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Heavy Metals Contamination of Soils and Plants at E-waste Burning Site in Idhna in Hebron Governorate, Palestine.

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To my true source of hope, to the people who keep my going through struggles, to reason of what I become today, my parents.

To my lovely brothers and sisters, your encouragement and continuous support are only matched by your big hearts and pure souls.

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List of Abbreviations

Al	Aluminum
As	Arsenic
Cd	Cadmium
Co	Cobalt
Cr	Chromium
Cu	Copper
EC	Electrical conductivity
EDTA	Ethylenediaminetetraacetic acid
EPA	Environmental Protection Agency
E-waste	Electronic waste
FAO	Food Agriculture Organization
Fe	Iron
Hg	Mercury
LECAs	Light expanded clay aggregates
Mn	Manganese
Mo	Molybdenum
Ni	Nickel
OM	Organic matter
Pb	Lead
PCBs	Polychlorinated biphenyls
POPs	Persistent organic pollutants
TF	Transfer factor

VOCs	Volatile organic compounds
WHO	World Health Organization
Zn	Zinc

Abstract

Electronic waste (E-waste) is a global environmental issue, which is threatening wildlife, human health and the environment. Idhna village is located in Hebron governorate and received about 200-500 tones daily of E-waste. All of this amount is burning in different and random site at this village to extract of worthy and valuable metals. Therefore, continuous release of several contaminants i.e heavy metals and PCB to surrounding environment form an essential need for investigation of soil pollution load, so this study aims to analyze heavy metals as a key step for determination of their concentrations of soils and plants and their distribution and potential mobility in contaminated site.

Soil at burning area and the surrounding agricultural lands has analyzed to determine its heavy metals level, in addition to analysis of their level in grown plants at each area. The results showed that, all soil samples that collected from Idhna were highly contaminated with Cu, Pb, Ni and Zn, and burning area had the highest level at its center with decreasing content in relation to its distance from it.

The mean concentration of Cu, Pb, Zn and Ni at burning area soil's were 10392.860, 1892.150, 2503.170 and 699.170 ppm, respectively and it's too high in comparison to control. The content of wild plants that grown there of Cu, Zn, Ni and Fe were 802.830, 334.906, 2981.554 and 2573.301 ppm which greater than 10.834, 125.937, 2066.695 and 517.402 ppm, respectively in plants at control area.

The high pollution load of heavy metals at the studied site and their high accumulation in plant shoots showed urgent need for remediation, so this study also aims to remediate this site by most protective amendments. Light expanded clay aggregates (LECA) and clay particles called locally “Huar” were used to reduce Cu and Pd bioavailability in contaminated soil. The results show that, both adsorbents significantly ($\alpha = 0.05$) reduce bioavailable Cu and Pb in soil in comparison to control, and Pb had the highest adsorption affinity than Cu. The percentage of Cu and Pb reduction based on control for Huar were 43.9 and 80.9 %, respectively.

Keywords: Heavy metals, Electronic waste, Soil, Plant, Contamination, Characterization, Remediation.

Introduction

The third industrial revolution which is also known with digital revolution, analog electronic and mechanical devices have developed to the digital devices that use nowadays. However, while the digital revolution has the power to change the world positively, these technologies threaten environment negatively. For example, due to rapid acceleration in technology, the life of electronic devices became short due to the poor-quality devices that produced by the commercial electronics companies which are focusing on the economic side regardless of the quality of electronic devices (Borisenko, 2018).

Moreover, people want to keep up the acceleration of technology, as a result of that people replace their electronic things i.e. laptops, printers, DVD player, TVs, tablet, smartphones, headphones, batteries, air conditioners, refrigerators and other household appliances from time to time, whether from breakdown, slow-down, or just to follow the fashion of a newer model. Consequentially, rejected broken or old model electronic devices produce large quantities of electronic waste, approximately more than 20-50 million tons of electronic waste annually is generated around the world (Perkins, Drisse et al., 2014).

Electronic waste which is also known as E-waste is a global environmental issue, which is threatening wildlife, human health and the environment. Nowadays, most of the countries worldwide used burning method of the E-waste to get the copper and other precious metals, which can be released heavy metals, acids, alkaline materials and toxins substance that can be contaminated soil and in turn, can be reached to surface water by runoff and groundwater by leaching (Adesokan, Adie et al., 2016; Zhang, Ying-Xin et al., 2012; Dharini, Cynthia et al., 2017), moreover, can be polluted atmosphere with many toxic compounds (Dharini, Cynthia et al., 2017) . Unfortunately, most of E-waste generates in the world is sent to developing countries such as India and Nigeria where the E-waste is collected, and most of these wastes are burning to get the precious metals (Sthiannopkao and Wong, 2013).

In Palestine thousands tons of E-wastes are coming daily from surrounding and neighbor countries and most of these waste come from Isreal occupation, and transfer to E-waste recycling sites for dismantling or burning of their components at random, unsafe burning sites in order to get most of valuable materials for economic purposes (ARIJ, 2012).

The main environmental problem associated with burning E-waste is contamination of soil and atmosphere. The heavy metals from E-waste parts are eventually released to surrounding environment in high concentration and mainly accumulated in soil.

1. Literature Review

1.1. Electronic waste contamination (E-WASTE)

The consumption of electronic equipment is highly growing over the years, unfortunately, after a while the life of these equipment will end up, and will be released to environment as waste. These wastes contain some of valuable materials and many harmful substances like heavy metals, polychlorinated biphenyls (PCBs), volatile organic compounds (VOCs) and Persistent organic pollutants (POPs). For example, cathode ray tubes in televisions contain more than 400 g lead per Kg (Adesokan, Adie et al., 2016; Zhang, Ying-Xin, et al., 2012; Luo, Liu et al., 2011).

Disposal of E-waste is a major problem causing several threats to surrounding environment. Nowadays, E-wastes have been burning at unsafe, random burning sites in order to obtain valuable metals such as copper, aluminum and iron. And because E-wastes contain high quantity of heavy metals such as lead, cadmium, arsenic, nickel etc. so, during the extraction process which usually done by burns E-wastes, all of these heavy metals and other toxic materials will be released to soil and in turn, will contaminate soil and then surface and groundwater. Moreover, the fine particulate matter, VOC and the toxic gases will be polluted atmosphere (Dharini, Cynthia et al., 2017).

Palestinian environment suffers and threats negatively from the received E- waste from its neighbor, due to their improper disposal. Most of these wastes are randomly burning to extract some of precious materials without any controls or considerations of their adverse effects and impacts on the environment. In Palestine, there is little studies on the impact of E-waste on the environment. ARIJ, 2012 studied the general impact of E-waste on the environment and on human health at Idhna, Hebron as one major E-waste burning area in Hebron.

Adesokan, et al. (2016) reported that the analysis of soil samples at several E-waste recycling sites at Nigeria were contaminated with heavy metals and their concentrations follow this sequence Pb > Cu >> Cr > Ni >> Cd. Zhang, et al. (2015) found that, the major heavy metals, that were presented at E-waste disassembling site, were Cd, Cu, Pb and Zn. The content of these metals decreased toward deep soil layers. A study in heavy metals distribution at E-waste recycling sites, which included E-waste burning, showed that, Cu, Pb and Zn were the major highly concentrated metals occurred at sites. The measured concentrations of lead and copper ranged between 115 – 9623, 329 – 7106 ppm, respectively.

Luo, Liu et al. (2011) analysis of heavy metals levels at E-waste burning sites surrounding areas’ in south China showed high soil content of Cu, Pb, Zn and Cd at levels about 11140, 4500, 3690 and 17.1 ppm, respectively, and the collected wild plant shoots had high level of Cu, Pb and Zn at 94.3, 54.8 and 143 ppm, respectively, and these levels were greater than allowable limit for food in China. In general, the concentration of most analyzed heavy metals is higher in dry season than wet (Isimekhai, Garelick et al., 2017).

Olafisoye, Adefioye et al. (2013) studied heavy metals (Cu, CR, Pb, Zn and Ni) concentration and distribution around E-waste dumpsite in Nigeria as a function of samples distance and sampling time, and the results indicated that the decline of heavy metals concentration with distance from E-waste dumping site, and their higher levels higher in dry season.

1.2. Soil

Soil is an important abiotic resources for human to be used in agricultural or industrial activities. Moreover, soil protects the groundwater from pollution by prevent the movement of nutrients and other contaminants to groundwater, since the different layers of soil is acting as filters. Currently, soil suffered from several anthropogenic and natural environmental problems including erosion, salinity and soil pollution with organic and inorganic contaminants. One of the major soil concerns is soil contamination with heavy metals (Keesstra, Geissen et al., 2012; Sun, Zhou et al., 2010). Nowadays, the highly demand of foods, energy and raw materials due to rapidly increasing in population, causing huge contamination and pollution to natural resources. Since several pollutants and contaminants are discharged to the environment and contaminated soil with several ways. Improper disposal of industrial wastes, burning of waste, intensive use of pesticides and fertilizers and vehicles emissions are the major sources of soil contamination (Sun, Zhou et al., 2010).

1.3. Heavy metals

Heavy metals are defined as metals or metalloids that are toxic to living organisms and human being, it is including cadmium (Cd), arsenic (As), lead (Pb), mercury (Hg), chromium (Cr), copper (Cu), molybdenum (Mo), cobalt (Co) and nickel (Ni) (Li, Zhou et al., 2019; Vodyanitskii, 2016). Heavy metals classified into two groups based on their hazards according to general toxicological Russian GOST; the strongly hazardous metals include As, Cd, Hg, Pb, and Zn, whereas the moderately hazardous elements are Co, Ni, Mo, and Cr (Vodyanitskii, 2016). Heavy metals contaminated soil is a critical environmental issue.

Heavy metals end up in the soil from geogenic resources (natural) and anthropogenic processes (human activities). Natural sources include volcanic emissions and biogeochemical weathering of heavy metals containing minerals. Heavy metals are also released to soil as a result of human activities include metals mining, textile and tanning, the combustion of fossil fuels, wastewater treatment and natural fertilizers like livestock manures and municipal sewage sludge that used to supply plants with macro- and micro-nutrients requirements (Wuana and Okieimen, 2011).

Recently, burning E-waste is also another source for soil contamination. The heavy metals from E-waste parts are eventually released several toxic heavy metals to surrounding environment in high concentration (Adesokan, Adie et al., 2016; Zhang, Ying-Xin et al., 2012; Dharini, Cynthia et al., 2017). These heavy metals can be leached into the groundwater or be washed out of the soil surface into surface water, mainly to streams and rivers (Dharini, Cynthia et al., 2017). Table A.1 shown the major sources of some heavy metals.

Soil contamination with heavy metals has been investigating worldwide. Several researchers investigated soil contamination with heavy metals and determined their concentrations in studied areas. i.e. the urban soils in Shenyang, China, are contaminated with heavy metal, were collected and analyzed in seven districts in term of Pb, Cu, Cd and Zn. The results showed that the average concentrations of Pb, Cu, Cd and Zn were up to 75.29, 51.26, 0.42 and 140.02 ppm, respectively. These concentrations were exceeded the standard values (Sun, Zhou et al., 2010).

In Palestine, there is little studies on soil contamination with heavy metals and its concentrations. Swaileh, et. al (2001) were analyzed heavy metals (Cu, Cd, Pb and Zn) in roadside soil and plant along Nablus-Ramallah main road in the West Bank. The results of this study showed that, roadside soil sample contain higher concentration of measured heavy metals than those found in control sample. The average roadside soil concentration of Cu, Zn, Cd and Pb were: 23.8, 128.3, 0.45 and 149.9 μg/g, respectively, whereas control sample contents of these metals were 13.71, 85.14, 0.122 and 10.46 μg/g, respectively. Moreover, the average concentration of Cu, Zn, Cd and Pb metals in plant's leaves that were planted along Nablus-Ramallah main road were 5.20, 4.48, 0.55 and 2.19 μg/g, respectively. There is no little literature studies pollution load and the concentration of heavy metals in the typical E-waste burning areas of west bank.

1.3.1. Heavy metals mobility and toxicity

In soil, heavy metals existing in several oxidation state which is called speciation. Speciation is an important charactarestic of heavy metals. The most important factors that control metals speciation are pH and redox potential. Table 1.1 shown the species of some heavy metals. Speciation controls the mobility, toxicity and the adsorption affinity of heavy metals to be binded into soil particles including clay minerals, aluminum (Al) and iron (Fe) (hydr)oxides and organic matters.

Table 1.1: Oxidation state of some heavy metals

Heavy metal	Speciation	Soil pH for metal bioavailability	References
Pb	0, II, IV	Pb^{+4} <5.2 Pb^{+2} >6.4	Kushwaha, Hans et al., 2018 Ashworth and Alloway, 2008
Cr	III, VI	Cr^{+6} leachability increase with pH Cr^{+3} solubility decrease with pH (<5.5 soluble)	Wuana and Okieimen, 2011
As	-III, 0, III, V	As^{+5} < 2.3 As^{+3} > 9	Mello, Roy, et al., 2006; Yaghi, 2015
Cd	II	4.5 - 5.5	Mulligan, Yong et al., 2001
Cu	0, I, II	Highly at 5.5	Wuana and Okieimen, 2011
Hg	0, II	No general trend Optimum at 5&11	
Ni	II, III	Low pH	Mulligan, Yong et al., 2001
Zn	II	Low pH	Wuana and Okieimen, 2011

For healthy plant growth, macronutrients (nitrogen N, phosphorus P and potassium K) and micronutrients (Cu, Fe, Mn, Mo, Ni, and Zn) are required. Due to huge population growth and their remarkable huge need of food for sustainability, so agricultural fertilizers and pesticides are used in large amounts, which are sources of heavy metals accumulation in soil. Healthy soil should contain heavy metals below intervention values that have developed by Department of Petroleum Resources as shown in table 3, above these values soil is threatened with serious damage. Target values are also developed to indicate standard soil quality essential for sustainability (Wuana and Okieimen, 2011).

Heavy metals in soil causes several serious environmental threats. They are non-biodegradable and accumulated in soil and food chain for long period. Continuous addition and release of heavy metals to the soil results in reduction of soil capacity to retain heavy metals, that causes release of heavy metals to soil solution available for plant uptake (Sharma, Agrawal et al., 2007). Plants can accumulate them in their edible parts such as roots, stems and leaves. Finally, it causes serious threat to human beings through food chains (Li, Zhou et al., 2019; Swaileh, Rabay'a et al., 2001; Zhang, Wang et al., 2013).

Heavy metals present in soil at several fraction: mobile; exchangeable; bound to carbonates; bound to organic matter; bound to Fe, Al and Mn and residual (Adesokan, Adie et al., 2016). The weakly adsorbed fraction of heavy metal is called exchangeable fraction, and it can be released by ionic exchange process. The fraction that bounded to carbonate group is precipitated or co-precipitated with carbonate, and it can release by change of pH or through ionic exchange. Iron, aluminum and manganese oxides can adsorb heavy metals at the adsorption site on their surface area. Organic- bound fraction is associated with organic materials present in soil through complexation or bioaccumulation process. Residual fraction is stable and strongly adsorbed within the structure of soil minerals (Ashraf, Maah et al. 2012; Peng, Song et al., 2009).

For example, Lead (Pb) can occur in soil at several forms such as Pb-hydroxy complexes and Pb^{+2}. Both forms consider the most stable form of lead contamination in soil, however, it can be competing some essential macro-nutrients including calcium and potassium in soil particles sites., Pb^{+2} is the most abundant stable form mainly as ionic compounds. Whereas Pb^{+4} which is strong oxidants is formed in strong oxidation conditions and mainly form covalent compounds (Mulligan, Yong et al., 2001; Wuana and Okieimen, 2011). Lead can accumulate in body organ and cause adverse effect to kidneys, central nervous system and brain poison which leads to death. In general, plants don't take up lead in large quantities from contaminated soil, but at high concentration, lead-dust deposition at plant forms the risk accumulation, and affects plant and microorganisms growth which includes cell division, root enlargement and chlorophyll production (Wuana and Okieimen, 2011; Kushwaha, Hans et al., 2018). The probability of occurrence of other forms decline respectively: bound to organic matter, exchangeable- weakly adsorbed metals, bound to Fe-Mn oxides and bound to carbonates (Adesokan, Adie et al., 2016), its solubility in soil increases at pH less than 5.2 (Kushwaha, Hans et al., 2018).

Chromium (Cr) can be released from electroplating and tanning processes. The available chromium form in contaminated sites depends on pH and environmental conditions. Cr^{+6} is the common form that can be found. Cr^{+3} may occur in soil by reduction of Cr^{+6} by soil organic matter and iron Fe^{2+} under anaerobic conditions, and it is the dominant at pH below 4. Under alkaline condition, Cr^{+3} mobility decreased due to its adsorption to clay particles or iron oxide, also at high pH, its solubility decline due to chromium hydroxide formation (Wuana and Okieimen, 2011).

Cr^{+6} is the toxic form of Cr which can cause irritation of the skin, liver diseases and lung cancer (Li, Zhou et al., 2019). The leachability of soluble Cr $^{+6}$ increased as soil pH increases, and it is precipitated in the presence of metal cations such as barium Ba^{2+} accumulation (Wuana and Okieimen, 2011), and it is mainly present in exchangeable phase, it's weakly adsorbed and can be released to the environment by ion exchange process. Cr^{+3} is strongly adsorbed by negative-charge soil surfaces under alkaline and slightly acidic soil. In general, Cr has high potential mobility (Ashraf, Maah et al., 2012; Choppala, Bolan et al., 2010).

Arsenic (As) is a natural element occurs in soil from volcanic emission and weathering of parent materials that contain arsenic at average concentration of 1- 40 ppm, and it can also be released from human activities including mining, combustion of fossil fuels and intensive use of pesticides. Its mobility in soil mainly depends on soil content of iron and aluminum hydr (oxide) which As mainly binds with iron, aluminum and manganese oxides, in addition to minor dependence on presence of organic matters. As^{+3} is more mobile than As^{+5} due to its high dissociation constant and dissolution of iron oxide, which As binding with it, under reduction conditions. Arsenic mobility depends on its speciation which affected by soil pH (Mello, Roy et al., 2006; Yaghi, 2015; Cai, Cabrera et al., 2002, Yaghi and Hartikainen, 2018).

Cadmium (Cd) is one of heavy metals that has no any known biological function. It is used as a pigment of electronic compounds, or in Lead/ Cadmium batteries as a rechargeable source. Cd^{+2} can release from refined petroleum products and fertilizers, and its mobility increases as soil pH decreases and plant uptakes of Cd takes place. Cd^{+2} is soluble form but can form bounds with organics or oxides. Cd affects human enzymes and can cause kidney diseases, lung and prostate cancer due to its chronic accumulation (Mulligan, Yong et al., 2001; Wuana and Okieimen, 2011; Li, Zhou et al., 2019).

Copper (Cu) is an important micronutrient for growth of plants and animals. Cu is needed for plants' diseases resistance and seed production. High concentration of Cu in soil affects plant growth, causes reduction of crop yield and threats human health through food chain due to plant uptake of Cu. Copper in high concentration causes kidney damage and stomach irritation. Ashworth and Alloway (2008) found Cu has U-curve for solubility with high mobility at high and low pH and minimum solubility at intermediate pH as shown in figure 1.1. Copper is highly soluble at pH 5.5 (Wuana and Okieimen, 2011). It mainly occurs bounded with Fe, Al and Mn oxides or carbonates or organic matter that available in soil (Adesokan, Adie et al., 2016).

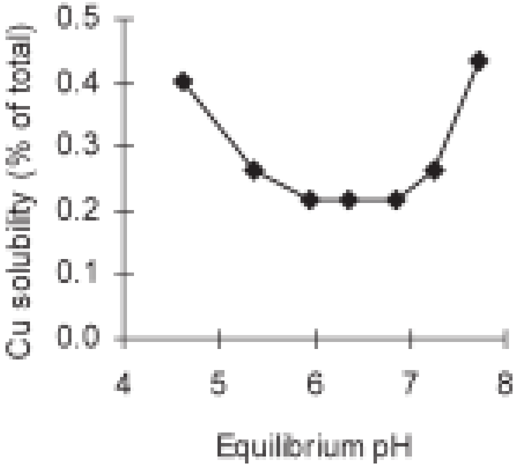


Figure 1.1: The effect of soil pH on copper solubility (reprint from Ashworth and Alloway (2008))

Nickel (Ni) released to soil from mining and metal plating industry and fossil fuel combustion. Ni that is released highly to soil will immobilized and adsorbed on soil particles, however, at low pH, Ni in soil exist as nickelous ion (Ni^{+2}) and becomes more mobile and leaches down. Stable precipitates of nickelous hydroxide ($Ni(OH)_2$) exit at neutral to slightly alkaline condition, and it is dissolved in acid conditions to form Ni^{+3}. Nickel oxides are unstable at high pH. Nickel is unknown to accumulate and uptake by plants (Wuana and Okieimen, 2011).

Zinc (Zn) occurs naturally in soil and its important as micronutrient for plants, but its concentration can be increased by its release from mining and waste combustion. At low pH, Zn^{+2} is the available form and it's mobile, whilst, zinc sulfide can precipitate under alkaline, anoxic condition (Mulligan, Yong et al., 2001). High level of Zn in soil has negative impact on activity of microorganisms and earthworms, and this will lead to delay of organic matter degradation. Traces of zinc is needed for human health, where high concentration can lead to gastrointestinal irritation, kidney and liver failure accumulation (Wuana and Okieimen, 2011; Li, Zhou et al., 2019).

Heavy metals mobility and toxicity is varied among soil type and affected by several soil characteristics, such as soil pH, organic matter contents, content of calcium carbonate and iron, aluminum and manganese oxides (Zeng, Ali et al., 2011).

1.3.1.1. Soil pH

The most important propriety that affects heavy metal speciation and mobility is soil pH. In general, heavy metals mobility and its bio-accessibility and bio-availability for plant uptake increase as soil pH decreases, and that is mainly found for Cd, Pb and Zn (Zeng, Ali et al., 2011). For Cd, Pb, and Cu, soil particles adsorption is highly depending on soil pH as a dominant property. Soil adsorption of heavy metals generally increases with increase of pH, since metals competition with hydrogen ions for binding and forming covalent bonds with oxygen on surface of soil particles deceases and leads to form precipitate of metal hydroxide (Basta, Pantone et al., 1993; Elliott, Liberati, et al., 1986). Gomes, Fontes et. (2001) found that, for heavy metals adsorption in eight different Brazilian soils, Cu, Cr and Pb have strong selectivity and competitive ability to adsorb in comparison to Cd, Zn and Ni.

In general, heavy metals mobility decreases as soil pH increases, due to cation exchange capacity (high the adsorption affinity between soil particles and heavy metals). At high pH, competition between dissolved metals and H^+ ions significantly decline, so cation exchange to negative charge clay–soil particles increases through adsorption, that leads to reduction of heavy metals mobility (Ashworth and Alloway, 2008; De, Fontes et al. 2001; Peng, Song et al., 2009).

Copper, iron, manganese, nickel, and zinc are the small molecules that are mainly adsorbed to soil particles at high pH when H^+ ions decline. These elements are available within soil at pH of 5-7, and their mobility and plant uptake decline (McCauley, Jones et al. 2009).

Ashworth and Alloway (2008) found that, Cd, Ni and Zn solubility declined with increasing pH above 6.4. Pb has high solubility at high pH, and Cu has U-curve for solubility with high mobility at high and low pH and minimum solubility at intermediate pH (Fig 1.1).

For cadmium, it’s very mobile at pH ranges 4.5 to 5.5. However, it’s immobile at pH above 7.5 (Mulligan, Yong et al., 2001). Chromium mobility dependence on pH varies with its speciation, Hexavalent chromium $Cr^{+6}$is not significantly depends on soil pH and organic matters content as it affects with iron and aluminum soil contents which play important role in its adsorption, and it is weakly adsorbed under alkaline condition. Cr^{+6} is more mobile than Cr^{+3}. Trivalent chromium mobility is highly depending on pH, as soil pH increases, available negative-charged surfaces on soil increase and its availability and mobility declines (Choppala, Bolan et al., 2010).

Arsenic mobility mainly depends on soil content of iron hydr(oxide) which As binds with it, As^{+3} is more mobile than As^{+5}. Arsenic speciation depends on soil pH and redox potential. As^{+5} occurs under extremely acidic, well oxidized conditions at pH less than 2.3 as H_3AsO_4, and As^{+3} occurs under alkaline, reduced environment at pH higher than 9 as H_3AsO_3, and its oxyanion is not commonly adsorbed to negative-charged soil surfaces (Mello, Roy et al., 2006; Yaghi, 2015; Cai, Cabrera et al., 2002).

1.3.1.2. Organic matter contents

Organic matter is important to provide essential nutrient to soil and to prevent pH change. It is coming from biodegradation of living organism residues, and the available organic matter is a net amount of the accumulated material from decomposed plant, animal residues and microbial products (McCauley, Jones et al., 2009).

Soil organic matter contains phenols and carboxylic acid functioning groups that form complexes with heavy metals, but readily degraded fraction of organic matter form soluble complex with these metal and that increased their solubility in soil after their degradation by oxidation (Ashworth and Alloway, 2008; Ashraf, Maah et al., 2012).

Basta, Pantone et al. (1993) and Ashworth and Alloway (2008) found that, Cd and Pb adsorption by soil is affected by soil organic matter contents (OM), these heavy metals adsorbed by organic matter due to their high affinity to form complex with humic organic matters than other soil particles and their soil adsorption is declined as organic matter contents decrease. However, this bounding is relatively stable, but can be destroying under strong oxidizing conditions (Ashraf, Maah et al. 2012).

1.3.1.3. Iron, aluminum and manganese oxides

Iron (Fe), aluminum (Al) and manganese (Mn) oxide contents in soil affect the availability of heavy metals. Iron oxide capable to adsorb and link with heavy metals, and that decreases their mobility. Iron oxide adsorption affinity varies from one heavy metals to other (Ashworth and Alloway, 2008). Iron, mainly Fe^{+3}, aluminum, Al and manganese, Mn^{+4} -oxides may be available as a cement, they are superior adsorbents with large surface areas and these oxides have O_2^-, OH^- or H_2O functional groups which contribute in exchange and binding with available heavy metals in soil. However, atbasic media or at anoxic conditions Fe^{3+} and Mn^{+4} will be reduced to Fe^{2+} and Mn^{3+} respectively, this reaction pattern enders Fe and Mn soluble and releases heavy metals retained by them to soil solution. In contrast to Fe and Mn, Al oxide is not redox sensitive, thus will retain heavy metals at different redox conditions (Yaghi, 2015). Among heavy metals, Zn is mostly present at bounding phase to oxides (Ashraf, Maah et al., 2012).

Bradl, 2004 reported that, lead had the highest adsorption affinity by Mn oxides in comparison with other studied metals- Co, Cu, Mn, Ni, and Zn. Chromium adsorbed on the surface of these oxides, hexavalent chromium can efficiently adsorb on hydroxyl groups which present on the surfaces of Fe, Al and Mn oxides at low pH, whereas trivalent chromium adsorbed by Fe and Mn oxides with increase of pH.

1.3.1.4. Clay minerals

Clay minerals is another factor that play an important role in soil physical and chemical properties, these usually come from chemical weathering of parent rocks. These minerals have tetrahedron and / or octahedron structures, the tetrahedron sheet is formed by coordination of silicon ions with oxygen on four sides, whereas octahedron is the coordination of aluminum, iron, or other cation as magnesium or manganese ions with oxygen/ hydroxyl ions on eight sides, and these sheets connected to each other in certain proportion and coordination to provide different clay soil types.

Because the center atom in clay is either Al, or Fe, heavy metals that exists as oxyanion, hydroxide or oxide are strongly binding to clay by ligand exchange mechanisms, which occur at neutral, positive and/ or negative surface site. Ligand exchange mechanisms, which is firstly describe by Hingston, and it's a process of binding of heavy metals to clay minerals through replacement of heavy metals- oxyanion, hydroxide or oxide with H_2O or OH^- groups on the clay surface, then formation of complexes with these metals. Ligand exchange is more dominant under acidic condition, due to high formation and presence of H_2O groups, which can easily replace by heavy metals than OH^- group (Yaghi, 2015).

1.4. Remediation of heavy metal contaminated soil

There are intensive efforts toward remediation of contaminated soil with heavy metals. Remediation and protection of contaminated soil can be achieved through implementation of appropriate techniques. Some techniques are gentile and provide safe use of remediated soil, whereas, other are harsh and prevent subsequent hazards to plant and human without probable use of soil.

Remediation techniques

Remediation of heavy metal contaminated soil is important and urgent to manage and reduce heavy metal soil content. Remediation technologies are mainly categorized into in-situ and ex-situ technology. In in-situ soil remediation, the contaminated soil is treated in their original site without removal to anyplace. However, the ex-situ remediation is conducted by removal and transfer of soil to other place for treatment (Wuana and Okieimen, 2011; Li, Zhou et al., 2019). For both techniques several approaches used to ameliorate contaminated soil as shown in table 1.2; including physical, bioremediation and chemical remediation (Zhang, Wang et al., 2013). The selection of most suitable one is based on its financial and commercial availability, its applicability and acceptance, in addition to site characteristics and types and amount of pollutants (Li, Zhou et al., 2019; Wuana and Okieimen, 2011).

Physical remediation aims at stopping the continuous deterioration of soil by use of surface capping; isolation and thermal treatment. Surface capping involves soil replacement with uncontaminated soil, where barriers are used for prevention of pollutant dispersion through isolation process. Thermal treatment is applied by heating soil, and it is based on pollutants’ volatility (Li, Zhou et al., 2019).

Bioremediations are conducted through biological mechanisms by assist of plants and microorganisms, which work to destroy, reduce or immobilize of pollutants. Plants are used to remove or stabilize pollutant, that called phytoremediation. As well, microorganisms transform and remove contaminants, however, this method it is not practical for heavy metal remediation (Li, Zhou et al., 2019).

In Palestine, Alhousani (2012) implemented phytoremediation in heavy metal contaminated site with Cr, Mn and Zn, he used Corn, *Zea mays* and tobacco, *Nicotianatabacum* for bioaccumulation of these metals. He found that, leaves of these used plants highly accumulated the detected heavy metals in comparison to other plant parts. Cr was effectively adsorbed by corn, whereas Mn was highly adsorbed by Tobacco and for Zn, both plants gave the same efficiency in Zn accumulation.

Chemical remediation uses chemical reagents and reactions for treatment of contaminated soil. It is involved pollutant stabilization/ solidification for immobilization; vitrification and soil washing and flushing for contaminant extraction (Li, Zhou et al., 2019; Wuana and Okieimen, 2011).

Soil flushing and washing are applied to remove pollutants from soil through desorption of pollutants by use of washing agent. There are several washing solutions can be used such as water and organic acids. Ethylenediaminetetraacetic acid (EDTA) for example is the most efficient one, due to its high efficiency, low cost, low biodegradability and low adverse effects on soil microorganisms (Li, Zhou et al., 2019). Vitrification is solidification/ stabilization process with thermal energy for heating of contaminated soil and added glass forming material at 1400–2000°C. It's highly efficient, but it's costly and limited to small area of soil (Mulligan, Yong et al., 2001; Li, Zhou et al., 2019).

Moreover, there are intensive efforts toward remediation of contaminated soil with heavy metals through adsorption due to its low cost, easy and fast implementation with high efficiency in reduction of heavy metals bioavailability under regular monitoring of soil conditions mainly soil pH (Li, Zhou et al., 2019).

Adsorption is one of major principle of heavy metals sorption mechanisms along surface precipitation and fixation or absorption processes. Surface precipitation is the formation of new solid phase as metal- oxide, hydroxide, carbonate, phosphate or sulfide which precipitate onto soil. Fixation is a diffusion of heavy metals that adsorbed onto clay surface sites into lattice structure and fixed in pore spaces of clay minerals (Bradl, 2004).

Adsorption is an accumulation of matter at the solid phase and formation of complex by interaction between dissolved solute- adsorbate and functional group at surface of solid-adsorbent. Adsorption can be selective and irreversible reaction which called specific or chemical adsorption, or weak, less selective and reversible bound between heavy metals and negatively charged surfaces through exchanged with cation near the surface and that is physical adsorption. Chemical adsorption includes formation of inner sphere surface complex with soil functional groups (hydrous oxide minerals and organic matter) (Bradl, 2004).

Many efforts have been done to develop several soil amendments and adsorbents that are effectively stabilized heavy metals. Adsorbent materials can be natural like clay particles (i.e. Huar), lime, calcium carbonate, zeolite and plat straw, or man-made adsorbents like light expanded clay aggregates (LECA) and biochar.

Cruciferous rape, *Brassica napus L.* straw was used by several researcher as organic adsorbent. Yang, Wang et al. (2015) found that, cadmium (Cd) concentration and uptake in the shoot of cucumber were declined after application of rape straw at rate of 45% compared to control.

Biochar is an effective amendment that is a product of pyrolysis of biomass and it's rich in carbon, so it can enhance soil productivity in addition to soil remediation. It has a high cation exchange capacity, so high capacity to adsorb pollutants in soil. Biochar can immobilize and fix heavy metals through several mechanisms: cation exchange with its calcium (Ca), magnesium (Mg) and other divalent cations- monovalent cation exchange is negligible- that leads to co- precipitation and complexation with biochar oxides or humic matter; surface complexation of heavy metals with different functional groups such as free hydroxyl; physical adsorption and surface precipitation with phosphate and carbonate. Biochar can be reduced mobility of Cd, As, Pb, Cu, Zn and Cr. For example, biochar that derived from hardwood and produced at 450 °C can adsorb Cd and Zn (Zhang, Wang et al., 2013). Immobilization approaches are not practical for heavy metals that are not soluble like mercury and hexavalent chromium (Mulligan, Yong et al., 2001).

Huar (حور) is a natural adsorbent of clay particles that formed in soil and found in nature. LECA is man-made product from expansion of special type of expanded clay that has been shaped as sintered pellets under heating at high temperature of 1200 ^{o}C, which burning organic matter off and forcing pellets to expand and form honey combed of light weight, porous, non-biodegradable and non-combustible brown to black aggregates. LECA has negatively charged surface due to substitution of cations, and its main components are Si, Al and Fe at 66.7% as Si-oxide, 16.57% as Al-oxide and 2.46 % as Fe-oxide. Adsorption at the layer edges of LECA depends highly on soil pH (Malakootian and Hossaini, 2009).

Table 1.2: Application of available remediation techniques of heavy metal contamination soil

Technique	Target pollutant	Results	Notes	Reference
Metal extraction	Pb	EDTA were completely removed lead	Recovery can be achieved by addition of cationic or anionic precipitate under alkaline condition	Hong, Banerji et al., 1999
		The maximum removal of lead using EDTA, NTA, and water were 64.2, 19.1, and 5.8% respectively	The removal of lead was pH-dependent	Peters and Shem, 1992
Immobilization	Pb	Both red mud and lime decrease pb availability	In the first year red mud at 5% was the most efficient, but by year both amendments had the same effectivity. Addition of P with red mud or lime decreased Pb concentration	Gray, Dunham et al., 2006

Phytoremediation	Cd, Cu, Pb and Zn	Cadmium accumulation by vetiver, Chrysopogon zizanioides was 218 g/ha at a soil Cd concentration of 0.33 ppm	Approximately four croppings may be required to extract the excess Cd with vetiver	Chen, Zheng et al., 2000
Extraction-soil washing	Cd and Pb	Rhamnolipid biosurfactant removed 92% of Cd and 88% of Pb after 36 h	Doesn’t only removed the leachable or available forms	Juwarkar, Nair et al., 2007
		Tap water removed 2.7% of Cd and 9.8% of Pb	Removed freely available or weakly bound forms	
Extraction-soil washing	Cd and Zn	Saponin removal efficiency was 90-100% and 85-98% for Cd and Zn, respectively	Saponin is plant derived biosurfactant. Soil pH increased to 10.7, so the metals removed as hydroxide precipitate.	Hong, Tokunaga et al., 2002
Phytoremediation	As	Chinese brake fern, P. vittata accumulated 3280 - 4980 ppm As in their tissues		Jadia and Fulekar (2009)

Phytoremediation	Cu	Brachiaria decumbens accumulated Cu 70 and 585 ppm of dry mass shoots and roots, respectively	Evaluation was taken after 47 days of growth in greenhouse	Andreazza, Bortolon et al., 2013
Bioremediation	Cd	The removal efficiency of sulfate-reducing bacteria is 70% of exchangeable Cd and 45-60% of oxide bending form of Cd	Experimental evaluation was conducted for 33 days	Jiang and Fan, 2008

In-situ heavy metal immobilization and chemical amendments

Several soil amendments in-situ, such as adding biochar, zeolite, red mud, lime and crop straw such as cruciferous rape (*Brassica napus L*.) enhance heavy metals stabilization and immobilization, which reduce their accessibility and bioavailability and in turn, their toxicity based on soil physicochemical properties. these methods are costly effective and environmental amendments (Castaldi, Melis et al., 2009; Zhang, Wang et al., 2013; Yang, Wang et al., 2015).

For remediation of heavy metal contamination site, in-situ heavy metal immobilization has listed among several best technologies due to its economic and environmental sounds. Ex-situ immobilization can easily apply by mixing of amendments with transferred contaminated soil, but it’s produced large amounts of waste that require careful control and storage in special landfill. In-situ immobilization is an easy, inexpensive and immediate technique for a wide range of pollutants, but pollutants remain in soil and its mobility can change with alteration of surrounding environment (Wuana and Okieimen, 2011).

Heavy metals immobilization can be conducted through stabilization/ solidification processes. Solidification is an encapsulation of pollutants in solid matrix by use of chemicals such as cement, it’s fast in-situ and ex-situ remediation of highly contaminated soil but it’s costly. Stabilization is chemical reaction between contaminated soil and added reagents, as shown in table 1.3, that decline pollutants’ mobility and solubility. It’s easy to implement and provide effects rapidly. Since contaminants remain in soil, it’s required regular monitoring of soil conditions (Mulligan, Yong et al., 2001; Li, Zhou et al., 2019).

Immobilization technique uses organic or inorganic amendments to produce stable phase of the available pollutants and decrease their mobility through precipitation, complexation or sorption due to their high cation exchange capacity. They should have high sorption capacity, low water solubility and stability under various conditions (Wuana and Okieimen, 2011; Peng, Song et al., 2009).

Heavy metals fixation or immobilization depend on amounts and form of present metals, in addition to added amendment properties (Guo, Zhou et al., 2006).

There are several organic amendments used to fix and immobilize heavy metals and provide low level of nutrients, these include poultry and cattle manure that released from farm, and they are capable to immobilize Cu, Pb, Zn and Cd. In addition to rice hulls from rice processing and straw that immobilize Cd, Cr and Pb. Sawdust can effectively fixe Cd, Pb, Hg and Cu mainly due to polyhydroxy groups of tannin that form high content of sawdust.

This group plays important role in adsorption process and form a chelate when the ion exchange occurred (Wuana and Okieimen, 2011; Guo, Zhou et al., 2006).

Inorganic amendments such as lime is efficiently immobilized Cd, Cu, Ni, Pb and Zn, also fly ash that released from thermal power plant can be used for immobilization of Cd, Pb, Cu, Zn and Cr. The two last amendments contain pozzolanic materials, that consist of small spherical particles that enhanced heavy metal stabilization (Wuana and Okieimen, 2011), other amendments are shown in table 1.3.

Several organic and inorganic amendments had used by Yang, Wang et al., (2015) to compare and evaluate their efficiency in reduction of Cd mobility. Red mud, zeolite, corn straw and cruciferous rape straw were applied in pot experiment. For red mud, the stabilization of Cd related to Cd sorption by Al and Fe oxide which mainly present in red mud. For organic amendments- straw, Cd immobilized through formation of solid complex with organic straw, and rape straw is more efficient than corn, since volatile sulfur compound is the major component of rape, which provides higher adsorption capacity of Cd. Among these, red mud was the most efficient one in immobilizing Cd.

Castaldi, Santona et al. (2005) used zeolite, compost and calcium hydroxide to remediate contaminated soil with Pb, Cd and Zn. The results showed that, these amendments reduce heavy metals solubility and mobility. Plants uptake of heavy metals in amended soil are reduced, also plant growth and above- ground and root biomass are enhanced and increased in amended soil compared to non-amended one.

Table 1.3: The application of some available chemical amendments for heavy metals immobilization

Chemical amendment	Target pollutant	Added amount (%)	Results	Notes	Reference
Calcium carbonate	Cd	0.2; 0.4	Addition of calcium carbonate reduced yields of rice, where 0.2% steel sludge increased yield of rice grain, but the other amounts decreased it.	Furnace slag is most efficient in reduction of Cd uptake by the plants, may be due to its high content of silicon	Chen, Zheng et al., 2000
Steel sludge		0.2; 0.4; 0.6			
Furnace slag		0.2; 0.4; 0.6	Furnace slag had no significant effect on yields		
Composts From municipal wastes	Acidic contaminated soil with As, Cu, Pb and Zn		Reduced heavy metals concentration and raised soil pH and nutrient levels	pH monitoring must be taken to ensure correct pH (5–6) to sustain plant growth	Farrell and Jones, 2010

Compost from industrial eggshell	Pb and Zn		Pb and Zn mobility declined more than 95% due to increase of soil pH above 6	It's conducted in acidic contaminated soil	Soares, Quina et al., 2015
Lime **Activated carbon** **Clay** **Zeolite** **Sand** **Cement**	Pb	1:5, 1:10, 1:20, 1:40, 1:50, 1:75, and 1:100 amendment: soil ratios	Lime at 1: 20 ratio, immobilize 88% of Pb and 99% at 1: 15 cement to soil ratio	Activated carbon, clay, zeolite and sand are not very efficient	Alpaslan and Yukselen, 2002
Zeolite	Pd, Cd and Zn	10	The most efficient one for reducing plant uptake of Cd		Castaldi, Santona et al., 2005
Compost		10	Efficient for reduction of Pd and Zn uptake		
Calcium hydroxide		0.05			
Red mud	Cd	0.1	Red mud more efficient than zeolite	It's conducted in calcareous soils	Yang, Wang et al., 2015
Zeolite					
Straw (corn and rape straw)		0.5	Cruciferous rape straw more efficient in reduction of soluble Cd		

2. Objective

Little literature studies pollution load and the concentration of heavy metals in the typical E-waste burning areas of south west bank, Hebron. Therefore, this study aims to determine the pollution load in term of heavy metals in soil and plant at E-waste burning site, and to investigate their potential mobility and plant uptake of heavy metals at E-waste burning site. After that, implementation of most feasible remediation approach and evaluation of its potential to reduce heavy metals availability and mobility by use of financially effective and environmentally protective amendments.

The study targets the following specific objectives:

- Analyzing soil and plant samples collected from E-waste burning site to determine their heavy metals concentrations.
- Determining potential transfer of heavy metals from contaminated soil to edible plant parts.
- Reviewing the soil contamination of heavy metals remediation techniques and determining the most feasible technique to be implemented in Palestine.
- Implementation of most feasible and environmentally sound amendments.

3. Methodology

3.1. Study area

This study was conducted at burning sites in Idhna rural in Hebron governorate, Palestine, which is located 15 Km west to Hebron city as shown in figure 3.1. The average annual temperature is 19 ºC and the annual rainfall ranges between 410-440 mm (AREJ, 2012). The daily amount of E-waste that Idhna received is about 200-500 tones. For extraction of worthy metals, burning of these wastes is one of major process used (Khlaif and Qumsiyeh, 2017).

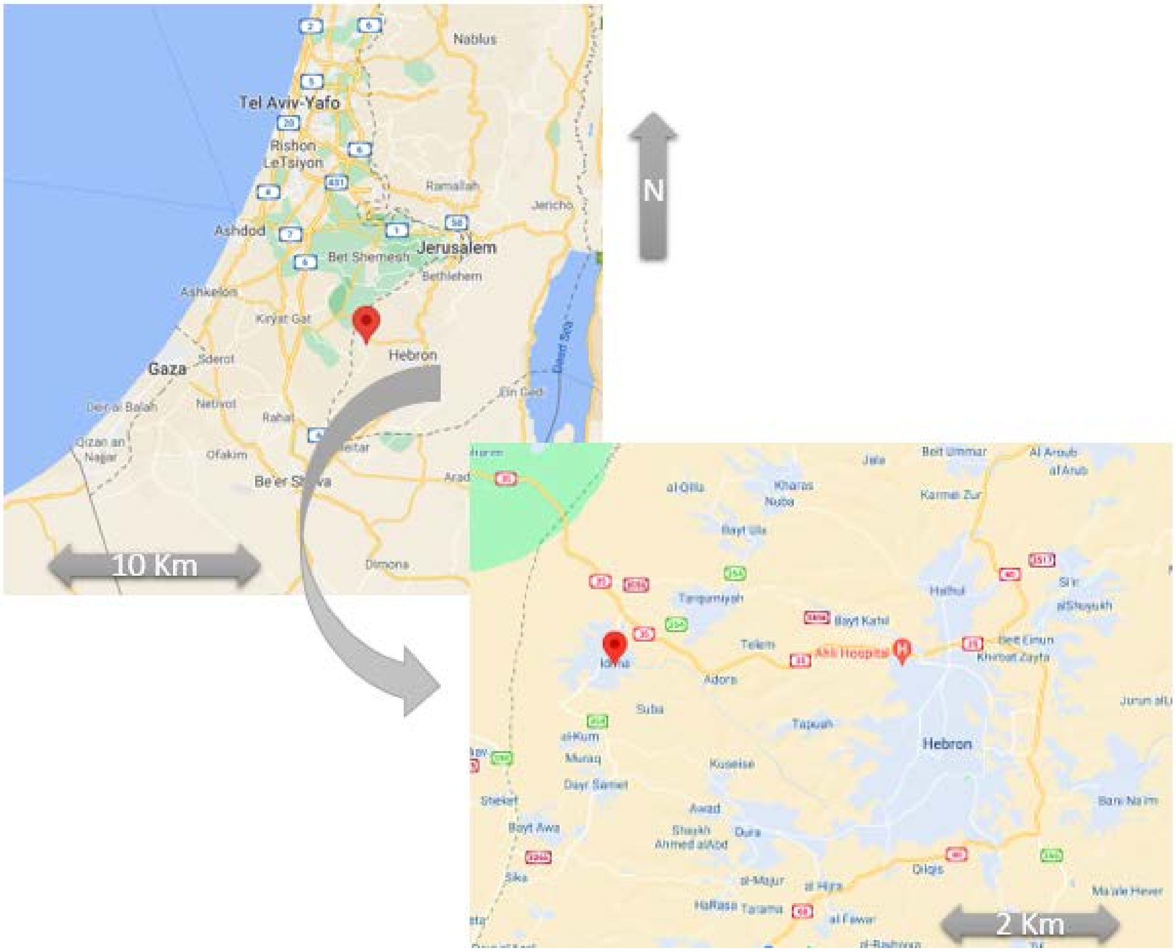


Figure 3.1: Map of Hebron and Idhna sampling site (Google Maps)

3.2. Soil and plant sampling

The burning site was selected for sampling in addition to control site (C). Burning site was northwest to Idhna center and stratified into three key areas: burning area (B); upward (U) and downward (D) burning areas as shown in figure 3.2. The control area (C1) is in Idhna and it’s more than 3 Km away from burning site and Idhna center whereas (C2) is located in Hebron city with more than 15 Km away from burning site.

Samples were collected at the end of February of 2019, soil samples from burning area were extracted till an average depth of 30 cm, by divided each core into 0-10 cm, 10-20 cm and 20-30 cm and subsequent subsample were collected to form composite sample. About 0.5 kg of soil samples were randomly collected from each point, and they include samples at burning center (B1), 2 m (B2) and 5 m (B3) away from B1 with 3 replicates. Soil samples from upward area was collected at 20 m (U1), 40 m (U2) and 100 m (U3) away from the center of burning site, moreover, soil samples from downward area were collected from 30 m (D1), 50 m (D2) and 80 m (D3) away from the center of burning site. Upward and downward composite samples collected at depth 0-20 cm. Scheme 3.2 shown the location of samples. Soil samples (n=51) were stored in marked plastic bags for further analysis.

Plants, that were growing at randomly selected sampling sites, were collected in paper bags (n=29) for analysis of their heavy metals content.

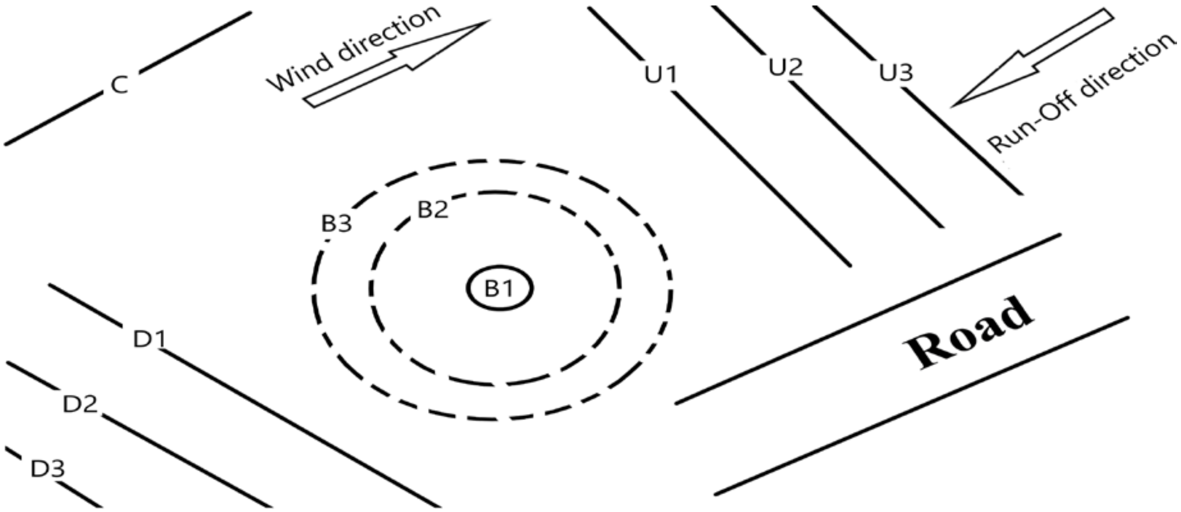


Figure 3.2: Scheme of sampling areas and the location of samples (prepared by author)

3.3. Soil physical and chemical analysis

Collected soil samples were air-dried for a week. After that soil samples were sieved through 2 mm sieve, then oven- dried at 105-110 ºC for 24 hours. Soil texture was analyzed by pipette method, which used hydrogen peroxide (25% H_2O_2, Sigma-Aldrich) to digest organic matter and sodium hexametaphosphate ($(NaPO_3)_6$) (Sigma-Aldrich) to separate soil particles. After that the percentages of sand, silt, and clay were determined. Soil bulk density was measured by use of paraffin wax which coated soil clods to determine its volume through buoyancy principle. Particle density was determined by use of graduated cylinder method (Estefan, Sommer, et al., 2013).

For pH and electrical conductivity (EC) measurements, (1: 2.5, soil: H_2O) was shaken for 1 hour after that, suspension was prepared and pH values of the filtrate measured by pH meter (model - HANNA) and EC by conductivity meter (JENWAY 4320 conductivity meter). Organic matters were determined by Walkley-Black method through use of potassium dichromate ($K_2Cr_2O_7$) (Sigma-Aldrich) wet combustion analysis to determine percentage of oxidizable organic carbon, total organic carbon then soil organic matter. 10 ml of 1N of $K_2Cr_2O_7$ and 20 ml of concentrated sulfuric acid (98% H_2SO_4) added to 1g dry soil and allow to stand for 30 min. 200 ml distilled water and 10 ml of concentrated orthophosphoric acid (H_3PO_4) added and left to cool. 10 drops of diphenylamine indicator added for titration with 0.5 M ferrous ammonium sulfate solution until the color changes from violet-blue to green (Estefan, Sommer, et al., 2013).

Soil samples were analyzed to determine their contents of heavy metals (Pd, Cr, Ni, Cu and Zn) by di-acid block digester method, the extraction was conducted with nitric acid (HNO_3) and perchloric acids ($HClO_4$) (Sigma-Aldrich). 3 ml of concentrated nitric acid was added to 1 g soil sample and heated in block digester at 145 ºC for an hour then 4 ml of concentrated perchloric acid added and heated for another hour at 240 ºC, after that tubes left to cool to room temperature, then diluted to 100 ml with distilled water and filtrated. The filtrate analyzed by use of atomic absorption mass spectrophotometer (PERKIN ELEMER AAnalyst 100) (Estefan, Sommer, et al., 2013).

For herbaceous plant, shoots are analyzed to determine their content of heavy metals by tri-acid block digester by use of concentrated nitric acid (HNO_3), sulfuric acid (H_2SO_4) and perchloric acid ($HClO_4$) (Sigma-Aldrich) at ratio of 10:1:4. Plants were oven-dried at 70 ºC for 48 hours. Thereafter 0.5 g of grand plant material was dissolved in acids, where 5 ml of concentrated H_2SO_4 added and heated in block digester at 145 ºC for an hour then5 ml of tri-acid mixture added and continued heating to 240 ºC for 12 hours, then tubes left to cool to room temperature, then diluted to 50 ml and filtrated. The obtained filtrate was analyzed by atomic absorption mass spectrophotometer (PERKIN ELEMER AAnalyst 100) to determine heavy metals concentration (Estefan, Sommer, et al., 2013).

3.4. Adsorbents characteristics

The used adsorbents in remediation experiment were clayey particles which called “Huar”, which was collected from the local area- Halhual, Hebron, Palestine and light expanded clay aggregates (LECA) with neutral pH, 0-3 mm in diameter and 650-850 Kg/m^3 density (Söğüt Toprak Mining Industry Inc.).

pH of adsorbents was determined by pH meter (HANNA), and iron content determined by di-acid block digester method which mentioned in previous section (3.3).

3.5. Remediation experiment

The contaminated soil samples that used for remediation experiments were collected from burning area at depth 0-30 cm, then air dried and sieved through 2 mm sieve. 50 g of soil was translocated to each experimental unit of nine polyethylene pot.

The used amendments in this experiment were applied at the rate of 0 and 5% -percentage weight. 2.5 g adsorbents-clay particles and LECA were added to soil samples and thoroughly mixed by hand. All treatments were conducted in three replicates and that included three control pots which set up without amendment. Amended and control pots were kept in incubator at 25 °C and watered regularly for one month. All pots were arranged in a completely randomized design.

Thereafter, pH of all treatments were determined by pH meter (HANNA). The content of bioavailable fraction of heavy metal- soil solution, exchangeable and carbonate bound were determined after extraction with 40 ml of 0.11 M acetic acid (CH_3COOH) then shaking for 16 hours. After that, the suspension centrifuges at 3000 rpm for 20 min according to BCR scheme (Vodyanitskii, 2006), the filtrate diluted to 50 ml and analyzed by using of atomic absorption mass spectrophotometer.

3.6. Statistical analysis

All collected data of soil and plant samples were statistically analyzed by one-way analysis of variance (ANOVA) using SAS Software System (SAS 9.4 software). Means of physiochemical properties, mainly total metal concentrations, among different sampling sites were compared using Fisher's least significant difference (LSD) test at $\alpha = 0.05\%$ (probability of error). Pearson correlation was conducted for analysis of correlation between heavy metals at $\alpha = 0.05\%$.

4. Results and Discussion

4.1. *Soil physical and chemical properties*

Soil texture of soil at burning area have determined to be clay soil with mean clay content of 50.92 ± 4.32 % and mean of sand content of 39.65 ± 2.95 %, and their mean bulk and particle densities were 1.2 ± 0.19 and 2.38 ± 0.04 g cm^{-3}, respectively, with porosity of 50%.

Clay particles play an important role in soil physical and chemical properties, and it is a charged surface with several functional groups for ion exchange and heavy metals adsorption. The measured soil bulk and particle density indicate soil aeration condition which affects heavy metals speciation and oxidation and reduction potential, and the soil has many pore spaces for optimum balance of air and water contents.

Heavy metals contamination and pollution loads in soil from E-waste burning processes mainly influenced by pH, soil organic matter and iron, aluminum and manganese oxides. Thus the major chemical properties were determined. The analyzed physiochemical characteristics of soil at different sampling sites within burning area, upward area, downward area and control are shown in table 4.1.

Table 4.1: The pH, SOM (%), EC (mmho/cm) and metals- Mn and Fe concentrations (ppm) at e-waste burning area and different surrounding areas (mean ±SD), while different letters show significant differences (α = 0.05) as measured by LSD test (one-way ANOVA)

Sampling unit		**Depth**	**pH**	**O.M**	**EC**	**Mn**	**Fe**
Burning area (B)	B1	0-10 cm	7.540 ±0.192b	5.000 ±1.894b	1.723 ± 1.112a	462.420 ±109.50a	10781.357 ±4775.02ab
		10-20 cm	7.603 ±0.258b	6.765 ±0.049a	2.641 ±1.884a	435.337 ±59.24a	13179.823 ±1005.75a
		20-30 cm	7.593 ±0.196b	5.700 ±1.40a	1.555 ±1.711ab	455.863 ±85.45a	11903.030 ±2553.54a
	B2	0-10 cm	7.740 ±0.223ab	5.025 ±1.252b	0.438 ±0.123b	356.663 ±64.09b	8955.660 ±1092.67bc
		10-20 cm	7.857 ±0.307a	6.263 ±0.646a	1.057 ±1.197b	438.757 ±64.09a	10029.597 ±2982.02b
		20-30 cm	7.840 ±0.212a	4.460 ±0.0bc	1.198 ±1.147b	339.557 ±41.48bc	9158.517 ±1252.59b
	B3	0-10 cm	7.665 ±0.318b	6.230 ±0.707a	0.376 ±0.069b	315.615 ±101.59b	9558.255 ±885.96b
		10-20 cm	7.755 ±0.290a	5.525 ±0.403a	0.283 ±0.035b	305.355 ±43.54c	7276.135 ±1733.95c
		20-30 cm	7.530 ±0.269b	4.920 ±0.905b	0.295 ±0.037b	341.270 ±50.8b	11052.825 ±1784.56a
Upward area (U)	U1		7.825 ±0.046a	5.167 ±0.154b	0.341 ±0.093b	479.800 ±17.78a	13042.600 ±131.94a
	U2		7.937 ±0.006a	4.743 ±0.978b	0.30 ±0.043b	479.810 ±27.15a	13060.500 ±384.86a

	U3	7.936 ±0.015a	4.837 ±0.832b	0.297 ±0.039b	495.20 ±5.13a	13406.55 ±53.7a
Downward area (D)	D1	7.983 ±0.032 a	5.843 ±0.773a	0.412 ±0.056b	438.760 ±51.31a	12553.360 ±699.28a
	D2	7.908 ±0.056a	5.523 ±0.42ab	0.439 ±0.007b	428.500 ±30.79ab	12613.020 ±428.95a
	D3	7.817 ±0.115a	5.32 ±0.854b	0.393 ±0.075b	517.430 ±25.83a	13478.140 ±423.19a
Control	C1	7.810 ±0.02a	3.420 ±0.689c	0.430 ±0.095b	418.233 ±41.05ab	11987.337 ±526.84a
	C2	7.815 ±0.163a	3.233 ±0.543c	0.254 ±0.038b	472.967 ±21.363a	13496.037 ±219.947a

All sampling areas were slightly alkaline with pH varies from 7.63 at burning area to 7.90 at downward area, and the lowest obtained value at burning area can be related to released acid from combustion processes in addition to acids added from organic matter decomposition. According to these pH values, the majority of metals are immobile due to low competition with low level of hydrogen ions in soil, therefore, their adsorption to negatively charged- clay and organic matter surfaces are high. Most of metals (Cu, Ni, Zn, Mn and Fe) are existed as a complex with soil minerals or organic matter, or as a precipitate at pH above 7. According to measured pH values, there was no significant difference ($\alpha = 0.05$) in these values among all sampling units at different area and within soil profile, and this result similar to Adesokan, Adie et al. (2016) results for soil pH range from 7.1 to 7.9.

Soil organic matter ranged from 3.23% to 5.84%, with maximum level at burning area which was highly concentrated at burning center. All soil samples are significantly different ($\alpha = 0.05$) in comparison to control, and their levels are higher than Adesokan, Adie et al. (2016) results for organic matter content (1.14- 2.10%) from near E-waste recycling activities, but lower than levels that found by Isimekhai, Garelick et al. (2017) at E-waste recycling and dismantling sites (6.20–26%). In semi-arid region, soil normally contains organic matter less than 1.5%, and all sampling areas in our study had more organic matter content than this value. E-waste equipment consist of wires, cables and other parts, most of these are made of plastic. Moreover, polyaromatic hydrocarbons (PAHs), phthalate and fatty acids which is rich in organic carbon, where organic matter contains 58% organic carbon, that could contribute to high level of organic matters in soil. High soil organic matter content generally decreases mobility and bioavailability of metals in soil due to form a stable complex with humus and another stable organic compound.

The electrical conductivity (EC) gives general indicate of the concentration of dissolved solids and bioavailable heavy metals in soil and that reflects soil microorganism activity which influence key soil processes. Soil EC at B area is significantly ($\alpha = 0.05$) high in comparison to control and surrounding areas, and it has the high level of water soluble matters.

Iron and manganese oxides were analyzed to indicate soil heavy metals status. Some fraction of available soil heavy metals is stabilized and immobilized by their adsorption on large surface area with high adsorbing capacity of iron, aluminum and manganese oxides, such as zinc which is mainly occurred as a form of bounding to oxides. Their soil contents were high in general as shown in table 4.1, but the lowest level of iron and manganese were observed at burning area with mean concentration of 10156.75 and 395.1 ppm, respectively.

4.2 Heavy Metals Contamination in Soil

4.2.1 Heavy metals contamination at different sampling areas

Burning of E-waste resulted in high pollution load to surrounding environment, which involved release of particulate material with smoke and high level of accumulated heavy metals in soil and plant.

Heavy metals concentration varies from one area to another as shown in table 4.2 based on its main applied process and use, its topographical and geographical aspects and environmental factors including wind direction, which all influenced metals abundance and mobility.

Table 4.2: Soil heavy metals- Cu, Cr, Pb, Zn and Ni concentrations (ppm) at e-waste burning area and different surrounding areas (mean ±SD), while different letters show significant differences (α =0.05) as measured by LSD test (one-way ANOVA)

Sampling unit	**Depth**		**Cu**	**Cr**	**Pb**	**Zn**	**Ni**
Burning area (B)	B1	0-10 cm	13271.227 ±960.33a	194.690 ±51.56a	2355.073 ±1431.63b	3056.827 ±326.67a	1110.860 ±671.12a
		10-20 cm	15835.94 ±1548.970a	194.692 ±103.13a	4017.387 ±1541.53a	3226.50 ±243.03a	723.390 ±387.47a
		20-30 cm	13686.743 ±1415.30a	150.037 ±68.21a	2312.990 ±1060.69b	3111.017 ±113.83a	1110.860 ±671.12a
	B2	0-10 cm	8808.057 ±7044.87b	105.383 ±68.21b	608.587 ±473.8c	2767.230 ±821.11a	465.077 ±223.71b
		10-20 cm	12214.510 ±7392.39ab	75.613 ±25.78b	1807.980 ±1294.21b	2784.107 ±616.22a	594.233 ±447.41ab
		20-30 cm	8095.240 ±5556.20bc	90.497 ±77.35b	2439.240 ±2083.48b	3159.873 ±1058.62a	400.500 ±111.86b
	B3	0-10 cm	3952.655 ±2135.2cd	135.150 ±0.0ab	1039.945 ±44.64bc	1159.345 ±229.9b	529.655 ±273.98b
		10-20 cm	3995.640 ±2363.15c	68.170 ± 31.58b	913.695 ±223.18c	1114.040 ±226.13b	723.390 ±0.0a
		20-30 cm	3807.585 ±1854.06c	45.840 ±0.0b	1229.325 ±491.01b	1283.270 ±258.17b	723.390 ±0.0a
Upward area (U)	U1		207.760 ±74.37d	90.500 ±44.66b	166.700 ±72.89c	169.740 ±40.1c	465.080 ±223.71b
	U2		118.130 ±133.5d	60.730 ±25.78b	166.710 ±36.45c	116.450 ±20.01c	465.080 ±223.97b
	U3		67.977 ±64.47d	68.17 ±22.33b	124.62 ±0.0c	131.96 ±11.99c	239.052 ±96.87b
	D1		472.740 ±376.32 d	60.730 ±25.78b	208.790 ±96.43c	219.500 ±123.80c	465.080 ±223.71b

Downward area (D)	D2	236.330 ±125.93d	60.730 ±25.78b	208.790 ±96.43c	151.100 ±37.91c	465.080 ±223.71b
	D3	64.400 ±22.37d	45.840 ±0.0b	124.620 ±63.13c	125.330 ±2.67c	335.920 ±0.0b
Control	C1	85.890 ±77.74d	75.610 ±51.56b	82.533 ±36.45c	112.900 ±41.84c	465.077 ±223.71b
	C2	2503.737 ±4163.04c	60.727 ±25.78b	588.213 ±747.19c	940.83 ±1185.13b	465.077 ±223.71b
WHO/ FAO limits		100d	100b	100c	300c	50c

Figure 4.1 and 4.2 shown that, pollution load and metals concentration in general were descended at burning area, nearby areas (downward area and upward area) and control area, respectively with some exception of some metals.

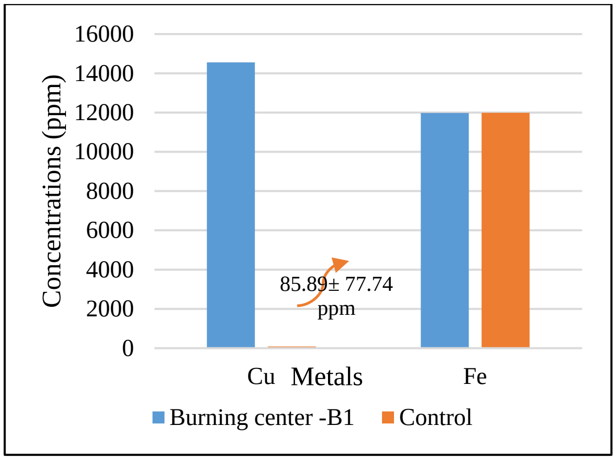


Figure 4.1 a: Heavy metals- Cu and Fe concentration at burning area center in comparison with control

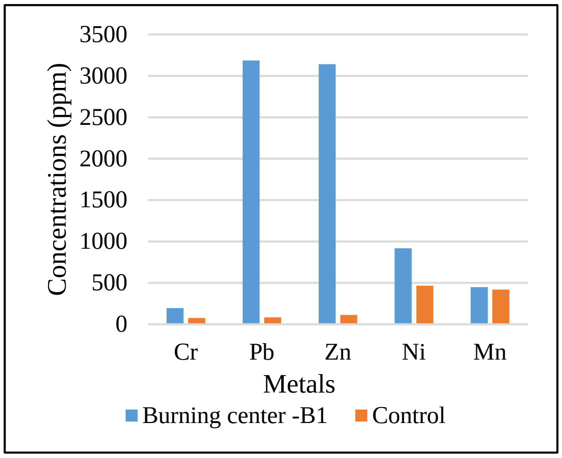


Figure 4.1 b: Heavy metals- Cr, Pb, Zn, Ni and Mn concentration at burning area center in comparison with control

Burning area (B) was highly contaminated with heavy metals, mainly copper (Cu) as shown in figure 4.1a. Since burning processes were conducted at this area, heavy metals from E-waste were released and accumulated in these areas at high level. Downward area (D) was highly contaminated than upward area (U) as shown in figure 4.2, since downward area had the lowest slope aspect and many of soluble fraction of heavy metals were carried with runoff and transferred by gravity from B and U areas to this D area. Obtained result of heavy metals concentration among different areas completely agrees with Luo, Liu et al. (2011).

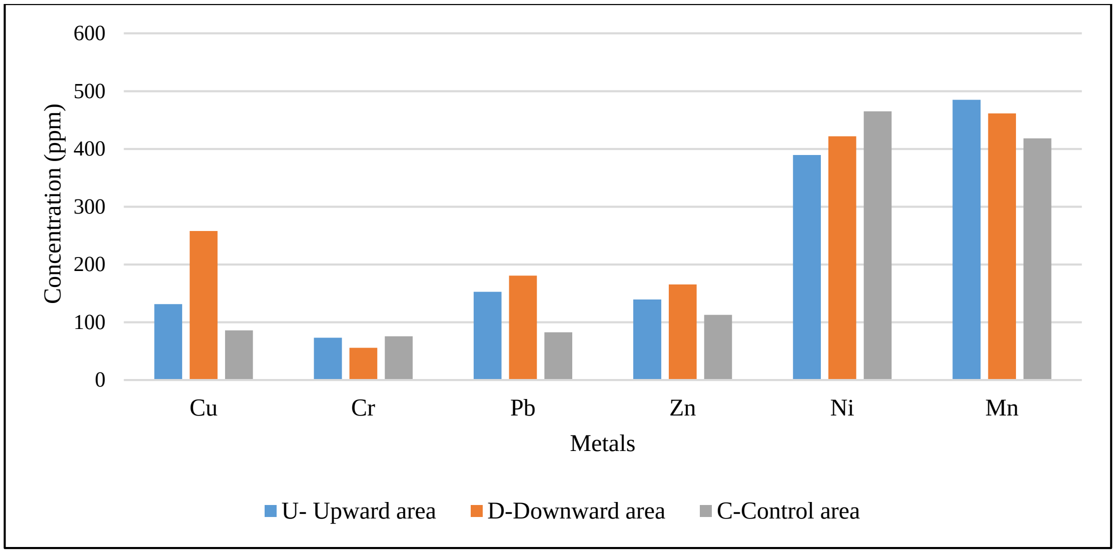


Figure 4.2: Heavy metals concentration at surrounding areas in comparison with control

Heavy metals contamination in upward area was noticeable and relatively high, since this area was located in the direction of wind, and many of volatile metals that released with smoke were carried by wind to this area and deposited by rainfall or under windless conditions. All areas had high content of heavy metals which were significantly ($\alpha = 0.05$) greater than control area as shown in figure 4.1 and 4.2 for most of heavy metals (Cu, Pb and Zn).

4.2.2 Heavy metals contamination at burning area (B)

Figure 4.1 shown the concentration of analyzed metals at B, the concentration of different heavy metals followed the following order Cu > Fe >>> Zn > Pb >> Ni > Mn > Cr. This result is similar to the result obtained by Isimekhai, Garelick et al. (2017), which found E-waste recycling sites in Lagos State, Nigeria were highly contaminated with copper, and the heavy metals soil concentration followed this order Cu, Pb and Zn, Moreover, its agrees with the results obtained by Adesokan, Adie et al. (2016) results on heavy metals concentration at E-waste recycling sites in Ibadan, Nigeria followed this trend Pb > Cu >>

Cr > Ni >> Cd. These differences are mainly related to soil type and its clay content which plays important role in retention of metals, and rate of E-waste burning and its type which depend on its main components, in addition to climatic and edaphic factors which affected heavy metal mobility and leachability with time.

Copper concentration was very high at this area as shown in table 4.2 and its about 120 and 208 times higher than its level in control and Moradabad guideline value (50 ppm), and that was greater than that was found in previous study in, India, where Singh, Dwivedi, et al. (2018) found that the Cu level at burning site was 40 times higher than Moradabad guideline value. Most of electronic parts are mainly contain copper in their components, so their burning will be releasing huge amount of copper at burning site at level ranging from 2324.64 to 17605.45 ppm as reported in Table 4.2, which is close to studies carried out in India that was ranging from 915.3 to 13646.6 ppm (Singh, Dwivedi, et al., 2018), and 1374 to 14253 ppm in Guiyu, China at open burning site (Wong, Wu et al., 2007), the little difference returned to types and amount of E-waste burned.

The mobility and solubility diagram of Copper has U- curve, it is highly dependent on soil pH as found by Ashworth and Alloway (2008) and shown in figure 1.1. Moderate soil pH (7.63) indicates that low copper mobility and exchangeability occurred due to its strong affinity to be formed chelation with the functional groups in organic matter that presented at high level (5.84%). Furthermore, it adsorbed onto the surface of Fe- and Al- oxide.

Burning area was also polluted with large amount of lead and zinc, which their concentrations were about 23 and 22 times greater than that in the control (table 4.2). Lead is a main component of cathode ray tubes in televisions, computers, etc., burning of these equipment released lead at concentration ranging from 124.62 ppm to 5742.83 ppm at burning center with mean concentration of 1892.15 ppm. The obtained results of the measured soil samples similar to results obtained by Singh, Dwivedi, et al. (2018) at burning sites which were ranged from 693.3 to 1832.6 ppm. Moreover, the results of Pb concentration also similar to the results obtained by Isimekhai, Garelick et al. (2017), that ranged between 115–9623 ppm, and relatively close to the results obtained by Wong, Wu et al. (2007), where the measured concentrations of Pb ranging from 856 to 7038 ppm at E-waste recycling sites, which included E-waste burning.

Zinc contamination at burning area was obviously presented at mean level of 2503.17 ppm which was lower than mean value (3690 ppm) that found in previous study in China E-waste incineration site (Luo, Liu, et al. 2011). For lead at pH above 6, it is immobile and mainly bounds with soil minerals and element to form insoluble lead sulfide, lead phosphate and lead oxides. It is highly adsorbed on soil organic matter than soil particles (Adesokan, Adie et al., 2016). At alkaline and anoxic conditions, zinc mainly presents as zinc sulfide which can precipitate and be unavailable in soil solution (Mulligan, Yong et al., 2001).

Also, there was a presence of chromium and nickel metals at mean level of 132.36 and 699.17 ppm, respectively. The measured concentrations of chromium and nickel in our study were higher than their maximum allowable limits according to WHO/ FAO (100 and 50 ppm, respectively), and they were 2-fold greater than C1 value, however, this result was close to Luo, Liu et al. (2011), where found that the concentration of chromium and nickel were 1.36 and 4.17 times higher than control.

In general, the concentration of all heavy metals are very high at B1, B2 and B3, moreover, their concentration is remarkably declined when moved to B2 and B3 except nickel as shown in figure 4.3b.

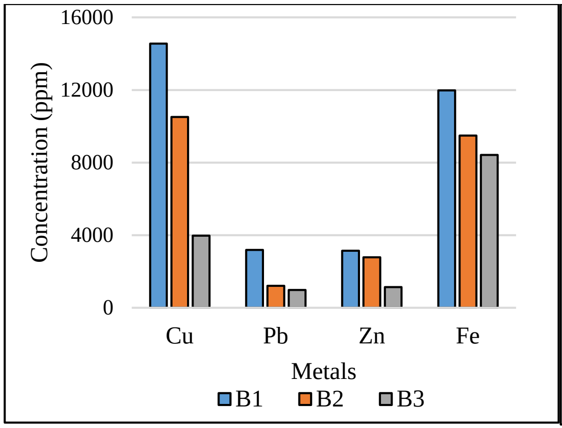


Figure 4.3 a: Heavy metals- Cu, Pb, Zn and Fe concentration in relation to their distance from the center of burning at burning area

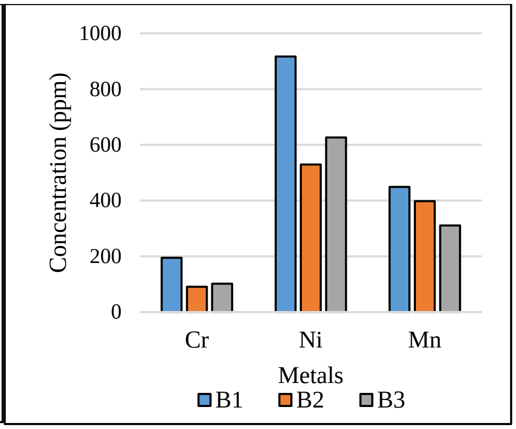


Figure 4.3 b: Heavy metals- Cr, Ni, Mn and Al concentration in relation to their distance from the center of burning at burning area

Generally, heavy metals concentration varies within soil profile due to difference in soil properties, mainly soil organic matter, clay content and Fe- and Al- (hydr) oxide which are changed within soil profile. Figure 4.4 shows heavy metals concentration in soil profile at different soil layers with 10 cm depth in B area.

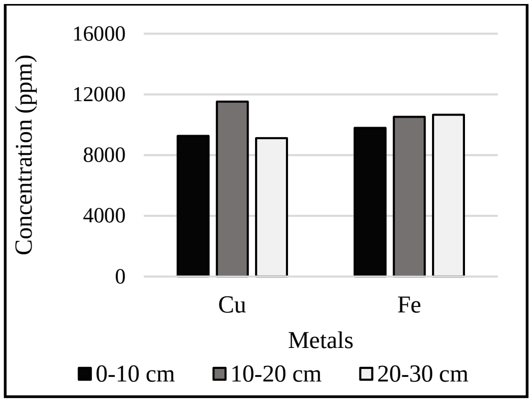


Figure 4.4 a: Heavy metals- Cu and Fe concentration in relation to their depth in soil profile at burning site

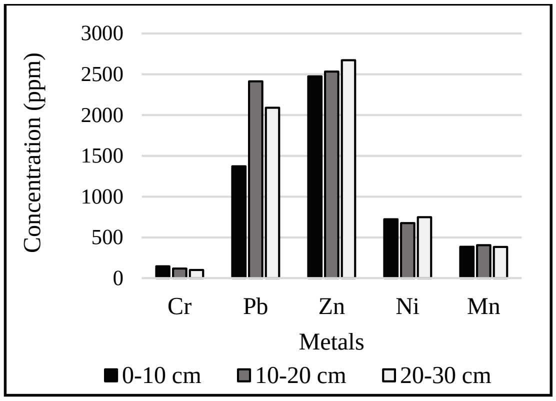


Figure 4.4 b: Heavy metals- Cr, Pb, Zn, Ni and Mn concentration in relation to their depth in soil profile at burning site

The trend of heavy metals concentration change with depth differs among each metal. For chromium, their level declined with depth and became low at deeper soil layer as shown in figure 4.4. Chromium presented at the highest mean level of 146.315 ppm at topsoil (0-10 cm), then its level declined in the second layer (10-20 cm) and it found to be about 118.407 ppm, after that it reached to their lowest level of 101.66 ppm at deeper layer (20-30 cm). Iron and zinc have the opposite trend (4.4). Most of Cr in deeper soil profile adsorbed onto the surface of Fe oxide, Thus the decline in the concentration of Cr with increase of soil depth leads to decline it’s leachability and mobility, and this concentration was significantly high in top soil than other layers which were not significantly differed from each other. In general, the results are relatively similar to result of Zhang, Ding et al. (2015); Isimekhai, Garelick et al. (2017), who did not find any significant difference ($\alpha = 0.05$) in chromium concentration with soil depth.

Chromium occurs naturally in soil from its parent material, and its released at high level from circuit broad and other electronic products in burned E-waste. Its speciation depends on soil pH, organic matter and presence of some elements. The highly toxic and soluble hexavalent chromium (Cr^{+6}), which uses in electronic products mainly for prevention of corrosion, is weakly adsorbed and can easily exchange mainly at high pH, although it can be adsorbed in soil that high in iron and aluminum oxide. Therefore, most of chromium species in this study may immobile and they’re not bioavailable in soil solution due to high level of iron (10156.75 ppm). Furthermore, Cr^{+6} is expected to be reduced to less toxic and most stable form; trivalent chromium (Cr^{+3}) due to presence of high organic matter (5.84%). Moreover, the mobility of Cr^{+3}decreasing as soil pH increasing which tends to adsorbed onto soil particles and forms hydroxide precipitate under alkaline condition which occurs in our analyzed burning area at pH 7.633.

The obtained behavior of chromium didn’t observe for other metals, and each one had its own behavior. For copper the maximum concentration found in second layer (0-20 cm) at level of 11517.83 ppm and followed by top soil (0-10 cm) with concentration of 9267.9 ppm, this behavior indicates that the vertical leaching of copper within soil. Since copper has strong adsorption affinity to organic matter, therefore, most of copper are bonded with soil organic matter in second layer where the content of organic matter (6.2%) is high. This trend relatively closed to results found by Isimekhai, Garelick et al. (2017), which copper concentration slowly increased with depth.

There was no general significant trend ($\alpha = 0.05$) of heavy metals concentration that followed with soil depth at our study, and it was similar to Isimekhai, Garelick et al. (2017) conclusion, but differed from the results obtained by Adesokan, Adie et al. (2016), which found general decrease of Pb, Cu, Cr and Ni concentration with depth with some exception. In addition to Zhang, Ding et al. (2015), who found that, Cd, Cu, Pb and Zn were highly concentrated at E-waste disassembling site, and their contents were high at top soil and then decreased toward deep soil layers.

4.2.3 Heavy metals contamination and mobility at surrounding agricultural areas

Since the location of E-waste burning site occurred randomly, in turn will cause a serious pollution the burning area as well as the vicinity lands. Moreover, the nearby land will be contaminated with burning residues by several ways such as air-born waste and water run-off.

Heavy metals, that released from burning process mainly as ash or as a volatile material can be transferred to atmosphere, and in turn its deposited to the surrounding environment and accumulated there at level exceeded their maximum standard values. In this study, an agricultural area was surrounding the burning site. The agricultural area was divided into two sub-areas; upward area and downward areas due to the differences on their topographical and then in their climatic-aspects. Both areas were covered with herbaceous plants mainly barley (*Hordeum vulgare*).

Figure 4.5 shows the concentration of heavy metals in the upward area, the contamination of this area by heavy metals followed the following sequence based on their measured soil content Mn > Ni > Zn > Pb > Cu > Cr. The different sequence of heavy metals content and order from those at burning area indicated difference in their mobility. Because U area located in the direction of dominant wind, the majority of transported and accumulated heavy metals carried by wind, and small fraction deposited by rainfall.

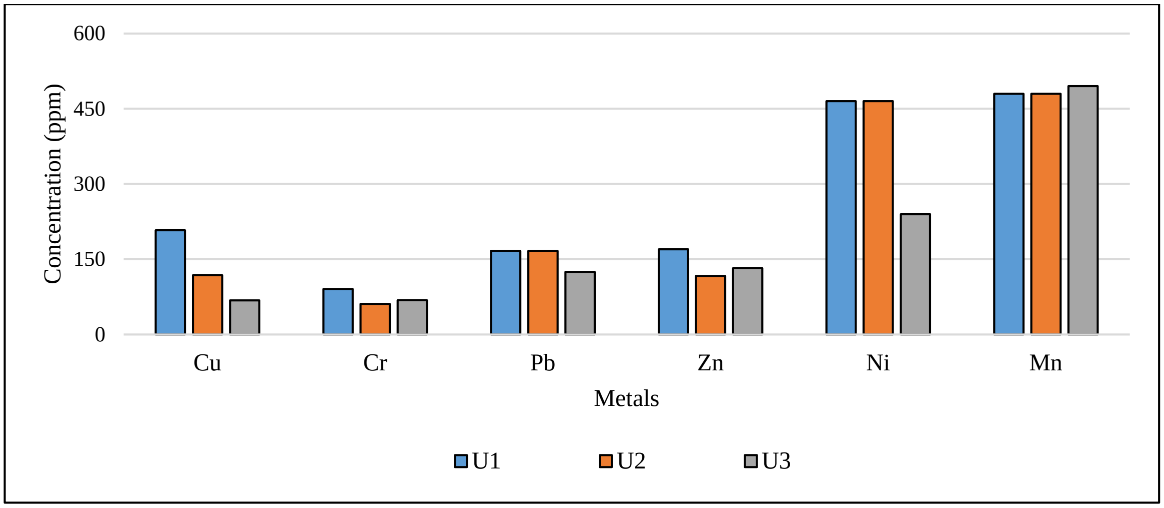


Figure 4.5: Heavy metals concentration at upward area as a function to distance from the center of burning site

According to the results in figure 4.5, soil contamination with heavy metals decreased with increasing the distance from burning center, and that related to wind activity which couldn’t carry heavy metals- contained ash for long distance, and the carried residues early deposited at close distance. This result agreed with the result of Olafisoye, Adefioye et al.

(2013) which indicated that the decline of heavy metals concentration with distance from E-waste dumping site. At U1, the soil maximum content of Ni, Cu and Cr were 465.08, 207.76 and 90.5 ppm, respectively, and Ni level is significantly ($\alpha = 0.05$) greater than WHO/ FAO limit at 50 ppm, where Cu and Cr concentrations were not significantly ($\alpha = 0.05$) differ in comparison to WHO/ FAO limits (100 ppm for both of them).

An exception for manganese was existing, whereas the data of soil sample from U3 showed the highest content of Mn with concentration about 495.20 ppm, but within WHO/ FAO maximum limit (2000 ppm). However according to the result that showed in table 4.1, figure 4.2 and 4.3, the concentration of Mn at burning site is lower than its concentration at upward area, this result indicates that Mn mainly occurrence from natural sources and there is no correlation between the soil's contents of Mn and E-waste burning, but its concentration is not significantly differ between B, U and D areas ($\alpha = 0.05$). Howe, Malcolm et al., (2004) reported that the mean concentration of Mn in soil is ranging from 300-600 ppm, this refer to the naturally occurrence of Mn is soil crust (0.1%) resulting from weathering the parent material in addition to other anthropogenic sources such as fuel combustion and mining industries.

The concentration of Cu, Pb, Zn and Ni at D area were more than that at U area, but not significantly differ ($\alpha = 0.05$) from each other, that mainly related to more affective transporting agents at this area. Heavy metals and other materials are transported and deposited to downward area either by gravity (colluvial), or by water runoff (Alluvial), in addition to wind carrier of particulate metals (Eolin). Figure 4.6 shows that, the concentration of heavy metals in D area increased with decreasing the distance to burning center site, which may be related to their adsorption at soil particle surfaces which rich with clay minerals and organic matter- 5.84% at D1 site, and that provided high retention of adsorbed metals.

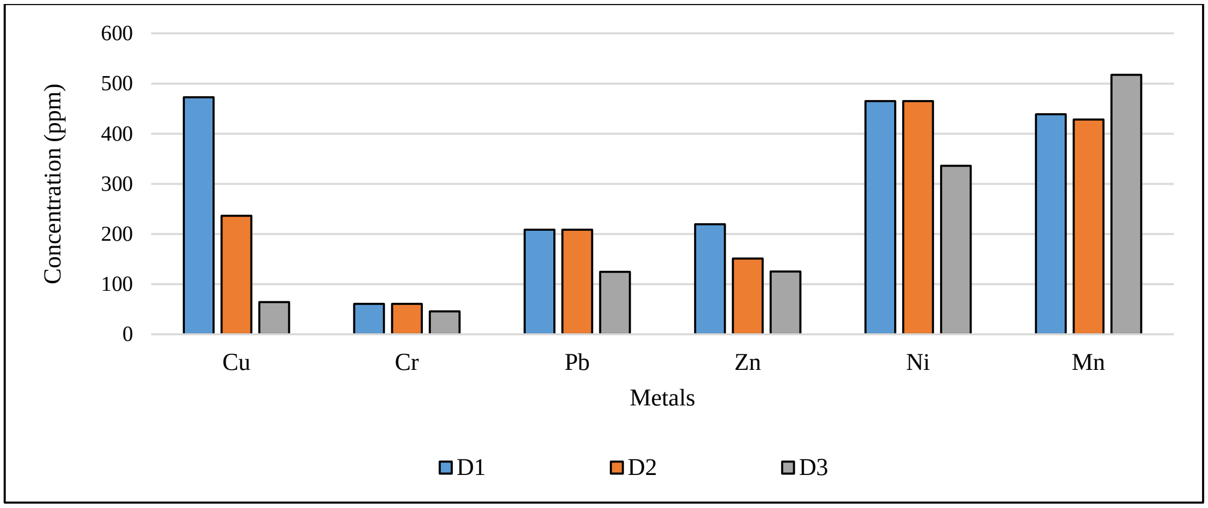


Figure 4.6: Heavy metals concentration at downward area as a function to distance from the center of burning site.

D1 is heavily contaminated with Cu and Zn than other areas. The Cu level was about 472.74, 236.33 and 64.4 ppm at D1, D2 and D3, respectively, and that shown reduction of its mobility with increase of distance more than 2 times from D1 to D2 and more than 3.5 times from D2 to D3.

Once more, there was no specific profile for Mn, since its concentration at D area does not affect at all with E-waste burning, this finds confirmed our previous prediction that the main source of Mn in soil is coming from natural sources not from burning.

In general, heavy metals content obviously declined but not significant ($\alpha = 0.05$) with distance due to reduction of their transporting agents' ability to carry them longer, and the trend of heavy metals concentration decline with distance was clearer at D area than U area. For Cu and Pb, figure 4.7 and 4.8, respectively shown the trend of their contents decline with distance at both surrounding areas.

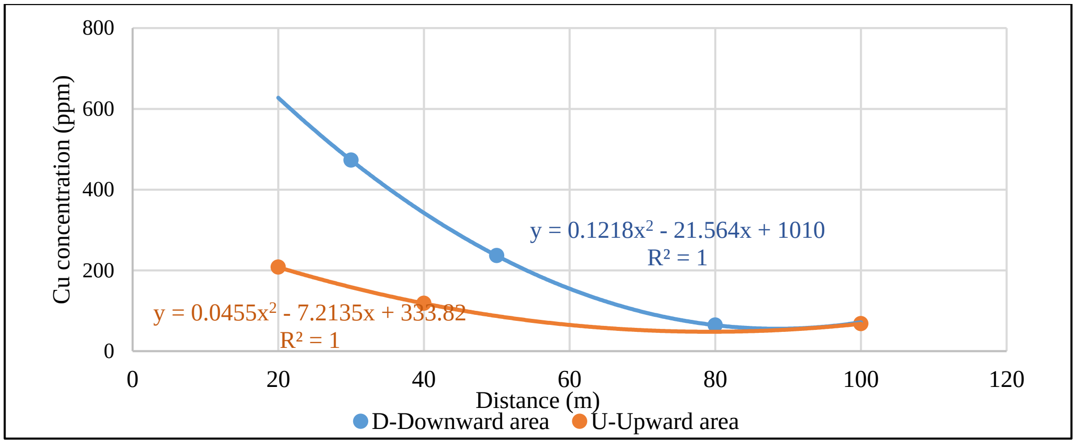


Figure 4.7: Copper concentration at upward and downward area as a function of distance

Cu and Pb concentration as a function of distance from burning center have curved trend with many flocculation in polynomial trend. The obtained equation with 1 regression can be used for estimation of Cu and Pb concentration at any point away from center. For Cu (figure 4.7), the obtained upward and downward area equations are $Y = 0.0455x^2 - 7.2135x + 333.82$ and $Y = 0.1218x^2 - 21.564x + 1010$, respectively, where Y is Cu concentration (ppm) and x is a distance (m).

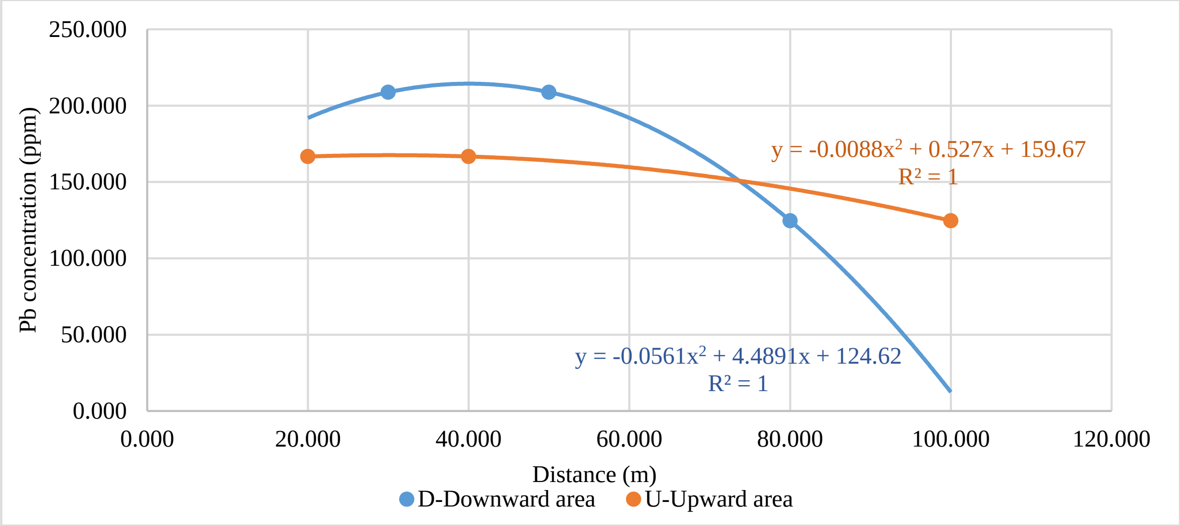


Figure 4.8: Lead concentration at upward and downward area as a function of distance

From figure 4.8 for Pb concentration at U and D areas as a function with distance, the obtained equations are $Y = -0.0088x^2 + 0.527x + 159.67$ and $Y = -0.0561x^2 + 4.4891x + 124.62$, respectively, where Y is Pb concentration (ppm) and x is a distance (m).

Iron content at D and U areas was very high which are equaled up to 12881.5 and 13169.88 ppm, respectively. Iron can release from E-waste, such as printer toner cartridges, However, it is noteworthy that the Fe is the fourth most abundant element in earth crust after oxygen, silicon and aluminum, and it occurs naturally in soil from weathering of minerals. According to US EPA (2019), soil natural content of iron ranging from 20000 to 55000 ppm. Thus, the measured iron levels at these areas were within the natural range and there was a high probability to be come from natural sources.

Luo, Liu et al. (2011) studied the concentration of Cu in soil at vegetable gardens nearby to E-waste incineration site, he found that the concentration of Cu higher than other metals with mean concentration of 324 ppm, however, the concentration of Cu at this study was 131.29 ppm and 257.84 ppm at U and D areas, respectively. Moreover, Luo, Liu et al. (2011) found that the concentration of Pb about 95.6 ppm, whereas in this study its concentration was 152.68 and 180.73 ppm at U and D areas, respectively. However, this is mainly referring to the differences in climate especially to the annual precipitation as well as to land sloop (topography) of the area.

Wu, Leung et al. (2015) reported that the concentration of Cu, Pb and Zn in soil at several E-waste burning site and vegetation field, the concentration of Zn was 194 ppm at burning site and 46.9 ppm in vegetation field, and, the concentration of Pb was 206 and 14.3 ppm, respectively. The concentration of zinc in this study at B, U and D area were 2503.17, 139.38 and 165.31 ppm, respectively.

A study of soil analysis for a nearby area located 500 m away from open burning site was carried out by Wong, Wu et al. (2007), and they found that Cu, Pb and Zn concentration are ranging from 59.4 – 114.0, 97.8 – 123.0 and 6.0 – 42.4 ppm, respectively. The result of this study found the concentration of these metals at U3 was 67.98, 124.62 and 131.96 ppm, respectively, which similar to Cu and Pb concentration and slightly greater than Zn concentration.

Generally, all analyzed samples had higher contents of heavy metals than control, and the highest levels at α = 0.05 were found at B area. E-waste burning processes are the major source of heavy metals contamination at the studied site, since all heavy metals- Cu, Pb, Zn, Ni and Cr are highly (0.5) or moderately (0.3-0.49) positively correlated to each other as shown in table 4.3 at high probability less than 0.003. These metals are also moderately correlated with soil pH in negative manner, where soil with high content of Cu, Pb, Zn, Ni and Cr will have lower pH value than normal one has lower content of heavy metals, and that is supported by the negatively moderate correlation between pH and EC, which reflects dissolved solid soil content. For other metals- Fe and Mn, they aren’t significantly correlated with found heavy metals (Cu, Pb, Zn, Ni and Cr) and that means Fe and Mn come from other different source, and they are mainly come from natural sources.

Table 4.3: Pearson correlation coefficient (r) among metals and soil physicochemical properties

	Cu	**Cr**	**Pb**	**Zn**	**Ni**	**Mn**	**Fe**	**pH**	**EC**	**OM**
Cu	1									
Cr	0.606*	1								
Pb	0.816*	0.586*	1							
Zn	0.903*	0.571*	0.777*	1						
Ni	0.530*	0.533*	0.501*	0.422*	1					
Mn	-0.121	0.167	-0.137	-0.246	0.053	1				
Fe	-0.056	0.088	0.051	-0.298**	0.147	0.597*	1			
pH	-0. 393*	-0.478*	-0.383*	-0.445*	-0.366 **	0.125	0.138	1		
EC	0.568*	0.590	0.509*	0.536*	0.423*	0.061	0.049	-0.49*	1	
OM	0.242	0.212	0.328**	0.207	0.165	0.099	-0.064	-0.189	0.158	1

* Correlation is significant at probability < 0.003

** Correlation is significant at probability < 0.05

4.3 Heavy Metals Contamination in Plant

For plant growth and development, several essential elements are required at certain range for each plant and soil type. Iron, manganese, copper, zinc, boron, cobalt, chlorine and molybdenum are micronutrients with significant role in plants mainly in plant enzymes. These elements are required at relatively trace quantities and plant can’t continue its life cycle in their absence. Moreover, no other elements can substitute their deficiencies. However, their occurrence at high level from natural or anthropogenic sources causes problem in balance of nutrients uptake.

Iron is important for chlorophyll synthesis and energy transfer. Its uptake reduces soil pH, since the release of hydrogen ions through ion exchange for iron uptake and increase its solubility in alkaline soil. Iron high levels cause brown spots on leaves and imbalance of nutrients uptake, and it mainly competes zinc, manganese, nickel and molybdenum.

Copper is one of enzyme constituents and it’s important for respiration and photosynthesis, excess Cu presence in soil inhibit seed germination and stunt plant, in addition to obstruction of other nutrients mainly iron uptake due to competition between them, and its uptake depends on strength of root system. Zinc plays important role on regulation of many metabolic activities and for good root system development, and it’s a strong competitor with copper.

Other non-essential elements including nickel, aluminum and lead are useful for some plant and toxic for most other plants. Excess of Al inhibits root function and macronutrients uptake.

Chromium naturally occurs in soil at low level from parent materials of rocks, and its high-level affect seed germination, root growth and height and macro- and micro- nutrients uptake. Its effect depends on its speciation, where hexavalent chromium is toxic. Also lead at high level affect plant growth negatively, due to its impact on soil microorganism.

The concentration of heavy metals in collected plant samples are summarized in table 4.4. The analyzed plants included herbaceous wild plants at burning area and cultivated herbaceous mainly barley (*Hordeum vulgare*) in surrounding areas.

Table 4.4: Heavy metals- Cu, Cr, Pb, Zn, Ni, Mn, Al and Fe concentrations (ppm) in plants from E-waste burning area and different surrounding areas (mean ±SD), while different letters show significant differences (α =0.05) as measured by LSD test (one-way ANOVA)

Sampling unit		**Cu**	**Cr**	**Pb**	**Zn**	**Ni**	**Mn**	**Fe**
Burning area (B)	B1	602.837±54.72b	19.338±4.3a	312.91±105.21a	352.489 ±21.91a	3143.0 ±645.78a	87.04 ±19.75e	2764.72 ±709.93a
	B2	847.607±715.50ab	24.3±7.44a	172.63±121.486ab	333.242 ±54.04a	2712.478 ±372.84a	92.739 ±19.75d	2446.517 ±477.31a
	B3	1035.662±367.26a	24.2995±10.53a	260.305±74.395a	311.03 ±75.38a	3143.0 ±913.28a	98.439 ±48.37d	2476.349 ±548.45a
Upward area (U)	U1	53.597±27.36c	21.819±11.37a	277.84±160.711a	84.51 ±27.74b	2066.694 ±372.84a	92.739 ±9.87d	1392.463 ±419.06b
	U2	35.687±10.34c	21.819±4.3a	312.91±182.23a	127.444 ±15.6b	2927.739 ±745.69a	126.946 ±9.88cd	1094.148 ±397.26b
	U3	29.717±27.36c	16.86±12.89a	102.49±0.0b	130.406 ±40.06b	2927.739 ±372.84a	167.053 ±34.51b	417.963 ±78.93d
Downward area (D)	D1	41.657±17.91c	16.857±7.44a	312.91±105.21a	131.886 ±36.18b	2281.956 ±986.45a	149.75 ±17.10bc	447.795 ±136.71d
	D2	41.657±31.02c	19.338±11.37a	242.77±60.74a	120.041 ±7.69b	2497.217 ±1118.53a	92.739 ±26.13de	398.076 ±45.57d
	D3	11.807±10.34c	19.338±4.3a	242.77±60.74a	97.764 ±22.21b	2712.478 ±372.84a	87.038 ±9.87e	467.683 ±45.57d
Control	C	10.834±11.28c	24.3±7.44a	207.7±105.21a	125.964 ±11.18b	2066.695 ±745.69a	92.739 ±26.126d	517.402 ±91.14bc
WHO/ FAO limits		73c	-	0.3c	100b	67b	500a	425d

The analyzed shoots of plant samples had high concentration of Ni, Cu, Pb and Fe (table 4.4 and figure 4.9). The high concentration of metals in plant sample indicates that the potential of mobility of these metals in soil, thereafter, these metals will transfer to plant through root by diffusion, then they are translocated and accumulated at edible plant shoots.

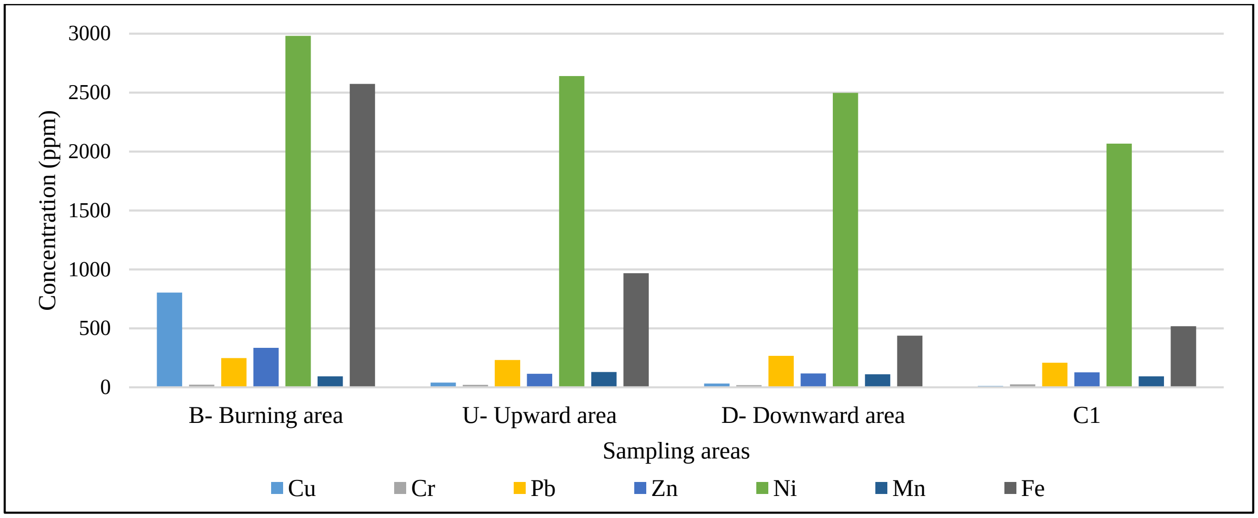


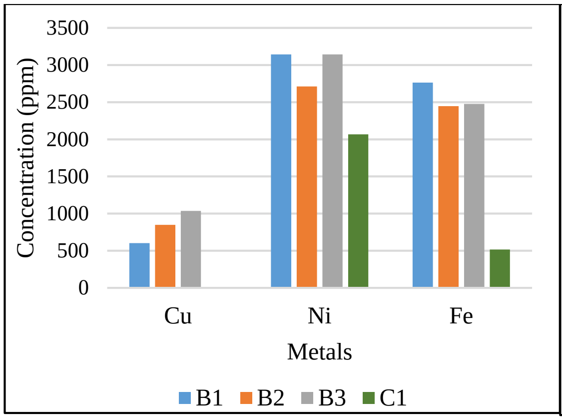
Figure 4.9: Heavy metal concentration in plant at different areas

Figure 4.9 shown that, plants at B area were highly concentrated and contaminated with metals that accumulated from burning E-waste, where at U and D areas plants were generally less contaminated with some exception, and that agreed with the result of study carried out by Luo, Liu et al. (2011), which analyzed wild plants at burning site and vegetables at nearby gardens, and they found the content of heavy metals in wild plants are higher than that in other areas.

Plants’ content of nickel was the highest one, and there is no known benefit of nickel for healthy plant growth. Nickel level in burning area herbage was about 2981.55 ppm and it was not significantly higher ($\alpha = 0.05$) than what were found in barley at U and D areas at level of 2640.72 and 2497.22 ppm, respectively, but their levels is significantly higher than 67 ppm according WHO/ FAO vegetation maximum allowable limit if Ni. In the environment, there are several plant species can accumulate metals at high level in their tissues, which called hyperaccumulators. *Alyssum betolonii* leaves’ contain Ni at level more than 10000 ppm. The analysis of wild plants and barley showed their high level of accumulated Ni and they are Ni tolerant plants (Prasad, M., 2005; Kramer, U et al. 1996)

At B area, Cu, Zn, Ni and Fe had the highest level in this area in comparison with U, D and C areas, due to its high contamination with metals that released from burning process, which was heavily conducted at this area, and B is significantly ($\alpha = 0.05$) concentrated and contaminated with Cu and Zn than U and D. After that mobility of available metals and accumulation in plants tissues as shown in the results of plant analysis, which summarized in table 4.4.

Copper and iron are micronutrients that essential in small quantities for plant growth, but their availability at level greater than plant needs, leads to improper growth of plants which significantly decreases and diminish the yield and its quality by playing a negative vital role in biochemical and physiological functions of plant. Iron concentration in soil at B area was too high than that in C area, the Fe level at B1 was 2764.72 ppm which was relatively greater than its levels at B2 and B3 that equal 2446.52 and 2476.35 ppm, respectively. Figure 4.10 shows that, at B area there is no significant difference ($\alpha = 0.05$) in plants content of heavy metals in relation to their location and distance away from burning center due to complex behavior of plants in uptake of nutrients available in water solution.



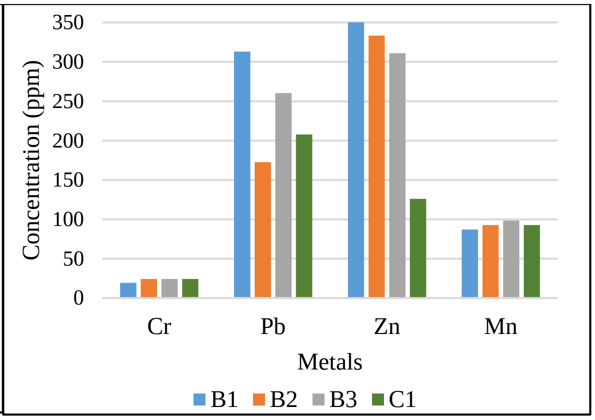


Figure 4.10 a: Heavy metal- Cu, Ni and Fe concentration in plants at burning area in relation to their location

Figure 4.10 b: Heavy metal- Cr, Pb, Zn and Mn concentration in plants at burning area in relation to their

Plants' content of heavy metals at different distances within burning area was significantly higher than that found in control as shown in figure 4.10, but there was no significant trend ($\alpha = 0.05$) in heavy metals levels in analyzed plants shoots as a function in their distance from burning center.

In comparison of this study with previous literature, shoots of our collected wild plants at burning area had high contents of Cu, Pb and Zn and the highest content of nickel at level of 802.83, 247.15, 334.91 and 2981.55 ppm, respectively. These results are greater than the obtained results by Luo, Liu et al. (2011), who found the level of Cu, Pb and Zn in wild plant shoots at burning site were 94.3, 54.8 and 143 ppm.

Transfer factor (TF) is used to evaluate potential transfer and uptake of heavy metals from soil to plants' edible parts. The high TF indicates high potential ability of plants to uptake of these metals and transfer to its tissues as shown in table 4.5. Cu concentration is generally high in soil, but its TF is low and ranging between 0.099 to 0.422, which shows low mobility and transfer of Cu to plants tissues. Whereas, Ni has the highest TF with mean of 5.93 and it has high mobility and potential uptake from soil to plant, and Pb and Zn have moderate mobility and transfer in comparison to other analyzed metals and they have TF of 0.098- 2.517 and 0.112- 1.116, respectively.

Table 4.5: Transfer factor of heavy metals from soil to plant shoots, while different letters show significant differences (α =0.05) as measured by LSD test (one-way ANOVA)

Sampling unit		**Cu**	**Cr**	**Pb**	**Zn**	**Ni**
Burning area (B)	B1	0.041b	0.099a	0.09c	0.112c	3.427b
	B2	0.081b	0.269a	0.143b	0.120b	5.121b
	B3	0.260a	0.239a	0.266b	0.274b	5.017b
Upward area (U)	U1	0.258a	0.241a	1.667a	0.498a	4.444b
	U2	0.302a	0.359a	1.877a	1.094a	6.299b
	U3	0.437a	0.247a	0.822a	0.988a	12.247a
Downward area (D)	D1	0.088ab	0.278a	1.499a	0.601a	4.907b
	D2	0.176a	0.318a	1.163a	0.794a	5.369b
	D3	0.183a	0.422a	1.948a	0.780a	8.075b
Control1	C1	0.126ab	0.323a	2.517a	1.116a	4.444b

There are several regulatory limits of heavy metals concentration in soil and plants have been developing by several organizations and countries. Table 4.6 showed permissible level of heavy metals in soil and plants, in addition to their normal range in barley.

Since there are no exact permissible limits of their levels on soil and plant, mainly in plant which its content depends on its species, soil and plant contents of heavy metals at contaminated site compared with control samples that collected from other uncontaminated sites at Idhna.

Table 4.6: The permissible level of heavy metals in soil and plants

Element	**Alberta tier criteria contaminated soil assessment and remediation- ppm** (Protection, 1994).	**WHO permissible limits- ppm** (WHO, 1996)		**WHO/ FAO and Ewers maximum allowable limits- ppm**		**Allowable range –ppm** (Onyedikachi, Belonwu, et al., 2018)		**Normal range in barley –ppm** (Zeng, Pu, et al., 2018)
	Soil	Soil	Plant	Soil	Vegetation	Soil	Edible plant	
Cd	2	0.8	0.02	3	0.1	0.4-1.9	0.21	-
Zn	120	50	0.6	300	100	50-150	47.4	18-56.8
Cu	80	36	10	100	73	36-75	3	7.2-35
Cr	100	100	1.3	100	-	-	-	0.9-2.1
Pb	50	85	2	100	0.3	15-85	0.43	-
Ni	40	35	10	50	67	-	-	-
Fe	-	-	-	50000	425	-	20	100-412
Mn	-	-	-	2000	500	20-10000	2	23-54

4.4 Bioavailability of Cu and Pb after remediation

In-situ remediation is conducted by application of naturally available amendments at rate of 5% (w/w %), including LECA and clay particles- Huar with neutral or slightly alkaline pH as shown on table 4.7. The used amendments are clayey soil which has high content of iron and aluminum which play important role on adsorption and immobilization of available heavy metals, the physiochemical properties of LECA and Huar shows that, Huar has Fe content significantly ($\alpha = 0.05$) higher than LECA.

LECA is a porous aggregate of expanded clay, and has neutral pH. Its surface is negatively charged due to non- stoichiometric substitution of cations, and that plays important role on heavy metals adsorption as mentioned previously in section 1.4.1.

Table 4.7: Physiochemical properties- pH and Fe- content (ppm) of used amendments

Amendment name	**pH**	**Fe**
LECA	7.72 ±0.05 a	3805.441 ±408.9 b
Huar	7.95 ±0.06 a	6372.007 ±240.86 a

Heavy metals immobilization is affected by their solubility which depends on soil pH. In general, solubility of heavy metals decreases with soil pH increasing as mentioned previously in section 1.3.1. Inorganic fraction of soil is the most responsible for metals sorption, this fraction includes clay minerals with many functional groups and oxide and hydrous oxide of Fe and Al. Soil organic matter (5.64% at B) is also important for heavy metals adsorption and it has charged surface with important functional groups (carboxyl, phenolic, etc). In soil heavy metals usually adsorbed into the surface of soil particles by chemical or physical adsorption. Chemical adsorption is very strong and irreversible, thus, the metal cannot be released to soil solution, and in turn does not mobile. However, physical adsorption is very weakly adsorption and its reversible, which is means, this fraction is exchangeable, and it can be released either by cation exchange or anion exchange mechanisms when pH or redox potential of soil has been changed, and in turn they can be mobile in soil as mentioned in section 1.4.1.

The remediated soil with Huar has significantly ($\alpha = 0.05$) the lowest pH (7.67) than other treatments (table 4.7), whereas LECA maintain the similar pH (7.71) as control (without amendments). The low pH of Huar- remediated soil may have related to its high content of metals such as Fe, which their levels is negatively correlated with soil pH as shown by Pearson correlation coefficient (Table 4.3).

The remediation experiment shows reduction of Cu and Pb bioavailability in comparison with control (without amendments) as shown in table 4.8. The bioavailable fraction of heavy metals according to Community Bureau of Reference (BCR) includes exchangeable and weak acid soluble fraction (Vodyanitskii, 2006).

The concentration of available Cu in Huar- remediated soil (499.85 ppm) was not significantly ($\alpha = 0.05$) differ than its available level in LECA- remediated soil (623.55 ppm), and the bioavailable Cu in both of them is significantly ($\alpha = 0.05$) lower than control. The percentage of Cu reduction based on control for Huar and LECA were 43.9 and 30.1 %, respectively.

For Pb, Huar and LECA are significantly (α = 0.05) effective in reduction of bioavailable Pb in soil in comparison to control. The reduction percentage of Pb by Huar and LECA were 80.9 and 86.8 %, respectively.

Huar and LECA have the same effect in reduction of Cu and Pb bioavailability due to their adsorption by Al, Fe and Mn oxide, which have O_2^-, OH^- or H_2O functional groups. They are more effective in immobilization and stabilization of Pb than Cu, since the used amendments have high adsorption affinity to Pb and produce more stable phase and its solubility under various conditions decreases through precipitation, complexation or adsorption due to their large surface area and high cation exchange capacity, this result match with Bradl, 2004, who found that Pb had the highest adsorption affinity by Mn oxides than Cu.

Table 4.8: Remediated soil pH and its bioavailable content of Cu and Pb (ppm)

Treatment	Applied dose (%)	pH	Cu	Pb
Huar	5	7.67 ±0.03 b	499.85 ±25.54 b	107.38 ±50.27 b
LECA	5	7.71 ±0.01 a	623.55 ±160.12 b	74.47 ±38.00 b
Control	0	7.71 ±0.01 a	891.42 ±23.23 a	562.66 ±312.66 a

5. Conclusion and Recommendations

The sever environmental impacts that associated with intense E-waste burning processes at Idhna spur us to study this site, and analyze physiochemical characteristics of soil and heavy metals contents in plant at burning area and at several surrounding areas. This analysis is a key step for management and remediation of this contaminated area with heavy metals that released from burning of E-waste.

Burning area soils' is highly concentrated with copper, lead and zinc, and the high levels of nickel, copper and iron accumulated in plants in comparison with control. And heavy metals leachability decreased with increased distance away from burning center. Barley can be planted as Ni tolerant plant and used in phytoremediation of Ni in environment. Further study should use barley (*Hordeum vulgare*) as a hyperaccumulator of Ni and study its efficiency in accumulation of Ni and reduction of its total soil concentration.

There is urgent need for heavy metals immobilization and site remediation to decrease their availability for plant for its healthy grow. LECA and Huar are efficient in immobilization and reduction of Cu and Pb bioavailability, and it is cost effective and environmentally sound amendments. It's an easy approach with rapid effects, but it's required regular monitoring of soil conditions such as pH and aeration, since heavy metals remain in soil.

The further study should study the effect of amendments in heavy metals immobilization with different dosage to determine the most optimum rate, in addition to study immobilization efficiency as a function of applying time and pH to determine the optimum remediation conditions to achieve the most effective stabilization of heavy metals.

Aluminum content in contaminated soil and the used amendments was planned to be analyzed, but due to technical problems in Al- lamb for atomic absorption mass spectrophotometer device, and its level should be taken in consideration due to its important role in sorption of heavy metals with functional group at its surface.

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Appendixes

Table A.1: Sources and adverse effects of some heavy metals on contaminated soil and human health and their allowable levels in soil

Heavy metals	**Sources (Wuana and Okieimen, 2011; Li, Zhou et al., 2019)**	**Effects**		**Target value (ppm) (Wuana and Okieimen, 2011)**	**Intervention value (ppm) (Wuana and Okieimen, 2011)**
		On soil (Wuana and Okieimen, 2011)	Human effects (Li, Zhou et al., 2019)		
Lead(Pb)	Metal mining and municipal sewage sludge	Plants don’t take up Pb in large quantities, but lead-dust deposited at plant at high concentration	Renal system damage and neurons damage	35	210
Chromium (Cr)	Electroplating and tanning processes and municipal sewage sludge	At low pH, Cr (III) mobility decreased due to its adsorption to clay particles or iron oxide, while at high pH, its solubility decline due to hydroxide formation.	Itching of respiratory tract, liver diseases, lung cancer and irritation of the skin	20	240
Arsenic (As)	Municipal sewage	Its mobility in soil mainly	Skin cancer and circulatory	----	----

	sludge, animal waste, mining, combustion of fossil fuels and intensive use of pesticides.	depends on content on soil content of iron hydr (oxide) which As binds with it, mainly iron/manganese oxides.	system problems		
Zinc (Zn)	Electroplating, mining and waste combustion	Affect microorganisms and earthworms activity, and delay of organic matter degradation	Gastrointestinal irritation, kidney and liver failure	----	----
Cadmium (Cd)	Pigments of electronic compounds, Lead/ Cadmium batteries, refined petroleum products and fertilizers	Cd mobility increases as soil pH decreases and plant uptakes of Cd takes place	Bone and kidney diseases, lung and prostate Cancer	100	380
Copper (Cu)	Electroplating industry, mining and biosolid	High Cu -soil concentration affects plant growth and crop production	Liver and kidney damage and metabolic disorders	0.3	10

Nickel (Ni)	Mining and metal plating industry and fossil fuel combustion	Soil microorganisms' growth can decline in the presence of Ni, but after that, they develop resistance to Ni. It is not known to accumulate in plants.	Cardiovascular diseases, kidney diseases, lung and nasal cancer	140	720

الملخص

النفايات الإلكترونية هي قضية بيئية عالمية تهدد الحياة البرية وصحة الإنسان والبيئة. تقع قرية إذنا في محافظة الخليل وتستقبل حوالي 200-500 طن من النفايات الإلكترونية يومياً. كل هذه الكمية تحترق في مواقع مختلفة وعشوائية في هذه القرية لاستخراج معادن قيمة. لذلك ، فإن الإطلاق المستمر للعديد من الملوثات مثل المعادن الثقيلة وثنائي الفينيل متعدد الكلور إلى البيئة المحيطة يشكل حاجة أساسية لدراسة وتحديد مدى تلوث التربة ، لذا فإن تحليل المعادن الثقيلة هوخطوة أساسية لتحديد تركيزاتها وتوزيعها في الموقع الملوث.

تم تحليل التربة في منطقة الاحتراق والأراضي الزراعية المحيطة بها لتحديد مستوى المعادن الثقيلة فيها ، بالإضافة إلى تحليل مستواها في النباتات المزروعة في كل منطقة. أظهرت النتائج أن جميع عينات التربة التي تم جمعها من إذنا كانت شديدة التلوث بالنحاس والرصاص والنيكل والزنك ، وكانت منطقة الاحتراق أعلى مستوى في مركزها مع تناقص المحتوى بالنسبة لبعدها عنها.

كان متوسط تركيز النحاس والرصاص والزنك والنيكل في تربة المنطقة المحترقة 10392.860 و 1892.150 و 2503.170 و 699.170 جزء في المليون على التوالي وهو مرتفع للغاية مقارنة بمجموعة التحكم. كان محتوى النباتات البرية التي نمت هناك من النحاس والزنك والنيكل والحديد 802.830 و 334.906 و 2981.554 و 2573.301 جزء في المليون والتي تزيد عن 10.834 و 125.937 و 2066.695 و 517.402 جزء في المليون على التوالي في النباتات في منطقة التحكم.

أظهرت التراكيز المرتفعة للمعادن الثقيلة في الموقع المدروس وتراكمها العالي في براعم النباتات الحاجة الملحة لمعالجة هذا الموقع. تم استخدام مجاميع الطين الخفيفة (LECA) وجزيئات الطين المسماة محليًا "الحور" لتقليل التوافر البيولوجي للنحاس والرصاص في التربة الملوثة. أظهرت النتائج أن كلا الماصتين تعمل معنويا ($\alpha = 0.05$) على تقليل من النحاس والرصاص المتوفر حيويا في التربة مقارنة بالعينة التحكم ، وأن الرصاص لهما أعلى توجه للامتصاص من النحاس. كانت النسبة المئوية لتخفيض النحاس والرصاص على أساس التحكم بواسطة الحور 43.9 و 80.9٪ على التوالي.

الكلمات المفتاحية: المعادن الثقيلة ، النفايات الإلكترونية ، التربة ، النبات ، التلوث ، التحليل ، المعالجة.