



Emerging airborne contaminants in India: Platinum Group Elements from catalytic converters in motor vehicles[☆]



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ABSTRACT

Platinum Group Element (PGE) pollution on the Indian subcontinent is a growing concern because vehicle sales in India have rapidly increased over the last decade, and it is well known that automobile catalytic converters are one of the major source of anthropogenic PGE in the environment. Despite the rapid growth of the Indian automobile industry, the sources and magnitude of PGE contamination in Indian airborne particles are unknown. In this study we report PGE and mercury (Hg) concentrations, as well as osmium isotope ratios ($^{187}\text{Os}/^{188}\text{Os}$) of airborne particles (PM_{10}) collected in Kanpur, a large industrial city in India. We estimate that $61 \pm 22\%$, $32 \pm 24\%$, and $7 \pm 3\%$ of the total Os fraction are derived from eroding upper continental crust, catalytic converters fitted in the exhaust system of motor vehicles, and fossil fuel combustion, respectively. Only one sample had a ten times higher ($\sim 76\%$) than average contribution from fossil fuel. Unlike Os, Pt is predominantly ($84 \pm 10\%$) derived from anthropogenic sources. Platinum Group Element and Hg concentrations are not well correlated. However, the highest concentration of particulate Hg corresponds to the most radiogenic $^{187}\text{Os}/^{188}\text{Os}$ isotope ratios (4.6). Our results further indicated that PGE/Ir ratios could be successfully used to quantify the relative proportions of natural and anthropogenic PGE sources in aerosol samples. Since PGE and Hg data on Indian environmental samples are scarce, this study provides an interpretive framework that calls for additional assessments of PGE and Hg concentrations in environmental samples from India.

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1. Introduction

Human activities have significantly altered the biogeochemical cycles of Platinum Group Elements (PGE) (Sen and Peucker-Ehrenbrink, 2012). Mining, fossil fuel and biomass burning, construction, and human contributions to net primary productivity are moving 2 Mg (1 Mg = 10^3 kg) of Os, 5 Mg of Ir, 20 Mg of Ru, 40 Mg of Rh, and 187 Mg of Pt every year between different surficial geochemical reservoirs. Such large anthropogenic displacements of PGE are many orders of magnitude larger than mass transfer

through natural processes such as riverine transport, primary production, wind erosion, volcanic eruption, sea-salt spray, and cosmic dust fluxes (Sen and Peucker-Ehrenbrink, 2012). As a result, the natural biogeochemical PGE cycles are disturbed. PGE derived from anthropogenic sources have been detected in snow, rainwater, soil, aerosols, vegetation and are no longer restricted to urban and rural locations (Barbante et al., 2001; Gómez et al., 2001, 2002; Kanitsar et al., 2003; Whiteley and Murray, 2003; Morcelli et al., 2005; Rauch et al., 2005a, b, 2006; Hooda et al., 2007; Moldovan et al., 2007; Chen et al., 2009; Soyol-Erdene et al., 2011; Sen et al., 2013; Alméjija et al., 2015). Anthropogenic PGE are found in some of the most pristine and isolated landmasses such as Antarctica (Soyol-Erdene et al., 2011). PGE are partially bioavailable in the environment (Schäfer et al., 1998; Wiseman and Zereini, 2009). For example, up to 30% of Pt emitted from catalytic converters is bioavailable in rats (Ek et al., 2004). Since PGE are

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bioavailable and studies have linked elevated concentrations of PGE in fine atmospheric particulate matter (PM_{2.5}) to increased morbidity and mortality rates, increasing PGE contamination is an emerging global concern (Wiseman and Zereini, 2009).

PGE in the environment can be derived from natural and anthropogenic sources (McCandless and Ruiz, 1991; Esser and Turekian, 1993; Palacios et al., 2000; Moldovan et al., 2002; Poirier and Gariépy, 2005, Rauch et al., 2009; Jackson et al., 2010; Baïoumy et al., 2011; Funari et al., 2016). The dominant source of anthropogenic PGE in the environment is thought to be catalytic converters in automobiles (Palacios et al., 2000; Moldovan et al., 2002). Catalytic converters are emission control devices that are installed in the exhaust system of vehicles and are used to reduce emissions of NO_x, CO, as well as partially burned and unburned hydrocarbons. The catalytic surfaces in these devices are primarily composed of Pt, Pd and Rh, whereas Os is present as a contaminant in trace amounts (Rauch et al., 2009; Poirier and Gariépy, 2005). During vehicle operation, PGE particles are thermally mobilized and mechanically abraded from the device and released into the environment. A substantial body of published information already exists on the sources and magnitudes of PGE pollution in North and South American countries (Rauch et al., 2005a, b, 2006; Bocca et al., 2006; Rauch et al., 2006; Sen et al., 2013), China (Pan et al., 2009), and European countries (Moldovan et al., 2007; Zereini et al., 2012). With the exception of very recently published study (Diong et al., 2016) that reports elevated Pt, Pd and Rh concentrations in PM_{2.5} and PM₁₀ samples from downtown Kolkata, studies on the sources and magnitude of PGE pollution in airborne particulate matter are still missing in India, despite the fact that PGE pollution is a growing concern there (Sen, 2013). Some anthropogenic processes that release PGE (fossil fuel combustion, mining and biomass burning) also emit mercury (Hg) at a global annual rate of 38 ± 2.4 Gg (1 Gg = 10^6 kg) (Sen and Peucker-Ehrenbrink, 2012), yet limited information exists on concentrations and sources of Hg in airborne particulate matter in India.

The sources of Os in the environment can be traced by using the Os isotope (¹⁸⁷Os/¹⁸⁸Os) composition, because potential natural and anthropogenic end-members have distinct ¹⁸⁷Os/¹⁸⁸Os ratios. For example, most anthropogenic sources such as catalytic converters and industrial waste have ¹⁸⁷Os/¹⁸⁸Os values ranging between 0.1 and 0.2 (Poirier and Gariépy, 2005), whereas eroding continental crust has an average ¹⁸⁷Os/¹⁸⁸Os value of ~1.2 (Peucker-Ehrenbrink and Jahn, 2001). Here, we report on PGE, Hg, and ¹⁸⁷Os/¹⁸⁸Os systematics of airborne particulate matter collected in Kanpur, a large industrial city in northern India. The main objective of the study is to understand the magnitude and source(s) of PGE contamination, as well as concentrations of Hg in airborne particulate matter in an area that is likely significantly contaminated. Our secondary aim is to investigate relationships between PGE and Hg, as anthropogenic Hg and PGE emissions share some (e.g. fossil fuel combustion), but not all (catalytic converters) emission sources. Hg concentrations might therefore be useful to refine PGE source apportionment. This study also provides a baseline and framework for future, more comprehensive studies of PGE contamination in India.

2. Materials and methods

2.1. Sample collection

Eleven aerosols were collected between March 1–21, 2013, using a high volume (1000 L/min) Envirotech PM₁₀ sampler (model number: APM 460 DXNL) on the campus of the Indian Institute of Technology Kanpur (IIT-K, latitude: 26°30′47.69″ N; longitude: 80°13′56.39″ E). The aerosol sampler was placed on the roof of a 15 m tall building. The sampler was used for ~9 h each day between

9:00 a.m. to 6:00 p.m. (Indian Standard Time) and approximately 530 m³ of air per sample was pumped through each 20 cm × 25 cm preconditioned (heated at 550 °C for 12 h) quartz fiber Whatman™ filter (Table 1). The sampling site is ~16 km northwest of Kanpur City, one of the largest industrialized centers in Uttar Pradesh, India. The site is located ~5 km North of a coal fired thermal power plant (Panki Thermal Power Plant) and a kilometer west of National Highway (NH-91). The types of vehicles using NH-91 include light and heavy trucks, buses, tractors, passenger cars and jeeps, motorcycles, and three-wheelers (Vikram auto rickshaw). It is estimated that on average every hour approximately 800 vehicles are passing in both directions on NH-91 in front of IIT Kanpur campus (Shukla et al., 2012).

In order to understand the source regions of the air parcel pumped through the filter, air mass trajectories were computed 12 h back in time at 6 h intervals from 12:00 UTC at an elevation of 500 m, 1000 m, and 1500 m above ground level during the sampling period using the HYSPLIT (Hybrid Single Particle Lagrangian Integrated Trajectory) model of the U.S. National Oceanic and Atmospheric Administration (Draxler and Rolph, 2003). The archived data file GDAS1 was used for computations. The aerosol-laden quartz fiber filters were dried at 50 °C and then powdered using a ceramic shatter box that was preconditioned with quartz fiber material at Woods Hole Oceanographic Institution, and were analyzed for PGE, Hg and ¹⁸⁷Os/¹⁸⁸Os isotopes. Note that direct gravimetric analyses of PM₁₀ particles were not done and PM₁₀ concentration data are therefore unavailable. A different aliquot of the sample powder was also analyzed for Pb isotope ratios and trace metal compositions to understand the sources of atmospheric lead in Kanpur. The results of these analyses are reported in Sen et al. (2016).

2.2. Sample preparation

PGE were pre-concentrated from ~1.5–2 g of powdered filter paper (total weight of aerosol laden filter powder ~3.5 g) using the NiS fire assay technique (Ravizza and Pyle, 1997). Samples were only processed once, as the method consumed the entire sample split available for PGE analyses. PGE concentrations were determined by isotope dilution. Briefly, the sample powder was mixed with a solution enriched in the following isotopes: ¹⁹⁰Os, ¹⁰⁵Pd, ¹⁹¹Ir, and ¹⁹⁸Pt. This mixture was then fused with 5 g of nickel-sulfur-borax powder in a ceramic crucible at 1050 °C for two hours. Nickel and sulfur formed an immiscible NiS melt, which extracted the PGE from the melt and cooled at the end of the experiment to form a solid NiS bead. The yields for the NiS bead were between 55% and 75%. The NiS bead was isolated from the ceramic crucible, and thereafter dissolved in boiling ~6.2 N HCl. Following the dissolution of the NiS bead, the ~6.2 N HCl solution was cooled and passed through a 0.45 μm cellulose filter paper to capture the insoluble PGE-rich particles. The 0.45 μm cellulose filter paper that contained the PGE-rich particles was stored in acid cleaned Teflon beakers. Additional details of the NiS fire assay technique can be found in Ravizza and Pyle (1997). On the day of analysis, 1 mL of concentrated HNO₃ was added to the filter paper, and the clean beaker was placed on a hotplate at ~130 °C for 60 min. Afterwards, the sample solution was chilled and diluted ~5-fold with 18.2 MΩ cm water from a Millipore water purification system.

2.3. ¹⁸⁷Os/¹⁸⁸Os and PGE analyses

The ¹⁸⁷Os/¹⁸⁸Os isotope and PGE analyses were carried out in the Woods Hole Oceanographic Institution Inductively-Coupled Plasma Mass Spectrometry Facility (WHOI-ICPMS Facility). For Os analysis,

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