The Assessment of Soil Contamination for Some of Basrah province Technology Regions Using ICP-GCMS

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Abstract

This study determined that soil pollutants considered widespread, available, and toxic to the environment include cadmium, aluminum, nickel, cobalt, copper, iron, lead, zinc, and arsenic. For this study, seven areas were selected in Basra governorate, including Safwan, Juaibda, Rumaila, Nahran Umer, Al-Najibiya, Abu al-Khaseeb, and Karmat Ali (Garden of the College of Science). Some soil factors were estimated, such as pH, salinity, total organic carbon, and soil texture. The highest value for pH was 8.21 at Karmat Ali, and the lowest value, 7.75, was detected at Juaibda, where the alkalinity of soil was available for all locations. As to salinity, the highest was 41.984 mg/l at the Nihran Umer location and the lowest at Juaibda at 2.854 mg/l, and values of the total organic carbon for soils were distinguished at the Abu al-Khaseeb location, where the highest values were detected at 0.27 mg/l and the lowest at 0.03 mg/l at Juaibda. The results showed a significant variance in the accumulation of pollutants for soils under study, where the highest values for Al, Ni, Fe, Cu, Pb, Co, Mn, Zn, and arsenic were 546.3, 81.67, 15739, 26, 20, 39.8, 87, 476.32 and 3.39 ppm respectively at Abu al-Khaseeb location. It was the most contaminated area. As to cadmium, the highest value was at 2.44 ppm at the Rumaila location, lead registered the highest value at 39.8 ppm at Safwan, and magnesium registered the highest value at 476.32 ppm at Rumaila. The lowest values were found at Juaibda, such as aluminum, iron, and copper at 151.88, 2911, and 5.8 ppm, respectively. The lowest accumulation for nickel was 11.46 ppm at the Najibiya location, cobalt was at 3.9 ppm at the Rumaila location, zinc and arsenic 56 and 0.36 ppm respectively at Safwan, and manganese was the lowest at 221 ppm at Najibiya. Besides.

Keywords: ICP, SEM-GCMS, pollutants, soil, accumulation, cadmium, aluminum.

Introduction

Mineral contamination results from discharging heavy elements into the environmental system. This is attributed to many reasons. The main reason is that human sources such as waste discharged to the environment through factories and plants, which could be liquid, solid or gas waste, are considered significant commercial lines in transporting oil globally (Al-Rubayai, 2002).

The human source is divided into developing and movable sources, where thousands of metric tons of gases flow at all energy locations that work using fuel, gas flame, and the like into the local atmosphere. Recently, car exhausts have become the main

source of pollution, including human sources and small industrial plants that cause gas emissions. These increase the traffic and the problem of high environmental emissions (Al-Hasan, 2011). Knowing the distribution and concentration of heavy elements in soil will help explore and determine contamination sources with heavy minerals and control pollutants (Al-Sultani, 2006). Concerns about soil contamination are increasing in every region. The United Nations Assembly for Environment (UNEA-3) has adopted a decision calling for accelerating actions and cooperation for treating and managing soil contamination. This consensus, carried out by more than (170) states, is a clear sign of the global importance of soil contamination and the readiness of these states to develop tangible solutions for curing the causes and effects of such a significant threat (Oldeman, 1991). Soil contamination cannot be evaluated or seen directly, making it a hidden danger and harmful to any organism that is not targeted (FAO and ITPS, 2015). Also, soil pollution has resulted from incomplete combustion of many materials and deposition of radioactive materials from air weapon tests and nuclear incidents. Besides, new concerns have been disclosed regarding emerging pollutants such as pharmaceutical and beauty cosmetics, hormones, toxins, and bio-pollutants such as bacteria and viruses. Soil contamination could severely damage the main ecosystem services that soil provides (Huan Feng *et al.*, 2008).

Moreover, soil contamination belittles food security via decreasing crop yields due to toxic levels of pollutants. And crops produced from contaminated soil are unfit for human and animal consumption (Chen and Gallie, 2005). Pollutants directly cause damage to micro-organisms and large organisms in the soil, then affecting the bio-diversity of soil and services provided by affected organisms. Risks to human health come from contamination caused by heavy elements such as arsenic, lead, cadmium, and organic chemicals such as polychlorinated biphenyls and PAHs (Swartjes, 2011). It is highly demanded to reduce soil contamination of the agricultural sources through implementing the world Sustainable Administrative Practices for Soil (Cachada, *et al.*, 2018).

Materials and Methods
Study Area:
For the collection of soil samples, seven areas in Basra governorate, South of Iraq, were selected in Basra governorate including Safwan (Juaibda between safwan and Rumaila), Rumaila, Nahran Umer, Najibiya, Abu Al-Khaseeb, and Karmat Ali (Garden of the College of Science). Soil samples were collected from the nominated areas, sent to the laboratory, cleaned of plant residues, sifted with a 63- micron sieve, then placed and stored in containers to be used later for required tests.

Soil Texture:
To identify the size of granules, (10) grams of soil were taken, and the percentages of the sizes of these granules (sand, silt, and clay) were calculated based on the volumetric pipette method according to the procedure detailed in Folk (1974).

Evaluation of pH:
By taking (25) grams of soil, pH was estimated for each under the study. Then (75) ml of distilled water was added, mixed well in a glass flask, left for (24) hours, then filtered. The pH was measured, and the quantity of salinity of the same mixture. The result was shown in ml/l. (Allison,1973).

Total Organic Carbon:
The Total Organic Carbon was estimated by Weaver and Ball (1964) using an incineration method, where a quantity of soil was taken from areas under study. Then, it was placed in a weight-known basin. Later, it was sent to an incineration kiln at (550) Celsius for (48) hours. Samples were got out of the kiln using a plier, samples weighted, then organic carbon was calculated according to the following equation:
Total carbon weight % = weight of basin with soil before burning – basin weight after burning 100*

Analysis Using ICP – MS:
To estimate the quantity of heavy elements in soil by using SEM-GCMS, the following is carried out:
1. Soil samples were taken and analyzed following ROPME (1987) as follows:
A weight of (1) gram of soil samples for each study area, placed in pipes of analysis, and (10) ml of Aqua regain solution was added, which consisted of (3) volumes of the concentrated

hydrochloric acid to (1) volume of the concentrated nitric acid, then samples were heated in the analysis device at (90) Celsius degree for two hours. Following analysis, a part of the digest solution was placed in a volumetric flask, and volume was completed to be (50) ml using distilled water free of ions. Samples are stored until the time of conducting measures using an inductively coupled plasma – Mass Spectrometer (ICP – MS). Also, samples were photographed using SEM-GCMS to determine the distribution of elements on soil granules' surfaces. Besides, soil samples were photographed by the SEM device.

Results and Discussion
Soil Physical and Chemical Tests
pH

Figure (1) explains spatial changes in the pH values, which is considered a measure of the acidic, alkaline nature of soils under study.

Results showed that the alkaline pH was prominent in the areas of study, where the highest values were found at the area of the College of Science garden (comparison location), registered at 8.21, which was attributed to continuous irrigation with the high salinity water of Shatt al-Arab that the soil was vulnerable to. This, in turn, leads pH to become alkaline, while the lowest pH value was found in the Juaibda area, at 7.75. This was attributed to the structural nature of the soil in this area, which is usually sandy (silica) and free of salts that affect the value of pH (Al-Jandeel, 2001). Besides, the pH values among soils under study was attributed to different root discharges in plant roots in addition to its content of gypsum, decomposed organic materials, salt concentration, and sodium ion concentration (Al-Azzawi, 2016).
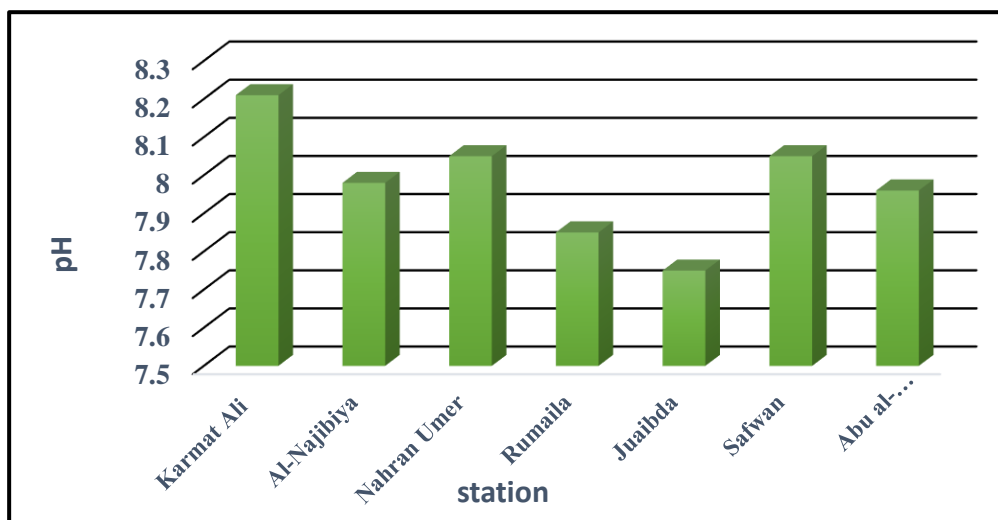

Figure 1: pH values in soils of the study areas

Salinity:

Figure (2) represents spatial changes in the salinity of the studied areas. Results showed a variation in the salinity content among the study areas, where the highest values in the salinity percentage were registered at Nahran Umer at 41.984 mg/L. The main reason behind this was the dry climate, hot weather accompanying these areas, high temperatures, and scarcity of rainfall, which brought about high levels of water

evaporation from the soil, then caused an increase in salinity. Second, the lowest salinity value was registered at Juaibda, amounting to 2.8544 mg/L, and was attributed to soils characterized by its dry sandy texture, poor ions, and distance from water sources and estuaries. Also, results reflected variation in salinity values among other study areas attributed to the variation in a physiographic location for study areas between the highest and lowest, and saline ground water levels were affected. This led to the movement of water salts in the

capillary action and their gathering on the surface (Al-Zubaidi, 2011). Besides, some areas are in the vicinity of marshes. These areas, especially Karmat Ali area, represented by the University of Basra location – the garden of the College of Science, are irrigated by waters headed from Shatt al-Arab affected by current tidal waters, sewage, and heavy industrial waters (Smith, 2004; Johansson, 2004).
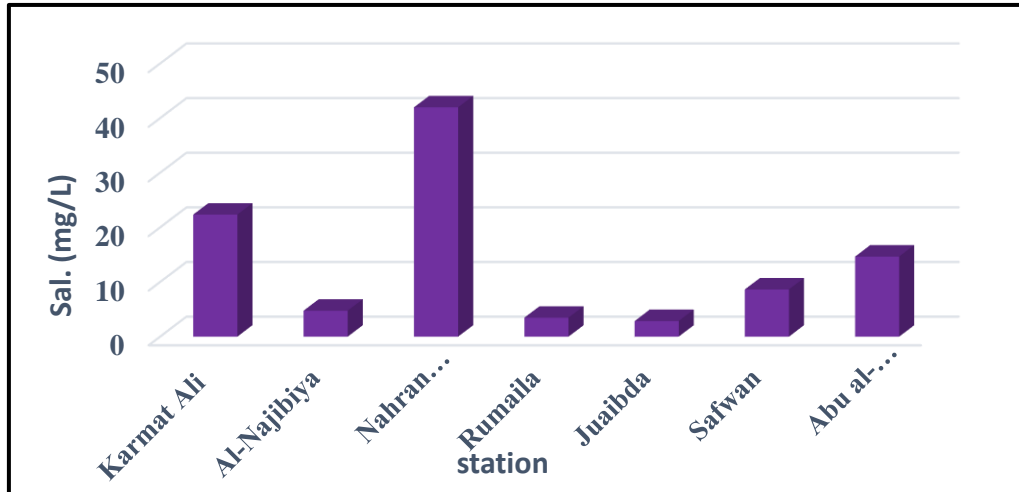

Figure 2: Salinity values in soils of areas under study

Total Organic Carbon (TOC):

Figure (3) pinpoints spatial changes in the soils' organic carbon values for studied areas. The said figure indicated the highest value of organic carbon in Abul Khaseeb area, amounting to 0.27 ml/1g of soil. This might be attributed to the fact that these areas are agriculturally affected by fertilizers containing high percentages of agricultural residues and fertilizers (Sharply, 2000).

Secondly, the burning of plants, accumulation of animal waste in that area, and the use of such areas as agricultural and grazing areas contributed to raising the percentage of organic materials in soils (Al-Jaberi, 2013), in addition to human usage and household waste that take part in raising values (Farid, 2017). Finally, low organic materials concentrations were in the Juaiba area, amounting to 0.03 ml/1g soil. This was due to many reasons: high temperatures and the non-agricultural regions, and the difficulty of plants growing in such areas as they fell in the desert range (Haller *et al*., 1974). It is worth mentioning that organic materials become less as long as human activities are limited (al-Shamsi *et al*., 2016).
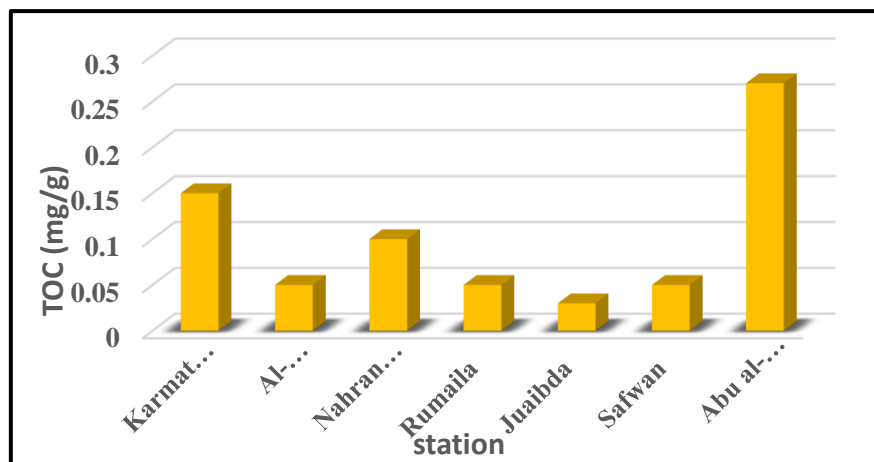

Figure 3: TOC values in soils of areas under study

Soil Texture:

Results of soil texture indicated that most of the study areas were characterized by their different nature. Abul Khaseeb area is characterized by its clay soil due to its high percentage of clay, which amounted to %53. In contrast, the Juaibda area was characterized by its smooth sandy soil, as the percentage of soil in it amounted to %88. As to other areas, it ranged between silt sandy and clay silt (mixture) according to the following table1

Table 1: Percentage of soil granules and their texture in the study areas

Area	% Clay	% Silt	% Sand	Texture
College garden	20	46	34	Loam
Najibiya	18	30	52	Silt sand
Nahran Umer	15	55	30	Silt clay
Rumaila	7	33	60	Silt clay
Juaibda	3	9	88	Loamy Sandy
Safwan	11	22	67	Sand silt
Abul-Khaseeb	53	26	21	clay

Heavy Elements in Soil:
Cd

Figure (4) showed light on the amount of the Cd element accumulated in the Basra governorate soil study areas. The highest value appeared at Rumaila, which amounted to 2.44 ppm. This was because this area is close to oil exploration sites and industrial operating sites, which largely contributed to the increase in the soil content of Cd. Also, keep discharging pollutants in abundance through oil extraction and refining operations, human activities, and disposal of different waste such as iron and automobile waste, etc. Moreover, mineral soils containing their natural materials may be the reason behind an increase in cadmium in soil (Al-Bassam, 2011), while the soil of the College of Science's garden recorded the lowest values, which amounted to 0.9 ppm. Such decrease was attributed to the fact that these locations are not contaminated with residues of crude oil, being away from the primary contamination areas or flame locations, being an agricultural area where their soils are vulnerable to being continuously washed by irrigation, and being away from the movement of automobiles and fuel burning (Chronopoulos *et al.*, 1997). Usually, these are considered high compared to Cd percentage in soils ranging between 0.01 – 0.70 ppm (Sarkar, 2002).
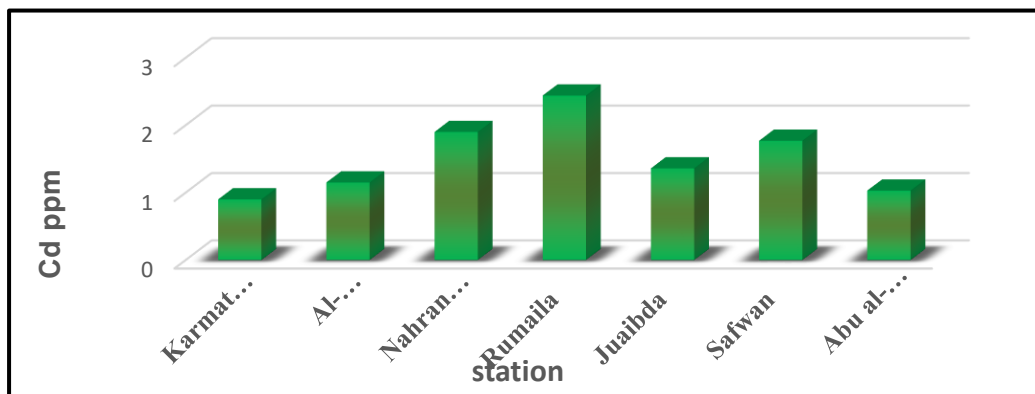

Figure 4: Cadmium element accumulated in soils of areas under study

Al

First of all, figure (5) shows an aluminum element accumulation in the study area's soil. Results brought to light that the highest value of aluminum was at 546.3 ppm at Abul Khaseeb area due to the high density of traffic and human activities such as waste of aluminum-manufactured doors and windows factories along with human waste such as beverage cans, plastic bags, pot lids and cans made from aluminum. This element (Al) is considered one of the widespread minerals used in packaging drinks and foods; therefore, it causes contamination (Neto *et al*., 2009). Second, compared with the rest of the study areas, a notable variation was detected in values of Al, where the lowest value was at 151.88 ppm of soil samples at Juaida area. This area is far from human presence locations and aluminum-manufactured waste. This variation made a clear reference to the availability of industrial waste and human activities and their impact on the presence of mineral elements at high or low levels relying on soils' distance from contamination sources (Kara *et al*., 2017).
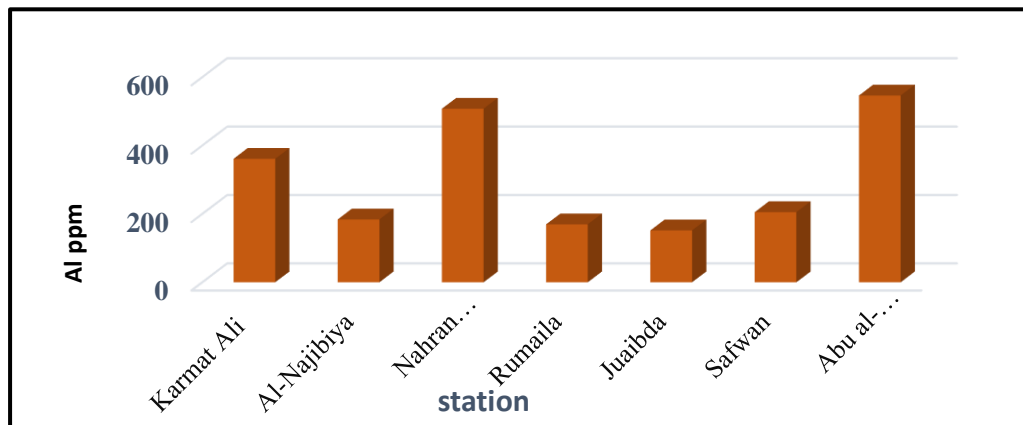

Figure (5): Aluminum values in soils of study areas

Ni

Firstly, results of nickel element accumulation in soils of the study areas demonstrated an increase in the value of nickel element in Abu al-Khaseeb area at 81.67 ppm compared to the rest of the study areas. Different values for nickel elements were recorded, where the lowest values were recorded in Najibiya area at 11.46 ppm. This variation referred to the percentage and contamination volume arising from automobile exhausts, traffic movement emissions, waste landfill burning, and fumes from the burning process. Also, such variation is caused by animal fertilizers, fertilization processes that these areas are vulnerable to, and municipal and industrial wastes (Barbafieri, 2000; McBride, 1994). Results were consistent with a study conducted by Davila *et al*. (2010) which demonstrated that an emission discharged to the environment came from heavy minerals such as nickel through sources of human contamination. Usually, the concentration of such emission is proportional to the environment depending on the distance from activities leading to an increase in the concentration of such minerals (figure 6).
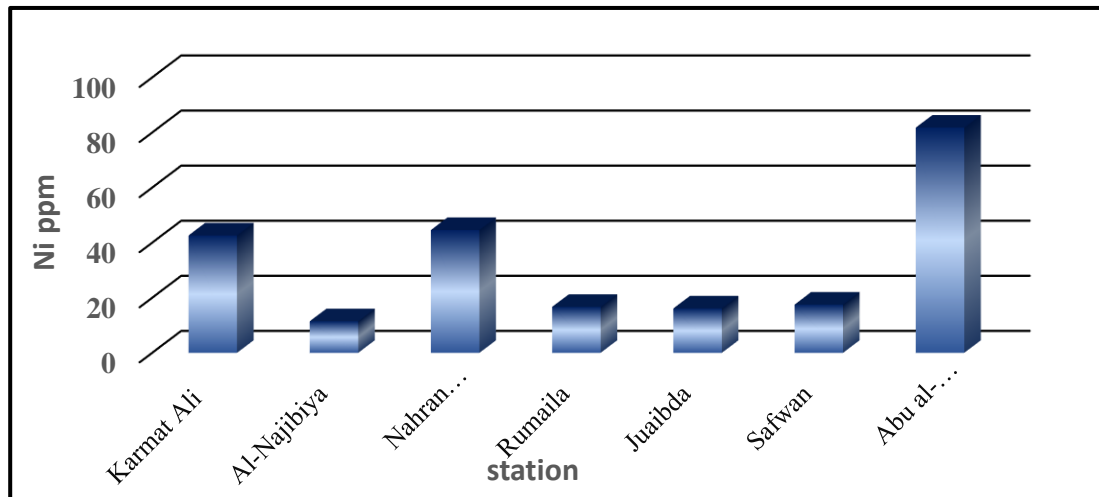
Figure 6 : Nickel values in the soils of study areas

Fe

First, as figure (7) showed, there were discrepancies in the percentages of iron (Fe) accumulation in soils of areas under study. The concentration of iron was high in soils rich in animal fertilizers, organic materials, and decomposed plant residues, leading to an increase in the iron ion, becoming highest in Abul Khaseeb area, which amounted to 15739 ppm. Second, the impact of discharges of workshops, factories, vehicles, and dust filled with sand from different sources multiplies iron in the soil. This result is consistent with a study conducted in Al-Qaraqhuli (2005). A clear decrease in values of the iron concentration was seen at Juaibda, which recorded the lowest accumulation in comparison with other study areas, which amounted to 2911 ppm. This was due to the said area's distance from human presence, activities, and agriculture. The variation in the concentration of heavy minerals, disregarding different soil areas, was consistent with a study conducted by Wuana and Okieimen (2011), which indicated that the concentration and distribution of mineral pollutants among areas are directly affected by numerous factors, including soil quality, mechanism of mineral transport to such areas and chemistry of underground waters and different industrial and agricultural activities. (Fig. 7).
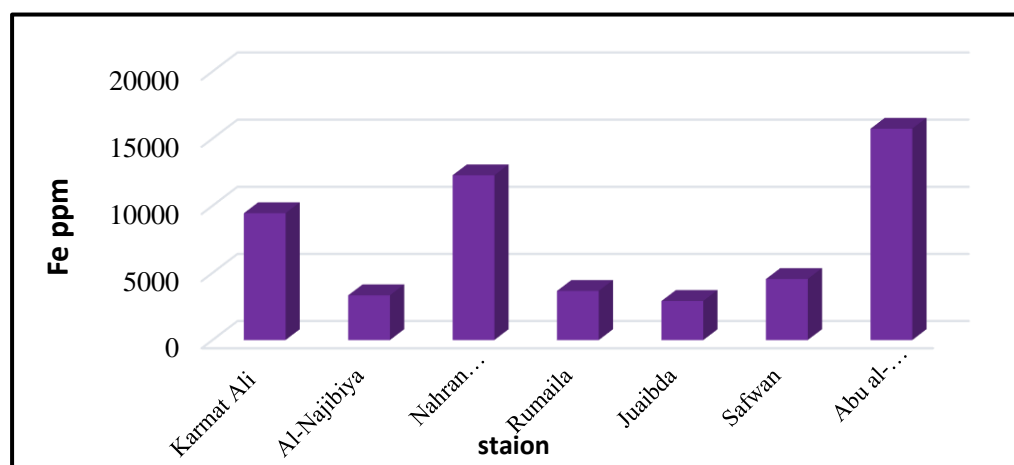

Figure 7: The values of iron in soils of areas under study

Cu

First, the accumulation percentage was noted in the Abul Khaseeb area and its decrease in Juaibda area, respectively. The rest of the study areas got different percentages of copper's accumulation. This was ascribed to existence of direct relationship between percentages of the copper accumulation values with contamination by animal fertilizers, contamination to the (Cu) element, as confirmed by Kabata – Pendias (2011), that resulted from modern human sources and proportional fertilization in the content of copper, which could be caused by environmental contamination and low concentrations in areas far away from areas of human and agricultural existence and different activities (Al-Hasan, 2011), (figure 8).
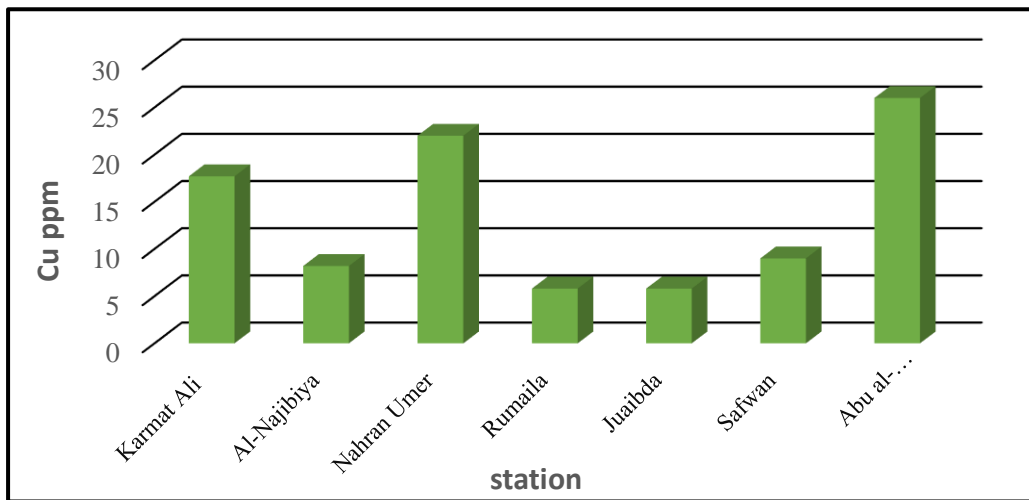

Figure (8): Cu values in soils of the study area

Co

Taking cobalt into consideration, the highest values were registered in the Abul Khaseeb area at 20 ppm compared to other concentration values in other study areas. Percentages were different, where the lowest value of cobalt concentration was measured in Rumaila area at 3.9 ppm, as shown in figure (10). As Al-Maliki (2005) disclosed, this variation among study areas was ascribed to miscellaneous human activities such as irrigation processes, the impact of sewage and drainage waters, and waste accumulation disposed of by close residents (houses) and automobile repair workshops disposed waste in soil and then transferred through ground layers. Secondly, these heavy mineral pollutants are usually caused by many operations such as fertilization, fuel burning, and sewage discharge (Varalakshmi and Ganeshmurthy, 2010).
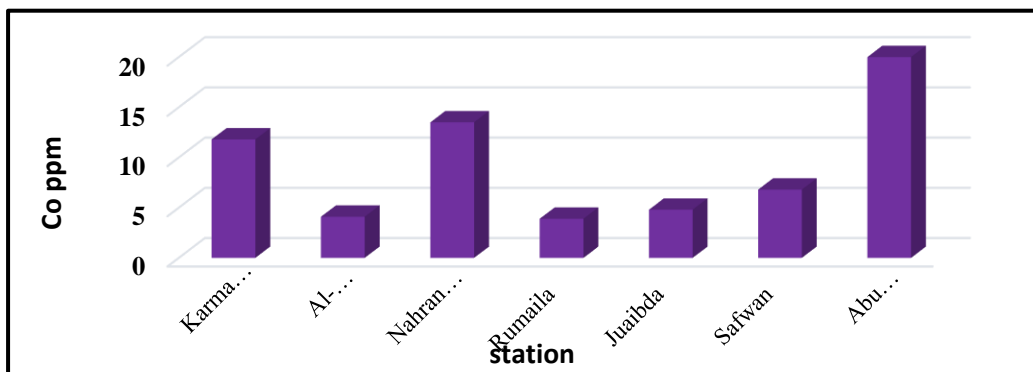

Figure 9: Values of CO element in soils of the study areas

Pb

First of all, figure (10) disclosed the accumulation of the Pb element in the soils of the study areas, where the highest accumulation value was registered at 39.8 ppm in Safwan area. This was attributed to many reasons, including industrial contamination as this area is enriched with oil products, transport means, mining, wells drilling, an increase in underground waters, and the like. The results of this study were consistent with a study conducted in Luo *et al*. (2005), which stated that soil contamination with lead is caused by the fall of dust, fine particles, chimneys dust, mining places, and their fumes. Second, there were high concentrations of Pb everywhere, which is correlated with the density of high traffic movement of automobiles operated by benzene containing Pb (Al-Khafaji,

1996). At the same time, the lowest values of accumulation were registered at the garden of the College, at 15.94 ppm. This was ascribed to the rarity of contamination sources in this area and its distance from industrial locations. Third, according to the value of Pb in this study, it was clear that the environment was less contaminated to moderately contaminated. These results were consistent with a study conducted by Chronopoulos *et al*. (1997), which pinpointed that there was a decrease in the concentration of the Pb element in gardens compared to its concentration in the soils of automobile parks, places vulnerable to automobile exhausts due to continuous wash that soils of such places are exposed to, and availability of plants that work on absorbing this element.
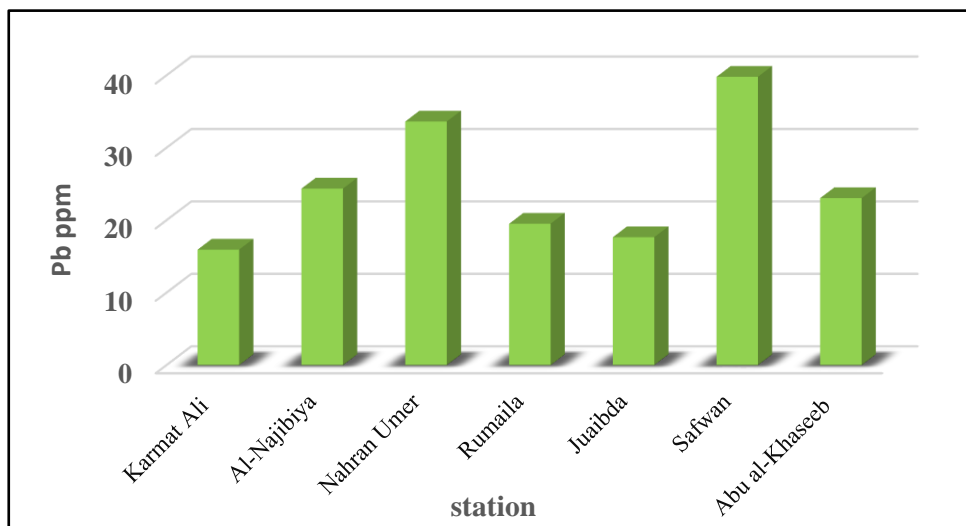

Figure (10): Pb values in the soils of study areas

Zn

Figure (11) referred to the accumulation of Zn elements in the soils of study areas, where a variation was seen among the study areas' soils. As to the values of Zn element accumulation, high values were registered at Abul Khaseeb area, where the value was at 87 ppm. This was attributed to the fact that the soil of this area lies within agricultural areas, to which fertilizers and pesticides are constantly added. Also, discharge operations resulting from sewage treatments were causes of such variation (CGWB, CPCB,

2000). Besides, the presence of organic materials from animal waste transferred to the area and the high level of underground waters and its mixture with sewage waters were other reasons for the increase in the Zn element. These results were consistent with a study by Salih (2008). Moreover, another reason for this element increase in this area is that Zn element is deposited in pH values in the range of (7-9) in the form of zinc sulfate ($ZnSo_4$). This accounted for the Zn presence in this area for the rise of pH value higher than (7). At the same time, the lowest

value of Zn element accumulation was (56) ppm in Safwan area due to high temperatures, exposure to drought, and being a non-agricultural area, free of animal fertilizers. The results were consistent with a study by Eisler (1993), which demonstrated that the main sources of zinc are of human origin, including industrial and household activities resulting from packaging materials with zinc. Moreover, zinc is used in agriculture as a fungicide, indicating zinc's high value in Abul Khaseeb area, of an agricultural nature and human activity. In addition, Uddin (2017) found that the zinc element is accumulated from natural sources such as ground waters and rocks and non-natural sources including mineral smelting, electroplating, and poultry manure (Zhang *et al.*, 2011).
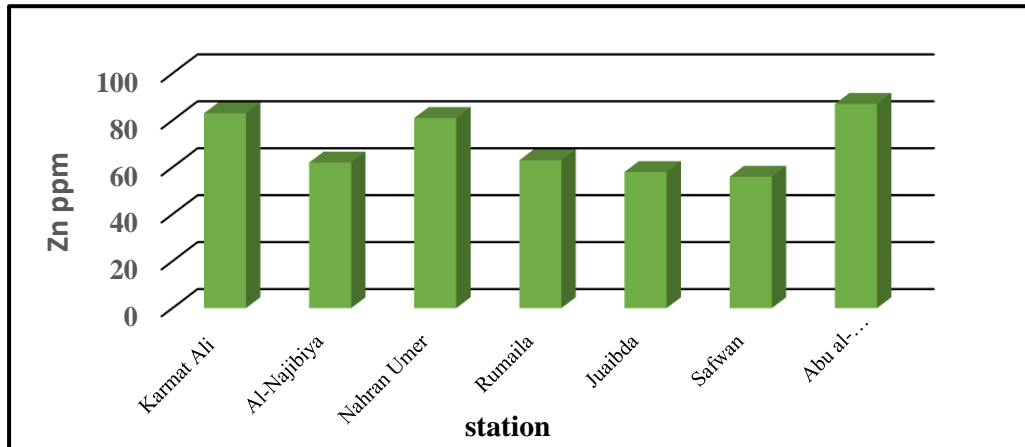

Figure (11): Zn values in the soils of study areas

Mn

Figure (12) denoted the accumulation of Mn element in the soils of study areas, and a variation among areas was detected, where the highest values were registered at Rumaila area (476.32) ppm. This may be attributed to the fact that this area is highly contaminated with oil materials, is close to fumes sites, transport, smoke and gases emitted from oil refineries loaded with manganese and accumulated different industrial residues. The results of this study were consistent with a study conducted by Kara *et al.*.(2017), which found that there was an increase in the manganese element so long as there was a rise in industrial activities, including steel manufacturing and iron alloys, mineral and oil and its products extraction. Whereas the lowest value of accumulation was registered in Najibiya area at (221) ppm. This value denoted that this area is away from emission and oil waste locations. It is known that industrial and urban pollutants could be the main source of the existence and accumulation of the Mn element in soil (Feng *et al.*, 2008).
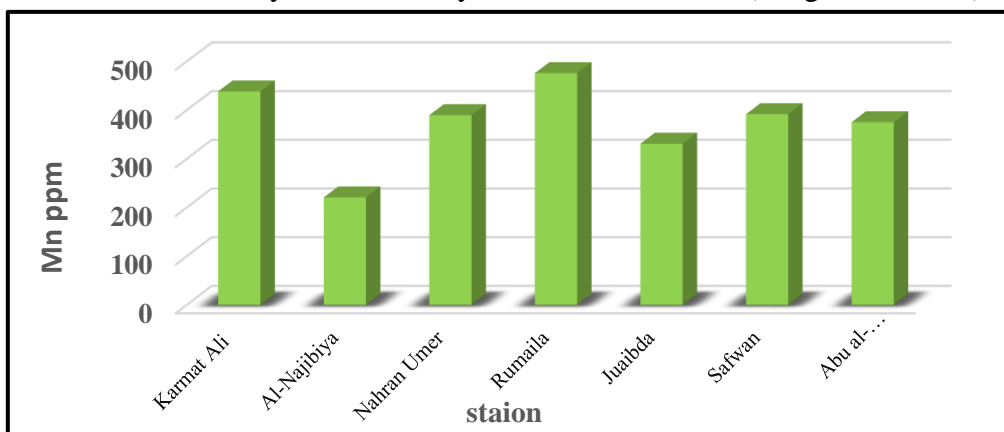

Figure (12): Mn element in the soils of study area

As

Figure (13) made clear that there was an accumulation of the As element in Abul Khaseeb area at (3.539) ppm, which was ascribed to the use of pesticides, animal fertilizers, and trees and plants burning. Also, the accumulation of As elements came from many products such as cement, mining, paints, glass, and contamination from smelting copper, lead, and zinc. As the lowest accumulation value, it was registered in Safwan area, which amounted to (0.36) ppm, which was attributed to being a non-agricultural area, containing no animal fertilizers and being away from human activities that increase arsenic in soil.
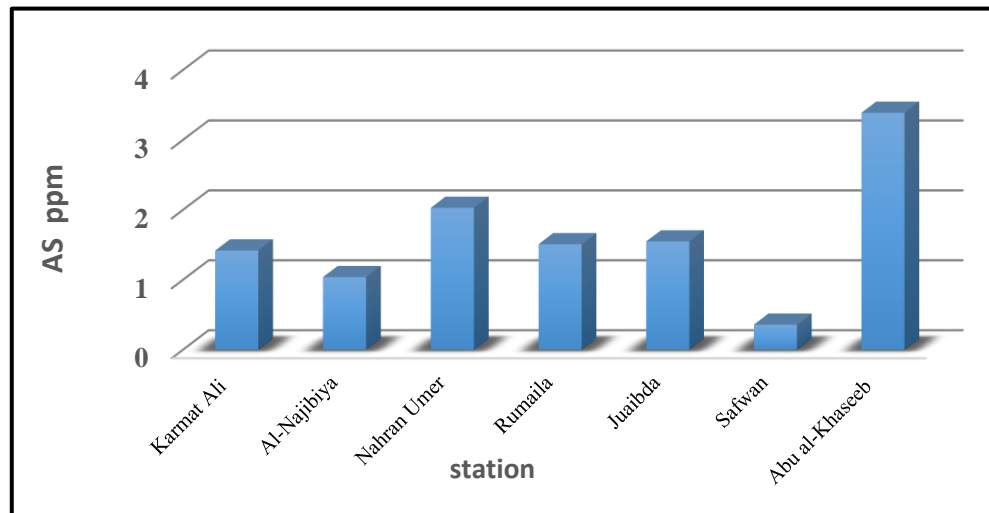

Figure (13): refers to values of As elements in the soils of study areas

Conclusions

Most of the soils of Basrah Governorate suffer from severe contamination with heavy metals, especially cadmium and lead.
The study sites varied in the distribution of pollutants (studied heavy elements) between medium and high.

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تقييم تلوث الترب لبعض مناطق محافظة البصرة باستعمال تقنية ICP-MS

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المستخلص

تم في هذه الدراسة تحديد العناصر الملوثة للترب والتي اكثر انتشاراً وتواجداً وسمية للبيئة وهي الكادميوم والالمنيوم والنيكل والكوبلت والنحاس والحديد والرصاص والخارصين والزرنيخ، واختيرت لذلك سبعة مواقع في محافظة البصرة وهي سفوان وجويبدة والرميلة ونهران عمر والنجيبية وابو الخصيب وكرمة علي (حديقة كلية العلوم) ، وتم تقدير بعص العوامل للتربة ومنها الاس الهيدروجيني والملوحة والكاربون العضوي الكلي ونسجة التربة، اذ كانت اعلى قيمة للاس الهيدروجيني 8.21 في موقع كرمة علي واقل قيمة 7.75 في جويبدة اذ كانت التربة في الجانب القاعدي لجميع المواقع. اما الملوحة فكانت اقصاها 41.984 ملغم/لتر في موقع نهران عمر وادناها 2.854 ملغم/ لتر في جويبدة. كما ان قيم الكاربون العضوي الكلي للترب (TOC) تميز موقع ابو الخصيب بتسجيل اعلى القيم له اذ بلغ 0.27 ملغم/غم تربة واقلها 0.03 ملغم/غم تربة في محطة جويبدة.

اما العناصر الثقيلة فقد بينت نتائج الدراسة الحالية التباين الكبير في تراكم الملوثات لترب المواقع المدروسة، اذ سجل اعلى قيمة للعناصر الالمنيوم والنيكل والحديد والنحاس والكوبلت والزنك والزرنيخ فبلغت 546.3 و81.67 و15739 و 26 و20 و87 و 3.39 جزء بالمليون على التوالي في موقع ابو الخصيب فكانت اكثر المحطات تلوث. اما الكادميوم فاعلاها 2.44 جزء بالمليون لموقع الرميلة وعنصر الرصاص بلغت اعلى قيمة 39.8 جزء بالمليون في سفوان وكذلك سجل عنصر المنغنيز اعلى قيمة 476.32 جزء بالمليون في الرميلة. اما ادناها فتميزت موقع جويبدة بتراكم اقل العناصر في تربه مثل الالمنيوم والحديد والنحاس 151.88 و 2911 و 5.8 جزء بالمليون على التوالي، واقل تراكم لعنصر النيكل 11.46 جزء بالمليون في موقع النجيبية والكوبلت 3.9 جزء بالمليون في موقع الرميلة والزنك والزرنيج 56 و 0.36 جزء بالمليون على التوالي في سفوان والمنغنيز ادناها 221 جزء بالمليون في النجيبية.