

Thesis

by Shiza Zafar

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**ANALYSIS OF SOIL RECALIMED BY INSTALLATION OF KASUR
TANNERY WASTEWATER PRE TREATMNET PLANT FOR ITS
TOXICITY**

By

Shiza Zafar

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Supervised by: Dr. Muhammad Rafiq Khan

Abstract

Kasur is a district of Central Punjab in Pakistan. It has long standing tradition of tanning and thus it houses more than 240 tanneries. These tanneries produce huge amount of wastewater which contains different obnoxious heavy metal compounds. Cr based carcinogenic compounds may be especially highlighted in this context because it is the major player in chrome tanning process extensively practiced in Kasur.

The tannery wastewater flooded more than 400 acre of land in the vicinity of the tannery cluster. After the installation of the wastewater pretreatment plant installed to dispose of wastewater, the land has been reclaimed but there yet exists the danger that the heavy metals contaminants which might have penetrated in the soil may ultimate become a part of the food chain because some crops are being grown in this area. The physiochemical analysis of affected soil seemed to be of major concern to assess whether the heavy metal content of the soil was suitable for cultivation of agricultural crops. Thus the goal of the research work undertaken here was to conduct analysis of the contaminated soil to judge its suitability for agriculture.

Physicochemical analysis of the tannery contaminated reclaimed soil was carried out by standard methods. The concentrations of various parameters such as pH, EC, OM, OC, P, K, Na, total metal content for Cr, Cd, Cu and extractable/available metal content for Cr, Cu, Cd, Zn and Fe were determined, computed and compared with the various international standards for agriculture recommended by different international organizations and individual or groups of experts. The results revealed that the concentrations of available/extractable Cu (24.66 mg/kg), Zn (10.11 mg/kg), and Fe (44.80 mg/kg) in agricultural soil are above the safe limits while total metal concentrations of heavy metals (Cr, Cd) are within permissible limits with exception of few areas exceeding the limits. The results for other parameters such as pH, EC, OM, OC, K and Na are in accordance with the prescribed limits but P (7.05-148.61 mg/kg) in soil exceeds the satisfactory range of P in agricultural soil.

Thus, it may be concluded that the reclaimed land area around Kasur tanneries is almost appropriate for agricultural practices. However, the problem of the exceeding

limits of extractable/available metals (Cu, Fe, Zn) can be addressed by bringing them within permissible limits by phyto-remediation, cultivating metal hyper-accumulator plants, heap leaching using chemicals or bio-remediation with microbes or manure/sludge.

Dedication

This dissertation is dedicated to my beloved mother, SHAFQAT SULTANA who forms the rock on which I balance my existence.

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First of all, I pray to Almighty Allah in thanks Who gave me the courage and ability to complete this task. All respect and regards are for the Holy Prophet Mohammad (Peace Be Upon Him), the source of knowledge and torch bearer for whole mankind to illuminate the track that leads to the Ultimate Reality.

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List of Acronyms

CEPT	Common Effluent Primary Treatment Plant
Cr	Chromium
Cd	Cadmium
Fe	Iron
Zn	Zinc
Cu	Copper
BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
As	Arsenic
NaCl	Sodium chloride
OM	Organic Matter
B	Boron
Ca	Calcium
Mg	Magnesium
NEQS	National Environmental Quality Standards
UNIDO	United nation industrial development organization
UNDP	United Nations Development Programme
KTPCP	Kasur Tannery Pollution Control Project
KDA	Kasur Development Authority
KTWMA	Kasur Tannery Waste Management Agency
Hg	Mercury
Cr ⁺³	Trivalent Chromium
Cr ⁺⁶	Hexavalent Chromium

As	Arsenic
Ag	Silver
Ni	Nickel
OC	Organic Carbon

Chapter 1

Introduction

Tanning is considered to be a potential environmental concern majorly because it produces large amounts of harmful tannery wastewater (Mwinyihija, 2010). The generation of extensively varying highly concentrated wastewater distinguishes tanneries as intensive pollution complexes. Tanning industry falls in the category of hazardous industries as it bears highest noxious strength per unit output (Vasudevan et al., 2012).

Leather products come in the category of consumer goods because these are used in everyday life which makes these products greatly demanded not only in Pakistan but all over the world. This is the reason that leather production is dealing with legal environmental restrains. Tanning industry plays a fundamental role in the economy of Pakistan but simultaneously it is also generating negative externalities to the community by harmfully affecting humans and environment. The extensive and unrestricted discharge of untreated tannery wastewater is one of the chief problems in Pakistan because massive volumes of potentially toxic tannery effluents contain poisonous heavy metal chromium (both hexavalent and trivalent), which are harmful for human beings and also for agricultural practices being carried out in the area (Shakir et al., 2012). The tanning process being the source environmental degradation on soil, air and water, is causing enormous direct and indirect damages to the state (Afreen, 2009). Many developed countries have banned tanning process on their lands because of the noxious effluents from tanneries and predominantly because of the presence of chromium in high quantity. But the manufacture of chrome tanned leather cannot be stopped for the reason that it is the need of the people worldwide. This fact provides the economic benefit to the developing countries like Pakistan to produce leather and earn money by exporting the leather to developed countries. To keep from falling, various ways have been adopted to recover chromium from tannery wastewater before its drains into rivers or other water bodies (Khan, 2007).

Tanneries in Pakistan are mostly located in the form of clusters or small industrial sectors in Sialkot Kasur, Karachi, Multan, Peshawar, Gujranwala, Lahore and Faisalabad. These include the small to medium scale industries and also some large

well-structured and organized, industries of international level, particularly in Karachi (UNDP, 1996).

In various tannery areas the environmental problems have reached such a stage that it is the basis of immediate health problems to the inhabitants of the area and particularly by contaminating the water sources. This demands urgent corrective measures to lessen the harmful influence on the environment. Hence, to deal with this serious problem the treatment of discharged water is essential for every setup, wherever it is.

For the small scale leather industries it is challenging to build and run the individual wastewater treatment plant for every industry because of the large space treatment plant demands and the lack of manpower to run the treatment plant. However, the cumulated effluent discharge quantity of these tannery clusters may be more than the discharge of large industries; therefore, the establishment of a common effluent treatment plant can be encouraged as a solution.

Considering the importance of environmental and health hazards in Kasur, United Nations Development Programme (UNDP) initiated Kasur Tannery Pollution Control Project(KTPCP) in collaboration with the Kasur Development Authority (KDA) under Punjab Government by Kasur Tannery Waste Management Agency (KTWMA). This project was signed in January, 1996 and UNDP allocated 2.5 million dollars while local input was Rs. 199 millions. Considering the measures to be taken regarding environmental conditions in Kasur, the aims of the project were achieved as below:

- The construction of outfall sewerage drain i.e. Final outfall or the Green Channel to Pandoki Outfall and in function;
- The evacuation of stagnant lagoons done and ready for reclamation;
- The pre-treatment adjustments in every tannery were made which involves installation of grease chambers, coarse screens and water flow meters and in operation;
- The waste water pollution control system for industrial and sanitary water in tanning industry clusters constructed/repaired and in function;
- The installation of the Common Tannery Effluent Primary Treatment Plant (CEPTP) constructed accompanied by a control laboratory and to be in constant function;

- The handling, transfer and disposal of sludge produced by CEPTP and disposal of tannery solid waste.
- The installation of chrome recovery plant and in operation;
- To provide assistance to almost 1000 landowners, include mostly small farmers from the recovery of stagnant pools which have been constantly flooding the surrounding land of more than 400 acres and unfavorably influencing crop fields on extended 311 acres of land, during monsoon time of the year (UNDP, 1996).

Now, that the project has been successfully completed, the Common Effluent Primary Treatment Plant with the capacity of treating 13000 cubic meters per day is operative, the solid waste disposal site has been constructed and the pilot chrome recovery plant has also been installed.

This is the bad luck of the region that the plant is not working properly and its efficiency is not meeting the requirements. The plant is often closed and is not used to run properly which is a big weakness of the authorities of the Kasur. The plant is also not cleaned properly and its maintenance is not done properly. The most alarming fact is that the whole of the waste coming from the tanneries is not sent for the treatment to the plant, instead, one full drain of wastewater out of two drains is let to pass into the Pandoki Drain without any treatment directly which is further going to degrade the Sutlej river water (Nawaz, 2011).

The pre treated water has been declared unfit for agriculture by the international consultants. The land that has been reclaimed by elimination of the stagnant pools is now being used for agricultural practices. The matter needs investigation both from the agricultural as well as residential point of view. The chelates of tannery water might have been absorbed in the soil and out of their components chromium seepage particularly is of special concern. Now, if agricultural practices will take place on this contaminated land there is every likelihood that the toxic substances may transfer to crops grown on land and then may enter the food chain to cause different diseases. The major diseases prevailing among the people living around tannery clusters are Diarrhea, Typhoid, Respiratory problems and Dysentery (HRW, 2012).

The work undertaken here is focused on the physico-chemical composition of the soil to assess the level of toxicity caused by the penetration of the tannery water in it.

Following are the aspects which are directly or indirectly related to the work undertaken here.

1.1 Environmental Pollution

Environment is characterized as whole circumstances around a living organism or group of living beings particularly, the combination of exterior physical conditions that influence and impact the development, advancement and survival of creatures (Farlex, 2005). It includes both biotic (flora and fauna) and abiotic (terrestrial, atmospheric, and aquatic habitats) factors (Duruibe et al., 2007).

Any such substance in the environment that causes undesirable effects by disrupting the safety of the environment, impairing the quality of life and may eventually cause death is called a 'pollutant'. These kinds of substance have to be entered in the environment in a specified limit so that it may not remain harmful. These limits can be defined by setting a tolerance limit which can be acceptable or desirable. Thus, environmental pollution can be defined as the existence of any pollutant in any of these three media of environment (air, soil and water) which may be noxious, toxic and harmful for the living organisms in the polluted region (Duruibe et al., 2007).

Human beings rely upon their surrounding physical environment for the resources they require for their continued existence but they have exploited these resources which is the cause of environmental decomposition. Due to expanded urbanization and industrialization, the issue of environmental contamination has been intensifying for many decades. All these problems are the ultimate effects of disposal of industrial wastes of all forms (effluents, solid wastes or noxious gaseous) which on coming in contact with water, soil and air harmfully affect their quality. There are many studies which reveal the fact that the areas in the vicinity of the industries are reported to have problems of contamination of agriculture lands, soil and water (Jan et al., 2010). Water bodies and soil have been used for dumping of wastes which has deteriorated these valuable resources (Quazilbash et al., 2006). Fact of ecological issues is accentuated by humanity's growing interest toward the harm brought to the environment. The fundamental part of this interest is joined with the conservation of living organisms on earth (Kolomaznik et al., 2008).

1.2 Industrial Pollution

Industrial pollution has been and keeps on being a significant reason for depletion of natural resources. Various studies have reported that communities in the vicinity of industries are observed to have high pollution of water, air and soil. Thus, these practices are causing harm to the water we drink, soil we grow crops on and air we breathe in, and finally spreading diseases among the habitants of the polluted region (Kabir et al., 2012).

There is an ever-increasing demand of water in commercial, domestic, industrial and agricultural practices. This raise in demand is because of the reason that the population is increasing and that more than half of the earth's population lives in cities enhancing the trend of urbanization all over the world. The developing urbanization expands the residential water utilization while supplying waste water that could be utilized for non-potable uses, for example, agrarian watering system (Jan et al., 2010).

Generally, pollutants from the industries are categorized into three forms i.e. solids, liquids and gases. But there are some other forms as well such as noise and odor (Wen, 2009). Following are some pollutant types from different industrial sectors:

Table.1.1. Pollutants from different industries

Industrial Sectors	Pollutant Forms			
	Gas	Solid waste and soils	water	Others
Iron and steel	SO _x , NO _x , HC, CO, H ₂ S, toxic chemicals	Slag, wastes, sludge form effluent treatment	BOD, COD, oil, metals, acids, phenol, cyanide	Noise, particulates
Textile and leather	SO _x , HC	Sludge (chromium) from effluent treatment	BOD, solids, sulfates and chromium, dyes	Odor, noise, particulates

Continued

Pulp and paper	SO _x , NO _x	Sludge from effluent treatment	BOD, COD, solids, chlorinated organic compounds	Odor, noise, particulates
Petrochemicals and refineries	SO _x , NO _x , HC, CO, H ₂ S, Toxic chemicals	Spent catalysts, tars, sludge	BOD, COD, oil, phenols and chromium	Odor, noise, particulates
Chemicals	Organic chemicals	Sludge from pollution treatment and process waste	COD, organic chemicals, heavy metals, solids and cyanide	Odor, toxic chemicals

Water utilized as a part of commercial ventures makes a waste that is a potential peril for our surroundings on account of the presentation of different contaminants, for example, heavy metals into soil and water assets (Danazumi & Bichi, 2010). Since the start of the industrial revolution, contamination of the biosphere with poisonous metals has increased drastically. The rise in population and industrialization has lifted the living standards which ultimately cause the debasement of environment because of the disposal of wastes from these industrial sectors (Tiwari et al., 2008). The wastewater from the industries consists of both inorganic and organic compounds and other substances which are least biodegradable. These contaminants affect the soil structure and ground water quality and cause severe issues (Karthikeyan et al., 2010). There is an increasing sense of worldwide concern on the subject of contamination of our surroundings by an exhibit of chemicals utilized within different practices (Palaniappan et al., 2009).

Right now, there are two key contamination related issues: the transfer of extensive amounts of litter that are ceaselessly being generated and the elimination of dangerous exacerbates that have been gathering at waste disposal sites, in the water bodies and in soils over the course of the last few decades (Hsu et al., 2006). The inappropriate industrial waste administration is one of the main reasons for groundwater and soil depletion in the developing nations. The circumstances get antagonistic when the people are exceptionally reliant upon groundwater assets for farming drinking purposes (Rashid et al., 2012). In the same way as other developing countries, the urbanization and industrialization have outstripped with ecological wellbeing in Pakistan, bringing about detrimental impacts of industrial waste discharge on nearby soils or streams. The country has experienced the extreme defilement of groundwater in industrial areas by industrial discharges which are released randomly without any system of regulations (Samina et al., 2004).

1.3 Tanning Industry

In the process of making leather from animal hides, tanning is a fundamental part. It is an intricate and arduous process which includes the usage of excessive amounts of 130 various chemicals, differing upon the material of raw hide and the required finished leather form (Riaz et al., 2006).

Tanneries are known to be a major environmental hazard worldwide. There is a diverse range of chemicals which are used in the process of tanning. The usage of huge volumes of water which are eventually disposed as bulks of chemically concentrated tannery wastewater is one of the serious concerns. The chemicals present in wastewater involve large quantities of heavy metal Cr, lime, sulfide and organic matter (Tariq et al., 2005). The developing countries have a common exercise of disposing the effluents produced by tanning industries on the nearby land area or in big lagoons without any treatment of wastewater or any prescribed procedure of its disposal (Scholz & Lucas, 2003). The deleterious substances from these effluents penetrate into the soil, leaving it unfit for agriculture (Kisku et al., 2000). On the other hand, the constant seepage of these effluents into the soil leads to the pollution of groundwater reservoirs (Ma et al., 2003).

1.4 Tanning industry in Pakistan

The leather industry of Pakistan is the second most astounding foreign trade earners for the nation. About 80% of the leather products are exported. As agriculture is the chief livelihood of the major population of the country, it has inherent benefit of large animal production.

Pakistan's leather industry is the 2nd highest foreign exchange earners for the country. Almost 80% of production is exported. As the country is predominantly agricultural, it possesses natural advantage in the area of livestock population. This industry adds about 7% to the aggregated exports and 5% to GDP of the state. The main leather items created in Pakistan incorporate leather clothing, footwear, footballs, purses, leather gloves, wallets and so on. Almost 60% of the locally generated leather is utilized by the shoe-making centers, 30% is distributed alike in leather furniture and garment industry and the 10% is used to make leather handbags and gloves etc. there are around twenty five hundred workers serving the leather industry of Pakistan (Din & Ghani, 2005).

Pakistan houses about 2500 tanneries and footwear-fabricating industries, primarily in Lahore, Kasur, Karachi and Sialkot. Tanning clusters in Kasur only focus on the preparing final leather from the raw hides while the tanneries in Lahore, Karachi and Sialkot also the have aptitude in assembling of attire/pieces of clothing, shoes, and gloves (Logistics Consulting Group, 2006).

The provinces of Sindh and Punjab provide the animal hides and skins which are the basic raw-materials of the leather industry. A few numbers of hides are also imported. The top period for the leather sector starts after Eid-ul-Azha which then prolongs to about 2-3 months. The industry production reaches twice than the casual days. In Pakistan, chrome tanning is the most commonly used method while vegetable tanning or the combination of both methods is also practiced. This is a multi-stages process which involves the usage of large volumes of water and salts/chemicals to be applied on the raw hides. These chemicals can be classified into four main categories i.e. pre-tanning, tanning, wet finishing and final finishing chemicals. Pakistan's tanning industry utilizes groundwater extensively for the process of tanning (Federation of Pakistan Chambers of Commerce and Industry, 1999).

There are several parameters to assess the environmental harm caused by tannery effluents which includes total suspended solids, sulfides, biological oxygen demand (BOD), sulfates, nitrogen, Cr and chemical oxygen demand (COD). In case of Pakistan, most tanneries release their wastewater without any treatment in nearby water bodies which is antagonistically influencing the aquatic creatures as well as human wellbeing. ISO 14001 was applied to all-scale industrial sectors in 2005. Hence, currently, the overseas traders are more attentive toward choosing the best ecological safe methods/measures to be taken during the whole process of leather making. This is the reason that the tannery industry in the country is facing enormous pressure to treat the tannery effluents before their discharge so that Pakistan's leather sector can sustain in worldwide business sector. Therefore, a prompt installation of treatment systems in the tanneries is evidenced especially in the tanneries which are more into exportation of leather goods. In many tanneries the primary treatment arrangements are either wholly or partially done. Now, to go along with the National Environmental Quality Standards (NEQS), few of the tanneries intend to make secondary wastewater treatment arrangements. For this purpose, large number of industries has started to use activated sludge method (Haydar & Aziz, 2009).

The fowl thing about the tannery clusters is that they are mostly situated in the proximity of agricultural area or in the human inhabited area. There are the chances of serious environmental hazards and effects on human wellbeing and soil in these areas (Tariq et al., 2009).

Tanneries produce all kinds of wastes (solid waste, air emissions and effluents). However, tannery effluent is the most concerned safety issue to be tackled by Pakistani tanneries.

1.4.1 Effluents

About 60 liters of water is utilized in processing of one kilogram hides, but accurate amount differs with various tannery procedures. In some audits of tannery clusters in Pakistan it is revealed that many tanneries are consuming three times more water than necessary. The general water release also shows a high level of occasional and day by day variability. Most of the tanneries follow the ritual to release the untreated effluents into the nearby environment.

Table.1.2. Chemical composition of tannery effluent and NEQS values (Safdar et al., 2002)

Parameters	Effluent	NEQS
pH	3.5-9.4	6-10
Total suspended solids, TSS (mg/l)	1000-1240	150
Total dissolved solids, TDS (mg/l)	1520-15850	3500
Sulphate, SO ₄ (mg/l)	1000-1300	600
Chloride, Cl (mg/l)	1200-6500	1000
Chromium, Cr (mg/l)	20-100	1.0
Biological Oxygen Demand, BOD ₅ (mg/l)	800-1200	80
Chemical Oxygen Demand, COD (mg/l)	1800-2700	150

1.4.2 Solid Waste:

The solid waste generated from tanneries is of two categories:

- I. Tanned waste
- II. Un-tanned waste

The solid waste production by tanneries is calculated to be around 5,500 kg per day (estimate for a tannery processing ten thousand kilograms of hides per day). This solid waste consists of trimmings (wet, raw, dry), salts, packaging material, shavings (wet and dry) and buffing material etc.

It is observed that tannery solid waste is sold in the market because it can be used further after some processing. The major uses are poultry feed making and glue production. But the problem is the presence of chromium content which can be a

cause of severe health issues in chickens as well as among the consumers of poultry products.

1.4.3 Air Emissions

Boilers and generators are the two main sources of air emissions from tanneries in Pakistan. These emissions were found to be lower than the NEQS limits. The emission of hydrogen sulphide while mixing of alkaline effluents with acidic effluents during drainage and ammonia production in the process of washing and handling of drums, is important because it can pose serious health impacts. The solution to eliminate hydrogen sulphide emissions is to discharge the alkaline and acidic wastewaters through separate drains (Haider, 2010).

1.5 Kasur Tannery Cluster

Kasur is a district which is situated in the central Punjab of Pakistan. This district consists of a large area of land which is used for agriculture. The irrigation water is supplied from groundwater by installing tube wells or from Indus River. There are about five million people who earn from the agriculture practices in this area. Cotton, corn, wheat, sugarcane and rice are the cash crops of Kasur. This city accommodates around 50% tanneries of Pakistan and as chrome tanning method is majorly implied thus 90% tanneries are found to be using this process.

All the effluents are released into the nearby drain “Rohi Nala” and open land area to convert these productive soils into large lagoons of stagnant tannery wastewater (Tariq et al., 2009).

In response to the critical ecological and health risks and the occupational safety and environment problems, Kasur Tanneries Pollution Control Project (KTPCP) was commenced. This project was a joint effort of Governments of Punjab and Pakistan and tanners association of Kasur and it was signed in 1996. While, United Nations Industrial Development Organization (UNIDO) provided the technological support to complete the project. Around 199 million rupees were provided by the local government and 2.5 million US dollars were contributed by UNDP. The aim of the project was to eliminate and decrease the environmental damage occurred due to the tannery wastes by providing mechanical and management assistance; by improving

the working industrial conditions and by publicizing the importance of environment to create awareness among people so that the Kasur tanning industry can lead to sustainable progress. KTPCP was considered to deal with stagnant poll evacuation, providing effluent drainage and collection system, constructing common effluent pre treatment plant and sanitary landfill for solid waste disposal, and incorporating in-house waste minimizing measures such as low-waste leather processing, chromium recovery and occupational health improvement (Nawaz, 2011).

Common Effluent Primary Treatment Plant (CEPTP) in Kasur was built in 1994 and came into operation on October, 2001. This treatment plant was built on the land of Railway Pakistan in the area leading to Ferozpur District. This land was not in any use after the war of 1971, so Government decided to construct a treatment plant there. This treatment plant is treating the wastewater produced by the leather tanneries. The plant is doing only primary treatment and the type of treatment plant is carried in aerated lagoon. In the CEPTP after passing manual and mechanical screening, the effluent enters the equalization tanks, which are fitted with the aerators for homogenization. The homogenized effluent is pumped into the settling tanks, which are equipped with the sludge and scum scrapers to throw sludge into the sludge pit. The settled sludge so collected into the sludge pumping pit where lime dosing prepared in the concrete tanks is added by pumps for sludge stabilization, preventing the sludge anaerobic decomposition and helping emission of noxious gases. From sludge pumping pit, the sludge is occasionally pumped to the permanent sludge lagoons. The sludge after 5 – 10 years will be either left as it is or removed from the sludge lagoons and shifted to solid waste disposal site located at far end of the plant. The clarified effluent from settling tanks flows through the measurement zone, which has facilities to measure flow, pH, temperature, etc. The clarified effluent further travels through effluent treatment lagoons in a zig zag pattern. After zig sagging through the lagoons, the clarified effluent is passed through a 36" Dia RCC pipe line into the outfall channel and then into the Pandoki Drain and ultimately into the Sutlej River (Nawaz, 2011).

KTPCP has reduced the magnitude of pollution generated by more than 240 tanneries of Kasur to a huge level but the problems are not eliminated completely. The odor issues in the area remain the same and the wastewater being released from Common

Effluent Pretreatment Plant (CEPTP) still exceeds the limits of hazardous substances set by NEQS. The large lagoons of tannery sludge have been formed due to the discharge of sludge into open land which can become a serious environmental hazard in coming years. Hence, concluding remarks are that there is still a strong need to fill the loopholes in the existing pollution control system of Kasur (EM Research Organization, 2002).

1.6 Heavy Metals Pollution

Heavy metals are the metallic elements which possess a comparatively high density and can be hazardous and lethal even at minor doses (Lenntech, 2004). The metals and metalloids in the periodic table are communally referred as 'Heavy metals. Their density is usually higher than 4g/cm^3 which is five times more than the density of water. The chemical characteristics are of more importance than their density. The elements found in platinum group and chromium (Cr), cadmium (Cd), iron (Fe), mercury (Hg), zinc (Zn) silver (Ag) arsenic (As), copper (Cu), lead (Pb) come under the heavy metal group (Durubie et al., 2007).

In large variety of toxic substances heavy metals stand out because of their persistence in all environments which makes them a strong pollution marker. Heavy metals cannot be decomposed to less hazardous substances by natural, biological or chemical processes like the organic contaminants. Hence, the harm caused by these metals to the living beings and natural environments may be significant and enduring despite of all the corrective measures. Some metals (cadmium, manganese, lead, copper, etc) are regarded as symbolic metals for environmental contamination because of the fact that their certain concentrations in environment indicate considerable pollution (Mahimairaja, 2000). The heavy metals are discharged in bulk amounts to the lands and waters in proximity. This causes the harmful depletion of quality of water, soil and air which is the emerging problem all over the world right now (Babel & Kurniawan, 2003).

The heavy metals acquire the atomic mass of more than 20. Zinc, cadmium, mercury, copper, lead and chromium are among the most widespread metal pollutants. Metals are also found in soil in background level being naturally present in the soil. Cobalt, nickel, manganese, copper and zinc are the essential micronutrients required for the

health of plants while mercury, lead and cadmium may have unexpected effects (Gaur & Adholeya, 2004).

The contamination caused by metals has disastrous impacts on natural systems because these are non-biodegradable. Cadmium, lead and cobalt can be distinguished from other metal contaminants as they can be accumulated in bodies of living organisms but cannot be bio-decomposed. Thus, these metals can be the cause of different illnesses and ailments even at very minor quantities (Pehlivan et al., 2009). Heavy metals can stay in soil for thousands of years which are the reason behind various health issues to organisms. They also negatively affect plant health by ceasing their growth or genetical changes (Roy et al., 2005). Heavy metals are reputed not to be easily biologically or chemically degradable thus need to be manually eliminated from the site or convert into less harmful substances (Gaur & Adholeya, 2004).

Another major concern rising all over the world regarding heavy metal pollution is their removal from the contaminated sites (Tariq et al., 2006). The spoiling of nature with heavy metals is a genuine issue. Due to sewage sludge applications and industrial exercises these metals are founded to be in extensive amounts in the natural environments. The existence of heavy metals in mechanical and urban wastewater is one of the primary drivers of soil and water contamination (Wang et al., 2005). Since the different developmental activities like tanning, smelting, metallurgy, mining and sewage have come into being, there is a threat to the lives of flora and fauna (Zeng et al., 2009). The harm to nature's domain by the risky tannery wastewater is turning into an intense issue in Pakistan. The chrome tanning procedure brings about lethal metals; particularly Cr^{+3} entering into the effluents cannot be removed by simple treatment procedures (Franco et al., 2005). The presence of high salt and organic content and highly toxic metal chromium makes the tannery effluents distinctive from others (Colak et al., 2005).

There is an increased attention towards the ecosystem and health impacts of heavy metals now a day. During the previous decades, enormous elevation in the utilization of heavy metals has predictably caused the expanded flux of metallic substances in nature. There are few metals which are lethally poisonous on accumulation, having the ability to incorporate and pile up in the muscular tissues of living bodies triggering

antagonistic physiological impacts. Zn, Cr, Ar, Hg, Cd, Pd and Cu are the frequently found metals at the effluents contaminated sites (Sundar et al., 2010).

As the metal containing wastes are directly discharged into the surface waters and soils which has posed severe hazards to organisms' health and also made the ecological conditions vulnerable. Eventually, these metallic compounds seep into the soil and reach the groundwater and as a consequence there are several surveys reporting the alarming problems in living beings. The heavy metals can easily find their route to enter in the bodies of living organisms. The toxicity after coming in contact with these metals can be chronic as well as acute. These metals mostly attack liver, respiratory organs and kidneys. Whereas, lead, chromium and cadmium are harmful even at little doses while zinc is a substantial metal for plants but can be harmful at high doses. The intake of these metals in large amounts into the body can lead to cancer and ultimately death (Olayinka et al., 2011).

1.7 Soil Toxicity

Soil is the most important component of the environment, but it is the most undervalued, misused and abused earth's resource. Soil pollution has become a major subject of concern in all industrialized areas of the country. The eventual sink for the released pollutants into the nature is soil. Soil is the home to certain microorganisms or animals and it also provides nutrients and compounds required for the growth and development of the plants. There are several incidences which report about the deleterious effects of harmful pollutants on soil life. The source of all the pollutants whether organic or inorganic is the discharge of the industrial wastewaters (Gowd et al., 2010). The presence of the trace metals or micronutrients in the phytotoxic concentrations produces highly unfavorable impacts on plants as well as pose potential hazard to the human wellbeing. As a part of biosphere pollution by the let outs of the industries, plant growth has also faced a potential decrement in the development. Plants which grow in heavy polluted areas were found to be affected by the toxic metals (Agoramoorthy et al., 2009).

The alteration in growth rate and metabolic processes are correlated with physiological processes in plant cells due to the toxicity of the pollutants. The process of respiration, photosynthesis and mitotic activity are greatly affected. The pollution

potential of the effluents from the tannery industry produces phytotoxic effects and uptake of heavy metals in high concentrations which on getting accumulated in plants results in stress for the plant life (Chidambaram et al., 2009).

The contamination of soil is broadly distinctive as compared to the water or air contamination because the endurance of heavy metals in soil is evidenced to be extensive periods of time than other sections of the environment. Heavy metals such as chromium are very hard to be eliminate, once accumulated in the soil they may permanently reside there. Heavy metals emitted either from anthropogenic or natural activities can disperse in environment and may ultimately get deposited in the soil. Plants growing in such areas may absorb heavy metals in their body. Although heavy metals like iron, molybdenum, manganese, zinc, copper, magnesium, copper, selenium and nickel have a major role for growth and development of plants, but may be toxic beyond certain level. The most common heavy metals found in soil are Zn, Cd, Pd, Cu, Hg and Cr (Marques et al., 2008). With regard to the agricultural practices the heavy metal containing sludge application on farmlands is one of the most important matters. In spite of the fact that sludge utilization on land has been carried out in several parts of the world very less quantity of sludge is used in other industries even if it is advised to be useful because of its rich nutrient value as compost(Xiamei et al., 2005)..

1.8 Accumulation of Heavy Metals in Agricultural Soils

Due to the increasing trend of industrialization in the past centuries, the contamination of soil by heavy metals is raising all over the world. The main areas of heavy metal pollution are mostly lie in the vicinity of the industrial regions where the agronomic field crops in the nearby lands get adversely affected. The use of phosphate containing fertilizers and sewage sludge is another cause of metal accumulation in soil (Puschenreiter et al., 2005).

The long term residence time of heavy metals in soil is the major ecological concern. This can lead to extensive interference in the characteristics of soil; let it be physical, biological or chemical. This is also the cause infertility and reduced efficiency of the terrestrial/agriculture soil. Heavy metals like Zn, Cu, Cd and Cr can change the metabolic activities of plants by triggering or hindering the normal growth of plants. It

is reported that when humans utilize vegetables contaminated with heavy metals, about 80% of these metals enter into the human bodies (Grigalavičienė et al., 2005).

The deposition of heavy metals in fertile and productive agriculture soils is concerning problem because it can generate extensive food and health safety issues and also become a hazard for the soil biota. The heavy metals possess specific characteristics such as they are all the time there in the soil in background levels; they are non-degradable; they are essential for plants in specified limits and can be detrimental on crossing those limits and they are usually present as cations that can easily mingle with the soil substances. The change in environmental circumstances can cause these metals to become mobile (Facchinelli et al., 2001). These elements come in the environment from the parent rock or the human inputs. The anthropogenic activities involve waste discharge, urban and industrial effluents, application of sludge and fertilizers, gaseous emissions from fuel burning and use of sewage and industrial wastewater for irrigation purposes (Koch & Rotard, 2001).

Other than the anthropogenic supplies the factor that influences the deposition of metals in soil is the physicochemical characteristics of soil. The parameters that extensively influence the soil properties to sustain the heavy metal content are pH and organic matter. Thus, to study the effects of these parameters on the heavy metal deposition in soil and vice versa is vital. The information regarding the source of heavy metals, their accumulation in soil, and their way to interface with soil characteristics are important goals in ecological analysis (Qishlaqi & Moore, 2007).

If the accumulation concentrations of metals are low at the moment, it may not cause any immediate effects but it can generate severe detrimental consequences later in time (Puschenreiter et al., 2005). Most of the studies have shown that metals are mainly absorbed in stem and edible parts of the plants which can be a hazard to the consumer's health. The accumulation of heavy metals in plants is strongly affected by quality of soil and climatic conditions under which the plants are cultivated and the stage of development of plant when harvested. The other considerable factor to measure the heavy metal accumulation in fruit plants is the understating of the nature of soil. This is for the reason that soil is the retaining and residing location of pollutants. The presence of heavy metals in agricultural soils can cause ever-lasting

impacts on living wellbeing which can lead to extinction of species and their habitat (Omoloye, 2009).

1.9 Effects on Humans

The existence of hazardous compounds in the industrial wastewaters is a widespread environmental issue because of the dissolved metallic ions which can eventually enter into the food chain and become detrimental for human health (Mythili & Karthikeyan, 2011). These hazardous compounds can enter into the food chain through different ways; first they enter into the plants via soil then into the plant eating animals and later into the consumers of those animals or the milk extracted from those animals. The sludge is widely applied on agricultural lands. This unrestricted discharge of contaminated water is adversely disturbing the quality of soils and groundwater reservoirs present in the tannery areas. The surrounding areas of tanning industries have been evidenced to be distressed by chromium and other detrimental chemicals used in tanning. There is a dire need to develop integrated cleaner production of leather because of the environmental problems arising due to the industrial practices so that the leather sector can develop in line with the sustainable environment (Scholz & Lucas, 2003).

The toxic chemicals mainly get into the human bodies through drinking the contagious water and eating contaminated food (Santos et al., 2004). The consumption of heavy metal accumulated crops can cause serious illnesses in organisms. Humans intake of these toxic metals by eating the polluted vegetables and by inhaling the foul air emissions (Jan et al., 2010).

The entrance and persistence of heavy metals in food chain through anthropogenic sources is the worldwide evidenced concern. As these heavy metals have the tendency to retain into the environment for longer periods of time without any degradation or conversion, they can aggregate into the fundamental human organs including liver and kidneys. This accumulation is also the reason behind enormous other fatal illnesses. The toxicity of metals can be chronic and acute while they can also cause cancer, mutations, and nervous system problems and ultimately may lead to death. The potential to damage particular body organs vary metal to metal. The health disorders

related to aluminium, lead, zinc, copper and mercury are dysentery, vomiting, diarrhoea, paralysis, blood poisoning, paralysis etc (Singh et al., 2009).

When the vegetables are cultivated in the soils having higher content of heavy metals, they absorb these metals and deposit them in their roots, stems, leaves and flowers or fruits. These metals can be accumulated in such amounts that can pose serious health disorders among the people who are involved in the consumption of these heavy metal containing plants. This is because of the reason that once bio-accumulated in human body, there are no affective treatments to remove them from the body. The heavy metals like Cd and Cu are the precursors of the gastrointestinal ailments and cancer. These are believed to be so harmful because of their long persistent nature, non-biodegradability, and their capability to get bio-accumulate into the organisms' tissues (Ahmad & Goni, 2010). Gastrointestinal cancer is one of the most prevailing illnesses caused by the intake of heavy metals while other health problems include slow or hindered growth, weak immunity systems and psychological impairments (Jan et al., 2010).

Several health surveys have determined that nervous system, kidneys and heart are among the chiefly affected organs in response to the ingestion of heavy metals in excessive amounts. Hence, the regular analysis of soil toxicity by heavy metals and the recognition of their origin is primary and essential step to evaluate the extent of health related problems in the area (Tariq et al., 2008). Common hazards caused by the metals released from industry are summarized in Table 1.3 (Mashi and Alhassan, 2007).

2

Table.1.3. Common hazards caused due to metals released from industry

Metals	Health hazards
Cadmium	Inhibits functioning of enzymes, affects gastro intestinal tract, lungs and bones, causes renal problems
Mercury	Headache, intestinal problem, blood malfunctioning
Chromium	Carcinogenic, leads to kidney disorders, ulcer, nervous disorder
Lead	Anemia, abdominal pain, damage to nerves, convulsion, hypertension
Arsenic	Liver damage, ulcers, kidney problems, dermatological disorders
Copper	Mental stress, coma, uremia
Zinc	Kidney problems, pain in legs, vomiting
Nickel	Decreases body weight, damages heart and liver, causes skin irritation
Fluoride	Fluorosis
Aluminum	Weakens nervous system

1.10 Effects of Chromium

The direct disposal of bulks of wastewater generated by tanneries onto the virgin lands in the proximity of the tanning industry is a common practice in developing nations. This practice has posed detrimental effects on the physical and biological quality of surface and ground water and soil, leaving them unfit for human utilization. These conditions have also caused the serious health problems like skin diseases, headache, stomach disorders, night blindness and several other ailments. Chromium is the most excessively utilized heavy metal involved in the process of tanning. In spite of the fact that there is vast establishment of cleaner leather processing technologies to reduce the deleterious hazards caused by these tanneries because of the presence of chromium which has got no substitute yet. In the traditional way of tanning procedures large amounts of chromium salts freely go to the tannery wastewater. The analysis of the discharged water revealed that the chromium salts is found in highest concentrations than other metals and these concentrations are way larger than the prescribed limit (0.5-15mg/l) (Tariq et al., 2006).

There are two different oxidation states of chromium which are hexavalent (Cr^{+6}) and trivalent (Cr^{+3}). Both of these states possess distinctive features with regard to bioaccumulation and bioavailability. Hence, the hazards and impacts are solely rely on the oxidation state of Cr. The trivalent chromium is more hazardous and soluble as compared to the hexavalent chromium (Pandey & Sharma, 2003). This metal enter into the body by eating the plants accumulated these metals. Chromium has deleterious impacts on the plants also. The higher concentrations of Cr may lead to the permanent loss of vegetation by intensively affecting the biological factors. Hence, the fertile land turns into barren land, eventually (Abdul-Ghani et al., 2011).

The phytotoxic impacts of chromium involve chlorosis, inhibited root growth and restrained germination of seeds. Several researches have carried out on the toxicity of chromium on crops. This metal substantially disturbs the metabolic activities among wheat, barley, vegetables, maize etc (Abdul-Ghani et al., 2011). The presence of high amounts of Cr in the soils of plant growth produces impairment in the growth or

production processes of plants and also causes plant diseases to spread (Nematshahi et al., 2012).

Cr^{+3} is involved in the regulation of glucose in human body, hence, it is the necessary micro nutrient. This is less mobile, more stable, less toxic, and have higher propensity to build strong complexes. Currently, Cr^{+6} is evidenced to be the cause of certain serious diseases such as lung cancer, stomach ailments, skin problems and ulcers. The solubility of hexavalent chromium is very high which makes it almost impossible to eliminate from the wastewaters without any chemical or biological treatment. The common practice is to reduce hexavalent Cr into trivalent Cr. Kasur tannery cluster releases about 13,000 m³ of extensively polluted effluents per day. There are around fifty thousand people in Kasur who are living and working in this area, face potential danger to be affected from the deadly ailments like cancer associated with the tannery generated wastes (Rashid et al., 2012).

Chapter 2

Literature Review

The environmentalists have analyzed the effluents of dangerously polluting industries, i.e. textile, tannery and leather and have also studied their effect on the surrounding soil and ground water in the vicinity of these industries. Due to the worldwide famous polluting tannery cluster site in Kasur a large number of studies have been undertaken from time to time on air, soil and water pollution due to existence of different tanneries in suburbs of this town.. Most of the studies have shown exceeding limits of metal contents (especially Chromium) in the study area. The highest concentration of chromium detected in the effluent from the tanneries in Kasur district of Pakistan is to be 3,956 mg/L which is high enough to pose serious pollution stress on the environment in the proximity of the tanneries. Large variation in chromium concentration in soils in a leather tannery district in Italy ranging from 42.9 mg/kg to 10,590 mg/kg with mean of 610 mg/kg was observed (Rashid *et al.*, 2012). There are also several studies on decontamination of soil from metals but just on experimental basis. But due to the large pollution level and with the laws regarding dumping of effluents poorly implemented across Kasur it seems that the problems encountered in Kasur will not be overcome easily or quickly. There is no study available to provide the information of contamination of the soil particularly of the whole 400 acres area of land that has been a stagnant pool for four to five decades.

A brief review of the research relating to the undertaken study from Pakistan with reference to the related aspects is reviewed below in chronological order.

2.1 Tannery Effluents Contaminated Soil Toxicity Assessment

Saadia R. *et.al* (2005) conducted the multivariate analysis of 12 metals (K, Na, Mg, Ca, Fe, Mn, Cd, Cr, Zn Co, Ni, and Pb) in tannery effluents and related soil. Thirty eight tanning units situated in Kasur, were selected. The metal analysis was carried out by atomic absorption spectrophotometry. The levels of Cr (391, 16.7 mg/L) and Na (25,519, 9369 mg/L) were reported that were in exceeding limits in tannery effluents and soil samples, respectively. The study confirmed that soil Cr was strongly associated with that of tannery effluents.

Sinha *et.al* (2006) studied physicochemical properties of the soil irrigated with treated tannery wastewater and the study revealed higher values for electrical conductivity, salinity, available phosphorous, sodium and potassium content while Calcium and Magnesium content was found less than the standard limit. The plant available metal content was also found high i.e. Fe (529.02-2615 $\mu\text{g g}^{-1}\text{dw}$), Ni (3.12-10.51 $\mu\text{g g}^{-1}\text{dw}$) and Cr (33.26-114.26 $\mu\text{g g}^{-1}\text{dw}$).

Barajas *et.al* (2007) assessed the effect of high levels of Cr^{3+} and Cr^{6+} on microbial (dehydrogenase) activity and nitrogen and carbon mineralization in semi arid soils. Addition of Cr^{6+} alone inhibited the CO_2 production rate, nitrification and dehydrogenase activity in soil while significant reduction in inhibition of CO_2 production and dehydrogenase activity was observed on addition of tannery sludge to Cr^{6+} amended soils but it increased the inhibition of nitrification in soil. Cr^{3+} added alone or Cr^{3+} plus tannery sludge added to soil showed no specific effect. The measurement of dehydrogenase activity turned out to be the best tool for assessment of the harmful effects of Cr^{6+} on soil microbial activity in semi-arid soils.

F.akbar Jan (2010) carried out multivariate statistical analysis of heavy metals contamination of industrial area of Peshawar and indicated that effluents streams strongly affect the adjacent soil. The collected soil samples showed significantly higher mean concentration of metals as compared to effluent stream water, which clearly indicated that the adjacent soil retained heavy metals. Mean concentrations of metals in soil were recorded as Cr 0.256 mg/L, Zn 0.672 mg/L, Pb 2.006 mg/L, Ni 0.359 mg/L and Mn 3.148 mg/L.

A study by Deepali and Gangwar (2010) showed exceeding limits of all metals (Cr, Fe, Mn, Cu, Pb and Cd) in effluents and associated soil from textile and tannery industry area near Haridwar. Cr contamination was observed only in samples collected from nearby tanneries and it was found more than other metals. The average value of chromium recorded in tannery associated soil was 743.80 $\mu\text{g/gm}$.

Another study of soil contaminated with tannery effluents by Rabah and Ibrahim (2010) revealed higher counts of bacteria and fungi in all the sampling sites. On the other hand, the physiochemical analysis of soil showed higher contamination of soil

with chromium (0.20-0.26mg/g), ammonia (0.40-0.60mg/g), and sulphide (0.35-0.44mg/g). All these levels were higher than the tolerable limits and a threat to local community.

F.akbar *et.al* (2010) reported that industrial wastewater irrigation significantly increased both bioavailable and total metal content in soil. The concentrations of several heavy metals ranged higher than permissible limits by WHO/FAO Zn (38.38-296.29 mg/kg), Cd (0.04-0.20 mg/kg), Pb (0.1-0.28 mg/kg), Ni (29.55-66.46 mg/kg), Cu (36.22-78.72 mg/kg), Cr (0.98-2.10 mg/kg), Mn (61.86-156.24 mg/kg) in food crops grown on wastewater irrigated soil. The intake of Cd, Pb and Cr was found highest for all the vegetables, while intake for Zn, Ni, Cu and Mn was the lowest in humans.

A comparative statistical analysis of soil affected by chrome and vegetable tanning effluents of Kasur and Mian Channun was done by Saadia *et.al* (2012). This study evidenced that Kasur district had enhanced levels of Cr and other metals in the soil due to the chrome tanning as compared to soil of Mian Channun due to vegetable tanning. The major contributing metals in the soils of Kasur were Na, Ca, K and Mg with mean values of 18,765mg/kg, 1335mg/kg, 610.4mg/kg and 137.2mg/kg respectively, while the levels of Cr varied from 2.0mg/kg to 26.0 mg/kg.

Moneeza *et.al* (2012) did the heavy metal toxicity analysis of few high risk areas of Kasur, Pakistan. The values of three metals Cr, Mn and Ni were reported as 3.859 ± 0.510 mg/Kg, 0.5243 ± 0.0691 mg/Kg and 0.4759 ± 0.0318 mg/Kg, respectively. Highest levels of these metals were found in the areas in contact with tannery effluents. Disease pattern in the area also illustrated that tannery industry was affecting not only water, soil and air but also population of the area.

Rashid *et.al* (2012) The results of two bore holes near Rohi Drain in Kasur tannery area showed no significant soil contamination in area adjacent to this effluent drain. The overall values for retained hexavalent chromium content ranged from 2.5 to 8.1 mg/kg, for total chromium content from 6.4 to 48.8 mg/kg. The retention of hexavalent chromium was found to be relatively higher at the depths near the water table. The leaching values for hexavalent chromium (0.002 to 0.02 mg/L) and for total

chromium (0.01 to 0.06 mg/L) were observed. All these values were less than standard values. The higher retention of total chromium was observed higher for the silt and clay proportion in soil.

Karim (2013) conducted a study of Hazaribagh, Bangladesh tannery effluents contaminated site and reported very high contamination of soil with Cr up to 37,000 mg/kg dm, mineral oils, and extractable organohalogenic compounds. Sulfur concentrations were also very high. Most severe pollution was confined up to top 10–20 ft of soil. Chromium in subsoil was founded to be very stable but less mobile in from of Cr³⁺ specie.

2.2 Plants Uptake of Heavy Metals

A study on accumulation of heavy metals in crop plants and naturally growing weeds by Barman *et.al* (2000) identified the plants (*Alternanthera sessilis* and *Cynodon dactylon*) as hyper accumulators of heavy metals when grown in fields irrigated with industrial wastewater. Fe and Cr were the highest accumulated metals. The concentrations of Cd, Pb, Cr and Ni were much higher in wheat and mustard and were beyond standard human consumption level.

An analysis by Sinha *et.al* (2006) for metal accumulation in twenty five different vegetables/crops grown in long term treated tannery wastewater irrigated fields showed that leafy vegetables had higher accumulation of toxic metals in edible parts, especially Cr in these parts was higher than edible parts of fruit bearing/non-leafy vegetables. Ni was not detected in all the plants and Cr was the most accumulated metal. Few vegetables such as potato, turmeric and garlic ($11.81\mu\text{g g}^{-1}$ dw, $20.86\mu\text{g g}^{-1}$ dw, $19.27\mu\text{g g}^{-1}$ dw respectively) accumulated lowest levels of Cr, while, maize, bitter gourd, jack tree, egg plant, and okra showed no accumulation for Cr and thus were suitable to grow in area.

Tudunwada (2007) assessed that Millet and Sorghum crops when grown in a field soil amended with tannery sludge showed accumulation of heavy metals (Cr, Cu, Co, Pb, Mn, Fe, Zn and Ni). The analysis of shoots and grains revealed that millet crop

accumulated higher concentrations of Co, Pb, Zn, Cr and Cu than sorghum. Thus, sorghum was most suitable crop to grow as it accumulated less heavy metals.

Chandra *et.al* (2008) reported that wheat and mustard plants irrigated with distillery and tannery effluents contained metal concentration higher than permissible limits of WHO/FAO. Wheat plant accumulated less metal content as compared to mustard plant and Fe was the most accumulated metal (340mgkg^{-1}) in wheat root and (560mgkg^{-1}) in mustard leaves). An increase in photosynthetic pigment, protein content and antioxidant content was observed as biochemical effect of toxic metals (Cu, Cd, Cr, Zn, Fe, Ni, Mn, and Pb).

A study of Luna *et.al* (2009) Cr toxicity on wheat, oat and sorghum plants indicated that Cr^{6+} was more mobile in soil than Cr^{3+} and had greater toxicity effects on seedlings of all three plants even at minor Cr concentrations. Most sensitive assessment for Cr-toxicity of soil was root growth as compared to seed germination and shoot growth. Cr^{+3} and Cr^{+6} affected Sorghum and wheat germination significantly. Root and shoot growth of all plants decreased with the increase in Cr concentration. Leaves of wheat were affected by chlorosis when exposed to Cr^{6+} (50mgkg^{-1}).

Bioconcentration factor (BCF)/plant concentration factor (PCF) is a parameter used to describe the transfer of trace elements from soil to plant body. A study by Jasim Uddin Ahmad (2010) on vegetables grown in heavy metals contaminated soil showed that although the Cu concentration was within permissible limit in soil; the BCF value for Cu of tomato was highest among all studied heavy metals. Tomato (for Cu, Cr, and Fe), cabbage (for Ni, Pb, and Zn), and egg plant (for Cd) showed highest metal accumulation.

Olayinka *et.al* (2011) estimated accumulation of metals in three vegetable samples (*Amaranthus viridis*, *Corchorus olitorius* and *Celosea argentea*) grown in metal contaminated soil. The plant *A. viridis* was observed to accumulate highest concentration of the metals analyzed in its tissues Cd ($1.4\text{-}5.2\text{ mgkg}^{-1}$), Cr ($43.0\text{-}96.0\text{ mgkg}^{-1}$), Pb ($20.0\text{-}49.5\text{ mgkg}^{-1}$) and Zn ($78.1\text{-}112\text{ mgkg}^{-1}$). Sequential extraction of soil before growing the vegetable samples indicated that Cd and Zn were the most

potentially bioavailable metals as they were mainly present in acid exchangeable and reducible fractions. The values of soil-to-plant transfer factor for metals decreased.

2.3 Phytoremediation

A study of Lombi et.al (2001) phytoextraction on *Thlaspi caerulescens* and maize (*Zea mays* L.) indicated that *T. caerulescens* removed more than 8 mg kg⁻¹ cadmium and 200 mg kg⁻¹ zinc from industrial contaminated soil but could not survive in high copper concentration. Maize with EDTA treatment accumulated smaller concentrations of Cd and Zn. EDTA did increase metal solubility but formed metal and EDTA persistent complexes which could be an environmental risk.

The pot experiment by Sampanpanish et.al (2006) for phytoremediation of Cr contaminated soil led to the result that *Cynodon dactylon* (152.1 mg/kg dw) and *Pluchea indica* (151.8 mg/kg dw) showed highest accumulation of total chromium for 100 mg/kg soil input of Cr (VI). Most of the Cr uptake occurred within 30 days after the input. *Pluchea indica* was found more suitable for phytoaccumulation of Cr with total chromium uptake 27%, 38%, and 35% in roots, stems, and leaves, respectively.

Abou-Shanab et.al (2007) conducted a pot experiment to study the growth and metal accumulation of five plants (*Zea mays*, *Sorghum bicolor*, *Helianthus annuus*, *Conyza discoridies* and *Cynodon dactylon*). The roots and shoot lengths and dry weights were found to be reduced in all plants. *C. dactylon* shoot showed highest accumulation of Cr (6.4 g kg⁻¹). *Z. mays* and *S. bicolor* were more suitable for phytostabilization as translocation of metal from root to shoot was restricted in these plants. The highest accumulation of metals in shoots of *Conyza discoridies* made it best specie for phytoremediation of Zn, Cu and Pb.

Gupta and Sinha (2007) found that the two plants *Sida. acuta* and *Cassia. Fistula* were found most suitable to decontaminate a tannery sludge disposal site from most of the metals. The correlation analysis between DTPA extractable metals and metal accumulation in the plants gave better value of correlation for metals in *S. acuta* and

C. fistula. Moreover, *S. acuta* showed better soil to plant transfer factor for most of the tested metals, especially Cr.

Khilji and Firdaus-e-Bareen (2008) studied the removal of toxic heavy metals from tannery sludge by an anchored hydrophyte (*Hydrocotyle umbellata*) to assess its rhizofiltration capabilities. For all the prepared concentrations of wet sludge *H. umbellata* showed a good tolerance. The reduction in chlorides and chemical oxygen demand (COD) was observed. The accumulation of Cr (18,200 mg kg⁻¹) was highest followed by Zn (15,560 mg kg⁻¹), Na (7,692 mg kg⁻¹) and Cu (6,660 mg kg⁻¹) in roots after 90 days. The study suggested that harvesting these plants three times with a 60% sludge concentration will remove all metals from tannery sludge.

Sakthivel and Vivekanandan (2009) revealed that three, stress enduring and fast growing tree species (*Melia azedarach*, *Azadirachta indica* and *Leucaena leucocephala*) could be employed in tannery polluted agricultural land by phytoremediation. The plants grew well in higher sludge concentrations of calcium, magnesium, nitrates and total nitrogen. The dark green color was observed in plants. The increase in polypeptides, biomolecules and CO₂ absorption was observed. The assimilation of chromium in the leaves ranged from 2.39-3.45 mg/g dw.

Mahimairaja (2011) examined the phyto-remediation potential of several flower and oilseed crops *Jasminum sambac* (Gundumalli), *J.grandiflorum* (Jathimalli), *Polianthus tuberosa* (Tuberose) and *Nerium oleander* (Nerium) for Cr-contaminated soil. The Cr content in plants varied from 0.74-4.83 mg kg⁻¹ in flowers, 1.69-7.85 mg kg⁻¹ in leaves and 2.83-14.02 mg kg⁻¹ in roots. Non-edible flower crops showed no toxicity symptoms for Cr concentration of up to 14.02 mg kg⁻¹, thus were most suitable for phyto-remediation. The *Jasminum* and *Sunflower* species showed highest tolerance towards soil Cr but the high accumulation of Cr (5.10 mg kg⁻¹) in sunflower seeds diminished its potential for phyto-remediation. The Mustard plant could not establish seeding even.

Firdaus-e-Bareen and Tahira (2011) conducted a study on phytoremediation by local species of plants grown on tannery effluent contaminated lands of Kasur. *Suaeda fruticosa* was used for experimentation because of its higher phytoextraction abilities.

EDTA treatment was given to both field and pot experiment soils which helped in leaching of Cr. Results showed significant bioaccumulation of Na and Cr by leaves of *S. fruticosa* with small doses of EDTA.

2.4 Sludge Composting

Haroun *et.al* (2007) studied fate of heavy metals in tannery sludge by composting for 50 days. A higher removal of Cr, Cd and Pb was observed while Zn and Cu were removed in least concentrations. Overall, every metal concentration was decreased in the end by leaching. 70–80% of the metals were bound to the residual fraction while 12–29% fraction were resistant to extraction. Only 2% of the metals were potentially bioavailable for plants.

An analysis of heavy metals during 60 days of tannery sludge composting by Haroun *et.al* (2009) revealed that all parameters reached their stable limits. C/N ratio was optimal, inorganic nitrogen was transformed into stable organic form. Leaching of heavy metals during composting left very small concentrations of Cr, Zn, Cu, Pb and Cd making the compost fit for agriculture. 97% germination of Chinese lettuce and cabbage showed that final compost was non-phytotoxic.

Mahimairaja (2011) assessed that the experiment of application of coir pith and poultry manure on Cr-contaminated soil proved to be a good bioremediation practice. It resulted in significant reduction in Cr-bioavailability due to reduction of toxic and soluble Cr (VI) to non-toxic and less soluble Cr (III) and formation of organo-chromic complexes (immobilization).

2.5 Microbial Metal Bioremediation

Heavy metals found in wastewaters are harmful to the environment and their effects on biological system are very severe. An efficient and economic treatment for their removal and reuse needs to be developed. Microbial metal bioremediation is an efficient strategy due to its low cost, high efficiency and eco-friendly nature. Recently advances have been made in understanding metal-microbe interaction and their application for metal detoxification. Microorganisms in soils are sensitive to the high

concentration of heavy metals like zinc, manganese, cobalt, copper, chromium, cadmium, mercury and silver. Smrithi and Usha (2012)

Following are some studies showing effectiveness of microbial bioremediation:

Megharaj *et.al* (2003) checked detoxification ability of two bacterial species (*Arthrobacter* sp and a *Bacillus* sp) isolated from a long-term tannery waste contaminated soil. Both bacteria tolerated Cr (VI) concentration of 100 mg ml⁻¹ with 50% glucose in minimal salts agar medium. *Arthrobacter* sp was not only able to grow in medium but also reduced Cr (VI) up to 50 µg/ml while *Bacillus* sp reduced only 20 µg/ml. *Arthrobacter* sp. showed great potential for bioremediation of Cr (VI) contaminated soils.

The fungal isolates of *Aspergillus niger* from tannery effluent contaminated soil showed higher removal of chromium than other fungal species. The absorption of chromium was observed at pH 6, temperature 30 °C. *A. niger* removed more than 70% chromium in soil microcosm at 250 and 500 ppm concentration of chromate. The chromium-contaminated soil mixed with compost (5% and 10%) removed chromium remarkably in presence of *A. niger* report. Srivastava and Thakur (2006)

Gomez and Bosecker (2010) reported that bioremediation with iron and sulfur-oxidizing and metal resistant bacteria (*Thiobacillus ferrooxidans* and *T. thiooxidans*) solubilized more than 50% of most of the heavy metals (As, Cd, Co, Cr, Cu, Ni, Zn). Cd, Co, Cu, and Ni were completely leached out by *T. ferrooxidans* strains while *T. thiooxidans* mobilized more than 80% of Cd, Co, Cu, and Zn. Both species showed good potential for bioleaching of heavy metal contaminated soils.

A study by Masood and Malik (2011) showed that *Bacillus* sp. strain FM1 was identified as Cr (VI) reducing strain from tannery wastewater irrigated soil. This strain showed resistance to toxic heavy metals including Cr (VI), Cr (III), Cd²⁺, Cu²⁺, Co²⁺, Ni²⁺ and Zn²⁺ and completely reduced 100 mg/L Cr(VI) within 48 h at 37 °C and pH 8. The addition of glucose enhanced Cr (VI) reduction. This bacterium showed great potential for Cr (VI) detoxification.

Smrithi and Usha (2012) carried out a study with an objective to remediate the tannery effluent contaminated soil by microorganisms. Results showed that the Cr-resistant isolated *Bacillus* sp reduced 85.9% of chromium from the culture medium after 96 hours by adding Potassium dichromate ($K_2Cr_2O_7$) at $10\mu\text{g/mL}$. *Bacillus* sp showed maximum heavy metals degradation at 2.0 mg/mL for chromium, nickel, zinc, copper and cadmium.

Yasin and Faisal (2012) studied growth of *Zea mays* (Lin) plants grown in tannery-contaminated soil by inoculation of four bacterial strains (*Cellulosimicrobium cellulans*- CrK16, *Exiguobacterium*-CrK19, *Bacillus pumilus*-CrK08 and *Bacillus cereus*-CrK20) that could resist up to 25 mg ml^{-1} of Cr (VI). Physical changes such as delayed flower budding, feminization of male flowers, burning of leaves and reduction in shoot length and dry biomass. Biochemical changes resulted as increasing 14-26% acid phosphatase activity, 50% carotenoid content, 17-38% soluble proteins content, 34% chlorophyll a and 70% chlorophyll b.

Non-inoculated plants showed higher Cr uptake (114 mg kg^{-1}) as compared to inoculated plants (49.4 mg kg^{-1}). Both bacteria and maize turned out to be good candidates for reclamation of tannery contaminated areas.

Negative effects of Cr induced stress on plants can be minimized using bacteria having an enzyme called 1-amino-cyclopropane-1- carboxylic acid (ACC)-deaminase. Shahzadi *et.al* (2013) reported that inoculation with ACC-deaminase producing bacterial strains increased the growth of wheat significantly as compared to uninoculated wheat seeds. The two strains (*Pseudomonas fluorescens* (Q14) and *Bacillus thuringiensis* (KAP5)) remarkably increased the root and shoot length. Significant Cr accumulation ($80.8\mu\text{g/g}$) was also observed in dry mass of root and dry mass in shoot ($69.9\mu\text{g/g}$). Thus, ACC-deaminase producing bacterial strains was most likely to enhance the bioremediation process of Cr contaminated sites.

Basu *et.al* (2014) experimented bioremediation of Cr (VI) by isolating bacterial specie *Bacillus subtilis* from Cr contaminated soil. The bacterial strain showed 97%, 89% and 55% removal of at initial concentration of Cr 2.5 mg/L , 5 mg/L and 7.5 mg/L , respectively in 24 hours from culture medium. Cr (VI) removal was best observed at 30°C . Percentage removal was decreased with increase in chromium concentration.

The Bacillus strain had the potential for the end of the pipe treatment of chromium (VI) contamination.

2.6 Chemical Extraction

Continuous application of wastewater leads to the enrichment of soil with heavy metals. Oxidation state, phase and form of heavy metals strongly affect their bioavailability. Chemical extraction techniques provide a well established mean of identification and characterization of different fractions of heavy metals in soil.

The leaching of several metals (Cu, Zn, Cd, Ni, Pb, Fe and As) from industrial heavy metal polluted soil of Lahore, Pakistan was evaluated by Hussain and Islam (2010). Five different leaching liquors (0.01M CaCl₂ , 1 M HNO₃ , 1:1 mixture of 0.1M HCl and 0.1M NaCl, 0.01M, EDTA) were applied and pH was controlled using 0.5M acetic acid tested for extraction of heavy metals out of which HNO₃ result highest extraction of heavy metals . EDTA also showed significant extractive efficiency. The results for few leached metals were as (78.7ng/ml) in 0.01M EDTA, Zn (1.81µg/ml) and Fe (898.96µg/ml) in HNO₃.

Chromium (Cr) chemical fractionation was studied by 5 hour citric acid (CA)/sodium citrate (SC) washing. A four-step sequential extraction proposed by the Community Bureau of Reference (BCR) was carried out. The results indicated that the process not only helped in Cr removal but also released the soluble and exchangeable fractions of Cr in soil. This proved to be an advisable choice for remediation of soils contaminated with Cr. Li *et.al* (2012)

Goals and Objectives

The brick by brick model of the research studies narrated in the review of literature presented to this point made the base of the research study undertaken by us. The goal and objectives of the project undertaken were fixed as follows:

The goal of the study will be the complete physicochemical analysis of the Kasur tannery wastewater contaminated soil reclaimed by the of Common Effluent Pre treatment Plant (CEPTP) that is used for agricultural practices and identification of certain toxicity and conservation measures to render the contaminated soil fit for agriculture.

The objectives will be as follows:

1. Sampling of the reclaimed Kasur tannery wastewater contaminated soil.
2. Physico-chemical analysis of reclaimed soil for toxic ingredients particularly heavy metals which are most hazardous if enter in food chain.
3. Identifying the toxicity level in soil by comparing with specified international standards.
4. Suggestions and recommendation of suitable measures to avoid impact of toxicity on ecosystem and human health.

Chapter 3

Materials and Methods

3.1 Study Area

The present study deals with approximately 400 acres of land area contaminated with tannery waste water in Kasur district. Instead, the area is shown in the map shown in Fig.1 which covers the areas along Deepalpur Road and Mangal Mandi Road, Ali Garh, Deen Garh and areas along Tannery Wastewater Pre-treatment Plant, Kasur.

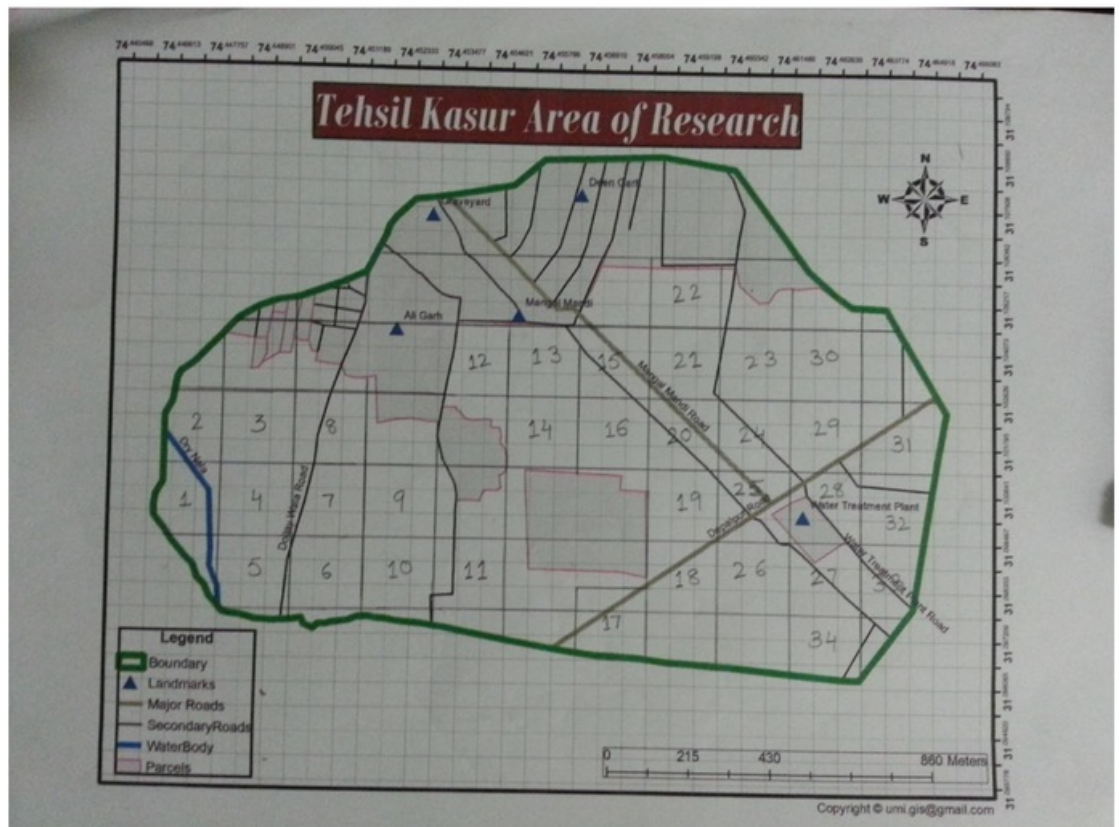


Fig.3.1. Map of Kasur research area showing grid and sampling sites

3.2 Sampling Plan

The major objective of the study was the analysis of reclaimed soil in Kasur to check its suitability for agriculture. The sampling plan was prepared with the help of professionals of Soil and Water Testing Laboratory for Research, Thokar Niaz Baig, Multan Road, Lahore. Grid sampling was done which involves subdividing the area of concern by using a square or triangular grid and collecting samples from each grid. A grid is constructed over the whole site. The distance between sampling locations in

the grid is determined by the size of the area to be sampled and the number of samples to be collected. Grid sampling is often used to delineate the extent of contamination and define contaminant concentration gradients. As a general guideline, one single or composite (bulk) sample per 4 hectare (approximately 10 acres) should be collected from the top 0-15cm of the soil profile with an auger or spade. Thus, a map was prepared with the help of GIS (Geographical Information System) which was divided into 3*3 grids; each grid covering an area of 9 acres. Composite sampling technique was used to carry out sampling. From each grid four/five grab samples were taken and mixed to form one composite sample. Total forty samples were collected in the same manner from all grid sites using GPS (Global Positioning System) device.

3.3 Sampling Sites

The criterion for selection of the sampling sites was the possible contamination due to standing of tannery wastewaters. The soil samples were collected from thirty-four different sites. Each composite sample was representative of the area of each grid. Map of the Kasur research area is shown in the Fig. 1. One small box represents land area of one acre and one big box the area of 9 acres. Longitudes and latitudes are also indicated.

3.4 Parameters Measured

The selected parameters for the physicochemical analysis of reclaimed soil of Kasur research area were pH, electrical conductivity (EC), Organic Matter (O.M), Organic Carbon (O.C), Nitrogen (N), Phosphorus (P), Potassium (K), Sodium (Na) and heavy metals i.e. chromium (Cr), Cadmium (Cd), Arsenic and Nickel (Ni). The physicochemical analysis of samples was carried out in Soil and Water Testing Laboratory for Research, Thokar Niaz Baig, Multan Road, Lahore and in science laboratory of Lahore School of Economics. There were total thirty-four (34) samples and each sample consisted of three replicates. The selected parameters are shown in Table 3.1.

Table.3.1. Parameters for physiochemical analysis of soil

Parameters	Unit
pH	
Electrical conductivity	mS/cm
Organic Carbon	%
Organic matter	%
Phosphorus	mg/kg
Sodium	mg/kg
Potassium	mg/kg
Heavy Metals	mg/kg

3.5 Sampling Procedure:

Samples were collected according to the guidelines given in US-EPA Field Sampling Guidance Document #1205. Standard sampling techniques were followed in each sampling site to ensure the integrity of the samples. The samples were collected in accordance with required and established methods. Extreme care was taken during sampling, sample handling, sample preservation, identification, transportation and storage. Samples were collected and handled carefully to avoid contamination before they reached laboratory. They were stored in appropriate container to maintain the integrity of the samples. To obtain reliable results, the samples were analyzed as soon as possible.

3.6 Sample Collection

Samples were collected with the help of professionals provided by Environmental Protection Department, Gaddafi Stadium, Lahore and Tannery Wastewater Pre-treatment Plant, Kasur. A hand auger consists of a sample bucket attached to the bottom of a length of pipe that has a crossbar at the top. Bucket augers are better for direct sample recovery. These, are fast, and thus provide large volume of sample.

The following procedure to collect soil samples with a hand auger was followed and precaution taken.

1. Decontaminated equipment was used to collect the soil sample.
 2. Auger was inserted into the material to be sampled at a 0° to 45° angle from vertical. This orientation minimizes spillage of the sample from the sampler. Extraction of samples may require tilting of the sampler.
 3. Auger was rotated once or twice to cut a core of material.
 4. Auger was slowly withdrawn, making sure that the slot was facing upward.
 5. Grab sample was transferred into an appropriate sample or homogenization container.
 6. Grab samples were mixed thoroughly and foreign materials like roots, stones, pebbles and gravels were removed.
 7. Bulk was reduced to about half to one kilogram.
 8. Sample was collected in a clean polythene bag.
 9. Chemical preservation of solids is generally not recommended. So samples were kept at general atmospheric temperature.
 10. Bag was labeled with information:
 - i. Sample type (Composite, grab)
 - ii. Sample date and time
 - iii. Sample identification number
 - iv. Sample grid number
- Soon after sampling, the samples were brought to the Lahore School of Economics (LSE) and Soil & Water testing laboratory, near thokar niaz baig, Lahore, for Laboratory analysis.

3.7 Sample Processing and storage

Following steps were followed for preparation and preservation of soil samples:

1. Sample numbers were assigned and entered in the laboratory soil sample register.

2. Sample collected from the field was dried in shade by spreading on a clean sheet of paper after breaking the large lumps, if present.
3. Soil was spread on a paper or polythene sheet on a hard surface and the sample was powdered by breaking the clods to its ultimate soil particle using a wooden mallet.
4. Soil material was sieved through 2 mm sieve.
5. Powdering and sieving were repeated until only materials of >2 mm (no soil or clod) were left on the sieve.
6. Material passing through the sieve was collected and stored in a clean polythene bag with proper labeling for laboratory analysis.
7. If the samples are meant for the analysis of micronutrients at-most care is needed in handling the sample to avoid contamination of iron, zinc and copper. Brass sieves were avoided and stainless steel or polythene materials were used for collection, processing and storage of samples.



Fig.3.2. Sample collection on site using a steel auger



Fig.3.3. Sample preparation: Sample air drying and sieving



Fig.3.4. Grounded and sieved labeled sample

3.8 Laboratory Analysis

3.8.1 pH

pH of soil samples was measured by 2210 pH meter (company HANNA instrument). 50g of soil sample was taken and a paste was prepared. Overnight stay was given to the soil paste sample so that it may be stabilized. The paste was rejuvenated next morning if desired. The electrode was dipped in the paste, the reading was noted when it was stabilized. The electrode was washed with distilled water and dried with tissue paper before dipping in new soil paste sample. (Schofield and Taylor 1955).

3.8.2 Electrical Conductivity

Electrical conductivity of soil samples was determined by Conductivity meter (HANNA HI8633). 10 g of sieved soil was weighed in 500ml plastic beaker and 100 ml of distilled water was added. After stirring, the solution in the bottle was left to stay overnight. The probe of the meter was first rinsed with distilled water and then immersed in the sample (USDA Handbook 60). The readings were noted in mS/cm.

3.8.3 Organic Matter

Chromic Acid method was used to find organic matter content in soil. 1.0 g air dried soil was weighed, soil sample was ground and transferred to a 500 ml conical flask, 5 ml $K_2Cr_2O_7$ was added and contents were mixed well. 10 ml sulphuric acid was added and mixed. The flask was allowed to stand for 30 minutes. Then 100-150 ml distilled water was added. 3 ml phosphoric acid or 0.5 g sodium fluoride, 5-10 drops of indicator were added and finally titrated against standard ferrous sulphate to sharp green end point through blue color. Blank sample was run and sample reading was subtracted from blank to get the actual volume of ferrous sulphate used to reduce potassium dichromate. (Walkey, 1947) The organic matter was calculated applying the following formula.

$$\% \text{ O.M} = \frac{\text{MI for blank} - \text{MI for sample}}{\text{Weight of sample (g)}} \times 0.698^*$$

3.8.4 Organic Carbon

Organic carbon was calculated by the following formula:

$$\% \text{ O C } = \% \text{ organic matter } / 1.724$$

3.8.5 Sodium and Potassium

Sodium and Potassium in soil were determined using a Flame Photometer. 2.5 g air dried, grounded and sieved soil sample was weighed, and transferred to a 250 ml conical flask in which 50 ml extracting reagent (1N Ammonium Acetate) was added. The contents were shaken on a flat bed reciprocal shaker for 30 minutes and filtered. (USDA Handbook 60) Sodium and potassium extracted in the filtrate were estimated by flame photometer in ppm using graph readings.

Calculations:

The calculation of sodium and potassium was done as under:

$$\text{Sodium (mg/kg)} = \text{Reading of flame photometer (ppm)} \times 20$$

$$\text{Extractable Potassium (mg/kg)} = \text{Reading of flame photometer (ppm)} \times 20$$

3.8.6 Extractable Soil Phosphorus (Olsen's method)

1.25 g air dried and ground soil sample was weighed and to it was added 25 ml extracting solution (0.5 M Sodium Bicarbonate). It was shaken for 30 minutes and filtered with Whatman No. 42. 5 ml aliquot was pipette out. 5 ml of color developing reagent was added in 25 ml volumetric flask and shaken to remove gas bubbles and left to stand for 15 minutes. The volume was made up to mark. Bluish color was developed. (Concentration of phosphorus in soil is directly proportional to the intensity of blue color developed.) Reading was taken on concentration mode at 880 nm wavelength on Spectrophotometer (PD-303S). (Olsen *et al.*, 1954)

Calculations:-

$$\text{Extractable phosphorous in soil (mg/kg)} = \frac{\text{Reading (ppm)} \times A \times 25/5^*}{Wt}$$

$$A = \text{Total volume of Extractant (25ml)}$$

$$Wt = \text{Wight of air-dry soils (1.25g)}$$

$$*25/5 = \text{dilution factor} \quad \frac{\text{Final volume (25/5)}}{\text{Aliquot taken}}$$

3.8.7 Metal Analysis by ICP- OES (Inductively coupled plasma atomic emission spectroscopy)

A. DTPA (Diethylene Triamine Pentacaetic Acid) Extractable Metals

This method is used to estimate the readily available metal content for plants. The five extractable metals Iron, Copper, Zinc, Cadmium and Chromium were determined by ICP- OES (Inductively coupled plasma atomic emission spectroscopy).

Reagents/Media required:

- I. 0.005 M DTPA
- II. 0.01 M CaCl₂
- III. 0.01 M TEA (Tri-ethanol amine, adjusted to pH 7.3 with dilute HCL)

DTPA solution was prepared by dissolving 3.934 g of DTPA and 2.94 g Ca Cl₂ and 25.3 ml of TEA in approximately 200 ml of distilled water. After the DTPA was completely dissolved, 2 liter volume was made. pH was adjusted to 7.3 with 1:1 HCl while stirring.

Method:

20 g of dried soil was added in 40 ml of DTPA solution. The sample solutions were put on horizontal shaker for 2 hours at 200 rpm (rotations per minute) and filtered with Whatman No.42. The filtrates were transfer to number/referenced test tubes for ICP analyses. A blank solution (0 ppm) containing all reagents except soil were also run with samples as blank. These were then directly analyzed using ICP- OES which was calibrated and standardized according to the method as appropriate per laboratory QA/QC protocols and manufacturer's recommendations. (Lindsay and Norvell, 1978)

Calculations:

The dilution factor for this method is 2. Normal reporting for micronutrient concentrations is in parts per million (ppm or mg/kg) on the soil basis. Therefore, the final ICP-OES analysis result of the extract is multiplied by 2 to provide mg/kg of soil.

Formula:

$$\text{Micronutrients (ppm or mg/kg)} = \text{Reading of ICP-MS} \times 2$$

B. Total Metal Content

This method is used to determine the total metal content that could become environmentally available. The total metal content for three metals Copper, Cadmium and Chromium was determined by ICP- OES.

Solid samples for ICP- OES are first dissolved in appropriate acid by digestion process or dry ashing. Thus, acid digestion was carried out as follows.

Acid Digestion/ Wet Ashing: Double Acid Method (HClO₄ and HNO₃)

Reagents:

1 Perchloric Acid and Nitric Acid Mixture (1:2): 167 ml (70%) Perchloric acid was added in 333 ml Nitric acid (69-70%), mixed well and stored in an amber glass bottle.

Procedure: (On hot plate)

This digestion method is used for multi-element analysis. This method can be used preferably for flame emission spectrophotometer. 5.0 g of soil was weighed in glass digestion tubes in which 17.5 ml of double acid mixture was added. Digestion tubes were shifted on hot plate. Brown fumes of the color of content in the digestion tubes became light yellow. Heating was continued at 175°C until clear transparent solution formed with white dense fumes at the end. These copious white fumes were the indication of complete digestion process. Digestion tubes were cooled. (However, this clear solution may have slight amber to yellowish tint which usually disappears when distilled water is added.) By using the volumetric flask made the volume 50 ml with distilled water or as desired when contents in the digestion tubes were still warm/taped. All samples were then filtered with filter paper Whatman No.42. The filtrate was transferred to the plastic bottles, stored in refrigerator. The digests were then directly run on ICP- OES for analysis. Care was taken that samples should not be dried on hot plate during digestion.

Calculations:

The dilution factor for this method is 10. Normal reporting for metal concentrations is in parts per million (ppm or mg/kg) on the soil basis. Therefore, the final ICP- OES analysis result of the extract is multiplied by 10 to provide mg/kg of soil.

Formula:

$$\text{Total metal content (ppm or mg/kg)} = \text{Reading of ICP-MS} \times 10$$

Table.3.2. Standard methods and Equipment used for physicochemical analysis of tannery contaminated soil samples

Serial No.	Parameters	Standard specification/ Techniques/ Equipment used
1.	pH	pH meter
2.	Electrical conductivity	EC meter
3.	Organic Matter	By Chromic Acid Method
4.	Organic Carbon	By Organic Carbon Formula
5.	Sodium	Flame Spectrophotometer
6	Potassium	Flame Spectrophotometer
7	Extractable Soil Phosphorus	Spectrophotometer
8	DTPA-Extractable or Available metals (Cu, Cd, Cr, Fe, Zn)	ICP- OES
9	Total Metal Content (Cu, Cd, Cr)	ICP- OES

Chapter 4

Results

The results of the physicochemical analysis of thirty-four (34) samples (with three replicates each) are interpreted below in the form of the graphs. The physicochemical analysis include pH, Electrical Conductivity (EC), Organic Matter (OM), Organic Carbon (OC), Available Phosphorus (P), Potassium (K), Sodium (Na), Extractable Heavy Metals (Cr, Cu, Z, Fe, Cd) and Total Metal Content for Cr, Cd, Cu and each composite sample was representative of the area of each grid. To interpret the data descriptive statistics is applied which includes mean and standard deviation (\pm SD). The resulted values are compared with the international standards specified for each parameter. The bivariate correlation coefficient of the mean value of each parameter is computed and the significance is tested against 5% level. To test the difference in the mean value of each parameter across different sites one way ANOVA is also applied at the significance level of 0.05.

In Fig. 4.1, the graph reveals the resulted values of pH for the reclaimed soil samples from all the grids in comparison with International Agriculture Soil Standards. The maximum mean value of pH with \pm SD is 8.80 ± 0.021 at the grid G₂₈. The minimum mean value of pH with \pm SD is 7.36 ± 0.042 , which is observed at grid G₁₂. The permitted range for pH is 4-8.5 given in International Agricultural Soil Standards (Alloway, 1990). pH values for all the grids lie within permissible limit except grids G₁₅ and G₂₈. The results of the ANOVA table indicated that the mean pH value across different sites show significant difference indicated by the P value=.000 (as shown in appendix 3a).

The graph in Fig. 4.2 shows measurement of electrical conductivity (mS/cm) in reclaimed soil samples from all the grids as compared to the International Agricultural Soil Standards. The grid G₃₀ has highest mean value with \pm SD i.e. 1.45 ± 0.035 (mS/cm) for electrical conductivity while grid G₂₇ has lowest mean value with \pm SD i.e. 0.143 ± 0.030 (mS/cm). The values for electrical conductivity recorded for all the grids are within the range of standard limit i.e. 4.0 (mS/cm) prescribed by International Agricultural Soil Standards (Alloway, 1990). The results of the ANOVA

table indicated that the mean EC value across different sites show significant difference indicated by the P value=.000 (as shown in appendix 3b).

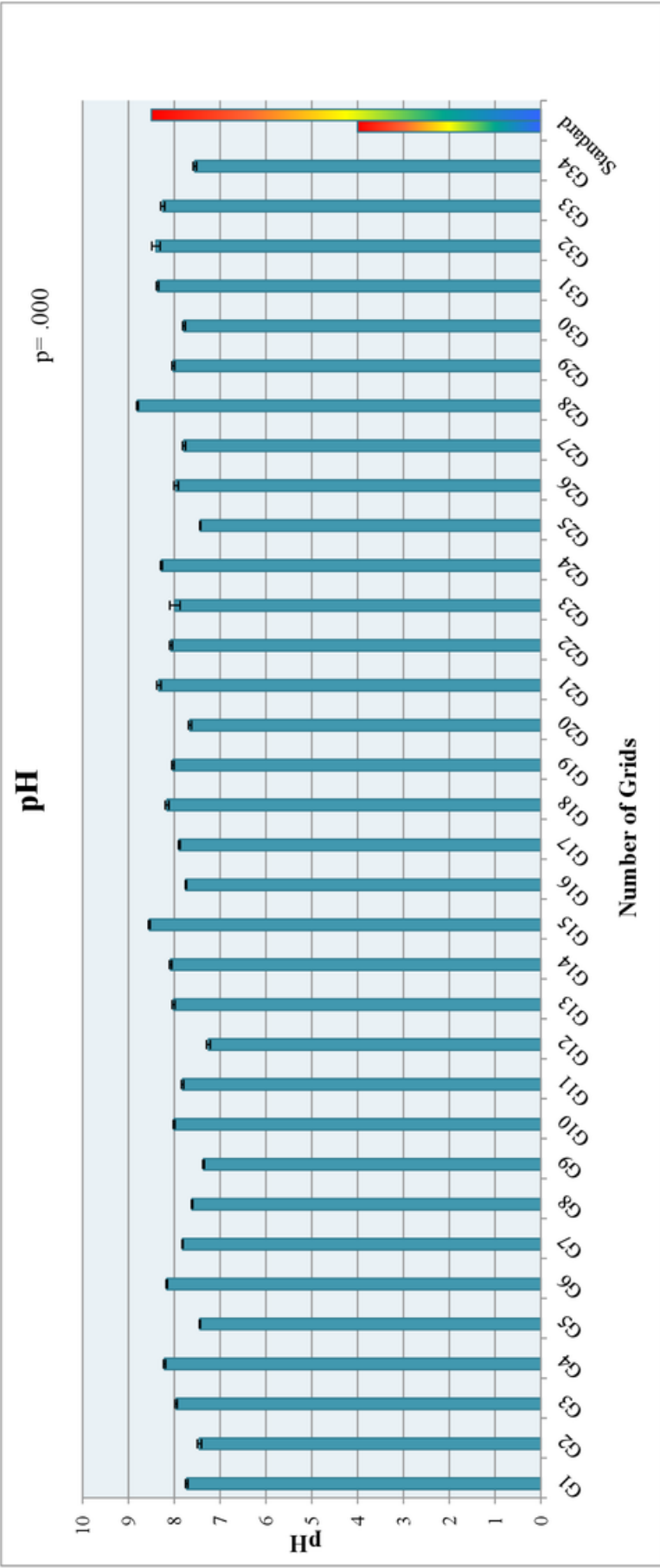


Fig. 4.1: Graph illustrating the mean values of pH for soil samples from all grids and their comparison with the proposed standard of pH by International Agricultural Soil Standards (Alloway, 1990).

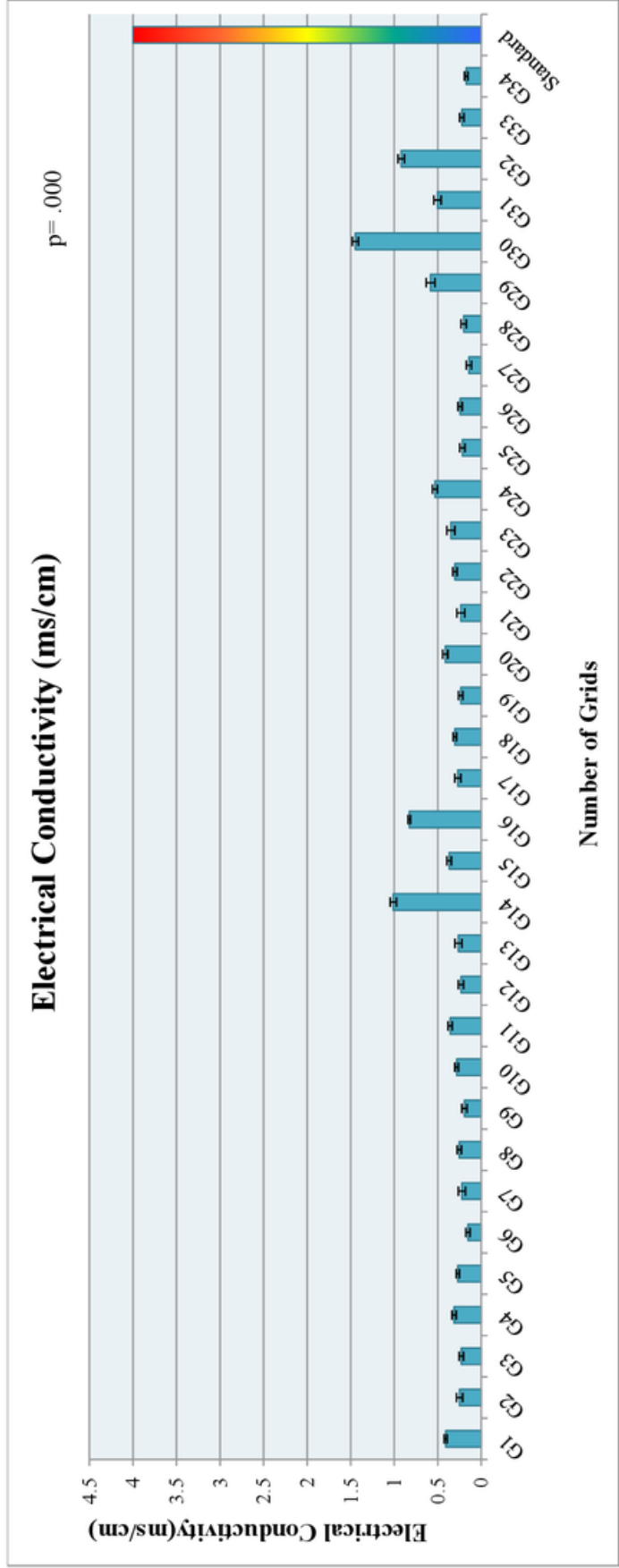


Fig. 4.2: Graph illustrating the mean values of EC for soil samples from all grids and their comparison with the proposed standard of EC by International Agricultural Soil Standards (Alloway, 1990).

In Fig. 4.3, the graph illustrates the results for organic matter (%) measured in reclaimed soil samples from all the grids. It is observed that every reading of organic matter is within the standard limit which is 3.4% described by European Union, 2009. The highest mean value with \pm SD is observed at grid G₁₆ which is $2.5 \pm 0.020\%$. The lowest mean value with \pm SD is observed at grid G₃₃ which is $0.50 \pm 0.050\%$. The results of the ANOVA table indicated that the mean OM value across different sites show significant difference indicated by the P value=.000 (as shown in appendix 3c).

The Fig. 4.4 shows the graph which represents the data for resulted values of organic carbon (%) in reclaimed soil samples from all the grids as compared with the standard limit. The organic carbon at grid G₁₆ is the greatest mean value with \pm SD which is $1.53 \pm 0.025\%$. The lowest mean value with \pm SD is observed at grid G₃₃ which is $0.21 \pm 0.03\%$. The standardized limit for organic carbon is 2% according to European Union, 2009 and all resulted values of this research are below the limit. The results of the ANOVA table indicated that the mean OC value across different sites show significant difference indicated by the P value=.000 (as shown in appendix 3d).

The graph in Fig. 4.5 reveals results of available phosphorus (P mg/kg) present in reclaimed soil samples as compared to the permissible limits given by two different standards. Standard 1 is taken as International Agricultural Soil Standards (Alloway, 1990) and Standard 2 is the satisfactory range of phosphorus in soil given by Malik et al., 1984; Motsara, 2002. The lowest mean value of phosphorous with \pm SD is observed at G₃₃ which is 7.05 ± 0.08 (mg/kg). The highest mean value of phosphorous with \pm SD is observed at G₁₅ which is 148.61 ± 0.10 (mg/kg). According to standard 1, the permissible limit value is >7 (mg/kg) and according to standard 2 the satisfactory range of phosphorus in soil is 7-14 (mg/kg). All the resulted values of phosphorus for current studies are far higher than the prescribed limits given by both standards. The results of the ANOVA table indicated that the mean P value across different sites show significant difference indicated by the P value=.000 (as shown in appendix 3e).

The graph in Fig. 4.6 depicts the resulted data for analyzed values of potassium (K mg/kg) in reclaimed soil samples from all the grids in comparison with two different standard references which are Standard 1 i.e. International Agricultural Soil Standards (Alloway, 1990) and Standard 2 i.e. satisfactory limit of K in soil described by Malik

et al., 1984; Motsara, 2002. The greatest mean value of potassium with \pm SD is observed at G₃₀ which is 920.03 ± 0.02 (mg/kg). The lowest value with \pm SD is observed at G₆ which is 40.08 ± 0.13 . In standard 1, the permissible limit is >80 (mg/kg) while in standard 2, satisfactory value of K was considered as 90-180 (mg/kg). With respect to standard 1 only grid G₆, G₁₀, G₁₆ and G₃₃ are in permissible limit. According to standard 2, most of the readings are in permissible limit except grids G₁, G₂, G₄, G₅, G₇, G₉, G₂₂, G₂₃, G₂₄, G₂₉, G₃₀, G₃₁ and G₃₂. The results of the ANOVA table indicated that the mean K value across different sites show significant difference indicated by the P value = .000 (as shown in appendix 3f).

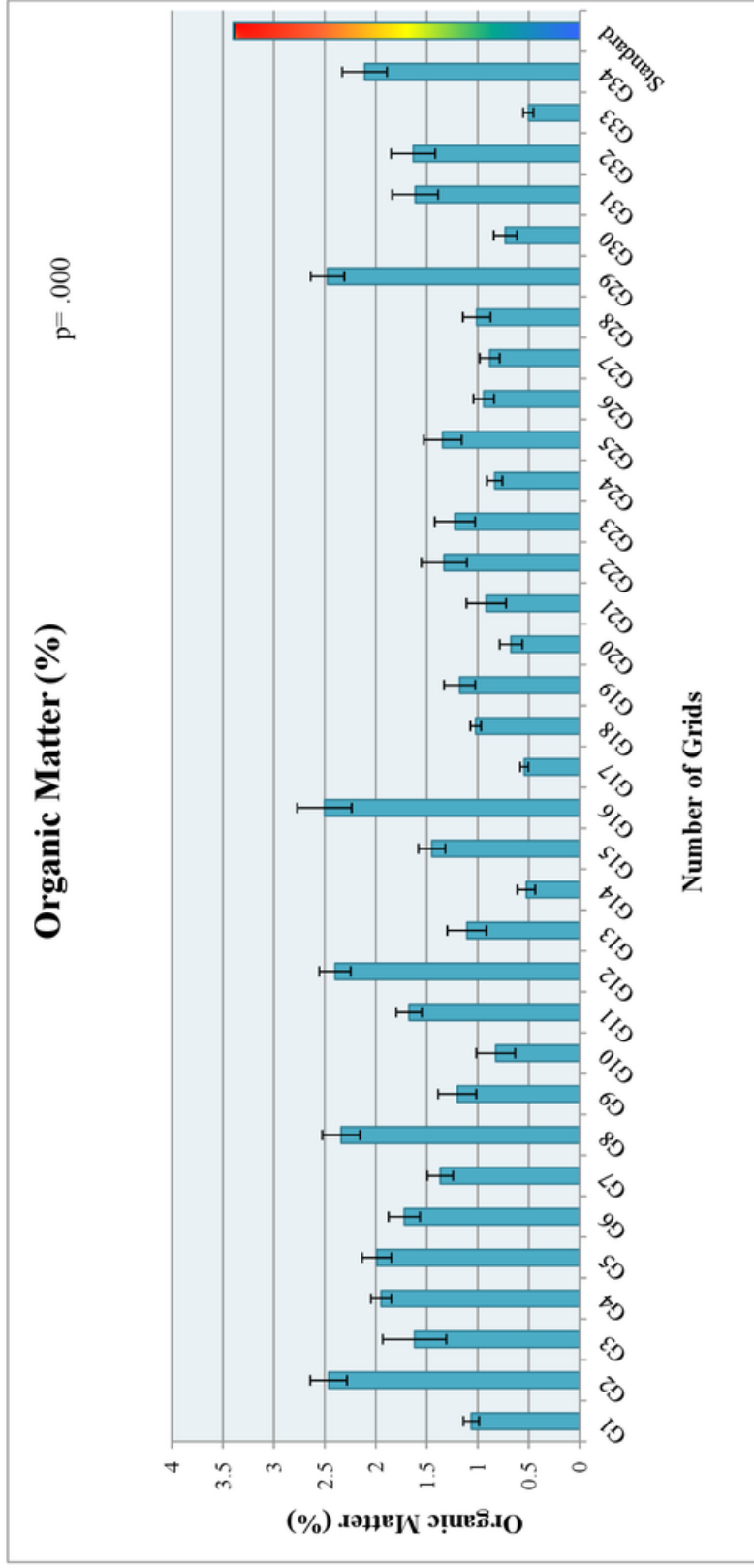


Fig. 4.3: Graph illustrating the mean values of Organic Matter for soil samples from all grids and their comparison with the proposed standard of Organic Matter in soil by European Union, 2009

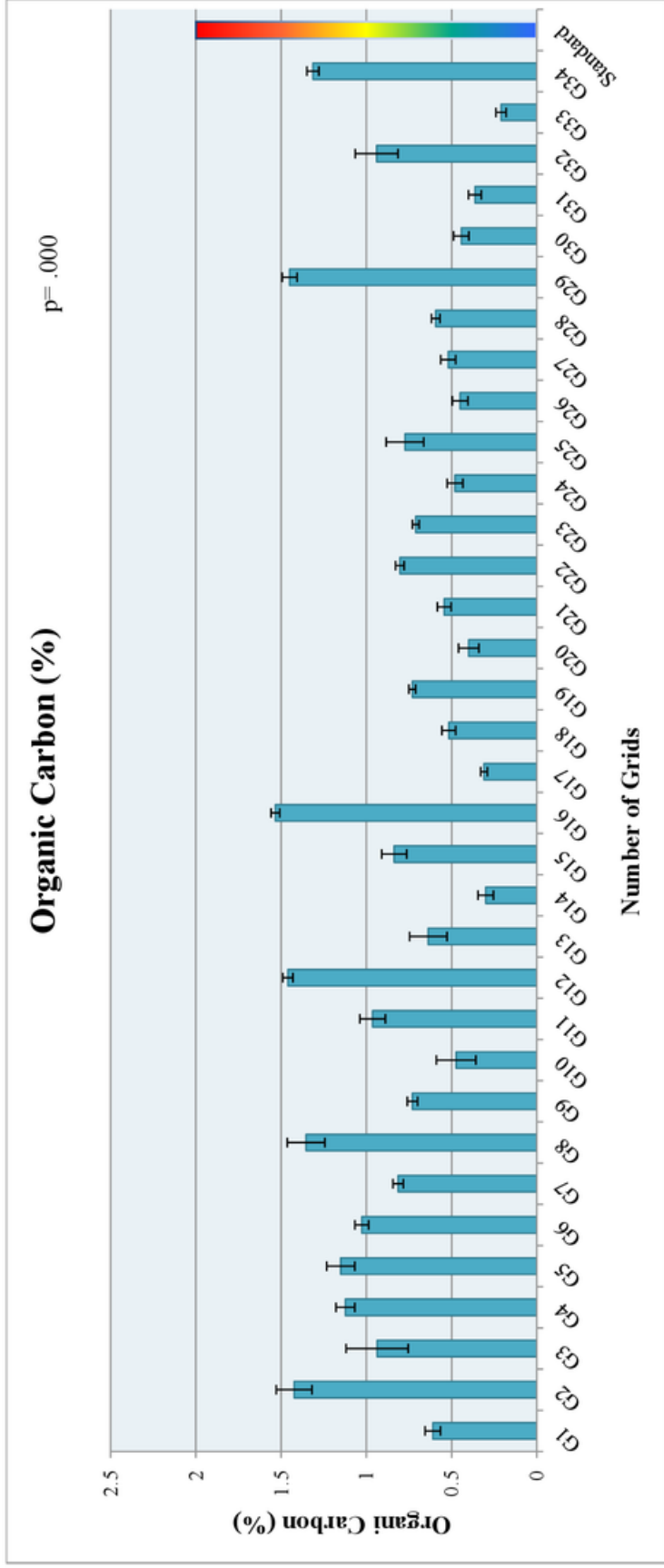


Fig. 4.4: Graph illustrating the mean values of Organic Carbon for soil samples from all grids and their comparison with the proposed standard of Organic Carbon in soil by European Union, 2009

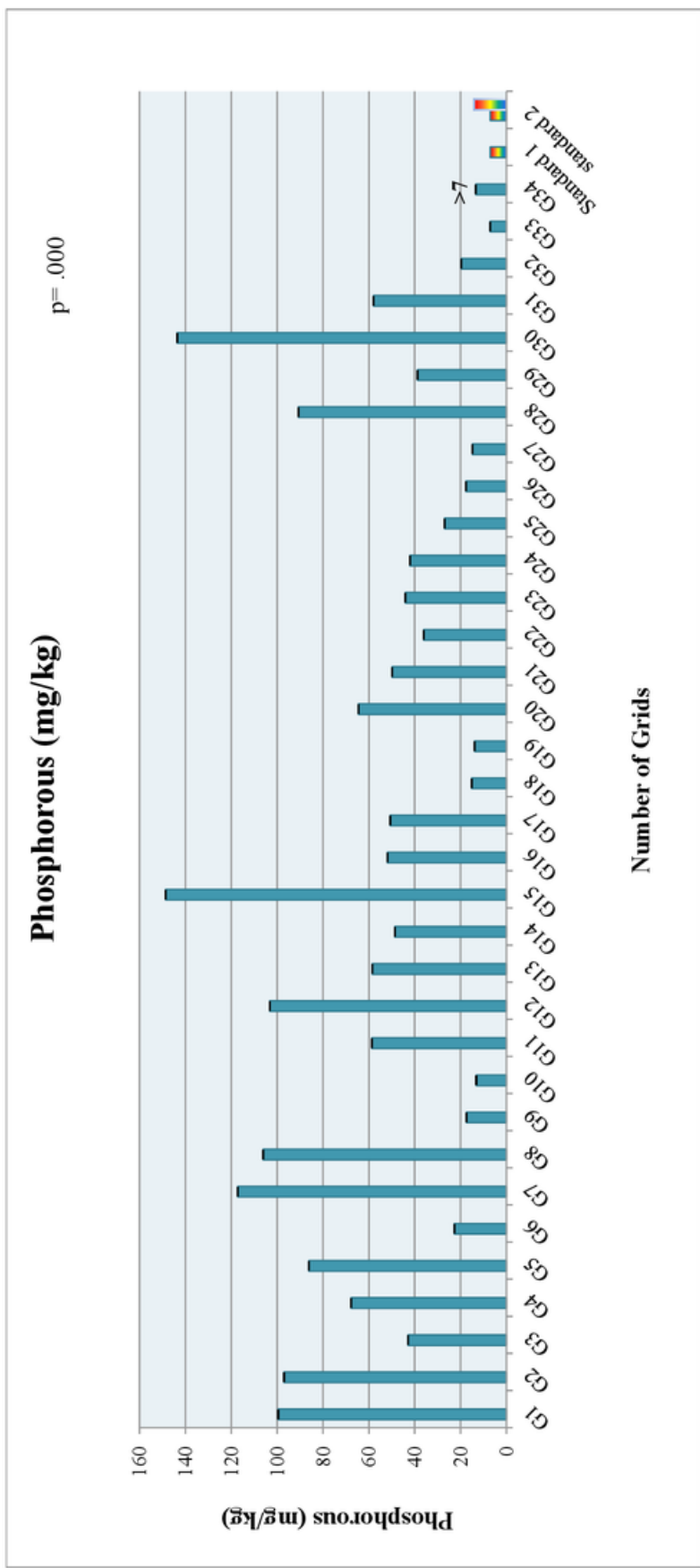


Fig. 4.5: Graph illustrating the mean values of Phosphorus for soil samples from all grids and their comparison with the proposed permissible

limits of Phosphorus in soil by *Standard 1 and **Standard 2

*Standard 1: International Agricultural Soil Standards (Alloway, 1990)

**Standard 2: Malik et al., 1984 and Motsara, 2002

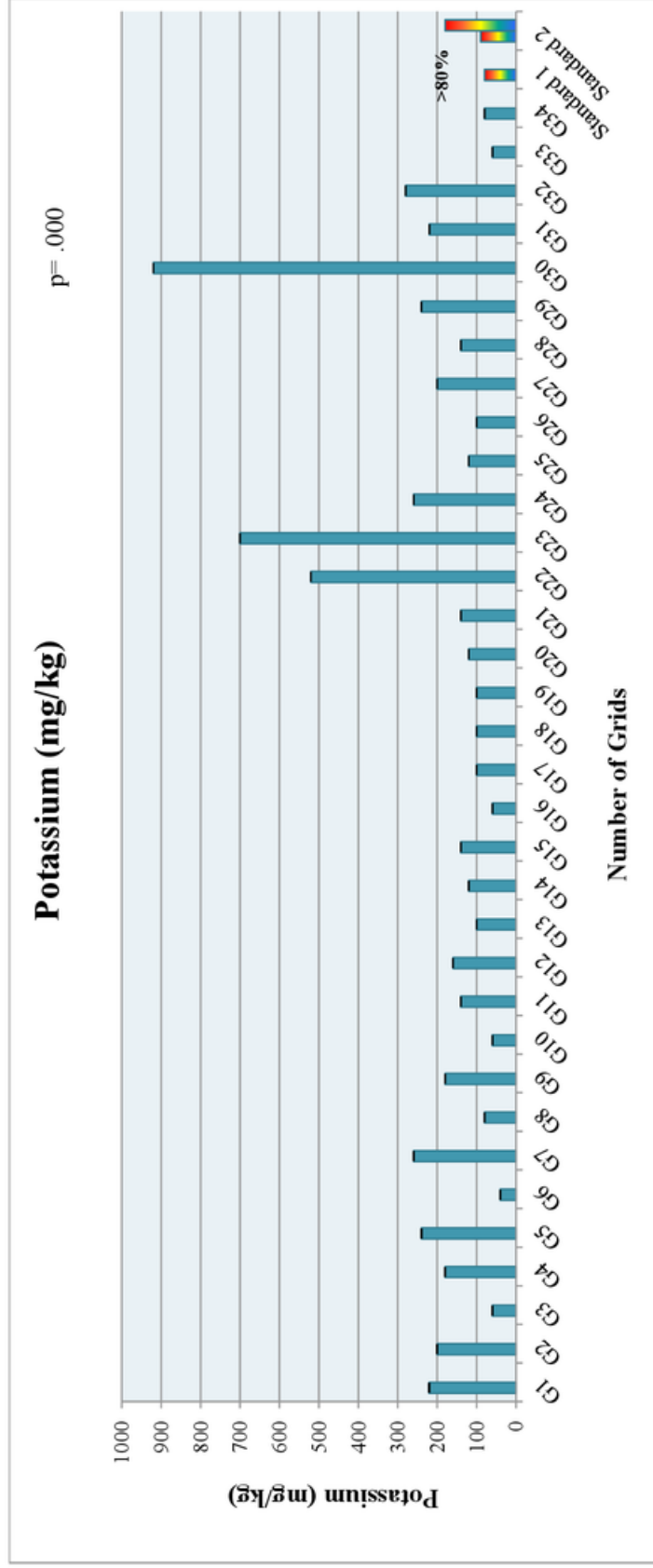


Fig. 4.6: Graph illustrating the mean values of Potassium for soil samples from all grids and their comparison with the proposed permissible limits of Potassium in soil by *Standard 1 and **Standard 2

*Standard 1: International Agricultural Soil Standards (Alloway, 1990)

**Standard 2: Malik et al., 1984 and Motsara, 2002

In Fig. 4.7 the graph represents the results of sodium (Na mg/kg) in reclaimed soil samples collected from all the grids in comparison with the permissible limit of sodium in soil for better plant growth. It is noted that every reading of sodium is below the detrimental range of sodium in soil which is 1550-2300 (mg/kg) described by Marschner, 1986. The highest mean value with \pm SD is observed at grid G₃₂ which is 1360.217 \pm 0.351(mg/kg). The lowest mean value with \pm SD is observed at grid G₈ which is 99.99 \pm 0.15 (mg/kg). All the readings are below the harmful described limit. The results of the ANOVA table indicated that the mean Na value across different sites show significant difference indicated by the P value=.000 (as shown in appendix 3g).

It is important to mention that there are no international standards or documented critical limits available in the literature in terms of DTPA-extractable heavy metals (Elgawad et al., 2007). For current study the results of DTPA-extractable metals are compared with the permissible limits described by Soltanpour, 1985; Maclean et al., 1987 which involves Ammonium Bicarbonate-DTPA for metal extraction that is a slightly different reagent from the reagent used in current study.

Fig. 4.8 exhibits the graph showing the concentration of extractable chromium (Cr mg/kg) in reclaimed soil samples as compared to the permissible limit of extractable Cr in agriculture soil given by Soltanpour, 1985; Maclean et al., 1987. The highest mean value of Cr with \pm SD at grid G₁₃ is found to be 0.221 \pm 0.033 (mg/kg) while lowest mean value of Cr with \pm SD at grid G₂₉ is found to be 0.011 \pm 0.003 (mg/kg). The permissible limit is 8.0 (mg/kg) and mean values at all the grids are below the permissible limit. The results of the ANOVA table indicated that the mean extractable Cr value across different sites show significant difference indicated by the P value=.000 (as shown in appendix 3h).

Fig. 4.9 presents the graph showing the values of extractable copper (Cu mg/kg) for reclaimed soil samples from each grid as compared with the proposed limit of extractable Cu in agriculture soil by Soltanpour, 1985; Maclean et al., 1987. The proposed limit is 0.5 (mg/kg). Every grid has higher value of Cu in reference to the proposed limit. The maximum averaged value of extractable Cu is measured with \pm SD for grid G₆ 24.660 \pm 0.020 (mg/kg). While the minimum averaged value of

extractable Cu is measured as \pm SD; 4.067 ± 0.012 (mg/kg) for grid G₁. The results of the ANOVA table indicated that the mean extractable Cu value across different sites show significant difference indicated by the P value=.000 (as shown in appendix 3i).

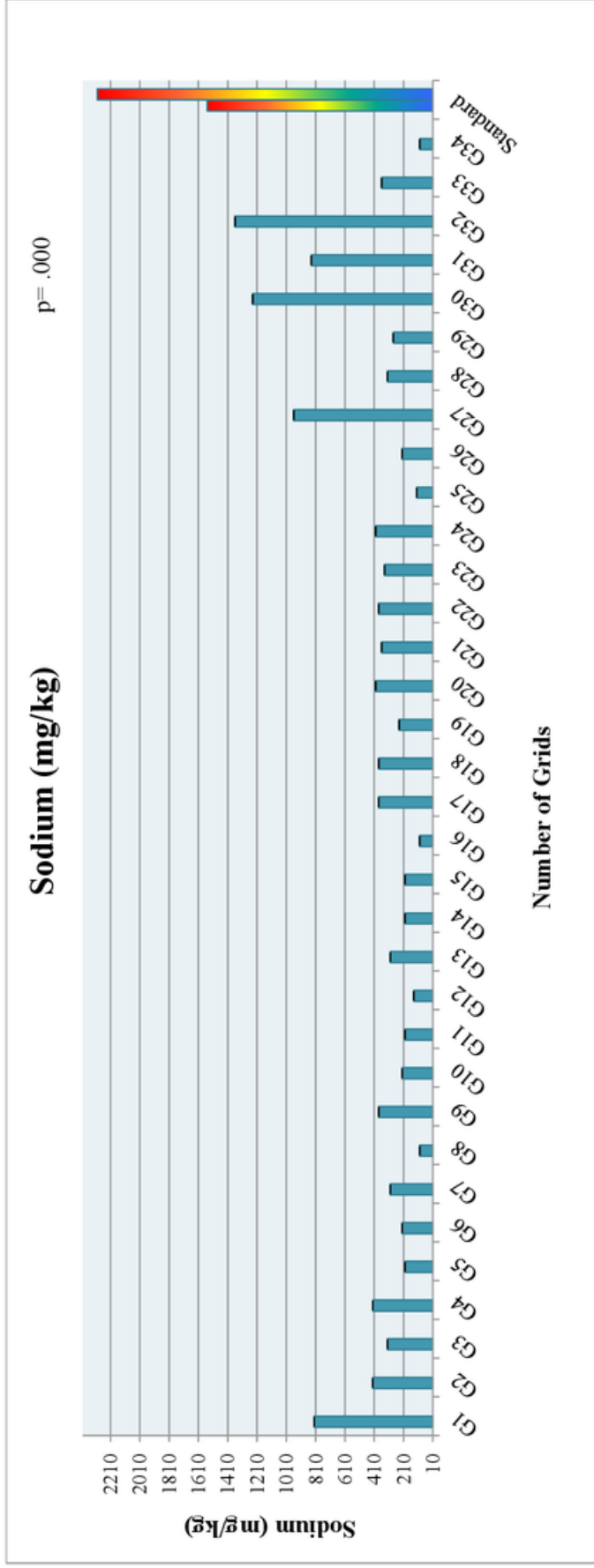


Fig. 4.7: Graph illustrating the mean values of Sodium for soil samples from all grids and their comparison with the proposed permissible limits of Sodium in soil by Marschner, 1986

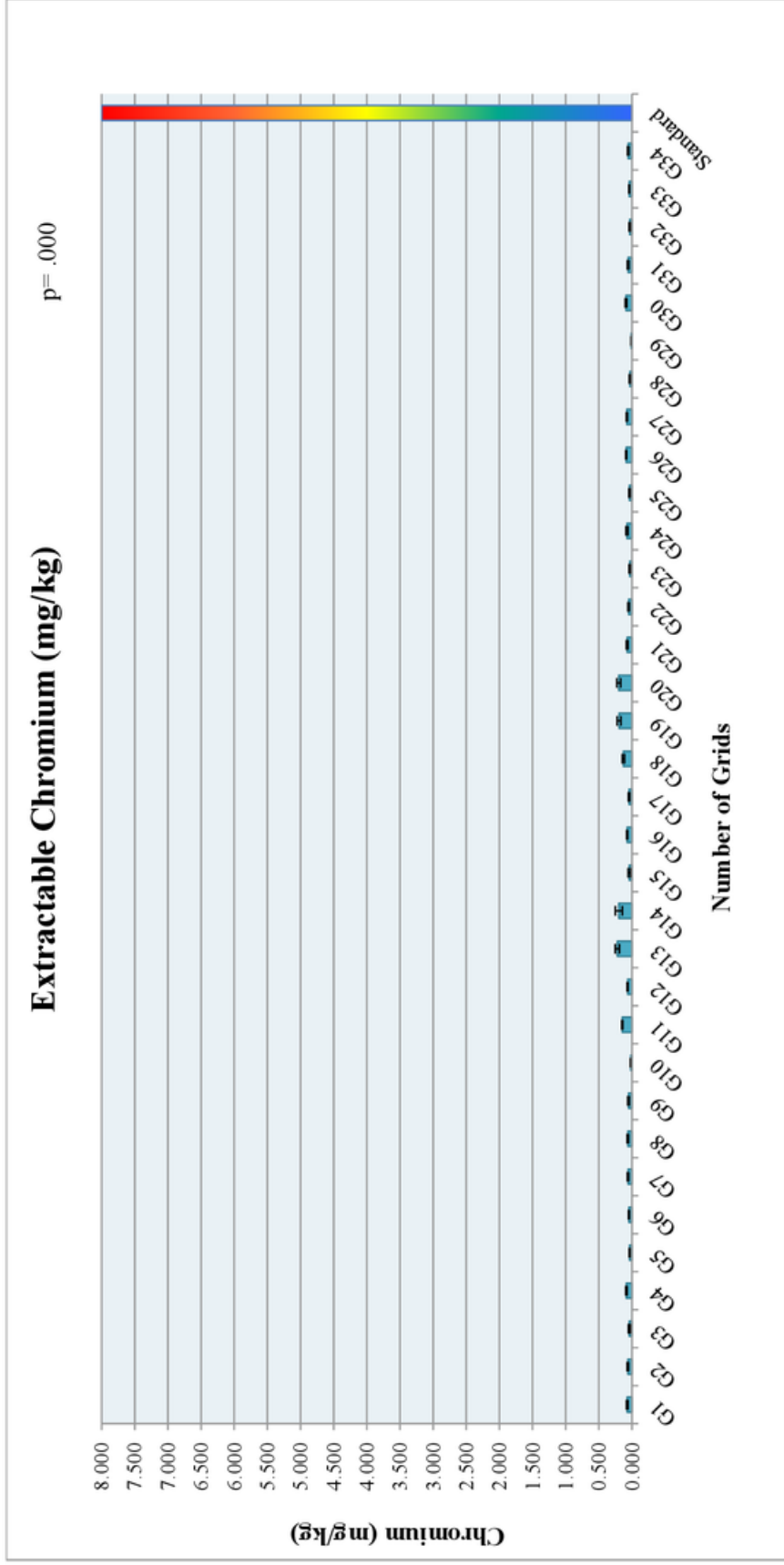


Fig. 4.8: Graph illustrating the mean values of Extractable Chromium for soil samples from all grids and their comparison with the proposed permissible limits of Extractable Chromium in soil by Soltanpour, 1985; Maclean et al., 1987

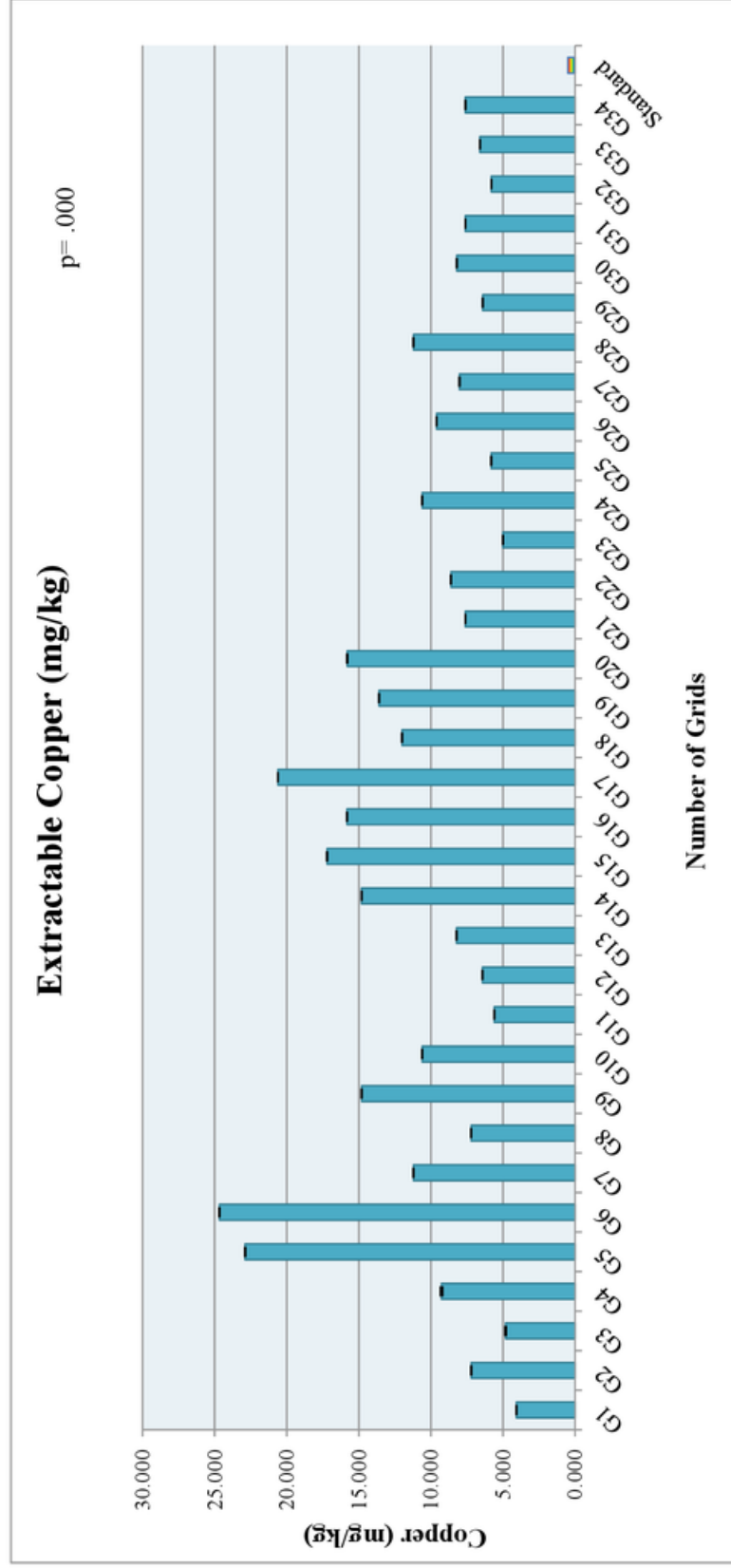


Fig. 4.9: Graph illustrating the mean values of Extractable Copper for soil samples from all grids and their comparison with the proposed permissible limits of Extractable Copper in soil by Soltanpour, 1985; Maclean et al., 1987

Fig. 4.10 displays the graph describing the results of extractable cadmium (Cd mg/kg) of soil samples in all grids in reference to the proposed limit of extractable Cd in agriculture soil. The acceptable limit of Cu in agriculture soil is 0.31 (mg/kg) (Soltanpour, 1985; Maclean et al., 1987). The highest averaged concentration of Cd with \pm SD is resulted as 0.106 ± 0.007 (mg/kg) at grid G₆. While lowest averaged concentration of Cd with \pm SD is resulted as 0.013 ± 0.005 (mg/kg) at grid G₂₁. The results of cadmium concentration is observed to be within the permissible range at all the grids. The results of the ANOVA table indicated that the mean extractable Cd value across different sites show significant difference indicated by the P value=.000 (as shown in appendix 3j).

Fig. 4.11 delineates the graph which shows the results of extractable zinc (Zn mg/kg) concentration in soil of each grid in comparison with the prescribed limit of extractable Zn in agriculture soil which is 1.5 (mg/kg) (Soltanpour, 1985; Maclean et al., 1987). The resulted bars show that maximum mean concentration of Zn with \pm SD is noted for grid G₂₀ i.e. 10.110 ± 0.125 (mg/kg) and the minimum mean concentration of Zn with \pm SD is noted for grid G₆ i.e. 1.633 ± 0.067 (mg/kg). The concentration of Zn is noted to be quite higher than the permissible limit in all the grids. The results of the ANOVA table indicated that the mean extractable Zn value across different sites show significant difference indicated by the P value=.000 (as shown in appendix 3k).

Fig. 4.12 represents the graph depicting results of iron (Fe mg/kg) concentration in reclaimed soil samples from all the grids in comparison with the acceptable limit of iron in agriculture soil. The maximum mean value of iron with \pm SD is observed at grid G₁₀ which is 44.803 ± 0.015 (mg/kg) while minimum mean value of iron with \pm SD is observed at grid G₂₄ which is 5.807 ± 0.012 (mg/kg). The acceptable limit of iron in agriculture soil is 5.0 (mg/kg) (Soltanpour, 1985; Maclean et al., 1987). All the grids have far higher concentrations of iron in reclaimed soil as compared to the acceptable limit. The results of the ANOVA table indicated that the mean extractable Fe value across different sites show significant difference indicated by the P value=.000 (as shown in appendix 3l).

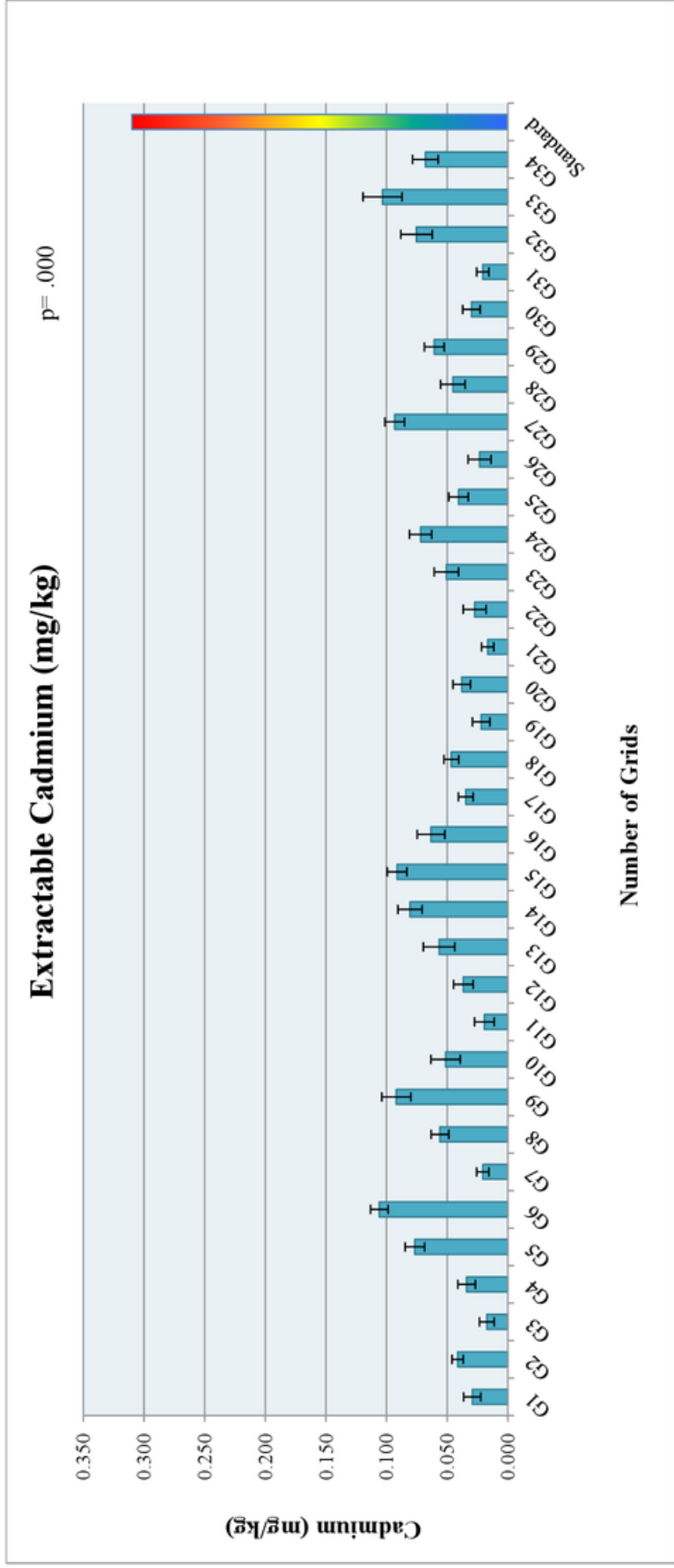


Fig. 4.10: Graph illustrating the mean values of Extractable Cadmium for soil samples from all grids and their comparison with the proposed permissible limits of Extractable Cadmium in soil by Soltanpour, 1985; Maclean et al., 1987

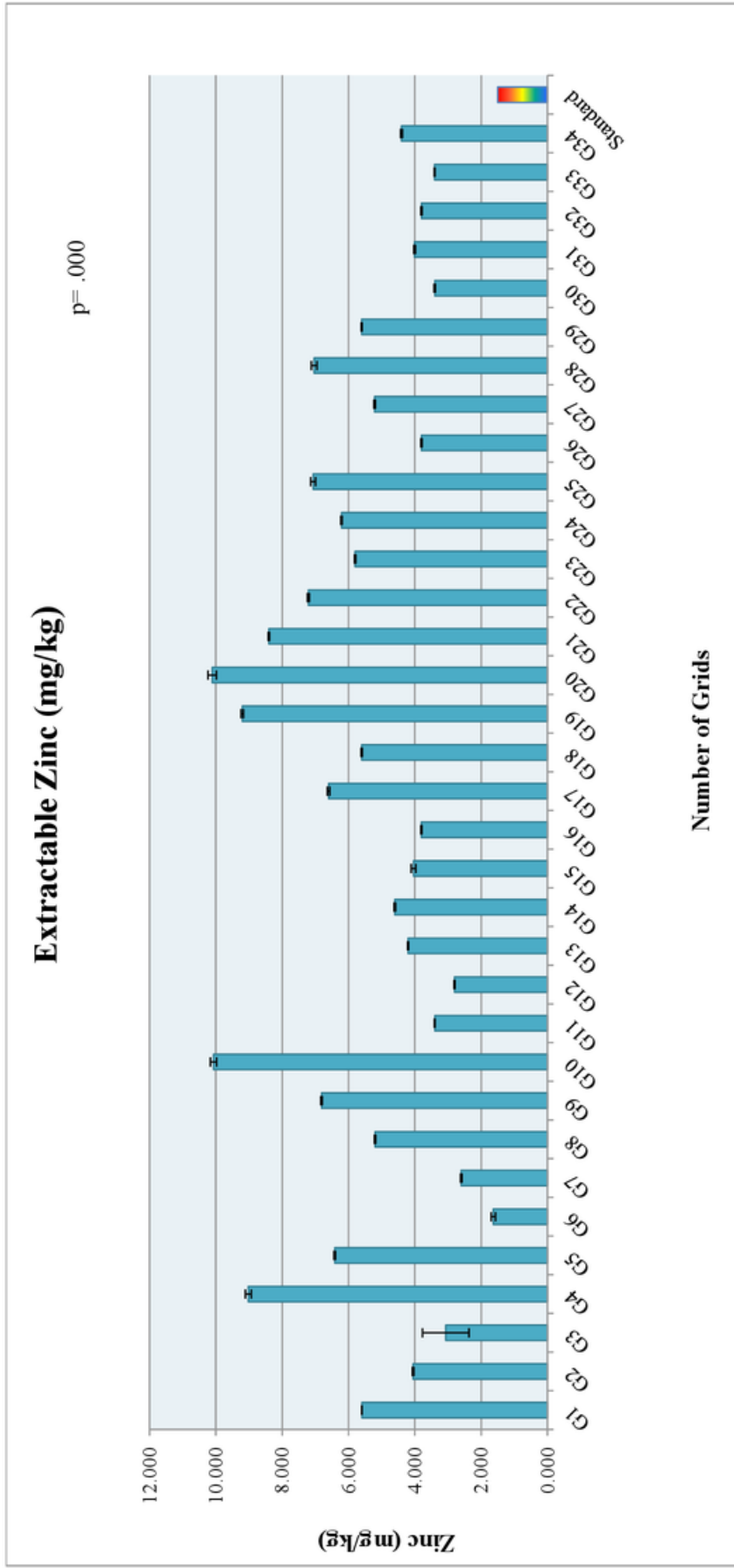


Fig. 4.11 : Graph illustrating the mean values of Extractable Zinc for soil samples from all grids and their comparison with the proposed permissible limits of Extractable Zinc in soil by Soltanpour, 1985; Maclean et al., 1987

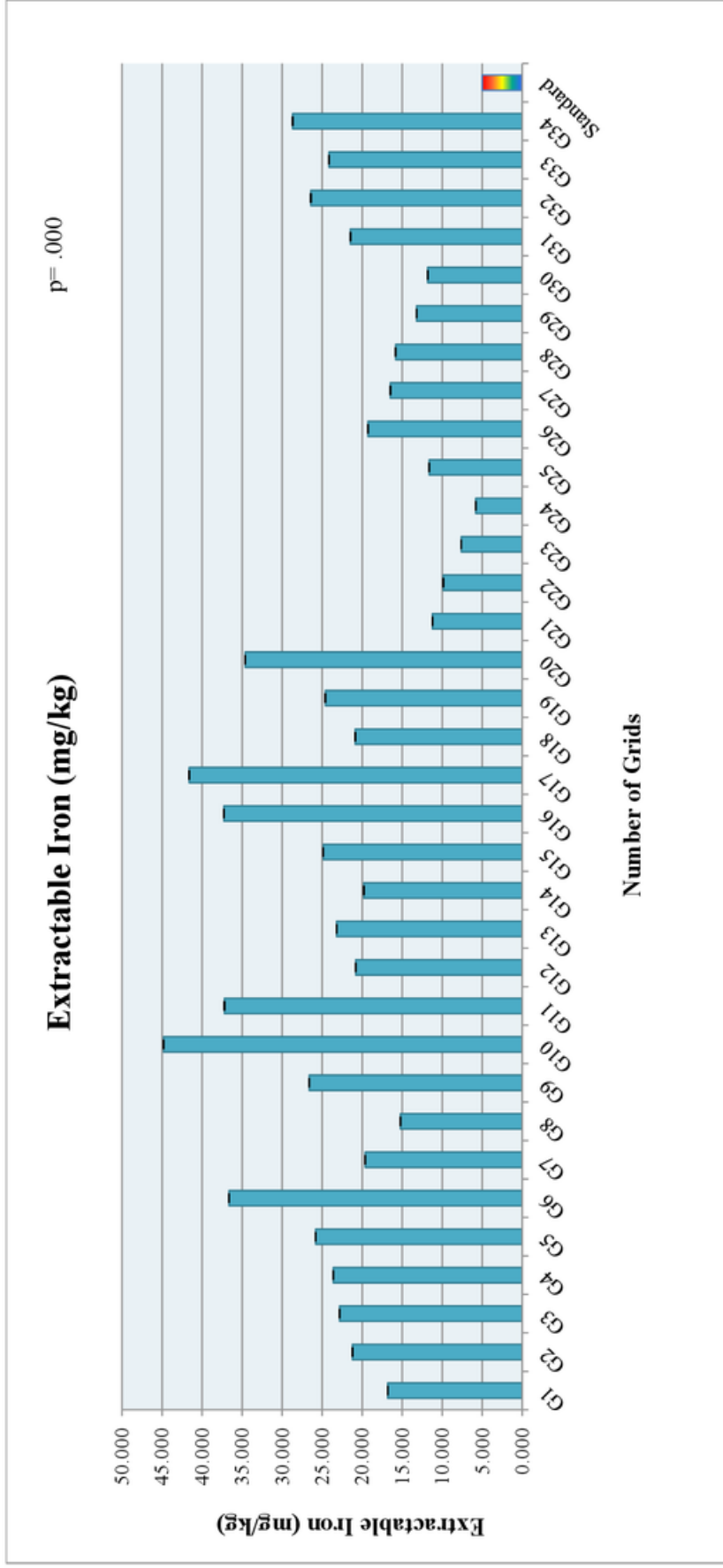


Fig. 4.12: Graph illustrating the mean values of Extractable Iron for soil samples from all grids and their comparison with the proposed permissible limits of Extractable Iron in soil by Soltanpour, 1985; Maclean et al., 1987

The graph in Fig.4.13 represents the total metal concentration for chromium (Cr mg/kg) in all reclaimed soil samples from all the grids in comparison with the four different standard references. 1st standard reference is International Agricultural Soil Standards (Alloway, 1990), 2nd standard reference is Indian Standards of Soil (Awasthi,2000), 3rd reference standard is permissible limits of heavy metals in soil given by European Community Commission (ECC, 1986) and 4th standard reference is permissible limits of heavy metals in soil given by Rowell, 1994. The greatest mean value of total Cr with \pm SD is observed at G₃₀ which is 950.687 \pm 0.035 (mg/kg). The lowest mean value with \pm SD is observed at G₅ which is 9.987 \pm 0.065 (mg/kg). According to standard 1 and standard 3 the permissible limit is 100 (mg/kg). Most of the resulted values are in permissible limit with these standards except grids G₁₃, G₂₂, G₂₃, G₂₄, G₃₀, G₃₁, G₃₂ and G₃₃ while there are no permissible limit given by standard 2 and standard 4. The results of the ANOVA table indicated that the mean total Cr value across different sites show significant difference indicated by the P value=.000 (as shown in appendix 3m).

The graph in Fig. 4.14 illustrates the total metal concentration for copper (Cu mg/kg) in all reclaimed soil samples from all the grids in comparison with the four different standard references. 1st standard reference is International Agricultural Soil Standards (Alloway, 1990), 2nd standard reference is Indian Standards of Soil (Awasthi,2000), 3rd reference standard is permissible limits of heavy metals in soil given by European Community Commission (ECC, 1986) and 4th standard reference is permissible limits of heavy metals in soil given by Rowell, 1994. The lowest mean value of total Cu with \pm SD is observed at grid G₁ which is 12.42 \pm 0.03 (mg/kg). The highest mean value with \pm SD is observed at grid G₆ which is 63.847 \pm 0.064 (mg/kg). All the resulted values are below permissible limits according to standard 1, standard 2 and standard 3 which are 100 (mg/kg), 135-270 (mg/kg) and 50-140 (mg/kg), respectively. According to standard 4 only grid G₁, G₂, G₁₁, G₂₀, G₂₁, G₂₃, G₂₄, G₂₅, G₂₆, G₂₇, G₂₈, G₂₉, G₃₁, are in permissible limit which is 20 (mg/kg). The results of the ANOVA table indicated that the mean total Cu value across different sites show significant difference indicated by the P value=.000 (as shown in appendix 3n).

The graph in Fig. 4.15 shows concentration of total cadmium (Cd mg/kg) in all the soil samples collected from grids as compared with the four different standard

references. 1st standard reference is International Agricultural Soil Standards (Alloway, 1990), 2nd standard reference is Indian Standards of Soil (Awasthi,2000), 3rd reference standard is permissible limits of heavy metals in soil given by European Community Commission (ECC, 1986) and 4th standard reference is permissible limits of heavy metals in soil given by Rowell, 1994. The total Cd at grid G₃₃ is the greatest mean value with \pm SD which is 6.843 ± 0.1 (mg/kg). The lowest mean value with \pm SD is observed at grid G₃ which is 0.13 ± 0.03 (mg/kg). In standard 1 the permissible limit for total Cd is 1.0 (mg/ kg), in standard 2 the permissible limit is 3-6 (mg/kg), in standard 3 the permissible limit is defined as 1-3 (mg/kg) while in standard 4, the permissible limit is given as 0.5 (mg/kg). According to standard 1 very few values are in permissible limit which includes grid G₁, G₂, G₃, G₄, G₇, G₈, G₁₁, G₁₂, G₁₃ and G₁₆. With respect to standard 2, only G₂₂, G₃₂ and G₃₃ exceeded the permissible limit. According to standard 3, grid G₂₂, G₂₉, G₃₁, G₃₂, G₃₃ and G₃₄ only exceeds the permissible limit. Grid G₂, G₃ and G₄ are only in permissible limit when the present study was compared with the standard 4. The results of the ANOVA table indicated that the mean total Cd value across different sites show significant difference indicated by the P value=.000 (as shown in appendix 3o).

Correlation between selected parameters is also determined as shown in Table.4.1. From the table it is revealed that there is a strong correlation between organic matter and organic carbon $p = .000$ ($r=0.991$) while, with other parameters organic matter shows no significant correlation. EC is found to be significantly correlated with K i.e. $p = .001$ ($r=0.530$) and Na $p = .002$ ($r=0.516$). Among metals total Cu and extractable Cu are moderately correlated i.e. $p = .000$ ($r=0.690$). Overall, there is less significant correlation observed among total metal content and available metal content.

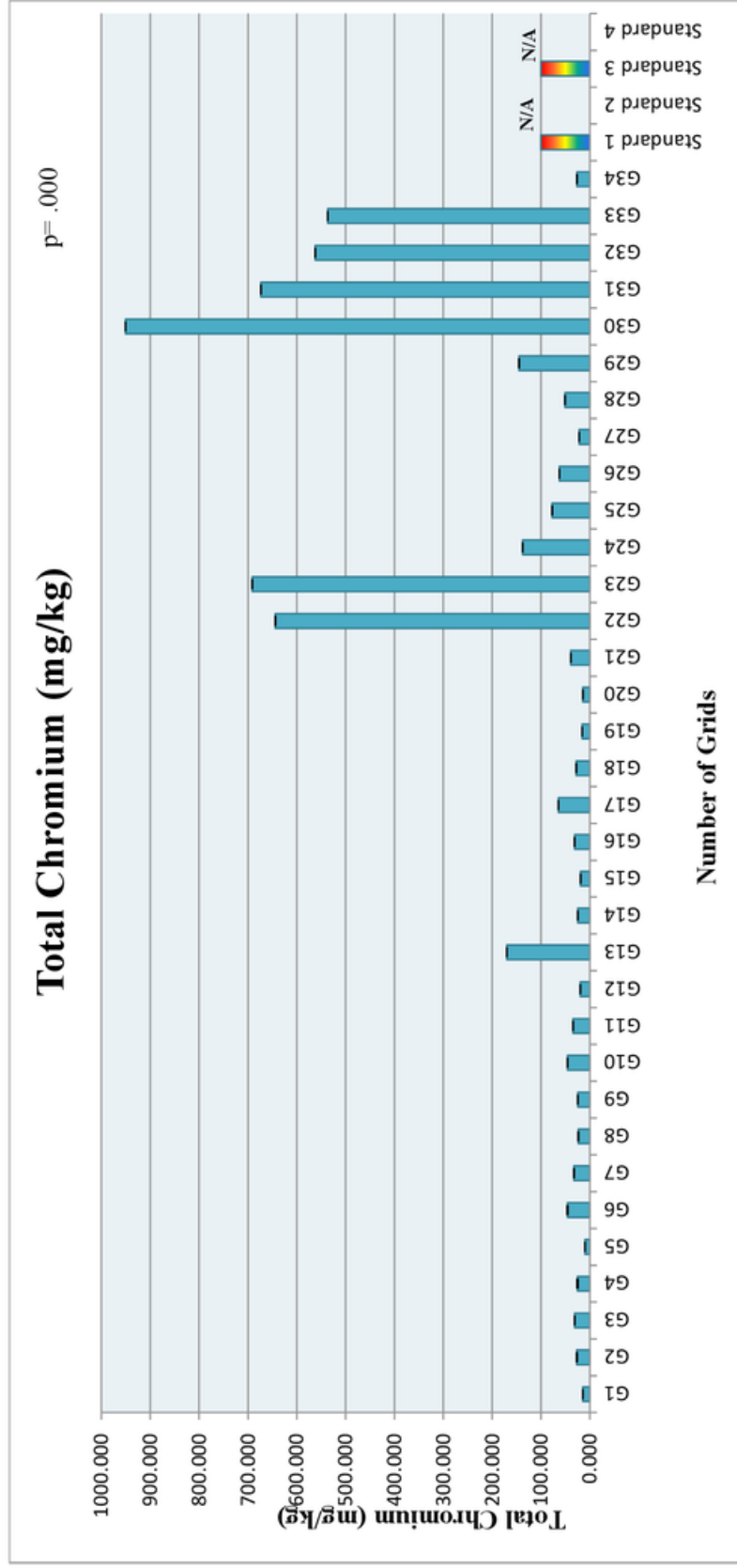


Fig. 4.13: Graph illustrating the mean values of Total Chromium for soil samples from all grids and their comparison with the proposed permissible limits of Total Chromium in soil by *Standard 1, **Standard 2, ***Standard 3 and ****Standard 4

*Standard 1: International Agricultural Soil Standards (Alloway, 1990)

**Standard 2: Indian Standards of Soil (Awasthi, 2000)

***Standard 3: Permissible limits of heavy metals in soil given by European Community Commission (ECC, 1986)

****Standard 4: Permissible limits of heavy metals in soil given by Rowell, 1994

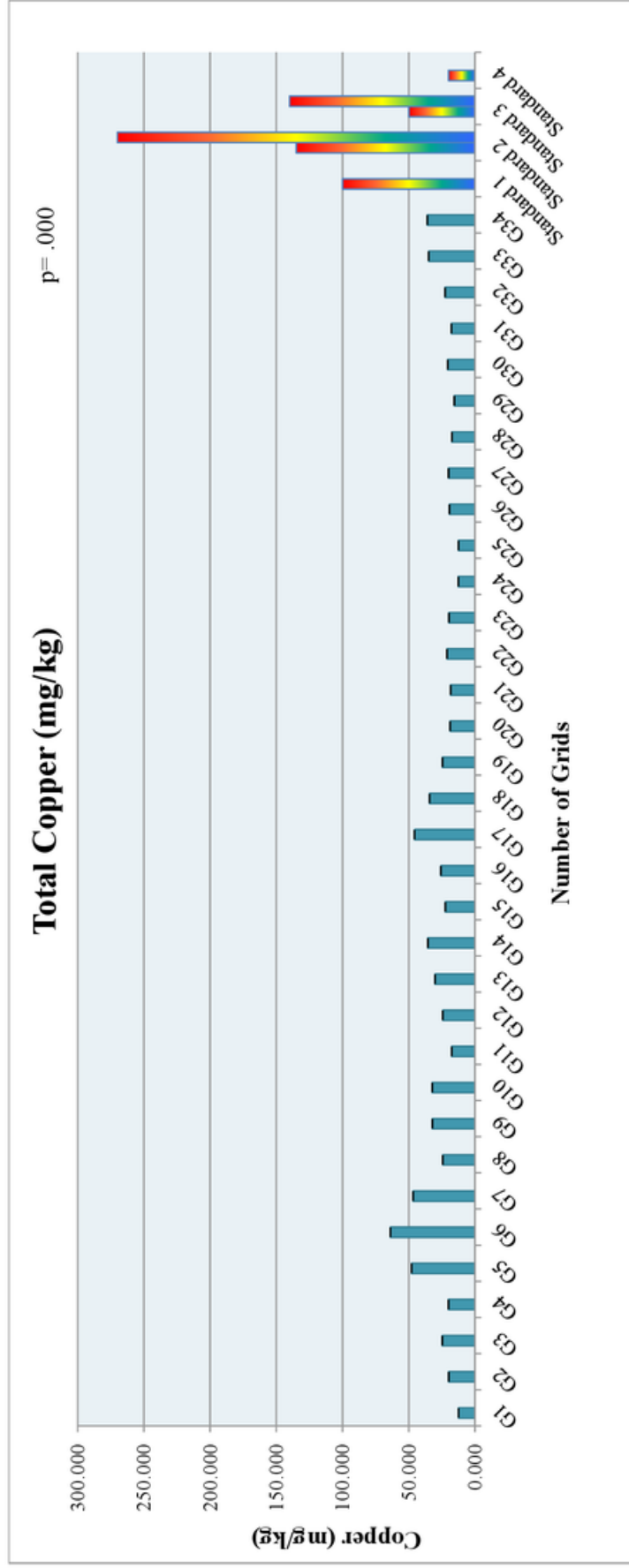


Fig. 4.14: Graph illustrating the mean values of Total Copper for soil samples from all grids and their comparison with the proposed permissible limits of Total Copper in soil by *Standard 1, **Standard 2, ***Standard 3 and ****Standard 4

*Standard 1: International Agricultural Soil Standards (Alloway, 1990)

**Standard 2: Indian Standards of Soil (Awasthi, 2000)

***Standard 3: Permissible limits of heavy metals in soil given by European Community Commission (ECC, 1986)

****Standard 4: Permissible limits of heavy metals in soil given by Rowell, 1994

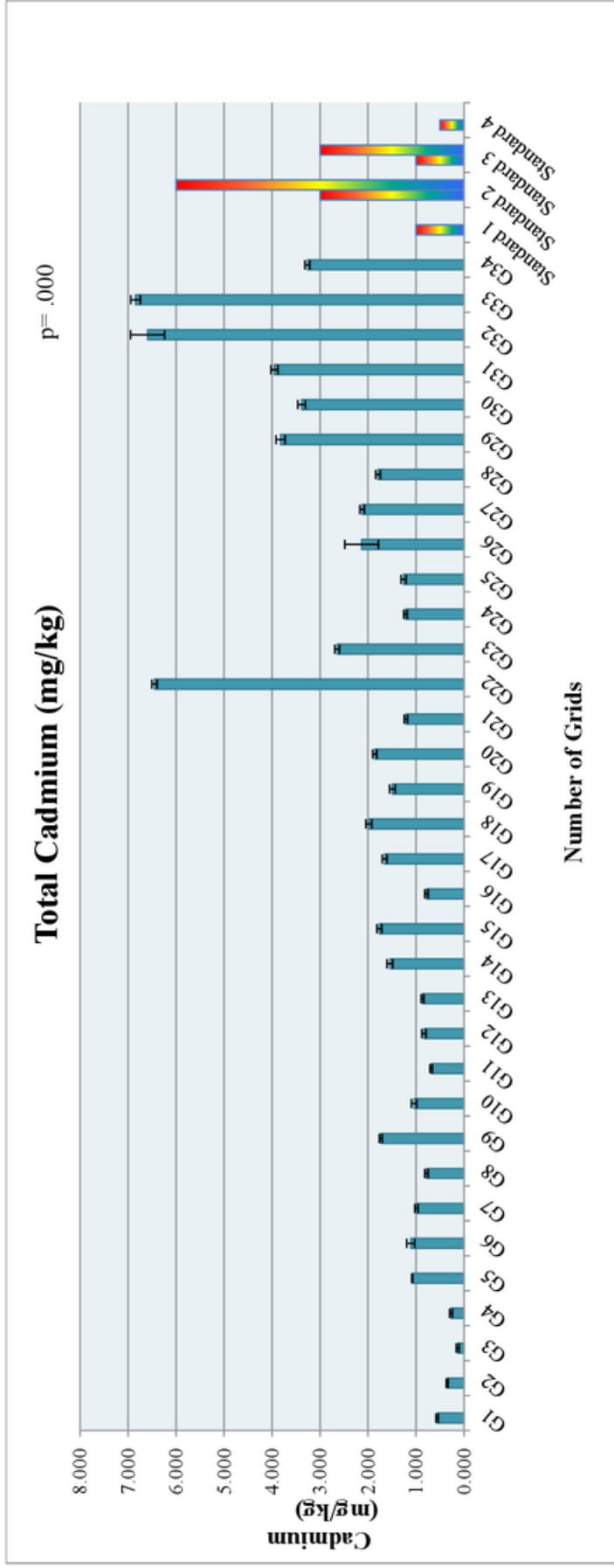


Fig. 4.15: Graph illustrating the mean values of Total Cadmium for soil samples from all grids and their comparison with the proposed permissible limits of Total Cadmium in soil by *Standard 1, **Standard 2, ***Standard 3 and ****Standard 4

*Standard 1: International Agricultural Soil Standards (Alloway, 1990)

**Standard 2: Indian Standards of Soil (Awasthi, 2000)

***Standard 3: Permissible limits of heavy metals in soil given by European Community Commission (ECC, 1986)

****Standard 4: Permissible limits of heavy metals in soil given by Rowell, 1994

Table 4.1. Shows correlation between different parameters

		Correlations													
		pH	EC	OM	OC	P	K	Nb	CuT	CdT	CrE	CuE	CdE	ZnE	FeE
pH	Pearson Correlation	1													
	Sig. (2-tailed)														
N		34													
EC	Pearson Correlation	.121	1												
	Sig. (2-tailed)	.496													
N		34													
OM	Pearson Correlation	-.345*	-.092	1											
	Sig. (2-tailed)	.045	.605												
N		34													
OC	Pearson Correlation	-.330	-.106	.991**	1										
	Sig. (2-tailed)	.057	.550	.000											
N		34													
P	Pearson Correlation	-.074	.261	.212	.185	1									
	Sig. (2-tailed)	.677	.137	.230	.295										
N		34													
K	Pearson Correlation	-.017	.530**	-.119	-.160	.332	1								
	Sig. (2-tailed)	.926	.001	.502	.365	.055									
N		34													
Na	Pearson Correlation	.202	.516**	-.254	-.265	.085	.519**	1							
	Sig. (2-tailed)	.252	.002	.147	.130	.631	.002								
N		34													
CrT	Pearson Correlation	-.240	.497**	-.219	-.253	.043	.761**	.588**	1						
	Sig. (2-tailed)	.172	.003	.214	.149	.809	.000	.000							
N		34													
CuT	Pearson Correlation	-.099	-.188	-.017	-.010	-.121	-.244	-.258	-.164	1					
	Sig. (2-tailed)	.579	.287	.926	.956	.496	.164	.141	.354						
N		34													
CdT	Pearson Correlation	.319	.262	-.176	-.184	-.309	.343*	.431*	.699**	-.060	1				
	Sig. (2-tailed)	.066	.135	.321	.298	.075	.047	.011	.000	.737					
N		34													
CrE	Pearson Correlation	-.044	.160	-.305	-.254	-.036	-.137	-.064	-.148	-.043	-.230	1			
	Sig. (2-tailed)	.806	.367	.079	.148	.839	.441	.720	.404	.811	.190				
N		34													
CuE	Pearson Correlation	.028	-.047	-.101	-.080	.026	-.240	-.277	-.302	.690**	-.213	.088	1		
	Sig. (2-tailed)	.873	.792	.568	.652	.883	.172	.113	.083	.000	.227	.622			
N		34													
CdE	Pearson Correlation	.058	.014	-.008	-.037	-.225	-.175	-.026	-.065	.398*	.226	-.166	-.393*	1	
	Sig. (2-tailed)	.746	.937	.965	.837	.200	.323	.883	.714	.020	.199	.347	.021		
N		34													
ZnE	Pearson Correlation	.056	-.186	-.299	-.262	-.218	-.055	-.106	-.184	-.270	-.100	.134	.093	-.209	1
	Sig. (2-tailed)	.752	.293	.086	.134	.215	.759	.550	.296	.122	.573	.450	.603	.237	
N		34													
FeE	Pearson Correlation	-.117	-.112	.053	.063	-.186	-.510**	-.197	-.320	.510**	-.179	-.104	.497**	.141	.025
	Sig. (2-tailed)	.511	.528	.767	.723	.293	.002	.264	.065	.002	.310	.558	.003	.428	.890
N		34													

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

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

Table.4.2. Shows comparison of average values of different parameters measured in present study with international standard limits

Parameters Measured	Resulted Ranges Observed in Kasur Study Area	Standard Limits
pH	7.36 – 8.80	4.0 – 8.5 ^a
Electrical Conductivity (EC)	0.143 – 1.45 mS/cm	4.0 ^a
Organic Matter	0.5 – 2.5 %	3.4 % ^b
Organic Carbon	0.21 – 1.53 %	2 % ^b
Phosphorus	7.05 – 148.61 mg/kg	a) >7 mg/kg ^c b) 7 – 14 mg/kg ^c
Potassium	40.08 – 920.03 mg/kg	a) >80 mg/kg ^a b) 9-180 mg/kg ^c
Sodium	99.9 – 1360.27 mg/kg	1550 – 2300 mg/kg ^d
Extractable Chromium	0.01 – 0.22 mg/kg	8.0 mg/kg ^c
Extractable Copper	4.067 – 24.660 mg/kg	0.5 mg/kg ^c
Extractable Cadmium	0.013 – 0.106 mg/kg	0.31 mg/kg ^c
Extractable Zinc	1.63 – 10.11 mg/kg	1.5 mg/kg ^c
Extractable Iron	5.807 – 44.803 mg/kg	5.0 mg/kg ^c
Total Chromium	9.987 – 950.687 mg/kg	a) 100 mg/kg ^a b) Not prescribed ^f c) 100 mg/kg ^g d) Not prescribed ^h
Total Copper	12.42 – 63.84 mg/kg	100 mg/kg ^a 135 – 270 mg/kg ^f 50 – 14 mg/kg ^g 20 mg/kg ^h
Total Cadmium	0.13 – 6.84 mg/kg	1.0 mg/kg ^a 3 – 6 mg/kg ^f 1 – 3 mg/kg ^g 0.5 mg/kg ^h

- a) International Agricultural Soil Standards (Alloway, 1990)
- b) European Union, 2009
- c) Malik et al., 1984 and Motsara, 2002
- d) Marschner, 1986
- e) Soltanpour, 1985; Maclean et al., 1987
- f) Indian Standards of Soil (Awasthi,2000)
- g) European Community Commission (ECC, 1986)
- h) Rowell, 1994

Chapter 5

Discussion

Soil contamination with heavy metals due to increased industrialization, urbanization, modern agricultural practices and inappropriate waste disposal methods is a major environmental problem in different parts of the world. Thus, the polluted soil is an important environmental issue to be resolved because the circulation of heavy metals in food chain causes serious ecological and health problems. Moreover, heavy metals accumulation in soils has led to elevated heavy metal uptake by crops (Wang et al., 2001) that add more to the gravity of the problem.

Physico-chemical properties of the soil are fundamental for soil quality because these are the most influential factors with reference to soil structure (Buscot, 2005). These characteristics of soil including pH, cation exchange capacity and organic matter regulate the fate of the metals (Kabata-Pendias, 2004). When the soil is exposed to environmental stresses, maintaining its structural ability is critical in prevention of soil erosion (Oades, 1993). Soil pH affects not only the metal bioavailability but also the process of metal uptake from roots. Gupta and Sinha (2006) reported that metal ions can be complexed with organic matter altering their availability to the plants.

The results of the physiochemical analysis of the soil from the area adjacent to Kasur tanneries are discussed below in comparison with other studies undertaken and finally compared with the international standards for agriculture, to judge whether the area is appropriate for agriculture.

The present study reports that the pH of the analyzed soil is alkaline i.e. 7.63-8.80 (Fig.4.1). There is a strong relationship between soil pH and nutrient availability. Alkaline soils with pH range 7-8 are generally deficient in Zn^{2+} , Fe^{3+} , P^{5+} and uptake of various plant nutrients is also pH dependent (Marschner, 1986). Most of the primary nutrients like nitrogen, phosphorous, potassium and secondary nutrients like calcium, magnesium and sulfur are best utilized by the plants when the pH range is 5.5-7.9. The uptake of most of the micronutrients also takes place at low pH (Lucas and Davis, 1986). In Pakistan, the soils have generally pH above 8 (Bhatti, 1999) and the undertaken studies also show almost similar results. At pH 5.5, fungi and algae generally dominate the soils (Trolldenier, 1973) where as at 6.0-8.2pH levels the bacteria are predominate (Mezhin, 1961). When compared to the International

Agriculture Soil Standards (Alloway, 1990) for pH which is 4-8.5, the analysis of the studied samples shows that most of the samples have pH value in permissible limit.

The results show that the electrical conductivity (EC) of soil samples ranges from 0.143-1.45 mS/cm (Fig.4.2). Yasin and Faisal (2013) reported the EC of contaminated soil as 15.1 mS/cm and Gupta and Sinha (2007) reported EC of sludge as 3.85 mS/cm. Both values are higher than those reported by present study. On the other hand, the present study is in agreement with the study of Sinha *et al* (2006) in which EC reported in the treated tannery wastewater soil is 0.53-1.44 mS/cm.

Maximum EC (1.45 mS/cm) was found in the sample taken from the soil near Depalpur Road. EC of the soil increases with the increasing concentration of salt. Mass and Hoffman (1986) reported that the EC more than the permissible limit can cause salinity problem over a long period of time while in the present study the EC-values of all samples are within permissible limit of 4 mS/cm prescribed by International Agriculture Soil Standards (Alloway, 1990) which shows that the soil of the studied area is less saline.

The range of organic matter (OM) percentage in analyzed soil is 0.50-2.65% (Fig.4.3). Liphadzi and Kirkham (2005) argued that high organic matter and cation exchange capacity are some of the most important soil factors which determine the bioavailability of metals to the plants. The organic matter is one of the factors that may reduce the ability of these metals to be phytotoxic in the soil due to metal-organic complexation. Amir et al (2005) argued that copper is strongly bound to OM and would be released slowly over time as the OM of the sludge is decomposed, whereas, Cd and Zn are not bound as strongly to OM as copper does. Yasin and Faisal (2012) observed that in tannery contaminated soil the organic matter is 7.92%, which might be due to the higher organic content in tannery wastewater. Thus this study controverts with the present work. While the conducted work is in agreement with Sinha et al., (2011) in which OM is reported from 0.49-2.5% in the tannery effluent contaminated soil.

Sahu et al (2007) reported that the OM in the tannery contaminated soil is 9.3-14.9%, which is not in accordance with the current study. Gupta and Sinha (2006) reported that metal ions can be complexed with organic matter altering their availability to the plants. Extraction of heavy metals is usually limited by availability of metals from the soil. According to the International Agriculture Soil Standards (Alloway, 1990), the

OM should be 3.4% in the soil. When compared to this value, all the recorded values are lower than the standard value.

Fig. 4.4 shows that the organic carbon average percentage in contaminated soil is 0.21-1.53% that is quite low and thus is in agreement with the opinion of Khalid et al(2012)who stated that organic matter in the soils of Pakistan is quite low; soil in Punjab province contained less than 1% organic carbon. The reported organic carbon content in contaminated soil due to tannery waste disposal by Mahimairaja *et al* (2011) is 0.47%, which lies within the range of conducted study's organic carbon values. According to the International Agriculture Soil Standards (Alloway, 1990) the organic carbon should be 2% in soil and thus the values of carbon average percentage reported in the present study are lower than the prescribed value.

Phosphorus in the examined soil varies from 7.05-148.61 mg/kg (Fig.4.5). Sinha et al (2006) reported that the available phosphorus in different soils receiving treated tannery wastewater of Jajmau, Kanpur, India ranged from 2.72-56.82 mg/kg which is slightly in line with the determined values of P. According to a study of agricultural field contaminated by tannery wastewater Sinha et al (2011) the available phosphorus ranges from 1.47-66.56 mg/kg while in soil samples studied here higher concentration of available phosphorus is observed as compared to this study. In Swapnil et al (2011) value of available phosphorus in contaminated soil was recorded as 81.662-121.66 mg/kg, which is in accordance with the result of the current study. In comparison with the two given limits by International Agricultural Soil Standards (Alloway, 1990) and the satisfactory range of phosphorus in soil given by Malik et al (1984); Motsara (2002) which are >7 mg/kg and 7-14 mg/kg, respectively, the phosphorus in soil is found to be far higher.

The value of K in studied soil samples ranges from 40.08-920.03mg/kg (Fig. 4.6). This is due to the reason that available K content of soil increases significantly by the sewage and tannery water application (Baddesha, 1997). Alkaline soils tend to have high concentrations of Potassium (Kim, 1994). As the soil here is relatively alkaline, result of this study is similar to Faryal et al (2007) which shows same pattern with regard to K ranging from 85-228 mg/kg. In many soils of Pakistan, the availability of K has become the limiting factor for crop production (White *et al.*, 1988). The optimum level of K for agricultural purposes is known to be 180-300ppm but the soils with less than 60ppm may show deficiency symptoms (Imran *et al*, 2010). In current research, there are very few samples which are K deficient if compared to both

international standards (Standard 1: International Agricultural Soil Standards (Alloway, 1990); Standard 2: Malik *et al.*, 1984 and Motsara, 2002). Fixation of K can be controlled by several factors such as soil type i.e. clay/ mineral, structural configuration, etc (White *et al.*, 1988).

The average value of Na ranges from 99.99-1360.27 mg/kg (Fig.4.7). In irrigated soil, Na can be accumulated to a greater extent because irrigation water often contains high amount of Na. Tannery wastewater also consists of large amount of Na due to greater use of NaCl in processing hides. Due to Na and K, salinity of the soil increases and thus high osmotic potential of soil solution makes Na unavailable for plants (Bohn *et al.* 2001). The water logging and salinity is another cause of enrichment of Na, Ca, Mg, Al (Nasreen, 2006). The amount of Na reported in the current study is in safe limit which contradicts the study of Tariq (2006) on tannery contaminated soil of Peshawar which shows that the Na content (11470-13751 mg/kg) is extremely higher than their natural abundance in soil. The reason can be the larger discharge of tannery wastewater with huge salt content. The Na in excess causes ionic toxicity and imbalance in Na^+/K^+ , $\text{Na}^+/\text{Ca}^{2+}$, $\text{Na}^+/\text{Mg}^{2+}$ ratios and causes salt injury to crops (Marschner, 1986). The continuous buildup of salts in soil surface may also adversely affect seed germination, seedling establishment and plant growth and may also deteriorate soil productivity (Mohammad and Mazahreh, 2003).

When compared to the detrimental range (1550-2300 mg/kg) of Na in soil (Marschner, 1986), the reported values of Na in soil in present study are below the given limit which makes it fit for agricultural practices.

The average range of total heavy metal content for three metals in soil is reported as Cr (9.98-950.68 mg/kg), Cu (12.42-63.84 mg/kg) and Cd (0.13-6.84 mg/kg) as shown in Fig.4.13, Fig.4.14 and Fig.4.15, respectively. Heavy metals accumulation in soils has led to elevated heavy metal uptake by crops (Wang *et al.*, 2001). Plants have a natural propensity to take up metals. The movement of metals through the soil profile was required to optimize agronomic practices. Some metals such as Cu, Co, Fe, Mo, Mn, Ni, and Zn are essential mineral nutrients. Others such as Cd and Pb have no known physiological activity (Lasat, 2002). Indiscriminate discharge of effluents loaded with heavy metals (especially Cr, Fe, Cd and Pb) into peripheral agricultural soils was clearly beyond levels prescribed for soil metal exposure through irrigating effluents, which is deteriorating soil quality and affecting plant growth (Ali *et al.*, 2013).

As reported by Alloway(1990); the permissible limit of chromium content in soils is 100 mg/kg. The results obtained in the current study (Fig.4.13) show that most of the samples have not exceeded the acceptable level of 100 mg/kg. Bini *et al* (2008) reported that large variation in chromium concentration in soils was observed in the leather tannery district in Italy, ranging from 42.9 - 10,590 mg/kg with mean of 610 mg/kg; same is the case with the studied soil in which Cr ranges from 9.98 - 950.68 mg/kg.

Tariq *et al* (2006) reported Cr concentration in tannery contaminated soil of Peshawar as 0.810 - 100.2 mg/kg, same is the result observed in the analyzed soil samples except few samples. The current study contradicts the study of Alvarez-Bernal *et al* (2006) in which copper was reported ranged from 7.2 – 20.5 mg/kg in soil of Leon, Mexico.

In accordance with Sahu *et al* (2007) the results show similar concentration of Cr (46.5 – 57.21 mg/kg) and Cd (2.9 – 4.3 mg/kg) in tannery contaminated soil while for the concentration of Cu (6.2 – 9.4 mg/kg) the study contradicts because of its higher Cu concentration. The findings in current research are similar to the findings of Asfaw (2013) for total heavy metal concentrations in the soils of tannery adjacent Ejersa area of East Shoa, Ethiopia which are Cr (92.86 – 126.17 mg/kg), Cd (0.19 – 0.74 mg/kg) and Cu (10.12 – 17.64 mg/kg). In another study by Iram *et al*(2013) the concentrations of heavy metals in Kasur soil were reported as Cd (2- 3.4 mg/kg), Cr (54.1-210.2 mg/kg), Cu (31.2-60.8 mg/kg) which resemble the values determined here with some variations.

Deepali and Gangwar (2010) cites that the value of Cr (630.85 – 815.25 µg/gm), Cu (0.03 – 0.05 µg/gm), Cd (0.03 – 0.05µg/gm) for tannery contaminated soil while in this study the value of total metal concentration is as Cr (9.987-950.687 mg/kg), Cu (12.42-63.847 mg/kg) and Cd (0.13-6.843 mg/kg). The present result when compared with Phatak *et al.* (2010) is similar for Cd and Cu concentration while contradicts Cr concentration.

When compared with the four standard limits i.e. 1st standard reference is International Agricultural Soil Standards (Alloway, 1990), 2nd standard reference is Indian Standards of Soil (Awasthi, 2000; Sharma *et al.*, 2006; Gupta *et al.*, 2008), 3rd reference standard is permissible limits of heavy metals in soil given by European Community Commission (ECC, 1986) and 4th standard reference is permissible limits of heavy metals in soil given by Rowell (1994), different conclusions are reached.

Total Cr is within permissible limit for most of the soil samples in comparison with standard 1 and standard 3. Total Cu is below the permissible limits according to standard 1, standard 2 and standard 3. According to standard 4 only thirteen soil samples are in permissible limit. According to standard 1 and standard 4 very few total Cd values are in permissible limits while according to standard 2 and standard 3 very few soil samples exceed the permissible limit.

Large differences in soil chromium concentration were observed in the site investigated with a very scattered distribution. The metal content of the polluted soil was also very high. The amount of Cr in tannery soil was very high as compared to normal soil. The higher values of Cr in all samples indicate that the majority of tanneries working in Kasur use the Chrome Tanning Process due to its high speed and cost effectiveness. However, this method of tanning is releasing a high concentration of Cr and other toxic pollutants into environment. In the present study Cr level was highest than other metals.

The analysis of soil evaluates the range of five extractable/available metals as Cr: 0.011- 0.22 (mg/kg), Cu: 4.06 - 24.66 (mg/kg), Cd: 0.013 – 0.11 (mg/kg), Zn: 1.63 – 10.11 (mg/kg), and Fe: 5.81 – 44.80 (mg/kg) as shown in Fig.4.8, Fig.4.9, Fig.4.10, Fig.4.11 and Fig.4.12, respectively. This study is in accordance with the study of Huq (1998) who reported extractable metals in the soil contaminated by tanneries in Bangladesh as Zn (23.4 mg/ kg), Cu (8 mg/ kg), Fe (226.4 mg/kg) and Cd (0.04 mg /kg), Cr (ND). According to Mitsios *et al* (2005), the concentration of extractable heavy metals ranged as Zn (0.03-5.5 mg/ kg), Cu (0.10-7.0 mg/ kg) and Cd (0.1-137 mg /kg) while in the inspected soil samples the extractable metals are found to be Zn (1.63-10.11 mg/kg), Cu (4.07-24.66 mg/kg) and Cd (0.01-0.11 mg/kg).

Khan *et al* (2013) studied the peri-urban area of Lahore where wastewater was used to irrigate the agricultural land and noted the level of extractable metals as Zn (1.58- 8.02mg/ kg), Cu (1.16- 5.42 mg/ kg), Fe (8.89- 35.03 mg/kg) and Cd (0.098- 0.52mg /kg) while in the undertaken study it is observed that the level of Zn and Fe are similar to the compared study but Cu level is higher and Cd level is found to be lower.

The calculated concentration of extractable Cd in inspected soil is in accordance with the determined concentration of DTPA extractable Cd (0.18 mg/kg) in agriculture soils of Fayoum District, Egypt (Elgawad *et al.*, 2007). According to Shanab *et al* (2007) mobile Cr (75.4 mg /kg), mobile Cu (1.1 mg /kg), mobile Zn (6.9 mg/kg) are

reported in multi-metal contaminated soil and the examined soil conflicts with these concentrations of mobile metals as it has lower concentration of all metals except mobile Zn which falls in range with it.

The studied soil has the lower concentrations of extractable metal content as compared to the observed values in tannery sludge by Gupta and Sinha (2007) which are as Fe (94.05 mg/kg), Zn (55.06 mg/kg), Cu (25.10mg/kg), Cr (19.59 mg/kg) and Cd (23.24 mg/kg). Similarly, Sinha *et al* (2006) studied extractable metals in soil of Jajmau, Kanpur, India receiving treated tannery wastewater and reported extractable Fe (62.56-2458 mg/kg), Cr (33.26-114.26mg/kg), Zn (6.73-190.82mg/kg), Cu (4.7-77.03mg/kg) while the concentration of all these extractable metals are lesser in the present research work.

The extractable metals Fe, Zn, Cu are not in the permissible limits when compared with the acceptable limit of these metals in agricultural soil prescribed by Soltanpour (1985) & Maclean et al (1987). It may be due to the presence of these metals in treated wastewater used for irrigation (Sinha et al., 2006). Extractable Cr and Cd are within permissible limit which shows that soil of the present studied area needs treatment to bring extractable Fe, Zn and Cu levels in soil within the permissible limits.

Conclusion:

From the foregoing discussion, it may be concluded that the reclaimed land area around Kasur tanneries is almost appropriate for agriculture practices. The mean values of available/extractable heavy metals Cr and Cd reported in different soil samples analyzed in present study are within the safe limits when compared with the prescribed permissible limits provided by International Agriculture Soil Standards (Alloway, 1990), Indian Standards of Soil (Awashti, 2000; Sharma et al., 2006; Gupta et al., 2008), European Community Commission (ECC, 1986) and other authors. However, concentrations of available/extractable Cu, Fe, and Zn in agriculture soil are above the safe limits described by Soltanpour(1985) and Maclean et al.,(1987), while total metal concentrations of all the heavy metals (Cr, Cd, and Cu) in the studied agricultural soil are within permissible limits prescribed by most of the compared standards with very few samples exceeding limits. The results for other parameters such as pH, EC, OM, OC, K and Na are in accordance with the prescribed limits but P in soil exceeds the satisfactory range of P in agricultural soil described by Malik et al., (1984) and Motsara (2002).

Recommendations:

Following are the recommendations based on the results of the study:

- I. Agricultural practice should be promoted in the area which is not only healthy utilization of land but will also provide labor opportunities to the people living in the surrounding area.
- II. A continuous monitoring of the soil quality of the agricultural land area should be done so that any kind of problem can be detected in time and solution can be provided.
- III. Further research on the soil to more depths should be carried out to clear the soil to clarify any in-depth contamination which can leach into groundwater.
- IV. Further research on the plants, vegetables and crops being grown on the agricultural land should be conducted to evaluate any possible contamination or entrance of heavy metals in food chain.
- V. To bring the exceeding limits of extractable/available metals (Cu, Fe, Zn) within permissible limit, phyto-remediation with metal hyper-accumulator plants, heap leaching by using chemicals or bio-remediation with microbes or manure/sludge addition may be practiced.

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Appendixes

APPENDIX: 1 (a)

CHEMICALS USED IN DETERMINATION OF ORGANIC MATTER IN SOIL.

- I. 1 N Potassium dichromate ($K_2Cr_2O_7$, F. wt. 294. 18): Dissolve oven dried 49.04 g potassium dichromate in distilled water, mix well and dilute to 1litre.
- II. 1.0 N ferrous sulphate standardised: Dissolve 278.02 g ferrous sulphate ($FeSO_4 \cdot 7H_2O$), in distilled water, add 15 ml concentrated sulphuric acid and dilute to one litre.
- III. Sulphuric Acid (96 %, specific gravity 1.84)
- IV. Phosphoric acid (H_3PO_4) 85 % or sodium fluoride (NaF)
- V. Barium diphenylamine sulphonate, 0.16 %: Dissolve 0.16 g barium diphenylamine sulphonate indicator in 100 ml conc. H_2SO_4 .

APPENDIX: 1 (b)

CHEMICALS USED IN DETERMINATION OF SODIUM AND POTASSIUM IN SOIL.

- I. A. 1 N NH_4OAC : Dissolve 77.1 g ammonium acetate (F.W. 77.1, CH_3COONH_4) in 800 ml distilled water and make the volume to 1 litre. Adjust pH 7.0 using either NH_4OH or HCl.
- II. B. Stock solution: Dissolve 1.907 g oven dried KCl/NaCl in distilled water and make volume 1-2. This solution contains 1000ppm K/Na.
- III. C. Prepare standard solutions from stock solution in 100ml volumetric flask.

APPENDIX: 1 (c)

CHEMICALS USED IN DETERMINATION OF EXTRACTABLE SOIL PHOSPHORUS (OLSEN'S METHOD)

- I. Sodium bicarbonate solution, 0.5 M $NaHCO_3$: Dissolve 42.0 g $NaHCO_3$ in app. 700 ml distilled water, shake well and make the volume 1000 ml . Adjust pH 8.5 using 4 N NaOH.

4 N NaOH = Dissolve 160g NaOH in distilled water and let it cool and make volume liter.
- II. Mixed reagent:

(a) Ammonium hepta molybdate 4.0 % ($(NH_4)_6MO_7O_{24} \cdot 4HO_2$ (f. wt. 1235.9)

Dissolve 12.0 g in distilled water and make volume 250 ml

(b) Potassium antimony tartrate ($\text{K}_2\text{Sb}_2\text{O}_7 \cdot \text{C}_4\text{H}_2\text{O}_6$)

Dissolve 0.291 g make volume to 100 ml with distilled water

(c) 5N H_2SO_4 . Dilute 140 ml concentrated sulfuric acid (in fume hood) in distilled water, let it cool and make volume 1 L.

(d) Add both the dissolved reagents (a + b) in 1000 ml 5 N H_2SO_4 and make volume 2000 ml with distilled water. Store in a Pyrex bottle in a dark, cool place

- III. Colour developing reagent: Weigh 0.528g ascorbic acid to 100 ml of mixed reagent. This reagent should be prepared freshly as required because it does not give accurate results after 24 hours.
- IV. Stock solution (1000 ppm): Dissolve 4.3937 g potassium dihydrogen phosphate (KH_2PO_4) in distilled water and make volume to 1 liter.

APPENDIX: 1 (d)

CHEMICALS USED IN DETERMINATION OF DTPA EXTRACTABLE METALS BY ICP-MS

IV. 0.005 M DTPA

V. 0.01 M CaCl_2

VI. 0.01 M TEA (Tri-ethanol amine, adjusted to pH 7.3 with dilute HCL)

DTPA solution was prepared by dissolving 3.934 g of DTPA and 2.94 g CaCl_2 and 25.3 ml of TEA in approximately 200 ml of distilled water. After the DTPA was completely dissolved, 2 liter volume was made. pH was adjusted to 7.3 with 1:1 HCl while stirring.

APPENDIX: 1 (e)

CHEMICALS USED IN DETERMINATION OF TOTAL METALS BY ICP-MS

I. ¹ Perchloric Acid and Nitric Acid Mixture (1:2):

167 ml (70%) Perchloric acid was added in 333 ml Nitric acid (69-70%), mixed well and stored in an amber glass bottle.

APPENDIX: 2 (a) STATISTICAL DATA INTERPRETATION OF THE SOIL SAMPLES COLLECTED FOR pH

pH					
Sample/Grid no.	R1	R2	R3	Average	±SD
G1	7.75	7.7	7.73	7.727	0.025
G2	7.4	7.46	7.49	7.45	0.046
G3	7.98	7.93	7.96	7.957	0.025
G4	8.2	8.24	8.2	8.213	0.023
G5	7.44	7.45	7.43	7.44	0.01
G6	8.18	8.15	8.16	8.163	0.015
G7	7.82	7.81	7.83	7.82	0.01
G8	7.63	7.6	7.61	7.613	0.015
G9	7.35	7.38	7.35	7.36	0.017
G10	7.98	8.02	8.01	8.003	0.021
G11	7.8	7.81	7.85	7.82	0.026
G12	7.24	7.3	7.22	7.253	0.042
G13	8.04	7.98	8.02	8.013	0.031
G14	8.1	8.05	8.09	8.08	0.026
G15	8.52	8.55	8.56	8.543	0.021
G16	7.74	7.76	7.74	7.747	0.012
G17	7.89	7.87	7.91	7.89	0.02
G18	8.2	8.12	8.15	8.157	0.04
G19	8	8.05	8.03	8.027	0.025
G20	7.62	7.66	7.69	7.657	0.035
G21	8.39	8.3	8.32	8.337	0.047
G22	8.1	8.08	8.04	8.073	0.031
G23	7.89	8.11	7.96	7.987	0.112
G24	8.26	8.3	8.28	8.28	0.02
G25	7.44	7.44	7.42	7.433	0.012
G26	7.91	8.01	7.96	7.96	0.05
G27	7.82	7.75	7.79	7.787	0.035
G28	8.82	8.78	8.81	8.803	0.021
G29	8.05	8.02	7.99	8.02	0.03
G30	7.79	7.76	7.82	7.79	0.03
G31	8.39	8.34	8.36	8.363	0.025
G32	8.42	8.3	8.48	8.4	0.092
G33	8.2	8.26	8.29	8.25	0.046
G34	7.58	7.51	7.56	7.55	0.036

APPENDIX: 2 (b) STATISTICAL DATA INTERPRETATION OF THE SOIL SAMPLES COLLECTED FOR ELECTRICAL CONDUCTIVITY (EC)

EC (ms/cm)					
Sample/Grid no.	R1	R2	R3	Average	±SD
G1	0.42	0.39	0.42	0.41	0.0173
G2	0.26	0.21	0.28	0.25	0.0361
G3	0.24	0.2	0.25	0.23	0.0265
G4	0.31	0.29	0.34	0.313	0.0252
G5	0.25	0.27	0.29	0.27	0.02
G6	0.13	0.18	0.15	0.153	0.0252
G7	0.18	0.23	0.26	0.223	0.0404
G8	0.25	0.23	0.28	0.253	0.0252
G9	0.22	0.16	0.2	0.193	0.0306
G10	0.26	0.3	0.29	0.283	0.0208
G11	0.33	0.38	0.36	0.357	0.0252
G12	0.26	0.2	0.24	0.233	0.0306
G13	0.22	0.27	0.3	0.263	0.0404
G14	0.98	1.05	1	1.01	0.0361
G15	0.35	0.36	0.4	0.37	0.0265
G16	0.84	0.81	0.83	0.827	0.0153
G17	0.31	0.26	0.24	0.27	0.0361
G18	0.32	0.28	0.31	0.303	0.0208
G19	0.21	0.26	0.24	0.237	0.0252
G20	0.44	0.38	0.42	0.413	0.0306
G21	0.28	0.24	0.19	0.237	0.0451
G22	0.33	0.28	0.3	0.303	0.0252
G23	0.36	0.39	0.3	0.35	0.0458
G24	0.55	0.5	0.55	0.533	0.0289
G25	0.19	0.25	0.21	0.217	0.0306
G26	0.24	0.27	0.22	0.243	0.0252
G27	0.11	0.15	0.17	0.143	0.0306
G28	0.23	0.17	0.21	0.203	0.0306
G29	0.53	0.59	0.63	0.583	0.0503
G30	1.48	1.41	1.45	1.447	0.0351
G31	0.49	0.47	0.55	0.503	0.0416
G32	0.91	0.89	0.96	0.92	0.0361
G33	0.2	0.22	0.25	0.223	0.0252
G34	0.19	0.18	0.15	0.173	0.0208

APPENDIX: 2 (c) STATISTICAL DATA INTERPRETATION OF THE SOIL SAMPLES COLLECTED FOR ORGANIC MATTER (OM)

OM (%)					
Sample/Grid no.	R1	R2	R3	Average	±SD
G1	1.13	0.98	1.08	1.06	0.08
G2	2.65	2.29	2.45	2.46	0.18
G3	1.52	1.97	1.37	1.62	0.31
G4	1.85	2.05	1.94	1.95	0.1
G5	1.95	2.15	1.87	1.99	0.14
G6	1.85	1.76	1.55	1.72	0.15
G7	1.5	1.25	1.35	1.37	0.13
G8	2.15	2.52	2.35	2.34	0.19
G9	1.26	0.99	1.35	1.2	0.19
G10	0.62	0.85	1	0.82	0.19
G11	1.55	1.8	1.67	1.67	0.13
G12	2.36	2.27	2.57	2.4	0.15
G13	0.95	1.32	1.05	1.11	0.19
G14	0.45	0.62	0.5	0.52	0.09
G15	1.35	1.6	1.4	1.45	0.13
G16	2.75	2.22	2.54	2.5	0.27
G17	0.55	0.58	0.5	0.54	0.04
G18	1.08	0.98	1	1.02	0.05
G19	1.12	1.06	1.35	1.18	0.15
G20	0.8	0.59	0.63	0.67	0.11
G21	0.87	1.13	0.75	0.92	0.19
G22	1.58	1.15	1.26	1.33	0.22
G23	1.4	1.01	1.26	1.22	0.2
G24	0.75	0.85	0.9	0.83	0.08
G25	1.52	1.15	1.36	1.34	0.19
G26	1.05	0.92	0.85	0.94	0.1
G27	0.797	0.99	0.86	0.88	0.1
G28	0.88	1.15	1	1.01	0.14
G29	2.66	2.35	2.41	2.47	0.16
G30	0.86	0.68	0.65	0.73	0.11
G31	1.52	1.87	1.45	1.61	0.23
G32	1.86	1.43	1.61	1.63	0.22
G33	0.51	0.55	0.45	0.5	0.05
G34	2.02	2.36	1.95	2.11	0.22

**APPENDIX: 2 (d) STATISTICAL DATA INTERPRETATION OF THE SOIL
SAMPLES COLLECTED FOR ORGANIC CARBON (OC)**

OC (%)					
Sample/Grid no.	R1	R2	R3	Average	±SD
G1	0.65	0.56	0.62	0.61	0.046
G2	1.53	1.32	1.42	1.42	0.105
G3	0.88	1.14	0.79	0.94	0.182
G4	1.07	1.18	1.12	1.12	0.055
G5	1.13	1.24	1.08	1.15	0.082
G6	1.07	1.02	0.89	0.99	0.093
G7	0.87	0.72	0.78	0.79	0.075
G8	1.24	1.46	1.36	1.35	0.11
G9	0.73	0.57	0.78	0.69	0.11
G10	0.35	0.49	0.58	0.47	0.116
G11	0.89	1.04	0.96	0.96	0.075
G12	1.36	1.31	1.49	1.39	0.093
G13	0.55	0.76	0.6	0.64	0.11
G14	0.26	0.35	0.29	0.3	0.046
G15	0.78	0.92	0.81	0.84	0.074
G16	1.59	1.28	1.47	1.45	0.156
G17	0.31	0.33	0.29	0.31	0.02
G18	0.62	0.56	0.81	0.66	0.131
G19	0.64	0.61	1.47	0.91	0.488
G20	0.46	0.34	0.29	0.36	0.087
G21	0.5	0.65	0.58	0.58	0.075
G22	0.91	0.66	0.78	0.78	0.125
G23	0.81	0.58	0.36	0.58	0.225
G24	0.43	0.49	0.52	0.48	0.046
G25	0.88	0.66	0.78	0.77	0.11
G26	0.6	0.53	0.49	0.54	0.056
G27	0.44	0.57	0.49	0.5	0.066
G28	0.51	0.66	0.58	0.58	0.075
G29	1.54	1.36	1.39	1.43	0.096
G30	0.49	0.39	0.37	0.42	0.064
G31	0.88	1.08	0.84	0.93	0.129
G32	1.07	0.82	0.93	0.94	0.125
G33	0.29	0.31	0.26	0.29	0.025
G34	1.17	1.36	1.13	1.22	0.123

APPENDIX: 2 (e) STATISTICAL DATA INTERPRETATION OF THE SOIL SAMPLES COLLECTED FOR AVAILABLE PHOSPHORUS (P)

Phosphorus (mg/kg)					
Sample/Grid no.	R1	R2	R3	Average	±SD
G1	99.62	99.42	99.54	99.53	0.1
G2	96.92	97.12	96.89	96.98	0.13
G3	42.79	42.9	42.87	42.85	0.06
G4	67.8	67.72	67.68	67.73	0.06
G5	86.22	86.15	86.1	86.16	0.06
G6	22.72	22.6	22.68	22.67	0.06
G7	117.24	117.05	117.15	117.1	0.1
G8	106.08	106.14	105.92	106	0.11
G9	17.46	17.33	17.42	17.4	0.07
G10	13.15	12.95	13.24	13.11	0.15
G11	58.62	58.74	58.68	58.68	0.06
G12	103.15	103.22	103.27	103.2	0.06
G13	58.42	58.5	58.48	58.47	0.04
G14	48.58	48.66	48.62	48.62	0.04
G15	148.61	148.58	148.65	148.6	0.04
G16	51.92	51.86	51.89	51.89	0.03
G17	50.65	50.56	50.72	50.64	0.08
G18	14.99	15.22	15.12	15.11	0.12
G19	13.88	13.75	13.92	13.85	0.09
G20	64.52	64.46	64.5	64.49	0.03
G21	49.92	49.83	49.86	49.87	0.05
G22	36.1	36.04	35.99	36.04	0.06
G23	44.12	44.06	43.97	44.05	0.08
G24	42.06	41.95	42.12	42.04	0.09
G25	27.08	26.95	26.88	26.97	0.1
G26	17.65	17.56	17.7	17.64	0.07
G27	14.78	14.82	14.92	14.84	0.07
G28	90.65	90.68	90.72	90.68	0.04
G29	38.84	38.75	38.7	38.76	0.07
G30	143.56	143.67	143.5	143.6	0.09
G31	58.05	57.95	57.88	57.96	0.09
G32	19.66	19.57	19.7	19.64	0.07
G33	7.14	6.99	7.02	7.05	0.08
G34	13.44	13.29	13.33	13.35	0.08

APPENDIX: 2 (f) STATISTICAL DATA INTERPRETATION OF THE SOIL SAMPLES COLLECTED FOR POTASSIUM (K)

Potassium (mg/kg)					
Sample/Grid no.	R1	R2	R3	Average	±SD
G1	221	219.2	220.8	220.33	0.987
G2	199.8	200.2	200.6	200.2	0.4
G3	59.8	60	60.6	60.133	0.416
G4	179.5	180.2	180.4	180.03	0.473
G5	240.5	239.3	240.2	240	0.624
G6	39.98	40.22	40.04	40.08	0.125
G7	259.8	260.3	260	260.03	0.252
G8	79.99	80.14	80.02	80.05	0.079
G9	180.06	179.88	180.12	180.02	0.125
G10	59.95	60.15	60.03	60.043	0.101
G11	139.96	140.12	140.05	140.04	0.08
G12	159.89	160.1	159.95	159.98	0.108
G13	99.95	100.05	100	100	0.05
G14	120.06	119.66	120.2	119.97	0.28
G15	140.05	139.98	140.13	140.05	0.075
G16	60.15	59.99	60.02	60.053	0.085
G17	99.99	100.15	100.04	100.06	0.082
G18	100.06	99.95	100.08	100.03	0.07
G19	99.89	100.2	100.05	100.05	0.155
G20	120.04	119.97	120.12	120.04	0.075
G21	140.13	140	140.03	140.05	0.068
G22	520	520.12	520.06	520.06	0.06
G23	700.05	699.98	700.12	700.05	0.07
G24	260.04	260.12	259.89	260.02	0.117
G25	120.04	120.15	120.07	120.09	0.057
G26	100.02	99.96	100.1	100.03	0.07
G27	200.05	200.04	200.02	200.04	0.015
G28	140.06	140.1	139.96	140.04	0.072
G29	240.05	239.89	240.12	240.02	0.118
G30	920.05	920.01	920.03	920.03	0.02
G31	220.05	219.88	220.12	220.02	0.123
G32	280	280.12	279.96	280.03	0.083
G33	59.96	60.04	60	60	0.04
G34	80.04	80	79.95	79.997	0.045

APPENDIX: 2 (g) STATISTICAL DATA INTERPRETATION OF THE SOIL SAMPLES COLLECTED FOR SODIUM (Na)

Sodium (mg/kg)					
Grid/Sample no.	R1	R2	R3	Average	±SD
G1	820	820.05	820.01	820.02	0.0265
G2	420.15	419.99	420.02	420.053	0.085
G3	320.15	320.02	320.1	320.09	0.0656
G4	420.08	420.02	420	420.033	0.0416
G5	200.05	199.96	200	200.003	0.0451
G6	220.12	219.88	220.04	220.013	0.1222
G7	300.04	300.1	300.15	300.097	0.0551
G8	99.85	100.15	99.98	99.9933	0.1504
G9	380.04	379.96	380.08	380.027	0.0611
G10	220.08	219.99	220.15	220.073	0.0802
G11	200.04	199.96	200.15	200.05	0.0954
G12	140.15	140.04	140	140.063	0.0777
G13	300	300.02	300.04	300.02	0.02
G14	200.07	200.01	200.11	200.063	0.0503
G15	200.04	200.01	200.08	200.043	0.0351
G16	100	100.02	100.05	100.023	0.0252
G17	380.08	380.45	380.16	380.23	0.1947
G18	380.05	379.87	380.12	380.013	0.129
G19	240.06	240	240	240.02	0.0346
G20	400.26	400.15	400.05	400.153	0.105
G21	360.05	360.14	360.1	360.097	0.0451
G22	380.08	380.01	380.02	380.037	0.0379
G23	340.14	340.2	340.03	340.123	0.0862
G24	400.08	400.11	400.01	400.067	0.0513
G25	120.05	119.92	120.18	120.05	0.13
G26	220.05	220.01	220.06	220.04	0.0265
G27	959.99	960.05	960.18	960.073	0.0971
G28	320.05	320.15	320.1	320.1	0.05
G29	280.04	280.16	280	280.067	0.0833
G30	1240.53	1238.88	1240.38	1240.15	0.9124
G31	840.06	840.02	840.08	840.053	0.0306
G32	1360.25	1359.85	1360.55	1360.22	0.3512
G33	360.08	360	360.01	360.03	0.0436
G34	100.05	99.98	100.01	100.013	0.0351

APPENDIX: 2 (h) STATISTICAL DATA INTERPRETATION OF THE SOIL SAMPLES COLLECTED FOR EXTRACTABLE CHROMIUM

Extractable Chromium (mg/kg)					
Grid/Sample no.	R1	R2	R3	AVERAGE	±SD
G1	0.060	0.070	0.084	0.071	0.012
G2	0.050	0.072	0.060	0.061	0.011
G3	0.052	0.026	0.044	0.041	0.013
G4	0.076	0.096	0.082	0.085	0.010
G5	0.030	0.042	0.038	0.037	0.006
G6	0.040	0.052	0.048	0.047	0.006
G7	0.070	0.050	0.056	0.059	0.010
G8	0.072	0.060	0.052	0.061	0.010
G9	0.042	0.064	0.050	0.052	0.011
G10	0.012	0.018	0.020	0.017	0.004
G11	0.136	0.154	0.148	0.146	0.009
G12	0.058	0.072	0.064	0.065	0.007
G13	0.208	0.196	0.258	0.221	0.033
G14	0.250	0.144	0.200	0.198	0.053
G15	0.022	0.054	0.046	0.041	0.017
G16	0.080	0.064	0.074	0.073	0.008
G17	0.038	0.058	0.040	0.045	0.011
G18	0.150	0.126	0.116	0.131	0.017
G19	0.220	0.166	0.200	0.195	0.027
G20	0.170	0.230	0.198	0.199	0.030
G21	0.060	0.074	0.084	0.073	0.012
G22	0.040	0.060	0.050	0.050	0.010
G23	0.036	0.024	0.044	0.035	0.010
G24	0.092	0.062	0.072	0.075	0.015
G25	0.046	0.028	0.040	0.038	0.009
G26	0.080	0.092	0.088	0.087	0.006
G27	0.084	0.066	0.080	0.077	0.009
G28	0.040	0.022	0.030	0.031	0.009
G29	0.008	0.014	0.010	0.011	0.003
G30	0.080	0.104	0.090	0.091	0.012
G31	0.068	0.044	0.060	0.057	0.012
G32	0.024	0.042	0.038	0.035	0.009
G33	0.038	0.048	0.042	0.043	0.005
G34	0.056	0.068	0.048	0.057	0.010

APPENDIX: 2 (i) STATISTICAL DATA INTERPRETATION OF THE SOIL SAMPLES COLLECTED FOR EXTRACTABLE COPPER (Cu)

Extractable Copper (mg/kg)					
Grid no.	R1	R2	R3	AVERAGE	±SD
G1	4.080	4.058	4.062	4.067	0.012
G2	7.220	7.180	7.200	7.200	0.020
G3	4.860	4.780	4.820	4.820	0.040
G4	9.180	9.290	9.330	9.267	0.078
G5	22.860	22.890	22.910	22.887	0.025
G6	24.680	24.640	24.660	24.660	0.020
G7	11.190	11.230	11.200	11.207	0.021
G8	7.180	7.210	7.220	7.203	0.021
G9	14.780	14.830	14.800	14.803	0.025
G10	10.590	10.620	10.600	10.603	0.015
G11	5.600	5.580	5.620	5.600	0.020
G12	6.420	6.400	6.440	6.420	0.020
G13	8.200	8.210	8.240	8.217	0.021
G14	14.800	14.800	14.820	14.807	0.012
G15	17.170	17.200	17.240	17.203	0.035
G16	15.800	15.820	15.840	15.820	0.020
G17	20.590	20.620	20.610	20.607	0.015
G18	12.010	11.980	12.020	12.003	0.021
G19	13.620	13.580	13.600	13.600	0.020
G20	15.770	15.810	15.830	15.803	0.031
G21	7.600	7.620	7.600	7.607	0.012
G22	8.610	8.590	8.620	8.607	0.015
G23	4.990	5.000	5.020	5.003	0.015
G24	10.600	10.620	10.600	10.607	0.012
G25	5.830	5.790	5.820	5.813	0.021
G26	9.580	9.610	9.620	9.603	0.021
G27	8.000	8.050	7.990	8.013	0.032
G28	11.180	11.210	11.220	11.203	0.021
G29	6.420	6.390	6.400	6.403	0.015
G30	8.190	8.220	8.200	8.203	0.015
G31	7.600	7.620	7.600	7.607	0.012
G32	5.810	5.790	5.810	5.803	0.012
G33	6.590	6.600	6.600	6.597	0.006
G34	7.620	7.580	7.610	7.603	0.021

APPENDIX: 2(j) STATISTICAL DATA INTERPRETATION OF THE SOIL SAMPLES COLLECTED FOR EXTRACTABLE CADMIUM (Cd)

Extractable Cadmium (mg/kg)					
Grid no.	R1	R2	R3	AVERAGE	±SD
G1	0.022	0.036	0.030	0.029	0.007
G2	0.036	0.044	0.044	0.041	0.005
G3	0.024	0.016	0.012	0.017	0.006
G4	0.028	0.042	0.032	0.034	0.007
G5	0.068	0.084	0.078	0.077	0.008
G6	0.100	0.114	0.104	0.106	0.007
G7	0.016	0.026	0.020	0.021	0.005
G8	0.050	0.064	0.054	0.056	0.007
G9	0.080	0.092	0.104	0.092	0.012
G10	0.040	0.064	0.050	0.051	0.012
G11	0.018	0.028	0.012	0.019	0.008
G12	0.038	0.028	0.044	0.037	0.008
G13	0.044	0.056	0.070	0.057	0.013
G14	0.070	0.082	0.090	0.081	0.010
G15	0.084	0.100	0.090	0.091	0.008
G16	0.054	0.076	0.060	0.063	0.011
G17	0.028	0.040	0.036	0.035	0.006
G18	0.040	0.052	0.048	0.047	0.006
G19	0.020	0.016	0.030	0.022	0.007
G20	0.044	0.030	0.040	0.038	0.007
G21	0.012	0.016	0.022	0.017	0.005
G22	0.038	0.024	0.020	0.027	0.009
G23	0.040	0.060	0.052	0.051	0.010
G24	0.062	0.074	0.080	0.072	0.009
G25	0.032	0.048	0.042	0.041	0.008
G26	0.016	0.034	0.020	0.023	0.009
G27	0.086	0.102	0.092	0.093	0.008
G28	0.036	0.044	0.056	0.045	0.010
G29	0.062	0.052	0.068	0.061	0.008
G30	0.022	0.036	0.032	0.030	0.007
G31	0.020	0.016	0.026	0.021	0.005
G32	0.062	0.076	0.088	0.075	0.013
G33	0.102	0.088	0.120	0.103	0.016
G34	0.080	0.060	0.064	0.068	0.011

**APPENDIX: 2 (k) STATISTICAL DATA INTERPRETATION OF THE SOIL
SAMPLES COLLECTED FOR EXTRACTABLE ZINC**

Extractable Zinc (mg/kg)					
Sample/Grid no.	R1	R2	R3	AVERAGE	±SD
G1	5.600	5.590	5.600	5.597	0.006
G2	4.040	4.080	4.040	4.053	0.023
G3	2.400	3.000	3.800	3.067	0.702
G4	8.950	9.000	9.120	9.023	0.087
G5	6.390	6.420	6.440	6.417	0.025
G6	1.600	1.710	1.590	1.633	0.067
G7	2.620	2.580	2.600	2.600	0.020
G8	5.220	5.180	5.200	5.200	0.020
G9	6.790	6.810	6.840	6.813	0.025
G10	9.970	10.100	10.150	10.073	0.093
G11	3.410	3.390	3.400	3.400	0.010
G12	2.790	2.820	2.800	2.803	0.015
G13	4.200	4.220	4.190	4.203	0.015
G14	4.580	4.620	4.610	4.603	0.021
G15	3.990	4.120	4.010	4.040	0.070
G16	3.790	3.820	3.800	3.803	0.015
G17	6.560	6.600	6.640	6.600	0.040
G18	5.580	5.620	5.600	5.600	0.020
G19	9.170	9.200	9.240	9.203	0.035
G20	10.230	9.980	10.120	10.110	0.125
G21	8.380	8.420	8.400	8.400	0.020
G22	7.210	7.180	7.240	7.210	0.030
G23	5.820	5.780	5.800	5.800	0.020
G24	6.210	6.190	6.230	6.210	0.020
G25	7.120	6.980	7.100	7.067	0.076
G26	3.780	3.800	3.820	3.800	0.020
G27	5.240	5.200	5.200	5.213	0.023
G28	6.950	7.120	7.040	7.037	0.085
G29	5.620	5.590	5.600	5.603	0.015
G30	3.380	3.420	3.400	3.400	0.020
G31	4.030	3.980	4.010	4.007	0.025
G32	3.780	3.820	3.800	3.800	0.020
G33	3.420	3.400	3.400	3.407	0.012
G34	4.370	4.400	4.430	4.400	0.030

**APPENDIX: 2 (I) STATISTICAL DATA INTERPRETATION OF THE SOIL
SAMPLES COLLECTED FOR EXTRACTABLE IRON (Fe mg/kg)**

Extractable Iron (mg/kg)					
Sample/Grid no.	R1	R2	R3	AVERAGE	±SD
G1	16.800	16.790	16.820	16.803	0.015
G2	21.250	21.190	21.220	21.220	0.030
G3	22.850	22.790	22.810	22.817	0.031
G4	23.650	23.580	23.600	23.610	0.036
G5	25.820	25.790	25.800	25.803	0.015
G6	36.620	36.650	36.610	36.627	0.021
G7	19.640	19.620	19.610	19.623	0.015
G8	15.210	15.190	15.240	15.213	0.025
G9	26.620	26.600	26.630	26.617	0.015
G10	44.820	44.790	44.800	44.803	0.015
G11	37.180	37.240	37.210	37.210	0.030
G12	20.780	20.820	20.800	20.800	0.020
G13	23.200	23.200	23.190	23.197	0.006
G14	19.780	19.820	19.800	19.800	0.020
G15	24.850	24.870	24.880	24.867	0.015
G16	37.260	37.270	37.280	37.270	0.010
G17	41.610	41.580	41.620	41.603	0.021
G18	20.860	20.890	20.850	20.867	0.021
G19	24.580	24.600	24.620	24.600	0.020
G20	34.620	34.600	34.620	34.613	0.012
G21	11.210	11.240	11.200	11.217	0.021
G22	9.900	9.858	9.841	9.866	0.030
G23	7.610	7.620	7.620	7.617	0.006
G24	5.820	5.800	5.800	5.807	0.012
G25	11.630	11.610	11.630	11.623	0.012
G26	19.270	19.250	19.280	19.267	0.015
G27	16.480	16.440	16.480	16.467	0.023
G28	15.820	15.800	15.840	15.820	0.020
G29	13.210	13.190	13.200	13.200	0.010
G30	11.800	11.800	11.820	11.807	0.012
G31	21.480	21.460	21.440	21.460	0.020
G32	26.380	26.410	26.430	26.407	0.025
G33	24.130	24.120	24.150	24.133	0.015
G34	28.710	28.660	28.680	28.683	0.025

**APPENDIX: 2 (m) STATISTICAL DATA INTERPRETATION OF THE SOIL
SAMPLES COLLECTED FOR TOTAL CHROMIUM (Cr mg/kg)**

Total Chromium (mg/kg)					
Sample/Grid no.	R1	R2	R3	AVERAGE	±SD
G1	14.200	14.550	14.320	14.357	0.178
G2	26.050	26.850	27.350	26.750	0.656
G3	30.900	31.060	30.970	30.977	0.080
G4	24.500	25.150	26.050	25.233	0.778
G5	9.990	9.920	10.050	9.987	0.065
G6	44.890	46.200	45.920	45.670	0.690
G7	32.250	33.100	32.000	32.450	0.577
G8	22.860	23.650	23.850	23.453	0.523
G9	24.220	24.450	24.620	24.430	0.201
G10	45.540	45.700	45.610	45.617	0.080
G11	34.480	34.550	34.500	34.510	0.036
G12	19.310	19.420	19.350	19.360	0.056
G13	170.200	170.150	170.080	170.143	0.060
G14	24.500	24.550	24.610	24.553	0.055
G15	19.120	19.080	18.950	19.050	0.089
G16	31.330	31.150	31.250	31.243	0.090
G17	64.360	64.410	64.300	64.357	0.055
G18	27.840	27.880	27.860	27.860	0.020
G19	15.650	15.680	15.700	15.677	0.025
G20	14.320	14.150	14.300	14.257	0.093
G21	39.150	39.220	39.280	39.217	0.065
G22	643.850	643.920	644.050	643.940	0.101
G23	691.280	691.050	691.150	691.160	0.115
G24	137.520	137.400	137.460	137.460	0.060
G25	77.210	76.980	77.130	77.107	0.117
G26	62.580	62.520	62.550	62.550	0.030
G27	21.830	21.850	21.880	21.853	0.025
G28	50.640	50.690	50.710	50.680	0.036
G29	0.000	0.000	0.000	0.000	0.000
G30	950.650	950.720	950.690	950.687	0.035
G31	673.610	673.590	673.540	673.580	0.036
G32	562.350	562.180	562.240	562.257	0.086
G33	536.720	536.650	536.680	536.683	0.035
G34	26.280	26.200	26.250	26.243	0.040

**APPENDIX: 2(n) STATISTICAL DATA INTERPRETATION OF THE SOIL
SAMPLES COLLECTED FOR TOTAL COPPER (Cu mg/kg)**

Sample/Grid no.	R1	R2	R3	AVERAGE	±SD
G1	12.390	12.450	12.420	12.420	0.030
G2	19.850	19.900	19.830	19.860	0.036
G3	24.600	24.630	24.720	24.650	0.062
G4	20.140	20.080	20.050	20.090	0.046
G5	47.940	48.100	47.900	47.980	0.106
G6	63.820	63.800	63.920	63.847	0.064
G7	46.750	46.680	46.700	46.710	0.036
G8	24.360	24.330	24.400	24.363	0.035
G9	32.150	32.080	32.160	32.130	0.044
G10	32.350	32.270	32.300	32.307	0.040
G11	17.620	17.520	17.580	17.573	0.050
G12	24.350	24.420	24.300	24.357	0.060
G13	30.160	30.170	30.190	30.173	0.015
G14	35.650	35.580	35.680	35.637	0.051
G15	22.350	22.380	22.410	22.380	0.030
G16	25.810	25.780	25.750	25.780	0.030
G17	45.650	45.580	45.610	45.613	0.035
G18	34.280	34.350	34.300	34.310	0.036
G19	24.580	24.600	24.540	24.573	0.031
G20	18.750	18.690	18.720	18.720	0.030
G21	18.460	18.400	18.420	18.427	0.031
G22	21.080	21.180	21.120	21.127	0.050
G23	19.710	19.620	19.650	19.660	0.046
G24	12.680	12.650	12.650	12.660	0.017
G25	12.440	12.460	12.430	12.443	0.015
G26	19.260	19.200	19.280	19.247	0.042
G27	19.980	20.110	19.900	19.997	0.106
G28	17.520	17.480	17.440	17.480	0.040
G29	15.600	15.680	15.560	15.613	0.061
G30	20.700	20.660	20.620	20.660	0.040
G31	17.880	17.830	17.850	17.853	0.025
G32	22.560	22.500	22.530	22.530	0.030
G33	35.020	34.920	34.900	34.947	0.064
G34	36.060	35.980	36.000	36.013	0.042

**APPENDIX: 2 (o) STATISTICAL DATA INTERPRETATION OF THE SOIL
SAMPLES COLLECTED FOR TOTAL CADMIUM (Cd mg/kg)**

Sample/Grid no.	R1	R2	R3	AVERAGE	±SD
G1	0.590	0.550	0.540	0.560	0.026
G2	0.350	0.370	0.330	0.350	0.020
G3	0.100	0.160	0.130	0.130	0.030
G4	0.300	0.270	0.240	0.270	0.030
G5	1.070	1.080	1.090	1.080	0.010
G6	1.020	1.180	1.130	1.110	0.082
G7	1.020	0.950	1.000	0.990	0.036
G8	0.740	0.810	0.790	0.780	0.036
G9	1.700	1.760	1.740	1.733	0.031
G10	0.980	1.050	1.090	1.040	0.056
G11	0.680	0.660	0.710	0.683	0.025
G12	0.790	0.830	0.880	0.833	0.045
G13	0.830	0.880	0.880	0.863	0.029
G14	1.480	1.550	1.600	1.543	0.060
G15	1.750	1.820	1.720	1.763	0.051
G16	0.750	0.820	0.770	0.780	0.036
G17	1.610	1.640	1.710	1.653	0.051
G18	2.050	1.930	1.960	1.980	0.062
G19	1.550	1.500	1.430	1.493	0.060
G20	1.810	1.900	1.870	1.860	0.046
G21	1.180	1.250	1.200	1.210	0.036
G22	6.390	6.460	6.500	6.450	0.056
G23	2.600	2.700	2.630	2.643	0.051
G24	1.190	1.210	1.260	1.220	0.036
G25	1.300	1.280	1.200	1.260	0.053
G26	1.800	2.500	2.100	2.133	0.351
G27	2.090	2.180	2.100	2.123	0.049
G28	1.790	1.740	1.840	1.790	0.050
G29	3.720	3.900	3.850	3.823	0.093
G30	3.300	3.390	3.460	3.383	0.080
G31	4.010	3.970	3.870	3.950	0.072
G32	6.960	6.570	6.250	6.593	0.356
G33	6.880	6.920	6.730	6.843	0.100
G34	3.240	3.320	3.220	3.260	0.053

Appendix 3(a): ANOVA calculated for pH

ANOVA

Ph

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	12.475	33	.378	264.644	.000
Within Groups	.097	68	.001		
Total	12.572	101			

Appendix 3(b): ANOVA calculated for Electrical Conductivity

ANOVA

EC

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	7.804	33	.236	241.946	.000
Within Groups	.066	68	.001		
Total	7.871	101			

Appendix 3(c): ANOVA calculated for Organic Matter

ANOVA

OM

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	36.399	33	1.103	40.854	.000
Within Groups	1.836	68	.027		
Total	38.235	101			

Appendix 3(d): ANOVA calculated for Organic Matter

ANOVA

OC

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	12.254	33	.371	21.400	.000
Within Groups	1.180	68	.017		
Total	13.434	101			

Appendix 3(e): ANOVA calculated for Phosphorus

ANOVA

P

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	148200.155	33	4490.914	739901.802	.000
Within Groups	.413	68	.006		
Total	148200.567	101			

Appendix 3(f): ANOVA calculated for Potassium

ANOVA

K

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	3319339.950	33	100586.059	1510078.895	.000
Within Groups	4.529	68	.067		
Total	3319344.479	101			

Appendix 3(g): ANOVA calculated for Sodium

ANOVA

Na

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	9185829.540	33	278358.471	8135172.067	.000
Within Groups	2.327	68	.034		
Total	9185831.866	101			

Appendix 3(h): ANOVA calculated for Extractable Cr

ANOVA

Cr E

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.294	33	.009	34.431	.000
Within Groups	.018	68	.000		
Total	.312	101			

Appendix 3(i): ANOVA calculated for Extractable Cu

ANOVA

Cu E

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	2692.082	33	81.578	137282.746	.000
Within Groups	.040	68	.001		
Total	2692.123	101			

Appendix 3(j): ANOVA calculated for Extractable Cd

ANOVA

CdE

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.070	33	.002	26.623	.000
Within Groups	.005	68	.000		
Total	.076	101			

Appendix 3(k): ANOVA calculated for Extractable Fe

ANOVA

Fe E

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	9137.331	33	276.889	682734.023	.000
Within Groups	.028	68	.000		
Total	9137.358	101			

Appendix 3(l): ANOVA calculated for Extractable Cu

ANOVA

Zn E

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	472.053	33	14.305	867.824	.000
Within Groups	1.121	68	.016		
Total	473.174	101			

Appendix 3(m): ANOVA calculated for Total Cr

ANOVA

Cr T

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	6443123.438	33	195246.165	2876451.045	.000
Within Groups	4.616	68	.068		
Total	6443128.054	101			

Appendix 3(n): ANOVA calculated for Total Cu

ANOVA

Cu T

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	13258.974	33	401.787	174690.040	.000
Within Groups	.156	68	.002		
Total	13259.130	101			

Appendix 3(o): ANOVA calculated for Total Cd

ANOVA

Cd T

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	300.659	33	9.111	914.855	.000
Within Groups	.677	68	.010		
Total	301.336	101			

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