Assessment of As and Hg in Mine Tailings and Indigenous Grass: A Case Study of Non-Functional New Union Gold Mine, South Africa

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ABSTRACT

The present study was carried out to assess the uptake of toxic metals, arsenic (As) and mercury (Hg), by Cynodon dactylon grass species at New Union gold mine tailings, Limpopo Province, South Africa. The samples were collected from New Union Gold Mine tailings and from Ka-Madonsi Village (control), and concentrations of As and Hg in soil and plant material were determined by ICP-MS. The average dry weight concentrations of As and Hg in mine tailing dam A were 2.53 and 1.18 μ g/g, respectively, and 2.24 and 0.91 μ g/g, respectively, in mine tailings B. The average dry weight of As and Hg in the control soil samples were 0.30 and 0.05 μ g/g, respectively. The C. dactylon, on average dry weight, absorbed 5.45 µg/g of As, and 1.72 µg/g of Hg from mine tailings A, and 4.29 μ g/g of As; and 1.55 μ g/g of Hg from mine tailings B. The control grass, on average dry weight, absorbed 0.53 μ g/g and 0.01 μ g/g of As and Hg, respectively. In most cases, significant differences were observed between bioaccumulation of Hg and As in plant tissue from mine sites and control sites. The study showed that the bioconcentration factor was less than 1 for the acidic mine tailings, with exception of the root and rhizome system which was greater than 1. This contrasted sharply with the control site where the pH was alkaline, and As and Hg levels were low. The pH values were significantly different (p < 0.05) between the soils originating from mine tailings and the control site. The electrical conductivity (EC) of soil at mine tailings A and B were 1847.35 and 1777.5 μ S/cm, respectively. The EC for the control site was significantly different (p < 0.05) at 543.3 µS/cm. C. dactylon was found to be capable of bioaccumulation of As and Hg, effective at soil stabilization, and grew well under the acidic conditions. The control grass was healthy and thrived under the alkaline conditions.

Keywords: toxic heavy metals; Cynodon dactylon; re-vegetation; mine tailings

INTRODUCTION

Mining operations contribute wealth to an economy in a variety of ways, but mine wastes can negatively impact the environment. Abandoned mine tailings sites are a source of environmental problems throughout the world and the number of these sites is on the increase (Lodenius and Malm, 1998; Bell *et al.*, 2001; Ogola *et al.*, 2002; Naicker *et al.*, 2003; Mendez *et al.*, 2007; Schuwirth *et al.*, 2007; Mulugisi *et al.*, 2009). This study focuses on the abandoned mine tailings at New Union Gold Mine, Malamulele, Limpopo province, South Africa, an arid region with limited rainfall. During the processing of the gold ore at New Union Gold mine, the gold was recovered after addition of amalgam (mercury) (Janisch, 1986). The mine operated from 1935 to 1998 in Giyani greenstone belt under various mining companies such as New Union Mining, Northfields Gold Pty Ltd, New Union Gold, Noorde, Offspring and Barberton until the exhaustion of the underground gold ore (Potgieter and De Villiers, 1986; Du Plessis, 2011). According to Potgieter and De Villiers (1986) the gold ore was associated with sulfur-rich arsenopyrite in garnetiferous, biotite-rich bands. Thus, the mine processing wastes were probably rich in arsenic (As) and mercury (Hg), and were discarded to the mine tailings dams. These mine tailings dams are thinly covered by vegetation on slopes and on the surface such that water and wind erosion are likely to occur (Figure 1).



Figure 1 Thinly covered vegetation at New Union Gold Mine tailings showing water erosion

The study of Rösner and Schalkwyk (2000) in the mine tailings of Witwatersrand goldfields, South Africa showed that water erosion contributed to loading of heavy metals in nearby and deteriorated water quality in nearby rivers. The studies of Mulugisi *et al.* (2009) and Magonono *et al.* (2010) at New Union Gold Mine demonstrated the presence of heavy metals such as manganese, zinc, copper, lead, As, cadmium, and cobalt in the mine tailings. The study of Winde *et al.* (2004) showed that the contamination of the streams adjacent to the Witwatersrand goldfields mine tailings posed

a health risk for the people in the nearby informal settlements who drink the river water without appropriate treatment.

It is known that some plant and, more specifically grass, species are able to remove heavy metals from contaminated soil and water (Comino et al., 2008). Plant species that accumulate large amounts of heavy metals from soils are referred as hyper-accumulator species (Madejón et al., 2002; Li et al., 2007). The use of plants to remove heavy metals from contaminated soils is an environmentally friendly and cost-effective method, termed phytoremediation (Cunningham et al., 1995; McLaughlin et al., 2000; Mulugisi et al., 2009). At New Union Gold Mine tailings an indigenous grass, Cynodon dactylon, has been growing in different patches on the mine tailings. According to Soleimani et al. (2009), C. dactylon can hyper-accumulate nickel and lead and was one of the candidate methods for cleaning up heavy metal contamination of soil and sediments in Shadegan wetland, Iran. C. dactylon has an extensive roots system which is suitable for soil stabilization (Smith et al., 1998; Rizzi et al., 2004), and the studies of Smith et al. (1998) and Madejón et al. (2002) also showed that C. dactylon has a widespread creeping ability, which is useful for the stabilization of mine tailings. A similar, but separate study of Nelushi et al. (2013) of C. dactylon under field conditions at New Union Gold Mine showed that the grass was able to bioaccumulate significant amounts of chromium and uranium. The study on the bioaccumulation potential of As and Hg uptake by *C. dactylon* under field conditions are rather limited. The main aim of this study was to assess the uptake of As and Hg in different parts of C. dactylon plants (roots, rhizomes, stems, and leaves) from the New Union Gold Mine tailings under field conditions. A second objective was to determine pH and electric conductivity (EC) of the mine tailings, and how these contribute to availability of the toxic metals, As and Hg.

METHODOLOGY

Sample collection and preparation

The samples were collected from tailings dams at the New Union Gold Mine and control samples from Ka-Madonsi village, South Africa, on June 2010. The study area is well described in Mulugisi *et al.* (2009). The samples, C. *dactylon* and soils were obtained from the same spot from the mine tailings and the control site. The samples were collected at the following geographical coordinates: 23°01′05″S and 30°43′50″E; 23°00′59″S and 30°43′53″E; 23°01′06″S and 30°43′47″E; and 23°01′04″S and 30°43′45E″; for sample tailings A1, A2, B1 and B2, respectively. The samples were then sealed in sample bags and transported in coolers to the laboratory at the University of Venda for further analysis.

The grass samples were washed with distilled water, oven dried at 55 °C (Vacutec oven, Labcon, South Africa) to constant weight for a week and subsequently cut into plant sections (roots, rhizome, stems, or leaves). After drying soil samples for a week, the individual samples were ground with a Retsch RS 200 grinding mill (Retch, United Kingdom) to 80% fine or < 75 μ m, and were then weighed to 5.00g, using an AS 220/C/2 analytical balance (Radwag, United Kingdom). All grass and soil samples were acid-digested following the procedure of the APHA (2006), and were sent, in duplicate, to the ARC Institute of Soil, Water & Climate, Pretoria, South Africa for metal analysis.

Determination of pH and EC

The soil samples were weighed to 50 g, (BP 1200 balance) and mixed thoroughly with 50 ml of distilled water (Sampanpanish *et al.*, 2006) prior to conducting pH and EC measurements, for which a Crison Basic Model meter was used. The pH and EC measurements were determined in duplicate.

Determination of metals, arsenic and total mercury

The acid digested samples were analyzed, in duplicate, for As and Hg using cold vapour/hydride generation ICP-MS (Chen *et al.*, 2008), using a Thermofischer ICP MS Model X Series II.

Data analysis

The concentrations of As and Hg were reported on a dry weight basis (d.w.). Statistical analyses were carried out using single factor ANOVA, with a significance level of p <0.05. The bioconcentration factor (BCF) was calculated as per procedure of Al-Qahtani (2012). The BCF ratio, which was calculated as metal concentration in plant divided by metal concentration in soil, represents the ability of the plant to bioaccumulate the metal in question.

RESULTS AND DISCUSSION

The pH and EC of soil samples mine tailings and control sites

The research findings, presented in Table 1, indicate that the mine tailing dams were highly acidic and the control site was neutral.

 Table 1
 Average pH and EC of soil samples from at New Union Gold Mine tailings and the control

Sample ID	pH	EC (µS/cm)
Mine tailing (A1)	3.55±0.04	1712.70±37.4
Mine tailing (A2)	3.49±0.01	1982.00±9.3
Mine tailing (B1)	3.62±0.01	1568.00±8.2
Mine tailing (B2)	3.66±0.05	1983.00 ± 14.8
Control site	7.59±0.17	548.33±0.7

site

The pH results for replicate mine tailings samples were not significantly different (p>0.05) from each other, but were significantly different (p<0.05) from the control site. The acidity of the mine tailings was probably due to oxidation of pyrite and other sulfide minerals of geological origin (Potgieter and De Villiers, 1986; Mulugisi *et al.*, 2009; Magonono *et al.*, 2010). According to Al-Qahtani (2012) and Nelushi *et al.* (2013), soil pH, EC, organic content, and metal speciation may influence the plant-bioavailability of metals. The EC values of soil samples from mine tailings were higher than those from the control site (Table 1). The EC values of the mine tailings A and B were not significantly different (p>0.05, and their relatively high EC values probably result from oxidation of pyrite and sulfide minerals exposed to oxygen and water (James, 1997). Electrical conductivity of the soil is an indirect measure of the Total Dissolved Solid (TDS) present in the soil,

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which has negative impacts on plant growth due to increased osmotic pressure of the soil solution, thereby inhibiting water and nutrient uptake by plants (James, 1997). Thus the acidic conditions are conducive to metal availability in the mine tailings soil coupled with easier metal uptake by the plants. Additionally, once the metals are in solution, they contribute to EC, as supported in this study. In contrast, the neutral conditions at the control site do not promote dissolution of metals, thus contributing to low electrical conductivity.

Concentrations of toxic metals in mine tailings and control sites

The research findings showed that As and Hg were significantly elevated in the New Union Gold Mine tailings in comparison with the control site (Figure 3). The range in concentrations of As and Hg in the mine tailings were 1.48 to 3.58 ug/g and 0.59 to 1.27 ug/g d.w., respectively. The levels of As and Hg in the mine tailings were higher than the control site, which may be attributed to the gold ore-amalgam processing and presence of sulfur-rich arsenopyrite in garnetiferous, biotite-rich bands.



Figure 3 Average dry weight concentrations, based on duplicate analyses, of As and Hg in mine tailings at New Union Gold Mine and at the control site, whiskers reflect standard error

For both As and Hg, the mine tailings A and B were not significantly different (p > 0.05) from each other, but were significantly different from the control for Hg, (p < 0.05), with an insignificant difference for As (p > 0.05). This supports that the source of Hg likely originates from the New Union Gold Mine, where Hg was used to extract gold during operations (Janisch, 1896). Additionally, as previously described, the presence of As in the mine tailings is probably geological, coming from sulfur-rich arsenopyrite (Potgieter and De Villiers, 1986).

These findings are in agreement with numerous studies from a variety of mine sites, such as Amono-Neizer *et al.* (1996) which reported 12.92 μ g/g and 0.93 μ g/g of As and Hg, respectively, in soils around the gold mining town of Obuasi in Ghana. Furthermore, the As concentrations are similar to the study of Madojen *et al.* (2002) at the Aznallcollar mine spill (SW Spain), who found levels of of 9.59 μ g/g in soils, and the study of Visoottiviseth *et al.* (2002), which reported As concentrations in soil of 14 μ g/g. The research findings are also in agreement with the study of

Fernandez-Martizer (2009) which recorded Hg concentrations ranging from 0.59 μ g/g to 1.59 μ g/g in soils.

Toxic metal concentration in different parts of Cynodon dactylon

The concentrations of As and Hg were also determined in the different plant parts (roots, rhizome, stem and leaves) of *C. dactylon* harvested from the study sites (Figure 4). The *C. dactylon* growing on the mine tailings accumulated more As and Hg in the leaves and stems than the *C. dactylon* growing on the control site (Figures 4a and b), with a significant difference of p < 0.05. There were significant differences in the accumulation of As and Hg in plant parts from the various mine tailings sites. *C. dactylon* collected from the mine tailing sites was shown to accumulate higher levels of As and Hg in leaves than in stems. The metals under study, As and Hg, have no known biological function in plants (Comino *et al.*, 2009) and are reportedly toxic to plants including the *C. dactylon*; being detrimental to plant health and wellbeing. According to Comino *et al.* (2009), the As-uptake by plants was inhibited by the presence of antimony and phosphate, but was promoted by the presence of molybdate.









Figure 4 Average dry weight concentrations, based on duplicate analyses, of As and Hg in (a) leaves, (b) stems, (c) roots and (d) rhizomes of *C. dactylon* mine tailings at New Union Gold Mine and at the control site, whiskers reflect standard error

Similar to observations from the leaves and stems, *C. dactylon* growing on the mine tailings accumulated more As and Hg in the roots and rhizome than the *C. dactylon* that was growing on the control site (Figures 4c and d), with significant differences from the control (p < 0.05). This was expected since the roots grow deeper into mine tailings than the rhizome. Significant differences (p<0.05) in the accumulation of As and Hg were observed among the mine tailings sites. The *C. dactylon* was shown to bioaccumulate more As than Hg in roots than rhizome. This was expected since soil samples from mine tailings had higher concentrations of As than Hg (Figure 3), and thus the *C. dactylon* had access to more As than Hg. It is also possible that As and Hg compete with each other for uptake, as was shown by the study of Comino *et al.* (2009) in tomato plants. In the same study Comino *et al.* (2009) also showed that the uptake of Hg by tomato plant was inhibited by selenate, which has chemical similarities to certain forms of As. It may, therefore, be possible that As was inhibiting Hg uptake with a similar mechanism, thereby leading to higher As uptake by *C. dactylon*.

Generally, the most toxic metals such as As and Hg are highly bioavailable to grass under acidic conditions, conditions in which metals are more soluble (Okunola *et al.*, 2007). The research findings are in agreement with Smith *et al.* (1998), who reported that *C. dactylon* may tolerate pollution of trace elements (e.g. up to 30,000 μ g/g of As in soil). The research findings are also in agreement with the study of Madejón *et al.* (2002), who reported that *C. dactylon* had a high bioconcentration of As (up to 75 μ g/g) in a contaminated site in Spain.

Bioconcentration factors of Cynodon dactylon

The availability of metals for uptake by plants is determined by factors such as soil pH, EC, natural organic matter in soil; and metal speciation (Al-Qahtani, 2012). The bioconcentration factor (BCF) was calculated as metal concentration in plant divided by the metal concentration in soil, which

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thus represented the ability of the plant to bioaccumulate the metal in question. Using this calculation, a BCF < 1 indicates lower bioavailability of a metal, while a BCF >1 indicates a higher bioavailable metal. The research findings showed that the BCF ratios were variable between the *C. dactylon* growing on mine tailings and that growing at the control site (Table 2). This BCF variability may be attributed to metal mobility and bioavailability as a result of acidic versus alkaline conditions. The study of Comino *et al.* (2009) showed that the uptake of As and Hg at the same time and space may interfere with each other, a finding that may support our results. Al-Qahtani (2012) stated that neutral to alkaline conditions restrained metal mobility and therefore the metal bioavailability in plant uptake and translocation into plant tissues. This is consistent with our study, where the alkaline conditions inhibited metal mobility and probably contributed to low BCF ratios for the control site. Our study showed that in the acidic mine tailings, the BCF was less than 1 with exception of the root and rhizome system which was greater than 1 for mine tailings such as A2 and B2 (Table 2). The location of accumulation of As in plant tissue was variable, but generally absorbed more in roots and the rhizome. Conversely, although the location of accumulation of Hg was also variable, it was generally absorbed more in leaves and the roots.

	Tailings A1 3.55		Tailings A2 3.49		Tailings B1		Tailings B2 3.66		Control 7.59	
pН										
	As	Hg	As	Hg	As	Hg	As	Hg	As	Hg
Leaves	0.2	0.6	0.5	0.1	0.4	0.8	0.5	0.3	0.0	0.0
Stem	0.2	0.3	0.5	0.1	0.7	0.4	0.5	0.2	0.6	0.0
Rhizome	1.4	1.1	0.2	0.1	0.1	0.2	0.1	0.0	0.7	0.2
Roots	0.1	0.2	1.6	0.4	0.5	0.7	1.1	0.6	0.5	0.0

Table 2 Bioconcentration factors (BCF) of C. dactylon for As and Hg

CONCLUSION

The ability of *C. dactylon* to uptake metals under acidic conditions and stabilize slopes as a result of creeping ability, makes it a suitable vegetation cover for the exposed mine tailings from a remedial perspective. However, this study showed that soil and *C. dactylon* samples at New Union Gold Mine tailings contain high levels of As and Hg in comparison to the control site. The acidic mine tailings likely solubilize the metals As and Hg, thus making these elements available for uptake by the *C. dactylon*. In contrast with control sample, the alkaline conditions were not conducive to metal solubility thus limiting uptake by *C. dactylon*. At the mine tailings sites in this study, the presence of As and Hg in the leaves and stem of this grass is worrisome, because grasses are frequently grazed upon by livestock and wild animals, which may lead to biomagnification in the food chain. The presence of animals at the mine tailings was shown by animal droppings. At the New Union Gold mine, there is presently no one to look after the property and the mine tailings are not fenced; the animals can thus freely graze on *C. dactylon* that was growing on the mine tailings.

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