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# Determination of Heavy Metal Levels in Soil Samples from Selected Areas in Mukuruwe-Ini Sub County, Nyeri County, Kenya

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**Abstract: Heavy metal contamination in soil is a significant environmental concern due to its potential risks to human health and ecosystem integrity. This study determined heavy metal levels in soil samples collected from two petrol stations and one control site with limited human activities in Mukuruwe-ini Sub County, Nyeri County, Kenya. The sampling sites were Muhito Petrol Station (operational for 15 years), Zinc Petrol Station (operational for 4 years), and Mugumoini, a control site away from petrol stations. Soil samples were collected from the surface layer (0–15 cm), digested using aqua regia (3:1 HCl:$HNO_3$), and analyzed by flame Atomic Absorption Spectroscopy (AAS) for lead (Pb), cadmium (Cd), chromium (Cr), zinc (Zn), and copper (Cu). Physicochemical parameters — pH, electrical conductivity, moisture content, and organic matter — were also determined. The mean Pb concentrations were 7.16 ± 0.78, 5.90 ± 0.63, and 2.09 ± 0.54 mg/kg at Muhito, Zinc, and Mugumoini respectively. Mean Cr concentrations were 16.72 ± 2.03, 5.04 ± 0.98, and 1.78 ± 0.65 mg/kg, while Cd was detected only at the petrol stations (0.13 ± 0.04 and 0.02 ± 0.003 mg/kg). Zn concentrations were 10.72 ± 1.02, 5.28 ± 0.89, and 7.44 ± 0.75 mg/kg, and Cu was 0.38 ± 0.07, 0.25 ± 0.05, and 0.62 ± 0.09 mg/kg respectively. Chromium had the highest concentration at Muhito Petrol Station (16.72 ± 2.03 mg/kg), likely due to stationary fuel combustion. All heavy metal concentrations were within WHO and KEBS permissible limits; however, regular monitoring is recommended to prevent escalation. Soil pH ranged from 5.70 to 8.30, electrical conductivity from 15 to 175 µS/cm, and moisture content was lowest at the petrol stations, indicating that contamination adversely affects soil physicochemical properties.**

***Keywords:*** *Heavy Metals, Soil Contamination, Petrol Stations, Atomic Absorption Spectroscopy, Mukuruwe-Ini, Nyeri County, Lead, Cadmium, Chromium, Zinc, Copper, Heavy Metals, Soil Samples, WHO, KEBS.*

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## I. INTRODUCTION

Heavy metal contamination of soil is a pervasive global environmental challenge, particularly in areas subject to intensive anthropogenic activities. Petrol stations represent a well-recognized category of point-source contamination, where activities such as fuel dispensing, vehicle servicing, underground tank leakage, and tire wear progressively introduce toxic metals into the surrounding soil matrix. Among the heavy metals of primary concern are lead (Pb), cadmium (Cd), chromium (Cr), zinc (Zn), and copper (Cu), which accumulate in soil and can enter the food chain through plant uptake and groundwater contamination [1].

Soil quality encompasses the physical, chemical, and biological properties that determine a soil's capacity to sustain plant and animal productivity. Contamination by heavy metals degrades this capacity by altering pH, electrical conductivity, moisture retention, and organic matter content, ultimately impacting agricultural productivity and ecosystem health [2]. In Kenya, rapid urbanization and proliferation of fuel retail infrastructure have intensified the risk of soil heavy metal contamination in peri-urban and rural towns, yet site-specific data remain scarce.

Flame Atomic Absorption Spectroscopy (AAS) is the gold standard for heavy metal quantification in environmental matrices, offering high sensitivity, specificity, and reproducibility. It operates on the principle that ground-state atoms absorb electromagnetic radiation at characteristic wavelengths, with absorbance proportional to atomic concentration in accordance with the Beer-Lambert law [3]. This study employed AAS to quantify heavy metals in soils from Mukuruwe-ini, a market town in Nyeri County, where petrol stations have expanded significantly in recent decades.

The objective of this study was to determine the levels of Pb, Cd, Cr, Zn, and Cu in soil samples from two petrol station sites and one control site with limited human activities in Mukuruwe-ini Sub County, Nyeri County, Kenya, assess their physicochemical parameters, and compare measured concentrations against WHO and KEBS permissible limits.

ISSN No:-2456-2165 https://doi.org/10.38124/ijisrt/26jul137

➢ *Specific Objectives*

The specific objectives of this study were to:

- Assess physicochemical parameters — pH, electrical conductivity, moisture content, and organic matter — in soils from the three sampling sites.
- Determine the concentrations of Pb, Cd, Cr, Zn, and Cu in soils from the two petrol station sites using AAS.
- Determine heavy metal levels in the control soil sample with minimal human activities.
- Compare measured heavy metal concentrations against WHO and KEBS permissible limits.

➢ *Justification and Significance*

Petrol stations are recognized sources of heavy metal contamination through fuel spills, exhaust emissions, lubricant leakage, and corrosion of metallic infrastructure. The proximity of petrol stations to residential areas, schools, and agricultural land in Mukuruwe-ini makes understanding soil contamination levels a public health imperative. Data generated by this study will inform environmental monitoring programs, support evidence-based policy development for soil protection, and contribute to the scientific knowledge base on heavy metal contamination in Kenyan peri-urban soils.

## II. LITERATURE REVIEW

➢ *Soil Physicochemical Properties*

Soil physicochemical parameters including pH, electrical conductivity (EC), moisture content, and organic carbon are critical indicators of soil health and contaminant mobility [2]. Soil pH governs nutrient availability and metal speciation: acidic soils tend to increase the solubility and bioavailability of most heavy metals, while alkaline conditions may precipitate metals as hydroxides or carbonates. EC reflects dissolved ion concentration in the soil solution; elevated EC in contaminated soils is diagnostic of high dissolved mineral loads [4]. Moisture content inversely correlates with contamination level in petroleum-affected soils — heavy metal contamination disrupts water balance and reduces water retention capacity [5]. Organic carbon influences metal retention through complexation, particularly for Cu and Zn [6].

➢ *Heavy Metals in Soil: Sources and Impacts*

- *Lead (Pb)*

Lead (Group IVA, Period 6; atomic number 82, atomic mass 207.2) is a naturally occurring bluish-grey metal with no known essential biological function. Its environmental burden has increased dramatically through the historical use of tetraethyl lead as a gasoline additive, industrial emissions, and paint. Lead accumulates in soil and enters the human body through ingestion, inhalation, and dermal contact. In children, it impairs physical and cognitive development; in adults, chronic exposure causes anemia, kidney damage, and neurological disorders [7].

- *Cadmium (Cd)*

Cadmium (Group IIB, Period 5; atomic number 48, atomic mass 112.4) is classified among the 'big three' heavy metal poisons alongside mercury and lead. It has no known essential biological function. Near petrol stations, Cd may originate from fuel impurities, metal infrastructure corrosion, and lubricating oils. Chronic exposure leads to kidney damage, bone demineralization (Itai-itai disease), and respiratory toxicity upon inhalation [8].

- *Chromium (Cr)*

Chromium (Group VIB, Period 4; atomic number 24, atomic mass 52.0) does not occur naturally in elemental form. Petroleum products — gasoline and diesel — contain trace chromium compounds that accumulate near fuel retail sites. Hexavalent chromium (Cr VI) is classified as a Group 1 human carcinogen by the International Agency for Research on Cancer (IARC), with prolonged exposure associated with elevated lung cancer risk [9].

- *Zinc (Zn)*

Zinc (Group IIB, Period 4; atomic number 30, atomic mass 65.4) is an essential micronutrient for plants and animals but becomes phytotoxic at elevated concentrations. Near petrol stations, it is released from tire wear, galvanized storage tanks, and engine components. Soil Zn concentrations of 70–400 mg/kg are classified as potentially phytotoxic [10]. Excessive Zn can reduce crop yields and soil fertility.

- *Copper (Cu)*

Copper (Group IB, Period 4; atomic number 29, atomic mass 63.5) is an essential micronutrient participating in hemoglobin synthesis and enzyme function. Near petrol stations, Cu originates from diesel engine components and copper-based lubricants. Cu is strongly complexed by soil organic matter and Fe/Mn oxides, concentrating in the upper soil horizons. Its solubility increases significantly below pH 5.5, enhancing bioavailability under acidic conditions [6].

➢ *Atomic Absorption Spectroscopy (AAS)*

AAS is a widely validated analytical technique for heavy metal quantification in environmental matrices. It is based on the absorption of characteristic wavelengths of electromagnetic radiation by ground-state free atoms generated by atomization of the sample in a flame (air-acetylene or nitrous oxide-acetylene). The method follows the Beer-Lambert law: absorbance is linearly proportional to the concentration of the analyte. Calibration curves constructed from standard solutions of known concentrations enable quantification of unknowns. The technique offers high specificity because each element absorbs at a unique wavelength, minimizing spectral interference. AAS is particularly suited for multi-element analysis of digested soil samples, providing reliable quantification at concentrations relevant to environmental monitoring [3].

## III. MATERIALS AND METHODS

➢ *Study Area*

The study was conducted in Mukuruwe-ini Central Ward, Mukuruwe-ini Sub County, Nyeri County, Kenya

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(catchment area: 13.93 km²). Soil samples were collected from three sites representative of contrasting levels of anthropogenic activity: two petrol stations and one control site with minimal human disturbance. The sampling sites are described in Table 1 and their locations are shown in Figures 1 and 2.

➢ *Instruments, Apparatus, and Reagents*

Instruments used included: Atomic Absorption Spectrometer with hollow cathode lamps specific to each element, a conductivity meter, an analytical balance, hot plate, muffle furnace, and desiccator. Apparatus included: 250 mL conical flasks, 100 mL and 250 mL beakers, watch glasses, reagent bottles, spatulas, and Whatman No. 42 filter paper. Chemicals used were: concentrated hydrochloric acid, concentrated nitric acid, and distilled/deionized water for aqua regia digestion; hydrated copper(II) sulphate, hydrated zinc(II) sulphate, lead(II) nitrate, cadmium sulphate, and hydrated chromium(III) chloride for standard solution preparation.

➢ *Sample Collection*

Composite soil samples were collected from five points within each of the two petrol stations and from the control site (Mugumoini). At each sampling point, 100 g of soil was excavated to a depth of 0–15 cm using a hoe and scooped with a sterilized spatula. Sub-samples were mixed thoroughly in sterilized aluminium foil to form a composite. Triplicate 100 g sub-samples were drawn from each composite, individually wrapped in aluminium foil, labeled, and sealed in polythene bags for transport to the Department of Chemistry, University of Nairobi. Samples were analyzed within one day of collection.

➢ *Physicochemical Parameter Determination*

- *Soil pH*

Two grams of soil was weighed and dissolved in 15 mL of distilled water in duplicate for each sample. The suspension was stirred magnetically and pH measured using a calibrated pH meter after equilibration.

- *Electrical Conductivity*

Two grams of soil was dissolved in 10 mL distilled water and stirred. The conductivity meter was calibrated using a KCl standard solution of known conductivity. EC was measured in duplicate for each sample and recorded in µS/cm.

- *Moisture Content*

Two grams of soil was weighed in a pre-tared weighing tin and dried in an oven at 105–110°C to constant weight. After cooling in a desiccator, the tin was re-weighed. Moisture content (%) = [(wet mass − dry mass) / dry mass] × 100.

- *Organic Carbon*

Two grams of oven-dried soil was placed in a pre-weighed crucible and ignited in a muffle furnace for 2 hours. After cooling, the crucible was re-weighed. Organic matter content was calculated from the difference in mass before and after ignition (loss on ignition method).

➢ *Soil Digestion*

One gram of air-dried, sieved (2 mm) soil was accurately weighed into a 250 mL conical flask. Twenty-five millilitres of aqua regia (3:1 HCl:$HNO_3$, v/v) was added and the mixture heated on a hot plate under a fume hood until near-dryness to eliminate nitrogenous compounds. The procedure was repeated for each sample in duplicate and a reagent blank was prepared concurrently. After cooling, the digestate was filtered through Whatman No. 42 filter paper, transferred quantitatively to a 50 mL volumetric flask, diluted to the mark with deionized water, and stored in labeled reagent bottles pending AAS analysis.

➢ *Standard Solution Preparation*

Stock solutions of 1000 ppm were prepared for each metal: Zn from 1.1160 g $ZnSO_4 \cdot 7H_2O$; Cu from 0.9923 g $CuSO_4 \cdot 5H_2O$; Pb from 0.4037 g $Pb(NO_3)_2$; Cd from 0.4731 g $CdCl_2$; and Cr from 1.3074 g $CrCl_3 \cdot 6H_2O$ — each dissolved in 1000 mL deionized water. Working standards of 100, 50, 10, 5, 1, 0.5, and 0.01 ppm were prepared by serial dilution for calibration curve construction.

➢ *AAS Analysis*

Digested samples were aspirated directly into the AAS flame (air-acetylene). Each metal was analyzed using its specific hollow cathode lamp at the characteristic absorption wavelength shown in Table 2. Calibration curves were constructed by plotting absorbance against standard concentration for each metal. Sample concentrations were determined by interpolation from the respective calibration curve. A one-way ANOVA was applied to assess significant differences in heavy metal concentrations across the three sampling sites; the F-statistic and p-value were used to evaluate inter-site differences.

## IV. RESULTS AND DISCUSSION

➢ *Physicochemical Parameters*

The physicochemical results for the three sampling sites are presented in Table 3. Muhito Petrol Station recorded the highest electrical conductivity (175 ± 3 µS/cm), reflecting a significant burden of dissolved minerals consistent with prolonged petroleum-related contamination. Zinc Petrol Station had intermediate EC (80 ± 2 µS/cm), while Mugumoini control site showed minimal EC (15 ± 5 µS/cm), confirming low dissolved heavy metal loads.

Moisture content was inversely related to contamination level: Muhito recorded the lowest moisture (5.40 ± 0.40%) and Mugumoini the highest (13.99 ± 0.28%), consistent with the well-documented ability of heavy metals to disrupt soil water balance and reduce water retention capacity [5]. Organic matter was also lowest at Muhito (0.4894 ± 0.023 g), consistent with progressive degradation of soil quality by heavy metal accumulation.

Soil pH ranged from 5.70 (Mugumoini) to 8.30 (Muhito). The WHO recommended pH range for soil is 6.5–

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8.5 and KEBS specifies 5.5–9.5. All three sites fell within these permissible limits. The elevated pH at Muhito is consistent with the alkalizing effect of petroleum product degradation and the presence of dissolved carbonates and bicarbonates from metallic infrastructure corrosion.

➢ *Heavy Metal Concentrations*

The mean heavy metal concentrations at each sampling site and comparison with WHO and KEBS permissible limits are presented in Tables 4 and 5 respectively.

- *Zinc*

Zn concentrations ranged from 5.28 ± 0.89 mg/kg (Zinc Petrol Station) to 10.72 ± 1.02 mg/kg (Muhito Petrol Station), with the control site recording 7.44 ± 0.75 mg/kg. Muhito had the highest Zn level, attributable to tire wear deposition, corrosion of galvanized fuel storage tanks, and Zn-containing fuel additives. The relatively elevated Zn at Mugumoini may reflect atmospheric deposition or water runoff from nearby roads. All values were well below WHO (300 mg/kg) and KEBS (200 mg/kg) permissible limits, indicating no current phytotoxic risk [10].

- *Lead*

Pb concentrations decreased with distance from petroleum activity: 7.16 ± 0.78 mg/kg at Muhito, 5.90 ± 0.63 mg/kg at Zinc Petrol Station, and 2.09 ± 0.54 mg/kg at Mugumoini. The gradient clearly demonstrates the influence of petrol station activity on Pb accumulation. Sources include residual leaded fuel from historical use, lead-containing lubricant additives, and lead-based paint on station infrastructure. All concentrations remained well within WHO (100 mg/kg) and KEBS (30 mg/kg) permissible limits, though the Mugumoini value suggests background contamination via water runoff requiring monitoring [7].

- *Cadmium*

Cd was detected only at the two petrol stations: 0.13 ± 0.04 mg/kg at Muhito and 0.02 ± 0.003 mg/kg at Zinc Petrol Station. At Mugumoini, Cd was below the AAS detection limit (BDL). Sources of Cd near petrol stations include lubricating oils, tyre rubber compounds, and corroded metallic components. Despite being among the most toxic heavy metals, both detected concentrations were far below WHO (3 mg/kg) and KEBS (5 mg/kg) limits, indicating no immediate health risk. However, even sub-threshold Cd exposure warrants vigilance given its long biological half-life and renal accumulation [8].

- *Copper*

Notably, Cu was highest at the Mugumoini control site (0.62 ± 0.09 mg/kg) compared to Muhito (0.38 ± 0.07 mg/kg) and Zinc Petrol Station (0.25 ± 0.05 mg/kg). This elevated control-site Cu suggests other anthropogenic sources unrelated to petrol stations — most likely the intensive application of copper-based fungicides in nearby agricultural areas, or deposition of metal scraps and organic residues. All three values were far below WHO (100 mg/kg) and KEBS (300 mg/kg) permissible limits [6].

- *Chromium*

Cr showed the steepest site gradient, with Muhito recording the highest concentration (16.72 ± 2.03 mg/kg), Zinc Petrol Station intermediate (5.04 ± 0.98 mg/kg), and Mugumoini the lowest (1.78 ± 0.65 mg/kg). Cr contamination near petrol stations is primarily driven by stationary fuel combustion, chromium-containing fuel system additives, and vehicle exhaust emissions. Although all values were within WHO (100 mg/kg) and KEBS (50 mg/kg) limits, the Muhito value is the highest of all metals at that site, and given the carcinogenic classification of Cr(VI), regular monitoring is particularly important [9].

➢ *Inter-Site Comparison and Statistical Analysis*

A one-way ANOVA confirmed statistically significant differences ($p < 0.05$) in concentrations of Pb, Cd, and Cr between the three sampling sites, with Muhito Petrol Station consistently showing the highest values. The pattern is consistent with the longer operational history of Muhito (15 years) compared to Zinc Petrol Station (4 years), confirming that duration of anthropogenic activity is a key driver of soil heavy metal accumulation. Cu was the only analyte with an inverse pattern (control > petrol stations), suggesting its primary source in this area is agricultural rather than petroleum-related.

## V. CONCLUSIONS

This study demonstrated measurable heavy metal contamination in soils surrounding petrol stations in Mukuruwe-ini Sub County, Nyeri County, with Muhito Petrol Station (15-year operation) consistently showing the highest heavy metal concentrations. The principal conclusions are:

All detected heavy metal concentrations (Pb, Cd, Cr, Zn, Cu) were within WHO and KEBS permissible limits at all three sampling sites. However, chromium was the most elevated metal at Muhito (16.72 ± 2.03 mg/kg), and cadmium was detectable only at petrol station sites, warranting precautionary attention.

Physicochemical parameters clearly reflected contamination gradients. Muhito Petrol Station showed the highest EC (175 µS/cm), alkaline pH (8.30), lowest moisture content (5.40%), and lowest organic matter (0.4894 g), while the Mugumoini control site showed the most favorable soil quality indicators.

Duration of petrol station operation significantly influences contamination levels. The 15-year Muhito station showed substantially higher metal burdens than the 4-year Zinc station across all analytes, underscoring the cumulative nature of petroleum-associated soil contamination.

Regular environmental monitoring is essential. Although current concentrations are within permissible limits, the upward contamination gradient relative to the control site indicates ongoing accumulation that could eventually exceed safe thresholds without intervention.

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## RECOMMENDATIONS

- Regular assessment of heavy metal concentrations in soils around petrol stations should be institutionalized to ensure levels remain within permissible ranges and trends are detected early.
- Community sensitization programs targeting people living and working near petrol stations should be implemented to raise awareness of heavy metal exposure risks and preventive measures.
- Petrol station infrastructure should be regularly inspected and upgraded to prevent underground storage tank leakages and surface fuel spills, which are primary vectors of soil heavy metal contamination.
- Health surveillance programs targeting workers at petrol stations and residents in proximity should be established to monitor for early indicators of heavy metal poisoning, particularly for Cd and Cr.
- Future studies should extend analysis to include additional metals (Hg, Ni, As) and investigate vertical metal distribution profiles (below 15 cm) to assess leaching risks to groundwater.

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**FIGURES AND TABLES**

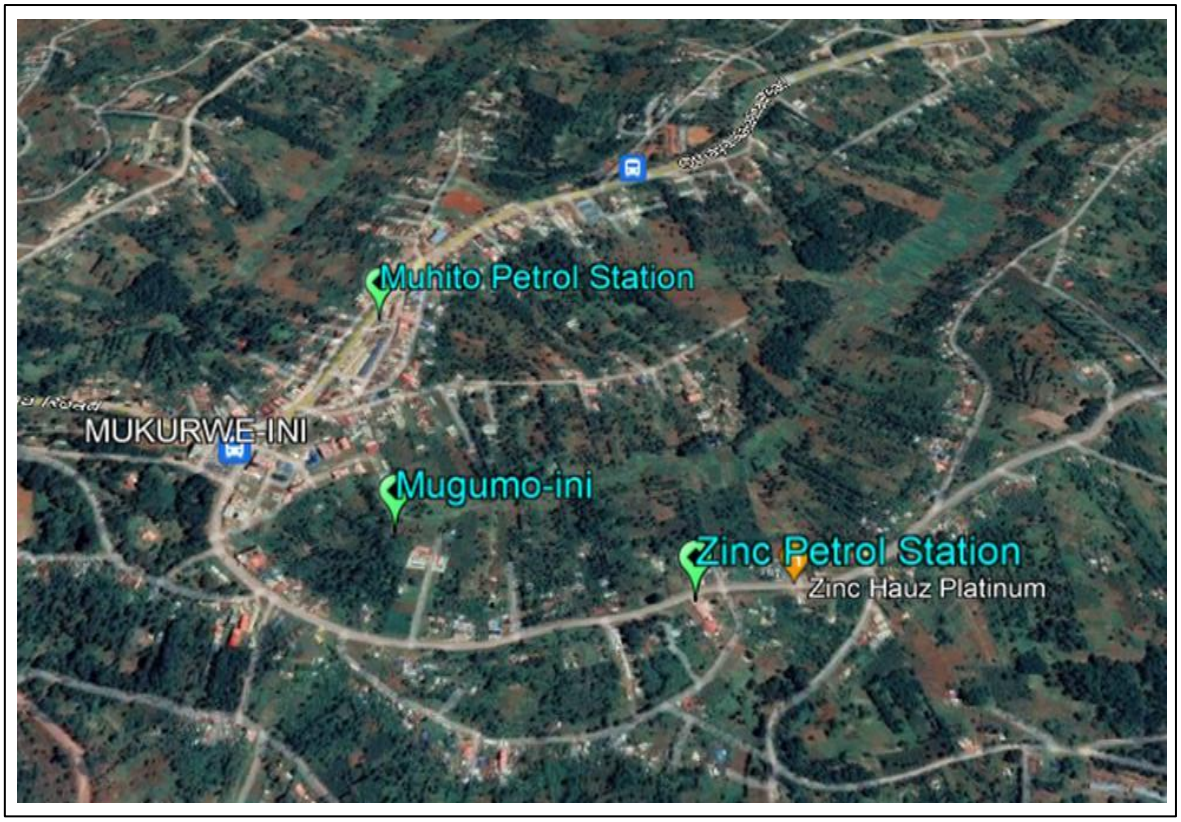


Fig 1 Aerial Map Showing the Three Sampling Sites: Muhito Petrol Station, Zinc Petrol Station, and Mugumoini Control Site, Mukuruwe-ini, Nyeri County (Source: Google Maps).


Fig 2 Administrative Map of Mukuruwe-Ini Sub County, Nyeri County, Showing the Location of the Study Area.

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Fig 3 Digestion of Soil Samples Using Aqua Regia (3:1 HCl:$HNO_3$) on a Hot Plate Under Fume Hood Conditions at the Department of Chemistry, University of Nairobi.

Table 1 Description of the Three Soil Sampling Sites in Mukuruwe-Ini Central Ward, Nyeri County.

| Site | Local Name | Coordinates | Human Activities |
|---|---|---|---|
| 1 | Muhito | Lat: 0°33′32.74″S Lon: 37°3′9.12″E | Petrol station (operational for 15 years) |
| 2 | Zinc | Lat: 0°33′49.46″S Lon: 37°3′24.29″E | Petrol station (operational for 4 years) |
| 3 | Mugumo-ini | Lat: 0°33′46.72″S Lon: 37°3′8.00″E | No human activities — control site away from petrol stations |

Table 2 AAS Instrument Parameters, Characteristic Wavelengths, and Limits of Detection (LOD) for the Five Analyzed Heavy Metals.

| Element | Wavelength (nm) | Flame / Gases | LOD (mg/L) | Lamp Type |
|---|---|---|---|---|
| Zinc (Zn) | 213.9 | Air / Acetylene | 0.01 | Hollow cathode |
| Copper (Cu) | 324.7 | Air / Acetylene | 0.01 | Hollow cathode |
| Lead (Pb) | 217.0 | Air / Acetylene | 0.01 | Hollow cathode |
| Cadmium (Cd) | 228.6 | Air / Acetylene | 0.01 | Hollow cathode |
| Chromium (Cr) | 359.0 | Air / Acetylene | 0.01 | Hollow cathode |

*LOD = Limit of Detection. All Metals Analyzed Using Hollow Cathode Lamp in Air/Acetylene Flame.*

Table 3 Physicochemical Parameters (Mean ± SD) for the Three Sampling Sites.

| Sampling Site | pH | Electrical Conductivity (µS/cm) | Moisture Content (%) | Organic Matter (g) |
|---|---|---|---|---|
| Muhito — Petrol Station | 8.30 ± 0.04 | 175 ± 3 | 5.40 ± 0.40 | 0.4894 ± 0.023 |
| Zinc — Petrol Station | 7.79 ± 0.02 | 80 ± 2 | 10.78 ± 0.35 | 0.5316 ± 0.034 |
| Mugumoini — Control Site | 5.70 ± 0.03 | 15 ± 5 | 13.99 ± 0.28 | 0.5583 ± 0.040 |

*WHO Recommended Soil pH: 6.5–8.5. KEBS: 5.5–9.5. All Sites within Permissible pH Ranges.*

Table 4 Mean Heavy Metal Concentrations (mg/kg, Mean ± SD) in Soil Samples from the Three Sampling Sites.

| Sampling Site | Pb (mg/kg) | Cu (mg/kg) | Zn (mg/kg) | Cd (mg/kg) | Cr (mg/kg) |
|---|---|---|---|---|---|
| Muhito Petrol Station | 7.16 ± 0.78 | 0.38 ± 0.07 | 10.72 ± 1.02 | 0.13 ± 0.04 | 16.72 ± 2.03 |
| Zinc Petrol Station | 5.90 ± 0.63 | 0.25 ± 0.05 | 5.28 ± 0.89 | 0.02 ± 0.003 | 5.04 ± 0.98 |
| Mugumoini (Control) | 2.09 ± 0.54 | 0.62 ± 0.09 | 7.44 ± 0.75 | BDL | 1.78 ± 0.65 |

*BDL = Below Detection Limit (< 0.01 mg/L). All Concentrations within WHO and KEBS Permissible Limits.*

Table 5 WHO and KEBS Permissible Limits (mg/kg) for Heavy Metals in Soil.

| Metal | WHO Permissible Limit (mg/kg) | KEBS Permissible Limit (mg/kg) |
|---|---|---|
| Zinc (Zn) | 300 | 200 |
| Copper (Cu) | 100 | 300 |
| Chromium (Cr) | 100 | 50 |
| Lead (Pb) | 100 | 30 |
| Cadmium (Cd) | 3 | 5 |

Sources: WHO (2021) Voluntary Guidelines for Sustainable Soil Management; KEBS Standards for Soil Quality.