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Lead And Associated Heavy Metal Distribution In El Paso, Texas

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LEAD AND ASSOCIATED HEAVY METAL DISTRIBUTION IN
EL PASO, TEXAS

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by

Ali Elkekli

2013

Dedication

This research is dedicated to my beloved mother for her support and prayer
My beloved wife and my family members for their constant support and encouragement

Without all of them

I would not have accomplished my goals.

LEAD AND ASSOCIATED HEAVY METAL DISTRIBUTION

IN EL PASO, TEXAS

by

ALI RAGAB ELKEKLI, B. S., M. S

DISSERTATION

Presented to the Faculty of the Graduate School of

The University of Texas at El Paso

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of the Requirements

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DOCTOR OF PHILOSOPHY

Environmental Science and Engineering

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Abstract

Contamination by lead and other heavy metals is one of the most important environmental concerns of today, locally and globally. This issue has led scientists and researchers to study the effect of heavy metals and their distribution in the environment. The aim of the present research is to document the concentration and geographic distribution of heavy metals in El Paso.

The selected heavy metals in the El Paso soil are lead, cadmium, chromium, zinc, antimony and copper. The soil sample for the study was collected during a previous community lead study (RO1 ESO11367; 2001-2006). 500 superficial soils samples were collected from public areas around 50 strata. Within each stratum, 10 blocks were randomly selected. The general procedures of EPA method 6200 for field portable XRF were followed for preparation of the samples, with slight modifications. These included grinding, mixing, pressing, and homogenization. The samples in present study 492 soil samples were analyzed by using x-ray fluorescence (Epsilon5). Statistical analyses were conducted to explore the relationships between lead and associated heavy metals. The detailed maps created by using the geographic information system techniques (GIS) for geochemical mapping of lead and associated heavy metals. The results of this study showed that the concentration of lead ranged from 10.8 to 420.9 ppm; for Cr ranged from 4.3 to 51.6 ppm; for Cu ranged from 6.5 to 385.8 ppm; for Zn ranged from 16.5 to 476.8 ppm; for Cd ranged from 0.4 to 11.9 ppm; and Sb ranged from 2.9 to 19.6 ppm with the mean value of 6.3 ppm. Therefore, the soil studied was highly contaminated with lead, copper, zinc and antimony and lesser extent in metals chromium and cadmium are detected in soil samples.

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Chapter 1: Introduction

1.1 Background

Heavy metals contamination is a major problem for our environment worldwide due to the ecological and health problems associated with it (Chernet, 2009). Metals are among the most dangerous environmental pollutants (Pundyte et al. 2011). Increased exposure to heavy metals is one of the consequences of human activities at the current stage of industrialization and demand for improved quality of life (WHO, 2007; Banerjee et al., 2011). The advance in detection techniques, methods and environmental chemistry, in addition to recent public awareness, has brought the topic of metal contamination to the forefront of the scientific community (Bergsten, 2006).

It is imperative that scientists explore the negative consequences of heavy metals on the ecosystem at local and global levels. The majority of heavy metals are considered among the most dangerous environmental pollutants. They are toxic to living organisms and have dramatically changed the composition and organization of soil. They do not disintegrate with physical processes, are bioavailable and biodegradable, and have a long biological half-life for elimination from the body (Pundyte et al., 2011). Lead, cadmium, chromium, zinc, copper, nickel, and mercury are the most common potential hazards and occurrences in contaminated soil (Chen, 2011; Alloway, 1995).

In spite of evidence of adverse health effects on humans and damages to the ecosystem from exposure to heavy metals, such metals are still being used in a wide range of applications. For example, lead, which is one of the oldest known metals in human history, saw a ten-fold increase in its global production from 1850-1990. Lead is utilized in many industries now,

especially in the manufacturing of chemicals. It is used in metal alloys, metallic paint, the plastic industry, batteries, nuclear power, oil, building materials, the ceramic industry, and water pipes. Mercury is still used in many parts of the world in the mining of gold. Arsenic and cadmium compounds are used with copper in timber preservation (DTSC, 2004; Jarup, 2003).

The worst incidence of lead release to the environment occurred during the 21st century when it was added to the gasoline fuel of vehicles. As refineries in the United States started adding lead compounds to gasoline in the 1920s, it became the dominant source of lead release in the United States (Pingitore et al., 2005; ATSDR, 2007). The use of lead in gasoline contributed significantly to the degradation of urban environments, the rising lead levels posing huge health risks to human populations, particularly children and women (Gihleman et al., 1999). Lead was gradually banned from gasoline in the U.S. between 1972 and 1996. The elimination of lead from gas is one of the great environmental achievements of all time; thousands of tons of lead have been removed from the air, and blood levels of lead in children is down by 70 percent (Browner, 1996).

Although the sources of lead release have been significantly reduced, and there has been a concurrent reduction in pediatric blood lead levels, the threat of lead exposure remains in the 21st century post-industrial era (Amaya et al, 2010). There is agreement among scientists, chemical policymakers and the public at large that research is needed to examine residual lead and other heavy metals contamination in the soil as well as to lower the levels of permissible standards of lead concentration blood levels (Alloway, 1995; Jarup, 2003).

Human land use affects the natural geological and biological redistribution of heavy metals through the pollution of air, water, and soil. Research conducted in communities in the United States to assess soil lead concentration and lead levels in blood show that there is a

relationship between human land use and environmental concentrations of heavy metals in urban soils (Elias et al., 2011). There is also correlation between lead levels in children and lead concentration in soils in urban areas (ATSDR, 2007). Additionally, an association has been found between ambient air lead levels and the concentration of lead in the surrounding soil (EPA, 1998).

There is much published data describing the range of heavy metals in the soil in El Paso, Texas. The major industrial activity responsible for heavy metals emissions in El Paso arises from the American Smelting and Refining Company (ASARCO). Most of these publications focused on soil lead in and around the ASARCO smelter. It has been considered the major source of lead and metallic contamination to the surrounding environment.

The studies also indicated that there was a significant association between soil lead and blood lead levels (Texas Department of Health, 2001). The lead levels found has significantly changed over the last quarter century; it has decreased between one and two orders of magnitude. Much of this decline is likely attributable to two transitions during that period: the phase-out of leaded gasoline and changes at the ASARCO smelter (Pingitore et al., 2005). In addition, investigations of particulate matter (PM) in the El Paso area indicated that vehicles have a relatively small contribution (< 20 percentage) to airborne particulate matter (Espinosa et al., 2005).

1.2 Statement of problem

The danger of soil contamination by heavy metals and their effect upon human, animal, and plant health is obvious and well understood. Awareness has been raised to reduce the risk of exposure to heavy metals, especially in the communities that experienced contamination. Mining and smelting are the most damaging and polluting activities for the soil. The industrial activity

from smelting in El Paso resulted in the accumulation of many heavy metals in the soil. Despite much research and investigation that studied the distributions and concentrations of environmental lead and other heavy metals since 1950 in El Paso, most of these studies focused on the environment near the El Paso smelter, which played an important role in measuring lead released into the environment. The status of lead contamination in El Paso has been studied more near the areas surrounding the ASARCO smelter as compared to other areas.

Therefore, this study seeks to address the under researched areas of El Paso. The need to conduct further study and research on soil contamination by lead and associated heavy metals, and to investigate the concentration levels and their geographical distribution is important to protect the environment and the residents in the contaminated areas. This research will investigate the concentration of heavy metals in El Paso by using the x-ray fluorescence analytical spectroscopic method.

1.3 Objectives of the study

The main objective of this study is to determine the concentration and distribution of heavy metals in the city of El Paso and El Paso County. This study is developed from The Encuentros Bi-national Lead Community Project with the following specific objectives:

1. To determine and evaluate the concentration of lead and associated heavy metals contamination in the study area;
2. To document the geographic distribution of lead and associated heavy metals in the soil of El Paso;
3. To evaluate the degree of human health risks;
4. To create detailed maps on the distribution and concentration of key metals.

1.4 Dissertation outline

The dissertation is planned as follows:

Chapter 1 provides an overall introduction background of heavy metals contamination.

Chapter 2 is an extensive literature review starting with a discussion of basic information and the concept of heavy metals and soil including soil contamination by heavy metals, classification of heavy metals in the environment and uses and benefits of heavy metals. Then introduced extensive literature reviewed for heavy metals contamination in El Paso is presented.

Chapter 3 draws the attention to heavy metal behavior and factors affecting heavy metal content in soil.

Chapter 4 begins with a review of background information, including area characterization, climate, soil, and flora followed by sources of contamination history of the study area. The methods for soil collection, preparation and procedure, and laboratory techniques used in analyzed the samples.

Chapter 5 focuses on a result and discussion of the study.

Chapter 6 present the summary finding, also brings out some of the recommendation and suggestions for future research on heavy metals.

Appendices and vita are included in the last part of the study.

Chapter 2: Literature review

2.1 Heavy metals in soil

2.1.1 Concept and definition of heavy metals

There is no clear single universal definition of what a heavy metal is (Jarup, 2003). There are many terms used in publications and legislation dealing with environmental science to describe and categorize metals, including trace metals, transition metals, micronutrients, toxic metals, and heavy metals (Isa, 2008; Lukkari, 2004). The first appearance of the term “heavy metal” in the literature goes back to European Journals in the 1890s (Moon et al., 2007).

Heavy metals constitute a very heterogeneous group of elements widely varied in their chemical properties and biological function (Raikwar, 2008). They are often used as a group name for metals and semimetals (metalloids) that have been associated with contamination and potential toxicity or eco-toxicity (Duffus, 2002). Several terms are used to refer to these elements, some based on density, some on atomic number or atomic weight, and some on chemical properties or toxicity. Density, in most cases, is taken to be the defining factor (Duffus, 2002). The metal as a subset of chemical elements with specific gravity that is at least 5 times the specificity of water (Sucui et al., 2009; Lied, 1992; Bone, 2004). Heavy metals tend to release electrons in chemical reactions and form simple cations. In the solid and liquid states, they are characterized by good heat and electrical conductivity, and are glossy and opaque. They have high melting and boiling points, and are malleable with usually monatomic pairs (Szyzewski et al., 2009).

2.1.2 Classification of heavy metals

The most current periodic table contains 108 elements of which 90 are considered metals (Horsfall, 2011). 23 of these are considered heavy metals: antimony, arsenic, bismuth, cadmium, cerium, chromium, cobalt, copper, gallium, gold, iron, lead, manganese, mercury, nickel, platinum, silver, tellurium, thallium, tin, uranium, vanadium, and zinc (Glaze, 1996).

According to the function and toxicity of heavy metals, they may be classified as essential, non-essential, and high toxic (Heiyan, 2003; Adage et al., 2011; Lin et al., 2011; Ibrahim et al., 2011; Iordache et al., 2010):

(I) - Essential for biological function: At low concentrations, some heavy metals are essential to health functions and the reproduction of microorganisms, plants and animals. These include cobalt, chromium, copper, manganese, molybdenum, nickel, selenium, and zinc. Exceeding the limit of these metals is either carcinogenic or toxic.

(II) - Non-Essential: Antimony and arsenic are non-essential metals, and cause toxicity above certain tolerance levels to plants and animals. They are difficult to metabolize and thus easily accumulate in organisms.

(III) - High toxic metals: Mercury and cadmium. These metals are non-essential.

The toxicity of both essential and non-essential heavy metals does not depend only on its concentration but also on the form of the metal (speciation) and the type and concentration of other toxicants (Reeder et al., 2006).

2.1.3 Soil composition

Soils are heterogeneous, complex mixtures of minerals solids and organic matter fractions found on the immediate surface of the Earth (Bandana, 2011; IAEA, 2004; Horsfall,

2011; Sdepanian, 2011). Soil is formed through the decomposition of rock and organic matter and living organisms over many years (Shayler et al., 2009). Soil develops slowly from various parent materials and is modified by time, changes in weather and climate, macro-microorganisms, vegetation, and topography (IAEA, 2004; Shayler et al., 2009).

Soil texture normally consists of liquid, gaseous, and solid components. Major components of the solid phase of soil include silicon, aluminum, iron, magnesium, calcium, and titanium, other traces, and varieties of soluble substance (Chatreewongsin et al., 2000).

According to Soil Science Society of America (SSSA), soil is a living system that represents a finite resource vital to life on Earth (IAEA, 2004). The properties of soil vary from one place to another (Shayler et al., 2009).

2.1.4 Soil contamination by heavy metals

Soils play a major role in element cycling and accumulating heavy metals in concentration orders of magnitude higher than in water and air (Ashraf et al., 2012). Soil is a major factor in reservoirs receiving many harmful constituents, elemental and biological, including heavy metals, and other human waste activity due to their high metal retention capacities (Dube et al., 2001). The contaminant is distributed horizontally, or between the particles of soil, because of mineral transformation or edaphological process (Flores et al., 2009). Metals in the soil distribute amongst various soil components. In some area of the world, it has been found that pollutants in the surface soil have reached a depth of half a meter (WHO, 2010).

Important soil characteristics that may affect the behavior and transfer of contaminants include soil texture, pH, amount of organic matter in soil, moisture level, temperature, presence of other chemicals, redox potential, and cation exchange capacity (LEF, no date; Shayler et al.,

2009). Heavy metals are among those chemicals that constitute the main group of soil pollutants that through their contamination of the environments affect all ecosystem components. The soil becomes contaminated by heavy metals if the concentrations of the metals are higher than the absorption capacity of the surface soil (Chatreewongsin, 2000). Soil contamination refers to the situation when the content of a natural or synthetic substance is higher than the background or natural content, whereby the soil loses its structure and both biological and chemical properties.

All metals are toxic at higher concentrations in soil because they cause oxidative stress by forming free radicals. In addition, some environmental conditions (e.g., pH, concentration of competing ions, concentration of complexing ligands in solution, the soil colloid, and characteristics of organisms in soil) may play an important role in determining metal mobility and bioavailability and toxicity (Yi et al., 2007).

Metals can exist as one of the following forms in soil (Schultz, 2006): (i) water-soluble free metal ions; (ii) carbonate complexes; (iii) metal ions occupying ion exchangeable sites and is specifically adsorbed onto inorganic soil constituents; (iv) organically bound metals; (v) compounds of oxides and hydroxides; and (vi) metals in the structure of silicate minerals.

The content of soil concentration of heavy metals depends on the composition of the parent material. The common total metal in unpolluted soils is below 1 mg/kg for cadmium, around 20 -30 mg/kg for copper, and below 20 mg/kg for lead in remote or recently settled areas. In soils with low-level pollution, between 30 and 100 mg/kg, range between 10 -300 mg/kg for zinc, below 10 mg/kg for arsenic, and less than 1 mg/kg for antimony (Sanchez & Ayuso, 2008).

2.2 Source of heavy metals in the environment

Different amounts of heavy metals may be found widely in our environment: terrestrial, aquatic, atmospheric, and limited amounts in the tissues of plants, animals, and human beings.

(Dube et al., 2001; Hei, 2002). The circulation and migration of metals in the natural environment are mainly related to the original lithological material, or created through anthropogenic processes (Flores et al., 2009). Generally, thousands of tons of heavy metals are released to the environment from all the sources and almost all of the released material becomes incorporated into the soil (Chernet, 2009).

2.2.1 Natural sources

Metallic elements occur naturally in all soils in one form or another in background levels that are regarded as trace ($<1000 \text{ mg kg}^{-1}$) and rarely toxic (Wuana & Okieimen, 2011), and are related to the soil parent material (Cancelac et al., no date). Natural geological processes are the most important source of heavy metals; these include alteration and weathering of high background rocks, and sediments (Sdepanian, 2011). Sand storms, forest fires and volcanic eruptions are the other natural phenomena through which heavy metals are released into the environment (Horsfall, 2011; Biosci, 2010; Lui, 2011; Chen, 2011).

2.2.2 Anthropological sources

Heavy metals are widely spread in the environment through many human activities, and form the major compounds that contaminate the soil because the most emitted metals to the atmosphere finally end up in soil (Lukkari, 2004). Anthropogenic sources include emission and disposal of waste by-products from metal processing industries, such as smelters, mining, coal and petroleum processing, municipal sewage discharge, home hold waste incineration, solid waste disposal, fertilizers and compost and internal combustion engine (Nriagu, 1989; Duce et al., 1991; Adelekhan, 2011; Horsfall, 2011). Heavy metals contaminants originating from anthropogenic sources are more likely the cause of the higher toxic concentrations in soil

(LeCoultré, 2001) and tend to be in a more mobile reactive form than the metals originating from native soil (Sdepanian, 2011).

2.3 Sources of heavy metals in contaminated soils

Soil becomes contaminated through natural activity as well as human activity. Certain chemical elements occur naturally in soil as a component mineral of the Earth's crust (Lin, 2011; SC&RM, no date). Heavy metals may occur through chemical, physical, and biological weathering of high background parent rocks and metal deposits (Adegoke et al., 2009), or may occur through geographical phenomena like volcanic eruption and earthquakes (Jung, 2008). The contamination of soil by metals has been dominated by various human activity (Lin et al., 2011; Adegoke et al., 2009), which has dramatically changed the composition and organization of soil, and increased the concentration of heavy metals (Sherametic et al., 2009).

Heavy metals have a wide range of applications in industry and agriculture (Adegoke et al., 2011). Mining and smelting operations are major sources of heavy contamination (Adegoke, 2009, Li et al., 2007). Activities such as mineral excavation, ore transportation, smelting, refining, disposal of tailings, and wastewater disposal around mines are the biggest sources of heavy metals in soil (Adegoke, 2009; Zhuang et al., 2009; Tetteh, 2010). Heavy metals are also derived from metallurgical industries (Ibrahim et al., 2011), the use of synthetic products (i.e. pesticides, paints, batteries) and land application of industrial or domestic sludge (USAD-NRCS, 2000), burning of various items such as wood, paper, tires (Mackay et al., 1997), waste incineration, and traffic emission (Ghiyasi et al., 2011).

Research indicates that soil in urban areas is contaminated by heavy metals, more so than suburban and rural areas, due to anthropogenic activities accompanying urbanization (Tahir et

al., 2007). Some studies in China, South Korea, and the United States showed that the areas near mines and smelters are at risk of contamination by heavy metals (Zhuang et al., 2009).

Atmospheric deposition is the main source of heavy metals in soil. Some metals are deposited by gas exchange at the sea surface, by fallout of particles (dry deposition) or are scavenged from the air column by precipitation (wet deposition). A thousand tons of metals are being added to the atmosphere annually by natural and anthropogenic sources. Table 2.1. (Valavanidis & Vlachogianni, 2010).

Table 2.1: Annual atmosphere emission of heavy metals by natural and anthropogenic sources

Metal	Natural sources tons/ year	Anthropogenic sources tons/ year
Nickel	26	47
Lead	19	450
Copper	19	56
Arsenic	7.8	24
Zinc	4	320
Cadmium	1.0	7.5
Selenium	0.4	1.1

2.4 Uses and benefits of heavy metals

Use of heavy metals has been closely linked to the activity of human beings for thousands of years (Biosci, 2010). The use of heavy metals in many activities is certainly not new to humanity. Heavy metal use extends back as far as 5000 years (Jarup, 2003), but the industrial revolution in the eighteen century, accompanied by non-management environment, and urban growth has led to the distribution of pollutants in all ecosystems (Pundyte et al., 2011).

Metals have useful properties such as strength, malleability, and conductivity of heat and electricity. Some metals exhibit magnetic properties and some are excellent conductors of

electricity (Sparks, 2005). Therefore, they are used in many industrial and agricultural applications. Metals are important components of our life; they play integral roles in the making automobiles, appliances, tools, computers and other electronic devices, and are essential to our infrastructure including highways, bridges, railroads, electrical utilities, food production and distribution, and other human needs such as medicines and treatment. In addition, certain metals are essential, required at low concentrations for plant growth and for animal and human health (Sparks, 2005). Some metals are used in diagnostic medical applications such as direct injection of gallium during radiological procedures, the use of lead as a radiation shield around X-ray equipment and the use of silver and mercury amalgam for tooth filling (Horsfall, 2011).

In addition, some heavy metals play an important role in biological systems. They are essential for good health life, for normal health growth, and reproduction by plants and animal in small trace amounts quantity. These metals such as copper, chromium and zinc (Iordache et al., 2010).

2.5 Toxicity of heavy metals

On the other hand, the majority of heavy metals are toxic to living organisms (Akbar et al., 2006). Metals are considered to be among the most dangerous environmental pollutants because they do not disintegrate through physical processes and have long biological half-lives for elimination from the body (Pundyte et al., 2011). They can adversely affect plant and animal metabolisms, and soil biological activity (Ezeh et al., 2011).

Toxicity of metals can vary according to their valence and their combination with other elements (Moore, 2002; Clark, 2001). The EPA ranked the heavy metals arsenic, lead and mercury as the top three most hazardous substances. The world health organization (WHO)

classified heavy metals as one of risks people have been exposed to through food (Banerjee et al., 2011). Cadmium, chromium, lead, zinc, and copper are potential hazards in soil, and are a high health risk (Chen, 2011; Alloway, 1995).

Plants absorb and accumulate heavy metals from the soil and water in the soluble form as salts by uptake through the roots. Heavy metals can influence physiological activities of plants such as photosynthesis, gaseous exchange, and nutrient absorption (Fagbote & Olanipekun, 2010). Absorption and accumulation of heavy metals in plant tissue depend upon many factors, which include temperature, moisture, organic matter, pH and nutrient availability (Jiwan & Kalamdhad, 2011).

In the human body, heavy metals affect psychophysical development (Szyzewski et al., 2009). The toxicity of a substance depends on three factors: its chemical structure, the extent to which the substance is absorbed by the body, and the body's ability to detoxify the substance and eliminate it from the body (HESIS, 2008). Heavy metal toxicity can result in damaged or reduced mental and central nervous function, lower energy levels, and damage to blood composition, lungs, kidneys, liver, and other vital organs (LEF, no date).

2.6 Review of previous researches in study area

The study of heavy metals in the El Paso area started in early 1970 (Srinivas, 1994) to investigate the effect of industrial pollution on the area. The studies focused upon the distribution and concentrations of environmental metals in soils, dust, air, and in the bloodstream of residents in selected areas in the El Paso del Norte region by local and state organizations (Dulin, 2005).

Pingitore et al. (2009) conducted a study to identify and quantify the major lead species, and its source in the airborne in El Paso. They stated that the sources and health threat of the low levels of lead in unleaded air remains a topic of scientific and public health interest in the United

States. They claimed that there is a need to further reduce the airborne particulate standard for lead, an assertion that is still argued between independent researchers and some members of the EPA's scientific advisory panel for stricter limits, as low as $0.02 \mu\text{g Pb m}^{-3}$. In this study, 20 samples of particulate matter (PM) were collected on woven silica fiber filters in 2005 and 1999 at three sites in El Paso. These samples were examined by synchrotron-based XAFS (X-ray absorption fine structure) to identify and quantify the major lead species. The study concluded that the local lead-contaminated soil was the major source of airborne lead in El Paso.

In 2006, Ketterer conducted a study for the Sierra Club. The purpose of this study was to characterize the possible contributions of ASARCO's inactive El Paso smelters to the burden of lead and other hazardous substances in the soils of three locations near the plant: residential areas in Ciudad Juarez, Chihuahua, Mexico; residential areas in Anapra, New Mexico; and areas near the facility in El Paso, Texas. The top 10 cm of soil from 97 locations from three areas were collected to investigate concentrations of ten elements lead, copper, zinc, arsenic, silver, cadmium, indium, antimony, thallium, and bismuth.

The study revealed a probable link between the smelting activities of the American Smelting and Refinery Company (ASARCO) and soil contamination in El Paso and the nearby communities of Anapra, NM, and Ciudad Juarez, Chihuahua, Mexico. This study concludes that the major source of soil contamination is the ASARCO smelter. The major findings of this study include that the presence of elevated levels of hazardous substances such as lead and arsenic is strongly correlated with the smelter. In sampled locations where lead and arsenic are present at the highest levels, the contaminants are always present at correspondingly high levels (Ketterer, 2006).

In 2005, Pingitore et al. conducted a study to investigate lead levels and the distribution of lead in El Paso, Texas, as a part of Encuentros Project. The researchers conducted a comprehensive study for soil lead levels in select areas of El Paso. A total of 500 surface soils samples were collected from 50 strata of public areas around selected municipal blocks. 339 surface composite samples have been analyzed with a Spectrace 9000 field-portable XRF unit equipped with three isotope excitation sources (^{55}Fe , ^{109}Cd , and ^{241}Am). The results of the study are represented in a uniquely detailed colored map of lead soil concentration in El Paso, based on the average lead soil concentration that shows the levels of lead were generally higher near ASARCO, in the old downtown part of the city, and neighboring commercial districts. Lower concentrations of lead characterized neighborhoods outside of this urban core. The study estimated the average concentration of lead for El Paso soil to be around 70 ppm. The maximum average block concentration was 421 ppm at a site near downtown, and the minimum value was below the detection limit of approximately 20 ppm. In addition, the study concluded that the geographic pattern of elevated lead values is obviously not random. The elevated values in the area near the ASARCO smelter have been attributed to operations at the plant for more than a century. The geographic distribution of lead in this study is similar to the pattern of lead in PM in air filters from around the city collected in the mid-1990s (UTEP Press Release, 2004; Dulin, 2005; Pingitore et al., 2005).

In 2002, U.S. Regional 6 through the U.S. Army Corps initiated a series of lead and indoor dust assessment in the El Paso region. A total of 112 soil samples from depths 0 to 1 inch were collected from University of Texas at El Paso (UTEP) campus, schools, and parks in El Paso. Samples were analyzed for lead and arsenic concentration. Elevated lead and arsenic concentrations above the human health threshold were identified at schools, parks, and the UTEP

campus in El Paso. The EPA took additional samples from the UTEP campus and in areas closer to downtown El Paso, and the results showed high concentration (exceeding 1000 mg/kg in some samples (Dulin, 2005).

In 2002, Weston Solutions Inc., collected 1,686 surficial and near-surficial soil samples from 341 locations at various depths (0- to 6-inch, 6- to 12-inch, 12- to 18-inch, and 18- to 24-inch) from various residences, daycares, schools, parks, churches, city properties, and undeveloped or industrial areas over an approximately 6-mile area in El Paso, El Paso County, Texas, and Sunland Park, Dona Ana County, New Mexico. Analytical results reported the presence of lead and arsenic within the majority of the sample locations. Lead was reported above the 500 mg/kg residential screening level in 28 sampling locations and arsenic was reported above the 24 mg/kg residential screening level in 45 sampling locations. At industrial sites, lead was reported above the 1000 mg/kg screening level at 12 sites and above the 200 mg/kg arsenic screening level at 7 sites (Weston Solutions, Inc., 2002).

In 1994, Srinivas collected 72 surface and subsurface (6-inch depth) samples from public parks in El Paso. The results of the sample analyses indicated that concentrations of metals were higher in surface soils than in subsurface soils. Arsenic was detected in only one sample, at the instrument detection limit of 55 mg/kg. Lead concentrations ranged from below the instrument detection limit of 30 mg/kg to 130 mg/kg. Srinivas found neither point sources nor large-scale contamination in east and northeast El Paso (Srinivas, 1994).

In 1994, Devanahalli collected 54 soil samples from the surface and at a 6-inch depth in public parks, playgrounds, and schools, a downtown area of El Paso, Texas, bounded by Interstate-10 to the north, the Rio Grande River to the south, the Sun Metro Terminal to the west, and Phelps Dodge Copper Refinery to the east. The results of the study showed that the arsenic

concentrations in the samples ranged from below the instrument detection limit of 13 mg/kg to 33 mg/kg. Lead concentrations ranged from the instrument detection limit of 17 mg/kg to 560 mg/kg (Devanahalli, 1994).

In 1993, Barnes conducted a study involving the collection of surface soil (0–2.5 cm) and subsurface soil (10–60 cm) beneath the surface samples from areas surrounding various facilities in El Paso, Texas, that were potential sources of metals contamination. Potential sources of contamination included the ASARCO Smelter, Memorial Park in central El Paso where a former smelter was located, and the Phelps Dodge Copper Refinery. Concentrations of arsenic, cadmium, copper, lead, and zinc were found at highest concentrations in the area around the ASARCO Smelter. Higher concentrations were found in the surface samples (2.5-centimeter depth) than in those samples taken from deeper locations. The highest concentration of lead (5,194 mg/kg) and arsenic (589 mg/kg) were found in the area identified by Barnes as ASARCO and decreased with distance from the smelter (Barnes, 1993).

In 1993, Ndamé collected and analyzed 78 soil samples at the University of Texas at El Paso campus, and at parks and public schools playgrounds within a 2 km radius of the campus. The samples were analyzed for several metals including arsenic, barium, cadmium, chromium, lead, and selenium. Sample results indicated the presence of arsenic in soils ranging from below the instrument detection limit of 51 mg/kg to 92 mg/kg. Surface soil concentrations of lead were reported as high as 1,500 mg/kg. Significant concentrations of arsenic and lead were not detected in any of the off-campus public schools or parks with the exception of a surface soil sample collected from Althea Park, which had a lead concentration of 840 mg/kg. The maximum observed concentrations for arsenic and lead were 13 and 79 times higher than their respective background soil concentrations in the western U.S. (Ndamé, 1993).

In 1989, the Texas Air Control Board (The Texas Commission on Environmental Quality) conducted an arsenic soil study in El Paso County. The study collected and analyzed surface soil taken from half-inch top samples in El Paso in the vicinity of schools and recreational parks. The highest value of arsenic detected was 1,100 milligrams per grams (part per million [mg/kg]) which were observed in the soil collected at the International Boundary and Water Commission, an area identified as being close to ASARCO and directly across from a brick manufacturing facility in Ciudad Juarez, Chihuahua (Texas Air Control Board, 1989).

In 1972, Miller documented the lead levels of soils of the Rio Grande Flood Plain in the “Upper Valley” and “Lower Valley” of El Paso. The study found lead contents of the soils ranging from 0.4 ppm to 35.0 ppm. No correlation was found between lead content and either vehicular traffic or soil type. Relationships were noted between lead content and distances from five potential point sources of lead contamination (Pingitore, 2005).

In 1971, the El Paso City-County Health Department (EPCCHD) collected soil samples between June and December of 1972 showing the highest concentrations of lead and other metals to be in surface soil from within 0.2 miles of the ASARCO smelter.

The investigations conducted around the ASARCO El Paso facility played an important role in identifying the potential public hazards caused by lead released into the environment (TDH, 2001).

2.7 Historical review of American Smelting and Refining Company

The American Smelting and Refining Company (ASARCO) smelter, constructed in the late 19th century (Health Consultation, 2001), was a major potential point source of metal contamination in El Paso. The smelter was located on the west side of El Paso, Figure 2.1, and

occupied 123 acres of 585 acres along the Rio Grande near U.S- Mexico border, at an elevation of approximately 3,600 feet above the mean sea level Figure 2.1.



Figure 2.1: Map and aerial view of El Paso smelter

The surface geology consists of a mix of colluvial sediments from the surrounding mountains and fluvial sediments from the Rio Grande River (Sher, 2009).

The smelter was constructed in 1887 as the Consolidated Kansas City Smelting and Refining Company. In 1899, it became part of the newly formed American Smelting and Refining Company (ASARCO). Ores of lead, copper, cadmium, zinc, and antimony were smelted at various times in the smelter during its operation. A copper smelter was added in 1910. In 1948, a zinc plant is installed. Slag fuming facilities were constructed to recover zinc from a lead blast furnace slag. In the late 1970s, the antimony plant was completed (Drexler, 2003; Health Consultation, 2001).

During its operation, ASARCO had environmental problems resulting from its smelting processing many by-products, some of which were released into the air or dumped as slag including such elements as arsenic, lead, cadmium and their compounds. The smelter was the source of particulate lead in soil, air, and dust. Heavy lead exposure was found throughout a wide radius in the city of El Paso and Juarez. High lead concentration was also found in children's bloods levels. It is estimated that the smelter emitted 1,100 tons of lead into the air from 1968 through 1971 (Anguelovski et al., 2008). In addition, ASARCO had emitted 508 metric tons of zinc, 12 metric tons of cadmium, and 1.2 metric ton of arsenic into the air (Health Consultation, 2001; Bernstein, 2004).

The smelter has received particular attention from local authorities and the EPA, The health department and the Centers for Disease Control and Prevention in 1972 as well as the Texas Air Control Board. Contamination by lead and other metals was calculated and measured in the environment. The results of these investigations found that ASARCO is responsible for elevated heavy metals levels in the El Paso environment. Heavy lead exposure was found throughout a wide radius in the cities of El Paso and Juarez. The lead concentration was also found in children's blood, and in residential properties (Soto, 2003). The EPA named ASARCO a potentially responsible cause of contaminated soils located throughout El Paso.

After the 1970's, ASARCO was accused of causing pollution in the air and in the soil by controlling pollution equipment and improving safety for employees. In 1951, ASARCO built a 610-foot chimney as demands increased for more pollutant control. In 1967, a 828-foot smokestack was completed; at the time, it was the largest in the world (Drexler, 2006). Based on complaints about air pollution, the city sued ASARCO in 1970 for violating the 1967 Air Safety Code and Texas Clean Air Act, citing numerous instances of specific violations. In

the mid 1980's, the antimony plant, with lead plant operations being suspended in 1985 followed by the closing and demolishment of the zinc plant, followed by closure of cadmium plants in 1992, and in 2005 ASARCO declared bankruptcy.

In 2009, the ASARCO El Paso smelter was shut down permanently on a mandatory three-year care and maintenance, and on April 14th 2013, the smelter was demolished.

The ASARCO facility was not the only smelter to operate in the El Paso community, though it was the largest and had the greatest longevity. Two additional smelters were located in El Paso as well. The International Smelter, at the present site of Guillen School in central El Paso, operated from 1888 until 1894, and the Federal smelter, which was located in central El Paso off Gold Street near what is now Memorial Park, operated from 1901-1904 (Health Consultation, 2001; Drexler, 2003). In addition, another area of interest is Phelps Dodge Copper refinery on the east side of El Paso, which was built in 1928.

Chapter 3: Discussion on the metals studied

3.1 General feature of investigated heavy metals

The following section will address the characteristics of several of the heavy metals, which the study explores. The study of the properties and the behavior of heavy metals through the environment are very important in design management strategies that minimize adverse environmental impact and avoid negative effects in human health and other living organisms. Design management strategies also help in finding the appropriate remediation methods to clean contaminated areas.

The discovery, abundance, uses, properties, sources and health effect of investigated heavy metals is provided below.

3.1.1 Antimony (Sb)

Humans have known antimony since ancient times. It has been found in the colored glazes used on beads, vases, and other glassware in ancient civilizations (Krebs, 2006). The natural sulfide of antimony was known and used in Biblical times as medicine and as a cosmetic (Kean, 2010).

Antimony is used in many applications. The most important use of antimony is in making compounds used in the manufacture of flame-retardant materials. It is also used to make alloys with a number of different metals (ATSDR, 2007).

Antimony is a rare element, naturally present in the Earth's crust in a very low concentration. It usually occurs as a compound. It is the 63rd most abundant element on the Earth's crust; the natural abundance of antimony is estimated to be about 0.2 ppm by weight, (0.00002%) in the Earth's crust (Krebs, 2006; Angima, 2010). The average concentration of

antimony in U.S soil is about 0.66 ppm with the range of about < 1-8.8 ppm (Shacklette & Boerngen, 1984). The total antimony content in unpolluted soils for antimony is below < 1 mg/kg (Sanchez & Ayuso, 2008). Concentration above 31 mg/kg in soil may be hazardous to human health (EPA, 2006).

Antimony is a semi- metallic element in period 5 and group 12 of the periodic table, and has the following chemical and physical properties: a moderately active, moderately hard, silvery-white, shiny metal. The melting point of antimony is 630°C (1,170°F) and its boiling point is 1,635°C (2,980°F). Its density is 6.68 g/cm⁻³ (Wuana & Okieimen, 2011; ATSDRS, 2007).

Antimony enters the environment and is transferred between media and makes its path through air, soil, and water by natural processes as well as anthropogenic activity (ATSDRS, 2007).

It releases into the environment naturally, from discharges such as windblown dust, volcanic eruption, sea spray, forest fires, and biogenic sources. It can be released due anthropogenic activities such as metal smelting and refining at coal-fired power plants (Krebs, 2006).

Antimony and its compounds are toxic to human beings. In 2011, the ATSDR ranked antimony as the 232nd most hazardous substance (SPL). Antimony poisoning occurs when a human being absorbs contaminants of the metal through breathing or ingestion. It can cause a variety of adverse health effects. The target organ systems affected by antimony are the cardiovascular and respiratory systems (ATSDR Tox FAQ for Antimony, 1992). Soluble antimony (III) salts can cause genotoxic effects in vitro and in vivo (WHO, 2008). Inhalation exposure to antimony was reported to be responsible for pneumonitis, fibrosis, bone marrow damage and carcinomas. In low levels, it can irritate the eyes and lungs, stomach pain, diarrhea,

vomiting, and stomach ulcers. Acute toxicity causes irritation of tissues, damage to the lungs, heart, liver and kidneys and may even cause death (IARC, 2010).

3.1.2 Cadmium (Cd)

German chemist Friedrich Stromeyer discovered cadmium in 1817 from an impurity in some samples of zinc carbonate (Krebs, 2006). Cadmium is produced mainly as a by-product from the processing of zinc, lead and copper extraction ores (EPA, 1997). The most important use of cadmium was in the electroplating of steel. Cadmium compounds are currently mainly used in batteries (especially rechargeable nickel-cadmium batteries). It is also used in pigments, coatings, plating, and the manufacture of plastic products, alloys, and pesticides (Hei, 2002; Morrison, 2000).

Cadmium is a relatively abundant element. It is found most commonly in ores of zinc as a mineral combined with other elements in the form of compounds such as cadmium oxide, cadmium chloride, cadmium sulfate, and cadmium sulfide (OSPAR, 2004). It is the 65th most abundant in the Earth's crust (Krebs, 2006). The natural abundance of cadmium is estimated to be about 150 ppm by weight, (0.00015%) in the Earth's crust (Shacklette & Boerngen, 1984). The total cadmium content in unpolluted soils is less than 1 mg/kg (Sanchez & Ayuso, 2008). Concentrations exceeding 37 mg/kg may result in effects on human health (EPA, 2006).

Cadmium is a transition element in period 5 and group 12 of the periodic table, and has the following chemical and physical properties: it is a bluish-white, soft, ductile, non-corrosive metal, with atomic weight of 112.4. Its melting point is 321°C (610°F) and its boiling point is 765°C (1,410°F). The density of cadmium is 8.65 g/cm³ (Wuana & Okieimen, 2011).

Cadmium enters the environment and makes its path into air, soil, and water from both natural processes and anthropogenic activity. Cadmium is released into the environment

naturally, mainly from the weathering of rocks, forest fire, volcanic activity, spray from oceans, biogenic material and forest fires (COWI, 2003). Cadmium can be released from anthropogenic activities such as the production of zinc metal, waste incineration and application of fertilizers and sewage sludge (Sparks, 2005; Iqbal, 2008).

All forms of cadmium are known to produce high toxicity effects on humans. In 2011, the ATSDR ranked cadmium as the 7th most hazardous substance (SPL). Cadmium poisoning occurs when a human being absorbs contaminants of the metal through breathing or ingestion. Food intake and tobacco smoking are the main routes by which cadmium enters the body (Wuana & Okieimen, 2011). Cadmium is toxic at very low exposure levels and has acute and chronic effects on human health (Jarup, 2003). The targeted organ systems are the liver, placenta, kidneys, lungs, brain, and bones (ATSDR Tox FAQs for Cadmium, 2010).

The most toxic form of cadmium is its ionic form. The inhalation of cadmium dust quickly creates deadly damages to the respiratory system and kidneys. The normal intake of cadmium is 1-3 micrograms/day. Ingestion of any significant amount of cadmium causes immediate poisoning and damage to the liver and kidney. In addition, cadmium can cause bones softness and loss of body mass. In extreme cases of cadmium poisoning, the mere body weight causes fractures (Amid, 2006).

High levels of cadmium accumulated in the human body can induce chronic pulmonary problems, diarrhea, erythrocyte destruction, muscular cramps, nausea, renal degradation, salivation, and skeletal deformity (WHO, 2008). Long-term occupational exposure to cadmium at excess concentrations can cause a wide variety of acute and chronic effects in humans. It can cause depressed growth, high blood pressure, kidney damage, cardiac enlargement, hypertension, fetal deformity, and cancer (Blacksmith Institute, 2008).

3.1.3 Chromium (Cr)

Chromium was discovered in a mineral known as Siberian red lead in 1797 by N. L. Vauquelin (Krebs, 2006). Chromium is primarily used in metallurgical, refractory and chemical industries; it is used also in alloys, and, the production of stainless steel. The applications of stainless steel include automobile and truck bodies, plating for boats and ships, construction parts for buildings and bridges, parts for chemical and petroleum equipment, electric cables, machine parts, eating and cooking utensils, and reinforcing materials in tires and other materials. Two other major uses of chromium are electroplating and the manufacture of refractory bricks in furnaces. Chromium is also used to tan leather, preserve wood, and make dyes and pigments for paints (Jalali, 2007; Greaney, 2005).

Chromium is rarely a pure element, naturally present in the Earth's crust. It does not occur as a free element. It is only found in combination with other elements such as chromium salts, and is found in complexes with oxygen, iron, or lead, in several different forms. The most common forms of chromium are chromium (0), trivalent or chromium (III), and hexavalent or chromium (VI). Its abundance is 21st among elements found in Earth's crust (Haroun, 2009; Krebs, 2006). The natural abundance of chromium in the Earth's crust is about 120 ppm (0.014%). The average concentration of chromium in U.S. soil is about 54 ppm with ranges about 1-2,000 ppm (Shacklette & Boerngen, 1984). Concentration of hexavalent above 30 mg/kg, and above 10,000 for trivalent may result in adverse health effects in human beings (EPA, 2006).

Chromium is a transition element in period 5 and group 12th of the periodic table, and has the following chemical and physical properties: Chromium is a fairly active metal. It is a steel-gray, lustrous, hard, brittle metal, and it can be highly polished with atomic number 24,

atomic mass 52, melting point 1875°C, and boiling point 2665°C. The density of chromium is 8.65 g/ cm⁻³ (Wuana & Okieimen, 2011).

Chromium enters the environment and makes its path into air, soil, and water as a result of both natural processes and anthropogenic activity. Naturally, chromium and its compounds releases into the environment through natural discharges such as the continental dust flux, volcanic eruption, sea spray, forest fires, and biogenic sources (Krebs, 2006). Chromium can be also released from anthropogenic activities such as metal smelting and refining, coal-fired power plants, steel industries, leather and textile manufacturing, electro- painting, the combustion of coal and oil, cement works, waste incineration, and fugitive emissions from road dusts (Jacobs & Testa, 2004; Krebs, 2006).

Chromium is known to cause various health effects in the human body. In 2011, the ATSDR ranked chromium, hexavalent as 17, chromium (VI) trioxide as the 66th, and chromium as the 78th, most hazardous substance (SPL). Chromium poisoning occurs when a human being absorbs contaminants of the chromium through breathing or ingestion, or through skin contact with chromium or its compounds. Food is the major source of chromium intake (WHO, 2008). The target organ systems are: immune system, urinary system or kidneys, and respiratory system (ATSDR Tox FAQs for Chromium, 2012).

Chromium (III) is an important component of a balanced human diet. It plays a role in normal body functions; it helps the body in monitoring sugar, protein, and fat, and in digesting food. Its deficiency causes a disturbance to glucose and lipid metabolism in humans and animals. In contrast, hexavalent chromium (VI) is a highly toxic carcinogen and may cause death in humans if ingested in large doses (Zayed & Terry, 2003).

At high levels, Chromium can damage the nose and cause cancer. Ingesting high levels of chromium (VI) may result in anemia or damage to the stomach or intestines. In larger amounts, chromium is harmful. Some compounds are especially dangerous, causing a rash or sores if spilled on the skin. They can also cause sores in the mouth and throat if inhaled. If swallowed, some chromium compounds can seriously damage the throat, stomach, intestines, kidneys, and blood (Chen, 2011; ATSDR, 2012).

3.1.4 Copper (Cu)

Copper was one of the earliest elements known to man. Humans have used copper since the Bronze Age. Copper has been used in north Iraq, China, the Roman Empire, and in the New World. Native Americans used copper objects as early as in 2000 B.C (Krebs, 2006). Copper and its compounds are used to make many alloys. The most important application of copper metal is electrical wiring. Alloys of copper, such as bronze and brass, are also used in construction. It also used as coloring agents in paints, ceramics, inks, varnishes, and enamels (USGS, 2009; Black, 1995).

Copper is a ubiquitous element naturally present in the Earth's crust, it is found in many minerals such as sulfides and oxides. It is 26th most abundant element in the Earth's crust (Krebs, 2006). The natural abundance of copper in the Earth's crust is estimated to be about 60 ppm (0.0068%). The average concentration of copper in U.S. soil is about 25 ppm with the range of about < 1-700 parts per million (Shacklette & Boerngen, 1984). The total copper content in unpolluted soils is around 20-30 mg/kg (Sanchez & Ayuso, 2008). Concentrations greater than 3,100 mg/kg may result in adverse health effects to human health (EPA, 2006).

Copper is a metallic, malleable, moderately active metal in period 4 and group 29 of the periodic table, and has the following chemical and physical properties: pure copper is usually

fairly soft and ductile, reddish-brown metal or red- orange, it has a melting point of 1,083°C (1,982°F) and a boiling point of 2,595°C (4,703°F). Its density is 8.96 g/ cm⁻³ (Wuana & Okieimen, 2011).

Copper enters the environment and makes its path into air, soil, and water by natural processes and as well as anthropogenic activity. Copper releases into the environment naturally mainly from wind- blown dust, decaying vegetation, forest fires and sea spray (Lui, 2011). It can be released to environment due to anthropogenic activities such as industrial manufactures and processes, uses of copper and compounds production of fertilizers, pesticides, and vehicle fluids (Amid, 2006).

Copper is an essential micronutrient for human beings, it is absorbed in small amounts on a daily basis to maintain good health. It is plays an important role in the human body, for the enzyme system in particular.

In 2011, the ATSDR has ranked copper as the 125th most hazardous substance (SPL). Copper poisoning occurs when a human being absorbs contaminants of the metal through breathing or ingestion. The target organ systems: gastrointestinal, hematological, hepatic (ATSDR Tox FAQ for copper, 2004). Inhalation of high levels can cause irritation to nasal passages. Ingestion of high levels can cause nausea, vomiting. Exposure to very high levels of copper can result in adverse health effects such as anemia, damage the liver, and kidneys, and may even cause death (Sharma et al, 2009; Greaney, 2005).

3.1.5 Lead (Pb)

The ancients discovered lead. There is a long history of public exposure to lead; it was reported in 370 BC that lead has been used since the prehistoric era. It has been mined and used by ancient Rome, Greece, and China as a sweetening agent, for transporting water, pigments, and

ceramics (Lesser, 1988). Lead is used in wide variety of products including paint, ceramic, pipes, solders, batteries, and cosmetic (Krebs, 2006).

Lead is rarely a pure element, naturally present in the Earth's crust, and is usually found in combination with zinc, silver, and copper as the mineral galena and lesser other lead forms (EPA, 1997). It is the 35th most abundant element in the Earth's crust (Krebs, 2006); the natural abundance of lead in the Earth's crust is estimated to be 16 ppm, (0.00099 %). The average concentration of lead in U.S. soil is about 19 ppm with the range of about < 10-700 ppm (Shacklette & Boerngen, 1984). The total lead content in unpolluted soils is less than 20 mg/kg in remote or recently settled areas, and between 03 -100 mg/kg in soils that experience low-level pollution (Sanchez & Ayuso, 2008).

Lead is an element in period 6 and group 14 of the periodic table, and has the following chemical and physical properties: lead is bluish-white, silvery, or gray solid and highly lustrous. It is very soft and ductile, with an atomic number of 82. The melting point of lead is 327.4°C (621.3°F), and its boiling point is 1,750 to 1,755°C (3,180 to 3,190°F). Its density is 11.34 g/cm⁻³ (Wuana & Okieimen, 2011; EPA, 1997).

Lead enters the environment and makes its path into air, soil, and water from both natural processes and anthropogenic sources. Lead is transferred continuously between ecosystem components by physical and chemical processes (ATSDR, 2007). Lead is released into the environment naturally mainly from activities such as the weathering of rocks, and volcanic activity (UNDP, 2010). Anthropogenic activity is the primary source of lead in the human environment (e.g. deteriorated paint, contaminated dust or soil, and some products). Human activities are responsible for increasing levels lead concentrations in environmental by more than 1,000-fold over the past three centuries because of the use of leaded gasoline (ATSDR, 2007).

Lead poisoning occurs when a human being absorbs contaminants of the metal, through breathing or ingestion. Lead is a highly toxic metal. In 2011, the ATSDR ranked lead as the 2nd most hazardous substance (SPL). The targeted organ systems are: the cardiovascular, developmental organs, gastrointestinal (digestive), hematological, musculoskeletal, nervous system, ocular (eyes), urinary system or kidneys, reproductive system (ATSDR Tox FAQ for Lead, 2007).

Absorbed lead enters the blood stream and accumulates in body tissue, particularly the kidneys, bones and nervous system. In children, lead poisoning occurs at lower blood lead levels than in adults where in the age range of 1-5 years is the most critical (CDC, 2010).

3.1.6 Zinc (Zn)

Zinc has been known since ancient times. It was reportedly known in Asia, in India, China, and Palestine before it was discovered in Europe. Zinc was rediscovered later in Europe. The first European to describe zinc was probably Swiss physician Paracelsus (1493-1541), and Andreas Marggraft in 1746 in Germany (Krebs, 2006).

Zinc is used to galvanize other metals, and make alloys. Alloys of zinc are used in a great variety of products, including automobile parts, roofing, gutters, batteries, organ pipes, electrical fuses, type metal, household utensils, and building materials (Jalali, 2007; Krebs, 2006).

Zinc is an element, which never occurs as a free substance and is naturally present in the Earth's crust. It is the 24th most abundant element in the Earth's crust, the natural abundance of zinc is estimated to be to be of about 70 ppm (0. 0078%) in the Earth's crust (Krebs, 2006). The average concentration of zinc in U.S. soil is of about 60 ppm with the range of about < 5-2.900 ppm (Shacklette & Boerngen, 1984). The total zinc content in unpolluted soils is between 10 - 300 mg/kg (Sanchez & Ayuso, 2008).

Zinc is a transition metallic element in period 4 and group 12 of the periodic table, and has the following chemical and physical properties: zinc is an inorganic substance, a fairly active element, fairly soft, lustrous, pure zinc is a bluish-white metal with a shiny surface, with atomic number of 30. Zinc's melting point is 419.5°C (787.1°F) and its boiling point is 908°C (1,670°F). Its density is 7.14 g/ cm⁻³ (Wuana & Okieimen, 2011).

Zinc enters the environment and makes its path into air, soil, and water from both natural processes and as well as anthropogenic activity. Zinc releases into the environment naturally occur from sea salt, the movement of soil dust particles in the air, forest fires and volcanoes (Krebs, 2006). Anthropogenic activity is responsible for elevated levels of zinc in the environment, including municipal and industrial effluents, and mining activity (Muwanga, & Barifaijo, 2006).

Zinc is an essential micronutrient element in small amounts for normal healthy growth and reproduction of human beings. Zinc plays an essential role in the manufacture of many important chemicals in the human body. The decrease or excess of zinc in human body can cause health problems. In 2011, the ATSDR has ranked zinc as the 75th most hazardous substance (SPL). The targeted organ systems are: the gastrointestinal, hematological and respiratory systems (ATSDR Tox FAQ for Zinc, 2010).

Zinc poisoning occurs when a human being absorbs contaminants of the metal, through breathing or ingestion. Breathing zinc dust may cause dryness in the throat, coughing, general weakness and aching, chills, fever, nausea, vomiting, acute renal tubular necrosis, chemical pneumonitis and interstitial nephritis. High concentrations of zinc can cause adult respiratory distress syndrome, acute renal tubular necrosis, chemical pneumonitis, interstitial nephritis, and irritation and corrosion of the gastrointestinal tract (ATSDR, 2010; Barceloux, 1999).

3.2 Heavy metals behavior in the soil

Heavy metals spread into various environment components through natural or anthropogenic activities. Human activities are responsible for the increased contamination of the environment through various wastes such as heavy metals. Metals do not undergo microbial or chemical degradation, and their total concentration persists for lengthy periods after being dispersed in soil (Wuana & Okieimen, 2011). The heavy metals accumulated in the surface soil layer may migrate into deeper layers over time (Dube et al., 2001).

Soil has the ability to both bind and transport heavy metals. The transport of heavy metals in soil depends mostly upon both the physical and chemical properties of the soil, the heavy metals, and binding form of the element in solid matrix (Sharman et al., 2009; Grabulosa, 2006). The chemical form and speciation of the metals are significant factors for the fate and transport of heavy metals in soil (Raymond & Wuana, 2011). Soil may contain metals in the solid, gaseous, or liquid phases, in some form of low solubility compounds and can exist in various forms as different forces keep them tightly bound to soil particles (Dube et al., 2000).

Once heavy metals reach the soil, they are subject to a wide range of complex chemical and biological reactions, which determined the mobility of heavy metals in the soil and their bioavailability, leaching and their toxicity. Also, the mobility of the metal changes as soil conditions change (EPA, 1997). Heavy metals are first absorbed by initial fast reactions followed by a slow adsorption reaction and are, therefore, redistributed into different chemical forms. These reactions last from minutes to days to years (Wuana & Okieimen, 2011). Reactions in the soil include sorption/desorption reaction, chemical complexation with organic and organic ligands and redox reactions, both biotic and abiotic.

The fate of heavy metals in the soil is determined by their interaction with the solid and the aqueous phases of the soil. Heavy metals can be found in the liquid phase of the soil as free cations or complexed with inorganic and organic ligands and in the solid phase retained at exchange sites or at specific sites of oxides, organic matter and in structures of primary or secondary minerals (Chernet, 2009).

Many factors control the reactions, and influence the fate and transport of heavy metal in soil. These factors include: the type and quantity of soil surface present, the concentration of metals, the concentration and type of competing ions and complexing ligands, both organic and organic redox status, pH, sorbent nature, presence and concentration of organic and inorganic ligands including humic and fulvic acids, microbial metabolites root exudates and nutrients (Violante et al., 2010; EPA, 1997; Matini et al., 2011; Ashraf et al., 2012; Szyzewski et al., 2009).

A brief description of mobility of investigated heavy metals is provided below.

3.2.1 Antimony

Antimony in soil is considered to be moderate mobility, or a relatively immobile metal under oxidizing conditions and/or with low available contents in soils (Sanchez & Ayuso, 2008). Most antimony ends up in soil, where it attaches strongly to particles that contain iron, manganese, or aluminum (ATSDR Tox FAQ for Antimony, 1995).

Antimony mobility in the soil depends on soil pH and redox potential, which are largely determined by the metalloid oxidation state and environmental reactions in soil systems. Soluble fraction is probably present as antimonite, especially under oxidizing and basic conditions, and could be adsorbed by the same soil constituent that bind phosphate and arsenate (Adriano, 2001).

3.2.2 Cadmium

Cadmium can enter the soil from manufacturing and processing facilities. Atmospheric deposition is a major source of cadmium in the soil. Other sources of cadmium are phosphate fertilizers, sewage sludge and municipal wastes.

Cadmium in the soil is more mobile, more bioavailable and bioaccumulation. Cadmium in the soil does not break down but can change into different forms, bind strongly to organic matter in the soil (ATSDR, 2012). This high mobility is attributed to the fact that cadmium adsorbs rather weakly on organic matter, silicate clays and oxides unless the pH is higher than 6 (Sanchez & Ayuso, 2008).

3.2.3 Chromium

Chromium enters the soil mainly from disposal of commercial products containing chromium, chromium waste from industry, and coal ash from electric utilities, disposal of commercial products, agricultural and food wastes. Chromium in soil is not very mobile (ATSADR, 2012).

Chromium is present in cationic form under natural environmental conditions (EPA, 1997). Chromium in the soil does not dissolve easily in water and can attach strongly to the soil particles (EPA, 1992). Chromium (III) in the soil is mostly present as insoluble carbonate and oxide of chromium (III); therefore, it will not be mobile in the soil. The solubility of chromium (III) in the soil and its mobility may increase due to the formation of soluble complexes with organic matter in soil, with a lower soil pH potentially facilitating complexation (Avudainayagam et al., 2003; ATSADR, 2007).

3.2.4 Copper

Copper enters the soil mainly from deposition from the atmosphere, tailings of mines and mills, agricultural use, and solid waste and sludge disposal (ATSDR, 2004). When copper is released into the soil, it can become strongly attached to the organic material and other components (e.g., clay and sand) in the top layers of soil and may not move very far when it is released (ATSDR, 2004).

In soil, copper is absorbed strongly on oxides, silicate clays and humus, and increasingly so as the pH is raised. Above pH 6 its precipitation as hydroxide, oxide or hydroxy-carbonates is also possible, nevertheless, under high pH conditions soluble hydroxyl- carbonate and organic matter complexes are formed increasing significantly the low mobility shown by this element in near-neutral soils (Sanchez & Ayuso, 2008).

3.2.5 Lead

Lead enters the soil mainly from various anthropogenic sources including flaking lead paint, or weathering paint, improper renovation of buildings and disposal of building materials, from incineration, and motor vehicles using leaded gasoline (ATSDR, 2007). Atmospheric deposition is the largest source of lead found in the soils (ATSDR, 2007). Lead deposited from the air is generally retained in the upper 0.7-1.1 inches of undisturbed soil (CDC, 1991).

Lead is present in cationic form under natural environmental conditions. In the soil, lead sticks strongly to soil particles and remains in the upper layer of soil (EPA, 1997). Complexation with organic matter, chemisorption on oxides and silicate clays and precipitation as carbonate, hydroxide or phosphate are the mechanisms responsible for lead immobilization, being all favored at higher pH. In alkaline soils, leads solubility may increase through the formation of soluble Pb–organic and Pb–hydroxy complexes (Sanchez & Ayuso, 2008).

3.2.6 Zinc

Zinc enters the soil from disposal wastes from metal manufacturing industries, smelter sludge and wastes, mine tailings of zinc, lead and cadmium ores, steel production, coal burning, and burning of wastes and fertilizers, and as a result of atmospheric deposition (ATSDR, 2005).

Zinc is relatively mobile in the soils and absorbs strongly into the soil particles (ATSDR, 2005). Its mobility in soil depends on the cation exchange capacity, pH, organic matter content, nature of complexing ligands, and the concentration of the metal and other ions in the soil solution (ATSDR, 1994; Alloway, 2008; UNEP, 2010). Under acidic conditions, zinc is one of the most soluble and mobile of the trace metal cations, being held in exchangeable forms in clays and organic matter. At higher pH, however, chemisorption of oxides and alumino-silicates and complexation with humus lowers its solubility markedly (Sanchez & Ayuso, 2008).

Chapter 4: Materials and Methods

4.1 The study Area Description

4.1.1 Location

El Paso, Texas, lies at the intersection of three states, Texas, New Mexico, and Chihuahua) and two countries, the U.S. and Mexico Figure 4.1. El Paso is limited with coordinates of $31^{\circ}47'25''\text{N}$ $106^{\circ}25'24''\text{W}$ (US Gazetteer files: 2011).



Figure 4.1: The study area location

El Paso is the 19th most populous city in the U. S. and the sixth most populous city in the state of Texas. According to the United States Census Bureau, the city has a total area of 256.3

square miles (663.7 km²). According to the 2010 census, the city's population is 649,121 (American Fact Finder, 2012; Geographic Identifiers, 2010).

4.1.2 Climate

The arid to semi-arid desert climate of El Paso County is characterized by an abundance of sunshine throughout the year, low humidity, and a very high evaporation rate in excess of 150 inches per year. More than half of the precipitation occurs in the summer during brief, but at times heavy, thunderstorms with annual precipitation averaging only 9 inches. In the summer, the daytime temperature frequently rises above 90° F and occasionally above 100°F, but most summer nights are comfortable because the temperature usually falls to the 60°'s (El-Hage et al., 1998; Rincon et al., 2005). The prevailing winds are westerly, with dust storms a common occurrence in the spring (Drexler, 2003).

4.1.3 Topography

The local topography is classified as complex terrain. It has the characteristic features of the trans-Pecos region. The Hueco Bolson, a broad, waste-filled lowland, is bordered on the west by the narrow north-south Franklin Range and on the east by the Hueco Mountains. The Rio Grande constitutes the western and southern boundary of the area (Richardson, no date). The city's elevation is 3,800 feet (1,200 m) above sea level. North Franklin Mountain is the highest peak in the city at 7,192 feet above sea level. The Franklin Mountains run north -south and divide the urban areas of west and north central/northeast El Paso.

4.1.4 Geology

The metropolitan area of El Paso lies primarily within the floodplains of the Rio Grande River, once dominated by a large lakebed (Lake Cabeza de Vaca). Millions of years of river

deposition resulted in a complex sedimentary sequence of gravel, silt, clay, and sand called the Fort Hancock Formation, accumulating to a thickness of more than 9,000 feet. Recent geological activity has been dominated by Basin and Range tectonics and the emplacement of young, 40,000 year old, basalt flows and cinder cones from the Potrillo Volcanic field (Drexler, 2003; Li et al, 1999).

The Franklin Mountains exhibit Proterozoic metasedimentary and igneous rocks that are capped by 2,500 m of Paleozoic sedimentary rocks with minor amounts of high angle reverse faulting during the Paleocene. The Franklin Mountains currently tilt west (average 35°) due to the faster rate of uplift of the eastern side of the range along the East Franklin fault (Avila, 2011).

4.1.5 Soil

According to the Soil of El Paso County Texas Survey (1977), the soil of El Paso is divided into two broad groups based on their relative abundance and association with the two major geographic features: high intensity survey and low intensity survey. High intensity survey covered soils that occur within the floodplains of Rio Grande. These include the following units: Anapra Silty Clay Loam, Barzito Fine Sand, Gila Series, and Glendale Series. Low intensity survey included unites of Delnorte-Canutio Hilly Association, Delnorte -Canutio Undulating Association, Blue Point Rolling Association and Lozner Association. There is no elevated metal such as lead, arsenic, zinc, copper, and cadmium in El Paso soils (Drexler, 2003).

4.1.6 Flora

The vegetation in the El Paso area reflects its aridity. The flora is dominated by desert shrub, desert grasslands, and pinyon-oak-juniper woodland (El-Hage et al., 1998). In the arroyos and near the Rio Grande, a variety of trees, including cottonwood, desert willow, mesquite, and salt cedar, are found. On the lower Franklin slope, small shrubs, creosote, and cactus plants

abound. Yucca and agave grow in abundance on the alluvial fans and lower mountain slopes (Ndame, 1993).

4.3 Sampling procedure and preparation

An X-ray fluorescence analytical spectroscopic method requires samples in the form of round, flat surface discs. In this study, sample procedures involved grinding and mixing of the soil to achieve homogeneity of the sample with particle grain size $\leq 40 \mu\text{m}$.

The general procedures of EPA method 6200 for field portable XRF, and PAN analytical article by The Analytical X-ray Company, and Handbook of Sample Preparation and Handling, SPEX, Sample Prep, LLC were adapted with slight modification for soil procedure and followed for preparation samples.

4.3.1 Soil sample preparation

The soil samples used in this study are composite samples collected during the Encounters Project. The soils were collected from public areas around selected municipal blocks in El Paso. The soils were taken in front of individual houses or structures around the blocks. The city area was divided into 50 strata Figure 4.2.

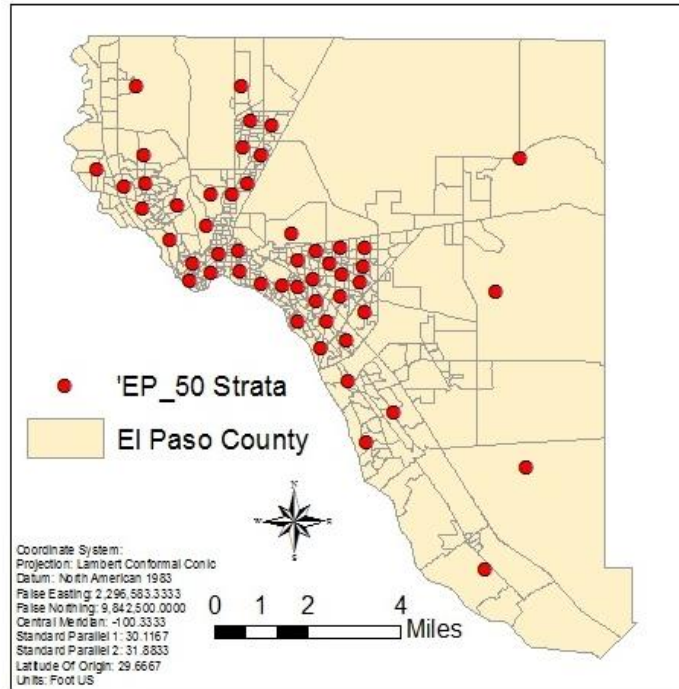


Figure 4.2: El Paso selected blocks per stratum

The strata were defined by uniform population size. Census tracts from the U.S. Bureau of Census were utilized to define strata, each stratum containing approximately $13,000 \pm 2,000$ individuals (Amaya, 2003). A total of 500 surface soil samples were collected Figure 4.3.

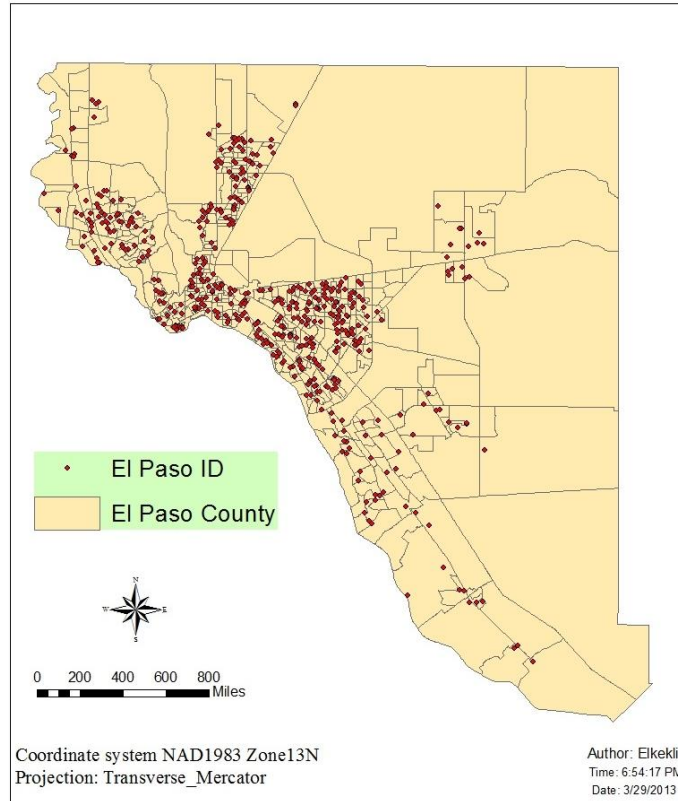


Figure 4.3: The selected soil samples from city blocks

To create a single composite sample to characterize each of the 500 blocks, a mix of equal volume of samples were taken from a single block (Pingitore et al., 2005). The composite sample was taken with a 10 ml cup that was emptied into sealable plastic bags, and stored in the lab for subsequent laboratory procedures (Pingitore et al., 2005).

4.3.1.1 Grinding

The samples were mixed thoroughly to achieve homogeneity. The samples were ground in Planetary PQ-T 04 Gear-Drive Planetary Ball Mill. Approximately 9.8 (\pm) grams of soil sample was weighed in balance, then put in 100 ml ceramic jar, and placed in the mill with 24 mill balls (10 mm diameter).

The jar was then placed in the mill for an operation time of 10 minutes at a speed 350 rpm with bidirectional interval time. Following this, the sample was transferred to a watch glass using a plastic strainer to separate the balls. A Teflon spatula was used to scrape the sample off the wall and bottom of the jar.

The soil sample was then sealed into a plastic bag with an identification number for subsequent laboratory procedures.

4.3.1.2 Mixing

Approximately 9.5 (\pm) grams of ground soil sample was weighed in a balance, and then placed in an 8 oz. translucent container. Then 1.15 (\pm) grams of cellulose binder (particle size $\leq 30 \mu\text{m}$) and 1.15 (\pm) grams of paraffin binder (particle size $\leq 20 \mu\text{m}$) were added, followed by 7 ml of methanol. The container was then closed and placed in the mill for an operation time of 4 minutes at a speed of 350 rpm with bidirectional interval time.

The container was removed from the mill, and then opened to allow drying and evaporation of the methanol by placing it in the hood for 24 hours. The sample was then stored in a sealed plastic bag with an identification number for subsequent laboratory procedure.

4.3.1.3 Pressing

The samples were prepared in the form of pressed pellets. The samples were pressed into pre-flared XRF SPEC-cap, with diameter of 31 mm, by using a RIIC, C- 30 manual 30 tons hydraulic lab press.

The sample was weighed at 11 g (± 0.005) in the balance, and emptied into the die set for pressing. The sample was pressed into the die bore between the polished steel pellet surfaces at 20 tons for 30 seconds. The pressure was then released within 15 seconds (bleed time), followed

by the die set being removed from the press. The sample pellet was taken out, and labeled by an identification number.

4.3.1.4 Homogenization

To monitor homogenization in sample soil, two methods were employed in this study. 10 grams of samples were taken, followed by the adding of 1.15 grams of cellulose binder, and 1.15 grams of paraffin binder. Then 0.5 grams of sodium fluorescence dye was added into the jar, and the mixture was ground in the planetary mill for 2 minutes at 350 rpm. Following the mixing, the sample was transferred into a watch glass, and examined under the microscope. When the dye was evenly distributed in the sample and no visible white spots appeared, homogenization was considered complete.

The second method was to examine the above mixture under ultraviolet light to assess the distribution of sodium fluorescence dye through the sample. If the dye appeared evenly distributed in the sample, and no visible white spots appeared, homogenization was considered complete (Sped Crete Prep Handbook, 1997; IAEA, 1997).

4.3.1.5 Standard and blank procedure

The same methods for soil procedure that include grinding and mixing have been used to prepare the standard, to verify the results and to calibrate the instrument. The following standards from the National Institute of Standards and Technology (NIST), and United States Geology Survey (USGS) were utilized:

USGS standards are BR-1, NOD-A-1, SDC-1, GLO-1, SRG--1, SCO-1, MAG-1, RGM-1

NIST standards are 2586, 2711, 2710, 2709 a.

Blank: Silica oxide, Teflon (Polytetrafluoroethylene).

4.4 Cleaning procedure

The following sequences were adapted in compliance with appropriate EPA protocols for cleaning. All apparatus used in this study, including jars, mill balls, plastic spoons, watch classes, Teflon spatulas, die sets, translucent containers, plastic strainers and stainless steel spatulas, were cleaned after every run off. The jars and mill balls were cleaned after every run sample as follows:

1. Wash with tap water.
2. Wash with cleaning solution. The cleaning solution used in this study was Citranox (10-20 ml per letter).
3. Rinse with tap water.
4. Dry the jars and mill balls with tissues, followed by blow dryer.

The jars were also cleaned after every 50 runs of the samples. The following steps were adapted:

1. Grind 10 grams of silicon (IV) oxide (99.5 %) for 5 minutes.
2. Rinse with tap water.
3. Mix 1 teaspoon silicon oxide with cleaning solution and hot water in the jar for 10 minutes at 350 rpm.
4. Rinse the jar with tap water.
5. Dry the jar with blow dryer.

4.5 Instrumentation and data analysis

The samples were analyzed via the X-ray Fluorescence (XRF) Spectroscopy. XRF is an instrumental approach used to identify elements through its characteristic x-ray emissions. The instrument also quantifies elements by measuring the intensity of characteristic emission lines.

In this study, the Epsilon5 instrument used to analyze the samples. The Epsilon5 is a fully integrated energy dispersive XRF analyzer consisting of spectrometer, x-y sample handler and software. The measuring program was set up in the software using Epsilon 5 wizard.

492 composite soil samples were analyzed. For each sample, the concentration of the metals was determined and recorded by ppm. The metals were lead (Pb), chromium (Cr), copper (Cu), zinc (Zn), cadmium (Cd), and antimony (Sb) as listed in (appendix A). The basic descriptive statistics, univariate analysis and bivariate analysis (for this purpose, correlations and the scatter plots) on the data were studied by Minitab 16 software. In addition, histograms were employed to check the normality of the data. In order to increase the readability of the scatter plots, log transformations have been used.

The maps of metals concentration distribution were produced by using Arc Info (ver. 10.1). The soil samples were collected from the blocks is symbolized by a four-colored symbol green, yellow, blue, and red.

Chapter 5: Results and discussion

5.1 Total metal concentration and spatial distribution

All results of soil samples analysis are given in (Appendix A).

5.1.1 Univariate analysis on El Paso data

The data obtained were statistically analyzed Table 5.1.

Table 5.1: Displays descriptive statistic of heavy metals in El Paso

Variable	N	Minimum	Maximum	Mean	St Dev.	Q1	Q3	Median
Pb	492	10.8	420.9	60.8	54.4	22.1	81.8	40.1
Cr	492	4.3	51.6	24.2	8.6	18.3	29.2	24.1
Cu	492	6.5	385.8	33.3	35.9	14.6	40.4	21.9
Zn	492	16.5	676.8	98.9	67.5	52.1	127.1	82.7
Cd	492	0.4	11.9	2.1	1.2	1.4	2.6	1.9
Sb	492	2.9	19.6	6.3	1.8	5.3	6.9	6.1

5.1.1.1 Lead in Soil

The total concentration of lead in the soil samples ranged from 10.8 ppm to 420.9 ppm, with the mean value of 60.8 ppm. The distribution of lead in samples is presented in Figure 5.1.

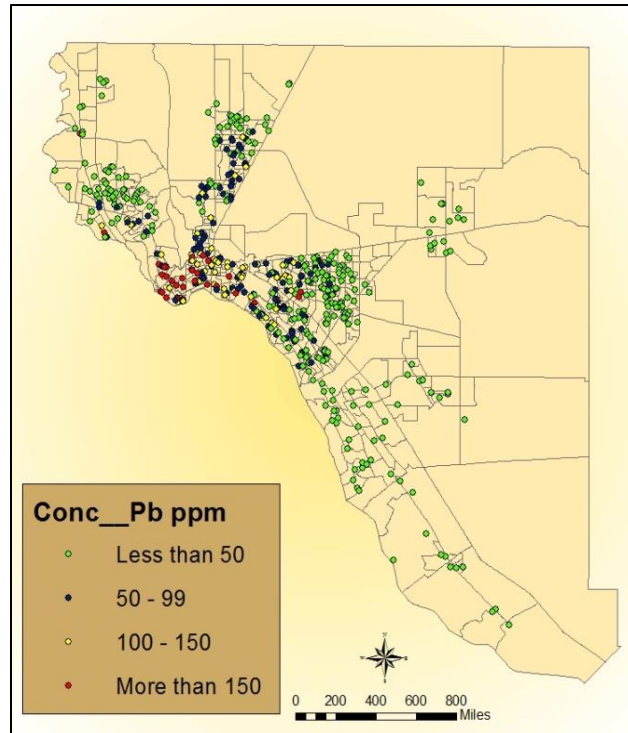


Figure 5.1: Lead levels in composite samples from blocks in El Paso

The lowest values (less than 50 ppm; in green blocks) of lead are encountered mostly in the study area, except in the central El Paso. The concentrations between 50 ppm and 99 ppm (blue blocks) are mostly recorded in the left side of east sections of the city and northeast areas. The yellow blocks representing the concentrations between 100 ppm and 150 ppm are scattered mostly in the central El Paso. Only two blocks in west side near the area surrounding ASARCO smelter, and two blocks in the northeast recorded. However, more of which are encountered in central area.

The highest values (more than 150 ppm; red blocks) of lead are recorded in the central area, which is concentrated in the downtown and central core district. Some blocks in east and northeast also have recorded more than 150 ppm, but very close to urban core.

The natural abundance of lead in the Earth's crust is estimated to be 16 ppm (Krebs, 2006), and the average concentration of lead in U.S. soil is about 19 ppm with the range of about < 10-700 ppm (Shacklette & Boerngen, 1984). The total lead content in unpolluted soils is less than 20 mg/kg in remote or recently settled areas, and between 03 -100 mg/kg in soils that experience low-level pollution (Sanchez & Ayuso, 2008). Using these guidelines, it can be observed that the majority of samples have high levels of lead that encountered in central and downtown El Paso, and to the west in the area of ASARCO smelter.

This is not surprising that these high levels of lead are found here because of all the activities that take place in these areas. The elevated lead levels can be attributed to the discharge of metals from industrial activities in the downtown district and adjacent area to the east of El Paso. The high levels may have resulted from businesses such as automobile repairing workshops and battery shops. The high levels are also possible due to the discharge of lead from the ASARCO smelter. Emission of heavy metals from the smelting tower stacks to the air and dispersed away by winds may have been increased the levels of lead and other heavy metals in the El Paso throughout the years resulting in deposited the metals in the soil (Gardea-Torresdey et al., 1996).

The levels of lead found in the present study are similar what other studies conducted in El Paso area. For example, Ndam (1993) found that lead concentrations steadily increased from the west part of UTEP campus to ASARCO. Develhalli (1994) found that lead in the downtown area ranged from 17- 560 mg/kg (ppm). Srinivas (1994) found that lead in Public Parks in El Paso area ranged from 30 to 130 mg/kg, and Pingitore et al, (2005) found a high concentration of lead in El Paso, 420 ppm in blocks at a site near downtown.

The concentration of lead in the soil of study area probably constitutes a major health hazard, and poses a threat to local population. The studies conducted in El Paso indicated that there was a significant association between soil lead and blood lead levels (Texas Department of Health, 2001). The children are more vulnerable and sensitive to exposure to lead and its poisoning occurs at lower blood lead levels than in adults where in the age range of 1-5 years. Figure 5.2 illustrates the concentration of lead levels in soil samples with correlation of children age 0-4 in El Paso area.

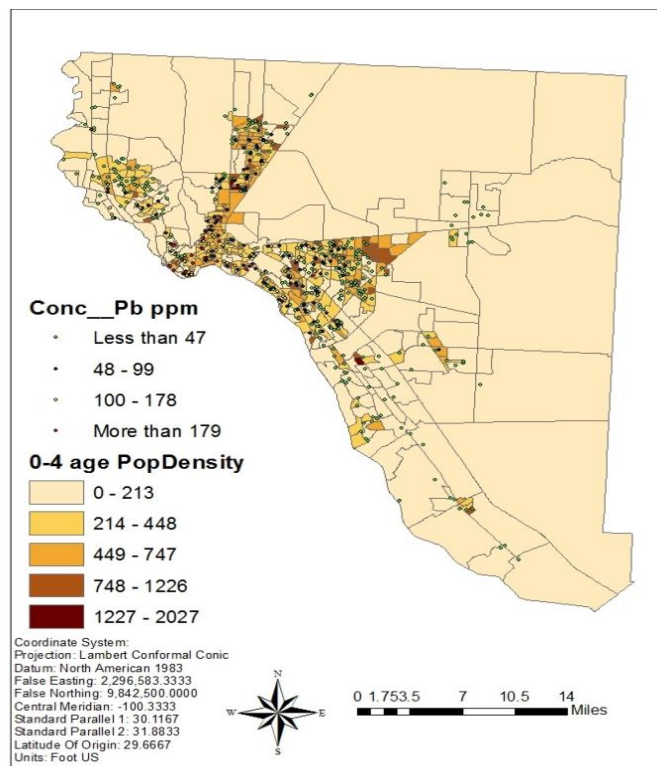


Figure 5.2: Population density of children age 1-4 to contaminated by lead soil in El Paso

For illustrate the risk of lead in El Paso area, risk map created to show which areas are risk to the children Figure 5.3.

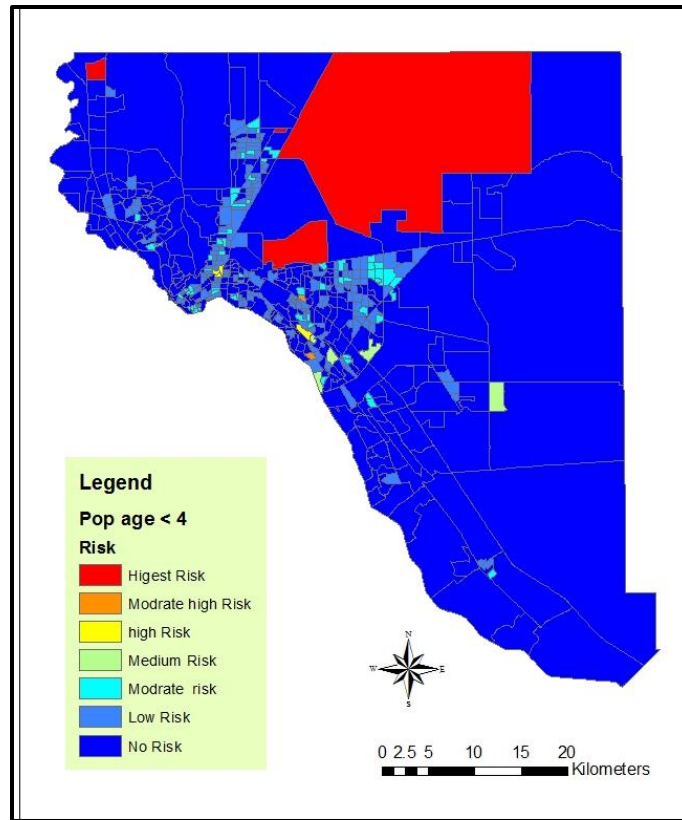


Figure 5.3: Risk lead area of children age 1-4 in El Paso

5.1.1.2 Chromium in Soil

The total concentration of chromium in the soil samples ranged from 4.3 ppm to 51.6 ppm, with the mean value of 24.2 ppm. The distributing of chromium in samples is presented in Figure 5.4.

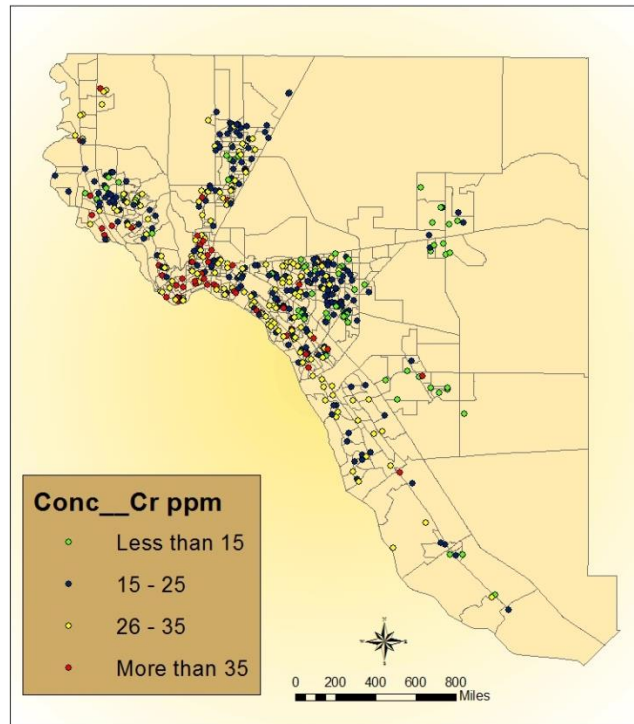


Figure 5.4: Chromium levels in composite samples from blocks in El Paso

Generally, the lowest values (less than 15 ppm; green blocks) of chromium are encountered in all the study areas. In the far east side of the city and surrounding areas, the soil has low soil chromium levels. However, the southeast section has higher levels of chromium than the far east side. Concentrations between 15 ppm and 25 ppm (blue blocks) are mostly encountered in the peripheral areas away from the urban core. Thus, the left side of the east sections of the city and surrounding areas has soil chromium levels between 15 ppm and 25 ppm.

The yellow blocks, representing the concentrations between 26 ppm and 35 ppm are scattered in all the study areas. However, more of these concentrations are encountered in the central area. The highest values (more than 35 ppm; represented by red blocks) of chromium are recorded in the central area, which covers the downtown and central core district.

It is clearly seen from the map that the level of chromium gradually decreases from the central to the east side.

The naturally occurring concentration of chromium in the Earth's crust is about 120 ppm and the average concentration of chromium in U.S. soil is about 54 ppm, with ranges about 1-2,000 ppm (Shacklette & Boerngen, 1984). Using these guidelines the results obtained from this study show that the concentration of chromium in El Paso is less levels. Therefore, no threat or health hazard to local population in El Paso.

5.1.1.3 Copper in Soil

The total concentration of copper in the soil samples ranged from 6.5 ppm to 385.8 ppm, with the mean value of 33.3 ppm. The concentration of the copper in samples is presented in Figure 5.5.

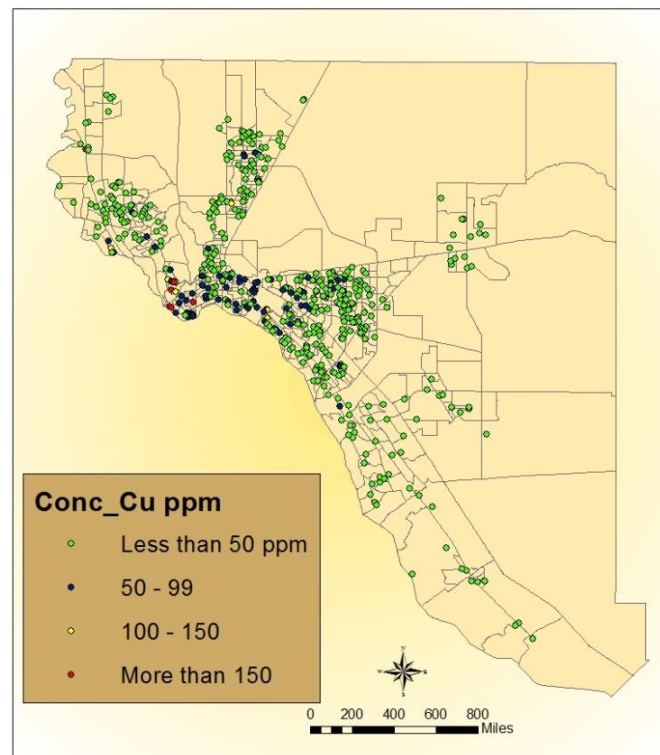


Figure 5.5: Copper levels in composite samples from blocks in El Paso

The lowest values (less than 50 ppm; represented in green blocks) of copper are encountered in the peripheral areas away from the urban core, such as the Far East, the west and surrounding areas. The conclusion is that all areas except the central El Paso have low soil copper levels. Blue blocks with 50 ppm to 99 ppm copper, seen in blue in Figure 5.5. The concentrations between 50 ppm to 99 ppm for copper are recorded from the central El Paso. Further, there are only a few blocks recorded for the northeast and the southeast.

Only a few blocks have copper levels between 100 ppm to 150 ppm (yellow dots). However, these blocks are limited only to the central El Paso. The highest values, those in excess of 150 ppm and depicted in red, are concentrated in the downtown and central core district. Therefore, it is unambiguous that the lower levels of copper are recorded in the areas away from the central El Paso.

The natural content of copper in the Earth's crust is estimated to be about 60 ppm, and the average concentration of copper in U.S. soil is about 25 ppm with a range of about < 1-700 ppm (Shacklette & Boerngen, 1984). The total copper content in unpolluted soils is around 20-30 mg/kg (Sanchez & Ayuso, 2008). Using these guidelines, the result obtained in this study show some areas have elevated copper levels especially in the central El Paso, which may result in adverse health effects in humans.

5.1.1.4 Zinc in Soil

The total concentration of zinc in the soil samples ranged from 16.5 ppm to 476.8 ppm, with the mean value of 98.9 ppm. The concentration of the zinc in samples is presented in Figure 5.6.

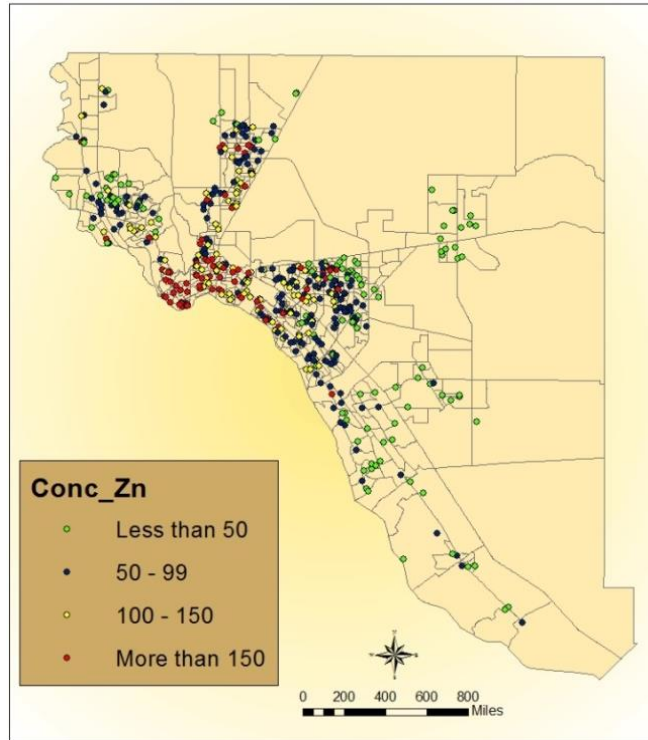


Figure 5.6: Zinc levels in composite samples from blocks in El Paso

The lowest values (less than 50 ppm, represented by green blocks) of zinc are encountered mostly in the far east side. Hence, this section of the city and surrounding areas has low soil zinc levels. However, the level of zinc gradually increases from Far East to left.

The concentrations between 50 ppm and 99 ppm (blue blocks) are mostly recorded in the left side of the east sections of the city and the northeast areas. Furthermore, some blocks in the northeast and the west side have zinc levels between 50 ppm and 99 ppm.

The yellow blocks, representing concentrations between 100 ppm and 150 ppm, are scattered mostly in the left side of the east sections, but not the peripheral areas. However, more of these concentrations are encountered in the central area.

The highest values (more than 150 ppm; red blocks) of zinc are recorded for the central area which is concentrated in the downtown and the central core district and some blocks in the east and the northeast, but very close to urban core. It is clearly seen from the map that the level of zinc gradually decreases from the central to the east side.

For comparison, the naturally occurring of zinc is estimated to be to be of about 70 ppm in the Earth's crust (Krebs, 2006), and the average concentrations of zinc in U.S. soil is of about 60 ppm with a range of about < 5-2.900 ppm (Shacklette & Boerngen, 1984). The total zinc content in unpolluted soils is between 10 - 300 mg/kg (Sanchez & Ayuso, 2008). Using these guidelines, the result obtained show that there is elevated high levels of the zinc concentrated in El Paso. These high levels of zinc probably cause health problems to the local population in the polluted area.

5.1.1.5 Cadmium in Soil

The total concentration of cadmium in the soil samples ranged from 0.4 ppm to 11.9 ppm, with the mean value of 2.1 ppm. The concentration of cadmium in samples is presented in Figure 5.7.

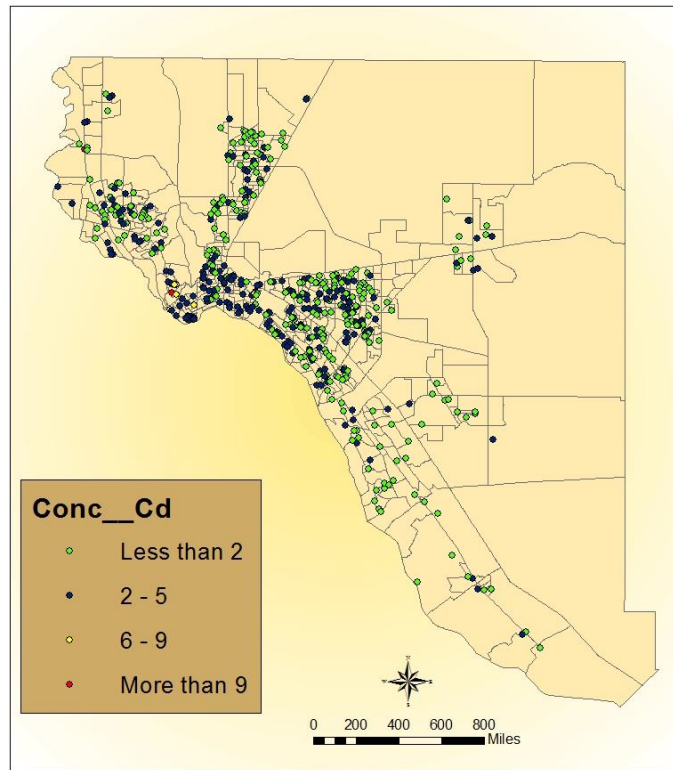


Figure 5.7: Cadmium levels in composite samples from blocks in El Paso

The lowest values (less than 2 ppm; green blocks) of cadmium are mostly encountered in the peripheral areas away from the urban core. However, green dot are scattered all over indicating lower soil cadmium levels. Blocks with 2 ppm to 5 ppm; cadmium, are seen in blue in Figure 5.7. The cadmium concentrations between 2 ppm and 5 ppm are recorded mostly in central El Paso. Further, these concentrations are scattered in the left side of the east side and in some in the west and northeast sides.

Only a few blocks have cadmium levels between 6 ppm and 9 ppm (yellow dots). However, these blocks are limited only to central El Paso. There is only one block with the highest value, that is in excess of 9 ppm, and it is depicted in red. This block is in the central

side. However, the lowest levels of cadmium are recorded from the areas away from central El Paso.

For comparison, the natural occurring of cadmium is estimated to be about 150 ppm in the Earth's crust (Shacklette & Boerngen, 1984) and the total cadmium content in unpolluted soils is less than 1 mg/kg (Sanchez & Ayuso, 2008). Using these guidelines we can conclude the study areas do not have highly elevated cadmium content, and therefore, there is no threat to human health.

5.1.1.6 Antimony in Soil

The total concentration of antimony in the soil samples ranged from 2.9 ppm to 19.6 with the mean value of ppm 6.3 ppm. The concentration of antimony in blocks as seen in samples is presented in Figure 5.8.

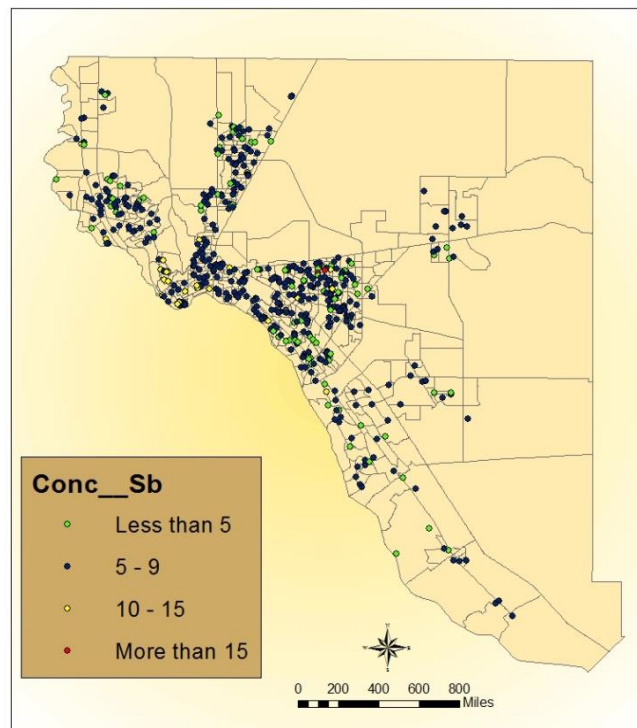


Figure 5.8: Antimony levels in composite samples from blocks in El Paso

The lowest values (less than 5 ppm; green dots) of antimony are mostly scattered in the peripheral areas away from the urban core. Blocks with 5 ppm to 9 ppm antimony, are shown in blue dots in Figure 5.7. Therefore, the concentrations between 5 ppm and 9 ppm for antimony are scattered all over the map.

Only a few blocks have antimony levels between 10 ppm to 15 ppm (yellow dots). However, these blocks are limited only to central El Paso. There is only one block with the highest value that in excess of 15 ppm, depicted in red. This block is in the left side of the northeast. The lowest levels of antimony are recorded from the areas away from central El Paso.

For comparison, the natural occurring of antimony is estimated to be about 0.2 ppm in the Earth's crust (Krebs, 2006; Angima, 2010). The average concentration of antimony in U.S soil is about 0.66 ppm with the range of about < 1-8.8 ppm (Shacklette & Boerngen, 1984). The total antimony content in unpolluted soils for antimony is below < 1 mg/kg (Sanchez & Ayuso, 2008). Using these guidelines the results show that the El Paso soil is highly polluted by antimony and may be hazardous to human being health.

The results of total concentration of the metals in El Paso indicated that the metal zinc has the highest concentration level of 476.8 ppm, and also the highest standard deviation, Q1, and median, Q3. The minimum concentration recorded for cadmium is 0.4 ppm. The minimum concentration of zinc is almost 50 times more than that of cadmium. This implies that in the El Paso soil samples, the highest concentration recorded is that of zinc.

We can also conclude that the elemental concentrations in soil samples are in the decreasing order of zinc > lead > copper > chromium > antimony > cadmium.

5.1.2 Bivariate analysis on El Paso data

In an attempt to understand the relationship between metals concentrations, scatter plots, and the Pearson correlation coefficient (r), were used to establish these relationships.

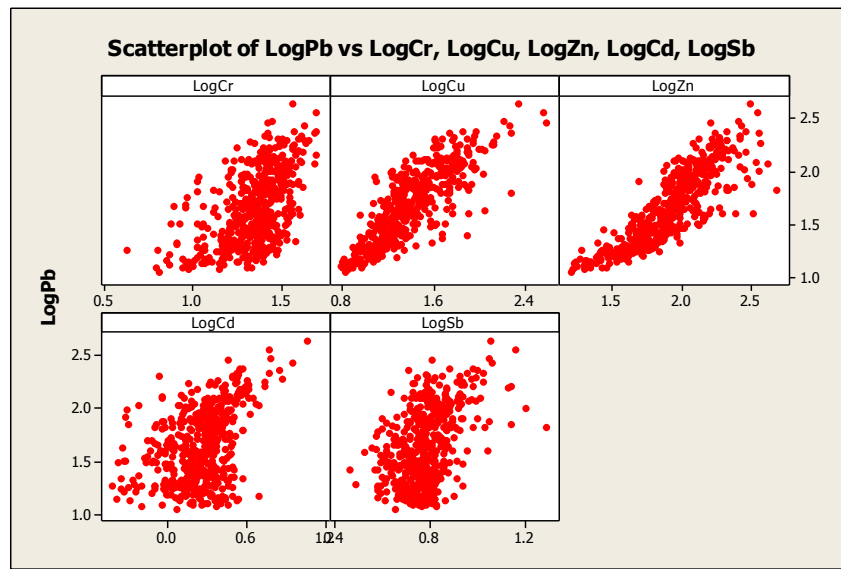


Figure 5.9: Correlation of Pb with Cr, Cu, Zn, Cd, Sb

From the above Figure 5.9, it can be observed that the variable lead shows a positive correlation with the two variables copper and zinc.

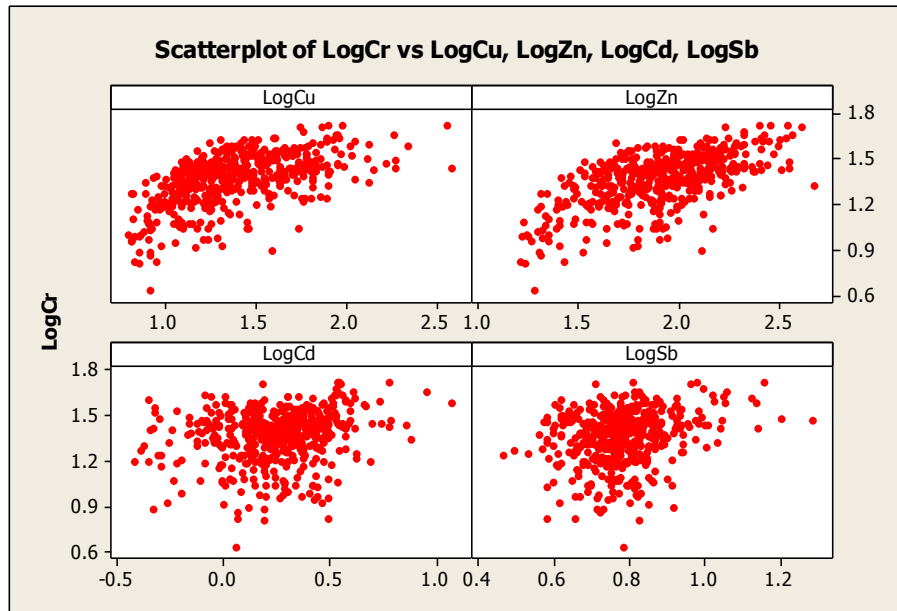


Figure 5.10: Correlation of Cr with Cu, Zn, Cd, Sb

From the above Figure 5.10, it can be observed that the metal chromium does not show a significant correlation with the other variable. However, it shows a minor positive correlation with the variable zinc and copper.

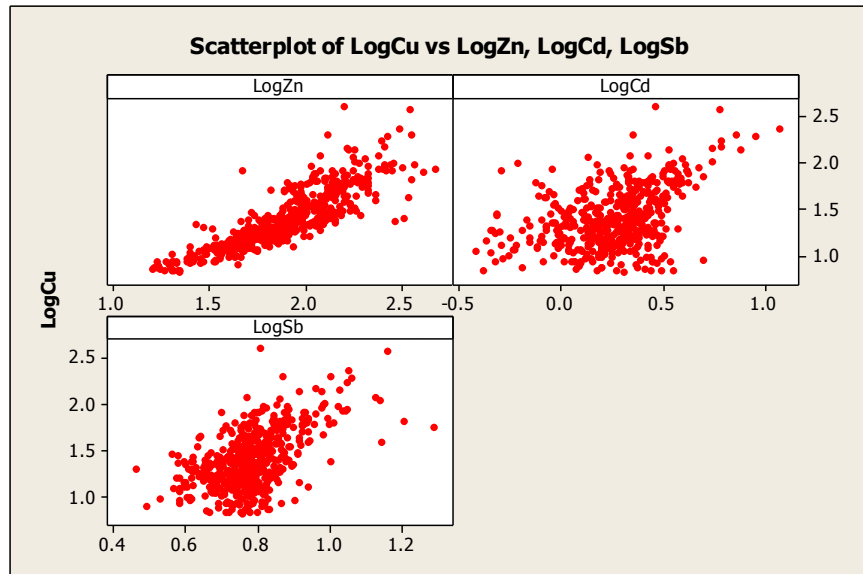


Figure 5.11: Correlation of Cu with Zn, Cd, Sb

By examining the above Figure 5.11, it can be observed that the metal copper exhibits a slight positive correlation with zinc.

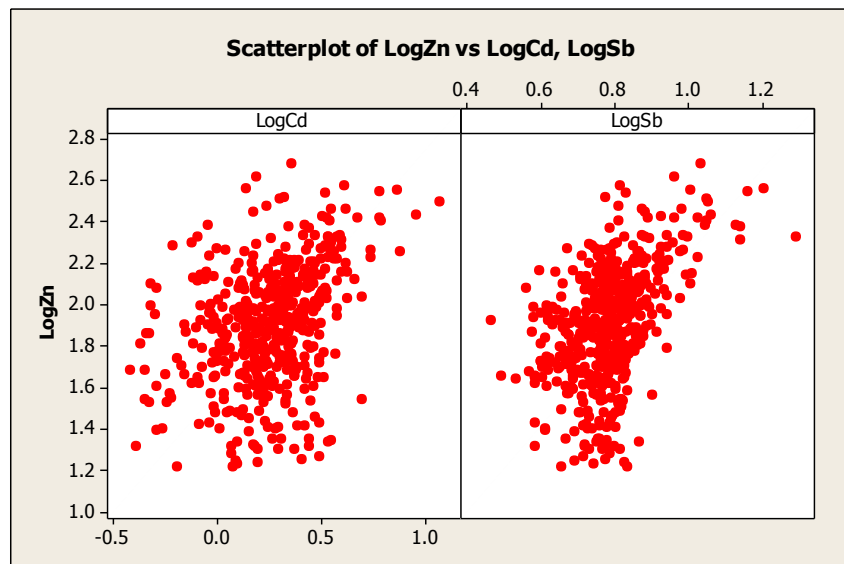


Figure 5.12: Correlation of Zn with Cd, Sb

By examining the above Figure 5.12, it can be observed that the metal zinc exhibits no considerably high correlation with other metals. However, it shows a minor positive correlation with the metal antimony.

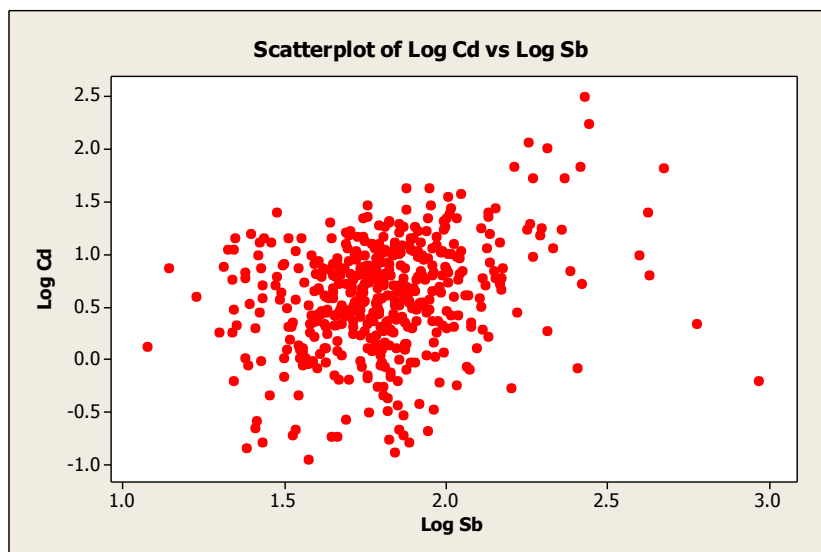


Figure 5.13: Correlation of Cd with Sb

By examining the above Figure 5.13, it can be observed that the metal antimony exhibits no significant correlation with metal cadmium.

To emphasize the observed results from the above scatter a plot, a correlation matrix was used Table 5.2.

Table 5.2: Correlations between the metals in El Paso soil

Correlations: Pb, Cr, Cu, Zn, Cd, Sb					
	Pb	Cr	Cu	Zn	Cd
Cr	0.538 0.000				
Cu	0.770 0.000	0.430 0.000			
Zn	0.741 0.000	0.567 0.000	0.658 0.000		
Cd	0.629 0.000	0.271 0.000	0.569 0.000	0.450 0.000	
Sb	0.483 0.000	0.281 0.000	0.537 0.000	0.586 0.000	0.354 0.000
Cell Contents: Pearson correlation P-Value					

As shown in above Table 5.2, the correlation coefficient (r) between soil metal content can be obtained.

Table 5.3: Computed Pearson correlation coefficient of heavy metals level

Correlation between metals	r value	P value
Correlation between Pb and Cr	0.538	0.000
Correlation between Pb and Cu	0.77	0.000
Correlation between Pb and Zn	0.741	0.000
Correlation between Pb and Cd	0.628	0.000
Correlation between Pb and Sb	0.483	0.000
Correlation between Cr and Cu	0.430	0.000
Correlation between Cr and Zn	0.567	0.000
Correlation between Cr and Cd	0.272	0.000
Correlation between Cr and Sb	0.281	0.000
Correlation between Cu and Zn	0.658	0.000
Correlation between Cu and Cd	0.567	0.000
Correlation between Cu and Sb	0.537	0.000
Correlation between Zn and Cd	0.446	0.000
Correlation between Zn and Sb	0.586	0.000
Correlation between Cd and Sb	0.356	0.000

As seen, in these observations, all the metal pairs show a significant correlation. However, these significant correlations may not have observed from the scatter plots due to the view of it. Lead and copper have the highest correlation. Further, it can be observed that the metals lead and copper have more influence or are more influenced by the other elements.

5.1.3 Checking the normality of the data

To check the normality of the data, the study employs histograms Figure 5.14.

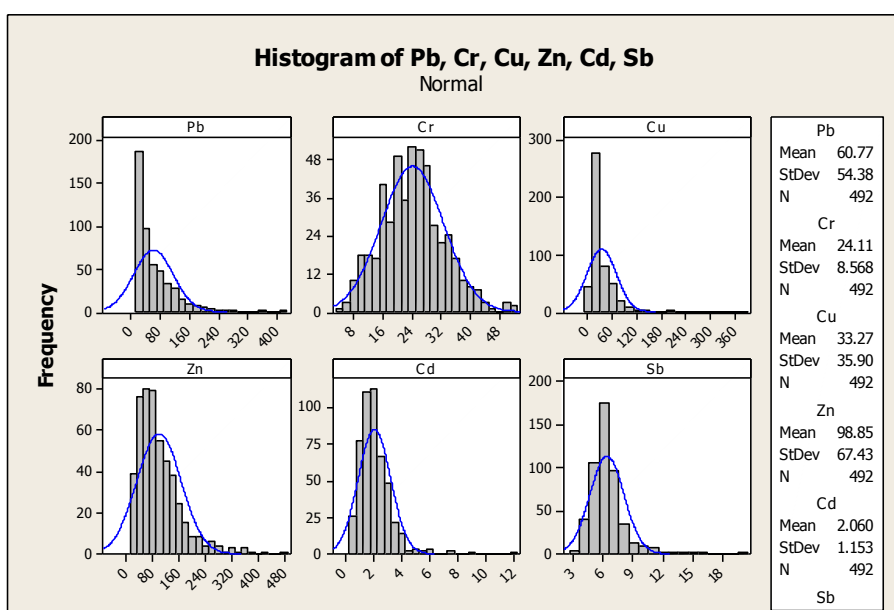


Figure 5.14: Histograms for the metals Pb, Cr, Cu, Zn, Cd, Sb

From the above figure, it can be observed that the metal chromium fits to approximately normal data. Further, the metals zinc and cadmium also show slightly normal data.

5.1.4 Checking for the outlying metals

For this purpose, dot plots have been used.

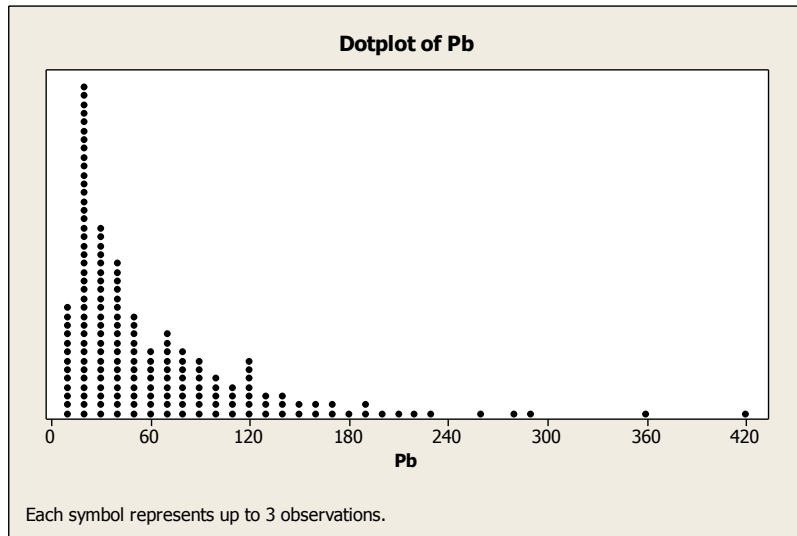


Figure 5.15: Dot plot for Pb

As seen from above plot, lead data is positively skewed. Further, there are some outliers in the upper end.

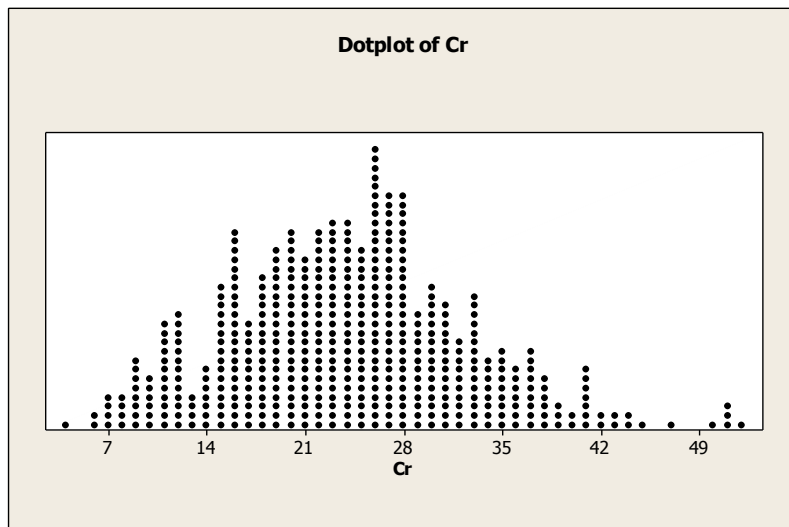


Figure 5.16: Dot plot for Cr

The above plot shows that chromium data is approximately symmetric. However, there are no significant outliers.

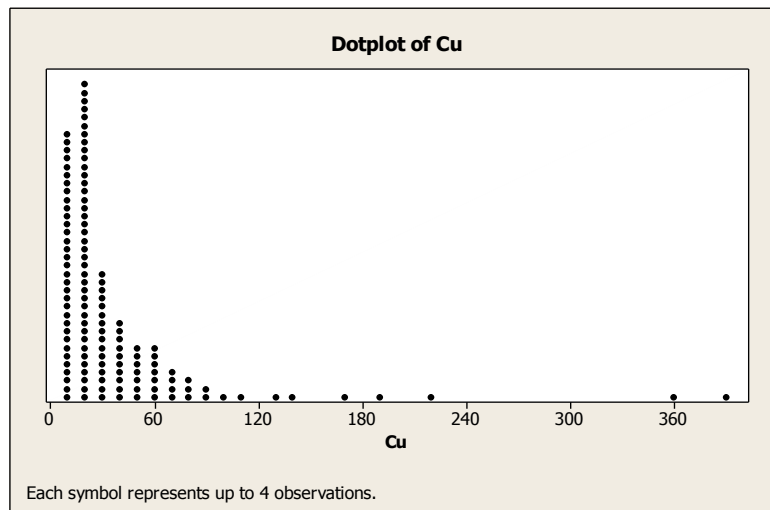


Figure 5.17: Dot plot for Cu

From the above plot, it is evident that the copper data is positively skewed. Further, there are some outliers in the upper end.

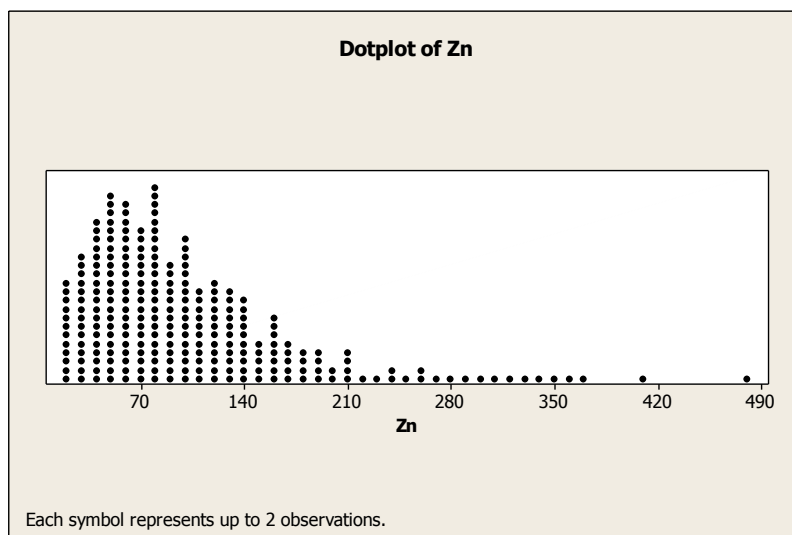


Figure 5.18: Dot plot for Zn

The above plot shows that zinc data is positively skewed. Further, there are some outliers in the upper end.

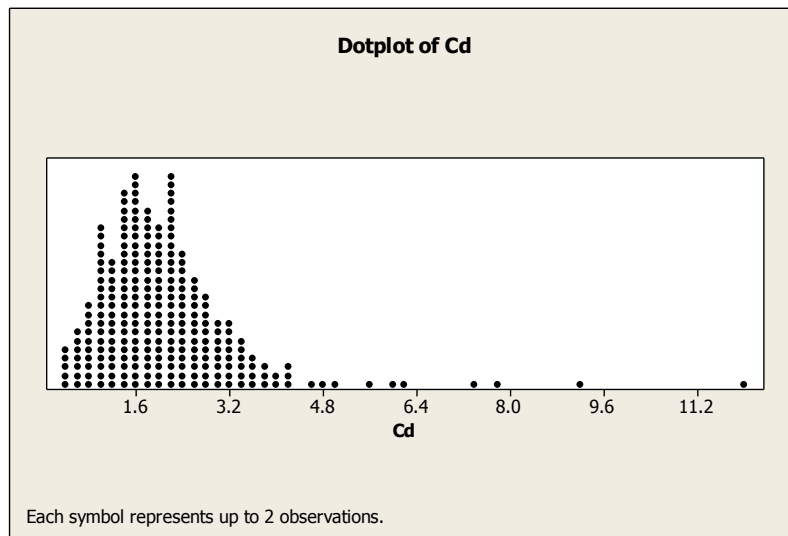


Figure 5.19: Dot plot for Cd

From the above plot, shows that cadmium data have some outliers in the upper end. When the outliers are ignored, slightly symmetric distribution is observed.

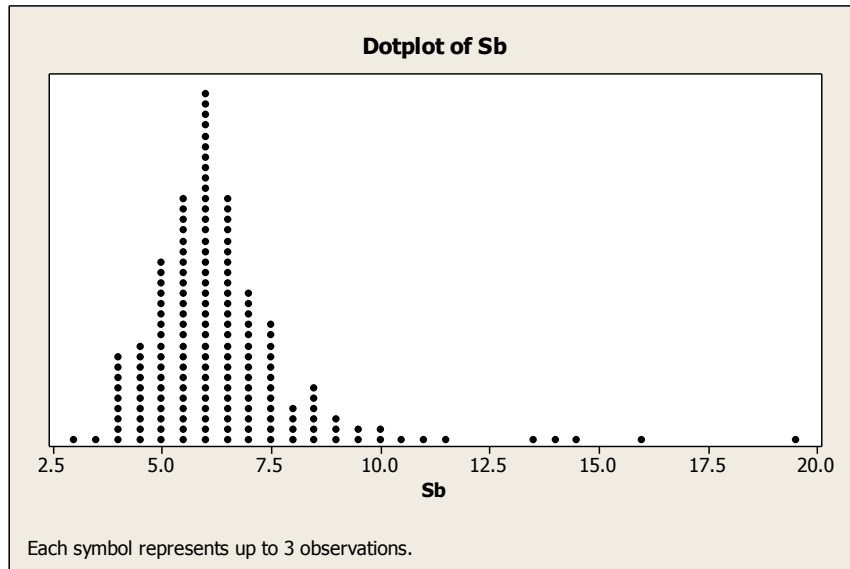


Figure 5.20: Dot plot for Sb

From the above plot, shows that antimony data have some outliers in the upper end. When the outliers are ignored, slightly symmetric distribution is observed.

5.2 El Paso regions data

In the following sections, analysis of data for each of the El Paso city regions has been conducted Figure 5.21. Further, comparison between the concentrations of different sides has been covered as well.

The study area is divided into the region following the geographic adapted maps for the city, west, east, northeast, and the central. The classification of the study area into regions give us a clear view about the concentration and distribution pattern of heavy metals in each regions, and allow us to make comparison between the regions.

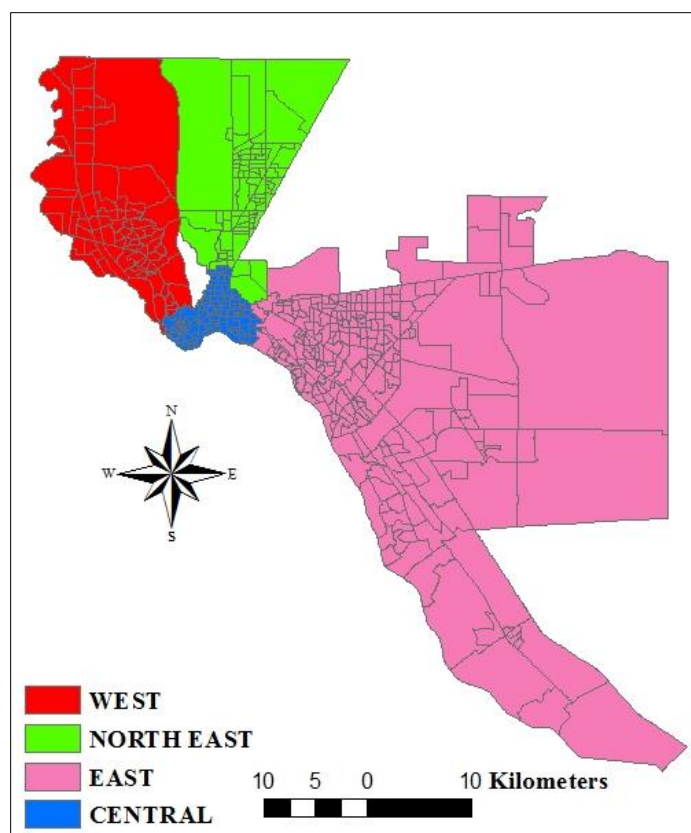


Figure 5.21: El Paso city regions

5.2.1 Central El Paso

Univariate and bivariate analyses were conducted on 74 samples from central El Paso.

5.2.1.1 Univariate analysis

The descriptive statistics obtained are shown in Table 5.4. The following observations can be made;

Table 5.4: Descriptive Statistics on heavy metals in central El Paso

Variable	N	Minimum	Maximum	Mean	St Dev	Q1	Q3	Median
Pb	74	50.8	355.3	138.4	61.4	91.6	170.5	126.1
Cr	74	17.9	51.6	32.1	8.6	25.8	37.7	30.1
Cu	74	19.6	385.8	68.9	62.2	36.3	76.3	52.9
Zn	74	67.8	413.4	181.7	77.2	124.2	214.7	164.5
Cd	74	0.9	9.2	3.3	1.6	2.3	3.7	2.9
Sb	74	4.4	14.6	7.6	1.9	6.2	8.7	6.9

5.2.1.1.1 Lead in soil

The statistical analysis Table 5.4 shows that the concentration levels recorded for lead ranged from 50.8 ppm to 355.3 ppm, with the mean value of 138.4 ppm. The distribution of lead in samples is presented in Figure 5.22.

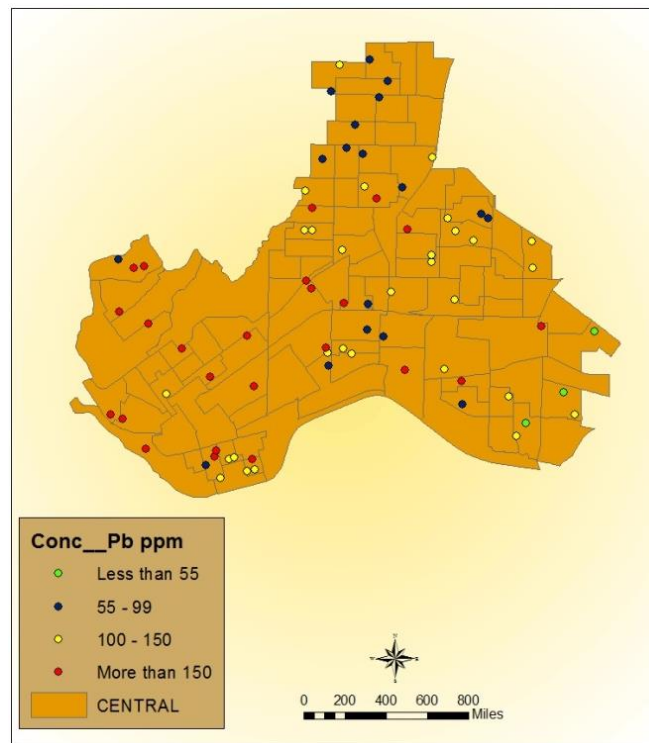


Figure 5.22: Lead levels in composite samples from blocks in central El Paso

The lowest values (less than 55 ppm; green dots) of lead are mostly encountered in the east part of central El Paso. However, only a few green dots can be found in the east central area indicating lower lead levels in the soil.

Blocks with 55 ppm to 99 ppm lead, seen in blue in Figure 5.22. Therefore, the concentrations between 55 ppm and 99 ppm for lead are recorded mostly in the central part of central El Paso.

Blocks having lead levels between 100 ppm and 150 ppm (yellow dots) are scattered all over the central part. However, it is mostly found in the east side of central El Paso.

Red dots depicting lead concentration levels more than 150 ppm are found in the west part of central El Paso. However, it seems the west part of central El Paso contains higher lead concentrations than the east part of central El Paso.

Figure 5.23, illustrates the concentration of lead levels in soil samples with correlation of children age 0-4 central El Paso area.

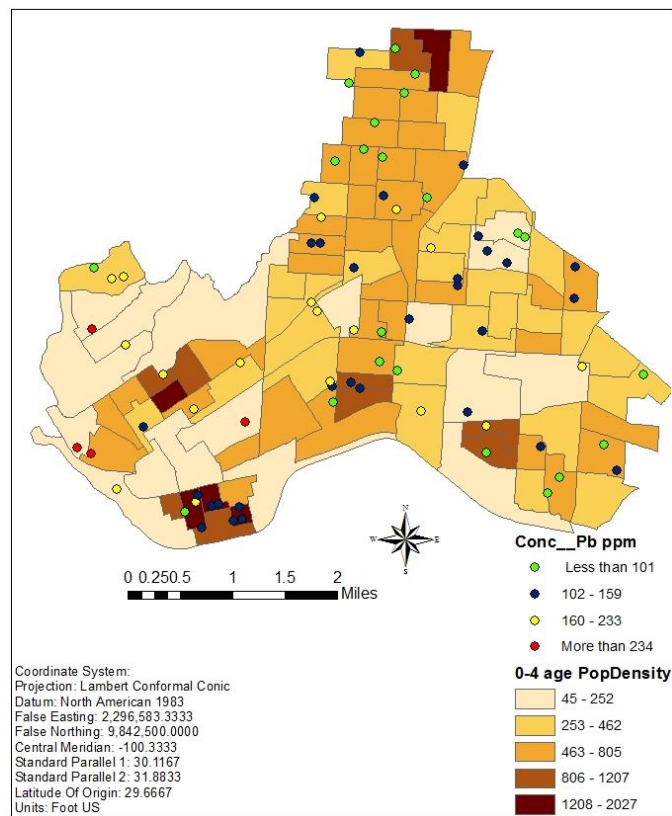


Figure 5.23: Potential population density of children and lead soil in central El Paso

5.2.1.1.2 Chromium in soil

Chromium levels ranged from 17.9 ppm to 51.6 ppm, with the mean value of 32.1 ppm. The distribution of chromium in samples is presented in Figure 5.24.

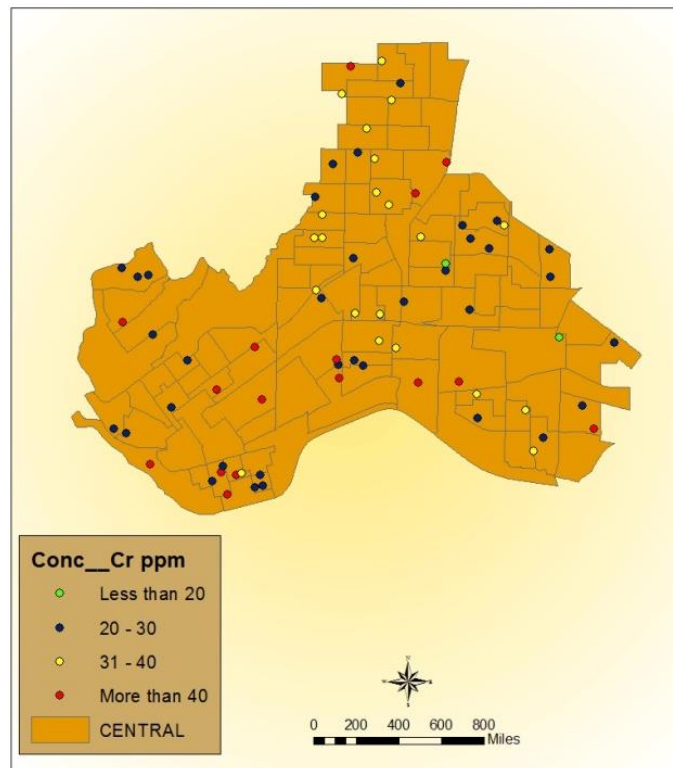


Figure 5.24: Chromium levels in composite samples from blocks in central El Paso

Only a few blocks were found to have the lowest values (less than 20 ppm; green dots) of chromium in central El Paso. Blocks with 20 ppm to 30 ppm chromium are seen in blue in Figure 5.24. Therefore, it is clear that concentrations between 20 ppm and 30 ppm for chromium are recorded all over the map.

Blocks having chromium levels between 31ppm and 40 ppm (yellow dots) are scattered mainly in the eastern part of central El Paso. However, there are few blocks with this level of

concentration in the other parts of the city also. Red dots depicting chromium concentration levels more than 40 ppm are found in the west part of central El Paso.

However, it seems the west part of central El Paso contains higher chromium concentrations than the east part of central El Paso.

5.2.1.1.3 Copper in soil

The concentration levels for copper ranged from 19.6 ppm to 385.8 ppm, with the mean value of 68.9 ppm. The distribution of Cu in samples is presented in Figure 5.25.

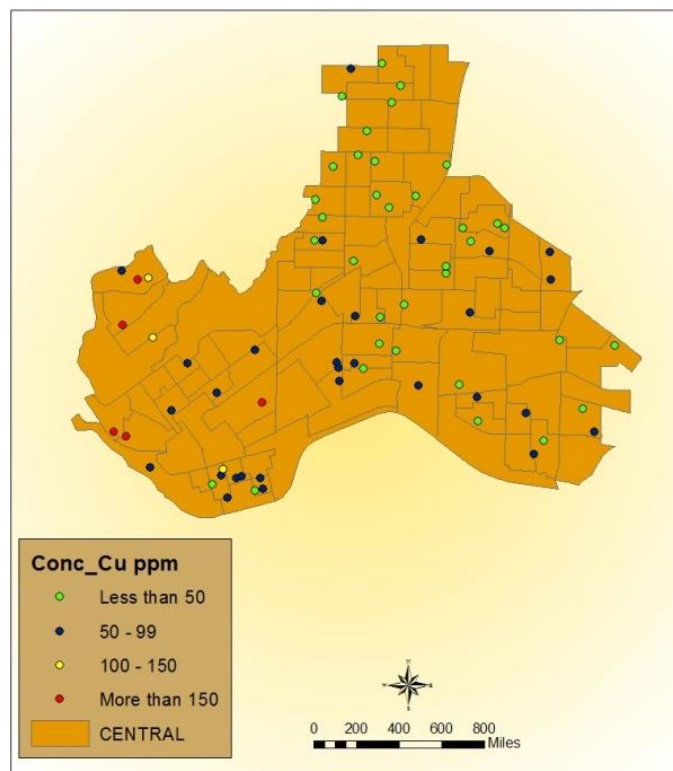


Figure 5.25: Copper levels in composite samples from blocks in central El Paso

Blocks having the lowest values (less than 50 ppm; green dots) of copper are encountered mainly in the east part of central El Paso. Only a few blocks in the west part have this lowest

copper concentration soil. Blocks with 50 ppm to 99 ppm copper, are seen in blue in Figure 5.25. Therefore, the concentrations between 50 ppm and 99 ppm for copper are recorded all over the map. However, most of these concentrations are encountered in the southern section of central El Paso. Only a few blocks having copper levels between 100 ppm and 150 ppm (yellow dots) are found in the map. These are scattered only in the west part of central El Paso. Red dots depicting copper concentration levels more than 150 ppm are found only in the west part of central El Paso.

However, it seems the west part of central El Paso contain higher copper concentrations than the east part of central El Paso

5.2.1.1.4 Zinc in soil

The concentration levels of zinc ranged from 67.8 ppm to 418.4 ppm, with the mean value of 181.7 ppm. The distribution of zinc in samples is presented in Figure 5.26.

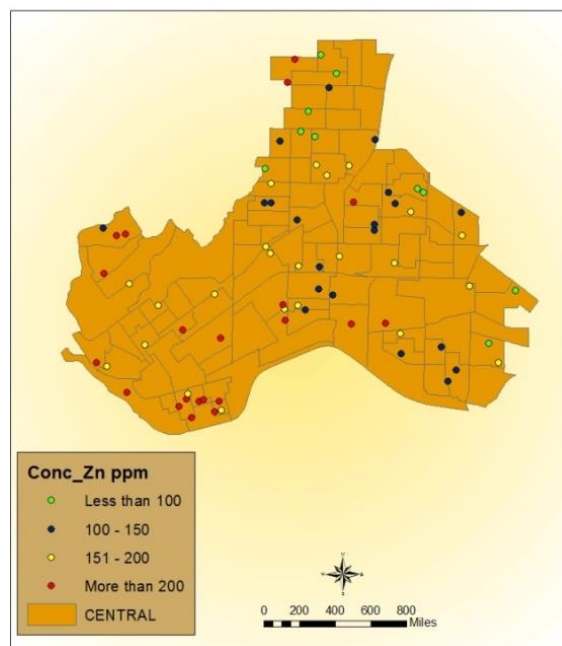


Figure 5.26: Zinc levels in composite samples from blocks in central El Paso

The blocks having the lowest values (less than 100 ppm; green dots) of zinc are found mainly in the east part of central El Paso. Blocks with 100 ppm to 150 ppm zinc are seen in blue in Figure 5.26. Therefore, the concentrations between 100 ppm and 150 ppm are also encountered in east part of central El Paso. Blocks having zinc levels between 151ppm to 200 ppm (yellow dots) are scattered all over central El Paso. The majority of red dots depicting zinc concentration levels more than 200 ppm is found in the west part of central El Paso. In the east part of central El Paso, there are only a few blocks having these levels of concentration.

However, it seems the west part of central El Paso contains higher zinc concentrations than the east part of central El Paso.

5.2.1.1.5 Cadmium in soil

The concentration levels for cadmium ranged from 0.9 ppm to 9.2 ppm, with the mean value of 3.3 ppm. The distribution of cadmium in samples is presented in Figure 5.27.

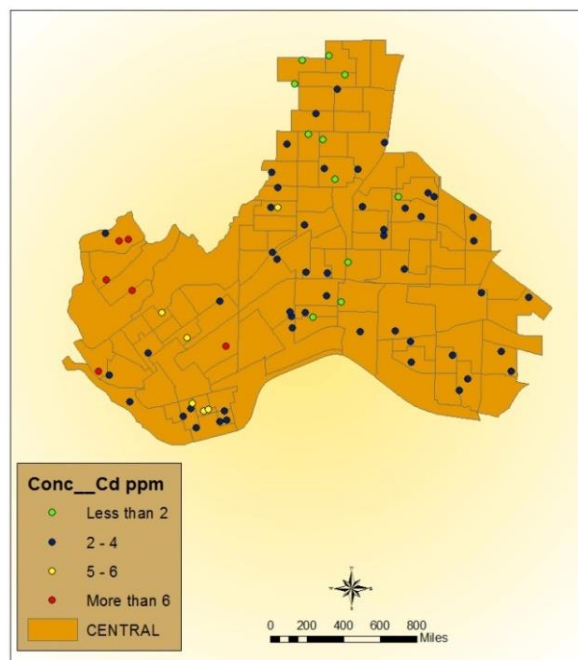


Figure 5.27: Cadmium levels in composite samples from blocks in central El Paso

The blocks having the lowest values (less than 2 ppm; green dots) of cadmium are found mainly in the central part of central El Paso. Blocks with 2 ppm to 4 ppm cadmium, seen in blue in Figure 5.27. Therefore, it is seen that concentrations between 2 ppm and 4 ppm for cadmium are encountered all over the map.

Blocks having cadmium levels between 5ppm and 6 ppm (yellow dots) are scattered mainly in the west part of central El Paso. Red dots depicting cadmium concentration levels more than 6 ppm are found only in the west part of central El Paso.

However, it seems the west part of central El Paso contains higher cadmium concentrations than the east part of central El Paso.

5.2.1.1.6 Antimony in soil

The concentration levels for antimony ranged from 4.4 ppm to 14.6 with the mean value of 7.6 ppm. The distribution of antimony in samples is presented in Figure 5.28.

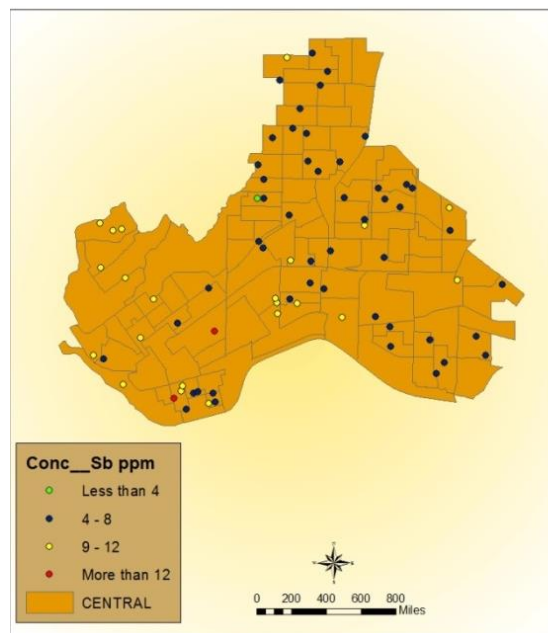


Figure 5.28: Antimony levels in composite samples from blocks in central El Paso

Only one block having the lowest values (less than 4 ppm; green dots) of antimony found in central El Paso. Blocks with 4 ppm to 8 ppm antimony, seen in blue in Figure 5.28. So the concentrations between 4 ppm and 8 ppm for antimony are encountered all over the map. However, the majority of them were found in the east part of the central El Paso.

Blocks having antimony levels between 9 ppm and 12 ppm (yellow dots) are scattered mainly in west part of the central El Paso. Nevertheless, there are a few blocks having this level of concentration in east part also.

Only a few red dots depicting antimony concentration levels more than 12 ppm found in the central El Paso. These blocks are encountered only in the west part of the central El Paso. It seems the west part of the central El Paso contains higher antimony concentrations than the east part of the central El Paso.

In central El Paso, the highest mean concentration value is recorded for the metal zinc at 476.8 ppm, which also has the highest standard deviation, Q1, and median, Q3. The minimum concentration is recorded for cadmium at 0.9 ppm, which is almost 60 times that of zinc. By considering the mean concentration, we can conclude that the concentration of heavy metals in the soil samples taken from central El Paso are in the decreasing order of zinc > lead > copper > chromium > antimony > cadmium.

5.2.3 Bivariate analysis

The metal concentration patterns are illustrated by scatter plots, as shown in Figure 5.29 - 5.33.

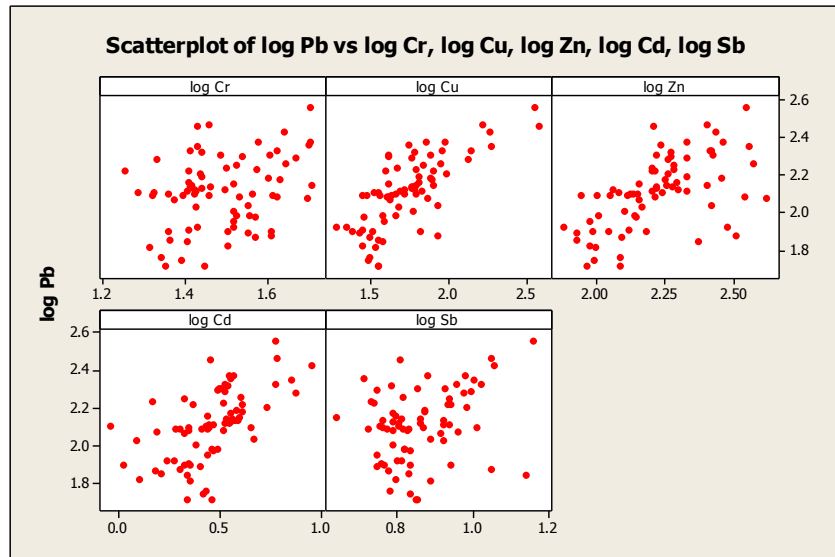


Figure 5.29: Correlation of Pb with Cr, Cu, Zn, Cd, Sb

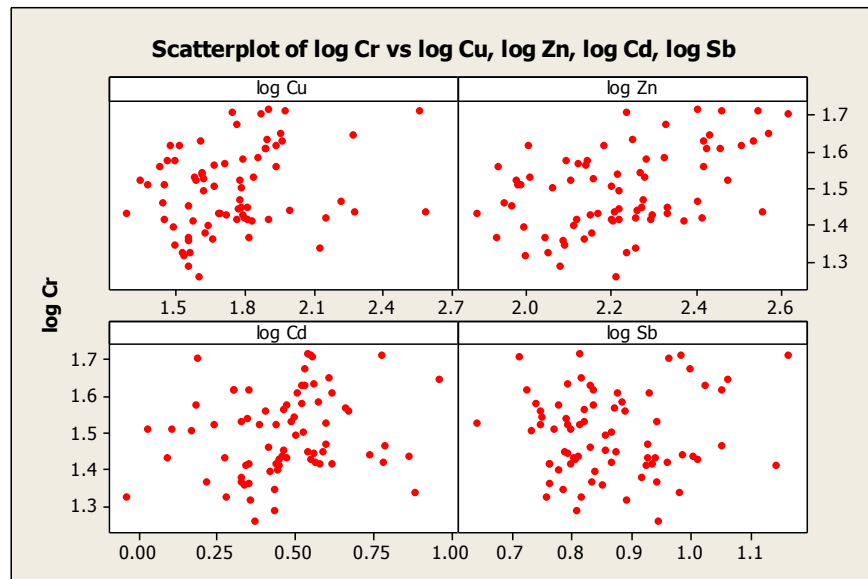


Figure 5.30: Correlation of Cr with Cu, Zn, Cd, Sb

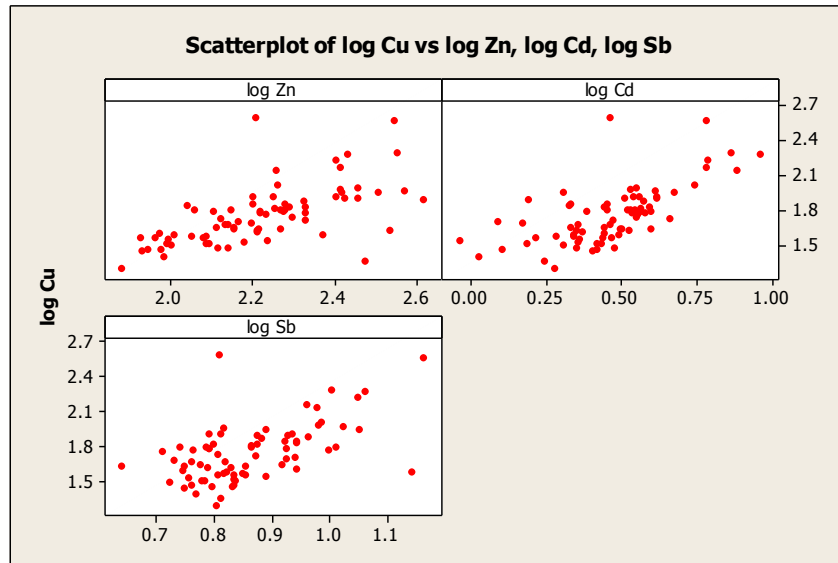


Figure 5.31: Correlation of Cu with Zn, Cd, Sb

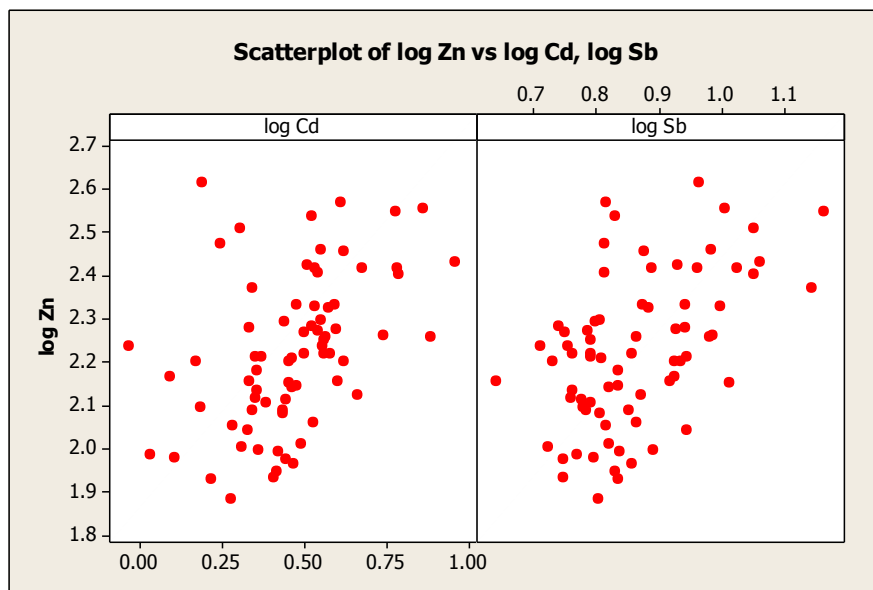


Figure 5.32: Correlation of Zn with Cd, Sb

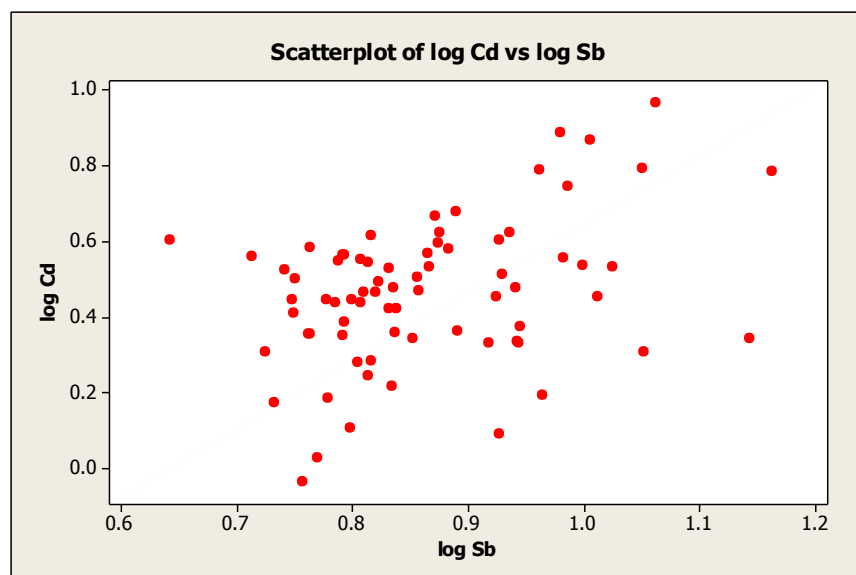


Figure 5.33: Correlation of Cd with Sb

As seen from the above figures, it can be summarized that the variable lead shows a positive correlation with the metals copper, zinc and cadmium. The metal chromium exhibits no significant correlation with other metals. However, chromium shows a positive relationship with lead. The metal copper has a minor positive relationship with zinc and cadmium. Further, it was clear that copper has a positive relationship with the lead concentration. The metal zinc does not show a significant correlation with cadmium and antimony. It is also observed that zinc shows a positive relationship with lead and copper. The metal cadmium exhibits no significant correlation with antimony.

To justify the observed results from the above scatter plots, a correlation matrix is used.

Table 5.5: Correlations between the metals

Correlations: Pb, Cr, Cu, Zn, Cd, Sb					
	Pb	Cr	Cu	Zn	Cd
Cr	0.337 0.003				
Cu	0.753 0.000	0.207 0.076			
Zn	0.512 0.000	0.524 0.000	0.456 0.000		
Cd	0.632 0.000	0.168 0.153	0.573 0.000	0.432 0.000	
Sb	0.400 0.000	0.135 0.250	0.499 0.000	0.516 0.000	0.444 0.000
Cell Contents: Pearson correlation P-Value					

According to Table 5.5, except for the metals pairs copper and chromium, cadmium and chromium, antimony and chromium all other variable pairs have significant correlations with a 5% significance level. Furthermore, these three pairs have the lowest correlation values. A linear correlation coefficient analysis (r) between soil metals was performed on the data. The result of correlation analysis is shown in Table 5.6.

Table 5.6: Computed Pearson correlation coefficient of heavy metals level

Correlation between metals	r value	P value
Correlation between Pb and Cr	0.337	0.003
Correlation between Pb and Cu	0.753	0.000
Correlation between Pb and Zn	0.512	0.000
Correlation between Pb and Cd	0.632	0.000
Correlation between Pb and Sb	0.400	0.000
Correlation between Cr and Cu	0.207	0.076
Correlation between Cr and Zn	0.524	0.000
Correlation between Cr and Cd	0.168	0.153
Correlation between Cr and Sb	0.135	0.250
Correlation between Cu and Zn	0.573	0.000
Correlation between Cu and Cd	0.281	0.000
Correlation between Cu and Cd	0.573	0.000
Correlation between Cu and Sb	0.499	0.000
Correlation between Zn and Cd	0.432	0.000
Correlation between Zn and Sb	0.516	0.000
Correlation between Cd and Sb	0.444	0.000

According to these observations, it is clear that the correlation between lead and copper is the highest ($r = 0.753$). Except for 6 pairs, all other metals pairs show less than 0.5 correlations. Furthermore, it can be observed that the metals lead and copper have more influence on, or are more influenced by the other elements. However, these significant correlations may not have observed from the scatter plots due to the view of it.

5.2.4 Check the normality of the data

To check the normality of the data, the study employs histograms Figures, 5.34-5.35, provides the histograms for the metals.

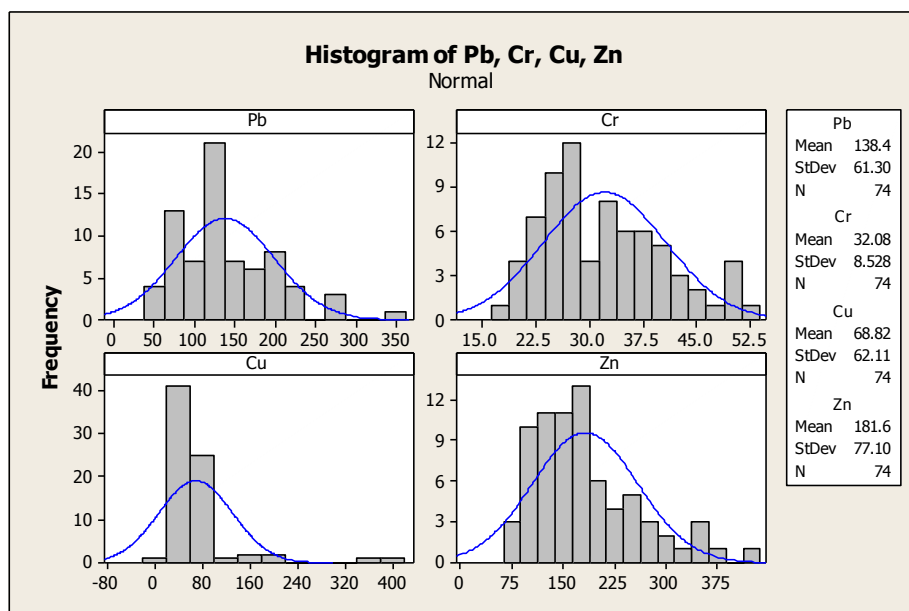


Figure 5.34: Histogram for the metals Pb, Cr, Cu and Zn

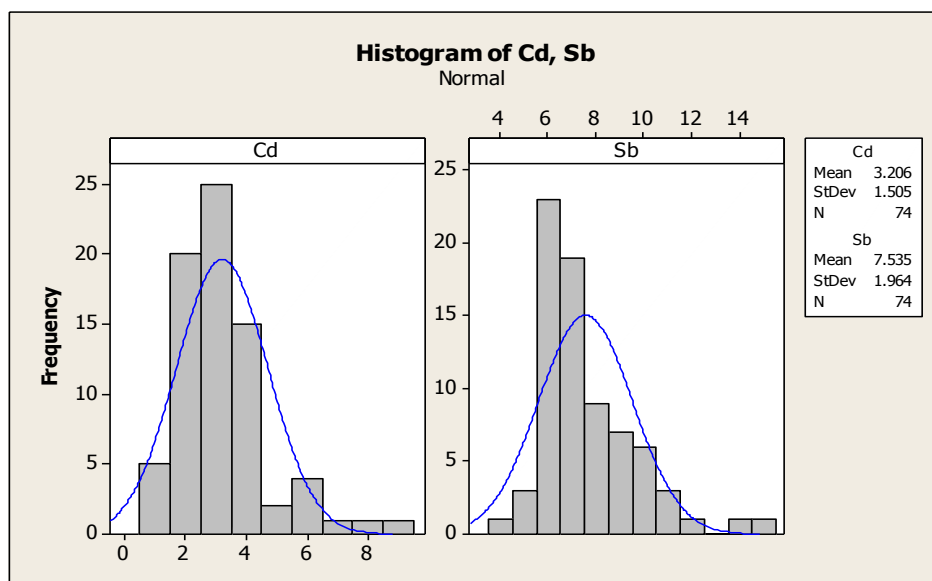


Figure 5.35: Histogram for the metals Cd and Sb

Figures 5.34 and 5.35 provide the histograms for the variables. From the output, it can be observed that the metal chromium fits to approximately normal data. Furthermore, the metals lead, zinc, cadmium and antimony also show slightly normal data.

5.2.5 Checking for the outlying observations

For this purpose, box plots have been used.

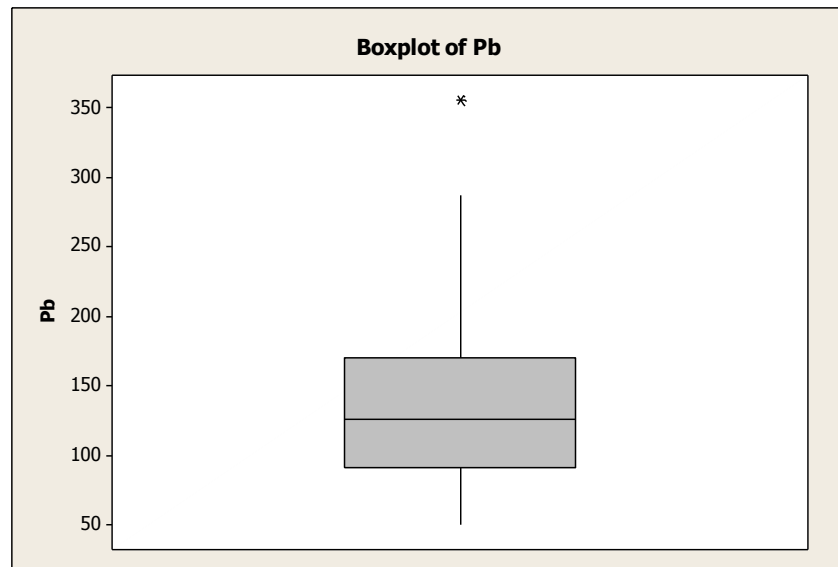


Figure 5.36: Box plot for Pb

From the above plot, it is noticeable that the data for lead is slightly normal. Furthermore, there are some outliers in the upper end.

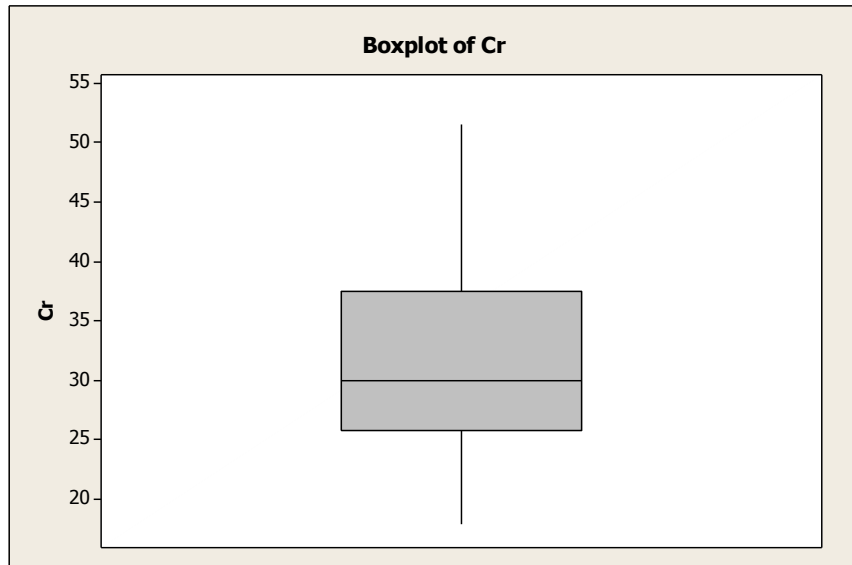


Figure 5.37: Box plot for Cr

From the above plot, it is noticeable that the data for chromium is slightly positively skewed.

Furthermore, there no significant outliers.

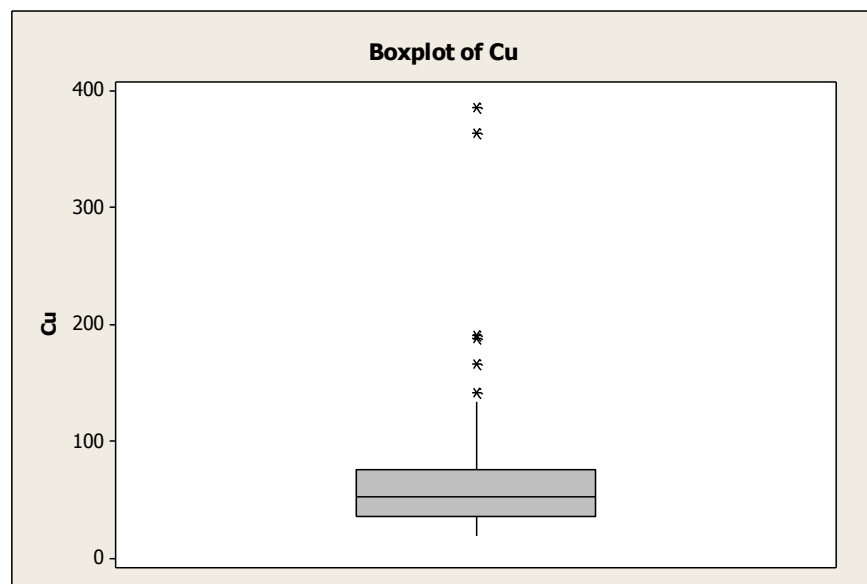


Figure 5.38: Box plot for Cu

From the above plot, it is noticeable that the data for copper is slightly symmetric. Further, there are some outliers in the upper end.

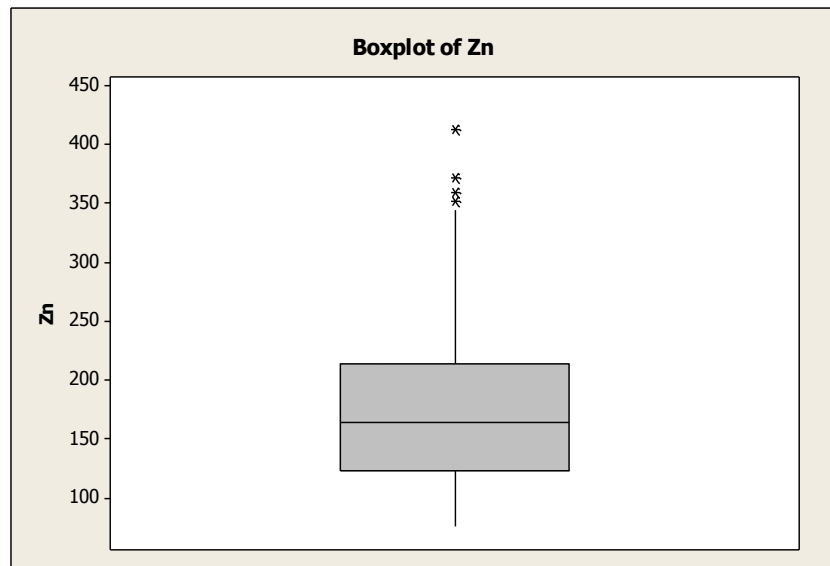


Figure 5.39: Box plot for Zn

From the above data, it is noticeable that the data for zinc is slightly symmetric. However, there are some outliers in the upper end.

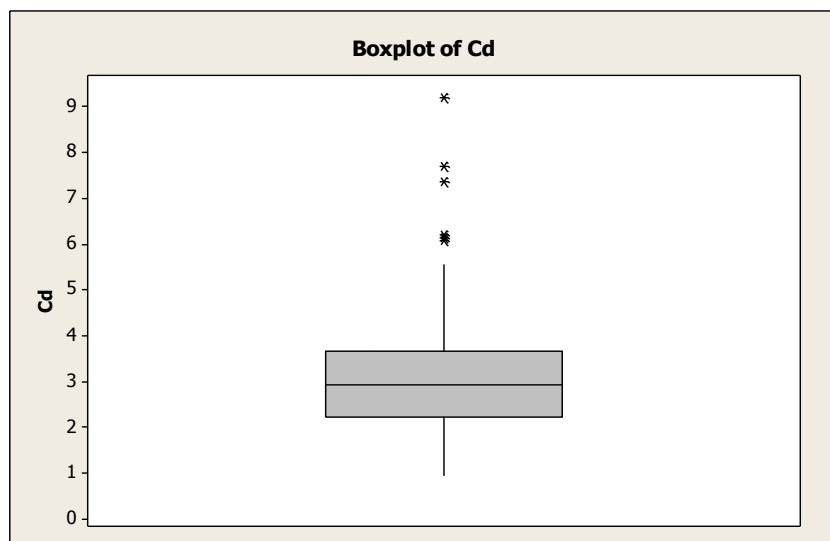


Figure 5.40: Box plot for Cd

From the above figure, we see that the data for cadmium is noticeable and some outliers appear in the upper end. If the outliers are ignored, slightly symmetric distribution is observed.

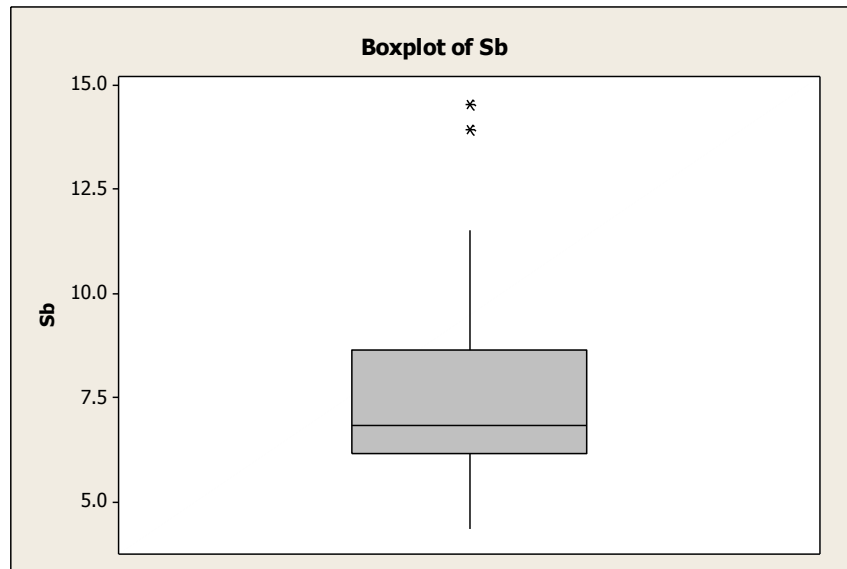


Figure 5.41: Box plot for Sb

The above plot shows that the data for antimony is noticeable and there are some outliers in the upper appear end. The data seems to be positively skewed.

5.3 East El Paso

Univariate and bivariate analyses were conducted on 266 samples from east El Paso.

5.3.1 Univariate analysis

The descriptive statistics obtained in east El Paso are shown in Table 5.7. The following observations can be made;

Table 5.7: Descriptive statistics on the metals of east El Paso

Variable	N	Minimum	Maximum	Mean	St Dev.	Q1	Q3	Median
Pb	266	10.8	197.9	44.6	36.4	18.6	58.1	30.9
Cr	266	6.3	44.1	22.6	7.9	16.3	27.9	22.3
Cu	266	6.5	191.1	27.9	237	13.2	35.8	19.9
Zn	266	16.5	467.8	80.2	53.6	44.2	101.4	69.7
Cd	266	0.5	5.6	1.9	0.9	1.3	2.3	1.8
Sb	266	2.9	19.6	6.1	1.7	5.9	6.7	5.9

5.3.1.1 Lead in soil

The concentration levels recorded of lead ranged from 10.8 ppm to 197.9 ppm, with the mean value of 44.6 ppm. The distribution of lead in blocks samples is presented in Figure 5.42.

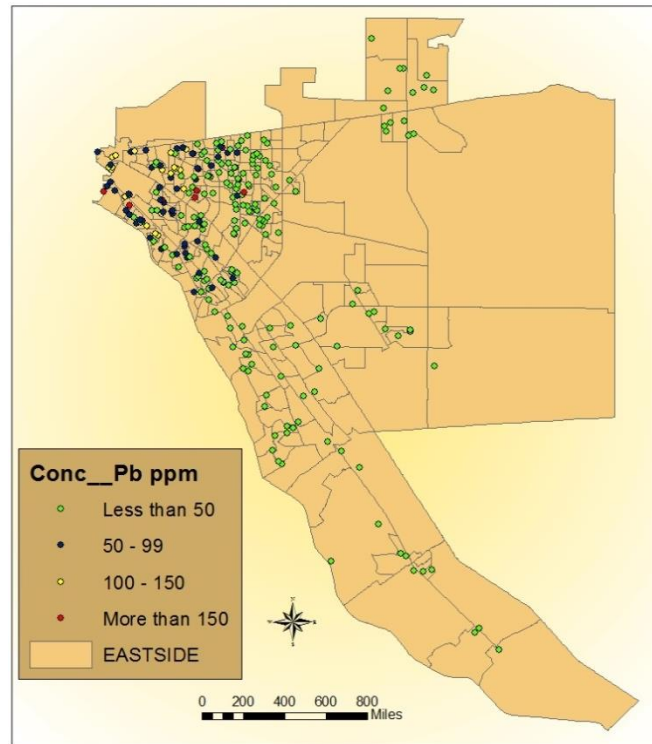


Figure 5.42: Lead levels in composite samples from blocks in east El Paso

The lowest values (less than 50 ppm; green dots) of lead are encountered all over the map. But the density of green dots seems to be lower in the west side of east El Paso. Blocks with 50 ppm to 99 ppm lead, seen in blue in Figure 5.42. Therefore, the concentrations between 55 ppm to 99 ppm for lead are recorded mostly from the west side of east El Paso.

Only a few blocks having lead levels between 100 ppm to 150 ppm (yellow dots) are encountered. However, all of them can be found in west side of east El Paso. A few red dots, depicting the lead concentrations levels more than 150 ppm are found in east El Paso. These blocks are situated in the central and the west part of east El Paso.

However, it seems west side of east El Paso contain higher lead concentrations than the east side of east El Paso.

Figure 5.43, illustrates the concentration of lead levels in soil samples with correlation of children age 0-4 in east El Paso area.

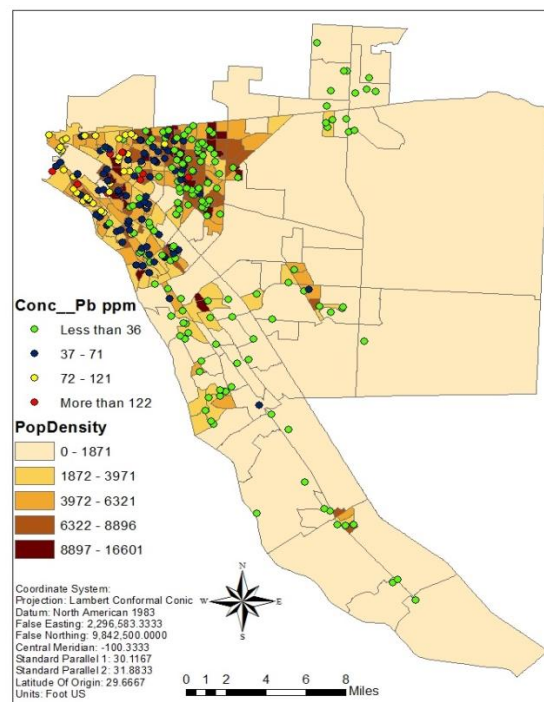


Figure 5.43: Potential population density of children and lead soil in east El Paso

5.3.1.2 Chromium in soil

The concentration levels of chromium ranged from 6.3 ppm to 44.1 ppm, with the mean value of 22.3 ppm. The distribution of chromium in blocks samples is presented in Figure 5.44.

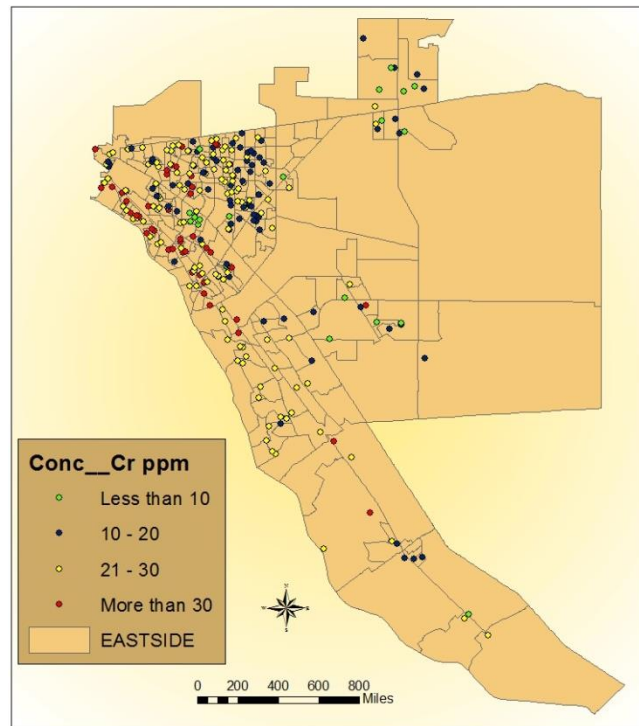


Figure 5.44: Chromium levels in composite samples from blocks in east El Paso

Only a few blocks having the lowest values (less than 10 ppm; green dots) of chromium are found in east El Paso. Blocks with 10 ppm to 20 ppm chromium, seen in blue in the Figure 5.44. Therefore, the concentrations between 10 ppm to 20 ppm for chromium are recorded all over the map. However, majority of them are recorded from central part of east El Paso.

Blocks having chromium levels between 21 ppm to 30 ppm (yellow dots) are scattered mainly in the west and the central parts of east El Paso. However, there are few blocks in this level of concentrate in the other side.

5.3.1.3 Copper in soil

The levels concentration of copper ranged from 6.42 ppm to 191.2 ppm, with the mean value of 27.9 ppm. The distribution of copper in samples is presented in Figure 5.45.

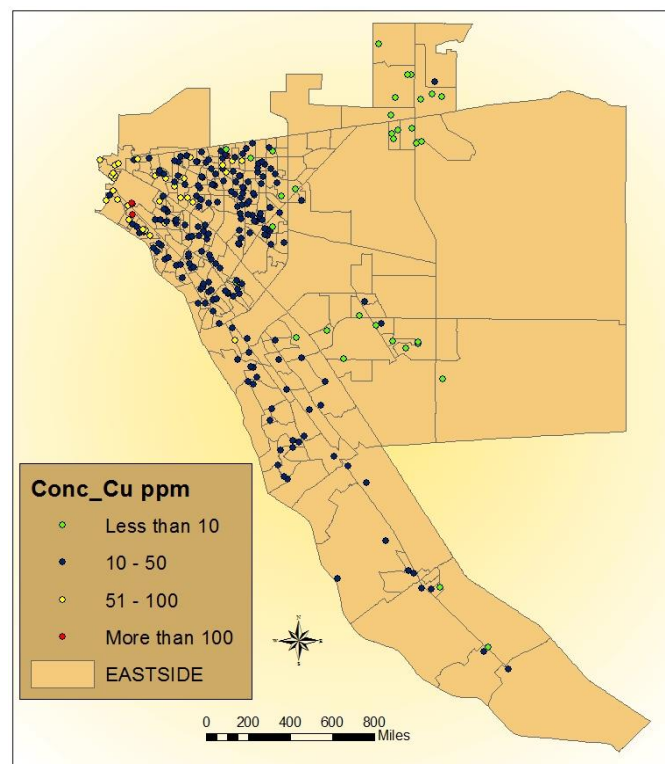


Figure 5.45: Copper levels in composite samples from blocks in east El Paso

Lowest values (less than 10 ppm; green dots) of copper concentrations are encountered more in the east side of east El Paso. Only a few blocks in the west and the central areas have this lowest copper concentration soil.

Blocks with 10 ppm to 50 ppm copper, are shown in blue in the Figure 5.45. Therefore, the concentrations between 50 ppm to 99 ppm for copper are recorded all over the map. However, density of blue dots is higher in the central section in east El Paso. Only a few Blocks having copper levels between 51 ppm to 100 ppm (yellow dots) are found in the map. These are scattered only in the west side of east El Paso.

5.3.1.4 Zinc in soil

The levels concentration of zinc ranged from 16.5 ppm to 476.8 ppm, with the mean value of 80.2 ppm. The distribution of zinc in samples is presented in Figure 5.46.

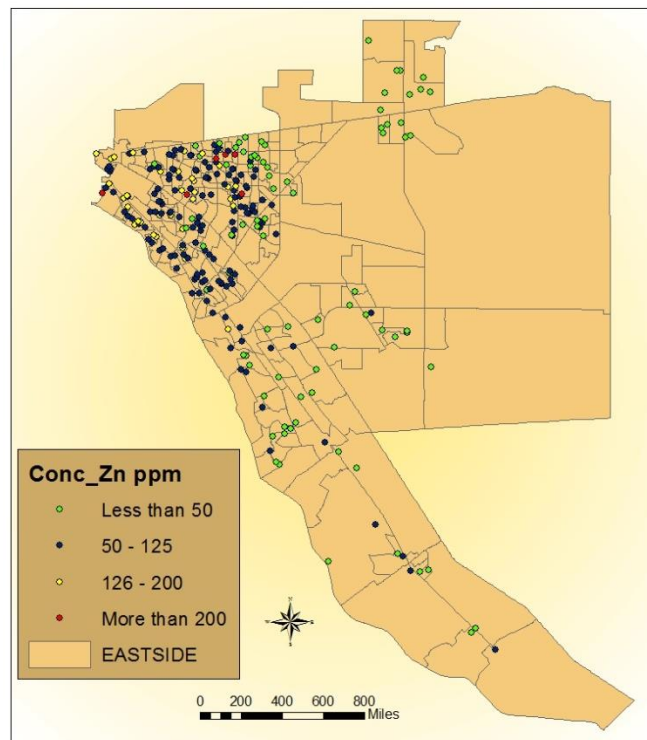


Figure 5.46: Zinc levels in composite samples from blocks in east El Paso

The blocks having the lowest values (less than 50 ppm; green dots) of zinc are found mainly in east side of east El Paso. However, there are some green blocks in central area of east

El Paso. Blocks with 50 ppm to 125 ppm zinc, seen in blue in the Figure 5.46. Therefore, the concentrations between 50 ppm to 125 ppm for zinc are also encountered in west and the central area of east El Paso.

Blocks having zinc levels between 126 ppm to 200 ppm (yellow dots) are scattered mainly from east west side east El Paso. Only a few red dots depicting the zinc concentration levels more than 200 ppm are found in the west and the central area of the east El Paso.

5.3.1.5 Cadmium in soil

The levels concentration of cadmium ranged from 0.5 ppm to 5.6 ppm, with the mean value of 1.9 ppm. The distribution of cadmium in samples is presented in Figure 5.47.

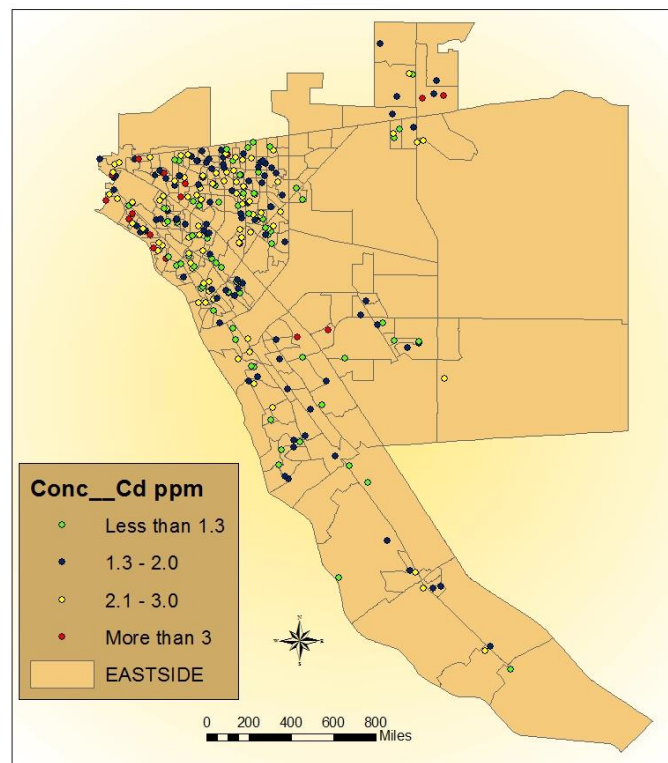


Figure 5.47: Cadmium levels in composite samples from blocks in east El Paso

The blocks having the lowest values (less than 1.3 ppm; green dots) of cadmium are found all over east area of east El Paso. Blocks with 1.3 ppm to 2 ppm cadmium, seen in blue in Figure 5.47. Therefore, the concentrations between 1.3 ppm to 2 ppm for cadmium are encountered in all over the map. Blocks having cadmium levels between 2.1 ppm to 3ppm (yellow dots) are also scattered all over east El Paso.

Red dots depicting the cadmium concentrations levels more than 3 ppm are found only in the west side of east El Paso.

5.3.1.6 Antimony in Soil

The levels concentration of antimony ranged from 2.9 ppm to 19.6 with the mean value of 6.1 ppm. The distribution of antimony in samples is presented in Figure 5.48.

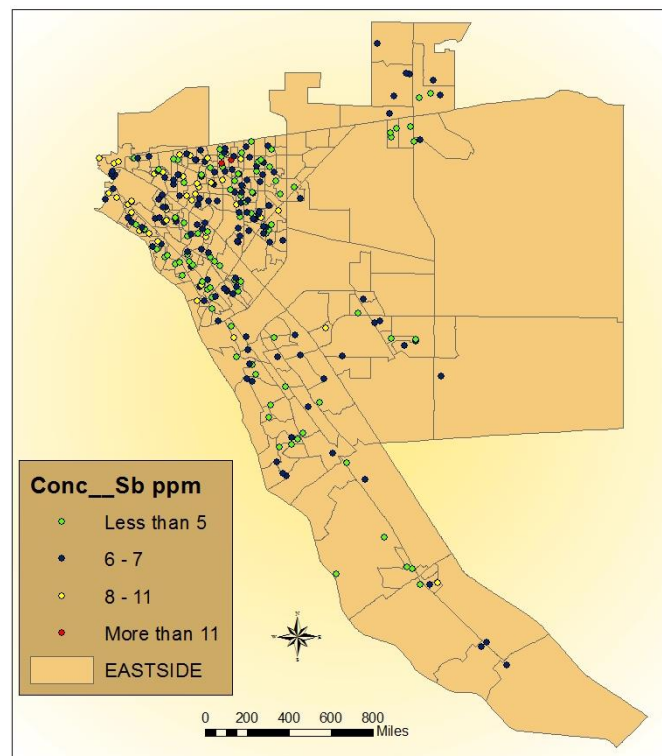


Figure 5.48: Antimony levels in composite samples from blocks in east El Paso

Block having the lowest values (less than 5 ppm; green dots) of antimony is found in all over the east El Paso. Blocks with 6 ppm to 7 ppm antimony, seen in blue in Figure 5.48. Therefore, the concentrations between 6 ppm and 7 ppm for antimony are also encountered in all over the map.

Blocks having antimony levels between 8 ppm to 11 ppm (yellow dots) are scattered mainly in west side of the east El Paso. However, there are few blocks having this level of concentration in the east side. Only two red dots depicting antimony concentration levels more than 11 ppm are found in the central area of the east El Paso.

However, it seems, generally west side of the east El Paso contains higher antimony concentrations than the east side of the east El Paso.

In the east El Paso, the highest mean concentration value is recorded for the metal zinc at 476.8 ppm, which also has the highest standard deviation, Q1, and median, Q3. The minimum concentration is recorded for cadmium at 0.5 ppm, which is almost 50 times than of zinc. By considering the mean concentration, we can conclude that the concentration of the soil samples taken from east El Paso are in the decreasing order of zinc > lead > copper > chromium > antimony > cadmium.

5.3.2 Bivariate analysis

Scatter plots, as shown in Figures 5.49 - 5.53, illustrate the metal concentration patterns.

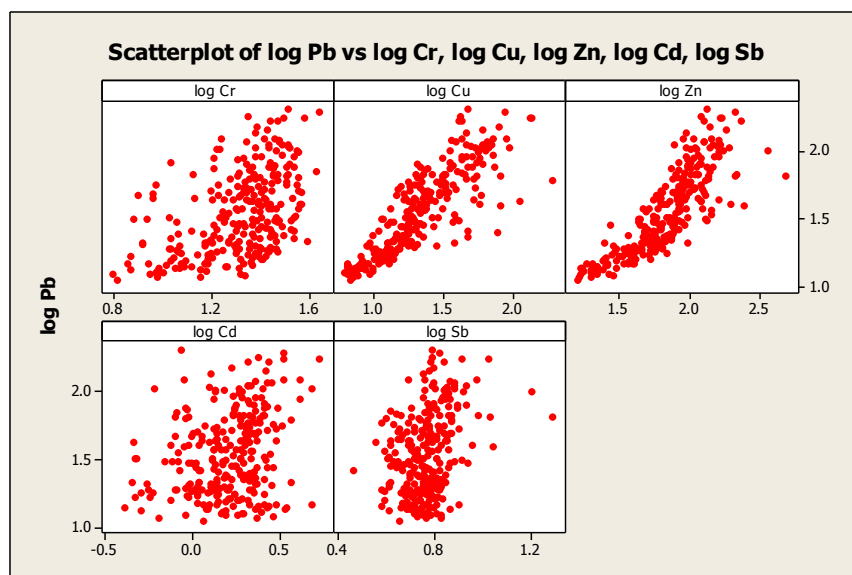


Figure 5.49: Correlation of Pb with Cr, Cu, Zn, Cd, Sb

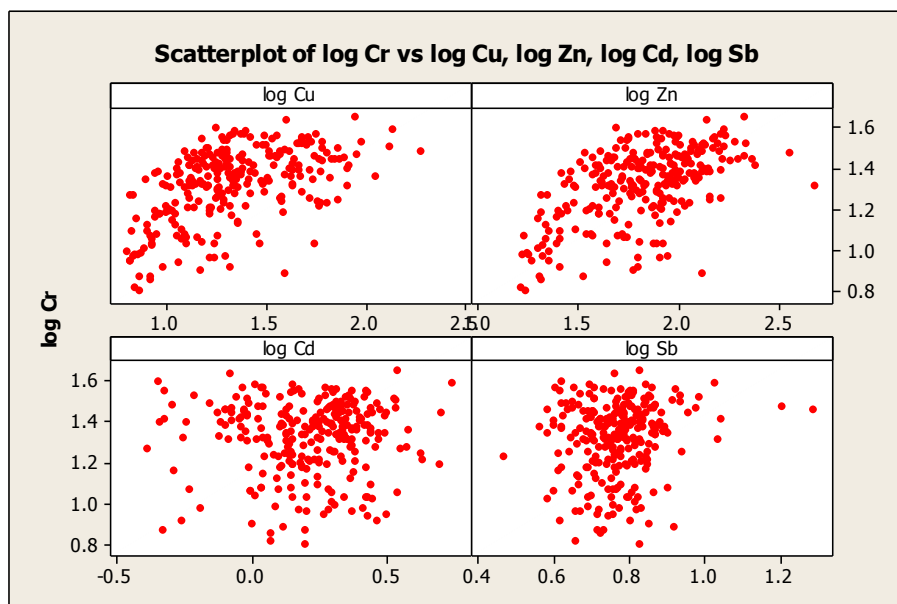


Figure 5.50: Correlation of Cr with Cu, Zn, Cd, Sb

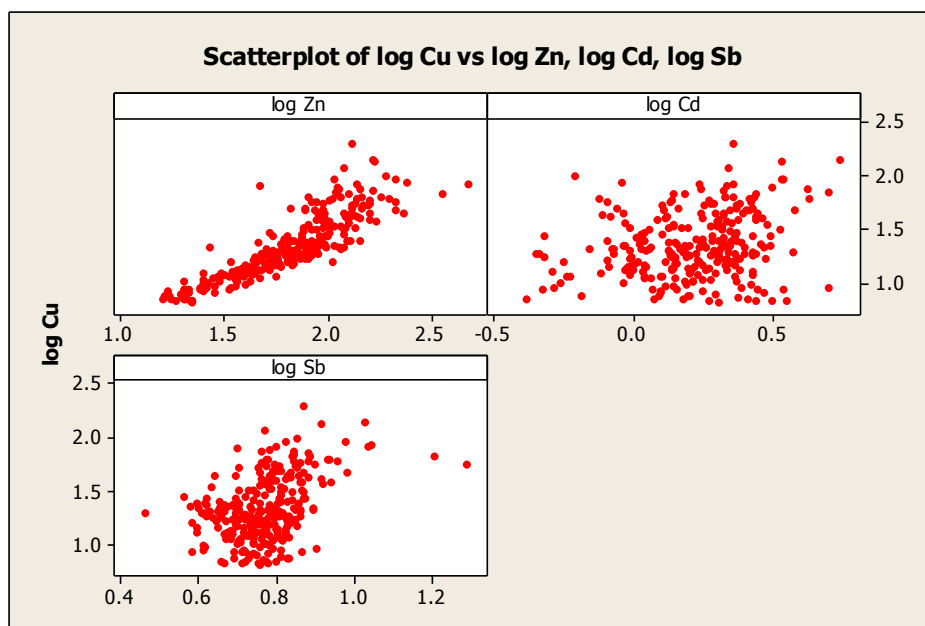


Figure 5.51: Correlation of Cu with Zn, Cd, Sb

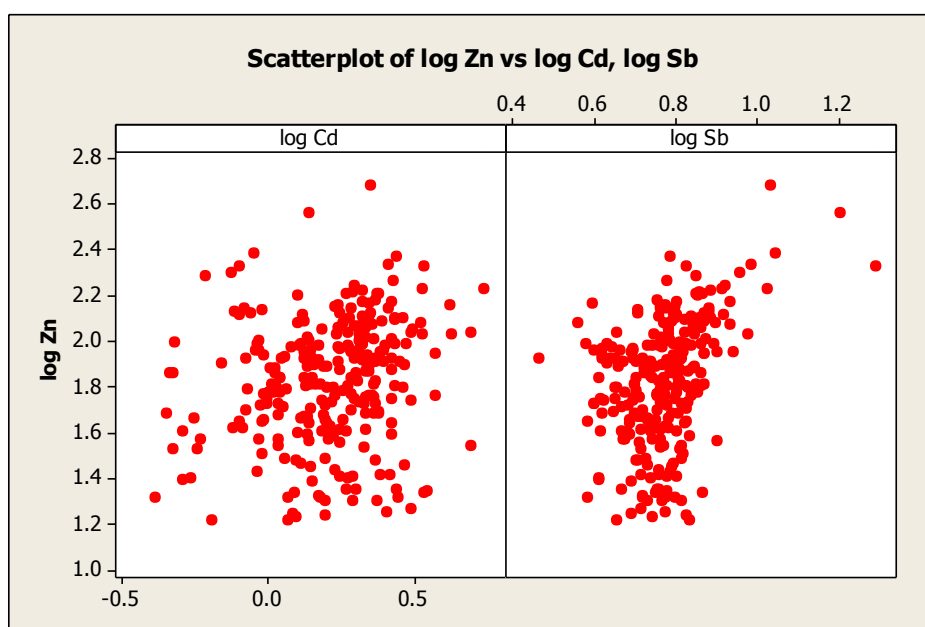


Figure 5.52: Correlation of Zn with Cd, Sb

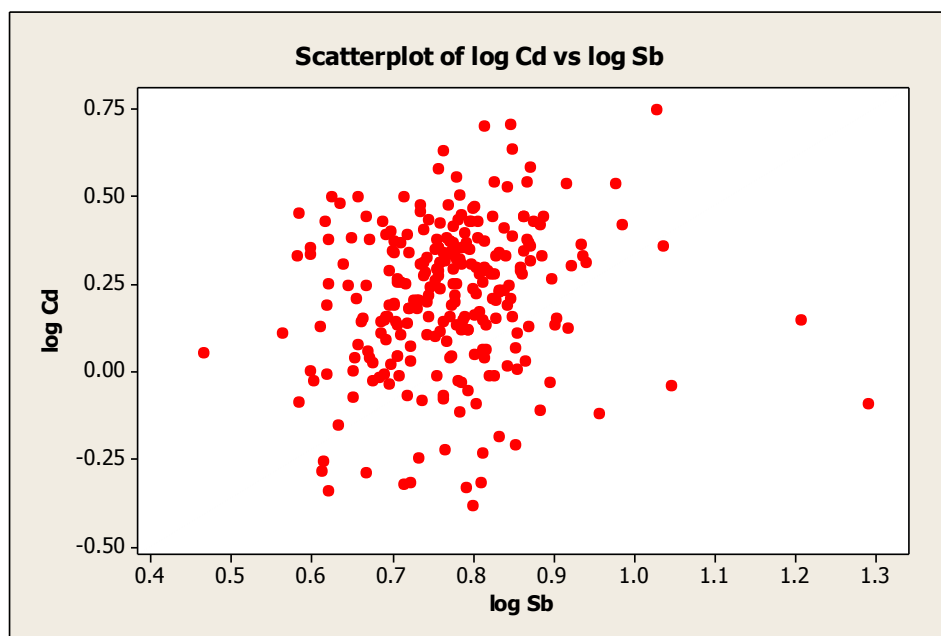


Figure 5.53: Correlation of Cd with Sb

By examining the above Figures, it can be summarized that the variable lead shows a positive correlation with two metals, copper and zinc. The metal chromium exhibits no significant correlation with other metals. However, chromium shows a positive relationship with lead. The metal copper has a minor positive relationship with zinc and cadmium. Further, it was clear that copper has a positive relationship with the lead concentration. The metal zinc exhibits no considerably high correlation with cadmium and antimony. However, it shows a minor positive correlation with the metal antimony. The metal antimony exhibits no significant correlation with other metals.

To emphasize the observed results from the above scatter plots, a correlation matrix can be used.

Table 5.8: Correlations between the metals

Correlations: Pb, Cr, Cu, Zn, Cd, Sb					
	Pb	Cr	Cu	Zn	Cd
Cr	0.443 0.000				
Cu	0.690 0.000	0.402 0.000			
Zn	0.656 0.000	0.434 0.000	0.673 0.000		
Cd	0.318 0.000	0.037 0.552	0.313 0.000	0.175 0.004	
Sb	0.325 0.000	0.162 0.008	0.445 0.000	0.565 0.000	0.127 0.039
Cell Contents: Pearson correlation P-Value					

According to Table 5.8, save for variable pair cadmium and chromium, all other variable pairs have significant correlations with a 5% significance level. Furthermore, these pairs have the lowest correlation values.

A linear correlation coefficient analysis (r) between soil metals was performed on the data. The results of correlation analysis are shown in Table 5.9.

Table 5.9: Computed Pearson correlation coefficient of the metals level

Correlation between metals	r value	P value
Correlation between Pb and Cr	0.443	0.000
Correlation between Pb and Cu	0.690	0.000
Correlation between Pb and Zn	0.656	0.000
Correlation between Pb and Cd	0.318	0.000
Correlation between Pb and Sb	0.325	0.000
Correlation between Cr and Cu	0.402	0.552
Correlation between Cr and Zn	0.434	0.000
Correlation between Cr and Cd	0.037	0.000
Correlation between Cr and Sb	0.162	0.000
Correlation between Cu and Zn	0.673	0.000
Correlation between Cu and Cd	0.313	0.000
Correlation between Cu and Sb	0.445	0.000
Correlation between Zn and Cd	0.175	0.000
Correlation between Zn and Sb	0.565	0.000
Correlation between Cd and Sb	0.127	0.039

According to these observations, it is clear that the correlation between lead and copper is the highest ($r = 0.690$). However, these significant correlations may not have observed from the scatter plots due to the view of it. Save for 4 pairs, all the other variable pairs show less than 0.5 correlations. Further, it can be observed that the variables lead, zinc and copper have more influence or are more influenced by the other elements. However, these significant correlations may not have observed from the scatter plots due to the view of it.

5.3.3 Checking the normality of the data

To check the normality of the data, the study employs histograms Figures 5.54 and 5.55 provide the histograms for the metals.

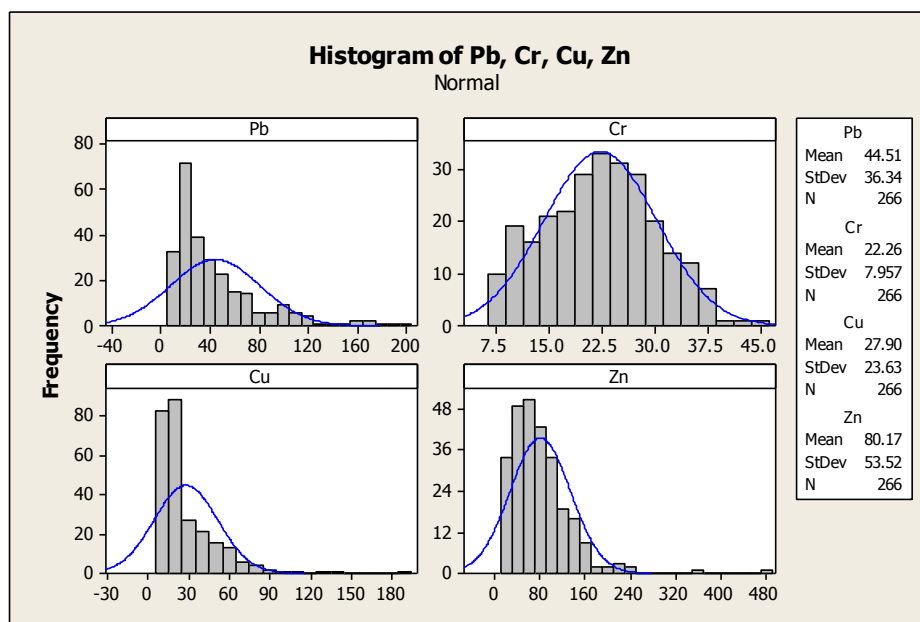


Figure 5.54: Histograms for the metals Pb, Cr, Cu and Zn

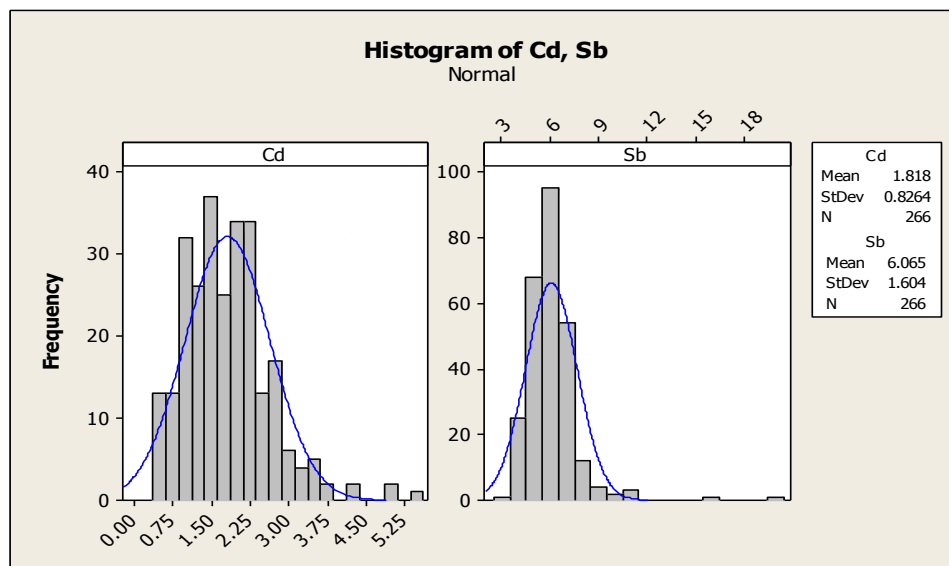


Figure 5.55: Histograms for the metals Cd and Sb

Figures 5.54 and 5.55 provide the histograms for the metals. From the output, it can be observed that the metal Cr fits to approximately normal data. Furthermore, the metals lead, zinc, cadmium and antimony also show slightly normal data.

5.3.4 Checking for the outlying observations

For this purpose dot plots have been used.

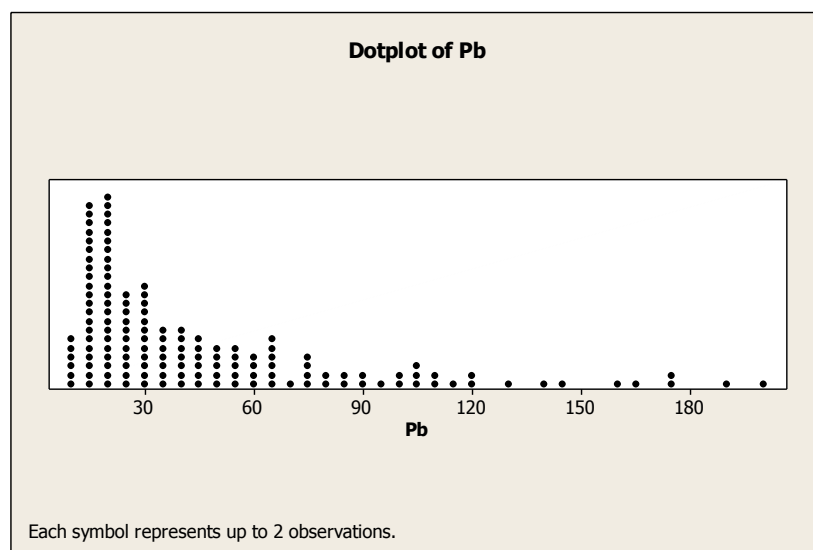


Figure 5.56: Dot plot for Pb

From the above plot, it is noticeable that lead data is positively skewed. Furthermore, there are some outliers in the upper end.

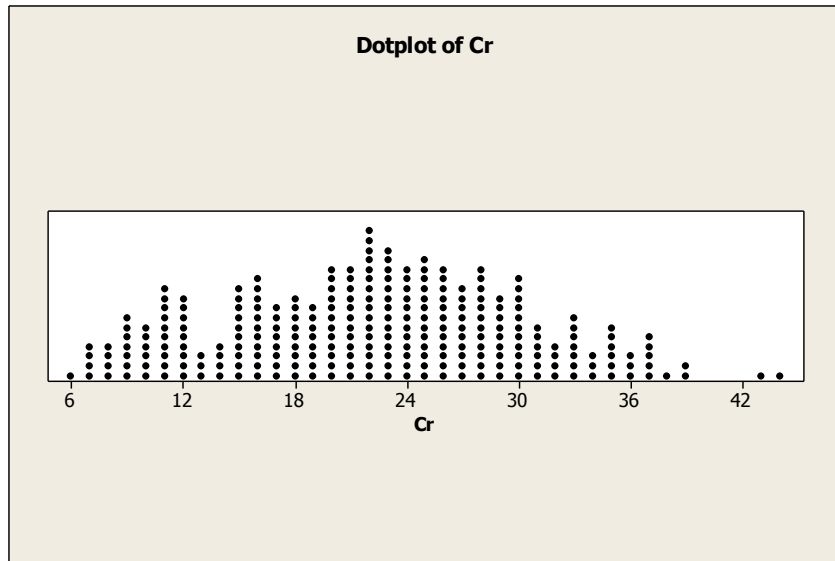


Figure 5.57: Dot plot for Cr

From the above plot it is noticeable that chromium data is approximately symmetric.

Furthermore, there are some outliers.

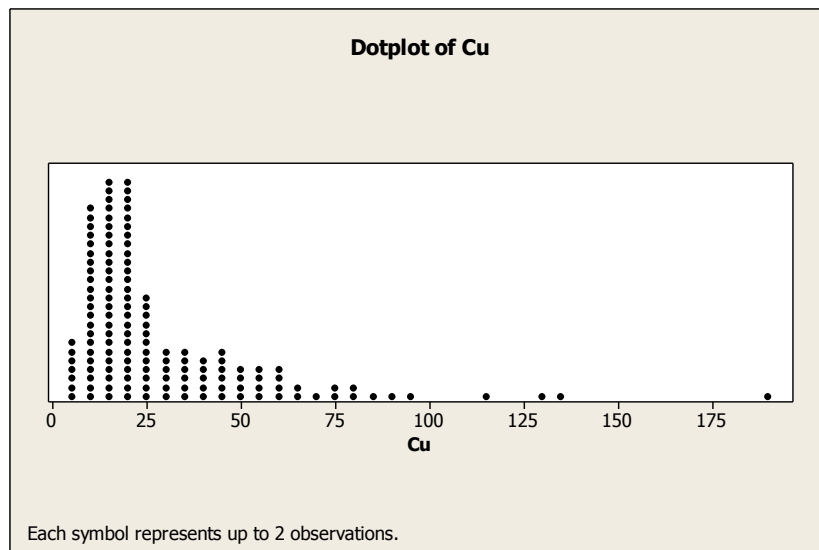


Figure 5.58: Dot plot for Cu

From the above plot, it is noticeable that copper data is positively skewed. Furthermore, there are some outliers in the upper end.

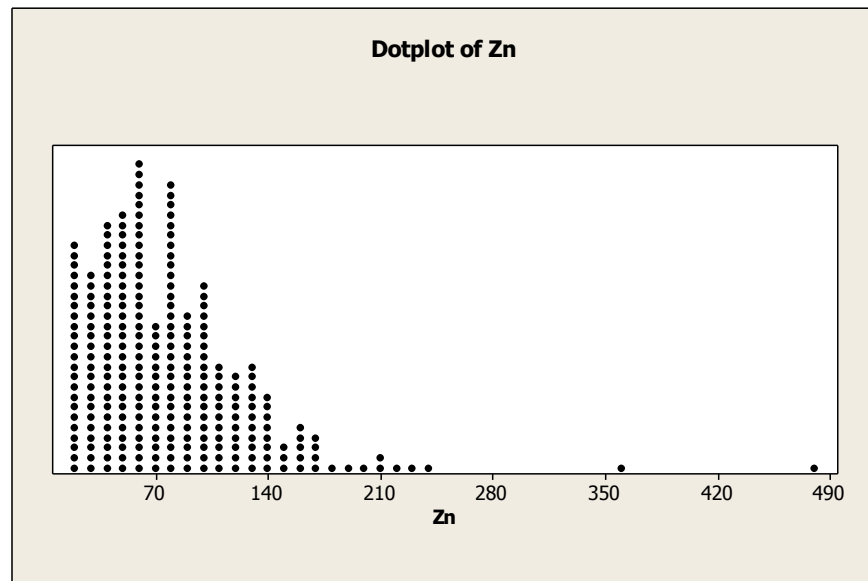


Figure 5.59: Dot plot for Zn

From the above plot, it is noticeable that zinc data is positively skewed. Furthermore, there are some outliers in the upper end.

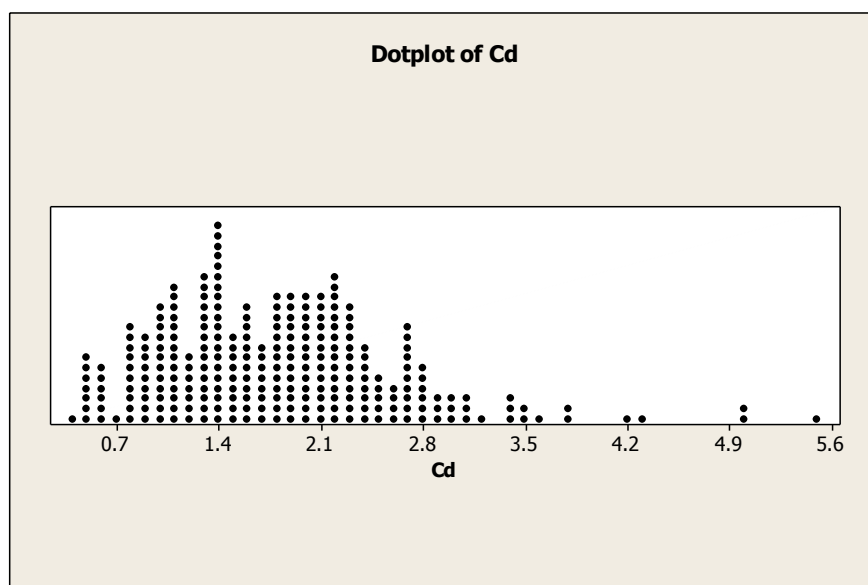


Figure 5.60: Dot plot for Cd

From the above plot, shows that cadmium data have some outliers in the upper end. When the outliers are ignored, slightly symmetric distribution is observed.

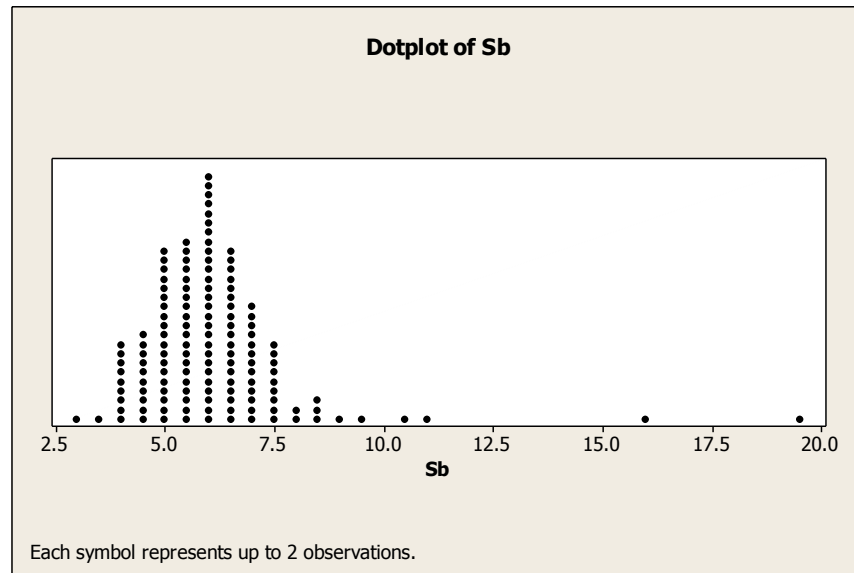


Figure 5.61: Dot plot for Sb

From the above plot, shows that antimony data have some outliers in the upper end. When the outliers are ignored, slightly symmetric distribution is observed.

5.4 Northeast El Paso

For the northeast side of El Paso, univariate and bivariate analyses were conducted on 75 samples.

5.4.1 Univariate analysis

The descriptive statistics obtained are shown in Table 5.10. The following observations can be made;

Table 5.10: Descriptive statistics on the metals of northeast El Paso

Variable	N	Minimum	Maximum	Mean	St Dev	Q1	Q3	Median
Pb	75	13.6	138.2	55.9	30.5	30.1	80.81	48.5
Cr	75	10.9	41.2	22.9	6.4	19.3	27.115	22.3
Cu	75	7.9	108.9	22.8	16.2	14.6	26.43	18.4
Zn	75	30.1	327.6	103.6	53.5	66.1	126.39	86.5
Cd	75	0.4	3.2	1.8	0.7	1.4	2.1190	1.8
Sb	75	3.2	10.2	5.9	1.3	5.3	6.7	5.9

5.4.1.1 Lead in soil

As Table 5.10 displays, the descriptive statistics analysis shows that the concentration levels recorded for lead ranged from 13.6 ppm to 138.2 ppm, with the mean value of 55.9 ppm. The distribution of lead in samples is presented in Figure 5.62.

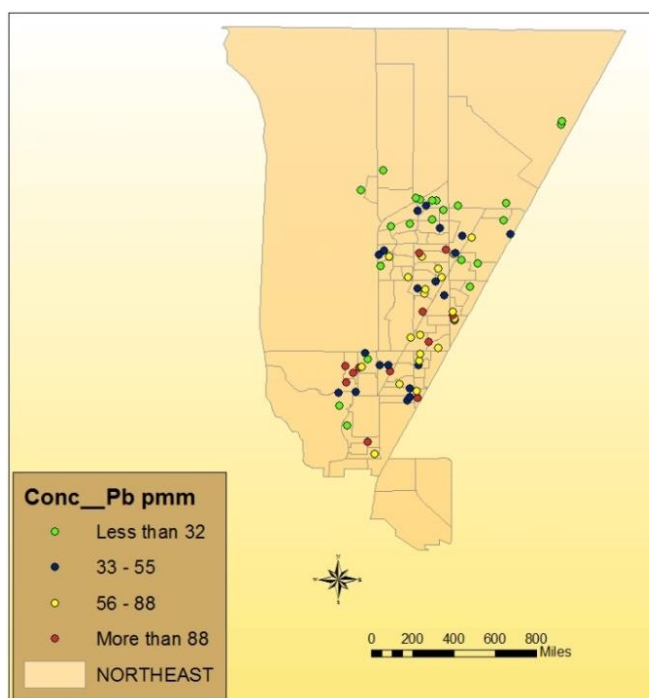


Figure 5.62: Lead levels in composite samples from blocks in northeast El Paso

The lowest values (less than 32 ppm; green dots) of lead are encountered mostly in the north part of northeast El Paso. However, there are a few green dots in the south part also.

Blocks with 33 ppm to 55 ppm lead are seen in blue in Figure 5.62. Therefore, the concentrations between 33 ppm and 55 ppm for lead are recorded mostly in the central part of northeast El Paso. Blocks having lead levels between 56 ppm and 88 ppm (yellow dots) are encountered in the southern central part of northeast El Paso.

Red dots, depicting lead concentration levels more than 88 ppm are also mostly found in southern central part of northeast El Paso.

However, it seems that the level of lead concentration is higher in the southern part than the northern part of northeast El Paso.

Figure 5.63, illustrates the concentration of lead levels in soil samples with correlation of children age 0-4 in northeast El Paso area.

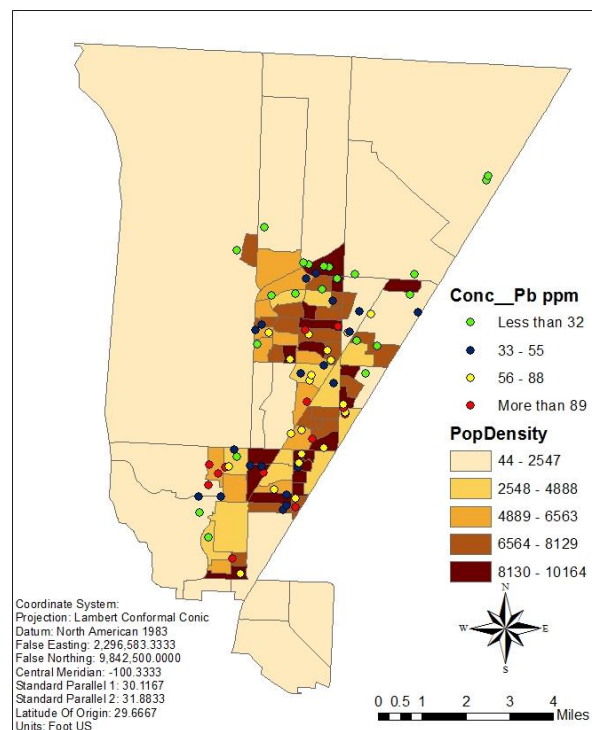


Figure 5.63: Potential population density of children and lead in the soil of northeast El Paso

5.4.1.2 Chromium in soil

The concentration levels of chromium ranged from 10.9 ppm to 41.2 ppm, with the mean value of 22.9 ppm. The distribution of chromium in samples is presented in Figure 5.64.

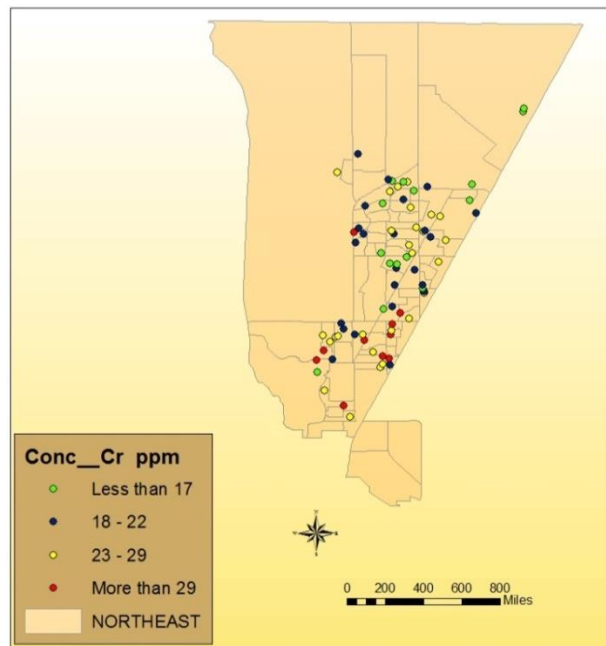


Figure 5.64.: Chromium levels in composite samples from blocks in northeast El Paso

The lowest values (less than 17 ppm; green dots) of chromium are scattered in the northeast El Paso. However, the north part contains more green dots than the south. Blocks with 18 ppm to 22 ppm chromium are seen in blue in Figure 5.64. So concentrations between 18 ppm and 22 ppm for chromium are recorded mainly in the central part of the map.

Blocks having chromium levels between 23 ppm and 29 ppm (yellow dots) are scattered all over the northeast part El Paso. Most of the red dots depicting chromium concentration levels more than 29 ppm are found in the southern area of northeast El Paso.

However, the map provides some evidence to believe that the southern area of northeast El Paso contains higher chromium concentrations than the north area of northeast El Paso.

5.4.1.3 Copper in soil

The concentration levels of copper ranged from 7.9 ppm to 108.9 ppm, with the mean value of 22.8 ppm. The distribution of copper in samples is presented in Figure 5.65.

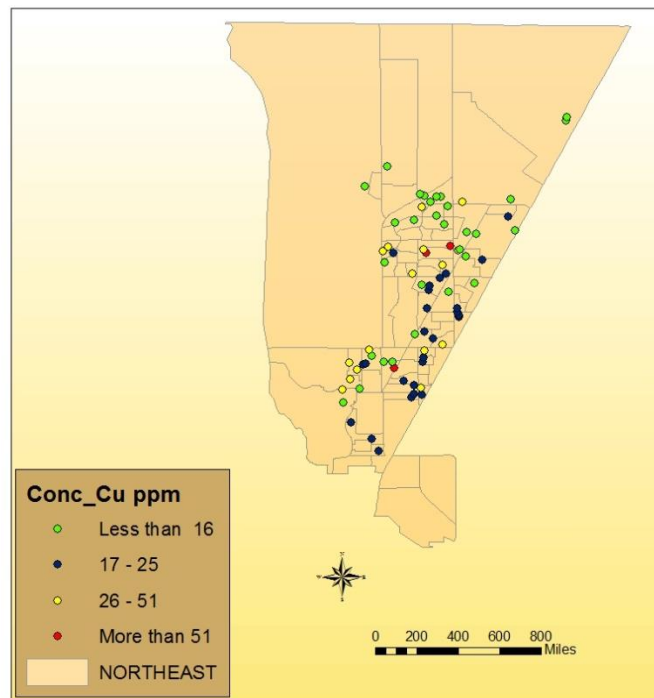


Figure 5.65: Copper levels in composite samples from blocks in northeast El Paso

Lowest values (less than 16 ppm; green dots) of copper concentrations are encountered more in the north central area of the northeast part of El Paso. Blocks with 17 ppm to 25 ppm copper are shown in blue in Figure 5.65. So the concentrations between 17 ppm and 25 ppm for copper are recorded mostly in the southern central area of the northeast part of El Paso.

Copper levels between 26 ppm and 51 ppm (yellow dots) are also found in the central part of the map. Only a few red dots depicting copper concentration levels more than 51 ppm are found in the central area of the northeast part of El Paso.

5.4.1.4 Zinc in soil

Zinc levels ranged from 30.1 ppm to 327.6 ppm, with the mean value of 103.6 ppm. The distribution of zinc in samples is presented in Figure 5.66.

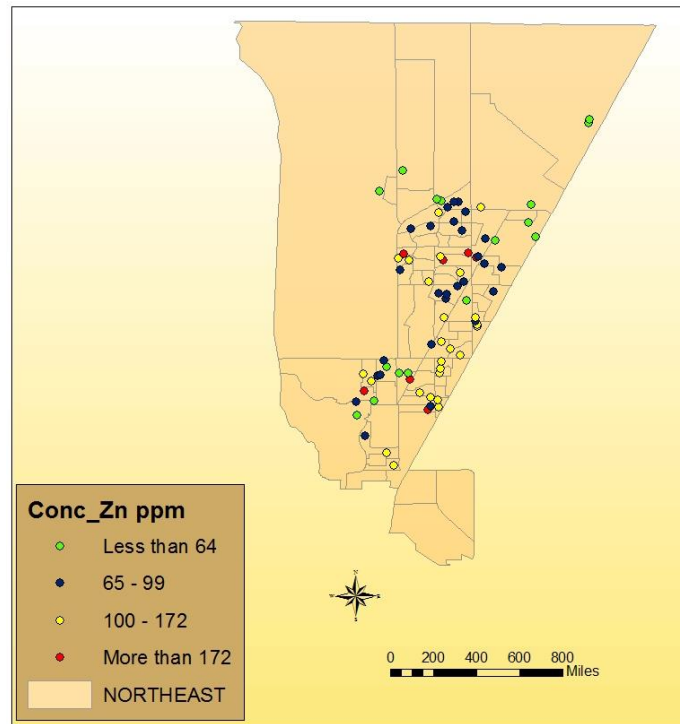


Figure 5.66: Zinc levels in composite samples from blocks in northeast El Paso

The blocks having the lowest values (less than 64 ppm; green dots) of zinc are scattered all over the northeast part of El Paso. Blocks with 65 ppm and 99 ppm zinc, are shown in blue in Figure 5.66. The density of blue dots is higher in the central area of the northeast El Paso.

Blocks having zinc levels between 100 ppm and 172 ppm (yellow dots) are scattered all over the northeast part of El Paso. Only a few red dots depicting zinc concentration levels more than 172 ppm are found in the north and central areas of northeast El Paso.

However, it seems the zinc concentrations are little higher in southern area than the north area of the northeast El Paso.

5.4.1.5 Cadmium in soil

Cadmium levels ranged from 0.4 ppm to 3.2 ppm, with the mean value of 1.8 ppm. The distribution of cadmium in samples is presented in Figure 5.67.

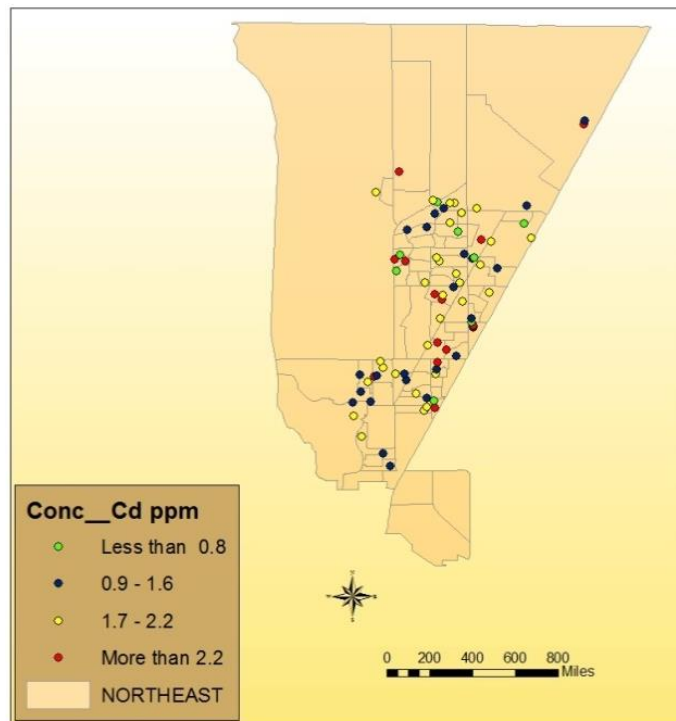


Figure 5.67: Cadmium levels in composite samples from blocks in northeast El Paso

The blocks having the lowest values (less than 0.8 ppm; green dots) of cadmium are found mainly in the central area of northeast El Paso. Blocks with 0.9 ppm to 1.6 ppm cadmium shows in blue in Figure 5.67. So the concentrations between 0.9 ppm to 1.6 ppm for cadmium are encountered in all over the map.

Blocks having cadmium levels between 1.7 ppm and 2.2 ppm (yellow dots) are also scattered all over the northeast part of El Paso. Red dots depicting cadmium concentration levels more than 2.2 ppm are found mainly in the central area of northeast El Paso.

5.4.1.6 Antimony in soil

The concentration levels of antimony ranged from 3.2 ppm to 10.2 with the mean value of 5.9 ppm. The distribution of antimony in samples is presented in Figure 5.68.

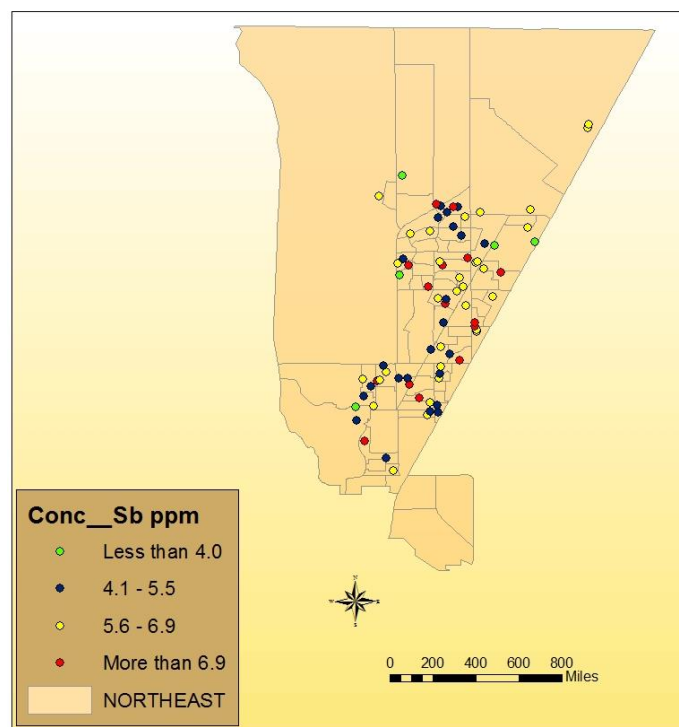


Figure 5.68: Antimony levels in composite samples from blocks in northeast El Paso

Only a few blocks having the lowest values (less than 4 ppm; green dots) of antimony are encountered from the northeast part of El Paso. Most of them are situated in the central area of El Paso. Blocks with 4.1 ppm to 5.5 ppm antimony show in blue in Figure 5.68. So the concentrations between 4.1 ppm and 5.5 ppm for antimony are encountered all over the map.

Blocks having antimony levels between 5.6 ppm and 6.9 ppm (yellow dots) are scattered all over the map in northeast El Paso. Red dots depicting antimony concentration levels more than 6.9 ppm are found mainly in the central area of northeast El Paso.

However, it seems, generally a specific pattern of the spread of antimony concentrations in northeast El Paso cannot be identified.

In the northeast El Paso, the highest mean concentration value is recorded for the metal Zn, 327.6 ppm, and has the highest standard deviation, Q1, and median, Q3. The minimum concentration is recorded for cadmium at 0.9 ppm, which is almost 50 times than zinc. By considering the mean concentration, we can conclude that the concentration of the metal in the soil samples taken from northeast El Paso are in the decreasing order of zinc > lead > chromium > copper > antimony > cadmium.

5.4.2 Bivariate analysis

Scatter plots, as shown in Figures 5.69 - 5.73, illustrate the metal concentration patterns.

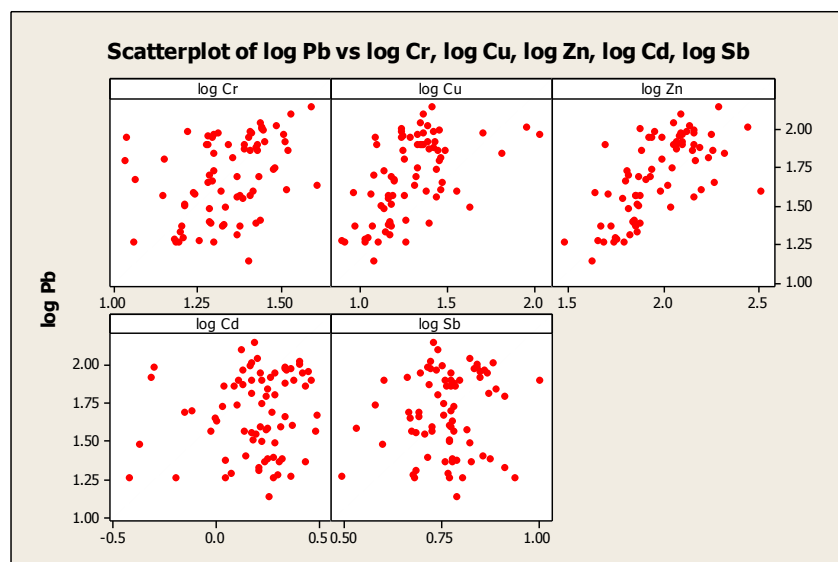


Figure 5.69: Correlation of Pb with Cr, Cu, Zn, Cd, Sb

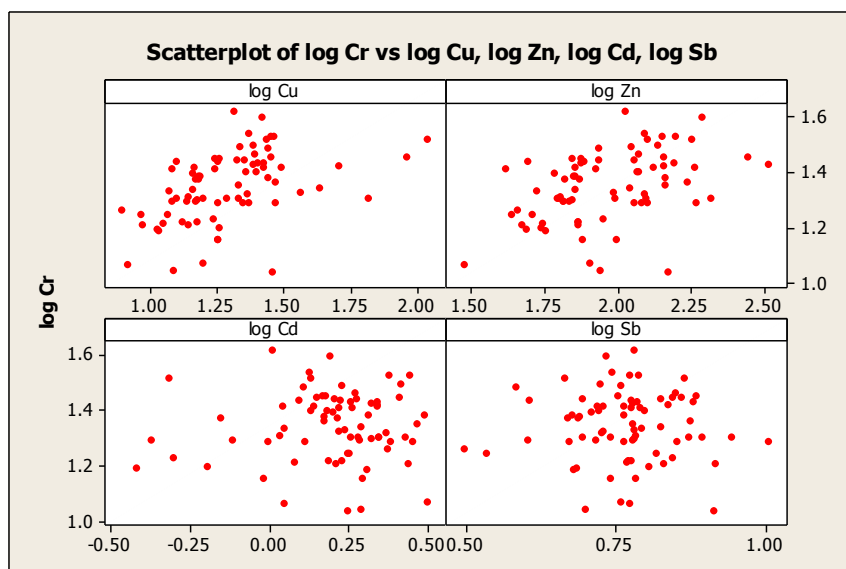


Figure 5.70: Correlation of Cr with Cu, Zn, Cd, Sb

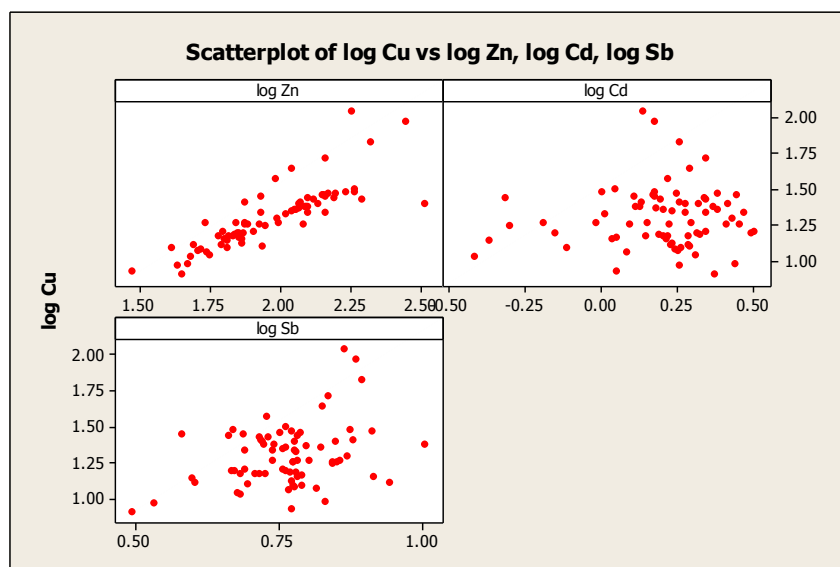


Figure 5.71: Correlation of Cu with Zn, Cd, Sb

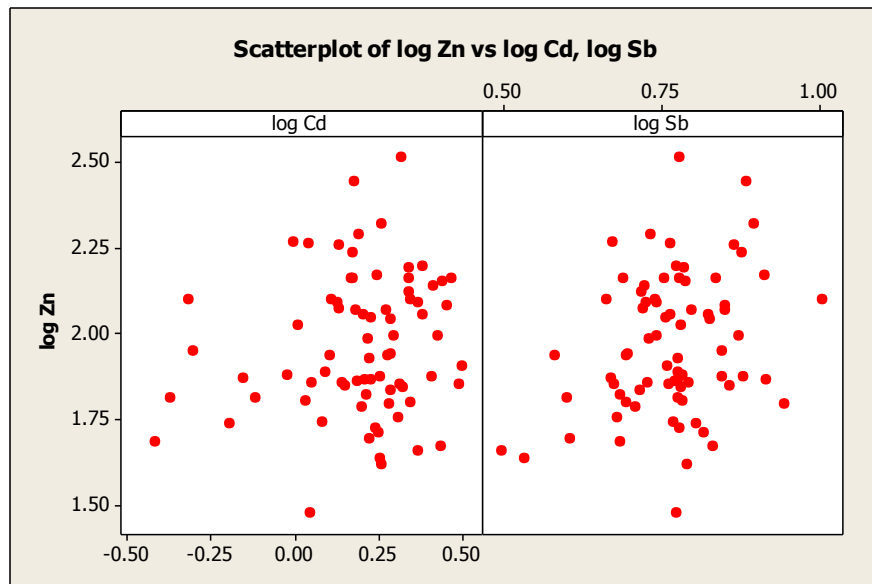


Figure1: Correlation of Zn with Cd, Sb

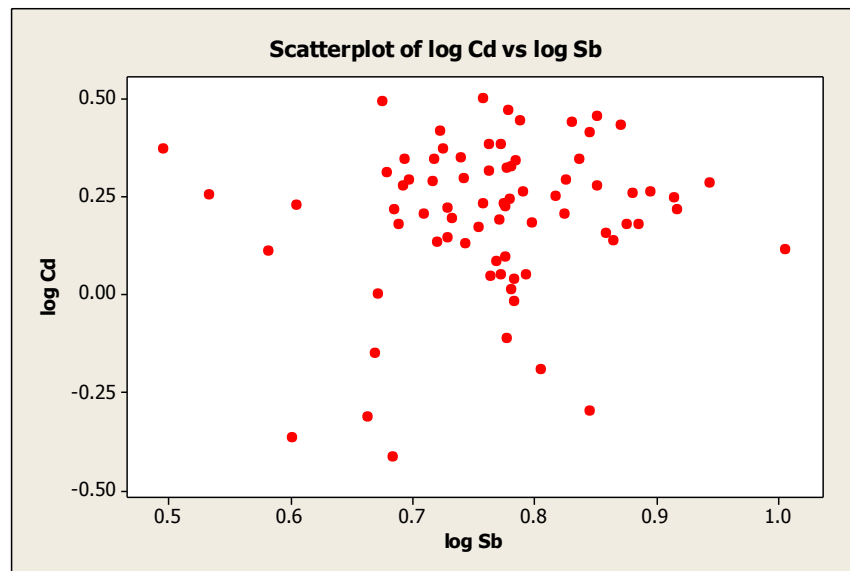


Figure 5.73: Correlation of Cd with Sb

From Figures 5.69 - 5.73, it can be summarized that the variable lead shows a positive correlation with the two variables copper and zinc. The metal chromium does not show a significant correlation with the other variables. However, it does show a minor positive correlation with the variable zinc and copper. The metal copper exhibits a slight positive correlation with zinc. Further, in Figure 5.69, we observed that lead also can influence or can be influenced by the amount of the element copper. Zinc exhibits no considerably high correlation with other metals. The variable antimony exhibits no significant correlation with other variables. To justify the observed results from the above scatter plots, a correlation matrix is used.

Table 5.11: Correlation of the metals

Correlations: Pb, Cr, Cu, Zn, Cd, Sb					
	Pb	Cr	Cu	Zn	Cd
Cr	0.429 0.000				
Cu	0.395 0.000	0.346 0.002			
Zn	0.516 0.000	0.391 0.001	0.667 0.000		
Cd	0.132 0.259	-0.015 0.902	-0.021 0.861	0.095 0.419	
Sb	0.131 0.262	-0.061 0.606	0.315 0.006	0.246 0.034	0.068 0.559
Cell Contents: Pearson correlation P-Value					

According to Table 5.11, the variable pair's cadmium and lead, cadmium and chromium, cadmium and copper, cadmium and zinc, antimony and lead, antimony and chromium, and antimony and cadmium have no significant correlations with a 5% significance level.

A linear correlation coefficient analysis (r) between soil metals was performed on the data. The result of the correlation analysis is shown in Table 5.12.

Table 5.12: Computed Pearson correlation coefficient of heavy metals level

Correlation between metals	r value	P value
Correlation between Pb and Cr	0.429	0.000
Correlation between Pb and Cu	0.395	0.000
Correlation between Pb and Zn	0.516	0.000
Correlation between Pb and Cd	0.132	0.259
Correlation between Pb and Sb	0.131	0.000
Correlation between Cr and Cu	0.346	0.002
Correlation between Cr and Zn	0.391	0.001
Correlation between Cr and Cd	- 0.015	0.902
Correlation between Cr and Sb	- 0.061	0.000
Correlation between Cu and Zn	0.667	0.000
Correlation between Cu and Cd	0.095	0.000
Correlation between Cu and Sb	0.315	0.000
Correlation between Zn and Cd	0.095	0.000
Correlation between Zn and Sb	0.246	0.034
Correlation between Cd and Sb	0.068	0.559

According to these observations, it is noticeable that the correlation between copper and zinc is the highest ($r = 0.667$). Except for 2 pairs, all other variable pairs show less than 0.5 correlations. However, these significant correlations may not have observed from the scatter plots due to the view of it.

5.4.3 Check the normality of the data

To check the normality of the data, the study employs histograms. Figures 5.74 and 5.75 provide the histograms for the metals.

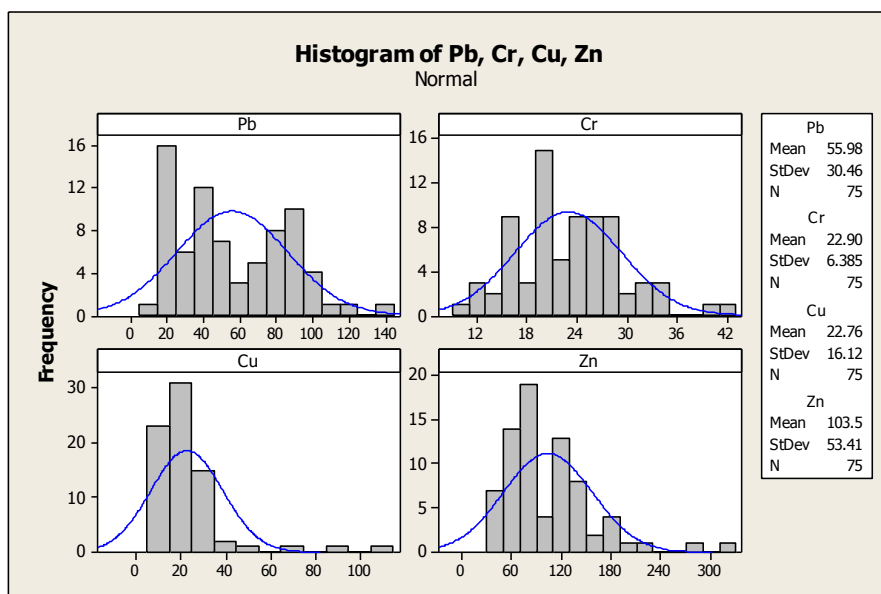


Figure 5.74: Histograms for the metals Pb, Cr, Cu, and Zn

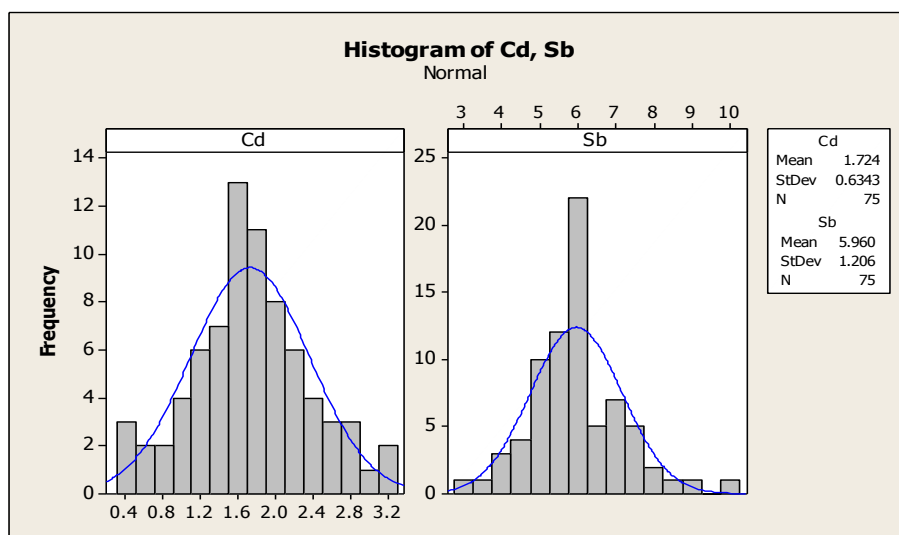


Figure 5.75: Histograms for the metals Cd, Sb

From Figure 5.74 and 5.75, it can be observed that the variables lead, chromium, cadmium and antimony fit to approximately normal data.

5.4.4 Checking for the outlying observations

To check for outlying observations, dot plots used.

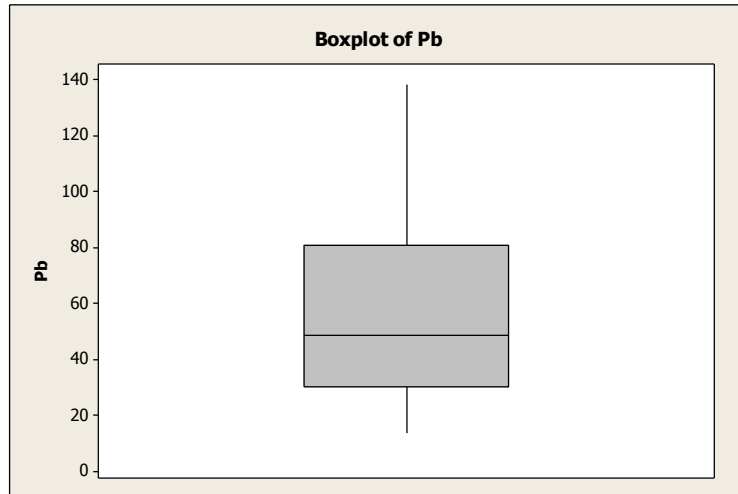


Figure 5.76: Box plot for Pb

From the above plot, it is noticeable that no significant outliers are present. However, the data seems to be positively skewed.

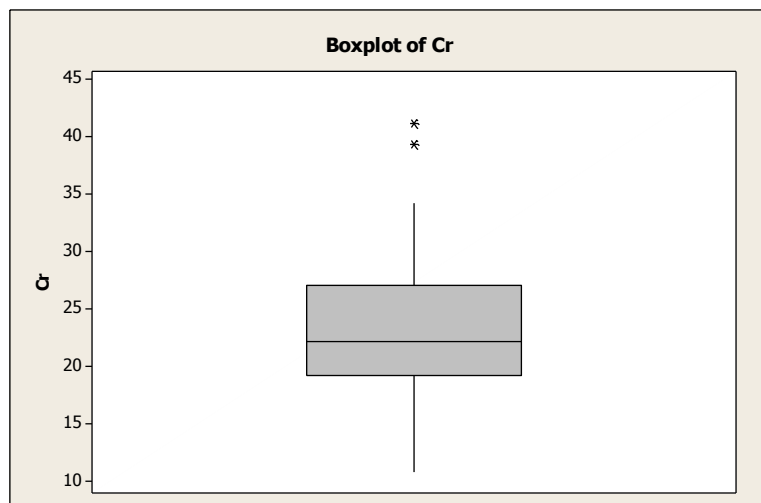


Figure 2: Box plot for Cr

From the above plot, it is noticeable that there are some outliers in the upper end. Furthermore, the data seems to be positively skewed.

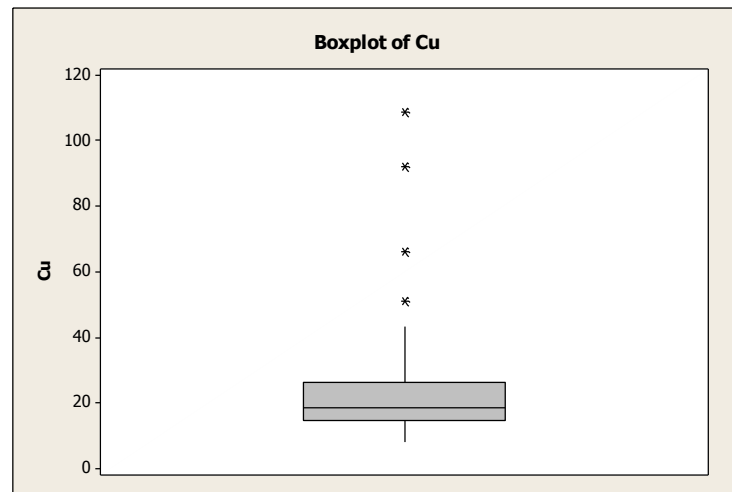


Figure 5.78: Box -plot for Cu

From the above plot, it is noticeable that there are some outliers present in the upper end. Furthermore, the data seems to be positively skewed.

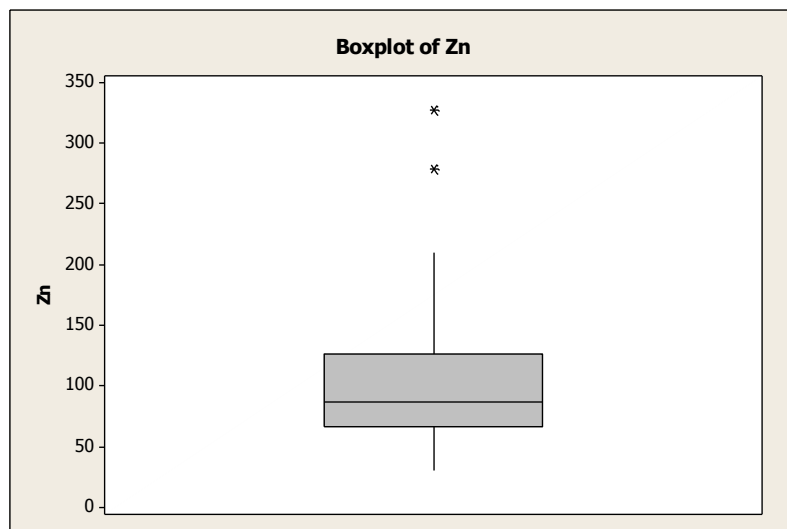


Figure 5.79: Box plot for Zn

From the above plot, it is noticeable that there are some outliers present in the upper end. Furthermore, the data seems to be positively skewed.

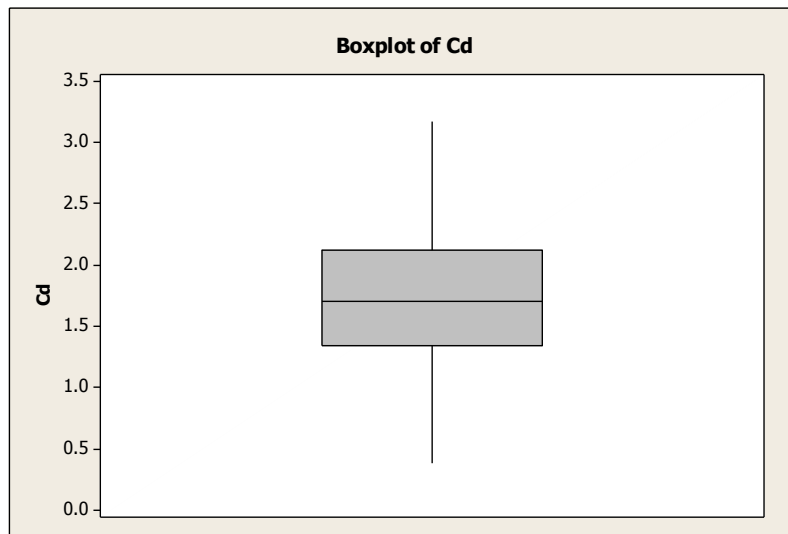


Figure 5.80: Dot plot for Cd

The above plot shows that there are no significant outliers. Furthermore, the data seems to be slightly symmetric.

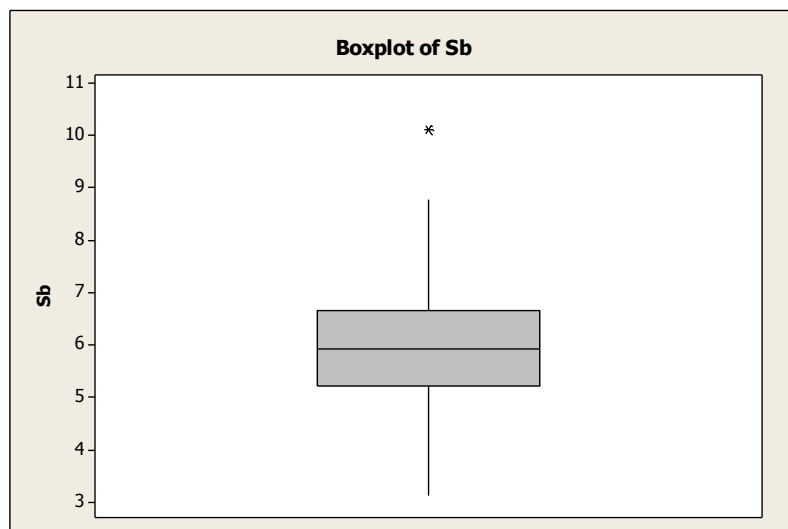


Figure 5.81: Box plot for Sb

From the above plot, shows that antimony data have some outliers in the upper end. When the outliers are ignored, slightly symmetric distribution is observed.

5.5 West El Paso

On the west side of the El Paso, univariate and bivariate analyses were conducted on 78 samples.

5.5.1 Univariate analysis

The descriptive statistics obtained are shown in Table 5.13. The following observations can be made;

Table 5.13: Descriptive statistics on the metals of west El Paso

Variable	N	Minimum	Maximum	Mean	St Dev	Q1	Q3	Median
Pb	78	13.5	420.9	52.9	64.4	21.5	61.2	29.4
Cr	78	4.3	44.1	24.2	8.5	17.7	29.9	24.3
Cu	78	8.3	224.3	33.4	41.9	13.7	28.1	18.9
Zn	78	19.2	359.5	86.1	65.5	44.4	103.8	69.8
Cd	78	0.1	11.9	2.4	1.8	1.4	2.9	2.1
Sb	78	3.8	13.9	6.4	1.9	5.4	6.7	6.2

5.5.1.1 Lead in soil

The concentration levels recorded of lead ranged from 13.5 ppm to 420.9 ppm, with the mean value of 52.9 ppm. The distribution of lead in samples is presented in Figure 5.82.

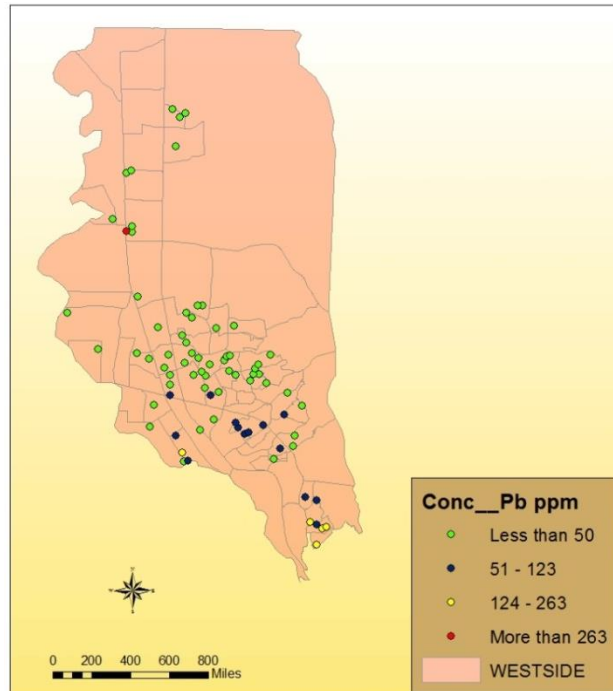


Figure 5.82: Lead levels in composite samples from blocks in west El Paso

The lowest values (less than 50 ppm) of Lead are scattered all over the map. The majority of the blocks in west side of El Paso have this level of lead concentration in soil. The concentrations between 51 ppm and 123 ppm (blue dots) are mostly recorded in the southern area of west El Paso.

Only a few yellow dots, representing the concentrations between 124 ppm and 263 ppm are found in this area. However, these blocks are scattered only in the southern area. Only one block having the highest values (more than 263 ppm) of lead is recorded. This block is situated in the north part of west El Paso.

Figure 5.83 illustrates the concentration of lead levels in soil samples with correlation of children age 0-4 in west El Paso area.

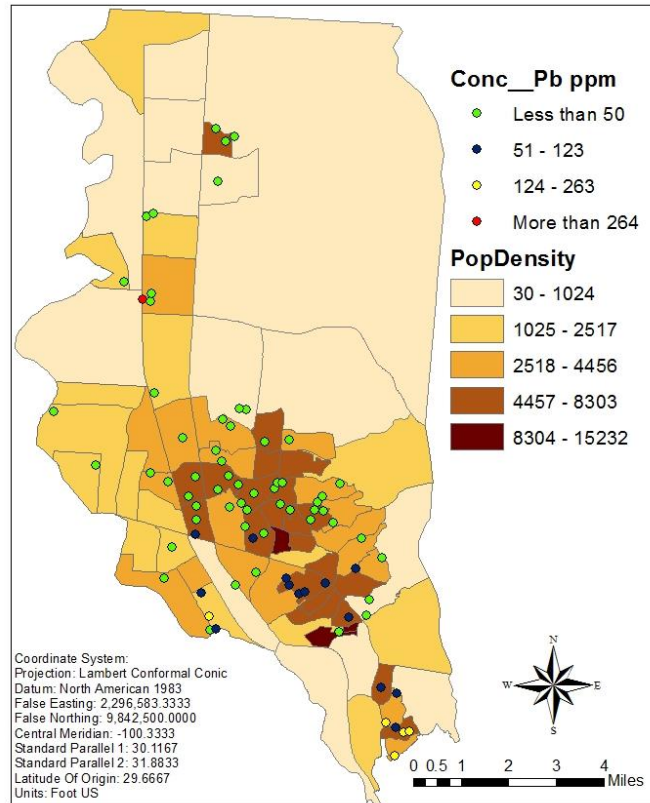


Figure 5.83: Potential population density of children and lead soil in west El Paso

5.5.1.2 Chromium in soil

The concentration levels of chromium ranged from 4.3 ppm to 44.1 ppm, with the mean value of 24.2 ppm. The distribution of chromium in samples is presented in Figure 5.84.

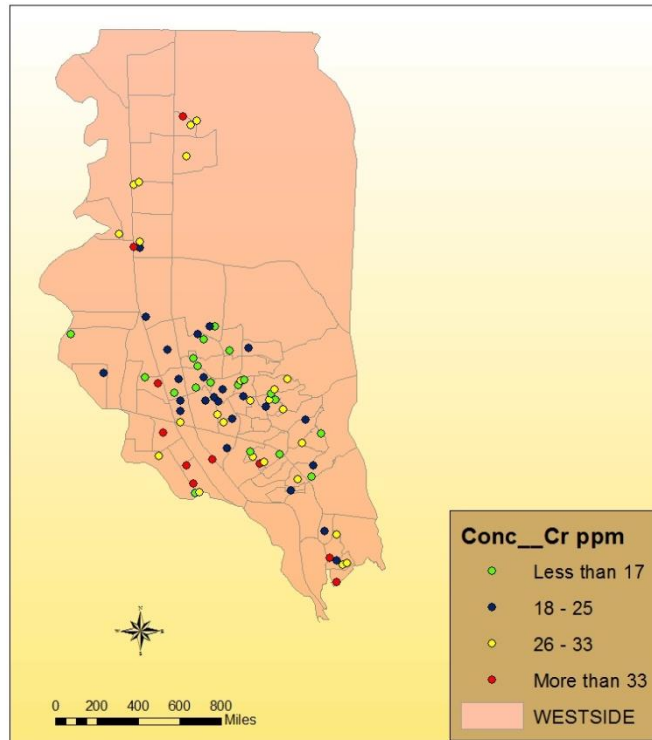


Figure 5.84: Chromium levels in composite samples from blocks in west El Paso

The lowest values (less than 17ppm) of chromium are encountered in the central area of the west El Paso. Therefore, these sections of the city and surrounding areas have low soil chromium levels. The concentrations between 18 ppm and 25 ppm are mostly encountered in the southern central area of west El Paso.

Yellow dots, representing concentrations between 26 ppm and 33 ppm are scattered in all the sides. The highest values (more than 33 ppm) of chromium are recorded mostly in the southern central area. However, there are some blocks in the north part of west El Paso having chromium concentrations more than 33 ppm.

5.5.1.3 Copper in soil

The concentration levels for copper ranged from 8.3 to 244.3 ppm, with the mean value of 33.4 ppm. The distribution of copper in blocks samples is presented in Figure 5.85.

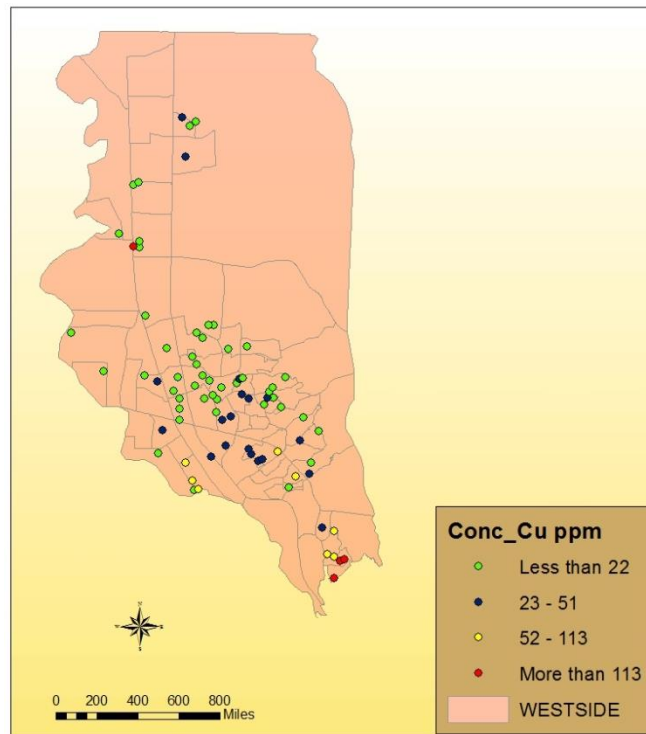


Figure 5.85: Copper levels in composite samples from blocks in west El Paso

The lowest values (less than 22 ppm; green dots) of copper are encountered all over the map. However, the density of the green dots is higher in the northern central part of west El Paso. Blocks with 23 ppm to 51ppm copper shoes in blue in Figure 5.85. So the concentrations between 23 ppm and 51ppm for copper are recorded from the southern central area of west El Paso. However, there are some blocks having this level of concentration in the north part of west El Paso. Only a few blocks have copper levels between 52 ppm to 113 ppm (yellow dots). However, these blocks are mainly situated in southern area of west El Paso. The highest values,

those in excess of 150 ppm and depicted in red, are concentrated in the southern part of west El Paso.

In general, the southern area of west El Paso shows more copper concentration levels in soil than the northern area of west El Paso.

5.5.1.4 Zinc in soil

The concentration levels of zinc ranged from 19.2 ppm to 359.6 ppm, with the mean value of 86.1 ppm. The distribution of zinc in samples is presented in Figure 5.86.

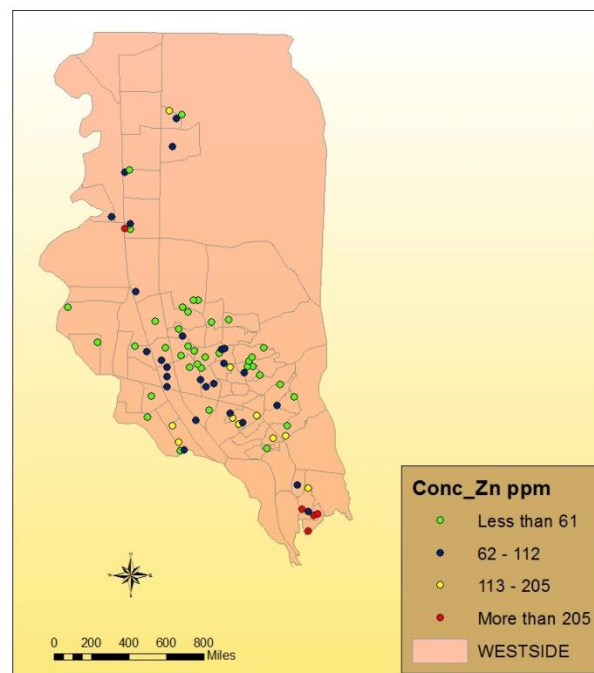


Figure 5.86: Zinc levels in composite samples from blocks in west El Paso

The lowest values (less than 61ppm) of zinc are encountered mostly in the Sothern central area of west side. The concentrations between 62 ppm and 112 ppm (blue dots) are recorded all over west El Paso. Yellow dots, representing the concentrations between 113 ppm and 205 ppm, are scattered mostly in the southern area of west El Paso. However, there is one

yellow block in the north part. The highest values (more than 205 ppm) of zinc are mainly recorded in the southern part of west El Paso.

In general, the southern section of west El Paso seems to have higher zinc concentrations than the northern section.

5.5.1.5 Cadmium in soil

The concentration levels of cadmium ranged from 0.5 ppm to 11.9 ppm, with the mean value of 2.4 ppm. The distribution of cadmium in samples is presented in Figure 5.87.

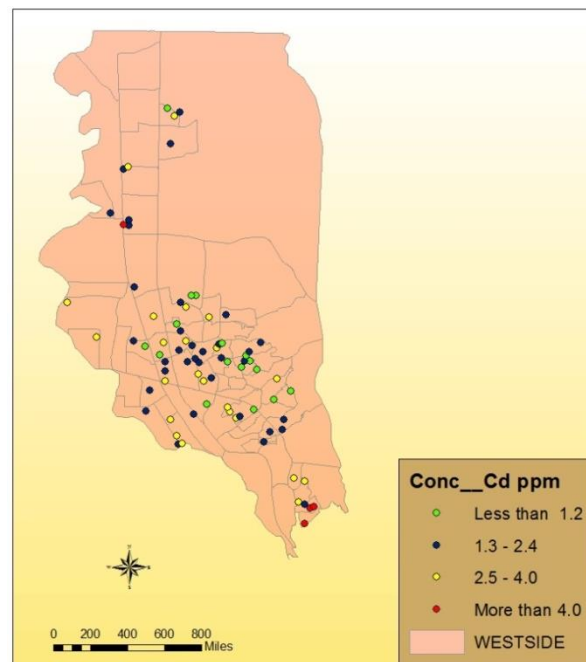


Figure 5.87: Cadmium levels in composite samples from blocks in west El Paso

The lowest values (less than 1.2 ppm; green dots) of cadmium are mostly encountered in the central area of west El Paso. However, there is a green block in the north area of west El Paso. Blocks with 1.3 ppm to 2.4 ppm cadmium, seen in blue in Figure 5.86. Therefore, the concentrations between 1.3 ppm to 2.4 ppm for cadmium are recorded from all over west El

Paso. Cadmium levels between 2.5 ppm to 4 ppm (yellow dots) are scattered all over the map of west El Paso. There are only a few red blocks depicting concentrations that exceed 4 ppm. These blocks are situated in the south part of west El Paso. However, there is one red block in the north area of west El Paso.

5.5.1.6 Antimony in soil

Finally, the concentration levels of antimony ranged from 3.8 ppm to 13.9 with the mean value of 6.4 ppm. The distribution of antimony in samples is presented in Figure 5.88.

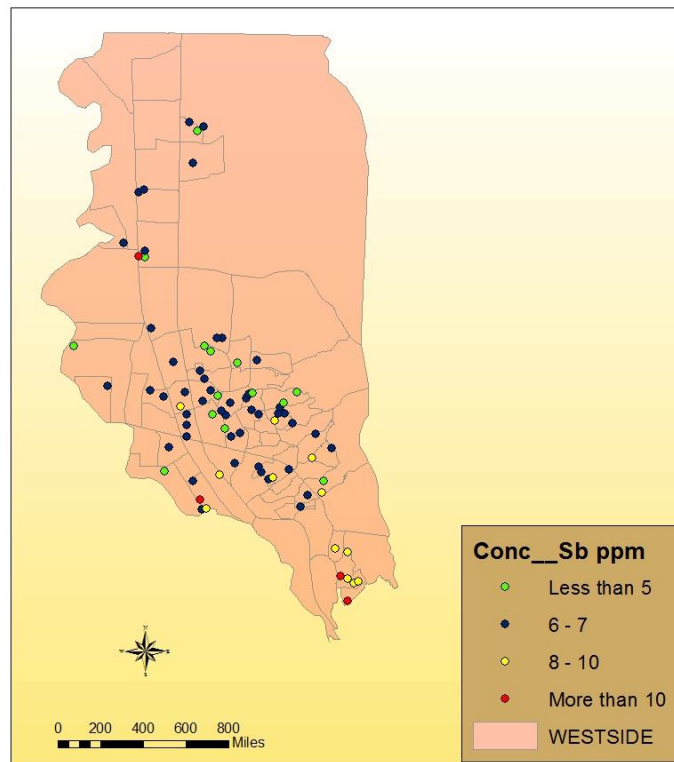


Figure 5.88: Antimony levels in composite samples from blocks in west El Paso

The lowest values (less than 5 ppm; green dots) of antimony can be found in the central and the north area of west El Paso. Blocks with 6 ppm to 7 ppm antimony are shown in blue dots

in Figure 5.88. So the concentrations between 6 ppm to 7 ppm for antimony are scattered all over the map except the south most area. Most of the blocks in west El Paso show antimony concentrations between 6 ppm and 7 ppm.

Yellow dots represent blocks having antimony levels between 8 ppm and 10 ppm. The density of the yellow dots in west El Paso is higher in the southern area. There are only a few blocks having the highest values, that is, in excess of 10 ppm, which are depicted in red. The majority of these blocks are in the southern part of west El Paso. However, there is one block in the north area.

In the west El Paso, the highest mean concentration value is recorded for the metal zinc at 359.5 ppm. However, the standard deviation relevant to zinc is also high. The minimum concentration is recorded for cadmium at 0.5 ppm, which is almost 50 times than zinc. By considering the above statistics, we can conclude the concentration of metal in the soil samples taken from west El Paso are in the decreasing order of Zinc > lead > chromium > copper > antimony > cadmium.

5.5.2 Bivariate analysis

The metal concentration patterns are illustrated by scatter plots, as shown in Figure 5.89 - 5.93.

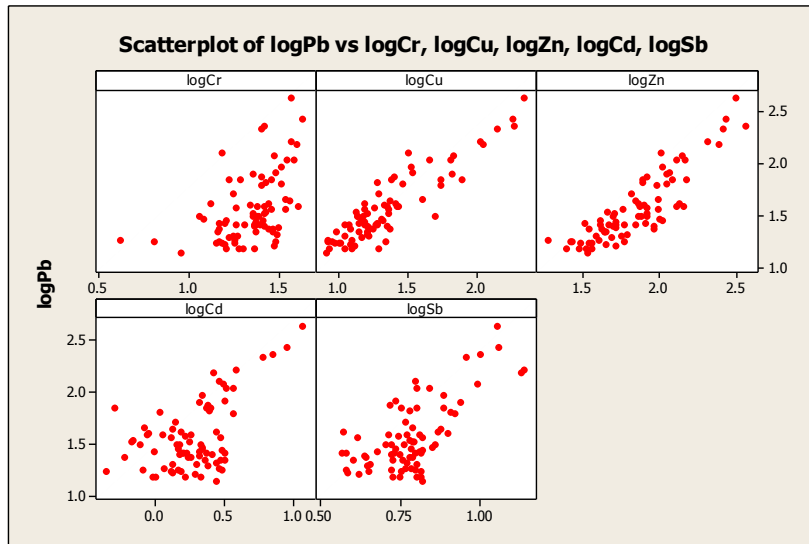


Figure 5.89: Correlation of Pb with Cr, Cu, Zn, Cd, Sb

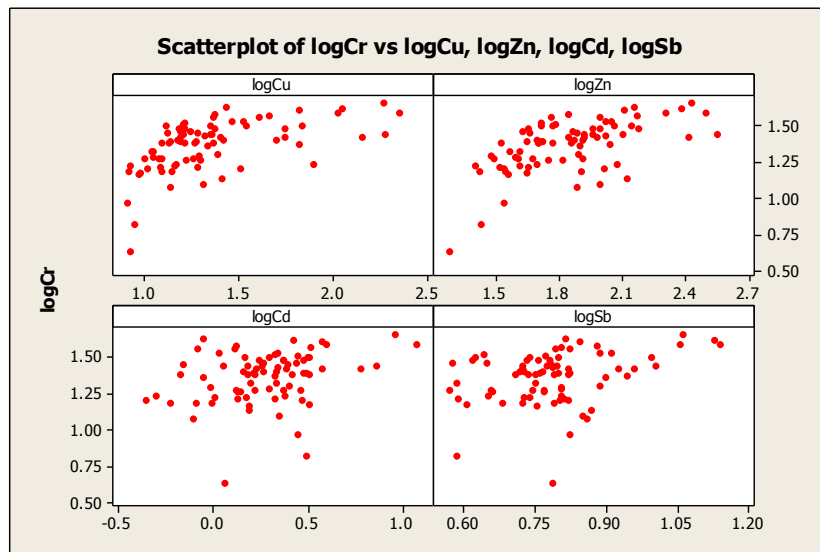


Figure 5.90: Correlation of Cr with Cu, Zn, Cd, Sb

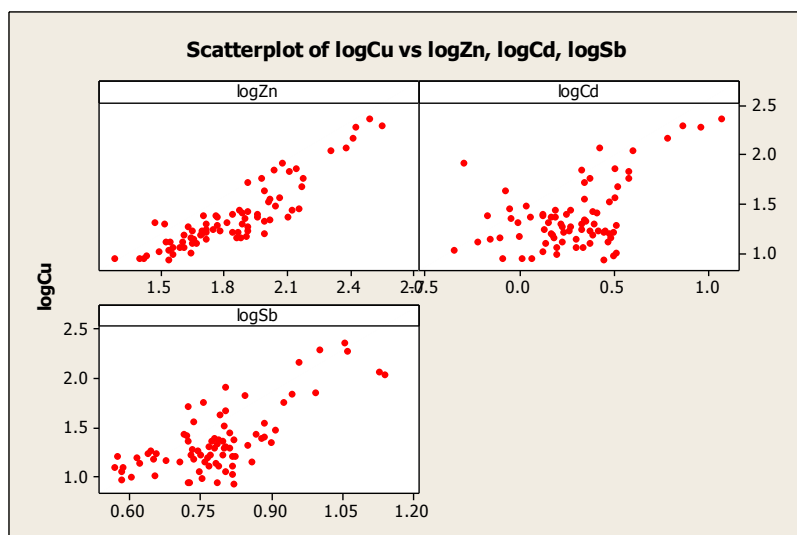


Figure 5.91: Correlation of Cu with Zn, Cd, Sb

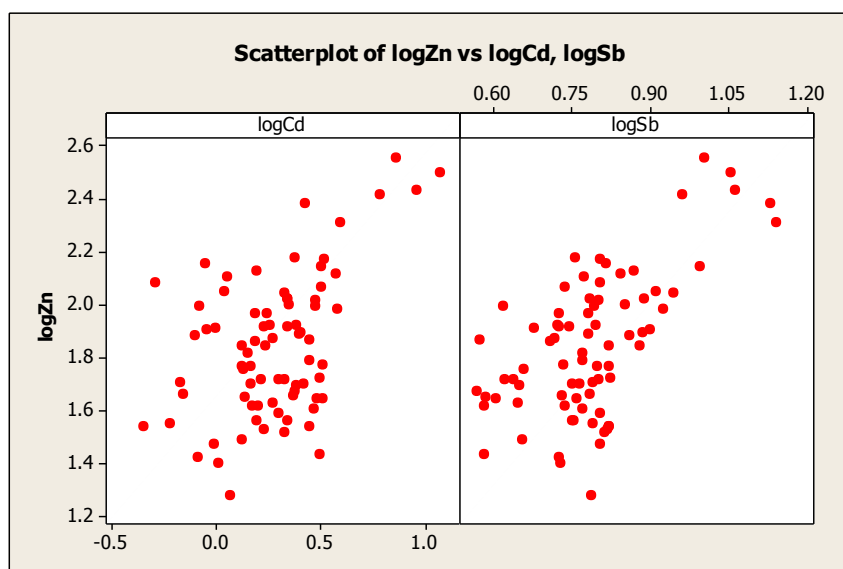


Figure 5.92: Correlation of Zn with Cd and Sb

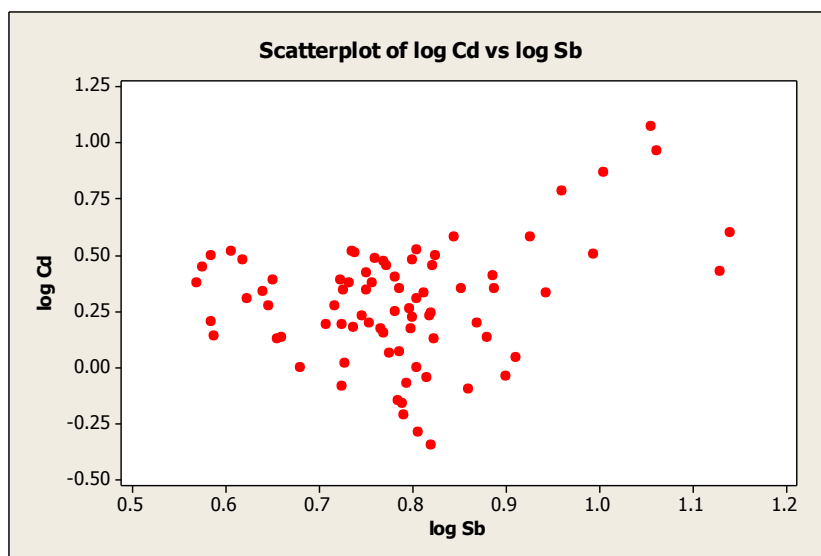


Figure 5.93: Correlation of Cd with Sb

By examining Figures 5.89 - 5.93, it can be summarized that the metal lead shows a positive correlation with the two variables copper and zinc. The variable chromium does not show a significant correlation with the other variables. However, it shows a minor positive correlation with the variable zinc and copper. The variable copper exhibits a slight positive correlation with zinc. The metal zinc exhibits no considerably high correlation with other variables. However, it shows a minor positive correlation with the variable antimony. The variable antimony exhibits no significant correlation with other variables.

5.5.3 Check the normality of the data

To check the normality of the data, the study employs histograms Figure 5.94 and 5.95 provide the histograms for the metals.

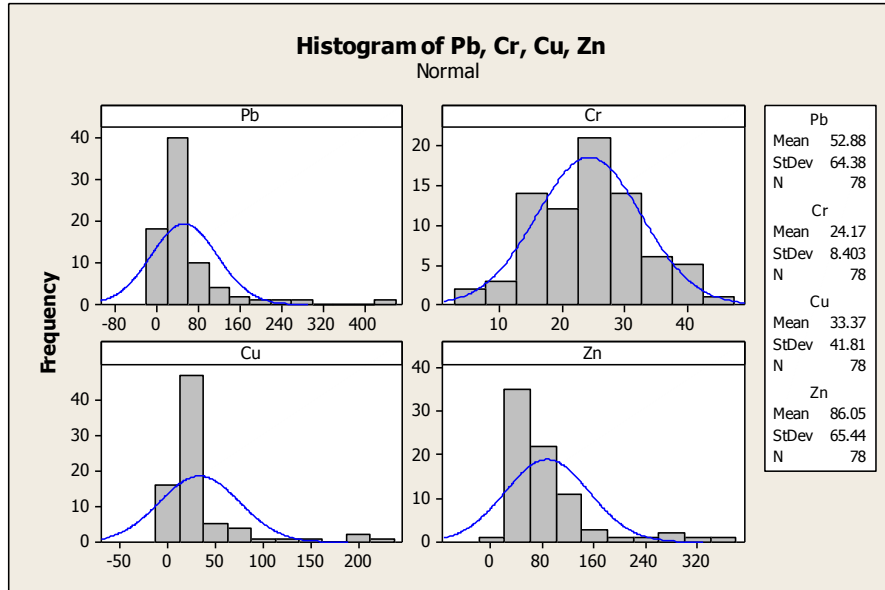


Figure 5.94: Histograms for the metals, Pb, Cr, Cu, Zn, Cd, Sb

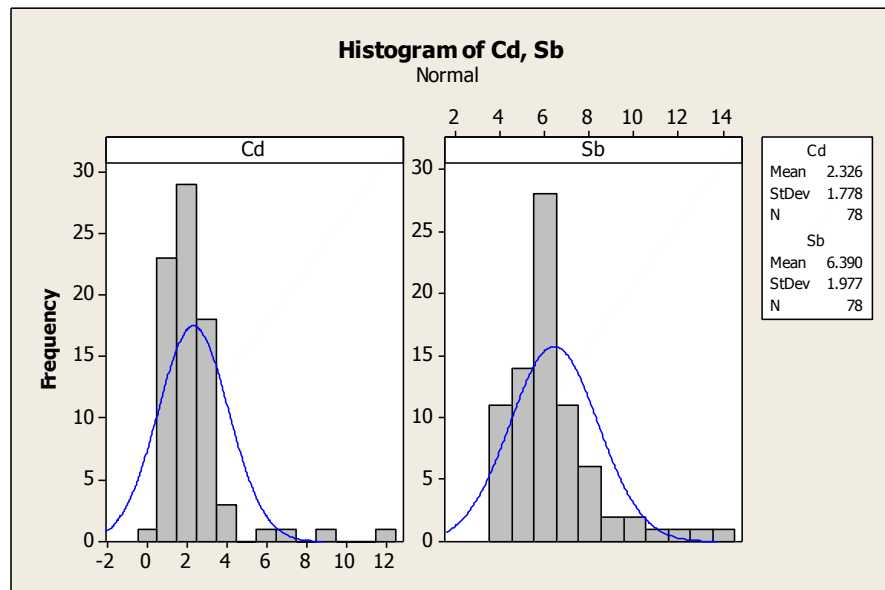


Figure 5.95: Histograms for the metals Cd, Sb

Figure 5.94 and 5.95, exhibit the histograms for the variables. From the output, it can be observed that the variable chromium fits to approximately normal data. Further, the variables zinc, cadmium and antimony also show slightly normal data.

5.4.4 Checking for the outlying observations

To check for the outlying observations, dot plots have been used;

Table 3: Correlations of the metals

Correlations: Pb, Cr, Cu, Zn, Cd, Sb					
	Pb	Cr	Cu	Zn	Cd
Cr	0.473 0.000				
Cu	0.946 0.000	0.477 0.000			
Zn	0.889 0.000	0.537 0.000	0.928 0.000		
Cd	0.864 0.000	0.367 0.001	0.829 0.000	0.733 0.000	
Sb	0.722 0.000	0.443 0.000	0.753 0.000	0.737 0.000	0.507 0.000
Cell Contents: Pearson correlation P-Value					

According to Table 5.14, all of the variable pairs have significant correlations with a 5% significance level.

A linear correlation coefficient analysis (r) between soil metals was performed on the data. The results of correlation analysis are shown in Table 5.15.

Table 5.15: Computed Pearson correlation coefficient of heavy metals level

Correlation between metals	r value	P value
Correlation between Pb and Cr	0.473	0.000
Correlation between Pb and Cu	0.946	0.000
Correlation between Pb and Zn	0.889	0.000
Correlation between Pb and Cd	0.864	0.000
Correlation between Pb and Sb	0.722	0.000
Correlation between Cr and Cu	0.477	0.000
Correlation between Cr and Zn	0.537	0.000
Correlation between Cr and Cd	0.367	0.000
Correlation between Cr and Sb	0.443	0.000
Correlation between Cu and Zn	0.928	0.000
Correlation between Cu and Cd	0.829	0.000
Correlation between Cu and Sb	0.753	0.001
Correlation between Zn and Cd	0.733	0.000
Correlation between Zn and Sb	0.473	0.000
Correlation between Cd and Sb	0.946	0.000

According to these observations, the significant correlations may not have observed from the scatter plots due to the view of it. It is noticeable that the correlation between lead and copper is the highest ($r = 0.946$). Except for 4 pairs, all other variable pairs show greater than 0.5 correlations. However, these significant correlations may not have observed from the scatter plots due to the view of it.

5.5.5 Checking for the outlying observations

For this purpose box plots have been used.

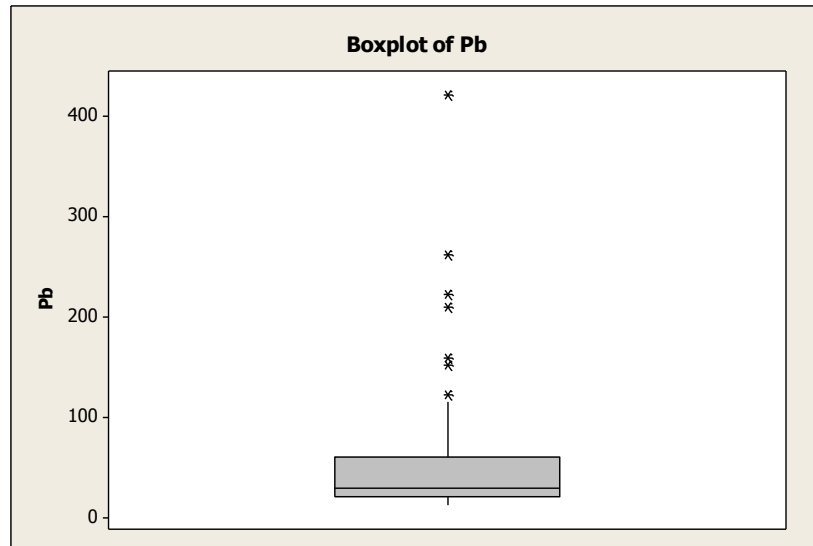


Figure 5.96: Box plot for Pb

According to the output, it is noticeable that there are a considerable number of outliers in the upper end. The data seems to be positively skewed.

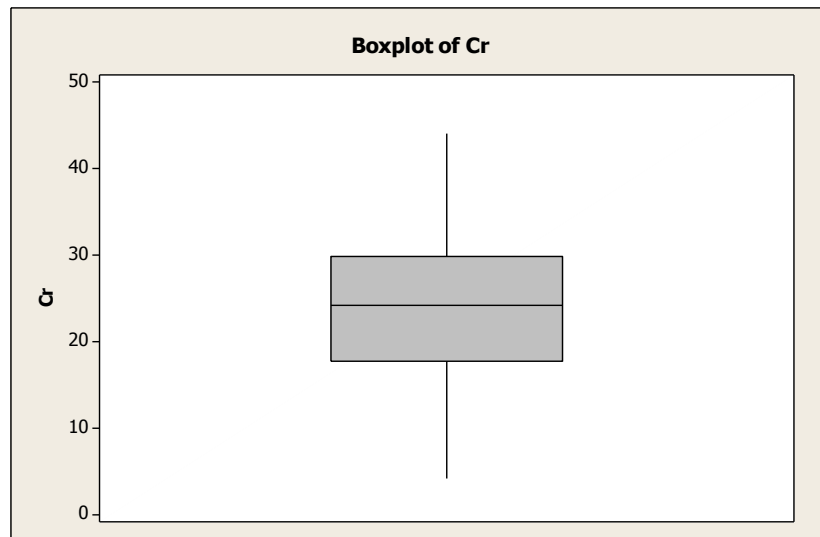


Figure 4: Box plot for Cr

According to the output, it can be observed that the data is approximately symmetrical. Further, there are no significant outliers.

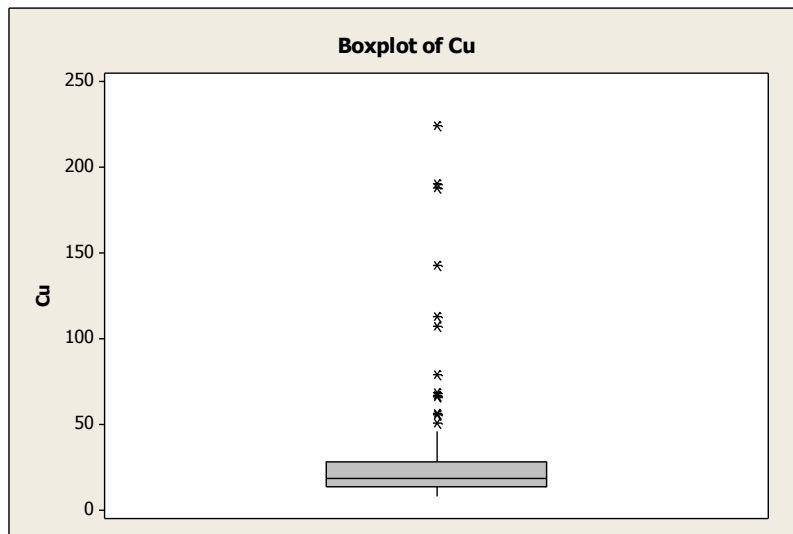


Figure 5: Box plot for Cu

According to the output, it is noticeable that there are a considerable number of outliers in the upper end. The data also seems to be positively skewed.

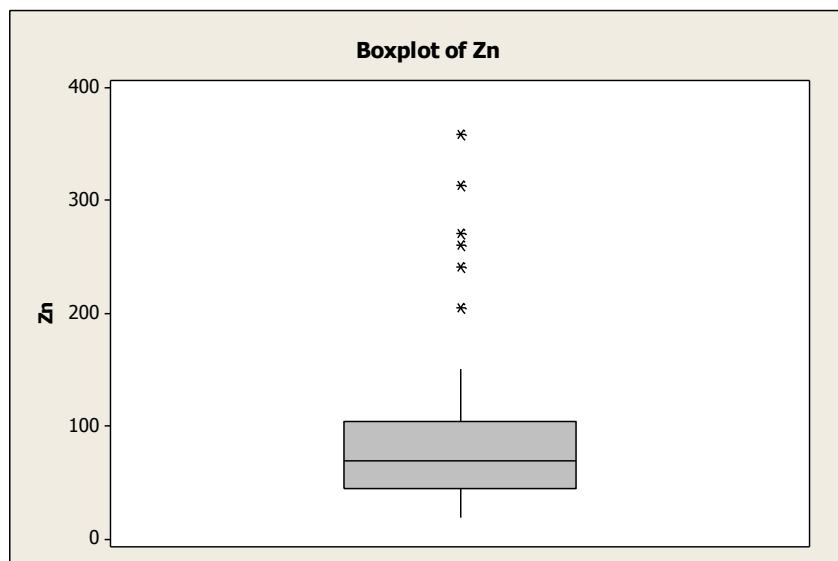


Figure 6: Box plot for Zn

According to the output, it is noticeable that there are a considerable number of outliers in the upper end. The data seems to be positively skewed.

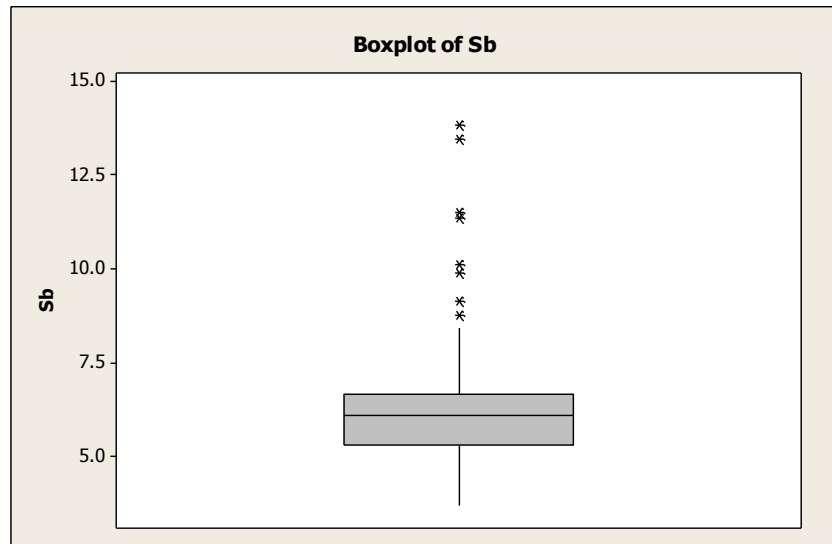


Figure 7: Box plot for Sb

According to the output, it is noticeable that there are a considerable number of outliers in the upper end. The data seems to be negatively skewed.

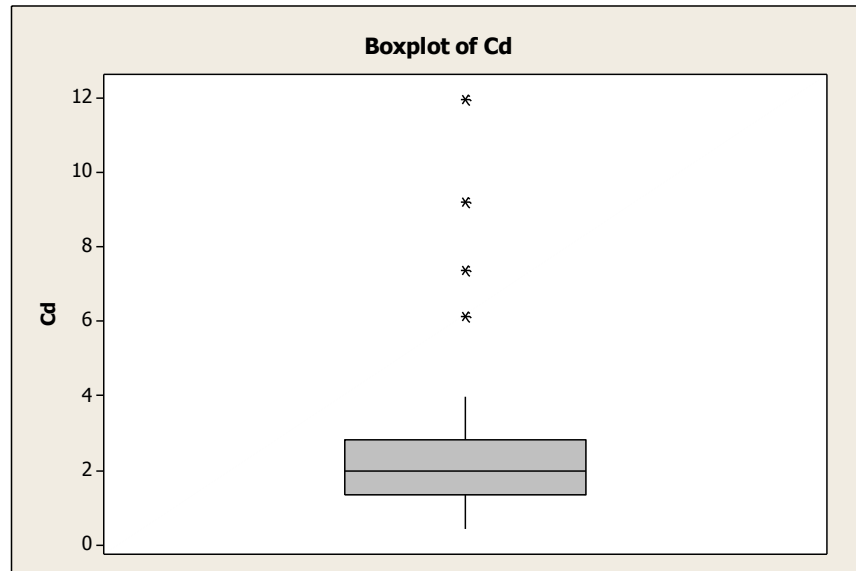


Figure 8: Box plot for Cd

According to the output, it is noticeable that there are a considerable number of outliers in the upper end. When the outliers are ignored, the data seems to be approximately symmetric is observed.

5.6 Comparing the elements in the four sides of El Paso

The Table 5.16 shows the mean, median and standard deviation of the elements for the four sides of El Paso.

Table 5.16: Comparing the elements in the four sides of El Paso

Element	Statistics	Central	East	North East	West
Pb	Mean	138.4	44.6	55.9	52.9
	StDev	61.4	36.4	30.5	64.4
	Median	126.1	30.9	48.5	29.4
Cr	Mean	32.1	22.3	22.9	24.2
	StDev	8.6	7.9	6.4	8.5
	Median	30.1	22.3	22.3	24.3
Cu	Mean	68.9	27.9	22.8	33.4
	StDev	62.2	23.7	16.2	41.9
	Median	52.9	19.8	18.4	18.9
Zn	Mean	181.6	80.2	103.6	86.1
	StDev	77.2	53.6	53.5	65.5
	Median	164.5	69.7	86.4	69.8
Cd	Mean	3.3	1.9	1.8	2.4
	StDev	1.6	0.9	0.7	1.8
	Median	2.9	1.8	1.8	2.1
Sb	Mean	7.6	6.1	5.9	6.4
	StDev	1.9	1.7	1.3	1.9
	Median	6.9	5.9	5.9	6.2

From above, it is observed that the mean values of the elements lead, chromium, copper, zinc, cadmium, antimony for central El Paso is higher than for the other sides.

Chapter 6: Summary of major finding and conclusion

6.1 Summary of major finding

The main objective of this study was to determine the concentration and distribution of heavy metals in the city of El Paso and El Paso County. The soil sample for the study was collected during a bi-national community lead project (2001-2005). 500 superficial soils samples were collected from public areas around 50 strata. Within each stratum, 10 blocks were randomly selected. The general procedures of EPA method 6200 for field portable XRF were followed for preparation of the samples, with slight modifications. These included grinding, mixing, pressing, and homogenization. The samples in present study 492 soil samples were analyzed by using x-ray fluorescence (Epsilon5). Statistical analyses were conducted to explore the relationships between lead and associated heavy metals. The detailed maps created by using the geographic information system techniques (GIS) for geochemical mapping of lead and associated heavy metals.

The results of the study in the El Paso, indicated that the soil samples concentration levels recorded for lead ranged from 10.8 to 420.9 ppm, with the mean value of 60.8 ppm; for Cr ranged from 4.3 to 51.6 ppm, with the mean value of 24.2 ppm; for Cu ranged from 6.5 to 385.8 ppm, with the mean value of 33.3 ppm. The concentration levels for Zn ranged from 16.5 to 476.8 ppm, with the mean value of 98.9 ppm, for Cd ranged from 0.4 to 11.9 ppm, with the mean value of 2.1 ppm; and Sb ranged from 2.9 to 19.6 ppm with the mean value of 6.3 ppm.

The results indicated that the elemental concentrations in soil samples in the El Paso are in the decreasing order of $Zn > Pb > Cu > Cr > Sb > Cd$.

In regards to the correlation between the metals, the results showed that Pb has a positive correlation with Cu and Zn. Metal Cr does not showed a significant correlation with the other metals, it showed a minor positive correlation with the metals Zn and Cu. Metal Cu exhibited a slight positive correlation with Zn. Metal Zn exhibited no considerably high correlation with other metals, it showed a minor positive correlation with the metal Sb. Metal Sb exhibited no significant correlation with metal Cd.

In the central El Paso, the concentration levels recorded for lead ranged from 50.8 to 355.3 ppm, with the mean value of 138.4 ppm; Cr levels ranged from 17.9 to 51.6 ppm, with the mean value of 32.1 ppm; for Cu ranged from 19.6 to 385.8 ppm, with the mean value of 68.9 ppm. The concentration levels for Zn ranged from 67.8 to 418.4 ppm, with the mean value of 181.7 ppm; Cd levels ranged from 0.9 to 9.2 ppm, with the mean value of 3.3 ppm and levels for Sb ranged from 4.4 to 14.6 ppm with the mean value of 7.6 ppm.

The results shows that the concentration of the soil samples taken from the Central El Paso are in the decreasing order of $Zn > Pb > Cu > Cr > Sb > Cd$.

In regards to the correlation between the metals in the central El Paso, Pb showed a positive correlation with the metals Cu, Zn and Cd. The metal Cr exhibited no significant correlation with other metals. Cr showed a positive relationship with Pb. The metal Cu has a minor positive relationship with Zn and Cd. The metal Cu has a positive relationship with the Pb concentration. The metal Zn does not showed a significant correlation with Cd and Sb. The metal Zn showed a positive relationship with Pb and Cu. The metal Cd exhibited no significant correlation with Sb. The highest correlation between Pb and Cu is recorded.

In the east El Paso, the concentration levels recorded for lead ranged from 10.8 to 197.9 ppm, with the mean value of 44.6 ppm; for Cr ranged from 6.3 to 44.1 ppm, with the mean value

of 22.3 ppm. The levels concentration for Cu ranged from 6.5 to 191.2 ppm, with the mean value of 27.9 ppm; Zn levels ranged from 16.5 to 476.8 ppm, with the mean value of 80.2 ppm, for Cd ranged from 0.5 to 5.54 ppm, with the mean value of 1.9 ppm; and Sb ranged from 2.9 to 19.6 with the mean value of 6.1 ppm.

The results showed that the concentration of the soil samples taken from east El Paso are in the decreasing order of $Zn > Pb > Cu > Cr > Sb > Cd$.

In regards to the correlation between the metals in the east El Paso, the results shows that the metal Pb has a positive correlation with metal Cu and Zn. The metal Cr exhibited no significant correlation with other metals. The metal Cr showed a positive relationship with Pb. The metal Cu has a minor positive relationship with Zn and Cd. The metal Cu has a positive relationship with the Pb concentration. The metal Zn exhibited no considerably high correlation with Cd and Sb; it showed a minor positive correlation with the metal Sb. The metal Sb exhibited no significant correlation with other metals. The highest correlation encountered between Pb and Cu.

In the northeast El Paso, the results shows that, the concentration levels recorded for lead ranged from 13.6 to 138.2 ppm, with the mean value of 55.9 ppm. The concentration levels, for Cr ranged from 10.9 to 41.2 ppm, with the mean value of 22.9 ppm. The concentration levels Cu ranged from 7.9 to 108.9 ppm, with the mean value of 22.8 ppm; Zn levels ranged from 30.1 to 327.6 ppm, with the mean value of 103.6 ppm; Cd levels ranged from 0.4 to 3.2 ppm, with the mean value of 1.8 ppm and Sb ranged from 43.2 to 10.2 ppm with the mean value of 5.9 ppm.

The results showed that the concentration of the metal in the soil samples taken from the northeast El Paso are in the decreasing order of $Zn > Pb > Cr > Cu > Sb > Cd$.

In regards to the correlation between the metals in the northeast El Paso, the metal Pb showed a positive correlation with the Cu and Zn. The metal Cr does not showed a significant correlation with the other metals, it showed a minor positive correlation with the variable Zn and Cu. The metal Cu exhibited a slight positive correlation with Zn. The metal Zn exhibited no considerably high correlation with other metals. The metal Sb exhibited no significant correlation with other metals. The highest correlation recorded between recorded Cu and Zn.

In the west El Paso, the results shows that the concentration levels recorded for lead ranged from 13.2 to 420.9 ppm, with the mean value of 52.9 ppm; Cr levels ranged from 4.3 to 44.1 ppm, with the mean value of 24.2 ppm; for Cu ranged from 8.3 to 244.3 ppm, with the mean value of 33.4 ppm. Zn ranged from 19.2 to 359.6 ppm, with the mean value of 86.1 ppm. Cd ranged from 0.5 to 11.9 ppm, with the mean value of 2.4 ppm. Finally, Sb ranged from 3.8 to 13.9 ppm with the mean value of 6.4 ppm.

The results showed that the concentration of metal in the soil samples taken from the west El Paso are in the decreasing order of $Zn > Pb > Cr > Cu > Sb > Cd$.

In regards to the correlation between the metals in the west El Paso, the results indicated that the metal Pb showed a positive correlation with metals Cu and Zn. The metal Cr does not showed a significant correlation with the other metals, it shows a minor positive correlation with the metal Zn and Cu. The metal Cu exhibited a slight positive correlation with Zn. The metal Zn exhibits no considerably high correlation with other metals; it showed a minor positive correlation with the variable Sb. The metal Sb exhibited no significant correlation with other variables. The results showed that the correlation between Pb and Cu was the highest value obtained.

6.2 Conclusion

From the result of this study, the following conclusion can be made:

- The present study revealed that some of soil studied was highly contaminated with lead, copper, zinc and antimony. Lesser extent in metals chromium and cadmium are detected in soil samples.

More than 150 ppm of lead is detected in soil samples, some areas have elevated copper levels excess of 150 ppm, more than 150 ppm of zinc is detected recorded, and antimony is detected with the highest value in excess of 15 ppm.

- This suggesting that some sites in the study area are polluted in the metals investigated; lead, copper, zinc and antimony and may pose potential hazards to residential population.
- The results indicated that the metals were distributed differently in soil, most of higher levels of the metals mainly recorded in the central and downtown El Paso.
- Lead is concentrated in the downtown and central core district, and in blocks in east and northeast, and to the west in the area of ASARCO smelter. Chromium is recorded in the central area, which covers the downtown and central core district. The highest values of chromium are recorded in the central area, which covers the downtown and central core district. Elevated copper levels recorded in the central El Paso.
- The results of this study confirm the expected levels of heavy metals like previous studies in El Paso.

For the future work, it is suggested the risk assessment hazardous of heavy metals in the El Paso would be potential topic.

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Appendix

Appendix 1: Concentration of soil samples (ppm)

Count	ID Block	Pb	Cr	Cu	Zn	Cd	Sb
1	2	36.332	14.145	17.994	75.712	0.96	6.073
2	16	45.929	11.72	15.859	80.81	3.173	5.739
3	17	62.951	14.247	18.139	98.719	1.98	5.521
4	22	86.161	19.952	19.497	98.247	2.698	7.44
5	52	90.778	20.031	21.504	125.767	2.221	5.504
6	92	17.98	20.085	12.7	62.081	1.924	8.792
7	95	35.365	23.669	27.649	145.719	1.501	4.883
8	109	23.473	21.531	14.542	71.848	1.125	6.208
9	135	31.846	16.426	15.187	72.95	1.543	5.916
10	170	24.533	19.421	14.823	68.552	1.937	5.213
11	173	31.086	16.477	13.212	73.544	1.707	5.959
12	187	48.077	23.608	15.361	74.226	0.706	4.68
13	230	35.897	23.989	15.497	71.428	3.114	4.741
14	236	49.307	19.484	12.186	65.232	0.767	5.99
15	237	70.905	25.836	31.182	183.985	1.106	5.812
16	271	100.849	28.135	92.078	279.365	1.507	7.677
17	274	91.862	26.24	51.058	144.47	2.202	6.876
18	278	68.448	20.132	66.148	210.028	1.818	7.86
19	308	75.364	26.84	26.831	156.081	2.194	6.099

20	315	86.755	25.604	17.559	84.492	1.672	5.973
21	327	44.441	19.292	29.7	185.088	0	4.703
22	331	39.429	33.365	29.386	157.527	2.41	5.928
23	337	87.989	19.317	17.972	121.192	2.855	7.107
24	344	30.061	19.475	13.841	65.199	0.429	3.992
25	403	61.731	10.837	28.821	148.701	1.767	8.211
26	420	37.888	17.55	9.301	43.449	1.8	3.417
27	421	18.032	15.772	18.333	54.811	0.642	6.389
28	423	78.603	27.115	12.679	49.481	1.688	4.029
29	428	23.853	19.759	15.099	69.559	2.119	6.039
30	436	25.134	27.759	18.358	70.118	1.425	7.229
31	477	23.003	24.163	15.34	71.119	2.068	5.791
32	501	78.48	19.207	23.451	126.389	1.3	10.131
33	505	93.854	16.845	17.363	89.399	0.502	7.009
34	507	77.143	19.28	22.272	113.785	2.412	5.802
35	508	108.13	27.653	22.552	113.387	1.607	6.678
36	528	37.257	17.6	11.68	51.328	1.782	6.566
37	580	78.467	22.242	21.612	145.558	2.945	6.011
38	582	86.411	11.037	12.354	86.775	1.953	4.986
39	607	103.669	31.031	24.503	137.503	2.6	5.289
40	614	63.379	23.031	29.685	172.389	1.502	7.52
41	645	82.139	28.73	24.692	117.466	1.883	7.103
42	652	42.272	41.133	20.725	105.791	1.025	6.048
43	661	48.428	27.507	21.318	86.019	1.897	4.935

44	672	38.641	26.461	24.433	327.545	2.098	5.995
45	679	71.846	33.631	28.342	141.912	2.78	6.152
46	695	72.535	24.845	25.139	118.191	1.36	5.256
47	699	54.519	30.783	21.756	110.894	1.706	5.729
48	722	80.811	32.792	27.414	126.154	0.484	4.605
49	728	93.163	20.648	23.378	123.228	2.341	5.311
50	762	97.225	28.294	28.617	144.444	1.475	5.679
51	766	94.779	25.897	26.793	132.536	2.204	5.226
52	784	138.188	39.402	26.435	194.8	1.561	5.403
53	801	18.889	15.348	10.834	56.803	2.041	4.776
54	819	53.831	30.43	27.768	86.398	1.286	3.817
55	824	52.066	20.158	13.936	63.949	1.088	6.075
56	833	38.978	21.151	36.548	96.565	1.661	5.367
57	839	99.38	27.927	17.573	75.026	2.592	7.006
58	840	71.644	27.271	17.962	77.173	1.241	5.971
59	846	23.115	21.386	11.909	52.859	1.745	6.023
60	907	34.978	24.707	14.589	60.89	1.598	5.127
61	911	44.648	20.006	15.847	63.093	2.217	4.937
62	916	90.881	32.488	108.98	180.441	1.365	7.331
63	951	124.125	34.239	23.412	123.861	1.344	5.542
64	971	78.48	24.953	23.061	116.679	1.523	6.292
65	1011	23.797	26.809	25.314	75.177	1.806	7.591
66	1097	65.359	32.048	28.73	95.373	1.279	6.278
67	1112	82.004	26.94	19.576	76.78	1.896	6.379

68	1136	116.591	50.35	75.372	413.395	1.552	9.21
69	1147	82.725	33.135	22.339	298.154	1.752	6.505
70	1206	92.696	37.588	29.418	139.268	3	6.855
71	1249	76.751	36.079	27.224	85.58	2.555	5.608
72	1305	70.528	23.152	36.126	85.064	1.652	6.836
73	1329	56.775	22.084	31.949	123.198	2.734	6.098
74	1367	121.534	28.791	28.28	88.868	2.625	6.791
75	1381	78.057	32.04	24.337	96.996	1.069	5.88
76	1398	121.108	41.145	30.557	101.213	2.033	5.314
77	1429	77.447	40.991	33.125	151.993	2.276	6.859
78	1441	118.68	34.238	41.689	163.476	2.242	6.184
79	1444	168.601	31.759	47.341	158.913	1.483	5.398
80	1451	69.493	16.973	79.425	120.52	0.512	6.406
81	1470	91.914	33.146	33.868	105.175	2.227	7.729
82	1473	107.34	36.042	45.871	147.966	3.311	6.399
83	1478	123.249	15.606	32.391	103.314	2.997	6.331
84	1480	80.144	30.898	34.97	116.761	3.23	5.485
85	1500	32.71	23.376	23.389	50.869	0.682	6.171
86	1530	68.757	29.591	55.593	150.584	2.382	5.727
87	1555	30.365	24.936	15.129	50.08	1.469	5.855
88	1574	15.033	20.426	11.033	36.667	2.198	5.634
89	1583	26.123	14.883	14.133	81.099	0	4.793
90	1593	13.438	9.132	8.274	34.552	2.816	6.646
91	1594	24.805	26.888	22.842	92.249	1.544	5.316

92	1608	15.768	30.735	13.269	52.26	2.005	4.201
93	1613	23.852	32.394	16.568	52.128	2.158	4.379
94	1646	34.031	27.546	13.399	45.627	0.705	6.1
95	1664	22.843	15.054	12.404	35.356	0.606	6.185
96	1666	17.706	4.224	8.452	19.151	1.168	6.128
97	1670	17.244	31.065	22.434	58.698	1.487	6.305
98	1675	39.441	22.323	21.757	80.009	0.904	7.963
99	1681	27.37	24.176	15.637	52.742	3.145	6.685
100	1688	63.669	33.299	29.383	112.04	1.099	8.158
101	1695	14.944	16.552	8.532	25.164	1.034	5.353
102	1713	25.595	18.548	12.092	47.38	2.382	3.722
103	1717	40.593	13.34	26.167	134.634	1.568	7.407
104	1745	30.63	24.614	50.812	82.542	2.202	5.341
105	1757	38.375	26.944	22.498	127.812	1.146	5.969
106	1769	25.293	24.018	19.054	52.444	1.659	6.328
107	1772	40.145	28.236	15.699	73.799	2.804	3.773
108	1788	37.955	24.45	26.545	74.912	1.871	5.229
109	1792	72.175	25.743	25.621	83.083	2.454	5.293
110	1858	18.033	18.332	12.471	40.449	2.949	5.894
111	1867	30.662	11.653	13.941	76.901	0.793	7.264
112	1883	37.289	18.514	18.22	82.614	1.696	5.583
113	1889	50.016	17.92	19.895	65.79	1.425	5.894
114	1896	64.427	27.53	19.318	77.6	2.5	6.053
115	1898	19.818	17.971	16.835	56.787	1.357	4.577

116	1900	19.552	18.867	11.206	39.008	2.013	6.392
117	1921	24.759	23.472	16.418	50.301	2.644	5.648
118	1926	16.18	16.044	12.202	44.902	1.372	3.871
119	1935	28.084	16.358	14.743	41.278	1.51	5.468
120	1943	42.659	37.32	23.709	69.712	1.346	7.598
121	1991	44.774	35.395	41.137	98.828	0.843	6.227
122	1996	17.029	14.34	9.424	36.334	1.578	5.689
123	2056	35.835	35.07	23.351	58.452	1.331	6.661
124	2101	22.789	28.075	17.813	42.677	1.874	4.439
125	2134	107.443	39.563	66.607	130.01	3.782	7.011
126	2142	159.927	37.865	107.566	205.021	3.989	13.844
127	2150	60.291	25.789	56.354	95.788	3.809	8.445
128	2151	25.784	16.117	19.181	33.016	2.151	6.498
129	2210	68.667	19.524	24.525	78.055	2.571	7.712
130	2220	116.037	30.623	69.131	139.174	3.198	9.892
131	2246	151.927	40.739	113.249	241.064	2.675	13.486
132	2259	210.263	26.003	142.616	260.506	6.122	9.148
133	2263	78.419	23.014	66.866	110.717	2.135	8.794
134	2275	222.803	27.045	190.85	359.421	7.344	10.118
135	2319	262.699	44.079	188.001	270.612	9.184	11.535
136	2375	187.86	21.589	134.933	181.601	7.705	9.552
137	2443	133.73	29.185	60.332	189.221	3.99	8.458
138	2483	286.729	28.868	167.176	253.317	6.181	11.247
139	2520	284.485	27.043	385.786	161.936	2.91	6.458

140	2651	199.382	40.522	78.844	265.777	3.243	8.496
141	2704	148.639	40.294	78.831	286.675	4.18	7.513
142	2705	106.53	35.945	86.815	262.228	4.75	7.762
143	2718	158.745	27.478	99.63	183.283	5.554	9.688
144	2730	137.864	51.586	81.169	254.443	3.48	6.504
145	2737	231.392	51.099	96.032	287.966	3.57	9.606
146	2742	69.242	25.621	38.299	235.799	2.205	13.917
147	2815	152.108	27.792	65.496	214.689	3.922	7.493
148	2823	126.909	26.753	49.888	214.627	2.991	8.739
149	2825	142.526	25.791	65.574	195.978	2.771	6.298
150	2898	355.294	50.977	364.268	352.356	6.062	14.547
151	2990	163.728	25.756	80.63	159.334	4.174	8.635
152	3028	178.452	44.514	90.747	372.092	4.102	6.558
153	3035	224.472	50.51	56.431	172.286	3.615	5.164
154	3067	193.638	34.818	41.872	186.061	3.16	5.632
155	3087	140.813	33.254	42.382	143.54	3.996	4.386
156	3088	122.663	36.786	52.577	133.142	4.608	7.45
157	3154	199.387	30.902	42.129	165.373	3.184	7.187
158	3157	206.198	27.803	61.549	187.097	3.508	6.131
159	3248	121.53	24.992	44.151	129.883	2.791	5.993
160	3298	120.396	20.904	36.816	112.985	1.923	6.56
161	3305	64.288	20.614	34.706	99.335	2.301	7.787
162	3307	88.203	33.239	39.323	94.9	2.78	5.598
163	3316	124.041	22.908	46.491	136.941	2.268	5.793

164	3326	136.622	26.223	63.148	180.691	3.683	7.342
165	3347	115.399	23.712	43.128	142.956	2.149	8.285
166	3381	125.245	19.324	36.124	120.421	2.744	6.42
167	3398	232.657	38.194	73.211	212.411	3.782	7.647
168	3440	129.279	26.691	53.301	198.215	3.566	6.412
169	3467	124.769	21.074	34.168	172.967	0.923	5.711
170	3485	94.585	36.349	46.802	138.534	2.923	6.615
171	3531	176.164	33.816	69.699	190.558	2.153	8.767
172	3555	95.233	33.756	38.366	102.363	3.112	6.64
173	3575	135.596	25.882	58.536	165.898	3.815	5.804
174	3575	121.589	36.997	60.384	163.786	2.5	8.483
175	3583	105.633	26.901	48.998	147.304	1.236	8.444
176	3613	74.237	40.975	86.635	321.703	2.03	11.273
177	3615	127.188	25.611	69.006	159.79	2.841	8.403
178	3615	113.685	26.788	59.308	159.168	2.96	7.6
179	3625	211.166	42.436	93.262	261.189	3.403	10.592
180	3669	73.083	37.477	31.613	124.506	1.532	6.016
181	3695	192.926	46.96	58.743	213.438	3.431	9.97
182	3751	119.715	42.217	40.957	344.359	3.359	6.787
183	3767	166.374	37.649	62.635	191.545	3.337	5.508
184	3778	78.748	25.752	28.786	131.355	2.254	5.78
185	3812	51.025	22.618	36.31	122.49	2.2	7.109
186	3821	100.678	33.196	60.717	127.643	2.437	6.212
187	3839	130.452	31.437	61.875	115.454	3.395	7.344

188	3875	54.632	24.635	31.44	98.431	2.646	6.885
189	3895	164.584	17.979	40.218	162.981	2.36	8.817
190	3935	122.444	26.612	62.466	141.742	2.845	10.294
191	3945	132.27	27.72	59.748	165.79	3.663	6.198
192	4060	113.38	22.153	66.232	126.849	2.76	7.749
193	4081	108.397	27.594	70.496	165.62	2.123	7.689
194	4100	79.411	10.774	55.571	84.061	2.663	6.286
195	4107	95.011	36.593	56.577	161.549	1.877	7.277
196	4119	104.096	27.461	68.351	109.577	5.036	7.034
197	4121	100.343	16.838	64.527	113.238	1.54	6.974
198	4125	101.164	17.197	57.809	103.329	1.38	5.8
199	4128	121.165	17.521	72.882	144.069	4.244	5.811
200	4133	67.175	20.813	43.523	93.474	1.757	4.423
201	4147	89.654	25.712	46.776	95.306	2.557	6.898
202	4252	36.662	19.989	23.073	46.629	1.348	5.1
203	4258	60.092	22.766	46.994	87.999	3.794	7.432
204	4261	31.447	10.688	29.593	77.635	2.214	5.671
205	4273	52.533	21.96	54.727	89.7	1.349	8.002
206	4282	147.169	24.59	81.089	140.431	1.715	6.313
207	4347	59.845	29.97	191.125	131.684	2.274	7.437
208	4348	41.466	22.797	113.094	119.916	2.187	5.935
209	4361	38.939	25.009	24.429	63.087	1.685	6.802
210	4363	43.353	34.31	34.439	82.019	1.397	6.514
211	4439	50.727	28.152	36.227	92.657	2.933	7.193

212	4446	146.711	42.896	79.197	178.439	3.645	6.201
213	4472	59.952	24.3	52.546	137.891	1.944	5.984
214	4505	78.031	33.32	61.472	117.461	2.292	8.606
215	4518	66.209	23.988	26.488	101.716	2.676	7.508
216	4524	189.698	44.093	89.184	212.596	3.468	6.722
217	4539	102.844	33.385	95.454	191.135	0.614	7.14
218	4563	173.108	31.427	132.397	169.861	3.422	8.254
219	4569	74.435	27.39	74.983	112.404	3.164	6.086
220	4574	84.924	20.479	43.297	97.711	2.118	6.761
221	4592	36.291	36.122	31.505	95.475	1.5	5.392
222	4596	88.884	35.014	51.865	150.751	2.358	5.691
223	4599	73.859	32.381	51.205	131.868	1.788	5.104
224	4606	39.868	27.083	24.071	66.355	2.035	5.756
225	4607	119.576	29.214	90.387	107.558	3.404	9.512
226	4618	88.244	24.261	43.225	162.14	1.979	7.245
227	4652	117.765	30.099	37.185	160.116	2.373	7.385
228	4655	113.443	30.412	39.337	125.738	2.916	6.306
229	4662	54.116	32.296	30.681	120.624	3.354	6.962
230	4664	49.865	28.077	23.357	89.327	2.455	4.92
231	4683	52.593	22.1	21.834	108.697	3.126	4.549
232	4705	31.15	25.616	17.189	72.063	0.477	5.29
233	4736	73.596	34.878	48.243	148.407	2.676	6.4
234	4752	62.252	36.515	21.803	90.495	0.934	4.005
235	4757	39.185	30.82	19.294	86.468	0.975	4.171

236	4769	42.869	16.02	16.832	81.341	1.379	5.07
237	4790	53.967	24.696	18.711	83.796	2.183	5.272
238	4791	28.872	29.688	20.172	72.15	1.063	7.339
239	4805	31.179	34.972	26.519	97.973	0.48	6.48
240	4810	41.48	23.484	27.905	120.337	1.277	3.664
241	4813	32.51	35.369	19.045	55.91	2.667	4.146
242	4824	26.789	31.279	16.147	48.74	2.405	4.465
243	4832	50.194	26.217	15.474	107.027	1.73	5.603
244	4852	39.528	36.696	24.043	69.112	1.102	5.093
245	4898	64.585	23.705	20.716	114.561	2.189	7.326
246	4920	43.575	26.303	20.179	115.728	2.063	6.094
247	4979	23.061	31.393	16.322	54.35	2.067	5.826
248	5013	25.149	34.909	48.528	78.642	1.444	6.36
249	5019	29.787	28.965	20.016	83.546	0.842	4.485
250	5048	39.292	27.759	58.796	198.109	0.756	9.07
251	5102	53.117	20.355	16.231	67.491	1.421	5.914
252	5112	29.355	11.488	14.374	55.852	0.998	4.483
253	5143	22.062	17.281	14.536	50.415	1.416	6.747
254	5151	16.107	7.407	8.381	33.609	0.473	5.199
255	5152	24.272	28.245	78.77	47.904	2.171	5.045
256	5155	39.025	37.448	22.244	84.16	1.424	4.965
257	5162	31.239	29.57	18.105	69.564	1.951	6.453
258	5168	58.058	26.29	18.354	91.037	2.505	4.993
259	5169	41.16	24.922	18.251	73.076	0.461	6.21

260	5195	26.158	26.483	17.854	63.354	1.355	6.045
261	5246	16.56	15.477	10.861	28.144	1.42	6.188
262	5247	28.404	20.596	22.053	59.926	1.053	4.758
263	5273	25.469	33.794	20.343	51.282	1.138	4.68
264	5284	50.07	36.508	24.665	62.69	1.084	4.52
265	5302	57.678	32.39	28.654	102.63	2.34	5.918
266	5313	55.198	36.027	20.833	99.721	2.071	6.027
267	5319	64.328	32.29	31.626	135.934	0.966	5.107
268	5329	57.977	21.828	22.768	96.635	2.123	3.828
269	5332	29.989	30.39	20.171	80.014	0.7	4.295
270	5370	44.707	20.83	25.568	96.206	2.109	5.543
271	5392	49.353	15.844	18.685	82.603	1.511	5.253
272	5406	35.327	23.804	23.625	144.914	2.252	3.97
273	5424	30.84	8.595	11.584	43.621	2.69	5.57
274	5430	36.863	21.395	13.508	51.97	1.575	6.009
275	5438	54.643	9.358	19.763	88.921	1.937	6.589
276	5446	46.888	9.141	16.672	80.922	2.368	4.697
277	5462	28.874	27.186	13.612	44.183	0.962	6.726
278	5475	43.429	9.153	17.433	63.125	1.6	4.533
279	5477	77.142	22.185	21.111	119.755	1.831	7.922
280	5484	46.228	7.958	14.937	59.193	1.011	7.168
281	5508	86.976	21.644	31.636	122.482	1.34	7.411
282	5536	65.422	13.42	22.964	80.702	1.755	4.655
283	5537	70.502	22.964	23.954	84.514	2.357	4.181

284	5540	68.933	42.995	40.413	138.688	0.831	5.804
285	5558	74.197	23.44	22	97.715	0.922	7.889
286	5566	138.405	27.102	60.959	182.951	2.701	6.049
287	5588	176.807	22.636	42.767	121.762	2.468	6.185
288	5602	54.644	17.073	38.046	94.193	1.212	5.861
289	5605	62.745	25.066	20.972	81.243	2.516	5.488
290	5609	46.178	16.971	60.206	81.941	2.135	6.005
291	5679	103.488	33.449	53.955	96.066	1.887	6.427
292	5680	132.33	24.217	46.471	96.228	1.29	5.76
293	5683	108.051	31.205	61.115	147.705	2.137	8.647
294	5693	42.848	26.713	26.163	55.167	3.122	4.22
295	5714	109.815	32.878	46.845	77.965	2.239	6.211
296	5719	89.809	31.029	72.731	114.791	1.755	7.02
297	5752	87.15	16.25	58.563	107.482	4.278	7.057
298	5753	103.317	24.075	59.342	139.312	2.605	7.661
299	5796	29.295	17.899	37.689	89.461	2.029	8.746
300	5802	38.263	25.658	82.964	242.158	0.907	11.13
301	5815	27.761	23.41	23.401	92.769	1.773	4.188
302	5821	48.693	25.57	34.708	128.538	2.24	5.74
303	5827	45.634	23.908	23.687	130.639	0.804	6.37
304	5829	33.433	18.723	22.19	80.683	2.859	5.444
305	5858	50.199	23.038	39.722	123.018	2.759	6.685
306	5862	30.133	24.674	41.951	133.394	0.772	7.655
307	5871	33.019	18.23	38.422	143.862	1.762	5.985

308	5872	31.484	17.317	19.575	68.658	1.338	4.096
309	5903	20.03	8.243	21.101	62.403	2.928	6.349
310	5936	21.74	10.752	17.468	75.459	2.679	6.261
311	5941	14.288	21.591	13.069	41.12	2.171	5.796
312	5942	21.03	18.691	19.028	57.545	3.766	5.719
313	5959	76.764	28.892	37.433	96.415	2.761	7.31
314	5965	79.808	27.934	35.844	103.166	2.173	5.954
315	5980	105.022	32.76	50.792	157.897	1.272	7.184
316	5987	23.579	11.583	18.07	49.774	1.936	5.729
317	6004	34.893	25.033	18.19	50.07	0.846	5.236
318	6008	121.432	26.3	43.453	91.09	0.917	4.971
319	6029	72.774	16.342	25.049	75.194	1.783	6.498
320	6030	65.066	28.581	32.873	109.008	1.893	6.647
321	6063	36.203	29.273	24.144	125.154	1.93	7.232
322	6068	97.052	35.854	35.993	173.167	1.991	8.368
323	6084	162.007	30.049	41.809	127.06	2.118	6.927
324	6088	197.828	32.951	48.132	133.291	0.879	6.245
325	6101	48.628	22.214	32.356	100.534	1.401	6.152
326	6136	19.272	11.825	28.73	52.929	1.089	6.524
327	6152	20.513	22.703	16.447	52.907	2.343	5.929
328	6153	25.7	16.857	19.503	83.397	1.118	2.933
329	6165	164.287	27.774	43.801	233.652	2.797	6.127
330	6179	42.047	22.071	26.317	91.844	1.926	4.987
331	6194	20.002	20.246	16.123	58.347	0.97	5.689

332	6240	20.646	15.206	38.951	97.708	1.3	6.236
333	6247	18.641	20.663	15.498	57.989	2.248	5.725
334	6255	23.823	23.403	18.261	73.033	2.019	5.435
335	6260	21.591	15.92	16.603	74.248	2.175	6.799
336	6265	42.409	19.494	20.588	61.165	1.16	7.131
337	6276	26.81	20.479	16.369	79.272	2.973	5.885
338	6278	23.717	14.653	21.318	76.838	1.599	7.034
339	6303	20.641	16.097	12.99	48.448	2.406	6.425
340	6514	21.776	24.26	13.982	44.367	3.06	5.766
341	6522	19.34	16.861	14.984	49.511	2.442	4.489
342	6612	13.578	25.675	12.103	41.634	1.826	6.178
343	6651	18.576	18.117	7.933	45.316	2.359	3.136
344	6668	17.896	15.402	10.704	48.546	0.384	4.839
345	6675	36.076	25.956	14.746	71.75	1.395	5.362
346	6678	20.224	23.544	14.843	66.025	1.649	4.848
347	6685	21.069	15.976	13.985	73.255	1.637	8.259
348	6704	18.029	11.585	8.295	30.016	1.123	5.928
349	6706	23.093	16.092	9.384	47.008	2.757	6.781
350	6723	19.118	16.347	11.304	55.468	1.21	5.881
351	6740	30.75	21.764	43.489	110.137	1.951	6.707
352	6776	25.264	25.603	15.649	69.73	1.727	6.619
353	6858	20.444	31.508	16.195	61.236	2.84	5.928
354	6861	27.924	26.221	21.047	105.639	2.221	6.125
355	6927	22	29.82	16.394	45.246	2.368	5.406

356	6931	38.021	41.281	27.602	143.453	0.893	6.538
357	6940	35.632	29.628	15.464	98.509	3.023	4.162
358	6960	23.298	29.854	23.94	92.3	1.777	6.059
359	7002	420.833	38.043	224.293	314.257	11.925	11.371
360	7006	32.557	26.902	16.235	83.075	1.828	6.283
361	7026	25.712	20.612	11.206	41.396	1.593	3.845
362	7066	30.207	23.36	13.712	72.822	1.541	5.12
363	7066	33.862	20.101	13.505	71.712	1.106	4.758
364	7085	25.252	23.465	18.773	58.917	3.281	5.439
365	7108	17.052	18.435	10.081	31.098	1.342	4.539
366	7110	14.818	19.421	19.615	29.897	0.988	6.392
367	7111	16.954	15.576	10.455	34.841	0.451	6.62
368	7129	17.677	6.446	9.043	27.094	3.147	3.847
369	7134	17.17	15.062	8.402	26.514	0.821	5.317
370	7138	28.552	12.201	20.731	99.442	2.249	7.121
371	7166	15.084	23.729	12.514	33.825	1.694	6.605
372	7222	22.023	14.698	9.621	44.279	3.258	4.042
373	7255	30.973	7.596	39.649	130.518	1.32	8.284
374	7258	15.737	11.172	12.024	25.562	1.975	6.395
375	7286	36.545	27.377	21.056	60.758	1.818	5.084
376	7302	52.586	21.504	33.089	106.506	2.073	6.095
377	7312	45.608	20.838	30.425	84.649	1.144	6.505
378	7314	73.24	28.642	35.652	101.157	0.939	6.047
379	7322	48.167	18.754	26.351	64.432	2.312	7.418

380	7324	61.179	19.131	31.391	77.293	1.562	5.551
381	7326	56.394	28.406	33.69	97.775	3.007	4.318
382	7449	13.785	12.194	8.092	25.454	1.768	6.031
383	7452	48.585	37.579	25.314	76.542	1.03	6.977
384	7467	10.793	6.513	6.956	16.399	1.187	4.561
385	7477	13.196	11.755	8.322	17.054	1.26	5.555
386	7512	12.253	10.136	7.767	19.979	1.97	6.537
387	7513	13.424	9.657	7.474	17.547	1.23	4.928
388	7567	11.378	14.256	7.167	20.032	2.383	5.853
389	7610	11.441	9.529	7.284	16.613	0.647	6.825
390	7671	14.325	15.34	8.827	34.663	4.994	6.535
391	7674	20.43	18.828	12.938	47.068	1.369	5.231
392	7723	27.629	16.313	21.092	27.47	1.721	5.748
393	7748	17.677	29.815	12.443	40.584	0.511	4.657
394	7810	25.499	27.666	19.982	61.147	0.852	5.812
395	7821	18.124	17.678	13.201	44.084	1.401	4.907
396	7842	12.004	20.848	9.607	26.761	0.923	6.118
397	7847	173.431	38.715	136.515	167.869	5.54	10.673
398	7849	66.064	30.031	33.248	116.584	2.004	6.11
399	7858	28.08	21.708	21.683	64.641	1.531	5.042
400	7867	64.307	20.464	81.204	476.724	2.278	10.872
401	7874	35.55	20.392	21.746	86.413	2.21	6.248
402	7887	63.807	28.65	55.245	213.69	0.804	19.53
403	7906	28.325	19.428	18.027	77.701	1.377	4.596

404	7916	98.5	29.528	64.562	361.038	1.394	16.111
405	7925	16.705	13.892	10.76	47.683	1.098	5.091
406	7929	16.167	26.535	11.615	32.245	0.967	6.631
407	7952	16.139	24.893	11.282	33.974	0.579	6.493
408	7955	13.936	10.444	8.448	20.886	2.803	3.841
409	8014	15.366	15.369	10.317	25.306	1.903	5.527
410	8018	16.939	15.752	10.415	36.232	1.781	5.151
411	8028	14.257	15.019	9.346	26.238	2.651	5.756
412	8035	14.45	14.944	11.075	39.966	1.275	4.865
413	8043	15.14	12.443	11.95	30.824	1.592	5.345
414	8047	18.943	25.21	19.836	64.941	1.475	6.453
415	8092	23.103	29.053	16.76	69.742	2.032	5.486
416	8093	65.15	33.032	46.05	215.335	2.621	9.669
417	8096	31.138	18.217	18.27	58.525	1.944	5.699
418	8117	20.619	14.866	16.737	45.466	0.979	4.899
419	8120	19.631	19.801	18.039	53.738	1.675	6.822
420	8130	20.915	15.569	16.737	64.603	1.418	7.087
421	8142	17.066	20.114	12.439	38.976	2.668	4.877
422	8143	15.851	15.962	13.967	40.355	1.653	6.394
423	8156	19.42	14.894	9.346	40.361	1.544	4.164
424	8195	20.545	8.26	9.615	25.353	0.55	4.127
425	8197	43.74	13.542	22.891	91.683	1.408	4.615
426	8216	42.155	17.866	52.631	161.592	2.408	7.081
427	8228	48.573	21.599	30.411	88.648	2.068	7.439

428	8247	25.02	20.238	18.357	48.118	2.324	6.214
429	8249	22.493	23.832	22.905	73.801	2.232	6.121
430	8250	27.02	25.638	27.488	75.81	1.067	5.294
431	8265	23.767	21.673	14.95	57.014	2.191	5.023
432	8297	13.714	13.094	8.007	21.68	1.247	5.676
433	8325	13.505	18.243	6.825	20.617	0.412	6.319
434	8340	12.473	9.516	6.942	17.768	2.572	5.972
435	8358	14.248	8.803	6.675	18.649	3.139	5.188
436	8365	11.918	6.273	7.343	17.211	1.58	6.761
437	8378	19.512	24.07	9.132	29.1	1.311	6.242
438	8448	12.706	15.214	10.003	20.686	1.534	5.952
439	8450	13.518	18.458	6.633	22.076	3.554	6.018
440	8453	12.816	7.449	7.364	20.187	1.586	5.383
441	9087	15.033	10.768	8.527	24.505	1.428	4.93
442	9458	13.057	14.391	8.897	24.733	0.517	4.111
443	9460	11.792	21.856	7.979	28.72	2.963	5.429
444	9471	14.177	7.141	8.355	20.664	1.173	5.283
445	9530	13.645	12.342	6.723	22.48	2.768	4.658
446	9534	12.348	9.707	6.416	22.497	2.031	5.745
447	9605	18.47	20.184	10.639	30.493	1.151	6.561
448	9820	27.857	20.5	13.043	45.041	1.813	5.667
449	9845	12.317	9.352	6.816	20.949	1.504	5.274
450	9928	13.126	11.34	8.458	21.617	3.471	7.377
451	9953	26.633	21.947	18.104	63.435	2.747	7.301

452	9964	13.979	23.446	8.835	26.227	2.454	5.229
453	9967	17.69	11.658	11.351	37.313	0.595	5.834
454	9969	22.806	19.207	48.509	66.476	2.348	6.519
455	9978	18.636	10.813	15.186	64.43	1.04	5.007
456	9989	17.985	11.372	12.683	53.367	0.999	3.982
457	9997	18.373	10.718	12.782	44.097	1.605	6.69
458	10010	16.973	24.197	14.669	69.222	1.43	5.558
459	10017	17.281	11.869	12.394	35.028	1.087	5.912
460	10075	15.399	25.421	14.323	53.649	2.147	3.982
461	10091	22.083	34.767	15.132	56.299	2.006	6.304
462	10106	14.762	23.26	11.298	37.133	1.09	4.701
463	10108	15.375	21.027	11.827	41.626	0.761	6.093
464	10130	22.499	27.899	17.09	47.495	1.557	5.038
465	10143	17.712	27.437	14.374	57.594	2.309	5.975
466	10181	21.801	25.367	15.989	58.082	1.7	6.895
467	10240	18.636	25.56	13.143	38.901	1.379	4.858
468	10244	25.418	24.677	17.582	63.487	1.895	6.721
469	10307	16.811	22.372	13.476	52.084	0.95	4.845
470	10316	13.249	20.586	10.101	30.243	2.346	5.056
471	10387	20.726	29.507	13.93	59.743	1.109	6.359
472	10397	18.391	22.829	10.195	42.527	1.639	5.99
473	10399	18.136	26.974	15.063	46.067	1.303	6.104
474	10441	18.585	20.674	15.184	46.148	0.562	5.421
475	10450	17.538	16.81	11.212	30.036	1.26	5.134

476	10455	15.68	23.454	11.609	38.546	1.696	6.838
477	10457	18.207	28.38	15.692	44.379	0.808	3.843
478	10493	15.573	25.866	13.156	40.38	1.864	5.498
479	10536	17.127	24.82	14.156	40.76	1.772	5.222
480	10609	36.781	28.339	19.198	83.974	1.343	6.571
481	10747	18.721	27.855	12.876	37.226	0.937	4.752
482	10754	30.17	34.105	19.586	55.44	1.535	4.98
483	10766	35.026	17.661	17.704	84.022	2.007	4.366
484	10775	30.549	23.531	11.888	45.05	1.59	5.403
485	10813	18.282	20.468	13.675	41.844	0.821	5.476
486	10836	21.086	39.294	17.957	48.656	0.451	4.194
487	11000	22.912	16.21	10.028	37.307	1.632	5.56
488	11008	14.284	11.943	9.06	36.741	1.403	8.014
489	11042	25.134	13.212	11.24	56.49	2.312	5.148
490	11114	12.013	8.851	6.625	22.413	1.864	5.724
491	11140	20.821	20.635	14.171	68.577	1.101	5.944
492	11146	18.243	29.389	15.172	34.317	2.158	5.834

Vita

The author of this work, Ali Elkekli, was born in Tripoli, Libya, in July 1962. He received his bachelor's degree in Botany from the University of Tripoli (formally Alfateh University) in 1985. He worked with the Libyan Environment General Authority from 1986 to 2008. During this period of his career, he served in several supervisory positions and performed leadership's tasks. These positions include; Director of the nature conservation department; Director of the administration & financial department, focal points, and national coordinators for international and non-governmental organizations, members of national and regional committees.

In, 2008, Elkekli earned his master's degree in Environmental Science from Higher Academic Researcher in Libya. His thesis was entitled "Environmental and Taxonomical Study of Vegetation in Farwa, Libya".

Ali moved to the United States in October 2008, and in 2010, was admitted to the doctoral program in Environmental Science and Engineering at The University of Texas at El Paso. While at UTEP, he worked as a research associate for Geological department and teaching assistant for the department of ESE.