

**Evaluation of the Mobility and Bioaccessibility of  
Potentially Toxic Metal Contents in Urban Soil of  
Lahore, Pakistan**



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*In The Name of Allah, The Most Gracious and The Most Merciful*

# DEDICATION

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*Dedicated To My Parents*

# DECLARATION

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This is to certify that this dissertation entitled “*Evaluation of the Mobility and Bioaccessibility of Potentially Toxic Metal Contents in Urban Soil of Lahore, Pakistan*” by **Mr. Yasir Karim Khan** is accepted in its present form by the Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan as satisfying the dissertation requirements for the degree of *Master of Philosophy* in *Analytical/Inorganic Chemistry*.

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Yasir Karim Khan  
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# TABLE OF CONTENTS

	<i>Page No.</i>
Dedication	iv
Declaration	v
Acknowledgements	vi
Table of Contents	vii
List of Figures	x
List of Tables	xii
Abstract	xiii
<b>CHAPTER 1 : INTRODUCTION</b>	<b>1-12</b>
1.1 Nature and Composition of Soil	1
1.2 Significance of Soil	2
1.3 Soil Pollution	4
1.4 Metals in Soil and their Health Effects	5
1.4.1 Cadmium	6
1.4.2 Chromium	6
1.4.3 Lead	7
1.4.4 Copper	7
1.4.5 Cobalt	8
1.4.6 Zinc	8
1.4.7 Manganese	9
1.4.8 Iron	9
1.5 Extraction Methodologies	9
1.6 Physiochemical Parameters of Soil	11
1.6.1 pH	11
1.6.2 Electrical Conductivity and Total Dissolved Solids	11
1.6.3 Soil Organic Matter	12
1.7 Objectives of the Present Study	12
<b>CHAPTER 2 : EXPERIMENTAL METHODOLOGY</b>	<b>13-26</b>
12.1 Site Description	13
2.2 Sample Collection and Storage	13

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2.3	Extraction Procedures	17
2.3.1	Glycine Extraction	17
2.3.2	EDTA Extraction	18
2.3.3	Acetic Acid Extraction	18
2.3.4	Nitric Acid Extraction	18
2.3.5	Aqua regia Extraction	19
2.4	Measurement of the Physicochemical Parameters of Soil	19
2.4.1	pH, Electrical Conductivity and Total Dissolved Solids	19
2.4.2	Soil Organic Matter	19
2.4.3	Soil Texture	20
2.5	Quantification of the Metal Contents in Soil	21
2.6	Quality Control and Quality Assurance	22
2.7	Statistical Analysis	22
2.8	Pollution Assessment	23
2.8.1	Contamination Factor	23
2.8.2	Geoaccumulation Index	24
2.8.3	Enrichment Factor	24
2.8.4	Degree of Contamination	25
2.9	Human Health Risk Assessment	25
	<b>CHAPTER 3 : RESULTS AND DISCUSSION</b>	<b>27-64</b>
3.1	Physicochemical Characteristics of Soil	27
3.2	Distribution of the Metals in Glycine Extract of Soil	30
3.3	Correlation Study of the Metals in Glycine Extract of Soil	32
3.4	Comparison of the Metal Levels in Glycine Extract of Soil from Various Areas	33
3.5	Distribution of Selected Metals in EDTA Extract of Soil	33
3.6	Correlation Study of the Metals in EDTA Extract of Soil	36
3.7	Comparison of the Metal Levels in EDTA Extract of Soil from Various Areas	37
3.8	Distribution of Selected in Metals Acetic Acid Extract of Soil	37
3.9	Correlation Study of the Metals in Acetic Acid Extract of Soil	40



3.10	Comparison of the Metal Levels in Acetic Acid Extract of Soil from Various Areas	40
3.11	Distribution of Selected Metals in Nitric Acid Extract of Soil	41
3.12	Correlation Study of the Metals in Nitric Acid Extract of Soil	44
3.13	Comparison of the Metal Levels in Nitric Acid Extract of Soil from Various Areas	44
3.14	Distribution of Selected Metals in Aqua regia Extract of Soil	45
3.15	Correlation Study of the Metals in Aqua regia Extract of Soil	47
3.16	Comparison of the Metal Levels in Aqua regia Extract of Soil from Various Areas	48
3.17	Comparison of the Average Metal Levels in Various Soil Extracts	49
3.18	Soil Texture	55
3.19	Evaluation of Pollution Status of the Metals in Soil	55
3.20	Multivariate Analysis of the Pseudo-total Metal Levels in Soil	60
3.21	Health Risk Assessment of the Metal Levels in Soil	62
3.22	Salient Findings of the Present Study	63
	References	65-75

## LIST OF FIGURES

	<i>Page No.</i>
Figure 1. Location of the sampling points in the study area (Lahore)	14
Figure 2. Comparison of the pH values in the soil samples	27
Figure 3. Comparison of the EC values ( $\mu\text{S}/\text{cm}$ ) in the soil samples	28
Figure 4. Comparison of the TDS values ( $\text{mg}/\text{L}$ ) in the soil samples	28
Figure 5. Comparison of the organic matter (%) in the soil samples	29
Figure 6. Comparison of average metal levels ( $\text{mg}/\text{kg}$ , $\pm$ SE) in glycine extracts of the soil	31
Figure 7. Quartile distribution of the metals ( $\text{mg}/\text{kg}$ ) in glycine extracts of the soil	31
Figure 8. Comparison of the average metal levels ( $\text{mg}/\text{kg}$ , $\pm$ SE) in glycine extracts of the soil samples collected from different areas	33
Figure 9. Comparison of average metal levels ( $\text{mg}/\text{kg}$ , $\pm$ SE) in EDTA extracts of the soil	35
Figure 10. Quartile distribution of the metals ( $\text{mg}/\text{kg}$ ) in EDTA extracts of the soil	35
Figure 11. Comparison of the average metal levels ( $\text{mg}/\text{kg}$ , $\pm$ SE) in EDTA extracts of the soil samples collected from different areas	37
Figure 12. Comparison of average metal levels ( $\text{mg}/\text{kg}$ , $\pm$ SE) in acetic acid extracts of the soil	39
Figure 13. Quartile distribution of the metals ( $\text{mg}/\text{kg}$ ) in acetic acid extracts of the soil	39
Figure 14. Comparison of the average metal levels ( $\text{mg}/\text{kg}$ , $\pm$ SE) in acetic acid extracts of the soil samples collected from different areas	41
Figure 15. Comparison of average metal levels ( $\text{mg}/\text{kg}$ , $\pm$ SE) in nitric acid extracts of the soil	43
Figure 16. Quartile distribution of the metals ( $\text{mg}/\text{kg}$ ) in nitric acid extracts of the soil	43
Figure 17. Comparison of the average metal levels ( $\text{mg}/\text{kg}$ , $\pm$ SE) in nitric acid extracts of the soil samples collected from different areas	45
Figure 18. Comparison of average metal levels ( $\text{mg}/\text{kg}$ , $\pm$ SE) in aqua regia extracts of the soil	46
Figure 19. Quartile distribution of the metals ( $\text{mg}/\text{kg}$ ) in aqua regia extracts of the soil	47

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Figure 20. Comparison of the average metal levels (mg/kg, $\pm$ SE) in aqua regia extracts of the soil samples collected from different areas	49
Figure 21. Comparison of average Cd levels (mg/kg, $\pm$ SE) in various extracts of the soil	50
Figure 22. Comparison of average Cr levels (mg/kg, $\pm$ SE) in various extracts of the soil	50
Figure 23. Comparison of average Pb levels (mg/kg, $\pm$ SE) in various extracts of the soil	52
Figure 24. Comparison of average Cu levels (mg/kg, $\pm$ SE) in various extracts of the soil	52
Figure 25. Comparison of average Co levels (mg/kg, $\pm$ SE) in various extracts of the soil	53
Figure 26. Comparison of average Zn levels (mg/kg, $\pm$ SE) in various extracts of the soil	53
Figure 27. Comparison of average Mn levels (mg/kg, $\pm$ SE) in various extracts of the soil	54
Figure 28. Comparison of average Fe levels (mg/kg, $\pm$ SE) in various extracts of the soil	54
Figure 29. Ternary diagram showing the soil texture in the studied samples	55
Figure 30. Comparison of average pseudo-total metal levels (mg/kg) in the soil with the earth crust levels	56
Figure 31. Comparison of the contamination factors ( $C_f$ ) of selected metals in the soil	57
Figure 32. Comparison of the geoaccumulation index ( $I_{geo}$ ) of selected metals in the soil	58
Figure 33. Comparison of the enrichment factors (EF) of selected metals in soil	59
Figure 34. Modified degree of contamination ( $mC_{deg}$ ) associated with the metal levels in soil	60
Figure 35. Cluster analysis of selected metals in aqua regia extract of the soil	61
Figure 36. Exposure risk assessment of the metal levels in soil through ingestion and dermal contact	62
Figure 37. Hazard quotient/index of the metal levels in soil through ingestion and dermal contact	63

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## LIST OF TABLES

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	<i>Page No.</i>
Table 1. Description of the sampling locations from Lahore, Pakistan	15
Table 2. Optimum analytical conditions maintained on the instrument (Shimadzu AA-670, Japan) for the analysis of selected metals using air-acetylene flame	22
Table 3. Statistical distribution parameters for selected metal levels (mg/kg) in glycine extracts of the soil	30
Table 4. Correlation coefficients among the metal levels in glycine extracts of the soil	32
Table 5. Statistical distribution parameters for selected metal levels (mg/kg) in EDTA extracts of the soil	34
Table 6. Correlation coefficients among the metal levels in EDTA extracts of the soil	36
Table 7. Statistical distribution parameters for selected metal levels (mg/kg) in acetic acid extracts of the soil	38
Table 8. Correlation coefficients among the metal levels in acetic acid extracts of the soil	40
Table 9. Statistical distribution parameters for selected metal levels (mg/kg) in nitric acid extracts of the soil	42
Table 10. Correlation coefficients among the metal levels in nitric acid extracts of the soil	44
Table 11. Statistical distribution parameters for selected metal levels (mg/kg) in aqua regia extracts of the soil	47
Table 12. Correlation coefficients among the metal levels in aqua regia extracts of the soil	48
Table 13. Principal component analysis of pseudo-total metal levels in the soil	61

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## ABSTRACT

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Present study is based on the measurement of potentially toxic metal contents (Cd, Cr, Pb, Cu, Co, Zn, Mn and Fe) in the urban soil of Lahore, Pakistan, employing five extraction methodologies aimed at the evaluation of the mobility and bioaccessibility of the metals in soil. Concentrations of the metals in the soil samples were determined by flame atomic absorption spectrophotometer and the metal data were subjected to the statistical analysis. Among the metals, Fe, Mn, Zn and Pb showed relatively higher contributions in various soil extracts. On the average basis, aqua regia and glycine extracts revealed comparatively higher concentrations for most of the metals; however, Cd, Pb, Co and Zn exhibited higher bioaccessibility and mobility/bioavailability in the soil while Cr, Fe and Mn were least mobile and bioavailable. Significant and strong positive correlations were found between Zn-Cu, Zn-Fe, Zn-Cr, Mn-Cr, Pb-Cr, Pb-Cu, Pb-Co, Co-Cd, Fe-Cr, Fe-Co and Fe-Mn in various soil extracts. Quartile distribution manifested that most of the metals demonstrated relatively broad spread in their concentrations. Physiochemical parameters and soil texture were also estimated and most of the soil samples were found to be sandy loam in texture. The pollution index associated with the metal levels was assessed by computing contamination factors ( $C_f$ ), geoaccumulation index ( $I_{geo}$ ), enrichment factor ( $EF$ ) and modified degree of contamination ( $mC_{deg}$ ). In comparison with the earth crust levels, mean concentrations of Cd, Pb and Zn in the soil were found to be higher in the present study. The pollution indices ( $C_f$ ,  $I_{geo}$ ,  $EF$ ) unfolded severe to significant contamination, accumulation and anthropogenic enrichment of Cd, Pb and Zn (along with Cu and Co, in some cases) in the urban soil of Lahore, while  $mC_{deg}$  associated with the metal levels in the soil divulged moderate contamination on the average. Multivariate analyses which include principal component analysis (PCA) and cluster analysis (CA) were performed for source identification/apportionment of the measured metal levels in the soil. PCA and CA of the pseudo-total metal levels pointed towards mostly natural contributions for Fe-Mn-Co, whereas Zn-Cu-Cr-Pb-Cd were predominantly anthropogenic in origin in the soil. Potential health risks associated with the metal levels were also assessed for ingestion and dermal adsorption along with the hazard quotient/index. No significant human health risk/hazard was associated with the prevailing metal levels in the urban soil of Lahore.

# Chapter 1

## INTRODUCTION

### 1.1 Nature and Composition of Soil

Soil is an intricate and diverse amalgamation of organics, inorganics, and other different components that control its physical, chemical and biological characteristics. It is formed by the weathering of parental rocks due to interactive geological, hydrological and biological processes and it is a variable combination of minerals, organic matter and water on the surface of earth supporting the plant life. The soil organic portion comprises plant biomass in numerous stages of decay; high populations of bacteria, fungi, and insects may be present in soil. Soil encloses air spaces, by and large, has a loose texture. The solid fraction of distinctive productive soil is about 95% inorganic matter and 5% organic matter (Friedlova, 2010; Ozba, 2011; Ponil *et al.*, 2013). With increasing depth, classic soil unveils different layers which are called horizons; they are formed by complex processes during weathering. Due to the biological activities, such as bacterial decay of remaining plant biomass, complexing compounds and organic acids that are percolated by water to lower horizons where they interact with clays and other minerals, the properties of the minerals are modified. The uppermost layer of soil (topsoil) has highest biological activity and comprises most of the soil organic matter. Metal ions and clay particles in uppermost layer are subjected to significant leaching. Subsoil collects material, such as organic matter, salts and clay particles seeped from the topsoil. After subsoil, the next horizon is constituted of worn parental rocks from which the soil originated. Water infiltrate through soil, carrying dissolved and colloidal solids, finally drops to lower horizons. Soil goes through constant interchanges of matter and energy with the hydrosphere, biosphere and atmosphere (Manahan, 1999).

Soil is the vital part of the geosphere for humans and most of the other organisms; it is the most essential requirement for agriculture. Although only a thin layer compared to the earth's total thickness, soil is the medium that produces most of the food needed by the living beings. It not only produces the food, but also acts as a receptor of large amounts of pollutants, such as particulate matter, toxic metals, fertilizers, pesticides, and other materials applied to the soil. Therefore, soil is a vital constituent of environmental chemical cycles (Manahan, 1999). It marks a large diversity of characteristics that are used

for their categorization for various purposes which include cultivation of crops, construction of roads, and disposal of waste. The parental rocks from which soils are originated obviously play a vital role in determining the soil composition. Other soil characteristics include soil particle size, permeability, strength, degree of maturity and workability. Under comparatively higher rainfall environment, in moderate regions of the world, alkaline earth metals, alkali metals and to a smaller extent, iron and aluminium seep from the topsoil. At higher pH in the subsoil, clays and hydrated iron oxides are redeposited. The mechanical properties of soil, which may have vital environmental repercussions in spaces, such as disposal of waste, are mainly assessed by particle size. United Classification System (UCS) has classified the soil into four major categories based on soil particle sizes: clays (less than 0.005 mm) < silts (0.005-0.075 mm) < sands (0.075–2 mm) < gravels (2–60 mm) (Manahan, 1999).

## **1.2 Significance of Soil**

Soil is an essential component of urban ecosystems affecting, directly or indirectly, the quality of life for the residents. It performs major role in biochemical reactions, the recycling of various elements, water filtration and plant's growth. One of the important roles of soil is: building infrastructure including recreational activities (Stroganova *et al.*, 1997). Urban soils are different from natural ones as anthropogenic activities influence greatly the nature of former (Bullock and Gregory, 1991). In contrast to agricultural soil, urban soil, especially of parks and residential areas, which is not used for food crops, may also have a direct influence on public health since it can be easily transferred into human bodies (De Miguel *et al.*, 1997; Mielke *et al.*, 1999; Madrid *et al.*, 2002). The chemicals are more likely to be added in the surface soil and may have an impact on inhabitant's health if they attain toxic levels. Metropolitan soil constitutes a fundamental part of the city scenery, presenting distinctive qualities that distinguish it from naturally formed soil. For instance, city soil normally does not have the typical vertical layers, classified by horizons, and may not have the chemical composition and mineralogy as of parent material (Wong *et al.*, 2006); nevertheless, a number of studies indicated the control of natural geochemical factors on the properties of soil even in heavily urbanized areas (Manta *et al.*, 2002; Rodrigues *et al.*, 2009).

The sources of potentially harmful chemicals in the urban soil can be either natural (inherited materials from the primary parent materials) or may be anthropogenic (Wong *et*

*al.*, 2006; Wei and Yang, 2010; Luo *et al.*, 2012). Anthropogenic metal in soil can remain in soil for many decades after termination of nonpoint source and point emissions because of the long residence times of these metals in the soil (Yesilonis *et al.*, 2008). Majority of the human population spends their lifetime in urban environment so the nature of urban ecosystems becomes very important (De Miguel *et al.*, 1998; Poggio *et al.*, 2008). Heavy metals in urban soil are very harmful for human health as these metals can enter the human body through food chains or inhalation of dust (Lu *et al.*, 2007). Heavy metals in urban soils may come from various human activities, such as industrial/energy production, construction, vehicle exhaust, waste disposal, as well as coal and fuel combustion (Komai, 1981; Ikeda and Yoda, 1982; Ritter and Rinefierd, 1983; Chon *et al.*, 1995; Wong and Mak, 1997; Martin *et al.*, 1998). The level of heavy metals in urban soil may be increased through traffic emissions (Hafen and Brinkman, 1996; Yassoglou *et al.*, 1987; Surthland *et al.*, 2000), industrial emissions (Schuhmacher *et al.*, 1997; Li *et al.*, 2008) and atmospheric depositions (Simonson, 1995; Han *et al.*, 2006). For that reason, the industrial growth rate and urbanization cause the rise of air and soil pollution levels (Golia *et al.*, 2008). Urban soil serves as a sink for potentially toxic metals and pollutants. Heavy metals in the soils can also generate airborne particles and dusts, which may affect the air quality (Chen *et al.*, 1997; Bandhu *et al.*, 2000; Cyrus *et al.*, 2003; Gray *et al.*, 2003).

Heavy metals in urban areas have been a subject of great attention because of their non-biodegradable nature and long half-lives for removal from the body (Radha *et al.*, 1997). Elevated levels of heavy metals have harmful effects on human health, particularly on the health of young children, as they have active digestion systems which result in higher rate of assimilation of the metals. Heavy metals may mount up in the body and damage the central nervous system, causing metal poisoning and may perform the role of cofactors in many other diseases (Hammond, 1982; Nriagu, 1988; Thacker *et al.*, 1992; Schwartz, 1994; Bellinger, 1995). In the last couple of decades, many studies were carried out for a better understanding of urban soil pollution and increasing research focused on heavy metals in urban soils may decrease the exposure of human population to potentially toxic metal contents (Lee *et al.*, 2006; Zhang, 2006; Manta *et al.*, 2002; Mielke and Reagan, 1998). Heavy metals are valuable indicators of pollution in top soil environments. The ecological importance of heavy metals in soils is closely related to human health due to their high transference potential. This is highly evident in urban areas where various stationary and mobile sources release large quantities of heavy metals into the atmosphere and soil, beyond the natural emission rates (Nriagu, 1989; Bilos *et al.*, 2001).



### 1.3 Soil Pollution

With excessive urbanization and industrialization in many parts of the world during last decades, the soil compartment is receiving greater attention to measure the pollutants from various sources (Wei and Yang, 2010). Urban soil geochemistry is getting serious consideration due to the potential enduring harmfulness of heavy metal pollutants (Alloway, 1995; Nyarko *et al.*, 2006; Ajmone-Marsan *et al.*, 2008). Soil contamination is an unwanted change in the physical, chemical and/or biological properties which reduces the land for cultivation and habitation (Khan *et al.*, 2010). Soil is the combination of heavy metals, mineral ingredients, biological matter, existing organisms, water, and air. High levels of potentially harmful metals in the soil are a threat to public health through percolation into groundwater, becoming part of the food chain, plant uptake, direct human intake via windblown dust or the hand-mouth passageway (Ajmone-Marsan *et al.*, 2008; Carr *et al.*, 2008; Morton-Berme *et al.*, 2009). The toxicological hazards of direct ingestion and inhalation of dust and soil, both as suspended dust and by direct contact via the hand-mouth pathway of soil particles, are specifically high for children because they are physiologically more susceptible (Calabrese *et al.*, 1991; Ajmone-Marsan *et al.*, 2008; De Miguel *et al.*, 1997; Abrahams, 2002; Davydova, 2005; Möller *et al.*, 2005).

Soil contamination may possibly threaten human health through its effect on the hygiene quality of food and drinking water, and also via its effect on air quality. Though not considerable thoughtfulness has been given to soil, paralleled with water, food, and atmospheric pollution, soil pollution has been highlighted more and more by many environmental safety organizations and societies. The metropolitan environment is influenced by extensive series of pollutants which fluctuate considerably within and between the cities. Exceptionally high concentrations of contaminants in soils are found in large number of industrial areas, disposal of waste and dumps that result from localized accumulations (Tiller, 1992). It is usually known that vehicular traffic is a main source of heavy metal contamination in urban soil (EEA, 1995; Oliva and Espinosa, 2007). Moreover, the level of heavy metals markedly declines in areas where there is low automobile traffic (Sezgin *et al.*, 2004; Zhu *et al.*, 2001). Atmospheric accumulation is also responsible for the main sources of heavy metal pollution in urbanized areas (Li *et al.*, 2001; Wong *et al.*, 2003; Chen *et al.*, 2005). Industrial and residential areas, roadside and busy commercial districts are well-known for exceptionally high metal levels (Cicchella *et al.*, 2008a; Imperato *et al.*, 2003; Li *et al.*, 2004; Chen *et al.*, 2005; Cicchella *et al.*, 2005;

Lee *et al.*, 2006; Zhang, 2006a). Level of contamination is also related to the time for which heavy metals from many pollution sources, have enriched urban areas (Li *et al.*, 2001; Chen *et al.*, 2005). In comparison to heavy metals in agrarian soil, those in metropolitan soil have more conceivable sources; together with automobile discharges (Madrid *et al.*, 2002; Chen *et al.*, 2005; Lee *et al.*, 2006; Cicchella *et al.*, 2008b), industrial emissions (Li *et al.*, 2004; Banat *et al.*, 2005; Morton-Berme *et al.*, 2009) and some other sources, including waste incineration (De Miguel *et al.*, 1998; Li *et al.*, 2001). Some studies have established that atmospheric wet and dry depositions signify prime pathways of anthropogenic contributions of toxic metals into the surface soil (Wong *et al.*, 2003; Chen *et al.*, 2005).

Soil pollution has emerged as an important environmental problem for developed countries because of changes in the land use pattern during the last couple of decades. When different kinds of pollutants are considered, toxic metals are particularly hazardous due to their long term persistence and toxicity (Adriano, 2001). Nowadays, soils have been assessed as a diagnostic tool for environmental conditions that impact health (Abrahams, 2002; Davydova, 2005). Anticipation of soil contamination and its role in health risks and hazards require some understanding of soil, including geochemical properties, human activities, and atmospheric contamination for the area of interest. Multivariate statistical methods have generally been employed to evaluate the sources of heavy metals in the urban soils (Zhu *et al.*, 2001; Manta *et al.*, 2002; Lee *et al.*, 2006; Zhang, 2006a).

#### **1.4 Metals in Soil and their Health Effects**

Soil is a long-standing sink for a number of potentially harmful metals, such as Cd, Cr, Pb, Cu, Co, Zn, Mn and Fe. Soil contamination by the toxic metals is global problem (Adriano, 2001; Kabata-Pendias and Mukherjee, 2007). Health risks with excessive exposures to the metals that cause harmful effects to the biological organisms are considered toxic metals of human concern. These toxic metals may include non-essential ones, such as Pb and Cd that can be harmful even at trace concentrations, and biologically essential metals, such as Zn and Cu, which might cause toxic effects at significantly higher concentrations. The nature of effects could be toxic (sub-chronic, chronic or acute), carcinogenic, neurotoxic, mutagenic and teratogenic. Health effects associated with some of the potentially toxic metals with their sources are discussed below.

### 1.4.1 Cadmium

Cadmium (Cd) is found naturally in combined form with other metals in the earth's crust (IARC, 2010). There are numerous sources of Cd in metropolitan environment; majority of the extracted Cd is used in the manufacturing of Ni–Cd batteries, pigments' coating/plating, production of automobile radiators, electronics component manufacture and photography. Components of tires, petrol, diesel and lubricating oils also contain Cd (Marsan *et al.*, 2010). Exposure risk due to inhalation of Cd may occur from road dust. After inhalation, its absorption may depend upon the particle sizes and their solubility. Cd, as yet, is not known to have any biological function; on the contrary, it is said to be highly toxic (Alloway, 1990). Compared with the other metals, Cd is more mobile in the soil, in relation to both leaching and availability to the plants (Tiller *et al.*, 1984). Its exposure can cause both chronic and acute health effects in living organisms (Faiz *et al.*, 2009). It can induce extreme toxicity in humans and is hazardous at very low levels. Elevated concentrations may result in obstructive lung disease and pneumonitis, due to inhaled dusts and fumes which result in cough, chest pain and the permanent ending of vital processes in the lining of the lung tissues. Depending on the extent of exposure, the symptoms of effects include vomiting, nausea and muscular weakness. Its exposure can lead to itai-itai disease (Godt, *et al.*, 2006; Nordberg *et al.*, 2002) and its compounds can also cause lung, kidney and prostate cancer (IARC, 2010).

### 1.4.2 Chromium

Chromium (Cr) plays a vital role in industrial sector especially in galvanic, metallurgical/steel and pigment industry. It is used as an alloy component to exhibit corrosion resistance properties. Its compounds are employed predominantly in wood preservatives, metal finishing and pigments (Hasnie and Qureshi, 2002). The leading source of Cr contamination is well-thought-out to be from leather tanning and dyestuffs whereby waste is discharged directly into the streams. It can increase the effects of insulin and may develop glucose tolerance. In Cr(III) form, which is a stable oxidation state, it is present in nature. In urban areas, motor vehicle exhaust, waste incineration and combustion of oil/coal may result in emission of Cr to the atmosphere. Naturally, soil originated from ultramafic rocks and, particularly serpentines, frequently have elevated concentration of Cr (Adriano 2001). Cr(VI) is considered toxic in nature and responsible for lung cancer. Positive relations have also been witnessed between Cr and cancer of the nose and nasal sinuses. Higher levels of Cr are generally associated with excessive

consumption of Cr from food (DRI, 2006; IARC 2012). According to IARC classification, Cr(VI) compounds are placed in Group 1 which are carcinogenic in nature.

### 1.4.3 Lead

Lead (Pb) is present in the earth's crust in low concentrations, mostly in the form of lead sulphide (*galena*); however, the extensive existence of Pb in our surroundings is the result of human activities. Mining is one of the main sources of Pb because it contaminates the environment at every stage, from starting activity to its final use (IARC, 2006). It has been utilized as an antiknock agent in gasoline for many decades and has been one of the main contributors of pollution in cities together with the paints. Pb pollution is also caused by soldering, glass and car batteries. In recent years, electronic products and wastes have become a considerable Pb source (Terazono *et al.*, 2006; Lincoln *et al.*, 2007). Unleaded gasoline is now used in most of the countries (IPIECA, 2003) and it is now banned for paint industry, but its long use and persistence in the soil have resulted in high level of Pb in urban areas. A lot of research work has been carried out in cities to evaluate its potential toxicological effects. It is found usually in the societies bustling with industrial activity and indication of the harmful effects of Pb on humans has been observed for many decades. As Ca and Pb have similar chemical properties, human body takes Pb in place of Ca when ingested and assimilates it into the nerve tissues, brain, bone marrow and kidneys (Ferner, 2001). Pb poisoning may result in inhibition of haemoglobin, kidneys' dysfunctions, damage to the joints and reproductive systems, cardiovascular system's disruption and chronic/acute impairment to the peripheral and central nervous system (Ogwuegbu and Muhanga, 2005). Its contamination can also damage urinary tract and gastrointestinal tract (McCluggage, 1991; INECAR, 2000; Ferner, 2001; Lenntech, 2004). Inorganic Pb compounds are possibly carcinogenic to humans-Group 2A (IARC, 2006).

### 1.4.4 Copper

Copper (Cu) is a vital trace metal that is extensively present in the environment. It is distributed naturally in elemental form and as a constituent of various minerals. Major sources of Cu are beverages, food, vegetables and animals' liver (Uauy *et al.*; 1998; DRI, 2001). Cu in the elemental form, does not transform in the environment, therefore, it tends to accumulate in urban areas. It is extensively used in electrical wiring and electronic equipment, thus, it is a major component of electrical and electronic industries (Lincoln *et al.*, 2007; Wong *et al.*, 2007). It plays an important role in biochemical process, such as

reductant in the enzymes superoxide dismutase, lysyl oxidase cytochrome oxidase and numerous supplementary oxidases that catalyze molecular oxygen. It is carried in the body of organism by the ceruloplasmin protein (Stern, 2010). Acute inhalation exposure to Cu dust or fumes at concentrations of 0.075-0.12 mg/m<sup>3</sup> may cause metal fume fever with symptoms such as cough, chills and muscle ache (US Air Force, 1990).

#### 1.4.5 Cobalt

Cobalt (Co) exists naturally in soil, water, air, rocks, animals and plants. As a result of wind-blown dust, it enters from soil into the water and air. It is widely employed in the industries: catalysts, stabilizers, inhibitors and preservatives. It forms main constituent of materials, such as pigments, paints, ink, fungicides, batteries, pesticides, fertilizers, dyes, adhesives, etc. It is used in many alloys (super-alloys for parts in gas turbine aircraft engines, corrosion resistant alloys, high-speed steels, cemented carbides), in magnets and magnetic recording media, as catalysts in the petroleum and chemical industries (Kanayochukwu *et al.*, 2015). Humans are affected by elevated concentrations of Co released from combustion of coal, mining, processing of ores and cobalt compounds. Co-dust may cause an asthma-like disease with symptoms ranging from cough, shortness of breath and dyspnoea to decreased pulmonary function, nodular fibrosis, permanent disability and death. Exposure to Co may cause weight-loss, dermatitis, and respiratory hypersensitivity (Kilburn, 1984).

#### 1.4.6 Zinc

Zinc (Zn) is a natural constituent of soil in terrestrial ecosystem. Various anthropogenic sources of Zn appear to concentrate in urban areas; apart from the metallurgic/galvanic industry and the common sources of metal contamination such as waste treatment and fuel burning; it is also present in tires, batteries and electronic equipment (Dagan *et al.*, 2007; Lincoln *et al.*, 2007). Its oxide is added as an activator during the vulcanizing process, comprising from 0.4% to 4.3% of the resulting tire tread (Smolders and Degryse, 2002). Zinc from the tire dust is a major pollutant in soil (Smolders and Degryse, 2002; Sadiq *et al.*, 1989; Solomons & Ruz, 1998). It usually occurs in low concentrations and is essential micronutrient and catalyzes enzyme activity, contributes to protein structure and regulates gene expression (DRI, 2001). It is essential component for plant growth as it serves an important role in plant structure and function (Kabata-Pendias and Pendias, 1984). It is considered comparatively non-toxic, particularly

if taken orally. Nevertheless, surplus amount can affect or dysfunction the systems resulting in impairment of growth and reproduction (INECAR, 2000; Nolan, 2003). The adverse effects associated with chronic intake of Zn include acute gastrointestinal effects, headaches, impaired immune function, changes in lipoprotein/cholesterol levels, reduced Cu status, Zn-Fe interactions, liver failure, kidney failure and anaemia (Fosmire, 1990; DRI, 2006).

#### **1.4.7 Manganese**

Manganese (Mn) is a vital nutrient for animals, plants and microorganisms. It occurs naturally and found in food, water, soil and rocks. Most of the Mn in soil comes from crustal rocks; other sources include wash-off from plant and other surfaces, direct atmospheric depositions, leaching from plant tissues and dead animal remains. Minerals which contain Mn are rhodonite, pyrolusite, rhodocrosite and hausmannite (NAS, 1973; Windholz, 1983; US EPA, 1984; HSDB, 1998). The main anthropogenic sources of Mn in environment encompass sewage sludge, municipal wastewater discharges, mining and mineral processing, emissions from iron production, combustion of fossil fuels and fuel additives (Wuana and Okieimen, 2011).

#### **1.4.8 Iron**

Iron (Fe) exists in large amounts in earth crust; it is a vital constituent in the metabolism and is a major catalyst. It is the main component of a number of proteins, including enzymes and haemoglobin (DRI, 2001). It is generally used to treat anaemia. It is also present in many vitamin supplements. Elevated concentrations of Fe may cause poisoning which is the main cause of fatal poisoning in young children. It starts with irritation of the stomach and digestive tract leading to bleeding. It can poison the cells, effecting their internal biochemical reactions (Abbaspour *et al.*, 2014).

### **1.5 Extraction Methodologies**

The effects of soil's metal contents on the plants and human health are normally assessed by evaluating their availability because the total metal contents in soil cannot characterize the factual amounts that are accessible for plants' absorption and human exposure (Freeman *et al.*, 1996; Fan *et al.*, 2011a,b, 2012). Various extraction procedures can discharge specific amounts of the metals in soil according to the potential of extractant

(Rao *et al.*, 2008), thereby making it possible to assess the mobile and phytoavailable fractions of the metal contents in soil. Neutral salt solutions can be employed to extract the soluble and/or exchangeable fractions of the metals in soil. Generally, they reveal strong association with the metal contents in plants (Gupta and Aten 1993; Houba *et al.*, 2009). Different extractants can release the metals on exchangeable sites or bond with soil organic matter. Selective extraction procedures can assess the quantities of mobile or potentially mobile fractions related with phytoavailable contents under specific environmental or agricultural conditions; these procedures are useful for the determination of the mobile species for the plant availability and also the data are extremely advantageous in the land use assessment. Large number of chemical reagents have been engaged to evaluate the metal's mobility and bioaccessibility by a series of extractions, such as weak/dilute acids like ethylenediaminetetraacetic acid (EDTA), acetic acid, dilute nitric acid or neutral salts ( $\text{CaCl}_2$ ,  $\text{NaNO}_3$ , etc.) (Keller and Hammer, 2004; Pueyo *et al.*, 2004; Rauret *et al.*, 2001; Sastre *et al.*, 2004; Sutherland, 2002).

Complexing reagents like EDTA have a greater advantage because of their strong complexing ability that can move the metals from insoluble organic complexes and those attached to inorganic soil components (Ure and Davidson 2001). It can form complexes with the free metal ions in solution thus lessening their reactivity in the solution and replicating their mobility and metabolism in plants (Atun and Meja, 1998). EDTA extractions are mostly used to assess the ecotoxicity and mobility of the metals in soil with respect to the plants or environmentally accessible trace metals (Anju & Banerjee, 2011). Similarly, the methods employed to evaluate the pool of soluble/available heavy metals contents of soils are based on extractions by dilute solutions of either weak acid (acetic acid) or strong acids ( $\text{HNO}_3$ ). Given the special environmental effects, such as acid rain and root secretions of the plants, dilute acid extractants are used to assess the release of metal ions from the soil in weak acid environment. It was proposed by Tipping *et al.*, (2003) to evaluate the mobility of the metals in soil using 0.43 M  $\text{HNO}_3$ .

The health risks related with the soil are generally gauged by the measurement of their total metal content, though it may also reveal the geological origin of the soil in addition to anthropogenic contamination from industrial processes. A more significant evaluation of the metals' pollution in the environmental perspective can be made by calculating the 'pseudo-total' metal contents by extracting the soil with strong aqua regia solution. Pseudo-total extraction/digestion is commonly employed to appraise the maximum potentially soluble or mobile contents of the metals and, in the case of

environmental pollution, it indicates all metal contents except the metals bound in silicates. Therefore, it is a measure of the maximum potential hazard that could occur in long-term or in extreme environmental regimes (Ivezic *et al.*, 2013).

## **1.6 Physiochemical Parameters of Soil**

The quality of soil depends on its constituents and their concentrations, which are mostly derived from the geological data. Besides, different physiochemical parameters such as pH, electrical conductivity, total dissolved solids organic matter, etc. can also play vital roles in the chemistry of soil. Their significance in the soil is briefly outlined as under.

### **1.6.1 pH**

It is the most important parameter controlling the accumulation and availability of the metals in soil (Ramesh *et al.*, 2010; Eneje and Lemoha, 2012). Generally, it is used to express the intensity of the acidic or alkaline conditions. Precisely, it indicates the concentration of hydrogen ions [ $H^+$ ] in the solution. It can alter the adsorption capacity of the minerals and organic colloids (Patil *et al.*, 2012). At low pH, the anion exchange capacity is dominant, while at higher pH the cation exchange capacity predominates (Tukura *et al.*, 2013). It is the measure of acid-base equilibrium for the soluble compounds as well as the extent of flocculation and coagulation of the chemicals (Nazir *et al.*, 2015).

### **1.6.2 Electrical Conductivity and Total Dissolved Solids**

Electrical conductivity (EC) is a measure of the concentrations of dissolved ions in water-extract. It is influenced by the presence of inorganic dissolved solids but the organic compounds, such as oil/sugars do not pass electrical current very well and, therefore, have a low conductivity. It is also affected by temperature; warmer solution show relatively higher value; therefore, EC measurements are reported at 25°C (Boman *et al.*, 2002). Similarly, total dissolved solids (TDS) are a measure of dissolved materials in water indicating the salinity behaviour. They help to regulate the flow of water in and out of organisms' cells. These have many implications in the control of biological and physical wastewater treatment processes. Water containing more than 500 mg/L of TDS is not considered desirable for drinking purpose, however, in unavoidable cases 1500 mg/L is also allowed (ISCA, 2011).



### **1.6.3 Soil Organic Matter**

It represents the organic constituents of the soil and may consist of animal and plant remains at numerous stages of decomposition. The results of organic contents on soil fertility, the use of animal composts for retaining the soil fertility and the effect of plant species on the transformation of humus show its importance in the biochemical reactions of soil. Generally, the soil organic matter is made up of a complex mixture of dominantly colloidal organic substances comprising acidic functional groups (Baldock and Nelson, 2000).

## **1.7 Objectives of the Present Study**

Considering the environmental significance of potentially toxic metal pollutants in soil, the present study is based on the following broad objectives:

- To develop the baseline data on present status of physicochemical parameters and the metal levels in the soil collected from metropolitan areas of Lahore.
- To evaluate the bioaccessibility and mobility of the metal contents in the soil.
- To appraise the comparative distribution of the metals in different soil extracts.
- To find out the mutual associations among the metal levels in the soil.
- To assess the pollution index associated with the metal contents in the soil in terms of contamination factor, geoaccumulation index, enrichment factor and degree of contamination.
- To identify the major pollution sources for the metals in the soil by multivariate statistical methods.
- To estimate the human health risks associated with the prevailing metal levels in the soil through ingestion and dermal adsorption.

## Chapter 2

# EXPERIMENTAL METHODOLOGY

### 2.1 Site Description

Lahore city is located on NE side of Punjab Province, Pakistan ( $31^{\circ}32'59''\text{N}$  and  $74^{\circ}20'37''\text{E}$ ); it is surrounded by fertile alluvial plains. In 1972, total population of the city was 2.17 million which reached 9.75 million in 2014 with an increase of almost 450% in four decades. This megacity is one of the most industrialized areas on the Asian subcontinent with severe pollution issues (Rattigan *et al.*, 2002; Ghauri *et al.*, 2007). In addition to the local industry, Lahore is a hub on the national highway system with an influx of heavy traffic (Waheed *et al.*, 2006). It is undergoing rapid population growth and the demands of residential areas has been increasing with increasing urban population. In 1972, land surface covered by built-up area of the city was  $103.4 \text{ km}^2$  which has jumped to  $1773 \text{ km}^2$  in 2012. Growing demand of the buildings for residential and administrative purposes has expanded the city tremendously; especially toward south-east of the city. It houses architecturally important buildings and monuments, many dating from the Mughal Empire (1526-1707), during which the city achieved great prominence. It is located in area with semi-arid type of climate. In summer, average temperature exceeds  $40^{\circ}\text{C}$  and, in winter, it touches freezing point with dense fog. Most of the precipitation is received during monsoon season that starts in late June and ends in September. The increasing population and changing land-cover of the city have adverse effects on its environment (Younas *et al.*, 1997).

### 2.2 Sample Collection and Storage

During the present study, soil samples were collected from various urban areas of Lahore including roadsides, parks/playgrounds and adjoining fields as shown in Figure 1. The detailed descriptions of the sampling locations are given in Table 1. Sampling was carried out during dry season (with no precipitation for at least preceding seven days) and the samples were collected from the areas where plants with superficial roots were not present. A total of 56 composite soil samples were collected in winter 2015. The samples were collected from 5–10 cm topsoil layer using a plastic spatula. Every composite sample was made of 5-10 sub-samples of equal proportion from an area of 10-20  $\text{m}^2$  and

thoroughly mixed. The soil samples were stored in zip-locked polythene bags for transportation and storage (Argyaki and Kelepertzis, 2014). The collected samples were carefully transported to the laboratory for further processing and analysis.

The soil samples were further processed in the laboratory. The large items such as, stones, wood pieces, grass, straws, etc., were manually removed from the samples. In the next step, the samples were dried in an electric oven at 80°C for at least 48 hours, disaggregated and sieved to < 2 mm fraction. The representative portion of each sample was stored in a pre-cleaned zip-locked polythene bag and placed in desiccators until further treatment.

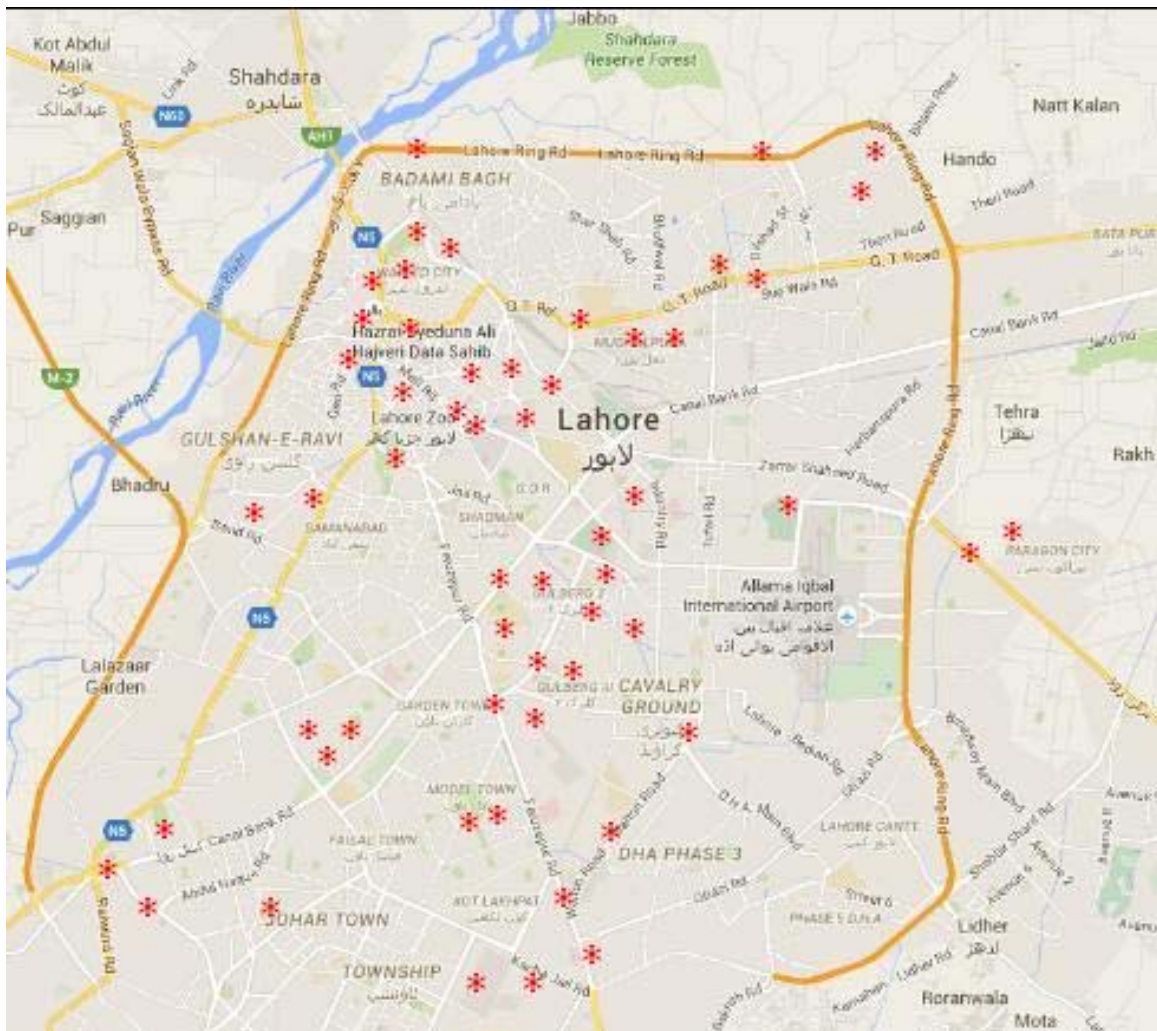


Figure 1. Location of the sampling points (\*) in the study area (Lahore)

Table 1. Description of the sampling locations from Lahore, Pakistan

Sample Code	Sampling Location
S-001P	Jam-Sherin Park, Ali Zeb Road, Gulberg-III, Lahore
S-002P	Society Linear Park, Ferozpur Road, Model Town, Lahore
S-003P	Model Town Park, Model Town, Lahore
S-004R	Ferozpur Road, Kalima Chowk , Lahore
S-005P	Punjab University Ground, Old Campus, Anarkali, Lahore
S-006R	Bahawalpur Road, Miani Sahib Graveyard, Chauburji, Lahore
S-007R	Lytton Road, Govt. College of Technology for Women, Lahore
S-008R	Mall Road, GPO, Lahore
S-009P	Jinnah Garden, Mall Road, Lahore
S-010R	Zarrar Road, Sadar Gol Chakar, VIP Store, Dharampura, Lahore
S-011R	Ring Road, WAPDA Grid Station Daegu, DHA Phases IV and V, Lahore
S-012A	Agricultural Land, Ring Road, DHA Phases IV/V, Lahore
S-013R	Barki Road, LSE, DHA Phase VI, Lahore
S-014A	Agricultural Land, Barki Road, LSE, DHA Phase VI, Lahore
S-015P	Park, Askari 10, Lahore
S-016R	Bakhsh Road, DHA, Lahore
S-017R	Ferozpur Road, Nishtar Colony, Lahore
S-018R	Ferozpur Road, Gajumata, Lahore
S-019A	Agricultural Land, Ferozpur Road, Gajumata, Lahore
S-020A	Agricultural Land, Main Rohi Nala, Double Road, Lahore
S-021R	Walton Road, Cantt, Lahore
S-022P	Cavalary Ground Park, Cantt, Lahore
S-023R	Davis Road, Total Fuel Station, Lahore
S-024P	Jilani Park (Race Course Park), Jail Road, Lahore
S-025A	Agricultural Land, PU New Campus, Canal Bank Road, Lahore
S-026P	Ground, Punjab University New Campus, Canal Bank Rd, Lahore
S-027P	Lawns, Punjab University New Campus, Canal Bank Road, Lahore
S-028P	Park, Old Anarkali, Lahore
S-029P	Park, Data Darbar Road, Lahore

Sample Code	Sampling Location
S-030P	Family Park, Multan Road, Lahore
S-031P	Shahi Qila, Fort Road, Lahore
S-032P	Iqbal Park, Minar-e-Pakistan, Circular Road, Lahore
S-033R	Hussain Chowk Gulberg-III, Lahore.
S-034R	Main Boulevard Road, Gulberg, Lahore
S-035P	Main Market, Gulberg, Lahore
S-036R	Mumtaz street, Allama Iqbal Road, Garhi Shaho, Lahore
S-037P	Shalimar Garden, GT Road, Near Baghbanpura, Lahore
S-038R	GT Road, Shalimar Garden, Near Baghbanpura, Lahore
S-039R	Lari Adda, Circular Road, Lahore
S-040R	Ravi Road, Total CNG, Niazi Chowk, Lahore
S-041P	Nur Jahan Tomb, Shahdara Bagh, Ravi Road, Shahdara, Lahore
S-042R	Ravi Road, Shahdra, Lahore
S-043R	Bund Road, Ravi Grid Station, Badami Bagh, Lahore
S-044R	GT Road, Railway Station, Lahore
S-045P	Railway Station Park, GT Road, Railway Station, Lahore
S-046R	Durand Road, Queen Marry College, Lahore
S-047R	Shami Road, Infantry Chowk, Cantt, Lahore
S-048R	Main Ghazi Road, Defence Thana, Defence, Lahore
S-049R	Stadium Road, G-Block Thana, DHA, Lahore
S-050R	Multan Road, Bader Pura Stop (Ever New studio), Hassan Town, Lahore
S-051R	Thokar Round, Rescue 1122, Thokar Niaz Biag, Lahore
S-052A	Agricultural Land, Thokar Niaz Baig Flyover, Thokar Niaz Baig, Lahore
S-053P	Bag-Stop Play Ground, Multan Road, Lahore
S-054R	Main Samanabad Road, Sozuki Motors, Saman Abad, Lahore
S-055P	Jangla Park, Allama Iqbal Town, Lahore
S-056P	Rahim Park, Gulberg III, Lahore

P= Parks, R= Roads, A= Agricultural Land

## 2.3 Extraction Procedures

Toxic trace metals can be present in soil forming physicochemical associations of different availabilities, such as simple or complex ions in soil solution, exchangeable ions, linked to organic substances, co-precipitated with oxides, carbonates and phosphates, or other secondary minerals and ions in the crystalline lattices of primary minerals (Soon and Bates, 1982). Therefore, the assessment of the environmental risks requires not only the total amount of toxic metals in the soil to be measured, but also the amounts of toxic trace metals in each association form particularly to evaluate their accessibility and mobility in the soil. Most widely used methods for the identification and evaluation of the availability and mobility of toxic trace metals in the soil involved leaching of the soil with different chemical extractants. Hence for the estimation of bioaccessibility and mobility of the metals in soil, following five extraction methodologies were applied in the present study.

### 2.3.1 Glycine Extraction

Due to bioethical considerations and constraints of costs and time, during the last few years in-vitro extraction tests are being developed to determine the oral bioaccessibility which shows the fraction of a substance that is soluble in the gastrointestinal environment and is available for absorption as a conservative estimate of its bioavailability. Human oral bioaccessibility of toxic metals in the soil can be assessed by physiologically based extraction test originally developed by Ruby *et al.* (1996) simulating the chemical environment of the human gastrointestinal system. Owing to its complexity, an in-vitro simple bioaccessibility extraction test (SBET) has been alternatively applied to several studies providing useful information on the solubility of potentially toxic metals in a medium compositionally similar to acid gastric fluids (Oomen *et al.*, 2002). It has a strong ability to extract the metals from soil, which is much greater than neutral salt extraction and close to dilute acid and complex extraction. In this method, the metals were determined by simulating the low pH conditions of the human gastric fluids. Initially, 50 mL of 0.4 M glycine extraction solution (adjusted to pH 1.5 with concentrated HCl) was added to 0.5 g of the soil. The suspension was quickly placed in a water bath and agitated at 37°C for 1 hour. The extracts were separated from the solid residue by centrifugation at 3000 rpm for 10 min. The supernatant was filtered through 0.45 µm filter paper and stored before analysis.

### 2.3.2 EDTA Extraction

EDTA forms strong complexes with many metals and it can be employed to extract the organically bonded metal contents in the soil. The EDTA extractable contents were obtained by mixing 4.0 g of soil with 40 mL of 0.05 M EDTA solution (adjusted to pH 7 with NaOH solution) at room temperature. The mixture was shaken on an auto-shaker at 25 rpm for 1 hour. The extracts were separated from the solid residue by centrifugation at 3000 rpm for 10 min (Ure *et al.*, 1993). The supernatant was filtered through 0.45 µm filter paper and stored prior to analysis.

### 2.3.3 Acetic Acid Extraction

The release of weakly bonded metals is promoted by ion exchange with cations. Ammonium acetate is generally the preferred reagent as its relatively high concentration and the metal complexing power of acetate prevents readsorption or precipitation of the released metal ions. However, ammonium salts of strong acids can lower the pH and promote the hydrolysis of clays, while the salts of weak acids such as acetate can tend to raise the pH with potential precipitation of metal hydroxides. Metal complexation by acetate counters this effect. Acetic acid also dissolves the exchangeable species but releases, in addition, more tightly bound exchangeable forms. It may partly attack the carbonate and silicate phases and dissolve the metals from specific sites on oxide minerals. In the present study, the mobilizable pools of potentially toxic metals were determined by treating 1.0 g of the soil sample with 40 mL of 0.43 M acetic acid solution at room temperature. The mixture was shaken on an auto-shaker at 25 rpm for 16 hours. The extracts were separated from the solid residue by centrifugation at 3000 rpm for 10 min (Houba *et al.*, 1996). The supernatant was filtered through 0.45 µm filter paper and stored till analysis.

### 2.3.4 Nitric Acid Extraction

The reactive/mobile forms of potentially toxic metals were assessed by using nitric acid extraction. In this method, 1.0 g of the soil sample was mixed with 40 mL of 0.43 M HNO<sub>3</sub> solution at room temperature. The mixture was shaken on an auto-shaker at 25 rpm for 2 hour. The extracts were separated from the solid residue by centrifugation at 3000 rpm for 10 min (Rodrigues *et al.*, 2010). The supernatant was filtered through 0.45 µm filter paper and stored before analysis.

### 2.3.5 Aqua regia Extraction

Aqua regia is commonly used for the digestion of solid samples and subsequent analysis as it has strong oxidizing effects. Nevertheless, the analyzed concentration after aqua-regia digestion cannot be called 'total content' since the dissolution is not complete for all kinds of matrices, especially the elements bound to the silicate matrix are not totally solubilized; hence it is often referred to as 'pseudo-total content'. The aqua regia extraction was performed by modifying the procedure recommended by the International Organization for Standardisation (ISO). In this procedure, 1.5 g soil sample was taken in 250 mL conical flask. First, the pre-digestion step was executed at room temperature for 16 h with 14 mL of HCl (37%) and HNO<sub>3</sub> (65%) in 3:1 (v/v) ratio. Then, the suspension was digested at 80°C for 2 hours on a hot plate (ISO 11466, 1995). The suspension obtained was then filtered through 0.45 µm filter paper, diluted to 50 mL with 2% HNO<sub>3</sub> and stored in polythene bottles for further analyses.

## 2.4 Measurement of the Physicochemical Parameters of Soil

### 2.4.1 pH, Electrical Conductivity and Total Dissolved Solids

In the present study, pH of soil samples was measured in their water extracts which were obtained by taking 20.0 g soil sample in 40 mL distilled water which was shaken for 30 minutes on an auto-shaker at 300 rpm. A pre-calibrated pH meter was employed for the measurement of pH of the soil solution. Buffer solutions of pH 4.0, 7.0 and 9.6 were used to calibrate the pH meter. After the calibration, the electrode was dipped in the soil solution and the pH was recorded. In case of drift, the reading was allowed to stabilize before recording (Radojevic and Bashkin, 1999). Electrical conductivity (EC) is related to the concentration of ionized substances in the soil sample. It is used as an approximate measure of the total concentration of soluble inorganic substances in the sample. In the present study, electrical conductivity (EC) and total dissolved solids (TDS) of the soil were determined in their water extracts as explained above. The multimeter was calibrated with 0.1 M and 0.01 M KCl solutions before recording the EC and TDS values of the soil solutions (Arain *et al.*, 2008).

### 2.4.2 Soil Organic Matter

Loss-on-ignition or dry-ashing serves as a rough indicator of the amount of organic matter present in the soil sample (Radojevic and Bashkin, 1999). For the determination of



moisture, about 1.0 g of the soil sample was placed in a pre-weighed crucible. The crucible along with the specimen was kept, without a cover, in the preheated drying oven (104-110°C). The oven was closed and the sample was heated for 1 hour; afterwards, the crucible was removed, covered immediately with lid, allowed to cool to ambient temperature in a desiccator and weighed. For dry-ashing, the crucible, along with the dried soil sample was positioned without cover in a furnace and the temperature was raised to 500°C. The temperature was maintained for 4 hours or until the sample reached a constant weight. The loss-on-ignition or organic matter was calculated by the weight difference before ( $m_1$ ) and after ( $m_2$ ) ashing the sample (Radojevic and Bashkin, 1999).

$$\text{Loss-on-ignition} = [(m_1 - m_2)/m_1] \times 100 \quad [1]$$

### 2.4.3 Soil Texture

In the present study, soil texture was determined by the ASTM 422 method (1998). Dried soil sample (50 g) was mixed with 125 mL of sodium hexametaphosphate (40 g/L) solution which was used as a dispersing agent. The resulting mixture was stirred until the soil got thoroughly wet. The soil was soaked for 16 hours at room temperature. Similarly, 125 mL of the dispersing agent was added into a control cylinder and diluted with distilled water up to the mark. Reading was taken as upper meniscus formed by the control solution and the hydrometer stem. The difference between the level of solution in the jar and the top of the meniscus is called the meniscus correction. Control cylinder was shaken to get its contents thoroughly mixed. Temperature and zero correction were noted by inserting thermometer and hydrometer, respectively. Soil slurry was thoroughly mixed after 16 hours, transferred to sedimentation cylinder and filled with distilled water up to the mark. Mixture was vigorously agitated by covering the open end of the cylinder with a stopper. Readings were taken by observing the upper meniscus formed by the hydrometer stem and the suspension. The hydrometer was slowly removed and put back into the control cylinder. Readings were taken after time period of 2, 5, 15, 30, 60, 250 and 1440 minutes. The suspension was transferred to a No. 200 sieve after taking the final hydrometer reading and washed with tap water until the wash water was clear. Residue, retained on the sieve No. 200 (75  $\mu\text{m}$  openings), was transferred to a suitable container dried in an oven at 105°C and was passed through a series of sieves of mesh numbers, i.e., 10 (1.68 mm), 25 (0.707 mm), 35 (0.420 mm), 48 (0.297 mm), 65 (0.210 mm), 100 (0.149 mm), 120 (0.125 mm), 140 (0.106mm), 170 (0.088 mm), 200 (0.075mm). Percentage of each fraction was calculated by determining the mass of each fraction retained on the sieve. In case of

hydrometer, the equivalent particle diameter ( $D$ ) was calculated by following equation:

$$D = K \sqrt{\frac{L}{t}} \quad [2]$$

where  $K$  is the constant that depends on the specific gravity of the soil particles and the temperature of the suspension;  $L$  is the effective depth for hydrometer in cm and  $t$  is the time in minutes. The percentage of each fraction was calculated by following relationship:

$$P = [(100000/W)G/(G - G_1)](R - G_1) \quad [3]$$

where  $P$  is the soil percentage in suspension as measured by hydrometer;  $W$  is oven-dried mass of soil in a total test sample;  $G$  is soil particles' specific gravity;  $G_1$  is specific gravity of suspension liquid;  $R$  is hydrometer reading with composite correction applied.

The percentage ( $P$ ) of different particles sizes present on the sieve was calculated by following equation;

$$P = \frac{\text{Mass.retained.on.each.sieve}}{\text{Initial.mass}} \times 100 \quad [4]$$

## 2.5 Quantification of the Metal Contents in Soil

Flame atomic absorption spectrometry (FAAS) is one of the most commonly used techniques in analytical laboratories for elemental analyses as it has a number of advantages, such as high selectivity, speed, fairly low operational cost and sensitivity up to ppm/ppb levels (Durana *et al.*, 2009; Ivanova *et al.*, 2004; Patnaik, 2010). This technique is similar to other high resolution spectroscopic techniques but it differs in the nature of radiation source and the use of heat energy to generate the absorbing species (Lagalante, 2004). Element selectivity and analytical sensitivities are important features of this technique. The working principle of the instrument is based on Beer's Law; absorbance is directly proportional to the concentration of analyte in the sample. In the present study, flame atomic absorption spectrophotometer (Shimadzu AA-670, Japan) was used for the quantitative measurement of potentially toxic metals (Cd, Co, Cr, Cu, Fe, Mn, Pb, and Zn) in the soil samples under optimum analytical conditions which are mentioned in Table 2. Quantification of the metals in the soil was conducted by calibration line method. Working standards were prepared from the stock solutions (1000 mg/L) of each metal which were procured from E-Merck or BDH.

Table 2. Optimum analytical conditions for the analysis of selected metals using air-acetylene flame (Shimadzu AA-670, Japan)

Metal	Wavelength (nm)	HC lamp current (mA)	Slit width (nm)	Fuel-gas flow rate (L/min.)	1% Absorption concentration (ppm)
Cd	228.8	4.0	0.3	1.8	0.02
Cr	357.9	5.0	0.5	2.6	0.09
Pb	217.0	7.0	0.3	1.8	0.20
Cu	324.8	3.0	0.5	1.8	0.09
Co	240.7	6.0	0.2	2.2	0.20
Zn	213.9	4.0	0.5	2.0	0.02
Mn	279.5	5.0	0.4	1.9	0.05
Fe	248.3	8.0	0.2	2.0	0.10

## 2.6 Quality Control and Quality Assurance

Quality control/assurance protocol prescribed by the US Environmental Protection Agency (USEPA) for metal analysis was followed in this study. In order to control the analytical procedure, precision of the analytical results was assured by replicate analysis. The laboratory glassware used for the analysis was washed with 0.1 M HNO<sub>3</sub>, rinsed at least thrice with distilled water and dried in an electric oven. All the chemical reagents used were of analytical grade procured from either BDH or Merck. Certified standard solutions (1000 mg/L) of Cd, Cu, Co, Cr, Fe, Mn, Pb and Zn were used for the preparation of working standards which were prepared afresh every time on the day of analysis. Reliability of the instrumental results was checked by analyzing the standard reference material (NIST SRM 2710). Generally, a maximum of  $\pm 2\%$  difference was observed in the measured and certified levels. Doubly distilled water utilized used for the preparation of samples, standards and reagents throughout this study.

## 2.7 Statistical Analysis

Descriptive statistical analysis included minimum, maximum, mean, median, standard deviation (SD), standard error (SE), skewness and kurtosis which showed the variations, dispersion and symmetry of the individual variables in the data-set. In order to explore the extent of mutual relationships between the variables, correlation study was

carried out in terms of Spearman correlation coefficients (Gong *et al.*, 2010). In addition, multivariate analysis comprising principal component analysis (PCA) and cluster analysis (CA) were performed on the data-set using the STATISTICA software (StatSoft, 1999). Multivariate statistical methods have many applications in environmental studies; they are particularly useful when there is a large volume of experimental result. Sometimes they provide insight into the multidimensional patterns in the data that may be overlooked with univariate analyses. They are used to differentiate between various sources that cause variations in the soil composition (Li and Feng 2012). PCA is the most widely employed tool in environmental sciences because it not only reduces the number of variables but also delineates that each extracted component is associated with a source characterized by its most representative elements (Mishra *et al.*, 2016). It is a method of source apportionment which was approved and recommended by the US Environmental Protections Agency. This was performed by utilizing the orthogonal transformation method with varimax rotation and retention of principal components whose eigen values were greater than unity (Almeida-Silva *et al.*, 2016). CA organizes a set of variables into two or more mutually exclusive unknown groups based on a combination of internal variables (Lu *et al.*, 2010). Clustering is the statistical operation of grouping the variables into a limited number of groups known as clusters or segments, which have two properties; they are not defined in advance by the analyst but are discovered during the operation and the variables with smaller distance are more similar than those with longer distances and, therefore, could be grouped within the same cluster (Cesari, 2007). The obtained results are displayed in a dendrogram, which exhibits degree of similarity among the variables. This is a very efficient method to explore highly stable group structures (Li *et al.*, 2013). PCA and CA are complementary techniques; both compress a large amount of data into more manageable groups and increase the significance (Guillen *et al.*, 2012; Iqbal *et al.*, 2016).

## **2.8 Pollution Assessment**

Pollution assessment related to the existing metal levels in the soil was executed by various factors/indices which are explained below.

### **2.8.1 Contamination Factor**

The potential soil contamination can be assessed using contamination factor ( $C_f$ ) in which the mean metal concentration measured in the soil samples is compared to the

baseline reference level in earth crust according to the following relationship (Hakanson,1980; Abraham and Parker, 2008):

$$C_f = \frac{C_n}{C_b} \quad [5]$$

where ‘ $C_n$ ’ and ‘ $C_b$ ’ refer to the mean concentrations of a metal in the soil and earth’s crust, respectively.  $C_f$  values were interpreted as  $C_f < 1$  — low contamination;  $1 \leq C_f < 3$  — moderate contamination;  $3 \leq C_f < 6$  — considerable contamination, and  $6 \leq C_f$  — very high contamination.

### 2.8.2 Geoaccumulation Index

Geoaccumulation index ( $I_{geo}$ ) is used to assess the level of soil contamination and/or pollution. It was computed using following equation developed by Muller (1969):

$$I_{geo} = \log_2 \left( \frac{C_n}{1.5B_n} \right) \quad [6]$$

where ‘ $C_n$ ’ is the average concentration of metal in the studied soil and ‘ $B_n$ ’ is the concentration of metal in the pre-industrial sample. The factor 1.5 is applied to minimize the probable variations in pre-industrial levels due to lithogenic effects.  $I_{geo}$  values were interpreted as;  $I_{geo} \leq 0$  — practically uncontaminated;  $0 < I_{geo} < 1$  — uncontaminated to moderately contaminated;  $1 < I_{geo} < 2$  — moderately contaminated,  $2 < I_{geo} < 3$  — moderately to heavily contaminated;  $3 < I_{geo} < 4$  — heavily contaminated;  $4 < I_{geo} < 5$  — heavily to extremely contaminated and  $I_{geo} > 5$  — extremely contaminated (Iqbal and Shah, 2011; Loska *et al.*, 2004; Saleem *et al.*, 2013).

### 2.8.3 Enrichment Factor

The extent of metal pollution due to anthropogenic activities in the soil samples can be gauged engaging enrichment factor (Duan *et al.*, 2010; Sutherland, 2000; Vega *et al.*, 2009). Enrichment factor ( $EF$ ) represents the pollution level in the soil and is a good tool to differentiate between the anthropogenic and natural sources of the metals. It can be calculated by following relation:

$$EF = \frac{[X / M_{ref}]_{sample}}{[X / M_{ref}]_{crust}} \quad [7]$$

where  $[X/M_{ref}]_{sample}$  and  $[X/M_{ref}]_{crust}$  refer to the ratio of mean concentrations (mg/kg, dry weight) of the target metal ( $X$ ) and the reference metal ( $M_{ref}$ ) in the examined soil and

continental crust, respectively. A number of different metals such as Al, Ti, Mn, Mg, Sr, Fe, etc. have been employed as reference metals in the previous studies. In the present study, Fe was considered as the reference metal. *EF* values were interpreted as:  $EF < 2$  — minor enrichment,  $EF = 2$  to  $5$  — moderate enrichment,  $EF = 5$  to  $20$  — significant enrichment,  $EF = 20$  to  $40$  — very severe enrichment and  $EF > 40$  — extremely severe enrichment (Abraham and Parker, 2008; Grant and Middleton, 1990; Loska *et al.*, 1997).

#### 2.8.4 Degree of Contamination

Hakanson (1980) proposed that the numeric sum of the contamination factors expressed the overall degree of soil contamination ( $C_{deg}$ ). Degree of contamination is generally defined as the sum of all the contamination factors ( $C_f$ ) for a given set of pollutants. It showed an overall degree of contamination in the soil using following equation:

$$C_{deg} = \sum_{i=1}^{i=n} C_f^i \quad [8]$$

where ' $C_f$ ' is the single metal contamination factor and sum of the  $C_f$  of all metals represented the degree of contamination ' $C_{deg}$ '. It is aimed at providing a measure of the degree of overall contamination in surface layers in a particular core or sampling sites.

## 2.9 Human Health Risk Assessment

In case of the soil, human exposure to the metals can occur through three main pathways (i) direct oral ingestion of the soil particles; (ii) inhalation of the suspended particulates through mouth/nose; (iii) dermal absorption of the metals in particles adhered to the exposed skin. Amongst these routes, oral intake and dermal contact are most significant exposure routes which can be calculated as (USEPA, 1989 & 2004):

$$Exp_{ing} = \frac{C_{soil/sed} \times IR \times CF \times EF \times ED}{BW \times AT} \quad [9]$$

$$Exp_{derm} = \frac{C_{soil/sed} \times CF \times SA \times AF \times ABS \times EF \times ED}{BW \times AT} \quad [10]$$

where  $Exp_{ing}$  is ingestion exposure (mg/kg-day);  $Exp_{derm}$  is dermal uptake (mg/kg-day);  $C_{soil/sed}$  is mean concentration of the metals in soil or sediments (mg/kg);  $IR$  is ingestion rate (mg/day);  $CF$  is unit conversion factor (kg/mg);  $EF$  is exposure frequency (days/year);  $ED$  is exposure duration (years);  $BW$  is body weight (kg);  $AT$  is average time

(years);  $SA$  is surface area ( $\text{cm}^2/\text{day}$ );  $AF$  is adherence factor for soil/sediments to the skin ( $\text{mg}/\text{cm}^2$ ) and  $ABS$  is dermal absorption from soil/sediments (unitless). These parameters are explained in Appendix I.

Non-carcinogenic risk in terms of hazard quotient ( $HQ$ ) can be computed following standard USEPA (2004) methodology as:

$$HQ_{ing/derm} = \frac{Exp_{ing/derm}}{RfD_o} \quad [11]$$

where  $HQ_{ing/derm}$  - hazard quotient through ingestion or dermal route (unitless);  $RfD_o$  - oral reference dose ( $\text{mg}/\text{kg}\text{-day}$ ). Generally, the hazard quotient values below unity are considered safe/non-hazardous.

To determine overall non-carcinogenic risk posed by all the metals, hazard index ( $HI$ ) is calculated using the following expression (USEPA, 1989):

$$HI = \sum_{i=1}^n HQ_{ing/derm} \quad [12]$$

## Chapter 3

# RESULTS AND DISCUSSION

### 3.1 Physicochemical Characteristics of Soil

The physicochemical parameters of the soil including pH, EC, TDS and organic matter were evaluated in the present study. The measured levels of the pH in the soil samples are shown in Figure 2 for comparative assessment. In the present study, the pH of the soil samples varied from 6.35 to 9.85, however, most of the samples exhibited the pH in the range of 6.5 to 7.5 and only a small number of samples exceeded this range. Thus, most of the soil samples exhibited nearly neutral pH or slightly alkaline nature. Similarly, comparison of the electrical conductivity (EC) values measured in the soil samples is presented in Figure 3. The EC values in the soil samples ranged from 212 to 5540  $\mu\text{S}/\text{cm}$ . Although most of the soil samples revealed EC values less than 1000  $\mu\text{S}/\text{cm}$  but about one third of the samples indicated EC levels in excess of 1000  $\mu\text{S}/\text{cm}$ . Thus, the soil samples manifested significant amount of dissolved minerals.

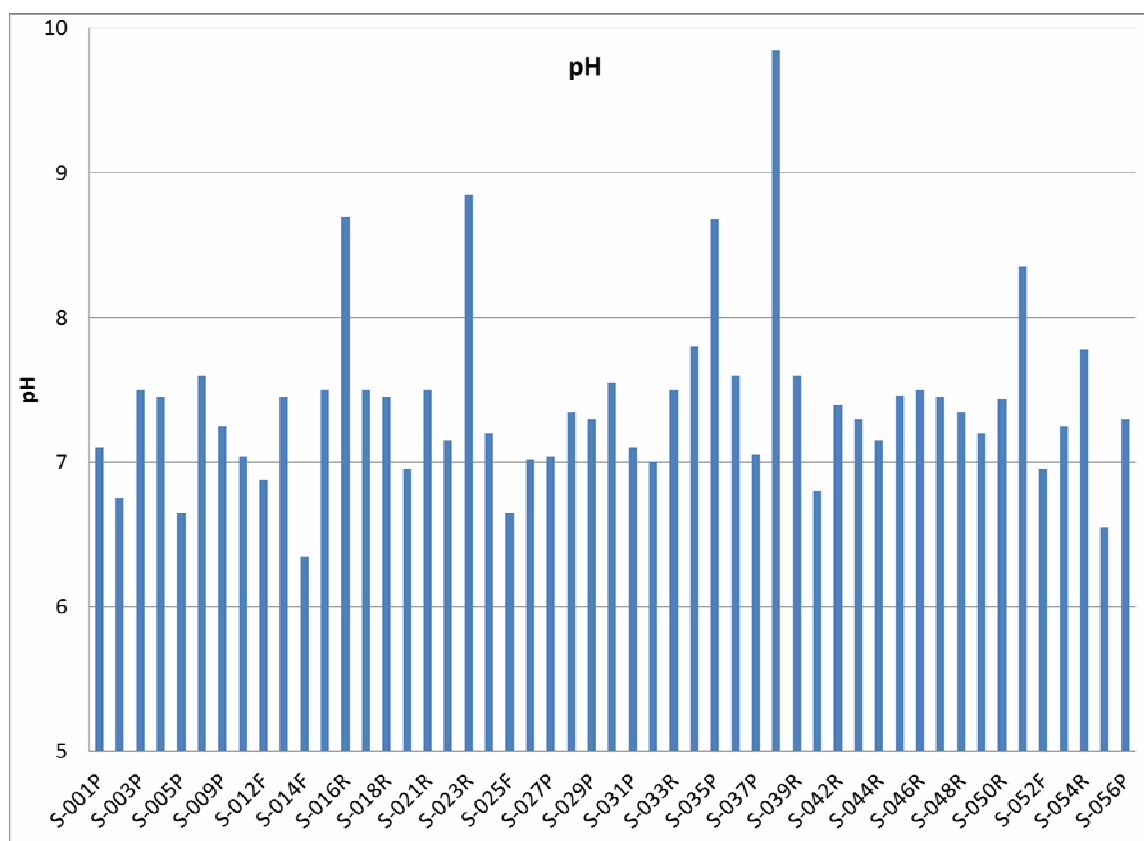


Figure 2. Comparison of the pH values in the soil samples



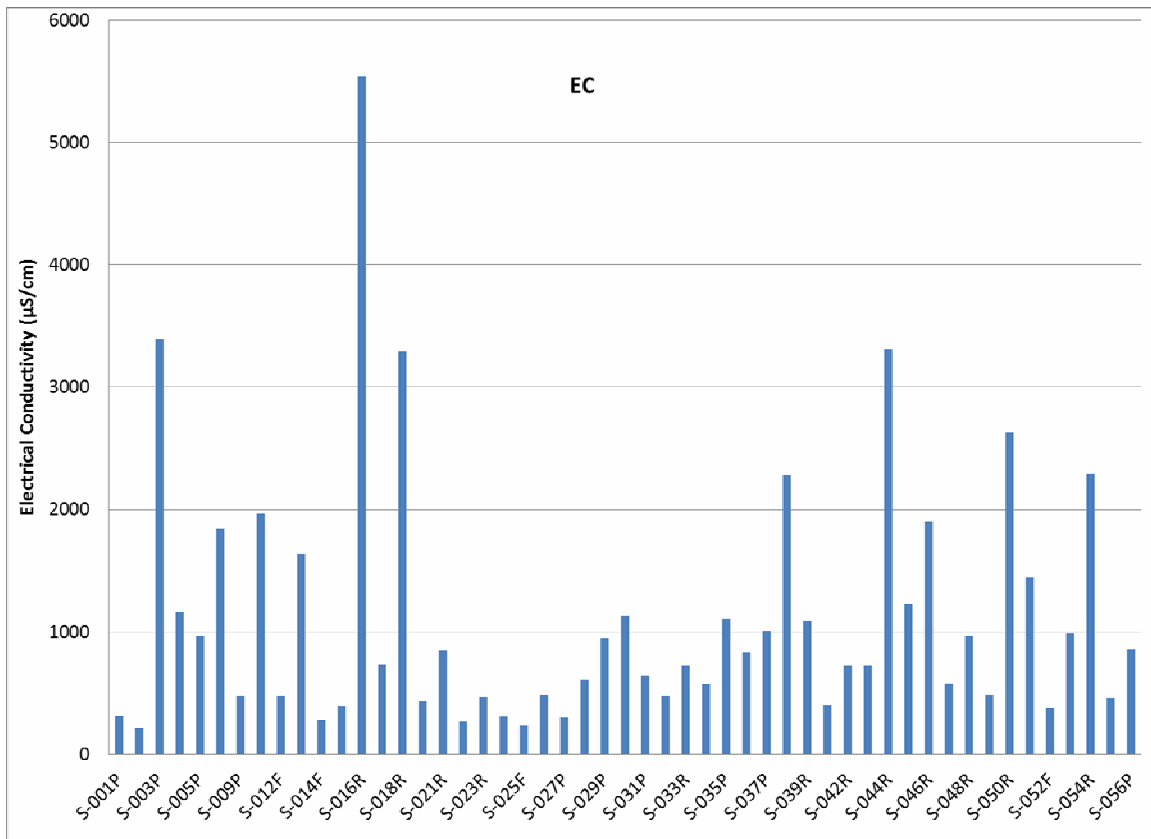


Figure 3. Comparison of the EC values (µS/cm) in the soil samples

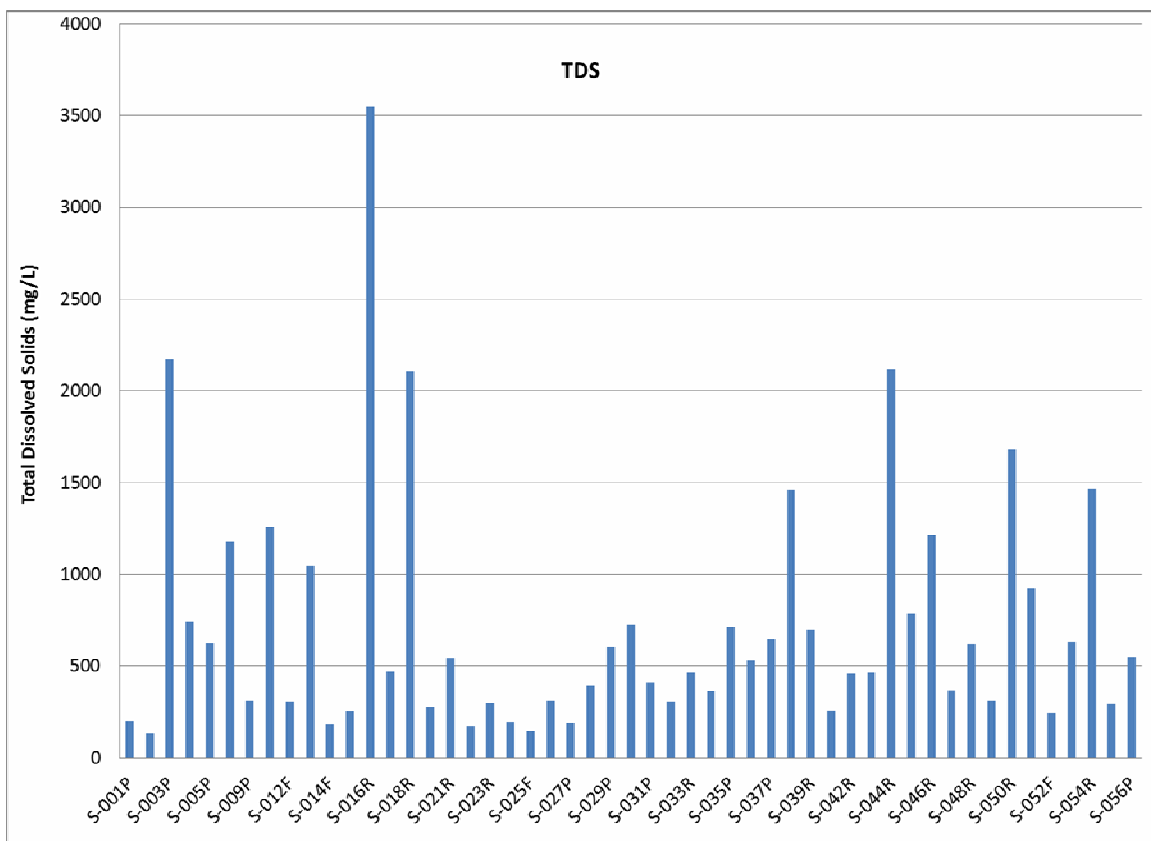


Figure 4. Comparison of the TDS values (mg/L) in the soil samples

Another parameter directly related to the EC is total dissolved solids (TDS) and the variations in TDS values in the soils samples are shown in Figure 4. In the present study, the TDS values ranged from 136 to 3546 mg/L. For majority of the soil samples, the TDS values remained less than 1000 mg/L and, once again it revealed significant amount of dissolved ions in the soil samples collected from the urban areas of Lahore. Another important characteristic of the soil is its organic content and the comparison of organic matter of the soil samples is shown in Figure 5. Organic content of the soil ranged from a minimum of 2.1% to a maximum of 10.5% in the present study; however, for majority of the soil samples, the organic matter was noted between 3 to 6%. Relatively higher amounts of the organic matter in the soil generally indicated the anthropogenic influence on the soil samples, although some natural processes including decaying vegetation also increased the organic content of the soil.

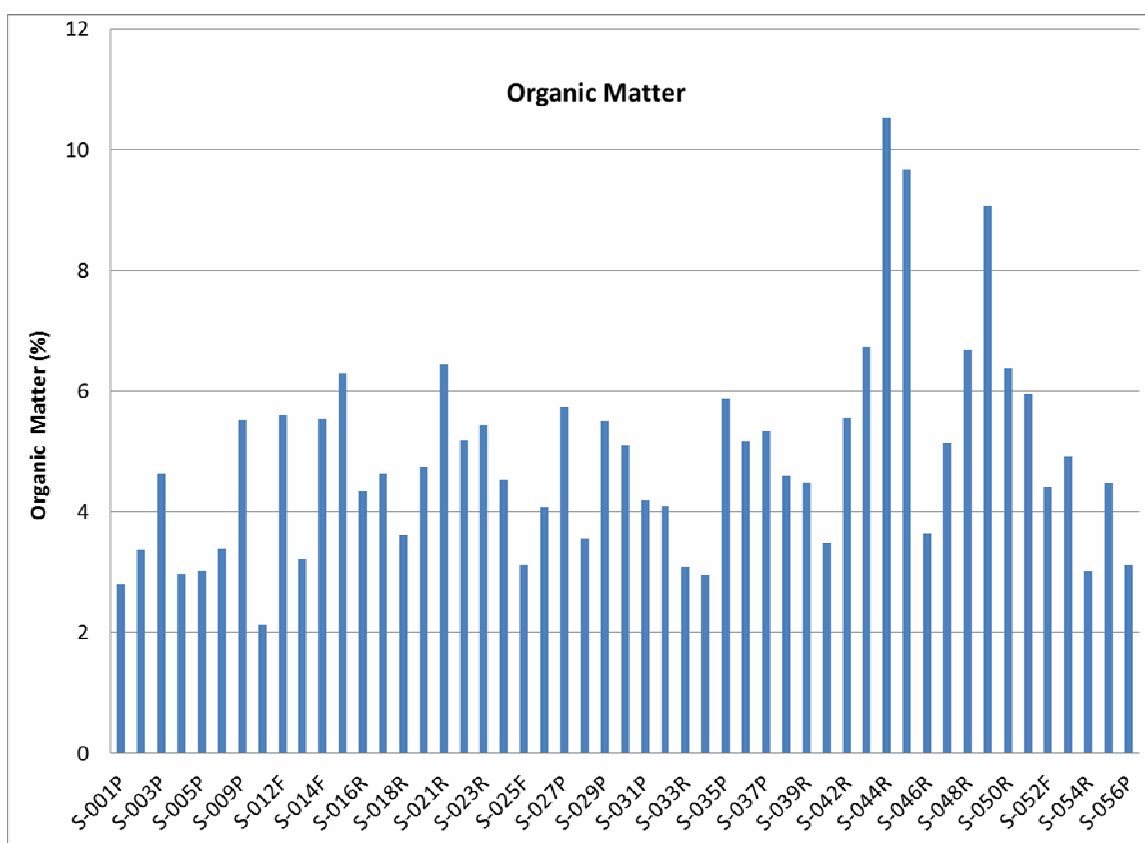


Figure 5. Comparison of the organic matter (%) in the soil samples

### 3.2 Distribution of the Metals in Glycine Extract of Soil

Metal fractions extracted in the glycine solution are generally considered as bioavailable and bioaccessible for humans particularly from the ingested soil particles. Table 3 gives selected metal concentrations (mg/kg, dry weight) in terms of the basic statistical distribution parameters in glycine extract of the soil. Large spread in the metal levels was observed as manifested by the minimum and maximum levels. On the average, highest contribution was recorded for Fe at 579.6 mg/kg, followed by Mn (174.2 mg/kg), Zn (74.72 mg/kg) and Pb (49.74 mg/kg), while mean concentrations of Co, Cu, Cr and Cd were found at 46.92 mg/kg, 19.28 mg/kg, 7.103 mg/kg and 3.357 mg/kg, respectively. More or less equivalent mean and median levels in the soil samples were noted for Mn thus suggesting consistent variations in the soil fraction. On the mean scale, metal levels in the glycine extract of the soil exhibited following decreasing trend as depicted in Figure 6: Fe > Mn > Zn > Pb > Co > Cu > Cr > Cd. Comparatively higher SD and SE values of Fe, Zn, Mn, Pb and Co divulged their large dispersion and predominantly random distribution in the soil fraction, while Cd, Cr and Cu showed relatively normal distribution pattern supported by reasonably lower SD and SE values (Mench and Martin 1991; Madrid *et al.*, 2008). Relatively lower kurtosis and skewness values for Cd, Pb, Co, Zn, Fe and Mn unfolded almost symmetric distribution in the soil samples; nevertheless, mostly asymmetric distribution pattern was noted for Cu and Cr as evident by rather higher values of the skewness and kurtosis. Overall, majority of the metals demonstrated relatively random/non-Gaussian distribution in glycine extract of the soil samples.

Table 3. Statistical distribution parameters for selected metal levels (mg/kg) in glycine extract of the soil

	Cd	Cr	Pb	Cu	Co	Zn	Mn	Fe
Min	0.183	0.956	0.636	5.347	0.200	7.002	105.1	156.4
Max	9.770	21.74	123.5	78.82	99.58	227.3	257.6	1287
Mean	3.357	7.103	49.74	19.28	46.92	74.72	174.2	579.6
Median	2.647	6.052	43.51	15.95	49.84	58.72	173.4	494.3
SD	2.745	4.905	31.54	13.41	26.84	52.91	32.32	316.3
SE	0.400	0.701	4.292	1.792	3.619	7.268	4.319	42.26
Kurtosis	-0.358	1.236	-0.505	7.005	-0.779	-0.095	-0.061	-0.465
Skewness	0.875	1.116	0.604	2.268	0.102	0.803	0.477	0.717

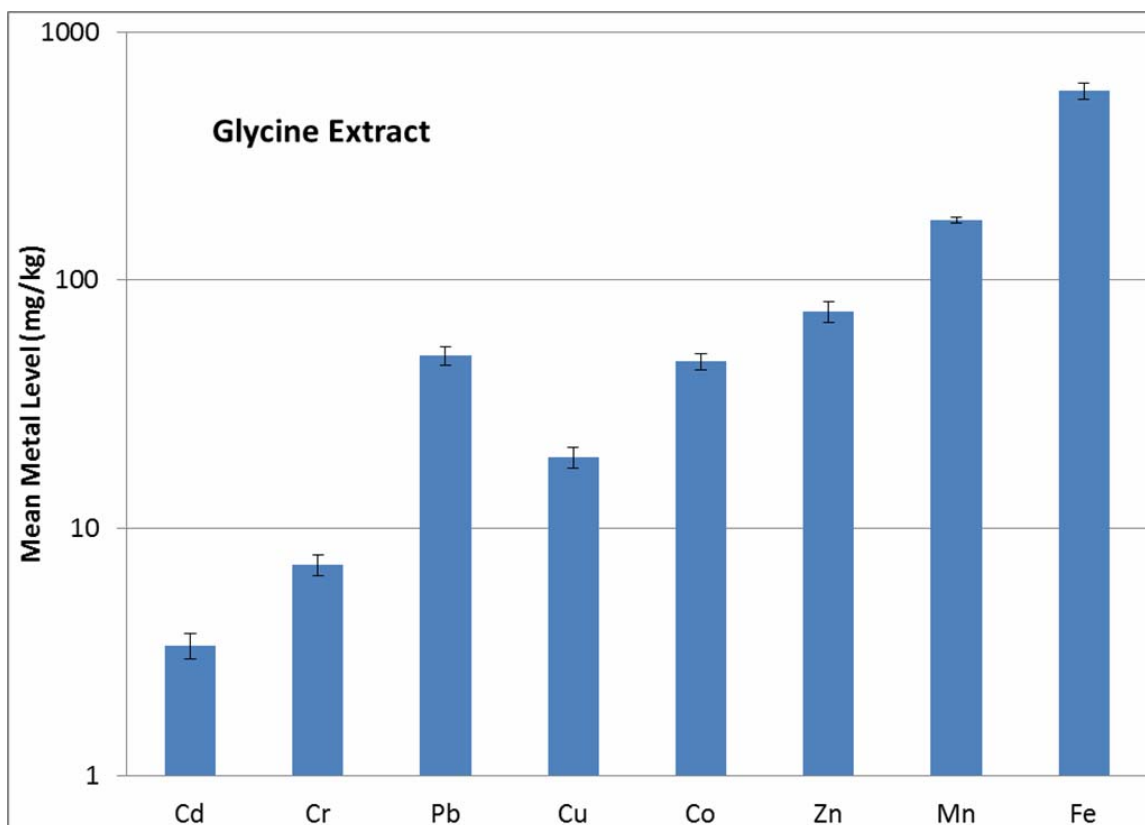


Figure 6. Comparison of average metal levels (mg/kg,  $\pm$  SE) in glycine extract of the soil

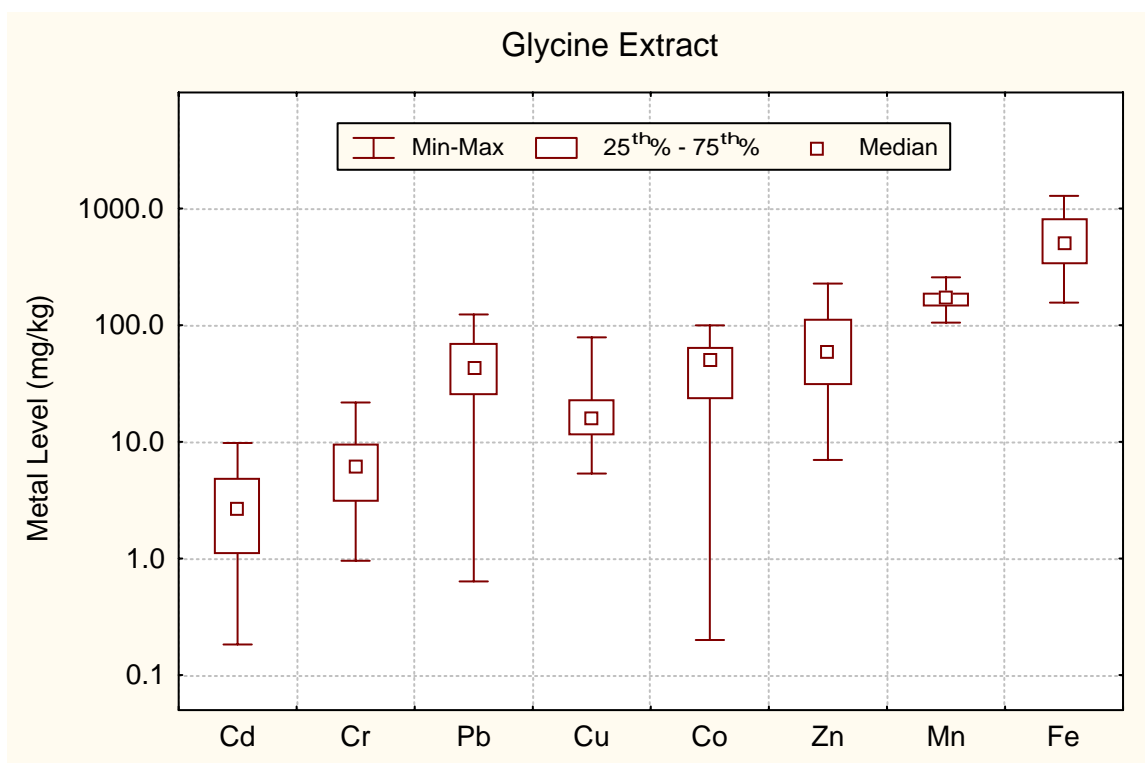


Figure 7. Quartile distribution of the metals (mg/kg) in glycine extract of the soil

Quartile distribution of the metals in glycine extract of the soil is portrayed in Figure 7 as box and whisker plot. Comparative variations of the metal levels in glycine extract of the soil revealed very broad and asymmetric spread in the distribution of Co and Pb followed by moderately broad distribution of Cu, Cr, Fe, Zn and Cd as manifested by their separate lower and upper quartiles. Nonetheless, among the metals, only Mn showed very narrow distribution as indicated by overlapping of lower and upper quartiles. Relatively symmetrical distribution was observed for Cr, Fe and Mn in the glycine extract of the soil samples.

### 3.3 Correlation Study of the Metals in Glycine Extract of Soil

Spearman correlation coefficients ( $r$ ) between the metal levels in various soil fractions were calculated to study their inter-relationships. Correlation coefficient matrix for the metal levels in glycine extract of the soil is shown in Table 4, wherein the significant  $r$ -values are presented in bold at  $p < 0.05$ . Most of the metal pairs exhibited insignificant correlations in the glycine extract of the soil. Some strong and significant relationships were noted between Zn-Cu ( $r = 0.703$ ), Fe-Zn ( $r = 0.685$ ), Fe-Cu ( $r = 0.682$ ), and Mn-Zn ( $r = 0.355$ ). The correlation study, thus, indicated mutual variations and probably common origin of Fe, Zn and Cu in glycine extract of the soil. However, Cd, Cr, Pb and Co unfolded statistically insignificant positive and negative correlations with other metals hence demonstrating their independent variations in glycine extract of the soil. Overall, the correlation study divulged mutual associations among Zn, Cu and Fe in this soil fraction.

Table 4. Correlation coefficients\* among the metal levels in glycine extracts of the soil

	Cd	Cr	Pb	Cu	Co	Zn	Mn	Fe
Cd	1.000							
Cr	0.270	1.000						
Pb	-0.065	-0.040	1.000					
Cu	0.295	0.303	0.101	1.000				
Co	0.222	0.071	-0.158	0.043	1.000			
Zn	0.132	0.175	0.114	<b>0.703</b>	-0.149	1.000		
Mn	0.218	0.184	0.007	0.255	0.051	<b>0.355</b>	1.000	
Fe	0.213	0.045	-0.049	<b>0.682</b>	0.103	<b>0.685</b>	0.247	1.000

\* $r$ -values shown in bold are significant at  $p < 0.05$

### 3.4 Comparison of the Metal Levels in Glycine Extract of Soil from Various Areas

In the present study, soil samples were collected from various urban areas which included roadsides, parks and fields. Comparison of the average metal levels (mg/kg,  $\pm$  SE) in glycine extract of the soil samples collected from different areas is shown in Figure 8. The comparative evaluation of the metal levels revealed that mean concentrations of Fe, Zn and Cu were predominantly higher in the roadside samples than the parks and fields while average levels of Cr and Co were found to be relatively higher in the samples collected from the fields. Among these metals, mean levels of Mn and Cd showed almost comparable contributions in the glycine extract of the samples collected from roadsides, parks and fields. Mean concentration of Pb in the samples collected from the fields and roadsides was almost equivalent but significantly higher than those observed in the samples collected from the parks which exhibited least contribution.

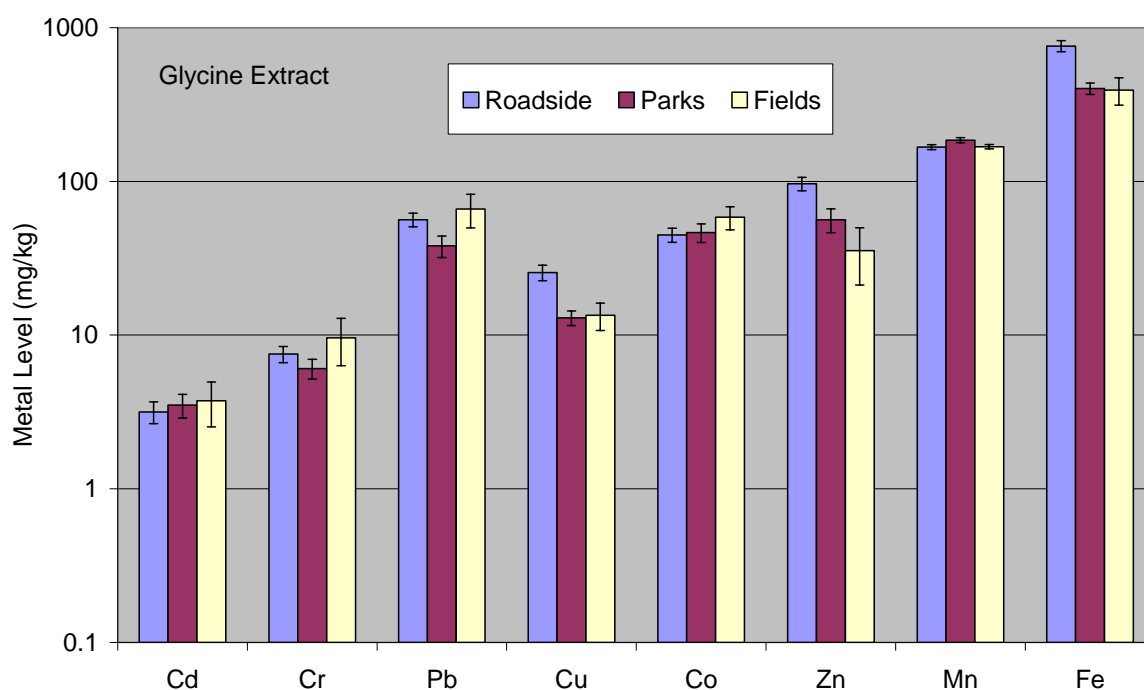


Figure 8. Comparison of the average metal levels (mg/kg,  $\pm$  SE) in glycine extract of the soil samples collected from different areas

### 3.5 Distribution of the Metals in EDTA Extract of Soil

Metal fractions extracted in the EDTA solutions are generally considered as highly phytoavailable. Statistical distribution parameters related to the concentrations of the

metals (mg/kg, dry weight) in EDTA extract of the soil are shown in Table 5. Among the selected metals, maximum concentration in this soil fraction was noted for Fe (243.6 mg/kg), followed by Mn (136.8 mg/kg), Co (88.45 mg/kg), Pb (66.68 mg/kg), Zn (60.55 mg/kg) Cu (26.88 mg/kg), Cr (3.179 mg/kg) and Cd (1.653 mg/kg) while the lowest concentrations were found for Cd (0.039 mg/kg), Cr (0.058 mg/kg), Pb (0.310 mg/kg) and Co (0.626 mg/kg). On the average basis, dominant contributions were demonstrated by Fe (84.05 mg/kg), Mn (47.73 mg/kg), Zn (27.87 mg/kg) and Co (27.26 mg/kg), while relatively lower mean levels were noted for Cd (0.608 mg/kg), Cr (0.617 mg/kg), Cu (8.314 mg/kg) and Pb (18.77 mg/kg). Comparison of the average concentrations of the metals in EDTA extract of the soil are given in Figure 9, which depicted following decreasing order: Fe > Mn > Zn > Co > Pb > Cu > Cr > Cd. More or less similar trend was also observed for the median metal levels in the soil fraction. Most of the metals exhibited almost comparable mean and median levels which indicated consistent variations of the metals in EDTA extract of the soil. Appreciably higher dispersion in the distribution was noted for Fe, Co, Mn, Zn and Pb as manifested by significantly higher SD and SE values. Among the metal contents in EDTA extract of the soil, Cd, Zn and Co showed fairly symmetric distribution divulged by rather lower skewness and kurtosis values, nonetheless, rest of the metals exhibited moderately asymmetric distribution in the soil samples. Overall, most of the metals unfolded relatively lower dispersion and asymmetry in EDTA extract of the soil compared with the previous case.

Table 5. Statistical distribution parameters for selected metal levels (mg/kg) in EDTA extracts of the soil

	Cd	Cr	Pb	Cu	Co	Zn	Mn	Fe
Min	0.039	0.058	0.310	2.931	0.626	3.651	22.66	23.65
Max	1.653	3.179	66.68	26.88	88.45	60.55	136.8	243.6
Mean	0.608	0.617	18.77	8.314	27.26	27.87	47.73	84.05
Median	0.555	0.480	16.77	6.618	18.82	24.73	41.47	74.38
SD	0.419	0.569	14.41	5.092	22.69	18.03	19.29	45.59
SE	0.062	0.079	1.926	0.680	3.059	2.431	2.578	6.093
Kurtosis	0.061	8.191	2.082	4.789	0.580	-1.060	8.730	1.354
Skewness	0.824	2.415	1.414	2.087	1.233	0.544	2.615	1.077

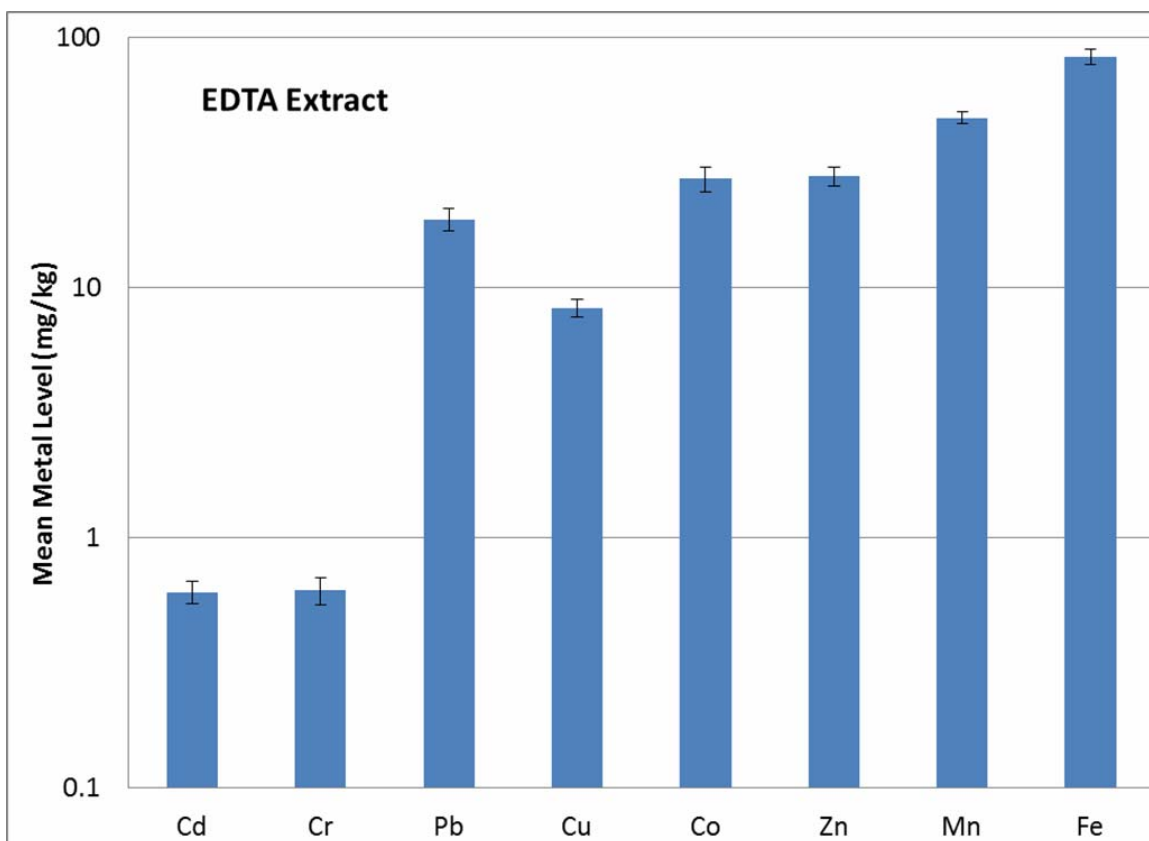


Figure 9. Comparison of average metal levels (mg/kg,  $\pm$  SE) in EDTA extract of the soil

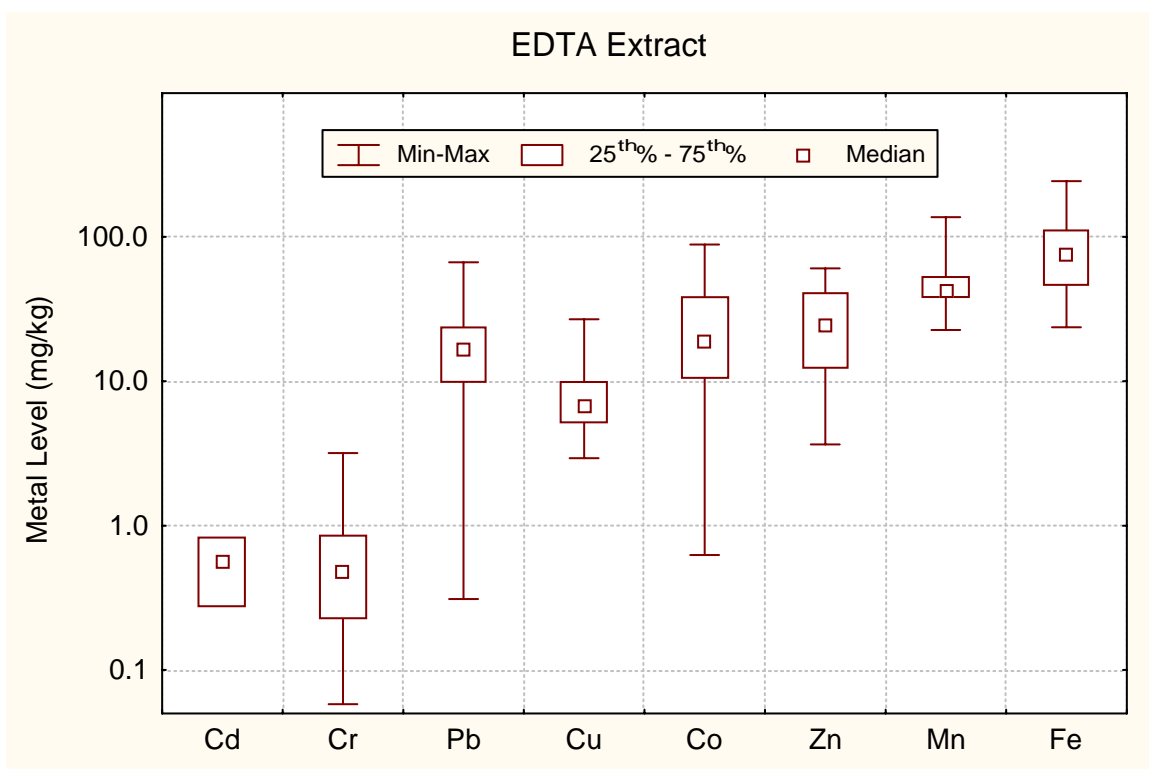


Figure 10. Quartile distribution of the metals (mg/kg) in EDTA extract of the soil



Box and whisker plot showing the quartile distribution of the metals in EDTA extract of the soil is portrayed in Figure 10. Most of the metals showed broad ranges and appreciably diverse quartile variations in the soil fraction. Highest spread was shown by Pb, followed by Co, and Cr while comparatively narrow spread and least variations were recorded for Mn and Cd. Among the metals, Fe and Cr demonstrated nearly symmetrical variations in their distribution while rest of the metals exhibited fairly asymmetrical distribution in the EDTA extract of the soil.

### 3.6 Correlation Study of the Metals in EDTA Extract of Soil

Correlation coefficients matrix for the metals in EDTA extract of the soil is given in Table 6, wherein the significant  $r$ -values are provided in bold at  $p < 0.05$ . A number of significant and strong relationships were observed between the metal pairs: strong and significant correlations were noted between Zn-Cu ( $r = 0.668$ ), Pb-Cu ( $r = 0.644$ ), Pb-Zn ( $r = 0.593$ ), Pb-Co ( $r = 0.467$ ), Mn-Fe ( $r = 0.452$ ), Pb-Cd ( $r = 0.395$ ), Zn-Co ( $r = 0.360$ ), Co-Cd ( $r = 0.353$ ), and Cr-Fe ( $r = 0.331$ ). The correlation study therefore indicated mutual variations and probably common origin of Pb, Zn, Cu, Co and Cd in EDTA extract of the soil while significant associations among Fe, Mn and Cr revealed their communal variations in the soil fraction. Overall, the correlation study manifested significant associations among the metals in EDTA extract which mostly consisted of organically bonded fractions of the metals in soil.

Table 6. Correlation coefficients\* among the metal levels in EDTA extracts of the soil

	Cd	Cr	Pb	Cu	Co	Zn	Mn	Fe
Cd	1.000							
Cr	-0.242	1.000						
Pb	<b>0.395</b>	-0.092	1.000					
Cu	0.304	-0.176	<b>0.644</b>	1.000				
Co	<b>0.353</b>	-0.065	<b>0.467</b>	0.210	1.000			
Zn	0.282	0.031	<b>0.593</b>	<b>0.668</b>	<b>0.360</b>	1.000		
Mn	0.004	-0.010	-0.165	-0.114	-0.342	-0.483	1.000	
Fe	-0.248	<b>0.331</b>	-0.063	0.128	-0.249	0.073	<b>0.452</b>	1.000

\* $r$ -values shown in bold are significant at  $p < 0.05$

### 3.7 Comparison of the Metal Levels in EDTA Extract of Soil from Various Areas

Average metal levels (mg/kg,  $\pm$  SE) in EDTA extract of the soil samples collected from different areas of Lahore are shown in Figure 11, for comparative evaluation. Among the metals, mean concentrations of Pb, Zn, and Cu were found to be higher in roadside samples followed by the parks while least contents were noted in the field samples. Conversely, Mn and Fe showed highest concentrations in samples collected from fields. Highest average levels were found in the field samples and lowest in the roadside samples. The samples collected from the parks showed comparatively higher contributions of Cd and Cr in the EDTA extracts. Average levels of Co were almost comparable in the roadside and park samples but significantly higher than those of the field samples (Figure 11).

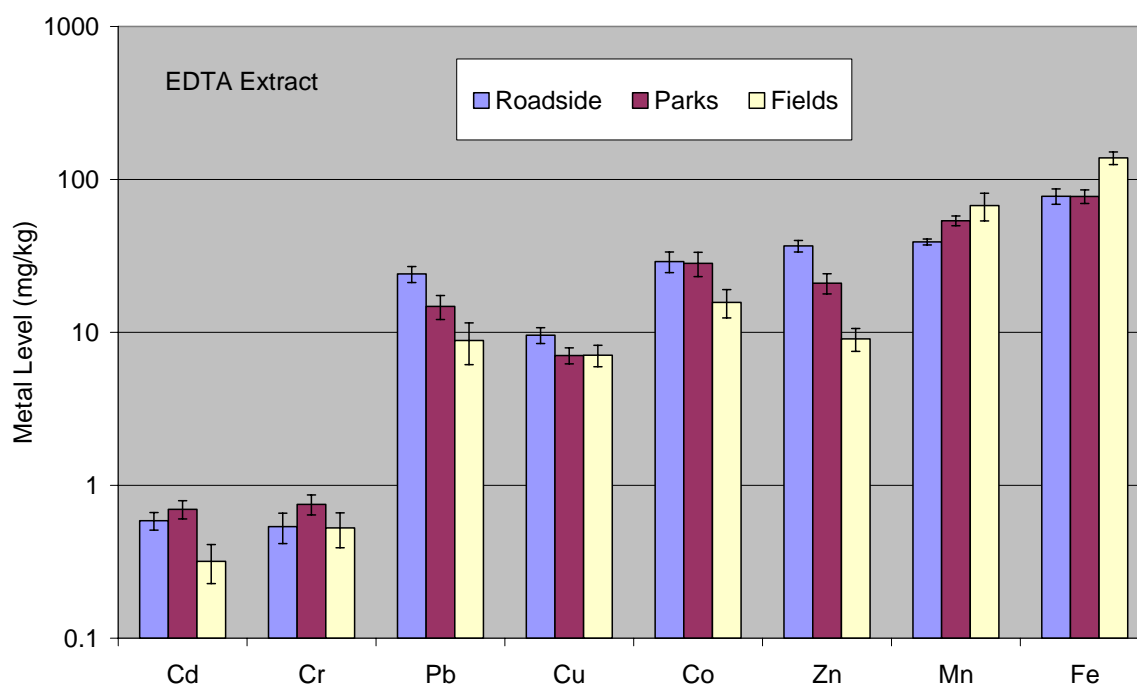


Figure 11. Comparison of the average metal levels (mg/kg,  $\pm$  SE) in EDTA extract of the soil samples collected from different areas

### 3.8 Distribution of the Metals in Acetic Acid Extract of Soil

Acetic acid extracts of the soil generally indicated easily exchangeable fraction of the metals in the soil. Distribution of the metal concentrations (mg/kg, dry weight) in terms of the basic statistical parameters in acetic acid extracts of the soil is provided in

Table 7. Most of the metals showed large spread in their concentrations; minimum level was found for Cd (0.117 mg/kg) while maximum level was revealed by Fe (644.7 mg/kg), followed by Mn (247.3 mg/kg). On the average basis, dominant contributions were observed for Fe at 227.0 mg/kg and Mn at 171.2 mg/kg. Some significant contributions were observed for Zn (69.32 mg/kg), Pb (27.05 mg/kg) and Co (25.24 mg/kg), while relatively lower mean levels were noted for Cd (2.611 mg/kg), Cr (2.770 mg/kg) and Cu (8.355 mg/kg). More or less, similar mean and median levels were observed for most of the metals which indicated their consistent their variations in acetic acid extract of the soil. Average metal levels in acetic acid extract of the soils were also compared as presented in Figure 12, which revealed following decreasing order: Fe > Mn > Zn > Pb > Co > Cu > Cr > Cd. Most of the metals exhibited significantly large dispersion as manifested by higher SD and SE values; highest dispersion was shown by Fe, followed by Zn, Mn, Co and Pb in acetic acid extract of the soil. Majority of the metals demonstrated relatively symmetrical distribution in the soil fraction as manifested by comparatively lower skewness and kurtosis values.

Table 7. Statistical distribution parameters for selected metal levels (mg/kg) in acetic acid extract of the soil

	Cd	Cr	Pb	Cu	Co	Zn	Mn	Fe
Min	0.117	0.196	1.251	0.229	2.312	6.600	117.5	5.885
Max	9.388	7.909	90.34	32.95	98.31	169.3	247.3	644.7
Mean	2.611	2.770	27.05	8.355	25.24	69.32	171.2	227.0
Median	1.651	2.457	23.54	5.384	15.33	55.69	170.2	195.8
SD	2.466	1.713	23.89	7.961	25.69	51.37	32.36	185.4
SE	0.345	0.233	3.345	1.064	3.464	6.865	4.325	24.78
Kurtosis	0.580	0.353	0.477	0.585	2.274	-0.904	-0.374	-1.219
Skewness	1.311	0.750	1.119	1.248	1.789	0.649	0.527	0.398

Quartile distribution of the metals in acetic acid extracts (exchangeable fraction) of the urban soil is represented in Figure 13. Significantly large spread and broad distributions were noted for Cu, Co, Pb, Cd, Zn, Cr, and Fe, hence, unfolding considerable variations in the metal levels in acetic acid fraction of the soil. Nevertheless, very narrow distribution and least variations were observed for Mn as evidenced by overlapping of the upper and lower quartiles; consequently, metal levels in the soil fraction were not significantly affected by the anthropogenic activities.

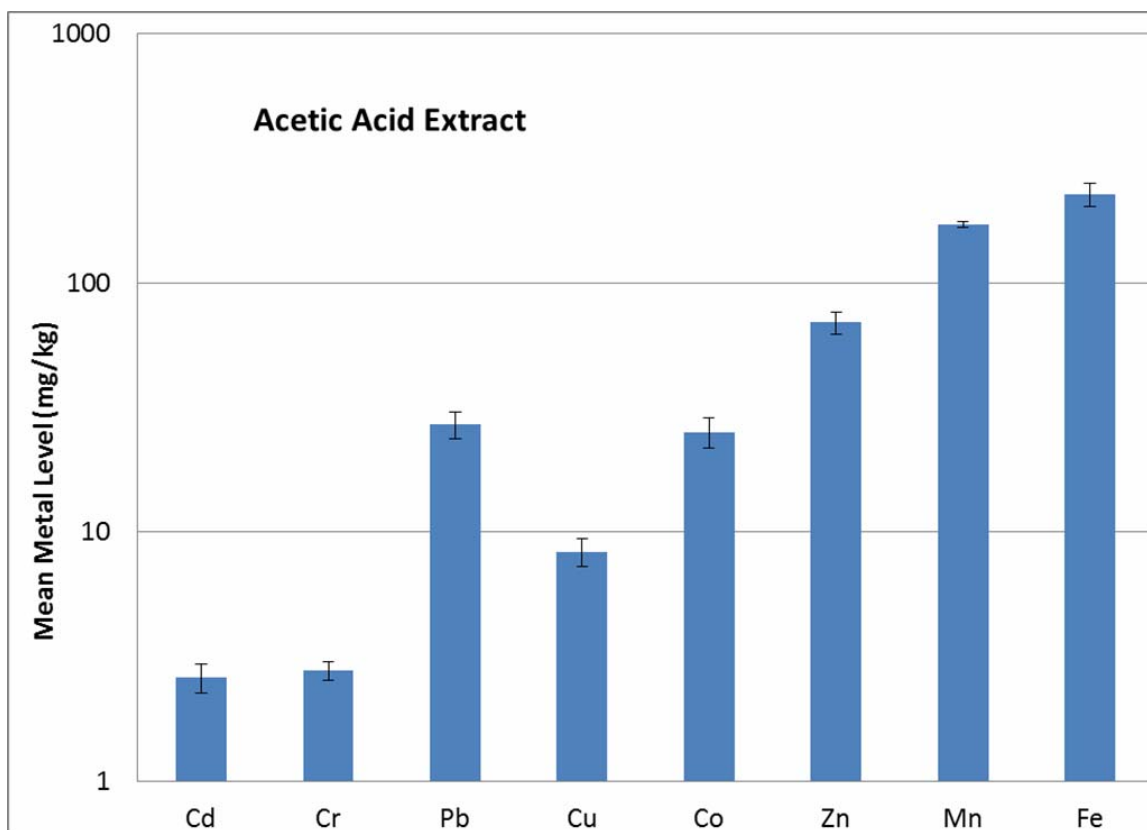


Figure 12. Comparison of average metal levels (mg/kg,  $\pm$  SE) in acetic acid extract of the soil

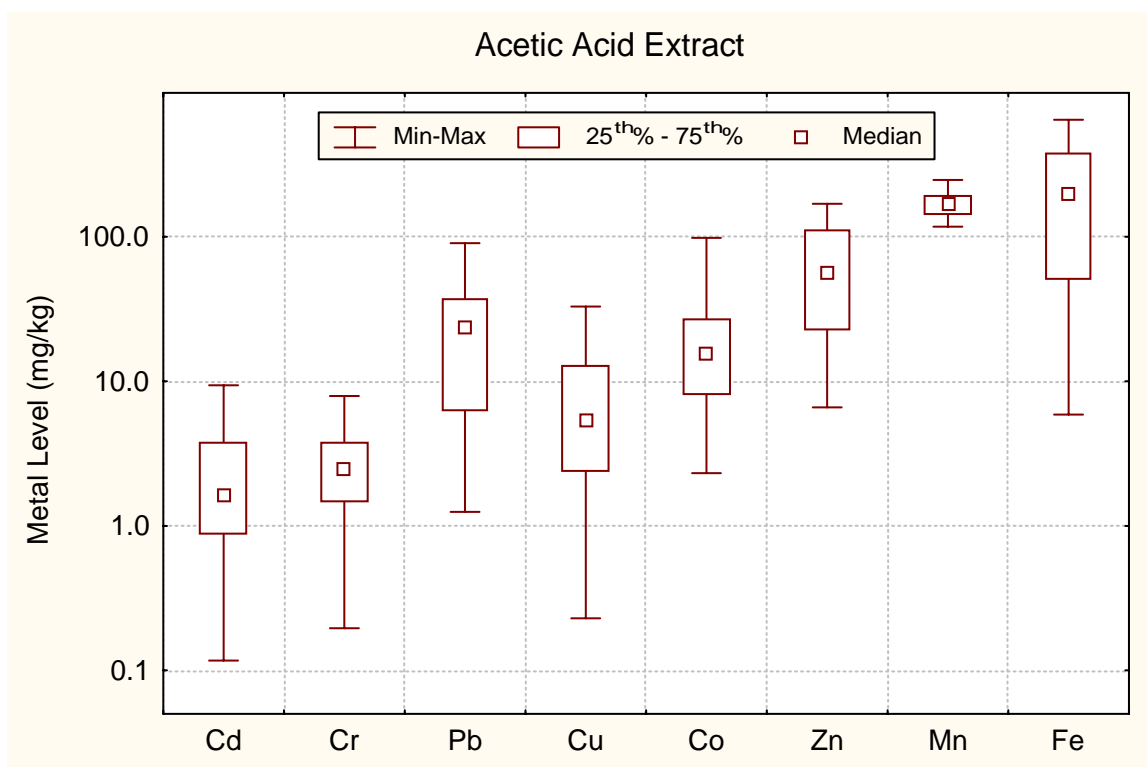


Figure 13. Quartile distribution of the metals (mg/kg) in acetic acid extract of the soil

### 3.9 Correlation Study of the Metals in Acetic Acid Extract of Soil

Correlation coefficients matrix for the metal levels in acetic acid extracts of the soil is given in Table 8, wherein the significant  $r$ -values are presented in bold at  $p < 0.05$ . Most of the metal pairs revealed insignificant relationships in the soil fraction; however, a few significantly strong correlations were noted between Fe-Cu ( $r = 0.784$ ), Zn-Cu ( $r = 0.717$ ), and Fe-Zn ( $r = 0.538$ ). The correlation study thus indicated mutual variations and probably common origin of Fe, Cu and Zn in acetic acid extracts of the soil. On the other hand, measured levels of Cd, Cr, Pb, Co and Mn showed statistically insignificant positive or negative correlations with other metals, hence, demonstrating their independent variations in the exchangeable fraction of the soil. Overall, the correlation study showed independent behaviour for most of the metals which proved that the metals were not contributed by communal sources and multiple factors/variables were responsible for their variations in the soil fraction.

Table 8. Correlation coefficients\* among the metal levels in acetic acid extract of the soil

	Cd	Cr	Pb	Cu	Co	Zn	Mn	Fe
Cd	1.000							
Cr	-0.007	1.000						
Pb	-0.292	-0.086	1.000					
Cu	-0.009	0.329	0.111	1.000				
Co	0.191	0.116	0.012	0.208	1.000			
Zn	-0.133	0.268	0.101	<b>0.717</b>	0.109	1.000		
Mn	0.238	-0.008	-0.222	-0.196	0.074	-0.059	1.000	
Fe	0.005	0.253	0.000	<b>0.784</b>	0.287	<b>0.538</b>	-0.161	1.000

\* $r$ -values shown in bold are significant at  $p < 0.05$

### 3.10 Comparison of the Metal Levels in Acetic Acid Extract of Soil from Various Areas

Comparison of the average metal levels (mg/kg,  $\pm$  SE) in acetic acid extract of the soil samples collected from different zones is shown in Figure 14. Most of the metals including Pb, Zn, Cu, Co, Fe and Cr revealed significantly higher contributions in the roadside samples compared with the park and field samples. It indicated build-up and

accumulation of the metals in the exchangeable fraction of roadside soil. Such accumulation may be associated with the excessive anthropogenic activities along roadside areas where most of the commercial activities were also witnessed. Among rest of the metals, Cd showed appreciably high concentration in the field samples while Mn exhibited almost comparable contributions in the soil samples collected from different urban localities of Lahore.

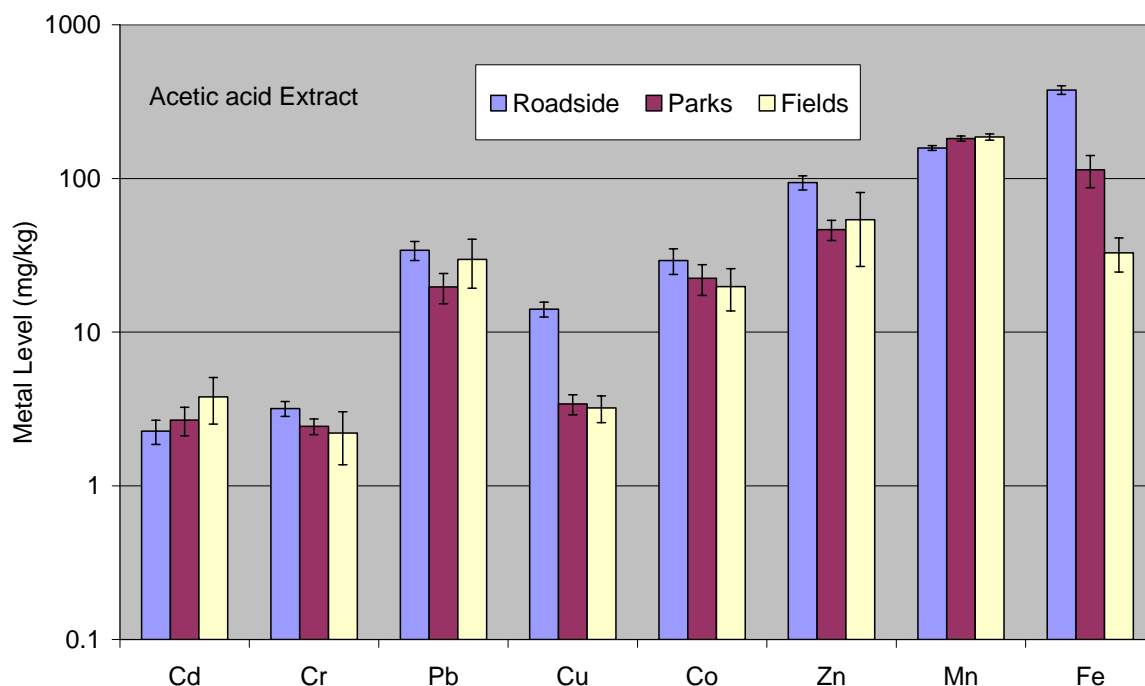


Figure 14. Comparison of the average metal levels (mg/kg,  $\pm$  SE) in acetic acid extract of the soil samples collected from different areas

### 3.11 Distribution of the Metals in Nitric Acid Extract of Soil

Nitric acid extract of the soil are considered to assess the total replaceable metal ions in the soil. Basic statistical parameters related to the distribution of the metal levels (mg/kg, dry weight) in the nitric acid extract of the soil are provided in Table 9. Most of the metals showed large spread in their concentrations as manifested by the minimum and maximum levels. Among the metals, Co indicated lowest concentration at 0.190 mg/kg while Fe showed maximum level at 1036 mg/kg. An examination of the metal data revealed highest average contribution for Fe (498.9 mg/kg) in this soil fraction, followed by Mn (162.4 mg/kg), while average concentrations of Zn, Pb, Cu, Co, Cr and Cd were recorded at 71.02, 50.24, 18.43, 15.23, 6.196 and 2.100 mg/kg, respectively. On the

average basis, metal concentrations revealed following increasing order in nitric acid extract of the soil as displayed in Figure 15: Cd < Cr < Co < Cu < Pb < Zn < Mn < Fe. Almost comparable mean and median values were observed for Mn and Cr which pointed out more or less normal distribution pattern of these metals in the soil. Considerably higher SD and SE values for Fe, Zn, Pb and Mn indicated their non-Gaussian distribution and higher dispersion in the soil fraction. Relatively higher kurtosis and skewness values were noted for Cu and Pb which divulged their asymmetric distribution in nitric acid extract of the soil while rest of the metals exhibited relatively symmetrical distribution in the soil fraction. Overall, most of the metals showed random variations and significant dispersions in nitric acid extract of the soil.

Table 9. Statistical distribution parameters for selected metal levels (mg/kg) in nitric acid extract of the soil

	Cd	Cr	Pb	Cu	Co	Zn	Mn	Fe
Min	0.216	0.906	8.303	5.121	0.190	4.153	111.8	120.2
Max	4.766	15.92	175.8	70.54	46.95	195.8	216.5	1036
Mean	2.100	6.196	50.24	18.43	15.23	71.02	162.4	498.9
Median	1.893	6.188	36.92	12.40	11.91	52.68	163.3	439.1
SD	1.280	2.806	36.41	14.31	11.73	55.43	26.96	237.5
SE	0.176	0.375	4.865	1.912	1.627	7.543	3.603	31.74
Kurtosis	-1.163	1.696	1.278	2.784	0.550	-0.505	-0.923	0.012
Skewness	0.198	0.645	1.154	1.749	1.058	0.854	0.089	0.919

Box and whisker plot demonstrating the quartile distribution of selected metals in the nitric acid extract of the soil is contained in Figure 16. The quartile distribution of the metals in nitric acid extract of the soil revealed very broad and asymmetric spread for Co, followed by Zn, Pb and Cd. However, very narrow distribution was observed for Mn, followed by somewhat moderately narrow variations for Fe and Cr in the nitric acid extract of the soil. Similarly, Cu levels manifested reasonably broad but asymmetric distribution in the soil fraction. By and large, the quartile distribution of the metals in nitric acid extract of the soil was considerably different from those observed in previous cases.

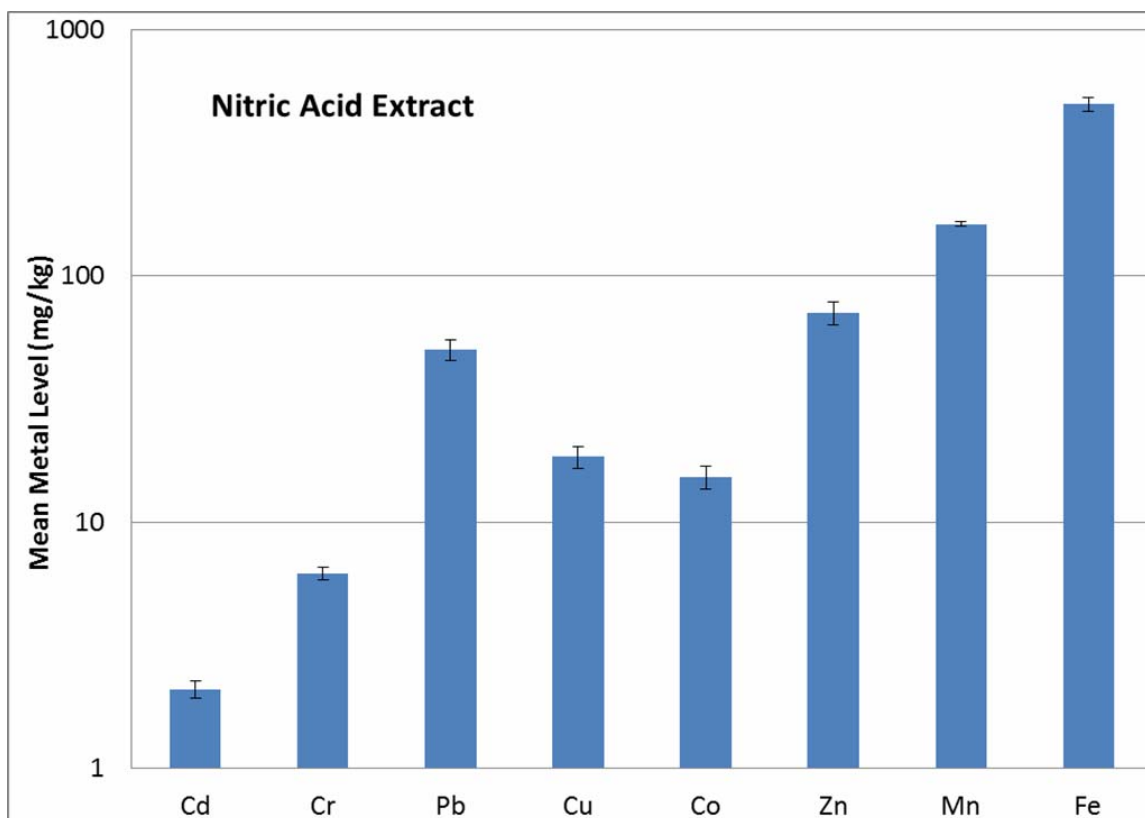


Figure 15. Comparison of average metal levels (mg/kg,  $\pm$  SE) in nitric acid extract of the soil

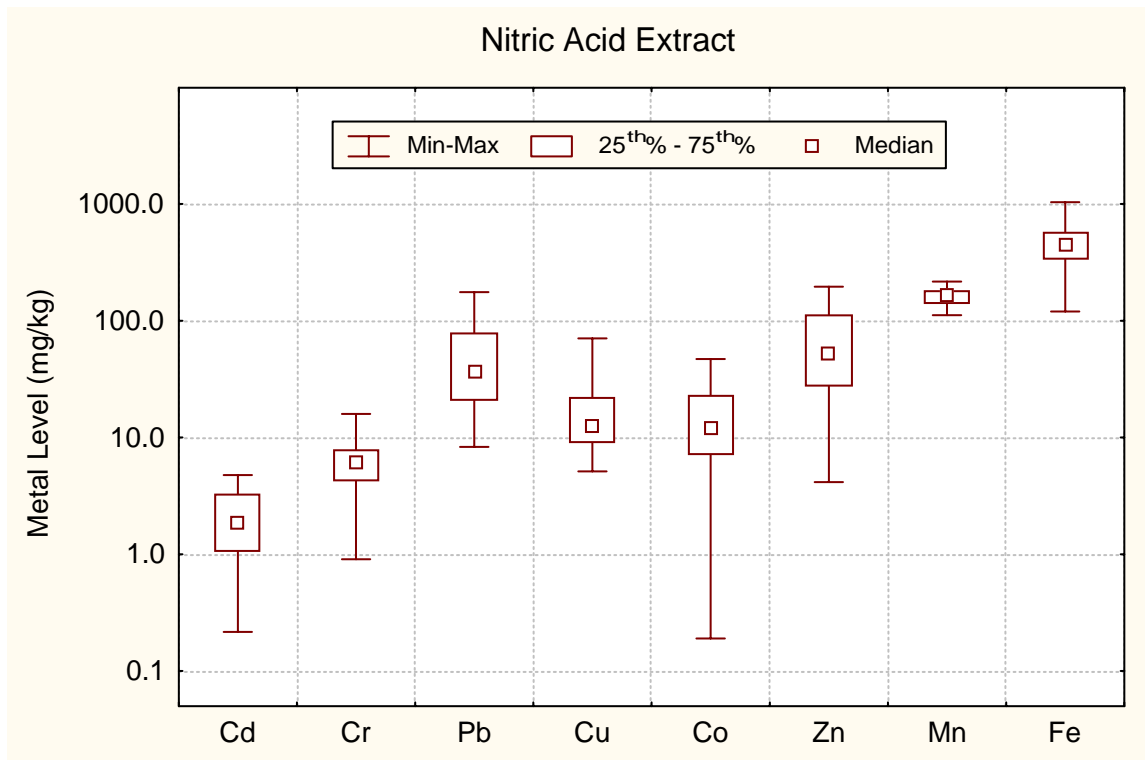


Figure 16. Quartile distribution of the metals (mg/kg) in nitric acid extract of the soil



### 3.12 Correlation Study of the Metals in Nitric Acid Extract of Soil

Correlation coefficients matrix for the metals in nitric acid extract of the soil is provided in Table 10, wherein the significant  $r$ -values are presented in bold at  $p < 0.05$ . Most of the metal pairs exhibited insignificant correlations in this soil fraction; however, some significant and strong relationships were noted between Zn-Cr ( $r = 0.409$ ), Cu-Pb ( $r = 0.424$ ), Cr-Cu ( $r = 0.450$ ), Zn-Pb ( $r = 0.561$ ) and Zn-Cu ( $r = 0.830$ ). Nevertheless, recorded levels of Cd, Co, Mn and Fe showed insignificant positive/negative correlations with other metals, thus, revealing their independent variations in nitric acid extract of the soil. The correlation study indicated mutual variations and probably common origin of Zn, Cu, Pb and Cr in this soil fraction while Cd, Co, Mn and Fe manifested least associations in the nitric acid extract of the soil.

Table 10. Correlation coefficients\* among the metal levels in nitric acid extract of the soil

	Cd	Cr	Pb	Cu	Co	Zn	Mn	Fe
Cd	1.000							
Cr	0.207	1.000						
Pb	0.079	0.143	1.000					
Cu	0.030	<b>0.450</b>	<b>0.424</b>	1.000				
Co	0.103	-0.263	-0.233	-0.232	1.000			
Zn	-0.022	<b>0.409</b>	<b>0.561</b>	<b>0.830</b>	-0.204	1.000		
Mn	-0.105	0.174	-0.116	0.159	-0.014	0.265	1.000	
Fe	0.310	-0.146	0.016	-0.010	0.185	-0.050	-0.150	1.000

\* $r$ -values shown in bold are significant at  $p < 0.05$

### 3.13 Comparison of the Metal Levels in Nitric Acid Extract of Soil from Various Areas

Average metal concentrations (mg/kg,  $\pm$  SE) in nitric acid extract of the soil samples collected from different urban regions of Lahore are shown in Figure 17, for comparative evaluation. The comparative study divulged that mean concentrations of Pb, Cu, Zn, and Cr were considerably higher in roadside samples followed by the samples collected from the parks while least contribution was noted in the field samples. On the mean scale, Cd and Co revealed appreciably higher concentration in the soil samples

collected from parks than the roadside and field samples. Similarly, average levels of Fe depicted relatively lower contribution in the park samples while mean contents of Mn were almost comparable in the nitric acid extract of the soil samples collected from various areas.

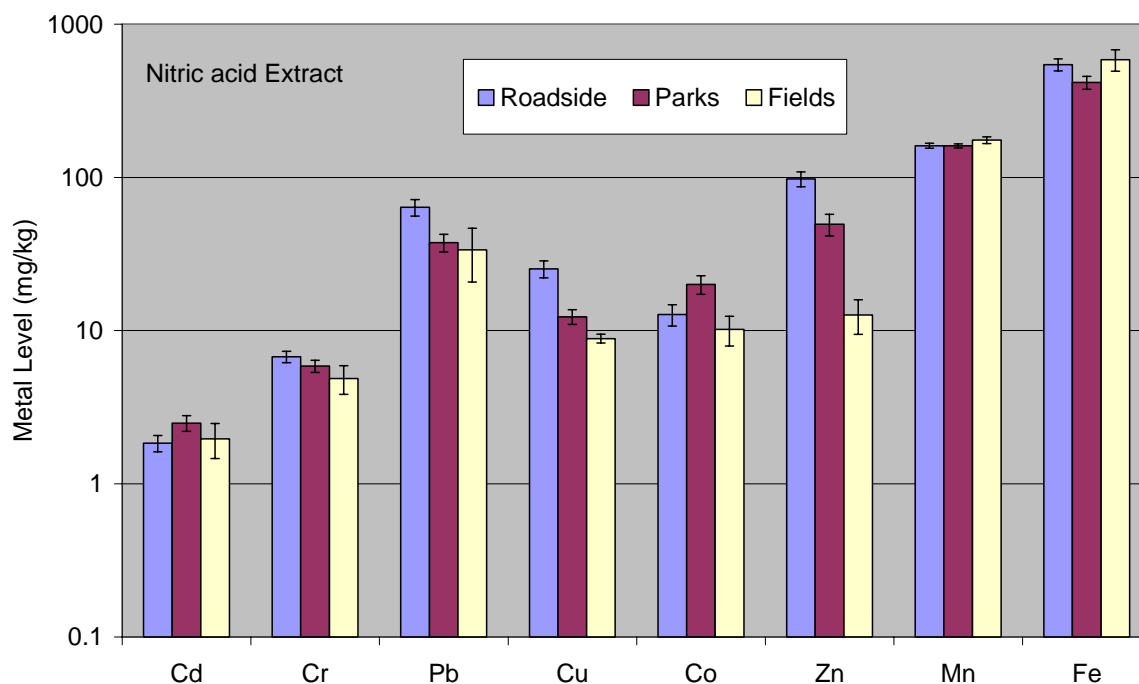


Figure 17. Comparison of the average metal levels (mg/kg,  $\pm$  SE) in nitric acid extract of the soil samples collected from different areas

### 3.14 Distribution of the Metals in Aqua regia Extract of Soil

Pseudo-total metal levels in the soil were evaluated in terms of aqua regia extract of the soil. The basic statistical parameters related to the distribution of selected metals in aqua regia extracts of the soil are given in Table 11. Maximum concentration in the soil samples was shown by Fe at 2158 mg/kg, followed by Mn at 700.6 mg/kg and Zn at 236.7 mg/kg, whereas minimum concentration was shown by Cd at 0.196 mg/kg and Co at 0.327 mg/kg. Most of the metals displayed large spread in their concentrations as judged from minimum and maximum levels. On the average basis, predominantly higher levels were observed for Fe (1566 mg/kg), followed by Mn (451.1 mg/kg) and Zn (114.8 mg/kg), while relatively lower mean concentrations were noted for Pb (52.84 mg/kg), Cu (39.15 mg/kg), Cr (24.82 mg/kg), Co (12.59 mg/kg) and Cd (3.953 mg/kg). Comparison of the

pseudo-total average metal levels in the soil is illustrated in Figure 18, which manifested following trend in the soil: Fe > Mn > Zn > Pb > Cu > Cr > Co > Cd. Almost similar trend was also noted for the median metal levels in the soil. Most of the metals showed large dispersion and relatively random distribution pattern as revealed by comparatively higher SD and SE values. Moderately higher kurtosis and skewness values for Cu, Co and Fe indicated their asymmetric distribution in the soil while rest of the metals exhibited relatively symmetrical distribution in pseudo-total contents of the soil.

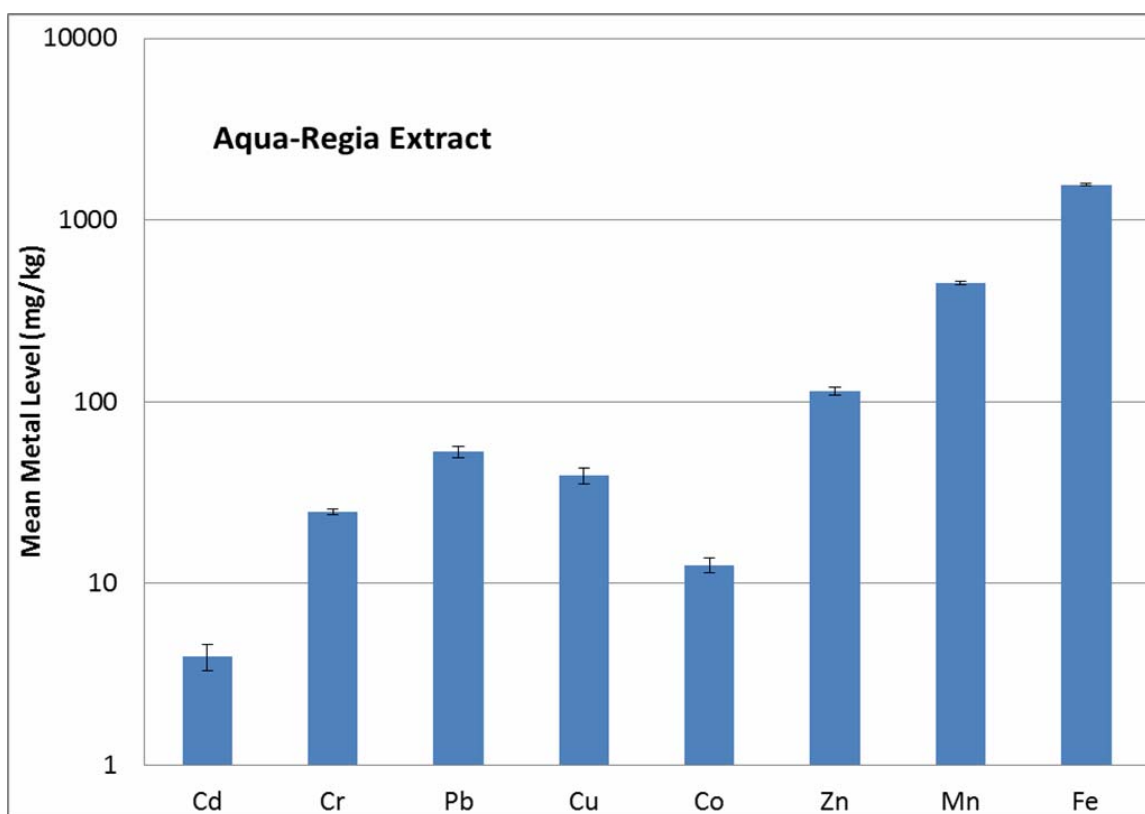


Figure 18. Comparison of average metal levels (mg/kg,  $\pm$  SE) in aqua regia extract of the soil

Figure 19 gives the box and whisker plot showing the quartile distribution of selected metals in aqua regia extracts of the soil. Most of the metals displayed relatively narrow and symmetric distribution in the aqua regia extract of the soil. Among these Fe, Mn, Cr, and Zn revealed very narrow spread with small variations in their median, minimum, maximum, 25<sup>th</sup> percentile and 75<sup>th</sup> percentile. On the other hand, Co and Cd demonstrated broad spread and relatively higher dispersion, therefore, indicating comparatively higher variations in most of the soil samples. Somewhat moderate variations in the quartile distribution of Pb and Cu were noted for their pseudo-total levels in the soil.

Table 11. Statistical distribution parameters for selected metal levels (mg/kg) in aqua regia extract of the soil

	Cd	Cr	Pb	Cu	Co	Zn	Mn	Fe
Min	0.196	11.50	8.436	11.24	0.327	45.47	266.9	1248
Max	16.19	46.15	140.7	130.1	41.95	236.7	700.6	2158
Mean	3.953	24.82	52.84	39.15	12.59	114.8	451.1	1566
Median	1.602	23.51	46.04	27.70	9.625	101.9	445.0	1506
SD	4.894	7.182	30.01	27.53	8.469	46.65	84.34	188.3
SE	0.660	0.960	4.010	3.679	1.153	6.234	11.27	25.17
Kurtosis	0.474	1.447	0.665	2.415	1.858	-0.209	0.319	1.466
Skewness	1.449	0.967	0.947	1.750	1.289	0.840	0.200	1.294

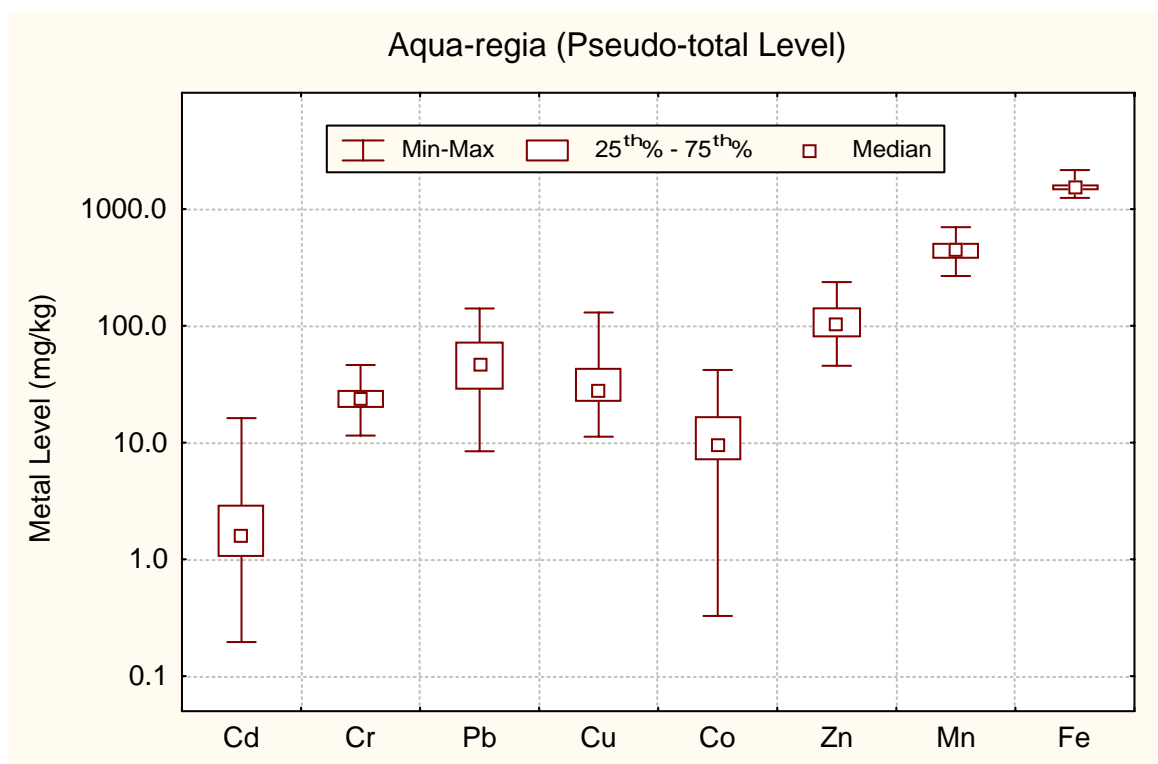


Figure 19. Quartile distribution of the metals (mg/kg) in aqua regia extract of the soil

### 3.15 Correlation Study of the Metals in Aqua regia Extract of Soil

Correlation coefficients matrix for the metals in aqua regia extract of the soil is presented in Table 12, wherein the significant  $r$ -values are placed in bold ( $p < 0.05$ ). Strong positive relationships were noted between Zn-Cu ( $r = 0.732$ ), Cr-Cu ( $r = 0.624$ )

and Zn-Cr ( $r = 0.601$ ). In addition, some significant relationships were noticed between Zn-Mn ( $r = 0.475$ ), Mn-Cr ( $r = 0.475$ ), Fe-Co ( $r = 0.470$ ), Mn-Cu ( $r = 0.452$ ), Cu-Pb ( $r = 0.420$ ), Zn-Cu ( $r = 0.732$ ) and Zn-Pb ( $r = 0.351$ ). Among the metals, only Cd showed independent variations as it was not significantly correlated with any other metal in aqua regia extract of the soil. Overall, the correlation study revealed mutual variations and common origin of most of the metals in aqua regia extract of the soil.

Table 12. Correlation coefficients\* among the metal levels in aqua regia extract of the soil

	Cd	Cr	Pb	Cu	Co	Zn	Mn	Fe
Cd	1.000							
Cr	0.201	1.000						
Pb	-0.020	0.213	1.000					
Cu	0.115	<b>0.624</b>	<b>0.420</b>	1.000				
Co	0.210	0.117	0.060	0.097	1.000			
Zn	0.157	<b>0.601</b>	<b>0.351</b>	<b>0.732</b>	0.078	1.000		
Mn	0.220	<b>0.475</b>	0.172	<b>0.452</b>	0.115	<b>0.475</b>	1.000	
Fe	0.092	0.148	-0.084	-0.019	<b>0.470</b>	-0.055	-0.035	1.000

\* $r$ -values shown in bold are significant at  $p < 0.05$

### 3.16 Comparison of the Metal Levels in Aqua regia Extract of Soil from Various Areas

Comparison of the average metal levels (mg/kg,  $\pm$  SE) in aqua regia extract of the soil samples collected from different localities is shown in Figure 20. The comparative study demonstrated that mean concentrations of Fe, Mn and Cr were nearly comparable in the soil samples collected from roadsides, parks and fields. However, average levels of Pb, Cu and Zn were considerably higher in the roadside samples, followed by the park samples while lowest levels were noted in the field samples. Similarly, mean levels of Cd were found to be comparatively higher in the field samples, whereas average contents of Co displayed slightly higher concentration in the samples collected from parks than the roadside and field samples.

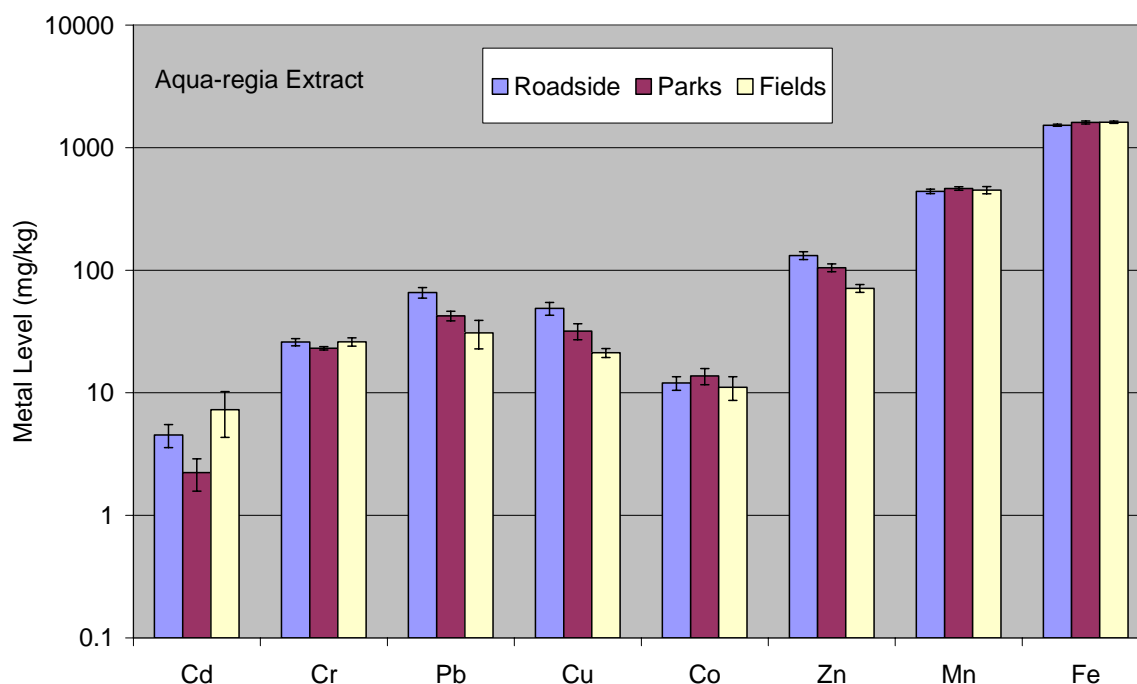


Figure 20. Comparison of the average metal levels (mg/kg,  $\pm$  SE) in aqua regia extract of the soil samples collected from different areas

### 3.17 Comparison of the Average Metal Levels in Various Soil Extracts

Concentrations of the metals (mg/kg, dry weight) in various extracts of the soil were compared to assess the availability in different leaching liquors and their bioaccessibility and mobility under different environmental conditions. Comparison of the average Cd levels in various soil extracts is presented in Figure 21. It showed maximum concentration in aqua regia extract (3.953 mg/kg), followed by the glycine extract (3.357 mg/kg), acetic acid extract (2.611 mg/kg), nitric acid extract (2.100 mg/kg), while the least contribution was noted in the EDTA extract (0.608 mg/kg). Consequently, significant contents of Cd in the soil were found to be bioaccessible thus revealing considerable mobility in the urban soil. Comparison of the average Cr levels in various soil extracts is given in Figure 22. Chromium unfolded predominantly higher contribution in aqua regia extract (24.82 mg/kg) while relatively lower levels were noted in the glycine extract (7.103 mg/kg), nitric acid extract (6.196 mg/kg), acetic acid extract (2.770 mg/kg) while the least availability was observed in the EDTA extract (0.617 mg/kg). Therefore, Cr exhibited lower availability and mobility in the soil samples.

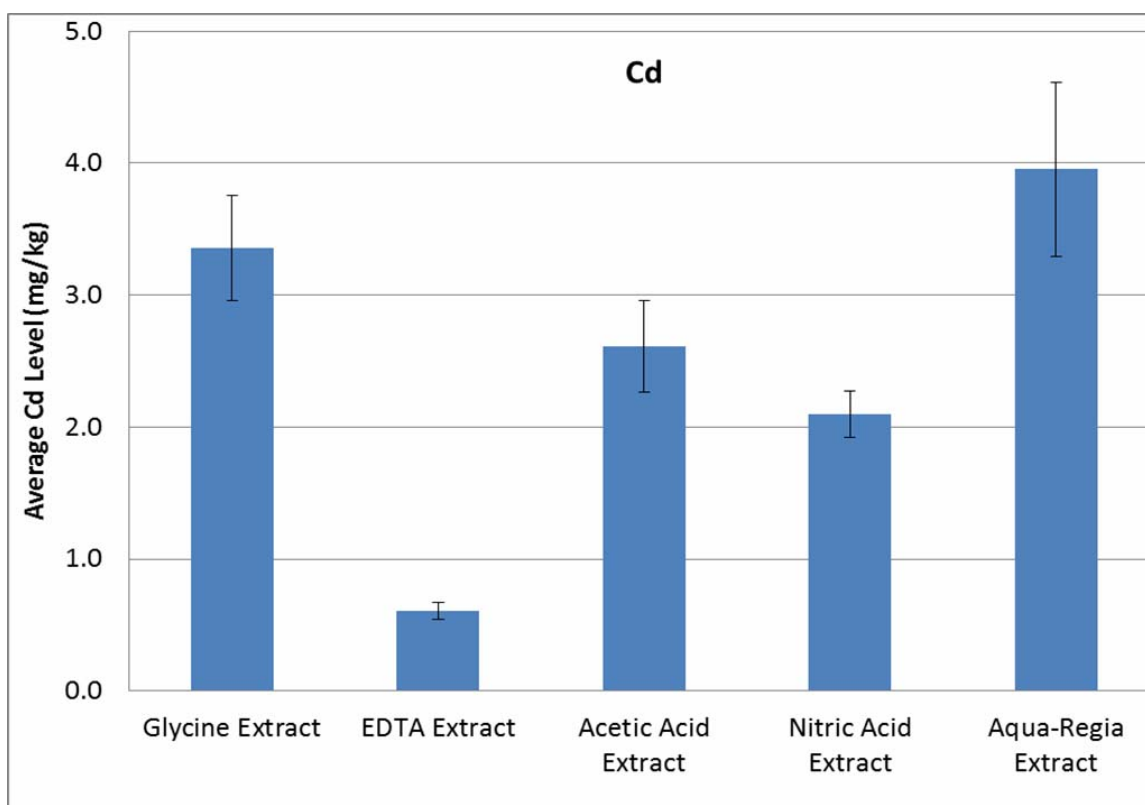


Figure 21. Comparison of average Cd levels (mg/kg,  $\pm$  SE) in various extracts of the soil

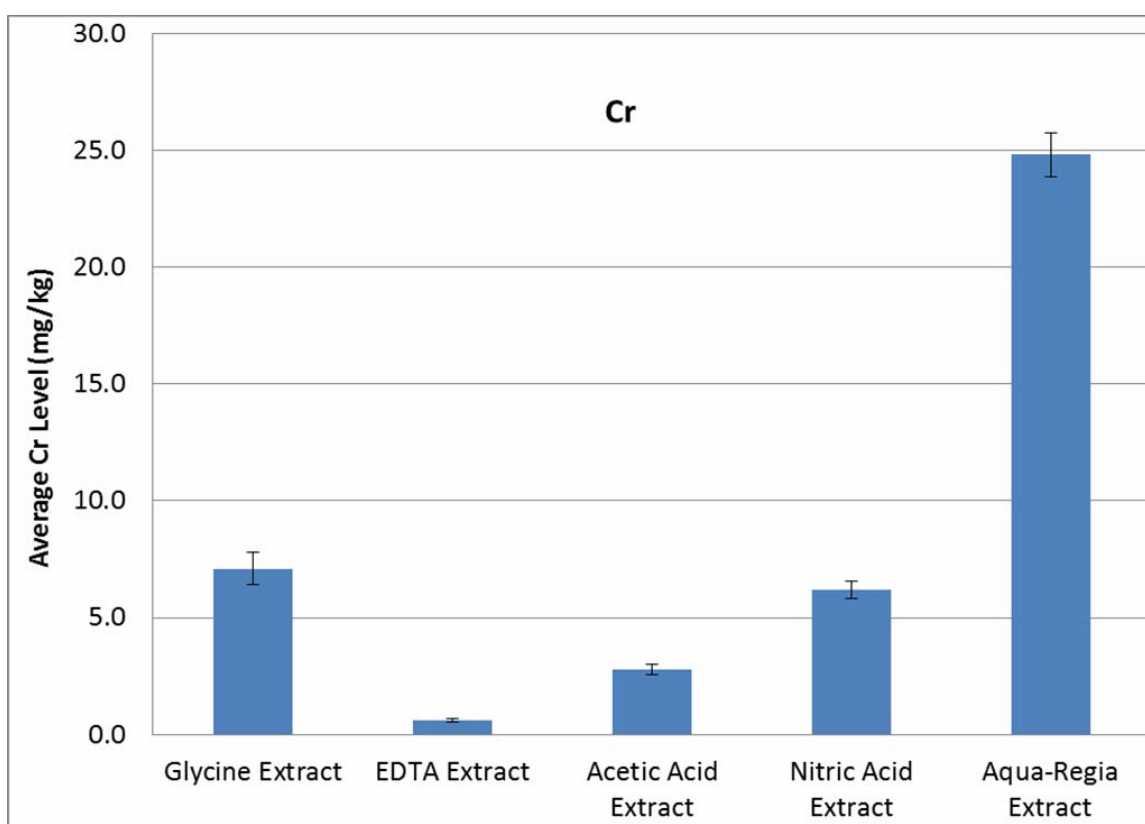


Figure 22. Comparison of average Cr levels (mg/kg,  $\pm$  SE) in various extracts of the soil

Comparison of the average Pb levels in various soil extracts is produced in Figure 23. It revealed maximum levels in the aqua regia extract (52.84 mg/kg), followed by considerably higher levels in the nitric acid extract (50.24 mg/kg), glycine extract (49.74 mg/kg), acetic acid extract (27.05 mg/kg), while the least availability was noted in the EDTA extract (18.77 mg/kg). Overall, Pb unfolded significantly higher bioaccessibility and mobility in the urban soil of Lahore. Comparison of the average Cu levels in various soil extracts is shown in Figure 24. It divulged highest concentration in the aqua regia extract (39.15 mg/kg), followed by relatively lower levels in glycine extract (19.28 mg/kg), nitric acid extract (18.43 mg/kg), acetic acid extract (8.355 mg/kg) while the least availability was experienced in the EDTA extract (8.314 mg/kg). Thus, Cu demonstrated relatively lower availability and mobility in the urban soil samples.

Comparison of the average Co levels in various soil extracts is illustrated in Figure 25. Cobalt manifested highest availability in aqua regia extract (46.92 mg/kg), followed by significant levels in the glycine extract (27.26 mg/kg), EDTA extract (25.24 mg/kg), acetic acid extract (15.23 mg/kg), and least concentration in nitric acid extract. Accordingly, Co offered significant bioavailability and mobility in the soil. Comparison of the average Zn levels in various soil extracts is contained in Figure 26. Comparison of the various soil extracts revealed that Zn exhibited highest contribution in aqua regia extract (114.8 mg/kg), followed by considerable contributions in the glycine extract (74.72 mg/kg), nitric acid extract (71.02 mg/kg), acetic acid extract (69.32 mg/kg) while relatively lower contents were observed in the EDTA extract (27.87 mg/kg). Therefore, Zn gave significant bioavailability and mobility in the urban soil.

Comparison of average Mn levels (mg/kg,  $\pm$  SE) in various extracts of the soil is displayed in Figure 27. It presented highest concentration in aqua regia extract (451.1 mg/kg), followed by considerably lower levels in the glycine extract (174.2 mg/kg), acetic acid extract (171.2 mg/kg), nitric acid extract (162.4 mg/kg), while the least levels were noticed in the EDTA extract (47.73 mg/kg). As a result, Mn showed relatively lower bioavailability and mobility in the soil samples. Comparison of average Fe levels (mg/kg,  $\pm$  SE) in various extracts of the soil is shown in Figure 28. It registered predominantly highest levels in the aqua regia extract (1566 mg/kg), followed by considerably lower levels in the glycine extract (579.6 mg/kg), nitric acid extract (498.9 mg/kg), acetic acid extract (227 mg/kg) while the least contributions were recorded in the EDTA extract (84.05 mg/kg). Consequently, Fe exhibited relatively lower mobility and bioaccessibility in the urban soil of Lahore.



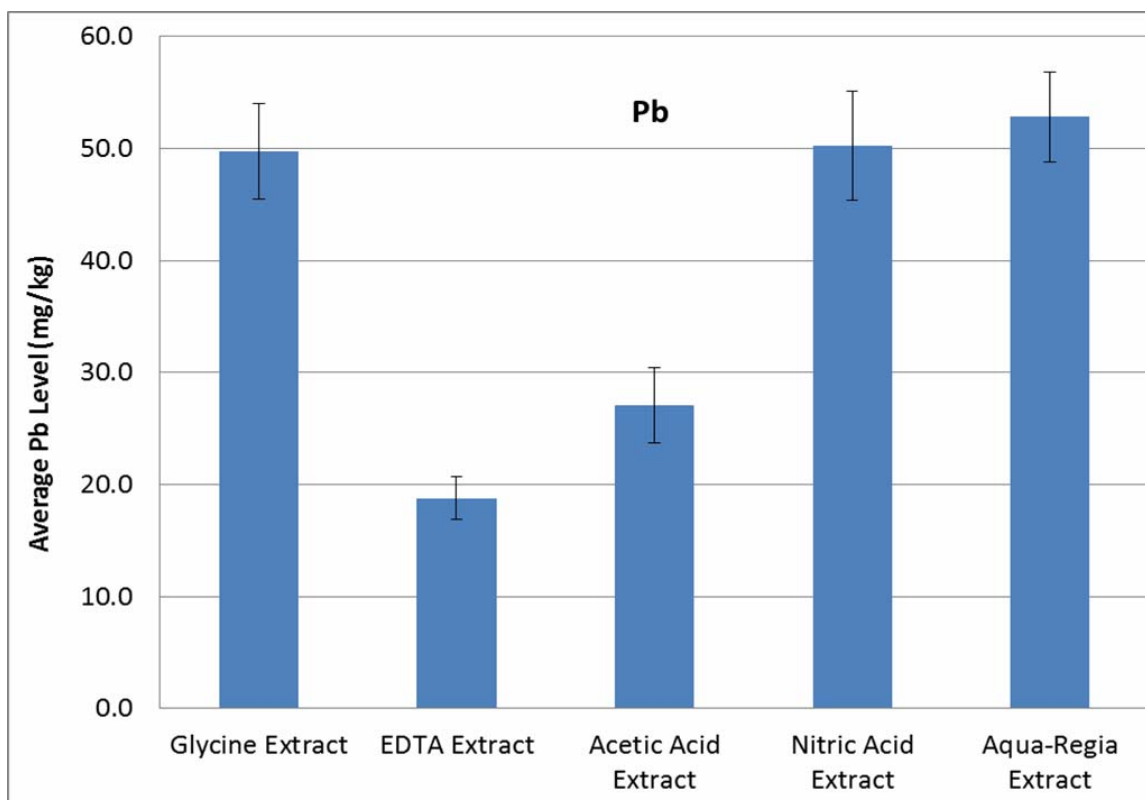


Figure 23. Comparison of average Pb levels (mg/kg,  $\pm$  SE) in various extracts of the soil

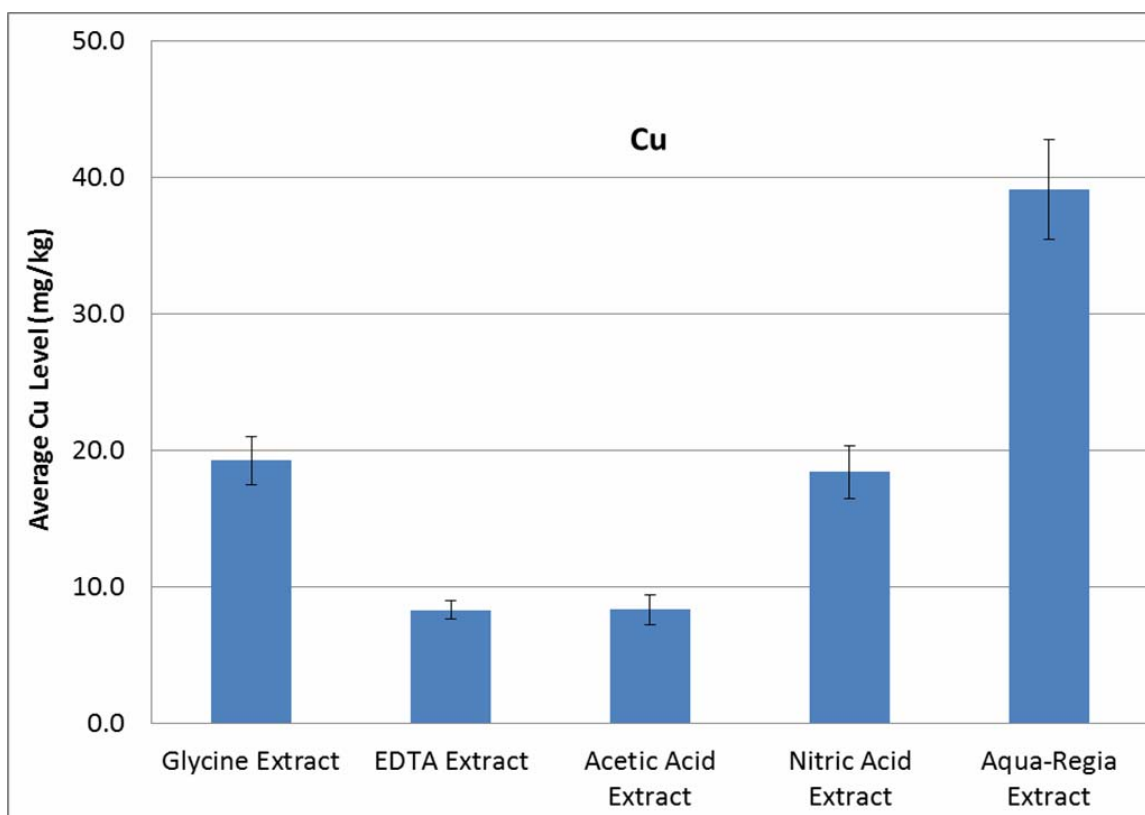


Figure 24. Comparison of average Cu levels (mg/kg,  $\pm$  SE) in various extracts of the soil

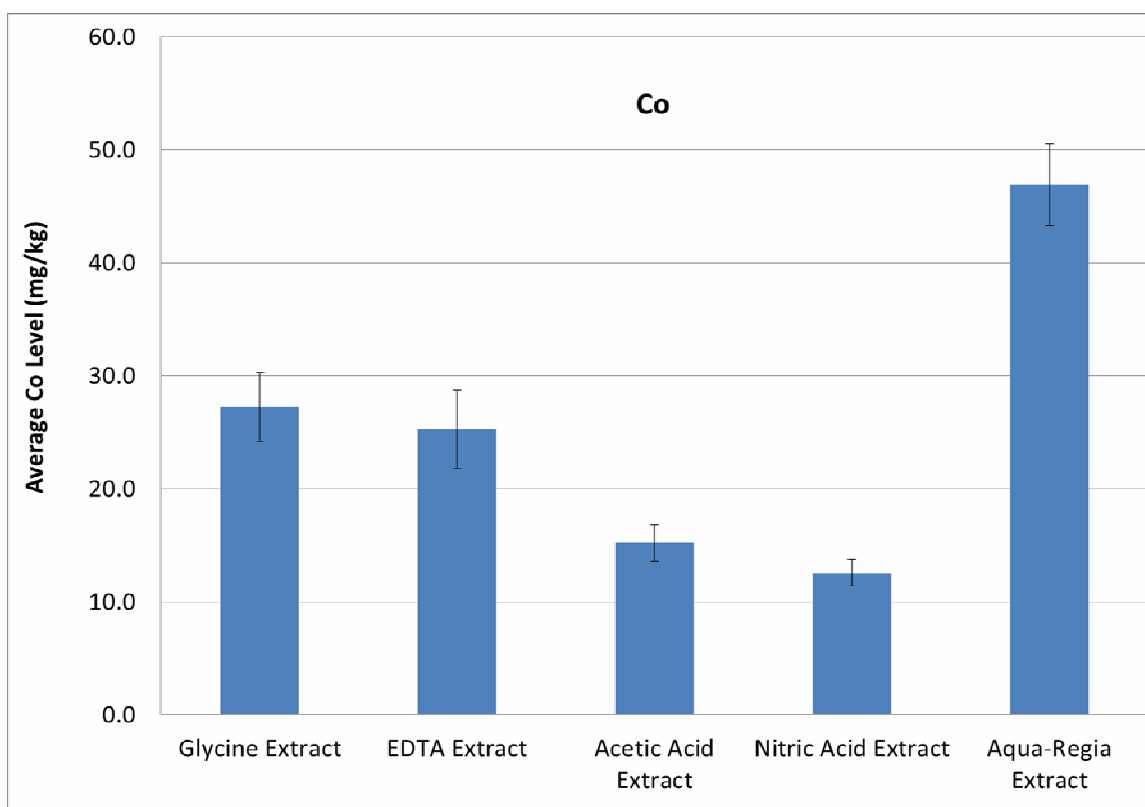


Figure 25. Comparison of average Co levels (mg/kg,  $\pm$  SE) in various extracts of the soil

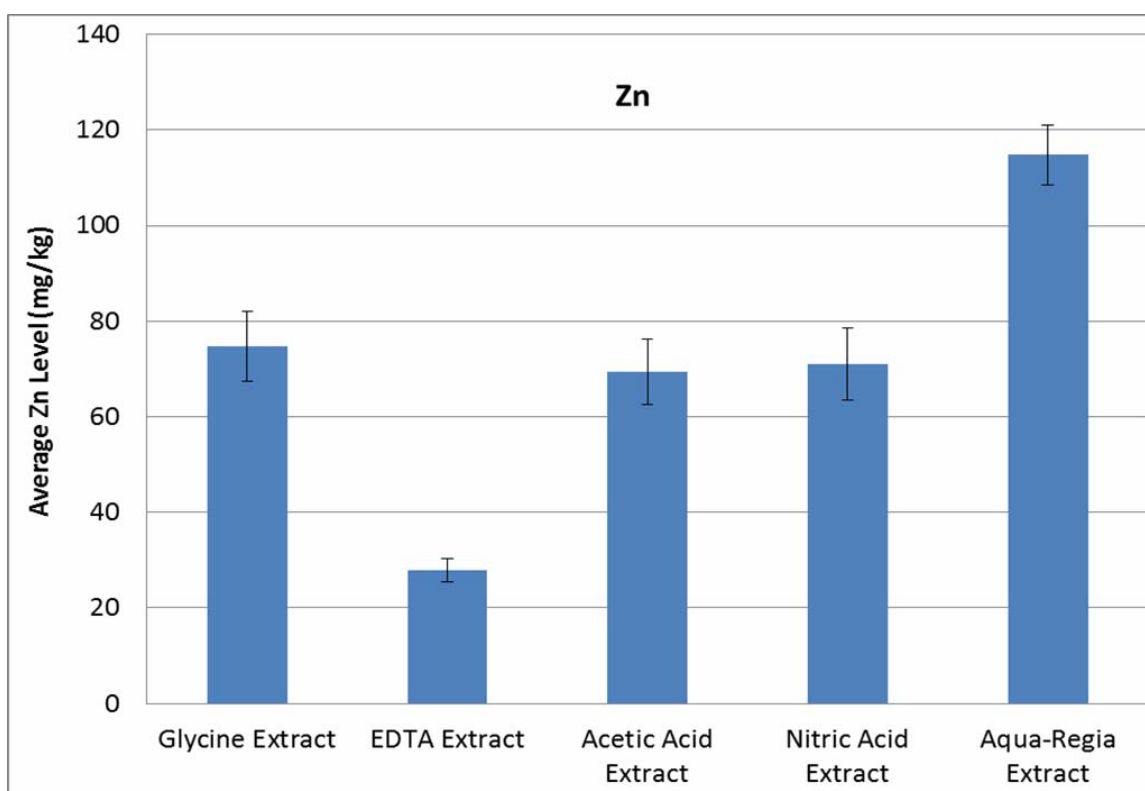


Figure 26. Comparison of average Zn levels (mg/kg,  $\pm$  SE) in various extracts of the soil

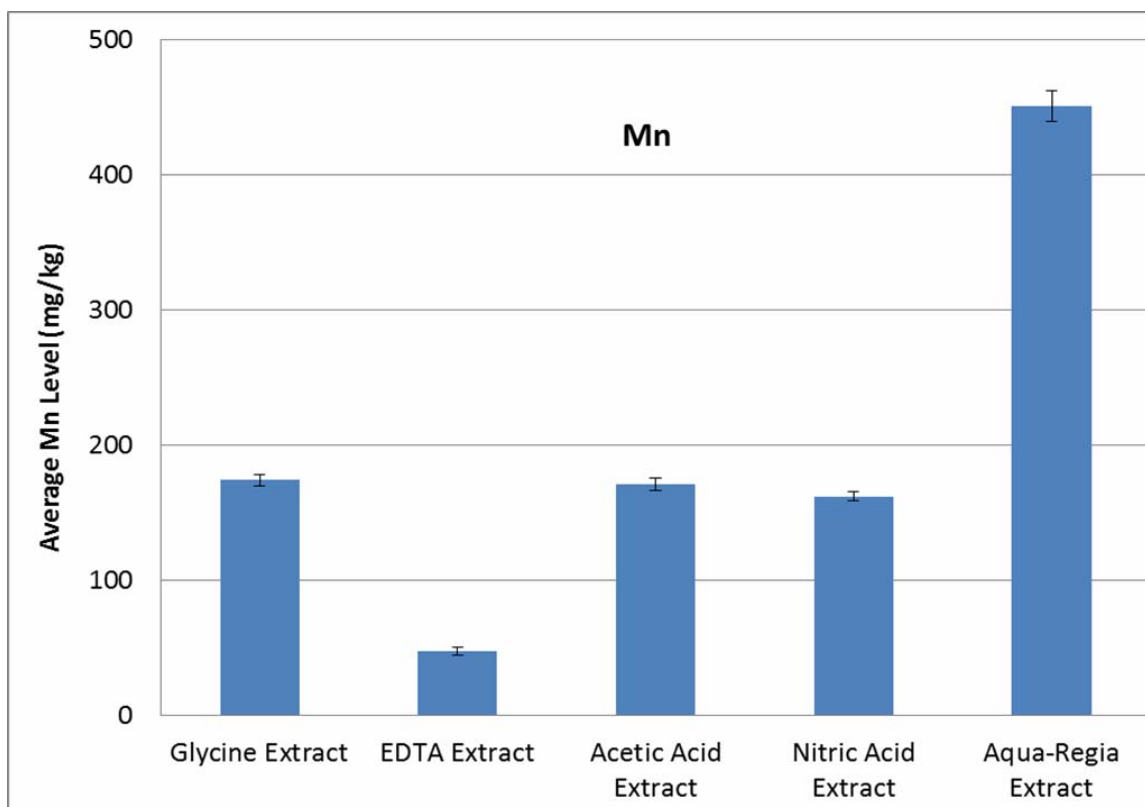


Figure 27. Comparison of average Mn levels (mg/kg,  $\pm$  SE) in various extracts of the soil

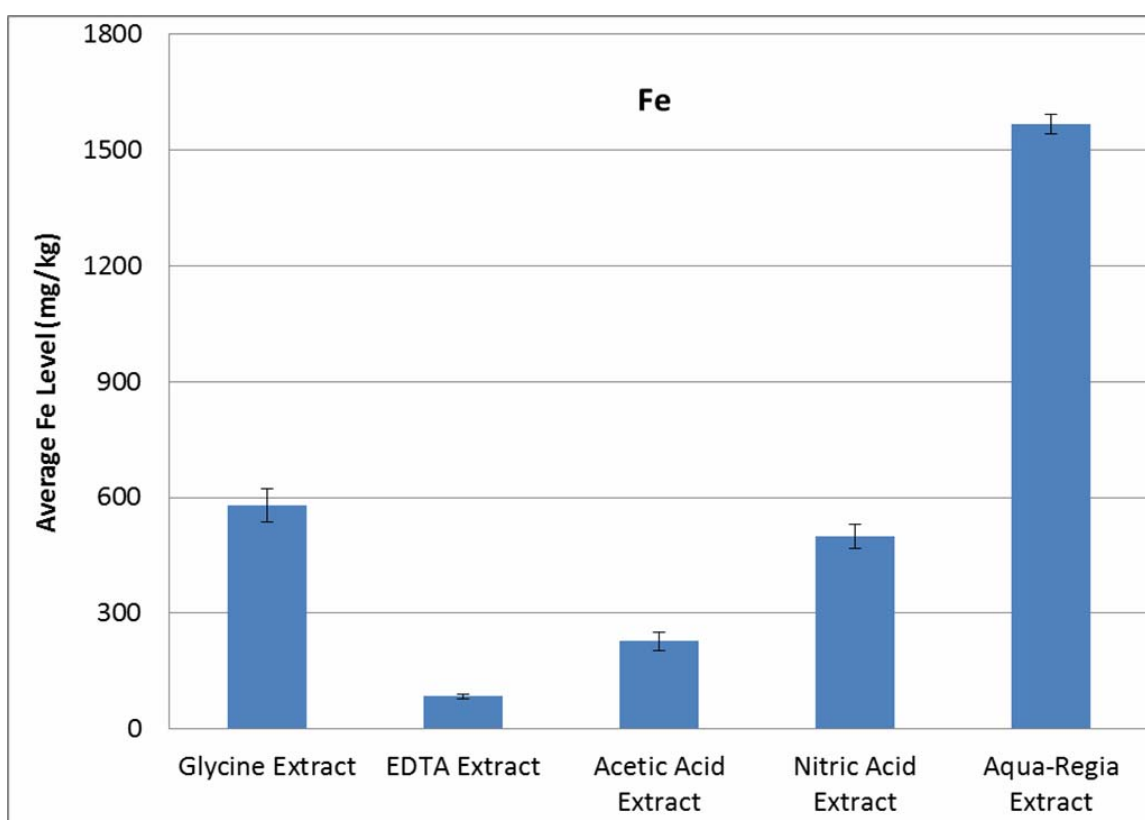


Figure 28. Comparison of average Fe levels (mg/kg,  $\pm$  SE) in various extracts of the soil



present mean levels of Cd, Pb and Zn unfolded higher concentrations than the earth's crust levels; it may be due to their anthropogenic accumulation/enrichment in the soil.

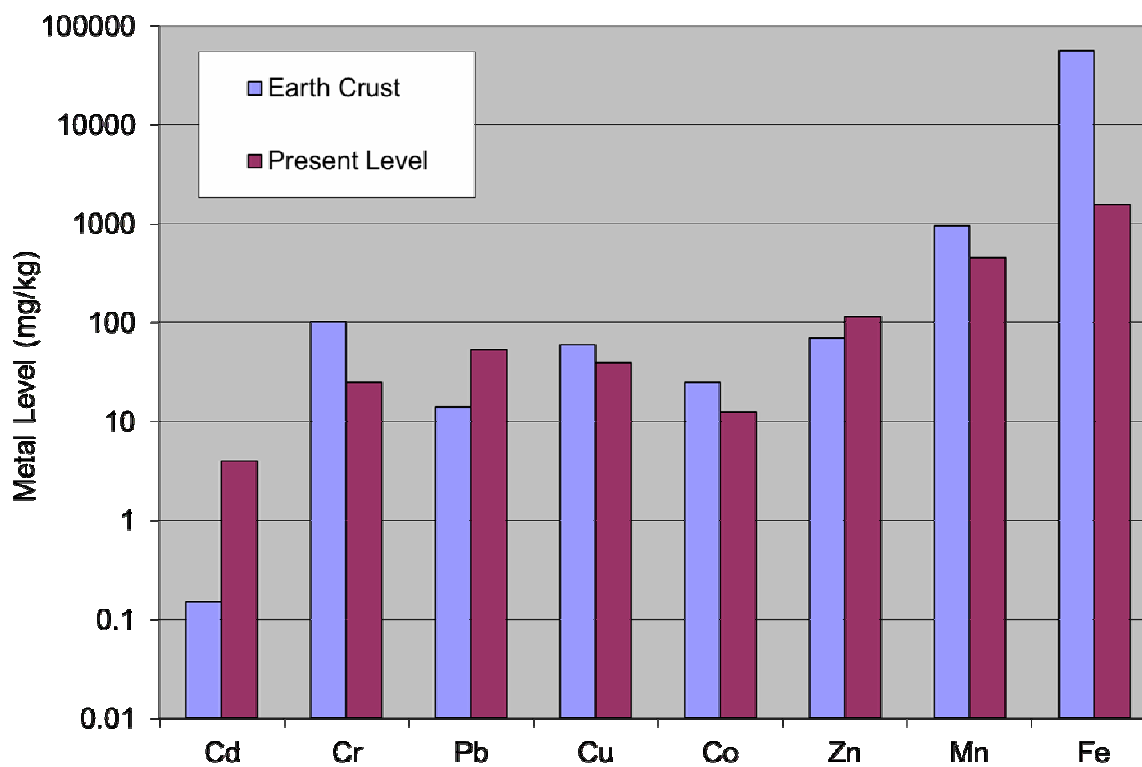


Figure 30. Comparison of average pseudo-total metal levels (mg/kg) in the soil with the earth's crust levels

Similarly, comparison of the maximum, minimum and mean values of contamination factors of the metals in the soil samples is illustrated in Figure 31. On the basis of pseudo-total metal levels in the soil, it is an effective tool to find the pollution load for a specific metal, which is categorized into following four levels (Hakanson, 1980):

1.  $C_f < 1$  low contamination
2.  $1 \leq C_f < 3$  moderate contamination
3.  $3 \leq C_f < 6$  considerable contamination
4.  $6 \leq C_f$  high contamination

The calculated contamination factors of the metals in the soil revealed high contamination for Cd on the average, followed by moderate to higher contamination for Pb and Zn. Maximum contamination factor values for Co and Cu indicated moderate contamination, whereas Cr, Mn and Fe revealed low contamination in the soil samples.

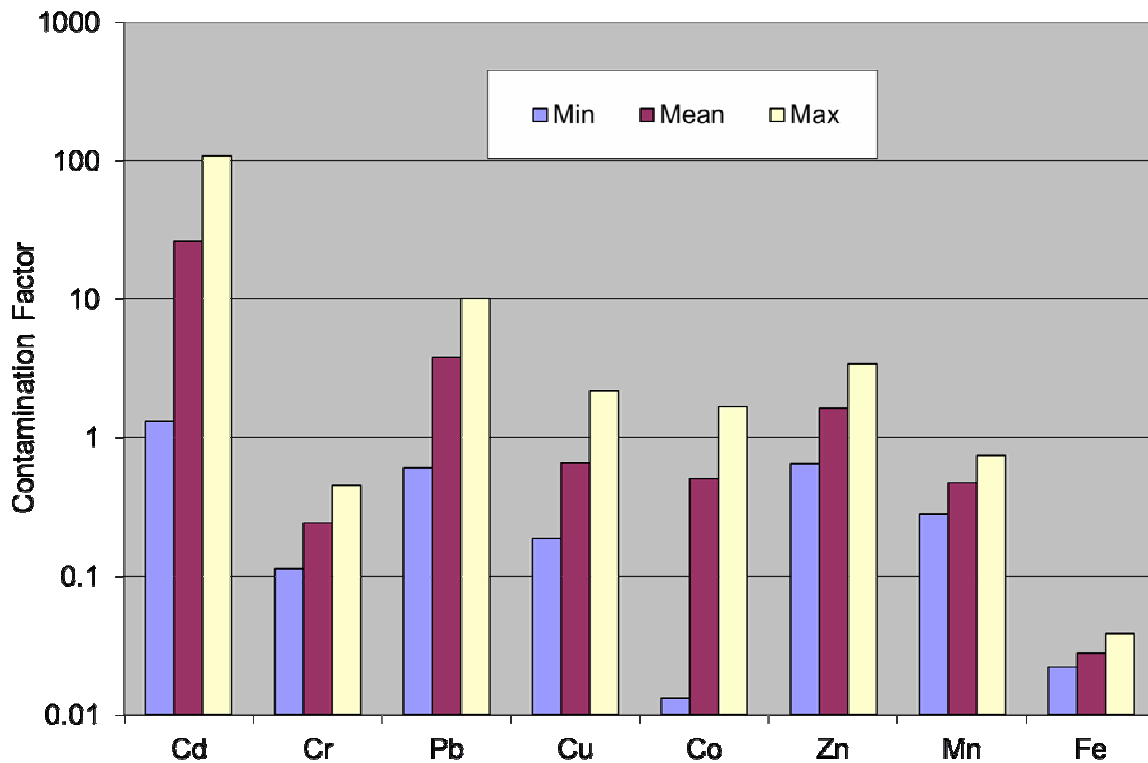


Figure 31. Comparison of the contamination factor ( $C_f$ ) of selected metals in the soil

The calculated geoaccumulation index for the metals in the soil samples is produced in Figure 32. These calculations were based on the pseudo-total metal levels in the soil. Geoaccumulation index is used to estimate the anthropogenic accumulation of the metals in soil. It is characterized into seven categories (Müller, 1969):

1.  $I_{geo} \leq 0$  practically uncontaminated
2.  $0 < I_{geo} < 1$  uncontaminated to moderately contaminated
3.  $1 < I_{geo} < 2$  moderately contaminated
4.  $2 < I_{geo} < 3$  moderately to heavily contaminated
5.  $3 < I_{geo} < 4$  heavily contaminated
6.  $4 < I_{geo} < 5$  heavily to extremely contaminated
7.  $5 < I_{geo}$  extremely contaminated

As presented in the Figure, Cd was heavily to extremely contaminated and accumulated in the soil while Pb was moderately to heavily contaminated and accumulated in the soil. However, maximum values of Cu, Co and maximum and mean values of Zn displayed uncontaminated to moderately contaminated status of the soil. Rest of the metals (Cr, Mn and Fe) showed practically uncontaminated status in the soil.

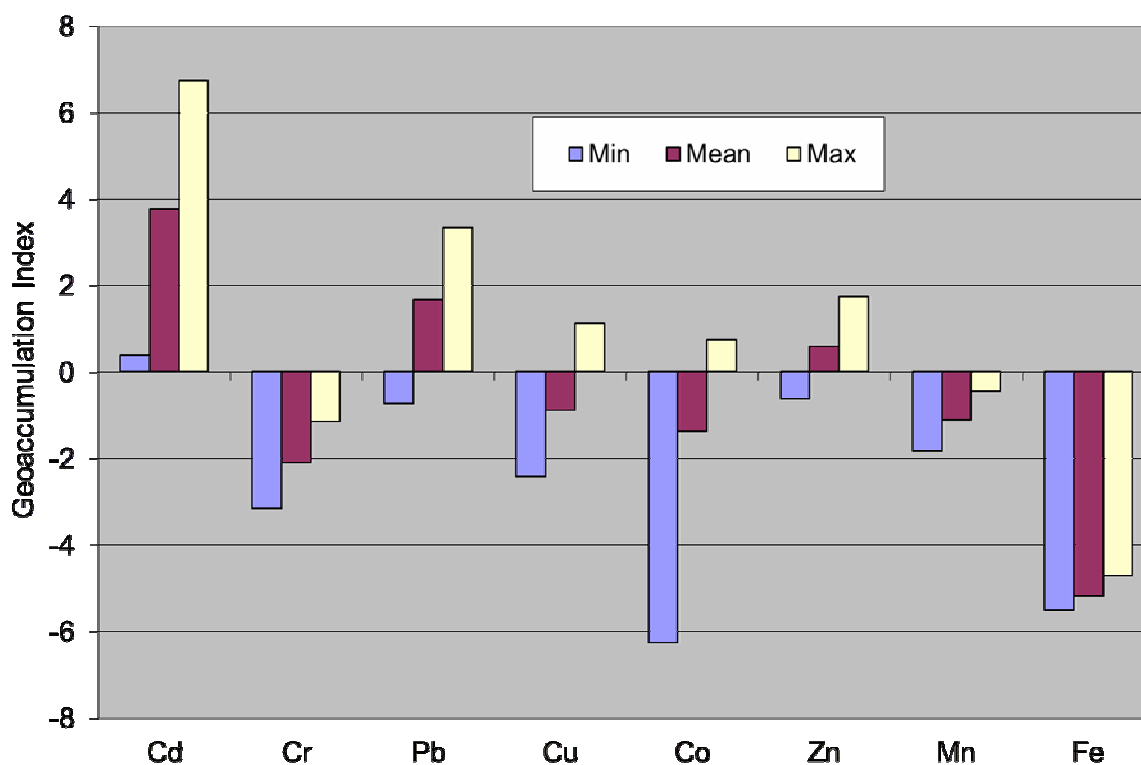


Figure 32. Comparison of the geoaccumulation index ( $I_{geo}$ ) of selected metals in the soil

Enrichment factors for the metal were also computed on the basis of pseudo-total metal levels in the soil samples. Comparison of the enrichment factors of the metals in the soil is shown in the Figure 33. Enrichment factors were employed to appraise the anthropogenic accumulation/enrichment of the metals in soil samples. Enrichment factors are classified into following five categories:

1.  $EF < 2$       minor enrichment
2.  $EF = 2 - 5$     moderate enrichment
3.  $EF = 5 - 20$     significant enrichment
4.  $EF = 20 - 40$     very severe enrichment
5.  $EF > 40$       extremely severe enrichment

On the average basis, among the metals, Cd, Pb and Zn demonstrated extremely severe enrichment in the soil samples, while mean and maximum values of Co, Cu and Mn exhibited significant to very severe enrichment in the soil due to anthropogenic activities. Similarly, Cr unfolded moderate to significant enrichment in the soil while Fe revealed least/minor enrichment in the urban soil samples.

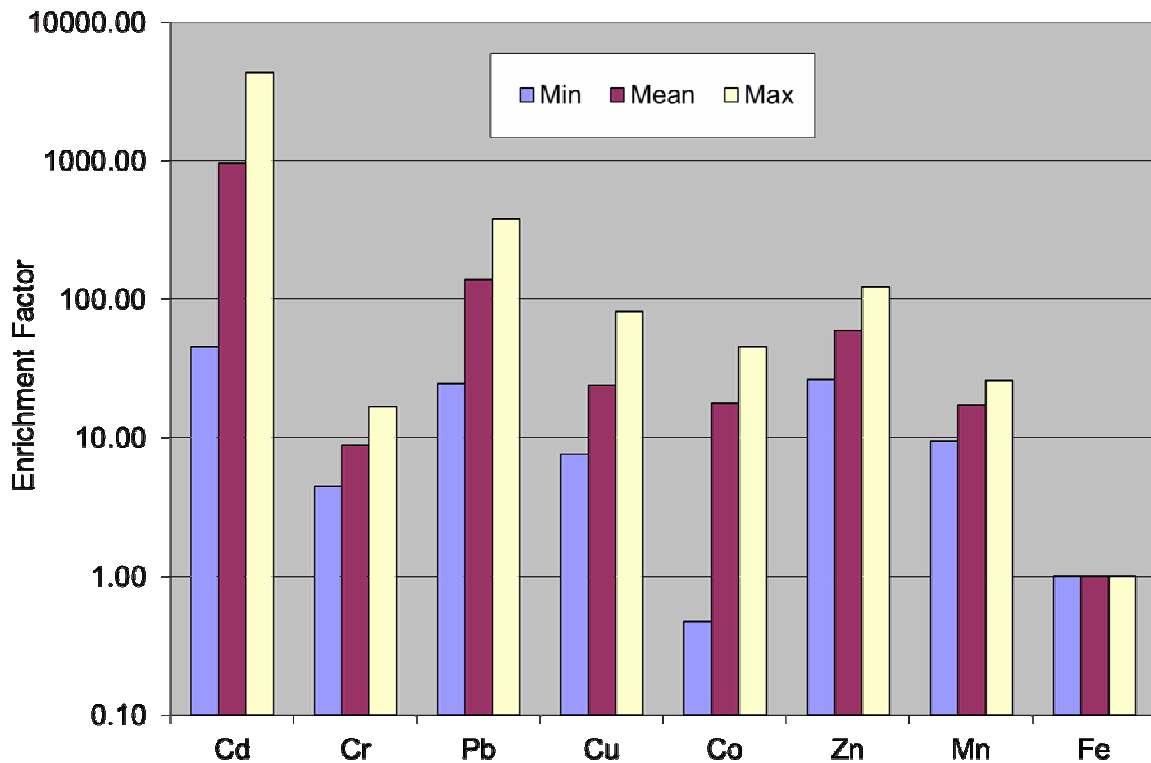


Figure 33. Comparison of the enrichment factors (EF) of selected metals in soil

Modified degree of contamination is used to determine the overall degree of contamination based on minimum, maximum and mean values of the metals in the soil. The calculated degree of contamination for the present metal levels in the soil is displayed in Figure 34. Pseudo-total metal levels in the soil were employed to determine the modified degree of contamination which is classified into following categories (Abraham & Parker, 2008):

1.  $mC_{deg} < 1.5$  Nil to very low degree of contamination
2.  $1.5 < mC_{deg} < 2$  Low degree of contamination
3.  $2 < mC_{deg} < 4$  Moderate degree of contamination
4.  $4 < mC_{deg} < 8$  High degree of contamination
5.  $8 < mC_{deg} < 16$  Very high degree of contamination
6.  $16 < mC_{deg} < 32$  Extremely high degree of contamination
7.  $mC_{deg} > 32$  Ultra-high degree of contamination

On the average basis, the modified degree of contamination for the metals in the soil indicated moderate degree of contamination; however, the maximum values suggested very high degree of contamination for the metals in the soil samples (Figure 34).



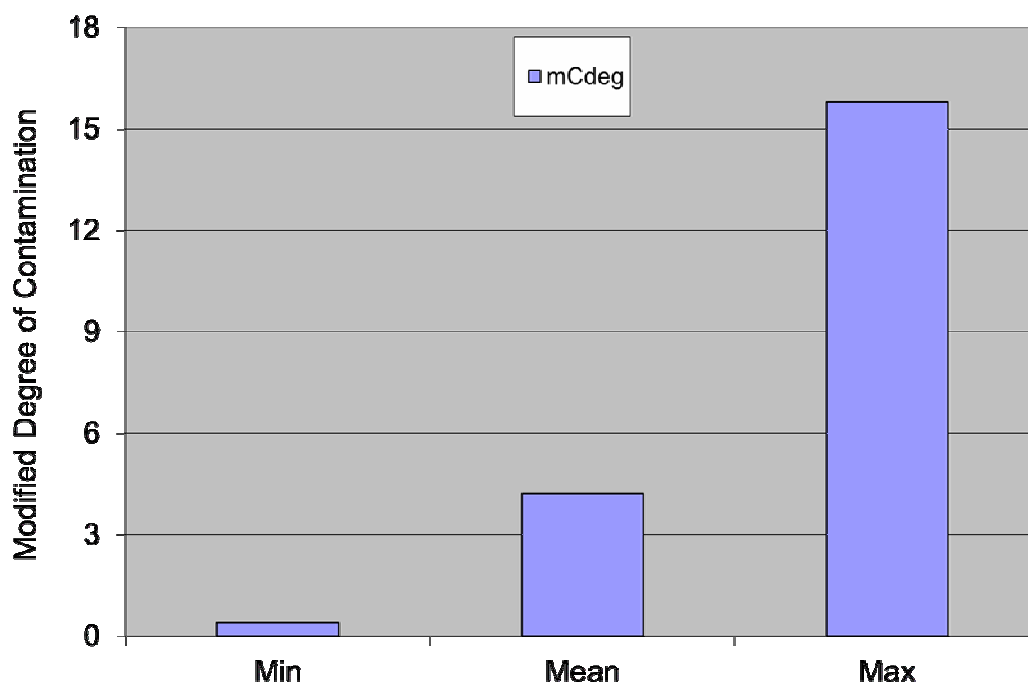


Figure 34. Modified degree of contamination ( $mC_{deg}$ ) associated with the metal levels in soil

### 3.20 Multivariate Analysis of the Pseudo total Metal Levels in Soil

Multivariate analysis was performed for the source identification and apportionment of the metals in aqua regia extract of the soil. Principal component analysis of the pseudo-total metal levels of the soil is displayed in Table 13, which manifested three significant principal components (PCs) with eigen values  $> 1$  and together explaining more than 67% variance of the data. The corresponding cluster analysis based on Ward's method is presented in Figure 35 in the form of dendrogram. The highest variance (37.57%) was given by PC 1 which revealed higher loadings for Cr, Cu and Zn. These metals were contributed by mixed sources in the soil as both natural and anthropogenic contributions were observed. PC 2 demonstrated higher loadings for Fe, Mn and Co, which were mostly contributed by the natural lithogenic sources in the soil. PC 3 exhibited significantly higher loadings for Cd and Pb, which were mainly contributed by the anthropogenic sources as these metals also unfolded significant pollution and contamination in the soil samples. The cluster analysis of the metals indicated two major clusters: first cluster consisted Fe, Mn and Co which was mostly natural in origin while second cluster comprised of Zn, Cu, Cr, Pb and Cd which showed contribution of anthropogenic sources in the urban soil. Overall, PCA and CA divulged significant anthropogenic contributions of the metals in the urban soil of Lahore.

Table 13. Principal component analysis of pseudo-total metal levels in the soil

	PC 1	PC 2	PC 3
Eigen Value	3.005	1.390	1.042
Total Variance (%)	37.57	17.38	13.02
Cumulative Variance (%)	37.57	54.95	67.97
Cd	0.255	-0.232	0.718
Cr	0.779	-0.176	0.112
Pb	0.283	-0.130	0.698
Cu	0.865	0.065	-0.164
Co	-0.148	0.583	0.050
Zn	0.866	0.045	-0.054
Mn	0.259	0.623	-0.163
Fe	-0.070	0.621	-0.137

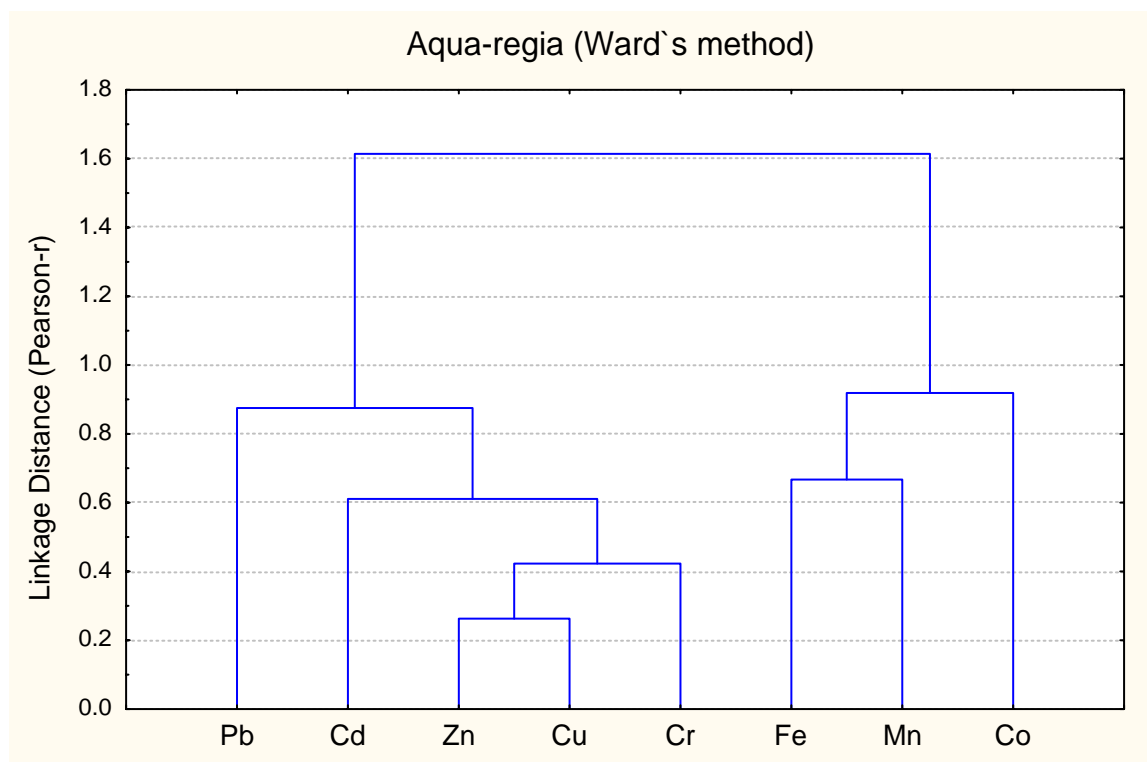


Figure 35. Cluster analysis of selected metals in aqua regia extract of the soil

### 3.21 Health Risk Assessment of the Metal Levels in Soil

Human health risks associated with the metal levels in the soil were also evaluated. Exposure risk assessment of the metal levels in the soil through ingestion and dermal contact were calculated and the results are illustrated in Figure 36. Exposure owing to ingestion was significantly higher than the exposure due to dermal contact. Highest exposure due to ingestion was shown by Fe, followed by Mn and Zn, whereas Cu, Pb and Cr offered comparatively similar exposure risk while Cd revealed the lowest exposure risk on the account of ingestion. More or less similar trend for the metals was also observed for the exposure through dermal contact.

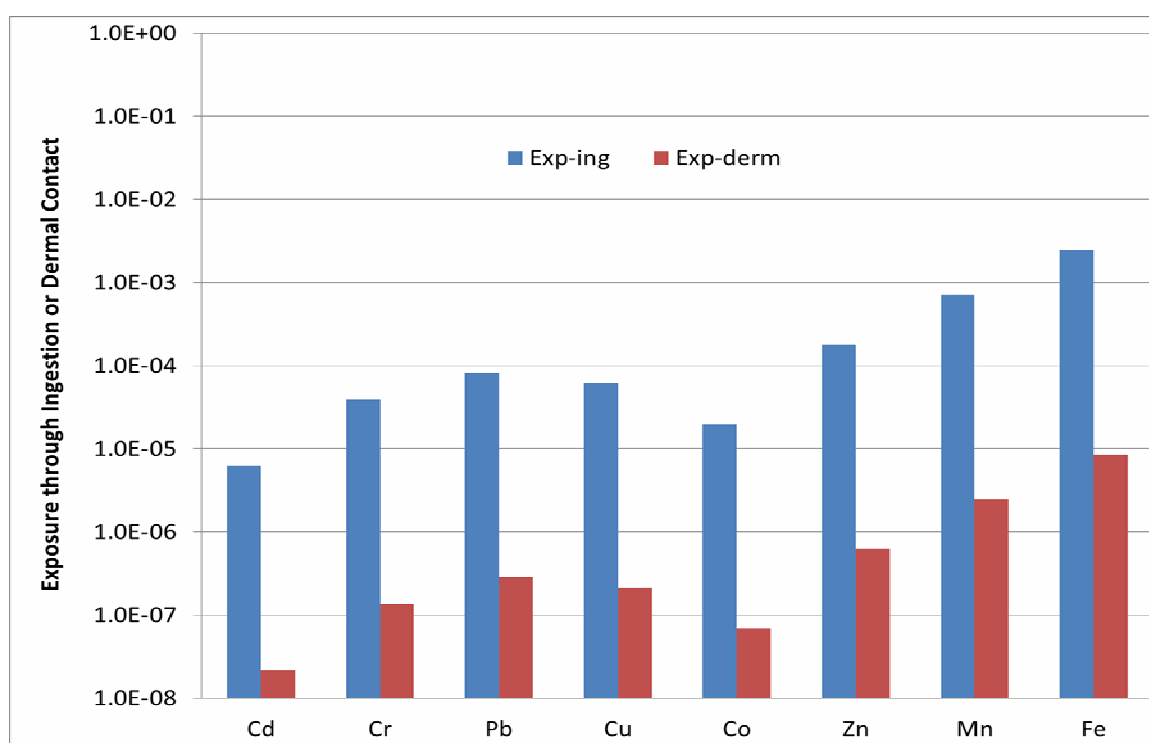


Figure 36. Exposure risk assessment of the metal levels in soil through ingestion and dermal contact

Non-carcinogenic risks associated with the metal levels in the soil were computed in terms of hazard quotient/index through ingestion and dermal contact as shown in Figure 37. The quotient/index value below unity (1) is generally considered safe for human health. By and large, the hazard quotients due to the ingestion were significantly higher than the quotients with respect to dermal contact. However, the calculated hazard quotients for both ingestion and dermal contact were considerably less than unity, so no significant health hazard was associated with these metal levels in the soil. Similarly, the

hazard index which is a cumulative parameter to evaluate the overall hazard was also calculated and for both ingestion and dermal contact the computed values were less than the safe limit (1). Therefore, the measured metal levels in the urban soil were not associated with any significant health hazard to the local population.

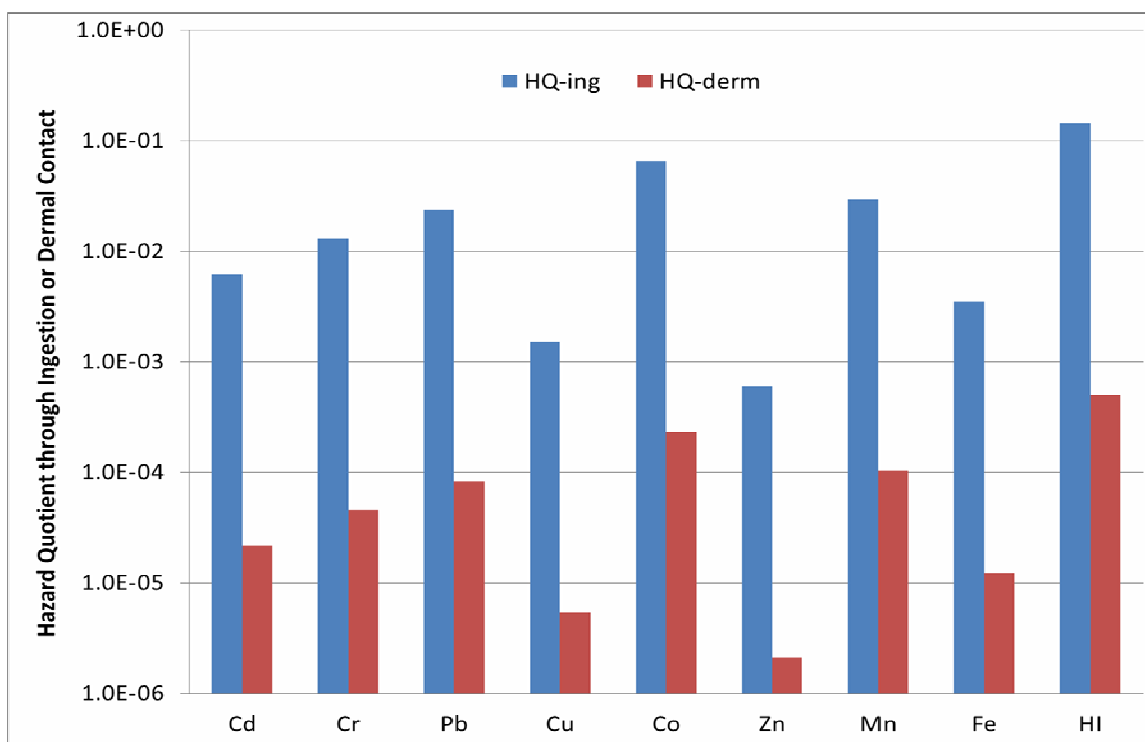


Figure 37. Hazard quotient/index of the metal levels in soil through ingestion and dermal contact

### 3.22 Salient Findings of the Present Study

Based on the deliberations put forward in foregoing sections, following salient features emerged from the present study:

1. Five types of extracting media were used to employed the bioaccessibility and mobility of potentially toxic metals in the urban soil of Lahore.
2. Among the metals, Fe, Mn, Zn and Pb showed relatively higher contributions in various soil extracts.
3. Aqua regia and glycine extracts revealed comparatively higher concentrations for most of the metals.
4. Among the selected metals, Cd, Pb, Co and Zn manifested higher bioaccessibility and mobility/bioavailability while Cr, Fe and Mn were least mobile and

- bioavailable in the soil samples.
5. Significant and strong positive correlations were found between Zn-Cu, Zn-Mn, Zn-Fe, Zn-Cr, Zn-Pb, Mn-Cr, Mn-Cu, Pb-Cr, Pb-Cd, Pb-Cu, Pb-Co, Co-Cd, Fe-Cr Fe-Co and Fe-Mn in various soil extracts.
  6. Quartile distribution demonstrated that most of the metals exhibited broad spread in their concentrations.
  7. Most of the soil samples were sandy loam in texture.
  8. In comparison with the earth's crust levels, mean levels of Cd, Pb and Zn in the soil were found to be higher in the present study.
  9. The pollution indices ( $C_f$ ,  $I_{geo}$ ,  $EF$ ) indicated severe to significant contamination, accumulation and anthropogenic enrichment of Cd, Pb and Zn (along with Cu and Co in some cases) in the urban soil of Lahore.
  10. Modified degree of contamination ( $mC_{deg}$ ) associated with the metal levels in the soil unfolded moderate contamination on the average.
  11. PCA and CA of the pseudo-total metal levels divulged common sources for Fe-Mn-Co, and Zn-Cu-Cr-Pb-Cd in the soil.
  12. No significant health risk/hazard was associated with the prevailing metal levels in the urban soil of Lahore.

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## *Appendix-I*

Description of input parameters for health risk assessment of the metals in soil

Parameter	Value	Unit	Reference
Exposure Frequency (EF)	350	days	USEPA, 1989 & 2004; Rovira <i>et al.</i> , 2011
Exposure Duration (ED)	30	year	USEPA, 1989 & 2004; Rovira <i>et al.</i> , 2011
Ingestion Rate (IR)	114	mg/day	Rovira <i>et al.</i> , 2011
Body Weight (BW)	70	kg	USEPA, 1989 & 2004
Sediments/Soil Adherence Factor (AF)	0.07	mg/cm <sup>2</sup>	USEPA, 1989 & 2004
Dermal Absorption Factor (ABS)	0.001 & 0.03 (As)	unit less	De Miguel <i>et al.</i> , 2007; USDoE, 2005
Exposed Skin Area (SA)	5700	cm <sup>2</sup>	USEPA, 2004
Averaging Time (AT)	10950	days	USEPA, 1989 & 2004
Conversion Factor (CF)	10 <sup>-6</sup>	kg/mg	USEPA, 1989 & 2004

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