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## **Soil and Rubble Pollution with Heavy Metals in the Gaza strip**

**MSc. Thesis By**

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**Ministry of Agriculture**

**A Thesis Submitted in Partial Fulfillment of the Requirements for  
the Degree of Master in Water and Environmental Studies**

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## **ABSTRACT**

In the last escalation of hostilities in Gaza (2014), about 36,000 tons of artillery shells (AS) and air force bombs (AFB) were dropped on Gaza Strip from 7<sup>th</sup> of July to 28<sup>th</sup> of August. As a result of using such massive amount of munitions 7,473 impact craters in agricultural and non-urbanized areas were recognized, as well as, two million tons of buildings rubbles were produced. Forty-five top soil and five rubble multi-increment composite samples were collected using systematic-random system from targeted soils and households, as well as 10 control, and two bar samples were collected from untargeted agricultural and isolated areas respectively, to assess the impact of the military activities on soil and rubbles pollution by metals in targeted locations. Digestion of samples was performed using Strong Acid Leachable Metals (SLAM) digestion method. Concentrations of Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn were detected using atomic absorption spectrometer (AAS), while concentration of aluminum was detected using UV/VIS Spectrophotometer. Soil properties (Soil texture, CEC and pH) were measured in order to predict the behavior of the metals in the soil profile of the targeted areas. The soil samples were grouped into categories. The T-test was used to compare the mean concentration of each metal among the different categories of soil in order to investigate the different aspects of the effect of the military activities on targeted soils. The mean concentration of the bar samples was considered as a normal limit of the natural contribution of the environment while, the mean concentration of the control samples was used as a normal limit for agricultural activities. The result showed that, the agricultural activities enriched the Gaza soils with, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn, while the content of Al is likely to be affected by the environmental contribution. Although military activities introduced significant amounts of Cd, Co, Cr, Cu, Mn, Ni, and Al in targeted soils, only Cd in (26.67%) and Cr in (20%) of the targeted soil samples were found with concentrations higher than the MACs of Chemical Constituents in Uncontaminated Soil listed by USEPA. The metals contents in targeted soil samples were not affected by the used type of munition (AFB and AS) except for Cu, where its content in samples collected from areas subjected to AS is significantly higher than that of samples collected from areas subjected to AFB. Although, the high sand content, as well as the low CEC values of Gaza soils increase the possibility of downward migration of metals in soil profile via soil solution, the slightly alkaline to moderately alkaline values of the soil pH decrease this possibility. Accordingly, relevant institutions should establish research programs to investigate the fate of metals and other explosive residuals in deep soil, groundwater and plants, as well as soil and rubble

contamination with other metals, explosive residuals and radioactive materials should be investigated. The results also revealed that, in terms of the investigated metals, rubble can be used in construction purposes or as a filling material without any restrictions, since their concentrations in rubble samples are lower than MACs of Chemical Constituents in Uncontaminated Soil Used as Fill Material listed by USEPA.

## ملخص الدراسة

اثناء الحرب الأخيرة على قطاع غزة تم القاء 36,000 طن من قذائف المدفعية والقنابل التي القتها الطائرات وذلك في الفترة منذ السابع من تموز وحتى الثامن والعشرون من أغسطس لعام 2014. وقد تسبب هذا الاستخدام المفرط للذخيرة في حدوث 7,473 حفرة في المناطق الزراعية والغير سكنية بالإضافة الى انتاج 2 مليون طن من مخلفات البناء، ولتقييم أثر الأنشطة العسكرية على تلوث التربة ومخلفات البناء بالمعادن في المناطق المستهدفة تم جمع 45 عينة تربة من المناطق التي تعرضت للقصف و 5 عينات من مخلفات البناء بالإضافة الى 10 عينات تربة ضابطة من المناطق الزراعية وعينت تربة من مناطق معزولة (Bar). هذا وقد تم هضم العينات باستخدام طريقة (Strong Acid Leachable Metals) ومن ثم تحديد تراكيز كل من الكاديوم والكوبالت والكروم والنحاس والمنجنيز والنيكل والرصاص والزنك باستخدام جهاز مطياف الامتصاص الذري بينما تم تحديد تركيز الألمنيوم في العينات باستخدام جهاز (UV/VIS Spectrophotometer) وبالإضافة الى ذلك تم قياس كل من قوام التربة والسعة التبادلية الكاتيونية والحموضة للتربة من اجل التنبؤ بسلوك المعادن عبر مقاطع التربة في المناطق المستهدفة.

تم تصنيف عينات التربة الى فئات، ومن ثم تم استخدام اختبار (ت) لمقارنة متوسط التراكيز لكل عنصر بين فئات التربة المختلفة من اجل التحقق من الجوانب المختلفة لتأثير الأنشطة العسكرية على التربة المستهدفة، حيث تم اعتبار متوسط التراكيز لعينات التربة المعزولة على انه الحد الطبيعي للمشاركة البيئية بينما اعتبر متوسط تراكيز العينات الضابطة على انه الحد الطبيعي للأنشطة الزراعية.

وقد أظهرت النتائج ان الأنشطة الزراعية قد ساهمت في زيادة تراكيز كل المعادن موضوع الدراسة في التربة الزراعية باستثناء الألمونيوم حيث ان تركيزه قد تأثر بالمساهمة البيئية، وقد أظهرت الدراسة أيضا انه على الرغم من ان الأنشطة العسكرية قد ساهمت في رفع تراكيز كل من الكاديوم والكوبالت والكروم والنحاس والمنجنيز والنيكل والألمونيوم في عينات التربة المستهدفة الا ان جميع التراكيز كانت تحت المستوى الذي قرره وكالة حماية البيئة الامريكية باستثناء تركيز الكاديوم في 12 عينة والكروم في 9 عينات. وقد بينت النتائج ان تراكيز المعادن في التربة لم تتأثر بنوعية الذخيرة المستخدمة باستثناء النحاس حيث كان متوسط تركيزه في المناطق التي تعرضت للقصف المدفعي اعلى منه في المناطق التي تعرضت لقنابل الطائرات.

على الرغم من ان كل من محتوى الرمل العالي والقيم المتدنية للسعة التبادلية الكاتيونية للتربة في قطاع غزة تزيد من احتمالية رشح المعادن الى التربة العميقة عبر محلول التربة الا ان حموضة التربة في قطاع غزة والتي تتراوح بين قليلة القلوية الى عالية القلوية تقلل من هذه الاحتمالية ولهذا توصي الدراسة

بان تقوم المؤسسات المعنية بإنشاء برامج لمتابعة محتوى المعادن في التربة العميقة والمياه الجوفية وكذلك للتحقق من احتمالية تلوث التربة ومخلفات البناء ببقايا المتفجرات والمواد المشعة ومعادن أخرى. وقد بينت الدراسة أيضا انه فيما يتعلق بالمعادن موضوع الدراسة فانه يمكن إعادة استخدام مخلفات البناء في عمليات البناء او الردم حيث ان تركيز هذه المعادن فيها تحت المستوى المقرر من وكالة حماية البيئة الامريكية.

## **DEDICATION**

*I dedicate this work to:*

*My kind and caring parents for their love, pray, and  
continuous sacrifices...*

*My loving wife and children, Lana, Ali, and Mohammed*

*My brothers and sisters*

*Emad Abu Krayem*

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## **LIST OF ABBREVIATIONS**

AAS	Atomic Absorption Spectrometry
AFB	Air Force Bombs
Al	Aluminum
ARIJ	Applied Research Institute - Jerusalem
AS	Artillery Shells
ASQG	Agricultural Soil Quality Guidelines
ATSDR	Agency for Toxic Substances and Disease Registry.
BGL	Background levels
CCME	Canadian Council of Ministers of Environment
CEC	Cation Exchange Capacity
CLAWR	Cold Lake Air Weapon Ranges
CMWU	Coastal Municipalities Water Utility
DNT	Dinitrotoluene
EDTA	Ethylenediaminetetraacetic acid
g	Gram
HEs	High Explosives
HMP	Hexametaphosphate
HMX	1,3,5,7-Octahydro-1,3,5,7 tetranitrotetrazocine
IARC	International Agency for Research on Cancer
IQ	Intelligence Quotient
ISQG	Industrial Soil Quality Guidelines
LFCA TC	Land Force Central Area Training Center
MAC	Maximum Allowable Concentrations
meq	Milliequivalent
ml	Milliliter
mm	Millimeter
N	Normality
NC	Nitrocellulose
NG	Nitroglycerin
nm	Nanometer
NQ	Nitroguanidine
NTP	National Toxicology Program

NWRC	New Weapon Research Committee
OCHAOPT	United Nations Office for the Coordination of Humanitarian Affairs Occupied Palestinian Territor
PCBS	Palestinian Central Bureau of Statistics
PWA	Palestinian Water Authority
RDX	1,3,5 Hexahydro-1,3,5-trinitrotriazine or Research Development Explosives
rpm	Round per minute
SLAM	Strong Acid Leachable Metals
TNT	2,4,6-Trinitrotoluene
UNEP	United Nations Environment Program
UNITAR	United Nations Institute for Training and Research
USA	United States of America
USEPA	United States Environmental Protecting Agency
UV/VIS	Ultraviolet-Visible
V	volume
W	weight
WWI	World War I

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# **CHAPTER ONE: INTRODUCTION**

## **1.1 Background**

Military activities during conflicts and training as well as improper management and disposal practices of energetic compounds involved in ammunition lead to high levels of environmental contamination. This contamination threatens not only humans but also all forms of life and ecosystems. In the United States of America (USA) alone, about 50 million acres are affected by military training activities including bombing as well as thousands of military sites are listed as polluted by energetic materials. This kind of contamination is not limited to USA; actually, it extends to cover greater areas in Europe and Asia (Pichtel, 2012). Explosive contamination always coupled with heavy metals contamination (Thiboutot et al., 2003).

In the last decade, Israeli occupation forces dropped thousands of tons of munition on Gaza Strip during frequent escalations of hostilities and incursions. These huge amounts of munition introduced significant amounts of many hazardous materials such as heavy metals to Gaza soil.

Heavy metals are metallic elements that characterized by its relatively high density (atomic density greater than 4g/cm<sup>3</sup>, or 5 times or more, greater than water) as well as they considered to be poisonous or toxic even at low concentration. When agricultural soils are polluted with heavy metals, they will accumulate in the plants growing in these soils. Animals that graze on the polluted plants will accumulate the heavy metals in their tissues and milk. All living organisms, living in such ecosystem including humans, that depend on these contaminated plants and animals in their food are also subjected to toxicity with heavy metals (Duruibe et al., 2007). If leaching from soil, heavy metals pollute groundwater specially in the case of acidic soil, since the mobility of these metals is increased in soil with low pH (Shomar, 2006). As heavy metals enter the human body by food, water or air they expose a great human health risk as they bio-accumulated in the body. The nature of heavy metals could be toxic (acute, chronic or sub chronic), neurotoxic, carcinogenic, mutagenic or teratogenic (Duruibe, et al., 2007).

Toxicity with heavy metals usually has very general symptoms, such as weakness or headache, which make the diagnoses in a clinical setting very difficult. The toxicity of metals commonly cause brain and kidney damage but some metals, such as arsenic, are clearly capable of causing cancer. Chronic exposure to lead at a high enough level cause chronic

toxicity effects such as hypertension, while exposure to such level of cadmium cause renal toxicity (McCally, 2002). Occupational exposure to a finely powdered metallic aluminum used in paints, explosives, and fireworks lead to death in some cases (ATSDR, 2008).

These metals are used in the casing, ignition system or explosive charge of the munitions (Thiboutot, et al., 2003). The concentrations of most common metals used in the casing of bombs used by USA army are iron (93%), aluminum (5%), copper (2%) and manganese (2%). Chromium, molybdenum, nickel, and titanium as well as boron (which is semimetal) also found in the bomb casing in lower percentage less than 0.02% (ATSDR, 2013). Trace amounts of, antimony, barium, cadmium, calcium, chromium, copper, lead, mercury, nickel, potassium, sodium, titanium, and zinc were found in explosive charges used by US army, while the predominant metal in explosive charges is aluminum, which accounted for as much as 21% of the explosive charge in some live bombs (Campbell et al., 2003).

Agricultural activities also pollute the soil with many heavy metals. The main sources of heavy metals contamination in agricultural soils include the application of pesticides and fertilizers, which contain considerable amounts of heavy metals (Su et al., 2014).

## **1.2 Problem Statement**

Gaza Strip is one of the most densely populated areas in the world. About 1.88 million inhabitants live in 365 km<sup>2</sup> (PCBS, 2016). During the last decade, Gaza Strip was subjected to frequent escalation of hostilities and incursions. Accordingly, a significant environmental footprint has developed in Gaza Strip. In the escalation of hostilities 2008 - 2009 about 2,692 buildings were completely destroyed or severely damaged. Roads and agricultural areas also were subjected to bombing. 120 Impact craters in roads and bridges as well as other 700 impact craters were revealed in open and agricultural areas. In addition to that, 180 greenhouses were destroyed in this escalation of hostilities (UNEP, 2009).

According to the research carried out by New Weapon Research Committee (NWRC), high levels of toxic material was detected in carters produced by bombing the agricultural areas of Gaza Strip. Two soil samples were collected from carters from Beit Hanoun city and Jabalia camp in July, 2006, and other two samples were collected from carters in Al Tufah, Gaza city in January 2009. The results of the samples showed high levels of contamination of Tungsten, mercury, Molybdenum, Cadmium, Cobalt, Nickel, manganese, copper, strontium and zinc. In January 2009, a sample was collected from powder inside a 155 mm white phosphorous artillery shell. High concentrations of aluminum, mercury, tungsten, nickel, cobalt, tin, lead,

uranium, lithium, boron, chrome, manganese, copper, zinc, arsenic, and cadmium were detected in the powder inside the artillery shell (NWRC, 2009).

Agricultural activities such as application of fertilizers, fungicides, sludge and wastewater have played a major role and enriched the agricultural soils of Gaza Strip with several metals such as Zn, Pb, Cu and Fe (Shomar et al., 2004).

### **1.3 Justification**

The last escalation of hostilities in Gaza (2014) is the most intensive and barbarian one, since the beginning of the Israeli occupation of 1967. This escalation of hostilities surpassing the length and severity of the escalation of hostilities of 2008-2009. Israeli occupation forces used thousands of tons of ammunition (ARIJ, 2014). About 36,000 tons of artillery shells (AS) and air force bombs (AFB) were dropped on Gaza Strip (Al-Najar et al., 2015).

As a result of using such massive amount of munitions about 44,300 housing units in Gaza Strip were affected. A total of 180,000 housing buildings were subjected to completely destruction or severe damage (OCHAOPT, 2014a). Accordingly, two million tons of rubbles were produced and 108,000 people became homeless (OCHAOPT, 2015). As well as 7,473 impact craters in agricultural and non-urbanized areas were recognized by United Nations Institute for Training and Research UNITAR's Operational satellite Applications Programme (UNOSAT) as shown in figure 1.1 (UNITAR, 2014). Since the heavy metals are a part of the munitions used to destroy the housing units and cause craters in agricultural and non-urbanized areas, it is expected that soil and rubble of affected areas are polluted with heavy metals.

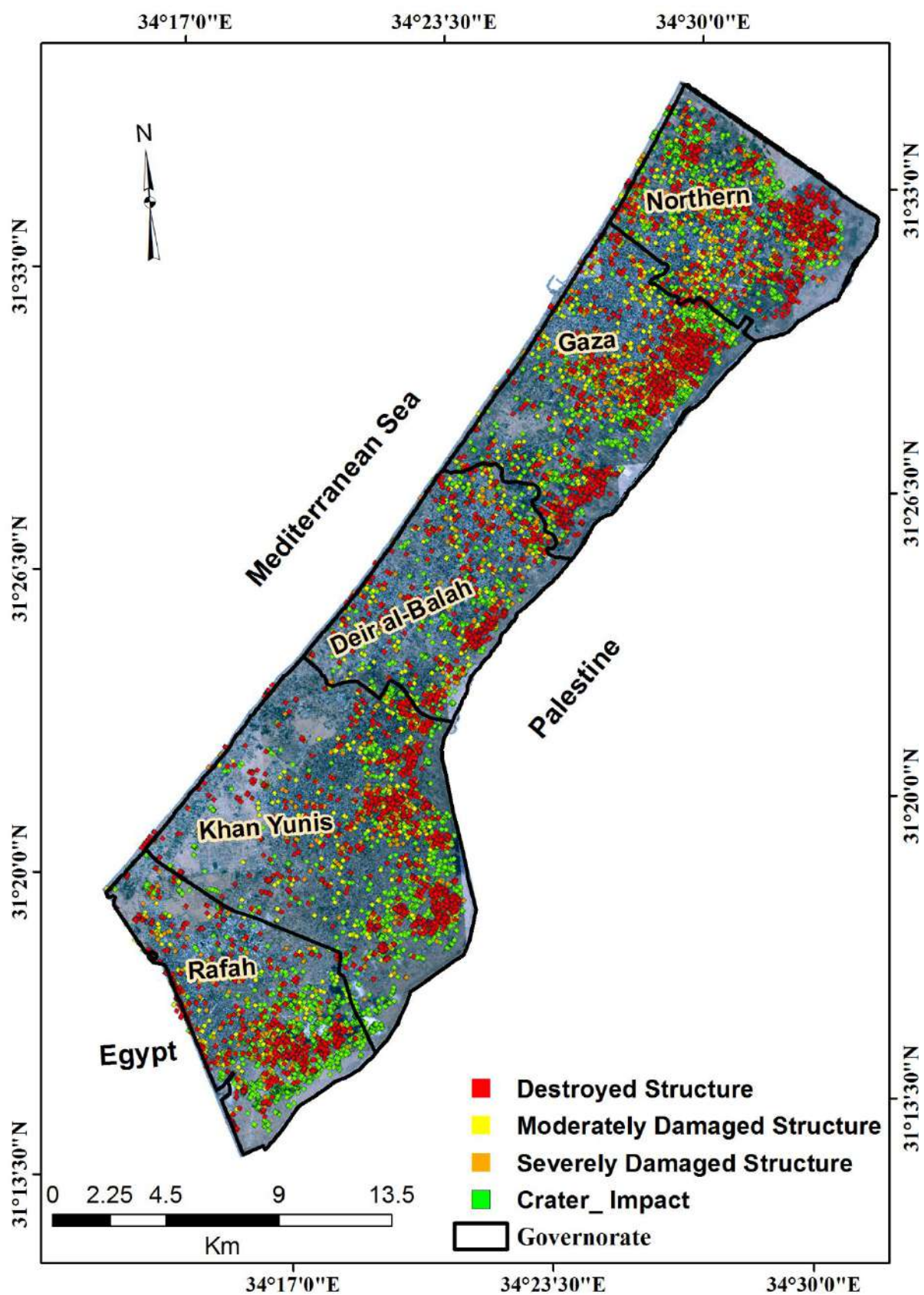


Figure 1.1: Satellite damage analysis (modified after: (OCHAOPT, 2014b))

## 1.4 Study area

Gaza Strip is located on the south-eastern coast of the Mediterranean Sea, between longitudes  $34^{\circ} 2''$  and  $34^{\circ} 25''$  east, and latitudes  $31^{\circ} 16''$  and  $31^{\circ} 45''$  north. The area of Gaza Strip is about  $365 \text{ km}^2$  and its length is approximately 45 km along the coastline. It has a 11km border with Egypt, near the city of Rafah, and a 51km border with Israel (Figure 1.2).

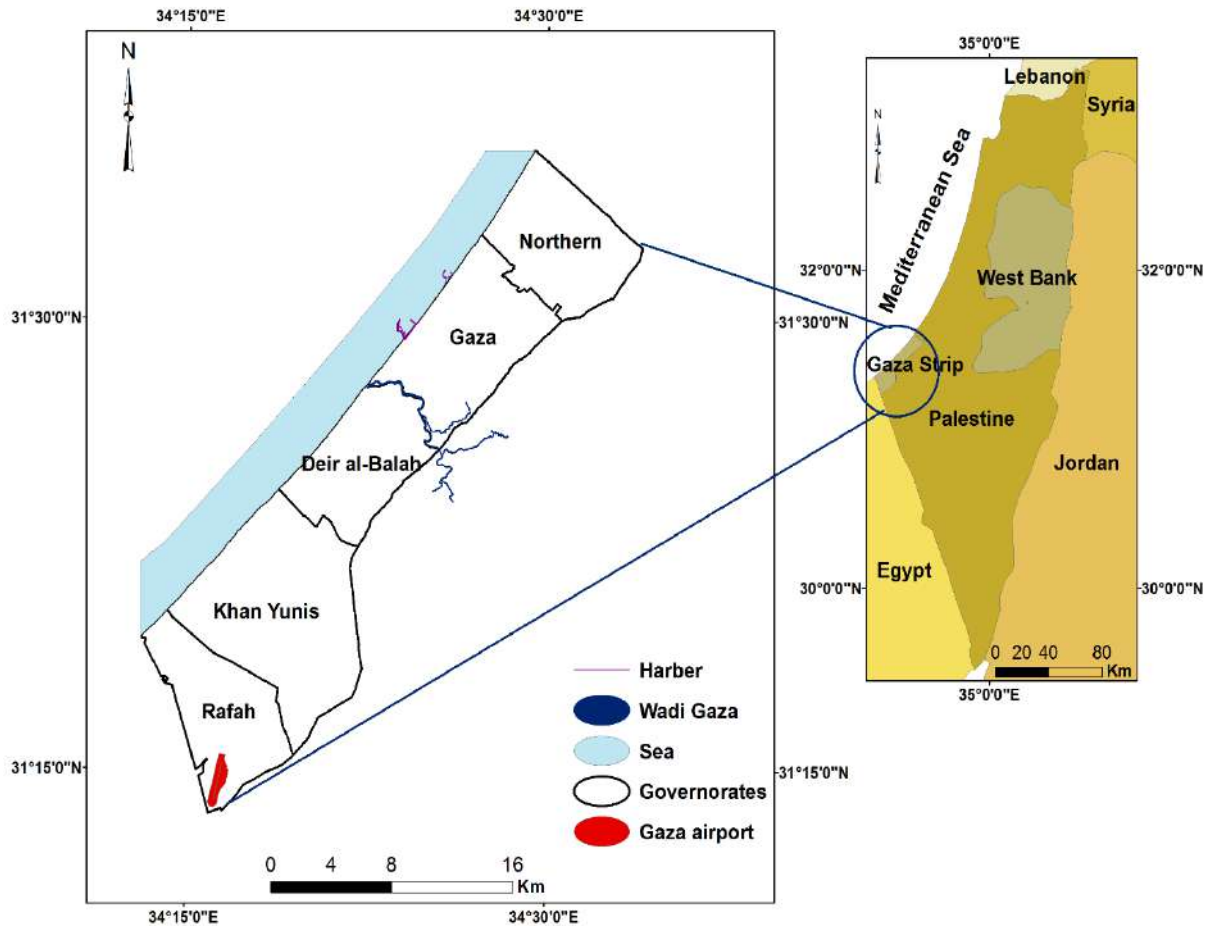


Figure 1.2: location map of the Gaza Strip

Gaza Strip is considered as one of the most densely populated areas all over the world. The number of inhabitants of the Gaza Strip is 1.88 million people, with natural rate of population growth of 3.3% (PCBS, 2016). The Gaza Strip is located in the transitional zone between the arid desert climate of the Sinai Peninsula and the semi humid Mediterranean climate along the coast. The temperature of Gaza Strip gradually changes through the year. The mean of the monthly maximum temperature ranges from about  $17.6^{\circ} \text{C}$  for January (winter) to  $29.4^{\circ} \text{C}$  for August (summer). The mean of the monthly minimum temperature for January is about  $9.6^{\circ} \text{C}$  and  $22.7$  for August. The relative humidity fluctuates between 60% and 85%. The rainy season in Gaza Strip is winter which stretches from October to April (Aish et al., 2004).The

rainfall which is the main source recharging the groundwater increases from south (200 mm/y) to north (400 mm/y), while the long term average rainfall rate in all over the Gaza Strip is about 317 mm/year (CMWU, 2011). The coastal aquifer is the main water source that people of Gaza Strip depend on to meet their different water needs (Agriculture, domestic, industrial, etc.). It represents 20% of a regional coastal aquifer that its natural boundary extends beyond Gaza Strip borders. Due to the over pumping, the Gaza coastal aquifer suffers from deficit. The over pumping results in sea water intrusion phenomena and upward movement of the saline water, the thing which negatively affects the quality of the ground water in terms of water salinity (PWA, 2012).

Sands, clay, and loess are the main three types composing soil in the Gaza Strip. The sandy soil extends along the coastline from south to outside the northern border of the Strip, at the form of sand dunes. The sand dunes have a hilly shape with a thickness ranging from two meters to about 50 meters. While clay soil is found in the north eastern part of the Gaza Strip, loess soil is found around Wadis (Aish, et al., 2004).

### **1.5 Scope and objectives**

The aim of this research is to assess the impact of the military activities on soil and rubble pollution by metals within the urban environment as well as on agricultural lands

The specific objectives of this research are:

1. To review the existing metals levels in agricultural soil.
2. To assess the degree of contamination by metals produced by AFB and AS in building rubble as well as in targeted agricultural areas after the escalation of hostilities in 2014.
3. To identify the number and types of locations that could be classified as potentially contaminated sites.
4. To investigate if the metal input in targeted locations is affected by the used type of munition (AFB and AS) or not.
5. To investigate if the contamination with metals is bounded in the craters formed by AFB and AS or if it is extended to areas surrounding these craters.

## **CHAPTER TWO: LITERATURE REVIEW**

### **2.1 Heavy metals - Historical review:**

The term "heavy metals" is used as a group name of metals and metalloids that are associated with pollution, toxicity or eco-toxicity. Many legal regulations specify lists of heavy metals, but, these lists differ from one set of regulation to another and sometimes the term "heavy metals" is used without specifying which heavy metals are covered. Although there is a general tendency to assume that all so-called heavy metals have highly toxic or eco-toxic properties, literatures have not specified authoritative definition for heavy metals. This inconsistent use of the term cause confusion regarding to its significance. Heavy metals have many different definitions some of them based on density, some based on atomic number or atomic weight and some based on chemical properties (Duffus, 2002).

Many literatures define the term heavy metal as it "refers to any metallic chemical element that has a relatively high density and is toxic or poisonous even at low concentrations (Lenntech, 2004). Another widely used definition of heavy metals is "a general collective term, which applies to the group of metals and metalloids with atomic density greater than 4 g/cm<sup>3</sup>, or 5 times or more greater than water"(Garbarino et al., 1996; Hawkes, 1997; Hutton et al., 1986; Nriagu, 1989) .

Heavy metals have been used since thousands of years in many locations over the world. For example, man has used lead in many applications since at least 5000 years. Lead has been used in water pipes, building materials and as pigments in ceramic manufacturing. In ancient Rome, Romans consumed about one gram of lead a day, as it was used in the form of lead acetate for sweetening old wine. Another heavy metal used by Romans was mercury, which was used for medication purposes. Romans used mercury as a painkiller for teething pain in infants. They also used mercury as a remedy for syphilis.

At the end of the 20<sup>th</sup> century production and emission of heavy metals decreased in developed countries. For example, in the United Kingdom, production of heavy metals decreased by about 50% in the period from 1990 to 2000 (Järup, 2003). While, production and emission of heavy metals increased steeply in developing countries, therefore, exposure to heavy metals continued and increased in these countries, although the adverse health effects of heavy metals have been well known (Järup, 2003; Su, et al., 2014).



## **2.2 Sources of heavy metals contamination:**

Sources of heavy metals can be divided into natural and anthropogenic sources.

### **2.2.1 Natural sources:**

Earth crust is the main source of heavy metals. 80% of the natural sources of heavy metals are weathered or eroded from the Earth's surface or they are released to the atmosphere via volcanic activities. Around 10% of the natural sources of heavy metals are contributed by forest fires, while biogenic sources account for the remaining 10% (Callender, 2003).

### **2.2.2 Anthropogenic sources**

Mining and smelting are the main sources of heavy metals contamination. Both of lead and zinc industry release considerable quantities of lead, copper, zinc and cadmium. Smelting of nickel and copper produce significant quantities of cobalt, zinc, manganese lead, nickel and copper. Due to its technological advances and increased importance, production and emission of chromium steeply increased during the period from 1970 to 1980. Manufacturing of steel and iron as well as using of chromium in pressure treated lumber are other reasons of increased production and emission of chromium (Callender, 2003).

Fossil fuel combustion, incineration of municipal wastes, production of cement and phosphate mining are important sources of heavy metals, since they release large quantities of heavy metals to the atmosphere. Discharge of wastewater and sewage sludge, use of commercial fertilizers and pesticides, and animal wastes are important sources of soil and aquatic environment contamination of heavy metals (Marfo, 2014).

## **2.3 Pathways of heavy metals contamination in contaminated soil**

### **2.3.1 Atmosphere to soil pathway**

The sources of heavy metals in the atmosphere are gas and dust, which are emitted from several activities including energy production, transportation, metallurgy and manufacturing of construction materials. Heavy metals are emitted to the atmosphere in the form of aerosol and later they deposit to the soil through natural sedimentation and precipitation. Wind allow heavy metals to transfer from point sources of pollution to surrounding areas. For example, the pollution of lead in down town Central Sweden was originated from copper plant, sulfuric acid plant, paint factory and other mining and chemical industries and then spread by wind and pollute surrounding areas (Gebreyesus, 2015).

Automotive transportation emit significant quantities of lead, zinc, cadmium, chromium and copper to the atmosphere and soil. Heavy metals come from burning leaded gasoline and the dust produced by automobile tire wear. For instance, in Nanjing-Hangzhou highway (China), contamination zones of lead, chromium and cobalt were formed along both sides of highway. The level of contamination of these metals was weakened as the distance increases from the both sides of the highway. Density of population, level of heavy industry, and traffic level obviously affect the quantities of heavy metals which deposit into the soil through natural deposition (Su, et al., 2014). Military activities is another source of heavy metals emission to atmosphere. When bomb impact the ground, the force of this impactation form a crater and the soil ejected from this crater and become airborne. Heavy metals previously found in the soil as well as those involved in explosive charge and the casing bomb emitted to the atmosphere. Although, most of soil and bomb particles including heavy metals fell to the ground, usually in a short distance from the crater, a portion of soil and the coupled heavy metals remain in the air becoming airborne and travel to surrounding areas by wind (ATSDR, 2003).

### **2.3.2 Sewage to soil pathway**

Irrigation of annual crops and fodders by wastewater has many advantages, including, year-round reliability, decrease disposal cost, and pressure alleviation on other water sources. The high content of nutrients in wastewater, increase productivity of the crops and fodders. Yield increase of crops such as eggplant, cauliflower, cabbage, and maize has been approved by several studies. Long-term irrigation of wastewater accumulate heavy in the soils and plants (Mok et al., 2014; Su, et al., 2014). This accumulation of heavy metals causes health risk for human and animals consuming crops irrigated by wastewater. However, heavy metals accumulate slowly in soil and the concentration of heavy metals takes decades to reach threshold concentration levels (Mok, et al., 2014).

### **2.3.3 Solid wastes to soil pathway**

Human activities worldwide generate huge quantities of solid wastes. Since generation of solid waste is an unavoidable aspect of human life, man can only manage rather than eliminate it. As a result of indiscriminate disposal of municipal, domestic and industrial solid wastes, the levels of heavy metal have been increased in the environment (Awokunmi et al., 2015). Solid wastes are varied in term of types and composition. Although all types of solid wastes could contain heavy metals, mining and industrial solid wastes are the most important.

The concentration of heavy metals in industrial solid wastes depends on many factors including, site-specific conditions, as well as the type and quantities of solid wastes (Hu et al., 2014). Heavy metals can move easily to surrounding water and soil during piling process, due to the facilitation of sunlight, rain and washing. Sludge produced from wastewater treatment plant is another important source of soil contamination of heavy metals. High content of organic matter, nitrogen and phosphorous in sludge encourage using of the sludge for fertilizing agricultural soil. Sludge usually contains high concentrations of chromium, lead, copper and zinc (Su, et al., 2014).

#### **2.3.4 Agricultural supplies to soil pathway**

Fertilizers, pesticides and mulch are the most important soil additives for agricultural production (Su, et al., 2014). Historically, agriculture is the oldest and main human activity that affect soil. Plants require both macronutrients (N, P, K, S, Ca, and Mg) and essential micronutrients (Co, Cu, Fe, Mn, Mo, Ni, and Zn) to grow and to complete lifecycle. Since some soils are deficient in these micronutrients, some crops require to be supplied by them as addition to soil or foliar spray, for healthy growth. In cereal crop fields, manganese and copper are occasionally added to soil to substitute their deficiency. In intensive farming systems, large quantities of fertilizers are added to the soil to provide adequate N, P and K for crops. Some heavy metals such as Pb and Cd, which have no known physiological activity, are found as impurities in the compounds of these fertilizers. Continuous addition of fertilizers to soil increase the concentration of these heavy metals to significant levels (Wuana et al., 2011). Heavy metals content in fertilizers vary according to the type of fertilizer. Generally, the content of heavy metals in phosphoric fertilizer > compound fertilizer > potash fertilizer > nitrogen fertilizer (Su, et al., 2014).

In the past, pesticides, which contained significant concentrations of heavy metals, were extensively used in agriculture and horticulture. In the recent past, about 10% of approved insecticides and fungicides in United Kingdom contained Cu, Hg, Mn, Pb, or Zn. Another example is arsenic containing chemicals, which were used largely to control cattle ticks and pests in banana in New Zealand and Australia. As a result of extensive use of such pesticides, many sites now are derelict, since the concentration of heavy metals in the soils of these locations greatly exceed background concentrations (Wuana, et al., 2011).

Recently, mulch has been largely used in many locations over the world. Application of mulch increases heavy metals concentration of soil, because heavy metals such as Cd and Pb

are contained in heat stabilizers, which always added during production mulch (Su, et al., 2014).

## **2.4 The impact of military activities on soil contamination with heavy metals**

Military activities is one of the most dramatic ways by which humans can affect soil properties. Warfare-induced disturbances to soil include physical, biological and chemical disturbances. Although the main aim of these disturbances is to cause direct problems to enemies, undesired indirect ramifications are resulted in most times. Physical disturbance includes creating of defense infrastructures, trenches, tunnels, compaction of soil by machinery and craters resulted by bombs. Chemical disturbance includes introducing of pollutants such as heavy metals, energetic compounds and oil to the soil. In most cases, biological disturbance takes place as a result of chemical and biological disturbances, but it can also occur by deliberated introduction of lethal microorganisms such as botulin or anthrax (Certini et al., 2013).

One of the most important chemical disturbances of soil is the introduction of energetic compounds. Energetic compounds are defined as those chemicals used in explosives and propellants. Energetic compounds from manufacturing operations, warfare, military training activities, as well as open burning and detonation of obsolete munitions are an important source of soil contamination worldwide .Most common energetic compounds used in explosives are 2,4,6-trinitrotoluene (TNT), 1,3,5 hexahydro-1,3,5-trinitrotriazine (RDX), and 1,3,5,7-octahydro-1,3,5,7 tetranitrotetrazocine (HMX), which are used as high explosives (HEs). Energetic materials used as propellant include nitrocellulose (NC), 2,4-dinitrotoluene (DNT), nitroglycerin (NG), and nitroguanidine (NQ) as well as various perchlorate formulations (Jenkins et al., 2005; Pichtel, 2012) .Since heavy metals represent significant parts of explosives, propellants, as well as the casing of bombs, the contamination of heavy metals always coupled with the contamination of energetic compounds. Characterization of certain heavy metals such as Aluminum, lead, cadmium, chromium, strontium, zinc and mercury should be conducted in parallel with energetic compounds in areas affected by military activities such as battlefields and training ranges (Thiboutot, et al., 2003).

Soils in battlefield are usually contaminated with heavy metals. For example, the results of 2,786 top soil samples (0-0.5m) collected from a battlefield around Ypres (West-Flanders, Belgium) showed that contamination with cooper had been occurred in this area. That area of 3,144 km<sup>2</sup> was used as a battlefield in which millions of copper containing shells were fired during the World War I (WWI). The median concentration of copper in soil samples

collected from battlefield area was 18 mg Cu/kg soil, while the median concentration of copper elsewhere is 12 mg Cu/kg soil. Since there is no evidence that another source of contamination with copper was found in this area, thus, it was concluded that about 2,800 tons of copper were introduced to the soil as an impact of warfare (Van Meirvenne et al., 2008). Another more recent study was carried out in the same area to evaluate the environmental impact of As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn. The results indicate that there is no pollution at regional scale, but sometimes the concentration of these heavy metals exceed the soil sanitation threshold specifically for copper, lead and zinc. The study proved that the contamination of copper and lead is associated to military activities occurred during WWI (Meerschman et al., 2011).

Beside battlefield, soils in training ranges and impact areas are subjected to contamination with heavy metals and energetic materials. Because many military sites are used as training ranges and impact areas, many needs emerged related to the identification and quantification of contaminants dispersed by munitions in these sites. In September 2007, soil samples were collected from 17 different training ranges at the Land Force Central Area Training Center (LFCA TC) Meaford, Canada to evaluate soil contamination by explosives and metals (phase I). The sampled training ranges include small arms ranges, skeet ranges, artillery firing positions and impact areas, anti-tank, grenade and other ranges. Of 135 soil samples, 79 samples were collected for energetic materials, and 56 for metals. The results showed that soils in all small arms ranges are contaminated with high concentrations of lead. Soils in some firing positions are contaminated with metals at concentrations higher than the industrial human health risk threshold criteria of the Canadian Council of Ministers of Environment (CCME) (Ampleman et al., 2009a). Another sampling campaign was done in August 2008 (Phase II). The new sampling campaign comprised re-collecting of soil samples from nine training ranges including Apeldorn range, Caen range, Cambrai range and other ranges. It was notable that there are some differences in the concentration of some metals in the two phases. These differences could be referred to the samples treatment, since different laboratories may use different sample treatment. Anyway, soil sampling in phase II was performed more accurately. Results of Phase II obtained from artillery impact area in Cambrai range showed that, the concentration of Cr, Hg, V and Ba exceeds the background levels (BGL), while the concentrations of Co, Cu, Pb, Sb, Ni, Se, Ag, As, Tl, Zn, and Cd exceeded the Industrial Soil Quality Guidelines (ISQG) (Ampleman et al., 2009b).

Soils in air force bombing ranges are also subjected to contamination with heavy metals. Results of soil samples collected from Jimmy Lake range, which is one of four ranges within

Cold Lake Air Weapon Ranges (CLAWR), showed that concentrations of Cd, Cr, Cu, Pb, Ni, V, and Zn are higher than BGL or Agricultural Soil Quality Guidelines (ASQG) and in some places higher than ISQG. Concentrations of Cd, Pb, Ni, V, and Zn in all soil samples exceeded the BGL, while concentration of copper exceeded the ISQG in many samples. Contamination with heavy metals is also revealed in soil samples collected from Shaver River range. This range is another training range within CLAWR. Air force bombs of 250, 500, and 1000 lbs are regularly dropped at stationary targets in this range. Results obtained from soil samples showed that the concentrations of Cu, Cd and Pb are detected at values higher than BGL and ASQGL (Ampleman et al., 2004; Pennington et al., 2005).

## **2.5 Specifications of soil sampling in locations subjected to bombing.**

As a result of military activities, explosive residues homogeneously distribute as particles of various size, shape and composition on the surface of areas of activities (Hewitt et al., 2007). Explosives contamination is coupled with heavy metals contamination as the both of them are dispersed at the surface of soil, vegetation, surface water and sediments (Ampleman, et al., 2004; Thiboutot, et al., 2003). When explosives in warhead detonate as designed (high-order detonation) they usually form a crater in the soil. The size of crater depends on the type of munitions, the physical properties of the soil and fuse setting. High-order detonation usually deposit microgram to milligram quantities per pound of explosive residues over hundreds of square meters of surface area. Higher concentration of energetic materials and heavy metals, are usually resulted by low-order detonation, dud or ruptured warheads (Hewitt, et al., 2007; Thiboutot, et al., 2003). The main objective of soil sampling is to obtain a representative sample. That means that the concentration determined for the sample should provide a valid estimate of mean concentration of the area of concern (Thiboutot, et al., 2003). Systematic-random multi-increment samples strategy is recommended to overcome the errors in estimation of mean concentration resulting by the heterogeneous distribution of explosive residues. Collection of 30 or more subsample in evenly distance is recommended by Hewitt, et al (2007), that it provides more reproducible results than either discrete samples or multi-increment samples collected using a totally random design (Pennington et al., 2006).

## **2.6 Factors affect mobility and Adsorption of heavy metals in soils**

Pollution problems take place when heavy metals are mobilized into the soil solution and thus become available for plants or transport to surface or groundwater. To predict the

environmental impact of heavy metals in the soil it is essential to understand the factors governing migration and plant availability of these metals. Solubility of heavy metals in soil solution is governed by reactions with solid phase. In soil, heavy metals may undergo one of the following fates: (i) adsorption/desorption, (ii) precipitation/dissolution, (iii) plant uptake and (iv) transfer through soil profile (Sherene, 2010). The main factors influence the mobility of heavy metals in soil are pH, organic matter, redox potential, clay content and soil structure (Carrillo-González et al., 2006).

### **2.6.1 pH**

Soil pH is the most important factor that affect the solubility and retention of heavy metals in soil (Orhue et al., 2011). Generally, the sorption increases when pH increases, accordingly, the lower pH value, the more solubility and mobility of heavy metals in soil. When pH value is lower than 5, the concentration of  $H^+$  significantly increased and the mobility of heavy metals is enhanced. In the other hand, when the pH of the soil solution is neutral or slightly alkaline, the mobility of heavy metals significantly decreased. The solubility of Pb in soil solution is highly affected by pH value. It increases as the pH lowered from 6 to 3, while there is no clear relationship between pH and Pb activity near neutral pH (Sherene, 2010). A study of the impact of soil pH on the adsorption of Pb, Ni, Zn, and Cu by two soils adjusted to various pHs ranging from approximately 4.3 to 8.3 revealed that the adsorption increased with pH (McLean et al., 1996). The pH dependence of adsorption reactions of heavy metals is due, in part, to the preferential adsorption of the hydrolyzed form of heavy metals in comparison to the free metal ion. For example, soil adsorption of Cu is more related to pH than Cd because hydrolysis of Cu occurs at pH 6, the thing which increases its retention to soil, while Cd hydrolysis does not occur below pH 8. Adsorption sites, such as Fe and Mn oxides, organic matter, carbonates, and the edges of clay minerals are pH dependent. When pH decreases, the number of negative sites available for cations decreases and in contrast the number of anions adsorption sites increases. In addition, as a result of the decrease in pH value, heavy metals face competition for occupying the negative sites by  $Al_3^+$  and  $H^+$ . The pH also plays an important role in dissolution of heavy metal hydroxide, oxide, carbonate, and phosphate precipitates which form only under alkaline conditions. When pH value lowered under 6, the oxides of Fe and Mn dissolve and thus allow the adsorbed metal ion to release into solution (McLean, et al., 1996).

### **2.6.2 Organic matter**

Soil organic matter can play important role in heavy metal solubility in soil, that it can affect the chemical, physical and biological conditions in soil. The most important role is that, it can increase the water holding capacity and Cation Exchange Capacity (CEC) of soils. Actually, it can increase the CEC far exceeding that of clay minerals and sand. Soil organic matter includes three main components which are (i) living organisms, (ii) soluble biochemical such as carbohydrates, amino acids, organic acids, proteins, lignin, etc. (iii) insoluble humic which act as exchange sites (Orhue, et al., 2011). Accordingly, it is important for the retention of metals by soil solids, and as a result it decreases the mobility and bioavailability of heavy metals (Sherene, 2010). It was reported that, some toxic elements and compounds are detoxified by interaction with soil organic matter (Orhue, et al., 2011). The study done on a sandy loam soils showed that, the Cd can move easily in this type of soils, but the organic matter in the surface layer acts as a sink for Cd and reduces its mobility in soil (Sherene, 2010). Anyway, because of the complexation of metals by soluble organic matter, further addition of organic matter can result in release of heavy metals from solids to the soil solution. It is known that, the solubility of humic acid increases as the pH increases and as a result, the dissolved organic matter increases. Extensive evidences proved that, in alkaline pH range, most of dissolved heavy metals are exist as metal soluble organic ligand complexes. Many studies observed that, the concentration of Zn increased in soil solution as the pH increased above 7.5. This observation was attributed to the solubility of organic complexes ligands (Sherene, 2010).

### **2.6.3 Oxidation reduction (redox)**

Many heavy metals have more than one oxidation state, and thus affected by the redox potential of the soil. For example, in soils having acidic to slightly alkaline pH, Fe(III) is highly adsorbed in the form of ferric hydroxide. Reduction of Fe(III) to Fe(II), result in mobility of ferrous iron and any metal which may be adsorbed on ferric hydroxide to the soil solution. Redox potential plays important role in Cr mobility in soil. Cr (VI) is toxic and relatively mobile in soil, while Cr (III) is less toxic and highly adsorbed to solid surfaces. Another example is selenate (Se (VI)) which is mobile but has less toxicity than Se (IV), which has less mobility. Generally, oxidizing conditions increase retention of heavy metals in soil, while reducing conditions increase mobility of these metals in soil solution (McLean, et al., 1996).



#### **2.6.4 Clay content and soil structure**

Although clays have different physical and chemical properties, but generally have high ion exchange capacity. Numerous studies proved that the ion exchange capacity of montmorillonite > illite > kaolinite and thus charged substances such as heavy metals can easily attach to the clay particles (Olaniran et al., 2013). Isomorphs substitution of  $\text{Al}^{3+}$  for  $\text{Si}^{4+}$  in the tetrahedral layers and substitution of  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ , etc. for  $\text{Al}^{3+}$  in tetrahedral aluminosilicate clay result in permanent net negative charge in clay minerals. This charge is permanent one since; it is not affected by the change in soil pH. In the other hand a pH dependent charge surfaces are associated with edges of clay minerals, as well as, the surfaces of oxides, hydroxides, carbonates and organic matter. The pH dependent charge is resulted by the association and dissociation of the protons from surface functional groups. For example, association of proton with iron oxide surface result in positive charge  $[-\text{Fe}-\text{OH}_2^+]$ , while under alkaline conditions, dissociation of protons result in a negative charge  $[-\text{Fe}-\text{O}^-]$ . Neutral charge appears at the point of zero net proton charge  $[-\text{Fe}-\text{OH}^0]$ . Anyway, for the pH organic and inorganic dependent surfaces, the number of negatively charged sites diminishes as the pH decreases and accordingly, the CEC is reduced. In contrast as the pH increases the number of negatively charges sites increase and thus the CEC increases (McLean, et al., 1996).

#### **2.7 Heavy metals in rubble**

Rubble represents the largest portion of all solid wastes in most countries. In 1996, about 127 million metric tons of rubble were generated in the USA (Townsend et al., 2004), while Europe produces about 461 million metric tons annually (Abel, 2015). Rubble consists mainly of concrete, wood, asphalt, gypsum wallboard, cardboard, metal, soil, rock and vegetative debris (Townsend, et al., 2004). The amount of rubble is increased dramatically during wars, as a result of bombing raids, which destroy building, streets and infrastructure. During the WWII about 55 to 110 million  $\text{m}^3$  of rubble were produced in Berlin, while in other cities such as Hamburg 40 million  $\text{m}^3$  were reported (Abel, 2015). In Gaza Strip, 400,000 tons of rubble were collected from ex-settlement after Israeli unilateral disengagement (El Kharouby, 2011). Furthermore, 600,000 tons of rubbles were generated during the war of Gaza 2009 (UNEP, 2009). The largest amount of rubble was produced

during the escalation of hostilities 2014, where, about two million tons of rubble were reported (OCHA OPT, 2015).

Although most constituents of rubble are inert, it may contain some materials that can pose risk to human health such as heavy metals. Rubble contamination with heavy metals can take place through several ways, including: (i) Contaminated soil, in case the constructions were established at sites previously contaminated by heavy metals, such as industrial facilities. (ii) Small pieces of hazardous building materials such as treated paint wood and paint ships. (iii) Leaching of hazardous materials mixed with rubble (e.g. lead, nickel and cadmium may leach from damaged batteries) (Townsend, et al., 2004). The result of 146 soil surveys from Berlin showed that, elevated concentrations of heavy metals are found in soil materials containing rubble produced during WWII, comparing to natural soil materials. The study revealed that 34, 71, 67, 68, 74% of the rubble containing sub-soils samples exceeded the precautionary values of the German Soil Conservation Act, regarding Cd, Pb, Cu, Zn, Hg respectively (Abel, 2015).

## **2.8 Studies concerning heavy metals in Gaza Strip**

In the last decade many studies discussed the issue of heavy metals contamination in different sectors in Gaza Strip

.Al-Najar, et al. (2015) assessed the impact of war activities on soil pollution in Gaza Strip. Soil samples were collected from craters of different sizes resulted by airstrike on agricultural lands. The concentration of (Ni, Cr, Cu, Mn, Co and Pb) were determined in 14 soil samples. The results revealed that, most soil samples had mean Ni concentration that was over four times higher than the control, Cr was five times, Cu was thirty one times higher, Mn was greatly higher than the control (114 times), Co was five times higher while Pb was twelve times higher than the control. The researchers recommended to follow up research program to investigate the fate of the metals in soil, groundwater and food chain.

Abou Auda et al. (2011) investigated the concentrations of Pb, Zn, Cd and Fe at three locations in the northern area of the Gaza Strip. The accumulation of these elements in the edible parts of some plants (spinach, wheat, strawberry, carrot, onion, squash, cabbage, potato, faba bean and cucumber) growing in these soils was investigated too. The researchers revealed that the concentration of metals were in the normal range in soil samples except for lead and iron which showed higher concentration in some locations such as Al-Monttar and

Gaza city center. Accumulation of metals in crop plants was also in the normal range except of lead which exceeded the normal ranges. The concentration of lead reached the toxic level only in onion bulb. Cadmium levels in concentration was low in soil samples and its accumulation in crop plants samples was very low and sometimes not detectable.

After the escalation of hostilities in 2009, UNEP as a part of its environmental assessment, investigated the contamination with heavy metals in rubble dust collected from destroyed house in the Al Shati Camp. The results of the collected sample revealed that, the rubble can be used in construction purposes without any restrictions (UNEP, 2009).

Shomar (2006), investigated the purity of pesticides used in Gaza in terms of trace elements. The concentration of 20 metal in the most commonly solid pesticides used in Gaza Strip were determined using a semi-quantitative EMMA-XRF technique and quantitative ICP/OES. The results shows that the used pesticides contain considerable amounts of elements and do not comply with the expected-theoretical structure of each species as well as they do not reflect the actual constituents listed in the trade labels. In addition to that, field survey and interviews with market owners revealed that, the pesticides were not pure and in some cases, local markets mixed them with minor inorganic species without a scientific basis. Shomar concluded that, the pesticides should be considered as a source of many metals such as Cu, Mn, Zn, Br, Sr and Ti, that may affect their concentrations in soil and groundwater as well as their plant uptake.

Shomar (2004) aimed to establish the current contents of trace metals and major elements in agricultural soils of the Gaza Strip and to identify the main anthropogenic activities that affect the contents of trace metals. 170 soil samples were collected from agricultural and nonagricultural areas representing a wide range of soil types and locations. The results revealed that the Gaza soils fall within the range of uncontaminated to slightly contaminated, where, up to 90% of the tested soils had metal contents equal to the international background values. Ten percent showed slight contamination, primarily by Zn, Cu, As, and Pb, due to anthropogenic inputs. The results also revealed that, the soil geochemistry is dependent on soil type and location and to a lesser extent on crop pattern as well as fertilizer and fungicide application. Anthropogenic inputs lead to the enrichment of Zn, Pb, Cu, and Cd in the agricultural soils. In addition to that, the application of Cd-containing phosphate fertilizers coupled with Cu containing fungicides may be an important source of Cd and Cu in several soils, while high Zn levels in several soils may be caused by sewage sludge.

## **2.9 Selected heavy metals and their human health effect**

The selected metals to be investigated in soil and rubble samples are Cadmium (Cd), Cobalt (Co), Chromium (Cr), Copper (Cu), Manganese (Mn), Nickel (Ni), Lead (Pb), Zinc and aluminum (Al).

### **2.9.1 Cadmium (Cd)**

Cadmium is a metal located in the second row of the transition metals in the periodic table. It has an atomic number 48, atomic weight 112.41, density 8.65 g/cm<sup>3</sup>, melting point 320.9 °C and boiling point 765°C (ATSDR, 2012a; Wuana, et al., 2011). In addition to mercury and lead, it is one of the big three heavy metals poisons (Wuana, et al., 2011). It is non-essential metal, present naturally in soils as Cd(II). Because cadmium has some chemical similarity to zinc, which is essential trace element, substitution of zinc by cadmium may occur and thus increase the Cd toxicity (Alloway, 2010; Wuana, et al., 2011). Soils are enriched by cadmium through atmospheric deposition as well as through application of phosphate fertilizers and sewage sludge. Cadmium is used in several industrial activities. The most important use of cadmium is in the production of rechargeable batteries. It was estimated that over 80% of cadmium consumption is used for this purpose. Since it is resistant to corrosion, it is widely used in coating of vessels and vehicles, especially marine vehicles. Beside using for cadmium as polyvinylchloride (PVC) stabilizer, other uses of cadmium include production of alloys and pigments. The toxicity of cadmium in soil is persistent, because its residence time exceeds decades and its bioavailability dose not reduced by time. Cadmium in soil can pose human health risk at concentrations well below the concentrations required to cause visual effects on plants and biota (Alloway, 2010). The main routes by which cadmium enters human body are food intake and tobacco smoking. In cadmium-contaminated soils, cadmium can accumulate through food chain and crops specially when applying sewage sludge and phosphate fertilizers to these soils. When cadmium enters human body, it can affect several enzymes. For example, it adversely affects the enzymes responsible for reabsorption of proteins in kidney tubules, which lead to renal damage and kidney dysfunction as well as increased excretion of Ca, which causes osteomalacia. The most publicized incidence of cadmium poisoning occurred in Toyama (Japan). Citizens consumed rice irrigated by Jintsu River which was contaminated by Cd produced from upstream mine producing Cd, Zn and Pb. The patients were affected by itai-itai disease, which is a bone disease with fractures and severe pain. Patients in that area suffered from osteomalacia and kidney malfunction

(Alloway, 2010; ATSDR, 2012a; Wuana, et al., 2011). Since cadmium is a severe pulmonary and gastrointestinal irritant, it can be fatal when inhaled or ingested. Symptoms appear after acute ingestion (15-30 min.) include abdominal pain, burning sensation, nausea, vomiting, salivation, muscle cramps, vertigo, shock, loss of consciousness, convulsions gastrointestinal tract erosion, pulmonary, hepatic or renal injury and coma. Finally, many regulatory agencies such as the International Agency for Research on Cancer (IARC) and the U.S. National Toxicology Program (NTP) classified cadmium compounds as human carcinogens (Tchounwou et al., 2012).

### **2.9.2 Cobalt (Co)**

Cobalt is a naturally occurring transition element with properties similar to iron and nickel. Cobalt has 26 radioactive isotopes, of which  $^{59}\text{Co}$  is the only stable one that has atomic number 27, density  $8.9\text{g/cm}^3$ , melting point  $1,495^\circ\text{C}$  and boiling point  $2,870^\circ\text{C}$ . Commonly it exists in 0, +2 and +3 valance states.  $\text{Co(III)}$  is a powerful oxidizing agent that can oxidize water and liberate oxygen, but much less stable than  $\text{Co(II)}$ . Cobalt is released to the environment from both natural and anthropogenic sources. Natural sources include wind-blown dust, seawater spray, volcanoes, forest fires, and continental and marine biogenic emissions. In the other hand anthropogenic sources, include burning of fossil fuels, sewage sludge, phosphate fertilizers, mining and smelting of cobalt ores, processing of cobalt alloys. Cobalt mobility in soil decrease with pH (ATSDR, 2004a; Howe et al., 2006). It is involved in many industrial processes such as cutting tools, super alloys, surface coatings, diamond tooling, magnets, ceramics and pigments (Gál et al., 2008). In trace amounts cobalt is essential for human and other mammals, as it is a component of vitamin  $\text{B}_{12}$ . Deficiency of cobalt in human body is similar to vitamin  $\text{B}_{12}$  deficiency resulting in anemia and nervous system problems (ATSDR, 2004a; Gál, et al., 2008). In the other hand, inhalation of air containing high concentration of cobalt result in serious effects on the lungs, including asthma, pneumonia, and wheezing.

### **2.9.3 Chromium (Cr)**

Chromium is a cubic crystal, steel-grey, lustrous, and very hard metal. It is a transition metal with atomic number 24, atomic mas 52 and density  $7.19\text{ g/cm}^3$ . Chromium has a melting point of  $1875^\circ\text{C}$  and boiling point of  $2665^\circ\text{C}$ . Chromium naturally presents in rocks, soils, plants and animals. It combines with other elements to form several compounds but never

found naturally in the elemental form(ATSDR, 2012b; Wuana, et al., 2011). Chromium has valence state ranging from Cr(II) to Cr(VI). Chromium (III) and Cr(VI) are the most stable forms of chromium respectively. Actually, the oxidation state of chromium depends on pH and redox conditions. Cr (VI) is the most toxic form of chromium and relatively has more mobility than other forms of chromium (Alloway, 2010; Wuana, et al., 2011). Chromium enters the environment through many natural and anthropogenic sources. Industrial activities which have the greatest contribution of chromium release include metal processing, tannery processing, stainless steel welding, chromate production, and pigment production. Chromium released into the environment from industrial activities mainly occurs in the hexavalent form Cr(VI), which is classified as human carcinogen by several regulatory agencies. Anyway, Cr(III) is an essential nutrient since it helps in strengthening insulin and thus plays important role in glucose, fat and protein metabolism (ATSDR, 2012b; Tchounwou, et al., 2012). Although Cr(III) is considered essential; there is no recognized diseases related to Cr(III) deficiency (ATSDR, 2012b). Chromium can enter human body via inhalation, which is limited to occupational exposure, or via ingestion of water and food containing chromium. It was reported that inhalation of Cr(VI) cause multi-organ toxicity such as renal damage, allergy, asthma, and cancer of the respiratory tract. Ingestion of high dose of Cr(VI) causes severe respiratory, cardiovascular, gastrointestinal, hematological, hepatic, renal, and neurological effects and finally leads to death. Reduction of Cr(VI) to Cr(III) is considered as detoxification process if it takes place at a distance from the cell, but if the reduction occurs inside the cell that will activate the chromium toxicity (ATSDR, 2012b; Tchounwou, et al., 2012).

#### **2.9.4 Copper (Cu)**

Copper is a reddish transition metal that occurs naturally in rocks, soil, sediments, water and also present at low concentration in air. It has an atomic number 29, atomic weight 63.5, density 8.96 g cm<sup>3</sup>, melting point 1083°C and boiling point 2595°C (ATSDR, 2004b; Bradl, 2005; Wuana, et al., 2011). Copper is widely used over the world, it is the third most used metal by man (Alloway, 2010; Wuana, et al., 2011). Although man had used copper since more than 10,000 years, 95% of copper has been extracted since 1900. The usage of copper includes electrical applications (65%), constructions (25%), vehicle industries (7%) and the remaining 3% are used in cookware, coins, musical instruments and sculptures (Alloway, 2010). It is usually introduced to agricultural soil via application of sewage sludge, fertilizers,

and pesticides (Alloway, 2010; ATSDR, 2004b; Bradl, 2005). Beside its elemental form, copper can be found in nature in Cu(I), Cu(II), and Cu(III) oxidation states (ATSDR, 2004b). It is strongly complexes with organic matter in the soil, although its solubility increased drastically at low pH (Alloway, 2010; Wuana, et al., 2011). At small quantities, it is essential for plant and animal growth. For plants it is vital for seed production and disease resistance, while in human body, it is involved in production of blood hemoglobin (Wuana, et al., 2011). At high dose, it can be toxic for human, that it causes anemia, liver and kidney damage as well as stomach and intestinal irritation (ATSDR, 2004b; Wuana, et al., 2011).

### **2.9.5 Manganese (Mn)**

Manganese is a naturally occurring, steel-gray, very brittle metal with molecular weight 54.94, density 7.26g/cm<sup>3</sup>, melting point 1,244°C and boiling point 2,095°C. Pure manganese does not occur in nature, rather, it combines with other elements such as oxygen, sulfur and chloride to form about 100 Mn minerals (ATSDR, 2012c; Bradl, 2005). It occurs in many oxidation states such as I, II, III, IV, VI, and VII, while, the II, IV, VI, and VII form the most stable salts. Manganese is strongly adsorbed by clay minerals and the adsorption increased as pH increases. Manganese is used in steel production to increase its hardness and strength and in the production of steel, copper and aluminum alloys. Furthermore, it is involved in the production of matches, alkaline batteries, electrical coils, ceramics, dyes, paints and other industries. The main anthropogenic sources of manganese are industrial activities, application of fertilizers, sewage sludge and animals wastes in agriculture, as well as atmospheric deposition of fossil fuel combustion (Bradl, 2005). Manganese is essential micronutrient for plants, animals and human. Inhalation of high dose of manganese affects the nervous system, cause irritation of the lungs, which could lead to pneumonia and Loss of sex drive and sperm damage (ATSDR, 2012c).

### **2.9.6 Nickel (Ni)**

Nickel is a transition element that occurs naturally in earth crust and found in all soils. It has atomic number 28, atomic weight 58.69, melting point 1,455 °C and boiling point 2,730°C. Nickel in its pure form is silvery-white metal, with unique properties that make it easily combine with other metals to form alloys (Fay, 2005). Normally nickel has 0 and +2 oxidation states, although it can be found as Ni(I) or Ni(III) in certain conditions (Alloway, 2010). In acidic conditions it occurs in the form of nickelous ion Ni (II), while in neutral to slightly alkaline solutions it precipitates in the form of nickelous hydroxide Ni(OH)<sub>2</sub> but in

very alkaline conditions it occurs as nickelite  $\text{HNiO}_2$  ion which dissolves in water. Nickel is used commonly in steel and other metals products. It is introduced to the soil via several sources including nickel mining, electroplating, combustion of fossil fuel and metal plating (Wuana, et al., 2011). Nickel can enter human body via breathing air containing nickel, ingestion of water and food containing nickel or when it contact with the skin. Small dosage of nickel is essential for human body but large dose can lead to several health problems. Breathing high concentration of nickel lead to chronic bronchitis, reduced lung function, and cancer lung nasal sinus cancer (Fay, 2005).

#### **2.9.7 Lead (Pb)**

Lead is a naturally occurring bluish-gray metal with atomic number 82, atomic mass 207.2, density 11.34 g cm<sup>3</sup>, melting point 327.4°C, and boiling point 1740°C (ATSDR, 2007). It is rarely found in nature in its elemental form, instead it usually found combined with other elements. Lead in its elemental form or as lead alloys when combined with other metals are used heavily in many industries including solders, cable covers, ammunition, plumbing, pigments, and caulking, while the largest use of lead is in the production of storage batteries (ATSDR, 2007; Wuana, et al., 2011). Lead commonly found in soils as Pb(II). Although the solubility of lead decreases as pH increases, because of the complexation with organic matter, sorption on oxide and silicate clay minerals, or precipitation as the carbonate, sulfate, or phosphate, the alkaline conditions in soil may increase its solubility due to the formation of Pb-organic and Pb-hydroxy complexes (Alloway, 2010; Wuana, et al., 2011). Lead enters human body through ingestion or inhalation and accumulates in body organisms such as bones and brain, leading to poisoning and even death. It can cause serious negative effect in gastrointestinal tract, kidneys, and central nervous system. Adults exposed to lead suffer from decreased reaction time, loss of memory, nausea, insomnia, anorexia, and weakness of the joints. While lead effect on children includes impaired development, lower IQ, shortened attention span, hyperactivity, and mental deterioration (ATSDR, 2007; Wuana, et al., 2011).

#### **2.9.8 Zinc (Zn)**

Zinc is an element that commonly found in the earth crust, it also presents in soil, water, air and food. It has an atomic number 30, atomic mass 65.4, density 7.14g/cm<sup>3</sup>, melting point 419.5°C, and boiling point 908°C (ATSDR, 2005; Bradl, 2005; Wuana, et al., 2011). In its elemental form, zinc is a shiny metal with bluish-white color. Due to its reactivity, it is found



in approximately 55 mineralized forms, but never found as free element in the nature, while the powdered zinc is explosive and when stored in a wet condition it may burst into flames (ATSDR, 2005). Although zinc naturally occurs in soil, its concentration in soil is rising as a result of anthropogenic activities (Wuana, et al., 2011). These activities include disposal of zinc wastes produced from industry, coal ash from electric plants, and application of sludge and fertilizers. It is used in many industries including galvanization of metals, production of alloys such as brass and bronze and manufacturing of dry cell batteries (ATSDR, 2005; Bradl, 2005). Zinc is an essential nutrient for both animals and humans, that it is required for membrane stability, present in about 300 enzymes, plays a role in metabolism of proteins and nucleic acids and male productivity. It is relatively non-toxic especially if taken orally, but high dose of zinc can cause anemia, impairment of growth and reproduction, as well as kidney and liver failure (Duruibe, et al., 2007).

### **2.8.1 Aluminum (Al)**

Aluminum is the most abundant and distributed metal in the earth crust. It is a light in weight, silvery-white colored metal, with atomic number 13, atomic mass of 26.98, density 2.7 g/cm<sup>3</sup>, melting point 660°C and boiling point 2,467 °C. Since it is a very reactive element, it is never found as free metal in environment, instead, it combines with other metals such as oxygen, silicon and fluorine. Aluminum is used in different purposes such as production of beverage cans, cookware, airplanes, siding and roofing, and foil. It is also used as pharmaceuticals and food additives and in water treatment as aluminum sulfate (alum). Powdered aluminum is usually used in explosives and fireworks (Aguilar et al., 2008; ATSDR, 2008). Aluminum can enter human body through inhalation of air containing aluminum, digestion of water and food contaminated with aluminum or through dermal contact. Some researches mention that, workers who breathe aluminum containing dust or aluminum fumes have suffered from decreased performance in nervous system tests'. Although some studies suggest that people who ingest high concentration of aluminum are subjected to develop Alzheimer's disease, other studies proved that, this is not true. Patients with Kidney disease accumulate excess aluminum in their bodies, and are subjected to develop bone or brain diseases (ATSDR, 2008).

### **CHAPTER THREE: MATERIALS AND METHODS**

To achieve the objectives of this research 62 samples, including 57 soil and 5 rubble samples were collected in September 2014, immediately after the cease-fire of the last escalation of hostilities (2014). Of the 57 soil samples, 45 top 5 cm soil samples were collected from the targeted locations (targeted soil samples) either by AFB or by AS, using a systematic-random multi-increment sampling system as described by Jenkins et al (2006) and Hewitt et al. (2007). Of the 45 targeted soil samples, 30 samples were collected from areas subjected to AFB, 18 of them were collected inside craters and the other 12 were collected from areas surrounding craters. As well as 15 samples were collected from areas subjected to AS, 9 of them were collected from craters and the remaining 6 samples were collected from areas surrounding craters. In addition to that, 10 control samples were collected from agricultural areas and household gardens, which have not been affected by military activities and, two bar samples were collected from isolated areas that assumed have not been affected by military or human activities. In the other hand 5 rubble samples were collected from households targeted by AFB and AS. GPS location for each sample was plotted during samples collection using Garmin GPS72. Locations of samples were plotted on maps using ARCGIS version 10.1. Types and numbers of soil and rubble samples are shown in table 3.1, while the locations of these samples are shown in figure 3.1.

**Table 3.1: Types and numbers of collected samples**

<b>Sample type</b>	<b>Craters</b>	<b>Areas surrounding craters</b>	<b>Subtotal</b>
<b>Targeted soil samples</b>	18	12	30

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<b>from areas subjected to AFBs</b>			
<b>Targeted soil samples from areas subjected to AS</b>	9	6	15
<b>Rubble samples</b>			5
<b>Control samples</b>			10
<b>Bar samples</b>			2
<b>Total</b>			62

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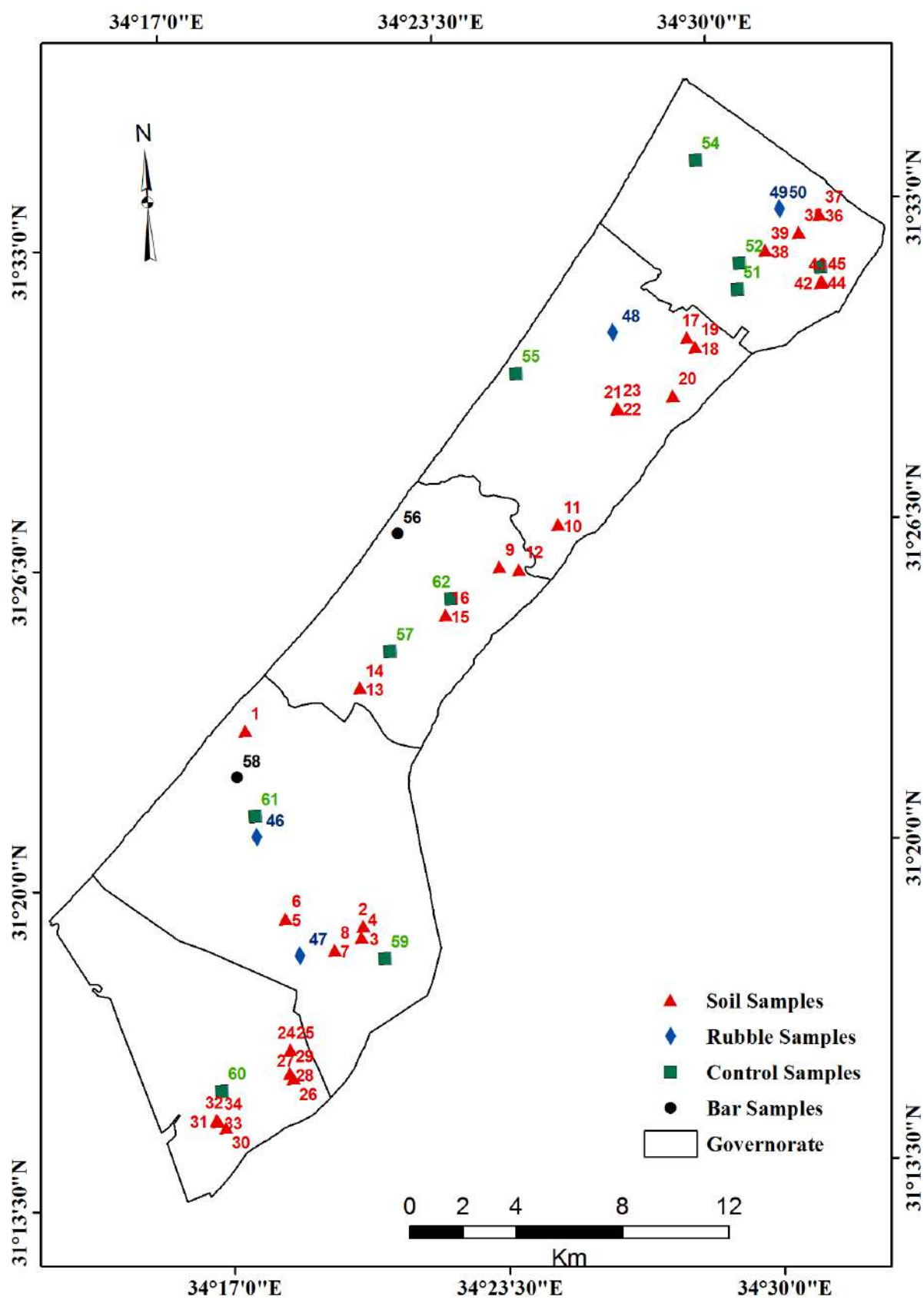


Figure 3.1: locations and types of collected samples.

### 3.1 Collecting of targeted soil samples

#### 3.1.1 Soil sampling inside craters formed by AFB

Soil samples were collected inside craters as described by Jenkins, et al. (2006). 18 composite samples were collected using systematic-random multi-increment sampling system. To build each composite sample, 50 increment surface (top 5 cm) soil samples, were collected by starting at a random location at the top edge and proceeding in a spiral pattern from the top to bottom collecting individual increments from the side walls and bottom (figure3.2). The weight of each increment sample was about 50 g. Thus, a 2.5 kg composite sample, were collected from each crater. The exact locations of these samples are listed in table 3.2.

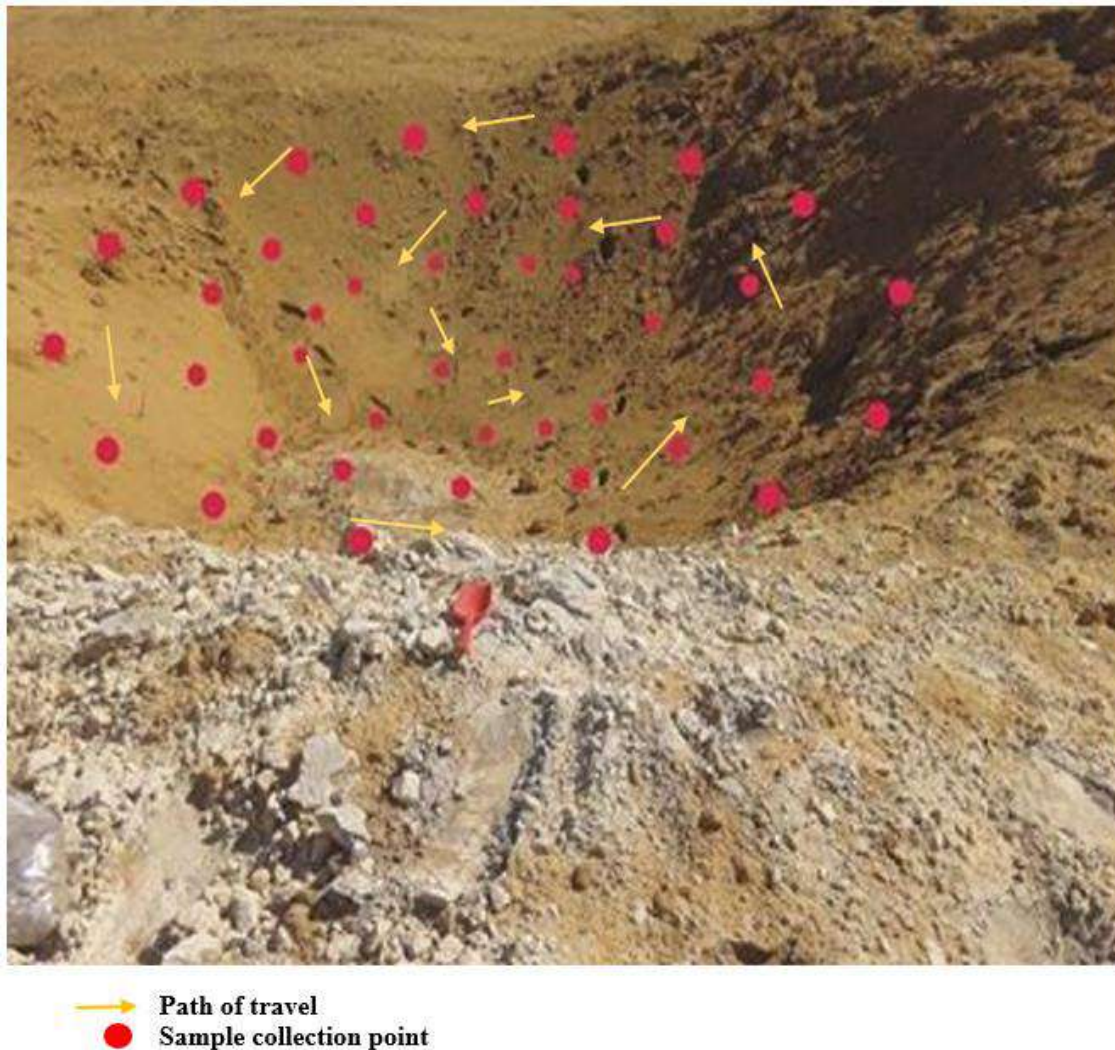


Figure3.2: Spiral pattern used to collect systematic-random multi-increment samples inside craters formed by AFB.

**Table 3.2: locations of samples collected from craters resulted by AFB (N\*=18)**

<b>Sample label</b>	<b>Governorate</b>	<b>location</b>	<b>Coordinates</b>	
			<b>North</b>	<b>East</b>
1	Khan Younis	Al Mwasy	34.300194	<b>31.3835</b>
2	Khan Younis	Abasan	34.341917	<b>31.3148889</b>
5	Khan Younis	Al Manarah	34.311389	<b>31.3191389</b>
7	Khan Younis	Al Fukhary	34.329917	<b>31.3074722</b>
9	Middle area	Al Buraij	34.404806	<b>31.4334444</b>
10	Middle area	Wadi Gaza graveyard	34.428972	<b>31.4465833</b>
13	Middle area	Dier El Balah El Jafrawy	34.346583	<b>31.3956111</b>
15	Middle area	Al Maghazi Abu Rashed	34.38225	<b>31.4183889</b>
17	Gaza	Gaza East Altofah	34.484667	<b>31.5069444</b>
18	Gaza	Gaza East Altofah	34.487806	<b>31.5035833</b>
20	Gaza	Gaza Karny	34.477694	<b>31.4875278</b>
21	Gaza	Gaza East Alzayton	34.455389	<b>31.4842222</b>
26	Rafah	Sofa	34.310361	<b>31.2649722</b>
30	Rafah	Rafah airport	34.282806	<b>31.24975</b>
31	Rafah	Rafah airport	34.279278	<b>31.2524167</b>
35	North of Gaza	Biet Hanon	34.531556	<b>31.54</b>
36	North of Gaza	Biet Hanon	34.540361	<b>31.54575</b>
38	North of Gaza	Biet Hanon Elshwa Hospital	34.517944	<b>31.5346944</b>

**N: number of samples**

### **3.1.2 Soil sampling outside crater formed by AFB**

12 Soil samples, were collected from areas surrounding to craters formed by AFB using systematic-random multi-increment sampling system as recommended by Hewitt et al. (2007). The area surrounding each crater was divided to a 50 X 50 m square grid centered on each crater. Accordingly, an area of 2500 m<sup>2</sup> was divided into 100 sub-square of 5mX5m area size. A sub-sample of about 50 g was collected from each sub-square to build a multi-increment composite sample. The area of the crater was deducted from the total area since the sampling area is surrounding the crater (figure 3.3). Accordingly the number of sub square is less than 100, and also the number of subsamples is less than 100. However, a composite sample of 2 kg were collected from each area. The exact locations of these samples are listed in table 3.3.

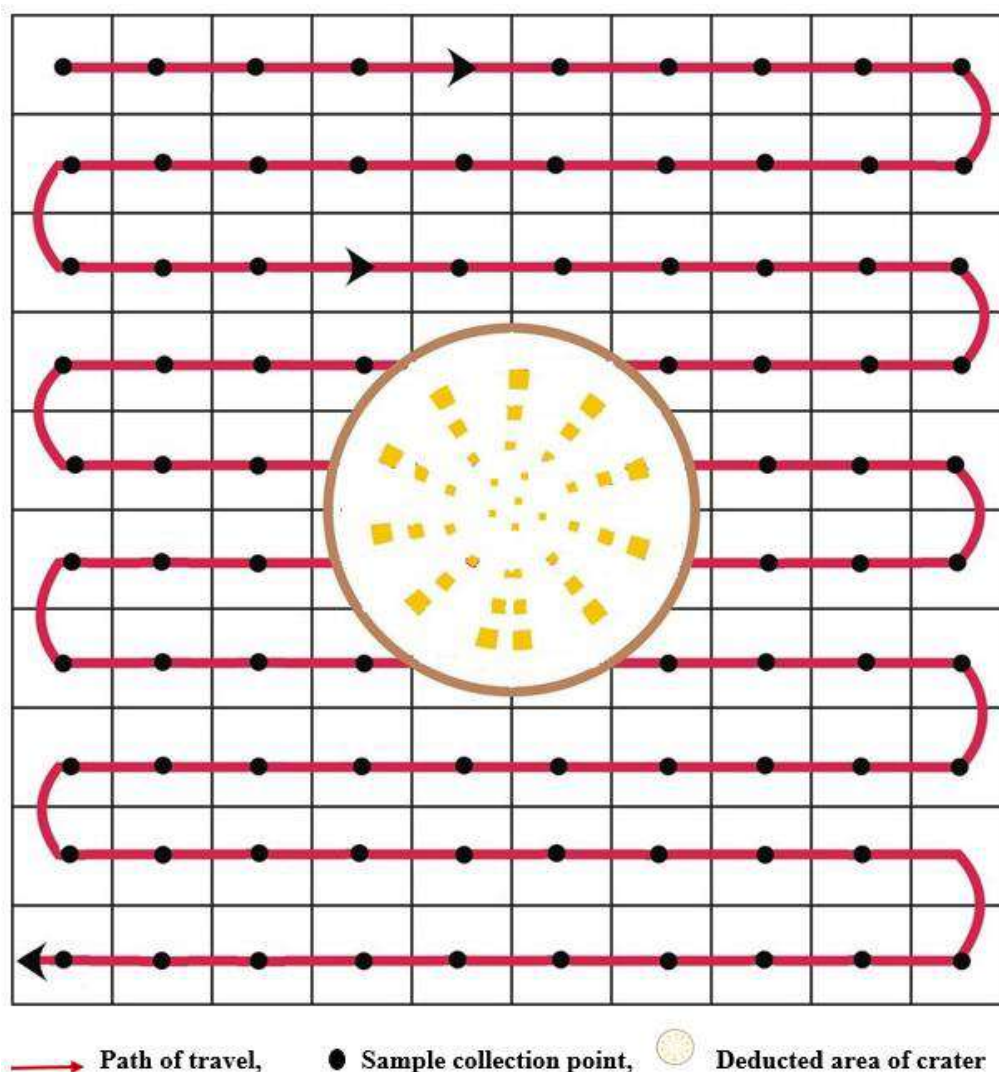


Figure 3.3: Systematic-random 50-increment sampling pattern used for collecting samples surrounding craters formed by AFB.

Table 3.3: locations of samples collected from areas surrounding craters formed by AFB (N=12)

Sample label	Governorate	location	Coordinates	
			North	East
3	Khan Younis	Abasan	34.341917	<b>31.3148889</b>
6	Khan Younis	Al Manarah	34.311389	<b>31.3191389</b>
8	Khan Younis	Al Fukhary	34.329917	<b>31.3074722</b>
11	Middle area	Wadi Gaza graveyard	34.428972	<b>31.4465833</b>
14	Middle area	Dier El Balah El Jafrawy	34.346583	<b>31.3956111</b>
16	Middle area	Al Maghazi Abu Rashed	34.38225	<b>31.4183889</b>
19	Gaza	Gaza East Altofah	34.487806	<b>31.5035833</b>
22	Gaza	Gaza East Alzayton	34.455389	<b>31.4842222</b>
27	Rafah	Sofa	34.310361	<b>31.2649722</b>
32	Rafah	Rafah airport	34.279278	<b>31.2524167</b>
37	North of Gaza	Biet Hanon	34.540361	<b>31.54575</b>
39	North of Gaza	Biet Hanon Elshwa Hospital	34.517944	<b>31.5346944</b>



### 3.1.3 Soil sampling from craters formed by AS

A total of 9 soil samples were collected by systematic-random multi-increment sampling system from craters formed by AS as recommended by Jenkins, et al. (2006). Since, AS usually form a small and shallow crater of about 1.5x1.5 m, 30 subsamples each of 50g were collected to build a composite sample of about 1.5kg from each crater. The locations of the sampled craters are listed in table 3.4.

**Table 3.4: locations of samples collected from craters resulted by AS. (N=9)**

Sample label	Governorate	location	Coordinates	
			North	East
4	Khan Younis	Abasan	34.341	<b>31.3111667</b>
12	Middle area	Alburaij East	34.412472	<b>31.4321667</b>
23	Gaza	Gaza East Alzayton	34.455389	<b>31.4847778</b>
24	Rafah	Sofa	34.310083	<b>31.2745833</b>
28	Rafah	Sofa	34.309278	<b>31.2666667</b>
33	Rafah	Rafah airport	34.279833	<b>31.2519722</b>
40	North of Gaza	Biet Hanon	34.539028	<b>31.5225278</b>
42	North of Gaza	Biet Hanon	34.539278	<b>31.5227778</b>
44	North of Gaza	Biet Hanon	34.539639	<b>31.5229444</b>

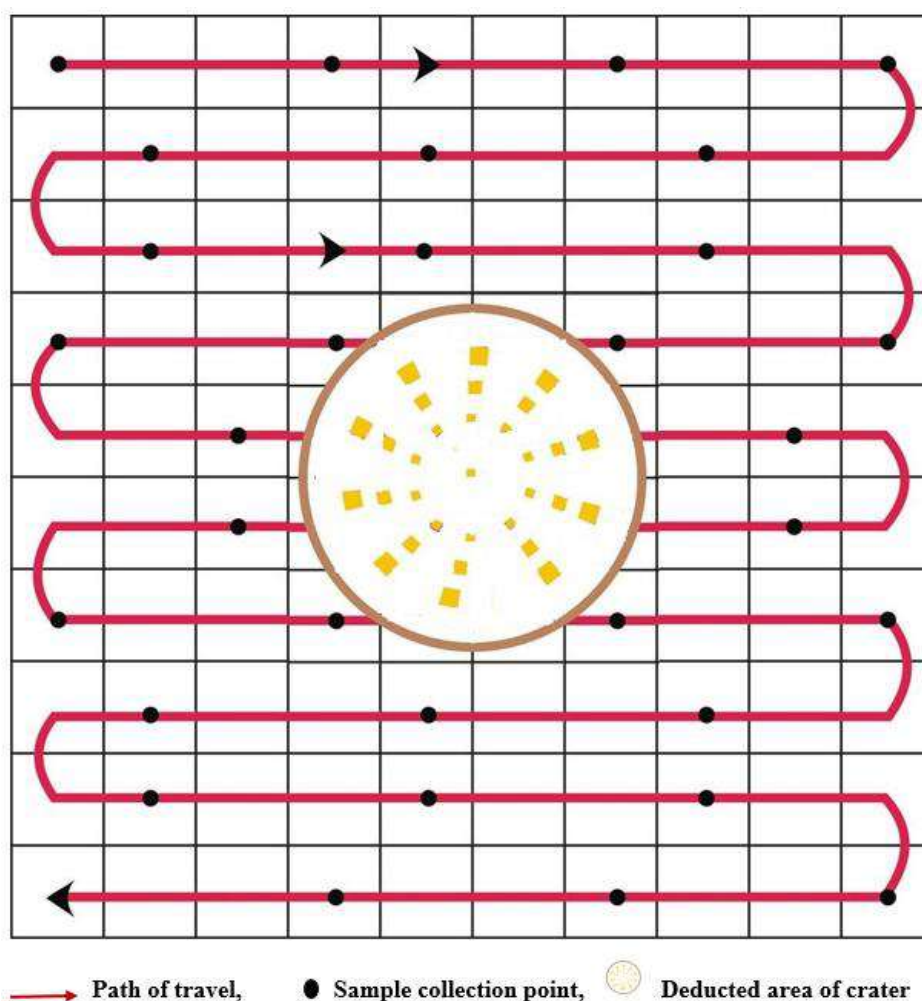
### 3.1.4 Soil sampling outside craters formed by AS

A systematic-random multi-increment sampling system, was used to collect six soil samples from areas surrounding craters formed by AS as described by Hewitt, et al. (2007). A 10X10 m square grid centered on each crater was drawn and thus, an area of 100 m<sup>2</sup> was divided into 100 sub-square. Each sub- square has an area of 1x1 m. A 30 multi-increment samples, each of 50g were collected to build a composite sample of about 1.5 kg. The area of the crater was deducted from the total sampled area surrounding the crater (figure 3.4). The locations of these samples are listed in table 3.5.

**Table 3.5: locations of samples collected from areas surrounding craters resulted by AS. (N=6)**

Sample label	Governorate	location	Coordinates	
			North	East
25	Rafah	Sofa	34.310083	<b>31.2745833</b>
29	Rafah	Sofa	34.309278	<b>31.2666667</b>
34	Rafah	Rafah airport	34.279833	<b>31.2519722</b>
41	North of Gaza	Biet Hanon	34.539028	<b>31.5225278</b>
43	North of Gaza	Biet Hanon	34.539278	<b>31.5227778</b>
45	North of Gaza	Biet Hanon	34.539639	<b>31.5229444</b>





**Figure 3.4: Systematic-random 30-increment sampling pattern used for collecting samples surrounding craters formed by AS.**

### 3.2 Collecting of control soil samples

Ten control samples were collected from agricultural areas and household gardens that have not been affected by military activities. The purpose of control samples is to establish the contribution of metals pollution resulted by agricultural activities versus the contribution of metals pollution resulted by military activities. The mean of the control samples was used as a normal limit for agricultural activities, and thus samples with values higher than the mean are considered to be affected by military activities. In each sampled location, an area of 10 X 10 m was divided to 100 sub-square and 30 Sub-samples were collected in systematic random design to build a composite sample of about 1.5kg. Types and locations of the control samples are listed in table 3.6.

**Table 3.6: Types and locations of control samples (N=10)**

Sample label	Governorate	Sample type	location	Coordinates	
				North	East
51	North of Gaza	Agricultural area	North of Jabalia (Safe Agricultural Society)	34.506	31.5223889
52	North of Gaza	Household garden	Jabalia - Tal Elzatar	34.507472	31.5311111
53	North of Gaza	Agricultural area	Biet Hanon - Alnazaz	34.539417	31.5280833
54	North of Gaza	Agricultural area	Biet Lahia - Alsayafa	34.492833	31.5669444
55	Gaza	Agricultural area	Gaza - Shekh Ejleen	34.416361	31.49875
57	Middle area	Agricultural area	Dier El Balah – East of Salah El deen St.	34.359444	31.4074444
59	Khan Younis	Agricultural area	Absan - El Taimat	34.349694	31.3036389
60	Rafah	Agricultural area	Rafah - El Shokeh	34.282083	31.2623889
61	Khan Younis	Household garden	El Amal St.	34.302028	31.3545278
62	Middle area	Household garden	El Maghazi - Sultani st.	34.384917	31.424

### 3.3 Collecting of bar soil samples

Two bar samples were collected from isolated areas that assumed have not been affected by military or human activities. The purpose of collecting bar soil samples is to establish a comparison between the agricultural activities and the environmental contribution of the metals in the soil. For each investigated metal, the mean of the bar soil samples was considered as a normal limit of the natural contribution of the environment, accordingly, samples with metal concentrations higher than the mean of the bar soil is considered to be affected by agricultural activities. The exact locations of the bar samples are listed in the table below.

**Table 3.7: Locations of bar samples (N=2)**

Sample label	Governorate	location	Coordinates	
			North	East
56	Middle area	El Nusairat - Tal OM Amer	34.365667	<b>31.44725</b>
58	Khan Younis	El Mwasay	34.295917	<b>31.3681944</b>

### 3.4 Collecting of rubble samples

Many researchers investigated the pollution of heavy metals in rubble. In these researches, collecting of samples was performed in recycling stage, where demolition of buildings usually transferred to be handled in special facilities. As far as the researcher knows, there are no approved sampling methods or protocols describe the collecting of rubble samples from households subjected to artillery or AFB before they are transferred to recycling facilities. For the purpose of this study, the rubble samples were collected from households, which are not completely destructed. Five rubble Samples were collected from households where the warhead penetrated the ceiling or the walls and detonated, spreading explosive residues inside the household. A multi- increment samples were collected from the floor and walls of these households using brush. About 1.5 kg composite sample were collected from each location. The locations of the rubble samples are listed in table 3.8.

**Table 3.8: Locations of rubble samples (N=5)**

Sample label	Governorate	location	Coordinates	
			North	East
46	Khan Younis	Al Saeqaly st.	34.302306	<b>31.3474722</b>
47	Khan Younis	Salah Eldeen St. (European Hospital)	34.316167	<b>31.3065278</b>
48	Gaza	Al Salam tower	34.455556	<b>31.5105556</b>
49	North of Gaza	Alnada Towers No.1 (Ground floor)	34.524806	<b>31.5486111</b>
50	North of Gaza	Alnada Towers No.1 (Apartment 18)	34.52475	<b>31.5485833</b>

### 3.5 Samples handling and treatment

Soil and rubble samples were collected, stored, labeled in polyethylene bags. Samples were grinded using a wood hummer. For homogenization of samples, each composite sample was divided into quarters. Each quarter mixed individually. Two quarters were mixed to form a half. The halves then mixed to form a homogeneous sample as described by USEPA (2014). As recommended by Horvath (2005), samples were dried at a temperature of  $60 \pm 5^{\circ}\text{C}$  for 24hours, and then sieved through 2mm (“10 mesh”) sieve. Fractions greater than 2mm were discarded. The samples then transferred to polypropylene containers (50 ml), closed tightly, labeled and stored for physical and chemical analysis.

### 3.6 Soil texture

The ratios of sand, silt and clay in each soil sample was determined using the hydrometer method described in Soil Survey Staff (2014). About 50g of air-dry soil < 2mm of each

sample were transferred to 1-L graduated cylinder. 100 ml of 50g/l sodium-hexametaphosphate (HMP) solution were added to the soil sample. Deionized water was added to bring the volume to 1L. A reference cylinder was prepared by adding deionized water to 100 ml of (HMP) to bring the volume to 1L. The samples and the blank were stirring using hand stirrer in an up and down motion for 30s. The hydrometer readings were recorded at 30s, 1min, 3min, 2h and 24h. The types of the soil samples were determined using soil texture triangle.

### 3.7 Cation Exchange Capacity (CEC)

CEC was measured according to the method described by Ryan et al., (2001). 4g of air-dry soil, were transferred to 40 ml centrifuge tube. Saturated with  $\text{Na}^+$  by adding 33ml of 1N sodium acetate trihydrate solution, shaken for 5 min and centrifuged at 3000 rpm and the supernatant liquid was discarded each time. This process was repeated a total of 4 times. Then a 33 ml of 95% ethanol was added to the soil, shaken for 5 min, centrifuged at 3000 rpm and then the supernatant liquid was also discarded. This process was repeated a total of 3 times. The  $\text{Na}^+$  then replaced by an index cation ( $\text{NH}_4^+$ ) by adding 33ml of 1N ammonium acetate solution, shaken for 5 min, centrifuged at 3000 rpm and supernatant liquid then collected in a 100 ml volumetric flask. This process was repeated a total of three times. The final volume was completed to 100 ml by adding 1 N ammonium acetate solution. The concentration of  $\text{Na}^+$  in the final extract was determined using a flame photometer at 767 nm wavelength.

CEC was calculated according to the following equation:

$$\text{CEC (meq/100g)} = \text{meq/l Na (from calibration curve)} \times \frac{A}{Wt} \times \frac{100}{1000}$$

Where, A is the total volume of the extract (ml),

Wt is the weight of the air-dry soil

### 3.8 Soil pH

Soil pH was measured using aqueous soil suspensions method (Pansu et al., 2007). Soil to water ratio used was 1:1 W/V. 30 ml of distilled water was added to 30g of soil sample, shaken for one hour and left for 30 min. WTW inoLab pH 720 device was calibrated using buffers at pH 4, 7 and 10 before immersing the electrode and record the readings.

### **3.9 Digestion of samples**

The aim of the acid digestion procedure is to completely transferee the analytes (metals) from the soil matrix into solution so that, they can be introduced to the instrumental analysis in liquid form for determination. Many digestion methods include using of the conventional heating of nitric acid or nitric and hydrochloric acids such as USEPA method 200.2, and USEPA method 3050, aim to extract environmentally available elements, while those bound in silicate structure are not normally released by these methods USEPA (1995).

In this research, the total concentrations of heavy metals and aluminum in soil and rubble samples, were extracted by digestion of these samples using Strong Acid Leachable Metals (SLAM) digestion method described by Horvath (2005). A sample of 4 g were transferred to a 250 ml conical flask. Each one gram of soil samples required 5ml of acids mixture for digestion, so 20 ml of concentrated nitric acid and hydrochloric acid (ratio by volume, 1: 1 nitric acid / hydrochloric acid) were added to the soil sample. Samples were fully covered by acid mixture. Sample and acid were mixed gently and left to sit at room temperature for about one hour. Mixtures were placed on a hot plate for about 2 hours at a temperature of  $90 \pm 5^{\circ}\text{C}$  and then were cooled to room temperature and diluted with distilled water to a volume of 25ml. Finally extracts were filtrated using Whatman 45  $\mu\text{m}$  filter paper and sample extracts were stored in a polypropylene containers (25ml) for instrumental analysis. Although, this method extracts the total heavy metals and aluminum, it does not completely dissolute metals bound in silicate structure. Accordingly, only environmentally available metals are extracted, while metals not dissolved by this method do not have environmental consequence, (Horvath, 2005).

### **3.10 Determination of heavy metals concentrations in samples**

Concentrations of the heavy metals (cadmium, cobalt, chromium, copper, manganese, nickel, lead and zinc) were detected using atomic absorption spectrometer (UNICAM 929 AA spectrometer).

### **3.11 Determination of Aluminum concentration in samples:**

Although aluminum concentration in soil can be measured by AAS using oxide–acetylene flame, but this method is not recommended, since it is not sensitive because aluminum is a refractory element. Comparing with AAS method, spectrophotometry method is much precise and inexpensive method (Pansu, et al., 2007). In this research, concentration of

aluminum was detected using Spectro UV/VIS Auto (UV-2602) Lab Med. Inc. at wavelength 535 nm. Aluminum extract solution was determined according to the method no. 3500-Al B described by Lenore, et al. (1998). Aluminum gives a red to pink complex with Erichrome Cyanine R dye. The concentration of aluminum influences the intensity of the developed color. Ethylene Di-amine tetra acetic Acid (EDTA) was used to provide a blank for deduction of color and turbidity resulting by other elements. Ascorbic acid was used to eliminate the interference caused by iron and manganese (Lenore, et al., 1998).

### **3.12 Statistical analysis**

Statistical analysis was performed using SPSS program version 20. Mean and standard deviation were calculated for each parameter. Correlation co-efficient was calculated to investigate the relationship among various parameters. Correlation coefficient among the CEC, pH, soil texture and the selected metals was calculated in order to investigate, interpret and predict the behavior of the selected metals in soil.

T-test was used to compare the mean concentration of each metal between targeted soil samples and control samples, to investigate if there is a significant statistical difference between the two means or not, and accordingly if the military activities affect the concentration of the investigated metals in the targeted locations or not. T-test was also used to compare the mean concentration of each metal between samples collected from areas subjected to AFB and areas subjected to AS, samples collected from craters formed by AFB and samples collected from areas surrounding to these craters and finally between samples collected from craters formed by AS and samples collected from areas surrounding to these craters. The purpose of the T-test analysis on the three previously mentioned categories is to identify if the targeted location is more affected by AFB or AS, and if there are significant differences between the concentration of the selected metals inside and outside craters formed either by AFB or by AS.

The concentrations of metals in control samples were compared with the mean concentration of the bar soil samples, (which considered as a normal limit of the natural contribution of the environment) to investigate the contribution of the agricultural activities. Then the results of targeted soil samples were compared with the mean of the control samples (which considered as a normal limit for agricultural activities) to investigate the contribution of military activities. Finally the concentrations of the metals in the targeted soil samples were compared

with the Maximum Allowable Concentrations (MACs) of Chemical Constituents in Uncontaminated Soil listed by USEPA (2011) to identify areas posing risk to human health. In the other hand, the results of the rubble samples were compared with Maximum Allowable Concentrations (MACs) of Chemical Constituents in Uncontaminated Soil Used as Fill Material listed by USEPA (2012).

## **CHAPTER FOUR: RESULTS AND DISCUSSION**

In this chapter, the results of the soil properties (Soil texture, CEC and pH) of the targeted soil, control and bar samples, as well as the results of the chemical analysis of the nine selected metals (Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn and Al) of both rubble and soil samples were discussed. Firstly, the results of the soil texture, CEC and pH of the targeted soil, control and bar samples were discussed and illustrated by figures and tables, in order to predict the behavior of the investigated metals in the soil profile in the targeted areas.

Secondly, the results of the chemical analysis of each metal in targeted soil samples were discussed separately in details. The soil samples were grouped into categories (bar samples, control samples, targeted soil samples, samples collected from areas subjected to AFB, samples collected from areas subjected to AS, samples from craters formed by AFB, and samples from areas surrounding craters and samples from craters formed by AS and samples from areas surrounding to these craters.). The T-test was used to compare the mean concentration of each metal between the previously mentioned categories in order to investigate if the military activities affected the concentration of the investigated metals in the targeted locations or not, and to identify if the targeted locations are more affected by AFB or by AS. In addition to that, the test was used to investigate if there are significant differences between the concentration of the selected metals inside and outside craters formed either by AFB or by AS. The mean concentration of the bar samples was considered as a normal limit of the natural contribution of the environment while, the mean concentration of the control samples was used as a normal limit for agricultural activities. The concentration of each metal in targeted soil samples was compared with the Maximum Allowable Concentrations (MACs) of Chemical Constituents in Uncontaminated Soil listed by USEPA (2011) to identify areas posing risk to human health.

Thirdly, because there is no base line data describing the rubble content of metals in Gaza Strip to compare with, measuring how much the military activities affected the concentration

of the selected metals in rubble is unreachable. Instead, the concentration of metals in rubble samples were compared with the Maximum Allowable Concentrations of Chemical Constituents in Uncontaminated Soil Used as Fill Material (MACs) listed by EPA to investigate the validity of using such rubble in construction purposes or as a filling material

#### 4.1 Soil texture

Most of targeted soil samples have a high sand content (80.24%) comparing with silt (15.53%) and clay (4.04%) fractions as illustrated in figure (4.1). That agrees with study done by Goris et al. (2001) and AbuSamra (2014). The sandy soil of Gaza Sstrip originated from the sand dunes, which have exceedingly low water holding capacity and high water permeability. In addition to the sandy soil, loess soil is found in Gaza Strip. Generally, the soils in Gaza Strip are rich in calcium, poor in aluminum and iron, as well as they are permeable by water, therefore leaching of minerals is predominant (Dudeen et al., 2001).

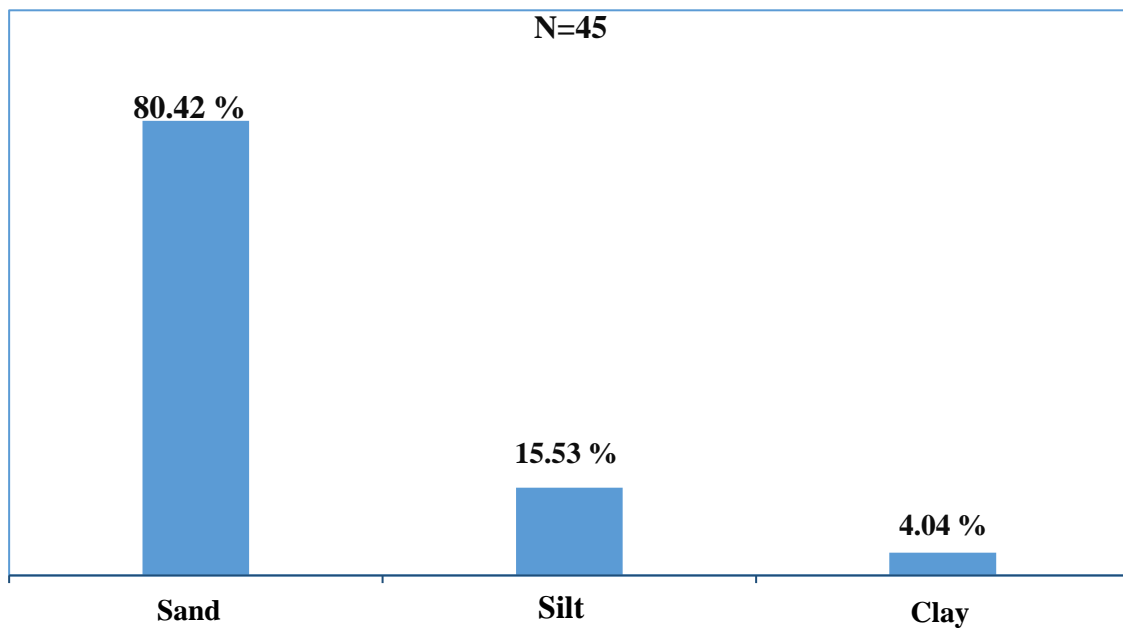


Figure 4.1: Average percentage of sand, silt and clay fractions in soil samples

According to the soil texture analysis, 37.77% of the soil samples (17 samples) have a sand texture, while the loamy sand texture represents the second highest ratio of 33.33% of the soil samples (15 samples). In addition to that, 24.44% of the soil samples (11 samples) have a sandy loam texture. Only one sample has a texture of sandy clay loam, and the another remaining sample has a loam texture. The results of soil texture analysis of the targeted soil are shown in table 4.1. In the other hand the soil types of control samples varied between



80% sand (8 samples) and 20% loamy sand (2 samples) as shown in table 4.2, while the type of the two bar samples is sand (table 4.3).

**Table 4.1: Samples characterization: CEC, pH, soil texture and soil types of targeted soil samples (N=45)**

Sample label	CEC (meq/100g)	pH	soil classification			Soil type
			sand %	clay %	silt %	
1	3.32	8.48	94	0	6	sand
2	13.92	8.41	66	5	29	sandy loam
3	10.58	8.85	85	4	11	loamy sand
4	7.82	9.13	83	4	13	loamy sand
5	9.12	8.89	83	5	12	loamy sand
6	8.82	8.69	93	2	5	sand
7	8.06	8.74	87	4	9	sand
8	7.83	8.69	89	2	9	sand
9	6.42	8.33	86	4	10	loamy sand
10	5.42	8.227	88	0	12	sand
11	6.25	7.99	92	0	8	sand
12	8.00	7.8	86	2	12	sand
13	18.23	8.02	65	6	29	sandy loam
14	7.50	8.09	93	2	5	sand
15	13.59	8	70	6	24	sandy loam
16	12.59	7.95	72	6	22	sandy loam
17	7.18	9.04	84	4	12	loamy sand
18	6.23	9.1	86	4	10	loamy sand
19	12.02	8.08	80	2	18	loamy sand
20	11.53	8.12	76	4	20	loamy sand
21	15.12	7.92	61	6	33	sandy loam
22	14.84	7.67	67	4	29	sandy loam
23	12.57	7.79	72	2	26	loamy sand
24	6.09	8.21	84	2	14	loamy sand
25	5.92	8.08	95	2	3	sand
26	9.51	8.24	82	6	12	loamy sand
27	6.22	8.28	93	2	5	sand
28	6.92	8.27	89	2	9	sand
29	6.42	8.15	93	2	5	sand
30	6.48	8.3	93	2	5	sand
31	7.38	8.53	89	4	7	sand
32	4.92	8.28	94	0	6	sand
33	4.35	8.37	93	0	7	sand
34	4.75	8.22	95	0	5	sand
35	23.27	8.04	46	16	38	loam
36	27.55	8.01	58	20	22	sandy clay loam
37	14.77	8.04	80	6	14	loamy sand

38	20.03	7.88	67	11	22	sandy loam
39	19.67	7.91	68	9	23	sandy loam
40	15.27	7.85	68	4	28	sandy loam
41	19.25	7.87	74	2	24	loamy sand
42	10.89	8.01	72	4	24	sandy loam
43	11.56	7.8	80	2	18	loamy sand
44	12.54	7.79	72	4	24	sandy loam
45	11.24	7.82	76	4	20	loamy sand

**Table 4.2: Samples characterization: CEC, pH, Soil texture and types of control samples (N=10)**

Sample label	CEC (meq/100g)	pH	soil classification			Soil type
			sand %	clay %	silt %	
51	6.03	8.15	86	4	10	Loamy sand
52	3.13	8.11	96	0	4	Sand
53	4.01	8.62	98	2	0	Sand
54	5.10	8.68	88	5	7	Sand
55	7.85	8.15	86	7	7	loamy sand
57	5.72	8.55	89	4	7	Sand
59	4.31	8.41	95	2	3	Sand
60	5.27	8.42	97	2	1	Sand
61	3.26	8.43	94	0	6	Sand
62	6.95	7.41	91	5	4	Sand

**Table 4.3: Samples characterization: CEC, pH, Soil texture and types of bar samples (N=2)**

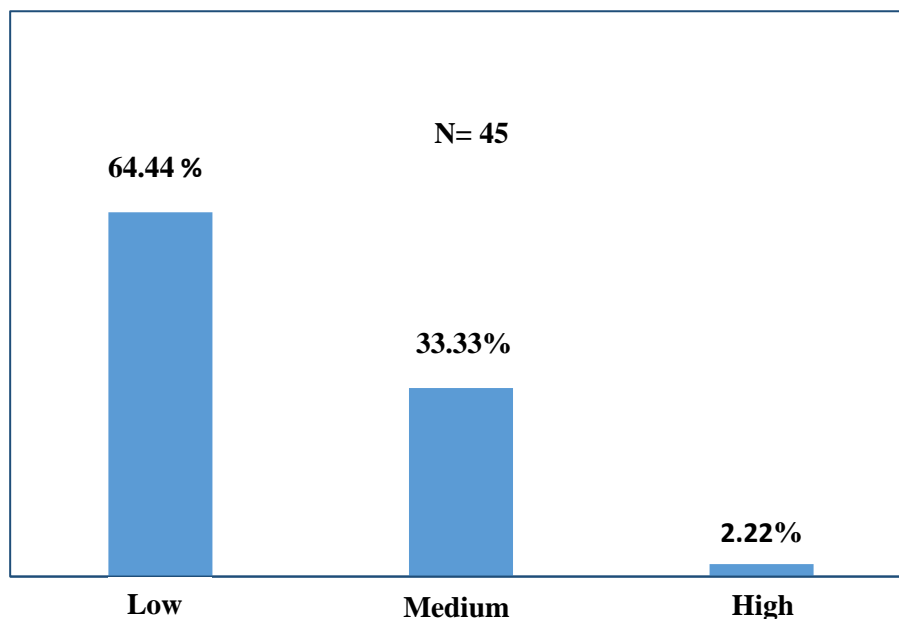
Sample label	CEC (meq/100g)	pH	soil classification			Soil type
			sand %	clay %	silt %	
56	3.87	8.64	98	2	0	Sand
58	0.79	8.75	100	0	0	Sand

## 4.2 CEC

Most of targeted soil samples (64.44%) have low CEC values ( $< 12$  meq/100g), whereas 33.33% of the samples have medium CEC values (12-25 meq/100g), while only one sample has a high CEC value (25.55 meq/100g) as show in figure 4.2. In this research the CEC rating (very low, low, medium and high) was defined as described by Hazelton et al. (2007). Since, high CEC value is an indicator for soils with more clay content, while low CEC is an indicator of sandy textured soils, the results of the CEC of the soil samples are compatible with the results of the texture analysis of the samples where 71.1% (32 sample) have sand and loamy sand texture. Since, low CEC is also an indicator for low soil organic matter content, the results of the CEC in this research agrees with the results obtained from the

research done by AbuSamra (2014), who revealed that the organic matter content in the soils of Gaza Strip are generally low (less than 1.5%).

The CEC values of the targeted soil samples range from (3.32 to 27.55) meq/100g. The lowest CEC values were found in samples label 1, 33, 34 and 32 respectively (table 4.1). These samples have a sand texture, with highest sand and lowest clay and silt ratios. In the other hand, the highest CEC values were found in samples label 36 (sandy clay loam) and 35 (loam) respectively. These results agree with the significant negative correlation between the CEC and the sand ratio of the soil samples ( $r = -0.899^{**}$ ), and the significant correlation between the CEC and the clay content ( $r = 0.832^{**}$ ), as well as the significant correlation between CEC and silt content ( $r = 0.804^{**}$ ) as shown in table 4.4. According to the CEC values of the soil samples, downward movement of metals is likely to occur in case of significant amounts of metals are added to these soils.



**Figure 4.2: CEC rating in targeted soil samples**

For control samples, table 4.2 shows that all control samples have low CEC values ranging from 3.13 meq/100g in sample label 52 to 7.85 meq/100g in sample label 55. However, these results agrees with results of soil texture analysis, where sample label 52 has no clay content, while sample label 55 has the highest clay content of 7%. In addition, the CEC values of the bar samples are very low (3.87 meq/100g in sample label 56 and 0.79 meq/100g in sample label 58) as shown in table 4.3.



Table 4.4: Correlation coefficient among all parameters in soil samples

	N= 45	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn	Al	CEC	pH	sand	clay	silt
<b>Cd</b>	Pearson Correlation Sig. (2-tailed)	1													
<b>Co</b>	Pearson Correlation Sig. (2-tailed)	0.181 0.234	1												
<b>Cr</b>	Pearson Correlation Sig. (2-tailed)	0.113 0.460	0.859**	1											
<b>Cu</b>	Pearson Correlation Sig. (2-tailed)	0.117 0.444	0.476**	0.489**	1										
<b>Mn</b>	Pearson Correlation Sig. (2-tailed)	0.056 0.712	0.827**	0.873**	0.395**	1									
<b>Ni</b>	Pearson Correlation Sig. (2-tailed)	0.049 0.750	0.849**	0.937**	0.462**	0.845**	1								
<b>Pb</b>	Pearson Correlation Sig. (2-tailed)	0.386** 0.009	0.624**	0.594**	0.347*	0.511**	0.545**	1							
<b>Zn</b>	Pearson Correlation Sig. (2-tailed)	0.067 0.660	0.594**	0.700**	0.690**	0.580**	0.691**	0.399**	1						
<b>Al</b>	Pearson Correlation Sig. (2-tailed)	-0.039 0.799	0.733**	0.697**	0.429**	0.706**	0.691**	0.265	0.589**	1					
<b>CEC</b>	Pearson Correlation Sig. (2-tailed)	0.060 0.695	0.837**	0.867**	0.519**	0.858**	0.833**	0.563**	0.688**	0.714**	1				
<b>pH</b>	Pearson Correlation Sig. (2-tailed)	0.289 0.054	-0.274	-0.367-*	-0.525-**	-0.213	-0.356-*	0.035	-0.576-**	-0.356-*	-0.462-**	1			
<b>sand</b>	Pearson Correlation Sig. (2-tailed)	-0.088 0.566	-0.772-**	-0.771**	-0.515-**	-0.795-**	-0.771-**	-0.470-**	-0.654-**	-0.717-**	-0.899-**	0.444**	1		
<b>clay</b>	Pearson Correlation Sig. (2-tailed)	0.086 0.576	0.782**	0.821**	0.218	0.837**	0.773**	0.607**	0.454**	0.549**	0.832**	-0.155	-0.766-**	1	
<b>silt</b>	Pearson Correlation Sig. (2-tailed)	0.077 0.616	0.663**	0.645**	0.570**	0.668**	0.665**	0.347*	0.649**	0.689**	0.804**	-0.505-**	-0.962-**	0.561**	1

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

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

### 4.3 Soil pH

The soil pH was classified according to Osman (2012). The results shows that the pH in 82.22% of the targeted soil samples (37 samples) are on the slightly alkaline and moderately alkaline side with pH values ranging from 7.6 to 8.5. Six samples (13.33%) are on the strongly alkaline side with pH values ranging from 8.7 to 9, while only two samples (4.44%) have pH values greater than 9 as shown in figure 4.3. The lowest pH value (7.67) was recorded in sample label 22, and the highest value (9.13) was measured in sample label 4 as shown in table label 4.1. Generally, the solubility of metals decreases as the pH increases. That is the lower pH value, the more metal can be found in soil solution. Nevertheless, higher solubility of metals in soil solution was attributed to enhanced formation of organic matter complexes, where extensive evidence exist that in alkaline pH range most dissolved metals are present as metal soluble organic ligand complexes (Sherene, 2010). Accordingly, since the organic matter content in soil Gaza soil are generally low, and the pH values of the soil samples are on slightly alkaline and moderately alkaline side, so it is expected that the downward mobility of metals in the soil profile is unlikely to take place.

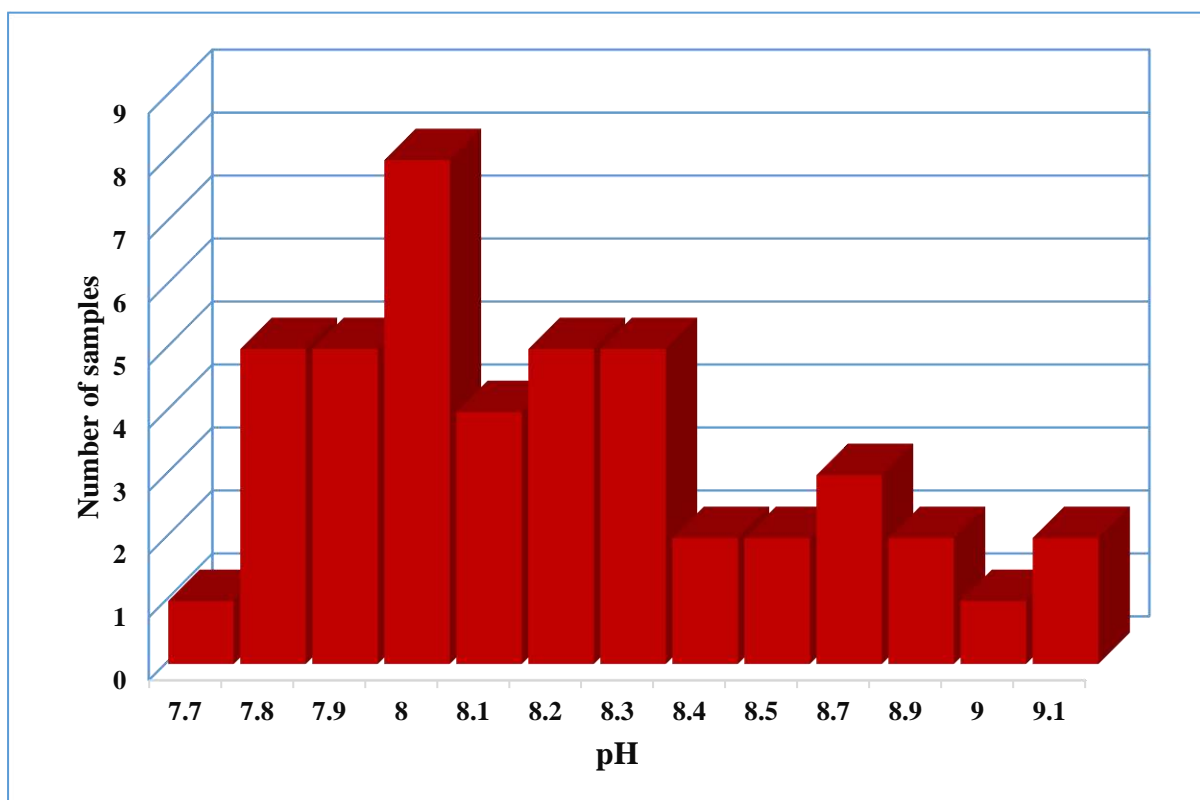
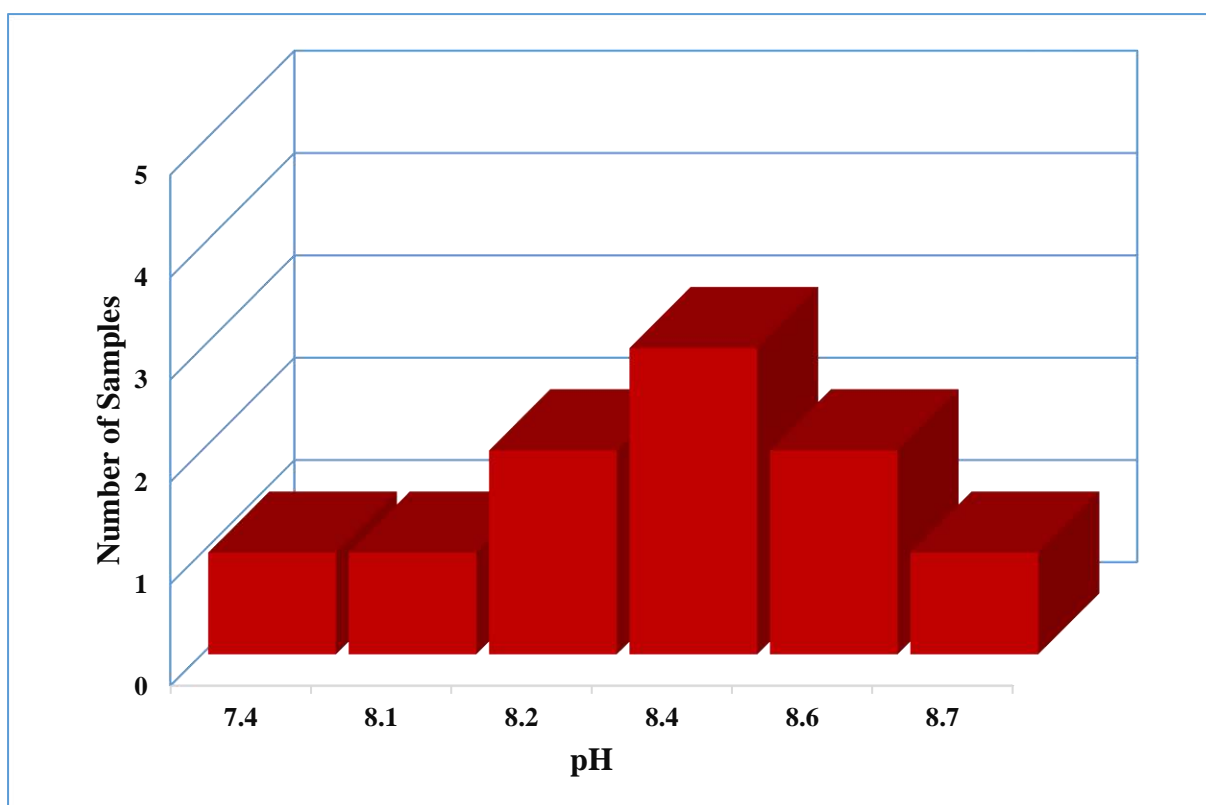


Figure 4.3: Frequency distribution of pH values in targeted soil samples



**Figure 4.4: Frequency distribution of pH values in control soil samples**

Figure 4.4 illustrates that, seven of the ten control samples have pH values on the slightly alkaline and moderately alkaline side with pH values ranging from 7.4 to 8.4, while the other remaining three samples have pH values on the strongly alkaline side ranging from 8.6 to 8.7. The result of the pH values of the control samples are listed in table 4.2. In addition to that, the two bar samples label 56 and 58 have pH values of 8.6 and 8.8 respectively, which are on the strongly alkaline side. The results of the pH values of the bar samples are listed in table 4.3. Although, the high sand content, as well as the low CEC values of Gaza soils increase the possibility of downward migration of metals in soil profile via soil solution, the slightly alkaline to moderately alkaline values of the soil pH decrease this risk.

#### **4.4 Metals in soil samples**

Excluding Cu in bar sample label 58, the selected metals (Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn and Al) were detected in all soil and rubble samples. The minimum, maximum, mean concentration and standard deviation of each metal are listed in table 4.5. For sample label 58, which has Cu concentration below the detection limit, a mean value equals to half of the detection limit was used in the statistical analysis instead of a missing data (Succop et al., 2004).

**Table 4.5: Mean concentration and standard deviation of metals in targeted soil, rubble, control and bar samples.**

	(mg/kg)								
	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn	Al
<b>Soil:</b>	N= 45 except for Al (N= 44)								
<b>min</b>	0.502	2.107	3.636	2.647	28.240	3.759	4.162	7.321	799.844
<b>max</b>	3.040	9.317	37.400	40.012	244.369	18.766	13.536	35.158	9507.166
<b>mean</b>	0.936	4.758	16.854	9.623	115.730	9.919	6.863	20.541	4493.672
<b>Sd*</b>	0.398	1.568	6.761	7.524	45.341	3.718	1.930	7.161	1925.902
<b>Rubble:</b>	N=5								
<b>min</b>	0.931	2.360	6.537	6.529	35.147	4.178	4.330	3.738	1150.508
<b>max</b>	4.112	11.733	12.665	110.203	51.601	9.297	43.423	27.878	16597.557
<b>mean</b>	1.827	5.041	10.135	50.469	42.970	7.172	15.895	16.808	4697.418
<b>Sd</b>	1.306	3.939	2.237	47.132	6.482	2.004	16.157	8.752	6662.332
<b>Control:</b>	N=10								
<b>min</b>	0.157	1.795	6.630	2.318	39.825	3.506	4.971	12.974	1197.407
<b>max</b>	1.129	3.861	17.307	13.464	108.827	7.610	29.871	51.230	3297.836
<b>mean</b>	0.496	2.761	11.715	4.801	74.884	5.493	9.886	25.484	1882.659
<b>Sd</b>	0.312	0.732	3.263	3.333	20.464	1.383	8.336	10.756	695.870
<b>Bar:</b>	N=2								
<b>min</b>	0.123	1.602	5.545	0.256	43.015	2.925	3.093	5.277	622.599
<b>max</b>	0.190	2.088	8.688	2.783	48.765	4.083	5.574	12.146	3899.922
<b>mean</b>	0.157	1.845	7.117	1.519	45.890	3.504	4.333	8.712	2261.261

\* Sd: Standard deviation

The mean concentration of the bar samples was considered as a normal limit of the natural contribution of the environment while, the mean concentration of the control samples was used as a normal limit for agricultural activities. Accordingly, samples with values higher than the mean of the bar soil samples are considered to be affected by agricultural activities and samples with values higher than the mean of the control samples are considered to be affected by military activities. The concentrations of the metals in bar and control samples are listed in table 4.6 and 4.7 respectively.

**Table 4.6: Concentrations of metals in bar samples (N=2)**

	(mg/kg)								
Sample label	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn	Al
<b>56</b>	0.123	2.088	8.688	2.783	48.765	4.083	5.574	12.146	3899.922
<b>58</b>	0.190	1.602	5.545	N/D*	43.015	2.925	3.093	5.277	622.599
<b>EPA</b>	1	20	21	330	630	20	23	1000	N/A

\* N/D: Not detected



**Table 4.7: Concentrations of metals in Control samples (N=10)**

<b>Sample label</b>	<b>(mg/kg)</b>								
	<b>Cd</b>	<b>Co</b>	<b>Cr</b>	<b>Cu</b>	<b>Mn</b>	<b>Ni</b>	<b>Pb</b>	<b>Zn</b>	<b>Al</b>
<b>51</b>	0.794	2.565	9.274	4.733	80.462	5.416	7.341	18.435	2081.312
<b>52</b>	0.157	1.795	6.630	2.829	39.825	3.788	4.971	22.842	1197.407
<b>53</b>	0.731	2.580	8.481	3.466	50.978	4.628	5.198	12.974	1861.011
<b>54</b>	0.492	2.804	12.268	3.033	77.983	5.794	6.250	26.803	1341.487
<b>55</b>	0.558	3.665	15.614	6.881	108.827	7.509	5.849	30.697	3297.836
<b>57</b>	0.323	3.517	12.719	4.718	88.229	6.353	9.089	21.582	1746.822
<b>59</b>	0.257	2.223	12.007	4.002	76.240	5.068	29.871	19.593	2830.049
<b>60</b>	0.324	2.799	13.086	2.566	74.239	5.259	5.451	18.772	1312.039
<b>61</b>	0.190	1.798	9.768	2.318	58.816	3.506	4.978	31.916	1326.951
<b>62</b>	1.129	3.861	17.307	13.464	93.238	7.610	19.858	51.230	1831.675
<b>EPA</b>	<b>1</b>	<b>20</b>	<b>21</b>	<b>330</b>	<b>630</b>	<b>20</b>	<b>23</b>	<b>1000</b>	<b>N/A*</b>

\*N/A: Not applicant

Targeted soil samples with concentrations exceeding the Maximum Allowable Concentrations (MACs) of Chemical Constituents in Uncontaminated Soil listed by USEPA, are considered posing risk to human health. Anyway, only Cd in 12 samples and Cr in 9 samples of the 45 targeted soil samples were found to be threatening human health risk. The concentrations of the metals in the targeted soil samples are listed in table 4.8.

The T-test was firstly carried out to compare the mean concentration of each metal between targeted soil samples and control samples. The test shows that, the targeted soil samples have significantly ( $P\text{-value} < 0.05$ ) higher concentrations of Cd, Co, Cr, Cu, Mn, Ni and Al than control samples, indicating that the military activities enriches the targeted locations with significant amounts of these metals. While for Pb and Zn, the T-test shows that, there are no significant statistical differences between the mean concentrations of them in targeted soil and control samples. Taking into account that the mean concentrations of Pb and Zn in control samples are higher than those of targeted soil samples (table 4.5), it can be concluded that, the concentrations of Pb and Zn in the targeted locations are not affected by military activities.

In addition to that, the T-test shows that, among the investigated metals, only the mean concentration of Cu in samples collected from areas subjected to AS is significantly higher than that of samples collected from areas subjected to AFB. The thing which refers to that, Cu represents 90% of the bronze-rotating band used in the artillery shells.

Finally, according to the results of the T-test, there are no significant statistical differences ( $P\text{-value} > 0.05$ ) between the mean concentration of all metals in samples collected from

craters formed by AFB (table 4.9) and samples collected from areas surrounding to these craters (table 4.11), as well as, between samples collected from craters formed by AS (table 4.10) and samples collected from areas surrounding to these craters (table 4.12). That refers to the high order detonation of bombs and artillery shells which is efficient to distribute the metals involved in the body of the shell or in the explosive charge over several hundreds of square meters (Hewitt, et al., 2007). The result of the T-test are shown in table 4.13.



**Table 4.8: Concentrations of metals in targeted soil samples (N=45)**

<b>Sample label</b>	<b>(mg/kg)</b>								
	<b>Cd</b>	<b>Co</b>	<b>Cr</b>	<b>Cu</b>	<b>Mn</b>	<b>Ni</b>	<b>Pb</b>	<b>Zn</b>	<b>Al</b>
<b>1</b>	0.975	2.107	3.636	6.449	28.240	3.759	6.636	9.572	799.844
<b>2</b>	1.034	6.042	18.907	6.326	134.861	11.119	8.366	19.296	5650.206
<b>3</b>	1.280	5.172	17.022	5.874	126.660	9.423	8.890	17.086	4705.362
<b>4</b>	3.040	4.382	16.790	4.348	99.050	7.302	8.128	12.254	3581.964
<b>5</b>	0.833	5.333	18.050	4.866	115.522	16.302	8.484	15.958	3575.407
<b>6</b>	1.170	4.824	15.958	6.590	112.724	7.990	8.897	16.371	3162.183
<b>7</b>	0.902	5.261	15.349	5.093	102.230	8.740	8.509	23.351	4417.633
<b>8</b>	1.241	5.018	13.731	5.222	101.338	8.846	8.955	16.305	3124.566
<b>9</b>	0.969	4.468	12.113	3.707	76.559	7.778	8.125	18.758	3653.730
<b>10</b>	0.703	3.156	7.220	2.647	39.770	5.735	5.840	7.321	2377.295
<b>11</b>	0.700	2.968	7.073	2.849	54.019	4.891	5.818	9.298	1899.166
<b>12</b>	0.768	3.588	10.674	4.249	81.749	6.749	5.443	15.393	3466.972
<b>13</b>	0.635	5.699	18.218	7.437	166.729	11.547	6.210	25.497	6758.895
<b>14</b>	0.699	4.027	14.263	4.131	107.380	7.227	7.484	15.195	4131.478
<b>15</b>	0.769	5.529	19.794	7.124	129.585	10.324	7.749	21.446	5248.310
<b>16</b>	0.502	3.943	14.279	7.549	105.097	7.030	4.683	15.640	4390.803
<b>17</b>	0.702	3.501	9.719	3.600	127.872	6.545	5.828	9.919	3433.768
<b>18</b>	0.679	3.147	8.158	4.734	153.835	4.897	5.442	8.349	2541.879
<b>19</b>	1.234	4.461	13.528	6.857	88.838	8.929	5.818	22.084	4204.461
<b>20</b>	0.768	2.795	10.431	7.007	72.511	6.815	4.677	25.965	3353.481
<b>21</b>	0.901	6.660	24.179	14.137	151.748	14.069	6.204	25.525	9078.105
<b>22</b>	0.701	3.411	25.511	11.375	173.478	15.174	6.590	31.265	4253.407
<b>23</b>	0.636	5.890	20.064	10.554	124.158	12.538	5.970	24.135	7276.194
<b>24</b>	1.415	4.473	15.842	12.424	100.714	8.884	7.878	35.158	2617.204
<b>25</b>	0.835	3.150	12.836	5.094	92.624	7.027	6.276	13.943	2495.233
<b>26</b>	0.837	4.652	21.490	7.557	125.279	12.599	6.988	19.843	3373.707
<b>27</b>	0.991	3.062	14.275	5.201	95.037	8.605	5.064	20.991	4144.678
<b>28</b>	0.745	3.056	10.779	7.319	82.835	7.355	4.162	24.303	3330.261
<b>29</b>	0.590	3.677	14.389	5.306	97.805	8.807	4.679	18.457	4328.915
<b>30</b>	0.658	3.592	16.320	4.742	83.055	7.786	4.428	13.614	2514.241
<b>31</b>	0.568	4.555	17.615	6.582	95.768	9.489	4.933	15.979	5501.064
<b>32</b>	0.768	3.500	13.307	5.198	74.135	7.502	4.295	14.806	3388.722
<b>33</b>	0.723	3.674	11.747	6.261	65.697	8.185	4.294	17.930	2991.533
<b>34</b>	0.568	3.853	12.234	4.133	71.353	6.065	4.424	16.572	3727.387
<b>35</b>	0.992	9.317	33.102	12.353	244.369	18.766	9.155	29.319	8686.522
<b>36</b>	0.972	8.106	37.400	12.174	214.866	18.611	13.536	29.507	5263.727
<b>37</b>	0.702	5.702	24.935	13.732	148.772	13.816	8.256	28.126	4203.405
<b>38</b>	1.235	8.072	27.667	13.933	208.750	18.190	7.356	28.316	7989.122
<b>39</b>	0.968	7.890	27.765	18.180	212.987	15.574	7.605	29.146	9507.166
<b>40</b>	0.901	6.221	25.617	40.012	150.162	13.523	9.009	31.693	5951.841
<b>41</b>	1.102	5.469	20.223	25.026	130.343	11.344	8.125	31.932	5933.930
<b>42</b>	1.264	4.031	17.393	17.305	109.899	10.548	7.525	23.558	5231.946
<b>43</b>	0.969	5.258	15.459	22.480	106.977	9.361	4.682	22.875	4605.746
<b>44</b>	1.035	5.358	17.174	26.931	108.024	10.447	10.035	31.302	6850.093
<b>45</b>	1.439	6.063	16.214	18.343	114.449	10.128	7.373	20.985	112.231
<b>EPA</b>	<b>1</b>	<b>20</b>	<b>21</b>	<b>330</b>	<b>630</b>	<b>20</b>	<b>23</b>	<b>1000</b>	<b>N/A</b>

Table 4.9 Concentration of metals, CEC, pH and soil texture in soil samples collected from craters formed by AFB (N=18)

Sample label	Concentration (mg/kg)									CEC Meq/100g	pH	Soil classification		
	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn	Al			Sand %	Clay %	Silt %
1	0.975	2.107	3.636	6.449	28.240	3.759	6.636	9.572	799.844	3.32	8.48	94	0	6
2	1.034	6.042	18.907	6.326	134.861	11.119	8.366	19.296	5650.206	13.92	8.41	66	5	29
5	0.833	5.333	18.050	4.866	115.522	16.302	8.484	15.958	3575.407	9.12	8.89	83	5	12
7	0.902	5.261	15.349	5.093	102.230	8.740	8.509	23.351	4417.633	8.06	8.74	87	4	9
9	0.969	4.468	12.113	3.707	76.559	7.778	8.125	18.758	3653.730	6.42	8.33	86	4	10
10	0.703	3.156	7.220	2.647	39.770	5.735	5.840	7.321	2377.295	5.42	8.227	88	0	12
13	0.635	5.699	18.218	7.437	166.729	11.547	6.210	25.497	6758.895	18.23	8.02	65	6	29
15	0.769	5.529	19.794	7.124	129.585	10.324	7.749	21.446	5248.310	13.59	8	70	6	24
17	0.702	3.501	9.719	3.600	127.872	6.545	5.828	9.919	3433.768	7.18	9.04	84	4	12
18	0.679	3.147	8.158	4.734	153.835	4.897	5.442	8.349	2541.879	6.23	9.1	86	4	10
20	0.768	2.795	10.431	7.007	72.511	6.815	4.677	25.965	3353.481	11.53	8.12	76	4	20
21	0.901	6.660	24.179	14.137	151.748	14.069	6.204	25.525	9078.105	15.12	7.92	61	6	33
26	0.837	4.652	21.490	7.557	125.279	12.599	6.988	19.843	3373.707	9.51	8.24	82	6	12
30	0.658	3.592	16.320	4.742	83.055	7.786	4.428	13.614	2514.241	6.48	8.3	93	2	5
31	0.568	4.555	17.615	6.582	95.768	9.489	4.933	15.979	5501.064	7.38	8.53	89	4	7
35	0.992	9.317	33.102	12.353	244.369	18.766	9.155	29.319	8686.522	23.27	8.04	46	16	38
36	0.972	8.106	37.400	12.174	214.866	18.611	13.536	29.507	5263.727	27.55	8.01	58	20	22
38	1.235	8.072	27.667	13.933	208.750	18.190	7.356	28.316	7989.122	20.03	7.88	67	11	22
Mean	0.841	5.111	17.743	7.248	126.197	10.726	7.137	19.307	4678.719					

Table 4.10: Concentration of metals, CEC, pH and soil texture in soil samples collected from craters formed by AS. (N=9)

Sample label	Concentration (mg/kg)									CEC Meq/100g	pH	Soil classification		
	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn	Al			Sand %	Clay %	Silt %
4	3.040	4.382	16.790	4.348	99.050	7.302	8.128	12.254	3581.964	7.82	9.13	83	4	13
12	0.768	3.588	10.674	4.249	81.749	6.749	5.443	15.393	3466.972	8.00	7.8	86	2	12
23	0.636	5.890	20.064	10.554	124.158	12.538	5.970	24.135	7276.194	12.57	7.79	72	2	26
24	1.415	4.473	15.842	12.424	100.714	8.884	7.878	35.158	2617.204	6.09	8.21	84	2	14
28	0.745	3.056	10.779	7.319	82.835	7.355	4.162	24.303	3330.261	6.92	8.27	89	2	9
33	0.723	3.674	11.747	6.261	65.697	8.185	4.294	17.930	2991.533	4.35	8.37	93	0	7
40	0.901	6.221	25.617	40.012	150.162	13.523	9.009	31.693	5951.841	15.27	7.85	68	4	28
42	1.264	4.031	17.393	17.305	109.899	10.548	7.525	23.558	5231.946	10.89	8.01	72	4	24
44	1.035	5.358	17.174	26.931	108.024	10.447	10.035	31.302	6850.093	12.54	7.79	72	4	24
Mean	1.170	4.519	16.231	14.378	102.476	9.503	6.938	23.970	4588.667					

**Table 4.11: Concentration of metals, CEC, pH and soil texture in soil samples collected from areas surrounding craters formed by AFB (N=12)**

Sample label	Concentration (mg/kg)									CEC Meq/100g	pH	Soil classification		
	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn	Al			Sand %	Clay %	Silt %
<b>3</b>	1.280	5.172	17.022	5.874	126.660	9.423	8.890	17.086	4705.362	10.58	8.85	85	4	<b>11</b>
<b>6</b>	1.170	4.824	15.958	6.590	112.724	7.990	8.897	16.371	3162.183	8.82	8.69	93	2	<b>5</b>
<b>8</b>	1.241	5.018	13.731	5.222	101.338	8.846	8.955	16.305	3124.566	7.83	8.69	89	2	<b>9</b>
<b>11</b>	0.700	2.968	7.073	2.849	54.019	4.891	5.818	9.298	1899.166	6.25	7.99	92	0	<b>8</b>
<b>14</b>	0.699	4.027	14.263	4.131	107.380	7.227	7.484	15.195	4131.478	7.50	8.09	93	2	<b>5</b>
<b>16</b>	0.502	3.943	14.279	7.549	105.097	7.030	4.683	15.640	4390.803	12.59	7.95	72	6	<b>22</b>
<b>19</b>	1.234	4.461	13.528	6.857	88.838	8.929	5.818	22.084	4204.461	12.02	8.08	80	2	<b>18</b>
<b>22</b>	0.701	3.411	25.511	11.375	173.478	15.174	6.590	31.265	4253.407	14.84	7.67	67	4	<b>29</b>
<b>27</b>	0.991	3.062	14.275	5.201	95.037	8.605	5.064	20.991	4144.678	6.22	8.28	93	2	<b>5</b>
<b>32</b>	0.768	3.500	13.307	5.198	74.135	7.502	4.295	14.806	3388.722	4.92	8.28	94	0	<b>6</b>
<b>37</b>	0.702	5.702	24.935	13.732	148.772	13.816	8.256	28.126	4203.405	14.77	8.04	80	6	<b>14</b>
<b>39</b>	0.968	7.890	27.765	18.180	212.987	15.574	7.605	29.146	9507.166	19.67	7.91	68	9	<b>23</b>
<b>Mean</b>	0.913	4.498	16.804	7.730	116.705	9.584	6.863	19.693	4259.616					

**Table 4.12: Concentration of metals, CEC, pH and soil texture in soil samples collected from areas surrounding craters formed by AS. (N=6)**

Sample label	Concentration (mg/kg)									CEC Meq/100g	pH	Soil classification		
	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn	Al			Sand %	Clay %	Silt %
<b>25</b>	0.835	3.150	12.836	5.094	92.624	7.027	6.276	13.943	2495.233	5.92	8.08	95	2	<b>3</b>
<b>29</b>	0.590	3.677	14.389	5.306	97.805	8.807	4.679	18.457	4328.915	6.42	8.15	93	2	<b>5</b>
<b>34</b>	0.568	3.853	12.234	4.133	71.353	6.065	4.424	16.572	3727.387	4.75	8.22	95	0	<b>5</b>
<b>41</b>	1.102	5.469	20.223	25.026	130.343	11.344	8.125	31.932	5933.930	19.25	7.87	74	2	<b>24</b>
<b>43</b>	0.969	5.258	15.459	22.480	106.977	9.361	4.682	22.875	4605.746	11.56	7.8	80	2	<b>18</b>
<b>45</b>	1.439	6.063	16.214	18.343	114.449	10.128	7.373	20.985	-	11.24	7.82	76	4	<b>20</b>
<b>Mean</b>	0.917	4.578	15.226	13.397	102.259	8.789	5.927	20.794	4218.242					

**Table 4.13: Summary of T-test on mean concentration of metals between different soil categories**

<b>Summary of T-test on mean concentrations of metals between targeted soil and control samples</b>				
<b>Metal</b>	<b>T-value</b>	<b>df</b>	<b>P-value</b>	<b>Level</b>
<b>Cd</b>	3.272	53	0.002	Significant
<b>Co</b>	6.072	30.263	0.000	Significant
<b>Cr</b>	2.331	53	0.024	Significant
<b>Cu</b>	3.133	32.422	0.004	Significant
<b>Mn</b>	2.771	53	0.008	Significant
<b>Ni</b>	6.268	40.005	0.000	Significant
<b>Pb</b>	-1.140	9.216	0.283	Not significant
<b>Zn</b>	-1.793	53	0.079	Not significant
<b>Al</b>	7.167	41.369	0.000	Significant
<b>Summary of T-test on mean concentration of metals between samples collected from areas subjected to AFB and areas subjected to AS</b>				
<b>Cd</b>	-1.221	15.731	0.240	Not significant
<b>Co</b>	0.647	43	0.521	Not significant
<b>Cr</b>	0.871	42.855	0.389	Not significant
<b>Cu</b>	-2.279	15.839	0.037	Significant
<b>Mn</b>	1.791	42.374	0.080	Not significant
<b>Ni</b>	1.090	42.921	0.282	Not significant
<b>Pb</b>	0.806	43	0.425	Not significant
<b>Zn</b>	-1.447	43	0.155	Not significant
<b>Al</b>	0.087	42	0.931	Not significant
<b>Summary of T-test on mean concentrations of metals between samples collected from craters and areas surrounding craters formed by AFB</b>				
<b>Cd</b>	-0.828	16.996	0.419	Not significant
<b>Co</b>	0.927	28	0.362	Not significant
<b>Cr</b>	0.319	28	0.752	Not significant
<b>Cu</b>	-0.328	28	0.745	Not significant
<b>Mn</b>	0.480	28	0.635	Not significant
<b>Ni</b>	0.711	28	0.483	Not significant
<b>Pb</b>	0.370	28	0.714	Not significant
<b>Zn</b>	-0.145	28	0.886	Not significant
<b>Al</b>	0.529	28	0.601	Not significant
<b>Summary of T-test on mean concentrations of metals between samples collected from craters and areas surrounding craters formed by AS</b>				
<b>Cd</b>	0.770	13	0.455	Not significant
<b>Co</b>	-0.100	13	0.922	Not significant
<b>Cr</b>	0.456	13	0.656	Not significant
<b>Cu</b>	0.167	13	0.870	Not significant
<b>Mn</b>	0.018	13	0.986	Not significant
<b>Ni</b>	0.603	13	0.557	Not significant
<b>Pb</b>	1.012	13	0.330	Not significant
<b>Zn</b>	0.830	13	0.421	Not significant
<b>Al</b>	0.412	12	0.688	Not significant

#### 4.4.1 Cadmium (Cd)

The concentration of cadmium in the soils of Gaza is affected by both military and agricultural activities. The Cd concentrations in targeted soil samples range from (0.5 mg/kg to 3.04 mg/kg) with mean concentration of 0.936 mg/kg, which is almost two times the mean concentration of control samples (0.496 mg/kg). The results of the T-test illustrated in table 4.13, show that, there is a significant statistical difference ( $P\text{-value} = 0.002$ ) between the mean concentration of Cd in targeted soil samples and the mean concentration of Cd in control samples, which indicates that the military activities affected the Cd concentration in the soils of targeted locations. Anyhow, that could be concluded from figure 4.5, which illustrates that all targeted soil samples have Cd concentrations higher than the mean of control samples.

In the other hand, figure 4.6 shows that all control samples have Cd concentrations higher than the mean concentration of the bar soil samples (0.157 mg/kg), indicating that the agricultural activities affect the Cd concentration in Gaza Strip, which may refer to the application of Cd containing phosphate fertilizers (Shomar, et al., 2004). That agrees with results shown in table 4.5, which reveals that, the mean concentration of Cd in control samples is 3.2 times the mean concentration of the bar samples. Figure 4.7, clearly shows that, the concentration of Cd in Gaza soils is much affected by military than agricultural activities.

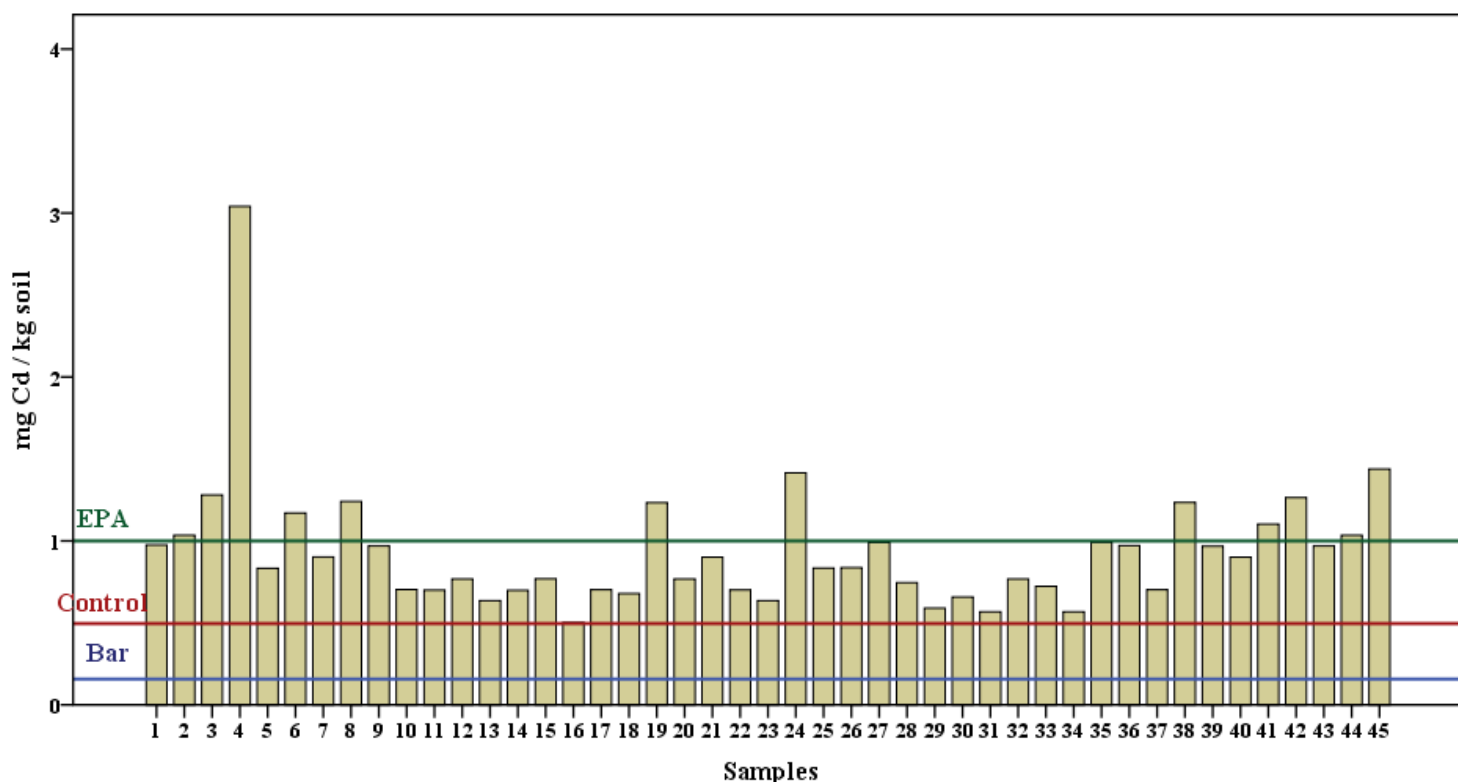




Figure 4.5: Concentration of cadmium in targeted soil samples

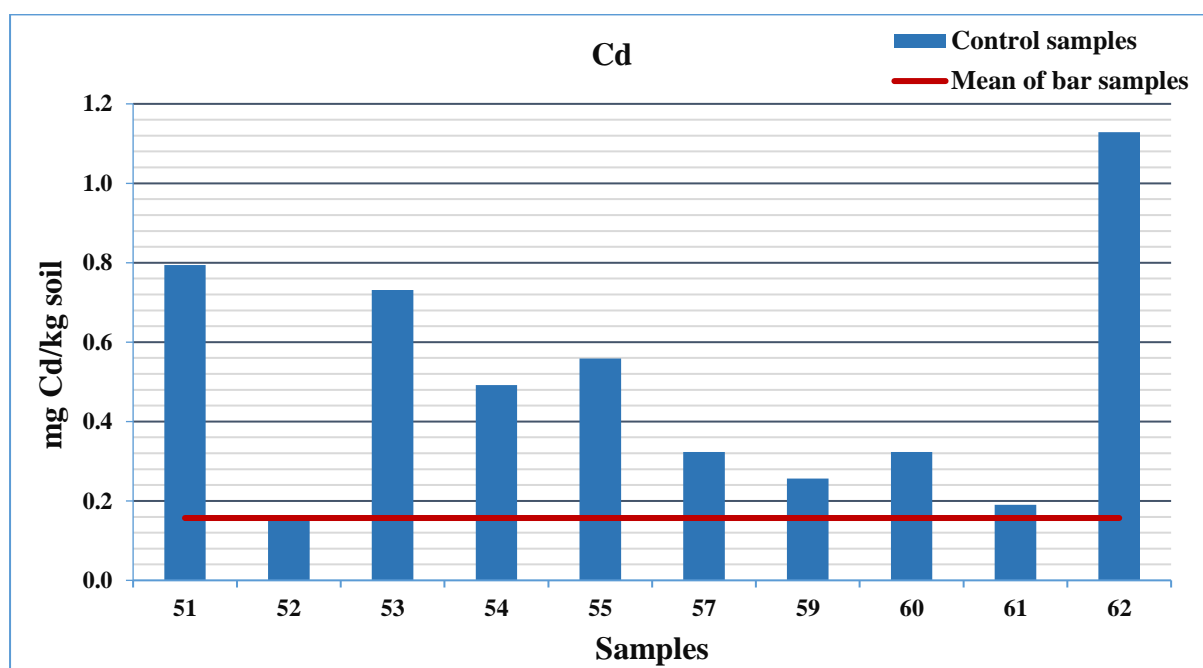


Figure 4.6: Concentration of cadmium in control samples

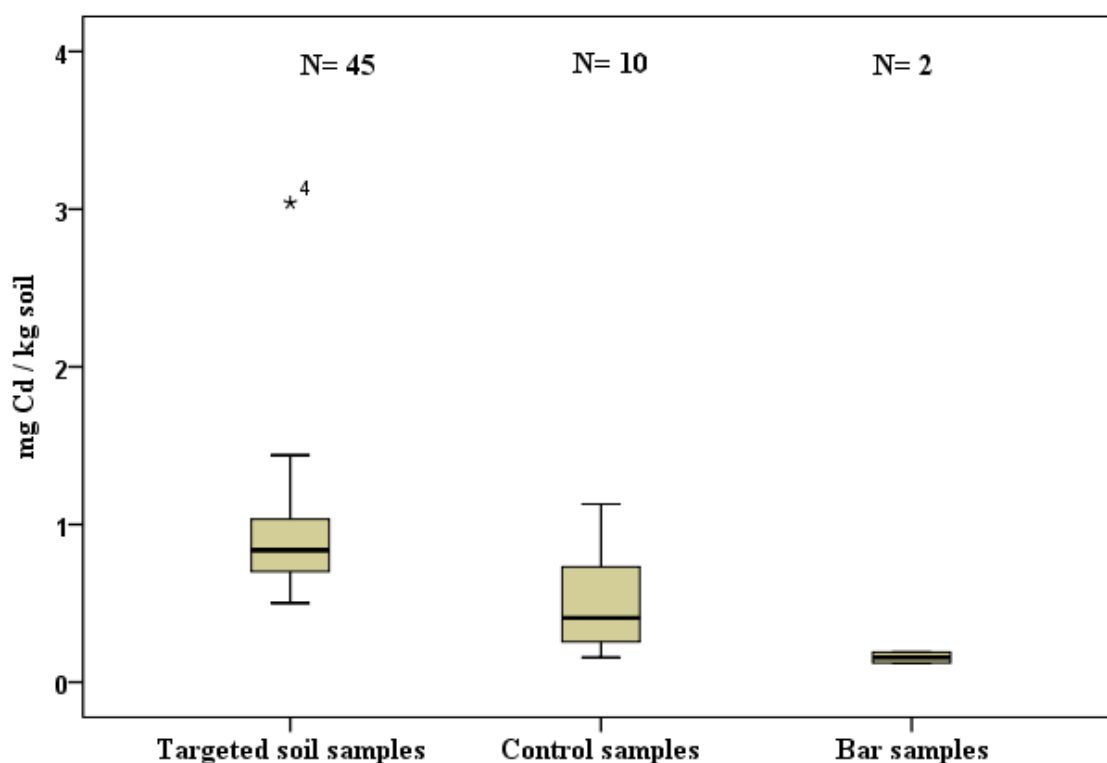


Figure 4.7: Concentration of cadmium in targeted soil vs. control and bar samples

Figure 4.5 shows that, the concentration of Cd in 26.67% of the targeted soil samples are higher than the value of (MACs) of Chemical Constituents in Uncontaminated Soil listed by USEPA (1 mg/kg), which means that, in these locations the concentration of Cd pose threat

to human health. Samples label 4, 45 and 24 have the highest Cd concentrations of 3.040, 1.439 and 1.415 mg/kg respectively, while the lowest concentrations (0.502, 0.568 and 0.568 mg/kg) were detected in samples label 16, 31 and 34 respectively as shown in table 4.8.

#### **4.4.1.1 Cd in soil samples from craters formed by AFB**

The concentration of cadmium in soil samples collected from craters resulted by AFB ranges from 0.568 mg/kg to 1.235 mg/kg, with mean concentration of 0.841 mg/kg as shown in table 4.9. The highest Cd concentration was detected in sample label 38, and the lowest was found in sample label 31.

#### **4.4.1.2 Cd in soil samples from areas surrounding craters formed by AFB**

The concentration of Cd in soil samples collected from areas surrounding craters formed by AFB range from 0.502 to 1.28 mg/kg with mean concentration of 0.913 mg/kg. Sample label 3 has the highest concentration of 1.28 mg/kg, while sample label 16 has the lowest concentration of 0.502 mg/kg. as shown in table 4.11.

#### **4.4.1.3 Cd in soil samples from craters formed by AS**

The concentrations of the Cd in soil samples collected from craters resulted by AS range from 0.636 mg/kg to 1.415 mg/kg with mean concentration of 1.17mg/kg as shown in table 4.10. The highest concentration was detected in sample label 4 and the lowest one was detected in sample label 23.

#### **4.4.1.4 Cd in soil samples from areas surrounding craters formed by AS**

The concentrations of Cd in soil samples collected from areas surrounding to craters formed by AS range from 0.568 mg/kg to 1.439 mg/kg, with mean concentration of 0.917 mg/kg. The highest concentration was detected in sample label 45 and the lowest was detected in sample label 34 as shown in table 4.12.

Table 4.13 shows that, there is no significant statistical difference (P-value = 0.240) between the mean concentration of Cd in samples collected from areas subjected to AFB and the mean concentration of Cd in samples collected from areas subjected to AS, indicating that both AFB and AS contains Cd which introduced to the targeted soils of Gaza Strip with Cd. The results of the T-test also shows that, there is no significant statistical difference (P-value = 0.419) between the mean concentration of Cd in samples collected from craters formed by

AFB and the mean concentration of Cd in samples from areas surrounding these craters. As well as there are no significant statistical difference ( $P\text{-value} = 0.455$ ) between the mean concentrations of Cd in samples collected from craters formed by AS and the mean concentration of Cd in samples from areas surrounding these craters. The concentration of Cd are very similar in the four previously mentioned categories in the term of minimum, maximum and mean concentrations. That refers to the high order detonation of bombs and artillery shells which is efficient to distribute the metals involved in the body of the shell or in the explosive charge over several hundreds of square meters (Hewitt, et al., 2007).

#### **4.4.2 Cobalt (Co)**

Cobalt concentrations in targeted soil samples range from 2.107 mg/kg to 9.317 mg/kg, with mean concentration of 4.758 mg/kg, which is 1.7 times the mean concentration of control samples (2.761 mg/kg) as shown in table 4.5. The results of the T-test illustrated in table 4.13, reveals that, there is a significant statistical difference ( $P\text{-value} = 0.000$ ) between the mean concentration of Co in targeted soil samples and the mean concentration of Co in control samples, indicating that the concentration of Co in targeted locations is affected by military activities. This conclusion is supported by figure 4.8, which illustrates that 97.77% of targeted soil samples have Co concentrations higher than the mean of control samples. Although of that, the concentration of Co in soil samples does not pose human health risk, since the Co concentration in all targeted soil samples are much lower than the MACs of Chemical Constituents in Uncontaminated Soil listed by USEPA (20 mg/kg).

In the other hand, figure 4.9, shows that 80% of the control samples have Co concentrations higher the mean concentration of bar samples, indicating that, the agricultural activities contributed in introducing Co to Gaza soils. This contribution may occur due to the application of phosphate fertilizers which contain cobalt (ATSDR, 2004a). Figure 4.10, indicates that the Co content in targeted soil samples are much higher than that of control and bar samples, indicating that, the soil content of Cd in Gaza soils is much affected by military activities than agricultural activities.

Samples, label 35, 36, 38 and 39, which were collected from Biet Hanoon city, have the highest Co concentration of 9.317, 8.106, and 8.072 mg/kg respectively. In the other hand the lowest Co concentration found in sample label 1 which was collected from Khan younis ( Al mwasy). Cobalt in soil samples is likely to adsorbed to soil particles and not to travel far through soil profile, because mobility of Co takes place under acidic conditions (ATSDR,

2004a; Howe, et al., 2006), while the pH of the targeted soil samples ranges from slightly alkaline to strongly alkaline (figure 4.3) and the organic matter and clay content in Gaza soils are generally poor.

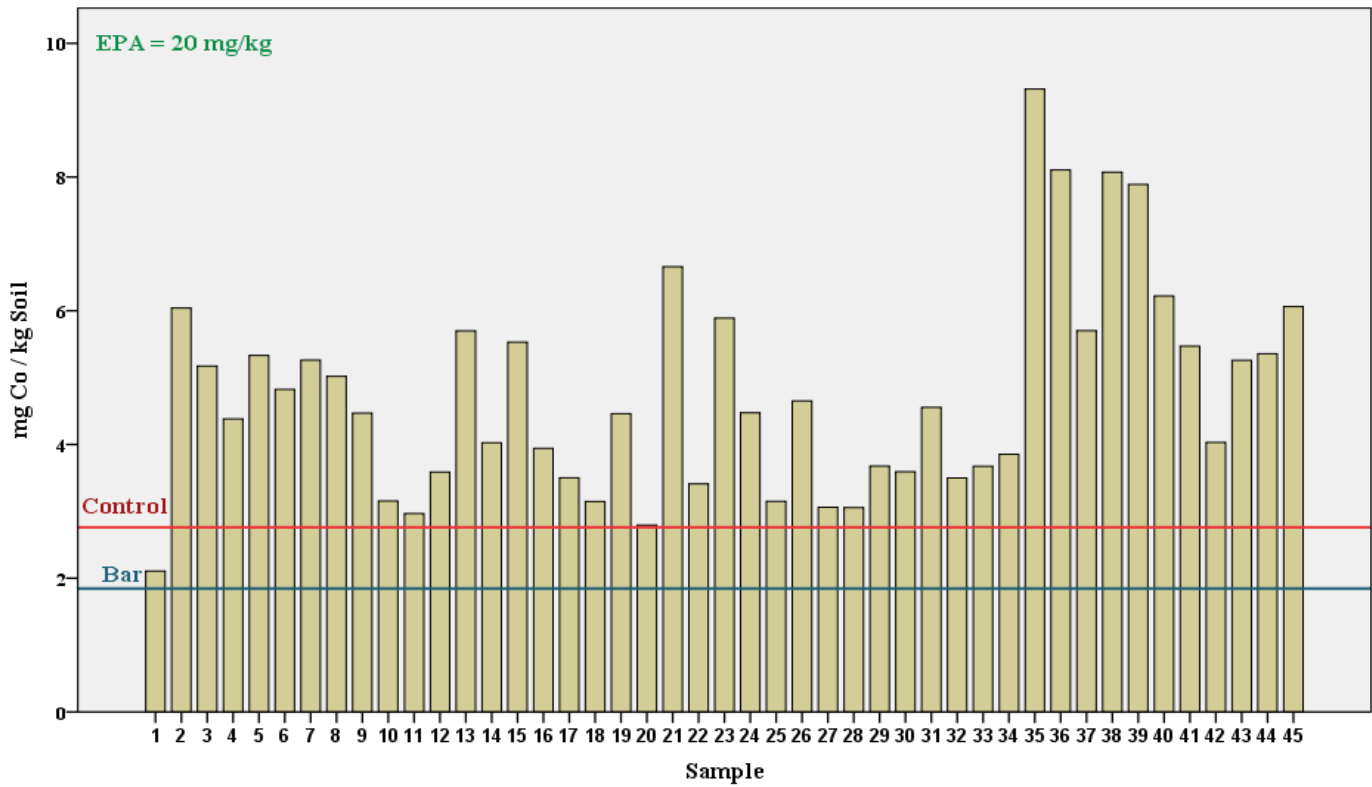
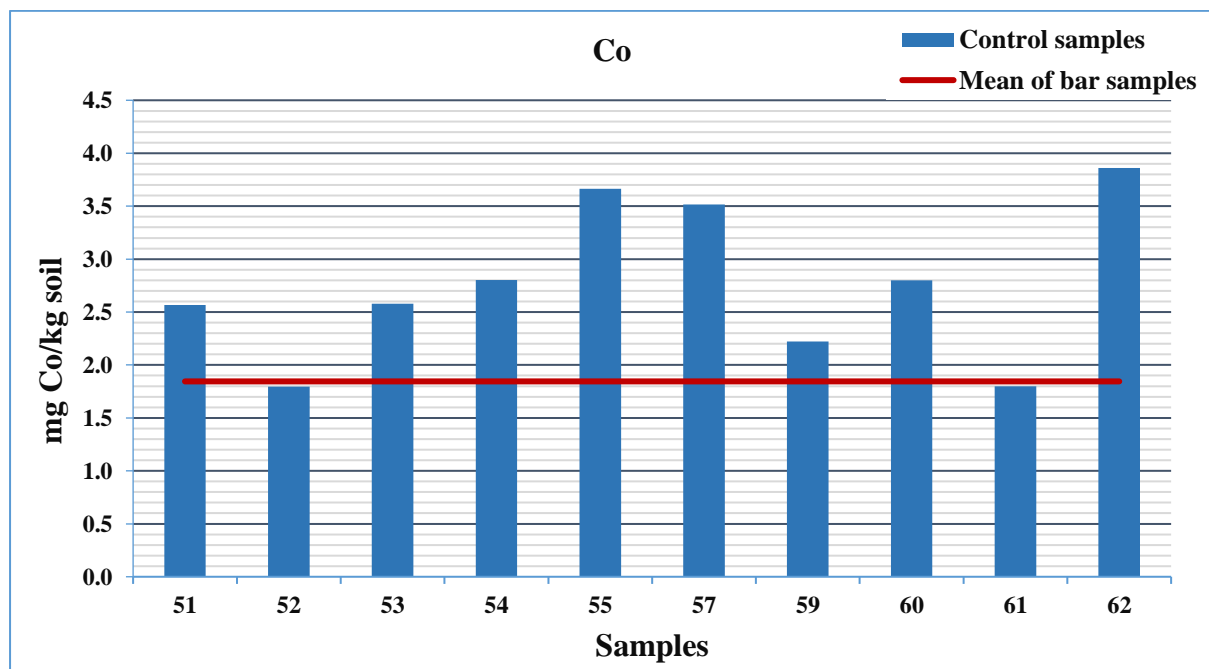
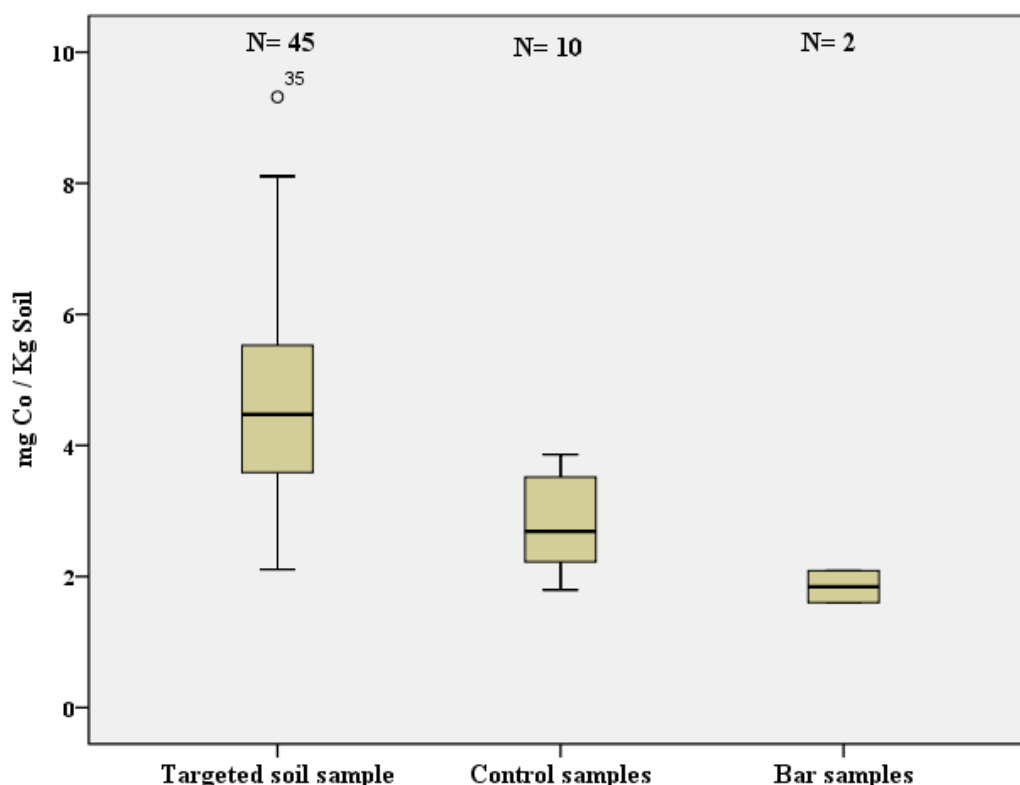


Figure 4.8: Cobalt concentration in targeted soil samples



**Figure 4.9: Concentration of cadmium in control samples**



**Figure 4.10: Concentration of cobalt in targeted soil samples vs. control and bar samples**

#### **4.4.2.1 Co in soil samples from craters formed by AFB**

Samples collected inside craters formed by AFB have Co concentration ranging from 2.107 mg/kg to 9.317 mg/kg with average concentration of 5.111 mg/kg. The highest concentration was detected in sample label 35 and the lowest in sample label 1 (table 4.9)

#### **4.4.2.2 Co in soil samples from areas surrounding craters formed by AFBs**

The concentration of Co in soil samples collected from areas surrounding craters formed by AFBs range from 2.968 to 7.890 mg/kg with average concentration of 4.498 mg/kg. Sample label 39 has the highest concentration while sample label 11 has the lowest concentration as shown in table 4.11.

#### **4.4.2.3 Co in soil samples collected from craters formed by AS.**

The concentrations of the Co in this category range from 3.056 to 6.221 mg/kg with average concentration of 4.519 mg/kg. The highest concentration was detected in sample label 40 and the lowest one was detected in sample label 28 as shown in table 4.10.

#### **4.4.2.4 Co in soil samples from areas surrounding craters formed by AS.**

The concentrations of Co in soil samples collected from areas surrounding to craters formed by AS range from 3.150 mg/kg to 6.063 mg/kg, with mean concentration of 0.917 mg/kg. The highest concentration was detected in sample label 45 and the lowest was detected in sample label 25 as shown in table 4.12.

It was noted that, there is no significant statistical difference ( $P\text{-value} = 0.521$ ) between the mean concentration of Co in samples collected from areas subjected to AFB and the mean concentration of Co in samples collected from areas subjected to AS, indicating that both AFB and AS enriches the targeted soils of Gaza Strip with Co (table 4.13). The results of the T-test also shows that, there is no significant statistical difference ( $P\text{-value} = 0.362$ ) between the mean concentration of Co in samples collected from craters formed by AFB and the mean concentration of Co in samples from areas surrounding these craters. As well as there is no significant statistical difference ( $P\text{-value} = 0.922$ ) between the mean concentrations of Co in samples collected from craters formed by AS and the mean concentration of Co in samples from areas surrounding these craters. The concentration of Co are close in the four previously mentioned categories in the term of minimum, maximum and mean concentrations, which refers to the high order detonation of bombs and artillery shells.

#### **4.4.3 Chromium (Cr)**

Chromium in the soils of Gaza Strip is affected by both agricultural and military activities. Its mean concentration in targeted soil samples (16.854 mg/kg) is 1.43 times the mean concentration of control samples (11.715 mg/kg) as shown in table 4.5. Taking into account that, there is a significant statistical difference ( $P\text{-value} = 0.024$ ) between the mean concentration of Cr in targeted soil samples and the mean concentration of Cr in control samples, that indicates that the military activities enriches the targeted locations with Cr. That was supported by the result illustrated in figure 4.11, which shows that 82.22% of the soil samples has Cr concentration higher than the mean concentration of control samples. Figure 4.11 also shows that 20% of the targeted soil samples have Cr concentrations higher than the value of (MACs) of Chemical Constituents in Uncontaminated Soil listed by USEPA (21 mg/kg), posing threat to human health. Chromium concentrations in targeted soil samples range from 3.636 mg/kg to 37.4 mg/kg soil. The highest concentrations were detected in samples label 36 and 35 respectively, while the lowest concentration was detected in sample label 1.

In the other hand, 90% of the control samples have Cr concentration higher than the mean concentration of bar samples (7.117 mg/kg), as shown in figure 4.12, indicating that, the agricultural activities participated in enrichment the Gaza soils with Cr. This result is supported by the result obtained from table 4.5, which reveals that, the mean concentration of control samples is 1.6 times the mean concentration of bar samples. That agrees with the study done by Shomar, et al. (2004), who revealed that, the most common fertilizers and fungicides used in Gaza Strip contain considerable amounts of Cr.

Figure 4.13, shows that the Cr content in targeted soil samples are much higher than that of control and bar samples, indicating that, the soil content of Cr in Gaza soils is much affected by military activities than agricultural activities.

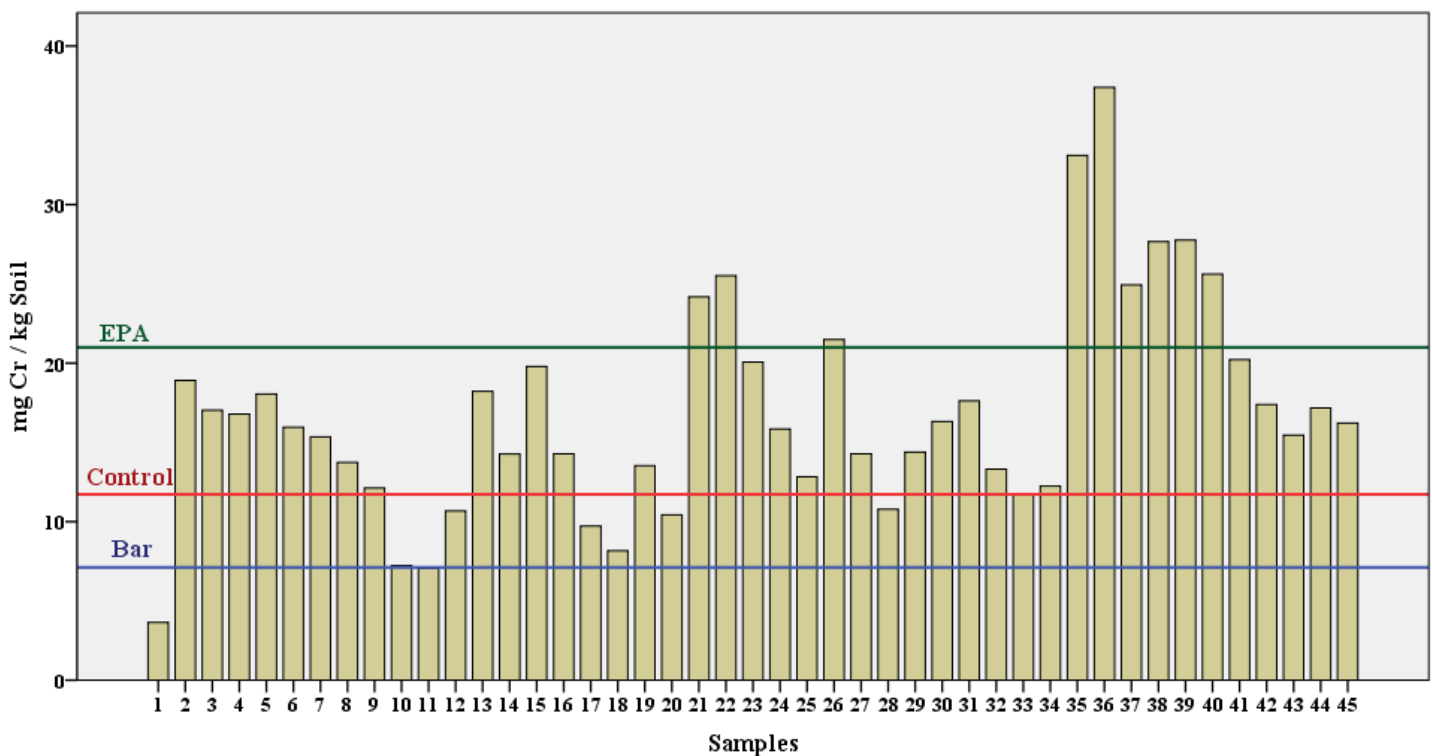


Figure 4.11: Concentration of chromium in targeted soil samples

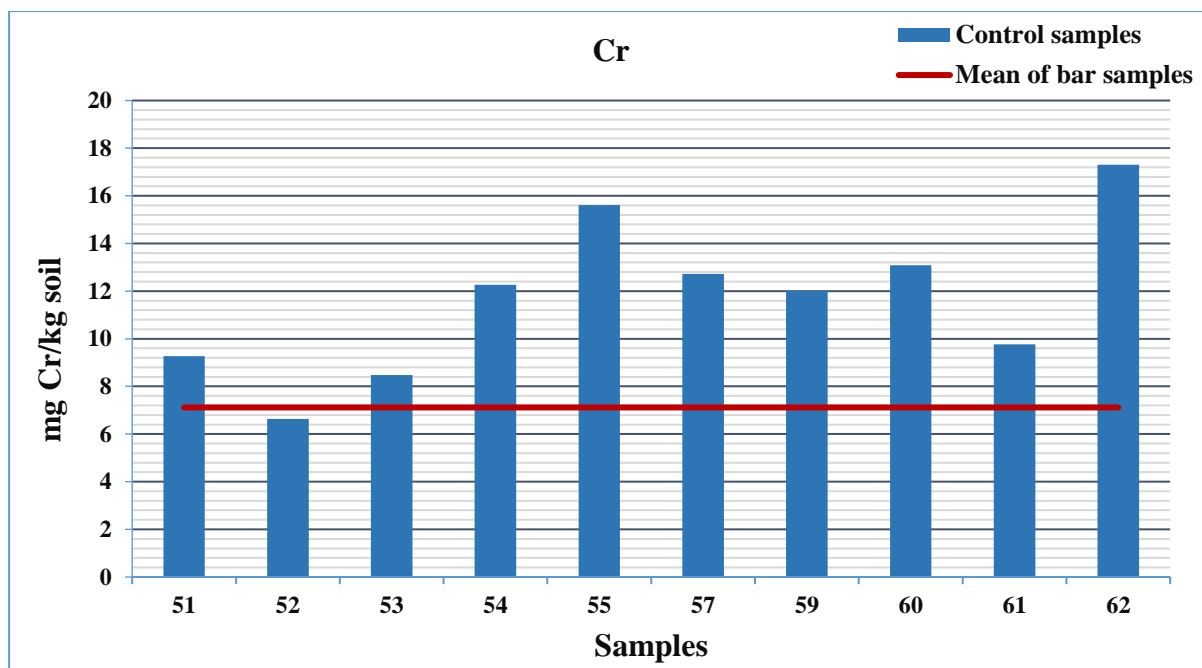


Figure 4.12: Concentration of chromium in control samples

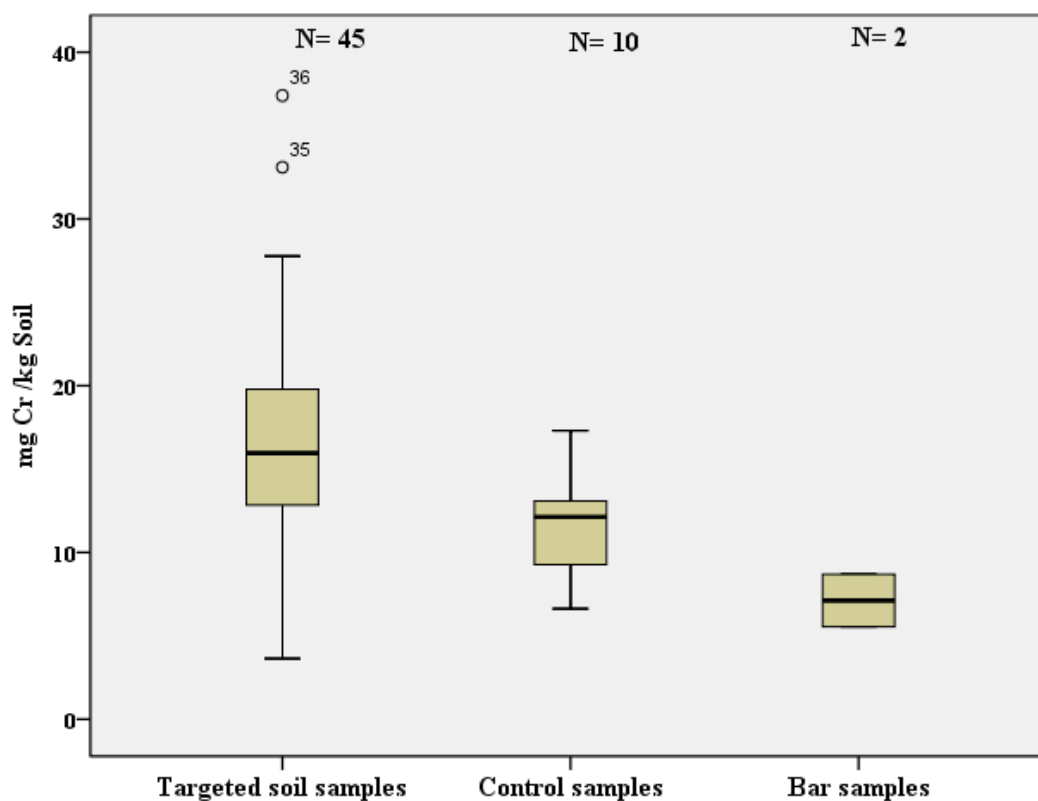


Figure 4.13: Concentration of chromium in targeted soil samples vs. control and bar samples



#### **4.4.3.1 Cr in soil samples collected inside craters formed by AFB**

Samples collected inside craters formed by AFBs have Cr concentration ranging from 3.636 mg/kg to 37.4 mg/kg with mean concentration of 17.743 mg/kg. The highest concentration was detected in sample label 36 and the lowest in sample label 1 (table 4.9)

#### **4.4.3.2 Cr in soil samples from areas surrounding craters formed by AFB**

The concentration of Cr in soil samples collected from areas surrounding craters formed by AFBs range from 7.073 to 27.765 mg/kg with mean concentration of 16.804 mg/kg. Sample label 39 has the highest concentration while sample label 11 has the lowest concentration as shown in table 4.11.

#### **4.4.3.3 Cr in soil samples from craters formed by AS**

The concentrations of the Cr in this category range from 10.674 to 25.617 mg/kg with mean concentration of 16.231 mg/kg. The highest concentration was detected in sample label 40 and the lowest one was detected in sample label 12 as shown in table 4.10.

#### **4.4.3.4 Cr in soil samples from areas surrounding craters formed by AS**

The concentrations of Cr in soil samples collected from areas surrounding to craters formed by AS range from 12.234 mg/kg to 20.223 with mean concentration of 15.226 mg/kg. The highest concentration was detected in sample label 41 and the lowest was detected in sample label 34 as shown in table 4.12.

Table 4.13 shows that, there is no significant statistical difference (P-value = 0.389) between the mean concentration of Cr in samples collected from areas subjected to AFB and the mean concentration of Cr in samples collected from areas subjected to AS, indicating that both AFB and AS enriches the targeted soils of Gaza Strip with Cr. The results of the T-test also shows that, there is no significant statistical difference (P-value = 0.752) between the mean concentration of Cr in samples collected from craters formed by AFB and the mean concentration of Cr in samples from areas surrounding these craters. As well as there is no significant statistical difference (P-value = 0.656) between the mean concentrations of Cr in samples collected from craters formed by AS and the mean concentration of Cr in samples from areas surrounding these craters. It can be concluded from the results of the T-test that, the content of Cr in both AFB and AS is spread over the craters and the areas surrounding craters formed by them, which occurs due to the high order detonation of the AFB and the AS.

#### **4.4.4 Copper (Cu)**

The copper content in the soil of Gaza is affected by both agricultural and military activities. The results of the T-test shows that, there is a significant statistical difference ( $P\text{-value} = 0.004$ ) between the mean concentration of Cu in targeted soil samples and the mean concentration of Cu in control samples. Taking into account that, the mean concentration of Cu in targeted soil samples (9.623 mg/kg) is 2 times the mean concentration of control samples (4.801 mg/kg), it can be concluded that the military activities enriches the targeted location with copper. This result was supported by the result obtained from figure 4.14, which shows that 77.78% of the targeted soil samples have Cu concentrations higher than the mean concentration of control samples. Anyway, the concentrations of Cu in targeted soil samples is much lower than the value of (MACs) of Chemical Constituents in Uncontaminated Soil listed by USEPA (330 mg/kg), and thus the soil content of copper does not pose threat to human health in the investigated locations. The highest Cu value (40.012 mg/kg) was detected in sample label 40 and the lowest value (2.647 mg/kg) was detected in sample label 10 as shown in table 4.8.

In the other hand, the mean concentration of control samples is 3.2 times the mean concentration of bar samples (1.519 mg/kg), as well as all control samples have Cu concentrations higher than the mean concentration of the bar soil samples (figure 4.15) indicating that the agricultural activities also affected the Cu content in Gaza soils. This result agrees with research don by Shomar, et al. (2004), who revealed that agricultural activities such as application of fertilizers and fungicides enrich several soils in Gaza Strip with Cu. Figure 4.16, shows that the Cu content in targeted soil samples are much higher than that of control and bar samples, indicating that, the soil content of Cu in Gaza soils is much affected by military activities than agricultural activities.

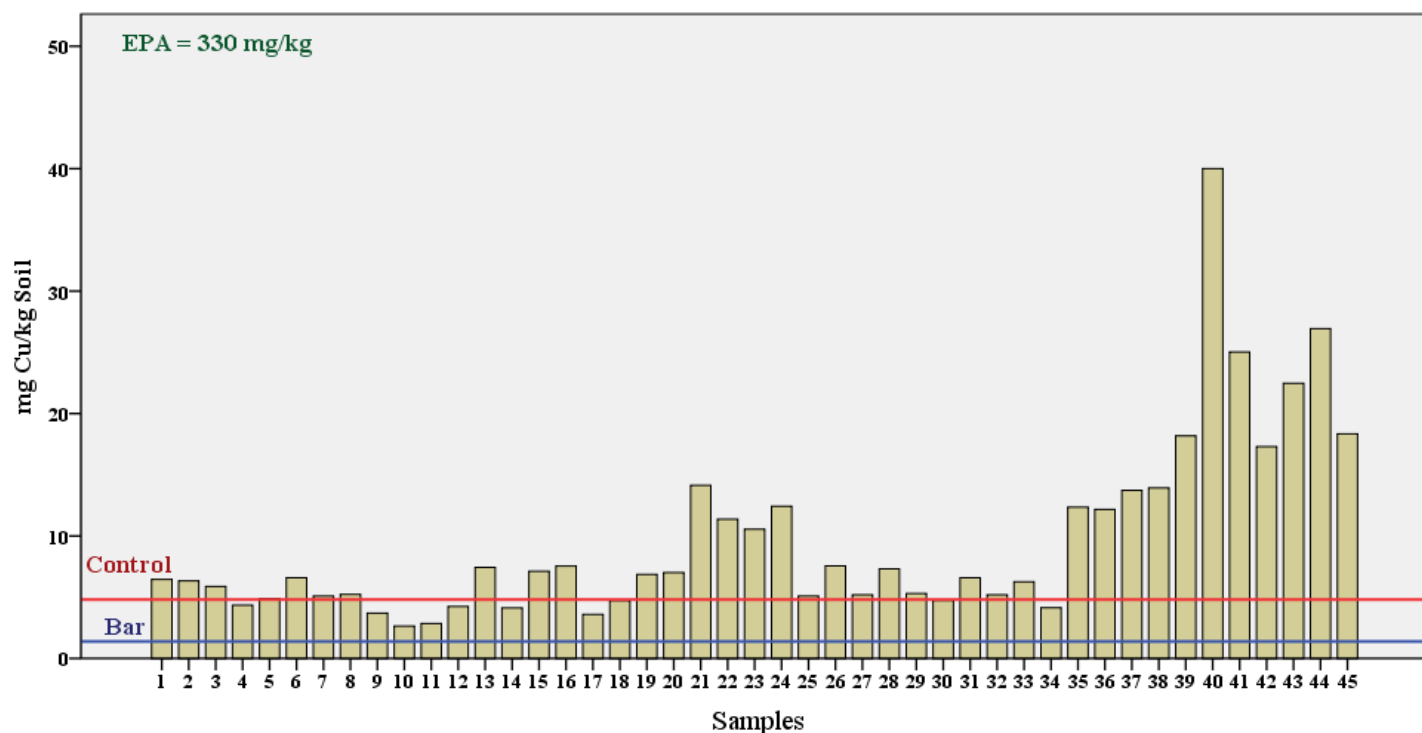


Figure 4.14: Copper concentration in targeted soil samples

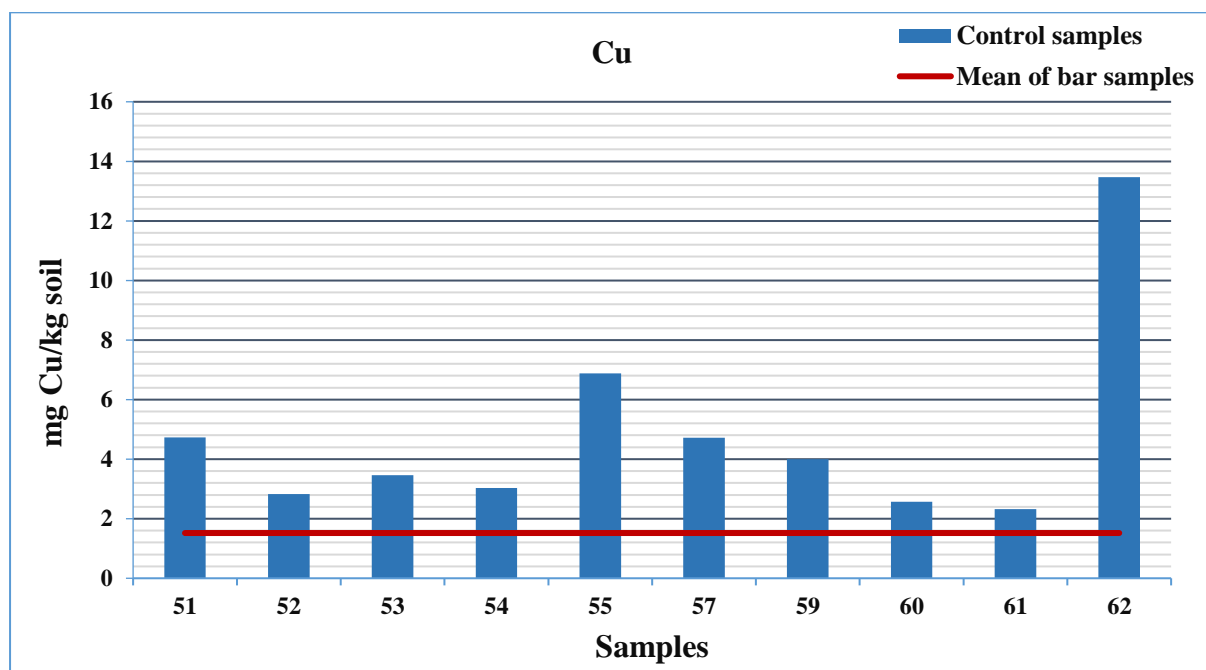


Figure 4.15: Concentration of copper in control samples

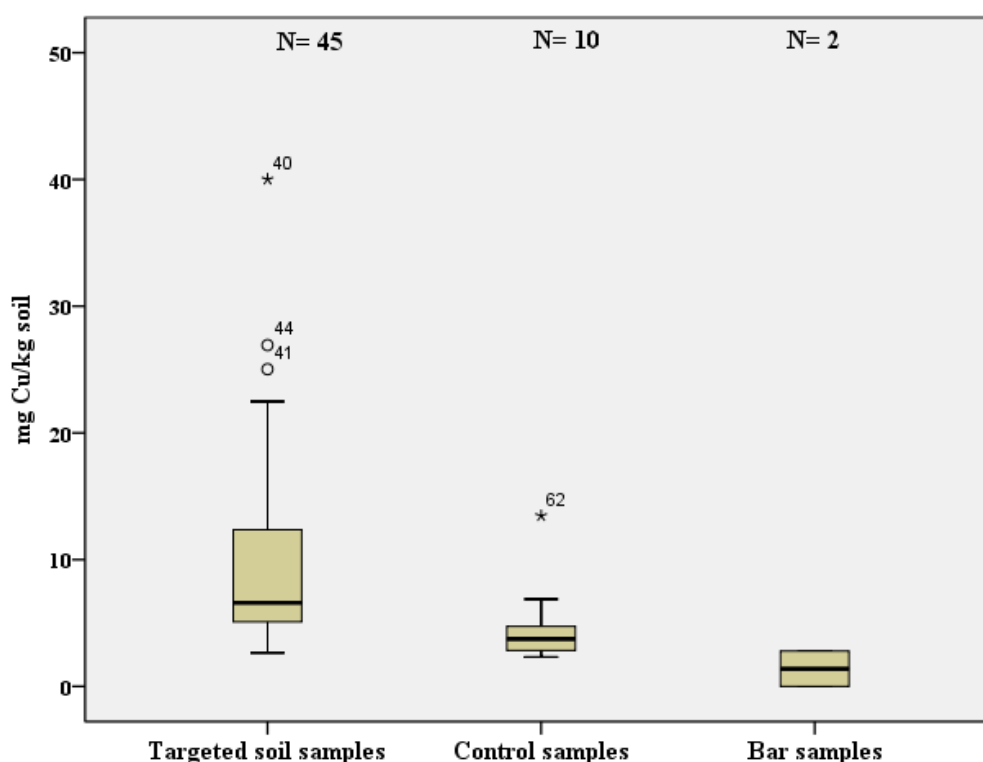


Figure 4.16: Concentration of copper in targeted soil samples vs. control and bar samples

#### 4.4.4.1 Cu in soil samples collected inside craters formed by AFB.

Samples collected inside craters formed by AFB have Cu concentration ranging from 2.647 mg/kg to 14.137 mg/kg with mean concentration of 7.248 mg/kg. The highest concentration was detected in sample label 21 and the lowest in sample label 10 (table 4.9).

#### 4.4.4.2 Cu in soil samples from areas surrounding craters formed by AFB.

The concentration of Cu in soil samples collected from areas surrounding craters formed by AFB range from 2.849 to 18.180 mg/kg with average concentration of 7.730 mg/kg. Sample label 39 has the highest concentration while sample label 11 has the lowest concentration as shown in table 4.11.

#### 4.4.4.3 Cu in soil samples from craters formed by AS.

The concentrations of the Cu in this category range from 4.249 to 40.012 mg/kg with mean concentration of 14.378 mg/kg. The highest concentration was detected in sample label 40 and the lowest one was detected in sample label 12 as shown in table 4.10.

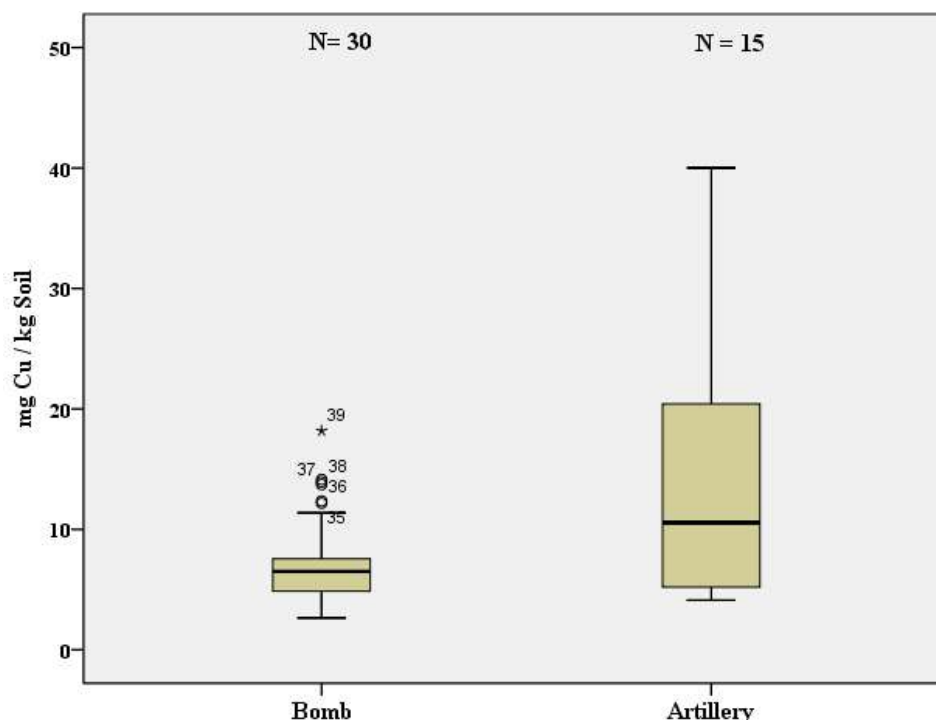
#### 4.4.4.4 Cu in soil samples from areas surrounding craters formed by AS

The concentrations of Cu in soil samples collected from areas surrounding to craters formed by AS range from 4.133 mg/kg to 25.026 with mean concentration of 13.397 mg/kg. The highest concentration was detected in sample label 41 and the lowest was detected in sample label 34 as shown in table 4.12. The result of the T-test shows that, there is a significant statistical difference (P-value = 0.037) between the mean concentration of Cu in samples collected from areas subjected to AFB and the mean concentration of Cu in samples collected from areas subjected to AS. Taking into account that, the mean concentration of Cu in samples collected from areas subjected to AS (13.986 mg/kg) is 1.9 times that of samples collected from areas subjected to AFB (7.441 mg/kg) as shown in table 4.14, it can be concluded that, AS introduced more Cu to the targeted soils than AFB. That agrees with the study done by Van Meirvenne et al. (2008), who revealed that the artillery shells fired in Ypres (West-Flanders, Belgium) during the WWI, polluted the battlefield soil with significant amount of copper. This was also supported by the research done by Boggs (2004), which revealed that the artillery shell has a bronze-rotating band at its base. 90% of the bronze used in the artillery shells composed of copper. In contrast, most of bombs has 1000 series steel in its munition casings, which does not contain copper (Boggs, 2004), accordingly artillery shells have more Cu content than AFBs.

**Table 4.14.: Mean concentration of metals in samples from areas subjected to AFB and AS**

	(mg/kg)								
	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn	Al
<b>AFB (N=30)</b>	0.870	4.866	17.367	7.441	122.400	10.269	7.027	19.462	4511.078
<b>AS (N=15)</b>	1.069	4.543	15.829	13.986	102.389	9.217	6.534	22.699	4456.373

Figure 4.17, clearly shows that, the samples collected from areas subjected to AS have more Cu than samples collected from areas subjected to AFB.



**Figure 4.17: Cu concentrations in locations targeted by bombs vs. locations subjected to artillery shelling**

The results of the T-test also shows that, there is no significant statistical difference (P-value = 0.745) between the mean concentration of Cu in samples collected from craters formed by AFB and the mean concentration of Cu in samples from areas surrounding these craters. As well as there is no significant statistical difference (P-value = 0.870) between the mean concentrations of Cu in samples collected from craters formed by AS and the mean concentration of Cu in samples from areas surrounding these craters. It can be concluded from the results of the T-test that, the content of Cu in both AFB and AS is spread over the craters and the areas surrounding craters formed by them, which occurs due to the high order detonation of the AFB and the AS.

#### 4.4.5 Manganese (Mn)

The manganese content in Gaza soils is much affected by military activities than agricultural activities. The T-test shows that, the targeted soil samples have significantly (P-value = 0.008) higher concentration of Mn than control samples, since its mean concentration in targeted soil samples (115.73 mg/kg) is 1.5 times its mean concentration in control samples (74.884 mg/kg), indicating that the soil content of Mn is affected by military activities. That was supported by the result obtained from figure 4.18, which shows that, 84.44% of the targeted soil samples have Mn concentrations higher than the mean concentration of control samples. The concentrations of manganese in targeted soil samples range from 28.24 mg/kg

to 244.369 mg/kg. The highest Mn value was detected in sample label 35 and the lowest value was detected in sample label 1 as shown in table 4.8. However, the Mn in soil samples does not pose threat to human health since its concentrations in targeted soil samples is much below the value of (MACs) of Chemical Constituents in Uncontaminated Soil listed by USEPA (630 mg/kg).

Table 4.5 shows that the mean concentration of Mn in control samples is 1.6 times the mean concentration of bar samples (45.890 mg/kg). This result is supported by figure 4.19, which shows that 90% of the control samples have Mn concentrations higher than the mean of the bar samples, indicating that the agricultural activities lead to enrich the soils of Gaza Strip with Mn. According to Shomar, et al. (2004), the pesticides used in Gaza Strip are considered as a considerable source of some trace metals such as Cu, Mn and Zn.

The soil content of Mn in Gaza soils is much affected by military activities than agricultural activities, since the Mn content in targeted soil samples are much higher than that of control and bar samples (figure 4.20)

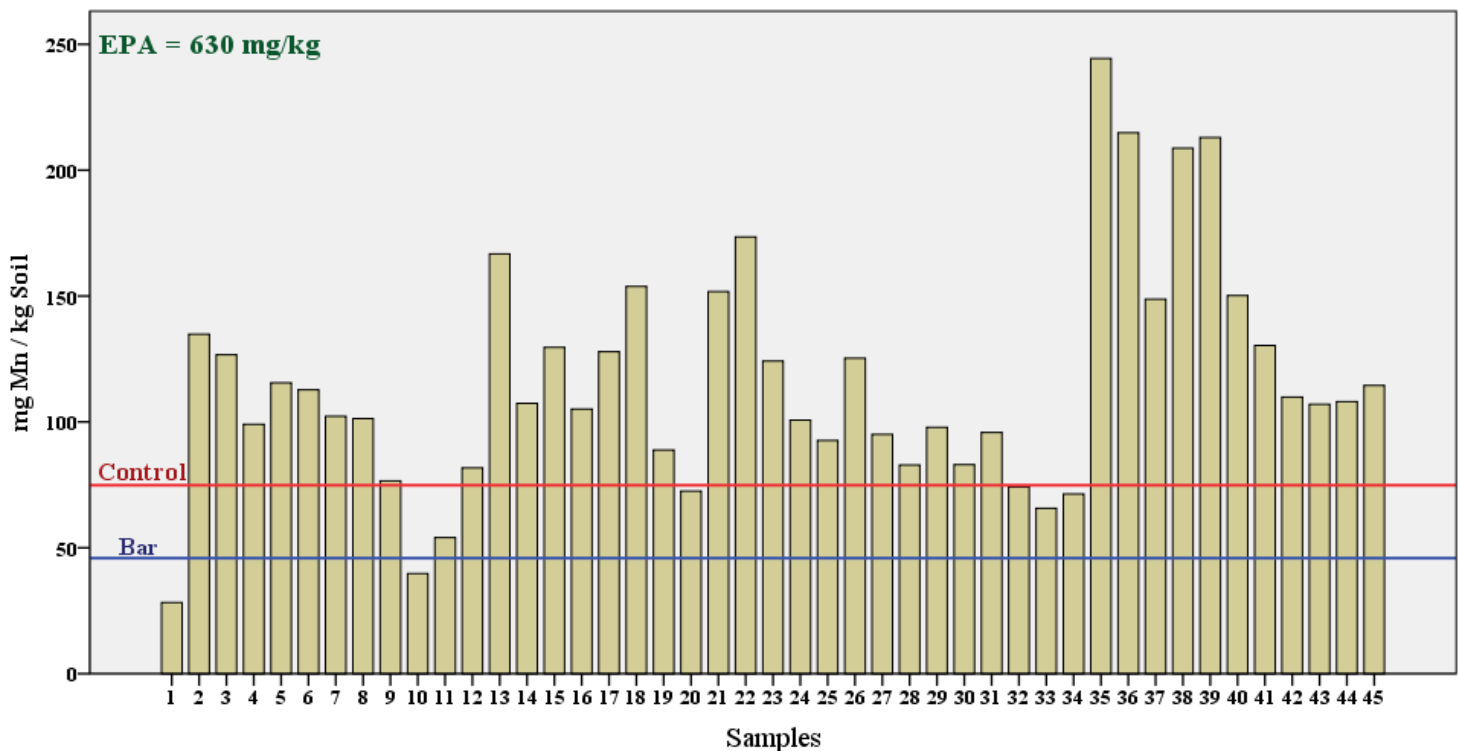


Figure 4.18: Manganese concentration in targeted soil samples

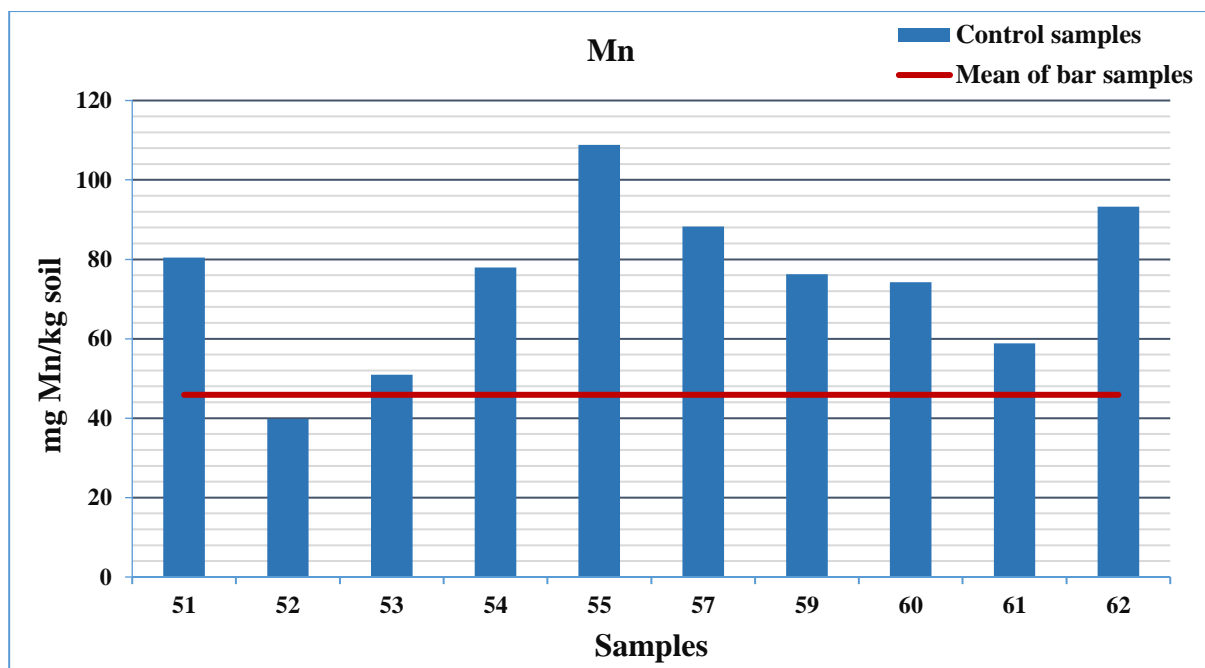


Figure 4.19: Concentration of manganese in control samples

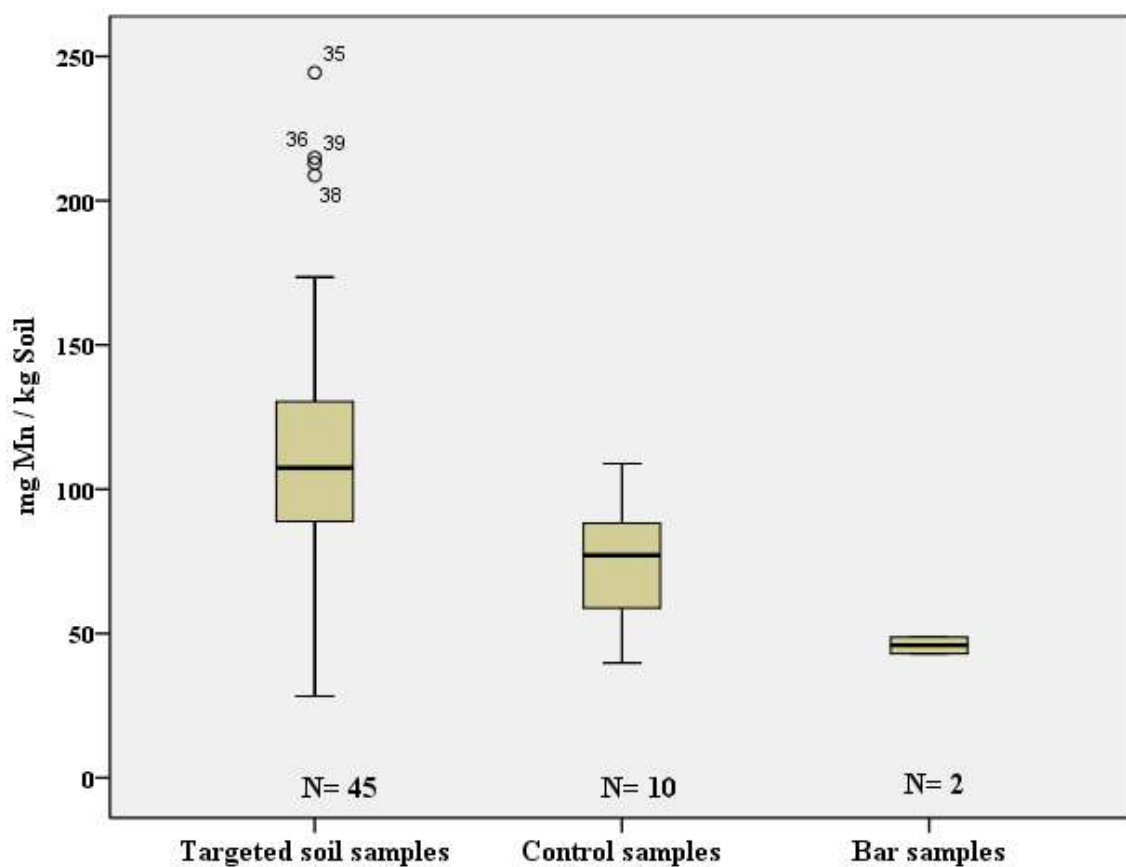


Figure 4.20: Concentration of manganese in targeted soil samples vs. control and bar samples



#### **4.4.5.1 Mn in soil samples collected inside craters formed by AFBs**

Samples collected inside craters formed by AFBs have Mn concentration ranging from 28.240 mg/kg to 244.369 mg/kg with mean concentration of 126.197mg/kg. The highest concentration was detected in sample label 35 and the lowest in sample label 1 (table 4.9).

#### **4.4.5.2 Mn in soil samples from areas surrounding craters formed by AFBs**

The concentration of Mn in soil samples collected from areas surrounding craters formed by AFBs range from 54.019 to 212.987 mg/kg with mean concentration of 116.705 mg/kg. Sample label 39 has the highest concentration while sample label 11 has the lowest concentration as shown in table 4.11.

#### **4.4.5.3 Mn in soil samples from craters formed by AS**

The concentrations of the Mn in this category range from 65.697 mg/kg to 150.162 mg/kg with mean concentration of 102.476 mg/kg. The highest concentration was detected in sample label 40 and the lowest one was detected in sample label 33 as shown in table 4.10.

#### **4.4.5.4 Mn in soil samples from areas surrounding craters formed by AS**

The concentrations of Mn in soil samples collected from areas surrounding to craters formed by artillery shelling range from 71.353 mg/kg to 130.343 mg/kg with mean concentration of 102.259mg/kg. The highest concentration was detected in sample label 41 and the lowest was detected in sample label 34 as shown in table 4.12.

Table 4.13 shows that, there is no significant statistical difference (P-value = 0.080) between the mean concentration of Mn in samples collected from areas subjected to AFB and the mean concentration of Mn in samples collected from areas subjected to AS, indicating that both AFB and AS enriches the targeted soils of Gaza Strip with Mn. That agrees with the research done by Boggs (2004) which revealed that Mn is widely used in munition casings.

The results of the T-test also shows that, there is no significant statistical difference (P-value = 0.635) between the mean concentration of Mn in samples collected from craters formed by AFB and the mean concentration of Mn in samples from areas surrounding these craters. As well as there is no significant statistical difference (P-value = 0.986) between the mean concentrations of Mn in samples collected from craters formed by AS and the mean concentration of Mn in samples from areas surrounding these craters. It can be concluded from the results of the T-test that, the content of Mn in both AFB and AS is spread over the

craters and the areas surrounding craters formed by them, which occurs due to the high order detonation of the AFB and the AS.

#### **4.4.6 Nickel (Ni)**

The concentration of Ni in soil samples is much affected by military activities than agricultural activities. The T-test shows that, the targeted soil samples have significantly (P-value = 0.000) higher concentration of Ni than control samples, since its mean concentration in targeted soil samples (9.919 mg/kg) is 1.8 times its mean concentration in control samples (5.493 mg/kg), indicating that the military activities introduced significant amounts of Ni to the targeted locations. That was supported by the result obtained from figure 4.21, which shows that, 93.33% of the targeted soil samples have Ni concentrations higher than the mean concentration of control samples. The concentrations of nickel in targeted soil samples range from 3.759 mg/kg to 18.766 mg/kg. The highest Ni value was detected in sample label 35 and the lowest value was detected in sample label 1 as shown in table 4.8. Concerning human health issue, the soil content of nickel does not pose threat to human health since, all targeted soil samples have Ni concentrations less than the value of (MACs) of Chemical Constituents in Uncontaminated Soil listed by USEPA (20 mg/kg), although many of these samples are very close to this value (figure 4.21).

In the other hand, figure 4.22 shows that all control samples have Ni concentrations higher than the mean of the bar samples (3.504 mg/kg) as well as, the mean concentration of Ni in control samples is 1.6 times that of bar samples. Although some pesticides used in Gaza Strip such as copper sulfate contains high amounts of Ni (Shomar, 2006), agricultural activities are not usually common sources of nickel. The source of nickel in control samples is likely to be associated to other anthropogenic activities. The lowest Ni concentration (3.759 mg/kg) was detected in sample label 1 and the highest concentration (18.766) was detected in sample label 35. Concerning human health issue, all soil samples have Ni concentrations less than the MACs (20 mg/kg), although many of these samples are very close to this value (figure 4.21). Figure 4.23, shows that the Ni content in targeted soil samples are much higher than that of control and bar samples, indicating that, the soil content of Ni in Gaza soils is much affected by military activities than anthropogenic activities.

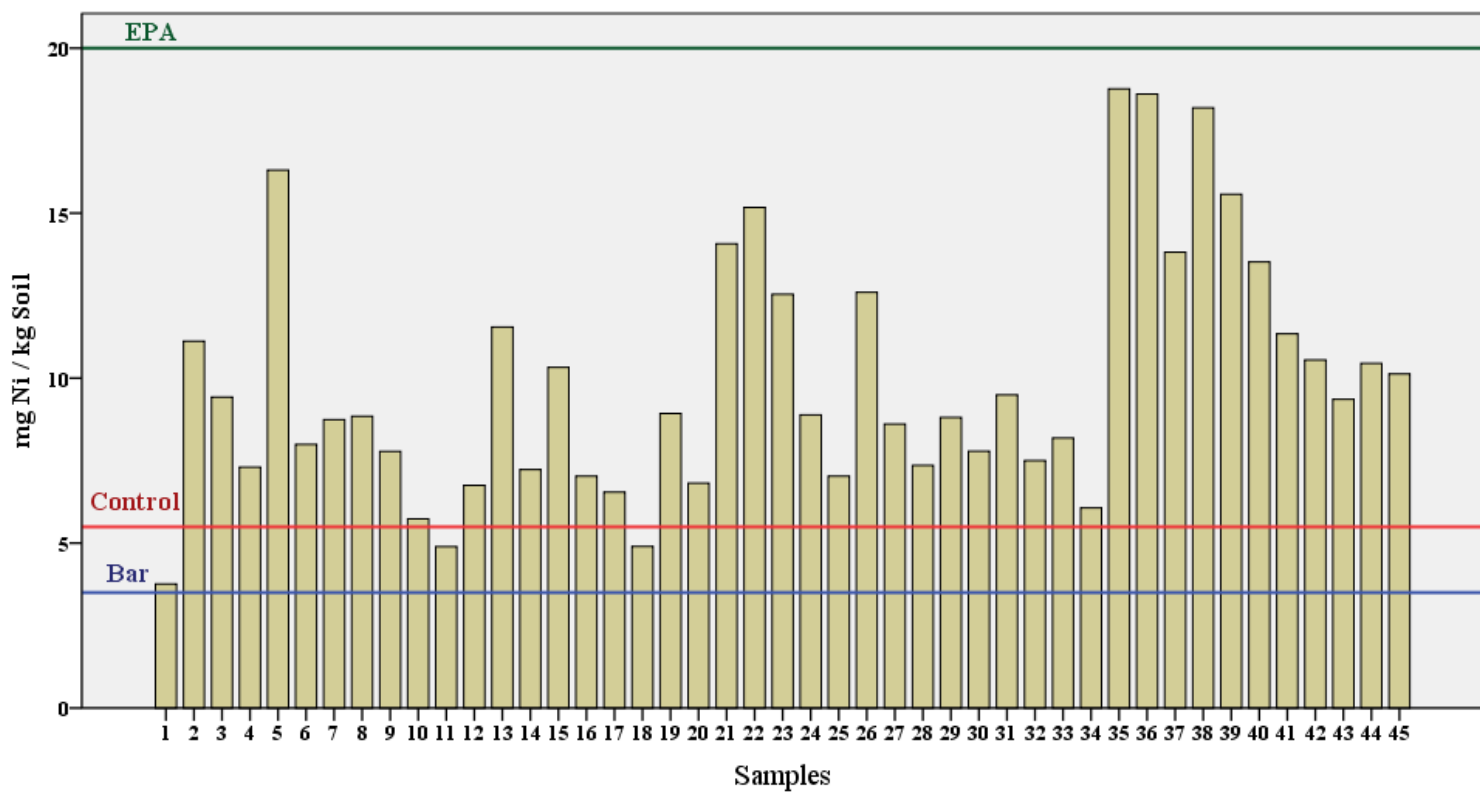


Figure 4.21: Nickel concentration in targeted soil samples

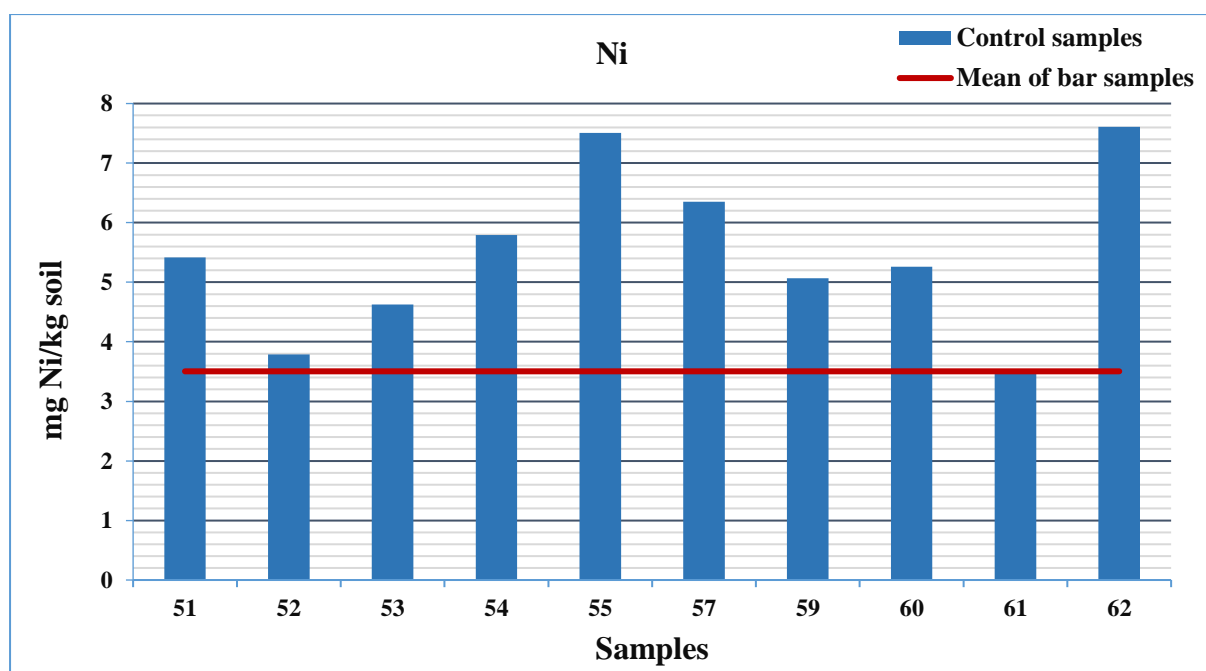


Figure 4.22: Concentration of nickel in control samples

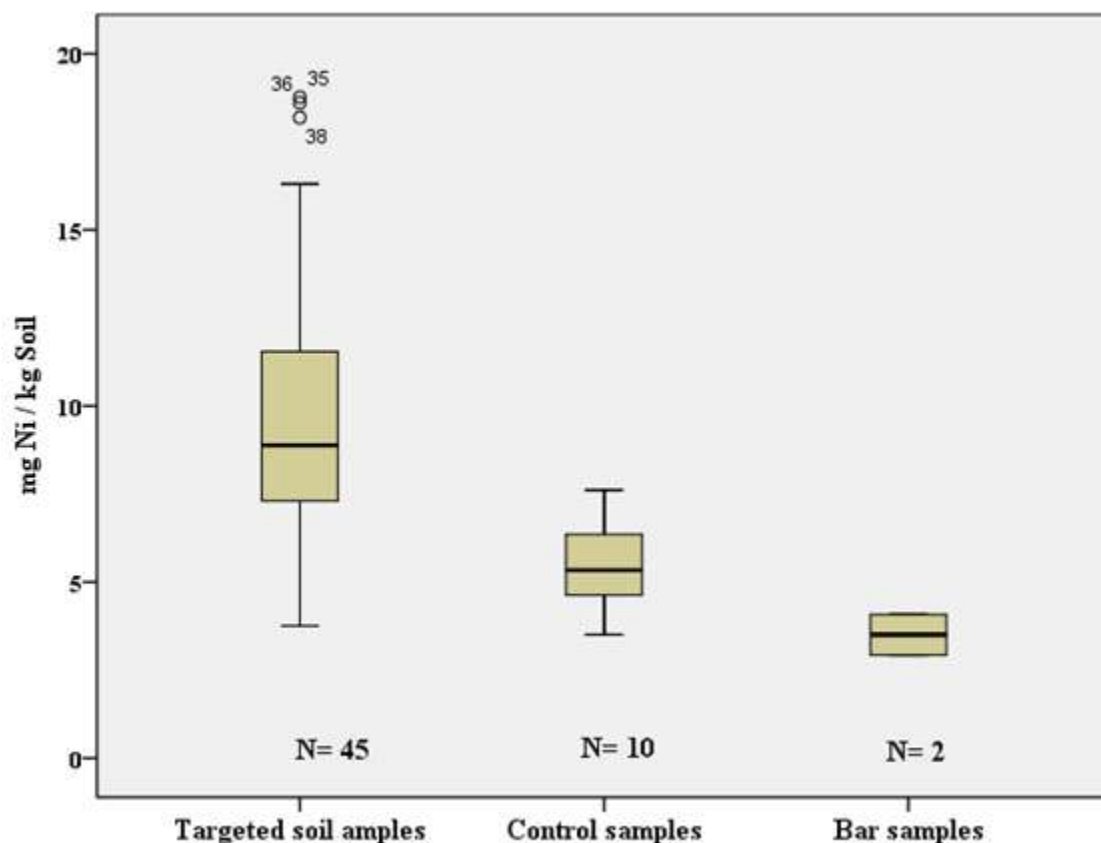


Figure 4.23: Concentration of nickel in targeted soil samples vs. control and bar samples

#### 4.4.6.1 Ni in soil samples collected inside craters formed by AFBs

Samples collected inside craters formed by AFBs have Ni concentration ranging from 3.759 mg/kg to 18.766 mg/kg with mean concentration of 10.726 mg/kg. The highest concentration was detected in sample label 35 and the lowest in sample label 1 (table 4.9).

#### 4.4.6.2 Ni in soil samples from areas surrounding craters formed by AFBs

The concentration of Ni in soil samples collected from areas surrounding craters formed by AFBs range from 4.891 mg/kg to 15.574 mg/kg with mean concentration of 9.584mg/kg. Sample label 39 has the highest concentration while sample label 11 has the lowest concentration as shown in table 4.11.

#### 4.4.6.3 Ni in soil samples from craters formed by AS

The concentrations of the Mn in this category range from 6.749 mg/kg to 13.523 mg/kg with mean concentration of 9.503 mg/kg. The highest concentration was detected in sample label 40 and the lowest one was detected in sample label 12 as shown in table 4.10.

#### **4.4.6.4 Ni in soil samples from areas surrounding craters formed by AS**

The concentrations of Ni in soil samples collected from areas surrounding to craters formed by AS range from 6.065 mg/kg to 11.344 mg/kg with mean concentration of 8.789mg/kg. The highest concentration was detected in sample label 41 and the lowest was detected in sample label 34 as shown in table 4.12.

Table 4.13 shows that, there is no significant statistical difference (P-value = 0.282) between the mean concentration of Ni in samples collected from areas subjected to AFB and the mean concentration of Ni in samples collected from areas subjected to AS, indicating that both AFB and AS enriches the targeted soils of Gaza Strip with Ni.

The results of the T-test also shows that, there is no significant statistical difference (P-value = 0.483) between the mean concentration of Ni in samples collected from craters formed by AFB and the mean concentration of Ni in samples from areas surrounding these craters. As well as there is no significant statistical difference (P-value = 0.557) between the mean concentrations of Ni in samples collected from craters formed by AS and the mean concentration of Ni in samples from areas surrounding these craters. It can be concluded from the results of the T-test that, the content of Ni in both AFB and AS is spread over the craters and the areas surrounding craters formed by them, which occurs due to the high order detonation of the AFB and the AS.

#### **4.4.7 Lead (Pb)**

The Pb content in the soils of Gaza is not affected by military activities; instead, it is affected by agricultural activities. The results of the T-test illustrated in table 4.13, show that, there is no significant statistical difference (P-value = 0.283) between the mean concentration of Pb in targeted soil samples and the mean concentration of Pb in control samples. Taking into account that, the mean concentration of Pb in targeted soil samples (6.863 mg/kg) is less than that of control samples (9.886 mg/kg) it can be concluded that the soil content of Pb is not affected by military activities. Anyhow, figure 4.24 shows that, 95.55% of the targeted soil samples have Pb concentrations lower than the mean of control samples. The concentrations of lead in soil samples range from 4.162 mg/kg to 13.536 mg/kg. The highest Pb concentration was detected in sample label 36 and the lowest was detected in sample label 28 (table 4.8). However, the concentrations of lead in all targeted soil samples are below the value of (MACs) of Chemical Constituents in Uncontaminated Soil listed by USEPA (23 mg/kg) as shown in figure 4.24, and does not pose risk to human health.

In the other hand, the mean concentration of control samples is 2.3 times the mean concentration of bar samples (4.333mg/kg), as well as all control samples have Pb concentrations higher than the mean concentration of the bar soil samples (figure 4.25), indicating that the agricultural activities affected the Pb content in Gaza soils. This result agrees with Shomar, et al. (2004), who revealed that the distribution of trace metals such as Pb, Cu, Zn, Cd and Mn in soils is governed by many factors including, soil types, crop patterns, and specific location. Shomar (2006) also mentioned that some pesticides which are used in Gaza, such as copper oxychloride contain high amounts of Pb.

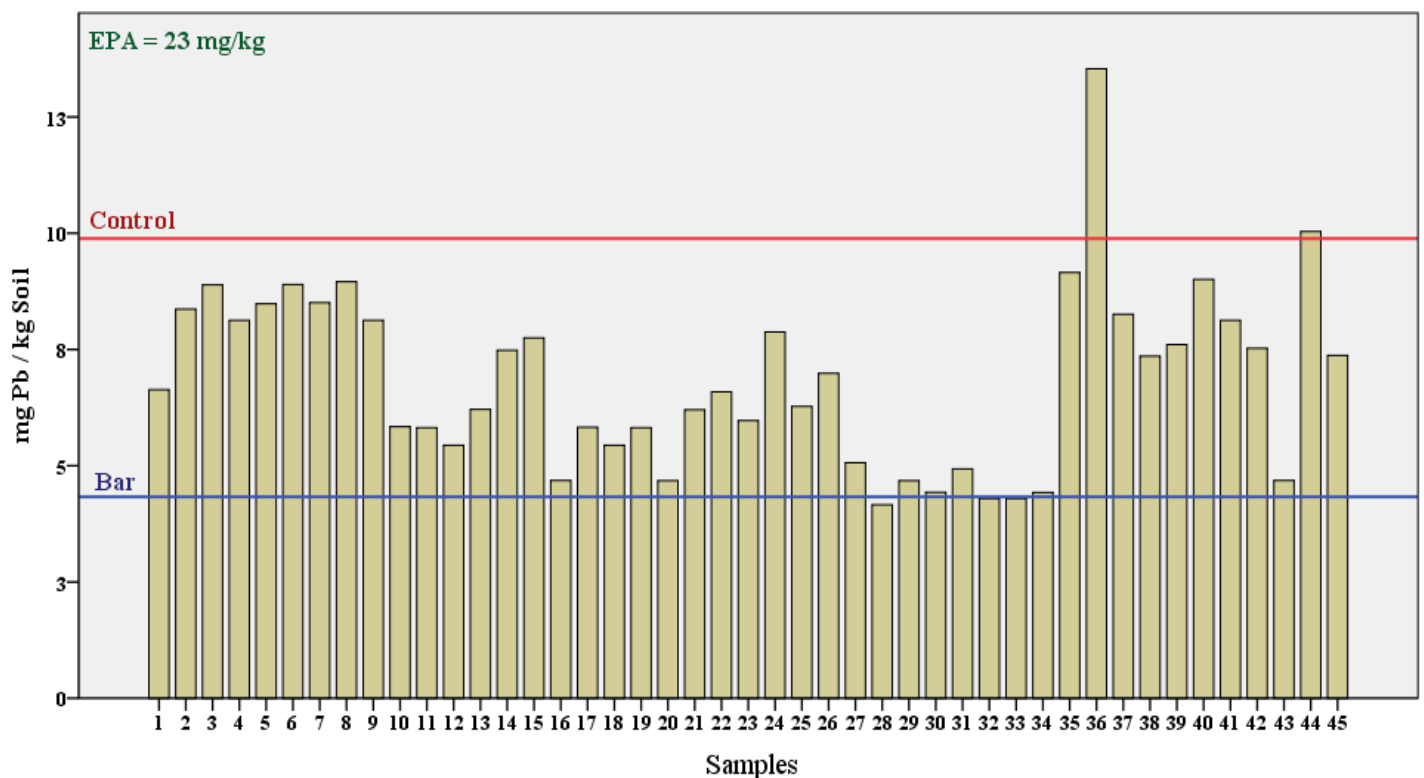


Figure 4.24: Lead concentration in targeted soil samples

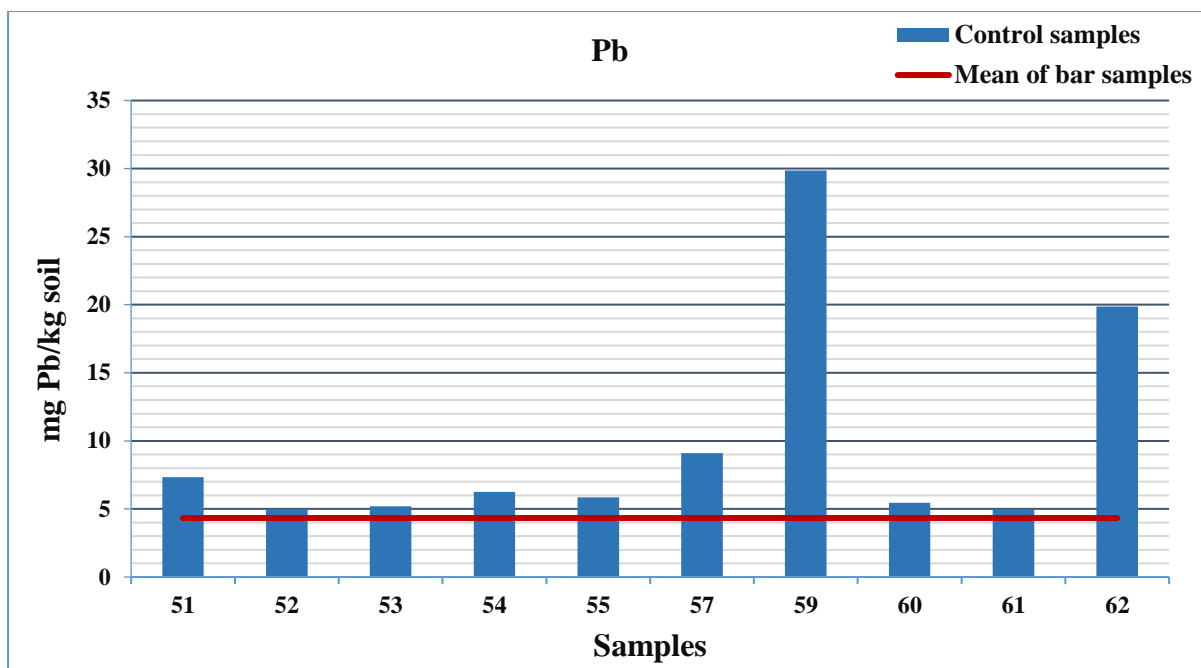


Figure 4.25: Concentration of nickel in control samples

#### 4.4.7.1 Pb in soil samples collected inside craters formed by AFBs

Samples collected inside craters formed by AFBs have Pb concentration ranging from 4.428 mg/kg to 113.536 mg/kg with mean concentration of 7.137 mg/kg. The highest concentration was detected in sample label 36 and the lowest in sample label 30 (table 4.9).

#### 4.4.7.2 Pb in soil samples from areas surrounding craters formed by AFBs

The concentration of Pb in soil samples collected from areas surrounding craters formed by AFBs range from 4.295 mg/kg to 8.955 mg/kg with mean concentration of 6.863 mg/kg. Sample label 8 has the highest concentration while sample label 32 has the lowest concentration as shown in table 4.11.

#### 4.4.7.3 Pb in soil samples from craters formed by AS

The concentrations of the Pb in this category range from 4.162 mg/kg to 10.035 mg/kg with mean concentration of 6.938 mg/kg. The highest concentration was detected in sample label 44 and the lowest one was detected in sample label 28 as shown in table 4.10.

#### 4.4.7.4 Pb in soil samples from areas surrounding craters formed by AS

The concentrations of Ni in soil samples collected from areas surrounding to craters formed by AS range from 4.424 mg/kg to 8.125 mg/kg with mean concentration of 5.927 mg/kg. The

highest concentration was detected in sample label 41 and the lowest was detected in sample label 34 as shown in table 4.12.

Table 4.13 shows that, there is no significant statistical difference (P-value = 0.425) between the mean concentration of Pb in samples collected from areas subjected to AFB and the mean concentration of Pb in samples collected from areas subjected to AS. The results of the T-test also shows that, there is no significant statistical difference (P-value = 0.714) between the mean concentration of Pb in samples collected from craters formed by AFB and the mean concentration of Pb in samples from areas surrounding these craters. As well as there is no significant statistical difference (P-value = 0.330) between the mean concentrations of Pb in samples collected from craters formed by AS and the mean concentration of Pb in samples from areas surrounding these craters. It was noted that, the concentrations of Pb in targeted soil samples are very close in areas subjected to AFBs and areas subjected to AS as well as in the four previously mentioned categories in the term of minimum, maximum and mean concentrations as shown in table (4.9, 4.10, 4.11, 4.12 and 4.14). However, it refers to that; the military activities did not affect the Pb content in the soils of targeted locations.

#### **4.4.8 Zinc (Zn)**

The content of Zn in Gaza soils is not affected by military activities; instead, it is affected by agricultural activities. The results of the T-test illustrated in table 4.13, show that, there is no significant statistical difference (P-value = 0.079) between the mean concentration of Zn in targeted soil samples and the mean concentration of Zn in control samples. Taking into account that, the mean concentration of Zn in targeted soil samples (20.541 mg/kg) is less than that of control samples (25.484 mg/kg) it can be concluded that the soil content of Zn is not affected by military activities. Anyhow, figure 4.26 shows that, 71.11% of the targeted soil samples have Zn concentrations lower than the mean of control samples. The concentrations of zinc in soil samples range from 7.321 mg/kg to 35.158 mg/kg. However, the concentrations of zinc in all targeted soil samples are below the value of (MACs) of Chemical Constituents in Uncontaminated Soil listed by USEPA (1000 mg/kg) as shown in figure 4.6, posing no threat to human health. In the other hand, the Zn mean concentration of control samples is three times the mean concentration of bar samples (8.712 mg/kg), as well as all control samples have Zn concentrations higher than the mean concentration of the bar soil samples (figure 4.27), indicating that the agricultural activities is the main source of Zn



in Gaza soils. This conclusion is supported by the research done by Shomar, et al. (2004), who revealed that Zn concentration in Gaza soils is governed by agricultural activities, including application of fertilizers and fungicides, which contain considerable amounts of Zn. That also, agrees with the finding that, the lowest Zn concentrations were found in samples label 10, 18, 11, 1, and 17 respectively. Samples label 10 and 11 were collected from uncultivated lands (Wadi Gaza graveyard) and samples label 17 and 18 were collected from uncultivated lands (east of El Tofah -Gaza). When sample label 1 was collected from Khan Younis, Elmwasi, this area was recently cultivated with citrus trees, which means that this area was not subjected to the application of fertilizers and fungicides for a long time.

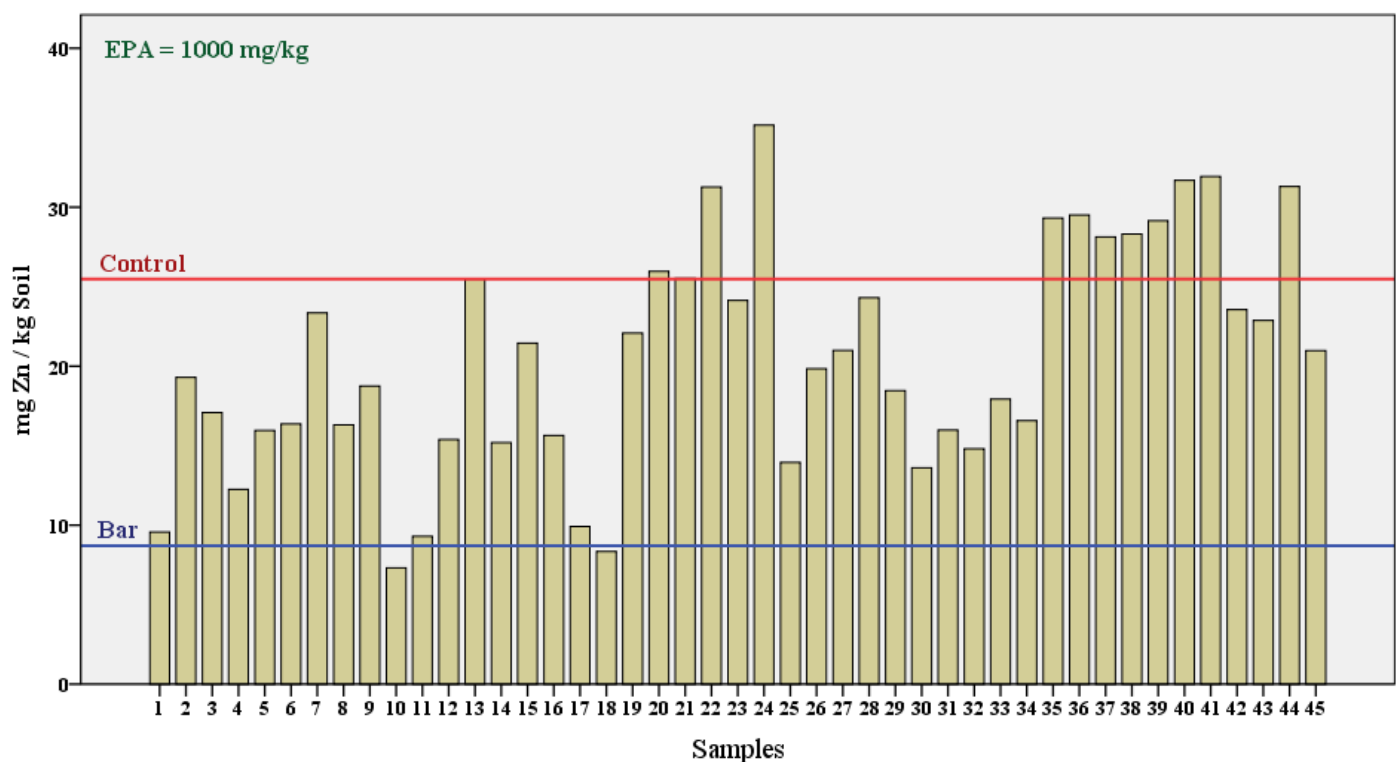


Figure 4.26: Zinc concentration in targeted soil samples

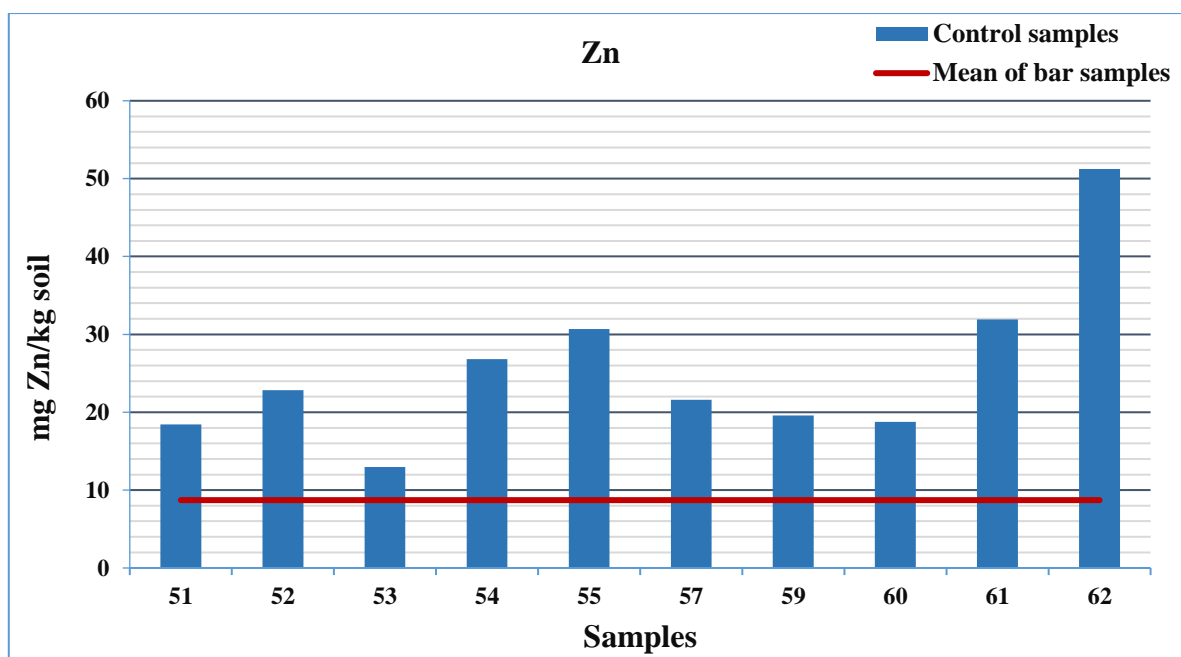


Figure 4.27: Concentration of zinc in control samples

#### 4.4.8.1 Zn in soil samples collected inside craters formed by AFBs

Samples collected inside craters formed by AFBs have Zn concentration ranging from 7.321 mg/kg to 29.507 mg/kg with mean concentration of 19.307 mg/kg. The highest concentration was detected in sample label 36 and the lowest in sample label 10 (table 4.9).

#### 4.4.8.2 Zn in soil samples from areas surrounding craters formed by AFBs

The concentration of Zn in soil samples collected from areas surrounding craters formed by AFBs range from 9.298 mg/kg to 31.265 mg/kg with mean concentration of 19.693 mg/kg. Sample label 22 has the highest concentration while sample label 11 has the lowest concentration as shown in table 4.11.

#### 4.4.8.3 Zn in soil samples from craters formed by AS

The concentrations of the Zn in this category range from 412.254 mg/kg to 35.158 mg/kg with mean concentration of 23.970 mg/kg. The highest concentration was detected in sample label 24 and the lowest one was detected in sample label 4 as shown in table 4.10.

#### 4.4.8.4 Zn in soil samples from areas surrounding craters formed by AS

The concentrations of Pb in soil samples collected from areas surrounding to craters formed by artillery shelling range from 13.943 mg/kg to 31.932 mg/kg with mean concentration of

20.794 mg/kg. The highest concentration was detected in sample label 41 and the lowest was detected in sample label 25 as shown in table 4.12.

Table 4.13 shows that, there is no significant statistical difference (P-value = 0.155) between the mean concentration of Zn in samples collected from areas subjected to AFB and the mean concentration of Zn in samples collected from areas subjected to AS. The results of the T-test also shows that, there is no significant statistical difference (P-value = 0.886) between the mean concentration of Zn in samples collected from craters formed by AFB and the mean concentration of Zn in samples from areas surrounding these craters. As well as there is no significant statistical difference (P-value = 0.421) between the mean concentrations of Zn in samples collected from craters formed by AS and the mean concentration of Zn in samples from areas surrounding these craters. It was noted that, the concentrations of Zn in targeted soil samples are very close in areas subjected to AFBs and areas subjected to AS, as well as in the four previously mentioned categories in the term of minimum, maximum and mean concentrations as shown in table (4.9, 4.10, 4.11, 4.12 and 4.14). However, it refers to that; the military activities did not affect the content of zinc in the soils of targeted locations.

#### **4.1.9 Aluminum (Al)**

The aluminum concentration in Gaza soils is not affected by the agricultural activities; instead, it is affected by the military activities. The T-test shows that, the targeted soil samples have significantly (P-value = 0.000) higher concentration of Al than control samples, since its mean concentration in targeted soil samples (4493.672 mg/kg) is 2.4 times its mean concentration in control samples (1882.659 mg/kg), indicating that AFB and AS supplied these locations with significant amounts of Al. That was supported by the result obtained from figure 4.28, which shows that, 95.56% of the targeted soil samples have Al concentrations higher than the mean concentration of control samples, and agrees with the researches done by Campbell et al. (2003) and Boggs (2004), which revealed that the amount of Al used in high explosive charge is in the order of 20%. Excluding sample label 45 which has unexpected result (112.231 mg/kg), the concentrations of aluminum in targeted soil samples range from 799.844 mg/kg, detected in sample label 1 to 9507.166 mg/kg detected in sample label 39. Although the concentrations of Al in targeted soil samples are relatively high comparing with other metals, the Al in targeted soil samples does not pose threat to

human health, since the maximum allowable concentration of Al is not listed in international standard such as EPA or Canadian standards.

In the other hand, the mean concentration of Al in control samples is less than that of bar samples (2261.261 mg/kg) as shown in table 4.5. As well as 80% of the control samples have Al concentrations lower than the mean concentration of the bar soil samples (figure 4.29), indicating that the Al concentration in the agricultural soils is not affected by agricultural activities, instead it is much affected by the environmental contribution of Al.

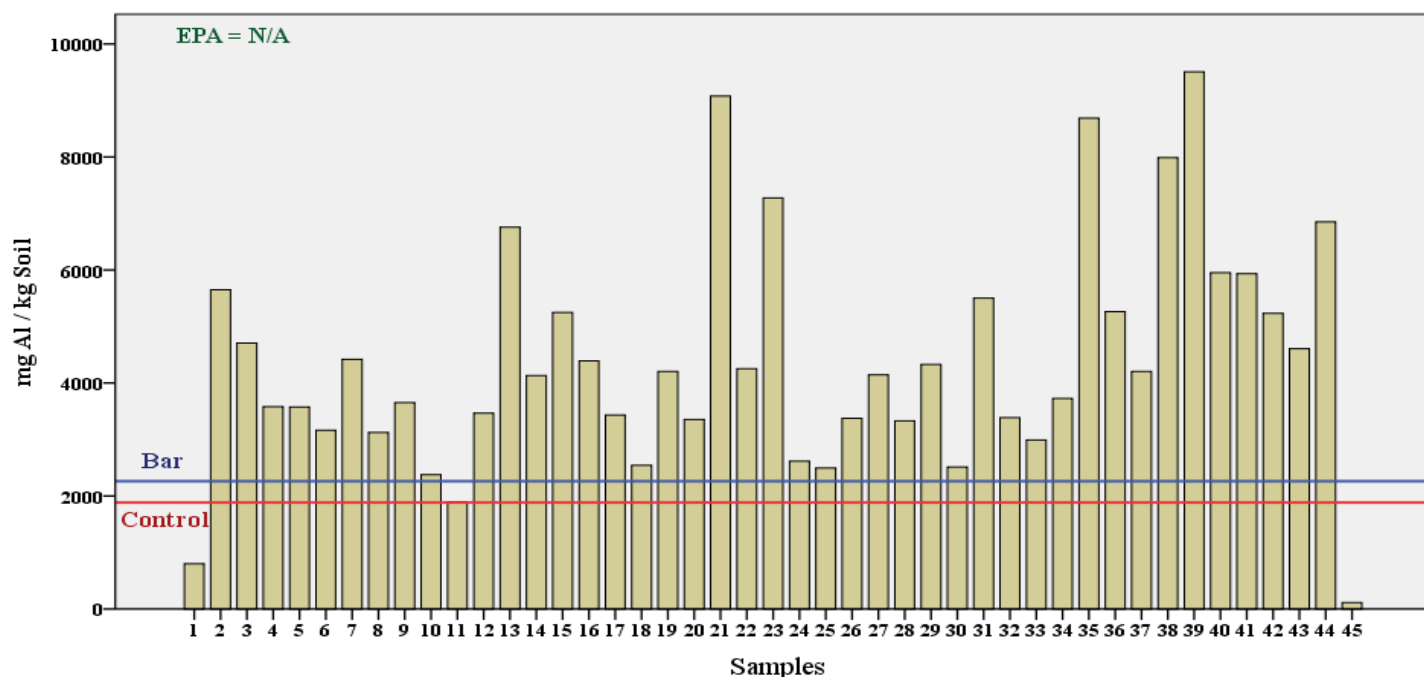


Figure 4.28: Aluminum concentration in targeted soil samples

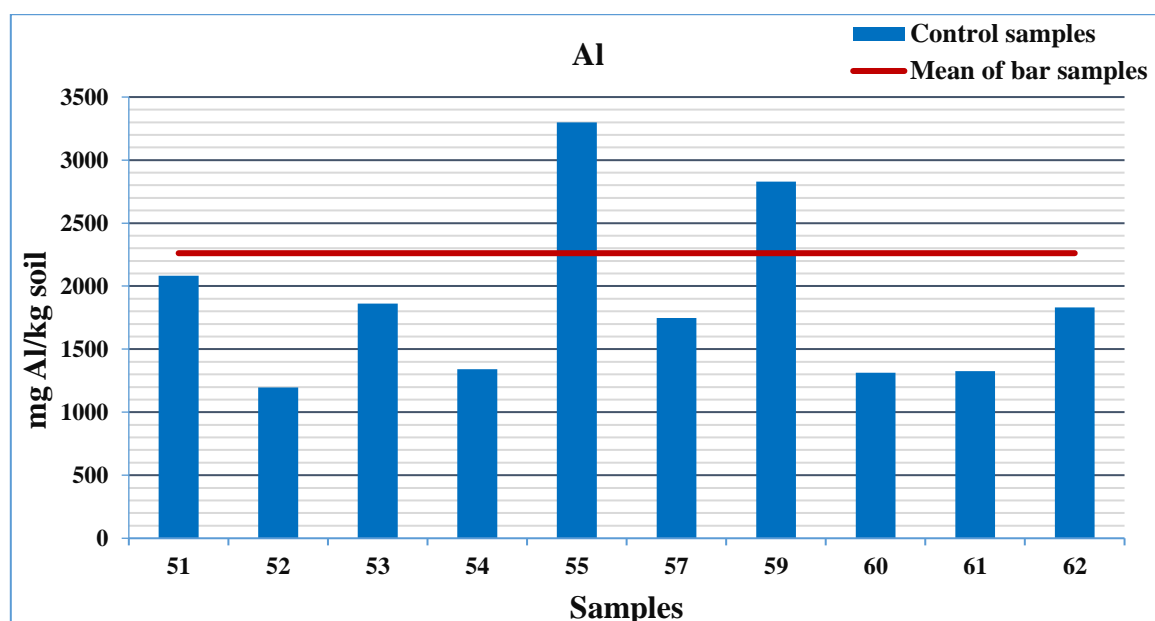


Figure 4.29: Concentration of aluminum in control samples

#### **4.6.9.1 Al in soil samples collected inside craters formed by AFBs**

Samples collected inside craters formed by AFBs have Al concentration ranging from 799.844 mg/kg to 9078.105 mg/kg with mean concentration of 4678.719 mg/kg. The highest concentration was detected in sample label 21 and the lowest in sample label 1 (table 4.9).

#### **4.6.9.2 Al in soil samples from areas surrounding craters formed by AFBs**

The concentration of Al in soil samples collected from areas surrounding craters formed by AFBs range from 1899.166 mg/kg to 9507.166 mg/kg with mean concentration of 4259.616 mg/kg. Sample label 39 has the highest concentration while sample label 11 has the lowest concentration as shown in table 4.11.

#### **4.6.9.3 Al in soil samples from craters formed by AS**

The concentrations of the Al in this category range from 2617.204 mg/kg to 7276.194 mg/kg with mean concentration of 4588.667 mg/kg. The highest concentration was detected in sample label 23 and the lowest one was detected in sample label 24 as shown in table 4.10.

#### **4.6.8.4 Al in soil samples from areas surrounding craters formed by AS**

Excluding sample label 45, the concentrations of Al in soil samples collected from areas surrounding to craters formed by AS range from 2495.233 mg/kg to 5933.930 mg/kg with mean concentration of 4218.242 mg/kg. The highest concentration was detected in sample label 41 and the lowest was detected in sample label 25 as shown in table 4.12.

Table 4.13 shows that, there is no significant statistical difference ( $P\text{-value} = 0.931$ ) between the mean concentration of Al in samples collected from areas subjected to AFB and the mean concentration of Al in samples collected from areas subjected to AS. The results of the T-test also shows that, there is no significant statistical difference ( $P\text{-value} = 0.601$ ) between the mean concentration of Al in samples collected from craters formed by AFB and the mean concentration of Al in samples from areas surrounding these craters. As well as there is no significant statistical difference ( $P\text{-value} = 0.688$ ) between the mean concentrations of Al in samples collected from craters formed by AS and the mean concentration of Al in samples from areas surrounding these craters. . It can be concluded from the results of the T-test that, the content of Ni in both AFB and AS is spread over the craters and the areas surrounding craters formed by them, which occurs due to the high order detonation of the AFB and the AS.

## 4.5 Metals in rubble

Measuring how much the military activities affect the concentration of the selected metals in rubble is unreachable, because there is no base line data describing the rubble content of metals in Gaza Strip to compare with. The concentration of metals in rubble samples were compared with the Maximum Allowable Concentrations of Chemical Constituents in Uncontaminated Soil Used as Fill Material (MACs) listed by EPA to investigate the validity of using such rubble in construction purposes or as a filling material. Concentrations of metals in rubble samples are listed in table 4.15.

**Table 4.15: Concentrations of metals in rubble samples**

Sample label	mg/kg								
	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn	Al
<b>46</b>	0.931	2.641	6.537	6.529	35.147	4.178	4.330	19.247	1715.306
<b>47</b>	1.046	3.002	10.540	110.203	39.263	6.540	5.756	14.722	1150.508
<b>48</b>	1.579	5.467	12.665	34.172	51.601	8.650	43.423	18.455	1878.916
<b>49</b>	1.465	11.733	10.844	11.217	47.104	7.193	8.929	3.738	16597.557
<b>50</b>	4.112	2.360	10.089	90.225	41.733	9.297	17.034	27.878	2144.804
<b>Mean</b>	1.827	5.041	10.135	50.469	42.970	7.172	15.895	16.808	4697.418
<b>EPA</b>	5.200	20	21	2900	N/A	100	107	5100	N/A

### 4.5.1 Cadmium (Cd)

The concentrations of Cd in rubble samples are relatively high comparing with that of soil samples, ranging from 0.931 mg/kg detected in sample label 46 to 4.112 mg/kg detected in sample label 50, with mean concentration of 1.827 mg/kg (table 4.15). In addition to its content in AFB and AS, the concentration of Cd in rubble may be affected by other sources such as paints (Abel, 2015) and damaged batteries (ATSDR, 2012a), which are commonly used in Gaza Strip due to the chronic crisis of electricity since the year of 2006.

Figure 4.30 shows that, all rubble samples have Cd concentrations lower than the Maximum Allowable Concentrations of Chemical Constituents in Uncontaminated Soil Used as Fill Material (MACs) listed by EPA (5.2 mg/kg)

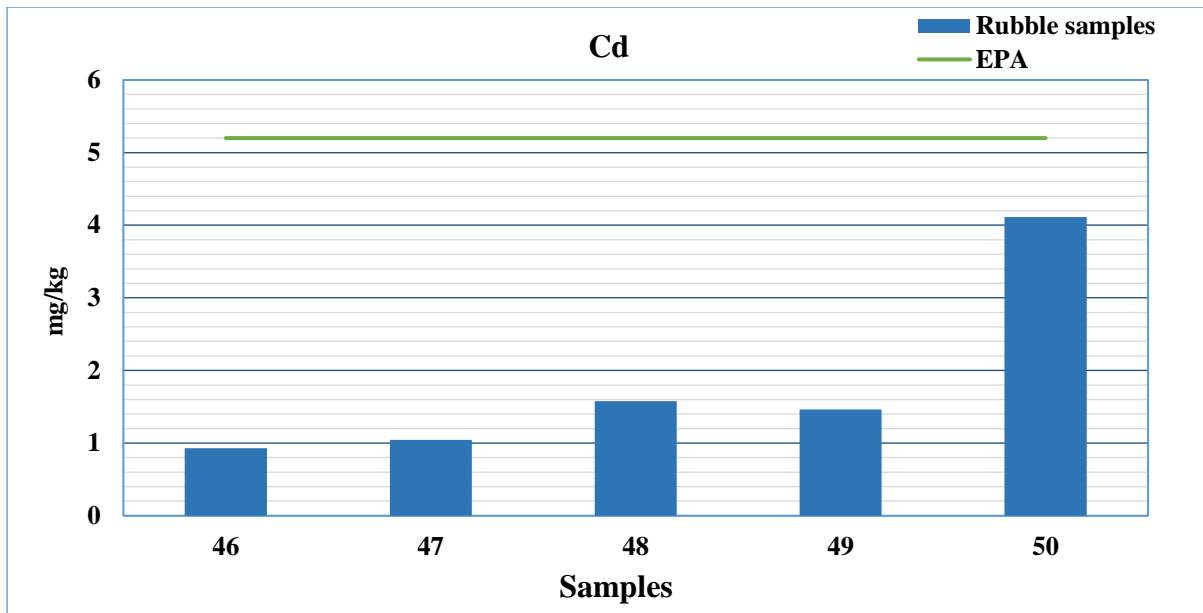


Figure 4.30: Concentration of cadmium in rubble samples

#### 4.5.2 Cobalt (Co)

Cobalt in rubble samples range from 2.360 mg/kg detected in sample label 50 to 11.733 mg/kg detected in sample label 49, with mean concentration of 5.041 mg/kg. Cobalt commonly used in paints and ceramics (ATSDR, 2004a), which with AFB and AS may affect its concentration in rubble samples. All rubble samples have Co concentrations lower than the Maximum Allowable Concentrations of Chemical Constituents in Uncontaminated Soil Used as Fill Material (MACs) listed by EPA (20 mg/kg) as shown in figure 4.31.

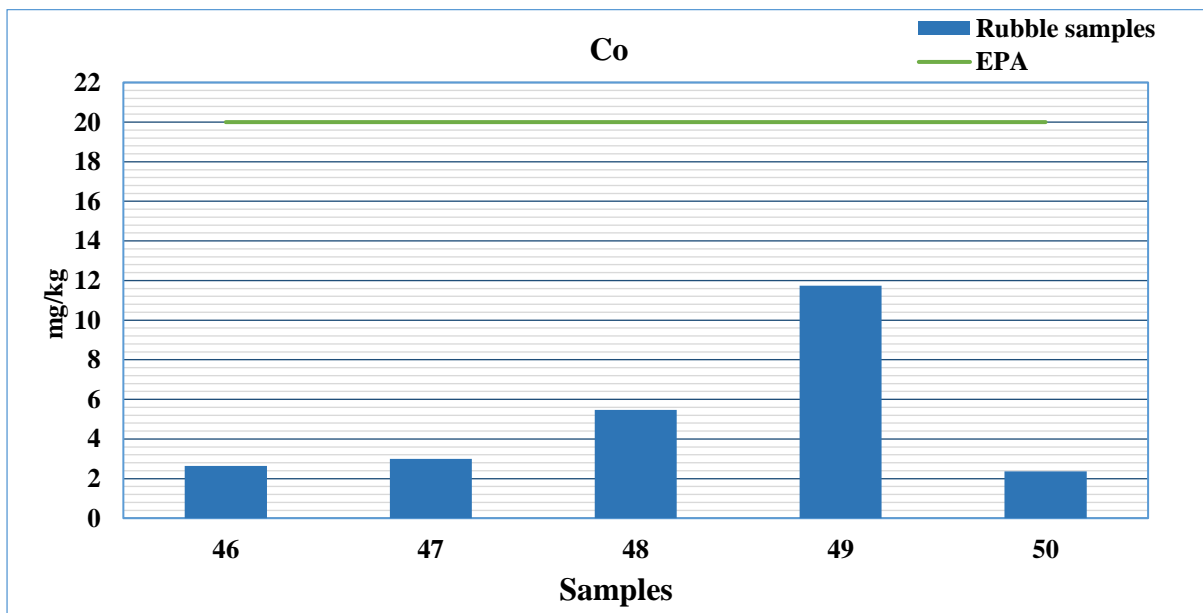


Figure 4.31: Concentration of cobalt in rubble samples

### 4.5.3 Chromium (Cr)

The lowest chromium concentration (6.537 mg/kg) was detected in sample label 46 and the highest concentration (12.665 mg/kg) was detected in sample label 48, while its mean concentration is 10.135 mg/kg (table4.15). Chromium concentration in all rubble samples are below the Maximum Allowable Concentrations of Chemical Constituents in Uncontaminated Soil Used as Fill Material (MACs) listed by EPA (21 mg/kg) as shown in figure 4.32.

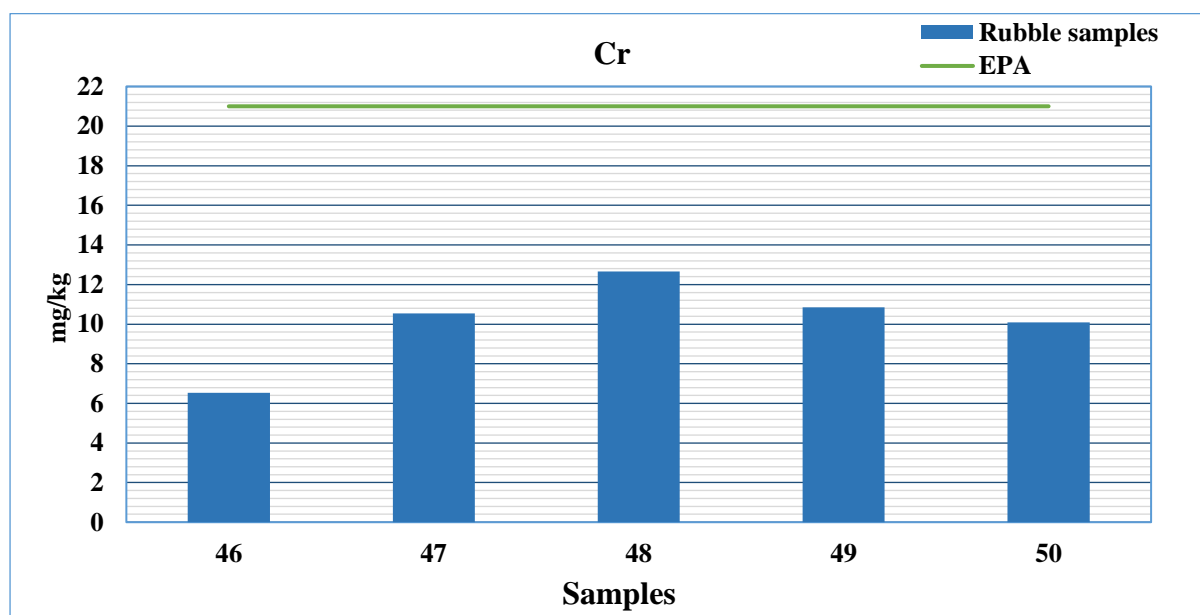


Figure 4.32: Concentration of chromium in rubble samples

### 4.5.4 Copper (Cu)

The lowest concentration of Cu in rubble samples (6.529 mg/kg) was detected in sample label 46, and the highest concentrations were found in samples label 47 (110.203 mg/kg) and sample label 50 (90.225 mg/kg) respectively, with mean concentration of 50.469 mg/kg. While there is no clear interpretation for the high concentration of Cu in sample label 47, the source of Cu in sample label 50 which was collected from apartment no. 18 of Al nada tower no. 1, is likely to be the dropped artillery shell. This type of shells has a bronze rotating band composed mainly of 90% copper (Boggs, 2004). Figure 4.33 shows that all rubble samples have Cu concentrations much lower than the Maximum Allowable Concentrations of Chemical Constituents in Uncontaminated Soil Used as Fill Material (MACs) listed by EPA (330 mg/kg).



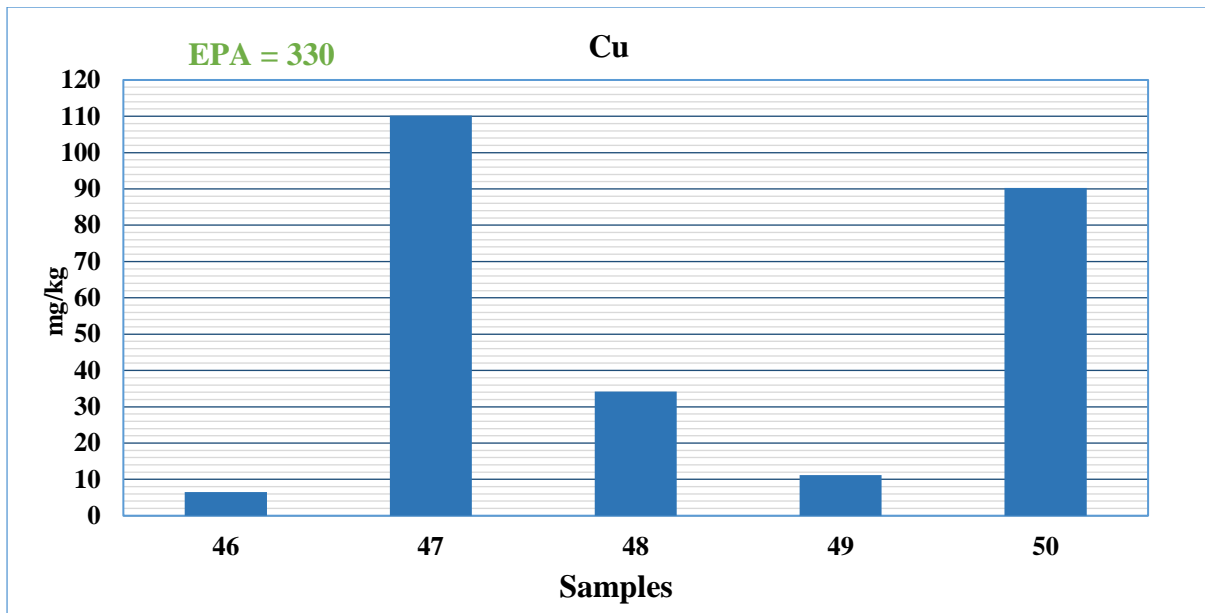


Figure 4.33: Concentration of copper in rubble samples

#### 4.5.5 Manganese (Mn)

Manganese in rubble samples range from 35.147 mg/kg detected in sample label 46 to 51.601 mg/kg detected in sample label 48, with mean concentration of 42.970 mg/kg. However, manganese is not listed the Maximum Allowable Concentrations of Chemical Constituents in Uncontaminated Soil Used as Fill Material (MACs) listed by EPA.

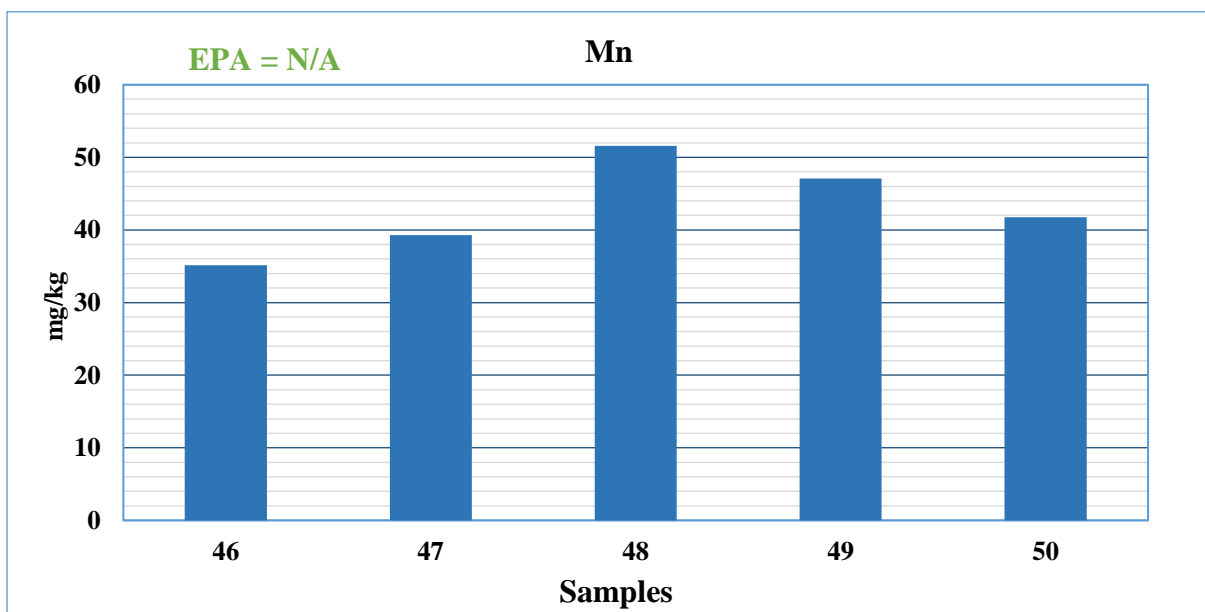


Figure 4.34: Concentration of manganese in rubble samples

#### 4.5.6 Nickel (Ni)

The concentration of nickel in rubble samples range from 4.178 mg/kg detected in sample label 46 to 9.297 mg/kg detected in sample label 50, with mean concentration of 7.172 mg/kg (table 4.15). Figure 4.35 shows that, the concentrations of Ni in all rubble samples are much below the Maximum Allowable Concentrations of Chemical Constituents in Uncontaminated Soil Used as Fill Material (MACs) listed by EPA (100 mg/kg).

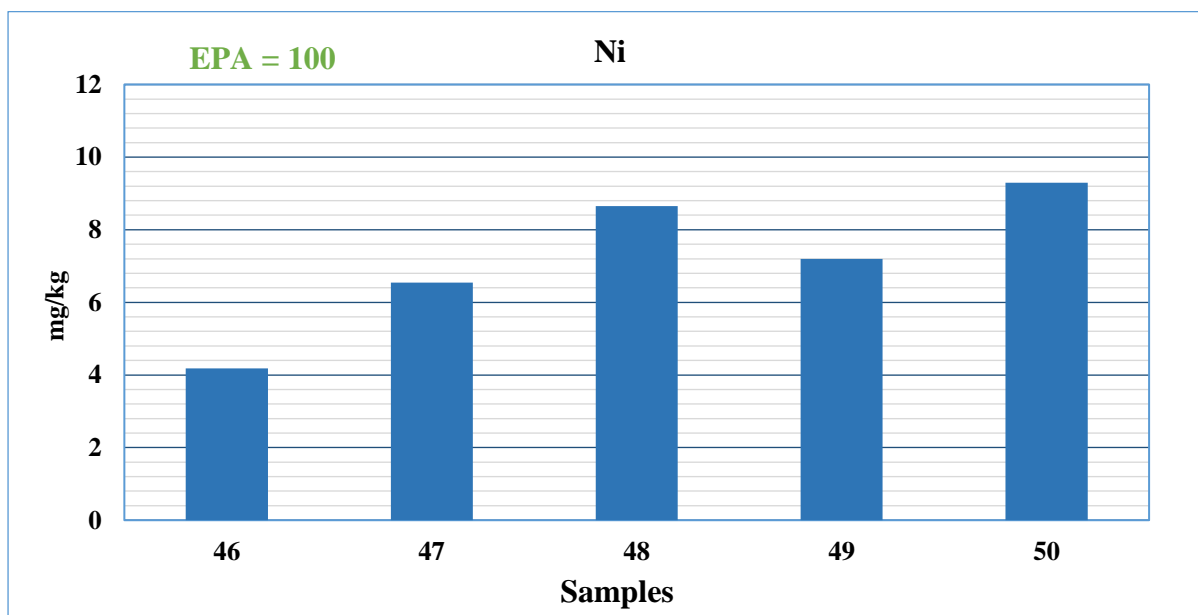


Figure 4.35: Concentration of nickel in rubble samples

#### 4.5.7 Lead (Pb)

Lead in rubble samples range from 4.33 mg/kg detected in sample label 46 to 43.423 mg/kg detected in sample label 48, with mean concentration of 15.895 mg/kg. However, the lead content in rubble samples is affected by many sources, including, ceramics, paints and storage batteries (ATSDR, 2007). Lead in all rubble samples is much below the Maximum Allowable Concentrations of Chemical Constituents in Uncontaminated Soil Used as Fill Material (MACs) listed by EPA (107mg/kg).

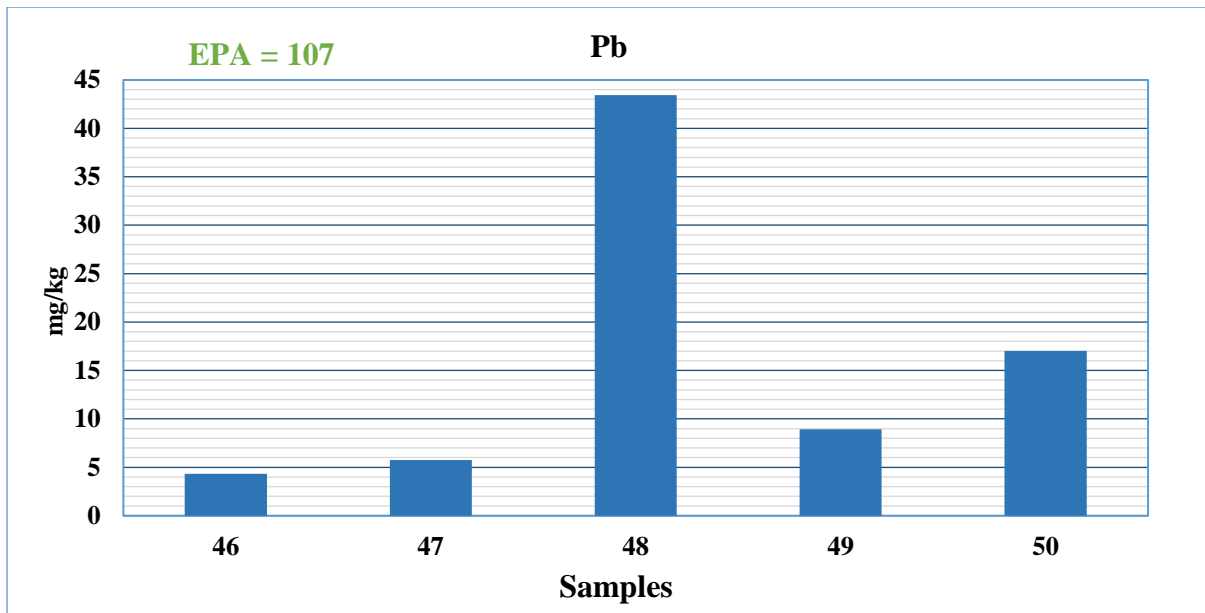


Figure 4.36: Concentration of lead in rubble samples

#### 4.5.8 Zinc (Zn)

The lowest zinc concentration (3.738 mg/kg) was detected in sample label 49 and the highest concentration (27.878 mg/kg) was detected in sample label 50, while its mean concentration is 16.808 mg/kg (table4.15). Zinc concentration in all rubble samples are much below the Maximum Allowable Concentrations of Chemical Constituents in Uncontaminated Soil Used as Fill Material (MACs) listed by EPA (5100 mg/kg) as shown in figure 4.37.

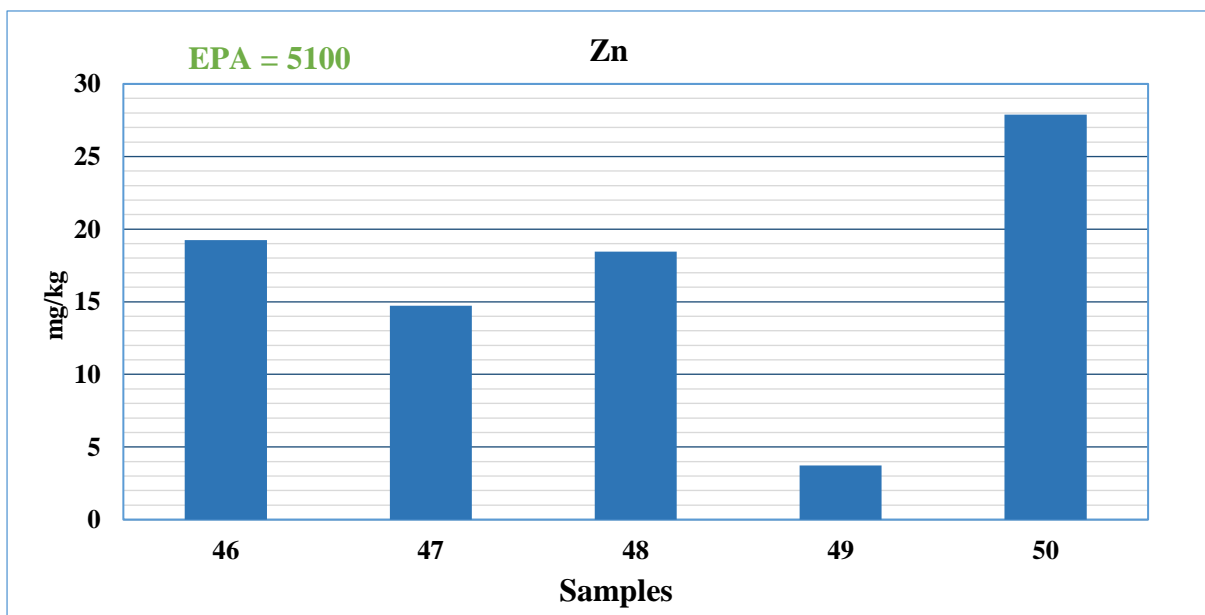


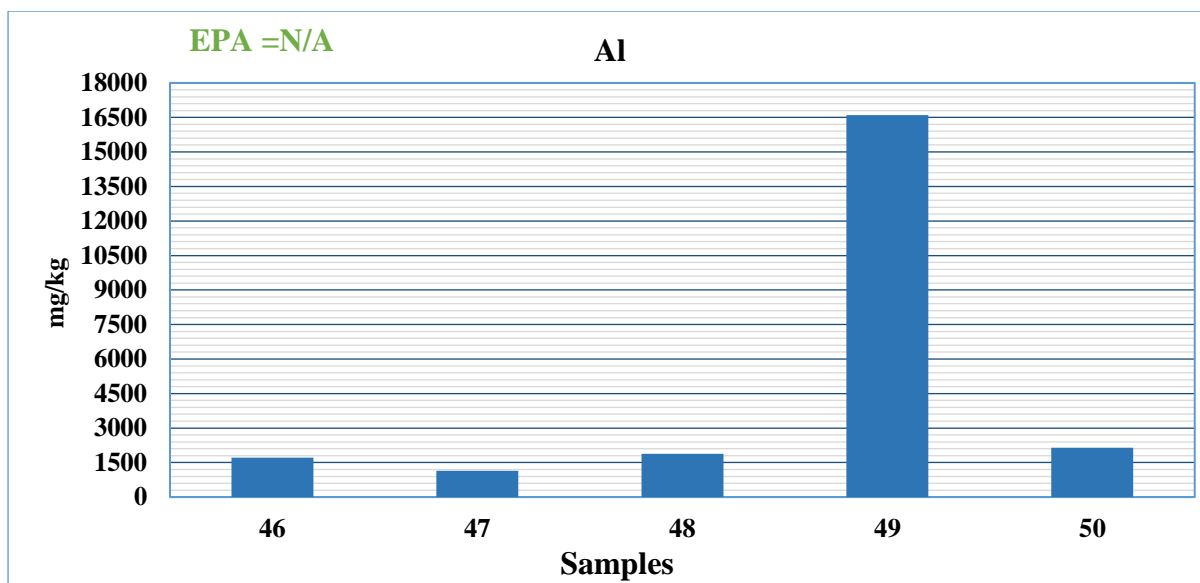
Figure 4.37: Concentration of zinc in rubble samples

#### 4.5.9 Aluminum (Al)

The concentration of Al in rubble samples range from 1150.508 mg/kg detected in sample label 47 to 16597.557 detected in sample label 49 with mean concentration of 4697.418 mg/kg (table 4.15). Sample label 49 was collected from the ground floor of Al nada tower no. 1. The source of Al in this in this sample is the explosive charge, since the bomb dropped over this tower was dud (not detonated) and the explosive charge spread in the place (figure 4.38). That was supported by Hewitt, et al. (2007), who revealed that, the higher concentration of metals, are usually resulted by low-order detonation, dud or ruptured warheads. This conclusion was supported by Boggs (2004) and Campbell et al. (2003) who revealed that the amount of Al used in high explosive charge is in the order of 20%. Anyway, aluminum is not listed the Maximum Allowable Concentrations of Chemical Constituents in Uncontaminated Soil Used as Fill Material (MACs) listed by EPA (figure4.39).



**Figure 4.38: Dud bomb dropped on Al Nada tower no.1**



**Figure 4.39: Concentration of aluminum in rubble samples**

Although, all of the investigated metals were detected in the rubble samples, the concentrations of these metals are below the Maximum Allowable Concentrations of Chemical Constituents in Uncontaminated Soil Used as Fill Material (MACs) listed by EPA (USEPA, 2012) as shown in table 4.15. Accordingly, in terms of the investigated metals, the rubble can be used in construction purposes or as a filling material without any restrictions. Anyway, that agrees with the results of the analysis of the heavy metals in rubble collected from a destroyed house in Al Shati camp, as a part of the environmental assessment carried out by the UNEP (2009).

## **CHAPTER FIVE: CONCLUSIONS AND RECOMMENDATIONS**

### **5.1 Conclusion:**

Soil and rubble pollution with metals in Gaza Strip was investigated in this research. A brief summary of the results is listed as follow:

1. Although, the high sand content, as well as the low CEC values of Gaza soils increase the possibility of downward migration of metals in soil profile via soil solution, the slightly alkaline to moderately alkaline values of the soil pH decrease this possibility.
2. The agricultural activities enriched the Gaza soils with, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn, while the content of Al is likely to be affected by the environmental contribution.
3. The mean concentrations of metals in targeted soil (mg/kg) were: Cd (0.936); Co (4.758); Cr (16.854); Cu (9.623); Mn (115.730); Ni (9.919); Pb (6.863); Zn (20.541) and Al (4396.306), so, these values followed the sequence: Al > Mn > Zn > Cr > Ni > Cu > Pb > Co > Cd.
4. Only Cd in (26.67%) and Cr in (20%) of the targeted soil samples were found with concentrations higher than the MACs of Chemical Constituents in Uncontaminated Soil listed by USEPA.
5. Both AFB and AS introduced significant amounts of Cd, Co, Cr, Cu, Mn, Ni, and Al, to the targeted soils in Gaza Strip, while the content of Pb and Zn in targeted soil is much affected by agricultural activities.
6. The metals contents in targeted soil samples were not affected by the used type of munition (AFB and AS) except for Cu, where, among the investigated metals, only the content of Cu in samples collected from areas subjected to AS is significantly higher than that of samples collected from areas subjected to AFB.
7. There are no significant differences between the metal contents inside and surrounding the craters formed by either AFB or AS, due to the high order detonation of the AFB and the AS, which is efficient to distribute the metals involved in the casing or in the explosive charge over several hundreds of square meters.
8. The mean concentrations of the metals in rubble (mg/kg) were: Cd (1.827), Co (5.041), Cr (10.135), Cu (50.469), Mn (42.970), Ni (7.172), Pb (15.895), Zn (16.808)

and Al (4697.418), so, these values followed the sequence: Al > Cu > Mn > Zn > Pb > Cr > Ni > Co > Cd.

9. The metal content in all rubble samples were found in values lower than the MACs of Chemical Constituents in Uncontaminated Soil Used as Fill Material.

## **5.2 Recommendations**

The main recommendations for this research can be summarized as follow:

1. Since they are important sources of many metals in Gaza soils, agricultural activities such as application of fertilizers and pesticides should be controlled.
2. In areas subjected to bombing, more studies should be conducted to investigate the soil and rubble contamination with other metals, explosive residuals and radioactive materials.
3. Relevant institutions should establish research programs to investigate the fate of metals and other explosive residuals in deep soil, groundwater and plants.
4. In terms of the investigated metals, rubble can be used in construction purposes or as a filling material without any restrictions, since their concentrations in rubble samples are lower than MACs of Chemical Constituents in Uncontaminated Soil Used as Fill Material listed by USEPA.
5. Since there are big differences in the international guideline values of metals in soil, due to the unique characteristics of soils in each country, a national soil standard should be established.

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