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Determination of Heavy Metals in Two Regions from Kirkuk City Using Sequential Extraction

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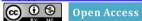Email: sabahkhaiat@gmail.com

Abstract

Soil is a major reservoir for heavy metals and other contamination as it possesses an ability to absorb these metals on the surface of clay minerals and bind various chemicals. These heavy metals and chemicals can exist in various forms in soil and different forces keep them bound to clay minerals and soil particles. The aim of the present work is to estimate the concentration levels of some heavy metals Zn, Cu, Pb and Cd in two sites of soil Kirkuk city. In this study the first sample was taken from inside the city of four areas around (Northern Oil Company) in Kirkuk city, while the second sample was taken from outside the city of four areas and both were randomly chosen. Sequential extraction procedure was applied to fractionate heavy metals which may help in the prediction of their mobility, bioavailability and fate of the metal contaminant. Results of sequential extraction showed that Cd and Pb were mainly bound to residual fraction, Cu was mainly bound to organic fraction and Zn was bound to Fe-Mn oxide fraction in the two sites of the study. The overall mean values obtained for the metals in the fractions gave the range: inside the city Cu (28.12 ppm), Zn (77.9 ppm), Pb (21.73 ppm) and Cd(4.21 ppm), and outside the city Cu (24.65 ppm), Zn (59.28 ppm), Pb (13.25 ppm) and Cd (2.38 ppm). The extracts were analyzed for heavy metal, using flameless-atomic absorption spectrophotometers (Flameless-AAS).

1. Introduction

In recent years, pollution by heavy metals from a metal recycling industry can become a very important source

of contaminated soils, air and water within the vicinity of the industry. Soil receives pollutants from a variety of sources, including automobile exhaust gases, and emission of factory chimneys, household electric power generators and dust storm [1]. Heavy metal contamination, which is common in soil throughout the world, poses a potential risk to human and animal health owing to migration through soil profiles into groundwater. Therefore, various remediation techniques have been applied to reduce the mobility and bioavailability of heavy metals in soil.

To effectively remediate heavy-metal-contaminated soil, it is necessary to know the amount of toxic elements in the soil. However, only determining the total concentration of heavy metals in soil is not sufficient because mobility and bioavailability are strongly dependent on the chemical phase of heavy metals in soil [2] [3]. Many researchers who studied the concentration of heavy metals in soils of Baghdad [4]-[6], Fallujah [7] Basra [8] and Babylon [9], also have estimated the effect of Kirkuk Oil Refinery on air of the city [10] [11]. Sequential selective extraction techniques are commonly used to fractionate the solid-phase forms of metals in soils. Many sequential extraction procedures have been developed, particularly for sediments or agricultural soils, and despite numerous criticisms, they remain very useful [12].

The theory behind sequential extraction is that the most mobile metals are removed in the first fraction and continue in order of decreasing of mobility. The number of successful applications of this method is rising because these extraction techniques provide information about heavy metal affinity to soil components and the strength of the bonds to the matrix [13]. One of the most widely-applied procedures was proposed more than 20 years ago by Tessier *et al.* (1979) [14]. A wide range of techniques is available whereby various extraction reagents and experimental conditions are used. These techniques involve a 5-step, 4-step [15], 3-step (BCR, Bureau Commune de Reference of the European Commission) [16] and 9-step [17] extraction, and are thus becoming popular and adopted methods used for sequential extraction.

2. Area of the Study

Kirkuk is one of the growing cities of Iraq and it is so largely due to presence of petroleum industrial resources also it is a centre for production and transporting petrol. Two areas were selected to study the concentration of heavy metal in soil. Four samples from the first area around (North Oil Company) within Kirkuk city. Another four soil samples were collected around 35 km to the north eastern Kirkuk city near the road between Kirkuk-Sulaimania, the distance between each sample around (1 km). The soil samples were collected using auger from 10 - 15 cm depth after removing surface organic materials.

The composite samples of soil were air-dried and milled so as to pass through a 2 mm sieve, homgenized and stored in plastic bags prior to laboratory analysis, the analysis of metals homogenised soil samples were ashed in a muffle furnace at 40°C for 1.5 hour and were digested by microwave assisted acid digestion [13]. Solution from digested soil samples were stored in 100 mL high-density polyethylene samples bottles at 4°C until analysis.

2.1. Aim of the Study

The aim of this paper is to study the effects of oil production and industrial activity of the (North Oil Company) on the soil pollution by heavy metals in the Kirkuk area, using sequential extraction method.

2.2. Reagents

All reagents were analytical reagent grade unless otherwise. Hydrogen peroxide, acetic acid, ammonium acetate, hydroxyl ammonium chloride, HCl and HNO_3 were of suprapure quality (Aldrich Chemie, Germany) All plastic and glassware were cleaned up by soaking dilute (1 + 9) and were rinsed with distilled water prior to use. Standard metals solution (1000 mg/l) were purchased from (BDH, Poole, UK) or prepared in lab from pure metals. All the soil samples were carried to laboratory and prevesed in a refrigerator at 3°C - 4°C.

2.3. Determination of Metals

Determination of cadmium, copper, zinc, and lead. The soil samples were digested using concentrated analytical grade HNO_3 and $HClO_4$. Approximate 0.5 g of dry soil sample was put into a glass vessel and 5 mL of concentrated HNO_3 was added. In succession, the glass vessel was heated on an electrothermal board at 150°C until the

mixture was nearly dried. Another 5 mL of concentrated HNO_3 and 3 mL of concentrated $HClO_4$ were added into the glass vessel and maintained at 150°C for 3 hrs. During the digestion process, a tundish was used to cover the mouth of glass vessel for preventing acid splashing. After cooling, the digested sample was decanted into a glass tube and diluted to 25 mL with 2% HNO_3. All AAS measurements were carried out using a Shimadzu AA-640 (graphite) AAS (Shimadzu Scientific Instrumental, Kyoto, Japan).

2.4. Sequential Extraction Procedure (SEP) [14]

The sequential extraction procedure used was similar to that of Tessier *et al.* [14] the procedure a pertionally groups heavy metals into the following five fractions:

F.1 = Soluble and exchangeable

The soluble and exchangeable metals from soil were extracted with 20 mL of a 1.0 M $MgCl_2$ solution adjusted to a pH of 7.0 by mechanical shaking for 1 h at 20°C.

F.2 = Bound carbonates

The carbonates in the residue from the previous step were extracted with 20 mL of a 1.0 M NaAc solution adjusted to a pH of 5.0 with HAc by continuously shaking for 4 h at room temperature.

F.3 = Bound to iron and manganese oxides

Metals bound to iron and manganese oxides were extracted from the residue of the second extraction by shaking with 50 mL of a 0.04 M $NH_2OH \cdot HCL$/25% HAc solution. The extraction was performed at 96 = 3°C for 5.5 h.

F.4 = Bound to organic matter

Metals bound to organic matter were extracted by pouring 7.5 mL of a 0.02 M HNO_3 solution and 12.5 mL of a 30% H_2O_2 solution adjusted to a pH 2.0 onto the residue from F3, then providing continuous agitation for 2 h at the temperature of 85°C. An additional volume of 7.5 mL of the 30% H_2O_2 solution adjusted to a pH of 2.0 is then added, while maintaining continuous and a temperature of 85°C for another 3 h. The solution was then cooled to room temperature. An aliquot of 12.5 mL of a 3.2 M NH_4Ac/20% NHO_3 solution was added and shaken for 30 min.

F.5 = Bounded to the soil (residual fraction)

The residue from F4 was quantitatively transferred into a digestion vessel and metals were dissolved in aqua regia using 7 mL of 10 M HCl and 2.3 mL of 15.8 M HNO_3. The temperature of the reaction mixture was slowly risen until reflux condition and maintained for >2 h. Three parallel extractions were carried out, in each case using 2.5 g soil. All solid/liquid separation was performed by centrifuging, at 5000 rpm for 15 min. The supernatant was removed and analyzed for metals. The residue was washed with 20 mL of de-ionized water. After centrifugation for 15 min the supernatant was discarded.

3. Results and Discussion

The total of the metals such as Copper, Zinc, Lead and Cadmium for the soil samples collected from two sites the first were collected from four areas within the city of Kirkuk and the second site were from four outside the city is presented in the **Tables 1-4** are from inside the city, which the **Tables 5-8** are from outside of the city.

Metal speciation in this context is taken to mean the fractionations of the total metal content in to exchangeable (bound to exchangeable sites of clay minerals), acid extractable (bound to carbonates and hydroxides), reducible (bound to Fe-Mn oxides), oxidisable (bound to organic matter) and residual (bound to clay minerals) forms. The chemical forms of the metal control its bioavailability or mobility [1]. The exchangeable and acid extractable fractions are mobile fractions that are easily bioavailable.

3.1. Bioavailable Species

The exchangeable and bond to carbonates species, corresponding to the first two fractions, are generally called "Bioavailable", as they exhibit a mobility relative to the environment and are potentially available for plants. Results show that the amounts of Zn, Cu, Cd and Pb in Bio-available from are very low, the abundance of metals in exchangeable fraction is (%1.35 Zn), (%3.75 Cu), (%10.96 Cd) and (%5.22 Pb) this for the soil inside the city, either with regard to percentages of the soil outside the city were ranged (%1.52 Zn), (%1.75 Cu), (%1.82 Cd) and (%5.29 Pb). Heavy metals in the exchangeable held by electrostatic adsorption represent the most mo-

Table 1. The concentration of heavy metal inside of Kirkuk city.

Cu	S1	S2	S3	S4
F1	0.1	0.5	0.6	0.8
F2	1.3	2.1	1.4	1.7
F3	4.7	3.5	2.9	2.0
F4	11.4	12.9	15.3	13.3
F5	8.4	8.2	11.6	9.8
Sum	25.9	27.2	31.8	27.6

Table 2. The concentration of heavy metal inside of Kirkuk city.

Zn	S1	S2	S3	S4
F1	0.6	1.3	0.9	1.5
F2	3.6	23	7.3	6.9
F3	41.0	48.1	57.3	63.5
F4	1.8	12	1.8	2.1
F5	8.9	5.3	15	10
Sum	55.9	89.7	82.3	84.0

Table 3. The concentration of heavy metal inside of Kirkuk city.

Pb	S1	S2	S3	S4
F1	1.8	0.4	0.9	1.3
F2	0.9	3.3	2.6	4.13
F3	2.4	1.7	2.8	0.66
F4	5.1	8.4	5.0	6.36
F5	9.2	6.1	15.6	8.3
Sum	19.4	19.9	26.9	20.75

Table 4. The concentration of heavy metal inside of Kirkuk city.

Cd	S1	S2	S3	S4
F1	0.2	0.3	0.7	0.6
F2	0.5	0.3	1.1	0.5
F3	1.2	0.5	1.4	1.3
F4	0.02	0.02	0.5	0.02
F5	1.7	0.9	2.8	2.3
Sum	3.62	2.02	6.5	4.72

Table 5. The concentration of heavy metal outside of Kirkuk city.

Cu	S1	S2	S3	S4
F1	0.6	1.7	0.9	0.6
F2	1.8	3.1	4.1	2.1
F3	2.1	4.3	3.3	2.6
F4	8.8	10.7	12.3	10.3
F5	6.2	7.6	9.1	6.4
Sum	19.4	27.4	29.7	22.0

Table 6. The concentration of heavy metal outside of Kirkuk city.

Zn	S1	S2	S3	S4
F1	0.1	0.09	1.8	1.6
F2	4.1	1.9	6.5	4.4
F3	21.1	24.6	39.4	26.4
F4	3.8	2.1	3.3	3.1
F5	14.2	18.1	17.3	18.6
Sum	**43.3**	**46.79**	**68.3**	**54.1**

Table 7. The concentration of heavy metal outside of Kirkuk city.

Pb	S1	S2	S3	S4
F1	1.3	0.7	0.3	0.6
F2	1.9	1.6	0.9	0.9
F3	2.6	2.0	4.0	2.8
F4	2.1	4.3	2.2	2.5
F5	4.7	5.3	6.8	5.5
Sum	**12.6**	**13.9**	**14.2**	**12.3**

Table 8. The concentration of heavy metal outside of Kirkuk city.

Cd	S1	S2	S3	S4
F1	0.0	0.0	0.02	0.3
F2	0.3	0.02	0.1	0.7
F3	0.5	0.3	0.4	0.9
F4	n.d.	n.d.	n.d.	0.3
F5	0.8	0.9	1.4	2.6
Sum	**1.6**	**1.22**	**1.92**	**4.8**

bile and readily available for biological uptake in the environment thus this fraction can be regard as a pollution indicator [18]. Whereas, the percentage of carbonate fraction for the soil within the city were (%12.35 Zn), (%10.97 Cu), (%12.69 Cd), and (%14.02 Pb), and the value of the metals from outside the city were (%7.82 Zn), (%5.825 Cu), (%10.044 Cd), and (%10.145 Pb).

3.2. Species Bound to Fe-Mn Oxide

In this fraction the results of sequential extraction shows that the percentages were (%68.05 Zn), (%12.34 Cu), (%26.74 Cd) and (%8.62 Pb) this for the inside the city, the outside of the city is (%51.9 Zn), (%11.84 Cu), (%23.85 Cd) and (%21.27 Pb). Zinc was highly abound to Fe-Mn oxides [19], in both samples more than the other elements, aboundace of Zn in other fractions is low and this refer to that Zn in this environment is more mobile than the metals that are mostly abundant in the residual fraction [20]. The residual fraction represents metal largely embedded in the crystal lattice of the soil fraction and should not be available for remobilization except under very harsh consideration [21]. Zinc strongly bound in the Fe-Mn oxides fraction and it has stability constants high enough to be concentrated in this fraction [22] [23]. Zn in high levels in the Fe/Mn oxide phase agree with (Fagbote. *et al.*, 2010) and (Jian-Min *et al.*, 2007) [23] [24]. According to Jian-Min results under reducing conditions metals present in the Fe-Mn oxide phase are unstable and easily released through dissolution releasing soluble metals. This implies that the potential risks of metal pollution will increase with time [25]. Also another regard that this fraction in comparison with carbonate minerals, Fe-Mn oxide minerals have relatively large area and surface site density. The Fe-Mn oxide, the reducible phase of the soil under oxidizing conditions is significant sink for the heavy metals [26].

Table 9. Mean concentration of heavy metals in soils from different cities in Iraq.

City	Pb	Zn	Cu	Cd
Baghdad	153.7 ppm	133.3 ppm	91.9 ppm	5.25 ppm
Basra	39.4 ppm	-	16.9 ppm	5.5 ppm
Fallujah	3.82 Mg/g	5.50 Mg/g	2.1 Mg/g	0.64 Mg/g
This study inside of Kirkuk city	21.73 ppm	77.9 ppm	28.12 ppm	4.21 ppm
This study outside of Kirkuk city	13.25 ppm	59.28 ppm	24.65 ppm	2.3 ppm

3.3. Species Bound to Organic Matter

Cu was mainly bound to this fraction in both sites of the study. The percentages of two sites were (%5.23 Zn), (%43.1 Cu), (%2.41 Cd), and (%29.43 Pb) this is for inside the city, but the percentages of the outside the city is (%5.95 Zn), (%46.93 Cu), (%1.56 Cd) and (%20.53 Pb). The results of sequential extraction in this study revealed that copper is mostly associated with organic matters fraction. Copper can be easily complex with organic matters because of high formation of organic-compounds [27] [28]. Heavy metals with high abundance in the phase bound to organic matter are more available than heavy metals in the Residual Fraction. The organic phase is relatively stable in nature but can be mobilized under strong oxidizing conditions due to degradation of organic matter [14] [27]. Heavy metals with high abundance in the phase bound to organics are more available than heavy metals in the residual fraction.

3.4. Spices in Residual Fraction

The results shows that Cadmium and lead were observed to be highest in the residual fraction but the percentages of Cu and Zn were lowest in both sites the results shows inside the city as follows (%12.99 Zn), (%29.81 Cu), (%45.83 Cd) and (%44.01 Pb) but outside the city the results were (%32.77 Zn), (%33.64 Cu), (%62.71 Cd) and (%42.41 Pb). Lead and Cadmium levels were mostly associated with the residual phase. This agrees with Ramirez *et al.*, 2005 who reported Cd and Pb were mostly abundant with the residual phase [29]. Metals present in the residual fraction are a measure of the degree of environmental pollution. The higher the metals present in this fraction, the lower degree of pollution and verse versa [30].

4. Conclusion

By the results we have concluded that the concentrations of the elements (Zn, Cu, Cd and Pb) in both regions were different. The results indicated that the areas within the city have the highest concentrations of the heavy metals than outside the city. The high concentration of the heavy metals in the Kirkuk city (first local) is due to oil producing and oil industry activity. This soil's region contain over the normal concentrations of heavy metals because of projectiles falling of brick factories on that zone where clay metals and organic materials in that soil adsorb these metals and increase their concentrations. **Table 9** shows the results of analysis of the concentrations of heavy metals in soils and areas in Kirkuk city, compared with the determinants of other cities soils in Iraq.

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