MONITORING OF HEAVY METALS IN SOIL SURROUNDINGS SOLIDWASTE DUMPSITES

By

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(2010-NUST-MSPhD-Env Sci-16)

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It is certified that the contents and form of the thesis entitled

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Submitted by

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have been found satisfactory for the requirements of the degree.

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This thesis is dedicated to my beloved parents and family

For their endless affection, support and encouragement

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Qurat ul ain Zahoor

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Abbreviations

MSW	Municipal solid waste
Cr	Chromium
Mn	Manganese
Zn	Zinc
Cd	Cadmium
Fe	Iron
AAS	Atomic Absorption Spectroscopy
XRF	X-ray Fluorescent Spectroscopy
Mg/kg	Milligram per kilogram
TOC	Total organic carbon
TN	Total Nitrogen
EC	Electrical Conductivity

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Abstract

The study aimed at the monitoring of heavy metals in soil surroundings solid waste dumpsites including I-14 dumpsite, Bhatta dumpsite and NUST. Soil samples were collected at three different depths i.e. (1-10 cm, 10-30 cm, 30-50 cm) from each solid waste dumpsite down the slope. The samples were analyzed for presence and concentration of Cd, Fe, Mn, Cr and Zn by using XRF and atomic absorption spectroscopy. Results showed that the accumulation pattern for the heavy metals in the soil profile follows the order Fe>Cr>Zn>Mn>Cd. The mean concentrations of Iron in surface soils in all three dump sites was 9.38 % while in 2nd depth 9.56 % and in 3rd depth the 9.48 %. While the mean concentration of Mn in surface soils were lies in 7.5 to 14.1 mg/kg while in 2nd Depth were in the range of 8 to 12.4 mg/kg and in 3rd Depth the values were lies 8.1 to 10.8 mg/kg. The mean values of Cd in all the dump sites and reference soil were in the range of 1.7 to 2.5 mg/kg while 2nd depth Cd values were in the range of 1.6 to 2.6 mg/kg and in 3rd depth 1.7 to 3.3 mg/kg. Similarly in surface soil Zn values were 115 to 242.7 mg/kg while in 2nd depth 104.9 to 210.5mg/kg and in 3rd depth 99.1 to 299 mg/kg were obtained and the mean concentrations of Cr in surface soils in all three dump sites were 72.2 to 132.8 mg/kg while in 2nd depth 45.3 to 134 mg/kg and in 3rd depth the values were 40 to 178.5 mg/kg. The concentrations of heavy metals found in the sites were below the threshold limits defined by USEPA (2001). While the levels found in these dumpsites were higher than the reference soil levels. Higher accumulations of these heavy metals were obtained in surface soil and within the depth concentration of heavy metals were

decreased. Statistically, the examined metals showed non-linear correlation with soil physicochemical properties which is suggestive that these metals arise from anthropogenic activities and may be the other parameters like hydrology and porosity are involved.

Chapter1

1.0 INTRODUCTION

1.1 Background

Municipal solid waste normally termed as “garbage”, “trash” or “refuse” is an inevitable byproduct of human activity. Solid waste includes domestic waste, chemical waste, hospital waste, industrial waste etc. Population growth and economic development lead to enormous amounts of solid waste generation by the dwellers of the urban areas. This waste is disposed off through the three basic methods of garbage disposal i.e. dumping, burning and burial, used since ancient times (Karishnamurti and Naidu, 2003). Unsustainable anthropogenic activities result in environmental pollution and substantial public health problems. Land pollution is one of the major forms of environmental catastrophe our world is facing today.

In developing countries open dumpsites are very common due to the low budget availability for waste disposal and non-availability of trained manpower. Open dumping of municipal waste is a frequent disposal method in Pakistan which causes adverse impacts like storm water pollution, leachate percolation, soil contamination and ground water pollution. The contamination of soil by heavy metals can cause adverse effects on human health, animals and soil productivity. Metal ions from the solid waste persist in soil and pose a serious threat to the environment which could be long lasting and this is a major concern of study due to the increasing level of toxic metal in soil. The existence of several heavy metals such as Mn, As, Cr, Cd, Ni, Zn, Co, Cu, and Fe in municipal solid waste dumpsites has been reported by several researchers (Amusan et al., 2005; Esakku et al., 2003; Ogundiran and Osibanjo, 2008; Smith, 2009). The movement, bio-availability and the consistent toxicity of a trace element in the soil is based on its chemical concentration in the soil solution, the nature of its association with other soluble ionic species and the soil's ability to release the trace element from the solid phase (Namurti and Naidu, 2003). Significant amounts of hospital waste, domestic waste, hazardous industrial wastes which are known to be sources of metals that are harmful in nature (Alloway and Ayres 1997, Pasquini and Alexander 2004, Woodbury, 2005). Household waste may also contain toxic materials coming from batteries, insect sprays, nail polish, cleaners, plastics, polyethylene or polyvinyl chloride (PVC) made bottles and other assorted products.

The estimated residence time of such heavy metals ranges between 1000-3000 years in temperate zones (Bowen, 1977). This means that these metals continue to disseminate for very long period of time in the soil in high concentrations. Presences of these pollutants degrade the environment and increased contents upset the environmental standards in and around the dumpsites. Therefore soil threshold limits have been identified particularly for the heavy metal content in dumpsites to recommend appropriate curative methods (Biswas et al., 2010).

1.2 Significance in Pakistan

Pakistan lacks proper sanitary landfill sites. Solid waste is managed improperly and polluting our natural resources (water, air and soil). The open dumping of solid waste has become a critical problem because the leachate produced by the waste can pose serious impacts on ground water resources. The heavy metal present in solid waste exerts a lethal impact on fauna and flora of lakes and streams (Eddy, 2004). Heavy metals are not biodegradable and have a toxic effect on living organisms at certain level of concentration. It also may cause blood and bone disorders, kidney damage and decreased mental capacity and neurological damage in human beings (NIEHS, 2004).

In Pakistan 65,000 tons of waste is generated daily while in Islamabad/Rawalpindi it amounts to 1600 tons per day. This study was designed to analyze the soil profile at Bhatta, I-14 and H-12 NUST dumpsites for the presence of heavy metals in response to waste dumping. It will help in quantifying the information on the environmental effect of these metals and suggested the techniques that control the heavy metal and will help in designing threshold limits of heavy metals in Pakistan. So this study can be used as a baseline study for the future work. For the monitoring of heavy metals, different techniques could be use but for the easy access in laboratory of IESE, XRF technique and Atomic absorption were used for the qualitative and quantitative analysis.

1.3 Objectives

The objective of the research is to

- Identify the sources of Heavy metals from the composition of waste.
- Quantify the distributions of heavy metals in soil near a dump site and compare their concentration.

Chapter 2

2.0 REVIEW OF LITERATURE

2.1 Municipal Solid Waste

Municipal solid waste is waste from family residential flats, hotels waste, institutional and commercial areas, demolition waste, street refuse, dead animals, and so on (Bishop, 2000). Due to the improper planning management and lack of finance, handling facilities are poor in developing and under developing countries which results into disposal of waste; it goes untreated in environment (Anikwe, 2000). Therefore, storage of waste and least exposure to human and environment has been fundamental rule of conventional landfills.

2.1.1 Disposal of the Solid Waste

Methods to dispose of the waste include sanitary land filling, incineration, barging it out into the sea, composting by bacterial agency (Garg, 1998). Landfills have been widely used for disposal of waste worldwide, because of availability of land. Developing countries consider it trustworthy and economical method.

1. Sanitary landfill, is more proper way with safety and care for the final dumping of solid waste without any threat to human and natural resources like ground water (Veslined, 2002).
2. Open dump "Open settlement of solid waste", where the solid waste is collected on the earth surface improperly without any treatment or to dispose off on landfill.

2.1.3 Solid Waste Leachate

Contaminants are leached from the solid waste, as water percolates through the landfill, a complex sequence of physical, chemical, and biological arbitrated actions occurs through solid waste that give rise to leachate (Vesilind, 2002).

Soil is a principal medium of solid waste storage as huge amount of waste from the different sources like industry, agriculture and domestic sources leach down into the soil (Nyles and Ray, 1999). Large amount of the toxic substance from the dump sites leach down into the soil and water ways during the rain, which ultimately contaminates the soil and ground water. Dumpsite soils have been reported to have high organic matter (Anikwe, 2000) due to this leachate.

In a study the trace metal contents in fine portions of municipal solid waste (MSW) taken from different depth levels of Perungudi dumping ground (PDG), near Chennai was analyzed. Heavy metal concentrations of MSW and leachate samples were differentiated with the water extracts arranged after the MSW fraction. The levels of As, Hg, Cr, Cd, Cu, Pb, Ni and Zn were determined and establish to be in mg/kg concentrations in MSW while in µg/L in leachates and water extracts. On the other hand, all values are in the threshold limits of United States Environmental Protection Agency (USEPA) standards.

2.1.4 Reasons upsetting leachate quality

Leachate feature is extremely variable. The difference in leachate quality can be ascribed to numerous interacting factors such as

- Densityof waste
- Depth and composition of waste
- Moisture and oxygen availability
- Landfill design and its operation
- Waste time period

The movement, presence and the corresponding toxicity of heavy metals in the soil based on different factors such as its nature of association with other ionic species and chemical level. (McBean *et al*., 1995, FCSHWM., 1998).

2.2 Heavy Metals in Waste

Heavy metal pollution has gained attention due to its toxic nature and can be mobile through the biochemical processes. These toxic chemicals affect the water supplies, damage food chains, ecosystems and human health. Heavy metals have a long persistence time and therefore enter food chain through plants and animals and they are considered as bioaccamulate in soil (Dosumu, 2003). Accumulation of some heavy metal ions in soil showed its relative immobility in the environment and that geochemical dispersion is not effective (Pinheiro et al., 1999).

2.2.1 Sources and Impacts of Heavy Metals

Leachate is the key source of heavy Metal pollution in soil and water. Environmental pollution has increased from the last few decades by heavy metals and chemicals due to the municipal solid waste, insecticides, pesticides, painting and coatings, industrial effluents, fertilizer and industrial chemicals (Sial *et al.*, 2006). Heavy metal contamination poses a severe problem for human health and for life in general. Table 2.1 is presents different heavy metals, their sources and impact on the human and environmental health.

Table 2.1 Sources and impacts of heavy metals in Municipal Solid Waste

Heavy metals	Sources	Impacts
Cadmium	Galvanized pipes, metal refineries, batteries and paints	Kidney damage, Bone defects in human and animals
Chromium	Steel and pulp mills, rubber, paper	Allergic dermatitis
Lead	Batteries, alloys, cebels, paints	Damage to nervous and reproductive system
Mercury	Industrial waste, emission from volcanoes	Damage brain and CNS
Antimony	Batteries, ceramics and glass	Nausea, vomiting and diaarhea
Copper	Corrosion of household plumbing system, natural deposits	Gastrointestinal distress , Anemia
Zinc	Galvanized metal, scraps, expired cosmetics and medicine and old building material.	Stomach cramps, skin irritations, vomiting nausea, anemia, damage pancreas and respiratory disorders
Iron	Metallic scraps co-deposited with domestic waste	Conjunctivitis, choroiditis and retinitis, chronic inhalation, lung and liver cancer, nausea, vomiting intestinal damage and diabetes
Manganese	Municipal waste water discharge, mining and mineral processing (particularly nickels, emissions from alloy,	Mn-induced anemia, Decrease in red blood cells, haematocinitis and mean cell volume.

	steel and iron production), combustion of fossil fuel and emissions from the combustion of fuel.	

Sources: (Alloway and Ayres, 1997) (Woodbury, 2005)

The discarding of trace metals is a result of several activities like chemical built-up, painting and coating, mining, extractive metallurgy, nuclear and other industries. Those metals employ a deadly influence on animals and vegetation of ponds and rivers. The level of soil contamination via trace metals and base metal ions specific of which were soil micronutrients is exact distressing. It has been detected that the more the city expanse, the lesser is the value of surroundings (Eddy., 2004).

Higher concentrations of heavy metals in soils hinder plant development, nutrient application and biological and metabolic progressions. This also results in chlorosis, damage to root tips, reducedwater and nutrientuptake and damage to enzymes (Baisberg., 1989, Toppi and Gabbrielli, 1999). Heavy metals, like other ecological stressors, too encourage antioxidant enzyme procedures in flora (Lannelli et al., 2002). Thesetoxic ions might remain in soil or leach-down and may pollute groundwater beside withthe soil itself and lastly arrive in the foodchain and basis of health danger in faunas and floras.

Levels of heavy metals in soil were measured in 19 sites near and around the old (MSW) dump site at four directions. It was found that the sites located in the southeast direction from dumpsite had the highest levels of total metals in soils. Of site close to the solid waste dumpsite at Abis contained the highest levels of total metals like Cd, Cu, Ni, Cr and Zn respectively. The concentrations of metals in leaves and roots of tomatoes, carrots and potatoes plants grown at the site close to Abis (MSW) dump site and decreased with increasing distance (Rashad and Shalaby, 2007).

In 2009, a research was conducted to know the impacts of municipal solid waste disposal in Ado-Ekiti metropolis, Ekiti-State, Nigeria soil samples from four waste dump sites (three samples from each location at 10 meters interval) and plant sample (root and leave) from Igbaletere dump site were investigated for heavy metals such as Cu, Mn, Fe, Cr, Pb, Co, Zn and Ni. High concentrations of Cu, Mn, Fe, Pb, and Zn were found in the soil samples collected at the centre of the dump sites. While the lesser concentration was gained in the soil samples taken at distance 20m away from the center of dumpsites. In the plant sample, concentration of Fe was highest in the root, whereas amount of Mn was highest in leaf (Adefemi, 2009). Concentration of all heavy metals in soil and plants are given in Table 2.2.

Table 2.2: Concentration of heavy metals in soil and plants

Heavy metals	Soil samples (center of dump site)	Soil samples (20 m away from dumpsite)	Plant samples (leaf and root)
Copper	232 mg/g	-	-
Manganese	292 mg/g	64 mg/g	109.7 mg/g
Iron	159 mg/g	110 mg/g	341.9 mg/g
Lead	205 mg/g	213 mg/g	-
Zinc	-	67 mg/g	-
Nickel	-	-	-

In 2010, a study reported levels of Cd, Hg, Pb, Cr, Fe, Co, Ni, Cu, Zn, Mo and As in soil and leaves from refuse dumpsites and background soils in two cities, a municipality and a rural community in Ghana by using a Thermo-Finnigan Element 2 high resolution inductively coupled plasma mass spectrometric (HR-ICP-MS) instrument. Concentration of Cd and Zn were higher as compared to other metals. The waste landfill soil as of the countryside community was smallest contaminated through the metals. Fe and Ni masses in vegetation as of the waste landfill soils in the cities and the city were outside the standard ranges.

(Agyarko *et al*., 2010).

2.2.2 Standards of Heavy metals in Soils

Because of exceeding pollution and resultant health impacts various state agencies have set a permissible limit to stop uncontrolled dumping. Few of them are given in Table 2.3.

Table 2.3 Standards of heavy metals applicable in various countries

Heavy metals	**European Community Limits mg/kg[a]**	**USEPA-FAO Limits mg/kg[b]**	**Indian Limits mg/kg[c]**
Cadmium	1-3	3	3-6
Manganese	NA	2000	NA
Nickel	30-75	50	75-150
Cobalt	NA	NA	NA
Zinc	150-300	300	300-600
Iron	NA	5000	NA
Lead	50-300	100	250-500
Chromium	100	100	NA

Sources: a= European community commission (1986), b= Ewers., 1991, Pendias and Pendias., (1992), c=Awashti., 2000, Mushtaq and Khan., 2010

2.3 Health Effects of Dumpsite

A study was conducted by Kimani (2010) on the Dandora waste dump site in Nairobi Kinya had shown higher concentrations of heavy metals, in soil samples collected from the site. A medical checkup of the children and adults having houses and schools adjacent to the waste dump site showed a higher occurrence of diseases which are connected by increased exposure to these heavy metal contaminants. Approximately 50% ratio of children who lived in schools adjacent to dumpsite had respiratory problems and higher levels of blood equal or higher than international threshold limit (10ug/dl of blood), whereas 30% had size and staining abnormalities of their red blood cells, approving higher introduction to heavy metal toxicity.

Results of the study evaluated that severe risks are associated with municipal waste dumps. Evaluation and monitoring of pollutants in different parts of the ecosystem has become a significant job in inhibiting danger to wildlife and public health on public health (Begun et al., 2009).

2.3.1 Uses of Dumpsites

Dumpsites are known to be rich in soil nutrients for plant growth and development because decayed and composted wastes enhances soil fertility (Ogunyemi *et al.*, 2003). Dumpsitesoils are similarly recycled to stop polythene bags and plant sales outlet pots to produce seedlings in plant nurseries. Dumpsites, in record of the third world states contain of a greater percentage (50–

90%) of biological constituents hence interpreting it proper for vegetal growth (Asomani and Murray, 1999).

2.4 Physico-Chemical Characteristics of Dumpsites

Municipal litters intensification the nitrogen, pH, cation exchange capacity, percentagebase saturationand organic matter of the unloading soils. Moreover, huge amount of waste in soil can raise concentration of heavy metals in soil and ground water which have injurious effects on soils, crop and human health (Nyle and Ray., 1999, Smith et al., 1996, Okoronkwo *et al*., 2006).

Electrical conductivity decreased with increase in soil depth, though not significantly. The highest value was recorded at 20–40 cm soil depth while soil depths 60–80 cm and 80–100 cm had the lowest values. The trend observed in the soil organic carbon (OC) was similar to that in the EC. The highest value was at the topmost soil layer while about 20% reduction in OC was recorded at the lowest soil layer (Azeez *et al.*, 2011).

Physical and chemical analysis of water and soil samples from three boreholes located near a landfill were carried out to assess the effect of dumpsite on groundwater quality and soil. The parameters determined were dissolved oxygen, iron, nitrate, nitrite, calcium, and heavy metals. The results showed very poor sanitation and damaging effects to health of users. Soil organic matter and organic carbon ranged from 2.44- 4.27% and 1.42- 2.48% respectively. Statistical analyses indicated significant differences at 95% level. Treatment of water before use and landfill redesigning were suggested.

2.4.1 Site Selection for Sampling and Analytical Techniques

Moderate environmental soil and dust analysis techniques are very slow and laborious and consequently there is a need for fast and accurate analytical methods. Extraction tests are generally used to revise the mobility of metals in soils and sediments. The outcome achieved by determining the extractable elements are relying on the extraction process applied. Single and sequential extraction procedure was used for heavy metal determination in contaminated soils and sediments. (Rauret, 1998)

Laboratory-based aqua-regia acid digestion of the soil samples were collected in the part and examined by the atomic absorption spectrophotometer (AAS) analysis established very high pollution, mainly by Pb, As, Cu, and Zn. Similar samples were investigated by portable X-ray fluorescence radioisotope and miniature tube powered (XRF, NITON instruments) and their performance was evaluated. Generally, the portable XRF technique showed outstanding correlation with the laboratory-based AAS method. (Radu and Diamond, 2009)

In 2011, a study was carried out to assess the heavy metals around the two municipal solid waste dump sites. The concentrations of heavy metals were measured at different distances and direction from the two dump sites in Alexandria for the ambient air and soil. The study indicated a steady decrease in the concentrations of total Cd, Cu, Ni, Cr and Zn in the ambient air at Abis area with distance from the municipal solid waste dumpsite. It was found that the soil of the site close to the dump site at Abis contained the highest concentrations of total metals (Ahmed *et* al., 2011). My study was based on the comparison between the three dumpsites in which one dumpsite had not been in use for several years.

A Research was carried out to extract soil solution samples from paddy soil near mine tailing dumps in an abandoned mine in Korea. Trace metals in the soil solution and soil solid (As, Cd, Cr, Cu, Ni, Pb and Zn) were analyzed, along with the mineralogical composition of the soil, using XRD. Cadmium, Pb and Zn concentrations go beyond the interference value of the Dutch standards, which requires remedial action. Arsenic, Ni and Cr were less than the values, signifying tiny or no contamination for these metals. Geochemical equilibrium modelling using PHREEQC shows the occurrence of solubility controlling solid phases for Cd and Pb, but Zn and Cu seem to be restricted by adsorption/desorption processes. (Lee, 2006)

2.4.2 Heavy Metal in Polluted Soil

A study was aimed to determine soil pollution in downstream area of the landfill, in relation to variations in soil chemical characteristics and heavy metal levels. The landfill was located in the southwest of Babol, North of Iran. Soil samples were taken at three depths (0-30, 30-60, 60-90 cm) and analyzed by atomic absorption spectrophotometer for Cd, Ni, Pb, Fe and Mn concentrations. Although in the soil vadose zone, heavy metals were found to be in their typical and normal ranges and within the background concentrations, by comparison their concentrations were higher in wet season. Variation in the concentration with depth suggests movement of the heavy metals either from the leachate or from naturally present sources of minerals in the soil (Marzieh, S *et al.,* 2010).

In 2010 a study was carried to analyze the impact of heavy metals concentrations in soils at Dump sites by collecting soil samples placed in Ikere and Ado Ekiti metropolis, South Western Nigeria. The soil samples were examined for concentrations of Cd, Co, Cr, Cu, Fe, Pb, Mn, Ni, Sn and Zn. Control soil samples were obtained at 200 m away from the last sampling point on each dump site down the slope and were also detected for the existence of these heavy metals. The results of the analyses show a significant difference in the concentration of these metals from the center of every dumpsite at interval of 10 – 70 m down the slope ($p < 0.05$). The dumpsites were found to comprise substantial quantity of toxic heavy metals. (Awokunmi *et al.,* 2010)

A research reported in 2011 in which Soil and groundwater samples from 7 municipal refuse dumps and a green uncontaminated control site in Ibadan, Nigeria were examined for Cadmium (Cd), Cobalt (Co), Lead (Pb), Chromium (Cr) and Nickel (Ni). Soil samples were took in triplicates at 3 different depths. Although Water samples were attained from dug wells at the dump sites. The values of Cd, Co, Pb, Ni and Cr in the dumpsites soil samples ranged from 0.75-16.30; 3.45-21.00; 45.00-624.50; 4.35-49.80 and 13.15-75.55mg/kg, individually.

Indication of pollution of these soils by Cd, Pb, Ni and Cr was apparent when compared to the control site. Ni was less than the threshold limit in all control samples but Pb and Cd were low than 0.05 and 0.002mg/kg, respectively .the concentrations measured were high when compared to the threshold limits sets for soils in some countries (Adelekan and Alawode, 2011).

2.4.3 Management System and its Implication

Azeez and coworkers (2011) studied soil distribution of heavy metals caused by municipal solid waste (MSW) deposition and its implications for MSW management system in emerging cities was investigated in Abeokuta, Nigeria. Results specified that the highest concentrations of Cu, Cr, Mn, and Zn were observed at 0-40 cm while Pb, Fe, and Ni collected at depths below 40 cm. Soils affected by waste deposits from market and auto-mechanic sites showed high levels of Fe, Cr, Pb, Cu, Mn, and Zn. The addition of heavy metals in the soils was maybe due to the formation of metal-organo-complexes. Hence, source separation of MSW with appropriate managing arrangements are suggested to recover the indiscriminate surface dumping experienced at present, while the use of wastes affected sites for cultivation should be dejected.

2.4.4 Effect of Unregulated Dumping Sites and Disposal Practices

Ukpebor in 2003 revealed the study about the heavy metals concentrations in sub- soil of refuse dumpsites. In this study, the concentration of heavy metals in tops soil samples from 3 refuse dumpsites in Benin city were determined. Results depicted the levels of metals in the 3 different places were less than the standard levels for commercial and industrial application, it can be utilized (Cd 30 m g/kg, Cr 800 mg/kg, Cu 500 mg/kg, Pb 1000 mg/kg, Ni 500 mg/kg). Cadmium content found in the study rendered the sites unsuitable for agriculture and resident applications heat even reclaimed, unless a level of remediation is administered to the soil. Enhanced concentrations of the heavy metals were observed for the soil samples from the dumpsites than soil samples taken 50 m from the dumpsites.

2.4.5 Use of GIS in Managing Dumpsites

Mufide and coworkers in 2009 distinguished the sample of leachate and soil with heavy metal pollution and distribution which were obtained from the unregulated dumping site area in Eskisehir/Turkey. These samples were examined for pH, cadmium, copper, iron, lead, nickel and zinc in spring, summer and autumn seasons. The sampling points were marked on an air photograph by using GeoMedia Professional 6.0 software. The results showed that levels of heavy metals were higher beside the agriculture areas of dumpsite. When physical-chemical study and conclusions obtained from GIS are calculated with organized, it was concluded that the EskiOehir dumping site will bring harm and threaten the environment and ecology of area in short and long periods so this site should be instantly transformed and rehabilitated.

The concentrations of trace metals were studied in soil profiles of eight municipal waste dump sites in Warri metropolis. The results designate that applications of trace metals diverse extensively amongst the different dumpsites and lessened with depths in a deliberate soil outline. The absorptions of metals established in these locations was under the Canadian threshold standards for land-living for agronomic, housing and commercial/industrial commitments excluding for the cadmium intensities in particular places that surpassed standard limits for agronomic and domestic.

Waste disposal applies have created indirect and yet stark environmental contamination and ecological deterioration in unindustrialized countries. In 2011, the work was started to calculate the Geochemical valuation of the effect of Aladimma dumpsite on the adjacent soil and surface groundwater. The level of parameters was higher in soil due to affinity between organic matter of soils and elements than in ground water. While the concentrations of heavy metals differ as shown: Fe > Zn > Cu > Mn > Cr > Pb > As. This may be because of high precipitation and subsequent weathering and leaching of metallic things from the dumpsite into the underground water (Amadi and Akobundu, 2011).

Chapter 3

3.0 METHODOLOGY

3.1 Study Area

The study carried out in Dump sites located in Islamabad and Rawalpindi are given below

1. I-14 Islamabad (S#1)
2. Bhatta, Rawalpindi (S#2)
3. NUST Islamabad (S#3)

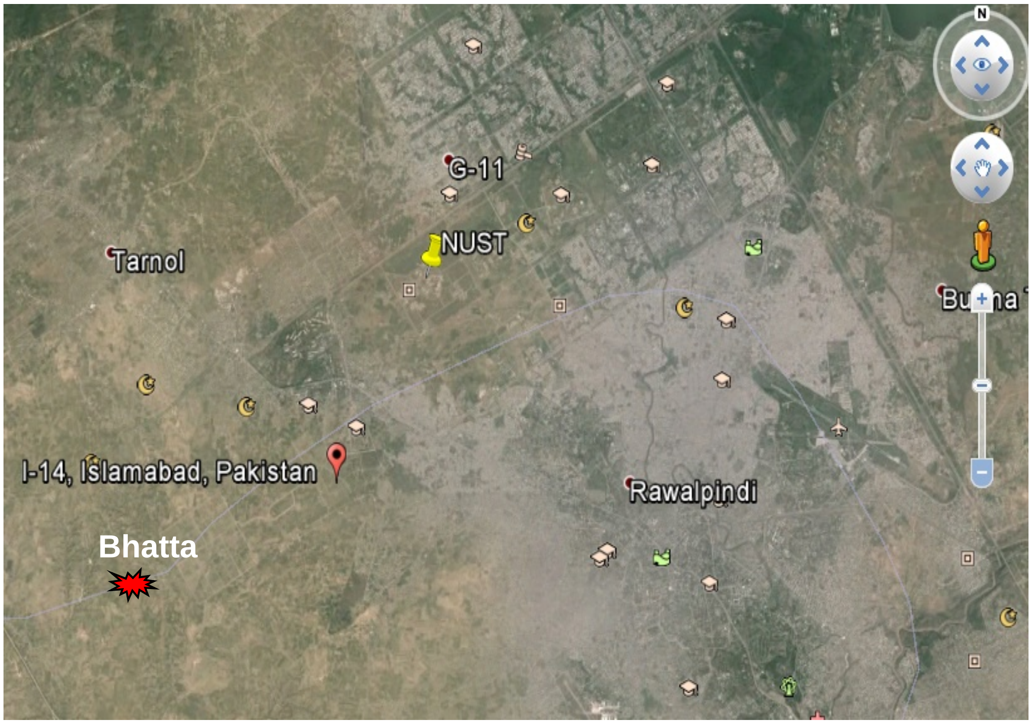

Figure 3.1 Sampling points shown on Google map for Islamabad and Rawalpindi

3.1.1 I-14 dump site

I-14 is taken care of by CDA Islamabad. Islamabad generates over 800 tons garbage daily. As per the agreement, CDA transports the garbage up to the green-belt between sectors I-14 and I-15. This land is not developed it is certainly not a healthy practice nor advisable to dump garbage like that over there.

Figure 3.2 Map location of sampling points in I-14 dump site

3.1.2 Bhatta dump Site

Bhatta is old dumpsite which is used by the Rawalpindi Cantonment Board development (RCBD) and Chaklala Cantonment Board (CCB). The collection vehicles from all over the Rawalpindi and Chaklala Cantonment Board Area transfer waste to Bhatta Chowk situated near Hajji Camp Rawalpindi. The total area of the dump site is 500 canals without a boundary wall. Almost 300 tons/day of solid waste from different wards of Rawalpindi cantonment board administered area and is carried to the dump site. Moreover the Hospital waste is also dumped with the Municipal solid waste, making the condition even worse.

Figure 3.3 Map location of sampling points in of Bhatta dump site (Rawalpindi)

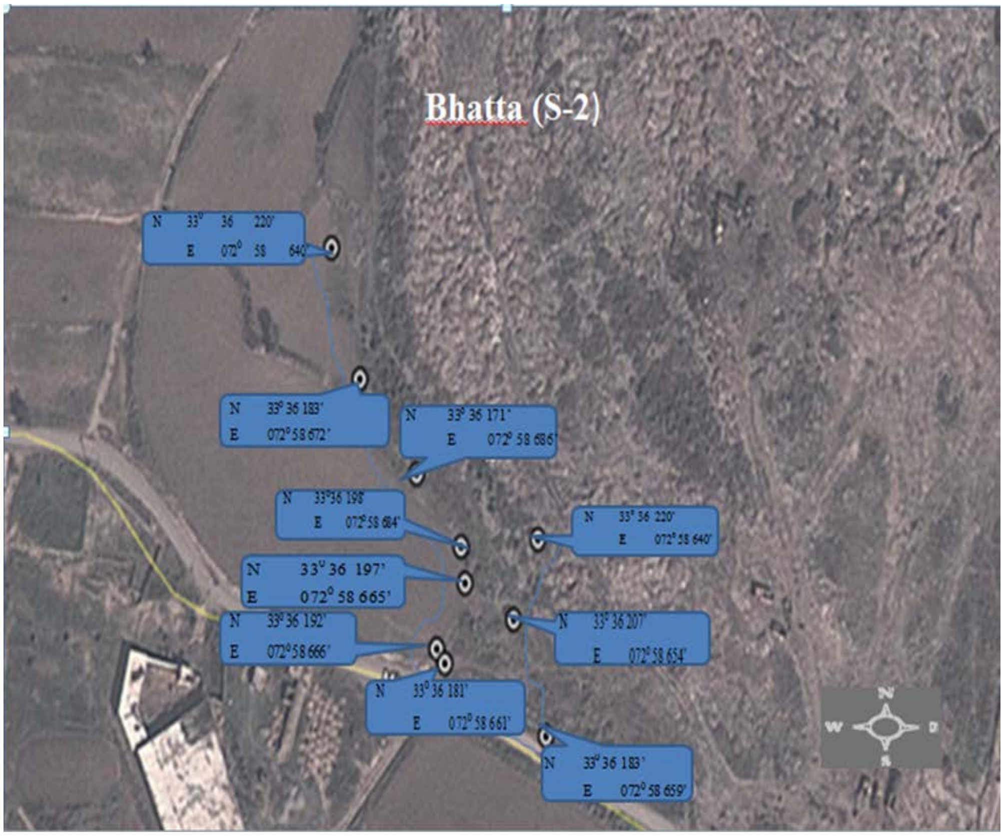

Figure 3.4 Scavenging at Bhatta dump site

3.1.3 NUST, H-12 Dumping site

H-12 is an abandoned dumpsite shifted by CDA to I-14 and it was used to be active since 1998 to 2003. Total 3 samples were taken from this dumpsite at 3 different depths. Soil near NUST café where plants are grown was taken as reference soil of the control site and only one sample was taken from this site.

Figure 3.5 Old Dumping of Islamabad located in H-12 (now NUST)

3.2 Sampling method

The sampling sites were selected based upon topography of dumpsite. The soil samples were collected from the sites in the direction of leachate movement depending upon elevation of ground. The sites coordinates were taken with a Global Positioning System (GPS).

3.3 Sample collection and preparation

Ten soil samples were taken from each dumpsite, three from NUST H-12 and one from natural reference soil at three different depths of 0–10 cm, 10–30 cm and 30–50 cm with auger. The samples were taken randomly from the locations to represent the entire dumpsite. Each sample was placed in a plastic bag, tightly sealed and transported to IESE laboratory where on arrival, analytical procedure was initiated.

Soil samples were air-dried at ambient conditions. After drying, soil was grounded by mortar and pestle, passed through a 2 mm mesh sieve and oven-dried at 120° C for 4h.

Figure 3.6 Soil sampling at Bhatta dumpsite at various depths

3.4 Physical and Chemical analysis of soil samples

Prior to the assessment of heavy metals, chemical properties of the samples were determined at the wastewater and analytical laboratory of IESE NUST.

3.4.1 pH

Soil pH was determined by a glass electrode using a soil to water ratio of 1:1 (Mcleans, 1982). The pH of the soil samples were measured in water by glass electrode (HOACH) method involving 1:1 soil: water mixture using pH meter. Each sample was analyzed thrice for verification. The results were recorded as mean value of the three different depths.

Figure 3.7 PH meter

3.4.2 Electrical conductivity

Electrical conductivity was determined by using a 1:5 soil to water suspension as for pH determination. The suspension was filtered using Whatman

No.42 filter paper in the funnel and the filtrate was transferred to 50 ml bottle and analyzed using conductivity meter (HOACH).

Figure 3.8 Conductivity Meter

3.4.3 Total Organic Carbon and Total Nitrogen

Samples were suspended 1:5 and then filtered to be analyzed for TOC and N. total organic carbon content and total nitrogen was analyzed through TOC analyzer. Results were recorded in triplicate and their average is given in results.

Figure 3.9 TOC Analyzer

3.4.4 Soil texture

3.4.4.1 Sieve Analysis

The procedure for the test is as following:

1. Set the sieves in order so that sieves with largest openings are on the top and gradually reduced size below.

2. Take oven dried soil sample about 300 to 500gmwhich has already been pulverized. Pour entire sample in to set of sieves.

3. Place the sieves set in the sieve shaker and shake for 5 to 10 minutes.

4. Remove the nest of sieves from the sieve shaker and obtain the mass of material retained on each sieve carefully. Compare sum of these mass to the actual mass taken.

3.4.4.2 Hydro meter Analysis

The procedure for the test is as following:

1. Take exactly 50 gm passing No.200 sieve of oven dry well pulverized soil sample and mix it with 125 ml of dispersing agent solution (The solution is prepared by dissolving 40gm of dry dispersing agent in one litter distilled water).

2. Allow the mixer to stand for about one hour. Transfer the soil mixer to the dispersing cup of the mixer. Be sure to wash all the soil from the dish into the mixer cup. If necessary add water until the cup is two thirds full. Mix for about 10 minutes.

3. Transfer all contents of the cup into the 1000 ml cylinder, taking care not to lose any material. Add water to fill the cylinder to 1000 cm^3 mark. Using the palm of the hand over the open end of the cylinder or rubber stopper, turn the cylinder upside down and back for a period of one minute to complete the agitation of the slurry.

4. Take hydrometer readings at the following intervals of time. 1, 2, 4, 8, 15, 30 minutes and 1, 2, 4 hrs along with the temperature readings. After each reading the hydrometer should be removed and placed in the control jar, for the dispersing agent correction. Hydrometer readings will be taken at the top of the meniscus. After 4 hrs of sedimentation, readings can be taken after 24 hours.

3.5 Elemental Analysis

3.5.1 Total elemental analysis by XRF

Qualitative analysis of prepared soil samples for heavy metals was carried out by energy dispersive x-ray fluorescence (XRF) spectrometry (JEOL. JSX-3202-M, Japan). It is used most widely for relatively non-destructive chemical analyses of rocks, minerals, sediments and fluids. From this study, Pellets were made from the 3g of soil and then pressed in Hydraulic press for the elemental analysis of soil composition, the instrument software allowed simultaneous multi-element spectral measurement and qualitative element analysis. Iron was calibrate to find the exact concentration of unknown through XRF by making 5%, 10%, 15% and 20 % pellets of iron sulphate and potassium bromide. The linearity of calibration curve has been give below:

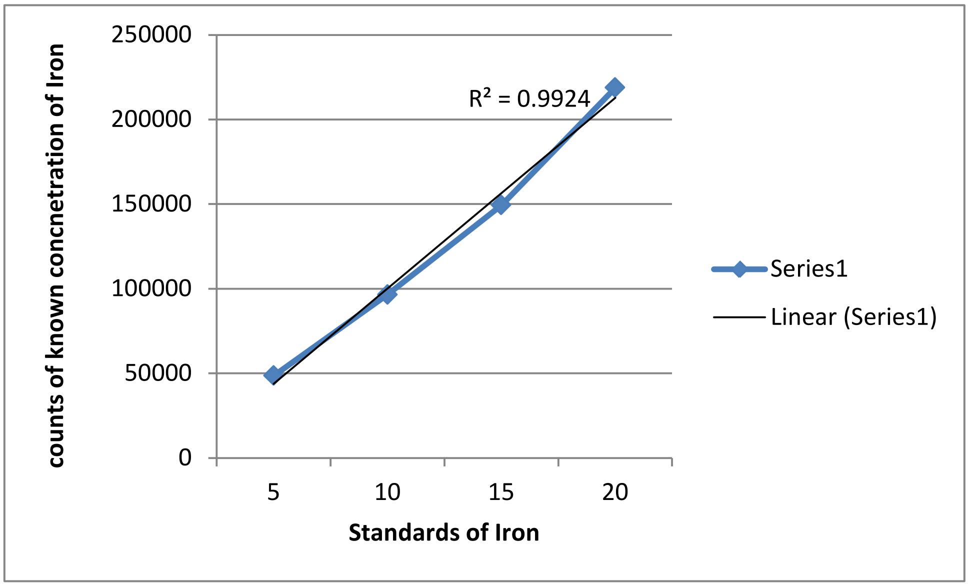

Figure 3.10 Calibration curve of Iron Sulphate

3.6 Quantitative Analysis

3.6.1 Sample preparation

The solution was concentrated on a hot plate till small amount of liquid was left in the beaker. Then, HNO_3 (2+98) mixture was added to the beaker. The beaker content then transferred to 25 ml volumetric flask and filled up to the mark with HNO_3 mixture the prepared sample was transferred to a polyethylene bottle and was analyzed on FAAS. Blank filters were prepared by digesting clean soil samples and the concentrations of analyte metals (Cd, Zn, Cr and Mn) were corrected against the filter blank.

Digested samples were preserved and stored according to the standard procedures at 4^{o}C in refrigerator in order to get the accurate results from the atomic absorption.

3.6.2 Atomic absorption spectroscopy (AAS)

AAS is an analytical procedure for the quantitative determination of chemical elements using the absorption of optical radiation by free atoms in the gaseous state. The quantitative analysis of metals in dumpsite soils were determined by flame atomic absorption spectrometer (Varian AA 290, USA) with air/acetylene burner. Each soil sample was digested by using the digestion reagents: hydrogen peroxide 35%, HCL 37% and nitric acid 65% (Merck, Germany) following similar open acid digestion. 1 g of soil was weighed from the weighing machine and transferred into a beaker to which 60 ml of HCL (1+1) and 10 ml of H_2O_2 were added. The beaker was enclosed with a watch glass and heated on a hot spot at 120^{o}C for 1 hr. After cooling, the solution was separated by using the filter paper (Whatmann 41). Another 40 ml of HCL (1+1) was added to the residual in the beaker and heated for 15 mins for a complete metal extraction. The beaker content was filtered again and filtrate was added to the filtrate of the previous step.

3.7 Statistical analysis

Statistical analysis of data was performed by using Microsoft Excel Analysis Tool Pak and SPSS. Box and whisker plots were used to show whether a distribution is skewed and whether there are possible unusual observations (outliers) in the data set. Box and whisker plots are ideal for comparing distributions because the mid, skewness and all data range are instantly apparent.

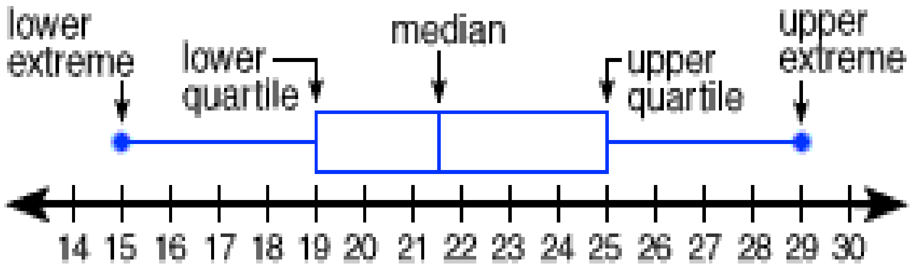

Figure 3.11 Box and Whisker plot

Chapter 4

4.0 RESULTS AND DISCUSSION

The study was carried out with an objective to identify the sources of heavy metals in soil containing solid waste its quantity and distribution in I-14, Bhatta and NUST dump site. Soil samples were collected from the dumpsites for the elemental XRF analysis and atomic absorption spectroscopy. Physio-chemical properties of soil samples were also determined by using standard methods (APHA, 2005). These characteristics include temperature, pH, total organic carbon, total nitrogen, electrical conductivity, magnesium, potassium, nitrogen and calcium. All these properties of soil help to determine the soil aeration, stability, absorbability for the pollutants.

4.1 Sources of Heavy metals in Solid Waste

The sources of heavy metals in solid waste depend on the composition of waste being disposed at dumpsite. It is varied according to the location, season, socioeconomic conditions, collection, sorting and disposal techniques of solid waste. Composition and percentage of solid waste in Eskisehir was 67.06 % of food waste, 5.62%plastics, and 10.07% paper-cardboards. 2.49% glasses, 1.26% metals, 3.86% ashes and 9.64% miscellaneous wastes and about 37% was humidity (Banar et al., 2009). However the composition and percentage of solid waste of study sites are given in Table No.1

Table No. 4.1 Composition and percentage of solid waste in dumpsites

Composition of waste	I-14 (%)	Bhatta (%)	Heavy metals in waste
Bones	1.03	4.8	Ca, Mn and Fe
Glass/ceramics	0.70	4.39	Ni, Pb, Cr, Zn, Cd and Cu
Grass/wood	21.26	8.7	Zn, Mn, K and Cu
Leather/rubber	2.9	4.76	Cr, Cd, Zn, Fe and Mn
Metals	0.96	2.96	Pb, Ni, Ar, Cr, Zn, Cd, Cu and Hg
Pampers	6.2	7.89	Ad, Zn. Au, As, Zn and Cr
Paper	2.70	5.82	Mn, Fe, Cu, Ar and As
Plastic	4.8	4.77	Ag, As, Au, Ba, Br, Cd, Cr, Cu and Fe
Shoppers	4.3	7.49	Cd, Cu, Fe, Cr, Zn, Ar and Ni
Textile	7.45	1.6	Cu, Cd, Zn, Mn and Fe
Vegetables	30.72	36.4	Cu, Cr, Zn, Fe and Cd
Miscellaneous	18.86	9.16	Zn, Mn, Cu, Ar, As, Cr, Hg, Pb
Total	100	100	

4.2 Characteristics of Dumpsite Soils

The parameters of the soil at different depths across all the experimental dump sites are presented in the table 4.2, 4.3 and 4.4.

4.1.1 pH

The Soil pH is important parameter to determine the availability of soil minerals. Soil is neutral to strongly alkaline in 1:5 soil water suspensions. At high pH, metals are locked up and cannot be used by plants and other metals become toxic (Braddy, 1999). Soil samples collected from the dump sites have an alkaline pH. The pH values of all the soil samples analyzed from 3 dumpsites were close, ranging from 7.6 to 8.9. Soil pH was slightly increased with the depth in I-14 solid waste dump site while in Bhatta dump site, pH varied slightly at three different depths, this may be due to the accumulation of heavy metals in soil with the plastic bags (Takura et al., 2007). Similarly, reference soil pH also slightly increased from 8.2 to 7.6 with the depth, while soil pH decreased from 8.9 to 7.5 at NUST. These values lie in the same range reported by Osake and Outaya (2008) but higher than the values recorded by Takura et al., (2007). The higher pH in soil of dumpsite may be due to the increased absorption/desorption of contaminants reported by Akopteva et al., (2010). It is also confirmed by the Matos et al., 2001 that with increase in pH there was an increase in the metals adsorption and there was also an increase in the precipitation of metals, so the reaction that governed the metals behavior was the precipitation.

4.1.2 Electrical Conductivity

Soil electrical conductivity (EC) represents the salt content. Results show that there is higher content of salt in soils of dumpsites. The increase in pH and iron content resulted in highest value of EC of dumpsites soils (Braddy and Weil., 1999). These higher values of EC for the soil around the dump sites compared to the reference soil values showed that solid waste dump sites had a great impact on the properties of soil in close proximity.

Electrical conductivity at I-14 ranges from 705 to 397 µS/ while the EC at NUST and Bhatta dump site showed a decreasing trend of values with the depth.

Concentrations varied at three different depths as Bhatta 695, 448 and 403 μS/cm. While in NUST, EC values were highest and decreased from 1432.6, 1119 and 464 μS/cm. Electrical conductivity values of three dump sites with the depth were greater than the reference value which were 249, 206.25 and 175μS/cm. Similar trend of EC values were observed within the soil depth between 5 dump sites by Elaigu et al., (2007) but higher than the values reported by Osake and Outaya (2008).

4.1.3 Total Organic Carbon

Total organic carbon (TOC) is the carbon (C) accumulated in soil organic matter (SOM). It is indicated the presence of organic matter and microbiological activities in the soil samples (Akpoveta at al., 2010). Interaction between dissolved OC released from manure (with pesticides) may affect pesticide movement through soil into groundwater. An increase in SOM, increase total C which leads to greater biological diversity in the soil, resulting in increase of biological control of plant diseases and pests (Edwards *et* al., 1999). The increase of the organic carbon values in dump site soils could also result from waste burning on the landfill (Christopher, 2012).

Results of the study showed that total organic carbon was highest in surface soils of Bhatta site of about 85 mg/kg, then in 2nd and 3rd depth concentrations were (55.6 mg/kg, 46.4 mg/kg). Concentrations were varied along the depth in both dumpsites and decreased along with depth across the Bhatta, I-14 and NUST sites. This may be due to the higher amount of organic matter and leaching of soil (Akopteva et al., 2010)

In I-14dump site surface soil concentration was 59.8 mg/kg while in 2nd and 3rd depth; concentrations were 53 and 49.5 mg/kg. Both the dump sites had a higher TOC values as compared to the reference soil values which were 27.29, 24.56 and 22.84 mg/kg but the NUST had a low values. There was no significant variation in the values of TOC obtained for all the soil samples analyzed. It is indicated that all sites might have a higher proportion of organic matter in soil. TOC values were quite higher than the values reported by Akopteva et al., (2010).

4.1.4 Total Nitrogen

Nitrogen is the most abundant element in our atmosphere, plants can't use it until it is naturally processed in the soil, or added as fertilizer. In extreme cases too much quick release nitrogen can cause burning of the leaf tissue and plant death. Total nitrogen represents high amount of green vegetation observed at the dump sites.

Total nitrogen is found to be decreased with the depth but higher in surface soil than the reference soil. In I-14 the surface soil, 2nd depth and 3rd depth was 30.6, 24.2 and 27.1 mg/kg and in Bhatta 33.57, 25.08 and 18.9 mg/kg while in NUST the concentration was low as compared to both the dump sites and that was 22.59, 9.17and 6.59 mg/kg. Anikwe and Nwabodo in 2002 endorsed that total nitrogen decreased with the soil depth in all the sampling points of dumpsites.

4.1.5 Soil Texture

In general, soils have a low clay content and organic matter so they tend to be permeable. This is the important characteristics of the soil which play an important role in plant species establishment and development and also affects the physical parameter of the soil. Clay texture played a significant role in differentiating normal soil of adjoining area than dumpsite soil (Tripathi and Misra, 2012). In I-14 the surface soil has 50% sand+50% fine silty clay while in 2nd depth 60% silty clay+40% Sand and in 3rd depth 50 % silty clay+50%Sand. So the maximum Equal amounts of sand and silt is present in the I-14 dumpsite soils. Similarly, In Bhatta dump site the texture of the soil was fine silty clay in which the surface soil has 60% fine silt (35% silt+5%clay). While in 2nd depth 80% silt clay (70% silt+10%clay) and 20 % sand and in 3rd depth 80% silty clay (70% fine silt+10%clay). This is may be due to the adjoining areas of the dumpsite are used for the agricultural purposes so the presence of silty clay is reasonable (Tripathi and Misra, 2012). While in NUST H-12 site, the texture of soil is silty and clay loam with gravels along the depth. This characteristic of soil at dumpsites are quite different and varies as compared to normal soil of undumped areas due to the mixed composition of solid waste in dumpsites (Tripathi and Misra, 2012).

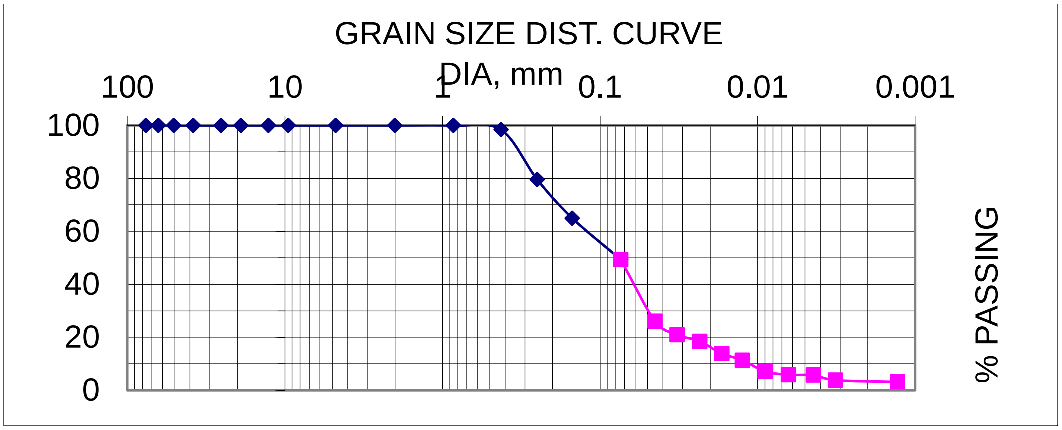

Figure 4.1 Grain size Distribution curve of Surface soil of I.14 Dumpsite

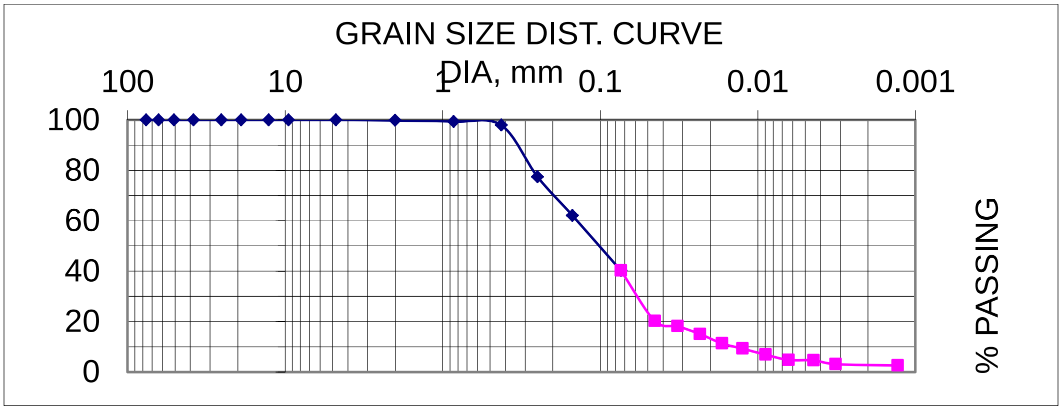

Figure 4.2 Grain size Distribution curve of 2nd Depth of I.14 Dumpsite

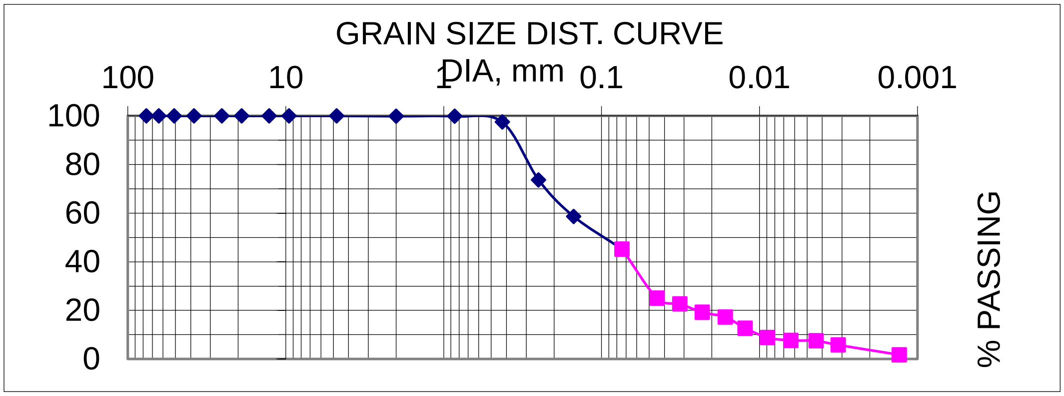

Figure 4.3 Grain size Distribution curve of 3rd Depth of I.14 Dumpsite

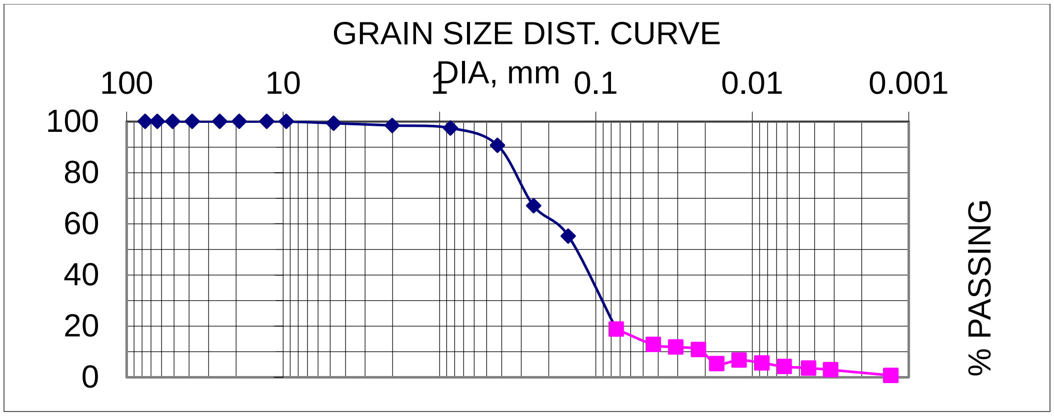

Figure 4.4 Grain size Distribution curve of Surface soil of Bhatta Dumpsite

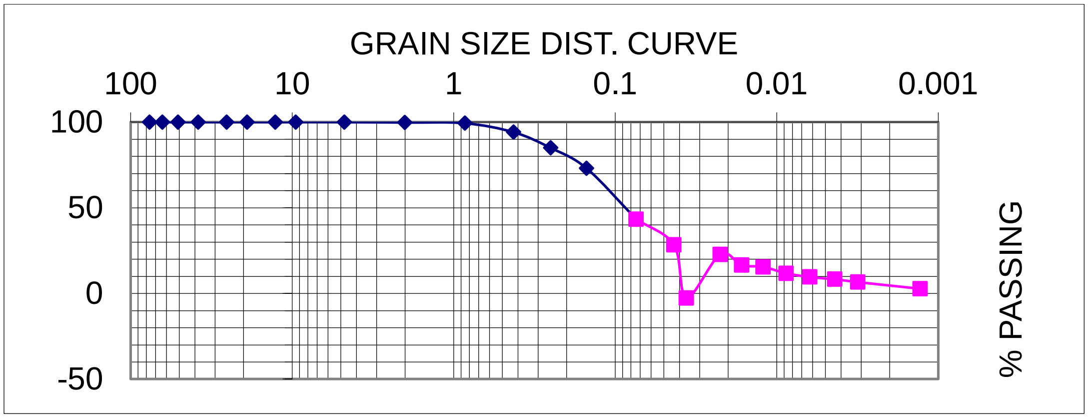

Figure 4.5 Grain size Distribution curve of 2nd Depth of Bhatta Dumpsite

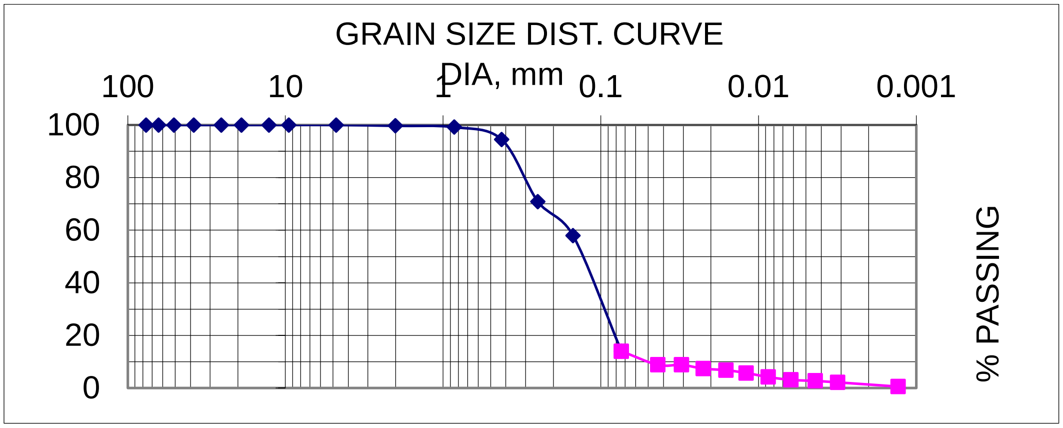

Figure 4.6 Grain Size Distribution curve of 3rd Depth of Bhatta Dumpsite

4.2 Elemental XRF Analysis

The qualitative analysis of solid soil samples were carried out by XRF in order to analyze the presence of selected heavy metals (Fe, Cd, Zn, Mn and Cr) of 3 dumpsites of Islamabad (S-1, S-2 and S-3. Before the quantification by FAAS, Selected soil sample was taken out for the qualitative analysis by XRF which displayed the presence and composition of all elements in soil samples in percentage and counts. All samples were analyzed and results showed the presence of Fe, Cd, Mn, Cr and Zn. In which the iron has higher percentage as compared to other metals against wavelength and counts. XRF spectrum of one such is shown:

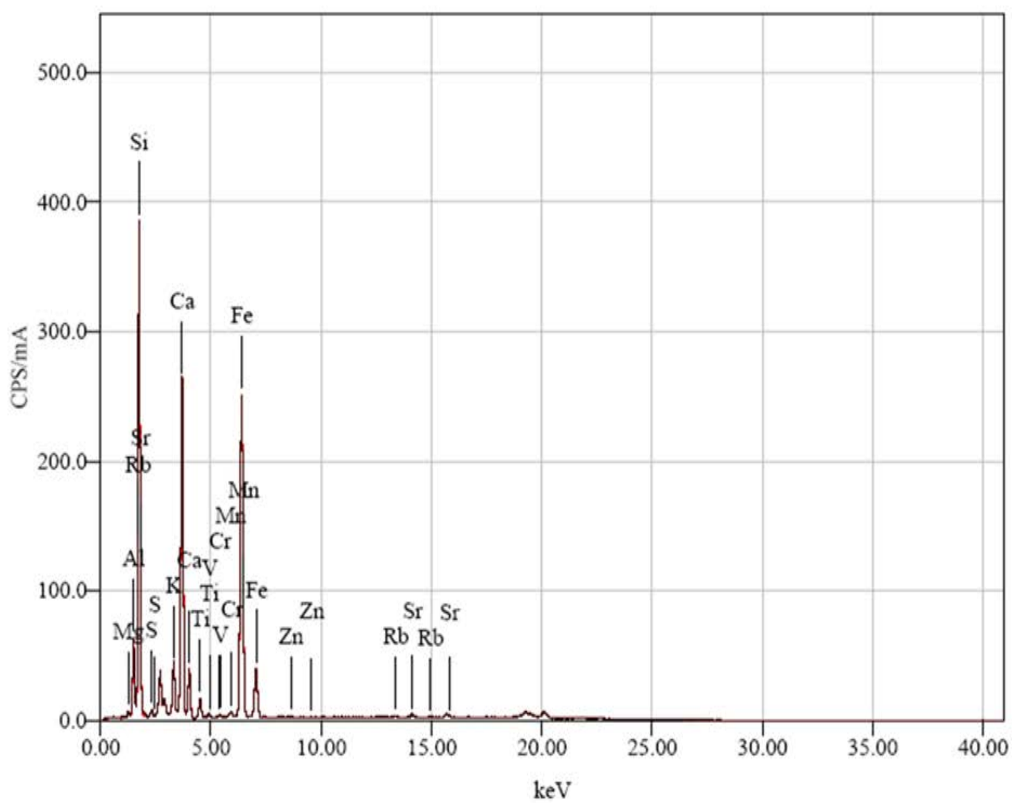

Figure 4.7 XRF Spectrum of Soil Sample

4.2.1 Concentration of Iron in Soil Profile

It is common metallic element in earth's crust. Total iron concentration in soil varies; its normal range is low of 200 ppm to higher than 10 percent (Tisdale and Nelson, 1966). 1% is equal to 10,000 mg/kg, so the 10 percent is equal to 100,000 mg/kg. The natural level of iron concentration ranged between 3,000 - 5,000 mg/kg. Graph 4.1 shows that mean concentrations of Iron (Fe) in soil of three dump sites. With changing depths, concentration of Fe decreased which represents the adsorption capacity of soil. Levels were higher in Bhatta dumpsite than I-14 dump site which had similar values at second and third depth. The concentrations of NUST H-12 and reference soil were more or less the same. The mean concentrations of surface soils in all three dump sites was 9.38 % while in 2nd depth 9.56 % and in 3rd depth the 9.48 %. The higher concentration might be due to higher background concentration as it is the most abundant element in earth crust and it may also due to the metallic scraps, metal tins and hospital waste. The concentration of iron in all soil profiles of the municipal waste dumps were high while I-14 had highest Fe concentration. The concentration of iron was higher than the 50,000 mg/kg threshold limit given by the USEPA, FAO (2001).

The concentrations of iron observed in the present study are higher than levels reported for soils around an oil field and those found in automobile spare parts market (Iwegbue et al. 2006).

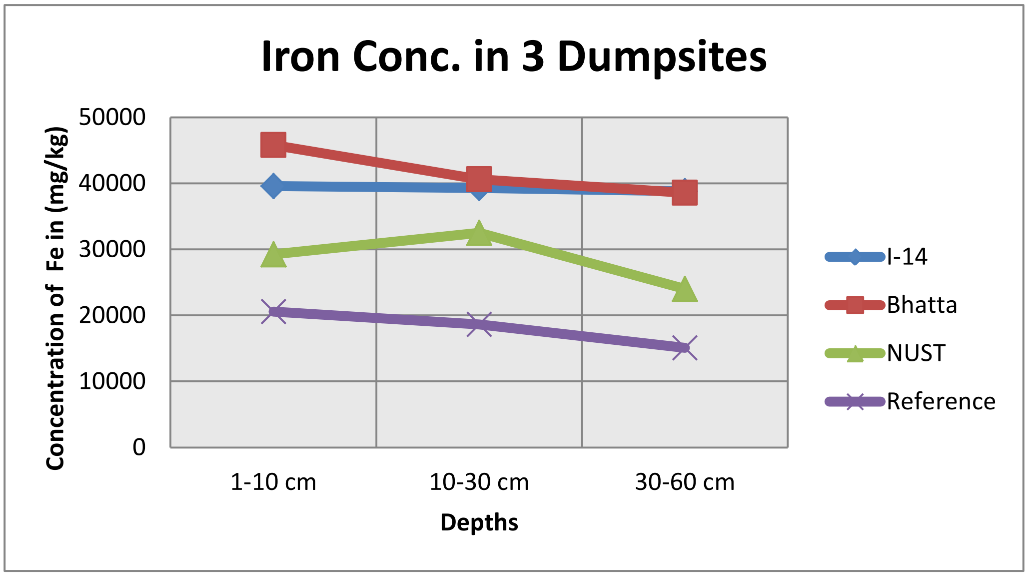

Figure 4.8 Iron concentration in surface soil, 2^{nd} and 3^{rd} depth of all the dump sites

4.3 Flame Atomic Absorption Spectroscopy (FAAS)

The actual concentration of heavy metal (Cd, Zn, Mn and Cr) at each sampling site was examined by FAAS. The calibration curves for all the four heavy metals showed the good linearity on the concentration range of heavy metals (0.1 to 20.0 mg/L) with a correlation co-efficient. Regression is in the range of 0.996 to 0.999.

4.4 Heavy Metal Content

A comparison of the average values of Cr, Mn, Zn, Cd and Fe with the corresponding normal range of soils. The values of Heavy metals at all sampling sites were considerably high. The heavy metal concentrations at Bhatta dump, I-14 and NUST H-12 sector were relatively high as compared to the reference values and threshold limits because of the high municipal solid waste and food waste. Other probable sources of high metal content are hospital waste, plastic, wood, metallurgies and batteries in Bhatta and I-14 dumpsite.

4.4.1 Concentration of heavy metals in Soils

4.4.1.1 Concentration of Manganese

Figure 4.3 shows the concentration of manganese at 3 different depths among the three dumpsites. It gives a clear view about the levels of heavy metals of three dumpsites in which the concentration of manganese in NUST is higher than the I-14 and Bhatta dumpsite. Concentration of manganese in NUST site was 3.5 times higher than the reference soil. The mean concentration of surface soils in all sampling sites (I-14, Bhatta, NUST and reference soil) were 11.03, 10.89, 14.54 and 10 .3 mg/kg while in 2nd Depth 8.83, 9.55,11.95 and 8 mg/kg and in 3rd Depth the values were 6.02, 7.75, 10.8 and 7.1 mg/kg. The lowest Concentration in surface soil was 4.5 mg/kg and highest concentration was 16.9 mg/kg obtained from the Bhatta dump site. While in I-14 the lowest value was 0.08 mg/kg to maximum concentration of 24.4 mg/kg was obtained. Both values were little low as compared to the NUST site but almost near to a value of reference soil. The concentration of manganese from all the dumpsites was lower than the 5000 mg/kg threshold limits defined by the USEPA-FAO. Therefore the manganese content within the depth was decreasing in all sites, it could be due to the mining and mineral processing specially nickels, emission from alloy, steel and iron production) or from the combustion of fossil fuel (Alloway and Ayres, 1997). Ukpebar and Unvigbe in 2003 reported that the higher content of manganese in some parts of refuse dumped might be associated with its use in electroplating in some parts of motor vehicles. Awokunmi (2010) found out that concentration of manganese ranged from 20 – 2210 mg/kg. However it was not detected away from the last sampling point on the dumpsite, where the highest range of concentration (2022 - 2210 mg/kg) was detected.

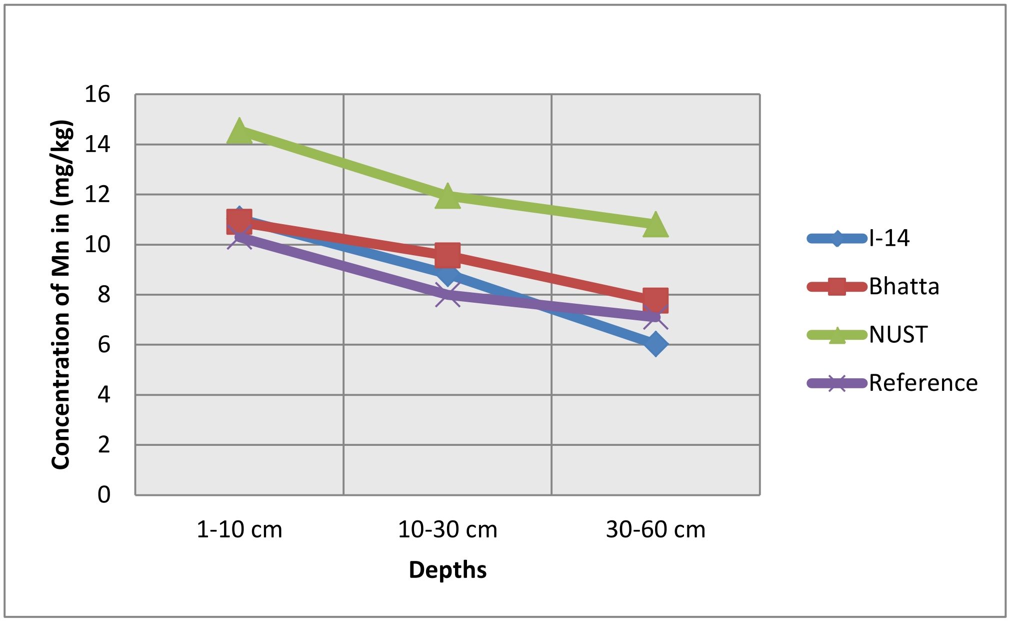

Figure 4.9 Concentration of Manganese in surface soil, 2nd and 3rd depth in different dump sites of Islamabad

4.4.1.2 Concentration of Cadmium

Figure 4.4 depicts the concentration of cadmium in surface soils among the three dumpsites. This demonstrates the level of cadmium in three different dumpsite in which concentration of cadmium in I-14 was higher than the Bhatta, NUST and reference soil. The mean values of Cd in all the dump sites and reference soil were 2.3, 2.5, 2.3 and 1.7 mg/kg while in 2nd depth 2.2, 2.6, 2.4 and 1.6 mg/kg and in 3rd depth 2.6, 3.3, 1.9 and 1.7 mg/kg as obtained. The values were lower than the 3 mg/kg limits given by the USEPA-FAO and also by 3-6 mg/kg limits given by the Indian standards. Cadmium was below the detection limit at some layers of the soil profile. The levels of cadmium may be related by plated steel, open burning of municipal wastes, wasted Ni-Cd batteries and plastics containing Cd pigments. On the other hand levels of cadmium in NUST H-12 and Bhatta dump site were closed and near to the value of reference soil. The study by Awokunmi et al. (2010) reported that the cadmium levels of 219 – 330 mg/kg at the soil surface layer of dumpsites and nil at 200m away. The results were same to those of Amusan et al. (2005) for soils of refuse dumpsite. The reason of this similarity in readings is not presently established (Adelkan and Alawode, 2011).

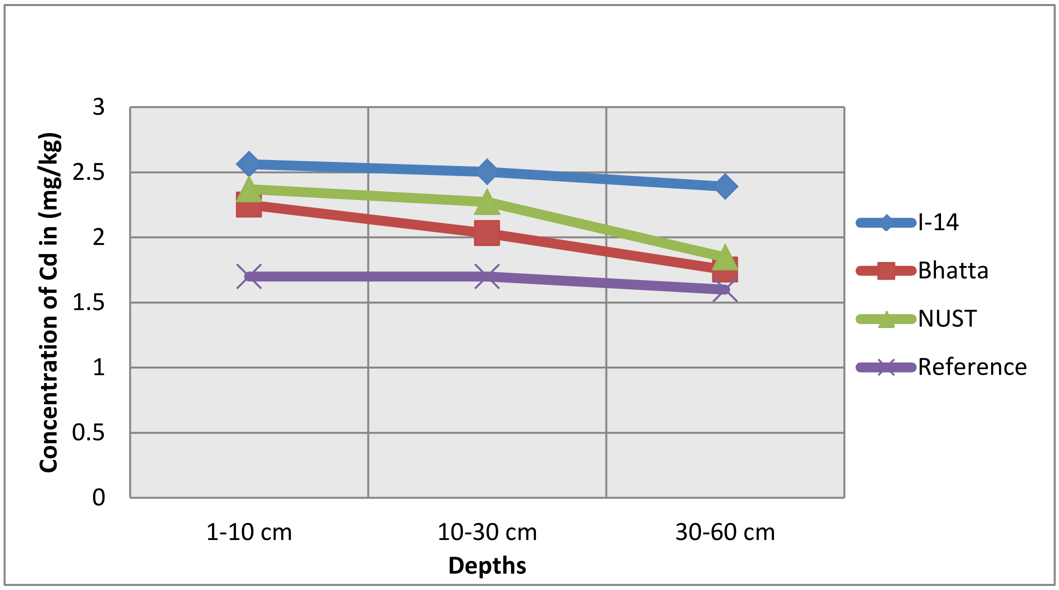

Figure 4.10 Concentration of cadmium in surface soil, 2nd and 3rd depth in different sites of Islamabad

4.4.1.3 Concentration of Zinc

Figure 4.5 shows the concentration of Zn at three different dump sites. In which the Zn concentration was higher in NUST dump site than Bhatta and I-14 dump site. Concentrations of all three dumpsites were higher than reference soil value. The mean values of Zn in all the dump sites (1-14, Bhatta and NUST) and reference soil were 131.04, 226.30, 260 and 132 mg/kg while in 2nd depth 98.8, 163.1, 192.9 and 114 mg/kg and in 3rd depth 92.8, 121.4, 133.8 and 105 mg/kg was obtained.

Total content of zinc in soil ranges from 10 to 300 ppm. The values taken were all lesser than the 300 mg/kg limit by the USEPA-FAO (2001) but zinc values of these were far less than 300-600 mg/kg standards given by the India. The higher values were may be due to source of Zn must be linked with the existence of galvanized metal scrap, expired cosmetics and medicines, old building materials, silver lining in wrappers etc. Akpoveta et al., (2010) found the higher content of zinc in Agbor and Abraka dumpsites of Nigeria. While Mufide (2009) reported that concentrations of zinc (according to average concentration) were lower than threshold limits. Similarly Zn content in soils of dumpsites obtained were within the normal range (10-300 mg/kg) confirmed by Anikwe and Nwobodo, 2002.

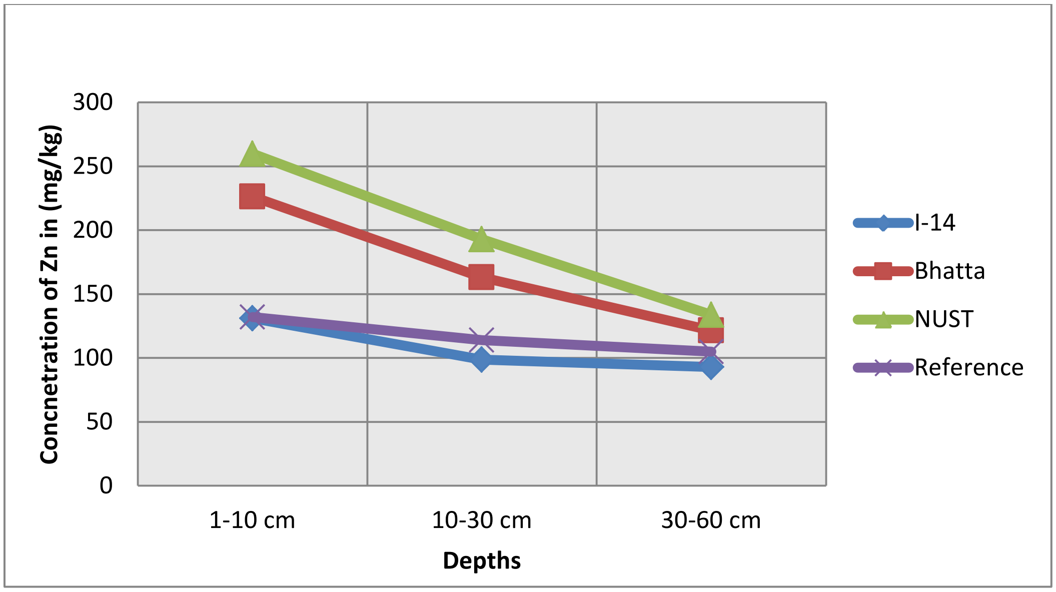

Figure 4.11 Concentration of Zinc in surface soils, 2nd and 3rd depth in different dump sites of Islamabad

4.4.1.4 Concentration of Chromium

Chromium toxicity in the environment is relatively rare, but it still pose some risks to human health since chromium can be accumulated on skin, lungs, muscles, fat, in liver, dorsal spine, hair, nails and placenta where it is traceable to various heath conditions (Reyes *et* al., 2007). Figure 4.6 shows the mean concentrations of Cr in soil of three dump sites. The level of chromium was higher in Bhatta site than I-14 and NUST dump site respectively. The mean concentrations of surface soils in all three dump sites were 109.3, 155, 72.2 and 83.5 132.8, 99.5, 72.2 and 83.5 mg/kg while in 2nd depth 92.42. 114, 45.33 and 42.7 mg/kg and in 3rd depth, values were 59.4, 53.43, 42.76 and 42.4 mg/kg. The lowest value of Cr was 30 to 212 mg/kg in I-14 dump site while in Bhatta site 37.5 to 512.5 was taken. Cr concentration of Bhatta site was higher because the waste dumped contains higher Cr concentration and dumping is still practicing in Bhatta. The concentration of chromium in NUST and reference soil was almost same may be because of the heavy metals drained out with rain water in past and settled at another place. Allowable limits of Cr in India are not given while the values were higher than the 100 mg/kg threshold limits defined by the USEPA-FAO (2001). Therefore most of the values obtained in this study were greater than the acceptable limits and posed a high risk to human health and environment. Other sources of chromium pollution are water erosion of rocks, liquid fuels, industrial and municipal waste. The values of Cr obtained were lower than the 900–2000 mg/kg reported by Adefemi and Awokunmi (2009) in dumpsites. However, Adelekan and Abegunde (2011) reported the same concentrations of Cr in dumpsites as observed in current study.

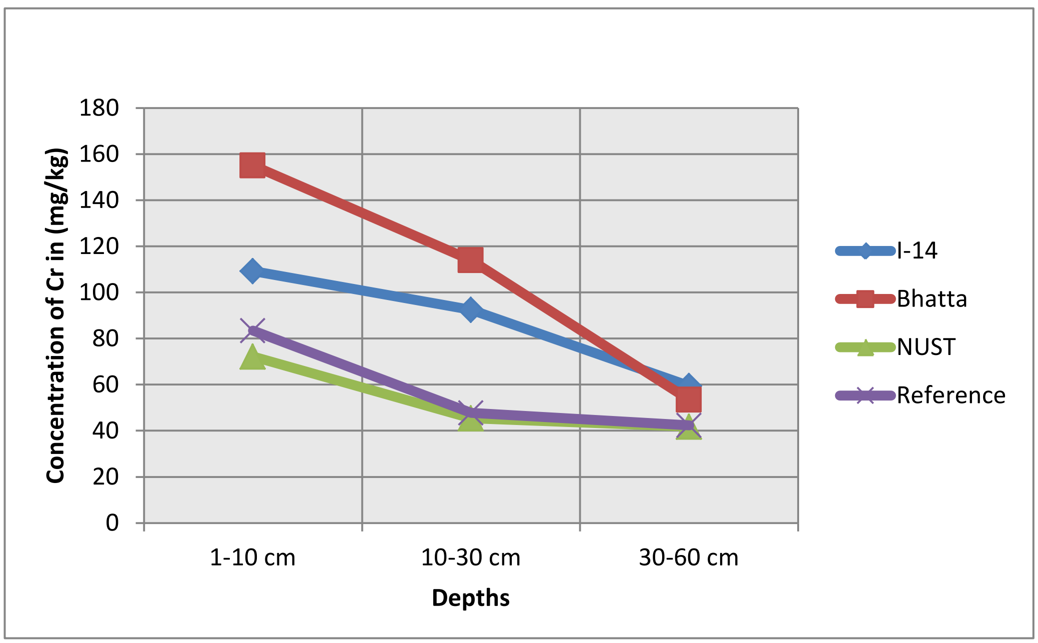

Figure 4.12: Concentration of Chromium in surface soils, 2nd and 3rd depth in different dump sites of Islamabad

4.5 Correlation matrix among the parameters

The significant relationships between concentration of heavy metals and physiochemical characteristics of dumpsites soil were done by performing the correlation analysis. The correlation matrix is one of the common and useful techniques in statistics which explain the degree of relationship between parameters.

4.5.1 Relationship of Heavy metals and Physiochemical Characteristics

The results showed statistically positive and negative correlation. In table 4.4 the correlation matrix of the pH at the surface soils showed a positive but weak correlation with chromium, manganese, zinc and cadmium but indirect and negative correlation with iron. Statistically, significant dependencies were recorded between pH with all parameters. It’s may be due to the pH is having a great impact on the absorption of soil and solute concentration reported by Osake and Otuga (2008). pH is reported as soil characteristic to show the good association to soil adsorption of elements such as Cd and Zn (Tyler and Mcbride, 1982., Christensen, 1984., King, 1988).

EC had positive correlation with TOC, TN, Cd and Fe but indirect with Cr, Mn and Zn. Negative or indirect correlation of Mn and Zn with electrical conductivity was not statistically significant which was confirmed by Mali et al., (2002) and Jayashree et al., (2012). EC may play major role in the relation. Similarly TOC had significant negative correlation with all the heavy metals except cadmium. The negative correlation with metals and physio-chemical characteristics could be due to the anthropogenic. The main sources of heavy metals in the municipal solid waste dumps include copper–cadmium alloy, nickel–cadmium batteries, PVC stabilizer and photovoltaic cells, etc.

Table 4.2: Correlation between the studied parameters in surface soils of all the dumpsites

Correlation	**Cr mg/kg**	**Mn mg/kg**	**Zn mg/kg**	**Cd mg/kg**	**Fe %**
pH	-0.172	0.088	0.182	-0.0158	0.174
EC	-0.060	-0.34	-0.011	0.077	0.092
TOC mg/l	0.132	-0.149	0.181	0.335	0.241
TN mg/l	-0.076	-0.0976	-0.015	-0.116	-0.044

In table 4.3 showed that 2nd depth pH had direct correlation with all the heavy metals except Cadmium. EC had slightly direct correlation with Zn and Cd which means that Zn and Cd had positive but weak interaction and are not increased with terms of electrical conductivity. Correlation existed positive with TN, Cd and Fe. TN was positive correlated with Cd.

Table 4.3: Correlation between the studied parameters in 2nd depth of all Dumpsites

Correlation	Cr mg/kg	Mn mg/kg	Zn mg/kg	Cd mg/kg	Fe mg/kg
pH	0.170	0.105	**0.0424**	-0.057	**0.0216**
EC	-0.40	-0.105	0.483	0.278	-0.479
TOC mg/l	-0.145	-0.196	0.090	0.32	0.189
TN mg/l	-0.168	-0.138	**0.00042**	**0.05**	**0.0189**

Table 4.4 showed that 3rd depth correlation patterns in pH were weak but positive relationship with all parameters except Cd. EC had moderately correlated with Zn but weak or statistically negligible with others existed with all the parameters except Cr and Fe. Positive correlation was found between Zinc with pH within the depths of all sites. However, Negative correlation of Zn with pH was not statistically significant which was reported by Deka and Sarma, 2012. TOC was positive but weakly correlated with Zn, Cd and Fe.

Table 4.4: Correlation between the studied parameters in 3rd depth of all the Dumpsites

Correlation	Cr mg/kg	Mn mg/kg	Zn mg/kg	Cd mg/kg	Fe mg/kg
pH	**0.006**	0.3008	0.1118	-0.009	0.370
EC	-0.233	0.074	0.539	**0.0177**	-0.339
TOC mg/l	-0.013	-0.186	0.275	0.0822	0.393
TN mg/l	-0.158	0.095	0.251	-0.333	0.438

Coefficient of correlation Between Heavy metals and other soil parameters established a weak linear relationship between the parameters. Similar results were obtained by Deka and Sarma, 2012. The lack of correlation between the physio-chemical and heavy metals in the study is concluding that there are other parameters which can also play an important role in leaching of heavy metals in soil samples. The positive weak correlation between the heavy metals showed that they probably have been from a same source and higher amount in heavy metals could be due to highest amount of carbon and electrical conductivity.

4.6 Box and Whisker Plots of All Dumpsites

Graph 4.6 shows surface soil parameter such as pH, EC, TOC, TN and heavy metals. The mean pH was 8.32 and standard deviation was 0.38. Minimum value was 7.68 in all the sites which is slightly alkaline but the maximum value was 8.86 which probably is due to any source of solid waste or other activities.. Similarly in case of electrical conductivity, mean value was 651 μS/cm with a minimum value of 176.50 μS/cm and maximum was 1511 μS/cm. the data was skewed from 74 % in EC. Mean of Total organic carbon was 63.78 mg/l with a minimum value of 2.39 which were observed in NUST site but the maximum value was 224.6 mg/l observed in soil sample of 1-14 dumpsite which could be due to high organic matter content. The data skewed from 4 % in all the sites. Similarly total nitrogen mean in all the sites was 30.85 mg/l with a minimum value of 1.81 mg/l and maximum value of 129 mg/l. These all were physio-chemical characteristics of soil which effects on the concentration of heavy metal, their mobility and availability. Heavy metal chromium had a mean of 123 mg/kg of all the dump sites but the minimum value was 52.5 mg/kg and maximum value 240 mg/kg. The concentration was considered as higher.

Similarly, in case of manganese, mean value of manganese was 11.38 mg/kg with a minimum value of 0.08 and maximum value 24.4 mg/kg taken in sample of i-14 dump site. The data was as swayed to 60% in all solid waste dump sites. Zinc value was higher with a mean of 191.4 mg/kg in all the sites with a minimum value of 86.10 mg/kg and maximum value of 473.5 mg/kg. While cadmium was low in all the sites as compared to the threshold limit and reference value. Mean of cadmium content was 2.24 with a minimum value of 0.75 mg/kg and maximum value of 3.10 mg/kg which was taken in sample of I-14 dump site. Iron had a mean of 4.01 % with the minimum value of 2.05 % with the maximum value of 5.6 %.

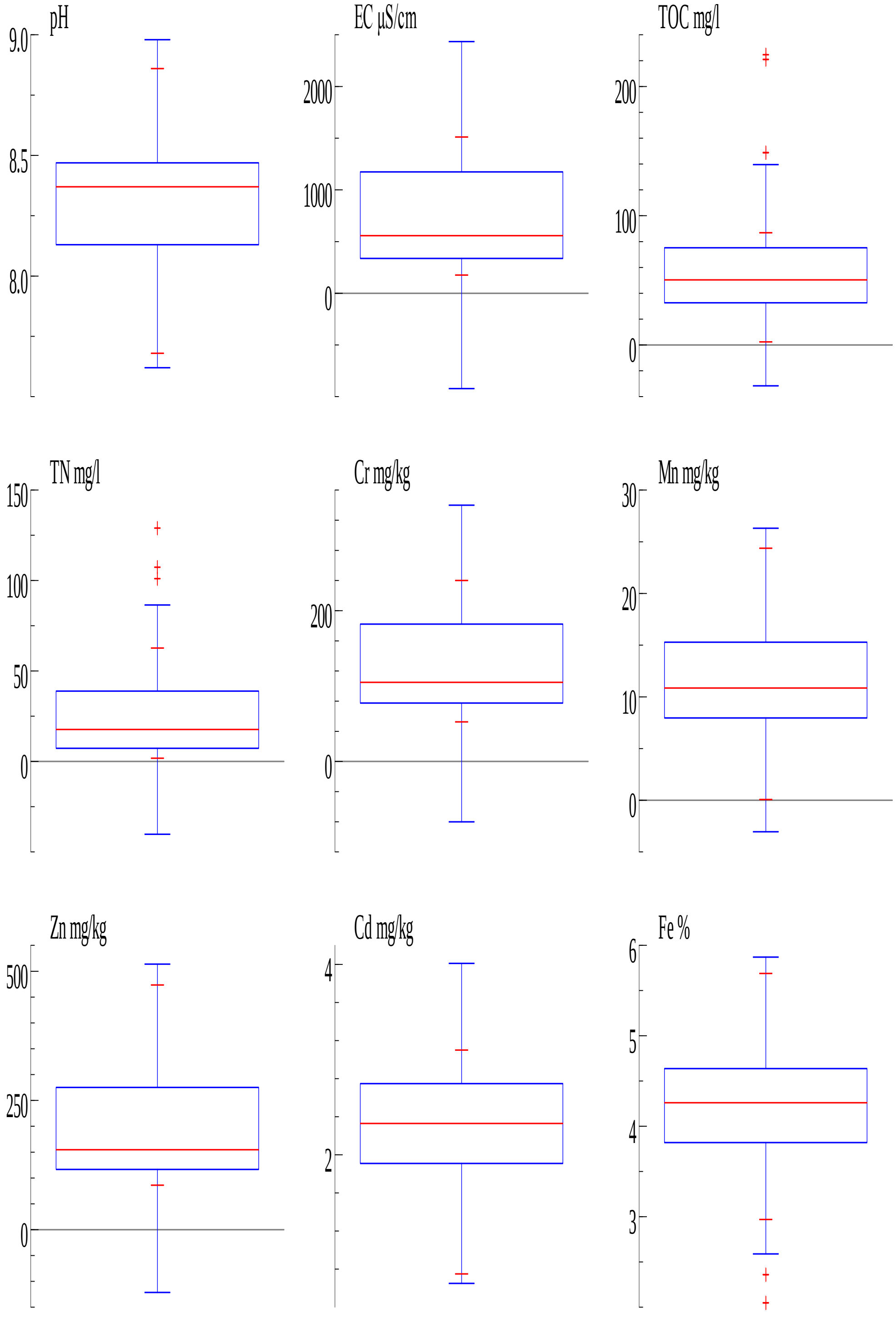

Figure 4.13 Box and whisker plot of surface soil parameters of all the dumpsites

The second depth was taken at 10-30 cm. In this depth mean of pH was lower than the surface soil. Mean of pH was 8.13 with a minimum value of 7.57 taken at I-14 solid waste dump site and maximum value was 8.8 which was the soil sample of NUST site. Mean of electrical conductivity was 578.8 µS/cm with minimum value of 148.5 µS/cm and maximum value of 1599.5 µS/cm and standard deviation was 443.65. In case of total organic carbon the mean value was 53.5 mg/l with a minimum value of 14.09 mg/l and maximum value of 196.4 mg/l. Mean of Total nitrogen was 21.54 mg/l and minimum value of 1.13 mg/l with a maximum value of 92.3 mg/l. the standard deviation was 21.13 of all the dump sites values. Mean of chromium metal was 93.87 mg/kg with a minimum value of 33.42 mg/kg and maximum value of 199.3 mg/kg. The values were decreasing in 2^{nd} depth of soil samples of all the dump sites. Similarly manganese concentration was decreased within the depth in all the dump sites. Mean of manganese was 9.48 mg/kg with a minimum value of 0.03 mg/kg and maximum value of 21.3 mg/kg in all the dump sites. Zinc mean of 142.9 mg/kg which was lower than the surface soil but the minimum value of 69.01 mg/kg and maximum value of 326.6 mg/kg was lower than the surface soil values of soil samples. Cadmium value with a mean of 2.89 mg/kg which was almost similar to surface soil value mean. Minimum value of cadmium was 0.75 mg/kg and maximum value of 3.07 mg/kg in 2^{nd} depth of all the dump sites soil. Iron was considers as an outlier in the box and whisker plot so it was avoided in the graph. Mean value of iron was 4.08 % with minimum value of 2.05 % and maximum value of 5.6 %.

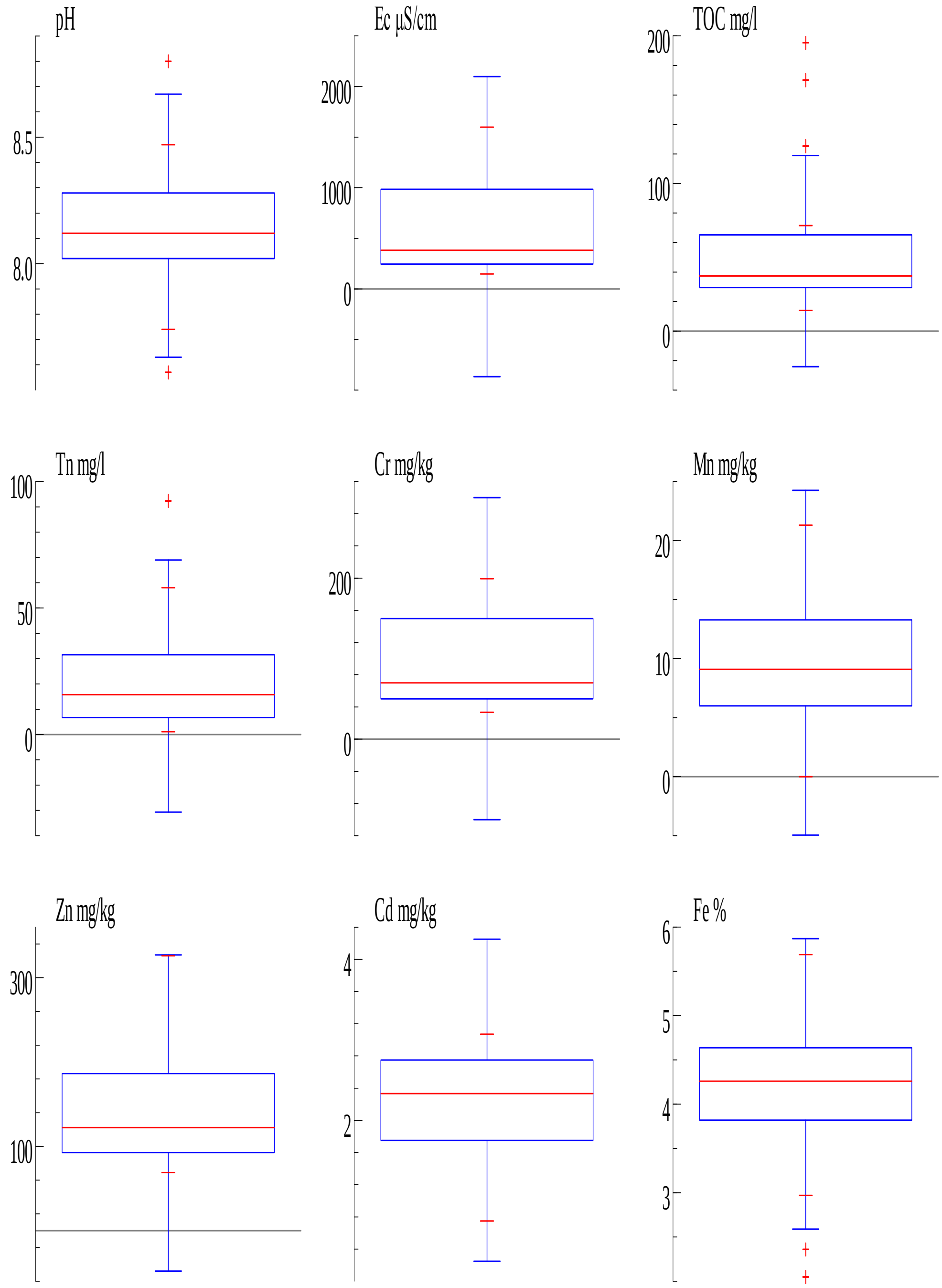

Figure 4.14 Box and whisker plot of 2nd Depth parameters of all the Dumpsites

In 3rd depth the distance from the soil surface was 30-60 cm. in this the pH mean 7.95 was lower than the 2nd depth with a minimum value of 7.28 and maximum value of 8.49. Electrical conductivity was lower than the 2nd depth with the mea 484.8 µS/cm. The minimum value was 135.20µS/cm but the maximum value 2097 µS/cm was higher than the 2nd depth value taken from the all dump sites. Similarly mean of total organic carbon was 42.7 mg/l with a minimum value of 8.3 and maximum value of 140 mg/l. The data showed a large variability could be because of the random sampling in all the sites to saw the variation in quantities. Mean of total nitrogen was 68.86 mg/l with a minimum value of 0.63 mg/l and maximum value was 210 mg/l.

Chromium value with mean of 62.29 mg/kg with minimum value of 28.06 and maximum value of 187.5 mg/kg. So here it was concluded that chromium concentration was decreasing with the depth but the manganese concentration was lower as compared to the 2nd depth with a mean of 7.38 mg/kg and minimum value of 0.03 mg/kg with a maximum value of 18 mg/kg. Mean of zinc value was110.3 mg/kg with a minimum value of 61.54 mg/kg and maximum value of 199.4 mg/kg. The standard deviation of the sites was 34.7. Mean of cadmium was 2.01 mg/kg higher in 2nd depth of all the dump sites with a minimum value of 0.50 mg/kg and maximum value of 3.67 mg/kg. Mean of iron was 3.58 % with a minimum value of 1.21 % and maximum value of 4.79%.

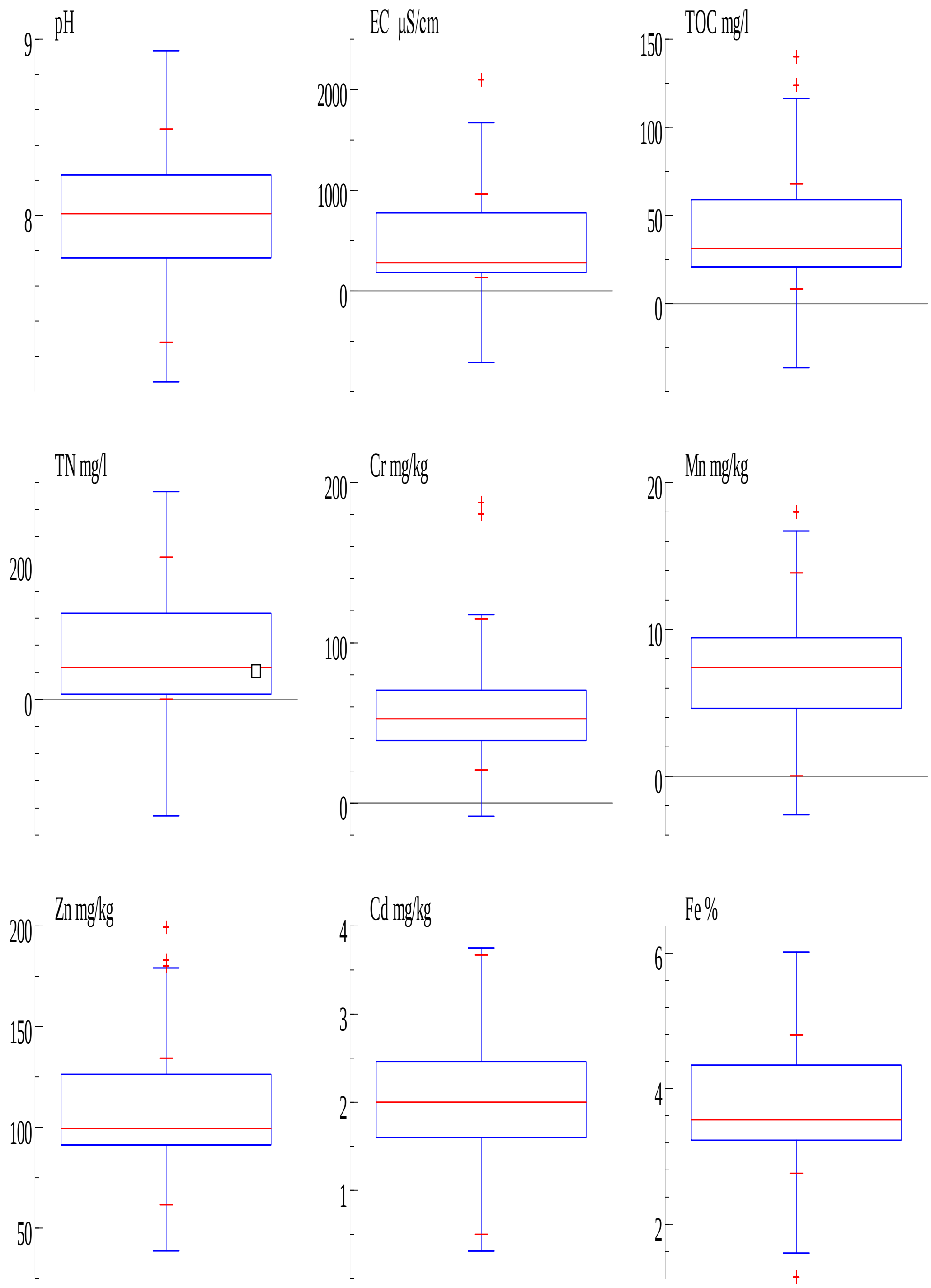

Figure 4.15 Box and whisker plot of 3rd Depth parameters of all the Dumpsites

CONCLUSION

- It provides a baseline study for the researcher and scientists to make standards for the heavy metals soils especially dumpsites.
- Soils close to the Dumping sites were found to be more contaminated.
- Concentrations higher than reference soil but within the Safe limits (Cr=100 mg/kg, Fe=50,000 mg/kg, Mn=2000 mg/kg, Cd=3 mg/kg, Zn= 300 mg/kg) except for Zn and Cr.
- Further in-situ and in-vitro bioaccumulation studies can also performed by using the information in this study.
- Non-linear relationships have been found between the heavy metals with physico-chemical characteristics like (pH, EC and TOC).

RECOMMENDATIONS

- Steps should be taken to control open dumping.
- Artificial reclamation with soils is recommended for these sites.
- Findings from this study will be of immense help to researchers and environmental regulators in developing countries.
- Enforcement of a directive to prevent any form of farming on the dumpsites.
- Studies must be conducted to find the movement of Heavy metals and taken up by vegetation and on speciation of various metals and measures to control.

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Appendix

APPENDIX-I
Characteristics of Dumpsite Soil

A-1.1 Characteristics of soil surface of all Dumpsites

Sites	pH	Ec µS/cm	TOC mg/l	TN mg/l	Cr (mg/kg)	Mn (mg/kg	Zn mg/kg)	Cd (mg/kg)	Fe (%)
Ref soil	8.2	249.2	24	3.46	83.5	10.3	132	1.7	2.06
1	8.01	384.5	50.39	14.25	195	24.38	150.33	2.28	3.82
2	7.98	490	75	11.36	155	17.05	116.73	2.82	4.15
3	8.12	557	59.77	17.71	212.5	4.2	217.47	2.46	4.15
4	8.3	1184	148.8	107.4	62.5	10.64	104.35	2.01	2.36
5	8.37	212	33.09	9.4	90	14.94	88.45	2.46	4.5
6	8.47	911	26.15	6.53	62.5	7.22	124.68	2.46	4.26
7	8.48	341	27.48	5.86	105	7.96	120.37	2.28	4.67
8	7.68	1176	80.8	15.06	80	0.08	86.1	3	3
9	8.39	285	36.25	16.92	77.5	10.75	147.31	3.07	4.36
10	8.13	1511	60.73	129	52.5	13.11	154.65	2.75	4.29
11	8.4	1225	221	39	150	12.5	225.35	3.1	5.69
12	8.24	1231	224.6	62.68	115	8.17	381.08	2.75	4.18
13	8.86	322	75.38	29.61	215	8.17	276.25	2.75	4.64
14	8.11	644	31.31	20.91	240	10	167.79	1.5	4.66
15	8.15	787.5	86.9	23.84	202.5	10.86	330.08	1.75	4.88
16	8.27	1271	50.42	101.1	182.5	4.52	159.45	0.75	4.36
17	8.46	386	32.61	4.58	102.5	16.96	351.34	1.25	4.71
18	8.48	337	36.94	23.2	122.5	16.13	155.28	2.25	4.28
19	8.31	569	53.66	23.46	132	14.16	114.96	1.5	4.16
20	8.49	176.5	41.74	7.32	97.5	7.53	106.61	2	4.22
21	8.85	500.5	18.6	4.9	62.02	11.57	133.85	2.58	3.74
22	8.42	642	32.74	61.08	94.2	16.75	275.5	1.91	2.97
23	8.42	251	2.39	1.81	60.24	15.3	473.5	2.33	2.05

Reference soil, 1-10= I-14 Dumpsite, 11-20=Bhatta Dumpsite, 21-23=NUST H-12

A-1.2 Characteristics if 2nd Depth of all Dumpsites

Sites	pH	Ec µS/cm	TOC mg/l	TN mg/l	C (mg/kg)	Mn(mg/kg	Zn mg/kg)	Cd(mg/kg)	Fe (%)
Ref soil	7.6	175.15	21.29	3.17	42.4	7.1	105	1.6	1.51
1	8.18	220.7	50.93	11.6	180.5	18	126.45	1.75	3.67
2	8	417.5	46.99	7.87	115	3.02	61.58	2.12	4.65
3	7.69	280	36	7	187.5	3.12	94.65	1.81	3.11
4	8.21	962.2	124	59	52.5	4.63	99.53	1.62	4.35
5	8.23	184.2	23.19	12.93	42.5	0.33	74.31	2.37	3.32
6	7.76	576	52.71	12.71	30	7.11	70.77	2.46	3.18
7	8.32	136.3	20.88	5.13	55	6.56	107.31	3	4.68
8	7.64	921	63.6	10.09	55	0.03	92.22	2.4	4.66
9	8.15	156	16.61	7.51	40	9.46	99.56	3.67	3
10	7.88	222	60.53	160.6	35	7.96	102.01	2.7	4.22
11	8.17	919	140	190	39	7.5	183.11	2.5	4.25
12	7.28	917	59.07	47.5	20.63	5.06	121.91	2.85	3.47
13	8.49	182.5	29.54	180	50.38	7.42	95.49	2	4.79
14	8.07	190.6	28.36	210	96.34	9.03	101.05	1	4.27
15	7.94	625.5	67.88	132.5	53.85	8.82	199.42	1.25	3.54
16	7.84	484	30.41	120	56.91	2.35	106.61	0.5	3.53
17	8.39	248.5	19.62	127.5	20.8	13.02	134.42	1.25	4.48
18	8.29	135.2	31.3	105	55.45	13.12	94.1	1.5	3.26
19	7.41	165.5	39.48	102.5	70.49	6.08	85.75	2	3.24
20	8.26	158.75	30.62	112.5	70.52	5.14	91.32	2.25	3.65
21	7.45	483.5	8.25	22.52	49.51	8.36	89.05	1.6	3.24
22	8.01	778	11.88	0.63	28.06	10.22	132.4	1.9	2.75
23	7.97	2097	12.55	4.38	47.72	13.85	180.06	2.03	1.22

A-1.3 Characteristics of 3rd Depth of all Dumpsites

Sites	pH	Ec µS/cm	TOC mg/l	TN mg/l	Cr (mg/kg)	Mn (mg/kg	Zn mg/kg)	Cd (mg/kg)	Fe (%)
Ref soil	7.8	206.2	22.8	3.46	47.7	8	114	1.7	2.06
1	8.1	236.5	37.34	19.25	190	21.3	135.29	1.75	3.82
2	7.99	479.7	65.3	8.97	132.5	16.5	69.01	2.82	4.15
3	8.08	383	38.25	7.07	199.25	3.7	104.35	2.46	4.15
4	8.24	1117.6	125.3	58.04	60	8.3	91.1	2.01	2.36
5	8.02	248.5	32.47	16.16	42.5	6.9	81.38	2.46	4.5
6	8.47	741	63.66	14	52.5	6	85.8	2.46	4.26
7	8.33	240.3	18.77	6.46	80	6	117.93	2.28	4.67
8	7.74	986.3	71.57	24.9	70	0	76.31	3	3
9	8.28	224	42.88	15.74	50	10.7	109.36	3.07	4.36
10	7.95	254	35.01	92.33	47.5	8.8	117.74	2.7	4.29
11	8.2	928	170	34	62.5	10	186.47	2.95	5.69
12	7.57	999.5	195.4	46.93	47.5	5.5	226.26	2.75	4.18
13	8.8	297	36.65	3.52	170	8.1	163.62	2.75	4.64
14	8.08	245	29.53	31.62	150	9.6	108	1.5	4.66
15	7.98	551	69.66	33.87	162.5	9.1	216.58	1.75	4.88
16	8.25	591.5	41.61	28.11	177.5	2.4	151.11	0.75	4.36
17	8.23	278	28.08	31.18	57.5	14.4	236.4	1.25	4.71
18	8.08	148.5	34.89	6.42	115	14.2	141.37	1.50	4.28
19	8.12	270.8	42.58	9.78	120	15	127.47	1.50	4.16
20	8.33	166	31.73	5.39	82.5	7.3	92.71	2.00	4.22
21	8.06	1238.5	17.58	6.71	53.085	10.2	122.38	2.58	3.74
22	8.31	1460	14.09	11.94	49.51	13.3	229.25	2.21	2.97
23	8.2	1599.5	16.62	1.13	33.4225	12.3	326.1	2.33	2.05

A.1.4 Statistical Analysis of surface soil of all Dumpsites

	pH	Ec µS/cm	TOC mg/l	TN mg/l	Cr (mg/kg	Mn (mg/k	Zn mg/kg)	Cd (mg/kg	Fe (%)
Mean	8.32	651.80	63.78	30.85	123.00	11.38	191.40	2.24	4.01
SD	0.257274	407.4055	57.25657	35.59595	57.42558	5.186919	103.955	0.606032	0.902306
Max	8.86	1511.00	224.60	129.00	240.00	24.38	473.50	3.10	5.69
Min	7.68	176.50	2.39	1.81	52.50	0.08	86.10	0.75	2.05
Variance	0.06619	165979.3	3278.315	1267.072	3297.697	26.90413	10806.63	0.367275	0.814156
SK	-0.04728	0.738947	2.024592	1.729345	0.662023	0.191419	1.332275	-0.65395	-0.93862

A.1.5 Statistical Analysis of 2nd Depth of all Dumpsites

	pH	Ec µS/cm	TOC mg/l	TN mg/l	Cr (mg/kg)	Mn (mg/k	Zn mg/kg)	Cd (mg/kg	Fe (%)
Mean	8.13	578.77	53.41	21.54	93.87	9.48	142.92	2.19	4.01
SD	0.25	443.65	46.64	21.13	54.36	4.76	63.70	0.62	0.90
Max	8.80	1599.50	195.40	92.33	199.25	21.25	326.10	3.07	5.69
Min	7.57	148.50	14.09	1.13	33.42	0.03	69.01	0.75	2.05
Variance	0.06	196827.69	2174.84	446.60	2954.58	22.65	4057.27	0.38	0.81
SK	0.21	1.01	2.12	1.92	0.76	0.38	1.30	-0.52	-0.94

A.1.6 Statistical Analysis of 3rd Depth of all Dumpsites

	pH	Ec µS/cm	TOC mg/l	TN mg/l	Cr (mg/kg	Mn (mg/k	Zn mg/kg	Cd (mg/kg	Fe (%)
Mean	7.968	484.838	42.737	68.860	62.294	7.385	110.337	2.005	3.584
SD	0.327	450.706	32.541	70.410	43.154	4.296	34.711	0.692	0.920
Max	8.490	2097.000	140.000	210.000	187.500	18.000	199.425	3.665	4.790
Min	7.280	135.200	8.250	0.630	20.630	0.025	61.584	0.500	1.215
Variance	0.10714	203136	1058.92	4957.58	1862.3	18.4587	1204.85	0.47916	0.84552
SK	-0.5136	2.18446	1.82615	0.65498	2.07418	0.47065	1.34319	0.17336	-0.9629