



Sudan University of Science and Technology
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Sequential Extraction of some Minerals from Jebel Torja Area Soil

الإستخلاص المتتابع لبعض المعادن من التربة بمنطقة جبل طوريه

**A Thesis Submitted in Partial Fulfillment for the Requirements of
Master Degree in Chemistry**

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الآية

قال تعالى:

(فَتَعَالَى اللَّهُ الْمَلِكُ الْحَقُّ وَلَا تَعْجَلْ بِالْقُرْآنِ مِنْ قَبْلِ أَنْ يُقْضَىٰ إِلَيْكَ وَحْيُهُ وَقُلْ رَبِّ زِدْنِي عِلْمًا)

صدق الله العظيم

سورة طه (الآية 114)

DEDICATION

I dedicate this work,

To my lovely parents

To soul of my brother (Mohammed)

To my sisters

ACKNOWLEDGMENT

My deep thanks and prayers to Almighty Allah for giving me health and desire to complete this work successfully.

My deep gratitude would go to my supervisor, Dr. Omer Adam Mohammed Gibla, for his support, encouragement and valuable advice .

My thanks would be extended to all those who helped, taught and encouraged me during the achievement of this work.

ABSTRACT

Jebel Toria is a hill south of Omdurman, where different types of heavy machines are moving. The machines are moving rocks and crushing them to smaller sizes. Some rocks and stones are used in building foundations. Some rocks are crushed to be used in road manufacturing.

Samples of soils were taken at (20cm) depth. Four samples were collected at a distance of 100 meters far from Jebel Toria in the four principal directions. A fifth sample was taken from the east-north direction. The sixth sample was a reference sample. It was collected from 1000 meters far from the heavy machines moving area.

The aim of this study was determined if the soil around the hill is polluted by some metallic minerals or not.

The sequential extraction method (BCR) was used to extract the concerned minerals from the six soil samples.

Some physicochemical properties have been studied. These include ash content, moisture contents and concentration of Iron, Copper, Nickel and Chromium.

The analysis showed that the fraction number (4) of the extraction has the highest value of Iron, Copper, Nickel and Chromium concentration compared to the other three fractions.

ملخص البحث

يقع جبل طورية جنوب مدينة امدرمان، حيث تتحرك عدد كبير من الآليات الثقيلة المختلفة. وهي تعمل في تحريك الصخور وتكسيورها إلى أحجام أصغر. بعض هذه الأحجار يُستخدم في أساسات البناء. بعضها يكسر إلى أحجام أصغر يستخدم في صناعة الطرق.

أخذت عينات التربة بعمق (20 سم). أربعة عينات جمعت على بعد 100 متر من موقع حركة الآليات في الإتجاهات الأربعة الجغرافية، العينة الخامسة أخذت بنفس المسافة من الإتجاه الشمالي الشرقي للموقع. العينة السادسة فيها عينة حاكمة أو مرجعية وأخذت على بعد 1000 متر من موقع الدراسة.

الهدف من هذه الدراسة هو تحديد إذا ما كانت التربة حول هذا الموقع قد تعرضت للتلوث لبعض المعادن أو لا.

إستخدمت تقنية الإستخلاص المتتابع (BCR) لتحديد تراكيز المعادن المعنية في العينات الستة.

حددت الدراسة كل من محتوى الرطوبة ومحتوى الرماد بالإضافة إلى تراكيز الحديد النحاس، النيكل والكروم.

أظهرت عمليات التحليل أن خطوة الإستخلاص الرابعة حققت أعلى تركيز للأربعة أيونات (الحديد، النحاس، النيكل، الكروم).

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CHAPTER ONE

INTRODUCTION

1. INTRODUCTION

1.1 Heavy metals

Metals are classified as “heavy metals”, if they have a specific gravity of more than 5g/cm^3 in their standard state. There are about sixty known heavy metals. Heavy metals accumulate could have a negative influence on physiological activities of plants (e.g. photosynthesis, gaseous exchange, and nutrient absorption), causing reductions in plant growth, dry matter accumulation and yield (Devkota and Schmidt, 2000). There are many terms used to describe and categorize metals, including trace metals, transition metals, micronutrients, toxic metals, heavy metals. Many of these definitions are arbitrary and these terms have been used loosely in the literature to include elements that do not strictly meet the definition of the term. Metals are defined as any element that has a silvery luster and is a good conductor of heat and electricity (Mclean and Bledsoe, 1992).

1.1.1 Heavy metals in soil and environment

The incidence of heavy metal contamination from both natural and anthropogenic sources has increased concern about possible health effects. Natural and anthropogenic sources of soil contamination are widespread and variable (Tahir *et al.*, 2007). According to Ross (1994) the anthropogenic sources of metal contamination can be divided into five main groups: (1) metalliferous mining and smelting (arsenic, cadmium, lead and mercury); (2) industry (arsenic, cadmium, chromium, cobalt, copper, mercury, nickel, zinc); (3) atmospheric deposition (arsenic, cadmium, chromium, copper, lead, mercury, uranium); (4) agriculture (arsenic, cadmium, copper, lead, selenium, uranium, zinc); and (5) waste disposal (arsenic, cadmium, chromium, copper, lead, mercury, zinc). Heavy metal contamination of soil results from anthropogenic processes

such as mining (Navarro et al., 2008) smelting procedures (Brumelis et al., 1999) and agriculture (Vaalgamaa and Conley, 2008) as-well as natural activities. Chemical and metallurgical industries are the most important sources of heavy metals in the environment (Cortes et al., 2003). Industries such as plating, ceramics, glass, mining and battery manufacture are considered the main sources of heavy metals in local water systems causing the contamination of groundwater with heavy metals.

Heavy metals which are commonly found in high concentrations in landfill leachate are also a potential source of pollution for groundwater (Aziz *et al.*, 2004). Large areas of agricultural land are contaminated by heavy metals that mainly originate from former or current mining activities, industrial emissions or the application of sewage sludge. Metals exist in one of four forms in the soil: mineral, organic, sorbed (bound to soil), or dissolved. Sorbed metals represent the third largest pool, and are generally very tightly bound to soil surfaces. Although mineral, organic, and sorbed metals are not immediately absorbed by plants, they can slowly release metals into solution (Jones, 2003). The inability to determine metal species in soils hampers efforts to understand the mobility, bioavailability and fate of contaminant metals in environmental systems together with the assessment of the health risks posed by them, and the development of methods to remediate metal contaminated sites (D'Amore *et al.*, 2005). However, in some natural soils developed from metalrich parent materials, as-well as in contaminated soils, up to 30 to 60% of heavy metals can occur in easily unstable forms (Karczewska *et al.*, 1998). In soil, metals are found in one or more of several "pools" of the soil, as described by Shuman (1991):

- dissolved in the soil solution;
- occupying exchange sites in inorganic soil constituents;

- specifically adsorbed in inorganic soil constituents;
- associated with insoluble soil organic matter;
- precipitated as pure or mixed solids;
- present in the structure of secondary minerals; and/or
- present in the structure of primary minerals

In situations where metals have been introduced into the environment through human activities, metals are associated with the first five pools. Native metals may be associated with any of the pools depending on the geological history of the area. The aqueous fraction, and those fractions in equilibrium with this fraction, i.e. the exchange fraction are of primary importance when considering the migration potential of metals associated with soils (Mclean and Bledsoe, 1992). Heavy metals naturally occur in the environment, but may also be introduced as a result of land use activities. Natural and anthropogenically introduced concentrations of metals in near-surface soil can vary significantly due to different physical and chemical processes operating within soils across geographic regions (Murray *et al.*, 2004). Migration of metals in the soil is influenced by physical and chemical characteristics of each specific metal and by several environmental factors. The most significant environmental factors appear to be (i) soil type, (ii) total organic content, (iii) redox potential, and (iv) pH (Murray *et al.*, 1999). Although heavy metals are generally considered to be relatively immobile in most soils, their mobility in certain contaminated soils may exceed ordinary rates and pose a significant threat to water quality (Bunzl *et al.*, 2001). Organic manure, municipal waste, and some fungicides often contain fairly high concentrations of heavy metals. Soils receiving repeated applications of organic manures, fungicides, and pesticides have exhibited high concentrations of extractable heavy metals (Han *et al.*, 2000) and increased concentrations of heavy metals in runoff (Moore *et al.*, 1998).

Previous studies indicate that metal constituents of surface soil directly influence the movement of metals, especially in sandy soils (Moore *et al.*, 1998; Cezary and Singh, 2001).

1.1.2 Behavior of heavy metals in soil

Monitoring the endangerment of soil by heavy metals is of interest due to their influence on ground and surface water (Clemente *et al.*, 2008; Boukhalifa, 2007) and also on flora (Pandey and Pandey 2008; Stobrawa and Lorenc-Plucinska, 2008), animals and humans (Devries *et al.*, 2007). The overall behavior of heavy metals in soil is said to be governed largely by their sorption and desorption reactions with different soil constituents, especially clay components (Appel and Ma, 2002).

The chemical behavior of heavy metals in soils is controlled by a number of processes, including metal cation release from contamination source materials (e.g., fertilizer, sludge, smelter dust, ammunition, slag), cation exchange and specific adsorption onto surfaces of minerals and soil organic matter, and precipitation of secondary minerals (Manceau *et al.*, 2000). The relative importance of these processes depends on soil composition and pH. In general, cation exchange reactions and complexation to organic matter are most important in acidic soils, while specific adsorption and precipitation become more important at near-neutral to alkaline pH values (Voegelin *et al.*, 2003). EL-ghawi *et al.*, (2007). studied the trace metal concentrations in some Libyan soils and found that the concentrations in clay surface soil are higher than in sandy soil. The multiple regression analyses performed confirmed the importance of pH as well as other soil properties such as texture, electrical conductivity and organic matter or carbonates on the behaviour of nutrients and heavy metals (Soriano-Disla *et al.*, 2008). Increased anthropogenic inputs of Cu and Zn in soils have caused considerable

concern relative to their effect on water contamination (Zhang *et al.*, 2003).

Oxidizing conditions generally increase the retention capacity of metals in soil, while reducing conditions will generally reduce the retention capacity of metals (McClean and Bledsoe, 1992). Soil reduction has been shown to result in the coincident release of metals associated with minerals that are susceptible to reductive dissolution, in particular Mn and Fe oxides (Charlatchka and Cambier, 2000; Davranche and Bollinger, 2000). Filep (1998) stated that contaminants reaching the soil can be divided into two groups, namely micropollutants and macropollutants. Micropollutants are natural or anthropogenic molecules, which are toxic at very low concentration. Macropollutants are present in the environment locally and/or temporarily to a much higher degree than normal level. The main micropollutants of soils are inorganic or organic compounds. (i) Inorganic micropollutants are mainly the toxic and potentially toxic heavy metals (Pb, Cd, Ni, Cr, Hg, Cu, Zn etc.) (ii) Organic micropollutants include pesticides and certain non-pesticide organic molecules: e.g. aliphatic solvents, monocyclic aromatics, halogenated aromatics, polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs), surfactants, plastifiers. Frequent macropollutants are:

- Inorganic (nitrogenous fertilizers)
- Organic (crude oil and products of oil industry).

Toxic heavy metals and micronutrients utilized as metal ions exist in the soil as species with several types of mobility and take part in many interactions.

1.1.3 General features of the investigated heavy metals

1.1.3.1 Iron

Iron is the fourth most abundant element in earth's crust (after oxygen, silicon, and aluminum). The mean iron content of soil, sediment, and rocks is about 5%. Most of the iron in soils is present as iron oxides; in fact the typical soil colors (brown, red, yellow) are partly due to various iron oxides differing in their physical/chemical properties and their color. Iron, aluminum, and manganese oxide soil minerals are important sinks for heavy metals in soil and residual-amended soils (Basta *et al.*, 2005). Iron can occur in either the divalent (Fe^{+2}) or trivalent (Fe^{+3}) states under typical environmental conditions (U.S. EPA, 2003).

Due to their high specific surface area, iron oxides act as important sorbents for dissolved species, e.g. heavy metals, phosphate and arsenate (Rozan *et al.*, 2002; Appelo and Postma, 2005). Some characteristic features of iron oxides include low solubility, and thereby high stability, conspicuous colours, and high surface area making them very effective sorbents for a number of dissolved species. In principle, all organic matter is thermodynamically apt to reduce Fe(III), and due to the high affinity of carboxylate groups for Fe(III) in solution or on the surface of a hydrous Fe(III) oxide, this type of process is very likely to occur in natural water, soils, and sediments (Pedersen, 2006). In most well-aerated soils, the minimum solubility of total inorganic iron is fixed in the range of 10^{-8} to 10^{-6} mol/m³. The concentrations of soluble iron measured in soil solutions are usually higher than those calculated from equilibrium reactions and in the range of 10^{-5} to 10^{-3} mol/m³ due to the complexation of soil-Fe with soluble organic ligands (Olomu *et al.*, 1973).

1.1.3.2 Copper

Total Copper concentration in soil solution is normally low (0.01-0.6 $\mu\text{mol L}^{-1}$). It is essential to plants, animals, and microorganisms, but is toxic when its concentration exceeds a certain critical level (Baker, 1990). Soil quality criteria and legislation on Cu levels in soils generally rely on data for total Cu content based on chemical analysis (Tom-Petersen *et al.*, 2004). Copper in soils may exist in the following forms: (i) water soluble, (ii) exchangeable, (iii) organically bound, (iv) associated with carbonates and hydrous oxides of Fe, Mn, and Al, and (v) residual (Shuman, 1985). Copper and Zinc are two metals that are consistently added to soils in increasing quantities in the form of fertilizers, pesticides, livestock manures, sewage sludges and industrial emissions (Adriano, 1989). Both of these metals show moderate mobility under relatively acidic soil conditions (pH 5-7) because of increased solubility and formation of soluble complexes with organic ligands (Klamberg *et al.*, 1989). Copper is adsorbed into the soil, forming an association with organic matter, Fe and Mn oxides, soil minerals, etc., thus making it one of the least mobile of the trace metals (Ioannou *et al.*, 2003).

1.1.3.3 Chromium

Chromium is one of the most versatile and widely used elements. Its main uses in the metallurgical, chemical, and refractory industries are well known. It is an essential element in the production of a wide variety of stainless steels, tool and alloy steels, nickel-chromium heating elements, and plating metals. Its widespread use in the metallurgical industry is attributed to its capability of enhancing properties such as resistance to corrosion or oxidation, creep, impact strengths, and hardenability.

In Sudan, Chromite ore deposits occur in the Ingassana hills in the Blue Nile region. Other occurrences had been reported at Hamissana-sol

Hamed in the northern Red Sea Hills, the Nuba Mountains in southern Kordofan, JabalRahib northwest Sudan and Jabal El Tawil in central Butana in southern Sudan.

However, the Ingassanachromite ore is considered as one of largest chromite ore deposits in Sudan (Seifelnassr, *et al.*, 2011). Low-grade deposits and the fines resulting in the mining operations cannot be economically used. Therefore, beneficiation of low grade and finely disseminated ores is becoming important in recent years due to the shortage of high grade ore reserves.

Although gravity methods are well known and widely used for the concentration of chromites, such techniques fail to recover chromite from the fine size fractions below approximately 100 μm .

Flotation offers an alternative concentration process for the separation of the fine materials and the reduction of chromium losses. However, earlier results of flotation of lower-grade chromite ores were inferior to those obtained by tabling (Seifelnassr, *et al.*, 2011).

There are two general types of methods for separating chromium ore (chromite) values from associated gangue minerals by froth flotation techniques. In the first method chromite ore which has been deslimed is subjected to flotation at a pH of 1.5 to 5.5 with a long chain fatty acid collector was reported (Seifelnassr, *et al.*, 2011). The selectivity of the process is enhanced by adding a soluble fluoride compound such as hydrofluoric acid, sodium fluoride or sodium silicofluoride in the flotation medium (Seifelnassr, *et al.*, 2011).

The flotation process is typically conducted by adding 0.5 to 5.0 pounds fatty acid, 0.1 to 10.0 pounds soluble fluoride ion and 1.0 to 11.0 pounds sulfuric acid per ton of ore to the aqueous treatment medium containing the chromite ore. A typical product obtained by such a process, from an

ore containing 25.2% Cr₂O₃, is a recleaner concentrate containing 41.0% Cr₂O₃ and 2.5% SiO₂ with a chromium recovery of 77.0%.

In the second technique [U.S. Pat. No. 3,473,656], chromite ore flotation is achieved with an undeslimed ore at a pH of 11.5 using a long chain fatty acid collector (Seifelnassr, *et al.*, 2011).

The pH of the pulp is adjusted with NaOH with the pulp being dispersed by sodium silicate using carboxymethyl cellulose as a depressant for silicate gangue minerals.

Typically during processing, three pounds of sodium silicate, 1.0 to 3.0 pounds of tall oil, and 0.25 to 0.50 pounds of carboxymethyl cellulose per ton of ore are added to the flotation cell (Seifelnassr, *et al.*, 2011).

From an ore containing 18.13% Cr₂O₃ and 23.98% SiO₂, a flotation concentrate was obtained containing 52.16% Cr₂O₃ and 3.72% SiO₂ with a chromium recovery of 80.0%. Also, Pryor, (1965) reported studies on a Turkish chromite ore containing 30% Cr₂O₃, associated with oxides and sulphides and gangue minerals are chiefly serpentine and olivine. When grounded to -100µm the serpentine dominated the fines, chromite the medium particles and olivine the coarse. Strongly alkaline pulp (more than pH 10) was used, with sodium oleate and oleic acid to float the serpentine (Seifelnassr, *et al.*, 2011).

The pulp was then rendered acidic (pH 3) and chromite was floated with 0.75 lb/ton of fatty acid-amine collector. Olivine, which only floats in a neutral solution under these conditions, remained in the final tailing, the obtained concentrate grade was 45% Cr₂O₃ (Seifelnassr, *et al.*, 2011).

Preconditioning with fuel oil permitted flotation of the chromite from the flocculated siliceous-gangue slimes. Recoveries of up to 91 percent were realized with products containing up to 45 percent Cr₂O₃ (Seifelnassr, *et al.*, 2011). The Cr/Fe ratios ranged from 2.17 to 2.46. Oleic acid was used for flotation. Sodium fluoride and sulphuric acid yielded better results

than dilute hydrofluoric acid when these reagents were added to free the 'flocs' from the siliceous gangue.

A process developed for one ore does not usually yield optimum results for another ore of different origin. It is thought that differences in the composition of the gangue materials, as well as in the composition of the chromium spinels, are responsible for these variations in flotation behavior. Fundamental research is required to alleviate this problem. Investigations involving the flotation of a high grade chromite sample and a high grade serpentine using sodium oleate as the collector showed that the chromite can be floated at collector dosages between 0.3 and 1000 mg/l (Seifelnassr, *et al.*, 2011).

1.1.3.4 Nickel

Nickel is the 24th most abundant metal in the earth's crust and 5th most abundant element by weight after iron, oxygen, magnesium and silicon, constituting about 3% of the earth composition. It is a member of 1st row transition series and belongs to group 10 of the periodic table with other group members that include palladium, platinum and darmstadtium. In its elemental form, nickel is silver- white in colour, hard and lustrous, but in powdery form, it is reactive in air and ignites spontaneously (Yahaya, 2011). It has a density of 8.9 gcm⁻³, a melting point of about 1455°C and a boiling point of 2732°C. Its relative atomic mass is 58.71 and atomic number of 28. Nickel usually exists in the 0 and +2 oxidation states, but less frequently in the -1, +1, +3 and +4 oxidation states. Nickel possesses high electrical and thermal conductivities; hence, it is resistant to electrical erosion, oxidation and corrosion at temperatures of -20 to +30°C (Yahaya, 2011).

The most significant nickel ore are pentlandite; nickel - iron sulphide and garnierite as well as, nickel - magnesium silicate. Nickel is a relatively abundant and naturally occurring metal, widely distributed in the earth's

crust. Its status in soils is highly dependent on the nickel concentration of the parent rocks, but in surface soils, its content is also a reflection of soil-forming processes and pollution (Yahaya, 2011).

The lowest contents are found in sedimentary rocks that comprise of clays, limestones, sandstones and shales, while the highest concentrations exist in basic igneous rocks (Yahaya, 2011).

Nickel content in soils varied widely and have been estimated to range from 3 to 1000 ppm; for the world soils, the brand range is between 0.2 and 450 ppm, while the grand mean is calculated to be 22 ppm (Yahaya, 2011).

Moreover, nickel is apparently a heavy metal of environmental concern only in urban cities, but could become a problem resulting from decreased soil pH, due to reduced use of soil liming in agricultural soils and mobilization arising from increased acid rain in industrialized areas (Yahaya, 2011). With decreasing pH, the solubility and mobility of nickel increases, hence, soil pH is the major factor controlling nickel solubility, mobility and sorption, while clay content, iron- manganese mineral and soil organic matter being of secondary importance (Yahaya, 2011).

Generally, the distribution of nickel in soil profile is uniform, with typical accumulation at the surface soil due to deposition through anthropogenic activities (Yahaya, 2011). Nickel can also exist in several forms in soils that include; adsorbed or complex on organic cation surfaces or on inorganic cation exchange surfaces, inorganic crystalline minerals or precipitates, water soluble, free-ion or chelated metal complexes in soil solution. In the presence of fulvic and humic acids, the complexes are much more mobile, and may be prominent than the hydrated divalent cation in soil solution (Yahaya, 2011).

1.1.4 Pollution By heavy metals

Sudan is a very large country, therefore, the most suitable way to estimate the concentration of heavy elements over the whole country is to take samples from different parts, which have different locations taking in consideration climates and soil. Therefore samples should be collected from south, middle, east and west of the Sudan including desert, tropical and equatorial climate. Heavy metals are general collective term referring to the group of metals and metalloids with a density greater than 6 gm/cm^3 . Although it is only a loosely defined term, it is widely recognized and applied to the elements such as Cd, Cr, Cu, Hg, Ni, Pb and Zn, which are commonly associated with pollution and toxicity problems. An alternative, theoretical name for this group of elements is (trace metals) but it is not widely used. Unlike organic pollutants, heavy metals occur naturally in rocks and ore minerals, there is a range of normal background concentrations of these elements in soils sediments, water and living organisms. Pollution gives rise to anomalously high concentration of the metals relative to the normal background levels, therefore, presence of the metal is insufficient evidence of pollution, and the relative concentration is all important. In geological terms heavy metals are included in the group of elements referred to as trace elements which together constitute less than 1% of the rocks in the earth's crust: The macroelements (O, Si, Al, Fe, Ca, Na, K, Mg, Ti, H, P and S) comprise 99% of the earth's crust. These trace elements occur as impurities, isomorphously substituted for various macroelement constituents of the crystal lattice of many primary minerals. Primary minerals are those found in igneous rocks which originally crystallized from molten magma. In sedimentary rocks trace elements occur, sorbed to the secondary minerals which are the products of the weathering

(physical disintegration and chemical decomposition) of primary minerals. Heavy metal pollution can affect all environments but its effects are most long lasting in soils due to the relatively strong absorption of many metals onto the humic and clay colloids in soils. The duration of contamination may be for hundreds and thousands of years in many cases (Magdi Hassan, *et al.*, 2014). Pollution of the aquatic environment by inorganic chemicals and heavy metals is a major threat to human health and to aquatic organisms (Hamed A. S., *et al.*, 2011). Heavy metals pollution in aquatic ecosystem is growing at an alarming rate and has become an important worldwide problem (Magdi Hassan, *et al.*, 2014). According to the World Health Organization reports, about 5 million people die every year from drinking polluted water. Anthropogenic activities represent the major contributor to the contamination of aquatic environments. Drainage water containing pesticides and fertilizers, effluents of industrial activities, and sewage effluents contaminate water bodies and sediments with huge quantities of heavy metals (Hamed A. S., *et al.*, 2011). Heavy metal contamination is particularly significant in ecotoxicology since these metals are highly persistent and can bioaccumulate and biomagnify in the food chain, thus becoming toxic to living organisms at higher trophic levels. On the other hand, heavy metals are natural elements that occur in the earth crust. Some of these metals are necessary for human health and metabolic activities in trace amounts (Hamed A. S., *et al.*, 2011), while, others, such as mercury, cadmium, lead and chromium, are toxic even in low concentrations. Trace metals derived from natural inputs and anthropogenic emissions are ubiquitous in the global environment (Hamed A. S., *et al.*, 2011). Since, heavy metals cannot be degraded, they are deposited, assimilated or incorporated in water, sediment and aquatic animals and thus, causing heavy metal pollution in water bodies. Therefore, metals that are deposited in aquatic

environment accumulate in the food chain and pose a threat to human health due to biomagnifications over time (Hamed A. S., *et al.*, 2011).

1.2 Soil pollution

According to George et al., 2016 Soil contamination or soil pollution a part of land degradation is caused by the presence of xenobiotic (human-made) chemicals or, other alteration in the natural soil environment. It is typically caused by industrial activity, agricultural chemicals, or improper disposal of waste .The most common chemicals involved are petroleum hydrocarbons, polynuclear aromatic hydrocarbons (such as naphthalene and benzo(a)pyrene), solvents, pesticides, lead, and other heavy metals. Contamination is correlated with the degree of industrialization and intensity of chemical usage

The concern over soil contamination stems primarily from health risks, from direct contact with the contaminated soil, vapors from the contaminants, and from secondary contamination of water supplies within and underlying the soil .

Mapping of contaminated soil sites and the resulting cleanup are time consuming and expensive tasks, requiring extensive amounts of geology, hydrology, chemistry, computer modeling skills, and GIS in Environmental Contamination, as well as an appreciation of the history of industrial chemistry (George, *et al.*, 2016).

Soil pollution can be caused by the following (non-exhaustive list):

- Oil drilling
- Mining and activities by other heavy industries
- Accidental spills as may happen during deforestation activities, etc.
- Corrosion of underground storage tanks (including piping used to transmit the contents)

- Acid rain (in turn caused by air pollution)
- Intensive farming
- Agrochemicals, such as pesticides, herbicides and fertilizers
- Industrial accidents
- Road debris
- Drainage of contaminated surface water into the soil
- Waste disposal
 - Oil and fuel dumping
 - Nuclear wastes
 - Direct discharge of industrial wastes to the soil
 - Landfill and illegal dumping
 - coal ash
 - Electronic waste
 - ammunitions and agents of war

The most common chemicals involved are petroleum hydrocarbons, solvents, pesticides, lead, and other heavy metals. In a wider sense, genetically modified plants (GMP) can count as a risk factor for soils, because of their potential to affect the soil fauna (Snyder C., 2005). Any activity that leads to other forms of soil degradation (erosion, compaction, etc) may indirectly worsen the contamination effects in that soil remediation becomes more tedious. Historical deposition of coal ash used for residential, commercial, and industrial heating, as well as for industrial processes such as ore smelting, were a common source of contamination in areas that were industrialized before about 1960. Coal naturally concentrates lead and zinc during its formation, as well as other heavy metals to a lesser degree (Snyder C., 2005). When the coal is burned, most of these metals become concentrated in the ash. Coal ash and slag may contain sufficient lead to qualify as a "characteristic

hazardous waste", defined in the USA as containing more than 5 mg/l of extractable lead using the Toxicity characteristic leaching procedure TCLP procedure. In addition to lead, coal ash typically contains variable, but significant, concentrations of polynuclear aromatic hydrocarbons. It generally contains more contaminants such as organisms, pesticides, and heavy metals than other soil (Snyder C, 2005).

Contaminated or polluted soil directly affects human health through direct contact with soil, or via inhalation of soil contaminants which have vaporized; potentially greater threats are posed by the infiltration of soil contamination into groundwater aquifers used for human consumption, sometimes in areas apparently far removed from any apparent source of above ground contamination (Olawoyinr., *et al.*, 2012).

Health consequences from exposure to soil contamination vary greatly depending on pollutant type, pathway of attack and vulnerability of the exposed population. Chronic exposure to chromium, lead and other metals, petroleum, solvents, and many pesticide and herbicide formulations can be carcinogenic, can cause congenital disorders, or can cause other chronic health conditions.

Industrial or man-made concentrations of naturally occurring substances, such as nitrate and ammonia associated with livestock manure from agricultural operations, have also been identified as health hazards in soil and groundwater (Olawoyinr., *et al.*, 2012).

1.3 Sequential extraction process

The potential toxicity of trace metals in soil or sediment is a function of their mobility and bioavailability, which depend on the phase of the metals and the chemical and physical processes that govern

Transformations between phases. Trace metals cause damage to the nervous system and internal organs, as well as carcinogenic effects

(Ahmed Wali *et al.*, 2014). One of the most critical properties of trace metals that differentiates them from other toxic pollutants, is that they are not biodegradable. Metals and metalloids in soils originate from natural sources (e.g. weathering of soil and rock, erosion, and forest fires) and anthropogenic activities (e.g. industrial effluent, fertilizers, atmospheric deposition, agricultural drainage, and the phosphate industry).

Several studies have determined the total metal contents in contaminated and non-contaminated soils. However, the total contents of trace metals do not provide enough information to understand their various forms, mobility, bioavailability, or potential risks to the environment . In contrast, a metal speciation analysis of soil can provide a good indicator of the ecosystem quality. Metals may be present in soil in several different physicochemical phases, including sinks for soluble or exchangeable trace elements in the environment and amorphous material (Fe/Mn oxides) bound to organic matter, sulphides, or mineral fractions residual . Determining their fractionation is important because the mobility and bioavailability of trace metals are highly dependent on their specific chemical forms or behaviour of binding to each soil phase.

Sequential extraction procedures have recently been developed to determine the speciation of trace metals in soil matrices. These procedures provide more information on the origin, physicochemical availabilities, mobilisation, and transport of trace metals in natural environments . The pH, redox potential, and organic matter can stimulate the mobilisation and retention of trace metals in the natural environment. The European Community Bureau of Reference (1993) introduced a new three-step sequential extraction that has since been modified (Ahmed Wali *et al.*, 2014). The BCR sequential extraction method analyses different fractions of metals in the soil: acid-extractable (water soluble, exchangeable, and bound to carbonates), reducible (bound to Fe and Mn

oxides), oxidizable (bound to sulphides and organic matter), and residual (Esraa omer *et al.*, 2012).

Sediments act as adsorptive sites for heavy metals in an aquatic ecosystem. The similar sediment metalaccumulation pathways resulting from both natural and anthropogenic sources complicates the determination of metal origin in sediments (Okoro&Fatoki, 2012), therefore, identifying metal fractions in sediments by sequential extraction is the only appropriate means of assessing sources of metals in an aquatic environment due to the different potential bioavailability of metals associated with the various binding forms (Jain *et al.*, 2008). Sequential extraction of sediment-bound metals identifies the principal binding phases of metals and provides better understanding of the actual and the potential environmental effect of metals in sediments (Tessier *et al.*, 1979; Okoro&Fatoki, 2012). As sequential extraction involves the use of different reagents in isolating fractions of metals, the extractants are applied in successive order of reactivity that corresponds to the less mobility fractions of the metals (Filgueiras *et al.*, 2002). Several steps may be involved and therefore, the objectives of the extraction procedure and the physical characteristics of the sample concern are crucial factors which determine the choice of the sequential extraction method .

The success of sequential extraction scheme (SES) depends on a number of factors including (i) the chemical properties of the extractant used (ii) the efficiency of the extractant and iii) experimental parameter effects (Filgueiras *et al.*, 2002). However, in practice, several other factors such as, the sequence of individual steps, specific 'matrix effects' like eg cross-contamination, pH-buffering steps, readsorption and heterogeneity together with physical associations (eg. coatings) of the various solid fractions also affect sequential extraction (Filgueiras *et al.*, 2002; Ure& Davidson, 2002). All these factors have significant effects on SES

because extractants used are less specific resulting in extracting species of other phases (Filgueiras *et al.*, 2002). In order to ensure a successful sequential extraction scheme, these factors have to be critically evaluated before a suitable extractant is chosen for a specific extraction. These extractants are commonly classified as unbuffered salts, weak acids, reducing agents; oxidising agents and strong acids (Filgueiras *et al.*, 2002). The reactivity of extractants in relationship to the metal mobility in different phases of the sequential extraction.

Sequential extraction of heavy metals was originally established by Tessier *et al.*, (1979) as a reliable technique for partitioning metals into various fractions according to their binding forms in soils and sediments. According to these authors, metals can be partitioned into five different fractions, namely exchangeable, carbonate bound, Fe and Mn oxide bound, organic matter and sulphide bound, and residual. These fractions are also referred to as exchangeable, acid-soluble, reducible, oxidizable and residual fractions (Prasanth *et al.*, 2013). However, since sequential extraction is an operationally defined procedure, there have been several modifications made and published by many researchers on the basis that metals are not only fractioned into above five compartments, but are affected by complex chemical processes at and between the metal-sediment interface (Morillo *et al.*, 2004). As a result, literature is now dominated with several sequential extraction procedures with metal partitioning into four (Sposito *et al.*, 1982), six (Kersten&Förstner, 1986) and seven fractions (Silveira *et al.*, 2006). This introduces lack of uniformity in the approach. This lack of homogeneity in the sequential extraction schemes therefore does not allow intercomparison of results worldwide or validation of procedures (Quevauviller *et al.*, 1997). The European Union's Standards, Measurements and Testing programme (SM &T) therefore adopted a scheme to standardize and harmonize many

sequential extraction methods for determination of extractable metal fractions in soils and sediments (Tessier & Campbell, 1987; Quevauviller *et al.*, 1997).

This was accompanied with the use of two sediment certified reference materials (BCR- 601 certified for the BCR protocol for soil and BCR-701 certified for metals in sediment) for validation of results to minimize analytic errors (Guevara-Riba *et al.*, 2004). The BCR-SEP as a three-step analytic approach is similar to the original sequential extraction method developed by Tessier *et al.*, (1979) with the exception of combining the "exchangeable" and "carbonate" bound fractions in the first step since these fractions are deemed to be the most mobile phases of metals in environmental samples (Wang *et al.*, 2010).

Sequential extraction schemes have not been standardized and the results of different procedures are not always comparable due to the lack of uniformity in experimental conditions and the differences in extraction reagents (Qingsong HE, *et al.*, 2013). Previous works mainly focused on the development of new extraction schemes and application of sequential extraction for characterization of metal mobility for different variety of environmental samples. However, there is less information available about the comparison of different sequential extraction schemes for metal fractions in the soil. The objective of this study was to compare four sequential extraction procedures (Sposito, BCR, Tessier and Silveira scheme) to determine the fractionation of trace metals (Fe, Cu, Cd and Zn) in a mining-contaminated soil (Qingsong HE, *et al.*, 2013).

1.4 Objectives

- Extract the minerals (Fe, Cu, Ni and Cr) by using sequential extraction procedures.
- Determination the moisture content and ash content for soil samples.
- Determination of minerals contents in Jebel Toria soils by using Atomic Absorption instrument.

CHAPTER TWO

MATERIALS and METHODS

2. MATERIALS AND METHODS

2.1 Collection of samples

Five samples of top soil were collected at 100 meter far from Jebel Toria in different directions, East, North East, North, South and West. The sixth sample obtained from a far distance 1000 meter from Jebel Toria as a control sample. Samples were collected during winter season (December 2015).

2.2 Chemicals

- Glacial Acetic acid (assay 99%)
- Ammonium acetate (NH_4OAc)(assay 96%) CDH,India.
- Hydrogen peroxide (15.18M/L)
- Hydrochloric acid (assay 35-38%), 1.18 g/cm^3
- Hydroxyl amine hydrochloride ($\text{HONH}_2\cdot\text{HCl}$)(assay 98%)
- Nitric acid (assay 69-70%) , $1.41\text{-}1.42 \text{ g/cm}^3$

2.3 Instruments

- Sensitive balance. SHIMADZU (capacity 120gm)
- Mechanical Shaker
- Hot air oven. DAIHAN LAB TECH co.ltd
- Thermostatic water bath. DAIHAN LAB TECH co.ltd
- Atomic absorption spectroscopy instrument.

2.4 Method of analysis

2.4.1 Samples preparation and treatment

Samples were kept in clean, dry, plastic containers. They were then ground to fine particles by using mortar and pestles and left to dry at room temperature, and saved in clean, dry glass bottles.

2.4.2 Sequential extraction of minerals (the BCR procedure)

2.4.2.1 Extraction of exchangeable and acid soluble minerals

40 ml of 0.1M acetic acid were added to 5.00g of dry soil sample in 250ml conical flask. The mixture of each sample was shaken using mechanical shaker at 200 rpm for 3 hours, and left over night to settle. Each supernatant liquid was decanted into 50ml volumetric flask, then the volume was completed to the mark by 0.1M acetic acid. The residue was washed by adding 5ml of distilled water, shaken for 5 min, the second liquid was discarded without any loss of residue.

2.4.2.2 Extraction of Minerals bound to iron and manganese

40ml of 0.1M hydroxyl amine hydrochloride (adjusted to pH 2 with 2M nitric acid) was added to each residue from the first step. The mixture was shaken using mechanical shaker at 200 rpm for 3 hours, left over night to settle. Then the supernatant liquid was decanted into a 50ml volumetric flask, the volume was completed to the mark by 0.1M hydroxyl amine hydrochloride. The residue was washed using 5ml distilled water, and the second liquid was discarded without any loss of residue.

2.4.2.3 Extraction of Mineral bound to organic matter and sulphides

10ml of 8.8M hydrogen peroxide was carefully added in small portions to the residue in the conical flask the mixture was left for 1 hour with occasional shaking. The procedure was continued for further 1 hour at 85C using thermostatic water bath, till the volume was reduced to few milliliters by further heating in water bath. A second portion of 10ml hydrogen peroxide was added and the digestion procedure was repeated. The mixture content was then heated to near dryness, and 50ml of 1.0M ammonium acetate solution (adjusted to pH 2 with nitric acid) was added to the moist residue. The mixture was shaken using mechanical shaker at 200 rpm for 3 hours, The supernatant liquid was decanted in to 50 ml volumetric flask. The residue was washed using 5ml of distilled water, and the second liquid was discarded without any loss of residue.

2.4.2.4 Extraction of Minerals in the last residue

The treatment of the final residue was performed using aqua regia for mineral insoluble in the previous steps (F1, F2, F3). For this purpose, first 6ml of distilled water was added, followed by 15ml aqua regia solution. The residue was evaporated to near dryness on water bath further 10ml of aqua regia solution was added to the remaining residue. The mixture was evaporated to near dryness on water bath, 15ml of 1M nitric acid solution were added in small amount to the last residue in the flask. The extract was filtered through filter paper. The conical flask walls, were, carefully, washed using 10ml of 1M nitric acid.

2.4.3 Moisture content

5g of each sample was taken in a pre-heated crucible of known weight and dried at 115°C for 3 hours. The crucible was then cooled in a desiccator and allowed to cool to room temperature and then re-weighed. The moisture content of the sample calculated according to following equation:

$$\text{Moisture \%} = (A - B)/C \times 100$$

Where:

A= weight of crucible + sample (before drying).

B= weight of crucible + sample (after drying).

C= weight of original sample.

2.4.4 Ash content

5g of each sample was accurately weighed into a weighed porcelain dish. The dish and content were then transferred to (furnace) and ignited at 700°C. The dish and content were then removed and placed into desiccator. After cooling it was weighted and the results were determined and expressed as below:

$$\text{Ash content (\%)} = \frac{(B - C) \times 100}{A}$$

Where:

A = sample weight at grams

B = weight of crucible and dish content in grams.

C = weight of empty crucible in grams.

CHAPTER THREE

RESULTS and DISCUSSION

3. RESULTS AND DISCUSSION

3.1 Soil minerals contents

Heavy metals have a potential human health concern when concentrations are at high levels in soils. Metals may be harmful to humans through ingestion of edible plants containing metals through normal uptake, ingestion of plants splashed with contaminated soil or by accidental direct ingestion of soil usually happen by children. Breathing dust coming from soil may also pose a health risk. Total heavy metals extracted from the various soil fractions are tabulated in tables from table (3.1) to table (3.4), the values of metals were determined by using atomic absorption spectroscopy instrument. From results, all minerals (Fe, Cu, Ni and Cr) were showed highest values in fraction (4) comparable to other three fractions.

Iron (Fe)

The mean value of iron concentration in the study area was higher than the mean obtained by Millán *et al.* (1983) from agricultural soils of the Ebro Valley and Campos (1997) in the Granada Valley. In spite of elevated soil content, total iron content a good indicator of their plant availability. iron is mainly present in precipitated forms, such as oxides and hydroxides, in these soil samples because the highest concentrations were appeared in fraction number four.

Table (3.1): Atomic Absorption spectroscopy of Iron concentration

Sample No	F1 (ppm)	F2 (ppm)	F3 (ppm)	F4 (ppm)	total (ppm)	%
1	10.10	49.127	1.48	164.522	225.229	56.31
2	12.611	62.943	2.263	165.267	243.084	60.77
3	31.529	60.076	2.269	164.694	258.568	64.64
4	15.535	77.044	2.697	165.783	261.059	65.26
5	20.57	34.911	3.189	163.891	222.561	55.64
6	7.180	27.859	9.536	162.573	207.148	51.78

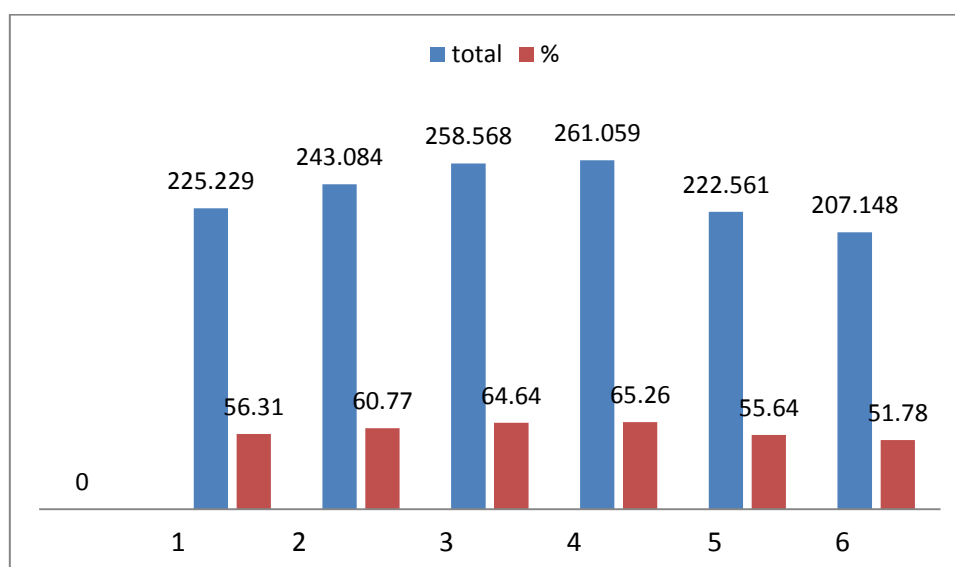


Figure (3.1): Total iron concentration and it percentage

Copper

Some studies have reported higher mean Cu values, such as that of Campos (1997) in the fertile Granada Valley, Marín *et al.* (2000) in vineyard soils of La Rioja and Millán *et al.* (1983) in the Ebro Valley, López and Grau (2004) from agricultural soils in Alicante. The normal Cu content of agricultural soils is 5 to 50 ppm. In this study, all

sampled were less than the normal range and none exceeded the reference value of Pérez *et al.* (2002) for agricultural soils in Murcia.

Table (3.2): Atomic Absorption spectroscopy of copper concentration

Sample No	F1 (ppm)	F2 (ppm)	F3 (ppm)	F4 (ppm)	total (ppm)	%
1	N.D	N.D	N.D	1.1	1.1	0.275
2	N.D	N.D	N.D	0.127	0.127	0.031
3	N.D	N.D	N.D	0.144	0.144	0.036
4	N.D	N.D	N.D	0.262	0.262	0.066
5	N.D	N.D	N.D	0.137	0.137	0.034
6	N.D	N.D	N.D	0.054	0.054	0.014

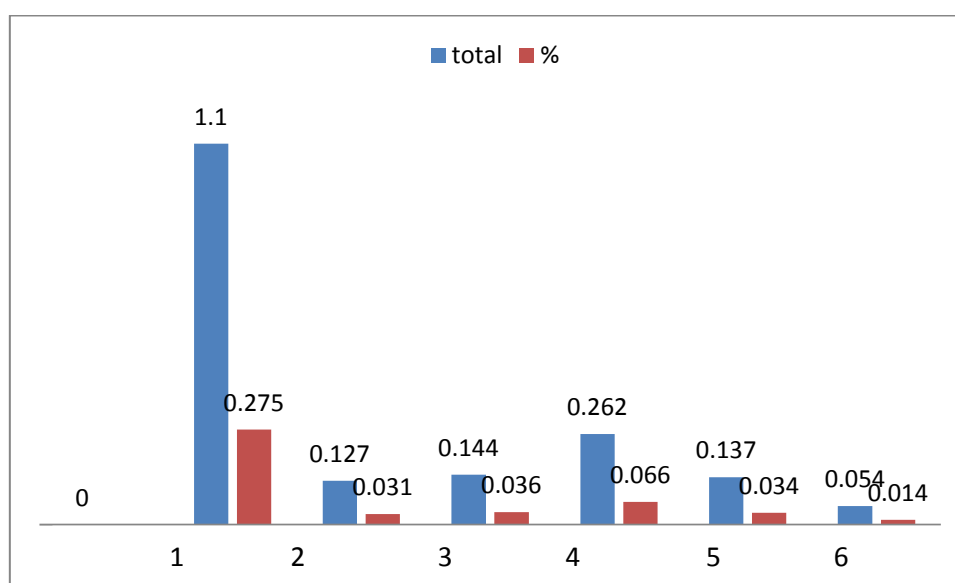


Figure (3.2): Total copper concentration and its percentage

Nickel

The mean value of nickel concentration in the study area was smaller than that reported by Andreu (1991), Boluda *et al.* (1988) in soils of Valencia and Campos (1997) in the fertile Granada Valley. The normal

soil Ni content varies from 1 to 100 ppm (Kabata-Pendias and Pendias, 2001). In this study all samples were less than the normal range.

Table (3.3): Atomic Absorption Results of nickel concentration

Sample No	F1 (ppm)	F2 (ppm)	F3 (ppm)	F4 (ppm)	total (ppm)	%
1	N.D	0.952	0.380	1.949	3.281	0.820
2	0.245	0.786	0.260	1.830	3.121	0.780
3	0.210	0.235	0.111	1.410	1.966	0.492
4	0.162	1.371	0.892	3.368	5.793	1.448
5	0.153	0.404	0.169	0.968	1.694	0.424
6	0.086	0.321	0.242	1.058	1.707	0.427

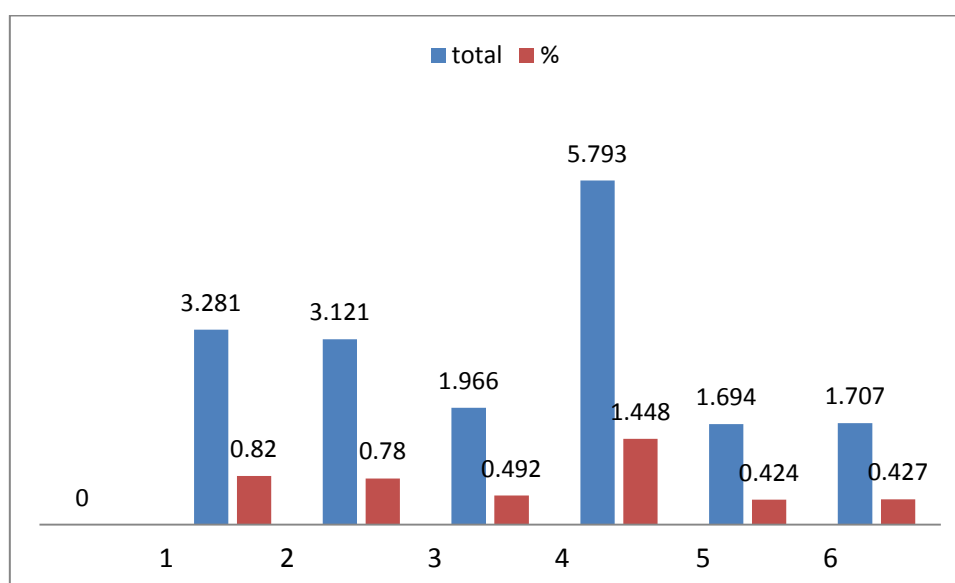


Figure (3.3): Total nickel concentration and it percentage

Chromium

The Cr mean value was lower than those reported by Aller and Deban (1989) in León or by Boluda *et al.*,(1988) in Valencia, (Adriano, 2001; Kabata-Pendias and Pendias, 2001), (Boluda *et al.*, 1988) and Pérez *et al.* (2002). Lower value indicate no contamination by Chromium in this area.

Table (3.4): Atomic Absorption Results of chromium concentration

Sample No	F1 (ppm)	F2 (ppm)	F3 (ppm)	F4 (ppm)	total (ppm)	%
1	0.321	0.141	0.138	2.318	2.918	0.729
2	N.D	N.D	N.D	2.318	2.318	0.579
3	N.D	N.D	N.D	2.795	2.795	0.699
4	N.D	N.D	0.146	3.682	3.828	0.957
5	N.D	N.D	N.D	1.467	1.467	0.366
6	N.D	0.136	N.D	1.390	1.526	0.382

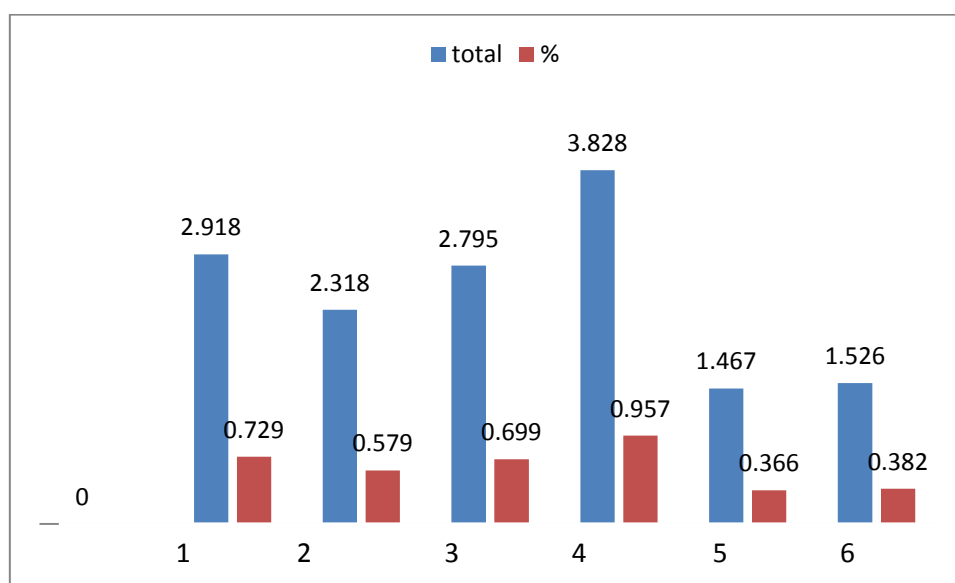


Figure (3.4): Total chromium concentration and its percentage

3.2 Some of proximate composition of soil samples

Analysis of some proximate composition (moisture content and ash content) gave information on the basic chemical composition of different soils. Moisture content value (23.03) and ash content value (28.49) in sample (2)North East jebel Toria site was more than other samples. Also

Moisture content value (9.50) and ash content value (20.71) in sample (1) East jebel Toria site was showed high value.

Table (3.5): Moisture content

Sample	Moisture content (%)
1	9.50
2	23.03
3	4.47
4	1.77
5	2.62
6	3.90

Table (3.6): Ash content

Sample	Ash content (%)
1	20.71
2	28.49
3	8.2
4	14.91
5	15.11
6	17.71

Samples (1&2) showed higher moisture content and ash content than the other four samples.

CONCLUSION

The analysis of heavy metals (Fe, Cu, Ni and Cr) for the different six soil samples showed the highest values for all metals in fraction (4), more than the other fractions. The values for (Cu, Ni and Cr) were less compared to other studies .this may indicates to that no contamination in this area under study.iron concentration was found to be more than other studies, increasing value of iron is very good. So the six samples which were taken from different sites showed that no pollution in these area.

Moisture content and ash content were high in samples (1) and (2).

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