ASSESMENT OF HEAVY METAL POLLUTION IN SOILS AND SELECTED CEREAL CROPS GROWN AROUND MUGHER AND ABYSSINIA CEMENT FACTORIES, ETHIOPIA

By

Yohannse Habteyesus

A Thesis Submitted to

Department of Applied Chemistry

School of Applied Natural Science

Presented in Partial Fulfillment of the Requirement for the Degree of Masters of Science in Chemistry (Analytical Chemistry)

Office of Graduate Studies

Adama Science and Technology University

Adama

December, 2017

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APPROVAL OF BOARD OF EXAMINERS

We, the undersigned, members of the Board of Examiners of the final open defense by **Yohannse Habteyesus** have read and evaluated his thesis entitled "**Assessment of heavy metal pollution in soils and selected cereal crops grown around Mugher and Abyssinia cement factories, Ethiopia**" and examined the candidate. This is, therefore, to certify that the thesis has been accepted in partial fulfillment of the requirement of the Degree of Masters of Science in Chemistry (Analytical Chemistry)

Eshetu Bekele (PhD)	_____	_____
Advisor	Signature	Date
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_____	_____	_____
Internal Examiner	Signature	Date
_____	_____	_____
External Examiner	Signature	Date

DEDICATION

To the farmers of Ethiopia!

BIOGRAPHIICAL SKETCH

The author was born on 19 September 1988 in North Showa and attended his high school and preparatory education at Woldia and Debrebrihan comprehensive school respectively. He joined Arba Mininch University in 2006 and graduated with B.Sc Degree in Applied Chemistry in 2009. After graduation, the author had worked in Ethiopia Institute of Agricultural Research as Assistance Researcher in the department of Agricultural and Nutritional Research Laboratories in Holetta. He joined Adama Science and Technology University, department of Applied Chemistry in 2016 to pursue his postgraduate studies in Chemistry (Analytical Chemistry).

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ACCRONYMS AND ABBRIVATION

AAS	Atomic Absorption Spectroscopy
BD	Bulk density
CEC	Cation Exchange Capacity
cmol	Centi mol
dS	Deci-Simens
DI	de-ionized water
AB-DTPA	Ammonium Bicarbonate-Diethylene Triamine Penta Aceticacid
EC	Electric Conductivity
HMs	Heavy metals
Igeo	Geo-chemical index
OC	Organic Carbon
PSA	Particle Size Analysis
TN	Total Nitrogen
SD	Standard Deviation
RSD	Relative Standard Deviation

Abstract

Different researches showed that cement manufacturing is one of the significant sources of heavy metal pollution in soil through precipitation and fallout. In this study, heavy metals pollution in soils and selected cereals (wheat and barley) grown around Mugher and Abyssinia cement factories were investigated. The level of heavy metals from factory effluents also investigated in the Mugher location. A total of 72 soil samples from 0-20cm & 20-40cm depths at different distance from the factory (0-500m, 500-1500m & ≈4000m),44 cereal samples (wheat and barley) and effluents sample were collected and analyzed at Holeta agricultural chemistry laboratory. The parameters analyzed includes: Available Heavy Metals using Ammonium Bicarbonate-Diethylene Triamine Penta Aceticacid extraction, total Heavy Metals after HNO_3-$HClO_3$ digestion and major physico-chemical properties (TN, Oc, K, P, pH, Moisture, soil texture, Bulk density,SO_4-S and Cation exchange capacity). Dry ashing method was used to determine the level of heavy metals in cereal samples. Heavy metals from effluents analyzed after HNO_3 digestion. Analysis for the concentration of heavy metals; Cu, Cr, Mn, Cd, Fe, Pb, As and Zn were conducted using AAS. One-way ANOVA were used to compare the mean values between treatments (distance b/n the factory) with SPSS statistical software. The Geo-accumulation Index and transfer factor of each heavy metal were computed and interpreted. Except to Pb in Mugher site, the Igeo values are below zero indicates that the soil quality is practically unpolluted. Cd and As were not detected in any of the cereals, soils and effluent samples. The results in soil physico-chemical properties showed that neutral to moderately alkaline soil pH, clay to clay loam soil texture, medium to high category of phosphorus, nitrogen, and potassium; Higher in soil bulk density nearer to the factory. The cement dust therefore effluence to enhance the pH level to the alkaline, as a result the contents of major soil physico-chemical properties declines near to the factory (in Mugher location). Heavy metals level from factory effluent, Mugher location, of Cu, Mn and Cr are above the permissible limit set by FAO use for irrigation activities. The factory therefore should be subject to mandatory monitor and control emanates cement dust & effluent before released to the environment. The values of heavy metals transfer factors from soil to crops are below one indicates that the crops have not influenced by metal pollutions by uptake heavy metals from cement dust polluted areas. The levels of heavy metals determined in the analyzed cereal samples also found to be below the permissible limit set by FAO/WHO; hence, the concentration of these heavy metals in the selected cereals analyzed, may not presently pose a health hazard and can as well serve as sources of essential trace metals to the population.

Key words: *Heavy metals, Atomic Absorption Spectrometer, pollution indices, transfer factor*

CHAPTER ONE

INTRODUCTION

1.1. BACK GROUND AND JUSTIFICATIONS

Environmental pollution related to urbanization and industrialization is inevitable unless proper measures are taken. Air pollution is one of the serious problems in recent times as a result of rapid increase in number of vehicles, cement factories, steel and coal industries and petrochemical industries coupled with deforestation of natural forest. In comparison to the effect of gaseous pollutants on the air quality, little attention is given to the effect of particulate pollutants on soil and vegetation properties [1, 2]. Globally, the problem of environmental pollution due to heavy metals has been a concern in most cities for it leads to geoaccumulation, bioaccumulation and biomagnifications in ecosystem [2]. Due to the increasing trends of heavy metals contamination in the environment and their negative impact on plants and other organisms, it is important to mitigate the toxicity of heavy metals from the environment which has become a burning issue.

Heavy metals enter the surroundings by natural means and through human activities. It is projected that the anthropogenic emission into the atmosphere is one-to-three orders of magnitude higher than natural fluxes [3]. The emission of anthropogenic heavy metal compounds causes considerable changes in biogeochemical cycles of some elements. Increasing industrialization and urbanization had anthropogenic contribution of heavy metals in biosphere and had largest availability in soil and to a relatively smaller proportion in atmosphere as particulate or vapors [4]. They are different sources of heavy metals in agricultural fields and corresponding crops; its availability to plants is due to mining activities, industrial exhausts & effluents, atmospheric depositions, waste disposals and agro-chemicals [5-8]. All sources of heavy metals can be divided into five categories as follows [9]:- 1, **geochemical sources**: in geological terms, heavy metals are included in the group of elements referred to as (trace metals) which together constitute less than 1% of the rocks in the earth crust; the macro elements (O, Si, Al, Fe, Ca, Na, K, Mg, Ti, H, p and S) comprise 99% of the earth crust. The natural enrichment of metals in the soils may still give rise to harmful effect to living organisms. 2, **agriculture**

material: agriculture constitutes one of the most important non-point sources of metals pollutants; the main sources are (impurities in fertilizers, pesticides, disscants, wood preservative, wastes from intensive pig and poulty productions, composts and manures, sewage sludge. 3, **metallurgical industries**. 4, **waste disposal**. 5, **other sources** in manufacture and disposal (include: batteries, pigments and paints, catalysts, polymer stabilizers, additive in fuels and lubricants).

Soil is of major importance for life since it represents a source of both water and nutrients for plants and soil-living microorganisms and animals. Metals and metalloids are significant natural components of all soils where their presence in the mineral fraction comprises a store of potentially-mobile metal species as important components of clays, minerals and iron and manganese oxides that, in turn, have a dramatic influence on soil geochemistry [10]. Metals are also present in the organic fraction, frequently as bound forms, with some metal recycling occurring as a result of organic matter decomposition. The aqueous phase provides a mobile medium for chemical reactions, metal transfer and circulation through the soil, to organisms, and also to the aquatic environment. Heavy metals and metalloids can be involved in a series of complex chemical and biological interactions. The most important factors which affect their mobility are pH, sorbent nature, presence and concentration of organic and inorganic ligands, including humic and fulvic acids, root exudates and nutrients. Furthermore, redox reactions, both biotic and abiotic, are of great importance in controlling the oxidation state and thus, the mobility and the toxicity of many elements, such as Cr, Se, Co, Pb, As, Ni and Cu.

The contamination of soil by heavy metals can be problematic on several levels because they do not degrade biologically, poses risks to humans and animals through ingestion of plants that have bio-accumulated toxic metals from contaminated soil [11]. These heavy metals may adversely affect soil ecology, agricultural production or product quality, and will ultimately harm to health of living organism by food chain. More detailed analyses showed that chemical properties of metals in soil and their retention in the solid phase of soil is affected by pH, quantity of the metal, cation-exchange capacity, content of organic matter and mineralogy of soil. Changes in chemical properties of soils affect concentration of free metals and result in changes in their availability for plants. With increasing pH, content of organic matter and clay the solubility of

most metals decreases due to their increased adsorption. The decreased availability of metals is affected by higher adsorption and precipitation in alkaline and neutral environments [12].

Cereal crops are mostly grown in temperate and tropical regions of the world and provide more food energy worldwide than any other type of crop. In Ethiopia, the most commonly cultivated crops are wheat, maize, barley, sorghum and rice. Its derived products are rich in carbohydrates, fiber, trace minerals, vitamins, and therefore, the base of a well balanced and healthy diet [13]. Cultivation of crops for human or livestock consumption on contaminated soil can potentially lead to the uptake and accumulation of trace metals in the edible plant parts around industrial areas with a resulting risk to human and animal health [14-16]. Metal contaminated soil poses risks to humans and animals through ingestion of plants that have bio-accumulated toxic metals from contaminated soil [17, 18]. These heavy metals may adversely affect soil ecology, agricultural production or product quality, and will ultimately harm to health of living organism by food chain.

Heavy metal toxicity in plants varies with plant species, specific metal, concentration, chemical form and soil composition and pH, as many heavy metals are considered to be essential for plant growth. Some of these heavy metals like Cu and Zn either serve as cofactor and activators of enzyme reactions [19]. Heavy metals such as Co, Cu, Fe, Mn, Mo, Ni, V, and Zn are required in minute quantities by organisms, excessive amounts of these elements can become harmful to organisms. Heavy metals such as Pb, Cd, Hg, and as (a metalloid but generally referred to as a heavy metal) do not have any beneficial effect on organisms and are thus regarded as the “main threats” since they are very harmful to both plants and animals, pollutant in the environment air, water and soil, may be poisonous or toxic and will cause harm to living things. Metals accumulate in ecological food chain through uptake at primary producer level and then through consumption at consumer levels and plants roots are the primary contact site for heavy metal ions. Whereas, in aquatic systems plant body is exposed to these ions and heavy metals are absorbed directly to the leaves due to particles deposited on the foliar surfaces.

Many research investigated the impact of the cement dust on soil properties, plant growth and a contamination source of heavy metals [20-26]. Air pollutants such as heavy metals, generated in the process of crushing limestone, bagging, and transportation of cement are carried by wind and deposited on soil, plants and water bodies [27].The dust deposition from cement factory influenced by wind velocity, particle size, and stack fumes. Among the metals especially recognized in environmental studies on emission from cement plants to have toxic effect on soil are arsenic, cadmium, lead, mercury, thallium, aluminum, beryllium, chromium, copper, manganese, nickel and zinc [26]. Arpita and Mitko (2011)[28] reported that top soils near a cement factory are enriched in Pb, Zn, Cr, Cd, V, Pb and Hg which are released into the air from the cement kilns.. The results of elementary chemical analysis, expressed in weight percent of oxides, conducted by (Young-Chull and Jae-Min, 2004) [29] showed that the raw material dust of the first grinding process primarily consisted of CaO (41.77), SiO_2 (11.72%), Al_2O_3 (3.45%), and Fe_2O_3 (1.47%). (Samuel and Aynalem, 2012) also reported that two soil depths (0-5 cm & 5-15 cm) are similarly categorized as moderately to heavily contaminated on the level of heavy metals around Messebo cement factory, Ethiopia.

Many instrumental analytical methods may be employed to measure the concentration level of heavy metals in various samples. The most predominant techniques are atomic absorption spectrometry (AAS); atomic emission/ fluorescence spectrometry (AES/AFS); inductively coupled plasma mass spectrometry (ICP-MS); inductively coupled plasma optical emission spectrometry (ICP-OES); neutron activation analysis (NAA), X-ray fluorescence (XRF); and anodic striping voltammetry (AVS). Various digestion methods are used to determine the mass concentration of trace elements in solid matrices [30]. Such digestion methods have been through the use of fluxes or inorganic acids such as HCl, H_3PO_4, HNO_3, $HClO_4$, HF, H_2SO_4 or their combination. These acids exhibit various peculiar properties which enables each acid to carry out specific functions during extraction [31].

Determining the physicochemical properties of soil, their trace metal content and the level of heavy metals in cereals is therefore important to monitor environmental pollution related to cement industries.

1.2. STATEMENT OF THE PROBLEM

The institute of Ethiopia Agricultural Research, department of Agricultural Chemistry has different mandates doing researches to solve the problem of the Ethiopian farmers. As far as we do researches relative to the quality of agricultural products, we had assessed information through survey on pollution of environment. One of the major survey result showed that the farmers compliant on the emission of cement dust from cement factories. The deposition of cement dust over the catchment was therefore very noticeable and of serious concern to the local community. Further assessments were followed by interviews from woredas' agricultural expertise, physical observation of cement dust polluted fields and cereal crops. Though then extensive literatures searched on the impact of cement dust pollution, many research investigated the impact of the cement dust on soil properties and plant growth. Many researches investigate the level of total forms of heavy metals rather than the available forms in soil and further extensive researches have shown no studies under taken in the level of heavy metals around Mugher and Abyssinia cement factories. This research therefore aimed on the investigation of heavy metals (available + total) levels in soil. In the study areas, around cement factories, cereals (especially wheat and barley) are dominantly harvested crops by the local farmers.

1.3. OBJECTIVES

1.3.1. General objective

- The main objective of this study was to investigate the level of heavy metals in selected cereal crops and soils around cement factories (Mugher and Abyssnia), central Ethiopia

1.3.2. Specific objectives

- To determine the level of heavy metals (Fe, Mn, Cu, Zn, Cd, As, Cr and Pb) in major cereal crops (wheat and barley) and in soils on which these crops grown
- To evaluate major physico-chemical properties of soil (pH, EC, Moisture, BD, TN, P, K, Oc, S, CEC and Soil texture) with respect to soil depths (0-20 cm and 20-40 cm)

- To investigate how the changes in soil physico-chemical properties due to pollutants from cement factories affects the level of heavy metals in cereal crops and soil around these factories

1.4. SIGNIFICANCE OF THE STUDY

The result of this study provide useful baseline information regarding to the level of heavy metals in soil, selected cereal crops and the major soil physico-chemical properties of the study areas. The factories also use the information to take attentions to regulate the deposition of cement dust that fallout to soil and plants.

CHAPTER TWO

LITRATURE REVIEW

2.1. HEAVY METALS AND SOURCES

The category of "heavy metals" includes several elements Cd, Cu, Cr, Co, Fe, Hg, Mn, Mo, Ni, Pb, Zn, to be defined by their metallic properties (conductivity, ductility and stability as cations), atomic number greater than 20 and density greater than 5.6 kg/dm^3 .They are persistent and non-biodegradable, have a long biological half-lives and they can be bio-accumulated through the biologic chains. Their existence is mainly due to anthropogenic sources such as industrial and agricultural activities [32]**.** Once liberated into the environment through the air, drinking water, food, or countless varieties of man-made chemicals and products, heavy metals are taken into the body via inhalation, ingestion and skin absorption. If heavy metals enter and accumulate in body tissues faster than the body's detoxification pathways can dispose off, then a gradual build-up of these toxins occurs. High concentration exposure is not a necessity to produce a state of toxicity in the body, as heavy metal accumulation occurs in body tissues gradually and, over time, can reach toxic concentration levels, much beyond the permissible limits [33]**.**

Heavy metals enter the surroundings by natural means and through human activities. Various sources of heavy metals include soil erosion, natural weathering of the earth's crust, mining, industrial effluents, urban runoff, sewage discharge, insect or disease control agents applied to crops, and many others [34]. Heavy metal contamination may occur due to factors including irrigation with contaminated water, the addition of fertilizers and metal based pesticides, industrial emissions, transportation, harvesting process, storage and/or sale [35, 36].

The heavy metals essentially become contaminants in the soil environments because (i) their rates of generation via man-made cycles are more rapid relative to natural ones, (ii) they become transferred from mines to random environmental locations where higher potentials of direct exposure occur, (iii) the concentrations of the metals in discarded products are relatively high compared to those in the receiving environment, and (iv) the chemical form (species) in which a metal is found in the receiving environmental system may render it more bio-available [37].

A simple mass balance of the heavy metals in the soil can be expressed as follows [38, 39]:

$$Mtotal = (Mp + Ma + Mf + Mag + Mow + Mip) - (Mcr - Mi)$$

where “M” is the heavy metal, “p” is the parent material, “a” is the atmospheric deposition, “ f ” is the fertilizer sources, “ag” are the agrochemical sources, “ow” are the organic waste sources, “ip” are other inorganic pollutants, “cr” is crop removal, and “l” is the losses by leaching, volatilization, and so forth.

Heavy metals in the soil from anthropogenic sources tend to be more mobile, hence bio-available than pedogenic, or lithogenic ones [40]. Metal-bearing solids at contaminated sites can originate from a wide variety of anthropogenic sources in the form of metal mine tailings, disposal of high metal wastes in improperly protected land fills, leaded gasoline and lead-based paints, land application of fertilizer (trace amounts of heavy metals as impurities), animal manures, biosolids (sewage sludge), compost, pesticides, waste water (such as: sanitary sewage, chemical waste water, industrial mining waste water and urban mining mixed sewage). coal combustion residues, petrochemicals, and atmospheric deposition (airborne sources of metals include stack or duct emissions of air, gas, or vapor streams, and fugitive emissions such as dust from storage areas or waste piles) [41]. Table 1 also shows various sources of heavy metals contaminating soils in the world.

Table 1: Different sources of HMs contaminating soils annually in the world (1000 t • a^{-1}) [42]

Sources	**As**	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
Agriculture and food waste	0~0.6	0~0.3	4.5~90	3~38	0~1.5	6~45	1.5~27	12~150
Farmyard manure	1.2~4.4	0.2~1.2	10~60	14~80	0~0.2	3~36	3.2~20	150~320
Logging and timber Industry wastes	0~3.3	0~2.2	2.2~18	3.3~52	0~2.2	2.2~23	6.6~8.2	13~65
Municipal wastes	0.09~0.7	0.88~7.5	6.6~33	13~40	0~0.26	2.2~10 7	18~62	22~97
Municipal sludge	0.01~0.24	0.02~0.34	1.4~11	4.9~21	0.01~0.8	5.0~22	2.8~9.7	18~57
Organic wastes	0~0.25	0~0.01	0.1~0.48	0.04~0.61	-	0.17~3.2	0.02~1.6	0.13~2.1
Metal processing solid wastes	0.01~0.21	0~0.08	0.65~2.4	0.95~7.6	0~0.08	0.84~2.5	4.1~11	2.7~19
Coal ash	6.7~37	1.5~13	149~446	93~335	0.37~4.8	56~279	45~242	112~484
Fertilizer	0~0.02	0 .03~0.25	0.03~0.38	0.05~0.58	-	0.20~3.5	0.4 2~2.3	0.25~1.1
Marl	0.04~0.5	0~0. 11	0.0 4~0.19	0.15~2.0	0~0.02	0.22~3.5	0.45~2.6	0.15~3.5
Commodity impurities	36~41	0.78~1.6	305~610	395~790	0.55~0.82	6.5~32	195~390	310~620
Atmospheric deposition	8.4~18	2.2~8.4	5.1~38	14~36	0.63~4.3	11~37	202~263	49~135
Total	**52~112**	**5.6~38**	**484~1309**	**541~1367**	**1.6~15**	**106~544**	**479~1113**	**689~2054**

2.2. HEAVY METAL POLLUTIONS IN SOIL AND PLANTS

Soil is of major importance for life since it represents a source of both water and nutrients for plants and soil-living microorganisms and animals. Quantitatively, micronutrients are negligible constituents of soils, but the concentrations and availability of these nutrients are still of great importance for plant development and for obtaining high yields in crop production. Soil micronutrients are derived from minerals in the geological parent material, where the composition of the bedrock, the texture and the degree of weathering of the mineral soil have a large influence on the amount of micronutrients stored and released. In addition to these background concentrations, total micronutrient concentrations in arable soils are influenced by anthropogenic inputs such as mineral and organic fertilizers, liming products, agrochemicals and atmospheric deposition.

Metal contaminated soil poses risks to humans and animals through ingestion of plants that have bio-accumulated toxic metals from contaminated soil [43]. Crops grown in soils contaminated with heavy metals have greater accumulation of heavy metals than those grown in uncontaminated soil [44].The rate at which heavy metals are accumulated in the soil depends on the physiochemical properties of the soil and the relative efficiency of crops to remove the metals from the soil [45]. Metals from soil enter plants primarily through the root system and concentrate in tissues of plants which are often proportional to levels in soils on which they are cultivated. Differences in accumulation among plants are dependent on sensitivities of plants to adverse effects and magnitude and duration of exposure, presence or absence of nutrients and other chemical species in soil that are determinants of the bio-available fraction [46].

The heavy metals that are available for plant uptake are those that are present as soluble components in the soil solution or those that are easily solubilized by root exudates [47]. Although plants require certain heavy metals for their growth and upkeep, excessive amounts of these metals can become toxic to plants. The ability of plants to accumulate essential metals equally enables them to acquire other nonessential metals [48]. As metals cannot be broken down, when concentrations within the plant exceed optimal levels, they adversely affect the plant both directly and indirectly.

Some of the direct toxic effects caused by high metal concentration include inhibition of cytoplasmic enzymes and damage to cell structures due to oxidative stress [49]. An example of indirect toxic effect is the replacement of essential nutrients at cation exchange sites of plants [50]. Further, the negative influence heavy metals have on the growth and activities of soil microorganisms may also indirectly affect the growth of plants. For instance, a reduction in the number of beneficial soil microorganisms due to high metal concentration may lead to decrease in organic matter decomposition leading to a decline in soil nutrients. These toxic effects (both direct and indirect) lead to a decline in plant growth which sometimes results in the death of plant [51].

It is important to note that certain plants are able to tolerate high concentration of heavy metals in their environment. Baker, 2001[52] reported that these plants are able to tolerate these metals via three mechanisms, namely, (i) exclusion: restriction of metal transport and maintenance of a constant metal concentration in the shoot over a wide range of soil concentrations; (ii) inclusion: metal concentrations in the shoot reflecting those in the soil solution through a linear relationship; and (iii) bioaccumulation: accumulation of metals in the shoot and roots of plants at both low and high soil concentrations.

2.3. MOBILITY AND BIOAVAILABILITY OF HEAVY METALS IN SOIL ENVIRONMENTS

The biogeochemical cycle of heavy metals has been greatly accelerated by human activities. Accumulation of metal ions in different compartments of the biosphere, and their possible mobilization under environmentally changing conditions induce a perturbation of both the structure and function of the ecosystem and might cause adverse health effects to biota [53]. Heavy metals enter an agroecosystem through both natural and anthropogenic processes. Some soils have been found to have a high background of some trace elements, which are toxic to plants and wild life, due to extremely high concentrations of these elements in the parent materials. Anthropogenic processes include inputs of heavy metals through use of fertilizers, organic manures, and industrial and municipal wastes, irrigation, and wet and/or dry deposits. These processes contribute with variable amounts of heavy metals to the agroecosystem. Only a small portion of heavy metals in soil is bioavailable. The mobility and availability of these

pollutants are controlled by many chemical and biochemical processes such as precipitation–dissolution, sorption– desorption, complexation-dissociation, and oxidation–reduction. Not all the processes are equally important for each element, but all of them are affected by soil pH and biological processes. Therefore, it is crucial to understand some major reactions in soils that control the release of a specific trace element in the soil and the environment in order to overcome problems related to deficiency and contamination of these elements.

The bioavailability of heavy metals, their biological uptake, and their eco-toxicological effects on the soil biota can be better understood in terms of their chemical speciation. The mobility and bioavailability, and hence potential toxicity of metal in the soil depend on its concentration in soil solution, the nature of its association with other soluble species, and soil ability to release the metal from the solid phase to replenish that removed from soil solution by the plants [54, 55]. Mobility and plant uptake of trace elements proceed through the solution phase. However, plant uptake of an element depends not only on its activity in the solution, but also on the relation existing between solution ions and solid phase ions. Plants take up essential and nonessential elements from soils in response to concentration gradients inducted by selective uptake of ions by roots, or by diffusion of elements in the soil. The accumulation level of heavy metals differs between and within species [56]. A number of biochemical reactions occur in plants stressed by heavy metals. Most of these reactions are produced by the displacement of protein cationic centres or the increase of reactive oxygen species. Those plants with better ability to adjust to toxicity effects are able to survive in heavy metal/metalloids impacted sites.

2.4. FACTOR AFFECTING THE LEVEL OF HEAVY METALS IN SOIL AND PLANT

The concentration of heavy metals in soil is influenced by various physicochemical characteristics of soil such as pH, particle size distribution, organic matter, cation exchange capacity, and moisture content of the soil [57]. The method of binding heavy metals, and hence their bioavailability, depends on several soil properties, which include [58]: Organic matter content, granulometric composition, occurrence and form of cations, pH value, content of macro and micronutrients, oxidation-reduction potential, activity of microorganisms, bioavailability for plants. Soils having granulometric composition characteristic for clay, silt and dust, and those with a high content of organic matter, have a high sorption capacity and a strong

ability to bind metallic elements [59]. Soil pH is a major determinant of metal mobility in the soil, as pH decreases the solubility of the metal cation increases due to desorption from soil minerals such as carbonates, metal oxides and hydroxides [60]. The increase of hydrogen ion concentration affects the mobilization intensity of heavy metals. In highly acidic soils, the mobility of metallic elements is much higher than in soils with neutral and alkaline reaction. Mobility of metals in soils with low pH decreases in the order: Cd > Ni > Zn > Mn > Cu > Pb [61].

The transfer and accumulation of the heavy metals into the plant organs is usually substantially influenced by various factors: primarily by heavy-metal content in soil and by soil characteristics (e.g. the mould and clay minerals content), by soil reaction, by cation exchange capacity, or by Ca / Mg content ratio [62]. Absorption of heavy metals by plants depends largely on the mechanical composition of soils. Heavy soils, as compared to light soils, due to large amounts of suspended fraction, have a greater ability to retain metallic elements. On the other hand, light soil does not have such ability of sorption. At a comparable state of heavy metal pollution, it may contain metals in dissolved form, easily available for plants. Light soils are also more susceptible to acidification, which is an additional factor causing metallic elements to run in them [63]. Increasing the amount of organic matter in the soil, helps to minimize the absorption of heavy metals by plants. The binding of heavy metals by organic matter is a complex process, due to the diversity of its connections with the mineral phase. Sorption capacity of organic matter is well above the mineral sorption capacity of the soil [64].

2.5. IMPACTS OF CEMENT EMISSIONS IN ENVIRONMENT AND SOIL AVAILABLE MICRONUTRIENTS

The cement industry is an energy intensive and significant contributor to climate change. The major environment health and safety issues associated with cement production are emissions to air and energy use. Cement manufacturing requires huge amount of non renewable resources like raw material and fossil fuels. It is estimated that 5-6% of all carbon dioxide greenhouse gases generated by human activities originates from cement production [65]. Raw material and Energy consumption result in emissions to air which include dust and gases. The exhaust gases from a cement kiln contains are nitrogen oxides (NOx), carbon dioxide, water, oxygen and small

quantities of dust, chlorides, fluorides, sulfur dioxide, carbon monoxide , and still smaller quantities of organic compounds and heavy metals [66]. Toxic metals and organic compounds are released when industrial waste is burnt in cement kiln. Other sources of dust emissions include the clinker cooler, crushers, grinders, and materials-handling equipment. These emissions are not only deteriorating air quality but also degrading human health. Emissions have local and global environment impact resulting in global warming, ozone depletion, acid rain, biodiversity loss, reduced crop productivity etc [67]. Scientific evidence indicates that air pollution from the combustion of fossil fuels causes a spectrum of health effects from allergy to death [68]. The results of several studies showed that these emissions are adversely affecting human health in a variety of ways, like itchy eyes, respiratory diseases like tuberculosis, chest discomfort, chronic bronchitis, asthma attacks, cardio-vascular diseases and even premature death [69].

2.6. TOXICITY OF HEAVY METALS

Heavy metals toxins contribute to a variety of adverse health effects. These exit over than 20 different heavy metals toxins that have impacts on human health. Excessive content of metals i.e. beyond maximum permissible level leads to number of nervous, cardiovascular, renal, neurological impairment as well as bone diseases and several other health disorders [70]. The degree to which a system organ tissue or cell is affected by a heavy metal toxin depends on the toxin its self and the individuals degree of exposure to the toxin [71]. The toxicity of heavy metals can be listed in order of decreasing toxicity as Hg> Cd> Cu> Zn> Ni> Pb> Cr> Al> Co, also this is only approximate as the vulnerability of species to individual metals varies. Heavy metal-polluted food can severely reduce some vital nutrients in the body that are accountable for declining immunological defenses, growth delay, reduced psychosocial abilities, incapacities related with malnutrition and greater occurrence of upper gastrointestinal cancer degrees [72]. Metals are non-decomposable and are recognized as main environmental contaminants causing cytotoxic, mutagenic and cancerous (carcinogenic) effects in animals [73].

CHAPTER THREE

MATERIALS AND METHODS

3.1. DESCRIPTION OF THE STUDY AREAS

The first study area is in Mugher, around Mugher cement factory, which is located 90 km North West of Addis Ababa. It lays at an elevation of 2450 m above sea level. The average wind speed at a height of 10 m above ground level was 1.0 km/h between October- November and 0.72 Km/h between April- May [74].The farmers around in this area harvests cereal crops such as wheat, barley, teff and sorghum once in a year from October to November. The second study site is in Chancho, around Abyssinia cement factory, which is located 40 km north of Addis Ababa. It lays at an elevation of 2500 m above sea level. In this study area barley, wheat and teff are dominant cereal crops that harvests in November once in a year.

Three treatments (0-500 m, 500-1500 m and ≈4000 m from the factory), twelve cereal fields (barley and wheat field) were chosen. The treatment selection was carried out based on the availability of selected cereal samples, proximity to the study areas and the probabilities of prevalence of dust particles depositions. The approximate to 4000m from the factory were considered as a control.

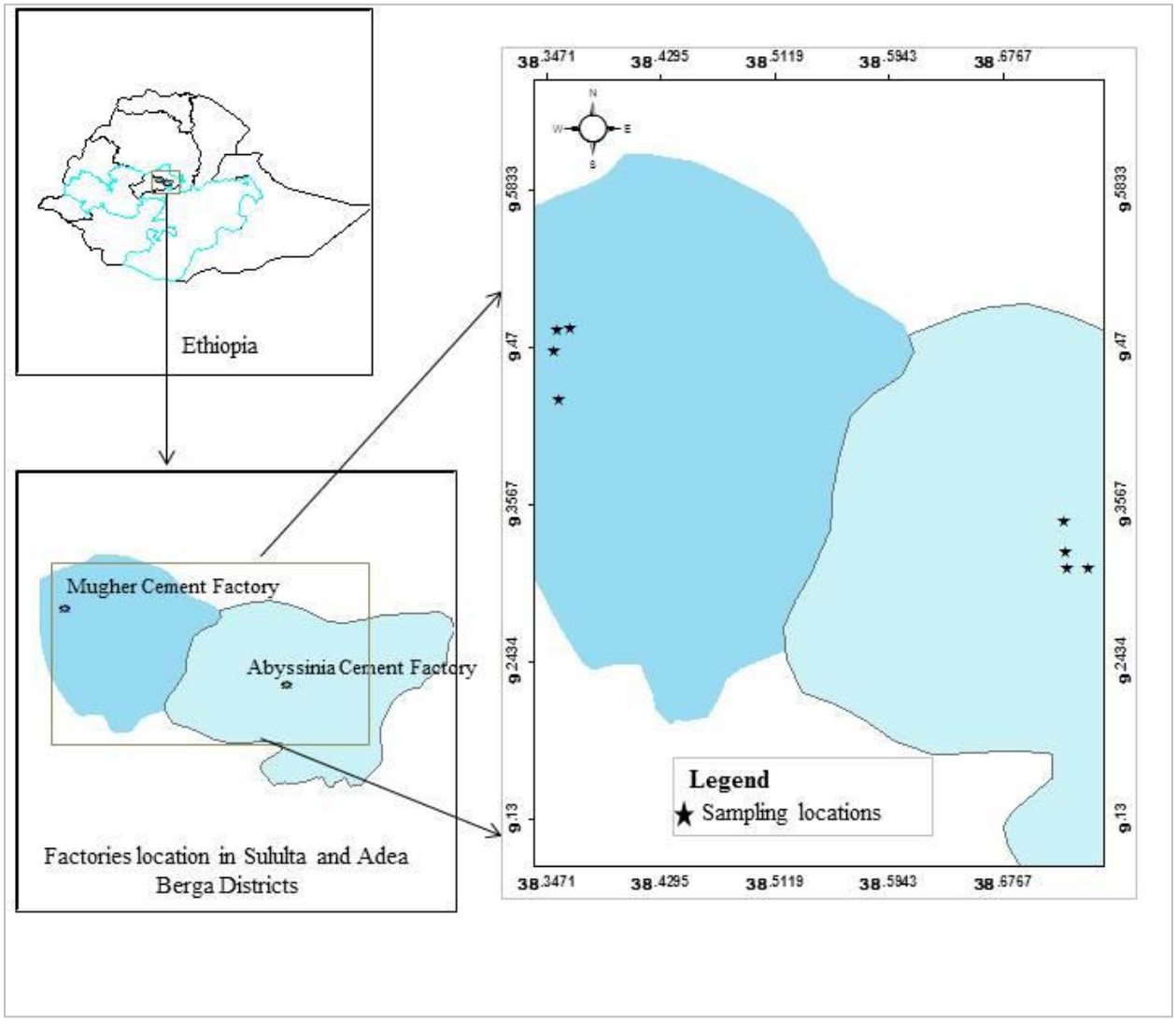

Figure 1: Location map of the study areas, North and West Shewa Zones, Oromiya region, Ethiopia.

3.2. INSTRUMUMENTS, CHEMICALS AND REAGENTS

3.2.1. Instruments and apparatus

The instruments and apparatus that used in this study were: Atomic Absorption spectrophotometer (Agilent, 200 Series AAS), spectro photometer (Janway 6300), pH meter (HI 9017 microprocesser HANNA),conductivity meter (Janway 4310), Muffle furnece (for crop sample ashing), drying oven (for drying crop & soil samples), reciprocal shaker (shak soil for extractable heavy metals), analytical balance (0-210 g, 0.0001 readiblity), pistel and mortar (for grinding soil sample), grinding machine (for grinding crop sample).

3.2.2. Chemicals and reagents

The list of chemicals that used in this study were: Nitric acid (HNO_3, AR, MW:63.01, assay: 52.5-55%), Sulfuric acid (H_2SO_4, AR, MW:98.07, assay: > 95%), Perchloric acid ($HClO_4$,AR, MW:100.46, assay: 60-62%), Hydrochloric acid (HCl, AR, MW:35.5, assay:35-37%), Sodium hydro oxide pellets (NaOH, AR, MW: 40, assay: > 98%), Boric acid (HBO_3, AG, MW: 61.8, assay: > 99.8%), Potassium dichromate ($K_2Cr_2\ O_7$, AR, MW:294.19, assay: > 99.9%), Ammonium acetate ($C_2H_7NO_2$, MW: 77.08, assay: >97%), Ethyl alcohol(C_2H_5OH, assay:> 95%), Ammonium bicarbonate ($NH_4\ HCO_3$, AR, MW: 79.06, assay:> 99%), Sodium bicarbonate ($NaHCO_3$, MW:84.01, assay:> 99.5%), Ammonium molybdate ($(NH_4)_6Mo_7O_{24}.4H_2O$, AR, assay: > 99.7%), Ascorbic acid ($C_6H_8O_6$, MW: 176.12, assay: 99.7%), pH buffer solutions (NIST Buffer color coded a tolerance of ± 0.02 pH Units at 20°C), 1000 mL heavy metals stock solutions(for each metals: Fe, Cu, Mn, Zn, Pb, Cr, As and Cd)

3.3. SAMPLE COLLECTIONS

3.3.1. Soil sample collections

The soil samples were collected at the time of harvesting cereal crops in December 2016. The cement dust deposition is NW-SE wind directions, considering this; random sampling techniques were followed to collect soil samples in the treatments of: 0-500 m, 500-1500 m and ≈4000 m from the factories regards to the cement dust concentration gradients. Soil samples collected from 0-20 cm (consider crop growth, deposition of the cement dust and nutrient uptake) and 20-40 cm (consider as a control & to see the variation from the top soil) depths. About 1 kg soil

sample from each spots were taken using auger in polyethylene bags and core samplers used for bulk density sampling in separate. Four spot samples from the eight polluted fields, composite samples from the four control fields a total of 72 soil samples (36 samples per location) were collected. Every sample was coded properly, the sample bags marked with codes using permanent marker. All the sample information regarding sampling locations, source, date of collection and allotted codes were recorded in the observation register and brought to Holetta Agricultural Research laboratory for preparation and analysis.

3.3.2. Cereals sample collections

Before sowing at the time of harvesting, a total of 44 cereals crops (22 samples per cereal and location) were collected from the spots of soil samples taken (i.e. about 100g, five sample each from the eight cement dust fields and four composites from the control fields). Polyethylene bags were used to store the collected sample and brought to Holetta Agricultural Research laboratory for preparation and analysis.

3.3.3. Effluent sample collections

The effluent samples were collected from Mugher site for heavy metals, pH and electric conductivity determination. Manual method, eight grab sample taken at equally spaced time (30 minute) intervals over the sampling period combine in equal volumes, were followed [75] and collected both types of effluent(about 1 L) in triplicates each. The collected samples stored in container which soaked overnight with 5% HNO_3 followed by rinsed with distilled water prior to pretreatment.

3.4. SAMPLE PREPARATIONS AND PRETREATMENTS

3.4.1. Cereals sample preparations and pretreatments

The collected cereal samples were threshed, placed in clean acid washed porcelain crucibles and oven dried at 70 ^{o}C for 24 hour in drying oven. The dried samples were then grounded in to a fine powder and kept in desiccators before analysis begun [78].

3.4.2. Soil sample preparations and pretreatments

The collected field soil samples were transferred to plastic trays and break up the large clods to speed up drying. The sample then air-dried, crushed with mortar and pestle and passed through a 10-mesh (2-mm opening) stainless steel sieve [76, 77].

3.5. PROCEDURES FOR LABORATORY ANALYSIS

3.5.1. Heavy metals for cereal crops

Dry ashing

1.0 g of grounded cereal samples were weighed in crucible, placed in muffle furnace to 550 ^{o}C for 2 hours. The ash dissolved with 1 mL concentrated hydrochloric acid and filtered in 100 mL volumetric flask marked with distilled water [78]. Dilution applied when the sample reading was not in acceptable working standard range with distilled water. Measurements of elements were done by using the atomic absorption spectrophotometer (Model: Agilent, 200 Series AA). The standard condition, preparation of working solution and calibration are summarized in section 3.6.

3.5.2. SOIL PHYSICO-CHEMICAL ANALYSIS PROCEDURES

3.5.2.1. Moisture

5 g soil sample were weighed to moisture can with 0.001 g accuracy, was dried overnight at 105^{o}C, moisture can was removed from oven, cooled in desiccator and weighed. The moisture content in wt % (w/w) is calculated by [76]: $Moisture\ (wt\ \%) = \frac{[fresh\ weight - dry\ weight]}{dry\ weight} \times 100$

3.5.2.2. Bulk density (Core method)

The collected soil samples in core sampler were weighed (soil + core sampler), dried overnight at 105 ^{o}C, removed from oven, cooled in desiccator and weighed. The BD in g/cm^3 calculated as [79]. $BD = \frac{Wtsc}{V} \times 100$, where: V = volume of soil core ($\pi r^2 h$), Wtsc= Dried weight of sample.

3.5.2.3. Electrical conductivity

20 g soil sample were weighed into a beaker, 20 mL water added, stirred thoroughly, and allow the suspension to stand for 15 to 20 min. The conductivity cell inserted to the suspension and read the electrical conductivity [80]. The result reported is in µS/cm.

3.5.2.4. Particle-size analysis

Hydrometer method

40 g soil sample were weighed into 600 mL beakers, 5 % 50 mL calgon solution and 25ml water were added. The beakers were covered with a watch glass and allowed to leave overnight. It was then transferred to the cup of mechanical stirrer and stirred for 5 minutes. The dispersed soils were transferred to a hydrometric jar and were mixed with a plunger. The mixture made to mark with distilled water. Reading was taken from immersed hydrometer. The jars were kept undisturbed for 3 hours and were taken the second reading. The result is reported as % clay, % silt and % sand [81].

$$\%(\text{Clay} + \text{Silt}) = R - B(\pm T)X\frac{100}{wt} \qquad from\ the\ first\ reading$$

$$\%\ Clay = R - B(\pm T)X\frac{100}{wt} \qquad from\ the\ second\ reading$$

$$\%\ silt = \%(Clay + Silt) - \%\ Clay$$

$$\%\ Sand = 100 - \%(Clay + Silt)$$

$$where: R = hydrometer\ reading, B = blank, T = Temprture$$

3.5.2.5. pH

The pH of soil sample was measured potentiometrically in the suspension of a 1:2 soil liquid mixtures. 20 g soil sample were weighed and poured 40 mL of distilled water. The mixture was allowed to stand for 30 min and measured by inserting electrode. Reading then taken (after 30 to 60 s) to the nearest 0.1 pH unit.

3.5.2.6. Total nitrogen

The micro-kjeldahl procedure was followed. The samples were digested in concentrated sulphuric acid with selenium as catalyst. The solution was then made alkaline with 38% sodium hydroxide; the distillate (evolved ammonia) was trapped in 1% boric acid and titrated with standard acid with 0.01 *M* HCl [76].

3.5.2.7. Organic carbon

The Walkley-Black procedure was followed. A wet combustion of the organic matter involved with a mixture of potassium dichromate and sulphuric acid. The residual dichromate were titrated against ferrous sulphate and reported as g/kg [76].

3.5.2.8. Phosphorus soluble in sodium bicarbonate

(Extraction according to Olsen et al.)

The samples were extracted with a sodium bicarbonate solution of pH 8.5. Phosphate in the extract was determined colorimetrically with the blue ammonium molybdate method with ascorbic acid as reducing agent [77].

3.5.2.9. Potassium and Cation Exchange Capacity

Ammonium acetate methods were followed to extract exchangeable potassium. 5 g soil sample weighed in 100 mL beaker and socked overnight by 50 mL ammonium acetate. It was filtered and leached 5 times with 30 mL portion in 250 mL volumetric flask. The solutions kept for potassium determination. The residue further leached with 95% ethyl alcohol, distilled by alkaline with MgO for CEC determinations [82].

3.5.2.10. Heavy metals in soils

Reagent preparation of extraction reagent, NH_4HCO_3–DTPA

0.005 M diethylene triamine pentaacetic acid solution was prepared by adding 9.85 g diethylene triamine pentaacetic acid to 4500 mL water in a 5000 mL volumetric flask. It was shaked constantly for 5 h to dissolve the DTPA, and brought to 5000 mL with distilled water. This solution is stable with regard to pH. To 900 ml of the 0.005 M DTPA solution, 79.06 g

ammonium bicarbonate (NH_4HCO_3) gradually added and stirred gently with a rod to facilitate dissolution and prevent effervescence when bicarbonate is added. The solution was diluted to 1000 ml with the 0.005 M DTPA solution, mixed gently with a rod and the pH adjusted to 7.6 with drop wise additions of 2M hydrochloric acid (HCl) and slow agitation with a rod.

Extraction Procedure

10 g soil sample were weighed in a 125 mL conical flask and 20 mL extraction reagent was added and shake on reciprocal shaker for 15 min at 180 cycles/min with flasks kept open. The extracts were filtered immediately through Whatman 42 filter paper [83].

3.5.3. HEAVY METALS IN EFFLUENTS

Nitric Acid digestions were followed: 100 mL sample measured to a beaker and 5 mL conc. HNO_3 poured to it. The mixture were then boiled and evaporated on hot plate to 20 mL. After digestion completed, it was transferred to 100 mL volumetric flasks [84]. The pH and Electric conductivity were determined directly with pH meter and conductivity meter respectively. The solution kept in refrigerator for heavy metal analysis.

3.5.4. QUALITY CONTROL ANALYSIS

Batch quality control analysis

The internal laboratory (Holetta Agricultural Research) control soil sample was used for QC analysis of soil chemical properties. For soil parameters, duplicates (same sample & equal weight for repeatability) and spikes (same sample & 2x weight for repeatability) used in each batch of chemical analysis. % Recovery and RPD (relative percent deviation) calculated as:

$\%\ \text{Recovery} = \frac{\text{spiked}}{\text{unsiked}} \times 100$, $\text{RPD} = \frac{(D1-D2)}{(D1+D2)/2}\ X\ 100$, D1: concentration of analyte in the sample, D2: concentrations of the analyte in the second (duplicate) sample, the result on QC are summarized in Tables 16 & 17.

Between triplicates of a single sample

Outliers of triplicates measurement checked with the relative percent deviations (% RSD), computing by: % RSD $= {}^{(Sp}/_{\mu)} \ * 100\%$, Sp: standard deviation, μ: mean

3.6. STANDARD CONDITION, PREPARATION OF WORKING SOLUTION, CALIBRATION AND INSTRUMENT CONDITION

Working standard solutions of copper (Cu), iron (Fe), zinc (Zn), manganese (Mn), chromium (Cr), arsenic (As), lead (Pb) and cadmium (Cd) were prepared from the stock standard solutions (1000 ppm) using dilution formula: $C1 \times V1 = C2 \times V2$. The instrument was calibrated with five series of calibration standard solutions: Fe (6, 12, 18, 24 and 30 ppm), Mn (2, 4, 6, 8, and 10 ppm), Zn (0.3, 0.6, 0.9, 1.2 and 1.5 ppm), Cu (2, 4, 6, 8 and 10 ppm), Cr (0.5, 1, 1.5, 2 and 2.5 ppm). Measurements of elements were done by using the atomic absorption spectrophotometer (AAS) (Model: Agilent, 200 Series AA).

Table 2. Instrument operating conditions and detection limit of AAS

HMs	Wavelength (nm)	Slit width (nm)	Flame type	Required detection limit (mg/l)	Instrument detection limit (mg/l)
Fe	372.0	0.2	Air-acetylene	0.50	0.0060
Mn	403.1	0.2	Air-acetylene	0.20	0.0020
Zn	213.9	1.0	Air-acetylene	0.10	0.0010
Cu	324.8	0.5	Air-acetylene	0.50	0.0030
Pb	283.3	0.5	Air-acetylene	1.00	0.0010
Cr	429.0	0.5	Air-acetylene	0.25	0.0060
Cd	228.8	0.5	Air-acetylene	0.20	0.0020
As	197.2	1.0	N_2O- acetylene	1.00	0.3

3.7. STATISTICAL ANALYSIS

Statistical analyses were carried out using SPSS software, version 20. One way ANOVA, descriptive statics, was used for comparing the mean concentration of soils, cereals and effluent sample. Significance difference among treatments indicated for each parameter at $p< 0.05$ and the results were reported as mean ± standard deviation.

3.8. DATA QUALITY CONTROL

Appropriate quality assurance procedures and precautions were carried out to ensure reliability of the results. De-ionized water was used to the reagent preparation and sample dilution throughout the study. The analytical balances, drying oven, muffle furnace and glass wares used in the laboratory were calibrated by the calibration body and certified to use it. The analytical balance (using check weights), drying oven and muffle furnace (using thermocouple) calibrated in houses and corrective action were taken during the analysis. Before begun to the laboratory analysis, we were participated in proficiency test scheme in major physico-chemical parameters with the international proficiency test providers to see the competency of Holetta Agricultural research laboratory on delivery same test.

For each soil physic-chemical parameters of soil samples: triplicate analyses were conducted together with the internal laboratory (Holetta agricultural research) control sample to verify the precision and accuracy of the results. The internal quality control sample is the sample used as a control by the laboratory in each soil physico-chemical parameters. It has known method validation summary: - precision (reproducibility and repeatability), measurement uncertainty and known Mean±SD values. Outliers between triplicates measurement of sample analysis were checked by verifying the % RSD (percent relative standard deviation).

During analysis with AAS; freshly prepared working standards, method blanks and duplicates were used. Instrumental sensitivity was checked during calibration with absorbance reading of prepared working standard. Each sample, reagent bank and standard results obtained from the instrument by averaged three points (<5 % between duplicates) of a single measurements. The correlation coefficient values of working standards in all the data obtained is >0.9998. The instrument shows flag as 'un calibrated' if r^2 of working standards is <0.9998 and corrective

action is done by recalibration and proper standard preparation. Re-calibration and re-slop were done in the intervals of 30 sample measures (referred by the instrument default value, i.e. 50). Duplicates and spikes used during each batch of analysis and the summery of the result are indicated in Tables 17 &18.

CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.1. EFFECT OF POLLUTION FROM ABYSSINIA CEMENT FACTORY ON THE LEVEL OF SOILS HEAVY METALS CONTENT

Table 3: Available heavy metals in soil extracted with Ammonium Bicarbonate-Diethylene Triamine Penta Aceticacid solution

Soil Profile	Treatments	Field	Fe	Mn	Zn	Cu	Cr	Pb
			---------- (ppm) ----------					
0-20 cm	**0-500m**	Barley	384.66±13.01b	16.54±0.90c	10.41±1.18ab	4.43±0.69ab	1.94±0.37ab	1.36±0.37a
	500-1500m	Barley	437.00±15.10a	35.10±2.21b	12.40±1.55a	3.44±0.52b	2.40±0.50a	1.44±0.21a
	≈4000m	Barley	418.00±19.47a	40.34±3.36a	8.66±1.61b	5.22±0.52a	1.33±0.49b	1.12±0.02a
20-40 cm	**0-500m**	Barley	383.00±13.00a	16.47±1.20b	9.47±1.12a	4.17±0.38b	1.70±0.60a	1.32±0.08a
	500-1500m	Barley	360.00±17.78ab	35.41±2.27a	11.35±2.17a	3.41±0.52b	2.13±0.59a	1.39±0.23a
	≈4000m	Barley	348.33±17.10b	35.00±2.51a	8.68±0.91a	6.04±0.25a	1.97±0.56a	1.29±0.04a
0-20 cm	**0-500m**	Wheat	432.00±35.03b	6.72±1.05b	4.46±0.20b	4.03±0.18a	2.07±0.40a	0.68±0.18b
	500-1500m	Wheat	563.33±23.50a	36.78±2.71a	11.57±2.52a	3.97±0.55a	1.24±0.04b	1.81±0.64a
	≈4000m	Wheat	233.33±23.59c	8.05±0.31b	5.29±0.68b	4.27±0.28a	2.47±0.11a	0.69±0.35b
20-40 cm	**0-500m**	Wheat	445.33±38.44b	6.89±1.03 b	4.94±0.23b	3.36±0.42a	1.16±0.22b	0.56±0.07b
	500-1500m	Wheat	520.67±29.02a	34.74±1.97a	11.90±1.82a	3.48±0.49a	1.20±0.20b	1.47±0.22a
	≈4000m	Wheat	253.67±25.92c	7.51±0.42b	5.20±0.87b	3.97±0.81a	2.43±0.38a	0.41±0.11b

Location one, around abyssinia cement factory. The mean±SD is the value obtained from four numbers of random samples in each soil depths, treatments (0-500m, 500-1500m and ≈4000m) and fields (Barley and Wheat fields). The level of HMs expressed in ppm (mg/kg). The significance difference at $p<0.05$ among treatments indicated as 'a', 'b' and 'c' from higher to lower order.

Table 3 has shown that the mean concentration of available heavy metals of soil in Barley and Wheat fields. Ammonium bicarbonate-diethylenetriaminepentaacetic acid) extracting solution was used to extract available forms of heavy metals from the soil sample. It is widely accepted that determining the total content of heavy metals in a soil is neither sufficient to understand their relative mobility and ecological availability as contaminants nor particularly useful as a tool to estimate potential risks. The level of cadmium and arsenic were not detected in any of sample in the study area. One- way ANOVA, descriptive statics at $P < 0.05$, were used to analyzed the mean concentration of available heavy metals between treatments (0-500 m, 500-1500 m & ≈4000 m) in each cereals field and soil depths (0-20 cm &20-40 cm). From the result on Table 3, the variation and significance difference of heavy metals availability between cement dust polluted (0-500 m and 500-1500 m) and unpolluted (≈4000 m) are inconsistent with the distance factor from the factory. It is well known that metals solubility in soils mainly depends on soil pH, organic C, CEC, and clay contents [85, 86]. In both fields (wheat and barley), the variation of availability of heavy metals collarets to the pH variation which have shown in Table 7. So that in the slightly acidic soil of treatment two (500-1500 m from the factory) is more availability of heavy metals than the neutral - moderately alkaline soils of the other treatments (0-500m and 500-1500m from the factory). Higher extractable heavy metals of barley experimental field in treatment three (≈ 4000m) might be due to the lowest cation exchange capacity and organic carbon contents as have shown in Table 8. Limits described by MacLean [87] on Cr, Pb and Cd level extracted with AB-DTPA are 8µg/g, 13µg/g and 0.31µg/g respectively. Therefore extractable chromium, lead and cadmium level in the study area are below the critical permissible levels. In barley field, except to Fe; there is no significance difference on the level Mn, Zn, Cu, Cr, and Pb among soil depths (0-20 cm to 20-40cm).

Table 3: The level of total heavy metals around Abyssinia cement factory in soil digested with HNO_3-$HClO_4$

Soil Profile	Treatments	Field	Fe (%)	Mn (ppm)	Zn (ppm)	Cu (ppm)	Cr (ppm)	Pb (ppm)
0-20 cm	**0-500m**	Barley	66.78±0.04a	1599.08±339.89b	124.91±11.87a	45.85±5.10a	24.53±3.15a	13.85±2.35a
	500-1500m	Barley	63.71±4.68a	1987.90± 64.23a	96.60±0.03b	42.40±2.32a	20.54±4.15a	12.90±0.77a
	≈4000m	Barley	39.77±1.34b	587.00±17.61c	74.36±2.23c	28.48±1.22b	14.55±0.45b	5.78±0.40b
20-40 cm	**0-500m**	Barley	63.13±2.59a	1126.08±75.50b	105.81±5.86a	32.44±3.27a	24.27±6.09a	13.29±2.50a
	500-1500m	Barley	61.29±4.21a	1499.23±70.10a	98.22±0.26b	35.79±2.20a	13.52±2.57b	10.29±1.02a
	≈4000m	Barley	37.85±1.26b	597.00±13.24bc	68.11±1.89c	29.00±0.89b	8.94±0.70c	5.39±0.34b
0-20 cm	**0-500m**	Wheat	74.55±0.49a	1318.15±62.69a	93.52±16.08a	48.01±3.55a	15.35±2.17b	12.98±2.31a
	500-1500m	Wheat	66.46±0.18b	1837.87±62.51b	101.58±5.94a	55.28±9.27a	20.85±2.55a	14.38±0.64a
	≈4000m	Wheat	13.17±0.03c	114.89±3.45c	63.80±2.24b	26.76±0.10b	8.05±0.04c	4.59±0.07b
20-40 cm	**0-500m**	Wheat	70.81±3.54a	1275.21±55.21a	88.56±12.30a	45.26±2.67a	14.11±2.52b	13.86±2.10a
	500-1500m	Wheat	66.37±0.09b	1760.78±5.53b	99.18±5.50a	51.81±9.00a	17.87±3.16a	13.15±1.32a
	≈4000m	Wheat	11.28±0.03c	110.00±2.23c	20.12±0.80b	20.55±0.09b	7.34±0.04c	4.49±0.04b
Permissible limit (ECC 1986)			**-----**	**----**	**150-300**	**50-140**	**100**	**50-300**

Note: *ECC, limits described by European community commission. Location one, Chancho site, around Abyssinia cement factory. The mean ± SD is the value obtained from four numbers of random samples in each soil depths (0-20cm and 20-40cm), treatments (0-500m, 500-1500m and ≈4000m) and experimental fields (Barley and Wheat fields). Except to Fe that expressed in percent (%); Cu, Mn, Zn, Pb and Cr level are expressed in ppm (mg/kg). The significance difference indicated as 'a', 'b' and 'c'.*

Table 4 has shown that the mean concentration of total heavy metals in Barley and Wheat fields. The di-acid wet oxidation carried out by employing oxidizing acids, HNO_3-$HClO_4$. In both fields of analyzed heavy metals, the control fields (≈4000 m from the factory) significantly different and lower in contents than the polluted areas of the treatments (0-500 m and 500-1500 m). The levels of Fe, for both fields, consistently decline towards go away from the factory. Young-Chull [88] pointed out that the results of elementary chemical analysis on the raw material dust of the first grinding process consisted of 1.47% Fe_2O_3.This is therefore enhances the level of iron in the study area with respect to the control (≈4000m from the factory). The Mn, Zn, Cu, Cr and pb levels of the study areas also significantly different and higher than the control. Organic materials contain high concentrations of stabilized humic substances, which can influence metal availability by adsorption and forming stable complexes. The comparable result obtained (on the content of Mn, Zn, Cu, Cr and pb) between treatment one (0-500 m from the factory) and treatment two (500-1500 m from the factory) are in accordance with the contents of CEC and organic matter as have shown in Table 7. Even though there is no significance difference among soil depths at $p<0.05$, the result on Table 3 have shown that the top soils (0-20 cm) heavy metals level are enriched than the bottom soil (20-40 cm).

Table 4 shows the pattern of heavy metals pollutions of cement dust polluted areas with respect to unpolluted. The values calculated for each heavy metal is with respect to the control (the value obtained ≈4000 m) i.e. treatment one/control & treatment two/control in wheat and Barley experimental fields. Igeo is calculated through the following equation as applied by [89-91]. $Igeo = \log_2 10[\frac{Cn}{1.5Bn}]$, where Cn represents the measured total concentration of metals in the soil (mg/kg); and Bn represents the geochemical background values of the metals (mg/kg). For the analysis of the geochemical background values of heavy metals (Bn), uncontaminated surface soils were used where both anthropogenic and industrial activities are minimal and can represent geological background with reference to heavy metals. The constant 1.5 is introduced to minimize the effect of possible variations in the background values which may be attributed to lithological variations in the soils [92]. The constant 1.5 also helps to analyze natural fluctuation between the content of a given substance in environment and very small anthropogenic influences.

Table 5: Geo-accumulation Index

Experimental Plot 1	Barley experimental plot			**Experimental Plot 2**	Wheat experimental plot		
	HMs	Igeo= $\log_2 [^{C}n /1.5B_n]$			HMs	Igeo= $\log_2 [^{C}n /1.5B_n]$	
		0-500m /≈4000m	500-1500m /≈4000m			0-500m /≈4000m	500-1500m /≈4000m
	Fe	-0.25	-0.27		Fe	0.28	0.25
	Mn	-0.04	0.05		Mn	0.58	0.69
	Zn	-0.25	-0.36		Zn	-0.31	-0.28
	Cu	-0.27	-0.31		Cu	-0.22	-0.16
	Cr	-0.25	-0.33		Cr	-0.20	-0.06
	Pb	-0.09	-0.13		Pb	-0.02	0.02

Location one,Chancho site, around Abbysinia cement factory. The pollution indices, the pattern of metal contamination in the area.

From the Table 5 the Igeo values of heavy metals (Fe, Mn, Zn, Cu, Cr and pb) in Barley experimental fields; Zn, Cu, Cr and pb in Wheat experimental fields are below zero. Table 6 refers that the seven ranges of contamination values have been determined to assess the degree of trace metals' pollution [93]. According to Galkus and Boszke [93, 94], the value indicated Igeo< 0 that the soil quality is practically unpolluted. Whereas Fe and Mn in wheat experimental plots are $0 < Igeo < 1$, this refers that the soil quality in the study site are unpolluted to moderately polluted [93].

Table 6: Igeo classes with respect to soil quality

Class	Value	Soil quality
0	Igeo< 0	Practically unpolluted
1	0 < Igeo < 1	unpolluted to moderately polluted
2	1 < Igeo < 2	Moderately polluted
3	2 < Igeo < 3	Moderately to strongly polluted
4	3 < Igeo < 4	strongly polluted
5	4< Igeo < 5	strongly to very strongly polluted
6	5 < Igeo < 6	Strongly polluted

Therefore the pollution index and the permissible limit on soil quality have proved that the soils in the study area, around the Abyssinia cement factory, is unpolluted with heavy metal

4.2. EFFECT OF POLLUTION FROM ABYSSINIA CEMENT FACTORY ON MAJOR SOILS PHYSICO-CHEMICAL PROPERTIES

Table 7: pH, EC, BD and Texture

Soil Profile	Treatments	Field	pH	EC (µS/cm)	BD (g/cm^3)	Moisture (%)	Texture---- Clay (%)	Silt (%)	Sand (%)
0-20 cm	**0-500m**	Barley	7.73±0.14a	148.40 ±13.86a	1.324±0.03a	17.05±3.47a	44.06±8.38b	34.06±8.44ab	21.88±3.15ab
	500-1500m	Barley	6.54±0.30b	87.03±19.64b	1.289±0.03a	13.32±3.61ab	30.00±2.50c	43.15±6.57a	26.88±7.74a
	≈**4000m**	Barley	7.90±0.08a	65.60±4.30b	1.295±0.01a	12.13±0.64b	52.50±1.00a	28.75±1.30b	18.75±1.30b
20-40 cm	**0-500m**	Barley	7.57±0.33a	116.77±18.08a	1.309±0.09a	16.57±2.57a	45.31±9.91b	34.06±12.60a	20.63±3.15ab
	500-1500m	Barley	6.51±0.13b	93.58±5.07b	1.364±0.106a	17.75±6.87a	32.50±7.50c	38.75±3.23a	28.75±8.90a
	≈**4000m**	Barley	7.89±0.08a	69.90±2.00c	1.363±0.01a	11.65±0.73a	60.00±1.30a	26.25±1.50a	13.75±0.90b
0-20 cm	**0-500m**	Wheat	7.82±0.13a	116.0±17.97b	1.322±0.04a	16.20±1.49a	42.50±4.08b	37.50±4.79a	20.00±4.79ab
	500-1500m	Wheat	6.25±0.15b	49.25±3.31c	1.242±0.06b	19.78±4.04a	43.13±4.27b	31.87±2.39b	25.00±3.22a
	≈**4000m**	Wheat	7.87±0.06a	235.00±1.40a	1.339±0.01a	17.37±0.80a	70.00±0.90a	13.75±0.80c	16.25±1.10b
20-40 cm	**0-500m**	Wheat	7.76±0.14a	123.18±16.74b	1.332±0.03b	16.93±3.89a	41.25±3.23b	33.13±3.15a	25.63±1.25a
	500-1500m	Wheat	6.11±0.29b	73.50±3.58c	1.270±0.06b	19.40±5.32a	41.88±4.73b	32.50±4.08a	25.63±2.39a
	≈**4000m**	Wheat	7.94±0.05a	171.60±1.80a	1.565±0.02a	18.55±0.70a	65.00±0.60a	23.75±1.00b	11.25±1.00b

Location one,Chancho site, around Abyssinia cement factory. The significance difference of P^H, EC, BD and texture at $p<0.05$ for each cereal plots and soil depths are indicated with 'a', 'b' and 'c'.

The mean±SD of pH, EC, BD and Texture are summarized in Table 7. Soil pH is a crucial soil indicator defined as the negative log of the hydrogen ion activity. The pH range normally found in soils varies from 3 to 9. The significance of pH lies in its influence on availability of soil nutrients, solubility of toxic nutrient elements in the soil, physical breakdown of root cells, and CEC in soils whose colloids (clay/humus) are pH-dependent and biological activity. Most crops grow best when the soil pH is between 6.0 and 8.2. From the table, slightly acidic to moderately alkaline soil P^H was obtained in the treatments. Top soil (0-20 cm) relatively high value in the treatments (0-500 m & 500-1500 m) than bottom soil (20-40cm) is due to the liming effects from cement factory. where as in the treatment (≈4000 m) which far from the cement factory, the lower pH value is observed in surface soils (0-20 cm depths) mainly due to leaching of bases due to rainfall rather than liming.

Particle size distribution (soil texture) is an important parameter in soil classification and has implications for soil water, aeration, and nutrient availability to plants. Laboratory procedure [81] normally estimate percentage of sand (0.05 – 2.0 mm), silt (0.002 – 0.05 mm), and clay (<0.002 mm) fractions in soils. Soil texture triangle shows that the samples in the study area are clay to clay loam soil. The silt fractions among treatments are significantly differing for both experimental fields and it declines a long distance far from the factory, this indicates that the dust pollutions contribute to enhance silt fractions, siltation, in the experimental fields near to the factory. The size of cement dusts ranges 0.003 to 0.004 mm which supports the previous statement that cement dust pollution aggregates the soil by enhances siltation.

Soil bulk density (BD) is ratio of the mass (oven-dry weight) of the soil to the bulk volume which includes the volume of both solids and pore space at specified soil water content (usually the moisture content at sampling). Even though the BD among treatments are not significantly different (at $p< 0.05$) in both experimental fields, in all soil profiles consistently increased with increasing depth is might be due to loading effect of the top soils and the moisture contents. Soil moisture influences crop growth not only by affecting nutrient availability, but also nutrient transformations and soil biological behavior.

Soil salinity refers to the concentration of soluble inorganic salts in the soil. It reflects the extent to which the soil is suitable for growing crops. Values of 0 to 200 µS/cm are safe for all crops; yields of very sensitive crops are affected between 200 to 400 µS/cm; many crops are affected between 400 and 800 µS/cm; while only tolerant crops grow reasonably well above that level. I.e. Barley (*Hordeum vulgare*) upper tolerable limit is 1800 µS/cm and Wheat (*Triticum aestivum*) is 1300 µS/cm [79]. In the Table 7 the results have shown that the soil salinity (electric conductivity) is safe and suitable to grow wheat and barley cereals as well as for all crops.

Table 8: CEC, Organic carbon, Total nitrogen, $S\text{-}SO_4^{-2}$, Phosphorus and potassium

Soil Profile	Treatments	Field	CEC ($cmol_c\ kg^{-1}$)	Corg. (g/kg)	Ntot.	$S\text{-}SO^{-2}_4$ ($mg\ kg^{-1}$)	P	K ($cmol\ kg^{-1}$)
0-20 cm	**0-500m**	Barley	30.06±4.24a	20.36±8.10a	1.72±0.69a	7.39±1.15a	19.45±4.35a	0.64±0.05a
	500-1500m	Barley	31.39±1.24a	20.92±1.76a	1.84±0.14a	9.29±2.74a	11.22±0.34b	0.62±0.04a
	≈4000m	Barley	17.58±0.00b	17.66±0.40a	1.68±0.02a	4.66±0.11b	5.58±0.08c	0.53±0.01b
20-40 cm	**0-500m**	Barley	30.99±5.02a	19.19±6.80a	1.63±0.58a	5.24±1.21b	17.36±7.76a	0.62±0.04a
	500-1500m	Barley	31.45±0.84a	19.00±0.77a	1.71±0.11a	8.35±2.48a	10.44±2.76ab	0.65±0.07a
	≈4000m	Barley	19.78±0.00b	17.19±0.23a	1.54±0.02b	3.32±0.13b	5.16±0.08b	0.53±0.02a
0-20 cm	**0-500m**	Wheat	31.49±2.02a	19.96±7.99a	1.71±0.66a	6.26±1.60b	21.28±7.27b	0.62±0.03a
	500-1500m	Wheat	28.32±0.81b	19.91±1.22a	1.85±0.08a	10.48±1.71a	7.74±0.52c	0.57±0.02b
	≈4000m	Wheat	24.50±0.00c	14.23±0.37a	1.02±0.01b	5.47±0.10b	32.94±0.49a	0.56±0.01b
20-40 cm	**0-500m**	Wheat	29.29±2.53a	19.41±7.66a	1.63±0.59a	5.81±1.79b	20.72±8.36b	0.60±0.04a
	500-1500m	Wheat	30.23±1.57a	18.21±0.62a	1.69±0.10a	9.43±1.21a	7.22±1.15c	0.59±0.03a
	≈4000m	Wheat	24.38±0.00b	10.74±0.24b	0.99±0.02b	5.03±0.14b	34.56±0.94a	0.54±0.01b

Location one,Chancho site, around Abyssinia cement factory. The significance difference of cation-exchange capacity, electric conductivity, organic carbon, total nitrogen, sulfur, phosphorus and potassium at $p<0.05$ for each cereal plots and soil depths are indicated with 'a', 'b' and 'c'.

Total nitrogen analysis measures N in all organic and inorganic forms. The organic fraction constitutes the majority of total N in soils (usually >95 %). It is composed mostly of plant and microbial remains, in variable composition. The inorganic phase of soil N is composed of ammonium (NH_4), nitrate (NO_3), and-very little though-nitrite (NO_2) forms. Environmental (temperature and moisture) and agronomic management (fertilization, cropping, etc.) factors influence its dynamic relationship with the organic fractions and also within the inorganic forms [79]. Only 1 to 4 percent of this total N becomes plant-available (converts via microbial activity from organic form to inorganic form) during a growing season [95]. From the Table 8 there is no significant differences in the treatments (0-500 m & 500-1500 m) however treatment (≈4000m, medium contents of TN) significantly different from the two treatments (0-500 m & 500-1500 m, high contents of TN) for both experimental fields.

Soil organic matter (OM) has a major influence on soil aggregation, nutrient reserve and its availability, moisture retention, and biological activity. As soil test interpretation guide [95], soil OM increases so does CEC, soil total N content, and other soil properties such as water-holding capacity and microbiological activity increases parallel. The result on Table 8 supports by soil interpretation guide that as the contents of organic carbon increases so does CEC and total nitrogen. In treatments (0-500 m & 500-1500 m) the contents of C_{org} is medium and low-medium in treatment (≈4000 m). As soil depths increases (0-20 cm to 20-40 cm) the content of total nitrogen and organic carbon declines consistently in both experimental fields. Sulfur (S) exists in soil and soil solution mainly as the sulfate (SO_4-S) and Plants absorb sulfur in this form. From the Table 8, treatment three (≈4000 m) significantly differ from the 0-500 m & 500-1500 m treatments. Its level categories are low in treatment three and medium for 0-500 m & 500-1500 m treatments. Along with N and P, potassium (K) is also of vital importance in crop production. From the Table 8 as CEC, treatment three (≈4000 m) is significantly different from the two treatments (0-500m & 500-1500 m). It has categorized that medium content of potassium in all treatments.

4.3. THE LEVEL OF HEAVY METALS IN BARLEY AND WHEAT CEREAL CROPS GROWN AROUND ABYSSINIA CEMENT FACTORY

Table 9: The average concentration of heavy metals, dry ashing, in cereal samples

Distance From factory	Crops	Fe	Mn	Zn	Cu	Cr	Pb
		---------- (ppm) ----------					
0-500m	Barely	326.79±31.68a	20.39±2.31a	18.90±1.59a	6.24±0.17a	1.27±0.05a	0.23±0.03a
500-1500m	Barley	311.62±7.32ab	18.32±1.25a	16.35±0.71b	5.29±0.16b	1.07±0.04b	0.18±0.02b
≈4000m	Barley	281.69±2.10b	18.08±0.70a	18.16±0.04ab	4.10±0.09c	0.82±0.02c	0.12±0.01c
0-500m	Wheat	265.21±26.16a	52.73±9.68a	27.30±5.16a	6.28±0.91a	1.31±0.17a	0.19±0.02a
500-1500m	Wheat	277.10±9.25a	47.72±2.45a	18.97±1.77ab	5.89±0.07a	1.20±0.01a	0.21±0.01a
≈4000m	Wheat	279.44±1.40a	49.16±1.10a	17.52±0.04b	3.70±0.03a	0.70±0.02b	0.08±0.01b
FAO/WHO		**425.5**	**500**	**99.4**	**73.3**	**2.3**	**0.3**

The level of heavy metals in each cereal crops, express in mg kg^{-1} dry weight. The significant differences at $p< 0.05$ for each crop types are summarized and indicated by 'a', 'b' and 'c'.

The mean value in each treatments and cereals obtained from five spot samples of triplicate tests. From Table 9 have shown that Arsenic (As) and Cadmium (Cd) were not detected in any of the cereal samples analyzed in the study. Significant differences among treatments at $p < 0.05$ in each cereals were summarized in the Table 9 indicated by 'a, b and c'. The levels of heavy metals determined in the analyzed cereal samples were found to be below the permissible limit set by FAO/WHO [96].The heavy metal transfer factor of each heavy metals from soils to crops is calculated using the formula [97]:- $TF = \frac{MP}{MS}$; Where: TF – transfer factor, Mp – metal content in plant (mg kg^{-1}), Ms – metal content in soil (mg kg^{-1}). By using the data of Table 9 for Mp and Table 4 for Ms, the result for all heavy metals analyzed are below one. If the ratios >1, the plants have accumulated elements, the ratios around 1 indicate that the plants are not influenced by the elements, and ratios <1 show that plants exclude the elements from the uptake [98]. Therefore the selected cereals crops (wheat and barley) in the study area are safe for consumptions.

4.4. EFFECT OF POLLUTION FROM MUGHER CEMENT FACTORY ON THE LEVEL OF SOILS HEAVY METALS CONTENT

Table 10: Extractable heavy metals (AB-DTPA), number of samples=4 for each: soil profile, treatments and experimental fields

Soil Profile	Treatments	Experimental Field	Fe	Mn	Zn	Cu	Cr	Pb
			---------- (ppm) ----------					
0-20 cm	**0-500m**	Barley	194.33±9.87c	1.25±0.16c	9.37±0.84c	0.90±0.18c	1.40±0.17a	0.73±0.09a
	500-1500m	Barley	335.33±20.79b	8.12±1.13b	22.44±4.27b	2.19±0.22b	0.19±0.00b	0.48±0.04b
	≈4000m	Barley	683.67±10.41a	11.26±0.99a	42.05±2.13a	2.68±0.02a	0.22±0.03b	0.20±0.03c
20-40 cm	**0-500m**	Barley	180.66±9.45c	1.18±0.17b	11.62±0.72c	1.27±0.08a	2.26±0.39a	0.54±0.12a
	500-1500m	Barley	339.00±26.85b	7.73±1.06a	21.33±3.29b	2.30±0.26a	0.23±0.03b	0.20±0.07b
	≈4000m	Barley	574.67±26.63a	8.08±1.62a	41.35±1.52a	3.40±0.04a	0.21±0.02b	0.15±0.05b
0-20 cm	**0-500m**	Wheat	221.33±16.29c	3.32±0.34b	40.18±2.25b	2.74±0.48b	5.61±0.63a	1.73±0.49a
	500-1500m	Wheat	621.67±19.60b	3.15±0.23b	58.00±6.13a	6.44±0.51a	0.20±0.06b	0.16±0.03b
	≈4000m	Wheat	855.33±31.26a	9.30±0.37a	41.35±2.97b	3.57±0.52b	0.23±0.03b	0.25±0.06b
20-40 cm	**0-500m**	Wheat	224.67±14.64c	1.43±0.49c	38.87±2.85b	2.85±0.27b	6.04±0.14a	1.81±0.21a
	500-1500m	Wheat	630.70±12.42b	9.88±1.27b	53.48±3.64a	7.37±0.54a	0.19±0.07b	0.19±0.05b
	≈4000m	Wheat	840.30±32.08a	13.46±0.21a	27.68±2.50c	2.62±0.18b	0.34±0.12b	0.15±0.04b

Location two, around Mugher cement factory. The mean±SD is the value obtained from four numbers of random samples in each soil depths (0-20cm and 20-40cm), treatments (0-500m, 500-1500m and ≈4000m) and experimental fields (Barley and Wheat fields). The level of HMs expressed in ppm (mg/kg). The significance difference indicated as 'a', 'b' and 'c'.

Table 10 has shown that the level of AB-DTPA extractable heavy metals in Mugher location of the study sites. As location one the level of cadmium and arsenics are not detected in any of soils sample. At $p< 0.05$ in barley field, the descriptive statics shows that there is significance difference among treatments (0-500 m, 500-1500 m and ≈ 4000 m away from the factories). Except to chromium and lead one way ANOVA revealed that higher and significantly different level of extractable heavy metals obtained go away from the factory. Again in wheat field the level of extractable chromium and lead in treatment one (0-500 m) are significantly different and higher than the respective treatments, high values of Fe and Mn obtained far away from the factory like to barley field. Therefore the variation of the extractable heavy metals (except to cr and pb) dominantly related with the pH variation of the study area that have showed in Table 13 (moderately acidic> neutral> moderately alkaline) comes from liming effects by the cement dust. The higher level of chromium and lead in the treatment (0-500 m near to the factory) might be due to the factory effluent which discharged and percolates to the 0-500 m study areas.

Table 11: The level of total heavy metals, around Mugher cement factory, digested with HNO_3-$HClO_4$

Soil Profile	Treatments	Field	Fe (%)	Mn	Zn	Cu	Cr	Pb
				(ppm)				
0-20 cm	**0-500m**	Barley	58.61±4.53a	1255.92±37.62a	105.66±8.11b	76.28±4.29a	15.55±2.63a	11.63±1.48a
	500-1500m	Barley	36.33±5.13b	734.32±57.06c	127.54±7.99a	57.06±2.69b	10.28±1.53b	5.81±0.57b
	≈4000m	Barley	29.89±1.20c	1101.18±33.10b	70.58±2.11c	52.02±0.89b	8.23±0.90ca	4.61±0.00c
20-40 cm	**0-500m**	Barley	55.75±0.70a	1121.10±54.99a	106.99±4.53b	72.51±4.82a	13.06±1.42a	6.11±0.77a
	500-1500m	Barley	34.47±2.84b	713.38±61.45c	119.56±3.55a	52.87±6.83b	11.32±2.97a	5.34±1.04b
	≈4000m	Barley	26.95±0.89c	912.30±27.36b	75.98±1.63c	55.46±1.00b	9.34±0.78b	4.80±0.14b
0-20 cm	**0-500m**	Wheat	71.35±1.93a	1264.47±131.23a	105.91±4.15b	66.66±2.37b	24.29±4.08a	15.3±0.51a
	500-1500m	Wheat	57.38±1.16b	1309.53±181.19a	117.62±5.79a	75.81±4.98a	13.82±2.62b	7.78±2.02b
	≈4000m	Wheat	57.22±0.07b	918.70±36.74b	63.34±1.20c	59.58±1.20b	11.08±1.04b	3.96±0.16c
20-40 cm	**0-500m**	Wheat	71.08±2.92a	1267.68±127.85a	106.73±8.50a	60.81±0.94c	19.97±5.19a	14.79±0.87a
	500-1500m	Wheat	57.56±1.55b	1372.72±73.05a	112.39±5.98a	72.07±4.40b	11.87±2.55b	6.95±1.14b
	≈4000m	Wheat	49.24±0.08b	774.16±28.17b	67.62±1.80b	68.87±0.70a	10.63±1.01b	3.73±0.08c
Permissible limit (ECC 1986)			**___**	**____**	**150-300**	**50-140**	**100**	**50-300**

***Note: ECC**, limits described by European community commission. Location two, Mugher site, around Mugher cement factory. The mean ± SD is the value obtained from four numbers of random samples in each soil depths (0-20cm and 20-40cm), treatments (0-500m, 500-1500m and ≈4000m) and experimental fields (Barley and Wheat fields). Except to Fe that expressed in percent (%); Cu, Mn, Zn, Pb and Cr level are expressed in ppm (mg/kg). The significance difference indicated as 'a', 'b' and 'c'.*

As location one, from the Table 11 have shown that the level of heavy metals except to Mn in barley filed are higher than the control site (≈4000m from the factory). Again the level of cadmium and arsenic are not detected in any of the soil samples analyzed. In wheat field, the level of Mn, Zn and Cu of treatment two (500-1500 m from the factory) significantly higher than the treatment one (0-500 m) is might due to the organic matter contents of soils which can influence metal availability by adsorption and forming stable complexes. The following table shows the pattern of heavy metals pollutions of cement dust polluted areas with respect to the control site.

Table 12: Geo-accumulation Index of Mugher site, around Mugher cement factory

	Barley experimental plot				Wheat experimental plot		
	HMs	Igeo= $\log_2 [^{C}n /1.5B_n]$		HMs	Igeo= $\log_2 [^{C}n /1.5B_n]$	
		0-500m /≈4000m	500-1500m /≈4000m		0-500m /≈4000m	500-1500m /≈4000m
Experimental Plot 1	Fe	-0.19	-0.40	Experimental Plot 2	Fe	-0.38	-0.47
	Mn	-0.42	-0.65		Mn	-0.33	-0.32
	Zn	-0.30	-0.22		Zn	-0.26	-0.21
	Cu	-0.31	-0.47		Cu	-0.42	-0.37
	Cr	-0.20	-0.38		Cr	-0.14	-0.38
	Pb	-0.07	-0.38		Pb	0.11	-0.18

Location two, Mugher site, around Mugher cement factory. The pollution indices, the pattern of metal contamination in the area. The value calculated for each heavy metal is with respect to the control (the value obtained ≈4000m) i.e. treatment1/control & treatment2/control in wheat and Barley experimental fields.

The data have obtained in the Table 12 shown that, except to pb in wheat filed, the pollution index of metals contamination are below zero. This again as Chancho sites and permissible limits of heavy metals in soil implies the soils in study areas of Mugher are not contaminated with heavy metals.

4.5. EFFECT OF POLLUTION FROM MUGHER CEMENT FACTORY ON MAJOR SOILS PHYSICO-CHEMICAL PROPERTIES

Mean values, in each treatments and soil depths, were obtained from four samples of triplicate analysis

Table 13: pH, EC, BD and Texture

Soil Profile	Treatments	Field	pH	EC (µS/cm)	BD (g/cm^3)	Moisture (%)	Texture Clay (%)	Silt (%)	Sand (%)
0-20 cm	**0-500m**	Barley	8.09±0.14a	133.08±18.29a	1.280±0.08ab	10.47±2.76a	46.25±16.89a	20.00±2.04a	33.75±15.07a
	500-1500m	Barley	6.93±0.21b	98.33±41.65ab	1.305±0.07a	9.20±2.24a	33.13±7.47a	26.88±7.18a	40.00±5.40a
	≈4000m	Barley	5.86±0.10c	68.00±17.20b	1.188±0.04b	9.13±1.10a	50.00±6.07a	25.00±0.70a	25.00±2.00a
20-40 cm	**0-500m**	Barley	8.15±0.17a	112.00±33.59a	1.296±0.12a	10.74±2.24a	48.13±18.53a	20.00±8.90a	31.88±11.06a
	500-1500m	Barley	6.98±0.17b	80.73±33.22a	1.353±0.02a	11.77±2.97a	35.62±5.54a	22.5±7.36a	40.63±11.61a
	≈4000m	Barley	7.02±0.10b	123.00±21.00a	1.337±0.01a	8.64±1.20a	42.50±4.00a	27.50±1.00a	30.00±3.00a
0-20 cm	**0-500m**	Wheat	8.08±0.10a	129.23±10.76a	1.347±0.07a	7.63±0.75a	31.25±4.33b	28.13±4.15b	40.63±8.07a
	500-1500m	Wheat	7.44±0.18b	117.25±37.10b	1.336±0.05a	10.31±2.09b	28.13±4.73b	37.50±5.00a	34.38±5.15a
	≈4000m	Wheat	5.74±0.09c	93.40±6.00c	1.267±0.01a	14.51±1.30c	57.50±1.20a	22.50±1.04b	20.00±2.00b
20-40 cm	**0-500m**	Wheat	8.03±0.13a	124.78±9.08a	1.377±0.08a	9.43±3.84b	29.38±2.39b	32.19±11.47ab	38.44±10.67a
	500-1500m	Wheat	7.34±0.14b	105.00±20.82a	1.390±0.01a	10.90±3.64b	31.88±5.54b	35.63±3.75a	32.50±7.36a
	≈4000m	Wheat	5.81±0.08c	60.70±4.20b	1.324±0.02a	16.03±1.27a	57.50±1.30a	22.50±1.30b	20.00±2.67b

Location two,Mugher site, around Mugher cement factory. The significance difference of pH, EC, BD and texture at $p<0.05$ for each cereal plots and soil depths are indicated with 'a', 'b' and 'c'.

In both fields (Wheat and Barley), pH value are significantly differ in all treatments in the order of treatment one (0-500m, moderately alkaline)> treatment two (500-1500 m, neutral)> treatment three (≈4000 m, slightly acidic). As location one among to soil depths (0-20 cm to 20-40 cm), significant differences have not observed in treatments of 0-500 m and 500-1500 m: may due to liming effects from cement factories. Whereas in treatment three (≈4000 m), significance difference has observed in soil depths (0-20 cm to 20-40 cm).The BD of barley experimental field among treatments is significant different and high value is observed near to the cement factory(0-500 m> 500-1500 m >≈4000 m) of the top soil might due to the dust particles make compacted the soil aggregates. In wheat experimental fields, even if no significance difference observed in treatments there is also higher value observed near to the factory. Consistently, the BD of top soil again in location one higher value than 20-40 cm soil depth might due to the loading effect of top-bottom soil. Soil texture triangle also shows that the sample in the study area is clay-clay loam soil.

Table 14: CEC, Organic carbon, Total nitrogen, $S\text{-}SO_4^{-2}$, Phosphorus and potassium

Soil Profile	Treatments	Exp. Field	CEC ($cmol_c\ kg^{-1}$)	Corg. (g/kg)	Ntot.	$S\text{-}SO^{-2}_4$ (mg kg^{-1})	P	K ($cmol\ kg^{-1}$)
0-20 cm	**0-500m**	Barley	40.30±8.71a	9.07±3.74c	0.64±0.32c	4.08±0.99c	25.25±17.36b	0.69±0.10a
	500-1500m	Barley	39.69±2.31ab	18.66±4.03b	1.46±0.28b	5.86±1.81b	51.15±14.17a	0.68±0.04a
	≈4000m	Barley	31.50±1.00b	35.52±0.00a	2.74±0.11a	6.83±0.09a	57.21±3.24a	0.76±0.00a
20-40 cm	**0-500m**	Barley	38.71±5.63a	8.99±4.82b	0.65±0.41c	3.14±1.22b	24.56±16.85c	0.60±0.06b
	500-1500m	Barley	39.13±4.55a	15.43±5.12b	1.32±0.39b	4.24±1.98b	49.33±19.22b	0.66±0.05b
	≈4000m	Barley	36.32±1.23a	27.92±0.00a	2.75±0.10a	5.89±0.09a	120.39±6.18a	0.86±0.02a
0-20 cm	**0-500m**	Wheat	33.36±1.74b	10.63±2.49b	0.86±0.10b	6.28±2.78b	14.77±3.24b	0.60±0.04b
	500-1500m	Wheat	40.22±5.82a	33.23±3.34a	2.64±0.48a	8.52±2.46a	116.78±70.43a	0.77±0.02a
	≈4000m	Wheat	32.04±0.64b	30.46±1.00a	2.34±0.09a	6.89±0.06b	7.91±1.34b	0.61±0.01b
20-40 cm	**0-500m**	Wheat	32.78±4.20b	10.79±3.09b	0.77±0.19c	5.03±2.27a	14.19±3.28b	0.63±0.05b
	500-1500m	Wheat	39.03±2.33a	26.80±4.39a	2.28±0.29a	6.66±0.71a	111.20±70.33a	0.75±0.04a
	≈4000m	Wheat	31.10±1.06b	25.50±1.37a	1.84±0.07b	6.88±0.06b	15.71±3.00b	0.56±0.02c

Location two,Mugher site, around Mugher cement factory. The significance difference of cation-exchange capacity, electric conductivity, organic carbon, total nitrogen, sulfur, phosphorus and potassium at $p<0.05$ for each cereal plots and soil depths are indicated with 'a', 'b' and 'c'.

In both fields (barley and wheat) the contents of total nitrogen and organic carbon of treatment 1(0-500 m) is significantly differ and lower than the respective treatments. Soil test interpretation guide [95] refers that the organic carbon and total nitrogen in soil are collarets each other, Table 14 (location two) & Table 8 (location one) also support the correlation. For barley experimental filed the level of phosphorus in treatment 1, near to the factory, is a medium content soil category and significantly differ from the respective treatments. In wheat field excessive P content of treatment two might due to the neutral pH. At neutral pH, the available p is not fixing with the acid forming cations and basic cations as a result have high contents of available p. The Low p content in treatment three have observed in acidic soil might due to fixing by acid forming cations. The content of phosphorus in barley filed at soil depth 0-20 cm to 20-40 cm increases and significantly different when the pH changes from moderately acidic (pH: 5.86) to neutral (pH: 7.02). This can be due to fixing of available P content in acidic soil with cations like Al.

4.6. THE LEVEL OF HEAVY METALS IN BARLEY AND WHEAT CEREAL CROPS GROWN AROUND MUGHER CEMENT FACTORY

Table 15: The average concentration of HMs in cereal samples

Distance from Factory	Crops	Fe	Mn	Zn	Cu	Cr	Pb
		---------- (ppm) ----------					
0-500m	**Barely**	199.09±5.88c	34.74±2.06a	26.16±2.19a	3.83±0.29b	0.77±0.08a	0.12±0.01a
500-1500m	**Barley**	289.90±11.53a	18.66±0.14b	20.68±2.09b	4.28±0.19a	0.83±0.05a	0.12±0.02a
≈4000m	**Barley**	256.40±3.00b	20.78±1.80b	20.01±0.98b	3.09±0.08c	0.65±0.01b	0.09±0.01a
0-500m	**Wheat**	187.62±8.19b	40.74±2.93b	23.67±1.93a	3.91±0.11a	0.77±0.05a	0.11±0.02a
500-1500m	**Wheat**	234.70±19.46a	17.21±0.83c	22.17±1.59a	4.04±0.21a	0.78±0.05a	0.11±0.02a
≈4000m	**Wheat**	146.81±4.60c	46.47±1.00a	18.55±0.69b	2.90±0.09b	0.61±0.02b	0.09±0.01a
FAO/WHO		**425.5**	**500**	**99.4**	**73.3**	**2.3**	**0.3**

The level of heavy metals in each cereal crops, express in ppm (mg kg−1) dry weight. The significant differences at p< 0.05 for each crop types and treatments are summarized indicated by 'a', 'b' and 'c'.

The mean value in each treatments and cereals obtained from five spot samples of triplicate tests. As Chancho site, Cd and As were not detected in any of the cereal samples analyzed. The levels of heavy metals determined in the analyzed cereal samples were found to be below the permissible limit set by FAO/WHO [96]. And the transfer factors of all HMs in the study sites were below one. Therefore the crops have not influenced by metal pollutions by uptake heavy metals from cement dust polluted fields.

4.7. THE LEVEL OF HEAVY METALS IN EFFLUENT SAMPLES SOURCES FROM MUGHER LOCATION, AROUND MUGHER CEMENT FACTORY

Table 16: Average values of pH, EC and heavy metals (Mean ± SD, n = 3) in effluent samples

Effluent Type	PH	EC (µS/cm)	Fe	Mn	Zn	Cu	Cr	Pb
			---------- (ppm) ----------					
Factory	7.68±0.05a	355±3a	1860±3.8a	2.59±0.02a	1.74±0.00a	0.59±0.01a	0.12±0.00a	0.03±0.01a
Toilet	6.82±0.06b	991±5b	93.33±1.00b	0.151±0.00b	0.012±0.00b	0.019±0.00b	0.007±0.0b	ND
(FAO)	**6.5-8.4**	**700**	**5.00**	**2.00**	**2**	**0.2**	**0.1**	**5.0**

Critical limits as described by FAO, (1985) for irrigation purposes, ND = Not detected, *both effluent samples are sources from Mugher cement factory. The mean values were obtained from three subsample of triplicate tests. The significance differences of average values between factory and toilet effluent indicated as 'a' and 'b'.*

The result of the analysis of heavy metals, pH and EC in effluent samples sources from Mugher site around Mugher is presented in Table 16. Both factory and toilet effluents were discharged to the agricultural fields towards to the treatment one (0-500 m). This result showed a variation in the concentration of heavy metals, pH and EC of analyzed effluent (factory and toilet) samples. The high concentration of heavy metals observed in factory effluent than toilet effluent. The Fe, Cu, Mn and Cr level of factory effluent are upper the permissible limit of the standard set by FAO, therefore the effluent cannot use for irrigation purposes. Cadmium (Cd) and Arsenic (As) were not detected in both effluent samples analyzed in the study. In addition to Cadmium (Cd) and Arsenic (As), lead (Pb) also was not detected in toilet effluent sample. The highest, above the permissible limit of electric conductivity obtained in toilet effluent samples.

4.8. QUALITY CONTROLS

Table 17: QC values of soil chemical properties

Duplicates								
No.	pH	EC (µS/cm)	CEC (cmol/kg)	OC (%)	TN (%)	P (mg/kg)	K (cmol/kg)	S (mg/kg)
1	5.93	76.4	32.40	1.838	0.196	7.411	0.58	8.39
	6.02	74.2	31.30	1.861	0.189	7.690	0.60	8.10
2	7.32	90.4	35.40	2.506	0.213	9.978	0.62	10.48
	7.47	93.1	33.90	2.540	0.220	9.706	0.61	9.99
3	7.97	131.2	31.48	1.297	0.099	24.360	0.66	5.81
	8.01	134.2	33.00	1.251	0.102	25.190	0.63	5.81
4	7.94	171.6	24.90	1.074	0.099	34.560	1.00	5.81
	7.89	175.3	24.38	1.112	0.103	35.780	0.96	5.67
5	7.90	97.0	37.44	1.532	0.121	41.595	0.62	5.86
	7.82	99.2	36.10	1.582	0.124	42.614	0.59	5.72
6	7.14	105.0	36.12	2.828	0.219	40.243	0.78	8.38
	7.23	108.0	35.11	2.871	0.211	40.991	0.76	8.38
7	7.01	77.4	37.46	1.793	0.168	59.672	0.68	3.77
	7.14	74.6	36.99	1.712	0.164	61.841	0.67	3.63
8	7.02	123.0	34.28	3.521	0.275	122.430	0.84	1.89
	7.14	117.2	35.32	3.574	0.271	118.012	0.81	1.80
RPD (range)	**0.50-2.03**	**2.13-4.83**	**1.26-4.71**	**1.24-3.48**	**1.24-3.64**	**1.84-3.70**	**1.48-4.65**	**0.00-4.87**
Spikes								
1				1.847	0.168	11.189	0.58	
				1.896*	0.161*	11.714*	0.59*	
2				1.423	0.102	32.938	0.76	
				1.397*	0.099*	31.847*	0.74*	
3				1.010	0.087	13.883	0.65	
				1.021*	0.084*	13.954*	0.62*	
4				3.552	0.274	57.21	0.76	
				3.641*	0.284*	54.76*	0.77*	
% recovery				**97.42-101.86**	**96.48-104.35**	**95.52-104.47**	**98.31-104.84**	

'***' refers spikes values**

The result showed in Table 17 showed the quality control values of soil sample analysis. Duplicates and spikes were used in each batch of chemical analysis. Relative percent deviation and recovery values are reported for duplicates and spikes quality control parameters respectively. In general, RPD ranges between 0.00 to 4.87 and % recovery from 95.52 to 104.84 in duplicates and spikes respectively.

Table 18: QC values for heavy metals in soil and cereals between average values

	Duplicates(for soil samples)						Duplicates(for cereal samples)					
	mg/kg						mg/kg					
No.	**Fe**	**Mn**	**Zn**	**Cu**	**Cr**	**Pb**	**Fe**	**Mn**	**Zn**	**Cu**	**Pb**	**Cr**
	421	37.25	10.90	4.01	0.182	0.512	185.045	38.060	21.637	3.998	0.803	0.080
1	416	35.92	10.40	3.87	0.179	0.492	180.240	39.146	22.107	3.988	0.804	0.081
	368	16.70	10.36	3.90	2.892	1.204	273.050	18.583	19.228	4.400	0.772	0.108
2	374	15.93	10.12	3.75	2.761	1.224	279.104	18.412	19.023	4.541	0.781	0.11
	359	9.23	25.80	2.08	2.304	0.525	245.740	46.334	22.083	5.598	1.201	0.204
3	342	8.97	24.90	2.10	2.208	0.500	254.81	45.395	21.997	5.675	1.222	0.209
	188	1.22	10.80	1.23	1.981	1.431	281.694	18.079	18.156	4.099	0.820	0.123
4	197	1.26	10.30	1.19	2.011	1.501	290.031	18.103	18.391	4.162	0.831	0.125
RPD (range)	1.19-4.85	2.86-4.72	2.34-4.74	0.96-3.92	1.50-4.63	1.64-4.65	2.19-3.62	0.13-0.28	0.39-2.15	0.24-3.15	0.16-1.70	1.24-2.31

Note: RPD , relative percent deviation between duplicate soil and cereal samples.

The result indicated in Table 18 showed that the quality control values of heavy metals in soil and cereals. The RPD in soils ranges from 0.96 to 4.85 and from 0.13 to 3.62 in cereal sample. The quality control results (Table 17 and Table 18) between duplicates and spikes in over all have shown that <5%, implies that it has in acceptable range [99].

CHAPTER FIVE

5.1. SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

Consuming the cereals contaminated with heavy metals has different detrimental effects on human health; therefore, monitoring contamination of heavy metals will allow for avoiding unnecessary exposures. The result of this study has revealed that the various concentrations of the heavy metals Cu, Fe, Zn, Mn, Cr, As, Pb and Cd in cereals (wheat and Barley) collected from Mugher and Chancho sites around in cement factories of the Oromia Regional State, central Ethiopia. The concentrations of heavy metals determined were Fe, Mn, Zn, Cu, Cr, Pb ; As and Cd were not detected in any of the cereal crops.

Generally, the levels of heavy metals obtained in both cereals (wheat and barley) are within the acceptable ranges and calculated values of transfer factor shows the crops not influenced by heavy metals that uptaked from the dust polluted fields in study areas. Therefore those crops harvested from cement dust polluted experimental fields do not pose any health hazard to the health of their consumers, may as well serve as sources of trace metals to the population consumes those cereals in the study areas. Further studies recommend to carried out on the yield of cereal crops grown around cement factories.

The following studies are being carried out on soil samples:-

- ✓ The concentration of HMs available to the cereals that extracted with Ammonium Bicarbonate-Diethylene Triamine Penta Aceticacid (AB-DTPA).
- ✓ The level of total HMs digested with Nitric acid-Perchloric acid (HNO_3-$HClO_4$), from this data-Igeo values were calculated for each heavy metal with respect to control (≈4000m far from the factories). The value indicated Igeo< 0 that the soil quality is practically unpolluted.
- ✓ Major soil physico-chemical properties: the status of pH, EC, BD, PSA, CEC, Oc, TN, S-SO_4^{-2}, Phosphorus and potassium have conducted in soil profiles (0-20cm & 20-40cm) and interpreted according to soil test categories for both locations. From these soil results conclude that:-

- The soils polluted with cement dust are higher in bulk density, poses siltation on soil texture which is due to the cement dust emanates from the factory, and this is therefore influences to restrict mobility of soil nutrients. This result parallel reflected to the physical observation during in survey that the soil was compacted in its structure.
- The soil are neutral (500-1500m from the factory) to moderately alkaline (0-500m from the factory) therefore liming effects from cement dust changes the pH level. This pH level is somewhat suitable for barley and wheat cereals (i.e. 6.5-7.5). However the trends of liming if does enhance more, the major soil nutrients like phosphorus will fixed and its availability to the crop are reduced.
- According to soil interpretation guide, the major nutrient status (i.e. phosphorus, nitrogen, and potassium) are medium to high category. The phosphorus, organic carbon, total nitrogen, potassium and sulfur contents of Mugher soil polluted with cement dust are decrease/significantly differ in contents than the control (≈4000m from the factory).

  Where as in Chancho, around Abyssinia cement factory, the contents are high near to the cement factory is due to the soil pH and less influence by cement dust than Mugher (year of the factory establishment and amount of dust emanate differ than the Abyssinia cement factory).

In general, the factory should monitor the dust pollution emanates during cement production that changes the physico-chemical properties of soil by enhancing the pH level and to the more compacted soil structure. It is recommended carrying out further study on the speciation of heavy metals in soil.

The levels of heavy metals in effluents sources from Mugher location, around Mugher cement factory, which discharged to the agricultural farm lands were analyzed. The result on total heavy metals analysis digested with Nitric acid has shown that the higher concentration, upper the permissible limit was discharged from the factory effluent. Owing to their toxicity and their possible bioaccumulation of these heavy metals which discharged from the factory, it should be subject to mandatory monitoring and controlling before released. As a result it might reduce the possible transfer of heavy metals from effluent to soil and again from soil to crops.

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7. APPENDICES

7.1. ANOVA result

7.1.1. Abyssinia wheat crops

Descriptives

		N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
						Lower Bound	Upper Bound		
Fe	0-500m	6	265.2082	26.16141	10.68035	237.7535	292.6629	228.18	294.94
	500-1500m	5	277.0964	9.24727	4.13550	265.6144	288.5784	269.35	287.22
	4000	5	279.4380	.00000	.00000	279.4380	279.4380	279.44	279.44
	Total	16	273.3701	17.16075	4.29019	264.2257	282.5144	228.18	294.94
Mn	0-500m	6	52.9300	9.67901	3.95144	42.7725	63.0875	43.04	64.58
	500-1500m	5	47.7206	2.44898	1.09522	44.6798	50.7614	45.01	51.67
	4000	5	49.1640	.00000	.00000	49.1640	49.1640	49.16	49.16
	Total	16	50.1252	6.18136	1.54534	46.8314	53.4190	43.04	64.58
Zn	0-500m	6	27.3030	5.16468	2.10847	21.8830	32.7230	21.35	33.06
	500-1500m	5	18.9738	1.76733	.79037	16.7794	21.1682	17.29	21.76
	4000	5	17.5230	.00000	.00000	17.5230	17.5230	17.52	17.52
	Total	16	21.6439	5.52915	1.38229	18.6976	24.5902	17.29	33.06
Cu	0-500m	6	6.2780	.91119	.37199	5.3218	7.2342	5.40	7.40
	500-1500m	5	5.8946	.06904	.03087	5.8089	5.9803	5.80	5.99
	4000	5	3.6990	.00000	.00000	3.6990	3.6990	3.70	3.70
	Total	16	5.3523	1.27670	.31917	4.6719	6.0326	3.70	7.40
Cr	0-500m	6	1.3103	.16759	.06842	1.1345	1.4862	1.12	1.49
	500-1500m	5	1.1958	.01381	.00618	1.1787	1.2129	1.18	1.22
	4000	5	.6980	.00000	.00000	.6980	.6980	.70	.70
	Total	16	1.0832	.28937	.07234	.9290	1.2374	.70	1.49
pb	0-500m	6	.1882	.02525	.01031	.1617	.2147	.16	.21
	500-1500m	5	.2128	.01511	.00676	.1940	.2316	.19	.23
	4000	5	.0770	.00000	.00000	.0770	.0770	.08	.08
	Total	16	.1611	.06177	.01544	.1282	.1940	.08	.23

7.1.2. Abyssinia barley crop

Descriptives

		N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
						Lower Bound	Upper Bound		
Fe	0-500m	6	326.7943	31.68476	12.93525	293.5432	360.0455	297.73	373.29
	500-1500m	5	311.6158	7.32730	3.27687	302.5178	320.7138	302.63	320.46
	4000	5	281.6940	.00000	.00000	281.6940	281.6940	281.69	281.69
	Total	16	307.9572	26.93091	6.73273	293.6067	322.3077	281.69	373.29
Mn	0-500m	6	20.3932	2.31590	.94546	17.9628	22.8236	17.17	23.47
	500-1500m	5	18.3244	1.25078	.55937	16.7714	19.8774	17.06	19.86
	4000	5	18.0790	.00000	.00000	18.0790	18.0790	18.08	18.08
	Total	16	19.0235	1.84815	.46204	18.0387	20.0083	17.06	23.47
Zn	0-500m	6	18.9022	1.59228	.65004	17.2312	20.5732	16.23	21.08
	500-1500m	5	16.3532	.70879	.31698	15.4731	17.2333	15.35	17.04
	4000	5	18.1560	.00000	.00000	18.1560	18.1560	18.16	18.16
	Total	16	17.8724	1.48303	.37076	17.0822	18.6627	15.35	21.08
Cu	0-500m	6	6.2425	.16638	.06793	6.0679	6.4171	6.08	6.40
	500-1500m	5	5.2948	.16051	.07178	5.0955	5.4941	5.09	5.50
	4000	5	4.0990	.00000	.00000	4.0990	4.0990	4.10	4.10
	Total	16	5.2765	.92284	.23071	4.7848	5.7682	4.10	6.40
Cr	0-500m	6	1.2737	.04902	.02001	1.2222	1.3251	1.23	1.33
	500-1500m	5	1.0724	.04059	.01815	1.0220	1.1228	1.02	1.12
	4000	5	.8200	.00000	.00000	.8200	.8200	.82	.82
	Total	16	1.0690	.19664	.04916	.9642	1.1738	.82	1.33
pb	0-500m	6	.2258	.02647	.01081	.1981	.2536	.18	.25
	500-1500m	5	.1824	.02361	.01056	.1531	.2117	.15	.21
	4000	5	.1230	.00000	.00000	.1230	.1230	.12	.12
	Total	16	.1801	.04803	.01201	.1545	.2057	.12	.25

7.1.3. Mugher, barley crop

Descriptives

		N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
						Lower Bound	Upper Bound		
Fe	0-500m	5	199.0948	5.88649	2.63252	191.7858	206.4038	193.71	208.14
	500-1500m	5	293.2646	8.99857	4.02428	282.0914	304.4378	279.38	301.24
	4000	5	256.3990	.00000	.00000	256.3990	256.3990	256.40	256.40
	Total	15	249.5861	40.51498	10.46092	227.1497	272.0226	193.71	301.24
Mn	0-500m	5	34.7426	2.06490	.92345	32.1787	37.3065	31.78	36.86
	500-1500m	5	18.6790	.15644	.06996	18.4848	18.8732	18.48	18.87
	4000	5	20.7790	.00000	.00000	20.7790	20.7790	20.78	20.78
	Total	15	24.7335	7.46199	1.92668	20.6012	28.8658	18.48	36.86
Zn	0-500m	5	26.1600	2.19152	.98008	23.4389	28.8811	24.12	29.25
	500-1500m	5	20.9762	2.19680	.98244	18.2485	23.7039	18.32	24.32
	4000	5	20.0060	.00000	.00000	20.0060	20.0060	20.01	20.01
	Total	15	22.3807	3.25126	.83947	20.5802	24.1812	18.32	29.25
Cu	0-500m	5	3.8946	.29053	.12993	3.5339	4.2553	3.38	4.10
	500-1500m	5	4.2590	.20604	.09214	4.0032	4.5148	4.10	4.60
	4000	5	3.0990	.00000	.00000	3.0990	3.0990	3.10	3.10
	Total	15	3.7509	.53628	.13847	3.4539	4.0479	3.10	4.60
Cr	0-500m	5	.7716	.08608	.03850	.6647	.8785	.62	.84
	500-1500m	5	.8430	.05285	.02364	.7774	.9086	.77	.92
	4000	5	.6460	.00000	.00000	.6460	.6460	.65	.65
	Total	15	.7535	.10010	.02585	.6981	.8090	.62	.92
pb	0-500m	5	.1182	.01370	.00613	.1012	.1352	.10	.14
	500-1500m	5	.1234	.02735	.01223	.0894	.1574	.08	.16
	4000	5	.0900	.00000	.00000	.0900	.0900	.09	.09
	Total	15	.1105	.02232	.00576	.0982	.1229	.08	.16

7.1.4. Mugher , wheat crop

Descriptives

		N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
						Lower Bound	Upper Bound		
Fe	0-500m	5	187.6150	8.18781	3.66170	177.4485	197.7815	179.04	196.39
	500-1500m	5	234.6992	19.46146	8.70343	210.5346	258.8638	207.36	254.45
	4000	5	146.8060	.00000	.00000	146.8060	146.8060	146.81	146.81
	Total	15	189.7067	38.84861	10.03067	168.1931	211.2204	146.81	254.45
Mn	0-500m	5	40.7376	2.92841	1.30962	37.1015	44.3737	37.67	43.88
	500-1500m	5	17.2078	.83426	.37309	16.1719	18.2437	16.02	18.18
	4000	5	46.4690	.00000	.00000	46.4690	46.4690	46.47	46.47
	Total	15	34.8048	13.20610	3.40980	27.4915	42.1181	16.02	46.47
Zn	0-500m	5	23.6726	1.93009	.86316	21.2761	26.0691	21.64	25.90
	500-1500m	5	22.1748	1.58510	.70888	20.2066	24.1430	20.12	24.32
	4000	5	18.5540	.00000	.00000	18.5540	18.5540	18.55	18.55
	Total	15	21.4671	2.59405	.66978	20.0306	22.9037	18.55	25.90
Cu	0-500m	5	3.9116	.11786	.05271	3.7653	4.0579	3.78	4.00
	500-1500m	5	4.0394	.20775	.09291	3.7814	4.2974	3.80	4.30
	4000	5	2.8990	.00000	.00000	2.8990	2.8990	2.90	2.90
	Total	15	3.6167	.54326	.14027	3.3158	3.9175	2.90	4.30
Cr	0-500m	5	.7728	.04964	.02220	.7112	.8344	.70	.82
	500-1500m	5	.7822	.04519	.02021	.7261	.8383	.75	.86
	4000	5	.6170	.00000	.00000	.6170	.6170	.62	.62
	Total	15	.7240	.08624	.02227	.6762	.7718	.62	.86
pb	0-500m	5	.1120	.01901	.00850	.0884	.1356	.08	.13
	500-1500m	5	.1102	.01644	.00735	.0898	.1306	.09	.13
	4000	5	.0890	.00000	.00000	.0890	.0890	.09	.09
	Total	15	.1037	.01724	.00445	.0942	.1133	.08	.13

7.2. Appendix Tables

Appendix Table 1: Extractable K and Olsen P soil test categories

	Extractable K	Olsen P (ppm)
Low	<150 ppm <0.4 meq/100 g soil	<10
Medium	150–250 ppm 0.4–0.6 meq/100 g soil	10-25
High	250–800 ppm 0.6–2.0 meq/100 g soil	25-50
Excessive	>800 ppm >2.0 meq/100 g soil	>50

Source: D.A. Horneck, D.M. Sullivan, J.S. Owen, and J.M. Hart (2011)Soil test interpretation guide

Appendix Table 2: soil P^H ranges

Soil P^H	Range
Strongly acidic	<5.1
Moderately acidic	5.2-6.0
Slightly acidic	6.1-6.5
Neutral	6.6-7.3
Moderately alkaline	7.4-8.4
Strongly alkaline	>8.5

Source: D.A. Horneck, D.M. Sullivan, J.S. Owen, and J.M. Hart (2011)Soil test interpretation guide

Appendix Table 3: SO_4^--S soil test categories (ppm)

SO_4^--S	Ppm
Very low	<2
low	2-5
Medium	5-20
High	>20

Source: Source: D.A. Horneck, D.M. Sullivan, J.S. Owen, and J.M. Hart (2011)Soil test interpretation guide

7.3. Annex pictures

Annex picture1: Dust pollution from Abyssinia and Mugher cement factories


Annex picture 2: Dust polluted cereal and effluent from the factory