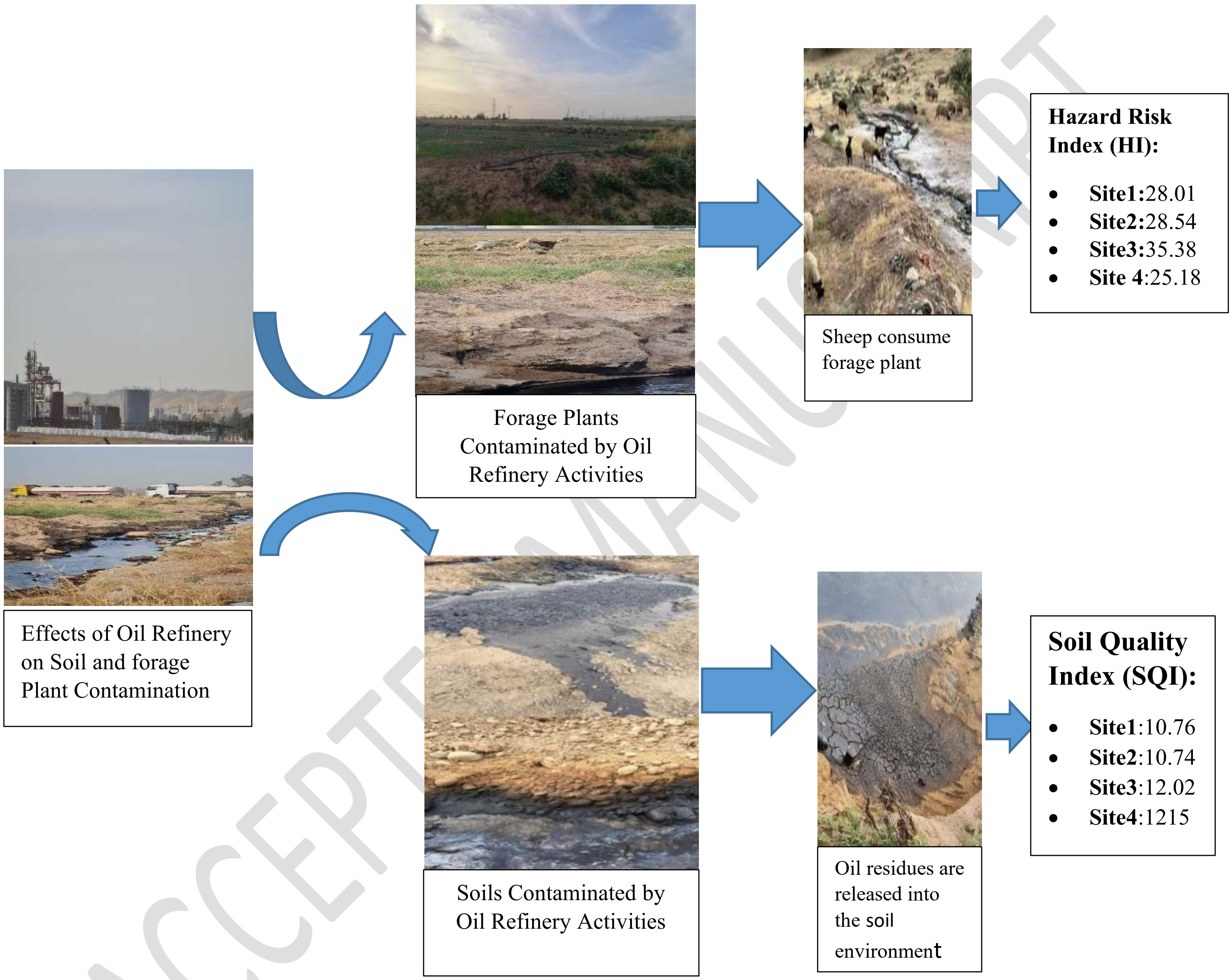
Integrated Assessment of Soil Quality Indices and Heavy Metal-Associated Hazard Risks in Area Impacted by Oil Refinery Residues

Graphical Abstract



Integrated Evaluation of Soil Quality Indices and Heavy Metal-Associated Hazard Risks in Area Impacted by Oil Refinery Residues

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Abstract

Oil refineries pollute nearby soils and forage plants with heavy metals, which can represent a potential threat to conservation and to the health of the population. The oil refinery discharges along Gwer Road in Erbil, Iraq, have deposited along a residual crude oil path in places of high pollution. The purpose of the present study was to evaluate the accumulation levels of heavy metals in soil and forage plants, evaluate the quality level for soil by using the soil quality index (SQI), assess the bioaccumulation factor from the plant (BCF), and estimate non-carcinogenic health risk through hazard quotients (HQ) and total health risk index (HI). Soil and four forage plant species were collected from four sites, and heavy metals were assessed and analyzed using X-ray fluorescence (Rigaku NEX CG). The soils were slightly acidic to neutral (pH 6.22 7.97) with variable electrical conductivity, organic matter, and texture, indicating moderate to poor fertility. All metals were above Environmental Baseline Standards (EBS), with the highest values of Cr (86.76 $mg.kg^{-1}$), Ni (67.8 $mg.kg^{-1}$), Cu (76.64 $mg.kg^{-1}$), Zn (73.38 $mg.kg^{-1}$), Cd (1.85 $mg.kg^{-1}$), and Pb (21.7$mg.kg^{-1}$). These results demonstrate that there is a great correlation between soil degradation and metal accumulation, it is possible to locate the hotspots of contamination, and present the valuable recommendations of the industrial soil management and a monitoring program.

Keywords: Heavy metals, Oil-contaminated soil, Forage plants, Soil Quality Index (SQI), Hazard risk, Geographic Information System (GIS) map.

1. Introduction

Refineries have significant environmental impacts and release effluents, resulting in serious ecological problems. The various activities within the oil industry, extraction, transportation, refining, and consumption, lead to the pollution of air, soil, and water, degradation of land, and even deforestation. Oil-related operations not only displace specific populations and cause changes in land value, but they also generate improperly maintained toxic waste that threatens the health of those who live nearby. Thus, the oil industry needs streamlined management and strict environmental regulations to reduce such impacts. (Akashraj and Mourwel, 2020).

The oil refinery processes generate sustainable negative externalities, such as toxic gases, carbon dioxide, carbon monoxide, sulfur, and nitrogen oxide emissions. Water footprints in refineries are also high, and the effluent discharged by refineries increases water pollution. The discharges of the midstream and downstream processes include volatile oil, leaks, and oily discharges that contaminate the air, water, and soil. These contaminants lead to decreased soil structure, compaction, and decreased permeability, which eventually changes the physicochemical balance of the soil. Oil refineries yield byproducts that are usually toxic in nature, i.e., they contain metals like lead, cadmium, and mercury, which result in malignancy, kidney damage, and lung damage. Additional water discharge- more is known to be a significant route of heavy metal pollution. (Fattahi et al.,2020; Ra et al.,2021; Samilia et al.,2023 and Ugboma et al.,2020).

Crude oil hydrocarbons have been observed to cause changes in soil physicochemical characteristics, which ultimately affect pH, aeration, nutrient availability, and microbial activity and community structure. where soil texture might remain stable, the ratio of sand, silt, and clay can be affected by contamination. The addition of crude oil raises soil pH and decreases electrical conductivity levels, resulting in lower soil fertility. The Soil Quality Index (SQI) methodology applied in the Niger Delta was effective in identifying the level of degradation, which can serve as a guideline to environmental risk assessment and remediation priorities. (Devatha et al., 2019; Kokah et al.,2019;Okafor et al., 2022). Industrial activities are a significant contributor to soil contamination, especially in arid and semi-arid conditions where there is little rainfall, and the soil experiences significant evaporation of water; the toxic elements are accumulated instead of attenuating naturally. Investigations adjacent to oil refining plants have revealed high levels of heavy metals such as chromium (Cr), nickel (Ni), copper (Cu), zinc (Zn), cadmium (Cd), and lead (Pb) that have a great effect on the physicochemical properties of soil and the poor quality of the soils. (Ayobami,2022; Li et al.,2024; Miletić et al.,2025; Tsamos et al.,2024).

The presence of heavy metals in contaminated soils is a great hazard to the food chain because metals may be passed down to plants and then on to animals and humans. Plant-eating animals are inebriated by eating contaminated pasture, and their predators store these toxins. Biomagnification poses a threat to the ecosystem because it decreases biodiversity, hinders the growth of plants and the activity of microbial organisms, which further disturbs nutrient cycling. (Bayata, 2020). The persistence and bioavailability of the metals in semi-arid climatic conditions make an oil refinery a serious ecological threat. (Shahzad et al., 2024; Zheng et al., 2024).

The Biological Accumulation Coefficient (BAC) is the capacity of a plant to accumulate metals relative to the concentration of the metal in the soil, therefore the degree of efficiency of the plant in accumulating and retaining heavy metals. Bioaccumulation is affected by the availability of metals, soil properties and plant species. The higher levels of toxic metals in the leaves and forage species in urban or industrialized areas can be dangerous to humans and animals. Oil is often considered one of the most serious threats to human health (Danjuma and Abdulkadir, 2018; Mohammed et al., 2024).In addition, environmental risk assessment research is evolving towards the necessity of incorporating soil quality indicators, plant bioaccumulation studies, and human health risk indicators including hazard quotient (HQ) and hazard index (HI) with the help of GIS-based spatial analysis to identify the hotspots of contamination and provide information to guide sustainable remediation efforts (Yi et al., 2024; Hendawy et al., 2025).

Oil refineries are a major cause of soil and subsoil pollution, and this is mainly attributed to the production of toxic substances and the use of heavy metals produced during their refining processes, storage, and disposal of their products. The semi-arid regions, like those in northern Iraq, have a low amount of precipitation and high rates of evaporation, and the toxic metals accumulate and concentrate in soils as they are not washed off. This is the first thorough evaluation of the combined effects of refinery operations on soil quality and related risk issues of hazards at this refinery location by examining the soil physicochemical properties, heavy metal concentrations (Cr, Ni, Cu, Zn, Cd, Pb), and the Soil Quality Index (SQI), and bioconcentration analysis in forage plants. The combination of soil quality measurement, plant bioaccumulation, and human health risk analysis in this study gives a more comprehensive evaluation of environmental degradation caused by the refinery in semiarid areas. Additionally, hazard risks were assessed on daily intake, hazard quotients (HQ), and total hazard index (HI). The semiarid area impacted by the refinery was identified as the hotspot of contamination using GIS-based spatial analysis, which is a scientific tool of risk-based decision-making, addressing complex issues, and sustainable environmental management of refinery-impacted semi-arid areas provides critical information to be used as a remediation tool and sustainable management of refinery-impacted semi-arid areas.

Research Questions

According to the context presented above, the following research questions are addressed in the study:

1. What are the refinery industrial activities of the semi-arid environments concerning the physicochemical properties of the soil?

2. What are the content, geographical distribution, and ecological hazard of heavy metals (Cr, Ni, Cu, Zn, Cd, Pb) in soils around the refinery site?

3. How much do polluted soils cause the bioaccumulation of heavy metals in forage plants and their transfer?

4. What are the human health risks in relation to the daily consumption, hazard quotient (HQ), and the hazard index (HI)?

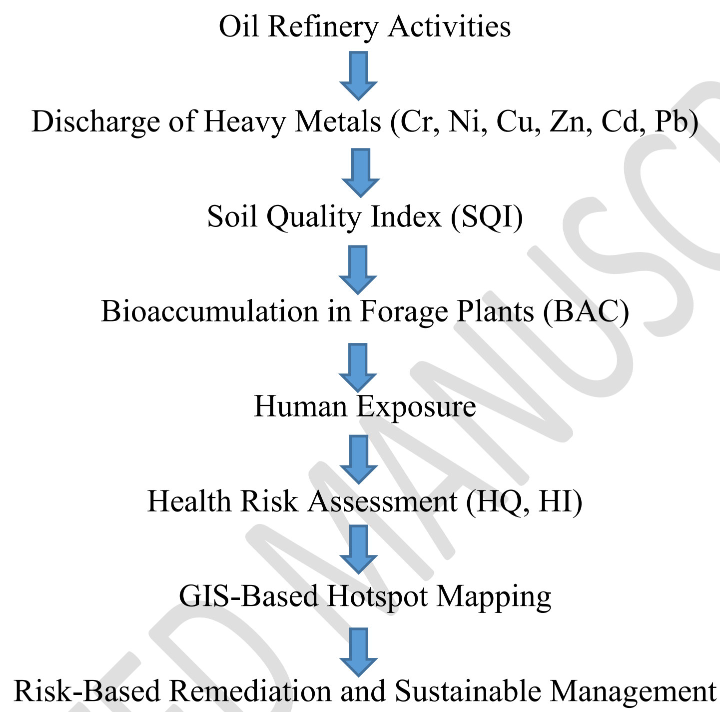


Figure 1. Theoretical framework that is used to identify the relation between refinery activities, soil contamination processes, environmental and hazard risk assessment

2. Materials and Methods

2.1. The Study Area Description

The study region was carried out in the Gwer Road, approximately 15 km southwest of the city of Erbil, in the Kurdistan Region, Northern Iraq, and at an elevation of 410-420 m above sea level. A GPS device was used to record the sampling coordinates (Table 1). Gwer is found in the Erbil Governorate with a latitude of about 35° 30′N and a longitude of 43°25′E. The soils of this area are calcareous, and most of them are based on the limestone and dolomite deposits, which are typical of the general geology of Erbil. Topsoil is usually 1-2 % organic matter and slightly alkaline because of the carbonate minerals. Gwer has a semi-arid climate that has Mediterranean conditions, hot and dry summers, and cool and wet winters. It has an average annual temperature of 12 °C during winter and 43 º C during the summer, with annual precipitation of 350 - 450 mm, with the rainy season mainly from November to April. The climatic and soil properties influence the natural plants as well as the distribution of pollutants in this region. There are several refinery facilities in the study area, with some of them being actively producing under 10,000 to 100,000 liters of petroleum products each day, and others have not been utilized in almost a decade. (Aziz et al., 2022; Aweez et al., 2021; Khudhur and Khudhur, 2015; Mirza and Ahmed, 2023).

Table 1: GPS reading of the study sites

Sites	**Latitude N**	**Longitude E**
Site 1	36° 8'32.10"	43°46'32.18"
Site 2	36° 8'31.10"	43°46'30.78"
Site3	36° 8'30.03"	43°46'29.39"
Site4	36° 8'29.09"	43°46'25.04"

2.2. Soil and Plant Sampling and Characterization

Soil and plant samples were collected in April 2024 in an oil refinery waste-contaminated site near Gwer Road, about 15 km southwest of Erbil city. The spatial variation was investigated by taking soil samples at positions of 0, 25, 50, and 100 m along the contamination gradient of waste-discharging stations. At each site, numerous subsamples were collected and amalgamated into four composite samples for each soil and plant species in order to characterize sites properly while minimizing analytical load. A satellite image of the study area is shown in Figure 1. Soil samples were stored in labeled plastic bags and air-dried, oven-dried at 105°C for 24 h, and sieved with a stainless-steel sieve of mesh size 106 µm to remove pebbles, large particles, roots, and debris. Soil pH was determined with a HANNA EDGE pH meter, organic matter content was measured using the Walkley-Black method, and particle size distribution by the Bouyoucos hydrometer approach; cation exchange capacity (CEC) was determined with 1N sodium acetate followed by 1N ammonium acetate. Soil sieves were homogenized with a porcelain mortar and pestle, placed in polyethylene containers, and analyzed for Cr, Ni, Cu, Zn, Cd, and Pb with the Rigaku NEX CG X-ray fluorescence spectrometer. A plant sample was collected from four forage type locations about 1 m distant from the leaching sites. Twenty-five samples (three replicates of each site) were collected 1-2 cm above the soil to avoid contamination, stored in sterile plastic bags tagged with a label, and transported to the Laboratory. plants were subjected to oven drying at 65 °C for 24 hours, subsequently crushed, and analyzed for heavy metals via XRF Rigaku NEX CG X-ray fluorescence (XRF) spectrometer. A Geographic Information System (GIS) was utilized for spatial analysis, visualization, and mapping of contamination patterns. (Aweez et al., 2021; Aziz et al., 2022; Khudhur and Khudhur, 2015; Meshabaz, 2024; Mirza and Ahmed, 2023).

Figure 2: Temporal Evolution of the Study Area as Shown in Satellite Images

2.3. CCME Soil Quality Index (SoQI)

The CCME (Canadian Council of Ministers of the Environment) soil quality index is a tool that prioritizes the assessment of relative risk by comparing the level of pollutant concentration to soil quality standards. The SoQI of polluted sites was determined based on three parameters: F1 (Scope), F2 (Frequency), and F3 (Amplitude) (Cepa, 2007; Bapeer and Darwesh, 2023).

$$F_1 = \frac{Number\ of\ failed\ contaminants}{Total\ number\ of\ contaminants} \times 100 \ldots (2.1)$$

$$F_2 = \frac{Number\ of\ failed\ tests}{Total\ number\ of\ tests} \times 100 \ldots\ldots\ldots\ldots (2.2)$$

$$Excursion_{-1} = \frac{Failed\ Test\ Vaue}{Guideline} - 1\ .\ .\ .\ .\ .\ . (2.3)$$

In instances where the test value must not be below the guideline:

$$Excursion_{-2} = \frac{Guideline}{Failed\ Test\ Value} - 1 \ldots\ldots (2.4)$$

$$ase = \frac{\sum_{i=1}^{n} Excursion\ i}{Number\ of\ failed\ tests} \ldots\ldots\ldots\ldots\ldots (2.5)$$

$$F_3 = \frac{ase}{0.01.ase + 0.01} \ldots\ldots\ldots\ldots\ldots (2.6)$$

$$SoQI = 100 - \frac{\sqrt{{F_1}^2 + {F_2}^2 + {F_3}^2}}{1.732} \ldots\ldots\ldots (2.7)$$

Table 2. Concern levels of the soil quality index

Site classes or level of Concern	Soil Ranking Categories of the SQI
Very low contamination	90-100
Low contamination	70-90
Medium contamination	50-70
High Contamination	30-50
Very high contamination	0-30

2.4. Bioconcentration Factor (BCF)

Displays the effectiveness of the plant in absorbing heavy metals in the soil and retaining them in the tissues. It is the ratio of the content of heavy metals in plant tissues (root, stem, or leaves) to the content of the soil. It is computed as follows (Aweez et al.,2023).

$$BCF = \frac{C\_plant}{C\_Soil}$$

$C\ \_plant\ = heavy\ metal\ concentration\ in\ plant\ tissues\ (stems\ and\ leaves)$

$C\ \_soil = \ heavy\ metal\ concentration\ in\ soil$

2.5. Daily Metal Consumption (DMC)

The daily metal consumption was evaluated using the formula

$$DMC\ (mg/day) = C\ factor \times C\ metal \times D\ food\ intake \times B\ average\ weight$$

$C\ metal = concentration\ of\ metals\ in\ forage\ (mg/\ kg)$

$D\ food\ intake = daily\ amount\ of\ forages\ consumed\ (kg/day)$

$B\ average\ weight = average\ body\ weight\ of\ sheep(kg)$.

$C\ factor = conversctor\ to\ convert\ green\ plant\ mass\ to\ dry\ weight$

The dry matter intake (DIM) of forage was 1.51 kg per sheep, which corresponds to an average body weight of 45 kg per sheep. A conversion factor of 0.085 was utilized to convert the green plant mass into dry weight. (Meshabaz, 2024; World Health Organization, 1996)

2.6. The Health Risk Index (HI)

Evaluates the severity of heavy metal risks by comparing the oral reference dosage with daily metal intake.

$$HQ = \frac{DMC}{RFD}$$

$DMC = daily\ metal\ consumption\ (mg\ kg^{-1}\ day^{-1})$

$RFD = oral\ reference\ dose\ for\ each\ heavy\ metal\ (mg\ kg^{-1}\ day^{-1})$

(Younis,2023)

Interpreting Hazard Index (HI)Values

The Hazard Index (HI) provides an overall measure of potential health risks from exposure to heavy metals. The interpretation of HI values is as follows:

$HI < 1\ Acceptable\ or\ negligible\ risk$

$HI = 1\ Threshold\ of\ concern$

$HI > 1\ Potentialth\ risk;\ remediation\ or\ intervention\ required$

The oral reference dose (RFD) is defined as the maximum daily intake that an individual can consume without significant risk of adverse consequences throughout their lifetime. The oral reference dose (RFD) values for cadmium (Cd) 0.001, chromium (Cr) 1.5, and zinc (Zn)0.3 mg kg^{-1} day $^{-1}$, respectively. The reference dosage (RFD) for lead (Pb) is 0.0035 mg kg^{-1} day $^{-1}$, whereas for copper (Cu) it is 0.04 mg kg^{-1} day $^{-1}$. The nickel concentrations were 0.02 mg kg^{-1} day $^{-1}$.

A Hazard Quotient (HQ) greater than 1 indicates that the health of the consumer population has been affected or that it poses a carcinogenic risk (World Health Organization, 1996).

The Total Hazard Index (HI) is obtained by summing the HQs of all assessed metals for each sample category:

$$HI = \sum HQ\ i$$

(Meshabaz, 2024; Younis,2023; World Health Organization, 1996).

2.7. Interpolation

The modelling of spatial variability of heavy metal concentrations was performed using the Inverse Distance Weighting (IDW) interpolation technique in GIS. IDW assumes that close points will share similar values, as compared to distant points. The concentration at a point not sampled is estimated by a weighted average of the nearest sample points, with the nearest point having a greater weight and the most distant point having a lesser weight. The method will allow methodically estimating the local differences in metal levels and locating pollution hotspots within the area of study. (Basnet et al., 2019; Mirza and Ahmed, 2023).

2.8. Statistical Analysis

To determine the significance of site and distance, SPSS statistical tests were performed to determine the interaction. All samples of heavy metal samples were subjected to a one-way factorial design experiment. A probability value below 0.05 ($p<0.05$) is considered to be statistically significant. The Pearson correlation coefficient was utilized to evaluate the association between heavy metals in the soil and those in the shoot. (Aweez et al., 2021; Mirza and Ahmed, 2023).

3. Result and Discussion

3.1. Effect of oil refinery residues on some of the physicochemical properties of the study sites

Table 3 presents the effects of oil refinery residues on the physical and chemical properties of the study sites ($p<0.05$).

The highest values of measured properties were pH 7.94 (Site4), Electrical Conductivity (EC) 218.07 dS/m (Site3), Cation Exchange Capacity (CEC) 45.45 meq/100g (Site4), Organic Matter (O.M) % 27.88 (Site 1), Calcium Carbonate $CaCO_3$% 27.88 (Site3), respectively. The lowest values were pH 6.44 (Site1), Electrical Conductivity (EC) 44.66 dSm^{-1} (Site1), Cation Exchange Capacity (CEC) 22.32 $meqL^{-1}$(Site1), Organic Matter (O.M) % 22.55 (Site 4), Calcium Carbonate $CaCO_3$ %3.86 (Site1), respectively. This result indicates that this change in soil pH (6.44 -7.94) suggests that there was an overall transition to a slightly alkaline environment as the distance to the crude oil source increased. The situation when the pH values are lowered near the contamination source due to the presence of acidic hydrocarbons and by the partial oxidation of petroleum compounds. On the other hand, the higher pH at more distant positions may be explained by the buffer of calcium carbonate and the accumulation of alkaline salts. High EC values at the contaminated sites indicate moderate to high salinity in the soil, probably referring to the dissolved salts and ionic compounds formed as a result of crude oil residues. Soluble ions, especially those of Ca^{2+} and $Mg^{2+,}$ build up, leading to the rise in salinity, which can also cause the rise in CEC. High CEC means increased soil ability to retain and exchange nutrients, but in the case of contaminated soils, this ability can also be used to retain the heavy metal cations. The comparatively large proportion of organic matter can be related to the inability of petroleum-based hydrocarbons to be degraded by microorganisms. Contamination with crude oil causes toxic, hydrophobic, and anaerobic environments, which prevent microbial activity and suppress the breakdown of organic residues, which changes the major physicochemical and physiological characteristics of soil. These results are in line with those that found the degradation of soils is caused by crude oil contamination and anthropogenic sources, including industrial effluents, agricultural runoffs, and disposal of municipal waste. These operations lead to the deposition of heavy metals (e.g., Cr, Cd, Pb, Hg, and As), leading to changes in the chemical and physical properties of the soil. High levels of heavy metals disrupt the structure of the soil by inhibiting the porosity, water-retention capacity, and aggregate stability, leading to the exacerbation of erosion and a deficiency of nutrients in the plants. (Angon et al., 2024; Mirza and Ahmed, 2023).

Table 3. Effect of oil refinery residues on some of the physicochemical properties of the study soil

Site	Location(m)	pH	EC dSm^{-1}	CEC $meqL^{-1}$	OM%	$CaCO_3$ %	Texture Name
Site 1	-	6.44 a	218.07 a	22.32 a	7.95 a	22.33 b c	SL
Site 2	25.00	7.15 b	194.73 b	33.33 b	6.73 a	22.55 b	SCL
Site3	50.00	7.93 b	94.66 c	25.65 ab	6.86 b	27.88 a	SCL
Site4	100.00	7.94 a	44.66 d	45.45 a	3.86 b	23.87 c	CL

3.2. Effect of oil refinery residues on heavy metals concentration in soils and soil quality index at the study sites

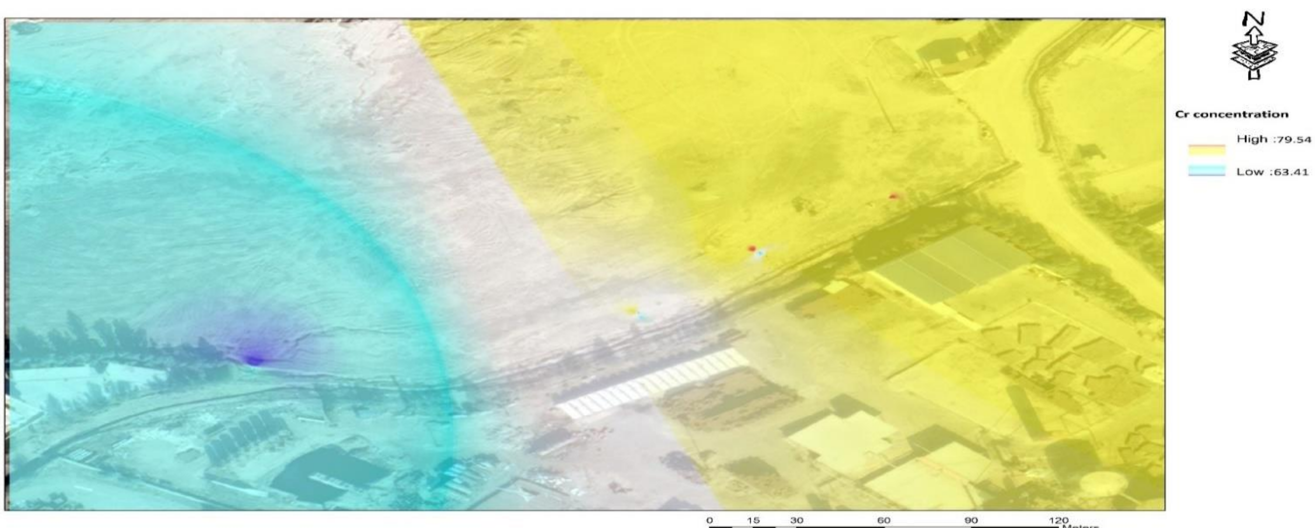
Table 4 presents the effects of oil refinery residues on heavy metal concentration and soil quality index of the study sites ($p<0.05$).

The highest values of heavy metal concentration were Chromium (Cr) 79.54 $mg.kg^{-1}$ Site 2, Nickel (Ni) 59.08 $mg.kg^{-1}$ Site1, Copper (Cu) 63.24 $mg.kg^{-1}$ Site1, Zinc (Zn) 72.41$mg.kg^{-1}$ Site1, Cadmium (Cd)1.85 $mg.kg^{-1}$ Site1, Lead (Pb)19.29 $mg.kg^{-1}$ Site4, and Soil Quality Index (SQI) 12.15 Site 4, respectively.

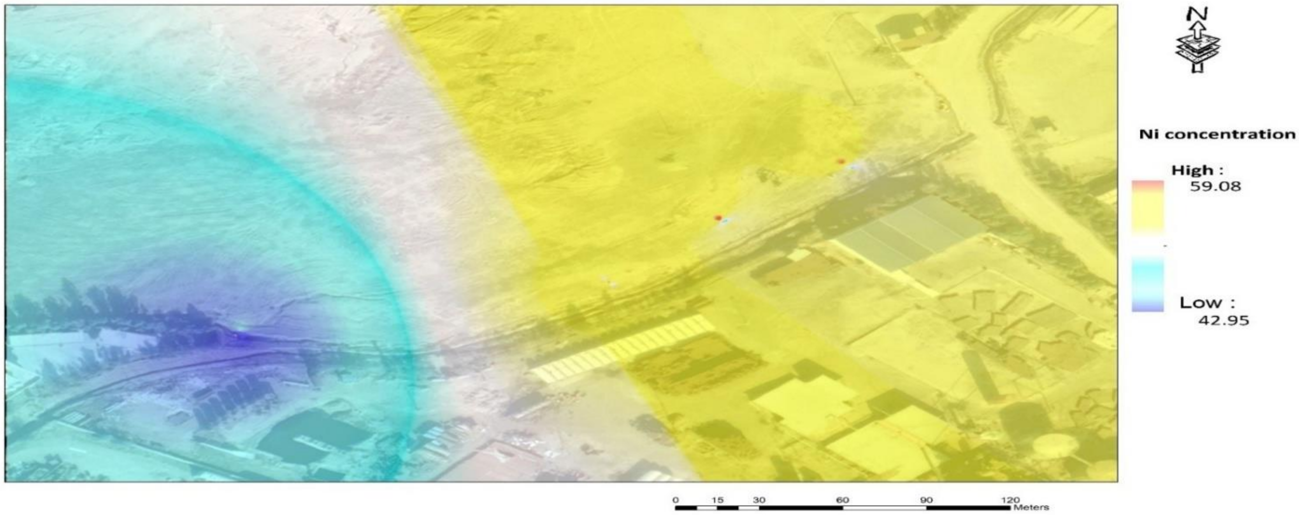
The lowest values were Chromium (Cr) 63.41 mg.kg^{-1} Site 4, Nickel (Ni) 42.9 5 mg.kg^{-1} Site 4, Copper (Cu) 53.34 mg.kg^{-1} Site 4, Zinc (Zn) 52.41 mg.kg^{-1} Site 4, Cadmium (Cd)1.41 mg.kg^{-1} Site 4, Lead (Pb)10.26 mg.kg^{-1} Site3, and Soil Quality Index (SQI) 10.74 Site3, respectively. The results indicate that the concentrations of heavy metals in soils in those areas that were near the oil refinery were much greater than those in distant areas, which means that there was a high spatial variability among the sites of the study. Such properties are attribute by a complex of factors, such as deposition of metals carrying particulates in the atmosphere due to refinery emissions, pipeline leakage, surface runoff, and runoff of contaminated sediments, and preferential retention of metals in soils depending on the content of organic matter, cation exchange capacity and soil texture. Also, the topographical differences and local hydrological routes could have also led to the non-uniform distribution of metals within the study area. There was significant contamination of the soil in the study area as all measured metals were higher than the Environmental Baseline Standards (EBS) reported by Hama and Darwesh (2019), which include Cr: 23, Ni: 34, Cu: 42, Zn: 23.8, Cd: 1.1, and Pb: 8.5 mg. kg $^{-1}$. The high Soil Quality Index (SQI) values also indicate extreme soil degradation, especially around industrial areas. The spatial distribution maps (Figures 3.1-3.6) produced with IDW interpolation in QGIS are used to demonstrate more concentrated areas of high metal content (yellow) and low metal content (blue), which show a clear image of localized accumulation of heavy metals on the topsoil layer (0-30 cm). The spatial patterns observed are probably due to combustion of fossil fuels, atmospheric deposition, pipeline leakage, industrial emissions, and surface runoff. The contaminated site analysis indicated that regions near the refinery were the most contaminated, with the metal levels decreasing with the distance to the source of pollution because of a lesser deposition intensity and dispersion effects. The findings agree with the findings of previous studies that reported heavy metal enrichment, localized pollution, and low soil quality due to the activities of refineries. Localized contamination and soil degradation, as evidenced by high concentrations of Cr, Ni, Cu, Zn, Cd, and Pb, especially in soils around the refinery, and poor Soil Quality Index (SQI) values, confirm that industrial processes are a major threat to ecological and public health. (Akporido et al., 2018; Useh and Dauda, 2018; Mirza and Ahmed, 2023; Bankole et al., 2024).

Table 4. Effect of oil refinery residues on the heavy metal concentration in soils and soil quality index at the study sites

Metal	Site1	Site2	Site3	Site4
Cr	70.24 a	79.54 b	64.31b	63.41c
Ni	59.08 a	55.69 b	47.30 b	42.95 ab
Cu	63.24 b	53.86 b	62.89 b	53.34a
Zn	72.41 a	65.14 b	56.30 a	52.41b
Cd	1.85 a	1.73 b	1.51a	1.41b
pb	17.64 b	10.42 a	10.26 a	19.29 a
SQI	10.76	10.74	12.02	12.15



3.1.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Ni concentration
High :
59.08
Low :
42.95
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90
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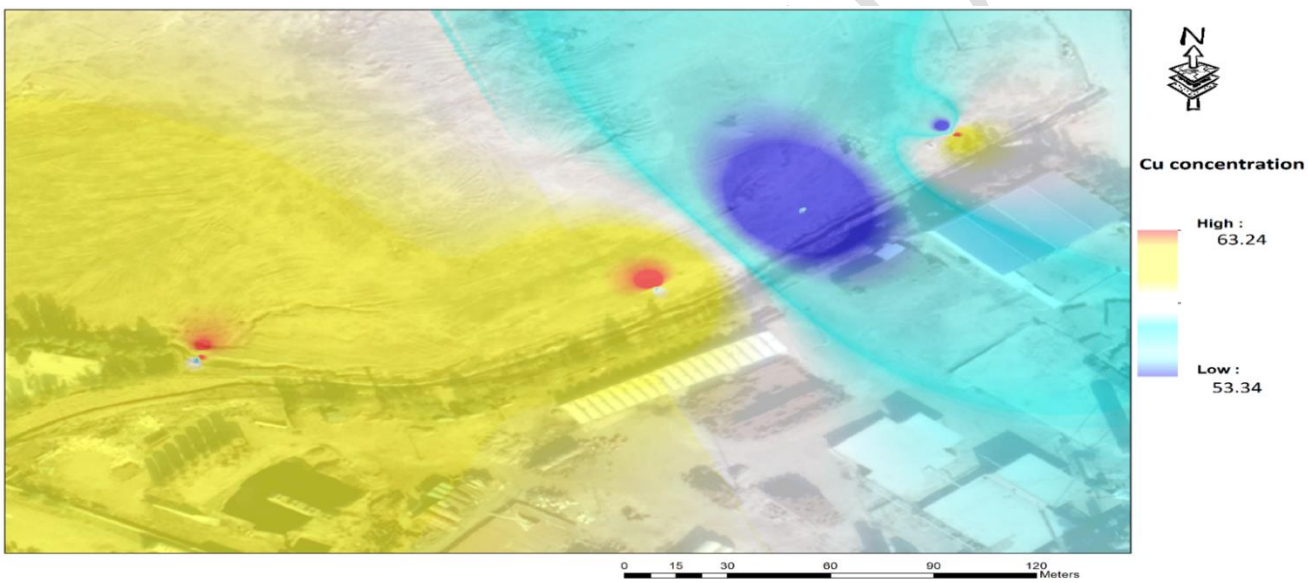
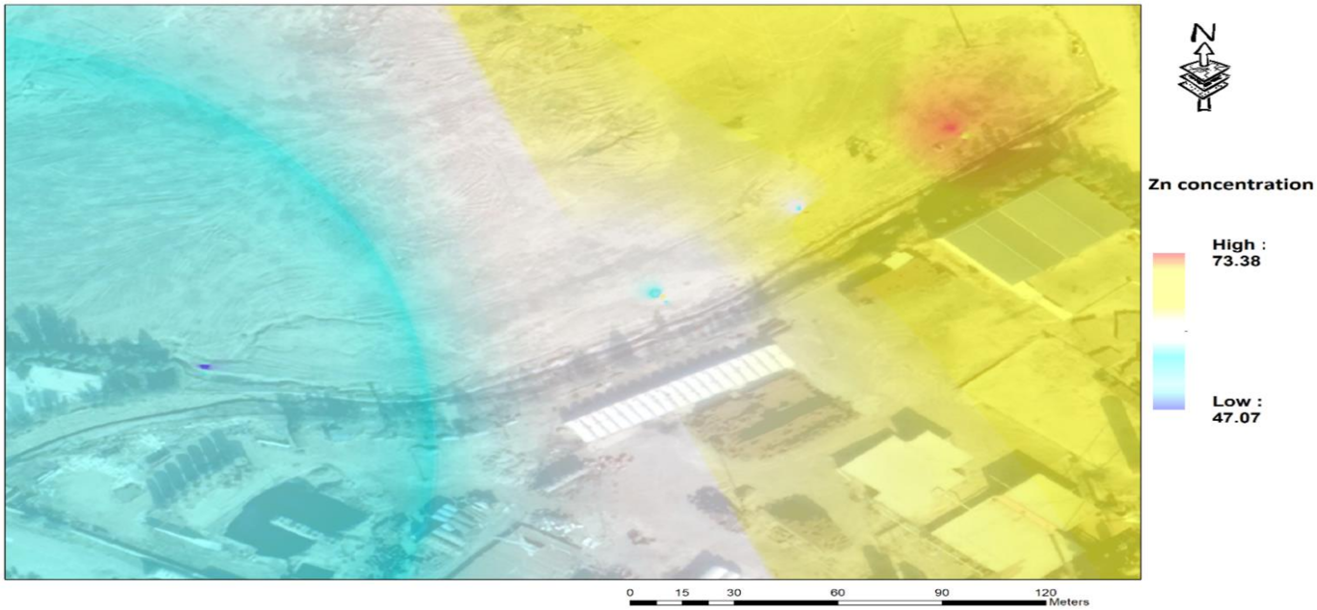
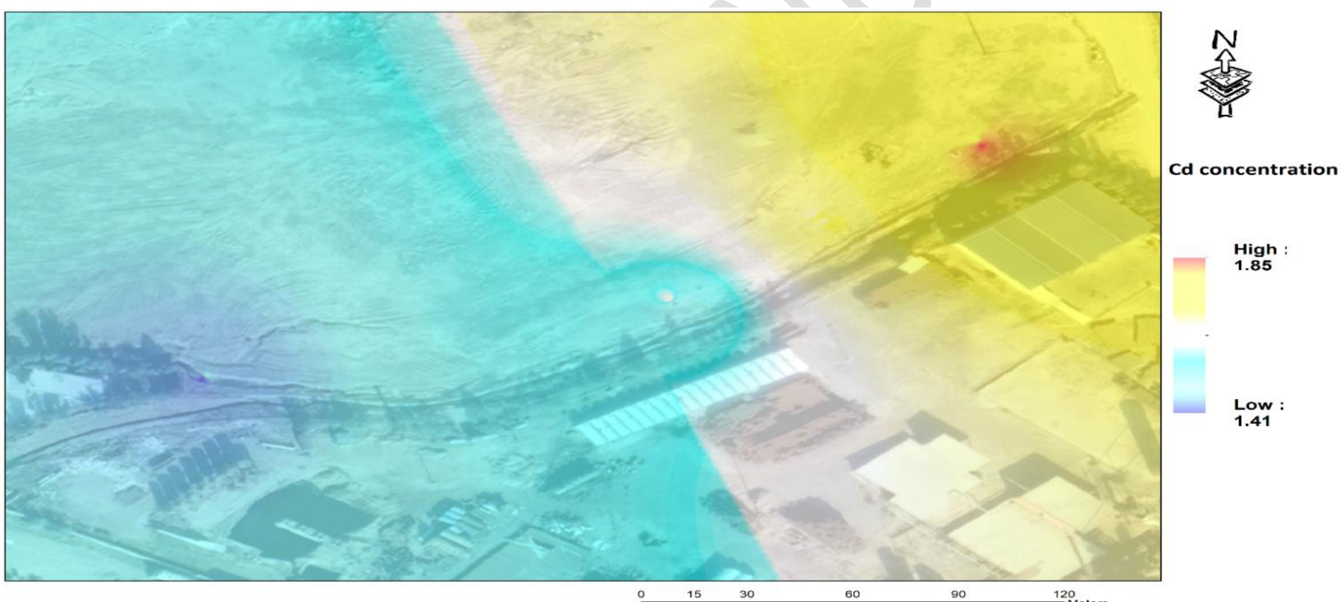
3.2.


N
Cu concentration
High :
63.24
Low :
53.34
0
15
30
60
90
120
Meters

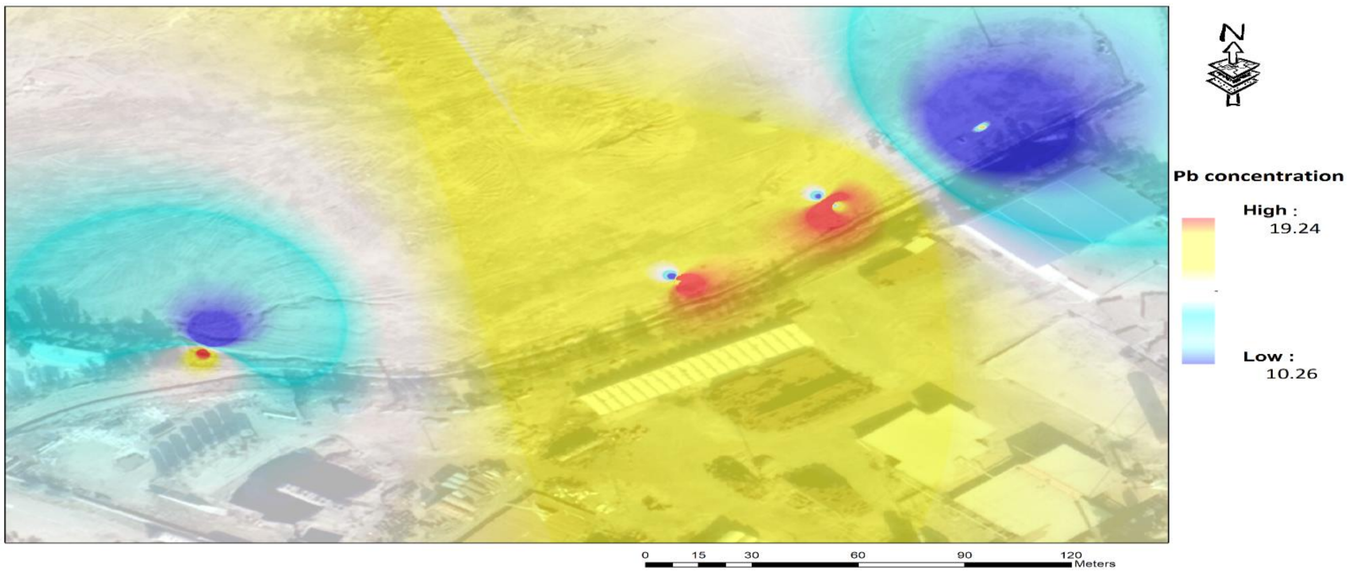
3.3.


N
Zn concentration
High : 73.38
Low : 47.07
0 15 30 60 90 120 Meters

3.4.


N
Cd concentration
High : 1.85
Low : 1.41
0 15 30 60 90 120 Meters

3.5.



3.6.

Figure (3.1), (3.2), (3.3), (3.4), (3.5), (3.6) Spatial distribution of Chromium (Cr), Nickel (Ni), Copper (Cu), Zinc (Zn), Cadmium (Cd), and Lead (Pb) Concentrations in soil, visualized using GIS mapping, with areas exceeding safe thresholds highlighted as contamination hotspots. Higher concentration in yellow and lower concentration in blue.

3.3. Effect of Oil Refinery Residues on Heavy Metal Concentration in Plants at the study sites

Table 5 present effects of oil refinery residues on heavy metal concentration in plants at the study sites ($p<0.05$)

The highest values of heavy metal concentration in the soil part were Chromium (Cr) 47.21 $mg.kg^{-1}$ Forage Plant 3, Nickel (Ni) 43.16 $mg.kg^{-1}$ Forage Plant 1, Copper (Cu) 65.60 $mg.kg^{-1}$ Forage Plant 3, Zinc (Zn) 75.20 $mg.kg^{-1}$ Forage Plant 3, Cadmium (Cd)47.48 $mg.kg^{-1}$ Forage Plant 1, Lead (Pb) 43.16 $mg.kg^{-1}$ Forage Plant 3, respectively. The highest values of heavy metal concentration in the shoot part were Chromium (Cr) 2.97 $mg.kg^{-1}$ Forage Plant 4, Nickel (Ni) 48.49 $mg.kg^{-1}$ Forage Plant 1, Copper (Cu) 42.79 $mg.kg^{-1}$ Forage Plant 3, Zinc (Zn) 116.75 $mg.kg^{-1}$ Forage Plant 3, Cadmium (Cd) 2.29 $mg.kg^{-1}$ Forage Plant 3, Lead (Pb) 25.14 $mg.kg^{-1}$ Forage Plant 3 respectively. The lowest values of heavy metal in the soil part were Chromium (Cr) 33.19 $mg.kg^{-1}$ Forage Plant 1, Nickel (Ni) 35.54 $mg.kg^{-1}$ Forage Plant 3, Copper (Cu) 51.67 $mg.kg^{-1}$ Forage Plant 2, Zinc (Zn) 29.80 $mg.kg^{-1}$ Forage Plant 2, Cadmium

(Cd) 3.31 $mg.kg^{-1}$ Forage Plant 3, Lead (Pb) 26.41 $mg.kg^{-1}$ Forage Plant 4, respectively. The lowest values of heavy metal concentration in the shoot part were Chromium (Cr) 1.82 $mg.kg^{-1}$ Forage Plant 1, Nickel (Ni) 24.99 $mg.kg^{-1}$ Forage Plant 4, Copper (Cu) 27.00 $mg.kg^{-1}$ Forage Plant 1, Zinc (Zn) 29.80 $mg.kg^{-1}$ Forage Plant 2, Cadmium (Cd) 1.43 $mg.kg^{-1}$ Forage Plant 1, Lead (Pb) 1.43 $mg.kg^{-1}$ Forage Plant 4 respectively. This result indicates that heavy metals in the soils and in forage plants are a significant source of oil refinery residues. The concentration of metals (Cr, Ni, Cu, Zn, Cd, Pb) in soils near the refinery was much higher, creating localized hot spots indicative of the spatial effect of the industrial emissions, surface runoff, and accidental spillage. Even though forage plants can absorb the metals in the contaminated soils, most of them are stored in the roots, implying that there is root-mediated sequestration as a natural defense mechanism that restricts, although does not eliminate, the translocation of metals to the shoot. Such a selective accumulation within roots not only enables the survival of plants through contaminated soils, but it also leads to long-term soil contamination, disrupting microbial activity and cycling of nutrients. All results were above the permissible limits established by the WHO (1996) for plant consumption, including Cr, Ni, Cu, Zn, Cd, and Pb (1.30, 10, 10, 0.60, and 2.0 $mg. kg^{-1}$), which indicated severe contamination and potential health hazards of consuming forage plants in such locations. Figure 4 supports this result, as Pearson correlation analysis identified a positive relation between soil heavy metals and their concentrations in shoots, indicating direct transport of metals from soil to plant tissues. Particularly concerning were the highest levels of Cd and Pb, due to their high mobility, potential for bioaccumulation, and toxicity, which may threaten ecosystem stability and food safety. The results are similar to the earlier studies that showed that refinery activities lead to enrichment of heavy metals, localized soil degradation, and ecological risks. Soil and plant contamination combination creates a considerable environmental and human health threat, which underscores the need for constant monitoring, cleanup operations, and cautious forage utilization in the contaminated areas. (Alsafran et al.,2021; Akporido et al., 2018; Bankole et al., 2024; Odiyi et al.,2020).

Table 5. Effect of oil refinery residues on heavy metal concentration in the plants at the study sites

plant name	Cr soil	Cr shoot	Ni soil	Ni shoot	Cu soil	Cu shoot	Zn soil	Zn shoot	Cd soil	Cd shoot	Pb soil	Pb shoot
Forage plant 1	33.19 a	1.82 a	43.16 a	48.49 a	53.33 c	27.00 ab	182.62 a	48.43 a	5.60 a	1.43 a	41.64 ab	18.03 a
Forage plant 2	43.75 a	1.84 a	41.03 a	31.85 ab	51.67 b	32.83 ab	43.44 b	29.80 a	3.38 a	2.15 a	27.12 b	18.79 b
Forage plant 3	47.21 a	1.98 a	35.54 b	30.16 b	65.60 a	42.79 ab	75.20 ab	116.75 ab	3.31 a	2.29 a	47.48 a	25.14 b
Forage plant 4	43.20 a	2.97 a	42.67 a	24.99 b	60.58 b	34.30 a	77.96 b	112.56 b	4.71 a	1.53 a	26.41 a	16.94 b

	Cr	Ni	Cu	Zn	Cd	Pb	Cr1	Ni	Cu	Zn
Cr	1	0.086	.620**	-0.177	0.008	0.161	0.025	0.045	.532**	-0.215
Ni		1	-.479*	-0.088	.552**	0.27	-0.052	.745**	-.448*	-0.15
Cu			1	0.108	0.036	0.224	-0.03	-0.299	.585**	-0.323
Zn				1	.616**	0.267	-0.188	0.367	-0.333	-0.109
Cd					1	0.258	0.039	.688**	-0.388	-0.331
Pb						1	-.623**	.424*	-0.055	-0.202
Cr							1	-0.318	0.293	.608**
Ni								1	-0.289	-0.351
Cu									1	0.206
Zn										1
Cd										
Pb										

Figure 4. Correlation is significant at the 0.01 level (2-tailed)

3.4. Effects of Heavy metal Concentration in Plants on the Bioconcentration Factor and Daily Consumption in the study sites

Table 6 presents the effects of heavy metal concentration in plants on the bioconcentration factor and plant daily intake in the study sites($p<0.05$)

The highest values of bioconcentration factor were chromium (Cr) 0.07 forage plant 4, Nickel (Ni)1.12 Forage plant 1, Copper (Cu) 0.65 Forage plant 3, Zinc (Zn)1.55 Forage plant 3, Cadmium (Cd) 0.69 Forage plant 3, Lead (Pb) 0.69 Forage plant 2, respectively. The highest values of plant daily intake were chromium (Cr) 0.01 forage plant 1,2,4, Nickel (Ni) 0.14 forage plant 1, Copper (Cu) 0.12 forage plant 3, Zinc (Zn) 0.33 forage plant 3, Cadmium (Cd) 0.01 forage plant 2,3, Lead (Pb) 0.07 forage plant 3, respectively. The lowest values of bioconcentration factor were chromium (Cr) 0.04 forage plant 2, forage plant 4, Nickel (Ni) 0.07 forage plant 4, Copper (Cu) 0.51 forage plant 1, Zinc (Zn) 0.27 forage plant 1, Cadmium (Cd) 0.26 forage plant 1, Lead (Pb) 0.43 forage plant 1, respectively. The lowest values of plant daily intake were Chromium (Cr) 0.01 forage plant 3, Nickel (Ni) 0.07 forage plant 4, Copper (Cu) 0.08 forage plant 1, Zinc (Zn) 0.08 forage plant 2, Cadmium (Cd) 0 Forage plant 1,4, Lead (Pb) 0.05 forage plant1, 2, 4, respectively. The findings indicate that the level of heavy metal accumulation is highly dependent on soil pollution and the absorption capacity of plants, as shown by the differences in the bioconcentration factor (BCF) and daily metal consumption (DMC) among sites and forage species. Sites that were nearest to the oil refinery (Sites 1 and 3) had greater amounts of soil metal that translated into greater BCF and DMC values in the related forage plants. Conversely, distanced sites (Site 4) were less contaminated and had less metal accumulated, which means that the exposures in distant locations are counteracted by dilution, dispersion, and decreased bioavailability. The largest BCF of metals studied were found in Zn and Ni, which were considered more mobile and bioavailable in contaminated soils. On the other hand, the BCF of Cr and Pb was lower, possibly because of their poor solubility and high affinity with soil particles, which restricts their movement to plant tissues. Differences in the metal uptake in plant species were also observed. Forage 1 and Forage 2 more effectively accumulated Cu and Zn, and Forage 4 accumulated Pb and Cd preferentially. The cause of these differences is probably species-specific differences, such as root morphology, rhizosphere chemistry, and intrinsic metal tolerance mechanisms. The results align with the previous research, indicating that pH, Cd, and Cr in crude oil-polluted soils are concentrated in plants, which exposes them to more risks of exposure due to ingestion and bioaccumulation (Chukwuma et al., 2019). Salih et al. (2025) reported significant heavy-metal concentration in plants cultivated around industries, and this supports the role of soil-plant transfer as an essential route of human and animal exposure.

Table 6. Effects of heavy metal concentration on the bioaccumulation factor, plant daily intake, at the study site.

plants	Cr		Ni		Cu		Zn		Cd		Pb	
	BCF	DITM	BCF	DITM	BCF	DITM	BCF	DITM	BCF	DITM	BCF	DITM
Forage plant 1	0.05	0.01	1.12	0.14	0.51	0.08	0.27	0.14	0.26	0	0.43	0.05
Forage plant 2	0.04	0.01	0.74	0.09	0.64	0.09	0.69	0.08	0.64	0.01	0.69	0.05
Forage plant 3	0.04	0.01	0.7	0.09	0.65	0.12	1.55	0.33	0.69	0.01	0.53	0.07
Forage plant 4	0.07	0.01	0.58	0.07	0.57	0.1	1.44	0.32	0.32	0	0.64	0.05

3.5. Effects of Heavy metal Concentration of plants on the Hazard Quotient Index (HQ) and Hazard Index (HI) in the study sites

Table 7 presents the effects of heavy metal concentration of plants on the Hazard Quotient Index (HQ) and Hazard Index (HI) in the study sites($p<0.05$)

The highest HQ and HI values were Chromium (Cr) 0.01 forage plant 4, Nickel (Ni) 6.9 forage plant 1, Copper (Cu) 3.04 forage plant 3, Zinc (Zn)1.11forage plant 3, Cadmium (Cd) 6.51 forage plant 3, Lead (Pb) 20.43 forage plant 4, and HI 35.38 forage plant 3, respectively. The lowest HQ and HI values were Chromium (Cr) 0 forage plant 1,2,3, Nickel (Ni) 3.55 forage plant 4, Copper (Cu) 1.92 forage plant1, Zinc (Zn) 0.28 forage plant 2, Cadmium (Cd) 4.08 forage plant 1, Lead (Pb)13.77 forage plant 4, and HI 25.18 forage plant 4, respectively. This result indicates that the health risk assessment is determined on the basis of hazard quotient (HQ) and hazard index (HI) value shows that there are significant non-carcinogenic risks that are noticed when forage plants are grown beside the oil refinery. Pb, Ni, and Cd had the highest HQ values, with the total HI reaching a peak of 35.38 in forage plant 3, which is above the safe level of 1. The HQ and HI values were lowest, but still showed continued risk, indicating that every site had been exposed to some extent to heavy metals by the average of forage intake. The identified difference in HQ and HI among sites and plant species can be explained by a few factors. The contamination of the soil by heterogeneous elements, especially near the refinery, led to sites with high metallic concentrations. This is the reason why there were higher risk values at certain locations, particularly forage plant 3 at Site 3. Additionally, the behavior of each species in uptake is a major factor in the risk, with plants like Forage 1 and Forage 2 accumulating more metal. were more efficient in accumulating metals like Ni, Cu, and Cd than other species. The physical properties of the soils, such as pH, the proportion of organic matter in the soil, and cation exchange capacity, were likely to influence metal bioavailability, and closeness to the refinery enhanced exposure through a concentrated source of contaminants. The findings highlight the importance of both the environmental and biological aspects of heavy metal accumulation in forage plants and that the product of soil contamination, plant uptake, and site proximity generally causes high HI values at each site. The results suggest a severe and chronic health risk to humans and animals that eat such plants, emphasizing that heavy metals around oil refineries are a major non-carcinogenic threat (Al Safran et al., 2021; Chukwuma, 2019; Odiyi et al., 2020; Khan et al., 2018; Morsy, 2020). This result is in line with these findings. Yi et al. (2024) found that the soils around industrial plants, including automobile manufacturing factories, were heavily toxic metal-contaminated, which led to the appearance of HQ and HI values exceeding the level of safe limits. which also proved the role of industrial contamination in increasing health risks. To mitigate these risks, this study emphasizes the importance of continuous environmental monitoring, ongoing remediation methods, and phytoremediation techniques in reducing metal exposure and preserving the environment's integrity and population health.

Table 7. Effects of heavy metal concentration of plants on health index (HQ), Hazard risk index (HI)

Plants	**Cr (HQ)**	**Ni (HQ)**	**Cu (HQ)**	**Zn (HQ)**	**Cd (HQ)**	**Pb (HQ)**	**Hazard Risk Index (HI)**	**Risk level**
Forage plant 1	0	6.9	1.92	0.46	4.08	14.65	28.01	High
Forage plant 2	0	4.53	2.33	0.28	6.13	15.27	28.54	High
Forage plant 3	0	4.29	3.04	1.11	6.51	20.43	35.38	High
Forage plant 4	0.01	3.55	2.44	1.07	4.34	13.77	25.18	High

3.6. Priority classification table based on soil quality index and hazard risk

Table 8 presents prioritization based on the Soil Quality Index (SQI) and Hazard Index (HI)in the study sites($p<0.05$)

The highest values of SQI were (12.15) Site4 and HI (35.38) Site3, respectively. The lowest values of SQI were (10.74) Site2 and HI 25.18 Site 4. This result indicates that the soils in the study site are undergoing severe degradation and are hazardous in terms of non-carcinogenic health conditions. The difference in SQI and HI of the sites represents a difference in the characteristics of the soil and the levels of contamination, although even the poorest scoring sites are characterized by low soil fertility and high threat, indicating that all sites are affected at an alarming rate. SQI and HI together present a complex and integrative method of measuring the state of soils, not only the determination of areas of priority in terms of remediation, but also the tracking of soil health over time. This two-index system, by measuring both soil quality and possible health risks, presents a powerful system of environmental risk assessment and can inform management choices to reduce the risk of ecological and human exposure. The SQI and HI outcomes, on the whole, contribute to the urgency of the soil management interventions, showing that any slight variations in soil quality indices cannot be seen as insignificant, and supporting the necessity of holistic remediation approaches at all sites of the study. These results align with earlier reports that chronic animal-generated contaminants of petroleum stimulate the deposition and build-up of toxic metals in upper soil, decreases the soil fertility and organic content, and raises the chances of metals being incorporated into plants (Gan et al., 2022; Nwankwoala et al., 2020). as demonstrated by (Ayobami, 2022) that toxic metals directly impair the quality of the soil, which is observed in reduced values of SQI, and at the same time enhances the possibility of the uptake of metals by the plants elevating the level of HI and the related health hazards.

Site	SQI	HI	SQI Statutes	Priority level	Recommended Action
Site 1	10.76	28.01	poor	High	immediate remediation and monitoring
Site2	10.74	28.54	poor	High	immediate remediation and monitoring
Site3	12.02	35.38	poor	High	immediate remediation and monitoring
Site4	12.15	25.18	poor	High	immediate remediation and monitoring

Table 8. Priority classification table based on soil quality index and hazard risk

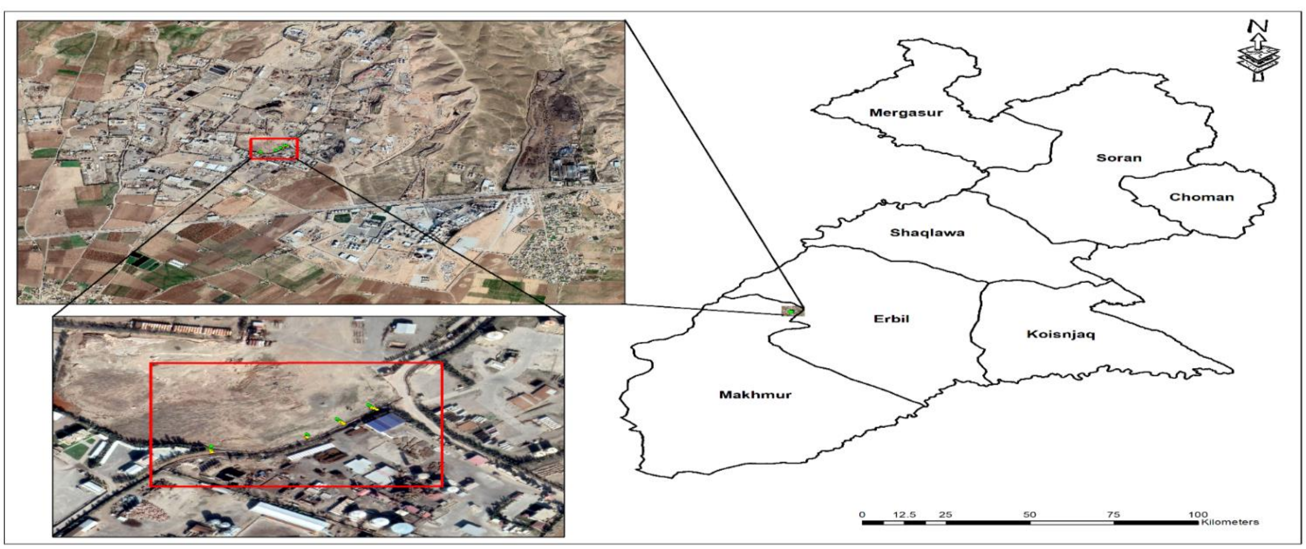


Figure 5. Location of the oil refinery and affected sampling sites in the study area.

6. Conclusion

This study demonstrated that soils and forage plants near oil refineries along the Gwer Road are significantly contaminated with chromium (Cr), nickel (Ni), zinc (Zn), cadmium (Cd), and lead (Pb), and the concentrations vary depending on the metal and the distance to the refinery. The pollution allowed significant alterations of the soil physicochemical characteristics, such as pH, EC, CEC, CaCO3, and OM, which indicated that the quality of the soil is quite poor. An increase in Soil Quality Index (SQI) and Hazard Index ($HI > 1$) means that there is an essential noncarcinogenic risk factor to human beings and animals through food chain transmission. Certain indigenous plants remain, which means that the individual forage species might be resistant to heavy metals; at the same time, the concentration of metals may cause certain hazards to the plant and be associated with food safety issues. Consequently, the remediation involving soil stabilization and removal, phytoremediation involving heavy metal-tolerant plants, and sustained GIS-based surveillance, are critical towards monitoring the success of the remediation practices and to reveal additional sources of contamination. The findings highlight the critical importance of the pervasive management of soils and policy-mandated remediation to maintain ecosystem health, sustainable land use, and protection of the population's health in industrialized areas.

Limitations of the Study

Despite the presented evidence being rather strong, certain limitations are to be considered. The sampling of soil and forage plants over a small area and time could not comprehensively reflect seasonal changes in heavy metal mobility and bioavailability. Besides that, the analysis was conducted on the surface soils and plant tissues only; other exposure routes, like groundwater contamination and atmospheric deposition, were not considered.

Future Prospects

Long-term monitoring of soil pollution and vegetation bioaccumulation with associated health risks is to be conducted in undertaking future work. The addition of groundwater and atmospheric pathways, more powerful source apportionment, remediation effectiveness (including phytoremediation with heavy-metal-tolerant plants, e.g., *Brassica juncea*, and GIS-based land-use and climatic variability modeling would go further to consolidate sustainable remediation planning and evidence-based environmental planning in refinery-impacted semi-arid environments.

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Abbreviation

Soil Quality Index	SQI
Bioaccumulation Factor	BCF
Health Risk hazard quotients	HQ
Total Health Risk Index	HI
Daily Metal Consumption	DMC
Environmental Baseline Standards	EBS

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