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Are Indexes of Ecological Risk Associated with Trace Metals Relevant for the Characterization of Mine Tailings and Polluted Soils in the Katangese Copperbelt (DR Congo) and for Assessment of the Performance of Remediation Trials

Serge Langunu [1,2,*], Jacques Kilela Mwanasomwe [1], Gilles Colinet [2,*] and Mylor Ngoy Shutcha [1,3]

[1] Ecology, Ecological Restoration and Landscape, Faculty of Agronomic Sciences, Université de Lubumbashi, Lubumbashi 1825, Democratic Republic of the Congo; jacqueskilela@gmail.com (J.K.M.); mylor.ngoyshutcha@unilu.ac.cd (M.N.S.)

[2] Water-Soil-Plant Exchanges, TERRA, Gembloux Agro-Bio Tech, University of Liège, 5030 Gembloux, Belgium

[3] Plant Ecology and Biogeochemistry, Université Libre de Bruxelles, 1050 Bruxelles, Belgium

* Correspondence: serge.langunu@uliege.be (S.L.); gilles.colinet@uliege.be (G.C.)

Abstract: This study aims to contribute to the characterization of Katangese Copperbelt's mining wastes and soils polluted with trace metals, using pollution indices and direct concentration measurements. The study also evaluated the use of these indices in assessing the success of remediation projects. Analytical data from previous studies and samples collected from six types of discharge and one polluted soil were used to address the first objective. Soil and plant samples were collected at Kipushi and Penga Penga for the second objective. The results revealed very high concentrations of As, Cd, Co, Cu, Mn, Pb, and Zn in all mine tailings and polluted soils, compared with local references. The degree of contamination (DC) values (from 72 to 5440) and potential ecological risk (RI) values (from 549 to 162 091) indicate very high-risk situations associated with polluted discharges and soils. Regarding revegetation trials, the results show lower concentrations and RIs in tree rhizospheres compared with unamended areas at both sites. However, trace metal concentrations are higher in tree rhizospheres compared with local references, and RI values are in the considerable risk range for Penga Penga (RI = 533) and very high (>1500) for Kipushi. Bioconcentration factor values are below 1, indicating low accumulation in roots, wood, and leaves, and low risk of contamination of the trophic chain. In this context, it seems that the pollution indices used are unsuitable for assessing the effectiveness of phytotechnology processes based on metal stabilization. Direct plant performance measurements combined with direct measurements of metals in substrates and plants to assess transfer and efficiency are more appropriate.

Keywords: trace metals; mining waste; phytoremediation; ecological risk indices; Katangese Copperbelt

1. Introduction

Mining activities in the Katangese Copperbelt (KCB) over more than a century generated huge quantities of mining waste. These result from ore extraction in mines and metallurgical processes for ore purification; a typology of mining waste in the KCB is provided in the literature [1,2]. Mining is responsible for metal dissemination and the related pollution of the environment as reported by numerous studies. Mining wastes cover large areas and are an important component of the landscape in the KCB, leading to socio-environmental and public health issues. Several studies have demonstrated the negative impact of mining activities on soils [3–6], surface, and groundwater [7,8]. Human exposure occurs via consumption of contaminated agricultural products [9–11] and fish [12]

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as well as direct ingestion of contaminated dust and water [13]. Evidence of the impact of high exposure to trace metals in the KCB are well documented. Banza et al. [13] produced one of the first reports highlighting the high exposure of populations living close (0-3 km and 3-10 km) to a mining site or refinery in KCB, with all analysed trace metals being above the World Health Organization's (WHO) threshold values. Several studies have reported the link between high exposure and the occurrence of specific diseases [13–17]. This high human exposure is exacerbated by the proximity of mining wastes and polluted sites to densely populated cities and urban areas.

Reducing or limiting human exposure to trace metals in the KCB needs a well-conceived remediation plan at a regional scale. Results from trials of mining waste and polluted soil remediation in the KCB are reported in the literature. Remediation is mainly based on the use of metal-tolerant plant species in phytoremediation strategies [18–21] or the use of woody species to enhance or improve the production of ecosystem services from vegetation to be established on mining wastes and contaminated soils [11,22,23]. In addition, reclaiming mining wastes based on their valorization in industry, to extract metals of interest (Cu, Co, Zn, etc.) and reduce their concentrations in the 'new' discharged wastes has been proposed [1,24–26]. To date, no study of the remediation trials of polluted rivers and lakes has been reported.

Up to now, most reported studies were limited to the comparison of metal concentrations in waste and contaminated soils to thresholds from the Democratic Republic of the Congo regulation or international standards, or assessing the potential of mining waste to release metals into the environment. To improve assessment of the risks associated with mining wastes by using pollution indices and suggest the most relevant remediation methods for each situation requires integrative methods for large scale characterization at the KCB level. This kind of large-scale integrated characterization is missing from former studies in the KCB.

In this context, the metal pollution indices used for the assessment of the hazardousness of mine wastes, sediments, and soils could also be a relevant tool to assess the metal concentrations themselves. Used as a mean for integrating the concentrations of a certain number of metals to quantify the level of contamination and the risks associated with mining wastes and contaminated sites for humans and the environment, these indices could potentially also be used to prioritize areas for remediation [27]. Numerous indices of the hazardousness of mining waste and contaminated sediments and soils have been developed to assess the risk associated with concentrations of individual (single indices) or several metals (multiple pollution indices) [27,28]. Among the most widely used are the enrichment factor and the contamination factor as single indices, and the degree of contamination, the pollution index, and the potential ecological risk index as multiple pollution indices. The use of indices based on metal concentrations to assess the potential risks for humans and environment is well documented [29–33]. However, their use in assessing the success of remediation trials is very poorly documented, with most of the studies limited to assessing the risks and identifying the phytoremediation potential of plant species [34–39].

Taking into account all the aspects described, the overall objective of this study was to contribute to better characterization and assessment of the risks associated with high concentrations of trace metals in mine tailings and polluted soils, and to evaluate the effectiveness of revegetation trials on tailings and contaminated soils in reducing ecological risks. More specifically, the objectives are to (i) characterize contamination in mine waste and polluted soils in the KCB using pollution indices as tools for prioritizing remediation and (ii) evaluate the use of ecological indices as tools for assessing the success of remediation trials based on revegetation with woody species. The results of this study are useful for identifying priorities and improving remediation processes for sites polluted with trace metals in the KCB.

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2. Materials and Methods

2.1. Study Area

This study was conducted in the Katangese Copperbelt, in the south-east of the Democratic Republic of the Congo. This region is rich in Cu and Co ores and has localized deposits of Zn, Mn, and U, making it one of the world's most important regions in terms of mineral supply [40,41]. KCB extends over an area more than 500 km long and 50 km wide from Kolwezi to Sakania (Figures 1 and 2). Its climate is humid subtropical with a rainy season from October to April and a dry season from May to September. Average annual rainfall ranges from 1200 mm to 1400 mm, and the mean annual temperature is 20°C [42,43]. The region's dominant soil types are laterites, tropical ferruginous soils, ferralitic soils, and vertisols [44]. The dominant vegetation in the region is miombo open forest [45].

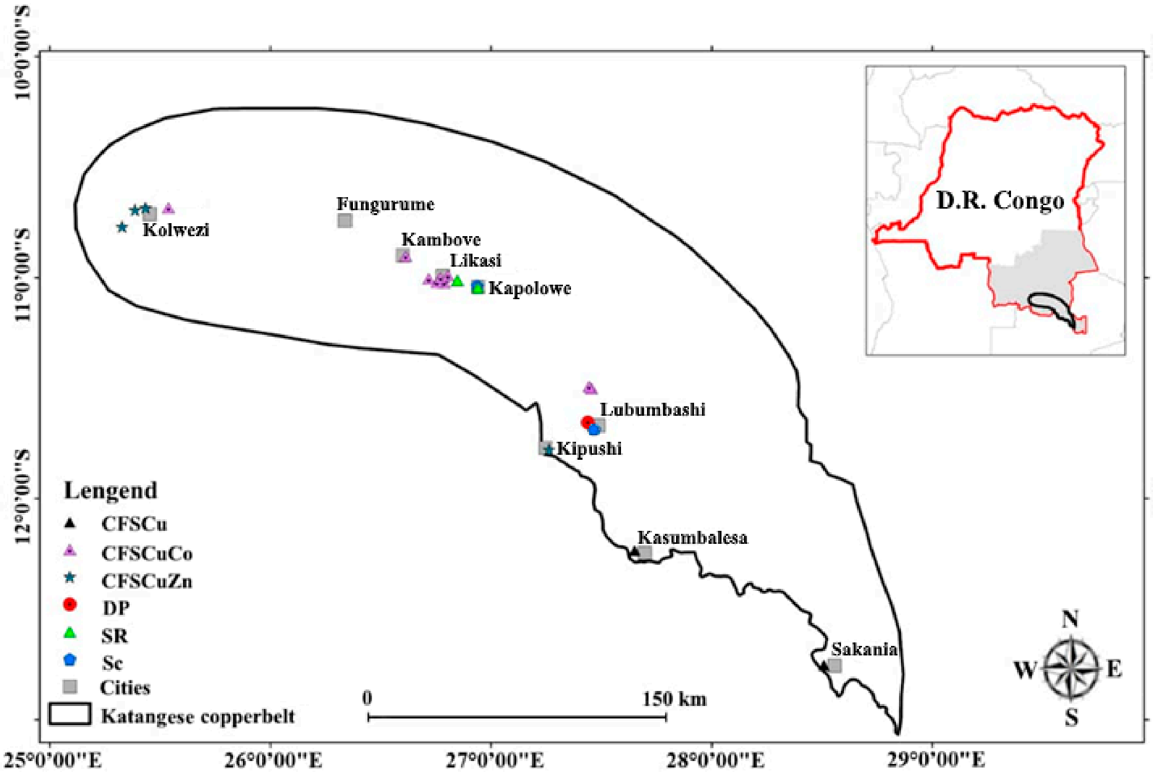

Figure 1. Spatial distribution of various mining discharges and polluted soil around the main towns in the Katangese Copperbelt. CFSCu = wastes from concentrates of Cu sulfides by flotation, CFSCuZn = wastes from concentrates of Cu and Zn sulfides by flotation, COCuCo = wastes from concentrates of Cu and Co oxides, DP = deposit from smelting emissions, Sc = slag, SR = river sediments from mining plants.

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Figure 2. Main types of mine tailings and polluted soil in the Katangan copperbelt. (**A**) soil polluted by emissions from the smelter, (**B**) wastes from concentrates of Cu and Zn sulfides by flotation, (**C**) river sediments from mining plants, (**D**) wastes from concentrates of Cu and Co oxides, (**E**) slag from the smelting process of copper.

2.2. Source of Data on Metal Concentrations

Primary and secondary data sources were used for this study. Primary data came from sample collection and analysis by the study team. A total of 95 samples were collected from the KCB. Secondary data were obtained from articles and grey literature (doctoral dissertations, Master's theses) based on work carried out in the KCB, as summarized in Table 1.

Table 1. Studies characterizing metal concentrations in different types of discharge to the KCB.

Reference	Aim of the study	Analyses
Kaniki [1]	Environmental characterization of mining and metallurgical wastes	pH, As, Cd, Cu, Co, Fe, Pb, Mn, and Zn. Extraction with aqua regia
Kitobo [24]	Remediation and reclamation of sulphide mine tailings	pH, As, Cu, Co, Pb, and Zn. Leaching test and extraction with HCl and NaOH
Ngenda [25]	Feasibility of the valorization of wastes from the Kolwezi zinc plants	pH, As, Cu, Co, Pb, and Zn. Leaching test and with HCl and NaOH

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Tshibanda [26]	Improving the metallurgical treatment of Cu-Zn sulfides from mining wastes in Kolwezi.	As, Al, Cd, Co, Cu, Hg, Pb, Zn, Mn, Fe, Ti, S, and Ni. Leaching test and X-ray fluorescence analysis
Narendrula et al. [4]	Assessing trace metal concentrations in polluted soils from smelting activities	pH, As, Al, Cd, Cu, Fe, Co, Pb, Zn, Mn, Mg, and Ni. Extraction with aqua regia
Mees et al. [46]	Concentrations and forms of heavy metals around two ore processing sites.	pH, As, Cr, Cd, Cu, Fe, Co, Pb, Zn, Mn, and Ni. Extraction with aqua regia
Pourret et al. [47]	Modeling of cobalt and copper speciation in metalliferous soils	Co, Cu, Fe, Mn, Mg, and Ca. Extraction with $HF+HClO_4+HCl$

2.3. Assessment of the Potential for Reducing the Ecological Risk Indices through Revegetation with Woody Species

To assess the potential for reducing the ecological risk of mining wastes and contaminated soils by revegetating with woody species, soil samples were taken in a long-term experiment (over 15 years) in the Kipushi tailing (contamination from concentrates of Cu and Zn sulphides by flotation) and in the residential plots of the Penga Penga neighbourhood (soil contaminated by deposits from the Gécamines Cu-smelter, see Shutcha et al. [19]). Details of the experiment are provided in Mwanasomwe et al. [22] for Kipushi and in Langunu et al. [11] for Penga Penga. The rhizosphere of the woody species considered correspond to areas that have been amended with organic matter filled in a ca. 1 m^3 area (Figure 3). In the Kipushi tailing, samples were collected from the rhizosphere surface horizons (0-20 cm) of five woody species: *Acacia auriculiformis* A. Cunn. ex Benth., *Albizia lebbeck* (L.) Benth., *Cupressus lusitanica* Mill., *Leucena leucocephala* (Lam.) de Wit, and *Syzygium guineense* (Willd.). Samples were taken from ten rhizospheres, with two profiles per species. Ten soil samples were also collected from the surface horizons of the unamended tailing areas. For Penga Penga, the species considered were *Mangifera indica* L., *Persea americana* Mill., and *Syzigyum guineense*. Soil samples were taken from the surface horizon in the rhizosphere of ten trees per species at Penga Penga. Ten samples were also collected from the surface horizon of unamended areas. Root, wood, and leaf samples were collected from individuals located in areas where soil samples were collected in Kipushi.

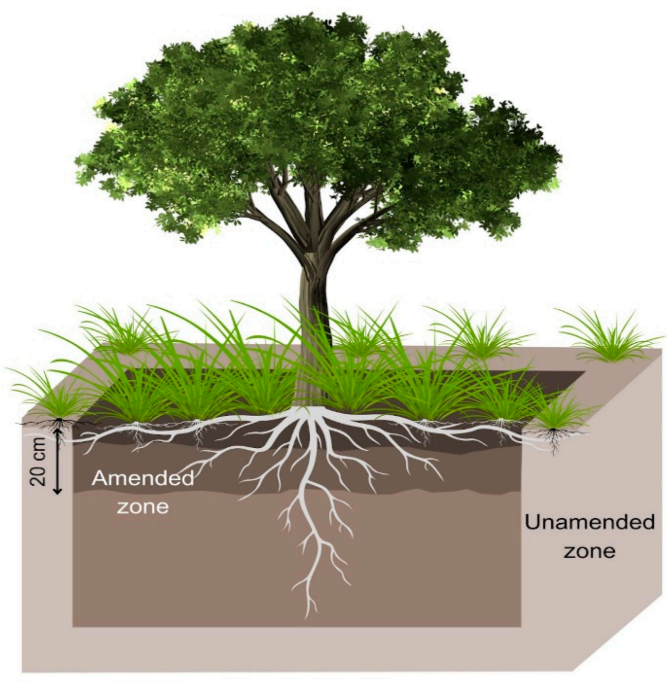

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Figure 3. Cross-section of a profile of edaphic conditions in the vegetated area of the Kipushi mine tailings.

2.4. Chemical Analysis

Air-dried samples were sieved at 2.0 mm, and a subsample was crushed to 200 µm. Methods were described in Lienard & Colinet [29]. Soil pH was measured potentiometrically in a 1:2.5 (W/V) suspension in water and in 1N KCl, while total organic carbon (TOC) was determined using the Springer–Klee method. Major (Ca, Mg, K, P) and trace (Fe, Mn, As, Cd, Co, Cu, Pb, Zn) element concentrations were determined after respectively (a) extraction with CH3COONH4 (0.5 M) and EDTA (0.02 M) at pH 4.65 (w:v 1:5 ratio) and agitation for 30 min (referred to as available metal concentration), and (b) aqua regia digestion following ISO 11466 (referred to as total metal concentration). The concentrations in the solutions were measured using flame atomic absorption spectrometry (AAS, Varian 220, Agilent Technologies, Santa Clara, CA, USA) for major elements, except P (colorimetry), and ICP-OES for aqua regia contents.

Leaf and root samples were washed with distilled water, then rinsed with 1% alconox solution to remove soil particles and avoid contamination [48], while bark was removed from wood. All samples were oven-dried at 95°C for 72 h for leaves and 120 h for roots and wood. Samples were ground to powder before being mineralized in a mixture of 65% HNO_3 and 75% $HClO_4$. Concentrations of As, Cd, Pb, Cu, Co, and Zn were determined using ICP-OES.

2.5. Calculation of Risk Indices

The enrichment factor (EF), the degree of contamination (DC), and the potential ecological risk (RI) were used as indices to assess the hazardousness of trace metal concentrations in mine tailings and affected soils in the KCB. All these indices were determined according to Håkanson's guidelines [27].

The EF was used to determine the degree of metal enrichment in discharges and soils compared with natural levels. It was calculated using Fe as the reference element [47,48] according to Formula 1. Seven enrichment levels are described as a function of EF values [33]: no enrichment if EF < 1, minor enrichment if EF < 2, moderate enrichment if 2 ≤ EF <5, moderately severe enrichment if 5 ≤ EF < 10, severe enrichment if 10 ≤ EF < 25, very severe enrichment if 25 ≤ EF < 50, and EF > 50 extremely severe enrichment.

$$EF = (C_{sample}/Fe_{sample}) / (C/Fe_{ref}) \quad (1)$$

Where C_{sample} = the concentration of the metal in the sample; Fe_{sample} = the concentration of iron in the soil; C_{ref} = the concentration of the reference soil metal, and Fe_{ref} = the concentration of the reference soil iron.

The DC is calculated on the basis of the sum of the contamination factor (CF) values for each trace metal analysed (Formula 2). The CF is calculated on the basis of the trace metal concentration values in the waste/soil samples and those of the reference geochemical background (3). Following the DC, four categories of contamination were used: low degree of contamination if DC < 8, moderate degree of contamination if 8 ≤ DC < 16, considerable degree of contamination if 16 ≤ DC < 32, very high degree of contamination if DC > 32.

$$DC = \sum CF_{M,} \quad (2)$$

$$CF = C_{sample}/C_{ref} \quad (3)$$

Where DC is the degree of contamination of a given release/soil, CF is the contamination factor for a particular metal, C_{sample} = the concentration of the metal in the release/soil analysed, and C_{ref} = the concentration of metal in the reference soil from the region.

The RI is the sum of the ecological factor (Er) values for each metal (Formula 4). The Er is used to determine the potential risk that each metal in the substrate presents to the environment and human health. The Er calculation involves the contamination factor (CF) and the toxicological

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response factor (Tr) values for each metal (Formula 5). Er were calculated using empirical values for the Tr of each metal (Table 2) [28,48].

$$RI = \sum Er \quad (4)$$

$$Er = CF \times Tr \quad (5)$$

Where RI = potential ecological risk index; Er = ecological factors (for each metal); Tr = the toxicological response factor for a given substance; and Cf is the contamination factor. Tr values for heavy metals by Håkanson [27] are given in Table 2. Based on the Er, the categories of ecological risk related to a single metal are as follows: Er < 40, low ecological risk; 40 ≤ Er < 80, moderate ecological risk; 80 ≤ Er < 160, considerable ecological risk; 160 ≤ Er < 320, high ecological risk; and Er ≥ 320, very high ecological risk. With regard to RI, the categories are as follows: RI < 150 = low risk; 150 ≤ RI < 300 = moderate risk; 300 ≤ RI < 600 = considerable risk; RI ≥ 600 = very high risk.

Table 2. Toxicological response factor (Tr) by Håkanson [27] and Duodo et al. [28].

Elements	Toxological response factor
As	10
Cd	30
Co	5
Cu	5
Mn	1
Pb	5
Zn	1

In addition to the RI, the bioconcentration factor (BCF) was calculated to assess the amount of trace metals taken up in roots, wood, and leaves of woody species planted at Kipushi. BCF is the ratio of metal concentration in organs to that in soil/substrate (Formula 6). [51–54].

$$BCF = C_{\text{tree } tissue}/C_{soil} \quad (6)$$

Where $C_{\text{tree } tissue}$ is the metal concentration in a given tissue and C_{soil} is the pseudo-total metal concentration in the soil.

2.6. Statistical Analyses

Descriptive statistical tests were applied to the mineral concentration data from the KCB mining wastes and polluted soils considered in this study. Detection Limit (DL)/2 imputation methods were used to integrate all data < DL in all analyses [55]. The Shapiro-Wilk normality test was applied to assess the distribution of data. As the data were not normally distributed, even after logarithmic transformation (no transformation for pH), the non-parametric Kruskal-Wallis test was applied to compare the concentration values of each parameter analysed among the sites. Principal component analysis (PCA) was applied as a multivariate model to compare sites by integrating all the parameters analysed.

Data from woody species revegetation trials and tree plantations at Penga Penga were also subjected to a Shapiro-Wilk normality test. The logarithmic transformation having corrected the data distribution, Student's *t*-test was applied to compare the mineral conditions and RI of the surface horizons of the rhizospheres of woody species and those of the surrounding unamended areas. The *t*-test was applied separately for each of the two sites (Kipushi and Penga Penga). A two-factor ANOVA was applied to compare metal concentrations in roots, wood, and leaves at Kipushi. The factors considered were species and organ. All analyses were performed using R Studio (4.0.1).

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3. Results

3.1. Concentration of Trace Metals in Mining Wastes and Contaminated Soils

Table 3 shows the descriptive statistics applied to parameters analysed on KCB's mining wastes and polluted soils. The range of pH values (water and KCl) observed for polluted sites (pH_{water}: 4.0-10.6; pH_{KCl}: 3.5-11.7) entirely covered that observed in unpolluted forest soils (pH_{water}: 4.0-7.3; pH_{KCl}: 3.8-5.8). Table 3 also highlights the high concentrations of metals in the mining wastes and contaminated soils considered in this study, compared with the forest soils taken as reference. Similarly to Fe, which is a major element (9890-320 000 mg kg^{-1}), all the measured trace elements showed high levels of variability. Cu and Zn were the trace metals with the highest average and ranges of concentrations, respectively 12 657 mg kg^{-1} (116-75 000 mg kg^{-1}) for Cu and 13 250 mg kg^{-1} (0.02-200 000 mg kg^{-1}) for Zn. The range of concentrations for the other elements were < 0.003-12 159 mg kg^{-1} for As, < 0.001-17 414 mg kg^{-1} for Cd, 2.52-2300 mg kg^{-1} for Co, 15-9600 mg kg^{-1} for Mn and < 0.003-58 000 mg kg^{-1} for Pb.

The Kruskal-Wallis test applied to all the parameters analysed showed strong variations between sites (Appendix A Figure A1). Slag (Sc) had the highest pH values ($p < 0.05$) (pH_{water} slag = 5.6-10.6 vs. 4.0-8.7 for other substrates). It is noted that classes cover ranges from acidic to strongly basic conditions and therefore pH should seldom be considered as an indicator of waste nature. Wastes resulting from Cu-Zn sulfide concentration by flotation (CFSCuZn) showed higher concentrations ($p < 0.05$) of As, Pb, and Zn, with values ranging from 7.8-12.2 mg kg^{-1} for As (vs. <LOQ-2395 for others), 498-58 000 mg kg^{-1} for Pb (vs. <LOQ-8000 for others) and 10 182-200 000 mg kg^{-1} for Zn (vs. 0.02-65 000 for others). Cd concentrations were higher ($p < 0.05$) in river sediments, with values of 24-17 414 mg kg^{-1} (vs. 0.003-2395 for others). Co concentrations were higher in wastes from Cu-Co oxide concentration and in slag, with respective values of 4310-26 700 mg kg^{-1} and 910-23 000 mg kg^{-1} vs. <LOQ-4900 mg kg^{-1} and 11-3839 mg kg^{-1} for the other substrates. For Cu, the Kruskal-Wallis test shows similar concentrations in all wastes and soils, except for river sediments. The latter showed lower concentrations ($p < 0.05$) compared with all other discharges (116-12 113 mg kg^{-1} for river sediments vs. 313-75 000 mg kg^{-1} for other discharges). The remarks made about pH can also be made about the metal content; even if there are significant differences between groups of wastes, the frequency distributions usually overlap each other.

Table 3. Descriptive statistics for concentrations of various trace metals (mg kg^{-1}) and pH. N = number of samples, SD = standard deviation, CV = coefficient of variation, Min = minimum, Max = maximum, Q1 and Q3 = first and third quartile, LOQ = Limit of Quantification , Reference = reference soil in the region (Shutcha et al., 2018; Mpinda et al., 2021).

	pH_{water}	pH_{KCl}	Fe	As	Cd	Co	Cu	Mn	Pb	Zn
All S2										
n	78	88	75	66	124	122	125	69	125	122
Mean	6.2	5.8	64764	1578	1751	826	12657	939	2096	13250
SD	1.48	1.78	76707	2695	4225	2673	14048	1909	7613	41111
Min	4	3.5	9890	< LOQ	< LOQ	2.52	116	15	< LOQ	0.02
Q1	5.13	4.8	21800	30.6	<LOQ	29.55	1317.5	109.5	31	15
Median	5.87	5.4	37850	314	28	94.13	7977	174	52	41
Q3	7.02	5.8	57150	1420	245	351	19513	750	712	694
Max	10.6	11.7	320000	12159	17414	23000	75000	9600	58000	200000
CV	24	30	119	178	243	315	149	198	370	317
Skewness	1.13	1.98	2.19	2.59	2.52	4.79	5.18	2.89	5.46	3.69
Kurtosis	1.10	3.72	3.52	6.37	5.06	24.66	39.42	8.38	32.7	12.82
Reference										
Mean	5.6	4.4	62954	-	1.3	20	187	119	40	69
Min	3.9	3.8	8971	-	0.1	0.1	3.1	4.3	0.3	2.0

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Max	7.3	5.8	112000	-	1.9	38	456	370	82	180

Projection of the variables in the CP1 x CP2 plane (59.1% total variation) of the PCA shows trends observed with the KW test (Figure 4). CFSCuZn are associated with the highest concentrations of As, Pb, and Zn, while SR are associated with the highest Cd concentrations but the lowest Cu concentrations. Slag and COCoCu are associated with the highest Co and pH values. Other wastes occupy intermediate positions.

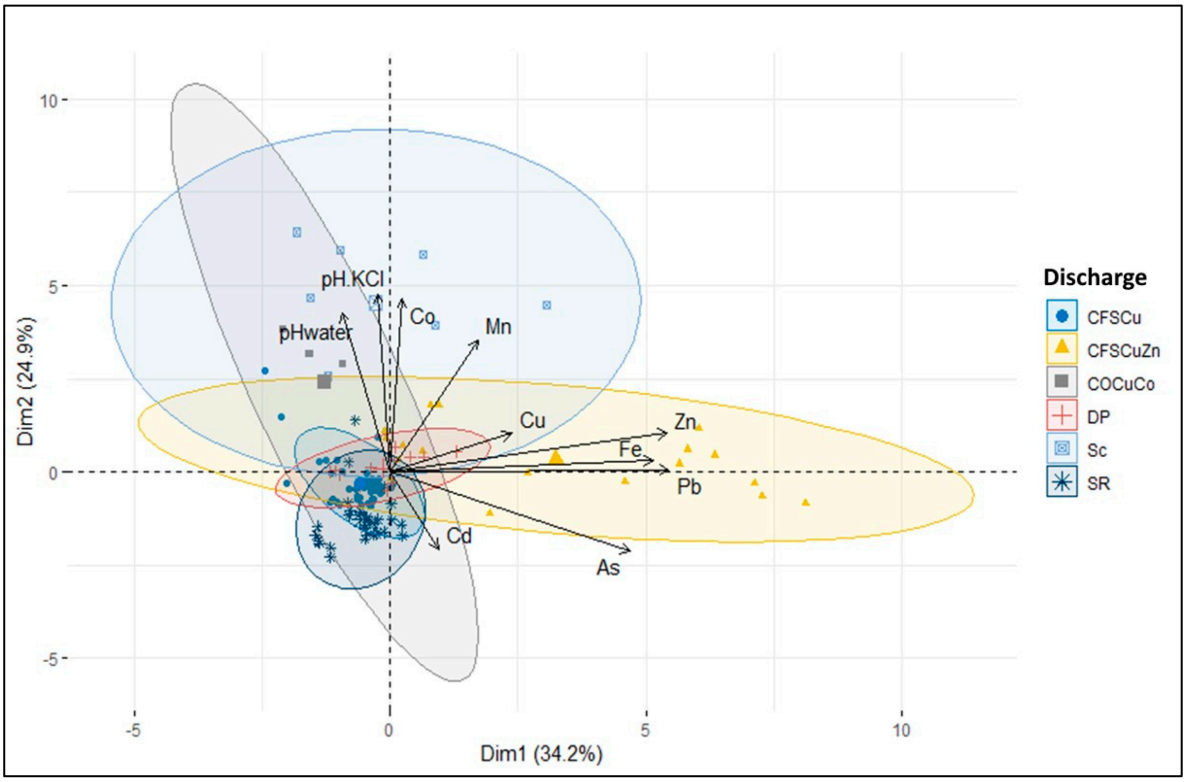

Figure 4. Principal component analysis showing the variability of the elements studied across 6 types of discharge. CFSCu = wastes from concentrates of Cu sulfides by flotation, CFSCuZn = wastes from concentrates of Cu and Zn sulfides by flotation, COCuCo = wastes from concentrates of Cu and Co oxides, DP = deposit from smelting emissions, Sc = slag, SR = river sediments from mining plants.

3.2. Ecological Risk Associated with Trace Metal Concentrations

The values for EF and CF were generally above 1, indicating enrichment and trace metal contamination. Only seven values (out of 42) for each index were less than or equal to 1. The DC values of all mining wastes and contaminated soil show very high levels of contamination as they exceeded 32 (Table 4). The decreasing order of DC values can be classified as follows: SR (5440) > CFSCuZn (2027) > Slag (338) > COCoCu (180) > DP (155) > CFSCu (72). The high DC values are mainly due to Cd for SR; Zn, Cd, and Pb for CFSCuZn; Zn and Co for slag; and COCoCu and Cu for DP.

RI values indicate high potential ecological risks associated with trace metal concentrations in all study sites. The decreasing order of mean RI values is as follows: SR (162091) > CFSCuZn (21959) > DP (1219) > slag (1109) > COCoCu (905) > CFSCu (549). The trends in the metals influencing RI values are the same as those observed for DC values. It should be noted, however, that DP presents a higher potential ecological risk compared to slag, contrary to the trends observed with DC values.

Table 4. Contamination factor (CF) and degree of contamination (DC) values for soil samples in discharge at KCB. CFSCu = wastes from concentrates of Cu sulfides by flotation, CFSCuZn = wastes from concentrates of Cu and Zn sulfides by flotation, COCuCo = wastes from concentrates of Cu and Co oxides, DP = deposit from smelting emissions, Sc = slag, SR = river sediments from mining plants.

Discharge	CF							DC
	As	Cd	Co	Cu	Mn	Pb	Zn	
CFSCu	0.001	7.7	2.9	59.2	1.1	0.5	0.4	72
CFSCuZn	176	593	3.7	61	3.4	222	968	2027
COCoCu	2.4	0.001	147	27.4	0.8	1	1.1	180
DP	6.3	20.8	9.4	71.8	0.1	18.3	28.6	155
Sc	0.1	0.001	131	39.6	7.6	21.3	138	338
SR	36.5	5388	2.9	3.8	0.2	7.2	0.9	5440

Table 5. Ecological risk factor (Er) and potential ecological risk factor (RI) values for soil samples in discharge of KCB. CFSCu = wastes from concentrates of Cu sulfides by flotation, CFSCuZn = wastes from concentrates of Cu and Zn sulfides by flotation, COCuCo = wastes from concentrates of Cu and Co oxides, DP = deposit from smelting emissions, Sc = slag, SR = river sediments from mining plants.

Discharge	Er							RI
	As	Cd	Co	Cu	Mn	Pb	Zn	
CFSCu	0.001	233	15	296	1.1	2.9	0.4	549
CFSCuZn	1760	17792	18.8	305	3.4	1111	968	21959
COCoCu	24	0.04	736	137	0.8	5.2	1.1	905
DP	63.6	625	47.4	359	0.1	94.4	28.6	1219
Sc	1.6	0.04	657	198	7.6	107	138	1109
SR	366	161653	14.7	19.4	0.2	36.1	0.98	162091

3.3. Impact on RI and BCF Values of the Localized Excavation and Replacement Approach for Revegetation

3.3.1. Profile of Edaphic Conditions and RI Values

Results show better fertility status in rhizospheres of trees at both sites with higher concentrations ($p < 0.05$) of P, K, and TOC compared with unamended areas (Table 6). In contrast, total trace metal concentrations were lower in the rhizospheres compared to the unamended areas at both Kipushi and Penga Penga. Co was the only exception to the general trend with higher concentrations in the rhizosphere of trees (932 ± 407 mg kg^{-1}) compared to unamended areas (102 at ± 57 mg kg^{-1}) in Kipushi.

Results show lower RI values in the rhizospheres of trees planted at Kipushi and Penga Penga. At Kipushi, the RI value averaged was 5704 ± 3222 in the unamended areas while it was 1522 ± 400 in the rhizosphere of the trees. At Penga Penga, the RI value is 1532 ± 503 in the unamended areas while it is 533 ± 493 in the tree rhizospheres.

Table 6. pH, total organic carbon (TOC), major elements and trace metal concentrations, and potential ecological risk (RI) values in surface horizons (0-20 cm) of unamended areas and tree rhizospheres in the Kipushi tailings pond from copper-zinc sulfide concentration by flotation and in polluted soil at Penga Penga. Mean ± standard deviation. Comparisons between unamended areas and rhizosphere done separately at Kipushi and Penga Penga. Values with the same letter (a,b) are not different after the Student's *t*-test ($p < 0.05$).

	Kipushi		Penga Penga		Reference
	Unamended	Rhizosphere	Unamended	Rhizosphere	(Forest soil)
pH_{KCl}	7.9 ± 0.2 a	7.0 ± 0.2 b	5.8 ± 1.7 b	7.7 ± 0.3 a	4.4 (3.8-5.8)
TOC (%)	2.2 ± 0.3 b	4.5 ± 1.9 a	1.4 ± 0.5	-	2.3 (1-5)
Ca (mg kg^{-1})	10060 ± 4002 a	4098 ± 425 b	11 ± 5.2 b	75 ± 43.7 a	-

Mg (mg kg^{-1})	2790 ±1824 a	2242 ± 352 b	1.7 ± 0.5	-	-
P (mg kg^{-1})	40 ± 14.1 b	148 ± 79 a	1.4 ± 0.5	-	-
K (mg kg^{-1})	20 ± 1.4 b	144 ± 49 a	1.2 ± 1.1 b	99 ± 36 a	-
As (mg kg^{-1})	2934 ± 2141 a	314 ± 155 b	1578 ± 2695 a	12.8 ± 14.2 b	-
Cd (mg kg^{-1})	159 ± 77.4 a	48 ± 16 b	1751 ± 4225 a	8.7 ± 12 b	-
Cu (mg kg^{-1})	9269 ± 1825 a	3533 ± 814 b	12657±14048 a	1379 ± 1371 b	187 (20-456)
Co (mg kg^{-1})	102 ± 57.1 b	932 ± 407 a	826 ± 2673 a	182 ± 113 b	20 (7.1-38)
Pb (mg kg^{-1})	4291± 1113 a	557 ± 230 b	2096 ± 7613 a	142 ± 131 b	40 (7.0-82)
Zn (mg kg^{-1})	22723 ± 11670 a	6725 ± 2650 b	13250 ± 4111 a	467 ± 312 b	69 (26-180)
RI	**5704 ± 3222 a**	**1522 ± 400 b**	**1532 ± 503 a**	**533 ± 493 b**	

3.3.2. Accumulation in Plant Tissues and Bioconcentration Factor Values at Kipushi

Co, Cu, and Zn concentrations were lower ($p < 0.05$) in wood compared with roots and leaves (results not shown). Cu concentrations were higher in roots (57.3 ± 22.5) than in leaves (17.8 ± 4.2). Co and Zn concentrations are similar in roots (Co = 3.8 ± 2.2, Zn = 289 ± 195) and leaves (Co = 2.7 ± 1.3, Zn = 293 ± 126) but lower in wood (Co = 1.2 ± 0.8, Zn = 67 ± 37). All BCF values were below 1, including all tissues (roots, wood, and leaves) of all species and all three metals analysed, ranging between 0.0004 and 0.09 (Figure 5). For all metals, BCF values were lower in wood compared to roots and leaves.

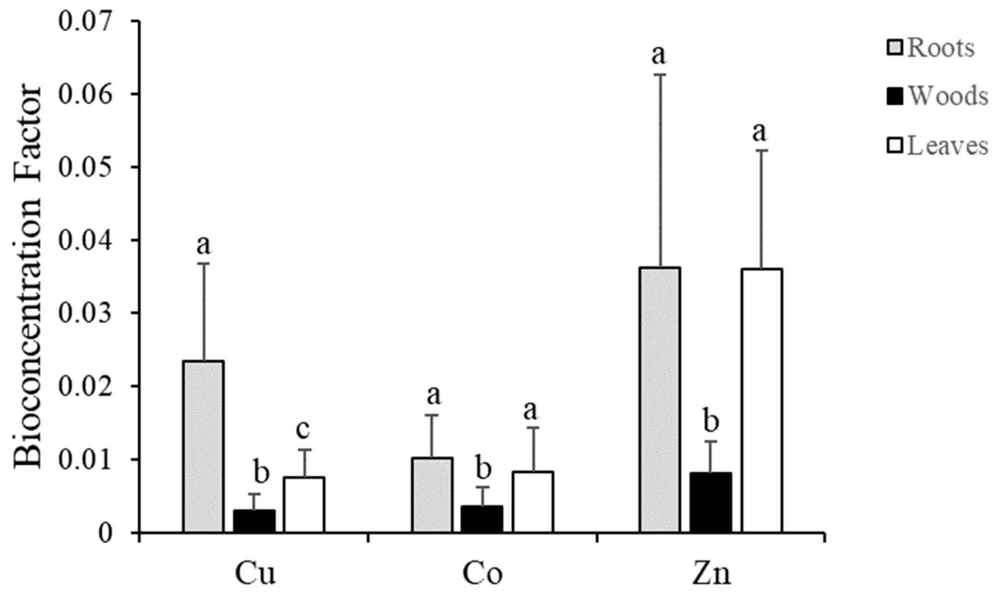

Figure 5. Bioconcentration factors for Cu, Co, and Zn in the tissues of five woody species grown for 15 years in the Kipushi tailing pond from the concentration of Cu-Zn sulphide by flotation.Values are represented by the mean ± standard deviation; means with the same letter are not significantly different ($p < 0.05$).

4. Discussion

4.1. Metal Concentrations and Ecological Risks Associated with Secondary Metal Habitats

The wide variability of values between mining wastes (for all parameters considered) in this study reflects the heterogeneity of the mineral composition of ores extracted from the KCB's metalliferous deposits, as well as the metallurgical processes and other treatments after their release from the plants. The variability of the chemical and mineralurgical composition of the deposits in the KCB is well documented and can be explained by the history of their emergence during geological eras [40,56,57]. Furthermore, the nature of ores (and therefore their chemical composition) leads to

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the application of different metallurgical schemes and the use of different inputs [58,59]. For example, oxide ores are subjected to hydrometallurgical processes, while sulfide ores are subjected to smelting processes [24,60]. The influence of ore origin is illustrated by the higher Zn concentration values in the tailing ponds from the concentration of Cu and Zn sulfide ores, while Co concentration is higher in discharges from Cu and Co oxide ores. In contrast, high pH values in wastes from ore concentrations (Cu and Zn sulfide ores, Cu sulfide ores, etc.) stored in sedimentation ponds most often illustrate the influence of treatments applied to the discharges, notably the application of lime for pH neutralization [2,26,61]. The high Ca and Mg values support this explanation.

Unsurprisingly, trace metal concentrations are much higher in mining wastes and contaminated soils compared to those reported from the reference geochemical background of non-metalliferous soils [62,63] as well as those reported from non-anthropized metalliferous soils [64]. This result explains the high values of DC (Table 4) and RI (Table 5). For example, the DC and RI values of mining wastes were 2 to 170 times (DC: 72–5440) the threshold of 'high contamination' (DC > 32) and 1 to 270 times the threshold for 'very high risk' (RI = 549–162 091). Such high levels of DC and RI are rarely reported in the literature [65–69] and would place KCB among the most trace-metal-polluted regions in the world. These results support the exceptionally high levels of trace metal exposure in KCB populations as reported by several authors over the past 15 years [13,14,16,17].

Results emphasize the contribution of certain trace metals, such as Cd and Pb, in the high ecological risk related to mining waste due to their toxicological characteristics despite relatively lower concentration levels compared to metals such as Cu and Zn (Table 5). They underline the need to analyse an extended set of trace metals for a better ecological risk assessment. For example, including all potentially harmful metals would help to refine the risk assessment associated with mining waste. In addition, given that the contamination classification usually used is not relevant for the sites studied, as we found DC values well over 32, we suggest that DC levels and the use of other pollution indices be developed.

4.2. Revegetation on the Basis of Excavation and Replacement and Ecological Risk Index

Revegetation trials with woody species installed since 2005 were based on localized excavation of planting sites followed by replacement of polluted sediments and soils with organic matter [11,23]. The present study represents a first assessment of the ability of this approach to reduce ecological risks using indices, previous ones being based mainly on edaphic conditions (based on AA-EDTA extractable Co, Cu, and Zn concentrations) and metal concentrations in aboveground organs without subtracting the influence of dust. The results of this study confirm an improvement in conditions in the rhizosphere surface horizons of the woody species evaluated (Table 6), thanks to better organic matter, P and K values, and generally lower trace metal concentrations compared with the surface horizons of the surrounding unamended substrates. Nevertheless, trace metal concentrations remain high (compared with regional references), probably due to metal release from surrounding substrates as argued by Langunu et al. [11] for the case of Penga Penga but also demonstrated for other regions [71]. Kaniki's [1] leaching test results also support the mobility of metals in the discharge of Cu and Zn sulfide concentrates at Kipushi.

The potential ecological risk was lower in the amended and planted areas thanks to lower concentration levels, particularly of the most hazardous metals such as Cd and Pb (Table 6). Nevertheless, the RI values correspond to considerable ($300 \leq RI < 600$) to high ($RI \geq 600$) risks. In other words, based on trace metal concentrations, the rhizospheres of trees planted in the Kipushi waste disposal and the Penga Penga polluted soil, made up of organic matter and other inorganic amendments (in the case of Penga Penga, e.g., termite mound soil, etc.), have been progressively enriched in trace metals to (total) concentrations that present significant ecotoxicological risks for the environment and human health. Although current results do not allow us to estimate trends with any certainty, concentrations in the rhizosphere may increase if metal release continues. This phenomenon of metal migration from contaminated substrates to rhizospheres made up of uncontaminated soil improvers should be further investigated in future studies. This is important as

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it will provide a better understanding of the success of revegetation methods for polluted sediments and soils based on localized excavation and replacement with unpolluted soil and soil improvers.

Nevertheless, the survival and performance of species over the last 15 years [22] combined with low accumulation levels and low BCF values (< 0.2 for all species and the three metals analysed, Figure 5) demonstrate a reduction in metal mobility and bioavailability. In this context, measurement of the ability of amendments to reduce metal mobility and prevent their transfer to other environment components seems to be key for the assessment of the success of such remediation approaches.

4.3. Implications for Remediation of Polluted Soil

The results of this study clearly indicate very high degrees of contamination and ecological risks associated with the high concentrations of trace metals in KCB's mine tailings and polluted soils. They justify the search for the best remediation and risk mitigation techniques undertaken by researchers over the past 20 years. These proposals include the use of physico-chemical processes with a view to revalorization via metallurgical processes while reducing metal concentrations [1,2,24,25] or the use of phytotechnology techniques using plant species tolerant to high concentrations of trace metals in the soil [18,19,21] or woody species [11,22]. It seems that no thought has yet been given to a global remediation strategy on the scale of the KCB region and to ways of assessing the effectiveness of these processes in reducing the risks of trace metal dissemination in the environment and human exposure. The results of this study argue in favour of such an approach, considering variations in the characteristics of mining wastes and polluted soils and their proximity to urbanized areas and natural unpolluted (or less polluted) ecosystems. They enable a better assessment of the overall pollution situation linked to mining activity over the whole area covered by the KCB and to determine priorities in terms of remediation and the most appropriate methods for each situation. As a result, the use of pollution indices appears to be an effective quantitative assessment tool over a large area when data (metal concentrations) are available. These results show the need for remediation trials to be extended to all mining wastes, particularly to river sediments and Cu and Zn sulfide flotation waste.

Results from the assessment of remediation trials on mine tailings and polluted soils showed that ecological risk values remain high in areas amended and vegetated with woody plants, although lower than in non-vegetated areas. These results tend to demonstrate that the ecological risk associated with trace metal concentrations in the amended areas of the KCB tailings and polluted soils potentially increases over time as a result of the release of metals from the unamended matrices, as explained above. In this context, the use of RI for the assessment of the effectiveness of the remediation seems to be insufficient as these indices only consider concentrations and toxicological characteristics of trace metals [50,72] and not the ability to prevent metal dissemination. It is clear that not all phytotechnology techniques are intended to reduce the concentrations and quantities of trace metals in the matrices concerned, this is primarily the case for phytostabilization for which the main purpose is to contain metals in the site and prevent their dissemination [73,74]. It would be wise to associate indicators of trace metal stability in the matrices concerned via describing physical characteristics and using appropriate extractions to assess mobility. On the other hand, the use of BCF and direct measurements of concentrations in aboveground organs as indicators of the success of risk reduction for contamination of the food chain seem more appropriate for assessing the success of phytostabilization. The results of the present study and those of Langunu et al. [11] support this view. The use of RI may be more appropriate for the assessment of phytotechnology techniques aimed at extracting trace metals and reducing their quantities (and concentrations) in soils and sediments, such as phytoextraction [75].

With a view to the overall remediation of unmanaged mining waste, a combination of approaches seems necessary in the case of the KCB. The varied characteristics of the wastes call for integrated approaches using existing research data. For example, where possible and with the means available, the reclamation of substrates with very high concentrations of metals of interest, as proposed by Kaniki and Tumba [2], should be considered upstream of revegetation actions for certain polluted sites. This would reduce the ecological risks associated with trace metals later on. In the

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absence of a waste reclamation project, revegetation according to the proposed models should be considered, including tolerant woody and herbaceous plants in the corridors [22,76] and potentially intended for biomass production [22]. Furthermore, for urbanized (and densely populated) areas established on the polluted soils of Penga Penga, a more participatory approach as recommended by Mwanasomwe [77] should be considered to better consider the needs of populations and the best technical itineraries for planting trees and tolerant grasses [19].

5. Conclusions

This study aimed to contribute to the assessment of risks related to KCB's mining wastes and soils polluted with trace metals, using direct concentration measurements and pollution indices. The study also assessed the feasibility of using these indices to evaluate the success of remediation projects based on localized excavation and replacement with non-polluted amendments, followed by planting of woody species. The results confirm high risks due to high concentrations of trace metals and high values of the potential ecological risks of mining wastes and contaminated soils considered in this study. The remediation strategy assessed led to the decrease of RI in the tree rhizospheres even if their values remain of concern as they still represent a considerable risk. The pollution indices used are not suitable for assessing the effectiveness of phytotechnology based on stabilization. This study suggests that pollution indices that take account of stabilization-based phytotechnology (excavation/replacement) should be developed to gain a better understanding of the ecological risks associated with this approach. In addition to direct measurements of transfer to the environment, the mechanisms by which metals are transferred from the untreated zone to the rhizosphere of plant species should also be studied in greater depth to assess the real ecological risk.

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Conflicts of Interest: The authors declare that this research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Appendix A

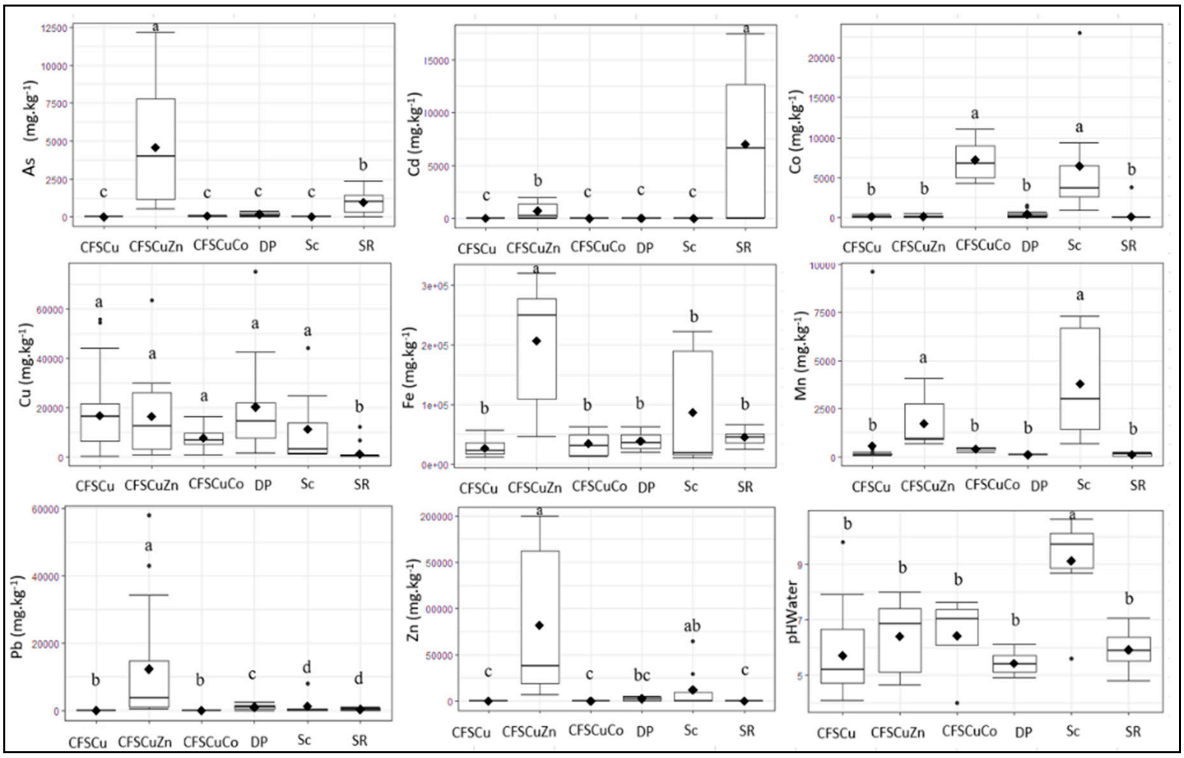

Figure A1. Comparison of metal concentrations in different types of discharge. CFSCu = wastes from concentrates of Cu sulfides by flotation, CFSCuZn = wastes from concentrates of Cu and Zn sulfides by flotation, COCuCo = wastes from concentrates of Cu and Co oxides, DP = deposit from smelting emissions, Sc = slag, SR = river sediments from mining plants.

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