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Geochemical Assessment of Heavy Metal Contamination in Soils from an Abandoned Quarry Mine in Nseleni, KwaZulu-Natal Province, South Africa

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Abstract**—** This study examined the heavy metal (HM) levels in five sub-soil samples (S1-S5) collected from an abandoned quarry mine (AQM) and a baseline sample (S6) taken from a nearby school to provide a comparison point in Nseleni, KwaZulu-Natal province. The pH and EC values for S1-S5 ranged from 3.3 - 5.0, and 1100 - 1400 µS/cm, respectively. The maximum HM concentrations for S1-S5 were in the following order: Al > As > B > Ba > Cd > Co > Cr > Cu > Mn > Na > Ni > Pb > Sb > Se > Sr > Ti > Tl > Zn. X-ray fluorescence analyses also revealed higher oxide concentrations (Na_2O, MgO, Al_2O_3, SiO_2, and P_2O_5) in S1-S5 where the contamination factor (CF) for each oxide indicated severe contamination. The detected oxides Al_2O_3 and MgO in the samples could accelerate acid rock drainage (ARD) processes, leading to HMs leaching into the groundwater and the environment, thus posing possible health risks to the Nseleni community.

Keywords**—**Acid Rock Drainage, Groundwater Contamination, Heavy Metal Contamination, Nseleni**,** Quarry Mine.

I. INTRODUCTION

South Africa, a nation celebrated for its rich geological diversity, is home to numerous quarry mines (QMs) spread across its provinces, including KwaZulu-Natal province [1]. This region is particularly notable for its variety of mineral deposits, such as stone quarries, aggregates, limestone, and sandstone, which have historically driven the local quarrying industry [2]. However, many of these quarry sites have been abandoned due to factors such as resource depletion, economic shifts, and evolving regulatory frameworks (Mhlongo et al., 2019). The challenges of operating in fragmented ecosystems or areas with geomorphological constraints often make continued quarrying unfeasible, leading to site abandonment (Devos et al., 2010). Geological complexities, such as fractures and structural basins, can exacerbate safety risks and operational difficulties, further prompting the cessation of mining activities. A significant issue contributing to this abandonment is the lack of adequate remediation efforts, which results in further environmental degradation [3].

Abandoned quarry mines (AQMs) typically present inhospitable conditions characterized by steep drop-offs, deep water, flooding, and poor drainage, all of which contribute to their abandonment [4]. The environmental impact of these sites is profound, leading to surface disturbances, soil erosion, and biodiversity loss. The presence of large debris, unstable solid mine waste, and contaminated soils creates significant stability challenges, making reclamation efforts less appealing [5]. These AQMs often feature quarry lakes (QLs) filled with water and mining debris, posing health, safety, and environmental risks to nearby communities. Heavy metals (HMs) such as Pb, Zn, Sb, Cu, Cr, Cd, As, and Mn are often found in these sites, where they significantly threaten soil and water quality [6, 7]. The extent of contamination is influenced by factors such as proximity to the AQMs, historical activities conducted at the sites, the types of rock present, weathering processes, and human activities that contribute to the enrichment of HMs in surrounding soils [8].

Despite extensive studies on soil contamination from active and abandoned mines in South Africa, particularly gold, coal, and platinum mines, there is a notable lack of research specifically addressing soil contamination in abandoned quarry mines (AQMs) in regions like Nseleni in KwaZulu-Natal province [9]. This gap underscores the need for focused studies to assess the environmental and health risks associated with AQMs, particularly in under-researched areas. As a result, this study was aimed at assessing the physicochemical parameters and HM concentrations from the AQM at Nseleni and assessing their impact on soil quality at the AQM at Nseleni.

II. MATERIALS AND METHODS

A. Study Area Description and Sample collection

This study focuses on the abandoned quarry mine (AQM) with the location of the geographic coordinates [28.655351°S,

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31.997542°E], situated in Nseleni, Empangeni, located in the KwaZulu-Natal province of South Africa.

Five random sub-soil samples (S1-S5) were collected in range of 100 to 200 m due to the steep and unstable sides of the Mayeni Dam (quarry lake) during the autumn season, with temperatures ranging between 24°C to 29°C. An additional sixth sample (S6) was taken from a local school approximately 2.5 km away from the AQM, serving as a baseline as recommended by [10]. All sub-soil samples were collected on the 10th of May 2024, using a RYOBI PA-200 Earth Auger at a depth of approximately 30 to 45 cm, in accordance with field soil sampling guidelines that incorporate judgment, haphazard, probability, and soil analysis methods as described by [11]. Prior to sample collection, the sampling sites were cleared of litter and surface rocks to ensure sample integrity. Approximately 1 kg of soil was sampled and then homogenized by mortaring into a composite sample, which was subsequently air-dried and sieved using a 2-mm stainless steel sieve, conforming to ASTM Standard E11. After sieving, the samples were carefully bagged into sterile polythene zipper-top bags to prevent contamination and labelled, then transported to the laboratory for further analysis. The coordinates of each sampling point were recorded using a Global Positioning System (GPS) device, and the sampling points were marked accordingly, as shown in Fig. 1.

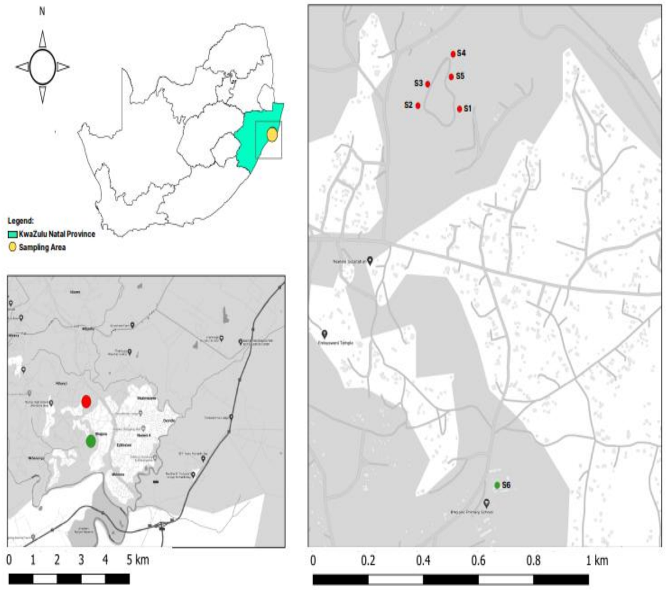

Fig.1. The Location of the study area and sampling points drawn using Geological maps were generated using Quantum GIS software (v. 2.18.11) and data from National Geo-Spatial Information (NGI), a component of the Department of Rural Development and Land Reform, South Africa.

B. *Paste pH and Electrical Conductivity Method*

The paste pH and Electrical Conductivity (EC) of the sub-soil samples were determined using a calibrated Portable Waterproof pH/EC/TDS Meter (High Range) - HI991301.

C. *Geochemical Analysis of Soil Samples*

The sub-soil samples were analyzed using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) for metal analysis while the X-ray Fluorescence (XRF) was used to determine the metal composition of the samples.

D. *Determination of Soil Contamination*

To assess the degree of soil pollution in the study area, the Contamination Factor (CF) was calculated using Eqn. 1 as adapted from the study by [12].

$$CF = \frac{C_1}{C_{Background}} \quad (1)$$

Where:

C_1 : is the concentration of the contaminant (heavy metal) in the soil sample.

$C_{Background}$: is the background concentration of the same contaminant, typically measured in an uncontaminated reference area (local school).

III. RESULTS AND DISCUSSION

The pH values of samples S1-S5 were observed to range between 3.3 and 5.0, while the electrical conductivity (EC) values spanned from 1100 to 1400 µS/cm, indicating acidic conditions with high ionic content and salinity. Sodium (Na) concentrations in these samples ranged from 92.6 to 137 g/kg, reflecting significant salinization of the soil, which could adversely impact soil structure and plant nutrient uptake. The baseline sample S6, collected from the local school, exhibited a near-neutral pH of 5.9 and an EC value of 439 µS/cm but had an exceptionally high Na concentration of 183 g/kg. This elevated Na level in S6, despite its neutral pH and lower EC, suggests localized factors contributing to high salinity, which may be associated with anthropogenic activities or specific soil management practices at the local school. The substantial Na content in S6 could pose risks of soil dispersion, reduced permeability, and potential toxicity to plants, contrasting with the slightly lower Na levels in S1-S5. Moreover, the observed variation in soil properties, particularly the pH, Na levels, cation exchange capacity, organic matter content, and available phosphorus (P_2O_5), with concentrations ranging from 0.12% to 0.45% for S1-S5 and 0.16% for S6, indicates a complex interplay between these factors and the mobility and bioavailability of heavy metals (HMs) in the soil [13].

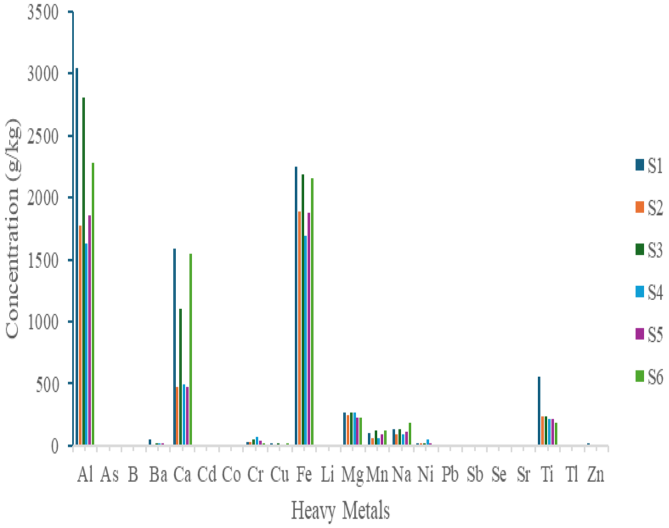

Fig 2: The heavy metal concentration profile of the sub-soil samples (S1-S6) which were sampled from the Nseleni, AQM.

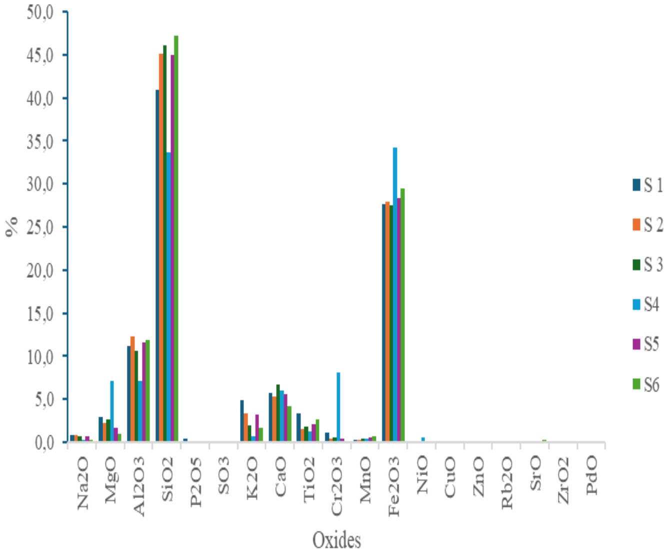

Fig 3: The mineralogical composition of the sub-soil samples (S1-S6) which were sampled from the Nseleni, AQM.

Fig 2 shows the metal concentrations within the sub-soil samples which were collected from the Nseleni AQM while Fig 3 shows the mineralogical composition of the same samples. The elevated Al concentrations in samples S1-S5, ranging from 1629 to 3046 g/kg, alongside the Al concentration in the local school sample (S6) measured at 2280 g/kg, suggest the presence of specific feldspar minerals, such as Orthoclase (potash or acid feldspar), which are prominent components of aluminosilicate minerals. These findings align with the reports by Niu et al. (2019), who identified similar mineralogical compositions in soils with high Al content. Al_2O_3 levels in S1-S5 range from 7.19% to 12.3%, while SiO_2, the most abundant oxide, ranges from 33.63% to 46.1% (Fig 3). SO_3 concentrations vary between 0.08% and 0.16%, and K_2O levels range from 0.68% to 4.87%. In contrast, the S6 sample displays an Al_2O_3 content of 11.9%, with higher SiO_2, SO_3, and K_2O concentrations at 47.2%, 0.13%, and 1.63%, respectively.

The presence of arsenic (As) in samples S2 (0.96 g/kg) and S5 (0.33 g/kg), coupled with its absence in samples S1, S3, S4, and S6, suggests that localized deposits or specific mining activities may be the primary sources of As in S2 and S5.

Iron (Fe) concentrations in abandoned quarry mine (AQM) soils can vary significantly, as evidenced in S1-S5, which exhibited Fe levels ranging from 1697 to 2247 g/kg, with corresponding Fe_2O_3 levels between 27.6% and 34.2%. These variations are primarily attributed to differences in mineral composition and weathering processes within the quarry environment, which lead to the accumulation of iron oxides in the soil. The presence of iron-bearing minerals such as hematite and goethite, typical of oxidized environments, suggests that these soils have undergone prolonged exposure to weathering processes specific to the AQM at Nseleni [14]. Similarly, the Fe concentration in the local school sample (S6) was recorded at 2153 g/kg, with an Fe_2O_3 content of 31.5%, consistent with the values found in the AQM soils. This consistency indicates that the local soil composition may be influenced by similar geological processes or the transport of iron-rich material within the study area. The slightly lower Fe concentrations in the school sample compared to the highest values in S1-S5 may suggest less intense weathering or the presence of different iron-bearing phases with lower Fe_2O_3 concentrations.

The soil samples collected from the abandoned quarry mine (AQM) at Nseleni exhibit significant variability in chromium (Cr) and copper (Cu) concentrations, reflecting the geochemical diversity of the site. In the quarry samples (S1-S5), chromium concentrations ranged from 25.6 to 70.4 g/kg, with corresponding Cr_2O_3 levels varying between 0.45% and 8.16%. Cu concentrations in these samples ranged from 12.3 to 17.3 g/kg, with CuO content between 0.04% and 0.05%. These findings suggest the presence of specific mineral phases influenced by the site's geological history and natural weathering processes [15]. Weathering, particularly chemical weathering, plays a critical role in shaping the distribution and form of metal oxides in these soils. Through weathering, metal oxides such as Cr_2O_3 and CuO may dissolve, thus releasing their constituent metals into the soil, and contribute to the formation of secondary minerals. In contrast, the soil sample from the local school (S6) displayed lower concentrations of Cr and Cu, recorded at 23.1 g/kg and 16.0 g/kg, respectively, with oxide contents of 0.20% for Cr_2O_3 and 0.10% for CuO. The differences observed between the AQM, and school samples may be attributed to varying degrees of mineralization and environmental exposure at the two sites.

The soil samples collected from the AQM denoted as S1 to S5, exhibited a wide range of manganese (Mn) and nickel (Ni) concentrations. Manganese (Mn) levels varied from 59.6 to 122 g/kg, with corresponding MnO content ranging between 0.26% and 0.51%. Nickel concentrations in these samples ranged from 18.2 to 49.7 g/kg, with NiO content varying from 0.13% to 0.58%. These variations in metal concentrations suggest a heterogeneous distribution of Mn and Ni within the quarry environment, likely influenced by the diverse mineralogical composition and weathering processes in the area [16]. In contrast, the soil sample from the local school, S6, displayed a different composition with MnO compared to the AQM samples. However, the nickel concentration in S6 was notably lower at 7.08 g/kg, with no detectable NiO.

Lead (Pb) was found to have significantly elevated levels in S3, reaching 1,04 g/kg, raising substantial public health concerns due to its potential to cause neurological damage, particularly in children. Elevated Antimony (Sb) and Selenium (Se) concentrations were also observed, especially in samples S3 and S4, respectively. These findings indicate significant anthropogenic influences, likely stemming from post-mining activities and waste disposal, as both elements are commonly associated with human activities such as mining [17]. The presence of Strontium (Sr) and Titanium (Ti) at the highest levels in sample S3, with concentrations of 2,99 mg/kg and 559,6 mg/kg, respectively, can be attributed to both natural occurrences in the soil and mineralogical contributions.

In relation to abandoned quarry mines, Thallium (Tl), although present in lower concentrations, was highest in S1 (1,63 g/kg), and Zinc (Zn) concentrations peaked in S1 (13,97 g/kg), reflecting extensive use in various industrial processes. The presence of Thallium, often associated with sulfide ores and released during mining and smelting activities, indicates residual contamination from historical mining operations [18]. These findings highlight the complex contamination patterns characteristic of the AQM site. The presence of these HMs necessitates targeted remediation strategies to mitigate the significant environmental and health risks they pose, particularly due to their potential for bioaccumulation and toxicity in both terrestrial and aquatic ecosystems.

IV. CONCLUSIONS

This study evaluated the extent of HMs contamination in an abandoned quarry mine based in Nseleni and observed that the site is heavily contaminated with various HMs. This may have a negative impact on the residents which are in close proximity to this site and therefore, mitigative strategies would need to be undertaken to ameliorate the contamination.

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