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PGEs and other traffic-related elements in roadside soils from São Paulo, Brazil

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Abstract

The distribution of platinum, palladium, and rhodium in soils adjacent to a major road in São Paulo, Brazil, is presented. Sampling was made at four sites with varying traffic volumes and driving styles (stop/start vs. constant speed). High-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) with NiS fire assay collection and Te coprecipitation was used as analytical procedure. The platinum group element (PGE) pattern distribution in the analyzed roadside soil was similar to that of other traffic-related elements such as Zn and Cu, characterized by a strong decrease of the PGE content with increasing distance from the traffic lane. The results indicate that the PGE concentrations in roadside soil are directly influenced by traffic conditions and distance, which characterize their catalytic converter origin. Pt, Pd, and Rh contents range between 0.3 and 17 ng g^{-1}, 1.1 and 58 ng g^{-1}, and 0.07 and 8.2 ng g^{-1} respectively. Lower levels of Pt and lower Pt/Pd ratios in relation to similar studies in other countries were observed due to the different Pt/Pd ratios in Brazilian automobile catalytic converters. This is the first study to assess traffic-derived Pt, Pd, and Rh deposition in Brazil.

Keywords: Rhodium; Platinum; Palladium; Catalytic exhausts; Urban pollution; Traffic-related elements

1. Introduction

Cars fitted with exhaust catalysts containing platinum group elements (PGEs) significantly minimize toxic gas emissions produced during gas combustion. Catalysts remove about 90% of carbon monoxide, unburned hydrocarbons, and nitrogen oxides (NO_x)

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from car exhaust and transform these pollutants into more innocuous carbon dioxide, nitrogen, and water (Palacios et al., 2000, Barefoot, 1999; Zereini et al., 2001). Both platinum and palladium are used to oxidize carbon monoxide and hydrocarbons. Rhodium must be present in order to reduce nitrogen oxides (Morton et al., 2001). However, catalytic converter surface abrasion and deterioration release these elements, adsorbed on small particles, into the environment, causing PGE deposits near roads, in vegetation, and in other environmental compartments such as rivers, as a result of wind and water transport (Zereini et al., 2001). Artelt et al. (2000), in engine bench test experiments, found emission factors ranging from 2 to 120 ng km^{-1}, depending on test conditions and catalyst age. The probable emission rate of Pt from vehicles equipped with catalytic converters has been estimated as 0.5–0.8 μg km^{-1} Pt (Helmers, 1997). The geogenic PGE concentration background in soils is estimated to be ca. 1 μg kg^{-1}, whereas contaminated soils along roadsides show contents up to several hundred micrograms per kilogram (Zereini et al., 2000).

The toxic effects of platinum emitted by automobile exhaust converters are only expected if platinum is bioavailable. Only soluble platinum compounds are of any possible toxicological relevance (Rosner and Merget, 2000). Respiratory sensitization to certain platinum salts is the relevant end-point for assessing the health risk potential of platinum. Platinum in dust emitted from automobile catalytic converters is mostly in metallic form, although small amounts of oxidized Pt(IV) have also been found in exhaust gases (Schlogl et al., 1987). Rhodium is present in the autocalyst in a metallic form and as an oxide. PGE transformations during vehicle operation might change the form in which PGE occurs in the autocatalyst (Rauch et al., 2000). Converter-emitted PGE may undergo rapid transformations in the environment and subsequently behave similarly to soluble PGE salts (Whiteley and Murray, 2003). Little work has been carried out with the bioavailability of Pt. Zereini et al. (1997) demonstrated the low Pt and Rh solubility both in soil and surface waters. Uptake experiments in plants showed that Pt and Rh present transfer coefficients below 0.1 (Schafer et al., 1998). Begerow and Dunemann (2000) reported that, in comparison with control groups, people heavily exposed to traffic do not show increased urinary Pt and Pd excretion and that, apparently, emissions from catalyst-equipped automobiles do not contribute to the internal background exposure of the general population.

Recent studies show that the cheaper price of Pd resulted in the development of catalytic converters with lower levels of Pt and constituted by Pd/Rh (Farrauto and Heck, 1999). This means that the potential effect of Pd to cause allergic reactions will become more important in the future (Jarvis et al., 2001).

There has been an increasing interest in determining PGE concentrations in environmental compartments along roadsides after the introduction of automobile catalytic converters (Jarvis et al., 2001; Gómez et al., 2001; Morton et al., 2001; Cinti et al., 2002; Cichella et al., 2003; Whiteley and Murray, 2003). A summary of the reports including measurement of PGE contents in environmental and biological samples (dust, vegetation, soil, sediments, water, blood, and urine) is found in Barefoot (1997). Most of the studies demonstrated increasing concentrations of PGE in roadside environments, providing evidence that the automobile catalysts are the predominant source of PGE (Whiteley and Murray, 2003).

Most of the studies have focused on Pt levels in a variety of environmental matrices, while Pd and Rh have only been monitored more recently (Helmers, 2000). According to Barefoot (1999), the concentration of Pt near German roads is about 70 times higher than background values. Schafer and Puchelt (1998) evaluated the concentrations and distribution patterns of Pt, Pd, and Rh in soil samples next to highways in Southwest Germany, and found high PGE concentrations in the uppermost soil layer, decreasing farther from the road. This is a result of large particle or whole catalyst piece emissions, which are deposited a very short distance from the roads (Rosner and Merget, 2000). In those catalytic converters produced between 1984 and 1992, there is a characteristic relationship between Pt and Rh, and a relatively constant Pt and Rh ratio (~5:1 or 6:1) can be observed in environmental samples (Zereini et al., 1997; Schafer and Puchelt, 1998). Since then, catalytic converter development has led to a wide range of Pt, Pd, and Rh combinations and concentrations, as well as to the introduction of Pd–Rh, Pt–Rh, Pt-only, or Pt–Pd–Rh catalysts. Therefore, these differences in composition may bring about concentration changes of these metals in environmental samples. Table 1 shows some results found for Pt, Pd,