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Spatial and temporal distribution of platinum, palladium and rhodium in Zagreb air

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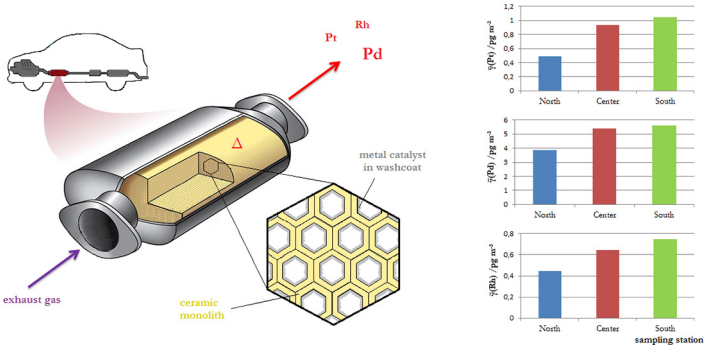
HIGHLIGHTS

- First measurements of Pt, Pd and Rh in PM_{10} and $PM_{2.5}$ in Croatia
- Higher concentrations of PGE related to higher traffic density
- Lower concentrations of PGE found in summer compared to winter
- Ratios of PGE found in PM_{10} similar to the ratio in automotive catalytic converters

GRAPHICAL ABSTRACT



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ABSTRACT

Platinum (Pt), palladium (Pd) and rhodium (Rh) are most widely used in the production of automotive catalytic converters that serve to reduce toxic emissions from motor vehicles. The aim of this study was to quantitatively determine the levels of platinum, palladium and rhodium in the PM_{10} and $PM_{2.5}$ fraction of airborne particle matter and find their spatial and temporal distribution at different polluted areas of the city of Zagreb, Croatia. The method used in this paper included weekly sampling of airborne particle matter on quartz filters, microwave digestion in acid under high pressure and temperature, and analysis by inductively coupled plasma mass spectrometry (ICP MS). The results have shown that the highest mean values at all three sampling stations (North, Center, South) were obtained for palladium (3.856 pg m^{-3}, 5.396 pg m^{-3}, 5.600 pg m^{-3}) and the lowest for rhodium (0.444 pg m^{-3}, 0.643 pg m^{-3}, 0.750 pg m^{-3}). The average mass concentrations of platinum group elements (PGE) in PM_{10} increased for all three elements in the direction North < Center < South which had to do with the traffic load nearby the monitoring stations. The ratio of measured mass concentrations to all measuring stations was similar to platinum, palladium and rhodium content in automotive catalytic converters. Factor analysis grouped platinum, palladium and rhodium at all of the monitoring stations, and their relation to other metals together with the aforementioned results indicate that their main source of pollution is traffic or precisely automotive catalytic converters. At all three of the monitoring sites, higher values were measured during the colder part of the year. The results of measuring platinum, palladium and rhodium levels in the city of Zagreb are the first results of their kind for this area and will provide insights into the contribution of catalytic converters to the presence of these elements in the environment.

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1. Introduction

Platinum (Pt), palladium (Pd) and rhodium (Rh) are considered strategic metals because of their specialized application in various industries (e.g. automotive, chemical, oil) as well as in dentistry, medicine, aerospace and agriculture. Due to their increasing application and the important role of these metals in the manufacturing of automotive catalytic converters, there research has been conducted in recent years on the quantitative determination of Pt, Pd and Rh in the environment, especially near roads (Rao and Trivedi, 2005). The assumption is that the health risks associated with human exposure to platinum group elements (PGE) in the environment are minimal. However, recent PGE toxicity studies, given their bioavailability and concentration in the environment and biologically important media, show that exposure to these metals can pose a health risk, especially at the chronic, subclinical level (Ravindra et al., 2004; Wiseman and Zereini, 2009). Platinum, palladium and rhodium can be easily mobilized and dissolved in various compounds often present in the environment, thereby increasing their bioavailability (Puls et al., 2012). Platinum group elements can be transformed into intoxicated compounds by inputting into the organism. Moreover, the elements of the platinum group and their complex salts pose a potential risk to human health by causing asthma, allergies, congenital conjunctivitis, and other serious health problems (Wang and Li, 2012). Wang and Li (2012) also described the bioavailability of Pt, Pd and Rh in the environment and their possible pathways in the organism. In addition to particulate matter, platinum elements have been found in dust and soil along the road, which then reaches surface waters and sediments and is transported to the coastal area (Wang and Li, 2012).

Previous research related to platinum group elements in the environment included water (Zimmermann et al., 2003), soil (Morcelli et al., 2005; Pan et al., 2009), plants (Hooda et al., 2007; Lesniewska et al., 2004; Pan et al., 2009), dust along the road (Lesniewska et al., 2004; Motelica-Heino et al., 2001), sewage sludge (Jackson et al., 2010; Motelica-Heino et al., 2001) and shells (Essumang et al., 2010; Sures and Zimmermann, 2007). All of the authors came to the conclusion that palladium is bioaccumulated to a much greater extent than other platinum metals. Kümmerer et al. (1999) analyzed platinum in the sewage waste of hospitals and hospital departments, and their results have shown that sewage waste is not the most important source of platinum in the environment, compared to platinum emissions from other sources, but its impact should not be ignored (Kümmerer et al., 1999). The main pathways of platinum metal intake into a human organism are by inhalation of fine particles (to which PGE is bound), through the skin and intake of food/water.

Determination of platinum metal requires high sensitivity, selectivity and rapid analytical methods, especially for recognition and quantitative determination. Spectral interference, matrix complexity, and instability of dilute aqueous solutions of platinum, palladium and rhodium represent a problem in the analysis of low concentrations of these metals in the environment. Due to all of the above stated, the methods of determining platinum, palladium and rhodium have been the subject of numerous investigations (Dubiella-Jackowska et al., 2007; Kulkarni et al., 2007; Rinkovec et al., 2017; Sucha et al., 2016).

The aim of this study was to quantitatively determine the concentration of platinum, palladium and rhodium in particulate matter in Croatia. Particulate matter was collected over two years at three locations in the various contaminated areas of the city of Zagreb. The research in this paper gives the first information on the levels of platinum, palladium and rhodium in Croatia and the region as well as their spatial and temporal distribution. The relationships between the mentioned elements and other metals bounded to particulate matter were investigated in order to determine potential sources of air pollution by platinum group metals.

2. Materials and methods

Weekly samples of particulate matter with an aerodynamic diameter < 10 μm (PM_{10}) were collected continuously from 27 April 2015 to 6 March 2017 on ø 90 mm quartz filter paper with a daily air flow of approximately 100 m^3 at three stations located in different parts of the city.

2.1. Monitoring stations

Zagreb has a population of approximately 790,000 inhabitants and over 350,000 registered vehicles (Statistical Yearbook of the city of Zagreb, 2017). The positions of the monitoring stations are shown in Fig. 1. The urban background site (NORTH) was situated in the northern residential part of Zagreb (45°50′6.83″N, 15°58′42.12″E), 168 m above sea level. The nearby road contains two lanes in both directions (north-south and south-north). Pollution at this site originates from domestic furnaces and moderate traffic. Monitoring site CENTER (45°48′39.6″N, 15°59′6″E) was located in the center of Zagreb and is characterized by heavy traffic and tall urban houses. The road around the monitoring station contains three lanes in the directions west-east and east-west; two lanes in the direction south-north and one lane in the north-south direction. This station is close to offices and schools. The measuring site SOUTH was located in the southern part of Zagreb (45°46′22.8″N, 15°58′44.4″E) and it is defined as an urban traffic monitoring station, burdened with heavy traffic and close to offices and schools. There is a big crossroads near the monitoring station with 3 lanes going in every direction (south-north, north-south, west-east and east-west). At measuring station North, in the period from 1 February 2016 until 6 March 2017, in parallel with the PM_{10} fraction, a fraction of $PM_{2.5}$ (particulate matter with an aerodynamic diameter < 2.5 μm) was sampled.

2.2. Determination of platinum, palladium and rhodium

The method for the determination of Rh, Pd and Pt in particulate matter used in this research was described previously by Rinkovec et al. (2017). It was tested using standard solutions, model samples, certified reference materials and real samples.

The method used included the preparation of collected quartz filters (Pall Life Sciences, Port Washington, NY, USA) by microwave digestion in acid (5 mL of 25% HNO_3) under high pressure and temperature (digestion system Ultraclave, Milestone, Sorisole, IT) for 30 min. Following digestion, 0.1 mL of concentrated HCl was added and diluted to 20 mL with distilled water and analyzed by inductively coupled plasma mass spectrometry (ICP-MS, 7500cx, Agilent Technologies, Santa Clara, CA, USA). The selected isotopes ^{103}Rh, ^{105}Pd and ^{195}Pt were used for analysis. ^{115}In was used as an internal standard. The ICP-MS spectrometer was tuned to obtain an oxide ratio and doubly charged ratio < 1%. The tuned operating parameters were: RF power 1550 kW, RF matching 1.72 V, carrier gas flow rate (Ar 5.0) 1.15 L/min, helium (He 6.0) gas flow rate 3.5 mL/min in the collision cell. The carrier and make-up gas flow rate were optimized to maximize the sensitivity and minimize interferences. Working standards (5% HNO_3/1% HCl (v/v)) were prepared from stock solutions (Inorganic Ventures, Santander, ES, 1000 μg mL^{-1}) of Rh, Pd and Pt at nine level concentrations (0.05–4.80 ng mL^{-1}) and calibration was carried out every time before sample analysis. The method detection limit for Pt was 0.045 pg m^{-3}, for Pd 0.908 pg m^{-3} and for Rh 0.177 pg m^{-3} and the accuracy of the method was determined by adding known amounts of Pt, Pd and Rh standard solution onto reference materials NIST 1648 and ERM CZ120 (PM_{10} like CRMs). The recoveries ranged from 86% to 100% for Pt, 92% to 115% for Pd and 90% to 104% for Rh. Vanadium(V), manganese (Mn), iron (Fe), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), cadmium (Cd) and lead (Pb) were also analyzed from the prepared samples in the same run as Pt, Pd and Rh. The method detection limits for V, Mn, Fe, Ni, Cu, Zn, As, Cd