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RESEARCH PAPER

Impact of Crude Oil discharge from Oil Refineries near Gwer Road of Erbil City on Soil Physico-chemical Properties and Metal Emancipations

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A B S T R A C T:
The study was carried out in October 2021 in oil refineries which are located near Gwer road and 15 km far away from Erbil city with GPS reading of (36° 8'32.31"N, 43°46'32.61"E, Altitude 325m), to investigate the impact of residual crude oil discharged from surrounding oil refineries on soil Physico-chemical properties and heavy metals contamination. A total of 108 soil samples were collected from (8) different locations, (4) distances, and (3) depths alongside the residual crude oil stream. By using (XRF) technique to determine total heavy metals concentration from collected soil samples. The range of soil pH was between (7.23 - 8.7) and an increase in crude oil quantity causes increases in soil pH. (Fe) has the highest total concentration of among the studied metals ranging between (11925.09 - 22394.37 mgkg-1) followed by (Mn) which ranged between (127.89 - 528.12 mgkg-1) and (Zn) ranged between (41.68 - 107.58 mgkg-1). According to Pearson's correlation, there is a significant positive correlation between (Fe and Mn) at ($p \leq 0.01$, r=.753**) which indicates both metals are derived from the same source. Moreover, there are a significant positive correlation between (Zn and Mn) at ($p \leq 0.05$, r=.338*) However, the correlation is less strong compared to (Fe and Mn) this mean (Zn) derived from multiple sources other than crude oil like automobile and truck tire which is one of the major sources for (Zn), since the study area was located next to the busy road.

KEY WORDS: Soil pollution, Heavy metals, Physicochemical properties, Oil refineries.
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1. INTRODUCTION:

As the world population increase, the demand for crude oil is increasing as well. Due to rapid industrialization, the exploitation, transportation, and storage of these organic compounds cause widely occur in the environment (Wang et al., 1999). Pollution appears when the balance of environmental structure and its function is disturbed due to a change in any material cycle in that environment (Deyanti et al., 2018).

One of the important sources of soil pollution came from various petroleum products which became a critical compound in basic human life (ATSDR, 2000). Nowadays, oil pollution is one of the major topics for global environmental issues (Soto-Onate and Caballero, 2017).

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During accidents, managed spills, or as unintended by-products of industrial activities, diesel, gasoline, and lubrication can be released into the environment and distributed in the environments (Park and Park, 2011). Crude oil can enter the soil at some point during leakage and goes deeper into the soil through infiltration causing alteration of soil physical and chemical properties (Wu et al., 2014). Soil odor and visual pollution are other consequences of entering crude oil pollutants into the soil (Yuniati, 2018).

Petroleum oil contains various amounts of trace elements and heavy metals (Akpoveta and Osakwe, 2014). There is potential contamination for our environment when heavy metals transfer into the food chains. Therefore, focused on the presence and concentration of heavy metals, and their toxicological effects on the environment it's important to restore our green eco-friendly, and healthy environment (Mishra et al., 2019).

Recent advanced technology for measuring elemental composition in soil pollution is portable XRF analyzer (pXRF) (Chakraborty et al., 2017). This device allows quantitating determination of multi-elemental content for contaminated soil at once without the need for digestion (Horta et al., 2015). The XRF technique transfers the inner electrons into an excitation state and emits radiation when relax and returns to their ground state (Radu and Diamond, 2009). XRF technique provides accurate elemental contents in soil samples (Reidinger et al., 2012).

Oil refineries near Gwer road has been operating for several years and discharging wastes of crude oil into the soil and water which has a significant impact on environment. It's necessary to investigate the impact of these oil refineries on soil quality, evaluate the degree of contamination, and health risk assessment. The aim of this study to monitor the soils polluted with heavy metals and their relation with soil Physico-chemical properties and to determine the effect of distance on the distribution of heavy metals in soil around the soil polluted with crude oil.

2. MATERIALS AND METHODS

2.1 Descriptions of the study area

The current study was carried out in October 2021 nearby oil refineries which are located near Gwer road and 15 km far away from Erbil city (36° 8'32.31"N, 43°46'32.61"E), to investigate the impact of residual crude oil discharged from surrounding oil refineries on soil pollution. (Fig. 1).

2.2 Oil refineries near Gwer road

Several oil refineries were located near the study area some of them were operating and producing between 10,000 to 100,000 Liters per day of petroleum products and the others are out of service from more than 5 years.

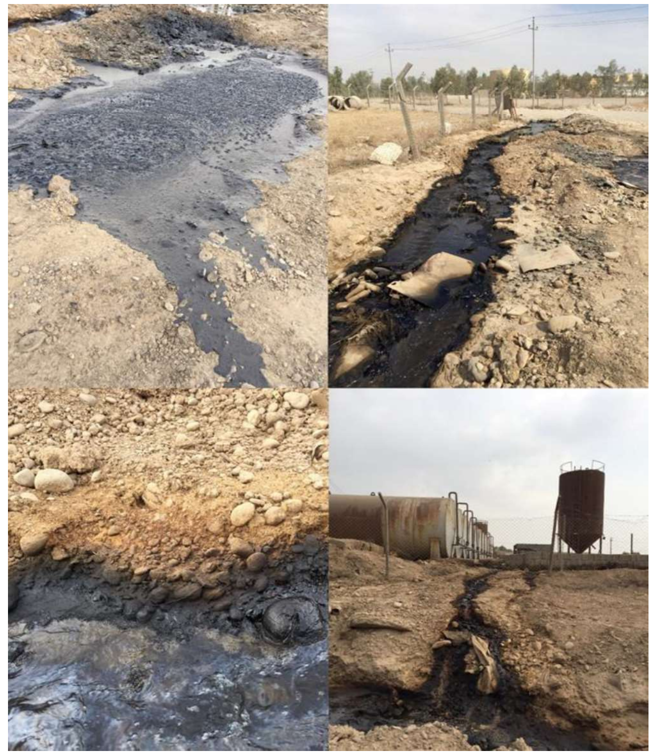

Figure 1: Residual crude oil from study area near the factories.

Some oil refineries that surround the area (Sabat oil refineries, Jawhar oil refineries, Shahab Kirkuk oil refineries, Dukan oil refineries, Ala oil refineries, Gwer oil refineries, and Rozh oil refineries). Multiple oil refineries were discharged their waste into the soil (36° 8'45.02"N, 43°46'42.05"E) as shown in (Fig. 2). In the refineries process the crude oil is heated up to (400 °C) and changed to petroleum products for energy consumption and daily basis like transportation, heating, paving roads, and generating electricity. The refining process breaks down crude oil into several components (Olsen, 2014).

2.3 Topographical history of the study area

The study area was facing several topographical changes during the last decade due to anthropogenic activities (Fig. 3), the satellite image from 2013 to 2020, shows that the "residual crude oil" pathway has been changed multiple times (GoogleMaps, 2020).

Figure 2: Study area and source of pollution as shown from satellite image.

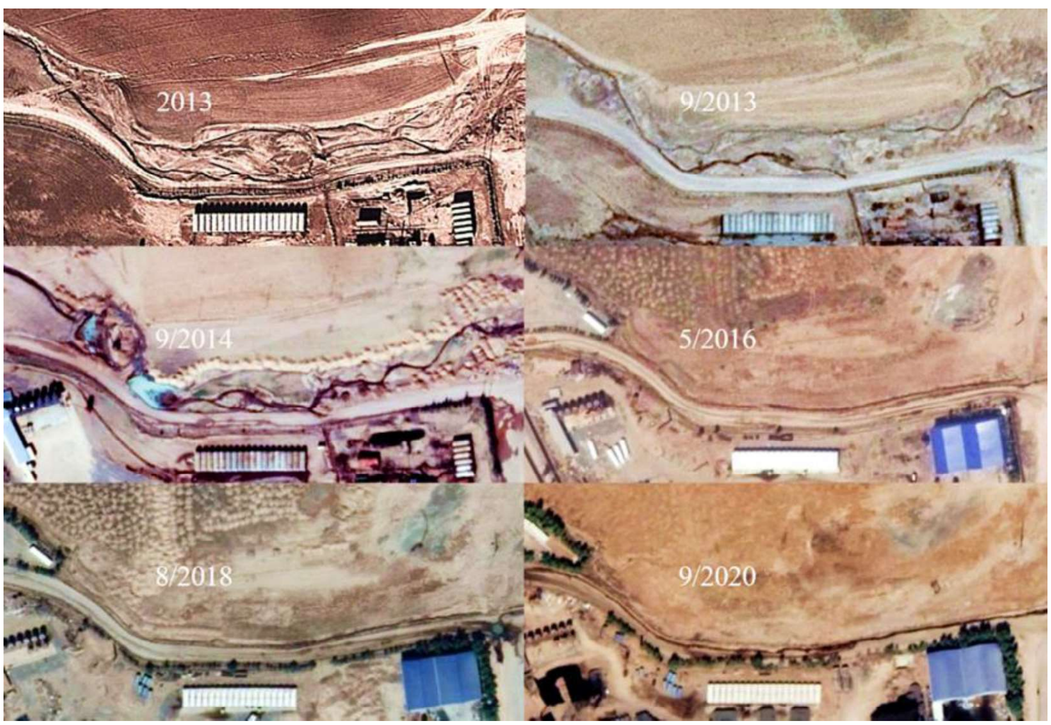

Figure 3: Evolution of study area as shown from satellite images.

From (9/2014) satellite image the residual pathway discharging their waste in randomize pathway into the soil surface in the nearby field, but in (5/2016) satellite image shows that the discharged crude oil waste is removed or filled with soil and the polluted land was leveled and small stream next to the field was created which stretched along with the dirt road next to it which then leading to Gwer road and finally dumped into the underground sewer. Since 2016 until now the contamination pathway remain the same as it is and continues to pollute the surrounding area (GoogleMaps, 2022).

2.4 Soil sampling

Soil samples were collected in (October 2021) from 2 directions, 8 locations, 5 distances, and 3 depths of soil around the polluted area. 108 soil samples in addition to one control sample (36°07'44.08"N, 43°50'54.08"E) stored in a labeled plastic bag. The distance from the original source of pollution and soil sample was approximately (650 m).

2.5 Soil physico-chemical analysis

Soil pH was determined by using (HANNA) pH-meter, model (EDGE) which extracted soil solution was measured by procedure of (Boyd and Tucker, 1992). Determination of total ($CaCO_3$) were conducted by using (Black, 1965) procedure. Organic matter of soil samples was measured by (Walkley and Black) procedure which was described by (Schulte and Hoskins, 1995). Particle size distribution was determined by (Bouyoucoous) hydrometer method according to (Klute, 1986).

2.6 Total heavy metal concentration in soil samples (mg kg^{-1})

Determination of total heavy metal concentration in soils were done by using portable XRF device (Skyray Instrument – Genius 5000XRF) (Chakraborty et al., 2017).

2.7 Statistical Analysis

The statistical analyses were performed by using (SPSS) statistical package for social science program version (Statgraphics-plus-professional-version 26.0) were used for determining person correlation coefficient. The correlation was produced at both 0.05 and 0.01 level of confidence (2-tailed). The level of significance and interaction between (distance, depth, location, and direction) for all heavy metal samples was conducted by using Duncan's multiple range test in two-way factorial analysis in Statistical Analysis Software (SAS) (Dabiri et al., 2016).

3. RESULTS AND DISCUSSION

3.1 Soil pH

The pH values from the studied soil sample was ranged (7.23 - 8.7) with an average value of (7.72). The highest value of pH (8.7) was measured at point (0 m), location (1) in the north direction at a distance of (1.5 m) away from the source of pollution, and the lowest value was (7.23) was measured at point (50 m), location (3) in the south direction at the distance of (2.5 m). Meanwhile, the pH value of the control (7.25) as shown in (Table 1).

In Table (1) indicates that the pH value of the control was (7.25) and according to USA acceptant classifications, this indicated that the pH of the control soil is neutral and the pH values of soil samples are ranged between neutral and strongly alkaline this finding come in agreement with those obtained by (Khudhur and Abdulla, 2016).

The high pH value of soil is caused by crude oil contamination. As the oil contamination increases the pH value increases as well this is agreed with (Wang et al., 2010) who observed a significant increase in soil pH value with the increasing quantity of crude oil in the soil. This due to the hydrophobic nature of crude oil could induce a potential drought in the surface and subsurface layers of polluted soil (Njoku et al., 2009), which could aggravate salinization, and thus raise the pH values compared with that in the control or increase in pH value due to the oil contamination in soil is associated with the accumulation of exchangeable base (such as Ca^{2+}, Na^{+}) and a decrease in exchangeable acidity and effective cation exchange capacity (ECEC), since increase in pH value causes increase in (ECEC). These mechanisms could also support the increase of pH values in the crude oil contamination soil (Benka-Coker and Ekundayo, 1995).

3.2 Calcium Carbonate ($CaCO_3$)

Total ($CaCO_3$) content in the soil sample was ranged between (13.7 - 31.75 %) and an average percentage of (24.58 %) with a high percentage of (31.75 %) was observed in both locations, first was located in the north direction at point (50m), location (6), and (5m) away from the source of pollution and the second was observed in the north direction at point (100 m), location (7) and (2.5 m) away from the source of pollution. The lowest percentage was determined in the north direction at point (100 m), location (7) and

(1.5 m) away from the source of pollution, this means the only (1 m) is the distance between the high and lowest ($CaCO_3$) percentage with the control sample has the highest ($CaCO_3$) percentage of (41.4 %) as shown in (Table 1).

Kurdistan region is well known for calcareous soils which are lands with an exceeded quantity of ($CaCO_3$) (Tariq et al., 2021). As shown in (Table 3) there is a positive significant relationship at the level (p ≤0.01, r=.431**) between (Ca) and ($CaCO_3$) in soil, since precipitation and dissolution processes of calcium carbonate in soil are mainly depended on the concentration of (Ca) in the soil and saturation index value as represented by the following equation (Durand et al., 2018):

$$Ca^{++} + 2HCO_3^- \leftrightarrow CaCO_3 + CO_2 + H_2O$$

On the other hand, the lowest ($CaCO_3$) percentage might be due to nutrient losses by wastewater discharged by oil refineries (SSSA, 2008) or leaching to subsurface soil (Hartemink, 2008).

3.3 Organic matter (O.M)

The organic matter content from soil samples ranged between (0.68 – 2.37 %) with an average percentage of (1.37 %). The highest percentage of (2.37%) was recorded in the south direction, point (100 m) at (0.5 m) away from the source which is the closest to the main pollution source and the lower percentage of (0.68 %) was obtained in the north direction, point (200 m) at (0.5 m) away from the source, with control sample having the lowest percentage of (0.46 %) as shown in (Table 1).

Many authors concluded that increases in organic matter content in the soil cause increasing in heavy metal concentration (Zhao et al., 2019); (Wiatrowska and Komisarek, 2019). But (Table 3) shows a negative significant correlation between (Mn and Fe) at (P ≤0.01, r=-.517**, -.445**) respectively this means increases in organic matter content cause decrease in concentrations of (Mn and Fe) and this was agreed with (Zhang et al., 2008); (Zhang et al., 2016); (Tang et al., 2020) which they also observed a decline in some heavy metals concentration as organic matter content increases.

3.4 Particle size distribution (PSD)

Sand fractions ranged between (302 - 729 gkg^{-1}) with a mean value of (519 gkg^{-1}). The highest percentage of sand was (729 gkg^{-1}) and it was recorded in the south direction, point (50 m) at (1.5 m) away from the source. Meanwhile, the lowest percentage of sand content is (302 gkg^{-1}) and it was recorded in the north direction, point (100 m) at (2.5 m) away from the source.

The silt content was ranged between (41 – 450 gkg^{-1}) with a mean value of (221.1 gkg^{-1}). The highest percentage of silt fraction is (450 gkg^{-1}) which was revealed in the north direction, point (100 m) at (2.5m) from the source. The lowest percentage of silt content is (41 gkg^{-1}) and it was determined in the north direction, point (0 m) at (10 m) from the source.

Clay content was ranged between (79 – 330 gkg^{-1}) with a mean value of (249 gkg^{-1}). The highest clay percentage is (330 gkg^{-1}) and observed in the north direction, point (0 m) at (1.5 m). The lowest percentage of clay content is (79 gkg^{-1}) which is located in the north direction, point (100 m) at (0.5 m) from the source and the sand, silt, and clay content in control sample was (367, 292, and 341 gkg^{-1}) respectively. (Table 1)

Increasing clay content in soil will increase the heavy metals concentration due to an increase in the number of the binding sites on the soil particle and (Srinivasarao et al., 2014); (Sungur et al., 2014) studies were concluded with the same results. Table (3) shows no significant correlation between clay and heavy metals concentration such as in results obtained from (Romić et al., 2004) they show no significant relation between clay content and heavy metals (Mn, and Zn).

3.5 Heavy metals concentrations in the surrounding soils of crude oil stream at various distances.

Table (2) shows that crude oil has a significant impact (P ≤ 0.05) on the surrounding soils of the study area. The average concentration of (Mn, Fe, and Zn) was: (351.44, 18409.67, and 64.35 $mgkg^{-1}$) respectively.

Iron had the highest concentration followed by manganese, and zinc had the lowest concentration (Fe>Mn>Zn) from the contaminated soil. Meanwhile, the average heavy metals

Table 1. Some physico-chemical properties along with GPS reading of the study area near oil refineries

Direction	Distance from the source (m)	Sample No.	Location from residual crude oil stream (m)	GPS reading		pH	OM%	Total $CaCO_3$ %	Particle size distribution g kg^{-1}			Soil texture
				Latitude N	Longitude E				Sand	Silt	Clay	
South	0	5	0.5	36° 8'32.02"	43°46'32.23”	8.22	2.33	20.16	629	191	180	Sandy L
		6	1.5	36° 8'31.99"	43°46'32.28"	7.46	1.29	30.06	454	216	330	Sandy clay L
		7	2.5	36° 8'31.97"	43°46'32.33"	8.18	1.88	22.75	529	166	305	Sandy clay L
		8	5	36° 8'31.87"	43°46'32.46"	7.53	2.11	28.26	554	191	255	Sandy clay L
	50	9	0.5	36° 8'31.01"	43°46'30.84"	7.52	1.48	21.4	669	116	215	Sandy clay L
		10	1.5	36° 8'30.98"	43°46'30.89”	7.54	1.75	19.15	729	91	180	Sandy clay L
		11	2.5	36° 8'30.95"	43°46'30.93"	7.23	2.22	17.68	619	166	215	Sandy clay L
		12	5	36° 8'30.86"	43°46'30.99"	7.55	2.15	25.87	554	166	280	Sandy clay L
	100	13	0.5	36° 8'29.93"	43°46'29.30"	7.52	2.37	20.5	504	241	255	Sandy clay L
		14	1.5	36° 8'29.92"	43°46'29.33"	8.16	1.94	17.35	629	141	230	Sandy clay L
		15	2.5	36° 8'29.91"	43°46'29.34"	7.94	1.57	28.26	579	141	280	Sandy clay L
		16	5	36° 8'29.89"	43°46'29.36"	7.66	1.64	20.5	587	225	188	Sandy L
	200	17	0.5	36° 8'28.97"	43°46'25.07"	7.28	0.83	17.68	427	250	323	Clay L
		18	1.5	36° 8'28.94"	43°46'25.07"	7.88	1	23.87	402	300	298	Clay L
		19	2.5	36° 8'28.88"	43°46'25.09"	7.32	1.22	19.37	577	150	273	Sandy clay L
		20	5	36° 8'28.80"	43°46'25.12"	7.39	0.95	31.63	527	175	298	Sandy clay L
North	0	1	0.5	36° 8'32.10"	43°46'32.18"	7.91	2.21	20.16	569	216	215	Sandy clay L
		2	1.5	36° 8'32.13"	43°46'32.18"	8.7	1.32	29.5	379	291	330	Clay L
		3	2.5	36° 8'32.16"	43°46'32.14"	7.95	1.83	29.5	354	416	230	L
		4	5	36° 8'32.24"	43°46'32.07"	7.34	1.69	30.17	429	266	305	Clay L
		33	10	36° 8'32.36"	43°46'31.97"	7.78	0.76	24.43	699	41	260	Sandy clay L
	50	21	0.5	36° 8'31.10"	43°46'30.78"	7.63	1.36	26.57	477	275	248	Sandy clay L
		22	1.5	36° 8'31.12"	43°46'30.74"	7.77	0.89	29.38	427	250	323	Clay L
		23	2.5	36° 8'31.17"	43°46'30.70"	7.71	1.03	30.85	352	400	248	L
		24	5	36° 8'31.21"	43°46'30.65"	7,68	0.95	31.75	392	325	283	Clay L
		34	10	36° 8'31.30"	43°46'30.58"	7.74	0.89	27.25	474	291	235	L
	100	25	0.5	36° 8'30.03"	43°46'29.39"	7.44	1.97	20.5	677	244	79	Sandy L
		26	1.5	36° 8'30.05"	43°46'29.37"	7.86	1.57	13.7	727	100	173	Sandy L
		27	2.5	36° 8'30.08"	43°46'29.36"	7.54	1.62	31.75	302	450	248	L
		28	5	36° 8'30.11"	43°46'29.32"	7.41	1.25	22.63	422	250	328	Clay L
		35	10	36° 8'30.16"	43°46'29.26"	7.35	1.01	22.75	574	166	260	Sandy clay L
	200	29	0.5	36° 8'29.09"	43°46'25.04"	7.73	0.68	29.05	367	350	283	Clay L
		30	1.5	36° 8'29.11"	43°46'25.06"	7.65	1.68	31.52	399	391	210	L
		31	2.5	36° 8'29.19"	43°46'25.08"	7.82	1.2	29.95	474	341	185	L
		32	5	36° 8'29.24"	43°46'25.08"	7.48	2.19	16.33	699	141	160	Sandy L
		36	10	36° 8'29.34"	43°46'25.08"	7.81	1.42	25.9	524	191	285	Sandy clay L

Table 3. Pearson’s correlation between the studied heavy metals and some of the Physico-chemical properties

	Ca	Mn	Fe	Zn	pH	OM	Sand	Silt	Clay	$CaCO_3$
Ca	1.00	0.30	0.17	-0.03	0.12	0.01	-0.23	0.23	0.08	**.431****
Mn		1.00	**.753****	**.338***	0.00	**-.445****	**-.330***	0.27	0.22	**.503****
Fe			1.00	0.31	-0.02	**-.543****	-0.32	**.363***	0.04	0.32
Zn				1.00	-0.04	-0.32	-0.07	0.12	-0.06	0.16
pH					1.00	0.07	-0.09	0.08	0.05	0.16
OM						1.00	**.398***	-0.20	**-.480****	-0.25
Sand							1.00	**-.877****	**-.575****	-0.14
Silt								1.00	0.11	0.15
Clay									1.00	0.04
$CaCO_3$										1.00

Concentration from the control sample (Mn, Fe, and Zn) had (10.17, 5263, and 0.098 mgkg^{-1}) respectively.

Iron had the highest concentration followed by manganese, and zinc had the lowest concentration (Fe>Mn>Zn) from the contaminated soil. Meanwhile, the average heavy metals concentration from the control sample (Mn, Fe, and Zn) had (10.17, 5263, and 0.098 mgkg^{-1}) respectively. The highest concentration of studied heavy metals (Mn, Fe, and Zn) were (528.12, 22394.37, and 107.58 mgkg^{-1}) respectively. The highest concentration of (Mn and Zn) were found in sample no. (28), meanwhile, the highest concentrations of (Fe) were found in sample no. (18). The lowest concentration of (Mn, Fe, and Zn) were (127.89, 11925.09, and 41.68 mgkg^{-1}) respectively. The lowest concentration of (Mn and Fe) is observed from sample no. (10, 14, and 11) respectively.

The contamination of soil by heavy metals results from crude oil discharge by oil refineries nearby the area and according to (Rasheed and Saleh, 2016) studies, they concluded that oil refineries have a big impact on heavy metals content in the soil. Heavy metals are toxic to the living organisms and can be categorized according to their level of toxicity (Crubellati et al., 2015): 1– Zn (super dangerous), 2– Mn (moderately dangerous), 3– Fe (low dangerous).

3.5.1 Zinc (Zn)

The highest amount of (Zn = 107.58 mgkg^{-1}) in sample no. (28) due to the soil being contaminated with crude oil, the same results are reported by (Pourang and Noori, 2014) who observed a high amount of (Zn) around the oil refinery. Moreover, the satellite image from (2013 until 9/2014) shows the residual stream near the same location where the highest concentration of (Zn) was reported (Fig. 3). However, according to (Ozaki et al., 2004) study one of the main sources of (Zn) on road is automobile exhaust and car tires which add a significant amount of (Zn) to the road, since our study was next to the busy off-road with cars and truck constantly using it (Fig. 3), therefore, this might be also another source for (Zn) in the study area this conclusion also proved by (Jeong and Technology, 2022) as the automobile tire mostly comprises of (Zn).

According to (Pendias and Pendias, 1992) world range of elements in non-polluted soils are between (17 – 125 mgkg^{-1}) and all analyzed soil samples are within this range. However, the contaminated soil sample is tremendously higher than the control sample (Zn = 0.098 mgkg^{-1}), in the same sites is more than (100 fold). The difference (Zn) between the studied soil sample and the control sample is considered the be the highest (Abd-alhamed, 2017).

Table 2: Heavy metals concentration (mg kg-1) in studied soils from different distances, directions, and locations.

Sample direction	Sample point (m)	Sample no.	Distance from source (m)	Heavy Metals (mgkg^{-1})		
				Mn	Fe	Zn
South	0	5	0.5	206.85^{e}± 34.13	17476.95^{V}±436.14	52.69 ^{h}± 2.68
		6	1.5	388.99^{N}± 68.21	15487.87^{a}±364.31	61.57^{V}±16.97
		7	2.5	333.7^{V}± 47.18	13147.81 ^{h}± 67.57	57.63 ^{b}±12.04
		8	5	395.74^{M}± 68.13	16412.9 ^{Y}± 275.45	41.69 ^{j}± 8.99
	Mean			331.32	15631.38	53.39
	50	9	0.5	323.99^{X}± 25.25	17329.13 ^{W}±97.29	95.14 ^{B}±35.92
		10	1.5	127.89 ^{i}± 15.02	15210.73 ^{c}± 153.5	64.83 ^{N}± 5.49
		11	2.5	175.53^{g}± 43.88	13574.67 ^{f}±404.21	43.1 ^{i}± 5.86
		12	5	290.11^{Z}± 27.54	13651.72^{e}±496.78	61.62 ^{T}± 4.34
	Mean			229.38	14941.56	66.17
	100	13	0.5	235.65 ^{b}± 51.6	13530.54^{g}±389.65	58.28 ^{Z}± 7.11
		14	1.5	189.88 ^{f}± 43.93	11925.09 ^{j}±212.76	49.28 ^{i}± 8.31
		15	2.5	404.88^{J} ± 19.09	14007.4 ^{d}± 647.33	66.6 ^{L}± 7.6
		16	5	230.9 ^{c}± 61.22	15589.04^{Z}±786.97	73.68 ^{F}± 3.65
	Mean			265.32	13763.02	61.96
	200	17	0.5	463.24^{F}± 53.21	21648.29 ^{D}± 287.5	59.35 ^{Y}± 7.45
		18	1.5	521.32^{B}± 60.65	22394.38 ^{A}± 287.7	68.94 ^{I}± 4.59
		19	2.5	286.08 ^{a}± 3.82	16891.03 ^{X}± 625.1	63.65 ^{O}± 2.71
		20	5	408.12^{I} ± 66.16	19464.16 ^{U}± 1177	58.22 ^{a}± 1.9
	Mean			419.69	20099.46	62.54
South			MAX	521.32	22394.38	95.14
			MIN	127.89	11925.09	41.69
North	0	1	0.5	366.96 ^{R}± 35.08	19898.88 ^{S}± 845	59.55 ^{X}± 1.49
		2	1.5	365.92 ^{S}± 37.08	20458.4 ^{R}± 685	56.07 ^{f}± 3.45
		3	2.5	500.16^{D} ± 49.55	21791.73 ^{C}± 716	69.76 ^{G}± 11.26
		4	5	372.93 ^{P}± 41.41	19653.86 ^{T}± 736	62.29 ^{R}± 11.99
		33	10	471.09^{E} ± 15.05	21377.4 ^{F}± 856.94	60.61 ^{W}± 7.08
	Mean			415.41	20636.05	61.65
	50	21	0.5	331.86^{W}±106.43	20478.45 ^{Q}± 988	61.87 ^{S}± 9.39
		22	1.5	369.06 ^{Q}± 26.04	20677.45 ^{N}± 1028	56.3 ^{d}± 13.83
		23	2.5	398.71 ^{K} ± 5.72	20524.75 ^{P}± 474	68.34 ^{J}± 6.39
		24	5	508.63^{C} ± 95.23	21892.52 ^{B}± 642	68.11 ^{K}± 4.27
		34	10	312.08 ^{Y}± 47.44	20956.78 ^{L}± 147	56.89 ^{c}± 5.44
	Mean			384.07	20905.99	62.30
	100	25	0.5	221.2 ^{d}± 50.54	15349.32 ^{b}± 763	74.29 ^{E}± 4.54
		26	1.5	138.97 ^{h}± 8.31	13134.27 ^{i}± 529	55.92 ^{g}± 4.97
		27	2.5	384.27 ^{O}± 12.91	20770.25 ^{M}± 182	69.08 ^{H}± 6.68
		28	5	528.13^{A}±125.07	21194.91 ^{I}± 414	107.59^{A}±33.45
		35	10	363.7 ^{T}± 18.62	21019.91 ^{K}± 36	62.66 ^{Q}± 8.42
	Mean			327.25	18293.73	73.91
	200	29	0.5	358.97 ^{U}± 22.5	21259.6 ^{G}± 725	82.2 ^{C}± 13.47
		30	1.5	430.53^{H} ± 14.43	21151.97 ^{J}± 653	63.53 ^{P}± 4.03
		31	2.5	396.9 ^{L}± 32.81	20571.71 ^{O}± 217	65.81 ^{M}± 9.5
		32	5	444.23^{G}±131.37	21629.02 ^{E}± 372	61.61 ^{U}± 5.44
		36	10	404.75^{J} ± 28.86	21215.24 ^{H}± 323	78.13 ^{D}± 8.17
	Mean			407.08	21165.51	70.26
Control				10.17	5263	0.0983
North		MAX		528.13	21892.50	107.59
		MIN		138.97	13134.27	55.92
Over all		AVG		351.44	18409.67	64.36
		MAX		521.32	22394.38	95.14
		MIN		127.89	11925.09	41.69

3.5.2 Manganese (Mn)

Manganese is one of the main heavy metals associated with petroleum products and this is agreed by (Chinedu et al., 2018), a high quantity of (Mn) in sample no. (28) due to the soil being polluted with crude oil since this location was facing untreated waste of crude oil discharged from nearby oil refineries such as (Arise et al., 2016) studies found a significant concentration of (Mn) in the area polluted with oil products. (Fig. 3) shows an image taken from the satellite from the year (2013 until September 2014), it explains the high concentration of manganese in the north direction, as well as, the highest concentration was detected in the same area where the waste oil dumping through. According to (WHO, 2000) standard permissible limit (SPL) for (Mn) is (437 $mgkg^{-1}$), while the mean concentration of (Mn =351.44 $mgkg^{-1}$) is below the (SPL) but in samples no. (3, 18, 24, 28, 32, and 33) it's higher than (SPL). The concentration of (Mn) in the control sample is (10.17 $mgkg^{-1}$) which is much lower than the nearby oil refinery soils. Therefore, indicating that the oil refiners have a great impact on the surrounding (Mn) content.

4.5.3 Iron (Fe)

(Table 2) shows the concentration of (Fe) is the highest among other studied heavy metals. The highest concentration in sample no. (18) may resulted from the accumulation of crude oil waste in the location this is also proven by (Rajesh et al., 2009) and (Chinedu et al., 2018) are concluded that a significant amount of (Fe) in the soil was derived from the oil spill. In (Fig. 3), both satellite images from (9/2014 and 9/2020) show a large pond of crude oil near the location where the highest concentration of (Fe) was recorded. The pond was providing continuous heavy metal to the surrounding soils this also proves the reason for the high (Fe) concentration at the farthest point from the main source which is located (800 m) away. Based on (WHO, 2000) standard, the (SPL) for soils (Fe) is (150 $mgkg^{-1}$) and according to (Ahmed, 2012) the range of iron in Erbil governorate soils is between (187.3 – 1073 $mgkg^{-1}$) compared to the mean concentration of iron and control sample its much higher than those ranges, but the range of total (Fe) concentration in soils according to (Kabata-Pendias and Pendias, 2001) between (5000 – 50000 $mgkg^{-1}$) and our samples still below the toxic limit.

5. CONCLUSIONS

Oil refineries near Gwer road in Erbil city have been discharging a large quantity of residual crude oil into the soil and providing it with the harmful pollutant. The results show that oil refineries have a significant impact on soil and it's the culprit for observing a high concentration of heavy metals in these areas. The soil near refineries was facing several anthropogenic activities like landfilling and excavation of soil which help to spread the contamination even faster.

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