

Original Research Article

Mobility and Fractionation of Cobalt in Some Calcareous Soils in Iraqi Centre

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Article History

Received: 03.11.2023

Accepted: 08.12.2023

Published: 13.12.2023

Abstract: Pollution is one of the major threats with potential risks to humans, animals and plants, especially pollution with heavy metals, which are characterized by their significant ability to accumulate in environmental systems and induce toxicity to living organisms, even at low concentrations and quantities. This study was conducted on some calcareous soils selected from the provinces of Babylon and Diwaniyah. Soil samples were collected from ten sites, five sites from each province, from a depth of 0-30 cm, to determine the concentration of cobalt in its chemical forms (available, bound to calcium carbonate, bound to organic matter and oxides, and residual) and total concentration, in addition to knowing the effect of different soil characteristics on these chemical forms. The results showed that there was a relatively wide range in the total cobalt concentration in the study sites (16.58 - 86.76 mg kg⁻¹), and the percentages of the available chemical phase of the metal ranged from 0.44% - 6.88%, and in the form associated with carbonates from 19.30% - 34.54%, and in the form associated with organic matter and oxides from 28.82% - 55.94%, and in the form associated with the residual fraction from 3.46% - 51.44%. Because the metals in these fractions might dissolve depending on environmental conditions, notably pH values, higher mobility levels of accessible metal ions and those partly bonded to calcium carbonate may suggest environmental contamination and a risk of toxicity in soils.

Keywords: Cobalt, Soil Pollution, Calcareous soil, Chemical fraction, pH.

INTRODUCTION

Pollution is one of the major threats with potential risks to humans, animals and plants, especially pollution with heavy metals, which are characterized by the great ability to accumulate in environmental systems and cause toxicity to living organisms even if it is in small concentrations and quantities (Dogan *et al.*, 2014). Some heavy metals are essential for plants as well as humans, but if their amount exceeds the permissible limit, it is considered a pollutant. These metals are likely to accumulate in the soil from natural and anthropogenic sources such as motor vehicles, industries, fertilizers, pesticides, and wastewater, thus the soil becomes a storehouse for these toxic elements. These factors are all responsible for soil and plant pollution and thus their impact on the health of living organisms (Khan *et al.*, 2020; Jadaa and Mohammed, 2023).

Heavy metals are non-degradable and can persist in the soil for extended period due to their adhesive characteristics, thus examining the factors affecting their solubility and availability in soil may shed light on appropriate methods for improving contaminated soil or water to achieve more acceptable environmental conditions, and thus clay minerals control their biological accessibility in soil (Rodrigues and Römken, 2018; Al-Mashhadi *et al.*, 2023).

Cobalt is one of the heavy metals that are essential to the existence of all living things. It primarily controls biological reactions, boosting the immune system's responsiveness to vitamins and hormones, and initiating the process by which heavy metals enter the food chain through plant absorption from the soil, and thus their transmission to humans and animals. Nevertheless, the concentration of heavy metals are mostly affected by the chemical properties of the substances and the physical properties of the soil such as pH, soil organic matter content, cation exchange capacity, calcium carbonate

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Citation: Ali Akram Abdulateef, Hazim Aziz Al-Robai, Layth Joudah Kareem Aldaini (2023). Mobility and Fractionation of Cobalt in Some Calcareous Soils in Iraqi Centre. *South Asian Res J Agri Fish*, 5(6), 81-87.

minerals ratio, soil texture and clay content. Primary and secondary minerals content of the metal is considered relatively safe because, the metal is not easily released under normal conditions (AL-Robai and Al-Jbouri, 2020).

Cobalt is one of the heavy metals found in the environment. Its sources include naturally occurring sulfides, arsenide minerals, metal oxides (from copper, nickel and iron), excessive use of fertilizers, waste water discharge, coal combustion processes and motor fuels. However, surpassing the acceptable cobalt levels in soil, water and air could potentially threat plants, animals and humans, leading to the development of severe diseases (Abdulateef and Naser, 2021; Tsamo *et al.*, 2022).

The cobalt content of the topsoil usually ranges between 1 to 40 mg kg⁻¹, and the majority ranges between 3 to 15 mg kg⁻¹. Contributing factors to cobalt deficiency in plants and grazing animals are mainly related to calcareous or alkaline soils, light soils, and their high content of organic matter. Since cobalt has a significant impact on plant growth, it is important to keep an eye on the amount of cobalt in the soil in order to determine its toxicity. 25–50 mg kg⁻¹ are the limiting critical limits for soil (Alloway, 2013). The purpose of this study was to ascertain whether certain calcareous soils in two provinces of Iraq were contaminated by chemical forms of this metal.

MATERIALS AND METHODS

Field and laboratory procedures

Babylon and Diwaniyah provinces-Iraq, were selected to collect soil samples from ten study sites at depth of 0-30 cm. Soil samples were air dried, then grounded and sifted through a 2mm sieve to prepare 1:1 soil extracts. Various physical and chemical of soil properties were determined under condition of this study. The pH of the soil was determined using the method presented in Jones (2001), and the electrical conductivity (EC) of soil samples were measured based on the method of water extracts described by Page *et al.*, (1982). The hydrometer method was used to determine soil texture (Raine *et al.*, 2003). Cation exchange capacity (CEC) was estimated by the simplified methylene blue method for calcareous soils, as detailed by Savant (1994), while organic matter (O.M) was estimated using the wet oxidation method according to the Walkley-Black method as described by Black *et al.* (1965). Total carbonate minerals (CaCO₃) were determined gravimetrically following the method mentioned in the U.S. Salinity Laboratory staff (1954). Table 1 showed the results of the determined soil properties for the selected soil samples.

A modified single sequential extraction technique

The metal fractions (chemical forms) in the soils were identified using a five-step single sequential extraction process (Badri and Aston, 1983; Ismail and Ramli, 1997). Five fractions of the heavy metal are separated by the modified and devised approach.

1. Fraction 1: *EFLE stands for easily, freely, or leachable and exchangeable.* 25 ml of 1.0M ammonium acetate (NH₄CH₃COO), pH 7.0, was constantly shaken with 5 g of the sample for 3 hours at room temperature.
2. Fraction 2: *metal bound to carbonate* 25 ml of 1.0M ammonium acetate (NH₄CH₃COO), pH 5.0, was constantly shaken with 5 g of the sample for 5 hours at room temperature.
3. Fraction 3: *Oxidisable-organic.* First, 7.5 ml H₂O₂ (R&M Chemicals, 35%) was added to 5 g of sample and heated to 90°C in a water bath. Following cooling, the metal extracted from the organic complexes was shaken constantly for three hours at room temperature using 25 milliliters of 1.0M ammonium acetate (NH₄CH₃COO), which had been acidified to pH 2.0 using HCl.
4. Fraction 4: *Residual.* The primary and secondary minerals contain the majority of the metal in this fraction (Wu *et al.*, 2004). The estimation process involved deducting the total fractionation fractions of the available cobalt element, as well as those linked to carbonates, oxides, and organic materials, from the total metal concentration, using the approach described by Fathi *et al.*, (2014).
5. Total fractions 5: *Total concentration of metal.* A 50 ml Pyrex vial was filled with 1 gram of the air-dried soil sample, which had been filtered through a 2 mm screen. 5 ml of nitric acid (HNO₃) was then added, and the mixture was allowed for a full day. The samples are heated to 80 °C for an hour, then they are allowed to cool naturally for a while. Next, 5 ml of perchloric acid (HClO₄) is added and heated to 180 °C for two to three hours, or until the samples' color changes from dark brown to a clear, colorless liquid. Jones (2001).

Table 1: General analysis of soil properties for the collected samples

No.	Site	pH 1:1	EC dS m ⁻¹	CEC Cmol(+) Kg ⁻¹	O.M %	CaCO ₃ %	Clay %	Silt %	Sand %	Soil Texture
1.	Babylon (Al Musayab)	7.50	6.53	18.15	0.67	18.45	15.77	63.11	21.12	Silt Loam
2.	Babylon (Al Nile)	7.22	7.73	15.97	0.43	14.77	10.58	48.81	40.61	Loam
3.	Babylon	7.48	6.81	17.36	0.54	15.88	13.44	69.50	17.06	Silt Loam

No.	Site	pH 1:1	EC dS m ⁻¹	CEC Cmol(+) Kg ⁻¹	O.M %	CaCO ₃ %	Clay %	Silt %	Sand %	Soil Texture
	(Abi Gharaq)									
4.	Babylon (Oufi)	8.12	2.11	25.11	1.28	28.96	41.80	33.60	24.60	Clay
5.	Babylon (Al Qassim)	7.74	4.03	23.42	1.03	24.38	32.06	53.60	14.34	Silty Clay Loam
6.	Diwaniyah (Al Saniyah)	7.59	5.14	19.28	0.75	20.52	17.40	67.60	15.00	Silt Loam
7.	Diwaniyah (Al dighara)	7.73	4.25	22.07	0.92	23.77	29.58	54.48	15.94	Silty Clay Loam
8.	Diwaniyah (Al shaamia)	7.61	4.59	21.43	0.82	21.62	23.33	58.97	17.70	Silt Loam
9.	Diwaniyah (Al shaafiaia)	7.17	10.53	13.46	0.37	14.06	3.77	52.08	44.15	Silt Loam
10.	Diwaniyah (Sumer)	7.92	3.19	24.64	1.17	27.02	35.07	40.56	24.37	Clay Loam

RESULTS AND DISCUSSION

Table 1 lists the general analysis of soil properties, in terms of pH, electrical conductivity, cation exchange capacity, organic carbon, calcium carbonate, and soil texture, the soils exhibited a wide range of soil attributes values. These calcareous soils have pH inherently somewhat alkaline with values range from 7.17 to 8.12. The obtained results showed a broad range of EC with lowest value of 2.11 dS m⁻¹ and a highest value of 10.53 dS m⁻¹. The range of results for cation exchange capacity were 13.46 to 25.11 Cmol(+) Kg⁻¹. The organic matter values ranged from 0.37 to 1.28 percent, whereas the range of calcium carbonate levels were 14.06 to 28.96 percent. The primary causes of these values in the examined samples are the carbonate rocks and their aridity.

The results of Cobalt available form (F1) showed a lowest percentage of 0.15% in Babylon province at Oufi study site, while the highest percentage in the Diwaniyah Province (Al-Shaafia study site) with percentage 6.88% with values of 0.13-1.14 mg kg⁻¹ of the total metal content as showed in Figures 1 and 6. Cobalt ions concentrations, which bound to carbonates (F2) of the studied soils, recorded the highest value of cobalt concentration in the province of Babylon (Oufi study site) 17.39 mg kg⁻¹, and the lowest value was in the province of Diwaniyah (Al-Shaafia study site) where it reached 5.95mg kg⁻¹. The highest percentage of cobalt associated with carbonates was in the province of Babylon (Al-Nile study site) represent 34.54%, and the lowest percentage was in the province of Diwaniyah (Sumer) represent 19.30% of the total content of metal (Figure 2 and 6). Figure 3 and 6 showed the concentrations of cobalt bound with organic matter and oxides in soil samples, where the lowest value was in the province of Diwaniyah (Al-Shaafia study site) where it reached 6.85 mg kg⁻¹ and the highest value of metal concentration was in the province of Babylon (Oufi study site) 25.94 mg kg⁻¹. The highest percentage was in the province of Babylon (Al-Nile study site) 57.11%, and the lowest percentage was in the province of Diwaniyah (Sumer study site) where it reached 28.82% of the total content of element,

The residual cobalt content in soil samples as displayed in Figures 4 and 6, showed that the study sites Oufi in Babylon province have the highest concentration of residual cobalt with values of 43.30 mg kg⁻¹ and Sumer in Diwaniyah province with percentage 51.44% have the highest residual concentration. While the lowest values of residual cobalt concentration in Al-Nile study site of Babylon province with value of 0.70 mg kg⁻¹ and percentage of (3.46%).

The total cobalt concentrations in soil samples as showed in Figure 5. The province of Babylon (Oufi study site) had the greatest cobalt content, with value of 86.76 mg kg⁻¹, while the province of Diwaniyah (Al-Shaafia study site) had the lowest, with value of 16.58 mg kg⁻¹.

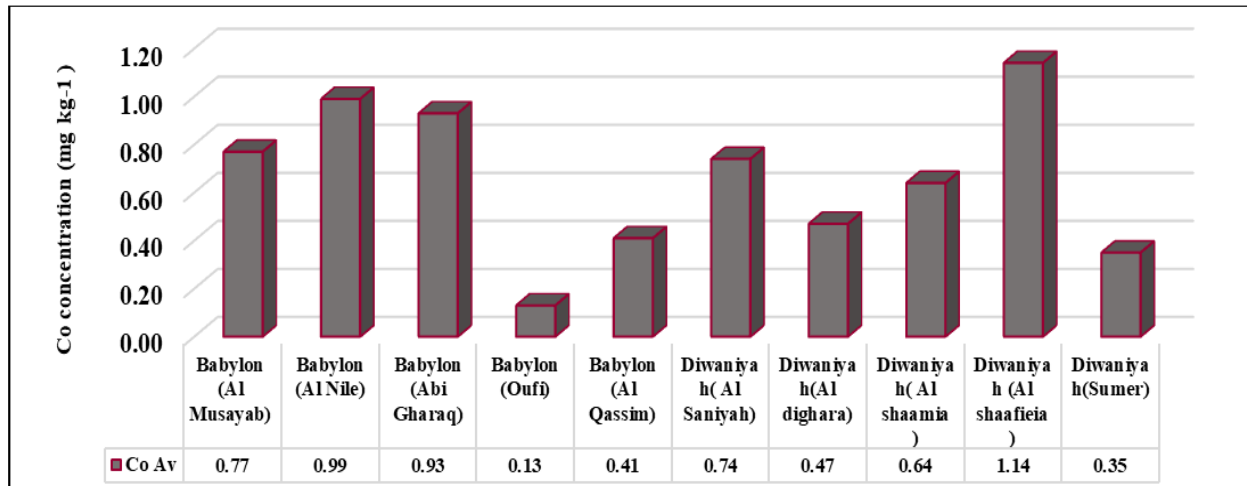


Figure 1: The concentration of available cobalt (mg kg⁻¹) in soil samples of study sites

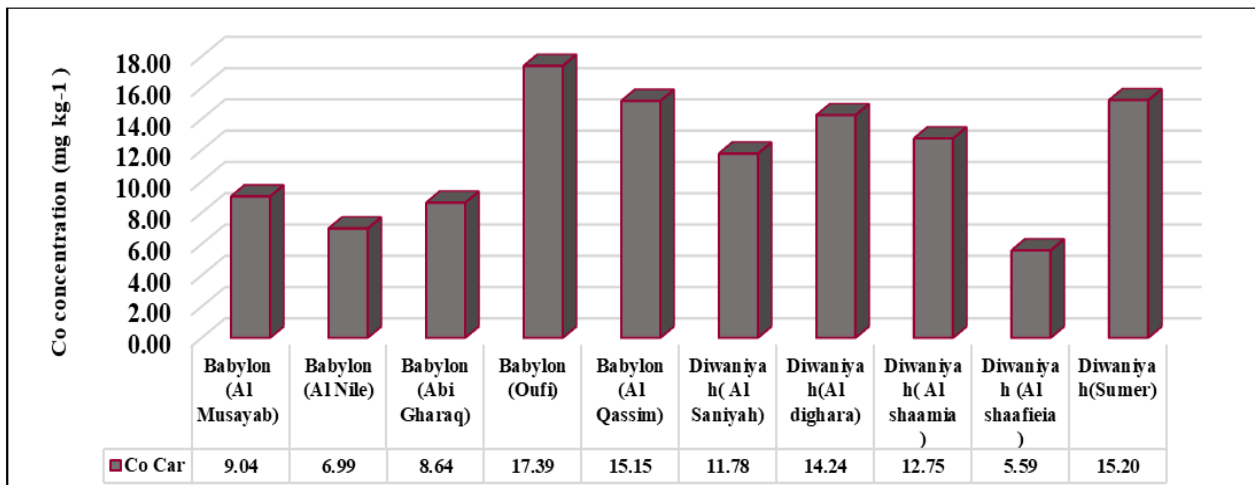


Figure 2: The concentration of cobalt bound to carbonate (mg kg⁻¹) in soil samples of study sites

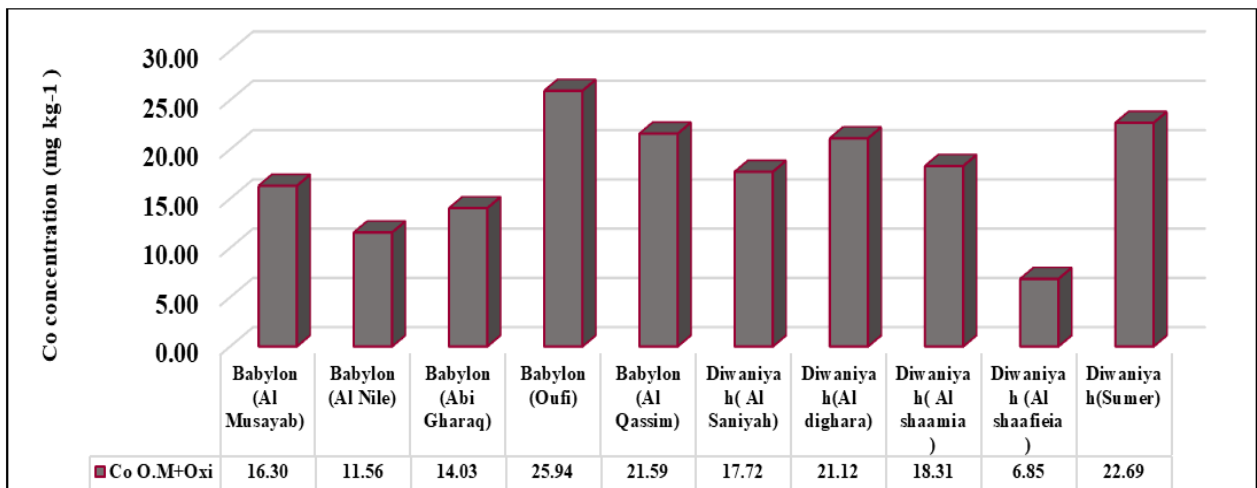


Figure 3: The concentration of cobalt bound to organic matter and oxides (mg kg⁻¹) in soil samples of study sites

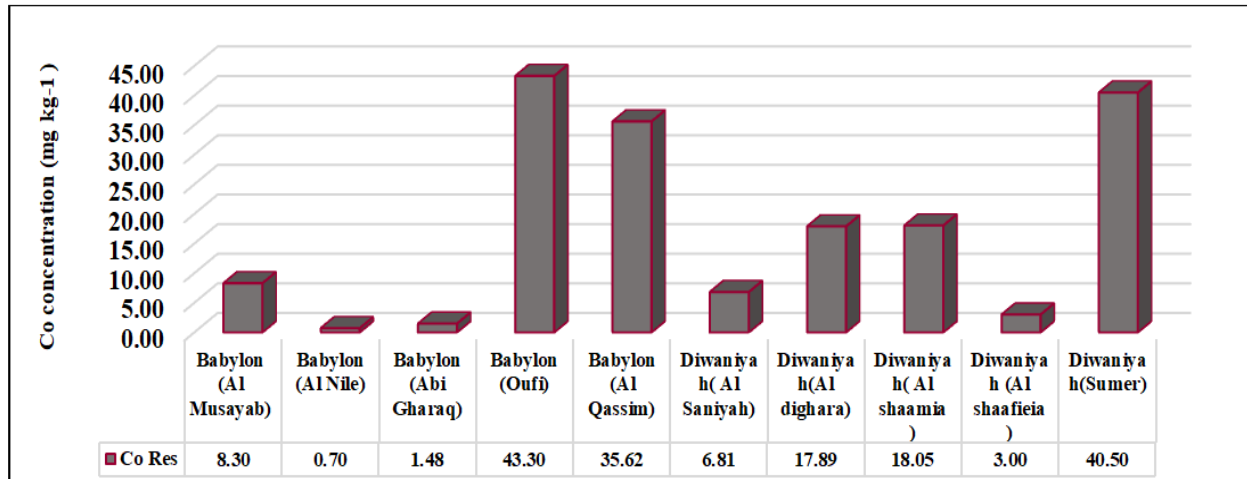


Figure 4: The concentration of residual cobalt (mg kg⁻¹) in soil samples of study sites

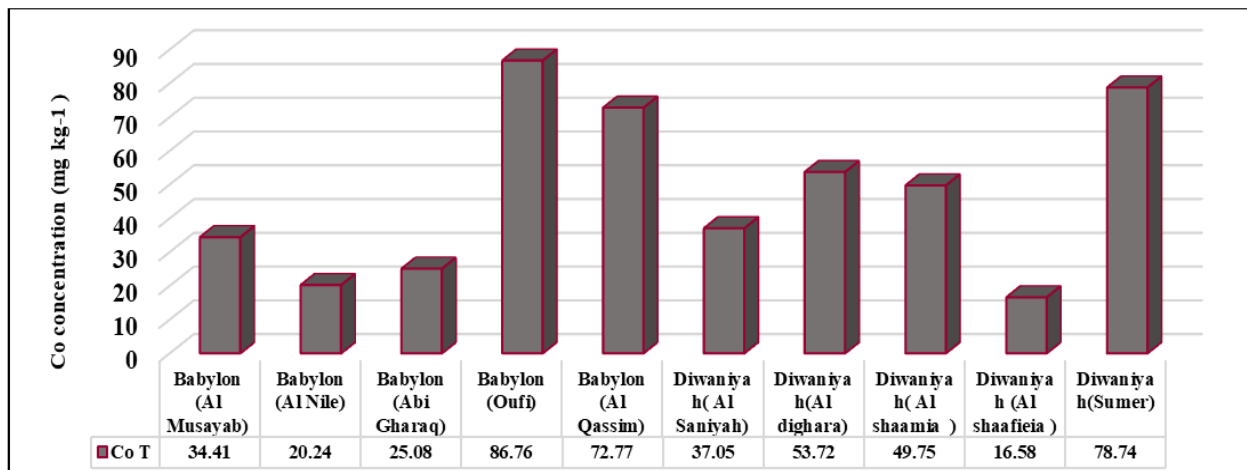


Figure 5: The total concentration of cobalt (mg kg⁻¹) in soil samples of study sites

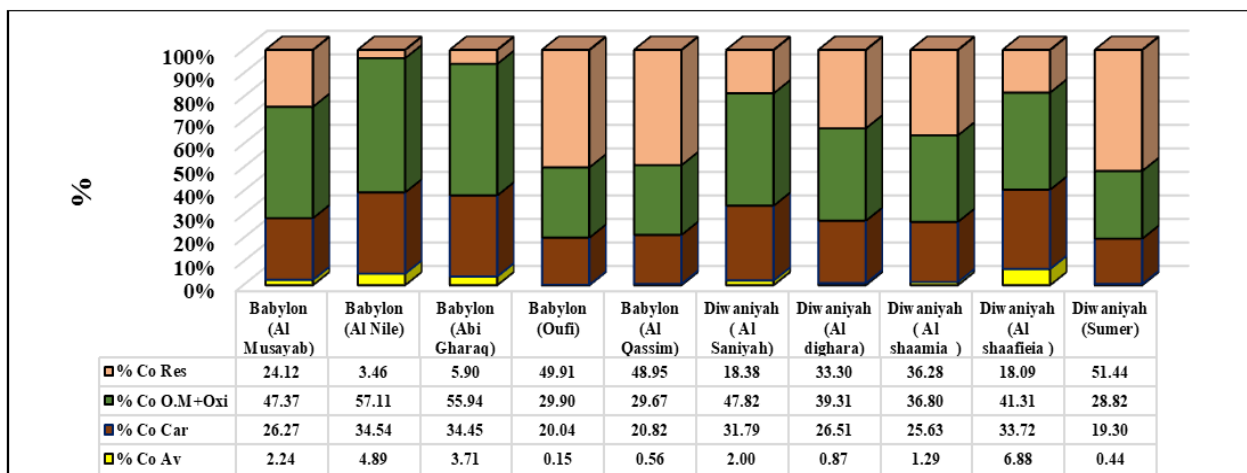


Figure 6: Chemical fractionation percentage of cobalt in soil samples from the study sites

According to the obtained results of this study, heavy metals concentrations are obviously affected by soil's pH, CaCO₃, organic matter content, and clay component content (Smith and Paterson 1995; Adriano, D. C. 2001; Moghal *et al.*, 2017).

The bioavailable concentrations of cobalt increased as pH decreased, as demonstrated by Table 1 and Figure 1 results. This is because a lower pH causes element and hydrogen ions to compete more for binding sites, by releasing ions

into soil by breaking down heavy metal complexes (Rama Krishnaiah and Somashekar 2002). According to the significantly correlation between bioavailable cobalt and soil properties the results of statistical analysis, showed a negative correlation ($r = -0.98^{**}$) between the bioavailable concentrations of cobalt ions and the pH values of soil samples. It was also shown that there is a significant positive correlation ($r = 0.98^{**}$) between the metal ions associated with carbonate minerals and the content of these minerals in the studied soils. It can result from the element forming free ions or from the metal binding to the surfaces of carbonate minerals as a bicarbonate complex by chemical adsorption (Hamza, 2005).

Due to the metal's strong affinity for organic matter (OM), there may be more complex formation between the metal and OM as OM content increases. This is supported by the presence of a positive significant correlation ($r = 0.97^{**}$) between cobalt ions associated with OM and the soil content of this material (Li *et al.*, 2020; Sungur *et al.*, 2015; Al-Jaba and Al-Robai, 2020).

Regarding the cobalt ions that are largely associated with the residual fraction represented by clay, it became clear that there is a significant positive correlation ($r = 0.94^{**}$) between them and the clay content of the soil. The reason for the low concentrations of cobalt ions associated with the residue fraction, despite having high exchange surfaces, may be due to the dominance of the competition process between the calcium ions prevalent in the study soil with the ions of this metal. On other hand the residual fraction considered relatively safe because, the metal is not easily released under normal conditions (AL-Robai and Al-Jbouri, 2020).

Because the metal ions in the 1 and 2 fractions can dissolve depending on environmental conditions, particularly pH values, and because these metals can be absorbed by organisms, greater mobility levels of Co may generally imply environmental contamination and a danger of toxicity in soils. The presence of high percentages of the available cobalt ions at Babylon 2 and 3 sites and Diwaniyah 4 site (Table 1), coinciding with a decrease in the total concentrations of the metal in these sites, indicates the presence of pollution that may come from human activities such as the use of sewage water, (Khan *et al.*, 2020), solid organic waste, and some fertilizers. The same applies to the metal ions associated with carbonates were concentrated in high percentages in the same sites above, which is another indication (partially) that their sources result from human activities.

On the other hand, the geological origins of the associated with residual form of cobalt could not be danger to the living organism, (Al-Hamdani *et al.*, 2016) due to their strong retention to the soil exchange sites.

CONCLUSION AND RECOMMENDATION

The study results lead to the conclusion that pH values significantly influenced the concentrations of available cobalt ions, particularly at Babylon sites 2 and 3, as well as Diwaniyah site 4. The elevated mobility of metal ions at these locations suggests potential environmental pollution stemming from human activities. Consequently, further investigations are recommended to assess the mobility of cobalt ions from contaminated soil to plants. Additionally, the study advocates for the implementation of environmental legislation to mitigate the disposal of pollutants into agricultural soil.

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