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Determination of traffic-related palladium in tunnel dust and roadside soil

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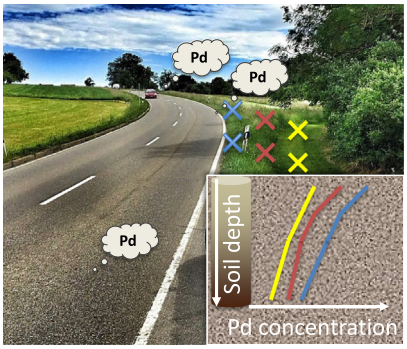
HIGHLIGHTS

- Pd emitted from car catalytic converters was studied in road dusts & roadside soils.
- Pd concentrations in dusts are in the range of few hundred μg kg^{-1}.
- Traffic-related Pd emissions accumulate in roadside soils up to 193 μg kg^{-1}.
- Aged soils/infiltration basins exhibit higher Pd concentrations.
- Depth profiles from 6 different sites reveal migration of Pd into deeper soil layers.

GRAPHICAL ABSTRACT



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ABSTRACT

Roadside dust and soil samples were collected at different sites in the area of Ulm and Munich in Germany. Road dust samples were collected in tunnels where the traffic-related dust is less influenced by atmospheric conditions. Soil samples were taken with a drill bar at varying distances to motorways, district and regional roads with different traffic densities. The soil cylinders of 30 cm length were divided into four sections in order to obtain depth profiles for palladium (Pd) distribution. Determination of Pd in total digests of the samples was performed by ligand-assisted selective separation and preconcentration of Pd(II) using solid phase extraction followed by high-resolution continuum source graphite furnace spectrometry. The analytical procedure was successfully validated using the certified reference material *BCR-723 Road Tunnel Dust* and by recovery experiments in spiked soil samples. The average Pd concentration found in the road dusts was 311 μg kg^{-1}, the maximum Pd concentration in the topsoil layer was 193 μg kg^{-1}. Pd depth profiles reveal transportation of Pd into deeper soil layers, where even at a depth of 25 to 30 cm a Pd concentration of 19 μg kg^{-1} was found, proving the high mobility of Pd. Different factors like traffic density and age of the soils are discussed in the context of the found Pd depth profiles.

1. Introduction

Palladium (Pd) exhibits excellent catalytic activity for various chemical reactions and is therefore together with platinum (Pt) and rhodium (Rh) the most frequently used catalytically active element in car

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exhaust-gas catalytic converters. More precisely, in recent years, usage of Pd has increased over that of Pt and Rh as the active species in automotive catalytic converters (Cowley, 2013). This application is the main source of anthropogenic Pd emissions to the urban environment, because mechanical stress and thermal stress cause emission of the platinum group metals (PGMs) together with the fast streaming exhaust gas. The amount of emitted PGMs ranges from 10 ng to several 100 ng/km and depends on the driving speed and condition of the road surface (Artelt et al., 1999). PGMs are emitted as particular matter (up to 90%) with particle sizes varying from >10 μm to <5 nm, however coarse particles consist of the precious metal bearing wash-coat and the ceramic carrier. Investigations of the emitted particles revealed, that up to one third by weight is emitted as particles smaller than 5 nm (Artelt et al., 1999; Ek et al., 2004; Herz et al., 1985). These Pd emissions from cars are initially found in airborne particular matter (Iavicoli et al., 2008) and obviously settle along roads where they are found in road dusts (Leopold et al., 2008) and roadside soils (Zereini and Wiseman, 2010). Moreover, some investigations show that even long-range transportation via air and water occurs and therefore Pd traces can be found in, sewage ashes, snow and water and may also enter biota (Ravindra et al., 2004). This is in agreement with Pd being the most reactive element among the PGMs resulting in a high mobility in the environment, high bioavailability, phytotoxicity, and allergenic potential (Ek et al., 2004). Moldovan et al. (2001) has shown that traffic-related palladium coming from a water runoff of a highway is bio-accumulated by fresh water isopod *Asellus aquaticus*. Speranza et al. (2010) observed adverse effects on the germination and vitality of Kiwi fruit pollen when exposed to Pd species similar to those emitted by catalytic converters (Pd(II) ions and Pd nanoparticles) indicating phytotoxic potential. Uptake and reduced biomass production were also observed by exposing barley plants to particulate Pd model substances (Battke et al., 2008). Moreover, the immunotoxic potential of Pd in form of nanoparticles has been studied in rats (Fontana et al., 2015; Iavicoli et al., 2015) and human blood cells (Petrarca et al., 2014) revealing immune response at higher Pd doses. Moreover, Pd was determined in foods, like bread, cereals, fresh meat and offal with a concentration range from 0.5 up to 2.2 μg kg^{-1} (Rose et al., 2010). Accordingly, it is likely that Pd emissions that are emitted locally along roads are further distributed. In this regard, three pathways have to be considered: 1. Transport via road drainage systems to sewage plants, 2. accumulation and/or transport in roadside soil and plants, and 3. further distribution by wind followed by dry and/or wet precipitation. In some urban areas as well as along motorways rainwater is not collected in road drainages, but seeps into designated roadside infiltration basins or planes. Thereby, the natural water cycle of rainwater is restored. At the same time, traffic-caused pollutants are supposed to be retained in the soil and thus are hindered to reach the aquifer. Of course, an exchange of the topsoil is necessary in discrete time intervals in order to maintain its retention capacity. Even though many pollutants are retained and accumulated in the soil, others possibly pass the topsoil, enter lower sediment layers and potentially reach the groundwater level (De Silva et al., 2016). At present, only very little is known about transportation of traffic-caused Pd emissions in soils. However, Pd is known to be much more reactive than other precious metals, forming a variety of different complexes (Bräse, 2013). Therefore, emitted particulate Pd can be dissolved and mobilised under environmental conditions (Jarvis et al., 2001; Zereini et al., 2015, 2016). In addition, a considerable part of traffic-caused Pd emission is fine particulate matter and could be transported in soils without prior dissolution. A few studies on spatial Pd distribution in roadside soils confirm its migration into the soil (Hangen and Dörr, 2015; Mihaljevič et al., 2013; Wichmann and Bahadir, 2015; Zereini et al., 2007). However, there are no comprehensive studies recording and comparing different factors, like traffic density and age of soils. with depth profiles of Pd in the soil. Here, the present work wants to contribute important data in order to assess mobility of traffic-related Pd in soils.

Anyway, Pd trace analysis in such complex environmental matrices is challenging because available detection techniques require highly selective separation and preconcentration of Pd traces in digests of the samples to overcome insufficient detection limits and/or severe interferences. In addition, verification of analytical procedures is elaborative since there is a lack of suitable reference materials. This is probably one reason why there is less data on traffic-related Pd emissions in comparison to other PGMs. In this work a combination of total digestion, selective solid phase preconcentration and ETAAS has been applied for Pd determination in soil and dust samples. Pd distribution in soils of infiltration basins from six different sampling sites and road dust from two tunnels were investigated.

2. Materials and methods

2.1. Reagents and materials

All purchased reagents were of analytical grade and ultra pure water (UPW) with a resistivity of 18.2 MΩ cm^{-1} was obtained from a MilliQ-Reference A+ system (Millipore GmbH, Schwalbach, Germany). All containers were thoroughly cleaned using nitric and hydrochloric acid baths and rinsed with UPW. Disposable polypropylene plastic vessels were used as purchased without further purification. Preparation of Pd calibration standards was performed by adequate dilution of Pd stock standard (1000 mg Pd L^{-1} in HNO_3 0.5 mol L^{-1}, CertiPUR, Merck, Darmstadt, Germany) in 0.5 M HNO_3.

2.2. Sample collection and pretreatment

The road tunnel dust samples were collected in 2012 in two tunnels in the city of Ulm (Germany), in particular in the *Eselsberg* tunnel (exact position: 48.41406°N, 9.97200°E) and in the *Bismarckring* tunnel (exact position: 48.39492°N, 9.97963°E). Tunnel dusts are less affected by weather and environmental influences and are therefore preferable over roadside dust samples for investigation of traffic-related emissions. The dust was collected from the tunnel wall using a disposable spatula (VWR International GmbH, Darmstadt, Germany) and a polystyrene container (VWR International GmbH, Darmstadt, Germany) for storage. The dust samples were dried for 24 h at 120 °C and homogenized in a ball mill. Sieving of the material was not required, as only small dust particles settle on the wall tiles.

Soil samples from side-strips along six different roads in the vicinity of Ulm and Munich in Germany and from a field near the University of Ulm were collected in 2008 and 2013. Samples were taken beside two German motorways A7 near Ulm (A7) and A 92 near Munich (A92), two district roads (*Uferstrasse*, Neu-Ulm; FS 6, Munich-Freising), a regional road in Neu-Ulm (*Heerstrasse*) and the entrance to a "park and ride" car park near Munich (*Car Park Fröttmaning*). The exact sampling sites are available as KMF file and presented on a map in Supporting information (Fig. S1). Soil sampling was performed according to DIN EN ISO 22475-1:2007-1. Briefly, soil samples were taken using a stainless steel soil sampler (Bürkle GmbH, Bad Bellingen, Germany) with an inner diameter of 14 mm and an outer diameter of 20 mm. The cylinder was pushed in the ground without turning, then turned for 180° and pulled out of the ground. The soil cylinder with a maximum length of 30 cm was divided into sections of 7.5 cm height each and transferred into polypropylene tubes (VWR International GmbH, Darmstadt, Germany) for transportation to the laboratory. Where possible, three distances to the road were distinguished and the 30-cm core sample was separated into four depth sections. However, at most sampling sites the topsoil layer was thinner than 30 cm allowing sampling of only 1 to 3 sections. The sample collector was cleaned with UPW in-between sampling. In 30, 50, and 70 cm distance to the road always 5 samples were taken and pooled to obtain a composite sample for each distance. Fig. S2 shows the sampling pattern.

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