Study of the Contamination of Soils Irrigated from Diwaniyah River with Lead / Iraq

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Abstract
This study was conducted to find out the effect of adding different pollutants (sewage water, liquid industrial water and heavy water) throwing into the river in Diwaniyah governorate on the concentration of Lead in river water and the effect of irrigation on the presence of this element in the soils during the different seasons of the year.

Soil samples were taken for two dimensions, the first at a distance of 100-150 meters from the source of pollution and for three depths, the first depth 0-30 cm, the second depth 30-60 cm, the third depth 60-90 cm, and the second dimension samples were taken at a distance of 5-5.5 km from the same source and also for three depths and three iterations for all sites and during four seasons: summer (July) 2019, autumn (October) 2019, winter (January) 2020, spring (April) 2020 with three locations, the first site is located at the entrance of Diwaniyah city (Sania area), which represents the control treatment as it is located before the various pollution ports that flow into the river (such as sewage, hospital waste, factory waste, sewage ... etc) and the second site in the city center (Rifaat quarter) and the third site in the (Sudair area), which represents the last site of the Diwaniyah city after the end of all estuaries and sources of pollution.

The results of the study were reached that the soil contamination with Lead was highest in the surface layer compared to the other of the depths, and the first dimension (100-150) m from the source of pollution is the highest compared with the second dimension (5-5.5) km, this indicated to a decrease in Lead concentration while moving away from the source of pollution.

The highest concentration of Lead in the summer was 3.11 micrograms.Kg⁻¹ in the first depth of the third site at a distance of (100-150) m, while the lowest concentration in the winter was 0.22 micrograms.Kg⁻¹.

At the third depth of the first site at a distance (5-5.5) km, this indicates that Lead contamination of soils is highest in the surface layer and increases with the slope of the river, and the concentration of Lead was decreasing with depth in all four seasons of the year and for all studied sites.

1. Introduction
Soil is an important environmental medium and is vulnerable to a number of pollutants, including heavy elements that are toxic by various human and natural activities. Therefore, soils contaminated with heavy elements have health risks for humans and other organisms in the ecosystem and have various methods of exposure to the organism such as direct swallow, contamination of drinking water. Edible crops, contact with contaminated soil and through the food chain [1]. Soil represents the final destination of the materials that are throwing into the environment from various human activities, whether they are organic or mineral pollutants, which accumulate in the soil due to its physicochemical properties, which causes dangerous problems for the environment in general, these substances affected to the chemical and physical balance of the soil and enter the food chain and reach to the human During the bioaccumulation process. When pollutant concentrations reaches higher values than the standard values specified in water, air and soil, which are described as a pollutant [2].

The total content of heavy elements in the soil expresses the sum of the concentrations of elements derived from minerals and geological origin materials in developed soils from the stone origin and the inputs from the wide range of sources of polluting human activities and includes air precipitates of airborne particles (Diameter less than 30 μm), container raindrops on heavy elements or in the form of gases for heavy elements, direct additions to agricultural fertilizers, whether they are mineral or organic (animal or vegetable), heavy water, food waste, remnants of industrial materials such as ashes, mine and mining residues and military projectiles, all of these can be polluted in the soil. So, the total concentration of heavy elements in soils is the sum of all those various inputs minus lost through pasture plants or harvested plants, erosion of soil particles through wind or water and washing down to the bottom of the soil and the lost through evaporation in the form of elemental gases [3]. Heavy elements are among the most dangerous substances thrown into the soil and their danger is centre on remaining in the soil for a long period of time without decomposing or undergoing any chemical changes. As a result of their presence in agricultural soils, they not only affect the growth of plants, but rather they pollute the grains and fruits that humans eat. [4].
Soil is the main source of the bio elements activity from plants and animals, also can be a source of heavy elements depending on their geological nature, and that the atmosphere can be a carrier of heavy elements in the form of gases or particles precipitates at different distances from their source. As for plants, they have a natural ability to accumulation of heavy elements and nutrients derived from soil, water and air are often used as bio indicators in monitoring heavy metals pollution [5].

Based on the above, the research aimed to study the effect of adding various pollutants (sewage and industrial water) on the concentration of Lead in the four seasons of the soils of Diwaniyah Governorate / Iraq.

2. Materials and Methods

The study area was chosen as three sites were identified on the Diwaniyah river for the purpose of taking water samples. The first site is in the Sania area, which represents the control treatment as it is located before the various pollution outlets that flow into the river and from different sources (such as sewage, hospital waste, factory waste ...... etc.).

The second site in the Rifaat quarter that represents the city center, and the third site is near the administrative boundaries of the Sudair district, which represents the last site of the Diwaniyah city after the end of all estuaries and sources of pollution. Soil samples were taken for the aforementioned sites and for two dimensions for each site, which are the first dimension (100-150 m) and the second dimension (5000-5500m) as a profile for each site and for each of the two dimensions above, by 6 profiles, were dug, and each profile contains 3 depths, for the same periods, the timings are summer (July) 2019, autumn (October) 2019, winter (January) 2020, and spring season (April) 2020.

After the soil transported to the laboratory, it was air dried in the laboratory and milled with a wooden hammer and passed through a sieve with a hole of 2 mm diameter and placed in polyethylene bags especially for preserving the samples on which the study area was fixed and the season in which the samples were taken and the depth which the samples were taken for the purpose of conducting laboratory analyzes as shown in Table (1).

2.1. Physical analyzes

2.1.1. Volumetric distribution of soil separators

The size distribution of the soil separators was estimated by the hydrometer method described in [6] to determine the proportions of the soil separators, as the weight of the separators (sand, silt, clay) was calculated, after the binders were removed from the carbonate minerals by adding acidified sodium acetate at pH=5, and the organic matter by hydrogen peroxide H2O2 at a concentration of 30%, with the addition of the dispersant, Sodium hexa meta phosphate, for the purpose of dispersing these separations.

2.1.2. Bulk Density

The bulk density was estimated using the Core Sample described in (6).

2.2. Chemical analyzes

2.2.1. The degree of soil reaction (pH)

The degree of soil reaction was measured by making an extract (1: 1) soil: water with a type WTW pH meter, according to what was mentioned in [7].

2.2.2. Electrical Conductivity (EC)

Soil electrical conductivity was measured in a soil extract: water (1: 1) by using the EC-meter WTW, according to [7].

2.2.3. Cation exchange capacitance (CEC):

The cation exchange capacity of the cationic ions was estimated using aluminum acetate and sodium acetate as reported in [6].

2.2.4. Carbonate minerals

It was estimated by equating it with (1N) of HCL and back titration with 1N of NaOH, as reported in the method of [7].

2.2.5. Organic matter

The organic matter was estimated by (Wet Digestion) using 1N of potassium dichromate K2Cr2O7, according to the Walkly and Black method, mentioned in [6].

2.3. Soluble Cations and Anions

2.3.1. Calcium (Ca2+)

Calcium was determined by correcting it with farsinite (Na2-EDTA) using the Ammonium Parpuate reagent according to Lanyon and Heald's method reported in [7].

2.3.2. Magnesium (Mg2+)

It was estimated by estimating calcium and magnesium together by titration with farsinite (Na2-EDTA) using Erichrome Black T reagent, then subtracting calcium from total calcium and magnesium according to the method of Lanyon and Heald that mentioned in [7].

2.3.3. Sodium (Na+)

Measure the sodium by using a flame Photometer as reported in [8].
2.3.4. Potassium (K')
Potassium dissolved in a soil extract: water (1: 1) was determined by using the Flame Photometer as indicated in the method suggested by Knudsen et al that mentioned in [7].

2.3.5. Sulfates (SO$_4^{2-}$)
Sulfate was determined by precipitation method as barium sulfate according to [6].

2.3.6. Carbonate and bicarbonate HCO$_3^{-}$ and CO$_3^{2-}$
The bicarbonate was determined by the titration method with sulfuric acid (H$_2$SO$_4$) at a concentration of (0.01N) in the presence of orange methylation index according to the method mentioned in [8].

2.3.7. Chlorine (Cl$^-$(i)
The chloride was determined by titration it with silver nitrate (AgNO$_3$) at a concentration of (0.01N) in the presence of potassium chromate, according to the method mentioned in [8].

2.3.8. Estimation of elemental lead in soil
The ready Lead Pb were estimated from the soil by the chelating compound (DTPA) Diethylene triamine penta aceticacid, and the total Lead Pb were extracted from the soil according to [9] method, and all solutions were measured with an Atomic Absorption Spectrometer [10].

3. Results and Discussion

3.1. Lead concentration in the soils for the four seasons.
Table (2) shows the concentration of Lead in soil samples for the summer season. The results showed that the highest concentration of Lead was 3.11 micrograms / kg$^-$ in the first depth of the third site, 100 meters from the water sampling site, while the lowest concentration was 0.51 micrograms.Kg$^-$ in the third depth of the first site, the control treatment is 5km away from the site, this is agree with [11], found that high concentrations of Lead are present in the surface layers of the soil, as the results are agree with [12], who found the depth of the soil is an effect on the soil content of Lead, as the highest concentration of Lead was in the surface layers of study soils that were collected from different places of Basra governorate, and the estrangement from soil sites of Lead pollution had a positive effect in reducing the level of Lead pollution, and soils that near from sources of pollution were exposed to contamination with an element Lead, especially at the surface layers of the soil, and these percentages and ranges are exposed to increase and not decrease, as in Figure (1).

Table (3) shows the concentration of Lead element in soil samples for the autumn season. The results showed that the highest concentration of Lead was 2.40 micrograms kg$^{-1}$ in the first depth of the third site, 100 meters from the water sampling site, and the lowest concentration was 0.40 micrograms.Kg$^-$ at the third depth of the second site and 5 km away from the water site, and it was close to the third depth in the first site, the control treatment, which amounted to 0.45 g.Kg$^{-1}$ and at a distance of 5 km from the water sampling site (and this may be due to the variation in adding pollutants to the first site in previous periods, this is agreement with [13], who found that high concentrations of Lead are present in the surface layers of the soil (Figure 2) due to sewage residues, pesticides, litter, etc. and the concentration of Lead decreases with increasing soil depth. We find from the results that all values were low in this season compared with the summer season and for all the sites and depths studied. This may be due to the decrease in the pollutant values in the river water as a result of the increase in water emissions, which reduces the added concentrations.

Table (4) shows the concentration of the element Lead in soil samples for the winter season. The results showed that the highest concentration of Lead was 2.34 micrograms.Kg$^{-1}$ in the first depth of the third site, 100 meters away from the water sampling site, and the lowest concentration was 0.22 micrograms.Kg$^{-1}$ in the third depth of the first site is the control treatment and at a distance of 5 km from the water site. This is in agreement with what [14], the high concentrations of Lead are concentrated in the surface layers of soil due to the presence of organic matter at the surface horizon [15,16].

[12], also indicated that the depth of the soil has an effect on the soil content of Lead, as the highest concentration of Lead in the surface layers of the study soil reached Figure (3). The results also showed a decrease in the concentration of Lead in this season in all sites and horizons as a result of increased releases. Hydroponics and rain, which reduced its concentration in the soil, and its concentration was high in the second and third horizons of the second and third sites in the winter season and the second and third horizons from the third site in the autumn season, and this may be due to the increase in the contribution of ground water.

Table (5) shows the concentration of Lead element in soil samples for the spring season. The results showed that the highest concentration of Lead was 2.65 micrograms.Kg$^{-1}$ in the first depth of the third site, 100 meters away from the water sampling site, and the lowest concentration was 0.25 micrograms. Kg$^{-1}$ in the third depth of the first site, the control treatment is 100 meters away from the water sampling site, we find from the results that the element concentrations began to rise in this season as a result of the decrease in water emissions and the increase in consumption and water uses in all sites and horizons Figure (4) in general it was decreasing with the increase in the distance from the place where water samples were taken, this is in agreement with what [5] stated, that the total concentration of heavy elements in soils affected by the waste of industrial establishments was higher than the comparison soils, which generally indicates the effect of these facilities on environmental pollution. [12], showed that soil depth had an effect on its Lead content and was highest in the surface horizons.
Table 1. Some chemical and physical properties of the study soil.

|        | Third depth | Second depth | First depth |
|--------|-------------|--------------|-------------|
| -      | 5.5-5.5 km  | 100-150m     | 5.5-5.5 km  | 100-150m     | 5.5-5.5 km  | 100-150m     |
| pH     | 7.99      | 8.12        | 7.94        | 8.12        | 7.98        | 8.04        |
| EC     | 39.44     | 0.986       | 0.950       | 0.891       | 0.986       | 0.831       |
| CEC    | 23.96     | 2.293       | 2.197       | 2.397       | 2.580       | 2.173       |
| Cations |           |             |             |             |             |             |
| Ca²⁺   | 0.565     | 0.341       | 0.302       | 0.564       | 0.589       | 0.47       |
| Mg²⁺   | 0.855     | 0.468       | 0.398       | 0.726       | 0.815       | 0.813       |
| Na⁺    | 1.470     | 1.071       | 0.642       | 1.386       | 5.104       | 1.743       |
| K⁺     | 1.833     | 0.851       | 1.522       | 0.958       | 2.552       | 1.845       |
| Anions  |           |             |             |             |             |             |
| Cl⁻    | 4.986     | 4.56        | 3.490       | 5.983       | 6.282       | 6.183       |
| SO₄²⁻  | 0.242     | 0.238       | 0.219       | 0.217       | 0.217       | 0.217       |
| CO₃⁻   | Nil       | Nil         | Nil         | Nil         | Nil         | Nil         |
| HCO₃⁻  | 0.155     | 0.145       | 0.134       | 0.134       | 0.134       | 0.134       |
| Bulk density | 1.49 | 1.51 | 1.38 | 1.37 | 1.43 | 1.38 |
| Texture | Lomy sand | Lomy sand | Lomy sand | Lomy sand | Lomy sand | Lomy sand |
| Soil isolated | 8129.81 | 8179.95 | 8323.48 | 8245.87 | 8300.82 | 8410.71 |

Table 2. Concentration of elemental Lead in soil samples for the summer season (July) (microgram.Kg⁻¹).

| Concentration | Depth | Distance | Site |
|---------------|-------|----------|------|
| 2.28          | First depth | 100m | First site |
| 1.80          | Second depth | 5km | Second site |
| 0.80          | Third depth | 100m | Second site |
| 1.15          | First depth | 5km | Second site |
| 0.91          | Second depth | 100m | Second site |
| 0.51          | Third depth | 5km | Second site |
| 2.78          | First depth | 5km | Second site |
| 2.02          | Second depth | 100m | Second site |
| 0.86          | Third depth | 5km | Second site |
| 1.30          | First depth | 5km | Second site |
| 1.01          | Second depth | 5km | Second site |
| 0.90          | Third depth | 5km | Second site |
Figure 1. Concentration of Lead element in soil samples in summer season (µg.kg⁻¹).

Table 3. Concentration of elemental Lead in soil samples for the autumn season (October) (micrograms.kg⁻¹).

| Concentration | Depth   | Distance | Site         |
|---------------|---------|----------|--------------|
| 1.90          | First depth |          |              |
| 1.21          | Second depth | 100m   |              |
| 0.69          | Third depth  |        | First site   |
| 1.02          | First depth  |        |              |
| 0.78          | Second depth | 5km   |              |
| 0.45          | Third depth  |        |              |
| 2.25          | First depth  |        |              |
| 1.83          | Second depth | 100m |              |
| 0.71          | Third depth  |        | Second site  |
| 0.87          | First depth  |        |              |
| 0.65          | Second depth | 5km  |              |
| 0.40          | Third depth  |        |              |
| 2.40          | First depth  |        |              |
| 1.89          | Second depth | 100m | Third site   |
| 0.78          | Third depth  |        |              |
Table 4. Concentration of elemental lead in soil samples for the winter season (January) (g.Kg\(^{-1}\)).

| Concentration | Depth    | Distance | Site      |
|---------------|----------|----------|-----------|
| 1.19          | First    | 100m     | First site|
| 0.54          | Second   |          | First site|
| 0.23          | Third    | 5km      | First site|
| 0.99          | First    | 5km      | First site|
| 0.43          | Second   | 100m     | Second site|
| 0.22          | Third    |          | Second site|
| 2.23          | First    |          | Second site|
| 0.99          | Second   | 100m     | Third site|
| 0.27          | Third    |          | Third site|
| 0.72          | First    |          | Third site|
| 0.55          | Second   | 5km      | Third site|
| 0.34          | Third    |          | Third site|
| 2.34          | First    |          | Third site|
| 1.16          | Second   | 100m     | Third site|
| 0.43          | Third    | 5km      | Third site|
| 0.81          | First    |          | Third site|
| 0.65          | Second   | 5km      | Third site|
| 0.37          | Third    |          | Third site|
| * 0.0958      | ---      | ---      | Value LSD |
Figure 3. Concentration of Lead element in soil samples for winter season (µg. Kg⁻¹).

Table 5. Shows the concentration of elemental lead in soil samples for the spring season (April) (µg. Kg⁻¹).

| Concentration | Depth     | Distance | Site         |
|---------------|-----------|----------|--------------|
| 1.55          | First depth| 100m     | First site   |
| 0.58          | Second depth| 5km     |              |
| 0.25          | Third depth|         |              |
| 1.04          | First depth|         |              |
| 0.47          | Second depth| 5km     | Second site  |
| 0.27          | Third depth|         |              |
| 2.44          | First depth|         |              |
| 1.32          | Second depth| 100m     |              |
| 0.33          | Third depth|         |              |
| 0.84          | First depth|         |              |
| 0.51          | Second depth| 5km     |              |
| 0.41          | Third depth|         |              |
| 2.65          | First depth|         | Third site   |
| 1.58          | Second depth| 100m     |              |
| 0.63          | Third depth|         |              |
| 0.87          | First depth|         |              |
| 0.68          | Second depth| 5km     |              |
| 0.41          | Third depth|         |              |

* 0.0938 --- --- Value LSD

Figure 4. Concentration of Lead element in soil samples for spring season (µg. Kg⁻¹).
References

[1] Soodan, R.K.; Y.B. Pakade; A. Nagpal and J.K. Katnoria. 2014. Analytical techniques for estimation of heavy metals in soil ecosystem: A tabulated review. Talanta, http://dx.doi.org/10.1016/j.talanta.02.033.

[2] Horta, C.G.; L. B. Casarrubias ; B. S. Ramirez ; M. C. Ishida; A. B.Hernandez ; D. G.Torres ; O. L. Zacarias ; R. J. Saunders ; Z. Drobra ;M. A. Mendez ; G. G. Vargas ; D. Loomis ; M. Styblo and L. M. Del Razo . 2015. A concurrent exposure to Arsenic and Fluoride from drinking water in Chihuahua, Mexico. Int. J. Environ. Res. Public Health, 12, 4587-4601.

[3] Alloway, B.J. 2013. Heavy metals in soils, Trace metals and metalloids in soils and their bioavailability, Third edition, Springer Dordrecht Heidelberg New York London. DOI 10.1007/978-94-007-4470-7.

[4] Ali, M.; M.I. Ali; S. Islam and Z. Rahman. 2016. Preliminary assessment of heavy metals in water and sediment of Karnaphuli River, Bangladesh, Environmental Nanotechnology, Monitoring & Management 5, 27-35.

[5] Farhan, Bassem Hussein 2020. Study of soil, water and plant pollution with some heavy elements from industrial wastes in Wasit governorate, PhD thesis, college of Agriculture - University of Baghdad.

[6] Black, C. A. (1965). Methods of soil analysis. part(1). physical properties. Am. Soc. Agron. Inc. publisher. Madison, Wisconsin, U.S.A.

[7] Dania Mohammed Danish Aladdin Sajadi, Akram Othman Esmail. (2020). Comparison Between Groundwater Quality at North East and South West of Erbil Governorate for Irrigation Using Some Global Systems and Principal Component Analysis. Al-Qadisiyah Journal For Agriculture Sciences, 10(2), 308-324.

[8] Jackson, M.L. 1958. Soil chemical analysis Prentice hall Inc. Englewood Cliffs, N.J.

[9] Jones , J. B. 2001. Laboratory guide for conducting Soil tests and Plant analysis /Includes bibliographical references and index CRC Press LLC.ISBN 0-8493-0206-4.

[10] Revision, 1992. Acid digestion of waters for total recoverable or dissolved metals for analysis by Flaa or Icp Spectroscopy . Method 3005A.

[11] Mihalievic . M.M. Zuna, V., Ettler .O . Sebek, L. Strand and V. Golias.2006. Lead fluxes, isotopic and concentration Profiles in apeat deposit near a lead smelter (Pribram, Czech Republic).Science of the Total Environment 372:334-344.

[12] Al-Halfi, Bidaa Allawi Hassan. 2010. Assessment of Lead pollution and behavior in some soils of Basra regions and its effect on the growth of yellow corn (Zea mays L.) at different levels of phosphate and organic fertilizer. Master thesis, College of Agriculture - University of Basra, Iraq.

[13] Mohammed, M.A. (2020). Structural, Optical, Electrical and Gas Sensor Properties of ZrO2 Thin Films prepared by Sol-Gel Technique. Neuroquantology, 18(3), 22-27. doi: 10.14704/nq.2020.18.3.nq20146

[14] Pichtel . J., K.Kuroiwa and H.T. Sawyerr. 2000. Distribution of Pb ,Cd, and Bain Soils and Plants of two contaminated Sites , Environ . Pollut .110:171-178.

[15] Yobouet  Y. A., Adouby K., Trokourey  A. and Y Ao B. 2010. Cadmium, Copper, Lead and Zinc speciation in contaminated Soils. International Journal of Engineering Science and Technology Vol.2 (5), p 802-812.

[16] Gismera , M. J.; J. Lacal ; P. Dasilva; R.Garcia ;M.T. Serilla and J.R.Procopio. 2004.Study of metal fraction in river Sediment. Acomparison between Kinetic and Sequential extraction Procedures. Environ . Pollut . 127: 175-182.