

Evaluation of Heavy Metals in Platinum Tailing Dam Site

Molebogeng P. Nkobane*, Ayo S. Afolabi, *Member, IAENG* and Ambali S. Abdulkareem

Abstract— Mining industry has been identified as the main sustenance of the South African economy, however the negative impacts of the industry on the ecological systems cannot be over emphasized due to the released waste which is mostly heavy metals into the environment. The study evaluated six heavy metal (Al, Cu, Fe, Ni, Pb and Cr) contents in a tailings dam from a specific mine site. A set of samples for the investigation were measured, that is, in the year 2012. The sample set was only taken at a distance profile of 500 meters from the foot of the dam. A kilogram of each sample was taken as per grid format. The samples at varied depths were taken at 0-cm depth for the top layer, 20 cm depth for the second layer, and 30cm depth for the third layer. The samples for the surface distance were taken at 1 m, 2m, 3m, and 4m away from the 500 m sampling point. 1. The results of this research study showed that when the concentrations of the six heavy metals at the Impala tailings dam site were compared, their prevalence followed the order $Al > Fe > Cr > Ni > Cu > Pb$ and the Anova tests confirmed that the difference between the group concentration means for each metal with respect to distance and depth was insignificant, and this finding agreed with the raw data analysis, which examined the concentration profile of each separate metal and showed that the average means were very similar.

Keywords — heavy metals, tailings dam

I. INTRODUCTION

Industrialization plays a vital role in sustaining the nation's economy and improving the wellbeing of its citizens. However, industrialization also has a negative impact, particularly in terms of the release by plants of unwanted by-products into the ecological system. Also, the long-term effects of industrial pollution on the environment may be disastrous for not only people but for all living organisms if not carefully controlled. This explains the current awareness among researchers of the need to monitor the activities of process industries, especially those that discharge heavy metals into the environment. Heavy metals occur naturally in the ecosystem, with large variations in concentration. In modern times, anthropogenic sources of heavy metals, that is, man-made pollution, have also been introduced to the ecosystem. The resultant build-up of heavy metals and sediments in the soil has caused acute concern in environmentalists. The main issues include the potential toxicity to plants and wildlife an overload of heavy metals may cause, and the inherent problems of biomagnification that may occur at several levels in the biological food chain. This in turn may lead to serious health problems in animals

and humans [1]. Yet another series of problems raised by an excess of heavy metals in soils is that of tropic accumulation and transport, which result in heavy metal contamination of groundwater by leaching, the pollution of waterways, and surface water runoffs that result in erosion. Once a groundwater aquifer has been contaminated, there is little chance that it can be put to use for several lifetimes [2].

The study focuses on the evaluation of heavy metal dispersion in soil, using as a case study a tailings dam at Impala platinum mine, which is located to the north of Rustenburg, on the western limb of the Bushveld Complex (Fig. 1).

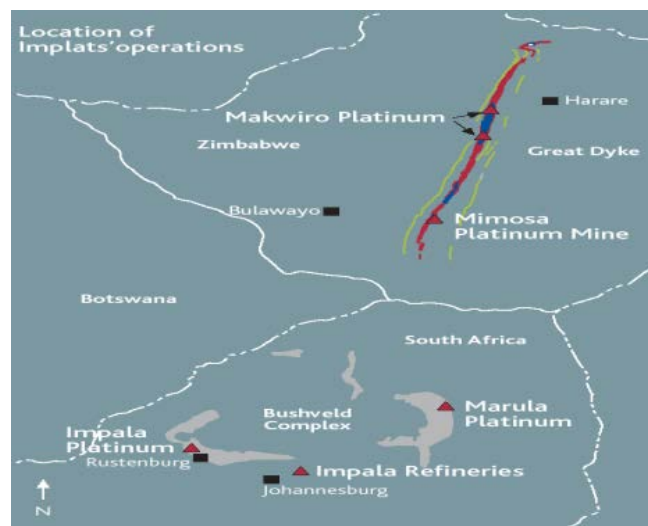


Fig. 1: Operations locations of Impala platinum mine

The Bushveld Complex contains two horizons, which are the sites of the Merensky and UG2 reefs, as shown in Figure 1. These two reefs are the host rocks for platinum group metals (PGMs), which are economically exploitable. The mineralogy of the two reefs is very complex. The Merensky consists of feldspathic pyroxenite, which lies between a footwall and hanging wall of anorthosite and norite respectively, with two layers of chromite stringers. The noble metals are usually associated with the two stringers [3]. The UG2 is a platiniferous chromitite seam that lies about 125 m below the Merensky reef, and comprises about 60–90 % of $[(Fe^{2+}.Mg)O(Cr.Fe^{3+}.Al)O_3]$ as shown in Fig. 2 [4].

The aim of this investigation was to evaluate the amount of heavy metals contaminants in platinum tailings dam environment. In this study, the soil samples of this site were analyzed to determine the concentrations of Al, Cu, Fe, Ni, Pb and Cr at various distances both in both vertical and horizontal directions at 500 m from the point of discharge. Avona variance statistical method was employed to determine the significant impact of these heavy metals contamination in these soil samples.

Manuscript received March 16, 2015; revised March 30, 2015.

Molebogeng Nkobane*, Ayo Afolabi and Ambali Abdulkareem are with the Chemical Engineering Department, University of South Africa, P/Bag X6, Florida 1710, Johannesburg, South Africa, (*Corresponding author: phone: +27 11 471 2156; e-mail: nkobamp@unisa.ac.za).

II. MATERIALS AND METHODOLOGY

Investigations were carried out to analyze the soil contaminated by heavy metals by collecting samples at a distance of 500 meters from the foot (outer edge) of the dam; the dam basin and sludge from the effluent pipe feeding waste into the dam. These locations are marked as points 1, 2 and 3 in Figure 2. The results of an analysis of these three samples by the ICP MS were used to provide a basic comparison of the occurrence of heavy metals in these three locations. They also served as points of reference for the assessment of the results obtained from sampling on sites at a distance from the tailings dam, so that the extent of soil contamination in the area surrounding the tailings dam could be determined.

Point 1: Pipeline connected to the metallurgical plant discharging tails into the dam.

Point 2: The dam basin.

Point 3: Location 500 m away from the edge of the dam.

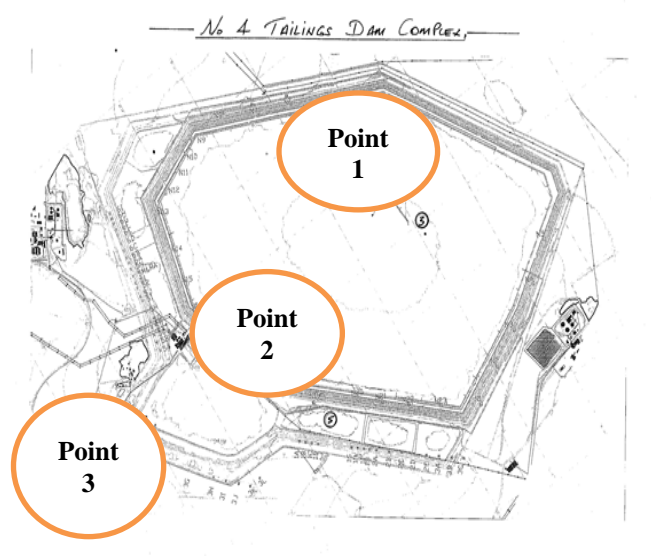


Fig. 2: Illustration of sampling locations near the tailings dam

A distance of 500 m from the outer edge of the dam in a straight line (point 3) in the direction of the water run off near the foot of the dam was measured before the samples were taken, the surface of the soil was scraped to remove any plant residue, as a preliminary to marking out a sampling grid in which three soil samples were taken spaced one metre apart, and at three levels of depth, as shown in Fig. 3.

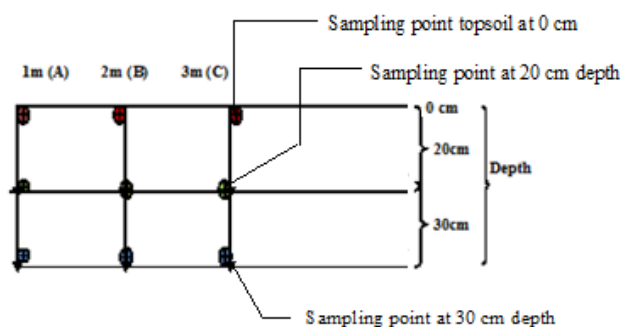


Fig. 3: Soil sampling pattern 500 m from the tailings dam

Nine (9) one-kilogram samples from the locations marked 500 m were taken and three sampling sites were

designated on the surface at one-metre intervals which was therefore 1, 2 and 3 m away from the marked point. These were identified as A, B and C respectively. Samples were taken from these sites at three different depths which were 0 cm for the surface layer, 20 cm for the second, and 30 cm for the third (thus, A at 1 m included the surface sample and the two layers below at 20 and 30 cm; B at 2 m refers to the same three layers and so on). The samples were tagged and bagged on site in clean colourless polyethylene bags to avoid contamination, and were then taken to the laboratory for analysis. In the laboratory, the samples were dried, ground in a 4mm jaw crusher, and split on a rotary splitter. They were then pulverized for six minutes. Sub-samples of 12 g each were removed from the well-mixed composite obtained from each sampling point, and these were each mixed with 3 g wax micro powder for binding. The mixture was then put into an Intelli-mixer at 99 rpm to ensure adequate blending.

The homogenized powder samples collected were then prepared for analysis by an inductively coupled mass spectrometer (ICP MS). First, each sample was subjected to a sequence of digestion procedures carried out in open vessels on a hot-plate. All samples were placed in digestion tubes in a block heater which was set at a temperature of 130°C. The heating continued for the duration of 14 hours. Then the samples were cooled for about 7 minutes. 30% hydrogen peroxide was added to each sample at a ratio of 1 mL per sample and the tubes were placed back onto the block heater for further heating which was between 20 and 30 minutes. The tubes were then taken off from the block heater and then cooled and 30% of hydrogen peroxide was then added and digested by reheating for another 20 - 30 minutes. Then the tubes were taken off from the block heater and 50 mL of water was added to each tube and these samples had to rest for 30 minutes or more. This process of digestion with different acids was to dissolve most of the silicate minerals and liberate most of the analyte. The resultant liquids was pipetted into the argon plasma of the ICP MS and analysed.

III. RESULTS AND DISCUSSION

The soil samples were analysed to determine the contents of the six heavy metals studied (Al, Fe, Pb, Cu, Ni and Cr). The results are presented both graphically and in table format. The F-test was applied (named after Sir Roger Fisher) to the findings on heavy metal concentration levels relative to the various distances and depths at which the samples had been taken for each of the six types under consideration. The F-test is a statistical tool by means of which a scientist can establish whether the data obtained are significant to his or her enquiry. The data obtained from the test were used to plot graphs of heavy metal concentration for each separate metal, which were compared in terms of both distance and depth. Both bar-type and line-type graph formats were used in order to establish trends that could be followed up in discussion. The statistical analysis tool ANOVA (analysis of variance) was then used to compare the results for the occurrence of each heavy metal.

The means, standard of deviation and variance for distance at 500 m at three different depth levels were calculated. The mean and standard of deviation of the differences obtained from these calculations using MS Excel were then used to calculate the 95% limits of agreement and the associated confidence limits for each metal. ANOVA

was used to determine the differences in mean concentration attributable to depth and distance.

The conditions of the test and equations used were as follows.

- **The null hypothesis, H_0** , is that the means of all members of the group are equal. $H_0: \mu_1 = \mu_2 = \mu_3 = \mu_4$. (In other words, the mean concentrations at varying distances are equal.)
- **The alternative hypothesis, H_1** , is that at least two of the group means are different.
- **The significance level of 5% is $\alpha = 0.05$ (95% probability):**

$$\bar{x} = \frac{\sum x}{n} \tag{i} [7]$$

$$\text{s.d.} = \sqrt{\frac{\sum (x - \bar{x})^2}{n}} \tag{ii} [7]$$

where; sd = standard deviation, x = sample, \bar{x} = sample mean, \sum = summation, n = sample size

The Anova table (Table I) shows the general format of an analysis of variance table.

TABLE I
ANOVA TABLE (FOR K GROUPS, TOTAL SAMPLE SIZE.....N)

Source	S.S	Degrees of freedom	M.S.S.	F
Between groups	SSG	k - 1	$\frac{SSG}{k-1} = MSG$	$\frac{MSG}{MSE} = F$
Errors	SSE	(N-1) - (k-1)	$\frac{SSE}{N-k} = MSE$	
Total	SST	N - 1		

Total variance = between systems variance + variance due to errors

- **SST**- Total sum of squares between systems
- **SSSys**- Sum of squares between systems or groups (SSG)
- **SSE**- Sum of squares of errors.
- **SSE** = SST - SSSys

In this table, the test statistic is the F-value calculated from the ANOVA table, which is then compared with the critical value read from the F-tables, $F_{\alpha}(v_1, v_2)$, with the given two degrees of freedom for the groups (v_1) and the errors (v_2). The two F values are then compared. The result of this process leads to either acceptance of the null hypothesis or its rejection.

Fig. 4 (a&b) indicates the different profiles of chromium behaviour in soil at various depths and distances for the 500 metre samples.

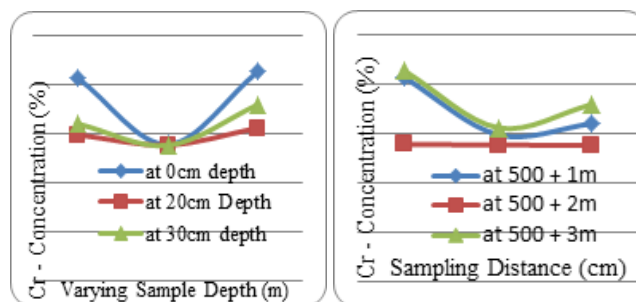


Fig. 4: Chromium variation in concentration at 500 m (a) depth (b) distance

The concentration of chromium was higher at 1 metre as compared to both 2 metre and 3 metre. 1 metre is a point closer to the dam and as the distance increases the concentration decreases at the furthest point from the dam this could be attributed to the fact that the nearer the sampling point is to the source of contamination (the dam), the higher the concentration of contaminant in the soil and in terms of varying depth the highest concentration is at 0 cm depth and this is in agreement with previously published reports on this subject which supported a decreasing order in chromium concentration in soil vertically [5]. Chromium most stable states are Cr (III) and Cr (VI), since the heavy metal exists in a number of oxidation forms. Cr (III) is the most prevalent form of chromium in most soils because it precipitates easily in soil aggregates, especially when the pH is greater than 6, and it is considered less mobile than other chromium states as it adheres strongly to soil aggregates [5].

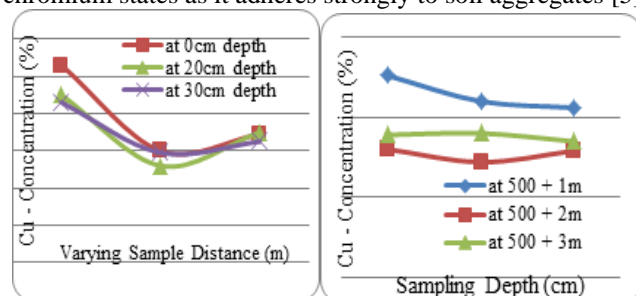


Fig. 5: Copper variation in concentration at 500 m (a) depth (b) distance

Similarly to the concentration of chromium, the copper concentration was higher at 1 metre as compared to both 2 metre and 3 metre. 1 metre is a point closer to the dam and as the distance increases the concentration decreases at the furthest point from the dam this could be attributed to the fact that the nearer the sampling point is to the source of contamination (the dam), the higher the concentration of contaminant in the soil and in terms of varying depth the highest concentration is limited to the upper 0 cm depth. Previous studies have shown that when soluble Cu is added to soil it reacts with phosphates, clays and organic matter, which reduces its solubility considerably and results in greater retention of copper in the soil. The results also show that Cu is abundant in the topsoil and is least concentrated in the 30 cm layer. Butkus and Grasso [6] explained this in terms of drying, which hinders Cu mobility and because the topsoil is dryer than the subsoil, the copper is concentrated in the top layer of the soil.

Fig. 6 (a & b) provide more detailed information on the presence of lead in the soil at various distances and depths.

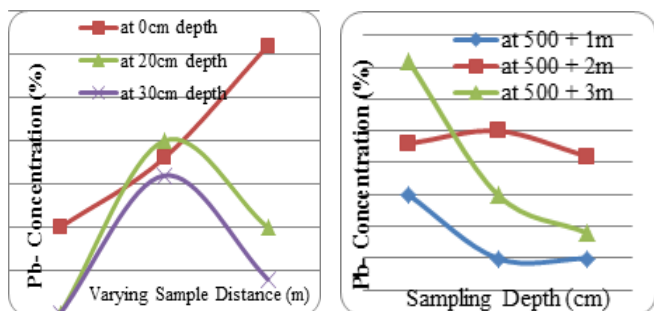


Fig. 6: Lead variation in concentration at 500 m (a) depth (b) distance

The lead (Pb) concentration declined slightly from the surface downward: in other words, the most significant contamination was limited to the surface of the soil.

Fig. 7 (a & b) present the different profiles of iron behaviour in soil at various distances and depths.

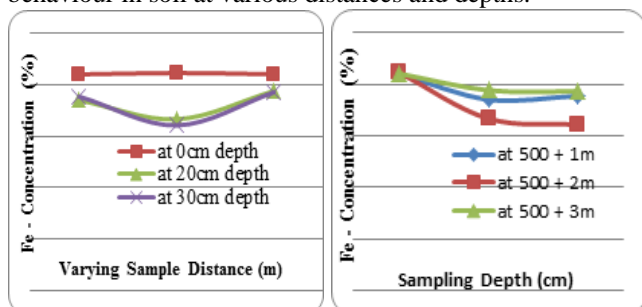


Fig. 7: Iron variation in concentration at 500 m (a) depth (b) distance

Iron is a common constituent of soils and groundwater. It participates readily in subsurface redox reactions, and under some conditions can cause problems in groundwater remediation systems. Iron occurs in higher concentrations in the effluent from the tailings plant, and is already present in the soil. Nonetheless an increasing order of agreement was found between the three sampled layers: most of the iron was found at the surface (0 cm).

Fig. 8(a & b) show the profiles of Al₂O₃ occurrence in soil at various distances and depths.

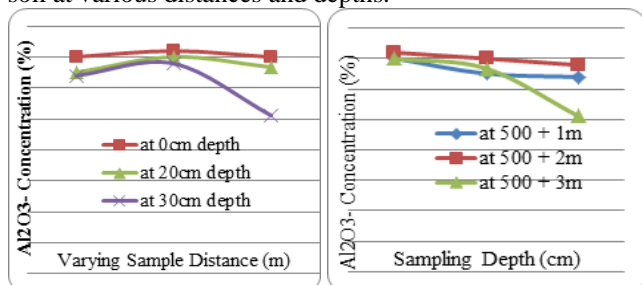


Fig. 8: Al₂O₃ variation in concentration at 500 m (a) depth (b) distance

Aluminium is strongly complexed in soils and most commonly occurs as Al₂O₃, which exerts a strong influence on the sorption of heavy metals through competitive effects and similarly to iron, aluminium has an increasing order of agreement which was found between the three sampled layers and most of them were found at the surface 0 cm.

Fig. 9(a & b) that follow which chart the profiles of nickel behaviour in soil at various distances and depths.

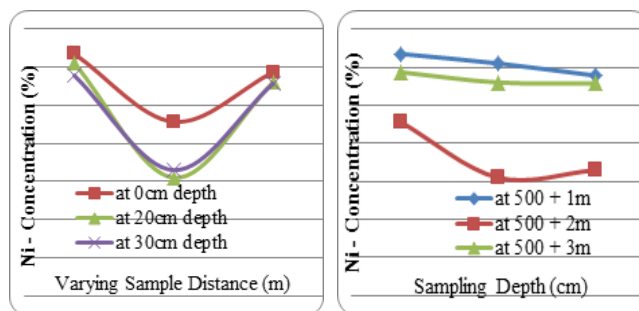


Fig. 9: Nickel variation in concentration at 500 m (a) depth (b) distance

TABLE II
ANOVA-F TEST VARIATION BY DEPTH AND DISTANCE

Samples at 500 m						
Variation by depth						
	Cr	Cu	Ni	Pb	Fe	Al
Distance (m)	500	500	500	500	500	500
F-Calculated	0.011	0.546	0.778	0.341	0.178	0.011
F-Table	5.14	5.14	5.14	5.14	5.14	5.14
Statement	Fcal < Ftab	Fcal < Ftab	Fcal < Ftab	Fcal < Ftab	Fcal < Ftab	Fcal < Ftab
Conclusion	Accept Ho there is no significant difference between the group means					
Variation by distance						
F-Calculated	0.027	0.073	0.011	0.175	0.096	0.027
F-Table	5.14	5.14	5.14	5.14	5.14	5.14
Statement	Fcal < Ftab	Fcal < Ftab	Fcal < Ftab	Fcal < Ftab	Fcal < Ftab	Fcal < Ftab
Conclusion	Accept Ho there is no significant difference between the group means					

The statistical analysis results for all six metals: chromium, copper, nickel, iron, aluminium and lead from the samples revealed that the group means are not significantly different from each other (Table II), which suggests that there is no significant difference in heavy metal concentration with respect to both depth and distance. The comparative average concentrations of the results obtained leads to the conclusion that the tailing dam does not introduce significant amounts of all these six heavy metals into the soils surrounding the dam.

IV. CONCLUSIONS

The analyses of the results of the evaluation of the heavy metal in platinum tailing dam site indicated that regardless of the manner in which heavy metals are introduced into the soil, the soil will generally act like a sieve and retain these metals. The migration of the heavy metals into groundwater or the atmosphere is normally not expected to occur as long as the retention capacity of the soil is not exceeded. In the soil, the extent of heavy metal movement in the y-direction (that is, horizontal to the surface) was found to be closely related to the chemical properties specific to each metal and solution on the surface.

The results also showed that there was no particular descriptive pattern showing the behaviour of each of these metals in soil. The findings all agreed with the same conclusion: that the group means did not differ significantly. The inference to be drawn is that the tailings dam does not introduce considerable amounts of the heavy metals and

there is no concentration profile for these heavy metals (Al, Fe, Pb, Cu, Ni and Cr) into the soils surrounding it.

The analyses of the results of study also showed that the concentrations of the six heavy metals at the tailings dam site followed the order Al>Fe>Cr>Ni>Cu>Pb. For samples taken at 500 m the Anova tests confirmed that the difference between the group concentration means for each metal with respect to depth (0 cm, 20 cm and 30 cm) was not significant. This was in agreement with the raw data analysis, which provided a concentration profile for each metal and led to the conclusion that the average means were very similar.

REFERENCES

- [1]O. Suruchi and M. Pankaj, Assessment of heavy metal contamination in different vegetables grown in and around urban areas. *Environmental Toxicology*, (5) (2011), 162-179
- [2]M. Olade, A. Van de Kraats and E. Ukpong. Effects of environmental parameters on metal dispersion patterns in stream sediments from the lead-zinc belt. *Geologie en Mijnb*, 58, (1978); 341-351.
- [3] C. Lee, A review of mineralization in the Bushveld complex and some other layered intrusions. In *layered intrusions. Elsevier*, (1996), 103-145.
- [4]C. Vermaak and L. Hendriks. A review of the geology of the Merensky reef, with specific reference to new data on the precious metal mineralogy. *Economic Geology*, 71, (1976); 1244-1269.
- [5] S. Smith, P. Peterson and K. Kwan. *Toxicology environmental Chemistry*, 24, (1989); 241-251.
- [6] M. Butkus and D. Grasso. *Environmental Engineering Science*, 16, (1999); 117.