A novel flow-injection method for simultaneous measurement of platinum (Pt), palladium (Pd) and rhodium (Rh) in aqueous soil extracts of contaminated soil by ICP-OES

Esther Herincs, a,b Markus Puschenreiter, b Walter Wenzel b and Andreas Limbeck * a

Abrasion of modern car catalytic converters has resulted in increased deposition of anthropogenic platinum group elements (PGEs; Pd, Pt, Rh) in roadside soils, but still little is known about their solubility, bioavailability and reaction with the soil solid phase. As the extremely low PGE concentrations along with matrix interactions represent a major analytical limitation for studying the fate of PGEs in soils, we propose an advanced flow-injection (FI) system for measuring Pd, Pt and Rh within the same analysis using inductively coupled plasma-optical emission spectrometry (ICP-OES). A combined set of alumina micro-columns along with optimised eluents was employed for concurrent separation of disturbing cations and analyte enrichment to minimise interferences and improve the limits of detection (LOD) by a factor of 5 to 10 compared to conventional measurements, with satisfactory relative standard deviations (RSD) of 2–7%. The method proved to be suitable for simultaneous measurements of PGEs in weak soil extracts of contaminated soil representing potentially bioavailable fractions and sorption envelopes, providing information about the interaction of PGEs with the soil solid phase. The method offers new opportunities to explore the fate of PGEs in soils and similar environmental samples.

1 Introduction

Since the late 1980s, catalytic converters have been employed successfully in European automobiles for the reduction of noxious gas emissions of hydrocarbons, carbon monoxide and NOx. The catalytic effect is obtained by platinum group elements (PGEs), i.e. platinum (Pt), palladium (Pd) and rhodium (Rh). While air quality has significantly improved, exhaust catalysts have become the primary source of anthropogenic PGE emissions into the environment.1,2 Highly straining conditions during the operation of the vehicle lead to the abrasion of the catalytic material, resulting in the emission of finely grained PGE particles in metallic form associated with the so-called “washcoat” particles,3–4 which deposit along road-sides. The size range varies from sub-micrometer to several micrometers, with emission rates on the order of several ng PGEs per vehicle and km.4–6

Initially, PGEs (being noble metals) were believed to stay in metallic form after deposition and not to interact with biota. However, there is evidence of increasing PGE accumulation in the environment, plants (e.g. beans and cucumber) and sediments.4,7–9 Total PGE concentrations in uncontaminated soils are typically around 0.4 (Pt, Pd) and 0.06 μg kg–1, respectively.10 Thus, along roadsides and in urban areas, especially those with high-density stop-and-go traffic, the PGE concentrations in topsoils have been globally increasing by 1–3 orders of magnitude since the introduction of PGE-containing exhaust catalysts.10,11

To this end, some PGE compounds are already known for their allergenic and cytotoxic properties. While Pd shows a sensitising effect, Pt is well-known as a cytostaticum in anticancer-research; as a result, the interest in this topic has steadily grown over the last few years and decades.4,5,12

The uptake and accumulation of PGEs in plants is linked to the bioavailability of these elements in soils, which are open biogeochemical systems and act as a sink and a source of nutrients and potentially toxic compounds while serving as a medium for plant growth. The potential bioavailability and toxicity of any element entering the soil largely depends on its partition between the solid and the aqueous phase, the so-called soil solution, and on the chemical speciation in the latter. The partition between the soil solid phase and solution is typically determined by measurements of so-called sorption envelopes (or isotherms) in batch experiments that show the change of concentration in the solid phase as a function of the

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equilibrium concentration in soil solution.\textsuperscript{13–15} Important compounds in the soil solid phase that participate in surface reactions include iron and aluminium oxides, clay minerals as well as complex structures of organic matter. Especially, organic matter is considered to be an effective sorbent. Modelling of sorption processes in soil using sorption envelopes is an important premise for assessing the potential bioavailability and risk of leaching into the groundwater.\textsuperscript{15,16} Therefore, we decided to determine sorption envelopes for a better understanding of the fate of PGEs in Austrian soil, since they have not been provided previously.

The use of standard procedures for the determination of all three PGEs in real samples without sample pre-treatment prior to measurement is limited. While even for high-end analytical tools such as ICP-mass spectrometers problems related to numerous interferences, high content of dissolved organic matter (DOM) and high ion concentrations coming from environmental samples are persistent and require cautious optimisation, conventional ICP-OES analysis is not sensitive enough. Thus, the determination of sorption envelopes especially for Pd and Rh is a challenging task due to methodological limitations caused by the complex matrix composition of the soil extracts.\textsuperscript{17–20}

Here we present a novel, optimised flow-injection (FI) procedure for selective and sensitive determination of Pt, Pd and Rh in aqueous soil extracts over a wide concentration range, analysed by ICP-OES. The procedure involves steps for matrix elimination and analyte enrichment. We demonstrate the applicability of the method for the investigation of real soils by presenting data on sorption envelopes covering low to high concentrations of the three elements in Austrian soil.

2 Experimental

2.1 Instruments

Elemental analysis of aqueous soil eluates was performed using a Thermo Scientific ICP-OES spectrometer (ICAP 6500 series, radial view) equipped with an APEX E high efficiency sample introduction system with a Meinhard concentric nebuliser and a cyclonic spray chamber (ESI Elemental Scientific, USA). For conventional measurements, an autosampler CETAC ASX-520 coupled to the ICP-OES was used.

The advanced flow-injection (FI) system for matrix separation and pre-concentration consisted of two activated alumina micro-columns connected with two six-port, two position injection valves (VICI, Cheminert C22, USA). The micro-columns used for matrix elimination and analyte enrichment were produced by filling polyvinyl chloride (PVC) pump tubing (2 mm inner diameter) with powder of $\text{Al}_2\text{O}_3$ (approximately 20 mm bed length, 60 $\mu$L bed volume), and sealing the ends of the tubes by means of porous frits. For the connection to the FI manifold, various conventional push fit connections were employed. All connections within the FI-system were made of polytetrafluoroethylene (PTFE) tubes with 0.7 mm inner diameter. Transportation of reagents and sample solution was performed by the peristaltic pump of the iCAP 6500 ICP-OES.

For measurements of pH and electric conductivity (EC), instruments of the WTW series inoLab were utilised (pH-electrode SenTix 41, pH 730, plus A 102108112 and EC-TetraCon 3, Terminal 740). Total organic carbon ($C_{\text{tot}}$) and nitrogen ($N_{\text{tot}}$) were measured using an elemental analyser NA 1500 (Carlo Erba, Milan, Italy). The dissolved organic carbon (DOC) of the untreated aqueous extracts was determined using a Shimadzu TOC-5000 (Shimadzu GmbH Europe, Duisburg, Germany) equipped with an ASI-5000 autosampler.

Microwave assisted UV-digestion of the soil extracts and standard solutions was conducted with a Multiwave 3000 (Anton Paar, Austria) equipped with an 8XQ80 rotor and XQ80 quartz vessels. The UV lamps (electrode-less Cd low-pressure discharge MW lamps in quartz glass with Mo-wire possessing emission domains in the UV-regions 228 nm and 326 nm) were provided in an UV Digestion Set (Anton Paar, Austria).

For equilibration of soil and solution during the adsorption experiment, an overhead shaker, type GFL 3040, was used. For centrifugation, Nalgene vessels (28.5 $\times$ 104 mm) and a Beckman J2-HS Centrifuge (JS-7.5 rotor: 7500 rpm, $r_{\text{max}}$ 165 mm, $k$-factor 5287, 10 $\times$ 395 $\times$ g) were used.

2.2 Reagents and materials

All chemicals were of pro-analysis grade or higher purity. Hydrochloric acid (HCl, 37%), nitric acid (HNO$_3$, 65%), suprapure grade quality hydrogen peroxide (H$_2$O$_2$, 30%) and ammonia solution (NH$_3$, 25%) as well as certified stock solutions of Pt, Pd and Rh (Pd and Rh: Fluka, Atomic Spectroscopy standard solution 1.000 g L$^{-1}$; Pt: Merck, Certipur standard solution) were purchased from Merck (Darmstadt, Germany) and Sigma Aldrich (Steinheim, Germany); standard solutions for measurement were prepared by appropriate dilution of these stock solutions on the day of use and kept in high-density polyethylene (HDPE) vessels. Aluminium oxide ($\text{Al}_2\text{O}_3$-powder) for thin layer chromatography (Fluka, Switzerland) was used as sorbent material for the micro-columns.

The buffer solutions for calibration of the pH-electrode (Orion application solutions, pH 4.01 orion 910104 and pH 7.00 orion 910107) were provided by Thermo Scientific. For the calibration of the EC electrode, a 0.01 M KCl (1.41 mS cm$^{-1}$) solution provided by SI Analytics GmbH (Mainz, Germany) was employed.

Calcium nitrate tetrahydrate ($\text{Ca(NO}_3)_2 \cdot 4\text{H}_2\text{O}$, Riedel-de Haén) for incubation of the soil was purchased at Sigma Aldrich (Seelze, Germany); cellulose acetate membrane syringe filters (Pall, 22 mm, 0.45 $\mu$m) from VWR collection were used.

All vessels (PE, HDPE) used for and during the soil experiment were prepared by acid washing (cleaned by keeping in 5% HNO$_3$ for at least 12 hours), rinsed at least 3 times with distilled water (Milli-Q system, Millipore) and dried before use. For the analytical procedure, high purity water was obtained by double distillation of deionised water derived from a reverse osmosis/ion exchange combination (Euro 20 plus-5G water system, Germany) using an in-house quartz apparatus, and used throughout the analysis.
Table 1 Working parameters for ICP-OES, iCAP 6500 series

<table>
<thead>
<tr>
<th></th>
<th>On-line (FI)</th>
<th>Conventional</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF – power (W)</td>
<td>1200</td>
<td>1350</td>
</tr>
<tr>
<td>Nebulizer flow rate (L min⁻¹)</td>
<td>0.8</td>
<td>0.75</td>
</tr>
<tr>
<td>Auxiliary flow rate (L min⁻¹)</td>
<td>0.4</td>
<td>0.5</td>
</tr>
<tr>
<td>Plasma gas flow rate (L min⁻¹)</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>Observation height (mm)</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>Sample flow rate (mL min⁻¹)</td>
<td>0.8–1.3</td>
<td>1.5</td>
</tr>
</tbody>
</table>

2.3 Analysis

2.3.1 ICP-OES measurements. Table 1 summarises the chosen instrumental parameters for conventional analysis of the soil extracts (without enrichment) and the results of the on-line measurements using the developed FI-procedure on ICP-OES, after certain optimisation steps. For conventional measurement, the samples were acidified with 1% HCl (v/v) for storage and measured by means of ICP-OES after each experiment.

Background corrected emission signals were measured at two wavelengths for each element $\lambda = 324.2$ and $340.4$ nm (Pd), $\lambda = 214.4$ and $265.9$ nm (Pt) and $\lambda = 343.4$ and $369.2$ nm (Rh) for quality control. Since the data showed good accordance, the more sensitive wavelengths $\lambda = 340.4$ nm (Pd), $\lambda = 214.4$ nm (Pt) and $\lambda = 343.4$ nm (Rh) were selected for method optimisation as well as calculations and data depiction of the sorption envelopes. On-line measurements were performed in transient signal mode, 60 data points per 180 seconds. Conventional analysis provided 5 replicates at a rate of 5 seconds each.

2.3.2 Enrichment procedure. To address the low concentrations of PGEs in the aqueous soil extracts as well as expected matrix interferences, we developed a novel procedure for simultaneous separation and enrichment of the analytes prior to determination by ICP-OES. To this end, we employed micro-columns filled with aluminium oxide as sorbent material. In an acidic milieu (reflecting the experimental conditions), platinum group elements form anionic chloro-complexes which are retained by anion exchange on the sorbent, whereas the interfering cationic matrix elements can pass through the column. Degradation of DOM was required prior to analysis. For the subsequent F1-procedure, the acid and oxidant concentration utilised for digestion had to be kept low because the efficiency of the enrichment procedure decreases with increasing acidity. To this end, 15 mL of sample were digested in the presence of 150 μL 10% HCl (v/v) and 150 μL H2O2 at approximately 230 °C and 60–65 bar (6.5 × 105 kPa) for a total time of 40 minutes in a microwave-assisted UV-digestion apparatus. This digestion method provides continuous radiation by the microwave-energised UV-source while the solution is simultaneously heated by microwave radiation. Afterwards all samples were transferred into pre-cleaned HDPE vessels and stored in the refrigerator until measurement.

2.4 Adsorption experiments

2.4.1 Soil collection and characterisation. The experimental soil (expected to be non-contaminated soil) was collected from an A horizon of a Cambisol located in a farmland area near Gmunden, Upper Austria. The soil was air-dried at room temperature, passed through a 2 mm mesh screen, mixed and stored in plastic bags. A subsample was dried in an oven at 105 °C to determine the factor for dry-weight. Important soil characteristics (Table 3) were measured using standard procedures and are briefly described below.

The soil pH was determined in the supernatant solutions of both deionised water and 0.01 M CaCl2 in a soil to solution ratio of 1 : 1 (w/v). The electric conductivity (EC) was measured in a saturated soil–water extract obtained by equilibrating a soil to solution ratio of 1 : 1 (w/v) for one hour. Total organic carbon (Ctot) (ISO 10694:1995) and total nitrogen (Ntot) (ISO 13878: 1998) were measured by a thermoconductivity detector (TCD) after dry combustion. The carbonate equivalent was determined by treating the soil with 10% HCl (w/v) and subsequent
For the next sample continue with step 2

<table>
<thead>
<tr>
<th>Step no.</th>
<th>Valve position</th>
<th>Operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A</td>
<td>MC1: pre-conditioning – 0.001 M HCl is purged through the column (flow rate 1.3 mL min⁻¹)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MC2: cleaning – the column is flushed with 0.9 M HCl (flow rate 0.8 mL min⁻¹)</td>
</tr>
<tr>
<td>2</td>
<td>A</td>
<td>MC1: sample application (anionic analyte species are retained on the column, while cations pass through)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MC2: still rinsed with 0.9 M HCl (“cleaning”)</td>
</tr>
<tr>
<td>3</td>
<td>A</td>
<td>MC1: wash step – rinsed with 0.001 M HCl to remove residual sample</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MC2: still in elution mode (“cleaning”)</td>
</tr>
<tr>
<td>4</td>
<td>A → B</td>
<td>Simultaneous switching of both valves to change eluent and flow direction; start of measurement and elution of MC1</td>
</tr>
<tr>
<td>5</td>
<td>B</td>
<td>MC1: elution – 0.9 M HCl is directed through the column at a flow rate of 0.8 mL min⁻¹ for removal of the retained analytes from the column and subsequent injection into the ICP-OES for measurement</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MC2: rinsed and conditioned with 0.001 M HCl</td>
</tr>
<tr>
<td>6</td>
<td>B</td>
<td>MC1: eluted and rinsed with 0.9 M HCl</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MC2: loading with sample solution</td>
</tr>
<tr>
<td>7</td>
<td>B</td>
<td>MC1: cleaning – 0.9 M HCl is purged through the column</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MC2: wash step – rinsed with 0.001 M HCl to remove residual sample</td>
</tr>
<tr>
<td>8</td>
<td>B → A</td>
<td>Simultaneous switching of both valves</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Start of measurement and elution of MC2</td>
</tr>
<tr>
<td>9</td>
<td>A</td>
<td>MC1: conditioning with 0.001 M HCl – repeating cycle (step 1)</td>
</tr>
<tr>
<td>10</td>
<td>—</td>
<td>MC2: purging with 0.9 M HCl for elution</td>
</tr>
</tbody>
</table>

Table 2: Sequence and operational conditions of the separation and pre-concentration steps employed in the flow-injection (FI) system. MC 1, MC 2: micro-columns one and two filled with aluminium oxide

Table 3: Physical and chemical characteristics of experimental soil

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH (H₂O)</td>
<td>6.3</td>
</tr>
<tr>
<td>pH (0.01 M CaCl₂)</td>
<td>5.6</td>
</tr>
<tr>
<td>EC (µS cm⁻¹)</td>
<td>190</td>
</tr>
<tr>
<td>Ntot (g kg⁻¹)</td>
<td>4.0</td>
</tr>
<tr>
<td>Ctot (g kg⁻¹)</td>
<td>52.7</td>
</tr>
<tr>
<td>OC (g kg⁻¹)</td>
<td>52.5</td>
</tr>
<tr>
<td>Texture (g kg⁻¹)</td>
<td>Sand: 275, Silt: 725, Clay: 0</td>
</tr>
</tbody>
</table>

volumetric measurement of the evolved CO₂ (Scheibler method)₂³,²⁴. Organic carbon (OC) was calculated from Ctot by deducting the carbon contained in the carbonates. Soil textural fractions (sand 2000–63 µm, silt 63–2 µm, clay < 2 µm (ref. 16)) were determined using a combined sieving and sedimentation procedure.²⁵

Prior to use in the sorption experiment, we incubated the soil with calcium nitrate solution adjusted to the same electric conductivity (EC) as measured in the saturated soil–water extract (EC 190 µS cm⁻¹). This was done by frequent moistening using a squirt or aerosol bottle and circulation of the soil in the storage bag several times manually, incubating for 10 days at room temperature (20–25 °C). For matrix-matched calibration used during analysis and determination of LODs in the presence of a soil matrix, we spiked blank soil extracts obtained from uncontaminated experimental soil with standard solutions containing various concentrations of PGEs. PGE addition to the blank soil extracts for matrix-matched calibration standards was conducted after MW-assisted UV-digestion of the solutions.

2.4.4 Determination of the equilibration time required for the adsorption experiment. Adsorption envelopes are commonly measured by equilibrating an adsorptive solution of known volume and composition with a known amount of adsorbent (soil) under agitation, at constant pressure and temperature for a period required to obtain steady state.¹⁴,³⁸ The degree of agitation for the equilibration process should be strong enough to warrant good mixing, but not too vigorous to minimise adsorbent modifications. Ionic strength and pH are also controlled in most sorption experiments.

In a preliminary experiment we determined the time required to obtain equilibrium of Pt, Pd and Rh adsorption on the experimental soil. To this end, standard solutions with PGE concentrations of 100 µg L⁻¹ were analysed using the conventional ICP-OES technique after stirring with soil for various time intervals ranging up to 96 hours. The concentrations were selected to meet the requirements given by the LODs of the conventional ICP-OES analysis. The experiment was performed at a soil to solution ratio of 1 : 5 (w/v). The solutions were centrifuged and passed through 0.45 µm membrane filters and acidified to obtain a final concentration of 1% HCl (v/v) in solution for stabilisation until measurement by ICP-OES.

2.4.3 Adsorption envelopes. Regarding the sorption experiment, after equilibrium is reached, the solution and the adsorbent are separated by settling, centrifugation or filtration. Finally, the derived soil extracts are analysed. Evolving from the experimental data, usually an isotherm according to the Langmuir or Freundlich equation can be fitted.¹⁴,³⁸

The sorption envelopes for Pt, Pd and Rh were determined by shaking the soil horizontally (lowest rotation adjustment, 2 rpm) at a soil : PGE solution ratio of 1 : 5 (w/v) and a
temperature of ~25 °C for the equilibration times determined in the preliminary experiment, using calcium nitrate (EC 190 μS cm⁻¹) as the background electrolyte. The PGE concentrations used were 0, 2, 5, 20, 50, 150, 3000, and 5000 μg L⁻¹.

After equilibration, the solutions were centrifuged for 10 minutes and passed through cellulose acetate membrane filters and stabilised by adding diluted HCl to obtain a final concentration of 0.1% (v/v) HCl in solution for subsequent microwave digestion and measurement. Control solutions, i.e. aqueous PGE standard solutions without soil, were carried throughout the experiment to monitor possible losses of PGEs onto vessel walls and to assure quantitative recovery of the analytes during the experiment. All adsorption envelopes and blanks were measured in duplicate.

3 Results and discussion

3.1 Effect of vessel and filter materials on PGE recoveries

To identify potential analyte losses along the whole analytical chain, we conducted recovery tests for each critical step of the adsorption experiment and subsequent sample treatment steps up to analysis. The tests were performed using standard solutions of varying concentrations up to 5 mg PGE L⁻¹, the highest concentration used in the final adsorption experiment. The tests should address potential losses due to PGE sorption onto walls of vessels and filtration materials used for equilibration, storage and digestion steps in the sorption experiment, including the effect of inappropriate adjustment of pH. However, none of the steps (centrifugation, filtration) after the first stage of the experiment resulted in significant analyte losses. Only the shaking vessels caused Pd losses between 5 and 13%, which was accounted for in the subsequent measurements. For Pt and Rh, the recoveries were satisfactory (losses < 0.2%), i.e. deviations from the expected concentration were generally less than the uncertainty of the ICP-OES measurements. For Pd, sample acidification was required to avoid sorption of this element to vessel walls during storage and thus keeping the deviations within the uncertainty limits of the method.

3.2 Effect of the soil matrix on LODs obtained by the conventional ICP-OES method

For the improvement of the ICP-OES analysis, the major interferences coming from the components of the soil extracts should be known and were characterised by ICP-OES measurements using standard conditions provided by the manufacturer. According to literature, Pd measurements by ICP-OES may suffer from interferences caused by Fe, Cu and Ti. For Pt, interferences caused by Fe, Mg, Cr and Mn are known, whereas Rh measurements may be affected by the presence of Fe, Cr and Ti.²⁶

Aqueous soil extracts may also contain large concentrations of dissolved organic matter (DOM) which may deter detection limits by influencing the sample introduction and the atomisation and excitation procedure as well as the stability of the background signal. We measured the dissolved organic carbon (DOC) as an indicator of DOM. The yellowish to brownish coloured solution contained 87.4 mg DOC L⁻¹, clearly indicating the need for removal of the organic fraction prior to PGE measurements.

The elemental composition of the aqueous soil extracts (soil : solution ratio 1 : 5) obtained in the sorption experiments is shown in Table 4. Among the elements causing interferences with PGE measurements, Fe and Mg are present at concentrations in the mg L⁻¹ range, with all others in the μg L⁻¹ range (Table 4). Soluble fractions of the PGEs in soils are expected to be considerably smaller. Even the largest PGE concentrations remaining in the aqueous phase after the addition of standard solutions containing 100 μg PGEs L⁻¹ to the experimental soil were well below those of the interfering elements. These results suggest that in particular Fe and Mg have strong potential to deter the LODs for PGE measurements in aqueous soil extracts. The large concentration of Sr in the soil extracts (Table 4) reinforces the need for alternatives to ICP-MS for the measurement of Pd as Sr is known to cause strong interferences.¹⁹

Table 5 presents the LODs calculated according to 3σ criteria (3σ) for the PGEs in aqueous standards and spiked soil extracts as determined via conventional ICP-OES analysis. For analysis of aqueous standard solutions, LODs were 0.5 to 1.3 μg L⁻¹. In the presence of a soil matrix, however, LODs ranged between 1.2 and 8.5 μg L⁻¹, indicating interferences by DOM and inorganic matrix components. The relative standard deviation (RSD %) was calculated for solutions of 25 μg L⁻¹ with n = 15 measurements. The RSDs in soil extracts were inferior to the aqueous ones by a factor 2 to 13 depending on the element. Hence, conventional ICP-OES measurements using routine conditions without sample pre-treatment such as decomposition of organic carbon, matrix elimination and analyte enrichment showed insufficient sensitivity and reproducibility for the determination of low PGE concentrations. Our results clearly demonstrate the demand for a method with improved detection

<table>
<thead>
<tr>
<th>Elements in soil extracts</th>
<th>Known interference to (in ICP-OES)²⁶</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Calcium</td>
</tr>
<tr>
<td></td>
<td>(mg L⁻¹)</td>
</tr>
<tr>
<td>Pd</td>
<td>X</td>
</tr>
<tr>
<td>Pt</td>
<td>X</td>
</tr>
<tr>
<td>Rh</td>
<td>X</td>
</tr>
</tbody>
</table>

| Table 4 Composition of soil extracts obtained in the sorption experiment (X = major interference expected; x = interference expected) |
limits for the determination of PGEs in aqueous soil extracts and solutions obtained in sorption experiments.

3.3 A novel flow-injection (FI) procedure for analyte separation and enrichment

In a first step, we tested and optimised the flow-injection (FI) procedure using aqueous standard solutions, addressing the flow rate and HCl concentration of the sample solution in the conditioning step of the enrichment micro-column, the retention of the analytes on the sorbent, and the flow rate of their subsequent determination by ICP-OES. Subsequently, we further optimised the conditions for PGE measurements in real soil extracts by introducing a pre-treatment step for decomposition of DOM.

3.3.1 Optimisation of the FI procedure using standard solutions. As the target analytes Pt, Pd and Rh are retained as anionic chloro-complexes on the sorbent material (Al₂O₃) while (interfering) cations are deemed to pass through the column, proper adjustment of the HCl concentration in the samples is a prerequisite for complete PGE retention. We investigated the effect of the HCl concentration in a range of 0.006–0.06 M on PGE retention in the columns and found 0.0012 M HCl to be the optimal concentration. Below this value lower signals are observed, indicating incomplete chloro-complex formation and thus partial analyte retention on the sorbent. At larger concentrations, excess chloride ions competed with the PGE-chloride complexes for retention in the column, again resulting in incomplete PGE retention on the sorbent.

Similarly, we optimised the elution step to obtain complete removal of the PGEs from the column for subsequent analysis. To avoid the use of rather noxious eluents⁷ such as ammonia or cyanide⁸ or organic solvents⁹ which are frequently applied as eluents in column-based enrichment procedures for PGEs,²⁸ we decided to use HCl.²⁷,²⁸ Hydrochloric acid is operating as an eluent for PGEs by introducing competitive chloride anions in excess, which have a higher affinity to the sorbent material than the analyte ions. Using HCl as an eluent moreover helps to avoid alterations of the baseline by continuous eluent flow into the detection system. For optimising the procedure, we tested HCl concentrations in the eluent ranging between 0.3 and 1.2 M. At concentrations <0.3 M, elution was incomplete. Concentrations around 0.6 M improved the elution efficiency, still providing unsatisfactory broad peak shapes. The best peak shape was achieved using 0.9 M HCl as eluent solution. Larger concentrations entailed smaller peaks but caused signal suppression in the plasma.

3.3.2 Sample pre-treatment step for decomposition of DOM and further optimisation of the FI procedure for the measurement of soil extracts. To address possible interferences of large DOM concentrations in soil extracts with PGE measurements using the novel FI procedure, we designed and tested a microwave-assisted UV-digestion procedure. Previous findings suggest that DOM may impede the quantitative formation of anionic analyte-chloro-complexes,²⁷,²⁹ a prerequisite for complete retention of the PGEs in the micro-columns of the FI method. In preliminary experiments, we tested HCl concentrations ranging from 0.01% to 0.2% (v/v) for their effect on the PGE sorption to the vessel walls and the DOM degradation in the soil extracts by H₂O₂. In the case of low acidity (0.01% HCl solutions), incomplete degradation indicated by the maintenance of the yellowish-brown coloured solutions of the soil extracts and poor recovery caused by either losses in the quartz vessels or incomplete retention in the micro-column were determined. After the MW-assisted digestion with HCl concentrations ≥0.1% (v/v) however, colloid-free thoroughly transparent solutions were obtained. Furthermore, complete recovery of the PGEs in the spiked soil extracts compared to aqueous standard solutions was found, indicating that no sample losses occurred during sample pre-treatment and DOM has been removed efficiently. Thus, PGE addition for matrix-matched calibration could be conducted after the MW-assisted digestion step since HCl concentrations ≥0.1% (v/v) impeded analyte losses in the quartz vessels.

In contrast, the high acid content required for the quantitative elimination of DOM impeded quantitative retention of the formed chloro-complexes on the alumina columns as excess chloride competes with the anionic PGE chloro-complexes for sorption. We therefore neutralised the sample solutions by means of 1.15 M NaOH and 1.34 M NH₃ before application to the columns. To identify an optimum for the retention of the target elements on the enrichment column, NaOH and NH₃ additions to 5 mL solution were evaluated in a range of 15–120 µL and 10–80 µL, respectively. Moreover, various combinations of both bases (1 : 2, 1 : 4, 1 : 10) were investigated. Neutralisation using 40 µL NaOH for 5 mL sample solution resulted in the best recoveries of Pt and Pd, whereas 30 µL of NH₃ performed best for Rh.

The different bases required for sample neutralisation do not allow for simultaneous retention of Pd and Pt with Rh in the same column. Therefore, column 1 was assigned for the
separation and enrichment of Pd and Pt using NaOH, whereas column 2 and NH₃ were used for Rh. Flow rates for loading and elution were again optimised for this modified FI procedure, and detection parameters for ICP-OES measurement were recorded. For the elution process, the flow rates were varied from 0.6 to approximately 1 mL min⁻¹, pinpointing the best peak shape and areas at a flow rate of 0.8 mL min⁻¹ for an injected sample volume of 5 mL. After use, the micro-columns were rinsed with water and dried by pumping air through the system for storage.

### 3.3.3 Analytical figures of merit

As mentioned in Section 3.2, aqueous soil extracts contain several elements as well as DOM at elevated concentrations, which are known to interfere with PGE analysis by ICP-OES. Thus, for an accurate assessment of sorption envelopes, an efficient separation is required. To investigate the ability of the developed procedure for separation of the analytes from potential interfering elements, solutions of various concentrations of major and trace elements (Ca, Co, Cr, Cu, Fe, Mg, Mn, Sr, and Ti) were applied on the micro-column and the eluates measured by conventional ICP-OES analysis. Considering the applied amount of each analyte on the column and the measured concentration in the eluate, the separation efficiency has been calculated. Hence, minor and trace elements displayed a decrease of >97 to even >99% in most cases of the analytes at an applied sample volume of 25 mL at a concentration level of approximately 1 mg L⁻¹ analyte, with the only exception being Ti, for which 21–29% was determined in the eluate. In natural extracts, however, low Ti concentrations are expected due to its low solubility. Ca, Fe, Mg and Sr, on the other hand, were applied up to concentration levels of approximately 100 mg L⁻¹ and a volume of 25 mL to mimic concentrations worse than our soil extracts, demonstrating 99.4% (Fe) to >99.9% (Ca, Mg, Sr) lessening of the analytes in the eluate, respectively.

For signal quantification of the PGE measurements, external calibration with matrix-matched standards was performed. All experiments were conducted with spiked soil extracts to keep the matrix the same for the calibration and sample solutions throughout all measurements. To investigate the reproducibility and potential memory effects during measurement, several standard solutions were analysed in the course of a day’s measurement. Blanks and correlation solutions were carried throughout the whole procedure to identify potential effects of preparation, digestion and measurement on reproducibility.

For the calculation of the LODs, procedural blanks (soil extracts without spiked PGEs) were repeatedly measured to obtain a minimum of 7 measurements per micro-column. The LODs presented in Table 6 were calculated using the 3σ criterion.

<table>
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<tr>
<th>Table 6 Method detection limits and relative standard deviations obtained by the final FI procedure (n = 15)</th>
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<tr>
<td>Pd</td>
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<td>Pt</td>
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<td>Rh</td>
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Removing interfering inorganic and organic matrix components by the new FI procedure resulted in improved reproducibility, in particular 7%, 2% and 3% instead of 11%, 39% and 17% for Pd, Pt and Rh, respectively, although an even lower concentration was used for detection (10 μg PGE L⁻¹ instead of 25 μg PGE L⁻¹). In addition, a significant enhancement for the sensitivity was achieved, since the values shown in Table 6 represent method detection limits for the whole procedure (i.e., experiment, filtration, degradation and analysis), whereas the results reported in Table 5 represent instrumental values only.

We also evaluated the performance of the micro-columns. Numerous equally produced micro-columns did not show any significant differences between the columns in terms of reproducibility. Diverse sample volumes ranging from 4 to 10 mL containing 5 and 10 μg L⁻¹ PGEs were examined showing a linear correlation. The determined linear correlation between the obtained ICP signals and the used sample volume indicates that analyte losses due to complex leaching from the micro-column can be excluded up to a sample volume of 10 mL. Thus a further improvement of the LODs could be expected for increased sample volumes. With an applied sample volume of 5 mL, the columns show a linear range up to a concentration of 150 μg L⁻¹ PGEs with flattening of the slope at 200 μg L⁻¹ PGEs and a durability of approximately 190 to 200 measurements. Usual calculation of the enrichment factor by comparing the calibration slopes of the methods could not be performed since peak areas were obtained from the on-line procedure, whereas with standard procedures counts per second (cts s⁻¹) are obtained impeding a simple comparison. Thus, a theoretical enrichment factor of 6 was obtained by calculating the ratio of the applied sample volume of 5 mL and the elution volume derived from a peak width of approximately one minute at an eluent flow rate of 0.8 mL min⁻¹. In reality, an improved enrichment factor (EF) could be expected since on-line measurement of transient elution profiles usually leads to a further increase of sensitivity. For the characterisation and comparison of pre-concentration systems, the consumptive index (CI) was determined. The consumptive index is defined as the ratio of the sample volume V (mL) and the obtained enrichment factor (EF): CI = V (mL)/EF.³⁹ Thus, the consumptive index for our method is 0.83 mL, which indicates efficient sample utilisation improvement compared to other pre-concentration methods for PGE determination.²⁶,³¹–³⁴

### 3.4 Application of the FI-procedure: adsorption envelopes of Pd, Pt and Rh in soil

#### 3.4.1 Determination of equilibration time

As little is known about the time required to obtain equilibrium for
The obtained dataset was used to calculate the amounts of the three elements. The solute concentrations of Pd, Pt and Rh were measured at two wavelengths (λ) for each element: 214.4 nm (Pt) and 343.4 nm (Rh). Since the data of both wavelengths showed good agreement, the more sensitive wavelengths (λ = 340.4 nm (Pd), λ = 214.4 nm (Pt) and λ = 343.4 nm (Rh)) were chosen for depiction of the results. Fig. 2 shows that a minimum of 90 hours equilibration was required to reach equilibrium for all three PGEs. The measured concentrations ranged from 12.1 to 77.2 μg L⁻¹ for Pd, Pt and Rh after 30 minutes and decreased to values <LOD. While Pd was quickly adsorbed, resulting in solute concentrations below the LOD of the conventional ICP-OES measurements after 3 hours, equilibration required 15 hours for Pt and >72 hours (5.6 μg L⁻¹) for Rh (Fig. 2). Hence, for the subsequent simultaneous sorption experiments, Rh was the decisive analyte. Considering its LOD and an interpolation predicting a trend from 72 to 96 hours, we decided to choose 93 hours as the equilibration time.

### 3.4.2 Adsorption envelopes (utilising the FI-procedure)

We applied the new flow-injection ICP-OES approach for measuring the solute concentrations of Pd, Pt and Rh after 93 hours of equilibration of PGE solutions with the experimental soil. The obtained dataset was used to calculate the amounts of the three PGEs adsorbed in the soil solid phase and fit adsorption envelopes (Fig. 3). As mentioned before, for depiction of the measured data, the more sensitive wavelength of each element was used. Sorption envelopes allow the prediction of element concentrations in the soil solution from the total concentrations in the soil solid phase which provides important information on its potential bioavailability and mobility in soil. For evaluating the accuracy of the measurements, we included multiple blank solutions (i.e., without soil) ranging from zero to 5000 μg PGEs L⁻¹.

The concentrations remaining in the solutions after 93 hours varied from values below the respective detection limits (Table 6) to tens of μg L⁻¹. Only for the sorption experiments with initial PGE levels of 3 and 5 mg L⁻¹ were elevated concentrations of 63, 758 and 3800 μg L⁻¹ (Pd, Pt and Rh respectively) found in the soil extracts. Sample concentrations exceeding the linear range of the calibration were properly diluted for measurements.

Compared to PGE adsorption observed for other soils from semi-arid soils and sediments, the experimental soil of our study adsorbed more than 99% of Pt and Pd even from a solution containing up to 5 mg L⁻¹. In contrast, the capacity of the soil for Rh adsorption reached a plateau at added solution concentrations of 1.5 mg Rh L⁻¹, with 24% of the added Rh being adsorbed at the highest addition.

According to literature, four general types of sorption envelopes or curves, i.e., S, L, H and C type, may be distinguished. The sorption of metals on the soil solid phase usually follows L-curved envelopes characterised by a non-linear sorption pattern and mathematically described by either the Langmuir equation or the van Bemmelen–Freundlich equation. The L-shaped envelope is delineated by a decreasing slope with increasing concentration as the number of available adsorption sites is decreasing with increasing binding of the adsorbent. For the S-type curve, the slope initially increases with adsorptive concentration, but eventually decreases and reaches zero when available adsorption sites are totally occupied. This type indicates that at low concentrations the affinity of the surface for the adsorptive is low, but it increases at higher concentrations. The H-shaped isotherm is a special type of the L-shaped curve, where a plateau and thus saturation of the soil is not reached. It is specific for strong adsorbate–adsorptive interactions, typically caused by the formation of inner-sphere complexes. The C-type can either occur due to constant distribution of the adsorptive between the interface area and the soil solution or because of a proportional increase of the adsorptive surface when concentration increases, for instance when the adsorbent is creating new adsorptive surfaces by itself. It is independent of the concentration until the maximum adsorption is reached.

Interestingly, for sorption of PGEs to the experimental soil, each element follows a different type of envelope. While Pd and Pt can be described by H- and L-shaped isotherms, respectively, Rh shows S-type behaviour. The H-type isotherm, which describes the course of Pd in soil, is an extreme version of the L-shaped isotherm, indicating a very high affinity of the soil for this element. van der Waals interactions of adsorbates with large organic molecules and inorganic polymers may cause
H-shaped isotherms. The L-shaped isotherm, which is the most common and most widely used, is the result of the high affinity of the metals towards the soil at low surface coverage. Within the experimental range of the solution concentration, the characteristic decreasing slope with increasing concentrations is only displayed partially by Pt, as the saturation concentration (plateau) was not reached. The adsorption of Rh is best described by S-type, indicating different influences on the interaction between the adsorbate with the soil solid phase and the dissolved Rh compounds, leading to the characteristic sigmoidal shape. The initial small incline of the slope might be explained by complexation of Rh by DOM retaining this element in solution. As soon as the Rh concentration exceeds the complexing capacity of DOM, sorption strongly increases; the part where the isotherm reaches saturation could be explained by the competition with other elements in solution.16

The sorption envelopes indicate that Pd solubility in the experimental soil is limited over a wide range of added Pd. Therefore uptake in and toxicity to plants and micro-organisms as well as leaching into groundwater is expected to be of minor concern even in highly affected soils such as along roadsides. In contrast, Rh is adsorbed to a much lesser extent, suggesting higher potential of transfer to groundwater and uptake in and toxicity to biota. However, not only soil characteristics but also the activities of soil microorganisms, plants and soil animals may influence the solubility of elements in soil, thus further enhancing the complexity of the system.

4 Conclusion

The inherent limitations of conventional analytical methods such as matrix effects have limited the investigation of the fate of PGEs in soils and other environmental media at realistic, i.e. typically low concentration ranges. We developed and tested a novel FI procedure for PGE measurements in aqueous soil extracts using ICP-OES. The method simultaneously enriches the target analytes and separates them from inorganic interfering elements such as Fe, Mg and Mn on Al2O3 micro-columns of the FI-system while avoiding the use of noxious reagents during the analysis. Moreover, we introduce a pre-treatment step to digest interfering DOM by H2O2 in a HCl milieu in a microwave assisted UV-digestion procedure. A current drawback of the proposed method relates to the need for a readjustment of the sample pH after this digestion, which necessitates different reagents for Rh (NH4)3 compared to Pd and Pt (NaOH). As a consequence, Rh enrichment requires a separate micro-column.

The novel FI procedure proved to be useful for studying PGE solubility and sorption in an experimental soil. The much improved LODs for the FI-method as well as the prevention of interferences as compared to conventional ICP-OES measurements allowed for the determination of PGE concentrations in the low μg L−1 range apart from the large DOM, Fe, Mg and Mn concentrations in the aqueous soil phase. The combination of parallel valves furthermore enabled a high sample throughput for quick and time efficient measurements. Improvements of sensitivity and reproducibility of the analysis allowed us to establish sorption envelopes for all three PGEs with good coverage of the relevant concentration ranges. The extension of data availability in the low concentration range enabled us to identify the differential sorption behaviour of the elements in the experimental soil, a prerequisite to assess the potential risk of PGE transfer into the food chain and leachability into groundwater. It is believed that the novel method presented here will prove useful in further studies of the fate of PGEs in soils and similar environmental samples. Combined with ICP-MS, improved sensitivity could be obtained, allowing even PGE measurements of soils in the low (natural) background range.

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