Platinum-Group Elements in Urban Fluvial Bed Sediments—Hawaii

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Abstract Results from a detailed examination of the abundance, spatial variability and grain-size fractionation of platinum-group elements (PGEs; iridium, Ir; palladium, Pd; platinum, Pt; and rhodium, Rh) in bed sediments of an urban stream in Honolulu (Hawaii, USA) indicate significant contamination of Pd, Pt, and Rh. PGE concentrations in sediments located in close proximity to storm drains followed the sequence of Pt (10.3–24.5 ng g^{-1}) > Pd (5.9–12.6 ng g^{-1}) > Rh (0.82–2.85 ng g^{-1}) > Ir (0.11–0.23 ng g^{-1}). From a contamination perspective, enrichment ratios followed the sequence of Rh (25.3) $\gg$ Pd (6.9) = Pt (6.8) $\gg$ Ir (2.3). Iridium was primarily geogenic in origin, while the remaining PGEs indicated significant anthropogenic contamination. Attrition of the PGE-loaded three-way catalytic converters and their release to the road environment is the most likely source of PGEs in the stream sediments examined. PGE enrichment of bed sediments likely resulted from direct transport of sediment-associated road runoff via storm drains. Preliminary work on grain-size partitioning showed preferential enrichment and mass loading of Pd, Pt, and Rh in grain-size fractions ranging from 63 to 1,000 μm. Data from this study have direct implications for contaminant transport, and sediment source identification in urban catchments. Rhodium, in particular, emerged as an element potentially useful for sediment fingerprinting.

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1 Introduction

Platinum-group elements (PGEs) Pd, Pt, and Rh, are incorporated in three-way catalysts (TWCs) to reduce vehicle emissions. These noble metals promote three main reactions: reduction of nitrous oxides to N and H_2O, oxidation of CO to CO_2, and final combustion (oxidation) of residual hydrocarbons (Lucena et al. 1999). Three-way catalyst systems destroy more than 90 % of engine emissions (Acres and Harrison 2004). Since the mandatory use of catalytic converters in new gasoline automobiles in the UK (1993), substantial health benefits have accrued (Hutchinson and Pearson 2004). The estimated net societal health benefits by 1998 were approximately £500 million, and by 2005 they were estimated at £2 billion.

Countering their importance in reducing automobile-related atmospheric contamination, is the concern the PGEs are released to the road environment and atmosphere in exhaust emissions following TWC wear/attrition (Ravindra et al. 2004; Kalavrouziotis and Koukoulakis 2009; Wiseman and Zereini 2009). Modern manufacturing processes produce catalytic converter washcoats covered in PGE particles of 0.3 μm down to nanoparticle sizes (Prichard and Fisher 2012). Alumina is commonly employed as a high surface area support for washcoats and act as a carrier for dispersed PGEs, CeO_2-ZrO_2 mixed oxides, and barium and/or lanthana oxides (Kaspar et al. 2003). Fragments of TWC have been found in the road-deposited sediments of London and Sheffield, U.K., with sizes of 25 μm and between 40 and 80 μm covered in minute PGE particles (<0.3 μm). Dynamometer studies have indicated automotive outputs of PGEs to the environment are typically only tens to hundreds of ng km^{-1} (Palacios et al. 2000). However, low emission rates of PGEs are greatly magnified by the large vehicle numbers in urban environments. The introduction of PGEs to the environment from vehicles is therefore significant—particularly when considering that the concentrations of PGEs in bedrock are typically at the ultra-trace level: Ir, Pd, Pt, and Rh are 0.05, 0.4, 0.4, and 0.06 ng g^{-1}, respectively (continental crust; Wedepohl 1995).

In addition to localized deposition of PGEs on road surfaces (Ely et al. 2001; Zereini et al. 2001; Sutherland et al. 2007; Mathur et al. 2011; Spada et al. 2012), roadside soils (Morton et al. 2001; Whiteley and Murray 2003; Marcheselli et al. 2010; Akrivi et al. 2012; Lee et al. 2012), and roadside vegetation (Djingova et al. 2003; Riga-Karandinos and Saitanis 2004; Pan et al. 2009; Fumagalli et al. 2010), there is increasing evidence of deposition in a variety of sedimentary sinks following particle-associated transport of PGEs throughout urban catchments (Tuit et al. 2000; Rauch et al. 2004; Jackson et al. 2007; Pratt and Lottermoser 2007; Prichard et al. 2008). Early PGE research in Sweden by Wei and Morrison (1994a, b) found Pt to accumulate in roadside 'gullypots' and in downstream sediments. More recently, PGE concentrations, well above background levels, have been found in a roadside detention basin in England (de Vos et al. 2002), and in stormwater infiltration basins in Australia (Whiteley and Murray 2005).

To date, only limited research has focused on quantifying the abundance of PGEs in fluvial bed sediments receiving direct runoff from urban watersheds (e.g., Jackson et al. 2007; Prichard et al. 2008). This is surprising given the ability of PGEs to bioaccumulate (Ek et al. 2004; Zimmermann et al. 2005 Nischkauer et al. 2013; Wren and Gagnon 2014), as well as their significant environmental solubility and bioavailability (Jarvis et al. 2001; Fliegel et al. 2004; Colombo et al. 2008a, b; Puls et al. 2012).

The aims of this paper are to present results of a baseline survey of PGE concentrations (Ir, Pd, Pt and Rh) and enrichment ratios in fluvial bed sediments in an urban Hawaiian stream impacted by direct road runoff via storm drains. Our working hypothesis was that anthropogenic enrichment of PGEs, if present, would be associated with road sources. We also examined the distribution of PGEs within a range of grain size fractions to test the commonly held notion that elements are often found most in abundance in small grain-size fractions.

2 Experimental

2.1 Study Area

Nuuanu catchment (11.7 km^2), located in Honolulu, Hawaii (USA) was the subject of a prior investigation on automotive-associated Cu, Pb and Zn contamination (Andrews and Sutherland 2004), and PGEs in road-deposited sediments (RDS) (Sutherland et al. 2008). The catchment is situated on the southern side of the Koolau Volcanic range on the island of Oahu. Much of the valley is now covered with layers of alluvium and soil. The underlying geology consists of basaltic lavas.

Nuuanu Valley is one of the oldest developed valleys on Oahu. Fifty-one percent of the surface area in catchment is forested conservation land, and 49 % is developed. Developed land in the lower catchment consists of: manufacturing/industry (6 %), commercial (~9 %), social services (9 %), open space (14 %), public infrastructure (16 %), and residential (46 %) (Steve Anthony, US Geological Survey, personal communication, 2002). The population density in the catchment is 1,287 persons per km^2 (Brasher and Anthony 2000). Daily traffic volumes on streets range from 3,440 to 19,500 vehicles per 24 h, with highway counts between 37,800 and 46,000.

2.2 Sample Collection and Processing

Bed sediment samples were collected in 2002 at seven storm drains in Nuuanu Stream under baseflow conditions (see Fig. 1 in Andrews and Sutherland 2004). Archived samples from three of these sites have been reexamined for the present study (Judd, Vineyard and Beretania). Sampling locations were selected based on access, the presence of sediment deposition zones, and a direct and obvious connection from the road inlet to the storm drain outlet into Nuuanu Stream. The Judd Street outlet primarily drains residential areas and has the lowest traffic densities.

Vineyard and Beretania Street outlets are closer to the mouth of Nuuanu Stream and Honolulu Harbor; and they drain mostly commercial land uses and have high traffic densities. To explore spatial patterns in PGE abundance, bed sediment samples were collected at the drain outlet (0 m) and 5, 10, and 20 m above, and below the outlet. Three baseline bed sediment samples were collected in a remote but accessible unnamed small tributary to Nuuanu Stream, located in headwaters of the catchment. At all sampling locations, six cores were extracted from the stream bed with an acid-washed plastic cylinder to a depth of 5 cm, and then composited.

Samples were oven-dried in the laboratory at 105 °C to a constant mass. Dried samples were gently disaggregated and passed through a 2-mm stainless steel sieve. The material retained on the 2-mm sieve was discarded. All material passing the 2-mm sieve was further sieved with a <63 μm stainless steel sieve for 10-min on a Ro-Tap shaker (W.S. Tyler, Mentor OH). The <63 μm size fraction was retained for analysis, as this is the most commonly measured size range in environmental contamination studies dealing with soil and sediment (e.g., Radakovitch et al. 2008; Aleksander-Kwaterczak and Helios-Rybicka 2009; Milacic et al. 2010; Owens et al. 2011; Akrivi et al. 2012; Gao et al. 2012, 2014; Saeedi et al. 2013). Material retained on the 63 μm sieve for the Vineyard storm drain outlet (0 m) sample was further fractionated using a 'nest' of stainless steel sieves. The mass in each of the grain size fractions was determined to a precision of ±0.001 g. The six fractions retained for PGE analysis and their sedimentological equivalents in parentheses were: <63 μm (silt and clay), 63–125 μm (very fine sand), 125–250 μm (fine sand), 250–500 μm (medium sand), 500–1,000 μm (coarse sand), and 1,000–2,000 μm (very coarse sand). Samples >63 μm were ground in tungsten carbide vials, with tungsten carbide balls to enhance homogeneity during digestions. All material was subsequently passed through a 63-μm nylon mesh screen.

2.3 Chemical Analyses and Quality Control

Details of the analytical methods are reported elsewhere (Sutherland et al. 2007). Briefly, samples weighing 100 mg were placed in sealed Teflon vials and digested at 180 °C with aqua regia (3:1 volumetric ratio of HCl and HNO_3) for 48 h. The solution was taken to dryness and re-dissolved in 6 N HCl, dried again and taken up in 2 mL of 0.5 N HCl. This solution was centrifuged and loaded onto a chromatography column containing 2 mL of pre-cleaned AG50-X8 200-400# cation exchange resin (Bio-Rad Laboratories, Hercules, CA).

Column yields for Ir, Pd, Pt and Rh varied between 98.8 and 101.2 % (n = 4). Column blanks were <1 pg for Ir, 1 pg Rh, 6 pg for Pd and 10 pg for Pt. Total analytical blanks were routinely 6 pg for Ir, 10 pg for Rh, 13 pg for Pd and 30 pg for Pt. Procedural detection limits were <10 pg g^{-1} for Ir, 10 pg g^{-1} for Rh and <30 pg g^{-1} for Pd and Pt.

Samples were analyzed at the Department of Earth Sciences (Durham University) on a Perkin Elmer Sciex Elan 6000 (Wellesley, MA) inductively coupled plasma-mass spectrometer (ICP-MS) equipped with a CETAC Aridus desolvating nebulizer (Omaha, NE). The following isotopes ^{103}Rh, ^{105}Pd, ^{191}Ir, and ^{195}Pt were used for quantification of elemental abundances.

Oxides of concern during the analysis of environmental samples contaminated by catalytic converter products include ^{87}Sr^{16}O, ^{86}Sr^{17}O and ^{89}Y^{16}O, as they interfere with the determination of ^{103}Rh and ^{105}Pd. The oxides of Sr and Y were quantitatively retained by the cation column relative to PGEs, thus effectively separating them and causing minimal interference problems (Sutherland et al. 2007). In addition, on-line correction was also conducted for these species in case that there may have been inefficient separation. Interference from isobaric oxides of Hf (^{179}Hf^{16}O) and Zr (^{90}Zr^{16}O) was greatly reduced by using the desolvating nebulizer. Therefore oxide generation levels were maintained at or below 0.05 % of the total metal signal, and these were readily corrected from PGE analyte signals (Sutherland et al. 2007).

Classical precision and accuracy were measured with the BCR-723 certified reference material, which is a tunnel dust sample (Zischka et al. 2002a, b). This is the only available environmental reference material with certified PGE concentrations for selected elements. Mean certified concentrations (±standard deviation) in BCR-723 are: Pd, 6.0 ± 2.19 ng g^{-1}; Pt, 81.3 ± 4.60 ng g^{-1}; and Rh, 12.8 ± 1.59 ng g^{-1}. Four independent dissolutions of BCR-723 were performed using the methods previously described. Precision for Pd, Pt, and Rh ranged from 2 to 6 %. Precision was lower for Ir, but still acceptable at 12 % given the ultra-trace concentrations (0.29 ± 0.036 ng g^{-1}). Accuracy for Pt and Rh were +3 % and −7 %, respectively. The accuracy for Pd was −25 %, but the concentration of 4.47 ± 0.26 ng g^{-1} was statistically the same as that measured for BCR-723 by Meisel et al. (2003) using isotope dilution ICP-MS following a HCl and HNO_3 digestion (i.e., 4.52 ± 0.23 ng g^{-1}). Sutherland (2007) questioned the veracity of the certified value of Pd in BCR-723, as 7 of the 48 values used in the certification process had values ≥ 10.1 ng g^{-1}. Following removal of these potential outliers, the median Pd value for BCR-723 becomes 4.9 ng g^{-1}, similar to that determined by Kanitsar et al. (2003). Accuracy could not be determined for Ir as this element is not certified in BCR-723. However, our data agree closely with the mean value of 0.26 ± 0.047 ng g^{-1} determined by Meisel et al. (2003) after removal of an extreme outlier.

2.4 PGE Enrichment Ratios and Grain-Size Fractionation

Grain-size normalized enrichment ratios (ERs) were computed to evaluate the level of contamination:

$$\mathrm{ER_{PGE}} = \frac{\mathrm{C_{PGE}\ Sample}}{\mathrm{C_{PGE}\ Baseline}}$$

where, ‘C’ represents the concentration of a given PGE in either a storm-drain associated bed sediment sample, or the mean (n = 3) baseline value determined for sediments in a remote area of Nuuanu catchment.

A preliminary examination of the total element loading (GSF_{Load}) for one outlet stream sediment sample (Vineyard, 0 m) was determined using concentration data for each of the six grain-size fractions with their mass grain size percentages (Sutherland 2003; Sutherland et al. 2008):

$$GSF_{Load} = \left[\frac{Pt_i \bullet GS_i}{\sum_{n=i}^{6} Pt_i \bullet GS_i} \right] \bullet 100$$

where in this example, Pt_i is the platinum concentration in an individual grain-size fraction (e.g., <63 μm) in ng g^{-1}; and GS_i is the mass percentage of an individual fraction (0–100 %).

3 Results and Discussion

3.1 Baseline PGE Concentrations

The bed sediment samples in the headwaters of Nuuanu catchment had the following mean concentrations (±1 SD): Ir = 0.080 ± 0.00 ng g^{-1}, Pd = 1.39 ± 0.20 ng g^{-1}, Pt = 2.49 ± 0.18 ng g^{-1}, and Rh = 0.067 ± 0.006 ng g^{-1}. These data are comparable to those for three baseline soil samples, analyzed using the sample methodology, in a nearby catchment (Sutherland et al. 2007): Ir = 0.095 ± 0.010 ng g^{-1}, Pd = 1.12 ± 0.19 ng g^{-1}, Pt = 1.98 ± 0.63 ng g^{-1}, and Rh = 0.070 ± 0.014 ng g^{-1}. The baseline Pd and Pt values from Nuuanu catchment bed sediments are substantially greater than the 0.4 ng g^{-1} values associated with data for the continental crust compiled by Wedepohl (1995) from European greywackes, or the values from Chinese loess, representing upper continental crust, determined by Park et al. (2012), with Pt and Pd concentrations of 0.60 and 0.53 ng g^{-1}, respectively. The significantly higher Pd and Pt abundances in Hawaii reflect the dominance of basalt in the islands versus this igneous rock’s proportion in the continental crust.

Baseline Ir concentration data from this study are similar to the 1919 basaltic flow on the island of Hawaii (BHVO-1), and the tholeiites from Kohala Volcano (Table 1). They are also significantly lower than the tholeiite basalts from Kilauea, and Mauna Loa Volcanoes. Palladium and Pt baseline data were most similar to those for tholeiites analyzed by Tatsumi et al. (1999) and Crocket (2000). Baseline Rh data are similar to those for BHVO-1, as Meisel and Moser (2004) report Rh concentrations ranging from 0.054 to 0.27 ng g^{-1}.

Table 1 Summary of average (±SD) PGE concentrations (ng g^{-1}) in geologic materials from Hawaii

Geologic material	No.	Ir	Pd	Pt	Rh
Picrites[a]	10		3.41 ± 2.32	4.10 ± 1.32	
Unaltered tholeiites[b]	18	0.376 ± 0.140		2.40 ± 1.04	
BHVO-1[c]	5	0.085 ± 0.018	3.06 ± 0.074	3.08 ± 0.99	0.113 ± 0.091
BHVO-1[d]	5	0.096 ± 0.012	2.86 ± 0.18	2.42 ± 0.42	
Koolau Volcano glass[e]	13			5.08 ± 1.71	
Tholeiites (Mauna Loa)[f]	4	0.289 ± 0.060	1.94 ± 0.26	3.13 ± 0.71	0.154 ± 0.046
Tholeiites (Kilauea)[f]	5	0.418 ± 0.046	2.10 ± 0.22	2.55 ± 0.29	0.152 ± 0.033
Tholeiites (Kohala)[g]	7	0.100 ± 0.085		2.66 ± 1.34	
Tholeiites (Kilauea Iki Lava Lake)[h]	32	0.296 ± 0.243	2.78 ± 1.94	4.29 ± 6.78	<0.5

[a] Bennett et al. (2000), includes Kilauea (3), Loihi (2), Mauna Kea (1), Hualalai (1), Mauna Loa (1) and Koolau (2)

[b] Crocket (2000), includes Kilauea Summit (4), Kilauea East Rift (12), and Hilina Pali (2)

[c] BHVO-1 basaltic *pahoehoe* lava from the Hawaii Volcano Observatory that overflowed from the Halemaumau crater in 1919. BHVO-1 is a US Geological Survey reference material (*minerals.cr.usgs.gov/geo_chem_stand/pdfs/basalt**bhvo**2.pdf*). Data from Meisel and Moser (2004)

[d] Data from Peucker-Ehrenbrink et al. (2003)

[e] Data from Norman et al. (2004)

[f] Data from Tatsumi et al. (1999)

[g] Data from Jamais et al. (2008), shield-building stage, Pololu Volcanics

[h] Data from Pitcher et al. (2009), olivene-rich lava formed during 1959 summit eruption of Kilauea Volcano

3.2 Storm-Drain Associated Bed Sediment PGE Concentrations

Mean PGE concentrations in the <63 μm fraction follow the sequence (Table 2): Pt (17 ng g^{-1}) > Pd (10 ng g^{-1}) > Rh (1.7 ng g^{-1}) > Ir (0.18 ng g^{-1}). Palladium, Pt and Rh concentrations in storm-drain associated bed sediments exceed baseline values for Nuuanu catchment (Fig. 1). The range of concentrations in the bed sediments for Pd, Pt and Rh are less than those found in Nuuanu Valley road-deposited sediments (Sutherland et al. 2008). Moreover, the mean bed sediment concentrations were significantly lower (unpaired t-test) than those in RDS for Pd (P-value = 0.010), Pt (P-value = 0.006), and Rh (P-value = 0.005). There was no significant difference between Ir concentrations in road and bed sediments (P-value = 0.57). The consistently greater concentrations of Pd, Pt and Rh in road sediments versus bed sediments suggests dilution of PGE contaminated road sediment delivered to the stream via storm drains, with sediments from the less-developed headwater areas of Nuuanu catchment.

There are some data to support the dilution of autocatalyst-associated PGEs along sediment transport pathways in urban watersheds. For example, the average

Table 2 Platinum-group element concentrations (ng g^{-1}) in the <63 μm grain size fraction of bed sediments from Nuuanu Stream, Oahu, Hawaii (n = 21)

Statistic[a]	Ir	Pd	Pt	Rh
Mean ± SD	0.18 ± 0.063	9.67 ± 5.14	16.9 ± 9.6	1.69 ± 1.05
CV (%)	35.1	53.2	56.9	62.4
Minimum	0.080	3.16	5.76	0.32
Maximum	0.28	20.5	40.2	3.46
25th percentile	0.12	5.68	9.06	1.04
Median	0.18	8.44	15.1	1.35
75th percentile	0.24	13.6	24.1	2.71

[a] SD is the standard deviation and CV is the coefficient of variation

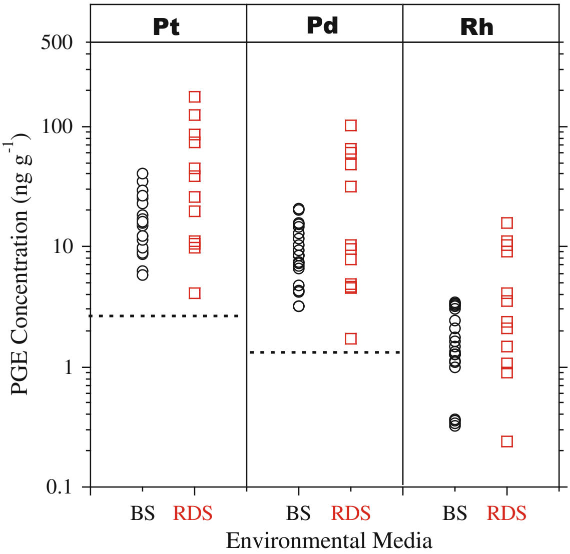


Fig. 1 Concentrations of Pt, Pd and Rh in the <63 μm fraction of 21 bed sediment (BS) samples and 12 road-deposited sediments (RDS) from Nuuanu watershed. The RDS data are from Sutherland et al. (2008). Note the *horizontal dotted line* across the Pt and Pd 'panels' represent the average baseline concentrations for Nuuanu watershed, 2.5 ng g^{-1} and 1.4 ng g^{-1}, respectively. The baseline value for Rh (0.07 ng g^{-1}) is less than the minimum value on the y-axis and is not plotted

Pt concentrations in roadside 'gullypot' sediments in Goteborg, Sweden (7.1 ± 4.0 ng g^{-1}), measured by Wei and Morrison (1994a), were higher than the bed sediment Pt concentrations in nearby rivers (<0.5–2.2 ng g^{-1}) (Wei and Morrison 1994b). Concentrations of Pd, Pt, and Rh in a sediment retention basin associated with the M20 motorway in England were significantly higher than those in the nearby River Stour, Kent (de Vos et al. 2002). Available PGE data for RDSs reported by Whiteley and Murray (2003), for West Coast and Leach Highways in Perth, Australia, were combined with those reported for stormwater infiltration basins in the same locations (Whiteley and Murray 2005). These data indicate that road sediments had higher PGE concentrations than those ‘downstream’ in the infiltration basins. For example, Pt, Pd, and Rh concentrations were 1.9–2.9 times, 2.6–5.4 times, and 2.4–3.3 times greater in RDS, respectively. Finally, data from Prichard et al. (2008) indicate an order of magnitude greater concentration of Pd, Pt, and Rh in RDS in Coisley Hill, Sheffield compared to bed sediments in the nearby Shire Brook.

3.3 Spatial Variation in Bed Sediment Concentrations About Storm Drain Outlets

Bed sediment data from three storm drains (Judd, Vineyard and Beretania Streets) were examined in detail to determine the effect of location on PGE contamination near drains (Table 3). Results from the Kruskal-Wallis test (Zar 1996) indicated at least one significant pair-wise difference for Pd (P-value = 0.0027), Pt (P-value = 0.0067), and for Rh (P-value = 0.0021). Pair-wise comparisons (Mann-Whitney U-test followed by a Bonferroni correction) indicated sediments associated with the furthest upstream storm drain outlet (Judd St.) had the lowest concentrations of Pd (5.9 ng g^{-1}), Pt (10.3 ng g^{-1}) and Rh (0.8 ng g^{-1}). Iridium concentrations were highest in Judd (0.23 ng g^{-1}) and Vineyard (0.20 ng g^{-1}) bed sediments. Similarity in data for two very different locations support the notion that traffic and land use had limited influence on the spatial distribution of Ir in the bed sediments of this system.

Conversely, Vineyard bed sediment-associated concentrations of Pd (12.6 ng g^{-1}), Pt (24.5 ng g^{-1}), and Rh (2.9 ng g^{-1}) were significantly greater than

Table 3 Mean ± SD (median in parentheses) for PGE concentrations (ng g^{-1}) in the <63 μm grain size fraction of bed sediments associated with three storm drain outlets to Nuuanu Stream, Oahu, Hawaii

Outlet[a]	Ir[b]	Pd	Pt	Rh
Judd	0.23 ± 0.036^{d}	5.94 ± 3.67^{c}	10.3 ± 4.66^{c}	0.82 ± 0.68^{c}
	(0.24)	(4.26)	(8.89)	(0.37)
Beretania	0.11 ± 0.017^{c}	10.5 ± 5.23^{d}	15.8 ± 11.0^{cd}	1.38 ± 0.25^{cd}
	(0.11)	(8.33)	(12.3)	(1.35)
Vineyard	0.20 ± 0.042^{d}	12.6 ± 4.52^{d}	24.5 ± 6.74^{e}	2.85 ± 0.78^{d}
	(0.19)	(11.7)	(25.5)	(3.20)

[a] The Judd site is the most upstream of the storm drain outlets sampled and is characterized by residential land use, and has the lowest traffic levels. Both Vineyard and Beretania sites are primarily influenced by commercial land use, and have significantly higher traffic densities

[b] Outlet concentrations for a given element (column-wise) are not significantly different at α = 0.05 if followed by the same letter (c, d, e)

those for the Judd St. outlet. Palladium and Rh were similar between the downstream Vineyard and Beretania storm drain outlets. Platinum was highest in Vineyard sediments. Both Beretania and Vineyard sites are primarily influenced by commercial land uses and have significantly higher traffic densities than the upstream Judd St. outlet. Thus, these three elements show an enrichment that is likely related to the direct delivery of contaminated road sediment to Nuuanu Stream via storm drains.

The autocatalyst-associated Pd, Pt, and Rh exhibited no consistent pattern of higher concentrations at the outlet or immediately downstream (Fig. 2). Although, the PGE values at the Judd outlet (0 m) were generally higher than those upstream (note negative values, i.e., −5, −10, and −20 m, on Fig. 2 reflect upstream sample locations). These patterns suggest that once road runoff, and transported road sediments with their sorbed contaminants, reach the stream via storm drains, they are largely dispersed by unidirectional fluid flows. Thus, the areas in the immediate vicinity of storm drains in Nuuanu Stream do not represent hotspots of contaminant storage.

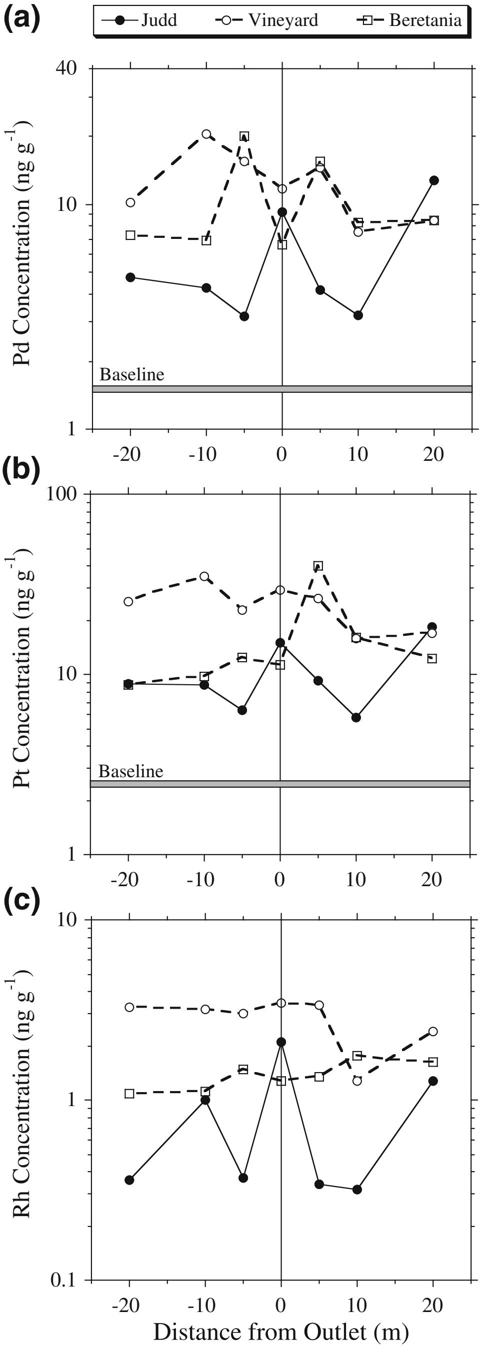
3.4 Bivariate Bed Sediment PGE Concentration Associations and Ratio 'Fields'

Palladium, Pt, and Rh were highly correlated (P-values < 0.0004), with Spearman correlation coefficients (r_S) between 0.79 and 0.87. Highly significant PGE correlations are suggestive of a common source, and we suggest that the most likely source would be release to the environment from automotive catalytic converters. No statistically significant correlation was observed between Ir and the other PGEs (P-values ranged from 0.47 to 0.85). The linear relationships on log-log axes are shown for Pt and Pd (Fig. 3a), Pt and Rh (Fig. 3b), and Pd and Rh (Fig. 3c). Data from 12 RDS samples from the Nuuanu catchment are also shown in Fig. 3a–c.

The close association of bivariate PGE concentration ratios for solid environmental media with those typical of TWCs has been used to infer anthropogenic inputs from autocatalysts (e.g., Whiteley 2005). Three common ratio 'fields' for TWCs have been defined by Ely et al. (2001, p. 3822) based on data published between 1995 and 2000, Pt/Pd 1–2.5, Pt/Rh 5–16, and Pd/Rh 4–9 (superimposed on Fig. 3).

The average (±SD) Pt/Pd ratio for Nuuanu bed sediments (<63 µm) was 1.80 ± 0.46, with a range from 0.62 to 2.59. Nineteen of the 21 bed sediment samples from this study were within the Pt/Pd 'field'. The Nuuanu Pt/Pd ratio was similar to bed sediment data from River Stour, Kent, UK (de Vos et al. 2002) and River Don and tributaries, UK (Prichard et al. 2008). In comparison, the mean Pt/Rh ratio for bed sediments was 12.5 ± 7.0, with a range from 7.0 to 30.0. Sixteen of the 21 bed sediment samples fell within the Pt/Rh 'field'. This ratio is comparable to the average value of 14 from River Stour (de Vos et al. 2002), but higher

Fig. 2 **a** Spatial variation in Pd concentration for bed sediments (<63 μm) associated with three storm drain outlets to Nuuanu Stream. Note *negative values* indicate upstream sample locations. The *horizontal line* represents the average baseline concentration. **b** Pt concentration. **c** Rh concentration, baseline concentration is 0.07 ng g^{-1} (not shown)



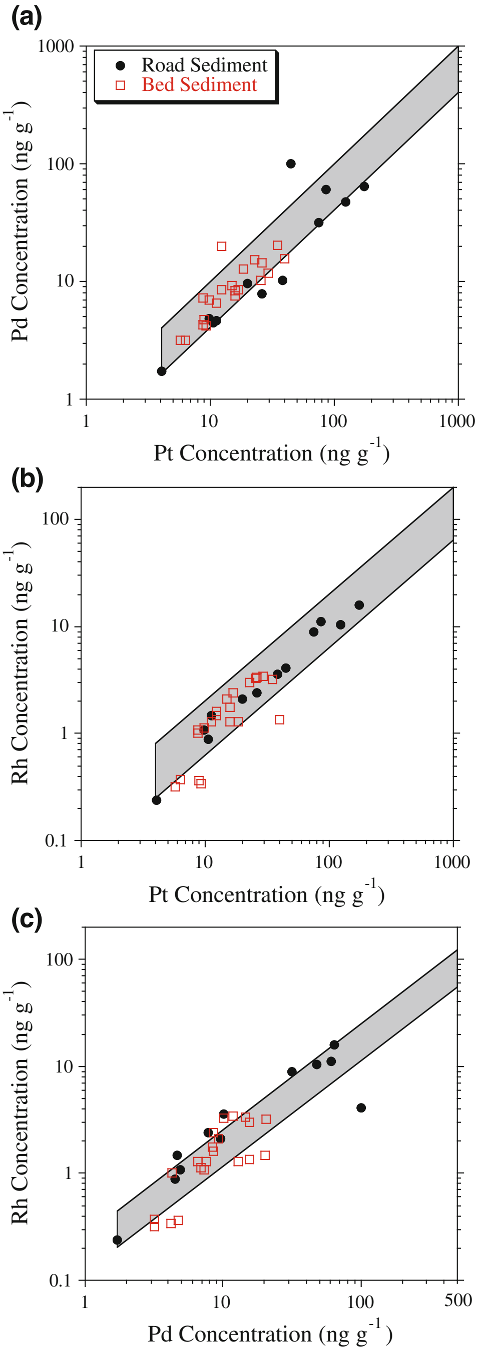


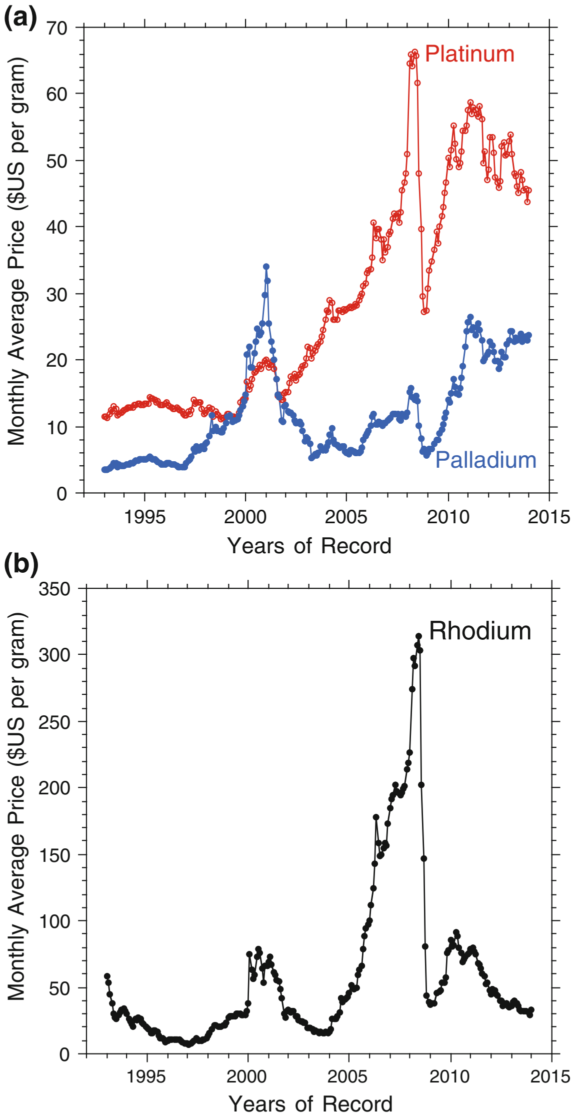
Fig. 3 **a** Bivariate scattergram of Pt and Pd concentrations in bed sediments (<63 μm) from Nuuanu, Stream. The *shaded area* reflects the Pt/Pd 'field' of 1–2.5 defined by Ely et al. (2001) for autocatalysts. Data for Nuuanu road deposited sediments are from Sutherland et al. (2008). **b** Pt and Rh concentrations. The *shaded area* reflects the Pt/Rh 'field' of 5–16 defined by Ely et al. (2001) for autocatalysts. Data for road sediments are from Sutherland et al. (2008). **c** Pd and Rh concentrations. The *shaded area* reflects the Pd/Rh 'field' of 4–9 defined by Ely et al. (2001) for autocatalysts. Data for road sediments are from Sutherland et al. (2008)

than those determined for Shire Brook and River Don, 4.3 and 7.0, respectively (Prichard et al. 2008).

Finally, the average Pd/Rh ratio for this study was 7.0 ± 3.4, with a range from 3.1 to 13.6. The Pd/Rh ratio was the most poorly constrained for Nuuanu, with only 12 of 21 sediment samples falling within the Pd/Rh 'field' defined by Ely et al. (2001). Whiteley and Murray (2005) found only 38 % of their infiltration basin sediments had Pd/Rh ratios that fell within the typical TWC 'field'. They argued that the low inclusion rate was a function of the increased solubility of Pd along the sediment transport path. Furthermore, the Pt/Pd ratio of infiltration basin sediments were statistically greater than those for the contributing RDSs. This was not the case for the Pt/Rh ratios from Nuuanu, which were not statistically different between media. There is evidence in the literature indicating preferential Pd solubility (i.e., Bowles and Gize 2005). Data from the present study indicated no statistically significant difference between RDS and bed sediment Pt/Rh (P-value = 0.38) and Pd/Rh (P-value = 0.57) ratios. However, the Pt/Pd ratio in the source area (i.e., RDS) was significantly greater (P-value = 0.034) than in the sink (bed sediments), 2.3 versus 1.8. These preliminary results do not support preferential loss of Pd along the limited sediment transport pathway from road to river in Nuuanu catchment.

It should be noted that the close approximation of the PGE ratios, especially Pt/Pd and Pt/Rh, in this study to the TWC 'fields' of Ely et al. (2001) reflect the sample collection date of Nuuanu sediments (i.e., 2002). The typical range of values compiled by Ely et al. (2001) do not reflect recent changes in PGE pricing, advances in catalyst washcoat technology, changes in fuel quality, tightening of emission standards, etc. (Cooper and Beecham 2013). The main driver impacting the proportional distribution of PGEs in light-duty gasoline vehicles is pricing. For example, from 2003 through 2010 the cost of Pt significantly exceeded Pd (Fig. 4a) by a factor of 3.1- to 4.5-fold. This price differential can be combined with an order of magnitude increase in the annual pricing of Rh from 2003 ($17.06 US per gram) to 2008 ($210.56 US per gram), and a maximum monthly mean value for Rh of $314.33 US per gram in June of 2008 (Fig. 4b). These price fluctuations have resulted in increased use of Pd at the expense of Pt, and significant thrifting of Rh in TWCs. Today the majority of TWCs are Pd/Rh with Pt much less common (Cooper and Beecham 2013). The temporal variation in PGE proportional loading on TWCs is currently reflected in the PGE ratios observed in solid environmental media (Table 4). It is clear from Table 4 that most cited studies with PGE samples collected after 2004 have ratio 'fields' different from those compiled by Ely et al. (2001). For example: (1) Pt/Pd ratios are more frequently below 1.0, than between 1 and 2.5; (2) Pt/Rh ratios are more frequently below the range of 5–16; and (3) Pd/Rh ratios are equally as likely to fall below or above the typical range of 4–9 compiled by Ely et al. (2001).

Fig. 4 **a** Monthly variation in Pd and Pt pricing from January 1993 to January 2014. Data accessed January 10, 2014 (www.platinum.matthey.com). **b** Monthly variation in Rh pricing



3.5 Grain Size-Normalized PGE Enrichment Ratios

Median bed sediment ERs (<63 μm) follow the sequence (Table 5): ER_{Rh} (20) > ER_{Pd} (6) = ER_{Pt} (6) > ER_{Ir} (2). Median comparisons between the different solid environmental media indicate anthropogenically impacted ERs for Pd, Pt, and Rh in road sediments exceed those in the stream channel by a factor of 1.2–2.2

Table 4 Summary of selected average PGE ratios for solid environmental media

Location	Media	Date collected	Pt/Pd	Pt/Rh	Pd/Rh	Reference[a]
Europe	Unused autocatalyst	2008	0.68	8.55	12.6	1
Sheffield, U.K.	River sediment (Shire Brook)	2006	0.92	4.33	4.93	2
Sheffield, U.K.	River sediment (Don River)	2006	1.46	7.00	5.00	2
Sheffield, U.K.	Road-deposited sediment	2006	0.92	3.35	4.64	2
Sheffield, U.K.	Estuary sediment	2006	1.10	5.50	5.00	2
Beijing, China	Roadside soil	2007	1.91	3.94	2.06	3
Guangzhou, China	Roadside soil	2007	0.88	2.90	3.30	3
Hong Kong, China	Roadside soil	2007	1.61	5.76	3.58	3
Macao, China	Roadside soil	2007	0.88	4.21	4.80	3
Qingdao, China	Roadside soil	2007	1.00	3.24	3.25	3
Kolkata, India	Roadside soil	2007	1.98	5.43	2.75	3
Mumbai, India	Roadside soil	2007	0.40	9.75	24.2	3
Varese, Italy	Leaf-deposited dust	2004–2005	0.86	1.59	1.84	4
Varese, Italy	Leaf-deposited dust	2007	0.29	0.54	1.85	4
Sheffield, U.K.	Sewage sludge	2004–2006	0.98	23.0	20.0	5
			(0.45–1.51)[b]	(9.00–40.0)	(16.5–26.5)	
Sheffield, U.K.	Incinerator ash (raw)	2004–2006	0.94	7.44	9.55	5
			(0.66–1.30)[b]	(3.40–16.8)	(3.44–17.7)	
Birmingham, U.K.	Sewage sludge	2004–2006	1.41	29.3	18.8	5
			(0.77–1.70)[b]	(8.71–32.0)	(11.2–20.8)	

(continued)

Table 4 (continued)

Location	Media	Date collected	Pt/Pd	Pt/Rh	Pd/Rh	Reference[a]
Birmingham, U.K.	Incinerator ash (raw)	2004–2006	0.91	14.1	15.1	5
			(0.80–1.13)[b]	(11.4–21.5)	(11.9–19.8)	
Modena, Italy	Nature reserve soil	2004	0.60	2.40	4.00	6
Modena, Italy	Agricultural soil	2004	0.68	2.87	4.20	6
Modena, Italy	Suburban soil	2004	0.65	5.20	7.94	6
Modena, Italy	Urban soil	2004	0.76	6.53	8.59	6
Hyderabad, India	Road-deposited sediment	2007	0.80	6.83	9.28	7
			(0.14–7.50)[b]	(2.00–16.0)	(2.00–30.0)	
Beijing, China	Road-deposited sediment	2010	0.49	2.88	5.87	8
U.S.A.	Spent autocatalyst	2011	0.71	4.42	6.24	9
Texas, U.S.	Washburn Tunnel dust	2013	0.70	3.2–4.4	5.2	9
Houston, TX, U.S.	Road-deposited sediment	2013	1.5–3.5	11.5–20.9	3.9–14.1	9
Guangzhou, China	Road-deposited sediment	2009	0.87	3.33	3.84	10
Texas, U.S.	Washburn Tunnel $PM_{2.5}$	2012–2013	0.31	2.3	7.6	11
Texas, U.S.	Washburn Tunnel PM_{10}	2012–2013	0.24	1.4	5.9	11
Europe	Various	1995–2000	1.0–2.5	5–16	4–9	12
This study	Fluvial bed sediment	2002	1.84	8.73	5.53	
			(0.62–2.59)[b]	(7.03–30.0)	(3.11–13.6)	

[a] 1. LGC Limited (2008), ERM-EB503a; 2. Prichard et al. (2008); 3. Pan et al. (2009); 4. Fumagalli et al. (2010); 5. Jackson et al. (2010); 6. Marcheselli et al. (2010); 7. Mathur et al. (2011); 8. Gao et al. (2012); 9. Spada et al. (2012); 10. Zhong et al. (2012); 11. Bozlaker et al. (2014); 12. Ely et al. (2001)

[b] Median values with minimum and maximum values in parentheses

Table 5 Mean ± SD (median in parentheses) enrichment ratios for PGEs in bed sediment (BS) and road-deposited sediment (RDS) in Nuuanu watershed, Oahu, Hawaii

Element	Bed sediment (n = 21)	Road-deposited sediment[a] (n = 12)	Median $\frac{RDS}{BS}$
Ir	2.3 ± 0.8	2.8 ± 4.2	0.74
	(2.3)	(1.7)	
Pd	6.9 ± 3.7	20.9 ± 23.3	1.2
	(6.1)	(7.1)	
Pt	6.8 ± 3.9	20.8 ± 21.3	2.1
	(6.0)	(12.9)	
Rh	25.3 ± 15.8	77.7 ± 76.4	2.2
	(20.2)	(44.6)	

[a] Computed using data compiled during the Sutherland et al. (2008) study

(Table 5). Iridium displayed a geogenic signal, having a higher median ER in bed sediments than in road sediments (ratio = 0.7).

When median ERs were computed using data reported by Ely et al. (2001) for 13 roadside soils and background soil data from Indiana, a sequence similar to Nuuanu was found: ER_{Rh} (15) > ER_{Pt} = ER_{Pd} (4). Similarly, ERs for 12 infiltration basin sediments and one wetland sediment in Perth, Australia were computed using the background soil data reported by Whiteley and Murray (2005). The median ER sequence was: ER_{Pt} (55) > ER_{Rh} (30) > ER_{Pd} (15). Enrichment data from the Nuuanu study, combined with those from the literature provide evidence of a strong anthropogenic signal for Pd, Pt, and Rh.

Rhodium may therefore be one of the most useful elements to fingerprint vehicle-associated sediment inputs to catchments over the last 20–30 years. For example, its limited post-depositional environmental mobility compared to Pd is an asset. Rhodium typically has significantly lower background concentrations in soil and bedrock compared with Pt. In the present study, average background concentrations of Pd and Pt exceed Rh by 21- and 37-fold, respectively. Despite the higher inputs of Pt from autocatalysts to the environment, ER_{Rh}-values are typically as high or higher than Pt. This has recently been documented for Washburn Tunnel (Houston, Texas) dust samples, and for $PM_{2.5}$ and PM_{10} samples collected in the same tunnel (Spada et al. 2012; Bozlaker et al. 2014). Further support for Rh as an indicative element for anthropogenic contamination comes from the fact that Pt is a common element in antitumour agents (cisplatin and carboplatin) and is highly concentrated in the waste stream of medical facilities (Ravindra et al. 2004). Inadvertent release of Pt to the fluvial environment prior to treatment, or even after treatment to coastal ecosystems, would complicate the interpretation of the Pt fingerprint signal in sedimentary sinks.

3.6 Grain-Size Fractionated Storm-Drain Associated Bed Sediment Sample

The limited attention paid to the variation of PGEs in different sediment or soil grain size fractions in the environmental literature may be based on the general assumption that element concentration typically increases with decreasing grain size, because of greater surface area and greater sorption potential (*cf.* Horowitz 1991). In contrast to this notion, Sutherland et al. (2008) found significantly higher concentrations of autocatalyst PGEs in fractions >63 μm for road sediments. Data for the fractionated Vineyard storm drain outlet sample examined in this study also exhibited higher concentrations of autocatalyst PGEs in fractions coarser than 63 μm (Table 6). Considering analytical error, concentrations of Ir were similar in all grain size fractions examined. The maximum concentration for Pd was in the coarse sand-sized fraction (500–1,000 μm) at 35 ng g^{-1}. The maximum concentration for Pt was in the fine sand-sized fraction (125–250 μm), containing 63 ng g^{-1}; and the maximum concentration of 6.8 ng g^{-1} for Rh was found in the very fine-sized sand fraction (63–125 μm). The ratio of the grain-size fraction with the maximum concentration to the concentration in the <63 μm fraction were 1.0 (Ir), 2.0 (Rh), 2.1 (Pt), and 3.0 (Pd) (Table 6).

Median enrichment values for the five Vineyard sediment fractions >63 μm (minimum and maximum values in parentheses) followed the order: $\text{ER}_{\text{Rh}} = 47$ (6–102) > $\text{ER}_{\text{Pd}} = 16$ (1–25) = $\text{ER}_{\text{Pt}} = 14$ (1–21) ≫ $\text{ER}_{\text{Ir}} = 1.5$ (1.4–1.6). Except for the coarsest fraction analyzed (1–2 mm), the autocatalyst PGEs exhibited significant anthropogenic enrichment in bed sediments of Nuuanu Stream.

Maximum mass loading (GSF_{Load}) for Pd and Pt were observed in the coarse sand-sized fraction (500–1,000 μm) at 60 % and 32 %, respectively (Fig. 5).

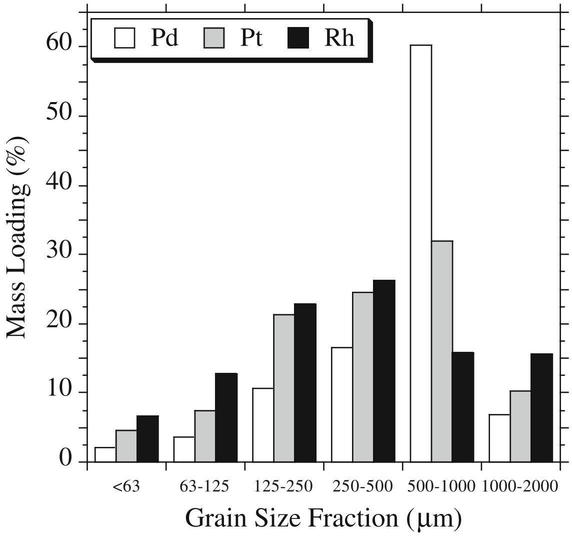
Table 6 Grain size distribution and PGE concentrations (ng g^{-1}) in specific size fractions isolated by sieving of the Vineyard storm drain outlet bed sediment sample, Nuuanu Stream, Oahu, Hawaii

Grain size (μm)	Sedimentological description	Mass (%)	Ir[a]	Pd	Pt	Rh
<63	Silt and clay	2.5	**0.17**	11.7	29.4	3.46
63–125	Very fine sand	2.4	0.12	22.2	48.6	**6.79**
125–250	Fine sand	5.4	*0.11*	29.1	**62.6**	5.46
250–500	Medium sand	11.0	0.13	22.2	35.3	3.10
500–1,000	Coarse sand	25.6	0.13	**34.6**	19.8	0.80
1,000–2,000	Very coarse sand	53.1	0.12	*1.9*	*3.0*	*0.38*
$\frac{\text{Max}^{\text{b}}}{<63}$	–		1	3.0	2.1	2.0

[a] For a given PGE, *italic* values reflect the minimum concentration observed, and those that are in **bold** reflect the maximum concentration

[b] For a given PGE, this index represents the ratio of the maximum element concentration to that for the <63 μm grain size fraction

Fig. 5 Mass loading percentages of Pd, Pt, and Rh in the grain-size fractionated Vineyard storm drain outlet sediment sample



For Rh, the maximum GSF_{Load} was in the medium sand-sized fraction (250–500 μm) at 26 %. Mass loading data indicate further attention must be given to quantifying PGEs in a variety of grain sizes, and not only in the most commonly analyzed fraction, e.g., <63 μm.

Jarvis et al. (2001) reported higher concentrations of PGEs in coarser fractions of road sediments above certain concentration thresholds. They speculated that agglomeration had occurred. This may partially account for the highest concentrations of PGEs in fractions >63 μm, as these elements have typical diameters of 1–10 nm when fixed on the surface of the washcoat of the monolithic honeycomb catalytic converters (Ravindra et al. 2004). Sintering and erosion of TWCs, with subsequent emission of PGEs in association with converter washcoat particles of γ–Al_2O_3 (Rauch and Morrison 2008) may also account for some of the PGEs in coarser fractions. However, we are not aware of any research that has shown emitted washcoat particles with associated PGEs coarser than 500 μm. Another possible reason for high concentrations of PGEs in coarse fractions is the charge characteristics of the organo-clay complexes in aggregated sediments in Nuuanu catchment. High cation exchange capacity (CEC) was observed for 11 bulk (<2 mm) sediment samples from Nuuanu Stream (Sutherland unpublished data). Mean CECs were 38.2 ± 3.9 meq 100 g^{-1}, with a range from 27.7 to 42.6 meq 100 g^{-1}. Additional grain size fractionated CEC data are not available to further test this hypothesis.

4 Conclusions

This is the first published study that combines both a detailed spatial examination of PGE abundance and grain size partitioning in fluvial bed sediments of an urban river. Data support strong anthropogenic contamination signals for Pd, Pt, and Rh in all bed sediment grain size fractions <1 mm. Rhodium was the element that was most enriched in Nuuanu streambed sediments, followed by Pd and Pt. The enrichment of PGEs in Nuuanu Stream is interpreted to be first from attrition of TWCs and subsequent emission via automotive exhaust and deposition on the road environment. Secondly, road runoff transfers the particle-associated anthropogenic PGEs via storm drains directly to the fluvial network.

Preliminary grain size partitioning data indicate that further attention should be given to examining PGEs in a variety of size fractions of solid environmental media. The finest grain-size fraction sampled for bed sediment in Nuuanu Stream (<63 μm) had the lowest autocatalyst-associated PGE concentrations and the lowest mass loading percentages. Further data are required to confirm the relationship of PGEs and grain size. Additionally, further examination of processes responsible for preferential association of PGEs with coarser grain size fractions is necessary. Accurate quantification of enrichment ratios can only be made with full knowledge of the grain size partitioning of the system under study. Finally, the use of Rh as an element for identifying urban sediment inputs in catchment sediment source and sediment budgeting studies should be further explored.

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