International Journal of Hygiene and Environmental Health xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

International Journal of Hygiene and Environmental Health

journal homepage: www.elsevier.com/locate/ijheh

Exposure of the German general population to platinum and rhodium – Urinary levels and determining factors

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ARTICLE INFO

Article history:
Received 31 May 2016
Received in revised form 22 July 2016
Accepted 25 July 2016

Keywords:
Platinum
Rhodium
Human biomonitoring
Dental restoration
Traffic emission

ABSTRACT

In this study the exposure of the general population in Germany to platinum and rhodium and its determinants was investigated in 259 participants (subdivided in three groups) by urine analyses and assessment of the dental status. Complementary, an interview including questions characterising possible exposure to traffic exhaust was conducted. The median excretion was 2.42 ng platinum/g creatinine and 7.27 ng rhodium/g creatinine. The detailed analysis of the collected data showed significant higher platinum excretion values with increasing number of surfaces covered with restorations containing precious metals ($R = 0.389$; $p < 0.001$), but also higher values for habitants of urban areas (median = 3.43 ng/g creatinine; *95th* percentile = 25.2 ng/g) compared with those of rural areas (median = 2.06 ng/g creatinine; *95th* percentile = 20.0 ng/g). Also, participants working in urban areas showed higher platinum excretion values (median = 3.27 ng/g; *95th* percentile = 19.6 ng/g). Male participants living and working next to highly frequented roads showed higher rhodium excretion values (median = 7.27 ng/g; *95th* percentile = 13.5 ng/g). In summary, the study showed that exhaust emissions have an influence on platinum and rhodium excretion, but for platinum this influence is rather low compared to the influence of precious metals containing restorations.

1. Introduction

Due to their catalytic properties and their resistance to corrosion and strength at high temperatures, platinum group elements (PGEs) are used in catalytic converters, like automotive exhaust catalysts or industrial catalysts. Further fields of application are dentistry, petrol, electrical and chemical industries, as well as glass and jewellery manufacturing (Johnson Matthey Public Limited Company, 2012; Lindell, 1997; NAS, 1977; WHO, 1991).

The purpose of using catalysts in cars is to reduce the hazardous components carbon monoxide (CO), hydrocarbon (HC) and nitrogen oxide (NO_x) in the exhaust gas (Gómez et al., 2002; Mooney, 2005). However, the ratio of the precious metals' composition varies between catalyst models due to persistent price increases for platinum and rhodium together with the efforts to optimize the performance of the catalyst (Koltsakis and Stamatelos, 1997; Palacios et al., 2000b; Spada et al., 2012; Zereini et al., 1997a). Basically the PGEs emission of automotive catalysts is caused by stress on the catalyst. Main factors for this stress are fluctuating operating temperatures, gas compositions and flow rates of the exhaust gases as well as the mechanical stress caused by vibration and aging (Artelt et al., 2000; Palacios et al., 2000b). König et al. (1992) determined in automotive exhaust gas a mean platinum emission of 3.3-39.0 ng/m^3. The reported emission of soluble PGEs averages 1% of the total PGEs released from catalysts (Artelt et al., 2000; König et al., 1992; Palacios et al., 2000a; Ward and Dudding, 2004). Additionally, an emission of elemental platinum in the nanometre size range with a bioavailability of up to 16% after 90 days has been described (Artelt et al., 1999). Moreover, there is some evidence that Pt mobilization from soil might increase over time (Zereini et al., 1997b). Since the reduction of the of exhaust emissions limits by the European Union in 1993 (Council of the European Union, 1993) which caused that new cars were equipped with automotive exhaust catalysts, an increase of PGEs in the environment has been found in several studies (Wichmann et al., 2007; Zereini et al., 2007).

A second major field of application for PGEs is in restorative dentistry. PGEs are part of noble metal alloys for prosthodontic

Abbreviations: PGE, Platinum group elements; PMA, Precious metal alloys; $N_{S\text{-}PMA}$, Number of surfaces covered with precious metal alloys.

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http://dx.doi.org/10.1016/j.ijheh.2016.07.019
1438-4639/

restorations. PGEs facilitate the manufacturing and prolong the stability of noble metal containing dentures. Furthermore PGEs are used to reduce the grain size and to improve elongation, tensile strength, yield strength, elastic modulus and porcelain-bonding properties of the alloys. Another reason for their usage is to get cheaper and more equally expensive alloys due to the inconstant price of gold (Wataha, 2002). The ratio of the different metals used for the dental alloys is highly variable. An influence of noble metal containing prosthetic restorations on PGEs excretion was described by Begerow (1999) with increased excretion values of PGEs after insertion of such restorations. Asides from dental restorations, platinum is used in other human implants, like cardiac pacemakers and silicone breast implants. The latter have shown to increase urinary platinum excretion significantly (Schierl et al., 2014). Other general environmental sources for PGEs, like diet components (i.e. meat, grain products, fruits and vegetables), have been identified too (Begerow et al., 1999; Bernstein et al., 2006; Kümmerer et al., 1999; Vaughan and Florence, 1992 Bernstein et al., 2006).

Typical routes of entry for PGEs in the human body apart from therapeutic administration are inhalation and gastrointestinal uptake. The majority of oral administered PGEs are released unabsorbed via faecal excretion. It is believed that absorbed PGEs are bound to proteins during distribution and for storage in the body (Artelt et al., 1999; Moore et al., 1975b). Absorbed PGEs are eliminated via renal and faecal excretion with the renal route being dominant (Artelt et al., 1999; Moore et al., 1975a, 1975b). Potential health effects are still discussed controversially (Dubiella-Jackowska et al., 2009), but there is evidence that PGEs facilitates the immune response to allergens (Paolucci et al., 2007).

Not yet satisfyingly clear is the impact of the various sources on the uptake in the general population and the different exposure routes on the internal exposure of the general population to PGEs. The present study investigated the urinary levels of platinum and rhodium as measure of internal exposure in individuals of urban and rural German population and the impact of two assumed determinants, automotive exhaust emissions and dental alloys of precious metals. Both PGEs included in the study are supposed to be used for manufacturing catalytic converters, but in contrast to platinum, only small amounts of rhodium are used for dental restorations and might therefore be a measure for automotive exhaust emissions rather than for the release from dental restorations. Therefore, Iavicoli et al. (2007) proposed that both, platinum and rhodium are suitable as biomarkers for traffic exposure.

2. Material and methods

2.1. Subjects

The study group consists of a total of 259 persons, split up into groups. The three groups chosen are representing very different subpopulations in terms of potential traffic exposure. The subjects of the first group (Group I) lived in an urban area, subjects belonging to the second group (Group II) lived in a rural area, and subjects of the third group (Group III) worked in areas with a high risk of exposure to automotive exhaust emissions. One hundred subjects subsumed in Group I, were recruited and examined in the Dental Clinic of the University Hospital Erlangen. The recruitment and examination of the 74 subjects of Group II had been carried out in a dental surgery in Amberg, a rural town in northern Bavaria. Both, Group I and II consist of patients in need of dental care as well as of routine check-up patients. Group III consists of 85 subjects with occupational exposure to automotive exhaust emissions. Twenty-six of them were employed as road maintenance staff in northern Bavaria. Their recruitment and examination was carried out at several maintenance depots at the beginning of the participants' shift. Another 6 subjects working as mechanics were recruited and examined at a local car workshop in the metropolitan area of Nuremberg (northern Bavaria). The remaining 53 participants of group III worked in the road construction sector in the same region. Recruitment and examination of these subjects was carried out at training courses. The participants of Group III lived in both urban and rural areas. Due to their creatinine levels (see below) or a history of chemotherapy in the past 37 and 2 participants, respectively were excluded from analyses.

All participants took part in an interview, their dental status was examined and a urine sample was obtained. Subjects gave written informed consent, according to the declaration of Helsinki. The study was approved by the ethics commission of the medical faculty of the university of Erlangen-Nürnberg.

2.2. Interview

An interview following a standardized questionnaire was performed to register anthropometric and lifestyle factors (such as weight, height, smoking behaviour) and potential sources of PGEs. Potential exposure to traffic, like volume of traffic at their residence and place of work or the main means of commuting, was enquired. Sources of PGEs that are relevant at the workplace, for example working with PGEs containing materials, but also the geographical position of workplace and residence, whether in urban or in rural areas, were assessed.

Additional data of the social status, potential medical PGEs sources, as well as diet customs were recorded. These data were evaluated in a separate study (Röß et al., in preparation).

2.3. Dental status

The interview was followed by the registration of the dental status of each subject. All examinations were performed by a licensed dentist and two dental students. Thereby missing teeth and all dental restorations were recorded in the dental status. For evaluation all surfaces covered with metallic restorations were counted to quantify a potential exposure to PGEs (Drexler and Schaller, 1998). The maximum count of surfaces for incisors and canines was four, for molars and premolars five. For pontics the maximum possible count was one count less than the maximum count of the correspondent tooth due to a reduced restoration surface being in contact with the salivary juice in the oral cavity. The surfaces were subdivided into "precious metal alloys", "base metal alloys" and "amalgam" containing, the surfaces of precious and base metal alloys were additionally subdivided in "veneered" and "not veneered".

2.4. Urine samples

A urine sample was obtained after interview and examination and stored frozen until analysis at −20 °C. All urinary data were related to their corresponding creatinine level to reduce the influence of the participant's fluid intake on the urinary excretion of PGEs. Creatinine adjustment has been found to be beneficial for analysing for many metals and other elements (Morton et al., 2014). Since highly reduced and increased fluid intake results in diluted or concentrated urine, inclusion criteria for further analyses were a creatinine values between > 0.3 and < 3 g/l.

2.5. Sample analysis

Platinum, rhodium and creatinine content were determined in urine. For platinum analyses samples were digested by UV-photolysis and analysed by inverse voltammetry (694 VA Stand, 693 VA Processor, Metrohm) (Ensslin et al., 1994; Schierl et al., 1998). In