



Platinum group elements (Pt, Pd, Rh) in airborne particulate matter in rural vs. urban areas of Germany: Concentrations and spatial patterns of distribution

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ABSTRACT

This study examines platinum group element concentrations (PGE) (i.e. platinum (Pt), palladium (Pd) and rhodium (Rh)) and their spatial distribution in airborne particulate matter fractions (PM) of human health concern in urban and rural areas of Germany. Fractionated airborne dust and PM₁₀, PM_{2.5} and PM₁ samples were collected along a busy road in Frankfurt am Main from July 2008 to April 2010. PM₁₀ was also sampled in Deuselbach and Neuglobsow between January 2008 and July 2009 to examine their concentrations at rural locations and potential for long-range transport.

Pt, Pd and Rh were isolated and pre-enriched in samples using a combination of Te and Hg co-precipitation methods. Concentrations were determined using isotope dilution ICP-Q-MS (in collision mode with He).

The highest airborne PGE concentrations were measured in PM₁₀ from Frankfurt (e.g. 12.4 pg Pt/m³ (mean)), while the rural locations of Deuselbach and Neuglobsow exhibited the lowest levels (e.g. 2 pg Pt/m³ (mean)). PGE concentrations were observed to decline with increasingly smaller PM size fractions from PM₁₀ to PM₁. All size fractions generally contained higher levels of Pd compared to Pt and Rh, an element of greater concern due to its solubility. PM_{2.5} collected in Frankfurt had a mean of 16.1 pg Pd/m³, compared to 9.4 pg/m³ for Pt. PGE concentrations also demonstrated a distinct seasonal relationship, with the greatest levels occurring in winter. Compared to a previous study in 2002, PGE concentrations in fractionated airborne dust have significantly increased over time. Elevated PGE levels were also measured for PM₁₀ sampled in Neuglobsow and Deuselbach, which could not be attributed to local emission sources. Using the diagnostic meteorological model, CALMET, trajectory analyses confirmed our hypothesis that PGE are being transported over longer distances from other areas of Europe.

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1. Introduction

Platinum group elements (PGE) are valuable rare elements, typically present at concentrations of 0.4 to 5 μg kg⁻¹ in the earth's crust (Wedepohl, 1995). Their chemical characteristics make them highly useful as catalysts in a variety of chemical and pharmaceutical processes. In particular, platinum (Pt), palladium (Pd) and rhodium (Rh) are widely used in a number of applications such as in hydration and dehydration reactions in pharmaceutical, pesticide and dyestuff production and in polymer processing (Zereini and Wiseman, 2010). Since the 1970s in North America and the 1980's in Europe, Pt, Pd and Rh have been used as the active catalyst material in automobile catalytic converters to reduce nitrous oxide, hydrocarbon

and carbon monoxide emissions. Today, the catalytic converter industry is the most important consumer of PGE, using a total of 38.7%, 57% and 80.4% of the global supply of Pt, Pd and Rh in 2009, respectively (Johnson Matthey, 2010). In particular, Pd has been used by the catalytic converter industry in increasingly greater amounts since the 1990s, from 22 t in 1993 to 126 t in 2009 (Johnson Matthey, 1996, 2010).

PGE are released in small amounts, together with particles from the wash coat of the catalytic converter, due to fast-changing oxidative and reductive conditions, high temperatures and mechanical abrasion of the catalytic material. This has led to increasing concentrations of these metals in the environment, as has been documented in a number of studies (e.g. Zereini et al., 2001a,b; Zereini et al., 2007; Gomez et al., 2000; Rauch et al., 2001; Kantisar et al., 2003; Wichmann et al., 2007; Leopold et al., 2008; Pan et al., 2009). Observed environmental increases of Pd concentrations, reflects the increased usage of Pd in place of Pt in catalytic converters since the

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1990s (Zereini et al., 2007). The chemical and noble metal extraction and processing industries are also important sources of PGE to the atmosphere (Zereini et al., 1998; Barbante et al., 2001; Rauch et al., 2006; Reimann and Niskavaara, 2006). Automobile catalytic converters have, however, received the most attention as a primary contributor of PGE to the environment.

Human biomonitoring studies of bus drivers and traffic police officers have demonstrated elevated levels of PGE in urine, as a function of exposures through traffic (Iavicoli et al., 2007, 2008). Observed increases in Pd concentrations and associated human exposures, is particularly a cause of concern, given the possible health risks associated with this element (Wiseman and Zereini, 2009). A couple of recent studies using physiologically based extraction tests to determine the solubility of PGE in automotive exhaust catalyst material have demonstrated a greater solubility for Pd in simulated lung and gastrointestinal fluids (Colombo et al., 2008a,b; Turner and Price, 2008). Other studies have also shown that Pd is more soluble and mobile in the environment compared to Pt, thereby having a greater potential to be taken up by organisms (Ballach, 1999; Rauch and Morrison, 1999; Eckhardt et al., 2000; Sures et al., 2001; Jarvis et al., 2001; Zimmermann et al., 2005; Zimmermann and Sures, 2006; Ek et al., 2004).

Several studies have reported elevated levels of PGE in airborne PM (e.g. Gomez et al., 2000, 2002; Rauch et al., 2006; Kantisar et al., 2003; Zereini et al., 2004; Limbeck et al., 2004). To date, the bulk of the research has focused on coarser PM fractions such as total suspended particulates (TSP) and PM₁₀. The availability of data on PGE concentrations in PM_{2.5} has been limited to date and information on these elements in even finer fractions (PM₁) is nonexistent. This highlights the need for more research on PGE associated with these finer fractions to support efforts to assess the potential risks of respiratory exposures (Iavicoli et al., 2008; Wiseman and Zereini, 2009) and inform shifting air quality policy efforts to regulate and monitor increasingly smaller airborne PM size fractions.

This research is part of a long time monitoring study funded by the German Umweltbundesamt (Title: "PGE-Metals in Fine Dust (PGE-Metalle im Feinstaub)"), which aims to further our knowledge base regarding the spatial distribution and concentrations of PGE in airborne particle size fractions relevant for human health. This includes an examination of the potential for PGE to be transported over longer distances, thereby impacting areas further away from the source of emissions. To fulfill these goals PM₁₀ samples were collected in three different areas of Germany, with assumed variable emissions levels as a function of known traffic densities and other local emission sources such as industries: (a) Frankfurt am Main, (b) Deuselbach and (c) Neuglobsow. In contrast to Frankfurt, these latter two sites were predicted to have negligible PGE concentrations, given their more rural locations. Meteorological aspects were considered in the selection of the rural locations. PM_{2.5} and PM₁ and fractionated impactor samples were also collected in Frankfurt. In this study, PGE concentrations in fine airborne particulate matter, PM_{2.5} and PM₁ are presented for the first time for Germany.

2. Sampling

Airborne PM (PM₁₀) samples were collected at three locations in Germany: Frankfurt, Deuselbach and Neuglobsow. Located in central Germany, the air quality in Frankfurt is impacted by a number of emission sources originating from both traffic and industry. Neuglobsow (53°08'34" N; 13°02'00" E) is situated in Brandenburg in northeast Germany, about 600 km away from Frankfurt. Deuselbach (49°45'47" N; 07°03'18" E) is located in Hunsrück, southwest Germany, about 170 km from Frankfurt.

PM₁₀ was collected at all three locations using high volume samplers (Digitel) and cellulose-nitrate filters with a pore size of 3 µm (diameter: 150 mm). In Frankfurt (50°07'28.56" N; 8°41'30.77" E),

samples were collected at the monitoring location of the Hessisches Landesamt für Umwelt und Geologie (Hessian State Office for Environment and Geology). Samples were taken at a height of 4 meters, directly at the roadside of a heavily driven street, which has four lanes and a traffic density of ca. 32, 500 automobiles/day (speed limit of 50 km/h). For most samples, only 48 hours were needed to collect enough sample material for analysis (mean air volume sampled: ca. 1350 m³).

In Neuglobsow, PM₁₀ samples were collected at the monitoring station of the Umweltbundesamt (Federal Environment Agency). Airborne PM₁₀ samples were collected in Deuselbach at the monitoring station of the Deutscher Wetterdienst (German Meteorological Office). Sampling time for the rural sites was longer (ca. 168 hours), due to the lower air pollutant levels compared to Frankfurt. The air volume filtered for most samples collected at Deuselbach and Neuglobsow ranged between 3350 and 4600 m³. Samples were collected at a height of 1.8 m above the ground at both locations. Meteorological aspects were considered in the selection of the rural locations. While the weather in Neuglobsow is strongly influenced by climatic fronts and conditions from the east and southeast, airstreams from the west and southwest dominate in Deuselbach. These locations allow for a determination of the impacts of the long-range transport of contaminants to the east and west portions of Germany.

A total of 270 PM samples were collected. In Frankfurt, 89 samples were collected between July 2008 and August 2009. One sample set was collected every two days during the first 12 months, while a second sample set was collected every 6 days from June to August 2009. In Neuglobsow, samples were collected every week from February 2008 to July 2009, yielding a total of 66 samples. In Deuselbach, 58 samples were collected from January 2008 to June 2009 (one per week).

Airborne PM_{2.5} and PM₁ samples were collected on quartz micro-fiber filters (filter diameter: 150 mm) using a high volume, fine particle size sampler (Digitel) in Frankfurt. PM_{2.5} and PM₁ samples were collected from September 2009 to April 2010 (29 PM_{2.5} and 28 PM₁ samples). Per filter, PM_{2.5} and PM₁ samples were collected over 72 and 96 hours at the monitoring station in Frankfurt, respectively. One sample of each particle size fraction was collected per week. Similar to PM₁₀ samples, PM_{2.5} and PM₁ samples were collected at a height of 4 meters above the ground. The air volume filtered for most PM_{2.5} and PM₁ samples was between ca. 2070 and 2150 m³.

Fractionated samples using an 8 stage Anderson impactor to determine the particle size distribution of airborne dust (9.0, 5.8, 4.7, 3.3, 2.1, 1.1, 0.63 and 0.43 µm) were collected simultaneously with the sampling of PM₁₀ at the same location in Frankfurt. A total of three Anderson impactors were used to collect samples from October 2008 to April 2009. Impactors were checked every 7 to 15 days using a gas meter to ensure a constant air flow of 29.5 L/min. Over a period of two weeks, air flow was found to be quite consistent, requiring only few adjustments. Sample collection using impactors ranged between 21 and 30 days. Similar to PM₁₀ samples, fractionated airborne dust was collected on top of the monitoring container at the monitoring station in Frankfurt at a height of 4 meters.

3. Experimental procedures

3.1. Sample preparation

An acid digestion procedure was used to prepare samples for analysis. For this, an acid mixture (aqua regia) of 1.5 ml 69% HNO₃ (Suprapur, Merck) and 4.5 ml 37% HCl (Suprapur, Merck) was added to samples in quartz glass vessels. To reduce the time required to achieve full digestion, samples were placed in a high pressure asher (HPA, Anton-Paar, Küner, Rosenheim, Germany) for 1 h at 320 °C (maximum of 130 bar). The samples were spiked with 1.2 to 15 ng of a ¹⁰⁵Pd (97%) and ¹⁹⁸Pt (95.7%) enriched solution prior to digestion (Cambridge Isotope Laboratories,

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