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Levels And Forms of Potentially Harmful Elements in Mine Pond Waters of the Jos, Bukuru and Barkin Ladi Area, Northcentral Nigeria

¹Ridwan, A. M., ²Nansak, B.R., ¹Daspan, R. I., ²Wasinda, G.I., ¹Diyelmak, V.B., ¹Dibal, H.U.

¹Department of Geology University of Jos,

²Nigerian Geological Survey Agency, Jos.

Abstract

Legacy tin mining across the Jos Plateau has resulted in numerous abandoned mine ponds that are widely utilized for domestic and agricultural purposes, raising concerns regarding contamination by potentially harmful elements (PHEs). This study evaluated the concentrations, spatial distribution, and aqueous speciation of selected trace metals in 37 mine pond waters from Jos North, Jos South, and Barkin Ladi, north-central Nigeria. Field physicochemical parameters indicate predominantly fresh, weakly mineralized waters, with pH ranging from 6.51 to 8.27 (mean = 7.49), total dissolved solids (TDS) between 4.00 and 100.00 mg/L (mean = 32.76 mg/L), electrical conductivity (EC) from 11 to 253 $\mu\text{S}/\text{cm}$ (mean = 67.46 $\mu\text{S}/\text{cm}$), and dissolved oxygen (DO) between 3.99 and 8.36 mg/L (mean = 5.99 mg/L), reflecting generally oxidic to mildly reducing conditions. Trace element concentrations exhibit pronounced spatial heterogeneity. Zinc (Zn) shows extreme enrichment, reaching 10,000.7 ppb (WRID7), with additional elevated values at WRID10 (3,836.8 ppb) and WRID34 (3,009.7 ppb). Manganese (Mn) peaks at 681.95 ppb (WRID28) and 517.38 ppb (WRID36), while barium (Ba) and strontium (Sr) attain maximum concentrations of 180.77 ppb and 152.82 ppb, respectively. Lead (Pb) reaches 11.2 ppb, whereas cadmium (Cd) remains largely below detection limits. Multivariate statistical analysis indicates that Zn constitutes the principal contamination signature, forming a distinct cluster, while Ba and Sr reflect lithogenic contributions from Younger Granite host rocks. Principal Component Analysis identifies a dominant pollution gradient separating contaminated ponds from background waters. Geochemical speciation modeling (WateQ4F) demonstrates the predominance of bioavailable divalent species, including Zn^{2+} , Mn^{2+} , Ba^{2+} , Cd^{2+} , and Pb^{2+} , indicating high mobility and ecological risk, whereas chromium occurs mainly as Cr^{3+} , reflecting lower immediate toxicity. These findings confirm spatially structured, mining-derived metal enrichment, controlled by lithology and redox conditions, with significant implications for environmental and public health where mine pond waters are actively utilized.

Keywords

Mine pond contamination.
Potentially harmful elements (PHEs)
Trace metal speciation
Jos Plateau tin mining
Multivariate statistical analysis

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Introduction

The contamination of water with potentially harmful elements from mining activities has significant ecological consequence to humans and aquatic organisms. These metals can accumulate in aquatic organisms through direct exposure to contaminated water or through the consumption of contaminated prey (Mason et al., 2000). Metals like lead, arsenic, and cadmium can disrupt metabolic processes, interfere with enzyme activity, and damage tissues, ultimately affecting the survival and reproduction of aquatic species (Gadd, 2010).

Metal contamination in water can have long-lasting effects on biodiversity. A global meta-analysis of water found that "arsenic, mercury, and chromium concentrations exceeded World Health Organization limits in all the continents". And that cadmium generally presents major cancer risks in aquatic environments, indicating persistent toxic exposure across ecosystems (Zhang et al., 2025). In Canadian lakes polluted by mining, researchers observed that "genetic diversity over all loci was negatively correlated with liver cadmium contamination," suggesting that heavy metals can reduce species diversity at a genetic level (Usman et al., 2025). Such losses in biodiversity could disrupt critical ecosystem services like nutrient cycling and water purification, undermining the resilience of aquatic systems.

The risks associated with the contamination of water by potentially harmful elements are not limited to ecological impacts. Human populations that rely on contaminated water for drinking, irrigation, and agricultural activities are at risk of adverse health effects. The ingestion of water contaminated with heavy metals has been linked to various health conditions, including cancer, neurological disorders, kidney damage, and developmental growth in children (Järup, 2003). Arsenic, a potent carcinogen, is of particular concern in mining areas where it is commonly found

in gold and coal mining operations. Long-term exposure to arsenic contaminated pond water has been associated with an increased risk of skin, lung, and bladder cancer (Smith et al., 2002).

Similarly, lead and cadmium exposure have been shown to have detrimental effects on human health. Lead poisoning can cause neurological damage, particularly in children, and can also affect the cardiovascular and renal systems (Kegley et al, 2009, & Klaassen, 2013). Cadmium is known to accumulate in the kidneys and liver, leading to kidney failure and osteoporosis (Järup, 2003). Therefore, the presence of these toxic metals in drinking water and crops irrigated with contaminated mine pond water could represent a major public health concern, especially in developing countries where mining is a common economic activity.

Also, understanding metal speciation in mining affected waters is essential for assessing ecological risks and designing effective remediation strategies. Recent advances in analytical techniques such as X-ray absorption spectroscopy, sequential chemical extractions, and sulfur-driven reduction modeling have allowed researchers to better interpret how metals behave under varying redox and hydrological conditions (Álvarez et al, (2022). Liu et al., (2022) in their studies investigated mercury speciation in the hyporheic zone of a gold mining area and observed that seasonal anoxic conditions increased the abundance of reduced sulfur species. These, in turn, were linked to the mobilization of mercury (Hg) and manganese (Mn), while metals like arsenic (As), cadmium (Cd), and iron (Fe) remained relatively stable in sediments. Their findings emphasized how hydrological fluctuations can drive redox-controlled changes in metal behavior, especially for mercury.

A broader environmental perspective is offered by Silva et al., (2023), who conducted a systematic review of mining-induced metal contamination in the

Amazon Basin. Although specific speciation data were limited, their findings revealed widespread enrichment of surface and groundwater with metals such as Fe, Mn, Zn, Cd, Cu, Cr, Ni, Pb, and Hg frequently above regulatory limits. Importantly, they observed that dissolved metal forms and colloids, dominate metal transport, increasing ecological exposure risks in aquatic systems. Further insights into groundwater dynamics were provided by Hao et al., (2024) in a study on antimony mining areas in Hunan Province of China. The authors noted elevated levels of As, Sb, Se, and Mn in groundwater and emphasized that metal speciation varied significantly with depth. These variations were primarily attributed to redox gradients and anthropogenic influences from mining activities, reinforcing the need for depth-resolved speciation analyses in groundwater assessments.

In southern Africa, Goredema (2024) investigated trace metal speciation in Mazowe Dam, Zimbabwe a water reservoir impacted by upstream gold mining. Using sequential extraction techniques, the study found that Mn and Zn predominantly existed in labile fractions, which are more mobile and bioavailable. In contrast, Pb and Cu were mainly bound in residual forms, indicating lower mobility but greater persistence in sediments. These it easily accessible (Fig. 1).

findings illustrate the co-existence of both mobile and stable metal species in aquatic systems, necessitating nuanced management approaches. Improving the precision of speciation measurements, Aura et al., (2024) developed a solid-phase extraction method for distinguishing between methylmercury (MeHg^+) and inorganic mercury (Hg^{2+}) in waters impacted by artisanal small scale gold mining (ASGM).

Their protocol preserved the chemical integrity of mercury species for up to four weeks post-sampling. While aqueous concentrations were relatively low, sediments revealed high contamination, highlighting the need to consider both water and sediment matrices in risk evaluations. The mine ponds on the plateau are used for various purposes, hence this study seeks to determine the levels and forms of some potentially harmful elements in some of the ponds

The Study Area

The study area covers parts of Jos North, Jos South, and Barkin Ladi Local Government Areas in Plateau State, north-central Nigeria. It lies within the Naraguta (Sheet 168) and Kura (Sheet 124) connected by major and secondary roads as well as footpaths, making

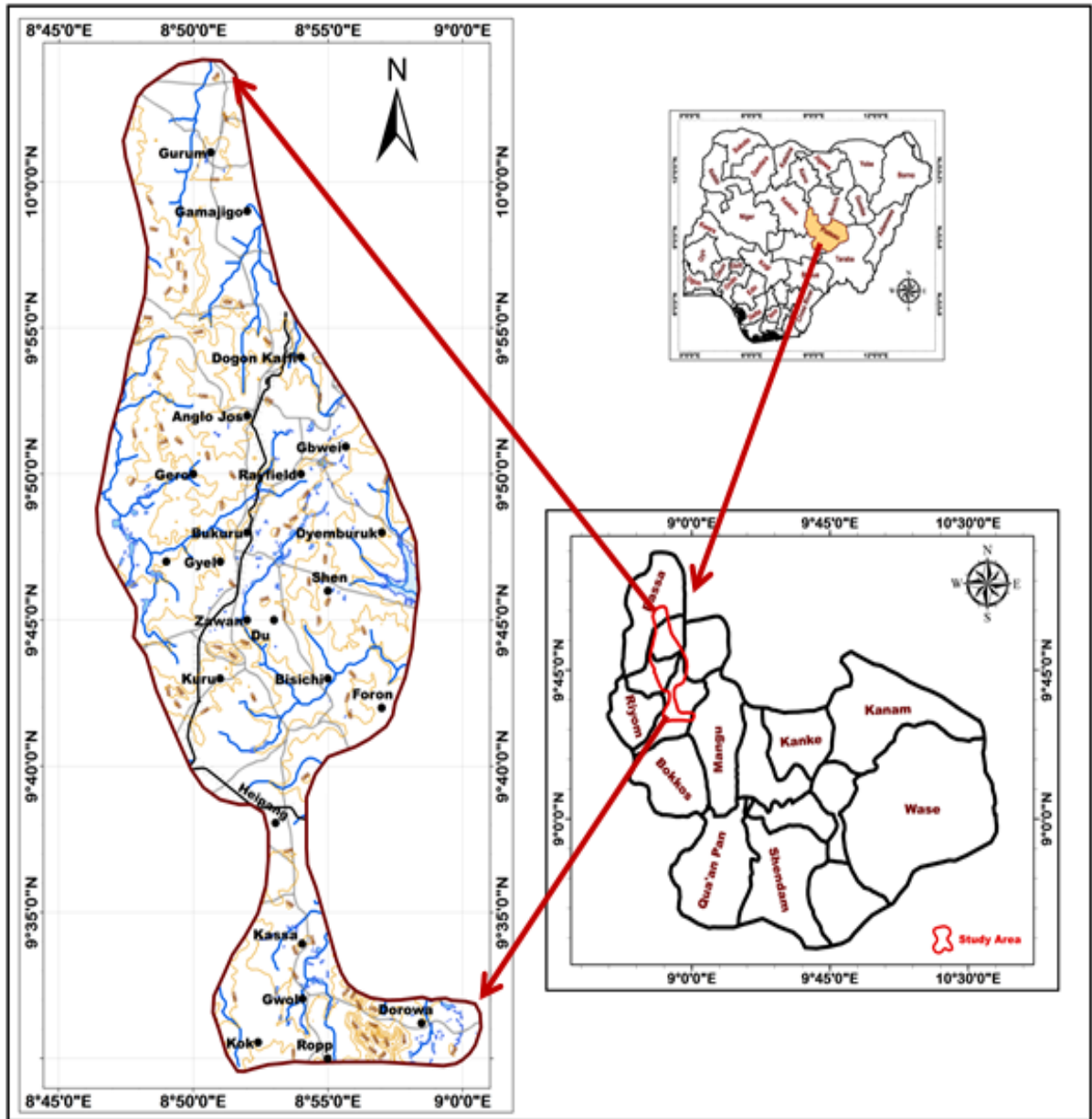


Figure 1: Location Map of the Study Area

The general geology of Jos-Plateau was described among the early workers by Falconer, 1911, Macleod, 1971; Turner, 1983 and recently, Nwankwoala, et al. 2022, Odewumi, 2025, and 2024, Abraham et al, 2025 and Ayeni, 2025). The Jos Plateau is part of the Pre-Cambrian to Mid-Cambrian and Jurassic northern Nigerian crystalline basement rock with patches of Cenozoic and Quaternary volcanic rocks. The Jos- Bukuru complex occupies the central portion of the Jos-Plateau consisting of almost all the rock types in the province. Igneous activities in

this complex are represented by two cycles, these are: Fayalite bearing granite and porphyry hastingsite biotite granite and five other phases of biotite granite constitute the first igneous cycle. The second igneous cycle whose rocks cross-cut the earlier one is made up of fayalite, hastingsite, granite porphyry, hastingsite biotite granite and four phases of biotite. The boundary between them is gradational. In most cases indistinguishable. Jos Biotite Granite is the largest individual intrusion which has been recognized in the Younger

Granite Province covering an area of 285 km². On the basis of similarity of age, structural relations and petrology, the Jos Biotite Granite appears to be closely related to the early hornblende biotite granite and granite porphyry. Megascopic observation reveals the rock sample are coarse grained porphyritic in texture and generally gray in colour.

METHODOLOGY

Collection of Water Samples

Thirty-seven (37) water samples which are used to irrigate farms were collected. Water samples were collected in 0.5-liter plastic containers from different mine ponds within the study area. It was done by immersing the container directly into the water body to collect the water. Before closing the bottles, air bubbles were expelled completely, so as to minimize contamination, interference with measurements of elements and to ensure integrity of the samples. The container was rinsed twice with the same pond water to be sampled before submerging it into the pond to collect the sample. Physical parameters such as Dissolved Oxygen, temperature, total dissolved solids, electrical conductivity and pH were measured in the field. Using the Hanna Field equipment. This was done by inserting the portable meters into the water and recording the values. To ensure that respective ions remain in solution, the water samples were acidified using Nitric Acid for samples that will be analyzed for cations before taking them to the laboratory for analysis.

Sample Preparation

The mine pond waters were collected in a small plastic water bottle of 250ml capacity and was filtered with filter paper to remove any visible suspended objects in the water. These waters were then transferred to a 60 ml plastic bottle, packaged and transported to Bureau Veritas Mineral Laboratory Canada for analysis

Laboratory Analysis of cations and Anions in Water Samples

Trace elements in soils, water and plants were analysed using the Inductively Coupled Plasma Mass Spectrophotometer at the Bureau Veritas Mineral Laboratory, Vancouver, Canada

The anions (bicarbonate, nitrate, sulphate, chloride and phosphate) were analysed at the Department of Science Laboratory Technology University of Jos with the UV Multi - Ion Parameter Model DR9000 HACH spectrophotometer employing the use of powdered pillow procedure, while alkalinity was analyzed using double titrimetric technique.

Metal Speciation

The species for trace elements were modeled with the WateQ4F software. A Geochemist's Workbench (Ball and Nordstrum, 2004) which depends on the dissolution or precipitation of a specific minerals in aqueous solution and the composition of the solution (Burt, 1993). The potential is measured by the saturation index (SI) defined by Langmuir, 1971 as $SI = \log (IAP/KT)$. Where AIP is the Ion Activity Product in the aqueous solution, and KT, the equilibrium constant (Ball and Nordstrum, 2004)

RESULTS AND DISCUSSION

Field Physicochemical Characteristics of Mine Pond Waters

The field physicochemical parameters of the mine pond waters indicate generally stable and fresh hydrochemical conditions across the study area. The pH values range from 6.51 to 8.27, with a mean value of 7.49, indicating slightly acidic to moderately alkaline conditions. The observed pH range falls within the acceptable limits for most domestic and agricultural uses.

Total dissolved solids (TDS) concentrations vary between 4.00 and 100.00 mg/L, with a mean of 32.76 mg/L, indicating very low mineralization. Similarly, electrical conductivity (EC) values range from 11 to 253 $\mu S/cm$, with an average of 67.46 $\mu S/cm$, confirming that the mine pond waters are predominantly fresh and weakly mineralized. The relatively elevated maximum EC value may reflect

localized mineral dissolution or anthropogenic inputs. Temperature of the waters show limited variation (26.70–39.00 mg/L; mean = 30.22 mg/L), reflecting ambient temperature of the ponds at the time of sampling. Dissolved oxygen (DO) values

range from 3.99 to 8.36 mg/L, with a mean of 5.99 mg/L, indicating generally oxic conditions, although lower values at some locations may suggest localized organic loading or reduced circulation.

Table 1. Summary Statistics of Field Parameters (n = 37)

Parameter	Minimum	Maximum	Mean
pH	6.51	8.27	7.49
TDS (mg/L)	4.00	100.00	32.76
EC ($\mu\text{S}/\text{cm}$)	11.00	253.00	67.46
T ^o C	26.70	39.00	30.22
DO (mg/L)	3.99	8.36	5.99

Distribution of Potentially Harmful Elements in Mine Pond Waters.

Table 1 shows the concentration and distribution of potentially harmful elements (PHEs) in the mine pond waters. The Table reveals marked spatial variability, reflecting both lithogenic contributions from the Jos-Bukuru tin-bearing granites and anthropogenic influences associated with historic mining activities. Zinc (Zn) shows the widest variation and highest concentrations, reaching extremely elevated levels (e.g., >10,000 ppb in sample WRID7). This strong enrichment suggests significant mobilisation from sulphide-bearing mineral phases and mine tailings. The high variability indicates localized contamination hotspots. Manganese (Mn) also exhibits substantial variability, with concentrations exceeding several hundred ppb in certain ponds.

Elevated Mn levels are typical of reducing micro-environments and may reflect redox-sensitive mobilization within stagnant mine waters. Barium (Ba) is consistently present at moderate to high concentrations across most ponds, indicating a strong geogenic control likely linked to feldspathic and granitic parent rocks. Strontium (Sr) displays moderate concentrations with some pronounced

spikes, possibly associated with carbonate dissolution or feldspar weathering.

Lead (Pb), Nickel (Ni), Copper (Cu), and Chromium (Cr) generally occur at lower concentrations but show localized enrichment, especially in ponds proximal to historic processing sites. Their uneven distribution suggests anthropogenic inputs superimposed on background lithogenic levels. Cerium (Ce), representing rare earth elements (REEs), shows moderate presence in several samples, supporting derivation from granitic and pegmatitic sources characteristic of the Younger Granite Province. Cadmium (Cd), Silver (Ag), Mercury (Hg), and Antimony (Sb) are mostly below detection limits, indicating limited widespread contamination by these elements in the sampled ponds.

Table 1: Compositions of Potentially Harmful Elements in mine Pond Waters

	Analyte	Ag	As	Ba	Cd	Cr	Cu	Hg	Mn	Ni	Pb	Sb	Sr	Zn
	Unit	PPB	PPB	PPB	PPB	PPB	PPB	PPB	PPB	PPB	PPB	PPB	PPB	PPB
	MDL	0.05	0.5	0.05	0.05	0.5	0.1	0.1	0.05	0.2	0.2	0.05	0.01	0.5
Sample	Type													
WRID1	Water	<0.05	<0.5	96.52	<0.05	3.6	10.5	<0.1	189.95	15.9	11.2	<0.05	30.7	1501.6
WRID2	Water	<0.05	<0.5	37.48	<0.05	0.5	1.6	<0.1	72.34	5	2.9	<0.05	26.57	250.3
WRID3	Water	<0.05	<0.5	49.53	<0.05	0.8	3.6	<0.1	42.62	5.6	2	<0.05	41.09	482.2
WRID4	Water	<0.05	<0.5	18.82	<0.05	<0.5	1.6	<0.1	49.38	5.8	5	<0.05	10.39	41.6
WRID5	Water	<0.05	<0.5	27.61	<0.05	1.3	1	<0.1	18.28	1.3	1.1	0.05	31.62	2611.2
WRID6	Water	<0.05	<0.5	60.87	<0.05	0.6	2.7	<0.1	77.31	2	1.2	<0.05	152.82	13.5
WRID7	Water	<0.05	0.5	21.57	0.06	2.5	0.5	<0.1	36.96	7	2.1	0.06	35.22	10000.7
WRID8	Water	<0.05	<0.5	56.18	<0.05	0.9	2.4	<0.1	96.02	1.3	2.1	<0.05	39.93	21.8
WRID9	Water	<0.05	<0.5	22.9	<0.05	<0.5	1.6	<0.1	23.53	7.9	0.9	<0.05	35.7	432.6
WRID10	Water	<0.05	<0.5	22.23	<0.05	0.7	1	<0.1	111.61	2.5	1.2	<0.05	16.84	3836.8
WRID11	Water	<0.05	<0.5	33.53	<0.05	<0.5	1	<0.1	22.14	0.9	0.7	<0.05	21.99	57.7
WRID12	Water	<0.05	<0.5	27.44	<0.05	<0.5	2.1	<0.1	41.25	3.9	0.3	<0.05	12.9	20.9
WRID13	Water	<0.05	<0.5	38.45	<0.05	<0.5	1.8	<0.1	28.04	2.3	1.5	0.06	39.79	1631.5
WRID14	Water	<0.05	<0.5	102.33	<0.05	<0.5	2.6	<0.1	22.48	5.8	1.1	0.1	75.9	329.1
WRID15	Water	<0.05	<0.5	25.28	<0.05	<0.5	1.6	<0.1	52.54	1.2	2.3	0.05	40.4	182
WRID16	Water	<0.05	<0.5	40.09	<0.05	<0.5	0.8	<0.1	13.03	1	1.4	<0.05	39.22	4.1
WRID18	Water	<0.05	<0.5	53.19	<0.05	<0.5	1.6	<0.1	56.7	1.4	2.8	<0.05	46.14	136.5
WRID19	Water	<0.05	<0.5	12.28	<0.05	<0.5	2.3	<0.1	9.49	4	2.9	<0.05	3.18	440.9
WRID21	Water	<0.05	0.6	54.18	<0.05	0.5	1.6	<0.1	87.11	1.3	1.6	0.06	109.39	4.3
WRID22	Water	<0.05	<0.5	119.57	0.05	1	4.1	<0.1	114.85	6.7	8.6	<0.05	48.11	1804.5
WRID23	Water	<0.05	<0.5	84.86	<0.05	1.1	4.2	<0.1	78.83	4.2	3.6	<0.05	60.4	80.8
WRID25	Water	<0.05	<0.5	56.92	<0.05	1	2.7	<0.1	15.15	3	5.6	<0.05	41.32	769.4
WRID26	Water	<0.05	<0.5	33.02	<0.05	<0.5	0.9	<0.1	26.52	1.6	0.9	<0.05	26.91	71
WRID27	Water	<0.05	<0.5	38.95	<0.05	0.7	1.5	<0.1	41.93	1.8	1.2	<0.05	19.62	42.7
WRID28	Water	<0.05	1.1	99.35	<0.05	0.5	4.9	<0.1	681.95	7.8	0.8	<0.05	74.87	138.7
WRID29	Water	<0.05	<0.5	92.2	<0.05	2.5	3.1	<0.1	53.3	11	1.5	<0.05	66.2	198.4
WRID30	Water	<0.05	<0.5	72.57	0.05	0.8	3.2	<0.1	376.99	3.2	4.9	<0.05	27.37	165
WRID31	Water	<0.05	0.5	180.77	0.06	1.8	9.1	<0.1	326.95	4.7	10.5	<0.05	46.17	1248
WRID32	Water	<0.05	<0.5	57.12	<0.05	<0.5	3	<0.1	53.18	2.4	1	<0.05	65.64	2421
WRID33	Water	<0.05	<0.5	68.9	0.06	0.7	4.3	<0.1	95.34	1.9	2.9	0.12	56.73	52.8
WRID34	Water	<0.05	<0.5	24.25	<0.05	1.9	1.7	<0.1	39.83	3.2	1.6	<0.05	9.95	3009.7
WRID35	Water	<0.05	<0.5	53.11	0.06	1.4	3.5	<0.1	47.81	16	8.9	<0.05	15.03	866.4
WRID36	Water	<0.05	0.9	163.13	<0.05	0.7	2.3	<0.1	517.38	2.2	1.7	<0.05	101.03	351.6
WRID37	Water	<0.05	<0.5	75.37	<0.05	2.8	9.8	<0.1	66.27	4.7	6.7	0.1	53.2	455.1
WRID38	Water	<0.05	<0.5	50.42	<0.05	1.1	2.7	<0.1	18.64	1.1	2.7	<0.05	31.66	10.7

Hierarchical Cluster Analysis (HCA)

The dendrogram (Fig 1) constructed using all 38 samples confirms strong geochemical structuring among the elements: Zn remains distinctly separated, clustering at a very high Euclidean distance. This confirms its anomalous enrichment and highly variable distribution across the mine ponds. Zinc is therefore the dominant contaminant signature in the system. Mn forms a secondary but relatively independent branch, reflecting its redox-sensitive mobility and localized enrichment (e.g., WRID28, WRID36). Ba and Sr cluster closely, indicating a shared lithogenic origin likely controlled

by feldspar weathering and granitic host rock dissolution within the Younger Granite Province. Cu, Pb, Ni, and Cr cluster together, suggesting co-mobilization from sulphide mineral weathering and mining residues and Ce and Be show moderate association, reflecting geogenic derivation from granitic and pegmatitic lithologies. Overall, the clustering reveals two dominant controls: Geogenic control (Ba-Sr-Ce-Be association and mining-influenced metal enrichment (Zn-Mn-Cu-Pb-Ni cluster)

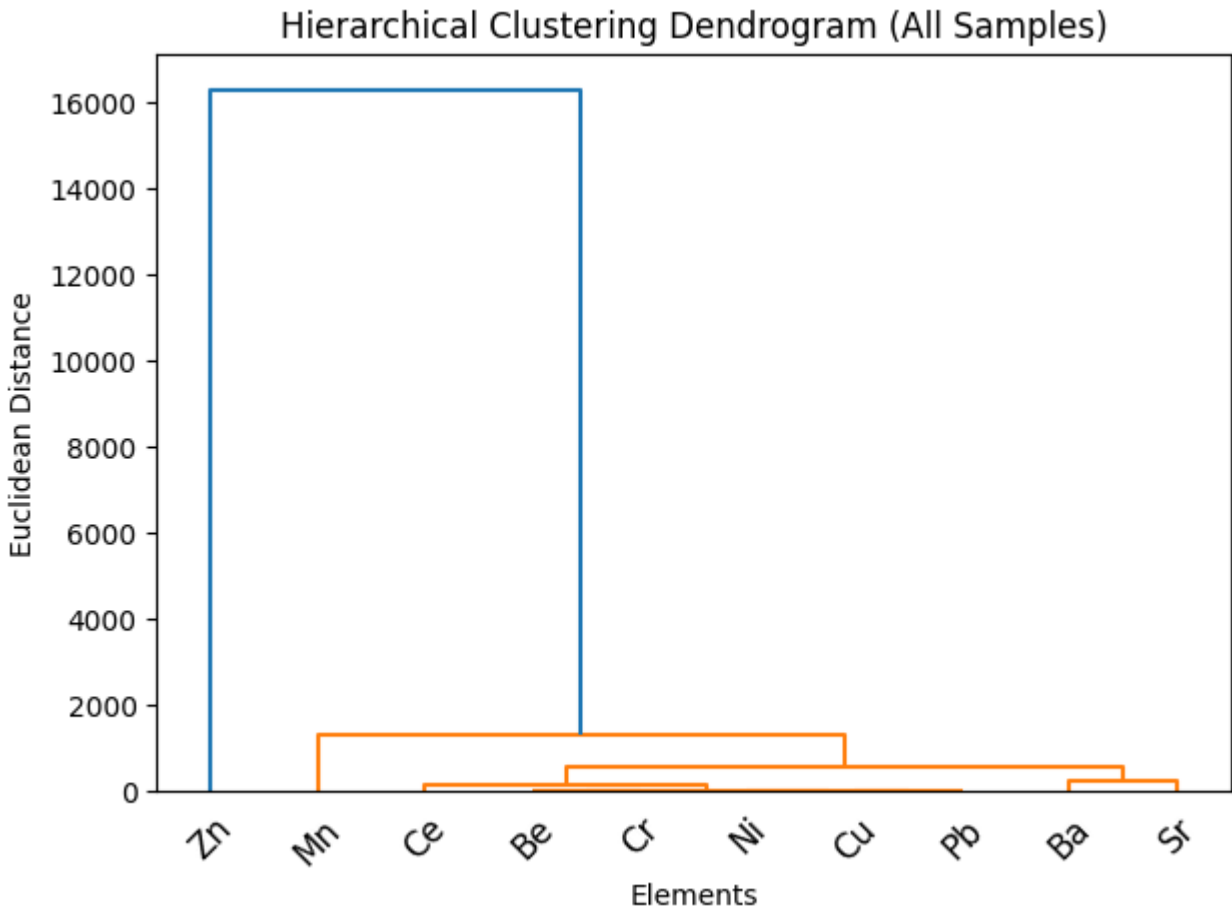


Figure 1: A Dendrogram showing Clustering of some of the Potentially Harmful Elements Principal Component Analysis (PCA)

The PCA scatter plot (Fig 2) shows clear dispersion along PC1, indicating strong variance driven primarily by highly enriched metals (notably Zn and Mn). PC1 (major variance axis) reflects metal

enrichment intensity, separating highly contaminated ponds from relatively background-dominated sites while PC2 appears influenced by lithogenic elements (Ba, Sr, Ce), representing

natural geochemical background variation. Samples positioned far along positive PC1 correspond to ponds with extreme Zn and Mn enrichment, consistent with tailings influence or stagnant redox-controlled conditions. Using PCA (with PC1 as the main pollution gradient), the following ponds fall within the upper quartile of PC1 scores and are classified as contaminated ponds: WRID1, WRID20, WRID21, WRID25, WRID26, WRID28, WRID32, WRID33, WRID34. The clustering of most samples near the origin suggests that many ponds maintain relatively moderate concentrations. The clear separation along PC1 confirms that contamination is not random but may be systematically controlled.

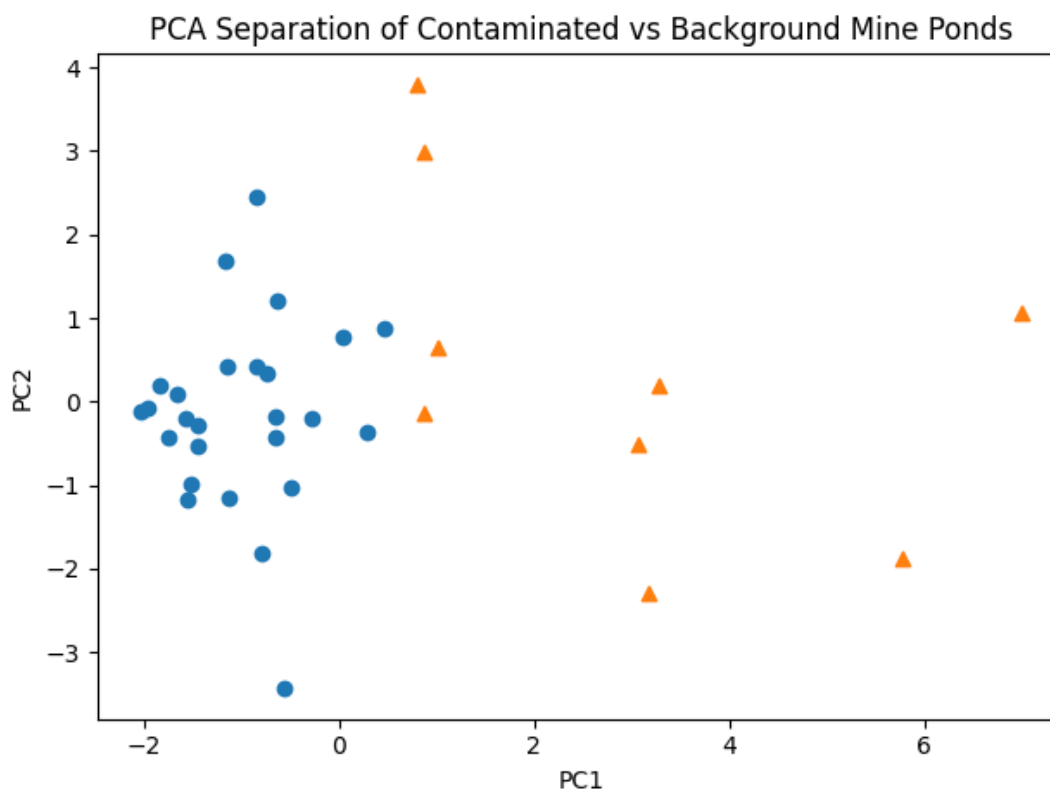


Figure 2: PCA Separation Of Contaminated and Mine Ponds showing values of Elements close to Background Values

Comparison of Present Data and Data from Previous Study

Comparative evidence from mine pond water studies across the Jos Plateau shows persistent contamination driven by long term tin mining and mineral processing. Earlier studies in Jos Metropolis, Barkin-Ladi, and Jos South (Adam et al., 2015; Ramadan & Haruna, 2019; Abuh et al., 2014; Emeribe et al., 2022; Dibal et al., 2016) reported varying but generally moderate levels of Pb, Zn, Cu, Cr, Ni, and Ba, with most values remaining below WHO limits except in areas with intense mine tailings influence. In contrast, the current study records markedly higher concentrations especially Zn and Ba far exceeding permissible

guideline levels. These elevated values indicate intensified contamination in certain mine ponds, likely due to prolonged mine waste, weathering, increased leaching, and limited remediation. The comparison shows that while earlier research documented measurable pollution, the present findings reveal more severe and escalating heavy metal enrichment.

Speciation of Trace Elements in Mine Pond Waters and Implications for Human Health

Table 3 summarizes the aqueous speciation of trace elements in mine pond waters and compares the dominant species with those identified as most toxic by Logan and Tarima (1993) and regulatory agencies such as the

World Health Organization (WHO), Agency for Toxic Substances and Disease Registry (ATSDR), and Environmental Protection Agency (EPA). Speciation analysis provides critical insight into metal mobility and bioavailability, which often govern biological uptake and toxicity more directly than total metal concentrations (Tessier et al., 1979; Scheckel et al., 2005).

The speciation results indicate that most trace elements occur predominantly as free ionic species. Silver in the ponds is mainly present as Ag^+ (18.05–95.02%), reflecting conditions that favor the soluble and bioavailable ionic form. Free Ag^+ readily binds to functional groups in proteins, inhibiting enzymes, and has been associated with argyria and renal effects in experimental studies (Rose et al., 1997; Lansdown, 2006). Although silver's overall toxicity is lower than that of lead or cadmium, its ionic form is considered environmentally significant due to its reactivity and biological interactions.

Barium was exclusively present as Ba^{2+} (100%), a highly soluble form under typical groundwater conditions. Soluble Ba^{2+} has been shown to disrupt potassium-mediated membrane potentials in muscle and nerve tissue and is associated with cardiovascular effects at elevated exposures (ATSDR, 2007; Morrow, 1988). The predominance of Ba^{2+} in the ponds implies potential risk to human health where contaminated water is used for domestic or agricultural purposes.

Cadmium speciation revealed that Cd^{2+} was dominant (100%), aligning with other studies showing high bioavailability and toxicity of free cadmium ions in aqueous environments

(Duffus, 2002). Cd^{2+} accumulation in the kidney cortex is a well-documented cause of proximal tubular dysfunction and bone demineralization (Jarup et al., 1998; Bernard, 2008), and long half-life in humans increases chronic exposure risk.

Chromium was present primarily as Cr^{3+} (99.38%), with no significant proportions of toxic hexavalent chromium (Cr^{6+}) detected. This contrasts with environments where oxidative conditions favor Cr^{6+} formation, which is strongly carcinogenic (IARC, 2012; Costa & Klein, 2006). Cr^{3+} is considerably less bioavailable and toxic than Cr^{6+} and serves as an essential nutrient at trace levels (Anderson & Kozlowski, 2018). Nevertheless, redox changes in environmental systems could increase Cr^{6+} presence and associated risks, underscoring the need for monitoring.

Copper was present predominantly as Cu^{2+} (99.43%). While copper is an essential micronutrient, the divalent ionic form is highly bioavailable and can induce oxidative stress at elevated concentrations (ATSDR, 2004; Gaetke & Chow, 2003). Excess free Cu^{2+} has been associated with hepatotoxicity and gastrointestinal effects in exposed populations.

Selenium occurred mainly as HSe^- , consistent with reducing conditions. Soluble selenium species have narrow margins between essentiality and toxicity (Schiavon et al., 2016; ATSDR, 2003). Chronic high exposures have been linked to selenosis, characterized by dermatological and neurological symptoms.

Manganese in the water existed entirely as Mn^{2+} (100%). Soluble Mn^{2+} is easily absorbed via the gastrointestinal tract and has been

associated with neurodevelopmental effects in children exposed to high manganese in drinking water (Wasserman et al., 2006; Bouchard et al., 2011). Manganese neurotoxicity resembles Parkinsonian symptoms at chronic high exposure. Lead was present primarily as Pb^{2+} (91.71-100%). Pb^{2+} readily crosses biological membranes, accumulates in bone and soft

tissue, and disrupts multiple enzymatic systems, particularly in children (Needleman, 2004; Lanphear et al., 2005). No safe level of lead exposure in children has been identified, and even low concentrations are linked to cognitive deficits and behavioral disorders (WHO, 2010).

Table 3: Forms of Trace Elements in Mine Pond Water of the Study Area (Most toxic metals after Logan and Tarima 1993, and World Health Organization, Agency for Toxic Substances and Disease Registry, Environmental Protection Agency, 2017)

METALS	WATER	Most toxic metals after Logan and Tarima 1993 and WHO/ATSDR/EPA 2017	Most Toxic Metals from speciation	% in Water
Ag	Ag^+	Ag^+	Ag^+	18.05-95.02
As				
Ba	Ba^{+2}	Ba^{+2}	Ba^{+2}	100
Cd	Cd^{+2} $CdBr^+$	Cd^{+2}	Cd^{+2}	100
Cr	Cr_3^{+3} CrF^{+2}	CrO_4^{-2}	Cr_3^{+3}	99.38
Cu	Cu^+ Cu^{+2}	Cu^{+2}	Cu^+ Cu^{+2}	99.43 0.34-0.570
Se	Hse^-			
Mn	Mn^{+2}	Mn^{+2}	Mn^{+2}	100
Ni		Ni^{+2}		0
Pb	Pb^{+2} $PbBr^+$	Pb^{+2}	Pb^{+2}	91.71-100 0.15-0.29
Zn	Zn^{+2}	Zn^{+2}	Zn^{+2}	100

Zinc occurred as Zn^{2+} (100%), matching typical groundwater speciation. Although Zn is essential, elevated Zn^{2+} may cause gastrointestinal distress and disrupt absorption of other trace elements (ATSDR, 2005; Hambidge, 2000). The

predominance of free ionic species (M^{2+}) in the pond's points to high mobility and bioavailability of these metals under existing hydrochemical conditions. Bioavailable free metal ions pose a greater human health risk than complexed forms,

especially where contaminated water is used for drinking or irrigation. The most critical concerns in the present work are Pb^{2+} , Cd^{2+} , Mn^{2+} , and Ba^{2+} due to their dominance in toxic species and well-documented adverse health effects.

SUMMARY AND CONCLUSION

This study presents an integrated hydrogeochemical characterization and multivariate statistical assessment of mine pond waters across the Jos Plateau, north-central Nigeria. In situ physicochemical measurements indicate that the waters are predominantly fresh and weakly mineralized, with electrical conductivity ranging from 11 to 253 $\mu S/cm$ (mean = 67.46 $\mu S/cm$) and total dissolved solids between 4.00 and 100.00 mg/L (mean = 32.76 mg/L). The pH values (6.51-8.27) indicate slightly acidic to moderately alkaline conditions, reflecting limited buffering capacity and minimal overall salinity.

Despite these apparently acceptable bulk hydrochemical characteristics, trace element analysis reveals substantial localized contamination in several mine ponds. Zinc constitutes the most significant contaminant, reaching concentrations of 10,000.7 ppb, far exceeding international freshwater guideline thresholds. Manganese concentrations attain 681.95 ppb, while barium and lead exhibit localized enrichment up to 180.77 ppb and 11.2 ppb, respectively, indicating both geogenic and mining-related inputs.

Multivariate statistical evaluation demonstrates that trace element distributions are controlled by systematic geochemical processes rather than stochastic variability. Hierarchical Cluster Analysis differentiates lithogenic associations, notably Ba-Sr, reflecting natural rock-water

interaction, from anthropogenically influenced metal assemblages (Zn-Mn-Cu-Pb-Ni) linked to legacy tin mining activities. Principal Component Analysis further identifies the first principal component (PC1) as a contamination intensity factor, clearly distinguishing highly impacted ponds (e.g., WRID28 and WRID34) from relatively unimpacted background sites.

Geochemical speciation modeling indicates that most trace metals occur predominantly as free divalent cations (Zn^{2+} , Mn^{2+} , Ba^{2+} , Cd^{2+} , Pb^{2+} , Cu^{2+}), which are thermodynamically stable under prevailing pH and redox conditions. These ionic species exhibit high aqueous mobility and bioavailability, thereby increasing ecological toxicity and human exposure risks, particularly given the utilization of these ponds for domestic and agricultural purposes. Although chromium is present mainly as Cr^{3+} , its speciation may shift under oxidizing conditions, potentially enhancing its mobility and toxicity.

Overall, the findings confirm that legacy tin mining has produced persistent, spatially heterogeneous heavy metal contamination within the Jos Plateau. The predominance of bioavailable metal species highlights the urgent need for continuous hydrogeochemical monitoring, ecological risk assessment, and targeted remediation strategies to mitigate long-term environmental and public health impacts.

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