Enrichment and Geoaccumulation of Pb, Zn, As, Cd and Cr in soils near New Union Gold Mine, Limpopo Province of South Africa

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Abstract Geo-accumulation index, enrichment factor, contamination factor and pollution load indexes were employed to evaluate Pb, Zn, As, Cd and Cr in soils near New Union mine dump. Arsenic and Cd were graded as unpolluted to moderately polluted whilst, Pb, Zn and Cr indicated no contamination (Igeo ≤0) in the soil. The EF values for Pb, Zn and Cr where attributed natural processes with no evidence of anthropogenic source. Meanwhile, As and Cd showed significant contamination in soil with CF>4. The PLI values for 95% of the sample sites were ≥1.5, which consequently indicated deterioration of soil quality.

Key words Geo-accumulation index, enrichment factor, contamination factor and pollution load indexes.

Introduction

Mining is one of the most important sources of toxic metals into the environment and mine tailing disposal may result in acid mine drainage and the release of metals of toxic levels that impact on human health and the environment (Davies and Rice, 2001). Many studies such as Forstner (1985), Giller et al. (1988), Kozak (1991) and Grzebisz et al. (2002) have shown that metals are extremely persistent in the environment, non-biodegradable and readily accumulate to toxic levels. Contamination of soil is a constant danger due to pollution by toxic metals resulting in the infertility and unsuitability of the soil for plant growth and thus affecting the organisms in the food web (Marques et al. (2011). These metals can accumulate to phytotoxic levels, especially in low pH soils and subsequently reduce plant growth and enter the food chain when plants are consumed by humans and animals (Chaney, 1993).

According to Du Plessis (2011), Potgieter and De Villiers (1986), New Union mine operated from 1935 to 1998 in the Giyani greenstone belt under various mining companies such as Northfields Gold Pty Ltd, New Union Gold, Noorde and Offspring mines until exhaustion of the underground gold ore. The gold mined was associated with sulphides such as pyrrhotite ($Fe_{1-X}S$), arsenopyrite (FeAsS), and (ZnS) sphelerite (Gan et al. 1986). A study by Mulugisi et al. (2009) and Mitileni et al. (2011) indicated elevated concentration of Pb, Cr, Cd, As and Zn at the mine tailings dump. Moreover, the tailings dam is thinly covered by vegetation and susceptible to water and wind erosion which may consequently enrich the surrounding environment with toxic metals. This study focused on the study of metal contamination (Ni, Cu, Pb, As, Cd and Cr) in the vicinity of New Union mine dump. The assessment of soil contamination was based on Geo-accumulation index (Igeo), enrichment factor (EF), contamination factor (CF) and pollution load indexes (PLI). The data on the distribution of these metals in soils near the mine dumb could provide valuable information on risk and exposure assessment of communities near the mine site.

Methods

Site Description

The area is located 10 km east of Malamulele town which lies between Giyani and Thohoyandou towns and falls under Thulamela Municipality and Vhembe District in Limpopo Province. It is also located < 1 km east of Madonsi Village and climate of the area is subtropical with hot and rainy summers and short cool and very dry winters. Lowest rainfall of 3 mm occurs mainly in July and highest 139 mm in January with average midday temperature range of 23°C in June and 30.5°C in January (SAWS, 1980-2003). Lithological assemblages include mafic and ultramafic sequences such as chlorite schist, talc schist, tremolite-actinolite schist, and amphibolite schist which are rich in seperntinites and pyroxene (Potgieter and De Villiers, 1986). Meta-quartzite, banded ironstones, are also prominent throughout the area.

Soil sampling

Surface soils samples were collected from a depth of 10-30 cm around the tailings dam and the sample spacing being 100 m. At least 20 samples around the mine dumb whilst, an additional 2 were collected 10 km from the tailings dam to represent background metal concentration. In all, 22 samples of approximately 2 kg of each were collected using a steel spade and stored in sealed polythene bags and transported to the laboratory for pre-treatment and analyses.

Chemical Analysis

The samples were oven dried at 105-110°C, sieved to -2 mm and then milled to 85% -75 µm. Weights of 10 g were digested in 60 ml freshly prepared aqua regia (1:3 HNO_3: HCl) on a hot plate for 2 hours. Standard stock solutions for all the elements were procured from Merck (Pty) Ltd South Africa and prepared in the laboratory for instrument calibration. The glassware used were thoroughly cleaned with deionised water and diluted nitric acid to remove any impurities. In addition, internal data quality control procedures were followed, that include in-cooperation of certified reference standards (CRMs) and blanks. The total concentrations of Ni, Cu, Pb, As, Cd and Cr were then determined using a Flame Atomic Absorption Spectrometer (AAS PerkinElmer Analyst 400).

Contamination Assessment Methods

Enrichment factor (EF) and Geoaccumulation index (Igeo) defined by Muller (1969) were used for assessment of soil contamination in the vicinity of the tailings dumb. Enrichment factor (EF) can be used to differentiate between the metals originating from anthropogenic activities and those from natural sources. Enrichment factor of the metals was calculated as the ratio of elemental concentration of sediment normalized to a reference Zr. The reference element is often the one characterized by low occurrence variability, such as the most commonly used elements; Aluminum (Al), Zirconium (Zr), Titanium (Ti), Iron (Fe) and Scandium (Sc) as stated by Reiman and Decarital (2000), and Blaser et al. (2000). The enrichment factor was calculated using the formula originally introduced by Buat-Menard and Chesselet (1979)

$$\boldsymbol{E} = \frac{C_x / C_{ref}}{B_x / B_{ref}} sample \qquad \text{(i)}$$

where:

Cx = content of the examined element in the examined environment, C*ref* = content of the examined element in the reference environment, Bx = content of the reference element in the examined environment and Bref= content of the reference element in the reference environment. Five contamination categories of EF were used in the study and a subsequent increase in EF values could correspond to the contributions of the anthropogenic origin of contamination (Sutherland, 2000) as foloows:

- EF < 2 is deficiency to minimal enrichment
- EF 2-5 is moderate enrichment
- EF 5-20 is significant enrichment
- EF 20-40 is very high enrichment
- EF > 40 is extremely high enrichment

Aquantitative measure of the extent of metal pollution in the studied soil was calculated using the geo-accumulation index proposed by Muller (1969), Abrahim and Parker (2008) as shown on below (tab. 1). This index (Igeo) of metal is calculated by computing the base 2 logarithm of the measured total concentration of the metal over its background concentration using the following mathematical relation (Muller, 1969):

$$I_{geo} = \log_2 \frac{Cn}{1.5 \times Bn} \qquad \text{(ii)}$$

Where C*n* is the average concentration of metal in the soil and B*n* is the background concentration of the metal. The factor 1.5 was introduced to minimize the effect of possible variations in the background values which might be attributed to lithologic variations in the soils.

Table 1 *The degree of metal pollution in terms of seven enrichment classes.*

I_{geo} Value	I_{geo} Class	Designation of sediment quality
>5	6	extremely contaminated
4-5	5	strongly to extremely contaminated
3-4	4	strongly contaminated
2-3	3	moderately to strongly contaminated
1-2	2	moderately contaminated
0-1	1	uncontaminated to moderately contaminated
<0	0	Uncontaminated

In order to give proper assessment of the degree of contamination, attempts were made to calculate the pollution load indexes (PLI) using the Thomilson et al. (1980) approach. The PLI represents the number of times by which the metal content in the soil exceeds the average natural background concentration, and gives a summative indication of the overall level of metal toxicity in a particular sample. The control samples were taken to represent natural background. The PLI of the place are calculated by obtaining the n-root from the n-CFs that was obtained for all the metals as follows;

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \ldots\ldots \times CF_n)^{1/n} \quad \text{(iii)}$$

Where, n is the number of metals (n = 5 in this study). PLI<1 implies that the site is free from contamination whilst, PLI = 1 implies to base line level of pollution and PLI> 1 = deterioration of site quality. The CF represents the individual impact of each trace metal on the soils obtained using the equation;

$$CF = \frac{C_n}{C_{ref}} \quad \text{(iv)}$$

Where C_n represents metal concentration in the studies environment and C_{ref} being the metal concentration in the background environment.

Results and Discussion

Metal Concentrations

Summary of the minimum, maximum, mean, standard deviation and median concentrations of Pb, Zn, As, Cd and Cr in 20 soil samples collected around New Union gold mine (tab. 2). The elements' dominance was in the order: Cr >As >Zn> Pb > Cd. The range of concentration (mg/kg) of metals in the studied areas were: Pb (7-26); Zn (8-75); As (5-47); Cd (0.4-0.8) and Cr (2-228). Arsenic and Cd were between 5 to 6 times above the normal soil level of 6 and 0.1 mg/kg (Bowen, 1979). The maximum Arsenic levels of 47 mg/kg were more than twice the WHO (2001) threshold of 20 mg/kg. Similarly, the maximum levels of Pb and Zn of 26 and 75 mg/kg was about four and two times more than the national threshold of 7 and 47 mg/kg respectively, but below the WHO (2001) limit of 50 and 300 mg/kg respectively. Since the contents of metals in soils are specific and depend on the lithology producing soil and the conditions of soil formation for determination of pollution level, the obtained results were also compared with the control sample which was considered as a background.

Table 2 *Basic statistical parameters for the distribution of metals at new Union mine (units are mg/kg).*

Variables	Pb	Zn	As	Cd	Cr
Minimum	7	8	5	0.4	2
Maximum	26	75	47	0.8	228
Mean	12	26	27	0.63	65
Median	12	25	27	0.6	49
Standard deviation	3.90	14.22	9.25	0.14	61.02
Average normal soil (Bowen, 1979)	14	90	6	0.1	-

Contamination Evaluation based on Geoaccumulation Index

The Igeo was used to calculate metal contamination level in the soils (fig. 1). The mean Igeo values for all metals ranged from -5.66 to 2.06, suggesting that some soils were not contaminated whilst, others were moderately contaminated. The Igeo values for Pb and Zn showed all the samples as uncontaminated class ((≤ 0). Chromium indicated only four sample locations as uncontaminated to moderately contaminated (classes 1 and 2 respectively). Igeo values for Cd indicated 95% of the samples being uncontaminated to moderately contaminated (classes 1 and 2) and similarly, As showed all sample locations being uncontaminated to moderately contaminated. However, there was no definable Igeo trends with distances ranging from 100 to 500 m from the tailings dump. This may be attributed to differences in the soil matrix such organic matter, changes in pH and redox potential.

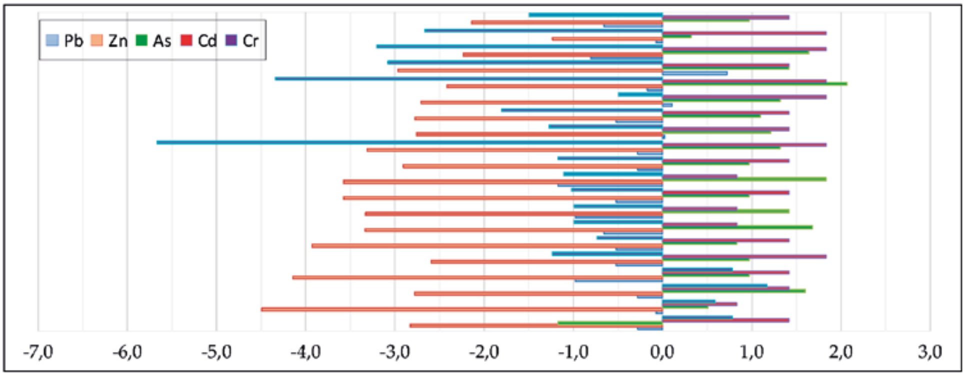

Figure 1 *The degree of metal pollution of soil samples according to the Geoaccumulation index.*

Enrichment Factor Analysis

The EF values for the studied metals obtained in this study are shown below (fig. 2). The control sampling point was considered to be the unpolluted or background point. The EF values for Pb, Cr and Zn observed in the present study were found not exceeding the level of moderately enriched with the EF values < 5. In general, it was found that the surface sediments were negligibly enriched with these metals. However, As and Cd indicated significant enrichment with EF mean of 6 and 7 respectively. The maximum EF values for these metals were 11 and 9 and consequently signifying significant soil enrichment by these metals. The findings also showed that all of the studied metals were evenly deposited throughout the sample stations. High As and Cd levels in sediments are detrimental to plants and can be transmitted through the food chain to higher organisms such as humans.

Contamination factor and Pollution load indexes The Pollution Load Index (PLI) calculated from CF indicated that the soils were uncontaminated, moderately to heavily contaminated by investigated metals. The values ranged from 0.97 to 2.63 indicating that some of the studied metals exceeded the background metal concentration. The overall contamination of soils at the site assessed based on CF indicated considerable contamination by Cd and As, moderately contamination by Pb, but showed no contamination by Zn and Cr (CF<1.5). On the basis of the mean values of CF, sediments were enriched with metals in the following order: Cd >As>Pb>Cr>Zn. This clearly indicated that the soils near New Union mine have been largely polluted by Cd and As which are projected to have been contributed directly and indirectly from the nearby mine dump. The highly contaminated sites with PLI>1.5 is mostly due to the mining activity where the metal occurs as a vital component in arsenopyrite present in the gold ores in the area (Gan and van Reenen, 1995) and Billay et al. (2008).

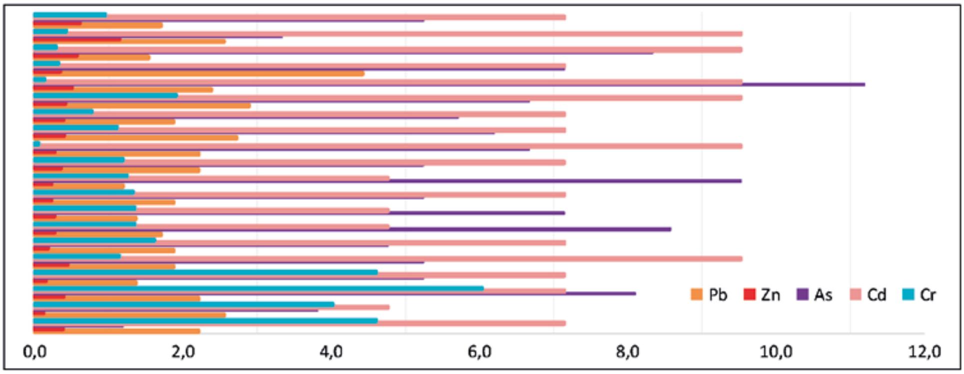

Figure 2 *Enrichment Factor of Pb, Zn, As, Cd and Cr in soils near New Union Gold Mine.*

Conclusion

Anthropogenically and geogenically impacted soils around New Union mine were assessed using geoaccumulation index, enrichment factor, contamination factor and pollution load indexes. The mean concentrations of metals in in the vicinity of the mine decreased in the following order Cr >As >Zn> Pb > Cd. Based on the Igeo, the soil was graded as unpolluted to moderately polluted with As and Cd whilst, being free from contamination by Pb, Zn and Cr (Igeo ≤ 0). Although the nature of calculating geoaccumulation indices (Igeo) is somewhat different from pollution calculation methods discussed in this study, the Igeo obtained from the studied metals are generally comparable to results reported for EFs and CFs. The EF values for Pb, Zn and Cr showed that these metals were derived mainly from natural processes or geogenic sources and were related to the exposure of the Earth's crust material, with no evidence of the tailings dump impacts. However, As and Cd indicated significant enrichment with a maximum EF values of 11 and 9 respectively. Arsenic and Cd also showed significant contamination in soil and made contribution to contamination of the soil expressed by contamination factor, CF (CF>4). The PLI values for almost all the 20 sites were ≥1.5, which indicated deterioration of soil quality. Since induced pollution can pose serious threats to water, soil, fauna, flora and undoubtedly human health of the area nearest to the mine site, calculating the CF and PLI from the pollution source and wind direction can provide more reasonable results. This study recommended an immediate plan for analysis of the quality of drinking water and some staple crops grown in the area to determine the levels of these noxious metals and uptake by plants, to be followed by a comprehensive mitigation or remediation plan.

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