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# The Ability of Different Calcareous Soil Textures to Lead Fixation in The Northern Iraq

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**Abstract.** This study was carried out on some calcareous soils in Nineveh province north Iraqi, to evaluate the ability of calcareous soils to Lead retention using the fractionation technique. Six surface and sub-surface soil samples have been taken 5 meters from the main roads between Nineveh governorate and affiliated cities. In the same sites 75 meters away from the main roads six soil surface and sub-surface samples have been taken as a control. All soil samples were triplicated Freundlich and Langmuir equations were applied to determine the maximum loading capacity for lead. Studied soils classified under Aridosol Calciorthids with slightly alkaline and low organic matter content. Results showed that Pb concentration increased by about (43.27%) near road sites compare to control surface soil because of car exhausts. While lead concentrations in sub-surface soil at depth (20 cm) for both sites were without any significant differences. The physochemical pathway of the lead distribution in calcareous conditions showed the following order: - Solid carbonates <Separates< Free oxides <Organic matter< available forms. It is clear that carbonate minerals in calcareous soils are regarded as a good lead resiviour with significantly related adsorption (R2=96).

**Keywords:** Calcareous Soil; Fractionation; Lead; Soil Fertility; Sustainable Agriculture.

## 1. INTRODUCTION

Emission of road and highway traffic is responsible for many heavy metals spread near highways and roads (1). Automobil and vehicle exhaust discharge could have significantly contributed to the deposition of heavy metals along the road (2). Heavy metal concentration and contamination level along roads depend on different factors such as site age, traffic density, automobile fuel nature, and some parameters influencing pollutant accumulation (3). High and/or medium traffic volume may impact more heavy metals on the soils, such as Cd, Cr, Zn, Cu, and Ni, but Pb is the most common pollutant that exists in surface soil among them (4). Lead is a heavy element that causes different inorganic chemical hazards for humans and ecosystems via soil and plant contamination, drinking contaminated groundwater, and the food chain (5). In order to prevent degradation and lead contamination of soils, adequate protection and restoration of contaminated soil ecosystems are required, which requires the characterization of contemporary legislation and respect for and protection of the environment and public health at the national and international levels (6). The characterization of soil lead gives insight into the state of the accumulated element and its bioavailability and remedies for contaminated soil by detecting the source of its contamination to maintain public health and the ecosystem (7). Heavy metals and metalloids penetrate agricultural ecosystems through natural and human processes. Some soils have a high ground content for some minor elements, some of which are toxic to plants and wildlife. This is due to the high concentrations of these

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elements in the soil's matrix. Human processes include the introduction of heavy metals through the use of chemical fertilizers, organic materials, and industrial and municipal waste. These processes contribute to the development of varying amounts of heavy metals in the agricultural environment (8). Only a small fraction of heavy metals and metalloids in the soil have an effect on biological activities. The movement of these pollutants is controlled by many chemical and biochemical processes, such as (dissolution, deposition, adsorption, desorption, complex formation, decomposition, oxidation, and reduction reactions). Not all of these processes are of equal importance to each element, but all are influenced by the degree of soil interaction and biological processes. Measuring the total content of these elements alone is not a good measure of biological readiness. Still, it is useful to quantify the pollutants and their environmental effort and human health risks. The total content in soils is a weak indicator of the toxicity of the element when this element is distributed over the different phases of the soil (9). The diagnosis and quantification of metals associated with soil phases or their constituents within the concept of fraction analysis give an idea about the heavy metals distribution in the solid phase in soil (10).Indicate that the average content of soil total lead is (16 mg. Kg-1) and that the content of calcareous soils is between (3 -10 mg. Kg -1) (11). The arrival of lead to the soil surface is distributed in its liquid and solid phases. The part associated with the solid phase is distributed to the mineral and organic soils depending on the interaction of this element with other components of the soil environment (12). These reactions have been identified by (5) in the following ways: dissolution, adsorption, complexity, migration, sedimentation, surface contamination, diffusion within metals, correlation with organic compounds, microbial adsorption, volatilization, and all these processes are controlled by the physiochemical properties of the soil. The main sites for the binding of lead with oxygen-containing active groups in organic matter are carboxylic and phenolic groups which are formed with lead chalets of different stability depending on the same element. In order to understand the interactions of this element in the soil and its transformations, measuring the total content of lead soil is a weak indicator of the toxicity of this element when it is taken into consideration that this element is distributed over the different solid phases of the soil. The indication of the readiness and movement of the element within the soil phases. (13) give the diagnosis and identification of the ion associated with the soil phases or their constituents called fraction analysis, through the use of successive extraction of a number of chemical extracts. This technique will provide us with accurate information about the movement and proliferation of heavy elements and their fate in the soil. Water extraction, solution extraction (DTPA), and mutual phase extraction include the portion associated with organic matter and extraction segment associated with the

carbonate minerals and extract the associated sand and silt that these conclusions successive will appear behavior of physiochemistry to distribute the total content in the soil and also explains the dynamics of the heavy element link components of soil. The aim of this study is to predict the distribution and fate of lead and evaluate calcium carbonate's ability to lead retention in some calcareous soil environments in Iraq using the fractionation technic.

## 2. MATERIALS AND METHODS

### Study area and samples collection

The roads that connect Nineveh Governorate and some of its affiliated cities are shown in (Table 1, Figure 1). In every studied location, we choose two sites, the first contaminated site is 5 meters away from roads and the second site represents control soil far 75 meters from the main roads. For every site, six surface and sub-surface (20cm depth) representative samples have been collected. Samples were dried, crushed, and passed through a 2 mm sieve, then the chemical and physical analyses were conducted. Soils belong to Haplocalcids, Vertic Haplo Calcids, according to (14). Chemical and physical characteristics were determined according to the methods of soil analysis. Also, soil textures were determined, organic matter by dichromate oxidation, and cation exchange capacity by treating soil with neutral 1N NH4OAC and 1N NH4OANa. (15,16,17). Electrical Conductivity (EC) (18) and soil (pH) were measured using 1:2.5 soil-to-water suspension (19,20) (Table 2). A paired t-test was used to compare the probability levels of 0.01 and 0.05 (21).

**Table 1.** The Coordinates of The Soil Sampling Locations In The Study Areas Using GPS.

| No. | Locations of soils in Mosul | | E (Longitude) | N (Latitude) |
|---|---|---|---|---|
| 1 | North | Nineveh Forests | 43.125403° | 36.361244° |
| 2 | | Alqiba | 43.034137° | 36.420108° |
| 3 | Northeast | Bieshiqa | 43.231027° | 36.547680° |
| 4 | | Alshilalat | 43.194889° | 36.455241° |
| 5 | East | Alqasr | 43.234571° | 36.220904° |
| 6 | West | Hamidat | 36.406012° | 42.976952° |

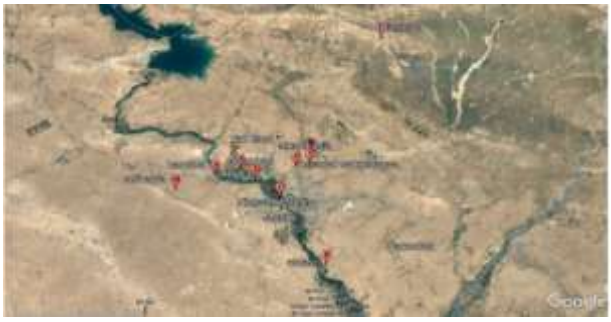

**Figure 1.** Soil Sampling Locations In Mosul, Iraq.

**Fractionation of total lead content:**

The total lead content has been fractionated using sequential extraction in order to identify the nature of the distribution of lead within the liquid and solid phase, linked to carbonate minerals, linked within the organic matter, iron oxides and linked within the soil grains according to the following context: -

Carbonate content: Soils were extracted using diluted hydrochloric acid (0.1) molar until the disappearance of burs and furans as evidence of the removal of carbonate minerals (22).

Associated with amorphous iron oxides: The lead part associated with amorphous iron oxides were extracted using a mixture solution of 0.25 M NH2OH.HCl + 0.25M HCl) (5: 50) (ie: solution: soil) with shaking for (23) minutes and heating in a water bath at a temperature of 50 ° C. The concentration of lead was estimated in the filtrate using the atomic absorption apparatus according to the method described in (23).

Organic matter content: After completion of the previous paragraph soils were treated with hydrogen peroxide (H2O2) until the color of the sample becomes pale (24).

Available content: Were obtained by using (DTPA) solution (0.005) molar and (0.1) molar Tri ethanol amine (TEA) with extraction ratio 2:1 (solution: soil) according to (25) method.

Residual content (sand, silt, clay): After the completion of the previous stage mentioned above soil samples were taken to the mechanical separation of sand was carried out using a sieve (50) micron clay and silt separated by the method of sedimentation and pouring, then each digested separately using the wet digestion method.

Sorption isotherm: In order to determine the maximum load capacity of studied soils, adsorption experiment was carried out in a plastic stoppered tube with 50 ml volume. Sorption isotherms for the lowest and highest calcium carbonate Soils were obtained by equilibrating (2 gm) Soil with (40ml) of lead solutions containing 5,10,20,40, 60, and 100 mg. L-1. Solutions were prepared using (Pb (NO3)2). Soil suspensions were shaken for 2 hours and allowed to dynamically equilibrate for 24 hours at room temperature (273k°). Suspensions were centrifuged and adsorbed lead in equilibration solutions were measured. Adsorbed Lead was calculated with the following equation:

SM= Cin-Cfi *V / W ……. (i)

Where (SM) is the amount of adsorbed metal mg. Kg-1. (Cin) is the initial metal Concentration in equilibrium Solution mg. L-1. (Cfi) is the final metal concentration in the

equilibrated solution after 24 hours., (W) is the weight of Soil (2gm). And (V) is the Volume of Solution (40ml).

Sorption parameters evaluation. Langmuir and Freundlich's equations were applied to evaluate Lead adsorption.

The logarithmic Freundlich equation is defined as follows.

logq= log kf +n logCe

Where:

(kF) is the Freundlich distribution coefficient

L.gm-1. (n) is a constant that has a value of less than (1).

And (Ce) is the metal concentration in equilibrated

Solution mg. L-1.

Straight line of the Langmuir equation was applied to evaluate Soils maximum adsorption capacity:

1/qx= 1/qmax KCe +1/qmax

Were. (qx) is the adsorbate concentration per unit of mass adsorbent µg.gm-1

(K) is the binding energy with unit L.gm-1.

(qmax) is the adsorption maximum. And (Ce) is the adsorbate equilibrium

Concentration mg. L-1

Lead in the solutions and extracts in the above solutions were measured using a GBC 933 plus atomic absorption device.

## 3. RESULTS AND DISCUSSION

Physochemical properties of the studied soil: -

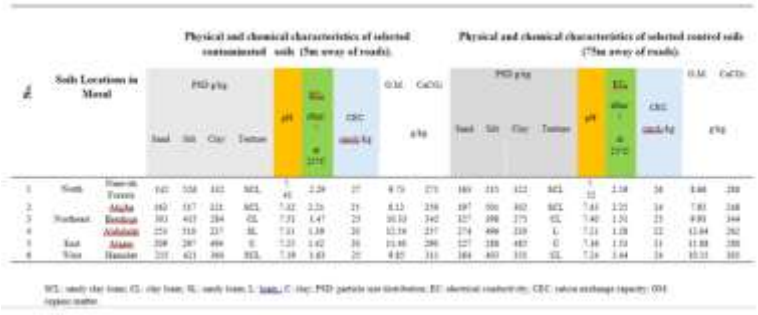

**Figure 2.** Physical And Chemical Characteristics Of Selected Soils.

Table (2) showed that the maximum value of carbonate minerals was (342) g. Kg-1, compared to the lowest value (257) g. Kg-1. The electrical conductivity values ranged between (1.39 -2.29 dScm-1). Soil pH ranges (7.11- 7.51) and high pH values of arid and semi-arid

regions, including Iraq, are due to high quantities of carbonate minerals. Carbonates have the regulatory capacity to resist changes in pH in those soils (26). Organic matter ranged between (8.12-12.54) g. Kg-1 and cation exchange capacity ranged between (20-27) Cmmolc kg-1.This is due to the difference in the low content of the organic matter and the clay content of studied soil, which is within the arid and semi-arid regions and characterized by the prevailing environmental conditions that increase in the annual temperature which increases the effectiveness of microorganisms that decompose organic matter as well as lack of moisture in the soil, as well as the lack of precipitation that does not lead to the formation of good vegetation helps to enhance organic soil (27).

These results indicate that studied soils were either basal or basal-alkaline, and may be due to factors and processes that in turn (28). Control soils. (75m away of roads) showed the same characteristics with few differences compared to polluted soils contaminated because it is affected by the same site conditions.

The successive extraction technique is used widely to predict the distribution and the fate of any element in Soil components and to provide accurate information about heavy metal migration through the soil profile. This technique also provides information about the heavy metal binding force with the solid soil phase. Table (3) shows the details of the successive extraction of studied soils.

**DTPA extraction**

This part expresses the formula contained in the aqueous solution balanced with the solid phase and its importance is that it reflects the potential of transition or ion migration (Potential Ion Migration) This extraction expresses the mobile fraction of lead ions in the soil and also expresses the formula on colloidal surfaces (clays and organic matter) that is in equilibrium with the liquid soil phase and its importance is that it expresses the potential Ion Migration of these ions towards the aqueous solution.

Figure (2) shows the values of lead extracted (0.005 molar DTPA) represented the extracted water-soluble and exchanged the lead on the surfaces of the solid phase sites, which ranged between (2.22 to 4.15) with a mean (3.11) mg. Kg-1 for control soil ranged between (5.28 to 7.65) with a mean (6.45) mg. Kg-1 contaminated soils.

The results obtained are in line with those obtained by (29). This can be explained by the fact that very small amounts of lead ions can be found in the solution at pH (7- 6) due to their high adsorption on the surfaces of different soil components.

This supports the hypothesis that sequence extraction doesn't begin with soluble ion extraction because a negligent amount of extracted ion will release, furthermore, the prevalence

of sedimentation in calcareous soil conditions and soluble yield values reduction for these elements compounds in the soil help to make these quantities very low (26).

**Organic Matter Extraction**

This extract solution breaks down the organic matter and releases all associated ions with organic matter, including lead. The results showed that the content of the studied soils, organic matter was low compared to the other component's content. However, this did not negate its role in the retention of lead ions, but this article has shown a high affinity to lead retention. Figure (3) shows the part of lead-related to organic matter and ranged between (0.98 to 3.51) with a mean (2.11) mg. Kg-1for control soil and ranged between (3.65 to5.67) with a mean (4.74) mg. Kg-1 incontaminatedsoils.

These results reflect the significant role of organic matter in the adsorption and retention of lead ions with high affinity. The high affinity shown by organic matter in the adsorption of heavy metal ions, including lead, may be due to the affinity and high preference of that material for metal cation ions, especially binary ones M+2 (30), as a result of its high qualitative surface. It has a high positive ion exchange capacity (150-300 Cmol.kg-1) (28).

This can be attributed to the variation in the effect of the surrounding conditions in the organic matter, moisture, reaction number, (C / N) percentage of the decomposing material , quantity and quality of clay are factors that influence the degree of degradation of the organic matter. Sometime the occurrence of overlaps between organic colloids and mineral colloids in the soil can be explained by two assumptions:- First: the sovereignty of montmorillonite in the soil can reduce the process of biodegradation of organic matter (12), Second, the formation of bonds or overlaps between organic colloids and mineral colloids (clay and oxide colloids) are soluble and insoluble with heavy elements which depend on the degree of medium reaction and the structural properties of the organic part causes the closure of available sites of exchange existing on colloids surfaces, leading to variation in values of exchange capacity of the positive ions of these colloids. The adsorption of the organic matter of the metal can be interpreted as an ion exchange process between hydrogen and metal on the surfaces of the active acidic groups (L) (31), as shown by the following equation.

$$Mx+ + >LHy = >L\text{-}M\ (x\text{-}y) + + yH+ \quad \text{(ii)}$$

Metal correlation with the active groups of organic matter will lead to the formation of inner-sphere complexes at pH (5.0) with covalent and ionic bonds. While low-priority metals tend to retain hydrophilic coating and remain interchangeable on organic soil material (32).

Retention of heavy element ions on charged organic surfaces (resulting from dissociation) and ionization of carboxylates and functional phenols fluids arise at pH> 6 and

be most severe at neutral conditions of pH 7-7.5 (33). The heterogeneous concentration of lead ions from one component to another depends mainly on the amount of this pollutant added to the ecosystems (28), as well as the physical, chemical, and biological conditions of the surrounding environment, especially the organic and inorganic protons and ions produced by plant roots and their effects change on medium reaction value.

**Oxides Extraction**

As shown in table (2) and figure (4) that the values of lead associated with oxides ranged between (3.17 - 5.21) with a mean (3.91) mg. Kg – 1 for control soil and ranged between (5.76 - 7.85) with a mean (6.95) mg. Kg-1 contaminated soils.

The low values of this part in this study soils can be attributed to the formative nature of the original material derived from Iraqi soils, which does not help the development of these soils much because of their modernity and containing high values of salts especially calcium carbonate (12). The high lead values associated with oxides compared to the clay content are due to high surface area of oxides. (34) found that only a small fraction of lead not exceed than (16%) was adsorbed on iron or aluminum oxides under pH = 7 conditions and its release conditions were increased by reduction of soil reaction due to its specific surface area. (5) described amorphous iron oxides as excellent scavengers for heavy and trace elements. These characteristics reflect the environmental importance of iron oxides and their ability to acquire the largest amount of heavy metal ions in soils with a reaction number higher than 7. This can be either in the form of casings or small partials or by combining two or more of the following processes (Co-precipitation, adsorption, surface complex formation, ion exchange, penetration between layers, or secondary Oxidative metal formation), which reduces the harmful effect of this ion on soil environment. In dry environmental conditions, more crystallization and stable structures are formed that can stabilize these elements. In this respect, the degree of soil reaction creates mutual competition of the proton with adsorbed lead on the surface of oxides, as well as the dependence of deposition, dissolving, oxidation and reduction of oxidizing oxidation depending on the degree of soil reaction (35). This means that oxides and organic matter have the ability to capture (scavenging) lead efficiently, our results showed that the amorphous iron oxides had a significant contribution to the retention of heavy lead ions compared to other soil components because of their high-quality surface area.

**Diluted hydrochloric acid extraction**

Acid dissolve lead-bearing carbonate minerals according to the following formula:

$$PbCO3 + 2HCl \longrightarrow PbCl2 + CO2 + H2O \ldots\ldots\ldots \text{(iii)}$$

In addition, hydrogen ions displace lead ions that may be present on carbonate surfaces that are not dissolved in acid. Fig (5) and Table (2) showed that lead values ranged between (15 to 30) mg. Kg-1 for the study sites with a mean (21.17), for control soil and ranged between (39.61 to 43.09) with a mean (41.08) mg. Kg-1 contaminated soils.

The soils of the present study are calcareous and their carbonate mineral content ranges between (257 to 324) gm.kg-1 for contaminated soils and (262 to 344) gm.kg-1 for control soils. The high carbonate mineral in studied soils is due to dry climate conditions characterized by low rainfall and high dissolved salts due to high evaporation of soil water, (26). Lead ion species may bind to the bicarbonate ions available in the study soil solution, forming a complex of bicarbonate, which has a very high binding coefficient, or they can bind to carbonate surfaces by chemisorption. The affinity of the lead ion to the carbonate surfaces is likely to return to the similarity of ionic radius between Pb and Ca according to the following equation:

$$Pb + CaCO3 \longrightarrow PbCO3 + Ca+2 \ldots\ldots\ldots \text{(iv)}$$

As a result of forming lead carbonate or lead bicarbonate complex, which reflects the high correlation of lead ions with carbonate minerals in the studied soils. This confirms that the lead ion was associated with carbonate minerals in the form of lead carbonate or complexes, which reinforces these results in that the soluble values of it are very low in the studied soils. According to the previous assumption, lead ion bonding with carbonate minerals gives great importance to the behavior of the ion in the study soil, especially its contaminated effect, and lead combines with colloidal surfaces which are more environmentally dangerous because of the easy release and entry into the food chain (29).

Therefore, the assumed situation of lead ion correlation with carbonate minerals in studied soils is strongly associated with the retention of relatively contaminated ions in the form of carbonate or lead bicarbonate complexes. The ability of carbonate minerals to adsorb lead ionic species could be explained by the presence of electric charge on the surfaces of carbonate minerals. An important pathway in the retention of heavy elements in calcareous soils is generally adsorption on the active surfaces of calcite, dolomite, and magnesite. This depends on the concentration of the element (26).

In the case of an increase in the soil solution, this leads to the formation of more layers on the surface and then the process of deposition, and there are various types of sedimentation facilities such as containment inclusion, adsorption and the formation of a solid solution, which

distinguishes by the type of association between the trace element and the host metal (27). Using calcium carbonate to restrain highly soluble heavy metals under acidic soil conditions is suitable because carbonate is a strong adsorbent material for these elements. Carbonates adsorption of positive ionic species of heavy elements is attributed to the presence of electric charge on carbon metal surfaces. This can be explained stages of the adsorption process on the roofs of carbonate plates:

a. Ion adsorption of the heavy element on carbonate metal surfaces.
b. 2 Ion diffusion phase into the degraded surface layer.
c. The formation of the M-OH-Carbonate nucleus (cell nucleus in the solution) grows and forms new crystalline materials of new calcium carbonate such as (PbCO3, X-OH).

**Residual Extraction**

The results indicate that the remaining part of the total lead after series extraction is located in the soil separators with values ranging between (6 -18). with a mean (11.83) mg .kg-1, for control soil and ranged between (30.14 to 34.60) with a mean (31.88) mg. Kg-1 contaminated soils, figure (6) and table (2).

Discussion of the remaining part (clay, silt, sand) of the fifth stage in the process of successive extraction was adopted on the basis of the effectiveness of clay because it is the only remaining colloidal part that adsorbed. This is of great importance in determining the physical and chemical properties of the soil because of its wide surface areas of about (15-20) m2.gm-1 for kaolinite to (280-500) m2.gm-1 montmorillonite. Thus, clay is a good material used as an absorbent for treating soils contaminated with heavy metals (35). The clay content of studied soils ranged between (230-485 gm. Kg-1) for control soils and (237- 494 gm. Kg-1) for contaminated soils, that indicating clay separation was somewhat high (Table2). The decrease in the quantity of heavy ions associated with the clay separation, despite its high surface area with the dominance of the montmorillonite metal of high cation exchange capacity within the study clay, can be attributed to the intense competition faced lead by the calcium ion available in the studied soils to occupy the exchange sites on the surfaces of the clay separator. Competition process between the calcium and lead ion to occupy the exchange sites are controlled by both the radius of the ion and its concentration within the soil solution. The lead ion has a radius of (0.97 A°), which is very close to the radius of the calcium ion of (0.99 A°), which facilitates the exchange and occupation of sites between them, but the nature of calcareous soils makes the calcium concentration superior to lead in the soil solution. Thus, removes it from the surfaces of the exchange sites, i.e., the dominant effect of ion concentration in the competitive state, which has led to a decrease in the amount of lead ions associated with

the clay-separated surfaces in the study soil on the other hand, increase their movement in the soil. The variation of lead values associated with the clay separation between the six soils may be due to the difference in the form of carbonate minerals may be found in those soils, that may surround the mud partially. Most of the carbonate minerals in Iraqi soils were in the form of a single or cement agent, and a few presents were in the form of wrappers around fine soil particles (often intended as mud-separated particles). The predominance of montmorillonite in soil clay is of environmental importance by trapping some of the heavy metal ions added to the soil with high binding force at specific adsorption sites to become restricted at those sites and not affected by the high concentrations of the main cations soil (Ca, Mg, Na) (34; 35). Ions associated with silt and sand represent the part associated with silicate and crystalline compounds associated with the heavy element, which represents the dissolved value of the concentrated acid. In the clay, the values we obtained express the inherited part of these particles.

**Adsorption isotherms**

Table (4) showed the Freundlich and Langmuir equation for Pb adsorption by two selected soils, the highest and lowest calcium carbonate content of studied soils. Both Langmuir and Freundlich curves are vertical and indicate that a positive relationship has been accrued between initial Pb concentrations in the equilibrium solution and adsorbed Pb on the solid phase. Pb adsorption capacity increased as initial Pb ion increased due to overcoming mass resistance to absorb more Pb in addition to highly negatively charged groups existing on carbonate Surfaces (39).

Even in a competitive interaction metals system, Pb Keeps increasing adsorption as initial metals concentration increases due to the high affinity between Pb and soil surfaces. (13,37). Pb adsorption by calcareous soils has been fitted to Freundlich and Langmuir equations. Table (4) shows the predicted values of both equation's parameters.

Determination coefficient (R) for Langmuir equation. Suggest that experimental results are close to Langmiur isotherm more than Freundlich. Maximum adsorption for studied soils, with lower and higher calcium carbonate content, is 1.428 mg. gm-1 and 1.666 mg. gm-1 respectively. The binding energy for both soils was very close to 0.012 and 0.013 L. gm-1 for lower and higher carbonate content respectively. These results support the efficiency of these soils to Pb retention when the maximum retention is obtained at pH (6-7). (39). Kf parameter is a distribution coefficient or adsorption capacity in Freundlich isotherm representing the ratio of metal retained in sold phase to its concentration in the equilibrium liquid phase (41). This parameter is very important to understand the distribution of heavy metals in the sold-solution

interface system and to predict heavy metal mobile towards sub-soil. Kf values for both studied soils are very close to 1.2706 and 1.2995 L. gm-1 for lower and higher carbonate content respectively. The highest Kf value is the more retained on the solid phase. The slope in the Freundlich equation represents the (n) value of adsorption intensity and the reciprocal of this parameter indicates the binding energy. The values of the (n) parameter are 0.8849 and 0.9407 L. gm-1 for lower and higher carbonate content in studied soils respectively and these values indicate favorable adsorption (42).

**Physicochemical lead pathway in soil environment:**

The results of the study appear that the chemical and physical properties of soils have an effect on the determination and dominance of lead within their different particles, and most of the lead parts were associated with carbonates and mineral particles. Carbonate mineral's lead content leads to conclude that the calcareous soil conditions (high degree of reaction and high content of carbonate minerals) contributed significantly to the association of this heavy element and its deposition in the form of carbonate heavy metals depending on the product of the solubility values of lead carbonates compared to carbonate minerals (7.4×10-14 - 2.8× 10-9) respectively, table (5) explains that carbonate minerals in surface soils retain appreciable amounts of Lead and sub-soil samples (20 cm depth) of both sites (contaminated and control soil) and showed no significant differences between both sites by the lead content.

In addition to the possibility of adsorption of this element on the surfaces of carbonate or entering into the crystal structure of the carbonate metal and this makes this soil a safe repository for the disposal of these heavy ions as part of the treatments. In order to illustrate the dynamics of the association of heavy lead ions with the soil components. This study proposed the following mechanisms: When the soil receives ions of heavy metals (lead) from different sources (irrigation water, phosphate fertilizers, and wind deposits), these ions are subject to bonding forces ranging from weak pulling forces to strong chemical bonding by soil solution ions on the one hand or by negative charges on colloidal surfaces on the other hand. These correlation forces depend on many factors including heavy-ion concentrations flowing into the soil, ionic activity, equivalence, ion size, substitution power, ion exchange constants, medium reaction number, type of negative charges and their density colloidal surfaces (40). As calcareous soils are calcite content in nature, calcium, and bicarbonate ions are predominantly in the soil solution, which makes them the dominant controllers of all chemical reactions taking place in the medium. Therefore, high-concentration calcium ions must compete with these ions on the adsorption surfaces (clay, oxides, carbonate minerals, and organic matter), which are most intense at the surfaces of the clay-separated particles because the majority of them and

have permanent negative charges compared to non-permanent charges based on the pH-dependent medium found on the surfaces of other soil components (oxides and organic matter). Therefore, the negative charges on the surfaces of the clay-separated particles are stronger than those on the surfaces of both oxides and organic matter. So, the attraction of calcium ions to the slurry-separated particles is faster and stronger in the first moments of the exchange compared to the surfaces of oxides and organic matter. This may lead to an increase in the movement of these ions in the soil body. This assumption is reinforced by the reduction of ions associated with the minerals of the soil particles compared to other soil components. The correlation of heavy lead ions in the studied soil with the carbonate surfaces can be explained according to the same assumption table (6). It is clear from the foregoing that the physochemical pathway of lead ions is the result of the physical, chemical, and biological effects in the ecosystems in which this ion exists and which in turn affects its biogeochemical cycle in those systems. The physiochemical pathway is illustrated in the calcareous soil conditions prevailing in the region. Solid carbonates> Residual > Free oxides> DTPA> Organic matter. As shown by the results obtained in Figures (7).

## 4. CONCLUSION

Road traffic emissions are responsible for different pollutants spread near highways and roads, including Lead. Lead is a toxic element and may cause many human health risks. In North Iraq (Nineveh province), different calcareous soil textures showed a high ability to lead to adsorption with high adsorption capacity. The fractionation technique is an adequate method to understand the heavy metal distribution in soil components. The fractional distribution of Lead in Mosul calcareous soil was in the order soil carbonate > residual>Fe-Mn oxides >DTPA > organic matter. The determination coefficient between Pb fractions and some studied soil properties was significant.

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**Authors' Contribution**

ZS = Fieldwork and sample collection.

SM = Laboratory work and sample analysis.

OK = Writing and interpreting its results.

MK = Statistical analysis.

HM = Manuscript revision and correspondence.

MA = General supervision, interpreting its results.

Compliance with ethical standards

Conflict of interest: Authors do not have any conflict of interests to declare.

Ethical issues: None

Declaration of generative AI and AI-assisted technologies in the writing process: None

**Table 3.** Lead Concentration in Studied Soils Fractions.

| **Type of Extractant** | **Lead concentration in studied soils fractions (control soils)** Soil Number | | | | | | | **Lead concentration in contaminated soils fractions Soil Number** | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | M* | 1 | 2 | 3 | 4 | 5 | 6 | **M*** |
| DTPA | 4.15 | 3.19 | 2.22 | 3.61 | 3.18 | 2.29 | 3.11 | 7.51 | 6.57 | 5.61 | 6.17 | 7.56 | 5.28 | **6.45** |
| Organic Matter | 3.51 | 2.56 | 1.85 | 1.59 | 2.14 | 0.98 | 2.11 | 5.13 | 5.67 | 3.65 | 4.88 | 4.27 | 4.84 | **4.74** |
| Oxides | 5.21 | 4.5 | 3.81 | 3.56 | 3.17 | 3.2 | 3.91 | 6.87 | 7.85 | 5.76 | 6.71 | 6.94 | 7.59 | **6.95** |
| CaCO3 | 30 | 27 | 21 | 18 | 16 | 15 | 21.17 | 41.99 | 40.69 | 43.09 | 39.61 | 39.75 | 41.32 | **41.08** |
| Residual | 18 | 16 | 12 | 10 | 9 | 6 | 11.83 | 33.11 | 30.14 | 31.2 | 30.33 | 31.9 | 34.6 | **31.88** |

*M refer to Mean

**Table 4.** Freundlich And Laungmiur Equation for Selected Two Selected Soils.

| **Soils Locations** | **Langmuir equation** | | | | **Freundlich equation** | | |
|---|---|---|---|---|---|---|---|
| | linear equation | Qmax, mg kg–1 | KL, L g–1 | KL b (MBC), L kg–1 | linear equation | n | Kf |
| **Soil3 high Calcium Carbonate** | y = 0.0458x + 0.0006 | 1666.67 | 0.0131 | 21.83 | y = 0.9407x + 1.2995 | 0.9407 | 1.2995 |
| **Soil4 low Calcium Carbonate** | y = 0.0568x + 0.0007 | 1428.57 | 0.0123 | 17.61 | y = 0.8849x + 1.2706 | 0.8849 | 1.2706 |

**Table 5.** Lead Content at Depth20 Cm In Studied Soils.

| **Type of Extractant** | **lead concentration in contaminated soils fractions (5m away of roads) at 20 cm depth** | | | | | | | **lead concentration in studied soils fractions (soil control, 75m away of roads) at 20 cm depth** | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Soil Number | | | | | | | Soil Number | | | | | | |
| | 1 | 2 | 3 | 4 | 5 | 6 | M* | 1 | 2 | 3 | 4 | 5 | 6 | M* |
| **DTPA** | 2.17 | 2.20 | 2.22 | 2.49 | 2.19 | 1.58 | 2.14 | 2.37 ns | 2.40 ns | 2.42 ns | 2.72 ns | 2.39 ns | 1.72 ns | 2.34 |
| **Organic Matter** | 2.42 | 1.76 | 1.27 | 1.10 | 1.47 | 0.68 | 1.45 | 2.64 ns | 1.93 ns | 1.39 ns | 1.20 ns | 1.61 ns | 0.74 ns | 1.59 |
| **Oxides** | 3.59 | 3.10 | 2.63 | 2.45 | 2.18 | 2.20 | 2.69 | 3.92 ns | 3.39 ns | 2.87 ns | 2.68 ns | 2.39 ns | 2.41 ns | 2.94 |
| **CaCO3** | 20.67 | 18.60 | 14.47 | 12.40 | 11.02 | 10.34 | 14.59 | 22.59 ns | 20.33 ns | 15.81 ns | 13.55 ns | 12.05 ns | 11.30 ns | 15.94 |
| **Residual** | 12.40 | 11.02 | 8.27 | 6.89 | 6.20 | 4.13 | 8.15 | 13.55 ns | 12.05 ns | 9.04 ns | 7.53 ns | 6.78 ns | 4.52 ns | 8.91 |

*M refers to Mean

**Table 6.** Coefficient's Determinants of The Lead Fraction with Soil Properties.

| Soil Property | DTPA | Oxides | Organic Matter | Diluted Hydrochloric Acid | Residual | Total |
|---|---|---|---|---|---|---|
| | R2 | | | | | |
| EC | 0.08 | 0.21 | 0.22 | 0.17 | 0.16 | 0.17 |
| pH | 0.78* | 0.66* | 0.71* | 0.57 | 0.67* | 0.65* |
| SOM | 0.61* | 0.65* | 0.62* | 0.68* | 0.71* | 0.69* |
| CEC | 0.95** | 0.90** | 0.98** | 0.91** | 0.95** | 0.94** |
| CaCO3 | 0.94** | 0.95** | 0.95** | 0.96** | 0.97** | 0.98** |
| Clay | 0.91** | 0.90** | 0.92** | 0.94** | 0.93** | 0.94** |

* and **: significant at 0.01 and 0.05 of probability, respectively.

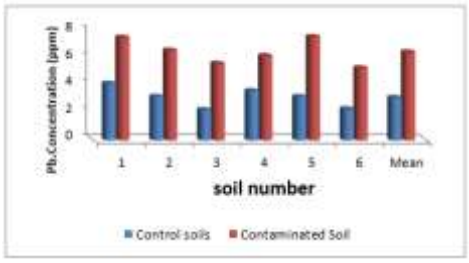


**Figure 3.** The Values of Soil Lead Extracted By DTPA Solution.

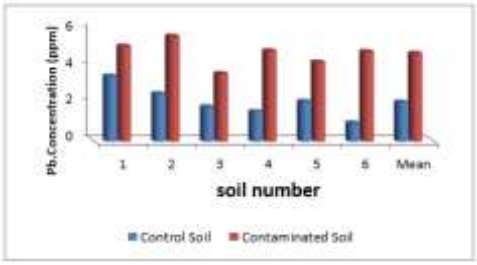


**Figure 4.** The Values Of Soil Lead Extracted By Sodium Hypochlorite Solution.

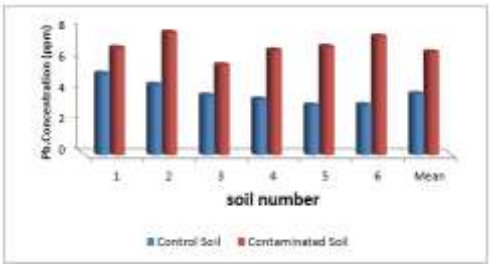


**Figure 5**. The Values Of Soil Lead Extracted By Sodium Dithionate.

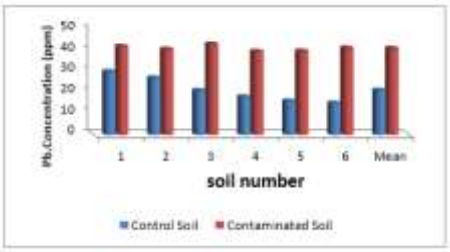


**Figure 6**. The Values Of Soil Lead Extracted By Diluted Hydrochloric Acid Solution.

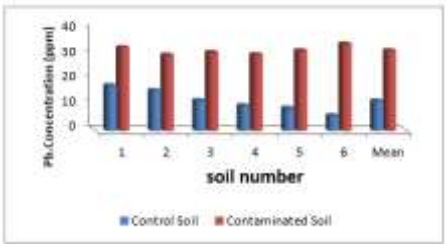


**Figure 7**. The Values Of Soil Lead In Soil Residual.

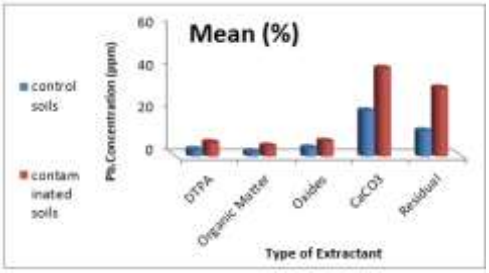


**Figure 8**. Chemical Pathway For Total Lead Distribution In A Calcareous Soil Environment (Soil Control And Contaminated S.

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