

*Article*



# **Assessment of Possibly Toxic Elements in Landfill Soils and Their Impacts on the Ecosystem in Alice, South Africa**

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**Abstract:** Soil contamination by metallic components is an obscure, detrimental, protracted, and irreparable predicament. Dumping of waste containing heavy metals into landfills, fertilizer and pesticide application, and coal combustion results in high toxicity of metallic elements, and their continuous accumulation in soil pollutes the environment, which, in turn, poses a threat to human health. The specimens were subsequently dehydrated, processed for mineralization, and carefully examined microscopically by scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM/EDX), which examined their mineral substance, crystalline configuration, and chemical composition. Thirteen (13) elements were detected, and only eight (8) metals were discovered (K, Mg, Na, Ca, Al, Fe, Au, Ba), including non-metals (C, O, Cl, P) and a metalloid (Si). The concentrations of possibly toxic elements obtained showed no consistent succession, as they fluctuated across the examined sites. The Al concentration ranged from  $3.78 \pm 0.23$  wt% to  $10.23 \pm 0.31$  wt%, while the Fe concentration fluctuated from  $4.14 \pm 0.40$  wt% to  $13.13 \pm 1.07$  wt%. Na and Mg levels were present in all samples, but their availability was minimal, at less than 2.0 wt%, ranging between  $1.44 \pm 0.20$  wt% and  $0.31 \pm 0.08$  wt%. The concentrations of Ca and K were low in all soil samples, ranging from  $0.91 \pm 0.14$  wt% to  $5.56 \pm 0.47$  wt% for Ca and from  $1.32 \pm 0.25$  wt% to  $4.87 \pm 0.18$  wt% for K. During the investigation at the designated and control areas, it was discovered that the concentrations of potentially hazardous metals exceeded the accepted limits established by the World Health Organization (WHO) > 100 ppm. The findings provide proof of metallic contaminants in the study region, which calls for proper monitoring, management, and remedial measures of metal-tainted sites, since the residents of this locality are at a significantly elevated risk of experiencing adverse effects due to their heightened exposure to these elements. As a result of that, there is an imperative need to monitor and regulate this area regularly and appropriately. The study recommends sustainable farming practices, where farmers could use natural fertilizers and compost, as well as, the implementation of proper waste management, effective recycling techniques, and proper disposal of substances containing heavy metals as byproducts. Further implement remediation techniques that effectively and safely restore soils contaminated by metals in an environmentally sustainable and economically efficient manner.

**Keywords:** metallic elements; waste; soil pollution; illegal disposal; SEM/EDX

# **1. Introduction**

Alice is a small town surrounded by numerous economic and academic activities, and faces the challenges of a densely populated area and increasing pollution. Recent studies have shown that the environmental condition in the community is deteriorating due to the presence of suppurating waste, poor solid waste management, and mismanaged landfill sites [\[1,](#page-9-0)[2\]](#page-9-1). The waste removal service has become inadequate and ineffective, leading to individuals disposing of their waste indiscriminately, even in areas where waste bins are available. However, these bins are constantly full as they serve a large population, resulting in unattended waste being left in the environment. The municipality



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still relies on landfilling as a waste management practice, but the Alice landfill site is poorly managed, and there is no proper waste management within the site. The soil is filled with waste products, such as plastics, gadgets, power sources, chemicals, and other hazardous materials, which are scattered carelessly. The accumulation of waste in the environment has compelled waste pickers to burn the garbage, resulting in the emission of hazardous fumes. These fumes linger above settlements, causing distress and discomfort to individuals with respiratory illnesses and other complications, while also exposing everyone to a harmful mixture of micro-chemicals [\[3\]](#page-9-2). These substances, when released into the environment, emit toxic compounds, such as heavy metals, that have the potential to poison animals, contaminate water sources, and negatively impact human health as they infiltrate the soil [\[4\]](#page-9-3). Potentially toxic elements (heavy metals) are defined as those elements with a density greater than 5.0 g $\cdot$ cm<sup>−3</sup>, such as Cd, Pb, Fe, Hg, Mn, Zn, and Cu. Although some elements (Fe and Zn) are essential for the growth and functioning of microorganisms, they can be harmful when present in large amounts. Local communities face the potential danger of being exposed to high levels of metal contamination, which is one of the most severe forms of environmental pollution due to its inherent toxicity and ability to infiltrate the soil, air, and water systems when present in large amounts [\[3\]](#page-9-2). Metal pollution in soils impacts biological function, leading to a slowdown in decomposition processes, which are crucial for providing the necessary nutrients for the growth of plants and organisms [\[3,](#page-9-2)[5\]](#page-9-4). Soil can naturally contain metallic elements due to pedogenetic processes, as well as being released into the environment through human activities, including vehicle emissions, energy production, industrial activities, and waste disposal [\[5\]](#page-9-4).

The study aims to critically evaluate the presence of potentially toxic elements in soil and their effects on human health, and to devise remediation processes to mitigate the growing problem of environmental pollution caused by potentially toxic metals. This research will assist municipal authorities in developing diverse methods to remediate soil contamination, with the goal of safeguarding all aspects of the environment (soil, water, and atmosphere), as well as public health, to promote a healthy and eco-friendly ecosystem [\[6\]](#page-9-5).

## **2. Materials and Methods**

## *2.1. Description of the Study Area*

The research team carried out the research in Alice township, Nkonkobe Municipality, in the Eastern Cape Province, focusing on the Alice dumpsite and the University of Fort Hare east campus as examination sites (Figure [1\)](#page-2-0). Latitudes 32◦48′24.88′′ S mark the location of the landfill. The landfill is approximately 2 km from the Happy Rest residential area, and the east campus, used as a control site, is 4 km from the disposal site. Vegetation surrounds the unpolluted site (Site 2 or D), located opposite the university barrier, providing it with effective protection from the natural environment. A, B, and C are the three sections that make up the landfill (Site 1), each with its own distinctive characteristics and waste management activities.

# *2.2. Collection and Preparation of Soil Sample*

Soil samples were taken at random at depths, ranging from 0 to 25 cm, over a period of four weeks. A clean soil auger was used to collect samples from three portions of Site 1 and Site D (reference site). The dry soil samples were collected and then placed in clean, labeled plastic bags before being sent to the laboratory for further examination [\[7\]](#page-9-6). The soil samples were ground with a pestle and mortar and then strained through a 2 mm mesh to obtain uniform and acceptable samples. Each sample was divided in half and stored at room temperature until the analysis [\[8\]](#page-9-7).

<span id="page-2-0"></span>

**Figure 1.** Presentation of a study area (landfill site, with three sampling sections A, B, & C) **Figure 1.** Presentation of a study area (landfill site, with three sampling sections A, B, & C) [\(www.](www.googleearthpro.com) (www.googleearthpro.com (accessed on 18 January 2024)). [googleearthpro.com](www.googleearthpro.com) (accessed on 18 January 2024)).

# *2.2. Collection and Preparation of Soil Sample 2.3. Elemental Analysis by SEM/EDX Spectrophotometry*

The soil samples were dried in an oven at 60 °C for 4 h to reduce moisture content and were crushed using an agate mortar into a fine powder, which was then sieved through a 0.2 mm screen. A scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) instrument was set to examine the samples. The instrument was operated at a working distance of 15 mm, with analytical conditions set at 15 kV. Count rates were adjusted to achieve more than 15–20 thousand counts per second (kcps), and the beam intensity was standardized using a clean copper (Cu) reference [\[9,](#page-9-8)[10\]](#page-9-9).

*2.3. Elemental Analysis by SEM/EDX Spectrophotometry*  load index (PLI); PLI is defined by the following equation: The concentration of metals has been determined at specific sites by using pollution

$$
\text{PLI} = \frac{\text{Ci}}{\text{Cb}}
$$

where *Ci* stands for metal concentration in investigated soil and *Cb* measures the concentration of reference value of the metal in soil  $[11, 12]$  $[11, 12]$  $[11, 12]$ 

#### $21.6$  to be adjusted to achieve more than 15–20 thousand counts per second  $\mu$ *2.4. Statistical Analysis*

 $t$  is beam international computation  $\frac{1}{2}$ The IBM Statistical Package for the Social Sciences (SPSS) 28, version 28.0, was utilized for data analysis (IBM, Armonk, NY, USA). Pearson's correlation was used to examine Hare University Research Ethics Committee (UREC) granted ethical approval for this project, with certificate number OYE021SMAP01/19/E. relationships between identified heavy metals and selected enzymatic activity. The Fort

#### where *Ci* stands for metal concentration in investigated soil and *Cb* measures the concen $t_{\rm r}$  referrence value of the metal in solution of the metal in solution of the metal in solution  $t_{\rm r}$ **3. Results**

# *3.1. Soil Morphology*

*2.4. Statistical Analysis*  Scanning electron microscopy (SEM) analyzes soil samples' surface morphology and structure. SEM images showing the topography of the soil samples from three sections of the landfill site and one control site are presented in Figures 2 and [3.](#page-3-1) All the soil samples consisted of micrometer-scale grains of varying particle sizes and non-uniform structures.<br>— The morphology and surface characteristics of the sample fragments exhibited significant

<span id="page-3-0"></span>variation due to their diverse sources, including partial oxidation of surface components, variation due to their diverse sources, including partial oxidation of surface components, variation due to their diverse sources, including partial oxidation of surface components,<br>veld wildfires, and waste incineration. The samples' surfaces appear uneven and rough in the SEM photos. The SEM images of the particles reveal irregular and asymmetrical shapes, as well as the presence of tiny pores. Pore size is crucial because it affects the permeability as well as the presence of tiny pores. Pore size is crucial because it affects the permeability<br>of the compost, which, in turn, determines the soil's water retenti[on](#page-9-9) capacity [10]. Samples displayed both large particle aggregates and a wide distribution of particle sizes.

The morphology and surface characteristics of the sample fragments exhibited significant significant



Figure 2. SEM images of soil samples collected from Site A, B, C, and D for the 1st and 2nd week.

<span id="page-3-1"></span>

**Figure 3.** SEM images of soil samples collected from Site A, B, C, and D for the 3rd and 4th week. **Figure 3.** SEM images of soil samples collected from Site A, B, C, and D for the 3rd and 4th week.

*3.2. Distribution of Major Elements*  The concentration of the the thirteen (13) is the table 13 identified elements in Table 1 and Table 1 and 1 *3.2. Distribution of Major Elements 3.2. Distribution of Major Elements*

The concentration of the thirteen  $(13)$  identified elements is tabulated in Table [1](#page-4-0) and measured in weight percentage (wt%). measured in weight percentage (wt%).



Table 1. Chemical composition of trace elements in soil samples' weight percentages (wt%).

<span id="page-4-0"></span>Note: Trace element concentration results are presented as mean values (M)  $\pm$  standard deviation (SD). \*\* Stands for detection below limit; N/A means not available. Conversion of 1.0 wt% is equal to 10,000 parts per million (ppm).

The concentrations of detected elements are presented in Table [1](#page-4-0) and were measured in weight percent (wt%) due to the elevated elemental content found in the analyzed samples. Thirteen elements were detected in soil samples through EDX analysis, namely: sodium (Na), calcium (Ca), aluminum (Al), potassium (K), magnesium (Mg), iron (Fe), silicon (Si), gold (Au), carbon (C), barium (Ba), oxygen (O), chlorine (Cl), and phosphorus (P). The spatial distribution of these components on the surface displays non-uniformity, suggesting a profoundly heterogeneous molecular structure and provenance. Elements such as Na, C, Ca, O, Fe, Mg, K, Al, and Si were detected in all soil specimens, albeit with varying levels from one sampling location to another. The soil samples manifested a notable chemical constitution, predominantly characterized by elevated concentrations of Al and Fe across all sampling sites, with Al levels ranging from  $3.78 \pm 0.23$  wt% to  $10.23 \pm 0.31$  wt%, and Fe levels oscillating between 4.14  $\pm$  0.40 wt% to 13.13  $\pm$  1.07 wt%. Despite the ubiquitous presence of Na and Mg in the samples, their abundance remained minimal, constituting less than 2.0 wt%, within the range of  $1.44 \pm 0.20$  wt% to  $0.31 \pm 0.08$  wt%. The concentrations of Ca and K were relatively scant in all soil specimens, varying from  $0.91 \pm 0.14$  wt% to  $5.56 \pm 0.47$  wt% for Ca and from  $1.32 \pm 0.25$  wt% to  $4.87 \pm 0.18$  wt% for K. Both the investigated and reference sites exhibited metal concentrations surpassing the permissible thresholds (>100 ppm) recommended by the World Health Organization (WHO), as delineated in Table [1](#page-4-0) and Figure [4.](#page-5-0) The results reported correspond with the documented findings by Shaibu et al., 2023, demonstrating heightened concentrations of Ca, Na, K, Mg, and Fe, while still adhering to the permissible ranges specified by the World Health Organization, apart from Fe levels that went beyond the acceptable limits [\[16\]](#page-9-14). The pollution load index defined the detected elements to have moderate contaminant effects on the surroundings, specifically Si and Ca, which were recorded between 1 to 3 (Appendix [A\)](#page-9-15).

<span id="page-5-0"></span>

**Figure 4.** EDX spectrum for significant elements in soil samples collected from Site A, B, C, and D for 2 the 1st, 2nd, 3rd and 4th week.

Au, Ba, Cl, and P were present in trace amounts, each constituting less than 1 wt%. These elements were not present in all samples; they were found at other sites with lower concentrations. Cl content was present during the first week of sampling at Site 1B, with a minimum concentration of  $0.84 \pm 0.11$  wt%.

Gold (Au) concentration was observed in some sampling sites but not in others, ranging from 0.26  $\pm$  0.16 wt% to 7.43  $\pm$  4.67 wt%. Meanwhile, the Ba composition was found in several locations, with recorded content ranging between  $1.72 \pm 0.47$  wt% and  $4.73 \pm 0.44$  wt%, which is less than 5 wt%. The P element was only discovered at Site 3A, with a concentration of  $0.57 \pm 0.10$  wt%.

# *3.3. Pearson Correlation Matrix*

The trace elements that were identified exhibited a robust correlation with each other as presented in Table [2.](#page-6-0) A notable positive statistically significant correlation was observed between Fe, Mg, Al, and K, while Fe correlated statistically significantly negatively with Ca concentration. A robust association among the detected metallic elements suggests their shared provenance within the studied area, with their alignments influenced by similar determining factors [\[17\]](#page-9-16). Conversely, a significant negative correlation was found between calcium (Ca) and Al, Na, Mg, and K. These data indicate that these elements originated from a shared source throughout the study area. Kadhim et al., 2023, found significant differences in metals, where metals (Ca, Mg, Na, Cu, Zn, Mn, and Fe) were significantly different ( $p < 0.05$ ) across study sites [\[18\]](#page-9-17).

<span id="page-6-0"></span>



Note: \*\* indicates a statistically significant difference at level  $p < 0.05$ ; \* means the value is statistically significant at level *p* < 0.01.

### **4. Discussion**

Soil specimens are comprised of clearly defined, heterogeneous particles exhibiting asymmetrical and porous configurations, as well as irregular fragments and elongated shapes. Scanning electron microscope (SEM) images reveal that soil specimens originating from diverse geographical locations possess unique morphologies and surface composition ratios. Clay, fine sand, and high-density fractions exhibit perforated surfaces, with textures ranging from fine to coarse. These results corroborate the discoveries made by Polakowski and colleagues (2021) [\[19\]](#page-9-18). The microscopic structure and distribution of soil aggregates have a significant influence on the biological, chemical, and physical attributes of the Earth's surface. Various human activities, such as agricultural practices, interactions, and processes involved in soil development, can introduce changes to the arrangement and constitution of soil aggregates [\[20\]](#page-9-19).

The ordering of the heavy metal elements with the highest potential for harm in this investigation were recorded in the following manner: iron (Fe)  $>$  aluminum (Al)  $>$  potassium (K) > calcium (Ca) > sodium (Na) > magnesium (Mg). An assessment was conducted to compare the levels and intensities of the identified elements at the contaminated locations against a control site. Kafle et al., 2022, reported a similar sequence of determined elements, where concentration and abundance of studied elements were found to be in the order of Si > Al > K > Fe > Ca > Na > Mg > Ti > P > S > Mn > Zn > Cr > Cd > V > Pb >  $Cu > Ni > As > Se$  [\[21\]](#page-9-20). The findings suggest that the polluted areas displayed elevated concentrations of Ca and Fe, in contrast to the reference site which showcased minimal levels. The increased presence of Fe in the soil can be linked to various factors, such as tire degradation, combustion of oil, wear of mechanical parts, and lubrication with oil. The concentration levels demonstrated variations within three specific areas of the observed vicinity [\[22\]](#page-10-0). Asafew and Chandravanshi (2021) observed the similar readings, and reported the higher concentration values of Na, Fe, Ca, Zn, and Pb obtained in the analyzed soil samples [\[23\]](#page-10-1). The variations in concentration levels at the monitored locations may be associated with land utilization, leaching processes, and adsorption [\[22\]](#page-10-0). Conversely, the reference sample exhibited higher concentrations of Na, Al, and Mg compared to the sample from the landfill site. It is of significance to highlight that all concentrations of the identified elements surpassed the recommended thresholds established by the World Health Organization (WHO) (refer to Table [1\)](#page-4-0). Recently, Kadhim et al., 2023, found the Fe in soil to have exceeded the concentration of the threshold limit recommended by WHO and FAO/WHO [\[18\]](#page-9-17).

The findings of this study reveal exceedingly high levels of metal contamination in soil (landfill sites and the control site). This study's findings corroborate the outcomes published by Abdullah et al. (2019), where they reported the metal concentrations to be elevated and recorded above the permissible limits suggested by the WHO [\[24\]](#page-10-2). Parvez and colleagues (2023) documented the elevated levels of Al, Co, Fe, and Pb in soil samples [\[17\]](#page-9-16). Meanwhile, the most substantial average levels in various soil categories for Ca, Mg, K, Na, and Mn were identified by Khan and Shah in 2023 [\[25\]](#page-10-3).

Nyika et al., 2019, reported the similar findings where the examination revealed that certain elements, such as Fe, Zn, Mn, Cu, and Ni, exhibited concentrations that exceeded the established threshold values at the majority of sampling locations, regardless of their proximity and depth relative to the landfill area [\[14\]](#page-9-21).

The study by Wanjala et al. (2019) reported different findings from this study; the Ca concentration was below WHO < 100 ppm, while Mg, Na, K, and Ni concentrations were recorded within the allowable limits set by WHO. The high values of Na were attributed to land-use practices [\[15\]](#page-9-22). In agreement with this study, Ullah et al. (2022) reported a similar finding, where polluted soil samples carried high potential toxic element concentrations, which were recorded above the permitted limits recommended by WHO [\[26\]](#page-10-4).

The increased occurrence of metallic elements in this region may be ascribed to anthropogenic endeavors, such as inadequate management of waste containing metals, incineration methods performed at the Alice landfill location, emissions from vehicles, and agricultural activities, which could also play a role in the buildup of toxic metals in the surrounding ecosystem. Agriculture plays a significant role in the local economy by providing livelihoods, ensuring food production, and generating income. Consequently, it is possible that these heavy metal contaminants originated from agricultural practices, particularly the use of fertilizers, such as P-fertilizers, which have been found to contain high levels of heavy metals. For example, superphosphate fertilizer, which contains Cd, Co, Cu, Pb, Zn, Cr, and Ni, may leach these contaminants into the soil [\[27\]](#page-10-5).

Some farmers in the region utilize livestock manures, primarily derived from poultry, cattle, and pig farming, as organic fertilizers. The application of these manures and the resulting compost to farmland is a common practice in agricultural crop production. However, these organic materials contain significant concentrations of elements such as Cu, Zn, Cd, Ni, Cr, As, Pb, and Hg, which can introduce a large number of contaminants into the soil [\[27\]](#page-10-5). Furthermore, the elevated concentration levels of metals in the soil may be attributed to the types of waste disposed of in the area, which contain these metals as

by-products of their manufacturing processes. Additionally, high levels of automobile emissions and other human activities along the highways passing through the region could contribute to the presence of these toxic substances in the environment [\[22,](#page-10-0)[24,](#page-10-2)[28\]](#page-10-6). These metals can enter the human body through the consumption of contaminated food or beverages, inhalation, or direct contact with the skin. Although they are essential elements, their elevated amounts have potential to cause damage to vital organs, such as the liver, nervous system, bladder, lungs, abdomen, skin, and reproductive systems [\[24\]](#page-10-2).

Silicon and oxygen are the most abundant elements in the Earth's crust and combine to form silicates, which are highly concentrated. Kafle et al., 2023 reported elemental concentration of Si as the most abundant (53.4%) element, followed by Al (12%) and K (11.4%) [\[21\]](#page-9-20). The level of silicon (Si) detected in our findings surpassed the typical average concentration of 29% found at the Earth's crust's outer layer, posing a potential environmental hazard to its surroundings [\[21\]](#page-9-20). Excessive amounts of silicon (Si) can lead to a condition known as silicosis, posing a significant health risk. Silica, a crystalline form of silicon, can interact with lung tissue cells and become toxic. The particles of silicates embed themselves in lung tissue, leading to the formation of nodular lesions and impairing breathing. Over time, this weakens the immune system and overall body condition [\[29,](#page-10-7)[30\]](#page-10-8). Soil dust primarily consists of silica and aluminosilicates, which have irregular shapes. Aluminosilicates with high levels of aluminum (Al), silicon (Si), and potassium (K) can originate from various sources, including the lithosphere, agricultural activities, fuel combustion, and waste incineration. Incineration processes release hazardous smoke into the environment, containing  $CO<sub>2</sub>$  and  $CH<sub>4</sub>$ . The release of these gases significantly contributes to the global aerosol mass and the accumulation of greenhouse gases in the atmosphere [\[31\]](#page-10-9).

## **5. Conclusions**

The Alice landfill has experienced insufficient management of solid waste, leading to a substantial buildup of metallic elements within the soil. Given the elevated levels of metallic elements reported in this study, the city must undertake joint efforts to mitigate pollution, promote sustainable practices, and safeguard both human health and the environment. Although, in general, the detected elements are significant in soil, they should be closely monitored to prevent potential ecotoxicity to the ecosystem. It is crucial for authorities to regularly monitor the soil and utilize soil testing methods to assess the concentrations of heavy metals present. Therefore, the study recommends sustainable farming practices, where farmers could use chemical-based natural fertilizers, pesticides, and compost. Also, the implementation of proper waste management, effective recycling techniques, and proper disposal of substances containing potential toxic elements as byproducts is imperative. Further application of novel and efficient site-specific remediation strategies, such as phytoremediation and bioremediation, can play a crucial role in this region, since these strategies could efficiently and securely rehabilitate soils and have environmentally friendly and cost-effective characteristics. Further investigation is needed to gain a more comprehensive understanding of metal dynamics in ecosystems unaffected by human activities in order to preserve soil quality. This will supply the necessary data to policymakers, which is essential for formulating efficient strategies for pollution control.

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**Data Availability Statement:** Data are available upon request.

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**Pollution Load Index Description**  $0 < PLI < 1$  Moderate contamination  $1 < PLI \leq 2$  Medium high contamination 3 < PLI ≤ 4 Relatively high contamination  $PLI \geq 5$  Extremely high pollution

<span id="page-9-15"></span>**Appendix A. The Description of Metal Pollution Load Index (PLI)**

**Conflicts of Interest:** The authors declare no conflicts of interest for this study.

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