DETERMINATION OF HEAVY METALS AND TOTAL PETROLEUM HYDROCARBONS IN SOIL SAMPLES AND PLANT LEAVES AROUND OIL REFINERIES LOCATED ON ERBIL-GWER ROAD

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ABSTRACT

Several refinery complexes exist in the Kurdistan Region of Iraq that produce various kinds of petroleum products. During the refining process, different types of gases, metals, hydrocarbons, and liquids are discharged into the environment. This study aimed to determine the concentration of eight heavy metals in soil and plant leaves collected around the refineries along Erbil-Gwer Road on two occasions throughout the study period. Additionally, we aimed to evaluate the levels of Total Petroleum Hydrocarbons (TPH) in the soil samples from the area. The results of the analysis revealed significant differences (P<0.05) in the concentrations of Pb, Ni, Cd, Cr, As, and Mn between the dry and wet seasons in the soil samples. However, no significant differences were observed for Cu and Zn between the two seasons. The levels of metals for both periods were as follows: Mn> Cr> Zn> Ni> Cu> Pb> As> Cd in successive forms. Regarding the plant leaves, significant differences (P<0.05) were found between the study periods for Pb, Cu, Zn, and Cd, whereas no significant differences were observed for the other metals. Furthermore, the concentration of TPH in the soil samples located alongside the refinery effluent stream was higher compared to the other areas.

KEYWORDS: Oil Refineries, Heavy metal, TPH, Soil, Plant leaves, XRF.

1. INTRODUCTION

Petroleum refineries play a crucial role in providing vital energy resources for industries and everyday life. However, the process of refining oil generates substantial quantities of harmful and long-lasting pollutants, including TPH and various heavy metals (HMs), such as total chromium, vanadium, zinc, iron, nickel, and copper, as well as, oil, grease, phenols including (cresols and xylenols), ammonia, sulfides, suspended solids, nitrogen compounds, and cyanides. These will be released and contaminate the environment (Côté, 1976). These pollutants pose significant environmental and health concerns due to their toxic and persistent nature. These toxic chemicals may enter the environment as a result of oil leakage and spillage from tanker trucks or oil tanks, waste oil dumping, and incomplete combustion of organic material (Tiwari et al., 2011).

Contaminants from oil refineries negatively impact soil quality, plant-physical, biological, and chemical characteristics. Various environmental studies on oil refineries and spill sites have revealed staggering amounts of environmental contamination and harmful effects on biota because of the hazardous nature of TPH and heavy metals. (Martí et al., 2009; Rahman & Singh, 2019; Teruhisa et al., 2003; Umechuruba, 2005). It has been determined that petrochemical industries are significant organic pollution emission sources (Nadal et al., 2007). A considerable quantity of organic contaminants, TPH, and HMs have been recorded in the vicinity of oil refineries (Adeniyi & Afolabi, 2002; Cetin et al., 2003; Iturbe et al., 2004; Mohebian et al., 2021; Tiwari et al., 2011).

The term "heavy metals" often refers to metals that are harmful to both living things and the environment and have a specific density greater than 5 g/cm^3 (Järup, 2003). Heavy metals can naturally enter the soil from parent rocks in concentrations that pose no risk to plants or animals. Even some elements, known as

micronutrients or trace elements such as Cu, Co, Mn, Fe, Zn, Mo, and Ni, play crucial roles in plant and animal cells (Appenroth, 2010; Serrano et al., 2005). However, high levels of these metals can have a detrimental effect on the physiological processes of plant growth and pose significant threats to the environment and people (Appenroth, 2010).

Heavy metals are characterized by a long residual period, a high degree of invisibility, limited mobility, a high level of toxicity, and complex chemical behaviors and eco-reactions. Also, it is well documented that HMs are among the most hazardous materials, and when their concentration exceeds a certain threshold, they pose a threat to the environment worldwide (Alloway, 1995; Khairiah et al., 2009; Oladebeye, 2017). In agricultural soils, an excessive accumulation of HMs can cause soil pollution as well as increased HM uptake by plants (Pourang & Noori, 2014).

According to (Alloway, 1995; Brunetti et al., 2009), in contrast to organic contaminants, HMs do not undergo biodegradation and typically remain immobile. As a result, the soil serves as a long-term repository for HMs, with retention periods varying from centuries to millennia depending on the particular element and the physicochemical characteristics of the soil.

On the other hand, the term total petroleum hydrocarbon (TPH) is often used to define a wide-ranging family of several hundred chemical organic compounds up to 17,000. These substances, including volatile organic compounds (VOCs), benzene, toluene, ethylbenzene, and xylenes (BTEX), as well as polycyclic aromatic hydrocarbons (PAHs) and other hazardous chemicals, are derived from crude oil. It is beneficial to quantify the total quantity of all hydrocarbons present in a specific sample of water, soil, or air (Bjorlykke, 2010; Gustafson et al., 1997). Some of these compounds are highly toxic and not only contaminate the environment, but they can also be toxic to humans and other

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species because of their specific characteristics (Yang et al., 2017).

The primary objective of this research was to assess the concentrations of certain HMs such as copper (Cu), lead (Pb), nickel (Ni), zinc (Zn), chromium (Cr), cadmium (Cd), arsenic (As), and manganese (Mn) in soil samples and plant leaves. The study was conducted in two distinct seasons (dry and wet) near the refineries situated along the Erbil-Gwer main road, with a focus on comparing the concentrations observed during both seasons. Additionally, the study was aimed at quantifying the TPH levels in soil samples collected in the dry season.

2. MATERIALS AND METHODS

2.1 Study Area

The study area is located southwest of Erbil city, the capital of Kurdistan Region-Iraq, along the main Erbil-Gwer Road, approximately 22 kilometers away from the city center (Figure 1). The area is closely surrounded by three villages: Lajan, Tarjan, and Qalata Soran. The study area is also close to the Erbil Steel Company. Several refineries have been working in the area for over 10 years and producing a variety of products, such as gasoline, diesel, benzene, asphalt, etc. Some of these refineries produce up to 100,000 liters of petroleum products per day (Mirza & Ahmed, 2023). These refineries discharge their effluents into the surrounding environment, as shown in Figure.

2.2 Sample Collection

Soil and plant leaf samples were collected on two occasions. The first was in the summer (dry season) of 2021, and the second was in the winter (wet season) of 2022. The sample locations were selected to cover the study area completely (sample coordinates are given in Tables 1 and 2). Soil samples were collected in 10 to 15 cm bellow soil surface using metal spades (Tan, 1995). A total of 14 soil samples were collected; three of them were collected of the long side of discharged wastewater stream of the refineries, and the other 11 samples were collected from different locations around the refineries. Samples were put in clean plastic bags for metal analysis and dark glass jars for TPH analysis. On the other hand, eight plant leaves were collected from Eucalyptus trees (*Eucalyptus camaldulensis*) Plant leaves were also kept in clean plastic bags. Then both soil and plant leaves were transferred to the laboratory on the same day of sampling for analysis.

2.3 Heavy Metals

2.3.1 Soil sample preparation:

After removing of stones and plant debris, soil samples were air-dried and sieved with the use of a 2.00 mm mesh stainless steel sieve at the Advance Laboratory of Environmental Science and Health Department, College of Science, Salahaddin University. Then, from each soil sample 50 gram was weighed and placed in an oven set at 105 °C for approximately 12 hours to ensure a constant weight. Subsequently, the samples were kept at room temperature in clean disposable plastic containers prior to analysis (Mason, 1992; Peris et al., 2008). Later on, soil samples were thoroughly homogenized and further sieved with the use of a 0.50 mm sieve to reduce the soil matrix effect (Kodom et al., 2012).

2.3.2 Plant leaf preparation:

The plant leaves were washed out with tap water to remove the dust, and then they were dried completely for 2 to 4 hours at a low temperature (~60 °C) in an oven. Then the leaves were ground to a powder using a grinder and kept in clean disposable plastic containers at room temperature prior to analysis (Reidinger et al., 2012).

The importance of drying the soil and leaf samples to avoid potential issues with the XRF analysis, particularly when the moisture content exceeds 20%. The concern is that excessive moisture could cause changes in the soil matrix, which might impact the calibration of the XRF spectrometer (Kodom et al., 2012).

2.3.3 XRF analyses:

The concentration of heavy metals was assessed using the Skyray Instrument-Genius 5000 XRF, a portable handheld X-ray fluorescent (XRF) device. XRF technology has become widely embraced in the environmental field as a practical analytical method suitable for field applications. The main reason for its widespread acceptance is mainly due to the effective excitation from the radioisotope source, along with sensitive detectors and advanced electronics. By utilizing XRF methodology, on-site analysis of various environmental samples becomes feasible in a cost-effective and time-efficient manner. Additionally, XRF offers several advantages over traditional methods commonly used for analyzing environmental samples (Melquiades & Appoloni, 2004).

Soil and plant leaf samples were placed in an X-ray sample cup, which was then covered with polypropylene film, and XRF measurements were performed in the laboratory using a portable test stand. The measurement time for each sample was 100 seconds. Concentrations of HMs were calculated through the built-in algorithm in the XRF (Hu et al., 2017).

Table 1: Soil sample coordinates.

| Sample ID	Coordinates	
	Latitude	**Longitude**
SS1[1]	36.1343679	43.7783929
SS2	36.1471751	43.7788948
SS3	36.1516110	43.7799161
SS4	36.1559040	43.7817829
SS5	16.1585390	43.7838881
SS6	36.1507219	43.7891550
SS7	36.1411531	43.7868908
SS8	36.1584220	43.7671481
SS9	36.1484110	43.7649370
SS10	36.1403211	43.7629300
SS11	36.1359341	43.7623319
SS12	36.1308639	43.7559100
SS13	36.1238151	43.7584960
SS14	36.1320860	43.7953851

[1] SS= Soil Sample
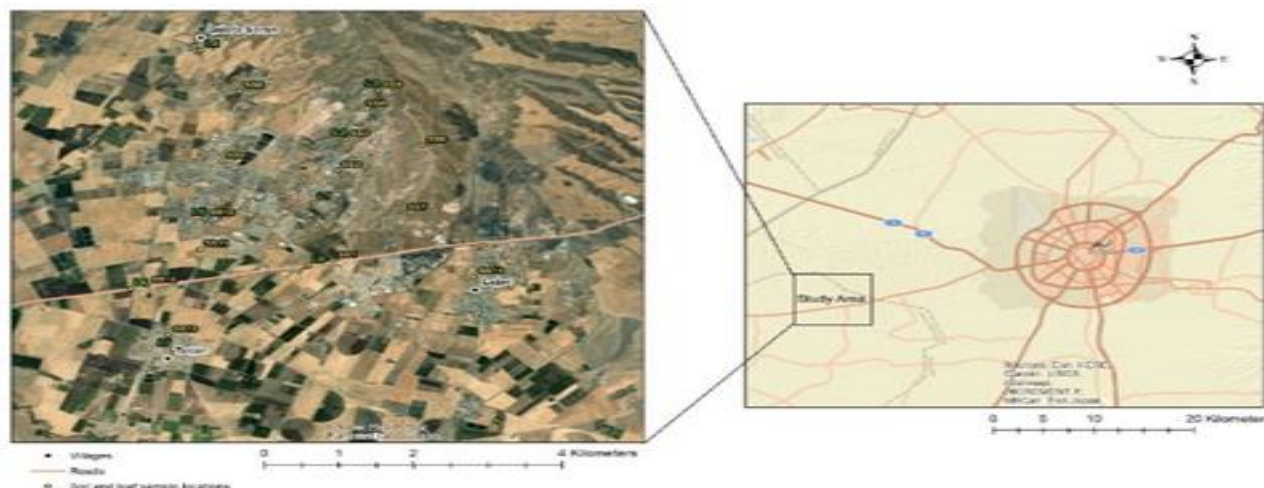
Figure 1: Satellite map of the study area and sample locations

Figure 2: Discharged effluents from refineries.

Table 2: Plant leaves sample coordinates

Sample ID	Coordinates	
	longitude	Latitude
L1[1]	36.1425750	43.7760430
L2	36.1516110	43.7799161
L3	16.1585390	43.7838881
L4	36.1641890	43.7624770
L5	36.1403210	43.7629300
L6	36.1303130	43.7540740
L7	36.1217650	43.7591430
L8	36.1336330	43.7753150

[1] L= Plant leaf

2.4 Total Petroleum Hydrocarbons (TPH)

Soil samples were analyzed for TPH measurement at Atmosphere Company for Environmental and Laboratory Services-Erbil, using the Gas chromatography–mass spectrometry (GC-MS) technique. GC-MS has gained significant popularity in environmental investigations because of its widespread application and effectiveness in analyzing a wide range of organic samples in various major categories (Almutairi, 2022).

2.4.1 Soil sample preparation and analyses:

Ten grams of the homogenized soil sample were taken and transferred into a 250-ml conical flask. Subsequently, 30 ml of high-purity (99.99%) n-Hexane solvent was introduced to the sample. Later on, for 10 minutes the solvent and sample were thoroughly mixed . To improve the extraction process, the sample was subjected to a rotary shaker for 1 hour. Followed by filtration to separate the liquid extract from the solid particles.

The mixture of sample and solvent was then passed through an evaporation process using a rotary evaporator in order to remove the solvent and concentrate the extract. Later on, the volume of extract was restored to 10 ml. Finally, the sample was analyzed for TPH by GS-MS.

2.4.2 GC-MS conditions

The condition of the GC-2030 was as follows: Temperature of the Column Oven: 50.0 °C, Temperature of the Injection: 320 °C, Mode of the Injection: Split less, Time for Sampling: 1.0 min, Control Mode for the Flow:

Linear Velocity, Pressure Condition: 33.5 kPa, Total Flow: 50.0 mL/min, Column Flow: 0.76 mL/min, Velocity of the Linear: 31.6 cm/sec, Purge Flow: 5.0 mL/min, Split Ratio: -1.0, High Pressure Injection: Auto, High Press. Pressure of the Injection: 250 kPa, High Press. Time of the Injection: 1.5 min, Carrier Gas Saver: OFF. Moreover, the GCMS-QP2020 NX conditions were: Temperature of the Ion Source: 230 °C, Temperature of the Interface: 320 °C, Time for the Solvent Cut: 2.50 min, Gain Mode of the Detector: Absolute, Detector Gain: 1.50 kV, Threshold: 0.0.

2.5 Statistical analysis

The obtained data were analysed statistically using GraphPad Prism (version 8.0). Paired t-tests and Wilcoxon matched-pairs tests were utilized to compare the levels of heavy metals in both soil and plants on each occasion. On the other hand, to compare the levels of heavy metals between soil and plants, unpaired t-tests and Mann-Whitney tests were employed.

3. RESULTS AND DISCUSSION

3.1 Soil heavy metals

The mean values of Ni, Cr, Zn, Cd, and As and the median of Pb, Cu, and Mn for soil samples of both periods (i.e., dry and wet seasons) are shown in Table 3. The results indicated that the median concentration of Pb in the dry season was 6.73 (1.47-12.26) mg/kg and in the wet season was 10.75 (6.66-18.35)

mg/kg DW. The median concentration of Cu in the dry season was 22.16 (16.79-43.96) mg/kg DW and in the wet season was 27.69 (11.96-51.54) mg/kg. The mean value of Ni in the dry season was 55.69±4.396 mg/kg DW and in the wet season was 35.72±2.632 mg/kg DW. The mean value of Cr in dry season was 101.0±12 mg/kg and in wet season was 70.06±6.714 mg/kg. Moreover, the mean values of Zn and Cd in dry season were 69.09±5.758 mg/kg and 0.3564±0.039 mg/kg respectively, while in wet season the mean values were 56.60±4.394 mg/kg and 0.48±0.013 mg/kg respectively. The mean concentrations of As in dry and wet seasons were 6.027±0.8 mg/kg and 3.381±0.33 mg/kg respectively. Median values of Mn in the dry season and wet season were 587 (235.3-908.7) mg/kg and 348.4 (153.9-549.8) mg/kg respectively.

According to the P-value results presented in Table 3, it is evident that significant differences (P<0.05) were observed between dry and wet season results for most of the studied metals, except for Zn. Additionally, it was found that the concentration of most of the metals were declined in wet period. Theses seasonal variations in the concentration of heavy metals in the soil can be attributed to atmospheric deposition through rainfall and heavy metal runoff, which leads to a decrease in the metal concentration in the soil (Ahmed et al., 2019; Oluyemi et al., 2008)

Level of metals for both periods were in a successive form, Mn> Cr> Zn> Ni> Cu> Pb> As> Cd. This sequential order is typically found in Iraqi soils, according to the literature.

The results arrived at in the present study were compared with those of Al-Dabbas et al. (2015). In their study, they determined the concentrations of Pb, Cu, Ni, Cr and Cd in October (considered as dry season) and March (considered the wet season) at Kirkuk Oil refinery and surrounding areas. The results obtained for metals examined in October were 5.7, 8.1, 32.4, 56.6, and 12.6 mg/kg , respectively, and in March, were 14.3, 5.3, 44, 66, and 7.4 mg/kg ,respectively. Upon comparison we observed that the mean concentration of Cd metal in our study was much lower in both seasons, in contrast; the average values of Cu in the present study were higher in both seasons. Moreover, mean values of Pb, Ni, and Cr were higher in dry season and lower in wet season. These results may be due to several factors, including differences in geographical location, soil conditions, soil types, as well as variations in emissions and waste generated by refineries.

Another study was conducted in Erbil Metropolis in which seven heavy metals, including As, Cr, Pb, Zn, Cu, and Cd were examined by Amjadian et al. (2016) in Erbil City. Mean values of the examined metals were 5.68, 39.61, 140.67, 262.8, 113.59, and 1.03 mg/kg, respectively. In comparison to these values, the mean concentrations of Pb, Zn, Cu, Cd, and As were lower in the current study, this is due to high traffic jams, high population and significant engine emissions from cars and diesel generators in Erbil Metropolis. The only exception is the mean concentration of Cr which was higher in this study. And this may be due to the effects of oil refineries, which release chromium into the environment, in different processes of their operation, including the combustion of fossil fuels, using chromium-containing catalysts and incineration of their waste (Zayed & Terry, 2003). The study results are also screened against WHO standards from 1996 for maximum permissible levels of elements (MPL) in unpolluted soils. The MPL for Pb, Cu, Ni, Cr, Zn, and Cd, are as follows 85, 36, 100, 50, 35, and 0.8 mg/kg, respectively (Table 7). From this, we found out that the mean concentrations of studied metals, Pb, Cu, Ni, and Cd, in both seasons were lower than the MPL employed by WHO, while Cr, and Zn concentrations in both periods were higher than WHO limits.

Additionally, the current study results were compared with Environmental Baseline Survey (EBS) results for HMs conducted by MapCom Company in 2010. EBS results were 8.5, 42, 34, 23, 23.8 and 1.1 mg/kg for the same heavy metals respectively (Table 7). This comparison indicated that mean values of Cu and Cd in both seasons and Pb in dry season were lower than the EBS results. While, mean values of Ni, Cr, and Zn in both periods and Pb in wet period were higher than EBS results.

Table 3: Comparison of soil sample heavy metals for dry and wet season

Elements (mg.kg)	Soil (n=14)		
	Dry season	Wet season	P-value
Pb	6.73 (1.47-12.26)	10.75 (6.66-18.35)	0.0004 ***
Cu	22.16 (16.79-43.96)	27.69 (11.96-51.54)	0.0203 *
Ni	55.69±4.396	35.72±2.632	<0.0001 ***
Cr	101.0±12	70.06±6.714	0.0055 **
Zn	69.09±5.758	56.60±4.394	0.0719 ns
Cd	0.3564±0.039	0.48±0.013	0.0099 **
As	6.027±0.8	3.381±0.33	0.0096 **
Mn	587 (235.3-908.7)	348.4 (153.9-549.8)	0.0004 ***

Wilcoxon matched-pairs test used for Pb, Cu, and Mn metals represented by Median (minimum-maximum); paired t test was used for the rest represented by Mean ±SE.

According to Zeng et al. (2015), soil pollution in the Tianjin Region, China, primarily resulted from the use of fertilizers and the introduction of manure in agricultural croplands. Consequently, the elevated levels of zinc in this study may be related to the use of zinc-containing fertilizers by farmers, as the area surrounding the refineries is agricultural land. Another source can be from parent material, the type of rock or mineral from which the soil derived from. The high levels of Ni can also be related to the use of fertilizers of pesticides from many years ago by farmers (Marinova, 2003). While higher levels of Pb in wet season could be from the atmospheric deposition of this metal which often associated with emissions from automobiles passing by area, because the area is located on a main road highway.

3.2 Plant heavy metals

The results of HMs in plant leaves (Eucalyptus) close to refineries showed that the mean ± standard deviation values for dry season of Pb, Zn, Cd, and As were 6.258±0.738, 73.21±5.38, 0.298±0.49, and 1.495±0.57 mg/kg, respectively, while in wet season values fluctuated between 16.15±1.101, 32.69±3.202, 0.621±0.026, and 0.597±0.22 mg/kg respectively. Also, the median of Cu, Ni, Cr, and Mn for dry season were 13.29 (0-17.44), 6.510 (0-31.71), 4.535 (0-50.74), and 330.3 (120.4-658.9) mg/kg, respectively, and in wet season values were 3.115 (0-5.84), 1.120 (0-3.19), 0 (0-19.91), and 188.6 (91.12-542.3) mg.kg , respectively (Table 4). The results also indicated that there is a significant difference (P < 0.05) between study periods for Pb, Cu, Zn, and Cd, while there is no significant difference between the rest of the metals.

As for soil samples, it was found out that most of the HMs in plant leaves showed decline in concentration during the wet season. These seasonal variations in temperature and

precipitation can have an effect on the mobility and availability of heavy metals for plant uptake in soil (Rajkumar et al., 2013). Another reason, it can be as a result of the heavy wind and rainfall during the wet season which wash and remove the contaminants from the surface of the leaves (Al-Dabbas et al., 2015).

Table 4: Comparison of plant sample heavy metals for dry and wet season

Elements (mg.kg)	Plant (n=8)		
	Dry season	**Wet season**	**P-value**
Pb	6.258±0.738	16.15±1.101	< 0.0001 ****
Cu	13.29 (0-17.44)	3.115 (0-5.84)	0.0469 *
Ni	6.510 (0-31.71)	1.120 (0-3.19)	0.125 ns
Cr	4.535 (0-50.74)	0 (0-19.91)	0.125 ns
Zn	73.21±5.38	32.69±3.202	0.0003 ***
Cd	0.298±0.49	0.621±0.026	0.0015 **
As	1.495±0.57	0.597±0.22	0.2563 ns
Mn	330.3 (120.4-658.9)	188.6 (91.12-542.3)	0.0547 ns

Wilcoxon matched-pairs test used for Cu, Ni, Cr, and Mn metals represented by Median (minimum-maximum); paired t test was used for the rest represented by Mean±SE.

Furthermore, the mean concentrations of HMs in plant leaves were compared to the WHO permissible values of 1996. The permissible limits set by WHO were 2 mg/kg for Pb, 10 mg/kg for Cu, 10 mg/kg for Ni, 1.3 mg/kg for Cr, 0.6 mg/kg for Zn, and 0.02 mg/kg for Cd (Table 7). It was found out that the average values of Pb, Cr, Zn, and Cd for both seasons exceeded the WHO permissible limits, while the mean values of Cu and Ni were below the WHO limits.

On the other hand, the results of the current study were compared with the findings of the study conducted by Salih and Aziz (2019) which have been done on Eucalyptus leaves of the same area. In their study, they determined the mean concentration of heavy metals, including Cu, Mn, Ni, Zn, As, and Pb and the results were as follows; 4.12, 521.3, 24.26, 879.52, 29.23, and 138.92 mg/kg, respectively. From this we found out that the mean values of the studied metals for both seasons of this study were much lower. And this may have happened because they were collected plant leave samples directly inside the steel factory, and the plants mostly affected by pollutants from the factory, whereas the samples of the present study were collected in the areas surrounding the oil refineries not directly inside these facilities.

Table 5 Comparison of soil and leave heavy metals for dry season

Elements (mg.kg)	Soil (n=14)	Plant (n=8)	P-value
Pb	6.241±0.906	6.258±0.738	0.9905 ns
Cu	22.16 (16.79-43.96)	13.29 (0-17.44)	< 0.0001 ****
Ni	57.44 (26.73-78.06)	6.510 (0-31.71)	< 0.0001 ****

Cr	94.31 (34.04-191.1)	4.535 (0-50.74)	< 0.0001 ****
Zn	69.09±5.758	73.21±5.38	0.6398 ns
Cd	0.356±0.0398	0.298±0.0493	0.3832 ns
As	6.027±0.8008	1.495±0.574	0.0008 ***
Mn	587 (235.3-908.7)	330.3 (120.4-658.9)	0.0288 *

Mann Whitney test used for Cu, Ni, Cr, and Mn metals represented by Median (minimum-maximum); Unpaired t test was used for the rest. Represented by Mean ±SE.

Table 6: Comparison of soil and leaf heavy metals for wet season

Elements (mg.kg)	Soil (n=14)	Plant (n=8)	P-value
Pb	10.75 (6.66-18.35)	16.01 (12.17-21.53)	0.0005 ***
Cu	30.22±3.088	2.906±0.756	< 0.0001 ****
Ni	38.65 (14.67-49.85)	1.12 (0-3.19)	< 0.0001 ****
Cr	68.97 (29.51-125.3)	0 (0-19.91)	< 0.0001 ****
Zn	56.60±4.394	32.69±3.202	0.0012 **
Cd	0.48±0.01301	0.621±0.0269	< 0.0001 ****
As	3.381±0.3307	0.5975±0.223	< 0.0001 ****
Mn	348.4 (153.9-549.8)	188.6 (91.12-542.3)	0.0102 *

Mann Whitney test used for Pb, Ni, Cr, and Mn metals represented by Median (minimum-maximum); Unpaired t test was used for the rest represented by Mean ±SE.

Table 5 and Table 6 show the comparison between the concentrations of metals in the dry and wet seasons, respectively. There was a significant difference between the levels of Cu, Ni, Cr, As, and Mn in soils and plant leaves in the dry season. During the wet season, significant differences between all HMs were observed. This suggests that the rainwater washes out the metals in the air, which then accumulate in the soil. The higher concentration of Pb in leaves for both seasons indicated the accumulation of this specific metal in the plant leaves (Salazar & Pignata, 2014).

Table 7: WHO and Environmental Baseline Survey results

Elements (mg/kg)	MPL of heavy metal (WHO, 1996)		EBS results (Hama & Darwesh, 2019).
	Unpolluted soils	**Plants**	**EBS Results**
Pb	85	2	8.5
Cu	36	10	42
Ni	100	10	34
Cr	50	1.3	23
Zn	35	0.6	23.8
Cd	0.8	0.02	1.1

3.3 Soil TPH

The TPH results for soil samples are shown in Table 8. TPH concentrations ranged from 9.826 to 4401.328 mg/kg DW, with an average value of 676.50 mg/kg DW. The highest TPH values were recorded at SS3, SS10, and SS12 with values of 2239, 4401.328, and 1597.071 mg/kg DW, respectively. These samples were taken alongside the effluent discharge stream from the refineries. This indicated that the refinery effluents negatively affected the soil quality. According to Mirza and Ahmed (2023) the pathway stream of the residual crude oil (effluents) from the refineries has changed many times from 2013 to 2020.

The other samples that were located inside the refineries area (i.e., SS1, SS2, SS9, and SS11) also had higher concentrations of TPH compared to the sites outside of the refineries area (i.e., SS4, SS5, SS6, SS7, SS8, SS12, and SS13). The TPH concentrations in the samples from inside the refinery area exceeded the safe limit for TPH in soil, which is generally considered to be 100 mg/kg (Michelsen & Boyce, 1993). However, it is important to note that the safe limit of TPH in soil varies depending on the specific use of the land. For example, the safe limit for residential soil is much lower than the safe limit for industrial soil. Additionally, it was observed that none of the soil samples recorded concentrations higher than the US EPA maximum permissible limit in soil, which is 10,000 mg.kg DW.

On the other hand, the results of this study indicated lower TPH concentrations compared to a study conducted on agricultural top soils vicinity to a petrochemical complex in Guangzhou, China (Li et al., 2012). In the Guangzhou study, TPH concentrations ranged from 1179.3 to 6354.9 mg/kg DW, with a mean value of 2676.6 mg/kg. In contrast, the TPH values obtained in the current study ranged from 9.82 to 4401 mg/kg DW, with an average value of 675.5 mg/kg. This difference can be referred to the age and production type of the refineries, spills or frequency of accidents in the study areas.

4. CONCLUSION

The refineries located on Erbil-Gwer Road are discharging a large quantity of effluents into the surrounding soils as well as a large number of gases into the air, which later precipitate and remain on plant leaves and soil. Based on the study's findings, the following conclusions can be drawn: Firstly, the Total TPH results clearly demonstrate that the area is contaminated with TPH, particularly in the vicinity of the refineries and their discharged wastewater. This contamination poses environmental concerns and warrants attention for its potential implications for soil and plant health. Secondly, the seasonal change affected the concentration of heavy metals in both soil and plant leaves. It was also observed that only the concentrations of Cr and Zn in soil samples for both seasons were higher than the WHO limits and EBS results. Whereas the concentrations of Pb, Cr, Zn, and Cd in plant leaves for both seasons were much higher than WHO guidelines.

The comparisons with other studies also indicated that the concentration of heavy metals was elevated in the study area but not reached toxic levels.

Table 8: TPH results of soil samples during the period of dry season

Sample ID	TPH concentrations in mg/kg DW
SS1	107.048
SS2	365.898
SS3	2239.51
SS4	39.675
SS5	57.905
SS6	70.592
SS7	9.826
SS8	70.905
SS9	232.076
SS10	4401.328
SS11	150.713
SS12	1597.071
SS13	50.052
SS14	78.515
Median (minimum-maximum)	92.78 (9.82-4401)

5. REFERENCES

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