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Platinum group element and cerium concentrations in roadside environments in Toronto, Canada

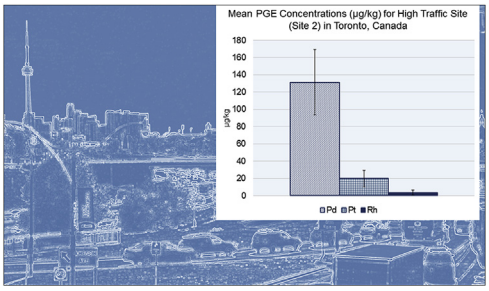
Clare L.S. Wiseman [a, b, *], Zahra Hassan Pour [c], Fathi Zereini [c]

[a] School of the Environment, University of Toronto, Toronto, Ontario, Canada
[b] Dalla Lana School of Public Health, University of Toronto, Health Sciences Building, Toronto, Ontario, Canada
[c] Institute for Atmospheric and Environmental Sciences, Department of Environmental Analytical Chemistry, J.W. Goethe University Frankfurt, Frankfurt am Main, Germany

HIGHLIGHTS

- Platinum, palladium, rhodium and cerium levels are reported for urban soil and dust.
- New data showing an urban enrichment of platinum metals in Canada is presented.
- Palladium occurs at the highest relative concentrations.
- Results confirm a shift from platinum to palladium use in exhaust converters.

GRAPHICAL ABSTRACT



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ABSTRACT

Platinum (Pt), palladium (Pd) and rhodium (Rh) are accumulating globally in the environment, due to their use as catalysts to control automotive exhaust emissions. While environmental increases in platinum metal concentrations have been well documented for a number of countries, published data for Canada have been missing to date. The aim of this study is to examine the concentrations of Pt, Pd and Rh, as well as Ce, in soils and dust as a function of traffic volume in Toronto, Ontario. Soils and road and underpass dust were collected from two sites with medium and high volumes of traffic. Samples were acid digested and co-precipitated with Hg (for Pd) and Te (for Pt and Rh), prior to measurement using ICP-Q-MS.

Palladium occurred at the highest levels in samples, followed by Pt and Rh. Median concentrations for all soil samples were 63 µg Pd/kg, 8.7 µg Pt/kg, 1.7 µg Rh/kg and 41 mg Ce/kg. The results support existing data regarding PGE accumulation trends in urban and roadside environments, due to their use as catalysts in automotive catalytic converters. This study also confirms a shift toward the heavier use of Pd as the catalyst of choice in recent years, as reflected in the higher concentrations measured for this metal relative to Pt and Rh. The results highlight a need to continue monitoring the accumulation of PGE, most notably Pd, in urban environments.

1. Introduction

Globally, environmental concentrations of platinum group elements (PGE), notably platinum (Pt), palladium (Pd) and rhodium (Rh), have been steadily increasing in urban areas over the last

* Corresponding author. School of the Environment, University of Toronto, 33 Willcocks St., Suite 1016V, Toronto, Ontario, Canada.
E-mail address: clare.wiseman@utoronto.ca (C.L.S. Wiseman).

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30–40 years. Sen and Peucker-Ehrenbrink (2012) evaluated the global flux of a range of elements and reported that Pt, Pd and Rh were among a total of 11 elements whose anthropogenic fluxes exceeded those of natural contributions. Studies have consistently demonstrated an environmental enrichment of PGE, documenting elevated levels of these elements in soils (Zereini et al., 1997, 2007; Whiteley and Murray, 2003) and airborne particulate matter (PM) (Rauch et al., 2001, 2005, 2006; Zereini et al., 2004, 2012; Kanitsar et al., 2003; Bozlaker et al., 2014), as well as street dust (Jarvis et al., 2001; Whiteley and Murray, 2003; Spada et al., 2012). While PGE are normally emitted in trace amounts in the ng/kg range, their accumulation in urban environments and demonstrated solubility in simulated lung fluids is a cause of concern (Zereini et al., 2012). Important source emissions of PGE include health care facilities (Turner and Mascorda, 2015), mining (Rauch and Fatoki, 2013) and the petrochemical industry (Bosco et al., 2005). However, most environmental contamination with PGE has been attributed to their use as exhaust catalysts in automotive catalytic converters, originally introduced in the 1970s in North America and in the 1980s in Europe, to control pollutant emissions. Platinum has a number of favorable properties, which makes it highly valuable as a catalyst, including its high oxidation potential, chemical stability and capacity to sorb simple gases such as CO (Reith et al., 2014). Initially, Rh/Pt catalysts were used for pollution abatement. Beginning in the mid-1990s, Pd was used in increasingly greater quantities, together with Rh and Pt in three way catalytic converters, to promote the oxidation of hydrocarbons. It was reported that the global gross demand for Pd as an autocatalyst increased from 4390 to 6970 metric tonnes between 1998 and 2013 (Johnson Matthey, 1999, 2013). A shift toward greater use of Pt in the future is likely, however, as more efficient hydrogen fuel cell automotive technologies require an estimated 3–10 times as much Pt for pollution abatement purposes (Alonso et al., 2012). The PGE are normally washcoated onto the monolith surface of the catalytic converter together with cerium oxide (CeO_2), typically in combination with zirconium oxide (ZrO_2), to promote thermal stability and oxygen storage (Kašpar et al., 2003). As such, Ce is commonly emitted with PGE exhaust catalysts. Nanoparticles of CeO_2 are added to diesel fuels in many countries such as the US and UK to improve the efficiency of fuel combustion, as well as reduce soot emissions (Cassee et al., 2011). While several studies have reported Ce concentrations and enrichment patterns in the environment (Whiteley and Murray, 2003; Zereini et al., 2005; Lyubomirova et al., 2011), emissions of this lanthanide and their potential human health implications have received limited attention to date.

Increases in the environmental concentrations of PGE have been documented for many urban areas, including Frankfurt am Main, Germany (Zereini et al., 2007, 2012), Gothenburg, Sweden (Rauch et al., 2001), Vienna, Austria (Kanitsar et al., 2003), Boston, US (Rauch et al., 2005), Mexico City, Mexico (Rauch et al., 2006), Buenos Aires, Argentina (Bocca et al., 2006) and Houston, US (Bozlaker et al., 2014). For Canada, however, there is no published data on traffic-associated concentrations of PGE in the environment. Data on the concentrations of Ce in Canada is also limited, especially in an urban context, with only one known published study having reported Ce levels for cultivated soils (Wiseman et al., 2013). The aim of this study is to contribute to the current body of knowledge regarding the PGE and Ce enrichment of urban environments and examine the concentrations of these metals in soils as a function of proximity to high and medium traffic volume roadways in a major Canadian city (Toronto, Ontario).

2. Materials and methods

Soil and road dust samples were collected at two different sites in Toronto, Ontario: 1. a public school located in Scarborough (43°45′19.6″N 79°15′53.7″W), which is situated in the East, and 2. a high traffic corridor in the West end of the city located close to Lake Ontario (43°38′20.0″N 79°27′30.0″W) (Fig. 1) (Hassan Pour, 2015). The prevailing wind direction at Site 2 is from the Southwest, with onshore/offshore winds often occurring in areas located close to Lake Ontario, most notably on warm, sunny days (Arain et al., 2009).

At Site 1, soil samples were collected in May 2013 from a series of raised garden beds situated in front (n = 10) and behind the school (n = 5), which had been established as part of a school agricultural program in collaboration with a non-profit organization in 2010. The beds at the front of the school are located at distances of 7, 9, 11, 13, 15, 17, 19, 21, 23 and 25 m away from a medium volume traffic road (ca. 24,100 vehicles/24 h weekday period), with 4 lanes and a tempo limit of 60 km/h. The beds behind the school were around 170 m away from the road. Apart from a small parking lot behind the school, the beds are surrounded by a community park. Three topsoil (0–5 cm) samples were taken from the middle and each end of the beds and composited. Pre-existing, uncultivated soils were also sampled directly adjacent to the road, at distances of 0.2, 2 and 5 m from the curb (each consisting of a composite of 3 discrete samples). In addition, 8 samples were each collected from the top 5 cm of the pre-existing soils at the front and back of the school and composited for comparative purposes.

For Site 2, two different transects, one running from East to West and another from North to South, were sampled in 2013 and 2014, respectively. The East-West transect involves a stretch which is bounded to the North by a municipal expressway situated close to Lake Ontario. The expressway, itself, is elevated between 2 and 5 m in height along this transect. It has 6 lanes of traffic, a speed limit of 90 km/h and a traffic volume of ca. 162,000 vehicles/24 h weekday period (City of Toronto, 2013). This transect is also bounded to the South by another major street, with 6 lanes of traffic, a speed limit of 60 km/h and a traffic volume of ca. 35,000 vehicles/24 h weekday period (City of Toronto, 2013). Over a stretch of ca. 250 m, three parallel soil samples were taken from the top 5 cm at intervals of 20 m and composited. A North-South transect was sampled at the same location in 2014, starting from the guardrail on the South side of the expressway and going in a southerly direction toward Lake Ontario. Three discrete soil samples were collected at distances of 1, 3, 5, 7, 10, 20, 30, 50, 80 and 120 m from the expressway and composited.

The North-South transect at Site 2 was extended northward from the expressway into a large city park in April 2014. This involved a stretch beginning at the North curb of the major road that runs parallel to the expressway on its North side (4 lane road, speed limit: 60 km/h, traffic volume: ca. 25,000 vehicles/24 h period (City of Toronto, 2013)). Again, 3 discrete samples were collected and composited, at distances of 0, 10, 20, 30, 40, 50, 120 and 170 m away from the curb. This sampling section involved a relatively steep gradient from ca. 20 to 50 m to the top of a hill. The sample collected at 120 m was situated on the hill, protected by trees, while the soil sampled at 170 m was located at the bottom of another steep gradient in a heavily treed area.

Additional samples were also collected in the vicinity of Site 2 in 2013 and 2014 to assess road dust inputs to soils: (1) dust and debris was sampled on the North and South sides of the expressway along the concrete foundations of a tunnel, (2) sidewalk samples consisting of dust from sweeps of between 5 and 14 m in length from two underpasses of the expressway, which connect the major roads that run parallel to the North and South of the expressway, (3) road dust from the shoulder of the major expressway (sweep of ca. 5 m in length), and (4) road dust collected from the curb of the major road located on the South side of the expressway (ca. 5 m of