Deanship of Graduate Studies

Al- Quds University

Determination of different trace heavy metals in ground and harvested rain water in certain regions of West Bank/Palestine by ICP/MS

Husam Thaher Malassa

M.Sc. Thesis

Jerusalem – Palestine

1435/2014

Determination of different trace heavy metals in ground and harvested rain water in certain regions of West Bank/Palestine by ICP/MS

By:

Husam Thaher Malassa

B.Sc. Earth and Environmental Sciences,
College of Science and Technology-Palestine

Supervisors: Dr. Mutaz Qutob

A thesis Submitted In Partial Fulfillment of Requirements for the Degree of Master of Environmental and Earth Science / Graduated Study

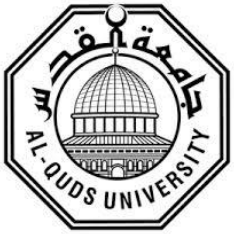
Al-Quds University

Jerusalem - Palestine

1435/2014

Deanship of Graduate Studies

Al- Quds University



Thesis Approval

"Determination of different trace heavy metals in ground and harvested rain water in certain regions of West Bank/Palestine by ICP/MS"

Student Name: Husam Malassa

Registration No: 21012862

Supervisor: Dr. Mutaz A. Qutob

Master thesis submitted and accepted date: 27 / 04 / 2014

The names and signatures of the examining committee members are as follows:

1- Head of Committee: Dr. Mutaz Qutob Signature:….....

2- Internal Examiner: Dr. Jawad Hasan Signature:…….

3- External Examiner: Dr. Subhi Samhan Signature:……..…

Jerusalem - Palestine

1435/2014

Dedication:

"To Our Profit Mohammad (Peace be upon him)".

"To My Family and Friends".

"To The Palestinians People".

Declaration

I Certify that this thesis submitted for the degree of Master of Science is the result of my own research, except where otherwise acknowledged, and that this thesis (or any part of the same) has not been submitted for a higher degree to any other university or institution.

Signed…….

Husam Thaher Malassa

Date: / / 2014

Acknowledgments:

Thanks to Allah, who gave me strength, determination, perseverance, and patience to complete this research. Peace and blessings be upon the first teacher and professor of all human beings Mohammed bin Abdullah.

I hereby give great recognition and acknowledgment to the generous funding through the research project (TRION) funded by the organisation (Deutsche Forschungsgemeinschaft), DFG.

I would like to express my sincere gratitude to my advisor Prof Dr. Mutaz Al-Qutob for his support, guidance, encouragement and invaluable helpful advice during this study and during the preparation of the thesis.

Special thanks to the staff of the Aquatic and Aquaculture research Laboratory for their help in the laboratory work especially Mr. Mahmoud Al-Khatib, and Dr. Fuad Al-Rimawi.

I would like to extend my special thanks and appreciation to my external and internal examiners.

Table of Contents:

List of Tables

List of Figures

List of Abbreviations	
°C	Celsius
amu	atomic mass unit
ANOVA	Analysis of Variance
ATSDR	Agency for Toxic Substances and Disease Registry
EPA	Environmental Protection Agency
GIS	Geographical Information System
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
MCM	Million Cubic Meter
ORS	Octapole Reaction System
pH	Potential Hydrogen
ppb	Parts-per-billion,(µg/L), 10^{-9}
ppt	Part-per-trillion, 10^{-12}
PWA	Palestinian Water Authority
RSD	Relative Standard Deviation
SD	Standard Deviation
SOPAC	Pacific Islands Applied Geoscience Commission
UNEP	United Nations Environmental Program
WHO	World Health Organization
WID	Waste Incineration Directive
r^2	Correlation Coefficient

Abstract

Surface and ground water contamination with heavy metals is one of the most important environmental issues as they are toxic even at low concentrations. This study was conducted to determine heavy metal concentrations in ground drinking water of north and south West Bank in addition to harvested rain water in south West Bank. Water samples were analyzed for different trace heavy metals (Tl, Pb, Bi, Cr, Mn, Co, Ni, Cu, Zn, Mo, Ag and Cd) and Al content by ICP/MS.

In North West Bank, three triplicates where obtained from five different wells. In South West Bank, three triplicates from ten groundwater wells were obtained in four different dates of the year (October 2012, November 2012, March 2013, and April 2013). The samples were analyzed for their pH, Electrical Conductivity, Total Dissolved Solids, and different trace metals content. The pH, Electrical Conductivity, and Total Dissolved Solids of all water samples were found to be within the U.S. Environmental Protection Agency guideline.

In South West Bank, Results showed that Pb, Al, Cr, Co, Ni, Cu, Zn, and Mo were detected in all water samples analyzed in this study, while Tl, Bi, Mn, Ag, and Cd were detected in 80%, 88%, 90%, 75%, and 95% of the water samples analyzed in this study, respectively. In general, 93% of all samples analyzed contained one or more of the 13 metals studied each in varying concentration. Furthermore, results showed that the concentration of Cr, Mn, Ni, Cu, Zn, and Mo is within the allowed WHO limits in drinking water. However the concentration of Pb, Cd, and Al are found to be higher than the allowed WHO limits in 40%, 8%, and 33% of the water samples analyzed in this study, respectively. Statistical analyses showed that concentrations of the metals studied were varied significantly between the ten ground water wells in south West Bank, indicating that the wells analyzed in this study is different from each other in terms of heavy metal content. Additionally, from the statistical results obtained, it was found that there is a significant difference in the concentration of the metals in each well during the wet and dry season, denoting that metal concentration in the wells varies significantly with sampling time.

At the North West Bank, Results showed that the concentration of trace metals (Cr, Mn, Ni, Cu, Zn, Mo, Pb, Cd, and Al) is within the allowed WHO limits in drinking water (50, 500, 20, 2000, 3000, 70, 10, 3, and 200 µg/L, respectively), however six metals of them

(Cr, Mn, Ni, Cu, Mo, and Al) were detected in 100% of the samples, while Pb, Cd, and Zn were detected in 80%, 60%, and 20% of the samples, respectively. On the other hand, Tl which is a very toxic heavy metal with allowed WHO limits of 0.01-1 µg/L, is detected in 100% of the water samples analyzed with a range of 0.02-0.12 µg/L, which indicates that such concentration level of Tl would be harmful for human being used these groundwater for domestic purposes. In general, 82% of all samples analyzed contained one or more of the 12 metals studied each in varying concentration.

Furthermore, harvested Rain water samples for drinking from West part of Hebron (south of West Bank in Palestine), were analyzed for different trace heavy metals (Cr, Mn, Co, Ni, Cu, Zn, Mo, Ag, Cd, Bi, and Pb) content by ICP/MS. A total of 44 water samples per houses cisterns were collected in November 2012 used to collect harvested rain water from the houses roofs. Results showed that concentrations of the heavy metals vary significantly between the 44 samples. Results also showed that the concentration of five heavy metals (Cr, Mn, Ni, Ag, and Pb) were higher than the WHO limits for these heavy metals in drinking water. The results obtained from this study suggest a possible risk to the population of the study area given the toxicity of these metals, and the fact that for many people in the study area, ground water and harvested rain water is a main source of their water supply.

Chapter One

Introduction and Literature Survey

1. Introduction:

Surface and ground water contamination with heavy metals is one of the most important environmental issues as they are toxic even at low concentrations (Momodu and Anyakora 2010, Vodela et. al. 1997, Marcovecchio 2007). Human activities have increased the concentrations of heavy metals in the environment. For example, anthropogenic activities e.g. industry, agriculture, solid waste disposal increase the contents of heavy metals in different environmental matrices (e.g. water, soil, air), fruits, vegetables, fish..etc (Batayneh 2010, Abderahman and Abu-Rukah 2006, Adekunle et. al. 2007, Chen et. al. 2007). There are 35 metals that concern us because of occupational or residential exposure; 23 of these are heavy metals: Antimony, Arsenic, Bismuth, Cadmium, Cerium, Chromium, Cobalt, Copper, Gallium, Gold, Iron, Lead, Manganese, Mercury, Nickel, Platinum, Silver, Tellurium, Thallium, Tin, Uranium, Vanadium and zinc (Ferner, 2001). Although small amounts of some elements are common in our environment and diet and they are may actually necessary for good health, but large amounts of any of them may cause acute or chronic toxicity. Health risks of heavy metals include reduced growth and development, cancer, organ damage, nervous system damage in extreme cases death. Exposure to some metals, such as mercury and lead, may also cause development of autoimmunity, in which a person's immune system attacks its own cells. Heavy metals become toxic when they are not metabolized by the body and accumulate in the soft tissues. Heavy metals may enter the human body via food, water, air or absorption through the skin in agriculture, industrial, or residential settings (Dupler, 2001).

Heavy metals are elements having Atomic Weights between 63.546 g and 200.590 g with specific gravity greater than 4.0 i.e. at least 5 times that of water. They exist in water in colloidal, particulate and dissolved phases, especially one that is poisonous, such as lead or mercury (Onwughara, 2011) Heavy metals pollution in subsurface environments come from natural and anthropogenic sources in some cases the weathering of minerals is one of the major natural sources. Anthropogenic sources include fertilizers, industrial effluent, waste recycling and leakage from service pipes (Leung and jiao, 2006). Recently, e-waste has become a subject of growing environmental concern in the West Bank due to the large volume of e-wastes that are imported from Israel for recycling. Many toxic substances including heavy metals contained in e-waste are released into the environment during disposal and recycling. Though some of the metals like Cu, Fe, Mn, Ni and Zn are essential as micronutrients for life processes in plants and microorganisms while many other metals

like Cd, Cr and Pb and many others have no known physiological activity, but they are proved detrimental beyond a certain limit (Marschner, 1995; Bruins, *et al.*, 2000). The deadlier diseases like edema of eyelids, tumor, congestion of nasal mucous membranes and pharynx, stuffiness of the head and gastrointestinal, muscular, reproductive, neurological and genetic malfunctions caused by some of these heavy metals have been documented (Johnson, 1998; Tsuji and Karagatzides, 2001; Abbasi, *et al.*, 1998). Therefore, monitoring these metals is important for safety assessment of the environment and human health in particular.

Heavy metals are considered as an important pollutant to groundwater, surface water, and harvested rainwater. Harvesting of rain water is a common practice in the West Bank and especially in South of the West Bank where there is a water scarcity. In these areas of West Bank during the winter, the rainwater is collected from the houses roofs and stored in cisterns. Two types of rain water catchment systems are used. One system works on a large scale to collect storm water runoff from the ground. This water is then stored in large reservoirs. The other system collects rain water on a small scale from controlled surfaces, such as a roof. This water is stored in small reservoirs, known as cisterns, constructed underneath or next to house. The average capacity of the existing cisterns is 70 m^3. According to Hebron Municipality, 60% of the inhabitants of the city have cisterns in their houses. In rural areas, the percentage of inhabitants using cistern collection systems is higher than in the city. This is because some of the small villages are not connected to water distribution networks, thus experiencing a shortage of water. Also, if connected, rural areas suffer from frequent shortage in water supply (ARIJ 1995).According to Luke Mosley from SOPAC Water Quality Office (Mosley,2005), heavy metals are contaminants commonly found in rainwater collection systems, where they come from dust particularly in urban and industrialized areas from roof materials (Mosley, 2005).

This study monitored the surface water considering the spatial and temporal variations for heavy metal more over to evaluate the status of the ground and surface water quality in the West Bank.

1.2 Literature Survey

Many studies have investigated the occurrence and monitoring of heavy metals in ground water and drinking water. The most important studies are described in the following two sections.

1.2.1 Worldwide Studies:

Momot et al. (2005) has investigated toxic aluminum and heavy metals in groundwater of middle Russia and results showed that some heavy metals (Hg, Cr, and As) were detected.

Gutierrez et al. (2008) has studied the occurrence of heavy metals in water of San Petro River in Mexico and results confirmed that the San Pedro River is contaminated with heavy metals and other contaminants that might affect human health as well as the health of the ecosystem.

Kar et al. (2008) has studied the assessment of heavy metals pollution in surface water in Ganga in West Bengal and results showed that the dominance of various heavy metals in the surface water of the river Ganga followed the sequence: Fe >Mn> Ni > Cr >Pb> Zn > Cu > Cd.

Magyar et al. (2008) has studied Lead and other heavy metals which are common contaminants of rainwater tanks in Melbourne where results showed that Concentrations of aluminum, cadmium, iron and zinc were found at levels exceeding acceptable health levels.

Despins et al. (2009) has assessed rainwater quality (pH, turbidity, colour, total and fecal coliforms, total organic carbon, total nitrogen, and total metals content) from rainwater harvesting systems in Ontario, Canada.

Iqbal and Gupta (2009), and Rajappa (2010) has studied the heavy metal pollution of groundwater in India, where results showed that some heavy metals are detected in groundwater samples.

Batayneh (2010) has studied heavy metal content in water springs of the Yarmouk Basin (Jordan) and results of the study showed that Yarmouk Basin in North Jordan are contaminated with heavy metals that might affect human health as well as the health of the ecosystem .

Momodu and Anyakora (2010) has assessed groundwater contamination with heavy metals (Pb, Cd) and Aluminum in Nigeria, and results showed that there is a significant risk for

the population from drinking groundwater as these metals were detected in 98% of water samples analyzed.

Laniyan et al (2011) as well as Oyeku and Eludoyin (2010) were also investigated the occurrence of heavy metals in groundwater in Nigeria.

A study by Amimand Alazba (2011) has focused on the sources of rainwater contamination in a rainwater harvesting system.

Ismail and Mat Saleh (2012) have analyzed different heavy metals in water samples from Malysia and results showed that the concentrations of heavy metals in water samples were below the detection limit.

It is obvious from this literature that studies on the occurrence and determination of heavy metals in water (ground, drinking, surface...Etc) is an important issue for the human health and for environment.

Voica et al. (2012) has determined different heavy metals in surface water from Transylvania/Romania and results showed that toxic heavy metals were detected in water samples in the range of few ppb.

Al-Omary (2013) has determined trace metals in drinking water in Irbid (Jordan), and results showed that the level of most elements determined (As, Ba, Cd, Pb, Cr, Cu, Fe, Zn, Mn, Ni, and Se) were within the Jordanian standards and WHO standards for drinking water.

1.2.2 Local Studies:

In Palestine, the principal water resources available include groundwater, springs, and harvested rainwater (UNEP, 2003). The West Bank lies over the Mountain aquifer which is divided into the eastern aquifer, the northeastern aquifer, and the western aquifer. The eastern aquifer and part of the northeastern aquifer flow east towards the Jordan River. The western aquifer and part of the northeastern aquifer flow westerly towards the Mediterranean Sea (Abed &Wishahi, 1999, Fathi M. Anayah 2009).

In Palestine, there are few studies that dealt with pollution of groundwater with different pollutants e.g. pesticides, nitrates, chlorides, heavy metals.

A study by M. Ghanem and N. Samhan in 2012 has focused on the assessment of pollution of groundwater in Tulkarem area with nitrate and chloride, and results indicated that there

are many samples with nitrate concentrations exceeding the WHO standards of 45mg/L for drinking water.

Ghanem et al (2011) has also investigated the groundwater pollution due to pesticides and heavy metals in north West Bank.

Anayah andAlmasri (2009) has also studied the trends and occurrences of nitrate in the groundwater of the West Bank, Palestine.

El-Nahhal (2006) has studied the contamination of groundwater with heavy metals in Gaza Strip where results showed that concentration of Cd, Pb, Fe, and Cr are above the EPA limits in some wells.

1.3 Research Motivations:

The following are the research motivations:

1. Site-specific characterization is needed to identify areas of high groundwater contamination.
2. Assessment of water quality and quantity in Palestine is vital. Groundwater is almost the sole water resource for the Palestinians.
3. There are not many studies on heavy metals in groundwater wells in the West Bank
4. Support and enhancement of management and assessment to the water resources.

1.4 Research Questions

The key purpose of this research is to address, and if possible to answer, the following questions:

1. What are the key and explanatory parameters that dictate the groundwater quality?
2. What is the spatial extent of the pollution occurrences in the groundwater resources of the West Bank in terms of heavy metals?

1.5 Main objective

1. To study the occurrence of different trace metals in ground water samples collected in West Bank for (Tl, Pb, Bi, Cr, Mn, Co, Ni, Cu, Zn, Mo, Ag, and Cd) and Al in ground water samples collected in West Bank.
2. To study the occurrence of different trace metals in harvested rain water used for drinking in Hebron (south West Bank/Palestine)

Chapter Two

Study area

2.1 Water Resources

The principal water resources available to Palestinians include groundwater, springs, and harvested rainwater (UNEP, 2003). There is little surface water and thus groundwater is the principal source of water in the West Bank. Both groundwater and surface water drain either westwards to the Mediterranean or eastwards to the Jordan River and Dead Sea. The lower Jordan River flows southwards at the eastern edge of the West Bank from Lake Tiberias to the Dead Sea (Abdul-Jaber et al., 1999).

The West Bank lies over the Mountain aquifer. The Mountain aquifer is divided into the eastern aquifer, the northeastern aquifer, and the western aquifer as depicted in Figure 2.1. The eastern aquifer and part of the northeastern aquifer flow east towards the Jordan River. The western aquifer and part of the northeastern aquifer flow westerly towards the Mediterranean Sea (Scarpa, 1994; Abed and Wishahi, 1999; PWA, 2001b; Anayah and Almasri 2009).

The quantity of cross boundary fluxes between the groundwater aquifer basins and the inter-aquifer flow within the basins are not well understood, making it difficult to accurately quantify the total groundwater storage and yield in each aquifer system (PWA, 2001). This uncertainty is reflected by the wide ranges given for each basin, as shown in Table 2.1.

Table 2.1: Reported annual recharge rates of the groundwater basins in the West Bank (PWA, 2001)

Aquifer basin	Annual recharge rate (mcm)
Eastern	100 – 172
North-eastern	130 – 200
Western	335 – 380
Total	565 - 752

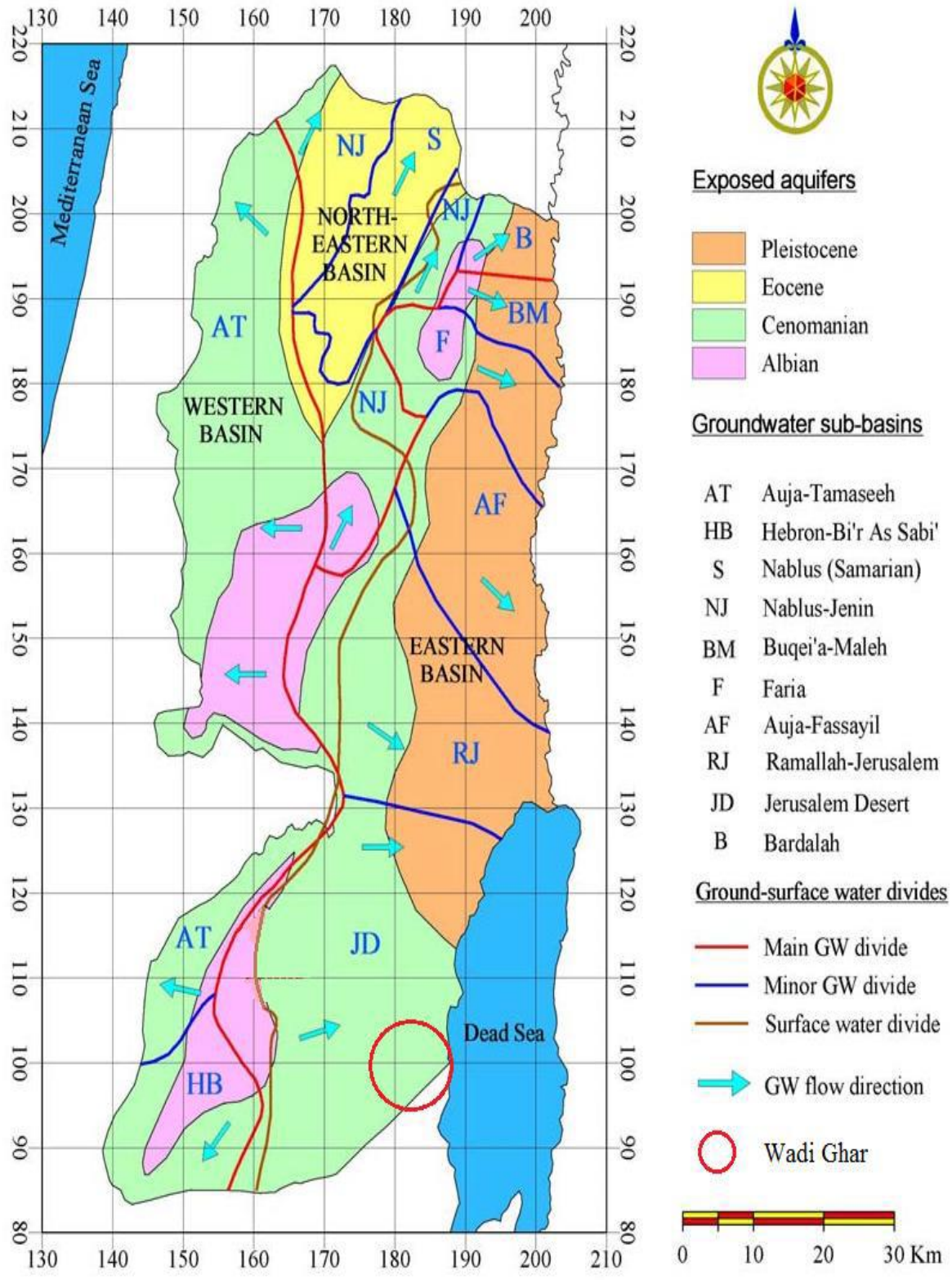


Figure (2.1): Groundwater basins and exposed aquifers in the West Bank / Palestine [modified after ARIJ 1995, Husary et al. 1996] (Qannam 2003)

The study area was divided into two areas north and south of the West Bank:

2.2 South West Bank

Water samples were obtained from south of West Bank /Palestine including three governors: Jerusalem, Bethlehem, and Hebron.

2.2.1 Climate

The climate of the southern part of the study area ranges from arid to semi-arid with an increase in aridity towards the Negev desert in the south and the Jordan valley in the east. The monthly average temperature of the study area ranges from 7.5-10 ^{o}C in the winter to 22 ^{o}C in the summer. The minimum temperature is -3 ^{o}C in January and the maximum is 40 ^{o}C in August. Most of the rain falls during December through February, although there may be rain from mid-October to the end of April. Water shortage is a serious problem facing the study area due to the arid and semi-arid climatic conditions (Environmental Profile for the West Bank, 1995).

2.2.2 Geography and Geology

South of West Bank including Jerusalem, Bethlehem, and Hebron have a highly varying topography and altitude; with the highest point at 1011 m above sea level and the lowest at 150 m above sea level. The study area has various topography as shown in Figure (2.2). In terms of geology, the majority of the study area is rocky mainly comprised of carbonate sediment such as limestone, chalky limestone and dolomite with marl. The geological rock age formations range from Turonian to Upper Cenomanian (Environmental profile for the West Bank, 1995).The study area has various geologic formations as shown in Figure 2.3.

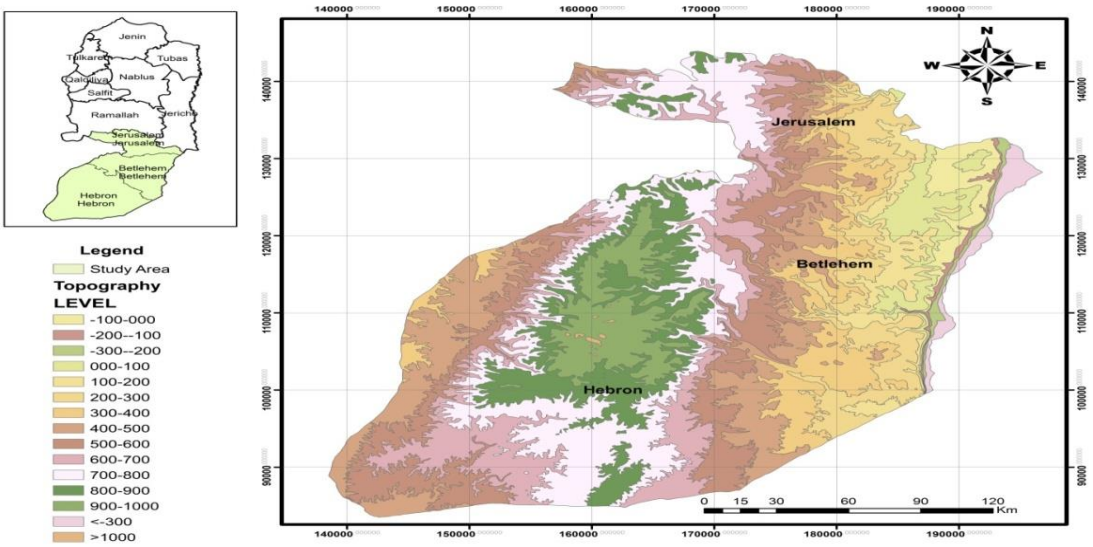


Figure (2.2): Topography of the study area in Southern West Bank. (Created in GIS Lab at Al-Quds University, 2013)

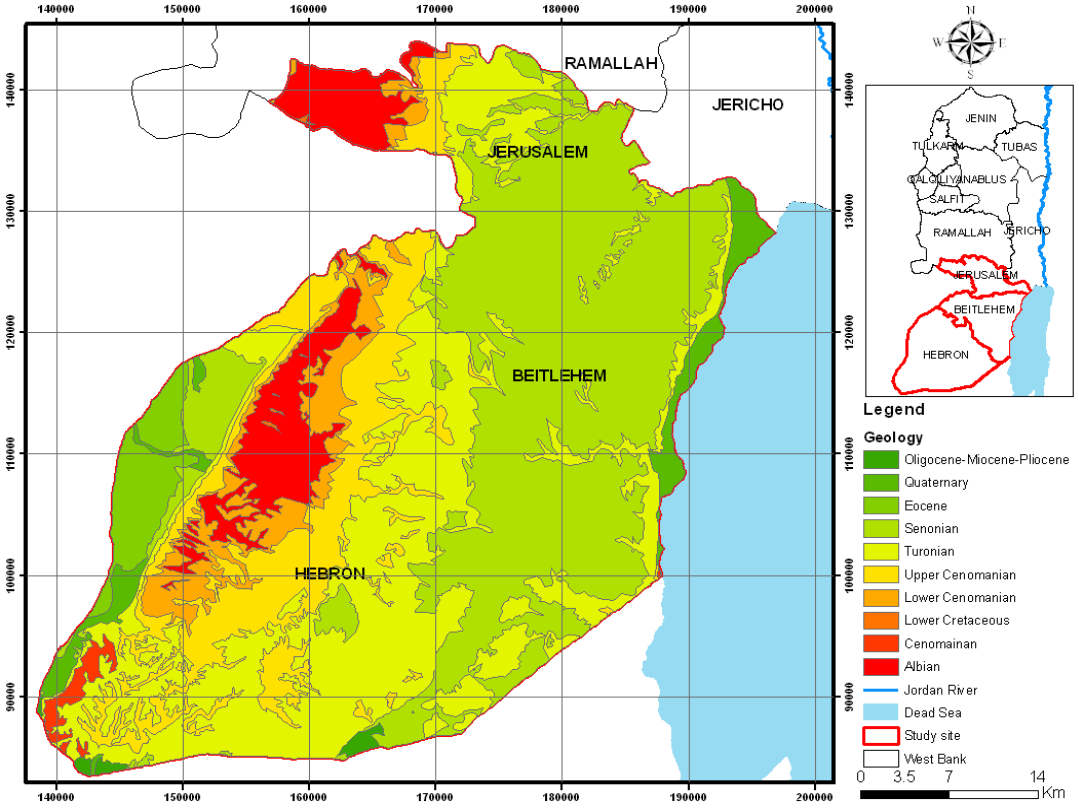


Figure (2.3): General geological and structural map of South West Bank. (Created in GIS Lab at Al-Quds University, 2013)

2.3 North West Bank

Water samples were obtained from Nablus and Jenin.

2.3.1 Climate

The climate in the North West Bank as the rest of the West Bank is affected by diverse ranges in topography and altitude and is influenced by the Mediterranean environment which is characterized by long, hot, dry summers and short, cool, rainy winters. The average annual precipitation in North West Bank is estimated at 640 mm for the period extending from 1952 to 2006 with a total of rainy days ranging from 57 to 75 during 1995-2006. The average annual precipitation in Jenin is 528 mm. The average yearly temperature is 27.1°C, while the average minimum temperature is 13.5°C and the mean annual humidity is 67.2% during the winter (Jenin Agricultural Department, 2004)

2.3.2 Geography and Geology

North of West Bank including Nablus and Jenin have a highly varying topography and altitude, with the highest point at 940 m above sea level and the lowest at 150 m above sea level for Nablus. The same goes for Jenin that has a peak height of 750 m above sea level while the lowest level is at 90 m above sea level. In terms of geology, the majority of the Nablus and Jenin area is rocky mainly comprised of carbonate sediment such as limestone, carbonate, chalk and marl. The geological rock age formations range from Cretaceous to Eocene (UNEP, 2003).

The study area has various geologic formations as shown in Figure (2.4).

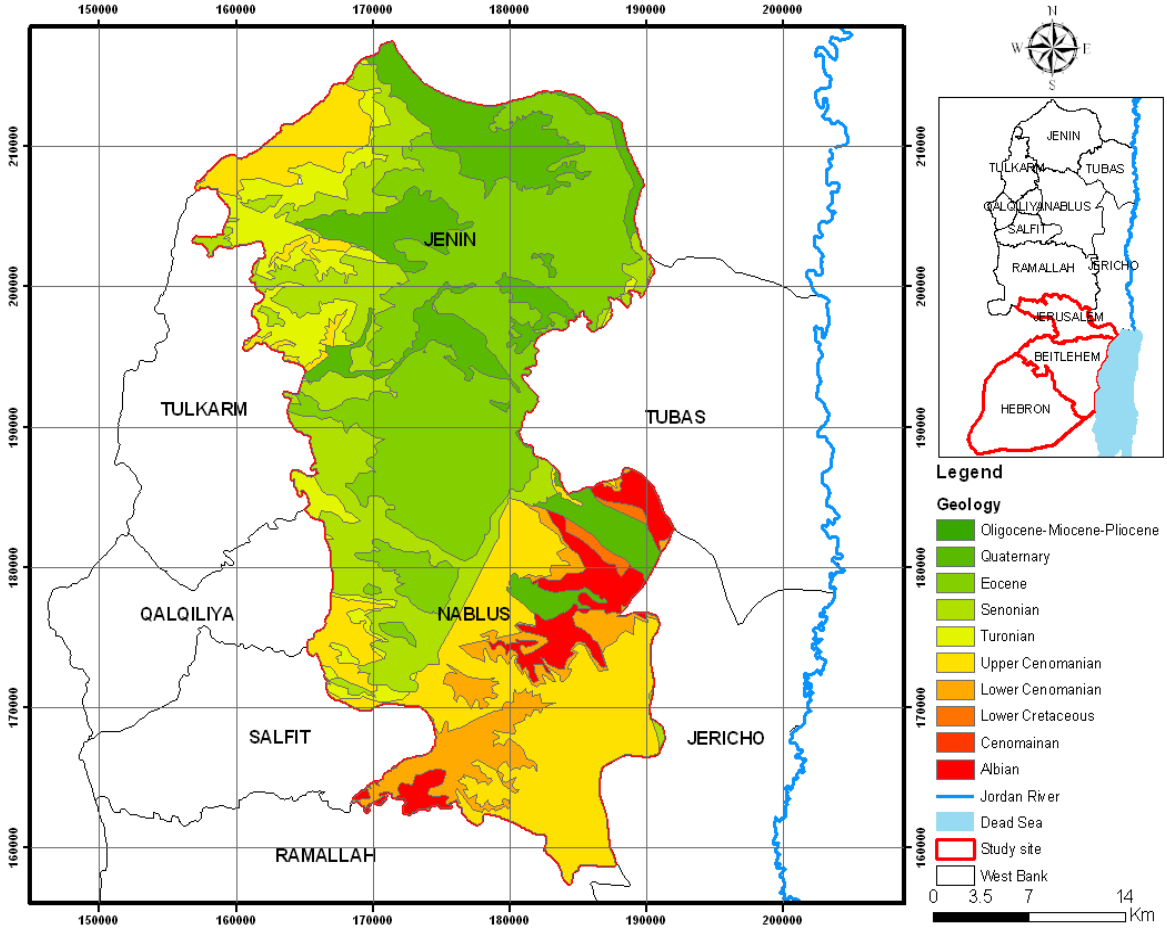


Figure (2.4): General geological and structural map of North West Bank. (Created in GIS Lab at Al-Quds University, 2013)

Chapter Three

Materials and methods

3.1 Sampling and analysis

3.1.1 Chemicals and Reagents

1- Ultrapure nitric acid. Merck catalogue number Z282541 304

2- multi-standard containing 22 metals (Ag 10 mg/L, Al 50 mg/L, B 50 mg/L, Ba 10 mg/L, Bi 100 mg/L, Ca 10 mg/L, Cd 10 mg/L, Co 10 mg/L, Cr 50 mg/L, Cu 10 mg/L, Fe 10 mg/L, K 100 mg/L, Li 50 mg/L, Mg 10 mg/L, Mn 10 mg/L, Mo 50 mg/L, Na 50 mg/L, Ni 50 mg/L, Pb 100 mg/L, Sr 10 mg/L, Tl 50 mg/L, Zn 10 mg/L, matrix 5% HNO_3) Fluka Analytical BCD1137 100990223.

3- Internal standard method was used using Indium (In) and Erbium (Er) as internal standard, Agilent Technologies G1820-60372.

4- Ultra-pure deionized water (18.2 MΩcm-1) from a Milli-Q analytical reagent grade water purification system, Millipore (Arium Pro DI) was used.

5- Filter paper - Whatman No. 41 or equivalent.

3.1.2 Preparation of solutions

Six solutions of the thirteen metals with concentrations: 1.0, 5.0, 100.0, 300.0, 500.0, and 1000.0 ppb were prepared from the stock multi-standard by dilution using 0.5% ultrapure nitric acid as diluent. These solutions were used for linearity and range study of the method. Each sample was analyzed three times and the results are expressed as mean ± SD (SD: Standard Deviation).

3.1.3 The instrument

Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

The Agilent Technologies 7500 Series ICP- MS (Agilent 7500)Figure (3.1) can measure trace elements as low as one part per trillion (ppt) and quickly scan more than 70 elements to determine the composition of an unknown sample with a Mass Hunter Workstation software automates the analysis and accurately interprets the resulting data. The ICP/MS

instrument consists of an on- board peristaltic pump that controls the flow of sample solution into and waste (drain) out of the instrument, a nebulizer (Micro Mist nebulizer) that uses a stream of argon to disperse the sample, an ICP Argon plasma torch using Argon as plasma gas, auxillary gas and nebulizer (carrier) gas, two pumps for evacuation, quadrupole mass analyzer with 0.8 amu resolution at 10% height, an Octapole Reaction System (ORS), and electron multiplier detector.

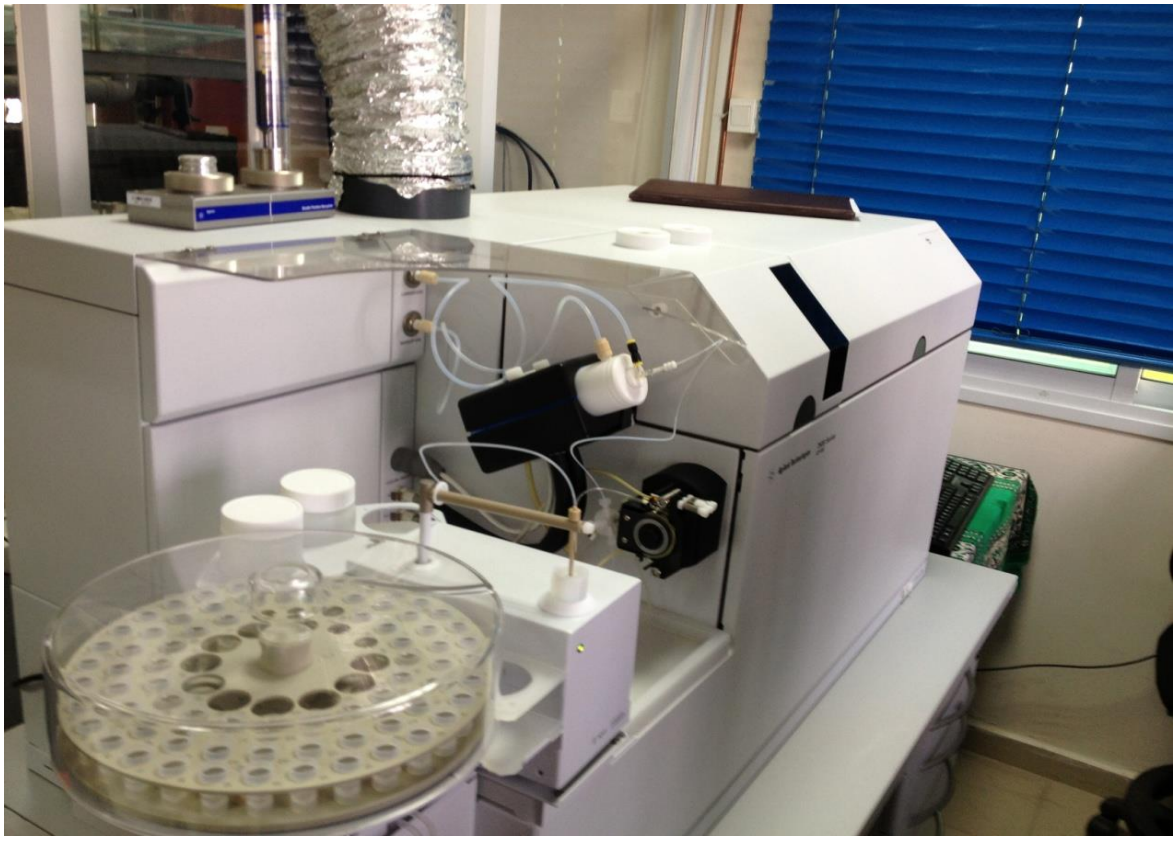


Figure (3.1): Agilent 7500 Inductively Coupled Plasma Mass Spectrometer (ICP-MS).

ICP- MS (Agilent 7500) with an on- board peristaltic pump, a nebulizer (Micro Mist nebulizer), an ICP Argon plasma torch, two pumps for evacuation, Quadrupole mass analyzer, an Octapole Reaction System (ORS), and electrom multiplier detector was used for analysis of the heavy metals in this study.

Overview of ICP-MS Major Components:

An ICP-MS instrument consists of several distinct parts:

• Sample introduction

• Ion generation in the ICP

• Plasma/vacuum interface

• Ion focusing

• Ion separation and measurement.

Sample introduction: The sample is typically introduced into the Inductively Coupled Plasma (ICP) as an aerosol, produced by passing the liquid sample through a simple pneumatic nebulizer. Larger aerosol droplets are removed from the gas stream by a spray chamber, and the remaining smaller droplets are swept into the central channel of the argon plasma. The Agilent 7500 Series is fitted with a Scott-type double pass spray chamber manufactured from high-purity quartz. Spray chamber temperature is precisely maintained with a thermoelectric (Peltier) device to prevent signal drift caused by large changes in room temperature and also to reduce solvent loading on the plasma. This reduced solvent loading leads to a higher plasma temperature, reducing oxide interferences, and assisting in matrix decomposition.(Agilent Technologies, 2005)

Ion generation in the ICP: The sample aerosol is passed into the plasma, which is generated in a stream of argon (Ar) contained in a quartz tube or "torch". The torch is located in the center of a cooled copper coil, through which a high power, high frequency electric current is passed. The intense magnetic field created by the electric current causes collisions between free electrons and Ar atoms, producing ions and more electrons, until a stable, high temperature plasma is formed. The high frequency current is produced by a Radio Frequency (RF) generator operating at powers up to 1600W. While two RF frequencies are approved for ICPs, 40.68 MHz and 27.12 MHz, the latter has been shown to result in higher plasma temperatures and is used in most modern and all Agilent ICP-MS instruments. The very high temperature of the plasma (up to 10,000K maximum and around 7,500K in the central channel) means that the aerosol droplets are rapidly dried, decomposed, vaporized and atomized, then ionized by the removal of one electron from each atom. The resulting ions, which are formed within about 10ms of the original aerosol droplet entering the back of the plasma, are present at the highest level at about 7mm from the end of the load coil, which is where the spectrometer interface is positioned. (Agilent Technologies, 2005)

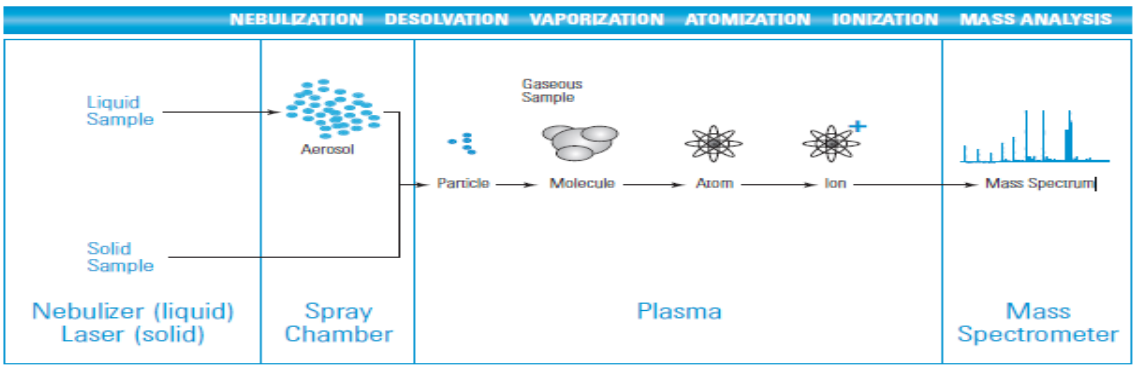


Figure (3.2): Schematic representation of processes in ICP-MS from sample introduction to mass analysis. (Agilent Technologies, 2005)

Interface: The positively charged ions that are produced in the plasma are extracted into the vacuum system, via a pair of interface "cones". The cones are essentially metal plates with central orifices through which the ions pass. Small orifices are used, typically 1mm diameter or less, to maintain the high vacuum in the mass spectrometer region. (Agilent Technologies, 2005).

Ion focusing: Electrostatic lenses keep the ions focused in a compact "ion beam" as they pass through the vacuum system to the final chamber, where the Mass Spectrometer (MS) and detector are housed. The ion lenses perform a second, essential, function of separating the ions from the photons and residual neutral material. Agilent uses a high transmission off-axis or Omega lens arrangement that separates the positively charged ions from the photons and neutral particles, which would otherwise reach the detector and increase random background noise. (Agilent Technologies, 2005)

Mass spectrometer: Three different types of mass analyzers have been used with ICP-MS; these are quadrupole, magnetic sector, and time-of-flight analyzers. By far the most common mass analyzer used in ICP-MS, and the one employed on the Agilent 7500 Series, is the quadrupole. The quadrupole uses a combination of DC (Direct Current) and AC (Alternating Current) electrical fields to separate ions based on their mass to charge ratio (m/z). Since the plasma produces almost exclusively singly-charged ions, the mass/charge ratio is equal to the mass of the ion, making the spectrum very simple to interpret. The ratio of the DC and AC electrical fields is fixed but the voltages can be changed. For a given voltage setting, only one m/z is stable and the quadrupole scans rapidly across the

mass range (2-260 amu), passing each mass of interest sequentially to the electron multiplier (EM) detector. (Agilent Technologies, 2005)

Ion detection: The electron multiplier detects each ion as it exits the quadrupole. The detector electronics count and store the total signal for each mass (m/z), creating a mass spectrum. The spectrum that is produced provides a simple and accurate qualitative representation of the sample. The magnitude of each peak is directly proportional to the concentration of an element in a sample; quantitative results are produced by comparing signal intensities to those generated by calibration standards. (Agilent Technologies, 2005)

3.2.1 Harvested Rain Water

Sampling has been carried out on November 2012 (the beginning of the rain season) where 44 water samples were collected from 44 house cisterns. Figure (3.3) shows the location of Hebron in West Bank and cisterns analyzed in this study. The water samples were collected in 1-liter high density polyethylene bottles (pre-cleaned with 10% nitric acid followed by repeated rinsing with bi-distilled water), stabilized with ultrapure nitric acid (0.5% HNO_3), preserved in a cool place (about 4 °C) and transported to the lab of Al-Quds University for further analysis. Temperature, pH, electrical conductivity, total dissolved solids, and dissolved oxygen were measured in the lab immediately after the arrival of the samples according to standard methods (APHA 1998). The samples were then analyzed for heavy metals content (Cr, Mn, Co, Ni, Cu, Zn, Mo, Ag, Cd, Bi, and Pb) by ICP/MS.

In order to get an accurate quantitative determination of heavy metals in harvested water samples, an internal standard method was used using Er as internal standard and a multi-standard calibration method: (29 metals standard with a concentration of , matrix 5% HNO_3). Samples were prepared by dilution of 1.0 mL of the water samples to 10.0 mL with 0.3% ultrapure nitric acid and analyzed by ICP/MS. Each sample was analyzed three times and the results are expressed as mean ± SD (SD: Standard Deviation). Relative Standard Deviation (RSD) of the three results are calculated and found to be less than 5% for all samples for all heavy metals analyzed in this study, reflecting the precision of the method for the analysis of these heavy metals. Calibration curves for all heavy metals analyzed were constructed by plotting the ratio of the intensity of the analyte heavy metal to that of the internal standard (Er) vs. concentration of the heavy metal (in µg/L), and

results showed that the calibration curves are linear with correlation coefficient (r^2) greater than 0.999 for the heavy metals analyzed with a concentration range of 1-1000 µg/L (Appendix A)..

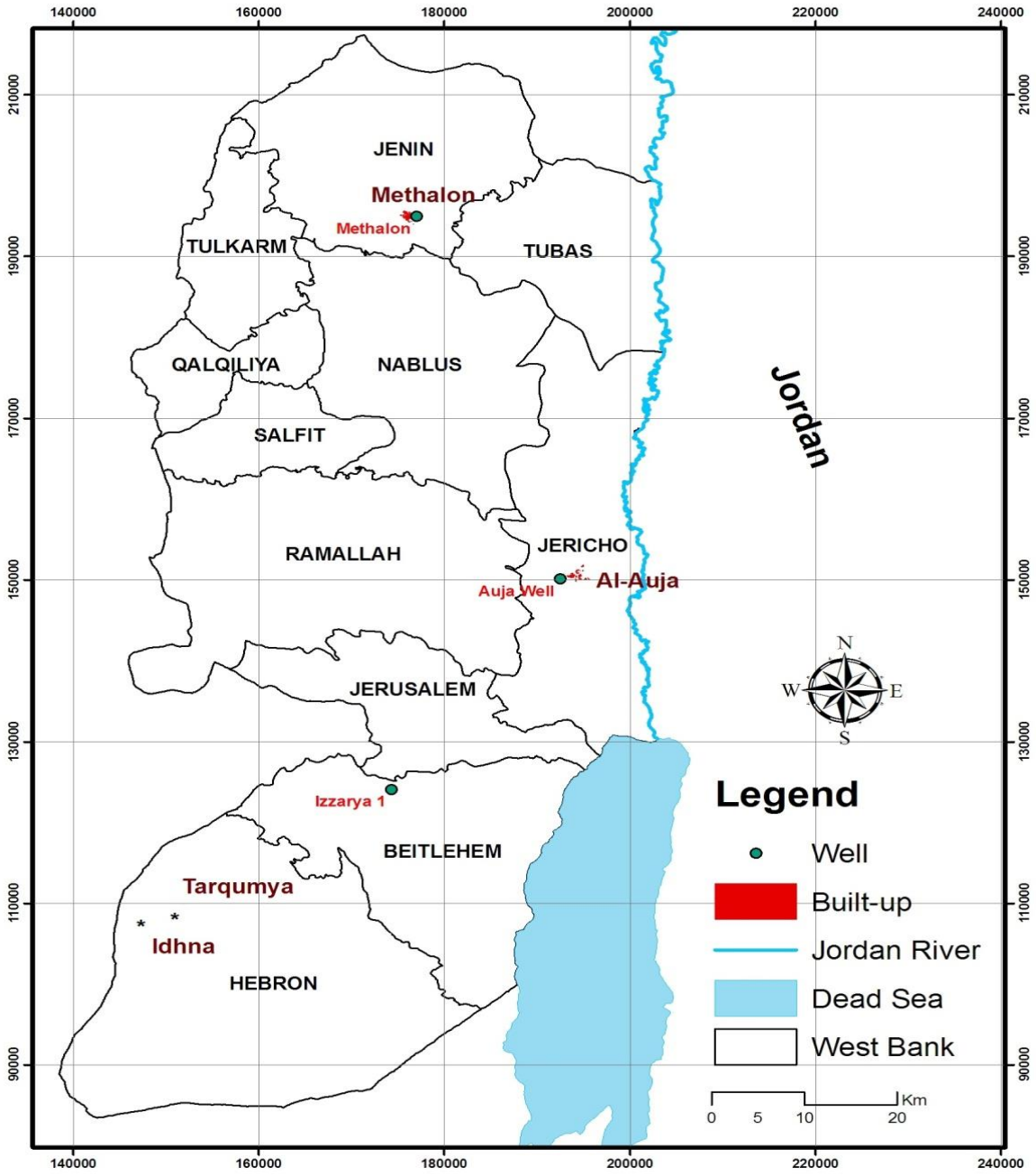


Figure (3.3): Map of West bank showing Hebron locality in south West Bank, and the location of cisterns (marked with *) containing harvested rain water analyzed. (Created in GIS Lab at Al-Quds University, 2013)

3.2.2 Ground Water of South West Bank

Ten groundwater wells were selected as representative wells of the study area. Figure (3.4) shows location of the wells in the study area analyzed in this study. Three samples were obtained from each well. The selected wells were sampled four times in four different dates of 2012 and 2013 (October 2012, November 2012, March 2013, and April 2013). A total of 120 water samples were collected from the ten wells. The water samples were collected in 1-liter high density polyethylene bottles (pre-cleaned with 10% nitric acid followed by repeated rinsing with bi-distilled water), stabilized with ultrapure nitric acid (0.5% HNO_3), preserved in a cool place (about 4 °C) and transported to the lab of Al-Quds University for further analysis. pH, electrical conductivity, and total dissolved solids were measured in the lab immediately after the arrival of the samples according to standard methods (APHA 1998). The samples were then analyzed for heavy metals content (Tl, Pb, Bi, Cr, Mn, Co, Ni, Cu, Zn, Mo, Ag, and Cd) and Al by ICP/MS (Agilent technologies 7500 series).

For accurate quantitative determination of heavy metals in ground water of south West Bank, an internal standard method was used using (In) as internal standard and a multi-standard calibration method: (22 metals standard (Ag 10 mg/L, Al 50 mg/L, B 50 mg/L, Ba 10 mg/L, Bi 100 mg/L, Ca 10 mg/L, Cd 10 mg/L, Co 10 mg/L, Cr 50 mg/L, Cu 10 mg/L, Fe 10 mg/L, K 100 mg/L, Li 50 mg/L, Mg 10 mg/L, Mn 10 mg/L, Mo 50 mg/L, Na 50 mg/L, Ni 50 mg/L, Pb 100 mg/L, Sr 10 mg/L, Tl 50 mg/L, Zn 10 mg/L, matrix 5% HNO_3). Samples were prepared by dilution of 1.0 mL of the water samples to 10.0 mL with 0.3% ultrapure nitric acid and analyzed by ICP/MS. Each sample was analyzed three times and the results are expressed as mean ± SD (SD: Standard Deviation). Relative Standard Deviation (RSD) of the three results are calculated and found to be less than 5% for all samples for all metals analyzed in this study, reflecting the precision of the method for the analysis of these heavy metals. Calibration curves for all metals analyzed were constructed by plotting the ratio of the intensity of the analyte metal to that of the internal standard (In) vs. concentration of the trace metal (in µg/L), and results showed that the calibration curves are linear with correlation coefficient (r^2) greater than 0.999 for the trace metals analyzed (Appendix A).

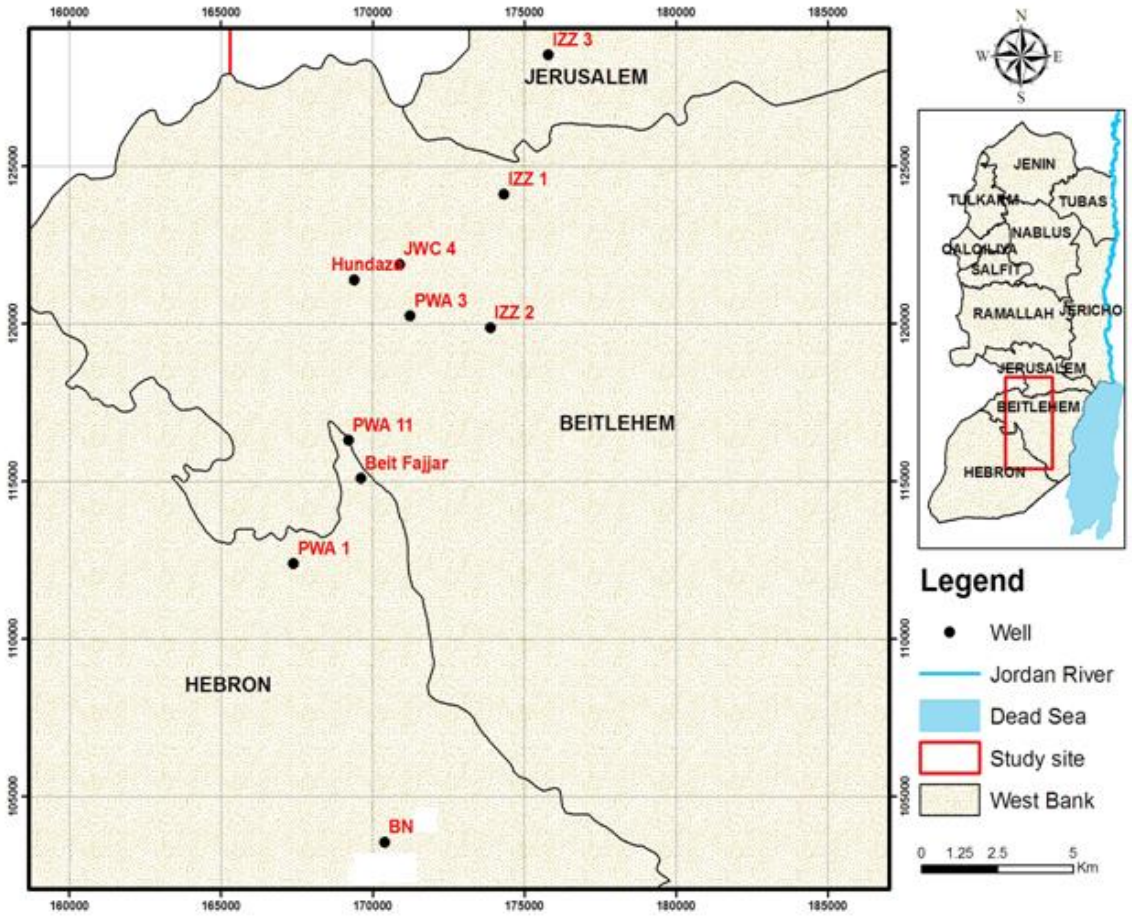


Figure (3.4): Map of West Bank and the study area showing location of the ground wells analyzed in this study (PWA1, Beit Fajjar, PWA3, JWC 4, BN, Hundaz, PWA 11, IZZ 1, IZZ 2, and IZZ 3).(Created in GIS Lab at Al-Quds University, 2013)

3.2.3 Ground water of North West Bank

Five groundwater wells which are used for drinking were selected as representative wells of the study area. Figure (3.5) shows location of the wells in the study area analyzed in this study. Three samples were obtained from each well at different times. A total of 15 water samples were collected from the five wells. The water samples were collected in 1-liter high density polyethylene bottles (pre-cleaned with 10% nitric acid followed by repeated rinsing with bi-distilled water), stabilized with ultrapure nitric acid (0.5% HNO_3), preserved in a cool place (about 4 °C) and transported to the lab of Al-Quds University for further analysis. pH, electrical conductivity, and total dissolved solids were measured in the lab immediately after the arrival of the samples according to standard methods (APHA, 1998). The samples were then analyzed for the following metals (Tl, Pb, Cr, Mn, Co, Ni, Cu, Zn, Mo, Ag, Cd, and Al) which are dissolved in water by ICP/MS.

In this case and for accurate quantitative determination of heavy metals in water samples of ground water of north West Bank, an internal standard method was used using (In) as internal standard and a multi-standard calibration method: (22 metals standard (Ag 10 mg/L, Al 50 mg/L, B 50 mg/L, Ba 10 mg/L, Bi 100 mg/L, Ca 10 mg/L, Cd 10 mg/L, Co 10 mg/L, Cr 50 mg/L, Cu 10 mg/L, Fe 10 mg/L, K 100 mg/L, Li 50 mg/L, Mg 10 mg/L, Mn 10 mg/L, Mo 50 mg/L, Na 50 mg/L, Ni 50 mg/L, Pb 100 mg/L, Sr 10 mg/L, Tl 50 mg/L, Zn 10 mg/L, matrix 5% HNO_3). Samples were prepared by dilution of 1.0 mL of the water samples to 10.0 mL with 0.3% ultrapure nitric acid and analyzed by ICP/MS. Each sample was analyzed three times and the results are expressed as mean ± SD (SD: standard deviation). Relative standard deviation (RSD) of the three results are calculated and found to be less than 5% for all samples for all metals analyzed in this study, reflecting the precision of the method for the analysis of these heavy metals. Calibration curves for all metals analyzed were constructed by plotting the ratio of the intensity of the analyte metal to that of the internal standard (In) vs. concentration of the trace metal (in µg/L), and results showed that the calibration curves are linear with correlation coefficient (r^2) greater than 0.999 for the trace metals analyzed (Appendix A).

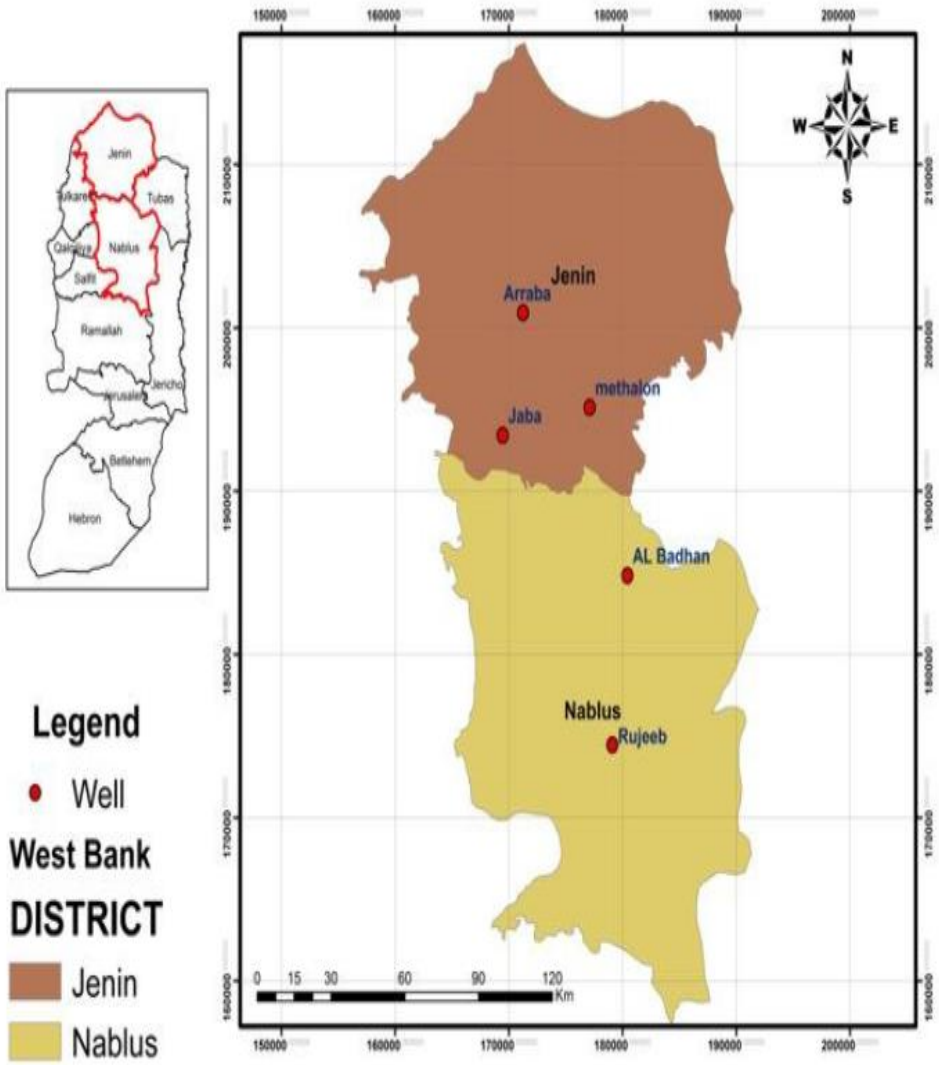


Figure (3.5): Map of West Bank and the study area showing location of the ground wells analyzed in this study (Arabba, Jaba, Al Badhan, Rujeeb, and Methalon).(in GIS Lab at Al-Quds University, 2013)

3.3Statistical analysis

Data were analyzed using Origin 9 software. Statistical differences were tested using one way ANOVA. Differences were considered significant at p values ≤ 0.05.

Chapter Four

Results and discussion

4.1 Harvested Rain Water

This study was conducted to investigate the quality of harvested rain water which is used for drinking in west part of Hebron (south of West Bank of Palestine). This region of Hebron has severe water scarcity so they depend mainly on the rain water harvested and stored in cisterns or wells. The pH of all water samples ranged between 7.1-8.2 (with mean temperature of 18.8 °C) which is neutral to slightly basic and in the allowed limit (6.5-8.5) according to WHO regulations. Electrical Conductivity, Total Dissolved Solids, and Dissolved Oxygen for water samples ranged from 240-1700 µs/cm, 136.7-1139 mg/L, and 8.3-9.15 mg/L, respectively. The limit for total dissolved solids in drinking water according to WHO is 1000 mg/L (WHO 2003) where our results showed that eleven samples have exceeded this limit indicating high amounts of dissolved salts e.g. heavy metals.

4.1.1 Heavy metals content

Results showed that eleven heavy metals (Cr, Mn, Co, Ni, Cu, Zn, Mo, Ag, Cd, Pb, and Bi) were detected in water samples analyzed (44 sample) in this study. Eight heavy metals (Cr, Mn, Co, Ni, Cu, Zn, Bi, and Pb) were detected in all samples, while Mo, Ag, and Cd were detected in 37, 18, 38 samples out of 44 samples, respectively. The concentration of Cr, Mn, Co, Ni, Cu, Zn, Mo, Ag, Cd, Pb, and Bi in water samples were ranged from: 22.6-165.5, 4.56-552.3, 0.34-4.93, 9.15-87.28, 21.93-925.5, 22.19-302.98, 0.0-6.17, 0.0-149.7, 0.0-2.19, 12.94-486.4, 1.33-96.52, respectively. Table 4.1 summarizes the concentrations of heavy metals which are detected in the harvested rainwater samples analyzed in this study (minimum, maximum, average, standard deviation, and relative standard deviation).

A one way ANOVA statistical test was used to test if the concentration of heavy metals is significantly different in the 44 water samples analyzed. Results showed that all heavy metals concentrations are significantly different in the 44 water samples analyzed in this study at 95% confidence level. This indicates that these 44 water samples are different from each other in terms of heavy metals concentration. This result confirms locational variations of heavy metals in the 44 water samples analyzed in this study. Figure (4.1) shows this variation for Pb in the 44 samples.

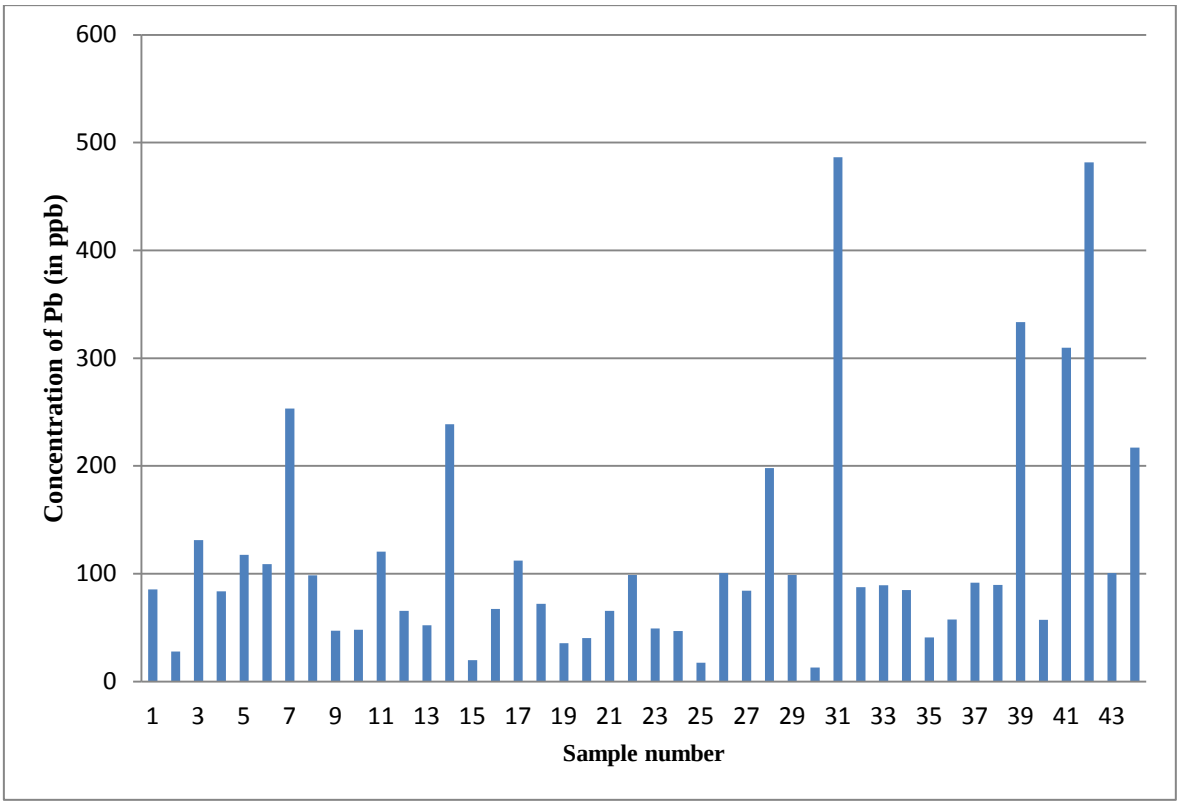


Figure (4.1): Concentration of Pb (in ppb) vs. sample number.

The sources of these heavy metals in harvested water used for drinking in the west part of Hebron might be attributed to uncontrolled burning (incineration) of solid wastes in illegal waste dumping sites, where it is expected that the ashes and dust of these incinerated wastes containing heavy metals is transported through wind to the house roofs and consequently to the harvested rain water in this region. It is noteworthy here to mention that people of this region (West part of Hebron) collect rainwater from their house roofs from the first rain which is expected to be highly contaminated with different micro pollutants e.g. heavy metals. In the study area, the most favored means of waste disposal is through burning. Additionally poor people of the study area burn specific solid wastes e.g. batteries, car wheels to get metals recovered from these wastes (iron, copper, silver...etc) to sell them.

The allowed WHO limit for Pb in drinking water is 10 µg/L, however our results showed that all samples analyzed in this study exceeded this limit with a range of 12.94 to 486.4. It has long been known that lead in drinking water is highly toxic. Exposure to lead is cumulative over time. High concentrations of lead in the body can cause death or permanent damage to the central nervous system, the brain, and kidneys. This damage

commonly results in behavior and learning problems (such as hyperactivity), memory and concentration problems, high blood pressure, hearing problems, headaches, slowed growth, reproductive problems in men and women, digestive problems, muscle and joint pain. Infants, children, pregnant women, and fetuses are more vulnerable to lead exposure than others because the lead is more easily absorbed into the sensitive tissue of actively growing bodies. According to the recently released lead toxicological profile for lead from Agency for Toxic Substances and Disease Registry (ATSDR), the adverse health effects of lead range from slight increases in blood pressure at 100 µg/L to severe retardation and even death at very high blood-lead levels of 1000 µg/L (WHO, 1993).

For Cr, the allowed WHO limit is 50 µg/L, however 26 water samples out of 44 have Chromium with concentrations larger than the allowed WHO limit. The highest Cr concentration was found to be 165.5 µg/L. The health hazards associated with exposure to chromium are dependent on its oxidation state; the hexavalent form is toxic. For Mn, the allowed WHO limit in drinking water is 500 µg/L; our results showed that two water samples were found to exceed this limit with concentrations of 538.9 and 552.4 µg/L. Regarding Nickel, our results showed that 15 water samples out of 44 have Ni concentration higher than the allowed limit (20 µg/L in drinking water) with the highest concentration of 87.28 µg/L. There is no limit for silver in drinking water according to WHO, however it is usually found in drinking water in the range 5-50µg/L, but our results showed that 2 samples of the analyzed water samples exceeded this upper limit (50µg/L) with concentrations of 52.0 and 149.7 µg/L.

Co and Bi have no limits in drinking water by WHO, however both metals were detected in all water samples analyzed in this study. Regarding Cu, Zn, Mo, and Cd, the allowed WHO limits in drinking water is 2000, 3000, 70, and 3 µg/L, respectively, and our results showed that these metals were found in the analyzed water samples within in these limits.

Table (4.1): Heavy metals concentrations which are detected in the harvested rainwater samples analyzed in this study (minimum, maximum, average, standard deviation, and relative standard deviation), as well as their WHO limits, and % of the samples that exceeded the WHO limit, and the % of the samples that found to contain particular heavy metal.

concentration (µg/L)	Heavy metal										
	Cr	Mn	Co	Ni	Cu	Zn	Mo	Ag	Cd	Pb	Bi
Minimum	22.6	4.56	0.34	9.15	21.93	22.19	0.0	0.0	0.0	12.94	1.33
Maximum	165.5	552.3	4.93	87.28	925.5	302.98	6.17	149.7	2.19	486.4	96.52
Average	56.1	112.6	3.16	26.7	143.6	111.8	11.3	39.7	1.17	45.8	32.8
SD	6.1	11.8	1.5	4.1	36.3	29.7	3.6	13.7	0.8	14.3	14.1
RSD (%)	10.9	10.5	47.5	15.4	25.2	26.6	31.9	34.5	68.3	31.2	43.0
% of samples that found to contain that heavy metal	100	100	100	100	100	100	37	18	38	100	100
Limits	50	500	No limits	20	2000	3000	70	No limits (usually found in concentration of 5-50µg/L)	3	10	No limits
% of samples that exceeded the limit	59	4.5	/	34	0	0	0	4.5(exceeded 50µg/L)	0	100	/

4.2 Ground Water of South West Bank

This study was conducted to investigate the quality of groundwater which is used for drinking in the study area. The study area has severe water scarcity so people depend mainly on the groundwater and on the rain water harvested and stored in cisterns or wells. The pH of all water samples ranged between 7.0-7.9 which is within the allowed WHO limit (6.5-8.5). Electrical conductivity and total dissolved solids of all water samples ranged from 196-1389 µS/cm, and 112.0-791.0 mg/L respectively. The limit for total dissolved solids in drinking water according to WHO is 1000 mg/L (WHO 2003), where our results showed that all water samples are within this limit.

4.2.1 Heavy metals content

Results showed that twelve heavy metals (Tl, Pb, Bi, Cr, Mn, Co, Ni, Cu, Zn, Mo, Ag, and Cd), and Al were detected in one or more water sample analyzed in this study. Table (4.2) shows the concentrations of metals detected in the groundwater samples analyzed in this study in four different sampling dates (October 2012, November 2012, March 2013, and April 2013). Results also showed that eight metals (Pb, Al, Cr, Co, Ni, Cu, Zn, and Mo) were detected in all water samples analyzed in this study, while Tl, Bi, Mn, Ag, and Cd were detected in 80%, 88%, 90%, 75%, and 95% of the water samples analyzed in this study, respectively. In general, 93% of all samples analyzed contained one or more of the 13 metals studied each in varying concentration. The concentration of Tl, Pb, Bi, Al, Cr, Mn, Co, Ni, Cu, Zn, Mo, Ag, and Cd in the ten wells analyzed in this study were ranged from: 0.0-1.0, 0.15-109.3, 0.0-215.7, 0.33-631.5, 0.08-28.6, 0.0-45.1, 0.01-6.2, 0.36-13.2, 0.53-243.6, 0.84-42.8, 0.1-11.5, 0.0-6.4, and 0.0-7.0 µg/L, respectively.

Furthermore, results showed that the concentration of six heavy metals (Cr, Mn, Ni, Cu, Zn, and Mo) is within the allowed WHO limits in drinking water (50, 500, 20, 2000, 3000, and 70 µg/L, respectively), however five of these metals (Cr, Ni, Cu, Zn, Mo) were detected in 100% of the water samples, and Mn was found to be existing in 90% of the water samples analyzed in this study. On the other hand, the concentration of Pb Cd, and Al are found to be higher than the allowed WHO limits (10, 3 and 200 µg/L, respectively) in 40%, 8%, and 33% of the water samples analyzed in this study, respectively. The highest concentration of Lead was found to be in well number PWA 1 with a concentration

of 109.3 µg/L (11 fold of the allowed WHO limits). Regarding Cd and Al, the highest concentrations of these metals were detected in well number Beit Fajjar (with concentration of 7.0 µg/L) and PWA 3 (with concentration of 631.5 µg/L), respectively. There is no limit for Ag in drinking water according to WHO, however it is usually found in drinking water in the range 5-50 µg/L. Our results showed that one sample contained 6.4 µg/L of Ag, while the rest samples contain lower than 5 µg/L. However it was found that 75% of water samples analyzed in this study contain this heavy metal (Ag). Co and Bi have also no limits in drinking water by WHO, however these metals were detected in 100% and 88% of the water samples analyzed in this study.

Thalium (Tl) is a highly toxic element that humans are exposed to mainly by consumption of drinking water and vegetables grown in soil with high Thallium content but also through inhalation of particles in the air. Thallium is also present in fossil fuels, alloys, and in electronic utilities. The increasing use of the element and emissions from notably energy production has lead to a higher load on the surface of the Earth. The allowed WHO limits of Tl in water is 0.01-1 µg/L (IPCS, 1996)**.** Our results showed that Tl is detected in 90% of the water samples analyzed with a range of 0.01-0.1 µg/L. This finding indicates that such concentration level of Tl is harmful to human being consuming this groundwater.

Table (4.2): Concentration of trace metals detected in groundwater wells analyzed in the South West Bank. Results expressed as Average ± SD for three samples (SD: standard deviation).

Well number (name)	Sampling date	Concentration of metals (µg/L)													
		Tl	Pb	Bi	Al	Cr	Mn	Co	Ni	Cu	Zn	Mo	Ag	Cd	Total concentration (µg/L)
1 (PWA1)	October-2012	0.1 ± 0.001	9 ± 0.14	11 ± 0.10	80 ± 0.27	5 ± 0.20	19 ± 0.05	0.6± 0.02	3.0± 0.09	43 ± 0.12	2.6± 0.05	1.3 ± 0.009	0.0	0.7± 0.04	177.6
	November-2012	0.4± 0.007	109 ± 1.1	125 ± 0.6	456 ± 0.7	2.3 ± 0.12	9.1± 0.09	0.2± 0.007	13.2± 0.04	7.4± 0.11	11.3± 0.14	1.08± 0.04	0.72± 0.007	1.4± 0.02	737.1
	March-2013	0.2 ± 0.005	3.5± 0.07	2.8± 0.1	82.5± 0.16	3.5± 0.08	6.6± 0.11	0.06± 0.008	1.1± 0.02	16.5± 0.08	21.0± 0.23	6.5± 0.005	2.1± 0.02	0.2± 0.009	146.6
	April-2013	0.03± 0.006	1.4± 0.04	1.1± 0.01	2.1± 0.02	0.2± 0.007	0.09± 0.003	0.04± 0.009	0.9± 0.06	3.7± 0.04	16.0± 0.04	2.4± 0.03	0.3± 0.007	0.03± 0.009	28.3
2 (Beit Fajjar)	October-2012	0.0	3.4± 0.03	1.8± 0.12	170.1± 1.21	2.8± 0.09	6.2± 0.003	0.3± 0.005	1.8± 0.09	31.1± 0.29	4.1± 0.007	0.1± 0.001	0.0	0.2± 0.011	221.9
	November-2012	0.1± 0.004	78.3± 0.03	44.4± 0.23	494.4± 2.2	2.3± 0.04	10.4± 0.06	6.2± 0.13	2.1± 0.002	3.0± 0.01	8.5± 0.08	1.1± 0.06	0.7± 0.008	7.0± 0.03	658.5
	March-2013	0.0	0.78± 0.001	0.35± 0.008	2.52± 0.009	0.24± 0.02	0.12± 0.003	0.03± 0.001	0.6± 0.008	3.8± 0.10	16.9± 0.20	1.6± 0.001	0.2± 0.03	0.02± 0.002	27.2
	April-2013	0.0	0. 8± 0.003	0.4± 0.01	2.5± 0.08	0.2± 0.004	0.1± 0.02	0.03± 0.002	0.6± 0.002	3.8± 0.001	16.9± 0.12	1.6± 0.001	0.2± 0.003	0.02± 0.004	27.2
3 (PWA3)	October-2012	0.02± 0.001	11.6± 0.21	138.1 ± 0.92	183.1± 1.0	8.0± 0.21	10.7± 0.09	0.3± 0.003	2.4± 0.11	53.6± 0.93	1.8± 0.006	1.9± 0.02	0.0	0.6± 0.02	412.2
	November-2012	0.2± 0.001	105.3 ± 0.85	18 ± 0.12	631 ± 2.6	2.3± 0.06	12.6± 0.02	0.4± 0.02	2.1± 0.001	16.5± 0.02	12.9± 0.11	1.1± 0.02	0.7± 0.02	6.7± 0.03	810.4
	March-2013	0.1± 0.01	17.5± 0.02	1.5± 0.005	84.5± 0.16	3.1± 0.03	2.1± 0.04	0.05± 0.003	1.1± 0.008	23.5± 0.20	27.5± 0.21	2.9± 0.04	1.9± 0.004	0.08± 0.006	165.8
	April-2013	0.04± 0.004	1.8± 0.001	0.0	0.7 ± 0.004	0.3± 0.001	0.0	0.02± 0.004	0.9± 0.02	4. 8± 0.11	14.5± 0.18	1.3± 0.002	0.04± 0.007	0.03± 0.002	24.4
4 (JWC4)	October-2012	0.04± 0.006	3.3± 0.02	43.5± 0.85	171.1± 1.2	4.7± 0.05	6.8± 0.04	0.4± 0.009	1.8± 0.10	31.4± 0.21	1.9± 0.004	0.8± 0.004	0.0	0.3± 0.003	266.0
	November-2012	0.1±	59.2±	5.4±	261.0±	15.9±	6.3±	0.6±	2.0±	1.0±	9.3±	1.1±	0.7±	0.7±	363.3

		0.002	0.25	0.003	0.82	0.08	0.008	0.005	0.04	0.001	0.42	0.008	0.01	0.005	
	March-2013	0.02± 0.008	4.8± 0.11	1.6± 0.06	97.5± 0.96	3.3± 0.008	3.7± 0.02	0.06± 0.005	1.1± 0.009	1.4± 0.01	2.0± 0.007	0.4± 0.001	0.4± 0.006	0.08± 0.003	116.4
	April-2013	0.01± 0.006	1.8± 0.03	0.0	1.3± 0.02	0.4± 0.002	0.0	0.02± 0.003	0.7± 0.10	7.8± 0.30	35.6± 0.08	0.8± 0.005	0.04± 0.003	0.06± 0.01	48.5
5 (BN)	October-2012	0.01± 0.006	1.5± 0.21	1.6± 0.003	188.2± 1.72	2.3± 0.003	4.0± 0.02	0.2± 0.003	1.0± 0.002	36.6± 0.82	0.9± 0.001	0.5± 0.003	0.0	0.0	236.8
	November-2012	0.1± 0.003	40.9± 0.21	3.4± 0.005	292.4± 0.75	2.3± 0.008	6.8± 0.32	1.8± 0.02	2.1± 0.06	3.7± 0.001	9.7± 0.20	1.0± 0.004	0.7± 0.03	2.9± 0.09	368.7
	March-2013	0.02± 0.003	5.0 ± 0.002	1.6± 0.02	522.0± 0.04	3.3± 0.002	8.0± 0.03	0.06± 0.004	1.2± 0.005	7.4± 0.42	6.3± 0.10	0.4± 0.02	0.2± 0.009	0.08± 0.002	555.6
	April-2013	0.0	2.3± 0.04	0.0	2.3± 0.10	0.2± 0.01	0.1± 0.006	0.02± 0.004	0.8± 0.002	4.7± 0.02	41.0± 0.51	1.1± 0.03	0.03± 0.005	0.09± 0.004	52.6
6 (Hendaza)	October-2012	0.06± 0.002	11.3± 0.21	2.9± 0.04	188.2± 0.98	5.0± 0.05	9.6± 0.76	0.3± 0.04	4.1± 0.10	60.3± 0.75	3.1± 0.04	0.2± 0.005	0.0	0.3± 0.02	285.4
	November-2012	0.1± 0.003	61.0± 1.0	5.3± 0.05	271.1± 1.32	2.3± 0.05	3.2± 0.02	2.7± 0.004	2.0± 0.03	4.4± 0.03	4.5± 0.03	1.1± 0.02	0.7± 0.02	4.7± 0.02	363.1
	March-2013	0.05± 0.005	10.8± 0.02	1.6± 0.03	505.1± 1.66	3.1± 0.05	24.1± 0.21	0.4± 0.005	2.6± 0.02	19.5± 0.82	19.0± 0.32	0.4± 0.02	0.2± 0.02	0.06± 0.002	586.9
	April-2013	0.02± 0.004	3.6± 0.02	0.0	1.3± 0.002	0.2± 0.003	0.0	0.02± 0.001	0.9± 0.005	5.0± 0.06	42.8± 0.78	0.6± 0.001	0.01± 0.001	0.3± 0.005	54.8
7 (PWA11)	October-2012	0.0	2.0± 0.06	4.7± 0.06	144.5± 0.92	4.7± 0.09	7.8± 0.05	0.3± 0.006	3.8± 0.12	9.5± 0.22	3.2± 0.005	1.0± 0.005	0.0	0.2± 0.003	181.7
	November-2012	0.1± 0.004	16.9± 0.03	5.1± 0.02	265.8± 1.13	2.3± 0.005	3.6± 0.001	0.2± 0.002	2.0± 0.01	2.2± 0.05	4.7± 0.05	1.1± 0.005	0.7± 0.002	0.9± 0.01	305.6
	March-2013	0.0	5.2± 0.03	1.6± 0.002	288.1± 0.50	3.3± 0.02	2.3± 0.01	0.05± 0.002	1.6± 0.002	9.0± 0.03	7.4± 0.02	0.4± 0.002	0.2± 0.002	0.08± 0.002	319.2
	April-2013	0.04± 0.001	0.2± 0.003	0.0	0.3± 0.002	0.08± 0.004	0.0	0.01± 0.002	0.4± 0.004	0.5± 0.009	0.8± 0.01	1.0± 0.009	0.01± 0.002	0.0	3.34
8 (IZZ 1)	October-2012	0.04± 0.002	38.8± 0.21	96.4± 0.23	144.1± 0.85	28.6± 0.23	39.5± 0.49	0.7± 0.11	3.9± 0.05	243.6 ± 0.92	4.3± 0.02	7.9± 0.09	0.0	0.9± 0.01	608.7
	November-2012	1.0± 0.02	90.9± 0.21	215.7 ± 0.81	322.3± 1.2	8.7± 0.15	5.9± 0.09	0.1± 0.004	2.1± 0.02	3.3± 0.002	6.6± 0.10	9.2± 0.05	6.4± 0.07	1.8± 0.009	674.0
	March-2013	0.0	2.7± 0.05	1.7± 0.008	86.5± 0.86	3.3± 0.08	3.6± 0.07	0.06± 0.005	1.1± 0.05	4.2± 0.02	9.2± 0.25	1.2± 0.11	0.2± 0.008	0.08± 0.008	113.8

	April-2013	0.1± 0.003	3.1± 0.03	3.1± 0.02	70.2± 0.52	2.4± 0.11	2.6± 0.08	0.04± 0.005	1.0± 0.03	3.1± 0.04	7.1± 0.02	1.0± 0.005	0.1± 0.005	0.06± 0.004	93.9
9 (IZZ 2)	October-2012	0.02± 0.001	5.5± 0.09	15.0± 0.31	179.2± 1.78	7.0± 0.21	11.5± 0.22	0.3± 0.005	2.9± 0.09	50.9± 0.88	2.3± 0.21	11.5± 0.34	0.0	0.3± 0.04	286.4
	November-2012	0.4± 0.02	80.7± 1.02	39.6± 0.23	436.7± 2.1	10.4± 0.20	3.0± 0.21	0.07± 0.005	2.1± 0.08	36.1± 0.23	4.1± 0.09	1.1± 0.002	0.7± 0.01	0.4± 0.005	615.4
	March-2013	0.02± 0.004	0.3± 0.003	1.7± 0.03	151.5± 0.79	3.3± 0.005	0.4± 0.008	0.06± 0.008	1.1± 0.02	1.2± 0.02	2.0± 0.02	0.4± 0.002	0.2± 0.01	0.08± 0.004	162.3
	April-2013	0.0	2.2± 0.03	2.6± 0.52	100.8± 2.11	2.6± 0.05	0.7± 0.03	0.04± 0.005	0.9± 0.002	1.1± 0.05	1.7± 0.08	0.3± 0.004	0.1± 0.005	0.07± 0.002	113.1
10 (IZZ 3)	October-2012	0.05± 0.001	18.4± 0.79	22.1± 0.11	150.9± 1.34	6.5± 0.07	31.8± 0.08	0.7± 0.007	4.5± 0.09	66.4± 1.0	5.5± 0.08	2.1± 0.04	0.0	1.7± 0.09	310.7
	November-2012	0.6± 0.02	61.5± 0.82	18.3± 0.52	319.8± 2.12	5.2± 0.31	9.7± 0.11	0.2± 0.02	2.1± 0.21	3.9± 0.10	14.5± 0.51	1.1± 0.09	0.7± 0.02	2.5± 0.08	440.1
	March-2013	0.05± 0.003	2.6± 0.12	1.7± 0.21	155.0± 0.03	3.3± 0.02	0.8± 0.005	0.06± 0.005	1.1± 0.02	3.4± 0.03	2.1± 0.01	0.4± 0.02	1.4± 0.02	0.08± 0.004	172.0
	April-2013	0.0	1.7± 0.02	1.7± 0.23	144.1± 2.10	2.7± 0.05	0.7± 0.005	0.04± 0.004	1.0± 0.01	2.3± 0.08	1.2± 0.008	0.2± 0.009	1.1± 0.03	0.07± 0.005	156.8
Average		0.10	22.0	21.1	195.7	4.27	7.9	0.44	2.1	20.8	9.8	1.7	0.53	0.89	
Standard deviation		0.19	32.1	45.2	162.9	5.0	10.4	1.1	2.1	40.5	10.7	2.5	1.0	1.7	
WHO guideline value	0.01-1	10	No limits	200	50	500	No limits	20	20	2000	3000	70	No limits	3	
Palestinian guideline value	No limits	10	No limits	200	50	1000 - 5000	No limits	No limits	50	1000-1500	5000	No limits	50	3	

4.2.2 Trace metals pollution in terms of well number

A one way ANOVA statistical test was used to test if the concentration of the analyzed metals is significantly different between the ten groundwater wells. Results showed that the ten wells in this study are different from each other at 95% confidence level in terms of heavy metal content. These findings confirm locational variations of the metals in the ten wells analyzed in this study. Figure (4.2) shows this variation for Pb as an example in the ten wells. This fluctuation in the concentration of trace metals in the ten wells analyzed in this study indicates that the sources of these metals are from anthropogenic and human activities e.g. arbitrary dumping sites, landfills, and industry.

From table 4.2, it was found that the highest concentration of Tl, Pb, Bi, Al, Cr, Mn, Co, Ni, Cu, Zn, Mo, Ag, and Cd were found in well IZZ 1, PWA1, IZZ 1, PWA 3, IZZ 1, Beit Fajjar, Beit Fajjar, PWA 1, IZZ 1, Hundaz, IZZ 2, IZZ1, and Beit Fajjar, respectively. As it is clear from this result, IZZ1 well is highly contaminated with heavy metals compared to others as this well is located near some industrial activities.

4.2.3 Effect of sampling date on the heavy metal content

Statistical analyses were conducted to test if there is significant difference in the concentration of the metals in the groundwater wells as a function of the sampling date (October 2012, November 2012, March 2013 and April 2013), results revealed that there is a significant difference, denoting that metal concentration in the wells vary significantly with sampling time. As it is seen in table (4.2), concentration of Pb is the highest on November and lowest on April. The same applies for Tl where highest concentration was detected on November, but the lowest concentration fluctuates between other months. For Bi, Co, and Ni the highest concentrations of these metals were detected in October and November, while the lowest in April. For Al, the highest concentration is detected in November for some samples and in March for other samples, while the lowest concentration remains in April. Regarding Cr and Mn there is fluctuation concentration (between October, November and March), but the lowest concentration remains in April. The highest concentration of Cd was found to be on November, but the lowest concentration fluctuates between October, March, and April. Concerning Cu, Zn, Mo and Ag, there is a fluctuation in the concentration of these metals and there is no trend in the

highest and lowest concentration. Generally high concentrations of trace metals are detected in October and November, while lower concentrations are detected in March and April (and especially in April). This result may be explained by the fact that such heavy metals which a rise from anthropogenic sources are collected and concentrated during no-rain months, and then washed in October and November (beginning of rainfall) with the rain runoff and leached to the groundwater through soil.

It was important to calculate the total concentration of all trace metals in the wells, and to compare this concentration in the ten wells in terms of sampling month. Results showed that the total concentration of the thirteen trace metals is highest in November and lowest in April in eight wells analyzed in this study (PWA1, Beit Fajjar, PWA3, JWC4, BaniNaem, IZZ1, IZZ2, and IZZ3). On the other hand, the total concentration for wells Hendaza, and PWA11 was found to be highest in March but the lowest total concentrations remains in April, see table (4.2). The high total concentration of trace metals found in November can be attributed to the leaching of theses heavy metals to the groundwater with rainfall in November, while in April these trace metals are diluted.

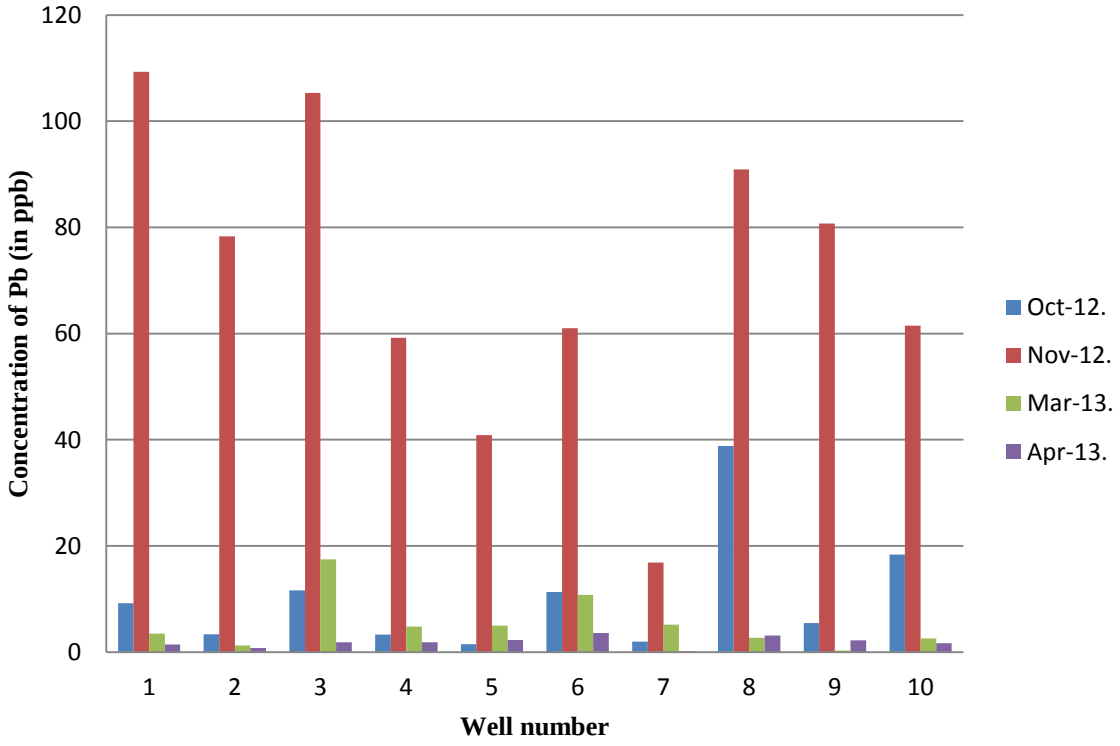


Figure (4.2): Concentration of Pb (in ppb) vs. well number obtained in October 2012, November 2012, March 2013and April 2013.

4.3 Ground Water of North West Bank

This study was conducted to investigate the quality of groundwater which is used for drinking in the study area. The people of the study area people depend mainly on the groundwater and on the rain water harvested and stored in cisterns or wells. The pH of all water samples ranged between 6.9 - 7.8 which is within the allowed WHO limit (6.5-8.5). Electrical conductivity and total dissolved solids of all water samples ranged from 394-1432 µS/cm, and 225.0-816.0 mg/L respectively. The limit for total dissolved solids in drinking water according to WHO is 1000 mg/L (WHO 2003), where our results showed that all water samples are within this limit.

4.3.1 Heavy metals content

Results showed that eleven heavy metal (Tl, Pb, Bi, Cr, Mn, Co, Ni, Cu, Zn, Mo, Ag and Cd) Al were detected in one or more water sample analyzed in this study. The concentration of Tl, Pb, Al, Cr, Mn, Co, Ni, Cu, Zn, Mo, Ag, and Cd in the five wells analyzed in this study were ranged from: 0.02-0.12, 0.0-1.35, 0.28-30.11, 0.07-1.77, 0.02-8.96, 0.03-0.06, 0.13-4.62, 0.52-16.11, 0.0-16.36, 0.38-8.75, 0.0-0.03, and 0.0-0.04 µg/L, respectively. Results showed that the concentration of nine trace metals (Cr, Mn, Ni, Cu, Zn, Mo, Pb, Cd and Al) is within the allowed WHO limits for drinking water (50, 500, 20, 2000, 3000, 70, 10, 3 and 200 ppb respectively), however six metals of them (Cr, Mn, Ni, Cu, Mo and Al) were detected in 100% of the samples, while Pb, Cd, and Zn were detected in 80%, 60% and 20% of the analyzed samples, respectively. In general, 82% of all samples analyzed contained one or more of the 12 metals studied each in varying concentration. Table (4.3) show the concentrations of metals detected in the groundwater samples analyzed in this study in sampling dates (March 2013).

Table (4.3): Concentration of trace metals detected in groundwater wells analyzed in the North West Bank. Results expressed as Average ± SD for three samples (SD: standard deviation), as well as their WHO and Palestinian guideline.

Well number (name)	Sampling date	Concentration of metals (µg/L)												
		Tl	**Pb**	**Cr**	**Mn**	**Co**	**Ni**	**Cu**	**Zn**	**Mo**	**Ag**	**Cd**	**Al**	Total concentration (µg/L)
1 araba	March-2013	**0.12** ± 0.001	**0.07** ± 0.01	**1.07** ± 0.002	**0.02** ± 0.003	**0.04** ± 0.002	**4.62** ± 0.12	**1.60** ± 0.01	**0.00**	**3.56** ± 0.13	**0.03** ± 0.002	**0.04** ± 0.002	**1.33** ± 0.29	12.50
2 jaba	March-2013	**0.02** ± 0.0006	**1.35** ± 0.03	**1.77** ± 0.04	**0.77** ± 0.009	**0.03** ± 0.001	**2.39** ± 0.02	**16.11** ± 0.08	**16.36** ± 0.37	**1.61** ± 0.02	**0.00**	**0.02** ± 0.0005	**3.21** ± 0.53	43.64
3 bathan	March-2013	**0.02** ± 0.006	**0.00**	**1.10** ± 0.01	**1.92** ± 0.02	**0.06** ± 0.002	**2.18** ± 0.04	**0.52** ± 0.005	**0.00**	**0.71** ± 0.008	**0.00**	**0.00**	**30.11** ± 0.34	36.65
4 rojeeb	March-2013	**0.02** ± 0.001	**0.03** ± 0.007	**0.29** ± 0.03	**0.01** ± 0.001	**0.03** ± 0.001	**0.13** ± 0.01	**1.43** ± 0.02	**0.00**	**0.38** ± 0.003	**0.00**	**0.00**	**0.00**	2.32
5 mythaloun	March-2013	**0.08** ± 0.004	**0.74** ± 0.04	**0.07** ± 0.002	**8.96** ± 0.04	**0.05** ± 0.004	**0.77** ± 0.008	**15.95** ± 0.09	**0.00**	**8.75** ± 0.05	**0.00**	**0.00**	**0.76** ± 0.14	36.13
Standard deviation		**0.05**	**0.60**	**0.69**	**3.78**	**0.01**	**1.74**	**8.14**	**7.32**	**3.44**	**0.01**	**0.02**	**12.93**	
WHO guideline value		**0.01-1**	**10**	**50**	**500**	**No limits**	**20**	**2000**	**3000**	**70**	**No limits**	**3**	**200**	
Palestinian guideline value		**No limits**	**10**	**50**	**100 - 500**	**No limits**	**50**	**1000 - 1500**	**5000**	**No limits**	**50**	**3**	**200**	

There is no limit for Ag in drinking water according to WHO, however it is usually found in drinking water in the range 5-50µg/L. Our results showed that all samples are within this limit. Co has also no limits in drinking water by WHO, however this metals were detected in 100% of the water samples analyzed in this study. Thalium (Tl) is a highly toxic element that humans are exposed to mainly by consumption of drinking water and vegetables grown in soil with high thallium content but also through inhalation of particles in the air. Thallium is also present in fossil fuels, alloys, and in electronic utilities. The increasing use of the element and emissions from notably energy production has lead to a higher load on the surface of the Earth. The allowed WHO limits of Tl in water is 0.01-1 µg/L (IPCS, 1996). Our results showed that Tl is detected in 100% of the water samples analyzed with a range of 0.02-0.12µg/L, which indicates that such concentration level of Tl would be harmful to human being consuming this groundwater.

A one way ANOVA statistical test was used to test if the concentration of the analyzed metals is significantly different between the five groundwater wells. Results showed that the five wells in this study are different from each other at 95% confidence level in terms of heavy metal content. These findings confirm locational variations of the metals in the wells analyzed in this study. Figure (4.3) shows this variation for Pb as an example in the five wells. This fluctuation in the concentration of trace metals in the five wells analyzed in this study indicates that the sources of these metals are from anthropogenic and human activities e.g. arbitrary dumping sites, landfills, and industry.

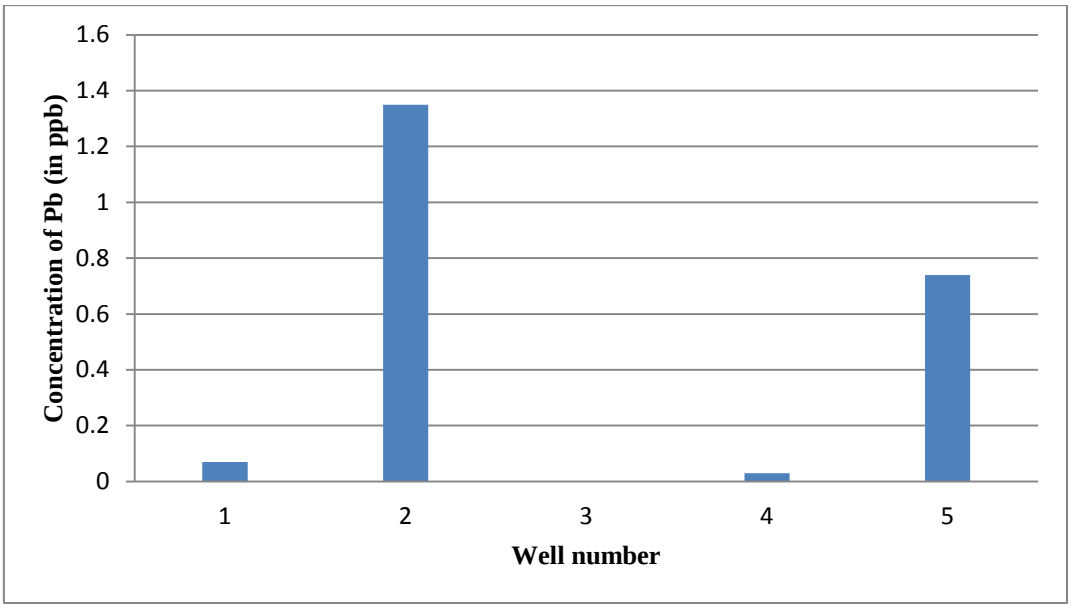


Figure (4.3): Concentration of Pb (in µg/L) vs. well number analyzed in this study.

4.3.2 Sources of heavy metals in the groundwater samples

Heavy metals exist in water in colloidal, particulate and dissolved phases (Adepoju-Bello *et al*., 2009) with their occurrence in water bodies being either of natural origin (e.g. eroded minerals within sediments, leaching of ore deposits and volcanism extruded products) or of anthropogenic origin (i.e. solid waste disposal, industrial or domestic effluents) (Marcovecchio*et al*., 2007). The most common heavy metals that humans are exposed to are Aluminium, Arsenic, Cadmium, Lead and Mercury. Aluminium has been associated with Alzheimer's and Parkinson's disease, senility and presenile dementia. Arsenic exposure can cause among other illness or symptoms cancer, abdominal pain and skin lesions. Cadmium exposure produces kidney damage and hypertension. Lead is a commutative poison and a possible human carcinogen (Bakare-Odunola, 2005).

The quality of ground water sources are affected by the characteristics of the media through which the water passes to the ground water zone of saturation (Adeyemi*et al*., 2007), thus, the heavy metals discharged by industries, traffic, municipal wastes, hazardous waste sites as well as from fertilizers for agricultural purposes and accidental oil spillages from tankers can result in a steady rise in contamination of ground water (Igwilo*et al*., 2006). Additionally, groundwater quality is influenced considerably by the quality of the recharge source. Variations in natural and human activities reflect spatial variations of the aquifer and the hydrochemical parameters of the groundwater. Pollution sources are classified as point sources and diffuse sources. Point sources are sources that can be clearly identified and pinpointed (such as landfill leachate). Diffuse sources cannot be pinpointed and are distributed over a large surface area (application of fertilizers and pesticides in agriculture) (El-Nahhal, 2006).

In Palestine, groundwater is one of the major sources of water. Efficient management of this resource requires a good understanding of its status. Groundwater management in the West Bank is affected by the randomly distributed dumping sites, solid waste landfills, cesspits, especially in rural communities, as well as agricultural and industrial practices. Accordingly, the shallow aquifer in the eastern and western groundwater basins is deteriorated; high concentrations of nitrate and sulfate were detected larger than the WHO standards (El-Nahhal, 2006). Microorganisms were detected in some springs inside rural communities in Ramallah area. This could be reflected on the water supply for these communities for the fact that these water sources are the major sources for drinking and agricultural purposes (Ghanem, 2011, El-Nahhal, 2006, . Abed, A., &Wishahi, S. 1999). Accordingly, the sources of the detected metals in groundwater wells of the study area which is used for drinking can be attributed to many sources, including, among others, dumping sites and landfills for solid waste disposal, cesspits, industries, traffic, as well as from fertilizers for agricultural purposes. The leachate of municipal wastes and landfills which contain heavy metals is transported to the ground water through soil. In addition to the leachate of landfills, uncontrolled burning (incineration) of solid wastes in illegal waste dumping sites and landfills may also results in the contamination of groundwater with heavy metals. The most publicized concerns from environmentalists about the incineration of municipal solid wastes involve the fear that it produces significant amounts of emissions in their ash and flue gases including heavy metals (Chang et al. 2003). Fly ash generated from waste incineration is usually contaminated with heavy metals and other dangerous

substances and have to be treated as a hazardous residue. As a result of solid waste incineration, diverse pollutants are formed and emitted in flue gas including heavy metals e.g. Hg, Cd, Tl, As, Ni, Pb, Sb, Se, Sn, Zn et…, especially when wastes contain batteries, leather, pigments, cans. The heavy metals emitted from solid waste incineration process can reach water (surface, ground, rainwater..etc) and pollute it. Europe has been strongly committed since the early 1970s to the environment protection of air. In this ambit, it should be mentioned the Directive 2000/76/EC of the European Parliament and of the Council, on the incineration of waste that aims "*to prevent or to limit as far as practicable negative effects on the environment, in particular pollution by emissions into air, soil, surface water and groundwater, and the resulting risks to human health, from the incineration and co-incineration of waste."* This Directive, known as Waste Incineration Directive (WID) states that continuous measurements of emissions including the following heavy metals such as (Cd, Tl, Hg, Sb, As, Pb, Cr, Co, Cu, Mn, Ni and V) is necessary (Directive 2000/76/EC of The European Parliament and the Council 2000). The emissions of heavy metals depend mostly on the waste characteristics and air pollution control devices. Air pollution residues produced in incineration processes are classified as hazardous solid waste mainly due to its high pH, and high content in volatile heavy metals (Quina et al. 2008b). As an example, cadmium is an environmental problematic toxic element that may arise in air emissions due to its thermal mobility. Although some countries restrict applications of Cd, frequent sources are electronic devices (including accumulators), paints, Ni-Cd batteries, and cadmium-stabilised plastics (BREF 2006). During incineration process, combustion temperatures determine the evaporation degree of heavy metals. Indeed, the following heavy metals: Hg, Cd, Tl, Sb, As, Pb, Cr, Co, Cu, Mn, Ni and V must be under control. These are very toxic metals since they are carcinogenic or may provoke respiratory damages. Lead and chromium are currently the most problematic heavy metals found in solid wastes residues that lead to a classification as hazardous waste (BREF 2006). Results of the current work have confirmed pollution of ground water collected in the study area, where thirteen metals including the toxic heavy metals: Pb, Cr , Cd, Mn, Co, Ni, Cu and Zn are detected.

In West Bank and especially in rural areas, people dispose their wastewater using cesspits which is one of the main pollution sources to groundwater. Most of these cesspits are emptied by vacuum tankers and disposed into wad is or to improper dumping sites. These dumping sites are located in agricultural lands and their sites were selected randomly

without any consideration to the soil characteristics, topography and climate as well as groundwater (El-Nahhal, 2006). As none of the existing dumping sites is designed to collect leachate from solid waste degradation, the leachate always finds its way through the soil to the groundwater, increasing concentration of pollutants including heavy metals to the water (El-Nahhal, 2006). In addition to municipal wastes and cesspits, urban, agricultural and industrial activities in the study area may also contribute to the contamination of the groundwater with heavy metals.

Chapter Five

Conclusions and Recommendations

5.1 Harvested Rain Water

Harvested rainwater from west part of Hebron in south West Bank contains different heavy metals with five heavy metals (Cr, Mn, Ni, Ag, and Pb) exceeding the WHO limits for heavy metals in drinking water. pH of the waters samples is within the WHO limits, while some water samples exceed the limits for total dissolved solids and electrical conductivity. Incineration of solid wastes in the study area may be responsible for the occurrence of heavy metals in harvested rain water. Uncontrolled consumption of harvested rainwater used for drinking in west part of Hebron may be dangerous for human health.

5.2 Ground Water of South West Bank

Groundwater from south West Bank contains twelve heavy metals (Tl, Pb, Bi, Cr, Mn, Co, Ni, Cu, Zn, Mo, Ag, and Cd) and one metal (Al) in 93% of samples analyzed from ten wells, with eight trace metals (Pb, Al, Cr, Co, Ni, Cu, Zn, and Mo) detected in 100% of water samples analyzed. Concentrations of six heavy metals (Cr, Mn, Ni, Cu, Zn, and Mo) detected in the water samples analyzed in this study are within the allowed limits, but they are detected in almost all water samples analyzed in this study. The concentration of three metals (Pb, Cd, and Al) are higher than the allowed WHO limits in 40%, 8%, and 33% of the water samples analyzed in this study, respectively. Municipal waste, landfills, cesspits, and incineration of solid wastes in the study area are responsible for the occurrence of the trace metals detected in the groundwater of the study area. It is concluded that uncontrolled consumption of groundwater which is used for drinking in the study area may be dangerous for human health.

5.3 Ground Water of North West Bank

Define Groundwater from north West Bank contains eleven heavy metals (Tl, Pb, Cr, Mn, Co, Ni, Cu, Zn, Mo, Ag, and Cd) and one metal (Al) in 82% of samples analysed from five wells, with nine trace metals (Cr, Mn, Ni, Cu, Zn, Mo, Pb, Cd, and Al) is within the allowed WHO limits in drinking water, however six metals of them (Cr, Mn, Ni, Cu, Mo, and Al) were detected in 100% of the samples. Although Co has no limits in drinking water by WHO, this metal was detected in 100% of the water samples analysed in this

study. Thallium (Tl), a highly toxic element with a WHO limit of 0.01-1 µg/L, is detected in 100% of the water samples analysed with a range of 0.02-0.12 µg/L, which indicates that such concentration level of Tl would be harmful to human being consuming this groundwater. There are locational variations in the concentration of metals in the wells analysed in this study.

5.4 Recommendations

1. The uncontrolled disposal of wastes and incineration of solid waste should be banned and responsible authorities have to monitor and control the quality of groundwater periodically (e.g. heavy metals content) in West Bank as this water is used for drinking especially in regions suffering from water scarcity.

2. Other studies should be conducted for monitoring heavy metals in water (surface, ground…etc) in other locations in Palestine.

3. Raising the awareness of all relevant institutions working in the fields of environmental pollution and discussing water treatment issues for the future is strongly recommended.

References:

Abbasi, S. A. Abbasi, N. Soni, R.1998. Heavy metal in the environment, 1st. Ed., Mital Publication, New Delhi, India

Abderahman,N and Abu-Rukah,Y. 2006."An Assessment Study of Heavy Metal Distribution within Soil in Upper Course of Zarqa River Basin/Jordan," Environmental Geology, Vol. 49, No. 8, pp. 1116-1124. doi:10.1007/s00254-005-0154-4.

Abed, A. and Wishahi, S, 1999. "Geology of Palestine: The West Bank and Gaza Strip. Palestine," Palestine Hydrology Group, Ramallah,.

Abdul-Jaber, Q., Rabbo, A., Scarpa, D., Qannam, Z., Younger, P. 1999. Wells in the West Bank: Water Quality and Chemistry. Report by Palestinian Hydrology Group, Bethlehem University, and Newcastle University to Ford Foundation. Irish Development Aid and Department for International Development.

Adekunle, I. Adetunji, M. Gbadebo, A and Banjoko, O. 2007. "Assessment of Groundwater Quality in a Typical Rural Settlement in Southwest Nigeria," International Journal of Environmental Research and Public Health, Vol. 4, No. 4, pp. 307-318. doi:10.3390/ijerph200704040007.

Adepoju-Bello, A. A. Ojomolade, O. O. Ayoola, G. A and Coker, H. A. B, 2009, "Quantitative Analysis of Some Toxic Metals in Domestic Water Obtained from Lagos Metropolis," Nigerian Journal of Pharmacy, Vol. 42, No. 1, , pp. 57-60.

Adeyemi, O. Oloyede, O. B and Oladiji, A. T.2007. "Physicochemical and Microbial Characteristics of Leachate Contaminated Ground Water," Asian Journal of Biochemistry, Vol 2, No. 5, pp. 343-348. doi:10.3923/ajb.2007.343.348.

Agilent Technologies, 2005." ICP-MS Inductively Coupled Plasma Mass Spectrometry A Primer" Publication Number 5989-3526EN, USA.

Alomary, A. 2013."Determination of trace metals in drinking water in Irbid City-Northern Jordan," Environ Monit Assess. 185(2): 1969-75.

Amin,M.T. Alazba,A.A. 2011. Probable Sources of Rainwater Contamination In A Rainwater Harvesting System and Remedial Options, Australian Journal of Basic and Applied Sciences, 5(12), 1054-1064.

Anayah, F. M. Almasri, M. N. 2009. Trends and occurrences of nitrate in the groundwater of the West Bank, Palestine, Applied Geography 29: 588–601.

APHA, 1998. (American Public Health Association), "Standard Methods for the Examination of Water and Wastewater," 20th Edition, Washington DC, p. 1294.

ARIJ, 1995. (Applied Research Institute, Jerusalem) Environmental profile for the West Bank, volume 3: Hebron District.

Bakare-Odunola, M. T. 2005."Determination of Some Metallic Impurities Present in Soft Drinks Marketed In Nigeria," The Nigerian Journal of Pharmaceutical Research, Vol. 4, No. 1, pp. 51-54.

Batayneh, A. T. 2010. "Heavy Metals in Water Springs of the Yarmouk Basin, North Jordan and Their Potentiality in Health Risk Assessment," International Journal of the Physical Sciences, Vol. 5, No. 7 , pp. 997-1003.

BREF. 2006. Integrated Pollution Prevention and Control- Reference Document on the Best Available Techniques for Waste Incineration, European Commission.

Bruins, M.R. Kapil, S. and Oehme, F.W. 2000. Microbial resistance to metals in the environment, Ecotoxicology and Environmental Safety, 45,pp 198-207.

Chang, M.B. Jen, C.H. Wu,H.T. 2003.Investigation on the emission factors and removal efficiencies of heavy metals from MSW incinerators in Taiwan. Waste Management & Research, 21: 218–224.

Chen, C. Kao, C. Chen, C. 2007. "Distribution and Accumulation of Heavy Metals in the Sediments of Kaohsiung Harbor", Taiwan. Chemosphere, 66: 1431-1440.

Despins, C. Farahbakhsh, K. Leidl, C. 2009. Assessment of rainwater quality from rainwater harvesting systems in Ontario, Canada, Journal of Water Supply: Research and Technology-AQUA, 58.2.

Directive 2000/76/EC of The European Parliament and the Council, of 4 December 2000, on the incineration of waste.,

Dupler, D. 2001. "Heavy Metal Poisoning," In: J. L. Longe, Ed., Gale Encyclopedia of Alternative Medicine, Gale Group, Farmington Hills, pp. 2054-2057.

El-Nahhal Y. 2006. "Contamination of Groundwater with Heavy Metals in Gaza Strip," 10th International Water Technology Conference, Alexandria, pp. 1139-1150.

Ferner, D.J. 2001. "Toxicity and Heavy metals," eMedicine Journal, Vol. 2, No.5, pp. 1.

Ghanem,M and Samhan,N. 2012. “Groundwater Pollution Assessment in Tulkarem Area, Palestine,” Journal of Earth Sciences and Geotechnical Engineering, Vol. 2, No. 4, pp. 1-16.

Ghanem,M. Samhan, S. Carlier, E and Wasim, A. 2011. “Groundwater Pollution Due to Pesticides and Heavy Metals in North West Bank,” Journal of Environmental Protection, Vol. 2, No. 4, pp. 429-434. doi:10.4236/jep.2011.24049

Gutierrez, R. Rubio-Arias, H. Quintana, R. Ortega, J and Gutierrez, M. 2008. “Heavy Metals in Water of the San Pedro River in Chihuahua, Mexico and Its Potential Health Risk,” International Journal of Environmental Research and Public Health, Vol. 5, No. 2, pp. 91-98. doi:10.3390/ijerph5020091.

http://www.water-observatory.net/sources/iwtc2006/15-1.PDF.

Igwilo, I. O. Afonne, O. J. Maduabuchi, U. J and Orisakwe, O. E. 2006. “Toxicological Study of the Anam River in Otuocha, Anambra State, Nigeria,” Archives of Environmental & Occupational Health, Vol. 61, No. 5, pp. 205-208. doi:10.3200/AEOH.61.5.205-208.

IPCS. 1996. Thallim international program on chemical safety, environmental health criteria.182. Geneva, Switzerland, WHO.

Iqbal , M. A and Gupta, S. G. 2009.“Studies on Heavy Metal Ion Pollution of Ground Water Sources as an Effect of Municipal Solid Waste Dumping,” African Journal of Basic & Applied Sciences, Vol. 1 No. 5-6, pp. 117- 122.

Ismail, I and Mat Saleh, I. 2012.“Analysis of Heavy Metals in Water and Fish (Tilapia sp.)Samples from Ttasik Mu- tiara, Puchong,” The Malaysian Journal of Analytical Sciences, Vol. 16, No. 3, pp. 346-352.

Jenin Agricultural Department.2004. “Meteorological Data about Jenin Governate,” Unpublished data, Jenin, West Bank,

Johnson, F.M. 1998. The genetic effects of environmental lead.Mutat. Res., 410: 123-140.

Kar, D. Sur, P. Mandal, S. 2008. “Assessment of Heavy Metal Pollution in Surface Water,” International Journal of Environmental Science and Technology Vol. 5, No. 4, pp. 119-124.

Laniyan, T. A.Kehinde Phillips, O. O and Elesha, L. 2011. “Hazards of Heavy Metal Contamination on the Ground- water around a Municipal Dumpsite in Lagos, South-western Nigeria,” International Journal of Engineering & Technology, Vol. 11, No. 1, pp. 61-69.

Leung C and Jiao J.2006."Heavy metal and trace element distributions in groundwater in natural slopes and highly urbanized spaces in Mid-Levels area, Hong Kong" Water Research, Vol.40.pp.753-767.

Magyar,M.I. Mitchell, V.G. Ladson,A.R and Diaper, C. 2008. Lead and other heavy metals: common contaminants of rainwater tanks in Melbourne, WATER DOWN UNDER.

Marcovecchio,J. E. Botte, S. Eand Freije, R. H. 2007. “Heavy Metals, Major Metals, Trace Elements”. In: L. M. Nollet, Ed., Handbook of Water Analysis, 2nd Edition, CRC Press, London, pp. 275-311.

Marschner, H. 1995. Mineral nutrition of higher plants, Academic Press, London.

Momodu, M. A andAnyakora,C. A. 2010. “Heavy Metal Contamination of Ground Water: The Surulere Case Study.” Research Journal Environmental and Earth Sciences, Vol. **2**, No. 1,, pp. 39-43.

Momot,O and Synzynys, B. 2005.“Toxic Aluminium and Heavy Metals in Groundwater of Middle Russia: Health Risk Assessment,” International Journal of Environ- mental Research and Public Health, Vol. 2, No. 2pp. 214-218. doi:10.3390/ijerph2005020003.

Mosley, L. 2005. SOPAC Water Quality Officer, water quality of rainwater harvesting systems, SOPAC Miscellaneous Report 579.

Ong, M. and Kamaruzzaman, B. 2009.An Assessment of Metals (Pb and Cu) Contamination in Bottom Sediment from South China Sea Coastal Waters, Malaysia. Amer. J. App. Sci., 6, 1418-1423.

Onwughara N., Umeobika U., Obianuko P and IloamaekeI.,(2011). "Emphasis on Effects of Storm Runoff in Mobilizing the Heavy Metals from Leachate on Waste Deposit to Contaminate Nigerian Waters: Improved Water Quality Standards" International Journal of Environmental Science and Development, Vol.2, No.1.pp.55-63.

Oyeku, O. T and Eludoyin, A. O. 2010. “Heavy Metal Con- tamination of Groundwater Resources in a Nigerian Ur- ban Settlement,” African Journal of Environmental Sci- ence and Technology, Vol. 4, No. 4, pp. 201-214.

Tsuji, L.J.S. and Karagatzides, J.D. 2001. Chronic lead exposture, body condition and Testis mass in wild Mallard Ducks. B. Environ. Contaminat.Toxicol., 67: 489-495.

Palestinian Standards Institution (PSI). 2004. Water quality standards. Ramallah, Palestine.

PHG. 2008. “Water For Life”, Water, Sanitation and Hygiene Monitoring Program (WaSH MP). (2007/2008).

PWA. 2001. Data review on the West Bank aquifers. Working Report SUSMAQ-MOD # 02 V2.0. Palestine: Sustainable Management of the West Bank and Gaza Aquifers, Water Resources and Planning Department, Palestinian Water Authority.

Quina, M.J. Santos, R.C. Bordado, J.C.M. 2008. Characterization of air pollution control residues produced in a municipal solid waste incinerator in Portugal, Journal of Hazardous Materials. 152: 853-869.

Rajappa, B. 2010, “Monitoring of Heavy Metal Concentration in Groundwater of Hakinaka Taluk, India,” Contempo- rary Engineering Sciences, Vol. 3, No. 4, pp. 183- 190.

Roberts, H. 1995. “Lead poisoning,” Available online at: http://www.setlet.com. (accessed 01-07-2013).

Scarpa, D. J. 1994. “Eastward groundwater flow from the Mountain aquifer,” In J. Isaac and H. Shuval (Eds.), Water for peace in the Middle East (Amsterdam: Elsevier Science Publications), pp. 193–203.

UNEP. 2003. “Desk Study on the Environment in the Occupied Palestinian Territories,” United Nations Environment Programme, Nairobi.

Vodela,J. K. Renden, J. A. Lenz, S. D. MchelHenney,W. H and Kemppainen,B. W.1997.“Drinking water contaminants,” Poultry Science, Vol.76, pp. 1474-1492.

Voical, C. Kovacs, M. H. Dehelean, A. Ristoiu, D and Iordache, A. 2012. "ICP-MS Determinations of Heavy Metals in Surface Waters from Transylvania," Romanian Journal of Physics., Vol. 57, No. 6-7, pp. 1184-1193.

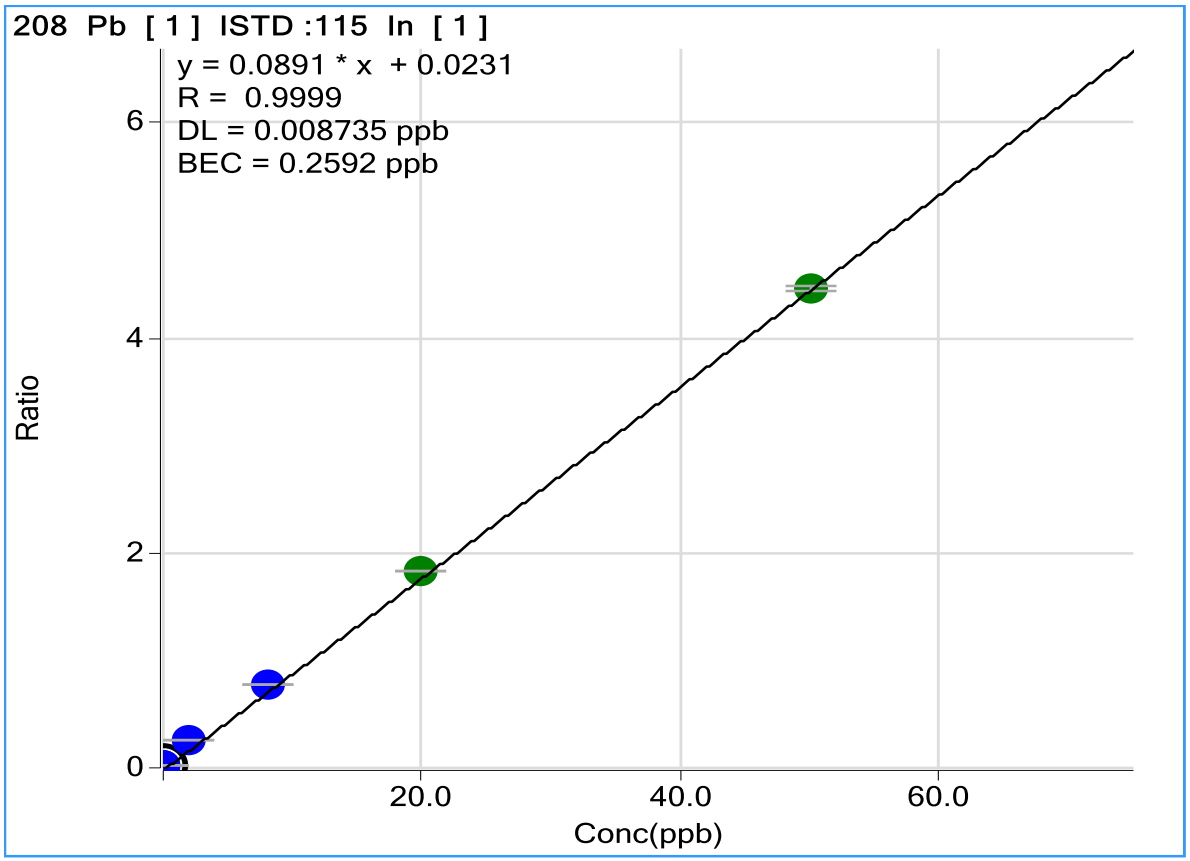
WHO. 2003. "Total Dissolved Solids In drinking water," Background Document for Development of WHO Guidelines for Drinking Water Quality (WHO/SDE/WSH/03.04/16)".

WHO. 1993. Guidelines for drinking water quality. 2nd edition. Volume 1: Recommendations. Geneva: WHO, 49-50.

Ziad Qannam. 2003. PhD thesis: A hydrogeological and environmental study in Wadi Al Arroub drainage basin, south West Bank, Palestine.

Appendix A

Calibration curve for various Lead concentrations using ICP-MS.

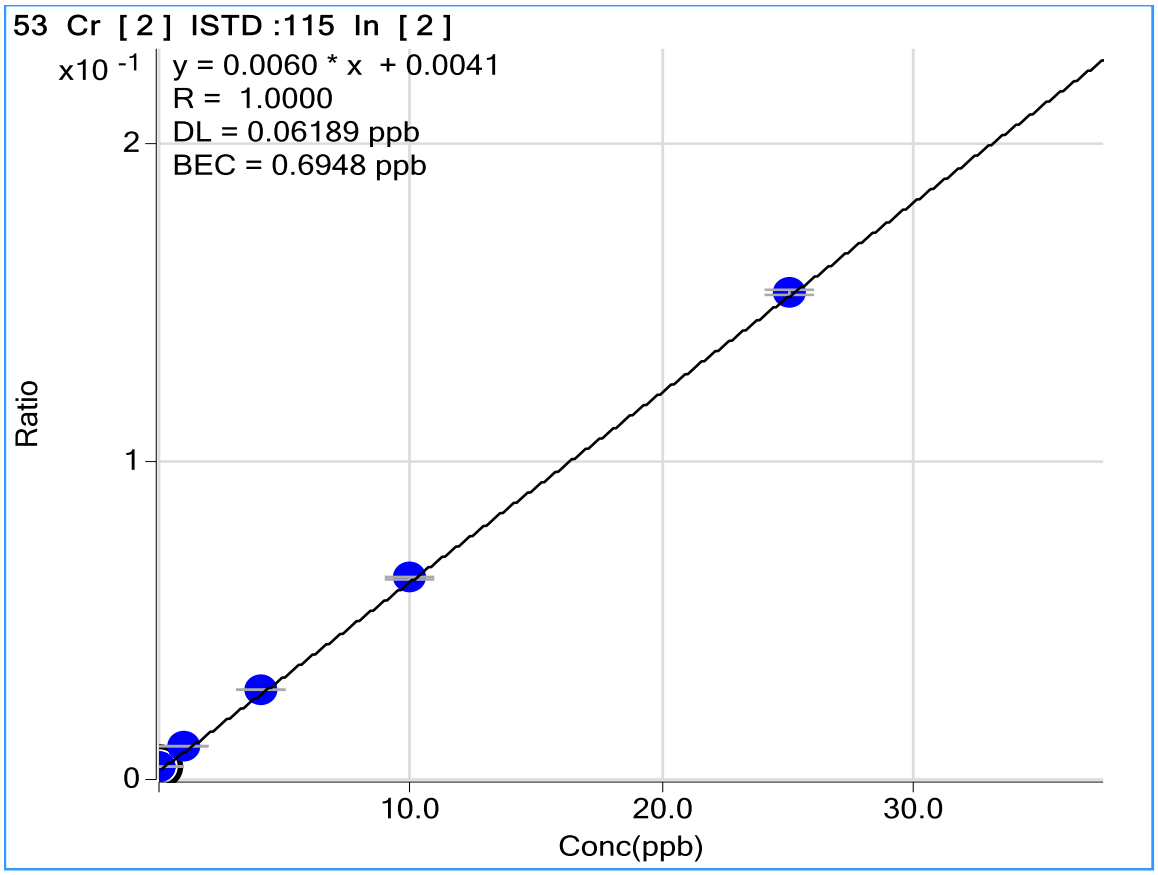


Ratio= Instrument Response (account/time)

DL : Detection Limit

BEC : background equivalent concentration.

Calibration curve for various Chromium concentrations using ICP-MS.

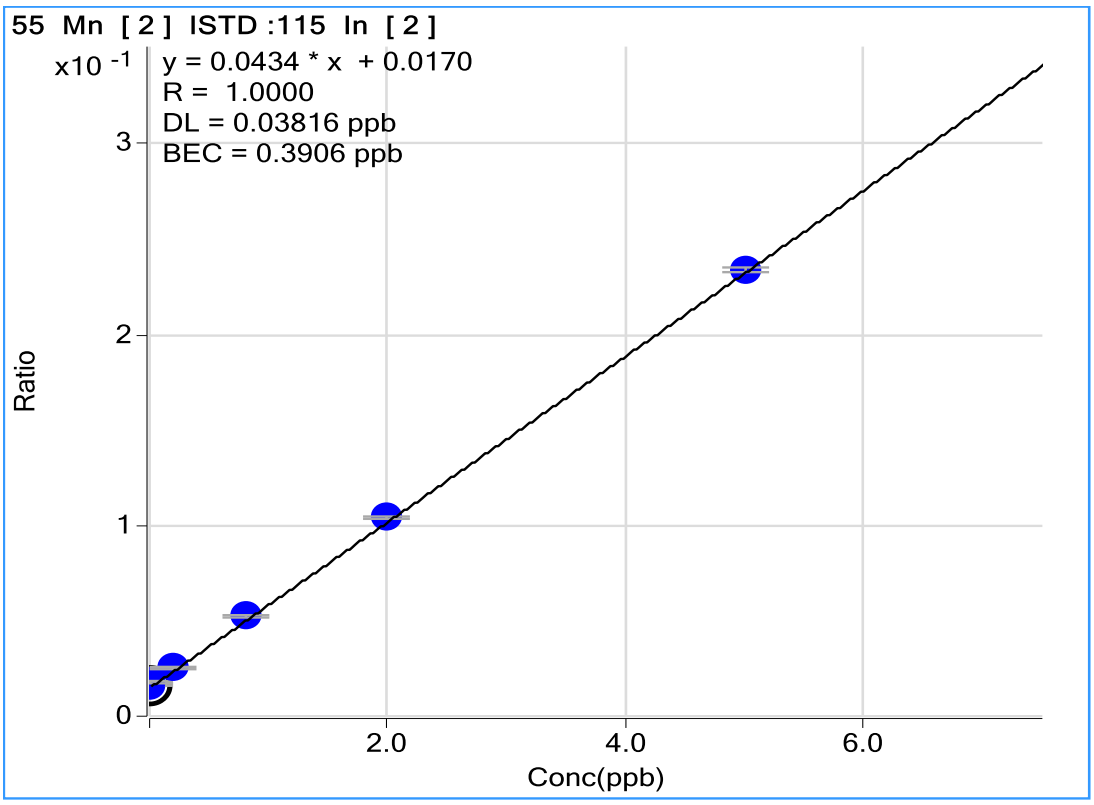


Ratio= Instrument Response (account/time)

DL: Detection Limit

BEC: background equivalent concentration.

Calibration curve for various Manganese concentrations using ICP-MS.

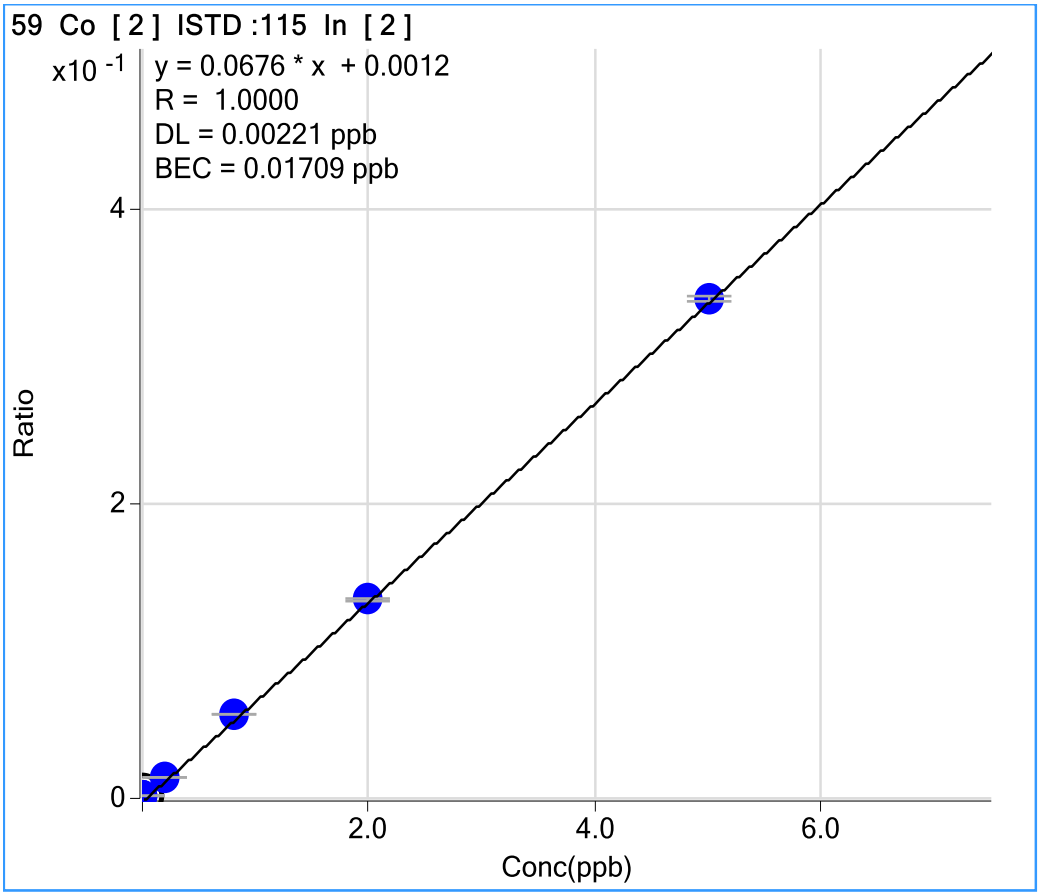


Ratio= Instrument Response (account/time)

DL: Detection Limit

BEC: background equivalent concentration.

Calibration curve for various Cobalt concentrations using ICP-MS.

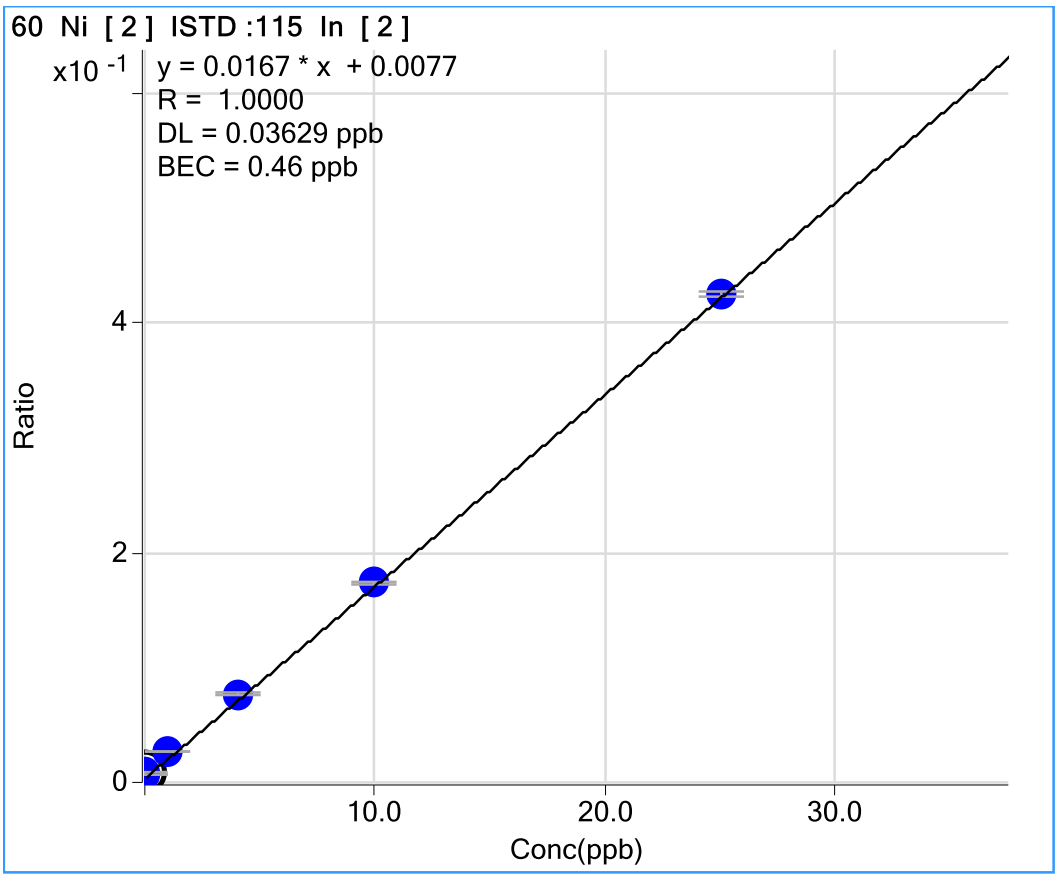


Ratio= Instrument Response (account/time)

DL: Detection Limit

BEC: background equivalent concentration.

Calibration curve for various Nickel concentrations using ICP-MS.

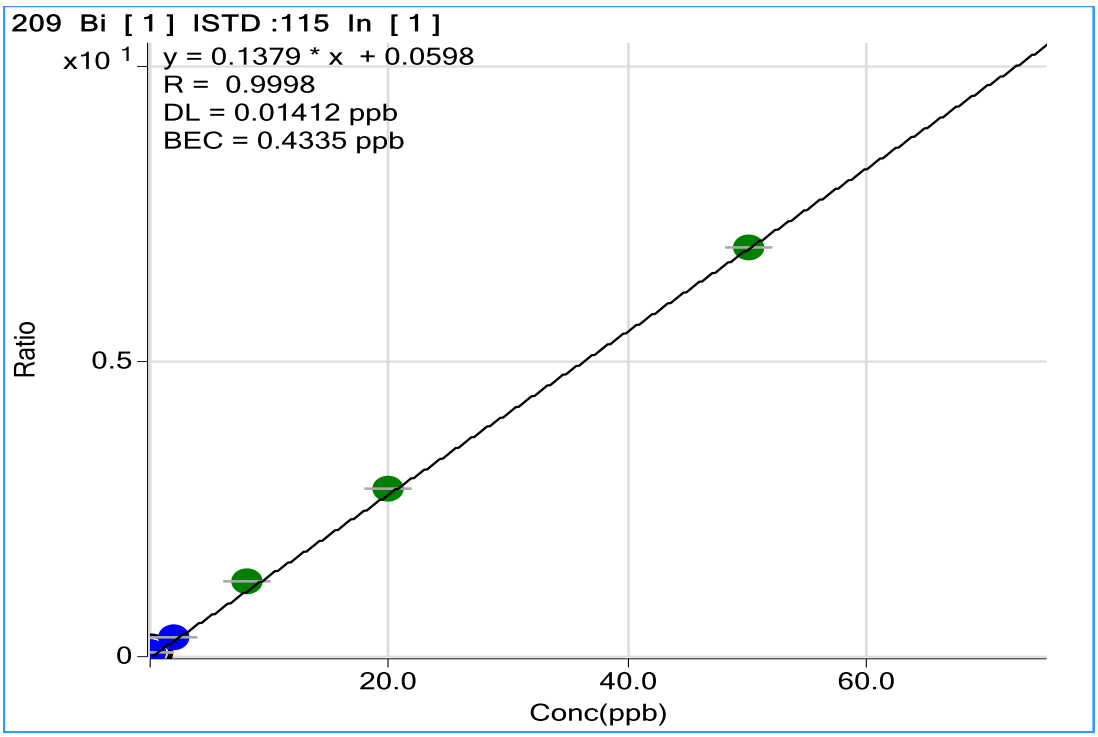


Ratio= Instrument Response (account/time)

DL: Detection Limit

BEC: background equivalent concentration.

Calibration curve for various Bismuth concentrations using ICP-MS.

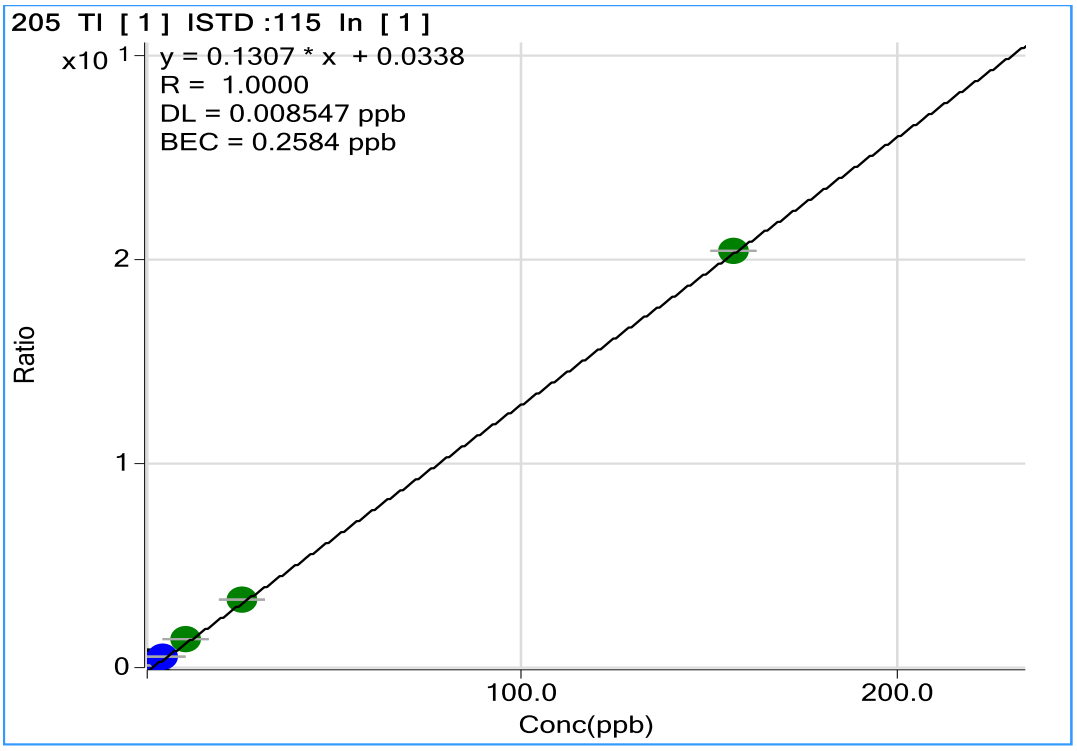


Ratio= Instrument Response (account/time)

DL: Detection Limit

BEC: background equivalent concentration.

Calibration curve for various Thallium concentrations using ICP-MS.

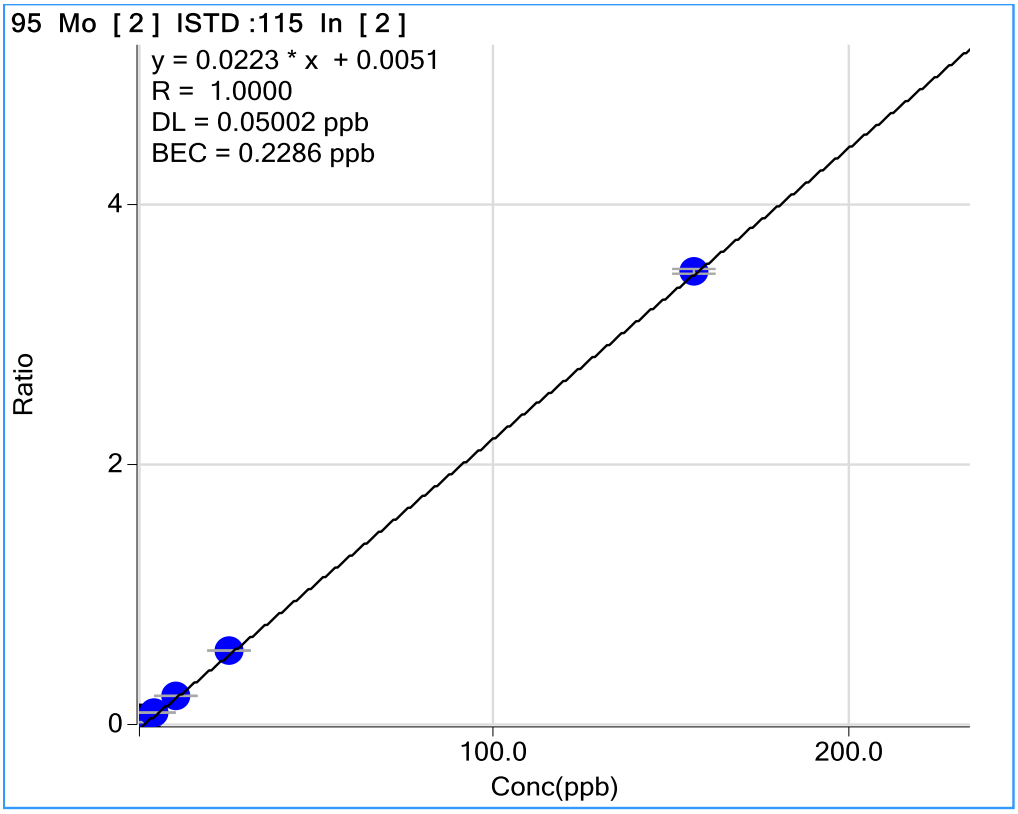


Ratio= Instrument Response (account/time)

DL: Detection Limit

BEC: background equivalent concentration.

Calibration curve for various Molybdenum concentrations using ICP-MS.

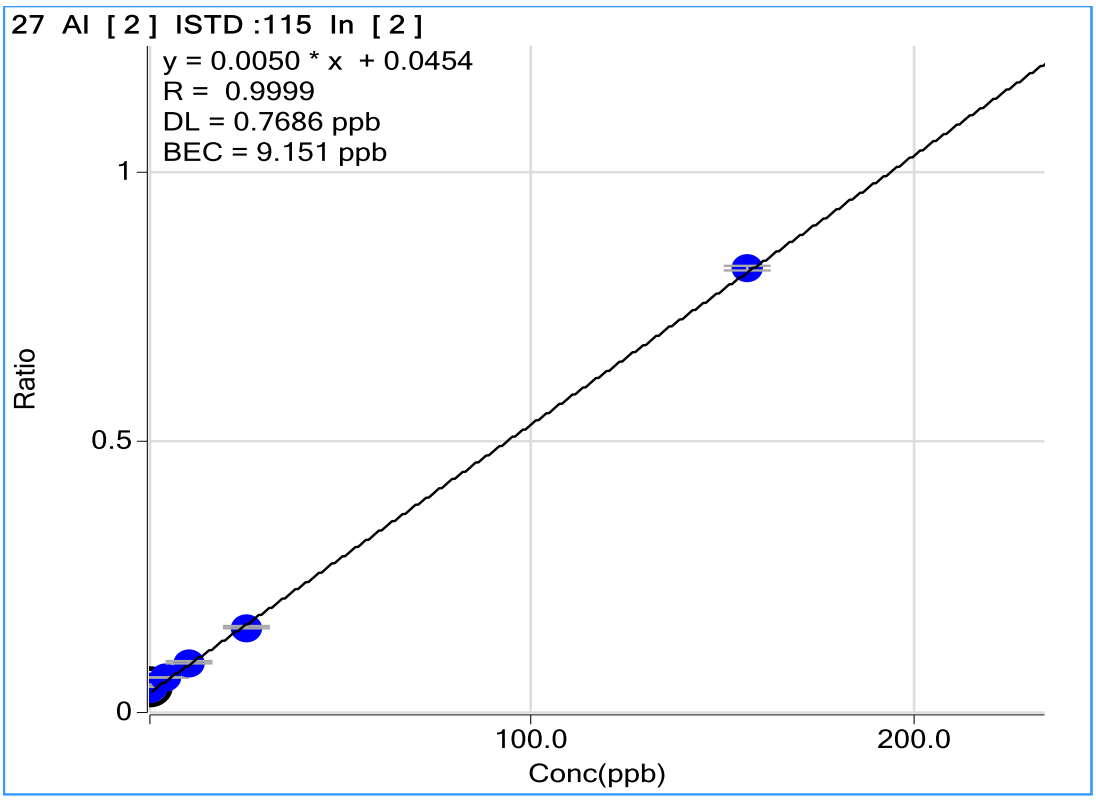


Ratio= Instrument Response (account/time)

DL: Detection Limit

BEC: background equivalent concentration.

Calibration curve for various Aluminum concentrations using ICP-MS.

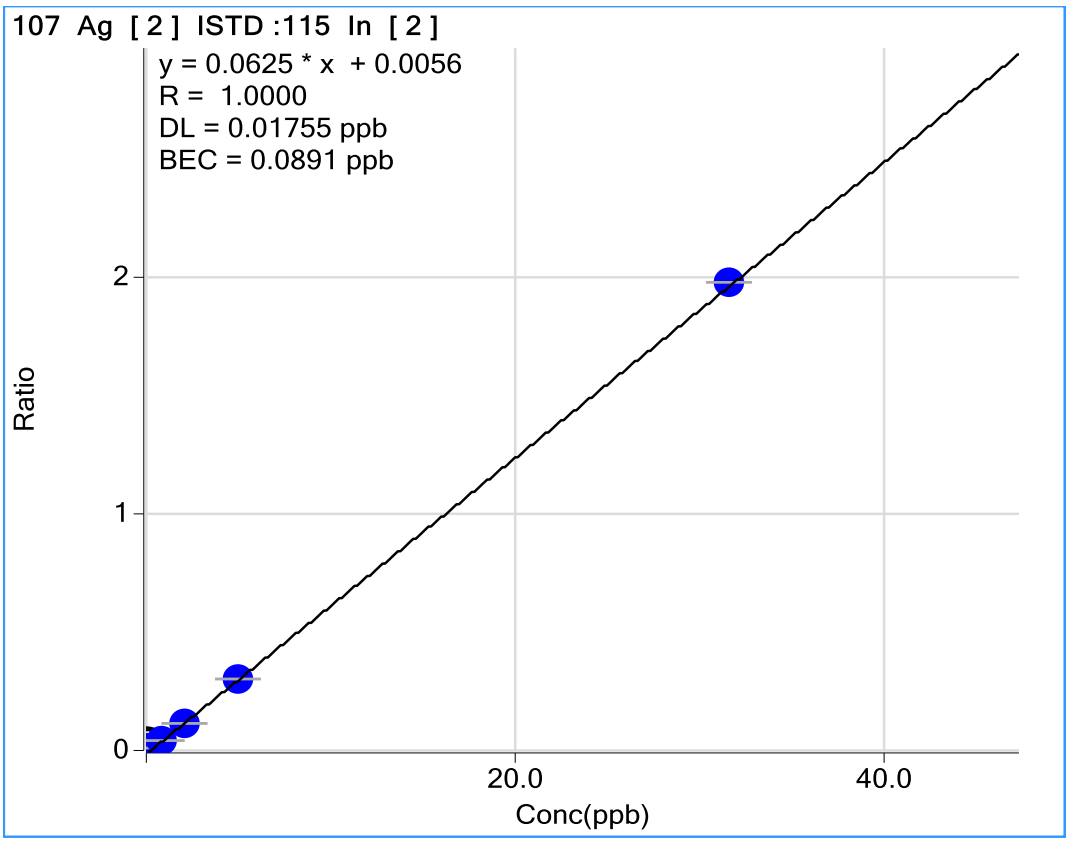


Ratio= Instrument Response (account/time)

DL: Detection Limit

BEC: background equivalent concentration.

Calibration curve for various Silver concentrations using ICP-MS.

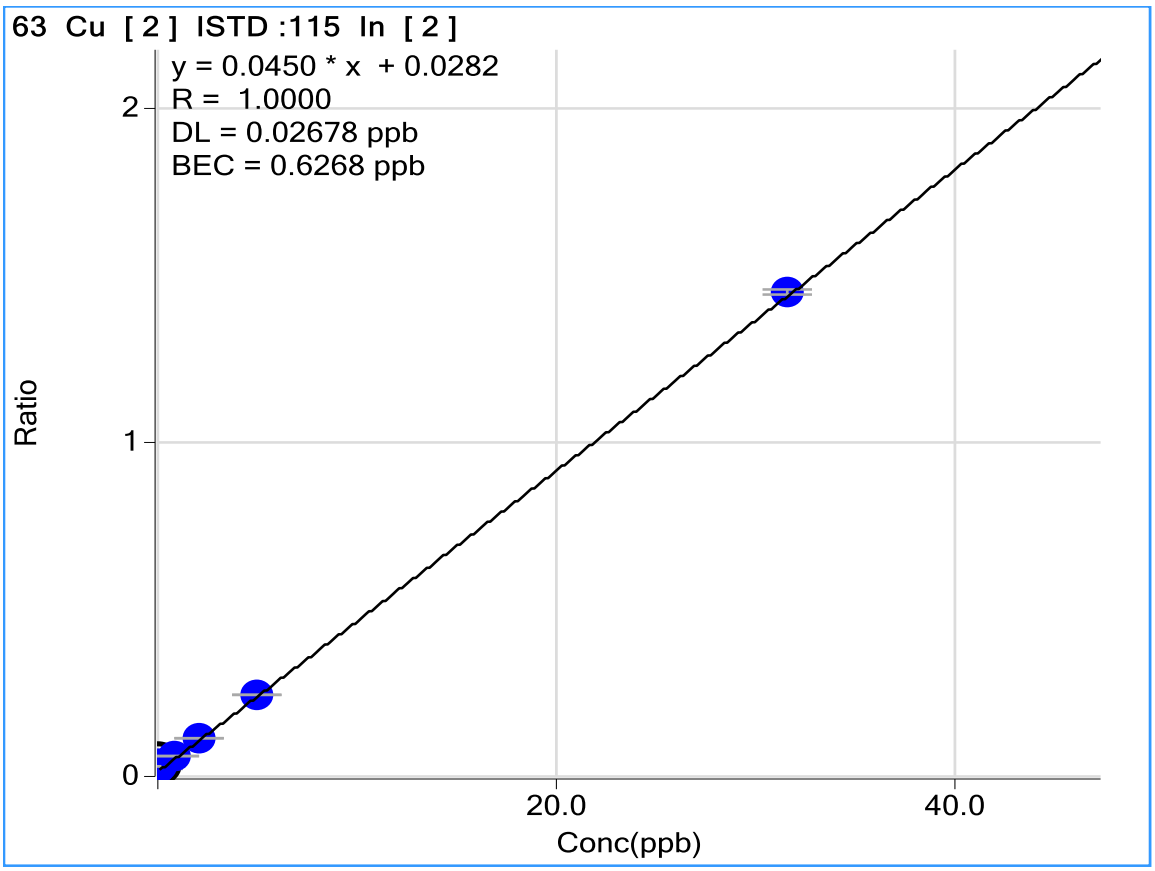


Ratio= Instrument Response (account/time)

DL: Detection Limit

BEC: background equivalent concentration.

Calibration curve for various Copper concentrations using ICP-MS.

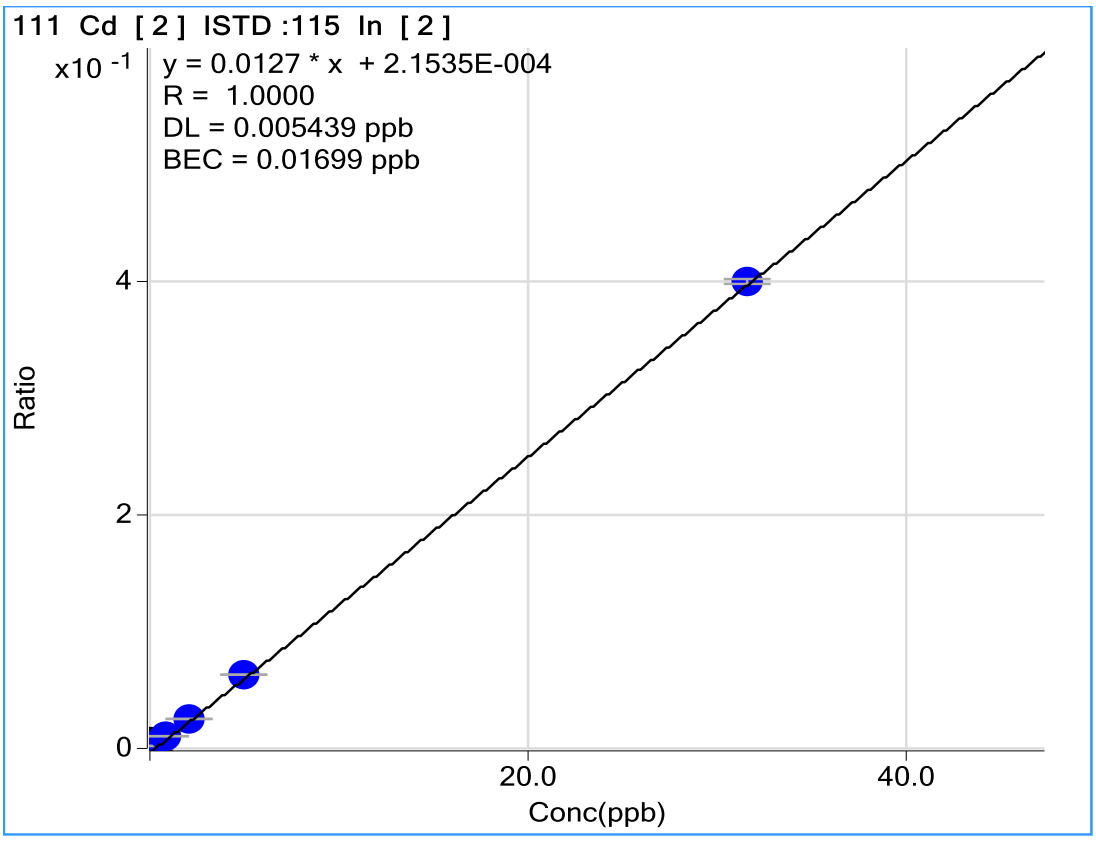


Ratio= Instrument Response (account/time)

DL: Detection Limit

BEC: background equivalent concentration.

Calibration curve for various Cadmium concentrations using ICP-MS.

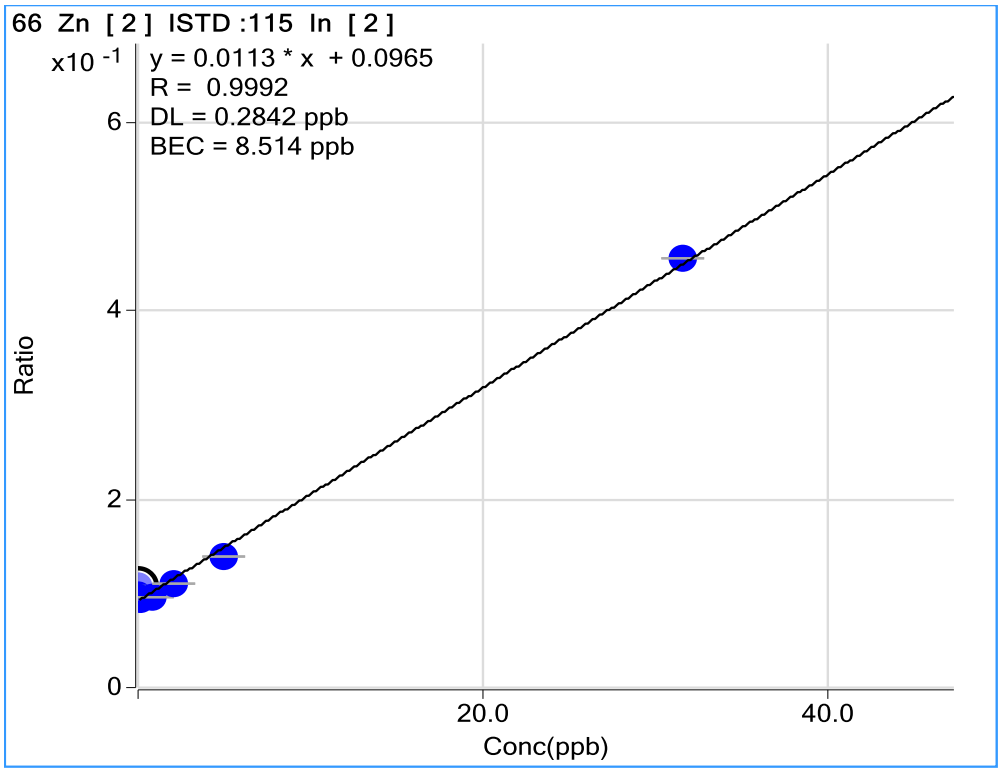


Ratio= Instrument Response (account/time)

DL: Detection Limit

BEC: background equivalent concentration.

Calibration curve for various Zinc concentrations using ICP-MS.



Ratio= Instrument Response (account/time)

DL: Detection Limit

BEC: background equivalent concentration

تقييم تلوث المياه الجوفية ومياه الأمطار بالمعادن الثقيلة في في مناطق معينة من الضفة الغربية / فلسطين بواسطة جهاز مطياف الكتلة البلازمي (ICP-MS).

إعداد:حسام ظاهر نمر ملصه

المشرف الدكتور: د. معتز القطب

الملخص:

تلوث المياه السطحيه والجوفيه بالمعادن الثقيلة هي أحد أهم القضايا البيئية ،لأنها تعتبر سامة حتى في تراكيز منخفضه. تم تقيم تلوث المياه الجوفيه بالمعادن الثقيله في الضفه الغربيه في فلسطين حيث تم تحليل العينات للمياه الجوفيه لمختلف العناصر الثقيله النادره (ثاليوم، رصاص، بزموت، كروم، منغنيز، كوبلت، نيكل، نحاس، الخارصين، موليبدنوم، فضه وكادميوم) بالاضافه للالمنيوم وذلك عن طريق مطياف الكتله البلازمي (ICP-MS).

هذه الدراسه تم اجرائها لتحديد نوعيه المياه الجوفية المستخدمة للشرب في منطقه الدراسه. حيث تم الحصول على عينات المياه من خمسه عشر بئر من ابار المياه الجوفيه وتم الحصول على ثلاثه عينات من كل بئر. تم في كل العينات قياس وتحليل درجه الحموضه، موصليه الكهرباء، مجموع المواد الصلبه الذائبه، والمحتوي لمختلف المعادن النادره.

لقد وجد أن درجه الحموضه، موصليه الكهرباء ومجموع المواد الصلبه الذائبه هي ضمن الحدود المسموح بها من قبل وكاله حمايه البيئه في الولايات المتحدة.

في جنوب الضفه الغربيه أظهرت النتائج أن: الرصاص، ألالمنيوم، كروم، كوبلت، نيكل، نحاس، الخارصين، وموليبدنوم، متوفره وتم الكشف عنها في جميع العينات التى تم تحليلها في هذه المنطقة، بينما تم الكشف عن الثاليوم، بزموت، منغنيز، فضه وكادميوم بنسبه 80%، 88 %، 90 %، 75%

و95% في عينات المياه التى تم تحليها في هذه الدراسه على التوالي. وبشكل عام 93% من جميع العينات التى تم تحليلها تحتوي على واحد أو أكثر من ثلاثه عشر عنصرا تم دراستها على تراكيز متفاوته.

بالرغم من ذلك أظهرت النتائج أن تركيز كل من: الكروم، منغنيز، نيكل، نحاس، الخارصين و موليبدنوم وجدت في النطاق المسموح به في مياه الشرب حسب منظمه الصحه العالمية. إلا أن تركيز كل من: الرصاص، كادميوم والألمنيوم وجد أنه أعلى من الحد السموح به في منظمه الصحه العاليمه في 40% ,8% و33% على التوالي لعينات المياه التى تم تحليلها في هذه المنطقة.

لقد اظهرات التحاليل الاحصائيه أن تراكيز العناصر التى تم دراستها في هذه الدراسة تتفاوت تفاوتا كبيرا بين عشره آبار من المياه الجوفيه، والجدير ذكره أن الآبار التي تم تحليلها في هذه الدراسة تختلف عن بعضها البعض من حيث احتوائها على المعادن الثقيلة.بالاضافه الى ذلك تبين أن هناك اختلاف كبير في تراكيز المعادن حسب النتائج الاحصائيه التى تم الحصول عليها لكل بئر على اختلاف أوقات أخذ العينات الاربع :(تشرين اول 2012، تشرين ثاني 2012، أذار 2013، ونيسان 2013)،كلها تدل على أن تركيز المعادن في الآبار تختلف بشكل ملحوظ مع أخذ العينات مع مرور الوقت.

في شمال الضفة الغربية أظهرت النتائج أن تركيز تسع من المعادن النزرة (الكروم، المنغنيز، النيكل، النحاس، الزنك، الموليبدينوم، الرصاص، الكادميوم ، وآلالومنيوم) ضمن الحدود المسموح بها في منظمة الصحة العالمية لمياه الشرب (50، 500، 20، 2000، 3000، 70، 10، 3، و 200 ميكروغرام / لتر) على التوالي ، ولكن تم الكشف عن تراكيز ستة من المعادن (الكروم ، المنغنيز ، النيكل، النحاس، الموليبدينوم وآلالومنيوم) في 100٪ من العينات، بينما الرصاص، الكاديميوم و

الخارصين تم الكشف عن تراكيزها بالنسب التاليه 80 ٪ ، 60 ٪ ، و 20 ٪ على التوالي . من ناحية أخرى، الثاليوم الذي هو معدن خطير وسام جدا مع حدود المسموح به من منظمة الصحة العالمية (0.1–1 ميكروغرام / لتر). تم الكشف عن تركيز هذا العنصر في 100٪ من عينات المياه التي تم تحليلها فوجد ان بعض العينات تحتوي على تراكيز اعلى من الحد المسموح به من منظمة الصحة العالمية بحيث أنه يمكن أن تكون ضارة للانسان. و بشكل عام فان 82 ٪ من جميع العينات التي تم تحليلها تحتوي على عنصر او اكثر من المعادن المدروسة بتراكيز متفاوتة.

وعلاوة على ذلك ، تم تحليل مياه الامطار من آبار التجميع من الجزء الغربي لمدينة الخليل (جنوب الضفة الغربية في فلسطين)، وهي أكبر مدينة في الضفة الغربية، تم تحليل مختلف المعادن الثقيلة النزرة (الكروم، المنغنيز، الكوبالت، النيكل، النحاس، الخارصين، الموليبدينوم، الفضة، الكادميوم، البزموث والرصاص) باستخدام جهاز مطياف الكتلة البلازمي (ICP–MS).

تم جمع 44 عينة مياه من 44 بئر تجميع لمياه الشرب من مياه الأمطار من أسطح المنازل في نوفمبر تشرين الثاني 2012. أظهرت النتائج أن تركيزات المعادن الثقيلة تتفاوت تفاوتا كبيرا بين العينات 44. وأظهرت النتائج أيضا أن تركيزخمسة من المعادن الثقيلة (الكروم، المنغنيز، النيكل، الفضة، والرصاص) هو أعلى من حدود منظمة الصحة العالمية لهذه المعادن الثقيلة في مياه الشرب. النتائج المتحصل عليها من هذه الدراسة تشير إلى مخاطر محتملة لسكان منطقة الدراسة نظرا لسمية هذه المعادن ، هذا وتعتبر المياه الجوفية ومياه الامطار المصدر الرئيسي لامدادات المياه لكثير من الناس في منطقة الدراسة.