

# Geochemical Investigation of Metals and Trace Elements around the Abandoned Cu-Ni Mine Site in Selibe Phikwe, Botswana

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## Abstract

Metals and trace elements may occur naturally in rocks and soils, but elevated quantities of them are gradually released into the environment by anthropogenic activities such as mining. The current study aims at characterizing the spatial distribution of trace elements and evaluate site-specific geochemical background concentrations of trace elements in the mine soils and river sediments and also to discriminate between lithogenic and anthropogenic sources of enrichment around a copper-nickel mining town in Selibe-Phikwe, Botswana. A total of 43 soil, 30 river sediments, and 9 river water samples were collected from an area of 500 m<sup>2</sup> within the precincts of the mine. The total concentration of Cu, Ni, Cr, As, Co and Zn in soils and sediments were determined using ED-XRF while river water samples were analyzed by ICP-AES. Geochemical pollution indices such as Geo-accumulation Index (Igeo), Enrichment Factor (EF) and Integrated Pollution Index (IPI) were employed for the assessment of metal and trace element contamination. The average metal concentration in soil of Cu, Ni, Cr, As, Co and Zn in the study area were 109.8, 107.1, 72.0, 2.3, 7.8 and 36.1 mg/kg, respectively. To calculate the geochemical baseline, Relative cumulative frequency curves and the 4 s-outlier test methods suggested by Matschullat et al. (2000) were incorporated. The estimated average baseline concentrations of Cr, Cu, Ni, Co, Zn and As are 53.8, 51.85, 53.95, 5.6, 32.36 and 4.27 mg·kg<sup>-1</sup>, respectively. Soil leachate, sediment leachate and river water pH levels ranged from basic (9) to very acidic (3) in areas closer to the mine. There is high variation in heavy metal concentration, e.g. Cu, depicting regional natural background concentrations while others depict anthropogenic sources. The calculated Igeo values revealed moderate pollution level by the same metals. The result of integrated pollution indices suggested a generally deteriorating site quality. The results of chemical analysis also indicate that the trace elements in soils decreased

with respect to distance from the mine; controlled mainly by water movement, wind direction, and topography.

### **Keywords**

Soil Contamination, Geochemical Baseline, Pollution Indices, Trace Elements

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## **1. Introduction**

Mining activities are responsible for different types of environmental problems all over the world. Heavy metals often find their way in the vicinity of high Cu, Ni and Zn sulphides ores, (Barrie et al. 2008), and their exploitation and processing (Ngole & Ekosse, 2012). In contrast to other pollutants such as petroleum hydrocarbons and domestic or municipal litter which may visibly build up in the environment, heavy metals in the environment often accumulate unnoticed to toxic levels. They tend to settle on river beds or persist in streams or land for long periods of time, providing a long-term source of contamination to the surrounding inhabitants. These heavy metals have the potential to harm the environment and human health as they continue causing damage long time after mining has ceased. Due to the deterioration of water and soil quality due to the impacts of heavy metals, there was a need to study the heavy metals around the defunct copper mining at Selibe Phikwe to establish their levels of concentration and dispersion in the area, as well as their source.

Numerous reports and publications have discussed the issue of anthropogenic contamination of soils in mining districts (e.g., Dudka & Adriano, 1997). The environmental degradation of the BCL mining area is poorly quantified in spatial terms because the availability of high precision and up-to-date regional geochemical data for both unpolluted and polluted regions is limited. Nonetheless, a study by Likuku et al. have examined the status of soil pollution and degree of pollution in this area, however, the research was mainly based on a few metals in soils but not in river sediments and water; information which in itself is limiting considering that the river might be receiving considerable amounts of heavy metal inputs from the mine, and therefore contaminated with many other metals as well. In addition, there is no information on ecological and health risk assessment of metal contaminants around the BCL mine. These assessments are essential as they provide policy makers with information on the extent of aquatic ecosystem contamination and are used as early-warning signals of ecological challenges. In order to assess the real heavy metal contamination status of surface sediments and surrounding soils of Selebi Phikwe area, we have carried out an investigation in this region. To achieve a comprehensive assessment of the impacts of heavy metals, we characterized the spatial distribution of trace elements in soils, sediments and river water and different indexes were applied including geo-accumulation index (Igeo), pollution load index (PLI) were applied. The main objective of this study is to get more information on the heavy metal

pollution status in this area by characterizing the spatial distribution of trace elements and investigating the degree of contamination of Cu, Ni and Zn in soils around the Selebi Phikwe Cu-Ni mine and provide guidance for dredging and remediation projects after mine closure.

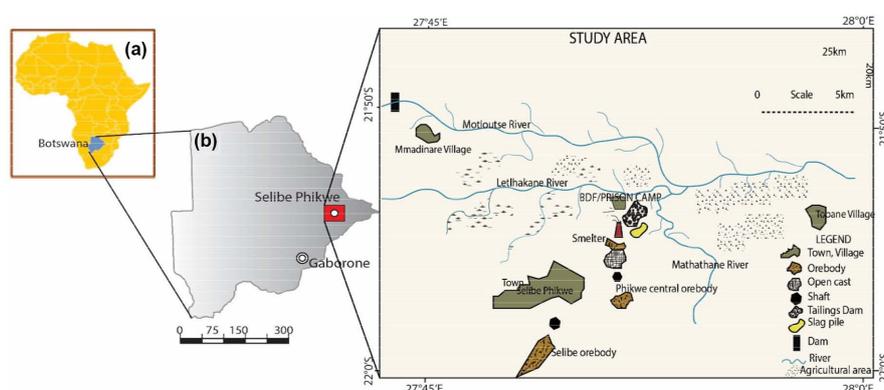
## 2. The Survey Area

### 2.1. Description of the Study Area

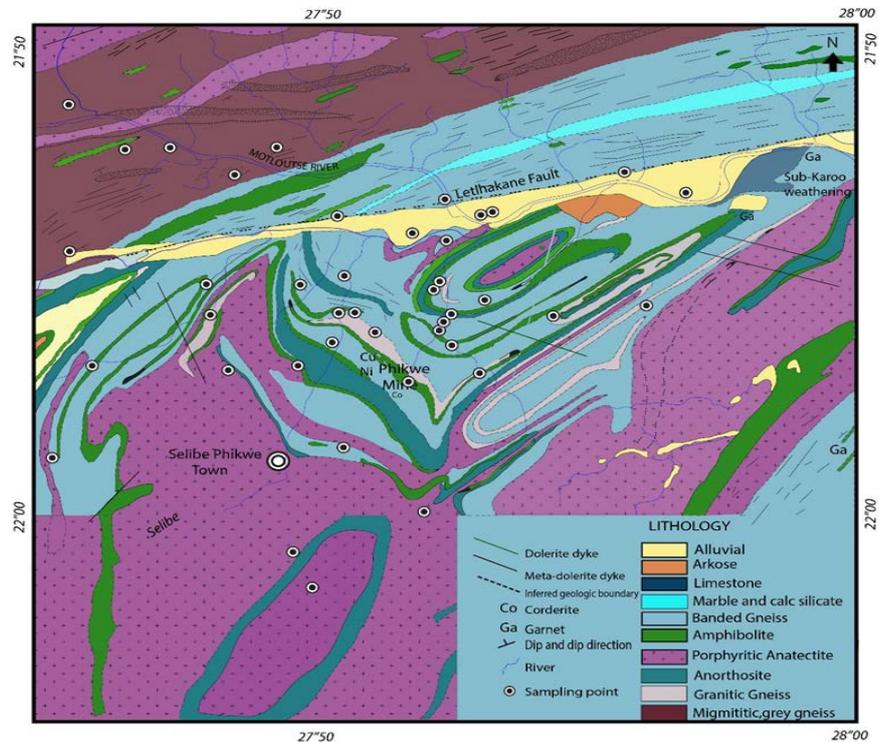
The study area is located in the eastern part of Botswana along the Motloutse River from Mmadinare in the west to Tobane in the south, roughly between latitudes  $21^{\circ}50'$  and  $22^{\circ}0'$  and longitudes  $27^{\circ}45'$  and  $28^{\circ}00'$  (**Figure 1**). Selebi Phikwe area receives an average annual rainfall of 418 mm, 90% of which is concentrated between October and March. The mean maximum temperature varies from low in June ( $13.0^{\circ}\text{C}$ ) to a high of  $39^{\circ}\text{C}$  in October. The mean minimum temperature ranges from  $5^{\circ}\text{C}$  in July to  $20^{\circ}\text{C}$  in January. The area is characterized by soils weathered from metamorphic and acid igneous rocks, as well as soils derived from alluvial sediments. The four main soil types are ferric luvisols, haplic luvisols eutric regosols as shown on **Figure 2**. Most of the soils in the area have a rustic moisture regime (between humid and arid) (De Wit & Bekker, 1990).

### 2.2. Geology

The study area is part of the Phikwe Complex, which falls within the Limpopo Mobile belt in Southern Africa. The Limpopo belt is situated between the Kaapvaal and Zimbabwe cratons, an Archean to early Paleoproterozoic granulite-facies metamorphic belt (Barton et al., 2006). The Phikwe Complex mainly consists of Archean (McCourt et al., 2004) quartzofeldspathic tonalitic hornblende-bearing and trondhjemitic gneisses, which host the mafic-ultramafic intrusions of the Selebi-Phikwe belt. The host rocks of the Selebi-Phikwe belt are medium to coarse grained, granoblastic to porphyroblastic granite gneisses with massive to weak foliations. Tectonically, The gneisses of the Selebi Phikwe complex are defined by variable north to northeast-trending planar fabrics with large-amplitude interference fold patterns vicinity of Phikwe and north-south in the



**Figure 1.** Location map showing (a) Map of Africa, (b) Botswana (c) Study area.



**Figure 2.** Detailed geological map of the study area showing different lithologies.

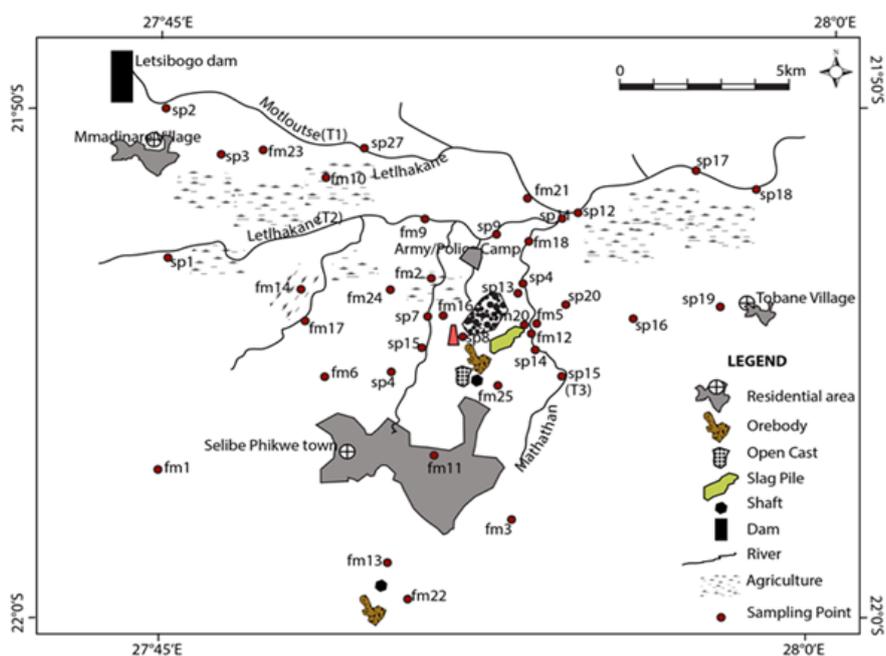
southern part of the complex. McCourt et al. (2004) estimated the age of granitic-gneisses to be between 2.6 and 2.65 billion years (Ga). The Phikwe copper deposit is one of the intrusions comprising the Selebi, central Phikwe and Selebi North deposits. Pyrrhotite, pentlandite and chalcopyrite are the main sulfide minerals in the study area (Maier et al., 2008). Bravoite, pyrite, marcasite and pyrite forms part of minor sulfides (Maier et al., 2008). Magnetite constitutes up to 20 volume percentage (vol. %) of the opaque fraction in the form of euhedral and anhedral grains. Most of the host rocks of the Selebi-Phikwe belt contain < 200 mg/kg sulphur, but sedimentary rocks with higher S contents reaching several 1000 mg/kg occur locally (Maier et al., 2008).

### 3. Materials and Methods

#### 3.1. Sampling Procedures

In the present study, stratified regular sampling method was adopted for soil sample collection as in geo-assessment of the variables estimated; the stratified regular sampling is more suitable because this kind of sampling draws homogenous error (Burgess & Webster, 1980; Burgess et al., 1981). The global positioning system (GPS) was used to identify the precise locations of all sampling sites. A total of 45 topsoil samples were collected from an area of about 500 km<sup>2</sup> to evaluate the spatial distributions of the heavy metals in the vicinity of the mine. Sampling locations are presented on **Figure 3**.

Two topsoil samples were taken away from the sampling area, far from people or industrial activity, representing soil background values. Soil samples were



**Figure 3.** Soil sampling locations.

obtained from a hand drilling auger with an inner diameter of 4' at a depth of 0 - 10 cm while sediment samples were collected using a portable plastic hand shovel. The samples were preserved in polyethylene (PE) bags. Samples were taken in mid-April, 2017, i.e. at the beginning of dry period. River water samples were collected from Motloutse River and its tributaries, labeled on **Figure 7** as T1, T2 and T3. The samples were brought to the laboratory where they were oven dried at temperatures of 80°C for 2hr and mixed thoroughly to obtain the representative samples. Soon after drying the debris and other objects were hand picked up and the samples were ground in a mortar to break up the aggregates or lumps, taking care not to break actual soil particles. Ultrapure water > 18 MΩ cm; Millipore Milli-Q) and analytical grade chemicals were used for the preparation of all solutions for heavy metal analysis.

### 3.2. Analytical Procedures

The physical parameters, pH, EC and temperature were measured in the field at the time of collecting samples. The pH of river water was also measured on site using a compact pH meter (Model: HI 8314 SHIMATSU instruments). A multi-range conductivity meter (Model: HI 9033 SHIMATSU) was utilized to measure the electrical conductivity (EC) of river water in all sampling sites.

### 3.3. Geochemical Analysis

Sieved and milled samples were then pressed into 32-mm internal diameter pellets using a hydraulic press operated at 200 kilojoules (kJ). All the metals and trace elements of interest, Cu, Ni, Cr, As, Co and Zn were analyzed by EDXRF spectrometer. To conduct elution tests, the soil concentration standard and

soil-leaching standard were carried out. Soil concentration standard involves acid elution which represents direct ingestion from soil or sediment, while soil leaching standard entails pure water elution which relates to groundwater ingestion from soil or sediments. The procedures were performed adopting the guidelines presented by Nakamura et al. (2016), 1.5 g of soil/sediment sample was mixed with 50 mL HCl (1.0 M), then shaken in a 200 rpm shaker for two hours to conduct the soil concentration standard tests. The soil leaching standard tests were performed by adding 50 ml pure water to 5 g soil sample, shaking in a 200 rpm shaker for six hours, then solutions were then filtered to 0.45  $\mu\text{m}$  membrane filter (Nakamura et al., 2016). Afterwards, the elements were analyzed in AIST, Geological Survey of Japan, Department of Geo-resources and Environment laboratory with Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES, SPS 3500DD, SII) using internal standard concentration. The pH and Electrical Conductivity (EC) of the soil and sediment-water elution filtrate were measured.

### 3.4. Pollution Assessment Indices

In this study, five different indices or criteria were used to properly assess heavy metal pollution in the environment around the BCL mine.

#### *Baseline determination*

The baseline was computed by incorporating the cumulative frequency method and the Iterative-2std-DEV technique both proposed by Matschullat et al. (2000). Matschullat et al. (2000) explained the 2std-DEV technique as a more radical and mathematically less robust method, that's why the two methods were incorporated to comprehend each other.

#### *Geoaccumulation index, $I_{\text{geo}}$*

Geoaccumulation index,  $I_{\text{geo}}$  indicates the degree of pollution of soil or sediments with regards to the geochemical background concentrations of the polluting heavy metals. The  $I_{\text{geo}}$  values were calculated using the equation first proposed by multiplying the geochemical background concentrations of the metals each time by a constant, 1.5 in order to allow content fluctuations of a given substance in the environment as well as very small anthropogenic influences. Geoaccumulation index is mathematically expressed below and distinguished classes shown in **Table 1**.

**Table 1.**  $I_{\text{geo}}$  classes and their corresponding classifications.

Class name	$I_{\text{geo}}$ value range	Classification
0	$I_{\text{geo}} \leq 0$	Practically uncontaminated
1	$0 < I_{\text{geo}} \leq 1$	Uncontaminated to moderately contaminated
2	$1 < I_{\text{geo}} \leq 2$	Moderately contaminated
3	$0 < I_{\text{geo}} \leq 3$	Moderately to heavily contaminated
4	$0 < I_{\text{geo}} \leq 4$	Heavily contaminate
5	$0 < I_{\text{geo}} \leq 5$	Heavily to extremely contaminated
6	$0 < I_{\text{geo}} \leq 6$	Extremely contaminated

$$I_{geo} = \log_2 \left( \frac{C_n}{1.5B_n} \right) \quad (1)$$

where,  $C_n$  = concentration of the examined element in the examined environment, and  $B_n$  = geochemical background of a given element in reference environment.

#### *Enrichment Factor (EF)*

EF is an indication of the degree of pollution or contamination. In this study, EF is calculated using the modified formula based on the suggested equation by Chester et al. (1985) and Sutherland et al. (2000) as:

$$EF = \frac{C_m \text{ sample}}{(\text{median } C_m \text{ Background} + 2 * \text{MAD } C_m \text{ Background})} \quad (2)$$

where  $C_m$  Sample is the concentration of a given heavy metal at contaminated sites. Median  $C_m$  Background is the median concentration of an element in the background soil sample and MAD  $C_m$  Background is the Median Absolute Deviation from the Median, defined in (3).

$$MAD = \text{median} \left[ \left| x_i - \text{median}(x_j) \right| \right] \quad (3)$$

Enrichment Factor (EF) was used to determine whether trace elements in soil or sediment were of anthropogenic origin. Iron (Fe) has been extensively and successfully used by several authors to normalize heavy metal contamination. For this reason, Fe was selected as the normalizing element for the present study. Data was re-analysed using the background values calculated in (1) above (therefore assumed to mimic pre-industrial data), and EFs were calculated using the formula reported in Chester et al. (1985) and Sutherland et al. (2000) given in (Equation (2)).

The five recognized and interpreted contamination categories on the basis of EF are presented in **Table 2**.

#### *Modified Degree of Contamination (mCd)*

The generalized pollution index equation by Likuku et al. (2013) for overall degree of contamination was modified and expressed as the sum of all CFs for a given set of heavy metals divided by the number of analyzed heavy metals. Hakanson (1980), mathematically expressed it as below and gradation for descriptive classification presented in **Table 3**:

$$mC_d = \frac{\sum_{i=1}^{i=n} C_f^i}{n} \quad (4)$$

where  $n$  is the total number of trace elements analyzed and  $C_f$  is the contamination factor calculated as shown in (5) below.

$$C_f = \frac{C_n \text{ sample}}{C_m \text{ Background}} \quad (5)$$

#### *Integrated Pollution Index, IPI*

The integrated pollution index (IPI) was proposed by Tomlinson et al. (1980) for reveal contamination which helps to make a comparison of pollution levels

**Table 2.** EF classes and their corresponding categories.

EF Class	Category
EF < 1.5	Non enrichment
1.5 ≤ EF < 5	Moderate anthropogenic enrichment
5 ≤ EF < 20	Significant anthropogenic enrichment
20 ≤ EF < 40	Very high enrichment
EF > 40	Extreme enrichment

**Table 3.** mCd classes and their corresponding descriptions.

mCd Class	Description
mCd < 1	Nil to very low degree of pollution
1 ≤ mCd < 1.5	Low degree of pollution
1.5 ≤ mCd < 2	Moderate degree of pollution
2 ≤ mCd < 3.5	High degree of pollution
3.5 ≤ mCd < 8	Very high degree of pollution

between various sites and at different times. The IPI was obtained as an elemental concentration factor of each heavy metal with respect to the background value in the sediment or soil. In this study, the values calculated in Equation (1) were taken as background for those trace elements. Angulo (1996) explained that the IPI is able to give an estimation of the heavy metal contamination status and the necessary action that should be taken. Equation (7) was employed to calculate the IPI.

$$IPI = (CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n)^{\frac{1}{N}} \quad (6)$$

where **N** is the total number of studied trace elements and CF is the contamination factor calculated as described in (Equation (5)).

#### *Statistical Analysis*

Raw data were used for statistical analysis using Excel Microsoft 2013 Package. Means of heavy metals concentration were determined and relationships between metals concentrations were established using Pearson's correlation coefficient in a two-tailed test ( $p < 0.01$  and  $0.05$ ).

## **4. Results and Discussions**

### **4.1. Physicochemical Parameter of Soil Samples**

The physico-chemical parameters that were measured in situ in the field were pH, electrical conductivity (EC) and temperature of the surface water. The mean river water pH levels recorded was (7.96) and ranged from 4.42 - 9.16. The mean electrical conductivity (EC) levels in river water samples demonstrated modest variations. The mean EC of river water was (3.56 mS/m). The highest mean water temperature of 29.1 (°C) was recorded at Letlhakane river while the lowest of

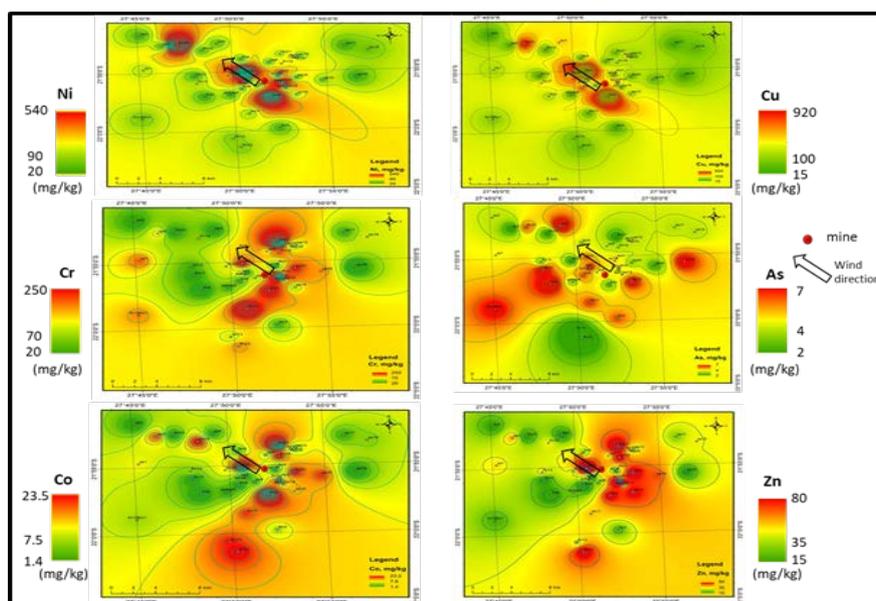
18.2 (°C) was obtained at downstream of Motloutse river. Stream and river temperatures varied relatively with response to environmental fluctuations of ambient air temperatures.

The mean pH of the soil was 7.9 (ranging from 3.79 to 7.70). Sampling sites located NW of the smelter, which is also the windward direction, had the lowest pH values. The average EC of soil in the studied area was 11.40 mS/m. Soil EC and other soil parameters are especially crucial in soil processes responsible for transportation and solubility of trace elements in soil (Matthews-amune & Kakulu, 2012).

The pH values of the stream sediments samples in all the sites ranged from 4.37 to 8.90 with a mean value of 7.65. pH values decreased with distance from the mine, indicating that mining activities play an essential role in the acidity of sediments.

#### 4.2. Total Concentration and Spatial Distribution of Heavy Metal in Soils, River Sediments and Rocks

Soil samples were collected from an area of 500 km<sup>2</sup> around the BCL mine area to evaluate the spatial distribution of metals and trace elements, as well as the influence of wind and water agents in regard to mine waste and the dispersal of trace elements in the surroundings. Generally, the results demonstrated some variations in the total concentration of trace elements in soil. According to many reporters, total concentration of metals in soil samples may reflect both natural differences in soil genesis, properties, and degree of contamination from anthropogenic sources. The spatial distribution of the total concentrations of the seven trace elements analyzed for this study are shown on **Figure 4** below. The statistical results of Cr, Cu, Co, Ni, Zn and As in soils are also shown on **Table 4**. Soil samples show very high mean total concentrations of Cu (109.84 mg/kg)



**Figure 4.** Spatial distributions of total concentrations of trace elements in soils.

**Table 4.** Descriptive statistics of total concentrations of trace elements in soil in (mg/kg).

Elements	Median	Mean	Max	Min
Cr	64.9	21.4	253.8	72.0
Co	6.2	1.3	23.6	7.8
Ni	50.9	18.1	543.7	107.1
Cu	50.6	15.3	921.1	109.8
Zn	34.8	15.3	83.5	36.1
As	4.1	1.8	7.0	2.3

and Ni (107.09 mg/kg). In sampling locations that are situated in the maximum direction of the wind (windward direction) and in the vicinity of the smelter plant, the contents of Cr, Cu, Co, Ni, Zn and As (**Figure 4**) are considerably higher.

The elevated total concentration of Cu and Ni in the soils are closely related to wind-transported pollutants. However, the distribution of Cr, As, Co and Zn do not show any relationship with wind effects. The concentration of Cr and Zn is higher at sampling points closer to the scrap metal dumping site located near the mine premises. The BCL smelter plant does not only refine the ore from the mine, but also treats the scrap metals and other metallic waste, therefore it's highly possible that the metal scrapes contributed to the elevated levels of trace elements. As total concentration in soil is significantly low, hence these levels may only represent the natural levels of As in soil. This anomalous distribution of metals is collateral to the soil concentration values around smelting plants reported by (Larocque & Rasmussen, 1998) and (Schroeder & Lane, 1988)

**Table 5** shows the lowest and highest concentrations of Cr, Cu, Co, Ni, Zn and As in river sediments, (see **Figure 1** for location). The most abundant trace elements in sediments is Ni with a minimum concentration of (8.7 mg/kg) and a maximum of (108.8 mg/kg), followed by Cr with a minimum concentration of (11.2 mg/kg) and a maximum of (50.4 mg/kg). Unlike in soils, the mean total concentration of Cu in sediments is considerably low. The same variation of elemental concentration is also observed in Co concentration, which has the lowest mean metal content in sediments. The highest concentrations of Cu, Ni and Cr are observed mainly in Mathathane River (T3) (**Figure 3**), which flows very close to the tailings dump and slag pile. The effluents and discharge from the mine directly disposed in (T3) are the main contributing factors to elevated concentrations of trace elements in sediments. Samples from upper stream and lower stream sediments recorded the lowest metal concentrations. While all other metals show a relationship with the distance from the mine, conversely As concentrations are considerably low and equally distributed in almost all the stream sediments. So, the general order of abundance of trace elements in river sediments is Cr > Ni > Zn > Cu > As > Co. This order may give an idea of the primary mineralogy of ore that was processed at the mine, Sphalerite, Chalcopyrite.

**Table 5.** Descriptive statistics of total concentrations of trace elements in sediments.

Elements	Median	Min	Max	Mean
Cr	11.2	11.2	50.4	22.7
Co	1.5	0.2	3.7	1.1
Ni	24.8	8.7	108.8	25.4
Cu	11.1	8.4	35.5	12.9
Zn	20.5	14.9	23.6	19.2
As	3.6	3.1	4.5	3.6

Mean trace element total concentrations of parent material are shown in **Table 6** below. The mean concentrations differ widely between the studied rock types, although in most of the cases the range of values between different rock types overlaps significantly. In the present study, only 8 rocks sample were collected due to lack of outcrops and time constricts. Rock samples collected from the study area were characterized according to their Si content and were allocated acidic, basic or ultramafic categories. Five samples were categorized as felsic rocks, two as mafic and there was only one ultramafic rock. Generally, concentrations of Cr, Co, Ni and Cu showed the highest concentrations in the mafic rocks and lowest in the felsic rocks. The felsic parent materials in the study area (granites, tonalite, and quartzite) primarily composed of quartz and plagioclase, with specs of biotite and other minerals. The mafic parent materials (gabbros, serpentinite, schist) are composed of varying parts of olivine, pyroxene, amphiboles, hornblend, and biotite. These minerals are the primary source of Cr, Co, Ni, and Cu. The geological influence of Ni and Cr content has been clearly demonstrated by many researchers (Alloway, 1995). The highest nickel concentrations are found in ultrabasic igneous rocks (peridotites, dunites and pyroxenites).

### 4.3. Statistical Analysis Results

The estimated average baseline concentrations of Cr, Cu, Ni, Co, Zn and As are 53.8, 51.85, 53.95, 5.6, 32.36 and 4.27 mg/kg, respectively. The estimated baseline values were compared with those reported in the literature by previous researchers. Soils were characterized by high baseline limit values for Ni and Cu. These anthropic baseline values were then used for the pollution assessment of selected trace elements around the BCL mine. On the other hand, baseline values of Cr, Cu, Ni, Co, Zn and As in sediments was computed from the two sampling stations away from the influence of anthropogenic inputs, and hence are believed to depict natural background values. The mean baseline values for Cr, Cu, Ni, Co, Zn and As in sediments were 14.6, 0.2, 23.8, 9.8, 15.8 and 3.2 respectively.

The application of the regional geochemical baseline values proposed in this study will allow comprehensive monitoring and the rapid identification of sites that could be affected by pollution due to historic mining exploitation in the area

**Table 6.** Major and minor elements concentrations in rock samples (mg/kg).

Sample number	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	Cr	Co	Ni	Cu	Zn	As	Pb	V	Rock type
5	77.9	13.0	3.6	-	-	9.9	17.8	18.6	10.2	49.7	3.0	Felsic
6	74.9	14.2	4.4	0.6	0.9	7.4	7.0	23.5	3.5	21.4	3.9	Felsic
7	51.8	10.7	2.6	35.4	66.4	53.4	245.6	117.6	0.0	2.6	280.7	Basic
8	71.8	14.9	5.3	-	3.5	6.5	7.5	45.7	4.2	24.2	30.2	Felsic
9	43.7	10.9	0.5	439.8	44.7	341.2	29.7	270.6	1.8	18.2	164.1	Ultramafic
10	50.9	26.6	2.7	20.4	3.0	18.1	6.6	33.6	0.5	9.3	28.3	Basic
11	68.3	16.0	0.5	12.9	6.9	9.8	5.7	22.0	0.9	11.0	46.8	Felsic
12	87.8	8.8	2.5	16.3	0.4	38.9	11.2	16.8	3.4	20.8	-	Felsic
<b>Mean</b>	<b>65.9</b>	<b>14.4</b>	<b>2.8</b>	<b>64.5</b>	<b>15.7</b>	<b>60.6</b>	<b>41.4</b>	<b>68.6</b>	<b>3.0</b>	<b>49.7</b>	<b>3.0</b>	

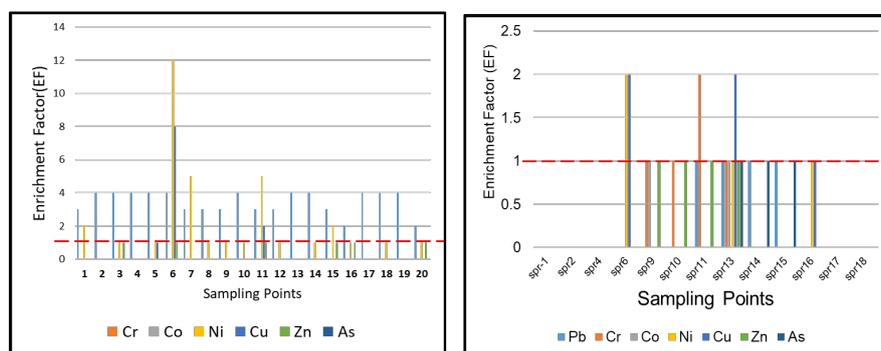
of Selibe Phikwe. In addition, this information will also be very useful in the process of land rehabilitation and proper restoration plan to try to ameliorate the detrimental environmental conditions caused by mining activities.

#### *Enrichment Factor (EF)*

In the present study, the enrichment factor (EF) was used to assess the level of contamination and the possible anthropogenic impact around the mine and the Selibe Phikwe town. In order to calculate the EF, the previously calculated geochemical baseline values were generally used. EF for Co, Cr, Cu, Ni as and Zn were found in the range of 0.06 - 7.48, 0.3 - 3.5, 0.26 - 4.41 and 0.46 - 2.39 respectively as seen on **Figure 5**. EF values between 0.5 and 1.5 indicate the metal is entirely from crustal materials or natural processes, whereas EF values greater than 1.5 suggest that the sources are more likely to be anthropogenic (Zhang & Liu, 2002); (Nowrouzi & Pourkhabbaz, 2014). EF values for Cu and Ni in soils were found to be the extremely high among sampling points 6, 7 and 11 with EFs 5 and 5 respectively for Cu. Sampling point 6 displayed high EF values for both Ni and Cu. The peaks in the EF graph of Cu and Ni are located in the vicinity of the mine, with high values on the windward direction from the smelter plant. The result of EF shows that the studied area is highly enriched in Cu followed by Ni when compared to all the other trace elements. Zn had moderate enrichment in soils only at locations 3, 6 11, 15, 16 and 20, on the other hand, Co, As and Cr has the lowest EF values much lower than 1.5, thus it is inferred that they represent the background concentration (Mmolawa et al., 2011) and that spikes of insignificant enrichment is probably due to the unidentified anthropogenic point sources. Zn also has a small spatial variation in EF values, with slightly higher EFs in southeast of the studied area. As no point sources were identified around the hotspots (showing only minor enrichment) in EF graph, the source of Zn at those locations might be of geogenic origin or from the dumping side of scrape metals.

#### *Modified degree of contamination (mCd)*

The results of the modified degree of contamination for soils suggest that the



**Figure 5.** EF values of trace elements at different sampling locations.

studied area is highly contaminated ( $mCd = 2.26$ ) (Table 7). When comparing the  $mCd$  values for soil with the previous studies (Likuku et al., 2013) in the study area, they are defiantly higher. This is proving that trace elements are gradually being added to the soils with time. When considering individual element degree of contamination, Cu and Ni fall under very high degree of contamination.

#### *Integrated Pollution Index, (IPI)*

In this study, IPI values varied from 0.217 to 2.75. IPI values were found greater than 1 on those sampling locations that were either close to the mine or the areas that were situated on the windward direction of the smelter plant. The overall IPI value (Table 8) for soil is 7.7, which indicates that overall situation of soils around the abandoned mine of BCL is showing significant heavy metal pollution and deteriorating site quality. The IPI values for the sediment of each site varied between 0.98 and 2.13. The intensity of heavy metal contamination increases as the IPI value increase (Suresh et al., 2012). IPI values above two were found at site 11 and 15, depicting deteriorating site quality borne by the input of waste discharged from the mine by the inflowing river located along the direction of the tailing dam and slag pile. However, the overall metal and trace element pollution classification suggests that river sediment exhibited insignificant pollution.

#### *Geo-Accumulation Index (Igeo)*

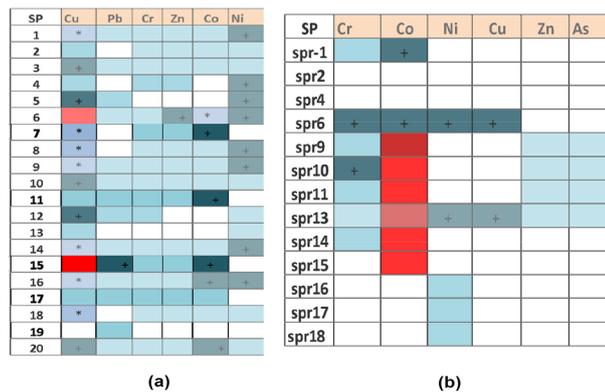
Igeo results for Cu, Ni, Cr, As, Co and Zn are presented in Figure 6. In the study area, considering the Igeo, most soils were included in Class 1 ( $0 < Igeo \leq 1$ ) and class 2 ( $1 < Igeo \leq 2$ ), that is, uncontaminated to moderately contaminated, with ~70% and ~20% of the samples, respectively, and only some soils in Class 3 ( $2 < Igeo \leq 3$ ), which were moderately to heavily contaminated by Cu and Co. A few sampling stations were included in Classes 4, heavily to extremely contaminated with Cu. Generally, it is revealed that soils in the study area is heavily contaminated with respect to Cu, moderately to heavily contaminate with Ni and Co and uncontaminated with the rest of the studied metals. Anthropogenic activities from mining processes such as smelting, slag piling and tailings dumping are the most important sources of Cu and Ni contamination in the study area.

**Table 7.** mCd values of trace elements in soil and sediments.

Heavy Metal	Soil	Sediments
Cr	1.46	1.31
Co	2.88	5.08
Ni	3.36	0.92
Cu	3.72	1.08
Zn	1.15	0.77
As	0.98	0.85
<b>C<sub>d</sub></b>	13.55	10.01
<b>mC<sub>d</sub></b>	2.26	1.67

**Table 8.** IPI values of trace elements in soil and sediments.

Metal	Soil	Sediments
Cr	1.5	1.3
Co	2.9	5.1
Ni	3.4	0.9
Cu	3.7	1.1
Zn	1.2	0.8
As	1.0	0.9
C <sub>d</sub>	13.6	10.0
mca	2.3	1.7
IPI	7.7	1.9



Class	Legend	Igeo range	Description
0		$I_{geo} \leq 0$	practically uncontaminated
1		$0 < I_{geo} \leq 1$	uncontaminated to moderately contaminated
2	+	$1 < I_{geo} \leq 2$	moderately contaminated
3	*	$2 < I_{geo} \leq 3$	moderately contaminated to strongly contaminated
4		$3 < I_{geo} \leq 4$	strongly contaminate
5		$4 < I_{geo} \leq 5$	strongly contaminate to extremely contaminated

**Figure 6.** Igeo and Pollution index values for soil (a) and sediments (b).

River sediments showed low Igeo values of Ni when compared to soils (**Figure 6(b)**), except for sampling location 6, 13, 16, 17 and 18. Most of these locations are upstream and downstream of Motloutse River. The Igeo values for copper revealed moderate contamination of sediments at sampling location 6 and 13. These sites are located at the streams flowing very close to the tailings and slag pile. Cr, Zn and As showed uncontaminated to moderate contamination. Co is the only trace element that showed strongly to extreme contamination for most sampling points.

#### **Value of Maximum Allowable Limits for Trace elements in Soil (mg/kg) from Different Countries as Compared to the Present Study**

Among the sampling sites, maximum total concentrations of all trace elements except Zn and As surpassed their corresponding background limits, the highest concentrations of Cu, Co and Ni were about 2.35, 2.4, and 1.6 times their corresponding standard limits **Table 9**. The concentrations of Cu and Ni at over 75% of the studied sites were beyond the values of all the referenced countries guideline limits as well as upper continent crustal values. When comparing the Chinese soil standard and results from this study, Cu and Ni demonstrated obvious trace element pollution around the Selibe Phikwe area. However, in comparison to the Japanese and Canadian limits, the concentrations of Cr was of a similar magnitude while Co and As were much less. When compared with upper crustal values, the concentrations of the eight priority trace elements were obviously higher, which was especially true for Co, Cu, Ni, which were 1.6, 2.3, and 2.4 times higher than their respective local background levels. The excessive loadings of trace elements respective to local background values might be a due to anthropogenic activities, more specifically from mining activities.

## **5. Conclusion**

Metals and trace elements assessment and source discrimination are essential for environmental improvement and protection strategy, especially for mineral resource producing countries. In the present study, selected trace element content in soil, sediments and water samples collected around the abandoned mine of BCL Cu-Ni mine has been studied. Comprehensive and robust environmental assessment methods were applied to carry out the geochemical analysis of the study area. These methods encompass contamination assessment, geochemical analysis, and spatial distribution of Cu, Ni, Cr, Co, Zn and As. The representative sampling points were meticulously chosen around the mine and along Letlhakane River and its tributaries. The geochemical baseline and the heavy metal contents in respective samples were evaluated. The mean geochemical baseline concentration of Cu, Ni, Cr, Co, Zn and As in soil samples were 38.23, 49.23, 65, 6.22, 34.93 and 3.93 mg/kg, respectively. Out of 42 soil-sampling stations, 14 locations had the values higher for Cu and Ni, 16 sites for Zn, 19 stations for Cr, 17 locations for Co and 19 for As than that of the geochemical baseline values, which may affect to a potential danger for the environment and the community of Selibe Phikwe mining town. Lower values for pH and higher levels of EC are

**Table 9.** Total average of soil trace elements and comparisons with local background values in upper crust and different countries.

Trace elements	Total average values <sup>a</sup>	Local background limit values <sup>a</sup>	UCC <sup>b</sup>	China <sup>c</sup>	Japan	Canada
Cr	79	89.8	35	200	-	75
Co	16	9.9	11.60	40	50	250
Ni	181	74.8	18.60	50	100	100
Cu	193	81.9	14.30	100	125	100
Zn	37	42.92	52	52	250	400
As	4	6.75	2	25	-	200

found in waters sampled immediately downstream of effluents passing through tailing dam and slag pile.

Enrichment factor, Geo-accumulation index, Pollution index were computed to assess the contamination status of the study area. Results of EF, Igeo and PI revealed that soil samples in the wind direction and central part of the study area where is close to the Copper Smelter and the waste dumps, respectively have higher contamination degree than the other soil samples. Soil samples located on the lee side and away from the waste dumps showed no significant anthropogenic sources, exhibiting minimum EF, Igeo and PI values for all analyzed metals. This fact reveals the adverse effects of anthropogenic sources (BCL Copper Smelter and BCL Copper Nickel mine) in the study area in the aspect of heavy metal pollution state. Results of EFs revealed a high degree of enrichment of Cu and Ni in soil and sediment. The outcomes of Igeo and EF were in agreement indicating a higher degree of metal pollution in the northwestern part of the windward direction of the study area. New indices, integrated pollution index (IPI) and modified degree of contamination (mCd) were proposed to assess metal pollution state in the study area based on trace element baseline values and their toxicity degree. Results of integrated indices (IPI and mCd) confirmed more metal pollution, and deteriorating site quality in the windward direction and on areas closer to the waste dumps when compared with other parts of the study area. Based on the application of different indices, it could be concluded that the primary anthropogenic sources of metals including BCL Copper smelter and abandoned BCL Copper mine had an adverse effect on metal pollution in soil and sediments samples. Comparing the concentration of trace elements with the other mining areas of the world, it can be concluded that the soils of the study area is moderately contaminated with trace elements, but if rehabilitation process is not commenced, the concentration of metals will increase to intolerable limits, which may create severe impacts on the soil environment and finally to the food chain.

## 6. Recommendations

Based on the findings of the present study, the following recommendations has

been drawn

- It is recommended to establish national soil and sediment contamination standard as well as soil and sediment background to examine and monitor the contamination level of the mine surroundings
- There is need for regular and periodic monitoring of soil surface and groundwater quality in order to ensure that the standards of trace elements constitutes as set by WHO are not exceeded.
- It is highly recommended to monitor elemental concentrations in surface soils routinely in future and accordingly to take necessary initiative by the local authority and government of Botswana.
- Study the potential human health risk for both non carcinogenic and carcinogenic risk of Cu, Ni, Cr, Co, Zn and As.

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### Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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