

# Assessing Heavy Metals Pollution in the Agricultural Lands of Gaza Strip that Has Undergone Three Successive Wars

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**Abstract** The intensive airstrikes on agricultural lands in the Gaza Strip create craters of 20 m diameter and 10 m depths. Samples from the craters are collected from fourteen different locations, were analyzed to assess the impact of war activities on soil pollution. Soil samples were analyzed for major heavy metals (Ni, Cr, Cu, Mn, Co and Pb) by using hotplate digestion and A Perkin-Elmer Analyst 600 GF-AAS analyzer, equipped with pyrolytically coated graphite tube with integrated platform Zeeman background and correction. The results showed that most of the soils 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. Due to its texture, some samples from sandy soil origins had not significant higher metals concentration than the control. Ni, Cr, Cu, Mn, Co and Pb clearly contributed by the content of munitions of the airstrike. Soil pollution by Cu, Mn and Pb was more widespread than the other heavy metals, which was contributed mostly by munitions. The results also indicate that the concentration of specific heavy metals depends on the type of the explosives material and the soil texture. The current research highlighted the danger and risk of munitions on the agricultural lands. It is highly recommend for the relevant institutions to monitor and follow up research program to investigate the fate of the metals in soil, groundwater and food chain to protect the environment and health.

**Keywords:** Gaza strip, soil contamination, heavy metals, munitions and airstrike

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## 1. Introduction

The area of the Middle East has been facing terrible and destructive disruption to its environment. This calamitous issue started ever since the beginning of the twentieth century. In this article a certain soil pollution issues arisen as result of the wars that endeavored Gaza Strip which lead to ecological destruction in all aspects of living and nonliving environments have been highlighted.

In the last six years, three successive wars occurred between Israel and Gaza Strip, the period between the war and the other almost two years, 2008-2009, 2012 and 2014 war. Tons of explosive materials have been dropped over the Gaza strip, left a serious impacts on all basics of life and on infrastructure as wells, water stations, water networks, sewage networks, electricity, and communication networks [1,2]. In particular, approximately 36000 ton of artillery heavy shells or rocket have been thrown on farmlands, formed craters with average diameter 20 meters and an average depth of 10 meter, where the agricultural sector has the largest losses in this war. The

losses estimated to be 550\$ million, of which 350\$ million direct losses and 200\$ million indirect losses. The total value of direct damages and losses hit the different branches of agricultural sectors at the north of Gaza Strip was 54.5 Million Dollars. Agricultural production losses about 76% of the total damage in the agricultural sector, and loss approximately 500 acres of agricultural land areas in the north of Gaza Strip alone [3].

The Gaza strip is a coastal area along the eastern Mediterranean Sea, 45 km long and between (6-12) km wide, with total area of about 365 km<sup>2</sup>. Gaza strip is located between longitudes 33<sup>0</sup>-2"east and latitudes 31<sup>0</sup>-16' north. The area forms a transitional zone between the semi-humid coastal zone in the north and the semi-arid loess plains of the northern Negev in the east, and the arid Sinai desert of Egypt in the south [4]. Administratively, Gaza Strip is divided into five governorates: the northern governorate, Gaza governorate, Middle governorate, Khan Younis governorate and Rafah governorate in the south bordering with Egypt, each governorate is then subdivided into municipalities. The northern governorate characterized by high rainfall rate compared with other Governorates due to its geographical location [5]. The

governorate soil classified as sandy and loamy clay soil. The North Governorate produce approximately 15.9% of the total agricultural production in Gaza Strip, the most famous crops are strawberries, apples, citrus and wheat [6]. Most of losses were in the agricultural sector presented as destruction and bulldozing of trees, crops, greenhouses and equipment's of irrigation wells. Due to the limited area and resources of the Gaza strip, the last three was caused serious pollution to the environment, all of these pollutants cause a serious risk to land and water resources. That affect human health directly and indirectly which needs a huge effort to mitigate them, but before suggest mitigation measures it requires to find the exact environmental pollution from munitions like heavy metal input, radioactive materials and toxic compounds. Therefore, the main objective of the current research is to investigate and determine the lands which are effected by the war in the northern governorate and the heavy metals input to the soil.

## 2. Study Area and Methodology

The study was conducted in the Northern Governorate. It is one of five governorates in Gaza Strip, with an area of 62 km<sup>2</sup> and accounts for 17% of Gaza Strip area. It has a population of 15% (270.245 inhabitants) of Gaza Strip population 1.800,000 inhabitants [7,8]. Northern Governorate constitutes of four urban communities: Jabaliya, Beit Lahia and Beit Hanoun and three rural communities: Om Al Naser village, Ezbet Beit Hanoun and Ezbet Abed Rabbo [9].

### Samples collection

The samples were collected from the center and sides of the craters directly after the ceasefire with dimensions of about 50 cm width and 70 cm depth, and with approximate weight of 0.5 kg. Control sample was collected from un targeted locations. Samples coordinates were determined using GPS as shown in Table 1 and Figure 1. The samples were placed in a drying oven for 6 hour at temperature 110°C. then cooled to room temperature, sieved in 4.7 mm sieve to remove any large object material then sieved in 2 mm to remove coarse material and grinded. Finally the samples were sieved in 500 µm.

Table 1. Samples coordinates

Samples	N	E
N01	31.54551	34.54089
N02	31.53168	34.54195
N03	31.52669	34.53564
N04	31.5283	34.53216
N05	31.5399	34.53124
N06	31.54112	34.51607
N07	31.54919	34.49757
N09	31.547	34.5005
N010	31.55889	34.48323
N11	31.558	34.48212
N12	31.52766	34.49456
N13	31.52487	34.48536
N14	31.52487	34.48536

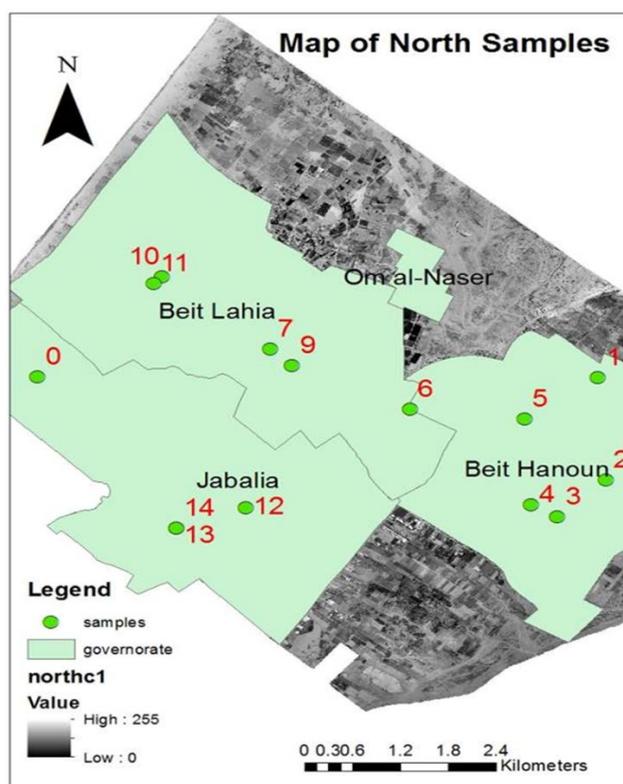


Figure 1. Samples locations in North Governorate

**Sample digestion:** Standard method for digestion of soil sample by hotplate digestion is used [10]. 10 ml of 1:1 nitric acid: water was added to 1 gram soil and heated to 85°C for about 10-15 minutes without boiling. Sample was cooled, then 5ml of concentrated nitric acid was added and heated again to 85°C for about 30 minutes without boiling. The solution was allowed to evaporate until reach 5 ml without boiling. Sample was cooled and 2 ml of water and 3 ml of 30% hydrogen peroxide was added, the beaker was returned to the hotplate for start peroxide reaction then cooled. Add (1-10) ml (No more than 10 ml) of 30% hydrogen peroxide until the general sample appearance is unchanged. The glass cover was removed and the acid peroxide digest was continued heating until the volume has been reduced to 5 ml. The beaker walls and bottom of the glass was rinsed with water and transferred to 100 ml volumetric flask, diluted to volume with water. The sample was filtered and the heavy metals were determined in the soil extract.

### Standards Preparation:

**Copper (Cu):** Stock solution of 1000 ppm Cu was prepared by dissolving 3.798g of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O in 1 L distilled water. 250 ppb from stock solution was prepared by dilution. Four working standard solutions with concentration 10,20,30,40 ppm were prepared from diluted solution 250 ppb.

**Chromium(Cr), Nickel (Ni):** Merck multi element standards have been used as a stock solution and all dilution have been made with highly pure water and highly pure HNO<sub>3</sub>. Samples have been acidified to 2% HNO<sub>3</sub> concentration. 20000 ppb was diluted to 100 ppb. Four working standard solutions with concentration 10,20,30,40 ppm were prepared from diluted solution 100 ppb.

**Manganese (Mn) and lead (Pb):** Merck multi element standards have been used as a stock solution and all

dilution have been made with highly pure water and highly pure HNO<sub>3</sub>. Samples have been acidified to 2% HNO<sub>3</sub> concentration. 100000 ppb was diluted to 100 ppb. Four working standard solutions with concentration 10,20,30,40 ppm were prepared from diluted 100 ppb.

**Cobalt (Co):** Stock solution of 1000 ppm Co was prepared by dissolving 4.9379 g of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in 1 L distilled water. 100 ppb from stock solution was prepared by successive dilution. Four working standard solutions with concentration 10,20,30,40 ppm were prepared from diluted 100 ppb.

**Table 2. A Analyst 600 AAS Furnace element Instrumental conditions**

Element	Co	Cr	Mn	Cu	Ni	Pb
Wave length (nm)	242.5	357.9	279.5	324.8	232	283.3
Time of reading (sec)	5	5	5	5	5	5
Slit width (nm)	0.2	0.7	0.2	0.7	0.2	0.7
Measurement	Peak Area	Peak Area	Peak height	Peak Area	Peak Area	Peak Area
Signal type of measure	AA-BG	AA-BG	AA-BG	AA-BG	AA-BG	AA-BG
Standard con. (µg/l)	10, 20, 30, 40					
Sample volume (µl)	20					

**Atomic Absorption Spectrometer:** A Perkin-Elmer Analyst 600 GF-AAS analyzer has been used, equipped with pyrolytically coated graphite tube with integrated platform Zeeman background and correction. An HCl lamp has been used as the light source. A Analyst 600 spectrometer, equipped with transversely heated graphite atomizer (THGA) and AS-80 auto sampler, was used. Hollow-cathode lamps (Perkin-Elmer) were used for (Cobalt, Nickel, Lead, Manganese, Chromium, Copper). (THGA) graphite tubes with integrated platform and was used for all elements. After the samples were located in (AAS), the instrumental conditions were programmed and samples were measured against calibration curve constructed from four aqueous standards as shown in Table 2.

### 3. Results and Discussion

#### Soil Texture:

Soil texture determined the chemistry of pollutants in the soil such as heavy metals, the clay soil has the ability to absorb the heavy metals while sandy soil has not this propriety [11,12]. Therefore the soil texture affects the mobility of elements and leaching to ground water. The percentages of sand in samples No. 6,7, 9, 10, 12,14 and control are 87%, 89.3%, 52.9%, 84.3%, 93.1%, 57.8% and 83.12% respectively. While samples No. S1, S2, S3, S4, S5, S11 and S13 have a high percent of silt and clay 56.3%, 83.1%, 59.3%, 89.13%, 85.4%, 51.2% and 73.2% respectively. Gaza soil characterized by high sand content [13]. According to Dudeen, 2001, the main soil type of the Gaza Strip including the study area originates from the dune sands. It is overlying alluvial soils in a shallow layer creating ideal conditions for fruit plantations. These dune sands have exceedingly low water holding capacity and very high water permeability. In addition to the sandy soils, loess soils are also occurring in the Gaza Strip. These soils owe their origin mainly to the dust storms of the desert. To a great extent, included in the are also locally weathered soils. They are rich in calcium but poor in iron and aluminium, have a high percentage of fine particles, which belong mainly to the fine sand fraction. They are easily permeable by water and air, therefore leaching of minerals is predominant in such soils [14].

The natural silty soil macro pores ranges from 4.0 to 8.0%, it reduced to 0.3- 2.5% after passing of heavy tanks in the area. Silty loam has macro pores ranges from 2.0 to

3.0% and changed to 0.8- 1.2%. While Silty clay is 0.5- 1.5% and changed to 0.1- 0.4%. The impacts of the various soil textures are very clear due military activities in the agricultural lands [3].

#### Metal contamination

In this research six heavy metals as potential pollution to the soil are measured (Ni, Cr, Cu, Mn, Co and Pb). The calibration curve for all measured elements is represented in Figure 2.

**Nickel (Ni):** Calibration curve for the determination of Nickel in the unknown samples is drawn based in the know concentration of Ni and the measured absorption in the AAS. The relation has  $R^2 = 0.999$  (Figure 2). The measured concentration of Nickel in control sample was 6.3 (mg/Kg soil) and for S1, S2, S3, S4, S5, S9, S11, S13 and S14 were 24.45, 13.76, 14.43, 22.61, 24.27, 11.88, 15.367, 10.8 and 11.72 (mg/Kg soil), respectively which are higher than the control (Figure 3). While S6, S7, S10 and S12 have Ni concentration lower than the control 1.93, 1.06, 1.1 and 0 (mg/Kg soil) respectively. Samples 6, 7, 10 and 12 contain high sand, so the heavy metals could be leached into the lower layers of the soil. Major concern for the impact and distribution of nickel in soils arises apparently from the role of soil as an ultimate sink for heavy metals and the consequence transfer through the food- chain to crops, fruits and vegetables grown in contaminated soils and their possible consumption by animals or humans [15]. The samples from sandy soils have lower Nickel concentration indicate the leaching of Nickel where sandy soils have lower content of organic matter to pertain the heavy metals.

**Chromium (Cr):** As shown in Figure 2, the correlation between the Cr concentration and the absorption is very high  $R^2 = 0.998$ . The measured concentration of chromium in control sample was 10.2 mg/Kg soil and for samples S1, S2, S3, S4, S5, S9, S11, S13 and S14 were 46.49, 44.32, 35.32, 51.07, 48.97, 26.39, 25.79, 22.42 and 30.97 mg/Kg soil, respectively which is higher than the control. Chromium in soil is mostly present as insoluble carbonate and oxide of chromium; therefore, it will not be mobile in soil. The solubility of chromium in soil and its mobility may increase due to the formation of soluble complexes with organic matter in soil, with a lower soil pH potentially facilitating complexation [16]. Samples S6, S7, S10 and S12 Cr concentration was 1.27, .15, 3.07 and 0 mg/kg soil lower than the control, it is noticeable that these samples have high sand content where sand pertains no heavy metals on its surface (Figure 4).

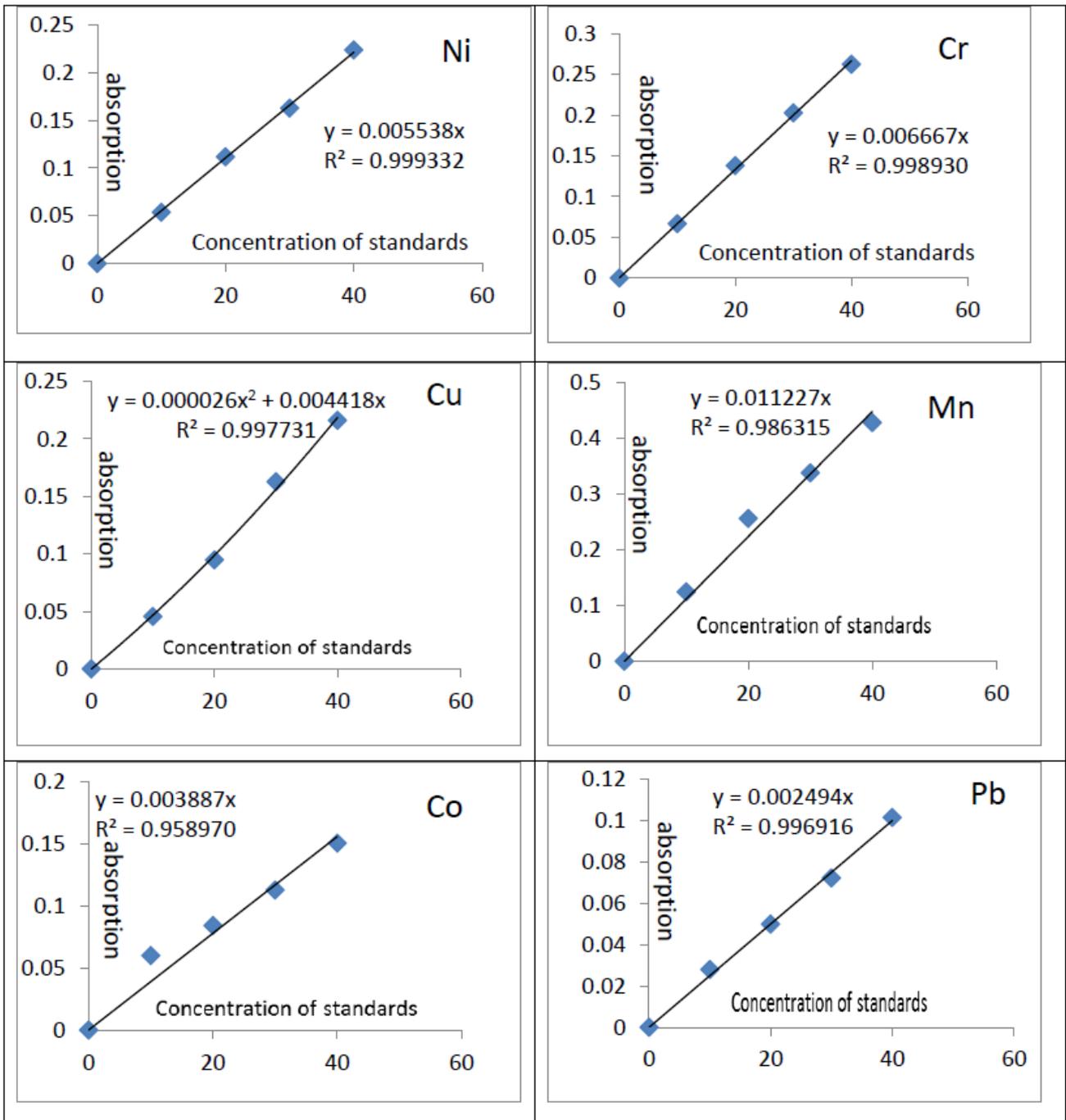


Figure 2. Calibration curve (concentration vs absorbance) for Ni, Cr, Cu, Mn, Co, Pb

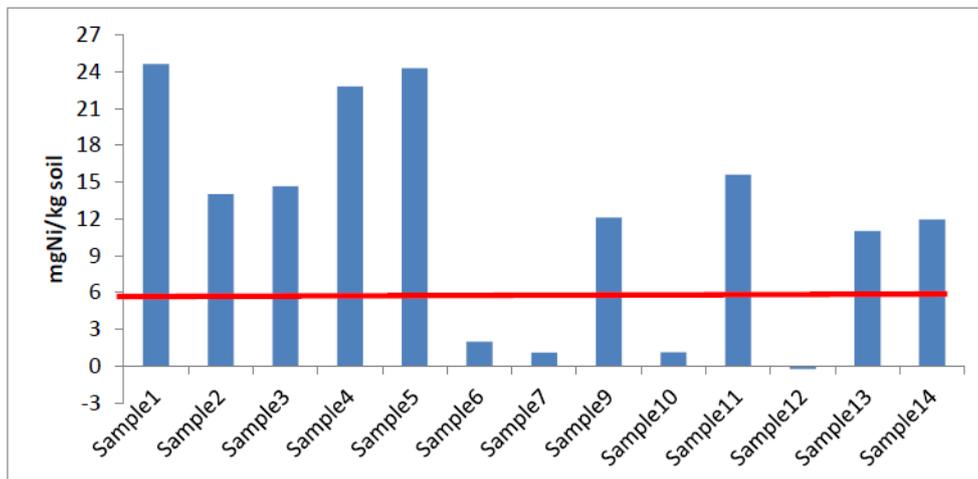


Figure 3. Nickel concentrations in various samples compared with the control

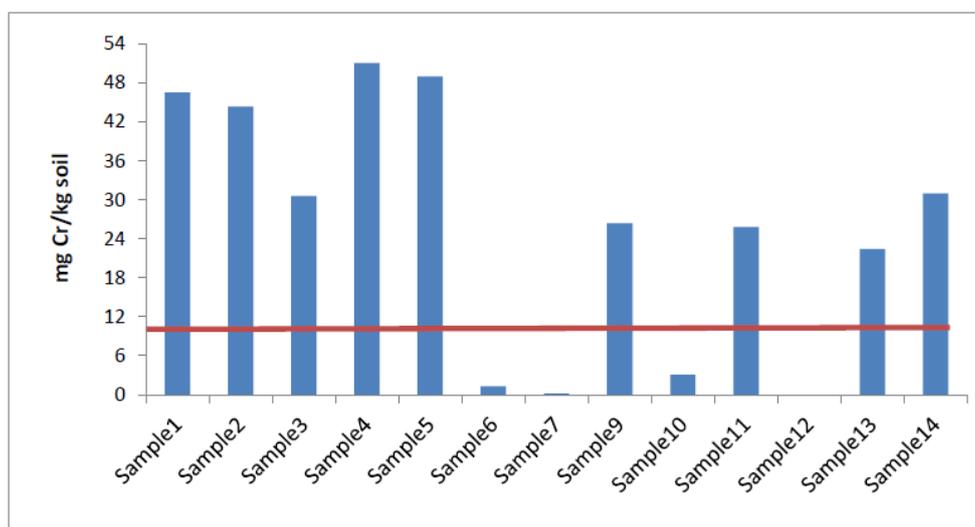


Figure 4. Chromium concentrations in various samples compared with the control

**Copper (Cu):** The measured concentration of Copper in control sample was 7.74 mg/Kg soil and for S1, S2, S3, S4, S5, S6, S7, S9, S10, S11, S13 and S14 were 43.35, 11.61, 63.57, 29.18, 13.31, 21.91, 10.58, 88.7, 8.59, 218.68, 17.09, 26.73 and 9.54 mg/kg soil, respectively (Figure 5) which are higher than the control. A substantial

amount of this copper can leach out of the soil during rain or irrigation. Copper movement is often associated with the movement of organic and inorganic constituents of soil [17]. As shown in Figure 2, the results obtained from the calibration curve at  $R^2 = 0.998$ .

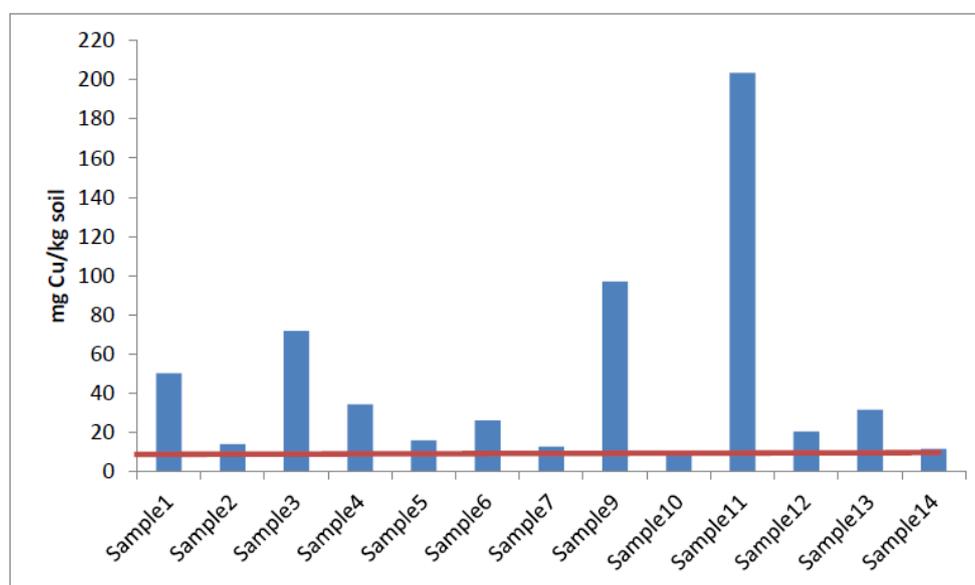


Figure 5. Copper concentrations in various samples compared with the control

**Manganese (Mn):** As shown in Figure 6, the measured concentration of Manganese control sample was 33.08 mg/Kg soil and for S1, S2, S3, S4, S5, S6, S9, S10, S11, S13 and S14 were 344.81, 238.35, 156.27, 200.32, 220.87, 65.91, 155.82, 43.68, 106.92, 41.9, 137.21 and 248.99 mg/kg soil, respectively which are higher than the control. Sample S7 was 14.83 (mg/kg soil) which is lower than the control. The correlation for Mn concentration and the absorbance is  $R^2 = 0.986$  (Figure 2). Manganese concentration in the collected samples was high compared to other heavy metals. Divalent manganese (Mn II) is the most soluble species of Mn in soil, whereas the solubility of Mn III and Mn IV are very low [18]. Mn oxides can form co-precipitates with iron (Fe) oxides, exhibiting amphoteric behavior. In addition, Mn interacts both with cations and anions in oxidation-reduction reactions involving Mn.

These reactions are influenced by a variety of physical, chemical and microbiological processes in the soil [19].

**Cobalt (Co):** The measured concentration of Cobalt control sample was 3.34 mg/kg soil and for S1, S2, S3, S4, S5, S6, S7, S9, S10, S11, S13 and S14 were 12.09, 11.70, 9.64, 16.20, 14.14, 6.68, 4.24, 11.83, 7.71, 13.89, 8.48, 11.84 and 17.23 mg/kg soil respectively, which is higher than the control (Figure 7). As shown in Figure 2, the calibration curve correlation is significant  $R^2 = 0.959$ . Cobalt deposited on soil is often strongly attached to soil particles and therefore would not travel very far into the ground. However, the form of the cobalt and the nature of the soil at a particular site will affect how far cobalt will penetrate into the soil. Both in soil and sediment, the amount of cobalt that is mobile will increase under more acidic conditions [20].

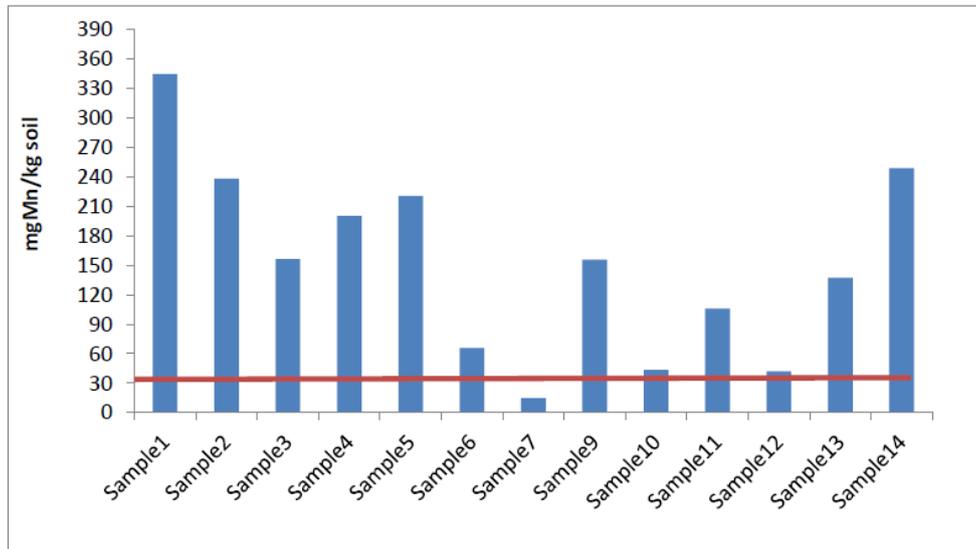


Figure 6. Manganese concentrations in various samples compared with the control

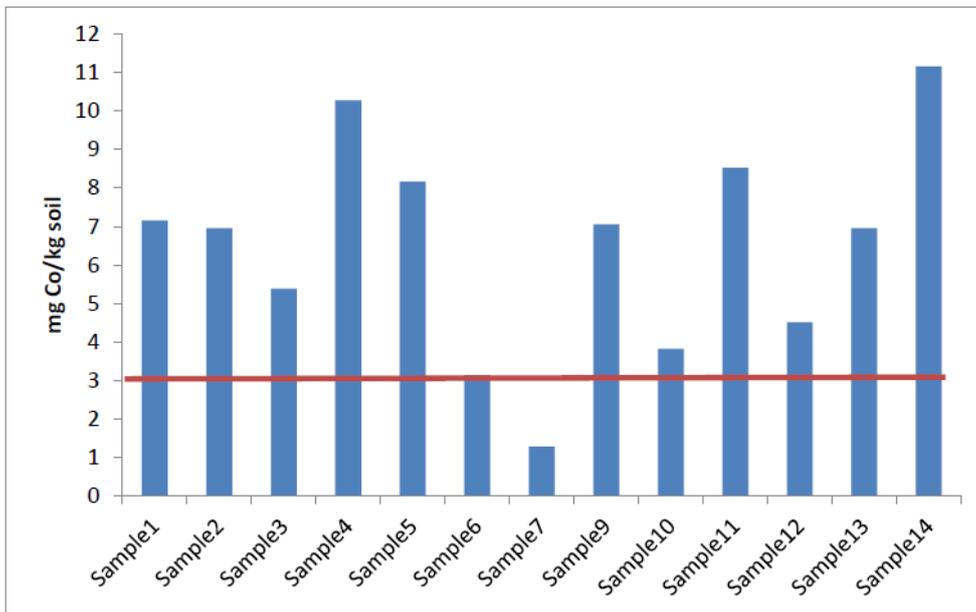


Figure 7. Cobalt concentrations in various samples compared with the control

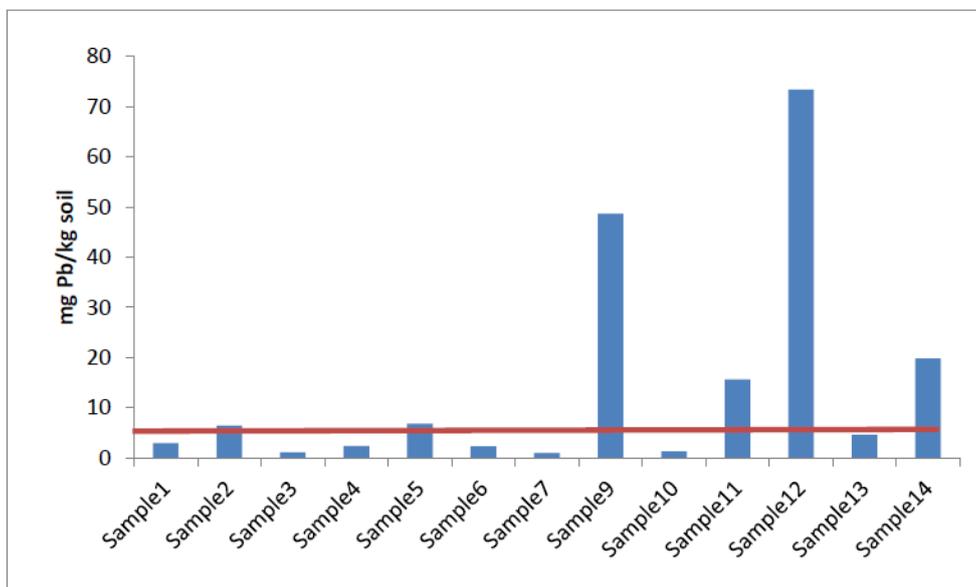


Figure 8. Lead concentrations in various samples compared with the control

**Lead (Pb):** The measured concentration of Lead control sample was 6.31 mg/kg soil and for S2, S5, S9, S11, S12 and S14 were 6.41, 6.82, 48.61, 15.63, 73.37 and 19.84 mg/kg soil, respectively (Figure 8) which are higher than the control. Samples S1, S3, S4, S6, S7, S10 and S13 were 2.98, 1.1, 2.4, 2.3, 1.00, 1.3, 4.61 mg/kg soil lower than the control. The nature of lead metal is volatile under high temperatures of bombs compared to other heavy metals and could be spread away from the center of the craters. The importance of heavy metals assessment in the soil plays essential role in food chain contamination and food safety. Soils polluted with heavy metals have become common across the globe due to increase in geologic and

anthropogenic activities. Plants growing on these soils show a reduction in growth, performance, quality and yield. Moreover it accumulates the toxic metals affecting the human health [21,22].

A study conducted by the New Weapons Committee Research Group in Italy [23] concluded that, the 2009 Israeli military activities in Gaza Strip, left high concentrations of toxic metals in the soil (Table 3). The results of the analysis of metal quantification by ICP/MS a type of mass spectrometry that is highly sensitive and capable of the determination of a range of metals and several non-metals) showed a presence, higher than the expected average quantity.

**Table 3. Heavy metals in the soil from 170 locations in Beit Hanoun, Jabalia Camp, Tufah and Gaza city [23]**

Element	Result	Effects on human health
Tungsten	Higher (20_42) expected average level in the soil	Genotoxic, Fetotoxic breathing and neurological pathologies
mercury	Higher (8_16) maximum level registered in 2003	a cancer- Fetotoxicity in animals
Molybdenum	Higher (25_300) the average levels in the soil	effects on spermatogenesis
Cadmium	7.3 times the average level	carcinogen
Cobalt	5 times the expected average level in the soil	mutagenic effects DNA breakage
Nickel, manganese	levels two times higher than the average	carcinogenic

Those metals can cause tumors and fertility problems, and cause serious effects on newly born babies, like deformities and genetic pathologies [24]. The metals are in particular tungsten, mercury, molybdenum, cadmium and cobalt. Significant amounts of tungsten (between 20 and 42 times the expected average level in the soil). Mercury (between 8 and 16 times higher than the expected average level in the soil (0.02- 0.41 mg/kg soil). Molybdenum is a rare element in the soil, has been found at high concentrations in all the examined craters. The amounts found range from 0.1 to 12 mg/kg soil, which means that they are between 25 and 3000 times higher than the average levels in the soil (0.004 mg/kg soil). Cadmium is an element normally present in low concentrations in the soil of Gaza (0.093 mg/kg soil).

The study has detected a high amount of cadmium up to 7.3 times the average level. Cobalt was found in craters with amounts reaching 26.2 mg/kg soil, about 5 times the expected average level in the soil (5.1 mg/kg soil). Nickel, manganese, copper and zinc were found in one of the craters with levels approximately two times higher than the average 4-55 mg/kg soil, 80-1300 mg/kg soil and 6-80 mg/kg soil, respectively. Results are summarized in Table 3 show the potential health impact in human beings.

## 4. Conclusion

Gaza Strip is high population density around 1.8 million inhabitants live in 365 km<sup>2</sup>, around 40% of the land is cultivated with vegetables and fruit trees. Three wars occurred within six years leading to the destruction of infrastructure and razing and change the physical, chemical and biological characteristics of the agricultural lands. The damage is not limited to destruction only, but to long term pollution of the agricultural lands which characterized by its light texture. The high sand content of the soil pertains no toxic metals in the upper layer, but there is a risk of toxic elements leaching to the groundwater. Research facilities and logistics are not

available to the research teams, the environmental effects of wars are limited to the researchers observations and the literature from similar areas. This research is the first attempt to investigate some of the environmental impacts especially in the agricultural lands as priority to prevent food chain contamination. Some other potential pollutions are not really investigated such as radioactive materials and inorganic pollutants from munitions source. It is highly recommend to start planned program with full capacity and logistics constitutes from the research institutions national and international levels and relevant governmental institution to investigate and mitigate the potential risk of war environmental impacts.

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