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# 1 **Platinum Group Elements contamination in soils: review of the** 2 **current state**

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## 10 **Keywords:**

11 platinum group elements (PGE), platinum, palladium, rhodium, urban environment,  
12 nanoparticles

## 13 **Abstract:**

14 Platinum group elements (PGE: Ru, Rh, Pd, Os Ir, Pt) are rare metals with low abundance  
15 in the continental crust. The elements of the palladium subgroup of PGE (PPGE: Pt, Pd,  
16 Rh) have been exploited more and more over the last thirty years for their physicochemical  
17 properties such as high melting point, high resistance to corrosion, mechanical strength  
18 and ductility. This led to emerging environmental contamination in different media such as  
19 air, road dust, soil, sediment, vegetation, and snow. The aim of this review is to summarize  
20 the available data on soil contamination by PPGE and its potential environmental impact.  
21 In this paper, the environmental issue of PPGE is discussed with regard to their  
22 anthropogenic emission and fate, which includes speciation, possible transformations into  
23 bioavailable forms and toxicity. Soil contamination by PPGE is described taking into  
24 account urban and non-urban areas. The analytical determination process is also  
25 discussed.

## 26 **1. Introduction**

27 The Platinum Group consists of 6 elements, Ru, Rh, Pd, Os, Ir and Pt (Platinum Group  
28 Elements, PGE). They are all siderophiles, and therefore concentrated in the core and  
29 mantle of the Earth while they are scarce in the continental crust. The natural abundance  
30 in the upper continental crust varies according to the considered PGE (namely, in  $\mu\text{g}$  (PGE)  
31  $\text{kg}^{-1}$  (rock): 0.030 (Ru), 0.018 (Rh) 0.526 (Pd), 0.031 (Os), 0.022 (Ir) and 0.599 (Pt) (Park  
32 et al., 2012; Peucker-Ehrenbrink and Jahn, 2001). The natural sources of PGE on the  
33 Earth's surface are volcanism, rock weathering and the deposition of extra-terrestrial  
34 matter (Mitra and Sen, 2017). Given that both continental crust concentrations are low and  
35 natural sources provide a limited amount of PGE to the Earth's surface, the fate of these  
36 elements in the environment should be of limited concern. However, anthropogenic PGE  
37 emissions started at the beginning of the industrial period, around the 1750s. This was  
38 evidenced because an accumulation of PGE in some soils was observed from that date.  
39 For instance, the increased accumulation of osmium found in a peat bog in northwestern  
40 Spain has been dated to this period (Rauch et al., 2010).

41 PGE are exploited due to their physical and chemical properties such as high melting  
42 points, high corrosion resistance, mechanical strength and ductility. PGE have a high  
43 economic value and are involved in many applications such as catalytic converters,  
44 electronics, drugs, and catalysts in the chemical industry. Due to their different  
45 physicochemical behaviour, PGE are divided into two subgroups: iridium PGE, also called  
46 IPGE and composed of Ir, Os, Ru, and palladium PGE, also called PPGE and composed  
47 of Pd, Pt, Rh (Mondal, 2011; Rollinson, 1993). The elements of the IPGE subgroup are  
48 more siderophile, refractory, associated with chromites as alloys and sulphides in dunites.  
49 The elements of the PPGE subgroup are more chalcophile than IPGE, associated with  
50 sulphides of Fe, Cu, Ni and gabbros, norites and dunites (Mondal, 2011; Rollinson, 1993).

51 The increasing use of PPGE (shown in Figure 1) and the release of these elements over  
52 the last thirty years have led to the emergence of environmental contamination.

53 This has also led to an emerging issue regarding the potential impacts of these elements.

54 From the resulting studies and monitoring, it appears that the PPGE concentrations are  
55 increasing in different environmental media (air, road dust, roadside soil, sediment,  
56 vegetation, snow...), these elements being significantly accumulated (Ely et al., 2001;  
57 Moldovan et al., 2007; Rauch et al., 2004; Schäfer et al., 1998; Sen et al., 2013). For  
58 example in Greenland, the concentrations measured in snow samples were  
59 approximatively 40- (Pt), 80- (Pd), and 120 times (Rh) respectively higher than the values  
60 in old ice (Barbante et al., 2001).

61 Therefore, in this review, an overview of the environmental issue of the PPGE emissions is  
62 first presented with respect to their sources, geochemical behaviour and potential toxicity  
63 in soil environments. Then, the focus is on PPGE soil concentrations in various types of  
64 areas (peri-urban and rural, urban, mining and roadside). This focus is motivated because  
65 soils are among the main primary receptors of PPGE emissions; soils are also dynamic  
66 environments where the physico-chemical states of these metals could change. Finally,  
67 analytical methods are described, since the PPGE determination is still critical in  
68 environmental samples. The goal of this review is to highlight the needs of research on this  
69 topic, including large-area assessments.

## 70 **2. Environmental issue**

### 71 *2.1. Anthropogenic emission of PPGE*

72 Anthropogenic emissions of PPGE come mainly from their production from ores (mining),  
73 the manufacture and use of products containing them and the resulting waste, as well as  
74 from fossil combustion and the use of carbon-based fossil materials containing traces of  
75 PPGE (Chyi, 1982; Finkelman and Aruscavage, 1981).

76 Mining activities have been identified as a significant source of PPGE in the environment  
77 (Rauch and Fatoki, 2015). The leading PPGE metal producing countries are South Africa  
78 (Bushveld Complex) and Russia (Kola Peninsula, Norilsk). In 2016, these two countries  
79 supplied 72% and 12% of the Pt production respectively (Johnson Matthey, 2017a). In  
80 particular, ore smelters in South Africa greatly contribute to local soil contamination; in  
81 Russia they are an important factor of local contamination of snow and soil. (Gregurek et  
82 al., 1999; Niskavaara et al., 2004; Rauch and Fatoki, 2013). These activities are also  
83 responsible for the transport of PPGE by airborne particles (Sen et al., 2013; Zereini et al.,  
84 2012). This leads to a dispersion of PPGE across the world with proven general  
85 contamination of surface seawater (Chen et al., 2009), snow from Greenland, the Alps and  
86 the Pyrenees (Barbante et al., 2001; Moldovan et al., 2007; Van de Velde et al., 2000), as  
87 well as probably soil contamination (no data available).

88 Regarding the manufacture and use of products containing PPGE, Figure 2 provides an  
89 overview of the relative distribution by industry of these elements. Nowadays, PPGE are  
90 mainly used for vehicle catalytic converters. The catalytic converter was first introduced in  
91 the US in the 1970s and later in Europe in the 1980s. This device is now compulsory in  
92 many countries in order to preserve air quality (e. g. EU Council Directive 91/441/EEC).  
93 The catalytic converter reduces emissions of carbon monoxide (CO), remaining  
94 hydrocarbons (HC) and nitrogen oxides (NO<sub>x</sub>) respectively by oxidizing CO and HC to  
95 carbon dioxide (CO<sub>2</sub>) and reducing NO<sub>x</sub> to nitrogen (N<sub>2</sub>).

96 The typical catalytic converter consists of: (i) a substrate, a ceramic monolith with a  
97 honeycomb structure; (ii) a washcoat of metal oxide (aluminium and cerium); (iii) the  
98 catalyst material, a mixture of Pt, Pd and Rh in nanocrystalline form attached to the metal  
99 oxide (Gandhi et al., 2003). Experiments showed that the Pt emissions from catalytic  
100 converter differ depending on its age, engine type and driving conditions (Moldovan et al.,  
101 2002; Palacios et al., 2000). For example, Artelt et al. (1999) measured the concentration

102 of Pt in the exhaust gases of new and used converters and found 22 and 14 ng m<sup>-3</sup>  
103 respectively. Pt emissions decrease because the platinum particles on the washcoat tend  
104 to agglomerate with age, so the particles are less abraded (Artelt et al., 1999). In order to  
105 comply with the latest air quality regulations and reduce particle emissions, newer diesel  
106 cars are also equipped with a Diesel Particle Filter (DPF) usually made of a honeycomb  
107 ceramic monolith. DPF may contain a PPGE catalytic coating (catalysed DPF) (Hartwig,  
108 1985). In tests performed on heavy-duty diesel vehicles operating at constant speed, the  
109 measured Pt emissions were found to be higher for vehicles equipped with catalysed DPF  
110 than for vehicles without DPF (Hu et al., 2009). DPF can also be placed after a catalytic  
111 converter. In this case, Cairns et al. (2011) found that DPF set on passenger cars fitted  
112 with catalytic converters reduced the emissions of PPGE by up to 97% for Pt. Annual  
113 global emissions of PPGE from cars are estimated at 14.5 tons Pt, 35 tons Pd, and 3 tons  
114 Rh. This corresponds to a contribution to the total surface deposition of 4.6%, 8.2% and 2%  
115 for Pt, Pd, Rh respectively (Mitra and Sen, 2017). The other possible emissions into the  
116 environment from other sectors of activity such as the chemical, electrical and electronic  
117 industry and jewellery are not documented to our knowledge. However, nowadays  
118 electrical and electronic equipment (EEE) contains traces of PPGE (e.g. 125 mg kg<sup>-1</sup> of Pd  
119 in smartphones (Cesaro et al., 2018)) and their waste accounts for up to 20 to 50 million  
120 tons worldwide each year (Cucchiella et al., 2015). Since waste management of EEE  
121 includes landfill and smelting (Gramatyka et al., 2007), it is likely this sector contributes to  
122 the release of PPGE to the environment.

123 In urban areas more specifically, and generally in areas containing hospital, water  
124 treatment plant or waste dump, sewage and solid waste are also sources of PPGE. The  
125 medical field uses Pt-based drugs (i.e. cisplatin, carboplatin) against cancer (Cowley and  
126 Woodward, 2011). Drugs excreted by patients can therefore be released into the  
127 environment. In hospital effluents, Pt was found with concentrations ranging from less than

128 10 ng L<sup>-1</sup> to 3500 ng L<sup>-1</sup> (Kümmerer et al., 1999). In several cities of the United Kingdom,  
129 the maximum concentrations found of Pt and Pd are respectively 192 and 191 µg kg<sup>-1</sup> in  
130 sewage sludge, and 602 and 710 µg kg<sup>-1</sup> in incinerator ash (Jackson et al., 2010). The  
131 increase in the Pd concentration in sewage sludge correlates with the Pd demand by the  
132 dental industry (Leopold et al., 2008).

133 In addition to these sources, there are emissions of PPGE, which are not directly related to  
134 the production, or use of these elements. Indeed, the combustion of coal for various uses  
135 also contributes to Pt emissions for quantities estimated at 0.001 to 0.2 tons per year  
136 (Rauch and Peucker-Ehrenbrink, 2015). The most recent estimates of annual emissions  
137 from coal combustion are 1 and 4 tons for Pt and Pd respectively (Mitra and Sen, 2017).

138 In summary, Figures 1 and 2 as well as the data presented above show that while vehicle  
139 exhausts are the main source of anthropogenic emission of PPGE, other sources such as  
140 industrial activities, fossil combustion and those related to urban life significantly contribute  
141 to the global quantities released into the environment. Atmospheric dispersion must also  
142 be taken into account because it contributes to the contamination of environments far from  
143 sources.

## 144 2.2. *PPGE in soil*

145 *Background.* In order to assess the contamination and identify the sources, the  
146 determination of the background concentration is therefore important. Since almost all  
147 studies on PPGE contamination focus on roadside environments, background values are  
148 usually taken as PPGE concentrations in areas with low population density and low traffic,  
149 without further details or selection criteria (Table 1). For example, Ely et al. (2001) used as  
150 background a sample collected 1 km from the road in South Bend (USA). They obtained a  
151 background concentration of Pt of 3.63 µg kg<sup>-1</sup>; however, this value was 7 times more than  
152 the mean abundance in the upper continental crust. Jarvis et al. (2001) collected as  
153 background a sample in a park outside an urban zone and measured Pt concentrations

154 lower than  $0.21 \mu\text{g kg}^{-1}$ , which was of the same order as that of the upper continental  
155 crust. In both cases, no information was available about the bedrock. For studies on  
156 roadside environments, this does not necessarily have any consequences because the  
157 PPGE accumulation is relatively high. However, in general, the influence and the nature of  
158 the bedrock should be taken in account. This is particularly the case in areas where there  
159 is no PPGE mining activity. To illustrate the variability of the background values, examples  
160 are given in Table 1. For instance, in Italy, soils formed on volcanic rocks have a slightly  
161 higher background values than soils formed on sedimentary rocks (Cicchella et al., 2008).  
162 It is the opposite in Germany where soil on quaternary sand have higher values than soil  
163 derived from volcanic formations (see Table 1) (Schäfer and Puchelt, 1998). Thus, from all  
164 these examples, it is obvious that knowledge of the geochemical background is crucial for  
165 any study, especially on non-urban areas. However, this value may be difficult to determine  
166 because field sampling is not always easily accessible and the analytical determination of  
167 very low concentration can be difficult.

168 *Peri-urban and rural areas.* Non-urban areas concern many environments with different  
169 characteristics, and more or less anthropized. Great variability of PPGE concentrations is  
170 therefore expected. Table 1 (median values) and Figure 3 (concentration ranges)  
171 summarize and illustrate this variability depending on the environment considered. Data on  
172 the concentration of PPGE in soils in non-urban areas are very scarce as very few studies  
173 were conducted in these environments. Existing data include those from forest and  
174 agricultural soil samples from Berlin surroundings, mainly in a peri-urban area (Table 1).  
175 The median Pt values in this area were  $2.98$  and  $5.83 \mu\text{g kg}^{-1}$  for agricultural and forest  
176 soils respectively (Birke et al., 2018). However, these authors showed that the source was  
177 not catalytic converters. For agricultural soils, contamination from agricultural activities  
178 may be possible because trace amounts of Pt in fertilizers were found up to  $2.3 \mu\text{g kg}^{-1}$  (Alt  
179 et al., 1997). In farms, wastewater is also used for irrigation and fertilization of agricultural



180 lands, and sewage sludge for soil amendment. As above-mentioned, these wastes can  
181 contain high concentrations of PPGE. Therefore, soil treated with wastewater or sewage  
182 sludge may be contaminated (Table 1). For example, in soils from farms around Berlin  
183 using field treatment with sewage, the maximum concentration of Pt was  $82.6 \mu\text{g kg}^{-1}$   
184 (Birke et al., 2018).

185 In rural environment, atmospheric contamination is lower than in urban areas (Zereini et al.,  
186 2012). Nevertheless, there is evidence for regional and global transport of PPGE from  
187 multiple anthropogenic sources (Rauch et al., 2005; Sen et al., 2013; Zereini et al., 2012).  
188 To our knowledge, only two studies were conducted to assess the spatial variability of  
189 PPGE in soil over a large area. Thus, the Kola Ecogeochemistry project investigated  
190 PPGE and Au concentrations in podzolic horizons and moss over an area of 188,000 km<sup>2</sup>  
191 in the European Arctic (Niskavaara et al., 2004). Median values are presented in Table 1. A  
192 Pd and Pt significant enrichment was observed close to the Russian mining areas.  
193 Geogenic sources of PPGE and Au were also identified with high metal concentrations in  
194 the deep horizon. In Southern Italy, topsoil samples were collected from the Campania  
195 region, including urban, suburban and agricultural areas. A relationship was established  
196 between high concentrations of Pt and Pd in soils, PM<sub>10</sub> airborne and high traffic areas  
197 (Zuzolo et al., 2018). Unfortunately, in this study, the influence of the bedrock could not be  
198 determined as the method detection limits were too high ( $2$  and  $10 \mu\text{g kg}^{-1}$  for Pt and Pd  
199 respectively).

200 *Urban areas.* Few studies were conducted focusing on the spatial distribution of PGE over  
201 an entire urban area and not only at the roadside (Birke et al., 2018; Cicchella et al., 2008;  
202 Orecchio and Amorello, 2011). This type of study is based on Geographical Information  
203 System (GIS). It enables PPGE sources to be characterised by multivariate statistical  
204 analysis. Thus, over a given area and depending on scale, the median local concentration  
205 and the geochemical baseline can be determined, and/ or a possible non-point source

206 identified. For example, in the low population density area of Benevento (Italia), PPGE  
207 concentrations close to the background were found with the exception of the industrial  
208 zone; on the contrary, in the high population density area of Salerno, the range of  
209 concentration was similar to that of the road environment; and concentrations of PPGE  
210 and other traffic-related heavy metals were found to significantly correlate, which  
211 established the car traffic as the source of contamination (Cicchella et al., 2008). From the  
212 Berlin inner city surveys, Birke et al. (2018) were also able to quantify the accumulation of  
213 PPGE over a 20-year interval, with increasing factors of 1.5 for Pt, 3.0 for Pd and 4.3 for  
214 Rh.

215 In order to identify the sources of PPGE, Pt/Pd, Pt/Rh and Pd/Rh elemental ratios can be  
216 calculated. Ely et al. (2001) compiled PPGE ratios in catalytic converters and defined the  
217 ranges: Pt/Pd from 1 to 2.5, Pd/Rh from 4 to 9 and Pt/Rh from 5 to 16. Although these  
218 ranges of values do not include any possible recent discrepancies in PPGE ratios in  
219 catalytic converter (e.g. the use of catalysts with Pd-Rh only), these ratios were used as  
220 indicators of the automotive source in many studies. For instance, Birke et al. (2018) found  
221 median ratios from roadside samples within the previously defined catalytic converter  
222 range: Pt/Pd 2.42, Pd/Rh 4.19 Pt/Rh 11.0. However, Rauch and Peucker-Ehrenbrink (2015)  
223 suggested that many studies were conducted with a presumption of potential sources and  
224 that the relative importance of different sources of PPGE depends on the specific  
225 characteristics of an urban area.

226 *Mining areas.* PPGE ores are naturally occurring in ultramafic to mafic-layered intrusions  
227 such as peridotite, pyroxenite and dunite. In the soils of PPGE ore zone, concentrations  
228 can reach very high values with a maximum up to  $1000 \mu\text{g kg}^{-1}$  (Figure 3). In this type of  
229 region contamination, the soil surface is contaminated from the rich geochemical  
230 background and surface pollution from mining activities, in particular smelters (Rauch and  
231 Fatoki, 2015).

232 *Roadside soil.* Early studies of PPGE contamination focused on roadside soils in cities or  
233 near highways, as these soils represent the closest environment to the main source of  
234 contamination from catalytic converters. Median values measured in different worldwide  
235 cities are summarised in Table 1. In addition, Figure 3 presents an overview of the PPGE  
236 concentration ranges found in soils. All of the median (or average) values compiled in the  
237 quoted studies exceed the element abundance in the earth crust. Most studies focused on  
238 the PPGE concentrations distribution with distance from the road. The following pattern  
239 was found: high values up to hundreds  $\mu\text{g kg}^{-1}$  for Pt, up to ten  $\mu\text{g kg}^{-1}$  for Pd and Rh, near  
240 the road, then decreasing concentrations with the depth and distance from the road (Ely et  
241 al., 2001; Jarvis et al., 2001; Schäfer and Puchelt, 1998; Zereini et al., 2007). Temporal  
242 studies clearly highlighted the increase and accumulation of PPGE in roadside soils over  
243 several years (Schäfer et al., 1999; Zereini et al., 2007). Some recent studies of urban  
244 soils and dust have pointed out that the increase in Pd concentration is particularly  
245 important (Spada et al., 2012; Wiseman et al., 2016). For example, near A5 highway in  
246 Germany, the median concentrations between 1994 and 2004 increased by 15 times for  
247 Pd, compared to only 2 and 1.6 times for Pt and Rh, respectively (Zereini et al., 2007).  
248 This reflects a greater current use of Pd in catalytic converters due to both the price  
249 difference between Pd and Pt and the better performances achieved with Pd (Cooper and  
250 Beecham, 2013).

251 In summary, there is clear contamination by PPGE in soils from urban area and mining  
252 zone, and near roads. Only little information is available about contamination in rural areas  
253 and their possible sources. Further large area assessments of soil contamination, based  
254 on a GIS approach, could help determine regional or national median concentration,  
255 spatial distribution and geochemical baseline, as well as identify a possible non-point  
256 source. It could also help to calculate the PPGE stock in soils since it was made for other

257 metals like Pb (e.g. Larcarce et al. (2012)). These assessments should be supported by  
258 well-established soil monitoring networks (Morvan et al., 2008).

### 259 2.3. *Geochemical behavior of PPGE in soils*

260 PPGE from catalytic converters are emitted as nanoparticles (NPs) in their oxidation state  
261 (0), or in water-soluble oxidized form. From bench tests, Artelt et al. (1999) found that  
262 more than 99% of platinum is emitted in the nanoparticle form. The presence of a  
263 predominantly particulate fraction in PPGE emissions is expected due to the fact that  
264 PPGE are actually in the form of nanoparticles (more reactive than the bulk metal) in  
265 catalytic converters (Lustig et al., 1998; Nachtigall et al., 1996). However, the experiments  
266 performed by Moldovan et al. (2002) revealed a soluble fraction was emitted, and this  
267 fraction was higher when catalyst aged due to physical and chemical alteration. Thus, in  
268 Madrid (Spain), the soluble fraction was estimated to be 10% of total city traffic emission  
269 for Pt, and 40% for Pd and Rh. Therefore, behavioural studies in soils of both soluble and  
270 nanoparticle forms of anthropogenic PPGE are of interest.

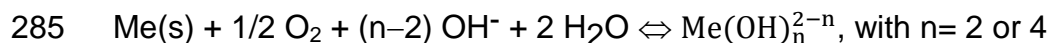
#### 271 2.3.1. *PPGE soluble forms*

272 The solubility and soluble species of PPGE are of interest to understand the environmental  
273 dispersion of PPGE. Studies were carried out to determine the solubility of PPGE under  
274 various physicochemical conditions similar to those found in the environment. Different  
275 thermodynamic studies have investigated the dissolution of PPGE metallic forms  
276 (Azaroual et al., 2001; Cobelo-García, 2013; Colombo et al., 2008; Suchá et al., 2016).  
277 The dissolution occurs by oxidation of PPGE leading to Pt(+II), Pd(+II) and Rh(+III)  
278 species. At the same time, these species can complex with various ligands. The hydroxide  
279 ion is a ligand playing a crucial role, the pH being one of the factors controlling the  
280 solubilisation of PPGE (Azaroual et al., 2001; Kalbitz et al., 2008; Suchá et al., 2016;

281 Zereini et al., 1997). The main processes leading to uncharged and charged species are  
282 as follows according to the considered PPGE:



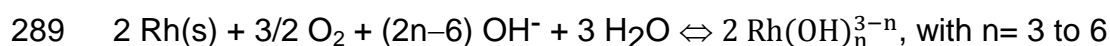
284 or



286 where Me represents Pt and Pd; and:



288 or



290 Different thermodynamic modelling was carried out on the PPGE speciation with pH.

291 Regarding Pt, two different speciation diagrams were proposed by Azaroual et al. (2001)

292 and Colombo et al. (2008). Azaroual et al. (2001) indicated that PPGE form hydroxyl

293 complexes over the entire range of pH except under very acidic and oxidizing conditions,

294 while Colombo et al. (2008) stated that PPGE form hydroxyl complexes whatever the pH.

295 In addition, according to Azaroual et al. (2001), Pt is predominant as  $\text{Pt(OH)}^+$  at  $\text{pH} < 9$

296 and  $\text{Pt(OH)}_2$  at  $\text{pH} > 9$ ; according to Colombo et al. (2008), Pt is predominant as  $\text{Pt(OH)}^+$  at

297  $\text{pH} < 1$ ,  $\text{Pt(OH)}_2$  at  $1 < \text{pH} < 11.5$ , and  $\text{Pt(OH)}_4^{2-}$  at  $\text{pH} > 11.5$ . Regarding Pd, Suchà et al.

298 (2016) reported that  $\text{Pd(OH)}_2$  is preponderant,  $\text{Pd(OH)}^+$  also existing at  $2 < \text{pH} < 3$ .

299 Colombo et al. (2008) found that the predominant dissolved species are  $\text{Pd(OH)}_2$  at  $2 < \text{pH}$

300  $< 12$ ,  $\text{Pd}^{2+}$  under oxidizing and acidic conditions, and  $\text{Pd(OH)}_3^-$  and  $\text{Pd(OH)}_4^{2-}$  at  $\text{pH} > 12$

301 and  $13$  respectively. Regarding Rh, Colombo et al. (2008) indicated that no

302 thermodynamic data were available for Rh–hydroxide aqueous complexes. More recently,

303 Cobelo-García (2013) reported that the following species coexist:  $\text{Rh}^{3+}$  ( $\text{pH} < 4$ ),  $\text{Rh(OH)}^{+2}$

304 ( $\text{pH} < 5$ ),  $\text{Rh(OH)}_2^+$  ( $2 < \text{pH} < 6$ ),  $\text{Rh(OH)}_3$  ( $2.5 < \text{pH} < 9.5$ ),  $\text{Rh(OH)}_4^-$  ( $5 < \text{pH} < 11.5$ ),

305  $\text{Rh(OH)}_5^{-2}$  ( $7 < \text{pH} < 13$ ), and  $\text{Rh(OH)}_6^{-3}$  ( $\text{pH} > 9$ ).

306 Leaching tests performed on different catalytic converters (gasoline and diesel, old and  
307 new) confirmed the quantities of soluble species released depended on both the pH and  
308 the wear state of the converter (Suchá et al., 2016). Leaching of Pt from contaminated  
309 soils, as well as arable and forest soils showed the same pH-dependence (Kalbitz et al.,  
310 2008; Zereini et al., 1997).

311 Other ligands capable to stabilise Pt(+II), Pd(+II) and Rh(+III) dissolved species were  
312 reported such as  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{PO}_3^{2-}$ . The quantitativity of PPGE solubilisation in  
313 presence of anions varies in this order:  $\text{NO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{PO}_3^{2-}$ , Pd being the most  
314 soluble element and Pt the least soluble (Zereini et al., 2017, 1997). Pyrophosphate and  
315 triphosphate anions also increase Pt solubility (Lustig et al., 1998); in this case, the  
316 kinetics of solubilisation of Pd from gasoline and diesel catalytic converters is faster in the  
317 presence of pyrophosphate. Another study of the interaction of PPGE with various ligands  
318 such as  $\text{OH}^-$ ,  $\text{NH}_3$  and  $\text{Cl}^-$  predicted that the predominant PPGE complexes depend on the  
319 ligand concentration (Colombo et al., 2008).

320 Naturally occurring organic complexing agents are also involved in the transformation of  
321 PPGE into soluble forms. Thus, the PPGE solubility was found to increase in the presence  
322 of fulvic acids, with likely formation of dissolved PPGE-humate complexes (Cobelo-García,  
323 2013; Koshcheeva et al., 2016; Wood, 1996, 1990; Wood et al., 1994). Nevertheless, long  
324 term leaching experiment (60 days) with PPGE from catalytic converters and fulvic acids  
325 showed that Pt and Pd were released from the catalytic converters and then immobilised,  
326 possibly due to flocculation of fulvic acids bound to metals (Šebek et al., 2011). In addition,  
327 Pt in solution and humic acids formed insoluble Pt-humic acid complexes (Lustig et al.,  
328 1998, 1996). Interestingly, experiments showed that  $\text{PtCl}_6^{2-}$  and  $\text{PtCl}_4^{2-}$  are re-complexed  
329 into insoluble species when mixed with humic soil while insoluble  $\text{PtO}_2$  was not affected by  
330 the presence of soil (Lustig et al., 1996).

331 Non-humic natural organic substances contain relatively low molecular weight molecules  
332 such as amino acids; simple organic fat acids and waxes can also complex PPGE. In soils,  
333 plant roots can freely and passively release these substances. Among them, the amino  
334 acids L-methionine and L-histidine were shown to form soluble complexes with Pt and Pd  
335 (Lustig et al., 1998; Zereini et al., 2016). Root exudates contain simple organic acids such  
336 as citric acid, which was also shown to complex Pt and Pd (Šebek et al., 2011; Zereini et  
337 al., 2016). In addition, the kinetics of complexation of Pt and Pd by citric acid was found to  
338 be rapid compared with other complexing agents such as pyrophosphate and fulvic acids  
339 (Šebek et al., 2011).

340 Soil components can be positively or negatively charged depending on the pH. Thus, the  
341 sorption behaviour of dissolved PPGE is important to access. Different studies were  
342 performed on soil minerals such as kaolinite, Mn/Fe-oxides, quartz, feldspar, calcite  
343 (Dikikh et al., 2007; Jean-Soro et al., 2013; Suchá et al., 2016). Kaolinite and Fe/Mn  
344 oxides have the highest sorption capacity compared to these other minerals (Dikikh et al.,  
345 2007). Thus, dissolved Pt, Pd and Rh are quantitatively sorbed by kaolinite, which can  
346 develop positive charges at a pH around 6 (100% removal from dissolved phase). At this  
347 pH, positive charges can develop on Al–OH sites, promoting the sorption capacity of  
348 kaolinite (Jean-Soro et al., 2013). Sorption capacity values up to 6,000  $\mu\text{g kg}^{-1}$  (kaolinite)  
349 and 1,200  $\mu\text{g kg}^{-1}$  (Fe oxide) were determined for Pt (Jean-Soro et al., 2013). Such  
350 capacities were due to the large surface area of the two materials, the oxide porosity, the  
351 pH and surface electric charges. All of these results indicate that dissolved PPGE are likely  
352 associated with clays in soils. Thus, the soil physical texture and mineral composition are  
353 important parameters driving the PPGE mobility.

### 354 *2.3.2. PPGE nanoparticle forms*

355 As mentioned above, PPGE are mainly released as NPs in the environment. Therefore,  
356 the behaviour of anthropogenic PPGE NPs is of interest. The mobility of Pt and Pd from Pt

357 and Pd nanoparticles coated with citrate (cPt/cPd NPs) and uncoated (Pt/Pd NPs) was  
358 evaluated relative to the metal salts, Pt(II) and Pd(II) (Leopold et al., 2018). Mobility  
359 increased in this order Pt(II) > cPd NPs > Pd(II) > Pd NPs > Pt NPs > cPt NPs. The higher  
360 mobilisation of Pd compared to Pt by dissolution of NPs can be explained by a possible  
361 oxidative decomposition of non-stabilised Pd NPs while Pt NPs were found to be more  
362 stable. For the coated nanoparticles, the difference in mobility came from the higher  
363 negative surface charge of the cPd NPs ( $\zeta = -70$  mV), which stabilised the nanoparticles to  
364 remain in suspension while the cPt NPs, which had a lower surface charge ( $\zeta = -14$  mV),  
365 could form hetero and homo-agglomerates. In addition, uncoated Pt NPs had a higher  
366 surface charge ( $\zeta = -28$  mV) than cPt NPs, which explains their higher mobility. Migration  
367 experiments were performed in the same study with the same Pd species in the soil and  
368 two other porous media, SiO<sub>2</sub> and sand. In all three media, cPd NPs were found to have  
369 the highest mobility. Pd(II) was highly retained due to the interaction with the mineral  
370 phase. The difference in migration between coated and uncoated particles can further be  
371 explained by their difference in surface charge, high negative values preventing  
372 aggregation. An in-situ migration experiment on two Siberian soils with platinum  
373 nanoparticles (Pt NPs) led to results depending on the following characteristics of the soils:  
374 organic matter content, porosity and particle size (Kulizhskiy et al., 2017). Thus, an  
375 adsorption of Pt NPs on humic layers was observed. Vertical migration of Pt NPs was also  
376 greater in sandy loamy soil than in loamy soil due to the greater porosity of the sandy  
377 loamy soil. Furthermore, a negative correlation between the Pt NPs concentration and the  
378 bulk density of soils was highlighted.

379 In summary, the PPGE emitted as NPs by the catalytic converter can be solubilised in soils  
380 and form stable complexes in the presence of natural inorganic and organic ligands, or can  
381 be sorbed on minerals (kaolinite, Fe/Mn oxides) and organic layers. Speciation depends  
382 on ligands present in the environment and on physicochemical conditions. In addition, soil



383 properties such as surface area, porosity, pH, surface electric charge, and density affect  
384 the PPGE mobility. As NPs, PPGE can aggregate or remain stable in suspension  
385 depending on the presence of a coating. Moreover, in the environment, engineered NPs  
386 are often coated by natural organic materials, which modify their properties (Surette and  
387 Nason, 2019). Therefore, further studies on this subject would be of interest to understand  
388 the fate of PPGE NPs.

#### 389 2.4. *Uptake and toxicity of PPGE to plants and soil life*

390 As shown in the previous section, PPGE can be transformed into water-soluble species.  
391 The question of bioavailability and uptake of PPGE by plants can therefore be raised.  
392 Table 2 presents typical PPGE concentrations found in plants from various environments.  
393 Concentrations of up to a few hundred  $\mu\text{g kg}^{-1}$  were found in native plants growing in the  
394 vicinity of PPGE ore deposits. This indicates that plants can significantly bioaccumulate  
395 these metals (Rencz and Hall, 1992). Therefore, bioaccumulative plants are used for the  
396 biogeochemical prospecting of PPGE (Kovalevskii, 2001). The most studied plant is grass,  
397 which usually grows on the roadside soil. The maximum Pt concentrations in grass were  
398  $30 \mu\text{g kg}^{-1}$  and  $256 \mu\text{g kg}^{-1}$ , respectively near highways and smelter, (Djingova et al., 2003;  
399 Rauch and Fatoki, 2013). In the study by Hooda et al. (2008), a significant correlation ( $r =$   
400 0.66) was found for Rh between its total concentrations in plants and soil. Nevertheless,  
401 the PPGE content in plants may not only reflect soil contamination but also atmospheric  
402 contamination, as is the case with grass sampled near smelters (Rauch and Fatoki, 2013).  
403 To overcome this difficulty, plants from the division briophyta (moss) can be used. This is  
404 because they do not have a root system. Therefore, they reflect atmospheric deposition  
405 and are used for biomonitoring of this process (Ayrault et al., 2006).  
406 The plant bioaccumulation factor was found to be low (up to 0.03) for Rye grass grown on  
407 a soil treated with Pt (Djingova et al., 2003). Similar results were obtained by Lustig et al.  
408 (1997) for Pt taken up by radish, potato and bean grown naturally on soil treated with Pt(s)

409 contained in tunnel dust. The authors suggested that Pt was first oxidised in the soil and  
410 then sorbed onto the soil matrix. Moreover, in cultivation experiments with contaminated  
411 soil, the soil-to-plant bioaccumulation factor of Pt, Pd, Rh was found to be similar to that of  
412 Cu, Pb, Cd, Zn (Schäfer et al., 1998). The bioaccumulation factor of PPGE in this  
413 experiment increased in this order  $Rh \leq Pt < Pd$ , making Pd the most bioavailable element.  
414 In a study by Verstraete et al. (1998), cucumbers were grown under hydroponic conditions  
415 in a Pt salt-containing medium ( $[Pt(NH_3)_4](NO_3)_2$ ). These experiments enabled the uptake  
416 and bioaccumulation of Pt in the roots to be highlighted, with a bioaccumulation factor up  
417 to 2098; translocation in the shoots was found to be limited, with a bioaccumulation factor  
418 of up to 42 (Verstraete et al., 1998). The distribution in the different plant parts was: root >  
419 leaf > stem (Bonanno, 2011; Kolodziej et al., 2007; Leopold and Schuster, 2011;  
420 Messerschmidt et al., 1994; Ronchini et al., 2015). The well-known toxic trace metals (Cd,  
421 Cr, Pb, Hg) have the same tendency of bioaccumulation in plants (Peralta-Videa et al.,  
422 2009). Negative biological effects were observed after exposure to PPGE. Typically, these  
423 effects are a decrease in germination rate of plant seeds, growth rate, biomass production  
424 and photosynthesis activity (Battke et al., 2008; Diehl and Gagnon, 2007; Farago and  
425 Parsons, 1994; Odjegba et al., 2007; Ronchini et al., 2015). They occurred for hydroponic  
426 PPGE exposure in the  $mg\ L^{-1}$  concentration range, while for non-essential metals such as  
427 Cd, Cr and Hg toxic effects occurred at lower concentration range ( $< 0.1\ mg\ L^{-1}$ ) (Das et al.,  
428 1997; Patra and Sharma, 2000; Shanker et al., 2005). For *Arabidopsis thaliana* L. under  
429 hydroponic conditions, photosynthesis appeared to be stimulated with Pt(II) concentrations  
430 below  $488\ \mu g\ L^{-1}$ , while growth inhibition and membrane damage were observed with  
431 higher concentrations, which is typical of the hormesis phenomenon (Gawrońska et al.,  
432 2018). Hormesis was also observed with peas (*Pisum sativum*) treated with a solution of  
433 Pd: the root diameter and volume increased with a Pd concentration lower than  $1\ mg\ L^{-1}$ ,  
434 while they decreased with higher concentrations. This biphasic response to a stress factor

435 is common in plants and has been observed with various non-essential toxic metals such  
436 as Cd, Cr, Al and Hg (Calabrese and Blain, 2009; Poschenrieder et al., 2013). Likewise, as  
437 non-essential metals, these hormetic effects seen with PPGE may involve various  
438 adaptive mechanisms, e.g. activation of the plant's general defence reaction with the  
439 metals acting as stimulators of antioxidant defences (Poschenrieder et al., 2013).

440 Little is known about the toxicity of PPGE to animals living in soils. The effects of PPGE on  
441 the nematode *Caenorhabditis elegans* were investigated (Schertzinger et al., 2017). Half  
442 maximal effective concentration (EC<sub>50</sub>) for Pt was determined for its effect on reproduction,  
443 fertility and growth (96h EC<sub>50</sub> = 497 µg L<sup>-1</sup> (exposure medium); 726 µg L<sup>-1</sup> and 808 µg L<sup>-1</sup>  
444 respectively). The 96h EC<sub>50</sub> for Pd ranged between 10 and 100 µg L<sup>-1</sup> for its effect on  
445 reproduction, while no significant trend was found for its effect on fertility and growth. No  
446 EC<sub>50</sub> was determined for Rh, as no effect on growth, fertility and reproduction was  
447 observed in the concentration range of 100 to 10,000 µg L<sup>-1</sup> (Schertzinger et al., 2017).  
448 Two other studies on soil-living invertebrates (collembolans *Folsomia candida* and soil  
449 worm *Enchytraeus crypticus*) were conducted with a longer exposure duration (28 days)  
450 (Havelkova et al., 2014; Nemcova et al., 2013, 2012). For both species, Pd appeared to  
451 have the lower EC<sub>50</sub>. This trend is the same as for nematodes with shorter exposure time  
452 (96h).

453 In summary, it is clearly established that plants accumulate PPGE, especially in the root  
454 part. However, the negative biological effects on plants occur over a range of mg L<sup>-1</sup>  
455 concentration range in an exposure solution, which is significantly greater than the  
456 expected concentration in the soil solution. Therefore, these effects are unlikely to be  
457 observed under real field conditions. Since little information is available on the toxicity of  
458 PPGE for animals, their possible transfer into the food chain, and human health, further  
459 studies should be carried out.

### 460 **3. Determination of PPGE in soil**

461 As this review focuses on PPGE in soils, only publications on the determination of PPGE  
462 in soils and solid environmental samples such as dust, sediment or sewage sludge are  
463 considered in this section. The most commonly used methods are shown in Table 3, along  
464 with the available analytical information. This table aims to compare the entire process of  
465 determination and not the instrumental performances. The PPGE determination remains a  
466 challenge due to the complexity of the matrices, the low PPGE concentrations, the  
467 numerous matrix effects and the numerous spectral interferences observed. Solid analysis  
468 techniques such as laser ablation, X-ray fluorescence or ion probe are generally not  
469 sensitive enough for the determination of PPGE in soil matrix. The general analytical  
470 process for the determination of PPGE involves: extraction from the matrix to release the  
471 analytes in the dissolved phase; possible post-digestion extraction of PPGE to remove  
472 chemical residues from the matrix, this step can be associated with a pre-concentration;  
473 and elemental determination by spectrometry or electrochemical techniques. These steps  
474 are discussed thereafter. It should be kept in mind that this section mainly presents the  
475 methods used in environmental studies; analytical developments for the determination  
476 PPGE are underway but they may not have yet been transposed into environmental  
477 studies.

478        3.1.        *Sample preparation*

479        *Sample decomposition.* As it is usually performed for the elemental determination, the  
480 matrix destructuring is obtained by digestion with a mixture of concentrated acid. Although  
481 the acid mixtures differ with studies, the acids generally used are nitric acid, and either  
482 hydrochloric acid or perchloric and hydrofluoric acids. Some authors reported that  
483 digestion with aqua regia alone is not sufficient to recover Pt and Pd from siliceous  
484 matrices (Borisov et al., 1997; Köllensperger et al., 2000; Totland et al., 1995; Tsogas et al.,  
485 2008). The process can also involve an evaporation step to remove HF and / or chlorides  
486 and possibly to concentrate the analytes, and the final volume can be adjusted with dilute  
487 nitric acid solution. An additional digestion step with HNO<sub>3</sub> can be performed and possibly  
488 repeated, in order to increase the quantity of analytes released in the dissolved phase  
489 (Orecchio and Amorello, 2011; Wiseman et al., 2016). However, these successive  
490 digestions do not always enable the matrix to be completely digested and therefore  
491 dissolved, total dissolution being the guarantee of total recovery of the analytes. In  
492 addition, these additional digestion steps can induce loss of analytes, contamination of  
493 samples, and are time consuming.

494        A specific method for determining noble metals using fire assay was also reported  
495 (Mihaljevič et al., 2013; Morcelli et al., 2005; Wichmann et al., 2007; Zereini et al., 2007).  
496 Fire assay using nickel sulphide (NiS) is widely used to determine PGE in environmental  
497 samples. This method enables not only the matrix to be destructured but also the metals  
498 soluble in NiS to be extracted and pre-concentrated (Wichmann et al., 2007; Zereini et al.,  
499 2007). The advantage of fire assay pre-treatment is the high amount of sample (10 – 50  
500 g), which solve the problem of low amount of PPGE. However, a high amount of Ni can  
501 lead to high blanks value during instrumental determination because Ni may contain PPGE  
502 impurities.

503 Another strategy for releasing analytes is to extract them directly from the solid matrix by  
504 sequential leaching. In that case, the objective is not to obtain the total concentration of  
505 elements but to determine the elements bound to the mobile fractions. For example, in the  
506 study by Van der Horst et al. (2018), a chemical sequential extraction procedure was used  
507 to extract the PPGE bound to fractions of organic matter, carbonates, and Fe-Mn oxides.

508 *Post-digestion extraction.* It is performed with a volume of digestate ranging from 1 to 100  
509 mL according to the publications (Jarvis et al., 1997; Kovacheva and Djingova, 2002; Wu  
510 et al., 2004). Two methods are often used: ionic (anionic or anionic) exchange and  
511 extraction based on co-precipitation with Hg or Te (Alsenz et al., 2009; Niskavaara and  
512 Kontas, 1990; Wiseman et al., 2016). The anion exchange resin is preferred over cationic  
513 resin because of the smaller volume required to elute PPGE (Kovacheva and Djingova,  
514 2002). Co-precipitation with Hg is more efficient than with Te, but involves a step of  
515 evaporation of Hg, which is neither respectful of health nor the environment (Alsenz et al.,  
516 2009). An organic solvent can also be used for extraction of PPGE. For example, methyl  
517 isobutyl ketone (MIBK) widely used for metal extraction was used for analysis of soils  
518 containing PPGE at environmental levels (Choudhury, 2016). However, this technique  
519 requires a relatively high amount of reagents.

520 *Pre-concentration.* This step can be carried out to overcome the dilution due to the  
521 digestion, and / or extraction. This is also necessary when the detection method is not  
522 sufficiently sensitive (discussed below). For example, Wu et al. (2004) used a YPA<sub>4</sub>  
523 chelating resin (aminoisopropylmercaptan type with a polythioether backbone, containing  
524 24.89% S and 7.82% N), either in batch or in column mode. The column appeared to be  
525 more efficient because the volume of digestate or extract used could be adjusted, with an  
526 enrichment factor up to 100 for a volume of 100 mL. Recently, new techniques of  
527 extraction and pre-concentration have been developed for the determination of  
528 contaminants in the environment: cloud point extraction (CPE) and dispersive liquid liquid

529 microextraction (DLLME). CPE is based on a surfactant in aqueous solution that can form  
530 micelles. When heated above the cloud point temperature, these micelles form a turbid  
531 cloud (the micellar solution) in which the hydrophobic metal complexes are “trapped” and  
532 concentrated. The advantages of this technique are simple operation, low cost, and high  
533 capacity to concentrate. For the Pd pre-concentration factor, up to 28 was reached (Table  
534 3). DLLME is based on solvents with high sorption capacity and dispersive solvents. The  
535 technique consists of the injection into an aqueous solution of fine droplets of the solvent  
536 that will preconcentrate the analyte. The phase separation is performed by centrifugation.  
537 An evaporation step may also be necessary depending on the instrumental determination.  
538 The advantages are the small volume of reagents and sample required, the simplicity and  
539 the high preconcentration capacity. Several solvents were used for the determination of  
540 Pd in soil samples, with a pre-concentration factor up to 156.

### 541 3.2. Elemental determination

542 Different analytical methods, mainly elemental spectrometric but also electrochemical,  
543 have been used to determine the PPGE in the (sub)  $\mu\text{g kg}^{-1}$  concentration range (Table 3).  
544 Several analytical aspects of these methods are discussed: vaporization process,  
545 sensitivity, accuracy and interferences.

546 *Vaporization process.* When atomic spectrometry without an inductively coupled plasma  
547 (ICP) source is used, special attention must be paid to the vaporization process of the  
548 sample. Some methods employed electrothermal vaporization (ETV) in a graphite furnace.  
549 However, this process, performed at a relatively low temperature (around 2200-2600°C)  
550 compared to plasma, can induce the formation of refractory compounds such as carbides,  
551 and memory effects due to the matrix. To overcome these problems, the matrix can be  
552 “neutralized” or removed. Thus, in the study by Wu et al. (2004), the YPA<sub>4</sub> chelating resin  
553 was used for preconcentration (as seen above) and also as a chemical modifier to prevent  
554 matrix effects. Under these conditions, the vaporization was quantitative at a temperature

555 of 1900°C. In the study by Zereini et al. (2007) as in the previous study quoted, a graphite  
556 furnace and electrothermal vaporization were also used. The PPGE were simultaneously  
557 extracted from the matrix and concentrated by a NiS fire assay. Under these conditions,  
558 usual temperatures of 2200°C to 2350°C were found to be sufficient for quantitative  
559 vaporization. The use of atomic spectrometry with ICP source overcomes these difficulties.

560 *Sensitivity.* The instrumental limits of detection (LOD), evaluated from the analysis of  
561 standard solutions of Pd, Pt and Rh, are as expected in atomic spectrometry: Inductively  
562 coupled plasma- Atomic Emission Spectrometry (ICP-AES) provides the highest LOD (in  
563 the range of  $\mu\text{g L}^{-1}$ ) and Inductively coupled plasma- Mass Spectrometry (ICP-MS) gives  
564 the lowest (from 0,08 to less than 0,0003  $\mu\text{g L}^{-1}$  depending on both the considered PPGE,  
565 the instrument, and the date of the study cited in Table 3). Graphite Furnace – Atomic  
566 Absorption Spectrometry (GF-AAS) and voltammetry although they are older techniques  
567 than ICP-MS may also offer competitive LOD (0,03 to 0,01  $\mu\text{g L}^{-1}$ ) compared to Q-ICP-MS.  
568 Flame Atomic Absorption Spectrometry (FAAS) is the less sensitive instrument with  
569 instrumental LOD that vary from to 0.1 to 6  $\mu\text{g L}^{-1}$ .

570 Given the objective of this section, i.e. the determination of PPGE in soils and solid  
571 environmental samples, it is also of interest to examine the LOD of analytical methods.  
572 Thus, the nature of the solid sample solid and the entire process, from preparation to  
573 detection, are taken into account. These LOD are shown in Table 3. Methods based on  
574 ICP-AES for soil analysis show LOD values of 15  $\mu\text{g kg}^{-1}$  for Pt and Pd without pre-  
575 concentration (Kovacheva and Djingova, 2002). In addition, studies based on FAAS  
576 obtained even higher LOD values up to 25  $\mu\text{g kg}^{-1}$  for Pd (Table 3). This is insufficient to  
577 determine background PPGE concentrations in soils. Sufficiently low LOD could be  
578 achieved with a pre-concentration step and ETV introduction, 0.15- 0.40  $\mu\text{g kg}^{-1}$  for Pt and  
579 Pd (Wu et al., 2004). The methods involving ICP-MS are the most widely used due to ICP-  
580 MS sensitivity (Table 3). In particular, very low LOD, under the  $\mu\text{g kg}^{-1}$  range can be



581 obtained with High Resolution-ICP-MS (HR-ICP-MS) when it is used in low-resolution  
582 mode (Rauch et al., 2000). With Quadrupole-ICP-MS (Q-ICP-MS), LOD varies between  
583  $0.03 - 1 \mu\text{g kg}^{-1}$  for Pt,  $0.03 - 1 \mu\text{g kg}^{-1}$  for Pd and  $0.01 - 0.9$  for Rh  $\mu\text{g kg}^{-1}$  (Table 3). In a  
584 recent study where the sample was pre-concentrated and then analysed either by  
585 differential pulse adsorptive stripping voltammetry or by Q-ICP-MS, very low LOD of the  
586 order of  $\text{ng kg}^{-1}$  were obtained in using voltammetry (van der Horst et al., 2018), confirming  
587 that this detection is suitable for PPGE determination.

588 *Accuracy.* Very few studies provide information about accuracy. Repeatability (express as  
589 relative standard deviation, RSD) and trueness (as recovery) are reported in Table 3.  
590 Usually, recovery is evaluated using standard solutions, spiked samples or certified  
591 reference materials. This issue is specifically discussed below. RSD was found to range  
592 over  $1 - 28\%$  for Pt,  $1 - 65\%$  for Pd, and  $5 - 14\%$  for Rh. Recovery was generally found  
593 between around 90 and 101% for the 3 PPGE. Comparing these values is critical, due to  
594 the limited number of studies and the variety of analytical and validation protocols used. In  
595 addition, some RSD and recovery values reported were overestimated, notably for Pd,  
596 likely due to difficulties in sample preparation or severe interferences (Wiseman et al.,  
597 2016). This illustrates the difficulties for PPGE determination. The choice of the calibration  
598 process is also important with regard to accuracy. External calibration appears as the  
599 procedure usually used. Köllensperger et al. (2000) determined Pt by external calibration  
600 and isotopic dilution and found similar repeatability (RSD  $\sim 6\%$ ). Nevertheless, isotopic  
601 dilution has helped improve repeatability when used in combination with extraction or pre-  
602 concentration techniques (Gómez et al., 2003; Müller and Heumann, 2000). In addition,  
603 some studies reported the use of internal standards (In, Ir, Tl) (Mihaljevič et al., 2013;  
604 Wichmann et al., 2007). However, from the studies in Table 3, no author focused on the  
605 effect of using an internal standard on accuracy. All this highlights the lack of analytical  
606 study.

607 *Interferences.* PPGE are usually present at ultratrace level in the matrix, which contains  
608 widely higher concentrations of Si, S, Zn, P, Fe, Ca, Pb, Co, Cu, Ni and Al as chloride or  
609 nitrate salts. This may cause interferences. In order to reduce these interferences, PPGE  
610 can be extracted to simplify the matrix, as discussed above. However, interferences may  
611 still remain. For example, atomic absorption of Pd (247.642 nm wavelength) in GF-AAS  
612 suffers of spectral interference from Pb (247.638 nm wavelength) (Brzezicka and Szmyd,  
613 1999); increasing the pyrolysis temperature of the graphite furnace to ensure the  
614 volatilization of Pb before the Pd atomization could eliminate this interference. Another  
615 sensitive Pd wavelength (244.791 nm) could have been suitable but it has a narrower  
616 range of linearity and also interference with Pb (247.638 nm) (Brzezicka and Szmyd, 1999;  
617 Frigge and Jackwerth, 1992). The determination of PPGE by ICP-AES is subject to several  
618 spectral interferences reported in Table 4. Some of these interfering species are major  
619 elements of soils (Al, Fe, Mn). The selection of the detection wavelength is therefore  
620 critical. Kim et al. (2018) thoroughly investigated the effects of interfering species  
621 (including Al and Fe) on six wavelengths of PPGE. They concluded that the most accurate  
622 wavelength was 265.95 nm for Pt, 340.46 for Pd and 343.49 nm for Rh (Kim et al., 2018).  
623 Interference also occurs in Q-ICP-MS. The known isobaric and polyatomic interferences  
624 for PPGE are reported in Table 5. The interferences are produced in the presence of  
625 elements frequently found in environmental samples (Cd, Cu, Hg, Pb, Zn, etc...).  
626 According to the literature, the three most abundant isotopes of Pt ( $^{194}\text{Pt}$ ,  $^{195}\text{Pt}$ ,  $^{196}\text{Pt}$ ) seem  
627 to be mainly interfered by HfO species. In order to overcome these interferences,  
628 mathematical corrections are used, assuming the only existence of HfO interferences (Kan  
629 and Tanner, 2004; Niemelä et al., 2004).  $^{106}\text{Pd}$  is the most abundant Pd isotope but  $^{105}\text{Pd}$   
630 is more often selected because it does not have mono-atomic interference. However, due  
631 to the abundance ratio between Pd isotope and its polyatomic interferences, it remains  
632 critical to mathematically correct Pd signals. Rh has only one isotope, therefore it not

633 possible to select another to overcome interference. In this case, mathematical correction  
634 remains reliable (Niemelä et al., 2004). Note that whatever the PPGE considered, a  
635 mathematical correction requires exhaustive knowledge of the elemental composition of  
636 the sample analysed, which can be critical to obtain. The use of HR-ICP-MS can be an  
637 alternative to overcome interference. Especially HR-ICP-MS seems very efficient in  
638 eliminating interference when determining Pt. The determination of Pd seems more critical  
639 because the mass resolution does not appear to be sufficient and interference remains  
640 (Table 5). For Rh, most of the interference can be eliminated, with the exception of  $\text{SrO}^+$ ;  
641 this can be an issue when the Rh concentration is low (Köllensperger et al., 2000; Rauch  
642 et al., 2000). The drawback of high resolution in ICPMS is the increased limits of detection,  
643 However they remain sufficiently low for the determination of PPGE in soils (Table 3). A  
644 sample introduction system in ICP-MS such as desolvating nebulizer can also help reduce  
645 interference (Köllensperger et al., 2000; Müller and Heumann, 2000; Sutherland, 2007).  
646 Desolvating nebulizers are made with a permeable membrane that filters the solvent,  
647 which increases sensitivity and reduces interferences from oxides.

648 Another solution to overcome interference is to use a collision/reaction cell (CRC) within  
649 Q-ICP-MS. CRC can minimize and even eliminate interference, but repeatability may be  
650 affected (Alsenz et al., 2009; Kan and Tanner, 2004; Satyanarayanan et al., 2011; Spada  
651 et al., 2012; Wiseman et al., 2016). Despite this possibility, only a few studies used CRC.  
652 CRC was always combined with a pre-treatment step as described above to eliminate part  
653 of the matrix and thus reduce the possible causes of interference. Studies carried out with  
654 standard solutions showed that CRC with He,  $\text{O}_2$  or  $\text{NH}_3$  as collision / reaction gas is  
655 effective in minimizing interferences (Alsenz et al., 2009; Moldovan et al., 2006; Simpson  
656 et al., 2001). He, used as a collision gas (non-reactive), reduces kinetic energy of  
657 polyatomic ions by collision, which enables fewer interfering species to enter the  
658 quadrupole. He has proven to be effective to reduce Ar-based interference (Moldovan et

659 al., 2006). O<sub>2</sub> acts as a dynamic reaction gas to oxidize interfering species that results in  
660 species with higher mass than the element of interest. For example, HfO interference on  
661 Pt forms HfO<sub>3</sub> in presence of O<sub>2</sub>, which enables the problem of mass superposition for Pt  
662 to be solved; Likewise, the ZrO interference on <sup>106</sup>Pd can be removed using O<sub>2</sub> (Simpson  
663 et al., 2001). NH<sub>3</sub> is also a reaction gas based on the transfer of electron from the  
664 interfering species to NH<sub>3</sub> molecules. Used alone or diluted in He, it was found to be very  
665 effective in minimizing <sup>89</sup>Y<sup>16</sup>O interference on <sup>105</sup>Pd (Moldovan et al., 2006). More recently,  
666 triple quadrupole ICP-MS (QQQ-ICP-MS) was proposed. QQQ-ICP-MS is based on two  
667 quadrupoles, and an octopole as CRC. Developments performed with standard solutions  
668 showed that QQQ-ICP-MS with NH<sub>3</sub> as reaction gas is effective in eliminating interference  
669 when determining Pt (mass-shift), Pd (on-mass) and Rh (on-mass) (Sugiyama and  
670 Shikamori, 2015).

671 Voltammetry also suffers from potential interference for Pt (with Cd, Co, Fe, Zn), Pd (with  
672 Cd, Co Cu, Fe), and Rh (with Cd, Co, Fe, Ni) (Locatelli, 2006; van der Horst et al., 2018).  
673 However, no study reported interference with these elements (Orecchio and Amorello,  
674 2011; van der Horst et al., 2018).

### 675 3.3. *Reference materials*

676 Certified reference materials (CRM) are essential for the validation of analytical  
677 procedures. Unfortunately, there is no CRM available for soil, vegetal and water (Jochum  
678 et al., 2005). There are some CRM for rocks and ores such as WMG-1 (Balaram et al.,  
679 2013; Mihaljevič et al., 2013). However, there is a limited number of CRM with certified  
680 PGE concentrations for environmental samples. A sediment, JSd-2, was used as a  
681 reference material in a few studies (Almécija et al., 2016; Cobelo-García et al., 2011;  
682 Djingova et al., 2003; Tsogas et al., 2008). It is a river sediment from the Geological  
683 Survey of Japan with preferable values for Pt and Pd. The only available CRM with Pt, Pd  
684 and Rh certified concentration is the road dust BCR-723 provided by the Joint Research

685 Centre of European Union (Zischka et al., 2002). The use of this sediment is preferable  
686 because it is an environmental matrix. However, the procedures for extracting PPGE from  
687 the matrix are cumbersome, complex and time consuming in order to recover PPGE  
688 quantitatively (Cobelo-García et al., 2011; Tsogas et al., 2008). Sutherland (2007a)  
689 reviewed the values of BCR-723 determined in studies and published in the literature: no  
690 statistical difference was found with the certified values. However, the same author re-  
691 examined the dataset used to certify the PPGE concentrations and found significant  
692 differences in the Pt and Pd concentrations provided by the laboratories. These differences  
693 appeared to come in part from the quantification methods used with ICP-MS, namely  
694 isotopic dilution or external calibration. In addition, for Pd only, the statistical distribution of  
695 its concentrations showed two populations. All of this reflects the difficulty of traceability  
696 and quality control in the PPGE analysis (Sutherland, 2007b). Therefore, the author  
697 advised to use the mean Pd concentration value as indicative value.

698 In the absence of CRM, validation can be achieved using at least two different  
699 independent methods and by checking agreement between the results. Some authors  
700 used samples spiked with PPGE standard solution (Hooda et al., 2007; Wichmann et al.,  
701 2007); but this is not recommended for solid samples, because the efficiency of digestion  
702 cannot be verified.

703 In summary, the determination of PPGE in environmental matrices remains a challenge  
704 because of the low concentration range and the numerous interferences occurring during  
705 detection. Given the most recent analytical developments, ICP-MS seems capable of  
706 achieving the required sensitivity, and overcoming interference using various strategies.  
707 The low number of certified PPGE materials makes traceability and quality control of  
708 analysis more difficult than for most of the trace metals studied. An effort should therefore  
709 be made to prepare new PPGE certified materials with different environmental matrices  
710 (soil, sediment, water...).

#### 711 **4. Conclusion**

712 Platinum group elements are used and released mainly by automotive exhaust catalysts.  
713 Therefore, their environmental concentrations have increased significantly over the past  
714 decades. However, while the main source of soil contamination is from the use of car  
715 catalytic converters, mining and industrial activities are also significant sources. It has  
716 been established that in soil, PPGE undergo transformations and may be converted into  
717 bioavailable forms. The risks posed by the environmental presence of PPGE are therefore  
718 real and discussions on the potential toxicity of emitted PPGE to living organisms are  
719 ongoing. In this review, we focused on soil because it is one of the environmental  
720 compartments the most exposed to PPGE deposits resulting from emissions. In urban  
721 areas, contamination and accumulation are well documented in many cities. However,  
722 information about soil contamination of rural zones and large surface areas is very scarce.  
723 The regulation on automotive exhausts is expected to be more stringent over the years.  
724 Therefore, with increasing use of PPGE-based catalysts, global contamination concern is  
725 also expected to increase. In this perspective, further studies should be conducted to  
726 examine the large-surface contamination, determine the spatial distribution, and assess  
727 the PPGE stocks, which would help determine the deposition rate and global fluxes. The  
728 analytical determination of PPGE remains a challenge. Therefore, there are only a small  
729 number of studies dedicated to these elements. Environmental contamination by PPGE is  
730 also a key issue. With the most recent developments in mass spectrometry, it can be  
731 expected that analytical issues will be solved and this will enable the PPGE contamination  
732 to be assessed more reliably.

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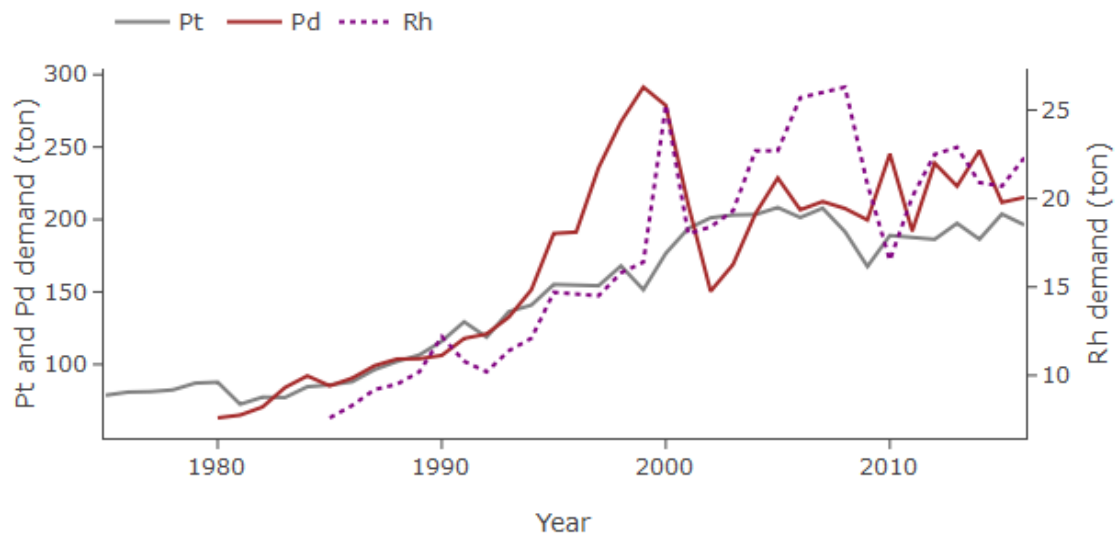


Figure 1: Evolution of the demand of Pt, Pd and Rh since 1976 (Johnson Matthey, 2017b).

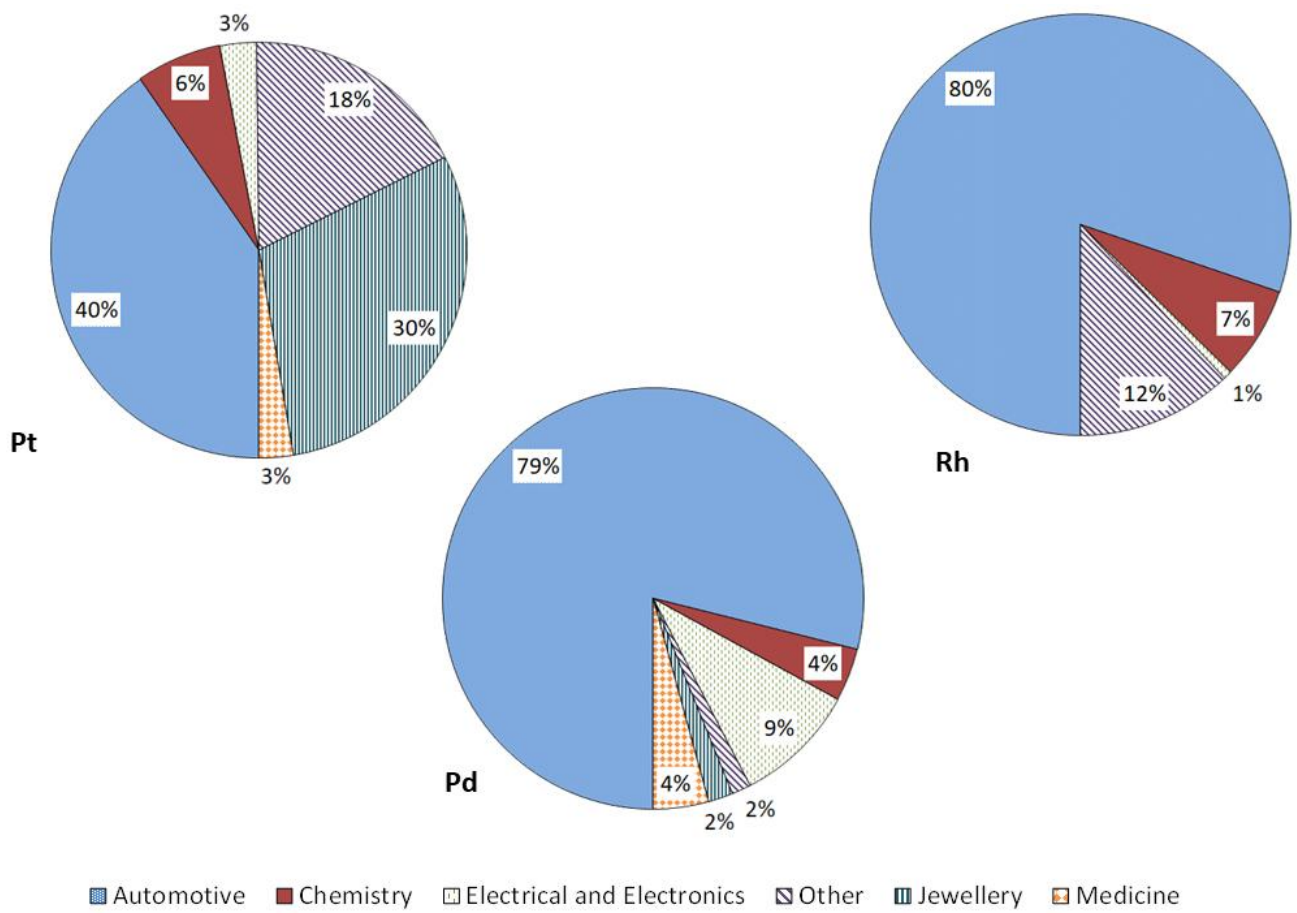


Figure 2: Pt, Pd and Rh demand (in percentage) by type of activities in 2016 (Johnson Matthey, 2017a).

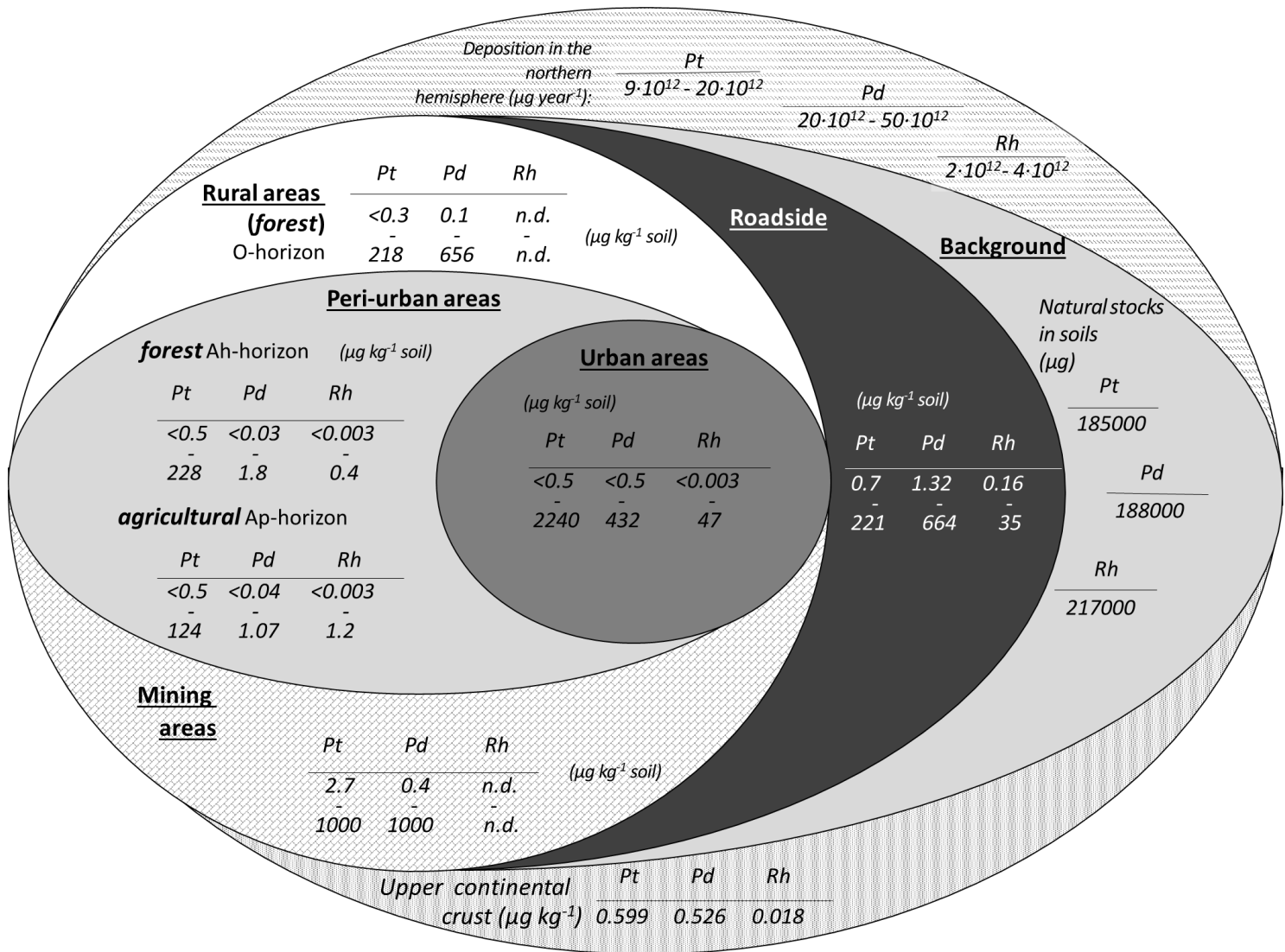


Figure 3: Ranges of concentrations and masses of PPGE in various environmental parts. Compiled values from : Birke et al., 2018; Cicchella et al., 2008, 2003; Ely et al., 2001; Fletcher, 1988; Hooda et al., 2007; Lee et al., 2012; Mitra and Sen, 2017; Niskavaara et al., 2004; Pan et al., 2009; Park et al., 2012; Rauch et al., 2005; Rauch and Fatoki, 2015; Whiteley and Murray, 2003; Wilhelm et al., 1997; Wiseman et al., 2016; Zuzolo et al., 2018

Table 1: Median concentrations ( $\mu\text{g kg}^{-1}$ ) of PPGE in soils classified by sampling zone and their analytical process (pre-treatment, detection) associated to their determination. The asterisk indicates average value. Abbreviations: NiS-FA, nickel sulphide fire assay, Pb-FA, lead fire assay, Q-ICP-MS, quadrupole-inductively coupled plasma-mass spectrometry; ID-ICP-MS, isotope dilution inductively coupled plasma- mass spectrometry; GF-AAS, graphite furnace atomic absorption spectrometry; DPV, differential pulse voltammetry; Arc AES, arc atomic emission spectrometry.

Crust abundance ( $\mu\text{g/kg}$ )	Pre-treatment	Detection instrument	Pt	Pd	Rh	Reference
Upper continental Crust	NiS-FA	Q-ICP-MS	0.599	0.526	0.018	(Park et al., 2012)
Bulk continental crust	n/a	n/a	0.4	0.4	0.06	(Hans Wedepohl, 1995)
<b>"Background" values (<math>\mu\text{g/kg}</math>)</b>						
UK, Ascot, Silwood Park Imperial College	NiS-FA	Q-ICP-MS	<0.21	<0.45	<0.16	(Jarvis et al., 2001)
USA, South Bend, background soil	Digestion ; cation exchange resin	Q-ICP-MS	3.63	1.54	0.09	(Ely et al., 2001)
Italy, Avellino, soils formed on volcanic rocks	Pb-FA	Q-ICP-MS	3.2	2.8	<0.05	(Cicchella et al., 2008)
Italy, Benevento, soils formed on sedimentary rocks	Pb-FA	Q-ICP-MS	1.3	1.1	<0.05	(Cicchella et al., 2008)
Italy, Caserta east, soils formed on sedimentary rocks	Pb-FA	Q-ICP-MS	1.1	0.9	0.3	(Cicchella et al., 2008)
Italy, Caserta west, soils formed on volcanic rocks	Pb-FA	Q-ICP-MS	2.7	2.3	0.3	(Cicchella et al., 2008)
Italy, Salerno, soils formed on sedimentary rocks	Pb-FA	Q-ICP-MS	1	1	0.4	(Cicchella et al., 2008)
Germany, Spöck, soil formed on quaternary sand	NiS-FA	Q-ICP-MS	4	<0.4	0.6	(Schäfer and Puchelt, 1998)
Germany, Michaelsberg, soil formed on claylike loess	NiS-FA	Q-ICP-MS	3	<0.4	0.4	(Schäfer and Puchelt, 1998)
Germany, Hohenhöven, soil on phonolith (0-10 cm)	NiS-FA	Q-ICP-MS	0.8	0.4	<0.1	(Schäfer and Puchelt, 1998)
Italy, Latium, sedimentary bedrock (average)	Digestion	Q-ICP-MS	2.5	n/a	n/a	(Cinti et al., 2002)
Italy, Latium, volcanic bedrock (average)	Digestion	Q-ICP-MS	4.1	n/a	n/a	(Cinti et al., 2002)

Table 1 (continued)

**Peri-urban and rural areas**

Germany, Berlin surroundings, agricultural soil Ap-horizon	Digestion; Te co-precipitation	Q-ICP-MS	2.98	0.167	0.0128	(Birke et al., 2018)
Germany, Berlin surroundings, sewage farm areas	Digestion; Te co-precipitation	Q-ICP-MS	5.83	1.86	0.221	(Birke et al., 2018)
Germany, Berlin surroundings, forest soil Ah-horizon	Digestion; Te co-precipitation	Q-ICP-MS	5.36	0.134	0.0121	(Birke et al., 2018)
Italy, Modena district, natural reserve soil	Leaching	Q-ICP-MS	2.51*	4.2*	1.05*	(Marcheselli et al., 2010)
Italy, Modena district, agricultural soil	Leaching	Q-ICP-MS	2.78*	4.07*	0.97*	(Marcheselli et al., 2010)
European Arctic, moss	Ashing ; digestion ; Hg co-precipitation	GF-AAS	<0.2	0.71	n/a	(Niskavaara et al., 2004)
European Arctic, podzol O-horizon	Ashing ; digestion ; Hg co-precipitation	GF-AAS	0.62	0.45	n/a	(Niskavaara et al., 2004)
European Arctic, podzol B-horizon	Ashing ; digestion ; Hg co-precipitation	GF-AAS	2.04	0.91	n/a	(Niskavaara et al., 2004)
European Arctic, podzol C-horizon	Ashing ; digestion ; Hg co-precipitation	GF-AAS	<0.5	0.91	n/a	(Niskavaara et al., 2004)
Italy, Campania Region, topsoil	Digestion	Q-ICP-MS	<2	<10	n/a	(Zuzolo et al., 2018)

Table 1 (continued)

**Urban areas**

Italy, Napoli metropolitan area	Digestion	Q-ICP-MS	1.6	8	n/a	(Cicchella et al., 2003)
Italy, Benevento's area low population density	Pb-FA	Q-ICP-MS	2.1	0.9	<0.05	(Cicchella et al., 2008)
Italy, Salerno's area high population density	Pb-FA	Q-ICP-MS	2.1	2.4	0.28	(Cicchella et al., 2008)
Germany, Berlin inner city area, 1992 survey	Digestion; Te-coprecipitation	Q-ICP-MS	1.35	0.24	0.04	(Birke et al., 2018)
Germany, Berlin inner city area, 2013 survey	Digestion; Te-coprecipitation	Q-ICP-MS	2.03	0.958	0.192	(Birke et al., 2018)
Italy, Palermo, high population density	Digestion	DPV	68	n/a	n/a	(Orecchio and Amorello, 2011)
United Kingdom, London, Richmond Borough	Pb-FA	Q-ICP-MS	1.04	n/a	n/a	(Farago et al., 1996)

**Mining zone**

Canada, Southern British columbia, Franklin mining district, A horizon	Pb-FA	Q-ICP-MS	26	29.5	n/a	(Fletcher, 1988)
Canada, Southern British columbia, Franklin mining district, B/C horizon	Pb-FA	Q-ICP-MS	9.5	18.5	n/a	(Fletcher, 1988)
South Africa, Bushveld Igneous Complex, topsoil (0-2 cm)	Digestion	Q-ICP-MS	97.5	n/a	n/a	(Rauch and Fatoki, 2013)
South Africa, Bushveld Igneous Complex, Main Zone (0-20 cm)	Digestion; charcoal/SnCl <sub>2</sub> pre-concentration	Arc AES	16	6.3	n/a	(Wilhelm et al., 1997)



Table 1 (continued)

**Roadside soil**

South Korea, Seoul	Digestion	Q-ICP-MS	49.7*	n/a	n/a	(Lee et al., 2012)
USA, South Bend	Digestion ; cation exchange	Q-ICP-MS	26.555	7.19	0.93	(Ely et al., 2001)
UK, multiple locations, 0m distance	Leaching	Q-ICP-MS	15.9*	120.8*	22.4*	(Hooda et al., 2007)
UK, multiple locations, 5m distance	Leaching	Q-ICP-MS	2.04*	84.2*	3.5*	(Hooda et al., 2007)
Australia, Perth	Digestion ; cation exchange	Q-ICP-MS	107.49	91.4	14.54	(Whiteley and Murray, 2003)
Canada, Toronto, 0 to 200m distance	Digestion ; Hg and Te co-precipitation	ID-ICP-MS	8.7	63	1.7	(Wiseman et al., 2016)
China, Beijing	NiS-FA	Q-ICP-MS	39.8*	20.8*	10.1 *	(Pan et al. 2009)
China, Hong Kong	NiS-FA	Q-ICP-MS	62.2*	38.7*	10.8*	(Pan et al. 2009)
India, Mumbai	NiS-FA	Q-ICP-MS	6.24	15.5	0.64	(Pan et al. 2009)
Germany, A5 Highway	NiS-FA	GF-AAS	132	83	20	(Zereini et al., 2007)
Germany, Pforzheim, A8 Highway	NiS-FA	Q-ICP-MS	46*	6*	7*	(Schäfer et al., 1999)
Russia, Moscow, southwest district	Digestion	Q-ICP-MS	88.5	34.2	6.7	Ladonin, 2018

Table 2: Typical PPGE concentrations in plants collected from field studies

Sample	Location	Sampling condition	Concentration ( $\mu\text{g kg}^{-1}$ )			Reference
			Pt	Pd	Rh	
Labrador tea ( <i>Ledum groenlandicum</i> )	Ferguson Lake, Keewatin District, Canada	Ni-Cu mineralisation, leaf sample	51	2103	97	(Rencz and Hall, 1992)
Dwarf birch ( <i>Betula glandulosa</i> )	Ferguson Lake, Keewatin District, Canada	Ni-Cu mineralisation, leaf sample	121	576	38	(Rencz and Hall, 1992)
Grass ( <i>Aristida bipartita</i> , <i>Bothriochloa insculpta</i> , <i>Digitaria eriantha</i> , <i>Ischaemum afrum</i> or <i>Panicum</i> )	Bushveld Igneous Complex, South Africa	Mining industry, near smelter	256	n/a	n/a	(Rauch and Fatoki, 2013)
Grass	United States	Highways, leaves and shoots only, washed samples	1.23	1.03	0.10	(Ely et al., 2001)
Ryegrass	Plateau Lorrain, France	Highways	1.4	6.8	3	(Tankari Dan-Badjo et al., 2007)
Grass ( <i>Calamagrostis</i> sp.)	Oulu, Finland	Highways	1.7	n/a	0.7	(Niemelä et al., 2004)
Plant leaves	Guangzhou, China	Near a main street, washed sample	3.52	1.55	1.16	(Pan et al., 2009)
Annual ryegrass (annual ryegrass)	Bonn, Germany	Highways	4.6	0.1	2.2	(Djingova et al., 2003)
Plantain ( <i>Plantago lanceolata</i> )	Saarbrücken, Germany	Highways	10.1	2.1	3.4	(Djingova et al., 2003)
Cocksfoot grass ( <i>Dactylis glomeratus</i> )	Oxfordshire, United Kingdom	Highways, 0m sampling	12.04	14.28	2.34	(Hooda et al., 2008)
Moss ( <i>Pleurozium schreberi</i> )	Oulu, Finland	Highways	27.4	n/a	4.6	(Niemelä et al., 2004)
Pine needles ( <i>Pinus pinea</i> L.)	Palermo, Italy	Urban zone	29	17	n/a	(Dongarrá et al., 2003)
Dandelion ( <i>Taraxacum officinale</i> )	Saarbrücken, Germany	Highways	30.0	3.1	7.0	(Djingova et al., 2003)

Table 3: Main characteristics of the analytical methods, found in or calculated from the cited articles, for the determination of the palladium platinum group elements (PPGE)

Sample	Pre-treatment			Instrument (introduction)	Other information	LOD in $\mu\text{g kg}^{-1}$ of sample (dry mass)			Repeatability as RSD in %			Trueness as recovery in %			Validation	References
	Matrix destruction (final amount)	Extraction (digest volume ; elution volume used)	Pre-concentration (enrichment factor)			Pt	Pd	Rh	Pt	Pd	Rh	Pt	Pd	Rh		
soil and road dust (0.2 g)	Digestion $\text{HNO}_3/\text{HCl}$ 1:3 (20 mL)	Dowex AG1-X8 anion exchange resin (20 ; 20)	-	Q-ICP-MS	Isotope Dilution; Desolvating nebulizer	0.15	0.075	-	28	25	-	98	76	-	CRM: WGB-1	Müller and Heumann, 2000
Road dust (3 g)	Digestion in Aqua regia (>40 mL)	Dowex 1-X10 anion-exchange resin (1; 42)	-	ICP-AES (2.5 mL/min continuous injection)	-	15	15	-	1.5	0.8	-	98.3	97.2	-	CRM: JSd-2	Kovacheva and Djingova, 2002
Soil (0.25 g)	Digestion in $\text{HNO}_3/\text{HCl}$ 1:3 (8 mL)	Dowex AG50W-X8 cation-exchange resin (-; 10)	-	Q-ICP-MS	In, Ir internal standards	0.1	0.5	0.1	9	6	12	100	98	102	CRM: BCR-723	Whiteley and Murray, 2003
Sediment (0.2g)	Digestion aqua regia (nd)	Dowex AG50W-X8 cation-exchange resin (2 ; 8)	-	Q-ICP-MS	Desolvating nebulizer	0,03	0,03	0,01	1,5	5,8	3,8	75	103	93	BCR-723	(Sutherland et al., 2007)
Sewage sludge (1.5 g)	Digestion in $\text{HNO}_3/\text{HClO}_4/\text{HF}$ 4 :2 :1 (10 mL)	YPA <sub>4</sub> chelating resin (100; -)	1 mL slurry prepared with the resin total mass (100)	ETV-ICP-AES (10 $\mu\text{L}$ injected)	-	0.145	0.40	-	3.7	5.6	-	101.4	99.1	-	CRM: NIST SRM 2557	Wu et al., 2004
Soil and sediment (5 g)	Ashing 650°C ; Digestion aqua regia (60 mL)	MIBK and $\text{NH}_4\text{SCN}$ as chelating agents (50 mL)	-	Q-ICP-MS	-	0,5	1	-	nd	nd	-	95	95	-		(Choudhury, 2016)
Soil (50 g)	Nickel sulfide fire assay (5)			GF-AAS	-	1.0	0.5	0.7	nd	nd	nd	90-95	90-95	90-95	nd	Zereini et al., 2007
Soil and airborne dust (50 g)	Nickel sulfide fire assay (5)			Q-ICP-MS	In internal standard; $\text{H}_2$ CRC	0.03	0.06	0.04	nd	nd	nd	> 90	> 90	> 90	Spiked samples	Wichmann et al., 2007
Soil (5g)	Nickel sulfide fire assay -			Q-ICP-MS	-	0.1	0.15	0.01	8	1	5	91	101	98	CRM: GBW07294	Pan et al. 2009
Soil (10 g)	Nickel sulfide fire assay -			Q-ICP-MS	In, Tl internal standards	0.65	0.45	0.08	2.8	2.5	14	95.5	98.9	93.5	CRM: WMG-1	Mihaljevič et al., 2013
Soil (10-15 g)	Nickel sulfide fire assay -			HR-ICP-MS	-	0.7	0.1	0.04	nd	nd	nd	nd	nd	nd	nd	Morcelli et al., 2005

Soil (-)	Ashing 600°C ; HNO <sub>3</sub> /HCl 1:3 (15 mL)	Based on co-precipitation with SnCl <sub>2</sub> / Hg (5; 4)	-	GF-AAS	-	0.5	0.2	-	1	2	-	99	99	-	CRM: SARM-7	Niskavaara et al., 2004
Road dust (0.2 g)	Digestion HNO <sub>3</sub> /HCl/HF 1:3:1 (25 mL)	Based on co-precipitation with SnCl <sub>2</sub> /Te (25;25)		Q-ICP-MS	Isotope Dilution	1	1	0.4	5	14	12	102	93	102	CRM: CW7 and CW8	(Gómez et al., 2003)
Soil and road dust (0.1 g)	Digestion in HNO <sub>3</sub> /HCl 6:2 (10 mL)	Based on co-precipitation with SnCl <sub>2</sub> / Te (Pt, Rh) or Hg (Pd), (3; 10)	-	Q-ICP-MS	Isotope dilution quantification	0.75	0.44	0.9	6	65	10	108	144	125	CRM: BCR-723	Wiseman et al., 2016
Soil (20g)	Digestion HNO <sub>3</sub> /HClO <sub>4</sub> 5:1 (12 mL)	CPE with BIMPI as chelating agent (28)		FAAS		-	25	-	-	3	-	-	98	-	Spike samples	(Tavallali et al., 2010)
Soil and road dust (0.4 g)	Digestion in HNO <sub>3</sub> /HCl/HF 1:3:1 (5mL)	CPE with TOMAC and Triton X-114 (20)		GF-AAS		0.5	-	-	2%	-	-	99	-	-	BCR-723	(Meeravali et al., 2014)
Soil (5 g)	Digestion in HNO <sub>3</sub> /HCl 1:3 (15mL)	DLLME with MBI as chelating agent (20)		FAAS		-	8	-	-	4%	-	-	99%	-	GPP-10	(Pouyan et al., 2016)
Road dust (2 g)	Digestion HNO <sub>3</sub> / HCl 1:3 (40 mL)	Magnetic graphene oxide nanosheet modified with polypyrrole-polythiophene copolymer (112)		FAAS		10	20	-	2	5	-	98	101	-	Spiked samples	(Jalilian et al., 2017)
Soil (1g)	Digestion aqua regia / HF (22 mL)	DLLME with Na-DDTC as chelating agent assisted with ultrasonic (156)		FAAS		-	24	-	-	9	-	-	96	-	Spiked samples	(Heydari and Ramezani, 2017)
Road dust (0.1 g)	Digestion in HNO <sub>3</sub> /HCl/HF1:3:1 (5 mL)	-	-	HR-ICP-MS	High resolution; Desolvating nebulizer	0.4	0.5	0.1	6	13	9	100	114	87	CRM: WPR-1	Köllensperger et al., 2000
Road dust and sediment (0.25 g)	Digestion in HNO <sub>3</sub> /HCl 1:3 (8 mL)	-	-	HR-ICP-MS	Low resolution	0.008	0.2	0.004	nd	nd	nd	nd	nd	nd	nd	Rauch et al., 2000
Road dust and sediment (0.25 g)	Digestion in HNO <sub>3</sub> /HCl 1:3 (8 mL)	-	-	HR-ICP-MS	High Resolution	0.15	0.3	0.02	nd	nd	nd	nd	nd	nd	nd	Rauch et al., 2000
Soil (0.5 g)	Digestion in HNO <sub>3</sub> /HCl 1:3 (10 mL)	-	-	DPV	Digest analysed in diluted H <sub>2</sub> SO <sub>4</sub> solution	0.3	-	-	< 5	-	-	nd	-	-	Standard solutions	Orecchio and Amorello, 2011

Soil and road dust (6.25 g)	3-step sequential leaching-based extraction (- ; 100, 100 and 70 mL)	ICP-MS	He CRC	0.03	0.03	0.01	1.12	1.58	1.37	na	na	na	Standard solutions	van der Horst et al., 2018
		DPAdSV	-	0.0006	0.0007	0.0020	1.18	1.44	0.93	na	na	na	Standard solutions	van der Horst et al., 2018

Abbreviations: ETV: electrothermal vaporization; DPV : differential pulse voltammetry ; DPAdSV : differential pulse adsorptive stripping voltammetry; CRC : Collision/Reaction Cell  
nd : not indicated in the publication ; na : not applicable  
Others: see the text

Table 4: Selected wavelength of Pt, Pd and Rh for ICP-AES determination (most sensitive) and their possible interferences reported in literature (Kovacheva and Djingova, 2002; Ojeda and Rojas, 2007; Petrova et al., 2010).

Element	Wavelength (nm)	Interference and wavelength (nm)	
Pt	214.42	Ir	214.42
		Cd	214.43
		Fe	214.44
		Al	214.54
		Ni	214.78
Pt	265.95	Mn	265.92
		Fe	265.92
		Ni	265.95
Pd	340.46	Fe	340.44
		V	340.44
		Zr	340.48
		Ti	340.50
		W	340.53
Pd	363.47	Th	363.42
		Fe	363.43
		Ce	363.43
Rh	233.48	Al	233.42
		Fe	233.48
Rh	343.49	V	343.54
		Al	343.94

Table 5: PPGE isotope abundances and possible interferences in ICP-MS (Köllensperger et al., 2000, Rauch et al. 2000). Isotopes with low abundance are not shown (<5%).

Isotope	Abundance (%)	Interfering ions	Required resolution m/ $\Delta$ m
<sup>194</sup> Pt	32.90	<sup>178</sup> Hf <sup>16</sup> O	8063
		<sup>176</sup> Hf <sup>18</sup> O	8775
		<sup>177</sup> Hf <sup>17</sup> O	9544
		<sup>176</sup> Yb <sup>18</sup> O	9261
		<sup>176</sup> Lu <sup>18</sup> O	9310
<sup>195</sup> Pt	33.80	<sup>179</sup> Hf <sup>16</sup> O	8108
		<sup>177</sup> Hf <sup>18</sup> O	8702
		<sup>178</sup> Hf <sup>17</sup> O	8881
<sup>196</sup> Pt	25.80	<b><sup>196</sup>Hg</b>	226550
		<sup>180</sup> Hf <sup>16</sup> O	8348
<sup>198</sup> Pt	7.20	<b><sup>198</sup>Hg</b>	176914
		<sup>182</sup> W <sup>16</sup> O	8001
<sup>104</sup> Pd	11.14	<b><sup>208</sup>Pb<sup>2+</sup></b>	1234
		<sup>63</sup> Zn <sup>40</sup> Ar	8313
		<sup>88</sup> Sr <sup>16</sup> O	29805
		<sup>104</sup> Ru	74431
<sup>105</sup> Pd	22.33	<sup>65</sup> Cu <sup>40</sup> Ar	7042
		<sup>89</sup> Y <sup>16</sup> O	24373
		<sup>88</sup> Sr <sup>17</sup> O	328855
		<sup>87</sup> Sr <sup>18</sup> O	35263
		<sup>87</sup> Rb <sup>18</sup> O	32102
		<sup>88</sup> Sr <sup>16</sup> O <sup>1</sup> H	31984
		<sup>68</sup> Zn <sup>37</sup> Cl	7319
		<sup>70</sup> Zn <sup>35</sup> Cl	9615
<sup>106</sup> Pd	27.33	<b><sup>106</sup>Cd</b>	35468
		<sup>66</sup> Zn <sup>40</sup> Ar	7033
		<sup>90</sup> Zr <sup>16</sup> O	27492
<sup>108</sup> Pd	26.46	<b><sup>108</sup>Cd</b>	369535
		<sup>68</sup> Zn <sup>40</sup> Ar	6474
		<sup>92</sup> Zr <sup>16</sup> O	27386
		<sup>92</sup> Mo <sup>16</sup> O	49724
<sup>110</sup> Pd	11.72	<b><sup>110</sup>Cd</b>	50834
		<sup>70</sup> Ge <sup>40</sup> Ar	5927
		<sup>94</sup> Mo <sup>16</sup> O	21265

		$^{94}\text{Zr}^{16}\text{O}$	27929
$^{103}\text{Rh}$	100.00	$^{206}\text{Pb}^{2+}$	1260
		$^{86}\text{Sr}^{17}\text{O}$	60603
		$^{63}\text{Cu}^{40}\text{Ar}$	7609
		$^{87}\text{Rb}^{16}\text{O}$	73241
		$^{66}\text{Zn}^{35}\text{Cl}$	7587
		$^{68}\text{Zn}^{35}\text{Cl}$	8719

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