



An Assessment of Selected Heavy Metals in Soil and Crops Grown on The Bauxite Soil of Guyana Using Pollution Indices and Background Concentration

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Abstract

This study aims to determine total heavy metal concentration presence in post mined bauxite land and its associated food plants grown in two physiographic regions along the bauxite belt of Guyana. Twenty-seven soil samples and twenty-four food plant samples (including Brassica rapa cv. chinensis; Spinacia oleracea; Cocos nucifera L, Manihot esculenta, Apium graveolens and Lycopersicon esculentum) were collected from four (three mined-out and one unmined) districts. The total concentrations of seven heavy metals (Al, Cd, Cr, Cu, Mn, Pb and Zn) were analyzed in the soil and paired food samples using ICP-MS. Background soil samples were analyzed using an ICP-OES. In addition, chemical parameters like soil pH and organic matter contents were determined by Act Lab Inc., an ISO 9001:2015; IEC/17025- accredited facility in Canada. With the raw data collected the geo-chemical index (Igeo) and bioaccumulation factor (BAF) were calculated and compared with the Codex Standards using one-way ANOVA and Pearson correlation using version 20 of the Statistical Package for the Social Sciences.

Bauxite mining alters the physicochemical properties of the soil and has increased the levels of some heavy metals in the soil. In descending order, the mean heavy metals concentration (mg kg⁻¹) in the soils were: Al > Mn > Zn > Cr > Pb > Cu > Cd. The heavy metal concentration in all soil samples did not exceed the permissible limits set by the Codex Standards. Post mined bauxite soils were found to have no effect on parameters like soil pH or organic matter content but had significantly higher levels of lead and zinc ($p < 0.05$). Higher total concentration of heavy metals was observed in unmined areas (T4-Hubu) compared to post-mined areas (T1-Wset Watooka, T2- Coomacka and T3- Three Friends). The Pearson correlation coefficient (r) test found a significant linear negative relationship between soil pH, % organic matter and total heavy metals in bauxite soil in T4 and post-mined T2 districts. However, in post-mined district T3 soil pH and organic matter showed a strong positive significant relationship ($r = 0.885^$) coupled with time. The quantitative Igeo results indicated pollution indices for various heavy metals, including Zn (0.8-1.2); Cu (0.8- 4.0), Cu (0.7-2.3); Mn (0.7-2.3) and Pb (0.3-1.7). Leafy vegetables (celery, pak choy, spinach), tomato, and cassava root tuber are effective bio-accumulators & hyperaccumulators of heavy metals, exceeding the Codex Standards while coconut fluid elicit heavy metal exclusion mechanism below Codex toxic permissible limits. This study indicates that some food crops grown in Guyana's bauxite soils may have higher than normal permissible levels of heavy metals. To the consumers they present serious health consequences moreso to vulnerable population that includes pregnant women and children. As such in order to grow crops on the mined-out bauxite soil the most desirable outcome would be to have a soil pH value of 6.4 and OM level of 11.05%.*

Results: Anomalous concentrations of Hg were identified beyond the natural background levels in West Watooka, suggesting the presence of numerous mining activities beyond bauxite extraction.

Keywords: Three Friends; Coomacka, West Watooka, Hubu, total heavy metals, soil pH, organic matter content, bioaccumulation factor, geo-accumulation index, post-mining bauxite soils

Introduction

Guyana is positioned on the northeastern corridor of South America. This English-speaking country is located on the Atlantic coast, positioned between 1°& 9° North Longitude and 57°& 61° West Latitude. The nation boasts approximately 214,970 km² in land area. Mining, forestry, agriculture and lately unearthed oil resources are its primary economic activities [1,2].

The agricultural sector is considered the backbone of the Guyanese economy. This sector comprises of conventional crops like rice and sugar cane as well as non-conventional food crops like fruits, vegetables, orchards, and coconut palms. This sector supplies products for exports as well as domestic use. The domestic agricultural sector provides food for the local population, of which leafy vegetables (Pak choy, celery and poi), root/tuber (cassava), coconut fluids and tomato are major components.

This subsector accounted for 23.8% of non-oil GDP in 2023, highlighting agri-diversification [3-6]. The mining sector of Guyana includes subsectors of gold, bauxite, diamonds, manganese, sand, and stones. In 2023, this subsector contributed 9.7% of GDP (approximately USD 888.2 million). Bauxite mining has been a significant subsector in Guyana, contributing 0.4% of GDP in 2023, roughly USD 79.6 Million [5].

Bauxite mining activities are centred around Linden. It is located at 107.5 kilometres from Georgetown, the capital of Guyana. Community and agricultural land located on reclaimed mining sites characterise the landscape of the bauxite sector. Approximately 12,000 hectares of land have been effectively reclaimed for agricultural food production. These lands are scattered throughout the bauxite belt, an arc about 300 km long and 25–40 km in width [2,7].

The mineralogy and origin of the Guyana bauxite commenced in the Paleoproterozoic epoch. These occurrences transpired some 2.2 billion years ago and produced the Guiana Shield. The mineralisation and origin of the bauxite deposits in Guyana are characterised by two theories: The first theory describes weathering as a result of successive physical, chemical, and biological processes acting on sedimentary and igneous parent rocks [8,9]. This process results in the formation of fragments that release their components [10]. The other theory posits that acidic rainwater modifies parent rocks, with an annual mean precipitation of 1700–2200 mm, an average annual temperature of 27.5 degrees Celsius, and short dry seasons [11,12]. Generally, soil formation comes from hydration-dehydration and silication-resilication [11,13] forming soft, and porous soils comprising coarse, medium and fine particles [9].

The bauxite deposit is also utilised to extract and concentrate leached minerals that have undergone massive weathering. During the process, fine sediments, silica (Si), free aluminium (Al), and iron (Fe) are reconfigured. The change results from the continuous breakdown of organic matter transforming gibbsite, feldspar, mica, and illite into kaolinite clay. Kaolinite coexists with gibbsite, having formed in situ and substituted the alumina in gibbsite with dissolved silicon. Clay gels are produced by these processes throughout the Tertiary age [9]. The kaolinite present comprises the elements Al, Si, Fe, K, and P, in addition to substantial quantities of contaminants on the soil surface [14].

The bauxite deposit results from weathering and rainfall modifications that mobilise heavy metals contained in clay, which encases gibbsite. It is possible from this clay that chemisorption is the main process by which Cr and other metals increase the contaminant concentration inside bauxite deposits. The bauxite deposit can be viewed as a vast reservoir for the sequestration of diverse heavy metals. The exploitation of the bauxite resource can generate pollutants to the surface of the land. The diverse nature of pollutants creates a significant impact on land quality.

After bauxite mining, bare land is consumed by adsorption-desorption processes of heavy metals [15]. The adsorption-desorption processes govern the chemical properties that regulate the accumulation and clearance of heavy metals, respectively [16,17], affecting heavy metal concentration, soil pH, organic matter and oxides [18,16,19] assert that heavy metals pose a risk to living organisms, even when Codex standards are not exceeded. Post-bauxite mining in India [20,21], Africa [22], Guinea [23], China [24] and Malaysia [25] reported increases in heavy metals toxicity in food and drinking water. However, there are challenges in physicochemical characteristics, which vary from site to site connected to reclamation of the land for agriculture after bauxite mining.

The pH of bauxite soil is a critical determinant in heavy metal adsorption-desorption. Heavy metal desorption escalates when pH falls below 5.5. The desorption and bioavailability of harmful heavy metals also increase at low soil pH [26-28]. On the other hand, researchers assert that an increase in pH leads to an increase in heavy metal adsorption. Soil pH can also affect the adsorption of heavy metals due to its ability to generate surface charges on aluminium, manganese and iron oxides [29,18,30]. Researchers found that in Australian bauxite soil systems with high pH, there were marked increases in negative charge sites on soil surfaces, which helped to increase the adsorption of Zn, but this effect decreased in acidic conditions [31,26,32]. Research on Zn adsorption under soil pH influences revealed that increased Zn adsorption levels were inversely correlated with soil pH [18,33,34]. The HM-Zn²⁺

behavior is entirely opposed to the established principles of soil pH and heavy metal adsorption or desorption. This contrasts with Cu and Cd adsorption in soil, which correlates to pH levels, preferential inclusion, and co-precipitation [35-38] and the exchange for same site in Cu and Zn. As such soil pH possess vital role over heavy metals interaction in the bauxite soil. In acid conditions, Al, Si, Fe and Mn oxides collect cation and anions [39], as they possess enabling energy obtained from discrete negatively charged surfaces due to imperfection or substitution or chemical dissociation reactive surfaces [11,15,17,13].

The remnants of aluminum (Al) ores extracted from the bauxite soils of Guyana retain a significant amount of Al, iron (Fe), silica (Si), and organic materials (OM) [11,40]. Under these conditions OM comes from plant matter, and detritus [41] and its aggregates are essential in extending the shelf life of soil for agronomy [28]. Soil organic matter (OM) exerts a contradictory influence on soil heavy metals, with some research indicating that elevated levels of OM may have a positive or negative effect. Organic matter possesses reactive sites that function as weak acids, chelating heavy metals. However, OM sorption was found for Zn, Pb, Al, and Cu in strong acidic conditions [42,43,44,35,40]. In tropical conditions, OM decomposition by oxidation can also liberate Al and Fe [45,42,40,9]. The incorporation of organic compost increased OM levels and reduced soil pH post-bauxite mining, according to studies by [46,47,48,41]. Chicken litter augments soil organic matter (OM), hence enhancing HM complexation, moisture retention, HMs chelation, and soil fertility owing to its negative charges [11,43,28].

Oxides are superior in the adsorption-desorption of heavy metals. Adsorption of Cr and Pb on Al oxides is more related to smaller hydrated ionic size and the presence of H⁺ ability to neutralise negative surface charges that easily adsorb by Al in a soil [49,50]. Aluminium has strong sorption affinity for oxygen-reactive anions and cations at the soil interface. Chromium binds effectively to oxygen due to analogous synergies and cooperation with Al [51,17,52]. In contrast, Cr desorption increases from pH 3 to 7, with no fluctuation at 7 [53]. The adsorption-desorption processes control the chemical properties that regulate HMs accumulation and clearance, respectively [16,17], affecting HMs concentration, the soil pH, OM, and oxides [18]. However, according to [16,19] HMs is risky to living organisms even if Codex Standards are not exceeded. In India [20-25] bauxite mining increases the HM toxicity in food and water.

Edible food plants include spinach (*Spinacia oleracea*) (Fam. Amaranthaceae), coconut *Cocos nucifera* L. (Fam. Arecaceae), celery (*Apium graveolens* L.) (Fam. Apiaceae), cassava (*Manihot esculenta* Crantz.), pak choi (*Brassica rapa* var. *chinensis* L.) (Fam. Brassicaceae), and tomato (*Lycopersicon esculentum* Mill.) (Fam. Solanaceae), which are extensively utilised for their nutritional content and sources of food. Food plants possess many mechanisms to manage HMs and the bioaccumulation of HMs in the edible portion of plants [54,16]. [55,56] report that leafy greens uptake metals ranging from 0.01 to 1300 mg kg⁻¹. Other researchers found that during a thirty-year span, coconut ecotypes developed exclusion and tolerance mechanisms to prevent HMs bioaccumulation.

Reclaimed bauxite soils are expected to include elevated concentrations of heavy metals (HMs) such as aluminum (Al), chromium (Cr), copper (Cu), cadmium (Cd), manganese (Mn), lead (Pb), and zinc (Zn) due to the breakdown of some of the minerals connected to bauxite deposits. The levels of these heavy metals in the reclaimed bauxite soils and their bioaccumulation in these crops cultivated in these soils have not been previously assessed. The purpose of this research is to fill this knowledge gap by analysing HMs levels in four communities engaged in crop production on reclaimed bauxite soil. Additionally, the study will also examine the presence of these HMs in six major crops grown in these regions.

Materials and Methods

This study was conducted at Three Friends (5.985352, -58.311274) and Coomacka (5.987821, -58.290713) in the white sand plateau and older peneplains to West Watooka (5.905325, -58.311324) and Hubu (6.822502, -58.457471) along the coastal plain. A total of 51 samples (determined using student reiteration T-test) were taken from four different treatment districts using a stratified random sampling method. There were 27 soil samples, 3 of which were background soil samples of the three mined-out locations, 24 soil samples and 24 plant edible samples (4 of which were coconut water samples). Samples were paired from plants and soil to soil alone. Samples of soil from coconut palms were collected in composites around the plants. To achieve homogeneity, samples were gathered in a zigzag manner as described in [57,58].

Approximately 500 grams of soil were collected from under plant roots for each representative sample. Soil composite was extracted from each location using a soil auger whose dimension comprises of 15 cm bucket depth and 10 cm diameter with 100 cm handle length. The 500 grams were weighed, labeled, and transported every day before being gently dried from 40 °C, 60 °C and 80 °C gradually for two days. Samples of edible plants were gathered at the precise location, and soil samples were obtained for each of the 24 sites. For each plant species representing the study districts (1500 grams of fresh weight) were collected for each species.

pH determination

Ground soil samples were weighed to a weight of 2.0 grams on a gravimetric scale. Then, 2.0 mls of distilled water were added to each beaker (100 ml) and vortexed (w/v). To dissolve any salt in the soil, the mixture was mixed and set aside for 10 minutes. After ten minutes, the material was vortexed once more, and the electrode was inserted for reading. The 2-point meter from Thermo Scientific, Waltham, MA, was calibrated for buffers 4.0 and 7.0. At the end of each sampling, the electrode was rinsed with distilled water and blotted dry. Activation Laboratory (Code 4F) in Canada gave readings from buffer 4.0.

OM determination

The Activation Laboratory's method of determining soil organic matter content (%) of soil involved using the loss on ignition method (Code 13). The organic matter is combusted at 550°C for 4 hours to remove organic and inorganic matter and at 1000°C for further 2 hours to remove carbonates and calculating the OM loss as described [58,59].

Background concentration analysis

Aqua regia reagents are used to digest 0.5 g of material for two hours at 95 °C. After letting the sample cool, deionized water is added to dilute it. After that, a Varian ICP for the 10-element suite (50% Aqua Regia – ICP-OES AQUAGEO) (Code -1E) is used to analyze the samples.

Soil analysis

Approximately 500 grams of soil were collected from under plants root for each representative sample. The soil auger (described in 3.2) was used to obtain composite soil samples from each site to obtain 500 grams of soil, which were placed in labelled bags and gently oven dried for two days. The sampled were then repackaged and shipped to Activation Laboratory for analysis. Digested samples are diluted by the UT4 Code described and analyzed by Perkin Elmer Sciex ELAN 9000 ICP/MS-OES by Activation laboratory package in Canada (Multi-Acid (4-Acid) Digestion).

Green coconut water analysis

Hydro-chemistry determination. Prior to water coconut analysis for heavy metals, samples were systematically collected from four locations in triplicates. Samples were collected in triplicates, stored in a cooler, and placed in vessels shipped cool to Activation Laboratories in Canada. All the samples have been analyzed for major HMs, using the standard method prescribed by Code 6 MB by Activation laboratory package.

Plant analysis

Samples of vegetable plants were gathered at each soil sampling location for each of the 24 sites. For each plant species representing the study districts (1500 grams of fresh weight) were collected for each species. Plants were uprooted from the soil, washed with distilled water to remove foreign materials that allowed to air-dry. These were then placed in large Ziploc bags and labelled for each site. Coconuts were taken in triplicates and stored in an ice cooler. At the laboratory, the plant samples were further cleaned and placed in paper wraps (non-aluminum) for dehydration gradually at 40 °C, 60 °C and 80 °C degrees Celsius for 24-48 hours. Before being shipped to Activation Laboratories in Canada, plant samples were pulverized using a mortar and pestle, put in sample bags, and weighed. In Canada, each samples were analyzed according to Vegetable Ash Package Digestion, ICP-MS, Code 2D [16]. Results for 59 elements were included in all plant-related reports from ACT Labs [16].

Geo-accumulation Index

The geochemical index (*I_{geo}*) is a commonly utilized metric for evaluating the presence and concentration of anthropogenic contaminants on the soil surface (Table 1). This index measure quantitatively determines soil contamination levels based on the actual bioavailable percentage (baseline value). This fraction is derived via the application of Muller [60]. Consequently, assessing the extent of metal pollution in agricultural areas impacted by industrial activities is crucial.

Table 1: Contamination categories for geo-accumulation index (Source: (Nowrouzi & Pourkhabbaz, 2014).

Geo-accumulation Index		
Class	Value	Classification
0	<0	Uncontaminated
1	0-1	Uncontaminated to moderately contaminated
2	1-2	Moderately contaminated
3	2-3	Moderately to strongly contaminated
4	3-4	Strongly contaminated
5	4-5	Strongly to extremely strongly contaminated
6	>5	Extremely contaminated

Geochemical index (*Igeo*) was originally stated by Muller (1969) [60]. In order to determine and define metal contamination in sediments by comparing current concentrations with preindustrial levels, *Igeo* is calculated as follows:

$$I_{geo} = \log_2 [C_n / 1.5B_n] \quad \text{Equation 1}$$

where B_n is the background value for the metal n , C_n is the measured concentration of the metal n in the soil, and the factor 1.5 is used to account for any fluctuations in the background data caused by lithological variances. The global average shale data is frequently used to construct the quantity *Igeo* [61]. Since the *Igeo* index was developed for this study this background data was used.

Bioaccumulation factor

The formula got bioaccumulation-a simple bioconcentration factor (BCF) model, sometimes referred to as bioaccumulation factor (BAF) [62]-assesses the metal content of plants based on the total metal concentration measured in the soil:

$$BAF_{sp} = \frac{M[p]}{M[s]} \quad \text{Equation 2}$$

Where:

[M]p = Total metal concentration in plant (mg kg^{-1})

[M]s = Total metal concentration in soil (mg kg^{-1})

BAF_{sp} = bio-concentration factor from soil to plant, being the ratio of metal concentration in plant to total metal concentration in soil [16].

2.9. Statistical analysis

The data collected was entered into the statistical software program SPSS 20 (International Business Machines Corporation, Armonk, NY, USA) in the analysis of the data. One-way analysis of variance (one-way ANOVA) was utilized to determine statistical significance at $p < 0.05$. To determine significant differences between treatments Duncan's multiple range post hoc test was employed at $p < 0.05$. Correlation between soil physical characteristics such as pH and OM with HMs concentrations in plant tissue (BAF) and HMs concentrations in the soil were conducted using a Pearson's correlation analysis.

Results

Soil pH

Table 2 demonstrates that there is no statistically significant difference ($p = 0.835$, by ANOVA) in mean pH values among treatment/district means. Bauxite mining does not affect soil pH. The finding corresponds with previous studies undertaken in Romania [63] and Indonesia [64] post bauxite mining sites. Figure 2

Table 2: One-way ANOVA of soil pH (mean $\pm$ SEM) in 4 bauxite districts in Guyana

Region	Mean $\pm$ S. E	Range
District 1	5.73 $\pm$ 0.2	4.63 - 6.62
District 2	5.68 $\pm$ 0.5	4.36 - 7.26
District 3	6.4 $\pm$ 1.1	4.62 - 11.8
District 4 (Control)	5.8 $\pm$ 0.5	4.29 - 7.18
p-value	0.835	-

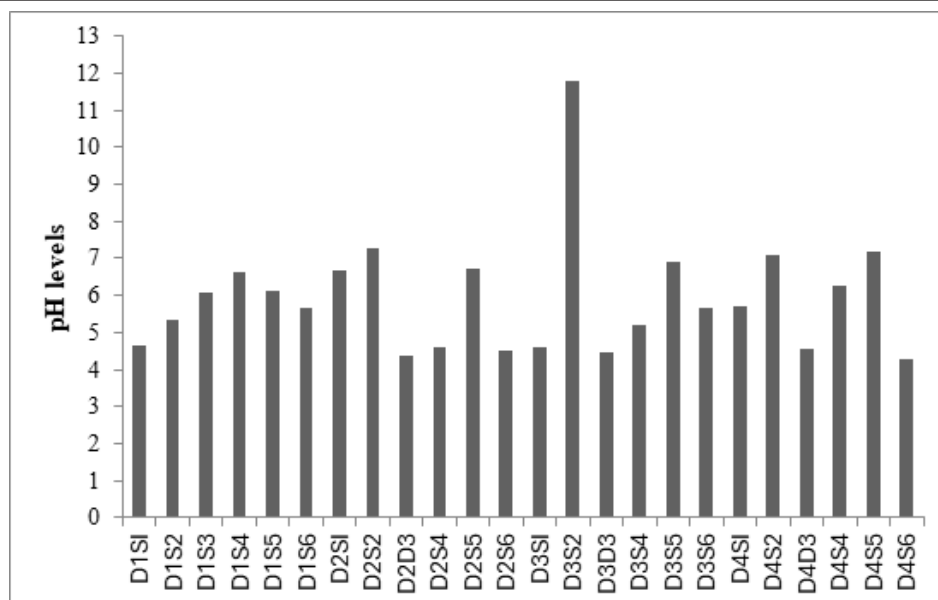


Figure 1: pH values for the soil samples from the study sites

Soil organic matter

Table 3 and Figure 2 Mean percent OM content is similar among treatment means ($p=0.788$) (Table 5). This would indicate that bauxite mining does not have significant effect on OM content in soil. Similar studies on post bauxite mining soil in Romania [63] and Brazil at various depths [65] have been cited.

Table 3: One-way ANOVA of organic matter content (%) for 4 bauxite mining districts in Guyana

Region	Mean $\pm$ S. E	Range
District 1	7.5 ± 1.3	1.1- 10.46
District 2	10.18 ± 1.1	7.3 – 13.24
District 3	11.05 ± 4.6	1.56 – 30.31
District 4 (Control)	9.7 ± 0.8	7.61 – 12.06
p-value	0.788	-

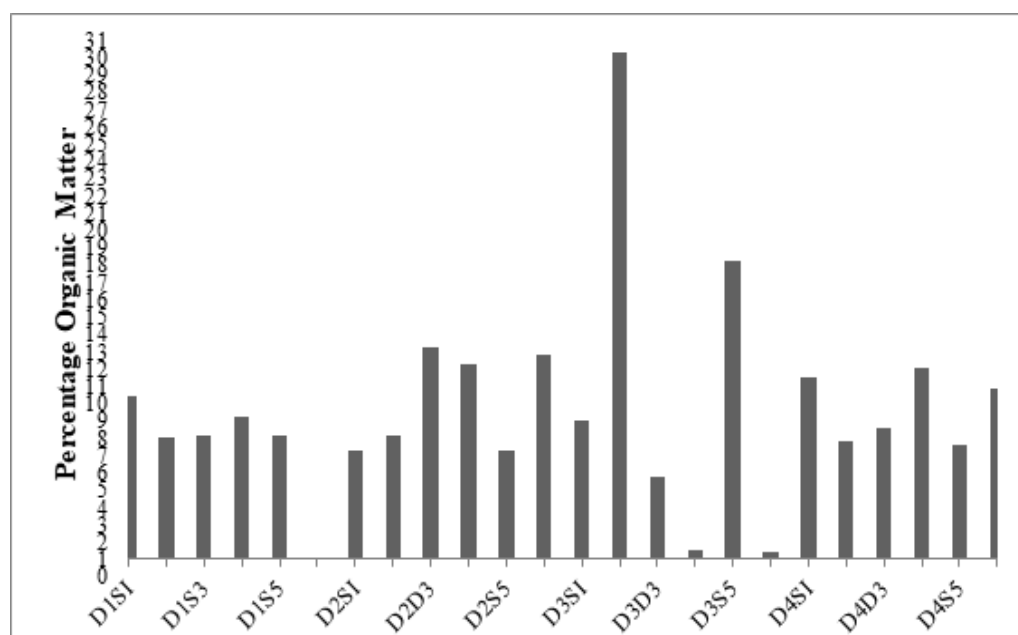


Figure 2: Organic matter (OM) content (expressed in %) in soil samples in the study areas

Soil total heavy metal concentration

Mining influences heavy metal concentration in bauxite soil

Table 4 shows the one-way ANOVA results show no significant difference in the treatment means ($p > 0.05$) of Al, Cd, Cu, Mn, and Cr in bauxite soil. The one-way ANOVA analysis in (Table 4, Figure 3) showed that the mean Pb concentration was significantly different among treatment means (F ratio = 9.28, $p < 0.05$). Figure 4 shows that the concentration of total Lead (Pb) was below FAO/WHO limits of 50 mg kg⁻¹ in soil. These values were observed to be below the CAC limit (Joint FAO/WHO Codex Alimentarius Commission, 2017) (i.e., 50 mg Pb kg⁻¹) for all soil samples towards human health safety [66]. The one-way ANOVA analysis in (Table 4) also shows that the mean Zinc (Zn) concentration was significantly different among treatment means (F ratio = 4.08, $p = 0.020$). However, in this study District 4 = District 2. Figure 5 shows that the concentration of total Zn in soil was below FAO/WHO limits of 10-300 mg kg⁻¹ in soil. These discoveries shed new insights into mining, particularly bauxite mining. A previous study [67] found contrastingly that mining was the main contributor to elevated Pb levels in the environment.

Table 4: One-way ANOVA analysis revealed the mean total heavy metal concentration (mg kg⁻¹) in soil for different treatment districts.

Treatments	Mean $\pm$ Std. Error						
	Total Al	Total Cr	Total Cd	Total Cu	Total Mn	Total Pb	Total Zn
District 1	40550 $\pm$ 3854	37.5 $\pm$ 4.3	0.1 $\pm$ 0.00	21.1 $\pm$ 5.7	171.3 $\pm$ 28.1	13.0 $\pm$ 1.3	37.9 $\pm$ 8.5
District 2	55400 $\pm$ 9098	37.0 $\pm$ 3.3	BDL	30.5 $\pm$ 10.3	108.1 $\pm$ 12.3	15.5 $\pm$ 1.7	59.1 $\pm$ 9.0
District 3	37583 $\pm$ 10571	34.1 $\pm$ 6.7	BDL	11.1 $\pm$ 4.1	107.5 $\pm$ 27.2	12.1 $\pm$ 2.9	31.4 $\pm$ 12.4
District 4	67350 $\pm$ 9996	35.8 $\pm$ 3.1	0.25 $\pm$ 0.05	16.7 $\pm$ 2.4	144.3 $\pm$ 17.0	27 $\pm$ 2.6	102.9 $\pm$ 26.6
p- values	0.091 ^{ns}	0.957 ^{ns}	0.091 ^{ns}	0.211 ^{ns}	0.133 ^{ns}	0.000*	0.020*

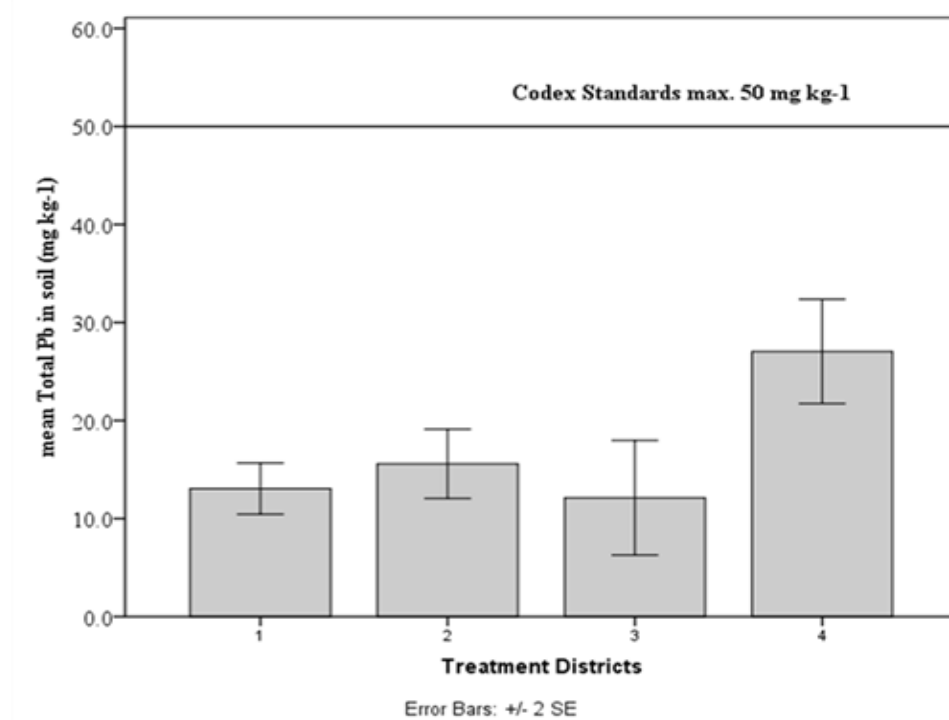


Figure 3: One-way ANOVA analysis revealed the mean Pb concentration (mg kg⁻¹) in bauxite soil

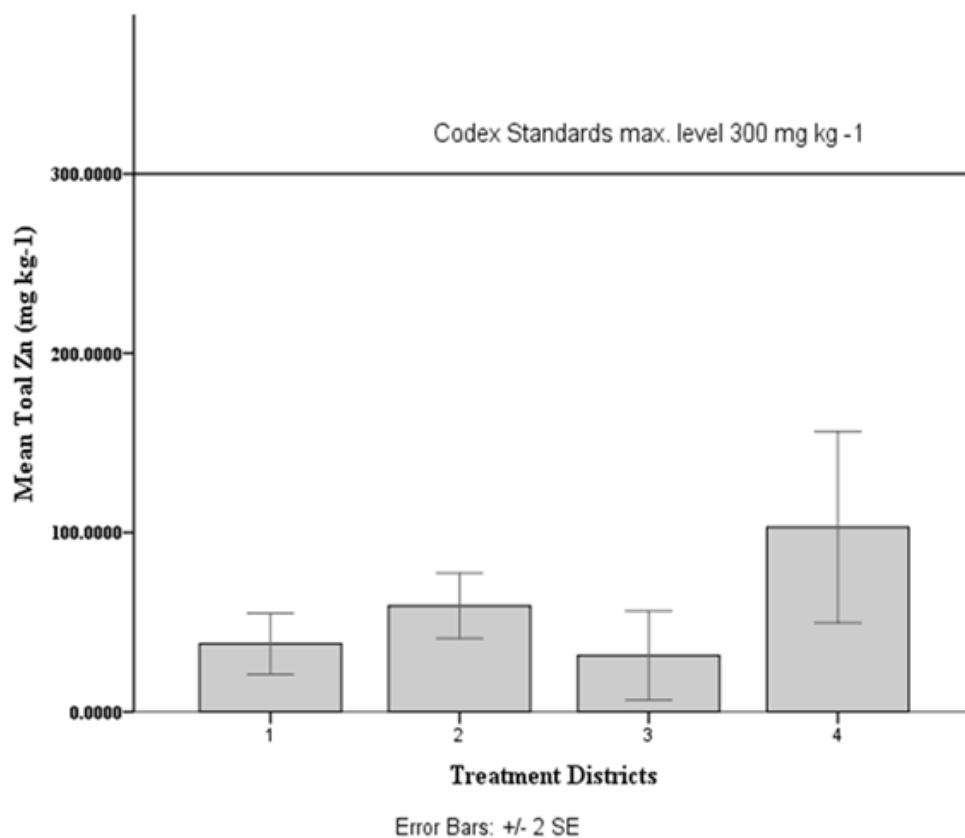


Figure 4: Mean total Zn concentrations in soil and CAC (WHO/FAO) limit

Pearson correlation output

Table 5: Results of Pearson correlation for treatment regions in the order 1-4

Parameters/ Regions	Post-mined regions			Unmined region
	West Watooka	Coomacka	Three Friends	Hubu
pH * OM	-0.132	-0.963**	0.885*	-0.451

*Significant at p value .05

**Significant at p value .01

Table 6: Heavy metals interaction in mined-out region (West Watooka)

	pH	OM	Al	Cd	Cu	Cr	Mn	Pb	Zn
pH	1								
OM	-0.132								
Al	-0.670	0.582							
Cd	. ^a	. ^a	. ^a						
Cu	0.695	0.387	-0.306	. ^a					
Cr	-0.727	0.018	0.722	. ^a	-0.774				
Mn	0.485	0.526	0.036	. ^a	0.821*	-0.304			
Pb	-0.601	0.750	0.963**	. ^a	-0.156	0.634	.215		
Zn	0.438	0.674	0.037	. ^a	0.930**	-0.586	0.828*	0.196	

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

a. Cannot be computed because at least one of the variables is constant.

Table 7: Heavy metals interaction in mined-out region (Coomacka)

	pH	OM	Al	Cd	Cu	Cr	Mn	Pb	Zn
pH	1								
OM	-0.963**								
Al	-0.255	0.300							
Cd	. ^b	. ^b	. ^b						
Cu	-0.427	0.311	0.806	. ^b					
Cr	-0.655	0.683	0.576	. ^b	0.470				
Mn	-0.090	-0.089	-0.777	. ^b	-0.279	-0.505			
Pb	-0.889*	0.757	0.299	. ^b	0.624	0.593	0.210		
Zn	0.013	-0.240	-0.034	. ^b	0.392	0.188	0.300	0.294	

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

b. Cannot be computed because at least one of the variables is constant.

Table 8: heavy metal interaction in mined-out region Three Friends

	pH	OM	Al	Cd	Cu	Cr	Mn	Pb	Zn
pH	1								
OM	0.885*								
Al	-0.132	0.114							
Cd	. ^b	. ^b	. ^b						
Cu	-0.093	0.222	0.866*	. ^b					
Cr	-0.162	0.065	0.997**	. ^b	0.828*				
Mn	-0.433	-0.302	0.880*	. ^b	0.617	0.907*			
Pb	-0.227	-0.017	0.908*	. ^b	0.859*	0.894*	0.866*		
Zn	-0.113	0.188	0.966**	. ^b	0.943**	0.949**	0.759	0.853*	

Table 9: Heavy metal interaction in unmined region Hubu

	pH	OM	Al	Cd	Cu	Cr	Mn	Pb	Zn
pH	1								
OM	-0.451								
Al	-0.851*	0.743							
Cd	. ^b	. ^b	. ^b						
Cu	0.762	0.123	-0.532	. ^b					
Cr	-0.225	0.668	0.579	. ^b	-0.053				
Mn	0.722	-0.159	-0.680	. ^b	0.817*	-0.058			
Pb	0.613	-0.750	-0.844*	. ^b	0.203	-0.672	0.235		
Zn	0.811	-0.800	-0.985**	. ^b	0.409	-0.555	0.584	0.895*	

** . Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

b. Cannot be computed because at least one of the variables is constant.

Background concentration

Background concentration results for the three mined-out study districts are presented in Table 6. This is the first data from Guyana. Similar, research has been conducted in countries like the USA, Belgium, India, Poland, Scotland, and Spain (Albright, 2004). Often, countries resort to shale values as a substitute for background values when calculating pollution indices, however, this practice is not ideal. The numbers obtained helped calculation of pollution index. It could make the best determining estimate of heavy metals sources from mining, anthropogenic, and environmental influences in soils as a whole.

Table 10: Results of Background Heavy Metal Concentration (mg kg^{-1}) as measured by ICP-OES (Code IE- 50% Aqua Regia ICP-AQUAGEO- Package) in Soils

Locations	Coordinates	Heavy metals (mg kg^{-1})							Hg report 2 (mg kg^{-1})
		Al	Cd	Cu	Cr	Mn	Pb	Zn	
District 1	5.908325 -58.311324	ND	BDL	5	ND	21	5	12	
District 2	5.987821 -58.290713	ND	BDL	1	ND	13	3	5	
District 3	5.925471 -58.306338	ND	BDL	3	ND	36	5	8	
Low Detection Limit (mg kg^{-1})		NA	0.5	1	NA	2	2	1	
Upper Detection Limit (mg kg^{-1})		NA	2000	10000	NA	100000	5000	10000	

Geo-accumulation Index

Results of the I_{geo} obtained for soil samples were calculated for the mined-out district and those values obtained from background concentration for specific mined-out treatment districts (Table 11). The I_{geo} , created by Muller, was used to assess field contamination by HMs. Using the average amount of I_{geo} for all HMs, the total assessment of HM contamination was performed for all the samples collected, allowing pollution to be identified for all HMs other than Al, for which no background value has been determined (Table 7).

Table 11: Geo-accumulation index classes for the HMs at the study post bauxite mine districts

Districts	Al	Cd	Cr	Cu	Mn	Pb	Zn
D1	-	Class 1	Class 2	Class 2	Class 3	Class 1	Class 2
D2	-	Class 1	Class 1	Class 4	Class 3	Class 2	Class 4
D3	-	Class 1	Class 1	Class 1	Class 1	Class 1	Class 1

Heavy metal uptake by food plants *Leafy greens*

Table 12: Indicates that leafy vegetables are efficient accumulators of heavy metals. These levels obtain can pose serious health risk to consumers.

Table 12: Analysis of variance showing heavy metals (mg kg⁻¹) uptake in leafy vegetables Pak chow Brassica chinensis; spinach Spinacea oleracea; and celery Apium graveolens from soil

Treatment	Genotype	Al	Cd	Cu	Cr	Mn	Pb	Zn
District 1	Pak choy	3170.0	2.4	125.0	95.0	1460.0	18.8	1020.0
District 2		1670.0	0.3	36.4	BDL	106.0	14.5	327.0
District 3		2780.0	0.6	51.3	7.0	401.0	8.8	601.0
District 4		2990.0	0.3	56.4	BDL	670.0	25.3	813.0
District 1	Spinach	1610.0	1.6	63.1	BDL	1230.0	8.1	533.0
District 2		1930.0	0.2	41.1	BDL	72.6	5.4	304.0
District 3		1490.0	0.2	27.8	BDL	502.0	7.5	173.0
District 4		1720.0	0.7	38.6	BDL	108.0	10.2	693.0
District 1	Celery	2400.0	5.5	4540.0	BDL	1020.0	7.40	730.0
District 2		ND	ND	ND	ND	ND	ND	ND
District 3		3140.0	0.2	42.3	7.0	266.0	38.40	456.0
District 4		1010.0	1.2	29.9	BDL	97.4	9.3	540.0
CAC Limits (mg kg ⁻¹)		NA	0.2	40.0	2.3	6.7	0.3	60.0

NA – Not available

Green coconut fluid

Table 13 indicates that green coconut fluid contains heavy metals at levels below the Joint FAO/WHO Codex requirements for drinking water quality. Except for manganese, which exceeds allowed amounts, manganese is an important microelement for the human body. Consequently, it seems to exist in a water-soluble form, facilitating its absorption.

Table 13: Uptake of heavy metals in coconut water (mg L⁻¹), *Cocos nucifera* L.

Treatment	Al	Cd	Cu	Cr	Mn	Pb	Zn
District 1	0.051	0.001	0.004	BDL	2.293	0.001	0.342
District 2	0.017	0.000	0.012	BDL	6.997	0.001	0.453
District 3	0.046	0.001	BDL	BDL	9.330	0.004	0.388
District 4	0.026	0.001	BDL	BDL	8.358	0.002	0.166
CAC Critical Limit (mg kg ⁻¹)	0.500	0.003	1.00	0.05	0.05	0.010	3.000

Tomato

Table 14 indicates that tomato is an effective accumulator of heavy metals with the exception of chromium, for which no quantities were detected. Tomato effectively absorbs Al, Cd, Cu, Mn, Pb and Zn above Codex acceptable limits.

Table 14: Uptake of heavy metals in tomato (mg kg⁻¹), *Lycopersicon esculentum* L.

Treatment	Al	Cd	Cu	Cr	Mn	Pb	Zn
District 1	332.0	0.33	58.70	BDL	124.00	12.60	242.00
District 2	375.0	1.95	90.50	BDL	215.00	7.50	387.00
District 3	1030.0	0.43	119.00	BDL	270.00	34.20	631.00
District 4	277.0	0.27	55.60	BDL	132.00	6.50	221.00
CAC Critical Limit (mg kg ⁻¹)	NA	0.2	40	2.3	6.7	0.3	100

Cassava tuber

Table 15 indicates that cassava tuber can effectively accumulate high levels, comparable to leafy greens and tomatoes, of heavy metals in their proliferous layer. These levels are far exceeding Codex acceptable standards.

Table 15 Uptake of heavy metals in cassava tuber (mg kg⁻¹), *Manihot esculenta* L

Treatment	Al	Cd	Cu	Cr	Mn	Pb	Zn
District 1	4340	0.12	49.40	11	156	15.40	459
District 2	20500	1.08	95.50	98	190	25.40	968
District 3	21900	0.07	67.40	44	549	59	545
District 4 (Control)	10300	0.34	64.60	29	560	23.60	662
CAC Critical Limit (mg kg ⁻¹)	NA	0.1	20	2.3	NR	0.1	50

Bioaccumulation of heavy metals by food plants

Pak choy BAF

Table 16: Bioaccumulation factor of HMs of leafy greens Pak Choy, *Brassica chinensis* L.

Treatment	Al	Cd	Cu	Cr	Mn	Pb	Zn
District 1	0.05	*	13.29	1.86	10.65	1.03	30.81
District 2	0.04	*	1.26	0.00	0.78	1.13	3.97
District 3	0.06	*	2.31	0.18	3.45	0.45	13.09
District 4 (Control)	0.04	*	2.31	0.00	3.40	1.27	11.53

Bold values – BAF above 1

Spinach BAF

Table 17: Bioaccumulation Factor of heavy metals in Spinach, *Spinacia oleracea* L.

Treatment	Al	Cd	Cu`	Cr	Mn	Pb	Zn
District 1	0.03	*	3.44	0.00	6.15	0.54	14.29
District 2	0.03	*	4.83	0.00	1.08	0.63	10.13
District 3	0.08	*	5.67	0.00	17.01	1.19	19.22
District 4 (Control)	0.04	3.40	1.85	0.00	0.69	0.28	3.91

Celery BAF

Table 18: Bioaccumulation factor of heavy metals in Celery leaf, *Apium graveolens*. L

Treatment	Al	Cd	Cu	Cr	Mn	Pb	Zn
District 1	0.070	55.80	130.08	0.00	6.18	0.66	12.67
District 2	ND	ND	ND	ND	ND	ND	ND
District 3	0.039	*	1.64	0.11	1.50	1.95	5.30
District 4 (Control)	0.028	4.033	1.67	0.00	0.51	0.27	2.75

Green coconut fluid BAF

Table 19: Bioaccumulation Factor of heavy metals in Coconut water, *Cocos nucifera* L.

Treatment	Al	Cd	Cu	Cr	Mn	Pb	Zn
District 1	0.00	*	0.00	0.00	0.01	0.00	0.01
District 2	0.00	*	0.00	0.00	0.05	0.00	0.01
District 3	0.00	*	0.00	0.00	0.07	0.00	0.01
District 4 (Control)	0.00	*	0.00	0.00	0.07	0.00	0.00

Tomato BAF

Table 20: Bioaccumulation factor of heavy metals in Tomato fruit, *Lycopersicon esculentum*

Treatment	Al	Cd	Cu	Cr	Mn	Pb	Zn
District 1	0.00	3.30	1.39	0.00	0.42	0.98	3.70
District 2	0.00	*	1.13	0.00	2.65	0.37	6.10
District 3	0.15	*	49.58	0.00	6.13	18.00	185.58
District 4 (Control)	0.00	*	3.15	0.00	1.12	0.26	3.68

Table 21: Bioaccumulation factor of heavy metals in Cassava, *Manihot esculenta*

Treatment	Al	Cd	Cu	Cr	Mn	Pb	Zn
District 1	0.13	*	5.95	0.27	1.62	1.73	58.84
District 2	0.37	*	3.43	1.96	1.91	1.37	13.01
District 3	0.53	*	11.62	1.15	3.49	3.88	24.43
District4 (Control)	0.11	*	6.21	0.85	5.49	0.915	12.70

Discussion

Soil physicochemical variables of bauxite soil of Guyana Soil Ph

The degree to which total heavy metals become available to their biological target is called bioavailability. Despite the absence of major alteration in soil pH, it is important to acknowledge that solubility and desorption of heavy metals are anticipated owing to the predominance of aluminium and iron oxides. Both one-way ANOVA and raw data are provided for clarification of the results. According to [68], mining often influences soil disturbances, leading to a noticeable increase in soil pH. The illustration in Figure 1 indicates soil pH variability across different sites. Soil samples had a pH range of 4.29 to 7.26 in water. They are classified as very acidic to alkaline [26]. An anomaly at site D3S2 (Three Friends) indicates a pH value of 11.8, classified as ultra-alkaline. These variations are often linked to mineralogy, which is affected by the chemical properties of the soil [68]. As a result, the CEC is expected to be above primary levels, mostly due to contributions from exchangeable cations. Similarity has been documented (Zhuang et al., 2009). According to [13,15], adsorbates like kaolinite (Al and Si oxides) and the subsequent neutralisation of the exchange sites for sesquioxides account for low CEC. This enables cations, in acidic condition, to substitute and fill vacant sites, potentially reducing permanent CEC. Al may discretely introduce pH-dependent charged sites that displace cations and encourage CEC. These charged sites are introduced by aluminium oxides. H^+ , $Al(OH)^{2+}$ and Al^{3+} that predominate the CEC complex under acidic conditions. This study substantiates the hypothesis that the increased presence of heavy metal complexes comes from a greater prevalence of oxide-rich mineralogy (Prado et al., 2015).

The highest pH value (pH 11.8) in sample D3S2 obtained from the Three Friends shows that the soil pH is alkaline. The mining operation at Three Friends was recorded in 1917 [11,69]. pH values above 6.9 (Coomacka-D2S2; Hubu-D4S2; D4S5), signify that the bauxite soils exhibit surface adsorption and Al precipitation as $Al(OH)_4^-$ attributed to different amounts of calcium oxide ($CaCO_3$), lacking below pH 7.0. Santini and Fey (2013) confirmed the presence of trace amounts of calcite (lime) in bauxite soil of Guyana. It lends itself to believing, reasonably so, to have contributed to the high soil pH. This site may possess substantial amounts of base cations, as the pH value of 11.8 markedly exceeds that of any other lateritic soils previously reported in India [8], Taiwan (Ko, 2014), the USA [68], Indonesia [64] and Australia [32]. These data demonstrate that the bauxite soil exhibits a frightening and inclusionary influence of HMs over a wide range of soil pH.

Soil Organic matter (OM)

Table 3 demonstrates that the average % organic matter content is similar among treatment means ($p=0.788$). This result suggests that bauxite mining does not significantly affect OM content in soil. Comparable studies on post bauxite mining soil in Romania [63] and Brazil at various depths [70] have been referenced. The OM content of the studied districts did not significantly change following bauxite mining. This information indicates that the soil is evolving under the influence of microbial activities that favor the improvement in soil fertility. Numerous studies on bauxite soil focused on variables like C:N ratio, C-organic and CEC where low CEC were linked to low organic carbon levels [71]. They recognized that organic matter is the factor that contributes to cation exchange capacity and organic carbon. The conclusions of [70] differ as they delineated the physical and chemical changes from mined lands to natural lands that may potentially augment microbial activity post-mining. Moreover, [72] explained that these changes improved soil structure due to triggers from microbial activity that release chemicals. In addition, OM serves as a source of soil charge derived from OM-functional groups [73,40,74]. The specified values indicate that OM levels at or below 5% are classified as deficient, while values above 18% are excessive relative to the present study [47].

The data obtained also suggests that OM is aligned in order to the movement of soil pH. That is, as percent OM increases, soil pH increases. Comparable results [75] in Australian lateritic soil indicated that the improvement of soil pH was attributed to the incorporation of organic matter. The highest value of 30.31% was obtained at the identical site (D3S2) where pH was 11.8. The most desirable outcome would be to have this localized high percentage of OM discovered distributed to all sites that show a considerably deficient amount. The link between high OM content and soil pH change can govern the amount of OM as well as the presence of important plant components and their metabolic byproducts. The finding of this research is supported by [75] in that the alkaline nature of plant materials (OM) results from the dissociation of organic acids as well as the release of H^+ ions from OM are linked to soil pH. According to [74] plant roots can provide 10% OM, whereas soil flora and fauna can offer 5% organic matter. Considering this development, it is abundantly evident that the soil's CEC/OM has a close connection to the pH of the bauxite soil. Similarly, in Nigeria, a decrease in CEC and pH was observed following OM removal from lateritic soil [76,77].

Soil OM is important to the bauxite soil in many ways [11,76,7,40]. Low values (1.34%) have been reported in the Brazilian bauxite soil [74]. These values are crucial because soil OM has a greater involvement in various processes that occur between soil OM and HMs. Likewise, [43,77,78] it has been reported that soil organic matter is connected to HMs adsorption. In the Brazilian bauxite soil, OM is connected to carboxylic compounds of HA, FA, and CEC [79,74]. The process of ligand exchange, which can compete with HMs, makes it possible for soluble OM to be adsorbed to bauxite soil. This process is explicitly carried out when soluble OM reacts with cations that become bound to the particle surface to form a soluble complex. The soil's surface would become more negatively charged as a result of OM absorption. This finding was also consistent with [79,8].

Heavy metal concentration in bauxite soil of Guyana

Total Lead and Zinc

The data on total lead indicates that the Pb concentration measured in District 4 is markedly greater than that in Districts 1-3, in terms of mean concentration. Bauxite mining considerably affects the concentration of lead in the bauxite soil of Guyana. The mean values obtained shows that in the unmined region possessed higher concentration of Pb than those when compared to the mined-out regions eliciting novel perspective about bauxite mining impact. A previous research [67] identified mining as the primary contributor to increased Pb levels in the environment.

The data on total Zn suggests that Zn levels at the control sites behave differently from those in the mined-out soil, due to the impact of bauxite mining and prolonged District 2 tailing discharge (District 2) that foremostly reaches the soil where crops are cultivated. The results also suggested that Zn^{2+} was the most likely ionic form in the bauxite soil under both alkaline and acidic conditions, which is expected to contribute to the exchange capacity of the soil, which is a concerning dimension. The bauxite soil inherently has an argillic and tensile deformation nature, with vast variation in OM content, perhaps low clay content, and multiple sites that could support Zn desorption and adsorption to aluminum sesquioxide inner sphere hydroxyl group, which function as acid/base sites on large surface area facilitating zinc binding via ligand and surface complexation [42,36,].

Pearson correlation of physicochemical parameters of the bauxite soil of Guyana

In the case of West Watooka, the solubility of heavy metals is contingent on OM constituents. Ligands and aminopolycarboxylic acids might enhance the extractability of heavy metals within pH 4-7 because of the magnitude of functional organic groups associated with weakened van der Waals forces, π - π , CH- π , and hydrogen forces, rendering them susceptible to adsorption-desorption processes. This property is derived from 1:1 clays like kaolinite that disperse to provide negative charges to particles. At pH > 7, both HA and FA acids are likely to attain dispersion from substitution by phenolic and carboxylic acids. Additionally, in Coomacka, soil pH affects heavy metal desorption in contaminated soil. This is offset by top-soil mixing, which contributes to a drop in soil pH. Even so, heavy metals are present in a range of valency states that can contribute to net H^+ ions elevating acidity. The bottom line is that an inverse significant relationship ($p < 0.01$) between pH and OM% contradicts the basic theory about OM accumulation primarily at the topsoil level. Acquiring a greater understanding of the physico-chemical properties of post-mining bauxite lands is essential for assessing the agricultural viability of the bauxite soil. The study's most ed result (Three Friends), with an r-value of 0.885 ($p < 0.05$), indicates a positive and substantial association between soil pH and OM. Out of all the treatment districts, this one has the highest mean pH at 6.4 ± 1.1 and OM at 11.05 ± 4.6 . The value of 11.05 % to attain pH and OM correlation is strikingly

incipient towards realistic connections for soil quality criteria that are cautious, based on the lower value. The study elicit a novel perspective derived from the accumulation of all sources which gives contextual understanding between total and the 50% aqua regia digestion in the background study. Accordingly, Three Friends mining occurred in 1917, marking a century-old mined-out region. Low content of soil OM (Hubu, unmined) in frequently cultivated lands decreased due to reduction in total organic matter inputs; increases in mineralization rates from tillage of organic matter; influence of the wetting and drying cycles and increase in temperature at the topsoil level.

Heavy metal interaction produced by Pearson's Correlation

Table 6 shows a positive significant ($p < 0.05$; 0.01) correlation between Cu and Cr, Pb and Cr, Zn and Pb. Higher aluminium and OM tend to capture more lead. In **Table 7** increases in soil pH appears to have a significant association with low OM and Pb in soil. **Table 8** has a strong positive correlation with Al (0.866^*); Pb (0.997^*) and Cr (0.828^*), suggesting close relationships, and that they increase together. Also, Mn (0.866^*) and Zn (0.966^*) levels tend to increase alongside Al levels pointing to similar behavior and co-occurrences. In Nepal Khadka et al. (2016) found r value of 41.8 % significant correlation between pH and Mn, which goes to show that soil pH and Mn-oxide progressively with OM controlled HMs, some of which are micronutrients, with superior positive r values between pH and OM. **Table 9** shows that as pH decreases Al (-0.851^*) levels increases, which is consistent with studies. Al, Zn (-0.985^{**}) and Pb (-0.844^*) tend to behave inversely. This expansive of data in the finding suggests co-occurrences, similar behavior of metals with the extent to which this complicates agriculture on the bauxite soil of Guyana. This complex nature demonstrates the role of pH and Al, Mn role in controlling the complex of the bauxite soil and also indicating that they tend to be present together.

Heavy metal uptake by crop plants

Food plants have a variety of mechanism to deal with HMs and the bioaccumulation of HMs in plants' edible parts [57,11]. Several researchers [11] reported leafy vegetables (celery, spinach, and pak chow), coconut fluid, tomato, and cassava bio-accumulated massive amounts of metals. It was reported that 97 percent of leafy greens absorbed heavy metals from contaminated locations, with 39 percent exceeding maximum limits of cadmium, copper, and lead collected from Egyptian markets [80]. The Joint FAO/WHO Codex Alimentarius Commission has implemented measures to ensure food safety, as food crops are grown on contaminated soil, thereby mitigating food consumption risks. The examination of edible food plants (11-15) and their bioaccumulation (16-21) concludes the research. Green leafy vegetables, tomatoes and cassava in human diets supply essential nutrients and enhance food and nutritional security. They respond to persistent demands for nutrition to shield the organ systems of the human body against chronic diseases. In people, chronic heavy metal illness resulting from uncontrolled consumption of contaminated food is linked to a diverse range of neurological, gastrointestinal, dermal and cardiovascular illnesses, including Parkinson's disease and Alzheimer's disease[55]. The findings reported above are in line with the body of literature that demonstrated that exposure to high concentrations of heavy metals poses serious health hazards to people (CAC, 2014, 2015; Gobas, 2001; Manikandan et al., 2019). As such, leafy greens and roots crops emanating from the farms on the bauxite soil present potential toxicities for consumers. The fluids from coconut palms consistently exhibited heavy metal levels below detection limits of ICP. This study consistently demonstrates the coconut crops may stabilize heavy metals via polyphenols, which play a role in blocking heavy metals and forming insoluble complexes that either include or exclude contaminants in food plants. These findings shed new perspective of heavy metals interactions, and the presence of Mn oxides with its role in the exchange complex. The studies by [81]; [27] and Shabala et al. (2015) suggested that aging mined-out lands is a beneficial tool for OM accumulation.

Conclusion

In summary, this study provides information on physico-chemical factors and the presence of total heavy metals concentration and their interaction through cooperation in the bauxite soil of Guyana. In addition, bauxite mining also alters total heavy metals concentration in the soil. In addition, the study revealed that five out of the six food crops are effective bio-accumulators of heavy metals. The pose serious health hazard to consumers.

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Conflict of interest

The author declares no conflict of interest

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