Long-Term Monitoring of Palladium and Platinum Contents in Road Dust of the City of Munich, Germany

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Abstract The concentration of platinum group metals (PGM), namely palladium, platinum and rhodium, has increased in all earth spheres, which is mainly due to the worldwide use of automotive catalytic converters containing these metals as active components. Especially high concentrations are therefore found near busy roads and in urban environments where PGM concentrations now have reached a level that has let scientists and engineers think about possibilities to recycle these precious metals in the context of urban mining strategies. Especially palladium has been classified as particularly critical as it shows a comparatively high mobility in environmental compartments and elevated toxicological effects. It is therefore advisable and necessary to monitor traffic related PGM emissions with particular focus on palladium. One way to do this is long-term monitoring of PGM emissions under largely constant conditions. In the present work this has been done by monitoring palladium concentrations in tunnel dust of the outer city ring (B2R) of Munich, Germany. Dust samples were collected from 1994 until 2012 from the roofs of emergency telephone boxes installed in the tunnels Landshuter Allee, Candid and Trappentreu and analyzed for their palladium and some of them for their platinum content. Major and minor matrix components have also been analyzed to ensure comparability of the samples. PGM Analysis was performed with Graphite Furnace Atomic Absorption Spectrometry (GFAAS) after complete sample digestion and enrichment of palladium and platinum with N,N-Dialkyl-N’-benzoylthioureas acting as highly selective chelating agents. Matrix characterization was performed by elementary analysis and Total Reflection X-ray Fluorescence (TXRF). The main matrix components determined in the road dust samples from 1994 to 2012 show, apart from one noteworthy exception (sulfur) a quite constant composition. The sulfur content in the dust samples of all three tunnels decreased significantly in the years after 1998. This is most probably attributable to the legally

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required reduction of the sulphur content in gasoline and diesel fuels. The average palladium concentration in the dust samples increased significantly from 1994 to 2007 where it reached a maximum. From 2009 onwards there was a steady decline in the average palladium concentration, reaching a minimum in 2012. The increase of the palladium concentration in the tunnel dust from 1994 to 2007 can easily be explained by the gradual replacement of platinum by palladium in automotive catalytic converters. In 2007 traffic density monitored by the municipal administration of the city of Munich also reached a high level which roughly remained the same up to today. Platinum concentration in the dust samples also reached a maximum in 2007 and declined from 2007 to 2012. The most likely explanation for the decline of the palladium and platinum concentration in the tunnel dust after 2007 is progress in the production of automotive catalytic converters and/or progress in automobile engine construction.

1 Introduction

In Europe car exhaust catalysts are legally prescribed for now 27 years, first in Switzerland (1986), later in Austria and Sweden and since 1993 they are a legal obligation for all newly registered petrol-engined cars in the European Union. Tax incentives first in Germany (1984) and later in other European countries further accelerated the use and the continued development of this technology until today. In parts of the United States of America which have advanced further in car exhaust cleaning technology catalysts have been legally prescribed as early as 1974.

As an inevitable consequence, the concentration of platinum group metals (PGM), namely palladium, platinum and rhodium, which are the catalytically active components in modern car exhaust catalysts, has increased significantly in all earth spheres, i.e. hydrosphere, atmosphere, lithosphere and biosphere. Even in Greenland ice samples an increase in PGM concentration has been detected (Barbante et al. 2001). This is due to the unavoidable discharge of PGM containing particulate matter mobilized by vibrations and material stresses mainly caused by the fast streaming exhaust gases leaving car engines after fuel combustion. Especially high concentrations are found near busy roads (Rauch et al. 2005; Whiteley and Murry 2005; Zereini et al. 2007; Jackson et al. 2007) and in other urban environments where PGM concentrations have reached a level that has let scientists and engineers think about possibilities to recycle these precious metals e.g. from road dust or solid residues of the street drainage system. It is conceivable that in the nearer future PGM recycling from traffic related emissions will be a part of urban mining strategies.

Among other PGM used in car exhaust catalysts palladium has been classified as particularly critical as it shows a comparatively high mobility in environmental compartments and elevated toxicological effects (Aberer et al. 1993; Schäfer et al. 1998; Kristine et al. 2004; Vamnes et al. 2004). It is therefore advisable and necessary to monitor traffic related PGM emissions with particular focus on palladium.

One way to do this is long-term monitoring of PGM emissions under largely constant conditions. In the present work this has been done by monitoring palladium concentrations in tunnel dust of the outer city ring (B2R) of Munich, Germany (Leopold et al. 2008). Dust samples were collected from 1994 until 2012 from the roofs of emergency telephone boxes installed in the tunnels Landshuter Allee, Candid and Trappentreu and analyzed for their palladium and most of them for their platinum content. Major and minor matrix components have also been analyzed to ensure comparability of the samples. These locations have been chosen for some reasons: (1) Weather related influences are reduced to a minimum. (2) Traffic is monitored by the municipal administration and the data are updated regularly. (3) The speed of vehicles in the tunnels is limited to 60 km h^{-1} and is subject to frequent inspection in order to achieve a regular and constant traffic flow (and a greater safety in the tunnels). (4) Only small dust particles settle on the roofs, course particles and litter do not.

2 Special Aspects in Trace and Ultra-Trace Analysis of Palladium

Quantification of palladium in the μg kg^{-1} and ng kg^{-1} range is not straight forward, especially in samples such as road dust, soil or sewing sludge ash, which represent a complex matrix consisting of a large number of elements and element species at concentrations usually exceeding that of palladium by several orders of magnitude. This is aggravated by the fact that some of the most sensitive determination techniques such as Neutron Activation Analysis (NAA) and ICP-MS suffer from severe interference by ubiquitous elements. From an analytical point of view it is therefore advisable to apply selective enrichment procedures, which eliminate matrix influences and, as an additional option, improve the detection limit to make palladium analysis accessible to determination techniques less sensitive but also less susceptible for interferences, e.g. Graphite Furnace Atomic Absorption Spectrometry (GFAAS) or Total Reflection X-ray Fluorescence (TXRF).

One of the oldest, but still very effective procedures to do so are fire assay techniques which do not require dissolution of the samples by aggressive solvents and as a consequence of the method inherent high sample weight, have less problems with statistically unequal distribution of the analyte within the matrix. This is a frequently underestimated problem in modern trace analysis usually performed with low sample weights of several milligrams up to 500 mg. However, before this advantage of fire assay techniques can be exploited to the full, large sample quantities of at least 100 g or more should be available. Fire assays also require special equipment and considerable experience and knowledge especially in finding the appropriate sample adapted mixture of chemicals, optimized temperature profiles and optimal dissolution conditions for the collector phase to avoid loss of analyte (Zereini et al. 1993, 1994, 2007).

Most of the established enrichment procedures require dissolution of the samples, e.g. by high pressure acid digestion, nowadays mostly performed with microwave assistance as a fast energy transmission and heating procedure. In this context it is of outmost importance to achieve a complete dissolution of the samples. The simple and very popular method of determining only the *aqua regia* soluble fraction of elements is very risky, especially in the case of silicate residues which due to their large amorphous surface pose a high risk to bind palladium species in the ng L^{-1} range. Own studies and experiments have demonstrated that between 5 and 90 % of palladium traces can be irreversibly and in a non-reproducible manner bound by silicate residues after *aqua regia* digestion of samples with high silicon content, e.g. road dust and grass samples. In practice, this means that hydrofluoric acid is crucial to completely dissolve silicon containing samples. In most cases the surplus of hydrofluoric acid has to be removed before measurement, e.g. by evaporating it in specially equipped exhaust hoods. This is a very unpopular approach and in addition to the always existing possibility of adsorbing palladium on vessel walls and other surfaces it is another source for loss of analyte e.g. by formation of volatile fluorine compounds or formation of analyte carrying aerosols. In some cases this problem can be overcome by the addition of boric acid and the resulting formation of tetrafluoroborate (BF_4^-). Tetrafluoroborate does not attack quartz and glass ware or silicon based adsorption materials such as normal or reversed phase materials for solid phase extraction (Boch et al. 2002) or application in chromatography.

In summary, the accuracy of trace and ultra-trace analysis of palladium in environmental samples stands and falls with collecting and measuring representative samples, which allow for an admissible extrapolation of the results and by performing reproducible digestion and enrichment procedures with high selectivity and highest possible enrichment of the analyte. Bearing this in mind the selection of a suitable quantification technique plays a subordinate but no less important role.

3 Selective Enrichment of PGM Using N,N-Dialkyl-N’-Benzoylthioureas

Coordination chemistry of platinum group metals is still a multifaceted and fascinating subject of current research e.g. in organometallic chemistry and in catalysis. From an analytical point of view the strong tendency especially of palladium to form very stable complex compounds with a variety of ligands is an interesting approach for the selective enrichment of palladium and other PGM from complex matrices. A ligand designed for this purpose should exhibit extraordinary high complex formation constants combined with a selective complexation behavior, high variability of the chemical and physicochemical properties of the ligand and the complexes to fine-tune polarity e.g. for phase transitions or optimized sorption behavior on stationary phases. A high chemical resistance against hydrolysis and oxidation is another prerequisite as traces of water soluble PGM species should be handled in acidic and oxidizing media to stabilize the analyte within the solutions.

In neutral or weakly acidic solutions colloidal PGM species can be formed by chemical reduction or formation of oxo-hydroxy compounds, which have a strong tendency to wall adsorption.

N,N-Dialkyl-N'-benzoylthioureas fulfil all of these requirements and were first utilized for selective PGM enrichment in 1985 and 1986 (König et al. 1985, 1986) followed by a series of investigations on the solvent extraction of PGM species (Vest et al. 1989, 1991) and patents e.g. (König et al. 1988, 1987). The chromatographic behavior of PGM and other complexes (König et al. 1984) as well as the crystal structure of N,N-Dialkyl-N'-benzoylthiourea complexes e.g. (Bensch and Schuster 1992) and fluorescence-labeled acylthiourea (Schuster and Unterreitmaier 1993, 1995) for fluorometric detection of heavy metals were subjects of further studies.

In 1996 the first fully automated enrichment and quantification system based on a flow injection (FI) approach utilizing N,N-Diethyl-N'-benzoylthiourea (DEBT) as a ligand for highly selective complexation of palladium was described in the literature (Schuster and Schwarzer 1996). It was intended for ultra-trace analysis of palladium in the lower ng·L^{-1} range from small sample volumes of 2−3 mL and provides an extraordinarily high overall selectivity with tolerance levels for commonly co-existing elements such as copper, nickel, cobalt, zinc and cadmium of up to 10 g L^{-1} and even more. Ubiquitous elements like iron and aluminum, earth alkaline and alkaline elements and others do not form stable complex compounds with DEBT in aqueous solutions. Due to the high chemical selectivity, it was even possible to measure palladium traces in ruthenium, rhodium, osmium, iridium, platinum, silver and gold standard solutions ($c_{metal} = 1$ g L^{-1}) intended for the use in atomic spectrometry. Validation was performed by recovery experiments in various matrices (98 ± 3 %) and by analysis of the reference material BCR-723 (found 6.0 ± 0.75 µg Pd kg^{-1}, certified value 6.0 ± 1.8 µg Pd kg^{-1}). Precision of the measurements is around 5 % in the lower ng L^{-1} range.

For determination GFAAS was chosen as it combines sufficient detection power, robustness and low operating costs for single element analysis. Small sample volumes of typically 20−40 µL applied by a high precision pipetting system is another advantage compared to sample introduction systems based on nebulizers which are much more susceptible to malfunction especially with regard to solvents with high viscosity/density and high concentrations of dissolved or dispersed analyte and/or matrix components. Volatilization of organic and other potentially interfering matrix constituents within the furnace temperature program is another pleasant tool provided by GFAAS. The flow injection system was also combined with Neutron Activation Analysis (NAA) to remove bromine and other elements which cause a strongly enhanced base line in the relevant energy range of the Pd-109 decay (Ag-109 m, 88.03 keV) (Schwarzer et al. 2000). With this setup it was possible to evaluate the palladium content in gasoline for the first time. Coupling of Electrothermal Atomization to Laser Absorption Fluorescence Spectrometry (ET LAFS) was performed for the determination of palladium in airborne particulate matter from Berlin, Germany (Tilch et al. 2000). In the meantime other research groups also utilized N,N-Dialkyl-N'-benzoylthioureas for trace analysis of PGM (Meeravali and Jiang 2008; Philippeit and Angerer 2001; Alshanaa and Aygüna 2011; Limbeck et al. 2004).

In the present work the determination of palladium in traffic related tunnel dust from the outer city ring of Munich utilizing the developed FI-GFAAS system and a specifically optimized digestion procedure (Boch et al. 2002) was continued and now includes the period from 1994 to 2012. For the determination of platinum in the same samples a new easy to perform separation and enrichment procedure based on cloud point extraction (CPE) with N,N-Di-(n-hexyl)-N'-benzoylthiourea (DHBT) as a selective reagent for complexation was used.

4 Selective Enrichment of Platinum Species by Ligand Supported Cloud Point Extraction

CPE is a very interesting analytical approach for trace metal enrichment as it combines high enrichment factors, a fast and easy assembly and the omission of (toxic) organic solvents (Pytlakowska et al. 2013). With N,N-Dialkyl-N'-benzoylthioureas as selective complexing agents CPE was first used for the decontamination of heavy metal polluted soils (Schuster et al. 1998). In aqueous solutions platinum occurs in two stable oxidation states Pt(II) and Pt(IV), normally existing as anionic complexes e.g. $[PtCl_4]^{2-}$ or $[PtCl_6]^{2-}$ which, depending on their concentration and chemical environment, have a strong tendency for ligand exchange reactions with small monodentate ligands (Al-Bazi and Chow 1984). After oxidizing digestion procedures Pt(IV) complex compounds are the dominating species, which show low reaction rates with N,N-Dialkyl-N'-benzoylthioureas at temperatures <40 °C. This is caused by a distinct kinetic inhibition of the complex formation (Vest et al. 1991) and allows for an effective separation of palladium traces from Pt(IV) containing solutions (König et al. 1988). To overcome the kinetic limitations tin(II) chloride ($SnCl_2$) is a good choice as it destabilizes Pt(IV) and also Rh(III) and Ir(III) species by the intermediate formation of $M[SnCl_3]_x$ complex compounds (Al-Bazi and Chow 1984) which in turn can be complexed by N,N-Dialkyl-N'-benzoylthioureas via ligand exchange. This ligand exchange is not kinetically limited and leads to the thermodynamically much more stable bidentate N,N-Dialkyl-N' -benzoylthiourea complex compounds. $SnCl_2$ also acts as a reducing agent, Pt(IV) can be reduced to Pt(II), a kinetically more labile species which forms very stable complex compounds with N,N-Dialkyl-N'-benzoylthioureas.

The enrichment procedure after sample digestion (Boch et al. 2002) and complex formation is easy to perform and utilizes the formation of micelles in surfactant containing aqueous solutions. N,N-Dialkyl-N'-benzoylthioureas, particularly those substituted with long alkyl chains like N,N-Di-n-hexyl-N'-benzoylthiourea (DHBT), form neutral, apolar complex compounds which can be effectively incorporated within micelles. Thermal induced coagulation of the micelles above the so called cloud point temperature leads to the formation of a surfactant rich phase which can easily be separated from the aqueous phase e.g. by centrifugation. The residual small surfactant droplet containing the platinum complex compounds is then dissolved in a small volume of a mixture of ethanol and hydrochloric acid and forwarded to GFAAS measurement without further treatment (Sievers and Schuster 2015). For platinum an enrichment factor of 60 and a limit of detection of 15 ng L^{-1} are achieved. Validation was performed by analysis of the reference materials BCR-723 (found 80.8 ± 3.87 µg Pt kg^{-1}, certified value 81.3 ± 3.3 µg Pt kg^{-1}) and SARM−7 (found 3.34 ± 0.44 mg Pt kg^{-1}, certified value 3.74 ± 0.045 mg Pt kg^{-1}). Precision is 5 % in the lower ng L^{-1} range.

5 Collection, Pretreatment and Matrix Characterization of the Tunnel Dust Samples

Tunnel dust samples were collected from the roofs of emergency call boxes in a height of about 2.3 m in three different tunnels (see introduction) and covered the years 1994, 1998, 2001, 2007, 2009, 2010 and 2012. After sampling the dust was completely removed from the roofs to avoid sampling of the same dust in subsequent years. The samples were dried for 24 h at 120 °C the gradual replacement and homogenized in a ball mill. Sieving of the collected dust was not necessary, since only small dust particles settle on the roofs of the boxes. Traffic statistics provided by the Department of Urban Planning and Building Regulation, City of Munich, Germany PLAN-HAI-31-1 are listed in Table 1.

Matrix characterization included quantification of relevant major, minor and trace elements. A selected compilation of elements is shown in the Figs. 1, 2 and 3. The major elements carbon, hydrogen, nitrogen, sulfur, and silicon were determined by elementary analysis. Other elements as well as minor and trace elements were determined by TXRF.

6 Results and Discussion

Matrix characterization of the main components carbon, hydrogen, nitrogen, sulfur, silicon, iron, zinc and calcium determined in road dust samples from 1994 to 2012 and 2001 to 2012 respectively show, apart from one noteworthy exception (sulfur) a quite constant composition. The sulfur content in the dust samples of all three

Table 1 Traffic-density monitored by the municipal administration of the city of Munich, Germany (average of vehicles within 24 h) in the city road tunnels "Landshuter Allee" "Candid" and "Trappentreu" from 1990 to 2007

Landshuter allee: vehicles 24 h^{-1}	Candid: vehicles 24 h^{-1}	Trappentreu: vehicles 24 h^{-1}
1992: 94,000	1990: 115,000	1991: 103,000
1994: 100,000	1996: 128,000	1994: 124,000
1997: 118,000	1997: 94,000	1998: 126,000
2005: 99,000	2007: 139,000	2007: 136,000
2007: 129,000	2011: 143,000	2011: 135,000

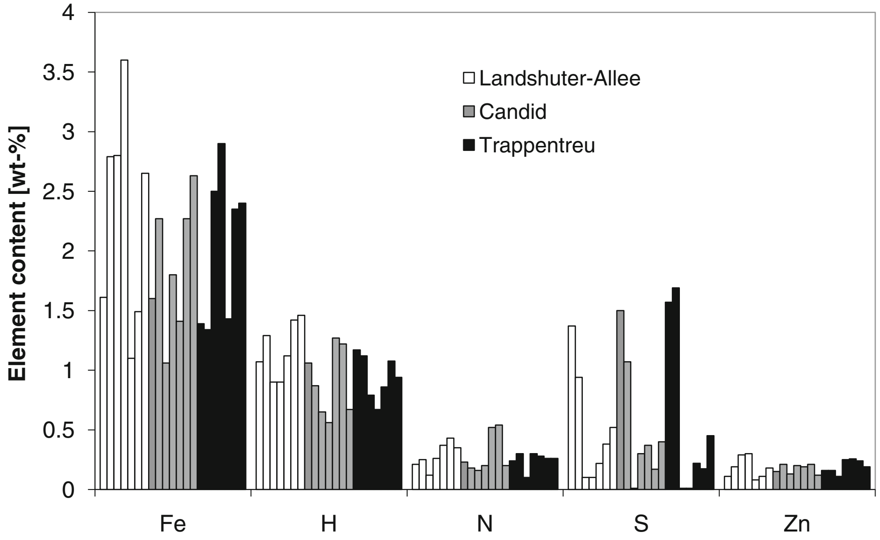

Fig. 1 Constituents of road dust of the years 1994, 1998, 2001, 2007, 2009, 2010 and 2012

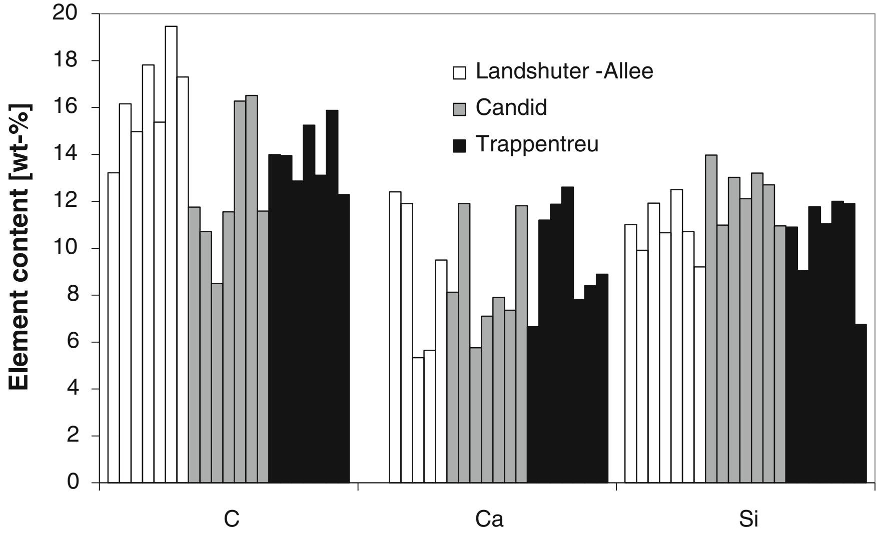

Fig. 2 Constituents of road dust of the years 1994, 1998, 2001, 2007, 2009, 2010 and 2012

tunnels decreased significantly in the years after 1998. This is most probably attributable to the legally required reduction of the sulphur content in gasoline and diesel fuels. The contents of the main components as well as the trace components chromium, copper and manganese reveal some fluctuations which are mostly of statistical nature but do not show a clear trend. These data support the assumption

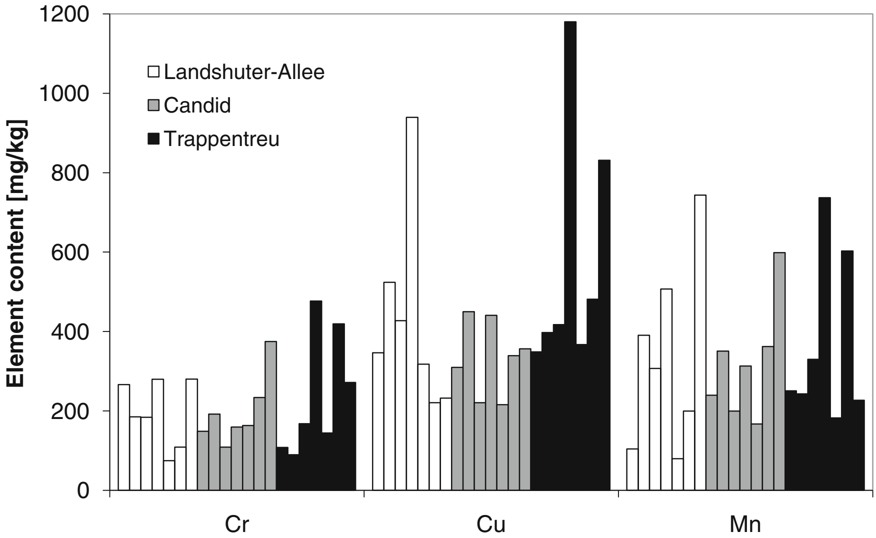

Fig. 3 Constituents of road dust of the years 1994, 1998, 2001, 2007, 2009, 2010 and 2012. Determination of Ca, Fe, Cr, Mn, Cu and Zn was performed by TXRF, other elements by elementary analysis

that the dust matrix remained constant over the years and that the sampling locations were well chosen to investigate long-term trends for ultra-trace elements like palladium or platinum.

The average palladium concentration in the dust samples increased significantly from 1994 (17.7 g Pd kg^{-1}) to 2007 (389 µg Pd kg^{-1}) were it reached a maximum. From 2009 onwards there was a steady decline in the average palladium concentration, reaching a minimum (236 µg Pd kg^{-1}) in 2012 (Fig. 4). The increase of the palladium concentration in the tunnel dust from 1994 to 2007 can easily be explained by the gradual replacement of platinum by palladium in automotive catalytic converters (Matthey 2012). In 2007 traffic density monitored by the municipal administration of the city of Munich also reached a high level which roughly remained the same up to today.

Platinum concentration in the dust samples increase between 1994 and 2001 and decline from 2001 to 2012 (Table 2). The increase in platinum content from 1994 to 2001 can be explained by the increasing use of automobile converters, promoted by the legislature. The decrease in the platinum content of the road dust samples since 2001 is mainly due to the replacement of platinum by palladium in the production of exhaust catalysts.The most likely explanation for the decline of the palladium and platinum concentration in the tunnel dust after 2007 is progress in the production of automotive catalytic converters and/or progress in automobile engine construction, a quite encouraging development, especially if taking into account that the pollutant emissions caused by traffic has also progressively been reduced.

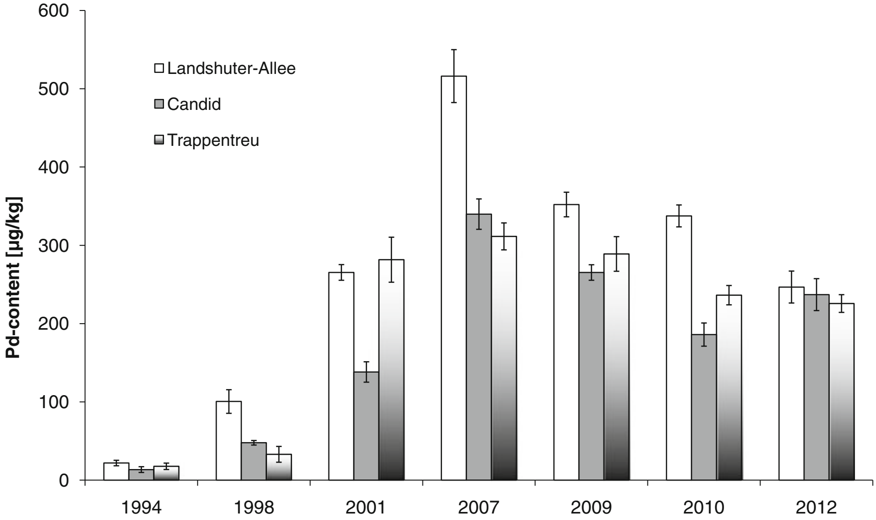

Fig. 4 Palladium content of road dust, determined by FI GFAAS (n = 3, error bar is the standard derivation of three independent samples)

Table 2 Platinum content of road dust, determined by GFAAS after CPE-enrichment (n = 3, error is the standard derivation of three independent samples)

	Landshuter allee	Candid	Trappentreu
	µg Pt kg^{-1}	µg Pt kg^{-1}	µg Pt kg^{-1}
1994	183.4 ± 16.3	–	182.7 ± 8.6
1998	306.4 ± 38.8	236.5 ± 45.8	251.4 ± 28.7
2001	641.9 ± 29.4	319.0 ± 14.8	543.9 ± 34.8
2007	308.4 ± 10.3	242.4 ± 7.2	269.6 ± 47.4
2009	–	255.3 ± 38.7	274.6 ± 29.8
2010	–	136.8 ± 28.6	172.1 ± 44.9
2012	143.2 ± 10.3	130.9 ± 21.7	126.8 ± 15.9

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