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Occurrence of palladium and platinum in human scalp hair of adolescents living in urban and industrial sites

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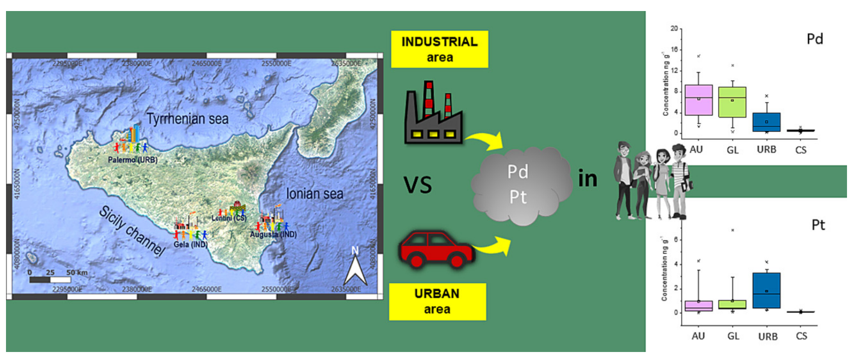
HIGHLIGHTS

- Human hair is a reliable tool to monitor environmental exposure to Pd and Pt.
- Pd and Pt play a crucial role as vehicle exhaust catalysts in environmental pollution.
- Pd occurs at the highest relative concentrations in industrial context.
- Gender-related differences in hair in studied areas were not found.
- Pd and Pt represent a potential health risk to the local population.

GRAPHICAL ABSTRACT



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ABSTRACT

Platinum group elements (PGEs) can be naturally found at very low concentrations in the Earth's crust. However, the increasing uses of PGEs in vehicle exhaust catalysts, in addition to some other applications (industry, jewelry, anticancer drugs) cause their anthropogenic emission and dispersion in the environment. The use of human hair samples analysis is considered a suitable biological indicator to assess human occupational and environmental exposure. It is an easily accessible material for individuals or population groups of non-invasive sampling. The aim of this study is a comparative analysis to investigate human hair content of Pd and Pt in adolescents, of both genders, residing near petrochemical plants of Augusta and Gela, in urban area of Palermo, and Lentini as control site (Sicily, Italy). A total of 108 samples were taken from school students (11–14 years old). Hair samples were cleaned, mineralized, and processed for analyses by inductively coupled plasma–mass spectrometry (ICP-MS).

The samples from the industrial sites of Gela and Augusta do not have statistically significant differences between them for either Pd for Pt; however, they differ from the samples relating to the city of Palermo. Median Pd concentrations are higher than Pt in industrial sites and control site. In urban site the levels of both metals were comparable. The study does not reveal any statistically significant difference between Pd and Pt concentrations in female and male samples. The data confirm that the study areas are heavily affected by industrial and urban emissions of Pd and Pt, representing a potential hazard to the local population.

1. Introduction

Platinum group elements (PGEs) can be naturally found at very low concentrations in the Earth's crust, and in the various environmental geospheres in ultra-trace quantities. Other known anthropogenic PGE sources to the environment are noble metal production, anti-cancer drugs, and coal combustion (Rauch et al., 2006; Reimann and Niskavaara, 2006; Zereini et al., 2012).

Since the introduction of automobile catalytic converters in the 1980s, platinum (Pt), palladium (Pd), and rhodium (Rh) have attracted increasing interest in environmental research as these metals are released in small amounts, together with particles from the wash coat of the catalytic

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converter into the environment, leading to increased concentrations of PGEs in environmental media such as air, soil, street dust, as well as in vegetation and organisms (Gomez et al., 2002; Djingova et al., 2003; Jackson et al., 2007; Colombo et al., 2008).

The growing use of PGEs in the automotive industry, as well as other applications in the industrial, jewelry, and pharmacological fields, has increased their diffusion in various environmental compartments. Initially, contamination of these metals occurred in airborne particulate matter, road dust, soil, and water, resulting in bioaccumulation in living organisms through several pathways (Ravindra et al., 2004). Therefore, there is a need to better understand their behavior in different environmental matrices, their potential bioaccumulation capacity, and above all their impact on human health. These elements are among those defined as "non-essential" as they do not play biological roles in the human body and are not involved in cell activity. For these elements there are no metabolic processes that regulate their concentration within the body, therefore they accumulate in the organs and tissues, and by increasing their concentration within the body, they represent a danger to human health (Wiseman and Zereini, 2009; Marcheselli et al., 2010). Several studies have reported elevated concentrations of PGEs in the fluids and tissues of occupationally exposed subjects, for example in precious metal refineries, or in bus drivers and traffic police officers (Ravindra et al., 2004; Iavicoli et al., 2007, 2008). The solubility of PGEs in the exhaust catalyst material was also tested using physiologically based extraction tests, demonstrating increased Pd solubility in simulated pulmonary and gastrointestinal fluids (Colombo et al., 2008; Turner and Price, 2008). Furthermore, studies on environmental matrices have demonstrated the greater solubility and mobility of Pd compared to Pt, with a consequent greater potential for absorption by organisms (Rauch and Morrison, 1999; Jarvis et al., 2001; Sures et al., 2001; Ek et al., 2004; Zimmermann and Sures, 2006). Therefore, the increase of Pd concentration in different environments is cause for concern for possible risks to human health (Wiseman and Zereini, 2009).

The effects of Pd and Pt on human health are not yet well defined. They come into contact with people both directly, through the inhalation of dust, and indirectly, through the food chain. The adverse health effect recognized by these metals is respiratory sensitivity, allergic reactions, dermatitis, lung diseases, and so on (Qiang et al., 2012).

The present study forming part of a larger research project on the dispersion of trace and ultra-trace elements in several environment matrices (vegetation, soil, air particulate matter, roadway dust, human hair) of Sicily (Italy). The study areas are located near a petrochemical complex and an urban area. Industrial sites are also subject to traffic-related air pollution, which can lead to additional toxic emissions and potential health risks from exposure and accumulation of elements potentially adverse to the population. In this study, we determined the levels of Pd and Pt in human scalp hair samples from adolescents (11–14 years) living near petrochemical complexes and urban areas.

In environmental and public health investigations, human biomonitoring is considered a valuable tool to evaluate the effects of chronic environmental exposure to pollutants in populations residing in geogenic (mining, volcanic areas) and anthropized areas (Gil and Hernández, 2009; Hernández et al., 2014; Varrica et al., 2022a). Human hair is considered a suitable matrix for estimating environmental exposures, is a non-invasive method (Esplugas et al., 2019), and better reflects long-term exposure (Gil et al., 2011). Human biomonitoring data analysis in adolescents is more interesting than that of adults (Esplugas et al., 2019). Adolescents are more susceptible to metal exposure due to their higher absorption rates in relation to their body weight, moreover, they have a low capacity for detoxification and excretion (Vella and Attard, 2019; Xie et al., 2017).

The main goals of this study were: to assess the potential exposure to Pd and Pt of adolescent populations living near petrochemical plants and urban areas; statistically verify whether there are significant differences in Pd and Pt concentrations in hair between adolescent groups, and then determine whether the degree of human exposure to Pd and Pt varies according to environmental factors; and evaluate the influence of gender on Pd and Pt content.

2. Materials and methods

2.1. Description of study areas

In this study, sampling sites representative of different anthropic pressures were chosen to evaluate the different exposures to Pd and Pt to which the population may be subject. Two industrial sites (Augusta and Gela), an urban area (Palermo) and a control site (Lentini) of the Sicily region (Italy) were selected (Fig. 1).

Augusta (34,000 inhabitants) is a town situated along the Sicilian Ionian coast in the province of Syracuse (37°13′53"N - 15°13′14″E). The petrochemical industry has contributed to the economic growth of the city and its urban and social transformation. The petrochemical complex is one of the largest in Europe with numerous oil and chemical refineries and energy production companies. The rocks outcropping in the study area are mainly of sedimentary origin characterized by alluvial and fluvial deposits together with coarse sands, calcarenites, and limestone as old as Late Cretaceous (Carbone, 2011).

The town of Gela (71,000 inhabitants) is situated along the Sicily channel coast (Italy) (37°4′53"N –14°13′ 53″E) and contains one of the largest petroleum refineries in Europe. The geology of the area is predominantly composed of limestone, clay, marly-clay, white and yellow quaternary biocalcarenites, and gypsum (Roda, 1966).

Palermo (670,000 inhabitants) is in the northwest of the island of Sicily, by the Gulf of Palermo in the Tyrrhenian Sea. The study area is entirely covered by sedimentary rocks (limestone, clay, marly-clay, and white or yellow quaternary biocalcarenite) (Abate et al., 1978). Potential sources of pollutants are mainly limited to vehicular traffic emissions.

The municipality of Lentini (SR) was chosen as the control site, representative of an area with low anthropic pressure. It is a hilly town located on the slopes of the Iblei Mountains (37° 17′ 4.55"N- 14° 59′ 54.76″E). The town is entirely covered by a limestone-clay complex from the Miocene period, the called Hyblean Plateau (Tortorici et al., 2006). The economy of the area is based on agricultural activities.

2.2. Sampling design and analytical procedure

A total of 108 human scalp hair were taken from school students of both genders (11–14 years old) living in Augusta (AU: 27 samples), Gela (GL: 43 samples), Palermo (URB: 22 samples), and Lentini (CS:13). Before sampling, all participant's legal representatives signed consent forms authorizing hair sample collection. All donors filled out a questionnaire to obtain information on their individual characteristics by responding to the following criteria: a place of origin, dietary habits, lifestyle, health status, smoking, recent surgery, or orthodontic treatment, and colored or treated hair. According to their responses, it was supposed that they share the same lifestyle and partially the same diet. To guarantee the anonymity of each participant, the answers were preserved without identification.

Hair samples, approximately 1–2 cm long, were cut with stainless-steel scissors from the nape of the neck close to the scalp and stored in plastic bags. Once in the laboratory, the samples were cut into smaller pieces with a sterile surgical scalpel to enhance the washing procedure, recommended by the International Atomic Energy Agency (Ryabukin, 1978; Subramanian, 1996; Sela et al., 2007). The washed samples were individually placed in glass beakers and dried for 24 h at 40 °C in a drying oven and then weighed. Five milliliter of HNO_3 (Ultrapure, Merck) were added to approximately 550 mg of the washed hair sample and digested for 24 h. Digestion was completed by adding 2 ml of H_2O_2 (Ultrapure, Merck) for another 24 h. The digestions were carried out at room temperature ($T = 20$ °C). After digestion, the solutions were diluted by the addition of 18 MΩ cm demineralized water to a volume of 20 ml and then filtered. Palladium and platinum determinations were carried out at the Department Scienze della Terra e del Mare (DiSTeM), University of Palermo by inductively coupled plasma mass spectrometry (ICP-MS, Perkin-Elmer, Elan 6100 DRC-e) after the addition of Y + Re as internal standards. All standard solutions were prepared with 18 MΩ cm demineralized water, the Pd and Pt

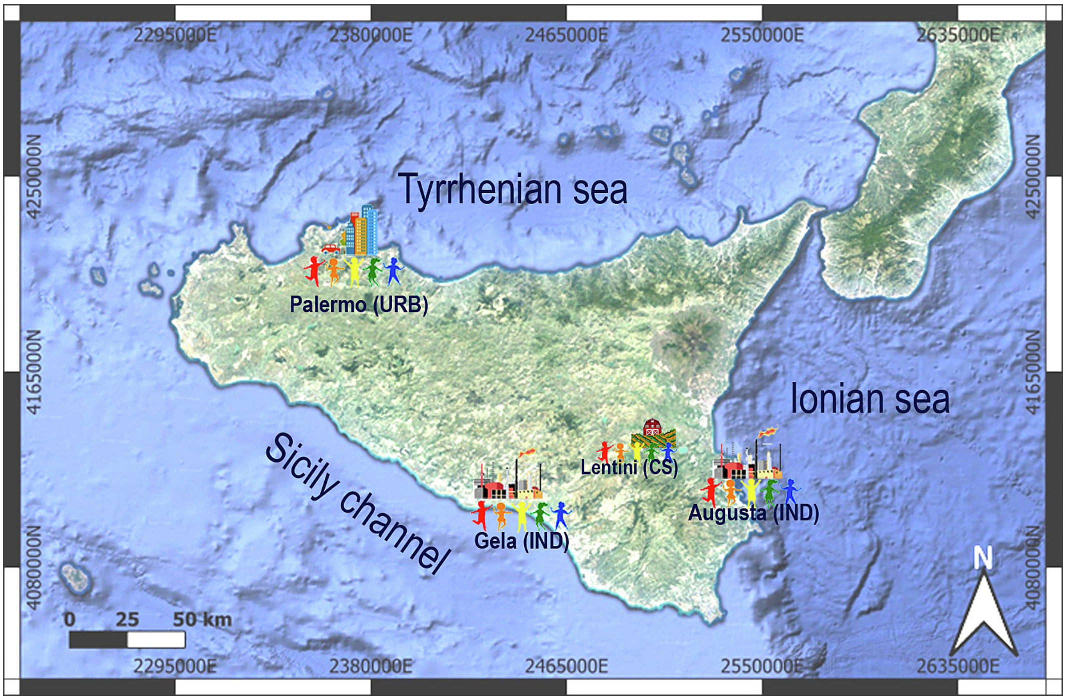

Fig. 1. Location of the study area with sampling sites. Augusta (AU), Gela (GL), Palermo (URB) and Lentini (CS).

CertiPUR standards (Merck). To minimize matrix effects, the calibration standard addition technique was used for all element determinations. The linear range was in 0–50 μg L^{-1} with a correlation coefficient of 0.9998 for both. The operational limit of detection (LOD) for Pd and Pt was calculated as three times the standard deviation of the analyte concentration in blank samples (Pd: 0.022 μg L^{-1}; Pt: 0.0014 μg L^{-1}). For internal quality control, certified reference material QMEQAS08H-02 (human hair) of the Institut National de Santé Publique – Centre de Toxicologie, Québec (Canada) was used. The reference material was spiked with Pd and Pt at two levels, in order to provide 1 μg L^{-1} and 10 μg L^{-1}. Spike recoveries were 80–94 % for Pd, and 95–99 % for Pt at both concentrations.

2.3. Statistical analyses

Data were analyzed statistically by the STATISTICA program (Tulsa, OK, USA), Statsoft version 6.0. All tests were considered significant at $p < 0.05$. The normality data distributions was verified by the Shapiro-Wilk test (W). A non-parametric Mann-Witney Test (U) was used to compare the differences between two or more independent groups. The Spearman correlation coefficient (R) was used to measure the association between variables in terms of rank.

3. Results

The main statistical parameters of Pd and Pt determined for human hair samples collected from adolescents living in the four study sites are shown in Table 1. Reference intervals calculated for each element differentiated by the site are also given. The results of the Shapiro-Wilk test (W) ($p < 0.05$) show a non-normal distribution for Pd and Pt in the urban site and in the industrial sites, except for the Pd in the Augusta site. Control site (CS) data show a normal distribution. The CV % calculated for all sites showed low variability for Pd for all industrial and control sites, however, in the urban site the CV% shows a wider variability. The Pt shows a large variability both in the urban site and in the industrial sites and a low variability in the control site.

Median Pd concentrations are higher than Pt in industrial sites (Pd_{IND}: 6.88 ng g^{-}1, Pt_{IND}: 0.44 ng g^{-1}) and control site (Pd_{CS}: 0.56 ng g^{-1}, Pt_{CS}: 0.12 ng g^{-1}). In urban site the levels of both metals were comparable (Pd_{URB}: 1.37 ng g^{-1}, Pt_{URB}: 1.56 ng g^{-1}). Reference intervals obtained underline a good overlap between Pd and Pt in the urban site and a different variability in the industrial sites. The overlap found between Pd and Pt in the urban area confirms that vehicular traffic is the only emission source for these elements compared to what was observed in the industrial sites

Table 1
Basic statistical parameters of Pd and Pt (in ng g^{-1} dry-weight basis) in adolescents' hair from industrial site (IND), AU, GL, URB, and CS. S·D.: standard deviation; CV indicated the coefficient of variation, which was calculated as CV(%) = 100 × S.D. × mean^{-1}. Test W: Shapiro-Wilk test, $p < 0.05$. Ref. Int.:Reference intervals. Reference intervals computed according to the non-parametric approach recommended by IUPAC (Poulsen et al., 1997). Test U: Mann-Whitney test, $p < 0.05$.

		N	Median	Mean	S.D	CV%	Test W	Ref. Int.	Test U
Industrial sites	Pd_{IND}	72	6.88	6.88	3.55	52	0.035	0.48–13.05	$0.0001_{(IND-URB)}$
	Pt_{IND}	70	0.44	1.00	1.33	133	0.001	0.04–4.28	$0.012_{(IND-URB)}$
	Pd_{AU}	28	6.94	6.70	3.67	55	0.285	1.35–14.81	$0.0001_{(AU-URB)}$
	Pt_{AU}	27	0.44	0.98	1.30	133	0.001	0.03–4.28	$0.036_{(AU-URB)}$
	Pd_{GL}	44	6.88	6.36	3.52	55	0.015	0.48–12.24	$0.0001_{(GL-URB)}$
	Pt_{GL}	43	0.44	1.01	1.36	135	0.001	0.09–5.33	$0.021_{(GL-URB)}$
Urban site	Pd_{URB}	22	1.37	2.26	2.33	104	0.001	0.21–7.18	$0.042_{(URB-CS)}$
	Pt_{URB}	22	1.56	1.80	1.45	81	0.005	0.25–4.19	$0.0001_{(URB-CS)}$
Control site	Pd_{CS}	13	0.56	0.60	0.28	47	0.781	0.09–1.22	$0.0000_{(IND-CS)}$
	Pt_{CS}	13	0.12	0.12	0.06	48	0.985	0.02–0.228	$0.0001_{(IND-CS)}$

(Pawlak et al., 2014). It is worth noting that the ranges of Pd and Pt coverage in anthropic sites are much wider than in the control site. Fig. 2 shows the data in terms of median, interquartile range (25–75 %), and experimental ranges of Pd and Pt, highlighting the similarity between industrial sites, and the difference with the urban and control context. The Mann-Whitney (U) non-parametric test highlights the statistically significant differences in Pd and Pt between the industrial, urban, and control sites. A good correlation between Pd and Pt is evident among the samples taken in urban area with Spearman's rank coefficient equal to 0.60 ($p < 0.05$) and in control site with $R = 0.92$. However, among the samples taken in industrial sites, a low Spearman's rank correlation coefficient ($R = 0.26$) is observed. In this study, we have considered gender as a potential discriminating factor. In Table 2, we reported the concentrations of Pd and Pt in the dataset broken down by males and females. Table 2 shows the overlapping of the distributions between females and males, which highlights an accumulation not linked to the gender factor. The non-parametric Mann-Whitney test (U) ($p < 0.05$), calculated for each site, does not report statistically significant differences between genders.

4. Discussions

Both urban and industrial areas are important sources of Pd and Pt emissions into the environment. These elements are present in nature in very low concentrations but their use, in various industrial fields, has dramatically increased their presence in the environment (Gomez et al., 2000; Rauch et al., 2001; Zereini et al., 2001; Wichmann et al., 2007; Pan et al., 2009; Zereini et al., 2012; Pawlak et al., 2014). The principal sources of environmental contamination with PGE were catalytic converters. Initially, Pd and Pt were used to reduce hydrocarbon and carbon monoxide emissions. Pd has been used in increasingly greater amounts over Pt, as it is cheaper and more chemically stable, leading to higher concentrations of this metal in the environment over time (Zereini et al., 2005). Pt is of great medical importance for the treatment of human carcinomas (Pawlak et al., 2014). These metals are also resistant to corrosion at high temperatures, have high melting points, and have good ductility. Due to these properties, there are used in the glass, petroleum, and electric industries, and the manufacture of jewelry. Pawlak et al., 2014, reports the different use of Pd and Pt in various industrial applications, underlining how in the last few years the quantities of Pd and Pt used in the automotive catalysts industry are similar.

To our knowledge, the current literature does not report examples of the determination of Pd and Pt in scalp hair from adolescents living close to anthropized or rural areas; therefore, the data obtained in this study represent a new contribution to the knowledge of exposure of these elements in human hair. The results reveal significant differences in the Pd and Pt concentrations between exposed and control samples (Table 1), underlining how the living environment influences the accumulation of these elements. A good correlation between Pd and Pt was found in the group of samples from the urban area and control site. In these two sites (Palermo and Lentini), it is possible to hypothesize a single source of Pd and Pt, related to vehicular traffic. In industrial sites, a low correlation was observed, therefore it is possible to hypothesize a double source of these elements, catalytic converters, and petrochemical activities, especially for palladium. In petrochemical plants, Pd catalysts are required to refine crude oil to produce aromatics and high-octane gasoline (Kim, 2013; Zientek et al., 2017). Based on the information provided (Table 1), the relative variability (CV%) of the dataset overall, exhibited Pd low variability across industrial and control sites but had wider variability in the urban site. On the other hand, Pt showed large variability in both urban and industrial sites but low variability in the control site. These differences between sampling sites are probably linked to the different anthropogenic contributions and small-scale environmental factors (Linhua, 2019).

In general, hair metals content depends on several factors which have a concomitant effect: age, site of residence, dietary habits, occupation, and gender (Christensen, 1995; Ali et al., 2019).

Gender-specific exposure has previously been observed in several studies (Chojnacka et al., 2010; Varrica et al., 2022b) but the statistical differences are mainly related to the role that the elements play in the functioning of the human body. The health effects of some toxic trace elements are also displayed differently between males and females, due to differences in kinetics, mode of action, or susceptibility (Vahter et al., 2007). In this study, the non-influence of the gender factor for these elements could be attributable to the non-role of Pd and Pt as essential elements for humans (Marcheselli et al., 2010; Wataha, 2013; Rentschler et al., 2018).

Several studies on the content of trace elements in different environmental matrices highlight the serious impact of local anthropic activities in the study areas (Alaimo et al., 2000; Bosco et al., 2005; Dongarrà et al., 2010; Varrica et al., 2022b). Varrica et al. (2022b) found higher concentrations of As, Cr, Ni, Pb, and V in lichens from the Augusta area, revealing a severe impact of local anthropogenic activities for many trace elements.

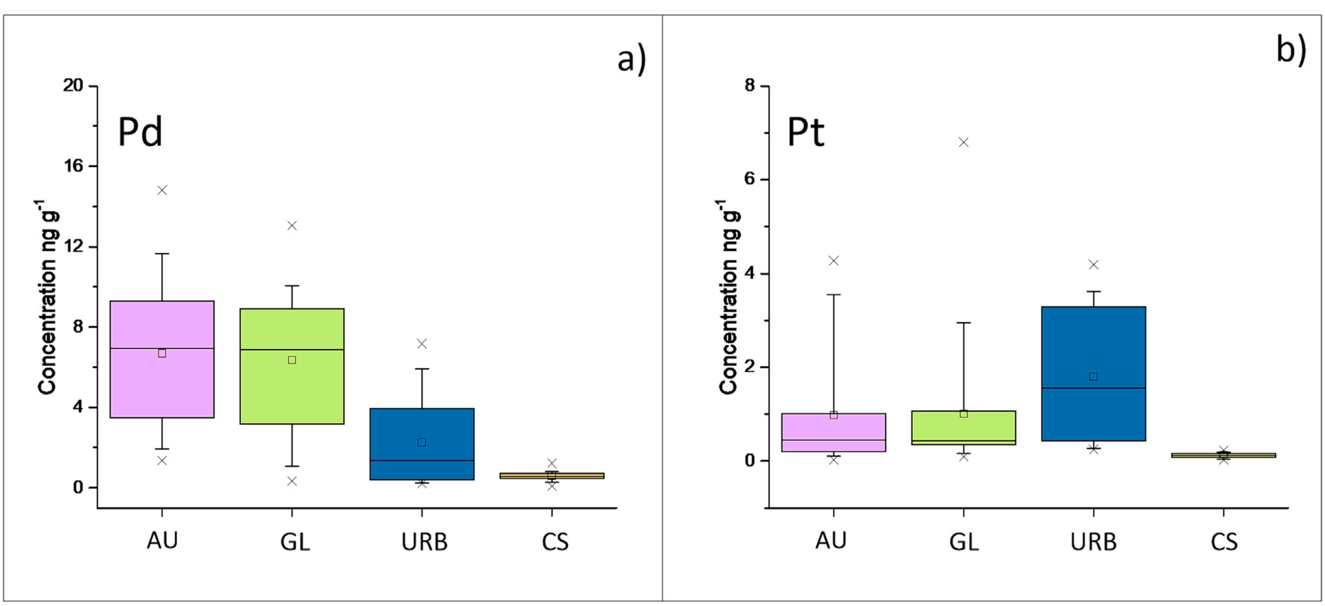

Fig. 2. Box plot of Pd (a) and Pt (b) in the analyzed hair samples. Boxes delineate the interquartile range (25–75 %) with the indication of the median (dark line); a small square inside the box marks the mean value; whiskers indicate the 10–90 % range; points outside the box are minimum and maximum. Data are given in ng g^{-1}.

Table 2
Basic statistical parameters of Pd and Pt (in ng g^{-1} dry-weight basis) in adolescents' hair from industrial site (IND), AU, GL, URB, and CS subdivided by gender. S.D.: standard deviation; Ref. Int.: Reference Intervals. Reference intervals computed according to the non-parametric approach recommended by IUPAC (Poulsen et al., 1997). Test U: Mann-Whitney test, p < 0.05.

		Industrial site (IND)		Augusta (AU)		Gela (GL)		Urban site (URB)		Control site (CS)	
		Female	Male	Female	Male	Female	Male	Female	Male	Female	Male
Pd	N	49	23	15	13	34	10	14	8	5	8
	Mean	6.50	6.48	6.61	6.79	6.45	6.07	2.34	2.11	0.72	0.52
	Median	6.87	7.34	6.54	7.34	6.88	6.92	2.04	0.48	0.71	0.56
	S.D.	3.41	3.91	3.66	3.82	3.36	4.21	1.93	3.06	0.33	0.23
	Ref. Int.	0.48–12.6	0.53–14.8	1.35–12.6	1.84–14.8	0.34–13	0.53–12.2	0.31–5.92	0.42–7.17	0.28–1.22	0.09–0.81
	Test U	Not significant		Not significant		Not significant		Not significant		Not significant	
Pt	N	48	22	14	13	34	9	14	8	5	8
	Mean	0.95	1.10	0.93	1.05	0.96	1.16	2.06	1.35	0.14	0.11
	Median	0.44	0.46	0.46	0.27	0.40	0.58	2.39	0.53	0.16	0.11
	S.D.	1.34	1.32	1.15	1.52	1.43	1.11	1.36	1.60	0.07	0.05
	Ref. Int.	0.09–3.87	0.04–4.28	0.03–3.54	0.04–4.28	0.09–6.80	0.14–3.32	0.25–3.98	0.28–4.19	0.03–0.23	0.02–0.19
	Test U	Not significant		Not significant		Not significant		Not significant		Not significant	

Surveys carried out on groundwater samples, pine needles, and road dust in Gela have shown high As, Ni, and V concentrations near the industrial plant (Bosco et al., 2005; Manno et al., 2006, 2007); the chemical composition of the bulk deposition showed an enrichment in Sb, Ni, Cr, and Cu, highlighting a contribution linked to both industrial activity and intense vehicular traffic (Boatta et al., 2014). Pine needles and leaves of *F. macrophylla* collected in urban area of Palermo revealed anthropogenic sources linked exclusively to gaseous emissions and the deterioration of the mechanical parts of motor vehicles (Alaimo et al., 2000; Alaimo and Varrica, 2020). Inorganic matter from roadway dust collected in the urban area of Palermo exhibits very high enrichment factors. Metal size distribution indicates that Pd, Pt, Au, Sb, Zn, S, Ni, V, Mo, and Cr substantially accumulate in the finest particles, whereas Pb, Br, As, Cu, Ag, and Ba are almost independent of the size fraction (Varrica et al., 2003). Varrica et al. (2022a) carried out a comparative analysis to investigate human hair metal profiles of adolescents residing near petrochemical plants and urban area. An industrial factor (As, Mn, Sr, U, and V) and an urban factor (Cd, Cr, Cu, Mo, Ni, and Sb) were distinguished by the multivariate statistical analysis.

The content of Pd and Pt was associated with trace element data determined by Varrica et al. (2022a) and Dongarrà et al. (2011) in the same hair samples. Relationships among the elements were evaluated by Spearman's correlation matrix for industrial and urban samples.

A good association between elements with $p < 0.05$, in industrial samples, was identified for As—Sr ($R = 0.36$), As—Pd ($R = 0.35$), and As—V ($R = 0.54$), highlighting industrial contribution. Furthermore, a good correlation between Pt—Cu (R = -0.57), Pt—Zn (R = -0.44), and Pt—Pd ($R = 0.60$) was also found in the urban samples. The link between these elements can be due to vehicular traffic.

Surveys on the Pd and Pt content in environmental samples mainly concern the analysis of road dust (Bosco et al., 2005; Varrica et al., 2003; Wiseman et al., 2016), atmospheric particulate matter (Zereini et al., 2012; Omrani et al., 2021), soils (Cinti et al., 2002; Wichmann et al., 2007; Cicchella et al., 2008), groundwaters (Ek et al., 2004), and vegetation (Dongarrà et al., 2003a, 2003b; Bosco et al., 2005; Bonanno and Pavone, 2015). A study conducted by Bosco et al. (2005) in the industrial area of Gela (Sicily, Italy) found different concentrations of Pd and Pt in pine needle samples taken within the urban center, in the vicinity of the petrochemical plant and rural zone. It underlined the higher concentrations of Pd found near the petrochemical plant (Pd:13 μg kg^{-1}; Pt: 6 μg kg^{-1}) compared to those found in the urban center (Pd:10 μg kg^{-1}; Pt:14 μg kg^{-1}) and in a rural area (Pd:5 μg kg^{-1}; Pt:4 μg kg^{-1}). Dongarrà et al. (2003a) show how the distribution of Pd and Pt within the city of Palermo is strongly linked to the distribution of car traffic. Pd and Pt concentrations in road dust reveal the increasing release of these elements into the environment from catalytic converters (Varrica et al., 2003). Studies on the content of these metals in human biological matrices mostly involved the use of biomarkers such as urine, blood, and plasma (Caroli et al., 2001; Ek et al., 2004; Iavicoli et al., 2004; Goulle et al., 2005; Falta et al., 2007; Rentschler et al., 2018). Surveys using hair as accumulators are very limited in the literature and are mainly aimed at occupationally exposed populations (Petrucci et al., 2005; Qiang et al., 2012; Marie et al., 2017). From these studies, it emerges that hair can certainly be used as a biomarker for these elements.

The greater dispersion of these elements has led to a greater degree of exposure and an increase in the risk for humans (Zereini et al., 2005; Wang and Li, 2012; Omrani et al., 2021). Wiseman and Zereini (2009) highlighted that Pd and Pt can be easily mobilized and solubilized by various compounds commonly found in the environment, thus increasing their bioavailability. A study was conducted by Sebek et al. (2011) to examine the action of ligands complexing PGEs. This group of elements is mainly emitted in metallic form, but some of them are transformed into soluble forms which become bioavailable (Moldovan, 2007). It was observed that substances found in the environment, such as PO_4^{3-} (derived from phosphate fertilizers), sodium chloride (used for road deicing), citrates (secreted by plant roots), and fulvic acid (formed by the decomposition of cellulose and lignin), can be listed among PGE ligands (Sebek et al., 2011). Humic substances have also been shown to increase the water solubility of Pd and Pt (Wood, 1996; Lustig et al., 1998; Zimmermann et al., 2003).

Available data on potential toxicity and evaluating the effects of exposure to PGEs, that are continuously emitted into the environment, are still limited today (Wiseman and Zereini, 2009; Wang and Li, 2012).

5. Conclusions

The use of hair as a biomarker in biomonitoring has proved to be a good screening tool for evaluating the exposure of individuals to potentially toxic elements of anthropic origin, even at low concentrations. Palladium and platinum, mainly released from vehicle exhaust catalysts, have been significantly accumulated in environmental matrices over the past decades. The presence of Pd and Pt in the environment they are used in the glass, petroleum, electric, and electronic industries, and the manufacture of jewelry. Besides, platinum metals are also used as an antitumor drug in cancer therapy. In this study, human hair samples from adolescents, both genders, residing near petrochemical plants of Augusta and Gela, in urban area of Palermo, and in Lentini as control site were analyzed. The samples from the industrial sites of Gela and Augusta do not show statistically significant differences between them for both Pd and Pt, however, they differ from the samples relating to the city of Palermo. Median Pd concentrations are higher than Pt in industrial sites and control site. In urban site the levels of both metals were comparable.

It is worth noting that the reference intervals of Pd and Pt in anthropic sites are much wider than in the control site. The results of our study suggest a relationship between the content of elements such as Pd and Pt in urban and industrial environments and human hair, highlighting the importance of biomonitoring for human health risk control. The study does not reveal any statistically significant difference between Pd and Pt between female and male samples as they are non-essential elements and therefore do not play any biological role within the body. All these factors highlight the need to monitor environmental levels of these metals and continue research into their bioavailability, behavior, speciation, and associated toxicity.

Therefore, the potential health risk from Pd and Pt should be assessed, especially for people living in urban environments and near industrial facilities. This study must be considered as an initial evaluation that needs further investigations (both experimental and model) in the future to better understand the behavior of PGEs in environmental matrices and above all the clear identification of the paths through which they come into contact with humans. There are few published data on the bioavailability of PGEs and their fate in the environment. It is therefore important to systematically monitor the concentration of these elements in the environment.

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CRediT authorship contribution statement

F. Lo Medico: Conceptualization, Data curation, Methodology, Formal analysis. **D. Varrica:** Conceptualization, Data curation, Methodology, Formal analysis, Funding acquisition, Supervision, Writing - original draft, Writing - review & editing. **M.G. Alaimo:** Conceptualization, Supervision, Data curation, Funding acquisition, Writing - original draft, Writing - review & editing.

Data availability

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declaration of competing interest

The authors declare that they have no competing interests.

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