Modified BCR Speciation Pattern of Heavy Metals in the Soil Sediments Around Areas of Mining Activities atRimin-Zayam, Toro LGA, Bauchi State of Nigeria, West Africa.

Ogunleye A.O[1] , Hassan U.F[2], Prof. Boryo D.E.A[2], Prof Adamu H.M[2]

[1]Department of Chemistry, Federal college of Education (T) Bichi, Kano state, NIgeria

[2]Department of Chemistry, Abubakar Tafawa Balewa University, Bauchi state Nigeria

Abstract.

BCR Speciation Patternof Heavy metals in soil sediments collected from the vicinity of the mining areas of RiminZayam, Toro LGA, Bauchi State were evaluated and the fractionation pattern were studied.Generalizing, the recorded high abundance of heavy metals such as cadmium, chromium, copper, iron, Lead, Nickel and Zinc, which were noted to be mainly bounded to the Residual fraction, pointing to their Lithogenic origins and thus the conclusion that they had nothing to do with the mining activity. However, Cobalt and Manganese being more abundantly speciated in the other fractions points to their anthropogenic origin, and their dispensation to being bioavailable and their tendency to be labile and mobile

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Keywords:*BCR Speciation Pattern,Heavy Metals, Soil Sediments, Rimin-Zayam and fractionation.*

Introduction.

Chemical partitioning can be defined as the process of determining and identifying specific chemical species or binding forms of heavy metals in the environment (Davidson *et al.*, 1999). Chemical partitioning has become an efficient and reliable tool for the assessment of environmental and ecotoxicological risk posed by heavy metals. Heavy metal partitioning has been harnessed in determining their potential bioavailability and remobilization within human, sedimentary, biotic and aquatic systems.

Studies on the distribution and partitioning of heavy metals in segments can provide not only information on the degree of pollution but especially the actual environmental impact on metal bioavailability as well as their origin (Ramirez *et al.*, 2005). It has generally been accepted that the most appropriate method to evaluate heavy metal is the selective sequential extraction procedure (Kot and Namiesnik, 2000). Selective extraction is widely used in soil and segment analysis to evaluate long term potential emission of pollutants and to study the distribution of the pollutants among the geochemical phases (Rauret*et al.*, 1999). They are also used to determine the metals associated with such constituents in the sedimentary deposit (Rubio *et al.*, 1991).

One of the importance of partitioning is the qualitative and quantitative signature it has given to specific metal species, which could be employed in the assessment of the index of toxicity impact of elements. A comprehensive knowledge of chemical partitioning and total metal concentration gives proper understanding of the interaction between the heavy metals and the segments. It explains the environmental impacts of these metals and reliably predicted their sources. The orientation of this research is therefore to study the partitioning of some heavy metals in artisanal mining site in Rimin Zayan, Bauchi State of Nigeria, West Africa.

Materials and Methods

In the preparation of all the solutions used in the research work, chemicals of analytical reagent grade purity and distilled water were used. Glass and plastic wares that were used, were washed with detergent solution, followed by 20.00 % (v/v) trioxonitrate (v) acid, rinsed with distilled water and finally with the solution that was placed in them. At the sampling sites, ploughing layer (that is, at a depth of 0 - 20 cm) was sampled with stainless steel trowel. The samples were air-dried in the laboratory for two weeks before been pulverized, using a ceramic pestle and mortar, then sieved through a 2 mm mesh plastic sieve. After which, it was dried to constant mass in an oven at 75°C and kept in a desiccator for further analyses. The metals were determined using Micro – Plasma Atomic Emission Spectroscopy (OMP-AES 4200 Model)

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BCR fractionation of the soil sediments.

Determination of Exchangeable Bound Metals

A 1.00 g of the soil sample was weighed into a 250 cm^3 conical flask and 10.00 $cm^3$of 1.00 mol/dm^3 sodium ethanoate solution was added. The pH was adjusted to 8.7 by the addition of ethanoic acid. The mixture was then shaking for 2 hours using Edmund Bahler Swip Mechanical Shaker and filtered into a 100 cm^3 volumetric flask using Whatman Filter Paper Number 1. The filtrate was then made up to the mark with water. The metals were determined using Atomic Absorption Spectrophotometer (AAS) and the residue was reserved for further fractionation (Ladigbolu et al., 2014 and Hassan et al., 2019).

Determination of Carbonate Bound Metals

The residue from the exchangeable metals was leached for 3 hours with sodium acetate solution and the pH was adjusted to 5.0 using acetic acid. The leachate was transferred into 100 cm^3 volumetric flask and made up to the mark with water. The laechate was analyzed for metals of interest using AAS and the residue was reserved for further analysis (Tessier et al., 1979, Ladigbolu et al., 2014 and Hassan et al., 2019)

Determination of Manganese Oxide Bound Metals

The residue from the carbonate bound soil was leached with 10.00 cm^3 of 0.10 mol/dm^3 hydroxylamine hydrochloride and 0.01 mol/dm^3 Nitric acid (the pH will be adjusted to 2.0 with acetic acid) after shaking for 3 hours using Edmund Balder Swip Mechanical Shaker. The leachate was quantitatively transferred into 10 cm^3 water. The leachate was used to analyze for metals of interest using AAS. The residue was reserved for further analysis (Tessier et al., 1979, Ladigbolu et al., 2014 and Hassan et al., 2019).

Determination of Iron-Manganese Oxide Bound Metals

The residue from the manganese oxide bound soil was extracted using 10.00 cm^3 of oxalate buffer of pH 3.0 after shaking for 12 hours at 90^0C in a water bath. The extract was filtered into a 100 cm^3 volumetric flask and water will then be added to the mark. The extract was then analyzed for the metals of interest using AAS. The residue was reserved for further analysis (Tessier et al., 1979, Ladigbolu et al., 2014 and Hassan et al., 2019).

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Determination of Organic Matter-Sulphide Bound Metals

The residue from the iron-manganese oxide bound soil was extracted by shaking it with 100.00 cm^3 of 30.00 % hydrogen peroxide solution. The pH was adjusted to 2.0 by the drop-wise addition of nitric acid and then heated for 6 hours at 90^0C in a water bath. This will be re-extracted at room temperature with 10.00 cm^3 of 1.00 mol/dm^3 ammonium acetate solution and the pH was still maintained at 2.0. After shaking for 3 hours, the first extract of the mixture will be filtered using what-man filter paper Number 1 into a 100 cm^3 volumetric flask and water will be added to mark. The extract will then be analyzed for all the metals using AAS and the residue was reserved for further analysis (Tessier et al., 1979, Ladigbolu et al., 2014 and Hassan et al., 2019).

Determination of Residual Metals

The residue from the Organic and sulphide bounded soil was digested with 10.00 cm^3 of agua-regia while heating in a digesting tube at a temperature of 250 ^0C. The clear digest was removed and allowed to cool then quantitatively transferred into a 100 cm^3 volumetric flask. This was made up to the mark with water and the solution was used to analyze for metals of interest (Tessier et al., 1979, Ladigbolu et al., 2014 and Hassan et al., 2019).

Results and Discussion.

Levels of heavy metal concentration in the soil.

The levels of heavy metal composition in the soil sediment taken from from mining areas at Rimi–Zayam with GPRS locations of $9^0$18’18” (active mining area), $9^0$18’36” (abandoned mining area) and $9^0$18’54” (non–mining area), from around Rimi–Zayam, Toro LGA, Bauchi State having been assayed and the data presented in Table 1. All the soil samples considered in this study were found positive for all the heavy metals analyzed, except for Cadmium and Copper which were observed to be below detection limit (BDL) in all the locations.

Table 1. Levels of the heavy metal concentrations present in the soil sediment sampled from the mining areas around Rimi–Zayam, Toro LGA, Bauchi State of Nigeria, West Africa.

Location	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Active mining site	BDL	0.73	BDL	168.91	1.25	0.92	BDL	6.58
Abandoned mining site	BDL	0.71	BDL	119.51	1.63	10.72	BDL	5.99
Non– mining areas	BDL	0.75	BDL	185.26	2.51	1.47	0.15	4.69

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The levels of Cadmium and Copper were found to be completely below detection limit in all the locations sampled. Which was contrary to reports made by Sanusi et al, (2017) of a mean concentration of Cd at 20.70 mg/kg in Nahuta China and 12.62 mg/kg in Sabon Target, both at Yelu, Alkaleri Local Government Area, Bauchi State. Far exceeding the WHO 2008 maximum permissible limit for cadmium at 0.35 mg/kg.

The mean levels of lead in the soil sediments were below detection limit at location active mining and abandoned mining sites, but found to be 0.15 mg/kg, for soil sediment in the non–mining area. This level of lead obtained in the soil sediment collected from the non – mining area is noted to be much lower than ranging reported by Sanusi et al., (2017) of 65 mg/kg - 658mg/kg, and even more than the 1162 mg/kg reported by Ezeh and Chukwu, (2011) in soils from South East Nigeria.

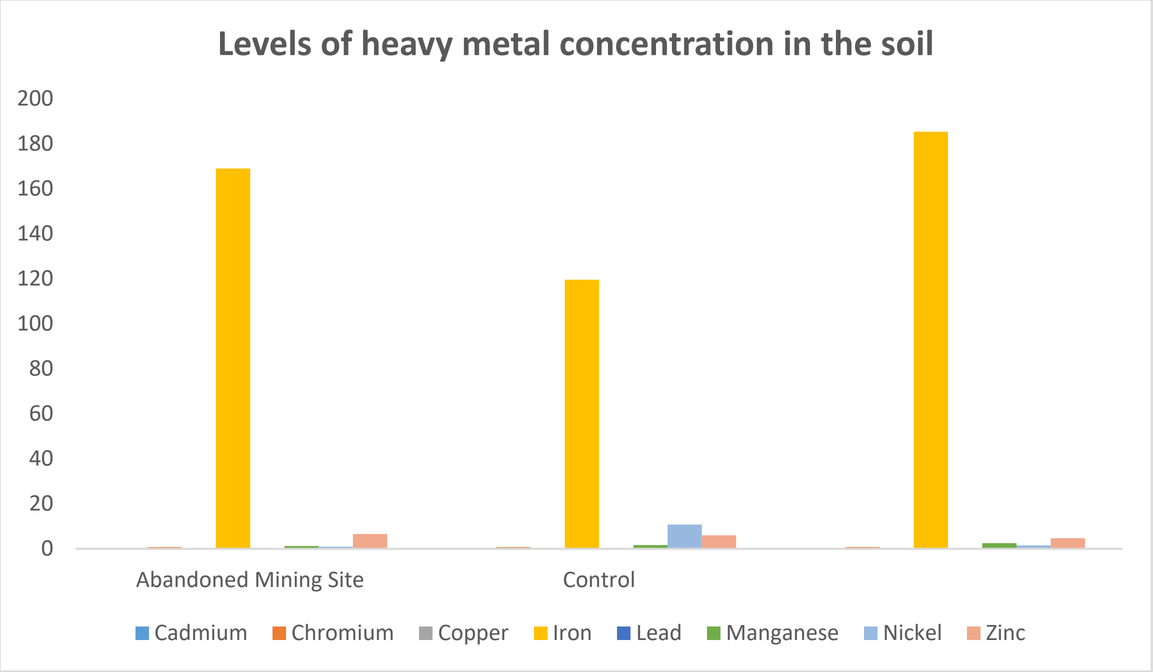

Figure 1. Levels of the heavy metal concentrations present in the soil sediment sampled from the mining areas around Rimi–Zayam, Toro LGA, Bauchi State.

The concentration of chromium in soil samples taken from the active mining, abandoned mining sites and non–mining area were found to 0.73, 0.71 and 0.75 mg/Kg, respectively. These levels as obtained are observed to be far less than the safe limit and of 100 mg/kg recommended value for agricultural soil as reported by Sharma et al. (2008)

The concentration of iron in soil samples taken from the active mining, abandoned mining sites and non–mining area were found to 168.91, 119.51 and 185.26 mg/Kg, respectively. These levels as obtained are observed to be far less than the safe limit. The outcome of the analysis done on the soil sediments clearly indicated that the all the samples are enriched with elevated concentrations of iron, are attributed to the ferrilitic nature of the soil, which is characteristic of the land in the tropics, and as such was used as the reference metal in subsequent data analysis.

Fractionation pattern of the BCR speciation of heavy metals present in the soil sediments sampled from the mining areas around Rimi–Zayam, Toro LGA, Bauchi State.

The BCR extraction of the heavy metals present in the soil sediment sampled from the mining areas around Rimi–Zayam, Toro LGA, Bauchi State where profiled into Exchangeable, Carbonate, Manganese, Iron–Manganese, Organic–Sulfide and Residual bound fractions.

Cadmium

Generally, it shows that Cadmium were mostly distributed between the Manganese and Organic/ Sulphide bound fractions, while sparsely in the others.At the abandoned mining site,

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the speciation pattern of cadmium in the soil sediment shows that it was mainly distributed in the order of: manganese > organic/sulfide > iron–manganese > residual > exchangeable bound fractions. This fractionation profile shows that cadmium was mostly bounded to the Manganese fraction, followed by the organic/sulphide fractions, while been equally distributed amongst the residual, iron–manganese and exchangeable bound fractions. At the active mining site, the speciation pattern of cadmium in the soil sediment that it was mainly distributed in the order of: manganese > organic/sulphide > iron–manganese > exchangeable > residual bound fractions. This fractionation profile shows that cadmium was bounded to the manganese fraction, followed by the organic/sulphide fractions, while been equally distributed amongst the exchangeable and iron–manganese fractions and least in the residual fraction. At the non–mining Area, the speciation pattern of cadmium in the soil sediment that it was mainly distributed in the order of: manganese > organic/sulphide > exchangeable > residual > iron–manganese bound fractions. This fractionation profile shows that cadmium was mostly bounded in equal proportions to the manganese and organic/sulphide fractions and also with significant and equal contributions the exchangeable and residual fractions and least in the iron–manganese fraction.

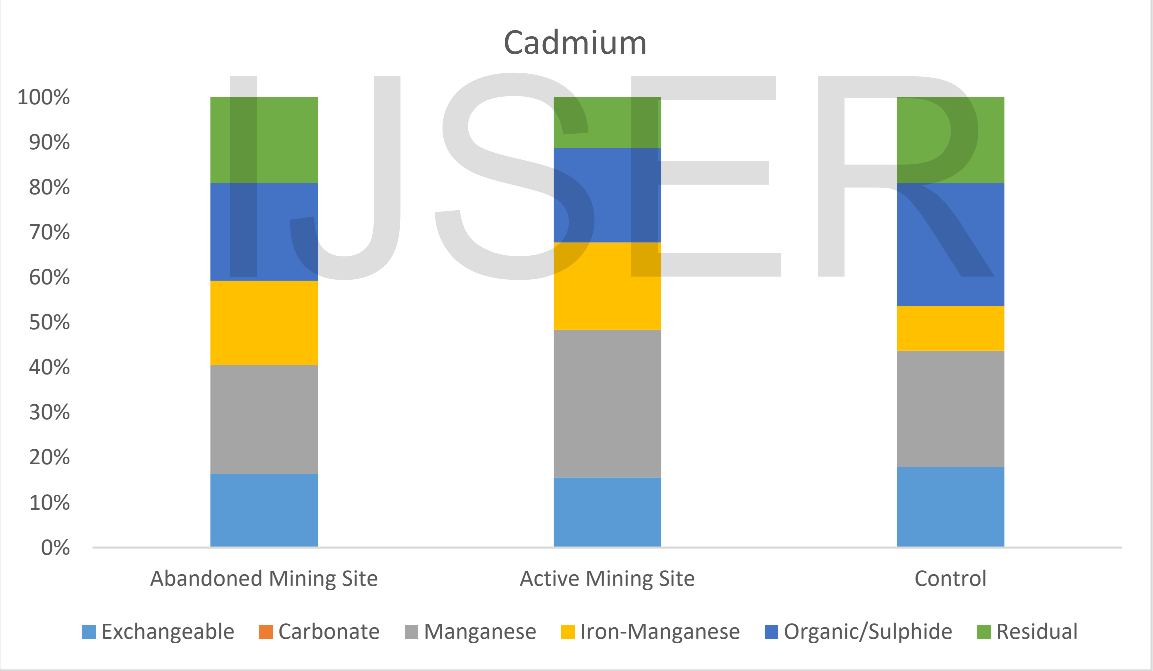

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Figure 2. Fractionation pattern of Cadmium present in soil sediments sampled from the mining areas around Rimi–Zayam, Toro LGA, Bauchi State.

Chromium

Generally, it shows that Chromium were mostly distributed between the Residual, Iron–Manganese and Organic/ Sulphide bound fractions, while sparsely or completely below detection limit in the others.

At the abandoned mining site, the speciation pattern of chromium in the soil sediment that it was mainly distributed in the order of: residual > iron‒manganese > organic/sulphide > exchangeable > manganese bound fractions. This fractionation profile shows that Lead was mostly bound to the residual fraction, followed closely by the iron‒manganese bound fractions and then the organic/sulphide fractions, while equally distributed amongst the exchangeable>manganese and completely absent in the carbonate fraction. At the active mining site, the speciation pattern of chromium in the soil sediment that it was mainly distributed in the order of: iron‒manganese > residual > organic/sulphide > manganese > exchangeable bound fractions. This fractionation profile shows that lead was mostly bound to the iron‒manganese fractions, equally amongst the organic/sulphide and residual followed by the manganese fractions and least in the exchangeable fraction. At the non‒mining Area, the speciation pattern of chromium in the soil sediment that it was mainly distributed in the order of: iron‒manganese > residua l> manganese > exchangeable > organic/sulphide > carbonate bound fractions. This fractionation profile shows that Lead was mostly bound to the iron‒manganese fractions, equally distributed amongst the residual, manganese and exchangeable fractions, followed by it distribution in the organic/sulfide and least in the Iron‒Manganese fraction.

Generally, it shows that Copper were mostly distributed between the Iron ‒ Manganese, Manganese and Carbonate bound fractions, while sparsely or completely below detection limit in the others.

At the abandoned mining site, the speciation pattern of copper in the soil sediment shows that it was mainly distributed in the order of: iron‒manganese > manganese > carbonate > exchangeable > organic/sulfide bound fractions. This fractionation profile revealed that copper was mostly bound to the iron‒manganese bound fractions, followed by its substantiate distribution in the manganese and carbonate fractions respectively, least in the exchangeable bound fraction and very negligible in the organic/sulfide bound fractions. At the active mining site, the speciation pattern of copper in the soil sediment shows it was mainly distributed in the order of: iron‒manganese > carbonate > manganese > residual > exchangeable bound fractions. This fractionation profile shows that copper was mostly and equally bounded to the iron‒manganese and carbonate bound fractions followed by their distribution in the manganese bound fractions then amongst the residual bound fraction and least in the exchangeable fraction. At the non‒mining Area, the speciation pattern of copper in the soil sediment that it was mainly distributed in the order of: iron‒manganese > manganese > exchangeable > carbonate > organic/ sulfide bound fractions. This fractionation profile shows that lead was mostly bound to the iron‒manganese fractions, followed by it distribution in the manganese fraction, then the exchangeable, next significant the residual fractions and least in the Organic/Sulphide fraction.

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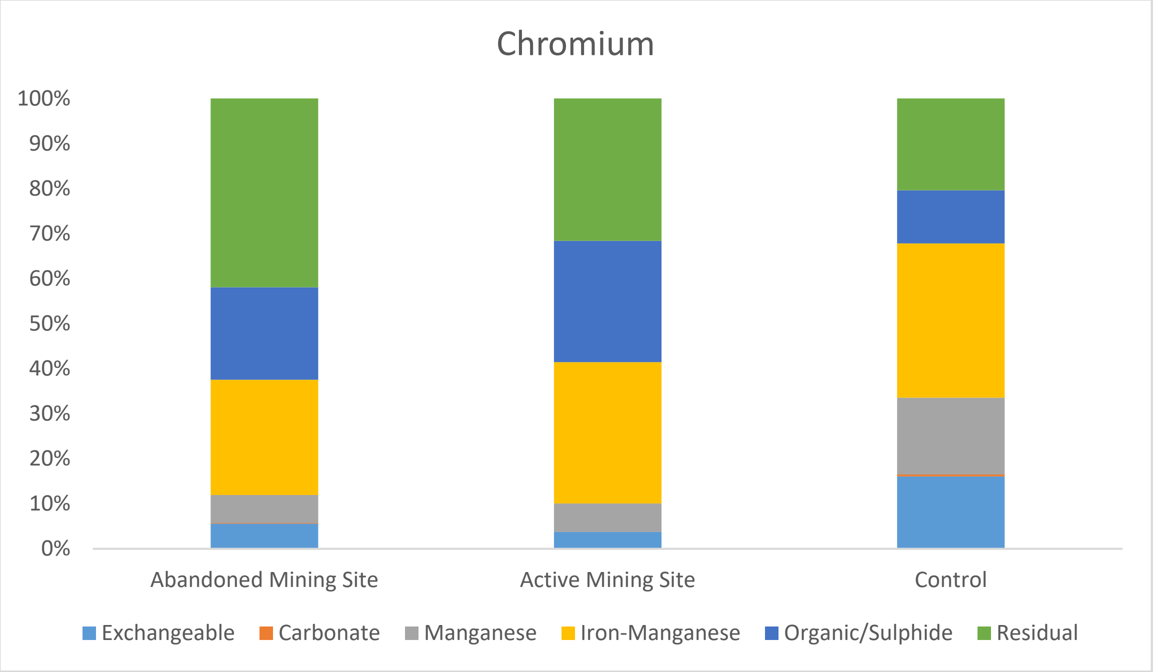

Figure 3. Fractionation pattern of chromium present in soil sediments sampled from the mining areas around Rimi–Zayam, Toro LGA, Bauchi State

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Copper

Generally, it shows that Copper were mostly distributed between the Iron – Manganese, Manganese and Carbonate bound fractions, while sparsely or completely below detection limit in the others.At the abandoned mining site, the speciation pattern of copper in the soil sediment shows that it was mainly distributed in the order of: iron–manganese > manganese > carbonate > exchangeable > organic/sulfide bound fractions. This fractionation profile revealed that copper was mostly bound to the iron–manganese bound fractions, followed by its substantiate distribution in the manganese and carbonate fractions respectively, least in the exchangeable bound fraction and very negligible in the organic/sulfide bound fractions.At the active mining site, the speciation pattern of copper in the soil sediment shows it was mainly distributed in the order of: iron–manganese > carbonate > manganese > residual > exchangeable bound fractions. This fractionation profile shows that copper was mostly and equally bounded to the iron–manganese and carbonate bound fractions followed by their distribution in the manganese bound fractions then amongst the residual bound fraction and least in the exchangeable fraction. At the non–mining area, the speciation pattern of copper in the soil sediment that it was mainly distributed in the order of: iron–manganese > manganese > exchangeable > carbonate > organic/sulfide bound fractions. This fractionation profile shows that lead was mostly bound to the iron–manganese fractions, followed by it distribution in the manganese fraction, then the exchangeable, next significant the residual fractions and least in the Organic/Sulphide fraction.

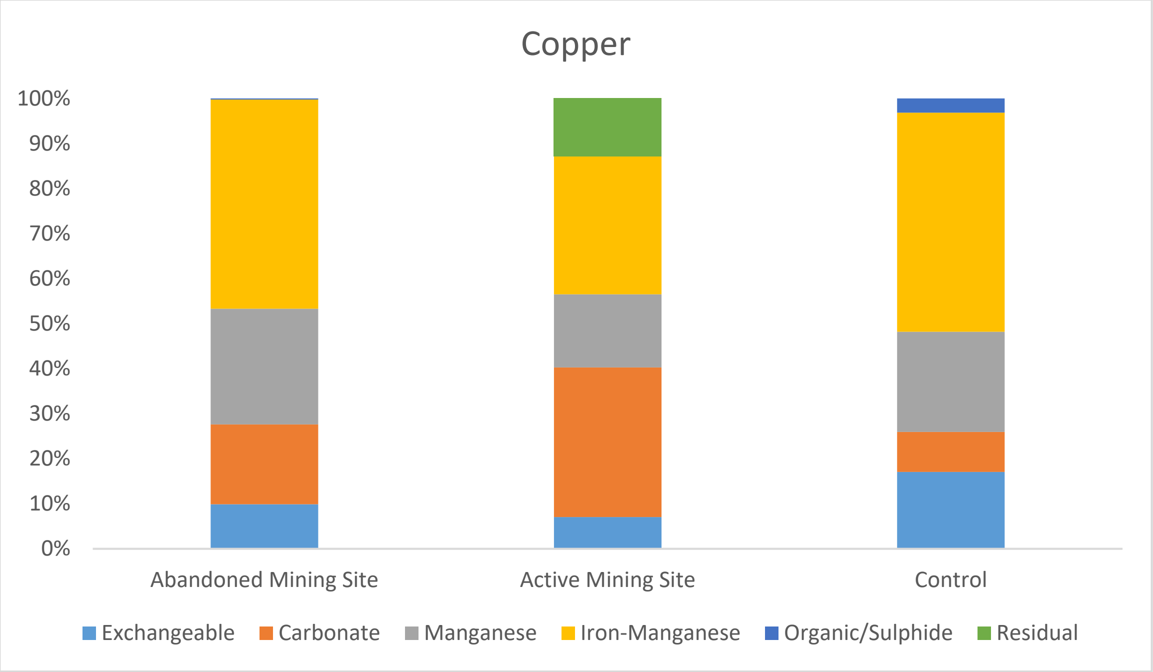

Figure 4. Fractionation pattern of copper present in soil sediments sampled from the mining areas around Rimi–Zayam, Toro LGA, Bauchi State

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Iron

Generally, it shows that Iron were mostly distributed between the residual iron–manganese and organic/ sulphide bound fractions, while sparsely or completely below detection limit in the others.

At the abandoned mining site, the speciation pattern of iron in the soil sediment shows that it was mainly distributed in the order of: residual > iron–manganese > organic/sulfide bound fractions. This fractionation profile shows that iron was in most part bounded to the residual fraction, with contribution from the iron–manganese and organic/sulfide fractions, while thinly distributed amongst the manganese bound fraction. At the active mining site, the speciation pattern of iron in the soil sediment shows that it was mainly distributed in the order of: residual > organic/sulphide > iron–manganese > manganese bound fractions. This fractionation profile shows that iron was mostly bounded to the Residual fractions, with contributions by the organic/sulfide and well as the iron–manganese fractions and least in the manganese fraction. At the non–mining area, the speciation pattern of iron in the soil sediment that it was mainly distributed in the order of: exchangeable > residual > organic/sulphide > carbonate bound fractions. This fractionation profile shows that iron was mostly bound to the exchangeable fraction, followed by it distribution in residual fraction, then the organic/sulfide bound fractions and least in the carbonate fraction, without any presence in the iron–manganese and manganese bound fractions.

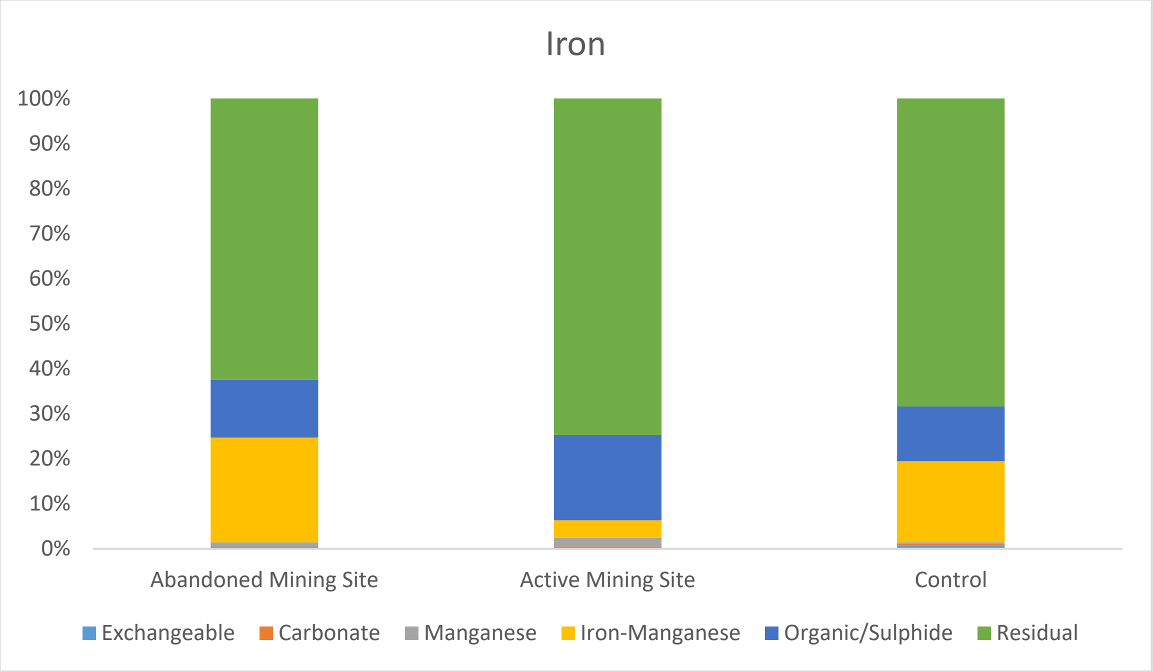

Figure 5. Fractionation pattern of iron present in soil sediments sampled from the mining areas around Rimi–Zayam, Toro LGA, Bauchi State

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Lead

Generally, it shows that lead was mostly distributed between the manganese and exchangeable bound fractions, sparsely, in the carbonate and organic/sulphide bound fraction and completely below detection limit in the residual bound fraction.

At the abandoned mining site, the speciation pattern of lead in the soil sediment that it was mainly distributed in the order of: exchangeable > manganese > iron–manganese > carbonate > organic/sulfide bound fractions. This fractionation profile shows that Lead was equally bounded to both the manganese and exchangeable fractions, with also equal contributions from the iron–manganese and carbonate fractions, while least distributed amongst the organic/sulphide fractions. At the active mining site, the speciation pattern of lead in the soil sediment that it was mainly distributed in the order of: exchangeable > manganese > iron–manganese > organic/sulphide > carbonate bound fractions. This fractionation profile shows that Lead was equally bounded to both the manganese and exchangeable fractions, with equal contributions from the organic/sulphide and iron–manganese while least in the residual fraction. At the non – mining Area, the speciation pattern of Lead in the soil sediment that it was mainly distributed in the order of: manganese > iron–manganese > exchangeable > carbonate > organic/sulfide bound fractions. This fractionation profile shows that Lead was mostly bound to the manganese, distributed in equal proportions in both iron–manganese and exchangeable fractions and also in equal proportions in both the Organic/Sulphide and carbonate fractions.

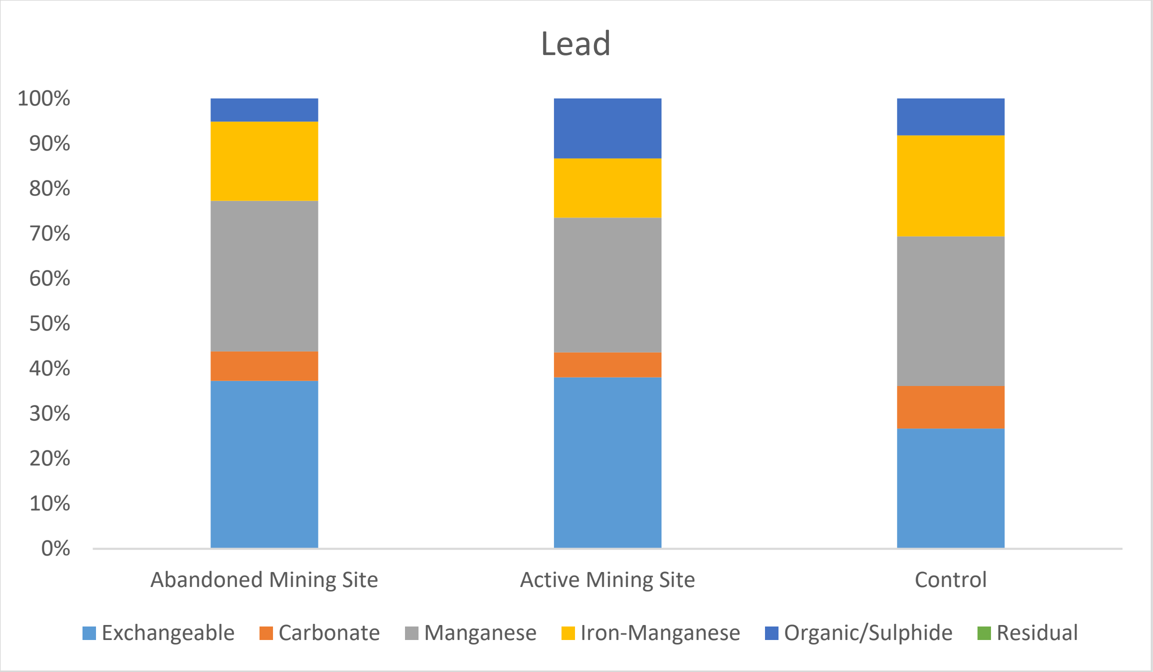

Figure 6. Fractionation pattern of Lead present in soil sediments sampled from the mining areas around Rimi–Zayam, Toro LGA, Bauchi State

Manganese

Generally, it shows that Manganese were mostly distributed between the manganese iron - manganese and residual bound fractions, while sparsely distributed or completely below detection limit in the others.

At the abandoned mining site, the speciation pattern of manganese in the soil sediment shows it was mainly distributed in the order of: manganese > iron–manganese > residual > organic/ sulphide > carbonate > exchangeable bound fractions. This fractionation profile shows that manganese was mostly bound to the manganese bound fractions, followed by the iron–manganese bound fraction then the residual fraction, followed by the organic/ sulfide fractions and insignificantly in the carbonate and exchangeable bound fractions. At the active mining site, the speciation pattern of manganese in the soil sediment that it was mainly distributed in the order of: manganese > residual > iron–manganese > Carbonate > exchangeable > organic/sulfide bound fractions. This fractionation profile shows that manganese was also mostly bounded to the manganese, then its distribution into the residual fractions, then the iron–manganese fractions, carbonates, the exchangeable and insignificantly in the organic/sulphide fraction. At the non–mining area, the speciation pattern of manganese in the soil sediment shows that it was mainly distributed in the order of: manganese > iron–manganese > residual > organic/sulphide > carbonate bound fractions. This fractionation profile shows that manganese was mostly bound to the manganese, with significant contribution in the iron–manganese fraction, then the residual fractions, least in the Organic/ Sulfide fraction and insignificantly in the Carbonate bound fraction.

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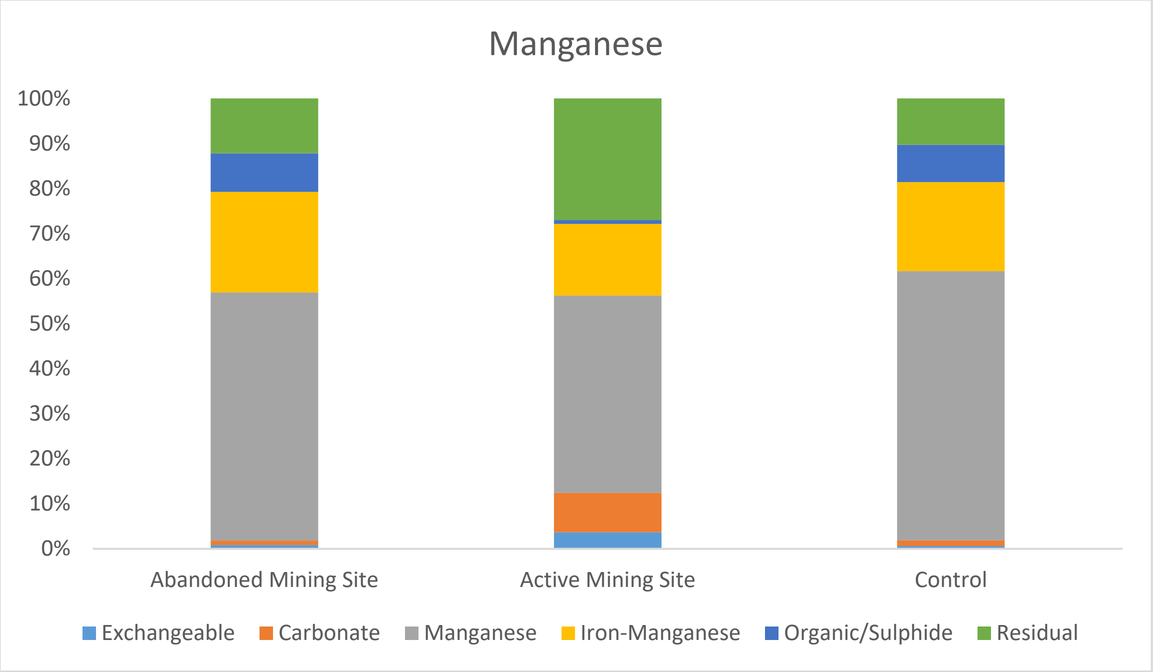

Figure 7. Fractionation pattern of manganese present in soil sediments sampled from the mining areas around Rimi–Zayam, Toro LGA, Bauchi State

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Nickel

Generally, it shows that nickel was mostly distributed between the residual, exchangeable and organic/sulphide bound fractions, while sparsely or completely below detection limit in the others.

At the abandoned mining site, the speciation pattern of nickel in the soil sediment shows that it was mainly distributed in the order of: residual > iron–manganese > organic/sulfide bound fractions. This fractionation profile shows that nickel was mostly bound to the residual bound fractions, with considerable contributions from both the iron–manganese and organic/sulphide fractions, while negligible in the other fractions. At the active mining site, the speciation pattern of nickel in the soil sediment shows that it was mainly distributed in the order of: residual > organic/sulfide bound fractions. This fractionation profile shows that nickel was mostly bound to the residual fractions, with contribution from the organic/sulphide bound fraction. At the non–mining area, the speciation pattern of nickel in the soil sediment shows it was solely distributed in the exchangeable bound fractions.

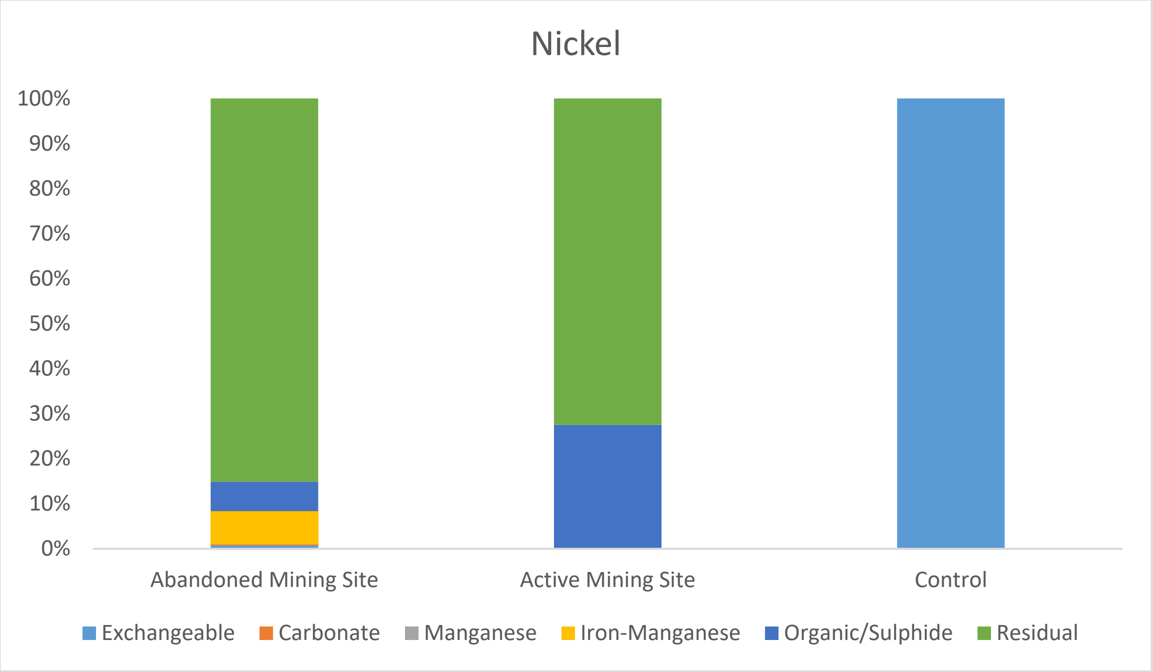

Figure 8. Fractionation pattern of nickel present in soil sediments sampled from the mining areas around Rimi–Zayam, Toro LGA, Bauchi State

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Zinc

Generally, it shows that zinc was mostly distributed in the exchangeable, manganese and organic/sulphide bound fractions, while completely below detection limit in the others.
At the Abandoned Mining Site and non–mining area the speciation of zinc was solely distributed in the exchangeable fractions.
At the active mining site, the speciation pattern of zinc in the soil sediment that it was mainly distributed in the order of: manganese > exchangeable > organic/sulfide bound fractions. This fractionation profile shows that zinc was mostly bound to the manganese bound fraction followed by the exchangeable fractions and least in the organic/sulphide fraction, while completely below detection limit in the others.

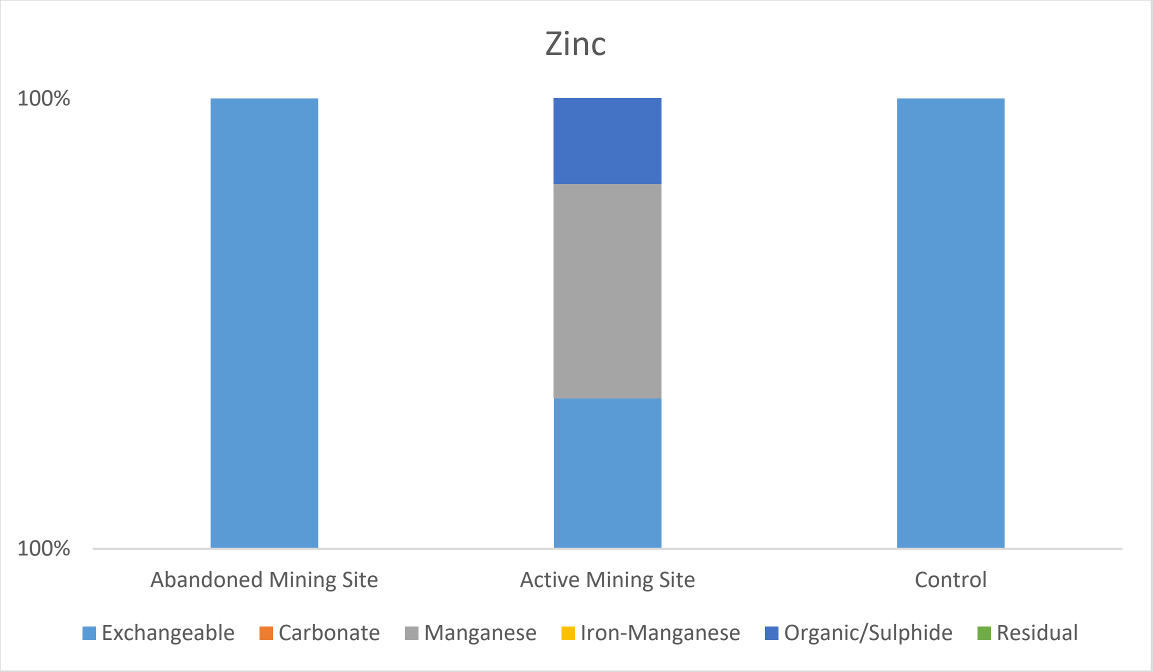

Figure 9. Fractionation pattern of Zinc present in soil sediments sampled from the mining areas around Rimi–Zayam, Toro LGA, Bauchi State

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Effect of the physico–chemical properties of the soil sediments on the bioavailability of heavy metals

Effect of Soil texture

Generally, Acosta et al. (2009) have established that the accumulation of metals in soils increases with the decreasing particle size, hence soil texture rich in clay fraction or organic matter have higher contents of trace elements than sandy horizons, and vice visa. This is based on the template that metals accumulate in fine-particle size fraction of soils due to high surface areas and negative charges associated with clay minerals and humic substances. Kabata–Pendias (1993) have been cited to observe that copper and chromium are present in higher concentrations in the topsoil than in the parent material while nickel tends to be more concentrated in minerals from the parent material than they appear in the surface horizon of soil, thus explaining the higher mobility of copper and chromium under chemical weathering. In all these, the main factors controlling the behaviour of trace metals in soils are organic matter content, iron and manganese hydroxides and redox potential. Metals fixed by Al, Fe and Mn hydrous oxides and other crystalline solid components are hardly mobile

Effect of pH

The physico–chemical properties of pH measured for the soil sediments taken from the study areas were relatively low within the ranges of 6.04–6.45. This variation in these values of the soil pH of the three areas could be attributed to the nature of the soils especially as it related to the bioavailability. Alkorta., et al, (2004) had observed that soil pH is considered one of the most important factors determining the concentration of metals in the soil solution, their mobility and hence, bioavailability. The increase of hydrogen ion concentration is noted to affect the mobilisation intensity of heavy metals. Hence, in highly acidic soils, the mobility of metallic elements is much higher than in soils with neutral and alkaline reaction. Generalizing Vamerali et al., (2010), stated that mobility of metals in soils with low pH decreases is in the order of: Cd > Ni > Zn > Mn > Cu > Pb. But also, noted that the effect of pH on the mobility of metallic elements in the soil is highly variable and dependent on the content and type of organic matter. Alkorta et al, (2004), also noted that just as anthropogenic factors, are linked with heavy metal introduction into the soils, so too it is with soil pH to their bioavailability.

Effect of Organic matter

The physico‒chemical properties of organic matter measured for the soil sediments taken from the study areas were reasonable high within the ranges of 0.729‒0.844. Generalizing, Organic matter is known to immobilize heavy metals, and under prevailing oxidizing conditions are induced to effect their release. Khalilova and Mammadov, (2007) have pointed out that some components in the organic matter are capable of acting as ligands to these many metal ions. Hence, might retain or facilitate their transport along the soil profile, which is a significant factor that affect their mobility. According to Isayev et al., (2007) Low content of organic matter in the soil is responsible for low cation exchange capacity, low buffering properties of soils, low water capacity and susceptibility to erosion, and it reduces microbial activity. Ociepa et al., (2010) had noted that land rich in organic matter actively retains metallic elements, since the sorption capacity of organic matter is well above the mineral sorption capacity of the soil.

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Conclusion.

The modified BCR speciation pattern shows that the heavy metals where present and spatially distributed across the six (6) fractions to various degrees. Generalizing, the recorded high abundance of heavy metals such as cadmium, chromium, copper, iron, Lead, Nickel and Zinc where noted to be mainly bounded to the Residual fraction, pointing to their Lithogenic origins and thus implying that they are primarily inherited from the parent material. Cobalt and Manganese being more abundantly speciated in the other fractions points to their anthropogenic origin, and their dispensation to being bioavailable and their tendency to be labile and mobile.

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