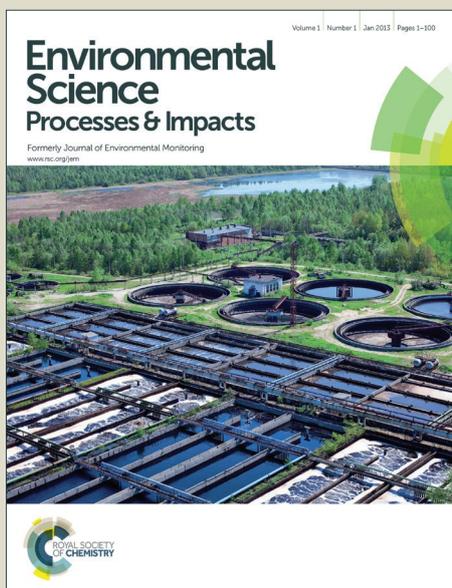


Environmental Science Processes & Impacts

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



rsc.li/process-impacts

1
2
3 Environmental concentrations of palladium (Pd) appear to be increasing at a greater rate relative
4 to the other platinum group elements, platinum (Pt) and rhodium (Rh), used in the control of
5 vehicular emissions. This study examines the effects of the organic complexing agents, L-
6 methionine and citric acid, on the geochemical behavior of Pd in soils and model substances. The
7 results confirm that Pd in soils readily complexes with organic chelating agents. The outer
8 atomic surfaces of Pd model substances were also observed to be partially oxidized when treated
9 with L-methionine and citric acid. The type of organic complexing agent used for experimental
10 purposes was determined to be the most important factor influencing solubility, followed by
11 solution pH and time of extraction.
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

[Type here]

6 Geochemical behaviour of palladium in soils and Pd/PdO model 7 substances in the presence of the organic complexing agents L- 8 methionine and citric acid

1 Received 00th January 20xx,
2 Accepted 00th January 20xx

3 DOI: 10.1039/x0xx00000x

4 www.rsc.org/

9 Fathi Zereini,^a Clare L.S. Wiseman,^{b,c,*} My Vang,^a Peter Albers,^d Wolfgang Schneider,^e Roland
10 Schindl,^f Kerstin Leopold^f

11 Abstract

12 Risk assessments of platinum group metal (PGE) emissions, notably those of platinum (Pt), palladium (Pd)
13 and rhodium (Rh), have been mostly based on data regarding the metallic forms used in vehicular exhaust
14 converters, known to be virtually biologically inert and immobile. To adequately assess the potential impacts
15 of PGE, however, data on the chemical behaviour of these metals under ambient conditions post-emission is
16 needed. Complexing agents with a high affinity for metals in the environment are hypothesized to contribute
17 to an increased bioaccessibility of PGE. The purpose of this study is to examine the modulating effects of the
18 organic complexing agents, L-methionine and citric acid, on the geochemical behavior of Pd in soils and
19 model substances (Pd black and PdO). Batch experimental tests were conducted with soils and model
20 substances to examine the impacts of the concentration of complexing agents, pH and length of extraction
21 period on Pd solubility and its chemical transformation. Particle surface chemistry was examined using X-ray
22 photoelectron spectroscopy (XPS) on samples treated with solutions under various conditions, including low
23 and high O₂ levels.

24 Pd was observed to be more soluble in the presence of organic complexing agents, compared to Pt and Rh.
25 Pd in soils was more readily solubilized with organic complexing agents compared to the model substances.
26 After 7 days of extraction, L-methionine (0.1 M) treated soil and Pd black samples, for instance, had mean
27 soluble Pd fractions of 12.4±5.9% and 0.554±0.024%, respectively. Surface chemistry analyses (XPS)
28 confirmed the oxidation of metallic Pd surfaces when treated with organic complexing agents. The type of
29 organic complexing agent used for experimental purposes was observed to be the most important factor
30 influencing solubility, followed by solution pH and time of extraction. The results demonstrate that metallic
31 Pd can be transformed into more bioaccessible species in the presence of organic complexing agents which
32 are ubiquitous in the environment.

33 A Introduction

34 Environmental concentrations of platinum (Pt), palladium (Pd) and
35 rhodium (Rh), which are used as exhaust catalysts to control
36 exhaust emissions, have been steadily increasing since automotive
37 catalytic converters came into widespread use in most
38 industrialized countries in the 1970s and 1980s.¹⁻¹⁰ Originally, Pt
39 emissions drew the most attention, as it tended to occur in higher
40 concentrations relative to the other platinum group elements
41 (PGE). Since the 1990s, a shift in the use of Pd over Pt as the active
42 catalyst in automotive catalytic converters has taken place,
43 however, resulting in relative increases of this noble metal in the
44 environment. In recent years, studies have demonstrated that Pd
45 now occurring at higher concentrations in environmental media

46 such as soils and dust in various countries such as the US,¹¹
47 Germany,² Bulgaria,¹² Brazil¹³ and Canada.¹⁴ Increased emissions of
48 Pd as a function of time have also been demonstrated by Sievers
49 and Schuster¹⁵ in their examination of tunnel dust. It is often
50 assumed that PGE are likely to have a low solubility and mobility
51 post-emission into the environment, as they are used in a metallic,
52 inert form in exhaust converters. Several studies have observed,
53 however, that PGE are soluble in environmental media and
54 bioaccessible to a variety of terrestrial and aquatic organisms.<sup>12, 16-
55 21</sup> In particular, Pd has been demonstrated to be more mobile and
56 readily bioaccessible compared to the other PGE.^{12, 22-25}

57 While gaps in knowledge continue to exist regarding the chemical
58 behaviour of PGE post-emission, several studies have shown that
59 PGE can be transformed into more reactive species in the presence
60 of various ions and common organic complexing agents.²⁶⁻⁴⁰ For
61 instance, Poprizki³⁸ reported an increased solubility of Pd in the
62 presence of Cl⁻ compared to NO₃⁻ and SO₄²⁻. Zereini et al.⁴⁰
63 confirmed the influence of these anionic species on Pt using a
64 platinum/aluminium model substance. Pd has also been shown to
65 form mobile complexes in various Cl⁻ rich solutions and in the
66 presence of O₂.^{33,34} Bruder et al.³⁹ measured a higher solubility for
67 PGE associated with urban airborne PM (PM₁₀) extracted with the
68 organic complexing agents L-methionine and
69 ethylenediaminetetraacetic acid (EDTA). Zereini et al.³⁵ also

^aInstitute for Atmospheric and Environmental Sciences, Department
Environmental Analytical Chemistry, Goethe University Frankfurt am Main,
Frankfurt am Main, Germany,

^bSchool of the Environment, Earth Sciences Centre, Rm. 1016V, 33 Willcocks St.,
University of Toronto, Toronto, Ontario, Canada M5S 3E8

^cDalla Lana School of Public Health, University of Toronto, Toronto, Canada

^dAQuora GmbH, Hanau-Wolfgang, Germany

^eUmicore AG & Co. KG, Hanau-Wolfgang, Germany

^fInstitute for Analytical and Bioanalytical Chemistry, University of Ulm, Ulm,
Germany

1 observed that metallic Pd in a model substance can be partially
 2 oxidized and transformed to PdOx ($x < 1$) when treated with EDTA in
 3 solution, using a combination of X-ray Photoelectron Spectroscopy
 4 (XPS) and Transition Electron Microscopy/Energy Dispersive X-Ray
 5 Spectrometry (TEM/EDX) techniques. Physiologically based
 6 extraction experiments provide further support for an increased
 7 solubility of PGE when exposed to simulated gastrointestinal and
 8 lung fluids.^{33-34, 41-42}

9 Overall, the results of various studies suggest that PGE are capable
 10 of being transformed into more mobile and bioaccessible species
 11 under ambient environmental conditions. Most studies have,
 12 however, conducted their experiments using commercially available
 13 model substances, standard reference materials and/or automotive
 14 catalyst material. Little data is available on the chemical behaviour
 15 of PGE post-emission under field conditions. As such, this highlights
 16 a need for experimental studies using field collected samples, to
 17 validate the existing findings of published studies. In light of this,
 18 the purpose of this study is to examine the chemical behaviour and
 19 transformation of Pd in field-collected soils treated with organic
 20 complexing agents, L-methionine and citric acid, employing isotope
 21 dilution (ID) ICP-Q-MS and XPS. L-methionine is an essential amino
 22 acid and plays an important role in plant metabolism.³⁹ Citric acid
 23 a low molecular weight organic acid commonly present in plants
 24 and can be released in significant quantities in soils via root
 25 systems.⁴³ For comparative purposes, chemical changes in the
 26 model substances Pd black and PdO are studied under the same
 27 experimental conditions. Palladium is the focus for two reasons: (1)
 28 available data on the chemical behaviour of this element in the
 29 environment is very limited, and (2) increases in the environmental
 30 concentrations of Pd have been shown to be greater relative to that
 31 of Pt in recent years.^{2, 11-15}

32 B Experimental

33 Materials

34 Soil samples ($n=6$) were collected directly along the Autobahn A5
 35 close to Frankfurt am Main, Germany, at depths of 0-3 cm. The A5
 36 is an 8 lane high traffic volume road with ca. 110,000 to 131,000
 37 vehicles/day (data from 2004, HSVV-Hessen). Two model Pd
 38 substances were used for experimental purposes: (1) Pd black,
 39 which is chemically similar to the bulk of the catalyst material used
 40 in exhaust converters, and (2) PdO, which is also present in catalytic
 41 converters. Pd black (99.36 % metallic Pd powder (Umicore)) has a
 42 specific surface area of 20 m²/g and a mean particle size ca. 22.2
 43 μm ($\pm 31.25 \mu\text{m}$).³⁵ PdO (99.9% in powder form (Aldrich, 520748-102
 44 5G), is finer, with a mean particle size of 4.49 μm ($\pm 5.88 \mu\text{m}$).³⁵ Two
 45 organic complexing agents with a high affinity for metals, which are
 46 commonly present in the environment, were used for experimental
 47 purposes: (1) L-methionine (Merck), and (2) citric acid (neo Lab.

48 Sample extraction and dissolution testing

49 Soil samples were air-dried, sieved to <2 mm and ground using an
 50 agate mill. About 1 g of sample material was transferred to dark
 51 brown, polyethylene bottles with 40 ml of 0.1 M L-methionine. The
 52 same was done with samples extracted with 0.1 M citric acid
 53 solutions. Extractions were done in triplicate with each respective
 54 solution. Samples were placed on a horizontal mixer (Laboshake
 55 300/16 (Gerhardt)) and alternately shaken for 15 minutes followed
 56 by 30 minutes rest for a total of 6 days at room temperature (23-25

°C). Samples were then filtered using cellulose-acetate membrane
 filters (pore size 0.2 μm (Sartorius AG)) to separate the solid from
 the liquid phase. Solid phase soil samples were digested in a
 microwave (MARS Xpress of CEM GmbH) with aqua regia (1:3 ratio
 of HCl to HNO₃ (Suprapur quality, Merck) for the determination of
 total Pd concentrations.

All samples (solid and liquid phase) were co-precipitated with Te
 according to the German Institute for Standardization's method DIN
 19741 to minimize molecular interferences in measuring Pd. Sample
 concentrations were measured using isotope dilution ICP-Q-MS
 (Varian 820-MS) in collision mode with He. Platinum and Rh
 concentrations were also measured in soil samples for comparison.
 Pd concentrations were calculated based on results for the isotope
 ratios ¹⁰⁵Pd/¹⁰⁶Pd, ¹⁰⁵Pd/¹⁰⁸Pd and ¹⁰⁵Pd/¹¹⁰Pd. The isotope ratios
¹⁹⁴Pt/¹⁹⁸Pt, ¹⁹⁵Pt/¹⁹⁸Pt and ¹⁹⁶Pt/¹⁹⁸Pt were used to determine Pt
 levels, while Rh concentrations were calculated based on the ¹⁰³Rh
 signal. The following instrumental set-up was used: plasma flow
 17.7 L/min, sheath gas flow 0.25 L/min, auxiliary flow 1.68 L/m,
 nebulizer flow 0.94 L/min, ICP RF power 1.40 kW, He gas flow 120
 ml/min.

Dissolution tests were also conducted with Pd and PdO model
 substances and the same organic complexing agents, citric acid and
 L-methionine, in separate batch experiments to assess the potential
 influence of solution pH, reaction time and ionic concentration on
 Pd solubility. Three different batch experiments were carried out in
 parallel with the respective extract solutions under the following
 conditions: (1) samples treated over a 6 day period with L-
 methionine and citric acid solutions of variable concentration
 (0.001, 0.01 und 0.1 M) at a constant pH (5.9 \pm 0.3 (L-methionine)
 and 2.2 \pm 0.3 (citric acid)) and dissolved O₂ concentration (8.4 \pm 0.03
 mg/L (L-methionine) and 8.3 \pm 0.02 mg/L (citric acid)), (2) samples
 extracted for 6 days with the respective complexing agents at
 variable pH levels (pH 6, 7, 8 and 9 for L-methionine and pH 2, 5, 7
 and 9 for citric acid, adjusted with the addition of NaOH) but at the
 same solution concentration of 0.1 M for both L-methionine and
 citric acid solutions, and (3) samples treated with a solution
 concentration of 0.1 M for both L-methionine and citric acid at pH
 of 7 until chemical equilibrium was reached. To determine this,
 sample aliquots were taken after the following time intervals: 6
 hours and 7, 14, 21, 42, 72, 100, 147, 190, 208 and 251 days. In
 addition to the batch experiments with organic complexing agents,
 the model substances were extracted with distilled water and
 NaClO₄ (0.1 M, pH 7) for comparison. Relatively high concentrations
 of L-methionine and citric acid were used for the extractions to
 effectively determine the effects of complexing agents on the
 solubility and chemical transformation of Pd. For each experiment,
 three parallel samples of the respective model substances (60 mg)
 were treated with 100 ml of solution at room temperature (23-25
 °C). Samples were alternately shaken for 15 min followed by 30 min
 rest during the reaction period. Following the extraction periods,
 samples were left undisturbed for 18 hours to settle. Sample
 aliquots of 50 to 100 μl were then transferred to centrifuge tubes,
 diluted to 10 ml with 0.5 % HNO₃ and centrifuged for 15 min at
 3500 RPM (Heraeus, Megafuge) prior to measurement.

The soluble Pd fraction was determined using ICP-Q-MS in collision
 mode with He using the same instrumental settings as described
 previously. It was not necessary to isolate and pre-enrich Pd in the
 sample extracts, as Pd is present at higher concentrations in the
 model substances and in a form with minimal matrix interferences.
³⁵

1 Particle surface chemistry analysis 58

2 Pd black samples (30 mg) were weighed and placed in capped, dark 59

3 brown polyethylene bottles with 20 ml of the respective organic 60

4 complexing agents, L-methionine solution and citric acid, at solution 61

5 strengths of 0.1 M. Samples were alternately shaken on a horizontal 62

6 mixer for 15 minutes, followed by 30 minutes rest, over two 63

7 different time periods of 6 and 251 days. 64

8 The solid (residue) phase was separated from the liquid phase of 65

9 treated samples using a blue ribbon filter for surface chemistry 66

10 analyses. Particle surface chemistry was analysed using XPS 67

11 (ESCALAB 250 Xi (Thermo Fisher Scientific)) to detect chemical 68

12 changes following the respective treatment periods. For this, 69

13 samples were placed on a tantalum sheet, introduced into the high 70

14 vacuum pre-chamber of the XPS spectrometer system and pumped 71

15 down at room temperature prior to analysis. The outer ca. 3-4 72

16 atomic layers of each single sample were analysed using targeted 73

17 monochromatic x-ray radiation (X-ray spot diameter: 900 μm) and 74

18 measuring the kinetic energy of the photo-emitted electrons.³⁵ 75

19 Measurements were carried out at Aqura GmbH, Hanau, Germany 76

20 More detailed information regarding XPS analysis can be found in 77

21 Reniers and Tewell⁴⁵ and Powell & Jablonski.⁴⁶ 78

22 Parallel Pd black samples were also treated with L-methionine and 79

23 citric acid solutions (0.1 M) under both O₂-rich and O₂-depleted 80

24 conditions in a separate experiment prior analysis using XPS. This 81

25 was done to assess differences in the chemical transformation of Pd 82

26 under aerobic and anaerobic conditions in aquatic systems. For this, 83

27 Pd black samples (30 mg) were placed in capped polyethylene 84

28 bottles with 50 ml of each respective organic complexing solution 85

29 Two different experiments were conducted with the respective 86

30 samples: (1) one where O₂ was added to sample solutions (8.6 mg 87

31 O₂/L), and (2) another with O₂ depleted solutions (1.8 mg O₂/L), 88

32 achieved by pumping N₂ into the samples. Samples were shaken 89

33 every 15 minutes, followed by 30 minutes rest, for 6 days. Following 90

34 the reaction period, sample residues were isolated from solutions 91

35 and analysed per XPS, as described above. 92

36 Samples treated under low O₂ conditions were prepared for XPS 93

37 measurement in a glove box with N₂, while those prepared with 94

38 higher O₂ levels were examined under ambient conditions. Pd 95

39 concentrations in sample solutions were determined using ID-ICP- 96

40 Q-MS. Pd black in untreated, powder form was measured via XPS 97

41 for control purposes. 98

42 Quality assurance and control 99

43 A number of steps were taken to ensure quality assurance and 100

44 control of sample preparation and analysis, also described in Zereini 101

45 et al.^{2, 35} Briefly, lab ware was pre-cleaned in acid baths, followed 102

46 by rinsing several times with purified water. All chemicals used 103

47 were of the highest grade (i.e. Suprapur quality, Merck). The 104

48 analytical methods employed are internationally recognized and 105

49 have been validated by rigorous testing methods (e.g. Round Robin 106

50 testing).^{2, 34, 47-50} 107

51 The following Pd isotopes were measured: ¹⁰⁵Pd, ¹⁰⁶Pd, ¹⁰⁸Pd and 108

52 ¹¹⁰Pd. The internal standards, ¹¹⁵In and ¹⁶⁹Tm (Merck), were used 109

53 for quality assurance and control. 110

54 Pd was measured in blanks of 0.5% HNO₃ (mean concentration: 111

55 0.021 \pm 0.012 $\mu\text{g/L}$), 0.1 M citric acid (mean concentration: 0.007 112

56 0.002 $\mu\text{g/L}$) and 0.1 M L-methionine (mean concentration: 0.144 113

57 0.042 $\mu\text{g/L}$). Pd standard solutions (certified level: 5 $\mu\text{g/L}$ Pd) were 114

also measured to validate instrumental accuracy (measured mean levels: 4.9 \pm 0.2 $\mu\text{g/L}$). The limit of detection (LOD), determined as 3 times the standard deviation of blanks, was 0.036 $\mu\text{g/L}$. This compares to the LOD given in the German Institute of Standardization's method, DIN 323645, of 0.028 $\mu\text{g/L}$.⁵⁰

XPS particle surface chemistry analyses were validated using reference data bases (certified values: Pd 3d5/2 (binding energy in eV): Pd (334.9 eV), PdO (336.3 eV), PdO₂ (337.9 eV), PdSO₄ (338.7 eV) and Pd(CN)₂ (339.2 eV). The binding energy scale for Au 4f7/2 (84.00 eV) was used for calibration.³⁵ The LOD was 0.1 atom-%.

C Results and discussion

Pd concentrations and behaviour in soils

The mean concentration of Pd in soil samples was 210 $\mu\text{g/kg}$ and ranged between 101 and 290 $\mu\text{g/kg}$. Mean levels of Pt and Rh were 14 and 4.4 $\mu\text{g/kg}$, respectively (min/max: 2.7/37 $\mu\text{g Pt/kg}$ and 2.5/6.4 $\mu\text{g Rh/kg}$). The results support recent studies which have observed a shift toward higher concentrations of Pd over Pt in various environmental media.^{2, 12, 14} Determined Pd concentrations are 20 times higher compared to levels measured in soils sampled in 1994 (mean: 8.9 $\mu\text{g/kg}$) along the same stretch of Autobahn close to Frankfurt am Main.³ Soil samples also collected from this site in 2004 had mean Pd levels of 83 $\mu\text{g/kg}$, representing an average 2.5-fold increase in Pd concentrations in the last 10 years.

This trend of increasing concentrations of Pd in soils over time can be attributed to the greater use of this PGE in automotive catalytic converters, including that for diesel-run engines.⁵¹ Similar trends have also been reported by Sievers and Schuster¹⁵ in their examination of Pd in tunnel dust over time.

Relatively high soluble Pd fractions were measured for soil samples treated with organic complexing agents, most notably with L-methionine. Soils extracted with 0.1 M L-methionine had a measured mean soluble Pd fraction of 12.4 \pm 5.9%. Pt and Rh solubility was lower, with means of 5.1 \pm 4.5 % for Pt and 1.4 \pm 1.2% for Rh. Soils treated with citric acid had comparatively lower soluble fractions of PGE, with mean levels of 7.3 \pm 4.3 % for Pd, 3.5 \pm 0.77% for Pt and 1.5 \pm 1.2 % for Rh (Figure 1). Pd solubility was twice as high in samples treated with L-methionine, despite the lower pH of the citric acid solution (pH 2 vs. pH 6).

The higher solubility of Pd relative to Pt and Rh highlight a need to consider the human and environmental health implications of exposures to this metal, especially in consideration of recent findings demonstrating increases in the environmental concentrations of Pd.^{2, 11-15}

Pd concentrations and behaviour in model substances

The solubility of model substances treated with the organic complexing agents was found to be considerably lower compared to soils. For metallic Pd (Pd black) treated with 0.1 M L-methionine at pH 7, the mean solubility of Pd was 0.20% (min/max: 0.18/0.21%) after a 6 day extraction period. The soluble fraction in Pd black treated with 0.1 M citric acid averaged 0.01% (min/max: 0.005-0.007%), about 120 times lower than that determined for Pd in soils extracted with this organic complexing agent. The differences in measured soluble fractions between soils and Pd black could be partially due to the particle size of the media examined. Pd black

1 has a mean particle size of ca. 22.23 μm (\pm 13.25 μm).³⁵ Pd emitted from exhaust converters can be emitted as particles of various sizes together with other PGE, including particles in the nano range which would be expected to be more soluble. A size-dependent solubility of Pd-containing particles has been confirmed elsewhere.^{33-34,39} Pd black is in metallic form, similar to the mostly insoluble catalyst material used in exhaust converters.⁵² In light of the results, the presence of a more reactive and soluble chemical Pd species in soils, formed post-emission in the environment, is likely. Pd in airborne PM collected in Vienna was also observed to be significantly more soluble than ground catalyst material using a physiologically-based extraction test,⁴² which lends support to the hypothesis that PGE are likely to be chemically transformed following emission.

Pd solubility was also observed to be influenced by the concentration of organic solutions used, solution pH and time of extraction. At a constant pH of 5.9 \pm 0.3, the solubility of Pd black increased with the concentration of the L-methionine and citric acid solutions used (0.01, 0.05 and 0.1M) (Figure 2). Mean soluble fractions were 0.280 \pm 0.009%, 0.352 \pm 0.005% and 0.554 \pm 0.024% for 0.01, 0.05 and 0.1 M L-methionine solutions, respectively. For citric acid, mean Pd solubility was 0.032 \pm 0.003 % (0.01 M), 0.068 \pm 0.005 % (0.05 M) and 0.097 \pm 0.004 % (0.1 M).

To compare, Pd black treated with distilled water was determined to have a mean solubility of 0.0003 \pm 0.0002 % (for PdO: 0.00002 \pm 0.000015 %), which was comparatively much lower. This provides further support that the presence of organic complexing agents contributes to an increased solubility of metallic Pd in the model substance.

PdO was observed to have a lower solubility than Pd black under the various conditions examined in this study, with L-methionine and citric acid having little influence on PdO model substance solubility. This observation was similar to that observed by Zereini et al.³⁵ in an earlier study employing EDTA solutions of variable strength. PdO samples treated with L-methionine solutions had measured soluble Pd fractions of 0.015 \pm 0.001 % (0.01 M), 0.017 \pm 0.001 % (0.05 M) and 0.020 \pm 0.001 % (0.1 M). Solubility was even less for citric acid solutions, with measured soluble fractions of <0.0002%.

The pH of organic solutions also influenced the solubility of model substances, with increasing amounts of Pd detected in solutions at lower pH levels. In Pd black samples treated with 0.1 M L-methionine, the highest soluble fraction was measured at pH 6, with a mean of 0.540 \pm 0.055 %. Solubility then decreased with increases in alkalinity, with means of 0.363 \pm 0.023 % (pH 7), 0.319 \pm 0.014 % (pH 8) and 0.286 \pm 0.007% (pH 9) (Figure 3). Similarly, PdO was slightly more soluble at a lower pH when treated with citric acid, with mean soluble fractions of 0.018 \pm 0.001 % (pH 6), 0.015 \pm 0.001 % (pH 7), 0.014 \pm 0.002 % (pH 8) and 0.008 \pm 0.001 % (pH 9). Of particular relevance to Pd solubility in field soils are results for samples treated with solutions having a neutral pH (pH 7), which falls in the typical pH range of most soils. The soils collected along the German Autobahn, for instance, had a pH of 6.9 \pm 0.15.

In addition to the concentration and pH of organic solutions, length of extraction period was observed to modulate model substance solubility. Most notably, the solubility of Pd black treated with L-methionine (0.1 M, pH 7) in the presence of NaClO₄ (0.1 M) steadily increased over time during the course of the extraction period. After 251 days, approximately 90% of the total metallic Pd present

in Pd black was measured in the soluble fraction. L-methionine was also more effective in solubilizing Pd black compared to EDTA solutions used in an earlier study with the same model substance.³⁵ Pd black extracted with citric acid had a soluble fraction of 0.0012% after 6 hours. This increased to 0.0057% after 7 days. Pd black solubility stagnated somewhat thereafter but increased again after 64 days, suggesting a time-dependent biphasic trend in solubility with citric acid.

Similarly, PdO was not that soluble in citric acid, with a soluble fraction of about 0.002% after 7 days. With NaClO₄ (0.1 M, pH 7, no complexing agents), Pd black and PdO had soluble fractions of 0.0013 \pm 0.0006 % and < 0.0001 %, respectively, after 7 days. This demonstrates that the organic complexing agents are more effective in inducing Pd solubility.

Metallic Pd black had the highest observed solubility in L-methionine, followed by treatment with EDTA³⁵ and citric acid, in solutions with similar concentrations (0.1 M), pH levels (7.1 \pm 0.15) and dissolved O₂ contents (8.33 mg/L \pm 0.14) (Figure 4). Similarly, Proprizki³⁸ also reported a low solubility (< 0.001 %) for metallic Pd when treated with ionic solutions containing anions of Cl⁻, NO₃⁻, SO₄²⁻, and PO₄³⁻.

Pd black kinetics

The thermodynamics of the model substances were modelled using data from the long term solubility studies, similar to that done in the Zereini et al. study³⁵ using data obtained from experimental studies with EDTA. Applying the slope of the linear regression, an initial reaction rate, r , of 8.08 \pm 0.29 $\cdot 10^{-12}$ mol L⁻¹ s⁻¹ was calculated for a reaction period of 1 to 21 days for L-methionine. The dissolution rate, R , normalized to the mass (0.501 g) and specific surface area (20 m² g⁻¹) determined for Pd black³⁵ was estimated to be 2.90 \pm 0.11 nmol m⁻² h⁻¹. The R for citric acid, calculated in the same way as for L-methionine (reaction period of 1 to 24 days), was estimated to be 0.05 \pm 0.01 nmol m⁻² h⁻¹, which is two orders of magnitude lower. Despite its lower pH, the R for citric acid is also two orders of magnitude lower than that calculated in earlier study for Pd black exposed to equimolar concentrations of EDTA (R = 2.01 \pm 0.17 nmol m⁻² h⁻¹).³⁵ Dahlheimer et al.³² estimated an R of 4.26 nmol m⁻² h⁻¹ for elemental Pd treated with a synthetic siderophore desferrioxamine-B (DFO-B). The results suggest that the type of organic complexing agent used is a more important modulating factor influencing elemental solubility than solution pH.

Surface particle chemistry of model substances

The surface regions of untreated Pd black particles, examined using XPS, are comprised mainly of metallic Pd (49.0%, binding energy (BE): 334.8 eV) and Pd (II) (39.1%, BE: 336.0 eV).³⁵ Pd is also present in a higher oxidized form but in comparatively small amounts, with 11.9% (BE: 336.8 eV). The outer atomic regions of Pd reference materials are dominated by Pd (0) (BE: 334.9 eV), Pd(II) (BE: 336.3 eV) and Pd(IV) (BE: 337.9 eV) (Pd(IV)).³⁵

The particle surface chemistry of Pd black changed little when treated with a solution consisting of distilled water only, with binding energies primarily measured in the range of 334.7 eV and 335.9 eV. In contrast, a weakly oxidized Pd species was detected on the surface of Pd black residues (solid phase) when treated with L-methionine (44.1 atom-%, BE: 335.0 eV) (Table 1). Significant amounts of Pd(II) were also detected (33.8 atom-%, BE: 336.3 eV).

1 In addition, Pd(IV) was present in the amount of ca. 9.2 atom-% 13 residues (solid phase) was observed to have a BE higher than 338.4,
 2 (BE: 337.8 eV). In sample extracts (liquid phase) of Pd black treated 14 suggestive of a higher oxidation status (Table 1). Most Pd in Pd
 3 with L-methionine, Pd was observed to have a higher oxidative 15 black residues was present as Pd(IV), with 70.7 atom-% (BE: 337.4
 4 status compared to that determined for sample residues. Pd in 16 eV), after 251 days. Lower amounts of Pd(II) are present, with 12.8
 5 solution was determined to be primarily present as Pd(II) (54.7 17 atom-% (BE: 335.9 eV). High binding energies were also detected in
 6 atom-%) and Pd(IV) (32.5 atom-%), with binding energies of 336.0 18 sample solutions (liquid phase) after 251 days, with BE's of 337.1 eV
 7 eV and 337.1 eV, respectively. 19 (35.4 atom-%) and 338 eV (55.7 atom-%). Clearly, the results
 8 The degree of oxidation on metallic Pd black surfaces treated with 20 show that longer time periods are conducive to the formation of
 9 L-methionine was observed to be time dependent, with higher 21 Pd/L-methionine complexes.
 10 amounts occurring at the end of the long term experiments (251
 11 days). Oxidized forms of Pd species lie in the range between Pd(II) 22
 12 and Pd(IV) (Figure 5). About 17 atom-% of the Pd in Pd black

Table 1: Results of the Gaussian-/Lorentzian line shape analysis of measured XPS signals for Pd black (untreated) and sample residues (R) and solutions (S) treated with 0.1 M L-methionine (binding energy in eV; atom-%) after 6 (short term test) and 251 days (long term test)

Element	Pd black (99,36% Pd)		Pd/L-methionine (R) (6 days)		Pd/L-methionine (S) (6 days)		Pd/L-methionine (R) (251 days)		Pd/L-methionine (S) (251 days)	
	eV.	Atom-%	eV.	Atom-%	eV.	Atom-%	eV.	Atom-%	eV.	Atom-%
C1s	284.1	57.1	283.2	5.6	283.1	13.2	284.2	48.7	283.4	6.7
	285.4	19.1	284.1	28.8	284.0	25.8	285.3	35.3	284.2	34.7
	287.3	16.6	284.9	32.7	284.9	38.8	287.2	8.2	285.0	46.0
	289.3	7.2	285.9	16.6	286.4	14.2	288.2	7.7	286.2	10.1
Cl2p3/2	-	-			198.3	90.2	-	-	198.8	83.5
					200.3	9.8			200.5	16.5
N1s	-	-	395.2	4.7	398.0	10.8	398.4	13.3	297.9	9.9
			397.5	20.1	398.4	43.1	399.4	45.0	399.1	49.2
			399.1	65.9	399.7	39.2	400.4	26.6	400.2	34.0
			400.6	9.3	401.2	6.8	401.5	15.0	401.6	6.9
Na1s	-	-	-	-	-	-	1071.9	100	-	-
O1s	527.1	3.6	526.3	1.4	529.7	20.5	530.5	10.8	530.0	1.8
	529.4	71.3	526.4	3.5	531.1	39.9	531.9	52.4	532.0	74.4
	531.6	25.2	530.0	95.1	532.4	39.7	533.4	36.8	533.0	23.7
Pd3d5/2	334.8	49.0	334.4	12.8	334.6	12.7	335.9	12.8	336.1	9.0
	336.0	39.1	335.0	44.1	336.0	54.7	337.4	70.7	337.1	35.4
	336.8	11.9	336.3	33.8	337.1	32.5	338.4	16.5	338.0	55.7
			337.8	9.2						

1

1 Compared to EDTA,³⁵ treatment with L-methionine results in a
2 greater shift in the binding energy of the outer 3-4 atomic shells of
3 Pd in the model substance. A maximum signal on the Pd 3d_{5/2}
4 peak of L-methionine treated Pd black was stronger compared to
5 that determined for samples treated with EDTA (337.4 eV vs. 335.3
6 eV). The stronger signals detected in this range are suggestive of a
7 greater degree of oxidation on the outer surfaces of Pd black. This
8 may also reflect the formation of strong coordination complexes
9 with ligands that serve as electron donors (e.g. S-containing ligands,
10 amino acid and carbonyl groups).

11 In addition, the binding energy and concentration (atom %) of
12 Cl(Cl2p), C(C1s), Na(Na1s), N(N1s) and O(O1s) was examined on the
13 particle surfaces of untreated and treated Pd black. These elements
14 were examined in the residue (solid) and solution (liquid phase) of
15 samples using XPS to obtain further information regarding the
16 presence and formation of Pd/L-methionine complexes. The results
17 yielded a broad spectrum for N1s. Unprotonated amino functional
18 N dominated (45 atom-%), followed by ammonium-N (26.6 atom-
19 %) and a weakly oxidized N-species with 15 atom-%. The
20 determined binding energy of S indicated the presence of sulfane-S
21 (69.3%), sulfide-S (17.1 atom-%) and sulfate/sulfonate-S (13.6
22 atom-%). Aliphatic C was mainly detected, with C-OOH functional
23 groups, from the methionine (Table 1). Oxygen was present mainly
24 as carbonyl and/or hydroxyl groups. The results for N₂, O₂, S and C
25 were similar for sample solutions. The presence of these substances
26 in both sample residues and solutions of Pd black treated with L-
27 methionine is an indication that Pd/L-methionine complexes are
28 formed. The importance of amino groups (NH₂) and S in forming
29 strong bonds with Pd was illustrated in an earlier study of the
30 crystal structure of Pd(II)(L-methionine)Cl₂-complexes.⁵³ Another
31 study of Pd(II) and methionine sulfoxide showed that bonds can be
32 formed with Pd via carboxylate and amino groups.⁵⁴ The production
33 and application of various commercially produced Pd/methionine
34 compounds for use in cancer chemotherapy are further examples of
35 the importance of such complexes.^{31, 55-58}

36 Compared to L-methionine, citric acid was less effective in
37 transforming the surface chemistry of metallic Pd black, with
38 oxidation occurring only in minimal amounts. Following treatment
39 with citric acid, about 35.3 atom-% of Pd (residue) remained in
40 metallic form (BE: 334.8). Circa 29 atom-% of Pd (residue) was
41 determined to be weakly oxidized (BE: 335.7 eV). An approximate
42 28 atom-% of the total was present in an oxidized form with a
43 higher binding energy in Pd residue. Similar results were observed
44 for sample solutions (Table 2).

45 Overall, the results demonstrate the L-methionine is highly effective
46 in transforming/complexing metallic Pd to Pd(II) and Pd(IV), while
47 citric acid does not appear to readily complex with Pd black. This
48 supports the results for soil samples, which showed that Pd present
49 in naturally-occurring soils is readily solubilized in the presence of
50 methionine, forming new organic-Pd complexes that are likely to be
51 more bio-accessible.

52

53

54

55 **Table 2: Results of the Gaussian-/Lorentzian line shape analyses**
56 **of measured XPS signals of Pd black residues (R) and solutions (S)**
57 **treated with 0.1 M L citric acid (binding energy in eV; atom-%)**
58 **after 6 days**

Element	Pd/citric acid (R)		Pd/citric acid (S)	
	eV.	Atom-%	eV.	Atom-%
C1s	284.4	30.5	284.1	14.8
	285.5	17.3	284.8	33.0
	287.0	16.7	286.1	8.6
	288.5	34.5	286.9	8.3
	290.6	1.0	288.7	35.3
O1s	529.9	33.5	530.4	7.6
	531.6	63.5	531.5	62.5
			532.7	29.8
Pd3d _{5/2}	334.8	35.3	334.4	26.1
	335.7	29.2	335.0	41.2
	336.9	28.1	336.3	20.9
	338.4	7.4	337.8	11.8

59 Pd solubility and transformation as a function of 60 dissolved O₂ content

61 A signal maximum of ca. 335 eV (44.1 atom-%) in the outer atomic
62 layers was detected for metallic Pd sample residues treated with
63 O₂-enriched L-methionine solutions. Surprisingly, a higher binding
64 energy value was detected in the sample treated with a reduced O₂
65 content (1.6 mg/L) (BE: 335.9 eV) (50.3 atom-%) (Figure 6). Similar
66 results were also seen for the liquid phase of treated samples (O₂
67 enriched: 336 eV, 54.7 atom-%; O₂ depleted: 336.6 eV, 45.3 atom-
68 %). (Table 3).

69 Pd in sample solutions (both O₂-enriched and O₂-depleted) was
70 found to be more oxidised compared to sample residues. Under low
71 oxygen conditions, metallic Pd treated with L-methionine had O₂
72 concentrations of 69.3 atom-% (BE: 530.4 eV) and 68.5 atom-% (BE:
73 530.8 eV) in the sample residue and solution, respectively (Table 3).
74 On the atomic surfaces of Pd black treated in the presence of higher
75 amounts of oxygen had O₂ concentrations (95.1 atom-%, BE: 530 eV
76 (residue) and 39.9 atom-%, BE 531.1 eV (solution)). Interestingly,
77 the results indicate that metallic Pd is more easily transformed to
78 Pd(II) and Pd(IV) under reduced O₂ conditions, findings of relevance
79 for sediments in aquatic systems. The Gaussian/Lorentzian curve
80 results demonstrate the transformation behaviour for Pd (Table 3),
81 with a higher binding energy of 335.9 eV for the O₂ depleted sample
82 (50.3 atom-%). The O₂-rich sample had a binding energy of 335.0
83 eV (44.1 atom-%). The results for citric acid treated samples confirm
84 that the surface chemistry of Pd changes little in the presence of
85 this organic substance, under both O₂-rich and O₂-depleted
86 conditions (Table 4). There was little difference in the concentration
87 of Pd species in residues of the respective high and low oxygen
88 citric acid treated samples. The results were, however, different for
89 sample solutions. Specifically, it was observed that species of Pd(IV)
90 dominate (46.9 atom-%, BE: 337.0 eV) in solution with low levels of
91 oxygen. In the oxygen rich sample solution, Pd with a binding
92 energy of 335.2 was more prominent (41.2 atom-%). There was
93 some variability in the oxidation of Pd in sample solutions, with one
94 O₂-rich sample having a measured O₂ concentration of 63.7 atom-%

1 (BE: 531.6 eV) vs. 66.8 atom-% (Be: 531.3 eV) for the O₂-depleted 4 result in Pd species with a higher oxidation status. This is also
 2 solution. This suggests that higher O₂ concentrations both in 5 confirmed by the results for Pd/L-methionine.
 3 solution and on the atomic surfaces of particles do not necessarily

Table 3: Results of the Gaussian-/ Lorentzian line shape analyses of measured XPS signals of treated Pd//L-Methionine residues (R) and solutions (S) (binding energy in eV; atom-%) under O₂-depleted and -enriched conditions after 6 days

Element	Pd/L-methionine (R)		Pd/L-methionine (S)		Pd/L-methionine (R)		Pd/L-methionine (S)	
	O ₂ concentration: 8.6 mg/L				O ₂ concentration: 1.6 mg/L			
	eV.	Atom-%	eV.	Atom-%	eV.	Atom-%	eV.	Atom-%
O1s	526.3	1.4	529.7	20.5	528.0	0.8	530.8	68.5
	526.4	3.5	531.1	39.9	530.4	69.3	532.2	31.5
	530.0	95.1	532.4	39.7	531.9	24.2		
					533.7	5.8		
Pd3d5/2	334.4	12.8	334.6	12.7	334.5	9.2	333.3	8.1
	335.0	44.1	336.0	54.7	335.9	50.3	335.1	17.1
	336.3	33.8	337.1	32.5	337.3	25.5	336.6	45.3
	337.8	9.2			338.4	15.0	337.4	29.5

Table 4: Results of the Gaussian-/Lorentzian line shape analyses of measured XPS signals of treated Pd/citric acid residues (R) and solutions (S) (binding energy in eV; atom-%) under O₂-depleted and -enriched conditions after 6 days

Element	Pd/citric acid (R)		Pd/citric acid (S)		Pd/citric acid (R)		Pd/citric acid (S)	
	O ₂ concentration: 8.6 mg/L				O ₂ concentration: 1.6 mg/L			
	eV.	Atom-%	eV.	Atom-%	eV.	Atom-%	eV.	Atom-%
O1s	529.9	36.5	530.0	7.6	529.8	33.2	530.0	7.3
	531.6	63.5	531.5	62.5	531.3	66.8	531.8	62.7
			532.7	29.8			533.0	30.0
Pd3d5/2	334.8	35.3	334.4	26.1	334.8	33.8	334.5	9.6
	335.7	29.1	335.2	41.2	335.8	27.8	335.9	32.6
	336.9	28.1	336.7	20.9	336.9	30.7	337.0	46.9
	338.4	7.4	338.0	11.8	338.4	7.8	338.1	11.0

22 The findings have important implications for exposed terrestrial and
 23 aquatic organisms. In light of the study results, documented
 24 increasing amounts of Pd relative to other PGE in the environment
 25 are a cause of concern that highlights the need for further
 26 monitoring.

1 Conclusions

2 Overall, the findings here demonstrate that the presence of organic
 3 complexing agents are likely to influence the solubility and
 4 bioaccessibility of emitted metallic Pd in the environment. Clearly
 5 certain organic complexing agents, notably L-methionine, are more
 6 effective in transforming metallic Pd into more soluble species. This
 7 finding is supported by the results for both field collected soils and
 8 Pd model substances, which showed that L-methionine is highly
 9 effective in transforming Pd into a more soluble species. This also
 10 implies, however, that different soil materials can have strong
 11 influence on the solubility depending on the presence or absence
 12 certain ligands. In addition to the type of organic complexing agent
 13 other factors play a role in modulating Pd solubility such as pH and
 14 reaction time. The solubility of Pd in soils was demonstrated to be
 15 higher compared to that in model substances, which highlights a
 16 need to conduct studies employing field-collected samples to
 17 adequately assess PGE behaviour and potential toxicity.
 18 The results of this study support more recent results that show that
 19 metallic Pd is likely to readily complex with organic substances
 20 commonly present in the environment, contributing to an enhanced
 21 reactivity and mobility of this element under ambient conditions.

27 Acknowledgements

28 This research was funded through the Deutsche
 29 Forschungsgemeinschaft (DFG project: GZ: ZE950/2-1 and
 30 ZE950/2-3) under the title "Experimental investigations into
 31 the influence of organic complexing agents and inorganic
 32 anions (Cl⁻, NO₃⁻, SO₄²⁻ und PO₄³⁻) on the transformation
 33 behaviour and the mobility of metallic palladium (Pd) and
 34 PdO". We would like to thank the Deutsche
 35 Forschungsgemeinschaft (DFG) for funding support for this
 36 project.

37 Notes and references

38 1 H. Wichmann, G. Anquandah, C. Schmidt, D. Zachmann, M.
 39 Bahadir. *Environ. Sci. Technol.*, 2007, **388**, 121-27.

ARTICLE

Journal Name

- 1 2 F. Zereini, H. Alsenz, C.L.S. Wiseman, W. Püttmann, 68
 2 Reimer, R. Schleyer, E. Bieber, M. Wallasch. *Sci Tot* 69
 3 *Environ*, 2012a, **416**, 261-68. 70
 4 3 F. Zereini F, C. Wiseman, W. Püttmann. *Environ Sci Technol* 71
 5 2007, **41**, 451-56. 72
 6 4 K. Leopold, M. Maier, S. Weber, M. Schuster. *Environ* 73
 7 *Pollution*, 2008, **156**, 341-47. 74
 8 5 MD Hays, SH Cho, R. Baldauf, J.J. Schauer, M. Shafer. *Atmos* 75
 9 *Environ.*, 2011, **45**, 925-34. 76
 10 6 A.P. Ribeiro, A.M.G. Figueiredo, J.E.S. Sarkis, M.A. Hortellani 77
 11 B. Markert. *Environ. Monit. Assess.*, 2012, **184**, 7373-382. 78
 12 7 A. Bozlaker, N.J. Spada, M.P. Fraser, S. Chellam. *Environ. Sci* 79
 13 *Technol.*, 2014, **48**, 54-62. 80
 14 8 O. Morton-Bermea, E. Hernández-Álvarez, S. Ordoñez 81
 15 Quiñonez, L.E. Beramendi-Orosco, J. Vega-Rodríguez, 82
 16 Amador-Muñoz, in *Platinum Metals in the Environment*, ed. 83
 17 F. Zereini, C.L.S. Wiseman, Springer-Verlag, 2015, pp. 257-64. 84
 18 9 S. Rauch, B. Peucker-Ehrenbrink, in *Platinum Metals in the* 85
 19 *Environment*, ed. F. Zereini, C.L.S. Wiseman, Springer-Verlag, 86
 20 2015, pp. 3-17. 86
 21 10 F. Zereini, C.L.S. Wiseman C. (Eds). *Platinum Metals in the* 87
 22 *Environment*. Springer Verlag, 2015, p. 492 88
 23 11 S. Chellam, A. Bozlaker, in *Platinum Metals in the* 89
 24 *Environment*, ed. F. Zereini, C.L.S. Wiseman, Springer-Verlag, 90
 25 2015, pp. 199-242. 91
 26 12 V. R. Lyubomirova, R. Djingova, in *Platinum Metals in the* 92
 27 *Environment*, ed. F. Zereini, C.L.S. Wiseman, Springer-Verlag, 93
 28 2015, pp. 243-255. 94
 29 13 A.M.G. Figueiredo, A.P. Ribeiro, in *Platinum Metals in the* 95
 30 *Environment*, ed. F. Zereini, C.L.S. Wiseman, Springer-Verlag, 96
 31 2015, pp. 131-44. 97
 32 14 C.L.S. Wiseman, Z. Hassan Pour, F. Zereini. *Chemosphere* 98
 33 2015, in press. 99
 34 15 H. Sievers, M. Schuster, in *Platinum Metals in the* 100
 35 *Environment*, ed. F. Zereini, C.L.S. Wiseman, Springer-Verlag, 101
 36 2015, pp. 187-198. 102
 37 16 H.J. Ballach, in *Emissionen von Platinmetallen, Analytik* 103
 38 *Umwelt- und Gesundheitsrelevanz*, ed. F. Zereini, F. 104
 39 Springer-Verlag, 1999, 217-27. 105
 40 17 N. Feichtmeier, K. Leopold, in *Platinum Metals in the* 106
 41 *Environment*, ed. F. Zereini, C.L.S. Wiseman, Springer-Verlag, 107
 42 2015, pp. 311-38. 108
 43 18 N. Ruchter, S. Zimmermann, B. Sures, in *Platinum Metals in* 109
 44 *the Environment*, ed. F. Zereini, C.L.S. Wiseman, Springer- 110
 45 Verlag, 2015, pp. 351-60. 111
 46 19 B. Sures, N. Ruchter, S. Zimmermann, in *Platinum Metals in* 112
 47 *the Environment*, ed. F. Zereini, C.L.S. Wiseman, Springer- 113
 48 Verlag, 2015, pp. 383-99. 114
 49 20 H.G. Zechmeister, S. Hann, G. Koellensperger, in *Platinum* 115
 50 *Metals in the Environment*, ed. F. Zereini, C.L.S. Wiseman, 116
 51 Springer-Verlag, 2015, pp. 339-49. 117
 52 21 S. Zimmermann, B. Sures, N. Ruchter, in *Platinum Metals in* 118
 53 *the Environment*, ed. F. Zereini, C.L.S. Wiseman, Springer- 119
 54 Verlag, 2015, pp. 361-81. 120
 55 22 J.D. Eckhardt, J. Schäfer, H. Puchelt, H. Stüben, 121
 56 *Anthropogenic Platinum Group Element Emissions*, ed. F. 122
 57 Zereini, F. F. Alt, Springer-Verlag, Berlin, 2000, pp. 47-55. 123
 58 23 S. Rauch, G.M. Morrison. *Sci. Total Environ.*, 1999, **235**, 251- 124
 59 68. 125
 60 24 S. Zimmermann, C.M. Menzel, D. Stüben, H. Taraschewski, B. 126
 61 Sures. *Environ. Pollution*, 2003, **124**, 1-5. 127
 62 25 S. Zimmermann, U. Baumann, H. Taraschewski, B. Sures. 128
 63 *Environ. Pollution*, 2004, **27**, 195-202. 129
 64 26 S. Wood, C. Tait, C. Vlassopoulos, D. Janecky. *Geochim. 130*
 65 *Cosmochim. Acta*, 1994, **58**, 625-37. 131
 66 27 F. Zereini, B. Skerstupp, F. Alt, E. Helmers and H. Urban, 132
 67 *Total Environ.*, 1997, **206**, 37-146. 133
- 28 S. Lustig, S. Zang, W. Beck and P. Schramel. *Mikrochim. Acta*, 1998, **129**, 189-194.
 29 K. Jarvis, S. Parry, M. Piper. *Environ. Sci. Technol.*, 2001, **35**, 1031-36.
 30 S. Wood and J. Van Middlesworth, *Can. Mineral.*, 2004, **42**, 411-21.
 31 G. Yang, C. Jin, J. Hong, Z. Guo, L. Zhu. *Spectrochem. Acta, Part A*, 2004, **60**, 3187-95.
 32 SR. Dahlheimer, CR. Neal and JB. Fein, *Environ. Sci. Technol.*, 2007, **41**, 870-75.
 33 C. Colombo, A.J. Monhemius, J.A. Plant. *Sci. Total Environ.*, 2008, **389**, 46-51.
 34 F. Zereini, CLS. Wiseman and W. Püttmann, *Environ. Sci. Technol.*, 2012b, **46**, 10326-10333.
 35 F. Zereini, C.L.S. Wiseman, M. Vang, P. Albers, W. Schneider, R. Schindl, K. Leopold. *Environ. Sci. Processes Impacts* 2015a, **17**, 915-21.
 36 Z. Ding, Q. Wang and X. Hu, *Procedia Environ. Sci.*, 2013, **18**, 679-85.
 37 M. Vang, Master's Thesis, Goethe-Universität Frankfurt am Main, unpublished, 2013
 38 J. Poprizki, Master's Thesis, Goethe-Universität Frankfurt am Main, unpublished, 2014.
 39 B. Bruder, C.L.S. Wiseman, F. Zereini, in *Platinum Metals in the Environment*, ed. F. Zereini, C.L.S. Wiseman, Springer-Verlag, 2015, pp. 265-75.
 40 F. Zereini, I. Müller, C.L.S. Wiseman, in *Platinum Metals in the Environment*, ed. F. Zereini, C.L.S. Wiseman, Springer-Verlag, 2015b, pp. 277-88.
 41 A. Turner and S., Price, *Environ. Sci. Technol.*, 2008, **42**, 9443-9448.
 42 C. Puls, A. Limbeck, S. Hann. *Atmos. Environ.*, 2012, **55**, 213-19.
 43 A.R. Angumeenal, D. Venkappayya. *LWT-Food Sci. Technol.*, 2013, **50**, 367-70.
 44 B.R. Tagirov, N.N. Baranova, A.V. Zotov, N.N. Akinfiev, N.A. Polotnyanko, N.D. Shikina, L.A. Koroleva, Y.V. Shvarov, E.N. Bastrakov. *Geochim. Cosmochim. Acta*, 2013, **117**, 348-73.
 45 F. Reniers, C. Tewell. *J. Electron Spectroscop Relat. Phenom.* 2005, **142**, 1-25.
 46 C.J. Powell, A. Jablonski. *J. Electron Spectroscop Relat. Phenom.*, 2010, **178**, 331-46.
 47 M.B. Gómez, M.M. Gómez, M.A. Palacios. *J. Anal. At. Spectrom.*, 2003, **18**: 80-3.
 48 J. Messerschmidt, A. von Bohlen, F. Alt, R. Klockenkämper. *The Analyst*, 2000, **125**, 397-99.
 49 H. Alsenz, F. Zereini, C. Wiseman and W. Püttmann, *Anal. Bioanal. Chem.*, 2009, **395**, 1919-1927.
 50 DIN 19741. Bodenbeschaffenheit - Bestimmung der Gehalte von Platingruppenelementen (Platin, Palladium, Rhodium) in Böden, Bodenmaterialien und Schlämmen, 2012.
 51 *Platinum 2013*, Johnson Matthey, 2013.
 52 R. Schlögl, G. Indlekofer, P. Oelhafen. *Angewandte Chemie*, 1987, **99**, 312-22.
 53 A. Caubet, V. Moreno, E. Molins, C. Miravittles. *J. Inorg. Biochem.*, 1992, **48**, 135-52.
 54 P. Corbi, F. Cagnin, L.P.B. Sabeh, A. Massabni, C.M. Costa-Neto. *Spectrochem. Acta Part A*, 2007, **66**, 1171-74.
 55 O. Vicol, N. Hurduc, I.A. Schneider. *J. Inorg. Nucl. Chem.*, 1978, **41**, 309-15.
 56 H.M. Marafie, N. Shuaib, S. El-Ezaby. *Polyhedron*, 1987, **6**, 1391-97.
 57 M. Calaf, A. Caubet, V. Moreno. *J. Inorg. Biochem.*, 1995, **59**, 63-77.
 58 B. Stypinski-Mis, G. Anderegg. *Anal. Chim. Acta*, 2000, **406**, 325-332.

Figure Captions

Figure 1: Mean Pd, Pt and Rh solubility (%) in soils treated with 0.1 M L-methionine (pH 6) and 0.1 M citric acid (pH 2) for 6 days

Figure 2: Box and whiskers plot of Pd black solubility (%) following treatment with L-methionine solutions (0.01 M, 0.05 M und 0.1 M) of pH 5.9 ± 0.3 (8.4 ± 0.03 mg O₂/L) after 21 days

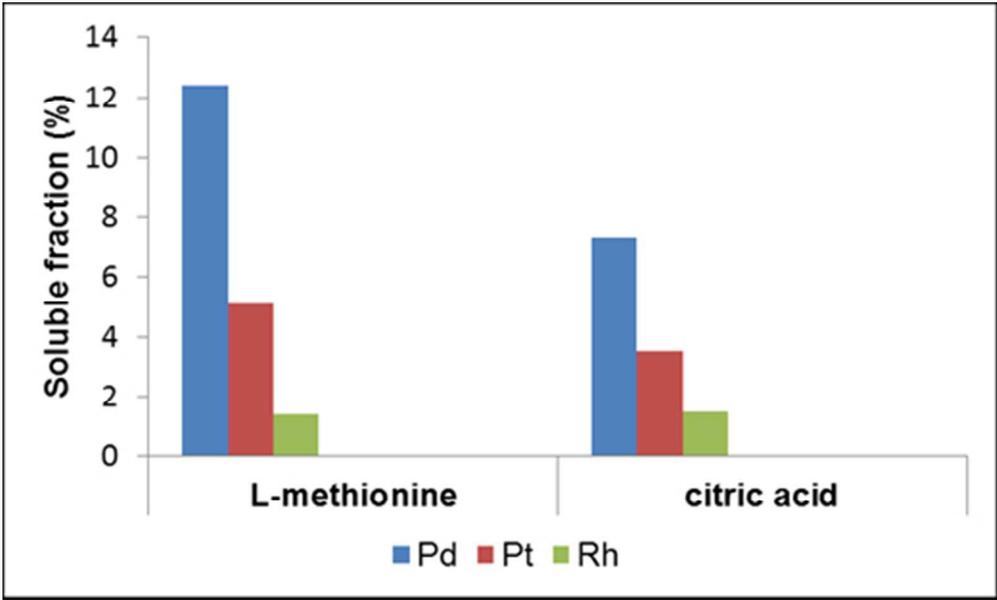
Figure 3: Box and whiskers plot of Pd black solubility (%) following treatment with 0.1 M L-methionine solutions of variable pH (6, 7, 8 and 9) after 21 days

Figure 4: Solubility (%) of Pd black in 0.1M L-methionine, 0.1 M ethylenediamine tetra acetic acid (EDTA)³⁵ and 0.1 M citric acid solutions (pH 7) after 21 days (individual samples depicted)

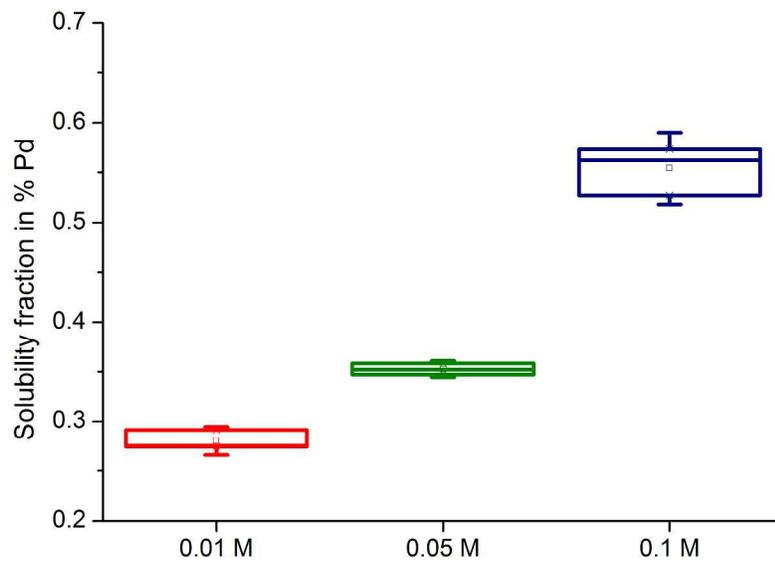
Figure 5: Binding energy (eV) of Pd black surfaces (outer 3-4 atomic layers) in untreated and L-methionine treated samples (long term test: 251 days)

Figure 6: Binding energy (eV) of Pd black residue surfaces (outer 3-4 atomic layers) in 0.1 M L-methionine treated under O₂-depleted (with N₂) (1.6 mg/L) and O₂-enriched (8.6 mg/L) conditions

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

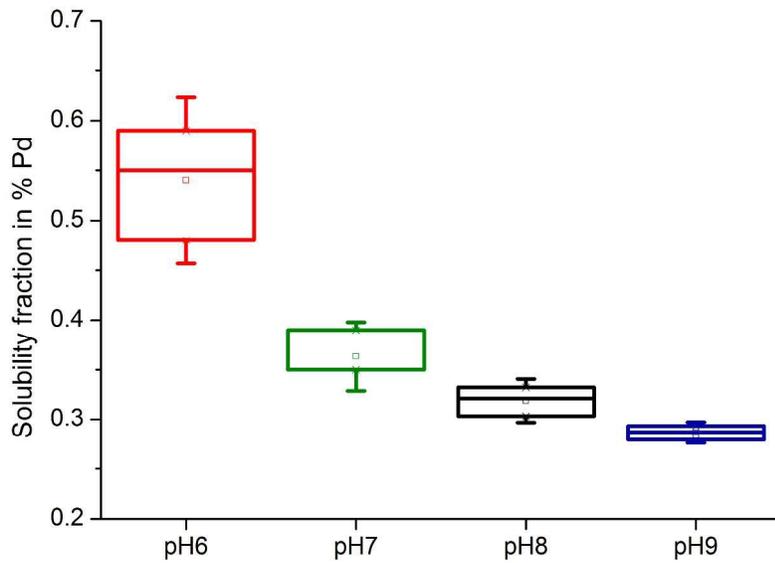


88x52mm (150 x 150 DPI)



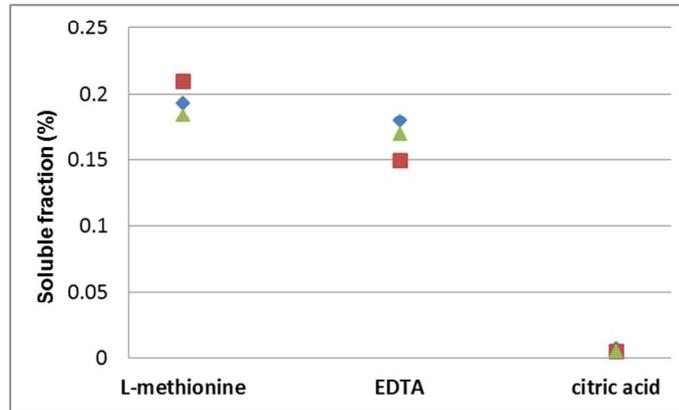
288x201mm (300 x 300 DPI)

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60



288x201mm (300 x 300 DPI)

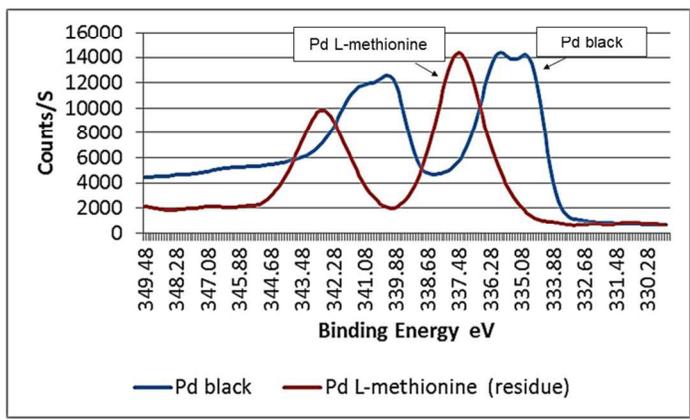
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60



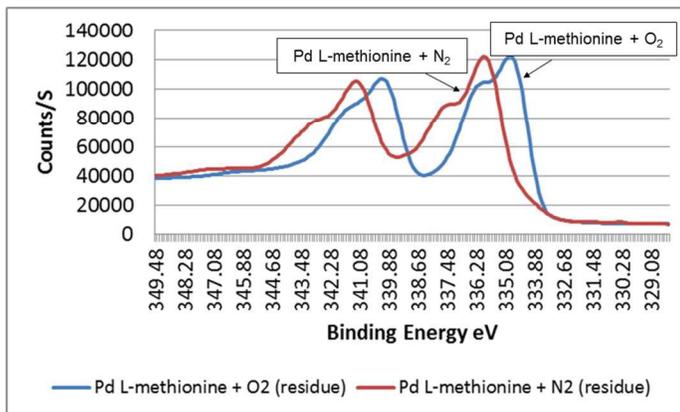
338x190mm (96 x 96 DPI)

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60



338x190mm (96 x 96 DPI)



338x190mm (96 x 96 DPI)

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60