

Original Research Paper

Sulfur Dioxide (SO₂) and Heavy Metals Accumulation in Soils around Oil Refineries: Case Study from Three Southern Oil Refineries in the State of Kuwait

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Abstract: Geochemical and statistical analysis of Sulfur dioxide, Total Organic Carbon (TOC) and heavy metal pollutants (Pb, Cd, Zn, Cu, Ni, Fe, Mn, Cr and V) was conducted to soil samples around major oil refineries (Mina Ahmadi, Mina Abdullah and Shuaiba), industries and scanty residential areas in Al-Ahmadi governorate at the southern region of the State of Kuwait. High level of SO₂ was found in soil samples of the adjacent area of the refineries (15,000-23,000) ug g⁻¹ and TOC ranging between 0.01 to 1.62 μg g⁻¹ in the soil samples. Furthermore, trace metal analysis in sediment samples revealed high metal levels in the sequence of Fe (17.15³ μg g⁻¹) > Zn (151.08 μg g⁻¹) > Ni (112.78 μg g⁻¹) > Pb (27.71 μg g⁻¹) > Mn (404.27 μg g⁻¹) > Cd (0.08 μg g⁻¹) > Cu (23.79 μg g⁻¹) > Cr (56.23 μg g⁻¹) > V (36.53 μg g⁻¹). Cr and V were within the permissible limit. Accordingly, the soil analysis demonstrated that the area around Mina Abdullah refinery was the most polluted area and Shuaiba refinery was the least polluted area, indicating the significance of pollution due to the increase of emissions from the refineries and factories in the area. The level of pollution is alarming, health effected and environmental monitoring is highly recommended.

Keywords: Air Pollution, Oil Refinery, Pollution, Soil, Trace Metals, Health Risk, Petrochemicals, Total Organic Carbon

Introduction

The State of Kuwait is located in the Middle East; in the Northern part of the Arabian Peninsula, occupying the northwestern corner of the Arabian Gulf. It is bounded in the east by the Arabian Gulf, in the South and South-West by Kingdom of Saudi Arabia and in the north and North-West by Iraq (Fig. 1). Air pollutions, industrial waste and Oil spills produced from refineries and other factories are a major threat to human life in the vicinity of the residential area. Pollution of the natural environment by heavy metals is a universal problem because these metals are indestructible and most of them have toxic effects on living organisms, when permissible concentration levels of these pollutants exceed their limit (Nriagu, 1988). Vehicle exhausts, as well as several industrial activities emit these heavy metals so that soils, plants and even residents along roads with heavy traffic loads are subjected to increasing levels of contamination with heavy metals.

Air pollution in Kuwait is generated by several sources, which include motor vehicles, power plants, oil fields, petroleum refineries, construction sites and other industries. The production capacity of Kuwait's southern oil refineries is approximately 936 thousand barrels/day that distributes as follows: Mina Al-Ahmadi Refinery (446 thousand barrels/day) consists of four flaring stacks, Al-Shuaiba Refinery (200 thousand barrels/day) has two flares and Mina Abdullah Refinery (470 thousand barrels/day) contains six flares (Fig. 2). The emission of these flares could cause pollution, which could have a severe influence on the industrial area and urban localities in the vicinity of oil refineries (Abdul-Wahab *et al.*, 2000). This study will access the present environmental condition of the adjacent areas near the three refineries Mina Ahmadi Refinery, Mina Abdullah Refinery and Al-Shuaiba Refinery using soil chemical analysis (Fig. 2). Measurements were taken for the Total Organic Carbon (TOC) and the selected trace metals such as Pb, Cd, Zn, Cu, Ni, Fe, Mn, Cr and V.



Fig. 1: Kuwait map showing oil activities



Fig. 2: Map showing the study area

The oil fields in the country are found in two main parts: The northern part which comprises the Ratqa, Raudhatain, Sabriya and Bahra oil fields (300 oil wells) and the southern part which includes the Greater Burgan, Managish, Umm Qudair and Wafra Oil fields (2021 oil wells).

Literature Review

It is known that an oil refinery can pollute the area surrounding the factories due to their emissions. A study by (Al-Jahdali and Bin Bisher, 2008) in Saudi Arabia examined the effect of oil refineries on soil and plants; their study monitored the cumulative levels of SO₂ in the soil and the plants' leaves in four different sites around the oil refinery. In addition to the soil samples, leaf samples of the dominant plants species, *Myoporum pictum*, were randomly collected from all sites (Al-Jahdali and Bin Bisher, 2008) concluded, "Highly significant levels of sulfate were found in soil and plant leaf samples at all sites compared to the control. The highest level of sulfate in the soil (9,000±1200 µg g⁻¹) and the plant's leaves (65,774±320 µg g⁻¹) were found in the south east side. This high content of sulfate indicates high levels of air contamination with SO₂ around the refinery which negatively effects the environment and public health at this populated area". The high concentration of heavy metals in soils is reflected by higher concentrations of metals in plants and consequently in animal and human bodies. Contaminated soils can be remediated using physical, chemical, or biological techniques. Nriagu (1988) studied the measurements of air pollution level over a period of one year in Shuaiba Industrial Area. Measurements of 15 parameters have been carried out every 5 minutes using a mobile laboratory fitted with an automatic calibrator and a data storage system. The pollutants studied include methane, Non-Methane Hydrocarbons (NMHC), carbon monoxide, carbon dioxide, Nitrogen Oxides (NO and NO_x), Sulphur dioxide, ozone and suspended dust. Meteorological parameters monitored simultaneously include wind speed and direction, air temperature, relative humidity, solar radiation and barometric pressure. The air quality data collected using the mobile laboratory has been used to calculate the diurnal and monthly variations in the major primary and secondary pollutants. Distribution levels of these pollutants relative to wind direction and speed have also been used in the analysis. The study showed some important results regarding pollutants. Nevertheless, factories also play a role in the pollution of the soil according to one study by (Yay *et al.*, 2008) in the urbanized area of Ankara and they found that "Concentrations of elements from human activity (e.g., Cd, Pb, Cr, Zn, Cu and Ca) in the urbanized area were higher than their corresponding concentrations in global average soil and soil in un-urbanized areas outside the urbanized area (IARC, 1982). Metal contents in soil were very high in densely populated districts and around some

industrial facilities. The only exception was Pb distribution, which was more dispersed, due to the nature of motor vehicle emissions. Alteration of the Cd, Zn, Cu and Cr content of soil was confined to the inhabited and industrial areas, whereas enrichment factors of these elements were close to unity in the remaining study area. Factor analysis identified two polluted soil factor associations (Connon *et al.*, 2007). One factor includes elements, such as Zn and Cd, which had high factor scores in inhabited areas and the other factor (high loading of Pb) represents soil polluted by motor vehicle emissions".

The soil in Kuwait is mainly sand in nature due to the desert that surrounds it (Al-Sarawi, 1995; 1996). The soil is also very fragile, can be affected by many factors and can have contaminants more than any other similar soil in the Arabian Gulf. The soil is usually as one research found by (Basaham and Al-Lihaibi, 1993) has "concentration and distribution of Cr, Cu, Co, Ni, V, Zn, Mn and Fe have been determined in sediments of the Western Gulf. The samples investigated are texturally classified into two main sediment classes: Sand and mud. Mud sediments were found in Kuwait area, whereas at sites extending south from Kuwait sediments grade to sand-size materials. The differences in trace element concentrations reflect the variation in the overall composition of their host. The elements analyzed were high in the mud samples from the Kuwait area and decrease to the south with an increasing sand fraction to attain their lowest concentration in the deposits of Qatar. The increase of trace element contents in the sand sediments of Saudi Arabia could be due to the presence of detrital sand size particles rich in trace elements. Thorough investigation has been completed to estimate the total emissions of major pollutants from flares in two petroleum refineries (Mina Al-Ahmadi Refinery and Al-Shuaiba Refinery) and to assess their impact on the air quality in industrial and suburban areas. The AMS/EPA Regulatory Model (AERMOD) was used to predict the ground level concentrations of pollutants to indicate the quality of air and certify the adequacy of the model by comparing the measured values of selected receptors. The present study is going to consider all three refineries in Kuwait and to measure the contribution of each source (Abdelrasoul *et al.*, 2010).

Materials and Methods

Field Approach

A total of 15 soil samples, (with reference point from each section adjoining the oil refineries) were randomly collected during a field survey in May 2017. The soil sampling sites were chosen to cover the whole study area that is divided into 3 sections forming arches around the 3 refineries (Fig. 3). The sampling was designed to investigate pollutants concentrations in representative soils

from stations: P1S1, P1S2, P1S3, P2S1, P2S2, P2S3, P3S1, P3S2, P3S3, P4S1, P4S2, P4S3, P5S1, P5S2 and P5S3 (Fig. 3). Soil samples were predigested in HNO₃:HCl (Aristar grade v/v ratio of 3:1) in a polystyrene sterile centrifuge tube and then waited overnight. The soil samples were treated with 1% HF for the complete mineralization and digestion (Bu-Olayan and Thomas, 2009). The samples were diluted in de-ionized water (50 mL) and digested in an automatic microwave digester. Spectrograph CEM was analyzed by using Inductively Coupled Plasma Mass Spectrometer-ICP-MS to determine the metals concentration. ICP-MS is the most sensitive elemental analysis technique available today. Detection limit can reach up to parts per trillion (1000,000,000) and is the preferred technique for trace metal analysis in environmental analysis and semiconductor industry.

Analytical Laboratory Analysis

Soil samples (100 g) below 5 cm from the sub-surface, were scooped and collected in sterile polyethylene containers and transported to the laboratory (Ghrefat and Yusuf, 2006) soil samples (5 and 100 g)

from each area were dried until constant weight at 50°C in an oven (GallenKamp II), respectively. Dried soil were powdered in the Agate mortar (Reutch), homogenized and sieved in 1.0 mm sieve mesh and stored in sterile vials (Djingova *et al.*, 1993; Ghrefat and Yusuf, 2006). The samples (0.2 g) are then used for TOC and trace metal analysis (Table 1). Basic chemical-physical properties were determined for the soil samples. Surface sediment samples were analyzed for sediment grain size using standard sieves in the Sedimentology laboratory at Kuwait University. All these parameters were analyzed by using statistical packages SPSS which provides correlation and assessment between the three refineries and the reference point in the open air between the soil samples (Table 2). Using Geographic Information System (GIS) ARC-INFO, the soil quality data (attribute) were linked to the sampling location (spatial) in ARCGIS and maps showing spatial distribution were prepared to easily identify the variation in concentrations of the above parameters in the groundwater at various locations of the study area using the curve-fitting technique of (IDW) and GIS Spatial analyst software.



Fig. 3: Location map for samples

Table 1: Total organic Carbon concentration in sediment samples

	Profile 1	Profile 2	Profile 3	Profile 4	Profile 5	Mean
Station 1	0.11	1.62	0.01	0.16	0.63	0.51
Station 2	0.38	0.02	1.01	0.03	0.25	0.34
Station 3	0.66	0.39	0.36	0.17	0.34	0.38
Mean	0.38	0.68	0.46	0.12	0.41	0.41

Maximum 1.62 Minimum 0.013 STD: Standard Deviation

Table 2: Descriptive Statistics analysis of TOC concentration in the study area

	N	Minimum	Maximum	Mean	STD
TOC	15	0.01	1.62	0.41	0.44

STD: Standard Deviation

Total Organic Carbon (TOC)

Total Organic Carbon (TOC) concentrations in sediment samples ranged from 0.01 to 1.62 $\mu\text{g g}^{-1}$ (Table 1). The over-all mean concentration of TOC is 0.41 $\mu\text{g g}^{-1}$, which is clarified in Table 2. The highest level of TOC is recorded at station P2S1 that is located behind Ahmadi area close to the south Oil farm, while the least level of TOC is recorded at station P3S1 (Table 1), that is located in Ahmadi along with Mina Shuaiba refinery (Fig. 4).

The chemical analysis of TOC showed that the mean concentration is higher than the mean concentration for clean sand in an earlier study done by (Al-Sarawi *et al.*, 1997). In the present study, Profiles 1 and 2 which are located in Al-Ahmadi area have the highest recorded TOC concentration (Fig. 5). On the other hand, Profile 3 located in Shuaiba area has the second highest TOC concentration (0.36 and 1.01 $\mu\text{g g}^{-1}$), which is also higher than the uncontaminated soil found by (Al-Sarawi *et al.*, 1997), but it is less than TOC concentration found in soil analyzed in Mojave in Eureka Valley, California and the Sahara near Abu Simbel, Egypt which were 7 and 1.7 $\mu\text{g g}^{-1}$, respectively (Cannon, 1963; Chen *et al.*, 1999).

The elevated TOC concentration might be related to the higher activity within Ahmadi's southern oil farm, Ahmadi refinery, Shuaiba Industrial area and to the daily activities along the highway.

Trace Metals in Sediment

The following section is describing the trace metal chemical analysis for each station. In Table 3 the overall mean concentration and standard deviation for each trace metal in the 15 stations, are statistically calculated using statistical methods.

Lead (Pb)

The Concentration of lead (Pb) in the sediment samples ranged between 14.81 to 65.01 $\mu\text{g g}^{-1}$ (Table 4). This is higher than concentration of lead in uncontaminated soil, which ranges between 10 to 30 $\mu\text{g g}^{-1}$ (Labunska *et al.*, 2000; Alloway, 1990). Figure 6 and 7 shows the variation and the highest concentration of Pb in the study area. The highest concentration recorded in P2S1 (65.01 $\mu\text{g g}^{-1}$), while the lowest level is recorded in P5S (14.8 $\mu\text{g g}^{-1}$).

The overall mean concentration of Pb 27.71 $\mu\text{g g}^{-1}$ and the standard deviation is 12.34 $\mu\text{g g}^{-1}$ (Table 5). Table 5 shows the mean concentration along profiles. Profile 2 recorded highest mean concentration of Pb (38.79 $\mu\text{g g}^{-1}$, STD: 22.86). This is higher than the overall mean concentration. This could be due to the activity at Ahmadi southern oil farm. Profile 4 also recorded highest mean concentration of Pb (35.68 $\mu\text{g g}^{-1}$, STD: 3.82 $\mu\text{g g}^{-1}$). This is higher than the overall mean concentration; this may be due to Mina Abdullah refinery and factories. The map in (Fig. 6) shows that the highest recorded concentration of Pb is 65.01 $\mu\text{g g}^{-1}$, present in station P2S1 at Al-Ahmadi,

Table 5 shows the mean concentration of Pb along stations. Station 1, recorded the highest mean concentration of Pb (31.69 $\mu\text{g g}^{-1}$, STD: 19.75 $\mu\text{g g}^{-1}$) which is higher than the overall mean concentration. Figure 7 shows no interaction between profiles and stations, so the stations along the five profiles follow a parallel trend.

From the above analysis for Pb it is recognized that the highest concentrations were recorded in P2S2 (Fig. 8), within Ahmadi city 65.01 $\mu\text{g g}^{-1}$ and P4S2 and P4S3 near Mina Abdullah, where the area is surrounded by industrial activities in addition to highway activity. This means concentration is higher than Pb concentration in uncontaminated soil (4.6 $\mu\text{g g}^{-1}$) and in contaminated soil (6.9 $\mu\text{g g}^{-1}$) in al-Ahmadi oil field recorded by Al-Sarawi *et al.* (1997). This favors to believe that the emissions due to fuel combustion and trace traffic could be the main possible causes of Pb pollution in the study area. Concentrations of lead found in uncontaminated sediments range from 10 to 50 $\mu\text{g g}^{-1}$ (Stephenson, 1998; Salomons and Forstner, 1984; Bryan and Langston, 1992; Licheng and Kezhun, 1992; Goncalves *et al.*, 1992).

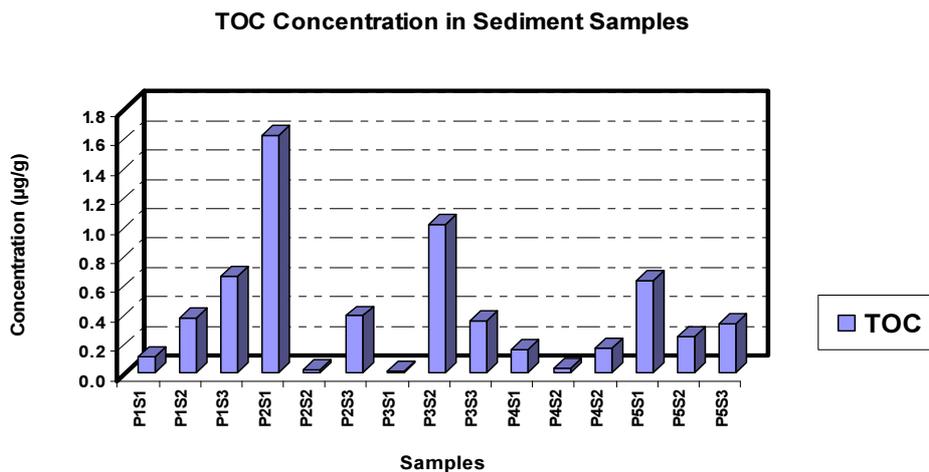


Fig. 4: Highest concentration of TOC recorded at station P2S1 close to Ahmadi south oil farm

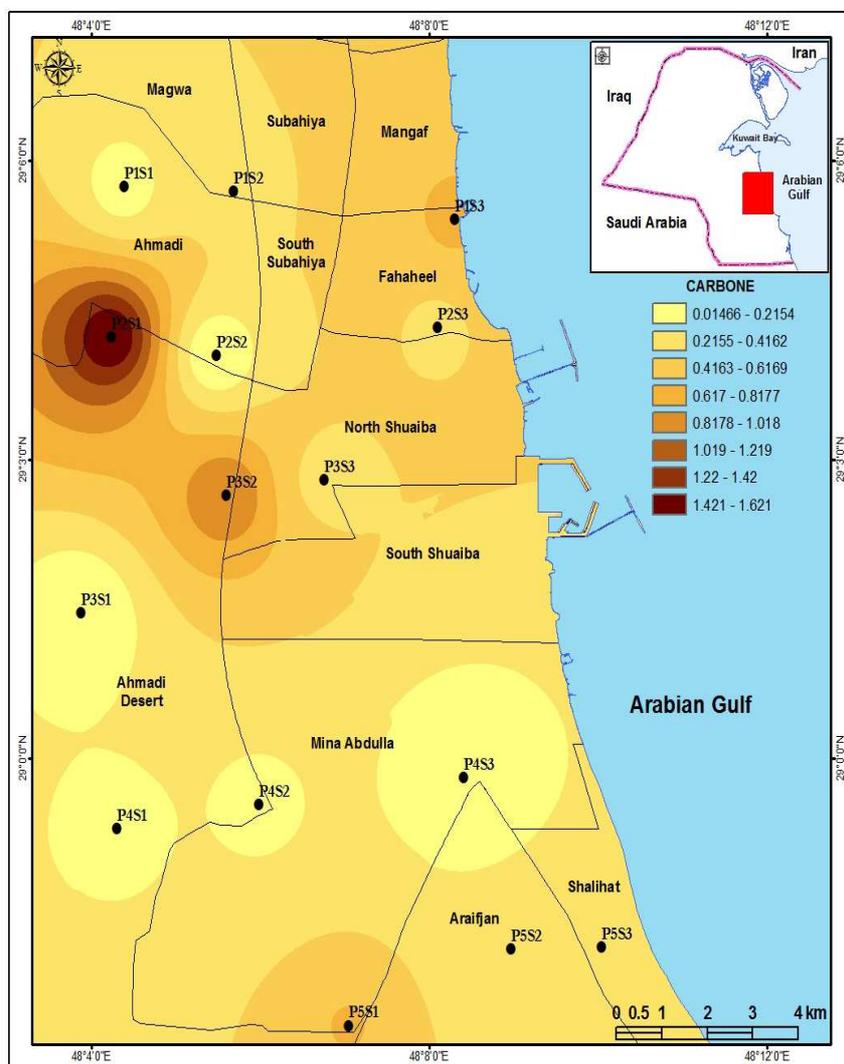


Fig. 5: Map shows TOC concentration at south oil farm at Ahmadi which has higher concentration in sediment samples ($1.62 \mu\text{g g}^{-1}$)

Trace metal Concentration in Sediment Samples

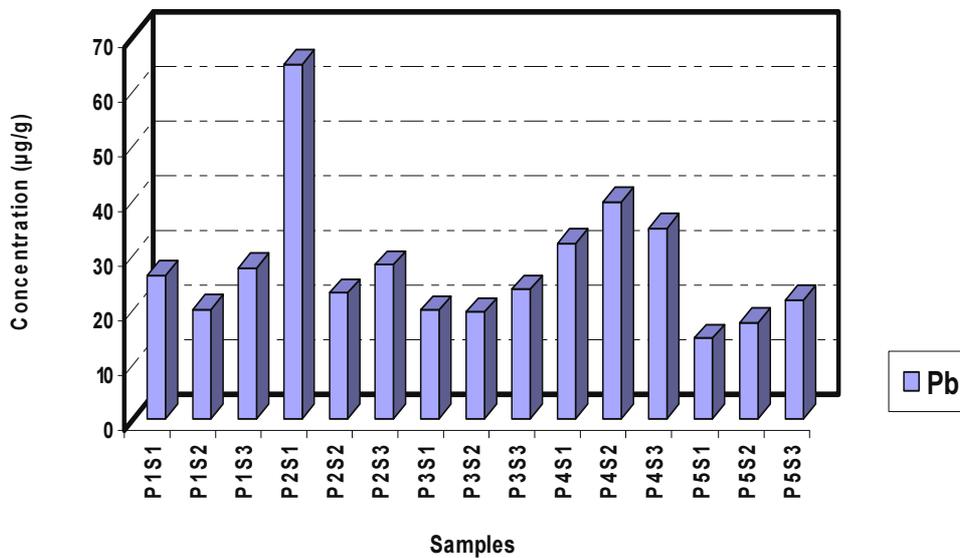


Fig. 6: Highest concentration of Pb is in P1S2 that is located at Ahmadi south oil farm

Estimated Marginal Means of Pb_variable

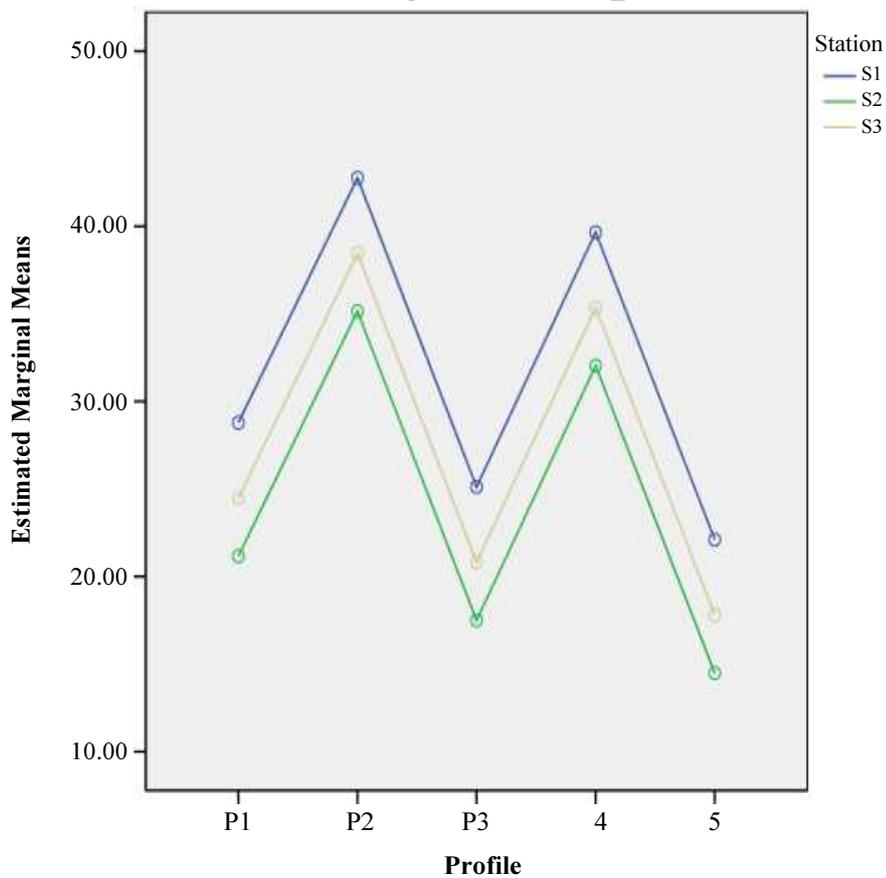


Fig. 7: No interaction between profiles and stations

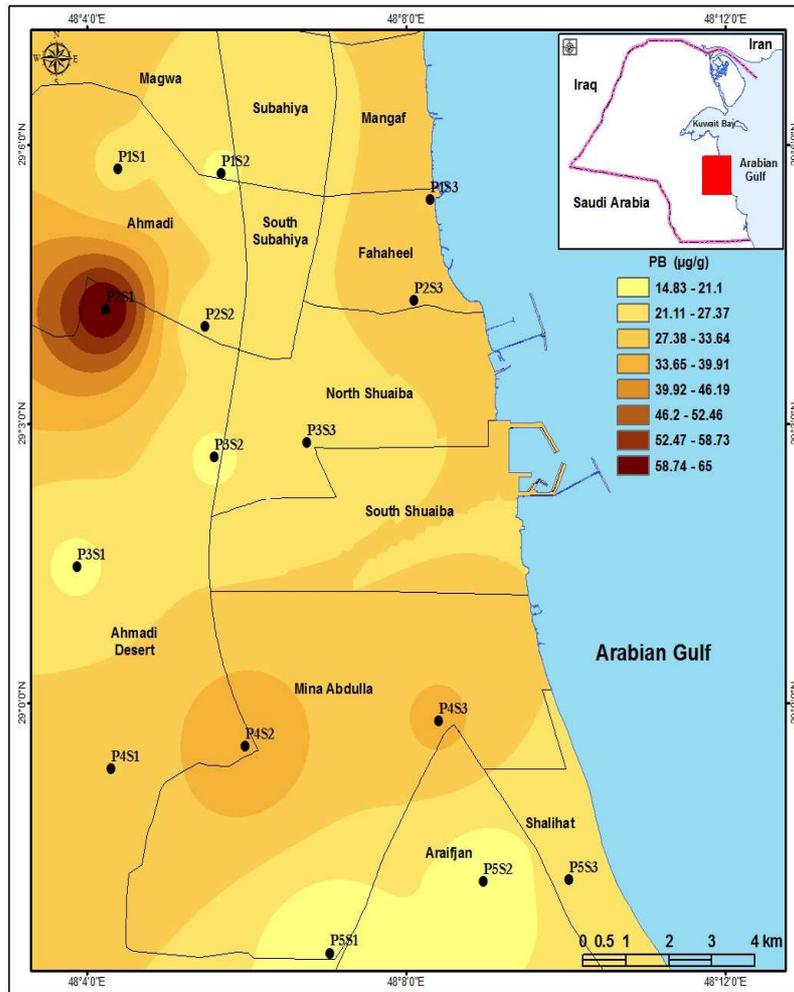


Fig. 8: Map shows the distribution of Pb in different stations

Trace metal Concentration in Sediment

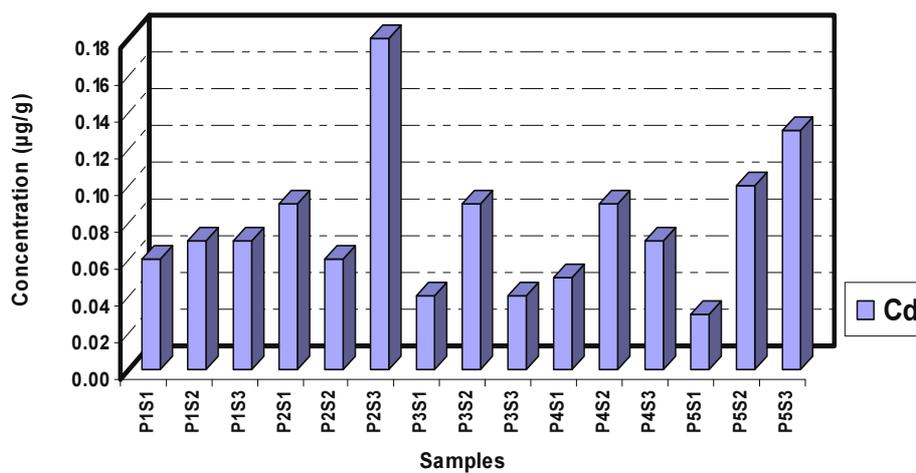


Fig. 9: Cd has higher concentration in P2S3 in Fahaiheel close to Ahmadi refinery

Cadmium (Cd)

The Concentration of Cadmium (Cd) in sediment samples ranged between 0.03-0.18 $\mu\text{g g}^{-1}$ (Table 6). The highest level of Cd is recorded in P2S3 0.18 $\mu\text{g g}^{-1}$, while the lowest concentration level of Cd is recorded in P5S1 0.03 $\mu\text{g g}^{-1}$. Figure 9 and 11 shows the variation of Cd along different stations.

The overall mean concentration of Cd is 0.08 $\mu\text{g g}^{-1}$ and standard deviation is 0.04 $\mu\text{g g}^{-1}$ (Table 7). This is higher than Cd concentration in the study conducted in al Ahmadi oil field by (Al Sarawi *et al* 1997, 0.056 $\mu\text{g g}^{-1}$),

but lower than Cd naturally found in the Earth's crust which averages 0.1 $\mu\text{g g}^{-1}$ (Labunska *et al.*, 2000; WHO, 2004). Profile 2 recorded the highest mean concentration of Cd that is 0.11 $\mu\text{g g}^{-1}$, STD: 0.06 $\mu\text{g g}^{-1}$. This is higher than the overall mean concentration in the area; this could be due to the activity at Ahmadi southern oil farm and Ahmadi refinery. Profile 4 also recorded a mean concentration higher than the overall mean concentration of Cd that is 0.09 $\mu\text{g g}^{-1}$, STD: 0.05 $\mu\text{g g}^{-1}$. It might be due to the Mina Abdullah refineries and industrial area.

Table 3: Trace metal overall mean concentration in sediment samples ($\mu\text{g/g}$). (Fe in thousands).

T.M	N	Min	Max	Mean	STD
Pb	15	14.81	65.01	27.71	12.34
Cd	15	0.03	0.18	0.08	0.04
Zn	15	51.77	416.28	151.08	130.64
Cu	15	11.78	50.83	23.79	10.56
Ni	15	59.32	232.04	112.78	51.21
Fe	15	12.61	23.94	17.15	3.28
Mn	15	287.17	473.88	404.27	59.43
Cr	15	35.89	80.41	56.23	13.35
V	15	27.33	48.65	36.53	6.42

N: Number of samples, STD: Standard Deviation

Table 4: Chemical and Statistical analysis of Pb concentration in Sediment Samples for each profile in ppm ($\mu\text{g/g}$)

	Profile 1	Profile 2	Profile 3	Profile 4	Profile 5
Station 1	26.44	65.01	19.97	32.20	14.81
Station 2	20.14	23.05	19.66	39.77	17.71
Station 3	27.85	28.30	23.80	35.06	21.87
Minimum	20.14	23.05	19.66	32.2	14.81
Maximum	27.85	65.01	23.8	39.77	21.87
Mean	24.81	38.79	21.14	35.68	18.13
STD	4.11	22.86	2.31	3.82	3.549

Maximum concentration 65.01, Minimum concentration 14.81, STD: Standard Deviation

Table 5: Statistical analysis of Pb concentration in sediment samples in ppm ($\mu\text{g/g}$)

	Station 1	Station 2	Station 3
Minimum	14.81	17.71	21.87
Maximum	65.01	39.77	35.06
Mean	31.69	24.07	27.38
STD	19.75	8.98	5.08

STD: Standard Deviation

Table 6: Chemical and Statistical analysis of Cd concentration in Sediment for each profile in PPM

	Profile 1	Profile 2	Profile 3	Profile 4	Profile 5
Station 1	0.06	0.09	0.04	0.05	0.03
Station 2	0.07	0.06	0.09	0.09	0.10
Station 3	0.07	0.18	0.04	0.07	0.13
Minimum	0.06	0.06	0.04	0.05	0.03
Maximum	0.07	0.18	0.09	0.09	0.13
Mean	0.07	0.11	0.06	0.07	0.09
STD	0.01	0.06	0.03	0.02	0.05

Maximum concentration 0.18, Minimum concentration 0.03, STD: Standard Deviation

Table 7: Statistical analysis of Cd concentration in sediment samples for each station in ppm ($\mu\text{g/g}$)

	Station 1	Station 2	Station 3
Minimum	0.03	0.06	0.04
Maximum	0.09	0.10	0.18
Mean	0.05	0.08	0.10
STD	0.02	0.02	0.06

STD: Standard Deviation

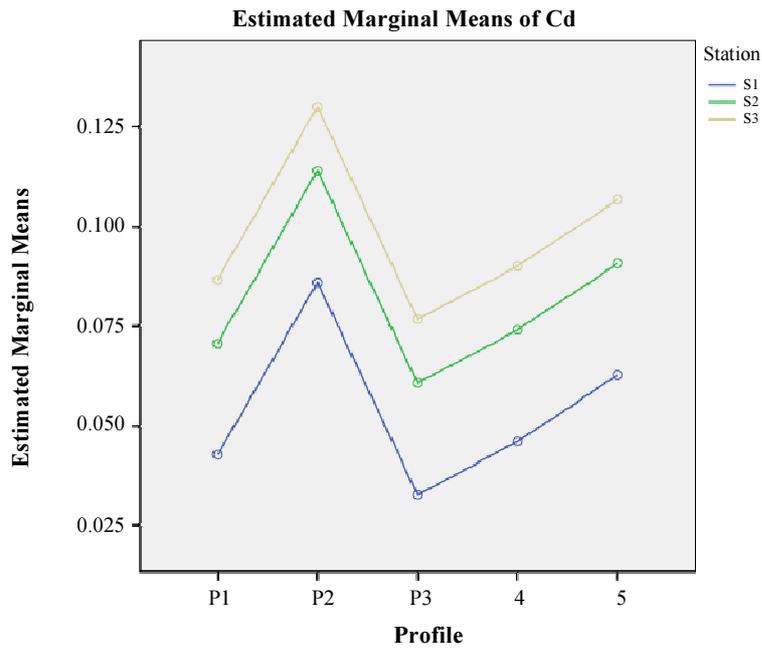


Fig. 10: No interaction between profiles and stations

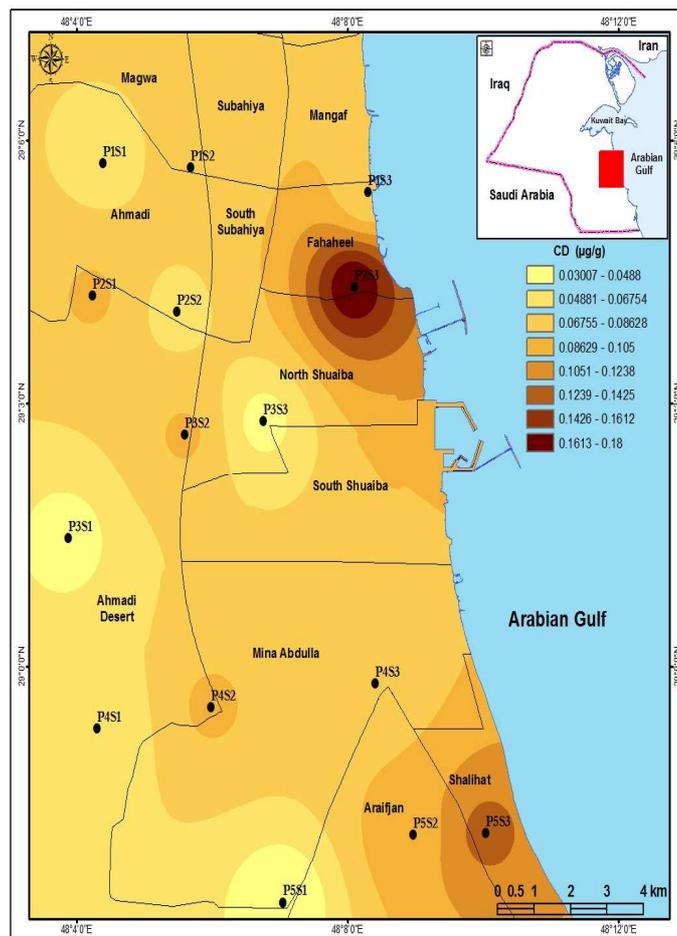


Fig. 11: Distributions of Cd concentrations in different stations

Figure 10 shows no interaction between profiles and stations, this means that similar station in the same horizon is sharing the same level of pollution. Figure 11 shows distribution of Cd in different stations.

Cadmium is a relatively rare metal; natural occurring Cd levels are extremely low. Reports indicate that Cd concentrations in non-contaminated soil vary from 0.01 to 5 $\mu\text{g g}^{-1}$ of soil (Kabata-Pendias, 2000). Regarding soil contamination, the UK Department of the Environment classifies a level of 0.1-1 $\mu\text{g g}^{-1}$ as being typical of uncontaminated soil. Anything above this is classified as contaminated and as such, restrictions on recreational and agricultural uses apply (Labunska *et al.*, 2000; Alloway, 1990). From the present study analysis for Cd it is been recognized that the highest concentration was found at P2S3 0.18 $\mu\text{g g}^{-1}$ which is within the range of ICRCCL classifications of uncontaminated sediment and the soil background concentration 0.01-2.0 $\mu\text{g g}^{-1}$ according to (USPHS, 1997; Labunska *et al.*, 2000; Alloway, 1990).

Cadmium is usually found in association with the sulphide ores of zinc, copper and lead, natural source of cadmium released to the atmosphere, emissions from wind-borne soil particles, forest fires, sea salt spray and biogenic processes. Anthropogenic sources of Cadmium is a by-product of zinc and lead mining and smelting. It is currently used mainly 37% for the production of nickel-cadmium batteries and 25% for metal plating, as pigments 12% for glasses and plastics, 22% as a stabilizer in polyvinyl chloride and as 4% a component of various alloys (Labunska *et al.*, 2000; USPHS, 1997; WHO, 2004).

Labunska *et al.* (2000) stated that Cadmium is a non-essential and toxic element, it has no biochemical or nutritional function and it is highly toxic to both plants and animals according to (USPHS, 1997; WHO, 2004). The inhalation of high levels of cadmium oxide fumes or

dust is intensely irritating to respiratory tissue, which can be fatal. There is strong evidence that following extended exposure, the kidney is the main target organ in humans and animals of cadmium toxicity.

Zinc

The overall mean concentration of Zn is 151.08 $\mu\text{g g}^{-1}$ and the standard deviation is 130.64 $\mu\text{g g}^{-1}$ (Table 7). This is considered high compared with mean of zinc for worldwide 64 $\mu\text{g g}^{-1}$ (Smith, 1973; Kabata-Pendias, 2000) and the background levels of zinc in sediment of 100 $\mu\text{g g}^{-1}$ according to (Stephenson, 1998; Sharma *et al.*, 2004; ATSDR, 1997; Licheng and Kezhun, 1992; Buszewski *et al.*, 2000). Table 8 shows the mean concentration of Zn along the five profiles. Profile 4 recorded highest mean concentration of Zn (298.92 $\mu\text{g g}^{-1}$, STD: 19.22 $\mu\text{g g}^{-1}$), which is higher than the overall mean concentration. This may be due to the activities in Mina Abdullah refinery and industrial area. Figure 12 shows the distribution of Zn in different stations. Profile 2 also recorded a high mean concentration of Zn, which is 216.80 $\mu\text{g g}^{-1}$, STD: 155.33 $\mu\text{g g}^{-1}$. This is higher than the overall mean concentration and may be due to the location, since profile 2 is situated in Ahmadi south oil farm and Fahaiheel which is close to Mina Ahmadi and Ahmadi refinery.

Table 9 shows the mean concentration of Zn in station along profiles. Station 3 and Station 2 recorded highest mean concentration of Zn (205.65 $\mu\text{g g}^{-1}$, STD: 169.70 $\mu\text{g g}^{-1}$) 152.43 $\mu\text{g g}^{-1}$, STD: 147.80 $\mu\text{g g}^{-1}$ respectively). There is no interaction between profiles and stations. This means that similar stations in the same horizon are sharing the same level of pollution and is due to their location that is near to the industrial area (Fig. 13).

Table 8: Chemical and Statistical analysis of Zn concentration in Sediment for each profile in ppm ($\mu\text{g/g}$)

	Profile 1	Profile 2	Profile 3	Profile 4	Profile 5
Station 1	79.96	160.76	62.46	92.08	80.53
Station 2	82.12	97.27	93.31	416.28	73.18
Station 3	97.92	392.38	97.75	388.41	51.77
Minimum	79.96	97.27	62.46	92.08	51.77
Maximum	97.92	392.38	97.75	416.28	80.53
Mean	86.67	216.80	84.51	298.92	68.49
STD. Deviation	9.81	155.33	19.22	179.67	14.94

Maximum concentration 416.28, Minimum concentration 51.77, STD: Standard Deviation

Table 9: Statistical analysis of Zn concentration in sediment samples in ppm ($\mu\text{g/g}$)

	Station 1	Station 2	Station 3
Minimum	62.46	73.18	51.77
Maximum	160.76	416.28	392.38
Mean	95.16	152.43	205.65
STD. Deviation	38.17	147.80	169.70

Trace metal Concentration in Sediment

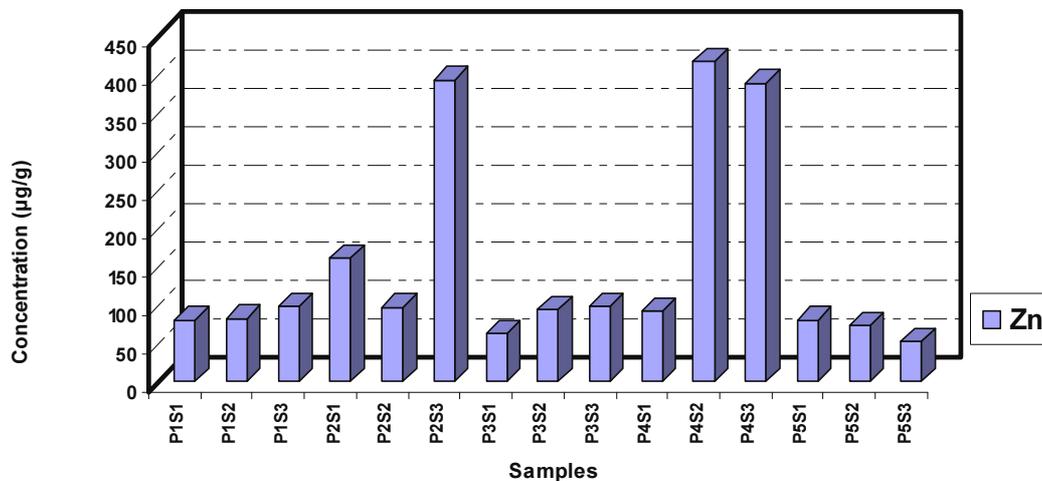


Fig. 12: Fahaiheel and Mina Abdullah have highest Zn concentration

Estimated Marginal Means of Zn

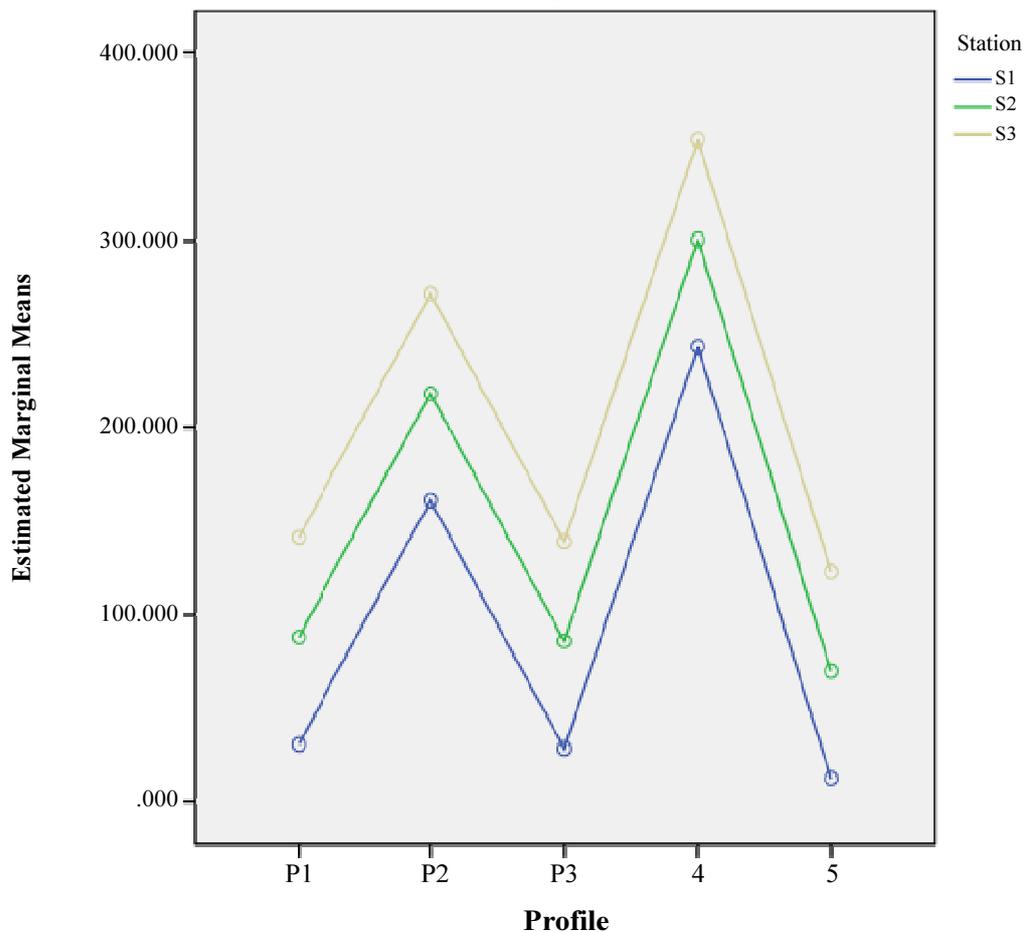


Fig. 13: No interaction between profiles and stations

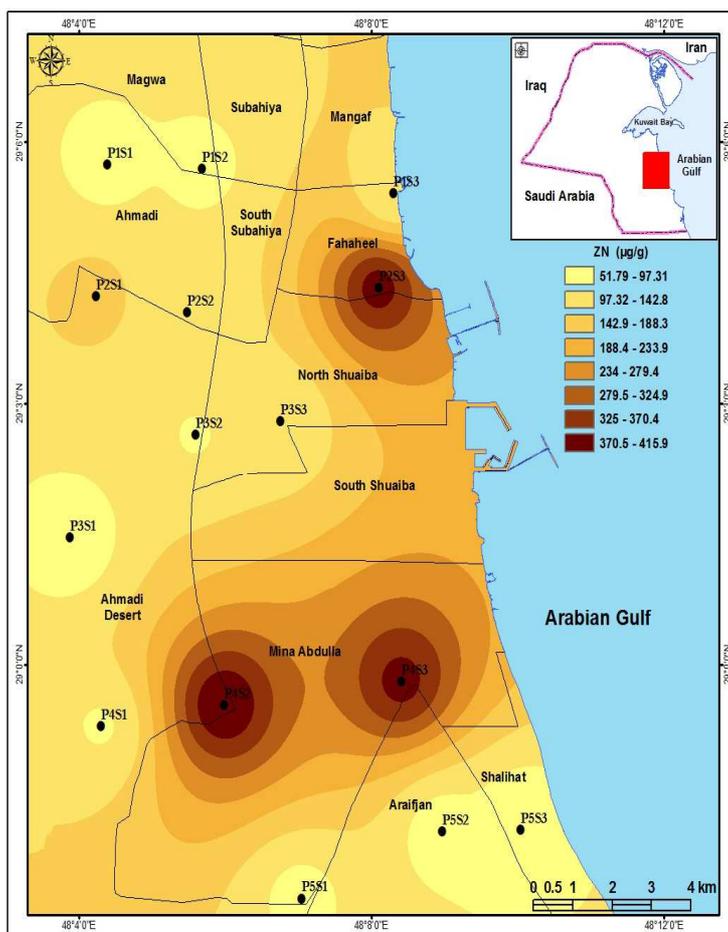


Fig. 14: Mina Abdullah industrial area contains highest Zn concentration

Zinc is an essential element for all living organism, but elevated level of it in the environment may be harmful near zinc-contaminated areas (USDOJ, 1998). In the present study, the analysis for Zn showed that the highest concentration was found at P2S3, which is located within Fahaiheel city that is situated close to Ahmadi refinery and P4S2 and P4S3 in Mina Abdullah refinery and industrials area (Fig. 14) add to that highway activity. (ATSDR, 1997) stated that a significant source of Zn is vehicular tire wear (UNEP/FAO/WHO, 1993) determined that increased Zn concentrations in sediment are related to increased vehicular traffic. Stephenson (1998; Buszewski *et al.*, 2000) stated that environmental releases of zinc from anthropogenic sources far exceed the releases from natural sources.

In terms of human health, most of the studies relating to the effects of zinc concentrate on exposure via inhalation. The recommended dietary allowances for zinc are 15 mg/day for men and 12 mg/day for women. If doses 10-15 times higher than these recommendations are taken by mouth, even for a short time, stomach cramps, nausea and vomiting may occur. Ingesting high levels for several months may cause anemia, damage to the pancreas and decreased levels of high-density

lipoprotein (HDL) cholesterol (Stephenson, 1998; Buszewski *et al.*, 2000; UNEP/FAO/WHO, 1993).

Copper (Cu)

In sediment samples the concentration of Copper (Cu) ranged between 11.780-50.83 $\mu\text{g g}^{-1}$ (Table 10). Figure 15 shows the variation of Cu in different stations. The highest level of Cu is recorded in P4S2 (50.83 $\mu\text{g g}^{-1}$) and P4S3 (41.86 $\mu\text{g g}^{-1}$) that are located in the same area, while the lowest level of Cu is recorded in P5S3 (11.78 $\mu\text{g g}^{-1}$).

The overall mean concentration of Cu is 23.79 $\mu\text{g g}^{-1}$ and the standard deviation is 10.56 $\mu\text{g g}^{-1}$ (Table 9). Table 11 shows the mean concentration of Cu along the five profiles. Profile 4, recorded highest mean concentration of Cu (37.77 $\mu\text{g g}^{-1}$, STD: 15.51 $\mu\text{g g}^{-1}$). This may be due to the industrial activities in Mina Abdullah refineries and industrial area. Profile 2 also recorded high mean concentration of Cu (25.08 $\mu\text{g g}^{-1}$, STD: 4.54 $\mu\text{g g}^{-1}$). This is higher than the overall mean concentration. This could be due to the activity at Ahmadi southern oil farm. Figure 18 shows the distribution of Cu in different

stations. Table 10 shows the mean concentration of Cu in each station. Station 2 recorded highest mean concentration of Cu ($26.736 \mu\text{g g}^{-1}$, STD: $13.66 \mu\text{g g}^{-1}$). Station 3 also has a high mean concentration of $26.88 \mu\text{g g}^{-1}$, STD: $10.76 \mu\text{g g}^{-1}$, which is higher than the overall mean concentration; the reason behind this maybe

because Station 3 is close to the industrial area of the three refineries. The line chart in Figure 16 shows no interaction between profiles and stations, meanings that similar stations in the same horizon are sharing the same level of pollution. The highest values of Cu concentration are recorded in Table 10.

Table 10: Chemical and Statistical analysis of Cu concentration in Sediment for each profile in ppm ($\mu\text{g/g}$)

	Profile 1	Profile 2	Profile 3	Profile 4	Profile 5
Station 1	11.78	20.90	21.22	20.63	14.28
Station 2	20.58	24.44	18.40	50.83	19.43
Station 3	29.66	29.91	14.71	41.86	18.28
Minimum	11.78	20.9	14.71	20.63	14.28
Maximum	29.66	29.91	21.22	50.83	19.43
Mean	20.67	25.08	18.11	37.77	17.33
STD	8.94	4.54	3.27	15.51	2.70

Maximum concentration 50.83, Minimum concentration 11.78

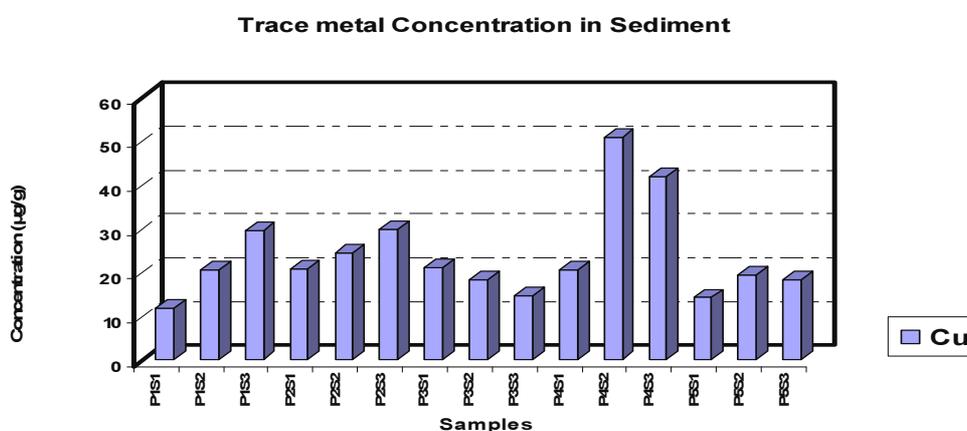


Fig. 15: Mina Abdullah industrial area contains highest Zn concentration

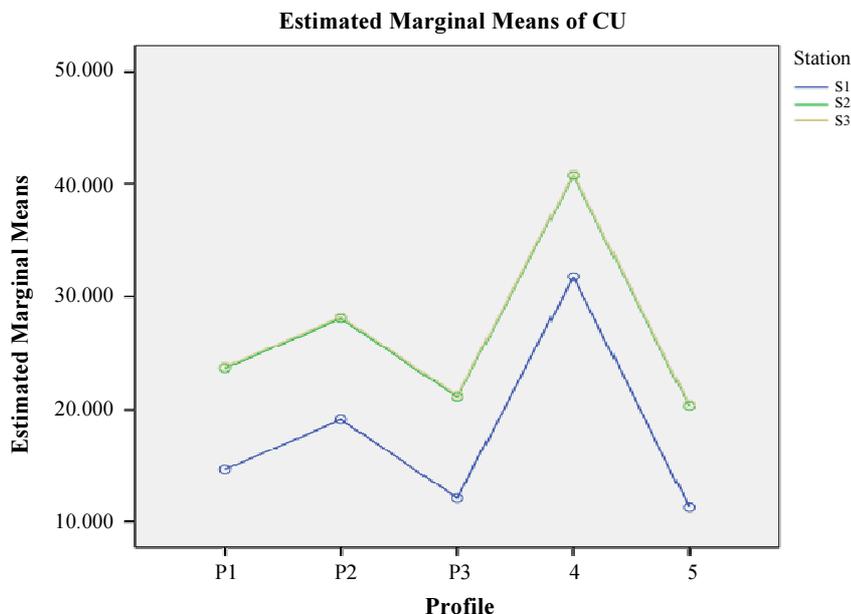


Fig. 16: No interaction between profiles and stations

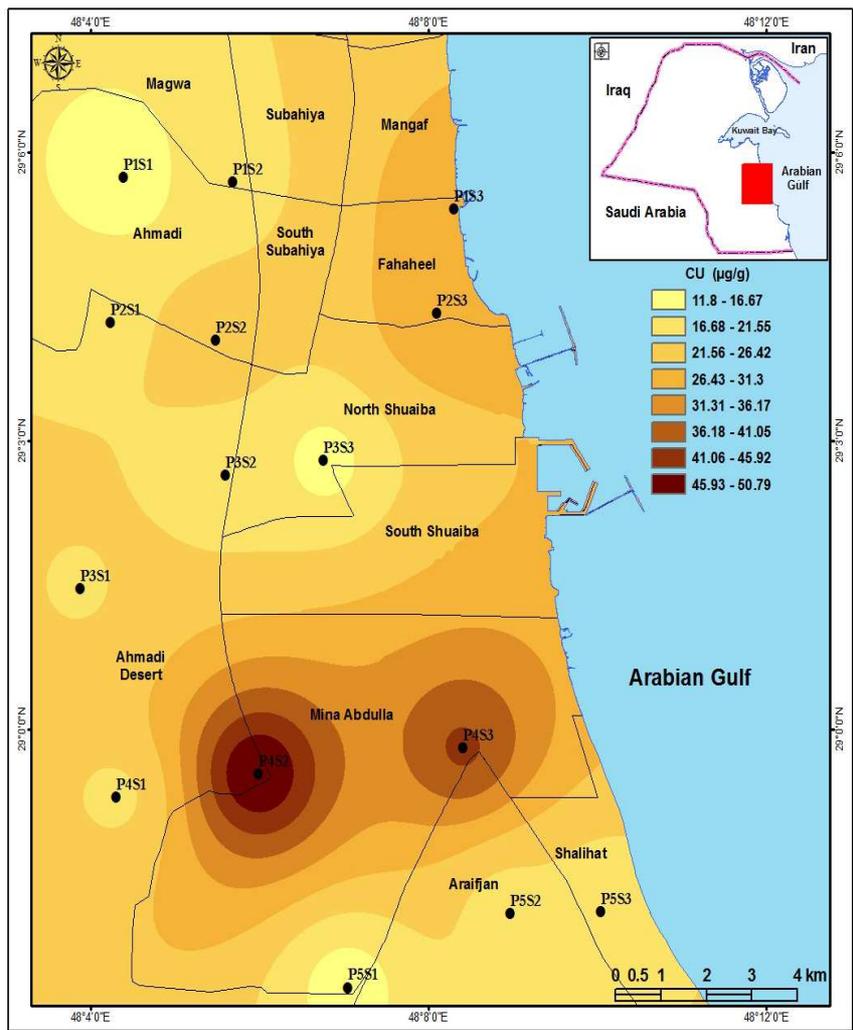


Fig. 17: Mina Abdullah contains highest Cu concentration

Trace metal Concentration in Sediment

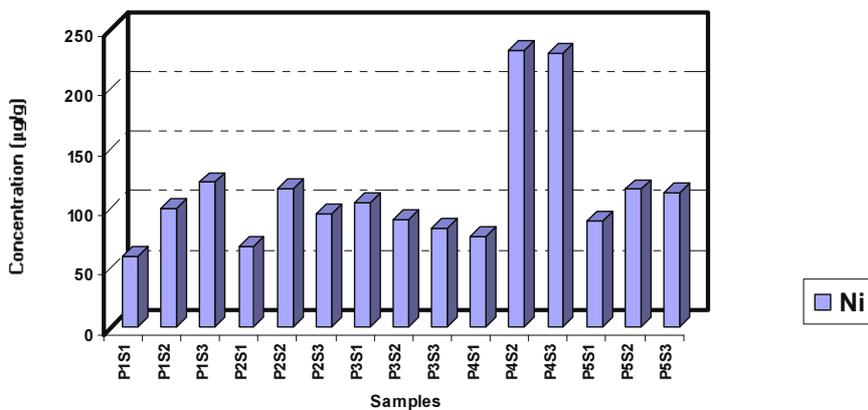


Fig. 18: Ni concentration is the highest at profile 4 at Mina Abdullah area

Abundance of copper in the Earth's crust is reported as ranging from 24-55 $\mu\text{g g}^{-1}$ (Alloway, 1990). The highest concentration of Cu in present study is found at P4S2 (50-83 $\mu\text{g g}^{-1}$) and P4S3 (41.86 $\mu\text{g g}^{-1}$) near Mina Abdullah (Fig. 17), where the area is surrounded by industries and P2S1 within Ahmadi city near south oil farm. These were found higher than the background concentration in soil (20-30 $\mu\text{g g}^{-1}$) according to (Alloway, 1990), yet within the limits of ICRCL level of uncontaminated soil, which is 1-100 $\mu\text{g g}^{-1}$ (Labunska *et al.*, 2000).

Copper is a highly malleable and ductile metal, as well as being an excellent conductor of heat and electricity. Cu major use is as an electrical conductor (copper cables and wires); it is also widely employed in coinage alloys, such as bronze (copper and tin), brass (copper and zinc) and Monel (copper and nickel), in corrosive-resistant and decorative plating, in munitions and in dental alloys. Copper compounds are used as chemical catalysts, algacides, fungicides, anti-fouling paints, disinfectants, nutritional supplements in fertilizers and feeds, in petroleum refining and as printing inks and dyes (Labunska *et al.*, 2000; USPHS, 1997; Wedepohl, 1978). Natural sources of copper released to the emissions include wind-borne soil particles, forest fires, sea salt spray and biogenic processes. The estimated total amount of copper released to the atmosphere from natural sources is 28,000 tones/year compared to an estimated anthropogenic load of 35,000 tones/year (Nriagu, 1988).

Nickel (Ni)

The concentration of Nickel (Ni) in sediment samples ranged from 59.32 to 232.04 $\mu\text{g g}^{-1}$ (Table 12). UK Department of the Environment (ICRCL) classifies a level of 0-20 $\mu\text{g g}^{-1}$ of Ni as being typical of uncontaminated level; anything above this is classified as contaminated (Kiss *et al.*, 2002). Figure 18 shows variation of Ni in different stations. The highest level of Ni is recorded in P4S2 (232.04 $\mu\text{g g}^{-1}$) and P4S3 (229.51 $\mu\text{g g}^{-1}$); both are located in Mina Abdullah industrial area, while the lowest level of Ni is recorded in P1S1 (59.320 $\mu\text{g g}^{-1}$) which is located within Ahmadi city.

The overall mean concentration of Ni is 112.78 $\mu\text{g g}^{-1}$ and the standard deviation is 51.21 $\mu\text{g g}^{-1}$ (Table 13). This is higher than the average (50 $\mu\text{g g}^{-1}$) that was stated by (USPHS, 1997) and the average of 40 $\mu\text{g g}^{-1}$ stated by (Alloway, 1990). Table 12 shows concentration of Ni along the five profiles which is found ranging between 92.37 to 179.34 $\mu\text{g g}^{-1}$. Profile 4 recorded highest mean concentration of Ni (179.34 $\mu\text{g g}^{-1}$, STD: 89.10 $\mu\text{g g}^{-1}$) in the study area. This may be due to the Mina Abdullah refineries and industrial area activity. Figure 19 shows distribution of Ni in different stations.

Table 13 shows that Station 2 recorded highest mean concentration of Ni is (130.73 $\mu\text{g g}^{-1}$, STD: 57.68 $\mu\text{g g}^{-1}$). Station 3, is also considered also high with mean concentration of 128.37 $\mu\text{g g}^{-1}$, STD: 58.53 $\mu\text{g g}^{-1}$ that is higher than the overall mean concentration. Figure 20 shows no interaction between profiles and stations, meaning that similar stations in the same horizon share the same level of pollution; this is due to their location in respect to the three refineries' activity.

Nickel the most abundant element in the Earth's crust, with an average concentration of 75 $\mu\text{g g}^{-1}$, (USPHS, 1997; Mmolawa *et al.*, 2011). In the present study, Ni is recognized with the highest concentration at Mina Abdullah refineries and industrial area (32.040 $\mu\text{g g}^{-1}$) and (229.510 $\mu\text{g g}^{-1}$) at P4S2 and P4S3 respectively where the area is surrounded by industries and the highway activity. The mean concentration is found to be 112.78067 $\mu\text{g g}^{-1}$, which is higher than natural Ni occurrence in soil.

Natural sources of Ni are emissions from wind-borne soil particles, forest fires, sea salt spray and biogenic processes. It is estimated that the total amount of nickel released to the atmosphere from natural sources is 29,000 tones/year, compared with an anthropogenic load of 52,000 tones/year (Labunska *et al.*, 2000; Nriagu, 1988). Worldwide anthropogenic inputs of nickel to soils sources are energy production (coal and oil combustion), manufacturing processes (metal, chemicals, paper and petroleum products), non-ferrous metal production (Ni, Cu, Pb), waste incineration (municipal refuse and sewage sludge), atmospheric fallout and agricultural and animal wastes (Labunska *et al.*, 2000; Nriagu, 1988; Warner and Solomon, 1990).

Iron (Fe)

The concentration of Iron (Fe) in sediment samples ranged between 12.61-23.94 $\mu\text{g g}^{-1}$ (Table 14). Figure 21 shows variation of Fe in different stations. The highest level of Fe recorded in P4S2 (23.94 $\mu\text{g g}^{-1}$) that is located at Mina Abdullah area followed by P5S2 and P5S3 with a range between concentrations 20.39 to 20.52 $\mu\text{g g}^{-1}$, while the lowest level of Fe is recorded in P5S1 (12.61 $\mu\text{g g}^{-1}$) that is located at Ali Sabah Al Salem area.

The overall mean concentration of Fe is 17.15 $\mu\text{g g}^{-1}$ and the standard deviation is 3.28 $\mu\text{g g}^{-1}$ (Table 14). Table 14 shows mean concentrations along the five profiles. Profile 4 recorded highest mean concentration of Fe (21.04 $\mu\text{g g}^{-1}$, STD: 2.52 $\mu\text{g g}^{-1}$). This could be due to the activity of Mina Abdullah industrial area. Profile 5, also recorded high mean concentration of Fe that is 17.84 $\mu\text{g g}^{-1}$, STD: 4.53 $\mu\text{g g}^{-1}$; this is higher than the overall mean concentration; this station is located at Ali Sabah Al Salem area that could be affected by Mina Abdullah industrial emissions. Figure 22 shows distribution of Fe in different stations.

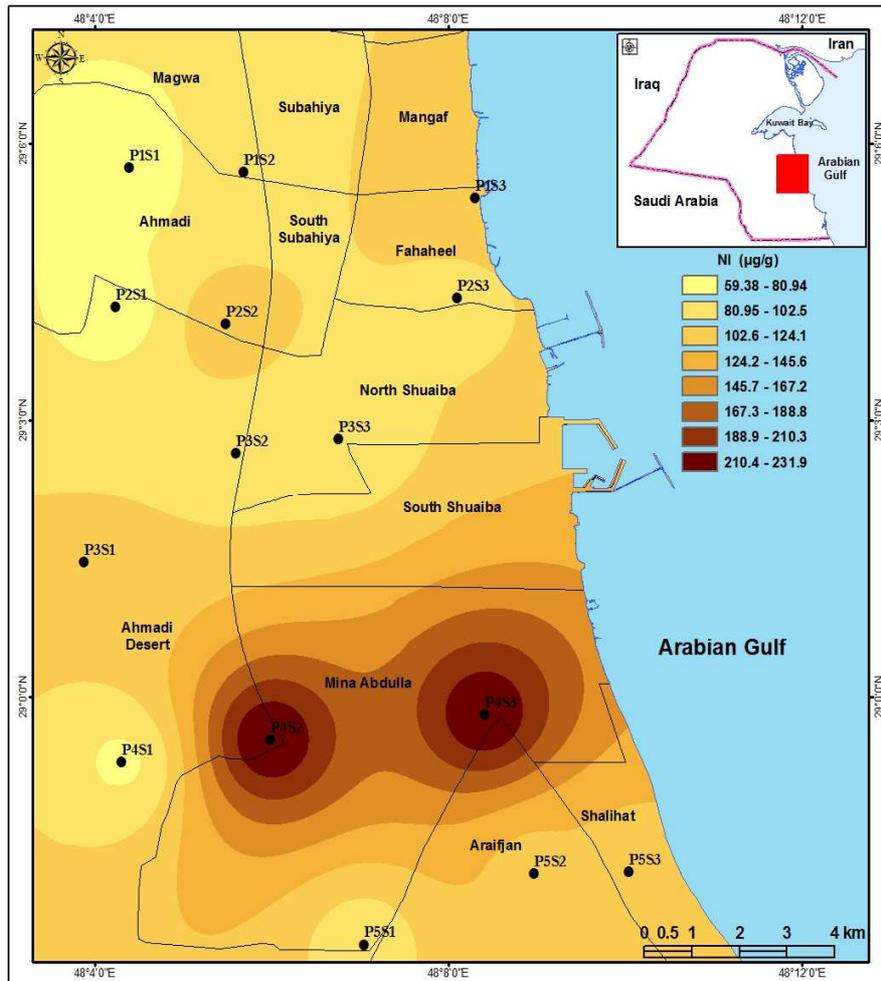


Fig. 19: The highest Ni concentration recorded in Mina Abdullah Industrial area

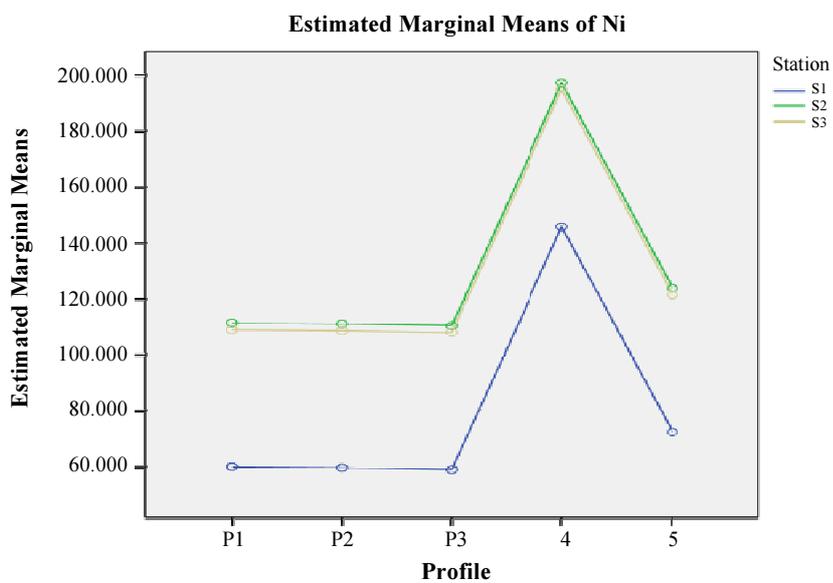


Fig. 20: : No interaction between profiles and stations

Table 15 shows the mean concentration of Fe in each station. Station 2 recorded highest mean concentration of Fe ($19.03 \mu\text{g g}^{-1}$, STD: $3.48 \mu\text{g g}^{-1}$). Station 3, is also considered high with mean concentration ($17.30 \mu\text{g g}^{-1}$, STD: $2.79 \mu\text{g g}^{-1}$), which is higher than the overall mean concentration. Figure 23 shows no interaction between profiles and stations, because the stations along the five profiles follow a parallel trend. It becomes clear that Profile 4 contain the highest Fe concentration in the

three stations. Iron toxicity with regard to soil content is $20\text{-}5000 \mu\text{g g}^{-1}$ (Venkataraman and Sudha, 2005).

From the above analysis, Fe is recognized with the highest concentration in the southern part of the study area at stations P4S2 and P4S3 near Mina Abdullah area and stations P5S2 and P5S3 in Ali Sabah Al Salem area that is close to Mina Abdullah industrial area and highway. Iron is the fourth most abundant element on Earth, with total Fe ranging from 0.7 to 55%.

Table 11: Statistical analysis of Cu concentration for sediment samples in ppm ($\mu\text{g/g}$)

	Station 1	Station 2	Station 3
Minimum	11.780	18.400	14.71
Maximum	21.220	50.830	41.86
Mean	17.762	26.736	26.88
STD	4.410	13.660	10.76

STD: Standard Deviation

Table 12: Chemical and Statistical analysis of Ni concentration in Sediment for each profile in ppm ($\mu\text{g/g}$)

	Profile 1	Profile 2	Profile 3	Profile 4	Profile 5
Station 1	59.32	67.38	104.060	76.48	88.96
Station 2	99.33	116.29	90.480	232.04	115.53
Station 3	121.46	95.38	82.570	229.51	112.92
Minimum	59.32	67.38	82.570	76.48	88.96
Maximum	121.46	116.29	104.060	232.04	115.53
Mean	93.37	93.02	92.370	179.34	105.80
STD	31.50	24.54	10.870	89.09	14.65

Maximum concentration 232.04, Minimum concentration 59.32, STD: Standard Deviation

Table 13: Statistical analysis of Ni concentration for sediment samples in ppm ($\mu\text{g/g}$)

	Station 1	Station 2	Station 3
Minimum	59.32	90.48	82.57
Maximum	104.06	232.04	229.51
Mean	79.24	130.73	128.37
STD	17.72	57.68	58.53

STD: Standard Deviation

Table 14: Chemical and Statistical analysis of Fe* concentration in Sediment for each profile in ppm ($\mu\text{g/g}$) In Thousand

	Profile 1	Profile 2	Profile 3	Profile 4	Profile 5
Station 1	13.15	13.76	16.74	19.35	12.61
Station 2	16.84	18.99	14.88	23.94	20.52
Station 3	17.15	14.80	14.32	19.84	20.39
Minimum	13.15	13.76	14.32	19.35	12.61
Maximum	17.15	18.99	16.74	23.94	20.52
Mean	15.71	15.85	15.31	21.04	17.84
STD. Deviation	2.23	2.77	1.27	2.52	4.53

Maximum concentration 23.94, Minimum concentration 12.61, * Fe was divided by 1000

Table 15: Statistical analysis of Fe concentration in sediment samples in ppm ($\mu\text{g/g}$)

	Station 1	Station 2	Station 3
Minimum	12.61	14.880	14.32
Maximum	19.35	23.940	20.39
Mean	15.12	19.030	17.30
STD. Deviation	2.85	3.478	2.79

* Fe was divided by 1000

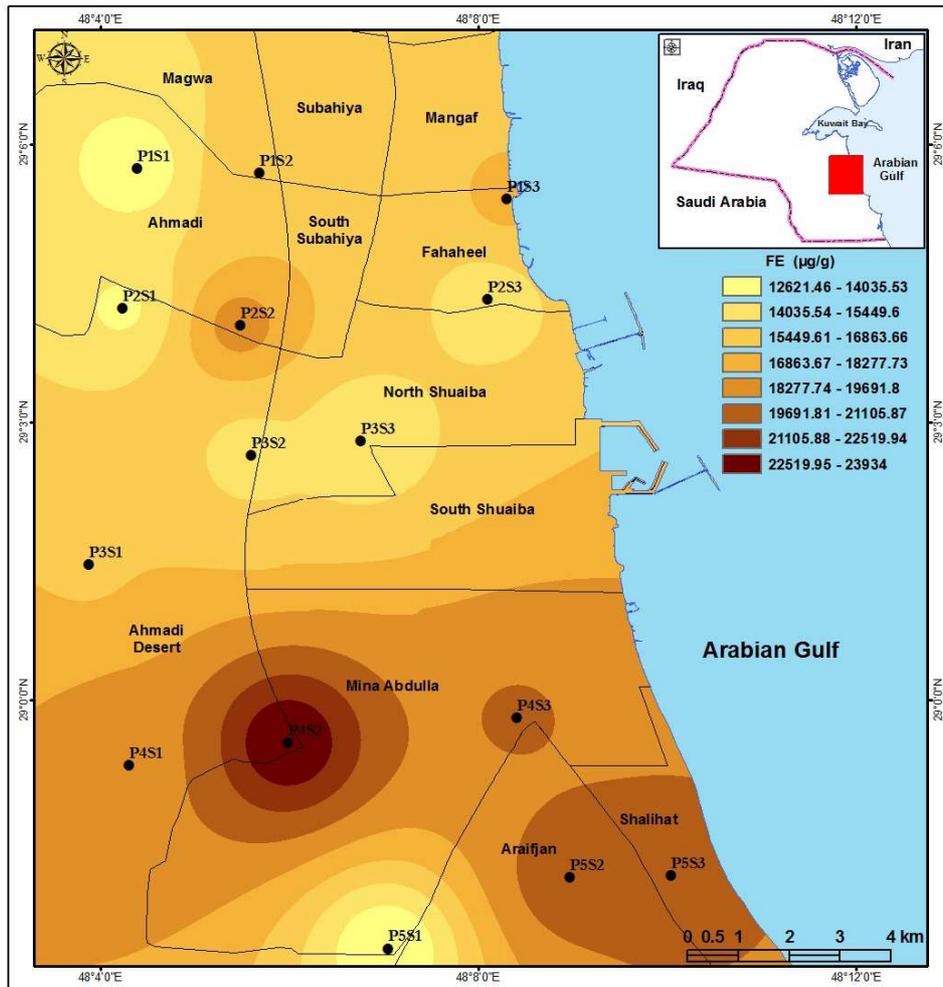


Fig. 21: The highest concentration of Fe is in P4S2 Mina Abdullah industrial area

Trace metal Concentration in Sediment

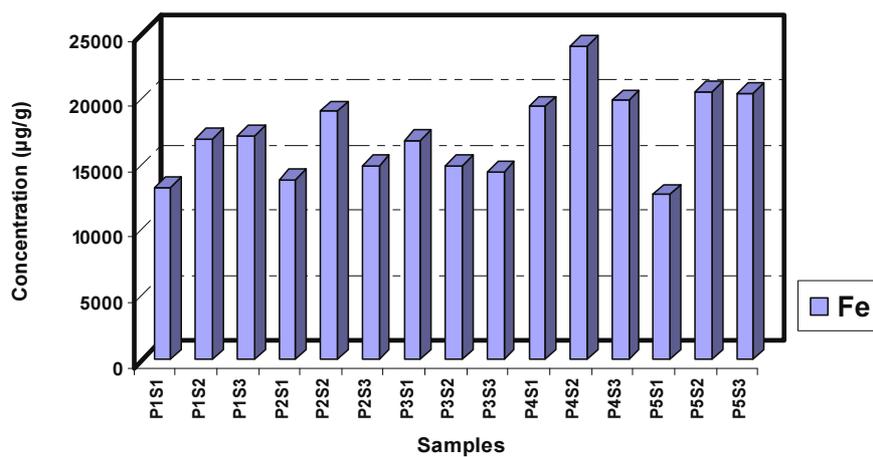


Fig. 22: Mina Abdullah industrial area is source of high Fe concentration

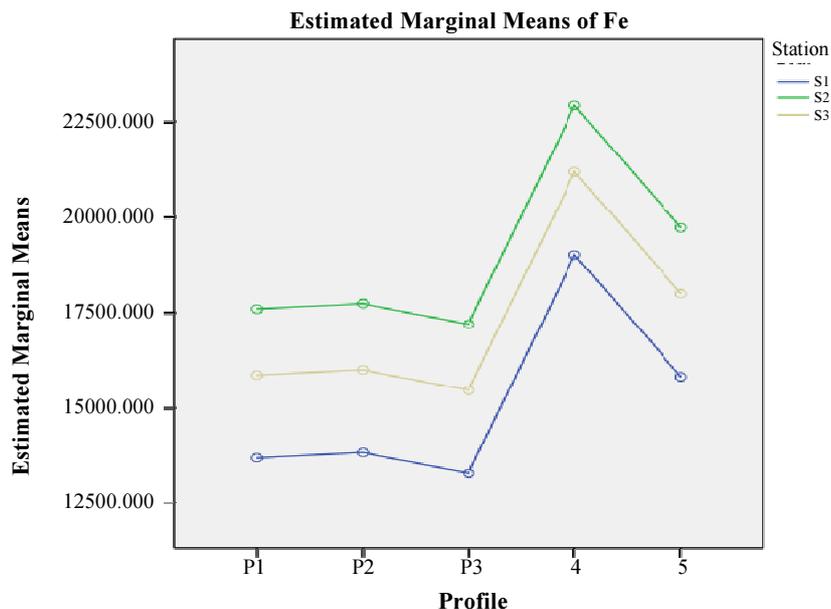


Fig. 23: No interaction between profiles and stations

Manganese (Mn)

The concentration of Manganese (Mn) in sediment samples is high in most of the stations with ranges between 287.17-473.880 $\mu\text{g g}^{-1}$ (Table 16). This is higher than quartzitic sandstone and grits that have Mn concentration of 170 $\mu\text{g g}^{-1}$. Carbonate rocks, particularly dolomite, may contain high concentrations of Mn, on average of 550 $\mu\text{g g}^{-1}$ (Bernad *et al.*, 2004). The variation of Mn in different stations is illustrated in Fig. 24. The highest level of Mn is recorded in P2S2 (473.880 $\mu\text{g g}^{-1}$) that is located in Ahmadi and P5S1 in Ali Sabah Al Salem residential area with an amount of 287.170 $\mu\text{g g}^{-1}$, while the lowest level of Mn is recorded in P2S1 in Ahmadi city.

The overall mean concentration of Mn is 404.27 $\mu\text{g g}^{-1}$ and the standard deviation is 59.43 $\mu\text{g g}^{-1}$ (Table 17). Table 17 shows the mean concentration of Mn along the five profiles ranges between 287.17 to 422.93 $\mu\text{g g}^{-1}$. Profile 1 recorded the highest mean concentration of Mn (406.23 $\mu\text{g g}^{-1}$, STD: 14.92 $\mu\text{g g}^{-1}$); it could be due to the activity at Ahmadi southern oil farm. Following Profile 1 is Profile 4, with a mean concentration of Mn of 422.93 $\mu\text{g g}^{-1}$, STD: 39.23 $\mu\text{g g}^{-1}$. Profile 5 also recorded a high mean concentration of Mn of 408.71 $\mu\text{g g}^{-1}$, STD: 103.70 $\mu\text{g g}^{-1}$. This is higher than the overall mean concentration; Profile 5 is situated at Ali Sabah Al Salem city that is close to Mina Abdullah. Figure 25 shows the distribution of Mn in different stations, the highest level is in Ahmadi, Mina Abdullah industrial area and Ali Sabah Al Salem area.

Table 16 shows the mean concentration of Mn in each station along the selected profiles. Station 2 recorded highest mean concentration of Mn (443.15 $\mu\text{g g}^{-1}$, STD: 35.50 $\mu\text{g g}^{-1}$). This could be because it is close to the

highway. Station 3 is considered to also have a high mean concentration that is higher to the overall mean concentration (409.82 $\mu\text{g g}^{-1}$, STD: 47.60 $\mu\text{g g}^{-1}$): It could be because it is close to the industrial area of the three refineries. Figure 26 shows no interaction between profiles and stations: This means that similar stations in the same horizon are sharing the same level of pollution and this is due to their location in respect to industrial activities.

Mn concentration is recognized to be high in the whole area with an overall mean concentration of 404.27 $\mu\text{g g}^{-1}$, but the highest mean was found at P2S2 within Mina Ahmadi Refinery and P4S2 and P5S3 and P5S3 near Mina Abdullah, where the area is surrounded by industrial area in addition to the effects of highway activity.

Like zinc, copper, nickel and chromium, manganese is an essential trace element. However, exposure to high levels can cause serious illness. Most of the toxicological information on manganese comes from studies of workers chronically exposed to high levels of manganese in the air. Many have suffered both mental and emotional disturbances (Stephenson, 1998; Buszewski *et al.*, 2000).

Chromium (Cr)

The concentration of Chromium (Cr) in sediment ranged between 35.89 to 80.41 $\mu\text{g g}^{-1}$ (Table 18). This is within the background concentrations range of chromium in sediment that ranges from less than 50 to 100 $\mu\text{g g}^{-1}$ (Salomons and Forstner, 1984). Figure 27 shows variation of Cr in different stations. The highest level of Cr is recorded in P4S2 (80.410 $\mu\text{g g}^{-1}$) which is located in Mina Abdullah while the least level of Cr is recorded in P1S1 and P2S1 in Al Ahmadi area with amount of 35.890 and 37.880 $\mu\text{g g}^{-1}$ respectively.

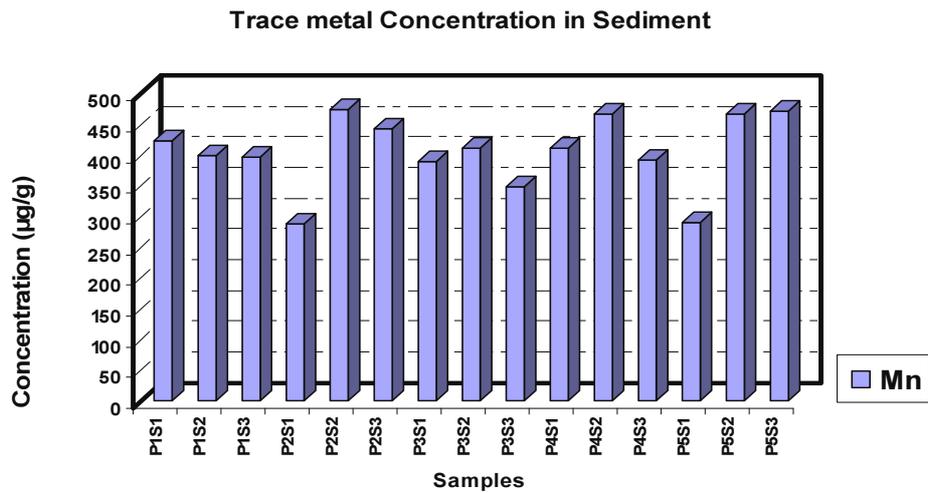


Fig. 24: Mn concentration is higher than the limit mostly in all stations

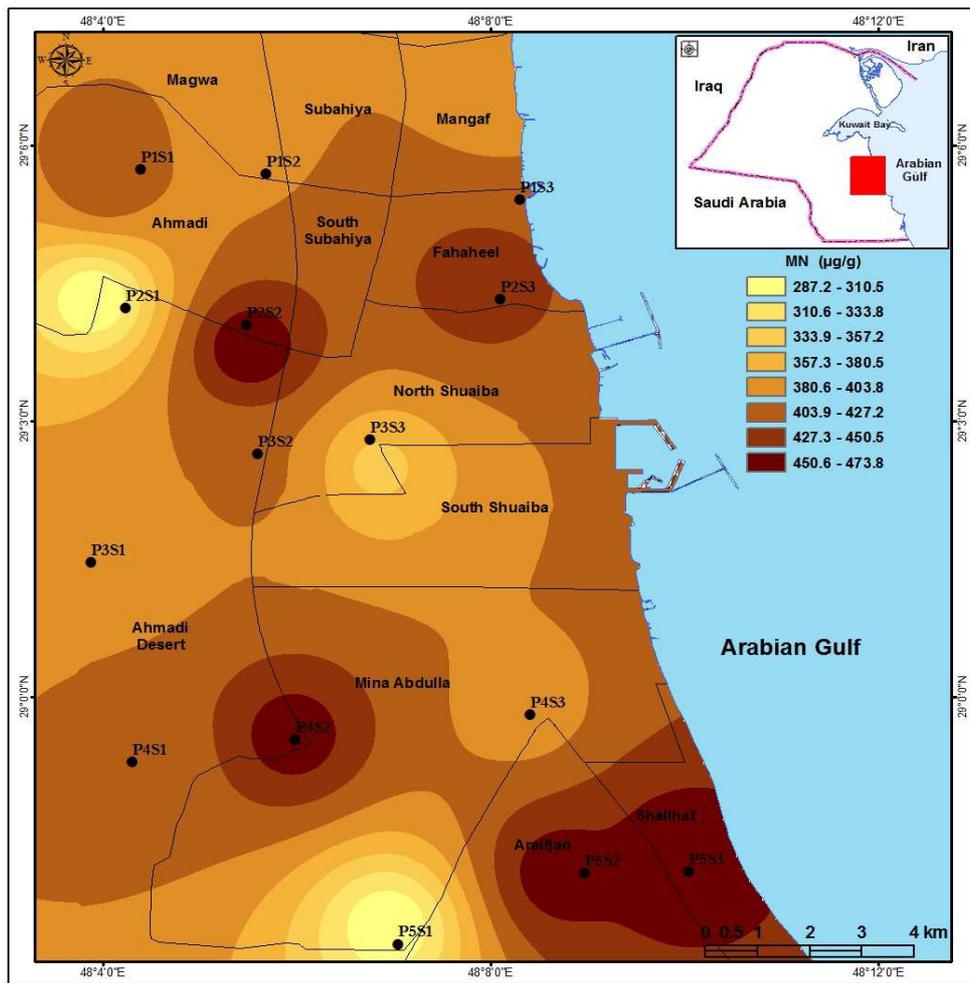


Fig. 25: Map shows the distribution of Mn in the study area, the highest level is in Ahmadi, Mina Abdullah industrial area and Ali Sabah Al Salem area

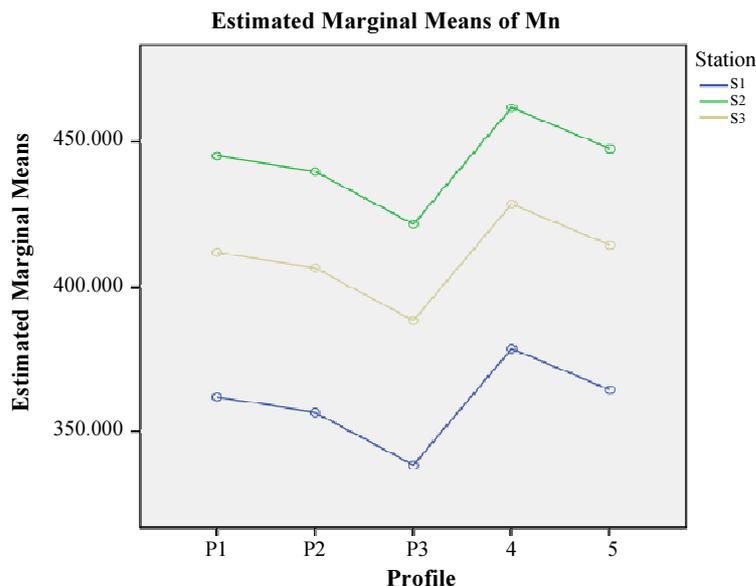


Fig. 26: No interaction between profiles and stations

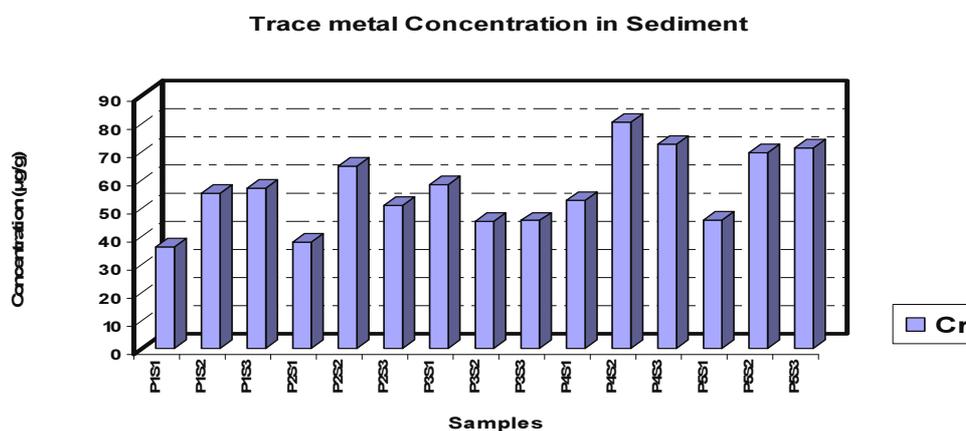


Fig. 27: The highest level of Cr recorded in P4S2 ($80.410 \mu\text{g g}^{-1}$)

Table 16: Chemical and Statistical analysis of Mn concentration in Sediment for each profile in ppm ($\mu\text{g/g}$)

	Profile 1	Profile 2	Profile 3	Profile 4	Profile 5
Station 1	423.370	287.17	389.16	410.50	289.01
Station 2	399.140	473.88	410.17	466.86	465.72
Station 3	396.180	441.47	348.62	391.42	471.40
Minimum	396.180	287.17	348.62	391.42	289.01
Maximum	423.370	473.88	410.17	466.86	471.40
Mean	406.230	400.84	382.65	422.93	408.71
STD	14.920	99.77	31.29	39.23	103.70

Maximum concentration 473.880, Minimum concentration 287.170, STD: Standard Deviation

Table 17: Statistical analysis of Mn concentration in sediment samples for each station in ppm ($\mu\text{g/g}$)

	Station 1	Station 2	Station 3
Minimum	287.17	399.14	348.62
Maximum	423.37	473.88	471.40
Mean	359.84	443.15	409.82
STD	66.63	35.50	47.60

STD: Standard Deviation

The overall mean concentration of Cr was $56.23 \mu\text{g g}^{-1}$ and standard deviation was $13.36 \mu\text{g g}^{-1}$ (Table 3). Table 18 shows the mean concentration of Cr along the five profiles where as Table 19 shows Cr concentration in sediment samples for each station 1, 2 & 3. Profile 4 recorded the highest mean concentration of Cr ($68.49 \mu\text{g g}^{-1}$, STD: $7.51 \mu\text{g g}^{-1}$). Profile 5 also recorded higher mean concentration of Cr that is $62.35 \mu\text{g g}^{-1}$ STD: $14.45 \mu\text{g g}^{-1}$. This is higher than the overall mean concentration; this may be due to the Mina Abdullah refineries and industrial area. Figure 28 shows the distribution of Cr in different stations. Table 18 shows the mean concentration of Cr in each station along all profiles. Station 2 recorded the highest mean concentration of Cr ($63.10 \mu\text{g g}^{-1}$, STD: $13.53 \mu\text{g g}^{-1}$). Station 3, is also considered high with mean concentration of $12.188 \mu\text{g g}^{-1}$, STD: $59.55 \mu\text{g g}^{-1}$, which is higher than the overall mean concentration. Figure 29 shows no interaction between profiles and stations, so the stations along the five profiles follow a parallel trend.

Chromium is a naturally occurring element found in plants, rocks, soils and volcanic dust and gases. Chromium is the seventh most abundant element on Earth, with an average concentration of $100 \text{ mg}\cdot\text{kg}^{-1}$ rock (Irwin *et al.*, 1997; Lener *et al.*, 1998). Concluding from the above analysis, Cr is recognized that the highest concentration was found at P4S2 and P4S3 near Mina Abdullah, even though the area is surrounded by an industrial area and highway activity. As (Stephenson, 1998)

stated the main source of high Cr is due to anthropogenic discharge especially chemical industries, but the area is still not contaminated. Possible sources of chromium may include paint chips, dust and grit from shipyard operations, leaching of anti-fouling paints from boat hulls and storm water runoff from industrial areas (Lener *et al.*, 1998).

Chromium is present in the environment in several different forms. Chromium is an essential nutrient that helps humans metabolize sugar, protein and fat. The World Health Organization classifies it as a human carcinogen. Ingesting large amounts of chromium can cause stomach upsets and ulcers, convulsions, kidney and liver damage and even death. Skin contact with certain Cr compounds can cause skin ulcers. Allergic reactions consisting of severe redness and swelling of the skin have been noted (Buszewski *et al.*, 2000).

Vanadium (V)

The concentration of Vanadium (V) in sediment samples ranged between $27.328\text{--}48.650 \mu\text{g g}^{-1}$ (Table 20). Figure 30 shows variation of V in different stations. V is like Mn and Cr that are slightly high in the whole area especially in the southern part of the study area. The highest level of V is recorded in P4S2 ($48.650 \mu\text{g g}^{-1}$) which is located in Mina Abdullah, while the least level of V is recorded in P1S1 and P5S1 in Al Ahmadi with amounts of 27.328 and $28.080 \mu\text{g g}^{-1}$, respectively.

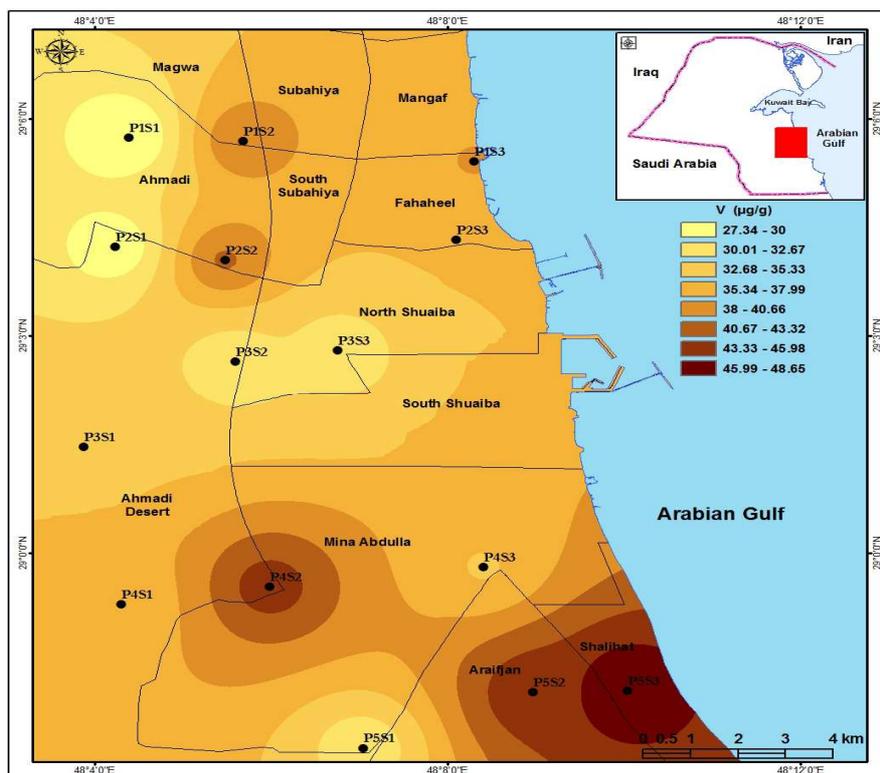


Fig. 28: The higher mean concentration is of Cr in P4S2 in Mina Abdullah

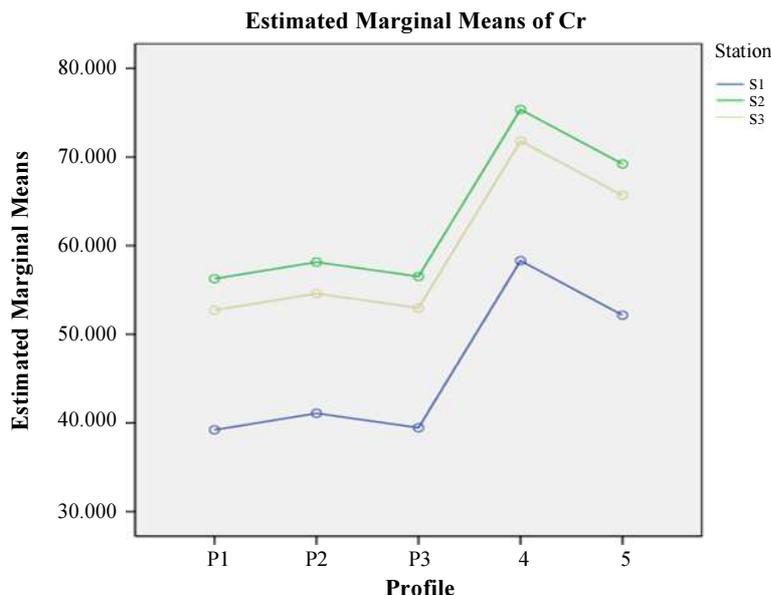


Fig. 29: No interaction between profiles and stations

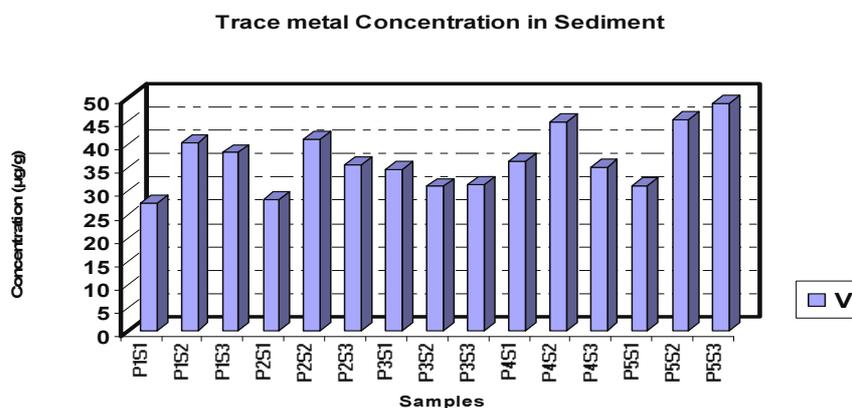


Fig. 30: V is within the limit but higher than the overall mean concentration $36.53 \mu\text{g g}^{-1}$ in Profile5

Table 18: Chemical and Statistical analysis of Cr concentration in sediment for each profile in ppm ($\mu\text{g/g}$)

	Profile 1	Profile 2	Profile 3	Profile 4	Profile 5
Station 1	35.89	37.880	58.320	52.440	45.690
Station 2	55.14	64.950	45.190	80.410	69.810
Station 3	57.18	50.990	45.430	72.630	71.540
Minimum	35.89	37.88	45.19	52.44	45.690
Maximum	57.18	64.95	58.32	80.41	71.540
Mean	49.40	51.27	49.65	68.49	62.35
STD	11.75	13.54	7.51	14.44	14.45

Maximum concentration 80.410, Minimum concentration 35.89, STD: Standard Deviation

Table 19: Statistical analysis of Cr concentration in sediment samples for each station in ppm ($\mu\text{g/g}$)

	Station 1	Station 2	Station 3
Minimum	35.89	45.19	45.43
Maximum	58.32	80.41	72.63
Mean	46.04	63.10	59.55
STD	9.51	13.53	12.18

STD: Standard Deviation

Table 20: Chemical and Statistical analysis of V concentration in Sediment for each profile in ppm ($\mu\text{g/g}$)

	Profile 1	Profile 2	Profile 3	Profile 4	Profile 5
Station 1	27.33	28.08	34.45	36.39	31.04
Station 2	40.19	41.02	30.95	44.64	45.17
Station 3	38.14	35.48	31.24	35.12	48.65
Minimum	27.33	28.08	30.95	35.12	31.04
Maximum	40.19	41.02	34.45	44.64	48.65
Mean	35.22	34.86	32.21	38.72	41.62
STD. Deviation	6.91	6.49	1.94	5.17	9.33

Maximum concentration 48.65, Minimum concentration 27.33, STD: Standard Deviation

Table 21: Statistical analysis of V concentration in Sediment samples in ppm ($\mu\text{g/g}$)

	Station 1	Station 2	Station 3
Minimum	27.33	30.95	31.24
Maximum	36.39	45.17	48.65
Mean	31.46	40.39	37.73
STD	3.93	5.71	6.58

STD: Standard Deviation

The overall mean concentration V was $36.53 \mu\text{g g}^{-1}$ and the standard deviation is $6.42 \mu\text{g g}^{-1}$ (Table 21). Profile 5 located in Ali Sabah Al Salem area, recorded the highest mean concentration of V ($41.62 \mu\text{g}$, STD: $9.33 \mu\text{g g}^{-1}$). Profile 4, also recorded a high mean concentration of V that is $38.72 \mu\text{g g}^{-1}$, STD: $5.17 \mu\text{g g}^{-1}$, this is higher than the overall mean concentration and may be due to the Mina Abdullah refineries and factories. Figure 31 show the distribution of V in different stations.

Table 21 shows the mean concentration of V in each station. Station 1, recorded the highest mean concentration of V ($40.39 \mu\text{g g}^{-1}$, STD: $5.711 \mu\text{g g}^{-1}$). V concentration in Station 3 is considered also high with mean concentration $37.7260 \mu\text{g g}^{-1}$, STD: $6.58424 \mu\text{g g}^{-1}$ which is higher than the overall mean concentration. Figure 32 shows no interaction between profiles and stations, meaning that similar stations in the same horizon are sharing the same level of pollution.

Soils typically have the following V abundance ranges: Sandstone and limestone derived soils 10 to 91mg kg^{-1} ; shales and argillaceous sediments, 20 to 150mg kg^{-1} ; and loess 27-110 to mg V kg^{-1} (Bernad *et al.*, 2004). Vanadium is important as an indicator of oil pollution since oil is one of the main contributors of vanadium to the environment and because most of the crude oil contains relatively high concentrations of vanadium $30.6 \pm 14.3 \mu\text{g g}^{-1}$ (Buszewski *et al.*, 2000). Vanadium contamination of soil may occur whenever petroleum or coal bi-products are accidentally discharged (Irwin *et al.*, 1997; Lener *et al.*, 1998).

In the present study, it was noticed that V content increases gradually toward the south of the study area at

P4S2 ($48.650 \mu\text{g g}^{-1}$) which is located in Mina Abdullah. This data is higher than the concentration of contaminated soil in Ahmadi oil field ($31.22 \mu\text{g g}^{-1}$) (WHO, 2004), but it is lower than sediment concentrations that range 20 to $200 \mu\text{g g}^{-1}$ (WHO, 2004). On the other hand, V concentration recorded in the study area is higher than the V concentration recorded in the study conducted by (Warner and Solomon, 1990) that stated that Vanadium in soils is at concentrations of 10mg/kg or more and is toxic for terrestrial plants.

The primary source of vanadium is titan magnetite deposits in which vanadium is present as a minor replacement for iron. Vanadium is also a trace element in fossilized organic matter, such as crude oils, coal and carbonaceous fossils and can be found in uranium-bearing minerals. It is used widely in metallurgy, the atomic energy industry, space technology, pharmaceutical industrial processes and other high-tech industries, making vanadium one of the most important metals for modern technology (Irwin *et al.*, 1997). Small amounts of vanadium in the environment tend to stimulate plants but large amounts are toxic. Vanadium toxicity is attributed to its ability to inhibit enzyme systems such as monoamine oxidase, ATPase, tyrosine, choline esterase and cholesterol synthetize (Venkataraman and Sudha, 2005; Mmolawa *et al.*, 2011). Effects of vanadium on human health and environment vary considerably depending upon the type and amount of the exposure to the metal (Lener *et al.*, 1998).

Figure 32 depicts that there is no interaction or interference between the stations S1, S2 and S3 with reference to estimated marginal means for the Vanadium.

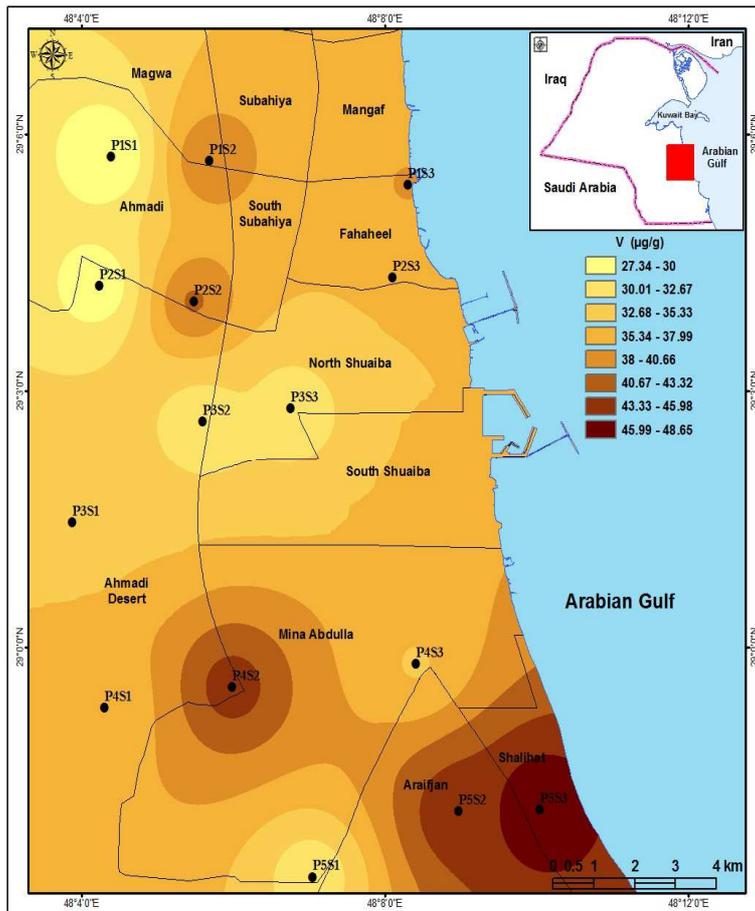


Fig. 31: Map showing the highest level of V in Ali Sabah Al Salem area

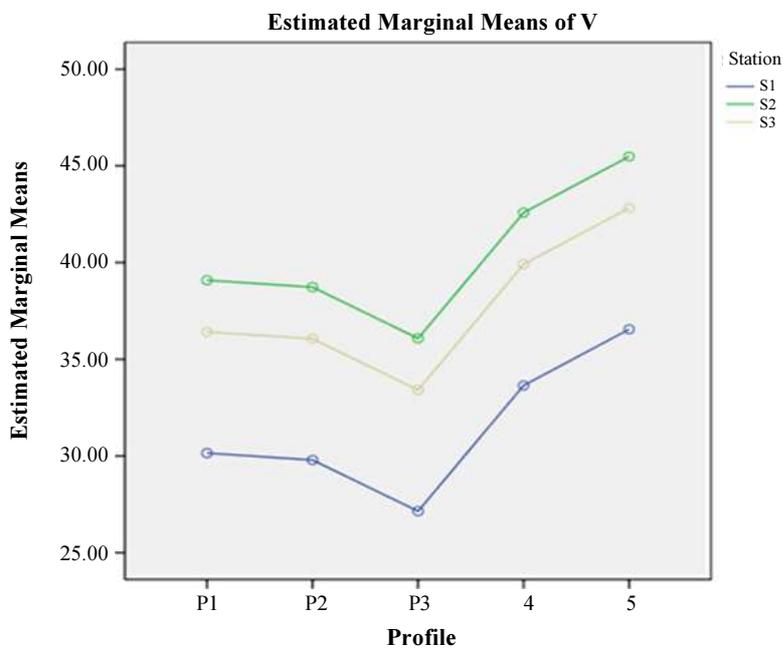


Fig. 32: No interaction between profiles and stations

Discussion

The air borne particulates in industrial and semi-urban areas are enriched with trace metals, particularly Pb, Zn, Ni and are being emitted by various industrial and transport sectors (Smith, 1973). In view of that, trace metals among the five profiles indicate the significance of pollution in the State of Kuwait due to the rapid internalized development, which increase the performance of industrial functions in addition to the rise in population that cause the higher traffic activity.

The chemical and statistical analysis revealed an elevated concentration of trace metal accumulating in soil of the southern part of Kuwait, the area surrounding the three major oil refineries. In comparison with the international standards and researches, the present study finds high TOC and trace metals levels in soil samples that were correlated with several factors including wind direction, rapid industrialization and anthropogenic sources. The chemical analysis showed that the elevated concentration of TOC in the area verifies that the pollutants in the area are of organic petroleum source, which is emitted mostly from the three refineries. Furthermore, the correlation between the TOC and the trace metal showed lateral relationship between TOC and Pb which is of petroleum source as mentioned previously. Moreover, the statistical analysis revealed a high concentration of trace metal bioaccumulation in sediment samples, in the sequence of Fe ($17.15 \mu\text{g g}^{-1}$) > Zn ($151.08 \mu\text{g g}^{-1}$) > Ni ($112.78 \mu\text{g g}^{-1}$) > Pb ($27.71 \mu\text{g g}^{-1}$) > Mn ($404.27 \mu\text{g g}^{-1}$) > Cd ($0.08 \mu\text{g g}^{-1}$) > Cu ($23.79 \mu\text{g g}^{-1}$) > Cr ($56.23 \mu\text{g g}^{-1}$) > V ($36.53 \mu\text{g g}^{-1}$). Chromium and vanadium were within the limit concentration, but their concentrations were higher than the overall mean concentration in profile 4 and profile 5. As for profiles, trace metal analysis revealed high level of metals in the sequence of P4>P2>P5>P1> P3, so Mina Abdullah has the highest trace metal content. It could be due to industrial activities in the area and/or highway activity, also Mina Abdullah acts as a sink for pollutants coming from the other refineries located at the north of it due to dominant wind direction. On the other hand, Mina Shuaiba soil samples had the least trace metal concentration. And as regards the stations, trace metal analysis revealed high metal levels in the sequence of S2>S3>S1, which indicated that the precipitations of the particulates in the refineries missions were close to the refineries' area.

The highest concentrations of Fe, Zn and Ni were determined in profile 4 in Mina Abdullah Industrial area, while the highest concentrations of Pb, Mn and Cd were

determined in Profile 2 in Ahmadi city. However, the concentrations of Fe and Mn were higher than the limited levels almost in all stations soil samples. Zn (0.088), Cu (0.052), Ni (0.086) and Fe (0.080) showed statistically significant differences among profiles. Furthermore, Fe (0.081), Cr (0.053) and V (0.059) are significantly different across different stations.

Statistical Analysis

This section discusse the relationship between different contaminants within the study area.

Significant Differences

Table 22 compares the mean concentration of the metal per profiles and per stations to see whether there are any significant differences in the study area between profiles and stations. To meet these objectives a multivariate analysis of variance technique was implemented to study the significant differences of stations and profiles for each metal and the possibility of interaction effect between the two. Decisions are made at $\alpha = 10\%$ level. If $P\text{-value} < \alpha = 10\%$ reject null hypothesis of insignificant relationships.

Accordingly, the above Table 23 indicates that there are significant differences between different profiles and different stations regarding some of the metal at $\alpha=10\%$ level. However, details concerning the metals are discussed thoroughly in the next section. The following Table 23 provides detailed findings of the effect of both profiles and stations on the amount of residuals of metals. As shown, there are significant differences between residuals including Zn, Cu, Ni and Fe, for different profiles, while regarding the stations there are significant differences between residuals including Fe, Cr and V, for different stations.

Profiles

Regarding profiles, the multivariate analysis test shows that there are significant differences between the five profiles at $\alpha = 10\%$ level. The results are that significant differances occur for Zn 0.088, Cu 0.052, Ni 0.086 and Fe 0.080 (Table 23). The multiple comparison test gives detailed findings of ranked mean concentration.

Profiles homogeneous sheet in Table 24 showed that the amount of Zn residuals in profiles 1, 3 and 5 are significantly less than the amount of Zn in profiles 2 and 4. Residuals for Profile 2 and 4 are higher which might be due to the activity at Ahmadi south oil field, that's why Profile 2 shows higher amount; also the amount of Zn in Profile 4 could be due to Mina Abdullah industrial area activities and/or the highway).

Table 22: Multivariate tests

	Effect	Value	F	Hypothesis df	Error df	Sig.
Profile	Pillai's Trace	2.700	1.038	32.000	16.000	0.485
	Wilks' Lambda	0.000	5.780	32.000	5.283	0.025
	Hotelling's Trace	.	.	32.000	.	.
	Roy's Largest Root	16356.957	8178.478 ^b	8.000	4.000	0.000
Station	Pillai's Trace	1.524	0.799	16.000	4.000	0.671
	Wilks' Lambda	0.000	10.181 ^a	16.000	2.000	0.093
	Hotelling's Trace	3236.873	0.000	16.000	0.000	.
	Roy's Largest Root	3235.772	808.943 ^b	8.000	2.000	0.001

Table 23: Tests of between-subjects effects

Source	Dependent variable	Type III sum of squares	df	Mean square	F	Sig.
Profile	Pb	988.403	4	247.101	1.981	0.191
	Cd	0.005	4	0.001	0.985	0.468
	Zn	124736.554	4	31184.139	2.982	0.088
	CU	842.742	4	210.685	3.786	0.052
	Ni	16989.770	4	4247.443	3.013	0.086
	Fe	68327.860	4	17081.970	3.121	0.080
	Mn	2552.447	4	638.112	0.174	0.946
	Cr	906.945	4	226.736	2.326	0.144
	V	161.490	4	40.372	1.581	0.269
Station	Pb	145.994	2	72.997	0.585	0.579
	Cd	0.005	2	0.002	1.865	0.216
	Zn	30532.732	2	15266.366	1.460	0.288
	CU	272.942	2	136.471	2.453	0.148
	Ni	8451.317	2	4225.659	2.998	0.107
	Fe	38414.140	2	19207.070	3.509	0.081
	Mn	17582.965	2	8791.482	2.399	0.153
	Cr	810.002	2	405.001	4.155	0.058
	V	210.451	2	105.225	4.120	0.059

Sig = significant differences; Trace metal that show significant differences between profiles Cu, Ni, Fe and Mn; Trace metal that show significant differences between stations Fe, Cr and V.

Table 24: Profiles Homogeneous sheet for Zn

Profile	N	Subset	
		1	2
5	3	68.49333	-
3	3	84.50667	-
1	3	86.66667	-
2	3	-	216.80333
4	3	-	298.92333
Sig.		0.134	0.354

Means for groups in homogeneous subsets are displayed. Based on observed means; N: number of stations; Sig: Significant differences; Alpha = 0.05

Table 25: Profiles Homogeneous Sheet for Cu

Profile	N	Subset	
		1	2
5	3	17.33000	-
3	3	18.11000	-
1	3	20.67333	-
2	3	25.08333	-
4	3	-	37.77333
Sig.		0.26500	0.07100

Means for groups in homogeneous subsets are displayed. Based on observed means; N: number of stations; Sig: Significant differences; Alpha = 0.05

Profiles homogenous sheet in Table 25 indicate that Cu content is different across profiles, however the multiple comparison test indicated that there are significant differences between profiles 1, 2, 3 and 5 as one group and Profile 4 as one group that has significantly higher mean weight. The reason for the high amount in profile 4 could be due to the presence of Mina Abdullah refinery and industrial area on one side and the highway on the other side.

Ni content also showed significant differences across profiles; however, the multiple comparison tests shown in profiles homogeneous sheet (Table 26) indicated that there are significant differences between profiles 1, 2, 3 and 5 as one group and Profile 4 as another group that has a higher mean concentration $179.34 \mu\text{g g}^{-1}$. The reason for the high amount in Profile 4 could be due to the presence of Mina Abdullah refinery and industrial area on one side and the highway on the other side.

Fe content is different across profiles as well; however, the multiple comparison tests (Table 25) indicated that there are significant differences between profiles 1, 2 and 3 as one group and Profile 4 and 5 as another group, which has a higher mean weight. Ali Sabah Al Salem area in Profile 5 is clearly affected by the higher activity in Mina Abdullah industrial area and refineries (Profile 4).

Stations

Regarding stations and whether there are significant differences between them, the result of the manova (multivariate analysis test), Table 27 indicates significant differences 0.093 between the three stations at $\alpha < 10\%$ level. In more specific detail, the findings are that Ni and Fe are significantly different across different stations P-values = 0.081, 0.053 and 0.059 respectively (Table 26, 27).

Stations homogeneous sheet (Table 28, 29 and 30) showed that Fe, V and Cr content is different across stations; however, the multiple comparison tests indicated that there are significant differences between the three stations. Fe in stations 2 and 3 as one group has significantly higher mean concentration than the mean concentration of Fe in stations 1.

Table 26: Profiles Homogeneous sheet for Ni

Profile	N	Subset	
		1	2
P3	3	92.37	-
P2	3	93.02	-
P1	3	93.37	-
P5	3	105.80	-
P4	3	-	179.340
Sig.		0.690	1.000

Means for groups in homogeneous subsets are displayed. Based on observed means; N: number of stations; Sig: Significant differences; Alpha = 0.05

Stations homogeneous sheet (Table 28) showed that V content is different across stations; however, the multiple comparison tests indicated that there are significant differences between stations 2 and 3 as one group, which has a higher mean concentration than station 1 as another group that have less mean concentration.

Table 27: Profiles Homogeneous sheet for Fe

Profile	N	Subset	
		1	2
P3	3	15.31	-
P1	3	15.71	-
P2	3	15.85	-
P5	3	17.84	-
P4	3	-	21.040
Sig.		0.248	0.132

Means for groups in homogeneous subsets are displayed. Based on observed means; N: number of stations; Sig: Significant differences; Alpha = 0.05

Table 28: Stations Homogeneous sheet for Fe

Station	N	Subset	
		1	2
S1	5	15.120	-
S3	5	-	17.300
S2	5	-	19.035
Sig.		0.180	0.275

Means for groups in homogeneous subsets are displayed. Based on observed means; N: number of profiles; Sig: Significant differences; Alpha = 0.05

Table 29: Stations Homogeneous sheet for V

Station	N	Subset	
		1	2
S1	5	31.4576	-
S3	5	-	37.7260
S2	5	-	40.3940
Sig.		0.0850	0.4280

Means for groups in homogeneous subsets are displayed. Based on observed means; N: number of profiles; Sig: Significant differences; Alpha = 0.05

Table 30: Stations Homogeneous sheet for Cr

Station	N	Subset	
		1	2
S1	5	46.04400	-
S3	5	-	59.55400
S2	5	-	63.10000
Sig.		0.06200	0.58600

Means for groups in homogeneous subsets are displayed. Based on observed means; N: number of profiles; Sig: Significant differences; Alpha = 0.05

Table 31: Correlation coefficient (r value) of heavy metals in soil (Correlation Matrix)

		TOC	Pb	Cd	Zn	Cu	Ni	Fe	Mn	Cr	V
TOC	Pearson correlation	1.000									
	Sig. (2-tailed)										
Pb	Pearson correlation	0.503*	1.000								
	Sig. (2-tailed)	0.056									
Cd	Pearson correlation	0.145	0.161	1.000							
	Sig. (2-tailed)	0.605	0.566								
Zn	Pearson correlation	-0.123	0.428	0.455	1.000						
	Sig. (2-tailed)	0.662	0.111	0.088							
Cu	Pearson correlation	-0.238	0.370	0.262	0.849**	1.000					
	Sig. (2-tailed)	0.392	0.175	0.346	0.000						
Ni	Pearson correlation	-0.372	0.139	0.092	0.705**	0.904**	1.000				
	Sig. (2-tailed)	0.172	0.622	0.743	0.003	0.000					
Fe	Pearson correlation	-0.510	0.037	0.178	0.328	0.661**	0.732**	1.000			
	Sig. (2-tailed)	0.052	0.895	0.525	0.232	0.007	0.002				
Mn	Pearson correlation	-0.629*	-0.312	0.458	0.160	0.314	0.334	0.683**	1.000		
	Sig. (2-tailed)	0.012	0.258	0.086	0.570	0.254	0.224	0.005			
Cr	Pearson correlation	-0.540*	-0.118	0.211	0.380	0.684**	0.819**	0.930**	0.633*	1.000	
	Sig. (2-tailed)	0.038	0.674	0.451	0.162	0.005	0.000	0.000	0.011		
V	Pearson correlation	-0.444	-0.244	0.359	0.074	0.374	0.465	0.842**	0.721**	0.861**	1.000
	Sig. (2-tailed)	0.097	0.381	0.189	0.794	0.170	0.080	0.000	0.002	0.000	

R ≥ 0.5 N=15: *Correlation is significant at the 0.05 level (2-tailed).: ** Correlation is significant at the 0.01 level (2-tailed)

Cr content is different across stations; however, the multiple comparison tests in Table 30 indicated that there are significant differences between station 1 as one group that has less mean concentration than stations 2 and 3 as another group that has a higher mean concentration.

All three-trace metals Fe, V and Cr (Table 28, 29 and 30) have higher mean concentration at stations 2 and 3 that are closer to the industrial area and the three refineries Ahmadi, Mina Shuaiba and Mina Abdullah in addition to activity of the highway.

Correlation Coefficient between Heavy Metals and TOC in Sediment

There is weak significant correlation that was found among TOC and some trace metals (Table 31). TOC correlated positively with Pb and negatively with Mn and Cr at (p<0.05) level. Strong significant positive correlation was found among trace metals at (p<0.01) level, i. e., Fe correlated with Cu, Ni, Mn, Cr and V. These metals are correlated with each other and with other metals in addition to Fe. Cu, Ni and Cr are significantly correlated with each other.

On the other hand, Cu and Ni are correlated with Zn at r = 0.849 and r = 0.705 respectively. Cr are correlated at (p<0.01) with Cu, Ni, Fe and V while with Mn at (p<0.05) where r = 0.633. Mn and V are also correlated positively and significantly (r = 0.721). The high correlation among heavy metals in this study

suggests that similar processes controlled metal associations in the study area.

Conclusion

From the research study and the full chemical analysis for soil samples, the study found that the concentration of total organic carbon is high in the sediment samples, which shows that the source of pollutant in the area is organic from petroleum base. Moreover, the concentration of trace metals level varied according to the location and the distance from the source of pollution. The concentration of trace metals in sediment sometimes exceeded the standard level assigned by the environmental and authorized institutions. The most polluted locations according to the level of trace metals is adjacent to Mina Abdullah Refinery and the results show that the concentration of trace metals is higher than the overall mean concentration found in the study area. The second polluted location is Mina Ahmadi refinery while Shuaiba refinery was as third in the level of pollution. It is found that the level of contamination of soils with trace metals in the study area, compared with different data from Nigeria, India, USA, China and WHO (Table 32), is higher and might cause health problems for both animals and humans. The source of contamination is varied between the following: The industrial area, the refineries, oil exploration and vehicles. Therefore, there is an urgent need to bioremediation to clean such soils.

Table 32: Concentration of trace elements in Kuwait surface soils in this study with comparison data from different sources

		Comparison data									
The present study Southern part of Kuwait (Refineries area)		Other studies									
		Recommended amount of trace metal trace metals in soil value									
		Niger									
T.M.	Concentration µg/g	Clean soil in Kuwait	Delta of Nigeria ¹	Florida soils ²	California soil ³	U.S. Soil ⁴	China Soil ⁵	World Soil	B. Conc	WHO	
Pb	14.81-65.01	27.71	3.4-4.6	1.20	4.1(0.18-290)	21.7	16	23.6	15	75.6	50-300
Cd	0.03-0.18	0.08	0.02-0.05	0.10	0.21(0.004-2.80)	0.26	NA	0.074	0.4	0.07	1-3
Zn	51.77-416.28	151.08	NA	3.20	12(0.90-169)	145	48	67.7	40	77.8	150-300
Cu	11.780-50.83	23.79	NA	NA	NA	NA	NA	20.0	12	28.7	50-140
Ni	59.320-232.040	112.78	6.9-18.0	0.40	6.5(0.04-375)	36	13	23.4	25	23.5	30-75
Fe	12.612-23.94	17.15	NA	20.0	NA	NA	NA	NA	NA	NA	NA
Mn	287.170-473.880	404.27	NA	NA	25(1.40-1642)	592	330	482	450	NA	NA
Cr	35.890-80.410	56.23	NA	NA	3.9(0.02-447)	76	37	53.9	50	87.0	NA
V	27.328- 48.650	36.53	10.4-12.1	NA	NA	NA	7-500 ^{***}	42.55 ¹⁰	100 ^{**}	NA	NA

B.Conc: Baseline concentration, WHO: World Health Organization, NA: Data Not available, ¹⁰ Lu et al 2010, ^{***}National Toxicology Program 2008

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Authors Contributions

Laila S. Ghari: Data collection, analysis and interpretation of the data , preparing the research paper.

Mohammad Al Sarawi: Supervision of the work and revision of the article.

Ethics

This article is original and contains unpublished materials. The corresponding author confirms that all the other authors have read and approved the manuscript and there are no ethical issues involved.

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