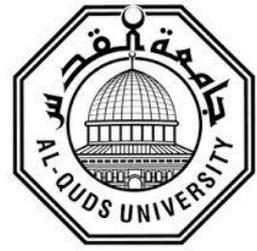


Deanship of Graduate Studies

Al- Quds University



**Determination of trace metals in rain water during the
November 2012 bombing in Gaza Strip**

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M.Sc. Thesis

Jerusalem – Palestine

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**Determination of trace metals in rain water during the
November 2012 bombing in Gaza Strip**

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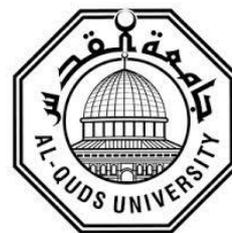
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Thesis Approval

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Dedication

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

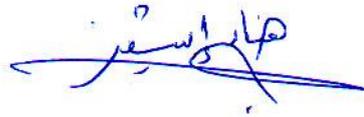
This thesis work is dedicated to my husband, Husam, who has been a constant source of support and encouragement during the challenges of graduate school and life. I am truly thankful for having you in my life. This work is also dedicated to my lovely parents, Imad and Fatima, who have always loved me unconditionally and whose good examples have taught me to work hard for the things that I aspire to achieve.

Declaration

I Certify that the thesis is submitted for the degree of master 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.

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Sing:

A handwritten signature in blue ink, appearing to be 'Hanà Imad Mohamed Shqair', written in a cursive style.

Date: 30/5/2016

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List of Abbreviations

°C	Degree Celsius
µg/L	Microgram per liter. (10^{-9})
mg/L	Milligram per liter
µs/cm	Micro Siemens per centimeter
amu	atomic mass unit
ANOVA	Analysis of Variance
ATSDR	Agency for Toxic Substances and Disease Registry
DU	Depleted Uranium
EC	Electrical Conductivity
EPA	Environmental Protection Agency
GIS	Geographical Information System
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
Km ²	Kilometer square
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
r ²	Correlation Coefficient
RF	Radio Frequency
RSD	Relative Standard Deviation
SD	Standard Deviation
TDS	Total Dissolve Solid
UNEP	United Nations Environmental Program
WHO	World Health Organization

Abstract

Surface 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 the water quality of harvested rain water used for drinking in Gaza after the 2012 bombing, and to assess the potential effect of bombing on the amounts of trace metals in harvested rainwater. In this study Gaza strip was divided in four areas (North (a) and (b)), Middle and Southern area.). A total of 43 water samples classified between bombed and non-bombed area, were collected in November 2012 during the first rain after eight days of bombings from 43 rain water pools and from an area that was hit by many rockets. Water samples have been analyzed for different trace (heavy) metals (Ba, Cu, Zn, Co, Mn, V, Al, Pb, Cr, Ni, As, U, and Cd) as well as phosphorous content by ICP/MS. The samples were analyzed for their pH, temperature, electrical conductivity, total dissolved solids. For some water samples the results were found to be within the U.S. Environmental Protection Agency guideline.

In North (a) Gaza Strip, Result showed that eight heavy metals Ba, Mn, Al, Pb, Ni, As, Cd and Cr have exceeded the WHO limits, the highest percent was for Ba metal in 93% of the 16 samples. Furthermore, results showed that the concentrations of three heavy metals Cu, Zn and U is within the allowed WHO limits in drinking water. However the concentration of Ba, Al, Pb, Mn, Ni, Cr, As, and Cd are found to be higher than the allowed WHO limits in 93%, 63%, 44%, 38%, 25%, 6%, 6%, and 6% of the water samples analyzed in this study, respectively. Potential contamination by different number of rockets F16 and a lot of destruction caused by shelling on the agricultural lands in this area are responsible for the occurrence of the trace metals with high concentration. The result showed using this water is dangerous for human health, especially when used for drinking and agriculture purpose.

In North b, Result showed that this area have been contaminated by twelve heavy metals (Ba, Cu, Zn, Co, Mn, V, Al, Pb, Cr, Ni, As, and Cd) in addition to P and U .Al metal was found in 73% of the analyzed eleven samples. On the other hand ten metals of them (Ba, Cu, Co, Mn, V, Al, Cr, Ni, As, and Cd) were detected in 100% of these samples, while the concentration of eight metals (Al, Pb, Ba, Mn, Ni, Cd, As and Cr) are higher than the allowed WHO limits in 73%, 63%, 45%, 36%, 36%, 36%, 27% and 18% of the water samples analyzed in this study, respectively. Phosphorous was also detected in all water samples analyzed in this study with high concentrations (range of 100.86-2467.48 µg/L

and average of 682.22 $\mu\text{g/L}$). These high concentrations of phosphorous was found in sample number 8 (Beirut Street, near to Abu Mazen Square) may be attributed to the white phosphorous munitions used in Gaza during the war. The area was hit by different number of missiles. Most of the samples in this area were potentially contaminated by eight to nine missiles, which were bombed very close to the building where people live. This is very danger for human health.

In Middle Gaza Strip (Nussairat area), Results showed that twelve trace metals (Ba, Cu, Zn, Co, Mn, V, Al, Pb, Cr, Ni, As, and Cd) were detected in all water samples analyzed. Furthermore result showed that the highest percent of samples that exceeded the limit of WHO limit was for Barium, in 83% of the samples analyzed in this region. Additionally twelve heavy metals (Ba, Cu, Zn, Co, Mn, V, Al, Pb, Cr, Ni, As, and Cd) were detected in 100% of water samples analyzed. Six heavy metals (Cu, Zn, Pb, Cr, Cd and U) were found in the analyzed water samples within in these limits. Phosphorous was also detected in all water samples analyzed in this region with high concentrations (range of 113.01-2855.07 $\mu\text{g/L}$, and average of 1039.4 $\mu\text{g/L}$). This high concentration of phosphorous was found in sample number 20 (sample from an area that was hit by 5 rockets) may be attributed to the white phosphorous munitions used in this war against Gaza. This area was also hit by many different number of missiles.

In the Southern area, Results showed that eleven trace metals Ba, Cu, Zn, Co, Mn, V, As, Pb, Cr, Ni and Al were detected in all water samples analyzed, the highest percent of samples that exceeded the limit of WHO limit, were for Al and Pb, with 90% of the samples analyzed exceeded this limit. Furthermore, result showed that the concentration of heavy metals (Al, Pb, Ba, Ni and As) exceeded the allowed WHO limits in 90%, 90%, 30%, 20% and 10% respectively. However the concentration of Ba, Cu, Zn, Co, Mn, V, Cr, Ni, As, U, P, Pb and Al) were detected in 100% of the water samples. Phosphorous was also detected in all water samples analyzed in this study with high concentrations (range of 286.61-7390.62 $\mu\text{g/L}$). These high concentrations of phosphorous was found in sample number 42 (sample from an area that was heavily bombed) the number of bombing was concentrated and heavy.

Furthermore, the concentrations of all heavy metals that were detected in the collected harvested rainwater from different areas vary significantly between the 43 samples. All of the metals were detected in all water samples that had been analyzed in this study.

Chapter One

Introduction and Literature Survey

Chapter One

Introduction and Literature Survey

1. Introduction:

One of the most important environmental issues is contaminated drinking water with trace metals 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 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 and Chen.et.al. 2007). In addition to these human activities, the use of weapons over the last century in conflicts and in training has polluted the environment with toxic compounds and heavy metals (Diaz 2003, Simini et. al. 1995). There are 35 metals that concern us because of occupational or residential exposure; 23 of these are heavy metals such as 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).

Trace metals, especially heavy metals, are well known to be toxic to human beings. Health risks of heavy metals include reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases may cause 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. This can lead to joint diseases such as rheumatoid arthritis, and diseases of the kidneys, circulatory system, and nervous system. Heavy metals also 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 (Roberts 1999, Dupler 2001).

Many studies have investigated the occurrence of heavy metals in groundwater, surface water, and harvested rain water. Contamination can spread from the soil and groundwater through physical migration or from uptake by organisms (Mueller et. al. 1995). Extensive

studies following explosions and bombing in inhabited areas of different countries have shown that the indiscriminate pulverization and incomplete combustion of a range of materials can release and distribute pollutants such as organic and inorganic e.g. trace metals, with worrying environmental and health consequences for human. The use of metals and heavy metals in weapons is implicated as the cause of the injuries without fragments. Also, the enhancement of already existing weapons of war by the utilization of particulate and potentially toxic metals has been described. This has led to the commissioning of weapons utilizing metals as augmenters, or as primary effective agents (small smart bombs, thermo baric grenades and shape charged weapons, to produce a molecular sieve of metal powder, capable of severing the human body) (Apperson, et. al. 2007). It is an important question whether the toxic and genotoxic potential of metals used in weapons could be a cause for long-term environmental (soil, water, air.etc), and health damage in exposed populations and the military.

An important toxic metal used in military weapons as high density penetrator is Depleted Uranium (DU). Usually alloyed with 1–2% other elements which enable at high impact speed, density, hardness, and pyrophoricity of the projectile destruction of heavily armoured targets. Increased rates of immune system disorders and other wide-ranging symptoms, including chronic pain, fatigue and memory loss, have been reported in over one quarter of combat veterans of the 1991 Gulf War(RAC, 2004) Combustion products from depleted uranium munitions are being considered as one of the potential causes by the Research Advisory Committee on Gulf War Veterans' Illnesses, as DU was used in 30 mm and smaller caliber machine-gun bullets on a large scale for the first time in the Gulf War. Veterans of the conflicts in the Arabian Gulf, Bosnia and Kosovo have been found to have up to 14 times the usual level of chromosome abnormalities in their genes (Schröder et al 2003). Also, in Iraq between 2005–2009 there was an increase in cancer and birth defects with infant mortality reached up to 13.6% in 2009/2010 which was attributed to DU (Busby et al 2010).Concentrations of DU in urine samples collected from bombed civilian areas in Jalalabad showed higher concentrations (80-400 ng L⁻¹) compared to typical concentration in the British population of ~5 ng L⁻¹ (Durakovic 2005).

A significant portion of Gaza's population is likely to have been exposed to these materials directly, through inhalation, and airborne materials would have settled on surfaces in a considerable portion of the densely inhabited areas of Gaza. Previous studies in 2006 and 2009 at Shifa Hospital in Gaza on toxic and carcinogenic metals, delivered by “not

fragmentation weapons” producing amputations, body charring, burns, and associated with white phosphorus burns, showed their presence in amounts higher than the minimal risk level for acute exposures, and then the known cumulative minimal risk level for chronic exposures (Skaik et al 2010). Important metals that were detected in excess over control in all biopsies were known human carcinogenic/teratogenic metals (class 1, IARC) like Mercury (Hg), Arsenic(As), Cadmium(Cd), Chromium (Cr), Nickel (Ni), and Uranium (U) (Skaik et al 2010). In another study on the potential contamination of the soil of Gaza due to Israeli bombing, 35 elements of 4 craters derived from 2 bombing events in Gaza in 2006, one in Beit Hanoun, one in Jabalia camp, and 2 bombings in 2009, both in Tufah, the Gaza suburb were analyzed by ICP/MS. In addition, powder remaining inside a shell of an exploded White Phosphorus bomb THS89D112-003 155MM M825E1 collected at Al Wafa in January 2009 was also examined. The study revealed significant amounts of Tungsten (170-350 ppm and 20- 42 folds the average level (8,5 ppm) expected in the soil) , higher than normal level of Mercury (0,082-1,634 ppm and 8-16 folds of the maximum level found the soil of Gaza, (0,01 ppm)) , Molybdenum, (0,1 to 12 ppm and between 25 and 3000 folds than average levels (0,004 ppm) in the soil), Cadmium(which is present in low concentrations in the soil of Gaza (0,093 ppm), (up to 7,3 folds)), Cobalt (was found in amounts up to 26,2 ppm (compared to 5,1 ppm average in the normal soil)), Nickel, Manganese, Copper , Zinc(were found at a 2 fold level than in soil), and Strontium (was found in amounts higher than average in earth crust in all craters). The powder contained also relevant amounts of Molybdenum (125-200 folds of the content in soil), Tungsten (up to 41 folds of soil content) and of Mercury (up to 160 folds), in addition to high amount of Aluminium (218000-524000 ppb) (Barbieri et. al. 2009).

The objective of the current study is, to study the effect of 2012 bombings and explosions of inhabited areas of Gaza strip on the quality of harvested rain water by determining content of trace metals in different harvested rainwater samples collected from bombed area of Gaza. Harvested rain water was selected as rainwater harvesting is a common practice in Gaza strip due to the shortage of water and to the high population density of Gaza. In Gaza, rain water is collected in tanks from roofs and used for both landscape irrigation and indoor purposes. Additionally, and in a large scale, rain water is collected from urban areas and stored in infiltration ponds. During the past twenty years, nearly 6300 cisterns were constructed in West bank and Gaza benefitting a more than 132,000

residents, and 434 ponds targeting 230,000 beneficiaries in the West Bank and Gaza. Captured rainfall can be stored either in cisterns as drinking water or in the soil for plant production or in the aquifer through artificial recharge to improve the water resources in the region. (Abdelmajid and Hamdan 2013).

In this regard, it is expected that the harvested rain water collected in the bombed area of Gaza would be contaminated with different metals. In the scientific literature, studies have been conducted to study the contamination of harvested rainwater with heavy metals; and according to Luke Mosley from SOPAC Water Quality Office (Luke, 2005), heavy metals are contaminants commonly found in rainwater collection systems, where they come from dust particularly in urban and industrialized areas(Luke, 2005).

1.1 Toxic Heavy metals impact on plant animal and human

A heavy metal: a metallic element with a specific gravity of 5.0 g cm⁻³ or more that is generally toxic in relatively low concentrations to plants and/or humans and animals. Heavy metals occur naturally in most soils and are taken up to some degree by plants. Cobalt, copper, and zinc are considered essential in the growth and development of higher plants, and the other heavy metals may benefit normal plant growth if available in very low concentration (Mengel and Kirkby 1978). All heavy metals, with the exception of barium and mercury, are necessary in very small amounts for the normal growth of humans and animals (Anke et al. 1984). Heavy metals are also considered a health hazard if present and available in the environment at levels in excess of their normal concentrations. Because of the potential health hazard associated with heavy metals in the environment, the World Health Organization has established guidelines for drinking-water quality that include concentrations of some heavy metals which can be used to assess the general surface-water quality (Table 1).

Table 1.1: Maximum Heavy-Metal Concentrations in Drinking water (WHO, 1993).

Heavy metal	concentration $\mu\text{g/l}$
Arsenic	10
Cadmium	3
Chromium	50
Copper	2000
Lead	10
Zinc	3000
Nickel	20

Arsenic (As):

There is no evidence that arsenic is essential for plant growth, but stimulation of root growth in solution cultures with the addition of small amounts of arsenic has been noted. Arsenic can be toxic to plants, and arsenic compounds were commonly used as insecticides and herbicides in agriculture until their replacement by organics. It has been reported that soil productivity is reduced where arsenic from sprays has accumulated in orchard soils. Arsenic has been added to the list of essential elements in the diet of mini-pigs, goats, and rats (Anke et al. 1984). Both acute and chronic exposure to arsenic may cause poisoning in humans and animals, but acute poisoning is rare today. Chronic poisoning usually results from exposure to contaminated air or drinking water or ingestion of arsenic in drugs or food. Arsenic poisoning among industrial workers is characterized by perforation of the nasal septum, skin changes, and peripheral neuritis. There is also evidence that arsenic may cause lung cancer (Ishinishi et. al.1986) and carcinogenic (Salnikow and Zhitkovich 2008, Beyersmann and Hartwig 2008).

Barium (Ba):

Barium is toxic to humans and animals because all water- and acid-soluble barium compounds are poisonous. Occupational poisoning by soluble barium salts is virtually unknown, but accidental poisoning with barium-containing household and medical products has been reported (Reeves 1986). Barium is not considered essential for plants or animals. It is not reported to be toxic to plants, and the uptake of barium by plants does not correlate with the total amount in the soil (Emsley 2001).

Cadmium (Cd):

Cadmium can be toxic to plants, animals, and humans. Some studies indicate plant growth is severely depressed with a relatively low accumulation of cadmium in plants. New research suggests cadmium is essential for rats and goats (Anke et al. 1984). Studies done in Japan indicate cadmium from polluted soil and water can be incorporated into the food web in sufficient quantities to be toxic to humans (Yamagata and Sigematsu 1970). Cadmium in the environment also has been implicated in human hypertension and cardiovascular problems (Järup 2003). Classified as carcinogenic by International Agency for Research on Cancer (IARC, 1987; Beyersmann & Hartwig 2008).

Chromium (Cr):

There is no conclusive evidence that chromium is essential for plants, but plant-growth stimulation in solution cultures with the application of low levels of chromium salts has been seen. High levels of chromium in the soil can severely stunt or kill plants. Chromium is essential for humans and animals, but at high levels in the diet, it can be toxic (Anke et al. 1984). Chronic exposure to chromate dust has been correlated with lung cancer, and oral intake has been associated with growth depression and liver and kidney damage in experimental animals (Järup 2003). It is carcinogenic (Salnikow and Zhitkovich 2008).

Cobalt (Co):

Cobalt is essential for microorganisms that fix nitrogen in the nodules of legumes, but it is also necessary for growth of higher plants (Mengel and Kirkby 1978). Cobalt can be toxic to plants when the concentration in the soil is relatively low. Cobalt is an essential element for humans and animals because it is required for the production of vitamin B12 (Emsley 2001). Cobalt is not considered highly toxic to human or animals, but the addition of cobalt to beer has caused endemic outbreaks of cardiomyopathy among heavy beer-drinkers, resulting in several fatalities. Animal studies also indicated cobalt may be carcinogen (Elinder and Friberg 1986).

Cobalt can inhibit DNA repair and cause DNA breakage (mutagenic) (Beyersmann and Hartwig 2008).

Copper (Cu):

Copper is an essential element for both plants and animals. A moderate deficiency of copper in plants normally results in a reduction in growth or yield, while more acute deficiencies cause dieback at terminal growth points. Excess copper also reduces growth and may cause iron chlorosis symptoms resulting from a depression of the iron concentration in plant leaves. Copper solutions were also used for herbicides and fungicides in agriculture until their replacement by organics (Emsley, 2001). Copper is an essential element for humans and animals because it is required for the function of several essential enzymes. Ingestion of a large amount of copper salts causes gastrointestinal disturbances, and chronic copper exposure may cause liver and kidney damage (Järup 2003). It is possible carcinogenic-classified as class 2 by IARC and fetotoxic (Luo et al 1993; IARC1987).

Lead (Pb):

Lead is not considered an essential element for plant growth, and no cases of lead deficiency in plants have been reported. Most observations of lead toxicity in plants are restricted to water-culture experiments, where acute toxic effects result in a reduction in growth, but acute toxicity is not generally seen in the field (Mengel and Kirkby 1978). Most research on lead in humans and animals deals with the toxic effect of this element,

but other research indicates that lead is essential in the diet of rats (Anke et al. 1984). Lead can bio accumulate in man and animals. One of the chief concerns of lead toxicity in humans is brain damage to children. There is evidence that elevated lead levels in the environment can induce aggressive behavior in animals (Järup 2003). Carcinogenic (Beyersmann and Hartwig 2008).

Nickel (Ni):

Nickel is found in most plants. It is not considered an essential element, and nickel deficiency in plants has not been reported. Excess nickel produces a chlorosis in many plants that resembles the symptoms of iron deficiency. Nickel is considered an essential element in the diet of chickens, rats, and goats (Anke et al. 1984). Dermatitis and lung reactions in the form of asthma have been attributed to sensitization caused by nickel (Järup 2003). Possible carcinogen in some forms, classified as class 2 by IARC (IARC, 1987, Salnikow and Zhitkovich 2008).

Zinc (Zn):

Zinc is an essential element for both plants and animals. One of the most common micronutrient deficiencies in plants is zinc, and it is becoming increasingly significant in crop production. Plants suffering from zinc deficiency often show chlorosis in the interveinal areas of the leaf, and terminal growth is usually affected. An excess of zinc commonly produces iron chlorosis in plants (Mengel and Kirkby 1978). Zinc is necessary for the function of various.

Enzymes in humans and animals. Symptoms and diseases related to zinc deficiency include acne, poor wound healing, loss of taste and smell, and poor growth in children. Large oral doses of zinc salts cause gastrointestinal disorders, but chronic zinc poisoning in humans has not been described (Emsley 2001). It complements as carcinogenicity and is fetotoxic (Järup 2003; Luo et al 1993).

Aluminium (Al) and Manganese (Mn):

Aluminium has no known function in biology, but it reduces plant growth on acid soils. Although it is generally harmless to plant growth in pH-neutral soils, the concentration in

acid soils of toxic Al^{3+} cations increases and disturbs root growth and function (Feng & Delhaize 2001). Aluminium excess is involved in degenerative diseases of the nervous system. Aluminium trespass placenta, if contamination occurs by skin exposure of the pregnant mother, and produces fetotoxicity. Manganese is an essential trace nutrient in all forms of life acts as cofactors in many classes of enzymes and also important in photosynthetic oxygen evolution in chloroplasts in plants (Emsley 2001). It is fetotoxic, possible carcinogenic-classified as class 2 by IARC and is involved in childhood developmental disorders and neurodegenerative diseases (Donald 1999).

Vanadium (V):

Vanadium is a rare, soft, ductile gray-white element found combined in certain minerals and used mainly to produce certain alloys. Most of the vanadium (about 80%) produced is used as ferrovanadium or as a steel additive. Mixed with aluminium in titanium alloys is used in jet engines and high speed air-frames, and steel alloys are used in axles, crankshafts, gears and other critical components. Vanadium alloys are also used in nuclear reactors because vanadium has low neutron-adsorption abilities and it doesn't deform in creeping under high temperatures (Makhijani & Yih 2000). Watering is an important way in which vanadium is redistributed around the environment because vanadates are generally very soluble. Vanadium is abundant in most soils, in variable amounts, and it is taken up by plants at levels that reflect its availability. Vanadium plays a very limited role in biology, and is more important in ocean environments than on land. Component of vanadium nitrogenase used by some nitrogen-fixing microorganisms. In humans it is used as dietary supplement for treating diabetes and for improving athletic performance in weight training. Inhalation of Vanadium peroxides could damage respiratory tract. Laboratory tests with test animals have shown, that vanadium can cause harm to the reproductive system of male animals, and that it accumulates in the female placenta, with DNA alteration in some cases. Classified as class 2B possible carcinogen by IARC (Soazo and Garcia 2007; IARC 1987, Beyersmann and Hartwig 2008).

1.2 Literature Survey

Many studies have investigated the occurrence and monitoring of heavy metals in harvested rainwater and ground water by contamination of environment and human health following bombing. The most important studies are described in the following two sections.

1.2.1 Worldwide Studies:

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

Schröder et al (2003) has focused in Bosnia and Kosovo. They have found up to 14 times the usual level of chromosome abnormalities in their genes due to the bombing.

Järup (2003) has studied the assessment, that the chronic effects of metal contamination can affect reproductive performance (fertility and malformation are potential effects) and children neurological development. The use of devices that carry and spread to unknown distances high amounts of toxic metals can cause widespread contamination of the soil, concurrent with the conditions of the displaced population that lives in this environment close to the ground and exposed to the possible contaminants, with the possibility of skin, respiratory and alimentary chronic contact. This is especially important for young people in reproductive age and for children due to the fact that chronic effects of metal contamination can affect reproductive performance (fertility and malformation are potential effects) and children neurological development.

Durakovic (2005) has studied the assessment of concentrations of DU in urine samples collected from bombed civilian areas in Jalalabad. He has measured higher concentrations of DU in Jalalabad civilian (80-400 ng L⁻¹) as compared to typical concentration in the British population of ~5 ng L⁻¹.

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.

Also, other studies were concerned of heavy metals pollution in surface, groundwater and harvested rainwater. Kar et al. (2008) has studied the assessment of heavy metals pollution

in surface water in Ganga in West Bengal. Their results showed that the dominance of heavy metals in the surface water of the river Ganga followed the sequence: Fe > Mn > Ni > Cr > Pb > Zn > Cu > Cd.

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.

Busby et al (2010) has focused in Iraq between 2005–2009 there was an increase in cancer and birth defects with infant mortality reached up to 13.6% in 2009/2010 which was attributed to DU.

Alaani S. et al (2011) have determined trace metals in hair samples from parents of children with congenital anomalies in Iraq and correlated this with the content of these contaminants in water samples. They have found high concentrations of heavy metals in hair samples, and have found a correlation between the metals found in the hair and in the drinking water, and concluded that the metals in drinking water is the sole source of these heavy metals in hair.

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

Other studies were also concerned with the significance of bombing in changing trace elements status in soil, water and even in plants. (Massol-Deyá et al, 2005 and Vidosavljević et al, 2013).

1.2.2 Local Studies:

In Palestine, the principal water resources available include groundwater, springs, and harvested rainwater (UNEP, 2003).

El-Nahhal (2006) has studied the contamination of groundwater with heavy metals in Gaza Strip. The results showed that concentration of Cd, Pb, Fe, and Cr are above the EPA limits in some wells. Skaik S. et al (2010) showed that metals, in particular known toxic and carcinogenic metals (e.g. lead, mercury, chromium, copper, arsenic, uranium, cadmium, zinc) were detected in wound tissues of victims from Gaza after bombing in 2006 and

2009. This study recommended also to conduct investigations on the effect of such bombing and weapons in Gaza on the environment (soil, water, air...etc.).

A study by Manduca P. et al in (2014) has focused on the heavy metals in hair of newborns, hair samples of newborns with congenital birth defects or developmentally premature birth were analyzed in a cohort of couples with documented parental exposure to military attacks in Gaza, and found high concentration of some heavy metals in hair samples. This study showed that the occurrence of birth defects is correlated to documented exposure of parents to weapons containing metal contaminants during attacks in 2009.

1.3 Research Motivations:

The following are the research motivations:

1. Assessment of water quality of harvested rain water used for drinking in Gaza after the 2012 bombing.
2. Assessment the potential effect of bombing on the amounts of trace metals in harvested rainwater.

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 types of heavy metals found in harvested rain water samples and how much is the concentration of each heavy metal?
2. Is the concentration of heavy metals compatible with the WHO stander or not?
3. What is the relationship between bombing and heavy metals?

1.5 Main objective

1. To study water Quality with respect to heavy metals concentrations in Gaza.
2. To study the effect of 2012 bombings and explosions of inhabited areas of Gaza strip on the quality of harvested rain water by determining content of trace metals in different harvested rainwater samples collected from bombed area of Gaza.
3. To assess the effect of bombing on the amounts of trace metals in harvested rainwater.

Chapter Two

Study Area

Chapter Two:

Study Area:

2.1 Study Area

The Gaza Strip is one of the most densely populated areas in the world, 4505 people per km². For administrative purposes; the area has been divided into five regions: North, Gaza, Middle, Khan Younis and Rafah. (Figure 2.1). Each governorate consists of municipalities that varied in number depending on the number of towns or villages and the population of each (Khalaf, 2005).

Gaza Strip is; a strip of land on the eastern coast of the Mediterranean Sea, located in the Middle East (at latitudes 31°16" and 31°45"N and longitudes 34°20" and 34°25"E) (Aish et al. 2004) bordered by the Mediterranean Sea in the West and the Negev Desert and Egyptian Sinai Peninsula in the South with a total area of 365 Km². Land surface elevations range from mean sea level to about 110 m in the eastern parts. Gaza's water resources are essentially limited to that part of the coastal aquifer that underlies its area (Al-Talmas et al. 2012).

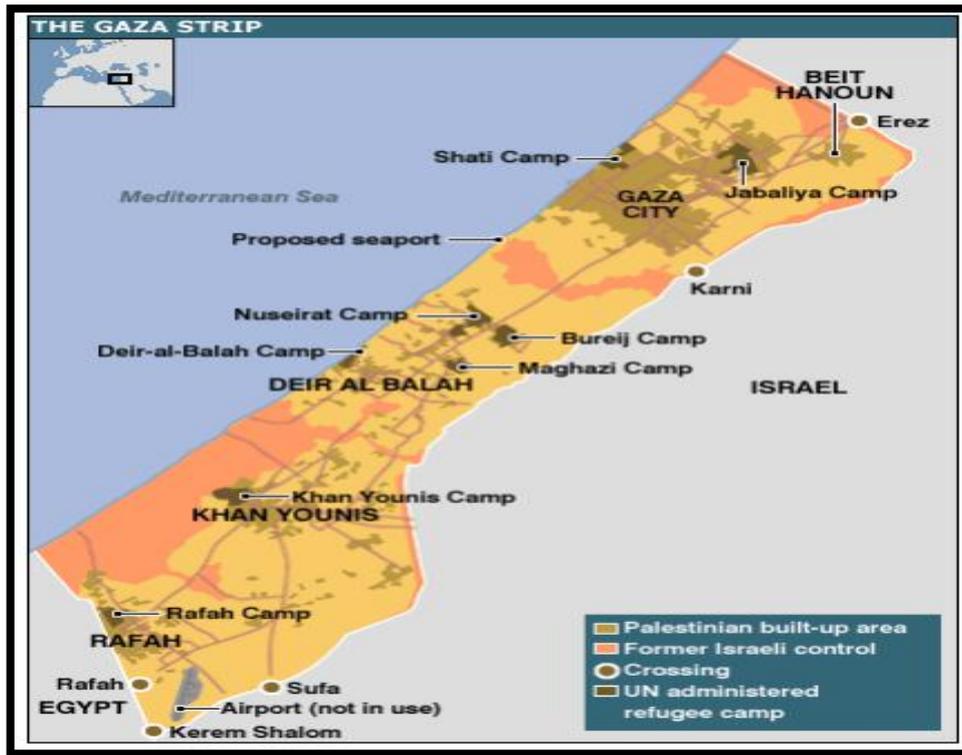


Figure 2.1: Gaza strip,location (Martin, 2014).

2.1.1 Topography

Gaza strip is a coastal foreshore plain according to a topography that refers to the altitude of the land surface. The topography of the area is flat, where the altitude of the Gaza Strip land surface ranges between zero meters at the shore line to about 90 meters above means sea level in some places. The height increases towards the east from 20 to 90 meter above the sea level (ARIJ- Part II 2001).

2.1.2 Population

Gaza Strip is estimated to be at approximately 4 million, according to the Palestinian Central Bureau of Statistics in 2009.

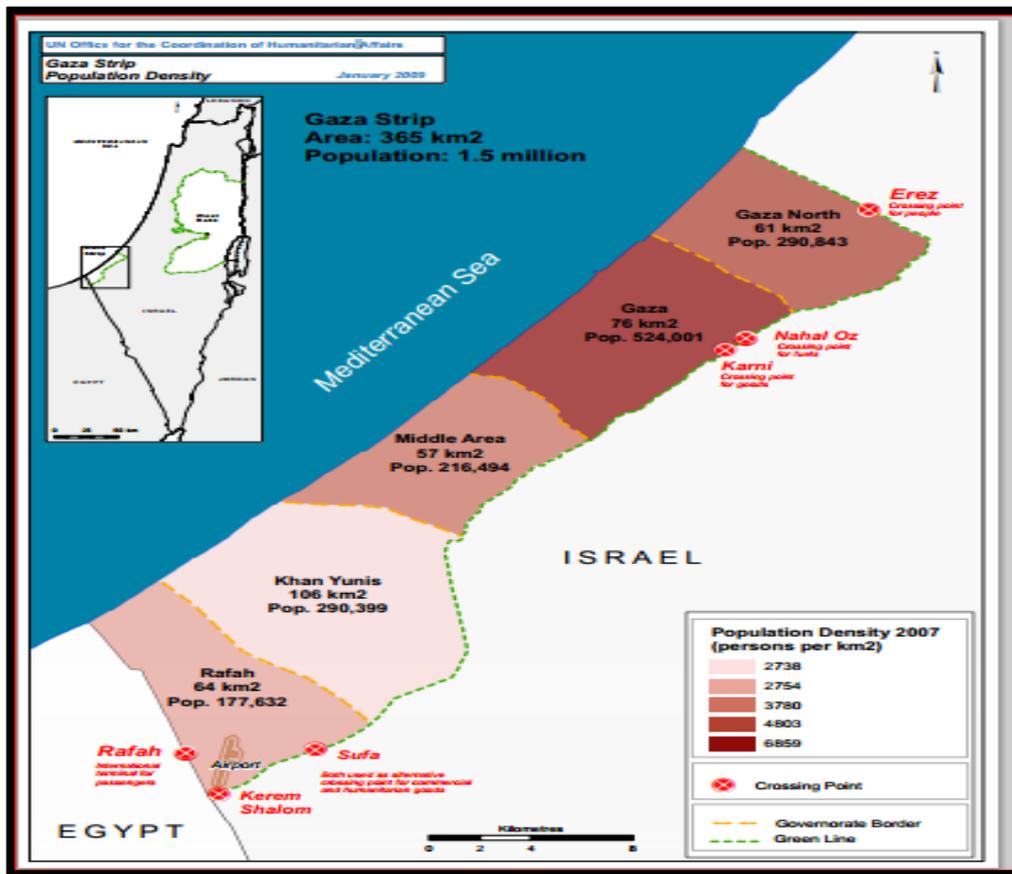


Figure (2.2): Gaza Strip, Population Density (UN Office for the Coordination of Humanitarian Affairs, 2009).

2.2 Meteorological Conditions

2.2.1 Rainfall

Generally; the climate of Palestine is of East Mediterranean type; identified as being hot and humid in summer and cold in winter. The US Environmental Agency has classified regions into arid and non-arid regions based on rainfall of 12.5 in/yr. (312.5 mm/yr.) to be the reference (Qrenawi 2006). The Gaza Strip area is classified as a semiarid region since the average annual rainfall is about 13.83 in/yr. (351.4 mm/yr.).

2.2.2 Temperature

The area has a Mediterranean dry summer sub tropical climate with mild winter; this is because of its locations as transitional zone between semi-humid Mediterranean climate and arid desert climate The highest mean annual temperature is 30.85 °C in August, while the lowest mean annual temperature is 13.50 °C in January, with the mean annual temperature of 19.90 °C (PMO, 2008).

2.2.3 Wind Speed

The wind velocity with northwest direction at 2 meter above the surface in the summer is about 1.5 m/ switch is less than that is during winter months where velocity reaches values of 2.8 m /s (D'Haeyer 2000).

Chapter Three

Material and methods

Chapter Three

Material and methods

3.1 Sampling and analysis

3.1.1 Sampling of Rain Water

In the days preceding and during the first rains, About 43 samples were taken by a team of professionals and volunteers from various organizations in Gaza. (Who gave laboratory sample collection bottles).

The location of each sample was mapped, and the samples were stored in refrigeration to perform various analytical tests, especially those related to heavy metals by using Agilent 7500 ICP-MS device.

Sampling has been carried out in November 2012 (the beginning of the rain season and after the end of war on Gaza) where 43 water samples were collected from 43 rain water pools and from an area that hit by many rockets. Harvested rain water in this area were classified into (North” a and b”, Middle and South area).

Harvested rainwater is used for drinking and agriculture in Gaza as it is located in the semiarid region and it is one of the scarce water countries. (Figure 3.1) shows the location of the part of Gaza where the samples were taken, and the location of the 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% HNO₃), preserved in a cool place (about 4 °C) and transported to the lab of Al-Quds University for further analysis. Temperature, 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 trace metals content and phosphorous by ICP/MS (Agilent technologies 7500 series).

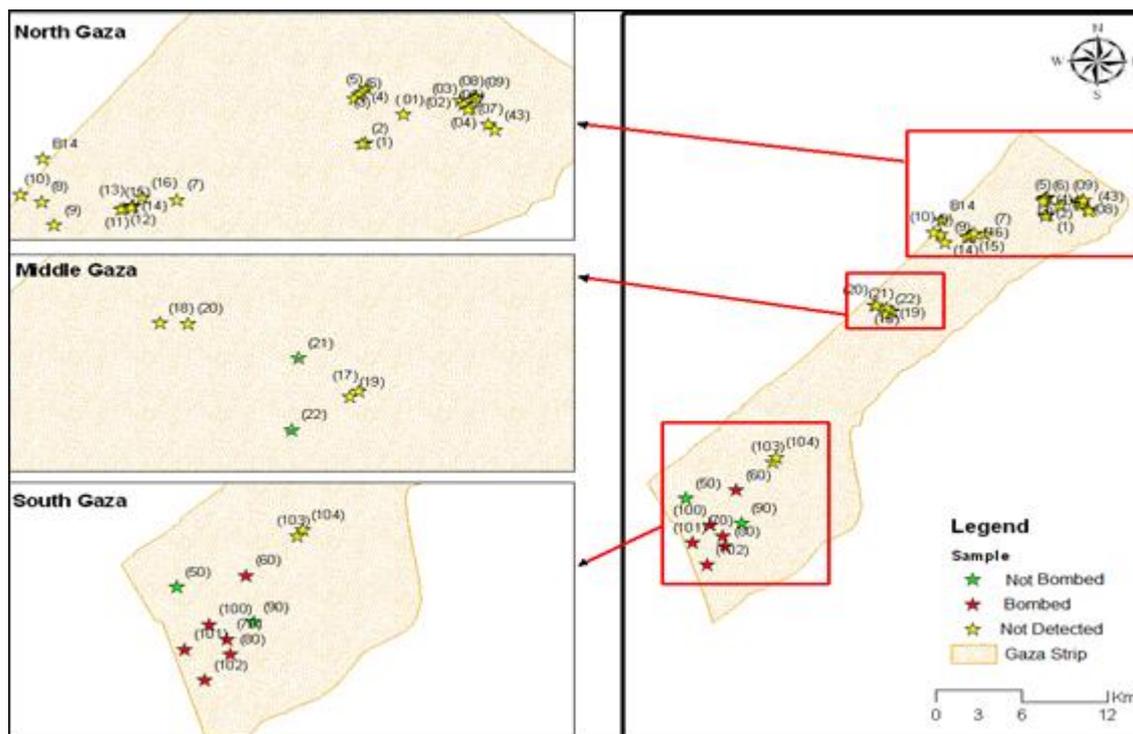


Figure 3.1: Map of Gaza strip showing the location of house wells and rain water pools sample marked with green color for non-bombed sample ,red color for bombed and yellow color for not detected) these sample containing harvested rain water analyzed in this work.(in GIS Lab at Al-Quds University, 2015).

3.1.2 Chemicals and Reagents

1- Ultrapure nitric acid. Merck catalogue number Z282541 304

2- Standard 1 and Standard 2 containing multi- 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% HNO₃) 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.

3.1.3 Preparation of solutions

Four solutions of the thirteen metals with concentrations: 5.0, 10.0, 25.0 and 50.0 ppb were prepared from the stock one and two 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 \pm SD (SD: Standard Deviation).

3.2.1 The instrument

Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

The Agilent Technologies 7500 Series ICP- MS (Agilent 7500) Figure (3.2) 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.

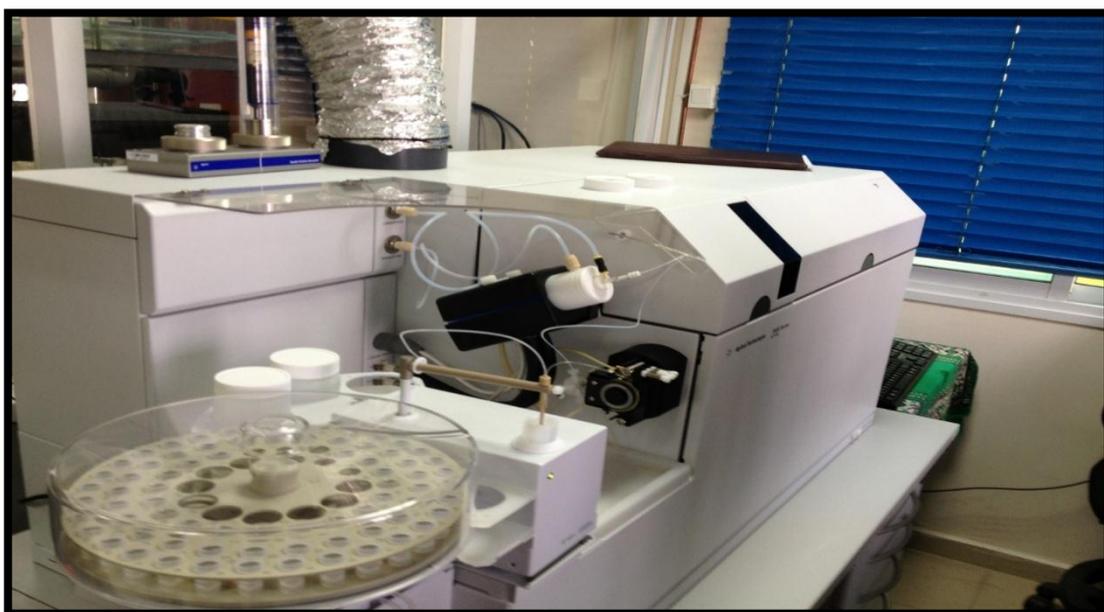


Figure (3.2): Agilent 7500 Inductively Coupled Plasma Mass Spectrometer (ICP-MS).

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)

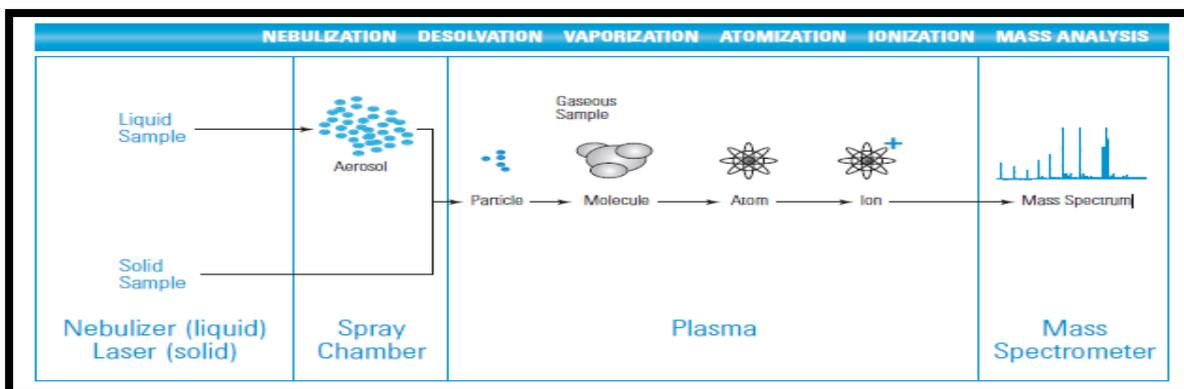


Figure (3.3): Schematic representation of processes in ICP-MS from sample introduction to mass analysis. (Agilent Technologies, 2005)

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)

For accurate quantitative determination of heavy metals in water samples, an internal standard method was used using (In) as internal standard and a multi-standard calibration method (29 metals standard, 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 \pm 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 vs. concentration of the heavy metal (in ppb), 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 ppb. (Appendix A).

3.3 Statistical analysis

Data were analyzed by using Origin 9 software and R program. Statistical differences between the same heavy metal from different water samples (43 samples) were tested using two way: ANOVA and correlation coefficient. Differences were considered significant at p values ≤ 0.05 for ANOVA test and more than 0.7 for strong correlation.

Chapter Four

Results and discussion

Chapter Four

Results and discussion

Harvested Rain Water

The pH of all water samples ranged between 7.2-7.9 (with mean temperature of (19.0 °C) which is neutral to slightly basic and in the allowed limit (6.5-8.5) according to WHO regulations. Electrical conductivity and total dissolved solids for water samples ranged from 170-5460 $\mu\text{s}/\text{cm}$ and 93.5-3003 mg/L, respectively. The limit for total dissolved solids in drinking water according to WHO is 1000 mg/L (WHO 2003). These results showed that two samples have exceeded the WHO limit. (Sample n1 and s35), indicating high amounts of dissolved salts that may contain heavy metals.

4.1 Harvested Rain Water in North area (a)

This area include: (Tal al Zaatar, Biet Lahia, and Biet Hanun- High Street and Shiekh zaid). This area was contaminated by bombing or agricultural activities. These regions were hit by different number of rocket as Shown in table 4.1. The pH of water samples in this area ranged from 6.83-8.18. Electrical conductivity and total dissolved solids for water samples ranged from 284-5460 $\mu\text{s}/\text{cm}$ and 156 -3003 mg/L, respectively as shown in table 4.2. Sample n1, has the highest values for EC and TDS, which may be attributed to bombing sources of pollution.

Table (4.1): Samples description in the North area (a) of Gaza Strip.

sample no.	Sample Description
n1	Bombing area: one rocket hit the house.
n2	Bombing area: One rocket hit the house.
n3	Agricultural empty lands: area was hit by 5 rockets f 16.
n4	Agricultural empty lands: area was hit by 5 rockets f 16.
n5	Agricultural empty lands: area was hit by 5 rockets f 16.
n6	Agricultural empty lands: area was hit by 5 rockets f 16.

n23	Bombing area: 5 rockets hit the area.
n24	Agricultural empty lands: area was hit by 2 rockets f 16.
n25	Agricultural empty lands: a lot of destruction by the shelling.
n26	Agricultural empty lands: a lot of destruction by the shelling.
n27	Bombing area lot of destruction by the shelling.
n28	Bombing area: 5 rockets hit the area.
n29	Bombing area: rockets hit the area.
n30	Bombing area: completely destroyed
n31	Bombing area: completely destroyed
n43	Bombing area: 5 rockets hit the area.

Table (4.2): Analysis of pH, EC and TDS, in the harvested rainwater samples in North (a).

sample no.	pH	EC (µs/cm)	TDS(mg/L)
n1	6.85	5460	3003
n2	7.89	1330	732
n3	8.18	573	315
n4	7.27	743	409
n5	7.67	611	336
n6	7.39	688	378
n23	7.34	469	258
n24	7.47	542	298
n25	7.53	329	181
n26	7.37	370	204
n27	7.52	390	215
n28	7.56	349	192
n29	7.58	323	178
n30	7.49	437	240
n31	7.94	461	254
n43	7.61	284	156

4.1.1 Heavy metals content:

Results showed that twelve trace metals (Ba, Cu, Zn, Co, Mn, V, Al, Pb, Cr, Ni, As, and Cd) were detected in all water samples analyzed (16 samples) in North area (a). All of them are heavy metals except Aluminum and Barium. The concentration (in $\mu\text{g/L}$) of these metals were found in the range of : 227.0-3484, 3.0-126, 0.34-813.0, 2.0-101.0, 55.0-13149.0, 4.0-30.0, 98.0-6101.0, 0.0-45.82, 1.0- 59.0, 3.0-95.0, 0.53-11.0 and 0.08-4.82, for Ba, Cu, Zn, Co, Mn, V, Al, Pb, Cr, Ni, As, and Cd respectively. In addition to these metals, Uranium and Phosphorous were detected in all samples analyzed in this area too, with ranges of 0.04-2.48, and 50.25-20166.1 $\mu\text{g/L}$, respectively as shown in table 4.3.

Table 4.3: Concentration of trace metals detected in harvested rain water after the November 2012 bombing in North (a), Gaza by using ICP/MS. Results expressed as average \pm SD for three samples (SD: standard deviation).

Sample no.	Concentration of metals ($\mu\text{g/L}$)													
	Ba	Cu	Zn	Co	Mn	V	Al	Pb	Cr	Ni	As	Cd	U	P
n1	530.25 ± 1.78	126.13 ± 3.51	282.72 ± 1.69	11.66 ± 0.07	251.5 ± 1.05	29.52 ± 0.11	6101.2 ± 31.5	45.82 ± 0.22	58.57 ± 1.77	63.99 ± 1.91	9.82 ± 0.32	0.8 ± 0.05	2.48 ± 0.03	901.27 ± 3.01
n2	315.51 ± 2.06	11.65 ± 0.2	268.46 ± 1.79	4.22 ± 0.06	177.12 ± 1.57	27.45 ± 0.19	131.51 ± 3.32	0.28 ± 0.01	4.58 ± 0.23	23.2 ± 0.08	9.35 ± 0.25	0.85 ± 0.07	1.52 ± 0.01	411.47 ± 2.18
n3	3483.56 ± 54.05	24.79 ± 1	509.92 ± 3.92	100.56 ± 2.19	13148.56 ± 173.15	15.04 ± 0.21	3247.31 ± 53.35	1.84 ± 0.02	6.24 ± 0.38	95.49 ± 3.39	11.37 ± 0.23	4.82 ± 0.16	0.08 ± 0.01	20166.1 ± 9.44
n4	606.28 ± 4.26	6.16 ± 0.04	0.3 ± 0.02	2.9 ± 0.03	77.93 ± 0.44	4.0 ± 0.05	97.6 ± 7.26	0.05 ± 0.01	0.67 ± 0.1	3.71 ± 0.03	4.86 ± 0.24	0.06 ± 0.02	0.64 ± 0.02	2254.64 ± 8.98
n5	373.97 ± 2.6	51.16 ± 0.46	812.9 ± 3.66	7.05 ± 0.04	675.72 ± 5.62	18.47 ± 0.16	3172.32 ± 27.99	34.13 ± 0.34	6.05 ± 0.22	20.3 ± 0.23	6.35 ± 0.02	1.26 ± 0.09	0.58 ± 0.01	2553.97 ± 7.30
n6	343.87 ± 0.98	38.86 ± 0.92	515.03 ± 1.53	4.8 ± 0.05	394.92 ± 0.82	12.63 ± 0.16	1284.72 ± 2.42	10.86 ± 0.03	3.98 ± 0.19	13.64 ± 0.2	7.02 ± 0.29	1.04 ± 0.07	0.41 ± 0.01	3358.28 ± 11.2
n23	376.38 ± 2.3	10.44 ± 0.04	58.82 ± 1.72	3.11 ± 0.1	100.61 ± 6.17	12.62 ± 0.14	103.33 ± 34.06	0.25 ± 0.23	5.11 ± 0.23	5.45 ± 0.12	4.23 ± 0.05	1.57 ± 0.05	0.04 ± 0.01	4528.35 ± 12.11
n24	226.71 ± 4.62	13.29 ± 0.21	40.27 ± 0.94	3.73 ± 0.06	256.37 ± 4.2	21.21 ± 0.51	109.73 ± 1.66	0.47 ± 0.01	14.1 ± 0.08	12.78 ± 0.39	4.6 ± 0.2	0.48 ± 0.07	1.05 ± 0.03	565.20 ± 4.06
n25	368.97 ± 6.36	21.1 ± 0.62	288.16 ± 5.57	8.8 ± 0.17	614.06 ± 11.81	26.36 ± 0.43	3970.67 ± 73.21	12.11 ± 0.24	19.37 ± 0.53	18.58 ± 0.53	2.94 ± 0.15	1.1 ± 0.1	0.94 ± 0.01	609.97 ± 3.02
n26	446.86 ± 2.91	21.14 ± 0.18	359.66 ± 1.01	17.8 ± 0.17	933.15 ± 8.01	24.7 ± 0.09	5312.33 ± 19.66	27.68 ± 0.24	26.23 ± 0.45	24.25 ± 0.63	3.24 ± 0.17	1.48 ± 0.08	1.06 ± 0.02	651.35 ± 4.72
n27	828.53 ± 4.3	2.87 ± 0.04	0.62 ± 0.05	2.4 ± 0.04	54.9 ± 0.14	16.69 ± 0.13	151.54 ± 12.09	0.11 ± 0.01	7 ± 0.25	2.91 ± 0.11	1.41 ± 0.04	0.09 ± 0.03	1.95 ± 0.03	134.29 ± 2.84
n28	915.08 ± 7.57	3.53 ± 0.1	3.92 ± 0.02	2.44 ± 0.01	81.65 ± 0.37	16.81 ± 0.05	220.45 ± 8.14	0.27 ± 0.01	7.63 ± 0.17	2.87 ± 0.21	1.38 ± 0.08	0.11 ± 0.02	1.77 ± 0.01	145.57 ± 1.73
n29	489.51 ± 4.92	3.56 ± 0.07	0.34 ± 0.15	3.21 ± 0.08	61.54 ± 0.67	12.66 ± 0.16	129.37 ± 2.6	0.17 ± 0.01	4.04 ± 0.01	2.85 ± 0.07	0.53 ± 0.01	0.2 ± 0.01	1.46 ± 0.04	50.25 ± 2.0

n30	393.66 ±3.02	30.75 ±0.48	565.45 ±5.2	17.75 ±0.1	1302.3 ±17.07	19.23 ±0.25	4165.73 ±54.19	14.5 ±0.15	5.35 ±0.07	18.73 ±0.14	1.92 ±0.08	2.87 ±0.12	0.52 ±0.01	996.68 ±4.55
n31	418.01 ±4.3	29.62 ±0.57	540.92 ±3.88	17.08 ±0.19	1245.94 ±10.77	17.92 ±0.14	3821.46 ±34.72	13.13 ±0.12	4.68 ±0.18	19.39 ±0.41	1.85 ±0.02	2.73 ±0.16	0.58 ±0.01	2876.13 ±8.77
n43	615.36 ±1.82	7.99 ±0.26	16.25 ±0.17	3.07 ±0.01	139.96 ±0.37	14.98 ±0.07	512.74 ±23.1	0.87 ±0.01	4.45 ±0.14	7.53 ±0.47	0.79 ±0.04	0.18 ±0.04	1.15 ±0.02	57.63 ±2.32

Table 4.3 summarizes the concentrations of heavy metals from the highest to lowest values which were detected in the harvested rainwater samples analyzed in this area.

From table 4.4 the concentrations of heavy metals which were also detected in the harvested rainwater samples analyzed in this area (minimum, maximum, average, median, standard deviation, and relative standard deviation). There was a significant difference between the average and median values indicating that there were differences in the concentrations of the metals in the water samples analyzed in this area. A one way ANOVA statistical analysis was used to test if the concentration of heavy metals is significantly different in the 16 water samples analyzed or not. Another statistical test (correlation coefficient) was also used for the different samples to determine if there is relationship between each element. Results showed that all metals concentrations are significantly different in the 16 water samples according to ANOVA test, which indicates that these water samples are different from each other in terms of heavy metals concentration. This result confirms locational variations of heavy metals in water samples analyzed in this area.

Figures (4.1), (4.2), (4.3) and (4.4) show this variation for Al, Ba, Ni and Pb in the 16 water samples.

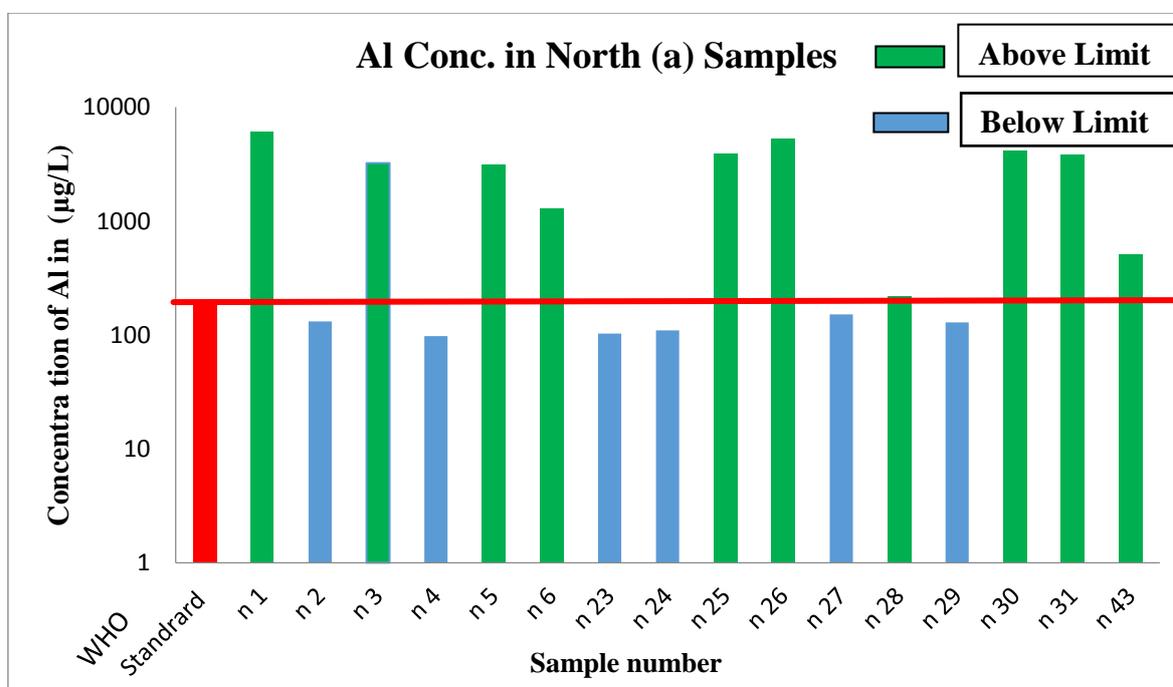


Figure (4.1): Concentration of Al (in µg/L) vs. (WHO Standard and sample number obtained in November 2012 in North (a) area.

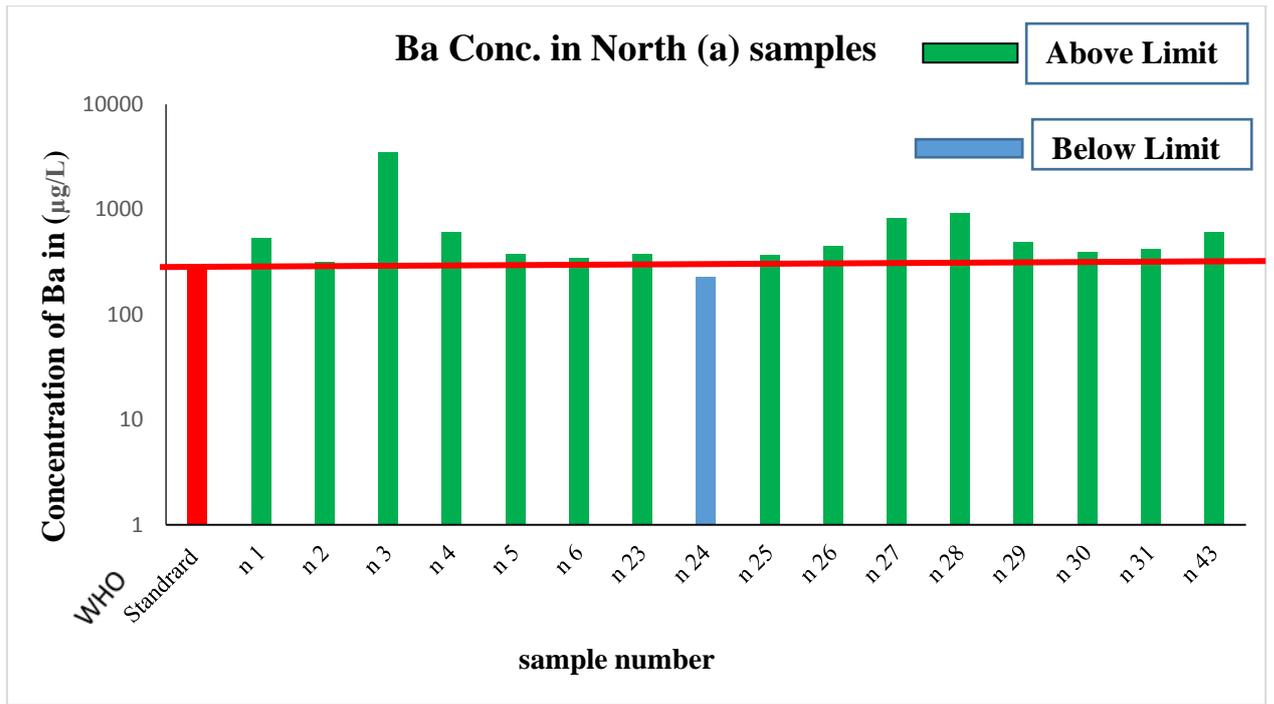


Figure (4.2): Concentration of Ba (in µg/L) vs. (WHO Stander and sample number obtained in November 2012 in North (a) area.

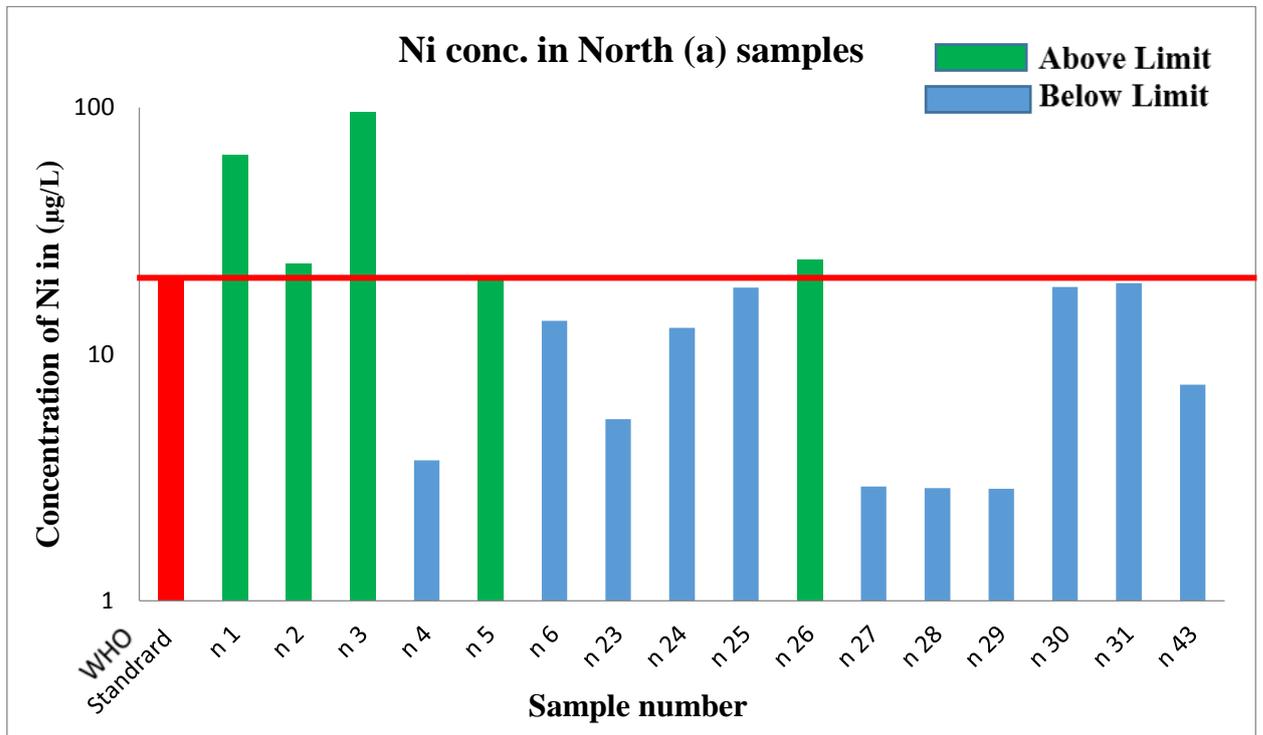


Figure (4.3): Concentration of Ni (in µg/L) vs. (WHO Stander and sample number obtained in November 2012 in North (a) area.

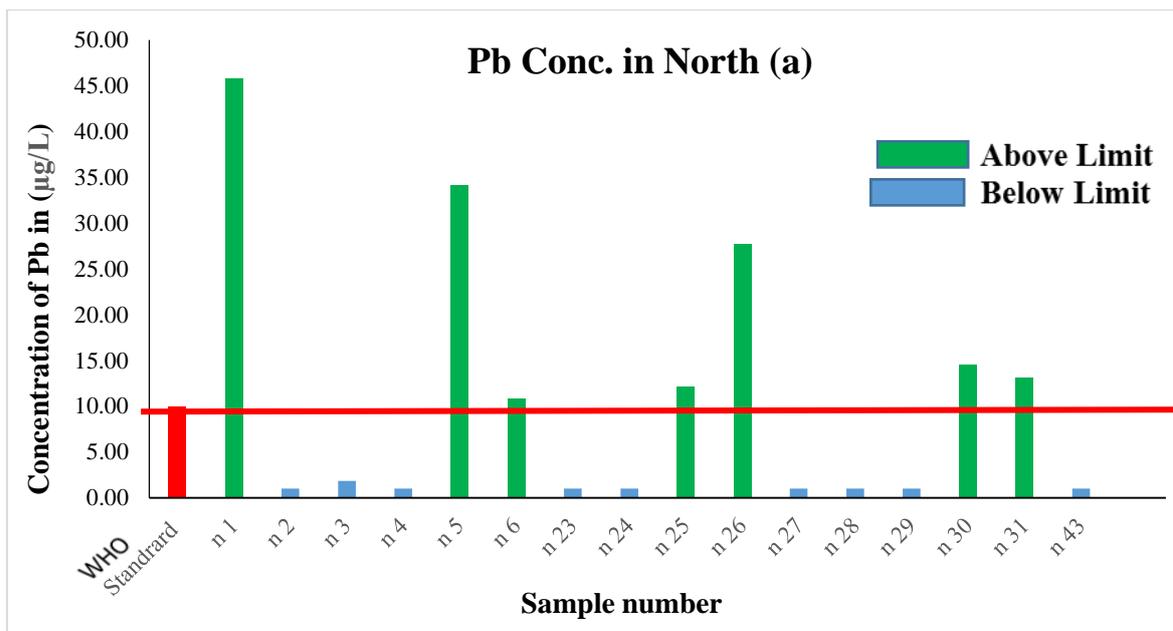


Figure (4.4): Concentration of Pb (in µg/L) vs. (WHO Stander and sample number obtained in November 2012 in North (a) area.

From these figures, results showed that some samples have exceeded the limit of WHO stander. Sample n1, has the highest concentration for Al and Pb metals. But in sample n3, Ba and Ni have the highest concentration values. This difference could be attributed to the different sources of contamination, which was bombing houses and agricultural empty lands for n1 and n3 respectively and to the variation of the number of rockets. These sites were hit by 1 to 5 rockets respectively.

The sources of these heavy metals in harvested water used for drinking and agriculture in the Gaza Strip might be attributed to bombing or agriculture activities. These regions had been hit by different number of rocket. The detected metals in the harvested rainwater samples analyzed in this area are of known human carcinogenic/teratogenic metals (class 1, IARC) as As, Cd, Cr, Ni (IARC, 1987), and of possible carcinogens (class 2B, IARC) as Co, V, and of known fetotoxic metals as Al, Cu, Ba, Pb, Mn (Jaerup, 2003, Siemiatycki et. al. 2004). Toxicological and experimental studies established that high concentrations of these metals disrupt body functions and have pathogenic effects in human respiratory organs, kidney and skin and affect sexual and neurological development and functions (Jaerup, 2003, Siemiatycki et. al. 2004, Domingo, 1994).

The allowed WHO limit for lead in drinking water is 10 µg/L (WHO, 1993), however our results showed that more than 44% of the samples analyzed in this region (7 out of 16) exceeded this limit with an average of 10.83 µg/L and the highest value is 45.82 µg/L. This may be attributed to the bombing and agricultural activities. It has long been known that lead in drinking water is highly toxic. Exposure to lead is also 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 Ba, the allowed WHO limit is 300 µg/L, however 15 water samples out of 16 have Barium with concentrations higher than the allowed WHO limit. The highest Ba concentration was found to be 3484.0 µg/L in sample n3, which was collected from agricultural empty land area that was hit by 5 rockets from F16. The health hazards associated with exposure to barium is toxic to humans and animals because all water- and acid-soluble barium compounds are poisonous. When people are exposed to Ba for short periods at levels above the maximum contaminant level, they may experience gastrointestinal disturbances and muscular weakness. Additionally, Ba has the potential to cause high blood pressure when humans exposed to levels above the limit for long periods of time (WHO, 2004).

For Mn, the allowed WHO limit in drinking water is 500 µg/L; results showed that six water samples were found to exceed this limit. The highest concentration was found to reach 13149.0 µg/L.

Regarding Ni, our results showed that five water samples out of 16 have Ni concentration higher than the allowed limit (20 µg/L in drinking water) with the highest concentration of 95.0µg/L.

For Al, the allowed WHO limit is 200µg/L, however 10 water samples out of 16 have Aluminum with concentrations larger than the allowed WHO limit. The highest Al

concentration was found to be 6101.0µg/L. The health hazards associated with exposure to Aluminium excess is involved in degenerative diseases of the nervous system, trespass placenta, if contamination occurs by skin exposure of the pregnant mother, it may produces fetotoxicity. Aluminum has been associated with Alzheimer's and Parkinson's disease, senility and presenile dementia (Bakare-Odunola, 2005).

As, Cr and Cd the allowed WHO limits in drinking water is 10.0, 50.0 and 3.0 µg/L respectively. Our results showed that these metals were found in the analyzed water samples. One sample only has As, Cr and Cd concentration higher than the allowed limit, with the highest concentration of 0.53, 1.0, 0.06µg/L, respectively.

Co, V and P have no limits in drinking water by WHO, however these metals were detected in all water samples analyzed in this study. Regarding Cu, Zn and U the allowed WHO limits in drinking water is 2000, 3000 and 30µg/L respectively. Our results had shown that these metals were found in the analyzed water samples within these limits. Phosphorous was detected in all water samples analyzed in this study with high concentrations (range of 50.25-20166.1 µg/L, and average of 26.41µg/L). These high concentrations of phosphorous may be attributed to the white phosphorous that was used in Gaza during the war. Uranium was also detected in all water samples analyzed in this area with a range of 0.08-2.48µg/L and average of 1.01µg/L, and it is attributed to the depleted uranium used in this war.

Table (4.4): Heavy metals concentrations in $\mu\text{g/L}$, which are detected in the harvested rainwater samples analyzed in North area (a) (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 ($\mu\text{g/L}$)	heavy metals													
	Ba	Cu	Zn	Co	Mn	V	Al	Pb	Cr	Ni	As	Cd	U	P
Minimum	227	4	0	2	55	4	98	0	1	3	0.53	0.06	0.08	50
Maximum	3484	126	813	101	13149	30	6101	45.82	59	95	11	4.82	2.48	20166
Average	670.78	25.19	284.23	13.16	1219.8	18.14	1925.4	10.83	11.13	20.98	4.48	1.23	1.01	2641
Median	432.44	17.20	285.44	4.51	253.54	17.37	898.73	1.84	5.70	16.11	3.74	0.95	1.00	776.31
SD	747.62	29.33	252.5	23.22	3106.4	6.38	2086.9	13.95	13.79	24.05	3.31	1.25	0.66	4729
RSD (%)	111.46	116.44	88.84	176.44	254.67	35.17	108.39	128.81	123.90	114.63	73.88	101.63	65.35	179.04
% of samples that found to contain that heavy metal	100	100	93	100	100	100	100	93	100	100	100	100	100	100
Limits	300	2000	3000	No limit	500	No limits	200	10	50	20	10	3	30	No limits
% of samples that exceeded the limit	93	0	0	/	38	/	63	44	6	31	6	6	0	/

4.1.1.1 Correlations between elements in North area (a)

Correlation coefficient between different heavy metals was calculated. Table 4.5 showed the correlation coefficient in North (a). Strong positive correlations (higher than 0.7) were detected for: P with Mn, Co, Ba, Ni and Cd. The Cd with Mn, Co, Zn and Ni. As with Ni. Cu with Al. Pb and Cr. Ni with Mn, Co and Ba. Cr with Pb. Also Pb with Al. Ba with Mn and Co. Finally there is a very strong correlation between Co and Mn.

Another correlation between different heavy metals was found in this area: Middle positive correlation (0.5 and 0.7) between, the following metals were found, P with As. Cd with Al. As with Mn, Co and Cu. Also Cu with Ni. Ni with Al. Cr with AL and V. Pb with V and Zn. Zn with Al. Finally V had correlation with Al. Middle negative correlation coefficient found for U with Cd and P.

Most of heavy metals in North (a) (table 4.5) were not associated to each other. Due to the differences between the 16 samples that were contaminated from different sources including bombing, agriculture contaminants or groundwater polluted sources. The large number of samples have a weak correlation between metals. But Mn, Ni and Co was intermediate association with other metals.

Mn had a strong correlation with Cu, Ba, Ni, Cd and P. P had a strong correlation with Mn, Co, Ba, Ni and Cd. Also Cd had a strong correlation with Mn, Co, P, Zn and Ni. Co had a strong correlation with Mn, Ba, Ni, Cd and P.

Table (4.5): Correlations between different heavy elements in North area (a) were determined by R program.

	Al	V	Mn	Co	Zn	Ba	Pb	Cr	Ni	Cu	As	Cd	P	U
Al	1.00													
V	0.57	1.00												
Mn	0.24	-0.09	1.00											
Co	0.35	-0.02	0.99	1.00										
Zn	0.65	0.25	0.34	0.39	1.00									
Ba	0.09	-0.19	0.95	0.93	0.13	1.00								
Pb	0.83	0.54	-0.10	-0.01	0.59	-0.20	1.00							
Cr	0.66	0.68	-0.09	0.00	0.04	-0.09	0.74	1.00						
Ni	0.58	0.33	0.81	0.85	0.44	0.74	0.37	0.45	1.00					
Cu	0.71	0.48	0.02	0.09	0.45	-0.05	0.87	0.80	0.55	1.00				
As	0.25	0.26	0.52	0.52	0.40	0.44	0.30	0.32	0.76	0.53	1.00			
Cd	0.50	0.06	0.81	0.85	0.65	0.64	0.12	-0.07	0.70	0.15	0.40	1.00		
P	0.18	-0.23	0.96	0.95	0.37	0.90	-0.11	-0.16	0.76	0.04	0.56	0.83	1.00	
U	0.02	0.48	-0.41	-0.38	-0.43	-0.24	0.22	0.56	-0.07	0.29	-0.10	-0.60	-0.56	1.00



Strong correlations

Middle positive correlation

Middle negative correlation

4.2 Harvested Rain Water in North area (b)

This area include: (Gaza City, Beirut Street, Tal Alhawa, Abu Ghadra, Main Street, former prison and King Street), most of these sites were contaminated by large number of missiles in different locations which was for building samples as shown in table 4.6. Eleven samples were taken from different sites in this area. The pH of water samples in this area ranged between 7.31-8.07 Electrical conductivity and total dissolved solids for water samples ranged from 170-1081 $\mu\text{s}/\text{cm}$ and 93.5-594.55 mg/L respectively, as shown in table 4.7. Result showed that there were a very strong correlation coefficient, with $R^2 = 1$; between EC and TDS as shown in Figure 4.5. The highest values of EC and TDS were in sample n11, contaminated by 8 missiles, which is a large number of rockets that contains a huge amount of pollutant that had affected on the location of the sample site.

Table (4.6): Description of each samples in North area (b), Gaza strip.

sample no.	Sample Description
n7	Potential Contamination: hit with 8 missiles
n8	Nearby bombs Westward in different locations
n9	Nearby bombs Westward in different locations
n10	Potential Contamination: hit with hit with 8 missiles
n11	Potential Contamination: hit with 8 missiles
n12	Potential Contamination: hit with 8 missiles
n13	Potential Contamination: hit with 9 missiles
n14	Potential Contamination: hit with 9 missiles
n15	Potential Contamination: hit with 9 missiles
n16	Sample taken from a small puddle created from the first rain on a cement paved road Potential Contamination: Bombing occurred 15 meters South-West from the sample, a fire started from the bombing and lasted for 10 hours burning construction debris and automotive equipment
n32	Potential Contamination: hit by missiles

Table (4.7): Analysis of pH, EC and TDS in the harvested rainwater samples in North area (b).

sample name	sample no.	pH	EC($\mu\text{s}/\text{cm}$)	TDS(mg/L)
7	n7	7.41	170	93.5
8	n8	7.31	828	455.4
9	n9	7.94	534	293.7
10	n10	7.94	424	233.2
11	n11	7.78	1081	594.55
12	n12	7.91	302	166.1
13	n13	7.50	692	380.6
14	n14	8.07	522	287.1
15	n15	8.02	667	366.85
16	n16	7.84	318	174.9
B14	n32	7.95	451	248.05

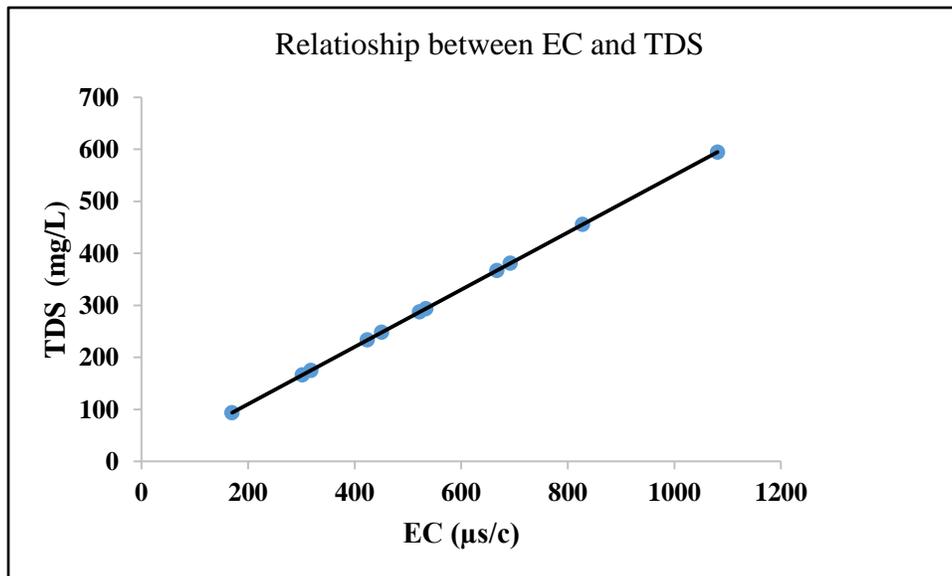


Figure (4.5): Concentration of TDS (in mg/L) vs. (EC (in $\mu\text{s}/\text{cm}$) for samples that obtained in November 2012 in North area (b).

4.2.1 Heavy metals content:

In North area (b), results showed that 11 trace metals (Ba, Cu, Zn, Co, Mn, V, Al, Pb, Cr, Ni, As, and Cd) were detected in all water samples. Results in (Table 4.8) were expressed as Average \pm SD for all samples that were analyzed in this sites. The concentration (in $\mu\text{g/L}$) of these metals were found to be in the range of : 178.98-1909.57, 3.16-672.44, 4.29-1074.30, 1.30-125.23, 115.09-9121.81, 4.23-155.11, 68.60-44046.43, 0.18-450.74, 3.45-112.18, 4.60-133.02, 0.43-24.99 and 0.39-12.61, 0.11-4.20, and 100.68-2467.48 $\mu\text{g/L}$, respectively. For Ba, Cu, Zn, Co, Mn, V, Al, Pb, Cr, Ni, As, Cd, U and P respectively. Table 4.9 summarizes the concentrations of heavy metals which were detected in the harvested rainwater samples analyzed in this area (minimum, maximum, average, median, standard deviation, and relative standard deviation).

Table (4.8): Concentration of trace metals detected in harvested rain water analyzed in the North (b) Gaza Strip. Results expressed as Average \pm SD for all samples (SD: standard deviation).

Sample no.	concentration of metals ($\mu\text{g/L}$)													
	Ba	Cu	Zn	Co	Mn	V	Al	Pb	Cr	Ni	As	Cd	P	U
n7	197.0 \pm 0.95	41.0 \pm 0.23	939.0 \pm 8.45	1.0 \pm 0.01	119.0 \pm 0.68	4.0 \pm 0.02	3610.0 \pm 18.2	53.0 \pm 0.5	5.0 \pm 0.03	12.0 \pm 0.22	1.24 \pm 0.04	1.71 \pm 0.04	382.0 \pm 5.39	0.34 \pm 0.01
n8	1910.0 \pm 31.99	158.0 \pm 4.74	1074.0 12.35 \pm	71.0 \pm 1.04	5012.0 \pm 59.55	67.0 \pm 0.6	23388 \pm 191.83	162.0 \pm 2.16	39.0 \pm 1.33	87.0 \pm 3.4	15.05 \pm 0.29	4.0 \pm 0.14	2467.0 \pm 12.69	4.0 \pm 0.03
n9	440.0 \pm 5.03	18.0 \pm 0.48	10.0 \pm 0.26	3.0 \pm 0.05	149.0 \pm 1.93	8.0 \pm 0.1	69.0 \pm 3.71	1.0 \pm 0.01	4.0 \pm 0.18	5.0 \pm 0.11	6.1 \pm 0.2	0.39 \pm 0.04	1018.0 \pm 15.52	0.89 \pm 0.01
n10	265.0 \pm 13.97	40.0 \pm 0.59	259.0 \pm 6.48	4.0 \pm 0.29	278.0 \pm 24.48	23.0 \pm 0.23	5543.0 \pm 52.68	78.0 \pm 0.59	24.0 \pm 0.59	10.0 \pm 0.3	6.13 \pm 0.08	0.91 \pm 0.06	374.0 \pm 8.56	0.84 \pm 0.02
n11	1756.0 \pm 50.31	259.0 \pm 6.52	989.0 \pm 31.36	125.0 \pm 3.97	9122.0 \pm 266.79	145.0 \pm 4.02	44064 \pm 1559.66	209.0 \pm 6.02	109.0 \pm 1.97	133.0 \pm 2.68	12.06 \pm 0.2	10.4 \pm 0.37	726.0 \pm 10.57	6.95 \pm 0.12
n12	1755.0 \pm 17.46	672.0 \pm 15.8	1001.0 \pm 19.39	49.0 \pm 0.49	3505.0 \pm 48.68	155.0 \pm 1.52	50840.0 \pm 688.87	451.0 \pm 5.14	112.0 \pm 3.02	70.0 \pm 2.01	24.99 \pm 0.57	12.61 \pm 0.36	1762 \pm 11.15	6.69 \pm 0.06
n13	179.0 \pm 2.55	82.0 \pm 2.74	310.0 \pm 5.13	4.0 \pm 0.04	119.0 \pm 1.24	15.0 \pm 0.22	2803.0 \pm 4.77	47.0 \pm 0.36	28.0 \pm 0.63	18.0 \pm 0.61	7.4 \pm 0.32	6.28 \pm 0.29	178.0 \pm 1.23	0.39 \pm 0.01
n14	205.0 \pm 0.76	20.0 \pm 0.33	460.0 \pm 1.66	3.0 \pm 0.02	231.0 \pm 1.23	6.0 \pm 0.03	148.0 \pm 1.58	1.08 \pm 0.01	3.0 \pm 0.13	7.0 \pm 0.26	2.21 \pm 0.12	1.13 \pm 0.07	215.0 \pm 3.69	0.11 \pm 0.01
n15	280.0 \pm 3.5	31.0 \pm 0.3	192.0 \pm 7.91	6.0 \pm 0.08	194.0 \pm 1.23	19.0 \pm 0.28	294.0 \pm 1.6	1.06 \pm 0.01	17.0 \pm 0.49	9.0 \pm 0.11	3.73 \pm 0.09	1.18 \pm 0	114.0 \pm 1.82	0.51 \pm 0.01
n16	697.0 \pm 2.95	3.0 \pm 0.11	4.0 \pm 0.13	3.0 \pm 0.03	621.0 \pm 5.05	6.0 \pm 0.03	153.0 \pm 2.97	0.18 \pm 0.01	3.0 \pm 0.03	40.0 \pm 0.88	0.43 \pm 0.04	0.4 \pm 0.04	167.0 \pm 4.05	0.81 \pm 0.02
n32	223.0 \pm 1.6	57.0 \pm 1.91	246.0 \pm 0.36	3.0 \pm 0.02	115.0 \pm 0.54	13.0 \pm 0.1	3042 \pm 3.65	63.0 \pm 0.2	22.0 \pm 0.9	8.0 \pm 0.23	1.35 \pm 0.04	1.54 \pm 0.11	101.0 \pm 0.36	0.3 \pm 0.01

Table (4.9): Heavy metals concentrations in $\mu\text{g/L}$, which were detected in the harvested rainwater samples analyzed in North (b). For 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 ($\mu\text{g/L}$)	Heavy metals													
	Ba	Cu	Zn	Co	Mn	V	Al	Pb	Cr	Ni	As	Cd	U	P
Minimum	178.98	3.16	4.29	1.30	115.09	4.23	68.60	0	3.14	4.60	0.43	0.39	0.11	100.86
Maximum	1909.57	672.44	1074.30	125.23	9121.81	155.11	50840.44	450.74	112.18	133.02	24.99	12.61	6.95	2467.48
Average	718.72	125.51	498.46	24.61	1769.50	41.91	12177.63	96.82	33.35	36.20	7.33	3.71	2.00	682.22
Median	280.25	41.47	309.50	3.51	230.79	15.39	3041.74	53.13	22.33	11.59	6.10	1.54	0.81	373.60
SD	682.13	187.25	399.33	38.75	2808.95	53.64	17845.77	129.67	38.16	40.57	7.11	4.07	2.51	741.78
RSD (%)	94.91	149.20	80.11	157.45	158.74	127.99	146.55	133.93	114.43	112.07	96.96	109.75	125.35	108.73
% of samples that found to contain that heavy metal	100	100	100	100	100	100	100	90	100	100	100	100	100	100
Limits	300	2000	3000	No limit	500	No limits	200	10	50	20	10	3	30	No limits
% of samples that exceeded the limit	45	0	0	/	36	/	73	63	18	36	27	36	0	/

From table 4.9, there was a significant difference between the average and median values indicating that there were differences in the concentrations of the metals in the water samples analyzed in this area. To support these results statistical analysis was done for each sample in this area. Two ways: ANOVA and R- program statistical test were used to prove, if the concentration of heavy metals were significantly different and if there was any correlation between each sample.

By using ANOVA statistical test, results confirm locational variations of heavy metals in the 11 water samples analyzed. Figures (4.6), (4.7), (4.8), (4.9) and (4.10) show this variation for Al, Cr, Ni, Ba and Pb respectively in the 11 water samples.

From these figures, results showed that Al, Cr and Pb had the highest concentration values in sample no. (n12), this area was hit by eight missiles, which was a large number of missiles that hit the same site of (n12) sample. While Ni and Ba have the highest concentrations in sample no. (n11), which also hit by the same number of missiles. Indicating that the sample n11 came from inside the prison, but n12 came from outside the prison.

Sample n11, has the highest values for: Ni and Ba, due to different reasons of contamination which was the main source from industrial metals and bombing in this area. Nickel, is used in the production of stainless steels. It has been estimated that 8% of nickel is used for household appliances (IPCS, 1991). Barium is a trace element that is never found freely in nature, and used in the electronics textile industries and, plastics. In the electricity industry it is used in spark plugs, fluorescent lamps and vacuum tubes. While sample n12 has the highest values for: Al, Cr and Pb, these results may be attributed to bombing.

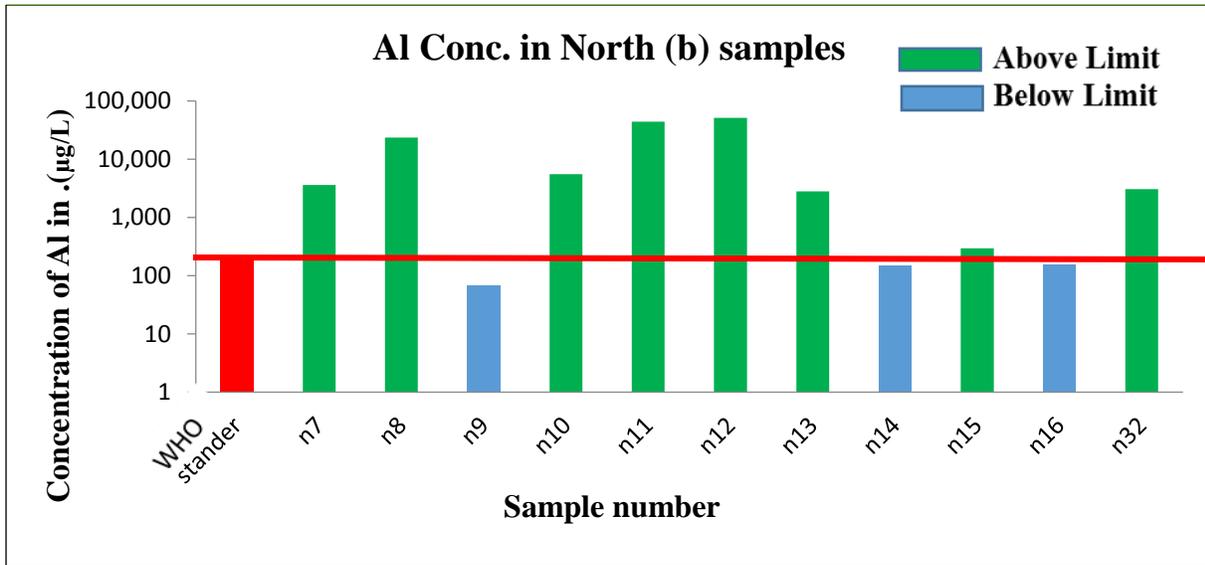


Figure (4.6): Concentration of Al (in µg/L) vs. (WHO Stander and sample number obtained in November 2012 in North area (b).

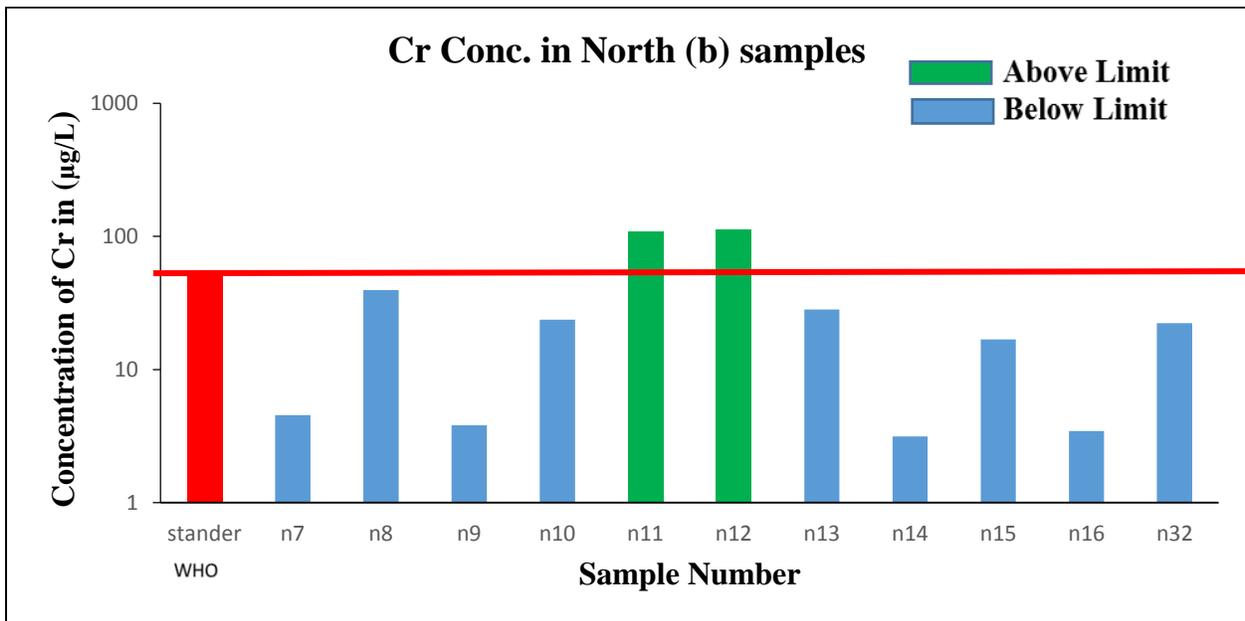


Figure (4.7): Concentration of Cr (in µg/L) vs. (WHO Stander and sample number obtained in November 2012 in North area (b).

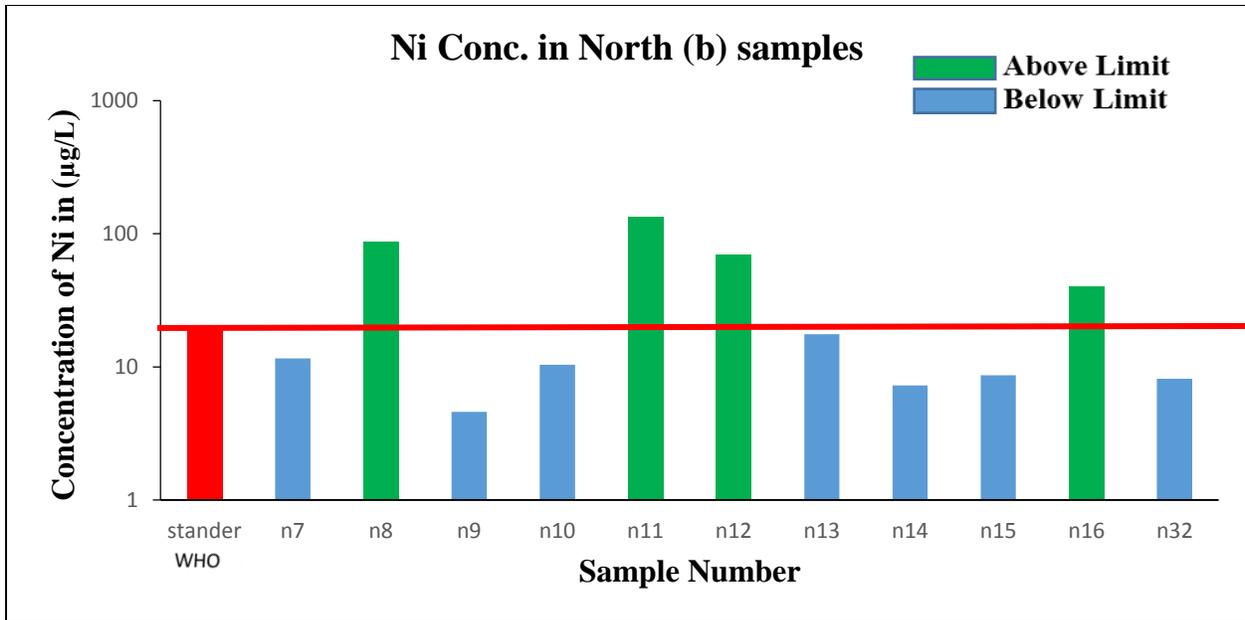


Figure (4.8): Concentration of Ni (in µg/L) vs. (WHO Stander and sample number obtained in November 2012 in North area (b).

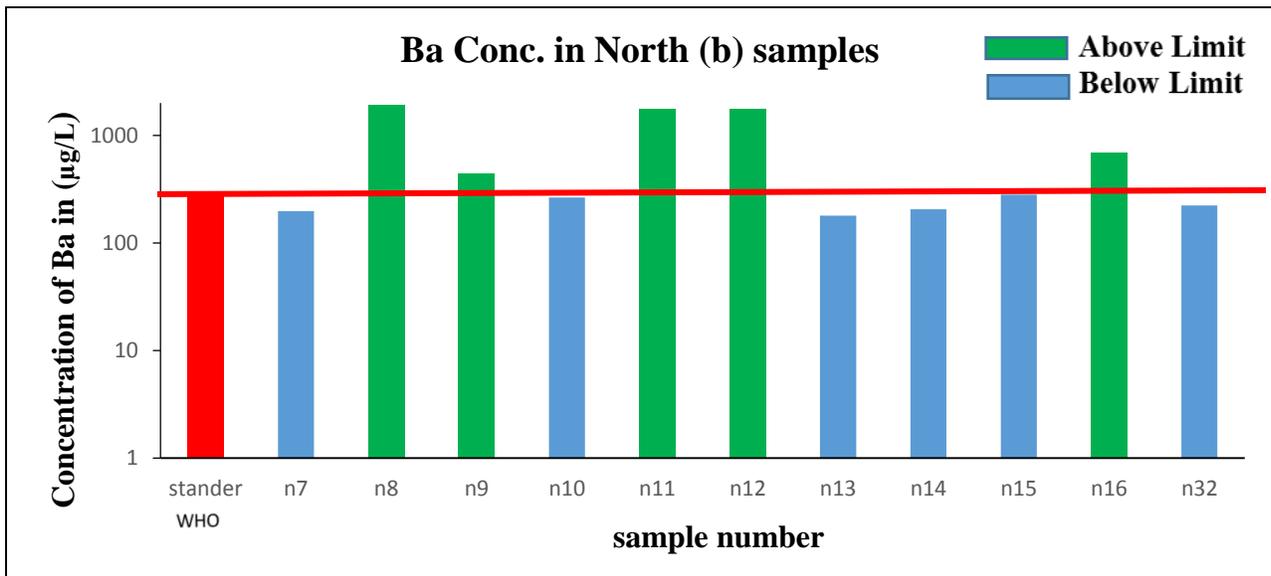


Figure (4.9): Concentration of Ba (in µg/L) vs. (WHO Stander and sample number obtained in November 2012 in North area (b).

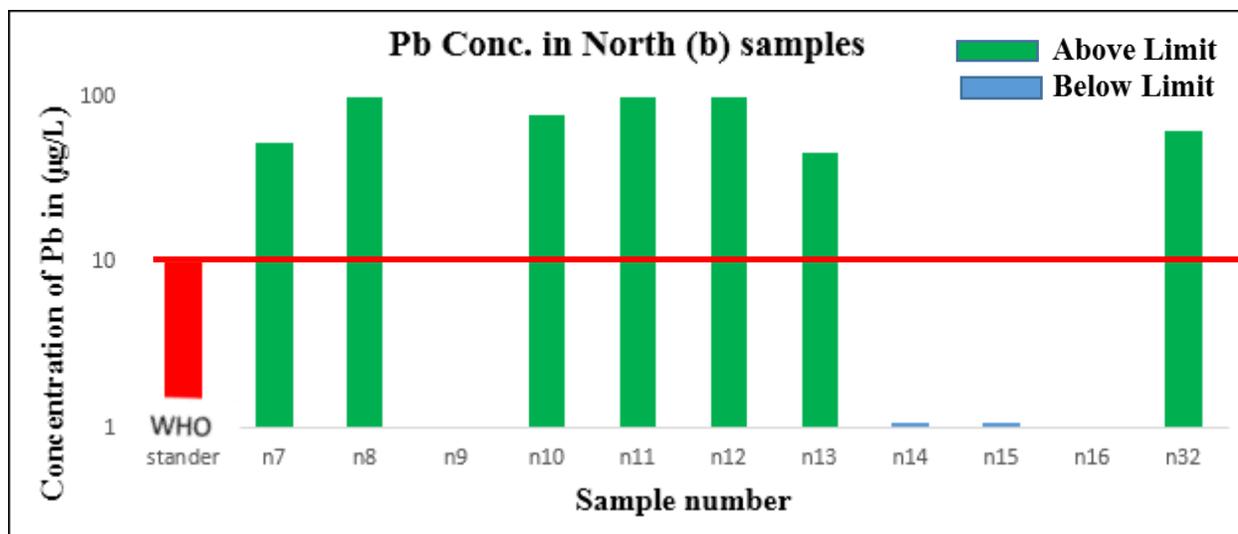


Figure (4.10): Concentration of Pb (in $\mu\text{g/L}$) vs. (WHO stander and sample number obtained in November 2012 in North area (b).

In North (b) area, the highest percentage of samples that exceeded the limit of WHO, was for Aluminum with 73% of the obtained samples. That mean 8 water samples out of 11 have aluminum with concentrations higher than the allowed WHO limit, which is $200 \mu\text{g/L}$, however the highest Al concentration was found to be $50840.44 \mu\text{g/L}$. The health hazards associated with exposure to Aluminium excess affect human health especially in degenerative diseases of the nervous system, trespass placenta, if contamination occurs by skin exposure of the pregnant mother, and produces fetotoxicity. Aluminum has been associated with Alzheimer's and Parkinson's disease, senility and presenile dementia (Bakare-Odunola, 2005).

The second heavy metal with high concentration is lead. Results showed that more than 63% of the samples analyzed in this study (7 out of 11) exceeded this limit with an average of $96.82 \mu\text{g/L}$ and highest value as 450.74 . Barium the allowed WHO limit is $300 \mu\text{g/L}$, however (5 out of 11) water samples had barium with concentrations larger than the allowed WHO limit, with 45% of the samples analyzed exceeded this limit. The highest Ba concentration was found to be $1909.57 \mu\text{g/L}$, with an average of $718.72 \mu\text{g/L}$. For Cr, results showed that two water samples found to exceed this limit with highest concentration $112.18 \mu\text{g/L}$. Regarding Arsenic, three water samples out of 11 contained As.

For Mn, Ni and Cd the allowed WHO limits in drinking water is 500.0, 20.0 and 3.0 µg/L, respectively, results showed that these metals had exceeded the limit of WHO by the same percentage which is 36% higher than the allowed limit, with the highest concentration of 9121.81, 133.02, 12.61µg/L, respectively. While Cu and Zn the allowed WHO limits in drinking water is 2000 and 3000µg/L, respectively, our results showed that these metals were found in the analyzed water samples within these limits.

Uranium allowed WHO limit in drinking water is 30 µg/L, results showed that these metal was found in the analyzed water samples within these limits. Uranium detected in all water samples analyzed in this area with range of 0.11-4.20µg/L and average of 2.00 µg/L, the highest value found in sample number 8, it might be attributed to the depleted uranium used in this war.

Co, V and P have no limits in drinking water by WHO, however these metals were detected in all water samples analyzed in North (b). Phosphorous was detected in all water samples analyzed in this study with high concentrations (range of 100.86-2467.48µg/L, and average of 682.22µg/L). These high concentrations of phosphorous was found in sample number 8 (Beirut Street, near to Abu Mazen Square) may be attributed to the white phosphorous that was used in this war.

4.2.1.1 Correlation between elements in North area (b).

The second way for statistical test by R- program. Correlation coefficient between different metals was detected in North (b). Show table 4.10.

Correlation coefficient gave strong correlation (higher than 0.7) for: U with Al, V, Mn, Co, Zn, Ba, Pb, Cr, Ni, Cu, As and Cd. Cd with Al, V, Mn, Co, Ba, Pb, Cr, Ni, Cu, and As. As with Al, V, Mn, Ba, Pb, Cr and Cu. Cu with Al, V, Mn, Ba, Pb and Cr. also Ni with Al, V, Mn, Co, Ba, Pb and Cr. Cr with Al, V, Mn, Co, Ba and Pb. Also Pb with Al, V, Mn, Zn and Ba. Ba with Al, V, Mn, Co and Zn. where Zn with Al, V, Mn and Co. Co was with Al, V and very strong correlation with Mn. Mn with Al and V. But V with Al. Finally P with Ba and As. P had a positive middle correlation with Al, V, Mn, Co, Zn, U, Pb, Ni and Cu. As also had the same correlation with Co, Zn and Ni. Cu had a middle correlation with Co, Zn and Ni too. Ni and Cr had another middle correlation with Zn. Finally Pb had a middle correlation with Co.

Table 4.10: Correlation between different heavy elements were determined by R program in North (b), Gaza Strip.

	Al	V	Mn	Co	Zn	Ba	Pb	Cr	Ni	Cu	As	Cd	P	U
Al	1.00													
V	0.99	1.00												
Mn	0.84	0.85	1.00											
Co	0.84	0.85	1.00	1.00										
Zn	0.76	0.70	0.70	0.71	1.00									
Ba	0.89	0.87	0.88	0.87	0.71	1.00								
Pb	0.94	0.91	0.61	0.62	0.71	0.78	1.00							
Cr	0.97	0.98	0.81	0.82	0.65	0.79	0.90	1.00						
Ni	0.85	0.85	0.98	0.97	0.69	0.92	0.65	0.81	1.00					
Cu	0.90	0.89	0.54	0.55	0.63	0.72	0.98	0.88	0.58	1.00				
As	0.89	0.87	0.62	0.63	0.64	0.82	0.93	0.84	0.64	0.92	1.00			
Cd	0.92	0.92	0.72	0.73	0.67	0.73	0.89	0.95	0.74	0.89	0.85	1.00		
P	0.63	0.58	0.54	0.55	0.63	0.82	0.65	0.48	0.57	0.59	0.80	0.47	1.00	
U	0.98	0.98	0.90	0.90	0.72	0.94	0.88	0.94	0.91	0.84	0.86	0.88	0.68	1.00

 Strong correlations
 Middle positive correlation

The correlation between heavy metals in North b region was very clear in contrast to North a. 11 samples were conducted in North b; so the source of potential contaminated was only from bombing area. The correlation coefficient was very strong in most elements in this area except P.

Ba had a strong correlation coefficient with all elements. While Al, V, U and Mn also had a strong correlation with all elements except with P. But P had a middle correlation with all elements except Ba and As.

4.3 Harvested Rain Water in Middle Area

Middle area includes: Nussairat- Almufti land between Sea Street and Salah al din and Nussairat- Abu Zekri land. Six samples have been analyzed in this region. For m17 and m19 were bombed by many rockets in this agricultural area. While m18 and m20 were hit by 2 to 5 rocket respectively. But samples m21 and m22 were not targeted by any missiles, as shown in table 4.11. The pH of water samples in this area ranged between 7.63-7.95. Electrical conductivity and total dissolved solids for water samples ranged from 217-573 $\mu\text{s}/\text{cm}$ and 119.35-315.15 mg/L, respectively as shown in table 4.12. Result showed that there was a strong correlations between EC and TDS. The highest values of EC and TDS were in sample m20, five rockets had hit the Nussairat area close to the sea, which was contaminated by a large number of rockets compared with other samples in the same area.

Table (4.11): Description of samples in Middle area, Gaza strip.

sample no.	Sample Description
m17	Agricultural area bombed which was hit by many rockets
m18	An area that hit by 2 rockets
m19	Agricultural area bombed which was hit by many rockets
m20	An area that hit by 5 rockets
m21	An area that has not been targeted by missiles
m22	An area that has not been targeted by missiles- the same area of 21

Table (4.12): Analysis of pH, EC and TDS, which were detected in the harvested rainwater samples in Middle area.

Sample no.	pH	EC ($\mu\text{s}/\text{cm}$)	TDS (mg/L)
m17	7.89	299	164.45
m18	7.79	217	119.35
m19	7.71	249	136.95
m20	7.63	573	315.15
m21	7.95	535	294.25
m22	7.63	501	275.55

4.3.1 Heavy metals content

Results showed that twelve trace metals (Ba, Cu, Zn, Co, Mn, V, Al, Pb, Cr, Ni, As, and Cd) were detected in six water samples analyzed in Nussairat area. Table (4.13) shows the concentrations of metals detected in the harvested water samples, results expressed as Average \pm SD for all samples that were analyzed. The concentration (in $\mu\text{g/L}$) of these metals were found to be in the range of :277.66-491.61, 3.59-30.37, 1.07-430.32, 2.58-8.80, 71.36-1006.25, 4.30-15.27, 53.65-3155.65, 0.05-8.28, 2.67-6.71, 2.30-28.48, 0.83-10.31, 0.13-1.07, 0.16-1.65 and 113.01-2855.07 $\mu\text{g/L}$, for Ba, Cu, Zn, Co, Mn, V, Al, Pb, Cr, Ni, As, Cd, U and P respectively. Table 4.14 summarizes the concentrations of heavy metals which were detected in the harvested rainwater samples analyzed in this area (minimum, maximum, average, median, standard deviation, and relative standard deviation).

Table (4.13): Concentration of trace metals detected in harvested rain water analyzed in the Middle area Gaza Strip. Results expressed as Average \pm SD for samples (SD: standard deviation).

Sample no.	Concentration of metals ($\mu\text{g/l}$)													
	Ba	Cu	Zn	Co	Mn	V	Al	Pb	Cr	Ni	As	Cd	U	P
m 17	456.0 \pm 5.73	4.0 \pm 0.08	1.0 \pm 0.18	3.0 \pm 0.04	71.0 \pm 0.85	15.0 \pm 0.15	54.0 \pm 0.99	0.07 \pm 0.01	5.0 \pm 0.18	2.0 \pm 0.05	1.0 \pm 0.07	0.13 \pm 0.01	1.65 \pm 0.03	113.0 \pm 2.25
m 18	429.0 \pm 7.08	8.0 \pm 0.23	85.0 \pm 1.43	4.0 \pm 0.09	519.0 \pm 10.16	14.0 \pm 0.26	2363.0 \pm 37.93	4.38 \pm 0.08	3.0 \pm 0.1	11.0 \pm 0.47	2.0 \pm 0.02	0.52 \pm 0.02	0.46 \pm 0.01	963.0 \pm 2.23
m 19	336.0 \pm 3.97	4.0 \pm 0.02	1.0 \pm 0.13	3.0 \pm 0.02	79.0 \pm 0.5	7.0 \pm 0.04	87.0 \pm 2.1	0.05 \pm 0.01	3.0 \pm 0.08	2.0 \pm 0.1	1.0 \pm 0.01	0.14 \pm 0.01	0.16 \pm 0.01	255.0 \pm 4.57
m 20	492.0 \pm 3.6	30.0 \pm 0.18	430.0 \pm 4.9	9.0 \pm 0.11	1006 \pm 9.04	4.0 \pm 0.07	3156 \pm 41.25	8.28 \pm 0.11	10.0 \pm 0.06	28.0 \pm 0.51	5.0 \pm 0.11	1.07 \pm 0.03	0.63 \pm 0.01	2855.0 \pm 45.71
m 21	313.0 \pm 3.74	9.0 \pm 0.7	20.0 \pm 0.1	4.0 \pm 0.02	154.0 \pm 1.37	15.0 \pm 0.13	89.0 \pm 4.27	0.21 \pm 0.01	7.0 \pm 0.14	9.0 \pm 5.13	9.0 \pm 2.32	0.25 \pm 0.04	0.27 \pm 0.01	1205 \pm 17.86
m 22	278.0 \pm 3.09	8.0 \pm 0.32	50.0 \pm 0.58	3.0 \pm 0.04	189.0 \pm 1.3	14.0 \pm 0.11	168.0 \pm 1.6	0.16 \pm 0.01	5.0 \pm 0.2	7.0 \pm 0.28	10.0 \pm 0.25	0.32 \pm 0.01	0.19 \pm 0.01	846 \pm 11.66

Table (4.14): Heavy metals concentrations in µg/L, which were detected in the harvested rainwater samples analyzed in Middle area (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 metals													
	Ba	Cu	Zn	Co	Mn	V	Al	Pb	Cr	Ni	As	Cd	U	P
Minimum	277.66	3.59	0.8	2.58	71.36	4.3	53.65	0.05	2.67	2.3	0.83	0.13	0.16	113.01
Maximum	491.61	30.37	430.32	8.8	1006.25	15.27	3155.65	8.28	9.52	28.48	10.31	1.07	1.65	2855.07
Average	383.96	10.61	97.81	4.24	336.43	11.68	986.18	2.19	5.37	10.14	4.58	0.4	0.56	1039.4
Median	382.74	8.24	34.91	3.47	171.81	13.77	128.94	0.19	5.24	8.3	3.06	0.28	0.37	904.18
SD	78.88	9.08	151.59	2.14	334.99	4.22	1275	3.14	2.34	8.81	3.83	0.32	0.51	898.26
RSD (%)	0.21	0.86	1.55	0.51	0.99	0.37	1.29	1.43	43.6	86.9	83.58	80.88	91.5	86.42
% of samples that found to contain that heavy metal	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Limits	300	2000	3000	No limit	500	No limits	200	10	50	20	10	3	30	No limits
% of samples that exceeded the limit	83	0	0	/	33	/	33	0	0	17	17	0	0	/

From table 4.14, there was a significant difference between the average and median values indicating that these water samples were different from each other in terms of heavy metals concentration according to different sources includes: (bombed, agricultures bombed area and area that hadn't targeted by any rocket).

To confirm these results, two statistical tests were done in this area on six water samples. One way ANOVA statistical analysis, results confirms that there was a variations between these heavy metals in the 6 water samples analyzed in Nussairat area. Figures (4.11), (4.12) and (4.13), show this variation for Mn, Ba and Al metals in the 6 water samples.

Results showed that Mn, Ba and Al had the highest concentration values in sample no. (m20) according to figures, (4.11), (4.12) and (4.13), this area contaminated by five rockets, which was the most sample exposed to bombing compared with other samples.

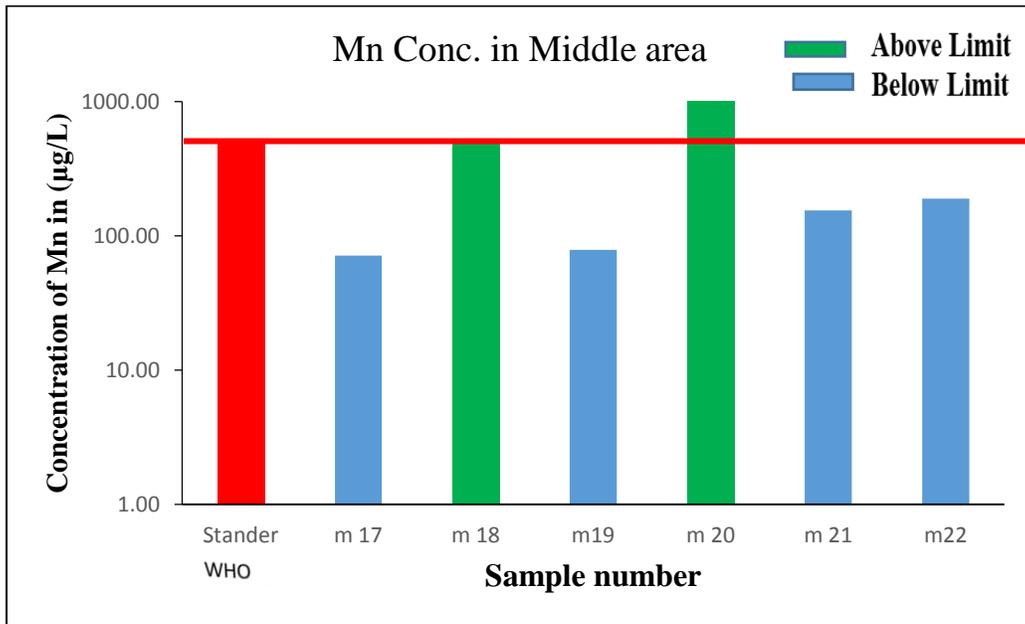


Figure (4.11): Concentration of Mn (in µg/L) vs. (WHO Stander and sample number obtained in November 2012 in Middle area.

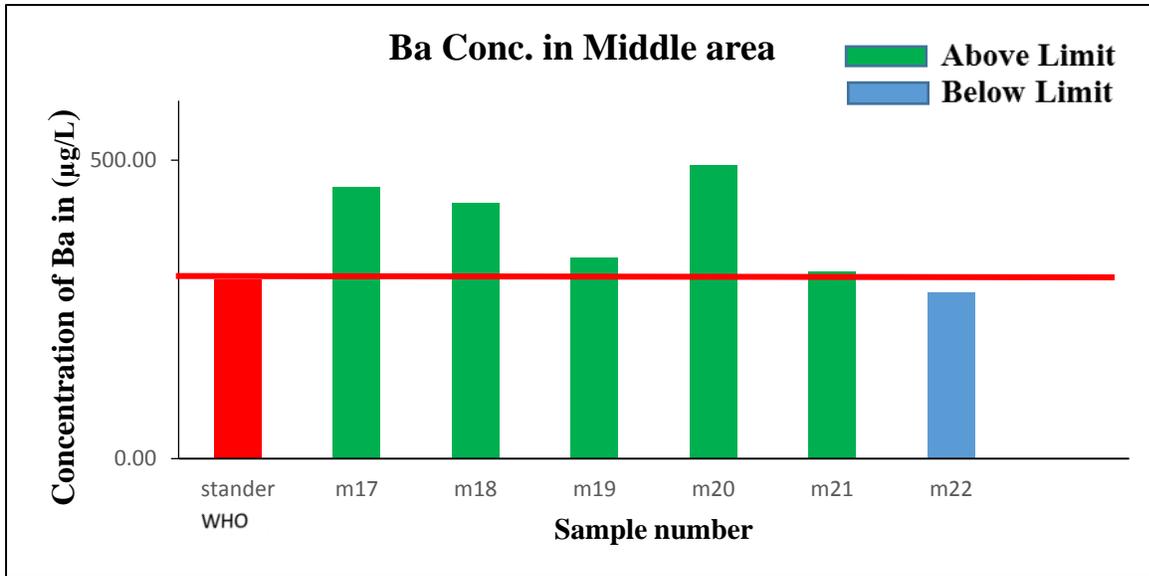


Figure (4.12): Concentration of Ba (in µg/L) vs. (WHO Stander and sample number obtained in November 2012 in Middle area.

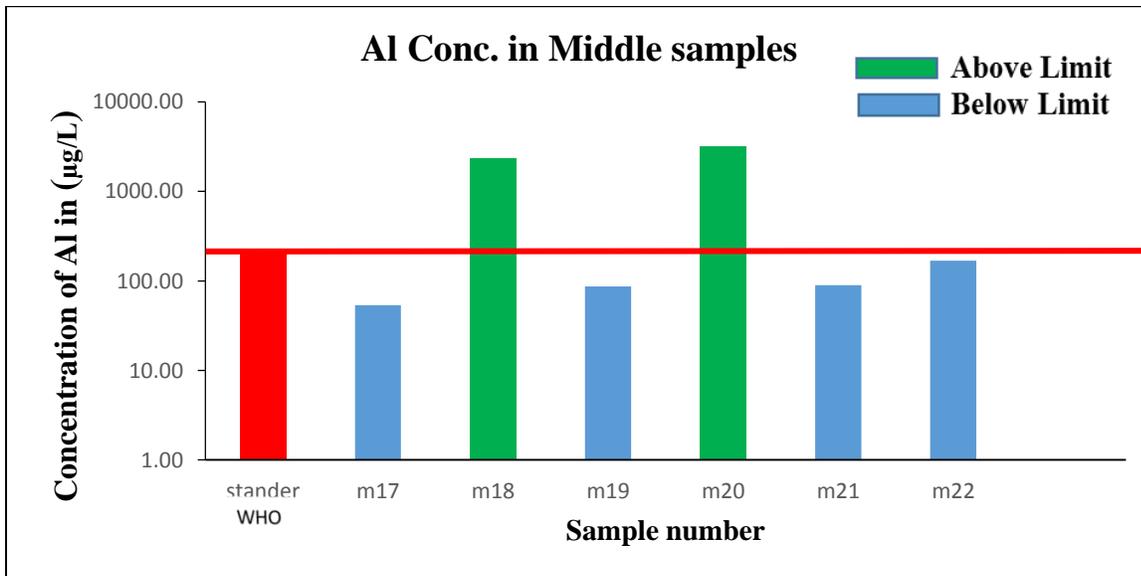


Figure (4.13): Concentration of Al (in µg/L) vs. (WHO Stander and sample number obtained in November 2012 in Middle area.

Middle area results showed that the highest percent of metals exceeded the limit of WHO, was for Barium. The allowed WHO limit is 300 µg/L, (5 out of 6), water samples have barium with concentrations higher than the allowed WHO limit, with 83% of the samples analyzed exceeded this limit.

The highest Ba concentration was found to be 491.61µg/L, with an average of 383.96 µg/L. The primary health effects in drinking water with a high concentration of soluble barium compounds over the short term may cause high blood pressure, breathing difficulties, stomach irritation, and changes in heart rhythm, muscle weakness, brain swelling, and damage to the kidney, liver, spleen and heart.

Aluminum and Manganese; were the second heavy metal important in this area with 33% of samples; that mean (2 out of 6), water samples have Al and Mn with concentrations larger than the allowed WHO limit, which is 200µg/L and 500µg/L respectively, however the highest Al concentration was found to be 3155.65µg/L in sample m20. The health hazards associated with exposure to Aluminium excess is involved in adverse effect on human health.

For Mn, the highest concentration was found to be 1006.25µg/L. Over exposure to manganese has been associated with toxicity to the nervous system which produces a syndrome that resembles Parkinson's disease. This effect is more likely to be found in the elderly. Manganese is of particular concern for young children, especially for infants who bottle-feed since some baby formulas contain manganese, and if prepared with water containing manganese, the infant receives a higher dose than the rest of the family. The young absorb more manganese than older age groups, while excreting less, so it is better for young children and pregnant women to drink water with a very low concentration of manganese (less than 500µg/L) according to WHO.

Results showed that 17% of the samples had exceeded the limit of WHO for Ni and As in drinking water, with the highest concentration of 28.48, 10.31µg/L, respectively. Regarding Cu, Zn, Pb, Cr, Cd and U the allowed WHO limits in drinking water is 2000, 3000, 10, 50, 3 and 30µg/L, respectively, results showed that these metals were found in the analyzed water samples within these limits. Co, V and P have no limits in drinking water by WHO, however these metals were detected in all water samples analyzed in the Middle area.

Phosphorous was detected in all water samples analyzed in this study with high concentrations (range of 113.01-2855.07µg/L, and average of 1039.4µg/L). The highest concentrations of

phosphorous was found in sample number 20 (sample from an area that hit by 5 rockets), which might be attributed to the white phosphorous that was used in this region bombing

4.3.1.1 Non- bombed sample in Middle area:

This included samples no. m21 and m22, in which both samples were taken from non-bombed Nussairat area. High concentrations of some heavy metals were detected in some agricultural regions of Gaza may be attributed to excessive use of pesticides in this area. It could also come from many factories that manufacture fruits canning. In addition to several factories for Concrete cement.

For example, Ba metal was detected in sample no. m21 with 313.28 $\mu\text{g/L}$ concentration and As metal was also detected for sample no. m22 with 10.31 $\mu\text{g/L}$ concentration.

4.3.1.2 Correlation between elements in Middle area

R- Program; was the second way for doing statistical analysis test in Middle area. The correlation coefficient was determined, as shown in table 4.15.

Correlation coefficient between elements in Middle area, gave a strong correlations (higher than 0.7) which is the correlation for: Al correlated with Mn, Co, Zn, Ba, Pb, Ni, Cu, Cd and P. Mn correlated with Co, Zn, Pb, Ni, Cu, Cd and P. Co correlated with Zn, Ba, Pb, Ni, Cu, Cd and p. Zn correlated with, Pb, Ni, Cu, Cd and P. Pb with Ni, Cu, Cd and P. Cr correlated with Ni, Cu and P. Ni correlated with Cu, Cd and P. Cu correlated with Cd and P. Cd with P.

Another correlation observed in Middle area which had positive middle correlation coefficient for these metals: Mn correlated with Ba and Cr. Ba correlated to Zn, Ni, Cu, Cd and U. Pb correlated with Cr. Finally Cr and Cd had positive middle correlation too. From Table 4.15, a strong negative correlation conducted between V and Zn. On the other hand, V had a middle negative correlation with Mn, Al, Co, Pb, Ni, Cu and Cd. Ba and As had middle negative correlation.

Table 4.15: Correlation between different heavy elements were determined by R program in Middle area, Gaza Strip.

	Al	V	Mn	Co	Zn	Ba	Pb	Cr	Ni	Cu	As	Cd	P	U
Al	1.00													
V	-0.52	1.00												
Mn	0.96	-0.62	1.00											
Co	0.88	-0.64	0.96	1.00										
Zn	0.85	-0.72	0.96	0.97	1.00									
Ba	0.70	-0.33	0.64	0.72	0.61	1.00								
Pb	0.98	-0.61	0.99	0.95	0.93	0.71	1.00							
Cr	0.39	-0.35	0.60	0.74	0.74	0.35	0.53	1.00						
Ni	0.86	-0.61	0.96	0.96	0.97	0.52	0.93	0.76	1.00					
Cu	0.80	-0.67	0.93	0.96	0.99	0.53	0.89	0.83	0.98	1.00				
As	-0.22	0.21	-0.04	-0.07	0.03	-0.64	-0.16	0.41	0.17	0.16	1.00			
Cd	0.93	-0.63	0.99	0.96	0.98	0.58	0.97	0.66	0.98	0.96	0.06	1.00		
P	0.79	-0.58	0.91	0.92	0.94	0.40	0.86	0.81	0.99	0.98	0.29	0.94	1.00	
U	-0.02	0.25	-0.05	0.10	0.00	0.66	0.01	0.17	-0.11	-0.04	-0.49	-0.08	0.19	1.00



Strong negative correlation



Strong correlations



Middle negative correlation



Middle positive correlation

In Middle area the correlation was dissimilar conversely to North (a) and North b. According to different sources of potential contamination from bombing and agricultures in six samples two of them were polluted from agricultures and the other samples were polluted from bombed area that was hit by different number of rockets. U and As didn't have any correlation with all heavy metals except Ba; U with Ba have a positive middle correlation, while As with Ba have a negative middle correlation. V had a negative correlation with all heavy metals; so the sources of V contamination differ than other element sources. Al had a strong positive correlation with most element except V, Cr, As and U. Co had a strong positive correlation but weak for V, As and U.

4.4 Harvested Rain Water in Southern Area

Southern area include: (Tal- AL sultan camp, Shabboura camp, Barazil camp, ALsalm camp, Yebna camp, Khan Yuen's and middle of Rafah). This area contains ten samples that had been analyzed. Different samples with different sources; collected from this area, samples (s34, s35, s36, s38, s39, s40, s41 and s42, contaminated by bombing. Bombing was varying with different number of rockets. Additionally, this area also includes two samples (s33 and s37), that were describe as not bombed area as shown in table 4.16. The pH of water samples ranged between 7.06-7.67. Electrical conductivity and total dissolved solids for water samples ranged from 340.0-2010.0 μ s/cm and 187.0-1105.5mg/L, respectively as shown in table (4.17). The limit for total dissolved solids in drinking water according to WHO is 1000 mg/L (WHO 2003), results showed that sample number s35 has exceeded the limit with 1105.5mg/L value.

Table (4.16): Description of samples in Southern area, Gaza strip.

sample no.	Sample Description
s33	not bombed area
s34	Collection of rainwater: Heavily bombed with 3 rockets
s35	Collection of rainwater : Heavily bombed area
s36	Collection of rainwater : Heavily bombed area
s37	non bombed area
s38	Collection of rainwater: Heavily bombed area
s39	Collection of rainwater : Heavily bombed area
s40	sample from an area that hit by 5 rockets
s41	sample from an area that hit by 5 rockets
s42	Collection of rainwater; middle of the camp - Heavily bombed area

Table (4.17): Analysis of pH, EC and TDS in the harvested rainwater samples in South area that were analyzed in this region.

Sample no.	pH	EC ($\mu\text{s}/\text{cm}$)	TDS (mg/L)
s33	7.60	671	369.05
s34	7.45	761	418.55
s35	7.13	2010	1105.5
s36	7.67	1397	768.35
s37	7.44	791	435.05
s38	7.46	340	187
s39	7.31	636	349.8
s40	7.28	980	539
s41	7.23	912	501.6
s42	7.06	1167	641.85

4.4.1 Heavy metals content

Southern area; results showed that eleven trace metals (Ba, Cu, Zn, Co, Mn, V, As, Pb, Cr, Ni and Al) were detected in one or more water samples analyzed (10 water samples in this study.) in different places in the southern area of Gaza Strip. Table 4.18, shows the concentrations of metals detected in the harvested rain water samples, results expressed as average \pm SD for all samples that were analyzed in different sites in Southern area.

By summarizing the concentrations of heavy metals, which were detected in the harvested rainwater samples after the November 2012, the analyzed results obtained in this area (minimum, maximum, average, median, standard deviation, and relative standard deviation). shows Table 4.19.

Table (4.18): Concentration of trace metals detected in harvested rain water analyzed in the Southern area Gaza Strip. Results expressed as Average \pm SD for samples (SD: standard deviation).

Sample no.	Concentration of metals ($\mu\text{g/L}$)													
	Ba	Cu	Zn	Co	Mn	V	Al	Pb	Cr	Ni	As	Cd	U	P
s34	142.21 ± 0.72	20.66 ± 0.45	206.75 ± 4.46	1.45 ± 0.02	96.41 ± 1.61	30.49 ± 0.39	1893.47 ± 27.18	16.73 ± 0.15	13.88 ± 0.35	7.69 ± 0.27	2.83 ± 0.07	0.35 ± 0.02	0.57 ± 0.01	286.61 ± 5.88
s35	164.26 ± 1.78	26.3 ± 0.59	272.82 ± 3.31	3.3 ± 0.04	142.3 ± 2.06	19.44 ± 0.23	2074.21 ± 22.19	13.86 ± 0.15	11.56 ± 0.27	10.63 ± 0.2	5.31 ± 0.16	0.27 ± 0.04	0.43 ± 0.01	372.27 ± 2.93
s36	200.82 ± 0.6	38.61 ± 0.51	289.27 ± 1.73	4.77 ± 0.03	169.59 ± 1.26	28.12 ± 0.19	3011.0 ± 18.62	32.16 ± 0.42	17.64 ± 0.39	12.14 ± 0.18	6.98 ± 0.17	0.41 ± 0.03	0.68 ± 0.01	453.94 ± 3.26
s37	212.93 ± 2.75	51.95 ± 0.96	474.75 ± 5.38	3.82 ± 0.06	253.96 ± 3.15	21.52 ± 0.26	2600.05 ± 35.1	98.07 ± 0.81	14.97 ± 0.33	15.67 ± 0.13	5.37 ± 0.06	0.83 ± 0.03	1.17 ± 0.08	829.14 ± 6.29
s38	325.73 ± 2.21	25.74 ± 0.36	381.87 ± 5.12	3.78 ± 0.05	317.1 ± 2.62	17.29 ± 0.18	2695.46 ± 43.41	44.56 ± 0.51	7.11 ± 0.08	9.42 ± 0.21	2.75 ± 0.07	0.75 ± 0.07	0.83 ± 0.01	914.66 ± 5.59
s39	344.92 ± 1.11	10.81 ± 0.13	4.15 ± 0.05	2.33 ± 0.01	141.48 ± 1.14	27.17 ± 0.26	40.92 ± 2.7	0.06 ± 0.01	6.27 ± 0.15	6.47 ± 0.04	6.19 ± 0.18	0.28 ± 0.01	1.50 ± 0.03	784.53 ± 7.30
s40	273.45 ± 2.49	48.5 ± 1.44	372.89 ± 4.26	6.51 ± 0.04	461.78 ± 4.25	28.68 ± 0.29	2246.33 ± 22.78	43.97 ± 0.18	9.15 ± 0.14	20.07 ± 0.72	8.13 ± 0.13	0.74 ± 0.06	1.68 ± 0.04	1650.29 ± 7.45
s41	168.37 ± 2.02	57.46 ± 0.45	146.24 ± 2.18	4.66 ± 0.05	242.34 ± 2.34	53.32 ± 0.68	2276.66 ± 17.8	10.74 ± 0.09	17.19 ± 0.33	11.43 ± 0.2	4.4 ± 0.15	0.55 ± 0.04	0.45 ± 0.01	309.9 3 ± 1.51
s42	531.16 ± 4.02	188.89 ± 3.92	1703.67 ± 13.9	8.56 ± 0.06	647.94 ± 6.8	42.09 ± 0.35	8807.74 ± 59.72	309.83 ± 2.51	31.32 ± 0.83	29.39 ± 0.81	10.64 ± 0.23	1.36 ± 0.03	2.16 ± 0.02	7390.62 ± 3.10

43	615.36	7.99	16.25	3.07	139.96	14.98	512.74	0.87	4.45	7.53	0.79	0.18	1.15	57.63
	±1.82	±0.26	±0.17	±0.01	±0.37	±0.07	±23.1	±0.01	±0.14	±0.47	±0.04	±0.04	±0.02	±2.32

Table (4.19): Heavy metals concentrations in harvested rainwater samples analyzed in Southern area, (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 ($\mu\text{g/L}$)	heavy metals												
	Ba	Cu	Zn	Co	Mn	V	Al	Pb	Cr	Ni	As	U	P
Minimum	142.21	10.81	4.15	1.45	96.41	17.29	40.92	0.06	6.27	6.47	2.75	0.43	286.61
Maximum	531.16	188.89	1703.67	8.56	647.94	53.32	8807.74	309.83	31.32	29.39	10.64	2.16	7390.62
Average	254.01	50.01	408.83	4.13	263.09	28.86	2794.39	62.72	14.13	14.06	5.86	1.01	1368.00
Median	206.88	35.23	281.04	3.80	205.97	27.64	2247.80	38.06	13.06	11.79	5.67	0.75	737.57
SD	113.58	48.33	449.36	2.04	163.69	10.61	2144.33	86.64	6.81	6.55	2.26	0.56	2043.6
RSD (%)	0.48	0.97	1.1	0.49	0.62	0.37	0.78	1.38	0.48	0.47	0.39	0.55	1.49
% of samples that found to contain that heavy metal	100	100	100	100	100	100	100	100	100	100	100	100	100
Limits	300	2000	3000	No limit	500	No limits	200	10	50	20	10	30	No limits
% of samples that exceeded the limit	30	0	0	/	0	/	90	90	0	20	10	0	/

From table 4.19, there is a significant difference between the average and median values indicating that these water samples were different from each other in terms of heavy metals concentration according to different sources, including a collection of water samples range between bombed and non-bombed area.

These results were confirmed by statistical test on all water samples in this area. One way ANOVA statistical test, results confirmed that there were variations between these heavy metals in the 11 water samples analyzed. Figures (4.14), (4.15) and (4.16), shows this variation for Al, Pb and Ni metals in the water samples.

Results showed that Al and Pb, have the highest concentrations value in sample no. s42.

Ni had the highest value for sample no. s41, according to figures, (4.14), (4.15) and (4.16). Sample s42 contaminated in the middle of the camp by heavy bombing ,while s41 was contaminated after it was hit by 5 rockets .

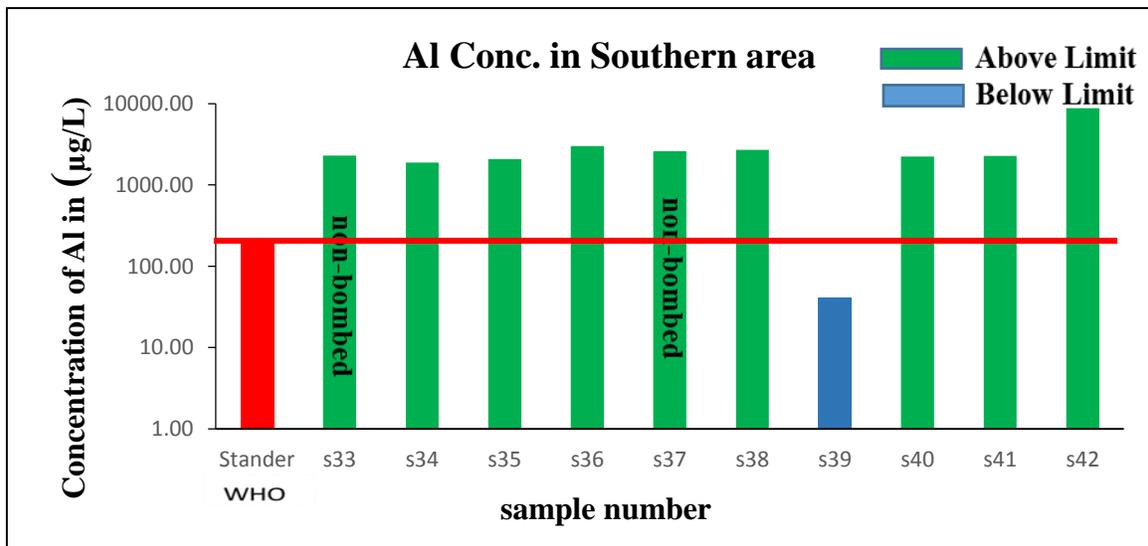


Figure (4.14): Concentration of Al (in µg/L) vs. (WHO Stander and sample number obtained in November 2012 in Southern area.

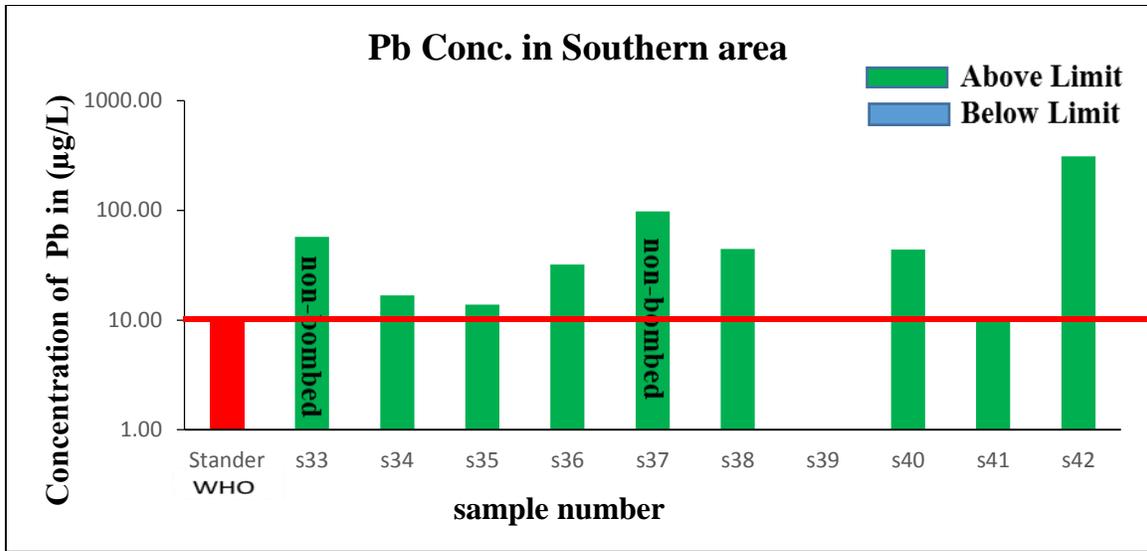


Figure (4.15): Concentration of Pb (in µg/L) vs. (WHO Stander and sample number obtained in November 2012 in Southern area.

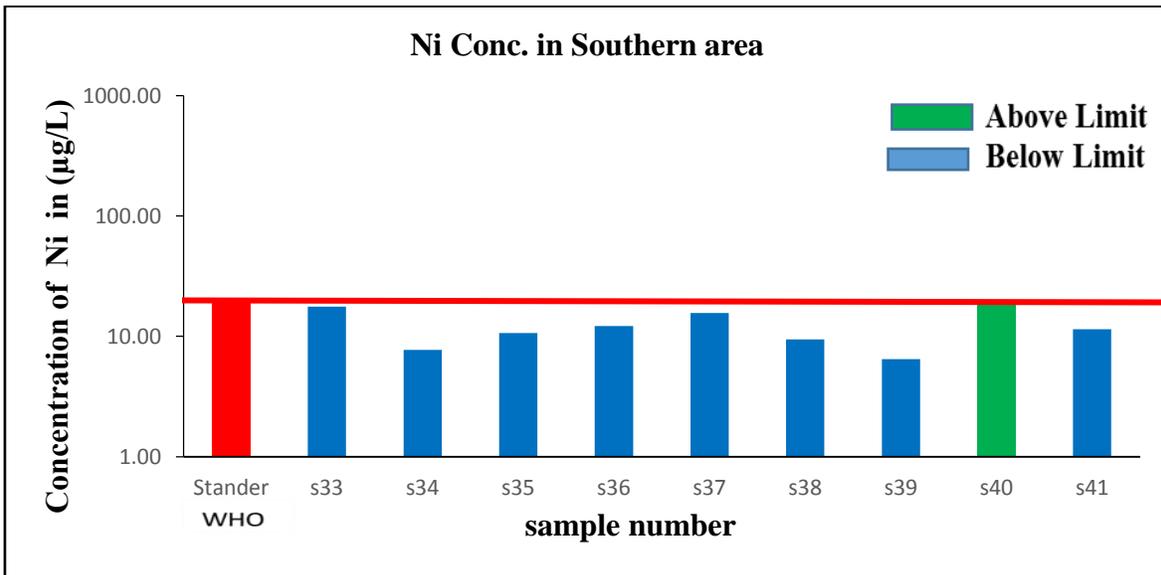


Figure (4.16): Concentration of Ni (in µg/L) vs. (WHO Stander and sample number obtained in November 2012 in Southern area.

In Southern area, results showed that Aluminum and lead, exceeded the limit of WHO, which is 200 $\mu\text{g/L}$, 10 $\mu\text{g/L}$ respectively, however, (9 out of 10) water samples have Al and Pb with concentrations higher than the allowed WHO limit, with 90% of the samples analyzed exceeded this limit. The highest Al concentration was found in sample s42 to be 8807.74 $\mu\text{g/L}$, with an average of 2794.39 $\mu\text{g/L}$, and the highest Pb concentration was found also in the same sample to be 309.83 $\mu\text{g/L}$, with an average of 62.72 $\mu\text{g/L}$.

Furthermore, results showed that the concentration of five heavy metals (Cu, Zn, Mn, Cr, and U) is within the allowed WHO limits in drinking water (2000, 3000, 500, 50 and 30 $\mu\text{g/L}$, respectively), however eleven of these metals (Ba, Cu, Zn, Co, Mn, V, Cr, Ni, As, U, P, Pb and Al) were detected in 100% of the water samples. On the other hand, the concentration of Ba, Ni, As, Pb and Al were found to be higher than the allowed WHO limits (300, 20, 10, 10 and 200 $\mu\text{g/L}$, respectively) in 30%, 20%, 10%, 90% and 90% of the water samples analyzed in this study, respectively. For Ba, the allowed WHO limit is 300 $\mu\text{g/L}$, however, (3 out of 10) water samples have barium with concentrations higher than the allowed WHO limit. The highest Ba concentration was found 142.21 $\mu\text{g/L}$. Exposure to barium is toxic to humans and animals because all water- and acid-soluble barium compounds are poisonous. When people are exposed to Ba for short periods at levels above the maximum contaminant level, they may experience gastrointestinal disturbances and muscular weakness. Additionally, Ba has the potential to cause high blood pressure when exposed to levels above the limit for long periods of time (WHO, 2004).

Co, V and P have no limits in drinking water by WHO, however these metals were detected in all water samples analyzed in Southern area. Phosphorous was detected in all water samples analyzed in this study with high concentrations (range of 286.61-7390.62 $\mu\text{g/L}$, and average of 1368.00 $\mu\text{g/L}$). These high concentrations of phosphorous were found in sample number s42 (sample from an area that was heavily bombed) the concentration of bombed was very high and heavy, it may be attributed to the white phosphorous munitions used in Gaza during the war, this area was hit with different number of missiles.

Ni and As the allowed WHO limits in drinking water is 20.0 and 10.0 $\mu\text{g/L}$, respectively, results showed that these metals have the same percent of sample which is 20% and 10% that exceeds

the limit of WHO, were found in the analyzed water sample (2 out of 10) and (1 out of 10) samples respectively only had Ni and As concentration higher than the allowed limit.

4.4.1.1 Non-bombed area in Southern area

This includes samples no. s33 and s37, which was found in (Tal alsultan camp- Rafah town and middle of Rafah) respectively. Results showed that the concentrations of some heavy metals found above the range of WHO limit, due to different sources of pollutant, which may be caused by a huge number of people working in many industrial professions. For example; Al and Pb metals were detected in samples no. s33 and s37 with (2298.13 -2600.05 $\mu\text{g/L}$) and (57. 24-98.07 $\mu\text{g/L}$) respectively.

4.4.1.2 Correlation between elements in Southern area

Second way to confirm our results by statistical analysis in southern area is, R- Program. The correlation was determined, as shown in table 4.20.

Correlation coefficient gave a strong correlations (higher than 0.7), which is the correlation for: P correlated with Al, Mn, Co, Zn, Ba, Pb, Cr, Ni, Cu and As. As correlated with Mn, Co, Pb, Ni and Cu. For Cu correlated with Al, Mn, Co, Zn, Ba, Pb, Cr and Ni. Ni correlated with Al, Mn, Co, Zn, Pb and Cr. For Cr correlated with Al, Zn, Ba and Pb. for Pb correlated with Al, Mn, Co, Zn and Ba. Ba metal correlated with Mn and Zn. Co correlated with Al and Mn. Finally Mn metal correlated with Al.

From different values conducted for some heavy metals correlation; a middle positive correlations coefficient range from (0.5 to 0.7) noted: Al correlated with Ba, As and U. V correlated with Cr and Cu. Mn correlated with Cr. also Co correlated with Ba and Cr and U. Zn correlated with As and U. For Ba correlated with Ni and As. And Cr correlated with As. Finally U correlated with Ni and Cu.

Table 4.20: Correlations between different heavy metals were determined by R program in Southern area, Gaza Strip.

	Al	V	Mn	Co	Zn	Ba	Pb	Cr	Ni	Cu	As	P	U
Al	1.00												
V	0.37	1.00											
Mn	0.80	0.35	1.00										
Co	0.78	0.47	0.92	1.00									
Zn	0.97	0.29	0.85	0.78	1.00								
Ba	0.67	0.19	0.80	0.67	0.77	1.00							
Pb	0.95	0.27	0.82	0.73	0.98	0.77	1.00						
Cr	0.89	0.59	0.57	0.66	0.83	0.44	0.83	1.00					
Ni	0.84	0.27	0.85	0.80	0.85	0.58	0.87	0.71	1.00				
Cu	0.96	0.52	0.85	0.84	0.96	0.73	0.95	0.90	0.86	1.00			
As	0.64	0.27	0.70	0.77	0.68	0.64	0.70	0.59	0.82	0.73	1.00		
P	0.92	0.36	0.87	0.79	0.96	0.87	0.96	0.77	0.84	0.95	0.76	1.00	
U	0.53	0.16	0.79	0.67	0.67	0.86	0.70	0.35	0.67	0.65	0.77	0.79	1.00

 Strong correlation
 Middle positive correlations

In Southern area, the correlation coefficient was clear conversely to other sites. Ten samples determined in this area. The source of contamination was only from bombing. Most of correlation between heavy metals was strong enough except V and U due to the different sources of heavy metals.

V didn't have a correlation with other elements except positive middle correlation with Cr and Cu. U had a strong correlation with P, As, Pb, Ba and Mn although U had positive middle correlation with Al, Co, Zn, Ni and Cu. On the other hand Cr had a strong positive correlation with Al, Zn, Ba, Ni, Cu and P. Cr had middle positive correlation with As, V, Mn and Cu. P had a strong correlation with all elements except V; due to all samples that bombed. Al had a strong correlation with Mn, Co, Zn, Pb, Cr, Cu and P.

Different between bombed area and non-bombed area in different heavy metals.

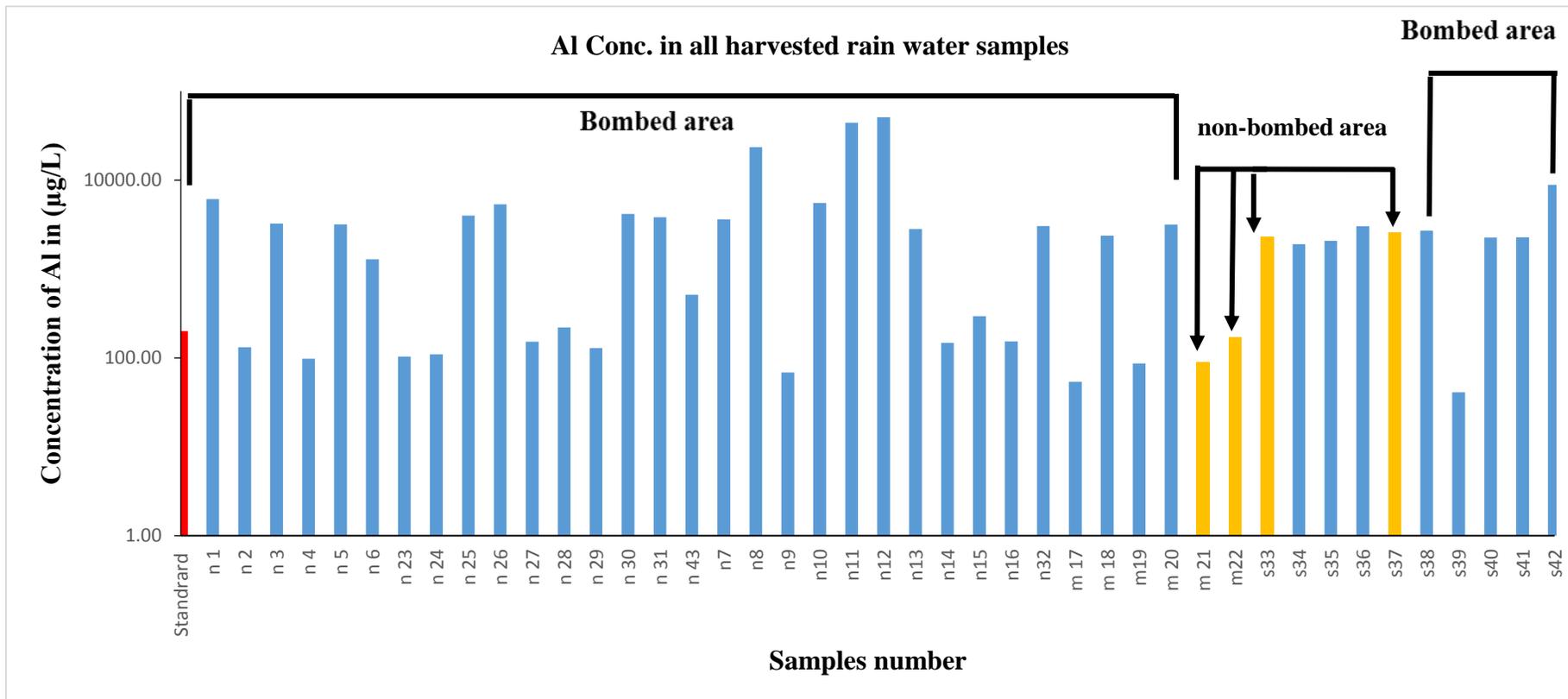


Figure (4.17): Concentration of Al (in µg/L) vs. (WHO Stander and sample number obtained in November 2012 in all water sample).

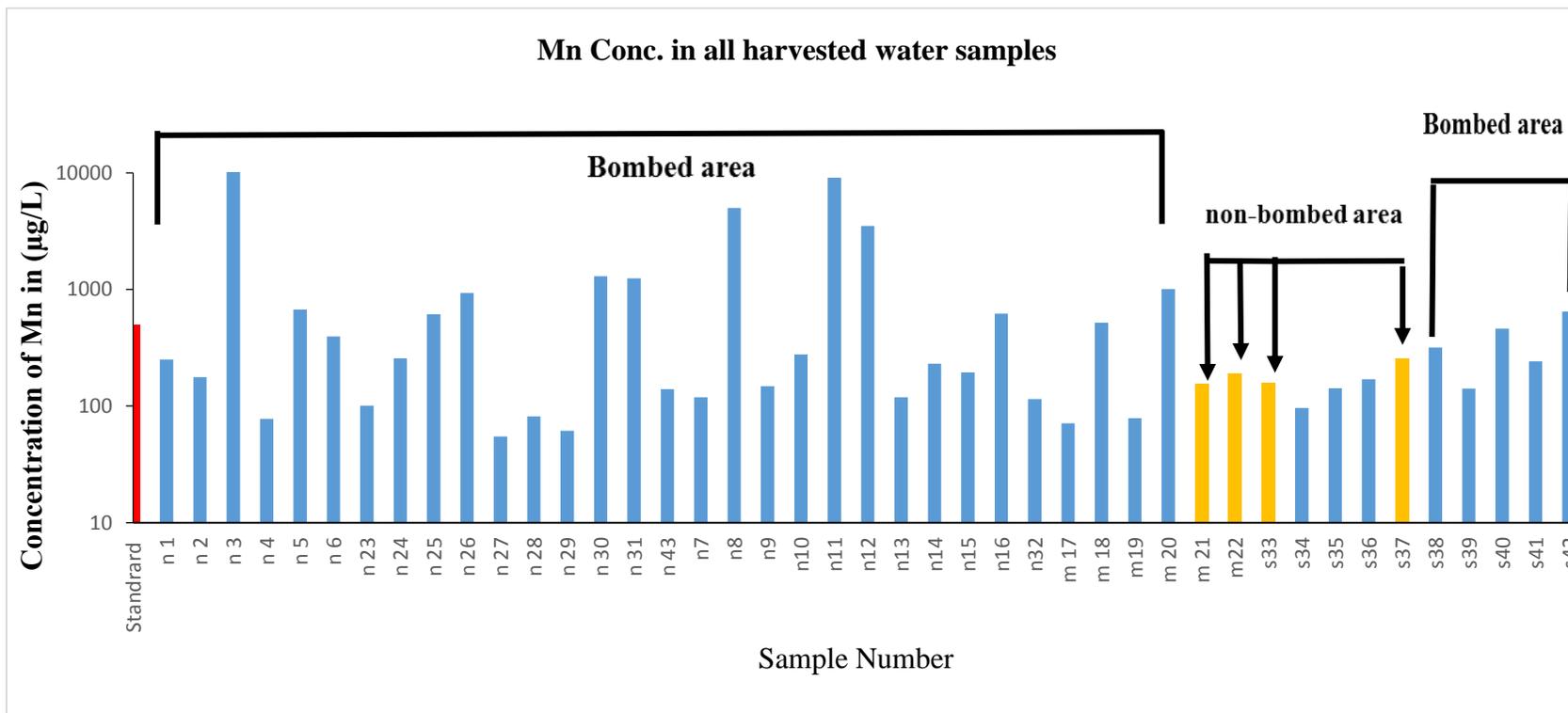


Figure (4.18): Concentration of Mn (in µg/L) vs. (WHO Stander and sample number obtained in November 2012 in all water sample).

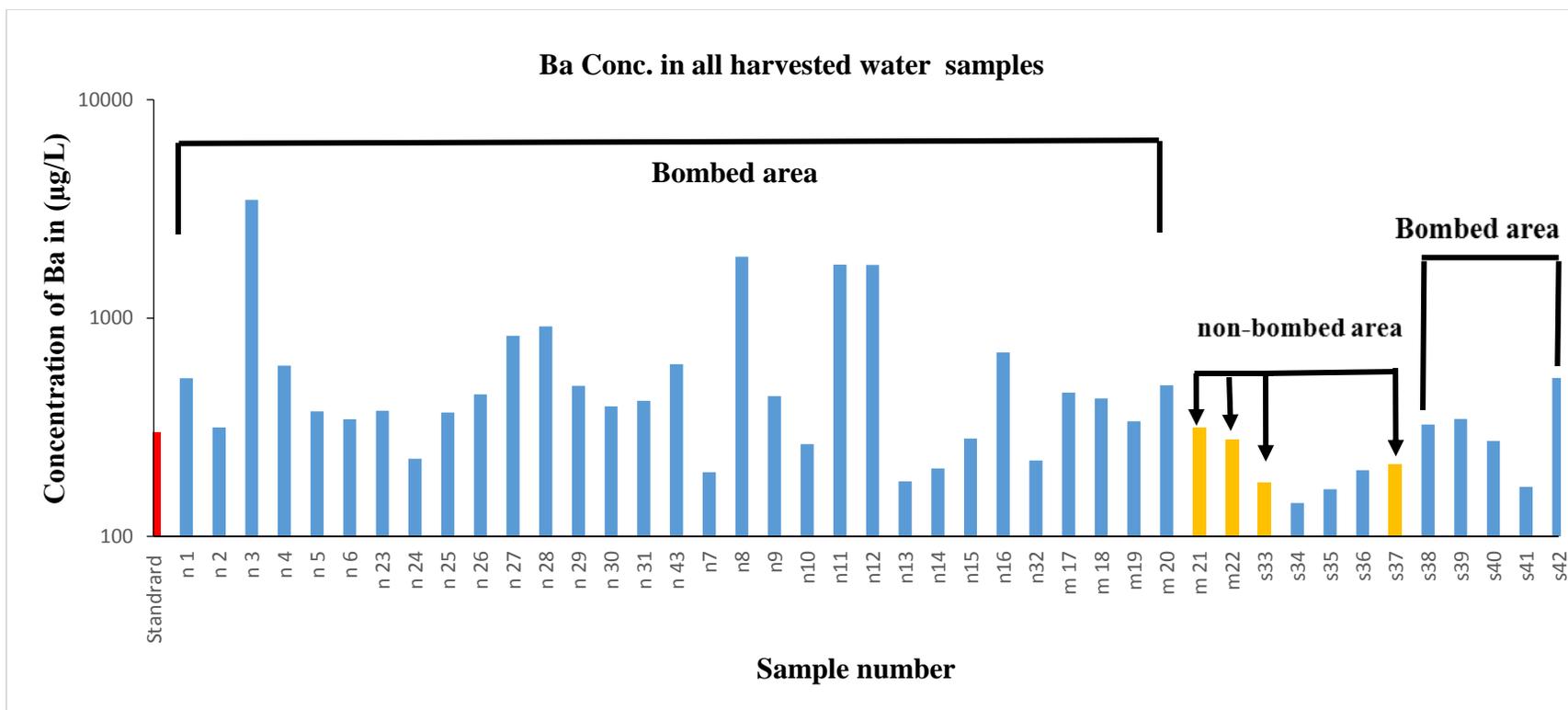


Figure (4.19): Concentration of Ba (in $\mu\text{g/L}$) vs. (WHO Stander and sample number obtained in November 2012 in all water sample).

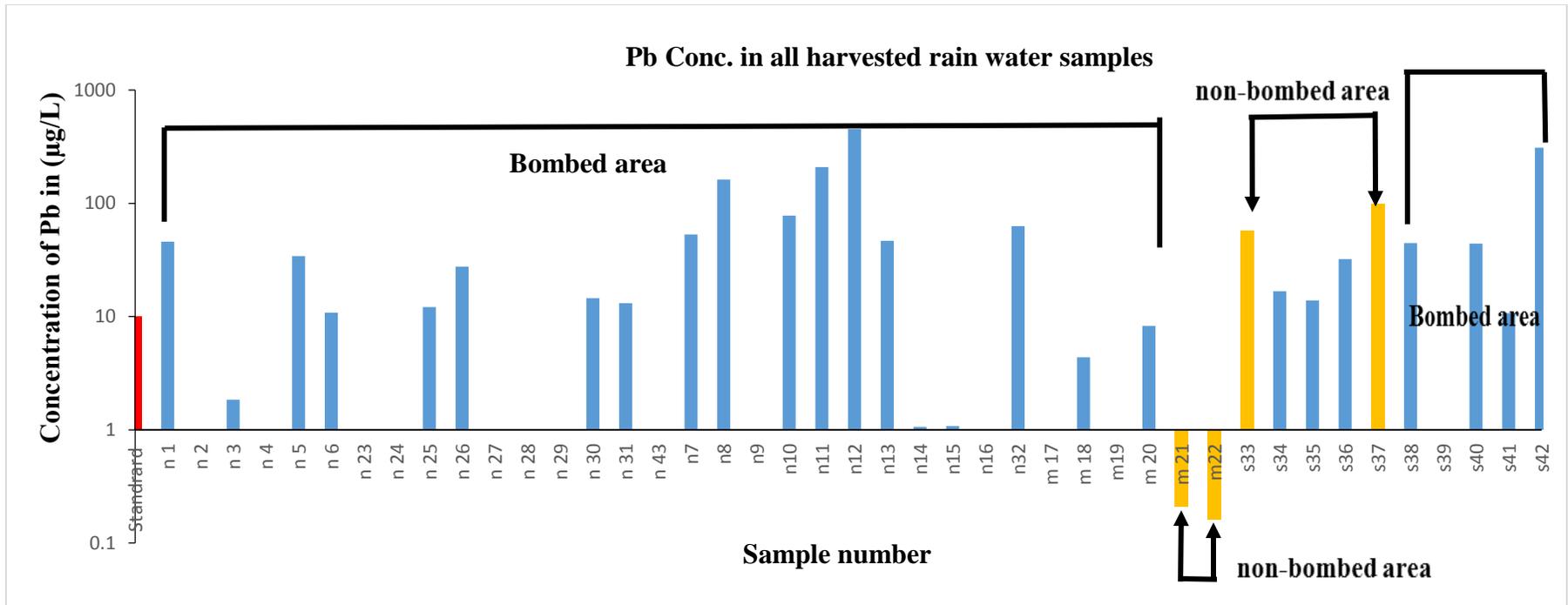


Figure (4. 20): Concentration of Pb (in µg/L) vs. (WHO Stander and sample number obtained in November 2012 in all water sample.

Chapter Five

Conclusions and Recommendations

Chapter Five

Conclusions and Recommendations

5.1 Harvested Rain Water

Harvested rainwater from bombed area of Gaza strip contains different trace metals with eight heavy metals (Ba, Mn, Al, Pb, Cr, Ni, As, Cd) exceeding the WHO limits in drinking water. pH of the waters samples is within the WHO limits, while some water samples exceed the limits for total dissolve solids and electrical conductivity. Based on the results of this study, it is believed that the bombing of Gaza in November 2012 may present one source of heavy metal and phosphorous contamination in the harvested rain water samples analyzed in this study.

However, pre-existing sources of heavy metal and phosphorus contamination resulting from agricultural or industrial practices must be taken into consideration as possible causes apart from bombing (UNEP, 2003). However other sources of waste contamination in this high populated region have not been controlled for. Uncontrolled consumption of harvested rainwater used for drinking in this region of Gaza may be dangerous for human health.

5.2 Recommendations

1. Other studies should be conducted for monitoring heavy metals in water (surface, ground...etc.) in other locations in Gaza.
2. Controlled the quality of harvested rainwater before using it for drinking in Gaza region especially in the exposed bombed areas.
3. Raising the awareness of all relevant institutions working in the fields of environmental pollution especially for bombing and discussing water treatment issues for the future is strongly recommended.

References

- Abdelmajid N., S. Hamdan, *Inter. J. of Emerg. Technology and Adv. Eng.*, 3 (2013) 316.
- 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.
- 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.
- Agilent Technologies, (2005). "ICP-MS Inductively Coupled Plasma Mass Spectrometry A Primer" Publication Number 5989-3526EN, USA.
- Aish, A., Smedt D., November (2004). *Hydro geological Study and Artificial Recharge Modeling of the Gaza Coastal Aquifer Using GIS and MODFLOW*, PhD thesis, Gaza.
- Alaani S., Tafash M., Busby C., Hamdan M., Blaurock-Busch E. (2011). Uranium and other contaminants in hair from the parents of children with congenital anomalies in Fallujah, Iraq. *Conflict and Health*. DOI: 10.1186/1752-1505-5-15.
- Al-Talmas, M., and Mogheir, Y. (2012). Risk Assessment and Mitigation of the Seawater Intrusion Using Modeling Approach, Gaza Strip. Islamic University of Gaza, Palestine.
- Amin M., Alazba 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.
- Anke M., Groppe B., Kronemann H. (1984). Significance of Newer Essential Trace elements in hair from the parents of children with congenital anomalies in Fallujah, Iraq, *Conflict and Health*, 5:15.

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

Apperson S., Shende R., Subramanian S., Tappmeyer D., Gangopadhyay S.(2007). Generation of fast propagating combustion and shock waves with copper oxide/aluminum nanothermite composites. *Appl Phys Lett*, 91:243109-11.

Applied Research Institute-Jerusalem ARIJ (2001). *Localizing agenda 21 in Palestine*.

Bakare-Odunola M. (2005). *The Nig. J. Pharm.*, 4. p.p. 51.

Barbieri M., Barbieri M., Manduca P.(2009). The Potentially Widespread Contamination of the Soil of Gaza Due To Israeli Bombing. Data of the analysis by ICP/MS of soil from 4 craters from bombing by Israel on Gaza strip in 2006 and 2009, and from the powder from an exploded WP bomb, 2009 are published in full in the <http://www.newweapons.org/>, under the title CRATERS GAZA 2006/09 and respectively WP BOMB GAZA 2009.

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.

Beyersmann D., Hartwig A. (2008). Carcinogenic metal compounds: recent insight into molecular and cellular mechanisms. *Arch Toxicol*. 82: 493–512.

Busby C., Hamdan M., Ariabi E. (2010). Cancer, Infant Mortality and Birth Sex-Ratio in Fallujah, Iraq, 2005–2009. *International Journal of Environmental Research and Public Health*.

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

D'Haeyer, T. (2000). *Net Irrigation Requirement for the Major Field Crops in the Gaza Strip*.

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.

Diaz E., Massol-Deya A. (2003). Trace element composition in forage samples from a military target range, three agricultural areas, and one natural area in Puerto Rico. *Caribbean Journal of Science* 39(2): 215-220.

Domingo J. (1994). *J Toxicol Environ Health* 42 p.p.123.

Donald B. (1999) Manganese. *Clinical Toxicology* 37 (2): 293.

Dupler D. (2001). Heavy metal poisoning. *Gale Encyclopedia of Alternative medicine*. Farmington Hills, Gale group. pp 2054-2057.

Durakovic C. (2005). The Quantitative Analysis of Uranium Isotopes in the Urine of the Civilian Population of Eastern Afghanistan after Operation Enduring Freedom. *Military Medicine*, 170(4) 277:284.

Elinder C.G., Friberg L., 1986 Cobalt in Vol. II: Specific Metals, *Handbook on the* Luke Mosley, SOPAC Water Quality Officer, WATER QUALITY OF RAINWATER HARVESTING SYSTEMS, SOPAC Miscellaneous Report 579, 2005.

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

Emsley J. (2001). Nature’s *Building Blocks: An A-Z Guide to the Elements*. Oxford, UK: Oxford University Press. pp. 249–253.

Feng M., Ryan P., Delhaize E. (2001). Aluminium tolerance in plants and the complexing role of organic acids. *Trends in Plant Science* 6 (6): 273:278.

Ferner, D. (2001). Toxicity and Heavy metals. *eMedicine Journal*, Vol. 2, No.5, pp. 1.

International Agency for Research on Cancer. (1987). Overall Evaluations of Carcinogenicity. IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Humans; Supplement 7. 440 pp. at www.iarc.fr/.

IPCS (1991) Nickel. Geneva, World Health Organization, International Program on Chemical Safety (Environmental Health Criteria 108).

Ishinishi K., Vahter M., Fowler B. (1986). Arsenic in Vol. II: Specific Metals, Handbook on the Toxicology of Metals, 2nd ed., L. Friberg et al. (editors), Elsevier, Amsterdam, Netherlands.

Jaerup L. (2003). British Medical Bulletin, 68 p.p.167.

Järup L. (2003). Hazards of heavy metal contamination. British Medical Bulletin 68: 167–82.

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.

Khalaf, A., (2005). Assessment of Rainwater Losses due to Urban Expansion of Gaza Strip.

Luke Mosley, SOPAC Water Quality Officer, WATER QUALITY OF RAINWATER HARVESTING SYSTEMS, SOPAC Miscellaneous Report 579, 2005.

Luo S., Plowman M., Hopfer S., Sunderman F. (1993). Embryotoxicity and teratogenicity of Cu^{2+} and Zn^{2+} for *Xenopus laevis*, assayed by the FETAX procedure. Ann Clin Lab Sci. 23:111–20.

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

Makhijani A., Yih K., 2000 Nuclear Wastelands: A Global Guide to Nuclear Weapons Production and Its Health and Environmental Effects . MIT Press.

Manduca P., Naim A., Signoriello S. (2014). Specific Association of Teratogen and Toxicant Metals in Hair of Newborns with Congenital Birth Defects or Developmentally Premature Birth in a Cohort of Couples with Documented Parental Exposure to Military Attacks: Observational Study at Al Shifa Hospital, Gaza, Palestine, Int. J. Environ. Res. Public Health, 11, 5208-5223.

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

Martin P. (2014). Israel Bombs Gaza Strip, Masses Army on Border. Global Research. Accessed January 12, 2016.

Massol-Deyá A., Pérez D., Pérez E., Berrios M., Díaz E. (2005). Trace Elements Analysis in Forage Samples from a US Navy Bombing Range (Vieques, Puerto Rico), *Int. J. Environ. Res. Public Health*, 2(2), 263–266.

Mengel K., Kirkby E. (1978). Principles of Plant Nutrition, International Potash Institute, Worblaufen-Bem, Switzerland.

Momodu, M. A and Anyakora, 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.

Mueller W., Bedell G., Shojaee S., Jackson P. (1995). Bioremediation of TNT Wastes by Higher Plants. Proceedings of the 10th Annual Conference of Hazardous Waste Research. Great Plains/Rocky Mountain Hazardous Substance Research Center. Overview of the Palestinian environment, Part II-C.

Palestinian Meteorological Office (PMO). (2008). Software data, Gaza, Palestine.

Qrenawi I. (2006). Environmental and health risk assessment of Al-akaidar landfill. M.Sc. Thesis, Jordan University of Science and Technology.

Reeves L. (1986). Barium, in Vol. II: Specific Metals, Handbook on the Toxicology of Metals. 2nd ed., L. Friberg et al. (editors), Elsevier, Amsterdam, Netherlands.

Research Advisory Committee on Gulf War Veterans' Illnesses, 2004 Scientific Progress in Understanding Gulf War Veterans' Illnesses: Report and Recommendations.

Roberts, H. (1999). Lead poisoning (Accessed 01-02-09). Available online at <http://www.setlet.com>.

Salnikow K., Zhitkovich A. (2008). Genetic and epigenetic mechanisms in metal carcinogenesis and cocarcinogenesis: nickel, arsenic, and chromium. *Chem Res Toxicol*. 21: 28–44.

Schröder H., Heimers A., Frentzel-Beyme R., Schott A., Hoffman W. (2003). Chromosome Aberration Analysis in Peripheral Lymphocytes of Gulf War and Balkans War Veterans. *Radiation Protection Dosimetry* 103 (3): 211–219

Siemiatycki J., Richardson L., Straif K., Latreille B., Lakhani R., Campbell S., Rousseau MC., Boffetta P. (2004). *Environ Health Perspect*, 112 p.p.1447.

Simini M., Wentzel R., Checkai R., Phillips C., Chester N., Major M., Amos J. (1995). Evaluation of soil toxicity at Joliet Army Ammunition Plant. *Environmental Toxicology and Chemistry* 14(4): 623-630.

SkaikS., Abu-Shaban N., Abu-Shaban N., Barbieri M., Barbieri M., Giani U., Manduca P. (2010). Metals detected by ICP/MS in wound tissue of war injuries without fragments in Gaza, *BMC International Health and Human Rights* 2010, 10:17.<http://www.biomedcentral.com/1472-698X/10/17>

Soazo M., Garcia G. B., 2007 Vanadium exposure through lactation produces behavioral alterations and CNS myelin deficit in neonatal rats. *Neurotoxicology and Teratology* **29** (4): 503–510.

Toxicology of Metals, 2nd ed., L. Friberg et al. (editors), Elsevier, Amsterdam, Netherlands.

UN Office for the Coordination of Humanitarian Affairs. (2009). OPT: Gaza Strip - Population Density.

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

Vidosavljević, D., Puntarić, D., Gvozdić, V., Jergović, M., Miškulin, M., Puntarić, I., Puntarić, E., Šijanović, S. (2013). Soil contamination as a possible long-term consequence of war in Croatia. *Acta Agric. Scand. Section B Soil Plant Sci.* 63, 322–329.

Vodela K., Renden A., Lenz, S., MchelHenney W., Kemppainen B. (1997). Drinking water contaminants. *Poultry Science*, Vol.76, pp. 1474-1492.

WHO. (1998) Guidelines for drinking-water quality.1.p.p. 10.

WHO. (1993) Guidelines for drinking-water quality.1.p.p. 49.

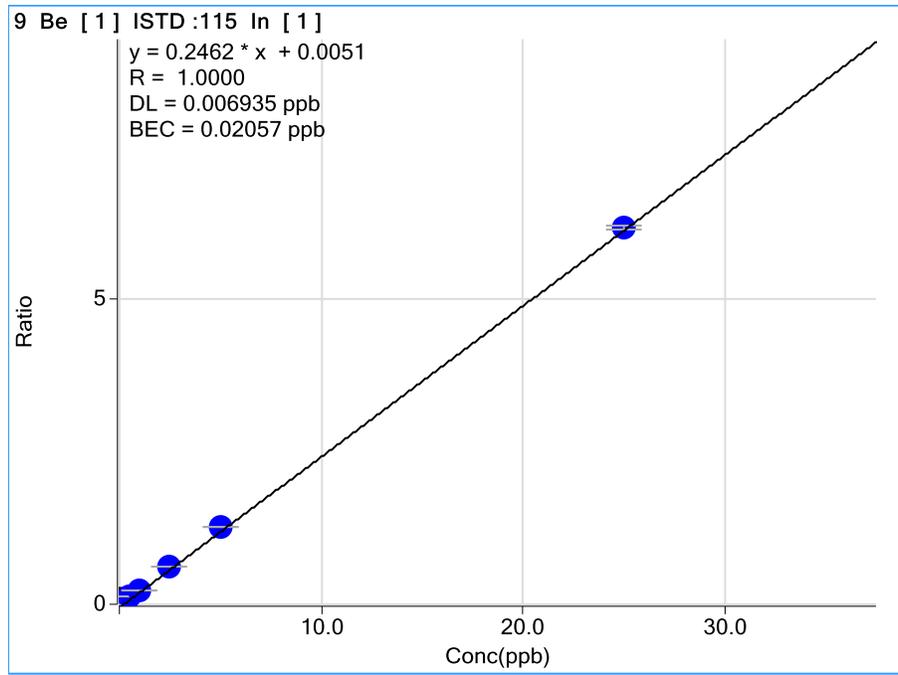
WHO. (2003). Background document for development of WHO guidelines for drinking water quality (WHO/SDE/WSH/03.04/16).

WHO. (2004). Guidelines for Drinking-water quality.1.

Yamagata N., Sigematsu I., 1970 Cadmium Pollution in Perspective, Bulletin 19:1-27, Institute of Public Health, Tokyo, Japan.

Appendix A

Calibration curve for various Barium concentration using ICP-MS.

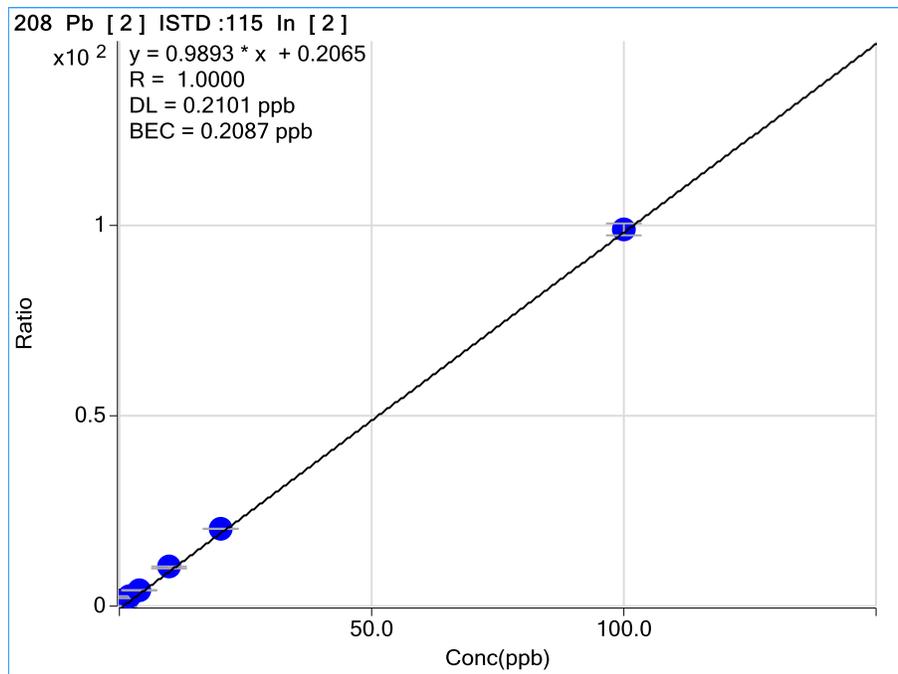


Ratio= Instrument Response (account/time)

DL : Detection Limit

BEC : background equivalent concentration.

Calibration curve for various Lead concentration using ICP-MS.

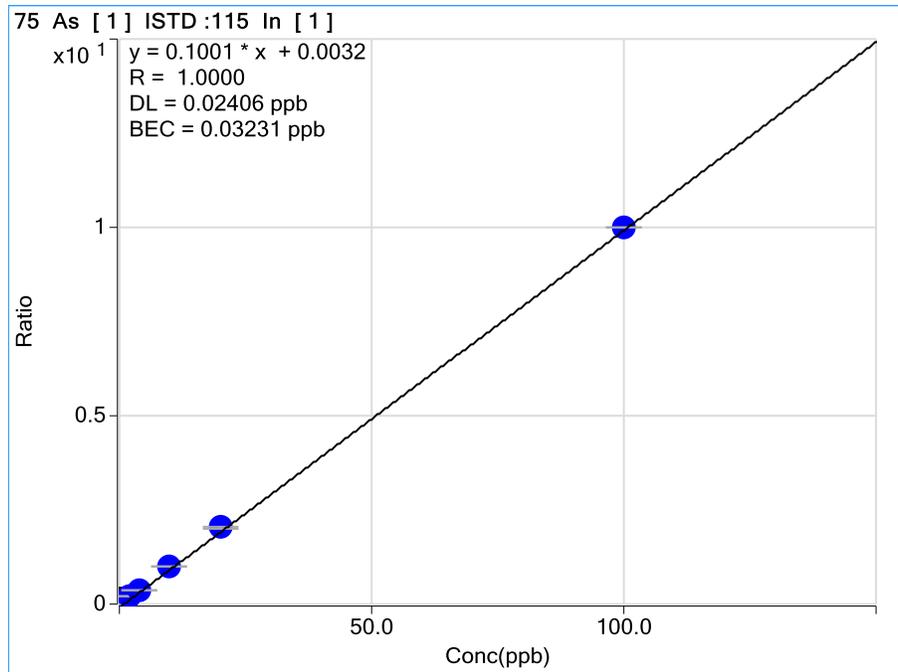


Ratio= Instrument Response (account/time)

DL : Detection Limit

BEC : background equivalent concentration.

Calibration curve for various Arsenic concentration using ICP-MS.

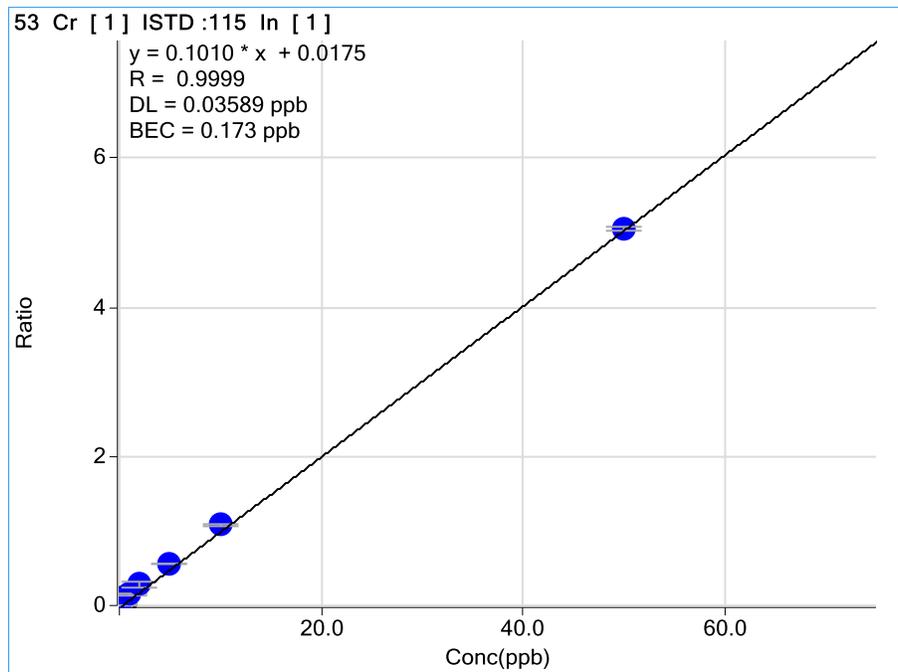


Ratio= Instrument Response (account/time)

DL : Detection Limit

BEC : background equivalent concentration.

Calibration curve for various Chromium concentration using ICP-MS.



Ratio= Instrument Response (account/time)

DL : Detection Limit

BEC : background equivalent concentration.

تقييم تلوث مياه الأمطار بالمعادن الثقيلة خلال الحرب على قطاع غزة

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الملخص:

تلوث المياه السطحية والجوفية بالمعادن الثقيلة هي أحد أهم القضايا البيئية، لأنها تعتبر سامة حتى في تراكيز منخفضة. ركزت هذه الدراسة على تقييم نوعية مياه الأمطار التي يتم استخدامها للأغراض الشرب في غزة بعد حرب 2012، وأيضاً تم تقييم النتائج الأولية لتأثير هذه القذائف من خلال فحص المعادن الثقيلة في مياه الأمطار. في هذه الدراسة تم تقسيم العينات الى أربعة مناطق في قطاع غزة (منطقة شمال غزة a ، منطقة شمال غزة b ، منطقة وسط غزة، منطقة جنوب غزة)، تم الحصول على ثلاثة وأربعين عينة في الشتاء الأول من سنة 2012، بعد ثمانية أيام من القصف. حيث تم الحصول على مختلف العينات من ثلاثة وأربعين موزعة بين أبار جمع، برك مائية و عدد من المناطق التي تم قصفها بأكثر من قذيفة تم في كل العينات قياس وتحليل درجة الحموضة، درجة الحرارة، موصلية الكهرباء، مجموع المواد الصلبة الذائبة، والمحتوي لمختلف المعادن النادرة (باريوم، نحاس، الخارصين، كوبلت، منغنيز، فاناديوم، ألنيوم، رصاص، كروم، نيكل، الزرنيخ، يورانيوم وكاديوم) بالإضافة للفسفور وذلك عن طريق مطياف الكتلة البلازمي (ICP-MS).

تم في كل العينات قياس وتحليل درجة الحموضة، موصلية الكهرباء، مجموع المواد الصلبة الذائبة، والمحتوي لمختلف المعادن النادرة. لقد وجد أن بعض عينات المياه هي ضمن الحدود المسموح بها من قبل وكالة حماية البيئة في الولايات المتحدة.

في المنطقة الشمالية (a)، أظهرت النتائج أن ثمانية عناصر ثقيلة هي باريوم، المنجنيز، الألمنيوم، الرصاص، النيكل، الكاديوم والكروم، قد تجاوزت حدود منظمة الصحة العالمية، وكانت أعلى نسبة لعنصر الباريوم في 93% من عينات 16. وعلاوة على ذلك، أظهرت النتائج أن تركيز العناصر الثقيلة ثلاثة النحاس والخاصين واليورانيوم هي ضمن المسموح به في منظمة الصحة العالمية لمياه الشرب. وكان تركيز الباريوم، الألمنيوم، الرصاص، المنغنيز، النيكل، الكروم والكاديوم أعلى من المسموح به لمياه الشرب لمنظمة الصحة العالمية في 93%، 63%، 44%، 38%، 25%، 6%، 6%، و 6% من عينات المياه التي تم تحليلها في هذه الدراسة، على التوالي. أظهرت النتائج ان تلوث المياه بالعناصر الثقيلة بتركيز عالي من المحتمل ان يكون نتيجة تعرض المنطقة والمناطق الزراعية لقصف بالصواريخ من F16، وان استخدام هذه المياه يشكل خطرا على صحة الإنسان، وخاصة عند استخدامها لأغراض الشرب والزراعة.

في منطقة شمال قطاع غزة (b)، أظهرت النتائج أن هذه المنطقة قد تلوثت باثنى عشر عنصرا وهي (باريوم، نحاس، الخاصين، كوبلت، منغنيز، فاناديوم، ألمنيوم، رصاص، كروم، نيكل، الزرنيخ وكاديوم). بالإضافة الى عنصرين الفسفور واليورانيوم، وأشارت النتائج الى ان تركيز عنصر الألمنيوم وجد في 73% من العينات، من ناحية أخرى عشرة عناصر وهي (باريوم، النحاس، كوبلت، المنغنيز، والفاناديوم، الألمنيوم، الكروم، النيكل، الزرنيخ والكاديوم) تم الكشف عنها في 100% من هذه العينات، في حين أن تركيز ثمانية عناصر وهي (الألمنيوم، الرصاص، الباريوم، المنجنيز والنيكل والكاديوم والكروم) أعلى من المسموح به في منظمة الصحة العالمية في 73%، 63%، 45%، 36%، 36%، 36%، 27% و 18% من عينات المياه التي تم تحليلها في هذه الدراسة، على التوالي. وتم اكتشاف عنصر الفوسفور أيضا في جميع عينات المياه التي تم تحليلها في هذه الدراسة مع تراكيزات عالية (تتراوح من 100.86-2467.48 ميكروغرام / لتر والمتوسط

682.22 ميكروغرام / لتر). هذه تراكيزات العالية من الفوسفور وخاصة في العينة رقم n8 (شارع بيروت، بالقرب من ساحة أبو مازن) ويمكن أن يعزى إلى ذخائر الفسفور الأبيض المستخدمة في غزة خلال الحرب. وكانت المنطقة قد تعرضت الى القصف بعدد مختلف من الصواريخ. معظم العينات في هذا المنطقة والتي قد تكون ملوثة تعرضت الى القصف بثمانية إلى تسعة صواريخ، وهذا هو خطر جدا على صحة الإنسان بسبب قربها على المباني السكنية.

في وسط قطاع غزة (منطقة النصيرات)، أظهرت النتائج أن اثني عشر عنصرا ثقيلًا وهي (باريوم، نحاس، الخارصين، كوبلت، منغيز، فاناديوم، ألمنيوم، رصاص، كروم، نيكل، الزرنيخ وكادميوم) تم الكشف عنها في جميع عينات المياه التي تم تحليلها. وعلاوة على ذلك أظهرت النتائج أن أعلى نسبة من العينات التي تجاوزت حدود منظمة الصحة العالمية المسموح بها كانت لعنصر الباريوم، في 83% من العينات التي تم تحليلها في هذه المنطقة. من ناحية اخرى اثني عشر عنصرا ثقيلًا (باريوم، نحاس، الخارصين، كوبلت، منغيز، فاناديوم، ألمنيوم، رصاص، كروم، نيكل، الزرنيخ وكادميوم) تم الكشف عنها في 100% من عينات المياه التي تم تحليلها. وعثر على ست عناصر ثقيلة وهي (النحاس، الخارصين، الرصاص، الكروم والكادميوم واليورانيوم) في عينات المياه في النطاق المسموح فيه. عنصر الفوسفور أيضا تم الكشف عنه في جميع عينات المياه التي تم تحليلها في هذه المنطقة مع وجود تراكيزات عالية (تتراوح من 113.01-2855.07 ميكروغرام / لتر، وبمعدل 1039.4 ميكروغرام / لتر). تم العثور على أعلى نسبة من الفوسفور في العينة رقم m20 (عينة من المنطقة التي تم قصفها ب 5 صواريخ) يمكن أن يعزى إلى ذخائر الفسفور الأبيض المستخدمة في هذه الحرب ضد غزة. وتعرضت هذه المنطقة أيضا للقصف بعدد مختلف من الصواريخ.

في جنوب قطاع غزة ، أظهرت النتائج أن احدى عشر عنصرا ثقيلًا وهي (باريوم، نحاس، الخارصين، كوبلت، منغنيز، فاناديوم، الزرنيخ، رصاص، كروم، نيكل والألمنيوم) تم الكشف عنها في جميع عينات المياه التي تم تحليلها. أعلى نسبة من العينات التي تجاوزت حدود منظمة الصحة العالمية المسموح بها كانت لعنصر الألمنيوم والرصاص بنسبة 90% من العينات. علاوة على ذلك أظهرت النتائج أن تركيز العناصر الثقيلة وهي: (الألمنيوم، الرصاص، باريوم، نيكل والزرنيخ) تجاوزت الحد المسموح به حسب منظمة الصحة العالمية بنسبة 90%، 90%، 30% و 20% و 10% على التوالي. ومن ناحية أخرى وجد أن تركيز كل من: (باريوم، نحاس، الخارصين، كوبلت، منغنيز، فاناديوم، كروم، نيكل، الزرنيخ، يورانيوم، فسفور، رصاص والألمنيوم)، تم الكشف عنها في 100% من عينات المياه. عنصر الفوسفور أيضا تم الكشف عنه في جميع عينات المياه التي تم تحليلها في هذه المنطقة مع وجود تراكيزات عالية (تتراوح من 286.61-7390.62 ميكروغرام / لتر). تم العثور على أعلى نسبة من الفوسفور في العينة رقم 42S(عينة من منطقه مقصوفة بعدد كبير من الصواريخ) ، حيث كان القصف في منطقة العيوق ثقيل وعنيف.

علاوة على ذلك ، تعد تراكيز جميع العناصر الثقيلة التي تم جمعها من مياه الأمطار بمختلف المناطق تتفاوت تفاوتًا كبيرًا بين 43 عينة المياه. جميع العناصر تم الكشف عنها في جميع العينات من خلال هذه الدراسة.