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# Chapter

# Evaluation of Trace Elemental Levels as Pollution Indicators in an Abandoned Gold Mine Dump in Ekurhuleni Area, South Africa

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# **Abstract**

In the Blesbokspruit area of Ekuhurleni, South Africa, previous gold mining activities resulted in many tailings dump sites. 20 representative soil samples were used in describing the distribution of metals. The soils were very strongly acidic ranging from 3.86 to 4.34 with a low cation exchange capacity (CEC). Based on X-ray fluorescence (XRF) analysis, elemental composition of the soils revealed average values of major elements such as Na2O (0.18%), MgO (0.63%), Al2O3 (6.51%), SiO2 (81.83%), P2O5 (0.04%), SO3 (3.40%), K2O (1.98%), CaO (0.45%), TiO2 (0.51%), Cr2O3 (0.17%), MnO (0.04%), Fe2O3 (3.59%), NiO (0.04%), As2O3 (0.02%), with Rb2O and SrO falling below 0.01%. Trace metals (TM) contamination levels in the soils were evaluated using various pollution indices which revealed that over 60% of the soils were between the high degree and the ultra-high degree of contamination classes. The concentration of various trace metals varies from 860.3-862.6 mg/kg for Cr; 324.9-328.4 mg/kg for Al; 200.9-203.4 mg/kg for As; 130.1–136.2 mg/kg for Fe; 121.9–125.8 mg/kg for Pb; 27.3–30.2 mg/kg for Co; 23.8–26.8 mg/kg for Ni; 7.2–9.2 mg/kg for Ti; 7.1–9.2 mg/kg for Cd; 4.0-5.6 mg/kg for Zn and 0.1-0.6 mg/kg for Cu.

**Keywords:** mine tailings, trace metal, pollution, contamination factor, geoaccumulation index

#### 1. Introduction

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South Africa like other developing countries is faced with the challenges of environmental degradation via the continuous release into the environment of trace element-containing chemicals through urbanization, agricultural and mining activities, as well as industrialization. Trace metals (TM) are naturally occurring elements that have a high atomic weight and a density at least 5 times greater than that of water, and some of the commonly found ones particularly at contaminated sites include Arsenic (As), Cadmium (Cd), Chromium (Cr), Copper (Cu), Lead (Pb),

Mercury (Hg), Nickel (Ni) and Zinc (Zn) [1, 2]. Attempts towards the assessment, mechanism and the characteristics of trace metal pollution in surrounding areas of mines has been and continue being a theme of various scientific gatherings.

Globally, the extraction and distribution of minerals from ore deposits has been one of the actions that contribute to environmental degradation due to industrialization. The extraction and beneficiation processes often result in the release of tailings that end up in natural percolations within the earth crust, thus paving a way for various kinds of risk elements entering the ecosystem. Such practices result in serious environmental complications due to the elevated concentrations and accumulation of trace metals which poses risk for human health [3–7].

The mining and processing of gold is associated with certain elements such as Copper (Cu), Antimony (Sb), Nickel (Ni), Selenium (Se), Mercury (Hg), Thallium (Tl), Titanium (Ti), Zinc (Zn), Silver (Ag), Cobalt (Co), Lead (Pb) and Uranium (U). Most of these metals are somewhat released into the environment via trophic links ranging from agricultural soils to plants, animals and humans [8–10].

Pollutants from various anthropogenic activities ranging from mine effluents such as wastewaters, tailings, runoff from agricultural pesticides and atmospheric deposition often contaminate the surrounding soils and water bodies thus posing threat to the ecosystem and humans. This occurs via direct ingestion or contact with contaminated soil, the food chain (soil–plant-human or soil–plant–animal-human), drinking of contaminated ground water, reduction in food quality (safety and marketability) via phytotoxicity, reduction in land usability for agricultural production causing food insecurity, and land tenure problems [11, 12]. In humans, several health challenges such as abortion, cancer, kidney damage and sometimes death, are some of the consequences of prolonged exposure to extreme concentrations of trace metals [13].

The importance of soil cannot be over emphasized as it is characterized as a complex and dynamic system that is made up of sediments that are different in relation to their physical, chemical, mineralogical and biological constituents. Soil is an essential resource for natural living conditions of plants, animals and humans. The role of soil as a collector filter of both organic and inorganic residues helps in protecting groundwater and in the sequestration of toxic materials [14]. The accumulation of excess metals and metalloids in soils over an extended period exposes humans and other animals to toxicity [15]. Assessing the spatial distribution of trace metals is soil is crucial to obtaining basic information about areas of concerns and to prioritize site mitigation strategies [16]. However, the quantification of element concentrations in soil as a single parameter is not enough in evaluating the extent of contamination due to differentiation between natural background levels and anthropogenic enrichment [3]. Indexes including geoaccumulation index ( $I_{geo}$ ) and contamination factor (CF) which are known to provide a better picture of the status of elemental contamination compared to the background concentration were used as pointers in identifying and quantifying the level of elemental pollution as well as the intensity of anthropogenic contaminants accumulated in the soil.

There are enormous impacts of mine tailings disposal sites with over 500,000 abandoned hard rock mines located in the United States, while Mexico alone is affected by 27.1 million hectares of mining activity [17–19]. Gold mine waste was reported in 2001 by South Africa's Department of Water Affairs and Forestry as the largest single source of waste constituting over 47% of mineral wastes generated in South Africa [20]. Previous studies indicate that there are close to 300 unlined and not vegetated tailings dumps covering over 400 km² surface area within the Witwatersrand Basin of the Republic of South Africa. With tailings dumps being a major source of contaminants, the Witwatersrand Basin's massive tailing dumps are a possible, environmental pollution threat [21]. Studies into the deposits in the mine regions of

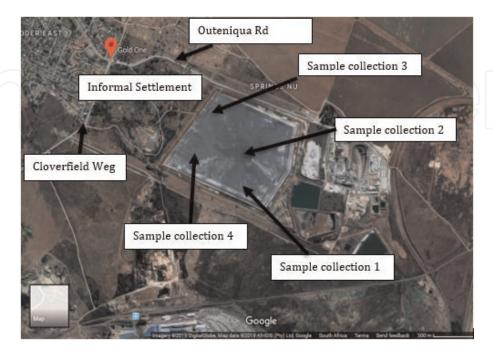
the Gauteng province of South Africa [17], revealed the deposits to be of great health concern; containing enormous amounts of toxic metals, such as U, As, Ra, Ni, Zn, etc.

Hence, this present study was aimed at determining the contamination level of identified trace metals in an abandoned mine tailing dump over time. In addition, findings from this study will assist the various stakeholders in resource management and policy implementation.

# 2. Materials and methods

# 2.1 Description of the study area

South Africa lies on the southernmost part of the African continent, and is known to have renowned varied topography, great natural beauty, and cultural diversity. It is a medium-sized country, with a total land area of 1,219,090 square kilometers. Ekurhuleni falls within the East Rand region and is characterized by rainfall known to be typical to the Highveld summer rainfall, which occurs from October to April. The average annual rainfall varies from 715 to 735 mm an indication that the study area has a distinct moisture deficit. Frost does occur frequently from mid-April to September, which makes temperatures below freezing common during winter times. This area is home to mild summers with temperatures seldom above 30°C. During spring and winter, northerly and north-westerly winds occur and during summer north-easterly to north-north-easterly winds occur [22]. There are many pans across the Ekurhuleni area. These pans cover a total area of 3559 hectares within the Ekurhuleni Metropolitan Municipality area and are mostly seasonal. There are also a few lakes created by mines, which are used for recreational parks. Germiston Lake, Benoni Lake and Boksburg Lake are the three main lakes used for recreational purposes within the Ekurhuleni Metropolitan Municipality area, but which fall outside the East Rand Basin area. The tailings dump has some informal settlements within its proximity with subsistence farming among the dwellers as shown in **Figure 1**. The specific description indicating coordinates of the



**Figure 1.** *Location of the sampling site.* 

Station no.	Latitude (S)	Longitude (E)
1	26 <sup>0</sup> 10 <sup>′</sup>	28° 27′
2	26 <sup>0</sup> 15 <sup>′</sup>	28° 35′
3	26 <sup>0</sup> 04 <sup>′</sup>	28° 40′
4	26 <sup>0</sup> 17 <sup>′</sup>	28° 44′
5	26 <sup>0</sup> 21 <sup>′</sup>	28° 50′
6	26° 30′	29 <sup>°</sup> 10 <sup>′</sup>
72	26° 00′	29° 15′
8	26 <sup>0</sup> 27′	29° 20′
9	26° 09′	29° 35′
10	26 <sup>0</sup> 38′	29 <sup>0</sup> 42 <sup>'</sup>
11	26 <sup>0</sup> 43 <sup>′</sup>	29° 47′
12	26 <sup>0</sup> 34 <sup>′</sup>	29° 50′
13	26 <sup>0</sup> 13 <sup>′</sup>	29 <sup>0</sup> 53 <sup>'</sup>
14	26 <sup>0</sup> 19 <sup>′</sup>	30° 10′
15	26° 48′	30° 15′
16	26 <sup>0</sup> 36′	30° 25′
17	26° 40′	30° 29′
18	26 <sup>0</sup> 14 <sup>′</sup>	30° 35′
19	26 <sup>0</sup> 23 <sup>'</sup>	30° 40′
20	26° 54′	30° 48′

Table 1.
Location of the Blesbokspruit gold mine tailings sediment samples.

sampling site located along Outeniqua Road & Cloverfield Weg in Springs, Ekurhuleni are illustrated in **Table 1**.

# 2.2 Sampling (material) description

In a bid to assess the level of trace metal contamination in the mine tailings, about 2 kilograms of 20 representative tailing samples were obtained from the dump. Preceding the removal of top tailing samples (2 cm) using an auger, samples were taken at a depth of 10 cm for every 50 m horizontal interval for a wider coverage. The collected soil samples (tailings) were kept cool in an icebox (<4°C) and transported to the laboratory for further analyses in sterile plastic bags.

# 3. Analysis

# 3.1 Experimental analysis

20 representative tailing samples of about 5 g each were oven dried at 100°C for 24 hours and passed through a 2 mm sieve. Aliquots of approximately 2 g of the various tailing samples were weighed into a Teflon crucible and moistened with 100 mL of 1 M HCl acid for the determination of the HCl-soluble fraction of heavy metals. The mixtures were covered and placed on a shaker for 12 hours at 130 rpm.

The solutions were filtered through a Whatman filter paper, and the filtrates were stored in sterile bottles prior to analysis of minerals using inductively coupled plasma-optical emission spectrometry (ICP-OES).

10 g each of the representative tailing samples were pelletized using a mold at very high pressure and then placed in the sample compartment of the X-ray fluorescence spectrometer (XRF; Rigaku ZSX PrismusII). This was done to analyze the major and trace element oxides of the tailing samples.

Physicochemical properties such as pH and EC (electrical conductivity) of the soil samples (tailings) were measured in a soil-to-water suspension (1,2.5, w/w) and a 1:5 tailings-to-water suspension using a Crison multimeter (model MM 41) respectively [23]. Loss on Ignition (LOI) analysis was used to determine the organic matter content (% OM) of the various tailing's samples [24]. The grain size distribution of tailing samples was determined using the hydrometer method [25].

# 3.2 Quality assurance and quality control

Apparatus and glassware used were acid-washed with 5% nitric acid for precision analysis while reagents were of analytical standard. The trace metals were determined using ICP-OES (Model - GBC Quantima Sequential) operated under specific conditions of 1300 W RF power, 15 L min $^{-1}$  plasma flow, 2.0 L min $^{-1}$  auxiliary flow, 0.8 L min $^{-1}$  nebulizer flow, 1.5 mL min $^{-1}$  sample uptake rate. Multiple levels of calibration standard solutions prepared from a Certipur ICP multi-element standard (Merck KGaA) was used in the calibration of the ICP-OES. Metal determination was done using Axial view, while 2-point background correction and 3 replicates were employed in the measurement of analytical signal. The emission intensities were determined for the most sensitive lines free of spectral interference. By diluting the stock multi-elemental standard solution (1000 mg L $^{-1}$ ) in 0.5% (v/v) nitric acid, the calibration standards were prepared. The calibration curves for all the studied elements were in the range of 0.01 to 1.0 mg L $^{-1}$ .

## 3.3 Data analyses

The history and degree of trace metal pollution in an environment can be ascertained from the surrounding sediments by comparing the pollutant metal concentration with an unpolluted reference material. The average shale concentration as an International standard reference for unpolluted sediment was utilized [26]. This study applied pollution indices such as (i) metal contamination factor, (ii) contamination degree, (iii) index of geoaccumulation, and (iv) pollution load index to assess heavy metal contamination.

## 3.3.1 Assessment according to contamination factor

By calculating the ratio of the concentration of a specific trace metal in the study area and the concentration of the background concentration of the corresponding metal, the contamination factor was determined. **Table 2** shows the various terminologies in describing contamination factor class and level [27]. CF is an effective tool for monitoring pollution over a period and for the respective metals was calculated using the equation as prescribed by [28].

$$CF = \frac{(\textit{Mean metal concentration at contaminated site } (\textit{Cm}))}{(\textit{Level of pre-industrial concentration of individual metal } (\textit{Cbackground}))}$$

CF	Description
CF < 1	Low contamination factor
1 ≤ CF < 3	Moderate contamination factor
3 ≤ CF < 6	Considerate contamination factor
CF ≥ 6	Very high contamination factor

**Table 2.** *Terminologies used to describe contamination factor* [27].

# 3.3.2 Assessment according to contamination degree

Contamination degree (CD) refers to the sum of all the contamination factor (CF) values of a specific sampling site. It is a diagnostic tool aimed at providing a measure of the degree of overall contamination in surface layers in a sampling site or core. In this study, CD was assessed using Eq. (2).

$$CD = \sum_{i=0}^{n} cf \tag{2}$$

A list of terminologies as prescribed by [29] used in describing the contamination degree of the site under investigation is summarized in **Table 3**.

# 3.3.3 Assessment according to geoaccumulation index

To quantify the level of heavy metal contamination associated with the study site, the geoaccumulation index (I-geo) was adopted. The  $I_{\rm geo}$  is an important method used for the interpretation of the quality of sediments in the sampling site. It is used to assess impacts due to anthropogenic activities and was determined using Eq. (3) as prescribed by [30].

$$I_{geo} = \log_2 \frac{Cn}{1.5Bn} \tag{3}$$

where  $C_n$  is the measure of the metal concentration in the examined metal n in the sediment, Bn is the background concentration of the element (average shale concentration) or reference value of the metal n, and 1.5 is the correction factor due to the lithogenic effect that could result in variations in the background values for a given metal in the environment. There are seven grades (0–6) ranging from unpolluted to highly polluted in the geoaccumulation index scale as described by [30] (**Table 4**).

CD	Description
CD < 6	Low contamination degree
6 ≤ CD < 12	Moderate contamination degree
12 ≤ CD < 24	Considerate contamination degree
CD ≥ 24	Very high contamination degree

**Table 3.**Terminologies used to describe contamination degree for soil [29].

$I_{geo}$ Value	Class	Contamination Level
$I_{geo} \le 0$	0	Uncontaminated
0 < I <sub>geo</sub> < 1	1	Uncontaminated/moderately contaminated
1 < I <sub>geo</sub> < 2	2	Moderately contaminated
$2 < I_{\text{geo}} < 3$	3	Moderately/strongly contaminated
$3 < I_{geo} < 4$	4	Strongly contaminated
4 < I <sub>geo</sub> < 5	5	Strongly/extremely contaminated
$5 < I_{geo}$	6	Extremely contaminated

**Table 4.**Classification for the geoaccumulation index (Igeo) [30].

# 3.3.4 Assessment according to pollution load index

Pollution load index, which is a useful tool in heavy metal pollution evaluation, refers to the number of times by which each heavy metal concentrations in the sediments (tailings) exceeded the background concentration in the soil, and it provides a summary of the overall level of heavy metal toxicity in a sample. The world average concentrations of metals using shale was used as background for identified heavy metals in this study [26]. The PLI can provide an estimate of the various metal contamination status and precautionary steps to be taking [31]. Using Eq. (4) as developed by [26], the PLI of the study site was calculated by obtaining the nroot from the n-CFs that was obtained for all the metals.

$$PLI = (CF1 \times CF2 \times CF3 \times ... \times CFn)^{1/n}$$
(4)

where CF is the contamination factor, CFn is the CF value of metal n, and n is the number of metals.

Interpretation of PLI values are categorized into two levels; polluted (PLI > 1) and unpolluted (PLI < 1) whereas PLI = 1 indicate trace metal loads close to the background level [32].

# 3.3.5 Assessment according to the United States environmental protection agency

The potential contamination of the tailing's sediments was evaluated using the proposed sediment quality guidelines by USEPA [19] **Table** 5. Illustrated the various criteria.

Metal	Not polluted	Moderately polluted	Heavily polluted	Present study
Cd	_	_	>6	7.1
Cr	<25	25–75	>75	860.3
Cu	<25	25–50	>50	0.1
Pb	<40	40–60	>60	121.9
Zn	<90	90–200	>200	3.9

**Table 5.**USEPA guidelines for sediments (mg/kg dry weights) in comparison with gold mine tailings sediments.

# 4. Results and discussion

# 4.1 Soil physical properties

Textural properties obtained from sieve analysis of the gold mine tailings sediments using classification as prescribed by [25] are presented in **Table 6**. These results reveal that fine sand (0.150–0.075 mm) and clay (0.075–0.053 mm) were the principal fractions of all sediment samples, with an average composition of 66.03% for fine sand, 23.08% clay and 10.89% silt respectively. With the larger portion of the sediments being fine sand, there is a likelihood for nutrients accumulation is high due to the higher surface-to-volume ratios [33].

Geochemical properties of the sediments such as the pH, EC and carbonate content (see **Table** 7) helps in ascertaining vital information to comprehend the soils potential to withhold heavy metals [34]. The results obtained for the sediment pH measurements, showed that the study area is very strongly acidic ranging from 3.86 to 4.34. The low pH values in the study area were related with heterogeneous deposits of sulfidic residues from the mine surroundings, which resulted in low pH values that is attributed to microbial sulfide oxidation and the resultant formation

Sample no.		Sieve size (ASTM) % Materials; Retains (gms)											
	No. 100	No. 140	No. 200	No. 270	PAN	TOTAL	% Sand	% Silt	% Clay				
1	5.68	45.51	15.84	10.25	22.72	100	67.03	10.25	22.72				
2	5.75	46.82	13.79	10.58	23.41	100	66.01	10.58	23.41				
3	5.40	46.52	13.61	10.62	23.85	100	65.53	10.62	23.85				
4	5.37	45.84	14.71	11.25	22.83	100	65.92	11.25	22.83				
5	5.42	45.93	13.93	11.81	22.91	100	65.28	11.81	22.91				
6	5.39	47.88	13.01	11.20	22.52	100	66.28	11.20	22.52				
7	5.42	48.23	11.87	10.78	23.70	100	65.52	10.78	23.70				
8	5.88	46.38	13.42	10.44	23.88	100	65.68	10.44	23.88				
9	5.94	46.82	13.00	10.32	23.92	100	65.76	10.32	23.92				
10	5.66	44.46	16.15	10.58	23.15	100	66.27	10.58	23.15				
11	5.86	47.20	14.22	9.88	22.84	100	67.28	9.88	22.84				
12	5.42	45.30	15.83	11.32	22.13	100	66.55	11.32	22.13				
13	5.38	45.92	13.68	11.84	23.18	100	64.98	11.84	23.18				
14	5.62	46.34	13.74	10.68	23.62	100	65.70	10.68	23.62				
15	5.48	46.82	13.81	10.31	23.58	100	66.11	10.31	23.58				
16	5.23	46.92	14.81	10.22	22.82	100	66.96	10.22	22.82				
17	5.98	48.22	11.62	11.69	22.49	100	65.82	11.69	22.49				
18	5.36	48.80	11.78	11.38	22.68	100	65.94	11.38	22.68				
19	5.92	48.24	11.34	11.75	22.75	100	65.50	11.75	22.75				
20	5.68	47.36	13.37	10.94	22.65	100	66.41	10.94	22.65				

**Table 6.**Sieve analysis of the gold mine tailings sediment samples.

of sulfuric acid [35]. Nutrient uptake by plants may be inhibited by the level of acidity as most plant nutrients are optimally available to plants within 6.5 to 7.5 pH range which also support plant root growth [36]. The low CEC values which correlates with the high proportion of sand fragment is an indication that the sediments may likely not have reliable soil sorption capacity [37]. LOI of studied soils were in the range of (5.0–5.4%)-dry weight, which could be, attributed to growing plants within the tailing's sediments.

## 4.2 Metal content

The summary of the determined heavy metal concentrations within the sediments of the study area by using ICP-OES are presented in **Table 8**. The concentration of various heavy metal varies from 860.3–862.6 mg/kg for Cr; 324.9–328.4 mg/kg for Al; 200.9–203.4 mg/kg for As; 130.1–136.2 mg/kg for Fe; 121.9–125.8 mg/kg for Pb; 27.3–30.2 mg/kg for Co; 23.8–26.8 mg/kg for Ni; 7.2–9.2 mg/kg for Ti; 7.1–9.2 mg/kg for Cd; 4.0–5.6 mg/kg for Zn and 0.1–0.6 mg/kg for Cu. Chromium (Cr) was identified as the most abundant heavy metal in the sediment samples. Mean concentration of the metals were Cr: 861.5 mg/kg; Al: 326.8 mg/kg; As: 202.2 mg/kg; Fe: 134.3 mg/kg; Pb: 123.7 mg/kg; Co: 28.8 mg/kg; Ni: 25.4 mg/kg; Ti: 8.5 mg/kg; Cd: 8.3 mg/kg; Zn: 4.5 mg/kg and Cu: 0.2 mg/kg dry weights. The average order of metal concentration is Cr > Al > As > Fe > Pb > Co >

Station no.	pН	C.E (mS/cm)	CEC (meq/100 g)	LOI (%)
1	3.86	1.30	8.5	5.1
2	4.34	1.50	8.8	5.4
3	4.28	1.80	9.0	5.0
4	4.30	1.90	8.3	5.1
5	3.92	1.40	9.1	5.3
6	4.34	1.60	8.8	5.1
7	3.89	1.40	8.5	5.4
8	3.87	1.40	9.1	5.1
9	3.86	1.40	9.0	5.2
10	4.27	1.80	8.8	5.2
11	4.28	1.80	9.4	5.4
12	4.28	1.80	8.5	5.1
13	3.88	1.40	9.3	5.2
14	3.86	1.40	8.7	5.2
15	4.30	1.60	8.3	5.4
16	3.87	1.40	9.1	5.1
17	3.86	1.40	9.0	5.1
18	4.31	1.50	8.5	5.2
19	4.27	1.90	8.8	5.1
20	4.28	1.80	9.3	5.2

**Table 7.**Geochemical properties of gold mine tailings sediments.

Ni > Ti > Cd > Zn > Cu. The mineral composition of the sediments and mining activities that took place within this region may be attributed to the high element concentrations in the soil samples.

In comparison to the interim sediment quality guidelines (ISQG) proposed by the Canadian Council of Ministers of the Environment [38], the elemental pollution status of the tailings (soil) were assessed **Table 8**. The heavy metals from the studied tailings sediments except for Zn and Cu all exceeded the ISQG. This implies that the sediments are toxic and could result in the introduction of sediment contaminants into the aquatic food web through predation by organisms at higher trophic levels.

In trace amounts, Arsenic is one of the priority toxic metals due to its several deteriorating effects to both plants and animals. The level of identified arsenic in the sediment is worrisome. As a non-essential element, Arsenic is not required for the growth of living organisms, though recent discovery reports a bacterium that

Station no.	Cr	Al	As	Fe	Pb	Co	Ni	Ti	Cd	Zn	Cu
1	862.6	327.4	201.7	134.1	125.6	28.4	26.1	9.0	9.2	4.7	0.6
2	860.4	327.9	203.4	136.2	122.9	30.2	25.3	8.3	8.8	4.0	0.1
3	861.3	328.0	202.9	133.7	123.1	29.5	26.4	9.2	8.1	4.1	0.2
4	862.4	328.4	202.4	130.1	124.7	28.8	24.7	8.1	7.9	3.9	0.2
5	862.1	326.5	202.1	132.5	121.9	29.6	23.8	8.7	7.2	5.6	0.3
6	861.5	325.7	201.7	134.9	122.1	29.3	25.1	7.9	8.3	4.3	0.1
7	860.6	324.9	203.0	135.3	123.5	28.7	25.7	8.5	7.5	5.2	0.1
8	861.1	328.1	201.9	135.1	123.2	29.2	26.3	9.0	7.9	4.9	0.3
9	860.7	327.9	202.6	135.9	124.1	27.5	26.8	9.2	9.0	4.2	0.1
10	860.3	326.3	202.1	132.7	124.8	29.1	25.2	8.1	8.5	5.1	0.1
11	860.6	325.4	201.7	136.0	122.3	27.3	25.7	8.3	7.1	5.3	0.1
12	861.0	326.7	200.9	131.8	122.5	27.9	23.9	8.7	8.7	5.0	0.2
13	862.1	326.1	201.2	135.9	124.9	28.7	24.3	7.6	8.3	5.5	0.6
14	860.5	327.9	201.4	134.1	123.1	28.3	26.0	9.1	9.1	4.5	0.1
15	862.5	328.2	203.0	133.7	122.7	28.0	25.8	9.2	8.3	5.0	0.2
16	862.3	326.3	202.6	134.9	125.8	29.1	24.6	8.3	8.5	5.3	0.3
17	862.4	325.9	201.5	133.5	123.7	29.5	24.2	8.0	8.1	4.1	0.1
18	861.9	327.4	202.3	134.2	125.1	29.7	26.5	7.2	8.0	4.8	0.4
19	861.6	326.1	201.9	134.9	124.3	28.1	25.7	8.4	8.5	4.4	0.5
20	862.0	325.6	203.1	135.7	125.3	28.4	26.3	8.7	8.8	4.6	0.1
Mean	861.5	326.8	202.2	134.3	123.7	28.8	25.4	8.5	8.3	4.5	0.2
Max	862.6	328.4	203.4	136.2	125.8	30.2	26.8	9.2	9.2	5.6	0.6
Min	860.3	324.9	200.9	130.1	121.9	27.3	23.8	7.2	7.1	3.9	0.1
B <sub>n</sub> ISQG	90 52.3	88,000 NA	13 7.24	47,200 NA	20 30.2	19 NA	50 NA	4600 NA	0.3	95 124.0	45 18.7

**Table 8.**Heavy metals concentration (mg/kg dry weight) in gold mine tailings sediments.

replaces phosphorus with As for a number of cellular functions [39]. Plants often accumulate As by root uptake from soil or by absorption of airborne As deposited on their leaves [40]. Arsenate, a dominant specie of Arsenic in soils, based on its similarity to phosphate usually compete for the same uptake carriers in the root plasmalemma of most plants. In so doing interrupts with several metabolic processes that end up inhibiting plant growth and development through arsenicinduced phytotoxicity [41, 42]. Some of the toxicity symptoms may include inhibition of seed germination, decrease in plant height, depressed tillering, reduction in root growth and some necrosis, decrease in shoot growth, lower fruit and grain yield, reductions in chlorophyll and protein contents, and in photosynthetic capacity and even death [41–46]. Due to migration and expansion of residential areas into former mining territories, the danger of human exposure to soil As has risen in the last two decades which have affected adversely the health of many [47]. Continued exposure to As results in several clinical manifestations such as melanosis (hyperpigmentation), keratosis, and leukomelanosis (hypopigmentation) of which cutaneous lesions are the highest reported [48, 49]. As is also a well-known carcinogen, causing skin, lung, bladder, liver, and kidney cancers [50, 51].

The average concentration of Copper (Cu) being 0.2 mg/kg was within the maximum acceptable concentration of 6.6 mg/kg for agricultural soil and safe limit of the Republic of South Africa [52].

As an important micronutrient, Cu is required for the growth of both plants and animals. In humans, it aids in the production of blood hemoglobin while plants utilize it in seed production, disease resistance, and regulation of water. In high levels, Cu could cause anemia, liver and kidney damage, as well as stomach and intestinal irritation [53]. Cu typically occurs in drinking water from Cu pipes, as well as from additives intended to control algal growth. The interaction of Cu with the environment is complex, however different studies revealed that most Cu introduced into the environment rapidly becomes, stable and results in a form which does not pose a danger to the environment [54, 55].

Zinc is an important metal due to its enzymatic and regulatory functions in biological systems. Being a readily mobile element, Zinc (Zn) when in high doses exhibit toxic and carcinogenic effects that could result in serious hematological and neurologic complications, liver and kidney disorders, hypertension, gastrointestinal misery, loose bowels, pancreatic harm and a host of other ailments in both humans and animals [56]. On the earth crust, Zinc is found in an average concentration of 80 mg/kg in association with ores of other metals such as Pb, Cu and Cd [57].

Chromium (Cr) has an average concentration of 100 mg/kg in the earth crust and the only known ore of commercial value is chromite (FeO.Cr<sub>2</sub>O<sub>4</sub>). Contamination by Cr could result in toxicity in plants depending on its state of valency since Cr (VI) due to its being highly mobile is toxic, while Cr (III) as less mobile is less toxic. The subsequent uptake, translocation, and accumulation of Cr by plants is dependent on its speciation. Cr in its trivalent (III) and hexavalent (VI) forms are known to be of biological importance. Generally, Cr poses the greatest threat to humans, animals and plants. Decreased seed germination, reduction of growth, decreased yield, inhibition of enzymatic activities, impairment of photosynthesis, nutrient and oxidative imbalances, and mutagenesis are some of the symptoms of Cr toxicity in plants [58]. In a previous study by López-Luna et al. [59], the toxicity of Cr (VI), Cr (III), and Cr tannery sludge were compared with respect to Cr mobility in soil and toxicity in wheat, oat, and sorghum plants and findings were that Cr(VI) was more mobile in soil and caused higher toxicity on those plant seedlings, while tannery sludge was the least toxic [60]. In humans, prolonged exposure results in kidney and liver disorders [61].

Lead (Pb) is the largely known immobile nonessential element among the heavy metals with most of its compounds being noxious in nature. Pb on the earth crust has an average concentration of 0.1 mg/kg. There is a gradual phase out of Pb from the materials regularly used by humans due to it being a metal toxicant. Mostly via food chain, Pb penetrates human or animal metabolism. The observed Pb content within the samples was very high and have been reported globally to be very harmful to humans and other animals as a long-term exposure could result in the bioaccumulation and biomagnification that end up in serious neurological health challenges. In plants, concentrations above 5 mg/kg of Pb causes severe growth retardation, discoloration, and morphological deformities. Pb accumulates in the body organs (i.e., brain), which may lead to poisoning (plumbism) or even death. The presence of lead often affects the gastrointestinal tracts, kidneys, and central nervous system. Infants exposed to lead are likely to suffer impaired development, lower IQ, shortened attention span, hyperactivity, and mental deterioration [62]. Adults usually suffer decreased reaction time, loss of memory, nausea, insomnia, anorexia, and weakness of the joints when exposed to Pb [63]. Lead performs no known essential function in the human body, it can merely do harm after uptake from food, air, or water.

Industrial waste materials, lime, fertilizer and sewage sludge constitute the major sources of nickel into soils [64]. Till date, nickel (Ni) remains a heavy metal of environmental concern as a result of decreased soil pH, due to reduced use of soil liming in agricultural soils and mobilization arising from increased acid rain in industrialized areas [65]. With decreasing pH, Ni exhibits increased solubility and mobility, thus, soil pH is the major factor controlling its solubility, mobility and sorption, while clay content, iron- manganese mineral and soil organic matter are of secondary importance [66]. Nickel (Ni) concentrations were observed to be high which could result in toxic effects to both plants and animals due to its ability to replace other metal ions in enzymes, proteins or bind to cellular compounds [65]. Nickel (Ni) is reported to interact with at least 13 essential elements namely calcium, chromium, cobalt, copper, iodine, iron, magnesium, manganese, molybdenum, phosphorus, potassium, sodium and zinc [67]. As a result, prolong exposure of humans to oxides and sulfides of nickel is linked with possible risk to lung and nasal tumors, skin allergies, nasal sinusitis, rhinitis and dermatitis [68]. Symptoms of nickel toxicity in plants besides inhibited growth include chlorosis, stunted root growth and brown interveinal necrosis [69].

Cadmium (Cd) is being discussed on a global platform as one of the most ecotoxic metals with a tendency of adversely affecting biological activities, plant metabolism, soil health and human health. The usage of Cadmium (Cd) is widely seen in Ni/Cd batteries, as rechargeable or secondary power sources exhibiting high output, long life, low maintenance, and high tolerance to physical and electrical stress. Observed levels of Cadmium was high and of great concern because it is very biopersistent and, once absorbed by an organism, remains resident for many years. In humans, Cadmium is known to affect several enzymes. Previous research revealed that renal damage that results in proteinuria is the consequence of Cd adversely affecting enzymes responsible for reabsorption of proteins in kidney tubules [70]. A prolong exposure to this metal even at very low concentration also reduces the activity of delta-aminolevulinic acid synthetase, arylsulfatase, alcohol dehydrogenase, and lipoamide dehydrogenase, which often cause anemia, cardiovascular disorders and hypertension whereas it enhances the activity of deltaaminolevulinic acid dehydratase, pyruvate dehydrogenase, and pyruvate decarboxylase [71].

Station no.		Conta	minatio	n factor	of sing	e metal	Degree of contamination			
	Cr	As	Pb	Co	Ni	Cd	Zn	_		
1	9.58	15.52	6.28	1.49	0.52	30.67	0.05	64.11	Very high	
2	9.56	15.65	6.15	1.59	0.51	29.33	0.04	62.83	Very high	
3	9.57	15.61	6.16	1.55	0.53	27.00	0.04	60.46	Very high	
4	9.58	15.57	6.24	1.52	0.49	26.33	0.04	59.77	Very high	
5	9.58	15.55	6.10	1.56	0.48	24.00	0.06	57.33	Very high	
6	9.57	15.52	6.11	1.54	0.50	27.67	0.05	60.96	Very high	
7	9.56	15.62	6.18	1.51	0.51	25.00	0.05	58.43	Very high	
8	9.57	15.53	6.16	1.54	0.53	26.33	0.05	59.71	Very high	
9	9.56	15.58	6.21	1.45	0.54	30.00	0.04	63.38	Very high	
10	9.56	15.55	6.24	1.53	0.50	28.33	0.05	61.76	Very high	
11	9.56	15.52	6.12	1.44	0.51	23.67	0.06	56.88	Very high	
12	9.57	15.45	6.13	1.47	0.48	29.00	0.05	62.15	Very high	
13	9.58	15.48	6.25	1.51	0.49	27.67	0.06	61.04	Very high	
14	9.56	15.49	6.16	1.49	0.52	30.33	0.05	63.60	Very high	
15	9.58	15.62	6.14	1.47	0.52	27.67	0.05	61.05	Very high	
16	9.58	15.58	6.29	1.53	0.49	28.33	0.06	61.86	Very high	
17	9.58	15.50	6.19	1.55	0.48	27.00	0.04	60.34	Very high	
18	9.58	15.56	6.26	1.56	0.53	26.67	0.05	60.21	Very high	
19	9.57	15.53	6.22	1.48	0.51	28.33	0.05	61.69	Very high	
20	9.58	15.62	6.27	1.49	0.53	29.33	0.05	62.82	Very high	
Average	9.57	15.55	6.19	1.51	0.51	27.63	0.05	61.01	Very high	

**Table 9.**Contamination factor (CF) and degree of contamination at various sampling station at the Blesbokspruit abandoned gold mine tailings site.

# 4.3 Pollution status

The assessment of the overall contamination of the studied area was based on the contamination factor **Table 9**. The average contamination factor for single metal from this study revealed the sediments as slightly contaminated with Ni and Zn, moderately contaminated with Co and highly contaminated with Cr, As, Pb and Cd. The highest average contamination factor value was that of Cd (27.63). Overall, the degree of contamination values of the sediments from the study site indicate very high contamination.

The average index of geoaccumulation values and contamination levels from the various sampling points within the study area as shown on **Table 10** reveals an uncontaminated status for Co (0.01), Ni (-1.09) and Zn (-3.39) respectively. However, Cr and Pb within the area showed a moderately contamination level with average  $I_{\rm geo}$  values being 1.85 and 1.42 respectively. The site was however moderately to strongly contaminated with As (2.34) and Cd (2.91).

As indicated in **Table 10**, Pollution load index (PLI) ranged from 2.56–2.75, with mean value 2.67. PLI values of the different stations are above 1 which strongly indicate that the sediments are all polluted by heavy metals, an indication of deterioration of the study site.

Station no.	Cr	As	Pb	Co	Ni	Cd	Zn	PLI	Description of PLI
1	1.85	2.34	1.43	0.00	-1.05	3.02	-3.51	2.72	Polluted
2	1.85	2.34	1.41	0.06	-1.09	2.97	-3.51	2.63	Polluted
3	1.85	2.34	1.41	0.04	-1.05	2.89	-3.51	2.61	Polluted
4	1.85	2.34	1.43	0.01	-1.11	2.87	-3.51	2.56	Polluted
5	1.85	2.34	1.40	0.04	-1.14	2.77	-3.22	2.67	Polluted
6	1.85	2.34	1.40	0.03	-1.11	2.91	-3.51	2.67	Polluted
77	1.85	2.34	1.42	0.01	-1.08	2.81	-3.22	2.64	Polluted
8	1.85	2.34	1.41	0.02	-1.05	2.87	-3.51	2.68	Polluted
9	1.85	2.34	1.42	-0.04	-1.02	3.00	-3.51	2.63	Polluted
10	1.85	2.34	1.43	0.02	-1.08	2.94	-3.22	2.68	Polluted
11	1.85	2.34	1.41	-0.04	-1.08	2.76	-3.22	2.66	Polluted
12	1.85	2.33	1.41	-0.02	-1.14	2.96	-3.22	2.65	Polluted
13	1.85	2.34	1.43	0.01	-1.14	2.91	-3.22	2.73	Polluted
14	1.85	2.34	1.41	-0.01	-1.05	3.01	-3.51	2.71	Polluted
15	1.85	2.34	1.41	-0.02	-1.08	2.91	-3.22	2.67	Polluted
16	1.85	2.34	1.43	0.02	-1.11	2.94	-3.22	2.75	Polluted
17	1.85	2.34	1.42	0.04	-1.14	2.89	-3.51	2.57	Polluted
18	1.85	2.34	1.43	0.04	-1.05	2.88	-3.51	2.69	Polluted
19	1.85	2.34	1.42	-0.01	-1.08	2.94	-3.51	2.68	Polluted
20	1.85	2.34	1.43	0.00	-1.05	2.97	-3.51	2.71	Polluted

**Table 10.**Geoaccumulation index (Igeo) and pollution load index (PLI) at various sampling station at the Blesbokspruit abandoned gold mine tailings site.

It is evident from the present study that the abandoned gold mine tailings site is not polluted with Zn and Cu, but heavily polluted with Cd, Cr and Pb when evaluated by comparison with the sediment quality guideline proposed by USEPA.

#### 5. Conclusion

The successful assessment of trace metal contamination of the abandoned gold mine tailings at Blesbokspruit-Ekurhuleni was done using indices such as geoaccumulation index, contamination factor, and degree of contamination and pollution load index. The sediment was mostly dominated by fine sand and silt/clay. Based on sediment quality guidelines proposed by the USEPA, the contamination of the sediment by Zn and Cu was negligible while Cd, Cr and Pb were detected at high concentrations. The evaluated pollution load index indicated that the sediments in the tailings dump are polluted while the geoaccumulation index revealed that Cr, Pb, and As contaminated the site, thus indicating very high degrees of contamination of the sediments at the mine dump. The high metal contaminants could be attributed to anthropogenic activities from previous extensive gold mining activities that took place within the area. Considering agricultural activities and human dwellers within the surrounding areas of the mine tailings, there are high tendencies of deleterious impacts. As a further precaution, this study strongly supports the call for analysis of the stream and drinking water quality, including the

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staple crops that are cultivated within the vicinity of the dump site, to ascertain the levels of heavy metals within such crops. Stringent mitigation plans or conversion of the tailings into value-added products should be considered.

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# Conflict of interest

The authors declare no conflict of interest.

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