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ORIGINAL PAPER

Determination of platinum and palladium released from autocatalysts in soil samples from different-sized urban agglomerations

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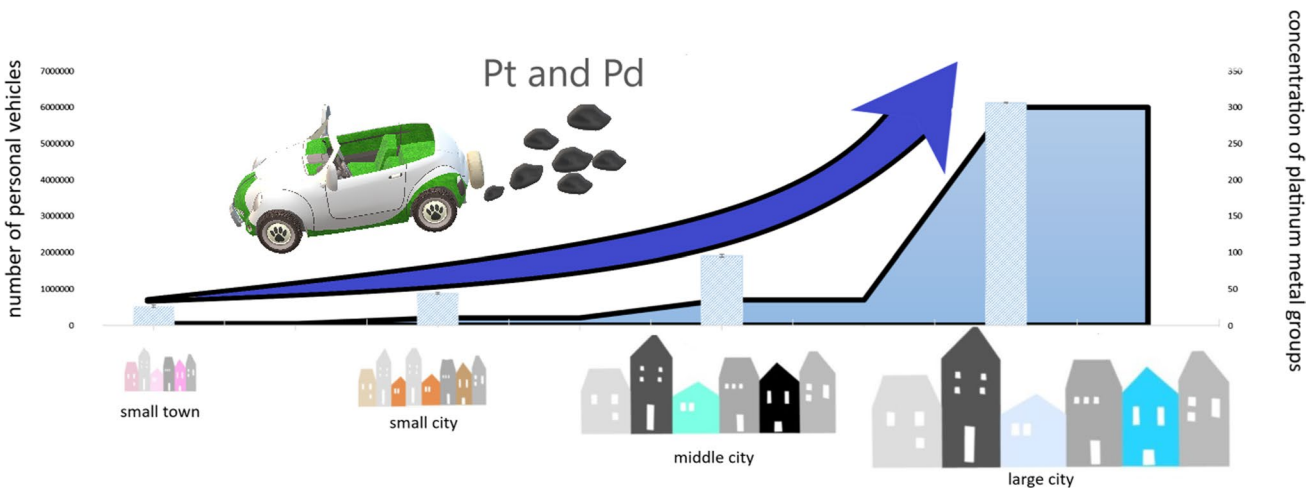
Abstract

The study is focused on environmental contamination with platinum metals and compares soil samples from four European cities: Jihlava (Czechia), Brno (Czechia), Vienna (Austria) and Moscow (Russian Federation). The research was aimed at determining the amount of platinum and palladium in soils that were sampled in different urban areas of the mentioned cities. The selection of sampling points was focused on crossroads and roads with a high intensity of car traffic, especially places which are frequent traffic jams in populated agglomeration. The results of this study show that the highest concentrations of platinum and palladium in the soil are close to these roads. The greatest release occurs when cars start on in places with low air circulation, such as tunnels, crossroads or highway entrances. Based on this fact, these localizations are the most interesting for research. Concentrations above the limit are also at places with poor dispersion conditions. This work includes monitoring the amount of platinum and palladium released into the environment due to automobile traffic. The measurement showed a connection between the increased traffic situation in individual cities and the concentration of platinum and palladium in the soil matrix. Platinum and palladium values ranged in the following ranges. For Jihlava, the concentration of platinum was determined from 16.93 to 38.72 ng g^{-1} and palladium from 2.705 to 8.452 ng g^{-1}. For Brno, the concentration of platinum was determined from 34.53 to49.71 ng g^{-1} and palladium 8.450–12.78 ng g^{-1}. For Vienna, the concentration of platinum was determined from 39.22 to 159.2 ng g^{-1} and palladium 18.45–98.21 ng g^{-1}. For the Moscow center, the concentration of platinum was determined from 5.897 (background value) to 352.9 ng g^{-1} and palladium 2.598 (background value) to 86.11 ng g^{-1}. For the Moscow circle, the concentration of platinum was determined from 249.7 to 520.9 ng g^{-1} and palladium 91.87–180.6 ng g^{-1}. This study was created in 2021–2022.

Graphical abstract



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Keywords Platinum · Palladium · Autocatalysts · Soil material · Traffic in the agglomeration · Solid-phase extraction

Introduction

Platinum and palladium occur naturally on Earth in very low concentrations; only in the mining areas, the metal content is higher, as described in Table 1. Amount of platinum and palladium in the urban environment. There is also an increased concentration of platinum and palladium near transport hubs. Both metals are used in several industries, one of the most important of which is the automotive industry. In this industry, metals are used in the production of auto-catalysts. At the same time, it is also the biggest polluter of the environment.

Autocatalysts are primarily used to convert CO, unburnt CH_x and NO_x in exhaust gases into non-toxic CO_2, H_2O and N_2 (Zhang et al. 2019a, b).

During use, the surface of catalysts is chemically, physically, rapidly changing redox conditions, high temperature and mechanically worn. This wear results in the release of platinum and palladium emissions into the environment. Depending on this fact, the highest concentration of platinum and palladium can be considered near traffic roads, mainly in larger urban agglomerations or at places with higher traffic density such as highways. Some studies estimate that up to 40% of platinum and palladium are released during the first 100,000 km driven (Wiseman et al. 2016).

The anthropogenic release of platinum and palladium from autocatalysts also depends on the type of catalyst used. The article (Palacios et al. 2000) compared the release of Pt and Pd in different types of autocatalysts at the start of operation and after 30,000 km. In this study, he compared 3 types of catalysts with different compositions of Pt and Pd. This study proved that Pt and Pd are released the most in a new car and gradually their release decreases. Compared to a new autocatalyst, emissions are reduced by up to 80–96% after driving 30,000 km.

Table 1 Amount of platinum and palladium in urban environment (Savignan et al. 2021; Zhang et al. 2019a, b)

Area	Pt μg kg^{-1}	Pd μg kg^{-1}
Rural area	< 0.3–218	< 0.1–656
Peri-urban area park	< 0.5–228	< 0.03–1.8
Peri-urban area agriculture	< 0.5–124	< 0.04–1.07
Urban area	< 0.5–2240	< 0.5–432
Roadside	< 0.7–221	< 1.32–662
Mining area	2.7–more than 1000	0.4–more than 1000

The fate of platinum and palladium in the environment

Autocatalysts are the main source of environmental pollution with platinum and palladium. Platinum metals are immobile on the surface of the catalyst, where they are exposed to changing chemical, physical and redox conditions that result in the wear of these catalysts. This wear and tear lead to the gradual release of the surrounding environment during the operation of the car. Platinum metals release elementary particles below 0.3 μm into the environment (Komendová et al. 2019).

In Fig. 1: regional and long-distance transport of accumulation in the environment. We can see how platinum and palladium get into the environment from autocatalysts.

Pt and Pd are emitted into the environment in the form of metal nanoparticles, which can be adsorbed on the catalyst support or parts of the exhaust gas.

Platinum and palladium in the airborne

The air is the primary component of the ecosystem into which platinum and palladium enter when released from autocatalysts.

After a certain period of time, which is dependent on climatic phenomena, platinum and palladium reach other parts of the environment by wet (precipitation) or dry deposition (caused by gravity sedimentation. Depending on climatic conditions, platinum and palladium can be transported over long distances. Platinum and palladium have also been found in central Greenland, where they reached precisely with the help of remote atmospheric transmission (Rauch et al. 2005). Table 2: concentration of platinum and palladium in airborne describes the contamination of these metals in different places in the World in the airborne.

Platinum and palladium in the soil

Pt and Pd are most often monitored in the area of busy traffic junctions. High concentrations of platinum and palladium are commonly found at these sites. However, even in locations that are not close to transport hubs, Pt and Pd can be found, of course in smaller concentrations. In urban agglomerations and near traffic transport hubs, as a result of anthropogenic activities, the physical, chemical and biological properties of soil differ significantly from natural uncontaminated soil. These unnatural soils consist of mixtures of in-situ natural products that enter the soil through

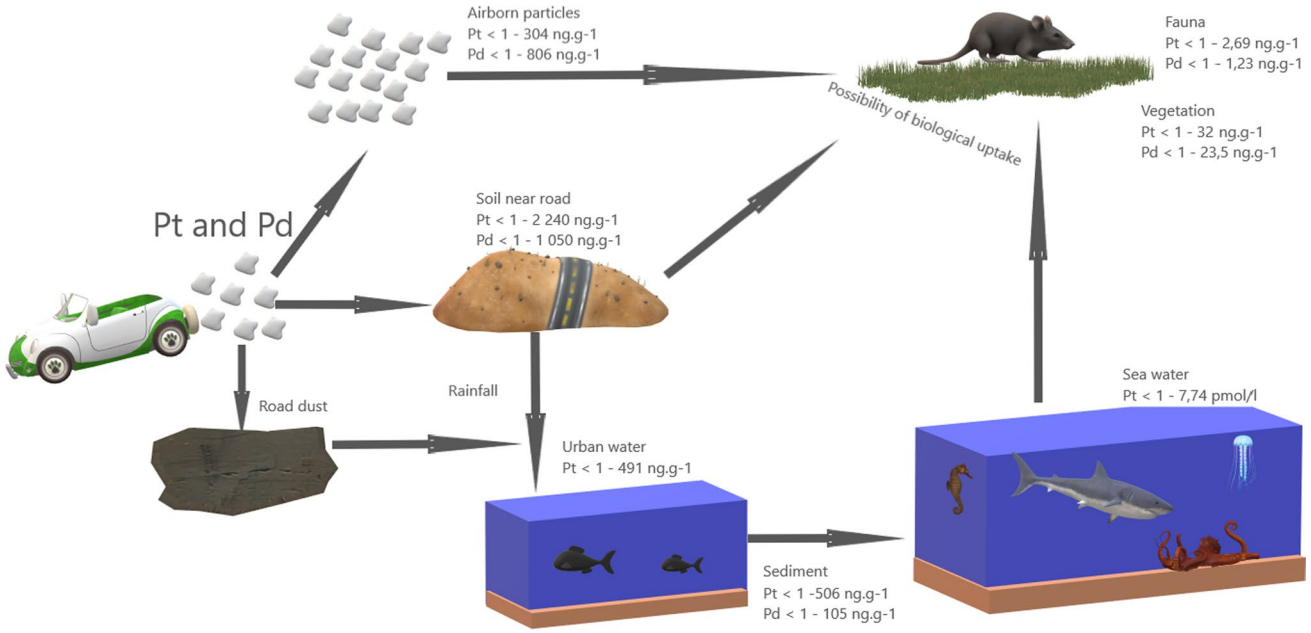


Fig. 1 Regional and long-distance transport of accumulation in the environment. Based on Tables 3, 4 and 5

Table 2 Concentration of platinum and palladium in airborne

Continent	Location	Method of determination	Concentration Pt ng m^{-3}	Concentration Pd ng m^{-3}	Reference
Asia	Kalkata, Indie	ICP-MS (inductively coupled plasma mass spectrometry)	0.86–12.3	2.7–111	Diong et al. (2016)
	Beijing, China	ICP-MS	7–304	< 1–24.75	Zhang et al. (2019a, b)
Europe	Frankfurt, Germany	ICP-MS	1.2–80.9	1.2–683	Zereini et al. (2012)
	Deuselbach, Germany	ICP-MS	< 1–37.5	< 1–13.3	Zereini et al. (2012)
	Neuglobsow, Germany	ICP-MS	< 1–19.3	< 1–10.9	Zereini et al. (2012)
	Budapest, Hungary	ET AAS	–	260–860	Atilgan et al. (2012)
	Istanbul, Turkey	ET AAS	–	< 1–640	Atilgan et al. (2012)
	Zagreb, Croatia	ICP-MS	0.488–1.071 pg m^{-3}	3.856–5.600 pg m^{-3}	Rinkovec et al. (2018)

weathering and anthropogenic materials of mostly unidentifiable sources (Savignan et al. 2021).

These sources can be from industry, construction activity, household waste, etc. Soil layers in urban areas have been mixed, destroyed or removed, the soil is vertically and spatially heterogeneous, it is compacted or closed under urban infrastructure, it can be enriched or contaminated with various inorganic and organic substances, the circulation of water, air and nutrients is greatly disturbed. Neutral to slightly or strongly alkaline soil pH values are also typical for urban soil, regardless of geological conditions (Gaberšek and Gosar 2021). Table 3: concentration of platinum and palladium in the soil samples present different concentrations of platinum and palladium metals in different parts of the world.

Platinum and palladium in the aquatic ecosystem

Aquatic ecosystems are anthropogenically contaminated mainly from two sources. The primary anthropogenic source is platinum and palladium-containing road dust runoff from autocatalysts. The second, relatively smaller and mostly point source, is wastewater (Brand et al. 2019). Cis-platinum is used to treat cancer. Even if hospital institutes have reliable wastewater treatment plants, platinum from treatment still enters the aquatic ecosystem. Another possibility of how they get into the aquatic ecosystem is after the patient leaves the treatment facility at home, from where platinum gets into water and sediments via wastewater (Vidmar et al. 2015).

Sediments are part of the aquatic ecosystem. It is a gravitationally settled heterogeneous system at the bottom of an

Table 3 Concentration of platinum and palladium in the soils samples

Continent	Location	Method of determination	Concentration Pt ng g^{-1}	Concentration Pd ng g^{-1}	References
Europe	Palermo, Italy	Voltametry	0.6–2240		Orecchio and Amorello (2011)
	Braunschweig, Germany	ICP-MS	< 1–50	< 1–43	Wichmann et al. (2007)
	Vienna, Austria	ETAAS	38–146	13–42	Limbeck et al. (2007)
	Rankweil, Austria	ICP-MS	2.8–134	< 1–24	Fritsche and Meisel (2004)
	Knittelfeld, Austria	ICP-MS	< 1–32	< 1–7	Fritsche and Meisel (2004)
	Sudost- Tangete, Austria	ICP-MS	2–39	< 1–6,5	Fritsche and Meisel (2004)
	Brno, Czechia	ET-AAS	< 1–12.8	–	Komendova and Jezek (2019)
	Sheffield, UK	ICP-MS	8–606	9–1.050	Prichard et al. (2008)
	Ulm, Germany	HR-CS-GFAAS	–	< 2–193	Leopold et al. (2017)
	Campania, Italy	ICP-MS	< 1–278.1	< 1–431.9	Zuzolo et al. (2018)
	Napoli, Italy	ICP-MS	1.6–52	8–110	Cicchella et al. (2003)
	Berlin, Germany	ICP-MS	< 1–366	< 1–75.5	Birke et al. (2018)
	Moscow, Russia	ICP-MS	88.5	34.2	Ladonin (2018)
Australia	Perth, Australia	ICP-MS	13–440	30–420	Whiteley and Murray (2003)
Asia	Hong Kong, China	ICP-MS	15–160	6–107	Pan et al. (2009)
	Shanghai, China	ICP-MS	< 1–100	< 1–101	Pan et al. (2009)
	Kaohsiung, Taiwan	ICP-MS	22.9	148	Hsu et al. (2013)
America	Sao Paulo, Brazil	ICP-MS	< 1–18	< 1–58	Morcelli et al. (2005)
	Toronto, Canada	ICP-Q-MS	26–69	10–121	Wiseman et al. (2016)
	Mexico City, Mexico	ICP-MS	3.1–332.7	2.5–101.1	Morton et al. (2001)

aquatic ecosystem. Sediment is made up of a number of organic or inorganic substances of natural and anthropogenic origin (Abdulbur-Alfakhoury et al. 2021).

The ratio between these substances determines the resulting state and its physicochemical conditions (especially adsorption), which is also related to the mobility of pollutant ions. In addition to the composition, pH and temperature also have a great influence on the physicochemical conditions.

Table 4: concentration of platinum and palladium in the aquatic ecosystem describes the concentration of platinum and palladium in sediments, rivers or oceans.

Although the concentration of platinum and palladium in aquatic ecosystems is lower compared to other environmental components, they can be expected to affect aquatic fauna and flora due to their ability to bioaccumulation (Pawlak et al. 2014).

Brand et al. (2019) studied the bioaccumulation of metals in the tissues of aquatic animals—the mussel—Dreissena polymorpha. The mussels were exposed to platinum in tanks with a precisely monitored concentration. Concentration series were selected—1; 10; 100 and 1000 µg L^{-1}. Only the highest concentration of 1000 µg L^{-1} led to mortality after 96 h of exposure. The other concentrations did not lead to the mortality of the test samples after exposure for 96 h.

Fischer et al. (2018) studied the concentration of platinum in the Pacific Ocean as a function of depth. The results of his study prove a conservative profile of platinum concentration in the entire water column to a depth of 4500 m. The platinum concentration ranged from 0.2 to 0.4 pmol L^{-1}. A similar study was also conducted by López-Sánchez et al. (2019). At this study, platinum was monitored in the Atlantic Ocean to a depth of 4500 m. The platinum concentration ranged from 0.11 to 0.32 pmol L^{-1}. The samples of both studies were taken in the open sea. The group of Mashio et al. (2016) focused on monitoring seawater closer to the coast. The results ranged from 0.29 to 7.74 pmol L^{-1}. It is therefore evident that platinum and probably palladium are higher near the coast.

Platinum and palladium in the fauna and flora

A significant group of monitored contaminated environmental components are plants growing near transport routes. Vegetation is suitable for use as biomonitoring. At this study Komendova (2020b), the lichen Hypogymnia physodes was used. In this work, the lichen was exposed for 150 days. The result of this study was the dependence of palladium accumulation on the lichen as a function of time.

Table 5: concentration of platinum and palladium in the fauna and flora present articles, which study different type of biological samples.

Table 4 Concentration of platinum and palladium in the aquatic ecosystem

Continent	Location	Method of determination	Concentration Pt ng g^{-1}	Concentration Pd v	References
Africa	Bushveld, South Africa	ICP-MS	River sediment < 1–491		Díaz-Morales et al. (2021)
Asia	Japan, Tokyo	ICP-MS	Rain water 0.12–0.62 Pmol L^{-1}	–	Mashio et al. (2016)
			River water 0.07–6.51 Pmol L^{-1}		
			Sea water 0.29–7.74 Pmol L^{-1}		
Europe	Mediterranean coast	AdCSV (adsorptive cathodic stripping voltammetry)	Sea sediment 6–15	–	Abdou et al. (2019)
	Prodelta, Portugal	AdCSV	River sediment 9.5	–	Cobelo-García et al. (2011)
	Sheffield, UK	ICP-MS	River sediment 2–64	River sediment 2–57	Prichard et al. (2008)
	Pacific Ocean	ICP-SFMS	Sea water 0.2–0.4 pmol L^{-1}	–	Fischer et al. (2018)
	Atlantic Ocean	AdCSV	Sea water 0.11–0.32 pmol L^{-1}	–	López-Sánchez et al. (2019)
Australia	Perth, Australia	ICP-MS	River sediment 9–103.8	River sediment 5.4–61.2	Whiteley and Murray (2003)
America	Hawaii		River sediment 4.44–506	River sediment 2.08–105	Sutherland et al. (2007)

Table 5 Concentration of platinum and palladium in the fauna and flora

Continent	Location	Method of determination	Concentration Pt ng g^{-1}	Concentration Pd ng g^{-1}	References
Europe	Sweden	ICP-MS	A freshwater crustacean < 1–38	–	Moldovan et al. (2001)
		ICP-MS	Sparrowhawk egg 0.54	Sparrowhawk egg 0.48	Ek et al. (2004)
		ICP-MS	Falcons part of body 0.2–2.69	Falcons part of body < 0.1–1.23	Ek et al. (2004)
		ICP-MS	Gryfalcon faeces 0.1	–	Ek et al. (2004)
	Italy	ICP-MS ET-AAS AdSV	Human urine 0.24–8.13 ng.L^{-1}	Human urine 0.71–17.2 ng.L^{-1}	Bocca et al. (2004)
	Brno, Czechia	ET-AAS	Grass < 1–11.6	–	Komendova and Jezek (2019)
	Brno, Czechia	ET-AAS	–	Lichen 5–23.58	Komendova (2020b)
	Austria	ICP-MS	Moss < 1–32	Moss < 1–25	Zechmeister et al. (2006)

Separation and preconcentration of platinum and palladium

Platinum and palladium in soils that are polluted by anthropogenic influences, i.e., near transport hubs and in urban agglomerations, are in very low concentrations compared to other contaminants. Often such low PMG concentrations cannot be determined directly, even using the most sensitive analytical techniques with very low limit of detection

Table 6 Typical detection limit values for platinum and palladium. (Komendova 2020a; Crespo Alonso et al. 2015)

Element	Method/LOD			
	ET-AAS (µg L^{-1})	ICP-OES (µg L^{-1})	ICP-MS (ng L^{-1})	Voltammetry (ng L^{-1})
Pt	4.5	20	0.01–0.1	0.054
Pd	0.5	2	0.01–0.1	–

Table 7 List, location and type of site where soil samples were taken

City	The name of the sampling site	GPS coordinates	Type of site	Sample identification
Jihlava	Street Znojemská	49° 22′ 42.0″ N 15° 35′ 24.6″ E	Exit of city	J1
	Street Telečská	49° 23′ 21.9″ N 15° 34′ 31.4″ E	Exit of city	J2
	Street Žižkova	49° 23′ 39.6″ N 15° 34′ 44.7″ E	City street	J3
	Street Okružní	49° 24′ 04.8″ N 15° 36′ 21.0 ″E	City street	J4
	Street Fritzova	49° 24′ 08.7″ N 15° 35′ 05.5″ E	City street	J5
	Street Okružní	49° 23′ 53.1″ N 15° 36′ 30.4″ E	Road crossroad	J6
	Street Březinova	49° 24′ 14.7″ N 15° 35′ 57.2″ E	Housing estate	J7
	Street Havlíčkova	49° 24′ 33.1″ N 15° 35′ 31.1″ E	City street	J8
	Street Romana Havelky	49° 24′ 37.4″ N 15° 34′ 47.7″ E	Exit to city circle	J9
	Street Jiráskova	49° 24′ 22.3″ N 15° 34′ 20.6″ E	Exit to city circle	J10
Brno	Street Hradecká direct to center	49° 13′ 47.7″ N 16° 34′ 47.7″ E	High traffic road	B1
	Street Hradecká direct to out of city	49° 13′ 48.7″ N 16° 34′ 49.8 ″E	High traffic road	B2
	Street Sportovní	49° 13′ 31.3″ N 16° 36′ 00.2″ E	City street	B3
	Street Kotlářská	49° 12′ 24.3″ N 16° 35′ 59.8″ E	City street	B4
	Street Koliště	49° 11′ 47.3″ N 16° 36′ 54.8″ E	City street	B5
	Street Poříčí	49° 11′ 13.0″ N 16° 35′ 42.8″ E	Crossroad	B6
	Street Gajdošova	49° 11′ 46.7″ N 16° 38′ 46.3″ E	City street	B7
	Tomkovo náměstí	49° 12′ 49.5″ N 16° 38′ 11.2″ E	Crossroad	B8
	Highway D2	49° 09′ 23.6″ N 16° 37′ 48.2″ E	Exit of city	B9
Vienna	Julius-Ficker straße	48° 15′ 55.7″ N 16° 27′ 13.5″ E	Crossroad	W1
	Wagramer straße	48° 14′ 21.9″ N 16° 25′ 50.9″ E	Crossroad	W2
	Lassallestraße	48° 13′ 25.5″ N 16° 24′ 03.8″ E	City street	W3
	Weihburggasse	48° 12′ 15.4″ N 16° 22′ 38.7″ E	City street	W4
	Neubaugurtel	48° 12′ 16.5″ N 16° 20′ 12.0″ E	High traffic road	W5
	Schloßalle	48° 11′ 17.7″ N 16° 18′ 49.9″ E	Crossroad	W6
	Rodauner straße	48° 08′ 25.3″ N 16° 15′ 37.1″ E	City street	W7
	Waldgasse	48° 06′ 41.8″ N 16° 11′ 15.3″ E	Park	W8
	Edelsinnstraße	48° 10′ 21.1″ N 16° 19′ 22.1″ E	High traffic road	W9
	Brigittenauer Lande	48° 13′ 53.2″ N 16° 21′ 47.6″ E	City street	W10
Moscow city	Akademicheskaya metro stanice	55° 41.252″ N 37° 34,468″ E	City street	M1
	Neskuchny sad 1	55° 42,710″ N 37° 35,181″ E	City street	M2
	Neskuchny sad 2	55° 42,742″ N 37° 35,235″ E	City street	M3
	Leninsky prospekt Gagarinovo náměstí	55° 42,621″ N 37° 35,043″ E	Crossroad	M4
	Dvorets Pionerov 1	55° 42,078″ N 37° 33,095″ E	Park near the road	M5
	Dvorets Pionerov 2	55° 42,036″ N 37° 33,030″ E	Park near the road	M6
	Vernadskogo prospekt	55° 42,060″ N 37° 32,818″ E	Crossroad	M7
	Universitsky prospekt 1	55° 42,145″ N 37° 32,614″ E	City street	M8
	Universitsky prospekt 2	55° 42,140″ N 37° 32,605″ E	City street	M9
	University forest	55° 42,555″ N 37° 32,088″ E	Forest in the city	M10
Moscow city circle	MKAD 1	55° 40′ 20.1″ N 37° 25′ 31.5″ E	Large urban circle—highway	MKAD 1
	MKAD 2	55° 48′ 50.5″ N 37° 23′ 25.1″ E	Large urban circle—highway	MKAD 2
	MKAD 3	55° 53′ 41.0″ N 37° 30′ 10.2″ E	Large urban circle—highway	MKAD 3
	MKAD 4	55° 53′ 43.8″ N 37° 39′ 43.0″ E	Large urban circle—highway	MKAD 4
	MKAD 5	55° 49′ 10.1″ N 37° 50′ 15.5″ E	Large urban circle—highway	MKAD 5
	MKAD 6	55° 40′ 04.3″ N 37° 50′ 14.9″ E	Large urban circle—highway	MKAD 6
	MKAD 7	55° 34′ 58.8″ N 37° 42′ 23.1″ E	Large urban circle—highway	MKAD 7

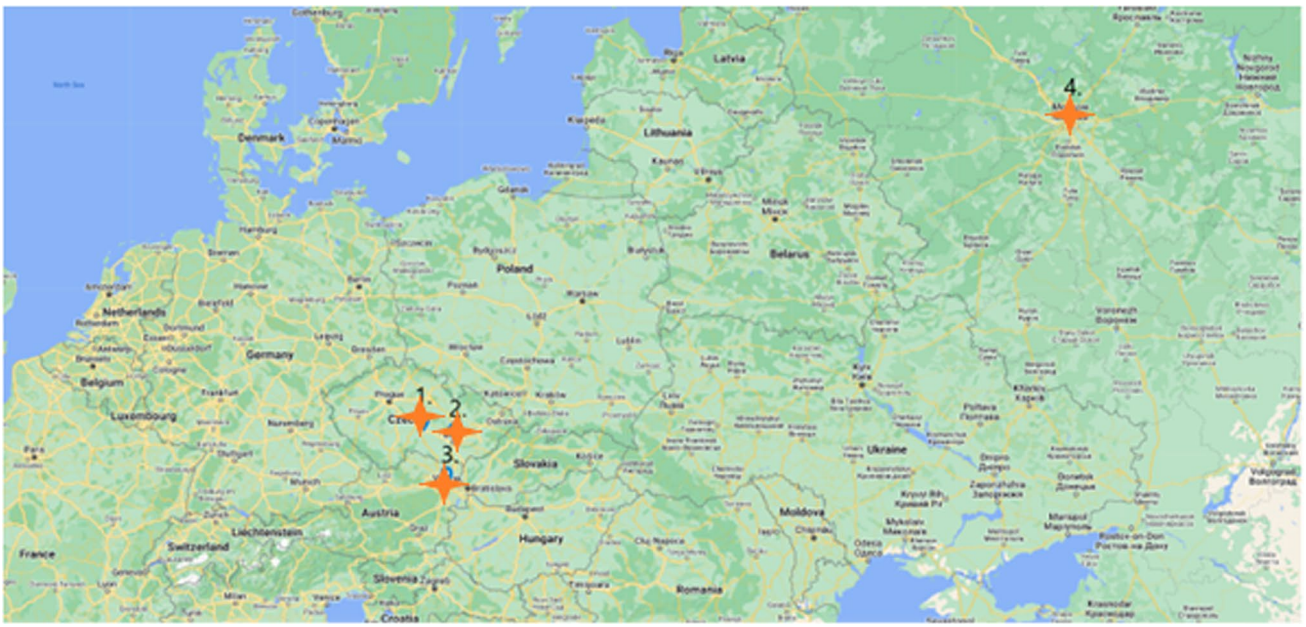
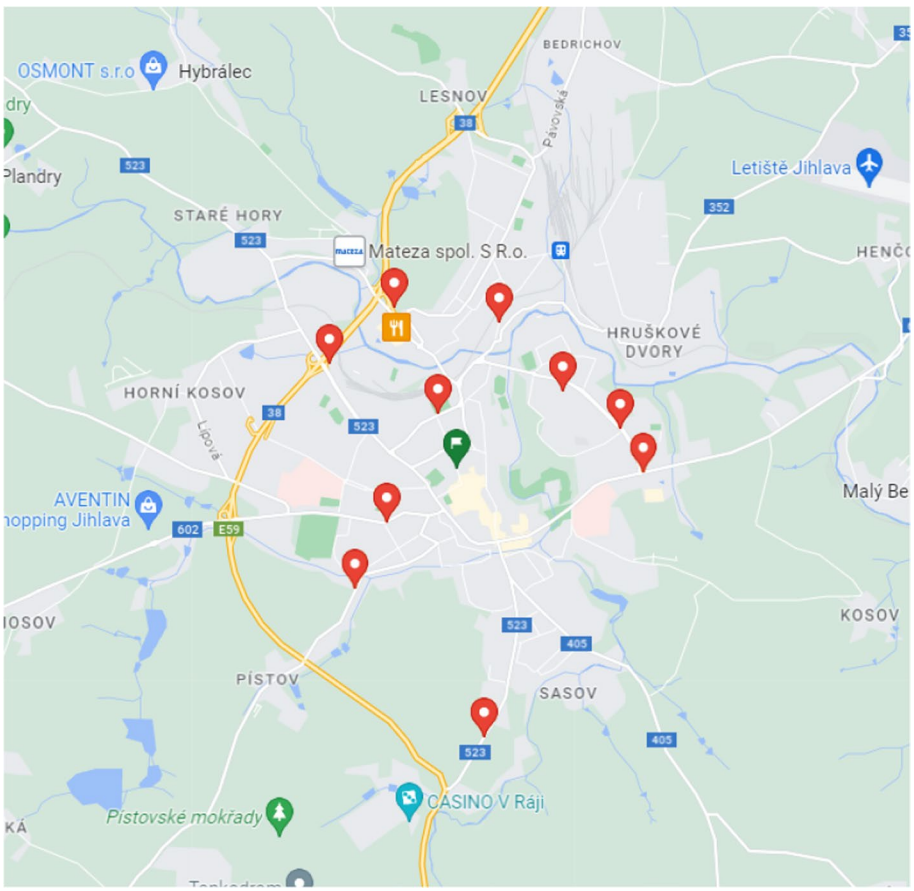


Fig. 2 Selected cities on the map. (1) Jihlava, (2) Brno, (3) Vienna, (4) Moscow

Fig. 3 Comparison of transport in city and population



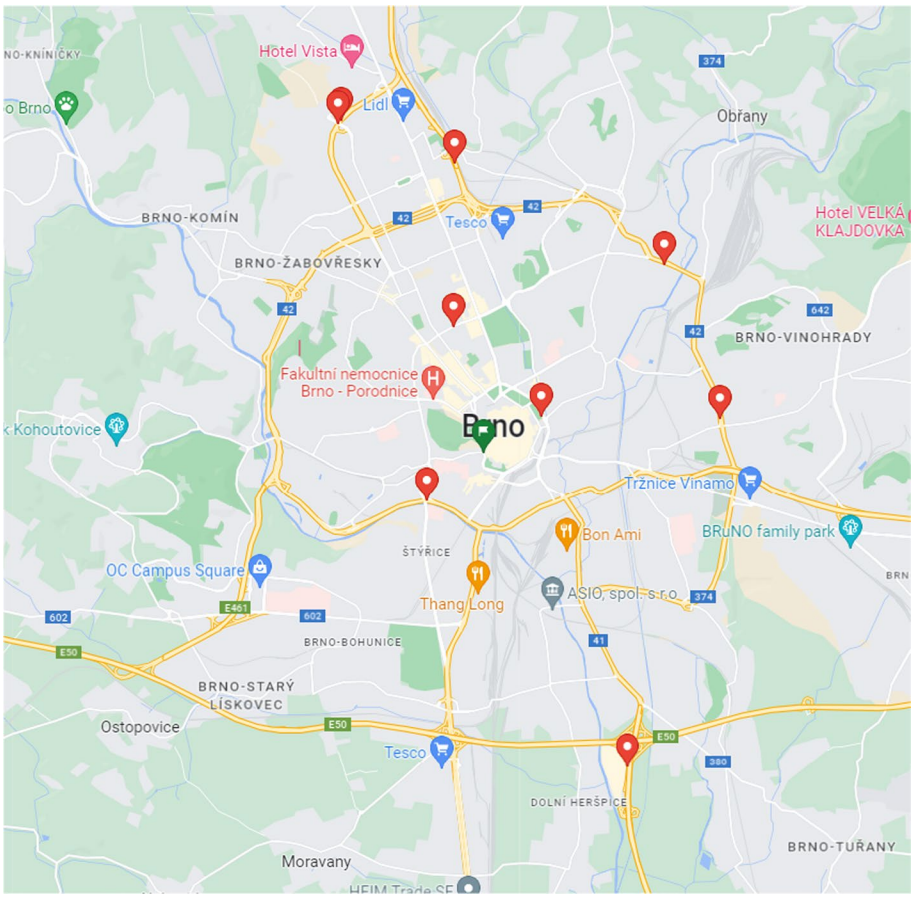


Fig. 4 Map of Jihlava with sampling points

(LOD) and limit of quantitation (LOQ) limits. For this reason, sorption techniques are used, which have the task of concentrating a specific metal to such a level that it is possible to determine the metals using more common analytical methods. One of the most effective methods of platinum and palladium concentration is the solid phase extraction (SPE) method. The advantage of this method lies in increasing the concentration of selected elements, but also their separation from the sample matrix (Komendova 2020a).

Adsorption

Metals are adsorbed on the solid phase through hydrophobic interactions or van der Waals forces.

Hydrophobic interactions occur if the solid sorbent is highly nonpolar (reversed phase). The most widespread sorbent of this type is Silicagel-C18 (which contains a saturated hydrocarbon chain—octadecyl). Polymeric reverse phases have emerged, especially copolymers of styrene and divinylbenzene, which provide additional π–π interactions when π-electrons are present in the analyte. Elution is usually performed with an organic solvent such as acetonitrile. These interactions are preferred in online systems as they are not very strong and can be broken quickly. Since most trace element species occur in the form of ions, they cannot be captured by this type of sorbent (Camel 2003).

Ion pairing

If a nonpolar sorbent is used, an ion pair reagent can be added to it. Such an agent contains a polar part (for example acids) and a nonpolar part (aliphatic hydrocarbon chain). Typical ion pair reagents are quaternary ammonium salts and sodium dodecyl sulfate. The nonpolar part interacts with the nonpolar reversed-phase sorbent, while the polar part forms an ion pair with the ionic species present in the matrix (Carson 2000; Nikoloski et al. 2015).

Chelation

Some functional groups of atoms are capable of chelating trace elements. These atoms include nitrogen and sulfur. Nitrogen is present in primary, secondary, and tertiary amines, in the groups: azo, diazo, nitro, nitroso, amides, and nitriles. Sulfur is present in disulfides, thiols, thiocarbamates, and thioethers. The character of the functional group provides selectivity of the ligands with respect to trace elements (Camel 2003).

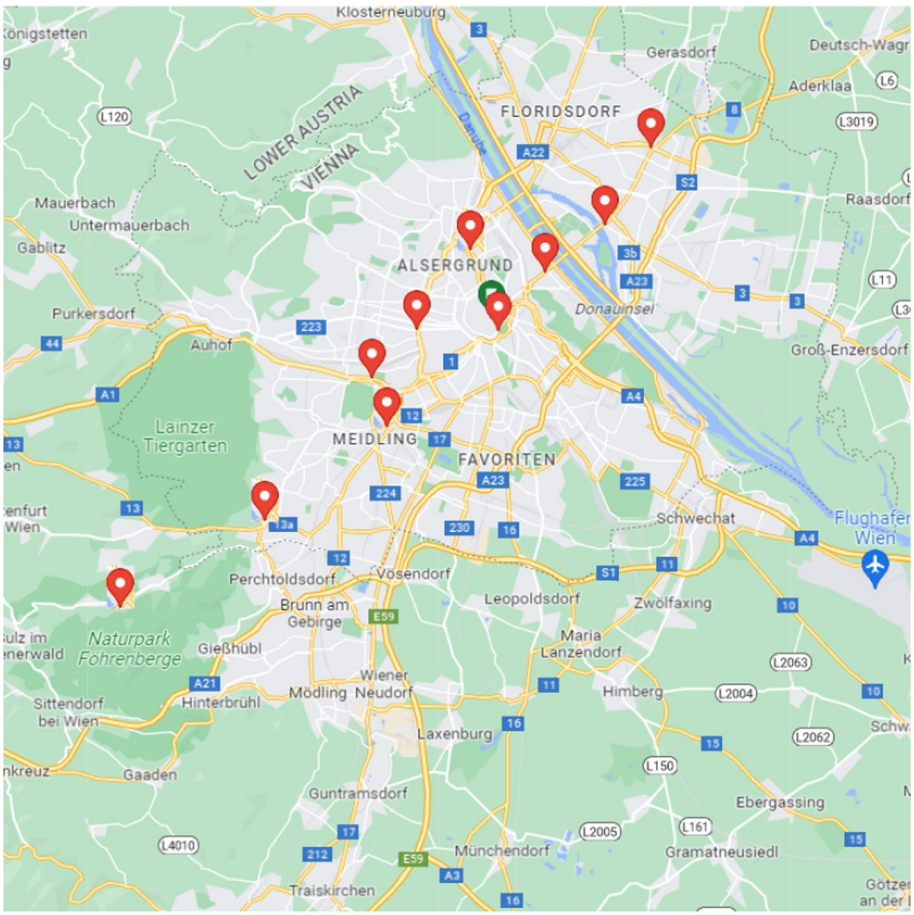


Fig. 5 Map of Brno with sampling points

Ion exchangers

This is one of the interaction variants in solid phase extraction (SPE), which uses cation–anion interactions. This is based on the electrostatic attractive forces between the charged ions of the functional group of the ion exchanger and the cation of the heavy metal, which, depending on the functional group of the ion exchanger, is either captured or passes through the ion exchanger without retention. According to the functional group used, we are able to distinguish between anionic ion exchangers and cationic ion exchangers (Nikoloski and Ang 2014).

Methods of detection

Platinum and palladium determination methods are mass spectrometry with inductively coupled plasma, atomic absorption spectrometry, atomic emission spectrometry with inductively coupled plasma (ICP-OES) or perhaps adsorption stripping voltammetry. Table 6 Typical detection limit values for platinum and palladium describes the difference in approximate detection limits depending on the determination method.

Materials and methods

Soil samples

Soil matrix samples were taken in close proximity to roads. Soil samples were taken at a depth of approximately 5 cm and were freed of unwanted biota. This was followed by homogenization and quaternization to a quantity of 10 g. The samples thus prepared were dried at laboratory temperature for 1 week. After drying, the samples were sieved on a Retsch sieving machine. For next step was the use of fraction size ≤ 200 mm. The sampling points from which the soil samples were taken were chosen according to the traffic density. These were busy city crossroad, city exit, city streets, highways, in construction sites where vehicles often stop, start or accelerate. But places that were far from busy road junctions were also chosen. The sampling locations are listed in Table 7. List, location and type of site where soil samples were taken. The GPS coordinates of the locations where the samples were taken are listed in the Table 7. At the same time, the type of location is indicated, which can be an crossroad, city road, expressway, park, or highway. The

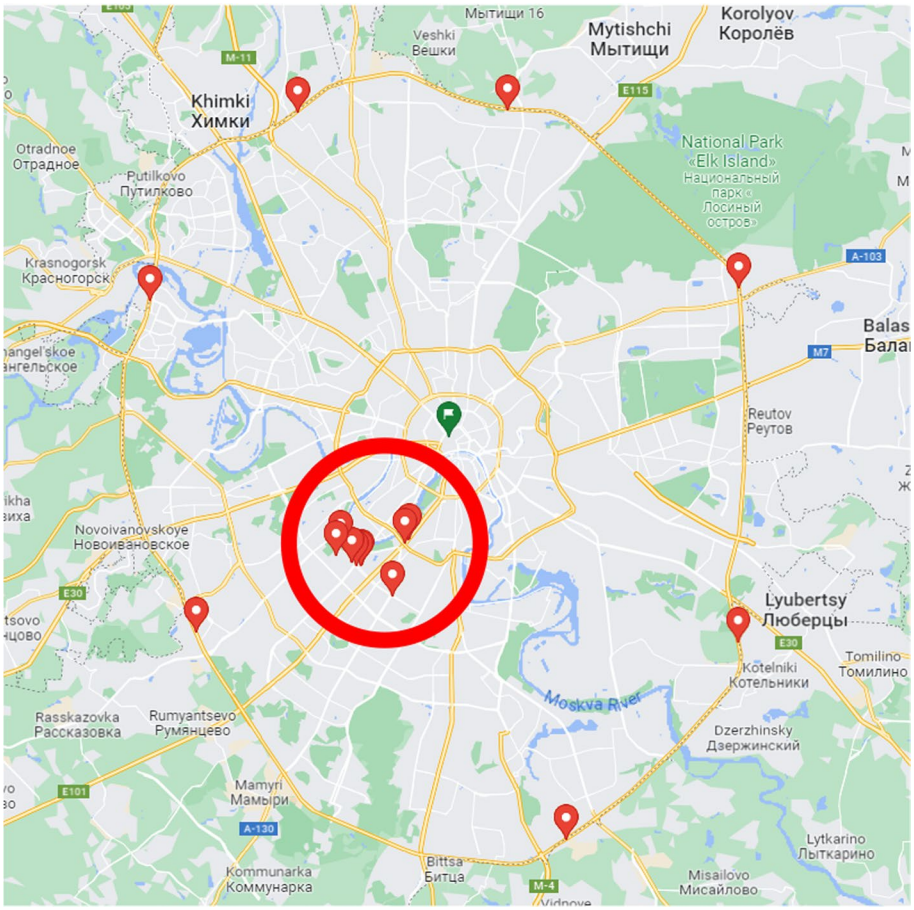


Fig. 6 Map of Vienna with sampling points

samples from Moscow were divided into two types. The first type are samples from the city center and the other type were samples taken from Moscow city circle.

Characterization of the sampled cities

Cities were selected to characterize cities in units of thousand, hundred thousand and million inhabitants. The individual collection points were chosen in such a way as to characterize the most frequented places in the given city. In Fig. 2: selected cities on the map, selected cities are shown.

Sampling sites in all cities were chosen to represent the characteristics of the cities. These are residential areas of the city, busy roads, crossroads, and cities exit or parks. In Fig. 3: comparison of transport by city and population we can see the dependence between the population in the selected city and the number of passenger vehicles in the city.

Jihlava (CZE)

Jihlava is a small regional town with a population of approximately 53,000. The town has a developed transport infrastructure. Because of its location in the middle of the highway connecting the two largest cities of the Czech Republic (Prague, Brno), Jihlava is a city with heavyt traffic. The number of passenger cars in Jihlava is around 51,000. In Fig. 4: map of Jihlava with sampling points is possible to see chosen locations, which characterize traffic in Jihlava.

Brno (CZE)

The urban agglomeration of Brno is the second largest in the Czech Republic. Approximately in the center of the South Moravian region. The population is about 390,000. The city has a developed transport infrastructure and industry. The number of passenger vehicles in Brno is approximately 206 000, i.e. 1.9 per passenger vehicle. In Fig. 5: map of Brno with collection points, it is possible to see selected locations that characterize transport in Brno.

Vienna (AUT)

The capital of Austria has a population of just under 2 million. It is the largest agglomeration in Austria. The city is a transport hub for Lower Austria. There are around 5 million

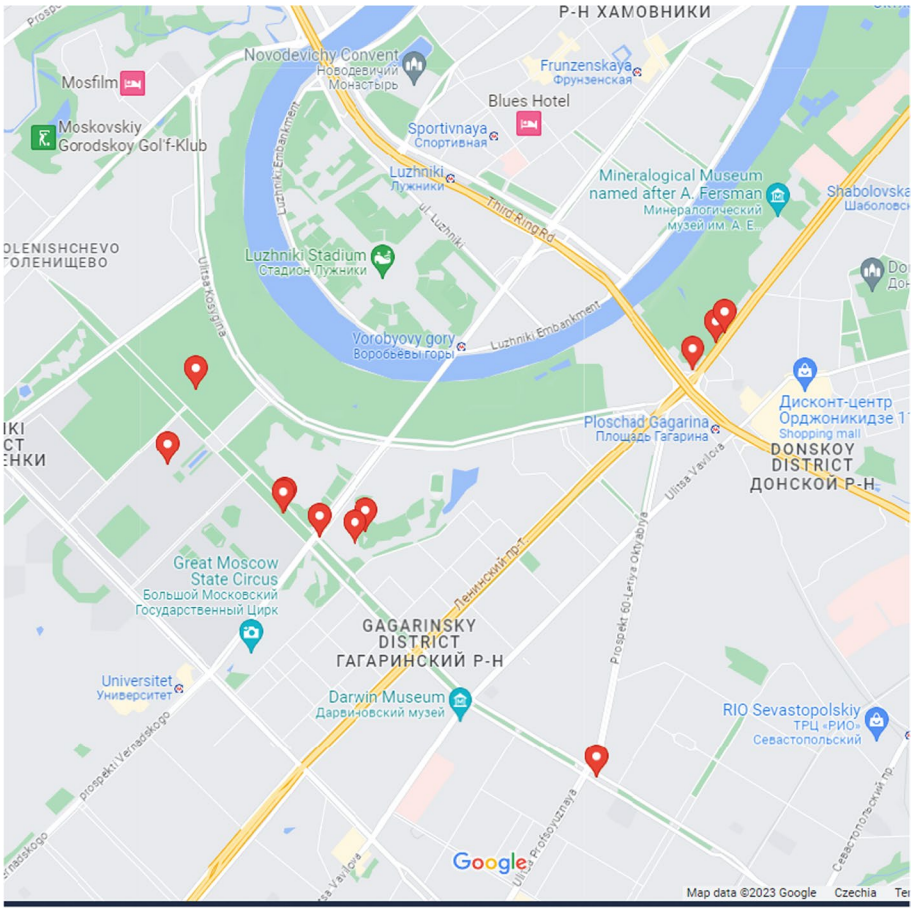


Fig. 7 Map of Moscow with sampling points—city center and circle

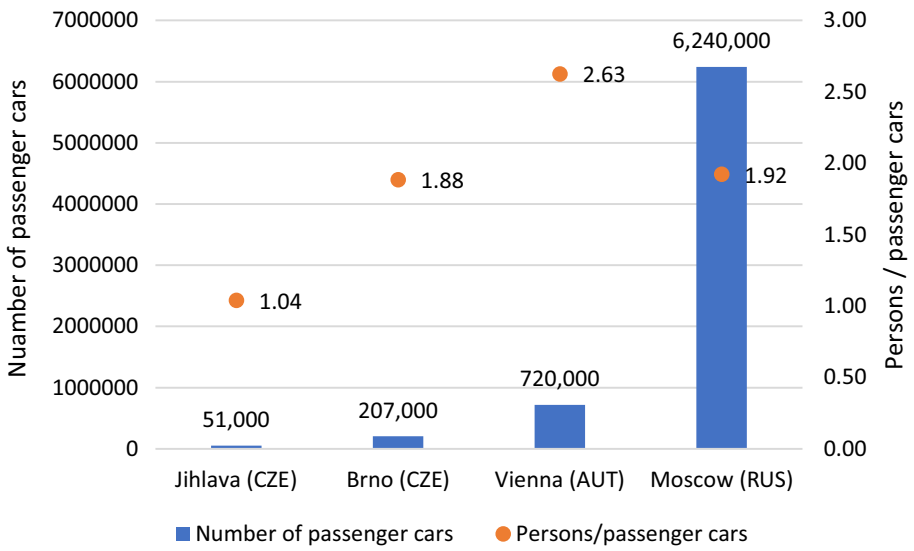


Fig. 8 Detail of city center sampling map—Moscow

Table 9 LOD and LOQ in the determination of Pt and Pd at a given wavelength

Metal	LOD (μg L^{-1})	LOQ (μg L^{-1})	Wavelength (nm)
Platinum	1.131	3.411	265.9
Palladium	2.210	5.895	247.6

registered motor vehicles throughout Austria. In Vienna are registered over 700,000 cars. In Fig. 6: map of Vienna with collection points, it is possible to see selected places that characterize transport in Vienna.

Table 10 Temperature program and measurement conditions applied for ContraAA 800D

Temperature program	Temperature (°C)	Temperature rise (°C/s)	Hold time (s)	Total time (s)
Drying 1	90	5	20	34
Drying 2	105	3	20	25
Drying 3	110	2	10	12.5
Pyrolysis	950	250	10	13.4
Atomization	2300	1400	6 Pd/8 Pt	6 Pd/8 Pt
Cleaning	2400	500	4.4	4.4

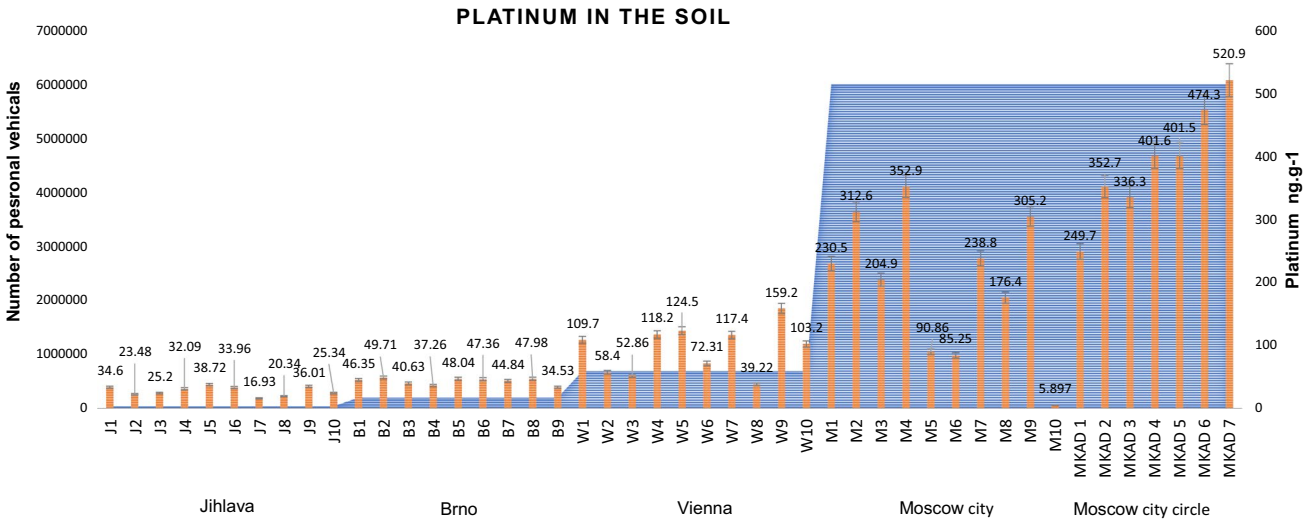


Fig. 9 Resulting platinum concentrations

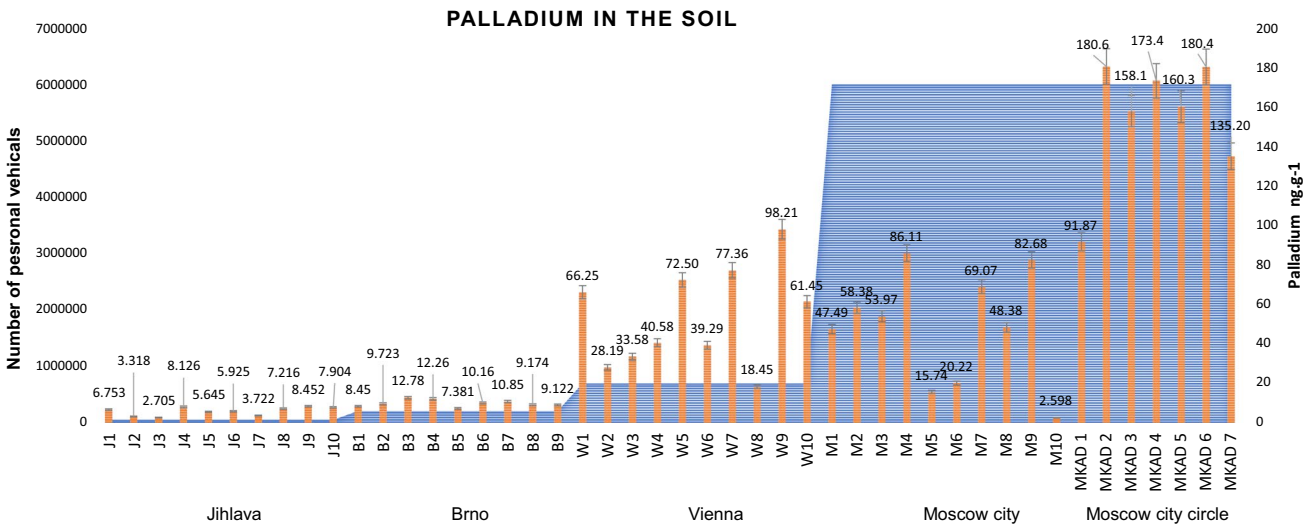


Fig. 10 Resulting palladium concentrations

Table 11 Concentration of platinum and palladium in the collected samples

City	Sample identification	Pt ng g^{-1}	Pd ng g^{-1}
Jihlava	J1	34.60 ± 1.73	6.753 ± 0.34
	J2	23.48 ± 1.17	3.318 ± 0.17
	J3	25.20 ± 1.26	2.705 ± 0.14
	J4	32.09 ± 1.61	8.126 ± 0.41
	J5	38.72 ± 1.94	5.645 ± 0.28
	J6	33.96 ± 1.69	5.925 ± 0.29
	J7	16.93 ± 0.84	3.722 ± 0.18
	J8	20.34 ± 1.01	7.216 ± 0.36
	J9	36.00 ± 1.80	8.452 ± 0.42
	J10	25.34 ± 1.26	7.904 ± 0.39
Brno	B1	46.35 ± 2.31	8.450 ± 0.42
	B2	49.71 ± 2.48	9.723 ± 0.48
	B3	40.63 ± 2.03	12.78 ± 0.69
	B4	37.26 ± 1.86	12.26 ± 0.61
	B5	48.04 ± 2.40	7.381 ± 0.36
	B6	47.36 ± 2.36	10.16 ± 0.50
	B7	44.84 ± 2.24	10.85 ± 0.54
	B8	47.98 ± 2.39	9.174 ± 0.45
	B9	34.53 ± 1.72	9.122 ± 0.45
Vienna	W1	109.7 ± 5.48	66.25 ± 3.31
	W2	58.40 ± 2.92	28.19 ± 1.41
	W3	52.86 ± 2.64	33.58 ± 1.67
	W4	118.2 ± 5.91	40.58 ± 2.02
	W5	124.5 ± 6.22	72.50 ± 3.62
	W6	72.31 ± 3.61	39.29 ± 1.96
	W7	117.4 ± 5.87	77.36 ± 3.86
	W8	39.22 ± 1.96	18.45 ± 0.92
	W9	159.2 ± 7.96	98.21 ± 4.91
	W10	103.2 ± 5.16	61.45 ± 3.07
Moscow city	M1	230.5 ± 11.53	47.49 ± 2.37
	M2	312.6 ± 15.63	58.38 ± 2.91
	M3	204.9 ± 10.25	53.97 ± 2.69
	M4	352.9 ± 17.65	86.11 ± 4.30
	M5	90.86 ± 4.54	15.74 ± 0.78
	M6	85.25 ± 4.26	20.22 ± 1.01
	M7	238.8 ± 11.49	69.07 ± 3.45
	M8	176.4 ± 8.82	48.38 ± 2.41
	M9	305.2 ± 15.26	82.68 ± 4.13
	M10	5.897 ± 0.29	2.598 ± 0.13
Moscow city cirlce	MKAD1	249.7 ± 12.49	91.87 ± 4.59
	MKAD2	352.7 ± 17.64	180.6 ± 9.03
	MKAD3	336.3 ± 16.82	158.1 ± 7.90
	MKAD4	401.6 ± 20.08	173.4 ± 8.67
	MKAD5	401.5 ± 20.07	160.3 ± 8.01
	MKAD6	474.3 ± 23.72	180.4 ± 9.02
	MKAD7	520.9 ± 26.05	135.2 ± 6.76

Moscow (RUS)

Moscow is the largest urban agglomeration in Russia and one of the largest on the European continent. There are currently over 6 million passenger cars in Moscow. With population growth, as residents of the Russian Federation migrate to large cities, there is also a sharp increase in passenger cars in these cities. In Fig. 7: map of Moscow with sampling points—city center and city circle present sampling points in full Moscow and Fig. 8: detail of city center sampling map—Moscow show detail near to Moscow state university (MSU).

Reagents

Hydrochloric acid 37% (HCl), Analytika spol s.r.o.

Nitric acid 67% (HNO3), Penta.

Acetone (C3H6O), Penta.

Ethyl alcohol absolute p.a. (CH3CH2OH) PentaAcetonitril (CH3CN),

Septonex PentaSeptonex®–carbaethoxypentadecyltrimethylammonium bromide (C21H44O2NBr), GNB a.s., Praha.

Certified reference material (CRM) platinum, palladium of concentrate 1 ± 0,002 g L^{-1} v 5% HCl, ASTASOL Analytika spol. s.r.o.,

Procedure

The samples were decomposed using microwave extraction. A maximum of 0.5 g was taken from the sieved samples and weighed from each sample. These samples were decomposed using microwave high-pressure extraction microwave digestion (MW) with the Ethos EASY system. Decomposition was carried out at a temperature of 180 °C for 25 min in a mixture of concentrated nitric acid and concentrated hydrochloric acid in a ratio of 1:3. After the decomposition was completed, the sample was transferred to a volumetric flask and filled to the required volume.

Preconcentration

Due to the content of interfering ions and the low concentration of platinum and palladium in the soil matrix, it is necessary to separate and concertize both metals. SPE extraction was chosen as a suitable method.

Extraction was carried out on SPE Bond Elut C-18 columns. SPE extraction is divided into 4 phase:

1. Phase is the conditioning of the sorbent with 10 ml of absolute ethanol, 10 ml of distilled water and then 10 ml Septonex® about concentration 0.005 mol L^{-1}.
2. Phase is the deposition of the prepared sample volume 100 ml.
3. Phase is to wash the sample with 10 ml of distilled water.
4. Phase is elution with acetonitrile in a volume of 10 ml. The eluate was evaporated on a Teflon dish and the evaporant was dissolved in 10 ml 0.1 mol L^{-1} hydrochloric acid.

Conditions of detection

An atomic absorption spectrometer ContraAA 800D (Analytik Jena, Germany) with a graphite furnace was used for the determination of platinum and palladium. The optimized temperature programs are shown in Table 9: temperature program and measurement conditions applied for ContraAA 800D. The following parameters were optimized for the method for the determination of platinum and palladium: wavelength, temperature program, slit width and the effect of acidity on the signal. Table 8: LOD and LOQ in the determination of Pt and Pd at a given wavelength present LOD and LOQ for ContraAA 800D.

All results obtained in this study were calculated as the average of three independent results. The resulting values of platinum and palladium concentrations in real samples are given as mass concentrations.

Results and discussion

Platinum and palladium were determined in a total of 46 soil samples from 4 different-sized cities—summarized in Table 10. Concentration of platinum and palladium in the collected samples. The lowest concentrations of Pt and Pd were determined in places with the lowest incidence of automobile traffic. This is, for example, background determination in the cities of Vienna and Moscow—both parks. The concentrations varied between Pt 5.897–39.22 ng g^{-1} and Pd 2.598–18.45 ng g^{-1}. Samples taken as background values were taken as far away from the road as possible. At the same time, the vegetation around the road, which serves as a barrier, was also taken into account. The samples from the parks were taken approximately 150 m from the road.

The highest concentrations of Pt and Pd were measured on the Moscow city circle (MKAD Moskovskaja kolcevaja avtomobilnaja doroga,), which serves as the main connecting node for the city with the suburban area, as well as a transportation hub for transportation from one end to the other. Unfortunately, due to the large number of passenger cars, which is almost comparable to the Czech Republic, there are almost always queues on this thoroughfare. Traffic congestion is at its worst in the morning and evening hours. It is then connected with the mobility of the city's inhabitants. Concentrations on MKAD ranged from 249.7 to 520.9 ng g^{-1} Pt and 91.87–180.6 ng g^{-1} Pd.

The concentration of Pt and Pd in cities is then directly proportional to traffic congestion. In Jihlava, which ranks among small towns, the concentration of Pt is in the range 16.93–38.72 ng g^{-1} a Pd 3.318–8.452 ng g^{-1}. There were concentrations in Brno, which ranks among the larger cities Pt od 34.53–47.98 ng g^{-1} a Pd 7.381–12.78 ng g^{-1}. In the Austrian metropolis of Vienna, Pt concentrations were in the range 52.86–159.2 ng g^{-1} and Pd 28.19–98.21 ng g^{-1}. In the largest of the monitored cities, Moscow, Pt concentrations were in the range 176.4–312.6 ng g^{-1} and Pd 15.74–86.11 ng g^{-1}. A graphical representation of the resulting values is shown in Fig. 9: resulting platinum concentrations from Fig. 10: resulting palladium concentrations.

Graphs are created based on the number of cars in a given city and the concentration of platinum or palladium.

In Vienna (marked W8) and Moscow (marked M10), background values were taken from the parks mentioned earlier in the text (Table 11).

Conclusion

The results of this study show that small, medium and large cities are exposed to platinum and palladium contamination from sources of automobile traffic. The study proves that the concentration of Pt and Pd depends very much on the intensity of car traffic and the style of driving. Soils near busy cities exit, interchanges, and highways are a significant anthropogenic source of Pt and Pd. Expressways have lower concentrations compared to crossroads. This is due to the driving style. Traffic is smoother on expressways. The traffic at crossroads is in a start/stop style. The highest concentrations were on the large city circle in Moscow. It is caused by traffic style and traffic congestion. This specific traffic artery is very congested mainly in the morning and afternoon rush hours. Even though it is an expressway, despite this, there are frequent traffic complications when vehicles drive very slowly in a start/stop style.

Already existing studies describe a negative effect on the health of the population. Even though the concentrations in the environmental components are low for drawing conclusions about the direct effect on the health of the population in areas with a high intensity of automobile traffic. Due to the ever-increasing number of cars in the world and the stricter requirements for exhaust gas emissions, it will lead to the more frequent use of platinum and palladium-based autocatalysts. For this reason, platinum and palladium will constantly be emitted into

the environment and may thus endanger the health of the population.

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Declarations

Conflict of interest The authors have no conflicts of interest to declare that are relevant to the content of this article.

Ethical approval This article does not contain any studies with human participants or animals performed by any of the authors.

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