

Environmental Geochemistry of Mine Tailings Soils in the Artisanal Gold Mining District of Bétaré -Oya, Cameroon

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Abstract

Changes in trace element concentrations in mine tailings (dry and wet) were investigated in the gold mining area of Bétaré-Oya, Eastern Cameroon. Forty-one surface sediment samples were analyzed using ICP-MS for heavy metals and pollution was assessed using Enrichment Ratio and Geo Accumulation Index (Igeo); using a sample from a remote area as control. Trace elements in mine tailings show significant increase compared to the background (control) values, with the exception of Sr and Nb. It is suggested that allochthonous deposition may account for Sr distribution. A strong correlation is observed between the lithophile elements; Y, Nb, Ce, La, and Pb. Their association with each other is also strong, i.e. Nb/Ce (.73) and La/Ce (.63). The close association of these elements in the samples may be an indication of the effect of resistant heavy minerals from felsic rocks (mainly granites and gneisses). Cu, Zn, Sr and Ba distribution is associated with mineralisation of sulphide-bearing minerals and clay formation from weathering of mica schist. Cu, Zn, As, W, Mo and Ag have been identified as potential pollutants. Compared to the Dutch soil quality guidelines, these elements are above the target values and below the intervention levels. Arsenic is considered to be the most threatening element, with regards to its potency. The distribution of As in this area appears to be controlled by mining activities.

Keywords: gold mining, trace elements, tailings, Cameroon

1. Introduction

1.1 Background

Environmental impacts due to mining are commonly associated with large-scale mechanised activities. However, several studies are reporting that artisanal, informal mining also gives rise to environmental problems (e.g. Tarras-Wahlberg et al., 2000; Hilson, 2002; Babut et. al., 2003; Waziri, 2014) and that the consequences could be more serious due to higher levels of exposure, in addition to the fact because these non-formal operations are hardly regulated by government agencies, their impact on the environment may go completely unnoticed.

During mining, a fine grind of the ore is often necessary to release metals and minerals, so the mining industry produces enormous quantities of fine rock particles, in sizes ranging from sand-size down to as low as a few microns (USEPA, 1994). These fine-grained wastes are known as "tailings". By far, the larger proportion of ore mined in most industry sectors ultimately becomes tailings that must be disposed of. In the gold industry, only a few hundredths of an ounce of gold may be produced for every ton of dry tailings generated (USEPA, 1994). These substances can be easily dispersed into the surrounding areas and can be carried off by processes of weathering into waterbodies. Tailings constitute a major source of pollution due to its potentially high chemical reactivity resulting from its large surface area. The potential for elements present in soils and sediments to be mobilised/immobilised and redistributed depends on several soil factors such as organic matter, type and amount of clay, pH, redox conditions and cation exchange capacity (CEC). Under the right geochemical conditions such as the pH and the prevailing redox conditions; and pathways, these elements can easily be mobilized and transmitted through for example, water and the food chain to humans. Previous researchers have highlighted the potentially negative environmental impacts of these processes on biodiversity, ecosystem function and ecosystem services (Malaviya, Munsu, Oinam & Joshi, 2010; Simmons et al. 2008). Amonoo-Neizer, Nyamah, & Bakiamoh (1995) reported the significant distribution of As and Hg in the top soils, plantain, water fern, elephant grass,

cassava and mud fish at Obuasi, (Ghana) and its environs. The aim of this work is therefore to assess trace element distribution and contamination in mine tailing from artisanal gold mining in Betare Oya, Cameroon.

1.2 Location, Climatic Setting and Drainage

Bétaré-Oya (Figure 1) is located on the south eastern edge of the Adamawa plateau, close to the Central African Republic (CAR) at 5°35'59" N, and 14°04'59" E. It lies in the transition zone between the equatorial forest to the south and the savannah to the north. It is found at an elevation of 779m asl with a regional topography comprising largely of monotonous, ridges, deep river valleys and gently undulating plains. This area is under the influence of a tropical, humid type A wet Equatorial climate with two seasons; the wet rainy season (March to October) with abundant rainfall and a short dry season (October to mid-March) with abundant sunshine. Humidity and cloud cover are relatively high and precipitation ranges from 1500 to 2000mm per year except in the extreme east and north regions where it is slightly less. Average annual temperature range from 22.8 °C to 24.7°C.

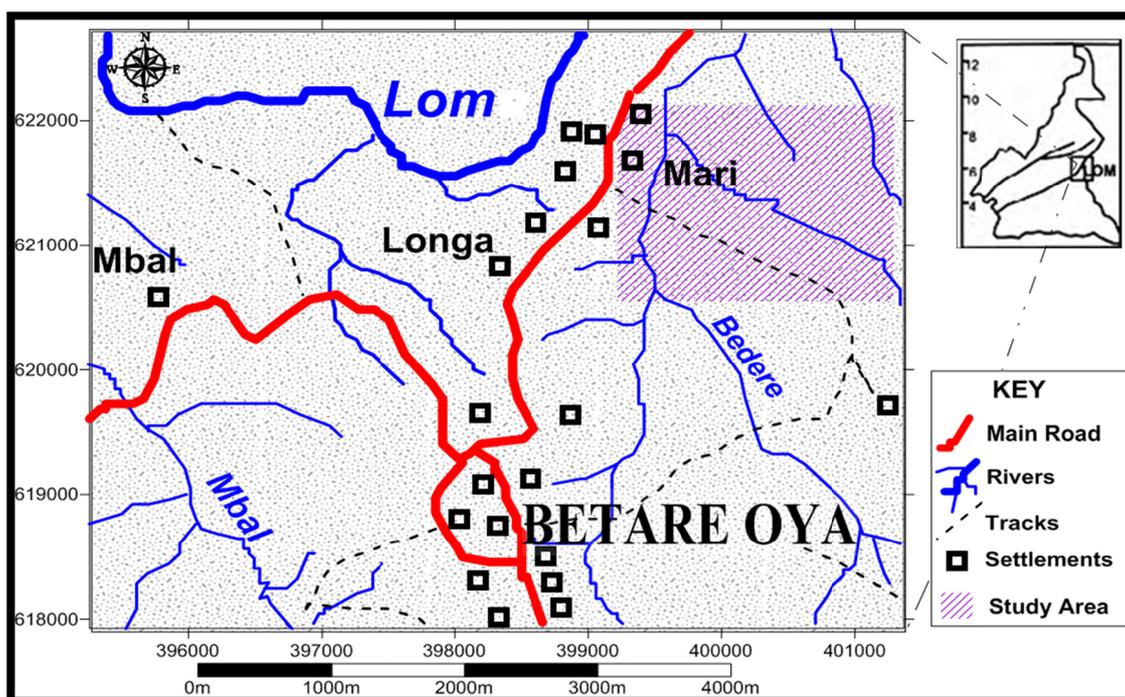


Figure 1. Map of the study area

The Bétaré-Oya gold district has several river systems that traverse the plains: the Nyong, Kadei, Boumbe and Lom rivers. These rivers flow all year round. Other secondary streams together with their tributaries also constitute a significant part of the drainage system e.g. the Mari River, Nguengue River, Mbigala, Lisso, Mbaya and Fofo, which drain into the Lom. The prevalence of metasedimentary rocks in the study area offers relatively uniform resistance to erosion, which favours dendritic configuration of the individual stream courses in the area. The vegetation is dominantly of primary nature comprising of low land tropical rain forest, which grows progressively thicker towards the south. The land area is sparsely cultivated and most of the natural vegetation is still intact.

1.3 Geologic Setting and Gold Mineralization

The regional geology is dominated by the Neoproterozoic volcano-sedimentary rocks of the Lom group, metamorphosed under low- to medium-grade conditions (Suh, Lehmann, & Mafany, 2006) and cross-cut by the Pan-African granitoids. The Lom Series is comprised of biotite schists, sericite and chlorite schists, quartzites and shales (Freyssinet, Lecomte, & Edimo, 1989). These rocks are characterized by a NE-SW steeply dipping foliation resulting from a regional right-lateral transpressive deformation. The granites are rich in quartz (SiO_2), feldspars $[(\text{K}, \text{Ca}, \text{Na})(\text{Al}, \text{Si})_3\text{O}_8]$, biotite and remnants of amphiboles and pyroxenes. Gold is hosted in quartz veins which are confined in brecciated and locally silicified metavolcanic and metasedimentary rocks, intruded

by post-tectonic mafic and felsic magmas of unknown age (Suh et al., 2006). Gold occurs as small particles disseminated within the quartz matrix and along microfractures within the veins. These veins have as much as 54ppm gold. The quartz matrix is associated with sphalerite (ZnS), pyrite (FeS), chalcopyrite (CuFeS₂), arsenopyrite [(As,Fe)S], galena (PbS) and barite (BaSO₄) and rare pyrrhotite. Freyssinet et al. (1989) identified Au-Mo-W-Pb-Bi element association in the host rock and overburden as pathfinder elements for gold in the Lom area. Other ore minerals produced by weathering in the quartz veins are hematite (Fe₂O₃), covellite and chalcocite (complex hydroxides of Cu and Fe), and psilomelane (Mn hydroxides) (Suh et al., 2006). Although Vairon (1986) attributed a Proterozoic age (2100–2200 Ma, Birrimian) to the Lom series, recent data (Soba et al. 1991) provide evidence of inherited Archaean ages (c. 2500 Ma) and Neoproterozoic ages (700–1100 Ma) on zircons from detrital material and Neoproterozoic ages (c. 700 Ma) from metavolcanic rocks in this district. The soil in the area is predominantly acrisols, alisols, plinthosols, acid soil with clay-enriched lower horizon and low saturation of bases.

2. Method

2.1 Sampling Analysis

Field work was done in the month of February. Sampling was random but purposive (only tailings) over the entire region of Mari artisanal gold mining site. Forty (40) samples were collected comprising of thirty (30) dry tailing samples from the tailing pile and ten (10) wet tailing samples from both active and inactive mining sites. A control sample was collected about 50km from Bétaré-Oya town at Ndokayo; a location remote from the mining area in the outskirts of Bétaré-Oya and far removed from the influence of mining activities. Forty one soil samples were shipped to ACME Analytical Laboratory, Canada for chemical analysis. The samples (0.5g) were leached in hot (95°C) Aqua Regia (HNO₃/HCl) for 2 hours. The digested samples were then cooled and diluted with deionised water and analyzed for their trace metal content by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Spiked duplicate samples were used to determine precision and bias. In order to allow for data analysis, concentrations below LOQ (limits of quantification) were replaced with half the LOQ for some of the trace elements (USEPA, 2000; Waziri, 2014). While those data points may not be very reliable, this is probably a better alternative to assigning zero concentration or removing the affected samples from the database (Waziri, 2014).

2.2 Data Treatment Procedures

Two pollution indices were used to assess the levels of contamination of the sediments: Enrichment Ratio (ER) and Geoaccumulation index, Igeo:

Enrichment Ratio (ER): Enrichment ratios, adopted from Albright, (2004) were calculated in order to assess the extent of enrichment and /or depletion of trace elements in the soils of the two study areas relative to their crustal concentrations. In this case, the control value was used as the background concentration (1).

$$ER = C_m / B_m \quad (1)$$

Where:

C_m is the concentration of an element measured in a sample and B_m is the background or baseline concentration, in this case the control value.

Geoaccumulation Index: The index of geoaccumulation (Igeo) actually enables the assessment of contamination by comparing the current and pre-industrial concentrations. Originally used with bottom sediments by Muller (1969), Igeo has widely been applied in the assessment of soil contamination (Likuku, Mmolawa & Gaboutloeloe, 2013). The geoaccumulation index (Igeo) is expressed as follows (Singh, 2001) (2):

$$I_{geo} = \log_2 \left(\frac{C_n}{1.5 \times B_n} \right) \quad (2)$$

Where:

C_n = measured metal concentration at sampling point; B_n = background concentration value for element; 1.5 = the background matrix correction factor. The factor 1.5 is introduced to minimize the effect of possible variations in the background values which may be attributed to lithologic variations in soils.

The geoaccumulation index assess contamination based on seven grades (0 – 6) ranging from unpolluted to very highly polluted. These seven descriptive classes are as follows: <0 = practically uncontaminated; 0 – 1 = uncontaminated to slightly contaminated; 1 – 2 = moderately contaminated; 2 – 3 = moderately to highly contaminated; 3 – 4 = highly contaminated; 4 – 5 = highly to very highly contaminated and >5 = very

highly/strongly contaminated.

3. Results and Discussion

3.1 Trace Element Concentrations

Table 1 is a summary statistics of chemical analysis of tailings samples (dry and sediment) and comparative concentrations of global crustal averages and trigger values. Gold has the lowest mean concentration followed by Cd and W, whereas Ba and Zr have the highest mean concentrations (579ppm and 651ppm respectively), similar observations were recorded in the Birim-Gwari (Nigeria) gold mine (Waziri, 2014). Ce, Zn, Sr and Nb have average values of about 50ppm, while the least abundant is Au; for the later, as the element of interest, it is most depleted in the tailings relative to the control soil. Low content can be as a result of low concentration in the original parent rock, and removal during mineral extraction and weathering processes. W, Ce and Nb are generally known to occur in trace quantities in rocks as reflected in the average continental crustal abundance. The elements with the highest concentration, Ba and Zr display different patterns that may have a bearing on the processes accounting for their distribution. The abundance of barite, micaschists and granatoids (Suh et al., 2006) of the parent rock which are host to Ba possibly accounts for the high Ba content. In addition, the substitution of Ba and Rb for K in K-feldspar and mica also serves as a source of this element. Mineralisation of feldspar will liberate Ba which adsorbs onto solid (secondary clay mineral)Fe-(oxy)hydroxides or phosphates particularly during the early stages of weathering (Price, Gray, Wilson, Fray, & Taylor, 1991). However, considering that K-bearing minerals are relatively more resistant to chemical weathering (Berner and Berner, 1996), release of Ba from them is likely to be limited. In addition, due to its lower solubility (relative to the other alkaline earth metals) Ba in aqueous systems is likely to be retained in neo-formed clays; thereby increasing its concentration in sediments. Mining activities seem to increase its concentration, such that it is a-par with the values of crustal abundances. Zr content in the control sample is higher relative to crustal abundance; the former is negatively affected in the mining area (as indicated by the test statistic), considering the mean and standard deviation. Zr is primarily present in zircon and other heavy minerals in the parent rock.

Table 1. Descriptive statistics for heavy metals and one-sample statistic t-test with test value as Control and comparative trigger concentrations of Continental crust and soils

| | This study | | | | | | Continental crust | | Trigger & intervention ^c |
|-----------|------------|------|--------|--------|---------|--------------|-------------------|-----|-------------------------------------|
| | Min | Max | Mean | SD | Control | P-value | A | b | |
| Au | .05 | 4.2 | 1.10 | 0.95 | .05 | 1.12E-08 | | | |
| Cu | 6 | 58 | 27.60 | 12.83 | 1 | 3.5E-16 | 25 | 25 | 140- 720 |
| Zn | 26 | 111 | 59.00 | 20.59 | 4 | 7.68E-20 | 71 | 65 | 50-100 |
| As | 5 | 43 | 19.78 | 12.55 | .05 | 1.5E12 | 1.5 | | 29- 59 |
| Sr | 20 | 152 | 53.33 | 24.20 | 50 | 0.195 | 350 | 333 | |
| Y | 16 | 82 | 39.35 | 12.09 | 20 | 9.07E-13 | | | |
| Nb | 23 | 99 | 48.28 | 14.37 | 52 | 0.055 | 25 | 29 | |
| Mo | 1 | 5 | 2.08 | 0.92 | .05 | 4.13E-17 | 1-5 | | |
| Ag | 2.1 | 18 | 8.21 | 3.90 | .05 | 2.75E-16 | | | |
| Cd | 1 | 2 | 1.20 | 0.41 | 1 | 9.38E-21 | | | 0.8- 12 |
| Sb | 5 | 11 | 6.68 | 2.22 | 1 | 1.31E-05 | | | |
| Ba | 220 | 990 | 578.95 | 183.66 | 112 | 4.19E-19 | 550 | 584 | |
| La | 10 | 54 | 20.25 | 10.71 | 8 | 5.18E-09 | 30 | 30 | |
| Ce | 36 | 164 | 80.85 | 26.07 | 14 | 3.15E-19 | 64 | 60 | |
| W | 1 | 13 | 3.88 | 3.41 | .05 | 7.74E-09 | | | |
| Pb | 18 | 54 | 31.33 | 8.23 | 5 | 1.4E-22 | 20 | 15 | 85- 530 |
| Zr | 369 | 1143 | 650.85 | 198.43 | 919 | 8.96E-11 | 190 | 203 | |

a: Upper continental crust, Taylor and McLennan, (1995); b: Wedepohl, (1995); c: Dutch values Bird et al., (2003)

The difference in concentration between the tailings sediment and the control is evaluated by the one sample t-test (with the control as the test value). The derived p-value ($\alpha=0.05$) of the test statistics, indicates that the null hypothesis can be rejected (i.e. the difference between the means is less than 0) for all elements with the exception of Sr and Nb. The statistically significant (compared to control) concentration of all elements introduced into the surface soil of the mining area, indicates increases in elemental concentrations in the mining area (i.e. Au, Cu, Zn, As, Y, Mo, Ag, Cd, Sb, Ba, La, Ce, W and Pb). Similar situations have been observed worldwide, such as in the Migori Gold Belt, Kenya, wherein the concentrations of heavy metals in the surface soil of this region, are above acceptable and background levels (Ogola, Mitullah, & Omula, 2001). Some of these elements can even exceed critical levels. Compared to the crustal abundances, Sr content in the control sample is lower (about three times), while Nb is almost twice as high relative to the crustal abundance. Mining has not affected the concentrations of these two elements (following the results of the test statistic). The behavior of Nb may be due to intense chemical weathering in both the mining and control site. Sr on the other hand may have its concentrations affected by allochthonous depositions in the control area, or leaching from the mining area; thereby maintaining concentrations between the two areas close/unchanged.

A comparison of the content of the tailings and published soil concentration guidelines is undertaken to assess the toxicity of certain elements. As is an element of particular concern in gold mining areas (Carvalho, Neiva, & Silva, 2009; Inam et al, 2011) where high releases are associated with pollution. Arsenic concentrations in the sediments are significantly higher compared to the control sample as evident in the results of the t-test; inferring a very strong possibility of potential environmental pollution. Gold mine tailings at Obuasi, Ghana for instance, contain very high amounts of As, averagely 8305 mg/kg (Ahmad & Carboo, 2000). This has been linked to the considerable level of naturally occurring arsenic at Obuasi, as well as liberations from arsenic-bearing gold ores during gold extraction (Amonoo-Neizer et al., 1995; Ahmad & Carboo, 2000; Kumi-Boateng, 2007). The As content in the study area is not comparable to that of Obuasi (Ghana). However compared to the soil quality guidelines (Dutch), the values (including standard deviation) have exceeded the target value. The Dutch target values indicate that if concentrations do not exceed this value, the site is considered clean with no eco-toxicological risk. Zn content also falls above the target value.

3.2 Pollution Indices

The ER provides an estimate of the changes in concentrations in the examined tailings soils, relative to the background or undisturbed soils (Table 2). Soil from the control area was used as baseline and is referred here as control sample soil. ER of 1 indicates that the soil or sediment is neither enriched nor depleted in a particular element relative to the soil in the control area. Enrichment and depletion are represented by ER values of >1 and <1 respectively. As (395.5) and Ag (164) show the highest mean enrichments whereas Zr (0.71) and Nb (0.93) are depleted. Considering that As content has been increased almost 400 times as a result of mining is a possible indication of sulphide oxidation processes. Mobility and loss of Zr during weathering in tropical areas have been reported in literature (Braun, Pagel, Herbillon, & Rosin, 1993; Colin, Alarcon, & Vieillard, 1993). Some elements of environmental concerns that have equally been enriched include Cu, Zn, Cd and Pb indicating that artisanal mining has contaminated the environment with these elements.

Table 2. Summary of indices of Enrichment Ratio (ER) for trace elements in tailings sediments (n=40)

| Element | Min | Max | Mean | SD |
|-----------|--------|--------|---------------|-------|
| Au | 1.00 | 84.00 | 21.93 | 18.9 |
| Cu | 6.00 | 58.00 | 27.60 | 12.8 |
| Zn | 6.50 | 27.75 | 14.75 | 5.1 |
| As | 100.00 | 860.00 | 395.50 | 250.9 |
| Sr | 0.40 | 3.04 | 1.07 | 0.5 |
| Y | 0.80 | 4.10 | 1.97 | 0.6 |
| Nb | 0.44 | 1.90 | 0.93 | 0.3 |
| Mo | 20.00 | 100.00 | 41.65 | 18.3 |
| Ag | 42.00 | 360.00 | 164.15 | 78.1 |
| Cd | 20.00 | 40.00 | 24.00 | 8.1 |

| | | | | |
|-----------|-------|--------|-------|------|
| Sb | 1.00 | 2.20 | 1.34 | 0.4 |
| Ba | 1.96 | 8.84 | 5.17 | 1.6 |
| La | 1.25 | 6.75 | 2.53 | 1.3 |
| Ce | 2.57 | 11.71 | 5.78 | 1.9 |
| W | 20.00 | 260.00 | 77.50 | 68.1 |
| Pb | 3.60 | 10.80 | 6.27 | 1.6 |
| Zr | 0.40 | 1.25 | 0.71 | 0.2 |

Table 3 is a summary of the results of the geoaccumulation index. Based on the *I_{geo}* classes, the results show that the study area may have problems relating to Ag, W and As pollution. Potential contamination problems linked to As and Ag have already been cited by ER values. Similarly, Cu, Zn, Mo and Cd with mean *I_{geo}* value ≥ 4 point to possible problems of contamination. Sr, Nb, Sb and Zr fall within the unpolluted class. Although the nature of the *I_{geo}* calculation, which involves the logarithmic function and a background multiplication factor of 1.5, is somewhat different from ER, the *I_{geo}* factors are in general comparable to results reported for ER, as observed in previous studies (i.e. Likuku et. al., 2013).

Table 3. Summary of indices of geoaccumulation, *I_{geo}* for trace elements in tailings sediments (n=40)

| | Min | Max | Mean | I_{geo} Class |
|-----------|------------|------------|-------------|------------------------------|
| Au | -0.58 | 5.81 | 2.68 | 3 |
| Cu | 2.00 | 5.27 | 4.00 | 4 |
| Zn | 2.12 | 4.21 | 3.20 | 4 |
| As | 6.06 | 9.16 | 7.67 | 6 |
| Sr | -1.91 | 1.02 | -0.62 | 0 |
| Y | -0.91 | 1.45 | 0.33 | 1 |
| Nb | -1.76 | 0.34 | -0.74 | 0 |
| Mo | 3.74 | 6.06 | 4.65 | 5 |
| Ag | 4.81 | 7.91 | 6.59 | 6 |
| Cd | 3.74 | 4.74 | 3.92 | 4 |
| Sb | -0.58 | 0.55 | -0.23 | 0 |
| Ba | 0.39 | 2.56 | 1.69 | 2 |
| La | -0.26 | 2.17 | 0.56 | 1 |
| Ce | 0.78 | 2.97 | 1.87 | 2 |
| W | 3.74 | 7.44 | 5.11 | 6 |
| Pb | 1.26 | 2.62 | 1.99 | 2 |
| Zr | -1.90 | -0.26 | -1.15 | 0 |

3.3 Geochemical Association

Geochemical association is performed with the aim of determining the possible sources of elements, especially potentially toxic ones in the soils and sediments. Multivariate statistical methods in the form of correlation matrix and principal component analysis were used to classify the elements into groups that may signify common origin.

Spearman correlation analysis was performed between all variables (with a level of significance: $p \leq 0.01$) and the multi-element correlation for sediment samples was determined and the results are given in Table 4. The strongest positive association is between Au and Ag. This association can be explained as the occurrence of Au-Ag alloys (Chapman, Leake, Bond, Stedra, & Fairgrieve, 2009) of type A in which Ag concentrations in the cores occur as discrete grains having sulfide inclusions and only minor variations in core composition. Cu and

Zn are strongly correlated (0.75), and these two elements are positively correlated with Sr and Ba and negative with Mo and W. Cu and Zn represent mineralization and weathering of sphalerite, chalcopyrite and other sulphide-bearing minerals. According to Teusch, Halicz, & Chadwick, (1999) Zn is likely to be associated with organic matter as well as with Mn and Al oxides and hydrous oxides, whereas Cu is probably associated with organic matter. Ba and Sr reflect weathering and mineralisation of alkali earth minerals which are hosted in minerals such as feldspars and micas. The association between these elements can partially be explained by the application of Ba/Sr ratios as proxy for the weathering of silicate rocks (Dalai, Krishnaswami, & Sarin, 2002). Negative association between Cu-Zn and W-Mo can be explained by the fact that they occur in different petrological associations; the former occur in the quartz matrix hosting the veins associated with the latter. The latter is associated with the gold grains in the veins; this assertion is supported by the identification of Au-Mo-W-Pb-Bi element association in the host rock and overburden as pathfinder elements for gold in the Lom area by Freyssinet et al. (1989). A strong correlation is observed between the lithophile elements: Y: Nb (.71), Ce (.79), La (.51), Zr (.31). The association with each other is also strong, i.e. Nb/Ce (.73) and La/Ce (.63). The close association of these elements in the samples may be an indication of the effect of resistant heavy minerals from felsic rocks (mainly granites and gneisses) on the geochemistry of soils and sediments in the area. Pb displays strong association with the lithophiles, i.e. 0.63, 0.63, and 0.55 for Y, Nb and La respectively. Here Pb could be hosted in the felsic rocks and the resistant heavy minerals. The close association of Pb with As and W could relate to Pb which is present in S-bearing minerals and two of these elements, W and Pb are pathfinder for gold in this area (Freyssinet et al. 1989).

Table 4. Spearman correlation matrix of trace elements, significance ($p \leq 0.01$)

| | Au | Cu | Zn | As | Sr | Y | Nb | Mo | Ag | Cd | Sb | Ba | La | Ce | W | Pb | Zr |
|----|-------------|--------------|--------------|-------------|--------------|-------------|-------------|--------------|--------------|--------------|--------------|-------------|-------------|-------------|--------------|-------------|--------------|
| Au | 1.00 | 0.06 | 0.21 | 0.08 | 0.12 | -0.01 | 0.11 | -0.15 | 0.83 | -0.01 | -0.22 | 0.24 | 0.09 | 0.06 | -0.16 | 0.31 | -0.07 |
| Cu | 0.06 | 1.00 | 0.75 | -0.25 | 0.47 | 0.21 | 0.20 | -0.47 | 0.00 | 0.02 | -0.08 | 0.43 | 0.07 | 0.17 | -0.41 | 0.15 | -0.18 |
| Zn | 0.21 | 0.75 | 1.00 | -0.21 | 0.58 | 0.29 | 0.24 | -0.38 | 0.07 | -0.08 | -0.19 | 0.54 | 0.04 | 0.20 | -0.31 | 0.30 | 0.08 |
| As | 0.08 | -0.25 | -0.21 | 1.00 | -0.30 | 0.07 | 0.16 | 0.26 | 0.00 | -0.23 | 0.31 | -0.08 | 0.24 | 0.12 | 0.65 | 0.40 | -0.09 |
| Sr | 0.12 | 0.47 | 0.58 | -0.30 | 1.00 | -0.10 | 0.09 | -0.21 | 0.01 | -0.24 | -0.35 | 0.53 | -0.23 | 0.18 | -0.23 | 0.04 | 0.20 |
| Y | -0.01 | 0.21 | 0.29 | 0.07 | -0.10 | 1.00 | 0.71 | -0.17 | 0.11 | -0.25 | 0.10 | -0.05 | 0.51 | 0.72 | -0.11 | 0.42 | 0.31 |
| Nb | 0.11 | 0.20 | 0.24 | 0.16 | 0.09 | 0.71 | 1.00 | -0.04 | 0.19 | -0.23 | 0.02 | -0.10 | 0.48 | 0.79 | -0.06 | 0.63 | 0.31 |
| Mo | -0.15 | -0.47 | -0.38 | 0.26 | -0.21 | -0.17 | -0.04 | 1.00 | -0.10 | 0.06 | -0.04 | -0.13 | 0.13 | -0.03 | 0.28 | 0.07 | -0.04 |
| Ag | 0.83 | 0.00 | 0.07 | 0.00 | 0.01 | 0.11 | 0.19 | -0.10 | 1.00 | 0.01 | -0.32 | 0.17 | 0.09 | 0.14 | -0.19 | 0.32 | 0.00 |
| Cd | -0.01 | 0.02 | -0.08 | -0.23 | -0.24 | -0.25 | -0.23 | 0.06 | 0.01 | 1.00 | -0.13 | -0.14 | 0.05 | -0.27 | -0.40 | 0.01 | -0.36 |
| Sb | -0.22 | -0.08 | -0.19 | 0.31 | -0.35 | 0.10 | 0.02 | -0.04 | -0.32 | -0.13 | 1.00 | -0.15 | 0.01 | 0.06 | 0.31 | 0.03 | -0.02 |
| Ba | 0.24 | 0.43 | 0.54 | -0.08 | 0.53 | -0.05 | -0.10 | -0.13 | 0.17 | -0.14 | -0.15 | 1.00 | 0.04 | 0.11 | -0.16 | 0.22 | 0.02 |
| La | 0.09 | 0.07 | 0.04 | 0.24 | -0.23 | 0.51 | 0.48 | 0.13 | 0.09 | 0.05 | 0.01 | 0.04 | 1.00 | 0.60 | -0.04 | 0.55 | 0.05 |
| Ce | 0.06 | 0.17 | 0.20 | 0.12 | 0.18 | 0.72 | 0.79 | -0.03 | 0.14 | -0.27 | 0.06 | 0.11 | 0.60 | 1.00 | -0.17 | 0.64 | 0.40 |
| W | -0.16 | -0.41 | -0.31 | 0.65 | -0.23 | -0.11 | -0.06 | 0.28 | -0.19 | -0.40 | 0.31 | -0.16 | -0.04 | -0.17 | 1.00 | 0.05 | -0.08 |
| Pb | 0.31 | 0.15 | 0.30 | 0.40 | 0.04 | 0.42 | 0.63 | 0.07 | 0.32 | 0.01 | 0.03 | 0.22 | 0.55 | 0.64 | 0.05 | 1.00 | 0.15 |
| Zr | -0.07 | -0.18 | 0.08 | -0.09 | 0.20 | 0.31 | 0.31 | -0.04 | 0.00 | -0.36 | -0.02 | 0.02 | 0.05 | 0.40 | -0.08 | 0.15 | 1.00 |

Principal component analysis was conducted in order to further assess the relationship patterns. While PCA does not show what controls the distribution of elements, it is useful for drawing inferences from elemental associations. Varimax orthogonal rotation was applied to the PCA in order to minimize the effects of non-normal data (Gong et al., 2010), especially the effects of high concentrations. Five components (Table 5), explaining about 71.16 % of the variance were extracted. Component 1 is associated with loadings of lithophiles (Y, Nb, La, Ce) along with Pb. This relationship has already been revealed in the correlation matrix and again is interpreted as an indication of effect of resistant heavy minerals from felsic rocks (mainly granites and gneisses) on the geochemistry of soils and sediments in the area. Component 2 is positively correlated with Cu, Zn, Sr and Ba. This relationship too has been indicated in the correlation matrix and is associated with mineralisation and clay

formation from weathering. The third component is negatively associated with Au and Ag; a relationship that has already been observed from the correlation matrix. The last two components have As and W which correlates positively and; Sr and Zr correlating negatively with Cd. The presence of Sr, along with Zr may support the fact that the distribution of this element may also be associated with anthropogenic and allochthonous deposition, as suggested by the insignificant variation between the mining and control areas.

Table 5. Total variance explained for trace element contents in tailings sediments

| Component | Initial Eigenvalues | | | Extraction sums of Squared loadings | | | Rotation sums of squared loadings | | |
|-----------|---------------------|--------|-------|-------------------------------------|--------|--------|-----------------------------------|--------|--------|
| | Total | Var. % | Cum % | Total | Var. % | Cum. % | Total | Var. % | Cum. % |
| 1 | 3.68 | 21.63 | 21.62 | 3.67 | 21.62 | 21.62 | 3.5 | 20.57 | 20.57 |
| 2 | 3.19 | 18.74 | 40.36 | 3.19 | 18.74 | 40.36 | 2.75 | 16.19 | 36.76 |
| 3 | 2.06 | 12.12 | 52.48 | 2.06 | 12.12 | 52.48 | 2.11 | 12.39 | 49.15 |
| 4 | 1.63 | 9.56 | 62.04 | 1.63 | 9.56 | 62.04 | 2.09 | 12.28 | 61.43 |
| 5 | 1.55 | 9.12 | 71.17 | 1.55 | 9.12 | 71.17 | 1.65 | 9.73 | 71.16 |
| 6 | 1.22 | 7.15 | 78.32 | | | | | | |

Table 6. Rotated component matrix for trace elements contents of tailings sediments

| Component | 1 | 2 | 3 | 4 | 5 |
|-----------|------|------|-------|------|-------|
| Y | 0.83 | | | | |
| Nb | 0.75 | | | | |
| La | 0.79 | | | | |
| Ce | 0.90 | | | | |
| Pb | 0.69 | | | | |
| Cu | | 0.86 | | | |
| Zn | | 0.87 | | | |
| Sr | | 0.55 | | | 0.59 |
| Ba | | 0.67 | | | |
| Au | | | -0.90 | | |
| Ag | | | -0.94 | | |
| As | | | | 0.86 | |
| W | | | | 0.81 | |
| Cd | | | | | -0.76 |
| Zr | | | | | 0.63 |

In conclusion, the results identify Ba and Zr to have the highest mean concentrations (579 and 651 ppm respectively). All the elements (i.e. Au, Cu, Zn, As, Y, Mo, Ag, Cd, Sb, Ba, La, Ce, W and Pb) with the exception of Sr and Nb have increased in the mining area and similar situations have been reported worldwide (e.g. Ogola *et al.*, 200; Waziri *et al.*, 2014). Nb trends can be attributed to its generally reported immobile nature, whereas for Sr, it is suggested that extensive leaching in the mining area and/or allochthonous deposition in the control area may influence its distribution. Pollution indices identified potential pollutants to include Cu, Zn, As, W, Mo and Ag. Compared to the Dutch soil quality guidelines, these elements are above the target values and below the intervention level. Among these As is considered the most threatening, considering its potency. The distribution of As in this area appears to be controlled by mining activities. Cu, Zn, Sr and Ba distribution is associated with mineralisation of sulphide-bearing minerals and clay formation from weathering of mica schist.

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