Botani : Publikasi Ilmu Tanaman dan Agribisnis
Volume. 3 Nomor. 3 September 2026
E-ISSN .: 3046-5494; P-ISSN .: 3046-5508, Hal. 13-31
DOI: https://doi.org/10.62951/botani.v3i3.616
Tersedia: https://journal.asritani.or.id/index.php/Botani

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

Saqr Mijbil Al-jumaily [1*], Zakiya Shihab Hamad [2]
[1] Tikrit University ،Faculty of Food Science / Al-Shirqat ،Department of Food Science and Technology, 34005, Salah Al Deen ،Iraq.
[2] College of Education for Pure Sciences, Department of Chemistry, Kirkuk University, Iraq
**Corresponding Author:* saqer.m.mohammed@tu.edu.iq

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 physiochemical 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

Among all anthropogenic sources of the formation of metal contamination, road transportation is one of the main sources of accumulation of heavy metals in roadside soils (1). Constant movement of vehicles leads to the release of heavy metals to the environment through exhaust gas emissions and wear of tires, brakes, lubricants, and other vehicle parts (2). The amount of heavy metal accumulation depends on numerous factors including traffic volume, road age, fuel composition, meteorological conditions, and physical and chemical properties of receiving soils (3). The high levels of cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), zinc (Zn), and especially lead (Pb) have been frequently reported in soils of roads with moderate to heavy traffic (4). As one of the most toxic pollutants, Pb is recognized due to its persistency, toxicity, and inability to degrade. Accumulation of Pb in soils can threaten terrestrial ecosystems as well as contaminates groundwater and agricultural crops as well as food chain which poses significant risks to the environment and human health (5). Thus, the reduction of soil degradation and Pb pollution needs effective environmental management and legislation and conservation practice at national and international levels (6). Besides, understanding the chemical behavior of Pb in soil is crucial to provide information about its origin, mobility, bioavailability and possible ecological risks (7). Heavy metals are able to enter the soil as a result of both natural geological processes and anthropogenic activities. As a result

Naskah Masuk: 13 Mei 2026 Revisi: 19 Juni 2026; Diterima: 20 Juli 2026; Tersedia: 22 Juli 2026

of weathering of parent materials, trace elements are introduced to the soil. Some of these elements may appear at the level that could be harmful for the growth of plants and other organisms. But the predominant source of enrichment of soil with heavy metals is related to the application of chemical fertilizers, organic amendments, industrial waste, municipal waste, and polluted irrigation water (8). The environmental behavior of heavy metals is defined by their total concentration in soil and chemical speciation. In general, the relatively low proportion of the total metal content is biologically available for plant absorption or environmental transport. They are regulated by different processes including dissolution, precipitation, adsorption, desorption, complexation, decomposition, oxidation-reduction processes, and microbiological interaction (9). However, determination of the total content of metals can give us little information about their toxicity or environmental risks since the metals are distributed in different stable and unstable solid phases (9). To solve this problem, the sequential fractionation analysis has become one of the effective approaches for distribution of heavy metals in the soil. It allows us to get important information about the interaction of metals with soil fractions and improve our understanding of their mobility, bioavailability, and behavior (10). Based on previous researches, it can be stated that the average content of total Pb in soils is about 16 mg/kg while the lead concentration in calcareous soils is about 3-10 mg/kg (11). After entering soil, Pb is partitioned between the liquid and solid phases. In the solid phase, Pb can become the part of mineral particles or soil organic matter depending on the interactions between Pb and soil (12). The interactions between Pb and soil are regulated by the following processes: dissolution, adsorption, complexation, migration, precipitation, surface sorption, diffusion into minerals, binding with organic substances, adsorption by microorganisms, and, finally, volatilization. All of these processes depend mostly on the soil physicochemical properties. Soil organic matter, especially its carboxylic and phenolic groups, is one of the main sorbents for Pb (5). They form the complex with lead which differs in stability in dependence of environmental conditions and composition of soil. As Pb exists in soil in different geochemical forms but not in one homogenous pool, total concentration of Pb cannot reflect its environmental behavior and biological availability (13). For this reason, Pb fractionation is conducted using the sequential extraction method. The procedure of Pb sequential extraction usually divides this metal into water-soluble, DTPA-extractable, exchangeable, carbonate-bound, organic matter-bound, and mineral-bound fractions. Therefore, the present study was designed to investigate the distribution of lead among different geochemical fractions and to evaluate the role of calcium carbonate in enhancing lead retention in selected calcareous soils of Iraq using the sequential fractionation technique.

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: -

1. 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).
2. 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).
3. Organic matter content: After completion of the previous paragraph soil were treated with hydrogen peroxide (H2O2) until the color of the sample becomes pale (24).
4. 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.
5. 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.
6. 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 ……... (ii)

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 …….... (iii)

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

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

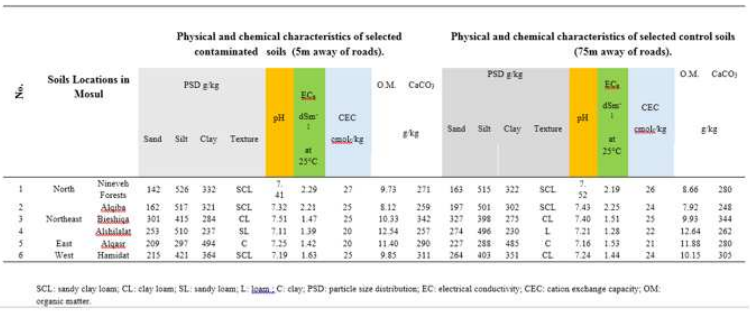
(qmax) is the adsorption maximum. And(Ce) is the adsorbate equilibrium

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

Physiochemical properties of the studied soil: -



No.	Soils Locations in Mosul		Physical and chemical characteristics of selected contaminated soils (5m away of roads). PSD g/kg Sand	Silt	Clay	Texture	pH	EC$_e$ dSm^{-1} at 25°C	CEC cmolc/kg	O.M. g/kg	CaCO$_3$ g/kg	Physical and chemical characteristics of selected control soils (75m away of roads). PSD g/kg Sand	Silt	Clay	Texture	pH	EC$_e$ dSm^{-1} at 25°C	CEC cmolc/kg	O.M. g/kg	CaCO$_3$ g/kg
1	North	Nineveh Forests	142	526	332	SCL	7.41	2.29	27	9.73	271	163	515	322	SCL	7.52	2.19	26	8.66	280
2		Alqiba	162	517	321	SCL	7.32	2.21	25	8.12	259	197	501	302	SCL	7.43	2.25	24	7.92	248
3	Northeast	Bashiqa	301	415	284	CL	7.51	1.47	25	10.33	342	327	398	275	CL	7.40	1.51	25	9.93	344
4		Alshalalat	253	510	237	SL	7.11	1.39	20	12.54	257	274	496	230	L	7.21	1.28	22	12.64	262
5	East	Alqasr	209	297	494	C	7.25	1.42	20	11.40	290	227	288	485	C	7.16	1.53	21	11.88	280
6	West	Hamidat	215	421	364	SCL	7.19	1.63	25	9.85	311	264	403	351	CL	7.24	1.44	24	10.15	305

SCL: sandy clay loam; CL: clay loam; SL: sandy loam; L: loam.; C: clay; PSD: particle size distribution; EC: electrical conductivity; CEC: cation exchange capacity; OM: organic matter.

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 extraction step was designed to decompose soil organic matter and liberate the metal ions bound to organic constituents, including lead. The analytical results indicated that the studied soils contained relatively low amounts of organic matter compared with other soil fractions.

Nevertheless, despite its limited abundance, organic matter exhibited a pronounced capacity to retain lead ions. As presented in Figure (3), the concentration of lead associated with the organic fraction ranged from 0.98 to 3.51 mg kg^{-1}, with an average value of 2.11 mg kg^{-1} in the control soils, whereas contaminated soils exhibited values ranging from 3.65 to 5.67 mg kg^{-1}, with a mean of 4.74 mg kg^{-1}.

These findings demonstrate the important contribution of soil organic matter to lead immobilization through strong adsorption mechanisms. The remarkable affinity of organic matter for Pb^{2+} is mainly attributed to the abundance of reactive functional groups and its exceptionally high cation exchange capacity, which ranges between 150 and 300 cmol kg^{-1}, enabling efficient retention of divalent metal ions (28,30). The retention efficiency of organic matter is influenced by several environmental and soil-related factors, including moisture content, soil pH, the carbon-to-nitrogen (C/N) ratio of decomposing residues, and both the quantity and mineralogical composition of clay. These variables regulate the decomposition of organic matter and consequently affect the availability of active adsorption sites. Furthermore, interactions between organic and mineral colloids have been explained by two complementary hypotheses. The first proposes that the dominance of montmorillonite in soil suppresses the biological decomposition of organic matter (12). The second suggests that organic colloids interact with clay minerals and oxide colloids to form soluble and insoluble organo-mineral complexes with heavy metals. The stability of these complexes depends on soil pH and the structural characteristics of the organic materials, frequently resulting in blockage of exchange sites on colloidal surfaces and consequent changes in cation exchange capacity. The interaction between lead ions and soil organic matter can also be interpreted as a cation-exchange process in which hydrogen ions associated with acidic functional groups are replaced by metal ions (31), according to the following reaction:

$$Mx^{+} + >LHy = >L–M(x–y)^{+} + yH^{+} \quad \text{..... (iii)}$$

After adsorption, lead becomes a part of stable inner-sphere complexes formed via covalent and ionic bonding with oxygen-containing functional groups, such as carboxyl and phenol groups, at moderate acidity (pH≈ 5.0). On the contrary, metals with lower affinity usually remain as exchangeable ions without losing their hydration shells on organic substrates (32). With increasing soil pH beyond 6.0, close to neutral (pH=7.0-7.5) conditions, dissociation of carboxyl and phenol groups creates extra negative charges, thus significantly enhancing adsorption and retention of heavy metal ions (33). The partitioning of lead among soil fractions not only depends on the amount of lead entering the ecosystem but also on the physical,

chemical, and biological environment in which this element is present. Chemical composition of soil solutions and organic/inorganic ions secreted by roots influences soil pH and directly affects the mobilization, translocation, and retention of lead in various soil compartments (28).

Oxides Extraction

According to Table (2) and Figure (4), the content of lead in the oxide fraction varied from 3.17 to 5.21 mg kg^{-1} with the average value of 3.91 mg kg^{-1} in control soils. However, for contaminated soils, the content of lead in the oxide fraction varied from 5.76 to 7.85 mg kg^{-1} with the mean value of 6.95 mg kg^{-1}. It can be explained by the pedogenesis properties of Iraqi calcareous soils. These soils usually develop recently from parent rocks with high contents of calcium carbonate and soluble salts. Such conditions hinder the accumulation of secondary oxides of iron and manganese. However, oxides are characterized by large specific surface areas and many adsorption sites. Thus, these minerals are very effective heavy metals sorbents. For this reason, the amount of lead sorbed by oxides was higher than that in the clay fraction. Several researchers have found that less than 16% of the total lead was sorbed by iron and aluminum oxides in neutral soils (pH≈7), while decreasing soil pH resulted in the increase in lead desorption due to oxide surface charge and adsorption properties' alteration (34). Similarly, iron oxides are considered to be very effective scavengers of trace elements and heavy metals due to their exceptional sorption properties (5). Oxide minerals are significant for the environment due to their capability to immobilize heavy metals by several physicochemical processes, such as co-precipitation, surface adsorption, specific surface complexation, ion exchange, interlayer diffusion, and oxidation/reduction of secondary oxides mineral phases. These processes effectively reduce lead mobility and its environmental risk. Oxide minerals in arid climates usually become more crystallized and structurally stable, and therefore, more capable of retaining heavy metals during prolonged period of time.

Soil pH plays a crucial role in these immobilization processes by regulating the competition of hydrogen ions and adsorbed lead ions for oxide surface sites, as well as regulating precipitation, dissolution, oxidation, and reduction of iron and manganese oxides (35). Both oxide minerals and organic matter can be considered as highly efficient scavengers of lead. It can be concluded from the obtained results that amorphous iron oxides contributed greatly to lead immobilization due to their large specific surface areas and abundance of reactive adsorption sites compared to other soil components.

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 examined in the present investigation were classified as calcareous, with calcium carbonate contents ranging from 257 to 324 g kg^{-1} in the contaminated soils and 262 to 344 g kg^{-1} in the control soils. The abundance of carbonate minerals is characteristic of arid and semi-arid environments, where limited rainfall, high evaporation rates, and the accumulation of soluble salts promote carbonate precipitation and persistence within the soil profile (26). Lead retention in calcareous soils is strongly influenced by the presence of carbonate minerals. In the soil solution, Pb^{2+} ions may react with bicarbonate species to produce stable lead-bicarbonate complexes or may become directly adsorbed onto carbonate mineral surfaces through specific chemical interactions. This strong affinity is largely attributed to the close similarity between the ionic radii of Pb^{2+} and Ca^{2+}, which facilitates ionic substitution within carbonate minerals according to the following reaction:

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

The formation of $PbCO_3$ or lead-bicarbonate complexes accounts for the pronounced association of lead with carbonates observed in the soils of study. The above assumption is further confirmed by the very low concentration of soluble lead in the soils, implying the substantial proportion of lead is present in the more or less stable form bound with carbonates. This process substantially impacts the environmental behavior of lead through decreasing its mobility in the soils. Nonetheless, lead associated with colloidal fractions can pose some environmental threat since the change of the soil conditions may cause its release and further migration into the food chain (29). Thus, it is clear that carbonates can be regarded as one of the major sinks for lead in the studied calcareous soils. The ability of carbonates to accumulate Pb^{2+} ions takes place primarily due to the electrically active surfaces of the carbonate minerals such as calcite, dolomite, and magnesite, where the adsorption reactions occur successfully. The degree of this process depends on the concentration of dissolved lead in the soil solution (26). Moreover, The increase of lead concentration in the soil solution leads to the gradual occupation of the adsorption sites at the surface of the carbonates, followed by precipitation

and crystal growth processes. Several processes of retention can act simultaneously in the case of carbonates, including surface adsorption, structural incorporation, co-precipitation, and formation of solid solutions with lead and carbonate minerals (27). Thus, calcium carbonates have proved to be an efficient agent for the immobilization of highly soluble heavy metals, especially in acidic soils. The adsorption process can take place in three main steps:

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 residual fraction is the part of total soil lead remaining after completion of the sequential extraction procedure. As is seen from Table (2) and Figure (6), this fraction varied from 6.00 to 18.00 mg kg^{-1} with the mean value of 11.83 mg kg^{-1} in the control soils and from 30.14 to 34.60 mg kg^{-1} with the mean of 31.88 mg kg^{-1} in the contaminated soils. The interpretation of the residual fraction was concentrated mainly on the clay fraction as the major component remaining after the sequential extraction process. Clay minerals make the principal contribution to the formation of soil physicochemical characteristics due to their exceptional high specific surface area varying from 15 – 20 m^2 g^{-1} in the case of kaolinite to 280 – 500 m^2 g^{-1} in the case of montmorillonite. Thus, clay minerals are well known as natural adsorbents for the immobilization of heavy metals in the contaminated soils (35).

The clay content in the studied soils varied from 230 to 485 g kg^{-1} in the case of the control soils and from 237 to 494 g kg^{-1} in the contaminated soils (Table 2). It indicates a high proportion of clay in all soils despite the high specific surface area and predominance of montmorillonite characterized by high cation exchange capacity. Nevertheless, the amount of lead retained by the clay fraction was rather low. It may be related to the serious competition between Pb^{2+} and Ca^{2+} ions for the exchange sites on the clay mineral surfaces.

The similarity of the ionic radii between Pb^{2+} (0.97 Å) and Ca^{2+} (0.99 Å) allows them to compete for the adsorption sites. However, the presence of high calcium content in calcareous soils leads to the domination of Ca^{2+} ions in the exchange complex, which displaces lead ions from the most adsorption sites. The competition with calcium ions decreases the amount of lead retained by the clay minerals but increases its mobility in the soil solution. The variations of lead concentrations associated with the residual fraction in the soils of the study may be explained by the differences in occurrence and morphology of the carbonates. In the

Iraqi calcareous soils, carbonate minerals occur in the form of cementing agents or discrete minerals. Only the small part of the carbonates occurs as coatings around the fine clay particles. It impacts the accessibility of the adsorption sites of the clay minerals and influences the distribution of the lead in the residual fraction.

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 current study indicated that the physicochemical properties of calcareous soils have a critical impact on the distribution and retention of lead in different soil fractions. Most of the retained lead is found in carbonate minerals and the residual fraction, suggesting that they are the main sinks for this metal. The predominance of lead in the carbonate fraction could be justified by the fact that the alkalic soil environment, along with the high amount of calcium carbonates in calcareous soils, facilitates lead immobilization via precipitation and adsorption. It can be attributed to the considerably lower solubility product of lead carbonate in comparison with calcium carbonate, which equals 7.4×10^{-14} and 2.8×10^{-9}, correspondingly. As a result, the precipitation of lead into the stable carbonate compounds occurs in the presence of an alkalic environment in soil. As shown in Table (5), carbonate minerals contained considerable amounts of lead in the upper and subsurface soil layers (20 cm) in both contaminated and control sites.

Besides the precipitation in the form of carbonate minerals, the immobilization of lead can also take place as the result of adsorption on the surface of carbonates or partial incorporation into the crystal structure of carbonate minerals. The mentioned processes decrease the mobility of lead and facilitate its usage as a natural barrier against heavy metal contamination. In order to describe the mechanisms underlying the distribution of lead in the investigated soils, the conceptual model based on the interaction between dissolved ions of lead and the soil components was suggested. After entering the soil via irrigation water, phosphate fertilizers, atmospheric deposition, or traffic pollution, Pb^{2+} ions participate in a series of physicochemical reactions varying from weak electrostatic attractions up to strong chemical bonds. These reactions can occur either with dissolved ions in the soil solution or negatively charged functional groups on the mineral and organic colloidal surface. The strength of the described interactions depends on such factors as metal concentration, ionic activity, ionic charge, hydrated ionic radius, exchange selectivity, cation exchange constants, soil pH, and the density and nature of the negative charge on the soil colloids (40). Since calcareous soils consist mainly of calcite, calcium and bicarbonate ions are the dominant constituents of the soil solution and thus have the strongest effect on the chemical equilibrium. The high amount of Ca^{2+} leads to the intensive competition between Pb^{2+} and Ca^{2+} for the adsorption sites on clay minerals, iron and manganese oxides, carbonate minerals, and soil organic matter. It takes place mostly due to the fact that clay minerals contain predominately permanent negative charge, while oxide minerals and organic matter have variable charges dependent on soil pH. Therefore, calcium

ions are likely to occupy numerous exchange sites on the clay surface in the course of adsorption, limiting the retention of lead in this soil fraction and increasing the mobility of Pb^{2+} ions in the soil solution. Such a suggestion is supported by the lower amount of lead retained by clay minerals in comparison with the carbonate and oxide fractions in the current study. Moreover, the strong association of lead with carbonate minerals can be explained in the same way, as shown in Table (6). Therefore, the environmental behavior of lead in calcareous soils is characterized by the combined effect of the physical, chemical, and biological processes taking place in the soil ecosystem. The mentioned processes regulate the mobility, redistribution, bioavailability, and stability of lead, thus defining its biogeochemical cycle in alkaline environment. Based on the sequential extraction results received in the current research, the proportion of lead in the investigated soil fractions could be defined in the following sequence: **Carbonate fraction > Residual fraction > Fe–Mn oxide fraction > DTPA-extractable fraction > Organic matter fraction**, as illustrated in Figure (7).

4. CONCLUSION

Road traffic is an important anthropogenic source of lead contamination in soils located adjacent to highways and urban roads. Owing to its persistence and toxicity, lead represents a significant environmental pollutant that may pose serious ecological and human health risks if it becomes bioavailable. The results of the present study demonstrated that the calcareous soils of Nineveh Province, northern Iraq, possess a considerable capacity to immobilize lead because of their high carbonate content and alkaline reaction. Sequential fractionation proved to be an effective technique for evaluating the distribution and environmental behavior of lead among different soil components. Lead was predominantly associated with the carbonate fraction, followed by the residual fraction, Fe–Mn oxides, the DTPA-extractable fraction, and finally the organic matter fraction. Furthermore, statistically significant relationships were observed between lead fractions and several physicochemical properties of the investigated soils, confirming the important role of soil characteristics in controlling lead retention and mobility.

Acknowledgments

The authors would like to thank the University of Mosul, University of Tikrit and University of Kirkuk, for providing the laboratory equipment to conduct this research, and also the anonymous reviewers, for helping us to improve the manuscript.

Authors' Contribution

ZS = Fieldwork and sample collection, Writing and interpreting its results, Statistical analysis.
SM = Laboratory work and sample analysis, Manuscript revision and correspondence, General supervision, interpreting its results.

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	4.51	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.

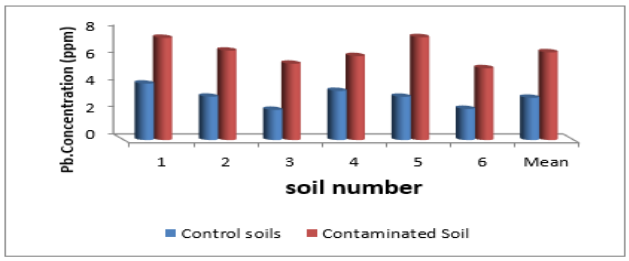


Figure 3. The Values of Soil Lead Extracted by DTPA Solution.

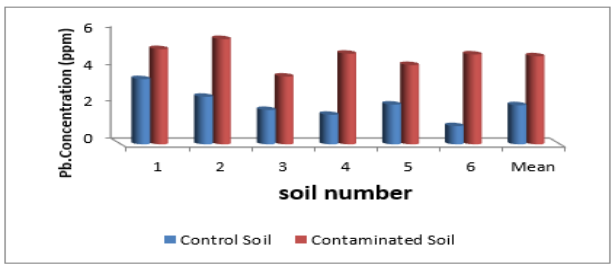


Figure 4. The Values of Soil Lead Extracted by Sodium Hypochlorite Solution.

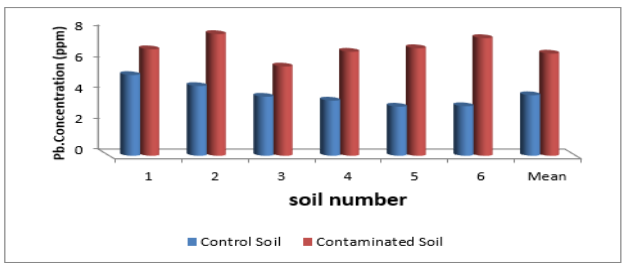


Figure 5. The Values of Soil Lead Extracted by Sodium Dithionate.

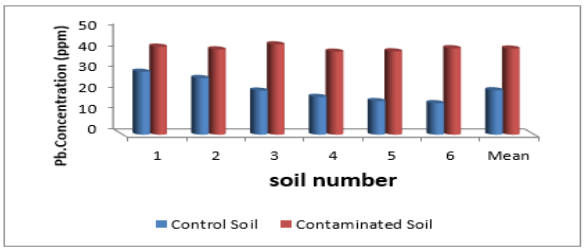


Figure 6. The Values of Soil Lead Extracted by Diluted Hydrochloric Acid Solution.

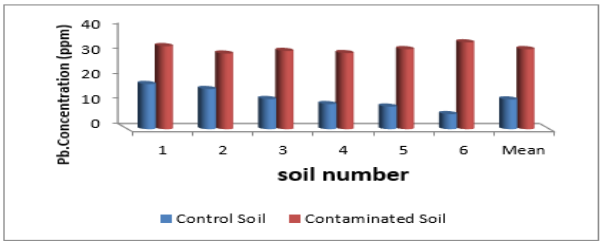


Figure 7. The Values of Soil Lead in Soil Residual.

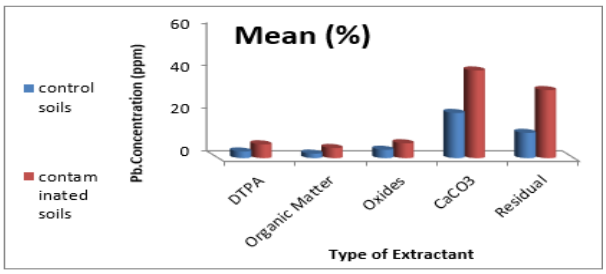


Figure 8. Chemical Pathway for Total Lead Distribution in a Calcareous Soil Environment (Soil Control And Contaminated Soil).

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