Occurrences and transport of trace metals in wastewater, sediment and soil. Case study Al-Qilt catchment, West Bank, Palestine.

Dissertation

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Abbreviations

APHA	American Public Health Association
ARIJ	Applied Research Institute / Jerusalem
BCR	Bureau Cmmunutaire de Reference
BMBF	Federal Ministry of Education and Research
Cm	Centimeter
^{0}C	degrees Centigrade
CC	Continental Crust
Co	Mean content of heavy or trace metals of sample
Cb	Mean content of heavy or trace metal of reference
CH_2mHill	Millennium Engineering Group
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
DP	Dissolved Phosphorous
DEV	Deutshe Einheisverfahren zur Wasser
EC	European Community
EPA	Environmental Protection Agency
EXACT	Maltilatral Peace Process Regional Project.
FIMS	Flow Injection Mercury System
EBS	Elemental Background for Soil
EF	Enrichment Factor
Eir	Monomial potential ecological risk factor
ERL	Effect Range Low
ERM	Effect Range Medium
G	Gram
HCA	Hierarchical Cluster Analysis
IC	Inorganic Carbon
ICP-MS	Inductive Couple Plasma - Mass Spectra
ICP-OAS	Inductive Couple Plasma – Optical Absorption Spectroscopy
I geo	Geo- accumulation Index
JIKA	Japanese International Cooperation Agency
Kd	Partition Coefficient
km	Kilometer
LAWA	Germany Working Group
LC	Lower Crust
l/s	Liter per second
LOI	Loss of Ignition

m.a.s.l	Meter above see level
m.b.s.l	Meter below see level
Mcm/a	million cubic meter per annual
M^3/d	Meter cube per day
Me	Metal
mm	Millimeter
µm	Micrometer
µg	Microgram
µg/g DW	microgram per gram of dry weight
mg/kgDW	milligram per kilogram of dry weight
µg/l	microgram per litter
mg/l	milligram per litter
ml	Millimeter
mm/a	millimeter per annual
mm	Millimeter
MPI	Metal Pollution Index
MPP	Maximum Permissible Pollutants
No or n	Number
N	Normalizer
NTU	Neuphlimetric Turbidity Unit
OC	Organic Carbon
PECDAR	Palestinian Economic Council for Development and Reconstruction
PEL	Probable Effect Level
PCBS	Palestinian Central Bureau of Statistic
pH	Acidity range
PHG	Palestinian Hydrology Group
PSI	Palestinian Standard Institute
PWA	Palestinian Water Authority
R	Correlation Coefficient
RH	Relative Humidity
RI	Ecological Risk Index
SEP	Sequential Extraction Procedure
SMART	Sustainable Management of Available Water Resources with Innovative Technologies
SM & T	Standard Measurement and Testing
SPM	Suspended Particulate Matter
SPSS	Stratigraphic Plus Software Statistic
SRM	Sediment Reference Material
SQG	Sediment Quality Guideline

TC	Total Carbon
TDS	Total Dissolved Solids
TEL	Threshold Effect Level
TKN	Total Khildahl Nitrogen
TOC	Total Organic Carbon
TN	Total Nitrogen
TP	Total Phosphorous
Tri	Metals toxic response factor
TS	Total Sulfur
UBA	Umweltbundesamt
UC	Upper Crust
UFZ	Helmholtz Center for Environment Research
UNEP	United Nation Environmental Program
USEPA	United States Environmental Protection Agency
WHO	World Health Organization
Wi	Weight for metal
Wt	Total weight for metals

General Overview

When discussing the issue of contamination in the aquatic environment, water pollution is still the major aspect that has been regulated and extensively studied, but poor attention has been devoted to sediments or soil. Sediments have been described as sink or as the storage place for contaminants in the environmental system through various pathways. Furthermore, sediments are recognized as either a carrier or some times as a possible source for contamination in the aquatic systems that may have effects on the groundwater. Both fluvial (rock material deposited or transported by flowing waters) and aeolian (wind borne) deposits are found in the rivers, wadis or lakes. Therefore, sediments provide historical information about chemical under investigation; this allows conclusions to be made on the prevailing media and environmental conditions at the time in question. This study will introduce three types of interrelation between sediments, wastewater and soil, then using the different types of factors in relation to trace and heavy metals in different environmental conditions.

The determination, occurrences, transport and fate of pollutants in sediments, soil and water are request to understand how to quantify and correlate with other dependent factors. Thus, this PhD will study and descripe the trace metal transportation, bonding and behavior as anthropogenic pollutants, then we will use the trace metals in sediments to calculate the environmental factors and to compare the results with local, regional or international guidelines.

This PhD work will contribute knowledge for researchers and certainly advice for design makers at the Palestinian Water Authority, moreover, we hope that this work can also assist in the preservation of the aquatic environment by providing the information that need for such vital areas as Al-Qilt catchment, since there are two different cases. The first case is located at the upstream and there are about 14,000 m^3/day of wastewater discharged from Palestinian communities and Israeli colonies, with only about 30% of these wastewater being treated, then it is mixed with raw wastewater and continue running to downstream.

The second case is downstream in which the water received from Ras Al-Qilt spring in the range of 17,000 m^3/day, this water is used for domestic purposes by the Palestinian.

In Palestine there are no technical analyses to evaluate the environmental impact of pollutants in the solid state or in total fractions, in which various carrier matrices must be considered in the soil or sediment. This work will focus in the soild form for pollutants from the environment in relation to geochemical, ecotoxicological and other environmental factor. Moreover, in order to determine the fractionations in the solid form, then to compare with total accumulation.

In a broad sense, fractionation has been defined as either the process of identifying and quantifying the different binding forms or to descripe 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 consider 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 allows 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.

It is recognized that there are risks and errors due to environmental analysis while sample preparation in addition to analysis steps. For this study, most of the precautions and limitations will be consider 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 sediments, water and soil. Furthermore, the guidelines adapted for sampling, field work, sample preparations, lab work, standards used as samples for sediments, wastewater and soil and even the quality control and quality assurance are adapted to minimize the error and to achieve high accuracy.

This thesis is written in five chapters, each chapter comprising an abstract, an introduction, material and method, result, discussion and conclusion. Most of these chapters are dedicated for publications in an international journal or conferences. Chapter five was published in "Journal of Environmental Studies on August, 2011 under the title of "Anthropogenic trace metals and their enrichment factors in Wadi Al-Qilt sediment, Palestine". Moreover, I am represent Palestinian Water Authority in several conferences such as in Morocco / Marrakech (INNOVA-Med project) on May 2010, under the title "Fate and occurrence of the anthropogenic pollutant due to wastewater at sediments: Case Study" Al-Qilt, West Bank, Palestine", and at Birziet University on May 2009 under the title "Occurrence of trace metal as anthropogenic pollutants in sediments “Case study Al-

Qilt / Jordan Valley, West Bank” from chapters 3 and 5. Furthermore, we are participated by posters in MENA training course at Sweden on Feb, 2009 from chapter 2 and in Martin Luther University conference on Sep, 2009 from chapter 5. Moreover, in the future we will present results from chapter 3 at Birziet University conference on Nov, 2011 under the title "Use of Principal Components Analysis (PCA) to assign the source of pollution in sediment; Case study Al-Qilt Wadi, West Bank, Occupied Palestinian Territory", also I am submit paper to International Conference on Integrated Water Resources Management. Management of Water in a Changing World: Lessons learnt and Innovative Perspectives 12-13 October 2011 Dresden, Germany, this is accepted as poster and it is from chapter 5 under the title of "Anthropogenic influence of trace metals in sediments at Wadi Al-Qilt, West Bank, Palestine".

Finally, Palestine Water Authority participate as partner in ENPI / call for proposal with Catalan Institute for Water Research (ICRA) / Barcelona, Spain as management issues for de-pollution and decrease the impact due to wastewater naturally recharged at Al-Qilt catchment.

General abstract

There are growing concerns over the potential accumulation of heavy and trace metals in sediments due to industrial and urban development; this will increase the reliance on anthropogenic pollutants. This study will answer two questions at the same time: the first quastion, what anthropogenic pollutants are detected in Al-Qilt catchment? The second question: Is the water used for domestic purposes at downstream safe for drinking? This study aims to understand the occurrences, fate, transport and mobility of these anthropogenic pollutants in order to identify the contaminated areas by using the trace metals in sediment, wastewater and soil from Al-Qilt catchment.

The Al-Qilt catchment is located in the West Bank on the western side of the Jordan Valley 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 m^3/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 (PWA, 2010).

Methods for investigation for sediment, soil and wastewater were applied by analyzed the parameters in relation to environment such as: normalization, grain size, water content, porosity, Suspended Particulate Mater (SPM) and Partition Coefficient (Kd) and environmental factors such as: Enrichment Factor (EF), Contamination Factor (CF), Geo-accumulation Indexes (I*geo*), Ecological Risk Indexes (RI), Metal Pollution Indexes (MPI) and the sequential extraction procedure called Community Bureau of Reference (BCR). All of these factors can be compare to Continental Crust and Elemental Background for Soil as references, furthermore, several guidelines will be use on the local level such as the Palestinian and Jordanian guidelines and on the international level such as LAWA (German working group) and Sediment Quality Guidelines (SQGs).

The occurrences of heavy and trace metal are normalized to Fe, Al and TOC as reference elements, results indicate that Fe is the best elemental normalizer. Result obtaine for grain

size from sediment show variable distribution between gravel to sand to muddy, the muddy being less than 63µm. On the otherhand, there are similarities in the distribution of soil grain size at Al-Qilt. For water contents the Loss of Ignition is variey according to sites and there is risk when there is high organic content due to wastewater. For porosity, results reveal that sediment samples have higher values for porosities compared with soil porosities at the upstream of Al-Qilt. Moreover, porosities for soil at spring sites are higher compared with sediments; this indicates that there is more space between soil textures. Furthermore, SPM is increase due to wastewater that discharged; this indicates that the trace and heavy metals in the particulate form are greater than in dissolved form, thus the trace metals can be transport either in suspended form or in turbulent movements. Results obtain for Kd had the highest values when the concentrations are equal for the dissolved and the particulate forms, such as in drinking water or spring samples. On the contrary, the wastewater samples are variey due to the incremental of one of the two forms.

Considering the environmental factors results obtain for EF indicate that Ag, Bi, Cd, Zn and Hg are anthropogenic and they enriched in sediments. This will give trend for these parameters are enriched in Al-Qilt catchment due to human activities. Faurthermore, results obtain for CF in sediments are contaminating with Zn, Ag, Cd, Hg, Bi and Hg, in clear world no site can be classified as ‘‘unpolluted’’ when looking at the calculations of the CF or MPI mainly at the three regions such as Sweanit, Ras Al-Qilt and Qalandiah.

Furthermore, results obtain for the I*geo* show that sediments in Al-Qilt have background concentrations for Al, Ti, Cr, Mn, Fe, Co, Ni, Rb and Ba and are unpolluted for V, Sr, and B and are moderately to unpolluted for Cu, Zn, As, Mo, Cd, Sn, Sb, Hg, Bi and Pb and moderately polluted for Ag.

Results obtain for RI reveal that the contribution percent of individual metals to the overall potential ecological risk show that Cd is considered in high risk with percentages of 67%, then Hg is rank as second among the metals contributing with a total of 20%. These are follow by 7% for Ag, 2% for Cu and As and 1% for Bi. It could be conclud that high RI is primarily dominated by the metals of Cd and Hg at Al-Qilt catchment with 87% from the total potential ecological risk. This result describes both an ecological risk caused by single pollutant and an overall risk or contamination from varied pollutants.

Results for I*geo* reveal that Cd, Hg and As are in the uncontaminated degree. However, RI results indicate that Hg, Cd and As must take with considerable interest due to their high toxicity and RI values are relatively very high. Thus, it is noticed that the I*geo* method is mainly focus on the accumulation levels of individual metals without taking into consideration the weight of the toxic response factor.

MPI results are less than one for most of the parameters, this classify the parameters as unpolluted. It is appear that most of the sites posed a risk for pollutions due to Hg, mainly at Qalandiah, Sweanit and Ras Al-Qilt.

Results from BCR summation and pseudo total digestion methods reveal that there is in consistances between the pseudo total digestion values and the summation of the BCR fractionations for both sediments and soil samples. The BCR fractionations give indication about mobility or transport for B, Cd, Sb, Pb, Cu, Hg and Sn and there are risks from their reallocation along Al-Qilt.

By using LAWA and SQGs Cu, Zn and Hg pose potential toxicity and they are exceeding the TELs and PELs values mainly at Sweanit, this due to the highest values for Hg and has the second value for Zn. By these concentrations the trace metals from sediments will have toxicity effect on microorganisms mainly by Zn, Hg, Cu and Cd, since these exceed TELs values. The incidence of toxicity is compared among samples for Cr, Ni, Cu, Zn, As, Cd and Pb in which Ni, Cu and Zn exceed the ERL values, moreover, the Zn and Cu are exceed the ERM mainly at the upstream of Al-Qilt.

Although there are incremental for trace metals in sediment and soil samples, on the other hand, these trace metals are not detected in water samples, mainly for Ag and Hg, since both are considered as anthropogenic pollutants and both are enriched in the sediment.

As conclusions, the capacity of the buffering zone between Sweanit, Fawwar and Ras Al-Qilt works well in removing the organic carbon and nutrients as self purification, but doing nothing with trace metals. These trace metals may have deleterious effects on the aquatic ecosystem and health of the rural dwellers whom use the spring for domestic purposes. This indicates that these springs are not granite, thus more policy management steps must be applied to decrease the wastewater discharge to protect both ground and surface water quality in the catchment with shallow water table from deteriration.

The sediments and topsoil are enriched clearly by anthropogenic pollutants due to discharge of raw wastewater, dumping sites, roadside and urban runoff, and sometimes due to natural effects. Therefore, trace metal inputs at Al-Qilt need to be kept under strict control in the future, since Ras Al-Qilt is considered one of the important springs in the area and it is used for domestic purposes, there are no guaranty from pollution if there is no management plan to decrease the pollution at the upstream of Al-Qilt. This means that if the buffering zone up to Ras Al-Qilt does not work efficiently to remove the pollution of trace metals the head of the spring will deteriorate.

If the three springs (Fawwar, Ras Al-Qilt and Sultan) are compared with each other for RI values, taking in considerations that Fawwar is located above Ras Al-Qilt or Sultan springs, but in terms of risk, Ras Al-Qilt spring has the highest RI values at Al-Qilt catchment.

Furthermore, the guidelines such as the CC, EBS and USEPA are available, but it is better to use the EBS, since there are high variations compared to CC values. Therefore, if EBS is used, then results will not be so far from the actual values from the study area. Beside these justifications there is a basic reason which is the difference in elevation between the upstream and downstream, that reaches to about 700m.

Chapter 1

Environmental background and basic informations

1.1 Introduction

Palestine, like many other areas of the Mediterranean region is experiencing an increase in urban activities that accompanied by rapid population growth, deterioration in natural aquatic ecosystems and minimal development in water resources. Furthermore, Palestine suffers from water detriarations of natural resources due to human activities. These activities are characterized by domestic or industrial wastewater, stone cutting, arbitrary dumping sites and urban runoff. These activities emit pollutants then they reach to the nearest wadis. These wadis have been used for long time for drinking, irrigation washing purposes and now most of these are pullulated and there are restrictions in usage. In the West Bank there are about 363 disposal sites to discharge the raw wastewaters into the environment (ARIJ, 2007). Eight of these sites are located in Al-Qilt catchment (Figure 1.1). The problem is maximize when people evacuate their septic tanks by trucks into wadis at arbitrary places, these will also mixed with urban runoff during the winter season. This makes it difficult to capture additional storm-water as runoff and it is estimated by 2.5 Mcm/a at Al-Qilt catchment.

All of mentioned make it difficult to have or guaranty potable water at downstream from the springs (Fawwar and Ras Al-Qilt), also the wells are shallow with water table ranging in 20-188 m in depth, so most of the pumping wells are from the upper aquifer and fed from rainfall (PECDAR, 2001).

In the Al-Qilt catchment there are 65,935 people from the cities, comunities and refugees camps of the Palestinians from the West Bank, and about 6,000 are living in East of Jerusalem (PCBS, 2005). Furthermore, there are six Israeli colonies with settlers estimated by 15,000 peoples living in the area (PCBS, 2003). In general, less than 30% of the wastewater discharged in the West Bank is treated efficiently, and more than 70% of the generated wastewater is discharged untreated to the environment to the wadis (ARIJ, 2007), this study estimates that 9500 m^3/d from the Palestinian communities and 4500 m^3/d from the Israeli colonies in the total 14,000 m^3/d of wastewater treated and untreated are discharged to the environment. Only Al Bireh, with 5000 m^3/d is treated, these wastewater represents 30% from the total, then these treated wastewater mixed with raw wastewater from Qalandiah and Stone Cutting quaries (1500 and 1300 m^3/d) respectively and all quantities continue running to downstream until they infiltrate and/or evaporate completely.

In Al-Qilt, there were few studies, for example, CH_2MHill, 1999 was one of these. They did a survey and monitoring for the Eastern basin of the West Bank. The main objective for their survey was to understand the wastewater potential and expected pollution to local resources in the Eastern basin; they monitored and analyzed the following parameters: Ammonia, Potassium, Nitrates, Chloride and TDS, Antimony, Lead, Selenium, Thallium, Iron, Beryllium, Mercury, Cadmium and Arsenic. Results revealed that there were incremental of trace metals in the springs downstream which used for domestic purposes. Moreover, Daghrah (2009) investigated the domestic water and wastewater in Al-Qilt catchment. Results indicate that there were high concentrations of Lead and Cadmium if compared to the Palestinian guidelines; these high concentrations were at Fawwar and Ras Al-Qilt that used for domestic purposes. Furthermore, results for wastewater samples from the wadis were contaminated by Cadmium and Lead when compared to the Palestinian guidelines for artificial recharge by infiltration (PSI, 2003). Also Daghrah indicated that there are major trends for decreasing tendencies in pollutant concentrations downstream due to dilution factors that caused by springs at the outflows and due to self-purification processes within the wadi bed. Furthermore, Helua, *et al*., (2007) revealed that effluents from different anthropogenic pollutants as sources from the Palestinian communities and Israeli colonies were varied due to storm intensity; this can be related to the length of the dry period between each rain event. Thus, the springs show shock to NO_3 and DOC values for several weeks after a significant storm event, and the DOC values in groundwater reach 12 mg\l at Ras Al-Qilt spring. This result is important to consider if the water will be treated for domestic purposes using the residual chlorine to avoid the risk of Trihalomethan formation. On the other hand, Mimi *et. al.*, (2006), investigated the urban runoff at Ramallah and Al Bireh district that located at the upstream of the Al-Qilt catchment. Results revealed that the analysis for trace metals in storm water such as Chromium (Cr), Zinc (Zn) and Lead (Pb) exceeded the PSI, (2003) and EPA guidelines for treated wastewater that could be artificially recharged by infiltration to the groundwater.

At the national level, the Palestinian Water Authority (PWA) has their monitoring program. This program is applied twice a year for chemical parameters such as: Ca, Mg, Na K, SO_4, NO_3, Cl and HCO_3 and physical parameters such as pH, temperatures, EC and turbidity, and one time each two months for biological parameters such as *Facal coliform* and *Total coliform*. Beyond these parameters such as trace metals, pesticides, herbicide and pharmaceuticals are only done for research purposes (PWA, 2010).

The monitoring programs for anthropogenic pollutants are not organized in routine in Palestine. Thus, this study will focus on trace metals in sediments, wastewater and soil according to the German Ministry of Environment (1993) the trace metals exist in low concentration in water and they have a propensity to associate preferentially with the sediments and attain considerable concentrations. For this reason, it is crucial to study the occurrence of trace metals in wastewater, sediment and soils samples, then to apply these calculations for environmental factors to evaluate occurrences, fate, mobility and transport of trace metals.

The current knowledge of post-deposition of trace metals in the environment are not investigated yet and there are needs to study the trace metal behaviour, then to use there concentrations to calculate the environmental factors such as: ecological risk assessment, contamination factor, enrichment factor, geo-accumulation indexes and metal pollution indexes. Therefore, there are a lot of questions we must answer for the processes that determine the occurrence, fate, mobility and transport of trace metals. Finally, there will an overview for the potential risk of sediments in relation to wastewater and soil in the environment.

Take in consideration that in most developing countries, point and non-point source pollution are major environmental problems that have effect on water quality. The situation is exacerbated by the lack of treatment for domestic wastewater (Iwata *et al*., 2003). For this study, we will verify the source of pollution using trace metals as anthropogenic pollutants in a semi arid region.

1.2 Area of study

The area of the Al-Qilt catchment is about 174 km²; it is situated in the east of the West Bank. It has a lot of tributaries such as Wadi Al-Ein (7.5 km), Wadi Mukhmas (9 km), Qalandiah (2 km) and Stone Cut (2 km), all of these wadis were located on the left bank of Al-Qilt catchment (Figure 1.1). The total distance of Al-Qilt wadi with its tributaries is in the range of 45-50 km. Al-Qilt is characterized by a steep relief and varies in elevation that rang from 800 m.a.s.l. at the western part to -300 m.b.s.l. at the eastern part. Furthermore, Wadi Al-Qilt is characterized by relatively steep slopes at Ramallah (west) running downstream to Jericho (east) and it becomes flat when passing Jericho.

The major drainage system for Al-Qilt is from the Judean Mountains between Jerusalem and Ramallah to the Jordan Valley with an average flow in the range of 3.0 Mm^3/a depending on the annual rainfall, and the largest flood occurred in 1991/92 when water level record heights and adjacent land (Forward, 1998). The runoff at Wadi Al-Qilt was observed in the middle of May 2007 and characterized as quite muddy, showing the extremely high sediment concentration and it was estimated the highest amount of sediments that transported downstream at the time of flooding that mixed with the wastewater discharged from some drainage, and all of these source were mixed with urban runoff as base flow from the surroundings (JIKA, 2008).

The hydrochemistry of water remains almost constant within the study area for groundwater wells, only by approaching the Jordan Valley it is characterized by an increase in Mg due to the change of the aquifer rocks from limestone to dolomite. On the other hand, wells that are close to the Jordan Valley will be high in TDS and Cl concentrations. Furthermore, the hydrochemistry shows high Cl values in the eastern part of Al-Qilt that are derived from three sources: 1) anthropogenic effect of sewage inflow or 2) deep brine water and 3) dissolution of salts from Lisan layers (Marie, personal communication 2008).

At Al-Qilt catchment there are few of springs, such as Fawwar, Ras Al-Qilt and Sultan. Sultan spring located just outside of the Al-Qilt catchment and we will use in this study just to compare with Al-Qilt springs such as Fawwar and Ras Al-Qilt, since it orginates from a deep aquifer and is expected not to be within an area (depthwise) for an anthropogenic impact due to human activities more informations about the springs given below:

- Fawwar: it is seasonal spring that emerges down of Sweanit wadi at an elevation of 75 m.a.s.l.
- Al-Qilt: it is emerges 4.5 km downstream of Fawwar spring at an elevation of 10 m.a.s.l. Its flow has little variation from winter to summer.
- Sultan: located to the east of Al-Qilt catchment and it is located below sea level.

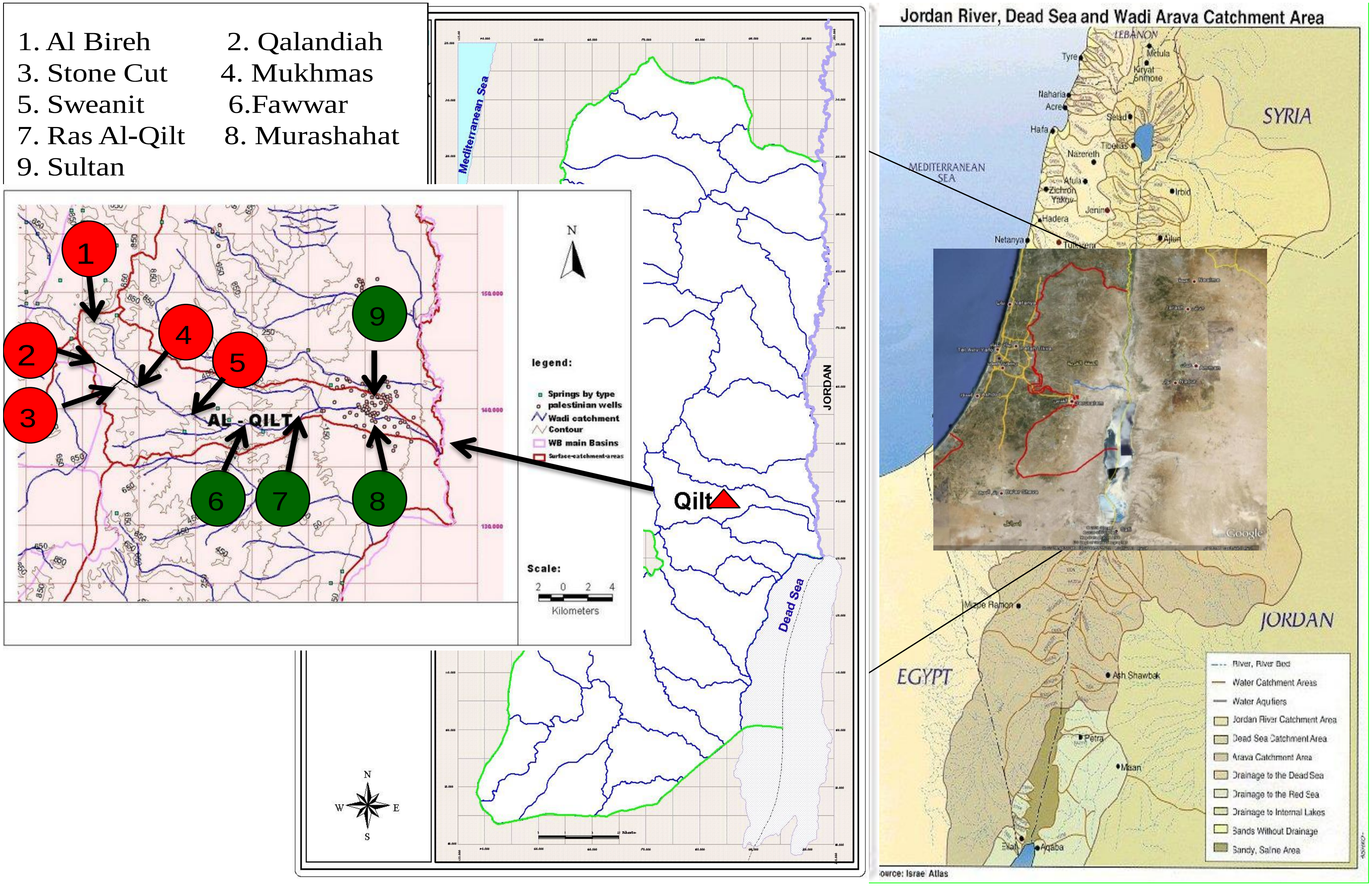

Figure 1.1: Study area of Al-Qilt catchment, springs, distance between sampling sites and major cities (PWA, 2009).

The Al-Qilt system is composed of two major tributaries, Fara and Sweanit that form the main stream of the Al-Qilt wadi after the combination of both tributaries before Fawwar spring, then both continue as one in the Al-Qilt wadi reaching Ras Al-Qilt spring and continue running downstream until reaching the Jordan River. At Fara spring all water are used by the Israeli colonies for recreation (as swimming pools), thus there is no water available to the wadi. Therefore, we will focus on the Sweanit tributaries that start from the Al Bireh wastewater treatment plant.

Wastewater, sediments and soil samples are taken from nine sites (Figure 1.2). Samples were collected for water and wastewater from July, August, and September 2007 and then each six months start from June 2008 for sediment, soil samples and water. Sediment samples are taken from each site using plastic grab sampler just beneath the top surface of about 5cm and the sample was then placed in a 250ml plastic Jar. For soil samples we take 1kg that were collected at 5cm from the surface and stored in a plastic jar. For water and wastewater, we collect about one liter and it is preserved in plastic bottle for trace metals, and all were preserved to 4^0C and send to the laboratory.

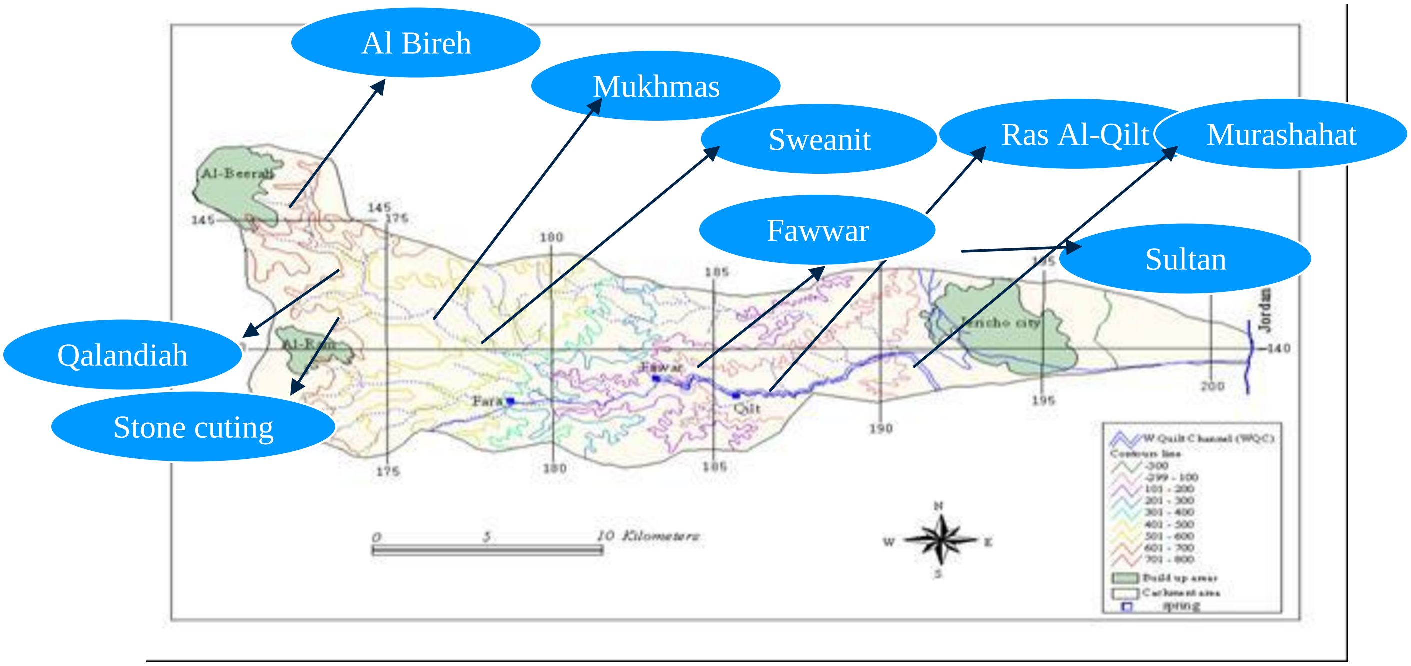

Figure 1.2: Study area Al-Qilt catchment and sampling sites at Al-Qilt catchment; source (PWA, 2009).

1.3 Purpose of the study

The knowledge of anthropogenic pollutants for organic and inorganic parameters, fate, occurrences, accumulations and transports are not investigated togather in Palestine. This due to the lack of experience and instrumentation that are necessary for sampling and analysis. Thus the Palestinian Water Authority through SMART project asked PhD student to have his topic to study the impact of pollutants due to wastewater in the Lower Jordan Valley, and to study the history of the pollutant and methods that are capable to describe pollutants variatins with time, then to use these different environmental factors to verify such pollution between sites.

Palestine suffer form water shortage, due to the lack of controlling to water resources and there are alot of restrictions from the Israeli side. The current water supply in Jericho area described as inadequate and insufficient for future development mainly for the agricultural, municipal and industrial sectors. Thus, PWA need a lot of efforts from the researcher targeting Jericho and the eastren aquifer to increase the quantity of water and to decrease the salinity at downstream. To achive this, there is no sufficient data for the quality of runoff or what are the types of anthropogenic pollutants that are flowing with such wastewater from the cities at the upstream?. Also there are Israeli colonies, as industrial and military zones they discharge their wastewater (treated and untreated) into the wadis, this will deteriorates the environment and then there will high potential to reach the water resources.

Based on EXACT, 2005 and CH_2MHill 1999 and 2000 studies for the wastewater and reuse. They monitore the groundwater wells and surface wastewater at the eastern basins of the West Bank. There objectives from the monitoring program were to get better understand for the potential pollution to the groundwater from the wadis that contain wastewater as base flow. For that survey about 10 wadis from the West Bank were selected for monitoring; Wadi Al Qilt was one of these, finally, there studies had a lot of recommendations summarised below:

1. There is no routine monitoring program for wastewater, neither at treatment plants, nor at the end-uses.
2. Insufficient data are available for wastewater quality and quantity and the quality of existing data is unclear and available sets are inconsistent.

3. Agencies responsible for wastewater monitoring have insufficient capacity to fulfil their tasks, and the existing laboratories cannot perform relevant analyses for routine analysis.
4. Available data are scattered among various agencies. No routine data are available for interpretation and funds are lacking to implement monitoring of environmental impact.

These informations indicate that more efforts and cooperation must be done between institutions such as: PWA, non-government, research centers and universities to formulate the framework to find the suitable methods or studies for the history of pollutants, since the amounts of pollutants in wastewater are not completely removed even if treated and the anthropogenic pollutants occurr from the surface water can be transported and reach to groundwater. In our case there are no treatment for wastewater, so many inorganic and organic species of pollutants are still available. Trace metals are one of these pollutants that have harmful and high toxic compound for humans even in low concentrations, take in consideration that at Al-Qilt the raw wastewater is discharged at upstream and it is naturally recharged by infiltration to the groundwater, then, it is used downstream from Ras Al-Qilt springs for domestic purposes.

This work will focus on sediments and will use the results from sediments, hence, the bottom of sediment serves as a reservoir for heavy and trace metals; this deserves special consideration in the planning and design of aquatic pollution research studies (Badri M and Aston S 1983; Pekey *et al*., 2004; Atgn *et al*., 2000). Moreover, sediments have a high storage capacity for pollutants if compared to any part of the hydrological cycle, since less than 1% are dissolved in water and more than 99% are stored in the sediments. Furthermore, human activities disturb the equilibrium between the metals in sediment/soils and ground or surface water, and the capacity of sediments to adsorb and retain contaminants that depend on their composition (Salomons and Stigliani, 1995). Also, sediments are important carriers of toxicants and can accumulate the toxicants over time. Moreover, sediments are used routinely to assign environmental assessment and to determine the potential toxicity as secondary sources of contaminants in aquatic systems (Birch and Taylor, 2000).

Heavy metals such as cadmium, mercury, lead, copper, antimony, boron and zinc are considered as serious pollutants due to their toxicity, tendency to incorporate into food chains and they have the ability to remain in an environment for a long time. Moreover, the heavy metal species in the aquatic environment is distributed among water-soluble species, colloids, suspended matter and sedimentary phases in relation with suitable environmental factors (Pekey *et al*., 2004).

Trace and heavy metals in sediments appear to have a potential threat to structure of ecosystems, so it is important to understand the mechanism that govern and alter fix the pollutnace:

1. Occurrences, fate and transport routes since they will be the key variables for the processes needed to identify the pollutants.
2. Ecological impact in aquatic ecosystems, since there are many different processes and factors that control the fate and transport pathways of pollutants.
3. It is proven fact that mobility, availability, toxicity and fate of an element depends on the form at which it occurs rather than its total concentration (Kishe M and Machiwa J., 2003; Pekey *et al*., 2004; Atgn *et al*., 2000; Birch GF and Taylor SE, 2000).

Therefore, there are three main reasons to study the distribution of trace metals in sediments:

1. An important fraction of trace metals is accumulation in sediment mainly that exists in unstable forms, making them available for incorporation into the surroundings.
2. Sediments can become a source of metals to the water column if the equilibrium between the surface sediments and the overlying water column is broken.
3. Trace metal data in sediments used to cover the pollution history of an aquatic system, because they are more widely available and more reliable than dissolved metal concentrations in water system.

1.4 Metrological data

1.4.1 Location and Geography

The Jordan Valley forms the eastern basin and it is considered as one of the main three basins in the West Bank. Structurally, the eastern basin is the eastern flank of the Judean anticline that dips steeply towards the east as a step fault escarpment. Surface water comprises the flood flows during the winter season and the base flow of springs that originate in the western mountainous area. This flow passes during its travel path to the Jordan River then to the Dead Sea, some of these flows percolate to the aquifers (Wishahi and Khalid 1999). Al-Qilt catchment is located in the eastern part of the West Bank and it includes parts of Ramallah, Al Bireh and Jerusalem and these comprises the western part, and then Jericho that comprises the eastern part (Figures 1.1 and Figure 1.2). The major drainage of the system was from the mountain aquifer area between Jerusalem and Ramallah downwards east to the Jordan River (Rofe and Raffety 1963).

1.4.2 Geology and hydrogeology

The geological map of Al-Qilt catchment, stratigraphic, structural resolution and prominent E-W striking indicates that more than 9 km long normal fault with throw of 80m down to the southeast has been identified. This fault causes structurally the spring outlets of Ras Al-Qilt and Sultan. Moreover, within the Judea group there were three sub-aquifers: the Shallow Turonian Aquifer feeding the springs with flow velocities that are quite high rainfall peaks and with average annual discharge about 9 x 10^6 m^3/a from Fawwar, Ras Al-Qilt and Sultan. Then the Upper Cenomanian and a Lower Cenomanian-Albian Aquifer by more than 81 production wells used mainly for agriculture and these wells are pumping relatively low quantities of about 4 Mcm /a (CH_2MHill, 2000).

Al-Qilt catchment is characterized by unique geologic formations due to the existence of the Jordan Valley Rift Fault that separates two types of formations these include quaternary deposits and some outcrops of carbonate rocks that bordering the Jordan Valley from the western side (Figure 1.3). The quaternary deposits consist of different deposition formations according to CH_2MHill (1999) as in the following sub sections:

1.4.2.1 Alluvial deposits

Alluvial deposits are present along the western side of Al-Qilt consists of unconsolidated lenticular beds of gravels, sands, clay and laminated marls, these are not defined either vertically or horizontally. The thickness of these deposits is highly variable and become relatively great near the foothills in the west and small in the east. These deposits are inter-fingering with the lacustrine sediments of the lisan formation (CH_2MHill, 1999).

1.4.2.2 Lisan formation

The Lisan formation covers a large part of the Jordan Valley, and consists mainly of laminated marl, gypsum and clay with some sand beds and pebbles. The best exposures are found along the sides of the Jordan River flood plain. The maximum thickness of this formation is not well known and according to many previous studies, this formation is acting as an aquiclude and underlying the alluvial deposits (CH_2Mhill, 1999).

1.4.2.3 Carbonate rocks

1.4.2.3.1 Abu Dies formation

Abu Dies formation crops out in the western part of the study area, as shown in the geological formations (Figure 1.3). This formation consists mainly of massive chalk with a distinctive twin band of cherty beds and little amounts of limestone. The total thickness of this formation is approximately rang from 200 to 450 meters (CH_2MHill, 1999).

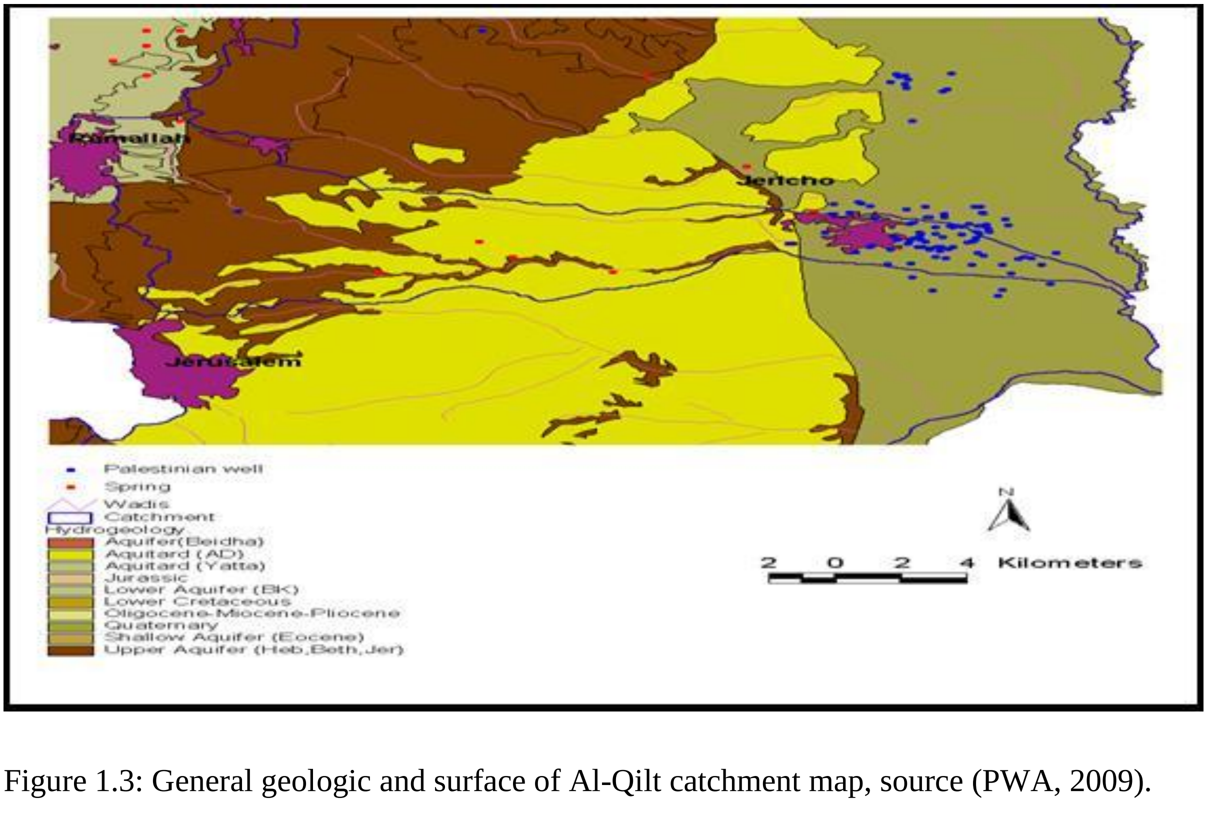

Figure 1.3: General geologic and surface of Al-Qilt catchment map, source (PWA, 2009).

1.4.2.3.2 Jerusalem formation

The Jerusalem formation covers a small area in Jericho as shown in (Figure 1.4). It is composed of limestone and dolomite limestone. In term of hydrogeology the groundwater in Jericho area is from the quaternary aquifer, which consist mainly gravels inter-fingering with impermeable layers of saline marl that deposited and transported from the western slopes of the Jordan Valley forming alluvial fans. Naturally, the infiltration of floodwater in Al-Qilt catchment is the main source of aquifer recharge during the winter season. Meanwhile, the water quality of this aquifer is varied with location and it is believed that this aquifer is overlaying the Lisan formation that acts as an impermeable or very low permeability layer (CH_2MHill, 1999).

1.4.3 Population

According to the PCBS (2005), there were 96,935 inhabitants from the Palestinian population in the Al-Qilt catchment. These inhabitants are distributed as: 38,192 in Al Bireh City, 10,103 in Kufr Aqab, 8,796 in Qalandia Camp, 2,238 in Borqa, 3,143 in Jaba', 1,823 in Mukhmas, 24,838 in Al-Ram, 5,916 in Hizma, 9,337 in Anata and 1,345 in Beit Hanina, where the population of Shu'fat and Shu'fat Camp was not estimated because they are considered as part of Jerusalem. Moreover, the number of Israeli settlers according to (PCBS, 2003) from the six colonies were 1,333 in Psagot, 3,922 in Kokhav Ya'kov, 998 in Ma'ale Mikhmas, 740 in Almon, 1,988 in Giv'a Binyamin (Adam) and 20,269 in Neveh Ya'kov. The population of Bisgat Ze'ev, Allon and Pisgat Omer are still unknown (Figure 1.1).

1.4.4 Climate

The West Bank has a typical Mediterranean climate with two distinct seasons: dry hot season from June to October and cold wet season from November to May. In Al-Qilt there are variation in the climate according to the drainage basin such as: in the western part, the climate is influenced by the Mediterranean climate; a rainy winter and dry summer. The climate in the eastern part is classified as arid with hot summers and warm winters (ARIJ, 1996).

1.4.5 Rainfall

Along the West Bank there are considerable variations in the quantity of the annual rainfall from year to year or from upstream to downstream. Moist air masses from the Mediterranean bring most of the rain that falls on the western part of Al-Qilt, since Ramallah and Jerusalem are on the upper mountains with annual rainfall of 500 to 700 mm/a (Abed Rabbo *et al.*, 1999). These rainfall values decrease down east to 150-200 mm/a (Ali *et al*., 1999). Moreover, rainfall in Al-Qilt is estimated at the range of 500-700 mm/a in the west and 150 mm/a in the east with an average rainfall over the catchment being about 400 mm/a (PWA, 2009).

1.4.6 Temperature

The average summer temperature in the West Bank varies between 20-23 ^{0}C reaching the maximum in the range of 40-43 ^{0}C. The average winter temperature is in the range of 10-11 ^{0}C with a minimum of 3 ^{0}C. These variations are expected due to the differences in elevation and distance from the coast and Jordan valley; hence, the temperature increase from north to south and from west to east. January is the coldest month and August is the warmest month (Ghanem, 1999). The temperature in the western part of Al-Qilt catchment is in the range of 6-12 ^{0}C and the coldest month is January and it is in the range of 7-19 ^{0}C. In the eastern part the tempreture reach 22-27 ^{0}C during August in the western part and 22-38 ^{0}C in the eastern part for the same month (ARIJ, 1996).

1.4.7 Relative humidity

In the West Bank, temperature increases from west to east and the main factors that controle the atmospheric moisture content is expressed as Relative Humidity (RH %). The RH % varies from north to south and the mean annual relative humidity is between 50 % in the eastern part of Al-Qilt catchment to 70.1 % in the western part (ARIJ, 1996).

1.4.8 Evaporation

Due to high temperature and low relative humidity of the air during the summer time in the West Bank, the evaporation rate is high and reaches 298 mm. The evaporation rate decrease in winter due to the increase in humidity and declince to 59 mm (PWA, Deab Abd Al-Ghafor personal communication and field trip, 2011).

1.4.9 Soil classifications in Al-Qlit

In Al-Qilt catchment, there are five major types of soil (Figure 1.4). These are arranged from upper to lower and are classified as follows:

1. Terra Rossa.
2. Mediterranean Brown Forest.
3. Coarse Desert Alluvium.
4. Brown Alluvium.
5. Desert Alluvium.

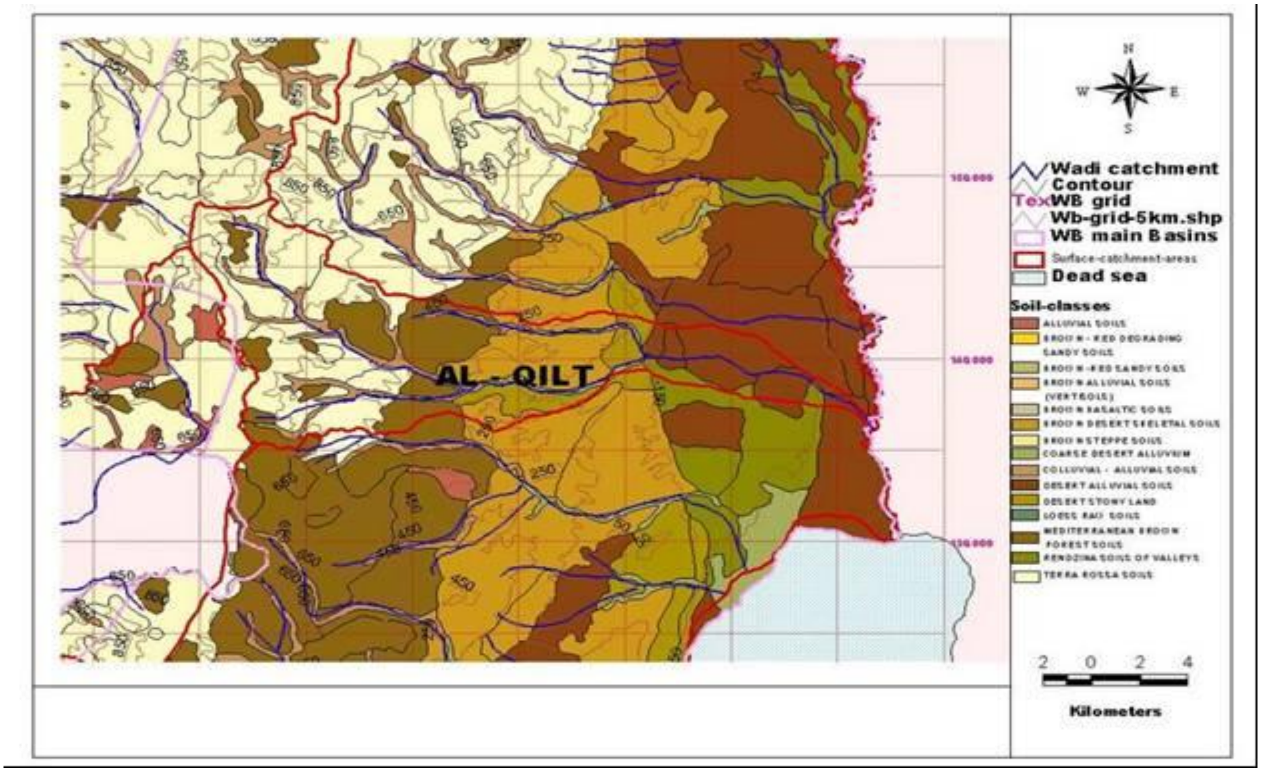

Figure 1.4: Soil classifications and elevations in Al-Qilt catchment: source (PWA, 2009).

1.5 Overall objectives

The aim of our research is to understand the occurrences, fate, transport and mobility of the anthropogenic trace metals in sediment, wastewater and soil at Al-Qilt catchment in order to identify the contaminated areas of the ecosystem and environment. Thus, this research will link the trace metal emissions to environment and its concentrations or available fractions. This linkage will provide ideas for the fractionation pathways and necessary parameters to control and evaluate the risk from exposure to such fractionations in the local environments. This can be achieved by studying the following factors:

1. Determine the physical-chemical parameters for sediment, wastewater and soil and other related parameters in relation to urban run off and deposition.

2. Calculate the environmental factors such as Elemental Background for Soil, Contamination Factor, Enrichment Factors, Ecological Risk Index, Metal Pollution Indexes and Geo-accumulation Index, these to evaluate ecosystem deterioration and its impact due to trace metals.

3. Self purification capacity for chemical transformation in the total and fractionations form, this to describe fate, transport and mobility of trace metals.
4. Use the statistical analysis correlations program and to compare between local, regional and international guidelines.

1.6 Methodology

1.6.1 Sampling

Fresh and grab samples from wastewater are collected during July, August and September of 2007 and for sediment, soil and wastewater during June and October of 2008 and June and October of 2009. These nine sampling sites represent the following type of samples (i) effluents of treated wastewater from Al Bireh wastewater treatment plant (ii) untreated wastewater from Qalandiah and Stone Cut (iii) wadis that carry wastewater and runoff from Mukhmas and Sweanit (iv) freshwater springs from Fawwar, Ras Al-Qilt, Murashahat and Sultan (Figure 1.2).

1.6.2 Field analysis and wet chemistry

The physical chemo-physical parametres such as discharge, turbidity, pH, temperature and dissolved oxygen were measured with suitable instruments at the field.

1.6.3 Sample preparation

At the laboratory, the sediment samples were frozen to – 25 ^{0}C by using deep freezer refrigerator for 6-8 hours in order to stop the microbial activities; then samples were incubated in “freeze-drying and evaporation” using CHRIST Delta 1-24 LSC for four days in order to dry the samples; then the sediment and soil samples were sieved into 63µm samples using the sieving analyzer Fritsch D-55743.

For wastewater, two samples were prepared one filtered to 45µm to investigate the dissolved trace metals, and the second from raw wastewater to investigate the total concentration of trace metals. All samples were acidified with HNO_3 to pH = 2 and then analyzed for the requested parameters after being digested using the aqua regia.

1.6.4 Aqua regia concentration (pseudo digestion)

About 0.25g from the mixed samples and Buffalo Reference Material (8704) were measured accurately into 100 ml teflon digestion tubes mixed with 6 ml of concentrated HNO_3 (65%) and 3 ml of concentrated HCl (37%). Afterwards, the samples digested for two hours using Microwave digester (MARS 5). Samples kept outside reaching room temperature, then the digested samples adjusted by water to 25 ml using Erlenmeyer flask, and then analyzed using Inductive Coupled Plasma Mass Spectra ICP-MS (Agilent 7500). The Hg is determined using Flow Injection Mercury System (FIMS 400).

Samples were analyzed according to Water and Wastewater Standard Methods (APHA, 2000), and according to the "Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung" special methods used by the Water Research Center (UFZ), Magdeburg, Germany.

1.6.5 Bureau Communautaire de Reference (BCR)

BCR method formed from four steps that classify in terms of reagent. The BCR sequential fractionation extraction is recommended as standard procedure for the characterization of heavy and traces metals in soil and sediment. 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 1.5) and discussed indetail in Chapter 4.

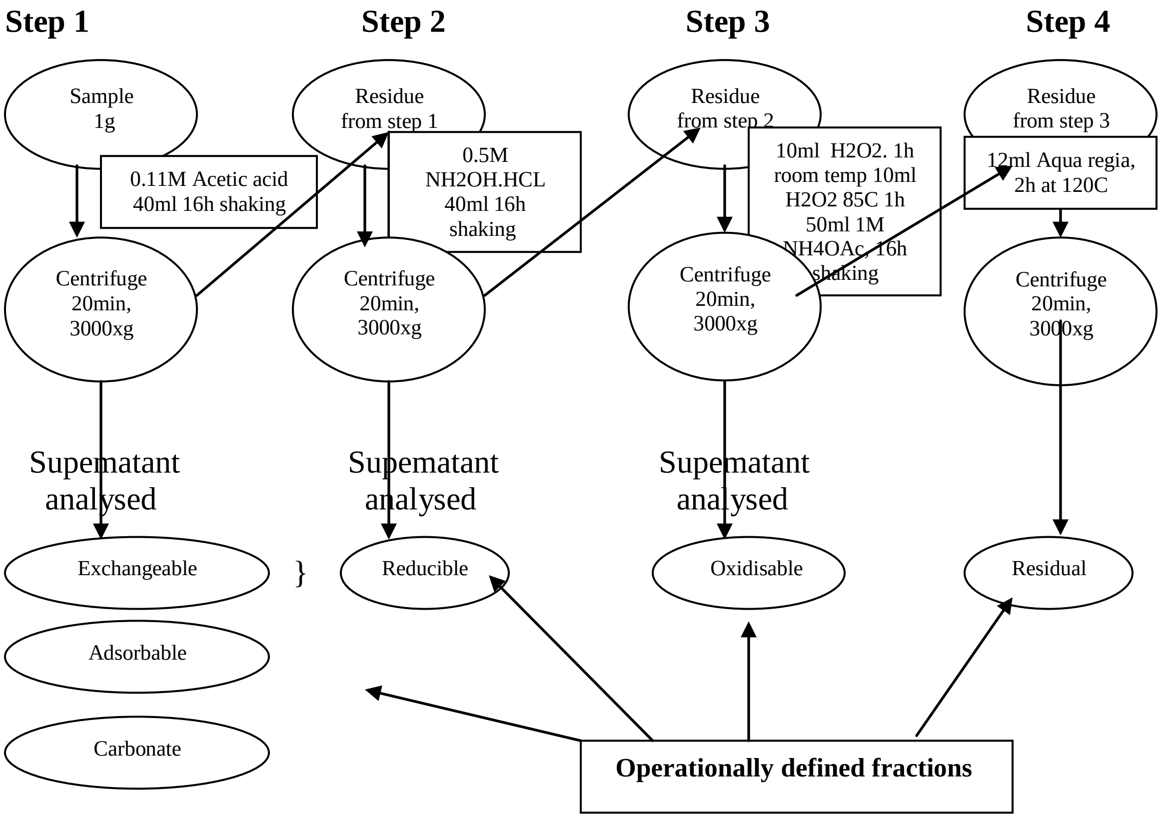

Figure 1.5: Schematic representation of the BCR four stage extraction scheme.

1.7 Guidelines

1. The elemental backgrounds will help in assigning the anthropogenic pollutants for the heavy and trace metals and the Averaged Shell values that will use according to Tuerkian and Wedepohl (1961) and Wedepohl (1995). Furthermore, the background value of an element is the maximum level of the element in an environment beyond the environment polluted by the element (Nasr *et al.*, 2006 and Barciela-Alonso *et*

al., 2003). For this study, we will use the Elemental Background for Soil (EBS) as reference from Sweanit, Fawwar, Ras Al-Qilt and Murashahat areas that are considered as pristine area from Al-Qilt catchment.

2. The LAWA guidelines used in Germany will use in this study for comparison, it is based on values of the Contamination Factors and we will evaluate the total concentrations and sequential fractionation of BCR values. This is important to understand the heavy and trace metals that release and transport to the environment.
3. Palestinian Standards (PS) will use as the limit for artificial recharge to the groundwater from the treated wastewater by infiltration (PSI 2003-742), also, the Jordanian guideline for the same purposes.
4. Availability and toxicity values from other areas similier in matrix for heavy metals, such as the Maximum Permissible Levels according to WHO they are used for drinking water and domestic purposes. These guidlines will give us clear information about pollution at the sites and the parameters that pose the highest risk to the ecosystem.

1.8 Quality assurance

Precision and accuracy for the data were checked through repeated analysis (n=5). For sediment and soil the Buffalo Reference Material (8704) for pseudo digestion and the Reference Standard Material (701) is used for BCR fractionation steps, furthermore, for wastewater we use Standard Reference Material (1643e).

Results are accepted if it is within ±15% of the certified values, this indicates consistance between the certified and the analyzed values for all samples, furthermore, the recovery values for the certified parameters were in the range of 80-110%.

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Chapter 2

Physicochemical proprieties for sediment, soil and wastewater at Al-Qilt catchment

2.1 Abstract

Aim of this chapter is to characterize sediment, soil and wastewater for grain size, physicochemical, organic carbon, nutrients and major parameters, these parameters are highly relate to transport factors and consider as indicators that have impact to the ecosystem. Then, we will use these parameters to describe the mechanism of transport between the sites of Al-Qilt catchment in density of 5-6 kilometer per site.

The grain size analyses for sediment show varied distribution between gravel to sand and muddy, the muddy form are predominant at less than 63µm at wadis, and it is decrease at the head of springs and at the sites for the wastewater discharge. Physicochemical, organic carbon, nutrients and major parameters have been analyzed for freshwater and wastewater, the results are in median, min and maximum values, it is for discharge 7344 (919-17458) m^3/d, pH is 8.16 (7.89-8.65), Temperature is 25.6 (19-28.8) ^0C DO is 3.38 (0.32-8.05) mg/l, Turbidity is 140 (2.15-766) NTU, TDS is 799 (297-1428) mg/l, Ca is 63 (30-87.5) mg/l, Mg is 26 (15.5-37.5) mg/l, K is 13 (3-36) mg/l, Na is 113 (18-293) mg/l, Cl is 189 (28-502) mg/l, SO_4 is 58 (13-119) mg/l, NO_3 is 20 (8-31) mg/l, NH_3 is 11.4 (0.2-34.8) mg/l, TKN is 15.5 (2.18-37.7) mg/l, PO_4 is 8.9 (0.2-25) mg/l, TP is 5.8 (0.04-17.7) mg/l, DP is 3.7 (0.05-12.8) mg/l, TOC is 82.6 (0.7-281) mg/l and DOC is 20.3 (0.5-80) mg/l, all these results are lower than allowe exept for the max values of Na and TOC that are higher if copmare to the Palestinian guidelines that used for recharged by infiltrations to the groundwater.

For Inorganic Carbon it is grater than Organic Carbon at all sites, this indicates predominates of carbonate mainly in the form of calcium carbonate. Furthermore, Suspended Particulate Mater (SPM) and Kd results indicate that Ag, Cd, Sn, Hg, Bi and Sb have low values for SPM, this indicates that these sites will be highly sensitive for pollution if the trace metals transport in suspend or particulate form. In addition to that Kd have low values for the trace metals in the particulate form and they are predominate over the dissolve form at Qalandiah, Stone Cut and Mukhmas, this indicates that the trace metals will transport in the suspended and particulate form.

Moreover; Principal Component Analysis (PCA) for the four factors are applied to major anions, caution, nutrients and organic carbon, this indicates that most of parameters located as one factor in PCA, this is consistence with results from Dendograph or Cluster Analysis (CA). Since, the pH located as second factor for PCA and with the same distance from the parameters in group one at the CA, then the temperature considered as third factor by PCA with the same distance from the other two groups at CA. This discrimination between these parameters in factors or cluster gives priorities for pollutants as anthropogenic and it is important to be consider in the monitoring program.

At Al-Qilt catchment the self purification processes work well to remove the pollutants load thus, self cleaning works well enough in karstic region to guaranty the springs "Fawwar, Ras Al-Qilt and Sultan" with safe water quality, this will need more management plan to decreases the untreated wastewater that discharges to the catchment from upstream to preserve water from deterioration at the head of springs.

As conclusion the pollutants load in term of nutrients and organic carbon still available and not remediate in the surface, thus there are possibilities for chemical interaction with the degraded organic carbon or inorganic parameters. Furthermore, there is impact from the transport or reallocate of these pollutants along Al-Qilt sites by different mechanisms.

2.2 Introduction

Physical properties for sediment, wastewater and soil at ecosystem help in studing the occurrence and transportation of fine particulate matter that alter the degree of associations between the solid and aqua's phase, hence; sediments and soil have the highest sorption capacities for pollutants that distribute according to the diagram (Figure 2.1) (Meili, 1992), furthermore; methods such as sorption, desorption, diffusion and re-suspensions are some of the reactions that regulate the particle association of solutes (Luoma, 1983).

In environment the main mechanisms for transport and spread of solutes with waters are advection and dispersion of streambed, these metals can retain extensive quantities of solutes that attached to particles (Helios Rybicka, 1996; Turner and Whitfield, 1980).

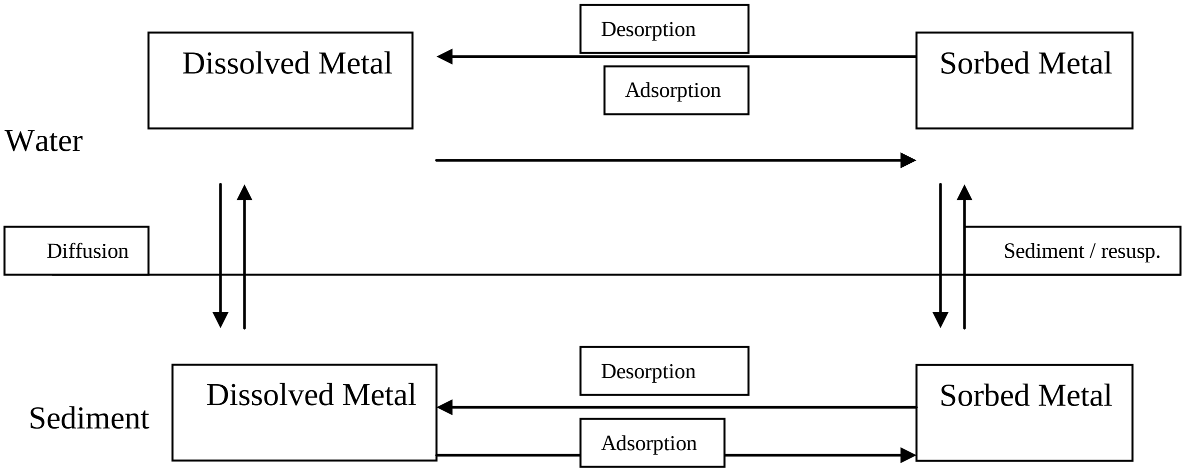


Figure 2.1: Processes that regulates the fate and transport routes and the ecological impact of substances in aquatic environments.

In the early of 1950s, aquatic geochemists made the distinction between dissolved and particulate metal fractions by using simple filtering membrane of size 0.45µm. by this we can discriminate between the two different phases. The continuous filtration of surface water to the bed of sediment allow numerous different chemical reactions to settle and accumulate. According to Stoke's law particles larger than 0.45µm are subjected to gravitational sedimentation depending on particle affinity, these are in the attached or suspended form and available between the sediment and the overlaying water surface for net exchange of the reactive species (Hakanson and Jansson, 1983).

At this chapter we will study the physical parameters for sediments, wastewater and soil grain size, porosity, water contents, Loss of Ignition (LOI), Inorganic and Organic Carbon, Suspended Particulate Matter (SPM), Partition Distribution Coefficients. These parameters will help to understand the occurrences and transportate of anthropogenic pollutants.

2.3 Guidelines and regulations

This study will use the Palestinian Standardization Institute PSI 2003-742 (PSI, 2003) and the Jordanian JS893/1995 (Government of Jordan, 1995) guidelines for reuse of the discharged wastewater that recharg by infiltration to the groundwater (Table 2.1)

Table 2.1: Palestinian Standards Institute and Jordanian guidelines of treated wastewater, as reuse for physicochemical, nutrient and organic carbon units are in mg/l.

Parameters	**PSI 2003-742**	**Jordanian JS893/1995**
TDS	1500	1500
pH	6-9	6-9
DO		> 2
NO_3-N	15	25
NH3-N	-	15
TN	-	50
Cl	600	350
SO_4	1000	1000
Na	230	230
Mg	150	60
Ca	400	400
PO_4-P	15	15
TOC	10	10

(-) not specified

Also it is important to use the guidelines as Maximum Permissible Levels for trace and heavy metals in drinking water according to WHO, (2004) or USEPA, there the nickel, lead, cadmium, and mercury were considered as proprietary substances, on the other hand; Decision 2455/ 2001/EC under the Water Field Directorate, metals such as arsenic, chromium, copper, iron, manganese, and zinc were recommended to add.

Current and international activities in terms of legislation, promotion of scientific research and waste management aim to make the environment safe; These were obtained from the United Nations Environmental Program (UNEP), United States Environmental Protection

Agency (USEPA), European Commission (EC) and German Environmental Protection Office, Umweltbundesamt (UBA).

For quality control standard (1µg/l) multi-element solution was used as quality assurance, furthermore; there are internal blanks that processed exactly as respective and regular samples are used to assess any background contamination that originate from sample manipulation and preparation. Accuracy was checked using Certified Standard Reference Matrix of Buffalo River Sediment (8704) for sediment and soil, and 1643e as certified standard for wastewater samples. Furthermore; some samples were taken duplicate and analyzed to check the results bias and accuracy, all samples were subsequently preserved in cool at 4 ^{0}C and acidify with HNO_3 pH = 2.

2.4 Objectives

1. To determine the physicochemical parameters for sediment and soil in term of water contents in relation to loss of ignitions and organic and inorganic carbon, grain size analysis, distribution coefficient and suspended particulate parameters. These parameters will use to control the transport routes and how these can potentially impact ecological from trace metals.
2. To determine the physicochemical parameters for water in term of discharge, pH, Temperature, Dissolve Oxygen, Turbidity, TDS, base cautions (Ca, Mg, K and Na), base anions Cl, and SO_4, nutrients (NO_3, NH_3, TKN, PO_4, TP and DP) and organics (TOC and DOC).
3. To determine controlling factors such as Principal Components Analysis and Cluster Analysis and other related correlation factors.

2.5 Material and Methods

2.5.1 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 a sediment size usually <63 µm (Birch and Taylor, 2000).

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 (Table 2.2) (Bubb *et al*., 1990).

Table 2.2: 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 percents of anthropogenic pollutants at fine-grain of less than 63µm, this will have higher pollutants percents compared to coarse-grain in the range of gravel (2mm) or in the range of sand that grater (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 in the range grater than 2mm are removed by hand-picking, then sieving using Fritsch D-55743 analyzer, furthermore; the gravel, sand and mud fractions are in the following series: gravel ≥ 200µm, Sand ≥ 63µm and the mud < 63µm (Rauret, 1998; Campbell and Bisson 1979).

2.5.2 Water content 105^{0}C, Loss of Ignition (LOI) at 550^{0}C and 900^0: is quantity of water contained in material called (moisture), the appreciable losses are occur below 105°C, this property is used in wide range of scientific and technical areas and expressed as zero for completely dry (* see references).

Water contents are measured for soil and sediment by taking 5ml samples to crucibles then dried in oven to 105 ^{0}C till it is constant in weight, then water content calculated according to the difference in weight, the samples are continued in drying in muffle furnace to 550 ^{0}C, then we calculate the LOI at 550 ^{0}C according to the difference in weight, then farther drying for the sample till it reach 900 ^{0}C to calculate the LOI at 900 ^{0}C.

2.5.3 Inorganic Carbon (IC) and Organic Carbon (OC): From the LOI we can calculate the organic contents and the carbonate minerals for sediment and soil. This is calculating by using the linear relations between LOI and the weight differences (Dean, 1974). The LOI at 550 ^{0}C will use to calculate the (OC) content, since at 550 ^{0}C the destructive of organic are responsible for removal of about 85% of organic matter from soil and sediments, moreover, Hosking (1938) justify that two hours of heating to sediment and soil at 550 ^{0}C are recommended to remove 99% of the organic matter from sediment and soil, furthermore; Juan *et al*, (2004) is demonstrated that farther two hour heating to 950 ^{0}C is reqested to calculate the (IC) content.

The analyses for IC and OC done as described by Schulte and Hopkins (1996) by using muffle furnace for the same samples. The samples dried after water quantities for further two hour and combusted to 550 °C in muffle furnace, then cooled in desiccators and weighed to calculate the organic carbon. Furthermore, the same samples are transferred for another two hours and combusted to 900 °C to calculate inorganic carbon (Bendell-Young *et al*. 2002 and Beaudoin, 2003).

2.5.4 Porosity: It is used for soil and sediment to describe the porous medium and the fractions of void space, this to void the containing air or water. Porosity is fraction in 0-1 rang and it is typically rang from less than 0.01 for solid granite to more than 0.5 for peat and clay and it is 0.2 for unsorted gravel size. Furthermore, the soil or sediments surfaces typically decreases as particle size increases, also, the subsurface samples from soil and sediments are lower than surface due to compaction by gravity (*).

Porosity measured by equivalent volumes (8g or 5ml) into 15ml crucibles. Then the samples are dried in oven Nabertherm (C19) to 105 °C for overnight, then cool in desiccators and weigh till constant weight, then the differences in weight were taken for porosity and water contents according to specail formulas.

2.5.5 Physicochemical, nutrients and organic carbon for water and wastewater: These parameters play key role in environment and ecological studies mainly for relation with anthropogenic pollutants due to domestic wastewater, urban runoff and other human activities. Furthermore, in developing countries, point and non-point pollution are major problems that impact and deteriorate the environmental system, this situation is exacerbated by scarcity of treatment for domestic wastewater and poor agricultural practices (Iwata *et al*., 2003).

In Palestine there are increases in population, deterioration in natural aquatic ecosystem, shortage of natural resources and deterioration of water resources, this due to human activities mainly the raw wastewater discharged without treatment from domestic and industrial wastewater, stone cutting, arbitrary dumping sites and urban runoff. In addition, there are lack in knowledge of post-deposition of anthropogenic pollutants that facilitate to understand of occurrences, fate, behavior and transport for pollutants and informations for ecological and environmental assessment, therefore, results will be helpful for Palestinian Water Authority to develop there water resources and research purposes.

The physicochemical parameters such as pH, Temperature, TDS, DO, Turbidity are measured using a portable electrodes "HANNA combo" sets that have been calibrated before the measurement by using suitable standard, the base cautions such as Na, K, Ca and Mg were measured by using ICP-OAS Perkin Elmer Optima (7300 DV) and base anion such as Cl, and SO_4 by using Ion Chromatography Dionex (ICS-3000), nutrients such as TKN by digestion, and PO_4 DP, TP, NH_3 analyzed by using Dr Lange Coda (200) spectrophotometer and organic carbon such as TOC and DOC measured by using DIMA-TOC (100). All of these laboratory work done in UFZ Central Laboratory at Magdeburg, Germany.

Furthermore, the discharge and water flow was measured at sampling point, the flow measurement monitored by Palestinian Water Authority (PWA) team using current meter.

2.5.6 Suspended Particulate Matter (SPM): SPM vary according to physiochemical conditions that change the degree of particles that associate in different types. SPM in water play fundamental role in aquatic system that regulates two major transport routes, the pelagic route (dissolved) and the benthic route (particulate) (Jorgensen and Johnsen, 1989), moreover, SPM directly related to many variables such as turbidity and color (Hakanson and Boulion, 2002).

Metals and inorganic compounds occur naturally in water at very little concentrations, this depend upon the local geological and hydrological conditions, since there are ranges of chemical forms for pollutants that available in water such as; free ions form, dissolved form or adsorbed form that bound to organic or inorganic matter in suspended or settled sediment (Meyer, 2002).

The SPM values are the difference in concentration between filtered (dissolved) and unfiltered (particulate) of the trace metals (Hakanson, 1999a).

2.5.7 Partition Coefficient (Kd): It is applied for wastewater as physical parameters that used to describe the fate and transport pathways in aquatic systems. The fact that there are many substances degrade slowly or accumulate on the top surface, this will have impact to the environment potentially that threat to the structure of ecosystems.

The Kd values were calculated in different methods:

1. Method that expresse the degree of particle association is the partition coefficient (Kd). Kd is generally defined as ($\mathrm{l\ kg^{-1}\ dw^{-1}}$) in relation to SPM:

$$\mathrm{Kd} = \frac{Cpart / SPM}{Cdiss}$$

Where: C*part* is concentration in the particulate form and C*diss* is in dissolve form.

The Kd values is equilibrium constant between substance in dissolved and particulate phases (Hakanson, 1999a).

2. Furthermore, we can express Kd values direct according to the following equation:

$$\mathrm{Kd} = \frac{Cdiss}{Cpart + Cdiss}$$

Where: Kd = partition or distribution coefficient.

C*part* = concentration of particulate (μg/l)

C*diss* = concentration of dissolved (μg/l)

2.5.8 Statistical analyses

By using SPSS 16 software packages SPSS Inc., Chicago, USA. The correlation analyses between each two parameters are presented in the form of Non-Parametric Spearman Correlation Coefficients to evaluate the pollution and distinguish the sources for cluster performed, then multivariate statistical approach is used to manipulate more variables in different distributions form.

The Hierarchical Cluster Analysis method was used between groups linkage during the classifying procedure. The averaging was performed overall pairs (x, y) of objects, where x is an object from the first cluster and y is an object from the second cluster. The mathematical function is calculate the distance between clusters X and Y is expressed as following:

$$D\,(X,\,Y) = \frac{\sum_{n=i}^{n=x}\sum_{n=i}^{n=y} d\,(xi, yi)}{NxXNy}$$

Where: X, Y two sets of objects, Vi. two clusters; D(X, Y) distance between clusters X and Y; d(xi, yj) distance between objects x ϵ X and y ϵ Y; Nx, NY-numbers of objects in clusters of X and Y respectively. The rescaled distance outcome was represented graphically as a dendrogram to identify relatively the homogeneous groups of variables in separate clusters and combines clusters until only one is left.

Principal Components Analysis (PCA), Cluster Analysis (CA) and Factor Analysis were used together to check the results of grouping for each variable within the total and they used as explanatory tools in multivariate statistical analysis to interpret the relationships between variables and they used together to check the results and provide grouping of each variable. Thus, it is widely used to reduce data and to extract small number of factors depending on the correlation matrix (Facchinelli, *et al.*, 2001; Jonathan *et al.*, 2004; Karbassi and Amirnezhad, 2004; Karbassi and Shankar 2005; Yongming, *et al.*, 2006).

2.6 Results

2.6.1 Grain size analyses

Sediment samples show variable distribution between gravel to sand to muddy, the muddy form are predominant of less than 63μm in samples from wadis. On the other hand, there are similarities in the distributions of soil grain size at Al-Qilt and if we classify these grain size for sediment and soil to sieving range such as: >2mm, 0.63mm, 0.2mm, >0.063mm and <0.063mm (Figure 2.2).

The grain size data for sediment and soil samples from Mukhmas, Sweanit and Sultan shows variable distribution between muddy sand and mud. Al Bireh, Qalandiah, Stone Cut, Fawwar, Ras Al-Qilt and Murashahat show distribution to gravel then sand and with low percent on the mud form, this due to high in slop, then to velocity of wastewater then to erosion.

The grain size analysis for fine fraction for sediments in mud rang is high at Mukhmas Sweanit and Sultan if compared to other sites, this mean that the specific surface of sediments will be more in fine form and there will affinity for adsorption processes for pollutants to positive charge ions such as trace metals.

Results reveal that sediment samples from wadis such as Mukhmas and Sweanit are finer than the soil, in general, the degree of sand and mud will be enrich more in sediments and it will impact the transport of these trace metals. Furthermore, results give significance and more positive for sediment to transport in the fluvial systems in the form of suspended particles matter, this dispersed sediment size and will distribute in appropriate way for transporte of sediment by dianamic flow.

Results reveal that sediment grain size is decrease with increasing flow such as at Qalandiah, Stone Cut, Fawwar, Ras Al-Qilt and Murashahat, this due to increase in the slope and erosion of fine material from the channel bed or banks.

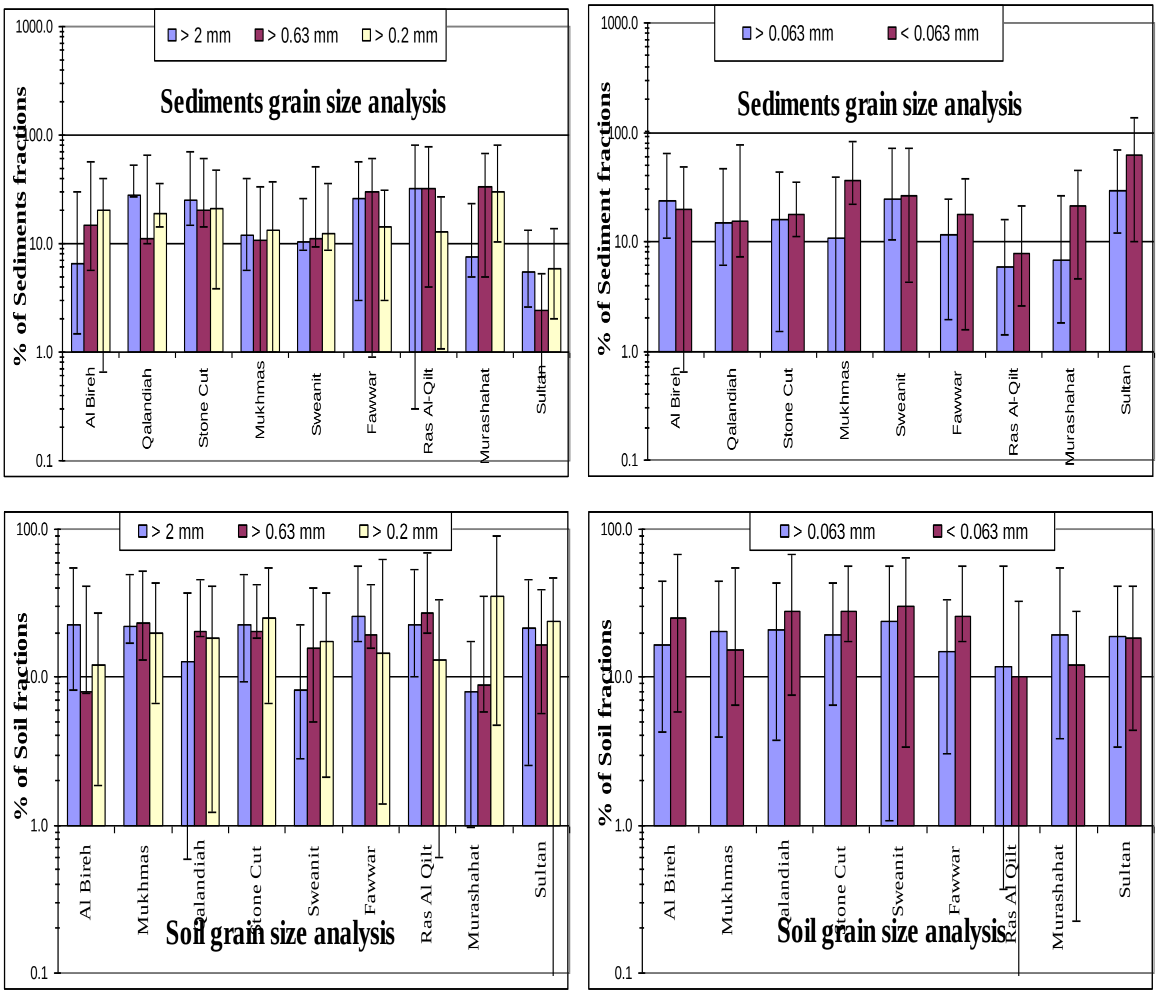


Figure 2.2: Grain size analysis for sediments and soil at Al-Qilt catchment.

2.6.2 Water content, Loss of Ignition (LOI) at 550°C and at 900°C

Results reveal that there are relationships between LOIs and water contents, this will reflect the sediment composition mainly for organic carbon and carbonate. Furthermore, water contents for sediment is high at Al Bireh, Mukhmas and Sweanit and the LOI 550 °C are low compared to LOI at 900 °C for the sediment samples, on the other hand, the LOI values at 900 °C are higher compared to LOI 550 °C for soils samples, this indicates that inorganic carbon as $CaCO_3$ will retarding the mobility or transport of trace and heavy metals.

As results there will retardation for the mobility in buffered and calcite media, this will appear more in the fractionations and more detail in Chapter 4 (Figure 2.3).

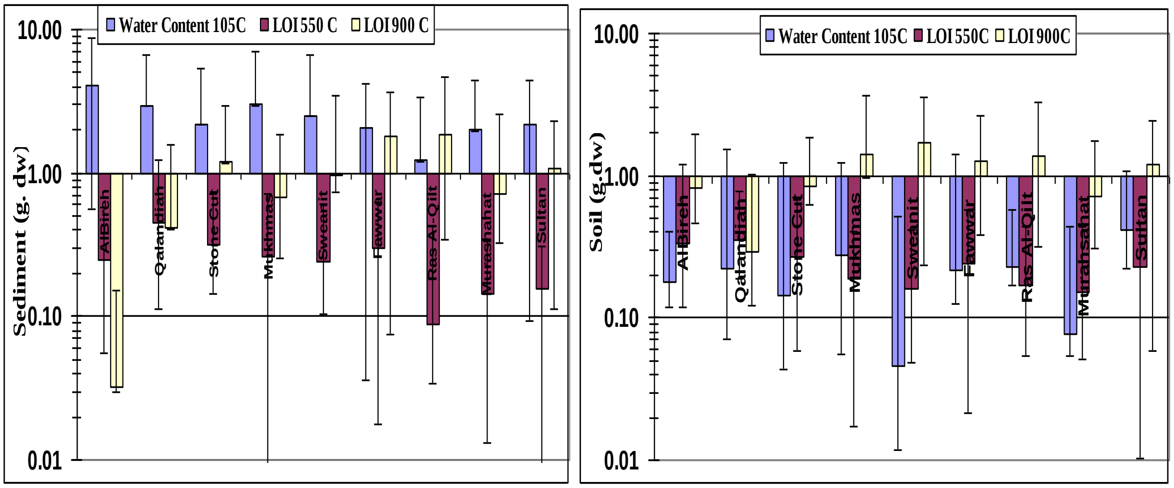


Figure 2.3: Water contents at 105 °C, LOI at 550 °C and LOI at 900 °C.

2.6.3 Inorganic and Organic Carbon

Results for organic carbon are calculated from the difference of water content at 105°C and LOI at 550°C, furthermore, the inorganic carbon is calculated from the difference of LOI at 550°C and LOI at 900°C.

Results reveal that inorganic values are high for sediment and soil mainly at Fawwar and Ras Al-Qilt springs if compared to Stone Cut, Mukhmas and Sweanit (Figure 2.4).

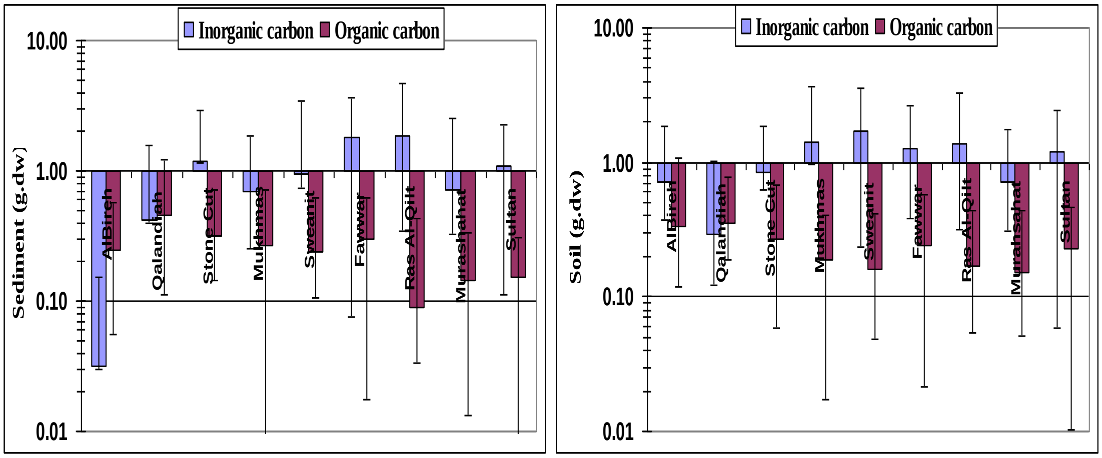


Figure 2.4: Inorganic and organic contents occurrences at Al-Qilt catchment.

2.6.4 Porosity

Results for porosity reveal that sediment samples are high for porosities if compared with soil porosities at upstream of Al-Qilt, this indicates that there still more space between sediments texture.

On the other hand, results for soil at springs are high if compared with sediments, this indicates that there still more space between soil texture (Figure 2.5).

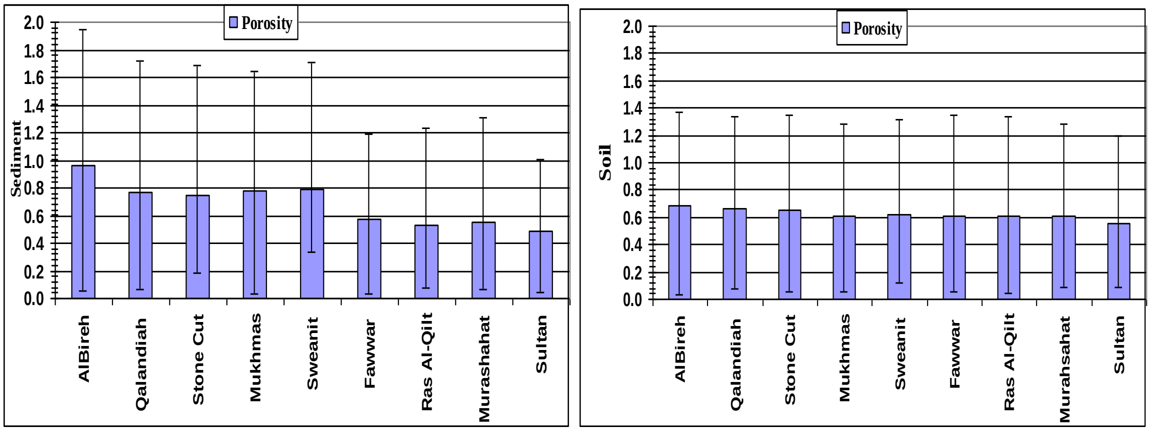


Figure 2.5: Porosity values for sediment and soil at the Al-Qilt catchment.

2.6.5 Suspended Particulate Mater (SPM)

Result reveal that the SPM for Ag, Cd, Sn, Hg, Bi and Sb are zero, this indicates that these trace and heavy metals have no difference between dissolve and particulate form, thus these trace metals are in equal values in both forms, this will increase the risk to transport in the dissolve form compared to particulate depending on the environmental conditions.

Results for trace metals (Figure 2.6), the risk increase for these trace with low SPM such as Cu, Zn, V, Cr, Co, Ni and Pb, this appear more at the springs downstream, this indicates that the dissolve form from these trace metals are grater than the particulate form due to infiltration from the upstream, this will increase the risks of these parameters, since they considered as anthropogenic pollutants.

Important to mention that the continuous filtration of water as dissolved solutes will allow numerous different chemical reactions to pass depend on its particle affinity. This will has implications for the net exchange of reactive solutes between the suspended sediment in turbulence and the overlaying with water, furthermore, the transport of solutes in water and in the sediment bed will dramatically alter the transport time, this will have large implications for the ecological effects of solutes in aquatic systems.

SPM has been demonstrate to exert an important control between dissolved and particulate phases of the trace metal, since if SPM is high this will depend more on the particle form of metals than dissolved phase form, this often represents only minor fraction from the total concentrations as dissolved or particulate phases. Balls, (1988) has concluded that mainly at sensitive areas, the changes in dissolved metal concentration was with low SPM loading.

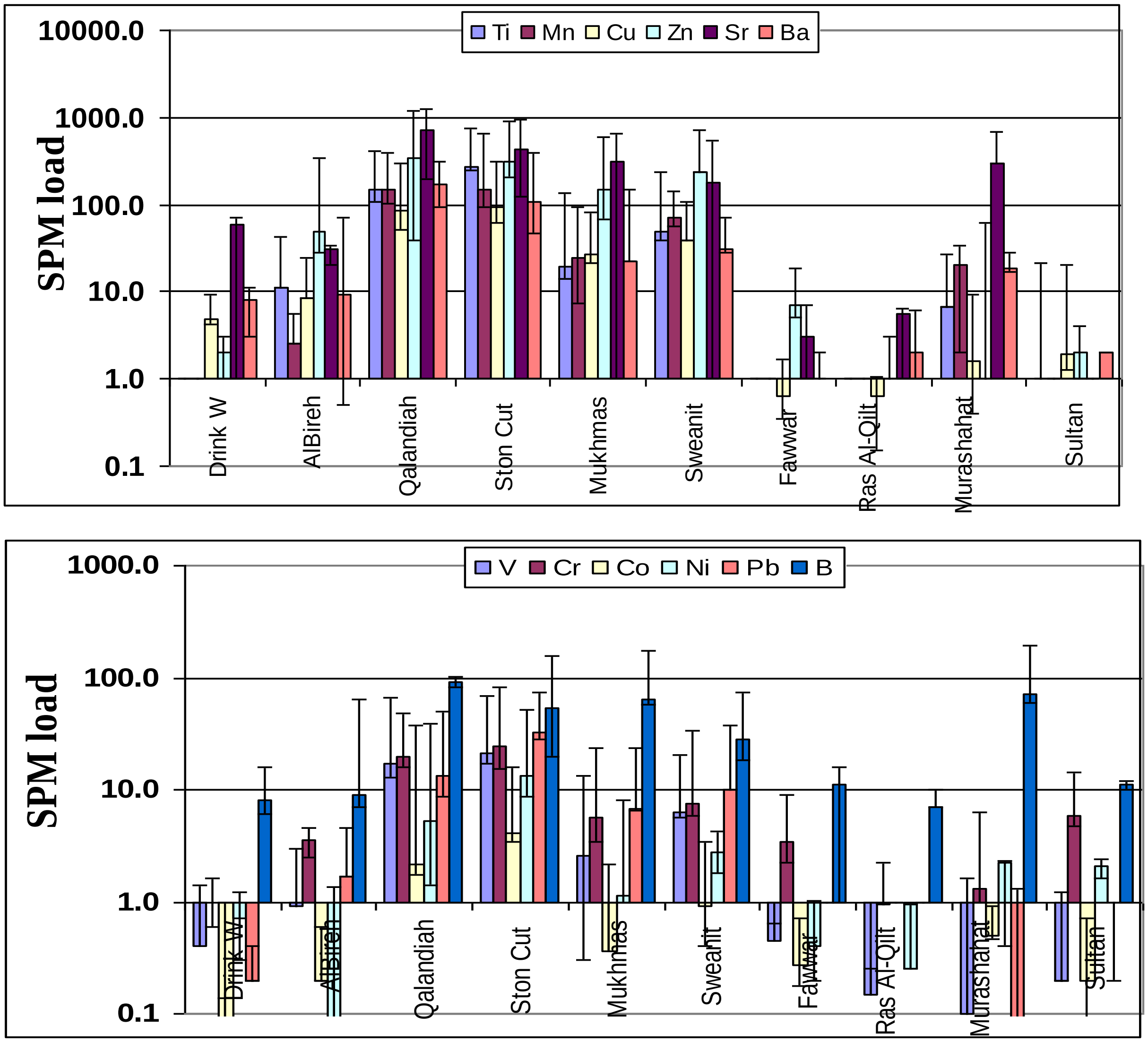


Figure 2.6: Suspended Particulate Matter of the studied trace metals in sediment.

Furthermore, results reveal that SPM increase due to wastewater that discharged mainly at Qalandiah, Stone Cut and Mukhmas, this indicates that the trace in the particulate form are grater than the dissolve form, thus, the trace metals can be transport on the suspended form or in turbulences movements. Since, the behaviour of Sr, Ba and B are the same and it is increase at the upstream mainly from the discharge points and it is decrease at downstream mainly at the head of springs, then it is appear again at Murashahat canal, this indicates that these trace metals are water soluble and can be easily transport between the saturated and unsaturated zone.

The dynamic nature of ecosystem environment work well to reduce the magnitude and to change the dissolved and particulate forms of trace metal concentrations, this blurring of signal is greatest in turbid areas for reactive metals such as Pb, Cu, Zn and Sb (Figure 2.6), then this appear with positive correlation between these species and give trend that it must monitored in the dissolve form for the reactive species in order to have better understand for the mechanism of transport of trace metals in the environment.

If the inter-element Spearman Nonparametric Correlation for SPM trace metals Turbidity, TDS, TOC and DOC are correlate (Table 2.3), results reveal that Ag and Hg not correlate with any parameters, since it is detected in the lower level and not varied in wastewater. Results with high positive correlation >0.9 at $P<0.01$ and $P<0.05$ is observed (red) and high correlation >0.70 at $P<0.01$ and $P<0.05$ is noticed (blue), moreover, moderate >0.5 at $P<0.01$ and $P<0.05$ is also noticed (yellow), furthermore, it is green when the correlation values less than 0.5 (Table 2.3).

The positive correlation between these different parameters is an indication for possible common pollution sources as well as their common media in the study area. Since, results indicate that the positive correlation for Zn/Cu, Sb/Cu, Sn/Cd, Pb/Cu, Pb/Zn, Pb/Sb, Turb/Sb and TOC/Sb, these correlations indicates that these trace metals are originates from the same source at Al-Qilt catchment, moreover Zn, Cu, Pb, Sb and Sn originate from wastewater, urban run off and road side, this is indication for possible processes and mechanisms that influence the metal associations and behavior, also give informations for bonding and retention mechanisms that might be explained by information on the geochemical phases (Mwamburi, 2003) this will be clear with more details in Chapter 4 and Chapter 5.

Table 2.3: Non parametric Spearman Correlations of SPM trace metals and physical parameters.

	Ti	**V**	**Cr**	**Mn**	**Co**	**Ni**	**Cu**	**Zn**	**Sr**	**Cd**	**Sn**	**Sb**	**Ba**	**Pb**	**Bi**	**B**	**Li**	**Turb**	**TDS**	**TOC**	**DOC**
Ti	1																				
V	0.86**	1																			
Cr	0.81**	0.83**	1																		
Mn	0.97**	0.79**	0.77**	1																	
Co	0.87**	0.73*	0.81**	0.90**	1																
Ni	0.70*	0.56	0.75*	0.76*	0.85**	1															
Cu	0.91**	0.90**	0.82**	0.86**	0.71*	0.70*	1														
Zn	0.87**	0.98**	0.86**	0.83**	0.75*	0.59	0.90**	1													
Sr	0.85**	0.65*	0.5	0.90**	0.76*	0.69*	0.77**	0.66*	1												
Cd	0.72*	0.70*	0.70*	0.71*	0.71*	0.70*	0.70*	0.69*	0.68*	1											
Sn	0.71*	0.70*	0.70*	0.72*	0.70*	0.68*	0.69*	0.70*	0.70*	0.98**	1										
Sb	0.99**	0.85**	0.78**	0.95**	0.83**	0.62	0.90**	0.85**	0.84**	0.73*	0.71*	1									
Ba	0.95**	0.75*	0.70*	0.97**	0.81**	0.76*	0.90**	0.77**	0.93**	0.69*	0.70*	0.92**	1								
Pb	0.92**	0.94**	0.76*	0.86**	0.70*	0.61	0.97**	0.91**	0.79**	0.72*	0.71*	0.91**	0.90**	1							
Bi	0.54	0.52	0.52	0.42	0.53	0.52	0.52	0.41	0.41	0.75*	0.58	0.55	0.41	0.54	1						
B	0.68*	0.47	0.6	0.80**	0.85**	0.75*	0.52	0.57	0.75*	0.49	0.55	0.66*	0.73*	0.46	0.17	1					
Li	0.75*	0.79**	0.6	0.74*	0.52	0.36	0.82**	0.83**	0.68*	0.32	0.38	0.75*	0.76*	0.82**	0.06	0.54	1				
Turb	0.90**	0.75*	0.74*	0.87**	0.83**	0.55	0.74*	0.77**	0.77**	0.70*	0.68*	0.93**	0.79**	0.74*	0.52	0.75*	0.66*	1			
TDS	0.83**	0.86**	0.73*	0.78**	0.64*	0.64*	0.95**	0.83**	0.77**	0.62	0.59	0.81**	0.83**	0.92**	0.52	0.53	0.84**	0.70*	1		
TOC	0.94**	0.76*	0.63	0.90**	0.72*	0.55	0.84**	0.73*	0.88**	0.62	0.59	0.93**	0.90**	0.87**	0.52	0.59	0.75*	0.85**	0.82**	1	
DOC	0.86**	0.71*	0.54	0.84**	0.65*	0.36	0.71*	0.72*	0.82**	0.51	0.53	0.88**	0.80**	0.76*	0.29	0.63	0.79*	0.90**	0.70*	0.93**	1

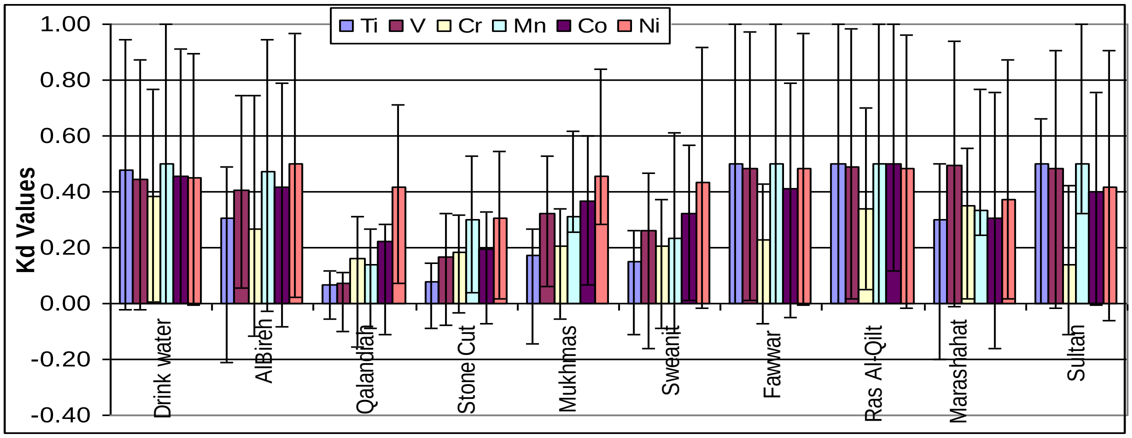
**. Correlation is significant at the 0.01 level (2-tailed).
*. Correlation is significant at the 0.05 level (2-tailed).
Sig. (2-tailed) and N=10

2.6.6 Partition Coefficient (Kd)

The chemical transformations of pollutants change from one phase to another, this often quantify by partition coefficient factor, this factor is called distribution coefficient. The simplest form of partition coefficient is the ratio of concentration for pollutant in the soil or sediment to water partition coefficient. Each value of Kd depend on the properties of the particular pollutant.

Results reveal that Kd has the highest values when the concentrations are equal for the dissolve or particulate forms such as drink water or springs samples, on the contrary, the wastewater samples are varied due to the incremental of one form, this variations will have impact in verifications of trace metal transport in particulate or dissolve form from one place to another, this is clear for Ti, V, Cr, Co, Cu, Zn, Sr, Cd, Sb, Ba and Pb (Figure 2.7).

The Kd values reveal that Ag, Sn and Hg are not change due to low detection limits in aqua's form, thus, there results will compare with drinking water. All wastewater samples have low Kd values will compare with fresh water samples, this will help in follow up the movement of contaminants depending on the Kd values, since movement of gradients are progressively slow moving contaminants with higher Kd values, since the dissolve form of the trace metals in the groundwater samples are similar in retardations according to their gradient movement, moreover, the soil serve as stationary phase and the extent of retardation is relate to the contaminant value of Kd as appear at downstream mainly at the springs.



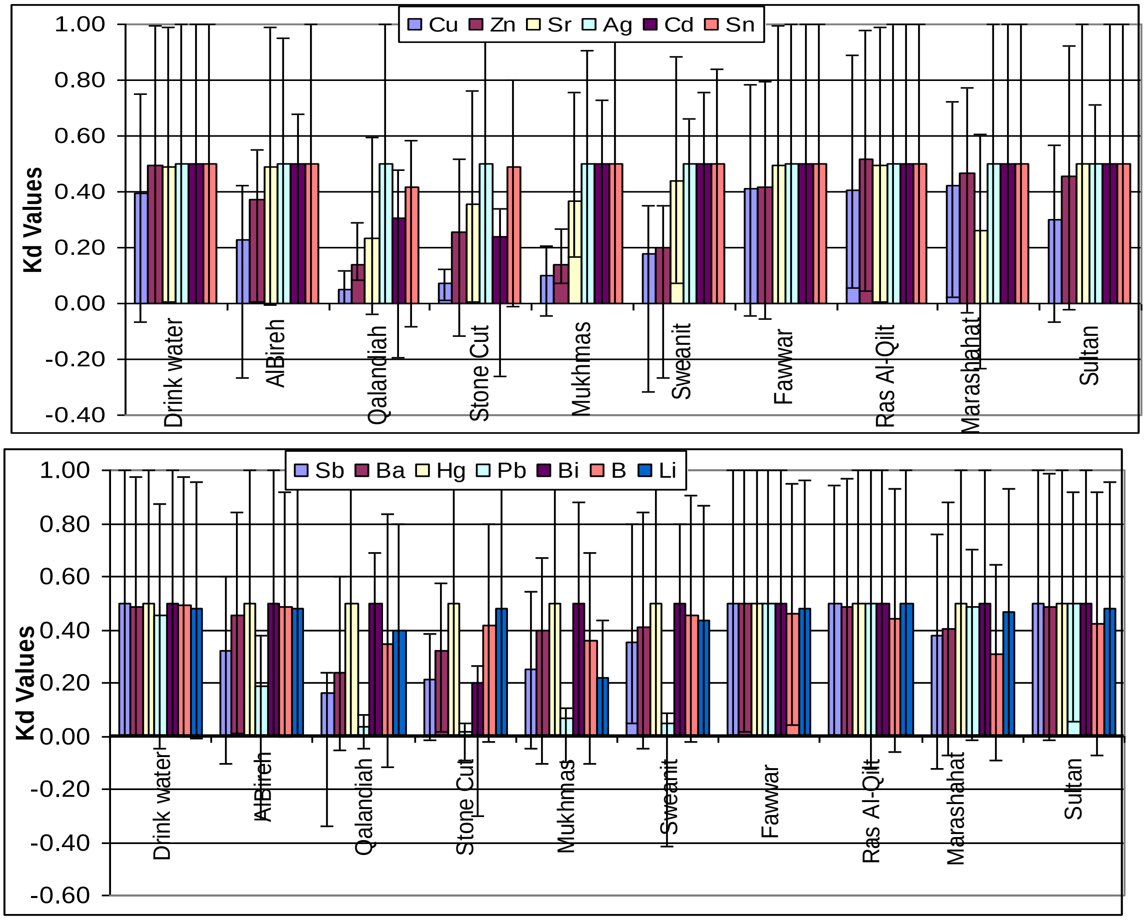


Figure 2.7: Kd values for trace metal along Al-Qilt catchment**.**

Furthermore, If the Inter-element Spearman Nonparametric Correlation of Kd is used for traces metals, Turbidity, TDS, TOC and DOC, results reveal that Ag and Hg not correlated with any due to low concentrations, since, there detection limits are 2 and 3 µg/l respectively in wastewater samples, moreover, there are very high positive correlation >0.9 at P<0.01 and P<0.05 is observed (red), high correlation >0.70 at P<0.01 and P<0.05 is noticed (blue), moderate >0.5 at P<0.01 and P<0.05 is noticed (yellow) and it is green when the correlation values less than 0.5 (Table 2.4).

The positive correlation between these different parameters are indicate for possible common pollution sources, also it is indication for possible correlations that might indicate the processes and mechanisms that influence the metal associations and behavior, furthermore,it reflect the bonding and retention mechanisms that will explain for the sediment geochemical Mwamburi (2003).

In terms of contaminant mobility and transports, the strongly sorbed contaminants remain sorbed to soil or sediment surfaces longer than weakly sorbed contaminants, they will move slowly through the subsurface to the groundwater and there will be in dissolve form. The movement of contaminants in dissolved form in the groundwater is analogous to the movement of pollutants through chromatograph media and each pollutant binds to soil and sediment with a unique binding strength that will move in different velocities and eventually become separated in space (Eugene, 2000).

Results indicate that Sn/Cd, Pb/Sn, Turbidity/Sb, TDS/Pb, TOC/Sb, DOC/Sb and TOC/Pb these correlations are similar with SPM correlation for Sn/Cd, Turbidity/Sb and TOC/Sb, this correlation indicates that trace metals distribute between water and solid phase for Sn, Cd, Pb and Sb, this correlation is with main turbulence factors such as Turbidity. These factors are behind the transport and the mobility of trace metal in the form of particulate "turbulence" or in dissolve form and example will be organic carbon.

Table 2.4: Kd trace metals Non Parametric Spearman Correlations with physical parameters.

	Ti	V	Cr	Mn	Co	Ni	Zn	Cd	Sn	Sb	Ba	Pb	Bi	B	Li	Turb	TDS	TOC	DOC
Ti	1																		
V	0.80**	1																	
Cr	0.36	0.54	1																
Mn	0.97**	0.77**	0.45	1															
Co	0.82**	0.54	0.56	0.82**	1														
Ni	0.47	0.16	0.42	0.42	0.79**	1													
Cu	0.77**	0.93**	0.67*	0.74*	0.54	0.22													
Zn	0.74*	0.82**	0.61	0.79**	0.62	0.13	1												
Sr	0.90**	0.51	0.06	0.84**	0.75*	0.48	0.5												
Cd	0.70*	0.68*	0.51	0.61	0.70*	0.54	0.42	1											
Sn	0.71*	0.70*	0.53	0.64*	0.68*	0.49	0.45	0.96**	1										
Sb	0.92**	0.81**	0.44	0.90**	0.73*	0.28	0.82**	0.71*	0.72*	1									
Ba	0.93**	0.66*	0.45	0.89**	0.86**	0.58	0.71*	0.68*	0.70*	0.92**	1								
Pb	0.94**	0.88**	0.38	0.88**	0.68*	0.38	0.71*	0.71*	0.69*	0.89**	0.86**	1							
Bi	0.41	0.41	0.29	0.3	0.52	0.52	0.17	0.75*	0.58	0.42	0.41	0.52	1						
B	0.5	0.07	0.36	0.54	0.72*	0.61	0.33	0.42	0.45	0.5	0.71*	0.29	0.17	1					
Li	0.58	0.4	0.42	0.68*	0.55	0.18	0.79**	0.03	0.14	0.59	0.64*	0.41	-0.29	0.54	1				
Turb	0.82**	0.67*	-0.47	0.81**	0.79**	-0.35	0.78**	0.70*	0.68*	0.94**	0.87**	0.75*	-0.52	-0.58	-0.55	1			
TDS	0.83**	0.87**	-0.45	0.74*	0.64*	-0.41	0.77**	-0.62	-0.59	0.80**	0.79**	0.91**	-0.52	-0.25	-0.45	0.70*	1		
TOC	0.90**	0.87**	-0.29	0.86*	0.66*	-0.27	0.73*	-0.62	-0.59	0.92**	0.86**	0.91**	-0.52	-0.46	-0.46	0.85**	0.82**	1	
DOC	0.82**	0.68*	-0.26	0.82**	-0.56	-0.04	0.81**	-0.51	-0.53	0.93**	0.81**	0.78**	-0.29	-0.48	-0.6	0.88**	0.68*	0.93**	1

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

Sig. (2-tailed) and N=1

2.6.7 Results for water flow and physical properties

2.6.7.1 Water flow: Water quantities at the upstream are calculated in median values, it is 5000 m^3/d at Al Bireh wastewater treatment plant, 1325 m^3/d at Qalandiah as raw wastewater, 1020 m^3/d at Stone Cut as raw wastewater, the three sites mixed at Mukhmas with total quantities of about 3374 m^3/d as mix of the treated and raw wastewater, then these quantities continue running by gravity to Sweanit 919 m^3/d (Figure 2.8), the total wastewater budget that discharged to Al-Qilt catchment from the Palestinian communities and Israeli colonies estimate for this study 14000 m^3/d, this depend on the discharge of population equivalents for consumption and the measured one (Chapter 1).

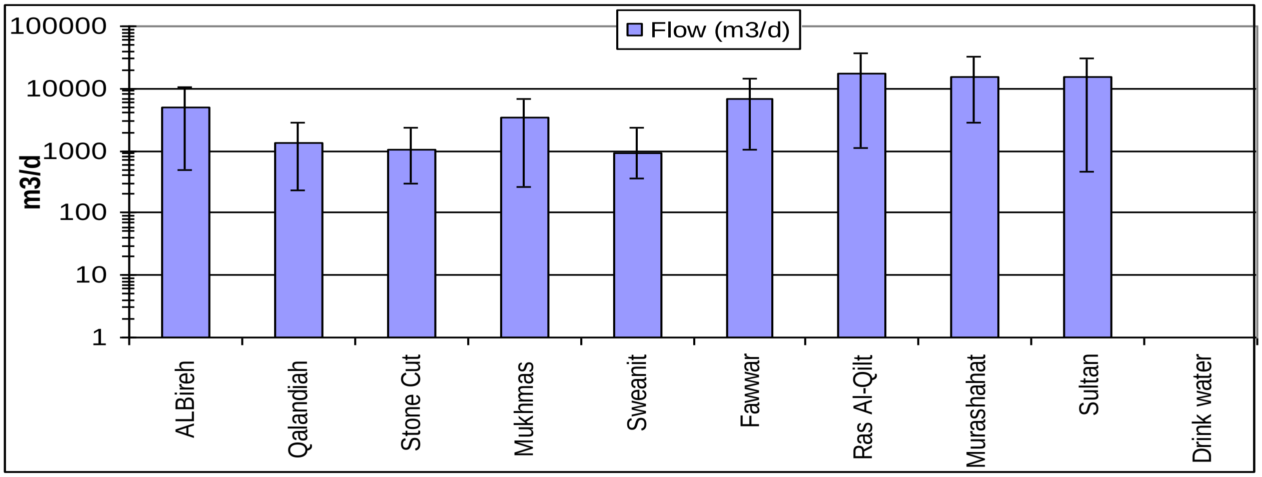


Figure 2.8: Flow meter measurement at Al-Qilt catchment.

The total distance for the wastewaters that run till it reachs Sweanit is 16 km, and then it is dry before reaching Fawwar spring 6 km from Sweanit, this means that all wastewater are infiltrate and evaporates. Result indicates that wastewater at Mukhmas 3374 m^3/d as results of 7345 m^3/d from Al Bireh, Qalandiah and Stone Cut, this mean that 46% of the water infiltrate and evaporate. At Al-Qilt the rate of evaporation reach to 28-30%, this mean that 15-17% are infiltrate to the groundwater take in consideration that the rate of evaporation increase downstream due to increase in temperature (PWA, 2011).

At downstream of Al-Qilt the water discharged from the springs such as Fawwar (6726 m^3/d), Ras Al-Qilt (17458 m^3/d) and Sultan (14900 m^3/d), moreover, it is discharged from Murashahat (15378 m^3/d) as water treatment plant (Figuer 2.9).

Figure 2.9: Measuring the discharge using the current meter at Al-Qilt catchment.

2.6.7.2 Turbidity: The turbidity variations depend on the source of discharged and distance of measurements, the values are in median and it is in the range of 766.6 NTU at Stone Cut and it is 21.8 NTU at Sweanit at the upstream, on the other hand, it is 4.2 NTU at Ras Al-Qilt spring and it is increase after running in the open channel to Murashahat and it is 27.6 NTU (Figure 2.10).

Results reveal that the lowest turbidity value is at Ras Al-Qilt due to infiltrate between Fawwar and Ras Al-Qilt springs. At this zone it has the capability to remove most of the suspended particulate matter from the top, on the other hand, the turbidity values are high at Qalandiah and Stone Cut due to discharge of raw wastewater, this will form slums like brewing and others suspend matter that will mixed with other pollutants and deposited into the wadi and continue in running to the downstream.

According to Spearman Correlation (Table 2.3) turbidity not correlated with pH, Temperature and it is correlated negatively with DO, furthermore, it is correlated strongly with TOC and DOC (0.92 and 0.91) respectively and it is correlated moderately with most of other parameters.

2.6.7.3 Total Dissolve Solid (TDS): Results reveal that values are varied at the upstream according to the source, since it is 1036.6 mg/l, 1428.3 mg/l and 933.3 (Figure 2.11) at Qalandiah, Stone Cut and Sweanit respectively, important to mention that these running water at the wadi infiltrate and recharg to the groundwater, hence, according to Palestinian and WHO guidelines the limit for TDS is 1500 mg/l (grey line Figure 2.11), also the green line is the allowed limit for Cl.

Results indicate that the major source for TDS is Cl and Na, since the concentrations of Cl and Na are increased by increasing the TDS and both of them are increased due to raw wastewater, this appears clear in Spearman Correlation (Table 2.3), since, TDS is not correlated with pH, Temperature and DO, but it is correlated strongly with Cl, this means that Cl is one of the main sources that responsible for TDS incremental. Moreover, TDS correlated good to moderate with other parameters Figure (2. 10).

Figure 2.10: Measuring physical parameters in the left (pH, Tempreture and TDS) and in the right the disolove oxygen at Al-Qilt catchment.

2.6.7.4 pH, Dissolve Oxygen (DO) and Temperatures values: In this study DO is low due to raw wastewater discharges and it has the highest at Al Bireh and Sweanit at the upstream sites. It is important to mention that oxygen utilized by organic decomposition; this will create anoxic conditions in the absence of oxygen. DO values are in median and it is 2.5 mg/l at Al Bireh, and 0.39 mg/l and 0.78 mg/l at Qalandiah and Stone Cut respectively, DO increase at wadi due to aeration and free runing, on the other hand, there are variations on temperature that reach to 2 ^{0}C at Stone Cut and 3 ^{0}C at Al Bireh, therefore, DO enrichment are not sufficient to over come for the temperature incremental. In addition, the temperatures are increase from west to east; this is accomplished with decrease in oxygen despite the aeration as wastewater run downstream.

These parameters are directly relate to acidification, solubility, oxidation reduction and other chemical interaction within the aquatic system, hence, it is not easy to monitor these parameters and their different relations in open field. since the solubility of nutrients and organics carbon are highly influence due to change of DO, Temperature and pH (Figure 2.11), these will enhance the nutrients and organic carbon either to dissolve or precipitate forms in the solution as a complex or organic fragments, this will has impact on the trace metals that transport and for mobility.

Important to mention that trace metals prefer low pH and high temperatures for transport in aquatic environments (Meza-Figueroa *et al*., 2007).

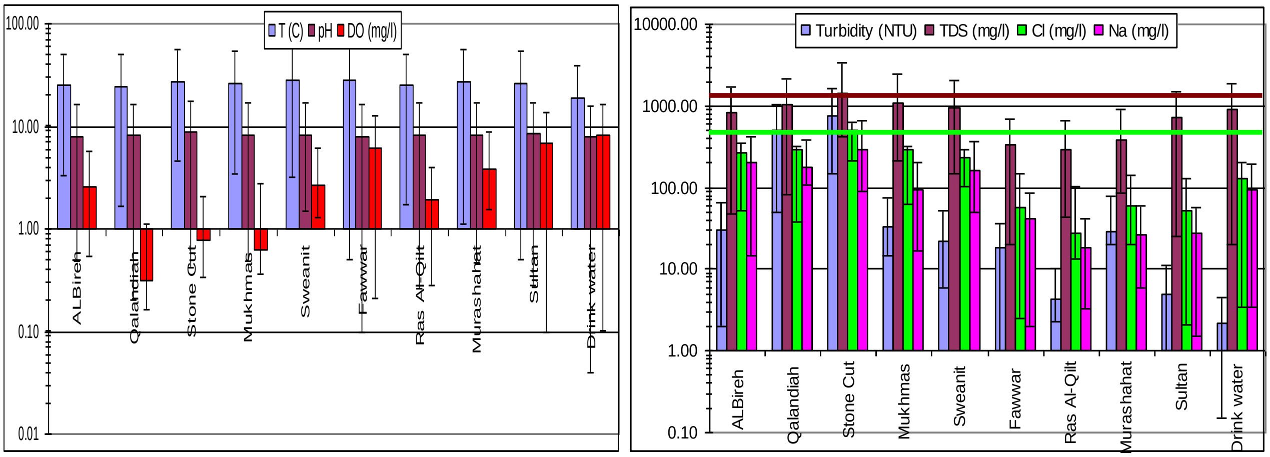


Figure 2.11: (left): Temperature (^{0}C), pH and DO (mg/l), (right): Turbidity (NTU), TDS (mg/l) Cl (mg/l) and Na (mg/l).

Furthermore, results reveal that pH is in median values, it is 7.89, 8.12 and 7.99 at Al Bireh, Qalandiah and Sweanit respectively (Figure 2.11), since the Palestinian guideline for pH used for recharged by infiltration is 6-9, this means that all values within this range and it is critical if the values are in acidic range, since it is preferable condition for trace metals as metallic form and it is easy to reallocate or transport, on the other hand, the pH values at the spring are in range of domestic purposes that can be use for drinking.

For temperature it is increase downstream from west to east and it is 24.4 ^{0}C, 26.5 ^{0}C and 27.9 ^{0}C at Al Bireh, Stone Cut and Sweanit respectively, moreover it is 24.7 ^{0}C at Ras Al-Qilt spring.

2.6.8 Nutrients

Nutrients such as NO_3^-, NH_4^+, TKN, PO_4-P, Total Phosphorus (TP) and Dissolve Phosphorous (DP) are analyses and investigate. Results for ammonium and nitrate are oppositely distributed within the nitrogen balance, this is strongly depend on the source, since NO_3 predominate over ammonium at Al Bireh, Mukhmas, Sweanit and springs due to nitrification process, also ammonium increase due to discharge of raw wastewater at Qalandiah and Stone Cut, this is accomplishe with declines of nitrates and increase of ammonium form in nitrogen balance (Figure 2.12.a). Nitrate is within the allowed limit according to Palestinian or Jordanian guidelines that used to discharge for the treated wastewater for infiltration, but there are still impact due to the accumulation and incremental of nitrate and there will be risks from the shook load for nitrate and organic carbon if they reach to the groundwater in karstic system these results discussed more by (Helua *et al.*, 2007) he found that there are shock load from nitrate at the head of Ras Al-Qilt due to karstic system.

NH_4 and NO_3 are behaves in different manners and there are chemical transform by nitrification and di-nitrification process, since the incremental of NH_4 mean that there are new raw wastewater by mixing (Figure 2.12.a), NH_4 usually available and release during decompositions of organic material and it is easily oxidized to NO_3. NH_4 in most cases are dominant in TKN form, this includes the organic nitrogen and inorganic nitrogen, these dominancy are clear at Qalandiah, Stone Cut and Mukhmas sites, furthermore, NH_4 become anoxic if there are no nitrified conditions, this will lead to have higher NH_4 and lower NO_3, this is explain the incremental in NH_4 that release, this will decrease NO_3 form, moreover, nitrate reduction can be relate to biological activities in micro organism consume the nitrate (Figure 2.12.a).

Results indicate that atmospheric oxygen increases the nitrogen in the form of nitrate and phosphorus in the form of phosphate by chemical transformation. In other worlds, oxygenation is quick solution to reduce the impacts of phosphorus and nitrogen pollution, this will increase the inorganic load in the surrounding, moreover, there will be incremental from the external load of phosphorus and nitrogen due to raw wastewater, this is clear at Qalandiah and Stone Cut at the upstream and extend till it reach Sweanit (Figure 2.12), furthermore, results for TP and DP are high at the sites mainly from the wastewater discharge. These parameters can play important roll for transport and reallocate the trace and heavy metals.

The phosphorus concentrations reflect the underlying geology and soil type of area, since it is enriched at soils from fertilizer and manure, moreover, the diffuse inputs of phosphorus are commonly the highest during winter storm events and the proportion of phosphorus will flush it into the stream under high flows, this will deposit and stored on the stream bed during the transport to downstream (Jarvie *et al*., 2005).

Furthermore, phosphorus plays an important role in buffering the soluble DP form, this will either absorb or release the trace and heavy metals depending on the concentrations of phosphorus at the surface (House & Denison, 1998).

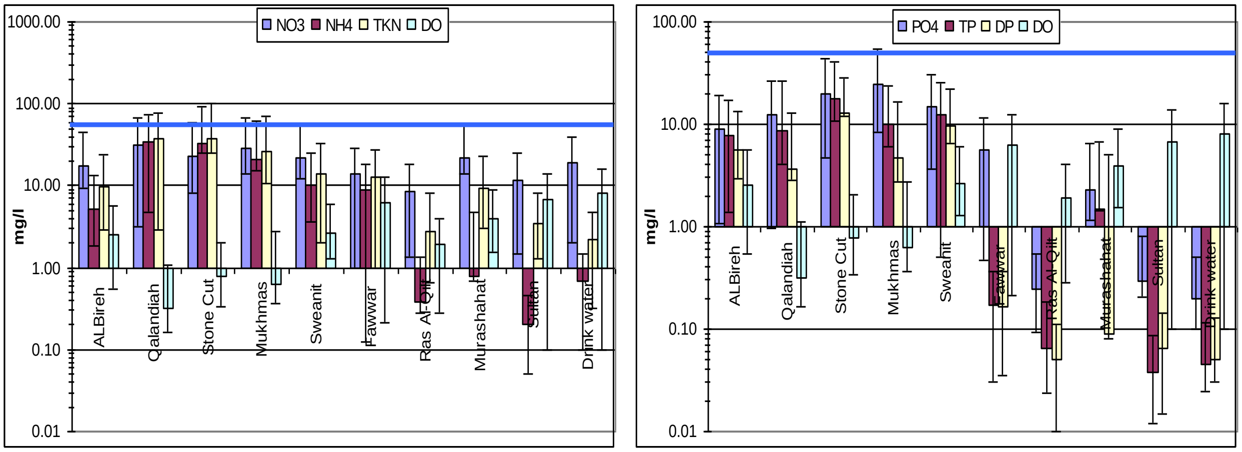


Figure 2.12: a (left); Nitrogen balance and DO measurements, b (right); Phosphate balance and DO measurements.

Jarvie *et al*., (2005) indicates that the interaction between the water column and bed of sediment is the key process governing the concentrations of both particulate (TP) and dissolved (DP) at the surface, this is due to the deposition or re-suspension of sediment. At Al-Qilt catchment the DP concentrations are increases due to anthropogenic emissions from the or diffuse sources such as raw wastewater from Qalandiah, Stone Cut, Mukhmas and Sweanit (2.12,b), so sediments will act as a sink for the stream water and will act as a source for DP to overly with water during the slowly flow conditions.

Phosphate values are low in compred to the Palestinian and Jordanian guidelines that used for infiltration to the groundwater, but phosphate will accumulate due to raw wastewater, this will have impact due to enrichment for the microorganism beside the nitrogen for the eutrophication process and will play important roll in transportation of trace metals at the environment. Moreover, it is important to consider the eutrophication at the surface and the TP load in aquatic system that can be transport or associate with sediment, this represent significant long-term source for potential and available phosphorus in the aquatic system, these results are similer to study done by (Sharpley *et al*., 1992).

The Palestinian guideline for treated wastewater and its reuse for infiltration for NO_3 and PO_4 are 15 mg/l and it is 10 mg/l for NH_4, results indicate that PO_4 at Mukhmas and Sweanit have the highest values and they are less than the allowed limit to reuse for infiltration or recharge after treatment, furthermore, NO_3 and NH_4 at Qalandiah, Stone Cut, Mukhmas and Sweanit have the highest values and they are less than the limit of the Palestinian guidelines for recharge by infiltration, moreover, if chemical transformation occurred then NO_3 will increase to reach the above limit as NH_4 decease, hence, the presence of both are unpleasant at the environment.

If we compare between the up and down streams the self purification process such as adsorption still function naturally and it is remediate most of nutrient and organics parameters and it is work to decrease the ammonia, nitrate at the springs at downstream (Figure 2.13).

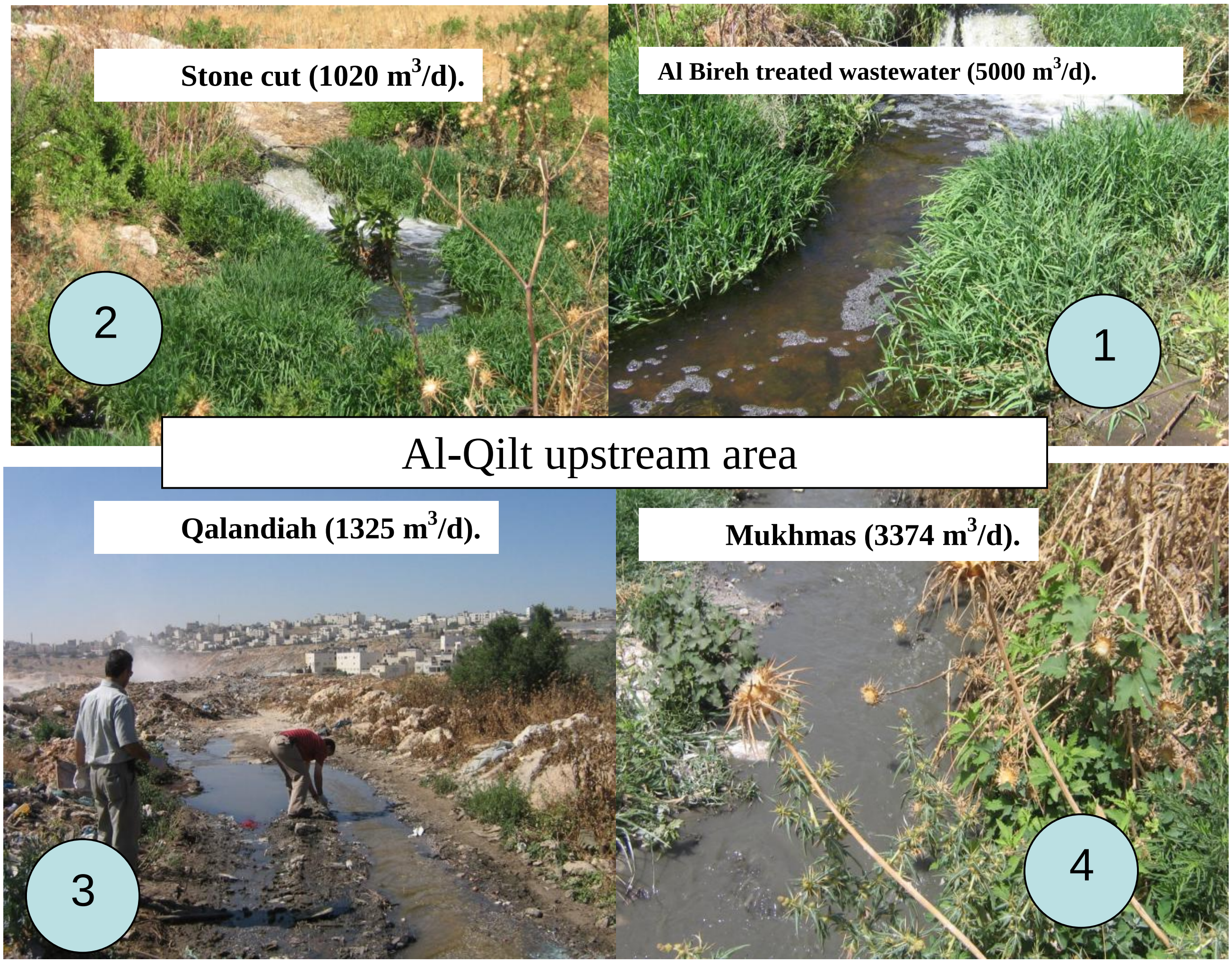


Figure 2.13: Wastewater discharged and quantities at sampling locations at Al-Qilt catchment

2.6.9 Organic carbon

Organic carbon are good indicators in aquatic environment, for example the TOC or DOC are used to identify biogeochemical form for soluble organic that can be transport within the water phase.

These parametres have possibility to reach the water table; moreover, they act as transporter for trace metals (Lions, 2004). The PS and WHO limits for artificial recharge by infiltration for TOC is 10 mg/l (Figure 2.14) in blue line, results indicate that all sites at Al-Qilt mainly at the upstream are above the limits. Moreover, NO_3 is 15 mg/l with red line (Figure 2.14) and there is no limit for DOC and can be related to TOC. Results indicate that organics decrease by retardation from soil layer, but this need suitable condition for bioremediation and it is not preferable if they reach the groundwater, this make the area more sensitive and its vulnerability will be high mainly for karstic system around the head of springs.

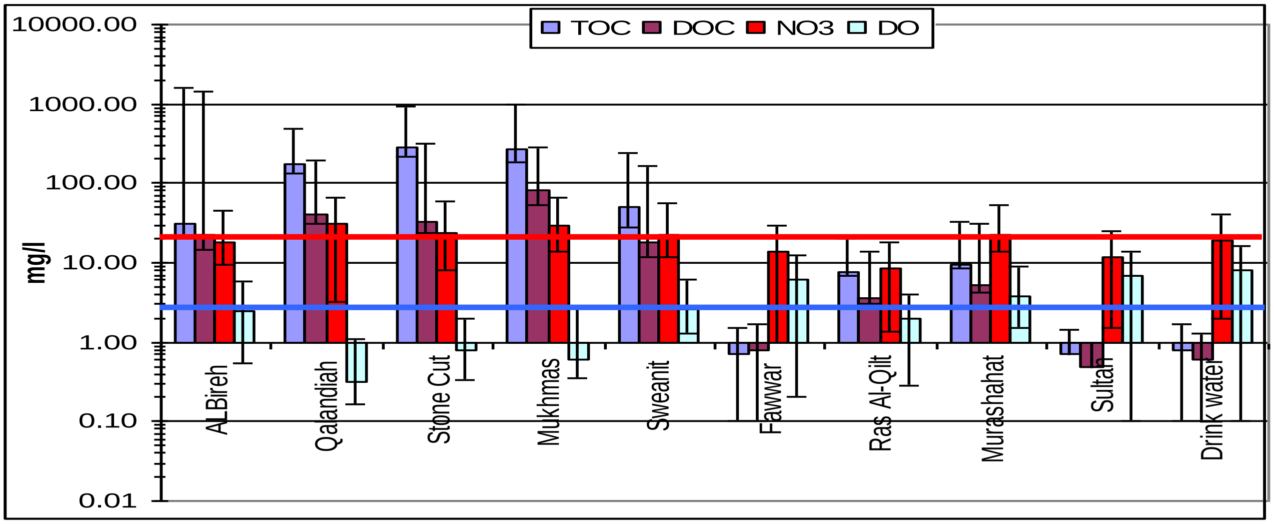


Figure 2.14: Organic measurement in term of TOC, DOC, NO_3 and DO**.**

Results indicate that the high values for TOC at Qalandiah, Stone Cut and Mukhmas are due to raw wastewater that discharged (Figure 2.14), furthermore, if results compared to PS and WHO limits it is reveal that TOC and nitrate are high at the upstream mainly at Qalandiah, Stone Cut and Mukhmas, on the otherhand, results for organic are low at the springs and Murashahat that used for domestic purposes, this due to consequence self cleaning or purification process between Sweanit and Fawwar and then between Fawwar and Ras Al-Qilt.

2.7 Statistical analyses

The physicochemical, nutrient and organics carbon parameters such as: discharge, pH, temperature, DO, turbidity, TDS, Ca, Mg, K, Na, Cl, SO_4, NO_3, NH_3, TKN, PO_4, TP, DP, TOC and DOC are statistically analyzed by using the descriptive analysis such as SPSS (Table 2.5). Results reveal that Na and TOC values are higher than the Palestinian guidelines that used for discharge by infiltration to the environment, thus the aquatic system will be in risk and there will be enrich or load with these pollutants. This load will decrease the buffering capacity of the filtrating zone, furthermore, it must take in considerations that Al-Qilt catchment is karstic area and the possibility for shock load is high and critical.

Table 2.5: Descriptive statistics for physical and chemical parameters in term of median, min and max values for wastewater samples at Al-Qilt catchment, units are in mg/l.

	N	Minimum	Maximum	Median	PS guideline for artificial recharge
Discharge	9	919	17458.33	7344.48	
pH	10	7.9	8.7	8.2	6—9
Temp	10	19	29	26	
DO	10	0.32	8.1	3	
Turbidity	10	2.2	767	141	
TDS	10	298	1428	800	1500
Ca	10	30	88	64	400
Mg	10	16	38	26	150
K	10	3	36	13	
Na	10	18	293	113	230
Cl	10	28	503	189	600
SO4	10	13	119	58	1000
NO3	10	8.5	31	20	60
NH3	10	0.2	35	11	
TKN	10	2.2	38	16	
PO4	10	0.20	25	8.9	60
TP	10	0.04	18	5.8	
DP	10	0.05	13	3.7	
TOC	10	0.7	281	83	10
DOC	10	0.5	80	20	
Valid N (listwise)	9				

The Inter-element Spearman Nonparametric Matrix for physicochemical, nutrients and organics carbon are correlate. Results reveal that there are high positive correlation >0.9 at $P<0.01$ and $P<0.05$ that observed between parameters in red color, high correlation >0.70 at $P<0.01$ and $P<0.05$ noticed between parameters in blue color. Moreover, moderate >0.5 at $P<0.01$ and $P<0.05$

also noticed between parameters in yellow color, and < 0.5 in green color that assign with no correlation these between parameters (Table 2.6).

Correlations between Cl/Na, Cl/TDS, TKN/Turbidity, TKN/NH_3, PO_4/TKN, TP/PO_4 (Table 2.6) indicates that these parameters caused by conmen sources from the wastewater samples. For example ammonium is correlates with all nutrients and organics parameters, this due to aerobic and anaerobic mineralization for organic matter by denitrification process. Moreover, the negative correlation of DO with nutrient indicates the nitrification consumes by oxygen and it is less than produced by mineralization from each type of nutrient and this consistence with (Song and Mueller, 1999).

The positive correlations between different elements give the following indication according to Mwamburi (2003) studies.

1. Possible common pollution sources in the aquatic system.
2. Indication for possible mechanisms that influence by the parameters in associations and behaviors.
3. Exact bonding and retention mechanisms are explained by the information on the geochemical phases for trace metals in sediment.
4. Correlations indicate similarties in the processes of sedimentation.

Table 2.6: Physical and chemical parameters correlation using Spearman Non-Parametric analysis, the colors, if the correlations > 0.9 Red, >0.7 blue, > 0.5 yellow, < 0.5 green according to LAWA classifications.

	pH	Tempreture	DO	Turbidity	TDS	Ca	Mg	K	Na	Cl	SO4	NO3	NH3	TKN	PO4	TP	DP	TOC	DOC
pH	1																		
Tempreture	0.31	1																	
DO	-0.33	0.14	1																
Turbidity	0.2	0.13	-0.77**	1															
TDS	0.26	-0.1	-0.52	0.70*	1														
Ca	-0.3	0.19	0.49	-0.24	-0.35	1													
Mg	-0.25	-0.04	0.61	-0.29	0.04	0.70*	1												
K	-0.03	0.21	-0.49	0.82**	0.72*	-0.01	0.16	1											
Na	-0.06	-0.07	-0.47	0.72*	0.81**	0.09	0.27	0.88**	1										
Cl	0.03	-0.13	-0.64*	0.86**	0.92**	-0.21	-0.01	0.86**	0.90**	1									
SO4	-0.13	0.01	-0.46	0.68*	0.61	-0.29	0.01	0.84**	0.73*	0.70*	1								
NO3	0.04	-0.09	-0.6	0.78**	0.81**	-0.55	-0.35	0.62	0.58	0.86**	0.55	1							
NH3	0.07	0.15	-0.72*	0.84**	0.75*	0.29	-0.35	0.75*	0.75*	0.87**	0.57	0.83**	1						
TKN	0.3	0.35	-0.72*	0.91**	0.72*	-0.24	-0.33	0.77**	0.72*	0.81**	0.6	0.73*	0.94**	1					
PO4	0.27	0.35	-0.70*	0.86**	0.75*	-0.33	-0.29	0.83**	0.70*	0.78**	0.75*	0.70*	0.86**	0.93**	1				
TP	0.21	0.31	-0.70*	0.83**	0.73*	-0.3	-0.19	0.89**	0.73*	0.82**	0.71*	0.72*	0.87**	0.88**	0.92**	1			
DP	0.14	0.4	-0.52	0.80**	0.68*	-0.03	0.06	0.95**	0.83**	0.77**	0.81**	0.54	0.77**	0.85**	0.90**	0.91**	1		
TOC	0.3	-0.03	-0.83**	0.85**	0.82**	-0.46	-0.25	0.80**	0.71*	0.88**	0.67*	0.80**	0.80**	0.79**	0.83**	0.91**	0.76*	1	
DOC	0.12	-0.08	-0.90**	0.88**	0.70*	-0.48	-0.44	0.75*	0.65*	0.83**	0.71*	0.79**	0.84**	0.81**	0.86**	0.86**	0.71*	0.93**	1

* Correlation is significant at the 0.05 level (2-tailed).

** Correlation is significant at the 0.01 level (2-tailed)

Furthermore, Principal Component Analysis (PCA) is applied to discover and interpret the relationships between variables. The results show different trend by displaying the loading factors with a varimax rotation as well as the eigenvalues, percentile of variance and cumulative percentage. In reference to the eigenvalues there are four factors extracted and have eigenvalues are summaried in (Table 2.7).

Table 2.7: Principal Component Analysis in four components for majors and organic carbon parameters.

	Component				**Initial Eigenvalue**		
	Factor 1	**Factor 2**	**Factor 3**	**Factor 4**	**Total**	**% of Variance**	**Cumulative %**
Discharge	-0.86	-0.07	0.25	-0.24	12.0	60	60
pH	0.30	0.34	0.78	0.03	3.3	17	76
Tempreture	-0.13	0.41	0.05	0.89	1.8	9.2	86
DO	-0.78	0.32	0.06	0.37	1.2	6.1	92
Turbidity	0.75	0.18	0.55	-0.19	0.72	3.6	95
TDS	0.94	0.14	0.07	-0.01	0.43		
Ca	-0.41	0.81	0.18	-0.12	0.32		
Mg	-0.17	0.89	-0.3	-0.2	0.19		
K	0.75	0.63	-0.24	-0.05	0		
Na	0.87	0.42	-0.07	-0.18	0		
Cl	0.97	0.22	0.03	-0.07	0		
SO$_4$	0.78	0.06	-0.59	-0.1	0		
NO$_3$	0.79	-0.45	-0.12	0.14	0		
NH$_3$	0.89	-0.18	0.3	0	0		
TKN	0.90	-0.17	0.29	0.05	0		
PO$_4$	0.91	-0.14	-0.14	0.26	0		
TP	0.95	0.23	-0.08	0.07	0		
DP	0.84	0.45	-0.09	0.1	0		
TOC	0.90	-0.2	0.25	0.04	0		
DOC	0.76	-0.48	-0.16	0.03	0		

From the PCA analysis at Al-Qilt it is classify to four factors, "factor one" characterized with high level, this give the paramteres the priorities to be consider in pollution mainly for: discharge, DO, turbidity, TDS, K, Na, Cl, SO_4, NO_3, NH_3, TKN, PO_4, TP, DP, TOC and DOC, these factors must taken in priorities as pollutants or must considered as cofactors that might be facilitate the transports of other parametrs such as trace metals. Discharge and dissolve oxygen have negative sign, this indicates that these parameters not considered as pollutants but working in the reveres process, for example, discharge could be considered interm of loading values and for DO you should consider the relations with other parameter such as TOC, NO_3 and DOC or oxidation reduction process. "factor two" characterized by Ca and Mg load, these indicate the geo formations and geological form for the surrounding environment, "factor three" characterized by pH that indicates the acidity effect, pH stand at the same distance from all parameters, "factor four" characterized by temperature, this indicates that it has the same distance from variations with all parameters.

The Cluster Analysis (CA) is performed using average linkage between groups rescaled distance as cluster (Figure 2.15). Although not substantially different from PCA and is used as a substitute method to confirm the results of PCA. The CA results if exclud the discharge can be illustrate in the dendrograms, this identify three clusters. Cluster one contains TP, DP, PO_4, pH, DO, K, NH_3, TKN, NO_3, Temperature, Mg, DOC, Ca, SO_4, Na, TOC, and Cl with the same distance, these parametrs make the second cluster with turbidity, then all did the third cluster with TDS. The physical parameters start from pH = 1, Temperature = 2, DO = 3, Turbidity = 4 and TDS = 5 are in the sequence distance despite they are found in three different group, then all inorganic stand at the same distance from each other, then the organics TOC and DOC are at 18 and 19 respectively.

Results from Dendogram for TP, DP, PO_4, pH, DO, K, NH_3, TKN, NO_3, Temperature, Mg, DOC, Ca, SO_4, Na, TOC, and Cl are with the same distance, then all associate with another cluster with Turbidity. These associations are consistence with PCA results and loading factors, furthermore, results show associate between organic such as DOC and TOC then nutrient such as phosphorus and nitrogen and other physical parameters such as pH, Temperature and DO.

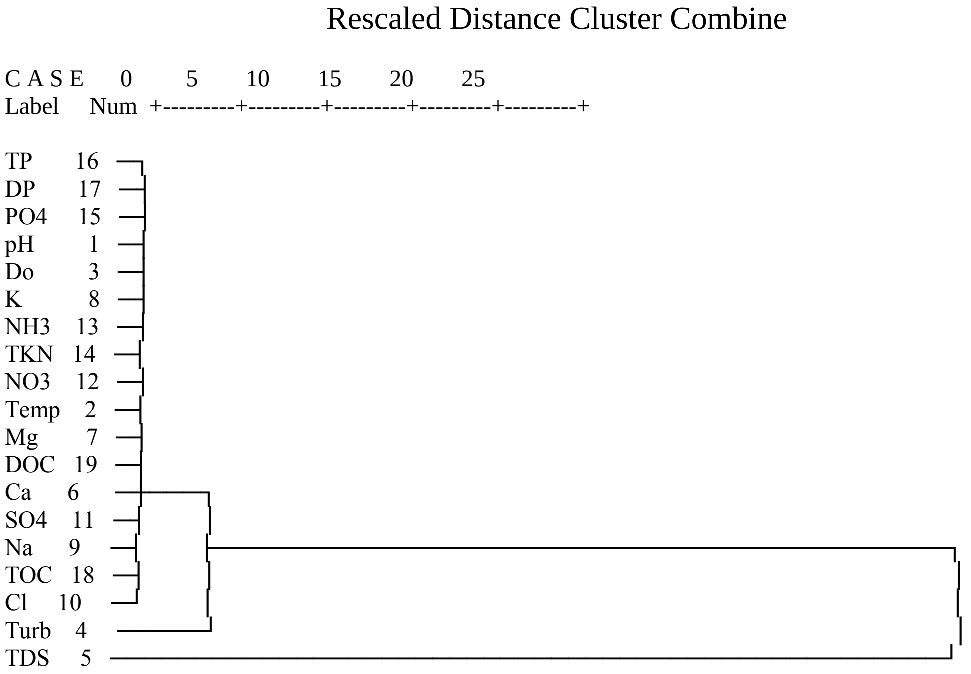


Figure 2.15: Dendrogram Hierarchical Cluster Analysis for average linkage between groups.

Results indicate that factor one in PCA include DO, Turbidity, TDS, K, Na, Cl, SO_4, NO_3, NH_3, TKN, PO_4, TP, DP, TOC and DOC, this consistence to results in cluster one. The TP, DP, PO_4, pH, DO, K, NH_3, TKN, NO_3, Temperature, Mg, DOC, Ca, SO_4, Na, TOC are at the same distance as group (Figure 2.15), this study clarify that the contribution and occurrence of these parameters are due to wastewater that discharge as source, this make the TDS with high concentrations and other parametrs easily ionized due to variation in caution and anion speceis. This explain the incremental load from these ions and other parameters that grouped together, this will have impact due to other physical parameters such as turbidity, furthermore, factor two consists from DO, Ca, Mg,

NO_3, NH_3, TKN, TOC and DOC, this associate with the first cluster in the Dendogram linkage.

Based to PCA (factors one and two) and CA (Cluster 2), there are similarity in correlation for both PCA and CA results, since TDS are repeate in both factors. The CA results show the relationship and associations between pH, Turbidity, Cl, TOC, DOC, Mg, Ca, SO4, Na and TDS at the distance (1, 4, 10, 18, 19, 7, 6, 11, 9 and 5) respectively, and according to Hsue and Chen (2000) the dissolved salts such as Na^+, Mg^{2+} Ca^{2+} and K^+ played an important role in buffering the pH if it change, since all are in carbonate media, this will influx of wastewater and urban runoff in major inputs for the selected cautions then it adsorb by the sediment. Moreover, Rubio *et al* (2000) explained that the association between Mg^{2+} Ca^{2+} and sand is strongly controlled by carbonates and plays an important role as dilatants material for the samples, since; carbonates are as dominant source of both parameters and it is abundant component in the surface area. Furthermore, the association of K^+ is explained as a function of ionic strength. K^+ is a monovalent caution with low replacing power compared with divalent cautions such as Ca^{2+} and Mg^{2+} (Hussien and Rabenhurst, 2001).

2.8 Conclusions

Grain size analysis for sediment samples are predominantly in the mud fraction, this will give significant for aggregate transportation of anthropogenic pollutant within the catchment; on the otherhand, the grain size analysis for soil samples are predominantly in gravel and sand fractions.

Buffering zone capacity between Sweanit and the springs (Fawwar and Ras Al-Qilt) work well to remove the organic carbon, nutrients and major ions by self purification process, in which the soil and rock work as filter, this buffering capacity has certain limit and this is highly restricted at Al-Qilt, since it is karst system.

Organic parameters are high in term of TOC and DOC, this is due to untreated wastewater that discharged at most of the sites, these organic parameters will decrease while it is run in environment and it is biodegradable, thus it is recommend to extend the study for inorganic parameters such as "trace metal", since they are not biodegradable in the environment and persistence to chemical transform.

The head of springs are not granites from anthropogenic pollutants, thus more than one step must be done to decrease the wastewater that discharge to Al-Qilt catchment, it is recommend to apply a strong precautionary principle regarding the organics and nutrients emission, these must based on best available techniques for wastewater treatment (point sources) and best available human practices to reduce the nutrients (diffuse sources). Furthermore, application of policy management must meet with the protection of both ground and surface water quality in the catchment area of Al-Qilt.

The impact of anoxic conditions stands behind preferable condition to release the trace metals; this will increase the possibility for trace metals to reallocate by surface water. Such these condition are at Qalandiah, Stone Cut and Mukhmas, there the urban activities, urban run off and arbitrary dump sites are available, these sites characterize with high concentrations for ammonium, phosphates and low DO, this is good media for ionization for the trace metals, this indicates that organic and nutrients loads are available at the upstream sites along Al-Qilt catchment and anoxic condition are predominates.

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Chapter 3

The occurrences of trace metal in wastewater, sediments and soil at Al-Qilt Catchment

3.1 Abstract

Wastewater, sediments and soil samples were collected four times every six months from nine sampling sites at Al-Qilt catchment. Sampling started on June, Julay, Augast of 2007 then each six month start from June, 2008, and end on October, 2009. Samples were analyzed for trace metals and compared with local and international guidelines to evaluate the pollution occurrence due to trace and heavy metals. Total concentrations of Ti, Sr, Mn, Cu, Zn, V, Cr, Ni, Ba, Ag, Sn, Sb, Cd, Pb, B and Co are determined by ICP-MS and for Hg by using FIMS, other instruments were used to analyze the TN, S, OC, TS and TC.

For wastewater results the trace metals are high at the points of the wastewater that discharged mainly at Al Bireh, Qalandiah, Stone Cut, then it is high at the sites for the urban run off and roadside that is deposited at Mukhmas, Sweanit and Stone Cut in which Cr, Pb, Cu, Co, Zn and Sb are predominates at the upstream of Al-Qilt. On the otherhand, result for Mn is higher than allowed if the water will use for recharge by infiltration at downstream. Farthermore, the correlations factors of trace and heavy metals indicate that the common sources of pollution are wastewater and then urban run off.

For sediment there are high concentrations for Cu, Zn, Ag, Hg and Mn in most of the site if compared to high polluted rang from Sediment Quality Guideline and USEPA guidelines. Trace and heavy metals are correlate with TN, TS, OC and TC and only metal-metal correlation is between Cd/Cr, other correlations confirm with the results in which the trace metals, TN, TC, TS and organics parameters are in one group, this give priorities to consider these relation for trace metals to transport and reallocate. Furthermore, results indicate that there are variations between the Continental Crust and Elemental Background for Soils values, these variations will affect the results if the Elemental Background for Soil is used for other calculations.

For soil there are high concentrations of trace and heavy metals for As, Co and Cr at the sites of wastewater discharge, then at urban run off sites. For example, Pb and Ni are high at Stone Cut, As is high at Mukhmas, Sn is high at Sweanit, Cd is high at Ras Al-Qilt and B is high at Murashahat.

Results indicate that there are variations in concentrations for trace metals at all sites, and there are high concentrations for Sn and Cd from the area that considered as pristine area; these areas are far away from the practices of human activities and only Israeli colonies are available. For correlations factors between trace metals at the soils, it is highly positive correlation between Pb/As and most of other correlations are between trace metals, TN, TS, OC and TC, this consensus with PCA group and CA clusters.

Although there are incremental for trace metals in sediment and soil samples, on the otherhand, there trace metal not detecte in water samples such as Ag and Hg, since both considered as anthropogenic pollutants and both are enrich in sediment only, important to mention that As and Mo are accumulate at Murashahat, this supply from Ras Al-Qilt spring and the water transport from Ras Al-Qilt spring to Murashahat treatment plant by open canal, this allow the soil to enter and transport or settle at the Murashahat site.

Results reveal that the capacity of the buffering zone between Sweanit and head of Fawwar then to Ras Al-Qilt are work well to remove the organic carbons and nutrient by self purification, but doing no thing with trace metal. These trace metals may have deleterious effect in the aquatic ecosystem and health of the rural dwellers whom use the spring for domestic purposes. This indicates that these springs are not granite and more management steps must applied to decrease the wastewater that discharge to Al-Qilt catchment.

3.2 Introduction

The problem of environmental pollution is attracting the attention of researchers around the world. The increased of urbanization and industrialization, intensified the demand on municipal water and the discharge of wastewater and industrial effluents.The disposal of industrial effluents and municipal wastewater is major problem that contaminate the surface water (Eletta, 2005).

Heavy and trace metals are pollutants that occur naturally in the earth crust at concentrations below 1000 mg/kg. They considered as toxic to flora, fauna or humas, even when occurred at such low contents. Beyond the natural occurrence of such metals, the anthropogenic pollution can occur once and emittied as particulates from the industrial vapor from waste incineration processes and automobile exhaust or wastewater discharged (Merian *et al*., 2008). Trace metals became one of the serious pollutants in natural environment due to there toxicity, persistence, non-biodegradabile and bioaccumulation, these can concentrate in the food chain. The occurrence and reallocation of heavy metals in the environment are considered with interest in the last decade due to there impact and accumulation (Wong, 2000 and Eja *et al*., 2003)

The aquatic ecosystems are vulnerable to water pollution over the environmental and human health impacts, since the aquatic ecosystem are often polluted with anomalously high level of toxicants (organic and inorganic substance), then they find their way to the aquatic system (Yang and Rose, 2005).

There are no clear demarcation between essentiality and occurrence of trace metals, few elements are considered as essential such as Fe, Zn, Cu, Mn and Co, and some are known to display toxic properties such as Cr, Cd, Pb and Hg (Clements, 1991). Thus, some of the trace metals are considered as essential elements to some organisms if they have the minimum requirements to supply their needs but if they maximum reach above the toxicity limits that occur, however, the minimum requirements is necessary because trace metals play essential role in the metabolic system of the organism and the range between the minimum and maximum is often called the window of essentiality (Hopkin, 1993). Moreover, there are trace elements in soil are used as result of human activities, since, there are 14 elements such as: Si, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo, I and F recognized as essential trace elements and others such as Bi, Sc, Se, Sc, Ba, Hg, Sb and Ti are present in small amounts, also Sn, Cu, As, Cr, Zn, Cd and Bi show wide range with risk of pollution from the last two groups (Bowen, 1979 and Mertz, 1981).

At West Bank, there are lack of knowledge about trace metal and their behavior, deposition and reallocation in the environment. So, monitoring program was organized by CH_2MHill for physical and chemical parameters mainly originated from waste emissions, Samples were collected from wadis, springs and wells and focused on the trace metal to understand the potential of pollutions. Results for heavy and trace metals indicate that Antimony, Lead, Selenium, Thallium, Iron, Beryllium, Mercury, Cadmium and Arsenic were reached the water table those as results from discharge of raw wastewater (CH_2MHill, 1999).

Water has been commonly used to monitor the quality, this need intensive sampling program, devices, analysis and more labors then the cost are higher (Horowitz *et al*., 1990). However, it has been recognized that short-term or past-pollution events is not reflected in water analyses, and the long-term infringement of water quality through release of sediment-bound metals are more significance (Chen *et al*., 1996), furthermore, heavy metal species in aquatic environment are distributed among water-soluble species, colloids, suspended matter and sedimentary phases, this mean that there trace metals distributed between water and sediment, this is strongly changed due to deposition or remobilization processes. Furthermore, trace metals distribution occurs between sediment and soil, this have special attention due to possible entries of pollutant into food chain (DelValla *et al*., 1998).

Thus, sediments have more storage capacity for pollutants and intermediate with any part of the hydrological cycle, since less than 1% of trace metals are actually dissolve in water and more than 99% are stored in sediments (Salomons and Stigliani, 1995). Moreover, sediment acts as sinks for trace elements and considered as sources for contaminants in aquatic systems Mucha *et al*., (2003), also, sediments act as integrators and amplifiers of the concentrations of trace metals from the water that pass over and transport with movement, this play an important role in the shallow water aquatic system, also, sediments have been widely used to identify the sources of contamination and to diagnose the environmental quality of aquatic systems (Luoma, 1989). Therefore, sediments have been employed to monitor the pollution of aquatic environments mainly for trace metals generally existing in low concentration and have propensity to associate preferentially with sediments (German Ministry of Environment, 1993).

As a result, heavy metals trapped and accumulated in sediments, these trace metals if not remediated still accumulate and will release and impact the water column (Wright and Mason, 1999).

Trace metals content in soil are derived from two main sources: natural weathering called geogenic from the base rock and soil formation, then the pedogenesis or anthropogenic through point source or diffuse pollution due to waste disposal in liquid or solid forms (Merian *et al*., 2004 and Boruvka *et al*., 2005). However, soil is composed of mineral constituents, organic matter (humus), water and air, these components as result from human activities, such as vehicle exhaust, lubricating oil residues, tires, weathered street surface particles, and brake lining wear particles and natural biogenic materials such as tree leaves and other plant matters that can be pulverized by passing traffic or direct contributor of dust or urban runoff (Omar *et al.*, 2007). Moreover, there will be incidental point sources of trace elements to soil, this include the corrosion of metal fragments, and dispersion of metallic ores during road transport, airborne dust, dispersion of combustion residue and any leach from spoil of waste materials.

The type and concentration of trace metals associated to emissions are introduced into soil that extremely variable and depend on specific conditions (Adriano, 1986). Furthermore, Purees (1977) reported some remarks that addressing some issues: (i) greatly elevated levels of Pb in soils along the routes used for trucks transport of lead ores in Missouri. (ii) High levels of Pb, Zn, Ag and Cd in soils nearby sites of mines and smelters ores. (iii) Greatly enhanced levels of As and Cu in soils that contaminated by drainage water and stream sediments from mining and smelting in South West England. (iv) level of available Cu, Pb, Zn and Cd contents in soils downstream from mines in Wales.

Heavy metals reaching the soil remain in the pedosphere for many years even after removing of pollution sources and increase the amounts of heavy metals in soils of urban areas this reported by many authors (Pichtel *et al*., 1997). However, the severity of pollution depends not only on the total of heavy metal in the soil, but to the proportion of their mobile and bioavailability forms, these are generally controlled by the texture and other physicochemical properties of the soils (Selim and Sparks 2001), there are many anthropogenic sources of trace elements that enter the soil amendments from liming materials, agrochemicals, refuse incineration, including the burning of municipal refuses and sewage sludge, wood combustion and automobile exhausts, atmospheric depositions from urban runoff and industrial activity, such these trace elements may travel long distance from the source through winds before deposited into the land and waters, the physical form and properties of the element changes in physical and chemical characteristics during transport, adsorption and solution processes occurring in the atmosphere and meteorological conditions (Nriagu and Pacyna, 1988).

On the otherhand, soil normally work as filters when the water moves downward, the filtration process leaves the water relatively free from contaminants by the time until it reach the groundwater. Soils have the properties that influence the trace metals movement through soil to the groundwater. These properties combined and rank the ability of each soil type to filter out the trace metals as well as to rank the tendency of each trace metals leach through the soil. Furthermore, trace metals enter the soil by number of pathways, then it is important to controlle their behavior and fate according to their source and species (Adriano, 1986).

Researches concerned with trace metals in soils that focused on the level of investigation and source of identification to the migration and transformation of metals among different environmental media (Meza-Figueroa *et al*., 2007). However, there were several approaches to detect the anthropogenic pollutants; these were based on the assumption that, if anthropogenic pollutants for any particular area had originated from the same source, then the pair wise relationships between the concentrations of these pollutants in sediments from various stations in the contaminated area would be linear. Nevertheless, this linear assumption could not always be real, because more than one source could occur in any area. For this reason, another method is prosed here, the statistical technique as multivariate analysis tool such as the Principal Component Analysis (PCA), and this does not need the above linear assumption. This PCA analysis establishes and quantifies the correlations among the original variables in data set, since the goal is to reduce the number of variables to smaller set of components that can allow an easier interpretation (Einax, 1997).

For wastewater, sediment and soil, the prevention of pollution involves the control of industrial production processes through legislation and monitoring. Thus, The United States Environmental Protection Agency (USEPA, 1991, 1994, 2003), considers 13 metals as top priority as anthropogenic pollutants such as Ag, As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se, Tl and Zn. Furthermore, the WHO (1984, 1996 and 2004) guidelines limit for trace metals in drinking water were highly restricted for most of these trace metals to control the surface and groundwater (Table 3.1).

Table 3.1: Guidelines for Maximum Permissible limits for heavy and trace metals use for drinking purposes according to USEPA and WHO from different publications.

Element	Surface water USEPA µg/l	Groundwater WHO µg/l	Remark
Antimony	6	5	
Arsenic	50	10	
Barium	2000	700	
Cadmium	5	3	
Chromium	100	50	For total chromium
Copper	1300	2000	
Cobalt		50	Desrable 0.1 WHO,1984
Lead	10	10	
Manganese	100	50	
Mercury	2	1	For total mercury (inorganic plus organic)
Molybdenum		70	
Zinc	2	5	
Nickel	20	20	

Current international and governmental activities in terms of legislation, promotion of scientific research and waste management aimed to make the environment more safe that can be obtained from United Nations Environmental Program (UNEP) (www.unep.org), United States Environmental Protection Agency (USEPA) (www.epa.gov.org), European Commission (EC) (www.europa.eu.int) and German Environmental Protection Office, (Umweltbundesamt ,UBA) (www.uba.de) websites.

Moreover, the guidelines from the Palestinian Standardization Institute (PSI) focus on reuse of wastewater that discharged to the sea at 500m and as artificial recharge to the groundwater by infiltration (Table 3.2).

Table 3.2: Palestinian guidelines for the reuse of treated wastewater concerning the physicochemical and trace metals, unit are in mg/l.

Characteristic	**Discharge into the sea- 500m far**	**Artificial recharge to groundwater**
Fe	2	2
Mn	0.2	0.2
Ni	0.2	0.2
Pb	0.1	0.1
Se	0.02	0.02
Cd	0.01	0.01
Zn	5	5
Cr	0.05	0.05
Hg	0.001	0.001
Al	5	1
Cu	0.2	0.2
Co	1	0.05
B	2	1
Li	-	1*
V	-	0.1*

(-) not specified and the (*) Jordanian guideline for reclaimed wastewater that use for artificial recharge, and for that discharge to sea 500m, no "JS893/1995".

3.3 Objectives

The objectives of this chapter are:

1. To determine the occurrences of heavy and trace metals concentrations such as Ti, Sr, Mn, Cu, Zn, V, Cr, Ni, Ba, Ag, Cd, Pb, Hg, B, Li, As, Rb, Mo, Sn, and Co and

to correlate these trace metals with major ions, nitrogen, sulfur, organic carbon and inorganic in wastewater, sediment and soil samples to help in interpretation of the mobility and transportations.

2. To determine the statistical analysis and controlle factors such as Principal Components Analysis, Factor Analysis and other factors in relation.

These objectives are based on two hypotheses: (1) dominant produces of trace metals as anthropogenic contaminants will have impacts on water table, (2) domestic, industrial wastewater and urban runoff increase and enriched by trace and heavy metals.

3.4 Material and Methods

Surface sediment and soil samples were from 5cm depth of each site, samples were taken from nine stations during June and Octber on 2008 then June and October on 2009 (Figure 3.1). The sediment and soil samples kept in icebox at 4^0C during transportation to the laboratory, then the sediment samples were treated by using deep freezer $–25^0$C for six hours to stop the bacterial activities, then sediment samples have been dried, frozen and evaporated for three days till they dried completely. Furthermore, the dried sediment and soil samples were mixed and homogenized using pestle mortared and sieved through 2mm, 630µm, 200µm, 63µm mesh screen and stored in polyethylene bags. For the determination of heavy and trace metals, then 0.25g from <63µm fraction was weighted from each sample and digested by 12ml Aqua-Regia with ratio 1:3 $HCl:HNO_3$ in Teflon bomb for 2h at 120^oC using Microwave (MARS 5) digester. Then, after cooling, the digested samples were filtered and kept in plastic bottles for analysis using the Inductive Coupled Plasma Mass Spectra ICP-MS (Agilent 7500 ICP-MS). For Hg Flow Injection Mercury System (FIMS 400) was used. Furthermore, for major parameters such as Na, K, Ca and Mg, Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) was used.

The Elementar Vario El CUBE elemental analyzer was used for the C, N, and S analyses. This model is equipped with an auto sampler, a combustion oven containing an oxidation catalyst and copper, Porapak GC column and thermal conductivity detector (TCD). Two different analyses methods were conducted with every sample, with or without a pre-treatment digestion with HCl 2N, these allowe us to determine the percentage of Total

Carbon (TC) (include the $CaCO_3$) and Organic Carbon (OC) and from the difference of TOC and OC the Inorganic Carbon (IC) was calculated.

Sampling jars and the laboratory apparatus were acid soaked in diluted nitric acid before the analysis of trace metals to ensure that any traces of cleaning reagent were removed then they were dried and stored in clean place. All laboratory works and analysis were done in UFZ Central Laboratory at Magdeburg, Germany.

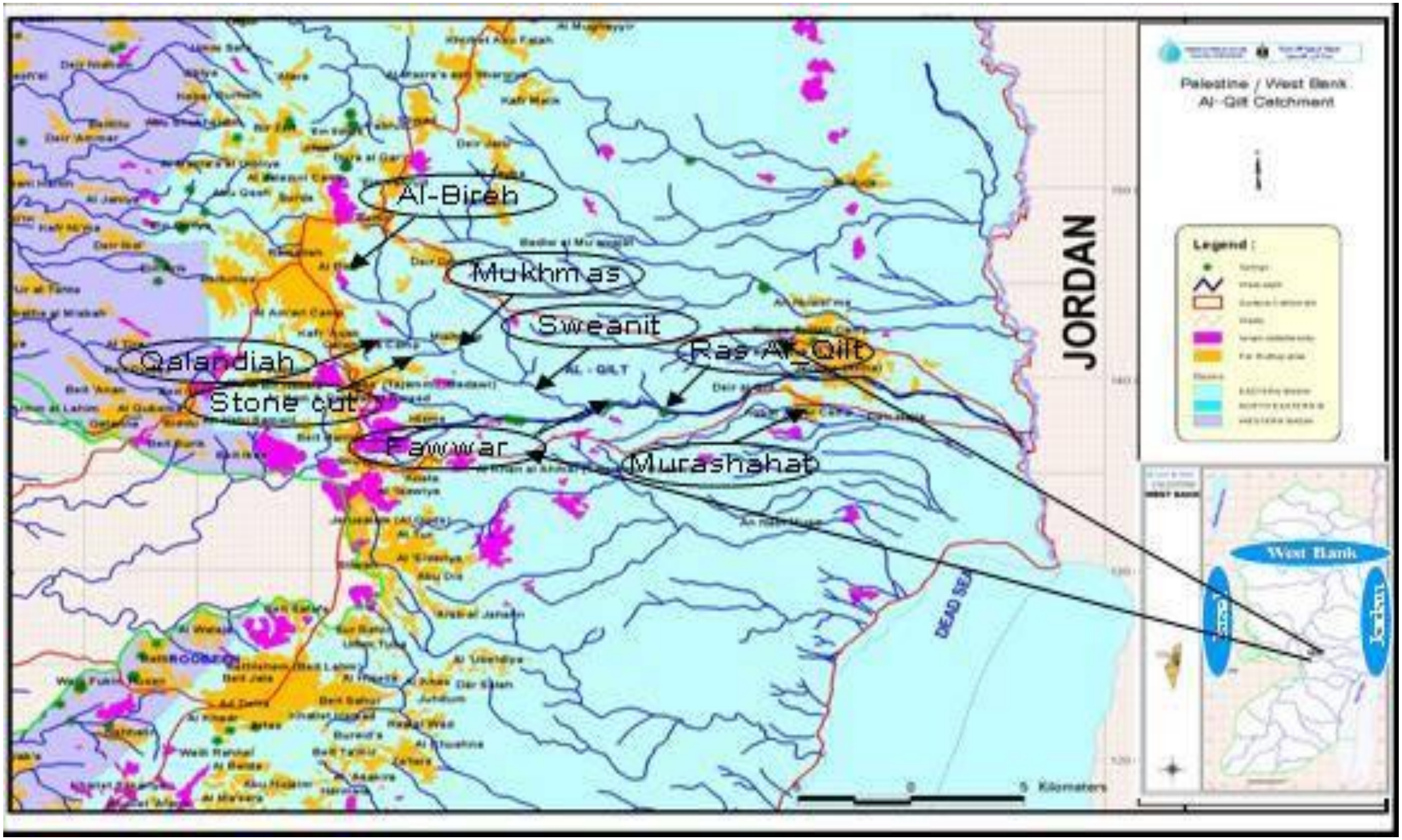


Figure 3.1: Study area of Al-Qilt catchment and sampling sites, Jordan Valley, West Bank, Palestine (PWA, 2009).

3.5 Quality control precautions

For quality control we use the intra-run quality assurance standard (1µg/l, multi-element standard solution), this is checked for deviation and accuracy of every 10 samples, moreover, blank samples were processed as regular sample and used to modify the background that originate from the sample matrixes. Furthermore, duplicate samples are collected from sampling sites that used to check the accuracy and precision, this is verified by using the certified standard for sediment and soil with name Buffalo (8047), also, for water we use the certified standard reference matrix No (1643e), beside these standareds other precautions for sampling and analysis are used as follow:

1. The analyte must prepared in the form of appropriate detection i.e. liquid form, this usually need dissolution and isolation steps, these steps usually affected by particle size, this reduced by grinding, sieving and mixing.
2. Matrix interference must remove by suitable treatment, hence, there are no selective methods for analysis, and this is known to alter the distribution of chemical species in sample matrix and expose this matrix with reagents using the suitable preservations.
3. Sample preparations are used to improve the selectivity, detect ability, reliability, accuracy and repeatability for analysis. Commonly they use the techniques in analysis of trace metals for environmental samples in the form of pseudo aqua ragia digestion (Stoeppler, 1994).
4. Appropriate digestion method is crucial prerequisite to use the pseudo aqua ragia digestion; this involves oxidizing acid such as concentrated nitric acid and hydrochloric acid in suitable vessel with heating under pressure (DIN S7, 1984). This digestion method generally require great deal for the operator attention, skill and experience in order to gain accurate and precise results, then sequances of addition of digestion reagent that formed from nitric acid and hydraulic acid, then the tube is tightly seal and placed in microwave oven, during heating the pressure built up due to the evaporation of digestion acids and gas evolved during the decomposition. However, the excessive build-up of pressure especially during the digestion of samples with high organic contents may cause rupture of sample vessel and subsequent loss of analyte, this is to avoid the over-pressures pre-

digestion of the samples that containing high carbonates concentrations, the sample kept for overnight at room temperature to digest slowly for organic to avoid foaming (Niazi S. *et al*., 1993).

3.6 Statistical background

The sources of anthropogenic pollutants are difficult to identify in local ecosystem environment, this need a lot of intensive analysis for sediment, soil and wastewater, furthermore, this need approach to describe and correlate the anthropogenic pollutants to their sources in different geochemical processes and conditions. So multivariate analysis will use to assists the contamination at the source, then it was possible to identify the current superficial sources of contaminate due to domestic, industrial and urban activities in one group.

Therefore, the Principal Components Analysis (PCA) is used as an exploratory, multivariate, statistical technique, environmental datasets to examine data variability, hence, these datasets is difficult to interpret and the inter-relationships between variables are difficult to identify and visualize, the multivariate techniques can describe many factors and control the data variability to reduce the variations between parameters (Boruvka *et al*., 2005), also it is used to discriminate variations between contaminant sources (Mudge and Duce, 2005), in addition it is used to identify key variables for environmental monitoring purposes (Shin and Lam, 2001).

Detailed descriptions of PCA and its applications can be found many texts (Shaw, 2003). Moreover, PCA is data reduction technique, since, the first principal component or factor is the greatest variability and factor loadings correlate with coefficients between the original variables that frequently used to investigate the processes and control the data variability. Factor scores indicate how strongly individual samples are associate with each factors, thus it can be used to investigate the similarity between samples, hence, samples with similar composition will have similar score and therefore have similar contaminant sources (Webster, 2001). Moreover, multivariate analysis applied as unambiguouse ascribe pollution sources for each parameter.

The assessment of the interactions between components are done by the application of multivariate statistical method due to strongly scattering territorial and temporal events that not compatible with many unvaried techniques (Anazawa *et al.*, 2004).

Furthermore, Factorial Analysis (FA) serve as tool for the recognition of variable structure and differentiated to evaluate the pollution in water, sediment and soil (Einax *et al.*, 1997). FA is powerful tool for characterization of anthropogenic and geogenic loads.

In this chapter we will use these statistical factors for the trace metals and other parameters in relation; this can be achieved through the following correlations and relations between groups such as:

1. Principal Components Analysis (PCA) and Cluster Analysis (CA) are used together to check the results and provide grouping for each variable within the total analysis. PCA and CA are explanatory tools in multivariate statistical analysis to discover relationships between variables (Yongming, *et al.*, 2006; Karbassi and Shankar 2005; Jonathan, *et al.*, 2004; Karbassi and Amirnezhad, 2004). Furthermore, Yongming, *et al.*, (2006) explained that PCA is used to reduce data and to extract a small number of factors that depend on the correlation matrix, whereas CA is performed to classify elements of different sources that base to their similarities properties.
2. FA in relation to CA are often used together to check the result and to provide grouping for each variable (Facchinelli, *et al.*, 2001).
3. Hierarchical Cluster Analysis done by using Dendograms to identify relatively the homogeneous groups of variables to separate clusters or combines clusters until only one left at the end.
4. Spearman Non Parametric Correlations done by use the Statgraphics Plus Software Statistics SPSS program to verify the source and correlations between the trace metals and other parameters in relation. Then multivariate statistical approach is used to manipulate more variables in different forms.
5. Trace metals concentrations will compare with Sediment Quality Guidelines (SQG) of USEPA**,** Continental Crust values according to Turekian and Wedepohl

(1961) and the Elemental Background of Soil (EBS). The EBS analyese for this study from the pristine area of Al-Qilt catchment.

3.7 Results and discussions

3.7.1 Trace metals in wastewater

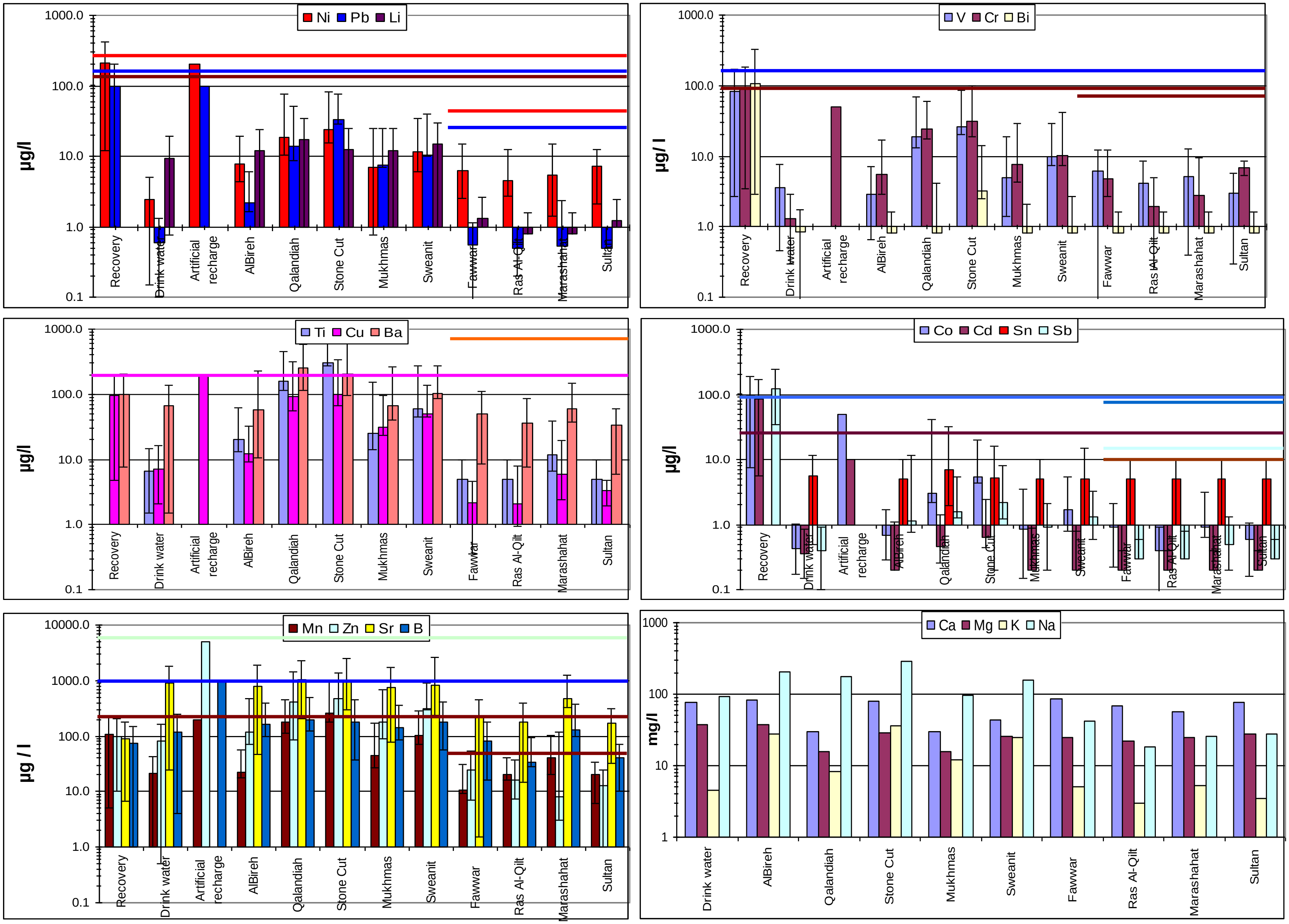
Results of the recovery values of the certified trace metals are ±10, this is acceptable for further interpretations. Results are compared with drinking water as base line and to the guidline for resue as artificial recharge by infiltration according to Palestinian guidelines, moreover, the Maximum Permissible Limit according to USEPA and WHO. Water and wastewater are analyese for major ions, nitrogen, sulfur, phosphorous, total organic carbon, dissolved organic carbon and trace metals. Results indicate that there are incremental of the trace metals at the sites of wastewater discharge such as "Al Bireh, Qalandiah and Stone Cut", furthermore, there are incremental of trace metals due to urban run off or roadside such as at Mukhmas, on the otherhand, there are decrease in the concentrations of trace metals at downstream from the springs due to natural retardation, this mean that pollutants still accumulate at the upstream locations (Figure 3.2).

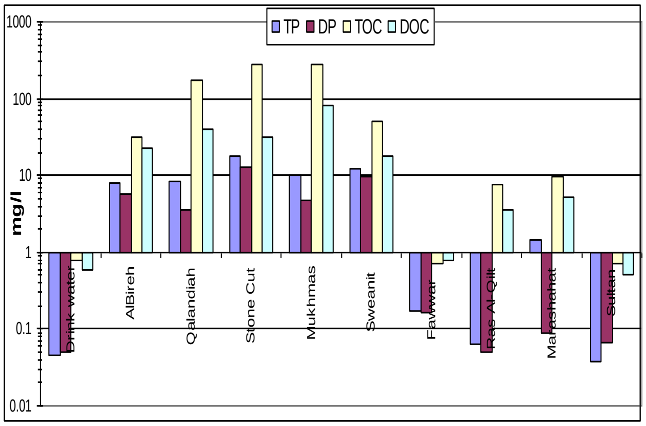
Results for Ag and Hg concentrations in water samples are less than detection limits for instruments. Result for other parameters if compare to Palestinian and Jordanian guidelines for Bi, Ti, Ba, Sn, Sb and Sr values are not considere as anthropogenic pollutance. Therefore, from the previous studies Pfeifer *et al.*, (2007) indicated that Ti and Sr were soluble elements, these parametres can be enrich from nature to the water phase till certain limits, also Ti will influence the sediments composition in relation to natural background or composition of soil, rock etc. moreover, for comparison purposes for Ba and Sb WHO guidelines are used for drinking purposes, these parameters have indications as anthropogenic pollutance. As results, also Bi and Sn have no limits in the artificial recharge by infiltration and according to Palestinian and Jordanian guidelines, thus it is good to study the sediment and soil samples in relation, since they contain cosidrable concentrations in the water phase.

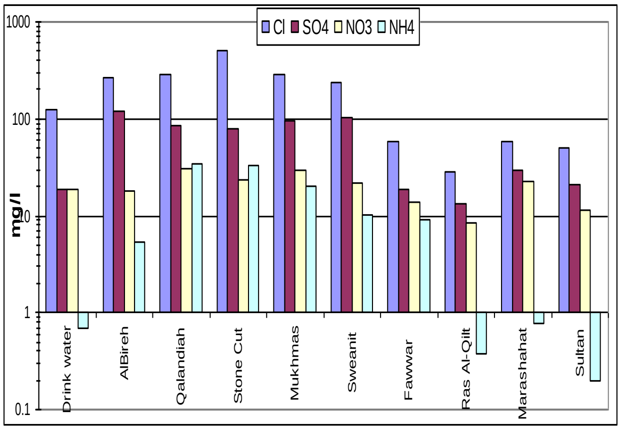
The WHO guidelines for domestic purposes are used to compare the trace metals values. Results indicate that the concentrations for trace metal at the head of the springs are less than the targeted values. On the otherhand, results at the upstream for Mn, Cu and Cr are in the range that are not accepted for reuse as reclaimed wastewater mainly for artificial recharge by infiltration (Figure 3.2).

Results reveal that trace metals are enrich and there are incremental in their concentrations due to discharge of raw wastewater and other human activities at Al-Qilt catchment if compared with guidelines that used for artificial recharged by infiltration, these trace metals are decreased downstream at the head of springs due to retardation or adsorptions, this mean that these trace metals still available at the environment.

Figure 3.2: Occurrences of trace metals at wastewater for major ions, nitrogen, total and dissolve phosphorus and organic carbon, the guideline for artificial recharge by infiltration at up stream, and at down USEPA and WHO Permissible Limit.







The trace metals values in wastewater samples are low if compare to the limits for artificial recharge by infiltration at all sites except for Mn at Stone Cut, furthermore, the trace metals concentration are predominated at Qalandiah and Stone Cut sites due to discharge of raw wastewater, then these wastewater are mixed togather and the source of these trace metals are due to urban run off and roadside mainly at Mukhmas.

Results indicate that B and Sr have the same behavior at the upstream and downstream of Al-Qilt, this due to their solubility in water phase, moreover, there is impact from the presence of B at downstream from the head of springs, since its occurrence mean that there is raw wastewater discharge if compared with WHO guideline that used for drinking water; 1000 µg/l for B and it is reach 200 µg/l at Murashahat site, there the Palestinian use the water for domestic purposes.

3.7.1.1 Spearman Nonparametric Correlation

The relationship between trace metals are verified as metal–metal correlation by using the inter-element Spearman Nonparametric Correlation. Since, high positive correlations >0.9 at $P<0.01$ and $P<0.05$ observed between parameters are labeled in red color, the high correlation >0.70 at $P<0.01$ and $P<0.05$ between parameters are labeled in blue, moreover, moderate >0.5 at $P<0.01$ and $P<0.05$ between parameters are labeled in yellow color and the correlation < 0.5 are labeled in green color (Table 3.3).

Table 3.3: Spearman Nonparametric Correlation for trace metals, major ions, nitrogen, sulfur, organic and in organic carbon for wastewater at Al-Qilt catchment, color for correlation according to LAWA calssifications.

	Cr	Mn	Co	Ni	Cu	Zn	Cd	Sn	Sb	Ba	Pb	B	K	Na	Cl	SO4	NO3	NH4	TP	DP	TOC	DOC
Cr	1.00																					
Mn	0.76^{*}	1.00																				
Co	0.85^{**}	0.78^{**}	1.00																			
Ni	0.95^{**}	0.71^{*}	0.80^{**}	1.00																		
Cu	0.81^{**}	0.94^{**}	0.78^{**}	0.78^{**}	1.00																	
Zn	0.77^{**}	0.78^{**}	0.70^{*}	0.75^{*}	0.90^{**}	1.00																
Cd	0.40	0.58	0.43	0.40	0.63^{*}	0.63^{*}	1.00															
Sn	0.25	0.47	0.29	0.25	0.54	0.54	0.95^{**}	1.00														
Sb	0.77^{**}	0.95^{**}	0.79^{**}	0.79^{**}	0.96^{**}	0.85^{**}	0.58	0.48	1.00													
Ba	0.58	0.88^{**}	0.71^{*}	0.53	0.89^{**}	0.82^{**}	0.74^{*}	0.73^{*}	0.87^{**}	1.00												
Pb	0.81^{**}	0.82^{**}	0.79^{**}	0.79^{**}	0.92^{**}	0.99^{**}	0.61	0.51	0.91^{**}	0.84^{**}	1.00											
B	0.77^{**}	0.91^{**}	0.83^{**}	0.79^{**}	0.95^{**}	0.84^{**}	0.56	0.50	0.98^{**}	0.88^{**}	0.90^{**}	1.00										
K	0.70^{*}	0.77^{**}	0.73^{*}	0.75^{*}	0.83^{**}	0.75^{*}	0.29	0.13	0.88^{**}	0.62	0.82^{**}	0.85^{**}	1.00									
Na	0.72^{*}	0.71^{*}	0.63^{*}	0.79^{**}	0.88^{**}	0.90^{**}	0.56	0.45	0.87^{**}	0.70^{*}	0.91^{**}	0.87^{**}	0.88^{**}	1.00								
Cl	0.73^{*}	0.88^{**}	0.73^{*}	0.71^{*}	0.95^{**}	0.88^{**}	0.63^{*}	0.54	0.93^{**}	0.84^{**}	0.92^{**}	0.93^{**}	0.86^{**}	0.90^{**}	1.00							
SO4	0.63^{*}	0.65^{*}	0.53	0.68^{*}	0.72^{*}	0.57	-0.02	-0.06	0.75^{*}	0.46	0.63	0.77^{**}	0.84^{**}	0.73^{*}	0.70^{*}	1.00						
NO3	0.61	0.86^{**}	0.75^{*}	0.49	0.83^{**}	0.65^{*}	0.53	0.51	0.79^{**}	0.86^{**}	0.72^{*}	0.83^{**}	0.62	0.58	0.86^{**}	0.55	1.00					
NH3	0.77^{**}	0.78^{**}	0.90^{**}	0.70^{*}	0.82^{**}	0.86^{**}	0.50	0.43	0.82^{**}	0.81^{**}	0.91^{**}	0.87^{**}	0.75^{*}	0.75^{*}	0.87^{**}	0.57	0.83^{**}	1.00				
TP	0.77^{**}	0.86^{**}	0.85^{**}	0.72^{*}	0.83^{**}	0.81^{**}	0.31	0.14	0.88^{**}	0.72^{*}	0.86^{**}	0.84^{**}	0.90^{**}	0.73^{*}	0.82^{**}	0.71^{*}	0.72^{*}	0.87^{**}	1.00			
DP	0.82^{**}	0.72^{*}	0.80^{**}	0.84^{**}	0.78^{**}	0.76^{*}	0.20	0.01	0.82^{**}	0.55	0.83^{**}	0.80^{**}	0.95^{**}	0.83^{**}	0.77^{**}	0.81^{**}	0.54	0.77^{**}	0.91^{**}	1.00		
TOC	0.72^{*}	0.92^{**}	0.71^{*}	0.65^{*}	0.86^{**}	0.80^{**}	0.44	0.31	0.90^{**}	0.75^{*}	0.81^{**}	0.83^{**}	0.80^{**}	0.71^{*}	0.88^{**}	0.67^{*}	0.80^{**}	0.80^{**}	0.91^{**}	0.76^{*}	1.00	
DOC	0.66^{*}	0.79^{**}	0.67^{*}	0.59	0.75^{*}	0.72^{*}	0.28	0.20	0.79^{**}	0.64^{*}	0.75^{*}	0.78^{**}	0.75^{*}	0.65^{*}	0.83^{**}	0.71^{*}	0.80^{**}	0.84^{**}	0.86^{**}	0.71^{*}	0.93^{**}	1.00

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

Results indicate that there are positive correlations between different elements "red color" in which Cu is predominate for correlations with Zn, Sb, Pb, B and Cl, this is indicate possible pollution in relatation to wastewater. Then Mn, Sb and Pb came next and correlate with Cu, Sb, B, TOC, B, Pb, TOC, Cl, B, Na, Cl and NH_3, such these correlations indicate that there are more than one geochemical structure and there are more than one source for pollution, for example, urban run off correlate with Cu with Zn, Sb and Pb parameters, and the industry and raw wastewater sources correlate Cu, B, TOC, Pb, Cl, Na, and NH_3. Furthermore, Sb is correlate with B, Pb, TOC and Cl, these parameters are known as indicator for wastewater, furthermore, the positive correlation of Sb and Pb are considered as sources for urban run off, roadside from brake lining and gazoline, since these correlations between trace metal in wastewater is good to understand the trace metal accumulation at the sediment, then this give information about bonding and mechanisms for the trace metal (Mwamburi, 2003).

Moreover, there are other correlations between TP, DP and K, Cl/Na and DOC/TOC that consider as indicator for wastewater due to salts and detergent in which TP/K and DP/K as result of wastewater detergent correlation and the table salts correlation in Cl/Na. furthermore, the correlation for geological indicator occurs between Ca, Mg, Ag, Bi are < 0.5, moreover, there are correlation such as Ag/Sn (0.5), Bi/Cd (0.77), Ca/Mg (0.7), Mg/Ag (0.5) and Mg/Bi (0.59).

3.7.1.2 Principal Component Analysis

The Principal Component Analysis (PCA) is used to identify the relationships between variables (Table 3.4), then Hierarchical Cluster Analysis (HCA) used to examine the relationships between the sampling sites (Reimann *et al*., 2002), the data are standardized by the median values, this will represent 50% of the results to minimize the effects that widely variey in the range among the parameters of PCA and HCA (Wayland *et al*., 2003).

Table 3.4: Total variance explained extraction method: Principle Component Analysis and related parameters.

Matreix Components*				**Initial Eigenvalues**			**Extraction Sums of Squared Loadings**			
	Factor 1	**Factor 2**	**Factor 3**	**Factor 4**	**Total**	**% of Variance**	**Cumulative %**	**Total**	**% of Variance**	**Cumulative %**
Cr	**0.94**	0.06	0.25	-0.18	16.87	64.89	64.89	16.87	64.89	64.89
Mn	**0.95**	0.09	0.25	-0.12	3.37	12.95	77.85	3.37	12.95	77.85
Co	**0.92**	0.22	0.23	-0.2	2.48	9.53	87.37	2.48	9.53	87.37
Ni	**0.94**	0.11	0.16	-0.21	1.65	6.34	93.71	1.65	6.34	93.71
Cu	**0.97**	-0.08	0.19	-0.03	0.92	3.52	97.24			
Zn	**0.97**	-0.02	0.06	0.07						
Ag	-0.24	0.23	0.36	**0.74**						
Cd	**0.75**	0.21	0.57	0.17						
Sn	0.44	-0.45	**0.62**	0.32						
Sb	**0.98**	0.11	-0.1	0.05						
Ba	**0.89**	-0.14	0.39	0.08						
Pb	**0.95**	0.21	0.09	-0.18						
Bi	**0.70**	0.56	0.14	-0.26						
B	**0.81**	-0.13	-0.21	0.44						
Ca	-0.33	**0.87**	0.12	-0.09						
Mg	-0.22	**0.82**	-0.1	0.49						
K	**0.74**	0.45	-0.48	0.05						
Na	**0.9**	0.31	-0.15	0.23						
Cl	**0.95**	0.12	-0.19	0.1						
SO4	**0.68**	-0.16	-0.62	0.25						
NO3	**0.70**	-0.54	-0.05	0.33						
NH3	**0.92**	-0.26	0.17	-0.1						
TP	**0.93**	0.06	-0.35	-0.02						
DP	**0.86**	0.27	-0.38	-0.03						
TOC	**0.84**	-0.24	-0.11	-0.16						
DOC	**0.60**	-0.55	-0.38	0.05						

[a] Extraction Method: Principle Component Analysis with 4 components extraction.

* Strong correlations >0.75 are in red color and moderate correlations >0.50 and < 0.75 in blue color.

Results for PCA analyses for four factors "components" and the Eigenvalue >1, the first four values from the results of percent variance is use for the initial analysis. The first factor has strong loadings for Cr, Mn, Co, Ni, Cu, Zn, Cd, Sb, Ba, Pb, B, Na, Cl, NH_3, TP and TOC, also it is moderately correlated with Bi, K, SO_4, NO_3 and DOC, these loading is represent 64.89% of variance. The second factor is strongly correlate or load by Ca and Mg with 12.95% of variance, the third factors moderately correlated with Sn as indicative of the redox in sensitive nature with 9.53% of variance, on the fourth factor it is moderately correlated with Ag with 6.34% of variance, these four loading are represent about 93.71% of cumulative loading of the analyzed parameters (Table 3.4). Results reveal that all trace metal in factor one must take in consideration as a priority when the anthropogenic pollutants are to consider for evaluation.

3.7.1.3 Dendrogram Hierarchical Cluster Analysis

Hierarchical Cluster Analysis (HCA) is used to identify the groups that have similar geochemistry, also to identify the average linkage between groups and cluster interrelations. Clustering part of trace metal in one group then major parameters as group for Ca and SO_4, then Mn and Ba form group with B and Na and both of these groups form group with TOC, since most of these groups indicate that they easily soluble in water except TOC. All formed groups form one group with Zn and Cl, this is perform to identify the trace metals that have similar in behavior and the distance between these trace metal as one group with other parameters (Figure 3.2).

Results of the cluster analysis is used to develop the fingerprints that identify the parameters that have priorities as anthropogenic pollutants and similar in behavior, such these associations explore and plot each parameter that form the cluster of groups to represent the area for fingerprints, this help in analysis and expect the impact of these trace metals and other related parameters from the surface water to the local eco-system (Wayland *et al.*, 2003). This indicate that all parameters behave the same but in varied distance till reach Zn and Cl at the end, other information is clear in group cluster of the related parameters for example, the numbering of the trace metals is recommend to consider as anthropogenic pollutants, furthermore, B and Na in the same group are highly soluble in the aqua's solutions, also Ca and SO_4 behave as good example for exchangeable and as strong oxidazable for trace metals, moreover, Mn and Ba behave the same as divalent trace metals with high concentrations in the water samples.

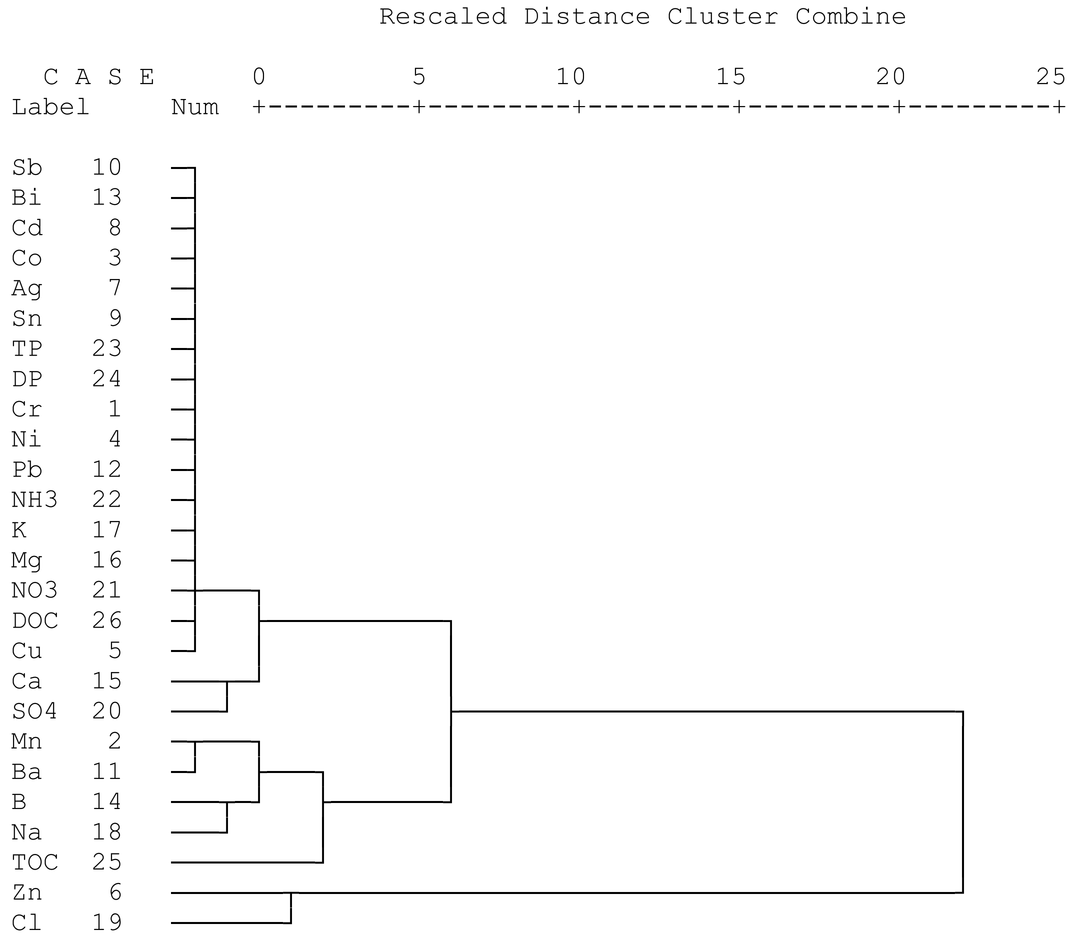


Figure 3.2: Dedrogram Hierarchical Cluster interrelation

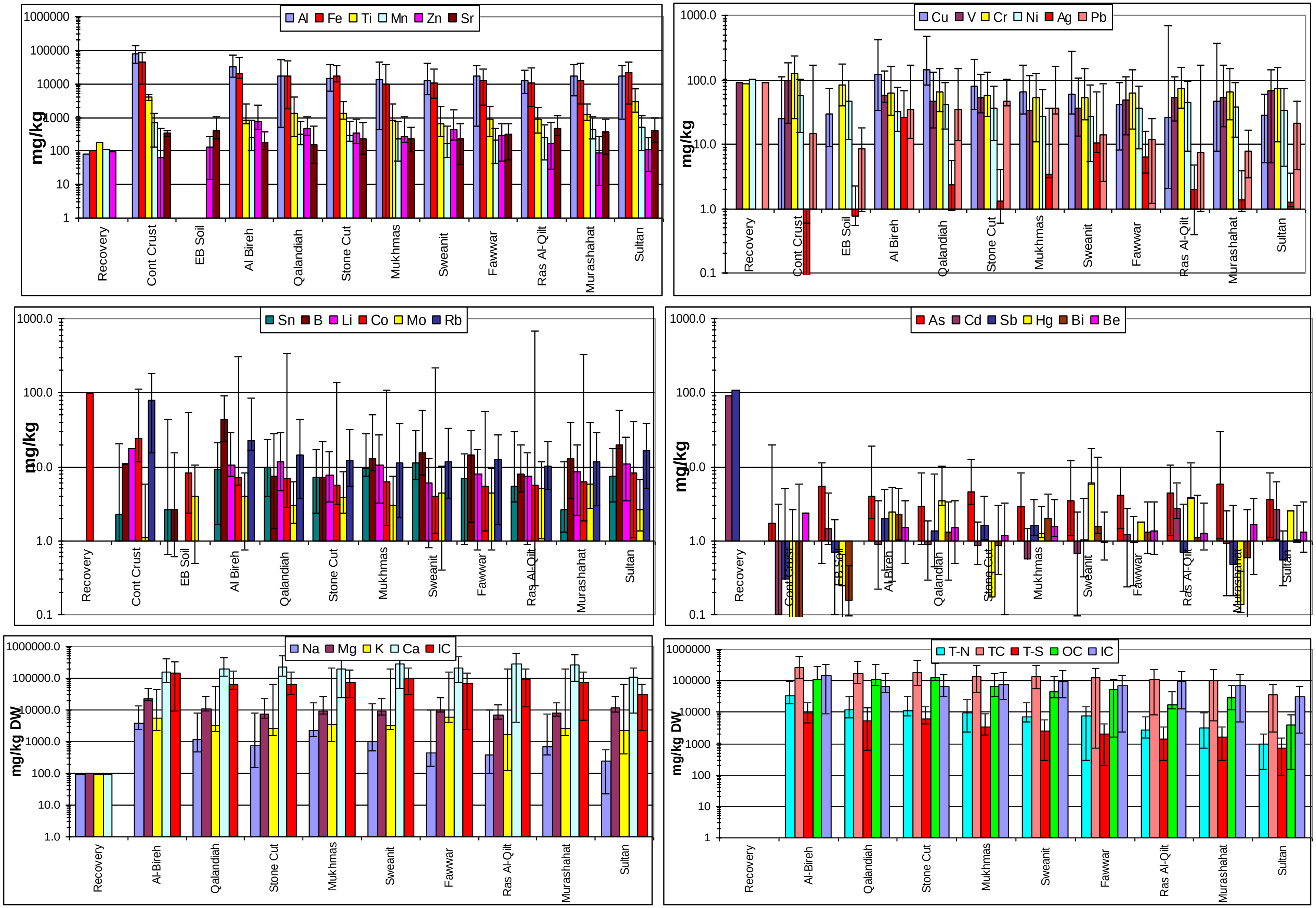
3.7.2 Trace metal in sediment

Results of trace metals in sediment show variation between the upper and lower of Al-Qilt catchment. Results indicate that Al, Fe, Ti, Mn, V, Cr, Co, Rb and Be are low if compare to the Continental Crust values and the Elemental Background of Soil, on the otherhand, the concentrations for Zn, Cu, Ag, Pb, Sn, B, Cd, Hg and Bi are high if compared to (CC) and (EBS), this give sense that these trace metals have external sources as anthropogenic pollutants for enrichments. Moreover, the major ions, sulfur, nitrogen, organic and inorganic carbons are use more in this chapter for statistical analysis and in correlation with trace metals; hence, the occurrences for all parameters are compared with CC, EBS and recovery values (Figure 3.3).

Results reveal that Al, Fe, Ti, Mn, Sr, V, Cr, Ni, B, Li, Rb and As concentration not significantly chang between the up and down streams of Al-Qilt. On the otherhand, Zn, Ag, Pb, Sn, Co, Mo, Cd, Sb, Hg, Bi and Be have significant incremental at the upstream and most of them decrease downstream due to retardation or adsorption by the soil layers. Results for Ag and Pb indicate that thier behavior are similar, since both of them are decreased downstream, then both are increased again at Fawwar spring, then decreased at Ras Al-Qilt spring. Moreover, B, Sn, Co and As occurrences in the surfaces and groundwater sediments during the monitoring they behave the same and most of them are enrich at the upstream, furthermore, B, Cd, Sn, As, Hg, Co, Ni, Cr and Pb are enriched at downstream in different ratios (Figure 3.4).

Trace metals in sediment are evaluated if compared with Sediment Quality Guideline (SQG), United States Environmental Protection Agency (USEPA), Continental Crust and Elemental Background of Soil, since, these values categorize in the range as not polluted, moderately polluted and heavily polluted. This will help in the evaluation and give indication for potential toxicity and possible enrichment for trace metals in the sediment samples (Table 3.5).

Figure 3.4: Occurrences and distributions of trace metals, major ions, nitrogen, sulfur and organic in sediment of Al-Qilt catchment.



Results reveal that most of trace metals in sediment at Al-Qilt catchment are in the range of moderately to heavy polluted, on the otherhand, Cu, Zn, Ag, Hg and Mn are in the range of heavily polluted at Al Bireh, Mukhmas, Qalandiah, Stone Cut, Sweanit and Fawwar (Table 3.5).

Table 3.5: Median values for trace metals in sediment, compared to SQG, CC and EBS values, units are in mg/kg DW (USEPA, 1991).

Sampling Stations	**Cr**	**Ni**	**Cu**	**Zn**	**As**	**Cd**	**Pb**	**Ag**	**Hg**	**Mn**
Buffalo Reference Material 8704	**121.9±3.8**	**42.9±3.7**		**408±15**		**2.94±0.29**	**150±17**			**544±21**
SBRM 8704	**121.90**	**42.90**		**408.00**		**2.94**	**150.00**			**544**
BRM 8704	**106.10**	**43.08**	**85.40**	**385.30**	**16.50**	**2.68**	**135.00**	**0.50**	**2.41**	**601**
Recovery	**87.04**	**100.42**		**94.44**		**91.16**	**90.00**			**110**
Continental Crust	**126.00**	**56.00**	**25.00**	**65.00**	**1.70**	**0.10**	**14.80**	**0.07**	**0.04**	**716**
Elemental Background Soil	**82.80**	**47.25**	**28.95**	**126.85**	**5.35**	**1.48**	**8.65**	**0.75**	**0.25**	**381**
Al Bireh	**61.70**	**32.05**	**119.05**	**744.10**	**4.00**	**0.88**	**34.77**	**26.35**	**2.48**	**255**
Mukhmas	**53.00**	**26.75**	**65.90**	**262.50**	**2.93**	**0.56**	**36.03**	**2.35**	**3.51**	**308.5**
Qalandiah	**64.40**	**40.85**	**144.00**	**478.50**	**2.90**	**0.89**	**35.10**	**1.30**	**0.17**	**282**
Stone Cut	**57.20**	**35.95**	**78.00**	**350.85**	**4.50**	**0.87**	**46.15**	**3.35**	**1.26**	**230**
Sweanit	**52.40**	**27.30**	**60.35**	**449.00**	**3.50**	**0.67**	**14.11**	**10.35**	**6.02**	**168.5**
Fawwar	**62.20**	**35.80**	**41.60**	**290.50**	**4.15**	**1.23**	**11.70**	**6.25**	**1.80**	**215**
Ras Al-Qilt	**72.30**	**44.90**	**26.00**	**160.00**	**4.40**	**2.68**	**7.45**	**2.00**	**3.86**	**248**
Murashahat	**64.44**	**37.94**	**45.89**	**88.15**	**5.82**	**0.91**	**7.84**	**1.35**	**0.14**	**447.55**
Sultan	**72.75**	**33.60**	**27.80**	**115.00**	**3.60**	**2.58**	**21.35**	**1.25**	**2.50**	**513**
Non polluted	**< 25**	**< 20**	**< 25**	**< 90**	**< 3**		**< 40**	**1.00**	**< 0.1**	**<300**
Moderately polluted	**25-75**	**20-50**	**25-50**	**90-200**	**3—8**		**40 – 60**	**1-2.2**	**-**	**300-500**
Heavily polluted	**> 75**	**> 50**	**> 50**	**> 200**	**> 8**	**> 6**	**> 60**	**>2.2**	**> 1**	**>500**

The highest concentrations of Cr are at Sultan and Ras Al-Qilt springs, both of them are in the range of moderately polluted, also there is variation for Cr if compared to CC and EBS in which Cr value in CC and EBS are considere as heavily polluted values. Furthermore, the highest concentrations of Ni is at Ras Al-Qilt spring and Qalandiah, this considere as moderately polluted, also the results for EBS is in the range of moderately polluted, moreover, the highest values for As, Cd and Pb are at Murashahat, Ras Al-Qilt and Qalandiah respectively, these results are in the rang of moderately polluted if compared to (SQG). On the otherhand, Cu, Zn, Ag and Hg are heavily polluted at Al Bireh, Mukhmas, Qalandiah Stone Cut, Sweanit, Fawwar, Sultan and Ras Al-Qilt. Results indicate that most of the trace metals pollutant originate from upstream due to raw wastewater, urban runoff and other human activities, since it is move to downstream and it is increase as it is reach Sweanit wadi.

Hall *et al*., (1997) consider the Cu and Zn as micronutrients for aquatic life in natural waters and sediments, since they become toxic to aquatic life at high threshold concentrations, however, both of them at Al-Qilt are in range of heavy polluted.

In order to quantify the hazards of trace metals at aquatic system in relation to SQGs benchmark, this study will use Cr, Ni, Cu, Zn, As, Cd, Pb, Ag, Hg and Mn in sediment, then the hazard indexes will calculate by dividing the median concentrations for each parameters at each sites to the value of heavily polluted of SQG (Table 3.6), then the benchmark in sediment values are determined based on the effect that observed during sediment toxicity if the ratio are higher than one, by this it will assume that these are used as indicator by sediment and there potentially associate with an adverse effect at the aquatic system by trace metals contamination.

Results for Cu, Zn, Ag, Hg and Mn are higher than one, this indicate that there will be adverse impact from these trace metals to the aquatic systems and there will be possibilities to transport or fractionate of the trace metals to other chemical forms and both will have impact to aquatic system.

Table 3.6: Ratio of the median value for trace metals in sediment samples from Al-Qilt divided to heavily polluted values**.**

Sampling Stations	Cr	Ni	Cu	Zn	As	Cd	Pb	Ag	Hg	Mn
Continental Crust	1.68	1.12	0.50	0.33	0.21	0.02	0.25	0.03	0.04	1.43
Elemental Background for Soil	1.10	0.95	0.58	0.63	0.67	0.25	0.14	0.34	0.25	0.76
Al Bireh	0.82	0.64	2.38	3.72	0.50	0.15	0.58	11.98	2.48	0.51
Mukhmas	0.71	0.54	1.32	1.31	0.37	0.09	0.60	1.07	3.51	0.62
Qalandiah	0.86	0.82	2.88	2.39	0.36	0.15	0.59	0.59	0.17	0.56
Stone Cut	0.76	0.72	1.56	1.75	0.56	0.14	0.77	1.52	1.26	0.46
Sweanit	0.70	0.55	1.21	2.25	0.44	0.11	0.24	4.70	6.02	0.34
Fawwar	0.83	0.72	0.83	1.45	0.52	0.21	0.20	2.84	1.80	0.43
Ras Al-Qilt	0.96	0.90	0.52	0.80	0.55	0.45	0.12	0.91	3.86	0.50
Murashahat	0.86	0.76	0.92	0.44	0.73	0.15	0.13	0.61	0.14	0.90
Sultan	0.97	0.67	0.56	0.58	0.45	0.43	0.36	0.57	2.50	1.03

At Al-Qilt catchment the calculated ratios below one are not associated with adverse biological effects; therefore, the presence of these metals in sediment at surface must not considere as potential for toxicity and will be more significant if calculated with other environmental factors. On the otherhand, the ratio range for Cu 1.21-2.38, Zn 1.31-3.72, Ag 1.07-11.98, Hg 1.26-3.86 and Mn 0.9-1.03, these results are use more for ecological interpretation and chemistry for sediment.

The high metal contents in sediments found at Al-Qilt indicates that there are anthropogenic sources and there are enrichment for Cu, Zn, Ag, Hg and Mn mainly at Al Bireh, Qalandiah, Stone Cut, Mukhmas, Sweanit and Sultan spring.

Moreover, in this chapter we use Cu, Zn, Ag and Hg to assess the harmful ecological effects that associate with the analyzed sediment (more detail in chapter 5). Results indicate that, it is better to use the Elemental Background for Soil, since they have one result for the ratio of 1.10 for Cr, this indicates that all other result considere as background values if compared with heavily polluted according to SQG values.

3.7.2.1 Spearman Nonparametric Correlation

The correlation between trace metals, major ions, nitrogen, sulfur, organic and inorganic carbon in sediment are varied, the metal–metal correlations are calculated by using Spearman Nonparametric Correlation. Since, high positive correlations >0.9 at $P<0.01$ and $P<0.05$ are observe between parameters are label in red color, high correlation >0.70 at $P<0.01$ and $P<0.05$ is notice between parameters and label in blue. Moreover, moderate >0.5 at $P<0.01$ and $P<0.05$ is also notice between parameters and labeled in yellow color and the correlation < 0.5 noticed and labeled in green color (Table 3.7).

Results reveal that Co correlation is < 0.5 except with Ca, Mn and Mg are moderate, also Ca is correlate highly with Mg and moderately with Mo and Pb, and other correlations are varied (Table 3.7).

The positive correlation between nitrogen, sulfur and organic carbon is excepted, but it is important to note that there are high correlations between Sb/TC, Sb/TS, Sb/OC, Cu/TN, Cu/TS, Zn/TC and Cd/Cr, since these correlations considered as indication for possible of common pollution or sources in sediment, otherwise, these trace metals Sb, Cu and Zn can be transported with nitrogen, sulfur and organic in complexes form, moreover, it is indicates that the processes or mechanisms that influencing the metal associations, and it is indication for the bonding might explain by information on the geochemical phases (Mwamburi, 2003).

Results reveal that Cd/Cr is highly correlates with each others along Al-Qilt catchment; this is possibile if the same sources of pollution for these parents of parameters have the same geochemical phases.

Results indicate that there are no similarities between parameters that correlate at wastewater and sediment, since more correlations between trace metal and trace metals and major ions in wastewater samples, on the otherhand, this is not found between sediment since the number of the correlated parameters are less and most of correlations are with organic, nitrogen and sulfur and some with trace metals.

Table 3.7: Spearman Nonparametric Correlation for trace metals, major ions, nitrogen, sulfur, organic and inorganic in sediment at Al-Qilt.

	Na	Mg	K	T-N	TC	T-S	OC	IC	Cr	Mn	Ni	Cu	Zn	As	Mo	Ag	Cd	Sn	Sb	Ba	Hg	Pb	Bi	B
Na	1.00																							
Mg	0.28	1.00																						
K	0.63	0.50	1.00																					
TN	0.85**	0.32	0.72*	1.00																				
TC	0.80**	0.20	0.55	0.92**	1.00																			
TS	0.87**	0.22	0.62	0.97**	0.97**	1.00																		
OC	0.75*	0.12	0.62	0.95**	0.92**	0.97**	1.00																	
IC	0.50	-0.02	0.25	0.20	0.32	0.25	0.07	1.00																
Cr	-0.70*	0.05	-0.57	-0.55	-0.67-*	-0.67-*	-0.62	-0.42	1.00															
Mn	-0.27	0.17	-0.48	-0.15	-0.28	-0.18	-0.15	-0.60	0.68*	1.00														
Ni	-0.45	-0.40	-0.48	-0.17	-0.20	-0.25	-0.15	-0.30	0.65	0.42	1.00													
Cu	0.87**	0.33	0.53	0.92**	0.85**	0.92**	0.87**	0.08	-0.53	0.05	-0.18	1.00												
Zn	0.72*	0.45	0.62	0.83**	0.92**	0.83**	0.75*	0.33	-0.57	-0.35	-0.22	0.77*	1.00											
As	-0.45	-0.53	-0.37	-0.28	-0.23	-0.22	-0.12	-0.05	0.28	0.20	0.43	-0.40	-0.45	1.00										
Mo	-0.16	-0.51	-0.18	-0.25	-0.15	-0.21	-0.24	0.54	0.00	-0.32	0.33	-0.34	-0.20	0.63	1.00									
Ag	0.65	0.37	0.75*	0.52	0.53	0.48	0.35	0.78*	-0.60	-0.73*	-0.47	0.35	0.67*	-0.37	0.23	1.00								
Cd	-0.80**	-0.02	-0.47	-0.58	-0.63	-0.70-*	-0.63	-0.28	0.92**	0.38	0.67*	-0.68-*	-0.48	0.38	0.20	-0.42	1.00							
Sn	0.62	0.48	0.38	0.43	0.52	0.47	0.33	0.18	-0.58	-0.30	-0.57	0.58	0.67*	-0.88**	-0.51	0.47	-0.65	1.00						
Sb	0.80**	0.22	0.58	0.88**	0.93**	0.93**	0.90**	0.27	-0.68*	-0.30	-0.38	0.78*	0.82**	-0.32	-0.36	0.48	-0.68*	0.53	1.00					
Ba	0.63	-0.05	0.38	0.72*	0.88**	0.82**	0.80**	0.17	-0.78*	-0.40	-0.18	0.73*	0.80**	-0.25	-0.10	0.38	-0.72*	0.58	0.78*	1.00				
Hg	-0.08	0.22	-0.17	-0.18	0.03	-0.18	-0.32	0.30	0.05	-0.32	0.03	-0.15	0.33	-0.52	-0.02	0.30	0.18	0.50	-0.05	0.12	1.00			
Pb	0.58	0.22	0.35	0.67*	0.63	0.72*	0.75*	-0.30	-0.50	0.12	-0.38	0.75*	0.48	-0.42	-0.75*	-0.03	-0.68*	0.55	0.77*	0.62	-0.27	1.00		
Bi	0.67*	0.48	0.72*	0.50	0.50	0.47	0.33	0.65	-0.57	-0.65	-0.65	0.35	0.63	-0.62	-0.18	0.88**	-0.47	0.63	0.60	0.32	0.35	0.22	1.00	
B	0.08	0.70*	0.30	-0.12	-0.10	-0.12	-0.27	0.38	-0.05	-0.17	0.67*	-0.17	0.10	-0.23	-0.09	0.47	0.00	0.25	-0.02	-0.30	0.23	-0.18	0.55	1.00

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

3.7.2.2 Principle Component Analysis (PCA)

Using PCA with five factors to analyze and correlate parameters in sediment, the interpretation of the group for variables that associate with a particular factors load of >0.6 will be consider. PCA technique is applied for 26 variables and represente by five principal components, results show that these variable categorized to five factors that extracte and describe of 93.33% of the common variance as follow: F1 46.75%; F2 16.53%; F3 13.05%, F4 10.46%, F5 6.65% (Table 3.9).

The first factor is highly load for Na, TN, TC, TS, OC, Cu, Zn, Ag, Sb, Ba, Pb, Bi and B and it is moderately loaded for Mg, K, IC, Cd and Sn, since it is negativly loaded for Cd. Positive loading for other parametrs indicate that there are influences of anthropogenic sources for trace metals and associate with contaminant inputs.

The second factor are highly loaded for Ca and Co and moderately loaded for Cr, Mn and Ba, furthermore, it is negatively loaded for Ca and Mn, this is highlights the influence of calcite-clay minerals and Mn-oxides in the bed sediments and its structure.

The third factor loading for As and Mo are positive and it is independent on the sediment matrix and compositions.

Hg is moderately and negatively loaded on the fourth factor, furthermore, Ni is loaded moderately and positively at factor five, this indicates that Ni is include in the geochemical matrix in sediment and it could be associate by this component with changing in the geochemical matrix, this due to change on concentrations of the anthropogenic input.

Table 3.8: Principal Component Analysis for percentage of variance as initial eigenvalues and correlation coefficient as component matrix.

	Component					**Initial Eigenvalues**			**Extraction Sums of Squared Loadings**		
	F1	**F2**	**F3**	**F4**	**F5**	**Total**	**% of Variance**	**Cumulative %**	**Total**	**% of Variance**	**Cumulative %**
Na	**0.88**	0.24	0.22	-0.04	-0.13	12.16	46.75	46.75	12.16	46.75	46.75
Mg	**0.73**	0.58	0.29	-0.17	0.03	4.30	16.53	63.28	4.3	16.53	63.28
K	**0.63**	0.08	0.24	-0.13	-0.3	3.39	13.05	76.33	3.39	13.05	76.33
Ca	-0.28	**-0.84**	0.39	0.08	0.15	2.72	10.46	86.79	2.72	10.46	86.79
TN	**0.93**	0.23	0.25	0.11	0.07	1.70	6.54	93.33	1.70	6.54	93.33
TC	**0.90**	-0.15	0.19	0.32	0.15	0.70	2.68	96.01			
TS	**0.90**	0.12	0.07	0.37	0.14	0.62	2.40	98.40			
OC	**0.77**	-0.12	-0.19	0.56	0.13	0.41					
IC	**0.70**	-0.13	0.64	-0.15	0.12	0					
Cr	-0.55	**0.62**	0.19	-0.01	0.51	0					
Mn	-0.53	**0.72**	-0.09	0.23	-0.11	0					
Co	-0.02	**0.96**	-0.2	0.13	0.06	0					
Ni	-0.45	0.1	0.23	0.43	**0.69**	0					
Cu	**0.77**	0.06	-0.21	0.31	0.30	0					
Zn	**0.95**	-0.03	0.09	-0.04	0.23	0					
As	-0.42	0.01	**0.72**	0.48	-0.19	0					
Mo	-0.32	-0.38	**0.84**	0.18	-0.03	0					
Ag	**0.80**	0.18	0.48	-0.27	0	0					
Cd	**-0.61**	0.42	0.07	-0.27	0.46	0					
Sn	**0.66**	-0.21	-0.51	-0.46	0.13	0					
Sb	**0.93**	-0.04	-0.17	0.22	-0.01	0					
Ba	**0.64**	**-0.64**	-0.24	0.13	0.18	0					
Hg	0.11	-0.3	-0.01	**-0.74**	0.53	0					
Pb	**0.64**	0.13	-0.57	0.44	-0.01	0					
Bi	**0.83**	0.06	0	-0.46	-0.09	0					
B	**0.63**	0.54	0.43	-0.28	-0.14	0					

3.7.2.3 Hierarchical Cluster Analysis

Hierarchical Cluster Analysis is used to identify groups with similar geochemistry, and to identify the linkage between groups and cluster interrelations. Results indicate that there are three clustering groups: trace metal, Na, K, TS, TN and Mg in one group, most of these parameters are easily soluble and oxidizable in water then all of these parameters are forming group with OC and IC, then these two groups form with the third group with Ca and then TC the total cluster (Figure 3.5).

Results of the analyzed cluster used to develop fingerprints that identify the parameters in similar behaviors, such these associations explore and plotting for each parameter from cluster in groups to produce fingerprints that use to analyse the impacts to local aquifer (Wayland *et al*., 2003). Again this indicate that all parameters behave the same except Ca and TC behave in different manner due to their contributions in the formation of the backbone of sediment texture from calcium carbonate and the high load of carbon from raw wastewater.

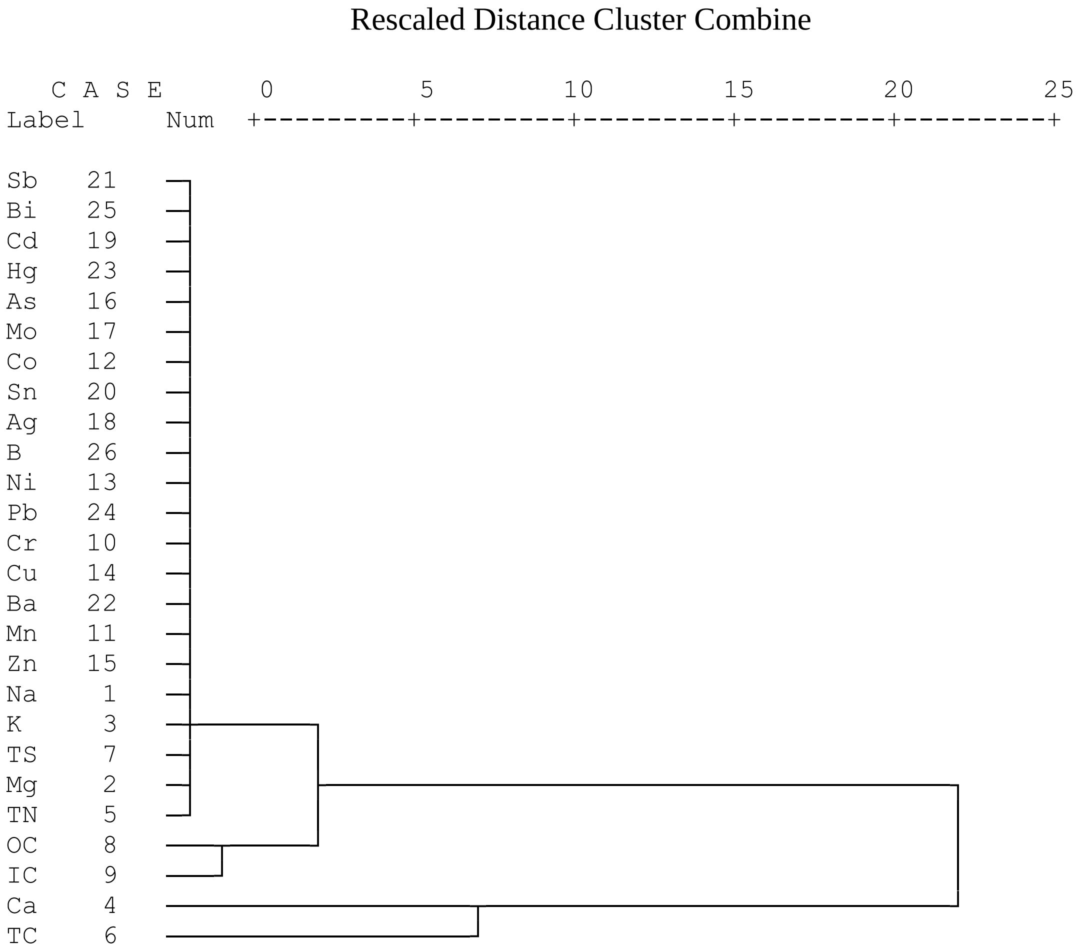


Figure 3.5*:* Hierarchical Cluster Analysis for trace metals, major ions, nitrogen and sulfur in sediment.

3.7.3 Trace metals in soil

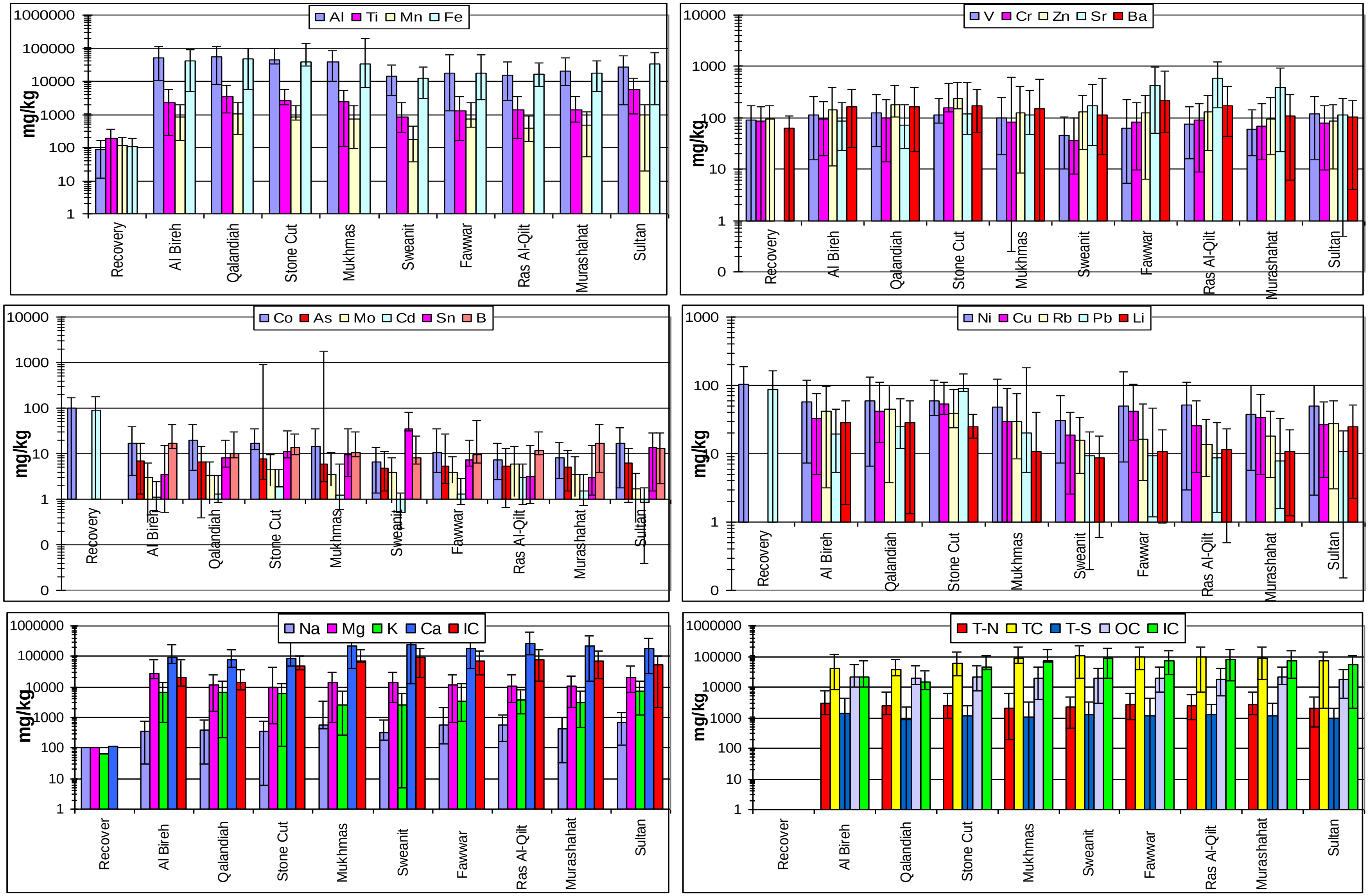
There are several sources for heavy and trace metals at Al-Qilt catchment, for example, raw wastewater, urban runoff, vehicles, industries waste from Israeli colonies and quarries from Palestinian communities, these activities are emitted their waste, this is increase for example trace metal occurrences and settled at the top of the soil, moreover, the results for trace metals with nitrogen, sulfur, total organic and inorganic carbon will be use for statistical analysis and correlations. It is important to mention that Pb is emitted to the environment from leaded gasoline and Cu, Zn and Cd are emitted from car components, tire abrasion, lubricants industrial and incinerators (Wilcke *et al*., 1998), furthermore, Li *et al*., (2001) realize that it is important to take in consideration the atmospheric deposition that emitte heavy metal in urban dust area, this play important role in atmospheric deposition and transportation for trace metal.

At Al-Qilt there is no information about the elemental background values such as heavy metal concentrations in soil, this Elemental Background for Soil (EBS) values will consider from pristine area of Al-Qilt. Therefore, the data of EBS will compare with the Continental Crust (CC) values from European soils (Utermann *et al*., 2004), other values such as threshold values were studied by (Eikmann and Kloke, 1993; Kloke, 1993), all these guidelines will be use in this study (Table 3.9).

Results reveal that the recovery values of the analyzed parameters are ±10, according to quality assurance and quality control it is acceptable, but it is with high value for Ti and it is low value for Ba, moreover, results for Ag, Sb, Hg, Bi and Be are below the detection limits (2, 2, 0.003, 1, and 2) mg/kg respectively. Moreover, the precision and accuracy are checked by control such as blank and quality control solutions, all of the measured parameters are within the accepted limits (Table 3.9).

Results reveal that Sr and Ba are predominated at Fawwar, Ras Al-Qilt and Murashahat springs, these sites are located at downstream of Al-Qilt, moreover, Sn is predominated at Sweanit soil, Mo, Cd are predominated at Ras Al-Qilt soil and B at Murashahat soil, Co and Li are predominated at Qalandiah soil, As, Ni, Cu, Pb, Cr and Zn are predominated at Stone Cut soil, these give sense to look more to chemical transformations (bonding) that responsible for reallocation for these trace metals and if possible to study their fractionations form (Figure 3.6).

Figure 3.6: Occurrences and distributions for trace metal, major ions, sulfur, nitrogen, organic and in organic carbon of soil at Al-Qilt, unit is in mg/kg DW.



For this study, the trace metals are divided according to the sources into three groups:

First group is the metals from decelerating activities such as Cu, Zn, Co, Sn and Ba, these are predominates at the upstream of Al-Qilt and all of these parameters are high if compared to Elemental Background of the Soil, thus there are anthropogenic sence.

Second group is metals as historical residue from the combustion of petrol such as Pb and Cd, since; Pb is high at Al Bireh, Qalandiah, Stone Cut and Mukhmas due to urban runoff and wastewater discharge.

Third group is non-source-specific metals such as Cr and Ni, since both are high if compared to (EBS) in particular at Al Bireh, Qalandiah and Ras Al-Qilt.

At Al-Qilt the soil samples have Cu, Zn, Cr, Co, As, Sn, Ba and Pb concentrations; these are high at roadside soil samples such as Mukhmas, Al Bireh, Qalandiah and Stone Cut. Moreover, the major source from road traffic are related to Cu and Sn as result to brake linings, tire abrasion, thus, it is significant to study these metals in more details to understand their fate and transport or reallocation, then there fractionations (Chapter 4).

Pb and Cd are high at Sweanit, Fawwar and Ras Al-Qilt if compared to (EBS), this indicates that the soil at these sites are despited these are located far away from human activities and these area considered as pristine area, but there are possibilities from weathering depositions from the Israeli colonies in the area.

Furthermore, the behavior of trace metals at Al-Qilt in the soil are decreased downstream due to retardations and adsorption at the top surfaces, this mean that they remain in complex in different form mainly the carbonate exchange, since calcium and magnesium are predominanted due to the nature and composition of rock (Figure 3.6), this will increase the time that need for transport or reallocate of these trace metals from reaching the water table.

Table 3.9: Median concentrations for soil compared to Elemental Background of Soil in Al-Qilt catchment.

Lab No	**Al**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Mo**	**Cd**	**Sn**	**Ba**	**Pb**	**B**	**Li**	**As**	**Rb**	**Sr**	**Zn**
Recovery	87	186	89	87	112	107	98	102			91		63	88						95
Al Bireh	52035	2184	112	95	859	42180	16.85	56.3	32.65	3	1.1	3.6	164.5	19.1	16.7	28	7.1	42	87	1445
Qalandiah	53940	3445	127	99	1021	46750	19.35	59.1	42.5	3.3	1.3	7.95	166.5	24.4	10.2	29	6.6	44	74	179
Stone Cut	44290	2602	116	157	825	39500	16.65	60	54.05	4.6	1.91	11	168	89	13.4	25	7.8	40	117	239
Mukhmas	37965	2470	98	84	726	32885	14.2	47.95	29.6	3.6	1.2	9.6	148	20.4	10.5	10.6	6.1	30	116	124
Sweanit	14560	868	45	37	174	12105	6.5	30.85	18.9	4	0.5	34.9	115	9.5	7.9	8.6	4.9	16	175	128
Fawwar	18210	1320	63	82	722	18170	10.4	49.2	42.1	3.9	1.3	7.2	218	9.3	9.4	10.6	5.4	16	423	127
Ras Al-Qilt	15655	1350	76	89	385	16275	7.3	50.8	26	5.8	2.93	3.1	170	8.7	11.7	11.3	5.4	14	597	128
Murashahat	20445	1396	60	70	467	17035	8	37.55	33.7	3.6	1.5	3.1	108	7.9	16.6	10.7	5.1	18	394	97
Sultan	27494	5778	119	80	991	34363	17.25	49.5	26.5	1.7	0.9	13.5	106	10.9	12.8	24.8	6.2	28	116	85
Elemtal Bacground				83			8.3	47.25	28.9	4	1.5	2.7	132	8.7	2.6		5.4		411	127
Conteental Crust				129			24	56	25	1.1	0.1	2.3	584	14.8	11		1.7		333	65
Utermann *et al*., 2004				9-56				7-39	7-24					9-6						25-100
MPP (USEPA) [a]			47 *					107		0.6*	4		302 *	84	1.7 *		8			

Utermann *et al*. (2004): range of heavy metal background values (medians) of European soils from calcareous rocks and clayey materials (Aqua Regia extraction).

[a] Maximum Permissible Pollutant concentrations in the receiving soils (USEPA, 1981 and 1992a).

*Values were computed numerical limits for these elements were within the range that is typical for soils.

According to USEPA values, the numerical values as limits for B, Be, Ba, Mo, Tl, and V, these empirical parameter values are estimated. These values will use for this study; results reveal that these values are high for V, Mo and B at all sites. The numerical limits for pollutants in soils expressed as Maximum Permissible Concentrations for the receiving soils as global reference, since it is estimatted as the upper limits. Moreover, most of the heavy and trace metal pollution are irreversible process in soil, once heavy metals enter the soil it is difficult to extract or dilute from the soil environment or they will be hazardous to organisms and then they influence the soil ecosystem structure and function (Zhou and Song, 2004) this will be investigate more on Chapter 4 and Chapter 5.

3.7.3.1 Spearman Nonparametric Correlations

In order to establish inter-element relationship for soil and correlation coefficients for trace metals. The high and positive correlations >0.9 at $P<0.01$ and $P<0.05$ are observed between parameters and label in red also, high correlation >0.70 at $P<0.01$ and $P<0.05$ is noticed between parameters and label in blue. Moreover, moderate >0.5 at $P<0.01$ and $P<0.05$ is noticed between parameters and label in yellow and that correlation < 0.5 is noticed and label in green (Table 3.10).

The significant correlation between metals indicates that there are common source for these metals (Table 3.10) most of the high correlations are related to parametres from texture such as Al, Fe, Mn, V and Li, since, metals are emitted due to decelerating activities such as Cu, Zn, Co, Sn and Ba, these will relate and correlate with each others, this will reflect the source for pollution as out side pollutants or its geoginic occurrencce.

Results for sediment, wastewater and soil are not similar if correlate for most of the sites, this indicates that each site must study in separate to use the suitable environmental factors in relation. At Al-Qilt it is important to consider the difference in elevation, since it is at Al Bireh about 700 m.a.s.l and it is about 20 m.a.s.l at Ras Al-Qilt spring, this give sense to consider the difference in the structure or composition of the soil along the area of study.

Table 3.10: Spearman Non Parametreic Correlations for trace metal, major ions, total carbon, organic carbon, sulfur and nitrogen in soil at Al-Qilt catchment.

	Na	Mg	K	Ca	TN	TC	TS	OC	IC	Cr	Co	Ni	Cu	Zn	As	Mo	Cd	Sn	Ba	Pb	B
Na	1.00																				
Mg	0.07	1.00																			
K	0.28	0.13	1.00																		
Ca	0.25	0.03	-0.72*	1.00																	
TN	-0.20	-0.14	0.09	-0.26	1.00																
TC	0.13	-0.03	-0.75*	0.83**	-0.09	1.00															
TS	-0.33	0.23	-0.41	0.46	0.51	0.45	1.00														
OC	-0.60	-0.25	-0.25	-0.28	0.49	-0.22	0.30	1.00													
IC	0.10	-0.10	-0.78*	0.95**	-0.27	0.90**	0.44	-0.22	1.00												
Cr	-0.17	-0.30	0.53	-0.62	0.24	-0.73*	-0.23	0.32	-0.72*	1.00											
CO	-0.08	0.14	0.77*	-0.93**	0.02	0.92**	-0.60	0.14	-0.96**	0.64	1.00										
Ni	-0.07	-0.23	0.77*	-0.72*	0.24	-0.77*	-0.27	0.15	-0.78*	0.93**	0.71*	1.00									
Cu	-0.22	-0.52	0.33	-0.78*	0.45	-0.55	-0.41	0.53	-0.70*	0.62	0.62	0.58	1.00								
Zn	-0.66	-0.27	0.20	-0.46	0.32	-0.42	0.14	0.37	-0.44	0.76*	0.33	0.70*	0.44	1.00							
As	-0.34	0.02	0.61	-0.82**	-0.02	-0.90**	-0.38	0.39	-0.84**	0.79*	0.88**	0.79*	0.56	0.58	1.00						
Mo	-0.10	-.691-*	-0.53	0.51	0.07	0.48	0.32	0.25	0.54	0.13	-0.61	-0.03	-0.01	0.26	-0.29	1.00					
Cd	0.09	-0.78*	-0.08	0.28	0.16	0.14	0.18	0.15	0.33	0.19	-0.39	0.19	0.07	0.14	-0.16	0.75*	1.00				
Sn	-0.29	0.33	-0.02	-0.14	-0.68*	0.03	-0.31	-0.16	-0.03	-0.17	0.21	-0.10	-0.17	0.03	0.26	-0.26	-0.51	1.00			
Ba	0.02	-0.38	0.03	-0.08	0.47	0.05	0.14	0.13	-0.17	0.58	-0.03	0.48	0.40	0.58	0.05	0.53	0.25	-0.35	1.00		
Pb	-0.29	-0.02	0.46	-0.68*	-0.23	-0.76*	-0.49	0.25	-0.73*	0.80*	0.80*	0.73*	0.49	0.60	0.93**	-0.16	-0.22	0.39	0.19	1.00	
B	0.09	-0.08	0.39	-0.26	0.31	-0.48	0.11	0.41	-0.29	0.21	0.26	0.29	0.19	-0.11	0.33	-0.13	0.40	-0.43	-0.31	0.03	1.00

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

3.7.3.2 Principal Component Analysis (PCA)

PCA is carried out to ascertain the possible contributing factors towards the metal concentrations and to determine the metals that have common of origin. This achieve by extracting the eigenvalues from the correlation matrix, the number of significant factors, the percent of variance that explained by each of them, all of these will calculate by using SPSS 7.5 and show in rotated component matrix (Table 3.11).

The results show that eigenvalues are grater than one, this will be consider and explain of ≈ 91% of the variance. The first five eigenvalues are selected and other values "but nonzero eigenvalues" are discarde for establishing the proper number of contributing factors. It is evident from the rotated component matrix that all metals analyeze are explained by five factors (Table 3.11).

First factor spanning the greater amount of variance 42.11% this factor has high load for K, Ca, TC, IC, Cr, Co, Ni, Cu, Cr, As, OC and IC and it is moderately for Zn and Pb. This factor indicates that the sources of pollution is industrial or urban runoff, this is evident from the presence of various metal processing industries as anthropogenic pollutants, these parameters from the first factor must be taken in considerations. The negative sing for Ca, TC and IC indicate that these are not anthropogenic pollutants and their loads must take in considrations.

Second factor has load for Mg, OC, Mo and Cd with 19.70% of variance, this could be air-borne emissions from various sources such as Cd (more detailed will be at Chapter 4), and Mg load is not as anthropogenic pollutants.

Third factor has load for TN, TS and B with 11.85% of variance, this is consider as source of mixed origin that includes industrial and domestic wastewater and contain oxidizable materials.

Fourth factor has load for Na and Sn with 10.77% of variance, this is consider as source from vehicular excused and tire abrasion, furthermore, there are evidence for atmospheric deposition more detail will be on Chapter 4 and Chapter 5.

Fifth factor has load for Ba with 6.66% of variance, this is not originate as anthropogenic source.

Table 3.11: Total Variance Explained, Extraction Method: Principal Component Analysis and Component for the five components.

	Component*					Initial Eigenvalues			Extraction Sums of Squared Loadings		
	1	2	3	4	5	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
Na	-0.33	-0.35	-0.28	0.77	-0.07	8.84	42.11	42.11	8.84	42.11	42.11
Mg	0.16	-0.70	0.51	-0.07	0.02	4.14	19.70	61.81	4.14	19.70	61.81
K	0.76	-0.50	0.03	0.15	0.14	2.49	11.85	73.66	2.49	11.85	73.66
Ca	-0.93	0.17	-0.04	0.24	0.11	2.26	10.77	84.43	2.26	10.77	84.43
TN	0.42	0.42	0.68	0.09	-0.32	1.40	6.66	91.09	1.40	6.66	91.09
TC	-0.90	0.31	-0.18	-0.06	-0.01	0.95	4.51	95.60			
TS	-0.32	0.39	0.67	-0.29	-0.03	0.65	3.08	98.68			
OC	0.42	0.48	0.43	-0.41	-0.07	0.28	1.32	100.00			
IC	-0.89	0.33	-0.16	-0.05	0.11	0.00	0.00	100.00			
Cr	0.84	0.37	-0.21	0.19	0.19	0.00	0.00	100.00			
CO	0.86	-0.46	-0.17	-0.01	0.03	0.00	0.00	100.00			
Ni	0.88	0.03	-0.13	0.38	-0.09	0.00	0.00	100.00			
Cu	0.80	0.40	-0.20	0.04	-0.15	0.00	0.00	100.00			
Zn	0.74	0.49	-0.28	-0.31	0.02	0.00	0.00	100.00			
As	0.93	-0.04	-0.13	-0.20	0.21	0.00	0.00	100.00			
Mo	-0.21	0.92	-0.09	0.15	0.12	0.00	0.00	100.00			
Cd	-0.12	0.67	0.07	0.48	0.46	0.00	0.00	100.00			
Sn	-0.41	-0.21	-0.36	-0.75	0.07	0.00	0.00	100.00			
Ba	0.38	0.46	-0.05	0.24	-0.73	0.00	0.00	100.00			
Pb	0.70	0.42	-0.33	-0.25	0.33	0.00	0.00	100.00			
B	0.31	-0.04	0.72	0.24	0.51	0.00	0.00	100.00			

* Extraction Method: Principal Component Analysis with five components extracted

3.7.3.3 Hierarchical Cluster Analysis

Hierarchical Cluster Analysis is performed to identify the groups that have similar geochemistry and to identify the linkage between groups and cluster interrelations. There are three clustering group: trace metal, Na, K, TS, TN, Mg and OC are in one group, most of these parameter are easily soluble and oxidizable in water. Moreover, the reactive mineral components in soils are in clay and oxyhydroxide minerals of Mg, Mn, etc, other substances are within the scope of OC and in carbonaceous materials such as charcoal. OC is usually the predominant sorbent unless the OC content is extremely low – other estimates suggest that less than 0.01% of organic carbon by weight – or unless the water content is low, then all parameters are grouped with TC and IC group, then these two group form with the third group as Ca to form the total cluster (Figure 3.7).

Results of the cluster analysis will use to develop the fingerprint that identifies the parameters in similar behavior. Such these associations explore and plotted for each parameter to form groups to produce fingerprints, this is used to analyeze the impacts for the local aquifer (Wayland *et al*., 2003). Again this indicates that all parameters behave the same except Ca behave differently due to their contributions in the formation of the backbone of the sediments texture, calcium carbonate and highly load, and there are considerable amount of carbon from raw wastewater.

The soil properties are characterized as high clay and $CaCO_3$ content and low Na^+, this will significantly impact the bioavailability and mobility of heavy metals through mobile colloids in soil samples. This will use as indicator to show the incremnetal of heavy metal and the fact that there are no secondary enrichment of heavy metals in subsoil horizons.

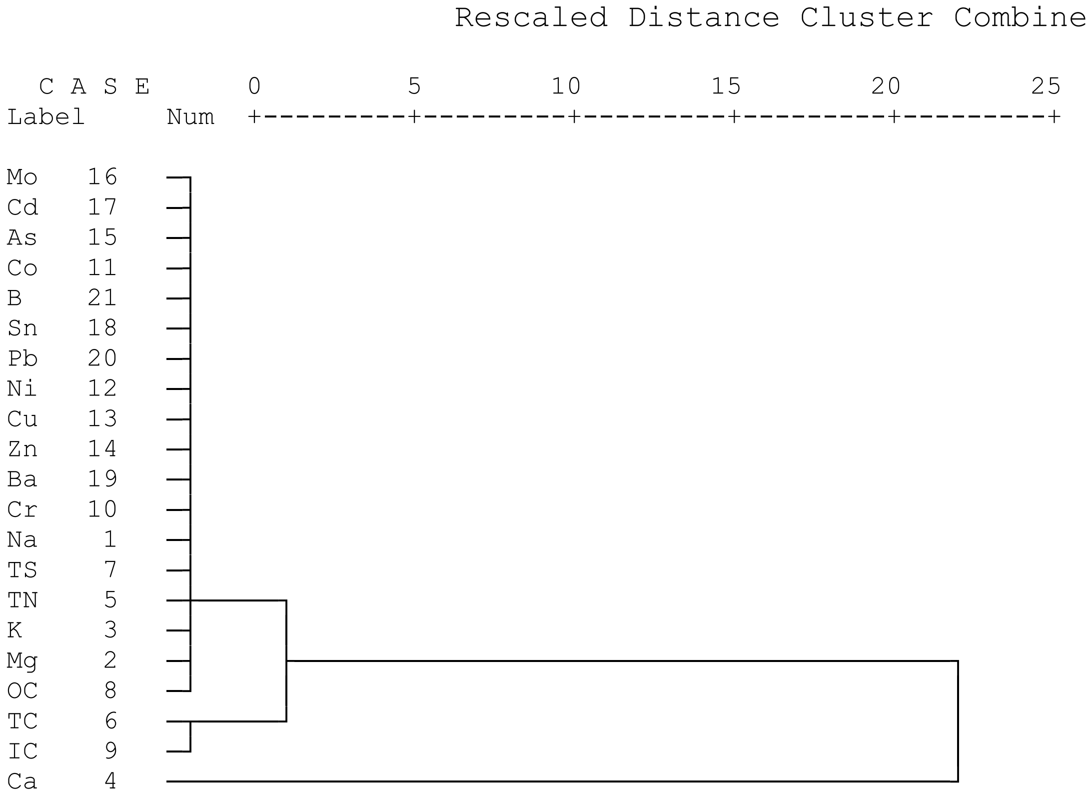


Figure 3.7: Hierarchical Cluster Analysis for trace metal in soil and other parameters.

3.8 Comparison between the trace metals in wastewater, sediment and soil

Results indicate that trace metals concentartions in wastewater samples are low; this is not significant to reflect the pollution sources or the enriched site if compare with sediment or soil samples. Sediment samples are predominated by trace metals and have the highest concentrations for Cu, Zn, Sr, Ba, Hg, Pb, Bi and B. On the otherhand, soil samples are predominated for Cr, Co, Ni, As, Mo, Cd, Ag, Sb, Sn, Li and Be, most of these trace metas are not available in water in detectable concentrations (Figure 3.8).

Mobility and transportation factors between water, soil and sediment for heavy and trace metals in Al-Qilt are depend on the pH change, this affect other parameters such as organic matter, sodium and carbonate contents. Since, clayey soils with moderate and alkaline pH with high $CaCO_3$ content are considered to have low mobility and bioavailability that based to binding capacity (Cameron *et al*., 1997). Moreover, no correlations are found between Ca as ion and IC as carbonate form with any of the trace metals, this indicates that the major and physical parameters are serving as media that retard or prevent the trace metals from free movement in the environment.

On the otherhand, the mobility and transportation of heavy metals are highly depend on the soil and sediment pH media, it is reported to transport by different pathways using Na^+-rich soils, hence, in situ mobilization colloid particles is important, this will decrease the ionic strength and cause increase in pH, moreover, the replacement of divalent cations by monovalent cations as Na^+ occurs (Kretzschmar *et al*., 1999). Na^+ is correlate with Zn^{+2} and Pb^{+2} in the wastewater samples, and not correlated with any parameters in sediment or soil, this resulte due to the higher solublility of Na^+ in water phase if compare to the solid phase, this make it easily to exchange the trace metals and then easily reallocate.

Heavy and trace metals are release in lower acidic pH conditions, and it will hold in case of the soil is highly buffered e.g. high carbonate content. Moreover, solubility of metals could increase at high pH due to binding for example with DOC values; this should dissolve more organic at high pH (Adriano, 2001). On the otherhand, OC are highly variey between wastewater, sediment and soil and it is highly correlate with Sb in wastewater and sediment, but there are no correlation with any of the trace metals in the soil, this mean that any increment in the pH values will increase the solubility for OC and more Sb will transport or reallocate in the wastewater along Al-Qilt.

Figure 3.8: Sediment, soil and wastewater comparison, units for sediment and soil mg/kg DW and for wastewater in µg/l.

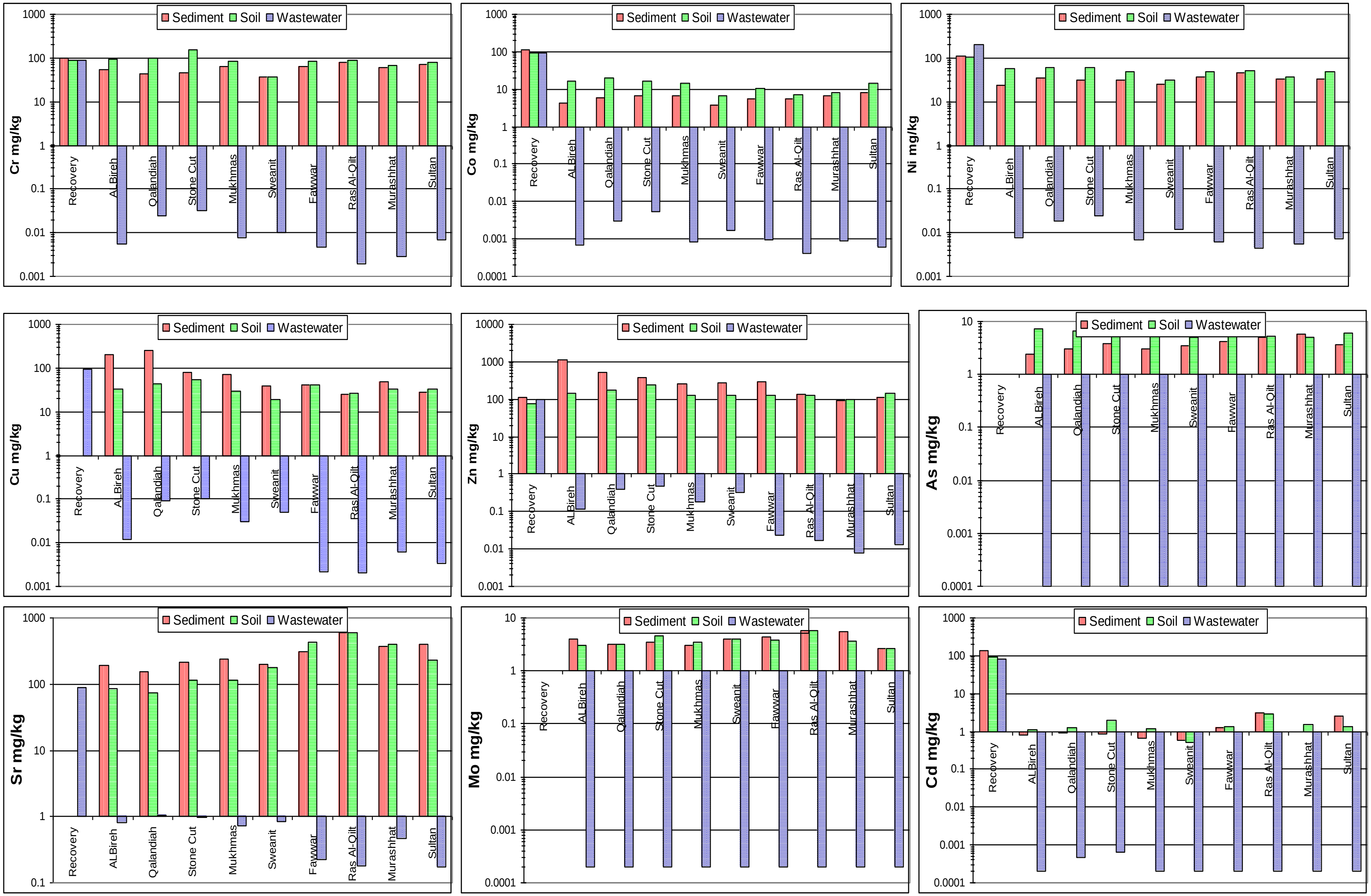


Figure 3.8: Sediment, soil and wastewater comparison, units for sediment and soil mg/kg DW and for wastewater are in µg/l.

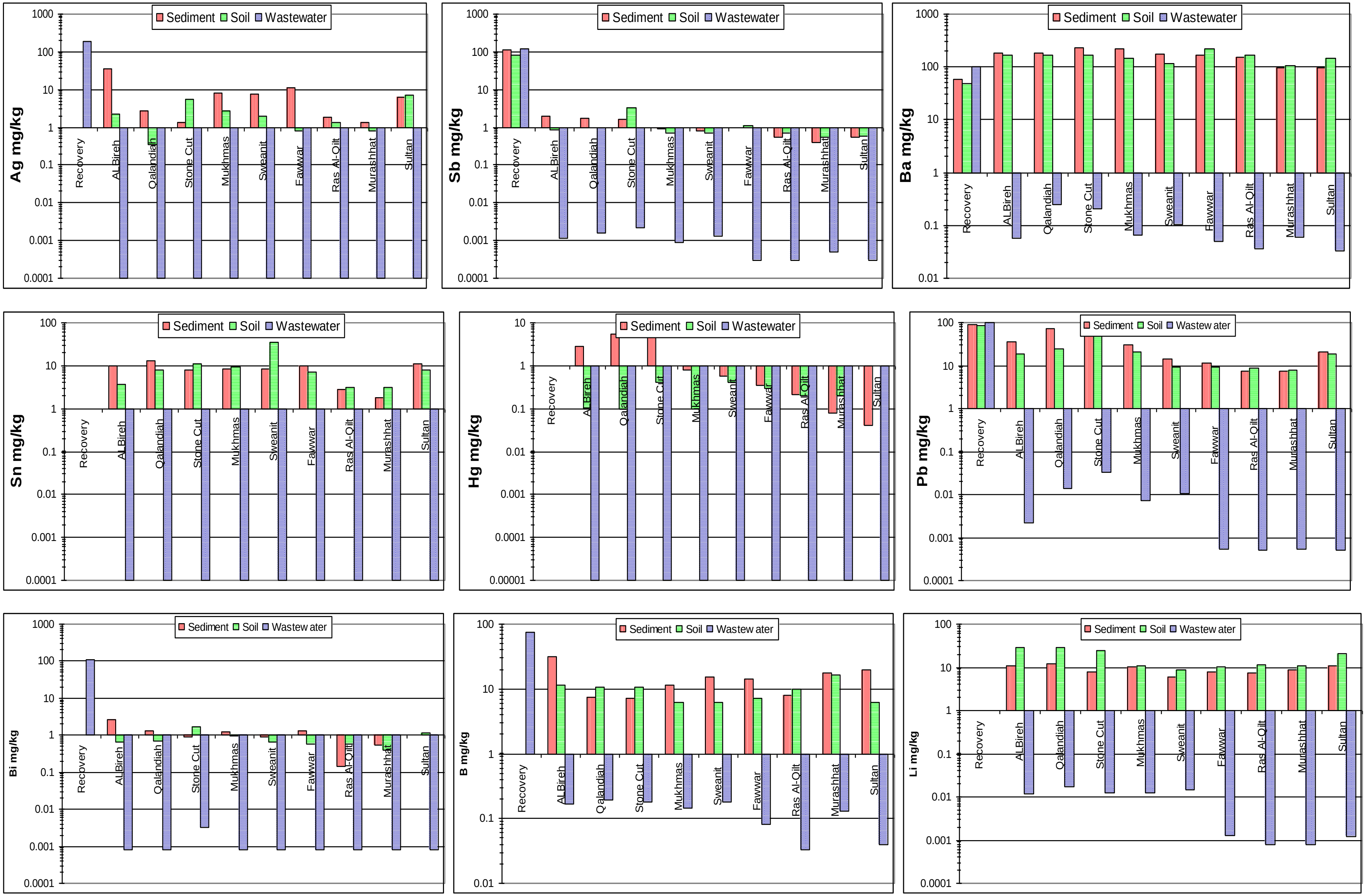
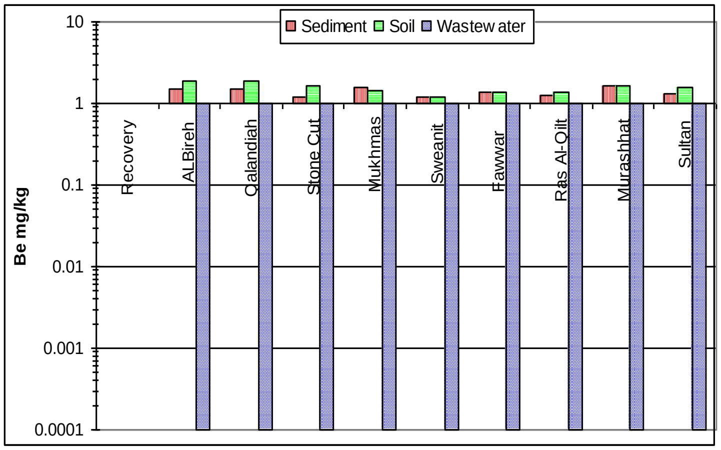


Figure 3.8: comparison among Sediment, soil and wastewater contents of the studied trace metals. Units for sediment and soil are in mg/kg DW and for wastewater in µg/l.



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Chapter 4

Sequential Extraction Procedures for Sediments and Soil Using the Bureau Communautaire de Reference (BCR) Method

4.1 Abstract

Sediment and soil samples are collected from nine different sites from Al-Qilt catchment. The samples include: wastewater discharge (raw and treated), industrial (quarry and industrial zone), traffic (roadside), wadis (open field) and springs (groundwater). The sediment samples are analyzed for trace metals. High concentrations of Zn, Ag, Sb, Bi, Cu, Hg, Pb and Ba are found at the upstream of Al-Qilt catchment, also high concentrations of Cd, Mo, As Cr, Co, Ni, Sr, Sn and B are found at downstream. For soil samples high concentrations of Co, Ni, As, Zn, Cu, Li, Be, Cr, Sb, Pb, Bi and Sn are found at the upstream and high concentrations of Ba, Sr, Mo, Cd, Ag and B at the downstream. There are similarities between sediment and soil samples for the occurrence of trace metals at the upstream for Zn, Sb, Pb, Bi and Cu, the occurrence of trace metals at downstream for B, Sr, Mo and Cd. This indicates that there are varation in there occurrenece and effected by accumulation of trace metals beside other anthropogenic sources of these parameters.

Sequential extraction procedure is applied according to the method recommend by the Standards Measurements and Testing program of the European Union (SM&T– formerly called BCR). This method is used to determine heavy and trace metals fractionation in sediment and soil samples. Results reveal that there are consence between the pseudo total digestion values and the summation of BCR fractionations values for both sediment and soil samples. Moreover, the BCR fractionation give indication for mobility or transport of B, Cd, Sb, Pb, Cu, Hg and Sn in an aquatic environment, this show that there is risk from their reallocation at Al-Qilt catchment.

Furthermore, by using the guidelines such as the Continental Crust (CC), Elemental Background for Soil (EBS) and USEPA, results reveal that it is better to use the EBS if they are highly varied if compared to CC values. Behind this there is basic reason for the difference in elevation between the upstream and downstream, this reach to 700m.

4.2 Introduction

Sediments play an important role in aquatic systems as sink and can trap various types of pollutants. Sediments also can store anthropogenic pollutants of the overlying water due to their ability to sequester metals, thus it is good indicator for water quality monitoring. Furthermore, it is important to record the anthropogenic effects before and after the re-suspension. Sediments are widely used in environmental pollution studies due to their low susceptibility from reach to water column. In addition, sediments charactaristics change according to environmental conditions such as pH or redox potential; this will effect the remobilization of the trapped metals (Baudo, 1990).

Trace and heavy metals exist in different mineral and combination forms in soils, rocks and sediments, this will vary according to various conditions, for example the pH, redox conditions, oxidation states, temperature and organic matter, then it will have influence on mobility, transformation and accumulation of trace metals in ecosystem. These factors strongly influence the geochemical cycles of elements in the environment mainly in acidic conditions, simple cations and complexes of chloride and sulfate exist in neutral and alkaline conditions as carbonate complexes, this will work as predominate and controlled by acidity (Kotand A and Namiesnik J, 2000).

Trace metals in sediments exist in different chemical forms and binding. For example, in unpolluted soils or sediments binding to silicates and primary minerals is relatively immobile whereas in polluted soils trace metals are generally more mobile and bind to sediment phases (Rauret, 1998). However, the evaluation of binding or fractionation is very difficult due to the intrinsic complexity of sediment-water system; different variables are determined the behavior of the aquatic systems or the genesis of these sediments (Forstner, 1993). In addition, the type of weathering and processes that control the transport and redistribution of the elements such as adsorption, de-sorption, precipitation, solubilization, flocculation, surface complex formation, ion exchange, and penetration of the crystal structure of minerals are relevant (Raiswell, 1983).

In particularlly, the Lead and Cadmium are two elements studied in street areas but very little attention has been given to other trace elements such as Cr, Cu, Zn and Ni that are frequently encountered in the urban environment (Sutherland R.A and Tolosa C.A., 2000).

Environmental and health effects of trace metal contaminants in dust depend initially on mobility and availability are function of their chemical speciation and partitioning within dust matrices. The identification of the main binding sites and phases associate with the trace metals in soils and sediments help to understand geochemical processes. This allows assessing the potential for remobilization with changes from the surrounding chemistry, especially pH and total solid (Hall *et al.*, 1996). It is difficult to solve these problems to understand the release processes and to control the availability and transportation of trace metals in the particle-water interfaces such as at Al-Qilt.

It is proven fact that the mobility, availability, toxicity or essentiality and fate of an element depends on the form it occurs rather than its total concentration. Recently, attention are shifted from the determination of total heavy metals in sediments to other techniques that focus on the determination of sequential extraction techniques to ascertain the solid-state fractionations for metals in sediment and soil to transport and store in the urban environment, this will give considerable loading to the metals that are received by water bodies that depend on the changes of the environmental conditions (Morrison *et al*., 1990).

With widespread accumulations of metals in sediment and soil, it is important to understand the processes in which the metals are held and mechanisms to mobilize, especially in environments that have organic soils (Tipping *et al*., 2003). It is essential to understand the processes by which metals are bind to the sediment or soil and the conditions for release. Such procedures are used to assess metal leaching from soil and sediment (Tokalioglu *et al*., 2003). For example, the use of reducing or oxidizing agents is related directly to the release of metals under different redox conditions (Ure *et al*., 1993 and Quevauviller *et al*., 1994).

Chemical speciation analyses deal with the determination of individual species such as fractionation or operational speciation; these involve the determination of elements that associated with predefined phases or fractions in the matrix. Fractionation is analyzed by attacking the particular phase with a selective reagent to release metals. A fraction describes the group of species in sample that can isolate from the matrix due to special properties. In addition, sequential extraction procedures have been applied to soils and sediments to characterize their respective metal fractions by selectively targeting and releasing metals that bound in certain geochemical phases such as carbonate, iron and manganese oxide/hydroxide, sulfide, organic and silicate (Tessier *et al*., 1979).

For solid phase fractionation the Sequential Extraction Procedures (SEP) are applied. In SEP there are several selective reagents are used to extract ‘‘operationally defined phases’’ from solid matrix in a set of sequence. The most commonly isolated phases in different sequential extraction schemes are: exchangeable "carbonate bound", Fe-Mn oxide bound (reducible), organic (oxidisable) and residual (Figure 4.1).

Although this method has some problems regarding of selectivity and re-sorption and there are agreements between different studies on soils, sediments and street dusts (Tessier *et al*., 1979).

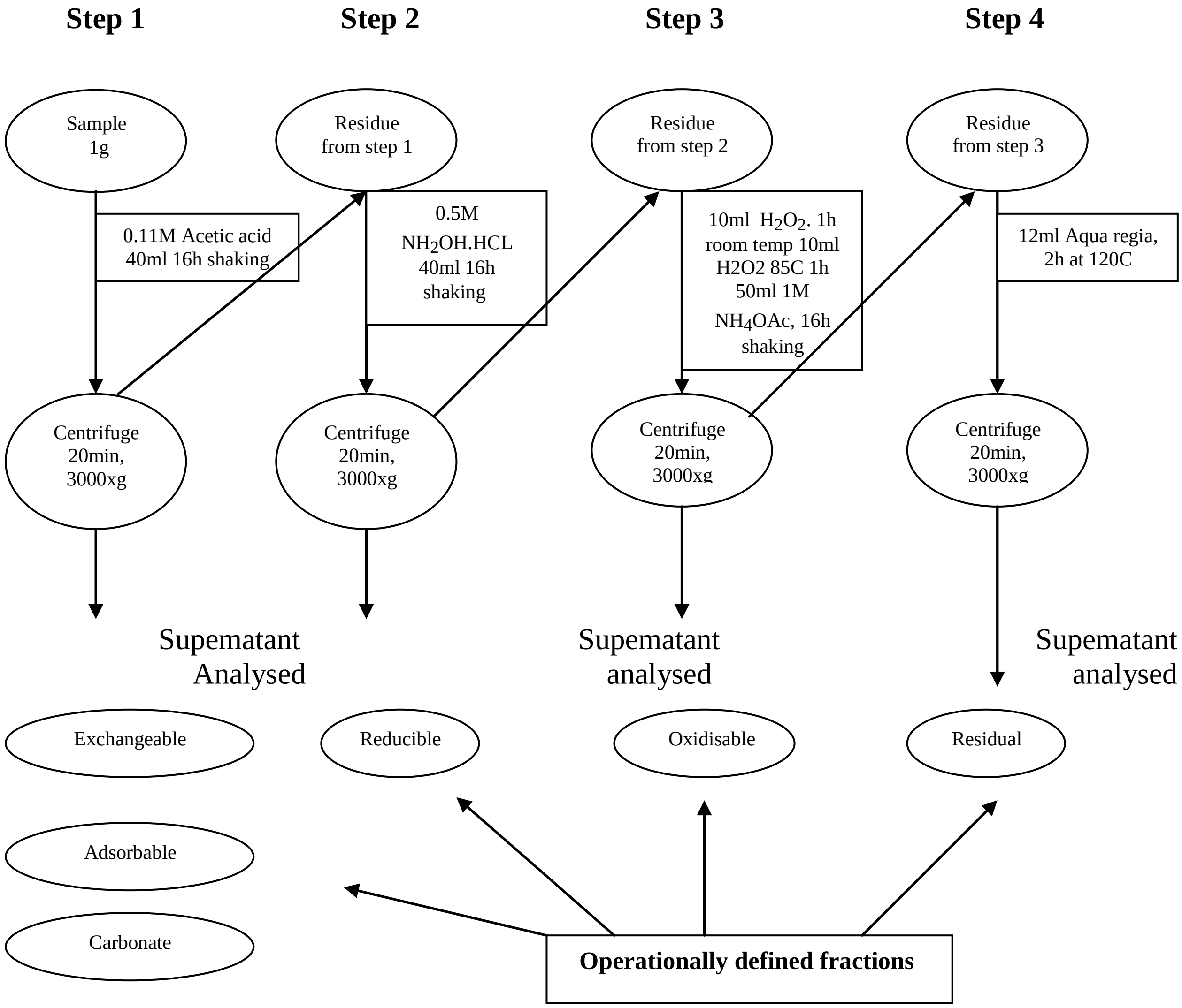


Figure 4.1: Schematic representation of the BCR 4-satges extraction scheme and reagents used.

Tessier *et al.* (1979) extraction scheme separates the elements into five operationally defined host fractions and does not distinguish between an easily reducible fraction that associate with 'new' manganese oxides and amorphous iron oxides and moderately reducible fraction that associate with 'aged' manganese oxides and crystalline iron oxides. In view to the previous study more comprehensive sequential extraction scheme used by Chester *et al.,* (1988), his study try to modify or answer to some questions in scientific manner. In addition, there is problem in the sequential extraction appear if the results from different procedures or data are compared, but no reference material and just depend on experimental conditions without taking into consideration the matrix effect between parameters in the sediment. This type of analysis does not enable the quality of measurements to control or verify their results (Lopez-Sanchez *et al*., 1993). Results are useful only if they correspond to well-defined and accepted procedures to assess acceptable accuracy and make the results comparable elsewhere (Griepink, 1998).

In previous discussion several terms are used such as: speciation, operational speciation (fractionation) and transformation species. Therefore, the IUPAC committee (2000) has offered definitions to clarify the situation as follows:

1. Speciation of an element is the distribution of defined chemical species of an element in the system; it is used to identify and quantify of chemical forms.
2. Fractionation refer to the process of classification of an analytic or group of analytic for certain sample according to physical (size and solubility) or chemical (bonding and reactivity) properties. It refers to quantify of binding forms that are extractable under different types of experimental and chemical condition.
3. Transformation species are describe as the change that occur between the leaching trace metals from soil or rock and their subsequent distribution in the aquatic environment.

Speciation and fractionation are used interchangeably as the main difference between two techniques that lies in speciation analysis, the true identification of definite species is sought while in fractionation of the total metal content of an operationally defined fraction is obtained.

For this study, the four steps of sequential extraction method will use with certifeid trace metal such as Sediment Reference Material (SRM 701). This method is named Community Bureau of Reference BCR as sequential extraction procedure Sahuquillo *et al*., (1999). The BCR proposed a sequential extraction procedure in 1992, this is accepted by large group of specialists were attended the "Workshop on Sequential Extraction in Soil and Sediments" held at Sitges, Spain (Ure *et al*., 1993).

4.3 Objectives

The objectives of this chapter are:

1. To study the occurrences of ubiquitous trace and heavy metals in sediments and soil using pseudo digestion.
2. To study the association of the trace metals and binding in sediment and soil in exchangeable, reducible, oxidisable and residual form by using the sequential chemical extraction procedures.

3. To assess the mobilization and release of trace and heavy metal inventories at the solid phase.

4.4 Methodology

4.4.1 Sampling and digestion by Aqua Regia

The samples are collected in June and October 2008 and June and October 2009 from nine sites. Samples are collected using Polyvinylchloride corer, placed in polyethylene Jar and then frozen when reaching the laboratory for analysis. The sediment samples are frozen using deep freezer for 4-6 hours to -30^{0}C, then, using "CHRIST, Delta 1-24 LSC" the samples are frozen-dried and evaporated for four days. About 200-250g from the sample has been sieved to <63µm using "Fritsch D-55743" sieving analyezer, 0.25g from each sample and Buffalo Reference Material (8704) as reference standard are measured 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.

Trace metal concentrations are measured using Inductive Coupled Plasma Mass Spectra ICP-MS (Agilent 7500 ICP-MS) for Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ag, Cd, Sn, Sb, Ba and Pb. Hg is analyezed using the Flow Injection Mercury System (FIMS 400).

For BCR fractionation analysis about one gram from the samples are weighted for the BCR four steps method (Figure 4.1). All analyses are done in the Water Research Center (UFZ), Magdeburg, Germany.

4.4.2 BCR sequential extraction procedure

The fractionation of native indigenous metal species is differ from anthropogenic indicator in which the mechanisms of sorption and subsequent desorption are different, these can be identified by use of sequential extraction procedures. Consequently, fractionation of metals defines in terms of extraction mechanism and used to release the metals rather than to discrete geochemical phases Gomez-Ariza, (1999). Sequential extraction schemes have been proposed for the determination of binding forms of trace metals in sediment and soil samples. This scheme is good to compare and provide practical method to give information for environmental contamination and risks in spite of being operationally defined procedures. The BCR is now the

Measurements and Testing Program of the European Commission summarized in Table 4.1 and Figure 4.1. According to Ure *et al*., (1995) and other researchers this method is recommended as standard procedure for the characterization of heavy metals in soils and sediments. The BCR procedure is applied to the readily available BCR 701 Lake Sediment Certified for the four step sequential extraction as Standard Reference Materials.

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 4.1):

Table 4.1: Reagents and conditions 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×*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.

4.4.3 Quality control for fractionation using BCR (701) and Sediment Reference Material (8704) for Pseudo total digestion

BCR 701 is used for fractionation steps and the Sediment Reference Material (8704) for total digestion; both are available on the market and those provide the extractable content of four-predefined fractions of the improved BCR and 8704 for total digestion. The shortcomings from the usage of these standards are two-fold: First, the material certified for the contents for some of popular trace elements. Second, the distribution of metals under batch static conditions is not expected and it is dynamic conditions.

4.4.4 Legislations and guidelines

For sediments and soils this study will use the Continental Crust (CC) values according to Wedepohl (1995) and the Elemental Background for Soil (EBS) from pristine area, these will use to compare the occurrences of trace metals in the national and regional level (Table 4.2).

Table 4.2: The CC values of trace and heavy metals according to Wedepohl, (1995) and the EBS median values, units are in mg/kg DW.

Parameters	**CC**	**EBS***	**Parameters**	**CC**	**EBS***
Cr	126	82.5	Cd	0.1	1.48
Co	24	8.3	Sn	2.3	2.7
Ni	56	47.5	Sb	0.3	0.7
Cu	25	28.9	Ba	584	132
Zn	65	126.9	Hg	0.1	0.25
As	1.7	5.4	Pb	14.8	8.7
Sr	333	410.5	Bi	0.1	0.16
Mo	1.1	4	B	11	2.6
Ag	0.1	0.75			

* This study

For soils the guidelines are used by the US Environmental Protection Agency (EPA, 1993) these are allowed to receive as pollutants by the soils. Of the eleven most common parameters that dominate and contaminate in the US National Priority List sites (called superfund sites) six of them were trace metals such as Pb, As, Cr, Cd, Ni and Zn. In addition, the USEPA (1993) is issue for metal that relative to soil applications of municipal sewage sludge on arable land and maximum cultivated loading. Then they reach the definition of Maximum Permissible Pollutant in the receiving soil (Table 4.3).

If the pollutants of industrial origin are not prevented from entering the wastewater collection and treatment systems, the land application of both reclaimed wastewater and sewage sludge must be carefully monitored as pollutant inputs, this may be substantial for the upper thresholds for pollutant loading concentrations in soils (EPA, 1993).

The values presented in the Table 4.2 are derived strictly from computation; these involved the empirical parameter values, these were estimated with applied method in the uniform system for the evaluation of substances (USEPA, 1993).

Table 4.3: The Maximum Permissible Pollutant concentrations in the receiving soils (USEPA, 1993) and (EPA, 1993):

Inorganic Element	Soil Concentrations (mg kg^{-1})	Inorganic Element	Soil Concentrations (mg kg^{-1})
Ag	3	Mo*	0.6
As	8	Ni	107
B*	1.7	Pb	84
Ba*	302	Se	6
Be*	0.2	V*	47
Cd	4	Sb	36
Hg	7		

*The computed numerical limits for these elements were within the range that is typical for soils.

The numerical limits for B, Be, Ba, Mo, Tl, and V were comparable to the typical concentration of soils around the world. The overlap of computed numerical limits to their respective typical concentrations in soils is indicated the in land application of reclaimed wastewater and sewage sludge. The margin of safety for these elements may be narrower than other elements. The USEPA can only provide approximations, the parameter values for B, Be, Ba, Mo and V require care evaluation and further refinement. The Maximum Permissible Pollutant concentration of soil is more suitable as reference point, it is establishes the upper limit without the need of accounting the possible past or future pollutant inputs from other sources.

4.5 Result and discussion

4.5.1 Result and discussion for trace metal in sediment

4.5.1.1 Pseudo digestion and summation of BCR steps for sediment

Summations for pseudo digestion, BCR steps and recovery values for the trace metals are calculated in median values (Figure 4.2). Recovery values are in range of ±15 for Co, Zn, Cd, Sb and Pb; results according to these certified parameters are acceptable and will support the interpretation for these elements. On the otherhand, the results for Cr, Ni and Ba are not consistent with the summations of BCR and pseudo digestion values. This is due to less solubility and different affinity for trace metals as complexes in sediments. However, there is inconsistances between the summations of BCR steps and pseudo digestion. Nevertheless, if we compare between the values at each site with the (CC) or (EBS) values, it is better to use the EBS, since there are variations if compared to CC values. Furthermore, for quality control of the BCR summation and pseudo digestion is applied and the BCR (701) is used as reference, also for pseudo digestion the Buffalo (8704) is used as reference are consistences with the certified values and most of the parametres are within the acceptable limits (Figure 4.2).

Results reveal that Zn, Ag, Sb and Bi have the highest values at Al Bireh "treated wastewater", Cu, Hg and Pb have the highest values at Qalandiah "raw wastewater", Ba has the highest values at Stone Cut "query", Cd has the highest values at Ras Al-Qilt "spring", Mo and As have the highest values at Murashahat "water treatment plant" and Cr, Co, Ni, Sr, Sn and B have the highest values at Sultan "spring" (Figure 4.2).

Results of Al-Qilt sediments reveal that Sn, Cu, Ag, Ba, Bi and B are high if compared to Elemental Background for Soil values, these incremental due to enrichment for different anthropogenic sources in Al-Qilt. On the otherhand Cr, Co, Ni, As, Sr and Cd are below the Elemental Background for Soil values, thus these parameters are considered as background values at all sites of Al-Qilt catchment.

Furthermore, results reveal that Sb, Zn, Hg and Pb are enriched more at the upstream sites such as Al Bireh, Qalandiah, Stone Cut, Mukhmas and Sweanit, on the otherhand, Mo, As, Cd, B, Sn, Sr, Ni, Co and Cr are enriched at downstream such as Fawwar, Ras Al-Qilt, Murashahat and Sultan, most of these trace metals are drived from the deep aquifer and Cd, As, Cr, Co, Ni and Sn, this indicate that there are accumulations for anthropogenic as trace metals in the sediment. The sources for these trace metals are varied and due to wastewater, urban run off and roadside parameters. However, Ras Al-Qilt is located far away from the road but it is under the effect of wastewater that discharge from the upstream or by air by weathering depositions from the Israeli colonies, then water from Ras Al-Qilt is discharged throught open canal to Murashahat (as water treatment plant), but as mentioned the Cd has the highest value at Ras Al-Qilt soil and Mo and As have the highest values in sediment at Murashahat, these variations raise two important questions. Is the distance (10-12 km in canal) between Ras Al-Qilt and Murashahat responsible for the enhancement of Mo and As?, and what are the sources of the Cd incremental at Ras Al-Qilt? For the first question and according to Acharya *et al*. (2000) the source of arsenic in deltaic plain of West Bengal is considered as arsenic-rich sediments that transport from Chotonagpur Rajmahal Highland was deposited in sluggish meandering streams under reducing conditions. This is similar to the Al-Qilt case, the running water in the canal with function of time are under the effects of sun light, such these conditions are responsible to give sufficient time and suitable media to reduce and mobilize the arsenic to move in the aqua's phase and then accumulate in sidement at Murashahat. Furthermore, Mo incremental is due to its increace in Ras Al-Qilt soil (Chapter 5), since it is transported by SPM in the canal and deposited at the Murashahat sediment.

The second question, most of studies consistent that Cd incremental and depositions is due to urban runoff and roadside vehicles. However, Ras Al-Qilt is located far away from cars even though the results for soil indicate that Ras Al-Qilt has the highest value for Cd if compared to other sites in Al-Qilt. Thus, Cd incremental is due to geogenic or natural effects and probably due to weathering deposition or other human practices at upstream of Ras Al-Qilt or it is from the Israeli colonies.

Furthermore, the highest values of Cr, Ni, Sn, Co and As indicate that there are possibility of common sources of these trace metals in Al-Qilt springs. However, there are no metal processing industries in Al-Qilt such as electroplating, pickling or galvanizing; but, it is not known what exists or what type of industries inside the colonies in Al-Qilt catchment. Hence, around the colonies only "green sites" were found around the colonies, they discharge their wastewater to the Al-Qilt Wadi. This is the reason to increase for Cr, Ni, Sn, Co and As in Al-Qilt springs at dowenstream, as these trace metals origin from automotive sources such as wear and tear of vulcanized rubber tyres, lubricating oils and corrosion of galvanized vehicular parts as well as from giogenic effects (Anju Banerjee, 2002). Moreover, at Al-Qilt sites the incremental of trace metals in sediments such as Zn, Hg, Ag, Sb, Pb and B that originates from domestic wastewater, urban runoff and roadside pollutants in most cases.

The pseudo digestion concentrations for trace metals not indicate the potential mobility or sediment bound metals, since the fractionation studies provide ideas of the different type and strength of metal associations in sediments and varied with the form of metal. Thus, the sequential extraction will provide more precise information; this will be with high value to the decision makers understand and to estimate the environmental risks that posed by heavy metals.

Figure 4.2: Recovery values for trace metals in sediment, pseudo-digestion values (pink) and summation of BCR steps (blue). Results compared with CC Wedepohl (1995) results in red and EBS from the same study in yellow.

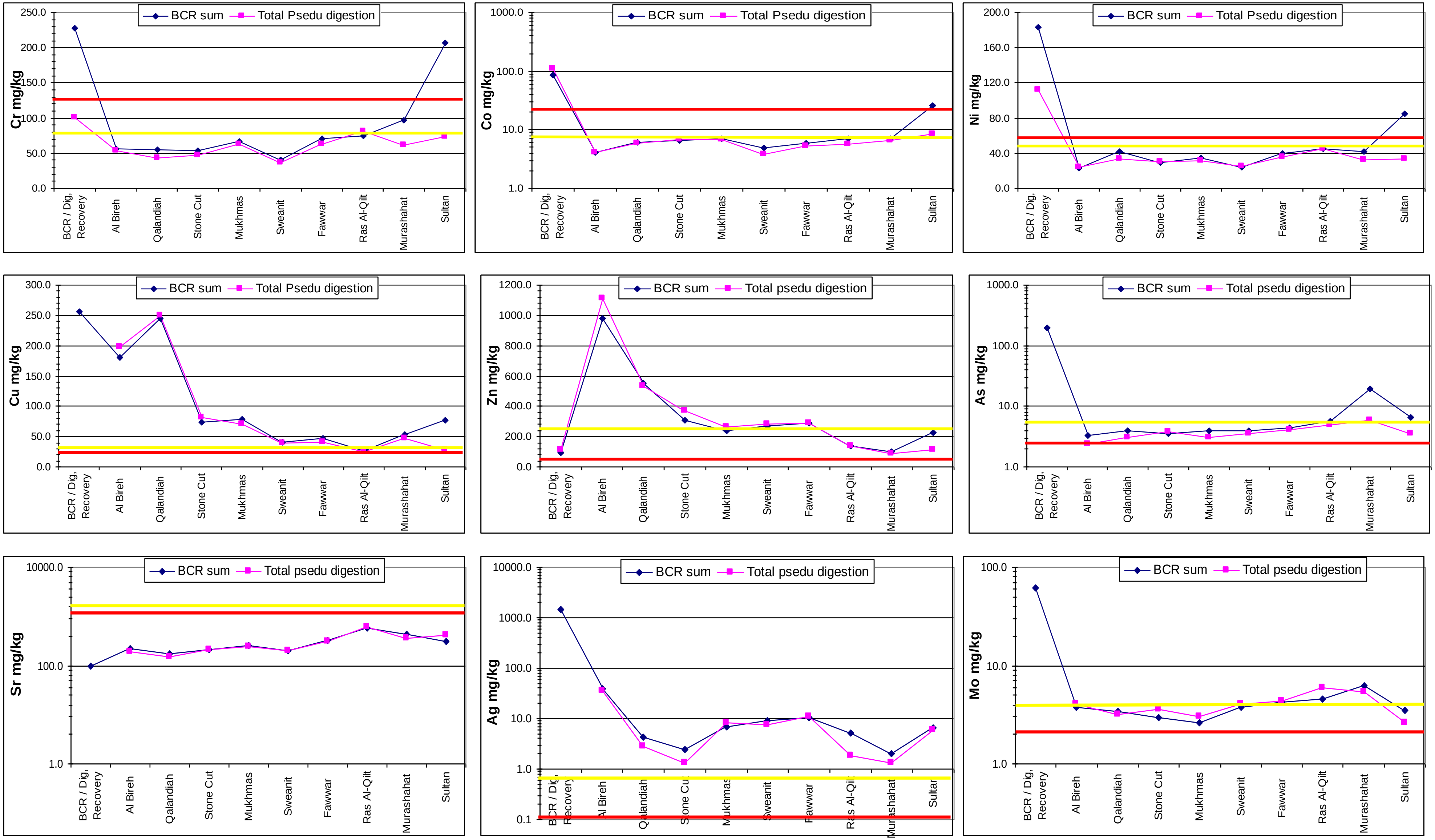
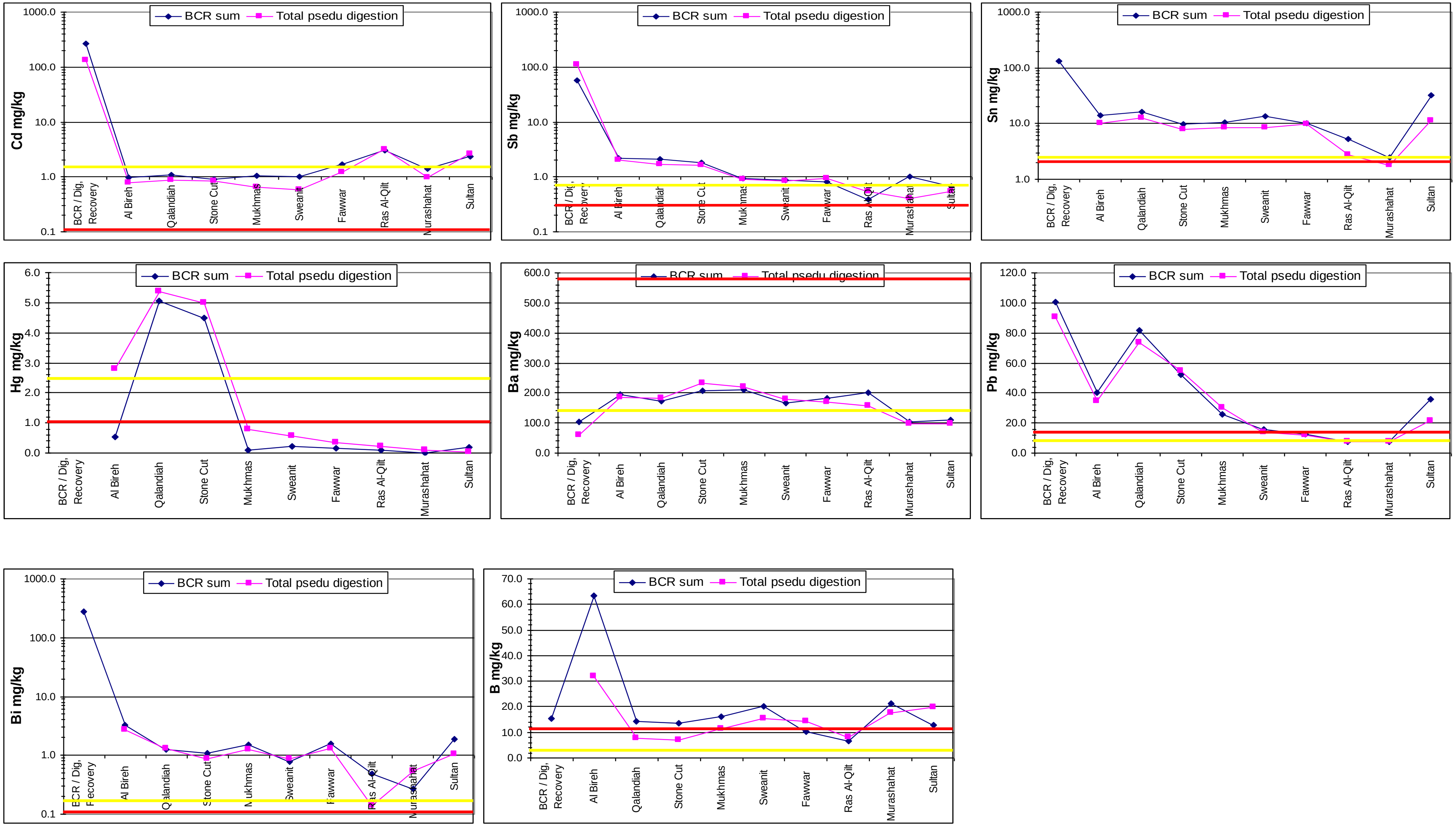


Figure 4.2: Recovery values for trace metals at sediment, pseudo-digestion values (pink) and summation of BCR steps (blue), these results compared with CC Wedepohl, (1995) in red line and EBS from this study in yellow.



4.5.1.2 BCR fractionation for sediments

Different metals from the same sampling sites show different behavior and fractionation pattern (Figure 4.3). For example, Sr and B exhibite more in exchangeable fractionation and predominates in most sites. Hence, the acid digestion method or exchangeable method indicates easy in mobility for the trace metals if there change from pH in the environment. Thus, there will be considerable amount of trace metal easly release to the environment if acidic conditions ocurrs. This exchangeable fractionation is in the sediment and soil; therefore, it is the most dangerous for the environment if it is predominant or even extended to the second fractionations.

The reducible fraction is predominated for Cd and Ba and the next fractionation is oxidisable for Cd and residual for Ba. This fraction theoretically represents the contents of metal that bound to iron or manganese oxides; these will release if the sediment are subject to reductive conditions (Panda *et al.*, 1995). Therefore, the results may be low if the carbonates have not been completely dissolved or if parts of the iron or manganese hydroxides have already been extracted in the previous stage. In this study the carbonates are in dissolve form at the reducible stage, since Cd and Ba have the highest concentrations at this stage. Furthermore, it is important to mention that these two stages (acid soluble and reducible) are the most mobile phases of the four fractionation stages; in addition they are the most dangerous for the environmente due to mobility and transport for trace metals. Thus, it is important to look at the next fractionations for the trace metals in the following two stages; it will have more impact if it is in exchangeable or reducible fractionations.

The behaviors of Bi, Co, Mo, Pb, Cu and Zn are in the oxidisable fractions and they predominate in most sites. These results are in consistence with other studies, for example Cu in most cases appears in oxidisable fractionations according to the studies by Licheng and Guijiu (1996). In addition, high proportion of Cu in the sediments may form bonding to organic matter and Cu easily that transport in the complex form, since, this fraction show the amount of metal bound to organic matter and sulfur and some time there is correlation between Cu and organic carbon and sulfur parameters (Chapter 3). These parameters are released to the environment if conditions become oxidative so this change may occur during dredging conditions (Forstner, 1989). In this fractionation there are a lot of parameters originated from urban runoff, roadside and wastewater that runs to the wadis. The runoff will have more time to form of complexes with organics and sulfur and then will leach if oxidative conditions occurr.

Moreover, results for the residual fractions are predominanted for Hg, Sn, Ag, Cr, Ni, Sb and As in most of sites. In this fraction the metals are associated strongly in the crystalline structures in mineral form, since it is difficult to separate them from the sediments or it is need extreme conditions to liberate the trace metals to the environments. The next fraction at this stage for Hg, Sn and Ag are exchangeable fraction at Murashahat, Fawwar and Sultan respectively, this will have impact from these parameters, since their occurrences are highly restricted if water is used for domestic purposes. Thus, these springs must be kept under control and monitored for these parameters, moreover the next fractionation for Sb, Cr, As and Ni is the oxidizable, this fraction is save if compare to the exchangeable and reducible fractions.

Considering these facts the metals under the least mobilized fraction will be at the residual, then oxidizable fraction, in which hard conditions are requested to release or liberate the trace metals. Trace metal in the residual fraction are at Al Bireh, Qalandiah, Stone Cut, Mukhmas and Sweanit, these are located at upstream of Al-Qilt from wastewater that discharge as raw or treated. Therefore, there are risks from its accumulations, these risks increase if the conditions are in exchangeable or reducible fraction due to their mobility and transport. This will be maximize if karstic system such as Al-Qilt catchment. On the otherhand, the behaviors for these parameters in the residual fraction are similar at downstream mainly at Fawwar, Ras Al-Qilt and Sultan springs except for Hg, Sn and Ag.

In general results for fractionation to Bi, Cu, Cr, Sb, Mo, As, Zn and Ni are increased at downstream if compared to upstream, this is influence by chemical transformation of bonded legend or the caution species, this will force the trace metals to react under saturated or unsaturated zone, if results at Al-Qilt are compared with studies from other countries for metal fractionations in sediment. For example, similar partitioning patterns that reported for Cr and Ni (Dollar *et al*., 2001) also for Ni (Klavins *et al*., 2000) and for Pb (Howari and Banat, 2001).

Moreover, results indicate that fast leaching metals are more accessible for trace metals to reallocate or transport, while slow leaching metals are less accessible and they need more time to release from the sediment to the environment. This leaching decreases from the exchangeable to the reducible to the oxidisable and then to the residual.

The sequential extraction procedure illustrates the variability of fractions of trace metal it is implay that the actual environmental threat pose by these metals will depend on the local environmental conditions.

As results, the four steps of fractionations are in comparative between trace metal and their affinities in different solid phase fractions, this can be arrange according to the stage of fraction, hence, the highest percentage of Sr and B are in the exchangeable and carbonate bound fraction, while Cd and Ba are the highest in reducible fraction and Pb> Cu> Zn> Bi> Co> Mo in oxidizable and Hg> Sn > Sb> Ag> Cr> Ni> As in residual fraction. Despite their high levels, the low percentages of these trace metals in four fractions indicate that there are limitations of the easly for mobility in the environment according to the tested parameters.

Furthermore, by assumption that the mobility is relate to the solubility or geochemical forms of the metals, it is decrease in the order of extraction fractionation from exchangeable to residual, the mobility and metal availability for these contaminated sediments guide to mention that mobility of metals in sediment, this can be estimate from the ratio of the extractable content / total metal content, they are decreased in the following order: Sr> B> Cd> Ba> Pb> Cu> Zn> Bi> Co> Mo> Hg> Sn> Sb> Ag> Cr > Ni >As.

Figure 4.3: BCR fractionations with regard to exchangeable (blue), reducible (violet), oxidizable (light yellow) and residual (light turquoise) for trace metal in sediments along Al-Qilt catchment.

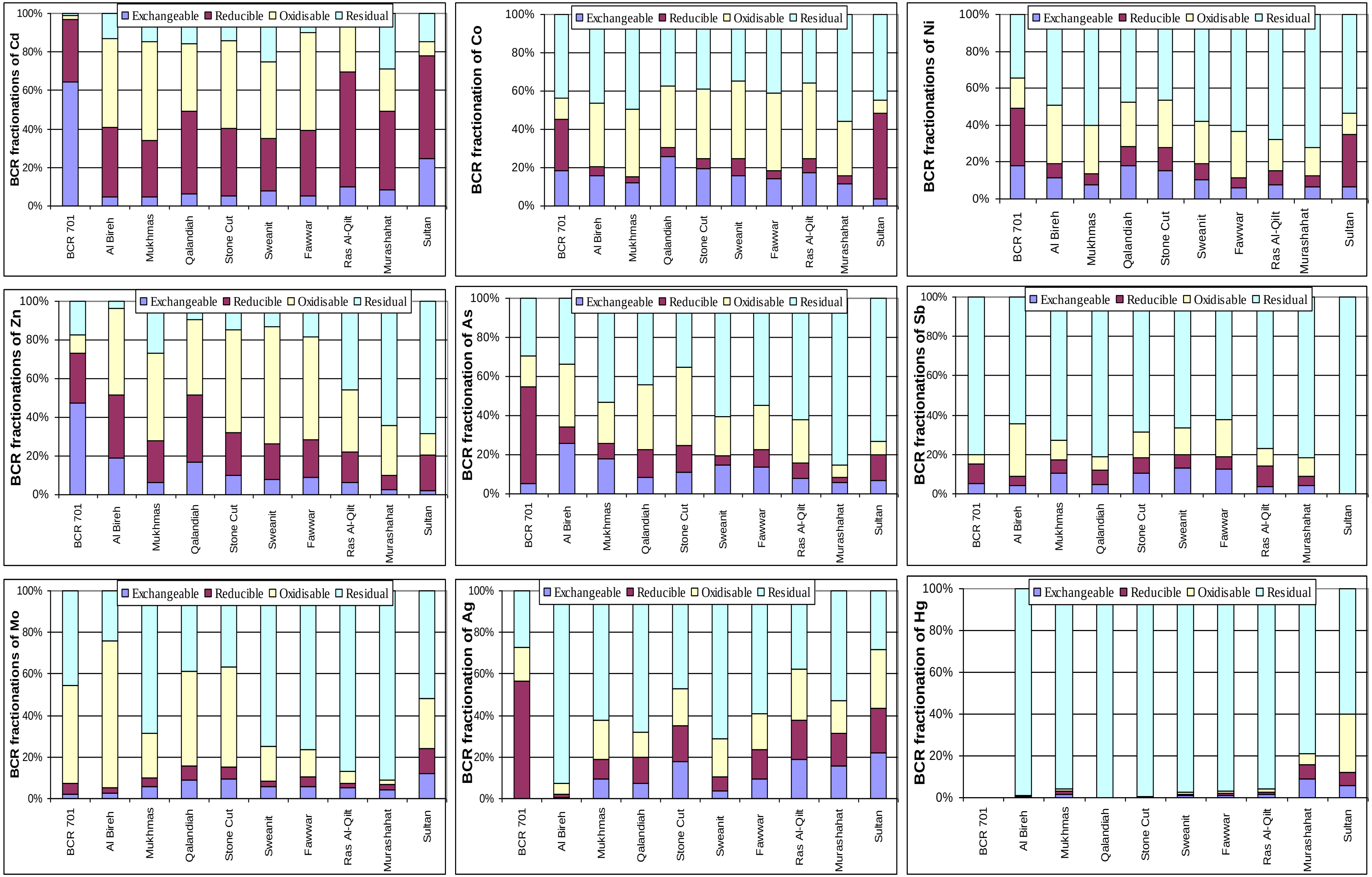
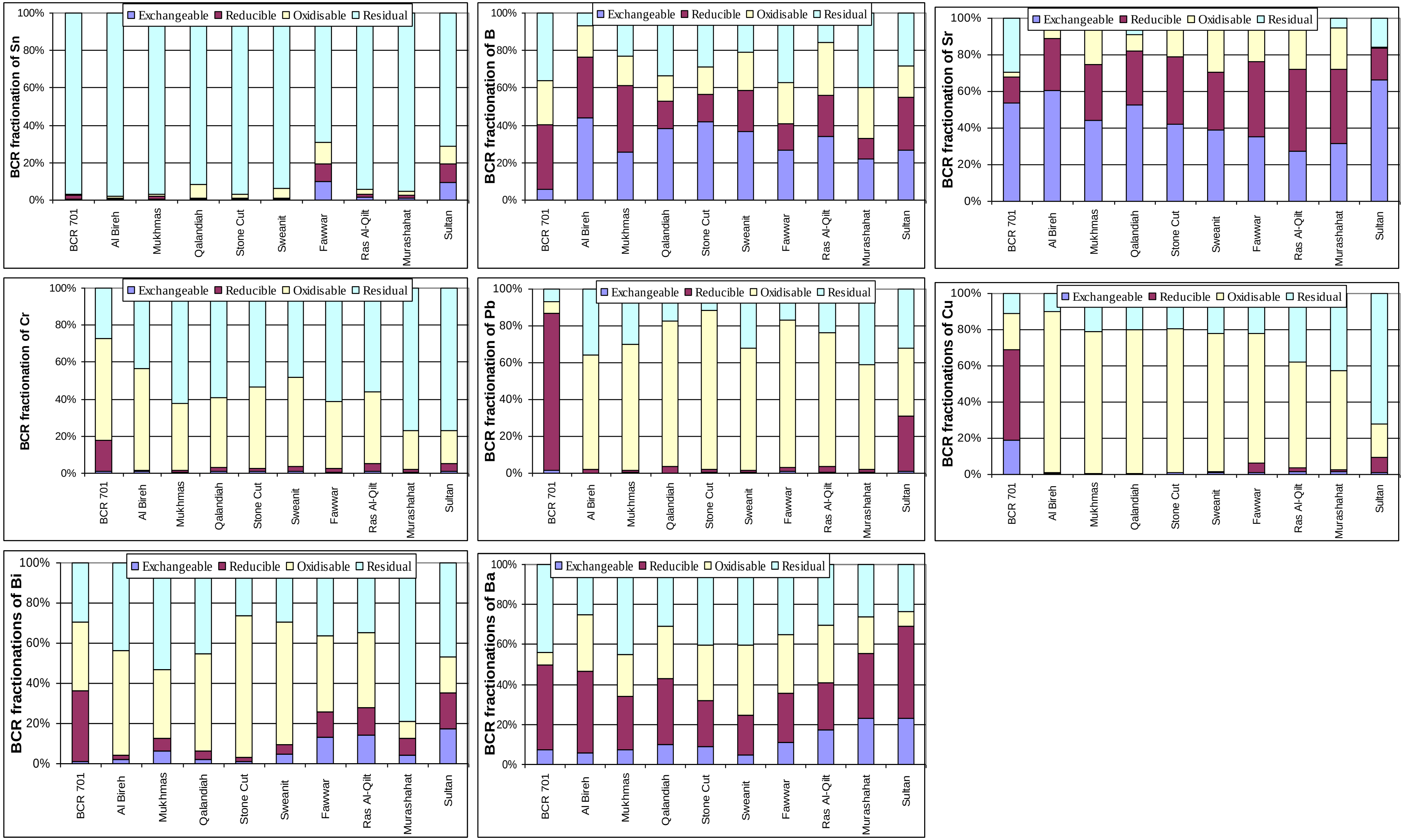


Figure 4.3: BCR fractionations with regard to exchangeable (blue), reducible (violet), oxidizable (light yellow) and residual (light turquoise) for trace metal in sediments along Al-Qilt catchment.



4.5.2 Results and discussion for trace metal in soil

4.5.2.1 Pseudo-digestion and BCR summation

Results for pseudo-digestion, BCR summation and recovery values for the certified parameters, all values are in median (Figure 4.4). The recovery values are in range of ±15 for the certified trace metals. This is acceptable except for Ba with 50% for pseudo digestion it is with in 85% for BCR summation steps. Furthermore, as quality control the BCR summation is controlled by using BCR (701) as reference material and for pseudo digestion is controlled by using the Buffalo (8704) as reference material, results are acceptable for the analyzed trace metals and support the interpretation for these elements to reduce the mineral component that varied within the soils matrix.

Result for Co, Ni, As, Zn, Cu, Li and Be are the highest values at Al Bireh soil, Cr, Sb, Pb and Bi are the highest values at Stone Cut soil, Sn is the highest values at Sweanit soil, Ba is the highest values at Fawwar soil, Sr, Mo and Cd, are the highest values at Ras Al-Qilt soil and Ag and B are the highest values at Sultan soil. These variations of trace metals within sites are relate to difference in elevation and impact of anthropogenic polutance from waterwater, hence, the elevation at Al Bireh is in range of 700m above sea level and it decreases until 60-20 meters above sea level at Fawwar and Al-Qilt springs. The difference in elevation of about 700m will have effect from the change in the soil layers. Also it should be responsible for the appearance of new rocks or new types of soil that appear downstream. The variations of results for Sn at Sweanit soil or Cd at Ras Al-Qilt soil despite these two areas are considered as pristine areas, since there are no human activities from the Palestinian comunities from the surroundings. On the otherhand, there are Israeli colonies and it is difficult to receive information about what types of industries or wastewater that discharged to the wadi. Also, it is difficult to monitor the weathering depositions in these two areas.

Results for Cr, Sb and Pb, are high in the soils that located around the roadside and at the quarry dust or Stone Cut site, since the dust deposition from the quarry and the mechanical instrumentations and hydraulics are the main sources that responsible for such incremental. In addition, surface soil at the roadside sites will have more organic concentrations if compared to other sites (see Chapter 3).

It can be concluded that Cr, Sb and Pb are derived and predominanted from the mineral soil and the atmospheric inputs, this will impact more the organic soils to transport and reallocate trace metals by complexes from one place to another.

On the otherhand, trace metals such as Co, Ni, As, Zn, Cu, Li and Be are the highest values at Al Bireh due to the arbitrary dumping sites, urban runoff and roadside. These incremental could be in reflection to accumulations of anthropogenic inputs from these trace metals at the soil surface. For example, Cu and Ni concentrations at Al Bireh soil are more with organic soils from flood or urban runoff. Results from Qalandiah, Mukhmas and Sweanit are variey due to raw wastewater discharge, quarries dust, urban runoff and solid waste from the surrounding.

Results for Cd, Sr and Mo are high at Ras Al-Qilt soil; while Cd is indicate that there is anthropogenic input due to atmospheric deposition. Cd has been deposited not only at or prior to the road works or exposed the mineral from the soil, but came from far distance such as the case of Ras Al-Qilt soil. By comparing with other studies, there is rapid development of industrial areas in which the heavy metals are deposited into the environment even if the area is considered pristine due to weathering (Watmough and Hutchinson, 1996; Dammgen *et al*., 2000). Both authors discussed separately the different cases in which Cd transfers distance from its sources. Furthermore, James Galloway *et al.*, (1979) emphasises that Cd show is increased the rates due to atmospheric depositions in the study area even if it is away from the source.

The Sultan soil that is used to compare with the Al-Qilt spring it shows that the soil has the highest concentrations for Ag, B, Be, Bi, Pb and Sn. It is important to mention that Sultan spring is the main source for domestic use in Jericho 15,000 inhabitants. This spring is discharged from deep aquifer and the recharge area is far away from the area of the spring.

Soil samples are compared with Continental Crust (CC) "red line", Elemental Background for Soil (EBS) "yellow line" and USEPA (1993) "green line" values. This indicates the following results: for Cr, Cu, Zn, As, Mo, Ag, Cd, Sn, Sb and Bi are greater than CC values, therefore, 50% of these parametres are less than CC values. Moreover, Cr, Cu, Ag, Sn, Pb, Bi and B are greater than EBS values; therefore, 50% of these parametres are less than EBS values. Furthermore, results for Mo and B are greater than USEPA values and Ni, As, Ag, Cd, Sb, Ba and Pb are less than USEPA values. This leads to the conclusion that EBS always are close to the target results of the study area and in more than one case differs from both CC and USEPA values, therefore it is better to use the EBS for farther calculations (Figure 4.4).

To conclude, pseudo-digestion for trace metal contents does not relate to or indicate for mobility or the type of soil-bound metals, since the severity of pollution depend not only on heavy and trace metal contents of the soil, but also to the proportion of their mobility and availability at the environments and the degree of expected risk. Thus, the fractionation studies provide an idea for different types of metal bond in soil (Selim H and Sparks L., 2001), moreover, this study will come up with more information that will provide important tools for decision makers to estimate and expect the environmental risk from these trace and heavy metals in the soil.

Figure 4.4: Pseudo-digestion for trace metals in soil samples in median values (pink), summation of BCR steps (blue), these results compared to CC according to Wedephol (1995) in (red) line, EBS from this study in (yellow) line and the USEPA (1993) guideline in (green) line.

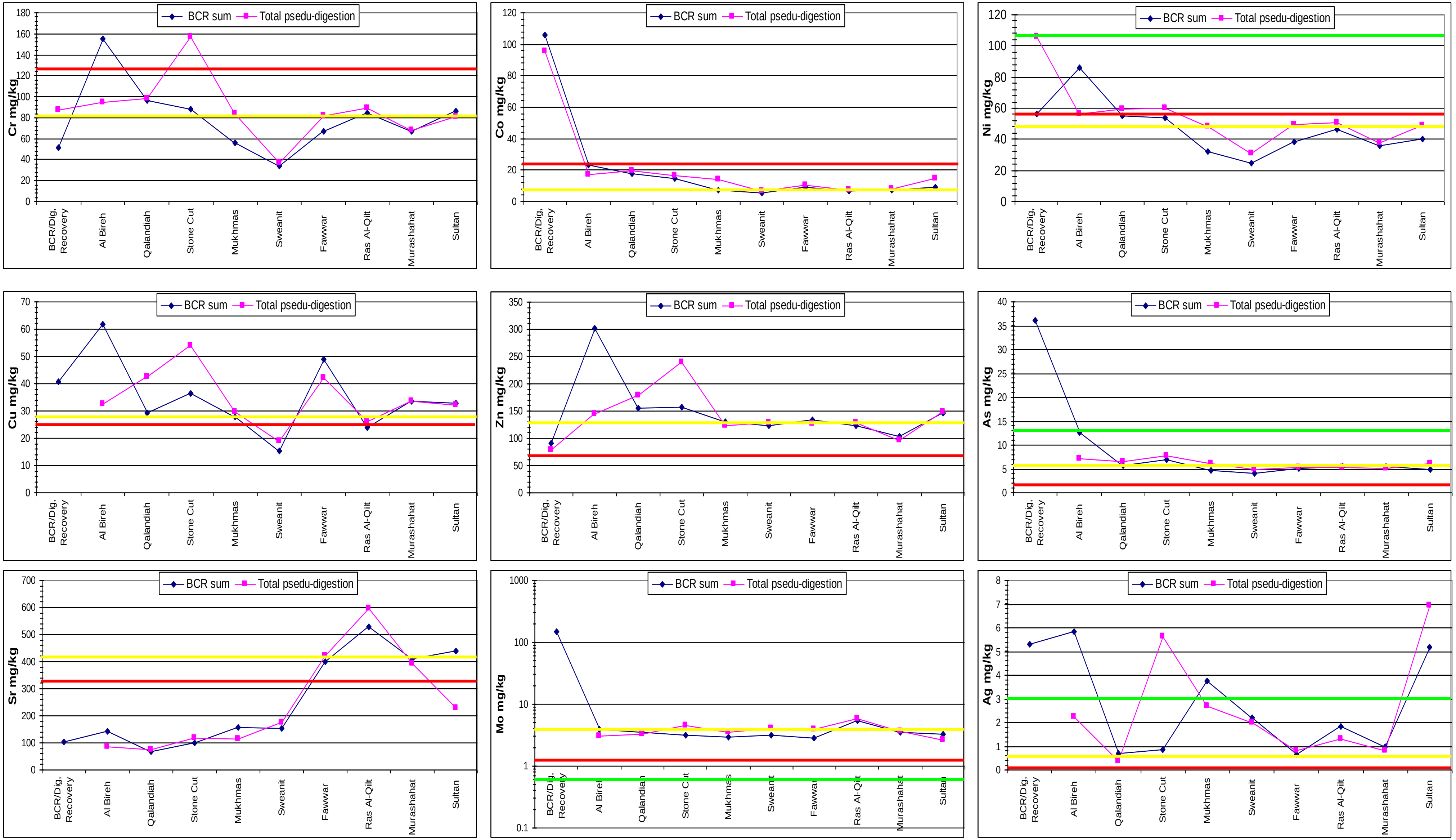
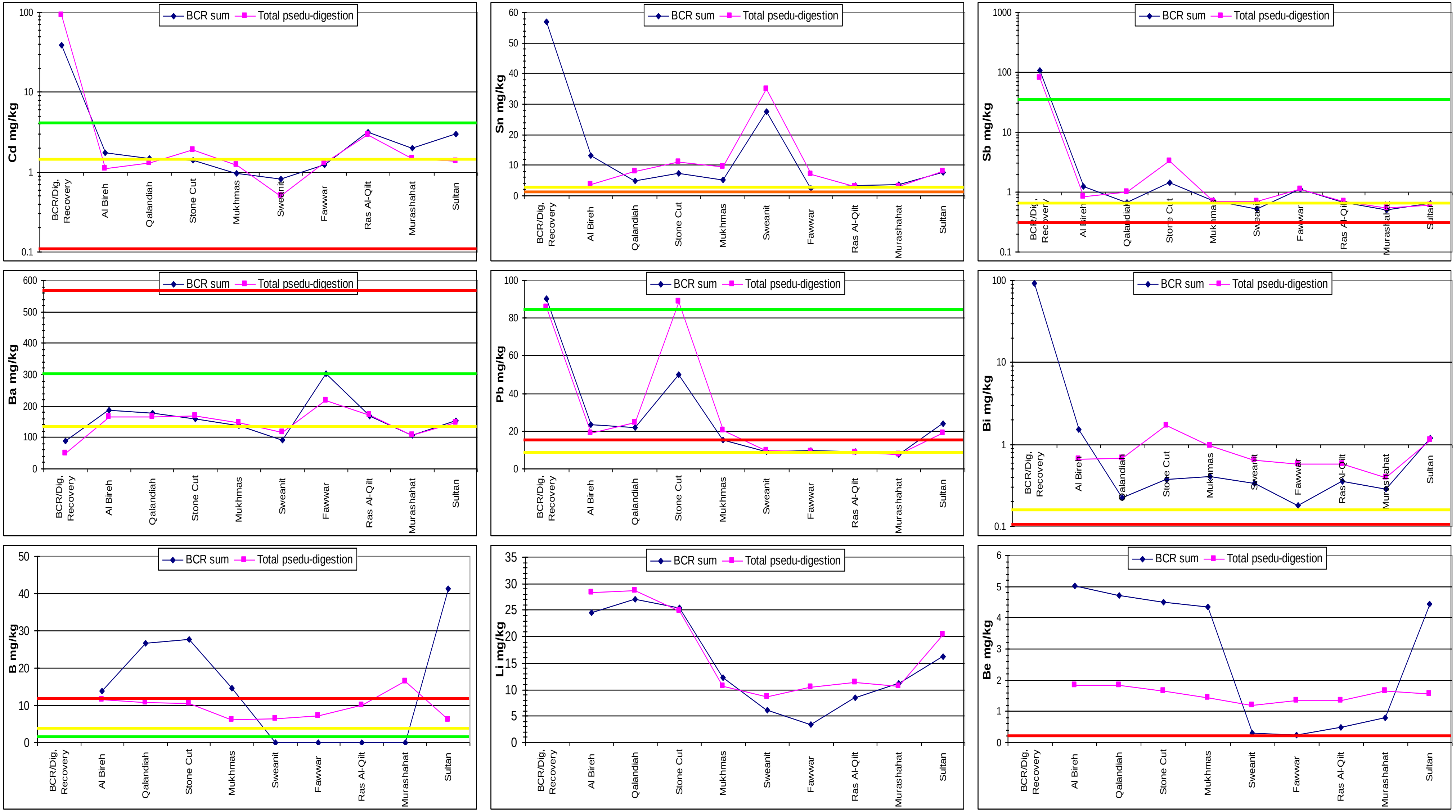


Figure 4.4: Pseudo-digestion for trace metals in soil samples in median values (pink), summation of BCR steps (blue), these results compared to CC according to Wedephol (1995) in (red) line, EBS from this study in (yellow) line and the USEPA (1993) guideline in (green) line.



4.5.2.2 Sequential fractionations for soil

There are differences in occurrences and fractionation forms for trace metals in soil samples. These variations cause difference in the behavior. Results reveal that the exchangeable fractionations are classified for Be, B and Sr and the next fractionation for Be and B is residual and for Sr is reducible, this indicate that Sr can easily mobile or transport, since the first and second fractionations are the most dangers for mobility and reallocate at the environment, moreover, exchangeable fractionation is acid soluble fraction, this phase prone to pH changes. This will exhibit fast leaching and it occurre in water soluble and easily exchangeable fraction. Therefore, this will have impact for mobility and it would be more worst if it follows by reducible fractionation like the case of Sr. Thus the fast leaching metals are more accessible, while slow leaching metals are less accessible according to (Quevauviller *et al.*, 1997). Therefore, it is good to consider the impact of the exchangeable fractionation for these metals in the complex form in soil, this is important to determine the mobility and transportation of trace metals (Figure 4.5).

In the case of Cd, Sb and Ba these are in the second extracting as reducing agent and they release the greatest proportion of the metal that present in the reducible fractionations. This stage contains metals associate with Fe–Mn oxides and can be dissolved by changes in redox potential change in the environmental, furthermore, the next fractionation is oxidizable for Cd and Sn and residual for Ba. Thus, from the study the Be, B, Sr, Cd, Sb and Ba is appear to occur in consistently available and leachable forms in soil samples.

Furthermore, the Cu and Pb extracte in the oxidisable fractionation and the next fractions are residual for both, since metals may be associating through complex accumulation process with various forms of organic material such as living organisms, detritus or coatings on mineral particles. Moreover, the oxidation of organic matter is typical for Mediterranean environments; this can make the metals more potentially and available (Kabata-Pendias A; Pendias H 1992). On the otherhand, Cu is removable or leach up to 95% by the addition of complex binder for Cu, thus the removal can occur at neutral to alkaline pH by adding ammonia. This is done by BCR method from the third step by adding ammonium acetate (Ottosen *et al.*, 2000). Also, Pb has low percentages of removal or leach (0%–10%) in studies of calcareous soil (Maini *et al.*, 2000), whereas around 50% removal or leach was obtained in studies of different sludges (Kim *et al.*, 2005) and highly successful removals in range (92%–98%) were obtained in studies of non calcareous soil besides from confirming the fact that acidification for trace metals (Ottosen *et al.*, 2005).

Therefore, buffer capacity is a determinant step for removal or leach for Pb in soil. However, it seems that long removal times are necessary for Pb from soil (Ottosen *et al.*, 2005).

Moreover, Bi, Cr, Ag Co, Li, Ni, Hg, Sn, Mo, Zn and As are found in the residual fractionations, since metals are distributed in the residual fraction show low risk of mobility and they prevalent indicate scant relatively for mobility (Filgueiras *et al.*, 2002), this increases the next step fraction that is the oxidaizable. For example, As is expected to be stable species of uncharged as (H_3AsO_3), thus it is not mobile form (Ottosen *et al.*, 2000).

The comparison of trace metal affinities in different operationally defined solid phase fractions estimate by taking the percent of trace metal for each site to the total concentration of the same metal for each fractionation, this shows the highest percentages of Sr, then B, then Be are in exchangeable and carbonate bound fractions, while Cd, then Ba,, then Sb are the highest in the reducible oxide fraction, and Pb, then Cu in oxidizable and Hg> Sn> Li> Mo> Ni > As> Bi> Cr> Ag >Co> Zn in the residual fraction.

In spite of their highest concentrations, the very low percentages of these traces in the four fractions indicate that their limited mobility according to the analysed parameters.

Results discussed above guide us to assign the degree of overall mobility that is highly influenced by many factors such as: pH, redox potential, organic matter processes from of the BCR fractionations by taking the ratio of exchangeable to total, also by assuming that the mobility is related to the solubility of geochemical forms of trace metals and decrease in order of extraction. Therefore, the mobility and potential metal availability for these contaminate in soils are arranged in the following order: Sr> B> Be> Cd> Ba > Sb> Pb> Cu> Hg> Sn> Li> Mo> Ni > As> Bi> Cr> Ag >Co> Zn.

Figure 4.5: BCR fractionations steps in terms of: exchangeable (blue), reducible (violet), Oxidizable (light yellow) and residual (black and green) for trace metal in soil at Al-Qilt catchment.

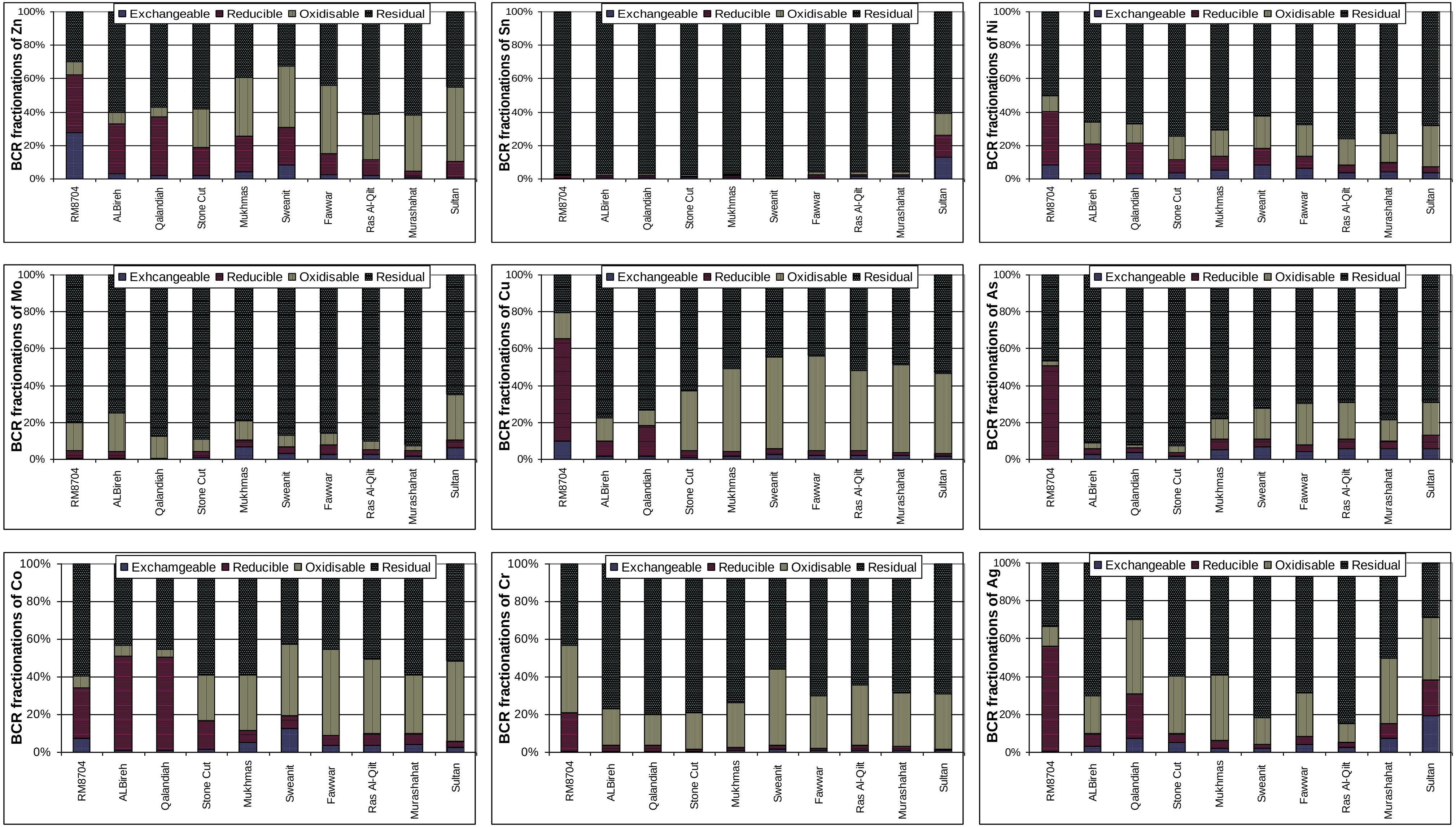
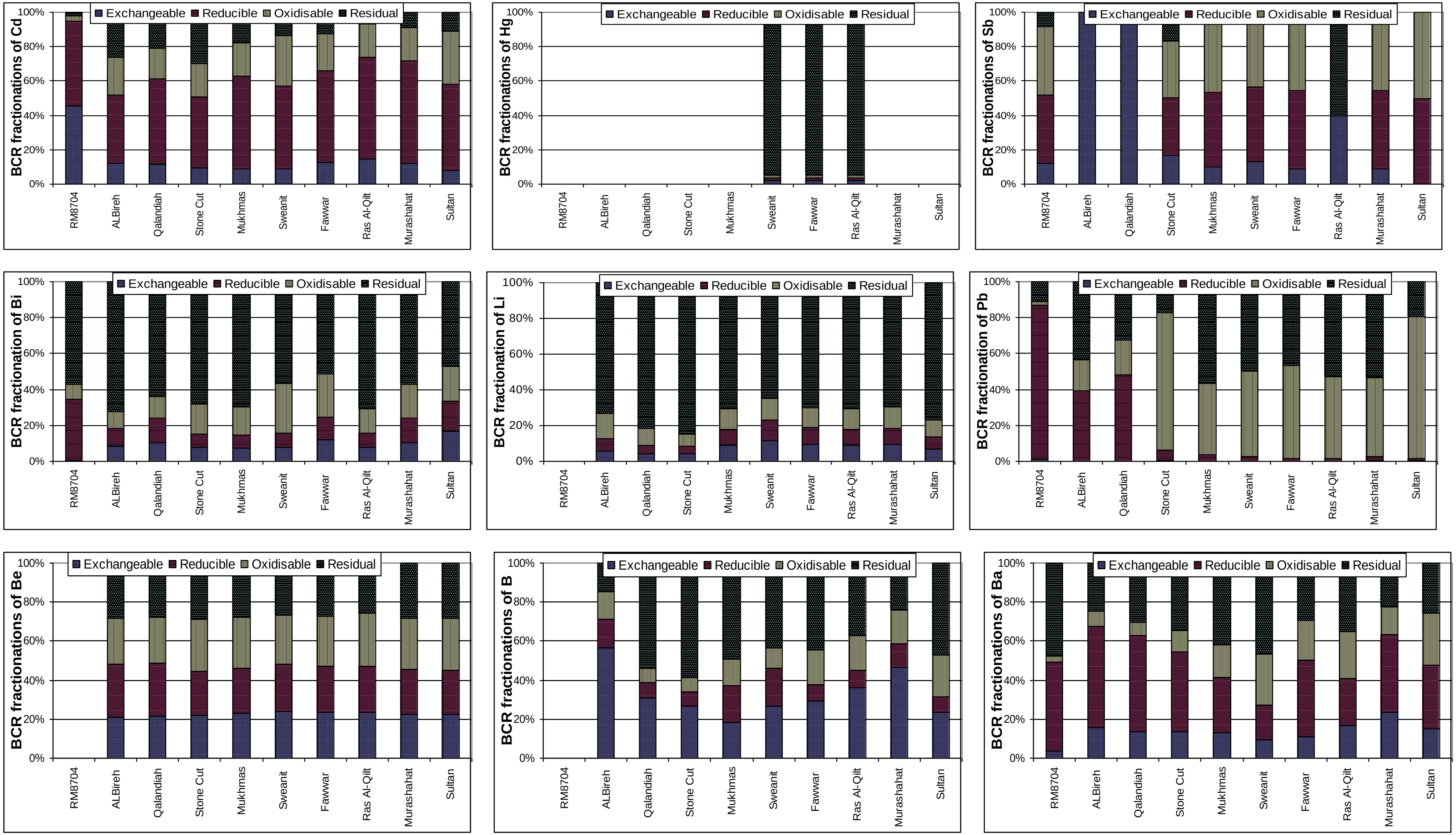


Figure 4.5: BCR fractionations steps in terms of: exchangeable (blue), reducible (violet), Oxidizable (light yellow) and residual (black and green) for trace metal in soil at Al-Qilt catchment.



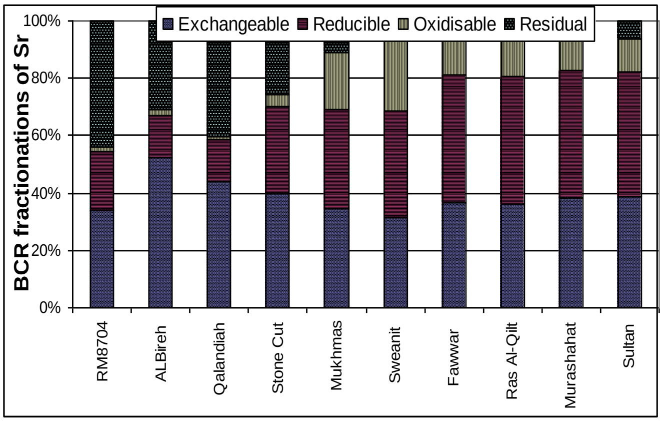


Figure 4.5: BCR fractionations steps in terms of: exchangeable (blue), reducible (violet), Oxidizable (light yellow) and residual (black and green) for trace metal in soil at Al-Qilt catchment.

4.6 Conclusions

Al-Qilt sediments and soil have been affected by human activities, this lead to high accumulation of trace and heavy metals. The sediments and soil are enriched clearly by anthropogenic pollutants due to discharge of raw wastewater, dumping sites, roadside, urban runoff and to certain extent due to natural effects that increase or decrease these trace metals in relation to the difference in elevation between upstream and downstream at Al-Qilt.

Trace metals in sediments are differe at up and down streams. The highest concentrations for Zn, Ag, Sb, Bi, Cu, Hg, Pb and Ba are prevalent at upstream sites while Cd, Mo, As, Cr, Co, Ni, Sr, Sn and B are prevalent at downstream sites. Spring sediments are enriched with anthropogenic pollutants such as Cd, Mo, As, Co, Ni, Sn and B. Most of these are caused by human activities around these springs despite there is no human activities and the possibilities to have pollutions vary due to atmospheric deposition, soil (natural) or direct contacts by infiltration from the upstream as the natural material and there are a lot of cavities in the area mainly from the Israeli colonies.

Furthermore, if the Continental Crust or Elemental Background for Soil are used for comparison purposes, it is better to use the Elemental Background for Soil, since it is not far away from the concentrations at each sites and it represents in most cases 50% of the values and it is highly varies if compared to Continental Crust values.

In addition, the BCR fractionations for trace metals, mobility and metal availability. In relation to this it is important to mention that mobility of trace metals in sediments at Al-Qilt catchment are estimated from the ratio of the extractable content / total metal content for each step and with each parameter this is decreases in the following order: Sr> B> Cd> Ba> Pb> Cu> Zn> Bi> Co> Mo> Hg> Sn> Sb> Ag> Cr > Ni >As.

For soil there are difference between the upstream and downstream at Al-Qilt such as Co, Ni, As, Zn, Cu, Li, Be, Be, Cr, Sb, Pb, Bi, and Sn are prevalent at upstream soil and Ba, Sr, Mo, Cd, Ag, B are prevalent at downstream. It seems that Mo, Cd, Ag, Sr and B have natural effect on the incremental of these trace metals in sediments at downstream. Furthermore, if the Continental Crust, Elemental Background for Soil and USEPA are used for comparison, then it is better to use the Elemental Background for Soil, since there values are vary compare with the other guidelines and in most cases it represents 50% for trace metals at Al-Qilt sites.

In addition to that if BCR fractionation is used for Al-Qilt soil to understand the mobility and potential metal availability for these contaminated soil samples, they can be arranged in the following order: Sr> B> Be> Cd> Ba > Sb> Pb> Cu> Hg> Sn> Li> Mo> Ni > As> Bi> Cr> Ag >Co> Zn.

4.7 Reference

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Chapter 5

Environmental factors as pollutant indicators at Al-Qilt catchment

(i) Anthropogenic pollutants and Enrichment Factor (EF)

(ii) Metal Pollution Index (MPI) and Contamination Factor (CF)

(iii) Ecological Risk Index and Geo-accumulation Index

5.1 Abstract

There are growing concerns for accumulation of heavy metals in sediments due to industrial and urban development; this increase the reliance of anthropogenic pollutants to infiltrate through soil to the groundwater. The aim of this chapter is to delineate the heavy metal pollution at Al-Qilt catchment for sediments of 5-10 cm depth with fractions of less than 63µm. Al-Qilt catchment is located in the east of Ramallah and Jerusalem district, both districs strongly influenced by wastewater from Israeli colonies and Palestinian urban areas. Thirty six surface sediment samples are collected during June and October 2008 and June and October 2009. The concentrations of trace metals are determined by pseudo-aqua regia digestion for Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Rb, Sr, Mo, Ag, Cd, Sn, Sb, Ba, Pb, Bi, U and B. These parameters are measured by ICP-MS, while Hg is measured by Flow Injection Mercury System and TOC is measured by TOC analyzer.

Heavy and trace metal concentrations are normalised by Fe, Al and TOC as reference elements to facilitate the comparison between sites for anthropogenic pollutants. Fe is good normalizer for Co, As, Mo, Cd, Sn, Sb, Hg, Bi, and U. Al is serve as good normalizer for Cr, Ni, Cd, Hg, Bi, and Be, and TOC is good normalizer for Cu, Zn, As, Sr, Sn, Sb, Ba, and Pb. Results indicate that Fe is the best as elemental normalizer, this lead to calculate Enrichment Factor (EF) in sediments and it is found that all sites svere from Ag and Bi and enriched mainly by Cd at Al Bireh, Sweanit, Fawwar, Ras Al-Qilt, Murashahat and Sultan. Furthermore, it is enriched with Zn at Al Bireh and Sweanit and with Hg at Al Bireh and Mukhmas. As a result, Ag, Bi, Cd, Zn and Hg are the most anthropogenic trace metals and their enrichment due to human activities and urban runoff.

Furthermore, the sediments are contaminated with trace metals at Al-Qilt, this evaluate through the three-pronged approach: (i) by comparison with other areas for trace metal concentrations using LAWA (German Working Group for Water) and Sediment Quality Guidelines values, (ii) by evaluate the contamination factors "total and fractionations using BCRs for each trace metal to calculate Metal Pollution Index (MPI), this is based on the difference in toxicity of trace metals, and (iii) by defining the potential level of biological risk by use the quality criteria such as the Threshold Effect Level (TEL) and Probable Effects Levels (PEL).

Sediment samples are contaminated with Zn, Ag, Cd, Hg, Bi and Hg. Although no site can be classify as ‘‘unpolluted’’ when looking at the calculated value for MPIs. Results

indicate that there are three regions; Sweanit, Ras Al-Qilt and Qalnadiah these sites are identified as critical sites for contamination. Trace metals input to Al-Qilt catchment is highly restricte to keep under strict control, since Ras Al-Qilt is considered one of the most important springs for the area and it is used for domestic purposes at Murashahat, thus there must be management plan to decrease the pollution at upstream of Al-Qilt to protect the springs from pollution at downstream.

5.2 Introduction

Regarding to the chemical status, only water samples were monitored twice year for major and physical parameters such as Ca, Mg, Na K, SO_4, NO_3, Cl and HCO_3, pH, temperatures and turbidity. Pollution due to heavy metals were monitored only in some special investigation programs and not in rotine (PWA, 2009), for this CH_2MHill (1999) monitored research to understand the potential pollution from raw wastewater that discharged to the groundwater. Results revealed that ammonia, potassium, nitrate, chloride, Total Dissolved Solids (TDS) and the trace metals such as antimony, lead, selenium, thallium, iron, beryllium, mercury, cadmium and arsenic were classified as pollutants mainly at Al-Qilt catchment.

Priju and Narayan (2007) and Marchand *et al*. (2006) were show that it is known that sediments act as sink for trace metals and considered as sources of contaminants in the aquatic systems. Also, Frignani and Bellucci (2004) demonstrate that human activities are significant sources for trace metals in the environment through effluents and atmospheric emission. Moreover, Liu *et al*. (2001) identify that sedimentation processes usually occur during the subsequent transport for metals of anthropogenic pollutants from the surface to the groundwater. Furthermore, Miroslav (2008), Audry *et al*. (2004) and Pekey (2006) were emphasized that heavy and trace metals derive from anthropogenic input such as industrial activities, automobiles, batteries, tires and wastewater were trapped in aquatic environments and accumulated in sediments.

Thus, in order to quantify sediments, several researches were used the method called "fingerprints" for tracing the anthropogenic pollutant sources. This method was applied at the Kishon River by Boris (1993). It is based on "if anthropogenic pollutants for any particular area had originated from the same source", then pair wise relationships between the concentrations of these pollutants in sediments from various stations would be linear for contaminations.

To reduce the heavy metal variability, the geochemical normalization has been used with various degrees of success by employ conservative elements, among these are Al and Fe (Dai *et al*. 2007). The normalization of trace metals by using Al and Fe has been used to reduce the natural effect of grain size and to estimate the extent of contamination (Daskalakis and O’Connor 1995). Therefore, several authors have been successfully used the Fe has priority for usage due to its abundance in the structure of clay minerals and according to the fact that it is associated with particle surfaces as an oxide coating. Fe also occurs from natural weathering processes and it is broadly used to normalize the metal in order to reduce particle grain size influence (Simeonov *et al*. 2000 and Zhang *et al*. 2007). Moreover, it is important to mention that Fe is clay mineral indicator element that has been used as an alternative to Al (Kennicutt *et al*. 1994). On the otherhand, Al is major constituent for fine grained aluminosilicate with bulk of trace metals that were associated (Shine *et al*. 1995). Moreover, Altun *et al*. (2008) and Unlu *et al*. (2007) show that most of the marine sediments were composed of aluminosilicate minerals that originate from continental weathering and erosion.

The usage of either Al or Fe as normaliser is problem if the contaminant source introduces large quantities for these trace metals (Morse *et al*. 1993). It is therefore good to use both of them to compare the correlation cofficeint, then we will choose the best based on thier correlations, moreover, the Total Organic Carbon (TOC) can be use as normaliser this was based on the assumption that it is serving as matrix on particle surfaces for metals and this show strong correlation between TOC and metal pollution in sediments (Daskalakis and O’Connor 1995, Shine *et al*. 1995). Most of the researchers use Al or Fe or TOC as normalisers for sediment and were compared between them. In this study the use of these parameters as elemental normalisers for sediments will be adapt to assign the anthropogenic sources, then to calculate the degree of metal contamination at Al-Qilt sites. The degree of metal contaminations were measured by several factors such as Enrichment Factor (EF), this define as the ratio of observed metal concentration to the normalizing element concentration for the sample, then divided by the background metal concentration to normalizing element ratio of the Continental Crust (Zhang *et al*. 2007).

Based to these knowledge, the anthropogenic pollutions due to heavy and trace metals can't be assign by doing the analysis only for wastewater samples. Good results can be achieved by doing the analysis for sediment and soil, then by using the average shall values in calculations accourding to Turekian and Wedepohl (1961).

Furthermore, soil samples will be use as reference samples from pristine areas for the study area mainly that located far away from human activities.

The CFs values are calculated and evaluated for the total concentrations and sequential fractionation method "Community Bureau of Reference" (BCR). This method show the binding of trace metals in four stages: exchangeable with carbonate, reducible (Fe, Mn), oxidisable (SO_4 and organic) and as residual. These four stages are important to understand the heavy and trace metals that release and transport to the environment. Beside this invistication it is important to relate the availability and toxicity and to compare with other studies that similar to the Al-Qilt catchment in terms of matrix and heavy metals. Then, the Metal Pollution Indexes (MPI) are calculated based to the Maximum Permissible Levels, this give clear information for the pollution to each site and for parameters that pose high risk to the ecosystem and human.

Trace metals in sediments have been used to monitor the pollution of aquatic environments as their existance with low concentration in the water column, this have tendency to associate preferentially with the sediments and attain considerable concentration (German Ministry of Environment 1993). Toxic metals were present in the environment in low concentrations as anthropoginic pollutance due to human activities. Moreover, metals can not be degraded or decomposed but were accumulated in the environment and concentrated in sediments, then they influence to the ecosystems (Steiner *et al*. 2007 and Imperato *et al*. 2003). It is noticeable that human induced metals (Pb, Hg and Cu) these have been detected in both Greenland and Antarctica snow samples due to human activitiers (Hur *et al*. 2007). Hence, sediments with contaminated metal may cause immediate toxicity to ecosystems on long term that will have adverse effects. For example, blood Pb level is 150 mg d/l and it is deadly (NSW LRC, 1997) and Agarwal *et al*. (2005), also identify that Pb is released to the water column from sediments in response to certain disturbances. Zheng *et al*. (2008) report that the distribution of heavy and trace metals in sediments adjacent to populated areas that used to investigate the anthropogenic on ecosystems, this will help in assessing the risk that posed by human waste discharges and deposited. But the problem is how we can measure such accumulation and with what values as guidlines we can compare as a reference.

There are international guidelines such as LAWA (Working Group of the Federal States on water) in Germany and Sediment Quality Guidelines (SQGs), this will use for comparison purposes to assign the deviations from the targeted values for trace metals in sediments. The ecological assessment was studied using the trace metals from surface sediments of open ecosystems and other geochemical factors of contamination based on: (1) Geo-accumulation indexes that base on the Muller Index, (2) Ecological risk index based on the Contamination Factor and (3) Sediment Quality Guidelines (SQG) used by USEPA (Perin *et al*. 1997) and LAWA working group.

The Geo-accumulation Index (*I*geo) was introduced by Muller (1969) to assess metal pollution in sediments and soil in order to determine the extent of pollution and to estimate anthropogenic inputs by using heavy and trace metals. The *I*geo include seven grades, these grade describe the degrees of enrichment. The highest grade (class six) reflects 100-fold enrichment above the background values. Moreover, the ecological risk index is calculated according to Hakanson (1980), MacDonald *et al*. (1996) and Long and MacDonald (1998). This index will take into consideration the following three categories: (1) Hg, Cd, Pb, Cu and Zn, these have been given as priority, (2) some representative trace metals quite often appear with similar pattern in the ecosystem sediments such as Cr, Ni, V, Mo and Co and (3) other non heavy metals found as trace metals. As, all times are suggested to be included as some forms of As that are very toxic and it appears to behave in very special way in aquatic systems. For this study we suggest to add all of them as they have the anthropogenic impact and there are no previous studies available on this subject at the area of study.

Sediments were classified as: not polluted, moderately polluted and heavily polluted, these were based on the numerical value of SQG and USEPA (Perin *et al*. 1997). These numerical values have been used in North America for both freshwater and marine ecosystems to identify contaminants in aquatic ecosystem (MacDonald *et al*. 2000), these guidlines will apply for sediments in Al-Qilt for comparison purposes, since there are similarities in matrix compositions. MacDonald *et al*. (1996), Long and MacDonald (1998), Long *et al* (1998) and Burton (2002) have been developed many potential toxic trace elements by applying two groups of SQGs to assess the eco-toxicological (a) Effect Range Low (ERL) and Effect Range Median (ERM) and (b) Threshold Effect Level (TEL) and Probable Effect Level (PEL) values. ERLs or TELs are concentrations below which adverse effects upon sediment dwelling fauna would be expected. In contrast, the ERMs and PELs represent chemical concentrations above which adverse effects are likely to occur.

There are a lot of interests in separation of geochemical values to discriminate between anthropogenic contribution and natural values (background) in sediments. This is probably even more critical than the separation between background and anomalies in geochemical prospecting studies. The term "geochemical baseline" indicates the actual content of elements in surfaces of the environment at a given point (Salminen and Gregorauskiene 2000).

5.3 Objectives

5.3.1 This chapter aims:

- ❖ To normalize trace metals in sediments.
- ❖ To compare the degree of contamination.
- ❖ To identify areas of contamination using the sediments.
- ❖ To evaluate sediment quality and eco-toxicity by using two sets of SQGs and other guidelines.

5.3.1 This can be achieved by:

5. Normalizing heavy and trace metals in sediments with Fe, Al and TOC to compare anthropogenic pollutants and then calculate the Enrichment Factor (EF) at each site.
6. Calculating the Contamination Factor for BCR steps at Al-Qilt and use LAWA as guidelines for comparison.
7. Calculating the Metal Pollution Indexes (MPI) by considering the weights of heavy and trace metals in relation to toxicity by comparing to SQGs.
8. Calculating the Geo-accumulation Index (I*geo*) and Ecological Risks Index.

5.4 Field and analytical work

5.4.1 Sampling

Surface sediment was collected four times from nine sites (Figure 5.1), these sites are in the range of 45-50 km of Al-Qilt catchment. The sampling took place during June and October 2008 and June and October 2009. Samples were not taken from areas of sub-aquatic with slope or inclination higher than 4-5° (height vs length) as the fine recent material could be very easily re-suspended (Hakanson, 1979). The collected sediment samples are taken using a plastic grab of about 300-400g just beneath the top surface in range of 5-10 cm and placed in 250ml plastic bottle (jars), then preserved at 4°C until analysis according to (APHA, 2000 and DEV, 2001).

Sampling sites are classified as follows: (i) effluents from treated wastewater (Al Bireh wastewater treatment plant); (ii) raw wastewater (Qalandiah and Stone Cut); (iii) Wadis carrying wastewater as base flow beside the runoff (Mukhmas and Sweanit); (iv) Springs (Fawwar, Ras Al-Qilt and Sultan); (v) water treatment plant for domestic use (Murashahat).

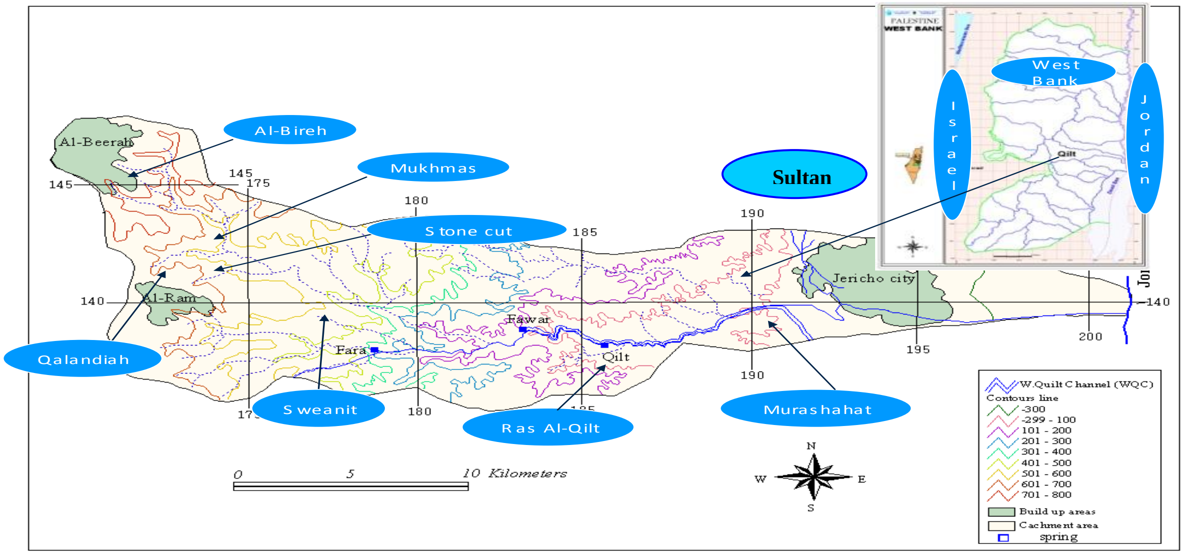

Figure 5.1 Al-Qilt catchment, elevation, major cities and sampling sites (PWA, 2009).

5.4.2 Laboratory analysis

At the laboratory samples are frozen to -30°C by using deep freezer refrigerator for 6-8 hours to stop microbial activity. Next step is “freeze-dried-evaporate” using CHRIST, Delta 1-24 LSC for four days until samples are dried. Then about 200-250g of sample is sieved through 2 mm, 630 µm, 200µm and 63µm using a Fritsch D-55743. Then weight of 0.25g from each sample of less than 63µm grain size fraction using high precision analytical balance (0.00001g) then prepare for pseudo digestion using aqua regia procedue.

5.4.3 Digestion by aqua regia

About 0.25g from the mixed samples and Buffalo Reference Material (8704) are measured accurately into 100 ml Teflon digestion tubes by adding 6ml of concentrated HNO_3 (65%) and 3ml of concentrated HCl (37%). Afterwards the samples are digested for two hours using Microwave digester (MARS 5). Samples are kept outside to reach room temperature and adjust with water to 25ml Erlenmeyer flask, then centrifuged and transferred to 50ml tubes for analysis using ICP-MS with proper dilution. Trace metal concentrations are measured for Cr, Co, Ni, Cu, Zn, As, Sr, Mo, Ag, Cd, Sn, Sb, Ba, Pb, Bi and B using an Agilent 7500 ICP-MS Inductive Coupled Plasma Mass Spectra ICP-

MS, and Hg is determined using Flow Injection Mercury System (FIMS 400). The laboratory works are at the Water Research Center (UFZ), Magdeburg, Germany.

5.4.4 BCR extraction procedure

The BCR method is applied for sieved sediment and soil samples from less tha 63 µm grain sizes, and using the Reference Standard Material (701) as quality control between the samples. One gram is weighted from samples and standard is transferred to glass tube and then BCR method is followed with its four steps (Chapter 4).

5.4.5 Quality assurance

Precision and accuracy are checked by repeat the analysis (n=2) of international standard for pseudo digestion sediment such as Buffalo Reference Material (8704) and Reference Standard Material (701), these are used to control the BCR fractionation steps. Furthermore, the water is used for dilution and blanks from double distillers with less than 18µsimen conductivity. The results for recovery values are within ±15% of the certified values, this indicates consistence between the certified and the analyzed values for sediment and soil samples, except for barium it is 61%.

5.4.6 Trace metals distribution graph

The median values are used in calculations and Spearman Correlations are selected for further statistical analysis due to fact that some parameters are not normally distributed, therefore they suitable more for the Spearman Correlation analysis (Figure 5.2).

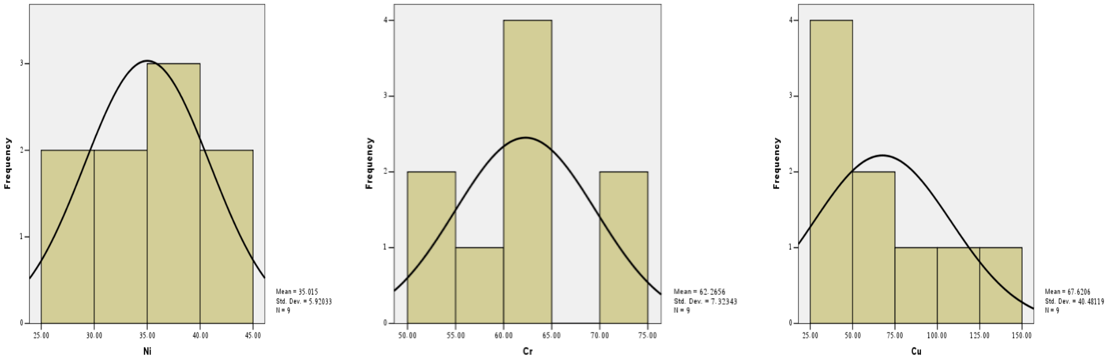

Figure 5.2: Varied samples from distribution graph such as Ni, Cr and Cu respectively.

5.5 Methodology

5.5.1 Correlation Coefficient (r^2)

Trace and heavy metals are graphed against Al, Fe and TOC to select the best reference elements; this will be use for further calculations along the Al-Qilt catchment sites. In this study the correlated metals with reference elements are calculated according to the correlation coefficient factors (r^2) with values approaches between 1 and -1 and the best correlations with highest values are categorized.

5.5.2 Normalization of trace and heavy metals

The normalization is based to the hypothesis that metal concentrations vary consistently with the concentration of reference elements unless the metals are due to anthropogenic origin. Normalization is a way to compensate for the natural variability of trace metals in sediments so any anthropogenic metal contribution may be detected and quantified by reducing the natural effect to assign the trace metal as anthropogenic pollutants (Daskalakis and O'Connor, 1995).

The normalization of trace metals with selected elemental normalizers are calculated by divide the metal concentrations for trace and heavy metals to the concentrations of selected reference, then the result is visualized in a suitable manner. Results that are greater than one will be considere as anthropogenic pollutants.

5.5.3 Enrichment Factor (EF)

The first step in calculation of an EF is to define the relation between metal and the normalizer, then to use this factor to identify anomalous metal concentrations that may have anthropogenic source to assign the enriched site. The elemental normalizer is divided by the same ratio in anthropogenic un-impacted geological material (background), this gives the definition of Enrichment Factor (EF) according to Jeong-Yul *et al*. (2004) and Feng *et al*. (2004), as in follwing equation:

$$EF = \frac{(Me/N)sample}{(Me/N)background}$$

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

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

Enrichment Factor is useful indicator that reflecte the status of environmental contamination. EF values are interpreted by Acevedo-Figueroa *et al.* (2006), if EF < 1 it 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 > 50 is extremely severe.

5.5.4 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 5.1) 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 5.1: Heavy and trace metal concentrations in the CC as average of UC and LC.

Elements	Concentration	Elements	Concentration	Elements	Concentration	Elements	Concentration
Al	79780 mg/kg[a]	Co	24 mg/kg[a]	Sr	333 mg/kg[a]	Ba	584 mg/kg[h]
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]	Ag	70 µg/kg[d]	Pb	14.8 mg/kg[a]
Cr	126 mg/kg[a]	Zn	65 mg/kg[a]	Cd	100 µg/kg[e]	Bi	85 µg/kg[e]
Mn	716 mg/kg[a]	As	1.7mg/kg[b]	Sn	2.3 mg/kg[f]	U	1.7 mg/kg[a]
Fe	43975 mg/kg[a]	Rb	78 mg/kg[a]	Sb	300 µg/kg[g]	B	11 mg/kg[j]

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).

5.5.5 Contamination Factor (CF)

The CF is describe the degree of pollution for given parameter as the ratio between the sediment metal content at the sampling locations and the reference value (locally named as Elemental Background for Soil and from international called Continental Crust values).

The CF is expressed as follows:

$$CF = \frac{Co}{Cb}$$

Where: *C*o is the mean content of heavy metals in the sediment.

Cb is the reference value for the heavy metals.

The CF is classified to four groups according to Hokanson (1980) and Pekey *et al*. (2004) and others, they use the following terminology: $CF < 1$ low contamination; $1 \leq CF < 3$ moderate contamination; $3 \leq CF < 6$ considerable contamination; $CF \geq 6$ very high contamination. Results of CF will use in the calculations of the Ecological Risk Indices.

5.5.6 German LAWA guidelines

LAWA (1998) "water group work" for all states in Germany, this group was targeted Hg, Cd, Zn, Pb, Cr, Cu and Ni with different classes summarized (Table 5.2). The aim from using the LAWA is to minimum requirements to monitor the pollution and not to far away from the high classes. For our study we will compare the result in sediment at Al-Qilt with LAWA values to assign sites that display the highest impact from trace metals as anthropogenic pollutants.

Table 5.2: Limits and classes for trace metals in sediment according to LAWA (1998) guidelines from all states as of the working group in Germany.

Class	**Hg**	**Cd**	**Zn**	**Pb**	**Cr**	**Cu**	**Ni**
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Target	0.8	1.2	200	100	100	60	50
I	≤ 0.2	≤ 0.3	≤ 100	≤ 25	≤ 80	≤ 20	≤ 30
I-II	≤ 0.4	≤ 0.6	≤ 150	≤ 50	≤ 90	≤ 40	≤ 40
II-III	≤ 0.8	≤ 1.2	≤ 200	≤ 100	≤ 100	≤ 60	≤ 50
III	≤ 3.2	≤ 4.8	≤ 800	≤ 400	≤ 400	≤ 240	≤ 200
III-IV	≤ 6.4	≤ 9.6	≤ 1600	≤ 800	≤ 800	≤ 480	≤ 400
IV	> 6.4	> 9.6	> 1600	> 800	> 800	> 480	> 400

5.5.7 Chemical and biological toxicity in sediments

Within the aim of defining the potential level for biological risk it is associated with the occurrences of trace metals in an aquatic environment, the results from this study we will compare by using the CFs in median, min and max values with numerical Sediment Quality Guideline (SQG), these will be in term of Threshold Effect Levels (TEL). TEL is the geometric mean of the 15th percentile in the effect data set and the 50th percentile in the no effect data set and Probable Effect Levels (PEL) will help to relate the biological abundance of microorganisms to heavy metals to relate this to the occurrences and then to toxicity according to studies by Taylor (1972), MacDonald (1994), Pekey (2006b) and Kucuksezgin *et al.*, (2006).

5.5.8 Metal Pollution Index (MPI)

MPI was defined as linear sum of concentration factors by taking the differences in weight of toxicity for different metals (Goncalves *et al.*, 1992 and Soares *et al.*, 1999) as in the following equation:

$$\mathrm{MPI} = \sum (Wi/Wt)CFi$$

Where CF_i is the contamination factor for metal i; w_i is the weight for metal i; and the wt = $\sum w_i$ is **(1870)** for the mentioned parameters.

The weight of trace metals are targeted according to Goncalves *et al.*,(1992) it is for Hg and Ni (1000 and 100) respectively and according to USEPA, (1976) and USPHS, (1962) are for As (100), Ba (1.4), Cd (333), Cr (20), Cu (2), Pb (20), Ag (20), Zn (0.05), Co (20), Sr (0.2), Mo (14), Sn (20), Sb (200) and Bi (20).

These weights are calculated by taking the inverse proportion of the Maximum Permissible Level in surface water that used for domestic purposes.

5.5.9 Geo-accumulation Index

This index was introduced by Muller (1969) and other researchers in environmental studies such as Abrahim and Parker (2008) and Lu *et al*. (2009) are defined in the following equation:

$$Igeo = \log 2\left(\frac{(Me)se\dim ent}{1.5(Me)backgound}\right)$$

Where: (Me) sediment: Is the concentration of heavy metal in the sample.

(Me) background: Is the values of metals as average of continental crust.

(1.5): Is the background matrix correlation factor, it is used for possible variations in the background data due to lithogenic effects.

The Geo-accumulation Index consists of seven grades according to Muller, it is in the rangs from unpolluted to very strongly pollute as summarized in (Table 5.3).

Table 5.3: Geo-accumulation Index results in relation to grade and pollution intensity.

Igeo (results)	Igeo (grades)	Pollution intensity
< 0	0	Unpolluted

0-1	1	Unpolluted to moderately polluted
1-2	2	Moderately polluted
2-3	3	Moderately to strongly polluted
3-4	4	Strongly polluted
4-5	5	Strongly to very strongly polluted
> 5	6	Very strongly polluted

5.5.10 Ecological Risk Index (RI)

The RI is due to toxic metals in sediments, it is carried out using the potential ecological risk index that proposed by Hakanson (1980). The RI method covers the variety of research that domains such biological toxicology, environmental chemistry and ecology. Parameters are calculated according to following formulas:

$$\mathrm{C}fi = \frac{Cni}{Coi}$$

$$\mathrm{E}ir = \mathrm{T}ri \ \mathrm{X} \ \mathrm{C}fi$$

$$\mathrm{RI} = \sum_{i=1}^{n} Eir$$

Where: C*fi* - single metal pollution index = CF

C*ni* - concentration of metal in samples;

C*oi* - reference value for metal;

E*ir* - monomial potential ecological risk factor;

T*ri* - metal toxic response factor.

T*ri* values for Zn =1, < Cr = 2, < Cu = Ni = Pb = 5, < As = 10, < Cd = 30, < Hg = 40 and by assumption the T*ri* values for Ag, V, Mo, Sr, Bi and B are 1 like the Zn (lowest value), since they are not considered before according to Hankanson (1980) or other studies.

Therefore, five categories for E*ir* and four categories of RI re defined in (Table 5.4).

Table 5.4: Ecological risk and the potential ecological risk grades for trace metals. The colors are according to LAWA scale.

E*ir* Values [a]	**Ecological risk of single metal**	**RI values**	**Potential ecological risk for the environment**
Eir <40	Low risk	RI < 150	Low risk
40 ≤ Eir < 80	Moderate risk	150 ≤ RI < 300	Moderate risk
80 ≤ Eir < 160	Considerable risk	300 ≤ RI < 600	Considerable risk
160 ≤ Eir < 320	High risk	RI ≥ 600	Very high risk
Eir ≥ 320	Very high risk		

[a] Hakanson, (1980).

5.6 Results and discussions

5.6.1 Coefficient of determination (r^2)

Heavy and trace metal concentrations are graphed as metals vs. reference elements such as Al, Fe and TOC, then the correlation coefficients are calculated (Figure 5.3). Results reveal that Fe is good normalizer for Ti r =0.75, V *r* =0.61, Co r = 0.59, Mo r = 0.25 Ag r = 0.35, B r = 0.22 and Li r = 0.34, and Al is good normalizer for Cr r = 0.63, Ni r = 0.69, Cd r = 0.64, Mn r =0.3, Bi r = 0.16 and Be r = 0.33. Furthermore the TOC is correlated Cu r = 0.72, Zn r = 0.22, Sr r = 0.32, Sn r = 0.13, Sb r = 0.87, Ba r = 0.35 and Pb r = 0.67 (Table 5.5). Fe is predominated over Al and TOC in correlation and will use as elemental normalizer, then as background to calculate the EF and other environmental factors as background.

Table 5.5: Correlation coefficient values (r^2) for trace and heavy metals are normalized with Al, Fe and TOC.

	metal/Al	**metal/ Fe**	**metal/TOC**		**Metal/Al**	**metal/ Fe**	**metal/TOC**
Mo	0.06	**0.25**	0.21	**Ti**	0.33	**0.75**	0.12
Ag	0.14	**0.35**	0.24	**V**	0.16	**0.61**	0.12
Cd	**0.62**	0.08	0.28	**Cr**	**0.63**	0.49	0.29
Sn	0.01	0.01	**0.13**	**Mn**	**0.3**	0.28	0.06
Sb	0.06	0.06	**0.87**	**Co**	0.25	**0.59**	0.07
Ba	0.21	0.02	**0.35**	**Ni**	**0.69**	0.16	0.01

Hg	**0.33**	0.08	0.01	**Cu**	0.05	0.03	**0.72**
Pb	0.02	0.21	**0.67**	**Zn**	0.02	0.01	**0.22**
Bi	**0.16**	0.03	0.02	**As**	0.04	0.01	**0.14**
B	0.05	**0.22**	0.13	**Li**	0.24	**0.34**	0.04
Be	**0.33**	0.01	0.06	**Sr**	0.02	0.03	**0.32**

It has been suggested that if the points in the regression plot between metal and normaliser concentrations are within the 95% confidence limits (Figure 5.3) the trace metal values in sediment are unlikely to be contaminated by human activities if the points are away from the best line. Then, this must be taken in consideration as anthropogenic and not naturally occuring (Coakley and Poulton, 1993).

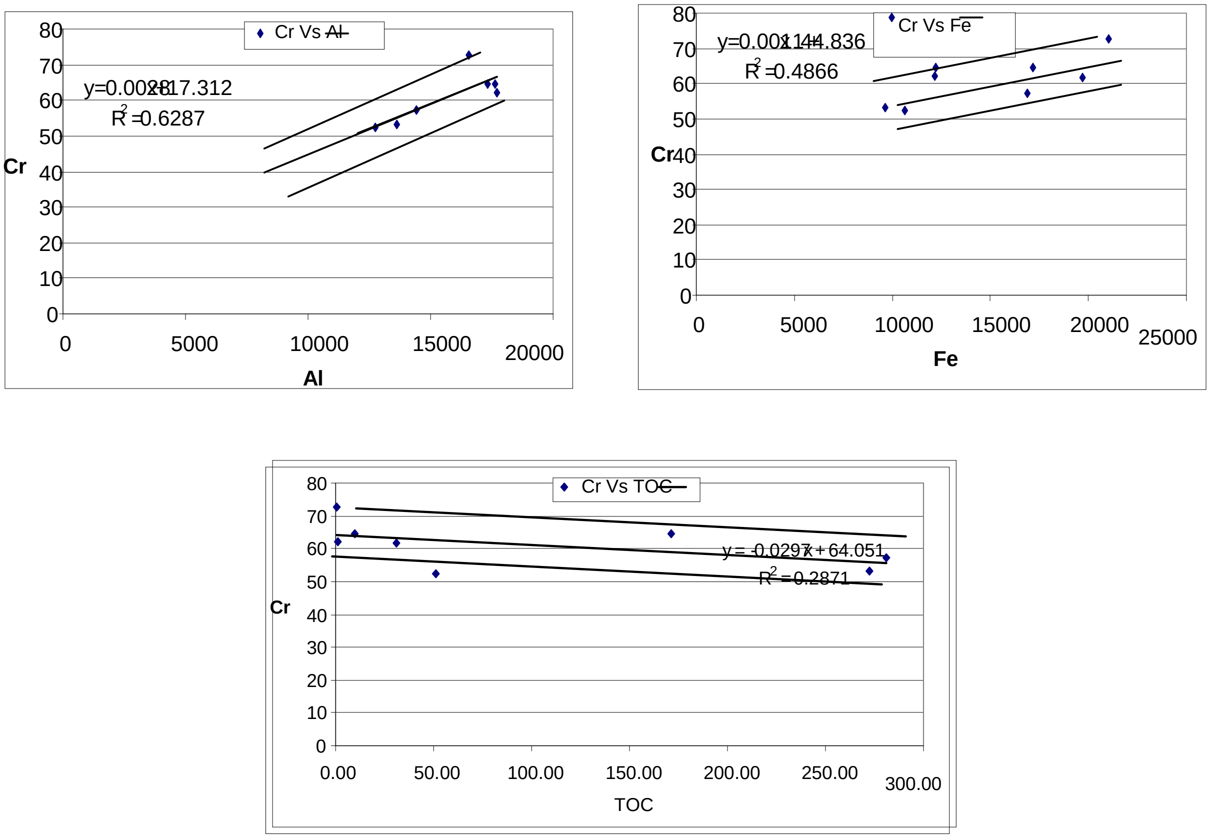

Figure 5.3: Correlation coefficient of trace and heavy metals with elemental normalizers and confident limit 95% without line points.

5.6.2 Metal/Al, Metal/Fe and Metals/TOC normalizations for anthropogenic parameters

Results reveal that metal /Al are less than one for Co, As, Rb, Mo, Ag, Cd, Sn, Sb, Hg, Bi, U, Li and Be, and are grater than one for Ti, Sr, Ba, Zn, V, Cr, Ni, Cu, Pb and B (Figure 5.4).

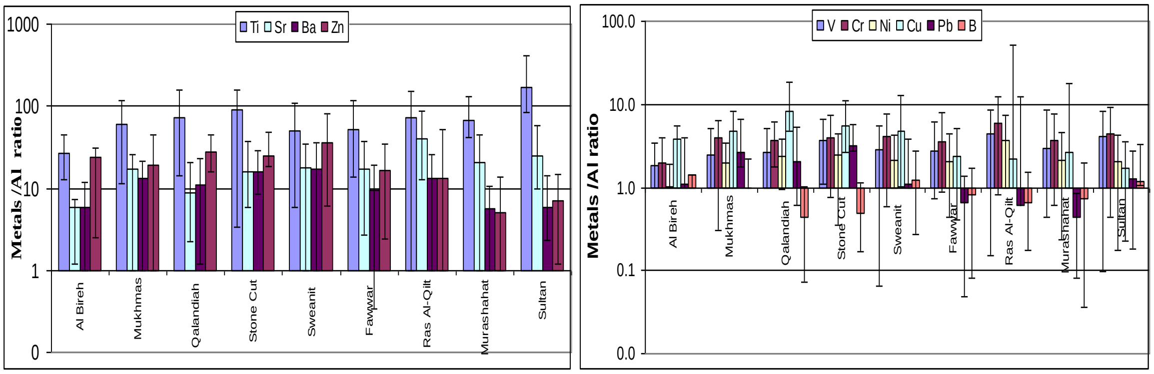

Figure 5.4: Metals / Al ratio for trace metals normalization, ratios higher than one.

Results for metals/ Fe are less than one for Co, As, Mo, Cd, Sn, Sb, Hg, Bi, U and Be, this indicates that these traces metals are not considere as anthropogenic pollutants at Al-Qilt sites. Metals/Fe are grater than one for Ti, Zn, Sr, Ba, Cu, Cr, V, Ni, Rb, Ag, Pb, B and Li (Figure 5.5), these trace metals must taken in considerations as anthropogenic pollutants.

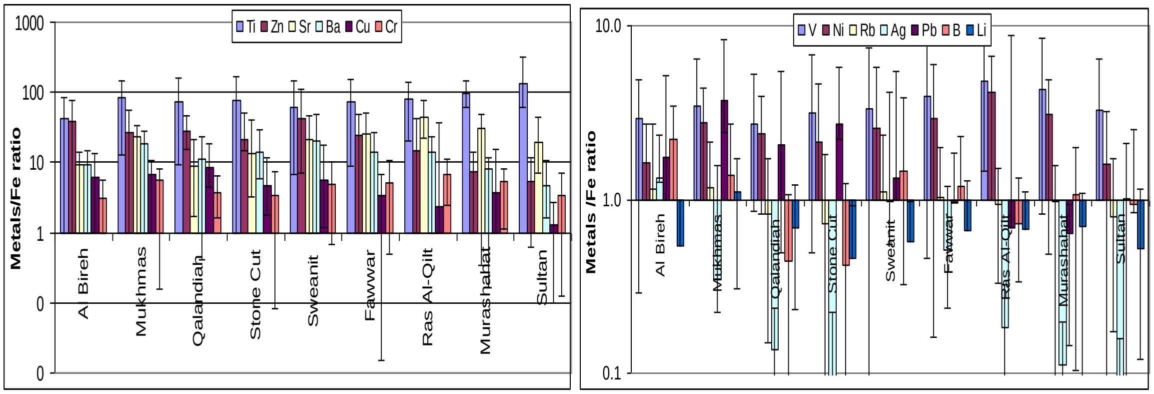

Figure 5.5: Metals/Fe ratio normalization for trace metals higher than one.

Results reveal that metals/TOC normalization for Sb, Hg, U and Be are less than one, so these are not considered as anthropogenic parameters. Moreover, it is higher than one mainly at downstream for Co, Ni, Cu, As, Rb, Mo, Ag, Cd, Sn, Pb, Bi, B, Li, Ti, V, Cr, Zn, Sr and Ba (Figure 5.6). These results are correlated with TOC concentration at the upstream due to high load of organics from wastewater. These load can be biodegradable in diffent ratio depending to the environemt factors while the wastewater runing and infiltrate till it reaches the springs downstream. Thus it is recommended to use the TOC if the trace metals are transport with organic in complex form.

It is important to mention that Sb, Hg, U and Be are not normalize with Fe, Al or TOC but must evaluate with other environmental factor mainly those are considered for toxicity.

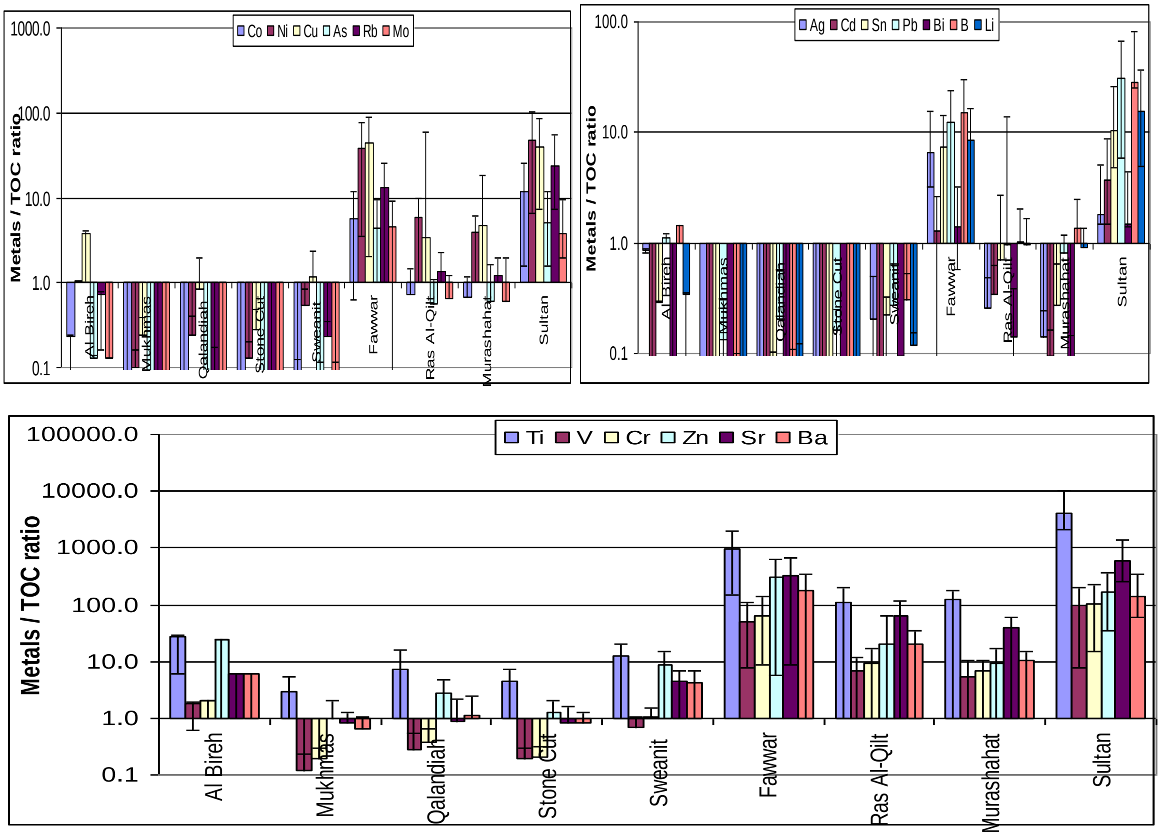

Figure 5.6: Metals / TOC ratio for trace metals higher than one.

Results indicate that there is similarity between Fe and Al in the behavior for assigning the trace metals as anthropogenic pollutants (Figure 5.4 and 5.5). Furthermore, results reveal that the normalization for Metal/Fe, Metal/Al and Metal/TOC indicate that Ti, Zn, Sr, Ba, Cu, Cr, V, Pb and B are assigned by the three normalizers, thus these trace metals must considere as top priority for the study as anthropogenic pollutants at Al-Qilt catchment, taking into consideration that trace metals like Cr, Pb, Zn and Cu originate from domestic wastewater and urban activities such as vehicles and urban runoff sites, these wastewater are discharged from Qalandiah, Mukhmas, Stone Cut and Sweanit and other Israili colonies. These results will quantify by using the sutaible environmental indicators.

5.6.3 Enrichment Factors (EF)

EF values from Al-Qilt catchment are summarized in Table 5.6. Results show that EF values for Al, Ti, Co, Rb, Ba, Li and Be are less than one, this indicates that these metals are derive from the crust and not consider as anthropogenic pollutants according to Zhang and Liu (2002).

The EF values for twenty three heavy and trace metals at Al-Qilt in sediment variy in the distributions and it is severe (red color) at all sites for Ag and Bi, moreover, it is enriched with Cd at Al Bireh, Sweanit, Fawwar, Ras Al-Qilt, Murashahat and Sultan. Furthermore, it is enriched with Zn at Al Bireh and Sweanit and with Hg at Al Bireh and Mukhmas. Therefore Ag, Bi, Cd, Zn and Hg are anthropogenic enriched in sediments. This shows the trend that Ag, Bi, Cd, Zn and Hg are enriched in the ecosystem at Al-Qilt catchment due to human activities.

Table 5.6 Enrichment Factors for trace metals at Al-Qilt catchment. If the EF<1 = dark blue; no enrichment, EF 1-3= light blue; miner, EF 3-5= green; moderate, EF 5-10= dark yellow; moderately, EF 10-25= light yellow; severe, EF > 25 red very severe.

Sampling Sites	**Al**	**Ti**	**V**	**Cr**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Rb**	**Sr**	**Mo**
Al Bireh	**0.67**	**0.56**	**1.18**	**1.21**	**0.61**	**1.41**	**13.76**	**31.94**	**7.88**	**0.72**	**1.52**	**8.23**
Qalandiah	**0.56**	**0.81**	**1.17**	**0.96**	**0.63**	**1.43**	**11.67**	**15.50**	**3.38**	**0.46**	**1.19**	**5.43**
Stone Cut	**0.57**	**0.90**	**1.54**	**1.23**	**0.71**	**1.81**	**8.74**	**13.32**	**8.01**	**0.40**	**1.80**	**9.68**
Mukhmas	**0.67**	**0.84**	**1.54**	**1.77**	**0.84**	**2.21**	**12.95**	**21.58**	**5.48**	**0.67**	**3.52**	**9.53**
Sweanit	**0.72**	**0.69**	**1.51**	**1.69**	**0.74**	**2.33**	**11.68**	**32.84**	**10.31**	**0.68**	**3.31**	**16.78**
Fawwar	**0.87**	**0.80**	**1.74**	**1.76**	**0.80**	**2.29**	**6.02**	**16.24**	**8.56**	**0.58**	**3.34**	**14.37**
Ras Al-Qilt	**0.60**	**0.87**	**2.19**	**2.31**	**1.06**	**3.23**	**4.48**	**10.39**	**10.43**	**0.54**	**5.86**	**18.49**
Murashahat	**0.68**	**0.78**	**1.84**	**1.60**	**0.86**	**2.25**	**7.47**	**4.64**	**14.32**	**0.47**	**4.16**	**21.70**
Sultan	**0.45**	**1.40**	**1.46**	**1.24**	**0.72**	**1.29**	**2.41**	**3.84**	**4.65**	**0.47**	**2.71**	**5.41**

Continue:

Sampling Sites	**Ag**	**Cd**	**Sn**	**Sb**	**Ba**	**Hg**	**Pb**	**Bi**	**B**	**Li**	**Be**
Al Bireh	**1334.40**	**26.67**	**9.20**	**19.90**	**0.85**	**30.38**	**10.33**	**70.83**	**10.58**	**0.78**	**0.33**
Qalandiah	**76.09**	**19.83**	**10.72**	**10.43**	**0.88**	**15.69**	**5.56**	**37.86**	**1.85**	**0.56**	**0.28**
Stone Cut	**48.34**	**23.27**	**7.70**	**13.58**	**0.99**	**4.73**	**7.82**	**26.63**	**1.73**	**0.52**	**0.21**
Mukhmas	**189.42**	**22.98**	**24.36**	**21.79**	**1.64**	**56.32**	**7.07**	**115.83**	**6.58**	**0.75**	**0.37**
Sweanit	**602.60**	**35.08**	**23.79**	**14.45**	**1.87**	**4.44**	**4.62**	**96.79**	**7.06**	**0.72**	**0.31**
Fawwar	**298.85**	**44.51**	**11.00**	**11.30**	**1.07**	**0.00**	**2.91**	**64.40**	**4.80**	**1.65**	**2.31**
Ras Al-Qilt	**114.84**	**107.83**	**9.42**	**10.72**	**0.89**	**7.07**	**2.18**	**44.09**	**2.88**	**0.73**	**0.42**
Murashahat	**39.28**	**32.38**	**3.23**	**5.81**	**0.61**	**1.33**	**1.59**	**22.70**	**3.76**	**0.46**	**0.42**
Sultan	**41.52**	**57.21**	**6.41**	**4.09**	**0.37**	**0.00**	**3.12**	**28.59**	**4.21**	**1.34**	**1.22**

5.6.4 Elemental Background for Soil (EBS) and Continental Crust (CC) as reference.

For this study the pristine soil samples are used from Sweanit, Fawwar, Ras Al-Qilt and Murashahat and name as Elemental Background for Soil (EBS). The Continental Crust (CC) values are used according to Turekian and Wedepohl (1961) as references in the calculations. Results in Figure 5.7 and Table 5.7 show that there are consistence between EBS and CC values in Cr, Ni, Cu, Sr, Sn and Pb. But there are inconsistence as appear in EBS for Zn, As, Ag, Mo, Hg and Cd and it is less for Ba. These variations will affect in the calculations for the contamination factor and it is important to identify the consistence between the EBS and CC values as reference.

Therefore, the results for CF is based on the CC and EBS values for Cr, Co Ni, As, Sr, Mo Cd and Ba are varied at different sites. Results show that it is lower if CC reference values are used for As, Cd, Mo, Ag, Sb, Hg, Bi. Furthermore, there is significant contamination based on the EBS values if compared to the CC values mainly for Cu, Zn, As, Sr, Mo, Ag, Cd, Sn, Sb, Hg and Bi, this indicates that there are significant variation in EBS and CC values for As, Mo, Ag, Cd, Sb, Ba, Hg and B (Figure 5.7 and Table 5.7). To conclude, it is better to use the soil as reference for the CF, since it have more concentrations compared with Continental Crust values.

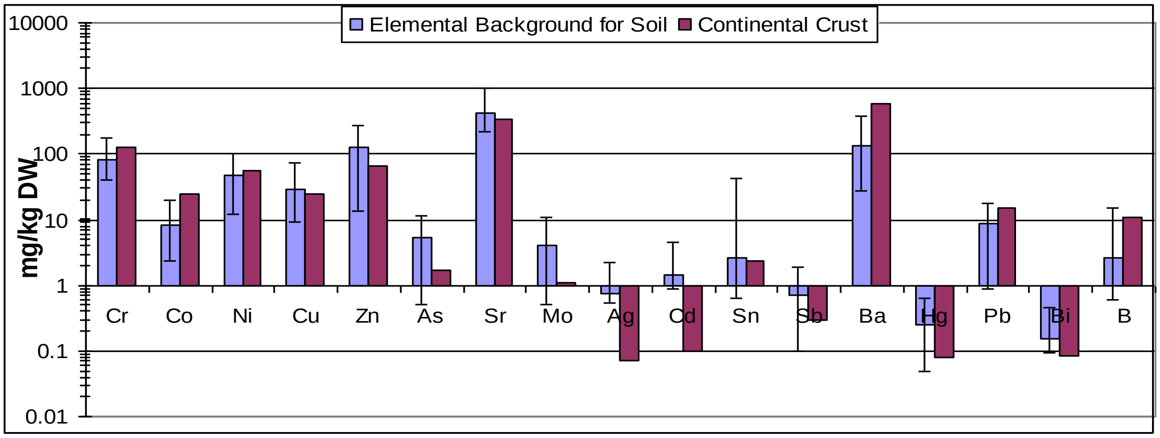

Figure 5.7: Elemental Background for Soil and Continental Crust as reference, values are in median, min and max for EBS.

Table 5.7: CF based on CC and EBS in median min-max of trace metal, n=4, average crustal, TEL and PEL values in sediments, units are in mg/kg DW.

Metal	CC[a]	CF/CC[b]		EBS[c]	CF/EBS[d]		This study [e]	
	mg/kg DW	Median	Min–Max		Median	Min-max	Median	Min-max
Cr	126.00	0.57	0.48-0.63	82.80	0.89	0.73-0.95	71.28	36.40-101.80
Co	24.00	0.28	0.20-0.40	8.30	0.81	0.58-1.14	6.70	3.10-13.00
Ni	56.00	0.70	0.50-0.89	47.45	0.82	0.59-1.05	39.10	25.30-55.50

Cu	25.00	1.99	0.91-6.40	28.95	1.72	0.78-5.53	59.60	22.70-670.00
Zn	65.00	5.25	1.28-10.32	126.85	2.69	0.66-5.29	284.00	76.00-1244.00
As	1.70	2.76	1.47-3.37	5.35	0.88	0.47-1.07	4.70	1.40-24.20
Sr	333.00	0.73	0.53-1.63	410.50	0.58	0.43-1.32	260.00	71.00-658.00
Mo	1.10	3.73	1.18-4.73	4.00	1.03	0.33-1.30	4.00	1.30-33.30
Ag	0.07	31.43	2.86-314.3	0.75	2.93	0.27-29.33	2.00	0.20-55.10
Cd	0.10	9.00	6.90-30.10	1.48	0.61	0.47-2.03	0.90	0.38-3.30
Sn	2.30	3.48	1.00-5.91	2.65	2.94	0.87-5.13	7.40	1.30-24.00
Sb	0.30	4.00	1.00-7.70	0.70	1.71	0.43-3.30	1.30	0.30-6.54
Ba	584.00	0.31	0.10-0.43	132.00	1.37	0.43-1.92	180.00	57.00-496.00
Pb	14.80	1.17	0.47-3.59	8.65	2.00	0.80-6.14	23.93	6.47-159.00
Bi	0.09	7.65	0.82-23.53	0.16	4.06	0.44-12.50	1.00	0.01-12.00
Hg	0.08	3.54	0.01-55.00	0.15	0.76	0.01-14.67	0.70	0.03-11.90
B	11.00	1.45	0.18-4.23	2.60	5.04	0.76-10.10	13.30	2.00-48.00

(a) Average of Continental Crust Taylor, (1972) and Trukian and Wodephol, (1961).
(b) Contamination Factors of this study based to Continental Crust.
(c) The Elemental Background for Soil (EBS) based on the results from pristine soils samples from Al-Qilt.
(d) Contamination Factors of this study based to (EBS).
(e) The concentrations for trace metal in median, min and max of this study.
Note: CF < 1 yellow, 1 ≤CF < 3 green, 3 ≤CF< 6 blue and CF ≥ 6 according to LAWA classifications.

5.6.5 Pseudo total concentration - Contamination Factors (CF)

If the total concentration are used to calculate the CF, results reveal that it posse risk at Al Berih, Qalandiah, Mukhmas, Sweanit, Fawwar, Ras Al-Qilt and then at Sultan mainly for Ag, Hg, Bi and B if compared with other sites based to soil as reference (Table 5.8).

Table 5.8: CF for trace metals by using the Elemental Background of Soil (EBS) as reference, values are in medium n=4 for each step, since CF < 1 blue, 1 ≤CF < 3 green, 3 ≤CF< 6 blue and CF ≥ 6 red according to LAWA classifications.

Sites	Cr	Co	Ni	Cu	Zn	As	Sr	Mo	Ag	Cd	Sn	Sb	Ba	Hg	Pb	Bi	B
EBS	82.8	8.3	47.45	28.95	126.85	5.35	410.5	4	0.75	1.48	2.65	0.7	132	0.15	8.65	0.16	2.6
AL Bireh	0.75	0.86	0.68	4.11	5.87	0.75	0.45	0.99	35.13	0.59	3.42	2.86	1.39	14.63	4.02	14.38	16.94
Qalandiah	0.78	0.83	0.86	4.97	3.77	0.54	0.38	0.75	3.60	0.60	3.77	1.93	1.42	23.39	4.06	8.09	2.90
Stone Cut	0.69	0.68	0.76	2.69	2.77	0.84	0.56	0.96	1.73	0.58	2.70	2.31	1.76	1.15	5.34	5.47	2.73
Mukhmas	0.74	0.87	0.67	2.95	3.76	0.81	0.46	0.88	22.67	0.45	3.66	2.00	1.35	2.63	3.36	10.25	6.79
Sweanit	0.63	0.48	0.58	2.08	3.54	0.65	0.55	1.10	19.60	0.45	4.83	1.46	1.63	2.41	1.63	10.78	5.96
Fawwar	0.75	0.64	0.75	1.44	2.29	0.78	0.75	1.09	14.53	0.83	3.74	1.36	1.28	1.13	1.35	8.28	5.54
Ras Al-Qilt	0.87	0.68	0.95	0.90	1.26	0.82	1.18	1.26	2.67	1.81	2.79	1.01	1.18	1.08	0.86	6.81	3.04
Murashahat	0.78	0.76	0.80	1.58	0.69	1.09	0.89	1.44	1.80	0.62	0.98	0.69	0.75	0.33	0.91	3.66	5.02
Sultan	0.88	1.00	0.71	0.96	0.91	0.67	0.99	0.66	8.13	1.74	4.28	0.79	0.75	0.13	2.47	6.47	7.62

5.6.6 Pseudo total concentration compare to LAWA and SQG guidelines.

LAWA (1998) is defined by Working Group of the Federal States on Water, (http://www.mosselmonitor.nl/Links/lawa_de/300715.pdf). According to LAWA and SQG guidelines for Hg, Cd, Zn, Pb, Cr, Cu and Ni will compare with sediments at Al-Qilt, then reults are summarized (Table 5.9).

Table 5.9: Trace metal results in median, min and max values for sediment and compare with LAWA target values, TEL and PEL.

		Hg	**Cd**	**Zn**	**Pb**	**Cr**	**Cu**	**Ni**
This study	**Median**	**0.76**	**0.90**	**284.00**	**23.90**	**71.30**	**59.60**	**39.10**
	Min-Max	**0.04-11.90**	**0.38-3.6**	**76-1525**	**4.8-134.5**	**29.8-101.8**	**22.7-670**	**16.1-55.5**
Sample Sites / target		**0.80**	**1.20**	**200.00**	**100.00**	**100.00**	**60.00**	**50.00**
AL Bireh J08		2.20	2.57	326.00	134.50	101.80	85.20	43.00
AL Bireh O08		2.76	0.66	817.20	41.54	50.00	141.50	25.80
AL Bireh J09			0.69	671.00	22.30	73.40	96.60	38.30
AL Bireh O09		2.19	1.07	1525.00	28.00	33.10	299.20	16.10
Qalandiah J08		7.60	0.71	525.00	159.00	36.40	670.00	37.10
Qalandiah O08		6.52	0.96	590.10	110.60	52.30	338.30	34.80
Qalandiah J09			0.90	481.00	33.60	76.50	160.10	46.90
Qalandiah O09		8.73	0.87	476.00	36.60	33.00	127.90	24.00
Stone Cut J08		0.20	0.88	76.00	6.47	70.40	40.00	39.10
Stone Cut O08		0.14	0.85	175.70	55.61	74.90	35.90	45.00
Stone Cut J09			0.94	536.00	53.10	44.00	115.20	32.80
Stone Cut O09		4.98	0.82	526.00	39.20	42.20	132.30	28.30
Mukhmas J08		0.90	0.38	180.00	125.40	56.20	43.60	28.20
Mukhmas D08		1.62	0.64	775.10	35.85	49.80	102.00	25.30
Mukhmas J09			0.88	284.00	36.20	75.00	57.60	43.60
Mukhmas O09		0.79	0.48	241.00	7.30	29.80	74.20	24.40
Sweanit J08		11.90	0.73	1244.00	71.94	60.40	215.50	26.70
Sweanit O08		0.14	1.79	238.50	11.51	95.90	30.40	55.50
Sweanit J09			0.60	570.00	16.70	44.40	72.90	27.90
Sweanit O09		0.58	0.57	328.00	11.40	28.80	47.80	21.90
Fawwar J09			1.47	341.00	12.90	79.00	49.80	44.30
Fawwar O09		0.34	0.99	240.00	10.50	45.40	33.40	27.30
Ras Al-Qilt J08		0.50	0.59	197.00	23.93	84.50	59.60	50.00
Ras Al-Qilt O08		0.11	3.30	131.60	6.54	85.00	23.90	50.00
Ras Al-Qilt J09			3.01	146.00	6.90	77.90	25.90	49.70
Ras Al-Qilt O09		0.21	2.34	174.00	8.00	66.70	26.10	40.00
Murashahat J08		0.25	0.91	78.95	7.30	71.28	41.57	39.97
Murashahat O08		0.03	0.91	83.30	8.38	57.60	38.00	35.90
Murashahat J09			1.59	187.00	8.60	83.70	325.50	50.00
Murashahat O09		0.07	0.73	93.00	4.80	40.20	50.20	25.30
Sultan J09			1.54	90.00	17.30	62.00	22.70	29.00
Sultan O09		0.04	3.62	140.00	25.00	83.50	32.90	38.20
TEL		**0.13**	**0.68**	**124.00**	**30.20**		**18.70**	
PEL		**0.70**	**4.21**	**217.00**	**112.00**		**108.00**	

Results reveal that 50% of the Hg, Cd, Pb, Cr and Ni are less than the targeted values and more than 50% of Zn is (262 mg/kg), this value is grater than the target value (200 mg/kg) according to LAWA. Moreover, 50% of the Cu values are (58.6 mg/kg) in the border of the targeted values (60 mg/kg).

Furthermore, the result indicates that the sources of trace metals is from wastewater that discharged from the upstream of Al-Qilt, hence, there are five cases above the (IV) grade of LAWA values, four of them are due to Hg, and three of these are from Qalandiah on dry and wet season, then the other values are high at Sweanit after wet season. The fifth case is with Cu from Qalandiah after wet season of June, 2008.

These results are consistence with the results from the TELs and PELs in which all trace metals (Table 5.9) at the upstream exceed the TEL values, on the otherhand, at downstream "springs" the trace metals values are not reach the TEL values during the study period, furthermore, PEL values are exceed at most of the sites at upstream mainly for Pb at Al Bireh J08, Qalandiah J08 and Mukhmas J08, and for Hg and Zn are exceed at most of sites during this study.

Therefore, results reveal that Cu, Zn and Hg have been pose potential toxicity and they are exceed the TELs and PELs values, mainly at Sweanit, there is has the highest values for Hg and has the second values for Zn.

By these concentrations for trace metals at Al-Qilt the sediments should compare thier toxicity effect on the microorganisms mainly to Zn, Hg, Cu and Cd due to exceed of TELs values, this means that 50% of the samples are above the TEL values and there about 15% effect data set of the samples according to definition of TEL values by (Pekey 2006b; Kucuksezgin *et al.,* 2006; Taylor 1972 and MacDonald 1994).

TELs and PELs include chemical concentrations observed or predicted to associate with the mentioned biological effects. Hence, samples were considered as ‘‘nontoxic’’ if concentrations were lower than TELs, also as ‘‘rarely toxic’’ if concentrations were lower than PELs (MacDonald, 1994; Jones *et al*., 1997).

For this study it is higher than TEL values for Cu, Zn, Cd and Hg ‘‘potentially toxic’’, furthermore, the concentrations are higher than both PELs and TEL values for Hg, Cu and Zn at Al Bireh, Qalandiah and Sweanit.

Furthermore, the highest concentrations of Cd is at Ras Al-Qilt, then Sultan and Fawwar springs, these concentrations are still in the range of nontoxic by comparing the chemical concentration and biological activities on the microorganisms according to TELs for Cd values in sediments (Figure 5.8).

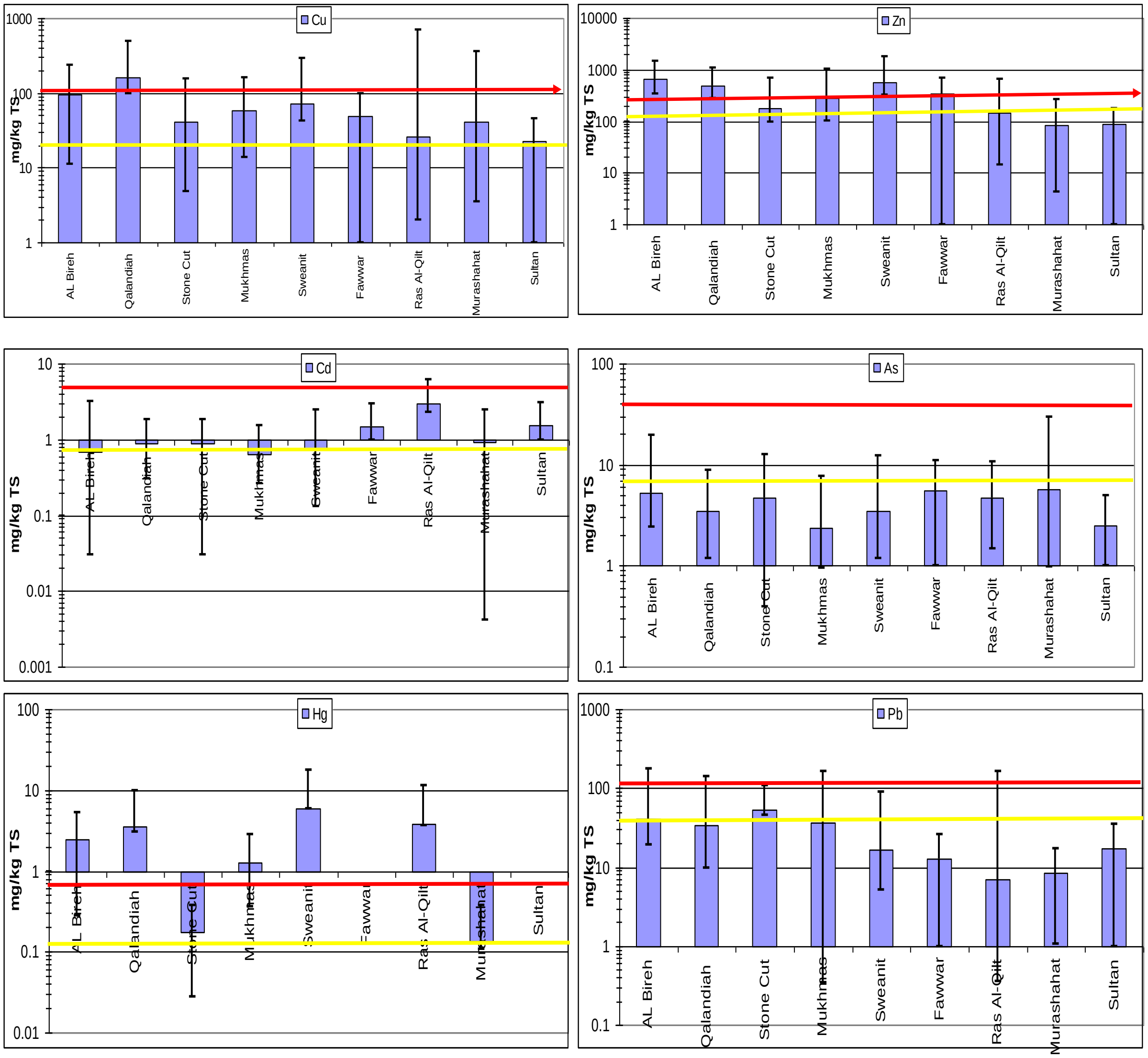

Figure 5.8: Trace metal in sediments are in median, min and max values are compared to TEL (yellow) and PEL (red) at Al-Qilt.

5.6.7 Eco-toxicological sense of trace element concentrations in sediment

The incidence of toxicity is compared among samples for Cr, Ni, Cu, Zn, As, Cd and Pb, results for Ni, Cu and Zn are exceed the ERL concentrations, moreover, Zn and Cu are exceed the ERM (Table 5.10) mainly at the upstream of Al-Qilt catchment due to wastewater that discharged and urban runoff, these results are consistences with TELs and PELs results mentioned before.

The same approach is used to evaluate the predictive and ability of the TELs / PELs (Long *et al.*, 1998). By considering the results for Ni, Cu, Zn and Pb, these are the most toxic due to the exceeding of PEL values at Al-Qilt catchment.

The assessment of sediment contamination according to Sediment Quality Guidelines (SQG) classified as: non-polluted, moderately polluted and heavily polluted, these are based to the SQG of USEPA and Perin *et al.*, (1997). The median values of trace metals from Al-Qilt sediment are summarized in (Table 5.10) and compared with reference baseline. Results show that Cu, Zn, Mo, Ag, and Hg are higher than the Continental Crust concentrations, thus sediments are heavily polluted by Zn, Cu, Ag and Hg, also it is moderately polluted by Mn and it is non polluted by Cr, Ni, As, Cd and Pb according to SQGs.

Table 5.10: Recovery values, Continental Crust, Elemental Background for Soil and trace metals are compared with SQG^{+} by USEPA and Long (1995)[a], units are in mg/kg DW.

Sampling Stations	**Cr**	**Ni**	**Cu**	**Zn**	**As**	**Cd**	**Pb**	**Ag**	**Hg**	**Mn**
Recovery	87.04	100.42		94.44		91.16	90.00			110.00
CC	126.00	56.00	25.00	65.00	1.70	0.10	14.80	0.07	0.04	716.00
EBS	82.80	47.25	28.95	126.85	5.35	1.48	8.65	0.75	0.25	381.00
Al Bireh	61.70	32.05	119.05	744.10	4.00	0.88	34.77	26.35	2.48	255.00
Mukhmas	53.00	26.75	65.90	262.50	2.93	0.56	36.03	2.35	3.51	308.50
Qalandiah	64.40	40.85	144.00	478.50	2.90	0.89	35.10	1.30	0.17	282.00
Stone Cut	57.20	35.95	78.00	350.85	4.50	0.87	46.15	3.35	1.26	230.00
Sweanit	52.40	27.30	60.35	449.00	3.50	0.67	14.11	10.35	6.02	168.50
Fawwar	62.20	35.80	41.60	290.50	4.15	1.23	11.7	6.25	1.80	215.00
Ras Al-Qilt	72.30	44.90	26.00	160.00	4.40	2.68	7.45	2.00	3.86	248.00
Murashahat	64.44	37.94	45.89	88.15	5.82	0.91	7.84	1.35	0.14	447.55
Sultan	72.75	33.60	27.80	115.00	3.60	2.58	21.35	1.25	2.50	513.00
TEL	52.30	15.90	18.70	124.20	7.20	0.68	30.20			
PEL	160.40	42.80	108.20	271.00	41.60	4.20	112.20			
ERL	81.00	20.90	34.00	150.00	8.20	1.20	46.70			
ERM	370.00	51.60	270.00	410.00	70.00	9.60	218.00			
Non polluted	< 25	< 20	< 25	< 90	< 3		< 40	1	< 0.1	<300
Moderately polluted	25-75	20-50	25-50	90-200	3—8		40 - 60	1-2.2	-	300-500
Heavily polluted	**> 75**	**> 50**	**> 50**	**> 200**	**> 8**	**> 6**	**> 60**	**>2.2**	**> 1**	**>500**

+ Sediment Quality Guidelines

[a] Long *et at.*, (1995).

Furthermore, if these trace metals for the upstream are correlated to each others, results reveal that Ni/Cr is highly positive correlated (red) > 0.9, then Zn/Hg, Pb/Hg, Cu/Hg and Cu/Zn are moderately correlated (yellow) > 0.7 and the green color is low correlation < 0.7, and the blue color for no correlations below 0.5. These correlations give sense to the source of pollutants, and all of these parameters are due to domestic and urban runoff (Table 5.11).

Table 5.11: Spearman Nonparametric Correlation for LAWA parameters, n=4 for all parameters and for Hg n=3.

Parameters	**Hg**	**Cd**	**Zn**	**Pb**	**Cr**	**Cu**	**Ni**
Hg	1.00						
Cd	-0.35	1.00					
Zn	0.83**	-0.35	1.00				
Pb	0.70**	-0.23	0.62**	1.00			
Cr	-0.43*	0.56**	-0.37*	-0.11	1.00		
Cu	0.85**	-0.38*	0.77**	0.56**	-0.37*	1.00	
Ni	-0.43*	0.50**	-0.41*	-0.16	0.90**	-0.32	1.00

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

Results reveal that Ras Al-Qilt is not save for domestic usage mainly after wet season, since, there are urban runoff in area and characterize by karstic system, moreover there are a lot of faults for the pollutants can penetrate to reach the water table and there are unexpected load as pollutants such as Hg at Sweanit, this is non dramatically appearance, since the distance between Qalandiah as sources for Hg to Sweanit are in rang of 10-12 km, important to mention that Hg is not appear at Mukhmas, since it that is in between the two points. Thus, it is important to keep Ras Al-Qilt under control and use other factors in relation to toxicity or further analysis in the fractionation form to evaluate the binding of trace metals in sediments.

Moreover, if the springs such as Fawwar, Ras Al-Qilt, Sultan and Murashahat as treatment plant are correlated for the mentioned trace metals, results reveal that only Ni/Cr is highly correlated and other parametres are not correlated. This indicates that the Ni and Cr are as results of same source from both upstream and downstream of Al-Qilt (Table 5.12).

Table 5.12: Spearman Nonparametric Correlation for the LAWA parameters at the springs n=4 for Hg, Cd, Zn, Pb, Cr, Cu and Ni and for Hg n=3.

	Hg	**Cd**	**Zn**	**Pb**	**Cr**	**Cu**	**Ni**
Hg	1.00						
Cd	-0.35	1.00					
Zn	0.55	0.07	1.00				
Pb	0.14	0.01	0.38	1.00			
Cr	0.19	0.41	0.29	0.23	1.00		
Cu	0.29	- 0.62*	0.30	0.10	0.08	1.00	
Ni	0.38	0.30	0.36	0.01	0.90**	0.15	1.00

5.6.8 BCR fractionations steps for trace metal using CF

If results are compared to LAWA it is reveal that the fractionations for Zn, Hg and Cu must be consider due to their high concentrations. Thus, the (CF) must be calculate for each step from BCR fractionations, this will base on the (EBS) fractionation, this will identify the type of bonding and heavy metals that capable to release in relation with (CF). For this reason the CF is good choise to describe the pollution in more detail (Table 5.13). On the otherhand, results for recovery of the certified parameters are within ±15% for the tested parameters except for Cd (132.5%) and for Ba (58.3%). Results for CFs reveal that Cr, Ni, As, Sr, Cd and Ba are less than six, this is not high risks for contaminations to the environments and ecosystems, moreover, the CFs for Co, Cu, Zn, Mo, Ag, Sn, Sb Pb, and Bi are greater than six grades for one of the fractionation steps from the BCR steps, this will indicate the type of bonding, then give ideas about the mobility or transport of these trace metals within the aquatic system, for example; Zn has the highest value of CFs in step one at Al Bierh (treated wastewater), Qalandiah (untreated wastewater) and Fawwar spring (groundwater), this mean that metals are released at this stage it is classified as exchangeable fraction, this step contain metals in loosely held surface that associate with carbonates, this step is easy to leached and can easily transport in aquatic system, on the otherhand, Co has the highest values of CFs for step two at Sultan spring "groundwater", this means that Co is released at this stage it is classified as being associate with the easily reducible fraction that consists of "new" oxides and oxy-hydroxides of Mn and amorphous Fe oxides. For steps three the CFs are higher than six grades for Cu, Zn, Mo, Ag, Sb, Pb and Bi at Al Bireh, also it is high for Cu, Ag, Sb and Bi at Mukhmas (wadi for wastewater), moreover, it is high for Cu, Mo, Sb, Pb and Bi at Qalandiah and it is high for Sb, Pb and Bi at Stone Cut, also it is high for Bi, Ag, Sn and Sb at Fawwar spring (groundwater), this means that these trace metas are released at this stage they classified as being associate with organic matter and sulfur or in oxidisable form. Furthermore; Ag and Bi are predominanted for step four at Al Bireh, Mukhmas and Fawwar for Ag and then at Al Bireh for Bi, this means that they are classified as "residual" this is not extracted in the previous three stages.

As results Zn, Ag, Pb and Bi trace metals fractionations are released from all steps, this will increase the risk for mobility and transport in the aquatic system in the exchange with carbonate, oxidazable, reducible or in residual forms. Moreover; the trace metal fractionation at the springs are behave in varied manners (Figure 5.1), for example, Fawwar is located at the upper of Ras Al-Qilt springs, but the Ag is released at steps three and four, this mean that it is in the oxidazable and residue form but at Ras Al-Qilt spring is released at steps one and two, this means that it is in exchange carbonate bonded and reducible forms as Fe and Mn bonded, these variations are due to stability of trace metals and there capability to complex in the unsaturated zone, rocks types and soil composition, since, it is more in carbonate form compared to Ras Al-Qilt. On the otherhand; Sultan spring is behave in different manner, Co and Pb are released at step two, this means that they are in the reducible form or bonded with Fe and Mn, thus it easily to reach the groundwater if complexes change despite the presence of carbonate form.

On the contrary; the CFs for Cr, Ni, As, Sr, Cd and Ba are never exceed the six grades for all BCR's fractionation steps, this put these values in category that not pose the impacts at Al-Qilt catchment otherwise; it is good to test these parameters with others environmental factors.

Table 5.13: Contamination Factors* for the BCR fractionation steps, values in median for all parameters, n =4 for each step, color according to LAWA scale.

Sampling sites	Cr	Co	Ni	Cu	Zn	As	Sr	Mo	Ag	Cd	Sn	Sb	Ba	Hg	Pb	Bi	B	Li	Be
Recovery	101.39	110.35	111.66		111.18					132.47		111.89	58.31	90.73					
Al Bireh Step1	0.71	2.17	1.61	2.10	61.94	3.08	0.93	1.25	6.00	0.25	1.00	3.33	0.44	8.13	5.00	6.50	6.49	0.60	0.50
Al Bireh Step2	0.33	0.50	0.71	0.89	19.03	1.30	0.39	1.00	10.00	0.61	1.00	2.50	1.73	8.57	5.00	6.50	17.17	0.58	0.50
Al Bireh Step3	1.82	0.61	1.35	19.42	11.51	1.59	0.35	13.68	19.50	1.52	2.50	60.50	2.33	26.67	9.02	31.00	4.08	0.93	0.60
Al Bireh Step4	0.55	0.48	0.48	1.41	0.58	0.32	0.58	0.35	72.30	0.86	3.70	2.42	1.01	71.89	2.35	8.60	0.65	0.92	0.63
Qalandiah Step1	0.68	5.00	3.21	1.10	28.71	1.35	0.59	3.13	6.00	0.39	1.50	3.33	0.70	6.88	7.50	3.00	1.28	0.55	0.50
Qalandiah Step2	0.60	0.75	1.25	0.67	10.89	3.05	0.29	2.00	10.00	0.84	1.50	3.75	1.21	7.14	12.18	6.00	1.75	0.60	0.63
Qalandiah Step3	0.99	0.84	1.30	24.30	5.21	2.25	0.38	6.84	5.00	1.36	21.00	15.00	1.92	14.17	15.95	14.10	0.77	1.03	0.53
Qalandiah Step4	0.60	0.55	0.60	4.04	0.76	0.58	0.81	0.42	5.50	1.21	4.35	2.83	1.09	320.81	1.59	4.37	0.74	0.97	0.60
Stone Cut Step1	0.78	4.00	2.21	1.40	9.66	1.35	0.63	3.13	10.00	0.28	1.00	5.67	0.74	6.25	9.00	1.00	1.33	0.58	0.50
Stone Cut Step2	0.43	0.88	1.23	0.28	4.06	2.10	0.49	1.50	10.00	0.59	1.00	3.13	1.04	34.29	5.56	3.00	1.67	0.53	0.50
Stone Cut Step3	1.27	1.02	1.18	7.43	4.18	1.98	0.89	6.58	5.00	1.54	3.50	20.50	2.46	81.67	15.61	17.20	0.77	0.68	0.55
Stone Cut Step4	0.59	0.60	0.48	1.19	0.66	0.34	0.67	0.37	2.70	0.93	2.75	1.83	1.74	312.03	0.96	2.17	0.60	0.51	0.55
Mukhmas Step1	0.64	2.83	1.34	0.50	5.00	2.67	0.83	1.88	10.00	0.25	1.00	3.33	0.66	7.50	3.75	7.50	0.95	0.55	0.53
Mukhmas Step2	0.36	0.63	0.71	0.28	3.26	1.50	0.51	1.00	10.00	0.51	2.50	1.63	1.29	7.86	1.12	7.50	4.83	0.55	0.53
Mukhmas Step3	1.37	1.13	1.47	7.38	2.99	1.29	1.39	2.89	10.00	1.75	1.50	10.00	1.94	7.50	3.45	8.10	0.96	0.73	0.60
Mukhmas Step4	0.90	0.89	0.76	1.31	1.00	0.63	0.89	0.67	6.60	1.00	2.43	1.17	2.07	10.14	0.69	4.17	0.57	0.98	0.63
Sweanit Step1	0.61	2.17	1.18	0.70	5.66	2.40	0.60	2.50	6.00	0.33	1.50	3.33	0.34	7.50	3.75	3.00	1.72	0.55	0.50
Sweanit Step2	0.57	0.88	0.70	0.39	2.51	1.00	0.43	1.00	10.00	0.37	1.00	1.25	0.81	7.86	0.91	3.00	3.67	0.53	0.50
Sweanit Step3	1.09	0.75	0.85	3.50	3.55	1.35	1.53	3.16	14.00	1.07	10.50	10.00	2.75	8.33	3.10	8.00	1.62	0.63	0.55
Sweanit Step4	0.41	0.35	0.48	0.66	0.44	0.78	0.44	1.04	10.90	1.36	3.25	0.83	1.54	18.11	0.67	1.27	0.65	0.52	0.55
Fawwar Step1	0.68	2.83	1.21	0.90	8.39	2.31	0.84	3.13	20.00	0.47	20.00	3.33	0.82	3.75	7.50	20.50	1.28	0.53	0.50
Fawwar Step2	0.77	0.63	0.79	2.89	3.29	2.00	0.86	2.00	29.00	1.05	20.00	1.25	0.94	4.29	1.47	20.50	2.50	0.53	0.50
Fawwar Step3	1.46	1.09	1.63	4.01	4.00	1.59	1.78	2.89	18.00	3.05	23.00	15.00	2.25	5.00	3.55	11.90	1.73	0.68	0.58
Fawwar Step4	0.95	0.61	0.95	0.81	0.78	0.74	0.69	1.25	12.40	1.21	2.37	0.83	1.31	7.57	0.34	3.80	1.18	0.77	0.58

Ras Al-Qilt Step1	0.73	3.17	1.74	0.70	2.34	1.42	1.10	3.13	10.00	1.67	1.00	0.50	1.00	8.13	2.00	3.00	1.02	0.53	0.50
Ras Al-Qilt Step2	2.30	1.00	1.14	0.44	1.09	1.98	1.57	1.00	10.00	3.25	1.00	1.00	0.73	6.43	0.97	3.00	2.33	0.53	0.50
Ras Al-Qilt Step3	1.62	0.97	1.17	1.54	0.96	1.68	4.05	1.58	6.50	2.91	1.50	3.50	1.75	10.00	1.46	1.60	1.42	0.65	0.55
Ras Al-Qilt Step4	0.90	0.49	1.07	0.65	0.79	0.92	0.42	1.65	2.00	0.71	0.95	0.50	0.91	9.86	0.21	0.50	0.31	0.38	0.55
Murashahat step 1	0.62	2.83	1.47	1.20	0.90	2.88	0.87	3.13	10.00	0.56	1.00	1.00	0.98	9.38	1.75	3.00	1.09	0.55	0.50
Murashahat step2	0.84	0.75	0.95	0.56	0.51	1.95	0.99	1.50	10.00	0.85	1.50	0.75	0.74	7.86	0.59	6.00	1.92	0.55	0.53
Murashahat Step3	1.05	0.95	1.09	2.63	0.74	1.33	2.42	0.79	5.00	0.91	1.50	6.50	0.81	7.50	1.39	1.20	2.23	0.65	0.55
Murashahat Step4	1.49	1.03	1.17	1.35	1.06	3.51	1.08	2.13	3.40	2.39	1.38	0.92	0.57	1.76	0.45	3.73	1.29	0.86	0.63
Sultan Step1	0.71	1.50	1.18	0.60	0.48	0.58	0.76	1.88	20.00	1.94	21.00	0.00	0.62	3.75	7.50	20.00	0.44	0.53	0.50
Sultan Step2	1.72	13.88	3.64	2.39	0.79	1.50	0.17	1.50	20.00	1.37	21.00	0.00	0.67	4.29	22.35	20.00	1.67	0.58	0.55
Sultan Step3	0.58	0.38	0.69	0.55	0.21	0.24	0.04	1.58	13.00	0.38	21.00	0.00	0.21	23.33	1.66	4.10	0.46	0.65	0.53
Sultan Step4	0.98	1.39	0.72	1.44	0.74	0.51	1.39	0.25	2.60	1.50	2.58	0.25	0.33	0.81	0.64	3.53	0.31	0.63	0.58

***** CF < 1 blue, 1 ≤CF < 3 green, 3 ≤CF< 6 yellow and CF ≥ 6 red according to LAWA classifications.

5.6.9 BCR fractionations for each step according to date and compare with LAWA parameters.

The values for each step of BCRs are compared with LAWA trace metals (Table 5.14), this indicates that Cu, Zn, Hg and Pb are high in the oxidisable and residual form at Al Bireh, Mukhmas, Qalandiah, Stone Cut and Sweanit, these posses risk from Cu at Qalandiah J08 in step three and from Hg at Stone Cut and Qalandiah on J09 and O09 at step four.

Table 5.14: BCR steps with time series in comparison with LAWA parameters, colors are according to LAWA classifications.

Sampling stations	CuJ08	CuO08	CuJ09	CuO09	ZnJ08	ZnO08	ZnJ09	ZnO09	HgJ08	HgO09	PbJ08	PbO08	PbJ09	PbO09
ALBireh step 1	0.60	1.00	1.60	1.10	191.00	148.90	193.00	230.00	0.01	0.01	0.10	0.07	0.10	0.20
ALBireh step 2	0.20	0.90	0.70	1.10	338.00	309.00	247.00	798.00	0.01	0.00	0.20	1.10	0.60	1.70
ALBireh step 3	209.80	112.50	66.00	387.10	623.00	275.00	138.00	747.00	0.02	0.01	44.50	15.43	17.70	34.10
ALBireh step 4	17.30	18.50	33.00	11.30	25.00	53.90	71.00	18.00	4.30	1.02	23.60	24.30	6.40	3.00
Mukhmas step 1	0.05	0.50	0.30	0.20	10.00	94.40	10.00	21.00	0.01	0.00	0.05	0.03	0.10	0.20
Mukhmas step 2	0.20	0.30	1.80	0.20	21.00	122.40	66.00	45.00	0.01	0.00	0.05	0.18	0.80	0.20
Mukhmas step 3	60.10	81.30	40.80	62.40	116.00	446.40	117.00	1.70	0.01	0.00	16.60	3.01	30.50	3.20
Mukhmas step 4	22.60	17.20	16.60	11.80	75.00	97.40	61.00	25.00	0.59	0.16	3.30	27.70	5.00	3.80
Qalandiah step 1	0.50	3.70	0.60	0.50	72.00	118.80	106.00	67.00	0.01	0.00	0.05	0.27	0.10	0.20
Qalandiah step 2	0.05	0.80	20.40	0.40	144.00	152.40	218.00	299.00	0.01	0.00	2.70	1.44	22.90	1.00
Qalandiah step 3	695.10	279.80	82.70	123.50	286.00	211.50	39.00	195.00	0.01	0.01	168.30	47.76	7.10	43.80
Qalandiah step 4	64.10	50.30	52.30	25.40	40.00	85.40	58.00	45.00	10.10	13.64	12.50	61.20	4.10	7.80
Stone cut step 1	0.05	0.80	0.60	0.80	1.00	8.90	51.00	69.00	0.01	0.00	0.05	0.16	0.30	0.20
Stone cut step 2	0.05	0.30	0.70	0.20	24.00	25.00	113.00	306.00	0.05	0.00	1.10	0.99	0.70	0.90
Stone cut step 3	37.50	14.90	85.90	131.90	102.00	49.70	248.00	224.00	0.06	0.04	103.50	30.45	43.30	46.30
Stone cut step 4	9.00	17.60	12.60	26.00	46.00	76.00	30.00	44.00	8.90	14.19	4.70	18.00	5.10	7.20
Sweanit step 1	0.30	0.40	1.00	0.30	2.00	16.10	100.00	19.00	0.01	0.00	0.05	0.01	0.10	0.20
Sweanit step 2	0.05	0.40	0.60	0.30	28.00	38.30	115.00	47.00	0.01	0.00	0.10	0.11	0.20	0.20
Sweanit step 3	19.40	11.40	58.90	38.70	51.00	56.60	244.00	220.00	0.01	0.00	12.00	3.49	14.30	5.80
Sweanit step 4	4.30	19.50	7.20	9.50	14.00	107.00	26.00	34.00	0.89	0.45	1.70	31.60	2.50	6.10
Fawwar Step1			0.70	0.20			40.00	12.00		0.00			0.10	0.20
Fawwar Step2			4.90	0.30			67.00	45.00		0.00			0.30	0.20
Fawwar Step3			36.90	29.70			137.00	175.00		0.00			10.70	9.70
Fawwar Step4			9.10	11.50			53.00	53.00		0.28			1.80	2.50
Ras Al-Qilt step 1	0.05	0.40	0.40	0.30	4.00	6.50	8.00	9.00	0.01	0.00	0.05	0.03	0.10	0.20

Ras Al-Qilt step 2	0.05	0.40	1.30	0.40	12.00	15.90	21.00	27.00	0.01	0.00	0.05	0.13	0.20	0.20
Ras Al-Qilt step 3	10.00	10.20	15.30	18.00	23.00	24.10	51.00	66.00	0.01	0.00	3.30	1.15	5.10	6.30
Ras Al-Qilt step 4	5.10	10.10	6.60	10.00	57.00	69.30	47.00	50.00	0.56	0.17	0.90	5.60	1.10	1.60
Murashahat step 1	0.05	0.50	5.80	0.70	0.10	2.60	7.00	3.00	0.01	0.01	0.05	0.02	0.10	0.20
Murashhat step 2	0.05	0.40	4.80	0.60	5.00	6.20	26.00	11.00	0.01	0.00	0.05	0.10	0.10	0.20
Murashhat step 3	38.60	16.70	18.90	24.70	26.00	14.20	37.00	32.00	0.01	0.00	4.00	2.35	4.00	5.30
Murashhat step 4	15.40	18.90	33.60	14.80	72.00	78.10	72.00	48.00	0.09	0.04	2.50	11.40	3.20	2.30
Sultan Step1			0.40	0.20			2.00	1.00		0.00			0.10	0.20
Sultan Step2			1.00	3.30			22.00	5.00		0.00			7.40	0.20
Sultan Step3			5.40	3.80			9.00	7.00		0.01			5.00	4.50
Sultan Step4			15.50	21.20			54.00	46.00		0.03			3.40	4.80

5.6.10 Chemical toxicity in relation to biological test

In the same manner, the results for Cu, Zn, As, Cd, Pb and Hg will compare with other area using the results for TELs and PELs (MacDonald 1994; Jones *et al.*, 1997), also the results for CC and EBS are compared with results for trace metals at Al-Qilt, these values includes chemical predicted values that associate with no biological adverse effects.

Results reveal that some of trace metals are posing and exceed the TELs values, other are posing and exceed the PELs values, moreover, according to TELs and PELs classifications, the samples are considered as ‘‘nontoxic’’ when the concentrations were lower than TELs such as for As, Cd and Pb and as ‘‘rarely toxic’’ when concentrations are lower than PELs and higher than TEL such as Cu and As, also as ‘‘potentially toxic’’ when concentrations are higher than both PELs and TEL such as Zn and Hg (Table 5.15).

Table 5.15: The CC and EBS in median for trace metal, results from this study, TEL and PEL values in sediments, units are in mg/kg DW and n=4.

Metal	**CC**[a]	**EBS**[b]	**This study** [c]		**TEL**[d]	**PEL**[d]
	mg/kg DW		**Median**	**Min-max**	**mg/kg DW**	
Cr	126.00	82.80	71.28	36.40-101.80		
Co	24.00	8.30	6.70	3.10-13.00		
Ni	56.00	47.45	39.10	25.30-55.50		
Cu	25.00	28.95	59.60	22.70-670.00	18.70	108.00
Zn	65.00	126.85	284.00	76.00-1244.00	124.00	271.00
As	1.70	5.35	4.70	1.40-24.20	7.24	41.60
Sr	333.00	410.50	260.00	71.00-658.00		
Mo	1.10	4.00	4.00	1.30-33.30		
Ag	0.07	0.75	2.00	0.20-55.10		
Cd	0.10	1.48	0.90	0.38-3.30	0.68	4.21
Sn	2.30	2.65	7.40	1.30-24.00		
Sb	0.30	0.70	1.30	0.30-6.54		
Ba	584.00	132.00	180.00	57.00-496.00		
Pb	14.80	8.65	23.93	6.47-159.00	30.20	112.00
Bi	0.09	0.16	1.00	0.01-12.00		
Hg	0.08	0.15	0.70	0.03-11.90	0.13	0.70
B	11.00	2.60	13.30	2.00-48.00		

(a) Average of Continental Crust Taylor, (1972) and Trukian and Wodephol, (1961).
(b) The Elemental Background for Soil (EBS) based on the results from pristine soils samples from the Al-Qilt wadi.
(c) The statistical concentrations for trace metal in median, min and max from this study.
(d) MacDonald, (1994) and Jones *et al*., (1997).
Note: Colors according to LAWA classifications.

5.6.11 Metal Pollution Index (MPI)

The evaluations for sediment contamination is conducted by calculate the MPI for Cr, Co, Ni, Cu, Zn, As, Sr, Hg, Mo, Ag, Cd, Sn, Sb, Ba, Pb and Bi, the results of MPI for Hg is grater than one during the four times sampling campaign, since the Maximum Permissible Limit for Hg is 1000, this is the highest values if compared to any other parameters (Figure 5.9).

The MPI results reveal that it is less than one for all parameters, this is classified them as unpolluted. Most of the sites are posed risk for pollutions due to Hg mainly at Qalandiah, Sweanit and Ras Al-Qilt (Figure 5.9).

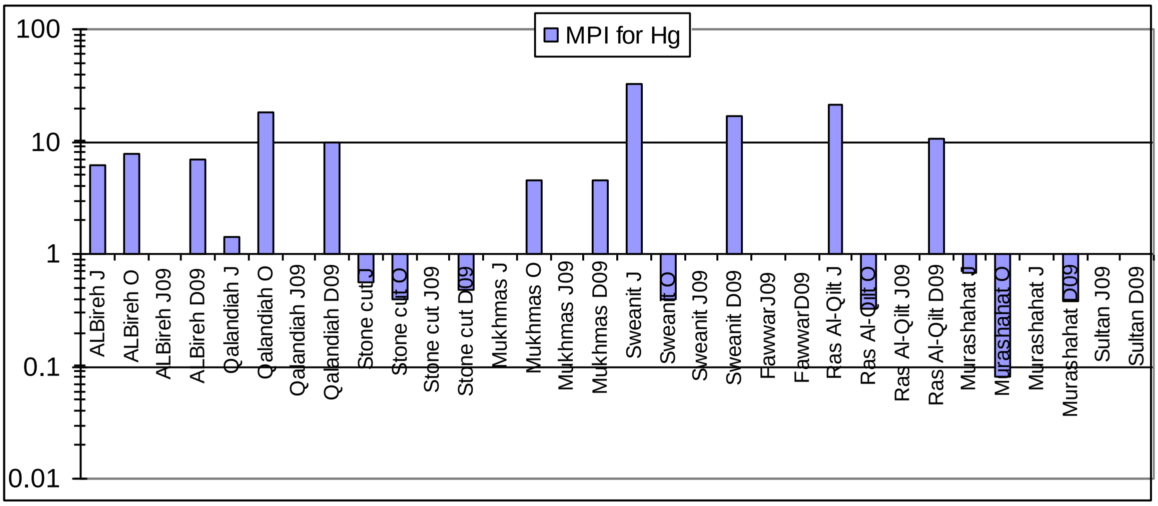

Figure 5.9: Metal Pollution Index for Hg from sampling sites at Al-Qilt.

MPI results are inconsistence after CC and EBS calculations, thus it is better to use the EBS in calculations, since the Elemental Background for Soil are varied and not consistences if compared to Continental Crust values (Figure 5.10).

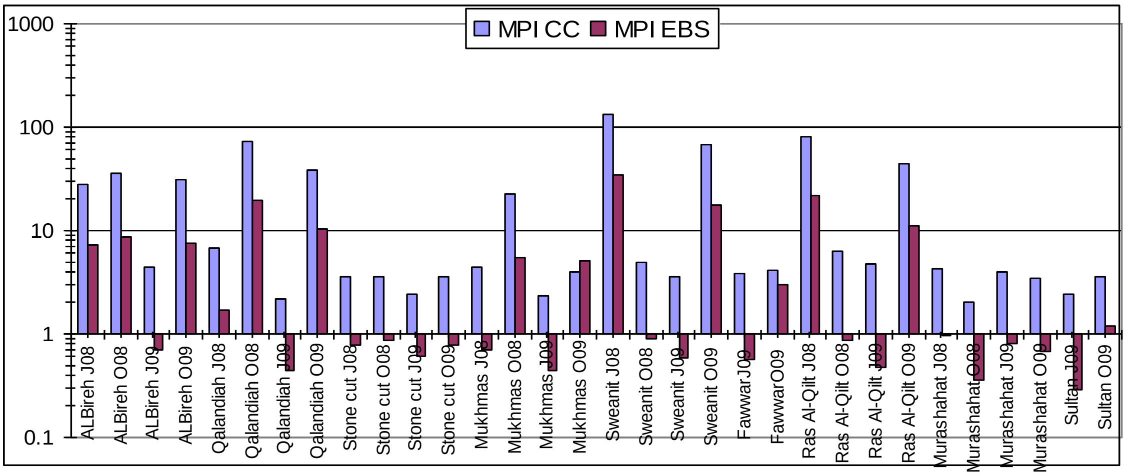

Figure 5.10: Metal Pollution Indexes (MPI) using (CC) and (EBS) as references.

Furthermore, there are seasonal effects due to urban runoff and raw wastewater that discharged to wadi, for example, results on 2008 are grater than 2009 due high rain fall on 2009, which is in range of 750mm if compared with 2008 which is in range of 550mm at the upstream area of Al-Qilt (PWA, 2010), this will cause dilution that increase the erosion to the sediments, on the otherhand, the MPI values are varied within the two seasons of the same year due to diffirance in wastewater discharged and urban runoff (Figure 5.10).

5.6.12 Geo-accumulation Index (Igeo)

The *I*geo values for trace and heavy metals are graphed (Figure 5.11). Results show variation between the sites for the analyzed parameters; these are highly related to pollution intensity and background concentrations. This factor will explain the chemistry of the wastewater in Al-Qilt catchment. Result for *Igeo* reveal that Sweanit is located at the upstream, but it is moderately polluted with Ag, Hg and Bi and there are variations due to seasonal effects. On the otherhand, Al Bireh and Mukhmas are located at the begnning of stream and they are moderately polluted with Ag. Furthermore, result from Qalandiah at the upstream is moderately polluted with Hg and there are variations due to seasonal effects. These calculations of *Igeo* for 26 trace metals aim to assign the anthropogenic pollutants for sediments from Al-Qilt catchment according to I*geo* classifications (Table 5.16).

Table 5.16: Trace metal classifications and pollution intensity for the trace metals are according to I*geo* class.

Heavy metals (I*geo* class)	Pollution intensity	(I *geo)*
Al, Ti, Cr, Mn, Fe, Co, Ni, Rb and Ba.	Background concentrations	< 0
V, Sr and B	Unpolluted	0-1
Cu, Zn, As, Mo, Cd, Sn, Sb, Hg, Bi and Pb.	Moderately to Unpolluted	1-2
Ag	Moderately polluted	2-3

Furthermore, using the I*geo* we can classify the pollutance according to the sites and location (Figure 5.11), results indicate that the upstream sites have the highest values due to enrichment from wastewater and urban runoff, but some parameters such as Ag, Cd, Sn, Sb, Hg and Bi are still have high concentrations at downstream of Al-Qilt.

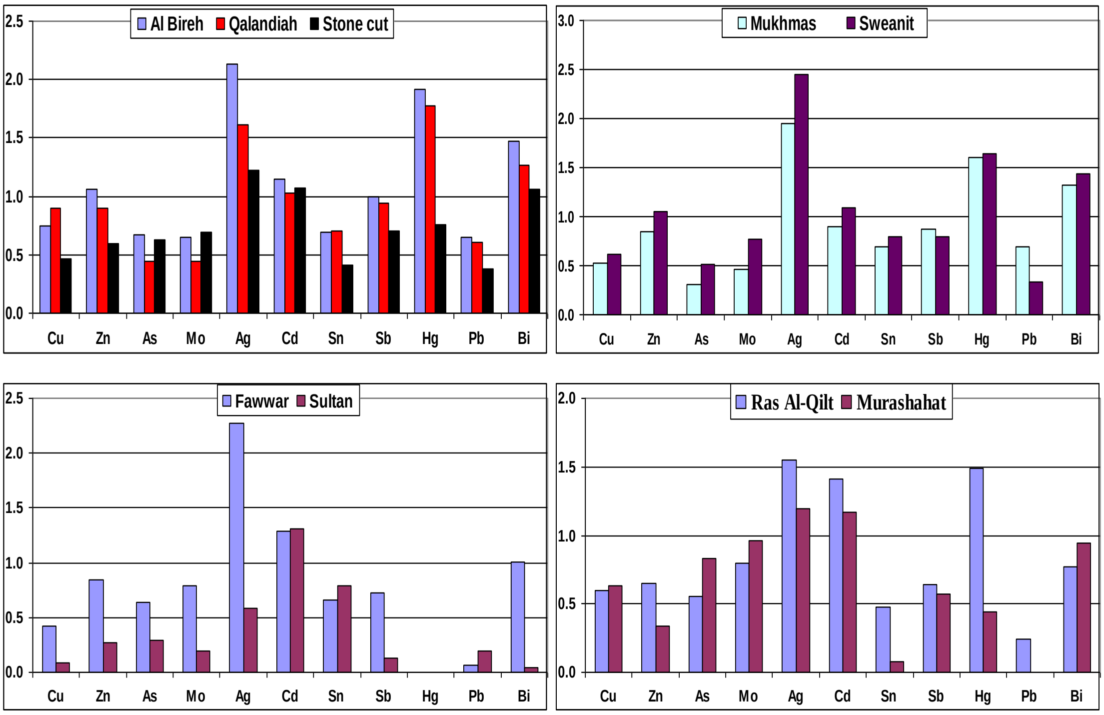

Figure 5.11: Geo-accumulation Index values for heavy and trace metals, the first two graphs are at upstream sites and the second two graphs are at downstream sites of Al-Qilt.

5.6.13 Ecological Risk Index (RI)

The RI values are characterized as the sensitivity of local ecosystem by toxic metals and represent to ecological risk from overall contamination; the ecological risk assessment is result from toxic metals at Al-Qilt (Table 5.17). It is found that the risk indices (Eir) values at upstream at Al Bireh, Qalandiah, Stone Cut, Mukhmas and Sweanit are ranked in the following order: Co < V < Cr < B < Ni < Mo< Sn < Sb < Zn < Pb < Cu < Bi < As < Ag < Hg < Cd while it is downstream at Fawwar, Ras Al-Qilt, Sultan and Murashahat are ranked as in the following order: Co < V < B < Cr < Zn < Sn < Sb < Ni < Mo < Bi < Pb < Cu < As < Ag < Cd < Hg. Moreover, results reveal that the average ecological risks (Eir) for the highest four values in both areas are similar and ranked in the order of As < Ag < Hg < Cd.

Table 5.17: RI values are based on Eir values, colors are based on the LAWA classifications.

Sampling Sites	**V E*ir***	**Cr E*ir***	**Co E*ir***	**Ni E*ir***	**Cu E*ir***	**Zn E*ir***	**As E*ir***	**Mo E*ir***	**B E*ir***
AL Bireh	0.58	0.98	0.30	2.86	23.81	11.45	23.50	3.59	**4.00**
Mukhmas	0.55	0.98	0.30	2.84	17.08	7.35	25.59	3.18	**1.60**
Qalandiah	0.47	1.02	0.29	3.65	28.80	7.36	17.06	2.73	**0.69**
Stone Cut	0.54	0.91	0.24	3.21	15.60	5.40	26.47	3.50	**0.65**
Sweanit	0.36	0.83	0.16	2.44	12.07	6.91	20.59	4.00	**1.41**
Fawwar	0.49	0.99	0.22	3.20	8.32	4.47	24.41	3.95	**1.31**
Ras Al-Qilt	0.53	1.15	0.24	4.01	5.20	2.46	25.88	4.59	**0.72**
Murashahat	0.53	1.02	0.26	3.39	9.18	1.36	34.21	5.24	**1.19**
Sultan	0.70	1.15	0.35	3.00	5.56	1.77	21.18	2.41	**1.80**
RI values	4.77	9.03	2.35	28.59	125.62	48.52	218.88	33.19	**13.36**

Continue:

Sampling Sites	**Ag E*ir***	**Cd E*ir***	**Sn E*ir***	**Sb E*ir***	**Hg E*ir***	**Pb E*ir***	**Bi E*ir***	**RI values**
AL Bireh	376.43	264.00	3.93	6.68	1100.00	11.75	27.06	1860.93
Mukhmas	187.14	199.50	4.22	4.67	0.00	9.82	19.29	484.11
Qalandiah	33.57	265.50	4.35	4.50	250.00	11.86	15.24	647.08
Stone Cut	18.57	259.50	3.11	5.40	72.05	15.59	10.29	441.03
Sweanit	147.86	199.50	4.91	3.42	70.80	4.77	18.53	498.55
Fawwar	89.29	369.00	3.00	3.17	0.00	3.95	0.00	515.77
Ras Al-Qilt	28.57	802.50	2.35	2.35	56.85	2.52	0.00	939.91
Murashahat	19.29	273.63	1.13	1.60	14.05	2.65	0.00	368.72
Sultan	17.86	774.00	3.20	1.83	0.00	7.21	0.00	842.01
RI values	918.57	3407.13	30.19	33.62	1563.75	70.12	90.41	6598.10

Results for As, Ag, Cd and Hg show that they pose risk to the local ecosystem (Figure 5.12), the highest percentage of E*ir* are due to As, Ag, Hg and Cd respectively in relation to other parameters.

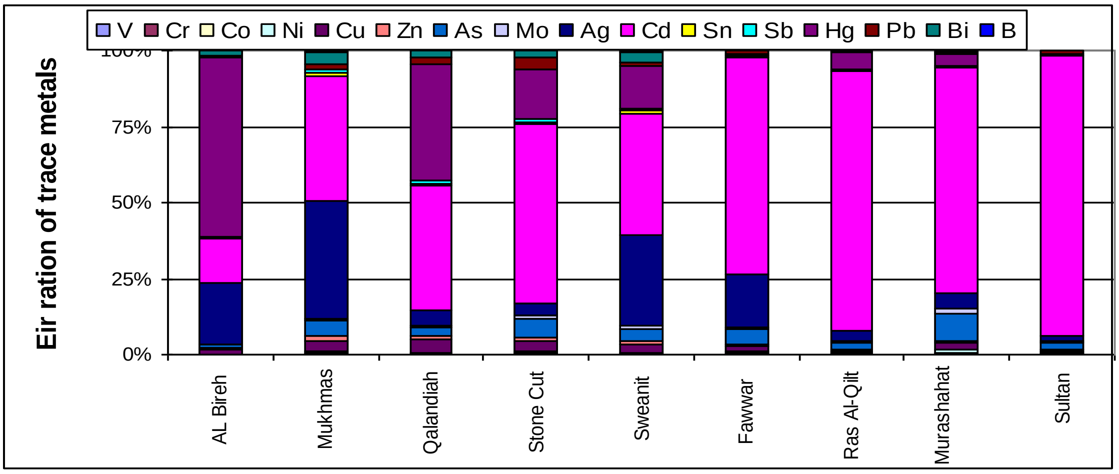

Figure 5.12: Contribution percentages of the sixteen trace metals to the total trace metals.

Results of percent contribution for individual metal to the overall potential ecological risk are in (Figure 5.12). Results show that Cd is posing the highest risk with percentages of 67% then Hg rank as second among the metals and contribute of 20% from the total followed by Ag with 7%, Cu with 2% and Bi, As with 1%. It is conclud that the highest ecological risk is dominated by Cd and Hg 87% from the total potential ecological risk. This result describes both the ecological risk for single pollutant and the overall risk or contamination from various pollutants.

In order to quantify the overall potential ecological risk at Al-Qilt, the calculations are based on the CF then the sum of risk factors for each site and parameters are calculated (Figure 5.13).

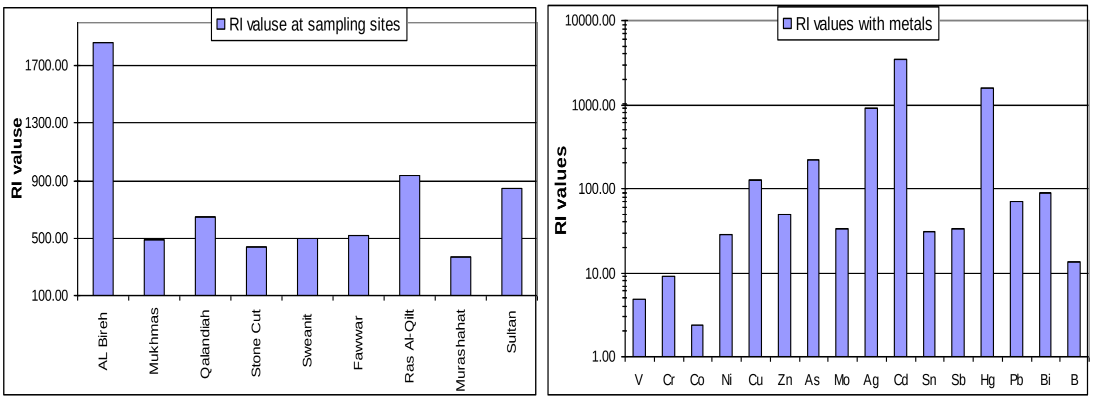

Figure 5.13: RI values are according to sample sites at the left and according to parameter at the righ.

The RI results at the upstream are range from 441 at Stone Cut to 1860 at Al Bireh. If the RI is ≥ 600 it means very high risk and we ranking the sites by Al Bireh > Qalandiah. Moreover, the RI at downstream range from 842 at Sultan spring to 940 at Ras Al-Qilt spring, both poses high risk according to the RI values and classifications.

If the three springs Fawwar, Ras Al-Qilt and Sultan are compared with each other for RI values, they are 516, 940 and 842 respectively. Fawwar is located at upstream of Ras Al-Qilt or Sultan springs but in terms of risks Ras Al-Qilt spring has the highest RI values from Al-Qilt springs (Figure 5.1). As conclusion, Ras Al-Qilt is highly risk in terms of ecological risk for trace metals if compared with other springs in the study area.

Results for geo-accumulation reveal that Cd, Hg and As are uncontaminated. However, ecological risk show that Hg, Cd and As are of considerable interest due to high toxicity and ecological risks. Thus the I*geo* method is mainly focus on the accumulation levels of individual metals without taking in consideration the weight of the toxic response factor.

5.7 Conclusions

Surface sediment from Al-Qilt catchment is characterized as industrial and densely populated areas. Trace metal is normalized against CC as background with Fe, TOC and Al, then Fe is used as elemental normalizer to identify the anthropogenic pollutants and to calculate the EF. Results for EF's indicate that it is extremely severe and enriched by Ag, Bi, Cd, Zn and Hg and Ag and Bi at all sites of Al-Qilt. Moreover, Cd is enriched at Al Bireh, Sweanit, Fawwar, Ras Al-Qilt, Murashahat and Sultan, also, Hg is enriched at Al Bireh and Mukhmas and Zn is enriched at Al Bireh and Sweanit.

CF results for Zn, Ag, Cd, Hg, Bi and B are high than six grades, thus, 50% of Zn values are higher than the targeted values according to LAWA classifications and 50% of the Cu values are in the rang of the targeted values. Furthermore, by using the BCR fractionations and CFs for Cu, Zn, Ag, Sb, Pb and Bi are higher than six, this increase the impact for the mobility of trace metals that may reach the water column. Therefore, SQGs values such as TELs and PEL for Zn, Hg and Cu. Results reveal that the high toxic sites are at Sweanit, Al Bireh and Ras Al-Qilt spring and the Hg has the highest values at Sweanit and the second highest values is for Zn after Al Bireh.

Moreover, the ecological risk assessment results show that Cd has 67% from the total and poses a potentially risk to the environment. The ecological risks are caused by Hg, Ag, Cu, As and Bi with 20%, 7%, 2%, 2% and 1% respectively. Moreover, if IR is considered Ras Al-Qilt spring has the highest risk in term of potential ecological risk if compared with Fawwar and Sultan springs. This indicates that the buffer zone at the stream up to Ras Al-Qilt does not work efficiently to remove the pollution of trace metals or the pollutance as trace metals that reach direct to Ras Al-Qilt without pass through Fawwar spring, this will not guarantee the purified water from Ras Al-Qilt for long time if the situation is not manage well at the upstream of Al-Qilt catchment.

Furthermore, the geo-accumulation indexes show that sediments at Al-Qilt have background concentrations for Al, Ti, Cr, Mn, Fe, Co, Ni, Rb and Ba and unpolluted for V, Sr, and B and it is moderately to unpolluted for Cu, Zn, As, Mo, Cd, Sn, Sb, Hg, Bi and Pb and moderately polluted for Ag, and it is heavily polluted due to urban runoff and wastewater that discharged directly without treatment.

Furthermore, the MPI values are considered with the toxicity weight of the metals in relation to concentrations; results indicate that Sweanit still pose the highest risks for pollution in term of Hg. Furthermore, Ras Al-Qilt is posed risk due to Hg and Cu if the CF consider for calculations as total or fractionations form for BCR, SQG or MPI, this is clear for most of the parameters and it is good to restrict the usage of water for domestic purposes without treatments.

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Statement of clarification

I affirm and clearly state that I have never submitted any kind of work for a doctor degree at any other university or institution.

Statement of Original Authorship

I hereby state that this submission is my own work and to the best of my knowledge and belief, the thesis contains no material previously published or written by another person, nor material which to a substantial extent has been accepted to the award of any other degree in the Martin Luther University Halle-Wittenberg, or any other institution, excluding where due reference is made in this thesis. Any contribution made to the research by others, with whom I have worked at the Martin Luther University Halle-Wittenberg or elsewhere, is explicitly acknowledged in this thesis.

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