Identification of Sources of Acidic Mine Drainage produced by Oxidation of $CuFeS_2$ due to copper mining activity using Energy Dispersive X-ray and K-means clustering.

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Abstract:

Rock mass is extracted from its initial location in the lithosphere as a result of mining activities. This activity results in Acidic Mine Drainage (AMD), which is produced due to oxidation of Pyrite bearing rock mass upon exposure to environmental influences such as air, water, and microorganisms. AMD is a source of heavy metals because of its high solubility and acidic nature. This metal-rich discharge travels to surrounding places through numerous drainage channels. In order to evaluate the pollution, this study measured the metal content of 10 sample locations. Energy dispersive X-ray was used to evaluate the samples for Copper (Cu), Manganese (Mn), Chromium (Cr), Cobalt (Co), Zinc (Zn) and Nickel (Ni). The correlation analysis of contamination level indicated the Copper in samples was highest and varied inversely with distance from the source. The correlation study also showed that the replacement of Manganese by Copper in the samples can occurs in presence of AMD. Two significant clusters in the dataset were found using K-means clustering. The samples were successfully divided into sources of AMD using the K-means clustering technique. Tailing Storage Facility and Mine Waste Dumps were found to be the research area's prospective AMD sites. Polluted areas were located close to mine waste dumps and tailing storage facilities, according to copper mapping. This research exposes and assesses the contamination brought on by acid mine drainage as a result of mining operations.

Keywords: Leaching, Sediment Contamination, Soil Contamination, Enrichment Factor, Contamination Factor, Pollution Load Index, Acid Mine Drainage

1. Introduction

Heavy metal pollution in soils and sediments is a common and important issue connected with mining. Mining operations such as blasting, drilling, and processing generate vast amounts of waste rock and tailings containing heavy metals. These pollutants can spread to neighboring soils when exposed to wind and rain (Kabata-Pendias, 2000)**.**

When sulfide minerals, particularly pyrite, which is typically found in mine waste, are exposed to oxygen and water, a sequence of chemical reactions occur, resulting in the creation of sulfuric acid and the liberation of heavy metals. The resulting sulfide-rich AMD has a low pH and high sulfate and heavy metal contents (Johnson & Hallberg, 2005).

When this AMD infiltrates the soil/sediments, it has the potential to significantly affect soil properties such as pH, organic matter concentration, and microbial activity. High acidity can cause nutrient leaching, diminishing soil productivity, and heavy metals can be harmful to many types of life (Gray, 1997).

A study to explore heavy metal contamination in agricultural soils of copper mining sites in Singhbhum shear zone, India, discovered elevated concentrations of heavy metals such as copper, manganese, zinc, and others. Copper, manganese, and zinc concentrations ranged from 54.3 to 3314.4 mg/kg, 111.7 to 1045.0 mg/kg, and 52.9 to 621.4 mg/kg, respectively. For almost all metals, the metal concentrations in the soil samples exceeded the average shale levels (Giri et al., 2017).

1.1. Stage of Pyrite (FeS_2) oxidation

The oxidation of pyrite involves a series of complex reactions in steps mentioned as follows:

a) Pyrite Oxidation:

This reaction is caused by the exposure of pyrite to oxygen and water, producing ferrous iron and sulfuric acid.

$$FeS_2(s) + 3.75O_2(g) + 3.5H_2O(l) \rightarrow Fe^{2+}(aq) + 2(SO_4)^{2-}(aq) + 4H^+(aq) \quad (1)$$

(Akcil & Koldas, 2006; Iakovleva et al., 2015; Moyo et al., 2023; Qureshi et al., 2016)

This reaction is exothermic and proceeds spontaneously in nature when pyrite is exposed to atmospheric oxygen and water (Blodau, 2006; Dugan, 1987; Mack et al., 2010; Singer & Stumm, 1970)

b) Ferrous Iron Oxidation:

Ferrous iron (Fe2+) is then further oxidized to ferric iron (Fe3+) in the presence of oxygen, generating more acidity. Bacteria, in particular Acidithiobacillus ferrooxidans, oxidize the ferrous iron (Fe2+) produced in the initial process to create ferric iron (Fe3+), which can then oxidize further pyrite. The reaction rate is greatly accelerated by this bacterial action, especially in acidic environments (Arrieta & Grez, 1971; Silverman & Ehrlich, 1964).

$$4Fe^{2+}(aq) + O_2(g) + 4H^+(aq) \rightarrow 4Fe^{3+}(aq) + 2H_2O(l) \quad (2)$$
(Akcil & Koldas, 2006)

c) Ferric Iron Hydrolysis:

The ferric iron produced reacts with water, creating iron hydroxides, commonly referred to as "yellow-boy," which precipitate out and coat stream beds, and additional acidity.

$$Fe^{3+}(aq) + 3H_2O(l) \rightarrow Fe(OH)_3(s) + 3H^+(aq) \quad (3)$$
(Blowes et al., 2003)

Moreover, the sulfuric acid produced through these reactions can dissolve other heavy metals found within the mine rock, such as copper (Cu), lead (Pb), and zinc (Zn), leading to high concentrations of dissolved metals in the acidic drainage (Blowes et al., 2003).

These reactions are all exothermic, meaning they release heat, which can further enhance the reaction rates and promote the formation of AMD (Blowes et al., 2003).

1.2. Study Area

The study area is an open-pit copper mine in the Indian state of Madhya Pradesh, in Central India. It is India's largest copper deposit. (Shukla et al., 2018). The project contains an open cast copper mine and an ore concentration/beneficiation plant with their waste disposal sites named as mines waste dump (MWD) and tailing storage facility (TSF)/tailing dam (TD) respectively, as shown in Google® Earth Pro™ image. (Figure 1). The principal ore mined is chalcopyrite ($CuFeS_2$) with 1.0% copper content (Tiwari et al., 2017). The length of the pit is 2.2 km in strike direction with an average width of 500 m. The study area lies between longitude 80.656717^0 E & 80.760728^0 E and latitude 21.940692^0 N to 22.083680^0 N. (Figure 2)

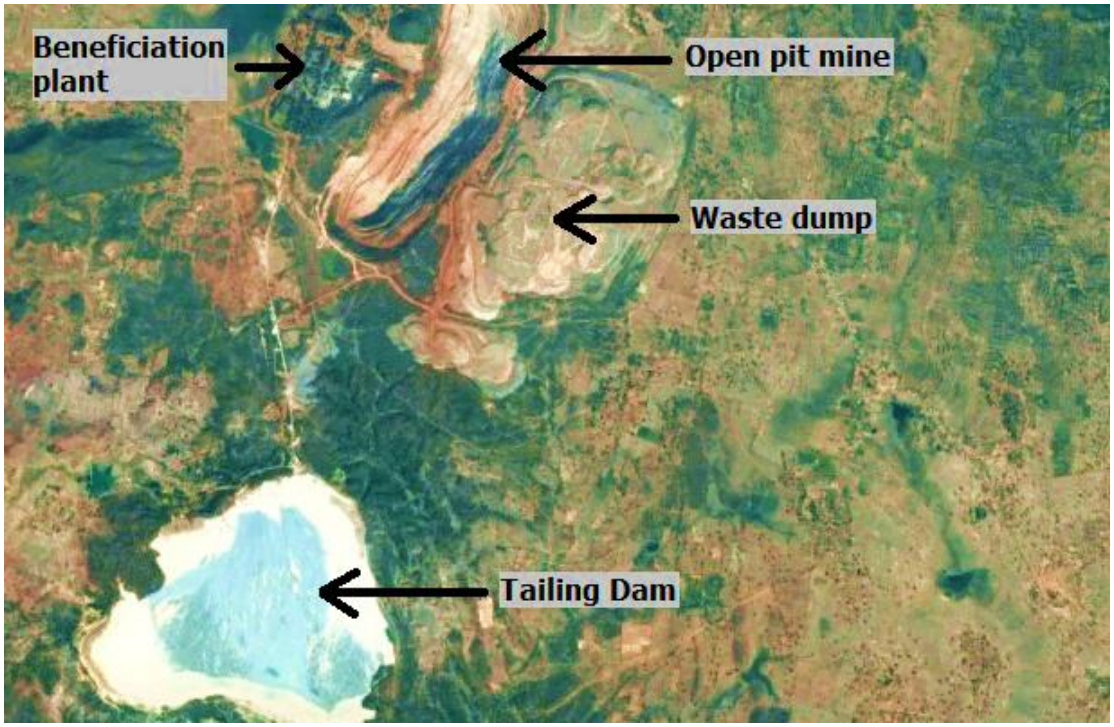

Figure 1: Study Area (Courtesy: Google Earth)

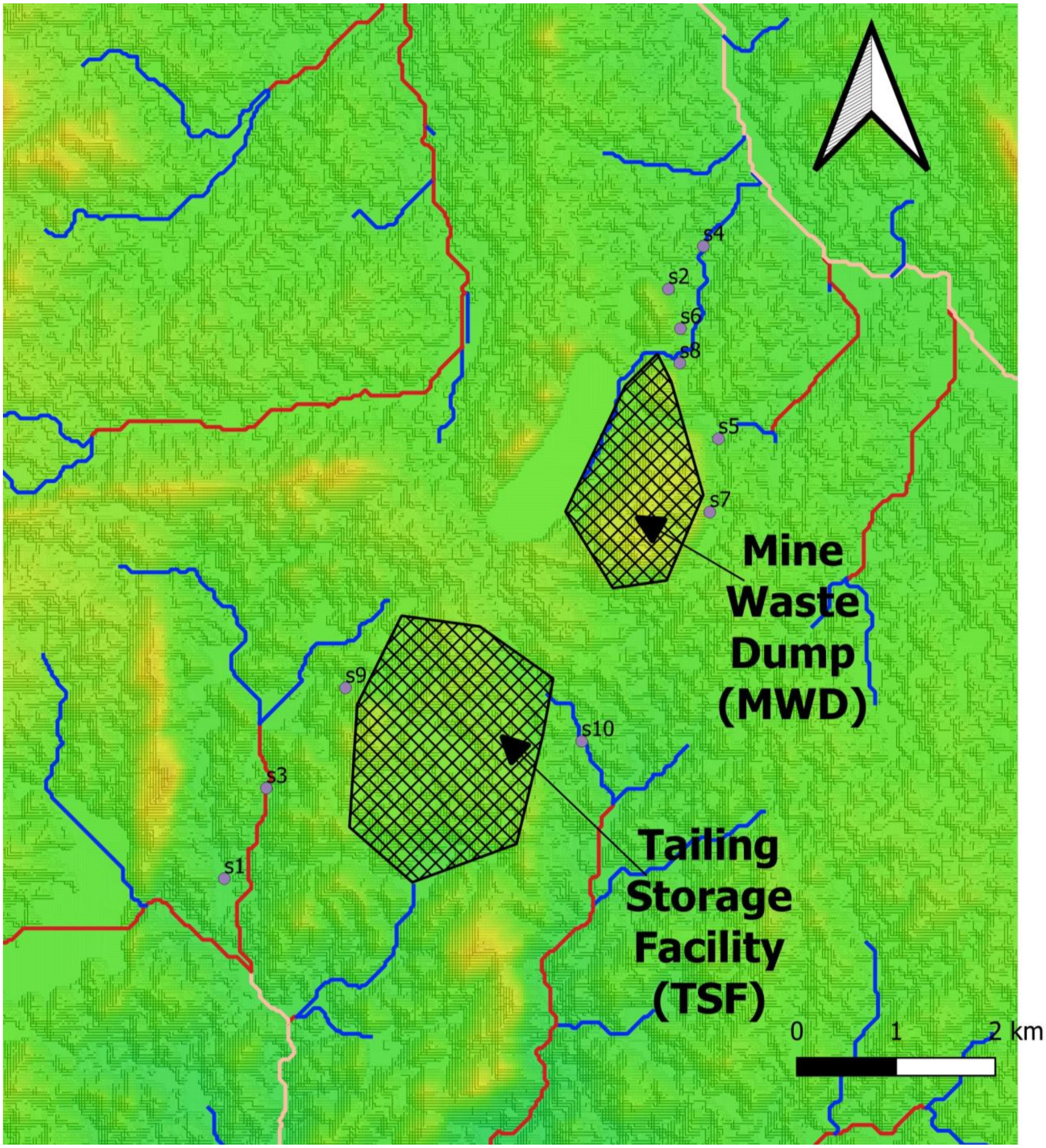

Figure 2: SRTM digital elevation model clipped to study area and drainage channels

Field visits were made to collect photographs near the copper mining project. The photographs showed green and brown colored precipitates covering soil surfaces (Figure 3 (a) – (d)). This green and brown colored precipitate was suspected to be due the oxidation states of Copper and Iron.

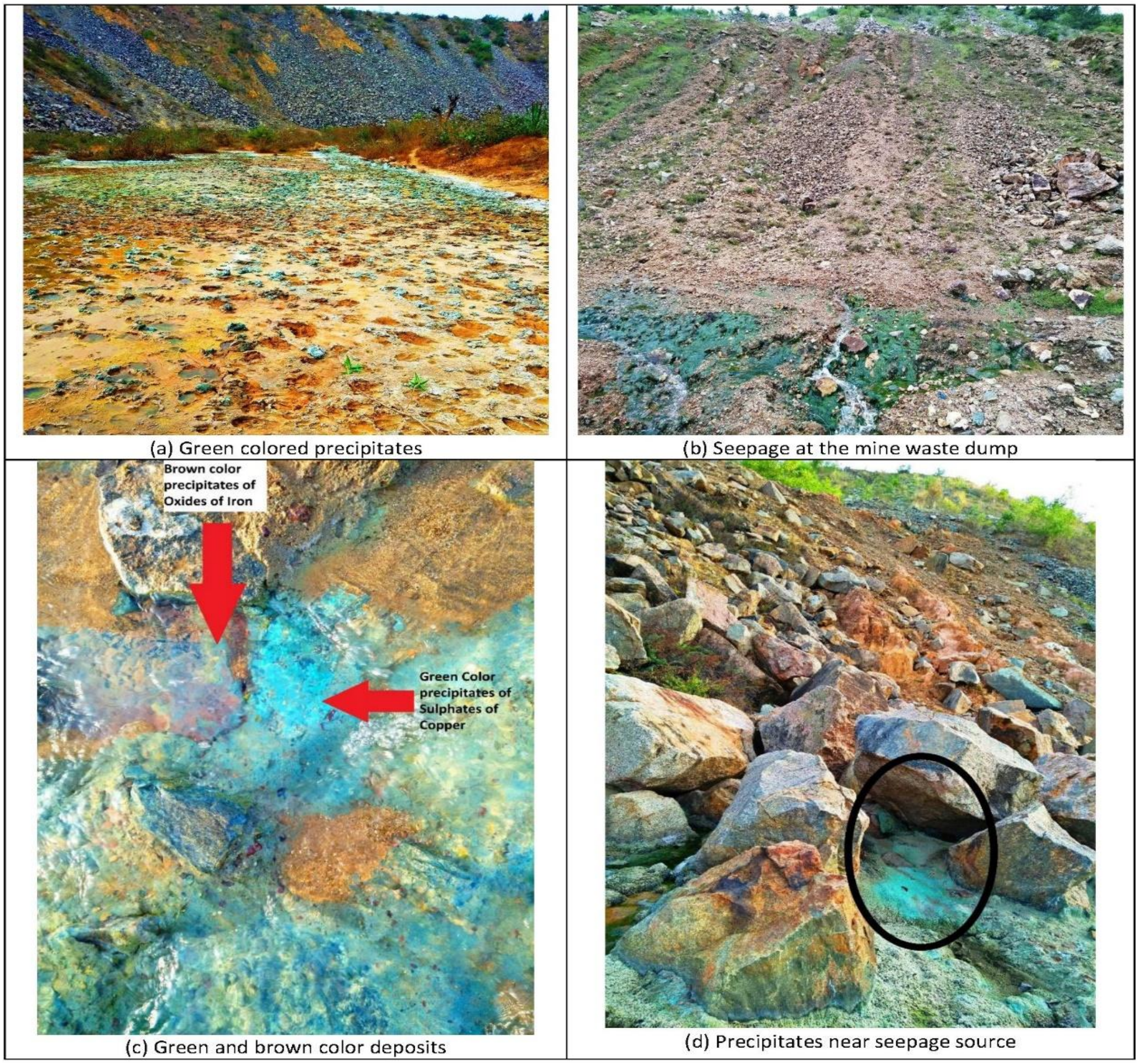

Figure 3: (a) to (d) Affected area with green colored deposits over soil surface adjoining a mine waste dump

2. Materials and Methods

2.1. Sample Collection and Analysis

The digital elevation model (DEM) was prepared from SRTM rasters (N21E080.SRTMGL1.hgt & N22E080.SRTMGL1.hgt) acquired from "Earthdata" web portal of NASA. The DEM and Drainage map was prepared using QGIS software LTR 3.10(QGIS Development Team, 2019). The sample locations were set based on the drainage map of the study area. The sample stations were positioned along the principal flow and deposition pathways. A total of 10 samples were collected in duplicate at a depth of 10 cm. In order to avoid contamination, the collection was done in duplicate with a separate plastic scrape and placed in a pre-labeled polyethylene Ziploc sampling bag. At each of the sample sites GPS coordinates were recorded. Pebbles, rock - chips and botanical bits were separated from the sample mass. The samples were processed in the following order: grinding was done using agate mortar, pulverized, and forwarded through 200 mesh sieves, and were kept in polyethylene bottles pre-washed using nitric acid and distilled water (3:1). Every sample was dried at 108^0 C to constant weight.

After all the samples had been dried, each sample was then subjected to SEM/EDX analysis using a ZEISS EVO Series Scanning Electron Microscope Model EVO 18 and Oxford-Energy Dispersive X-ray system (INCA 250 EDS with X-MAX 20mm Detector). The sample were coated with carbon using a Quorum-SC7620 Sputter Coater before EDX analysis. The samples were analyzed in normalized % weight for 'Cu', 'Cr', 'Mn', 'Co', 'Zn' and 'Ni'.

3. Results and Discussion

3.1. Evaluation of heavy metals in the samples

The heavy metals content (in %) observed in samples collected from mine waste locations in the study area are provided in Table 1.

Table 1: Heavy metals concentration near mine waste locations in the study area

	'Cu'	'Cr'	'Mn'	'Co'	'Zn'	'Ni'
s1	0.04	0.00	0.04	0.16	0.00	0.05
s2	0.88	0.02	0.02	0.05	0.00	0.11
s3	0.06	0.03	0.12	0.00	0.06	0.00
s4	0.18	0.00	0.08	0.02	0.00	0.06
s5	0.54	0.00	0.15	0.08	0.05	0.00
s6	0.42	0.00	0.05	0.06	0.00	0.00
s7	0.04	0.00	0.10	0.08	0.04	0.00
s8	1.50	0.00	0.02	0.03	0.00	0.00
s9	0.17	0.00	0.08	0.05	0.00	0.00
s10	0.10	0.00	0.14	0.19	0.06	0.00
Mean	0.39	0.01	0.08	0.07	0.02	0.02
Minimum	0.04	0.00	0.02	0.00	0.00	0.00
Maximum	1.50	0.03	0.15	0.19	0.06	0.11
Range	1.46	0.03	0.13	0.19	0.06	0.11
1st Quart	0.07	0.00	0.04	0.04	0.00	0.00
Median	0.18	0.00	0.08	0.06	0.00	0.00
3rd Quart	0.51	0.00	0.12	0.08	0.05	0.04
St. Dev	0.47	0.01	0.05	0.06	0.03	0.04

In Table 1, the mean content for heavy metals in the samples collected around the study area were found in order: Cu (0.39) > Mn (0.08) > Co(0.07) > Zn (0.02) = Ni > Cr (0.01). Among the heavy metals under study, Copper had the highest standard deviation indicating variability in the sample due to mining activity. The acidic drainage produced by the oxidation of pyrite can dissolve Copper along with other metals. Since, the study area is a copper mining area with chalcopyrite ($CuFeS_2$) as the main ore, highest mean content and highest standard deviation were observed for Copper. The sample s8 exhibited the highest concentration (Table 1) as this sample site is located closest to waste disposal site with distance of 3 m, on the other hand the sample s1 located about 1.4km from the waste site showed least copper content (Table 2).

Table 2: Samples with distance, elevation and copper content

Sample	Distance (m)	Elevation (m)	Copper content
s8	**3**	**572**	**1.5**
s2	5	566	0.88
s5	9	570	0.54
s7	15	576	0.04
s6	26	571	0.42
s9	553	574	0.17
s4	569	563	0.18
s10	581	561	0.1
s3	750	558	0.06
s1	**1452**	**546**	**0.04**

3.2. Correlation analysis and K-mean clustering

Table 3 shows the Pearson's correlation matrix for all the variables. The element copper showed negative correlation with distance (r = -0.574), which is due to the fact that as the distance from pollution source increases the effect of pollution dissipates. Manganese and Copper exhibit negative correlation (r = -0.544), as manganese gets replaced by copper in the soil matrix due copper rich drainage from mine waste disposal sites.

Table 3: Pearson correlation coefficient matrix

	Cu'	Cr'	Mn'	Co'	Zn'	Ni'	distance	elevation
Cu'	1	-0.005	**-0.544**	-0.330	-0.375	0.141	**-0.574**	0.359
Cr'		1	0.000	**-0.445**	0.279	0.294	0.060	-0.256
Mn'			1	0.218	**0.873**	**-0.524**	0.032	0.039
Co'				1	0.232	-0.055	0.386	-0.407
Zn'					1	-0.482	-0.019	-0.052
Ni'						1	0.121	-0.355
distance							1	**-0.863**
elevation								1

Similarly, other metals such as Cr, Co and Zn showed negative correlation with copper, because of displacement of such metals by copper in samples near the mine site. Since, Zinc and Manganese (r = 0.873) are important soil elements which occur together, therefore both exhibit strong positive correlation. Manganese and Zinc show near zero correlation with distance (r = 0.032 & r = -0.019 respectively) as these metals are commonly present in soil and does not vary significantly by distance. Although useful, the correlation analysis considers pairwise variation of data variables, however correlation analysis needs support from methods which analyze full data set. The K-means clustering analyses the whole dataset at once leading to better understanding of hidden sets in the data.

3.3. K-means clustering of EDX dataset

By performing k-means clustering, we can understand how different sample sites are grouped based on their pollution profiles. This can provide insight into possible sources of pollution (e.g., sites with similar pollution profiles might be influenced by the same source) and how pollutants disperse in the environment. It can also help identify areas of similar pollution levels, which could be useful for environmental planning and management (Shi & Zeng, 2014).

The k-means clustering methods produces different cluster settings, each with different silhouette score. The silhouette score analysis is a technique used to evaluate the quality of clustering results. It provides a measure of how well each data point fits into its assigned cluster and assesses the separation between different clusters. The higher the silhouette the better the clustering. (Everitt et al., 2011; Kaufman & Rousseeuw, 2005) .The silhouette scores are shown in Figure 4.

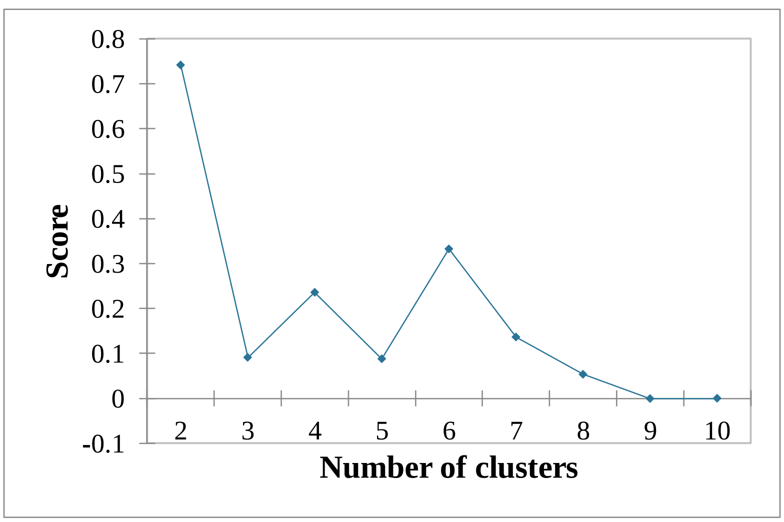

Figure 4: Evolution of the silhouette score with number of clusters

The silhouette score for cluster 2 was the highest hence, two cluster set was most well-defined cluster set. The result of cluster analysis is shown in Table 4.

Table 4: Cluster centroids

Cluster	Cu'	Cr'	Mn'	Co'	Zn'	Ni'	distance	elevation
1	0.110	0.006	0.092	0.084	0.024	0.022	781.000	560.400
2	0.676	0.004	0.068	0.060	0.018	0.022	11.600	571.000

It can be observed that the clusters 1 and 2 have very different copper content. Cluster 2(Cu: 0.676) has nearly 6 times the copper content of cluster 1 (Cu: 0.110). Similarly, the distance variable was significantly different in each cluster (Cluster 1: distance – 781meter & Cluster 2: distance – 11.6 meters). This indicates that copper and distance are differentiating variables and greatly influence the cluster definition. The samples belonging to each cluster are shown in Table 5 .

Table 5: Results by cluster

Cluster	Cluster 1	Cluster 2
Samples	s1	s2
	s3	s5
	s4	s6
	s9	s7
	s10	s8

Cluster 1 contains sample location s1, s3, s4, s9, s10 whereas cluster 2 comprises of sample locations s2, s5, s6, s7 and s8. The reason for cluster 2 samples i.e. s2, s5, s6, s7and s8 exhibiting high copper content is that these sample sites are located in the neighborhood mine waste dump and tailing storage facility and receive direct drainage resulting from oxidation of pyrite in these wastes. Although the chalcopyrite ore is mined to greatest extent possible, yet some chalcopyrite bearing rock may end up in the waste disposal areas. Similarly, the recovery parameter of beneficiation process is less than 100% and therefore tailings also contains ore particles which reach the tailing storage facility. The cluster analysis successfully identified the sources of pollution namely, Mine Waste Dump (MWD) and Tailing Storage Facility (TSF). The TSF & MWD are shown in Copper distribution map (Figure 5) generated with inverse distance weighing method using QGIS software. The location near Mine waste dump has the highest copper content shown in Red shade in the map.

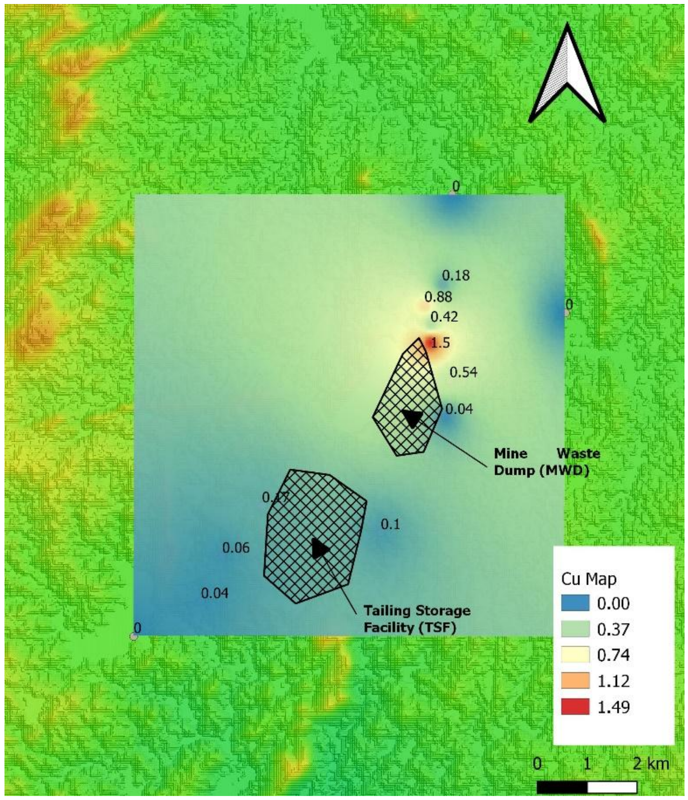

Figure 5: Copper distribution map for the study area

4. CONCLUSIONS

According to the findings of this study, the mining of copper exposes $CuFeS_2$ to atmospheric oxidation and subsequently an acidic discharge is generated. The release of copper into sediments/soils is caused by acidic mine drainage. In the course of the field survey that was carried out in the study area, it was observed that the affected surfaces were covered with precipitates of copper and iron. SEM-EDX analysis is helpful, time saving and non-destructive technique which can be used to assess heavy metal in soil/sediments. The copper concentrate was strongly related to the distance from mine waste disposal site. The correlation analysis indicated that replacement of Manganese by Copper in the samples can occurs in presence of AMD. K-means clustering successfully analysis the dataset and two prominent clusters in the data set was discovered. The clustering analysis successfully separated sample into sources of AMD. It was observed that TSF and MWD were the potential AMD sites in the study area. The mine waste is a potential environment hazard and therefore, it must be treated with care.

5. Conflict of Interest

All authors declare that they have no conflicts of interest.

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