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Environmental impact of fuel stations on some heavy metal concentrations in nearby surface crust soils in urban areas: A case study of soil heavy metal contamination.

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Abstract. In the present study, the chemical analysis, related to heavy metals (Pb, Ni, Zn, Mn, and Fe) which considered the main source of pollution in soils that come from several sources, was carried out near a three fuel stations to reveal their effect on heavy metals in the nearby soils. Samples were collected from soils which are near to three Fuel stations in Al Hilla city, as a case study, it was found that the concentrations of these metals are all below the value that should be available in average shale, except that for Pb. The average concentration of metals in samples was Pb (25.47 ppm), Ni (86.65 ppm), Zn (84.38 ppm), Mn (96.71 ppm), and Fe (112.38 ppm), and a statistical analysis is done for these results to find correlations coefficients among studied elements, and the results suggested that the fuel station may compromise the nearby soils by increasing Pb concentrations in them.

1. Introduction.

Soil ecosystem in the world have been extensively contaminated with heavy metals due to various human activities, possibly including mobilization of these metals up in the food chain, thereby threatening human health.[1][2]

As it is well known, environmental problems are the most escalading problems worldwide in the last 25 years. Problems such that-caused by the destruction of forests, erosion, rapid increasing of population, distorting urbanization and decreasing green areas, distortion of shores, chemicals used in industry, pollution of air, thermic power stations and Fuel stations are the ones that their solutions are searched in all over the world.[3][4][5][6] Air, water and soil pollution due to the industrialization and urbanization. especially the use of machines that depends on fossil fuel has been the reason for increasing air pollution in recent years.

Soils, whether in urban or agricultural areas, represent a major sink for metals released into the environment from a variety of anthropogenic sources.[5] Once in soil, some of these metals will be persistent because of their fairly immobile nature.[7] Other metals, however, will be more mobile migrating to either groundwater aquifer or plants (bioavailability). There is a large consensus among the scientific community to believe that the risks for living organisms associated to the presence of heavy metals.[1]

In addition, metals can be dispersed into the atmosphere, by natural geochemical cycling and by other anthropogenic processes (such as smelting and burning leaded gasoline and coal) and by

microbial activities; these metal fluxes must be considered in overall metal bioavailability studies. The use of tetraethyllead as a gasoline enhancing agent since the beginning of car manufacturing had and still have a great effect on lead contamination in soil, air and water.[8][9]

The uptake of toxic heavy metals from contaminated soils by food and forage plants comprises a prominent path for such elements to enter the food chain and will finally be ingested by humans.[10]

Ingestion and eventual accumulation of toxic heavy metals pose a threat to human health and, therefore, they should be minimized due to the sever negative effects that can cause to human and environment especially on newly born children.[7][11]

Fuel stations may contain hazardous risk on soil metal concentration due to its direct contribution on air pollution around the station and the possibility of oil product spillage on soil around the facility. The studied heavy metals in this paper have different sources, Pb is generated from leaded fuel combustion and sewage sludge as well as surplus ammo[12], Ni and Zn main source of contamination is the use of fertilizers[13][14], while Mn contamination is considered rare in soil due to the oxidation effect of some bacteria that transform it in to another form that is useful to planets[14] and the last one is Fe which considered as a refence element in earth crust and can presence in high concentrations without causing environmental problems.[15]

In this study, determination of some metal levels that considered the most toxic on human being (Pb, Ni, Zn, Mn, and Fe)[1] in the soil around three fuel station: (Al Hilla fuel station), (Ishtar), and (Hamurabi) in Hilla city, Figure 1 was developed by ArcGIS 10.5 program to represent the exact location of the study region and sampling points with the aid of GPS to locate the points.
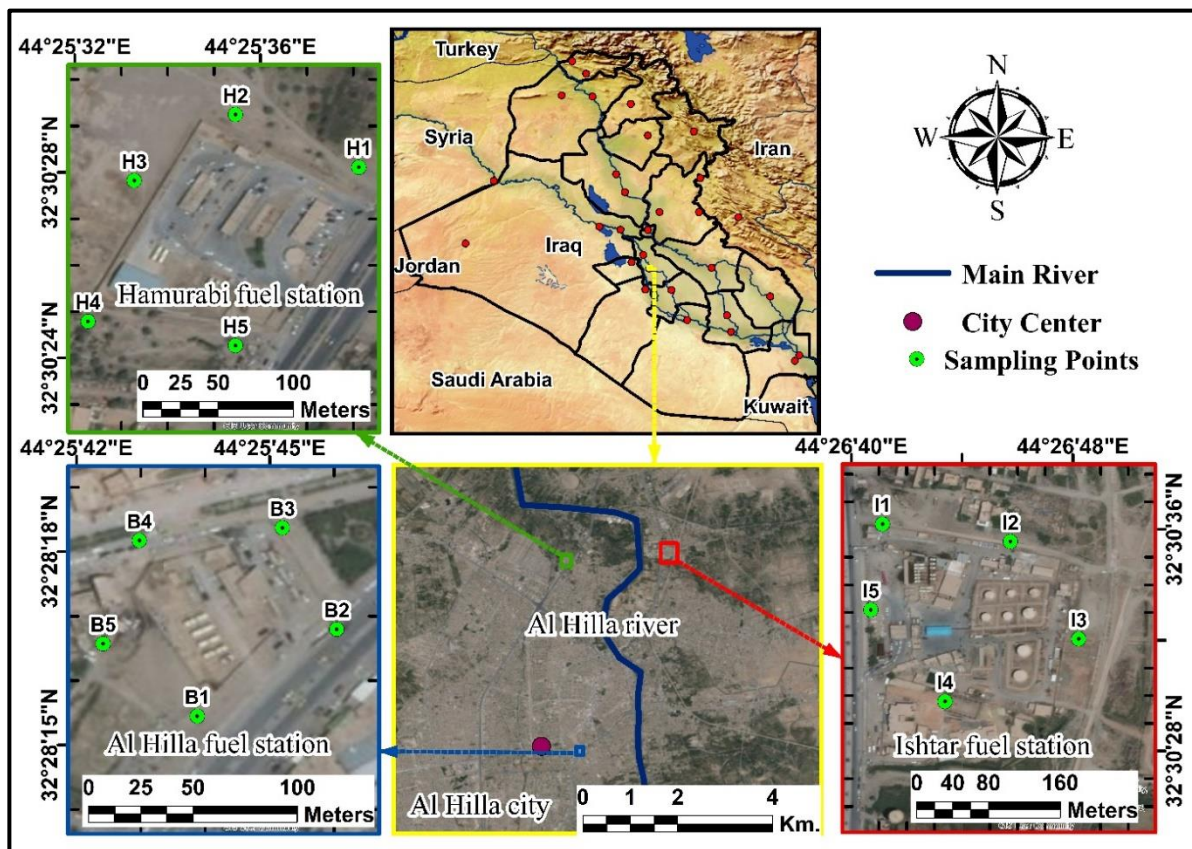

Figure 1. The location of the studied areas and sampling points

2. Materials and methods.

2.1 Sampling

In December 2018, five soil samples were taken randomly in each fuel station by selecting a suitable sampling sites with in distance not less than 50 meters from each one and from the centre of the station, after cleaning the surface debris first samples were collected from a depth of about 10 cm from the surface in the areas near (Bab-Almashhad), (Ishtar) and (Hamurabi) fuel stations, also, samples were kept in a glass containers washed with distilled water, after that the samples were passed through a 0.15 mm nylon sieve after grounding with an automated marble mortar, the fine fraction collected was stored in clean, dry and clearly labelled sample bottle.[15][16][17]

2.2 Preparation of specimens

A 1 gram digital balance measured soil samples were dried in an Oven, VEB-MLW Labortechnik ILMENAU, for 30 min. for each measured element at a temperature between 40 and 105 Cº depending on the water content , then the samples was digested using a mixture of concentrated hydrochloric and nitric acid that was added to the samples with great caution[18][16], after that a hotplate approach was conducted on the samples, the samples wat put in a hot plate and covered with a wet glass to reduce the rate of evaporation Figure 1, three replicants for each element for each sample were made, the digestion method often took up to two hours with the temperature just above the boiling point of the two acids.

Once cooled the digested samples were diluted with ultra-pure water to a volumetric glass washing out all the beaker content for quantitative transfer purpose, then the mixture was filtered, and the filtrate was calibrated and taken for the measurement of the desired elements.

Figure 2. putting the samples on the hot plate for digestion process

2.3 Measuring metal content

Flame atomic absorption spectrophotometer apparatus (Buck scientific 210 spectrophotometer) Figure 2, was used to measure the concentration of heavy metals in the specimens, after making the calibration graphs, three samples were taken for each element and the average concentration result is shown in the coming tables.
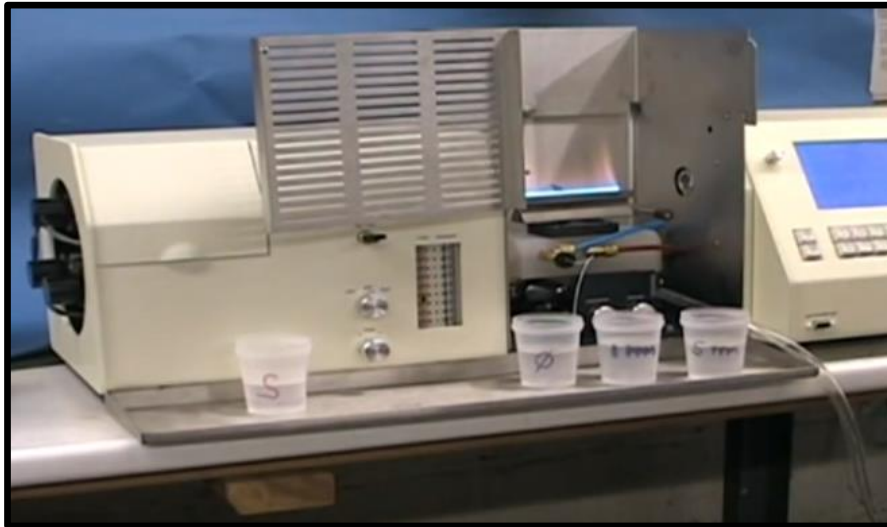
Figure 3. Atomic adsorption apparatus (Buck scientific 210)

3. Results.

The obtained concentrations shown in Tables 1-3 are all below the average shale concentrations [13][19][20] except that for lead.

Table 1. Heavy metals concentration in the soil near (Al Hilla fuel station) (ppm)

Sampling station No.	Pb	Ni	Zn	Mn	Fe
B1	25.2	35.6	32.8	26.4	44.8
B2	28.6	34.2	33.2	22.6	45.6
B3	22.8	30.2	35.8	25.3	48.1
B4	23.8	31.8	48.5	24.7	46.2
B5	26.7	33.4	41.2	24.5	43.5
Average conc. in shale	20	68	95	850	47200

Table 2. Heavy metals concentration in the soil near (Ishtar) fuel station (ppm)

Sampling station No.	Pb	Ni	Zn	Mn	Fe
I1	23.5	30.5	25.3	28.6	45.6
I2	24.6	31.8	26.8	27.9	42.5
I3	26.7	33.5	27.8	28.4	46.8
I4	23.5	35.6	28.5	26.5	45.9
I5	22.8	38.2	28.6	29.1	44.2
Average conc. in shale	20	68	95	850	47200

From the previously mentioned Tables, it is obvious that the results of the concentration of Pb are very high in all three fuel stations compared with the average value in earth shale, while Fe and Mn are extremely low, also, the measured concentrations of Zn and Ni are approximately quarter and half the average concentration in earth shale respectively.

In Table (4) the average amount of heavy metals and the three fuel stationed were calculated, to maintain a clear idea about the correlation between the different metal concentrations, Figure 3 is a graphical representation of the five measured heavy metals, and emphasise the fact that lead have values more than that should be available in average sedimentary earth shale soils.

Table 3. Heavy metals concentrations in the soil near (Hamurabi) fuel station (ppm)

Sampling station No.	Pb	Ni	Zn	Mn	Fe
H1	29.1	38.2	38.7	63.2	43.5
H2	24.8	37.5	37.6	63.5	43.6
H3	25.9	37.4	34.5	63.4	45.8
H4	26.3	37.5	33.2	62.8	44.5
H5	27.8	34.5	33.8	63.4	43.7
Average conc. in shale	20	68	95	850	47200

Table 4. The average concentrations of heavy metals in the soil around the fuel stations (ppm)

Fuel station	Pb	Ni	Zn	Mn	Fe
Al Hilla fuel station	25.42	82.6	95.75	61.75	114.1
Ishtar	24.22	84.8	68.5	70.25	112.5
Hamurabi	26.78	92.55	88.9	158.15	110.55
Overall average	25.47	86.65	84.38	96.71	112.38
Average conc. in shale	20	68	95	850	47200
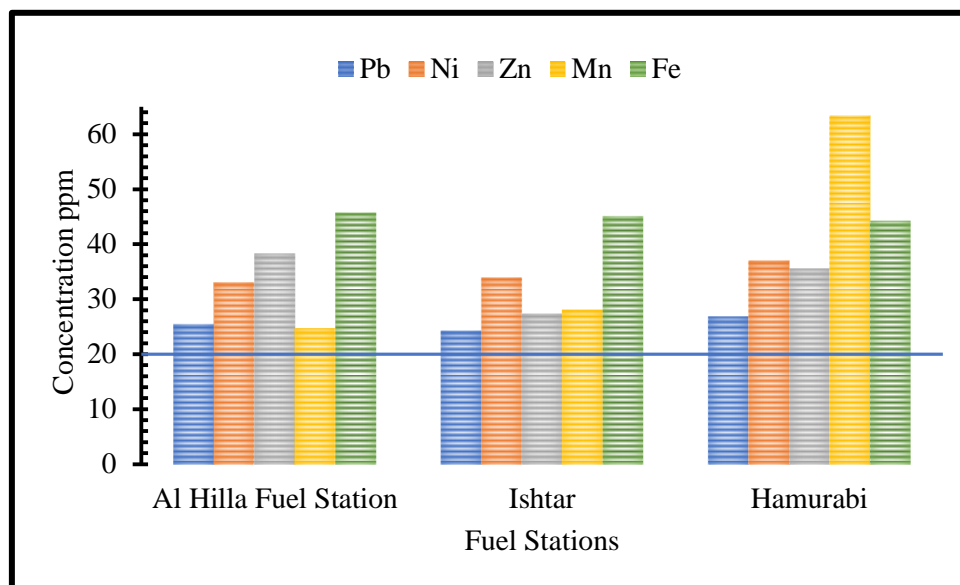
Figure 4. measured heavy metals in the three fuel stations

4. Discussion

It has been shown clearly from Tables (2-4) that the pollution levels of the studied elements in soils except Pb are all considered below the average shale concentration, this may be referred to the use of leaded fuel which may cause severe pollution problems when emitted from vehicles and generator exhaust systems, as well as, the pollution that comes from spillage and leakage from the fuel stations, affecting the nearby soil in the studied areas.[21]

Table 5. shows the moderate positive correlation coefficients between Pb and Ni, which means that since they come from the same pollution source, the increment in a metal concentration will lead to an increment in the other, and that what was clearly noticed in all three fuel station,

whenever there is an increase in Pb concentration there is an increase in Ni value in accommodation with it.

Table 5. the correlation coefficient between heavy metals

	Pb	Zn	Ni	Fe
Zn	-0.06809	---	---	---
Ni	0.37646	-0.31411	---	---
Fe	-0.62978	0.11754	0.21734	---
Mn	-0.64324	0.31164	-0.01172	0.47322

I the other hand, the study revealed that there is an adverse correlation between Pb and the two metals Fe and Mn, and that may be the reason behind the extreme negative difference between those two metals and the average value of them.

From all above, we can conclude from the results of the heavy metal concentrations and the correlation between them, that the concentration of Fe is far away from that it should be in the crust, we can say that the fuel stations have no effect on it.

From other hand, Mn concentration is also less than the average value in shale, which means that the presence of fuel stations have no effect on the metal concentration in the nearby soil, but it was noticed that the metal concentration in Hammurabi fuel station nearby samples was a little bit more than the other ones, and that may be connected to the significant role of Mn in soil health[22], as some times Mn plays an oxidant agent to Arsenic (As) and Chromium (Cr), although, further investigation on the last two mentioned metals should be carried out near by the three fuel station , to reveal their connection to Mn.

Also, Zn and Ni concentration values were almost as the same as the average shale value, and since these two metals are correlated to industrial activities, especially stainless-steel production[14], [23], it seems that the presence of the fuel stations have no impact on their concentrations in adjacent surface soils.

From other hand, the concentration of Pb was slightly above the average concentration in all three sites, which means that there is a direct effect for that rise from the fuel station in that area. The main reason behind that slightly elevated concentration of Pb is the use of tetraethyllead as fuel enhancer to reduce cracking noise in gasoline engines and that method is considered out dated and forbidden in many developed countries for its hazardous effect on the ecosystem[8], [12]

5. Recommendations.

Considering the research results with the discussion made on heavy metal concentrations, it is recommended that strict regulations on fuel handling and transportation should be endorsed legally to protect the surrounding environment, moreover, regulations should be amended to forbid the use of environmentally hazardous substances, such as tetraethyllead, as fuel enhancers and start to use alternatives substances that have no effect on the environment.

Also, great efforts on rising environmental awareness about the toxic and damaging effect of heavy metals to the ecosystem that might be generated from fuel combustion should be spend by the government organizations to incite people to be more careful by monitoring their vehicle and machines emissions regularly.

Further researches on the patterns by which heavy metals are distributed around fuel stations, especially Pb, should be conducted for the purpose of preventing further dispersion, also a heavy metal phytoremediation plants are suggested to be used for soil remediation process, and also an investigations on the Arsenic and Chromium concentrations in the soil around the stations should be curried out to find its connection to the declined Mn concertation.

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