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

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Abstract

Assessment of the environmental impact of platinum group elements (PGE) and other trace elements from mining activities is essential to prevent potential environmental risks. This study evaluates the concentrations of PGE in stream sediments of the Hex River, which drains the mining area of the Bushveld Igneous Complex (South Africa), at four sampling points. Major, minor and trace elements (Fe, Ca, Al, Mg, Mn, V, Cr, Zn, Cu, As, Co, Ni, Cd, and Pb) were analyzed by FAAS and ETAAS in suspended particulate matter and different sediment fractions (<63, 63-500 and 500-2000 µm), and Pt, Pd, Rh, and Ir were measured by ICP-MS after removal of interfering elements (cation exchange resin 50W-DOWEX-X8). Procedures were blank-corrected and accuracy checked using reference materials. Nickel, Cr, Pt, Pd, Rh and Ir show concentrations 3-, 13-, 18-, 28-, 48- and 44- fold the typical upper continental crust levels, respectively, although lower than concentrations reported for the parent rocks. The highest concentrations were observed closer to the mining area, decreasing with distance and in the <63 µm fraction, probably derived from atmospheric deposition and surface runoff of PGE-rich particles released from mining activities. Thus, mining activities are causing some disturbance of the surface PGE geochemical cycle, increasing the presence of PGE in the fine fraction of river sediments. We propose that indicators such as airborne particulate matter, and soil and river sediment quality, should be added to the protocols for evaluating the sustainability of mining activities.

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

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

Several studies have been focused on the geochemistry and mineralogy of river sediments and soils of the Bushveld Complex mining area to trace PGE-rich layers or to gain an understanding of PGE weathering processes and sedimentological characteristics (Cawthorn, 2001; Oberthür et al., 2004; Wilhelm et al., 1997). From an environmental perspective, Gzik et al. (2003) studied soils contaminated by trace elements associated with the Bushveld Complex mining activities and how contamination affects the biological communities, whereas Kaonga and Kgabi (2011) investigated the source of atmospheric particulate matter in the Marikana mining area and concluded that the mining activities are the source of metals in airborne particles in this area. Recently, Rauch and Fatoki (2013) studied the occurrence of platinum in soils and vegetation (grass) in the vicinity of mines in the Bushveld Complex; although
elevated concentrations in this area may be the result of natural sources, they found evidence of anthropogenic platinum enrichment linked to platinum mining activities due to atmospheric transport of PGE-rich particles from smelters. Also, Rauch and Fatoki (2013) concluded that atmospheric deposition is the main source of platinum in grass, while uptake of bioavailable Pt in soils has a minor impact on platinum levels in grass.

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

2 Materials and methods

2.1 Sampling

The Hex River flows in a northerly direction crossing the city of Rustenburg, the capital of the most populated municipality in the North West Province of South Africa, where almost 550,000 people live and where the main industrial activity is mining (Census 2011, Statistics South Africa). The Hex River drains one of the most important mining areas in the western limb of the Bushveld Igneous Complex (Fig. 1) where the PGE-rich Merensky Reef and the UG-2 chromitite layer are mined. Water and surface sediment were sampled at four points (A: upstream; B: urban; C: intermediate; and D: downstream) along the Hex River (Fig. 1) during high-flow conditions in March 2006. Water samples were collected using a telescopic pole with a bottle holder in acid-cleaned 1 L high-density polyethylene bottles that were subsequently kept in zip-lock bags and placed in a cooler box for transportation. For sediments, in order to ensure representivity of the samples, composite samples were obtained at each sampling point by mixing equal volumes of discrete grab samples of surface sediments (15-20 grab samples, ~ 5 Kg of sample) collected in an area of 15 m² covering both river banks. The surface sediments were collected using a plastic spatula and stored in zip-lock plastic bags. Samples were collected at least 10 m away from roads to avoid including the impact of PGE emissions from automobile exhaust catalysts (e.g. catalytic converters) on PGE concentrations (Schäfer et al., 1999).
Physicochemical variables, i.e. temperature, pH, conductivity and dissolved oxygen (DO) were measured in situ using a calibrated WTW 340i sensor package (Nova Analytics). In the laboratory at the University of Johannesburg, 100 mL aliquots of water samples were vacuum-filtered using an acid-cleaned Nalgene-type filtration unit fitted with acid-cleaned and pre-weighed 0.45 μm pore size polycarbonate filters (Pall Corporation). Filters with the retained suspended particulate matter (SPM) were stored frozen in plastic Petri dishes pending their analysis for major and trace elements. For the analysis of dissolved organic carbon (DOC), separate 100 mL aliquots of water samples were vacuum-filtered through pre-combusted GF/F filters (Whatman) in a Millipore glass filtration unit. Filters were stored frozen in Petri dishes, and filtrates were collected in pre-combusted glass vials, acidified with HCl (analytical reagent grade, Merck) to pH 2, and frozen until analysis.

Sediments were dried (<60 °C), sieved into three size fractions following the Wentworth Grain Size Class (Wentworth, 1922): i.e. silt and clay (<63 μm), fine-medium sand (63-500 μm) and coarse sand (500-2000 μm). After sieving, sediment samples were ground using an agate mortar and pestle, in order to homogenize the sample.

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

Dissolved organic carbon (DOC) was measured in the thawed samples by high-temperature catalytic oxidation using a total organic carbon analyzer (Shimadzu Carbon-5000), and air-dried GF/F filters were analyzed for total carbon and nitrogen using a CHN analyzer (Carlo Erba EA1110). Major and trace elements (Fe, Ca, Al, Mg, Mn, V, Cr, Zn, Cu, As, Co, Ni, Cd, and Pb) in suspended particulate matter and sediments were determined after microwave-assisted digestion in Teflon® bombs (MarsXpress, CEM) using a 3:1 mixture of HNO₃ (Hiperpur© 69% Panreac) and HF (Suprapur© 40% Merck); the selected program is specially suitable for sediments (heating: 20 min, digestion: 8 min, temperature: 180 ± 5 °C; EPA3052). Analysis of major elements in the digests was conducted by means of flame atomic absorption spectrophotometry (Varian SpectrAA 220FS), whereas trace elements were determined using electrothermal atomic absorption spectrophotometry (Varian SpectrAA 220). One blank was run every ten samples and results were therefore blank-corrected. The accuracy of the analytical methodology was checked using PACS-2 marine sediment reference material (NRC, Canada) and LGC6137 (LGC Standards) sediment reference material (which includes certified concentrations for all the elements analyzed); and results obtained were within the certified concentrations (Table 1).
2.3 Analysis of platinum group elements in sediments

A Thermo X series II ICP-MS, using external calibration, was used for the determination of the concentrations of platinum (Pt), palladium (Pd), rhodium (Rh) and iridium (Ir). A modified version of the procedure given by Sutherland et al. (2007) was employed for sample digestion and removal of isobaric and polyatomic interferences (Fig. 2); accordingly, about 100 mg of sediment was ashed in quartz crucibles for 5 hours at 450 °C in order to remove organic matter. The optimization of the ashing step (Table S1, Electronic Supplementary Material) was achieved using two certified reference materials: river sediment JSd-2 (Geological Survey of Japan) and road dust BCR-723 (European Institute of Reference Materials and Measurements). Ashed sediment samples were digested in aqua regia (HNO$_3$ 65% and HCl 30%, Suprapur® Merck) for 4 hours at 195 °C and then allowed to cool down; then, digest were syringe-filtered through 0.45 µm Supor™ hydrophilic polyethersulfone membranes (Pall®). The filtered digest was then evaporated until near dryness and re-dissolved using 2 mL of 0.5 M HCl, and then passed through a 2 cm$^3$ (0.4 cm diameter x 16 cm length) Teflon® column containing a cation exchange resin (50W-DOWEX-X8, hydrogen form, 100-200 mesh), that was previously acid-cleaned and conditioned with 10 mL of HCl 6 M and 10 mL of HCl 0.5 M. Samples were stored in Teflon® vials pending analysis. The presence of potential polyatomic and isobaric interferences was checked during analysis. Results for the reference materials (JSd-2: river sediment and BCR-723, road dust, Table S1, Electronic Supplementary Material) indicated a good recovery (>80%) except for Pd in BCR-723 where a recovery of 59% was obtained. However, previous studies (Meisel et al., 2003; Sutherland, 2007) concluded that the Pd certified value in BCR-723 was overestimated, proposing an average of 4-4.5 ng g$^{-1}$, which would lead to a Pd recovery greater than 80% in our study.

3 Results and discussion

3.1 Ancillary parameters

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$^{-1}$, 98-106 % of saturation) values obtained at sampling points A, B, and C indicated similar conditions and were in the range of other rivers draining the Bushveld Complex (Seanego and Moyo, 2013) (Table 2). However, the presence of a dam upstream of sampling point D reduced flow capacity and competence, producing a decrease in SPM levels of 80% and a slight increase in pH as a result of biological activity.
As the Hex River flows through Rustenburg, the amount of organic material in water due to urban and domestic inputs, here measured as DOC, POC, and PON, increased from sampling points A to B. Dissolved oxygen concentrations, saturated at all stations, showed that the system still had self-purification capacity (Seanego and Moyo, 2013).

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

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

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

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

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

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

3.5 Impact of mining activities on PGE concentrations

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

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

In order to assess whether the atmospheric deposition of fine PGE-rich particles derived from the mining activities had an impact on the sediments of the Hex River, the enrichment factors of the PGE concentrations in the silt and clay fraction (<63 µm) compared to the total, weighed-averaged concentrations (Table 3) were calculated (Fig. 6). Since higher concentrations in the fine sediments compared to coarser fractions may be the result of natural processes (e.g. most PGE minerals are < 50
µm, Oberthür et al., 2004), these ratios were also calculated for comparison with other relevant elements in this area (Cr, Ni, Cu). As observed in Figure 6, the PGE enrichment in the silt and clay fractions was clearly higher than for the other metals suggesting a main source of PGE-rich fine particles in this area, not observed for other elements (e.g. at sample point C, average PGE-enrichment factor and Cr-Ni-Cu were 7 and 2 respectively). The highest PGE enrichment factors (Fig. 6) were observed at sampling points B, C and D, 8, 4 and 7 respectively, which are situated close to or downstream of the mining activities and therefore are subject to a significant input of particles from direct atmospheric deposition and surface runoff. In contrast, the location of sampling point A upstream of the mining activities and therefore less affected by surface runoff could explain the lower PGE-enrichment factor in the fine fraction found (average PGE-enrichment factor= 2). Besides, the higher PGE concentration in the sand and coarse sand fractions than in the other sample points was a consequence of the direct erosion of the PGE-rich layer, since sample point A is located just after the river drains the the Merensky Reef; here, the Hex River is in its upper part and is still able to transport grains of different sizes (Figures 3 and 4), prevailing weathering and transportation over chemical processes explaining the highest PGE concentrations at this station (Cawthorn 2001).

4 Conclusions

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

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


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

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

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

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

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

Fig. 6: Enrichment factors for the silt and clay fraction, defined as the ratio of the element concentrations in the <63 μm fraction to the weighted-average total fraction.
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 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 near Rustenburg from Rudnick and Gao (2003) and Barnes and Maier (2002) respectively (data from PGE-rich layer are not included in the average).

<table>
<thead>
<tr>
<th>Sample point Fraction</th>
<th>FeO (%weight)</th>
<th>Al₂O₃ (%)</th>
<th>CaO (mg g⁻¹)</th>
<th>MgO (mg g⁻¹)</th>
<th>MnO (µg g⁻¹)</th>
<th>V (µg g⁻¹)</th>
<th>Cr (µg g⁻¹)</th>
<th>Zn (µg g⁻¹)</th>
<th>Cu (µg g⁻¹)</th>
<th>As (µg g⁻¹)</th>
<th>Co (µg g⁻¹)</th>
<th>Ni (µg g⁻¹)</th>
<th>Cd (µg g⁻¹)</th>
<th>Pb (µg g⁻¹)</th>
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<td>9.0</td>
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<td>642</td>
<td>80</td>
<td>525</td>
<td>72.7</td>
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<td>-</td>
<td>-</td>
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<td>28.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>134</td>
<td>1520</td>
<td>130</td>
<td>77.3</td>
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<td>62.9</td>
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<td>-</td>
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<td>69</td>
<td>1140</td>
<td>72.4</td>
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<td>22</td>
<td>210</td>
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<td>19.2</td>
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<td>519</td>
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<td>51.5</td>
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<td>238±83</td>
<td>17</td>
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<td>silt &amp; clay</td>
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<td>28.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>732</td>
<td>47.3</td>
<td>34.7</td>
<td>1.6</td>
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<td>-</td>
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<td>4.5</td>
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<tr>
<td>coarse sand</td>
<td>3.3</td>
<td>25.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>73</td>
<td>361</td>
<td>63.9</td>
<td>20.2</td>
<td>0.6</td>
<td>39.3</td>
<td>151</td>
<td>0.1</td>
<td>4.3</td>
</tr>
<tr>
<td>D downstream SPM</td>
<td>0.9</td>
<td>4.4</td>
<td>8.4</td>
<td>1.1</td>
<td>233</td>
<td>21</td>
<td>215</td>
<td>9.8</td>
<td>5.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>silt &amp; clay</td>
<td>4.3</td>
<td>17.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>87</td>
<td>1370</td>
<td>50.5</td>
<td>25.0</td>
<td>1.0</td>
<td>32.4</td>
<td>107</td>
<td>0.0</td>
<td>34.1</td>
</tr>
<tr>
<td>fine-medium sand</td>
<td>2.5</td>
<td>10.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>99</td>
<td>3220</td>
<td>34.3</td>
<td>7.1</td>
<td>0.3</td>
<td>34.0</td>
<td>105</td>
<td>0.0</td>
<td>3.4</td>
</tr>
<tr>
<td>coarse sand</td>
<td>2.6</td>
<td>10.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>70</td>
<td>1290</td>
<td>23.8</td>
<td>11.0</td>
<td>1.5</td>
<td>24.7</td>
<td>77</td>
<td>0.0</td>
<td>5.3</td>
</tr>
</tbody>
</table>

Upper Continental Crust: 5.0±0.5 15.4±0.8 3.59±0.2 2.48±0.35 775±77 97±11 92±17 67±6 28±4 4.8±0.5 17±1 47±1 0.09±0.01 17±1

Rustenburg Layered Suite (n= 14-24): 8.3±2.0 13.3±3.5 7.14±1.5 16.5±3.1 1140±160 92±15 2010±308 - 328±123 <0.5 79±15 1030±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±0.2 3.6±0.7 51.1±2.6 11.1±0.8 665±278 87±5 47±7 231±16 31.6±1.6 - - - - -

PACS-2 Values obtained: 5.3±0.1 25.0±2.1 - - - 131±4 84.5±6.1 374±14 291±21 30.8±3.6 11.4±0.6 41.2±4.2 1.9±0.5 182±10
Certified values: 5.3±0.2 22.5±0.5 - - - 133±5 90.7±4.6 364±23 310±12 26.2±1.5 11.5±0.3 39.5±2.3 2.1±0.2 183±8

4 Values: mean value ± 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).

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

*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).

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

Values: mean value ± standard deviation
**STEP**

- ashed (5 h, 450° C)
- digestion (*aqua regia*, 48 h 195° C)
- filtered (0.2 μm)
- evaporation (105° C)
- dissolution (2 mL 0.5 M HCl)
- passing sample through a cationic exchange column (DOWEX 50 W8X con base H⁺)
- elution of column (8 ml 0.5 M HCl)
- ICP-MS

**GOAL**

- remove organic material
- decompose mineral phases
- remove particulate material
- remove HNO₃
- optimal condition for column
- remove isobaric interferences
- recover all the PGE
- obtain data
C: intermediate

D: downstream
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