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Assessing the potential of inorganic anions (Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-}) to increase the bioaccessibility of emitted palladium in the environment: Experimental studies with soils and a Pd model substance☆

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ABSTRACT

Palladium (Pd) emitted from vehicles equipped with exhaust catalytic converters has been accumulating at a greater rate relative to other platinum group elements (PGE) in the last 10–20 years. Little is known, however, regarding the various environmental factors and conditions which are likely to modulate the chemical behavior and bioaccessibility of this element post-emission. To meet data needs, soils and a Pd model substance were treated with solutions containing common anions (Cl^-, NO_3^-, SO_4^{2-} und PO_4^{3-}) to shed light on the geochemical behavior of emitted Pd under ambient conditions. As part of this, the particle surface chemistry of treated residues (insoluble phase) and solutions (soluble phase) was examined using XPS to assess the chemical transformation of Pd in the presence of inorganic anions. The results show that Pd is the most soluble in the presence of anionic species, followed by rhodium (Rh) and platinum (Pt). Pd in field-collected samples was found to be considerably more soluble than the metallic Pd in the model substance, Pd black, when treated with anionic species. The results also demonstrate that the solubility of Pd black is strongly dependent on solution pH, concentration and the duration of reaction. The outer 3–4 atomic layers of metallic Pd was determined via XPS to be partially oxidized when treated with anion solutions, with the degree being dependent on anion type. The concentration of dissolved O_2 in solution was found to have little impact on the transformation of metallic Pd. Given the ubiquitous nature of the anions examined, we can expect that Pd will become more bioaccessible post-emission.

1. Introduction

Increases in the global environmental concentrations of the platinum group elements (PGE) have been documented for airborne particulate matter (Leopold et al., 2008; Zereini et al., 2012a; Bozlaker et al., 2014; Lyubomirova and Djingova, 2015) and soils (Lee et al., 2012; Figueiredo and Ribeiro, 2015; Wiseman et al., 2016). An enrichment of PGE has also been reported for vegetation (Hooda et al., 2008; Djiangova et al., 2003; Feichtmeier and Leopold, 2015; Lyubomirova and Djingova, 2015) and aquatic and terrestrial organisms (Rauch and Morrison, 1999; Ek et al., 2004; Moldovan et al., 2001; Ruchter et al., 2015; Zechmeister et al., 2015). Platinum group elements are released in automotive exhaust as a result of the mechanical and thermal stresses that

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commonly occur under operating conditions. Shifts in the environmental concentrations of Pt and Pd have been reported over time, since the introduction of the widespread use of automotive catalytic converters, which reflect their use as catalysts in relative terms. More recently, Pd has been observed to be accumulating in the environment at a greater rate relative to Pt, suggestive of its greater use as the catalyst of choice in automotive catalytic converters (Zereini et al., 2012b, 2016; Wiseman et al., 2016).

While the environmental concentrations of Pd have been increasing, our knowledge regarding its geochemical behavior and potential to be transformed into species with higher bioaccessibility and mobility post-emission is limited. The available evidence suggests that Pd is the most soluble and mobile PGE in the environment. However, less is known regarding the various environmental factors and conditions, which are likely to modulate the chemical behavior of this element post-emission. Earlier tailpipe emissions studies have reported a relatively low solubility of <10% for Pd (Moldovan et al., 2002). In contrast, experimental studies with street dust extracted with rain and deionized water (pH 3) measured a high solubility of over 35% for Pd (Jarvis et al., 2001). This same study observed that Rh and Pt solubility extracted with the same solutions was much lower, with fractions of 1.2 and 0.48%, respectively. Inorganic constituents such as Cl^- anions have also been reported to modulate Pd solubility and mobility (Tait et al., 1991; Bazarkina et al., 2014; Tagirov et al., 2013; Poprizki, 2014). For instance, Tait et al. (1991) identified the formation of the following species following the treatment of Pd(II) with Cl^- solutions of various concentrations and pH levels: $PdCl_4^{2-}$, $PdCl_3(H_2O)^-$, $PdCl_2(H_2O)_2$, $PdCl(H_2O)_3^-$ and $Pd(H_2O)_4^{2+}$.

Recent studies with organic complexing agents such as EDTA, L-methionine and citric acid have confirmed the higher relative potential of metallic Pd to be chemically transformed into more soluble and mobile species post-emission (Zereini et al., 2015b, 2016). Studies using simulated lung and gastrointestinal fluids to extract PGE in milled automotive catalyst and airborne particulate matter (PM) have provided further evidence for the potential of metal complexing agents to increase the solubility and bioaccessibility of Pd (Colombo et al., 2008; Turner and Price, 2008; Puls et al., 2012; Zereini et al., 2012b).

This study builds upon prior work examining the potential of L-methionine and citric acid (Zereini et al., 2016) and EDTA (Zereini et al., 2015b) to chemically transform Pd by examining the effect of inorganic ions (Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-}) on Pd transformation and solubility. An investigation into the effects of inorganic anions is particularly important in light of their ubiquitous presence in the environment and their known potential to form metal complexes. The occurrence of elevated levels of various anions associated with anthropogenic emissions from agriculture, fossil fuel combustion and other sources highlights a need to explore their potential impact on the behavior of Pd in soils in close proximity to such activities. The use of deicing salts can result in high concentrations of chloride, for instance, along roadways and in urban run-off (Novotny et al., 2009). In addition to agriculture, urban areas can be significant non-point sources of nutrients such as phosphorous, nitrogen and chloride (Steele and Aitkenhead-Peterson, 2011; Carey et al., 2013). Atmospheric sources of nitrogen have been estimated to be depositing as much as 10 kg N/ha/year in many world regions, due to human activities such as those related meat and agricultural production (Galloway et al., 2008). Given this, the potential of these inorganic anions to modulate the solubility and geochemical behavior of emitted Pd is in critical need of examination.

Field-collected soils and the model substance, Pd black, were treated with anion-containing solutions (Cl^-, NO_3^-, SO_4^{2-} und PO_4^{3-}) under different conditions such as variable solution concentrations, anion type, pH and reaction time. As Pd black is chemically comparable to the bulk of the metallic Pd (Pd^0) used as a catalyst in automotive catalytic converters, it can be used as an indicator substance to assess the potential for Pd-emitted particles to be chemically transformed into more soluble species post-emission. In addition, the role of dissolved O_2 on the oxidation of metallic Pd in the presence of inorganic anions was examined using anion solutions with low and high O_2 levels. The results of the latter are particularly important to assess the potential geochemical behavior of emitted Pd transported to aquatic systems via soil run-off processes. Finally, the particle surface chemistry of treated residues and solutions was examined using XPS to directly examine the chemically transformation of atomic surfaces of Pd particles in the presence of the respective anions in solution.

2. Experimental

2.1. Materials

Field-collected soils and Pd black were examined as part of this study. Soil samples (N = 6) were collected from the top layer (0–3 cm) of soil directly at the edge of the Autobahn A5 close to Frankfurt am Main, Germany. Soils had a mean pH of 6.7 ± 0.15. Following collection, soils were dried at room temperature, sieved to <2 mm and ground using an agate ball mill. Pd black, which is metallic Pd in powered form (99.36% Pd, Umicore) with a specific surface area of 20 m^2/g and an average particle size diameter of about 22.23 μm (±13.25 μm) (Zereini et al., 2015b), was used to represent the elemental form used in automotive catalytic converters.

Solutions containing low concentrations (0.001 M, 0.01 M und 0.1 M) of inorganic anions, Cl^-, NO_3^-, SO_4^{2-} und PO_4^{3-}, were prepared from the following acids (Supra quality, Firm Roth): 35% HCl, 69% HNO_3, 95% H_2SO_4 und H_3PO_4. The concentration of anion solutions used for extraction purposes was chosen to represent the potential range of levels present in the environment. The lowest solution concentration used (0.001 M) is generally comparable to background levels for these anions and falls in the range of permissible drinking water standards set by various regulatory agencies (e.g. Hessisches Landesamt für Umwelt und Geologie, 2012). Soils were treated with the highest solution concentration of 0.1 M to improve detection and reliability in the examination of potential shifts in the geochemical state of Pd, as weaker concentrations were predicted to yield results too close to the analytical detection limits.

2.2. Determination of total PGE concentrations in soils

Soil samples were digested in a microwave (MARS Xpress, CEM GmbH) with 6 ml aqua regia (1:3 ratio of HCl to HNO_3). Following digestion, samples were transferred to Teflon evaporating dishes with 2 ml HNO_3 (69%). Once samples were heated to near dryness, another 2 ml of HNO_3 was added and the samples reheated until a small amount of digest remained. This step was repeated third times before samples were transferred to centrifuge tubes, which were filled to 10 ml 0.5% HNO_3.

Sample digests underwent a pre-enrichment, co-precipitation procedure with Te in accordance with the German Institute for Standardization method, DIN 19741 (2012), developed to minimize the potential for matrix effects. Samples were spiked Pd (97% ^{105}Pd) (Cambridge Isotope Laboratories, Woburn, Ma, USA) and Pd was measured using isotope dilution ICP-Q-MS (Varian 820-MS) in collision mode with He. Pt and Rh were also measured in soil samples (pre-spiked with 95.71% ^{198}Pt). ^{115}In and ^{169}Tm (Merck) were used as internal standards. Pd and Pt concentrations were also determined based on the following isotope ratios: $^{105}Pd/^{106}Pd$,

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