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Metals Content, Occurance and Distribution in Soil of Al-Qilt Catchment.

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Dedication

To my great father and my wonderful mother, who raised me to be I am today....

To my brothers, my sister.

To my dear husband who stood by my side always had support and supportive to me.

To my beloved daughter Rittal who has given me strength and hope to complete this work.

To my grandfather and my grandmother.

To all teachers in my entire life.

To the memory of my dearest friend.

I dedicate this work

Acknowledgement

First of all, I would like to express my gratitude to ALLAH s.w.t. for helping me to complete my undergraduate study.

Many thanks and gratitude to my supervisors; Pro. Shehdeh Jodeh and Dr. Abd Alfattah Hassan for their academic, technical guidance and full support during thesis work.

Thanks also for Dr. Subhi Samhan for his help and providing useful suggestions.

I thank Palestinian Water Authority (PWA) for funding 50% for the tuition fees for my master study and helping me in providing the needed data.

Many thanks for University of Karlsruhe for their support and the Federal Ministry of Education and Research (BMBF) for their funding the Master work. Moreover, the technical assistance that was provided by the laboratory staff to the Helmholtz Centre for Environmental Research (UFZ) in Magdeburg is greatly acknowledged.

I am grateful to my Colleagues Moath Barri and Anas Al Ali to help me in completing this research.

My deepest gratitude to, my family; who enlightened my academic path with care and support.

<div align="right">Hanan Harb.</div>

الإقرار

أنا الموقعة أدناه مقدمة الرسالة التي تحمل العنوان:

Metals Content, Occurance and Distribution in Soil of Al-Qilt Catchment.

أقر بأن ما اشتملت عليه هذه الرسالة إنما هي نتاج جهدي الخاص، باستثناء ما تمت الإشارة إليه حيثما ورد، وأن هذه الرسالة ككل، أو أي جزء منها لم يقدم لنيل أية درجة أو لقب علمي أو بحثي لدى أية مؤسسة تعليمية أو بحثية أخرى.

Declaration

The work provided in this thesis, unless otherwise referenced, is the researcher's own work, and has not been submitted elsewhere for any other degree or qualification.

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List of Abbreviation

m.a.s.l	Meter above sea level.
m.b.s.l	Meter below sea level.
IUPAC	The International of pure and Applied Chemistry.
TEM	Transition Electron Microscope.
BCR	Bereau Communautaire de Reference.
CC	Continental Crust.
UP	Uper Crust.
LC	Lower Crust.
EGT	European Geo-Traverse.
ICP-MS	Inductive Coupled Plasma Mass Spectrometer.
$\mathbf{R^2}$	Correlation Factors.
EF	Enrichment Factor.
Me	Metal.
N	Normalizer.
E.B.S	Elemental Background for soil.
$\mathbf{m^3/d}$	Meter cubic per day
Mcm/d	Million cubic meter per annual
mm/a	Millimeter per annual
l/s	Litter per second
$\mathbf{g/cm^3}$	Gram per centimeter cubic
$\mathbf{Km^2}$	Kilo meter square

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Abstract

Heavy metals pollution in Palestine soils was ignored for decades; anthropogenic pollution of soil has negative effect on the environment and human life. Determination of elemental background and identifying the anthropogenic pollution in Palestine soils will help in screening the anthropogenic metal-based pollution.

The objective of this research was to determine the elemental background for soil's analysis in Al-Qilt Catchment Palestine due to lack of such information in literature.

Soil samples from pristine areas of Al-Qilt catchments were analyzed and assessed of their content for heavy and trace metals. The sources and impact of anthropogenic pollution in Al-Qilt catchment soils were also discussed.

Samples along Al-Qilt catchment were collected. Then were digested by aqua regia, and analyzed by using BCR fractionation method.

Data were analyzed by computing the correlation coefficient of heavy and trace metals, and graphed against Al and Fe as reference elements to

facilitate the comparison between Al-Qilt sites. Fe was chosen as elemental normalizer, based on the higher values of correlation factor (R^2) compared to Al. This allows identifying the trace metal as a manmade pollutant, then the Enrichment Factor (EF) was calculated, this lead to identification of anomalous metal concentrations that have an anthropogenic source.

The elemental background concentrations of anthropogenic pollution in the soil of Al-Qilt catchment were determined and compared to the continental crust values.

Results showed that metal/Al and metal/Fe normalization for Ti, V, Mn, Co, Rb, Ag, Li, B and Be were used as anthropogenic pollutants for most of Al-Qilt sites, As a comparison, the Fe was found to be the best elemental normalizer, The EF calculation showed that Pb had the highest value of trace metals in Ramallah and Stone cut areas, and there was a moderate values for Sn and Ag in Sweanit and Sultan respectively.

Sources for pollution in Al-Qilt catchment, from heavy metals concentration in the soils of Al-Qilt catchment were higher than the average values of continental earth crust, and thus such heavy metals are considered as soils' contaminants and affect the surface and groundwater, and ultimately the people in the surround.

Chapter one

1. Introduction

1.1. Research overview

The studies of heavy metal pollution in sediments and soils have increased in recent years [1-8], Heavy metals considered as serious pollutants of aquatic ecosystems, due to their environmental persistence [9], toxicity, and ability to combine with food chains [10], the human health risks that happened due to the pollution of the environmental materials such as sediment and soil, that due to the transfer of it to the water that uptake by the plants then to the human [11], the reference study of such pollution will contribute in protecting human lives and groundwater resources.

The soil pollution in urban regions may occur from other pollutants such as non-soil origin pollutants, with the continuation of dry conditions from the polluted soil particles. However, the main soil pollutants are radio nuclides, chlororganic compounds and Heavy metals. There are different pollutants sources such as the road infrastructures, vehicular traffic and manufacturing activities [12-15].

Heavy metals reaching the soil remain present in the pedosphere for many years even after removing of the pollution sources. Increased amounts of heavy metals in soils of areas that have been reported by many researchers [16-18].

1.2. Study area

Al-Qilt catchment is located in the West Bank on the western side of the Jordan Valley, and covering about 173 km²; it is characterized by a steep relief with elevations in the range of 700 m.a.s.l in the western part to the range of -250 m.b.s.l in the eastern part. At Al-Qilt, there are about 96,935 inhabitants from Palestinian communities and Israeli colonies, they discharge about 14,000 m3/d of wastewater and only about 30% of these quantities is treated, then it is mixed again with raw wastewater, moreover, at Al-Qilt the rainfall is estimated by 600 mm/a in the West and it is 150 mm/a in the East and the average rainfall over the catchment is 400 mm/a. The long term observations of flow mainly for Al-Qilt springs range from 3.0 to 12.0 Mcm/a, and the continuous base flow for the Ras Al-Qilt spring of around 300 l/s [19].

An environmental survey revealed that there are 363 disposal sites discharging raw wastewater into the environment in the West Bank [20]. Eight of these are at Al-Qilt catchment which starts from Al-Bireh wastewater treatment plant (5000 m3/d). The treated wastewater from Al-Bireh is discharged to Wadi Al-Ein and mixed downstream with untreated wastewater that is discharged from Qalandiah Camp and Al-Ram (1500 and 1300 (m3/d) respectively. Furthermore, there are Israeli colonies and other Palestinian communities discharging their wastewater to the wadi (figure 1.1). Moreover, the problem is exacerbated when people arbitrarily evacuate their septic tanks by tanker trucks into Al-Qilt wadi at different

places. All these sources are mixed with the urban runoff in addition to leachates from dumping sites during the winter season [21].
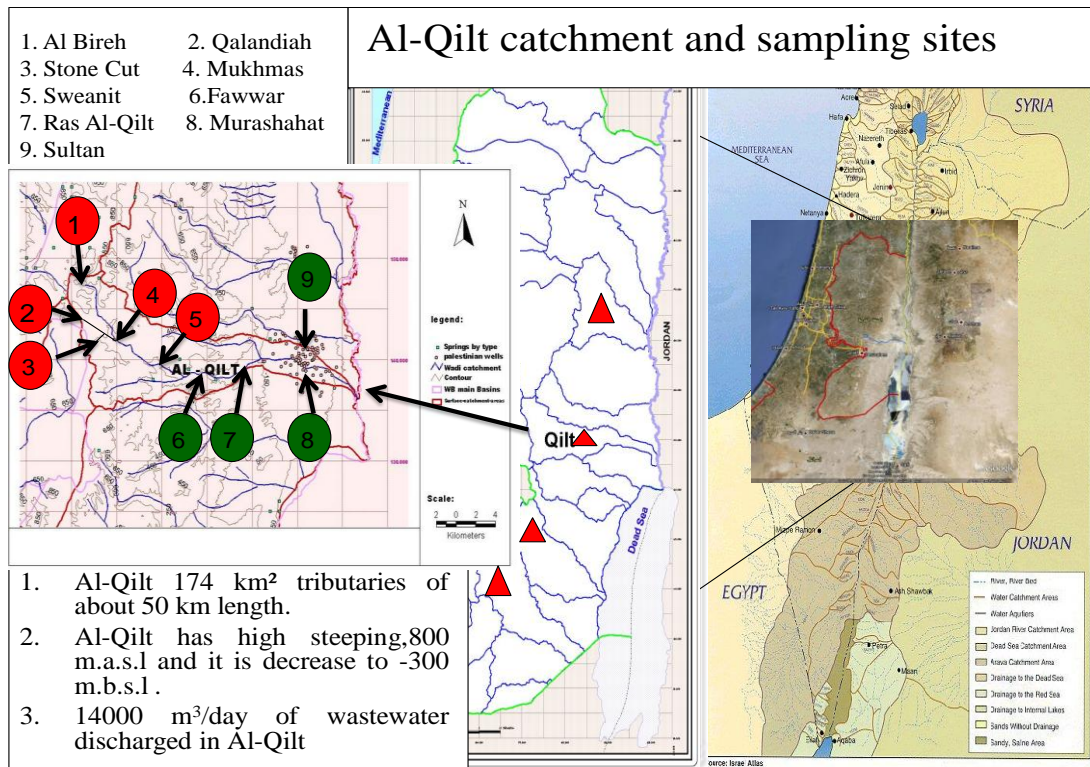
Figure1.1.location of Al-Qilt catchment.[21] Samhan ,2013.

1.3. Heavy metals

Criteria used to define heavy metals have included density, atomic number, atomic weight, or periodic table position [22]. Density criteria range from above 3.5 g/cm^3 to above 7 g/cm^3. There is a suggestion referring to heavy metals as "all the metals in groups 3 to 16 that are in periods 4 and greater [23]. There is no widely agreed definition of a heavy metal.

The origin of the term "heavy metal" is not clear. An early use when elements were divided into nonmetals, light metals and heavy metals

[24]. Light metals had densities of 0.860–5.0 gm/cm^3; heavy metals 5.308–22.000 [25].

Beryllium and Aluminum, although light metals, are sometimes counted as heavy metals in view of their toxicity (26-28).

Heavy metals are metals exhibit metallic properties where that mainly the transition metals or the metals that have d-block. There are other definitions that depending on different parameters such as the toxicity, chemical properties or atomic number ,The International Union of Pure and Applied Chemistry (IUPAC) consider the term "heavy metal" is a misinterpretation because of its lack of a "coherent scientific basis".[29] Toxic metals can be used as alternative term. However, there is no determined definition. As discussed earlier, according to the definitions, the elements lighter carbon are included to the heavy metals while some of the heaviest metals are excluded.

Different concentrations of the heavy metals can be occurred naturally in the aquatic system. Nowadays, one of the ecosystem pollutions source by heavy metals is human made.

on the other hand, heavy metals are important agents for medical and scientific applications. They have X-rays absorbance properties and thus are valuable in X-ray imaging, as with barium meal. Also, heavy metals can be used in transition electron microscope (TEM) to create specific contrast and expose fine detail.

Heavy metal such as lead (II) chromate as an example can be used in some pigments. Although organic dyes can have very high absorbance, they can be eventually bleached on exposure to sunlight, thus sunlight-stable inorganic heavy metal pigments have their uses.

1.4. Research question.

❖ To find elemental background for the heavy metals in the pristine area of Al-Qilt soil catchment by studying the occurrence of heavy metals in the pristine area soil's of Al-Qilt catchment, then to use them as references for studying and determining the levels of anthropogenic pollution in the soil of Al-Qilt catchment.

❖ Waste water discharged at high stream water consumed at low stream.

1.5. Objectives

The main goal of this research is to study the anthropogenic pollution in Al-Qilt catchment soil; other specific objectives of this research are will be helpful:

• To determine the soil elemental background of heavy-metals in Al-Qilt catchment.

• To screen heavy and trace metals contents of Al-Qilt's soil as either naturally occurring or resulted from anthropogenic activities.

Chapter Two

2. Literature review

2.1. Background

Human health in towns and cities is strongly dependent on the status of urban soils [30]. Strong compaction, contamination by wastes and atmospheric depositions, loss of organic matter, changes in soil reaction, structural degradation and infection by pathogenic microorganisms are only few of the many adverse processes that affect and modify the ecological functions of soils [31-34].

Soils act as a sink for heavy metals and other pollutants. The possible sources of pollution include vehicle emissions [35-38], industrial waste [39], the atmospheric deposition of dust and aerosol [40] and others. Most of heavy metals in high concentrations have an adverse effect on human health, especially on the health of young children, who have a higher rate of absorption of heavy metals because of their active digestion systems and sensitivity to hemoglobin. Heavy metals may accumulate in our body and affect the central nervous system, causing heavy metal poisoning and acting as cofactors in many other diseases [41-45].

The presence of high concentrations of metals in soils can have adverse impacts on terrestrial ecosystems [46-48]. They can also represent a threat to the health of people exposed either directly through soil contact or indirectly through the food chain [49]. There are two main sources of the

soil metals content [50]: either naturally from the geogenic weathering of base rock during soil formation (pedogenesis) or anthropogenically through point source or diffuse pollution and/or solid waste disposal [51]. According to the European Union and internationally, a set of studies has focused on the ecological risk assessment of metals in soils [52-55].

One of the core sources of heavy metal accumulation in soils is Atmospheric deposition reflected by high heavy metal concentrations in dust [56]. Key heavy metals are thereby Pb from leaded gasoline, Cu, Zn and Cd from car components, tyre abrasion, lubricants and industrial and incinerator emissions and urban runoff [57,58,59].

Samples in this research were analyzed by BCR fractionation, in a broad sense; fractionation has been known as either the process of identifying and quantifying the different binding forms or to describe the type of these fractions in steps which named as sequential extraction procedures "Bureau Cmmunautaire de Reference (BCR). This is an example for research activities that depend on pH and deem as tool for environmental assessment studies: this method is now standardized at the European Committee for Standardization and encompasses both single and sequential extraction methods into a scheme that let more direct relationships to make true speciation as derived from geochemical fractionation. These fractionations will give idea about the environmentally accessible and fate of pollutant "trace metal" mobility from sediments or soil to groundwater [21].

It is known that there are risks and errors due to environmental analysis while sample taken and preparation in addition to analysis steps. For this study, most of the precautions and limitations will be deem starting from sampling, sample pretreatment, storage and standards that use for analysis. All these issues were considered to be sure if we use the best way for sampling to soil. Furthermore, the guidelines adapted for sampling, field work, sample preparations, lab work, standards used as samples for soil and even the quality control and quality assurance are adapted to minimize the error and to achieve high accuracy [21].

BCR fractions are grouped into four steps: Acid soluble, reducible, oxidable and residual. Each extraction step and target phase is listed in order of least chemically aggressive reagents Table (2.1) [21]:

Table2.1: Reagents and conditions are employed for the (BCR) sequential extraction procedure.

Step	Fraction of solid phase	Reagent and conditions
1	Acid extractable "Exchangeable, water and acid soluble (e.g., carbonates)"	1 g of sample using 40ml 0.11 mol l^{-1} CH_3COOH, shaken for 16 hour at room temperature, centrifuged $3000 \times g$ for 20 minute, decant the supernatant, wash the solid, centrifuge then go to the next step. The supernatant for analysis.
2	Reducible "iron/manganese oxides"	40mL 0.5 mol l^{-1} $NH_2OH \cdot HCl$, shaken 16 hour at room temperature, centrifuged as in Step 1, then the supernatant for analysis.
3	Oxidisable "organic substance And sulphides"	Digested with 10ml 8.8 mol l^{-1} H_2O_2, 1 hour at room temperature, 1 hour at 85∘C and covered samples, 10ml 8.8 mol l^{-1} H_2O_2 added, 1 hour at 85∘C, reduced volume to 1 ml, extracted with 50mL of 1 mol l^{-1} NH_4COOCH_3, pH of solution 2-3, shaken 16 hour at room temperature, centrifuged as in Step 1, then the supernatant for analysis.
4	Residual "Remaining, non-silicate bound Metals"	7.5 mL 12 mol l^{-1} HCl, 2.5ml 16 mol l^{-1} HNO_3, Microwave digestion for 2 hour, cool, decant the supernatant, centrifuge, then sample for analysis.

Heavy metal contamination of the environment consider as worldwide phenomenon that has attracted a great deal of attention from governmental and regulatory bodies anxious to prevent further environmental deterioration and to examine possible methods of remediation.

2.2. Metals

In this research, 25 parameters of heavy metals were studied to make elemental background for anthropogenic pollution in Al-Qilt catchment's soil some of this metals are Al and Fe which are heavy metals we adopted one of them as normalizer.

2.2.1. Titanium

Figure2.1 Titanium [60].

Titanium is a chemical element with the symbol **Ti** and atomic number 22. It is a lustrous transition metal with a silver color, low density and high strength.

It is highly resistant to corrosion in sea water, aqua regia and chlorine.

The element occurs within a number of mineral deposits, principally rutile and ilmenite, which are widely distributed in the Earth's

crust and lithosphere, and it is found in almost all living things, rocks, water bodies, and soils.[61]

2.2.1.1. Toxicity of titanium:

Titanium is non-toxic and is not rejected by the body, It is not appears alone in the nature but it found combined with other elements, Titanium dioxide is of the titanium combined which is toxic.

2.2.2. Manganese

Figure 2.2 manganese [62].

Manganese is a chemical element, designated by the symbol Mn. It has the atomic number 25. Manganese is found as a free element in nature (often in combination with iron), and in many minerals. It is a metal with important industrial metal alloy uses, particularly in stainless steels

2.2.2.1. Toxicity of manganese:

Manganese overexposure is most frequently associated with manganism, a rare neurological disorder associated with excessive manganese ingestion or inhalation. Historically, persons employed in the production or processing of manganese alloys have been at risk for developing manganism [63, 64].

2.2.3. Bismuth

Figure 2.3 Bismuth [65]

Bismuth is a chemical element with symbol Bi and atomic number 83. Bismuth, a pentavalent poor metal, chemically resembles arsenic and antimony. Elemental bismuth may occur naturally, although Bismuth sulfide and oxide form important commercial ores. The free element is 86% as dense as lead. It is a brittle metal with a silvery white color when freshly produced, but is often seen in air with a pink tinge owing to surface

oxidation. It is the most naturally diamagnetic element and has one of the lowest values of thermal conductivity among metals.

Bismuth compounds account for about half the production of bismuth. They are used in cosmetics, pigments, paper, and a few pharmaceuticals, notably Pepto-Bismol. Bismuth's unusual propensity to expand upon freezing is responsible for some of its uses, such as in casting of printing type. It has unusually low toxicity for a heavy metal. As the toxicity of lead has become more apparent in recent years, there is an increasing use of bismuth alloys (presently about a third of bismuth production) as a replacement for lead.

2.2.3.1. Toxicology

Scientific literature concurs that bismuth and most of its compounds are less toxic compared to other heavy metals (lead, antimony, etc.) and that it is not bioaccumulative. They have low solubilities in the blood, are easily removed with urine, and showed no carcinogenic, mutagenic or teratogenic effects in long-term tests on animals (up to 2 years).[66,67].

 Bismuth poisoning exists and mostly affects the kidney, liver, and bladder. Skin and respiratory irritation can also follow exposure to respective organs. As with lead, overexposure to bismuth can result in the formation of a black deposit on the gingiva, known as a bismuth line.[68 -70]

Bismuth's environmental impacts are not very well known. It is considered that its environmental impact is small, due in part to the low solubility of its compounds.[71 -73].

2.2.4. Chromium

Figure 2.4 Chromium [74]

Chromium is a chemical element which has the symbol **Cr** and atomic number 24. It is the first element in Group 6. Chromium is a steely-gray, lustrous, hard and brittle metal [75].

2.2.4.1. Toxicity of Chromium

As Chromium compounds were used in dyes and paints and the tanning of leather, these compounds are often found in soil and groundwater at abandoned industrial sites, now needing environmental cleanup and remediation per the treatment of brown field land. Primer

paint containing hexavalent chromium is still used for aerospace and automobile refinishing applications [76].

2.3. Judgment and previous study:

Heavy metals contamination of rivers' soils was covered previously by different researches. A summary or relevant study is shown in Table (2.2).

Table2.2: summary of reviewed literature.

	Location	Targeted metals	Procedure of analysis	Main results	References
1	Al-Qilt catchment west bank, Palestine	Heavy and trace metals	the sequential extraction procedure called Community Bureau of Reference (BCR)	Results of Al-Qilt sediments reveal that Sn, Cu, Ag, Ba, Bi and B are high if compared to Elemental Background for Soil values	Sobhi A.R. Samhan , 2013
2	Al Qilt catchment area-Palestine	Trace elements	Physical ,chemical and biological parameters.	Most pollutant section throw wadi Al-Qilt is the part between AWWTP and wadi sweanit . Three springs located in the drainage basin are contaminated with heavy metals , whereas two springs are biological contaminated.	G.A Daghra and R Al-sa'ed (2009)
3	central Mexico,	boron, cadmium, chromium , mercury, lead and arsenic	modified Tessier method according to a six fraction scheme	The concentrations of total arsenic and mercury were below the detection limits (0.03 and 0.01 mg kg_1, respectively) except for 0.77 mg Hg kg_1 in one soil. The concentrations of total Cr and Pb did not exceed the maximum permissible levels set by the regulations of	Carlos A. Lucho-Constantin o et al. (2005)

				the European Union whereas total Cd was on the verge.	
4	reclaimed tidal wetlands in Pearl River estuary, South China	Cr and Ni	sequential extraction technique was used to produce five chemical fractions (exchangeable (F1), carbonate (F2), Fe–Mn hydroxide (reducible) (F3), organic (F4) and residual (F5))	generally the contamination levels increased with a longer history of reclamation (100> 40> 30> 10 years) whilst an undisturbed reference wetland was least affected.	Rong Xiao Junhong Bai et al. (2012)
5	Seyhan River, Turkey, Márk Horváth	Cd, Cr, Cu, Mn, Ni, Pb and Zn	a modified three-step sequential procedure	Pb > Mn > Zn > Cu > Ni > Cr in October 2009 and Mn > Pb > Zn > Cu > Ni > Cr in June 2010.	Orkun I.Davutluoglu, Galip Seckin et al. (2011)
6	Košice, Slovakia and Gödöllő, Hungary	heavy metal	BCR sequential extraction procedure supplemented with microwave-assisted HNO3/H2O2 digestion and another three-step method using supercritical CO2,	first step of the BCR with 0.11 mol dm−3 acetic acid and second and third steps of the alternative method with H2O and H2O+CO2, respectively) was similar in case of Cd, Ni and Cu in both biofilm and sediment samples.	Márk Horváth et al. (2012)
7	Guadalhorce river	Cu, Ni, Cr, Pb and Cd	microwave assisted sequential extraction	by using a CCD design we have been able to establish the optimum conditions for the proposed MW	M.L. Alonso Castillo, E. Vereda Alonso et al.(2011)

				procedure. The optimum conditions established in each step of the BCR procedure were applied to the determination of copper, nickel, lead, chromium and cadmium in sediments of different origins by ICPMS	
8	Tisza river sediments	Ni, Cu, Zn, Cr, Pb, Fe, and Mn	Tessier method	the Tisza River is slightly to moderately severely polluted with Cu, Zn, and Pb, and minorly polluted with Cr. It is concluded that sediments of the Tisza serve as a repository for heavy metal accumulation from adjacent urban and industrial areas	Sanja M. Sakan et al.(2009)
9	Spain	Fe,Pb,Zn, Cu, Mn,Ni and Cr	multivariate exploratory and BCR fractionation	the sum of the three BCR fractions, the elements showed a decreasing availability of: Fe > Pb > Zn > Cu > Mn > Ni > Cr.	R. Devesa-Rey et al.(2010)
10	Poxim river estuary of Sergipe State northeast Brazil	Cd, Cr, Cu, Ni, Pb and Zn	using the 3-stage sequential extraction procedure proposed by the European Community	Cd, Cu, Ni and Pb were associated with the oxidizable fraction, and Pb, Cr and Ni with	Elisangela de Andrade Passos et al.(2010)

			Bureau of Reference (BCR).	the reducible fraction. Principal component analysis (PCA) clearly separated the metals into three groups: I (Zn); II (Pb); III (Cd, Cu, Cr and Ni). These groupings were mainly due to different distributions of the metals in the various fractions, in sediments from the different locations	
11	Gomti River (India)	Al, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sn, Ti, V, and Zn	multi-way (three-way)		Kunwar P. Singh et al.(2005)
12	Spain	Pb ,Zn	modified BCR sequential extraction method	need to treat the mine tailings dumped in the mine area	L. Rodrı´guez et al. (2009)

2.4. Continental Crust as reference or background

Trace and heavy metal concentrations indicate anthropogenic pollution if they are compared with the Continental Crust (CC) as a background. The Upper Crust (UC) and the Lower Crust (LC) Table (2.3) were analyzed for rock samples and then the average values were taken and summarized according to Wedepohl (1995), Pekey *et al*. (2004), Buccolieri *et al*. (2006) and Alagarsamy (2006).

Table (2.3): Heavy and trace metal concentrations in the CC as average of UC and LC.

Element	Concentration (mg/kg)	Element	Concentration(mg/kg)	Element	Concentration(mg/kg)	Element	Concentration (μg/kg)
Al	79780 mg/kg[a]	Co	24 mg/kg[a]	Sr	333 mg/kg[a]	Sb	300 μg/kg[g]
Ti	4010 mg/kg[a]	Ni	56 mg/kg[a]	Mo	1.1 mg/kg[c]	Hg	40 μg/kg[i]
V	98 mg/kg[a]	Cu	25 mg/kg[a]	U	1.7 mg/kg[a]	Cd	100 μg/kg[e]
Cr	126 mg/kg[a]	Zn	65 mg/kg[a]	Pb	14.8 mg/kg[a]	Bi	85 μg/kg[e]
Mn	716 mg/kg[a]	As	1.7mg/kg[b]	Sn	2.3 mg/kg[f]	Ag	70 μg/kg[d]
Fe	43975 mg/kg[a]	Rb	78 mg/kg[a]	B	11 mg/kg[j]		
Ba	584 mg/kg[h]						

a : **UC:** Shaw et al. (1967, 1976), LC: Rudnik and Presper (1990) in the proportions of standard profile of the continental crust derived from 3000 km long Standard Profile of Continental Crust (European Geo-Traverse) (EGT)) generalized on the basis of worldwide mapping, petrological studies and chemical balances.

b: **UC** calculated from rock average of Onishi and Sandell (1995), Burwash and Culbert (197 9) in relate to EGT profile mentioned before LC: gabbro, gneiss minus 20%..

c : **UC:** calculated from rock average compiled by Manheim and Landergeren (1978) in proportion to EGT profile, gabbro, gneiss minus 20% granite.

d: UC, LC: calculated from rock average of Hamaguchi and Kuroda, (1995) in proportion to EGT profile, Cu/Ag in felsic rocks 300 to 450.

e: UC, LC: calculated from rock average of Heinrichs et al. (1980) in proportion to EGT profile.

f: UC: calculated from rock average compiled by Hamaguchi and Kurdoda (1969) and Smith and Burton (1972) in proportion to EGT profile, LC: Rundick and Presper (1990).

g: UC: calculated from rock average of Onishi and Sandell (1995) and Burwash and Culbert (1979) in the proportion of EGT profile, LC: estimated.

h: UC: calculated from rock average complied by Puchelt (1972) in proportion to EGT profile, LC: Rudnik and Presper (1990).

i: UC, LC: calculated from rock average complied by the present author partly from Marowski and Wedepohl (1971).and partly from unpublished data in the proportion of EGT profile.

j: UC: calculated from rock average complied by Harder (1974) and Shaw et al. (1986) in proportion to EGT profile, LC: data from Truscott et al (1986), Leeman et al. (1992) and harder (1974).

2.5. Grain size analysis:

It is used to characterize the sediments and soil in different textures in the range of gravel, sand, silt and clay forms, hence; the main reasons to study the trace metal in relation to textures size was: (i) smaller particles that have greater surface area that increase the metal scavenging and adsorption capacity (ii) the greater concentrations of metal adsorbing or binding to particle matter, these variations are reduced by analyzing the sediment to size usually <63 μm [77].

The interpretation of sediment contaminant data is complicated if there are variable in grain size, since, contaminants are frequently associate with the fine fraction of aquatic sediments due to an exponential that increase at surface area with decreasing the grain size[78].Table (2.4).

Table (2.4): Summery of grain size in term of textural and chemical properties.

Normalization	Size µm	Indicator	Role
Grain size	2000 - < 2	Granular variations of metal - bearing minerals / compounds	Determines physical sorting and depositional pattern of metals
Sand	2000 – 63	Coarse - grained metal - poor minerals / compounds	Usually diluents of trace metal concentrations
Mud	< 63	Silt and clay size metal – bearing minerals / compounds	Usually overall concentrator of trace metals
Clay	< 2	Metal - rich clay minerals	Usually fine – grained accumulator of trace metals

Grain size analysis for sediment and soil are critical factor that influence the percent of anthropogenic pollutants at fine-grain of less than 63µm, this will have higher pollutants percent if compared to coarse-grain in the range of gravel (2mm) or in the range of sand that is grater to 63µm, furthermore; the fine-grain particles have higher surface area to mass ratio if compared to coarse-grain, also they often sequester much higher of pollutants mainly for trace and heavy metals in sediment and soil due to difference in charges. As a consequence, there is often strong inverse correlation between grain size and metal concentrations; this relationship

is further enhanced by common accumulation from organic and inorganic matter in depositional zones, The grain size analysis for sediments and soil for the range that is greater than 2mm are removed by hand-picking, then by sieving using Fritsch D-55743 analyzer, furthermore; the gravel, sand and mud fractions are in the following series: gravel $\geq$ 200μm, Sand $\geq$ 63μm and the mud < 63μm [79].

Chapter Three

3. Methodology

3.1. Background

This methodology will be focused on studying the heavy metals content and distribution in the soil of Al-Qilt catchment in Palestine and to compare with regional or international studies, and to determine heavy metals in the pristine area to consider as elemental background for the anthropogenic pollution in Al-Qilt catchment soils.

3.2. Sampling

Ten soil Samples were collected in December, 2012 along Al-Qilt catchment, and from ten locations: Ramallah, Al Bireh, Mukhmas, Qalandiah, Stone-cut zone,Sweanit, Fawwar, Ras Al-Qilt ,Murashahat and sultan. Figure(3.1)
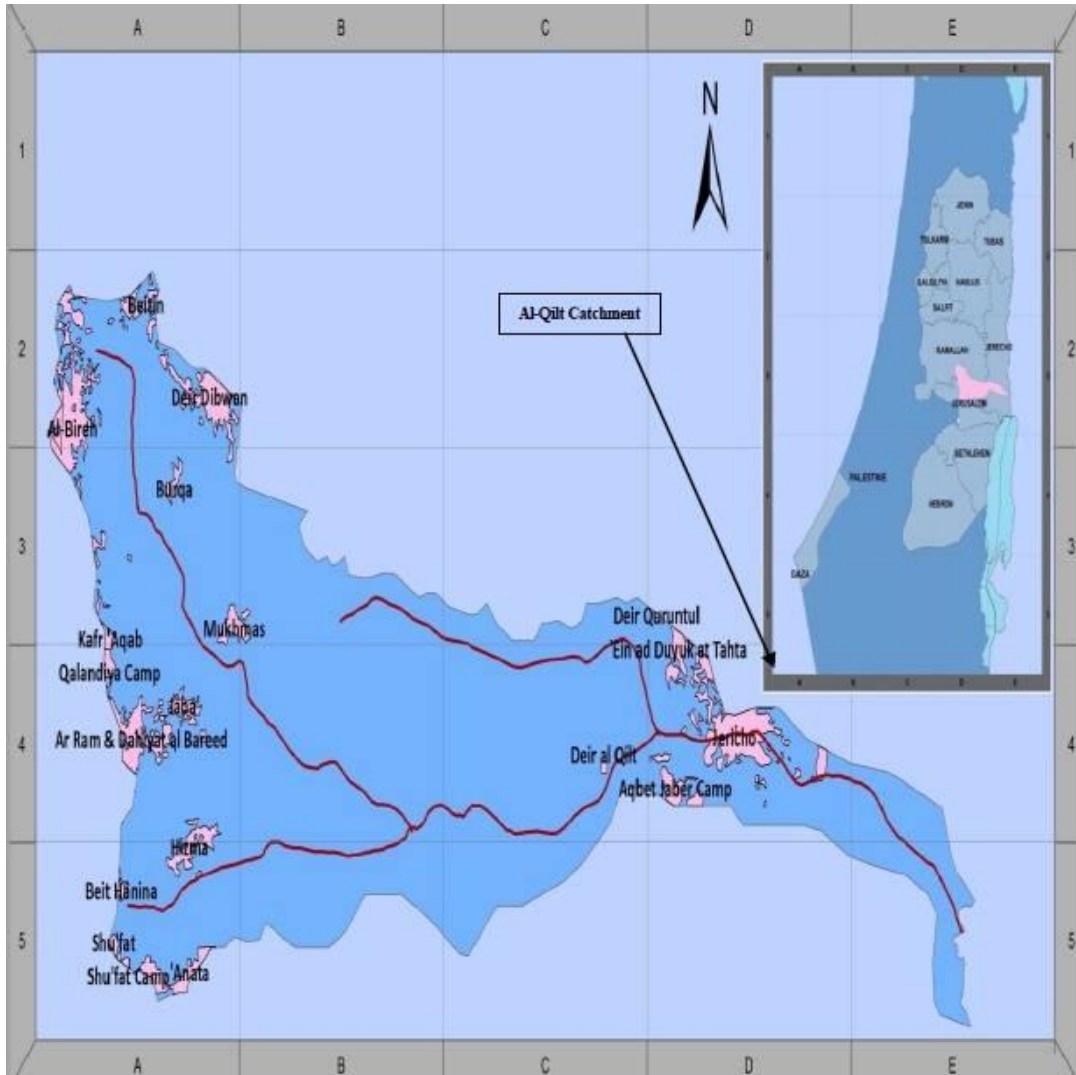
Figure (3.1): General map for Al-Qilt catchment. [80]

Samples were collected by polyvinylchloride-shovel, and then placed in polyethylene bottles, all samples have been refrigerated transferred to the laboratory for analysis.

3.3. Sample digestion and analysis by Aqua Regia:

• About 200-250g from each sample have been sieved to <63μm using "Fritsch D-55743" sieving analyzer.

- About 0.25g from each sample and Buffalo Reference Material (8704) as reference standard are weighted accurately in 100 ml Teflon digestion tube for Aqua Regia digestion.

- Then it is mixed with 6mL of HNO_3 (65%) and 3ml of HCl (37%).

- The samples digested for two hours using "Microwave MARS 5" digester and then the samples kept to reach the room temperature.

- Samples are centrifuged and the supernatant transferred to 50mL tube for analysis by doing the proper dilution. [21].

Trace metal concentrations of Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Rb, Sr, Mo, Ag, Cd, Sn, Sb, Ba , Pb, Bi, U, B, Li and Be were measured by an Inductive Coupled Plasma Mass Spectrometer (ICP-MS) (Agilent 7500) .

For BCR fractionation analysis about one gram from the samples are weighted for the BCR steps Figure (2.2). All soil samples analyses were conducted in the Water Research Center (UFZ), Magdeburg, Germany.

3.4. Bureau Communautaire de Reference (BCR)

BCR sequential fractionation extraction is recommended as standard procedure for the characterization of heavy and traces metals in sediment and soil, the BCR method is formed from four steps that classify in terms of reagent, This method is recommended by the Measurements and Testing Programme of the European Commission, The fractions of each method are grouped into four "equivalents" (acid soluble, reducible, oxidable, and

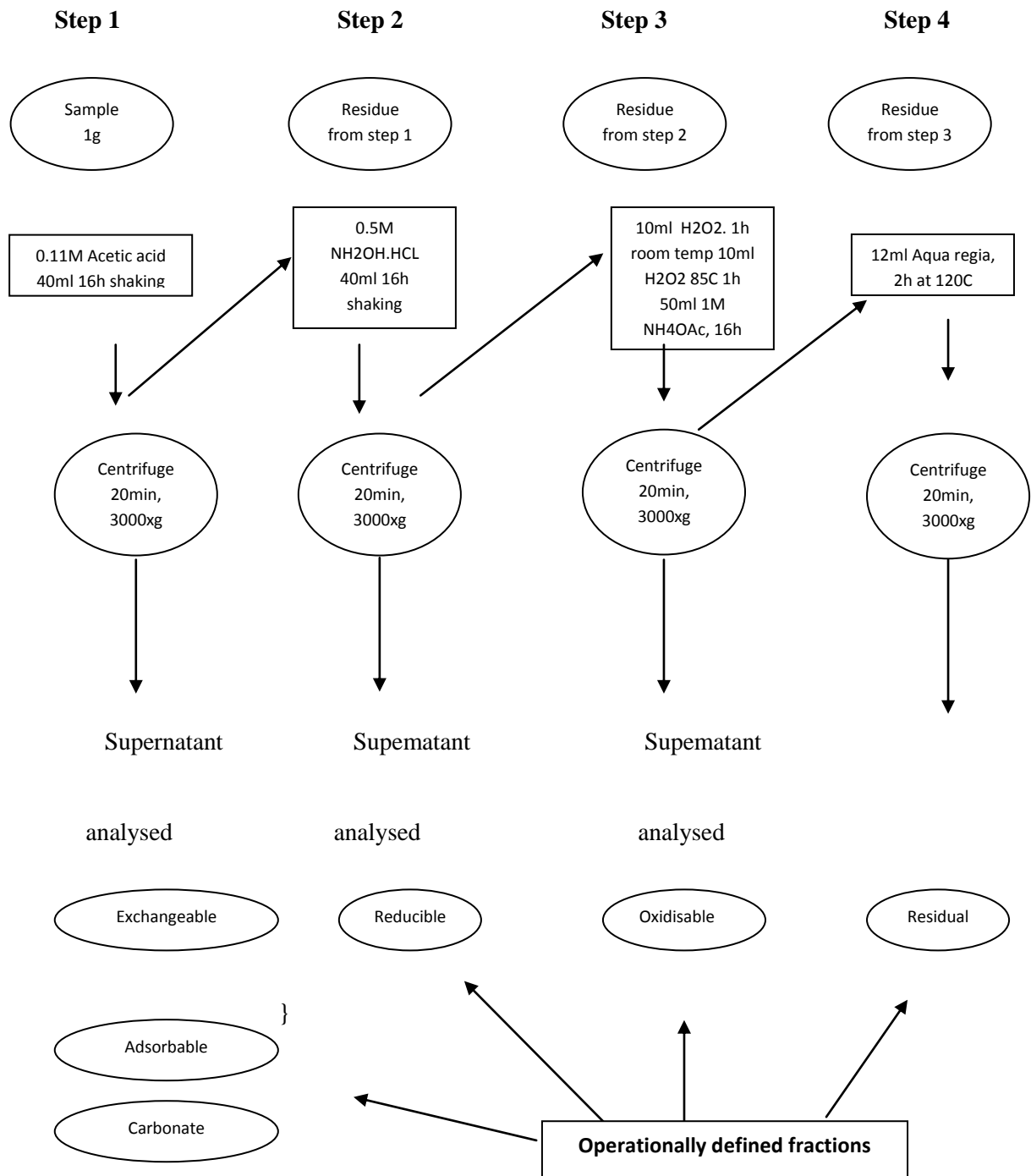residual), The BCR 4-stage extraction scheme is summarized in figure (3.2).

Step 1 **Step 2** **Step 3** **Step 4**

Sample 1g
Residue from step 1
Residue from step 2
Residue from step 3

0.11M Acetic acid 40ml 16h shaking

0.5M NH2OH.HCL 40ml 16h shaking

10ml H2O2. 1h room temp 10ml H2O2 85C 1h 50ml 1M NH4OAc, 16h

12ml Aqua regia, 2h at 120C

Centrifuge 20min, 3000xg
Centrifuge 20min, 3000xg
Centrifuge 20min, 3000xg
Centrifuge 20min, 3000xg

Supernatant Supematant Supematant

analysed analysed analysed

Exchangeable Reducible Oxidisable Residual

Adsorbable }

Carbonate

Operationally defined fractions

Figure (3.2): Schematic representation of the BCR four stage extraction scheme [21].

3.5. Data analysis

3.5.1. Correlation coefficient (R^2)

Heavy and trace metals were graphed against Al and Fe as reference elements to facilitate the comparison between Al-Qilt sites. The best correlated metals with elemental normalizers or reference element, depending on the correlation factors (R^2), since the best elemental normalizers will be in the range 1or -1, and we considered the best correlation with the highest values.

3.5.2. Normalization of heavy and trace metals

The normalization was based on the supposition that metal concentrations very consistently with the concentration of reference elements unless the metals were of anthropogenic origin. Normalization is away to compensate for the natural variability of trace metals in soils, so that any anthropogenic metal contributed may be detected and quantified by reducing the natural effect of grain size. This then allows us to identify the trace metal as a man-made pollutant [81].

The normalization method was based on the following assumptions:

(1) The concentration of metals is regular with the reference elements unless the metals were of anthropogenic origin.

(2) The normalization method is a way to compensate for the natural variability for trace metals in soil and sediments.

(3) Any anthropogenic metal contribution may be detected and quantified by reducing the natural effect of grain size.

These assumptions allow us to identify the trace metal as a man-made pollutant since many researchers have used Al and Fe as elemental normalizer.

3.5.3. Enrichment Factor (EF):

First step in the calculation of an EF is finding the relation between a metal and anomalizer, and then using this factor to identify anomalous metal concentrations that may have an anthropogenic source; then we can specify the enriched site. The selected normalizer can be divided by the same ratio of anthropogenic at un-impacted geological material (background). This permits the definition of Enrichment Factor (EF) parameters as (Me/N) sample/ (Me/N) background, where (Me/N) sample is: metal to normalizer ratio in the soil sample and (Me/N) background is: metal to normalize ratio in anthropogenic un-impacted geological material.[82,83].

$$EF = \frac{\left(\frac{Me}{N}\right) sample}{\left(\frac{Me}{N}\right) background} \qquad (1.1)$$

Me/N sample: is the metal or element to normalizer ratio.

Me/N background: is the natural background value of metal to normalizer ratio.

Enrichment Factor shows the status of environmental contamination .the EF values were interpreted by Acevedo-Figueroa et al.[84] , where EF □ 1

indicates no enrichment;1-3 is minor;3-5 is moderate; 5-10 is moderately severe; 10-25 is severe;25-50 is very severe ; and $\square$ 50 is extremely severe.

3.6. Elemental background for soil (E.B.S.):

Trace and heavy metal concentrations indicate anthropogenic pollution if they are compared with the elemental background, samples from pristine area (places with no known human activities) in Al-Qilt catchment were analyzed for soil to make the elemental background.

In this research, elemental background of Al-Qilt catchment was determined to assess the anthropogenic pollution in Al-Qilt catchment soil and to compare by using continental crust values (showed in section (2.4))

The pristine area considered as clean area because there is no human activity in it these area are: Sweanit, Fawwar, Ras Al-Qilt and Murashahat. So when these samples were analyzed it will give us a ratio of heavy and trace metals present in Al-Qilt soils naturally without the effects of human activities.

Chapter Four

4. Results and discussion

4.1. Introduction:

This chapter discusses the measured and calculated value of correlation coefficient values (R^2) for metals with Al, Fe and elemental background (E.B.S.), and Enrichment Factor (EF). This chapter also present the comparison between the values of metals in EBS and CC.

4.2. Results and discussion.

4.2.1 Correlation coefficient (R^2):

Heavy and trace metals concentrations of collected samples from Al-Qilt were graphed as metals vs References element such as Al and Fe and the correlation coefficient were calculated .

The correlation factor between the concentration of all measure metals against the Fe were higher than the Al, Al and Fe were found as a good normalizer due to the high R^2 values. (Table 4.1)

Table (4.1): Correlation coefficient values (R^2) for metals with Al, Fe and E.B.S. along Al-Qilt catchment.

|	Met/Al	Met/Fe	Met/E.B.S. [*]
Ti	0.0469	0.2087	0.8456
V	0.5503	0.7179	0.1000
Cr	0.3837	0.3331	0.8514
Mn	0.4211	0.4222	0.4153
Co	0.6711	0.7253	0.3590
Ni	0.3362	0.3155	0.0939
Cu	0.3602	0.1895	0.4960
Zn	0.3803	0.2362	0.0319
As	0.3942	0.2902	
Rb	0.6297	0.4987	0.0421
Sr	0.5678	0.6026	0.6554
Mo	0.1027	0.1393	0.3333
Ag	0.0068	0.0341	0.3086
Cd		0.0005	0.2727
Sn	0.0762	0.0365	0.1341
Sb	0.2772	0.1698	
Ba	0.1715	0.0194	0.6618
Pb	0.3577	0.2677	0.0884
Bi	0.0003	0.0795	
B	0.0982	0.1277	
Be	0.0727	0.2483	
Li	0.6862	0.7364	
U	0.4127	0.3041	0.0526

[*]**Met/E.B.S.** Correlation coefficient values (R^2) for metals with Al and Fe in EBS in the pristine area along Al-Qilt catchment.

Fe is prevailing over Al since its related more in correlation Table(4.1) this prefer use of Fe as elemental normalizer at Al-Qilt , and then to use it as background for EF calculation .

Met/Al, Met/Fe normalization for anthropogenic parameters: normalization procedures were adapted by dividing the concentration of any metal by the

concentration of the reference element, in this study we use the normalization procedure to recover the natural variability of trace metal in soil, in this way anthropogenic metal contributed could be detected and quantified, the normalization of metal/Al and Fe were calculated then the normalization results were visualized to have numerical numbers and not fractions, the highest value being considered as indication for anthropogenic pollutants.

The heavy and trace metals concentrations were graphed as metals vs reference elements , then the correlation coefficients were calculated Figure(4.1), (4.2)and (4.3)
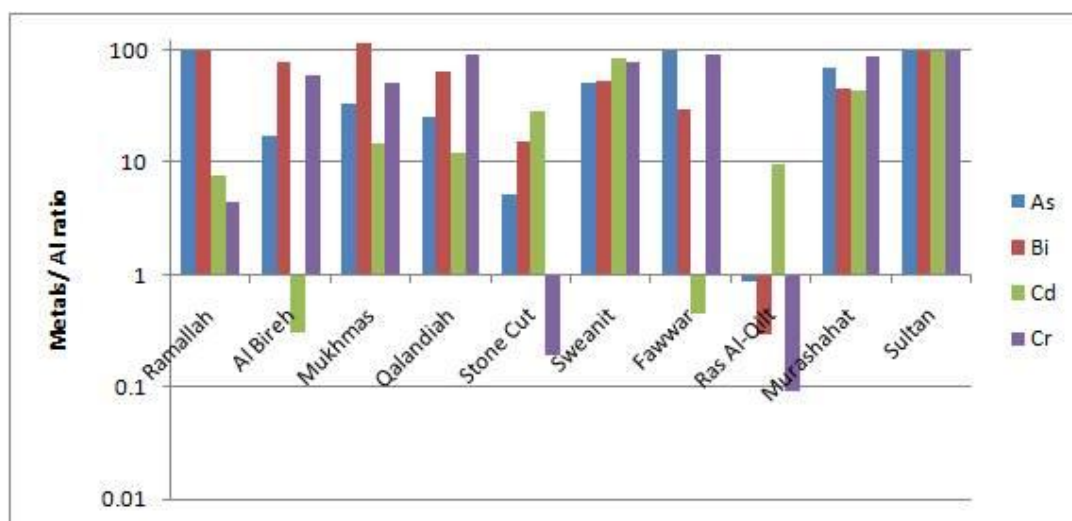
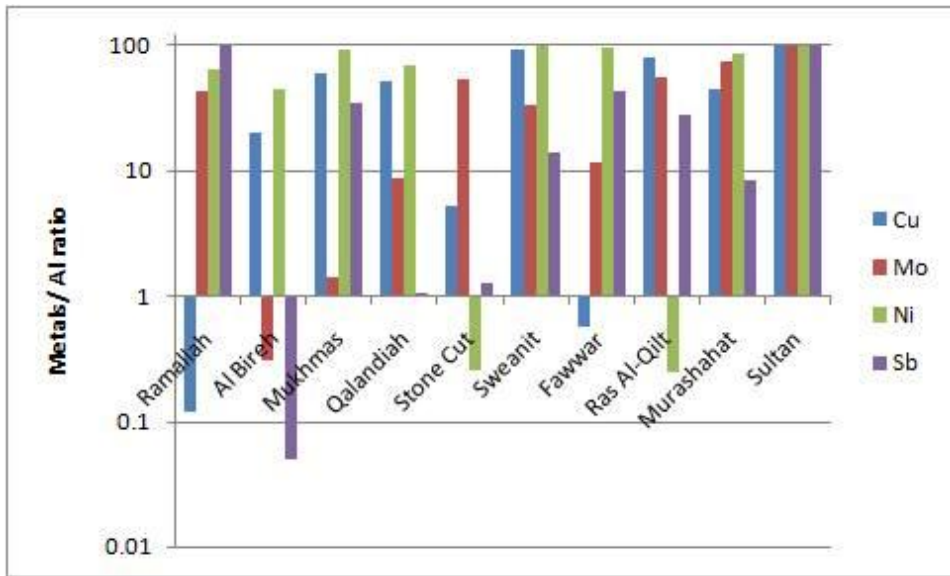**Figure(4.1)** metals/Al ratio less than 1 for As, Bi, Cd and Cr.

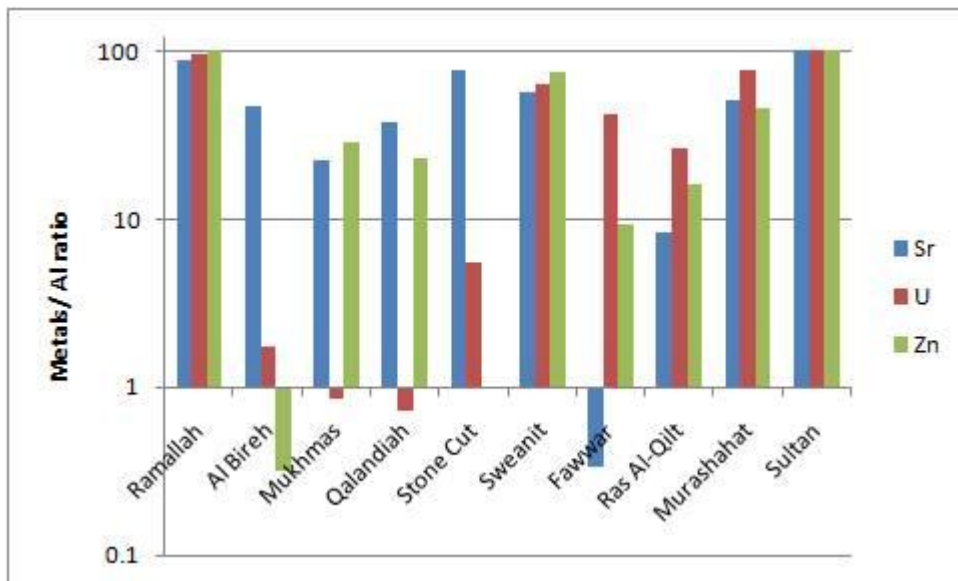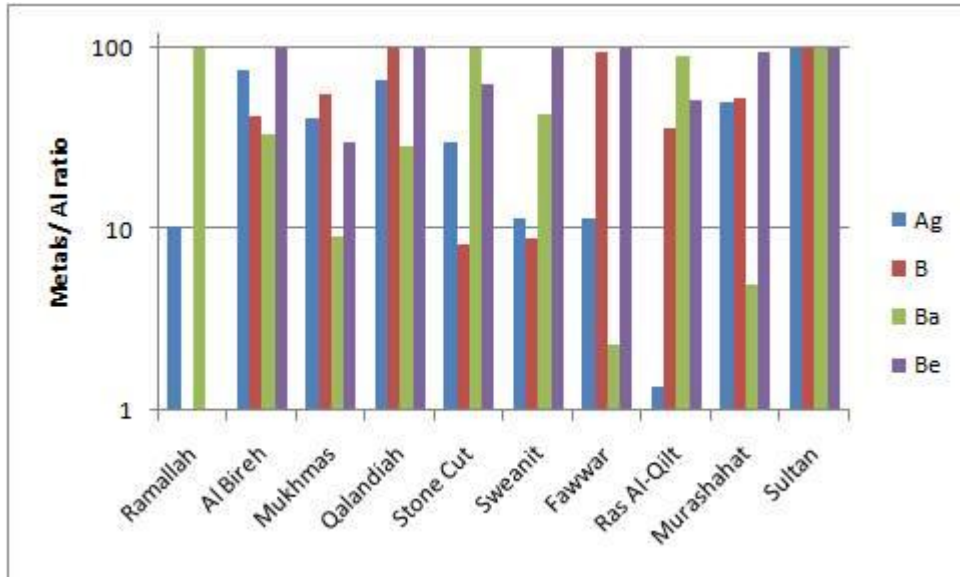**Figure (4.2)** metals/Al ratio less than 1 for Cu, Mo ,Ni and Sb.

Figure (4.3) metals/Al ratio less than 1for Sr, U and Zn.

Result showed that metal/Al were less than 1 for Cr, Ni, Zn , Cu, Sr, Cd, Sb, U, Bi, As and Mo , this indicates that these values for the mentioned parameters are to be considered as background or natural effects.
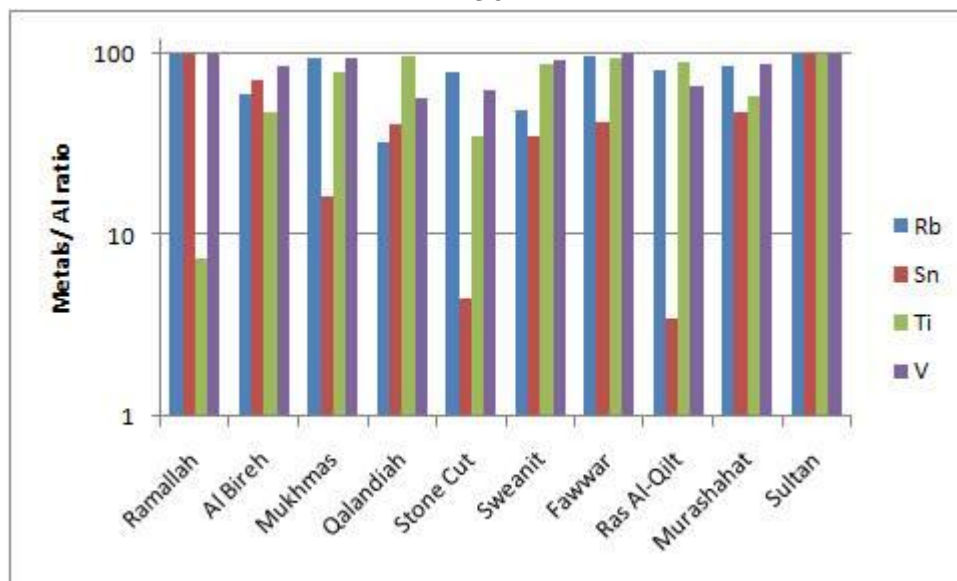
Value of metal/Al greater than one show at figure (4.4), (4.5) and (4.6) indicate anthropogenic pollution.

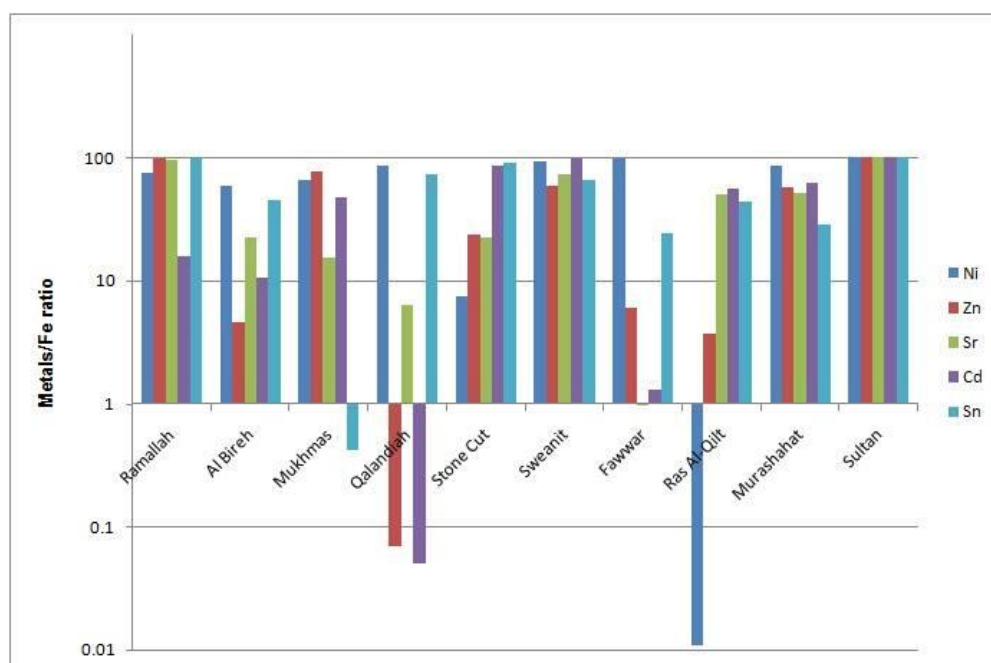**Figure(4.4)** Metals/Al ratio more than 1for Ag, B, Ba and Be.
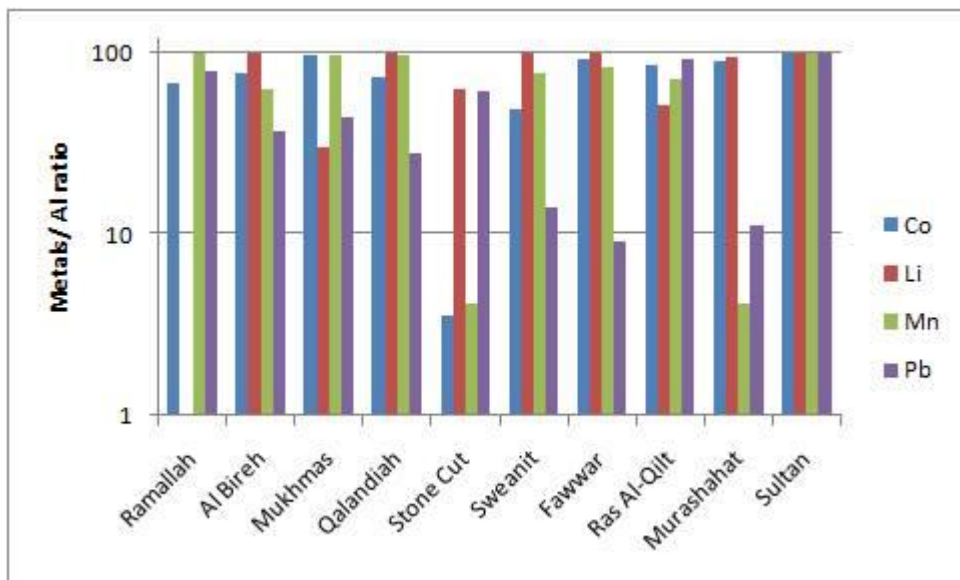
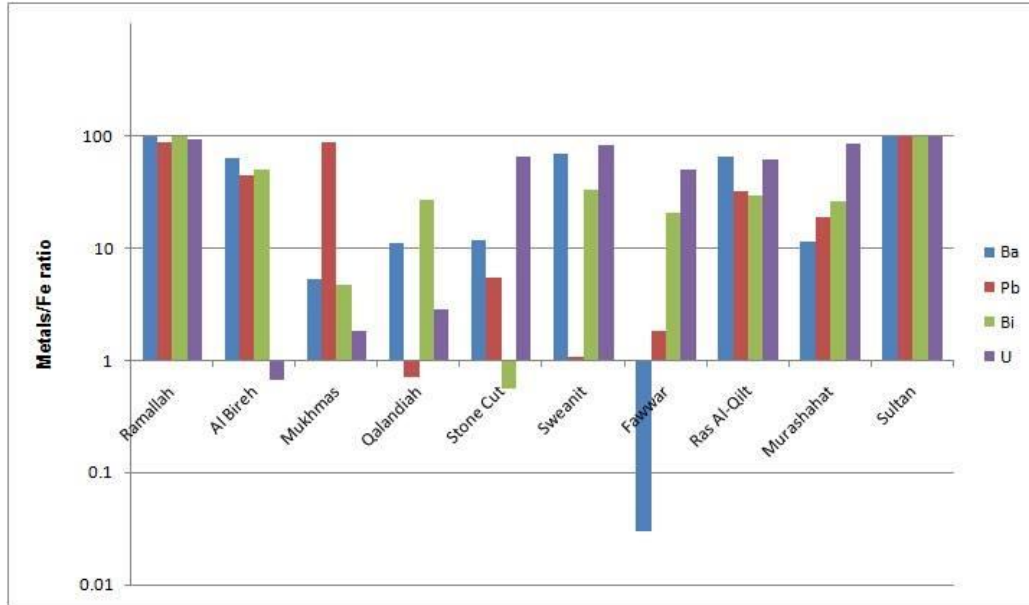**Figure(4.5)** Metals/Al ratio more 1 Co, Li, Mn and Pb.

Figure(4.6) Metals/Al ratio more 1for Rb, Sn, Ti and V.

Furthermore, results showed that metals/Fe results for Ni, Zn, Sr, Cd, Sn, Ba, Pb, Bi and U were less than one , and so these trace are not considered as anthropogenic pollutants at Al-Qilt sampling site Figures (4.7) and (4.8).

Figure(4.7) Metals/Fe ratio less than 1for Ni, Zn, Sr, Cd and Sn.

Figure(4.8) Metals/Fe ratio less than 1 for Ba, Pb, Bi and U.

Those greater than one, these are considered as anthropogenic indication for pollution were graphed at figure (4.9) , (4.10), (4.11)and (4.12).
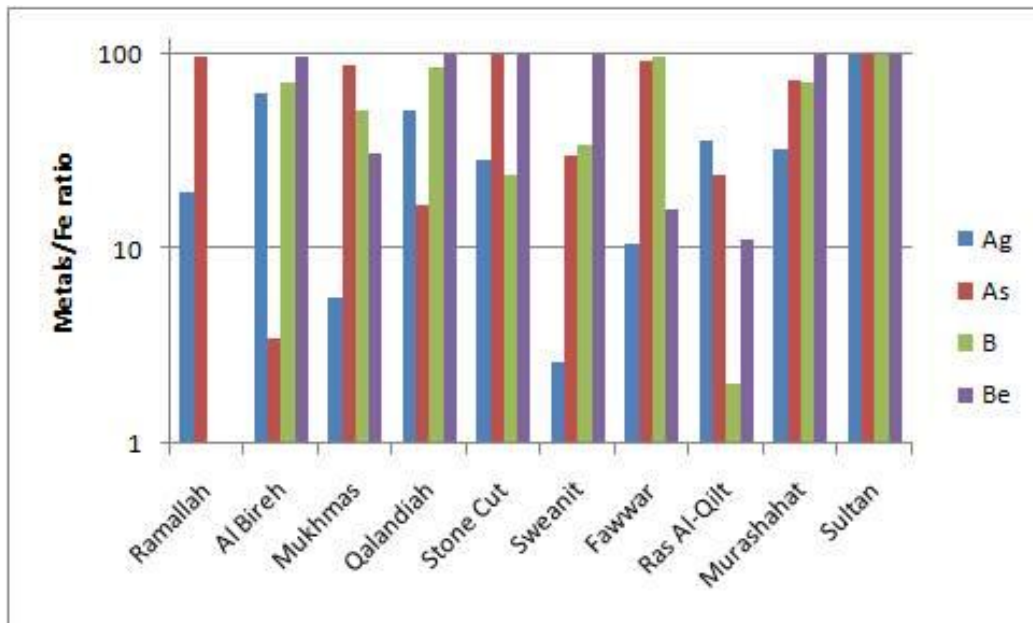

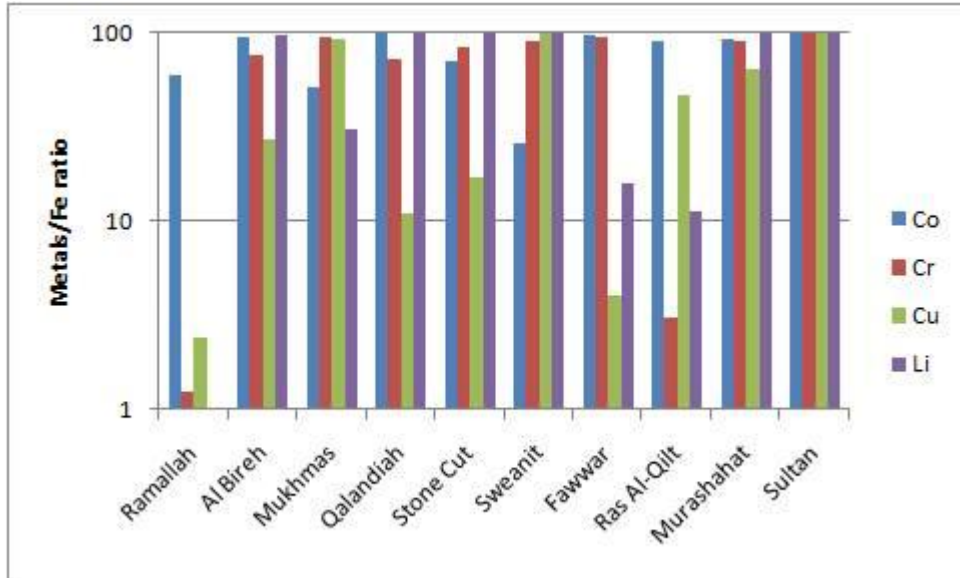**Figure (4.9)** Metals/Fe ratio more than 1 for Ag, As, B and Be.

Figure (4.10) Metals/Fe ratio more than 1 for Co, Cr, Cu and Li.
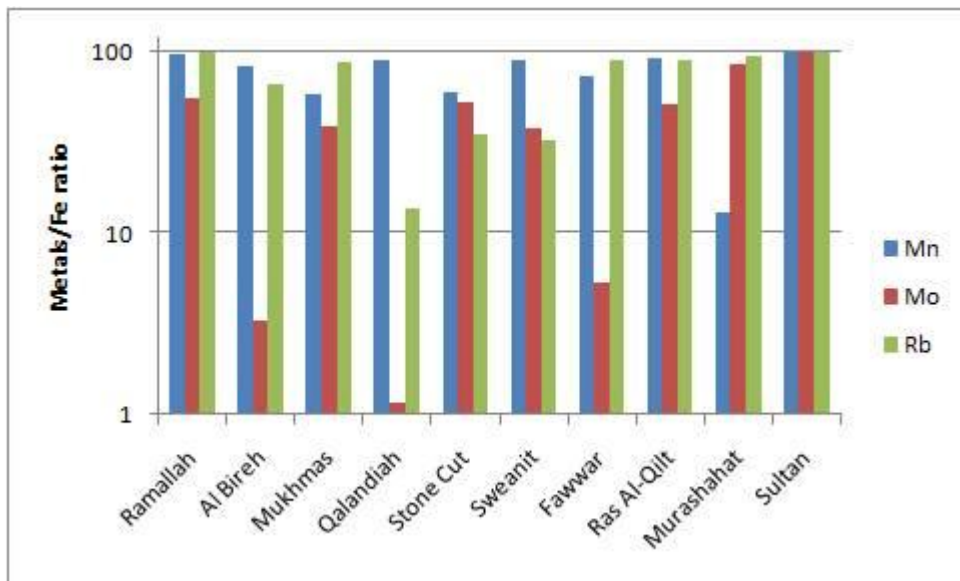

Figure (4.11) Metals/Fe ratio more than 1for Mn, Mo and Rb.
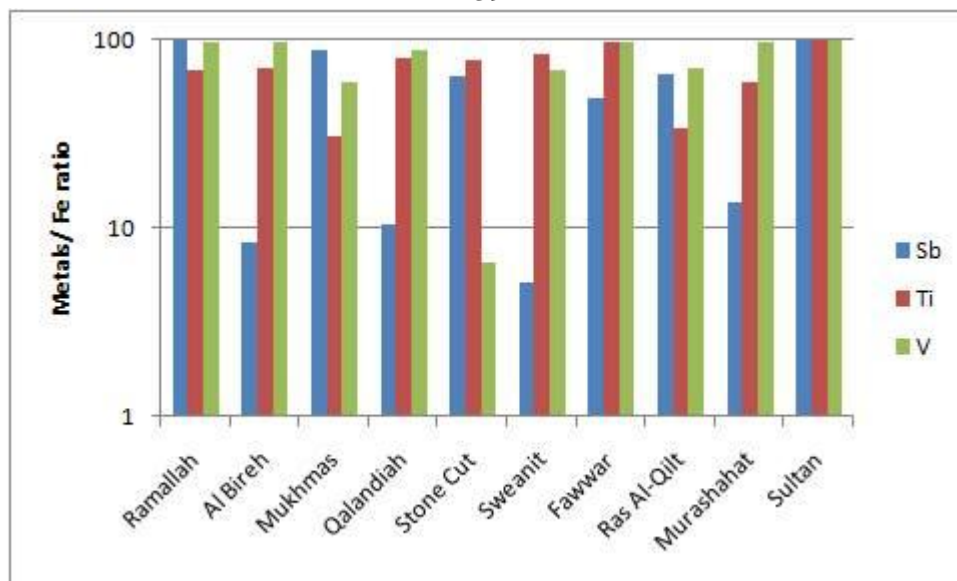
Figure(4.12) Metals/Fe ratio more than 1 for Sb, Ti and V.

Results showed that metal/Al and metal/Fe normalization for Ti, V, Mn, Co, Rb, Ag, Li, B and Be were to be considered as anthropogenic pollutants in most of Al-Qilt sites.

Furthermore, Fe was more suitable for normalization compared to Al for trace and heavy metals, and according to the normalization method we can assign the anthropogenic pollutants. Thus, we can use results of Fe as background values for the samples to calculate the Enrichment Factor (EF).

Fe was found to be the best elemental normalizer since it has the highest R^2 values compared to Al. table (4.1).

4.2.2. Enrichment Factor (EF):

Table (4.2) summarizes the results of enrichment factors at Al-Qilt catchment for trace metals tested at each site, if the EF values are between 0.5 and 1.5 the metal must be entirely from crustal materials or natural

weathering processes. If the EF is greater than 1.5 this suggests that a significant portion of the metal has originated from non-crustal or anthropogenic processes.

Table (4.2) enrichment factor along Al-Qilt since EF□ 1= blue, no enrichment, EF=1-3, yellow miner, EF=3-5, orange, moderate, EF=5-10, red moderately.

sampling situations	Ti	V	Cr	Mn	Co	Ni	Cu	Zn	As	Rb	Sr	
Ramallah	0.15	0.51	0.41	0.52	0.61	0.38	1.05	1.21	1.33	2.18	0.07	
Al Bireh	0.66	0.69	0.36	0.74	0.80	0.49	0.41	0.45	0.52	0.98	0.08	
Mukhmas	0.96	0.77	0.41	0.80	0.84	0.54	0.47	0.49	0.58	0.90	0.14	
Qalandiah	0.94	0.70	0.34	0.79	0.80	0.47	0.48	0.50	0.47	0.93	0.06	
Stone Cut	0.84	0.75	0.65	0.75	0.85	0.57	0.71	0.80	0.64	1.00	0.11	
Sweanit	0.92	0.96	0.50	0.58	1.14	0.96	0.82	1.40	1.31	1.31	0.57	
Fawwar	0.93	0.90	0.74	1.44	1.09	1.01	1.21	0.92	0.87	0.87	0.93	
Ras Al-Qilt	1.06	1.21	0.90	0.86	0.85	1.17	0.83	1.04	0.97	0.85	1.46	
Murashahat	1.05	0.91	0.66	0.99	0.93	0.83	1.04	0.75	0.93	1.04	0.92	
Sultan	2.16	0.90	0.38	0.20	0.98	0.54	0.41	0.32	0.55	0.80	0.13	
Continue sampling situations	Mo	Ag	Cd	Sn	Sb	Ba	Pb	Bi	U	B	Li	Be
Ramallah	0.33	0.00	0.64	0.31	1.87	0.63	5.71	0.50	0.21			
Al Bireh	0.25	0.60	0.21	0.12	0.37	0.40	0.81	0.50	0.16	0.55	1.00	0.60
Mukhmas	0.42	1.16	0.27	0.40	0.48	0.46	1.10	0.64	0.42	0.46	0.50	0.38
Qalandiah	0.22	0.00	0.19	0.22	0.34	0.37	0.93	0.45	0.15	0.29	0.93	0.54
Stone Cut	0.44	1.93	0.45	0.36	1.20	0.44	4.09	1.07	0.17	0.45	0.95	0.64
Sweanit	1.16	2.10	0.75	3.83	1.31	2.23	1.35	1.75	0.58	0.91	1.12	1.05
Fawwar	0.77	0.69	0.49	0.51	0.87	1.24	0.89	1.16	0.77	0.68	0.91	0.69
Ras Al-Qilt	1.30	0.78	1.67	0.24	0.97	1.08	1.00	1.30	1.73	1.01	1.02	0.78
Murashahat	0.82	0.74	1.06	0.23	0.93	0.65	0.85	0.00	0.82	1.37	0.97	1.49
Sultan	0.20	4.07	0.26	0.53	0.46	0.32	0.58	1.85	0.41	0.52	1.10	1.11

The EF for heavy and trace metals in soil at Al-Qilt were varied with years, Pb is moderately severe (red) in Ramallah, Pb, Sn and Ag it is moderate

(orange) in stone cut, Sweanit and sultan respectively ,yellow color show that there is minor effects of this metals.

The results show that there are no big problems in our calculation, mostly of the values of the FE in the Table (4.2) show there is no enrichment, some of trace and heavy metals have minor values, Pb, Sn and Ag have moderate values, Pb has the highest value in the table this value show that Pb has moderate value in Ramallah this value may refers to Wars and Military activities located in that region over the antiquity and that originate from urban activities such as vehicle , road and urban runoff.

4.2.3. Elemental back ground for soil VS continental crust values

Average values of heavy metals concentration for the elemental background Figure (4.13) showed that values of Zn, Cu, As, Sr, Mo, Ag, Cd, Sn, Sb, Bi, U and B are higher in the elemental background than those of the continental crust .
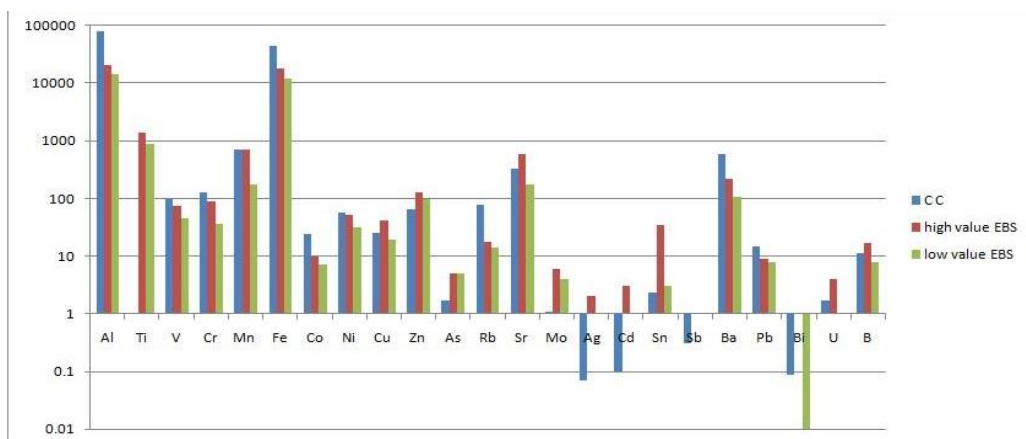

Figure (4.13) Elemental background Vs continental crust value

The nature of soil in the pristine area in Al-Qilt catchment has higher values of heavy and trace metals than the soils used in the continental crust value calculated.
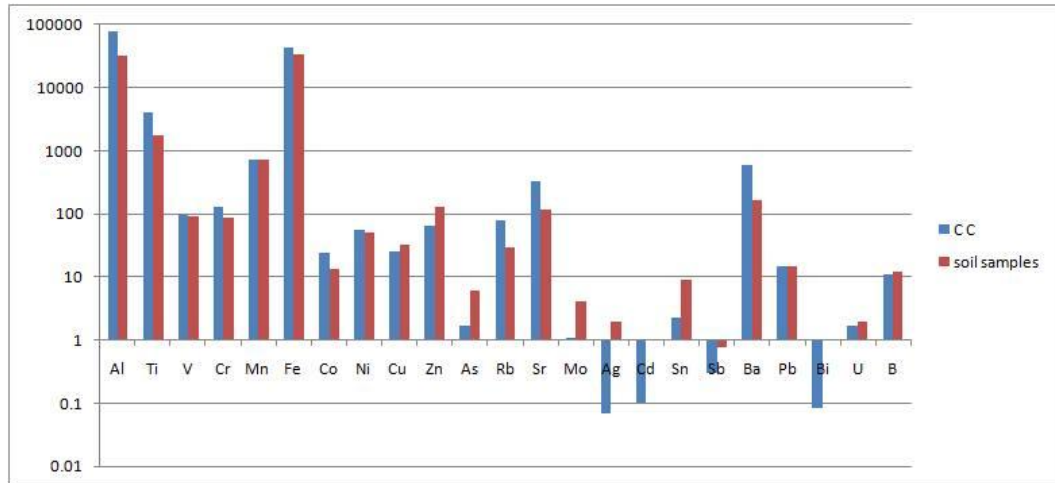

Figure (4.14) Continental crust value Vs soil samples.

Average values of heavy metals concentration for the collected sample Figure (4.14) show the different between the concentrations of heavy metals in the continental crust value were compared to the relevant concentrations of continental earth crust in order to further differentiate between anthropogenic pollution and naturally occurring of studied metals. and the soils samples in Al-Qilt catchment and this explain why the result in reference [21] showed that there is anthropogenic pollution in Al-Qilt catchment because of comparing the concentration of heavy metals of his samples with continental crust value, but compared this results with elemental background of CC so found there is no anthropogenic pollution, so heavy metals are considered as soils' contaminants in Al-Qilt catchment.

In Figure (4.14) show that the concentration of Cu,Zn,As,Mo,Ag,Cd,Sn,U and B in the soil of Al-Qilt catchment more than in the CC.

Anthropogenic pollution is for Pb , naturally occurring contamination for Sn, Ag ,Bi, Ti, Ba, Sb, Li, Be, Rb, Zn and Cu,

Chapter Five

Conclusion and recommendation

5.1. Conclusion.

Palestine suffers for long time from pollution due to experiencing different war conditions over time. The presence of the Israeli occupation and the colonies increased the rate of pollution in the Palestinian lands, anthropogenic pollution mainly transported with wastewater that flows from the Israeli colonies located in the West Bank to adjacent lands. Industrial activities in such colonies act as the main source for anthropogenic pollution.

Results based on metal/Al and metal/Fe normalization showed that :

1. Fe was found to be the best elemental normalizer since it has the highest R^2 values compared to Al, Thus, we used results of Fe as background values for the samples to calculate the Enrichment Factor (EF).

2. Ti, V, Mn, Co, Rb, Ag, Li, B and Be were to be considered as anthropogenic pollutants in most locations along of Al-Qilt wadi,

3. The EF calculation showed that Pb had the highest value of trace metals in Al-Qilt catchment (Ramallah site) because of the urban off, and there was a moderate values for Sn and Ag in some site in Al-Qilt catchment such as Sweanit and Sultan, result also showed that

4. there are no significant anthropogenic pollution in Al-Qilt catchment, almost of heavy and trace metals had no enrichment in the soil of Al-

Qilt Catchment, the elemental background made to be a reference for another researcher in the future.

5.2. Recommendations

Main recommendation of this research is that more studies are needed to evaluate:

1. The heavy metals pollution in ground-water and its imposed risk on people live in Al-Qilt catchment.
2. The concentration of heavy metals impregnated into surface water flowing downstream.
3. The effect of heavy metals on Graze lands in Al-Qilt catchment.
4. Needed remediation techniques to alleviate the heavy and trace metals pollution in the soils of Al-Qilt catchment.
5. Needed lows to limit the pollution in Al-Qilt catchment.
6. Study the source of pollution in Al-Qilt catchment.
7. Needed of E.B.S. for the others stream in Palestine which as Al-Qilt stream.

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جامعة النجاح الوطنية

كلية الدراسات العليا

محتوى المعادن، تواجدها وتوزيعها في تربة منطقة وادي القلط.

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قدمت هذه الأطروحة استكمالاً لمتطلبات الحصول على درجة الماجستير في الكيمياء بكلية الدراسات العليا في جامعة النجاح الوطنية في نابلس، فلسطين.

2015

محتوى المعادن الثقيلة وتوزيعها في التربة الطينية والرواسب في وادي الفارعة بفلسطين

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الملخص

التلوث بالمعادن الثقيله مهمل منذ زمن طويل ، بالرغم أن التلوث الناتج عن النشاط البشري له آثار سلبيه على البيئه وحياة الانسان.

ان تصميم مرجعيه للملوثات الناتجه عن النشاط البشري في تربة فلسطين ستساعد في تسهيل عمليه فحص وجود تلوث بمسببات بشريه ناتج عن المعادن.

الهدف من هذا البحث هو دراسة مواقع التلوث في تربة منطقة القلط ، ثم أخذ عينات من التربه النظيفه في منطقة القلط وتحليلها لمعرفة مكوناتها من المعادن الثقيله، وهي بشكل رئيسي تعزى الى النشاطات البشريه في المنطقة.

لقد تم جمع العينات على طول منطقة القلط بشكل شهري ، عينات التربه تم معالجتها بالماء الملكي ثم تحليلها بواسطه طريقة التجزئه BCR .

لقد تم التعامل مع المعطيات للنتائج من خلال حساب معامل الارتباط للمعادن الثقيلة ورسمها بيانيا مقابل عنصري الحديد والالمنيوم كعناصر مرجعية لتسهيل المقارنه بين مواقع المنطقة ، ولقد تم اختيار عنصر الحديد كمرجع اعتمادا على قيم معامل الارتباط بالمقارنه مع الالمنيوم .

ولقد استخدمنا التطبيع وهو وسيله للتعويض عن التقلبات الطبيعية من المعادن النزرة في التربة، بحيث يمكن الكشف عن اي معدن بشري ساهم في التلوث وتحديدة كميا بواسطة تقليل الحد من التأثير الطبيعي لحجم الحبيبات، هذا يساعد في تحديد المعادن النزرة كملوثات ناتجه عن نشاط

بشري ، ثم تم حساب عامل التخصيب كخطوة أولى للربط بين المعدن وأفضل مطبع له، وهذا يؤدي الى تحديد تراكيز المعادن الشاذة التي قد يكون لها مصادر بشريه.

تم تحديد المرجعيه لتركيز الملوثات الناتجه عن النشاط البشري في تربة منطقه القلط ومقارنتها مع قيم المعادن في القشرة الارضيه.

ان عملية تطبيع بعض المعادن مثل التيتانيوم والفناديوم والمنغنيز والكوبلت والربديوم والفضه والليثيوم والبورون والبيريليوم مع الالمنيوم والحديد أظهرت كنتائج انهم ملوثات ناتجة عن نشاط بشري في معظم مواقع منطقة القلط ز

ان حساب معامل التخصيب أظهر أن الرصاص له اعلى قيم في المعادن النزرة وتربة منطقة القلط وهناك قيم معتدله لكل من السناديوم والفضة في بعض الزمناطق وبالتالي هذه النتائج تظهر انه لا يوجد تلوث ناتج عن نشاط بشري في المنطقه.

وقد بينت قيم تراكيز المعادن الثقيله في تربه منطقة القلط النظيفة أعلى منها في القشرىة الارضية وبالتال العناصر الثقيله اعتبرت كمكون للتربه وممكن ان تاثر على المياه السطحيه والجوفيه وعلى السكان ان زادت نسبتها.

التوصيات لهذا البحث هي: عمل دراسات مستقبليه على تاثير التلوث بالعناصر الثقيله على المياه الجوفيه وتاثيرها على السكان وتراكيز المعادن في مياه الوادي، ودلراسه تاثير المعادن الثقيله على المياه السطحيه و وكذلك دراسة تأثيرها على ادارة الاراضي الصالحة للرعي ، ودراسة كيفية معالجة المعادن الثقيله والنزرة في تربة منطقة القلط .