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Evaluation and Study of Pollution in The Elements in The Baiji Refinery After the Recent Terrorist Operations

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ABSTRACT

The research is about the evaluation and study of heavy metal pollution in Baiji refinery after the recent terrorist operations. The samples were examined with an atomic absorption spectrometer (Atomic Absorption Spectrometer) model Shimadzu (AA6200) working with acetylene gas - in the laboratory of mechanical analysis - chemical engineering - Tikrit University, where the concentrations of heavy elements ranged (cadmium ≥ 4 mg/kg), nickel (16.8) - (4 mg/kg), copper (1.4-268.1) (mg/kg), zinc (21.6-554.8 mg/kg) and lead. (165.2 -2 mg/kg) (cobalt is less than (2 mg/kg), where the values of the pollution coefficient showed the presence of a low pollution coefficient in most areas and most of the elements, while there was (a very high pollution coefficient of zinc in the area of the loading arms, pumping and storage of fats Hydrogenation of fats, and less pollution of zinc (i.e., a significant pollution coefficient of zinc in the dewaxing division area), while the lead element was there (a very high pollution coefficient in the desalination of gases and northern refining), while for the copper element, there was significant pollution in the hydrogenation of fats. The results of laboratory tests have indicated that the values of some of the heavy elements taken within this study were outside the permissible limits when compared with the approved determinants for zinc, copper, cobalt, and lead.

Keywords- pollution, environmental, heavy metal, Baiji refinery, terrorist operations.

I. INTRODUCTION

Heavy metals are considered one of the important environmental pollutants due to their high stability and their unlimited permanence as they can move to areas, which are far from their original places and their concentrations can double through the food chain as some animals and plants become the end of the food chain and due to the high concentrations of these hazardous elements, they could be toxic and a great danger to the health (2). Attention to studying the heavy metals in the soil was focused as they are toxic and its constancy [(3)].

The hazard of these elements lie in their transport from the surface soil to the human body through the particles of the soil into the mouth through the inhalation of the soil particles or the dust that represents a potential danger to human health by means of inhalation [(4)].

1-1 Objective of the research

1. The access to a database that shows the pollution level all over the company.
2. Identifying the polluted locations and limiting the spread of pollution.
3. Evaluating the health dimensions of those elements and their impact on the working staff and attempting to decrease their negative effects.
4- Providing a safe environment for the field work in a way that guarantees the safety of the staff.

Three random areas were selected, in which the damage was very small so that these areas can be a benchmark for comparison. The first area is in the lube refinery (the energy of lube refinery) and it was compared with the infected areas (loading, plastic container manufacturing, oxidation section, pumping and storing the lubes, fat hydrogenation, wax removal and the area of RCR tank). The second area was AlShimal refinery area

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(AlShimal refinery firefighting), which was considered as a model that represents the unaffected areas and it was compared with the destroyed areas in AlShimal refinery area (AlShimal purification, Liquid gas unit LPG, Thermal cracking section 07 and gases analysis section 09). The third area was in Salah AlDeen refinery as the area of (the boilers of Salah AlDeen/2) as an area that is slightly affected compared to other affected areas (gasoline improvement S D/2, gasoline hydrogenation S D/2, After researching and resorting to the books and references and as this thesis is

II. PRACTICAL PART

In this part, the researcher discussed the method of samples collection, mentioning the devices and the chemicals used in this research.

2-1 Data collecting and data analysis

The area of the study is located inside the internal fence of North Refineries Company in Beiji district, Tikrite Governorate that is situated (180) kilometers to the north of Baghdad. The samples were obtained from the areas that were attacked with rockets, car bombs and explosive charges due to the terrorist operations to identify and investigate the polluted areas.

Twenteen(12) sites were selected to collect the soil samples with a depth of (0 – 10 cm) after removing the herbs, grass and strange objects. The samples were collected in August 2020 after obtaining the necessary approvals. Samples were kept in plastic bags and soil was dried and sieved using sieves with various diameters (4 micron, 2 micron and finally 1 micron). Samples were grinded in a ceramic mortar

2-2 Devices used

Table (1): Shows the devices Used

No.	Device	Origin
1	Flame Atomic Absorption Spector photo Meter-novAA-6200	Germany
2	Sensitive scale	Germany
3	(µm0.45) Millipore Filter Paper	Germany
4	Water Bath	England
5	Burette and various glass	China
6	A fridge for storing the samples	China

2-3 Chemical materials used in the study

The following chemical materials supplied by the companies mentioned below were used without purification as they highly pure as shown in table (2)

Table (2): Chemical materials used

No.	Name	Made in	Purity	Molecular Formula
1	Nitric Acid	R.D.H	....	HNO_3
2	Sulfuric Acid	R.D.H	....	H_2SO_4
3	Cadmium solution	Oxford /India	99%	Cd^{+2}
4	Cobalt solution	Oxford /India	99%	Cr^{+2}
5	Nickel solution	Oxford /India	99%	Ni^{+2}
6	Copper solution	Oxford /India	99%	Cu^{+2}
7	Zinc solution	Oxford /India	99%	Zn^{+2}
8	Lead solution	Oxford /India	99%	$pb^{+2,+4}$

2-4 Evaluation of the environmental pollution

In order to evaluate the level of contamination of the area soil, the contamination factor (CF) was used, which is used to classify the level of contamination by the elements in the soil samples by means of dividing the concentration of each element by the reference value of that element [(11).] The Contamination factor (CF) is calculated as follows:

$$(C_m)_{Background} / \mathbf{CF} = (C_m)_{sample}$$

where;

- $(C_m)_{Sample}$: A certain concentration in the soil
- $(C_m)_{Background}$: The concentration of the same element in the ground crust

Table (3): Shows the levels of environmental contamination factor

No.	Levels of contamination factor	Evaluation types
1	Low	CF > 1)less than 1(
2	Moderate	1>CF > 3)1-3(
3	High	3>CF > 6)3-6(
4	Very high	CF < 6) higher than 6(

Table (4) Abundance of elements in the earth crust

No.	Element concentration in the ground crust (18) **$(C_m)_{Background}$ ppm)(**	**Cadmium Cd.**	**Nickel Ni.**	**Copper Cu.**	**Cobalt Co.**	**Zinc Zn.**	**Lead Pb.**
1		20	20	55	10	70	14

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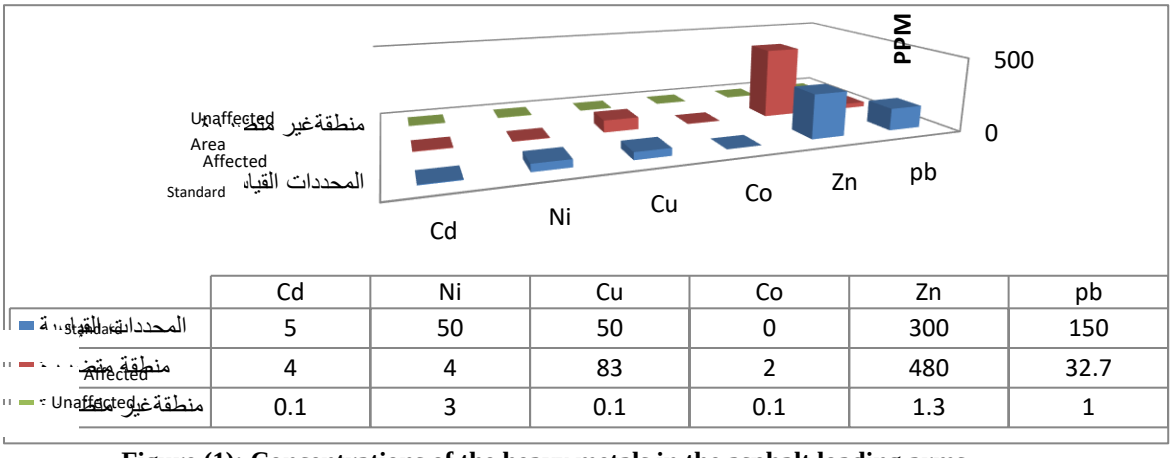
III. RESULTS AND DISCUSSION

Lube area		Area of AlShimal refinery	Area of Salah AlDeen refinery
1-	Asphalt loading arms	8- aerial purification	12- Gasoline improvement SD2
2-	Vessels manufacturing	9- Liquid gas unit	13- Gasoline hydrogenation SD2
3-	Oxidation section 108	10- Thermal cracking	14- Guest house
4-	Pumping and storing section 150	11- Gases sweetening	15- Old library
5-	Hydrogenation 105		
6-	Wax removal 204		
7-	PCR tank area		

3-1- Lubes area

3-1-1 Asphalt loading arms area

Concentrations of the heavy metals was measured in this area as shown in the image (2) and this area is located in the south. The concentration ranged between (2 – 480 ml/kg) as shown in figure (1). As for the contamination factor (CF) of zinc, it was very high and was moderate for lead and copper and the values for the rest of the elements was lower as shown in table (5). The values of contamination factor for zinc, copper and cobalt were higher than the limits of the World Health Organization. The reason behind the rise in the zinc concentration is due to the burning of fuel or wastes or the mechanical corrosion of vehicles or the solubility of the solid materials [12]. From the other hand the increase of the concentration of copper is attributed to the melting of the electrical cables (copper alloys) and the deterioration of the mechanical parts and emission to the environment [13]. When comparing with the unaffected areas (the energy of lubes refinery), it was clear that there were differences between it and the affected areas .



	Cd	Ni	Cu	Co	Zn	pb
المحددات القياسية Standard	5	50	50	0	300	150
منطقة متضررة Affected	4	4	83	2	480	32.7
منطقة غير متأثرة Unaffected	0.1	3	0.1	0.1	1.3	1

Figure (1): Concentrations of the heavy metals in the asphalt loading arms

Table (5)

Elements	Lead (Pb)	Zinc (Zn)	Cobalt (Co)	Copper (Cu)	Nickel (Ni)	Cadmium (Cd)
CF value	2.3	6.8	0.2	1.5	0.2	0.2
Category	Moderate contamination	Very high contamination	Low contamination	moderate contamination	Low contamination	Low contamination

3-1-2 Vessels and Barrels Factory

The area of manufacturing the vessels and barrels is located in the southern area. The concentrations of the heavy metals (as shown in figure 2) ranged between (2 – 61.5 ml/kg). As for the contamination factor (CF) (table 6), the contamination factor was low for all the elements. Nevertheless, the concentrations were within the acceptable limits except for the cobalt, which was high

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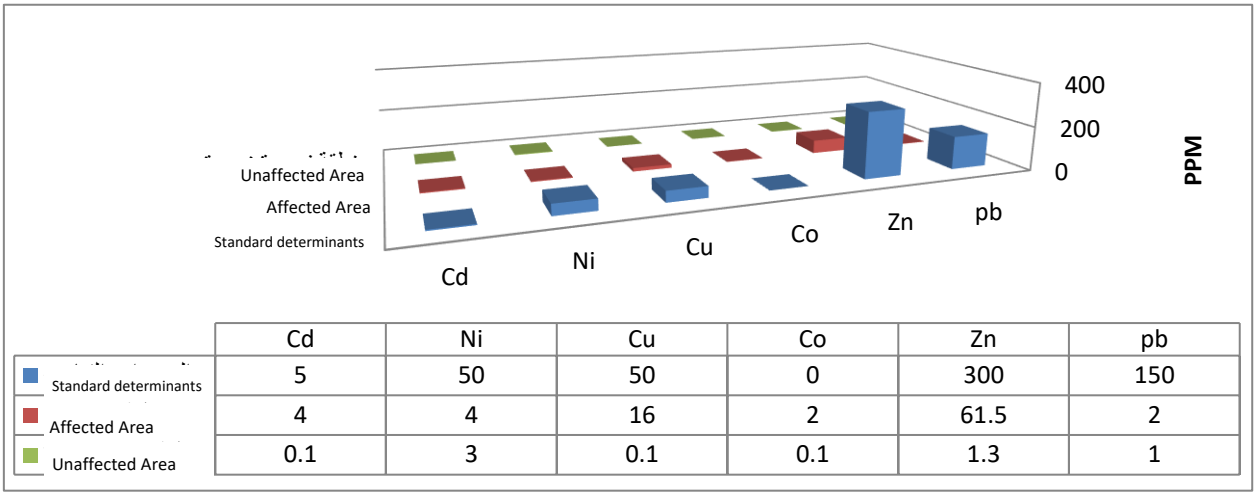
due to the combustion of the fuel especially in the furnaces and burners and after that it precipitates on the soil surface [14]. Comparison was made with the unaffected areas in the lube refinery and there were slight differences between them as shown below:



	Cd	Ni	Cu	Co	Zn	pb
Standard determinants	5	50	50	0	300	150
Affected Area	4	4	16	2	61.5	2
Unaffected Area	0.1	3	0.1	0.1	1.3	1

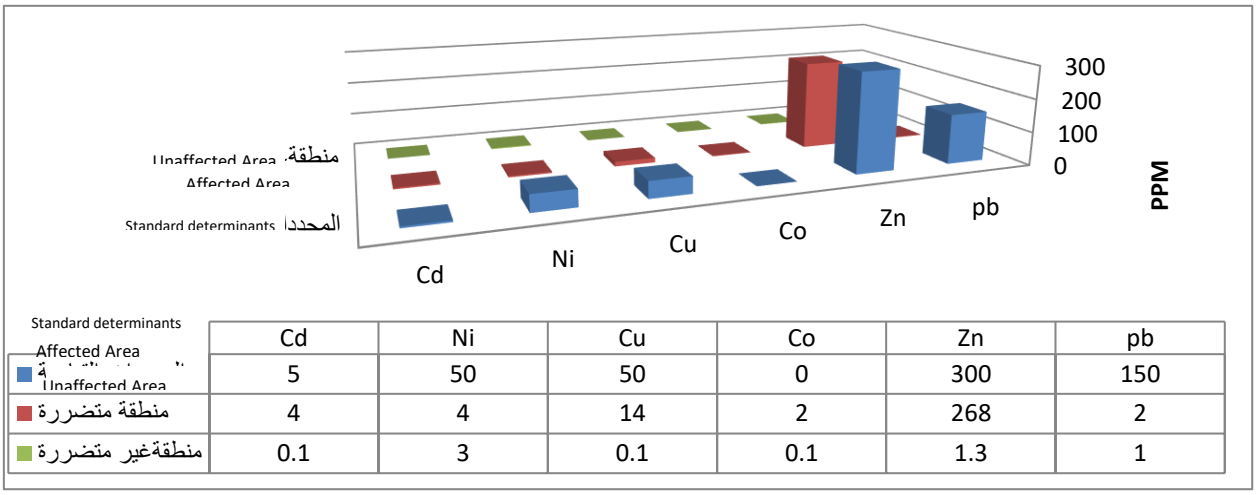
Figure (2): The concentrations of the heavy metals in the area of manufacturing the vessels and barrels

Table (6)

Elements	Lead (Pb)	Zinc (Zn)	Cobalt (Co)	Copper (Cu)	Nickel (Ni)	Cadmium (Cd)
CF value	0.14	0.8	0.02	0.3	0.2	0.2
Category	Low contamination	Low contamination	Low contamination	Low contamination	Low contamination	Low contamination

3-1-3 Oxidation Section Control

This section is located in the southern area ,The concentrations of the heavy elements, which ranged between (2 – 268 ml.kg), was measured (figure 3). The zinc values of contamination factor were moderate and the values for the rest of the elements were lowed (table 7). In general, the concentrations of the heavy metals in this site didn't exceed the acceptable limits, except for the cobalt and zinc [12, 14]. When comparing with other unaffected areas (lube energy), it was obvious that there were significant differences particularly for zinc and copper.



	Cd	Ni	Cu	Co	Zn	pb
Standard determinants	5	50	50	0	300	150
منطقة متضررة	4	4	14	2	268	2
منطقةغير متضررة	0.1	3	0.1	0.1	1.3	1

Figure (3): Concentrations of the heavy metals in oxidation section control

Table (7)

Elements	Lead (Pb)	Zinc (Zn)	Cobalt (Co)	Copper (Cu)	Nickel (Ni)	Cadmium (Cd)
CF value	0.14	3.8	0.2	0.25	0.2	0.2

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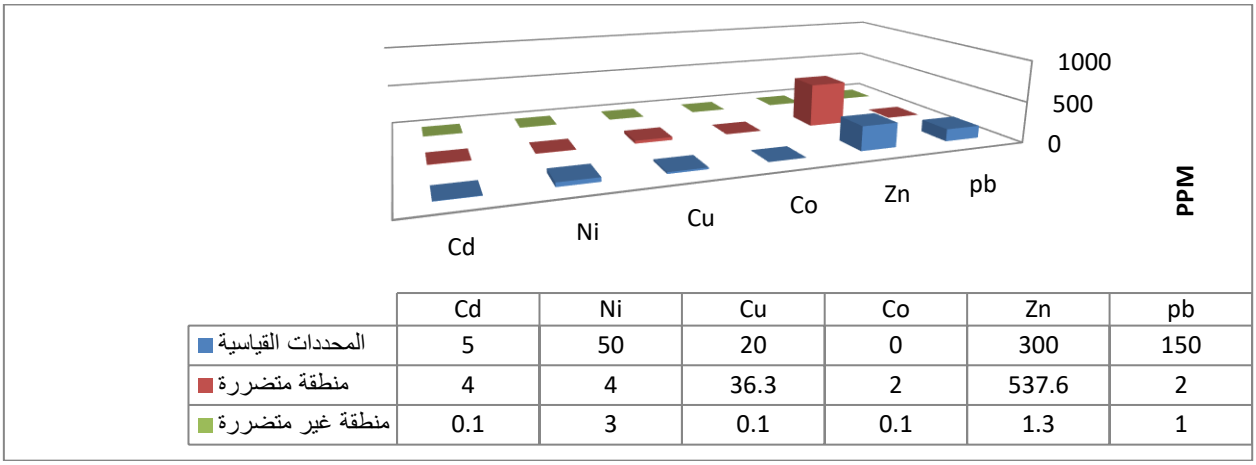
Category	**Low contamination**	**Low contamination**	**Low contamination**	**Low contamination**	**Low contamination**	**Low contamination**

3-1-4 Area Pumping and storing the lubes

This area is located in the southern location near from the oxidation section. As for the concentrations of the heavy metals, the values ranged between (2 – 537.6 ml.kg), as shown in figure (4). The value of contamination factor of zinc was very high, while the values of the rest of the elements were low (table 8). In general, the concentration values were within the acceptable limits, except for the zinc and copper [12,13]. When comparison is made with the unaffected areas in the refinery of lubes, there were significant differences especially for the zinc and copper.



	Cd	Ni	Cu	Co	Zn	pb
المحددات القياسية	5	50	20	0	300	150
منطقة متضررة	4	4	36.3	2	537.6	2
منطقة غير متضررة	0.1	3	0.1	0.1	1.3	1

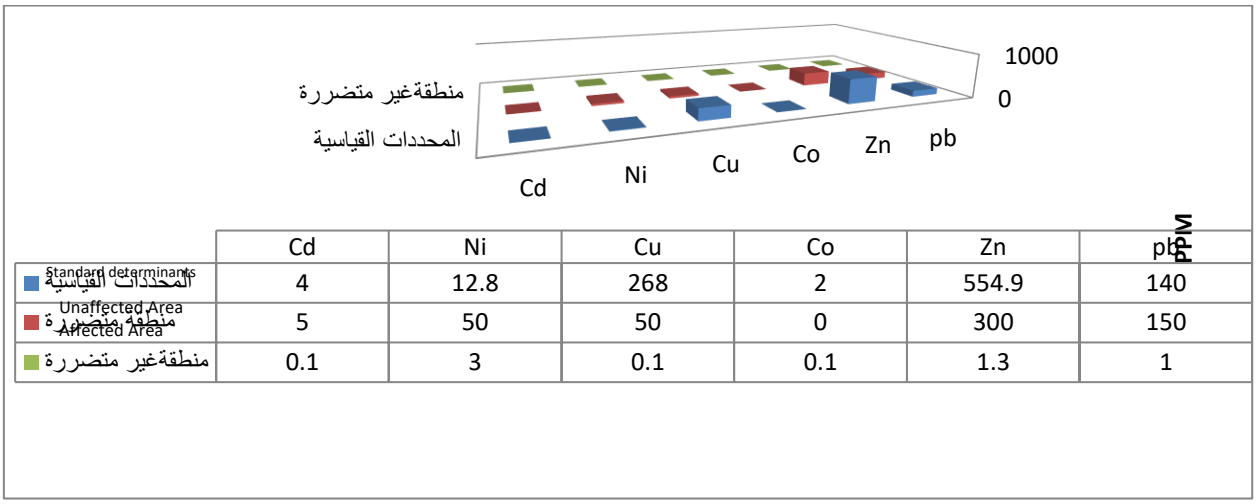
Figure (4): Concentrations of the heavy metals in the area of pumping and storing of lubes

Table (8)

Elements	**Lead (Pb)**	**Zinc (Zn)**	**Cobalt (Co)**	**Copper (Cu)**	**Nickel (Ni)**	**Cadmium (Cd)**
CF value	**0.14**	**7.6**	**0.2**	**0.65**	**0.00**	**0.005**
Category	**Low contamination**	**Very high contamination**	**Low contamination**	**Low contamination**	**Low contamination**	**Low contamination**

3-1-5 Lubes hydrogenation

This section is located near from the management of lube department. The concentrations of the heavy elements were (2-554.9 ml/kg) as shown in figure (5). The contamination factor (CF) of zinc was very high, high for copper, moderate for lead and low for nickel and cadmium. According to table 9, the concentrations of zinc, cobalt and copper ([12), (14), (13)] were higher than the acceptable limits and when comparison is made with the unaffected areas (are of lube energy), difference was clear for all the elements except for the cobalt, as shown in the following figure:



	Cd	Ni	Cu	Co	Zn	pb
Standard determinants المحددات القياسية	4	12.8	268	2	554.9	140
Unaffected Area منطقة متضررة Affected Area	5	50	50	0	300	150
منطقةغير متضررة	0.1	3	0.1	0.1	1.3	1

Figure (5): Concentrations of the heavy metals in lube hydrogenation area

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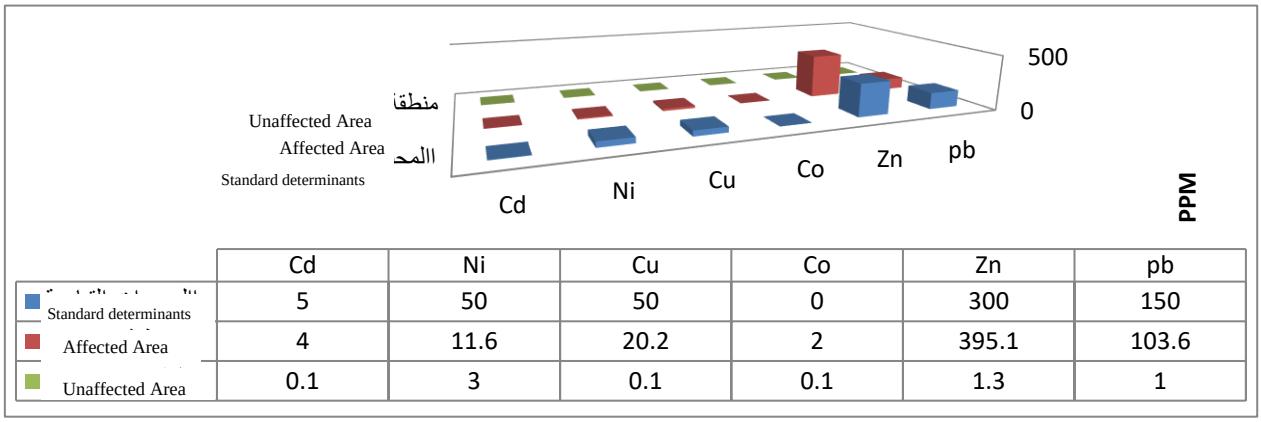
Table (9)

Elements	Lead (Pb)	Zinc (Zn)	Cobalt (Co)	Copper (Cu)	Nickel (Ni)	Cadmium (Cd)
CF value	1	7.9	0.2	4.8	0.6	0.2
Category	Moderate contamination	Very high contamination	Low contamination	High contamination	Low contamination	Low contamination

3-1-6 Dew axing section

The concentrations of the heavy metals ranged between (2-395.1 ml/kg) as shown in figure (6). As for the values of the contamination factor, the value was high for zinc and the value was lower for the rest of the elements as shown in table (10). All the concentrations were within the acceptable limit except for the values of zinc and cobalt [12), (14)] that exceeded the standard specification of the World Health Organization. There were significant differences with uncontaminated areas, as shown in the figure below:



	Cd	Ni	Cu	Co	Zn	pb
Standard determinants	5	50	50	0	300	150
Affected Area	4	11.6	20.2	2	395.1	103.6
Unaffected Area	0.1	3	0.1	0.1	1.3	1

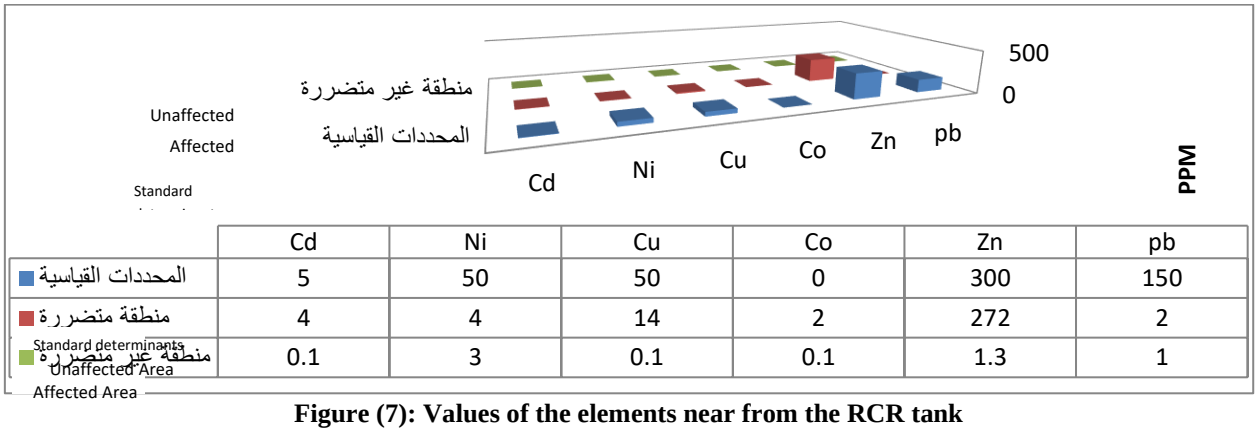
Figure (6): Concentrations of the heavy metals at the wax removal area

Table (10)

Elements	Lead (Pb)	Zinc (Zn)	Cobalt (Co)	Copper (Cu)	Nickel (Ni)	Cadmium (Cd)
CF value	0.7	5.6	0.2	0.36	0.58	0.2
Category	Low contamination	high contamination	Low contamination	Low contamination	Low contamination	Low contamination

3-1-7 Damaged tank site (RCR)

Samples were taken from the area near from the (RCR) tank, which is related to the lubes section (image 8). The concentrations of the heavy metals ranged between (2-272 ml/kg) as shown in figure (7). The values of the contamination factor was high for zinc and the value was lower for the rest of the elements as shown in table (11). All the concentrations were within the acceptable limits except for the values of zinc and cobalt [12), (14).] There were no significant differences with uncontaminated areas, except for zinc which was significant.



	Cd	Ni	Cu	Co	Zn	pb
المحددات القياسية	5	50	50	0	300	150
منطقة متضررة	4	4	14	2	272	2
منطقة غير متضررة	0.1	3	0.1	0.1	1.3	1

Standard determinants
Unaffected Area
Affected Area

Figure (7): Values of the elements near from the RCR tank

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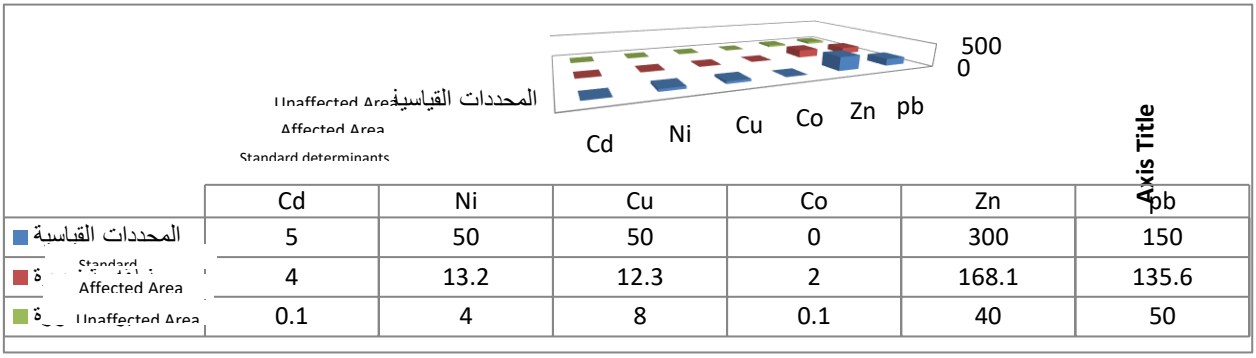
Table (11)

Elements	Lead (Pb)	Zinc (Zn)	Cobalt (Co)	Copper (Cu)	Nickel (Ni)	Cadmium (Cd)
CF value	0.14	3.8	0. 02	0.25	0.2	0.2
Category	Low contamination	high contamination	Low contamination	Low contamination	Low contamination	Low contamination

3-2 Alshimal refinery site

3-2-1 Alshimal purification (aerial purification)

Samples were taken from the area from the ground of the aerial purification tower at AlShimal refinery. The concentrations of heavy metals ranged between (2-168.1 ml/kg) as shown in figure (8). The values of the contamination factor for lead was very high and moderate for zinc as demonstrated in table (12). As for the concentrations of zinc, cobalt and lead [12], [14] the concentrations were higher than the acceptable limits internationally approved and this is due to the emission of high quantities of vehicle fuel and the chemical additives or the lead ethyl and it still reflects historical contamination considerably due to the long age of lead in the soil [22]. When comparing with the unaffected areas, significant differences were observed for all the elements, as shown in the figure below:



	Cd	Ni	Cu	Co	Zn	pb
المحددات القياسية	5	50	50	0	300	150
Affected Area	4	13.2	12.3	2	168.1	135.6
Unaffected Area	0.1	4	8	0.1	40	50

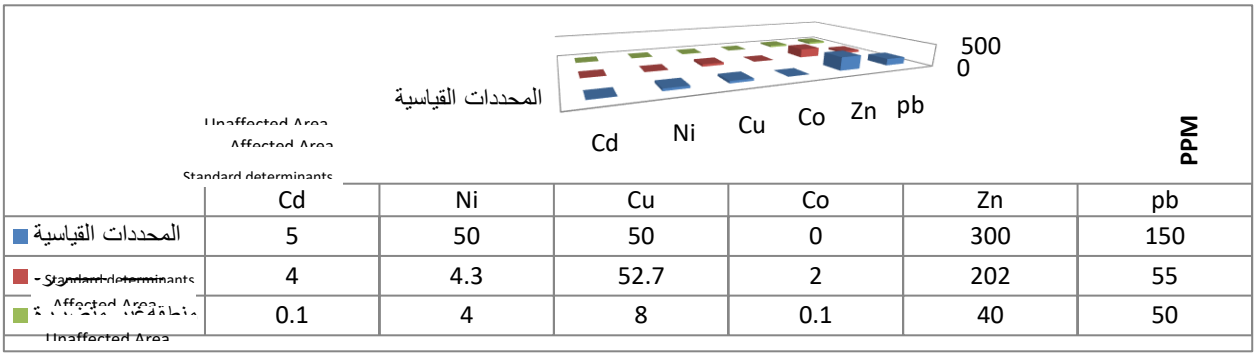
Figure (8): Concentrations of the heavy metals in AlShimal refinery

Table (12)

Elements	Lead (Pb)	Zinc (Zn)	Cobalt (Co)	Copper (Cu)	Nickel (Ni)	Cadmium (Cd)
CF value	9.6	2.4	0. 2	0.2	0.65	0.02
Category	Very high contamination	moderate contamination	Low contamination	Low contamination	Low contamination	Low contamination

2-3-2 Liquid gas unit (LPG) at AlShimal

Samples were taken from the area of the liquid gas at AlShimal refinery. The concentrations of heavy metals ranged between (2-202 ml/kg) as shown in figure (9). The values of the contamination factor of zinc was moderate and closer to high and contamination was low for copper and also low for nickel, while the values were lower for the rest of metals as shown in table (13). The concentration of all the elements were lower than the acceptable limit except for copper and cobalt [13], [14]. When comparison is made with the unaffected areas, it is found that there is variations in the concentrations as shown in the figure below:



	Cd	Ni	Cu	Co	Zn	pb
المحددات القياسية	5	50	50	0	300	150
Standard determinants	4	4.3	52.7	2	202	55
Affected Area	0.1	4	8	0.1	40	50

Figure (9): concentration of heavy metals in the liquid gas unit

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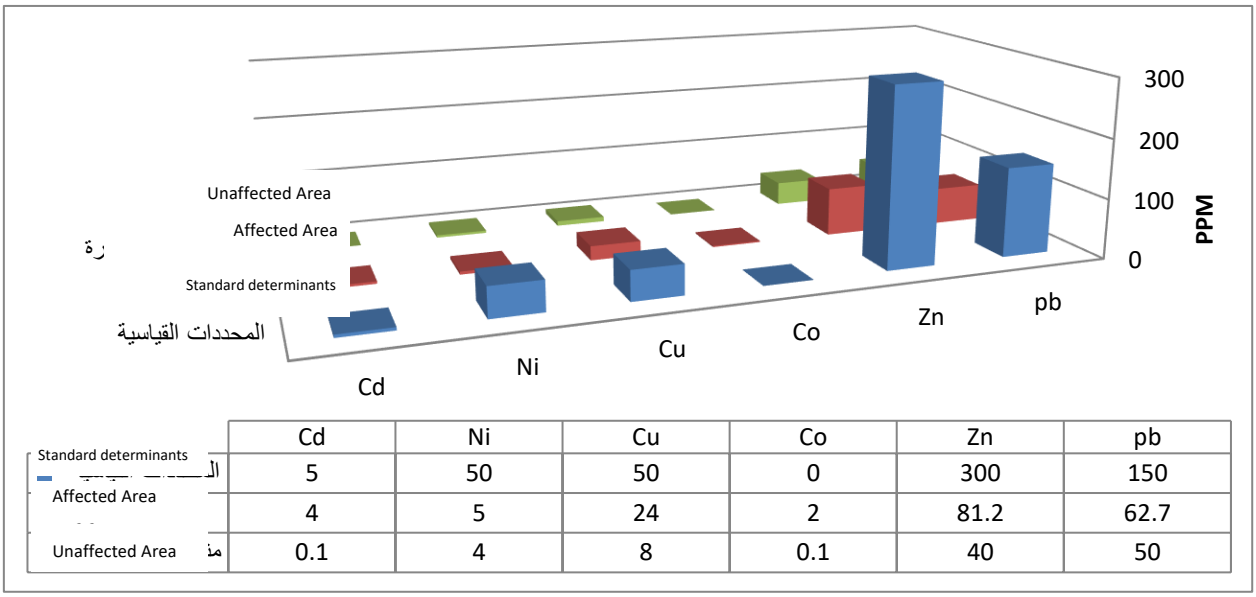
Table (13)

Elements	Lead (Pb)	Zinc (Zn)	Cobalt (Co)	Copper (Cu)	Nickel (Ni)	Cadmium (Cd)
CF value	0.14	2.8	0.2	0.94	0.2	0.2
Category	Low contamination	moderate contamination	Low contamination	Low moderate contamination	Low contamination	Low contamination

3-2-3 Thermal cracking at AlShimal (O7)

Samples were taken from the site of thermal cracking at AlShimal refinery. The concentrations of heavy metals ranged between (2-81.2 ml/kg) as shown in figure (10). The values of the contamination factor of zinc was moderate and closer to high and contamination was low for copper and also low for nickel, while the values of the rest of metals were as shown in table (14). The concentration of all the elements were lower than the acceptable limit except for cobalt [14]), which was higher than the acceptable value. When comparison is made with the unaffected areas (AlShimal refinery energy), it is found that there were variations in the concentrations as shown in the figure below:



	Cd	Ni	Cu	Co	Zn	pb
Standard determinants	5	50	50	0	300	150
Affected Area	4	5	24	2	81.2	62.7
Unaffected Area	0.1	4	8	0.1	40	50

Figure (10) Concentrations of the heavy elements in the thermal cracking unit

Table (14)

Elements	Lead (Pb)	Zinc (Zn)	Cobalt (Co)	Copper (Cu)	Nickel (Ni)	Cadmium (Cd)
CF value	0.14	1.1	0.2	0.17	0.2	0.2
Category	Low contamination	moderate contamination	Low contamination	Low contamination	Low contamination	Low contamination

3-2-4 Area of gases sweetening section (09):

Samples were taken from the site of gases sweetening unit at AlShimal refinery). The concentrations of heavy metals ranged between (2-165.2 ml/kg) as shown in figure (11). The values of the contamination factor showed a very high contamination of lead but for zinc it was moderate and low for the rest of the elements as shown in table (15). In general, the concentrations of all the elements were lower than the acceptable limits except for lead and cobalt ([14), (15).] When comparison is made with the unaffected areas (AlShimal refinery energy), it is found that there were differences in lead and zinc as in the figure below:

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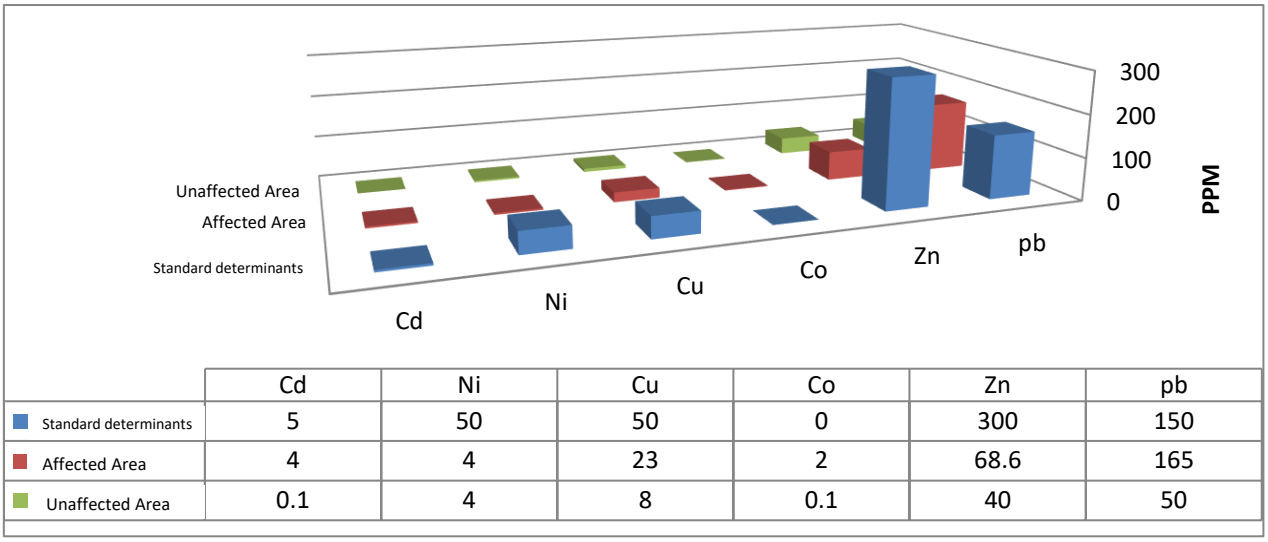


	Cd	Ni	Cu	Co	Zn	pb
Standard determinants	5	50	50	0	300	150
Affected Area	4	4	23	2	68.6	165
Unaffected Area	0.1	4	8	0.1	40	50

Figure (11): Concentrations of the heavy elements in gas sweetening unit

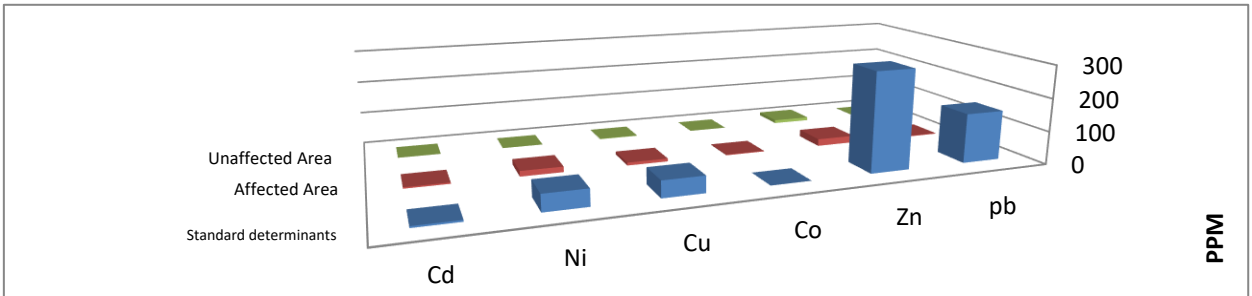
Table (15)

Elements	Lead (Pb)	Zinc (Zn)	Cobalt (Co)	Copper (Cu)	Nickel (Ni)	Cadmium (Cd)
CF value	11.8	1	0.2	0.43	0.2	0.2
Category	Very high contamination	moderate contamination	Low contamination	Low contamination	Low contamination	Low contamination

3-3 Salah AlDeen area

3-3-1 Gasoline improvement in Salah AlDeen refinery/2

Samples were taken from the site of gasoline improvement at Salah AlDeen refinery /1. The concentrations of heavy metals ranged between (2-21.6 ml/kg) as shown in figure (12). The values of the contamination showed low contamination as shown in table (16). In general, the concentration of all the elements was lower than the acceptable limit except for cobalt [14], which was higher than the acceptable value. When comparison is made with the unaffected areas, it is observed that there were no differences as shown



	Cd	Ni	Cu	Co	Zn	pb
Standard determinants	5	50	50	0	300	150
Affected Area	4	16.8	9	2	21.6	2
Unaffected Area	0.1	0.1	1	0.1	10.3	1

Figure (12): Concentrations of the heavy elements in the gasoline improvement unit

Table (16)

Elements	Lead (Pb)	Zinc (Zn)	Cobalt (Co)	Copper (Cu)	Nickel (Ni)	Cadmium (Cd)
CF value	0.14	0.3	0.2	0.34	0.8	0.2

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Category	**Low contamination**	**Low contamination**	**Low contamination**	**Low contamination**	**Low contamination**	**Low contamination**

IV. CONCLUSIONS & RECOMMENDATIONS

It was tested in the laboratory that the concentrations of the elements part within the study area (within the security fence of the northern refineries) and the largest part of them were within the standard limits, including the global health (who) And through the values of the active coefficients that are measured in an area, large innovations were discovered in most areas and most of the elements while there was (a very high coefficient of zinc production in the area of the loading arms, pumping and storage capacity, the degree of capacity). The contamination with zinc was lower, i.e. higher contamination factor in the wax removal unit. As for lead the contamination was very high in gases sweetening site and the purification in AlShimal) and a high contamination of copper in the site of lube hydrogenation. To limit the spread of these poisonous elements and to preserve the health of the company staff, it is recommended.

- Use the salt-free sterilized water to wash the contaminated soil to dissolve the salts using the Leaching technique.
- Spraying the contaminated area with Na_2EDTA with a concentration of (0.03 M) of the aqueous [16].
- Hydrochloric acid can be used as a solution for extracting the heavy elements [16].
- Cultivating certain plants near the contaminated areas that are called (plants hyper accumlatrices with high capability to absorb and uptake the contaminated materials and extract part of the heavy elements that exist in the soil. These plants include sunflower, Indian mustard and yellow corn) [17].
- Establishing the green belts projects around the units.
- Administer liquid milk to the staff who work near the areas that include the heavy elements.
- Conducting periodic surveys to the soil, especially the sites that are close from the storages of the petroleum products as they have negative effects on the environmental resources.

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