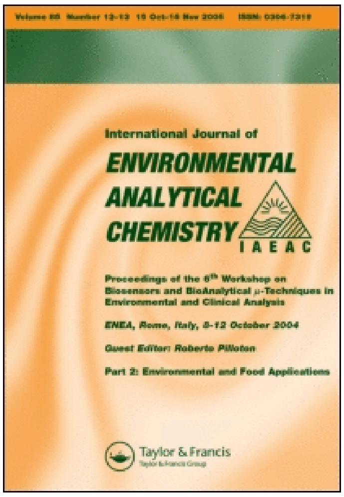

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Investigation of the solubilization of car-emitted Pt, Pd and Rh in street dust and spiked soil samples

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To cite this Article Ljubomirova, Valentina , Djingova, Rumyana , van Elteren, Johannes T. , Veber, Marjan , Kowalkowski, Tomasz and Buszewski, Boguslaw(2008) 'Investigation of the solubilization of car-emitted Pt, Pd and Rh in street dust and spiked soil samples', International Journal of Environmental Analytical Chemistry, 88: 7, 499 — 512
To link to this Article: DOI: 10.1080/03067310701809136
URL: http://dx.doi.org/10.1080/03067310701809136

Intern. J. Environ. Anal. Chem.
Vol. 88, No. 7, 15 June 2008, 499–512

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Investigation of the solubilization of car-emitted Pt, Pd and Rh in street dust and spiked soil samples

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(*Received 9 October 2007; final version received 14 November 2007*)

A sequential extraction procedure (three-step), proposed by the Standards, Measurements and Testing Programme (formerly BCR) of the European Union, was applied to street dust and spiked soil samples for the determination of PGEs. Analyses were carried out using inductively coupled plasma-mass spectrometry (ICP-MS). The results indicate that up to 5% from Pt, 70% from Pd and 14% from Rh are in mobile forms in street dust. The results for the soil samples spiked with crushed catalytic converter are significantly lower indicating that PGEs are oxidised more efficiently in natural conditions. Additionally Pt and Pd bound to humic acids were investigated.

Keywords: PGEs; BCR extraction scheme; speciation; soil; street dust; ICP-MS

1. Introduction

Interest in the determination of platinum, palladium and rhodium (platinum group elements, PGEs) in environmental materials has increased since the introduction of automobile catalytic converters, which are designed for the removal of carbon monoxide, unburnt hydrocarbons and nitrogen oxides from vehicle exhausts [1]. The PGEs present in the catalytic converters are known to be released during car operation, possibly due to abrasion mechanisms [2]. As a result, elevated concentrations of PGEs have been found in samples of airborne particulate matter [3], soil and dust [3,4], sediments [5,6], plants [7–10], human body fluids [11], etc.

The accurate determination of PGEs has been one of the difficult tasks in analytical chemistry because of their ultra-trace concentration in most geological, environmental and biological samples [12]. Inductively coupled plasma mass spectrometry (ICP-MS) is one of the most sensitive analytical techniques presently available for PGEs determination at trace levels generally having detection limits in the order of $\mathrm{ng\,g^{-1}}$ [6,9,13–17]. It is even more difficult to study the behaviour of PGEs in environmental systems which demands speciation investigations. However, in comparison with bulk analysis, speciation data can provide more important information about the origin, fractionation, transportation and alteration of PGEs in nature. The behaviour of PGEs depends on many parameters such as the size of the emitted particles, the form in

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ISSN 0306–7319 print/ISSN 1029–0397 online

DOI: 10.1080/03067310701809136
http://www.informaworld.com

which they are bound chemically to soil phases, as well as the soil conditions (pH, concentration of clay minerals and humic substances). The traffic-emitted PGEs occur in the form of metals or oxides of extremely small size (nm) and are considered as mostly inert under atmospheric conditions [18]. However, in contact with water or soil their reactivity can increase significantly. Lustig *et al.* [19] demonstrated that humic substances present in soil may dissolve Pt nanoparticles and form metal organic complexes. The behaviour of Pt compounds in soil is reported to be dependent on chemical (oxidation state and degree of complexation) [19] and physical (colloidal particle size) [20] characteristics.

The scarcity of information on the speciation and solubility of PGEs under real environmental conditions and the possible toxicological effects impose the necessity for further investigations in order to study the biotransformation processes, the ecotoxicological effects and the health hazards of the emitted PGEs. Only a few studies deal with platinum speciation, using hyphenated techniques for separation and quantification of Pt species [21–27]. Some other studies investigate association of PGEs with soil phases using sequential extraction schemes [6,28]. The procedures involves subjecting a solid sample (soil or sediment) to successive attacks with reagents possessing different chemical properties (acidity, redox potential, or complexing properties) in which each subsequent extract includes a part of the trace metals associated with a respective, stronger binding, soil phase [29]. Wei and Morrison [28] and Fliegel *et al.* [6] although using very different extraction schemes chose the same approach measuring Pt not in the extracts after each stage of the procedure but in the residue claiming high matrix effects in the solutions. The results reported in both papers indicate different dominating forms of Pt bonding in the investigated tunnel dust, street dust and gully samples. Additionally data about the type of bonding of the other PGEs are even scarcer.

The aim of the present paper is to present additional data on the solubility, mobility and speciation of Pt, Pd and Rh in the environment by means of the improved BCR sequential extraction scheme used for the determination of PGEs in soil samples, spiked with catalytic converters, Pt-chlorocomplexes species and in street dusts from different sites in Germany. The chosen extraction scheme is an operationally defined and standardised procedure [30,31], in which the reagent used at each stage is intended to release metals associated with a particular soil phase such as acid-soluble, reducible, oxidizable and residual.

Additionally the most probable Pt and Pd-humic acid species are investigated.

2. Experimental

2.1 *Samples and sample preparation*

A description of the samples and sampling sites is presented in Table 1. The soil samples were collected from two different regions in Bulgaria (Brown forest – south Bulgaria and Carbonic chernozem – North Bulgaria). The soil samples were sieved through a 2-mm PTFE sieve and well homogenised. Two kilograms of each type of soil were spiked with Pt (Pd) catalytic converter previously crushed and homogenised in a PTFE ball mill. The concentration of Pt (Pd) in the converter material was determined after total digestion both by the present method and by ICP-AES measurement (instrumental parameters given in Kovacheva and Djingova, 2002) [32] and were $750\,\mu g\,g^{-1}$ and $6000\,\mu g\,g^{-1}$, resp Since the concentrations were high enough and within the possibilities of ICP-AES this was a good opportunity to check the accuracy especially in the

Table 1. Soil samples, spiked with different Pt-species.

Soil type	Spiked of Pt or Pd	Pt or Pd added ($\mu g\,g^{-1}$)	Pt or Pd found* ($\mu g\,g^{-1}$)
Brown forest (pH 7.2)	Pt-catalyst	110	114 ± 4
	Pd-catalyst	150	148 ± 5
	K_2PtCl_4	14	14.1 ± 0.2
	K_2PtCl_6	20	21.3 ± 1.5
Carbonic chernozem (pH 8.0)	Pt-catalyst	50	50.8 ± 1.6
	Pd-catalyst	75	74.5 ± 1.8
	K_2PtCl_4	7	6.03 ± 1.04
	K_2PtCl_6	8	8.08 ± 1.04

Notes: *Determined by ICP-MS after MW-digestion.

determination of Pd where the interferences in ICP-MS might create a problem. The converter material was then mixed with the soils and well homogenised. Another batch of the above mentioned soil types was spiked with different Pt species and well homogenised. The added quantity of Pt (Pd) is given in Table 1. The spiked soil samples placed in flowerpots were irrigated with tap water at regular intervals. The street dust samples and sampling sites are described elsewhere [9].

By means of a riffler (ENDECOTTS, London, England) representative aliquots of 0.5 g of the samples were taken out.

2.2 *Reagents*

Suprapur chemicals and double deionised water (MilliQ) were used for preparing all solutions. Working standard solutions were prepared from multi-element calibration solution-III (Merck) by appropriate dilution in the respective matrix for each step. Blank determinations were run by using the same reagents in equal quantities as described in the analytical procedure throughout the experiment.

2.3 *Instrumentation*

Metal determination in soil extracts and digests was carried out using an Agilent 7500ce Series ICP-MS system with Babington nebulizer. The spectrometer is equipped with a collision reaction cell (CRC) for removal of multi-element interferences using He in an octopole reaction cell. The spectrometer is optimised to provide minimal values of the ratios CeO^+/Ce^+ and Ba^{2+}/Ba^+ and optimal intensity of the analytes. External calibration was performed. The calibration coefficients for all calibration curves were at least 0.99. The optimum ICP-MS measurement conditions for measurement of the elements of interest are given in Table 2.

A centrifuge (CENTRIC 322A, Tehtnica, Slovenia), for complete separation of the extracts from the residues, a mechanical rotator of the end-over-end type (Laboratoijsko mešalo, AC 220V, motor 12 VDC, Slovenia) and a pH meter (Iskra, MA 5736, Slovenia) were used throughout all the experiments. For the microwave digestion of the samples, a High Performance Microwave digestion system (MILESTONE mls 1200 mega) was used. The conditions are presented in Table 3.

Table 2. Measurement conditions for ICP-MS (Agilent 7500 ce).

RF power	1500 W
Ar plasma gas flow rate	15 L min^{-1}
Ar carrier gas flow rate	0.9 L min^{-1}
Ar makeup gas flow rate	0.15 L min^{-1}
He gas flow rate (octopole)	5 mL min^{-1}
Sampling depth	9.5 mm
Sampler cone	1 mm
Skimmer cone	0.4 mm
Peak pattern	Three points per mass
Measured masses (integration time per mass)	Cu-63 (0.15 s), Zn-66 (0.15 s), Sr-88 (0.15 s), Y-89 (3.0 s), Rh-103 (6.0 s), Pd-104 (6.0 s), Pd-105 (6.0 s), Hf-178 (0.15 s), Pt-194 6.0 s), Pt-195 (6.0 s)
Number of repetitions	2
Rinse solution	2% HNO_3

Table 3. Program for microwave digestion of soil and street dust samples.

Step	Time (min)	Power (W)
1	2	250
2	2	0
3	5	250
4	4	400
5	3	600

The evaluation of the accuracy in the determination of Pt, its concentration in the humic acid extracts and digests were measured independently with atomic absorption spectrometer with electrothermal atomization (Perkin Elmer Analyst 800, Shelton, USA). The quantitative analysis was carried out both by standard calibration and standard addition method.

2.4 *Spectral interferences*

The following equation was used for introducing corrections for interferences:

$$\mathrm{Scorr} = \mathrm{Smeas} - (\mathrm{Sinter}\,\mathrm{A}) \tag{1}$$

where Scorr is the corrected signal of the analyte, Smeas is the measured signal, Sinter the signal of the interfering element and A is the % formation of the respective interfering species (e.g. oxide).

For calculations the values of A are determined in model solutions with appropriate concentration of the interfering element and measured at the working conditions in Table 2.

To determine Sinter the interfering elements were measured in each samples and the isotope abundance was accounted for.

The determination of Pt, Pd and Rh was established for the most expected interferences. The isotopes of the measured interfering elements are shown in Table 2.

No significant interferences from HfO^+ was established in the determination of Pt (^{194}Pt and ^{195}Pt). The only isotope of rhodium ^{103}Rh was checked for interferences from $ArCu^+$ and SrO^+ and the % formation of the interfering species was $7.10^{-4}\%$ by $ArCu^+$ and 0.001% by SrO^+. The signal for Pd was mostly interfered by SrO^+(0.016%) for ^{104}Pd and for ^{105}Pd by YO^+(0.38%).

2.5 *Analytical characteristics-detection limits, precision and accuracy of the analysis*

The achieved detection limits (3σ) for Pt, Pd and Rh amount to $5.7.10^{-3}$, $5.4.10^{-3}$ and $1.9.10^{-3}$ ng/ml, respectively. It is possible to determine the elements in soil and street dust samples at background concentrations. The precision is in the interval 1–10%. Good reproducibility was obtained due to the homogeneous distribution of Pt, Pd and Rh after riffling in the samples.

The estimation of the accuracy is rather difficult since no reference material for sequential extraction of PGEs was available. Quality control was realised by parallel measurements of Pt and Pd by ICP-AES according [32] and ETAAS. Also, a confirmation for the accuracy of the present analysis is the lack of significant differences to the results obtained earlier for Pt, Pd and Rh in the street dust samples [9] using another version of ICP-MS [13], where additionally Pd has been determined after extraction.

The data obtained from ICP-MS and AAS determination of Pt in the humic acid extracts and digests were in very good agreement.

2.6 *The modified BCR three stage extraction procedure*

2.6.1 *Exchangeable metals*

Twenty milliliters of 0.11 mol L^{-1} acetic acid was added to dry 0.5 g soil and street dust samples in 50 mL polypropylene tubes. The mixtures were shaken for 16 h at 22 ± 3°C (overnight) at 30 rpm. The extracts were separated from the solid phase by centrifugation at 3000 rpm for 20 min. The supernatant liquid was decanted into 25 mL polyethylene tubes. The residue was washed by adding 20 mL double deionised water, shaking for 15 min on an end-over-end rotator and centrifuged at 3000 rpm for 20 min. The second supernatant liquid was discarded without any loss of residue.

2.6.2 *Metals bound to iron and manganese oxides*

Metals bound to iron and manganese oxides were extracted by adding 20 mL of freshly prepared 0.5 mol L^{-1} hydroxylammonium chloride (pH 1.5) to the residue from the first step. After shaking the mixture for 16 h at 22 ± 3°C (overnight), it was centrifuged for 20 min at 3000 rpm and then decanted into 25 mL polyethylene tubes. Using 20 mL of double deionised water, the residue was washed by shaking for 15 min on an end-over-end rotator, centrifuged at 3000 rpm for 20 min and the supernatant discarded.

2.6.3 *Metals bound to organic matter and sulphides*

Ten milliliters of 8.8 mol L^{-1} hydrogen peroxide was carefully added in small aliquots to the residue in the centrifuge tube. The vessels were loosely covered with the caps and the tube ingredients were digested at room temperature for 1 h with occasional manual shaking. The covers were removed and the digestion procedure was continued for 1 h at 85°C in a water bath till the volume was reduced to less than 3 mL. A second aliquot of 10 mL of hydrogen peroxide was added to the residue and the digestion procedure was repeated till the volume of the liquid was reduced to about 1 mL. Afterwards 25 mL of 1.0 mol L^{-1} ammonium acetate (adjusted to pH 2.0 with concentrated nitric acid) was added to the cool moist residue. The sample solutions were shaken and centrifuged, and the extracts were separated as described above.

2.6.4 *Aqua regia digestion*

About 0.5 g of the sample is placed in a Teflon pressure vessel and 6 mL aqua regia is added. The closed vessels are introduced in a microwave oven assisted sample digestion system and subjected to the microwave dissolution protocol given in Table 3. After cooling, the content of the pressure vessels is quantitatively transferred in 50 mL polypropylene tubes by washing with double deionised water and centrifuged. Afterwards the supernatant was decanted diluted to 35 mL with double deionised water. Before analysis 1 mL of the sample is taken and diluted to 10 mL with double deionised water.

2.7 *Extraction of humic substances from compost*

A volume of 10 mL of 0.1 mol L^{-1} sodium pyrophosphate was added to the dry compost sample (5 g), the mixtures were stirred for 1h at room temperature, centrifuged and the supernatant was transferred to a volumetric flask. The extraction was repeated four times, and the final volume was brought to 50 mL with double deionised water.

2.8 *Digestion of HA samples for total PGE determination*

Total Pt concentration was determined both directly in the HA-extract and after nitric acid digestion. The HA extracts were evaporated to less than 5 mL. Ten milliliters of sub boiled nitric acid (Chempur, 65%) and 2 ml H_2O_2 (30% pure p.o POCH, SA) were added to each sample and two blank samples were prepared containing only nitric acid and hydrogen peroxide. The samples were heated at 200°C on a Turboterm Block Digestor (Gerhardt) while adding 4 times sub boiled nitric acid and peroxide to digest remaining undigested humic acids. Once the digested samples were completely transparent and colourless they were boiled down to about 1 mL. The digested solutions were then transferred to 15 mL test tubes and diluted to 12 mL with distilled deionised water (18 MU cm^{-1}).

3. Results and discussion

3.1 *Soil samples, spiked with catalytic converter*

The results from the BCR extraction scheme show that Pt occurs in all fractions although the total extracted Pt is below 1% from the input. The lowest concentration is found in the exchangeable fraction which is about 0.01% and is almost equal in both types of soil. In the oxide fraction the concentration is higher and differs in the investigated samples. In the neutral soil the highest concentration of Pt is found in the organic phase. In the alkaline soil the concentration of Pt in the oxide fraction is slightly higher than in the organic fraction. In spite of this, there is not a significant difference in the reported values and it can be concluded that the solubility of Pt in soils spiked with catalytic converter does not depend strongly on the characteristics of the investigated soil types.

A higher degree of solubility (about 2%) is obtained for Rh. Similar to Pt, the results show the trend in the behaviour of Rh in the investigated soils. The percentage of extracted Rh in each step is comparable between the soil samples and increases from the exchangeable to the organic fraction. Organically bound Rh amounts to ~1%.

The total solubility of Pt and Rh amounts up to 0.37% and 1.49%, respectively for the neutral soil and 0.47% and 1.86%, respectively for the alkaline soil. These results are considerably higher compared with literature data (0.01–0.025% for Pt) and 0.05% for Rh, but they confirm that the relative solubility of Rh is higher than that of Pt, and that the Pt:Rh ratio fluctuates between 1 and 4 [33].

The highest solubility was established for Pd (27% in brown forest and ~65% in chernozem). Similarly to Pt and Rh the lowest concentration is found in the exchangeable fraction, and the extracted percentage is comparable with that of Rh for both types of soil. The highest concentration of Pd is found in the Fe/Mn-oxides fraction (15% for forest soil and 48% for chernozem) followed by the percentage in the organic fraction which resembles the typical environmental behaviour of heavy metals. The percentage of Pd in the oxide and the organic fractions, as well as of the total leached quantity differ significantly between the two soil samples, which shows that in contrast to Pt and Rh, the solubility of Pd depends on the soil characteristics.

3.2 *Street dust samples*

The results from the extraction of street dust samples are presented in Table 5. In contrast to soils samples no Pt is found in the exchangeable fraction. The extracted percentage in the oxide fraction is about 0.1% with the exception of Saarbrucken street dust, which reached 1.4%. The highest percentage was leached in the organic fraction and varies from 1% to 5% for the different samples. Thus, the total quantity of mobile Pt is less than 10%.

The comparison of the results with literature data shows, that the present results are significantly lower. Wei and Morrison [28] report 15% exchangeable, 10% carbonate, 32% Fe/Mn oxide and 26% organic bound Pt in road sediments and only 17% residual Pt. On the contrary the results of Fliegel *et al.* [6] indicate no Pt in the organic fraction of tunnel dust and about 30% in the easily mobilised fraction (carbonate fraction). Thus the present results confirm the data of Wei and Morrison [28] that a certain part of emitted Pt is converted to some organic complexes in the dust. It might be possible that the variation from the results of Fliegel *et al.* [6] are due to the different types of investigated samples – tunnel dust and street dust. It might be that in street dust transformations of Pt occur more easily than in tunnel dust, street dust being subjected to stronger and more direct climatic and anthropogenic influence (rain, snow, sun, splash etc.).

A higher degree of solubility (10–22%) was observed for Rh. In one of the street dust samples the highest percentage of Rh is established in the exchangeable fraction while in the other two samples (A-1 and A-61) Rh is mainly bound to Fe/Mn-oxides. Rh in the organic fraction is negligible (in A-61 it is 1.3%).

The highest solubility is observed for Pd. A significant part is leached in the exchangeable step, especially in the Saarbrucken street dust – 70%. The behaviour of Pd is similar to Rh in each street dust. In contrast to Pt which increases from the exchangeable to the organic fraction in all the street dust samples, Pd is established either in the exchangeable fraction (~70% in Saarbruecken) or in the oxide fraction (~61% in A-1). In A-61 the highest percentage is leached in the second fraction (both for Pd and Rh). Pd in the organic fraction is almost constant in all samples – about 4%. Thus Pd in the street dust samples has similar behaviour to Rh and not Pt.

Thus the trend in the behaviour of Pt is similar in the spiked soil and in the street dust samples. It increases from the exchangeable to the organic fraction and seems that the solubility and the formed species do not depend on the particular matrix. However in natural conditions the mobility of Pt is much higher than in the spiked samples.

In contrast to Pt, there is a difference in the behaviour of Rh in the soil and the street dust samples. In the soil samples, it behaves similar to Pt. In the street dust samples the lowest quantity is leached in the organic phase, which shows that the solubility depends on the matrix characteristics.

In contrast to the spiked samples where Pd was leached predominantly in the oxide and organic fractions in street dust it was established mainly in the exchangeable and oxide fractions. In the street dusts Pd is mobilised much more than in spiked samples similarly to Pt and Rh.

The results, obtained from street dust samples, show the great importance of using real samples instead of spiked model samples. The higher percentage of mobilised PGEs in street dust samples, compared with the spiked soil samples might be explained by several reasons: the transformation of emitted platinum into bioavailable species is a long-term process [19,34] and thus the 4 months of the present experiment were probably not enough for the species transformation in the spiked soils. Besides platinum in fresh automobile catalyst is not only present in metallic state, but also in the form of oxides, chlorides and bound to hydrocarbons [35], sulfur in the fuel might bind to Pt, which could increase the solubility of Pt [36] and lead to the higher levels of oxidised Pt in the real samples, compared with the soil samples, spiked with crushed catalytic converter. Examination of the released particulates showed that approximately 99% of Pt is in the metallic state with approximately 1% present as oxidised Pt, presumably in the form [37] of Pt^{4+}. The more efficient oxidation of Pt in this matrix can be related also to its nanocrystalline pore size and ultrafine dispersion which is in good agreement with other literature data [19,20,34]. It is worth mentioning that although the percentage of Pd leached in each step differs in the soil and the street dust samples the trend is the same. The highest concentration is found in the second fraction, followed by the third fraction. In the Saarbrucken street dust the highest percentage of Pd was established to be exchangeable, the same as for Rh.

The observation that PGEs are oxidised in soil and street dust samples to a significant degree as well as that the greatest part of platinum is eluted in the organic phase initiated further investigation of the probable platinum complexation to humic acid (Section 3.4).

3.3 *Soil samples, spiked with solutions of K_2PtCl_4 and K_2PtCl_6*

In the soil samples, spiked with Pt ions the trend of solubility of Pt is the same as in the previously discussed samples – it increases from the exchangeable to the organic fraction.

The lowest level of Pt is found in the exchangeable fraction and there is not a significant difference between the investigated types of soil (about 3% in the brown forest and about 5% in the carbonic chernozem soil) irrespective of the initial Pt ion.

Pt bound to Fe/Mn-oxides is higher and dependant on the soil type but independent on the type of ion.

A very high percentage of Pt (42 – 62%) is found in the organic fraction, independently of the soil type. This result indicates that when in ionic form (no matter if Pt^{2+} or Pt^{4+}) Pt predominantly forms organic complexes within the soil. The most probable organic-Pt complexes reported in the literature are Pt-humic acid complexes.

3.4 *Investigation of Pt-humic acid complexes*

The formation of platinum-humic acid complexes in soil samples was assumed already in the literature [19,34,38]. Experiments investigating the solubilization of metallic Pt black and tunnel dust-platinum by humic acid resulted in 0.12% of Pt black and 4.2% of tunnel dust-platinum. Recoveries of the chloroplatinates K_2PtCl_4 and $Na_2PtCl_6 \cdot 6H_2O$ in aqueous humic acid were 33% and 22% after 30 days [34]. Experimental work undertaken to illustrate the organic processes and the reaction timescale examined various reactions including those between Pt and Pd foil and humic and fulvic acids. Up to $195\,\mu g\,L^{-1}$ Pt and $102\,\mu g\,L^{-1}$ Pd in humic acid solutions exposed to metal foils were established for about a year at room temperature. These reactions appear pertinent to those that may occur between the PGE particles ejected by vehicle exhaust catalyst and the natural environment [39]. Wood [42] reports the formation of complexes of Pt with fulvic acid and indicates the extremely limited number of studies of the interaction of PGEs with humic substances which plays a very important role in the transport and fixation of metals in soils [39–42]. The identity of those complexes that are significant carriers of the PGE is unknown and the toxicity of the PGE-bearing complexes cannot therefore be determined [39].

3.5 *Extraction of humic substances from compost*

While choosing the extraction conditions for the analysis of compost, two aspects have to be considered: (i) the humic substances should be efficiently leached, possibly without changing their natural structure; and (ii) the native binding of the elements should not be altered. Because of the dissociation of carboxylic and phenolic functional groups, generally better solubility of humic substances is observed at elevated pH values using $0.1\,mol\,L^{-1}$ sodium pyrophosphate and $0.1–0.5\,mol\,L^{-1}$ sodium hydroxide and these leaching solutions are commonly used for soils, sediments and compost [43,44]. Furthermore, these two solutions have been used to obtain data on the amount of elements that were bound to organic matter. However there is some controversy over which of the extractants is more suitable: the use of sodium hydroxide has been criticised because of possible oxidation of humic constituents or hydrolysis of the elements and their readsorption on the reactive surface sites. Sodium pyrophosphate is thought to form ternary complexes between pyrophosphate and metal humate adducts. This can help in stabilising the metal humates in the extraction medium. Although the use of sodium pyrophosphate

Table 4. Results from the sequential extraction, aqua regia digestion and humic acid determination in soils spiked with catalytic converter.

	Elemental concentration in brown forest soil ($ng\,g^{-1}$)					Elemental concentration in carbonic chernozem ($ng\,g^{-1}$)				
El.	Fraction I	Fraction II	Fraction III	Me-HA	Aqua regia $\mu g\,g^{-1}$	Fraction I	Fraction II	Fraction III	Me-HA	Aqua regia $\mu g\,g^{-1}$
Pt	13.4 ± 4.6 **0.011%***	180 ± 12 **0.156%***	235 ± 29 **0.203%***	80.68 ± 0.87 **34%****	116 ± 6	7.21 ± 0.83 **0.014%**	134 ± 8 **0.26%**	101 ± 6 **0.196%**	42.97 ± 0.48 **43%****	52 ± 2
Rh	23.72 ± 5.02 **0.1%***	102 ± 8 **0.425%***	233 ± 28 **0.97%***	Not analyzed	24 ± 1	9.84 ± 1.28 **0.1%***	60.4 ± 3.6 **0.59%***	120 ± 6 **1.17%***	Not analyzed	10.0 ± 0.3
Pd ($\mu g\,g^{-1}$)	0.175 ± 0.038 **0.118%***	22.5 ± 1.5 **15.2%***	17.5 ± 2.1 **11.8%***	4.81 ± 0.16 **28%****	148 ± 13	0.094 ± 0.014 **0.126%***	35.7 ± 4.3 **48%***	12.7 ± 0.6 **17%***	7.3 ± 0	74 ± 4

Notes: *- % from the total concentration; **- % from the organic fraction.

could mitigate this problem the probability of structural changes in the humic substances might increase bridging effects [45].

Extraction of humic acid complexes was done as described in Section 2.6. The results are presented in Tables 4 to 6 as Me-HA both as concentration (ng g^{-1}) and as a percentage from the organic fraction (third fraction in Tables 4 to 6) of the respective spiked soil or street dust.

The Pt-HA is between 10 and 65% of the respective organic fraction depending on the sample type. Unexpectedly low Pt-HA is established in the soils spiked with Pt^{2+} and Pt^{4+} although the highest percentage of organic bound Pt was established in these samples. Obviously other types of Pt-organic complexes are formed between the Pt ions and the soil components. While there is no difference in the behaviour of both Pt ions in the forest soil there is a significant difference in the percentage of Pt-HA in chernozem formed by spiked Pt^{4+} (31%) and Pt^{2+} (10%). Obviously as already established by the sequential extraction, the soil type plays a significant role when solutions of Pt species are spiked in the soil.

A higher percentage of Pt-HA from the respective organic fraction is established in the soil spiked with catalytic converter (34% for forest soil and 43% for chernozem) the percentage in chernozem being higher.

Table 5. Results from the sequential extraction, aqua regia digestion and humic acid determination in street dust samples.

		Elemental concentration in street dust (ng g^{-1})		
Element	Fraction	Saarbrucken	A-1	A-61
Pt	I	ND***	ND***	ND***
	II	1.90 ± 1.16	0.35 ± 0.02	0.35 ± 0.03
		1.41%*	**0.12%***	**0.12%***
	III	6.93 ± 0.10	2.31 ± 0.05	6.31 ± 0.16
		5.13%*	**0.76%***	**2.25%***
	Pt-HA	3.29 ± 0.02	1.12 ± 0.47	4.08 ± 0.01
		48%**	**48%****	**65%****
	Aqua regia	135 ± 15	303 ± 40	280 ± 20
Rh	I	2.16 ± 1.08	3.49 ± 0.21	1.61 ± 0.11
		7.2%*	**8.31%***	**4.03%***
	II	0.60 ± 1.22	6.06 ± 0.73	2.21 ± 0.18
		2.0%*	**14.43%***	**5.53%***
	III	0.104 ± 0.028	ND***	0.517 ± 0.027
		0.35%*		**1.3%***
	Rh-HA	ND***	ND***	ND***
	Aqua regia	30 ± 5	42 ± 3	40 ± 2
Pd	I	62.98 ± 4.29	10.22 ± 1.68	3.08 ± 1.11
		69.98%*	**10.76%***	**3.76%***
	II	5.16 ± 1.61	58.42 ± 5.09	12.31 ± 1.07
		5.73%*	**61.49%***	**15.01%***
	III	4.28 ± 0.06	4.20 ± 0.43	3.60 ± 0.10
		4.75%*	**4.42%***	**4.39%***
	Pd-HA	4.31 ± 0.17	4.53 ± 0.55	3.23 ± 0.32
		100%**	**100%****	**90%****
	Aqua regia	90 ± 8	95 ± 2	82 ± 7

Notes: *- % from the total concentration; ** - % from the organic fraction; *** - not detected.

Table 6. Results from the sequential extraction, aqua regia digestion and humic acid determination in soils spiked with K_2PtCl_4, K_2PtCl_6.

	Elemental concentration in brown forest soil (ng g^{-1})					Elemental concentration in carbonic chernozem (ng g^{-1})				
Pt species	Fraction I	Fraction II	Fraction III	Pt-HA	Aqua regia µg g^{-1}	Fraction I	Fraction II	Fraction III	Pt-HA	Aqua regia µg g^{-1}
Pt^{2+}	454 ± 2 **3.12%***	795 ± 2 **5.46%***	6 914 ± 70 **47.5%***	1361 ± 26 **10%****	14.55 ± 0.56	311 ± 1 **5.08%***	1141 ± 9 **18.65%***	2580 ± 45 **42.18%***	268 ± 1 **10%****	6.12 ± 0.07
Pt^{4+}	649 ± 1 **3.01%***	1111 ± 6 **5.15%***	10760 ± 126 **49.85%***	1196 ± 13 **11%****	21.59 ± 0.32	371 ± 1 **4.52%***	1584 ± 14 **19.31%***	4 436 ± 38 **54.1%***	1383 ± 13 **31%****	8.20 ± 0.29

Notes: *- % from the total concentration; ** - % from the organic fraction.

Unexpectedly, the highest percentage of Pt-HA (48–65%) is established in the street dust samples although the organic fraction in the street dust is significantly less than in the soils spiked with Pt ions. It seems that the species emitted from catalytic converters are not in ionic form but in forms enabling the fixation by humic substances while other types of Pt-organic complexes are dominating in the spiked soil sample. Since to our best knowledge no other quantitative data are available in the literature; to further elucidate this problem investigations with HPLC-MS are in progress.

The trend for Pd-HA is similar to platinum. In soil spiked with catalytic converter Pd-HA is 28% from the organic fraction in brown forest soil and twice as high (57%) in chernozem. The percentage of Pd-HA in street dust is extremely high (90–100%) which indicates that all the Pd in the organic fraction is in the form of humic complexes.

4. Conclusions

The work presented here showed that metallic PGE, especially in natural conditions can easily be dissolved to a significant degree and bioavailable species can be formed.

Although higher mobility was established in natural conditions, the relative solubility increases in the order Pt < Rh < Pd, which is the same in the spiked soil samples and the street dust samples.

The results from the BCR extraction scheme showed that:

- Pd was mainly eluted in the Fe/Mn-oxides fraction;
- Pt forms mainly organic complexes both in the soil and the street dust samples; and
- In the spiked soil samples the greatest part of mobile Rh was eluted in the organic fraction in contrary to the street dust samples where the organically bound Rh is negligible or not determined at all. The data show that in the street dust samples Rh is found in the exchangeable and in the oxide fraction.

Investigations on the formation of humic acid complexes, showed that:

- In the street dust samples the main part of the organic Pd is bound to humic substances; and
- A significant part of the organic forms of Pt and Pd in the soil samples and Pt in the street dust samples were not identified.

In order to define the variety and the nature of the organic complexes of Pt and Pd further investigations are in progress by HPLC-MS.

Acknowledgement

One of the authors (Valentina Ljubomirova) is grateful to CEEPUS program for fellowships at the University of Ljubliana, Slovenia (CEEPUS NOPL-0004-05/06) and University of Torun, Poland (CEEPUS NO C11-PL004-02-0607-M-6415).

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