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# Biomonitoring Exposure to Platinum, Palladium and Rhodium in Young University Students from Leicester, England †

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**Abstract:** We assessed the dietary exposure to platinum group elements [PGEs; platinum (Pt), palladium (Pd) and rhodium (Rh)] in young adults (18–23 yrs old) at De Montfort University (DMU, England). A total of 111 (20.45 yrs old; 78 female) DMU students participated. PGEs were analysed in scalp hair by ICP-MS. Pt was detected in hair from sixteen female [median and IQR, in µg/g: 0.00014 (0.000036, 0.000551)] and two male participants [P95 = 0.00205, in µg/g]; Rh was detected in seven female [P95 = 0.0038, in µg/g] and six male participants [median and IQR, in µg/g: 0.00097 (0.00028, 0.00335)]. Our results suggest that DMU students show minimal exposure to PGEs.

**Keywords:** platinum group elements; Pd; Rh; human hair; dietary intake; university students

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## 1. Introduction

The rapid development and expansion of urban environments are occurring on a global scale, resulting in new and unprecedented environmental hazards to human populations. Within these hazards, metal and metalloid contamination has become a worldwide health concern, although not all trace elements are as well known as lead or mercury. Thus, since the obligation to manufacture European Union vehicles with catalytic converters as of 1 January 1993 [1], an increase in the presence of platinum (Pt), palladium (Pd) and rhodium (Rh) in different environmental compartments has been described in the literature [2,3]. These metals, also known as platinum group elements (PGEs), are the active components of catalysts [4] and are used to reduce emissions of various pollutants into the environment. Specifically, Pt and Pd oxidise carbon monoxide to carbon dioxide and hydrocarbons in water. Rhodium, meanwhile, is able to reduce a range of nitrogen oxides.

Despite the use of catalytic converters having a major benefit for the reduction in the emissions of important environmental contaminants such as lead, the potential effects of PGEs on human health in the short and long term have not been well established. Moreover, the environmental fate of these pollutants and their toxicokinetic in humans are not well understood yet. The amount of PGEs emitted by catalytic converters depends on the speed of the vehicle, type of engineering, age of the catalyst, and the additives used in the fuels. Moreover, Pt is also used in jewellery; as catalysts/additives in the chemical, electronic and glass industries; in dental amalgams [5], and in the manufacture of chemotherapy drugs [5,6]. Hospitals have also been described as a source of Pt emissions [7]. Rh has a number of significant applications in the chemical industry [8].

Once emitted, PGEs can travel short distances through the air due to their mass and are then deposited around the emission sources, primarily traffic lanes. Despite previous assumptions of their relative inertness, various authors have reported that PGEs can undergo a series of environmental transformations, resulting in the conversion of these metals into more reactive forms that could potentially become bioavailable [2,9].

Based on this, different studies have linked levels of PGEs in the blood and plasma of occupationally unexposed individuals to vehicle emissions [10]. Likewise, Caroli et al. [11] have found a strong linear correlation between urine Pd and Rh concentration with traffic density, but not for Pt.

While the human toxicity of Pt has been studied in detail, little is known about the pathophysiology of Pd and Rh [8,9]. In general, metallic forms are considered biologically inert, although Pt compounds such as tetrachloride and hexachloroplatinate are known to be allergenic and nephrotoxic. Moreover, platinum-based cytostatic drugs, for example cisplatin, are genotoxic [12]. The exposure to Pd compounds has also been linked to severe seizures and toxic effects on the heart and kidney [9,13]. Regarding the pathophysiology of rhodium salts, there is controversy [14], but it is largely unknown. PGEs accumulate primarily in the liver and kidneys and are eliminated through the urine [8].

Despite the increasing uses and environmental presence of PGEs, little is known about their chemical burden on the English population. As a result, a human monitoring programme was performed to determine the exposure to these pollutants in young university students attending an English University in Leicester, in the East Midlands, in the United Kingdom (UK).

## 2. Material and Methods

Leicester is one of the largest cities in the UK that supports a high population density; thus Leicester's 2024 population has been estimated at 570,858 [15]. Leicestershire has housed important industries related to textile production, coal mining, quarrying and brick manufacture, along with many engineering enterprises that have used different metals including iron, aluminium, cadmium, zinc and chromium.

### *2.1. Dietary Intake of PGEs*

Comprehensive nutrient intake was collected from 111 (20.45 $\pm$ 1.16 yrs.-old; 78 female) DMU students between 2015 and 2016 from three major ethnic backgrounds/continental origins (41 Asia, 41 Africa, 27 Europe) using a validated variant of the Nutrition Norfolk Food Frequency Questionnaire (version 6, CAMB/PQ/6/1205) [16] and a previous food frequency questionnaire (FFQ) used by our group [17]. Thus, some food items were modified and/or added to adapt the FFQ to the target population following the indications of McCance and Widdowsons's *The Composition of Foods* [18] for the most commonly consumed foods in the UK. A comprehensive literature review was carried out to include food items that are commonly consumed by the diverse populations living in Leicester (especially populations from China, Eastern and Central Europe and South Asia). FFQs are relevant tools in epidemiological studies to evaluate the relationship between diet and health outcomes [17]. Collected FFQs were processed with Nutritics® software (v.5.7 Research Edition, Nutritics Ltd., Dublin, Ireland). Underweight/overweight individuals were identified based on their body mass index (BMI; using the formula kg/m$^2$), depending on their ethnic background/continental origin [19].

### *2.2. Scalp Hair Samples*

PGEs were also analysed in scalp hair provided by 73 of these participants (58 female), as human hair has been described as a reliable tool to monitor environmental exposure to Pd and Pt [20]. Each hair sample (approximately 1.0 g) was washed with Triton X-100 (1%, *v*/*v*; bought from Sigma-Aldrich Co., Saint Louis, MO, USA) in ultrapure water

Milli-Q (resistivity 18.2 MΩcm) for 5 min in an ultrasonic bath and a second time only with ultrapure water Milli-Q to minimise the influence of exogenous contamination [21,22]. Once washed, samples were rinsed with ultrapure water Milli-Q and dried at about 50 °C to a constant weight. Triton X-100 was used to remove exogenous contamination without affecting the endogenous composition of metals [22].

The concentration of each PGE was determined by inductively coupled plasma mass spectrometry (ICP-MS, Perkin Elmer Elan 6000, Perkin Elmer Inc., Waltham, MA, USA), according to previous methods [23–25]. Blanks used during the acid mineralisation were also run every 5 samples. The limit of detection for these metals is provided in Table 1.

**Table 1.** Levels of PGEs in hair (µg/g) of university students from Leicester, England.

| Element | Population | LoD | Arithmetic Mean | Median | Range | Interquartile Range | *p*-Value |
|---|---|---|---|---|---|---|---|
| Female | Pd | 0.0057 | / | / | / | / | / |
| | Pt | 0.00046 | 0.0011 ± 0.0079 | 0.00014 | 0.00047–0.00895 | 0.00004, 0.0005 | 0.288 |
| | Rh * | 0.0014 | / | / | 0.01842–0.00835 | P95 = 0.00379 | 0.00392 |
| Male | Pd | 0.0057 | / | / | / | / | / |
| | Pt | 0.00046 | / | / | 0.00058–0.005511 | P95 = 0.00206 | 0.288 |
| | Rh * | 0.0014 | 0.0053 ± 0.0283 | 0.00097 | 0.00159–0.01653 | 0.00028, 0.0033 | 0.00392 |

LoD = limit of detection (µg/g); arithmetic mean results are presented as mean values ± S.D.; statistical significance: * ($p < 0.05$).

### *2.3. Statistical Analyses*

Statistical analyses were performed using the free software R-project, version 4.1.0 [12]. Data were processed with the statistical package "NADA" in R due to high presence of censored results (data presented as censored percentages for Pd, Pt and Rh, respectively: 100%, 75.34%, 82.19%). Significance scores were based on Kruskal–Wallis for nonparametric multiple comparisons; one-way analysis of variance was used for normal multiple comparisons. For normality, Shapiro–Wilk test was used. Differences were considered statistically significant at *p*-values lower than 0.05.

## 3. Results and Discussion

Palladium was not detected in any of the scalp hair samples monitored, which might suggest that the DMU students monitored had minimal environmental and/or dietary exposure to this element. However, to rule out exposure, PGEs should also be measured in urine in future studies, as these metals are mostly eliminated in the urine. Contrarily, Pt and Rh were detected in scalp hair collected from a few participants, as described in Table 1. Specifically, Pt was detected in hair from sixteen female [median and IQR, in µg/g: 0.00014 (0.000036, 0.000551)] and two male participants [P95 = 0.00205, in µg/g]; Rh was detected in seven female [P95 = 0.0038, in µg/g] and six male participants [median and IQR, in µg/g: 0.00097 (0.00028, 0.00335)].

Only Rh showed sex-dependency (*p*-value = 0.00392), possibly due to the high presence of censored values in female/male participants. The concentrations of Pt were similar to those reported in adolescents' hair from Palermo (data provided as median and reference interval; 0.00156; 0.00025–0.00419, all in µg/g), which also reported higher levels in females [20]. However, in previous human biomonitoring studies carried out by our research group, we detected Pd (9.24%) and Rh (5%) only in a few of the scalp samples collected in Spanish children (6 to 9 years old; 70 girls) born and residing in Alcalá de Henares (Spain); meanwhile, Pt was not detected in any of the samples monitored [25]. We originally attributed this distribution to the higher mobility and biological uptake rates described for Pd and Rh in comparison to Pt. However, a different trend has been observed in the hair of DMU students, which would highlight the necessity for further research into the assimilation and toxicokinetics of PGEs in humans.

In relation to their BMI values, 25.7% and 8.3% of this population were overweight (BMI between 25 and 29.9 kg/m$^2$) and obese (BMI $\geq$ 30 kg/m$^2$); meanwhile, 9.2% were underweight (BMI < 18.5 kg/m$^2$). Our results suggested that female individuals were slightly more likely to be overweight or obese, although without statistical differences ($p$-value = 0.2886). Moreover, the dietary intakes of Pt [underweight (0.00016) < overweight (0.000042) < normal weight (0.000034) < obese (<LoD); $p$-value = 0.496] and Rh [overweight (0.00011) < normal weight ($6 \times 10^{-5}$ < obese ($5.4 \times 10^{-7}$) < underweight (<LoD); all in µg/g; $p$-value = 0.500] showed tiny variations according to the BMI for all the individuals together, although without statistical differences, which might be attributed to the low/different number of responses. Similarly, levels of Pt and Rh did not show dependency according to their ethnic backgrounds/continental origins ($p$-values = 0.459, 0.072, respectively).

Regarding the dietary intake, Pt was positively correlated with fatty fish intake (r = 0.292; $p$-value < 0.05), and Rh was positively correlated with the intake of dairy products and fish (r = 0.293, 0.286; $p$-value < 0.05) and was very positively correlated with the intake of eggs, meat, crisps and snacks (r = 0.311, 0.315, 0.335; $p$-value < 0.01). The differences in intake of these foods might explain the sex differences found for Rh in hair. Thus, the intakes of eggs (17.625 vs. 16.998 g/day) and meat (271.55 vs. 193.06 g/day) were higher in male counterparts. Similarly for Pt, female participants eat more fatty fish (13.41 vs. 10.05 g/day). To date, there have been no proposals for concentration limits for platinum group elements in water or food. This is despite the fact that these metals could represent an emerging risk, given their continuous and increasing use and discharge into the environment. Further toxicological studies are required to inform any future proposals for concentration limits. This is particularly relevant for Pt, as it has been described that diet could represent a substantial contribution to the total Pt intake [26–28].

## 4. Conclusions

Our results suggest that, in general, DMU students had minimal exposure to PGEs, particularly palladium. However, their increasing number of applications in vehicles and electronic/medical industries highlight the importance of performing similar biomonitoring studies in the near future that also include the collection of urine samples to identify the potential risks to young British university students. Thus, for example, rhodium has a prominent role in fabricating three-way catalysts (TWCs) owing to its catalytic reactivity properties towards the decomposition of nitrogen oxides ($NO_x$), critical for NO reduction [29].

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