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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 μg (PGE)
31 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_x) respectively by oxidizing CO and HC to
95 carbon dioxide (CO₂) and reducing NO_x to nitrogen (N₂).

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⁻³
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⁻¹ 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⁻¹ to 3500 ng L⁻¹ (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⁻¹ in
130 sewage sludge, and 602 and 710 µg kg⁻¹ 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⁻¹; 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 km²
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, PM₁₀ 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.

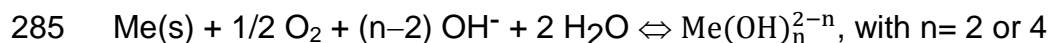
271 2.3.1. *PPGE soluble forms*

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:



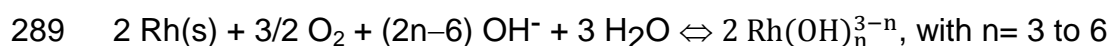
284 or



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 Pt(OH)^+ at $\text{pH} < 9$

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

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

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

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

300 < 12 , Pd^{2+} under oxidizing and acidic conditions, and Pd(OH)_3^- and 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: Rh^{3+} ($\text{pH} < 4$), Rh(OH)^{+2}

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

305 Rh(OH)_5^{-2} ($7 < \text{pH} < 13$), and 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 SO_4^{2-} , NO_3^- , Cl^- , 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 OH^- , NH_3 and 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 PtCl_6^{2-} and PtCl_4^{2-} are re-complexed
329 into insoluble species when mixed with humic soil while insoluble 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, SiO₂ 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 (EC₅₀) for Pt was determined for its effect on reproduction,
443 fertility and growth (96h EC₅₀ = 497 µg L⁻¹ (exposure medium); 726 µg L⁻¹ and 808 µg L⁻¹
444 respectively). The 96h EC₅₀ for Pd ranged between 10 and 100 µg L⁻¹ for its effect on
445 reproduction, while no significant trend was found for its effect on fertility and growth. No
446 EC₅₀ 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⁻¹ (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 EC₅₀. 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⁻¹
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 HNO₃ 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 YPA₄
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 YPA₄ 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 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}Pt , ^{195}Pt , ^{196}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}Pd is the most abundant Pd isotope but ^{105}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 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, O_2 or 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). O₂ 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 HfO₃ in presence of O₂, which enables the problem of mass superposition for Pt
662 to be solved; Likewise, the ZrO interference on ¹⁰⁶Pd can be removed using O₂ (Simpson
663 et al., 2001). NH₃ is also a reaction gas based on the transfer of electron from the
664 interfering species to NH₃ molecules. Used alone or diluted in He, it was found to be very
665 effective in minimizing ⁸⁹Y¹⁶O interference on ¹⁰⁵Pd (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 NH₃ 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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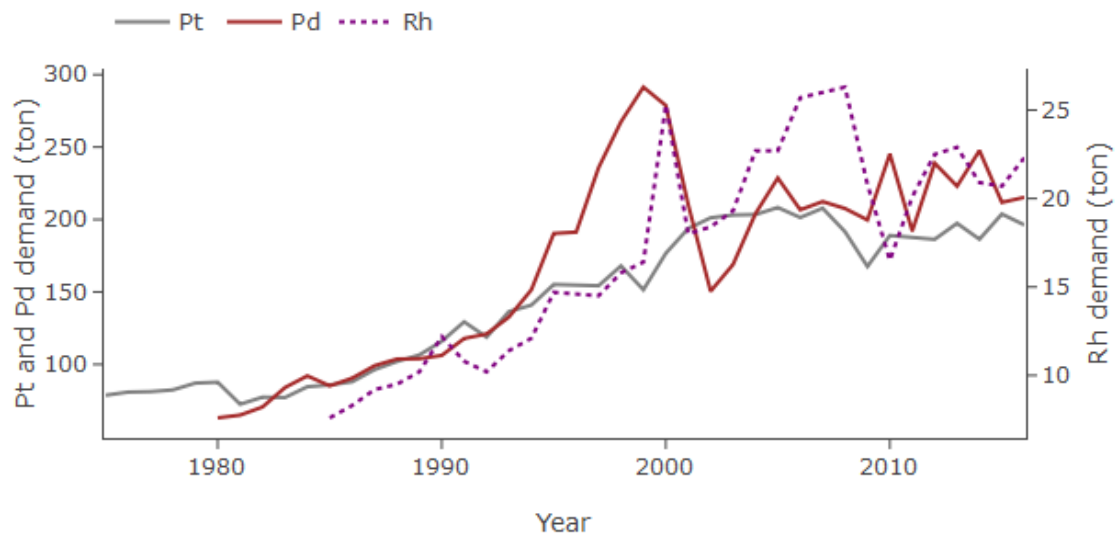


Figure 1: Evolution of the demand of Pt, Pd and Rh since 1976 (Johnson Matthey, 2017b).

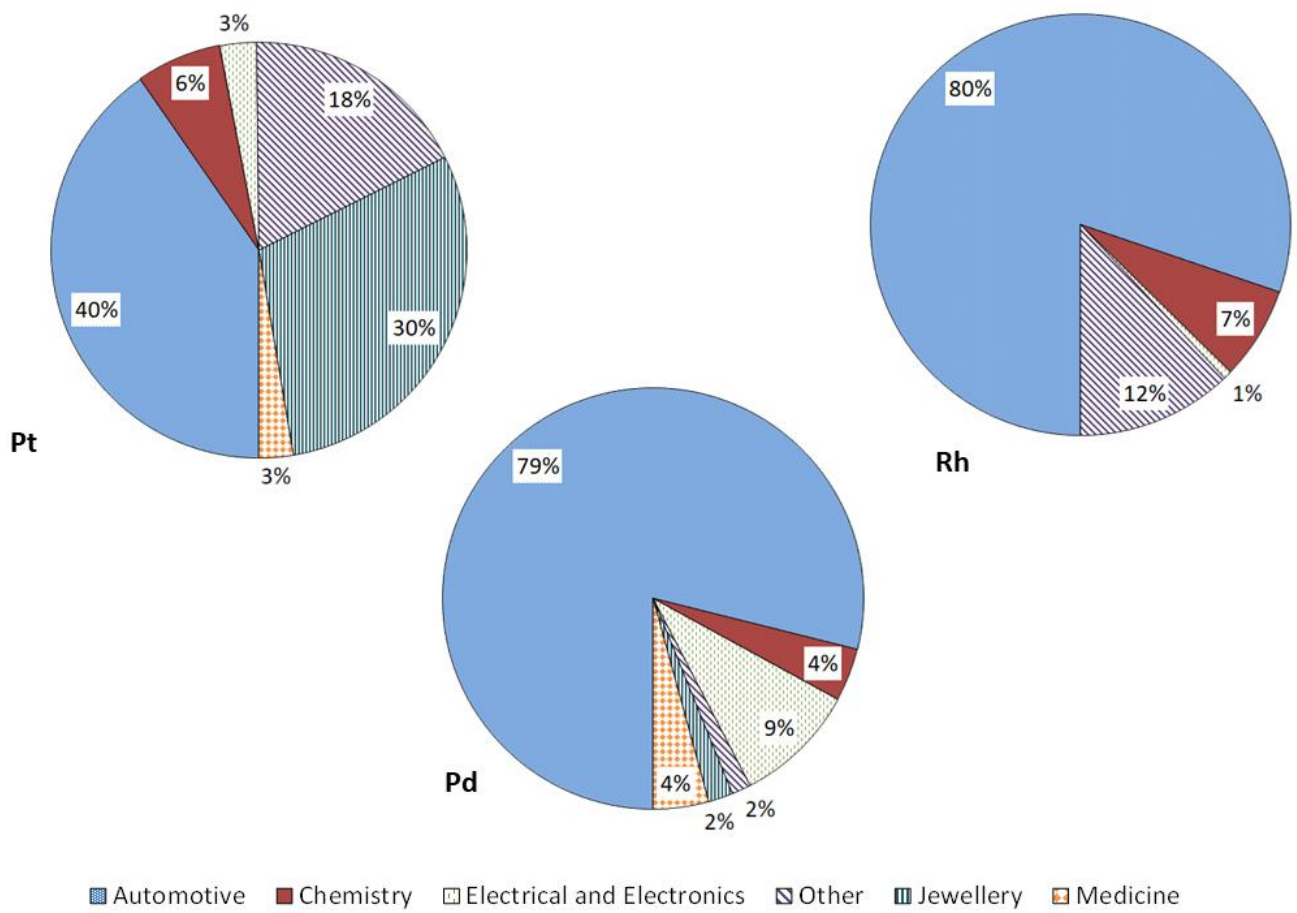


Figure 2: Pt, Pd and Rh demand (in percentage) by type of activities in 2016 (Johnson Matthey, 2017a).

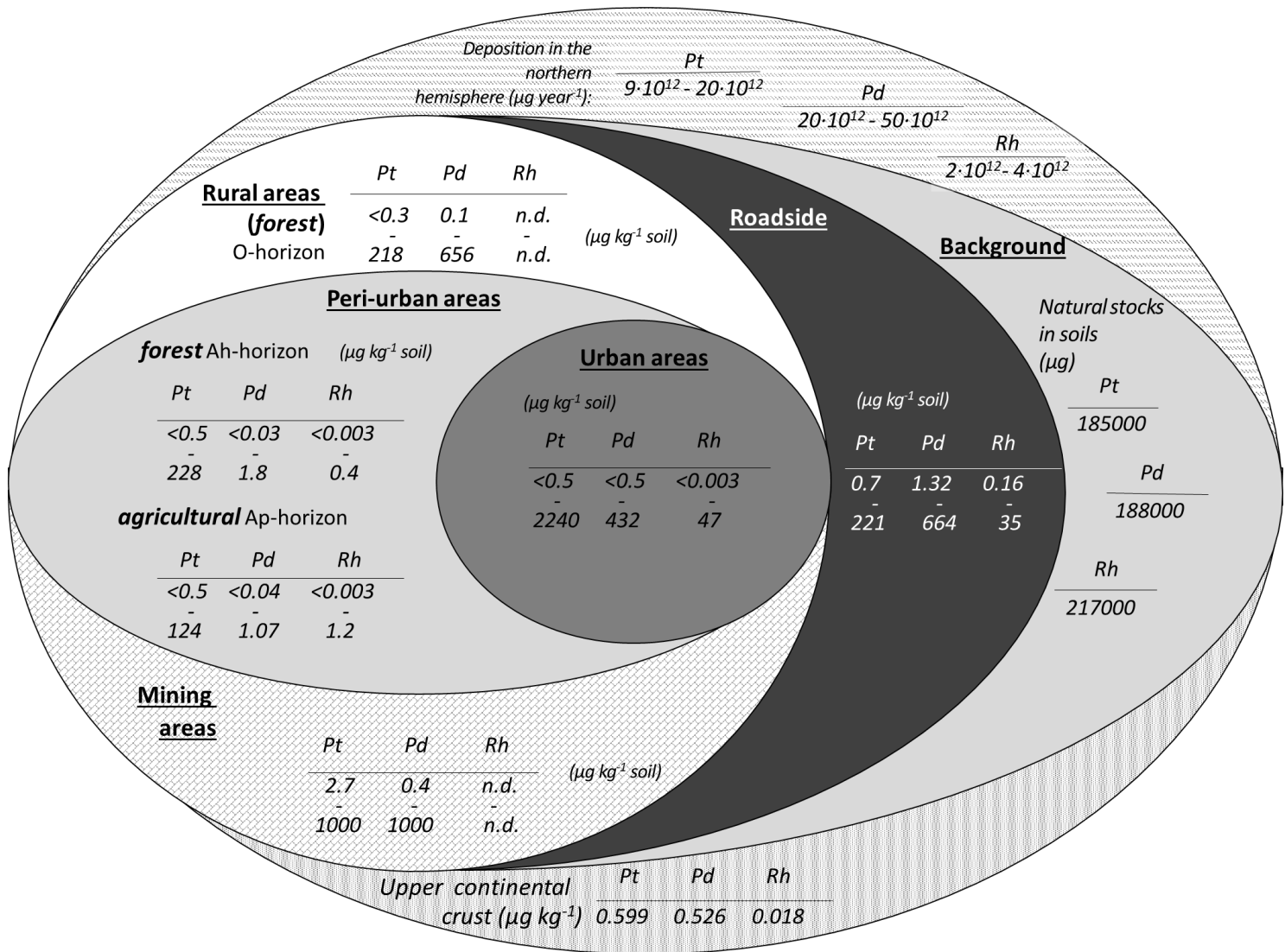


Figure 3: Ranges of concentrations and masses of PPGE in various environmental parts. Compiled values from : Birke et al., 2018; Cicchella et al., 2008, 2003; Ely et al., 2001; Fletcher, 1988; Hooda et al., 2007; Lee et al., 2012; Mitra and Sen, 2017; Niskavaara et al., 2004; Pan et al., 2009; Park et 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)
"Background" values ($\mu\text{g/kg}$)						
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 ₂ 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 HNO_3/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 HNO_3/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 ₄ chelating resin (100; -)	1 mL slurry prepared with the resin total mass (100)	ETV-ICP-AES (10 μL 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 NH_4SCN 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; 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 ₃ /HCl 1:3 (15 mL)	Based on co-precipitation with SnCl ₂ / 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 ₃ /HCl/HF 1:3:1 (25 mL)	Based on co-precipitation with SnCl ₂ /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 ₃ /HCl 6:2 (10 mL)	Based on co-precipitation with SnCl ₂ / 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 ₃ /HClO ₄ 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 ₃ /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 ₃ /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 ₃ / 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 ₃ /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 ₃ /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 ₃ /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 ₃ /HCl 1:3 (10 mL)	-	-	DPV	Digest analysed in diluted H ₂ SO ₄ 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/ Δ m
¹⁹⁴ Pt	32.90	¹⁷⁸ Hf ¹⁶ O	8063
		¹⁷⁶ Hf ¹⁸ O	8775
		¹⁷⁷ Hf ¹⁷ O	9544
		¹⁷⁶ Yb ¹⁸ O	9261
		¹⁷⁶ Lu ¹⁸ O	9310
¹⁹⁵ Pt	33.80	¹⁷⁹ Hf ¹⁶ O	8108
		¹⁷⁷ Hf ¹⁸ O	8702
		¹⁷⁸ Hf ¹⁷ O	8881
¹⁹⁶ Pt	25.80	¹⁹⁶Hg	226550
		¹⁸⁰ Hf ¹⁶ O	8348
¹⁹⁸ Pt	7.20	¹⁹⁸Hg	176914
		¹⁸² W ¹⁶ O	8001
¹⁰⁴ Pd	11.14	²⁰⁸Pb²⁺	1234
		⁶³ Zn ⁴⁰ Ar	8313
		⁸⁸ Sr ¹⁶ O	29805
		¹⁰⁴ Ru	74431
¹⁰⁵ Pd	22.33	⁶⁵ Cu ⁴⁰ Ar	7042
		⁸⁹ Y ¹⁶ O	24373
		⁸⁸ Sr ¹⁷ O	328855
		⁸⁷ Sr ¹⁸ O	35263
		⁸⁷ Rb ¹⁸ O	32102
		⁸⁸ Sr ¹⁶ O ¹ H	31984
		⁶⁸ Zn ³⁷ Cl	7319
		⁷⁰ Zn ³⁵ Cl	9615
¹⁰⁶ Pd	27.33	¹⁰⁶Cd	35468
		⁶⁶ Zn ⁴⁰ Ar	7033
		⁹⁰ Zr ¹⁶ O	27492
¹⁰⁸ Pd	26.46	¹⁰⁸Cd	369535
		⁶⁸ Zn ⁴⁰ Ar	6474
		⁹² Zr ¹⁶ O	27386
		⁹² Mo ¹⁶ O	49724
¹¹⁰ Pd	11.72	¹¹⁰Cd	50834
		⁷⁰ Ge ⁴⁰ Ar	5927
		⁹⁴ Mo ¹⁶ O	21265

		$^{94}\text{Zr}^{16}\text{O}$	27929
^{103}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
