

1 **Platinum group elements in stream sediments of mining zones: the Hex River (Bushveld Igneous**
2 **Complex, South Africa)**

3

4 **Clara Almécija^{1-2,*} Antonio Cobelo-García¹, Victor Wepener³ and Ricardo Prego¹**

5

6 ¹Grupo Biogeoquímica Mariña, Instituto de Investigacións Mariñas-CSIC, Eduardo Cabello 6, 36208-
7 Vigo, Spain

8 ²Unidad de Tecnología Marina, Fundación CETMAR, Vigo, Spain

9 ³Water Research Group, Unit for Environmental Sciences and Management, North-West University,
10 Potchefstroom, South Africa

11

12

13 ***Corresponding author:** e-mail: calmecija@cetmar.org

14

15

16 **Abstract**

17 Assessment of the environmental impact of platinum group elements (PGE) and other trace elements
18 from mining activities is essential to prevent potential environmental risks. This study evaluates the
19 concentrations of PGE in stream sediments of the Hex River, which drains the mining area of the
20 Bushveld Igneous Complex (South Africa), at four sampling points. Major, minor and trace elements (Fe,
21 Ca, Al, Mg, Mn, V, Cr, Zn, Cu, As, Co, Ni, Cd, and Pb) were analyzed by FAAS and ETAAS in
22 suspended particulate matter and different sediment fractions (<63, 63-500 and 500-2000 μm), and Pt, Pd,
23 Rh, and Ir were measured by ICP-MS after removal of interfering elements (cation exchange resin 50W-
24 DOWEX-X8). Procedures were blank-corrected and accuracy checked using reference materials. Nickel,
25 Cr, Pt, Pd, Rh and Ir show concentrations 3-, 13- 18-, 28-, 48- and 44- fold the typical upper continental
26 crust levels, respectively, although lower than concentrations reported for the parent rocks. The highest
27 concentrations were observed closer to the mining area, decreasing with distance and in the <63 μm
28 fraction, probably derived from atmospheric deposition and surface runoff of PGE-rich particles released
29 from mining activities.

30 Thus, mining activities are causing some disturbance of the surface PGE geochemical cycle, increasing
31 the presence of PGE in the fine fraction of river sediments. We propose that indicators such as airborne
32 particulate matter, and soil and river sediment quality, should be added to the protocols for evaluating the
33 sustainability of mining activities.

34

35 *Key words:* Platinum Group Elements, Bushveld Complex, stream sediments, mining environmental
36 impact.

37

38

39

40 **1 Introduction**

41 Platinum group elements (Ru, Rh, Pd, Os, Ir, and Pt; PGE) are highly siderophile elements and, as such,
42 the bulk of Earth's PGE budget is thought to reside in the core, estimated to be more than 99.8% (Lorand
43 et al., 2008), as evidenced by the relative depletion of PGE in Earth's upper mantle relative to chondrite
44 meteorites. This siderophile character explains the ultra-trace concentrations of PGE in the Earth's crust,
45 being amongst the rarest elements in the environment with average crustal concentrations ranging
46 between 0.02 ng g^{-1} (Ir) and $0.5 \text{ (Pt, Pd) ng g}^{-1}$ (Rudnick and Gao, 2003). Typical Pt and Pd
47 concentrations in mantle rocks are around $1\text{--}100 \text{ ng g}^{-1}$ as compared with $10^6\text{--}10^7 \text{ ng g}^{-1}$ in chondrites,
48 iron meteorites and, presumably, the Earth's core (Lorand et al., 2008).

49 The development of mantle partial melts and their intrusion into the crust, followed by particular
50 mechanisms -related to the cooling and fractional crystallization of a Ni-Cu sulphide liquid resulting in a
51 residual sulphide liquid highly enriched in Cu, Pt, and Pd forming PGE rich layers, (Naldrett et al., 2008)-
52 leads to the formation of economically viable PGE-rich deposits. An example of this is the Bushveld
53 Igneous Complex (South Africa; Fig. 1), a vast layered igneous complex settled within late Archean and
54 early Proterozoic rocks (Cole et al., 2013). Bushveld complex is divided in five zones depending on their
55 composition and stratigraphy, being the Critical Zone the most relevant regarding to the PGE contents, in
56 particular the Merensky Reef and Upper Group 2 layers which are the PGE-richest bodies ever described
57 (Eales and Cawthorn, 1996). About 75%, 52%, and 82% of the world resources of Pt, Pd, and Rh -
58 respectively- are estimated to be contained in the Bushveld Igneous Complex; its reserves are large
59 enough to meet the world demand for decades (Cawthorn, 2010).

60 Several studies have been focused on the geochemistry and mineralogy of river sediments and soils of the
61 Bushveld Complex mining area to trace PGE-rich layers or to gain an understanding of PGE weathering
62 processes and sedimentological characteristics (Cawthorn, 2001; Oberthür et al., 2004; Wilhelm et al.,
63 1997). From an environmental perspective, Gzik et al. (2003) studied soils contaminated by trace
64 elements associated with the Bushveld Complex mining activities and how contamination affects the
65 biological communities, whereas Kaonga and Kgabi (2011) investigated the source of atmospheric
66 particulate matter in the Marikana mining area and concluded that the mining activities are the source of
67 metals in airborne particles in this area . Recently, Rauch and Fatoki (2013) studied the occurrence of
68 platinum in soils and vegetation (grass) in the vicinity of mines in the Bushveld Complex; although

69 elevated concentrations in this area may be the result of natural sources, they found evidence of
70 anthropogenic platinum enrichment linked to platinum mining activities due to atmospheric transport of
71 PGE-rich particles from smelters. Also, Rauch and Fatoki (2013) concluded that atmospheric deposition
72 is the main source of platinum in grass, while uptake of bioavailable Pt in soils has a minor impact on
73 platinum levels in grass.

74 In order to provide additional information, the objective of this study is to assess the impact of mining
75 activities in the Bushveld Igneous Complex on the surrounding environmental compartments. To this
76 aim, a suite of platinum group elements (Rh, Pd, Ir, and Pt) and a range of other major, minor and trace
77 elements (Cu, Zn, Cr, V, Pb, Cd, Ni, Co, and As) were analyzed in the stream sediments of a river (Hex
78 River) draining the Bushveld Complex mining area. The results are discussed in terms of the
79 anthropogenic impact caused by mining activities on the environmental PGE concentrations in this area.

80

81 **2 Materials and methods**

82 **2.1 Sampling**

83 The Hex River flows in a northerly direction crossing the city of Rustenburg, the capital of the most
84 populated municipality in the North West Province of South Africa, where almost 550,000 people live
85 and where the main industrial activity is mining (Census 2011, Statistics South Africa). The Hex River
86 drains one of the most important mining areas in the western limb of the Bushveld Igneous Complex (Fig.
87 1) where the PGE-rich Merensky Reef and the UG-2 chromitite layer are mined. Water and surface
88 sediment were sampled at four points (A: upstream; B: urban; C: intermediate; and D: downstream) along
89 the Hex River (Fig. 1) during high-flow conditions in March 2006. Water samples were collected using a
90 telescopic pole with a bottle holder in acid-cleaned 1 L high-density polyethylene bottles that were
91 subsequently kept in zip-lock bags and placed in a cooler box for transportation. For sediments, in order
92 to ensure representivity of the samples, composite samples were obtained at each sampling point by
93 mixing equal volumes of discrete grab samples of surface sediments (15-20 grab samples, ~ 5 Kg of
94 sample) collected in an area of 15 m² covering both river banks. The surface sediments were collected
95 using a plastic spatula and stored in zip-lock plastic bags. Samples were collected at least 10 m away from
96 roads to avoid including the impact of PGE emissions from automobile exhaust catalysts (e.g. catalytic
97 converters) on PGE concentrations (Schäfer et al., 1999).

98 Physicochemical variables, i.e. temperature, pH, conductivity and dissolved oxygen (DO) were measured
99 in situ using a calibrated WTW 340i sensor package (Nova Analytics). In the laboratory at the University
100 of Johannesburg, 100 mL aliquots of water samples were vacuum-filtered using an acid-cleaned Nalgene-
101 type filtration unit fitted with acid-cleaned and pre-weighed 0.45 μm pore size polycarbonate filters (Pall
102 Corporation). Filters with the retained suspended particulate matter (SPM) were stored frozen in plastic
103 Petri dishes pending their analysis for major and trace elements. For the analysis of dissolved organic
104 carbon (DOC), separate 100 mL aliquots of water samples were vacuum-filtered through pre-combusted
105 GF/F filters (Whatman) in a Millipore glass filtration unit. Filters were stored frozen in Petri dishes, and
106 filtrates were collected in pre-combusted glass vials, acidified with HCl (analytical reagent grade, Merck)
107 to pH 2, and frozen until analysis.

108 Sediments were dried ($<60\text{ }^{\circ}\text{C}$), sieved into three size fractions following the Wentworth Grain Size Class
109 (Wentworth, 1922): i.e. silt and clay ($<63\text{ }\mu\text{m}$), fine-medium sand ($63\text{-}500\text{ }\mu\text{m}$) and coarse sand (500-
110 $2000\text{ }\mu\text{m}$). After sieving, sediment samples were ground using an agate mortar and pestle, in order to
111 homogenize the sample.

112

113 **2.2 Analysis of dissolved and particulate organic carbon, and major and trace elements**

114 Dissolved organic carbon (DOC) was measured in the thawed samples by high-temperature catalytic
115 oxidation using a total organic carbon analyzer (Shimadzu Carbon-5000), and air-dried GF/F filters were
116 analyzed for total carbon and nitrogen using a CHN analyzer (Carlo Erba EA1110). Major and trace
117 elements (Fe, Ca, Al, Mg, Mn, V, Cr, Zn, Cu, As, Co, Ni, Cd, and Pb) in suspended particulate matter and
118 sediments were determined after microwave-assisted digestion in Teflon® bombs (MarsXpress, CEM)
119 using a 3:1 mixture of HNO_3 (Hiperpur© 69% Panreac) and HF (Suprapur© 40% Merck); the selected
120 program is specially suitable for sediments (heating: 20 min, digestion: 8 min, temperature: $180 \pm 5\text{ }^{\circ}\text{C}$;
121 EPA3052). Analysis of major elements in the digests was conducted by means of flame atomic absorption
122 spectrophotometry (Varian SpectrAA 220FS), whereas trace elements were determined using
123 electrothermal atomic absorption spectrophotometry (Varian SpectrAA 220). One blank was run every
124 ten samples and results were therefore blank-corrected. The accuracy of the analytical methodology was
125 checked using PACS-2 marine sediment reference material (NRC, Canada) and LGC6137 (LGC
126 Standards) sediment reference material (which includes certified concentrations for all the elements
127 analyzed); and results obtained were within the certified concentrations (Table 1).

128

129 2.3 Analysis of platinum group elements in sediments

130 A Thermo X series II ICP-MS, using external calibration, was used for the determination of the
131 concentrations of platinum (Pt), palladium (Pd), rhodium (Rh) and iridium (Ir). A modified version of the
132 procedure given by Sutherland et al. (2007) was employed for sample digestion and removal of isobaric
133 and polyatomic interferences (Fig. 2); accordingly, about 100 mg of sediment was ashed in quartz
134 crucibles for 5 hours at 450 C in order to remove organic matter. The optimization of the ashing step
135 (Table S1, Electronic Supplementary Material) was achieved using two certified reference materials: river
136 sediment JSd-2 (Geological Survey of Japan) and road dust BCR-723 (European Institute of Reference
137 Materials and Measurements). Ashed sediment samples were digested in *aqua regia* (HNO₃ 65% and HCl
138 30%, Suprapur[®] Merck) for 4 hours at 195 °C and then allowed to cool down; then, digest were syringe-
139 filtered through 0.45 µm SuporTM hydrophilic polyethersulfone membranes (Pall[®]). The filtered digest
140 was then evaporated until near dryness and re-dissolved using 2 mL of 0.5 M HCl, and then passed
141 through a 2 cm³ (0.4 cm diameter x 16 cm length) Teflon[®] column containing a cation exchange resin
142 (50W-DOWEX-X8, hydrogen form, 100-200 mesh), that was previously acid-cleaned and conditioned
143 with 10 mL of HCl 6 M and 10 mL of HCl 0.5 M. Samples were stored in Teflon[®] vials pending
144 analysis. The presence of potential polyatomic and isobaric interferences was checked during analysis.
145 Results for the reference materials (JSd-2: river sediment and BCR-723, road dust, Table S1, Electronic
146 Supplementary Material) indicated a good recovery (>80%) except for Pd in BCR-723 where a recovery
147 of 59% was obtained. However, previous studies (Meisel et al., 2003; Sutherland, 2007) concluded that
148 the Pd certified value in BCR-723 was overestimated, proposing an average of 4-4.5 ng g⁻¹, which would
149 lead to a Pd recovery greater than 80% in our study.

150

151 3 Results and discussion

152 3.1 Ancillary parameters

153 The pH (7.30-7.39), SPM (28.6-31.9 mg L⁻¹), temperature (19.8-23.0 °C) and DO (8.65-8.98 mg L⁻¹, 98-
154 106 % of saturation) values obtained at sampling points A, B, and C indicated similar conditions and were
155 in the range of other rivers draining the Bushveld Complex (Seanego and Moyo, 2013) (Table 2).
156 However, the presence of a dam upstream of sampling point D reduced flow capacity and competence,
157 producing a decrease in SPM levels of 80% and a slight increase in pH as a result of biological activity.

158 As the Hex River flows through Rustenburg, the amount of organic material in water due to urban and
159 domestic inputs, here measured as DOC, POC, and PON, increased from sampling points A to B.
160 Dissolved oxygen concentrations, saturated at all stations, showed that the system still had self-
161 purification capacity (Seanego and Moyo, 2013).

162

163 **3.2 Grain-size characterization**

164 Attending to the grain-size, the Hex River samples are divided in two groups: sample A and D where sand
165 size (63-500 μm) predominates, and samples B and C where the % of sand and coarse sand (500-2000
166 μm) is similar. For all the samples, the silt and clay (<63 μm) represented the smallest fraction, especially
167 in sample point D. Data are represented in triangles of abundance in Figs. 3 and 4.

168

169 **3.3 Major and trace elements**

170 Remarkable elevated concentrations of Ni and Cr were observed in all sampling points and fractions,
171 compared with other trace elements (Figs. 3 and 4; Table 1). The concentrations of Ni and Cr were found
172 to be 3-fold and 13-fold higher, respectively, than typical upper continental crust values. These values are
173 in agreement with the concentrations of several trace elements in the Bushveld Complex rocks near
174 Rustenburg (known as Rustenburg Layered Suite), i.e. 22-fold for Cr and Ni, 12-fold for Cu and 5-fold
175 for Co (Barnes and Maier, 2002).

176 In general, higher concentrations of several trace elements (Cu, Ni, Co, Cr) both in sediments and SPM
177 were observed at sampling point A compared to the other stations (except for Cr in the sand fraction of
178 sample point D that showed a high Cr concentration). This may be explained by its location just
179 downstream of the Merensky Reef (Fig. 1), and therefore containing a significant fraction of eroded
180 metal-rich particles. Lower trace metal concentrations were recorded in the SPM fraction than in the
181 sediments at all the sampling stations, due to a higher proportion of non-detrital material (e.g. organic
182 matter) as observed by the lower concentrations of Al and Fe in the SPM fraction (Figs. 3 and 4).

183 In agreement with these elevated concentrations of trace elements (especially for Cr and Ni) found in
184 sediments and SPM of the Hex River, Gzik et al. (2003) also observed Cr and Ni enrichment in
185 agricultural and grassland soils in this area (on a farm 10 km east of Rustenburg); however, these high
186 concentrations did not have an inhibitory influence on micro-organisms or the enzyme activity of soils,
187 and no obvious influence on the health of animals was observed (Gzik et al., 2003).

188

189 **3.4 PGE concentrations**

190 Sediment samples from the Hex River showed a weighted average PGE concentration of $14 \pm 10 \text{ ng g}^{-1}$,
191 being the individual concentrations of $4.8 \pm 2.9 \text{ ng g}^{-1}$ for Pt, $7.3 \pm 6.2 \text{ ng g}^{-1}$ for Pd, $1.4 \pm 0.7 \text{ ng g}^{-1}$ for
192 Rh, and $0.54 \pm 0.13 \text{ ng g}^{-1}$ for Ir (Table 3, Figs. 3 and 4). A heterogeneous presence of rich-PGE particles
193 may explain the wide dispersion of PGE values in different replicates, the so-called “nugget effect”. In
194 terms of the spatial distribution of the respective platinum group elements, sampling point A showed, in
195 general, the highest weighted average for each element (9.0 ± 0.6 , 15.7 ± 1.1 , 2.4 ± 0.0 and $0.68 \pm 0.01 \text{ ng}$
196 g^{-1} for Pt, Pd, Rh and Ir, respectively) followed by sampling point B ~ C ~ D (Table 3). Concentrations of
197 PGE in the silt and clay fraction at each sampling point (A: 55.2 ± 5.7 , B: 98.1 ± 35.7 , C: 47.1 and D:
198 $42.0 \pm 2.9 \text{ ng g}^{-1}$, Table 3) were always higher than the average values ($14 \pm 10 \text{ ng g}^{-1}$). These values
199 indicate a PGE enrichment with respect to the upper continental crust of 10, 15, 23 and 29 times for Pt,
200 Pd, Rh and Ir, respectively (Peucker-Ehrenbrink and Jahn, 2001; Wedepohl, 1995), corresponding mainly
201 to natural levels in the parent rock in the study area (the Bushveld Igneous Complex), but are lower than
202 the concentrations reported by Barnes and Maier (2002) for a drill-core sample of the rocks near
203 Rustenburg, without considering the PGE ore layers (Table 3).

204 PGE-rich layers in the Bushveld Igneous Complex are associated with chromitite rocks enriched in Cr
205 and Cu-Ni (Barnes and Maier (2002). In fact, PGE extraction and purification includes Ni by-products in
206 many cases (Glaister and Mudd, 2010). Previous studies have reported typical Cr-PGE correlation
207 coefficients ranging between 0.829 (for Cr-Pt) and 0.946 (for Cr-Ir), controlled by their similar affinity
208 and the formation of Cr-spinels (Barnes and Maier, 2002; Lee, 1983). However, the Cr-Pd correlation
209 coefficient is only 0.224, showing different affinity since Pd geochemistry and accumulation is controlled
210 by sulphide phases (Barnes and Maier, 2002; Lee, 1983). This typical low correlation between Pd and Cr
211 is also observed in this study: sample D shows, for Pd and Cr, the lowest and the highest concentrations,
212 respectively. The PGE/Cr ratios reported in this study are consistent with those reported for other stream
213 sediments (Wilhelm et al., 1997) and drill cores of the parent rock (Barnes and Maier, 2002) in the area
214 (Fig. 5). The highest PGE concentrations (Pt 35 ng g^{-1}) in river sediments reported in the Wilhelm et al.
215 (1997) study are in line with elevated concentrations of Cu ($77 \text{ } \mu\text{g g}^{-1}$), Ni ($150 \text{ } \mu\text{g g}^{-1}$) and, especially, Cr
216 ($1\ 600 \text{ } \mu\text{g g}^{-1}$), but also of V ($134 \text{ } \mu\text{g g}^{-1}$) and Co ($54 \text{ } \mu\text{g g}^{-1}$). The recent study of Rauch and Fatoki (2013)

217 also reported elevated values of Pt (12-698 ng g⁻¹), Cu (22-136 µg g⁻¹) and Cr (43-340 µg g⁻¹) in soils
218 affected by the mining activities in the Bushveld Complex.

219

220 **3.5 Impact of mining activities on PGE concentrations**

221 As explained in the previous section, the soils and sediments of the Bushveld Complex are naturally
222 enriched in PGE and other elements (e.g. Cr, Ni) due to mafic-ultramafic intrusion which contains the
223 world's largest resources of Pt, Pd, and Rh (Cawthorn, 2010). The intensive mining and associated
224 activities (e.g. processing plants, smelters) in the Bushveld Complex may lead to an anthropogenic
225 increase in PGE concentrations over the –already– elevated background levels. Rauch and Fatoki (2013)
226 demonstrated such anthropogenic enrichment for Pt in soils from the Bushveld Complex; accordingly,
227 they found the highest concentrations of Pt in soils close to a smelter (698 ± 178 ng g⁻¹, < 125 µm), while
228 lower concentrations were recorded in processing plants, shafts and nearby towns. It was suggested that
229 such contamination was derived from the emission of fine Pt-rich particles (< 125 µm) from the smelters
230 in the Bushveld Complex and, importantly, this atmospheric deposition was the main source of Pt in the
231 local vegetation (Rauch and Fatoki, 2013).

232 The highest PGE concentration was observed to be in the silt and clay fraction at the sampling point
233 closest to the mining areas (B: urban) with a Pt concentration similar to that reported in previous studies
234 (34 ng g⁻¹, Wilhelm et al., 1997). Thus, although PGE minerals tend to occur naturally in the silt and clay
235 fraction (most PGE minerals in the PGE-rich layers occur in grain sizes of less than 50 µm, Oberthür et
236 al., 2004), atmospheric deposition of mining emissions also increases the Pt accumulation in this fraction
237 (Kaonga and Kgabi, 2011); Rauch and Fatoki (2013) reported that the Pt-rich particles in soils near mine
238 activities are <125 µm. In addition, the PGE concentration decreases with increasing distance to the
239 mining area; accordingly the closest point to the mining area (sample point A), exhibited the highest PGE
240 concentration in the silt and clay fraction, while the farthest point to mining activities (sample point D),
241 showed the lowest PGE concentration in the same fraction.

242 In order to assess whether the atmospheric deposition of fine PGE-rich particles derived from the mining
243 activities had an impact on the sediments of the Hex River, the enrichment factors of the PGE
244 concentrations in the silt and clay fraction (<63 µm) compared to the total, weighed-averaged
245 concentrations (Table 3) were calculated (Fig. 6). Since higher concentrations in the fine sediments
246 compared to coarser fractions may be the result of natural processes (e.g. most PGE minerals are < 50

247 μm , Oberthür et al., 2004), these ratios were also calculated for comparison with other relevant elements
248 in this area (Cr, Ni, Cu). As observed in Figure 6, the PGE enrichment in the silt and clay fractions was
249 clearly higher than for the other metals suggesting a main source of PGE-rich fine particles in this area,
250 not observed for other elements (e.g. at sample point C, average PGE-enrichment factor and Cr-Ni-Cu
251 were 7 and 2 respectively). The highest PGE enrichment factors (Fig. 6) were observed at sampling points
252 B, C and D, 8, 4 and 7 respectively, which are situated close to or downstream of the mining activities
253 and therefore are subject to a significant input of particles from direct atmospheric deposition and surface
254 runoff. In contrast, the location of sampling point A upstream of the mining activities and therefore less
255 affected by surface runoff could explain the lower PGE-enrichment factor in the fine fraction found
256 (average PGE-enrichment factor= 2). Besides, the higher PGE concentration in the sand and coarse sand
257 fractions than in the other sample points was a consequence of the direct erosion of the PGE-rich layer,
258 since sample point A is located just after the river drains the the Merensky Reef; here, the Hex River is in
259 its upper part and is still able to transport grains of different sizes (Figures 3 and 4), prevailing weathering
260 and transportation over chemical processes explaining the highest PGE concentrations at this station
261 (Cawthorn 2001).

262

263 **4 Conclusions**

264 The elevated concentrations of PGE and other trace elements (Cr-Ni-Cu) found in sediments of the Hex
265 River (South Africa) which flows through the Bushveld Igneous Complex, correspond mainly to natural
266 levels in the parent rock. However, mining activities in the Bushveld Complex cause some disturbance of
267 the surface PGE geochemical cycle. Accordingly, increased concentrations of PGE in the silt and clay
268 fraction ($<63 \mu\text{m}$) were observed, probably derived from atmospheric deposition and surface runoff of
269 PGE-rich particles released from mining activities. This is especially relevant since this atmospheric
270 deposition of PGE-rich particles in the Bushveld Complex is impacting the concentrations of PGE in the
271 local vegetation and may become an environmental risk in the area.

272 Based on the results reported in this and previous studies (Kaonga and Kgabi, 2011; Rauch and Fatoki,
273 2013) we propose that parameters such as airborne particulate matter, and soil and river sediments should
274 be considered in protocols for the evaluation of the sustainability of mining activities in order to enhance
275 the environmental quality and protection from potential hazardous effects.

276

277 **Acknowledgements** This work has been made possible thanks to the support of the Spanish-South
278 African action CGL2004-0383-E, CTM2011-28792-C02 project (Spanish MINECO) and *JAEPredoc*
279 program (CSIC) co-funded by *Fondo Social Europeo* for C. Almécija (predoctoral fellowship). Thanks to
280 Susana Calvo Rapado (IIM-CSIC) for technical work and to the *Universidade de Vigo* and *Facultade de*
281 *Ciencias do Mar* for the Ph.D. programme in Oceanography.

282

283 **References**

- 284 Barnes, S.-J., Maier, W.D., 2002. Platinum-group elements and microstructures of normal Merensky Reef
285 from Impala platinum mines, Bushveld Complex. *J. Petrol.* 43, 103–128.
- 286 Cawthorn, R.G., 2010. The platinum group element deposits of the Bushveld Complex in South Africa.
287 *Platin. Met. Rev.* 54, 205–215.
- 288 Cawthorn, R.G., 2001. A stream sediment geochemical re-investigation of the discovery of the
289 platiniferous Merensky Reef, Bushveld Complex. *J. Geochem. Explor.* 72, 59–69.
- 290 Census 2011, Statistics South Africa, <http://www.statssa.gov.za>
- 291 Cole, J., Finn, C.A., Webb, S.J., 2013. Overview of the magnetic signatures of the Palaeoproterozoic
292 Rustenburg Layered Suite, Bushveld Complex, South Africa. *Precambrian Res.* 236, 193–213.
- 293 Eales, H.V., Cawthorn, R.G., 1996. The Bushveld Complex, in: Cawthorn, R.G. (Ed.), *Developments in*
294 *Petrology, Layered Intrusions*. Elsevier, pp. 181–229.
- 295 EPA3052 report: microwave assisted acid digestion of siliceous and organically based matrices. United
296 States Environmental Protection Agency, <https://www.epa.gov/measurements>
- 297 Glaister, B.J., Mudd, G.M., 2010. The environmental costs of platinum–PGM mining and sustainability:
298 Is the glass half-full or half-empty? *Miner. Eng.* 23, 438–450.
- 299 Gzik, A., Kuehling, M., Schneider, I., Tschochner, B., 2003. Heavy metal contamination of soils in a
300 mining area in South Africa and its impact on some biotic systems. *J. Soils Sediments* 3, 29–34.
- 301 Kaonga, B., Kgabi, N.A., 2011. Investigation into presence of atmospheric particulate matter in
302 Marikana, mining area in Rustenburg Town, South Africa. *Environ. Monit. Assess.* 178, 213–
303 220.
- 304 Lee, C.A., 1983. Trace and platinum-group element geochemistry and the development of the Merensky
305 Unit of the Western Bushveld Complex. *Miner. Deposita* 18, 173–190.
- 306 Lorand, J.-P., Luguet, A., Alard, O., 2008. Platinum-group elements: a new set of key tracers for the
307 Earth's interior. *Elements* 4, 247–252.
- 308 Meisel, T., Fellner, N., Moser, J., 2003. A simple procedure for the determination of platinum group
309 elements and rhenium (Ru, Rh, Pd, Re, Os, Ir and Pt) using ID-ICP-MS with an inexpensive on-
310 line matrix separation in geological and environmental materials. *J. Anal. At. Spectrom.* 18,
311 720–726.
- 312 Naldrett, T., Kinnaird, J., Wilson, A., Chunnett, G., 2008. Concentration of PGE in the Earth's Crust with
313 Special Reference to the Bushveld Complex. *Earth Sci. Front.* 15, 264–297.
- 314 Oberthür, T., Melcher, F., Gast, L., Wöhr, C., Lodziak, J., 2004. Detrital platinum-group minerals in
315 rivers draining the eastern Bushveld complex, South Africa. *Can. Mineral.* 42, 563–582.
- 316 Peucker-Ehrenbrink, B., Jahn, B., 2001. Rhenium-osmium isotope systematics and platinum group
317 element concentrations: Loess and the upper continental crust. *Geochem. Geophys. Geosystems*
318 2: 1061.
- 319 Rauch, S., Fatoki, O.S., 2013. Anthropogenic Platinum Enrichment in the Vicinity of Mines in the
320 Bushveld Igneous Complex, South Africa. *Water. Air. Soil Pollut.* 224, 1–8.
- 321 Rudnick, R.L., Gao, S., 2003. Composition of the Continental Crust, in: Heinrich, D.H., Turekian, K.K.
322 (Eds.), *Treatise on Geochemistry*. Elsevier, pp. 1–64.
- 323 Schäfer, J., Eckhardt, J.-D., Berner, Z.A., Stüben, D., 1999. Time-dependent increase of traffic-emitted
324 platinum-group elements (PGE) in different environmental compartments. *Environ. Sci.*
325 *Technol.* 33, 3166–3170.

- 326 Seanego, K.G., Moyo, N.A.G., 2013. The effect of sewage effluent on the physico-chemical and
327 biological characteristics of the Sand River, Limpopo, South Africa. *Phys. Chem. Earth* 66, 75–
328 82.
- 329 Sutherland, R.A., 2007. Platinum-group element concentrations in BCR-723: A quantitative review of
330 published analyses. *Anal. Chim. Acta* 582, 201–207.
- 331 Sutherland, R.A., Pearson, D.G., Ottley, C.J., 2007. Platinum-group elements (Ir, Pd, Pt and Rh) in road-
332 deposited sediments in two urban watersheds, Hawaii. *Appl. Geochem.* 22, 1485–1501.
- 333 Wedepohl, K.H., 1995. The composition of the continental crust. *Geochim. Cosmochim. Acta* 59, 1217–
334 1232.
- 335 Wentworth, C.K., 1922. A scale of grade and class terms for clastic sediments. *J. Geol.* 30, 377–392.
- 336 Wilhelm, H.J., Zhang, H., Chen, F.L., Elsenbroek, J.H., Lombard, M., De Bruin, D., 1997. Geochemical
337 exploration for platinum-group elements in the Bushveld Complex, South Africa. *Miner.*
338 *Deposita* 32, 349–361.
- 339
340

341 **Fig. 1:** Geographic location of the sampling points in the Hex River draining PGE mining areas
342 (Rustenburg, in Bushveld Complex, South Africa). The two main land uses are urban and mining
343 activities (including mines, smelters, processing plants and shafts). The Marinaka Mining area is also
344 included (from Kaonga and Kgabi, 2011).

345

346 **Fig. 2:** Diagram of sample processing methods with associated objectives for each step.

347

348 **Fig. 3:** Major, minor and trace elements in each grain-size fraction of river sediments at sampling points
349 A and B (A – upstream sampling point, away from mining areas; river has eroded Merensky Reef; and B
350 – urban sampling point, the closest to mining area; river has crossed Rustenburg). Triangular diagram
351 shows the grain-size distribution of each sample. [SPM = suspended particulate matter, ND = no data]

352

353 **Fig. 4:** Major, minor and trace elements in each sieved fraction of river sediments at sampling points C
354 and D (C – intermediate sampling point; river near urban and mining area; and D – downstream sampling
355 point; river downstream urban and mining areas). Triangular diagram shows the grain size distribution of
356 each sample. [SPM = suspended particulate matter, ND = no data]

357

358 **Fig. 5:** PGE/Cr vs. PGE ratios in Hex River (this study), river sediment (Wilhelm et al., 1997) and Impala
359 Mine core (Barnes and Maier, 2002).

360

361 **Fig. 6:** Enrichment factors for the silt and clay fraction, defined as the ratio of the element concentrations
362 in the $<63 \mu\text{m}$ fraction to the weighted-average total fraction.

363

1 Table 1: Concentrations of major, minor and trace elements in suspended particulate matter (SPM >45 μm) and different size fractions (Silt & Clay <63 μm ; fine-medium
 2 sand 63-500 μm ; coarse sand 500-2000 μm) of river sediments at the Hex River sample points given in Figure 1. Average values for the upper continental crust and drill core
 3 near Rustenburg from Rudnick and Gao (2003) and Barnes and Maier (2002) respectively (data from PGE-rich layer are not included in the average).

Sample point	Fraction	FeO (% weight)	Al ₂ O ₃ (%)	CaO (mg g ⁻¹)	MgO (mg g ⁻¹)	MnO ($\mu\text{g g}^{-1}$)	V ($\mu\text{g g}^{-1}$)	Cr ($\mu\text{g g}^{-1}$)	Zn ($\mu\text{g g}^{-1}$)	Cu ($\mu\text{g g}^{-1}$)	As ($\mu\text{g g}^{-1}$)	Co ($\mu\text{g g}^{-1}$)	Ni ($\mu\text{g g}^{-1}$)	Cd ($\mu\text{g g}^{-1}$)	Pb ($\mu\text{g g}^{-1}$)
A upstream	SPM	5.0	9.0	1.8	1.5	642	80	525	72.7	33.5	-	-	-	-	-
	silt & clay	10.9	28.1	-	-	-	134	1520	130	77.3	4.9	62.9	399	0.1	45.1
	fine-medium sand	5.5	14.4	-	-	-	69	1140	72.4	38.3	1.8	34.3	224	0.1	16.2
	coarse sand	6.5	14.3	-	-	-	102	1040	113	49.9	3.8	51.9	244	0.1	24.5
B urban	SPM	1.3	7.1	12.7	0.6	111	22	210	11.5	5.8	-	-	-	-	-
	silt & clay	4.3	19.2	-	-	-	60	1220	74.6	30.1	0.9	30.5	130	0.1	26.6
	fine-medium sand	3.3	13.2	-	-	-	53	1120	40.4	7.7	0.6	31.5	96.2	0.0	5.4
	coarse sand	2.6	9.4	-	-	-	46	519	31.5	13.5	0.1	23.8	99.6	0.0	4.7
C intermediate	SPM	1.6	18.2	51.5	6.2	238 \pm 83	17	77	19	12.1	-	-	-	-	-
	silt & clay	4.0	28.9	-	-	-	47	732	47.3	34.7	1.6	27.6	123	0.1	28.0
	fine-medium sand	2.5	28.1	-	-	-	47	1250	31.3	14.3	0.2	23.1	85.0	0.0	4.5
	coarse sand	3.3	25.8	-	-	-	73	361	63.9	20.2	0.6	39.3	151	0.1	4.3
D downstream	SPM	0.9	4.4	8.4	1.1	233	21	215	9.8	5.9	-	-	-	-	-
	silt & clay	4.3	17.0	-	-	-	87	1370	50.5	25.0	1.0	32.4	107	0.0	34.1
	fine-medium sand	2.5	10.8	-	-	-	99	3220	34.3	7.1	0.3	34.0	105	0.0	3.4
	coarse sand	2.6	10.2	-	-	-	70	1290	23.8	11.0	1.5	24.7	77	0.0	5.3
Upper Continental Crust		5.0 \pm 0.5	15.4 \pm 0.8	3.59 \pm 0.2	2.48 \pm 0.35	775 \pm 77	97 \pm 11	92 \pm 17	67 \pm 6	28 \pm 4	4.8 \pm 0.5	17 \pm 1	47 \pm 11	0.09 \pm 0.01	17 \pm 1
Rustenburg Layered Suite (<i>n</i> = 14-24)		8.3 \pm 2.0	13.3 \pm 3.5	7.14 \pm 1.5	16.5 \pm 3.1	1140 \pm 160	92 \pm 15	2010 \pm 308	-	328 \pm 123	<0.5	79 \pm 15	1030 \pm 340	-	-
LGC6137	Values obtained	3.9	3.6	52.2	13.4	642	51.4	51.0	253.0	31.5	-	-	-	-	-
	Certified values	3.9 \pm 0.2	3.6 \pm 0.7	51.1 \pm 2.6	11.1 \pm 0.8	665 \pm 27	-	47 \pm 7	231 \pm 16	31.6 \pm 1.6	-	-	-	-	-
PACS-2	Values obtained	5.3 \pm 0.1	25.0 \pm 1.2	-	-	-	131 \pm 4	84.5 \pm 6.1	374 \pm 14	291 \pm 21	30.8 \pm 3.6	11.4 \pm 0.6	41.2 \pm 4.2	1.9 \pm 0.5	182 \pm 10
	Certified values	5.3 \pm 0.2	22.5 \pm 0.5	-	-	-	133 \pm 5	90.7 \pm 4.6	364 \pm 23	310 \pm 12	26.2 \pm 1.5	11.5 \pm 0.3	39.5 \pm 2.3	2.1 \pm 0.2	183 \pm 8

4 Values: mean value \pm error (confidence interval 95%)

Table 2: Parameters of Hex River water at the four sample points (SPM: suspended particulate matter; DO: dissolved oxygen; Sat DO: % saturation of oxygen; DOC: dissolved organic carbon; POC: particulate organic carbon; PON: particulate organic nitrogen). Sand River (Limpopo) data from Seanego and Moyo (2013).

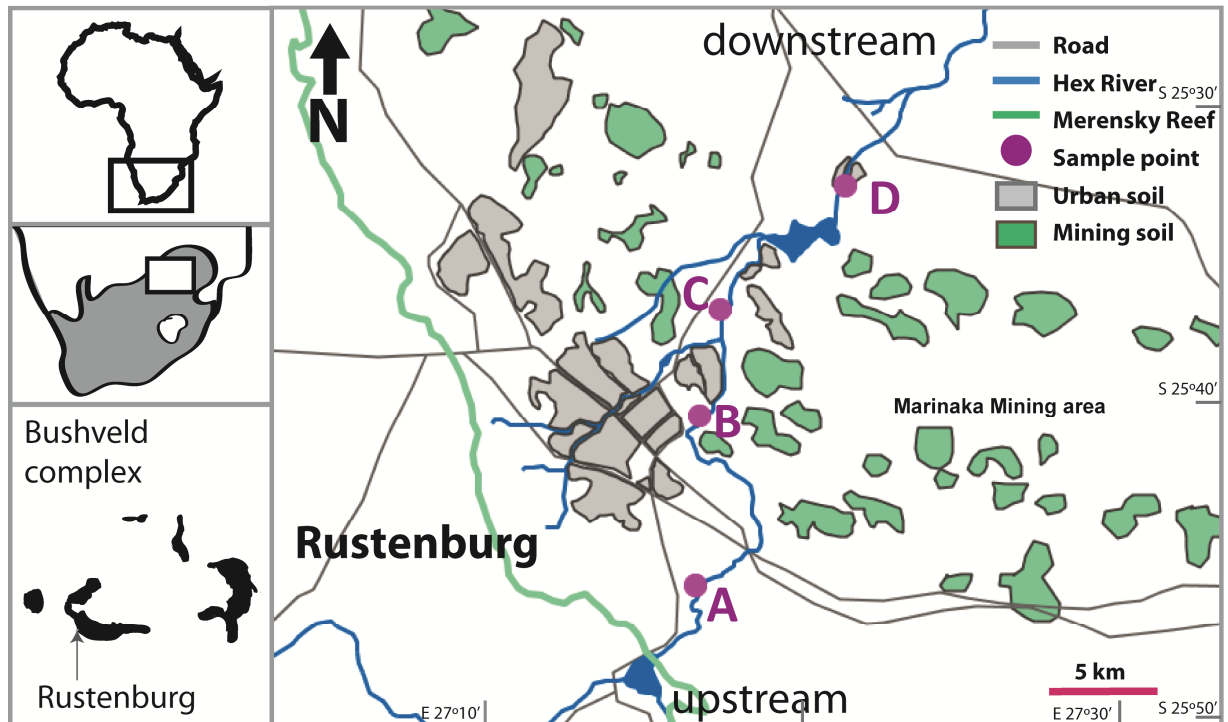
Sample point	pH	SPM (mg L ⁻¹)	Conduct (μ S cm ⁻¹)	Temp (° C)	DO (mg L ⁻¹)	Sat DO (%)	DOC (mg L ⁻¹)	POC (%)	PON (%)	C:N
A upstream	7.35	30.0	501	19.8	8.92	98	1.3	5.7	0.3	22
B urban	7.30	31.9	443	23.0	8.65	104	1.5	11.2	1.3	10
C intermediate	7.39	28.6	1015	21.5	8.98	102	2.2	11.0	1.4	9
D downstream	8.59	6.1	817	26.2	8.05	106	2.2	33.3	1.7	23
Sand River*	7.3±0.04	60±7	1100	-	-	-	-	-	-	-

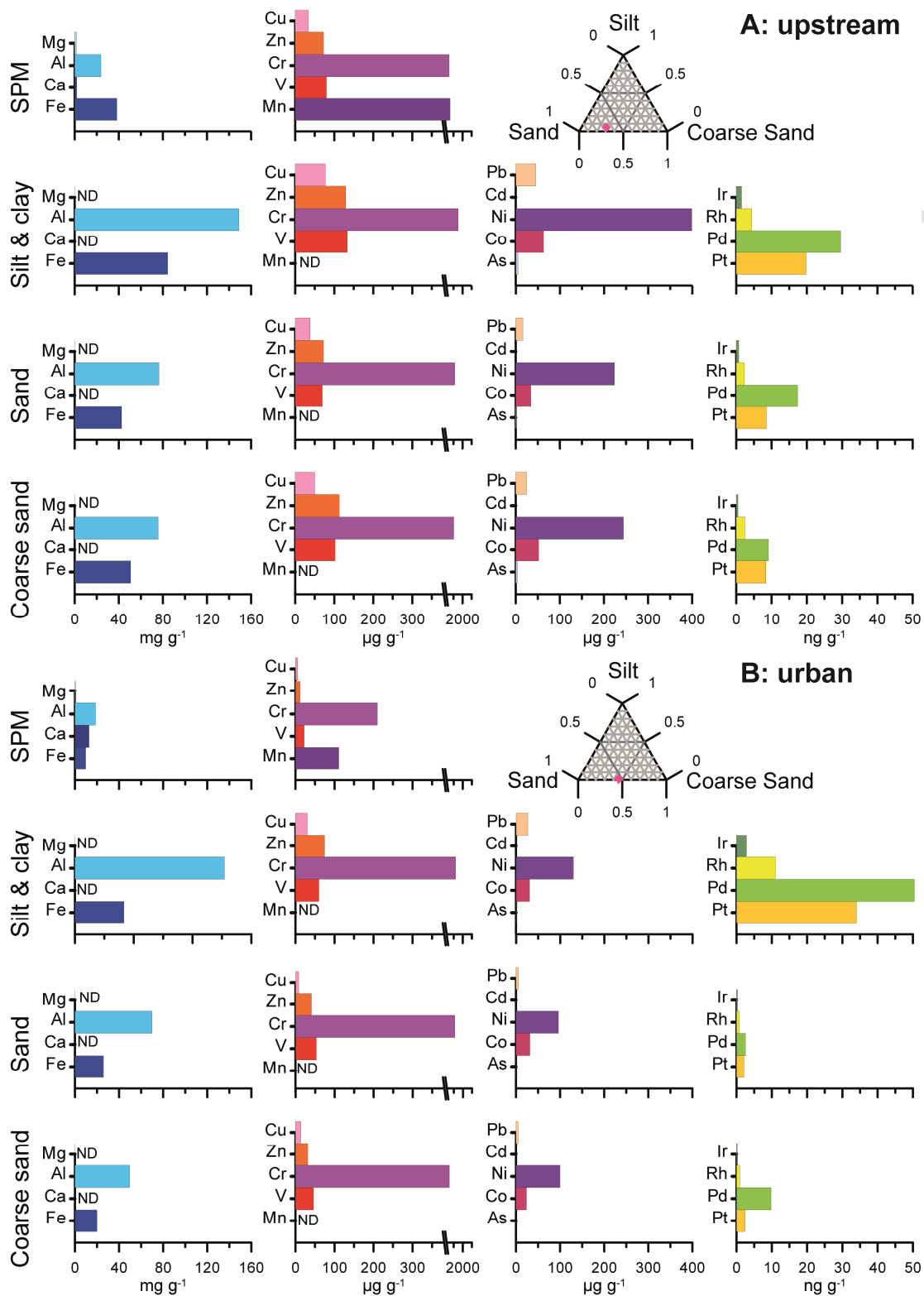
*value ± error (confidence interval 95%)

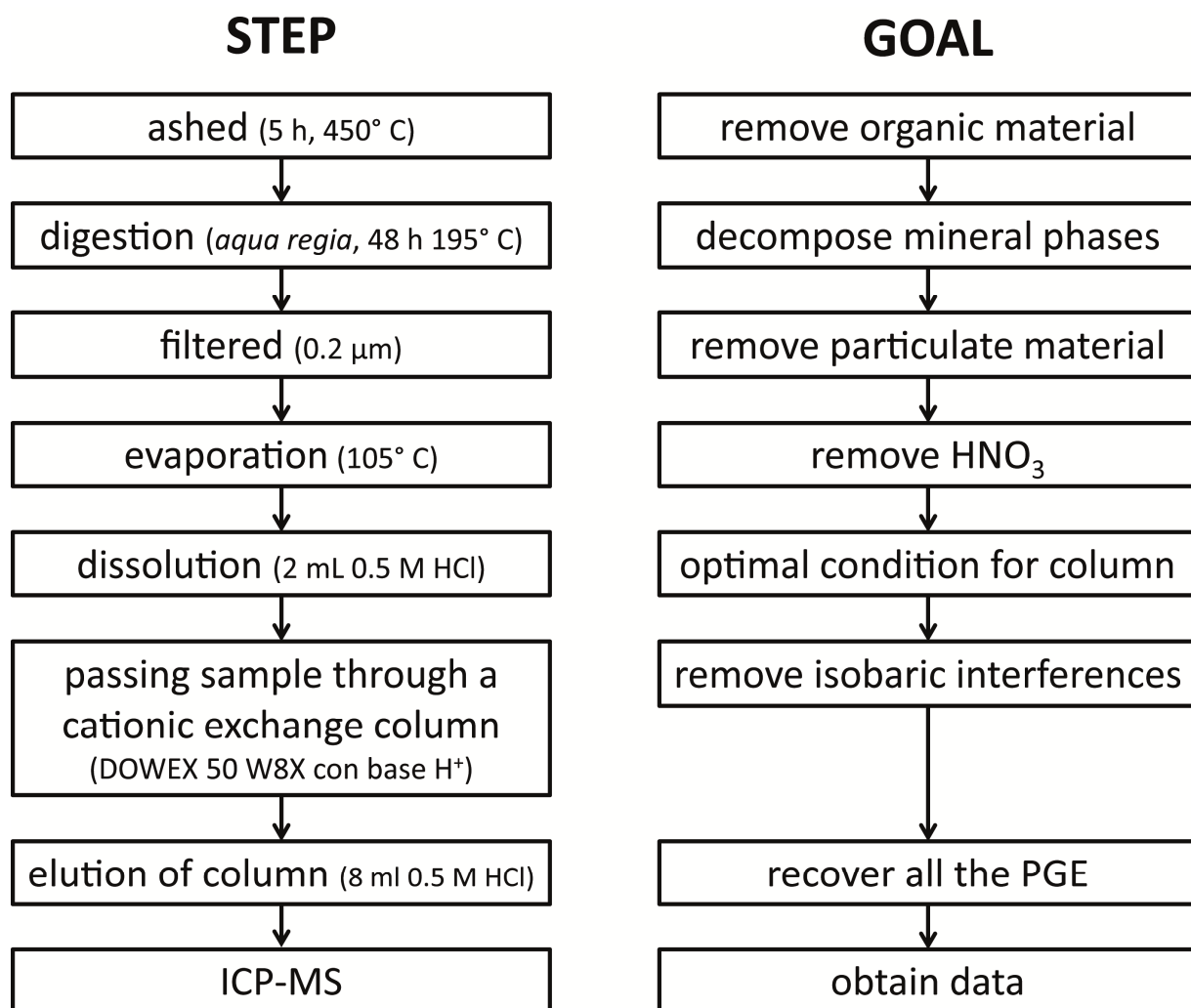
Table 3: PGE concentrations in grain size fractions (silt & clay <63 μm ; fine-medium sand 63-500 μm ; coarse sand 500-2000 μm) of river sediments at the Hex River sample points given in Figure 1. For the samples with results from two different digestions, both values are given. Average values for the upper continental crust and drill core near Rustenburg (data from PGE-rich layer are not included in the average) (Barnes and Maier, 2002; Peucker-Ehrenbrink and Jahn, 2001; Wedepohl, 1995).

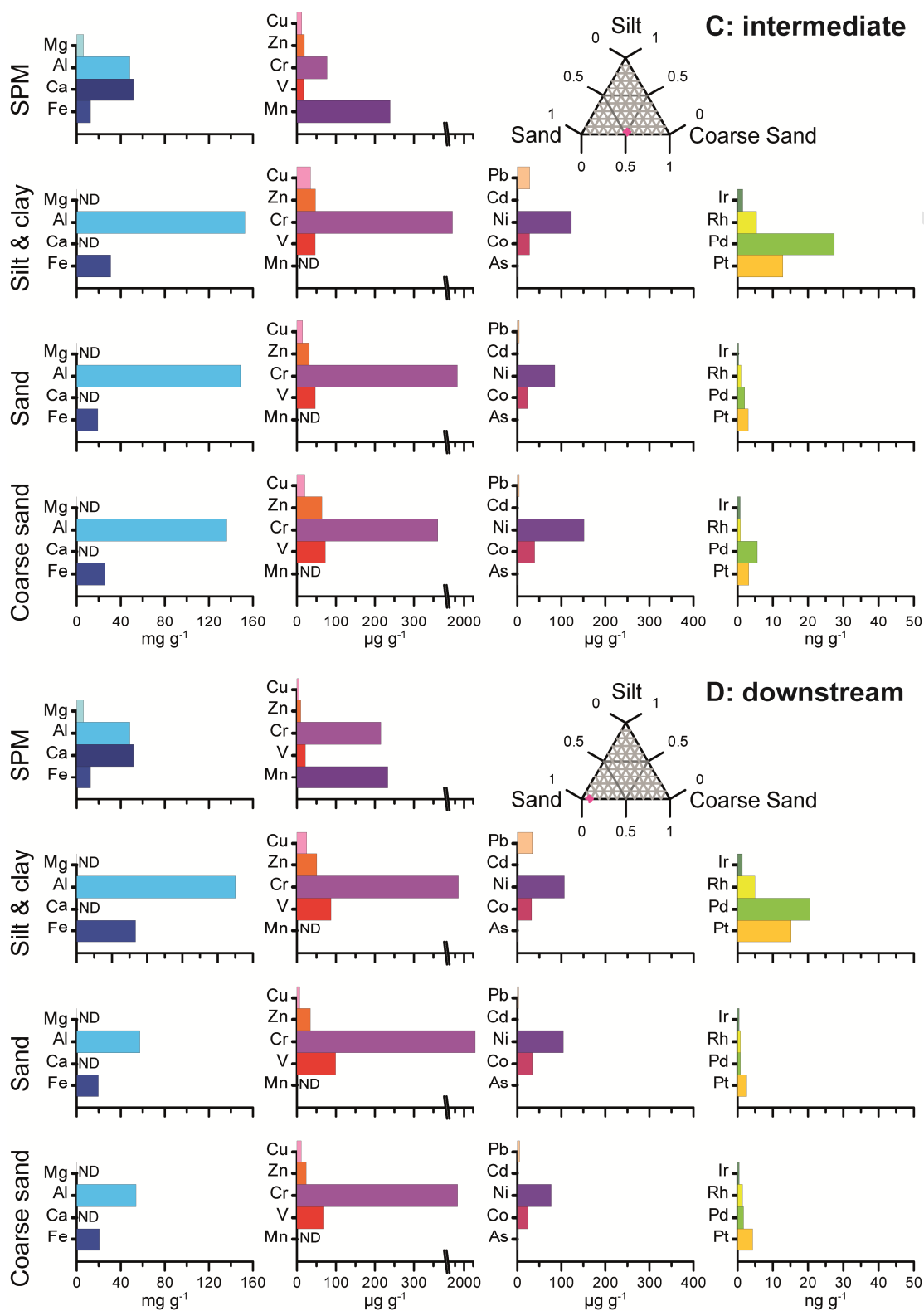
Sample point	Fraction	PGE (ng g^{-1})	Pt (ng g^{-1})	Pd (ng g^{-1})	Rh (ng g^{-1})	Ir (ng g^{-1})
A upstream	silt & clay	55.2 \pm 5.7	19–21	25–35	4.3–4.5	1.4–1.6
	fine-medium sand	28.9	8.5	17	2.3	0.70
	coarse sand	20.4 \pm 4.4	7.2–9.6	7.3–11	2.3–2.4	0.46–0.47
	<i>Weighted average (n=5)</i>	-	9.0 \pm 0.6	15.7 \pm 1.1	2.4 \pm 0.0	0.68 \pm 0.01
B urban	silt & clay	98.1 \pm 35.7	26–42	33–67	11	2.8
	fine-medium sand	5.7 \pm 4.5	1.5–2.6	0.1–5.0	0.7–0.9	0.16–0.42
	coarse sand	13.3 \pm 3.4	2.3–2.4	7.6–12	0.8–0.9	0.16–0.21
	<i>Weighted average (n=6)</i>	-	3.2 \pm 0.7	7.9 \pm 4.5	1.2 \pm 0.2	0.36 \pm 0.15
C intermediate	silt & clay	47.1	12.8	27.4	5.4	1.46
	fine-medium sand	6.4 \pm 0.1	3.0–3.1	2.0–2.1	1.0	0.26–0.30
	coarse sand	10.2 \pm 6.0	2.8–3.5	1.7–9.4	0.6–0.9	0.16–1.3
	<i>Weighted average (n=5)</i>	-	3.4 \pm 0.3	4.5 \pm 2.7	1.0 \pm 0.1	0.54 \pm 0.42
D downstream	silt & clay	42.0 \pm 2.9	14–17	17–24	4.9–5.0	1.4
	fine-medium sand	4.6 \pm 1.7	2.0–3.3	0.5–1.0	0.7–0.8	0.26–0.65
	coarse sand	7.9 \pm 0.4	3.8–4.8	1.1–2.4	1.4	0.42–0.56
	<i>Weighted average (n=6)</i>	-	3.5 \pm 1.1	1.2 \pm 0.6	1.1 \pm 0.1	0.58 \pm 0.32
Average values	14.1 \pm 9.5	4.8 \pm 2.9	7.3 \pm 6.2	1.4 \pm 0.7	0.54 \pm 0.13	
Upper continental crust	-	0.51	0.52	0.06	0.02	
Core from Rustenburg (n=14-24)	-	81 \pm 28	42 \pm 16	4.8 \pm 1.7	2.4 \pm 0.8	

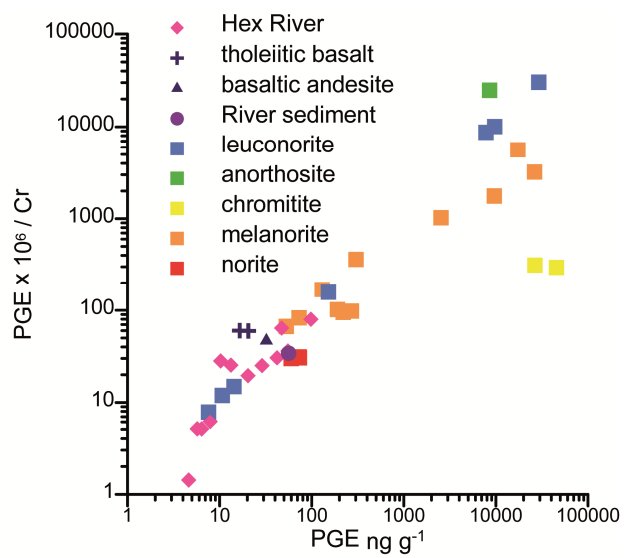
Values: mean value \pm standard deviation

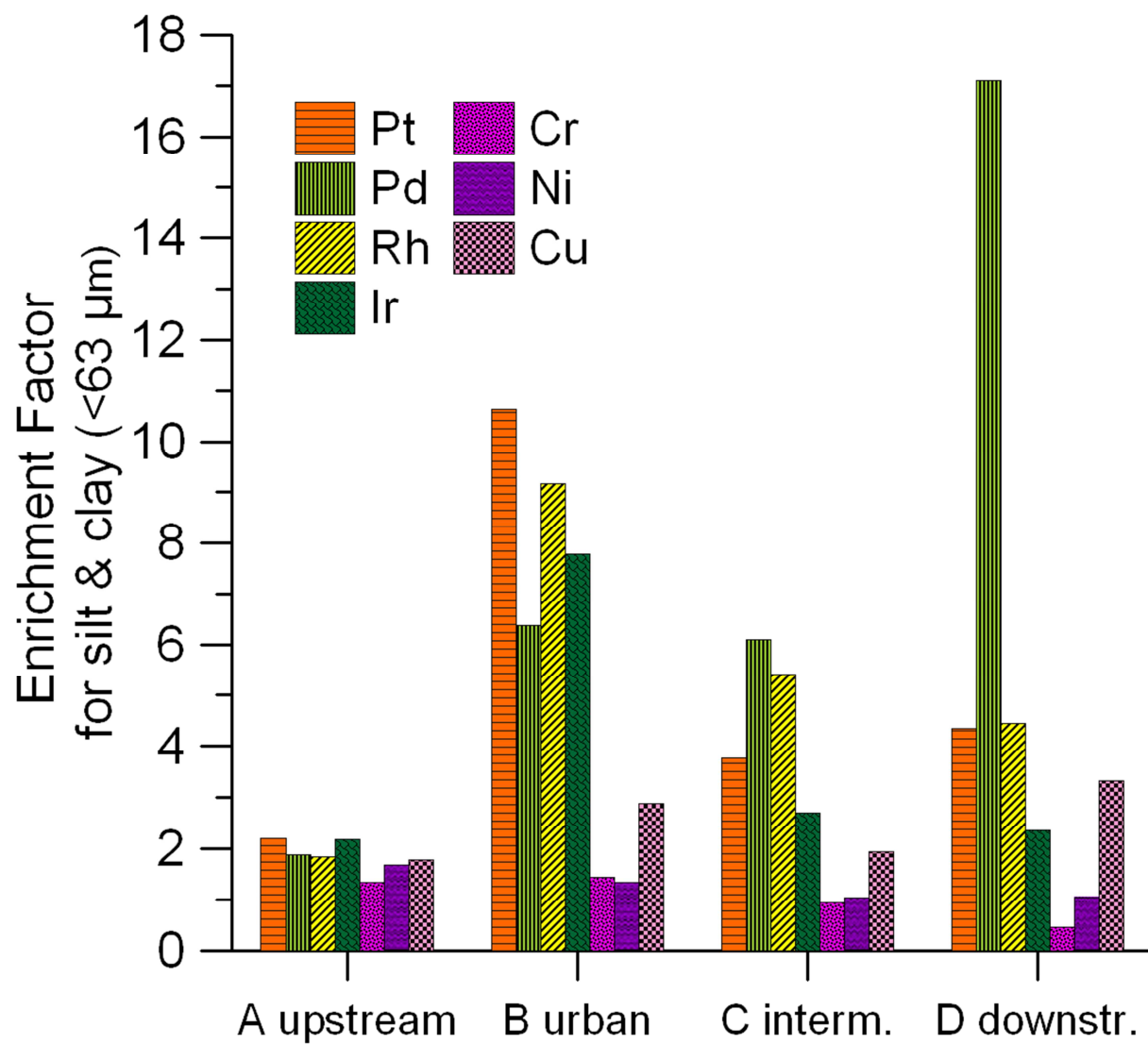












HIGHLIGHTS

Mining causes disturbance on the surface geochemical cycle of PGE

The impact of PGE mining activities is mostly on the silt and clay fractions

PGE concentrations decrease with the distance to the mining areas

River sediment quality should be taken into account for assessing mining activities

ACCEPTED MANUSCRIPT