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Grain size partitioning of platinum-group elements in road-deposited sediments: Implications for anthropogenic flux estimates from autocatalysts

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Grain size fractionation of road sediments indicates that fluxes of platinum group elements into the environment from autocatalysts may have been significantly underestimated.

Abstract

Twelve road-deposited sediment samples were analyzed for platinum-group elements (PGEs) and Pb in the <63 μm fraction of an urban watershed in Hawaii. Three samples were further fractionated into five size classes, from 63–125 μm to 1000–2000 μm, and these were analyzed for PGEs and Pb. Concentrations in the <63 μm fraction reached 174 μg/kg (Pt), 101 μg/kg (Pd), 16 μg/kg (Rh), and 1.3 μg/kg (Ir). Enrichment ratios followed the sequence Rh > Pt = Pd > Ir. Iridium was geogenic in origin, while the remaining PGEs indicated significant anthropogenic contamination. Palladium, Pt and Rh concentrations and enrichment signals were consistent with PGE bivariate ratios and PGE partitioning in three-way catalysts. Size partitioning indicated that the <63 μm fraction had the lowest PGE concentrations and mass loading percentages. These data suggest that autocatalyst PGE flux estimates into the environment will be significantly underestimated if only a fine grain size fraction is analyzed.

Keywords: Iridium; Palladium; Platinum; Rhodium; Lead; BCR-723; Grain size partitioning; Mass loading; Enrichment ratios; ICP-MS

1. Introduction

Early works by Haagen-Smit (1952) and Haagen-Smit et al. (1953) were instrumental in increasing our understanding of urban and vehicle-related photochemical smog production. Typical exhaust gas composition, for the three primary pollutants, at normal engine operating conditions are carbon monoxide (CO, 0.5 vol.%), unburned hydrocarbons (HC, 350 vppm), and nitrogen oxides (NO_x, 900 vppm) (Heck and Farrauto, 2001). Levels of tailpipe pollutants from American cars in the mid-1960s, were typically HC 9.4 g/km, CO 56 g/km, and NO_x 3.8 g/km (Twigg, 2005). These emissions contribute to the photochemical production of ozone, a greenhouse gas, and other secondary pollutants (Niemeier et al., 2006).

The enactment of the Clean Air Act in the US in 1970 was a major watershed in the subsequent reduction of vehicle-related atmospheric pollution. The Act set the 1970 CO emission standard at 21.2 g/km, and HC at 2.55 g/km. The 1975, 1983 and 2004 emission standards for CO were set at 9.32 g/km, 2.11 g/km and 1.06 g/km, respectively; for NO_x the standards were 1.93 g/km, 0.62 g/km, and 0.12 g/km; and for HC emission standards were 0.93 g/km, 0.16 g/km, and 0.08 g/km (Vermaak, 1995). To reach the legislated standards for primary pollutants from vehicles, after-treatment catalytic converter systems were developed. These systems can destroy more than 90% of the engine emissions for more than

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160,000 km (Acres and Harrison, 2004). However, even with their reductive efficiencies of 90% or more, road traffic globally emits 8.8 Tg N/year, 237 Tg CO/year, and 33.2 Tg non-methane HC/year (Matthes et al., 2005).

Hutchinson and Pearson (2004) estimated that since the mandatory use of three-way catalysts (TWCs) in new gasoline automobiles in the UK (1993), substantial health benefits have accrued. By 1998 estimated net societal health benefits were approximately £500 million, and by 2005 they were estimated to be £2 billion. Incorporation of PGEs (typically Pd, Pt and Rh) in automotive catalytic converters has been critical in reducing exhaust emissions. Typical gasoline autocatalysts contain 1.5–3 g of PGEs (Barefoot, 1997; Palacios et al., 2000a). Output of PGEs to the environment is typically in the order of 10s to 100s of ng/km, due to abrasion, attrition and erosion of the catalytic converter (Ek et al., 2004a; Ravindra et al., 2004). Despite the low emission levels of PGEs to the environment, there is concern because emissions are greatly magnified by the significant number of vehicles, and their association with urban environments. In the year 2000, the average number of automobiles (trucks in parentheses) per 1000 inhabitants was 508 (54) in Germany, 492 (158) in Japan, 482 (325) in the US, 469 (105) in France, 435 (116) in Canada, and 381 (53) in the UK (Niemeier et al., 2006). It is estimated that in the year 2000 there were >500 million passenger cars in use worldwide, with annual production of 60 million plus another 200 million passenger trucks (Heck and Farrauto, 2001). With a significant percentage of these vehicles equipped with catalytic converters, loss of PGEs is significant, particularly when the concentration of PGEs are typically at the ultra trace level for bedrock and uncontaminated soil. For example, Wedepohl (1995) estimates the continental crust concentrations of Ir, Pd, Pt, and Rh are 0.05, 0.4, 0.4, 0.06 μg/kg, respectively.

Bencs et al. (2003) stated that monitoring of PGEs originating from the attrition of automotive catalytic converters into the environment is of paramount importance with respect to estimating the future risk to human health and ecosystems. This awareness has spurred a substantial increase in research on PGEs in environmental media, with Europe being the primary geographic focus. Environmental matrices examined include road-deposited sediment (RDS), and tunnel dust (Wei and Morrison, 1994a,b; Ek et al., 2004a; Farago et al., 1996; Helmers and Mergel, 1998; Jarvis et al., 2001; Motelica-Heino et al., 2001; Sutherland, 2003a; Varrica et al., 2003; Fritsche and Meisel, 2004; Lesniewska et al., 2004; Niemelä et al., 2004; Whiteley, 2005); roadside soil (Schäfer and Puchelt, 1998; Ely et al., 2001; Jarvis et al., 2001; Morton et al., 2001; Cicchella et al., 2003; Sutherland, 2003a; Morcelli et al., 2005; Zereini et al., 2007); fluvial sediment (Moldovan et al., 2001; de Vos et al., 2002); lacustrine sediment (Rauch et al., 2004a); airborne particulate matter (Alt et al., 1993; Palacios et al., 2000a; Petrucci et al., 2000; Gómez et al., 2001; 2002; Rauch et al., 2001; Kanitsar et al., 2003; Zereini et al., 2005); biotic reservoirs (Helmers, 1996; Helmers and Mergel, 1998; Ma et al., 2001; Jensen et al., 2002; Sures et al., 2002; Djingova et al., 2003; Ek et al., 2004b); and snow and ice (Barbante et al., 2001).

Despite the increase in PGE related research in Europe, there has been a dearth of information on autocatalyst PGEs in environmental matrices from the US. The first study was conducted by Hodge and Stallard (1986), on dust deposited on roadside vegetation in San Diego, California. This was followed by a gap of 14 years, with the next US publication on environmental PGEs in Boston Harbor sediments (Tuit et al., 2000). Ely et al. (2001) explored PGEs in roadside soils in Indiana, US, and Ma et al. (2001) examined Pt in tree bark in Hawaii and San Francisco. Sutherland (2003a) presented preliminary data only for Pt in road sediments and roadside soils in Hawaii. Several recent studies have been published from Massachusetts on lake sediments (Rauch et al., 2004a), ombrotrophic peat bog deposits (Rauch et al., 2004b), and in urban airborne material (Rauch et al., 2005). Sutherland et al (in press) analyzed PGEs in road sediments in two neighboring watersheds in east Honolulu, Hawaii.

This study extends previous research conducted in Hawaii and in the US as we attempt to add to the growing body of information on archives of PGEs in urban watersheds. The objective of this study is to quantify PGEs in road-deposited sediments and to present the first detailed examination of PGE mass loading in different grain size fractions of this important urban environmental archive.

2. Materials and methods

2.1. Study area

Nuuanu watershed is located in Honolulu, Hawaii, and was the subject of a previous investigation on automotive-associated Cu, Pb and Zn contamination (Andrews and Sutherland, 2004). The study area is situated on the southern side of the Koolau volcanic range on the island of Oahu. The underlying geology consists of basaltic lavas. The watershed has a surface area of 11.7 km^2. Rainfall in watershed is spatially variable. From 1989 to 1999, mean annual rainfall at Nuuanu Reservoir No. 4 at an elevation of 320 m above sea level, varied from 189 to 322 cm, with an average of 256 cm.

Nuuanu Valley is one of the oldest developed valleys on Oahu. Fifty-one percent of the surface area in Nuuanu watershed is forested conservation lands, while 49% is ‘developed’. Developed lands in the lower watershed consist of: commercial (~9%), manufacturing/industry (6%), open space (14%), public infrastructure (16%), residential (46%), and social services (9%) (Steve Anthony, personal communication, 2002). The population density is 1287 persons per km^2 (Brasher and Anthony, 2000). Daily traffic volumes on streets range from 3440 to 19,500 vehicles per 24 h, with highway volumes between 37,800 and 46,000 (G. Okaneku, personal communication, 2001).

2.2. Sample collection and processing

Road-deposited sediments are an important archive in urban areas for assessing the degree of contamination of solid particulate matter entering the subsurface storm sewer system and potentially the river network (Wei and Morrison, 1994b; Sutherland and Tolosa, 2000; Sutherland, 2003a). Road sediments reflect accumulation of materials directly emitted or worn from vehicles, atmospheric deposition, and soil eroded from roadside areas. In the original study by Andrews and Sutherland (2004), 15 samples were collected from the curbside areas in 2002. Twelve of these have been reanalyzed for total Pb and PGEs in the present study. Acid-washed plastic scoops were used to collect sediments from curbside accumulation areas (the mean sample mass was ≈400 g). Sites were selected to provide representative coverage of all