Chemical fragmentation and Bioavailability for Lead in some calcareous soils from the city of Mosul

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Abstract. The first two sites were selected from the Aden district and geographically defined by coordinates N36° 21'21.5" E43° 12'39.1". In the course of valley Al- Danfili in the city of Mosul, which pours its cargo in the Tigris River at the site of the Al-Mazara district, which is geographically defined by coordinates N36° 19'50.2" E43° 09'49.05". We classified the soil suborder (Argids, Orthents) Respectively. The total content of the Lead was separated by extracting the soil in a sequential manner in order to identify the nature of its distribution within the different soil phases according to the following context: Water extraction and then (0.005 M) (DTPA) which is associated with carbonates with diluted hydrochloric acid solution (0.1M). The H$_2$O$_2$ extraction stage is 20% equilibrium for the purpose of determining organic matter content then associated with non-crystalline iron oxides (AFeOx) Amorphous Fe Oxides using a mixture solution (0.25M NH$_2$OH . HCl + 0.25M HCl) (10: 1) (solution: soil), This was followed by the final phase, which included mechanical separation of sand, silt and clay digest each separately by using a wet digestion method to determine residual content (sand, silt and clay). Lead was measured in the solutions and extracts in the solutions above using the (GBC 933plus) atomic absorption device. The results indicated the following:

- Water soluble fraction ranged from (0.33 to 0.34) mg.kg$^{-1}$ and by (0.10%),
- exchange from (15.14 to 7.01) mg.kg$^{-1}$ and by (3.31%),
- associated with oxides from (14.20 to 76.29) mg.kg$^{-1}$ and by (13.51%), which is related to the organic matter from (29.60 to 23.00) mg.kg$^{-2}$ and by (7.85%),
- associated with carbonates from (261.20 to 87.50) mg.kg$^{-1}$ and by (52.04%), and associated with clay from (43.84 to 10.77) mg.kg$^{-1}$ and by (8.15%), associated with silt from (22.23 to 3.59) mg.kg$^{-1}$ and by (3.85%) and associated with sand from (44.46 to 30.50) mg.kg$^{-1}$ and by (11.19%) of the total content from the Aden (clay) and the Al-mazara (sandy clay loam) districts Respectively. The physiochemical pathway for the distribution of Lead in the calcareous conditions prevailing in the following area is explained:

Solid carbonates > Oxides > Sand > Clay > Organic Matter > Silt > Exchange > Soluble.

Keywords: chemical fragmentation, Bioavailability, Lead.

Introduction

The biochemical cycle of heavy elements and metalloids increase in human activity and the accumulation of these formulas in different parts of the biosphere and the possibility of transmission under the conditions of environmental variability will hamper both the structure and function of the
ecosystem and the possibility of anti-health effect of the neighborhoods (Fedotov and Mirò', 2008). Heavy metals and metalloids penetrate the agricultural system through both natural processes and human processes. Some of the soil has a high floor for some micro elements, some of which are poisonous to plants and wildlife. This is due to the high concentrations of these elements in the mother material of the soil. The human processes include the introduction of heavy elements through the use of chemical fertilizers, organic materials, industrial waste, city and municipal waste and irrigation and wet and dry deposits. These processes contribute to the development of different quantities of heavy metals in the agricultural environment. Only a small fraction of the heavy metals and metalloids in the soil have an effect on bioavailability. The movement and readiness of these pollutants is controlled by many chemical and biochemical processes. For example, there are processes (solubility, sedimentation, adsorption and release, complex formation and degradation, oxidation and reduction reactions). Not all of these processes are equally important for each element but all are affected by soil reaction and biological processes. In order to understand some of the major interactions controlling the release and release of the heavy metal into the soil and the environment and the problems related to its lack or pollution of the soil. Measuring the total content of these elements alone is not a good measure of bioavailability but it is useful to quantify pollutants. Therefore, the total content in the soil is a weak indicator of the toxicity of the element when it is distributed on different soil stages. This gives an indication of the readiness and movement of the element within the soil phases (Krishnamurti and Naidu, 2008; Selim, 2011).

The identification and quantification of metals associated with soil phases or their components within the Fraction analysis (Templeton et al., 2000), using several extracts within the so-called sequential extraction, will provide accurate information on the movement and dispersion of heavy metals in the soil.

The variation in concentrations of heavy metal ions from one component to another depends primarily on the added amount of this pollutant to ecosystems (Vrbek et al., 2002), in addition to the physical, chemical and biological conditions of the surrounding environment, organic and inorganic ions and changes in the interaction number of the medium (Collins et al., 2003).

Research materials and methods

The first two sites of Aden district, geographically defined by coordinates N36° 21.5”, E43° 12.39.1” were selected in valley al-Danfili in the city of Mosul, which pours its load into the Tigris river at the location of the Al-Mazara district defined by coordinates N36° 19° 50.2” E43° 09° 49.05” where the nature of the agricultural exploitation in the first site vegetables with the use of organic manure (bird residues) and nitrogen for many years continued, the second was planted with vegetables and fertilizers with nitrogen and phosphate fertilizers in addition to spraying pesticides. These sites examined morphology and identified their horizons in the field. The soil of the first site was then classified to the order Aridisols suborder Argids and second to the order Entisols level the suborder Orthents level as indicated in the Soil Survey Staff (2010). After that, several random samples were taken for each site in order to obtain a composite soil sample where was dried and then crushed by a 2 mm diameter sieve and stored in plastic containers for analysis to estimate their physochemical properties. As shown in Table 1 according to the methods in Al-Zu’bi, et al. , 2013).

| Table (1) Some physiochemical characteristics of the study soil |
|---------------------------------------------------------------|
| Texture and classification | ECE (dS. m⁻¹) | pH | S | O.M | Soil content (gm.Kg⁻¹) | Soil Separation |
|---------------------------------------------------------------|
| Carbon | Organic Total | Carbonate | Minerals | Sand | Silt | Clay |
| CEC (cmol c kg⁻¹) | | | | | | |

2
Sequential Extraction Fractionation:

To divide the total content of the Lead by extracting the soil in a sequential way to identify the nature of its distribution within the various soil stages according to the following context: The first phase included the work of water balance using water distilled by (1: 20) (soil: water) left to equilibrium (48) hours after the filtration was separated by filtration method to determine the soluble content of Lead. The second phase was followed by the second extraction phase using (0.005M) (DTPA), (1: 2) according to the proposed method as defined by Lindsay and Norvell (1978). After the equilibrium for an hour, the stabilizers were separated for the purpose of Lead estimation. The third extraction phase was followed by dilute hydrochloric acid solution (0.1M) until the silt and furan disappeared as evidence of carbonate removal. Followed by the Lead extraction phase associated with amorphous Fe Oxides (AFeOx) in Phase fourth using a (0.25M NH₂OH solution. HCl + 0.25M HCl) and 5:50 (soil: solution) with stirring for 30 minutes and heating in a water bath at 50 ° C followed by the fifth extraction phase with 20% H₂O₂ solution until the color of the sample Pale. And then separated the stabilizers for the purpose of determining the content related to the organic matter followed by the sixth and final phase, including mechanical separation of sand using a 50 micron, clay and sludge in the manner of deposition and pouring according to the law of Stoke and then digested each separated by using wet digestion method to determine the residual content Residual content (Sand, Silt, Clay). Lead was measured in solutions and extracts in the solutions above using GBC 933 plus atomic absorption device.

Results and discussion

1. Water soluble part:

This phase expresses the ion type in the water solution balanced with the exchange part. It is important that it expresses the potential ion migration of these ions and expresses the ability of the water and the saline solutions to extract part of the exchange phase and part of the deposited minerals. The mobile fraction of the heavy metal ion is expressed in the soil. Table (2) shows the water soluble Lead values for the two study sites (0.33 to 0.34) mg.kg⁻¹ for the two textures (Argids) Clay and (Orthents) Sandy Clay Loam respectively, at 0.34 mg.kg⁻¹ and 0.10% The soluble fraction is very small in the soil of the study, although the study sites are irrigated with the water of the stream. This can be explained by Rieuwerts et al. (1998) that very small amounts of lead ions can be present in the solution at pH 6 or 7 higher by adsorption on the surface of different soil components, Reaction number (pH> 7). Which supports the hypothesis of not starting to extract dissolved ions by many researchers (Huang et al., 2002; Kashem and Singh, 2002) In addition, sedimentation in calcareous soil conditions and lower solubility values for soil element compounds help to make these quantities very low (Sabah, 2007)

| Part                      | quantities of Lead extracted during sequential extraction stages(mg.Kg⁻¹) | % from Total Content |
|---------------------------|--------------------------------------------------------------------------|----------------------|
| Soluble                   | 0.33                                                                     | 0.34                 | 0.34                | 0.10              |
| Exchange                  | 15.14                                                                    | 7.01                 | 11.08               | 3.31              |
| Carbonate Minerals        | 261.20                                                                   | 87.50                | 174.35              | 52.04             |
| Organic Matter            | 29.60                                                                    | 23.00                | 26.30               | 7.85              |

Table (2) quantities of Lead extracted during Sequential Extraction stages
2. Exchange part:

This phase or part expresses the formula on the surface of the collides (organic matter and Clay) which is in equilibrium with the balanced liquid soils. Its importance is expressed as the expression of the ionic migration or migration of these ions towards the water solution. As shown in Table (2) from (15.14 to 7.01) mg. kg\(^{-1}\), the values of the (Argids) Clay and (Orthents) Sandy Clay Loam respectively ranged at 11.08 mg. kg\(^{-1}\) and by 3.31% of the total content. They agree with what happened (Sabah, 2007) on the soil and sediments of Iraq with a calcareous origin. In general, they are relatively small compared to the ratio of ions associated with other soil components.

3. The part associated with oxides:

The results shown in Table (2) show that the Lead values associated with oxides ranged from 14.20 to 76.29 mg. kg\(^{-1}\) for both (Argids) Clay and (Orthents) Sandy Clay Loam respectively, at average 45.25 mg. kg\(^{-1}\) and 13.51% of the total content.

The high values of Lead ions associated with oxides, despite the fact that these oxides form a low percentage compared to clay deposits, are due to their high surface area. Helal (2006) found that small quantities of Lead parts do not exceed (16%) of the amount adsorption on iron or aluminum in the conditions (pH = 7) and that their release conditions increase with pH. This may be due to the high affinity of these oxides in the retention of the largest amount of heavy metals ions. This is confirmed by Hooda (2010) and Olaniran et al. (2013), who described the unfixed iron oxides as excellent scavengers of elements. This is reflected in the environmental importance of these oxides, which lies in the acquisition of the largest amount of ions of heavy metals contaminated in the With a pH of more than 7 (Bolton and Evans, 1996), either in the form of a pack or composition of small minutes or by combining two or more of the following processes (co-precipitation, adsorption, surface complex composition, ion exchange, or the formation of oxidizing secondary metals containing heavy metal), which reduces the harmful effect of these ions on the environment (Gu and Evans, 2008), which explains why the heavy drop of heavy Lead (soluble and exchange) in both soil is clearly reduced. In dry environmental conditions, the formation of more crystallization and stable structures that can stabilize the Lead. In this respect, the degree of soil reaction (pH) acts on the reciprocal exchange of the proton with the micro-adsorbsents on the surface of the oxides (Boparai et al., 2011) (pH) for sedimentation, solubility, oxidation and reduction of induced oxides (Cave and Talens-Alesson, 2005; Tack et al., 2006; Violante et al., 2010) that oxides have the ability to scavenging archaeological elements with high efficiency. The results obtained in Table (2) showed that non-crystallized iron oxides had a significant contribution to Lead ion capture compared with other soil components, because they did not have a high surface area.

4. The part related to organic matter:

The results shown in Table (2) show that the Lead values ranged from 29.60 to 23.00 for both (Argids) Clay and (Orthents) Sandy Clay Loam, respectively, at a rate of (26.30) mg. kg\(^{-1}\) and 7.85% of the total content. The high efficiency shown The organic matter in Lead ion adsorption may be due to the high affinity and preference of the material to the metal ionic ions, especially the two (M\(^{2+}\)) (Adriano et al., 2002) due to its high surface quality (800-900 m\(^2\) .gm\(^{-1}\)) and a high positive ion exchange capacity of 150-300 cmol c kg\(^{-1}\) soil (Al-Khatib, 2008), as well as to the variation in the effect of ambient conditions in the member material. Such as moisture, reaction number, C / N ratio of

| Oxides     | 14.20 | 76.29 | 45.25 | 13.51 |
|------------|-------|-------|-------|-------|
| Clay       | 43.84 | 10.77 | 27.31 | 8.15  |
| Silt       | 22.23 | 3.59  | 12.91 | 3.85  |
| Sand       | 44.46 | 30.50 | 37.48 | 11.19 |
dissolved material, quantity and quality of clay, which have an effect on the degree of decomposition of organic matter, or as a result of interferences between organic colloids and mineral deposits in soil (Tan, 2005) Two assumptions are:

First, the predominance of Smectite minerals in soil can reduce the bio-decomposition of organic material (Tan, 2005) which negatively impacts the process of providing new charged organic surfaces. Second, the formation of bonds or overlaps between organic colloids and metal colloids (clay colloids and oxides) is soluble and insoluble with heavy metals, which depend on the degree of reaction of the medium and the structural properties of the organic part, may cause the closure of the available exchange sites on the surface of the colloids, Variance in the exchange capacitance values of the positive ions of these colloids. The adsorption of organic matter to metals can be interpreted as an ion exchange between hydrogen and metals on the surfaces of the acid active groups (L) (Tan, 2005), as shown in the following equation:

$$M^{x+} + yLH^+ = L^-M^{(x-y)+} + yH^+$$ ........................................ (1)

The bonding of Lead with the active groups of organic matter will lead to the formation of inner-sphere complexes with covalent and ionic bonds. The adsorption process is a chemical adsorption process where the adsorption of organic matter is preferable to metals at the reaction level (5). To the formation of "inner-sphere complexes" with organic soil, while low-priority metals tend to retain the hydrogenic membrane and remain interdependent on organic soil matter (Erdogan et al., 2007; Sposito, 2008; Tang et al., 2014). The retention of heavy metal ions into the charged organic surfaces resulting from dissociation and ionization of the groups of carboxylates and active functional phenols. (Motuzova, 2012) arises at pH <6, and is strongest at the neutral conditions of the pH (7-7.5) (Evans et al., 2003). Although the ion capture mechanism is not yet clear by effective functional groups yet(Uchimiya et al., 2010; Cao et al., 2010). The physico-chemical path of heavy metal ions is the result of physical, chemical, and biological effects in the ecosystems in which these ions are present and which in turn affect biogeochemical processes in these systems, as shown in Figure 1.

![Figure 1](image.png)

**Figure 1.** Mechanical ion correlation of expected Lead in the components of the study soil
5. Carbonate-related part:

The results shown in Table (2) show that the Lead values ranged from 261.20 to 87.50 for both (Argids) Clay and (Orthents) Sandy Clay Loam, respectively, at a rate of 174.35 mg kg\(^{-1}\) and 52.04% of the total content. It appears from the results of Table (2) that Lead ion concentrations associated with carbonate minerals were relatively high compared to dissolved and exchange values. The present study assumes that heavy ions may be associated with the bicarbonate ions available in a soil solution, a complex component of the heavy metal bicarbonate, which can be symbolized by MHCO\(_3^+\), which has a very high correlation coefficient (Hirsch et al. 1989). Or can be linked to carbon surfaces by chemical adsorption (chemisorption).

It is clear that the important part of the ion's presence in the soil environment and its impact on the pollution process is the knowledge of the most ready-made image, which is the weakest image associated with colloids surfaces (Evans, 1989), and the most environmentally dangerous because of the easy release of the contaminated ion and its entry into the food chain (Lahucky et al., 2001). It is one of the important tracks in the retention of heavy metals in calcareous soils is the process of adsorption on the effective surfaces of calcite, dolomite and magnesite. These minerals exist in the soil and are characterized by their differing ability to absorb the ions on their surfaces. Calcium and magnesium ion may be substituted for Surface layer This depends on the concentration of the metal. In the case of an increase in soil solution, more layers are formed on the surface and sedimentation occurs (Ma et al., 2012; Sdiri et al., 2012). There are also various types of sedimentation such as containment Inclusion, adsorption and Solid solution formation formed by Trace element and mineral (Sposito, 2008). The results of (Brown et al., 2005; Gray et al., 2006; Geebelen et al., 2006; Chen et al., 2012), using calcium carbonate (Lime) in curbing heavy metals in high melting conditions The carbonate's ability to adsorb positive ionic species to heavy metals can be explained by the presence of an electrical charge on the surfaces of carbon metal The phases of the adsorption process can be explained on the carbonate surfaces:

1. Ion adsorption of heavy metal on carbonate surfaces. 2. The phase of the spread of the ion into the surface of the source. 3. Formation of the M-OH-Carbonate nucleus A cell nucleus in the solution grows and crystallizes new crystalline materials of new calcium carbonate such as \((\text{Pb (CO}_3\text{)}_{\times1} \text{OH})\) which can be represented in Figure (2) \(\text{M}^{+2}\) on the surface of carbonate-water (Calcite-Water): -
6. The clay-related part:

The results indicated in Table (2) that clay separators retained Lead values ranging from (43.84 to 10.77) for (Argids) Clay and(Orthents) Sandy Clay Loam respectively, at a rate of 27.31 mg.kg\(^{-1}\) and 8.15% of the total content.

The discussion of the remaining fraction of clay, silt, and sand from the fourth stage of successive extraction was based on the effectiveness of the clay as the only remaining colloid fraction that has adsorption. Which is of great importance in determining the physical and chemical properties of the soil because of the large surface areas where the surface quality of (15-20) m\(^2\).gm\(^{-1}\) of kaolin mineral, (280, 500) m\(^2\).gm\(^{-1}\) of montmorlonite mineral (Mustafa,2005) and so the clay is a good adsorbed used as a means to treat soils contaminated with heavy metals (Diaz et al.,2007; Sen Gupta and Bhattacharyya,2008 ; Chotpantarat et al.,2011; Pare et al.,2012;Mustafa et al.,2012). The reduction in the amount of heavy ions associated with clay separates despite its segregated disposal of a high surface area with the dominance of the montmorlonite mineral The exchange capacity of the high positive ions within the study periods is that the variation in the values of the Lead ion associated with the minutes separated by the Clay between the two soil may be due to the difference in the body that may Al-Kaysi (1983) found that most of the carbonate minerals in Iraqi soils were in single or bond form, and a few of them were in the form of wraps around soft soil minutes (Al-Dulaimi, 2000), when it was studied in the middle of Iraq, which is reflected in the efficiency of adsorption of clay-separated minutes to those ions. This variation can be attributed to the closure of the exchange sites and the inhibition of adsorption on the surfaces of those minutes through the formation of organic membranes or casings of crystallized iron oxides (Brown et al.,2005) The predominance of montmorlonite minerals in the soil of the study soil is of environmental importance by holding it to a section of heavy metal ions added to the soil with high binding strength at specific adsorption sites. These ions are restricted at these sites and are not affected by the high concentrations of the main cations in solution Soil (Ca\(^{2+}\), Mg\(^{2+}\), Na\(^{+}\)) (McLean and Bledsoe, 1992).

7. The part related to silt and sand:

This value reflects the fraction associated with the heavy metals and silica compounds that represent the dissolved value of the concentrated acid. Although the silt and sand separators do not have loaded surfaces, as in clay, the values we obtained reflect the inherited part of the separated component. From (22.23 to 3.59) for both (Argids) Clay and(Orthents) Sandy Clay Loam respectively for the silt average at 12.91 mg.kg\(^{-1}\) and 3.85% of the total content. As for the sand-related component, the values ranged from 44.46 to 30.50 for both (Argids) Clay and(Orthents) Sandy Clay Loam, respectively, at 37.48 mg.kg\(^{-1}\) and 11.19% of the total content. As shown in table (2). Al-Nuaimi (2011) found in her study of (12) a samples of river sediments from different areas along the eastern side of the Tigris River between the Mosul Dam and the Qasr area.

Physiochemical pathway of Lead in the soil environment:

The data of Figs. (3 and 4) showed that the physiochemical pathway of the Lead in the soil environment associated with the main soil components was distributed in the following order:

Solid carbonates >Sand> Clay> Organic matter >Silt> Exchange> Oxides> Soluble. (Aden district) of the clay texture (Argids).
Figure (3) Physiochemical behavior of the distribution of total Lead content in clay texture (Argids)

Solid carbonates > Oxides > Sand > Organic matter > Clay > Exchange > Silt > Soluble. (Al-Mazara district) of the sandy clay loam texture (Orthents).

Figure (4) Physiochemical behavior of the distribution of total Lead content in the sandy clay loam texture (Orthents)

It seems from the results of the study that the characteristics of soils and chemical and physical water have an impact on the determination and the dominance of Lead parts within their different separations. The results of the present study also show that the Al-mazara (sandy clay loam) soil has a
low organic matter content due to the low percentage of the associated part of the Lead as well as the decrease of its surface area and its exchange capacity through the part associated with the surfaces exchanged. In addition, most of the Lead parts have been associated with carbonate and separated in clay texture, as opposed to sandy clay loam. The separators were the least carbonate and were relatively interdependent and associated with organic matter. This may be due to the low soil content of organic matter. The increase in Lead within the carbonate separation leads us to the conclusion that the conditions of calcareous soil (high reaction rate and high content of carbonate minerals) contributed a large part of Lead bonding and deposition of Lead carbonate minerals based on melting ratio of these minerals compared to carbonate minerals, (7.4×10^{14}, 2.8×10^{9}) respectively, in addition to the possibility of adsorption of Lead on carbonate surfaces or entry into the crystalline structure of carbonate metal and thus make these soils a safe repository for the disposal of these heavy ions as part of the treatments. To illustrate the dynamics of heavy metal ions in soil components above, the current study suggested the following mechanisms:

When the soil receives the ions of heavy metal from different sources (irrigation water, phosphate fertilizers and wind deposits), these ions are subject to binding forces ranging from weak forces of attraction and strong chemical bonds by the ions of the soil solution on the one hand or by the existing negative charges on the colloidal surfaces on the other. These correlations depend on several factors: the concentration of heavy ions flowing into the soil, ionic efficiency, equivalence, ion volume, substitution capacity, ion exchange constants, mean reaction type and negative charge type and density on colloidal surfaces (Ugochukwu et al., 2012; Ali and Salem, 2012). Because the soil of the study is calcareous by nature, calcium ions and bicarbonates are certainly predominant in the soil solution, which makes them dominant over all the chemical reactions taking place in the center.

Therefore, high-concentration calcium ions must compete with these ions on adsorption surfaces (minutes separated by clay, oxides, carbonate minerals, and organic matter), which are most pronounced at the surface of mined clay, most of which carry permanent charges. Based on the pH-dependent number on the surfaces of other soil components (oxides and organic matter). Therefore, the negative charges on the surfaces of mined clay are stronger than those on the surfaces of both oxides and organic matter. Thus, the attraction of calcium ions to mined clay is faster and stronger in the first moments of the exchange process than its attraction to the surfaces of oxides and organic matter. Which may increase the movement of these ions in the soil body (McLean and Bledsoe, 1992). This assumption is further enhanced by the reduction of ions associated with the clay-separated minutes compared to other soil components. The bond of heavy metal ions in the soil solution of the study by the carbonate surfaces can be interpreted according to the presumption mentioned above (carbonated part).

In general, the overall rate of the study sites, regardless of texture, the physiochemical pathway of lead in calcareous conditions prevailing in the region was as follows:

Solid carbonates > Oxides > Sand > Clay > Organic matter > Silt > Exchange > Soluble.

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