Geochemical controls of potentially toxic element (PTE) release from the Gold One Tailings Dam Complex into the Randfontein area, Witwatersrand, South Africa

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Abstract

This study investigated the release of potentially toxic elements (PTEs) from the Gold One Tailings Dam Complex (TDC) in Randfontein, South Africa. The Gold One TDC generally comprised a PTE-leached upper oxidized zone and PTE-enriched lower oxidized, transition and reduced zones. Acid-base accounting determined that TD materials were largely acid-generating. According to sequential extraction procedures, Co and Pb yielded the highest potentially bioavailable concentrations, compared to Cu, Ni and Zn. The results suggest that Co and Pb may pose increased threat to the health of the environment and wildlife.

Keywords: Acid-base accounting; sequential extraction procedures; Randfontein; South Africa

Introduction

Tailings are one of the largest waste products associated with mining (Dold 2014). Tailings create potential threats to the environment largely in the form of acid mine drainage (AMD). AMD, which is formed via the oxidation of sulfide minerals (such as pyrite), which readily mobilizes potentially toxic elements (PTEs) in the environment (Tutu 2003). As a result, soils, surface water bodies and groundwater in the vicinity of tailings facilities can become contaminated with PTEs over time and thereby, potentially compromise the overall environmental, ecological-and public health of the area.

The Randfontein area in West Rand, South Africa, hosts several tailings facilities linked to gold mining (Abegunde *et al.* 2016). A number of studies have reported that this area is affected by AMD (Lusilao-Makiese *et al.* 2013; Shapi *et al.* 2021). Randfontein is located close to the Krugersdorp Game Reserve. Thus, it is crucial to investigate the geochemical controls of PTE release from these tailings facilities into surrounding areas, to mitigate their potential risk to the environment and game animals.

Methods

Twenty-nine samples were collected from three drill core sections (T001, T002 and T003) in the Gold One Tailings Dam Complex (TDC) located in Randfontein, South Africa (Fig. 1). The study site lies within the Witwatersrand Basin which comprises auriferous conglomerates of the

Witwatersrand Supergroup (Tutu *et al.* 2003). TD mineralogy was determined via X-ray diffraction (XRD) analysis. Major oxide and trace element chemistry was determined via X-ray fluorescence (XRF) and inductively coupled plasma mass spectrometry (ICP-MS), respectively. Total carbon and sulfur content were determined via LECO analysis. Total carbon and sulfide-sulfur were used in acid-base accounting (ABA) to estimate the acid-generating potential of TD materials. Sulfide-sulfur was determined by digesting sulfate contents in an ammonium oxalate-oxalic acid solution at pH 3 for 2 hours at 80 °C; and the sulfate contents was then subtracted from the total LECO sulfur. Finally, sequential extraction procedures (SEPs) were used to assess the mobility and potential bioavailability of PTEs in the TDC. The five-step SEP scheme used in this study is listed below. Solutions at each step were filtered to separate the liquid from solid residue and were analyzed via graphite furnace atomic absorption spectrometry (GFAAS). Associations among extractable elements were assessed using principal component analysis (PCA).

Step 1: Water-soluble. To 5 g of solid material, 90 ml of distilled H_2O at pH 7 was added, then agitated for 90 minutes at room temperature.

Step 2: Exchangeable and carbonate (*loosely bound fraction and/or sensitive to pH changes*). To the solid residue from step 1, 90 ml of 1 M ammonium acetate- $NH_4CH_3CO_2$ (buffered to pH 5 with ≈ 37 ml acetic acid) was added, then agitated for 90 minutes at room temperature.

Step 3: Hydrous Mn-oxide (*fraction typically sensitive to redox changes*). To the solid residue from step 2, 90 ml of 0.1 M hydroxylamine hydrochloride- $NH_2OH.HCl$ (buffered with 10 ml of 10% nitric acid- HNO_3) was added, then agitated for 90 minutes at room temperature.

Step 4: Hydrous Fe-oxide (*fraction typically sensitive to redox changes*). To the solid residue from step 3, 90 ml of 0.25 M $NH_2OH.HCl$ (buffered with 25 ml of 10% HNO_3) was added, then agitated for 90 minutes at room temperature.

Step 5: Residual (*strongly bound fraction*). (i) Two rounds of 25 ml of 60% hydrofluoric acid

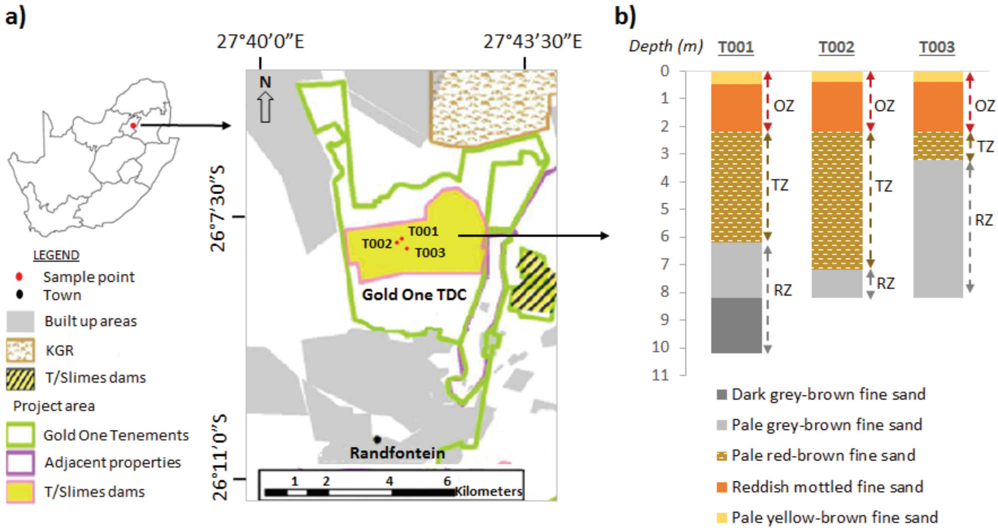

Figure 1 a) Location map of the Gold One TDC and Krugersdorp Game Reserve (KGR) near Randfontein in South Africa (modified after Gold One International Limited 2012) and b) the lithology of drill core sections T001, T002 and T003 (where 'OZ' is the oxidized zone, 'TZ' is the transition zone and 'RZ' is the reduced zone).

(HF) were added to 1 g of solid residue from step 4 and heated for 1 hr at approx. 100 °C in a sand bath; (ii) two rounds of 20 ml HF : 5 ml HNO_3 were added and heated for 1 hr at approx. 100 °C in a sand bath; (iii) 25 ml HNO_3 was added to 100 ml flasks and agitated for 5–6 hours; and (iv) flasks were topped to 100 ml with distilled water and 5 ml of 5% boric acid added to stabilize the ions.

Results and Discussion

Mineralogy and geochemistry

According to the XRD analysis, the Gold One TDC consisted of mainly quartz (41.7% – 63.7%), pyrophyllite (0.8% – 5.9%), pyrite (0.12% – 0.64%), gypsum (0.3% – 1.8%) and clinochlore (0.2% – 0.4%). These results are relatively consistent with the mineralogy of the Witwatersrand gold ore bodies (Phillips & Law 2000). However, gypsum is likely linked to the partial neutralization of AMD through liming (Tutu *et al.* 2008). Three weathering zones were distinguished in the TDC; namely, an oxidized zone 'OZ' (comprising upper pale yellow-brown fine sands and lower reddish, mottled fine sands), a transition zone 'TZ' (comprising pale red-brown fine sands) and a reduced zone 'RZ' (comprising pale to dark grey-brown fine sands) (Fig. 1). Of the drill core sections investigated, section T003 was seemingly the least weathered, showing the highest pyrite contents (approx. 0.42% – 0.64%) and the earliest onset of grey (reduced) fine sands. Paste pH ranges in the TDC were as follows: the OZ (2.9 – 5.2), the TZ (3.7 – 8.1) and the RZ (7.4 – 8.4). The acidic paste pH in the OZ is likely related to the oxidation of pyrite. Major oxide concentration ranges in the TDC were (in %): SiO_2 (81.4 – 93.3), CaO (0.02 – 1.43), Fe_2O_3 (1.37 – 4.79) and MnO (0.003 – 0.06). PTE concentration ranges in the TDC were (in mg/kg): Co (1.6 – 78.0), Ni (8.2 – 242), Zn (5.0 – 231), Cu (7.5 – 100.5) and Pb (11.4 – 67.5). Minimum PTE concentrations generally corresponded with the upper OZ; while maximum PTE concentrations generally corresponded with the lower OZ and RZ. In nearly all cases, maximum PTE concentrations coincided with maximum Fe and/or Mn oxide concentrations. Thus, Fe and/or Mn oxides, which are known scavengers of trace elements (Hall *et al.* 1996), may play important roles in the mobilization/immobilization of PTEs in the TDC.

Acid-generating potential

The acid-generating potential of the TDC was assessed using the Neutralizing Potential Ratio (NPR) which represents the ratio between acid potential (AP) and neutralizing potential (NP) (Fig. 2). Total carbon was used to represent NP (INAP 2009), with the assumption that all carbon in the sample is present as calcite ($CaCO_3$), and sulfide-sulfur selected to represent the AP. The AP ranged from 0.05 $CaCO_3$ kg/ton to 36.8 $CaCO_3$ kg/ton; while the NP ranged from 1.67 $CaCO_3$ kg/ton to 31.7 $CaCO_3$ kg/ton. The NPRs were interpreted according to Price *et al.* (1997). Thus, TD materials from sections T001, T002 and T003 were largely acid-generating. TD materials with non-acid generating potential occurred within the first 0.5 meters of sections T001 and T002. Thus, the two potentially non-acid generating samples appear consistent with the PTE-leached, pale fine sands of the upper oxidized zone, suggesting that oxidation was at its incipient stage at the time of sample collection.

PTE mobility and potential bioavailability

The bioavailable fraction of PTEs refers to the proportion of PTEs transported into, entering and accumulating in living organisms (NRC 2003). Potentially bioavailable PTE fractions are therefore considered to represent more accurately the potential toxicity of metals in the environment (Yiika *et al.* 2023). In general, water-soluble, exchangeable, carbonate and Mn/Fe oxide bound PTE fractions are considered potentially bioavailable; while residual (e.g. primary silicate)-bound PTE fractions are considered relatively stable under most environmental conditions (Siegel 2002). Fig. 3 shows that Co was largely bound to exchangeable and carbonate phases which corresponds with that of gold mine tailings in the Johannesburg area (Rösner & Van Schalkwyk 2000). Lead

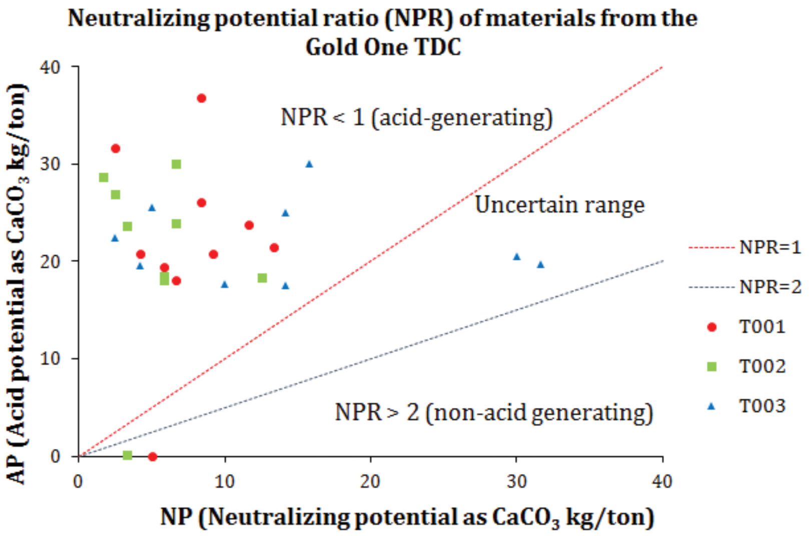

Figure 2 *Graph indicating the neutralizing potential ratio (NPR) of samples collected from the Gold One TDC.*

was largely bound to the hydrous Fe-oxide (reducible) phase which is fairly consistent with that of gold mine tailings dumps in the West Rand area (Fosso-Kankeu *et al.* 2015). Copper, Ni and Zn were largely bound to the residual phase which coincides with findings by Yiika *et al.* (2023). In general, the mobility and potential bioavailability of PTEs can be described in decreasing order as: Co > Pb >> Cu > Ni > Zn. When the weathering zones are compared with the SEP (Fig. 3), the highest water-soluble PTE fractions occurred largely within the OZ and upper TZ. This suggests that PTE fractions within the OZ and upper TZ are most susceptible to leaching by rainwater. This is important considering that the study area receives approx. 749 mm of annual rainfall (Climate-data.org 2025) and some of the highest PTE concentrations occurred within the lower OZ. PTE fractions within the lower TZ and RZ generally showed greater susceptibility to leaching under changing pH and redox conditions.

The PCA biplots of extractable elements in step 2 (the exchangeable and carbonate phase) and step 4 (the hydrous Fe-oxide phase), which were associated with the highest potentially bioavailable PTE contents, are shown in Fig. 4a and b, respectively. Fig. 4a shows that extractable Co in step 2 was associated mainly with Mn. A number of SEP-related studies have found that Co and Mn are positively correlated (Gray *et al.* 1999; Rösner & Van Schalkwyk 2000). Gray *et al.* (1999) suggested that extractable Mn in this fraction could represent Mn within carbonates, separate-phase $MnCO_3$ or highly soluble Mn oxides. Similarly, Fig. 4b shows that extractable Pb in step 4 was associated mainly with Mn which is supported by statements by Bradl (2004). The co-precipitation of Mn with Fe oxides (Sposito 1983) and incomplete dissolution of Mn oxide in step 3 (Chao 1972) provide possible explanations for the extractable Mn contents in step 4 of the SEP. The association of PTEs with Mn (Fig. 4) is consistent with the increased metal-scavenging capacity of Mn oxides, compared to Fe, which is partly attributed to their complex mineralogical structure (Hall *et al.* 1996).

Conclusions

Regarding PTE contents, the Gold One TDC was dominated by Ni and Zn, with lower concentrations of Cu, Co and Pb. The PTE contents appeared lowest in the pale yellow-brown fine sands in the upper OZ; and highest in the reddish mottled fine sands in the lower OZ and grey-brown fine sands in the RZ. According to the SEP, Co was mainly bound to the exchangeable and carbonate phase (appearing largely associated with Mn); Pb was mainly bound to the hydrous

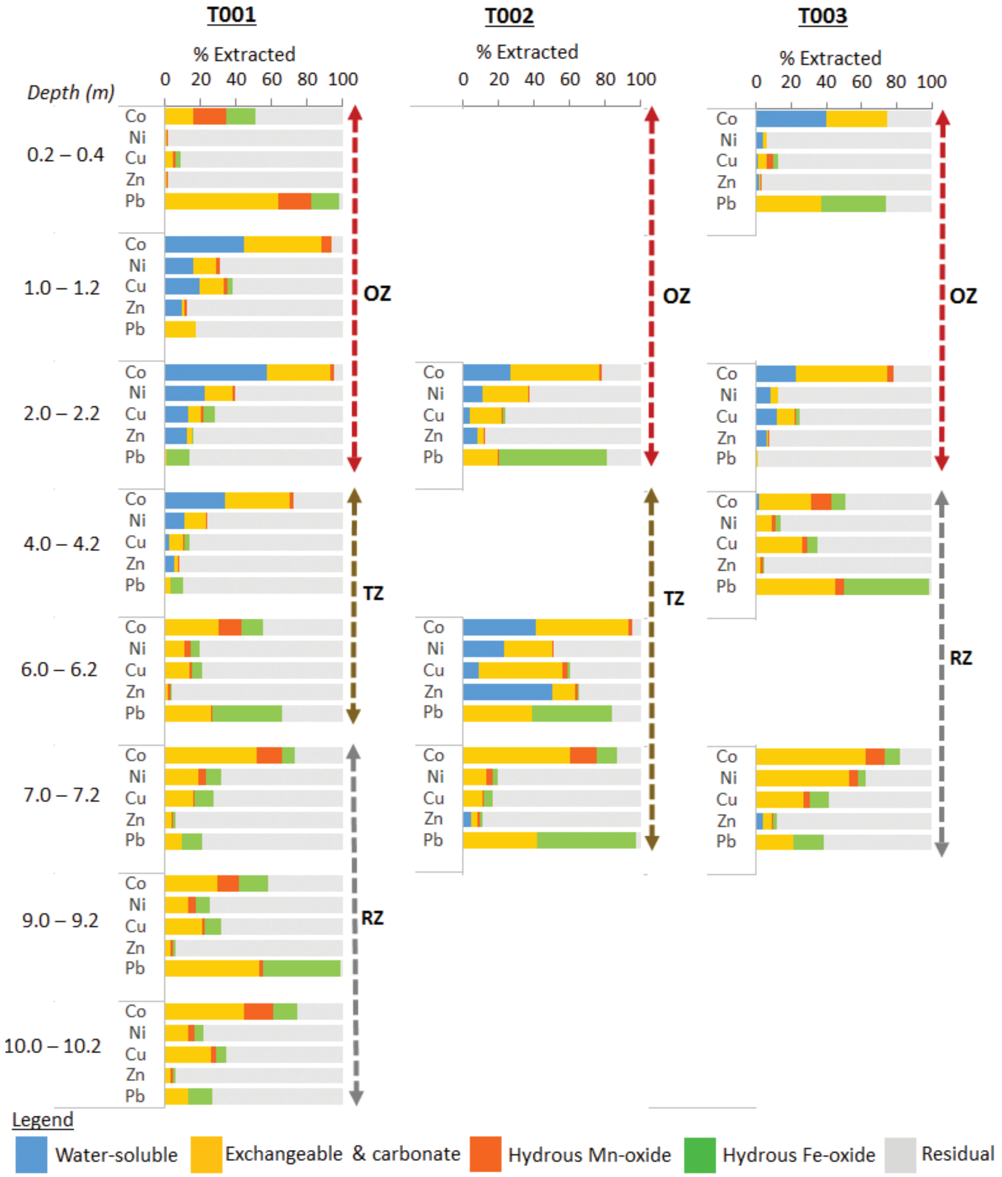

Figure 3 *Results of the SEPs performed on TD materials with depth. Depths shown are consistent across T001, T002 and T003 but are not shown to scale downhole to conserve space.*

Fe-oxide phase (appearing largely associated with Mn); while Cu, Ni and Zn were mainly bound to the residual phase. The results suggest that Co may have the greatest potential for release into the environment under changing pH conditions while Pb may be released into the environment under changing redox conditions. These findings are important considering that TD materials in the study site were largely acid-generating. The Gold One TDC may therefore pose potential threat to the health of animals in the nearby Krugersdorp Game Reserve. This study highlights the need to implement suitable mitigation strategies to minimize the potential environmental and ecological risks associated with the Gold One TDC. It is recommended that future

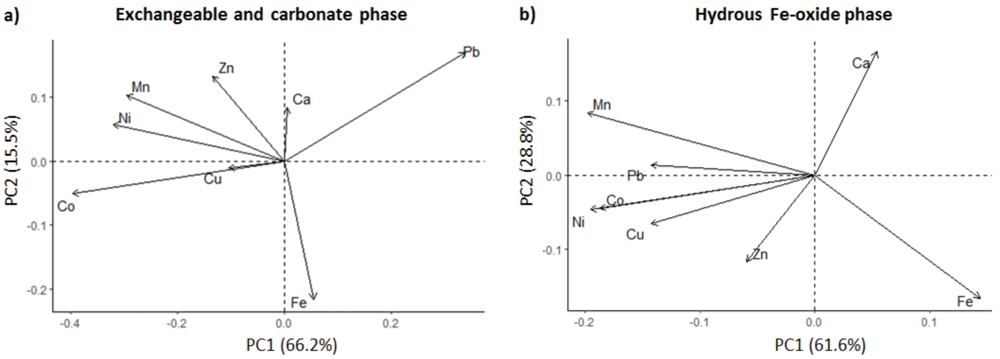

Figure 4 *Principal component analysis (PCA) biplots showing element associations in a) the exchangeable and carbonate phase and b) the hydrous Fe-oxide phase.*

studies incorporate leach column testing to monitor PTE release from the TDC long-term. In addition, it may be worthwhile exploring the use of hydro-geochemical modeling to predict PTE release from the TDC long-term.

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