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Sanata Dama

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CORRELATION OF ECONOMIC STATUS AND TRACE METALS CONCENTRATIONS IN SURFACE SOILS IN THE HOUSTON METROPOLITAN AREA

DISSERTATION

Presented in Partial Fulfillment of the Requirements for

the Degree Doctor of Philosophy in the Graduate School

of Texas Southern University

By

Sanata Dama, B.S., M.S.

Texas Southern University

2021

Approved By

Dr. Hyun-Min Hwang

Chairperson, Dissertation Committee

Dr. Gregory Maddox

Dean, The Graduate School

Approved By

Dr. Hyun-Min Hwang 10/26/2021

Chairperson . Date

Dr. Jason Rosenzweig 10/29/2021

Committee Member Date

Dr. Abate Wolde-Kirkos 10/27/2021

Committee Member Date

Dr. Tuan Phan 10/27/2021

Committee Member Date

CORRELATION OF ECONOMIC STATUS AND TRACE METALS CONCENTRATIONS IN SURFACE SOILS IN THE HOUSTON METROPOLITAN AREA

By

Sanata Dama, Ph.D.

Texas Southern University, 2021

Dr. Hyun-Min Hwang, Advisor

Urban surface soils are contaminated by trace metals from various anthropogenic sources such as traffic and industrial facilities. Socio-economically disadvantaged communities are generally located closer to these sources and likely exposed more to toxic metals. This study aims to investigate the surface soil contamination by trace metals. Surface soils were collected from parks (n=75) and playgrounds of elementary schools (n=6) located in 33 postal codes split into four groups with different economic status (average annual household income) and industrial emissions (releases reported to the Toxic Release Inventory). Postal codes were ordered into high/middle income (> $40,000/year) without emissions, high/middle income with emissions, low income (< $40,000/year) without emissions, and low income with emissions. Collected soil samples were analyzed for trace metals (Al, As, Cd, Cr, Co, Cu, Fe, Mg, Mn, Ni, Pb, and Zn) using microwave digester with nitric acid and ICP-MS. A confirmatory analysis was performed by XRF. The results showed that disadvantaged neighborhoods at the proximity of industrial facilities displayed the highest levels of Fe, Pb, Cu, Zn, Cd, Cr,

Co, Ni and Mn with the respective mean concentrations of 1.40%, 33.1 mg/kg, 12.7 mg/kg, 94.2 mg/kg, 0.26 mg/kg, 11.7 mg/kg, 4.07 mg/kg, 8.35 mg/kg, and 228 mg/kg. While the lowest mean concentrations of 1.40%, 0.48% 13.6 mg/g, 6.70 mg/kg, 38.1 mg/kg, 0.08 mg/kg, 4.96 mg/kg, 2.11 mg/kg and 3.76 mg/kg for Al, Fe, Pb, Cu, Zn, As, Cd, Cr, Co, and Ni were detected in the samples collected in affluent neighborhoods located far from industries. This study shows that closeness to industrial facilities is likely to be an important factor for the health risk of children living in economically disadvantaged communities.

TABLE OF CONTENTS

CHAPTER

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

ANOVA Analysis of the Variance

EF Enrichment factor

EJ Environmental Justice

EPA Environmental Protection Agency

ICP-MS Inductively Coupled Plasma Mass Spectrometry

Igeo Index of geo-accumulation

Lbs pounds

µg microgram

µm micrometer

mg/kg milligram per kilogram

mL milliliter

mm millimeter

MSA Metropolitan Statistical Area

PM Particulate Matter

ppb parts per billion

ppm parts per million

NIST National Institute of Standards and Technology

NPL National Priorities List

SD Standard Deviation

SIC Standard Industrial Classification

SCOs Soil Cleanup Objectives

SSL Soils Screening Levels

SRM Standard Reference Material

TCQE Texas Commission on Environmental Quality

TEL Tetraethyl lead

TRRP Texas Risk Reduction Program

TRI Toxic Release Inventory

TU Toxic Unit

∑**TU** Sum of Toxic Unit

US United States

XRF X-Ray Fluorescence

WHO World Health Organization

ZIP Zone Improvement Plan

VITA

2006……………………………………	B.S., Cadi Ayad University, Marrakesh, MOROCCO
2008…..…………………………………	M.S.,Cadi Ayad University, Marrakesh, Morocco
2008-2009……………………………….	Independent Consultant at GTZ -BURKINA FASO
2015-Present……………………………	Graduate Teaching Assistant, Chemistry Department Texas Southern University Houston, Texas
2018-2020………………………………	Title III Fellow Graduate Research Assistant Texas Southern University Houston, Texas
Major Field…………………………….	Environmental Toxicology

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CHAPTER 1

INTRODUCTION

The growth of urban population around the globe is without precedent (United Nations, 2001). From a population estimated at 6.1 billion in 2000, this number is expected to reach 8.3 billion by 2030. The statistics predict that two-thirds of the world population will be living in urban areas in one decade. In western countries, the urban population is projected to reach 80% by 2030. (Wong et al., 2005; Ajmone-Marsan et al., 2010). Urbanization has numerous positive impacts such as economic growth and development, it also has drawbacks. Thus, the rise of urban population has generated several issues in cities, among which environmental pollution including soil contamination and environmental justice.

Urban soils contamination

The rapid geographical growth of urban areas has an impact on both the environment and human health. Thus, soil, an essential component of the ecosystem, is subject to unplanned urbanization, rapid use change, strong sealing, and extreme industrialization. For instance, three million potential polluted sites have been estimated in Europe (EEA, 2014), and more than 1,300 polluted or contaminated sites are included in the Superfund National Priorities List (SNPL) in the United States (US) (USEPA, 2013). In Australia, the number of contaminated sites reaches 80,000. More alarming, 16 % of all Chinese soils are predicted to be polluted.

Due to anthropogenic activities, urban areas receive substantial amounts of contaminants such as trace metals (e.g., lead, copper, zinc), and organic compounds (e.g., formaldehyde1,3-butadiene, polycyclic aromatic hydrocarbons). Among the pollutants of great concern are heavy metals. Heavy metals include metals and metalloids such as arsenic (As) whose density exceeds 6g/cm^3. They are non-biodegradable, bioaccumulate, and extremely toxic to humans and other living organisms (Alloway, 2012). Naturally, metals are present in rocks and soils at trace levels (concentrations < 1,000 mg/kg) and are rarely harmful (Wuana et al., 2011). However, trace metal concentrations are amplified in urban environments due to human activities (Karakus, 2012). For instance, anthropogenic activities released copper, cadmium, zinc, and lead; 13 to 100 times more than natural processes (Ross, 1994).

Urban soil contamination exists due to extreme disturbance and intense anthropogenic activities. Many studies have described intensive traffic and industrial activities as principal anthropogenic activities causing urban soil pollution by trace metals (Yesilonis et al., 2008; Davis et al., 2009; Wu et al., 2010; Ha et al., 2014). Traffic-related activities may enhance urban soils with Pb, Cu, and Zn. Depending on the activities performed, industries may be associated with mercury (Hg), copper (Cu), manganese (Mn), magnesium (Mg), lead (Pb), copper (Cu), cadmium (Cd), chromium (Cr) and several other heavy metals. Due to atmospheric deposition, soils are the final sinks of pollutants. The upper 20 cm of the surface soils are particularly highly contaminated because of the reduced mobility of trace metals in surface soils. As a result, urban soils are enriched with more heavy metals than their surrounding agricultural soils (Johnson & Ander, 2008; Figuiredo et al., 2009; Davis et al., 2014). For example, Schwartz et al. (2006) found that the levels of Cd, Pb, and Zn in garden soils were twice the amount in surrounding agricultural soils. Additionally, Madrid et al. (2002) found that the older and most urbanized areas depict the highest concentrations.

Trace metal contamination in urban soils is a severe threat to human health in densely populated metropolitans (Clark et al., 2015). The health hazard originated from soil contamination is greatly intensified because of the distinctive disperse pattern of metal contaminants and the proximity of urban populations to contaminated soils (Ajmone-Marsan et al., 2010). Urban surface soils have a circumneutral pH and high organic content, particularly in residential and municipal parks, which restrict the mobility of trace metals (McBride et al., 2014). Open public places like parks and playgrounds near sources of pollution are heightened with significant levels of pollutants including heavy metals due to their accumulation into the surface soil. During outdoor activities in these areas, the exposure of children to trace elements significantly increased (Ng et al., 2003; DeMiguel et al., 2007). Children may ingest enormous amounts of soils laden with trace metals through putting their hands loaded with soil in their mouths frequently (Yu & Li, 2012; Nezat et al., 2017). As an illustration, lead exposure levels are greater during the summer months, as reported in many major cities in the US.

Trace metal contamination occurs via the direct ingestion of soil particles, the inhalation of suspended soil particles, and dermal contact of soil particles loaded with toxic trace metals, with ingestion being the principal pathway of urban exposure. Ingestion of contaminated soil constitutes a higher health risk in children than in adults. Based on EPA values for risk assessment, soil ingestions rates are 20 mg/day for infants of 0 to < 6 months, 30 mg/day for infants of 6 months to <1 year, 40 mg/day for children between the age group of 1 to < 6 years, 30 mg/day for children between the age group 6 to <12 years, and 10 mg/day for 12 years and beyond (USEPA, 2017). The inhalation of resuspended soil dust is another important route of exposure to trace metals. The soil dust inhaled is usually trapped, then ingested, and goes through the gastrointestinal tract. Nevertheless, a portion of dust is trapped inside the lungs, leading to ailments such as bronchitis, asthma, pneumoconiosis, and lung cancer (Botsou et al., 2020).

Children are more sensitive to trace metals due to their heightened metal absorption rates and fast body development, in particular, the rapidly developing nervous system (Ng et al., 2003; Tan et al., 2016). Heavy metal poisoning in children is one of the most prevalent health issues in pediatric medicine, all genders, races, and socio-economic conditions combined, due to the ubiquitous dissemination of heavy metals, long persistence, and high toxicity (Casey et al., 1994).

Trace elements can be divided into essential trace metals known as micronutrients (e.g., Cr, Cu, Fe, Mn, Mo, and Zn) and non-essential ones (e.g., As, Cd, Pb, and Hg). The dietary uptake of the first category is required for ideal human health. Insufficiencies of these metals lead to detrimental health effects, and excess ingestion induces toxicity (Panel on Micronutrients, 2001). For example, Cu is necessary for the formation of human hemoglobin. However, high uptake of Cu may result in anemia, liver, and kidney damage, stomach, and intestinal exasperations. Similarly, nickel (Ni) is needed in exceedingly small amounts, and high doses may cause cancers (Wuana et al., 2011). Cr (III) deficiency is linked to infertility, cardiovascular conditions, and diabetes, whereas Cr (VI) is highly toxic and causes cancers. Zn shortage can cause infertility in humans, and elevated levels negatively alter the biological functions.

Non-essential trace metals do not play any essential role in the human body, and exposure to these metals should be eliminated (Tchounwou et al., 2012). Among the non-essential trace metals, Pb is one of the most hazardous. Pb is a significant threat to human health, particularly to children's health. Adverse pediatric effects of Pb are well presented in the literature as the historical use of Pb in paint and gasoline. Pediatric Pb is identified as the leading cause of childhood poisoning to heavy metals. Pb is a neurotoxin, and children exposed to Pb are at risk of defective development, reduced Intelligent Quotient (IQ), reduced attention span, hyperactivity, and mental decline. Children under the age of six are at higher exposure risk (Wuana et al., .2011; Yang et al., 2021). Pb can also affect the nervous system, kidney function, and cardiac function in adults, leading to severe and irreversible health damages (Spivey 2007). Along with Pb, other non-essential trace metals can jeopardize human health. Cadmium (Cd) is highly toxic, and it may impair the heart, liver, bones, and kidneys (Manahan, 2003; Navratil et al., 2005). Cd can cause osteoporosis in children and has been associated with pediatric cancers (Yang et al., 2019). Arsenic (As) may damage the skin, affect~~s~~ the circulatory system, and cause cancers (Scragg, 2006).

Human exposure to urban soil pollutants is amplified as more people elect to live or are obligated to live in areas with past and present industrial activity and at the proximity of elevated atmospheric deposition of pollutants such as industrial facilities and busy roads with extensive traffic (Johnson et al. 2017). Environmental justice issues arise, as some people, due to socio-economic characteristics, have a disproportionate burden of environmental hazards. These communities living in the vicinity of sources of pollutants are likely at higher adverse health risks of trace metal toxicity (Han et al., 2017), precisely, their children during outdoor activities on schools' playgrounds and public parks.

Environmental Justice

Environmental Justice (EJ) is defined as the "*fair treatment of people of all races, income, and cultures with respect to the development, implementation and enforcement of environmental laws, regulations, and policies, and their meaningful involvement in the decision-making processes of the government*" in chapter 2 of the Not in my Backyard Executive Order 12,898 and Title VI signed by President Clinton in 1994.

A substantial body of literature has undeniably highlighted the disproportionate burden of pollutants on minorities and socio-economically disadvantaged communities compared to the overall population (Bullard et al., 2008; Bullard, 2008; James et al., 2012; Nance et al., 2016 and reference therein). Environmental Justice (EJ) has presented an association between income and the proximity to pollutant sources. Many studies, in the US and elsewhere have reported that pollutant sources were disproportionately located in low-income neighborhoods (Burke, 1993; Perlin and al.,1995; Pastor et al. 2006; Mohai & Saha 2007; Maantay et al. 2009; Chakraborty et al., 2011). For instance, several authors have indicated the disproportionate location of industries emitting toxic substances in disadvantaged communities (Perlin et al., 1995; Brooks & Sethi, 1997; Arora & Cason, 1999). Others have emphasized that the storage and disposal of hazardous pollutants were higher in areas populated by minorities and low-income communities (Anderton et al., 1994; Been & Gupta, 1997; Mohai & Saha, 2007; Bullard et al., 2008; Zwick et al., 2014). A study reported that 40,000 identified hazardous waste sites, including 1,200 most dangerous to human health, were found in low-income neighborhoods (Gray & Johnson, 2015 and the references therein). Houston and colleagues (2004) indicated that minorities and low-income communities in Southern California reside in proximity to busy traffic areas, known to be significant contributors to pollution.

Several factors such as income, race, ethnicity, age, gender nutrition, exercise, and residence can generate exposure and risk disparities to environmental hazards. However, income followed by race is recognized as the most crucial factor in environmental disparities (Brochu et al., 2011; Burger, 2011). For example, in many places like Washington, DC; Chicago, Illinois; Denver, Colorado; Los Angeles and San Francisco, California; and New York, NY, low ambient air quality was recorded in low-income predominantly black neighborhoods (Burger, 2011). Apelberg et al. (2005) reported higher toxic air risks in poor African American communities in Maryland. Similarly, in Houston, TX, higher levels of air pollutants were recorded in socio-economically disadvantaged neighborhoods (Linder et al., 2008; Figueiro et al., 2009; Johnson et al., 2014; Horney et al., 2017).

This uneven distribution of pollutants across a city leads to health disparities. Higher rates of asthma prevalence, emergency room visits rates, hospitalization, and mortality have been reported in low-income populations (Wright & Fischer, 2003; Akinbami 2006; Forno et al., 2009; EPA, 2013; Pacheco, 2014). Asthma occurrence was found to be greater in households living below the poverty level (Gray et al., 2015). The United States Environmental Protection Agency (USEPA) statistics portrayed higher rates of asthma emergency room visits at 330%, hospitalization rate at 220%, and death rate at 180% for African Americans compared to Caucasians (Gray et al., 2015). According to the Center for Disease Control and Prevention (CDC, 2012), asthma is more likely to be detected in 21% of non-Hispanic black children, and 16 % of them will remain suffering from it. In contrast, low percentages of 15 % and 10% for Hispanics, and 12% and 8 % for non-Hispanic White offspring are reported. Similarly, for low-income families, the percentages of children ever diagnosed with asthma and still suffering from it are 18 % and 13 %, respectively; and for affluent background families are only 12 % and 8 % (CDC, 2012). Likewise, lead blood levels are higher in predominantly African American low-income communities. Peters et al. (2011) indicated that poorer health in low socio-economic populations was associated with higher blood lead (Pb) levels. Lead blood levels in Hispanic and black children are higher than those in non-Hispanic and white children (Bell et al., 2012). Research reviews on childhood Pb blood poisoning, conducted in the U.S. from 2002 to 2012, revealed that African American children have greater blood Pb levels than white and Hispanic children (White et al., 2016).

Rationale

Due to the presence of a giant petrochemical complex like Houston Ship Channel (HSC) and 200 additional petrochemical facilities and power plants, massive traffic, active port, and major roadways, numerous sources likely contribute to polluting Houston MSA with trace metals, specifically in areas neighboring industrial facilities and highways. As an economically developed metropolitan area, the proportion of the population living in Houston MSA is rapidly increasing. Subsequently, the environmental quality of urban soils regarding human health is a growing concern. However, little information is available about soil metal contamination in Houston MSA, while knowledge about the outdoor environment in urban settings is vital.

In 2018, Houston Metropolitan Area (MSA) had 513 Toxic Release Inventory (TRI) facilities (USEPA TRI, 2018), mostly located in East and North East of Houston, 3 to 10 km away from Downtown Houston. In the same year, nearly ten billion pounds of toxic chemicals were disposed in and on-site of industries**.** Due to the lack of formal zoning into Houston MSA, residential areas neighborhood industrial facilities are more likely to be exposed to poisonous trace metals. Besides, grandfathering laws allow the industries to continue using their properties for its original purpose if they were in place before 1971 (Lewyn, 2003). EJ issues may arise in Houston MSA as most of this substantial industrial activity occurs on the east of Houston, where low-income and minority communities are located. In opposite, the west side of Houston is primarily composed of residential and commercial areas. Accordingly, an abundant amount of literature has illustrated social disparities in Houston's levels of air pollutants. Evidence of low ambient air quality in Houston's socio-economic disadvantaged communities has been presented by several scholars (Linder et al., 2008; Figueiro et al., 2009; Johnson et al., 2014). However, to the best of our knowledge, no similar study has been done regarding the economic disparities in Houston's surface soils.

In addition, the trend of industrial emissions reported to TRI (TRI,2017) suggests that the release of toxic heavy metals is higher in low-income Zone Improvement Plan (ZIP) codes compared to affluent neighborhoods (Figure 1). Communities living in low-income ZIP codes may have a disproportionate burden of environmental hazards, especially regarding surface soil trace metal pollution (Nicole, 2018).

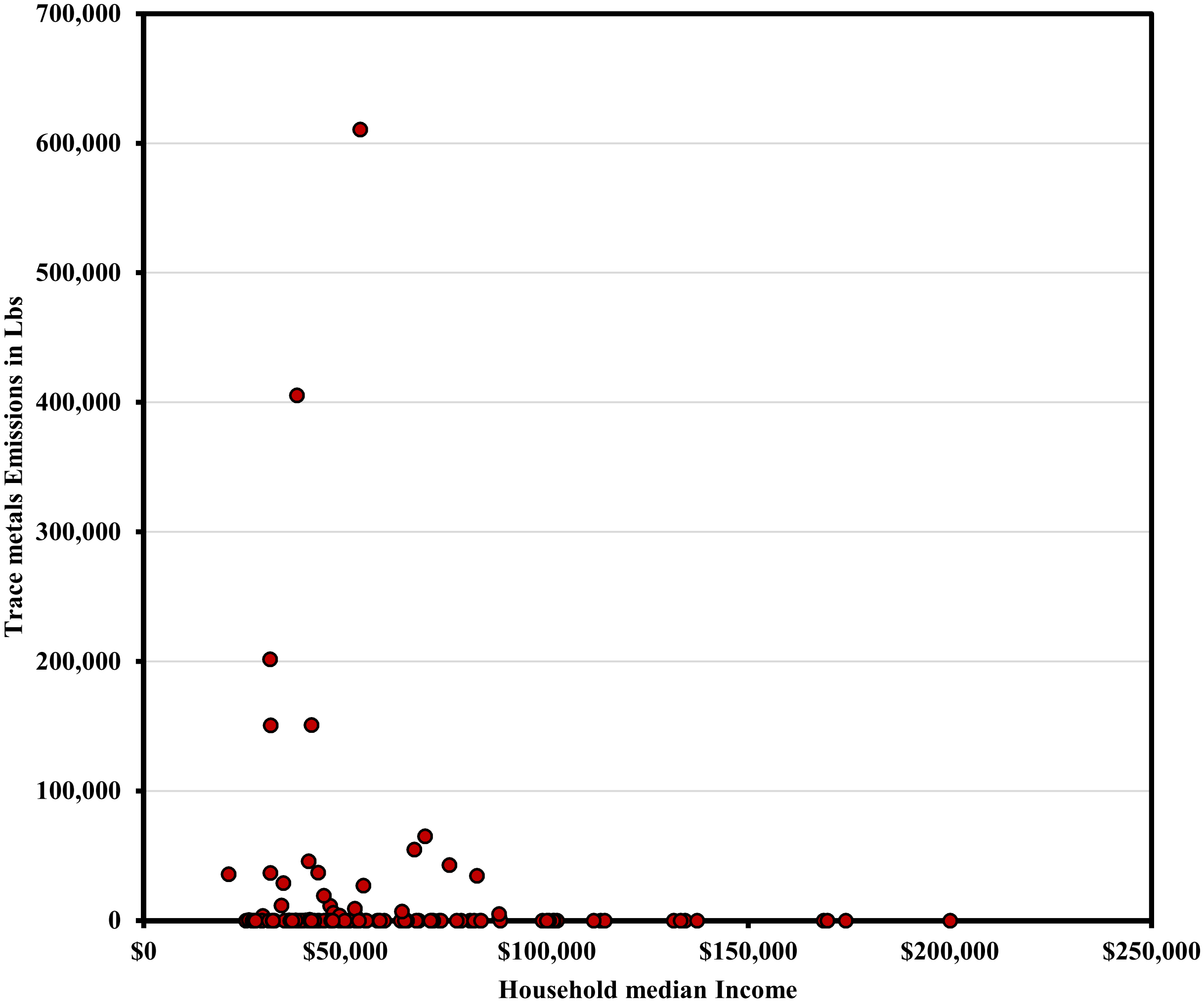

Figure 1 Industrial emissions reported to TRI vs Income
Trace metals emissions in lbs (TRI data ,2017, reported by industrial facilities to EPA) plotted against the median household income in $ (US Census Bureau data, 2010).

A type of EJ is to investigate whether communities of low socio-economic status face higher exposures to contaminants than wealthier communities (Clough et al., 2016). This study seeks to contribute to distributive EJ by investigating whether low-income communities living to proximity of industrial facilities face significantly higher exposure to surface soils trace metals.

Research hypothesis

Anthropogenic trace metal contamination in surface soils negatively correlate with income.

Research's objectives

The objectives of this study are:

1. To investigate Houston's surface soil contamination for 12 heavy metals and metalloids including Al, As, Cu, Co, Cd, Cr, Mg, Mn, Ni, Zn and Pb using data from an ICP-MS and XRF.
2. To explore the relationship between surface soils trace metal concentrations and economic status (annual income) and analyze the impact of closeness to industrial facilities on trace metal surface pollution
3. To compare regulations from various regulatory agencies regarding surface trace metal contamination

CHAPTER 2

LITERATURE REVIEW

Toxic Release Inventory

The Environmental Protection Agency (EPA) classifies the sources of pollution as point and nonpoint sources (EPA, 2018). The former point sources are identifiable and derived from stationary sources such as industries, mines, sewage treatment plants, and quarries. Accordingly, the pollution generated by these sources is traceable. On the contrary, pollution from nonpoint sources is not attributable since it is made from mobile sources such as vehicles (e.g., cars, buses, trains, and planes), stormwater runoff, and agriculture. EPA traces specific point sources through the Toxic Release Inventory (TRI).

TRI is a tool used by the EPA. Some industrial and waste facilities are required to report the amounts of TRI chemicals they manage, dispose of and release into the environment each year (EPA Toxic Release Inventory Program).

However, they are self-reporting to the TRI program (Johnson et al., 2014). A "release" of a chemical means that it is emitted to the air or water or placed in some sort of land disposal. The TRI Program currently covers 770 individually listed chemicals and 33 chemical categories. TRI chemicals include chemicals that can cause cancer or other adverse and/or acute human health effects and cause detrimental effects on the environment. Metals and metalloids like Pb, As, Hg, Ni, Zn, Al, Mn, Mg, and organic compounds such as benzene and ozone are examples of toxic chemicals monitored by the EPA.

Since only certain kinds of facilities are mandated to report their emissions, TRI data must be scrutinized. Industrial and processing establishments are obligated to report to TRI if they have at least ten employees; if the establishment is listed under the Standard Industrial Classification (SIC) codes 20–39; and if the facility produces, imports, or processes more than 25,000 pounds of any TRI chemical or otherwise utilized more than 10,000 pounds of a TRI chemical in a calendar year (EPA,1997). TRI numbers represent releases and other waste management activities. However, TRI environmental data does not convey information about whether (to a certain degree) the public has been exposed to these toxins. The evaluation of the releases alone is not enough evidence to find the exposure or assess the possible adverse effects on humans and the environment. TRI data combined with other evidence can be used in a general assessment assess of the exposure level generated by industrial and other activities associated with poisonous chemicals. Several factors must be considered for the estimation of the potential risk of a chemical: toxicity of the chemical, fate of the chemical and the volume and time of human or other exposure to the chemical after its release (EPA, 2020). Each facility reporting to TRI is also mandated to report its location, its SIC code and parent company. The Zone Improvement Plan (ZIP) code of the location of the facility combined with US census data can give information about the socio-economic characteristics of the neighborhoods (Arora & Canson, 1995).

Main sources of trace metals in urban environments

Urban soil is an essential compartment of the ecosystem that is subject to unplanned urbanization, a rapid use change, and extreme industrialization, resulting in pollution. Numerous studies have shown that the first layers of the soils are enhanced with several metals and other pollutants emanated by natural processes and anthropogenic activities. (Steinnes et al., 2011; Rodríguez-Eugenio et al., 2018). Trace metals in urban areas accumulate in the soil because of traffic-related activities and industrial activities (Li et al., 2004; Hamzeh et al., 2011; Faciu et al., 2012; Wang et al., 2018).

Industrial activities

Metals enter the environment during industrial processes when their compounds are crushed, heated, and dissolved. Industrial activities are accountable for releasing a large volume of pollutants based on the type of activity executed. The magnitude of emission depends on the particularity and proficiency of the industrial procedure. Consequently, trace metals in urban areas are found in elevated concentrations around mines, smelters, industrial complexes, and roadways (Navratil et al., 2005).

The global generation of metals has exponentially exploded over the years. For example, the production of Cu, Ni, and Zn has increased by two-fold in less than four decades. Table 1 displays the total annual production of some heavy metal(loid)s from 1973 to 2010 (Alloway, 2012). The amounts represent the entire element content except for barium (Ba), cadmium (Cd), and chromium (Cr).

Table 1 World mine production of heavy metals and metalloids (in ton of element content, except where stated) (Alloway, 2012)

		World production			
Elements	**Symbol**	**1973**	**1994**	**2004**	**2010**
Antimony	Sb	-	106,000	112,000	135,000
Arsenic	As	-	43,000	37,500	54,500
Barium*[a] (59%)	Ba	-	4,300,000	6,900,000	6,900,000
Cadmium*[b] (46.5%)	Cd	-	17,200	18,100	22,000
Chromium*[b] (46.5%)	Cr	-	9,570,000	17,000,000	22,000,000
Cobalt	Co	-	18,500	46,900	88,000
Copper	Cu	7,116,900	9,430,000	14,500,000	16,200,000
Gold	Au	-	2,300	2,470	2,500
Lead	Pb	3,487,000	2,800,000	3,150,000	4,100,00
Manganese*[c] (35-40%)	Mn	-	7,190,000	11,000,000	13,000,000
Mercury	Hg	9,300	1,760	1,750	1,960
Molybdenum	Mo	-	104,000	139,000	234,000
Nickel	Ni	710,000	906,000	1,400,000	1,550,000
Selenium	Se	-	1,880	1,500	2,260
Silver	Ag	-	13,900	19,500	22,200
Thallium (kg)	Tl	-	15,000	15,000	10,000
Tin	Sn	233,800	184,000	250,000	261,000
Tungsten	W	-	26,000	60,000	61,000
Vanadium	V	-	33,900	44,000	56,000
Zinc	Zn	5,709,400	6,810,000	9,100,000	12,000,000

* Tonnages of mined metal ores, rather than in metal (loid) content. [a]Barite = $BaSO_4$ (59% Ba) [b]Chromite = $FeCrO_4$ (46.5% Cr) [c]Mn ore (oxides) (35–54% Mn)

Industries that can potentially cause soil pollution can be categorized into six principal groups including energy industries; production and processing of metals; mineral industry, chemical industry, and installation; waste or textiles tanning of hides and skins; and production of carbon or graphite (García-Pérez et al., 2007). Selladurai et al. (2017) have also included and described salinization as a significant threat to soils, especially to those at the proximity of industrial facilities dealing with Chlor-alkali, textiles, glass, rubber production, animal hide processing, and leather tanning, and detergent production. Other industrial activities susceptible to polluting soil involve the manufacture of paper and board, production of fibers, poultry or pig rearing, industries employing organic solvents and pharmaceuticals, oil and gas drilling, pigment production, and ceramic production.

Similarly, the adverse impacts of the industries on the environment are well documented. Pollutants such as contaminants in gaseous form and radionuclides release into the atmosphere sink directly into the soil following atmospheric deposition or acid rain. Heavy metals are common in industrial sites and can result from dust, spillages of raw materials, wastes, final products, fuel, and fires (Alloway, 2013). The enormous amounts of dust emitted by industrial facilities contain As, Cu, and Zn, and other trace metals initiating surface soil contamination (Hu et al., 2018). Choppala et al. (2013) found that anthropic activities releasing Cr are generally solid waste disposal, sewage sludge, spills, and leaks from industries processing metals and other industrial processes. Multiple studies have also indicated that coal-fired power plants are the principal source of Hg (Streets et al., 2009; Zhang et al., 2015). Worldwide, industrial activities, lacking appropriate environmental procedures, are accountable for adulterating many soils with trace metals (Mackay et al., 2013; Lu et al., 2015; Podolský et al., 2015; Strzebońska et al., 2017). The improper chemical storage or direct discharge of waste into the ground, former industrial lands may still have enormous amounts of pollutants, including trace metals.

The adverse impacts of mining on the environment are countless (FAO and ITPS, 2015). Mining activities have intensively polluted various soils around the globe (Alloway, 2013). Mining and smelting industries produce copious amounts of many pollutants. Heavy metals and other poisonous elements are intensively introduced into the soil following the separation of minerals by metal smelting. These hazardous elements persist for extended periods, long after activities have ceased (Ogundele et al., 2017).

Human activities are primarily accountable for the occurrence of Pb in urbanized areas. Industrial sources of Pb include mining and smelting Pb ores or ores producing Pb as a byproduct or contaminant. Thus, soil, water, and air may receive a large volume of Pb during these processes. Fossil fuels such as coal also contain Pb as a pollutant. Likewise, electrical facilities that burn fossil fuels emit vast amounts of Pb in the flue form. EPA (2001) has estimated that the burning of 1 ton of lignite releases 4.2×10^{-4} pounds of Pb. For example, a boiler burning 1 million pounds of lignite coal emits 420 pounds of Pb into the air. Yedjou and colleagues (2012) estimated that the US industrial sector required a total of 1.52 million metric tons of Pb in 2004.

In 2001, the total amount of Cu generated in the US was estimated at approximately 5,050 metric tons. 91.9% of this production, equivalent to 4,360 metric tons, was released into the soil. Further, in the same period, 99.8% of the total amount of Cu compounds, approximately 454,000 metric tons was directly released to the soil (TRI, 2003). According to Perwak et al. (1980) the soil is the top receiver of Cu released by all sources combined. The principal sources of Cu are tailings and overloads, from Cu mines and tailings from mills. Most detrimental, Cu released from tailings is unrecoverable.

In 2015, the British Geological Survey estimated at 24,900 metric tons the global production of Cd (Brown et al., 2017). In 2016, the US Geological Survey (2017) estimated that 23,000 metric tons of Cd was produced worldwide (US excluded). All types of Zn ores contain Cd; therefore, substantial amounts of Cd are generated during Zn melting. Throughout Zn production, Cd dust is emitted and settled down in nearby soils (Bi et al., 2006; Hogervorst et al., 2007; Roy and McDonald, 2015). Every year, smelters and factories processing Cd emit 1,000 tons of Cd into the air, accounting for 45% of total Cd pollution (Navratil et al., 2005). Khan et colleagues (2016) highlighted that Cd's presence in urban soil is essentially due to industrial processes and vehicular emissions.

The destination of most of the Zn emitted is in the soils. Anthropogenic activities generating Zn into soils are released from smelter slags and wastes, mine tailings, coal and bottom fly ash, and commercial products such as fertilizers and wood preservatives containing Zn (ATSDR, 2005). Human activities, including power plants, smelters, mining wastes, and municipal, commercial, and industrial wastes producing ash residues, enhance urban soils with As. Ash originated by power plants may be combined with cement and other construction materials. Thus, ash residues used in roads and construction release As into the soil. In 1983, anthropogenic activities (mine tailings and smelter slag excluded) introduced between 52,000 to 112,000 metric tons of As with a median value of 82,000 metric tons (Nriagu et al.,1988: Pacyna et al. 1995). Mine tailings and smelter slags introduced between 7,200–11,000, and 4,500–9,000 metric tons, respectively. Abandoned mine tailings release As to soils to a greater extent.

Table 2 and table 3 give the possible trace metals associated with various type of industrial activity.

Table 2 Examples of possible combinations of heavy metal(loid) contaminants associated with different industries (Adopted from Alloway, 2012)

Industries	**Potential trace elements**
Chemical industry (general)	Ag, Sb, Se
Chlor-alkali (Cl_2 and NaOH) industry	Sb, As, Bi, Ba, Cd, Cu, Pb, Hg, Ag, Sn
Sulphuric Acid works	As, Cu, Pb, Ni, Pt, V, Zn
Nitric acid works	As, Cr, Co, Cu, Mo, Ni, Rh, V, Zn
Phosphoric acid works	As, Ba, Cd, Cu, Pb, U
Ceramics	Cd, Cr, Cu, Pb, Hg, Ni, Zn, Ce, Eu
Electrical components	Cu, Zn, Au, Ag, Pd, Pb, Sn, Y, Cr, Se, Sm, Ir, In, Ga, Re, Sn, Tb, Co, Mo, Hg, Sb, Hf, Ru, Ta, Te
Steel works	As, Cr, Pb, Mn, Mo, Ni, Se, Sb, W, V, Zn
Pesticide works	As, Cu, Cr, Pb, Mn, Zn, V, Th
Battery manufacture	Pb, Sb, Zn, Cd, Ni, Hg, Ag
Printing and graphics	Se, Pb, Cd, Zn, Cr, Ba
Catalysts	Pt, Sm, Sb, Ru, Co, Rh, Re, Pd, Os, Ni, Mo, Ag, Zn
Pigments and paints	Pb, Cr, As, Sb, Hg, Se, Mo, Cd, Ba, Zn, Co

Table 3 Sources of selected chemical compounds (Adopted from Navratil et al., 2005)

	Trace metals							
Paints & coatings	As	Cd	Cr	Pb	Cu	Hg	Sb	Zn
Crude oil processing	As	-	Cr	Pb	-	-	-	Zn
Iron & steel production	As	Cd	Cr	Pb	Cu	Hg	Sb	Zn
Nonferrous metal refinery	As	Cd	Cr	Pb	Cu	Hg	Sb	Zn
Plastic industry	-	Cd	Cr	Pb	-	-	-	Zn
Batteries, accumulators	As	Cd	Cr	Pb	Cu	Hg	Sb	Zn
Plant protection	As	-	Cr	Pb	-	Hg	-	Zn

Industrial activities in Houston MSA

There are 6,388 manufacturing establishments listed in the Greater Houston area.

Table 4 Manufacturing Overview Houston MSA 2018*

Manufacturing Industry	**Establishments**
Fabricated Metal Products	1,729
Machinery	806
Chemical	570
Computer and Electronic Products	318
Food	420
Petroleum and Coal Products	90
Plastics and Rubber Products	220
Nonmetallic Mineral Products	277
Electrical Equipment and Appliances	156
Transportation Equipment	136
Other Manufacturing	1,666
Total Manufacturing	6,388

** Four quarters ending Q3/18 Source: Texas Workforce Commission, Quarterly Census of Employment and Wages BASE* (Greater Houston Partnership, 2019)

The Houston Region is home to 570 chemical plants. Houston metropolitan bears 44.2 % of the total American base petrochemicals manufacturing capacity split in 48.7% butadiene, 48.1% ethylene, 47.0% of propylene, 39.1% benzene, 33.2 % xylenes, and 33.3% toluene of the country production (See Table 5). Base petrochemicals are the raw materials for manufacturing some of the essential plastics and resins. In addition, Houston MSA leads the US production of three main resins, including polypropylene, polyethylene, and polyvinyl chloride, with a production capacity of 47.8%, 44.2%, and 34.1%, respectively.

Table 5 Base chemical production capacity Houston MSA, 2019

	Million Metric Tons per year	**% of U.S. Total**
Butadiene	1.2	48.7
Ethylene	17.2	48.1
Propylene	14.8	47
Benzene	3.3	39.1
Xylenes	4	33.2
Toluene	1.9	33.3
Total	42.5	44.2

Petroleum Refining

The Spaghetti Bowl refers to a complex of many thousand miles of product pipeline connecting hundreds of chemical plants, refineries, salt domes, and fractionation plants along the Texas Gulf Coast. As stated by the US Energy Information Administration, in 2018, Houston Metropolitan had a crude operating capacity of 2.6 million barrels of refined petroleum products per calendar day. This number represents 13.8 % of the total US capacity (Houston Partnership, 2019). Table 6 shows the different petroleum refineries, daily barrel production, and the city where they are located.

Table 6 Petroleum Refining Capacity Metro Houston, 2018

Company	Barrels Per Calendar Day	City
Marathon Petroleum Co	571,000	Galveston Bay
Exxon Mobil Refining & Supply Co	560,500	Baytown
Deer Park Refining	275,000	Deer Park
Houston Refining	263,776	Houston
Phillips 66 Company	256,000	Sweeny
Valero Refining Co Texas	225,000	Texas City
Valero Refining Co Texas	199,000	Houston
Pasadena Refining Systems	112,229	Pasadena
Kinder Morgan Crude & Condensate	84,000	Galena Park
Petromax Refining Co	25,000	Houston
Total Metro Houston Capacity	2,571,505	
Percent of US Capacity	13.8	

Source: U.S. Energy Information Agency, Refinery Capacity Report January 1, 2018 (Release Date: June 25, 2018) (Greater Houston Partnership 2019)

Metal Recyclers Facilities

In 2015, the American metal recycling industry produced more than 20 million tons of ferrous and nonferrous metals. The total number of operating scrap facilities is estimated at 8,160. Texas ranks the second place with a total of 672 facilities. Of this number, 130 metal recyclers in operation are in Houston (Han et al.,2020).

Dangers of living in the vicinity of industrial facilities

Industrial complexes are significant sources of particulate matter (PM). Thus, living in the proximity of industrial facilities is a significant threat to human health. Communities in the vicinity of industrial centers, primarily metal industrial areas, are recognized to bear higher concentrations of toxic elements adsorbed to PM compared to neighborhoods distant from industries (Kim et al.,2006).

According to the EPA, nearly 150 catastrophic accidents occur annually in regulated industrial facilities. Fenceline communities in Houston well-illustrate the danger of living in proximity to industrial sites. Fenceline communities are neighborhoods that are directly adjacent to a company and are directly affected by the noise, odors, chemical emissions, traffic, parking, and operations of the company (Burke, 1999). These communities endure a greater burden of environmental hazards and a higher occurrence of industrial accidents such as accidental leakages and plants' explosions during which the amount of pollutants released is amplified (Union of Concerned Scientists, 2016). Moreover, the history of the burning of industrial facilities emanating dangerous chemicals is well sustained in Greater Houston. 425 chemical accidents occurred between the explosion in April 2013 at the West Texas fertilizer facility and August 2015. In 2017, the historical hurricane Harvey brought thousands of gallons of water in East Texas, causing several industrial accidents during this disaster, ranging from accidental leaks to industrial plants' fires. Several communities were then exposed to prominent levels of toxic pollutants, including trace metals.

Industrial accidents are not limited to Houston. Many investigations around the world have mentioned similar disasters. Activities related to oil products are essential point-sources pollution producing hydrocarbons and poisonous metals. In Denmark, Fritt-Rasmussen et al., (2012) reported the contamination by heavy metals due to the leakage of tanks situated in Greenland. In Tehran, Iran fortuitous leakages from oil refinery storages also caused soil pollution by heavy metals (Nabavi-Pelesaraei et al., 2017).

Industrial activities negatively impact the health of populations. Thus, in China, more than 5,000 brownfields are accountable for deleterious effects on the population health (Yang et al., 2014). Urban brownfields located in the centers of agglomerations are former industrial facilities presently relocated **(**Rodríguez-Eugenio et al., 2018).

Traffic related activities

The population growth associated with urban sprawl from 1945 to today, leads to the surge in use of motorized vehicles and the overall distance traveled. In the USA, from 74.4 million registered cars in 1974, this number sharply rose to 254 million in 2012 (USDOT, 2015). Also, the US total vehicle traveled distance went from 1.15 trillion km in 1960 to 4.75 trillion km in 2012 (USDOT, 2015). As a rapidly sprawling metropolitan, traffic in Houston MSA is one of the densest and most congested in the US, thus the presence of major roadways (Texas A&M Transportation, 2015).

A large body of literature has provided evidence that traffic-related activities constitute a significant source of environmental contamination, specifically in the urban environment (Hwang et al., 2016). Thus, in sprawling urban cities like Houston, pollutants from automobiles are more alarming because of the tremendous traffic volumes and congestion. Primary sources of pollutants released by motor vehicles include exhaust emissions and non-exhaust emissions. Exhaust emissions or tailpipe emissions comprise byproducts of lubricant volatilization and incomplete fuel combustion such as soot particles, carbon monoxide (CO), oxides of nitrogen (NOx), oxides of sulfur (SOx), volatile organic compounds (VOCs), and polycyclic aromatic hydrocarbons (PAHs). These byproducts are directly released into the atmosphere and eventually deposit into the soil (Faiz et al., 1996). Non–exhaust traffic emissions contain brake, tire, and pavement wear caused by abrasive forces, discharging particulate matter into the ambient air (Faiz et al., 1996; Viana et al., 2008). PM emitted into the atmosphere are laden with harmful trace metals including Pb, Cu, Zn, Cd, Cr, Co, Ni, and V. The particulate matter emitted into the air ultimately sinks into the soil causing contamination.

Road traffic emissions include vehicle exhaust, tire and brake wear, and resuspended dust (Soltani, 2015). Numerous studies on road traffic have demonstrated that the historical use of lead in gasoline and petrol was accountable for Pb urban soil contamination (Thorpe & Harrison, 2008; Pant & Harrison, 2013; Wang et al., 2017; Appleton, 2018). Accordingly, Pb principal source in surface soils is due to automobiles (Roberts et al., 2011). Pb has been widely used in the automobile industry. In the early 1920s, the discovery of tetraethyl lead (TEL) resulted in its addition to gasoline to improve engine performance. TEL and methyl-tertiary butyl ether (MTBE) were used as fuel additives and had caused substantial Pb environmental pollution (Nriagu, 1990; Faiz et al., 1996). TEL was alone responsible for 98% of the total Pb pollution. In 1984 leaded gasoline was alone responsible for 90% of all anthropogenic Pb productions (EPA 1996). The phase-out program of leaded gasoline was initiated in 1978 in the US and was complete in 1996. This phase-out was principally due to the harmful effects of leaded gasoline on human health and the environment. From mid-1920s to the complete phase-out of Pb-gasoline in late 1990, more than 7 million tons of Pb was introduced into the US (Hwang, 2016 and references therein). In Sydney, Australia, Kristensen (2015) estimated seven decades of leaded fuel use had generated approximately between 34,000 and 41,000 tons of Pb emitted from tailpipes.

In the US, Pb concentration in urban soils is still exceeding the background level despite the complete phase-out of leaded gasoline in 1996 (Newell & Rogers, 2003) due to Pb used in the wheel's weight balance. Over time, lead wheel weights break up into small particles by vehicle traffic (Root, 2000). In the mid-2000, approximately 64 million tons of Pb were annually used worldwide in the production of wheel balancing weight (Bleiwas, 2006). Another source of Pb from fossil fuel powered vehicles is acid batteries. Along with sulfuric acid and water, acid batteries contain Pb plates (Hwang and al., 2016). Pb enclosed in the Pb-acid-based battery represents more than 90% of Pb total amount in a car. Recent cars retailed in the US contain 10 kg for passenger cars and 12.5 kg for heavy-duty trucks of Pb in every Pb-acid-based battery. Within 2005 and 2009, nearly 3.6 billion kg of lead has been utilized in the production of cars and trucks (Statistics, 2014). Unfortunately, Pb lost by the acid battery during a collision, for instance, is practically impossible to recover, inducing the pollution of urban soils. According to Hwang et al. (2016), a meaningful fraction of Pb released by vehicles is left on urban surfaces.

Other vehicles emissions involve barium (Ba), Cd, Cu, Cr, and Zn produced by the wear of tires and brake linings, fuel combustion, and leaked fluids (Nezat et al., 2017). Fakayode et al (2003) found an association between high traffic density and trace metals concentrations. High concentrations of trace metals were recorded at high traffic density roads compared to moderate and low traffic density roads. Consequently, brake dust and tire wear have been extensively investigated in several studies on non-exhaust vehicle emissions because of the environmental concern of Cu and Zn. Brake dust and tire wear are associated to adverse effects on fish and other aquatic organisms resulting from Cu and Zn toxicity (Hwang et al. 2016). Lesser-known non-exhaust sources include wheel balancing weights, motor oil leaks, and pavement wear. (Hwang et al. 2016). Affixed to nonpermanent locations, lead wheel weights inevitably become loose due to wheel jarring, dislodge, and are pulverized into small particles by vehicle traffic (Root 2000). As a result, the abrasive forces on vehicle tires released into the environment, particulate matter, and trace metals from the pavements.

Cu is added to friction material in brake pads. When brakes are hit, brake pad friction material is heated following the contact with a disk rotor. A petite portion of the friction material is then released and deposited on traffic areas, parking lots, and neighboring soils. Hence, brake pads are accountable for an essential fraction of Cu in urban areas (Hwang and al., 2016). In the mid-1990s, the entire quantity of Cu originated from brake pad deterioration was evaluated at 1.42 million kg per year in the USA (Lifset et al., 2012). However, in 1998, Garg et al. (2000) assessed a different emission rate of Cu from the deterioration of brake pad in the US (approximately 1 mg/km per vehicle bringing up the total Cu emitted at 4.8 million kg in the US (Hwang and al., 2016).

In urban zones, Zn is essentially produced by tires and galvanized metals (CASQA, 2015; Vos & Janssen, 2009). Global substantial levels of Zn in urban soils indicate that tire wear is predominantly responsible for Zn pollution (Yuen et al., 2012). Tire production is the largest consumer of Zinc Oxide in the world and alone consumes more than half of the total production of Zn, estimated at 1.2 million metric tons (Walter, 2009). The percent of Zn in every tire is approximately 1.5% of Zn by weight (Councell et al., 2004). Therefore, the friction of tires delivers a large amount of Zn. For instance, Hwang et al. (2016) estimated that about 8.8 and 8.0 million kg of Zn were introduced to the environment during 1999 and 2012 due to tire wear. Councell et al. (2004) estimated that between 10 and 11 million kg of Zn were released from tires in the US in 1999. Similarly, galvanized crash barriers and road signs contribute to Zn and Cd pollution in urban soils (Legret & Pagotto, 2006; Kluge & Wessolek, 2012). Palm & Östlund (1996) estimated 17 tons of Zn were annually released by street furniture, tires, and buildings.

Industrial processes and vehicular emissions are Cd principal sources in urban soils (Khan et al., 2016). Cd use as a stabilizer in tires and automobile exhaust production has caused urban soil pollution (Ellis & Revitt, 1982). Motor oil leaks on pavement surfaces involve multiple trace metals depending on the oil formulation and engine wear. Trace metals in concrete and asphalt enormously fluctuate based on the actual supply of aggregates, binders, and filters (Thorpe & Harrison 2008). Fiala et al. (2019) estimated the motor vehicles releases of non-exhaust emissions in Houston MSA to be 149,000 kg, 58,000 kg, 54,000 kg, and 20 kg per year for Zn, Cu, Pb, and Cd, respectively. In table 7 are given the annual emissions in tons of trace metals by emissions source based on 6 million of vehicles.

Table 7: Emissions of trace metals (in tons per year) by car traffic per emissions source, based on 6×10^6 vehicles (Adopted from Ajmone-Marsan, 2010)

Contamination	**Exhaust**	**Oil leaks**	**Tires**	**Brakes**	**Radiator**	**Total**
As	0.17	0.015	0.013	0.004	-	0.20
Cd	1.2	0.002	0.73	-	-	1.9
Cr	1.7	0.014	2.6	0.518	-	4.8
Cu	0.25	0.061	3.65	9.072	50.9	63.9
Pb	240	1.96	-	0.022	0.072	242
Ni	1.7	0.007	2.48	0.285	0.192	4.7
Zn	2.3	1.49	175	0.117	0.168	179

Traffic related activities in Houston MSA

In 2019, a total of 5,478,148 vehicles were registered in the region. Public transportation is insufficient in the metropolitan. As a result, traffic in Houston Metropolitan Area is one of the densest and most congested in the country, ranking third in the US (Texas A&M Transportation, 2021) despite the 3,309 centerline miles and 10,759 lane miles of freeways and expressways in operation. Also, certain highways may exceed more than 350,000 vehicles per day (TxDOT, 2016). In 2019, motorists in the region traveled 96,685,315 vehicle miles per day, corresponding to an average daily Vehicle Miles Traveled (VMT) per vehicle of 17.6 miles (Greater Houston Partnership, 2020).

Danger of living in the vicinity of busy roadways

Scientific evidence has linked busy roadways to innumerable adverse health effects on nearby living populations (Reynolds et al., 2004; Holguin, 2008; Oakes et al., 2016 references therein). Deleterious health effects range from respiratory diseases including asthma, bronchitis, lung cancers, cardiovascular ailments, reproductive problems such as low birth rates, miscarriages, preterm births, stillborn, to death. Higher rates of autism have been reported in children living in the proximity of busy roadways (Volk et al., 2011).

Fate and transport of trace elements in the urban environment

A substantial amount of research has demonstrated that trace metals enter urban environments through atmospheric emissions. (Nriagu & Pacyna, 1988; Kubin & Lippo, 1996; Wong et al., 2003; Wong et al., 2006). Once emitted, trace metals adhere to PM to generate fine particulates and dust (Vesper &White, 2003). Particles loaded with trace metals prevail in the air until deposited in the soil and in water. Metal distribution and dispersion strongly depend on the particle size and the receptor substrate's surface properties.

Trace elements entering the environment are incessantly transported between the different compartments, including air, water, and soil, following natural chemical and physical processes such as weathering and precipitation. The principal pathways of trace metals are ground deposition surface runoff, dry deposition, air/water gas exchange, water/air gas exchange, wet deposition, groundwater, and surface water runoff. In urban soils, trace metals can easily be displaced, disseminated by wind, rain, and surface runoff (Callender et al., 2000).

Soils are the top sinks of pollutants due to the soil high chemical binding ability. Countless chemicals in various forms can be found bound in soil particles by diverse forces. In the environment, trace metals (metals and metalloids) are found in a wide range of compounds as free ions, inorganic and organic complexes, metal species associated to significant molecular organic materials (lipids, humic acids, polysaccharides), or adsorbed on clays and colloids. In evaluating metal mobility, biological activity, and toxicity, metal speciation is essential (Navratil et al., 2005). The toxicity of the metal in the environment ultimately depends on its form (Dube et al., 2001). The mobility of metals in soil depends on the clay content, the amount of organic matter, and the pH. In the surface layers of aerially polluted soils, metals persist for years. In aquatic media, metals may be trapped in the lowest sediments, where they remain for extended time periods. However, when the pH decreases, trace metals mobility in the soil increases. For such, acid rain is accountable for transporting trace metals deeper in soil, leading to the damage of deep-rooted plants and polluting groundwater (Walker et al., 2012).

Many studies have highlighted that urban dust and rural surface soils are strongly influenced by atmospheric deposition (Yu et al., 2016; Wand et al., 2018). Urbanization is accountable for huge impervious surfaces in urban areas. As a result, significant hard and impervious surfaces are characteristics of urban scenery. Blansett & Hamlett (2013) reported that impervious surfaces occupy two-thirds of the total surfaces in highly developed urban areas. Aerosol particles contained in the air, ultimately settle down on pervious and impervious surfaces due to atmospheric deposition. When aerosolized particles are deposited on pervious surfaces, trace metals can then infiltrate into the soil column (Fiala, 2017). On the contrary, particles left on the impervious surface are carried out by the stormwater runoff and brought to surface waters, enhancing them with trace metals. The enlarged fraction of impervious surfaces in urban areas considerably raises the volume and velocity of runoff during storms (Andoh, 1994). Klein (2019) emphasized that in cities, an increase in water imperviousness enormously contributes to the impairment of receiving water bodies. Thus, the impairment may be initiated when watershed imperviousness gets to 12 %, and values attaining 30% were likely to cause extreme damage (Klein, 1979). Consequently, receiving waters including ponds, lakes, streams, rivers, and bays (Legret & Pagotto, 1999; Hwang & Foster, 2006) may be impaired and sensitive aquatic organisms adversely impacted (Hwang et al., 2016).

Similarly, the wind and traffic associated forces may easily resuspend finer particles deposited on or at the proximity of roadways (Acosta et al., 2011). As a result, these finer particles may enter inside urban residences (Chu et al., 2012). Campbell et al. (2018) substantiated that trace metal contamination of indoor air and dust are a strong indication of elevated concentrations of trace metals in outdoor soil. Indoor dust enriched with trace metals is a significant source of exposure through inhalation and ingestion (Laidlaw et al., 2017).

Particles-laden with trace metals are carried to sediments due to their significant solid-water affinity. They can persist in sediments at elevated concentrations for an extended time, sufficient to cause harmful effects to benthic communities (Fleeger et al., 2003). Urban waters, as a result, are contaminated with more trace metals and often surpass sediment quality guidelines (Hwang et al., 2006; Barlow et al., 2014). The use of Pb in gasoline, prior to 1992, and in other parts of vehicles has contributed to intensively enhance urban areas with Pb. Most of the Pb emitted by motorized vehicles is deposited on an urban surface and is eventually washed off during storm events, carried to watersheds. Thus, legacies of leaded gasoline use can still be found in urban waters, sufficient to impair the quality of urban receiving waters.

Concentrations of trace metals in stormwater runoff found into the literature differ as they are described in dissolved or total (dissolved concentration combined to particle phases) concentrations. Thus, Pb is likely to be found in particle phase in aqueous solutions due to its solid-water partition coefficients (Kd) ranging from 10^3 to 10^5 L/kg (Sansalone & Buchberger, 1997).

Besides Pb, significant concentrations of Zn in urban stormwater runoff compromise the quality of receiving water bodies (Tuccillo, 2006; Nason et al., 2012). In many cities, an association, between Zn concentration in urban stormwater runoff and/or sediments and volume of fuel retailed, has been observed. The amount of fuel sold is an indication of the traffic volume in the city (Wiesner et al., 1998). Zn solid–water partitioning coefficients range between 10^2 and 10^4. More than half of the Zn contained in stormwater is in the dissolved form (Stead-Dexter & Ward, 2004). In a lot of urban environments, surface waters have concentrations of Zn surpassing water quality criteria due to high volume of stormwater runoff received (Vos & Janssen, 2008).

The urban mean concentration of Cu, in the air, is estimated at 200 ng/ m^3. In the air, Cu is related to particulates generated by suspended soils, combustion sources, production, or processing of Cu-containing materials, or mine tailings. Cu bounded to atmospheric particulates sinks on soil following gravitational settling (bulk deposition), dry deposition (inertial impaction characterized by a deposition velocity), in-cloud scavenging (attachment of particles by droplets within clouds), and washout. With 97 %

of Cu released sinking, soil is the environmental compartment the most impacted by Cu (Perwak et al. 1980). The concentration of Cu in natural waters (e.g., rivers, lakes, and oceans) is between 4 and 10 ppb, whereas mean Cu concentrations in urban stormwater runoff in the US vary between 12 and 159 ppb (Nason et al., 2012). Cu is transported in waters bounded to PM. In urban areas, impervious surfaces lead to runoff which significantly enhances receiving waters with Cu. A study conducted by Cole et al. (1984) found that concentrations of Cu in 96 runoff samples ranged from 1 to 100 ppb with a geometric mean of 18.7 ppb.

Trace metals adverse health effects

Evidence of metal adverse effects on humans and the environment has been widely presented by numerous scholars (Awofolu et al., 2005; Vigeh et al., 2006; Wirth et al., 2010; Yu et al., 2012; Kim et al., 2019; Niemeyer et al., 2020). Heavy metals can adversely impact living organisms by inhibiting cell organelles (e.g., cell membrane, mitochondria, lysosome, endoplasmic reticulum). They can deter enzymes involved in metabolism, body cleaning, and damage reparation. Heavy metals may cause oxidative stress, DNA alteration, and protein damage resulting in cycle modulation, carcinogenesis, or apoptosis (Tchounwou et al., 2012). Risks from elevated concentrations of trace metals in soils generally involve the contamination of the groundwater or the threat to the food chain through plant uptake. However, in urban environments, due to the closeness of populations to the soil, risk exposures arise following dermal contact, direct ingestion, and inhalation of soil particles rich in trace metals (Ajmone et al., 2010). Thus, in the risk assessment of contaminated sites, ingestion and inhalation of soil particles are of particular concern.

Concentrations of trace metals intensify in biological organisms with time compared to the environment due to a greater absorption rate than excretion rate.

High concentrations of PM are a primary environmental concern in large urban environments (Lee et al., 2005; Krzyzanowski et al., 2014). Air flows initiated by wind, and traffic-related forces resuspend the finest soil particles (<10mm) (Huo et al., 2003, Kassomenos et al. 2012), rising atmospheric PM levels. A significant amount of dust inhaled by humans is trapped, absorbed, and passed by the gastro-intestinal tract. Besides, a certain amount of dust is trapped inside the lungs. Lung physiology can be affected when particles are loaded with trace metals due to the metal high adsorption efficiency (60% to 80%) (Ajmone-Marsan, 2008). Once inhaled, coarse particles (PM_{10}) settle down in the upper respiratory tract. On the contrary, the finest particles settle down in the pulmonary alveoli. Over time, these particles trigger lung inflammation and initiate respiratory ailments like bronchitis, pneumoconiosis, asthma, lung cancer; and cardiovascular ailments (Dominici et al., 2004; Pope III et al., 2004; Sun et al. 2010; Xia et al., 2016). The lung's response to dust ultimately depends on the type and amounts of dust inhaled (Cohen et al., 2020). Research led by Yamamoto et al. (2006) revealed that the fine soil particles (modal size smaller than 39 mm) can bind to children's hands and potentially be ingested due to hand to mouth behavior. According to Davis et al. (2006), children have a daily ingestion rate of 37 to 207 mg/day compared to 23 to 625 mg/day for adults. The average amount of soil ingested by children under six years is estimated at 1,200 mg/day by EPA (2002).

Some trace elements such as Se, Cu, Zn, and Cr are essential micronutrients for life processes in minute concentrations, but in higher concentrations, they are all toxic (Amin et al., 2020). Cr has been related to the development of respiratory-related complications such as asthma and a decrease in the forced expiratory volume linked to other respiratory complications, including wheezing, coughing, nasal blockage, and facial erythema (Wilbur et al. 2012). Cr can also cause respiratory cancers. Similarly, high uptake of Cu may result in anemia, liver and kidney damage, stomach, and intestinal exasperations (Wilson disease). Zn is linked to anemia and tissue lesions (Brevik, 2013). Ni is responsible for many types of cancers.

Non-essential trace elements like As, Pb, Cd do not have established biological functions and should not be present in the organism. Arsenic can induce cardiovascular and peripheral vascular diseases, developmental anomalies, neurologic and neurobehavioral disorders, diabetes, hearing loss, portal fibrosis, hematologic disorders (anemia, leukopenia, and eosinophilia), and carcinoma. It can also damage the skin and affect the circulatory system (Scragg, 2006). Likewise, As is associated to diverse types of cancers including bladder, kidney, skin, and liver cancers. Cd is highly toxic. It may impair the liver, the bones, and the kidneys, and trigger lung cancer (Manahan, 2003). Chronic exposure to Cd can cause osteoporosis and alter pulmonary function. Pb is highly toxic and can impair various organs of the human body. Pb may adversely impact the kidneys, liver, central nervous system, hematopoietic system, endocrine system, and reproductive system. Due to the neurotoxin adverse effects, children are at greater health risk exposure to Pb (Yang et al., 2013, Zeng et al., 2019, Pan et al., 2020). In adults, Pb may affect the nervous system, kidney function, and cardiac function and lead to severe and irreversible health damage (Spivey 2007).

Techniques to determine trace metals' concentrations in soils

Standard methods for evaluating trace elements in soils include a combination of conventional wet chemistry/instrumental techniques such as atomic absorption spectrometry (AAS) inductively coupled plasma-atomic emission spectrometry (ICP-AES) or inductively coupled plasma-mass spectrometry (ICP-MS), wavelength dispersive XRF (WD-XRF), energy-dispersive XRF (ED-XRF), and portable ED-XRF (Byers et al., 2019 and references therein).

ICP-MS and XRF are common analytical methods used in soil analysis. Both techniques have their advantages and disadvantages, and the validity of a result has always to be checked. Common problems are spectral interferences of matrix components. Today, several legal regulations concerning pollutants in soils are found on extractable concentrations. This tactic can result in erroneous results since an uncontrolled amount of trace elements can be extracted from the fraction naturally present from rock erosion (Moor et al., 2001).

Soils represent a matrix with intrinsic heterogeneity and variable mineral composition, leading to analytical complexity. Analytical methods for the elemental analysis of soil usually involve the sample matrix's partial or total breakdown. Urban soils fluctuate critically in total and bioaccessible trace elements concentrations (Mooradi et al., 2015). Recoveries and precision of elements via pseudo-total and total digestion methods diverge depending on numerous factors, such as the mineral composition and origin of the soil, the digestion method, along with the elements of interest (Voica et al., 2012). The soil researchers have documented this challenge, and subsequently, acceptable precision and accuracy for digestion techniques have been reported as typically less than 20%.

Besides, the determination of some trace elements in the soil is challenging and may necessitate developing different specific methods for a comprehensive multi-elemental analysis. Techniques for total metal estimation are available and should be applied in combination with partial extraction techniques, the latter being comparable to the conditions of the natural processes leading to metals in the samples (Moor et al., 2001).

For these reasons, there is an increasing interest in finding alternative and/or complementary robust sampling techniques that directly analyze solid matrices.

CHAPTER 3

DESIGN OF STUDY

Study Area

Houston Woodlands-Sugar Land MSA is a nine-Texas county area that includes Austin, Brazoria, Chambers, Fort Bend, Galveston, Harris, Liberty, Montgomery, and Waller located along the Gulf Coast in Southeast Texas. This region has a total area of 10,062 sq miles (26,060 km^2) of which 8,929 sq mi (23,130 km^2) is land. The climate is classified as humid subtropical. Figure 3.1 shows a map of this area.

In 2019, the metropolitan's population was estimated at 7,066,140 people, making it the fifth most populous metropolitan in the US. This metropolitan hosts the fourth populous city in the US, Houston, and the third largest county in the US being Harris County. From 2010 to 2019, the region's population increased by 1.14%. The racial demographics are 35% White, 17% Black and African American, 8% Asian, 2% from two or more races, and 38% Hispanics and Latin Americans of any race. The median household income is estimated at $69,193 and the per capita income at $35,190. 12.9% of the residents, of which 18% of children under 18, live below the level of poverty (Greater Houston Partnership, 2020).

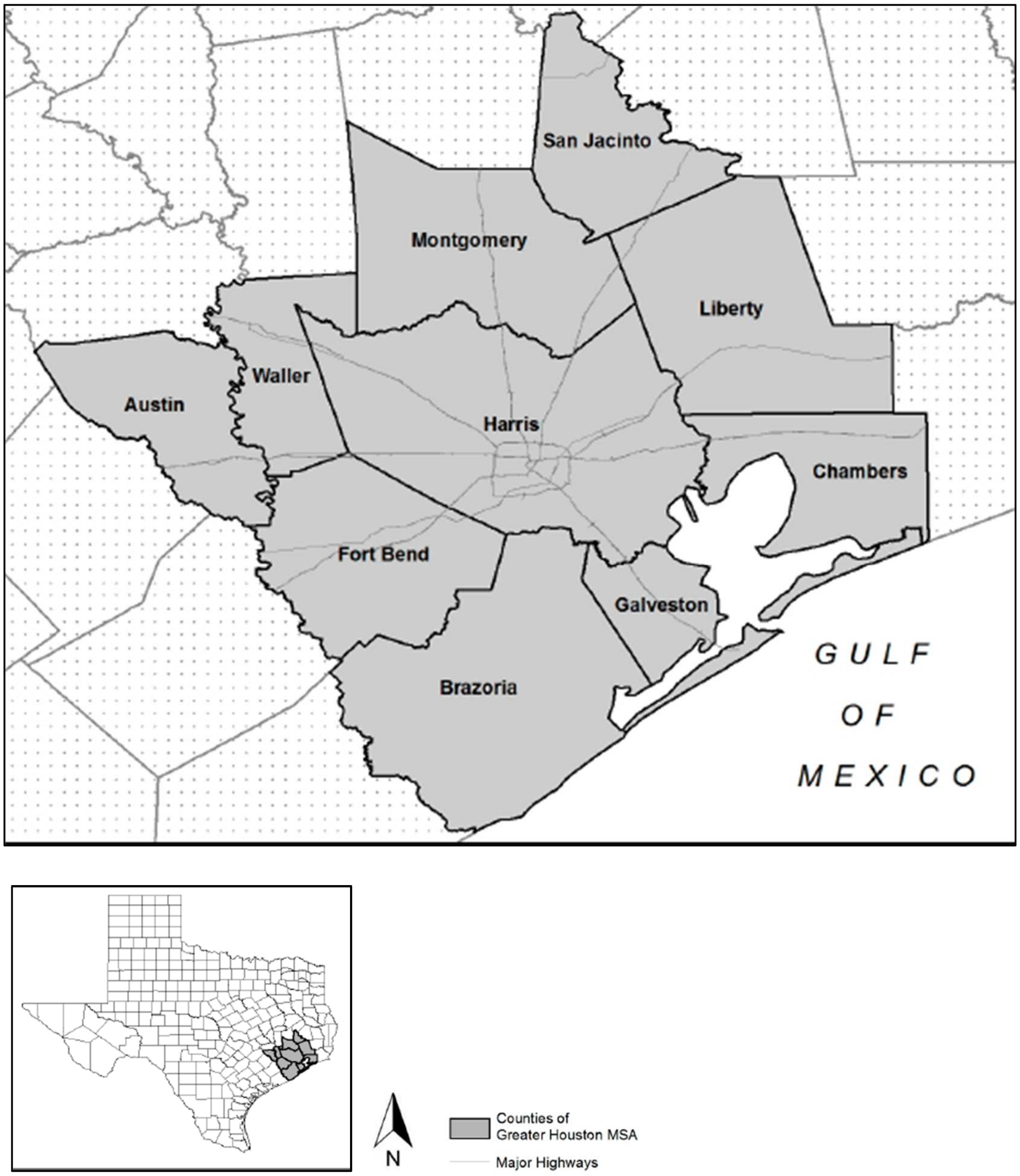

Figure 2 Location of the Greater Houston Metropolitan Statistical Area (MSA), 2021, Texas, USA

Study experimental design

Selection of ZIP codes

To investigate the relationship between income and soil pollution, trace metals' emissions were estimated using the TRI data, and the income was evaluated using the US 2010 Census data. For each ZIP code, historical TRI data from 2014 to 2018 were downloaded to estimate industrial facilities' environmental pollution. The TRI data provided an estimate of the volume of common trace metals generated in each ZIP code. ZIP codes were chosen based on reported industrial emissions (with and without industrial emissions).

To better understand household incomes in Houston MSA, US 2010 census data were employed. The economic status of communities was defined based on an annual household median of $40,000. Although, US Census Bureau estimated the annual median household income at $49,445 in the US (2010), in a survey complete in 2017, it used $40,000 as a threshold in separating low income and middle-high income households (US census survey, 2017). In the present study, ZIP codes with a household median income below $40,000 were considered low income. While ZIP codes with the annual median household income surpassing $40,000 were classified as middle- high income.

In total, 33 economically different zip codes were chosen in Houston and surrounding suburbs, including Alvin, Jersey Village, Bellaire, LaMarque, Galena Park, and Pasadena. The ZIP codes were split into four groups based on economic status (median annual household income) and industrial emissions (annual releases reported to the TRI):

Table 8 Income Groups and Emissions Range

Groups	*Income Groups & Emission Range*	*Zip codes*
Group A	Middle-High Income without industrial emissions	77004 77005 77098 77019 77079 77084 77094 77504 77568
Group B	Middle-High Income with industrial emissions	77015 77040 77041 77064 77590 77511 77571 77503 77507
Group C	Low income without industrial emissions	77020 77021 77022 77036 77051 77060 77067 77072 77057 77081
Group D	Low income with industrial emissions	77012 77013 77023 77029 77091 77547

Selection of sampling sites

For comparison, sampling sites were selected based on economic status and proximity to anthropogenic trace metals sources. Industrial facilities and highways are the primary anthropogenic sources of trace metals considered in this study. Thus, the selected sampling sites of parks and playgrounds in elementary schools were separated into four groups:

- Sampling sites at the proximity of highways and industries
- Sampling sites at the proximity of highways and distant from industries
- Sampling sites at proximity of industries and distant from highways
- Sampling sites distant from highways and industries

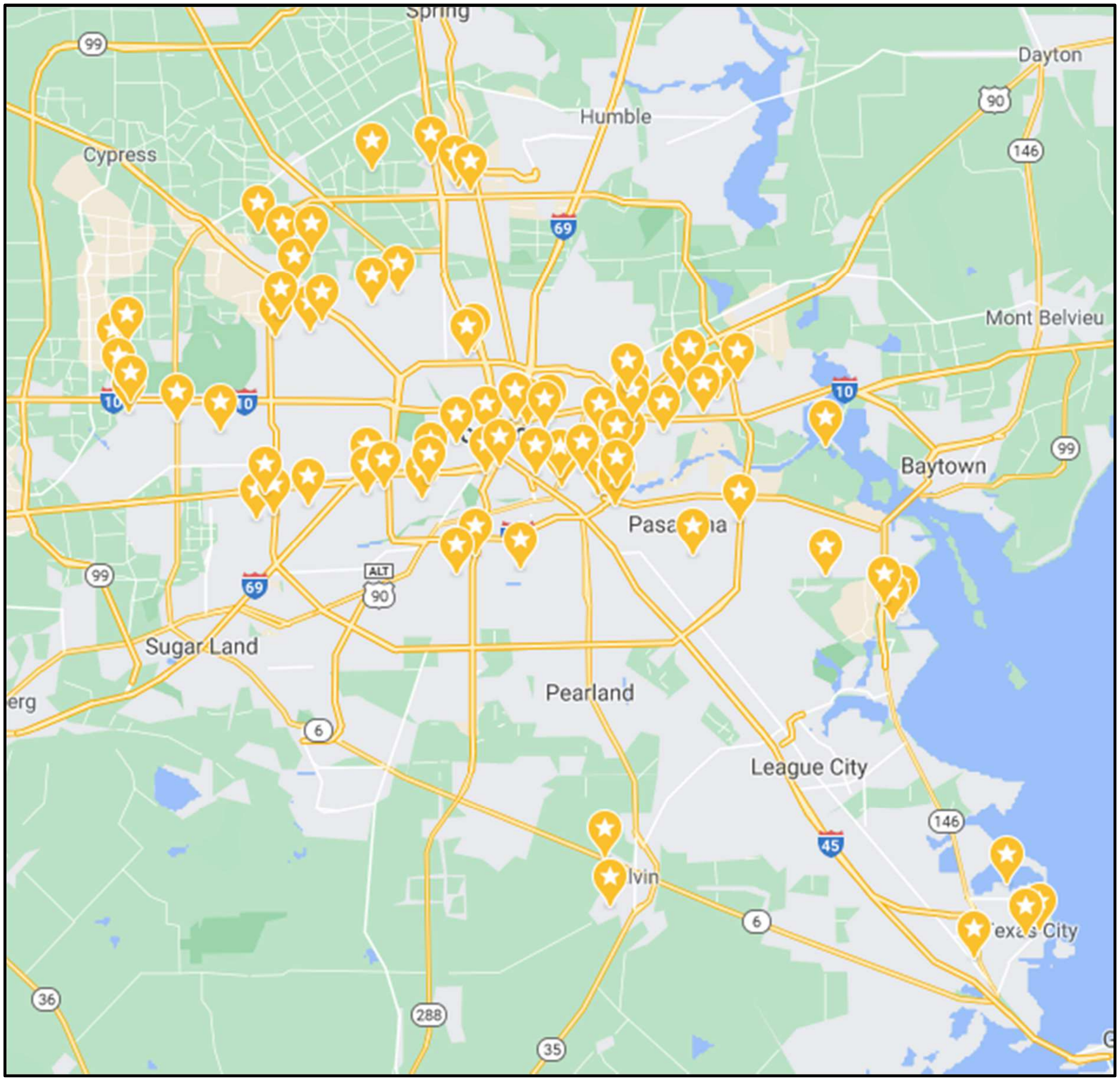

Figure 3 Soil sampling sites in Houston Metropolitan Statistical Area (Google map, 2019).

Sample collection and preparation

Surface soils were collected in Houston and surrounding suburbs of Alvin, Jersey Village, Bellaire, LaMarque, Galena Park, and Pasadena from January 2019 to May 2019. Eighty-one soil samples were collected from public parks (n=75) and playgrounds of elementary schools (n=6). Sample collection was done on sunny days and following seven consecutive days with dry weather. After removing organic matter and other coarse elements, surface soils were collected in 10 different spots in each sampling site park and playground. Composites samples of surface soils were collected to a depth of 2 cm using a plastic shovel. Then, the sub-samples were thoroughly mixed to get a bulk sample. The composite soil sample was stored in a sealed Ziploc plastic bag and refrigerated after collection. Upon arrival to the laboratory, the soil samples were placed in beakers and dried at 60°C in a drying oven for 72 hours. Once dried, soil samples were gently crushed using a mortar and pestle, and finally sieved to get 63 µm fractions. The sieved samples were stored in polypropylene tubes and refrigerated at -20 °C pending chemical analysis. Care was taken to avoid metal contamination during sampling, drying, grinding, and storage.

Instrumental analysis

Chemical Analysis by ICP-MS

To release the environmentally available concentrations of 11 trace metals including zinc (Zn), copper (Cu), cadmium (Cd), lead (Pb), arsenic (As), aluminum (Al), nickel (Ni), chromium (Cr), cobalt (Co), manganese (Mn) and magnesium (Mg), the pulverized soil samples (<63 µm fractions) were digested according to the EPA Method

3051 A *"Microwave-assisted acid digestion of sediments, sludges, soils, and oils"* (EPA, 2007) using 70% nitric acid (HNO_3).

Half a gram (dry weight) of the soil sample was placed in a digestion vessel (MARS Xpress). The vessels were priory washed and cleansed by soaking for 24 hours in a 10 % nitric acid solution and triple rinsed with distilled water and Milli-Q extra pure water. In each digestion vessel, already containing 0.5 g of the soil sample, 10 ml of 70% HNO_3 (high acid, reagent grade) was added. The vessels were kept in a closed system constituted by an appropriate microwave-accelerated reaction system (CEM Corporation, MARS6) for 8 minutes 40 seconds on a temperature ramp until reaching 175°C. Vessels remained at 175°C for 4 minutes 30 seconds. Once digested and cooled, the extracts were moved to 15 mL polypropylene centrifuge tubes. The tubes were centrifuged for 15 minutes in a centrifuge (Centrifuge Thermo Fisher) at 2,000 rpm to separate the soil particles from the solution containing the bioavailable fraction of trace metals.

After centrifugation, 0.25 ml of the supernatant was carefully pipetted, and the acid digested extracts diluted 21-fold by adding 5 ml of ultrapure Milli-Q water. Trace metals concentrations were found using an Inductively Coupled Plasma Mass Spectrometer Agilent Technologies ICP-MS 7800, Santa Clara, California, USA. ICP-MS standards were run every 5-10 measurements by performing a continuous check of variation (CCV), i.e., samples of a known 50 µg/L concentrate in an aqueous 2 % (v/v) HNO_3 solution). Similarly, a periodic estimation of blank samples showed no general contamination.

The ICP-MS is a mass spectrometer designed to detect elemental concentration in the order of part per trillion (ppt). The inductively coupled plasma ionized the prepared samples, then separates and quantifies the ions.

Method accuracy and precision

Calibration of standard solutions (Multi-elements standards, Agilent Technologies) containing elemental concentrations similar to their environmental occurrence was prepared from standard stock solutions. A standard solution of 10 ppm was diluted down to 100, 50, 10, 1, 0.5 ppb using 3% HNO_3.

Calibration curves were obtained with these diluted calibration solutions. The r^2 values of the curves ranged from 0.999 to 1.

Quality assurance and quality control

To validate quantification data, the samples were analyzed in a batch of 22 samples, including one procedural blank, two samples duplicates, and one Standard Reference Material SRM 2709a, San Jacinto soil acquired from the National Institute of Standards and Technology (NIST). The concentrations in the blanks were insignificant. The duplicate samples' Relative Percent of Difference (RPD) was within 20%. The levels of target trace metals in SRMs were within 30% of certified values except for Al, Cr, Fe and Pb which are recognized to be incompletely recovered using out nitric acid digestion method (Cook et al., 1997; Hornberger et al., 1999).

Chemical Analysis by XRF

Prepared soil samples (63 µm fractions) were analyzed using Field Portable-X-ray Fluorescence (XRF Niton™ XL2 FP-XRF Analyzer, Thermo Fisher Scientific, Grand Island, New York, USA) according to USEPA Method 6200 ‘‘*Field Portable X-Ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and*

Sediment'' (EPA, 2007). Method 6200 is a screening method to be used with confirmatory analysis with other techniques such as ICP-MS used in the present research.

XRF was intrusively used in prepared soil samples. One gram of the pulverized soil sample was placed on a prepared Polyethylene sample cup, carefully stuffed with a cotton ball, and covered with 2.5 µm X-ray window film. The probe window was directly put on the prepared sample cup, allowing the analysis and record of trace metals concentrations.

Calibrations were done using SRM San Jacinto 2709a National Institute Standard Technology (NIST), United States Geological Survey (USGA) standard, SiO_2 and Resource Conservation and Recovery Act (RCRA) standard.

XRF analysis quantifies the fluorescent (or secondary) X-ray emanated by a sample when excited by a primary X-ray source. In XRF analysis, a primary X-ray source excites a sample, then the emanated fluorescent or secondary X rays are quantified. Elements present in the sample have specific fluorescent X-rays or unique fingerprints that distinguish each of them.

Anthropogenic enrichment

Numerous pollution indicators are recommended by EPA, such as pollution index, geo-accumulation index, enrichment factor, and exposure risk model to evaluate soil metals pollution and estimate human beings' exposure risks. In the present study, the enrichment factor (EF) and the Geo-accumulation Index (Igeo) were considered to identify the degree of pollution of the different soils.

The EF for each trace metal was calculated to distinguish between anthropogenic input and natural occurrence of trace metals in the soil. EF analysis considers the natural trace metal variability (Schiff and Weisberg, 1999; Hornberger et al., 1999) in the environment due to various sources like rocks and volcanoes. Similarly, this pollution indicator is used to evaluate the degree of anthropogenic influence (Lu et al., 2014). The equation to calculate the EF is the following:

$$\text{EF} = \frac{(Cn/Creference)sample}{(Cn/Creference)background}$$

Where C_n represents the concentration of metal element n in the sample (mg/kg)

$C_{reference}$ is the concentration of the reference element (mg/kg) used to normalize metal n in the samples and background matrix.

EF values that range between 0.5 and 1.5 indicate that crust materials or natural processes entirely generate the concentrations of trace metals. On the contrary, EF values exceeding 1.5 suggest that anthropogenic activities are accountable for the concentrations found in the soil (Zhang and Liu, 2000). Furthermore, the contamination levels of the soils can be assessed with the EF values: $\text{EF} < 2$ indicates a deficiency to a minimal enrichment, $2 \leq \text{EF} < 5$ shows moderate enrichment, $5 \leq \text{EF} < 20$ significant enrichment; very high enrichment $20 \leq \text{EF} < 40$ or extremely high enrichment $\text{EF} \geq 40$.

In addition to the EF, the Igeo was calculated to investigate the anthropologic influence on soils. The Igeo was first introduced in the late 1960s by Muller (1969), this index is a geochemical measure to estimate the pollution level in soils and sediments.

The geo-accumulation index is calculated by employing the following formula:

$$\text{Igeo} = \log 2(\frac{Cn\ sample}{1.5Bn})$$

B_n is the geochemical background value of the corresponding metal (mg/kg)

To identify minor anthropogenic effects the coefficient *1.5* is used in the formula (Loska et al., 2004). The introduction of this coefficient 1.5 permits to seize all potential dissimilarities caused by background values generated by lithogenic discrepancies (Chen et al.,2015).

Cn is the evaluated concentration of the metal ions in soil or background value found in the soil (mg/kg). Muller (1969) has divided the I_{geo} into seven classes equivalent to soil level pollution, which are unpolluted ($I_{geo} \leq 0$), unpolluted to moderately polluted ($0 < I_{geo} \leq 1$), moderately to heavily polluted ($2 < I_{geo} \leq 3$), heavily polluted ($3 < I_{geo} \leq 4$), heavily to extremely polluted ($4 < I_{geo} \leq 5$), or extremely polluted ($I_{geo} \geq 5$).

The sum of toxic units(∑TU) was determined for each sampling site. Toxic units were calculated by dividing the concentration of each metal by reference value and then combining them all together for each sample to get the sum of toxic unit (∑TU).

$$\sum TU = \sum (C_n / C_{reference})$$

C_n Measured concentration of trace element i in the sampling site

$C_{reference}$ reference value of the regulatory agency

Statistical Analysis

Statistical analysis of the soil samples was performed using Microsoft Excel 365. Common relevant descriptive statistics variables were estimated. The parameters determined were mean, median, minimum, maximum, standard deviation (SD), and coefficient of variation (CV). To distinguish between distinct groups, one way Analysis of the Variance (one way ANOVA) pair-wise comparisons at 95 % confidence level was performed. Statistical analyses including ANOVA assume a normality of population distributions for each group, an equality of variances for all groups, as well as those observations are randomly and independently representative of the populations (Reimann et al., 2011). Linear regression of metal-metal correlation was performed to determine sources of trace metals (similar/natural and diverse/anthropogenic). Pearson's correlation coefficient was also calculated to compare EF and I_{geo} results, and XRF and ICPMS results. Error bars are presented as the mean ± standard deviation (SD).

CHAPTER 4

RESULTS AND DISCUSSION

Study 1: Comparison of XRF data and ICP-MS data

I. Analysis of trace elements recovery and concentrations

As shown in Figure 4, Figure 5, Figure 6 and Figure 7, all investigated trace metals were detected by ICP-MS. In contrast, XRF did not detect Mg, Co, Ni, Cd, and As, because the concentrations of these elements are below the detection limits of XRF (Figure 4 and Figure 5). Detection limits of ICP-MS are in the order of parts per billion (ppb) or lower, compared to higher detection limits in parts per million (ppm) for XRF. Even with repeated measurements, XRF cannot quantify trace metals at ppb or lower concentrations levels. ICP-MS is a multi-element technique for evaluating liquid samples, characterized by high selectivity, sensitivity, and detection limits much lower than other multi-element techniques, including XRF.

For some elements, including Al, Fe, Cr and Cu concentrations obtained by XRF are higher than those of ICP-MS. XRF is an elemental analysis technique (physical technique) i.e., it quantifies the total content of trace metals in the soil sample regardless of chemical bonds. ICP-MS measures the environmental available fraction of trace metals present in the acid digest. Total concentrations consist of all forms of the metal in the soil like ions adhered to the crystal structure of primary and secondary minerals; ions adsorbed to surfaces of secondary minerals (e.g., clays, oxides, and carbonates), ions bound in solid-state organic matter, free ions, and soluble organic and inorganic complexes in soil solutions (Alloway, 2012). The available concentration of metal in the soil refers to the estimation of the fraction of this metal found as free ions, soluble complexes or in readily insoluble (labile) forms.

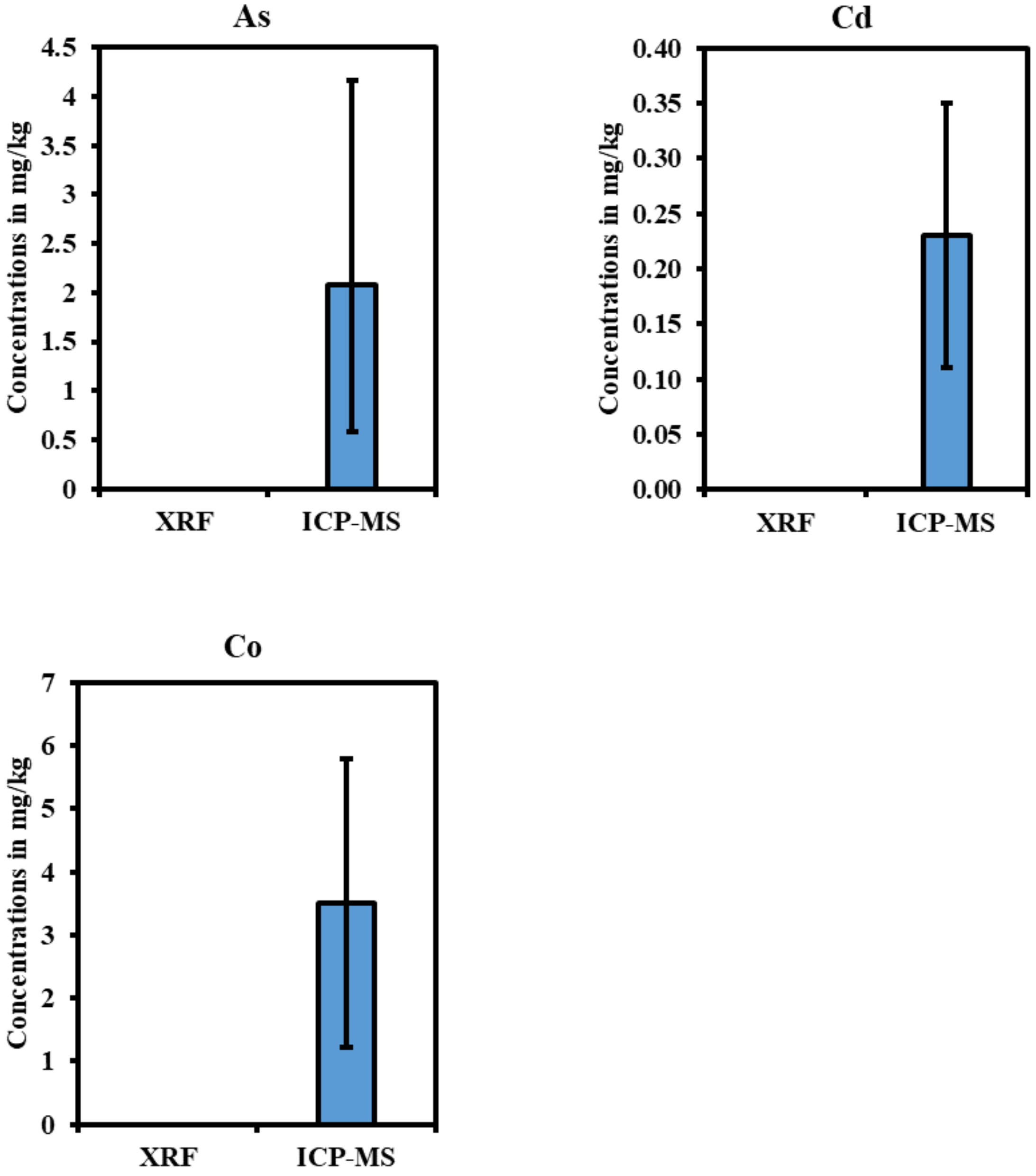

Figure 4 Comparison of As, Cd, and Co mean concentrations by XRF and ICP-MS . In blue ICP-MS mean concentrations and in red XRF mean concentrations. ***=significant difference with $p < 0.000$; * = significant difference with $p < 0.05$.

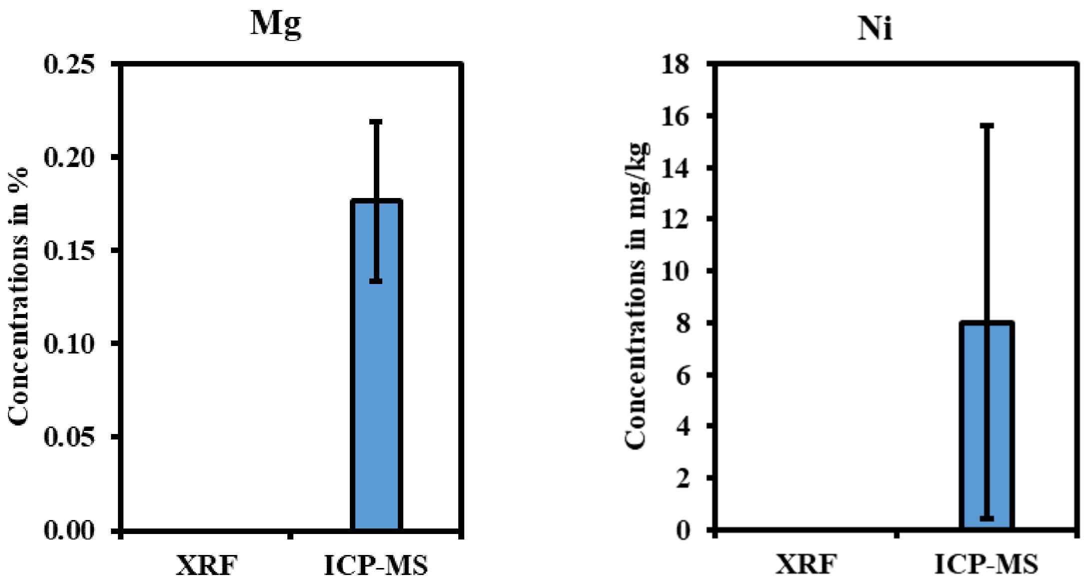

Figure 5 Comparison of Mg and Ni mean concentrations by XRF and ICP-MS .
In blue ICP-MS mean concentrations and in red XRF mean concentrations.
***=significant difference with $p < 0.000$; * = significant difference with $p < 0.05$.

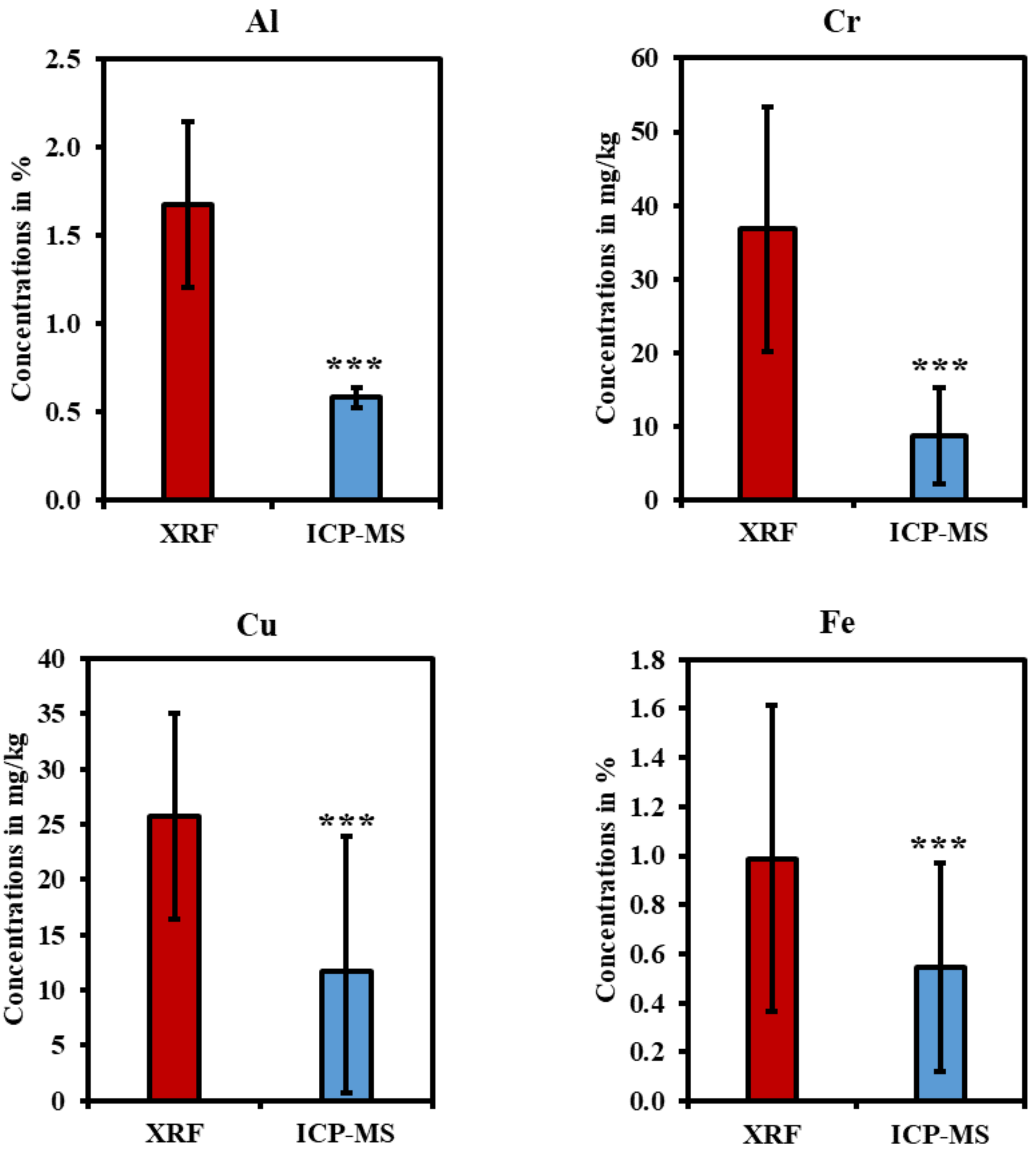

Figure 6 Comparison of Al, Cr, Cu and Fe mean concentrations by XRF and ICP-MS . In red XRF mean concentrations and in blue ICP-MS mean concentratrions. ***=significant difference with $p < 0.000$; * = significant difference with $p < 0.05$.

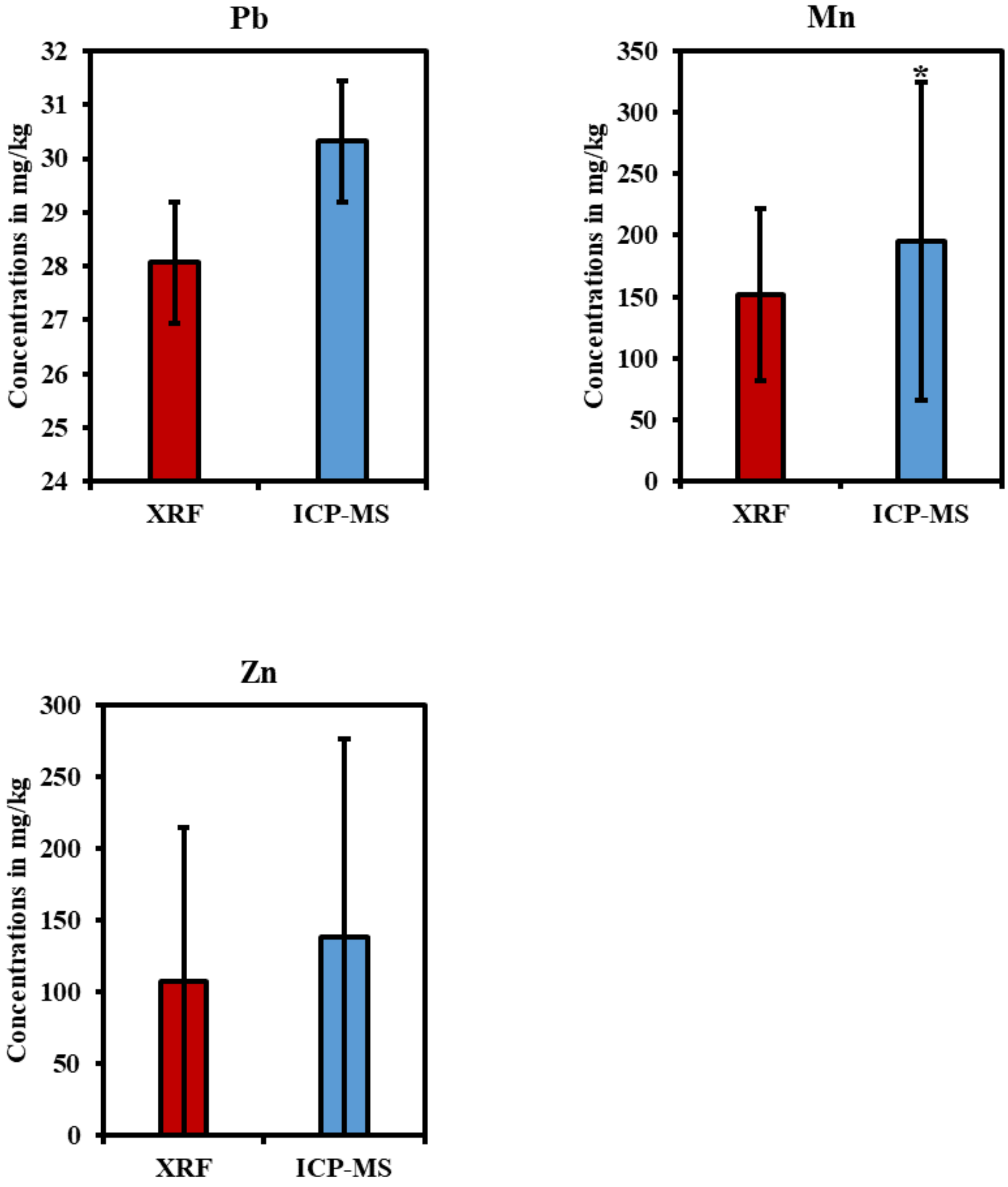

Figure 7 Comparison of Pb, Mn and Zn, mean concentrations by XRF and ICP-MS . In red XRF mean concentrations and in blue ICP-MS mean concentratrions. ***=significant difference with $p < 0.000$; * = significant difference with $p < 0.05$.

Recoveries of SRM San Jacinto 2709A by ICP-MS and XRF are reported in Table 4.1. The recovery of some elements including Al, Cr and Fe, was better attained with XRF compared to ICP-MS. The XRF/ICP-MS ratios for Al, Fe, and Cr varied between 1.14 and 7.83, 0.95 and 3.62, 1.77 and 13.1 respectively, with the arithmetic mean ratio of 3.60, 2.00, and 4.93, respectively. The recovery rates in HNO_3 for most elements in the SRM were within 80% and 120%, but much lower for Al (23-28%), Cr (41-53%), Pb (69-75%), and Fe (74-90%). The results indicate that digestion with nitric acid is satisfactory for the recovery of Mg, Mn, Ni, As, Cd, Co, Cu, and Zn, but low with Al, Pb, Cr and Fe. Thus, depending on the type of acid used in pretreatment steps before ICP-MS analysis, trace metals' recoveries vary. These results corroborate with previous studies, which have found satisfactory recoveries for Mn, Ni, As, Cd, Co, Cu, and Zn; and low recoveries for Pb, Cr, and Al when nitric acid digestion is performed prior to ICP-MS analysis. (Arunachalam et al., 1995).

The challenges related to the acids used in the pretreatment steps of ICP-MS have been broadly presented in the literature (Quevauviller et al. 1996, Baffi et al. 2002; Sandroni & Smith, 2002; Wang et al. 2004; Hassan et al., 2007; Congiu et al., 2013). The nature of the extractant employed to free the trace elements from the soil matrix is critical: different reagents release metals from various soil components and offer distinct forms of information. Hence, various acid extraction methods can lead to different concentrations of trace elements for the same sample. According to Ajmone-Marsan et al. (2010), the variability in the extraction methods may hamper the comparison of published data. Thus, different extraction techniques can result in a 20 to 30% variation between data.

Digestion with concentrated acids delivers near-total metal concentrations, compared to much fewer concentrations achieved with dilute acid digestion such as 0.5 N HNO_3 (Hwang et al., 2006). Dilute acids are likely to extract only the readily bioavailable fraction of trace metals in the samples (Peijnenburg & Jager, 2003). For instance, nitric acid (HNO_3), a mild acid, has a less efficient dissolving power than hydrofluoric acid (HF), a strong acid. Accordingly, concentrations of trace metals in nitric acid digests are lower than those in hydrofluoric acid digests. Besides, concentrated nitric acid digestion is not strong enough to completely dissolve some metals such as Al, Cd, Cr, and V, compared to hydrofluoric acid digestion, which can provide a total decomposition of soil samples (Cook et al., 1997; Hornberger et al., 1999). Concentrated HNO_3, even when heated, does not dissolve Al completely because it prompts the formation of an oxide layer that protects Al against further reaction (Michel et al.,1964). Thus, to achieve the dissolution of materials particularly resistant to acids, the use of concentrated HF is required (Congiu et al., 2013). Comparable low Al recovery (20-43%) associated with the nitric acid digestion process, in opposite to approximately 80% of Fe recovery, has been reported in several studies (Schiff and Weisberg, 1999; Hornberger et al., 1999). The incomplete digestion of alumina-silicate by nitric acid and high concentration of Al in soil samples also explains the low recovery of Al in nitric acid digests.

Data from this research investigation supports Amorosi et al. (2011)'s study in which a systematic higher efficiency of Cr determination by XRF analysis (60%) compared to ICP-MS (only 45%) was found. Variances in contamination source, pH organic carbon, and clay content may influence the percentage of extractable Cr in soil by different methods (Congiu et al., 2013 and reference therein). Besides, some minerals such as chromite

($FeCr_2O_4$) and zircon ($ZrSiO_4$) are highly resistant to acid digestion and persist undissolved even after repetitive treatments. Also, hexavalent chromium (Cr VI) is lost as chromyl chloride (chromic oxychloride, CrO_2Cl_2) during the acid decomposition procedure, leading to low recovery of Cr in soil samples by ICP-MS (Yamasaki et al.,2016). Many studies have emphasized that Cr is dominant in the residual, non-labile form of the soil, so Cr does not accumulate in the finest particles size and is scarcely bioavailable in this particle size (Lu et al., 2003; Davidson et al., 2006; Wang et al., 2006; Ajmone-Marsan et al., 2007). The increasing order of Cr in soil fractions is residual (92.9%) > organic (4.2%) > Fe–Mn oxide (2.7%) > carbonate (0.2%) > exchangeable (0.04%) (Lu et al., 2003). A plausible reason for low Pb recovery is that some fraction of Pb in soil samples is integrated into refractory minerals like zircon, known to contain Pb and not completely attacked by HNO_3 even under pressurized conditions (Arunachalam et al., 1995, Yamasaki et al., 2016).

Table 9 Summary of SRM recoveries (%) by ICP-MS and XRF

Trace metals	ICP-MS	XRF
Al	**23 - 28**	**61 – 62**
As	92 - 114	ND
Cd	100 -112	ND
Cu	91 - 108	**72 – 86**
Co	97 - 113	ND
Cr	**41 - 53**	76 – 87
Fe	**74 - 90**	98 – 99
Mg	86 - 105	ND
Mn	99 - 120	86
Ni	92 - 103	ND
Pb	**69 -75**	88-96
Zn	94 - 105	78 – 85

ND Not detected

In bold SRM recoveries not in the range of 80% -120%

The recovery of soil trace metals concentrations by acid extractions carries a considerable uncertainty. When comparing metal concentrations, special attention should be made to the type of acid used in the sample preparation performed before ICP-MS analysis. Also, care should be taken when Al is used as a reference element for normalization in order not to overestimate or underestimate the anthropogenic impact.

Even though commonly employed as a trustworthy method for accurately assessing metal concentrations at low levels (Griffith et al. 2009), ICP-MS has the disadvantage of necessitating substantial sample preparation and generates excessive amounts of hazardous wastes contrary to XRF. XRF analysis can be conducted without sample destruction since it does not require a pretreatment step with chemicals and acids, contrary to ICP-MS analysis. New methods and techniques have been developed to extend the potential of

XRF (X-ray fluorescence) to analyze liquid solutions. XRF can be performed without contact analysis of solid and liquid samples. It is high repeatable and demands negligible sample preparation as well as minimal operator training. (Moradi et al., 2015).

II. Analysis of correlation coefficients of ICP-MS and XRF data

Table 10 Correlation coefficients of ICP-MS and XRF trace elements data

Trace metals	Correlation coefficient
Al	0.80
Cu	0.96
Cr	0.68
Fe	0.88
Mn	0.92
Pb	0.99
Zn	1.00

The values of the correlation coefficients between ICP-MS-XRF are displayed in Table 10. The comparison of ICP-MS and XRF results indicates excellent correlations for elements present at concentrations that pass both ICP-MS and XRF detection limits (Zn, Pb, Cu, Mn, Al, and Fe). The correlation coefficients are 1.00, 0.98, 0.92, 0.96, 0.87, and 0.80 for Zn, Pb, Mn, Cu, Fe, and Al, respectively. The exception was made for Cr, which displays a low correlation coefficient of 0.68. These results align with those obtained by Niu and colleagues (2010), with correlation coefficients exceeding 0.84 for Fe, Mn, Zn, Pb, and Cu. Likewise, Al Maliki et al. (2017) found that ICP-MS corroborate XRF for Pb soil measurements with a high coefficient correlation of 0.94. Field-portable XRF is a rapid, low-cost technique which can detect some trace metal levels such as Pb, similar to those detected by digestion in samples sieved to less than 2 mm in a laboratory (Markey et al. 2008).

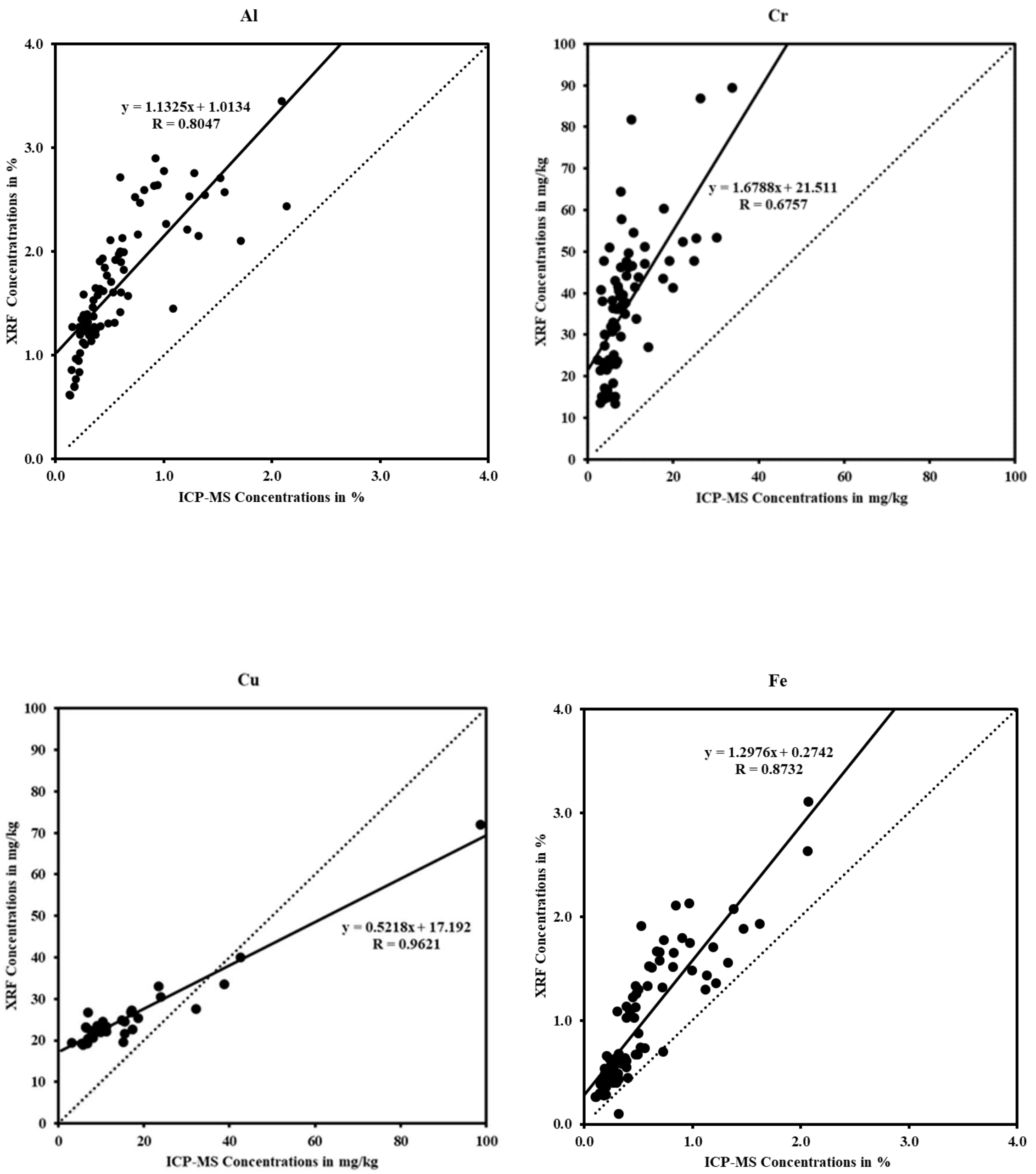

Figure 8 Correlation graphs of Al, Cr, Cu and Fe XRF data vs ICP-MS data.
XRF concentration data plotted against the values obtained by ICP-MS. The solid line is the linear regression line, and the dotted line is the 1:1 line (line of Y = X). R represents the coefficient of correlation.

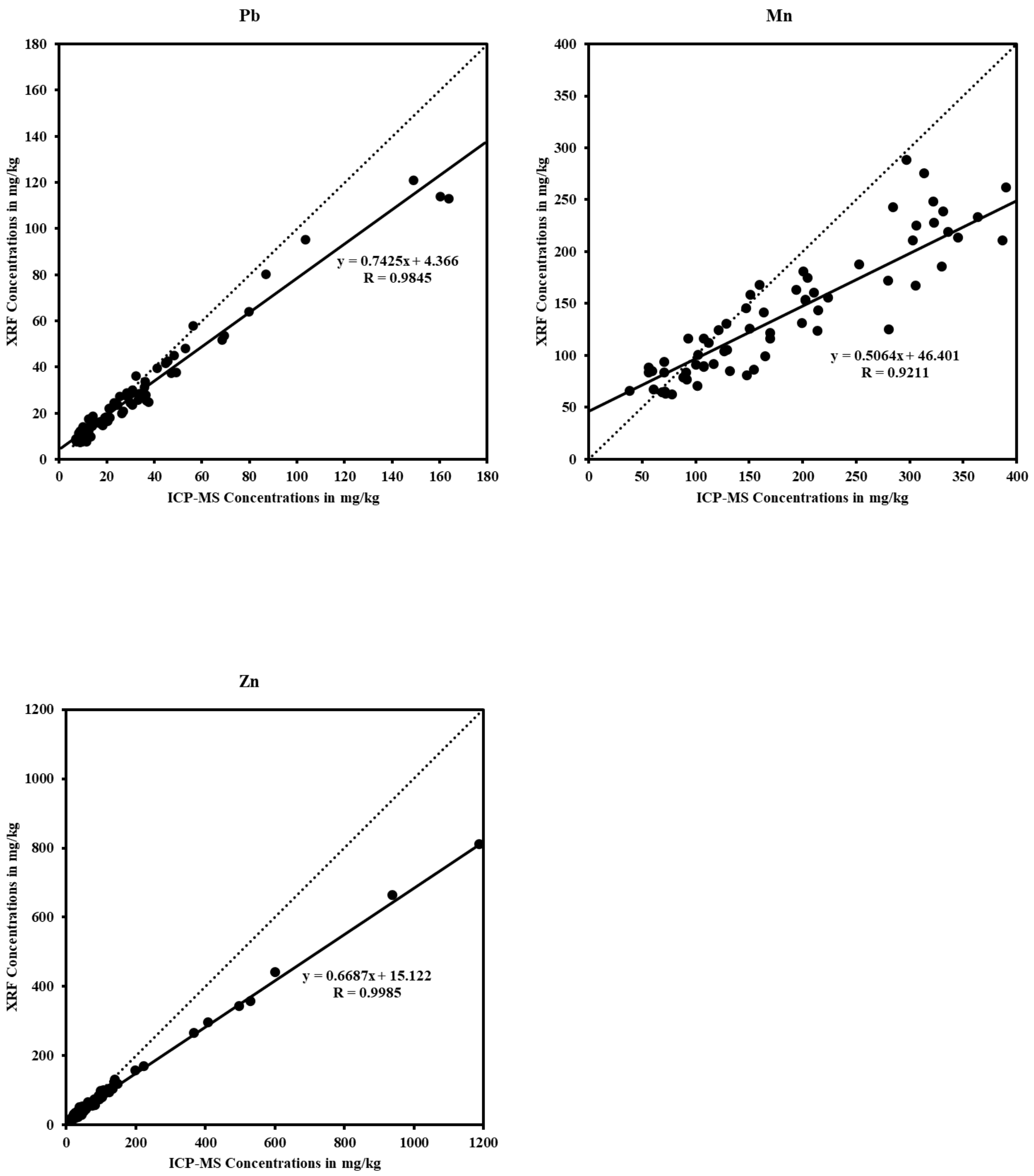

Figure 9 Correlation graphs Pb, Mn and Zn XRF data vs ICP-MS data.
XRF concentration data plotted against the values obtained by ICP-MS. The solid line is the linear regression line, and the dotted line is the 1:1 line (line of Y = X). R represents the coefficient of correlation.

As seen in Figures 8 and 9 dots above the 1:1 line are elemental concentrations underestimated by ICPMS, while dots below the 1:1 line are concentrations overestimated by XRF. Thus, the lower concentrations obtained by XRF for Mn, Zn, and for Pb are slightly underestimated. These underestimations are due to the lack of accuracy, an important limit of the XRF technique. The accuracy of XRF is based on the kind of samples (matrix and interelement ratios) used to calibrate the instrument. Concentrations reached by ICP-MS are slightly underestimated for Fe and Cu, and significantly for Al and Cr. The underestimated concentrations of IC-PMS are once again related to the acid used in dissolution steps.

ICP-MS and XRF provided comparable results for many elements, while ICP-MS was ideal for broader ranges of chemical information, including various trace elements. This is particularly essential from a geological and environmental point of view. ICP-MS data are undeniably strongly related to the digestion procedure and detection of trace elements by XRF requires high concentrations in soil samples. As a result, Al and Cr recovery was extremely low in nitric acid and XRF did not detect some elements (Mg, Co, Ni, Cd, and As). Nevertheless, ICP-MS is a reliable method for accurately determining metal concentrations at low levels. Likewise, XRF is a rapid, non-destructive method that can be employed to assess an abroad range of trace metals into the soils, including the challenging elements such as Al and Cr, strongly affected by the type of acid digestion used before ICP-MS.

Moving forward, the considered concentrations of Al and Fe are obtained by XRF, and for all other metals, the concentrations are attained by ICP-MS.

Study 2: Assessment of metal contamination in urban surface soils

I. Analysis of elemental concentrations in urban surface soils

Concentrations of trace metals in Houston MSA's surface soils

The concentrations in soil particle < 63µm (without removing outliers) are in the ascending order of Al > Fe > Mg> Mn >Zn > Pb >Cu > Cr> Ni > Co > As > Cd. As shown in Table 4.3, the mean concentrations of Al, Fe, Mg, Mn, Zn, Pb, Cu, Cr, Ni, Co, As and Cd are 1.67%, 0.99%, 0.18%, 201 mg/kg, 138 mg/kg, 39.0 mg/kg, 12.6 mg/kg, 10.1 mg/kg, 8.01 mg/kg, 3.51 mg/kg, 3.07 mg/kg, and 0.23 mg/kg, respectively. Except for Pb and Zn, the mean concentrations of the trace metals were below their according TCQE background values, 15 and 30 mg/kg, respectively (See details in Table 11).

The standard deviations (SD) values are high, indicating the heterogeneity of urban soils, as reported in many studies on urban soil samples (Romzaykina et al., 2020). The coefficients of variation (CVs), which are the percentage of the SD against the mean values, range from 37% to 216%, with the highest values exhibited by Cu (117%), Cd (169%), Zn (163%) and Pb (216%). High CVs suggest that various anthropogenic sources contribute to the soil contamination in Houston MSA. These results are in good agreement with those found by Zhank and colleagues (2009) in Fuyang County/China. The author found that the CVs of Pb, Zn, and Cu were high, suggesting their anthropologic origin. Likewise, in Sacramento, California, a high CV for Pb indicates the anthropogenic origin of Pb.

Linear regression of metal-metal correlation combined with the CV can assist in distinguishing between metals of similar/natural and those of diverse/anthropogenic sources (Table 12). Al has the lowest CV of 37 and is used as a reference element for comparison. Arsenic, Co, Cr, Fe, Mg, Mn, and Ni have strong to moderate positive correlations (r > 0.6), with Al suggesting these metals likely originate mostly from similar/natural sources. In contrast, Cd, Pb and Zn exhibit a very weak correlation with Al (r < 0.2), implying these metals likely emanate mainly from dissimilar/anthropogenic sources due to the large discrepancy between samples. Cu has a weak correlation with Al (r < 0.5), but has a strong correlation with Fe, which has the 2nd lowest CV (r greater than 0.6). Thus, this metal may have both natural and anthropogenic sources.

Table 11 Trace metal concentrations (in mg/kg) of Houston MSA soil particles < 63µm

Metal	10th percentile	Median	90th percentile	Mean	SD	CV
Pb	7.37	20.8	69.3	39.0	84.0	216
As	1.27	2.81	5.08	3.07	2.08	68
Zn	24.0	60.0	338	138	251	182
Cu	4.06	9.00	20.5	12.6	14.7	117
Ni	2.19	5.58	16.4	8.01	8.56	107
Co	0.92	3.06	7.24	3.51	2.28	65
***Fe**	0.38	0.68	1.87	0.99	0.15	63
Mn	56.8	160	401	201	138	69
Cr	3.31	6.63	21.7	10.1	10.6	105
Cd	0.05	0.13	0.43	0.23	0.39	169
***Al**	0.95	1.57	2.62	1.67	0.62	37
***Mg**	0.04	0.13	0.38	0.18	0.15	84

SD = Standard Deviation CV = Coefficient of Variation, * Al, Fe and Mg concentration unit is %

Table 12 Linear regression correlation (R) value for trace metals in Houston surface soils (<63μm)

	Al	**As**	**Cd**	**Cr**	**Co**	**Cu**	**Fe**	**Mg**	**Mn**	**Pb**	**Ni**	**Zn**
Al	1.00											
As	**0.74**	1.00										
Cd	0.24	0.59	1.00									
Cr	**0.61**	0.67	0.43	1.00								
Co	**0.84**	0.84	0.31	0.71	1.00							
Cu	0.47	0.59	0.72	0.69	0.65	1.00						
Fe	**0.92**	0.84	0.37	0.71	0.88	**0.65**	1.00					
Mg	**0.80**	0.75	0.31	0.62	0.82	0.59	0.80	1.00				
Mn	**0.62**	0.73	0.38	0.47	0.80	0.61	0.69	0.64	1.00			
Pb	0.16	0.43	0.72	0.41	0.31	0.76	0.41	0.11	0.37	1.00		
Ni	**0.70**	0.66	0.39	0.80	0.84	0.66	0.81	0.70	0.60	0.32	1.00	
Zn	0.14	0.34	0.88	0.56	0.31	0.83	0.31	0.26	0.20	0.79	0.50	1.00

R values in **bold** indicate similar sources
R values in regular indicate dissimilar sources

Table 13 TCEQ Background soil concentrations (in mg/kg) (Connor & Schaklette, 1975)

Trace metal	Background Concentrations
Al	3%
As	5.9
Cd	Unknown
Cr	30
Co	7
Cu	15
Fe	1.5%
Pb	15
Mg	Unknown
Mn	300
Ni	10
Zn	30

For comparison with the present research, average trace metals concentrations in urban soils reported in the US and other world cities, are also displayed in Table 14. Comparing data from studies with dissimilarities require caution. Discrepancies can arise from the sorting size (soil particle size), nature of the investigated soil (e.g.: sand, silt, clay), sampling and analysis methods (e.g., XRF vs ICP-MS), type of acids used in pretreatment steps (e.g.: strong acids vs dilute acids). In general, smaller size particles depict greater trace metals concentrations than larger particle size. Smaller particles have higher surface adsorption due to higher clay minerals, organic matter content, and occurrence of phases of Fe-Mn oxides that trap trace metals (Ajmone-Marsan, 2010).

The review of available urban soil concentrations indicates that the present data are within the reported ranges of concentrations of trace elements reported in other urban soils. Cd, Ni, and Cr in the current study are below the 30th percentile. Pb, Cu, and As are below the 45th percentile. As and Zn are at the 45th percentile and 60th percentile, respectively. A recent study conducted by Da Silva et al. (2021) on Florida backgrounds soil values has estimated similar concentrations of trace metals. The Florida urban soils concentrations (in mg/kg) for Pb, Zn, Cu, Cd, Cr, As, and Ni are 39.5, 54.6, 9.57, 0.21, 16.4, 1.37 and 3.55, respectively. Though, like other data, Pb and Zn concentrations are relatively elevated in the current study. Pb, Cu, and Zn are known as typical urban trace metals and usually exceed background values in cities (Biasioli et al., 2007; DeMiguel et al, 2008: Ajomone Marsan, 2010; Hwang et al., 2016). In the present study, Pb and Zn considerably surpassed background values compared to Cu. Lead and Zn appear to be the metals, the most impacted by anthropogenic activities in Houston. The high concentration of Pb is probably due to the legacy of the historical use of Pb in gasoline, prior to 1978. It can also be due to the extensive industrial activities taking place into the metropolitan. Pb's mobility is restricted in the soil, therefore, concentrations of Pb remain and accumulate in the soil for long time, even after frequent rain events such as in Houston (Gmochowska et al. 2019).

Table 14 Trace metals concentrations in urban soils (mg/kg)

Location	Value used	Land use	Pb	Zn	Cu	Cd	Cr	As	Ni	Particle size	Acid Used	Instrument
Houston MSA, TX [1]	Mean	Urban parks Playgrounds	39.0	138	12.6	0.23	10.1	3.07	8.01	< 63µm	HNO_3	ICP-MS
Urban average, FL[2]	Mean	Residential-commercial	39.5	54.6	9.57	0.21	16.4	1.37	3.55	< 2 mm	HNO_3, H_2SO_4	ICP-MS
Anniston, AL[3]	Mean	Residential peripheral areas	183	345	61.7	0.7	17.6	2.5	12	< 2 mm	HNO_3, H_2O_2	ICPMS
Baltimore, MD[4]	Median	Residential soils	33.8	68.5	13.6	0.2	13.5	2.5	9.7	< 2 mm	HNO_3, H_2O_2	ICP-MS
Gainesville, FL[5]	Median	Public parks	7.23	NR	NR	NR	NR	0.35	NR	< 2 mm	HNO_3, H_2O_2	GFAAS
Miami, FL[6]	Median	Public parks	82	NR	NR	NR	NR	3.29	NR	< 2 mm	HNO_3, H_2O_2	GFAAS
Pueblo, Co[7]	Median	Residential soils, playgrounds	89.8	NR	NR	2.6	NR	12.9 *	NR	< 2 mm	HNO_3, HF	ICPMS *HG-AAS
Sacremento, CA[8]	Median	Urban soils	52.6	120	105	0.34	NR	0.11	NR	NP	$HClO_4$, HNO_3, HF, HCl	ICPMS
Spokane, WA[9]	*GM	Urban parks	19	54	12.5	0.07	25.8	8.3	NR	< 2 mm	HNO_3, H_2O_2	ICP-OES

Los Angeles, CA[10]	Median	Urban parks	45	NR	NR	NR	NR	NR	NR	< 2 mm	HNO_3, HCl, H_2O_2	ICP-OES
Madrid, Spain[11]	Mean	Municipal playgrounds	22	50	14	0.14	17	6.9	NR	< 100 µm	HCl, HNO_3	ICP-MS
Beijin, China 2005[12]	*GM	Urban parks	55.2	82.5	59.6	NR	NR	NR	21.4 *	< 100 µm	HNO_3, H_2O_2	FAAS
Guangzhou City, China[13]	Median	Urban parkss	224	NR	NR	NR	NR	24.2	NR	< 250µm	HNO_3, HF, $HClO_4$	HG-AFS
Athens, Greece[14]	Median	Urban parks	101	146	42	Nr	84.3	nr	77.8	< 2mm	HNO_3, HCl	AAS
Khorramabad , Iran[15]	Mean	Urban parks	7.38	NR	NR	NR	NR	NR	NR	<149µm	HNO_3, HCl	AAS
Mexico Metropolitan, Mexico[16]	Median	Urban topsoils	82	NR	NR	NR	116	NR	39	< 2mm	$HClO_4$ HF	ICP-MS
Harcourt Metropolis, Nigeria[17]	Median	Urban parks	7.48	NR	8.37	0.72	NR	0.1	NR	< 2mm	HNO_3, H_2SO_4, $HClO_4$	AAS
Scotland, UK[18]	Median	Elementary school playgrounds	118	154	52.5	NR	NR	NR	NR	< 2 mm	HNO_3, HCl	ICPMS
Beijin, China 2020[19]	Median	Urban parks	32.6	137	32.4	0.47	53.1	12	26.6	< 125 µm	HNO_3, HF	ICP-MS

Perth, Australia[20]	Median	Urban parks	75.6	120	21.8	0.12	10.7	2.17	3.75	≲50 µm	HNO_3, HCl	ICP-OES
Peshawar City, Pakistan[21]	Median	Parks & Playgrounds	25.2	69.9	13.8	5.8	38.4	NR	51.5	< 2 mm	HCl, HNO_3, $HClO_4$	AAS
Urban average, Colombia[22]	Mean	School playgrounds	89	396	39	2.1	27	26	10.8	< 100 nm	NR	ICP-MS
Shenyang, China[23]	Median	Urban soils	70.1	182	71.1	0.54	65.1	17.6	NR	< 2 mm	HNO_3, $HClO_3$, HF	ICP-OES

*GM Geometric Mean NR Not Represented

References

1 Present study
2 da Silva et al., 2020
3 Ha et.,2014
4 Pouyat et al., 2007
5 Chirenje et al., 2003
6 Chirenje et al., 2003
7 Diawara et al., 2005
8 Solt and al., 2015
9 Nezat et al., 2017
10 Hung et al., 2018
11 De Miguel, 2007
12 Chen et al., 2005
13 Lu et al., 2010
14 Massas et al., 2010
15 Solgi et al., 2016
16 Morton-Bermea et al., 2016
17 Okereke et al., 2017
18 Davidson et al., 2019
19 Liu et al., 2020
20 Rate, 2018
21 Khan et al., 2016
22 Donado et al., 2021
23 Li et al., 2013

Comparison of trace metals concentrations by income groups and emission range

Table 15 displays the average concentrations of trace metals in Houston soils in particle size < 63 µm (after excluding outliers). The mean concentrations of trace metals in Houston Metropolitan soils vary between 1.67%, 0.99%, 0.18%, 201 mg/kg, 138 mg/kg, 39.0 mg/kg, 12.6 mg/kg, 10.1 mg/kg, 8.01 mg/kg, 3.51 mg/kg, 3.07 mg/kg, and 0.23 mg/kg, for Al, Fe, Mg, Mn, Zn, Pb, Cu, Cr, Ni, Co, As and Cd, respectively. Most trace elements concentrations are below their equivalent TCQE background values, except Pb (>15 mg/kg) and Zn (>30 mg/kg).

Table 15 Trace metal concentrations of Houston MSA soil particles < 63µm

Metal	10th percentile	Median	90th percentile	Mean	SD	CV
Pb	7.21	18.8	46.4	22.7	15.4	68
As	1.27	2.38	4.76	2.79	1.36	49
Zn	23.3	51.4	131	68.9	45.3	66
Cu	4.03	8.46	17.0	9.52	5.00	53
Ni	2.17	5.35	13.0	7.06	7.19	102
Co	0.91	3.02	6.58	3.41	2.13	63
% Fe	0.38	0.67	1.79	0.96	0.58	60
Mn	56.5	157	390	195	129	66
Cr	3.19	6.17	11.2	6.88	3.34	49
Cd	0.05	0.12	0.35	0.16	0.12	74
% Al	0.94	1.55	2.59	1.65	0.59	36
% Mg	0.04	0.12	0.34	0.16	0.12	74

The elemental concentrations by income group and emission range were compared to average Houston concentrations (data in Table 16, outliers removed).

Table 16 Concentrations of metals in soils from different income groups & emissions range (in mg/kg except for Al, Fe, Mg in %) *

	Al	As	Cd	Co	Cr	Cu	Fe	Mg	Mn	Pb	Ni	Zn
Group A: High/Middle Income without industrial emissions												
Mean	1.40	2.43	0.08	2.11	4.96	6.70	0.48	0.15	161	13.6	3.76	38.1
Median	1.36	2.03	0.07	2.04	4.69	5.54	0.47	0.06	114	12.5	3.49	36.6
SD	0.32	1.30	0.04	1.04	1.54	2.74	0.14	0.04	116	7.51	1.79	18.1
Min	0.86	0.69	0.03	0.42	2.60	2.85	0.26	0.03	32.8	5.74	1.12	11.7
Max	2.00	5.24	0.19	3.81	7.65	11.4	0.67	0.14	403	28.3	7.55	82.6
CV	23	54	53	49	31	41	28	47	72	55	48	48
Group B: High/Middle Income with industrial emissions												
Mean	1.58	2.45	0.11	2.72	6.97	8.55	0.82	0.18	128	14.2	5.01	64.9
Median	1.42	2.34	0.09	1.79	6.41	7.77	0.55	0.11	96.7	13.3	4.01	49.8
SD	0.66	0.98	0.06	1.85	3.27	4.49	0.56	0.12	71.3	5.50	2.85	38.1
Min	0.62	0.81	0.04	0.68	2.15	3.2	0.26	0.02	44.5	6.91	1.26	24.7
Max	2.71	4.41	0.25	6.15	14.2	18.7	1.88	0.39	280	23	11	147
CV	41	40	58	68	47	53	68	47	56	39	57	59
Group C: Low Income without industrial emissions												
Mean	1.82	2.94	0.16	3.95	6.38	9.43	1.14	0.21	196	25.2	8.29	58.1
Median	1.77	2.99	0.12	3.80	6.17	9.44	1.26	0.15	197	20.5	7.49	37.6
SD	0.66	1.26	0.12	1.82	2.46	4.29	0.46	0.12	88.4	19.8	4.74	38.9
Min	1.02	0.98	0.03	1.35	2.33	3.27	0.36	0.05	59.3	6.27	2.17	22.5
Max	2.89	4.74	0.48	7.76	10.9	18.2	1.79	0.46	364	79.7	16.8	134
CV	30	43	78	46	39	45	40	63	45	79	57	67
Group D: Low Income with industrial emissions												
Mean	1.78	2.73	0.26	4.07	11.7	12.7	1.14	0.16	228	33.1	8.35	94.2
Median	0.54	2.34	0.27	3.51	8.83	12.2	1.03	0.14	160	32.2	7.54	101
SD	0.57	1.17	0.11	2.31	7.07	5.23	0.58	0.08	134	13.3	4.41	33.0
Min	0.96	1.10	0.06	0.85	3.17	5.43	0.38	0.04	28.4	8.86	2.01	28.4
Max	2.75	4.90	0.46	8.43	25.4	23.5	2.1	0.28	495	56.4	18.1	145

CV	32	43	43	57	60	41	51	55	58	40	53	35

* Table 4.8 summarizes data (mean, min, max, median, and other relevant descriptive statistics from all sampling sites (parks and school playgrounds), without outliers. All element concentrations are offered on a dry matter basis. All concentrations represent ICP-MS data, except for Al and Fe which represent XRF data.

Among the income groups, *Group A* presents the lowest concentrations for most elements including Al (1.40%), As (2.43 mg/kg), Cr (4.96 mg/kg), Pb (13.6 mg/kg), Zn (18.1 mg/kg), Ni (3.76 mg/kg), Fe (0.48%), Cd (0.08 mg/kg), Cu (6.70 mg/kg), Co (2.11 mg/kg), and Mg (0.04%). None of the average concentrations surpassed the TCQE background value. These values are also below the average concentrations in Houston (See Table 4.8 for details). Compared to Houston MSA soil data, Ni concentration is below the 30th percentile. Co, Cr, and Cd concentrations are below the 35th percentile. Zn concentration is below the 37th percentile. Pb and Cu concentrations are below the 40th percentile. Arsenic concentration is below the 51st percentile. The low concentrations of trace metals recorded in these parks, suggest that industrial input is negligeable in this study area as shown by the TRI data. Additionally, the low concentrations reported in *Group A* suggest that the soils of this group can be used as background level income group and emission range to show concentrations of uncontaminated soils in Houston.

Followed by *Group A*, the second lowest concentrations are recorded in *Group B* with 1.58%, 0.82%, 0.12 %, 2.45 mg/kg, 0.11 mg/kg, 8.55 mg/kg, 14.2 mg/kg, 64.5 mg/kg, 5.01 mg/kg, 2.72 mg/kg, for Al, Fe, Mg, As, Cd, Cu, Pb, Zn, and Co, respectively. None of the concentrations in these soils surpassed the mean concentrations of trace metals in the metropolitan. Except for Zn (>30 mg/kg), all trace metals concentrations are below their corresponding TCQE background values. Mn is below the 40th percentile. Pb and Cd are below the 45th percentile. Co and As are below the 48th and 50th percentile, respectively. Cu and Ni are below the 55th percentile. Zn and Cr are below the 60th percentile.

On the other hand, the highest concentrations of most trace metals are recorded in *Group C* and *Group D*, with the latter group expressing the highest levels. In *Group C* the concentrations (in mg/kg) are 1.82 ,1.14, 0.21, 2.94, 3.95, 0.16, 9.43, 196, 8.29, and 58.1 for Al (%), Fe (%), Mg, As, Co, Cd, Cu, Mn, Ni and Zn, respectively. In this group, Pb, As, Mg, Mn and Ni are above the average concentrations of Greater Houston's soils. Moreover, Pb and Zn concentrations exceeded the TCQE background criteria. Pb concentration is in the 63rd percentile. Zn and Cr concentrations are in the 55th percentile. As and Mn concentrations are in the 60th percentile. The concentrations of Co, Ni, Mg, and Cd are in the 69th, 72nd, 73rd and 75th percentile, respectively. Though, without any industry reporting to TRI, concentrations are still elevated in this study area. A plausible reason may include that sources other than industrial exist at the proximity of these soils. Another plausible explanation may be the presence of industries not required to report to TRI. However, these industries conduct activities which can cause soil pollution. For example, Japhet park, located inf 77020, a socio-economically disadvantaged zip code; has prominent levels of trace metals. The concentrations of Pb (160 mg/kg), As (4.74 mg/kg), Zn (600 mg/kg), Cu (45.9 mg/kg). Ni (85.5 mg/kg), Fe (2%), Mn (653 mg/kg), Cr (57.8 mg/kg), and Cd (1.97 mg/kg) are extremely high. Pb, As, Zn, Cu, Ni, Mn, Cr Cd are approximatively 7, 2, 9, 5, 3.5, 8.5 and 12.5 times higher, respectively, than their according Houston's average concentrations. In this ZIP code, there is no industry reporting to TRI. But the park is surrounding by metal junk yards, metallurgic industries (e.g., Southwest Proler and Steel, Sun Belt Texas, Painted Metal Products, Rocking 8 Transportation), and metal recycling centers, including Angel recyclers and Sims metals. These are important contributors to trace metals contamination. Metal recycling activities engender dust (aerosol metals), smells, fume, noise, and traffic. During the breaking down of metals, the operations of torch cutting, shearing, shredding, or crushing occur in open areas in the scrap yards. Therefore, the generated aerosol metals may be transferred to the surrounding soils and cause metal contamination (Han et al., 2020).

Significant higher levels of most trace metals were recorded in *Group D*. In this group, the concentrations are 1,78%, 1.14%, 2.73 mg/kg, 11.7 mg/kg, 4.07 mg/kg, 0.26 mg/kg, 12.7 mg/kg, 228 mg/kg, 8.35 mg/kg, and 94.2 mg/kg for Al, As, Cr, Co, Cd, Cu, Mn, Ni and Zn, respectively. Compared to Houston soils, the concentrations of As, Mg, Zn, Mn, Co, Cu, Ni and Cr are in the 52nd ,62nd, 69th, 70th ,72nd ,77th 78th and 92nd percentile, respectively.

Mean concentrations of Fe, Cd, Cu, Pb, Cr, Co, Ni, and Zn are significantly higher ($p<0.05$) than those at *Group A* and *Group B* soils (See Figure 4.7, Figure 4.8, and Figure 4.9). For a better visualization of the data, the metal concentration variations in the income groups were plotted in individual graph (Figure 4.4).

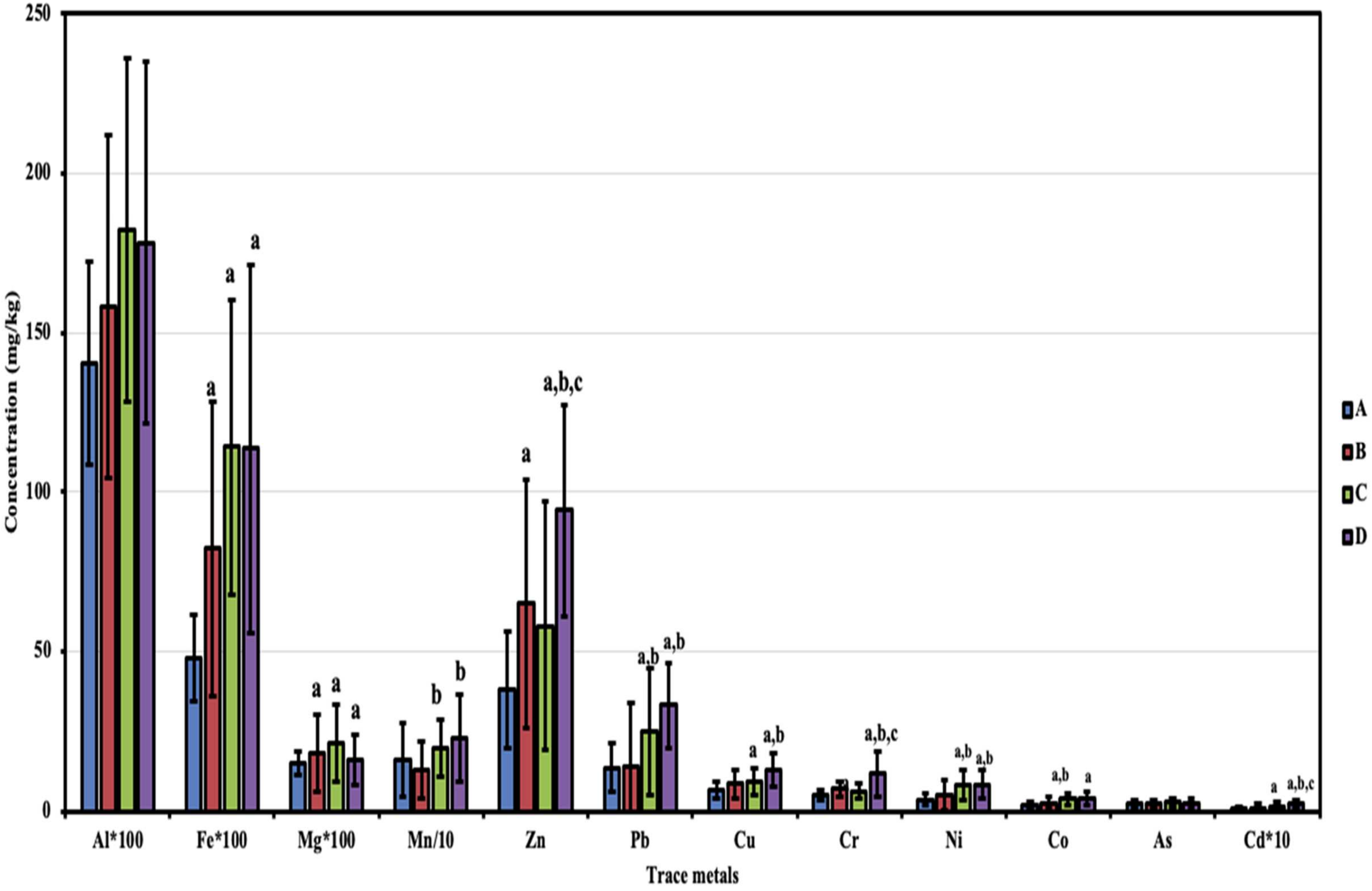

Figure 10 Trace metals concentrations in mg/kg

Concentration of Al, Fe, and Mg are in %. For a better visualization, some adjustments were made. Concentration of Al, Fe, and Mg are multiplied by 100, and Mn divided by 10. Cd concentration is multiplied by 10.

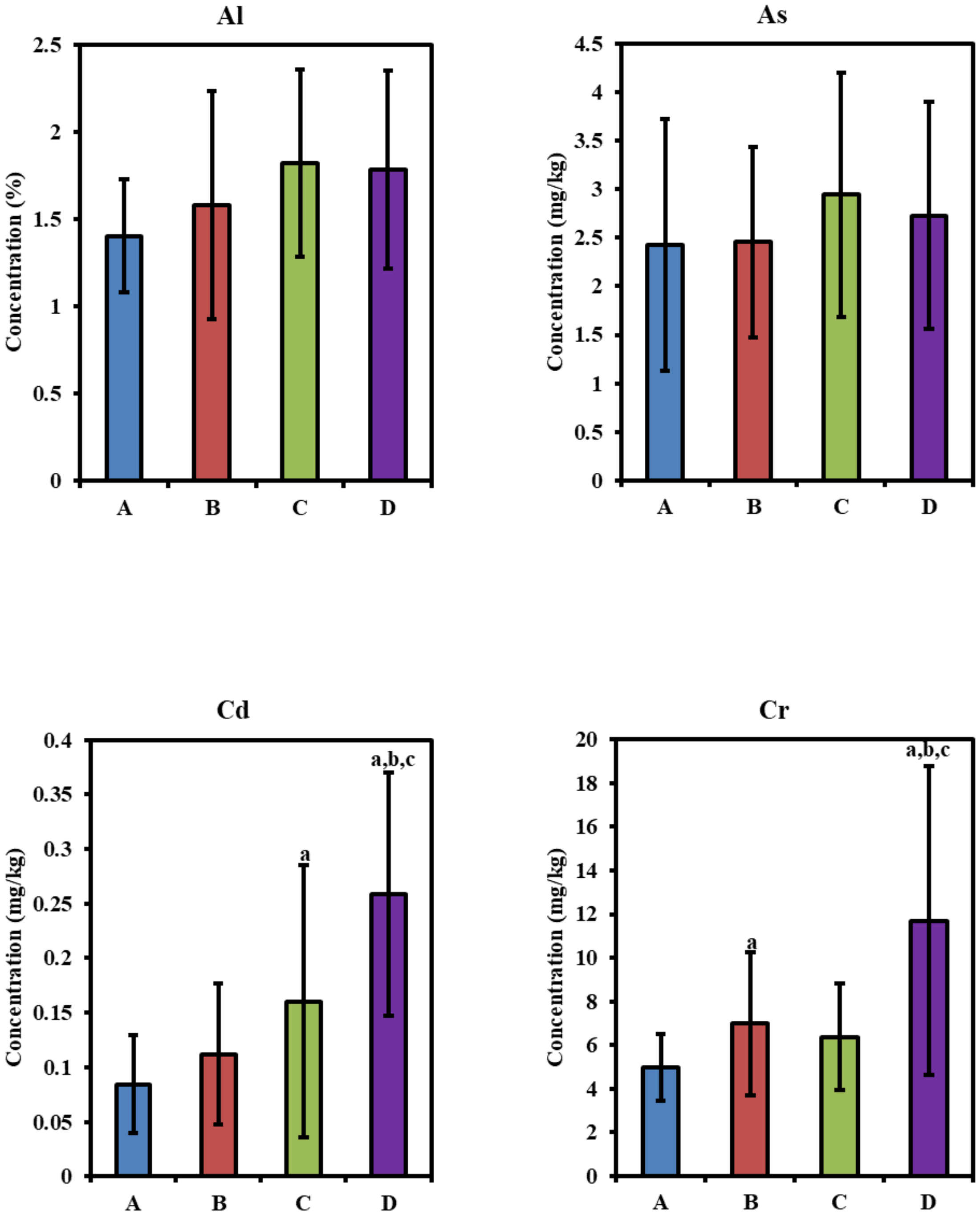

Figure 11 Graphs of Al, As, Cd and Cr mean concentrations in income groups.
Mean concentrations of As, Cd and Cr are in mg/kg, Al concentration unit is %.
a, b, and c refer to the difference at significance level of 0.05 ($p < 0.05$) with Group A, B, and C and D, respectively.

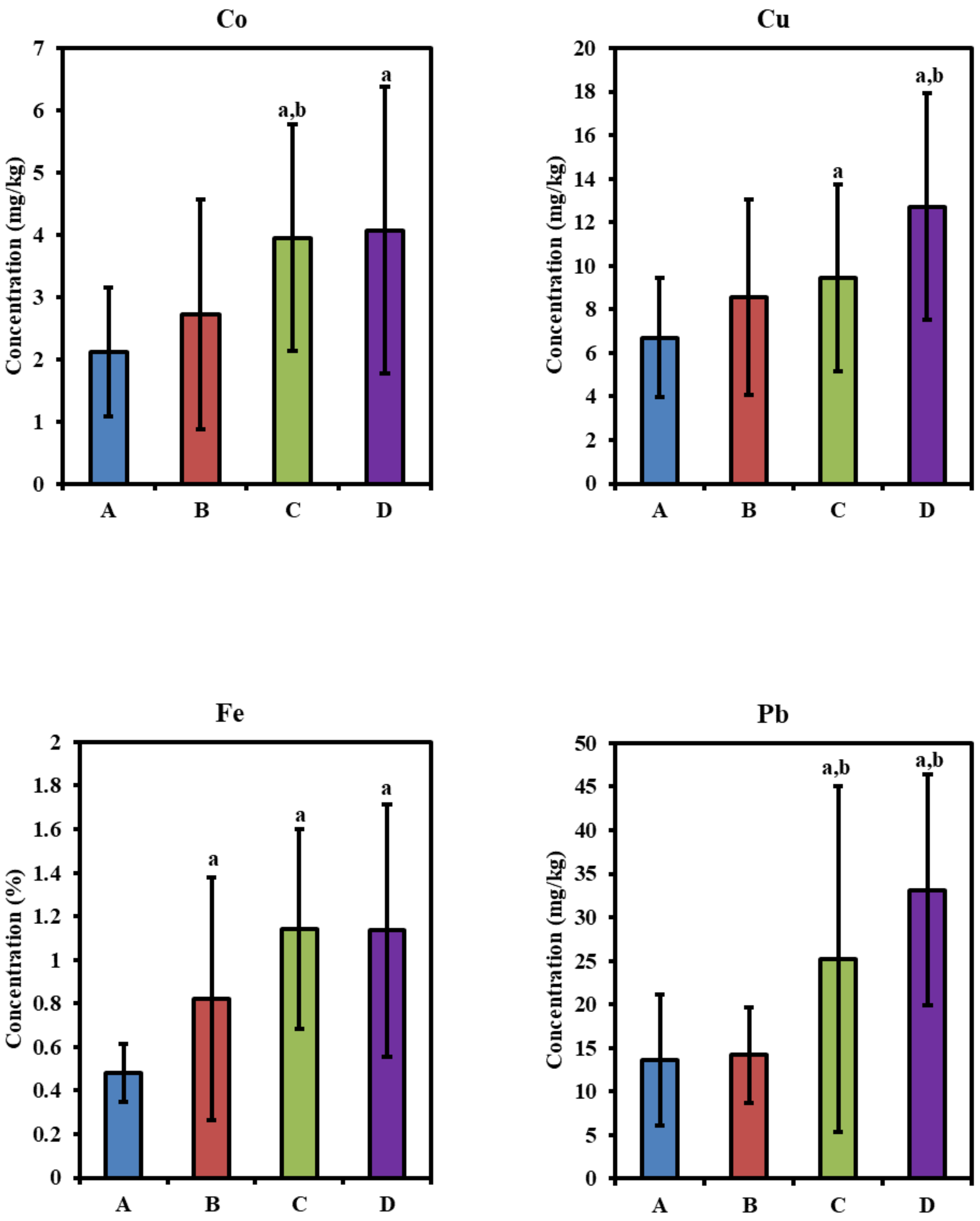

Figure 12 Graphs of Co, Cu, Fe, and Pb mean concentrations in income groups. Mean concentrations of Co, Cu, and Pb are in mg/kg, Fe concentration unit is %. a, b, and c refer to the difference at significance level of 0.05 ($p < 0.05$) with Group A, B, and C and D, respectively.

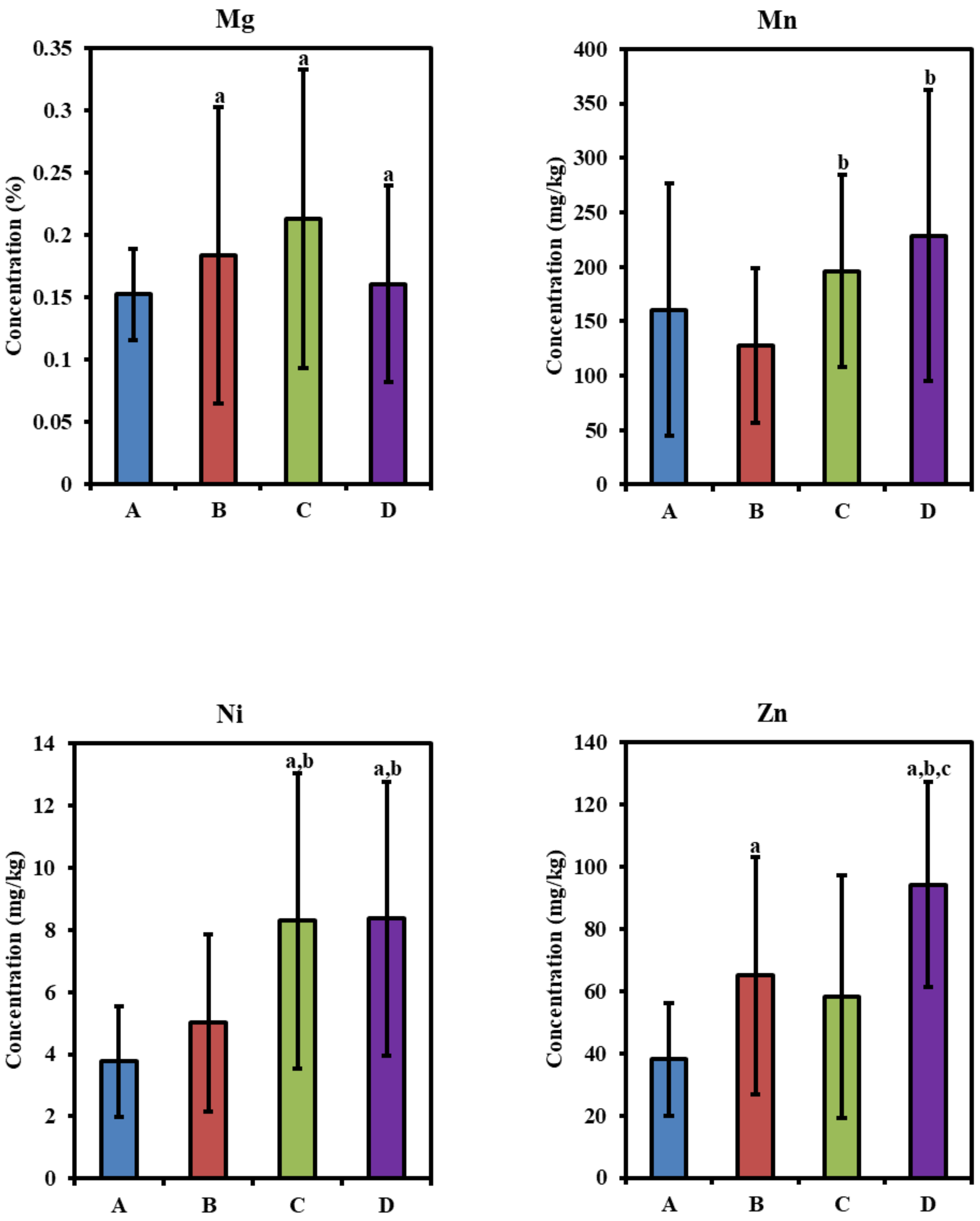

Figure 13 Graphs of Mg, Mn, Ni. and Zn concentrations in income groups. Mean concentrations of Mn, Ni, and Zn are in mg/kg, Mg concentration unit is %. a, b, and c refer to the difference at significance level of 0.05 ($p < 0.05$) with Group A, B, and C and D, respectively.

II. Assessment of contamination in soils

Contamination level of trace elements

The world and regional average or median of trace metals concentrations offer a basis for comparison of soil data at specific sites. However, they are of little use when interpreting soil data regarding contamination and potential toxicity. To understand the current situation of soil pollution, several indices have been employed to assess the soil pollution level. These methods include the geo-accumulation index (Igeo), monomial pollution index (Pi), threshold pollution index (PIT), enrichment factor (EF), and contamination factor (CF) and others (Yan et al., 2020).

In the present study, the enrichment factors and geo-accumulation factors are determined to distinguish between lithogenic values and anthropogenic origin of the trace elements.

Al, Fe, Mn, and Li are often elements used as reference elements. The natural occurrence of Al in the environment is 10,000 times greater than other trace elements. So, anthropogenic activities do not significantly affect Al concentration in soil. As a result, Al can be used to normalize concentrations in urban soils and natural background. In Houston MSA, Al was the trace element the most abundant and Texas background value of Al concentration is 1.5 times Fe concentration. Texas Background concentration of Li is unknown. Consequently, in the present study, Al is the best reference element to normalize the concentrations of urban soils and natural background. Houston background values of trace metals were from the United States National Geochemical Database (USGA, 2020).

Table 17 Concentrations of urban soils and natural background (in mg/kg) used in EF analysis

	Al (%)	As	Cr	Co	Cd	Cu	Fe (%)	Mg	Mn	Ni	Pb	Zn
Group A	1.4	2.43	4.96	6.7	0.08	6.7	0.48	0.15	161	3.76	13.6	38.1
Group B	1.58	2.45	6.97	8.55	0.11	8.55	0.82	0.18	128	5.01	14.2	64.9
Group C	1.82	2.94	6.38	9.43	0.16	9.43	1.14	0.21	196	8.29	25.2	58.1
Group D	1.78	2.73	11.7	12.7	0.26	12.7	1.14	0.16	228	8.35	33.1	94.2
Houston[1]	**1.2**	**1.97**	**15**	**5**	**ND**	**10**	**1.5**	**ND**	**70**	**5**	**10**	**26**

Group A High/Middle Income without industrial emissions.
Group B High/Middle Income with industrial emissions
Group C Low Income without industrial emissions.
Group D Low Income without industrial emissions
ND Not determined
1 United States National Geochemical Database (USGA, 2020).

Analysis of the Enrichment factors

The Enrichment factors (EF) are displayed in Table 18 and Figure 14. After removing the outliers, the enrichment factors varied between <1 to 5. The EF of Cd and Mg cannot be calculated since their background concentrations are unknown. The analysis of the EF shows that the lowest EF values are obtained in *Group A* while the highest are recorded in *Group D.*

In *Group A,* the enrichments of Cr, Co, Cu, Fe and Ni are within the range of natural concentrations. The soils have a minimal enrichment of As and are moderately contaminated with Mn, Pb and Zn. No metal is grossly contaminated by anthropogenic sources. Although the EF of the metals are higher (except for As) in *Group B* the trace metals lie in the same classes of EF as in the previous type of soil.

The overall enrichment of soils in Group D, based on the EF values, indicates that the soils are significantly enriched with Zn, moderately enriched with Ni, Mn, and Pb, minimally with As and Cu, but show no signs of enrichment with Cr, Co, and Fe. Similar classifications are observed in Group C at the exception of Zn which enrichment is within moderate.

Table 18 Al Enrichment factors (EF) of trace metals

	A	**B**	**C**	**D**
As	1.98± 1.45	1.90±0.66	1.83±0.74	1.76±0.41
Cr	0.52±0.13	0.72±0.35	0.52±0.23	0.93±0.37
Co	0.71±0.22	0.80±0.49	0.94±0.37	0.94±0.33
Cu	1.12±0.53	1.12±0.79	1.17±0.54	1.59±0.45
Fe	0.59±0.09	0.73±0.25	0.93±0.30	0.90±0.23
Mn	3.26±2.23	3.26±2.55	3.28±1.02	3.89±1.92
Ni	1.25±0.31	1.25±0.45	2.08±1.44	2.00±0.62
Pb	2.53±1.84	2.53±1.24	3.15±2.37	4.46±2.06
Zn	2.67±1.63	2.67±2.02	3.00±2.50	5.09±2.26

EF Mean values of trace elements ± SD

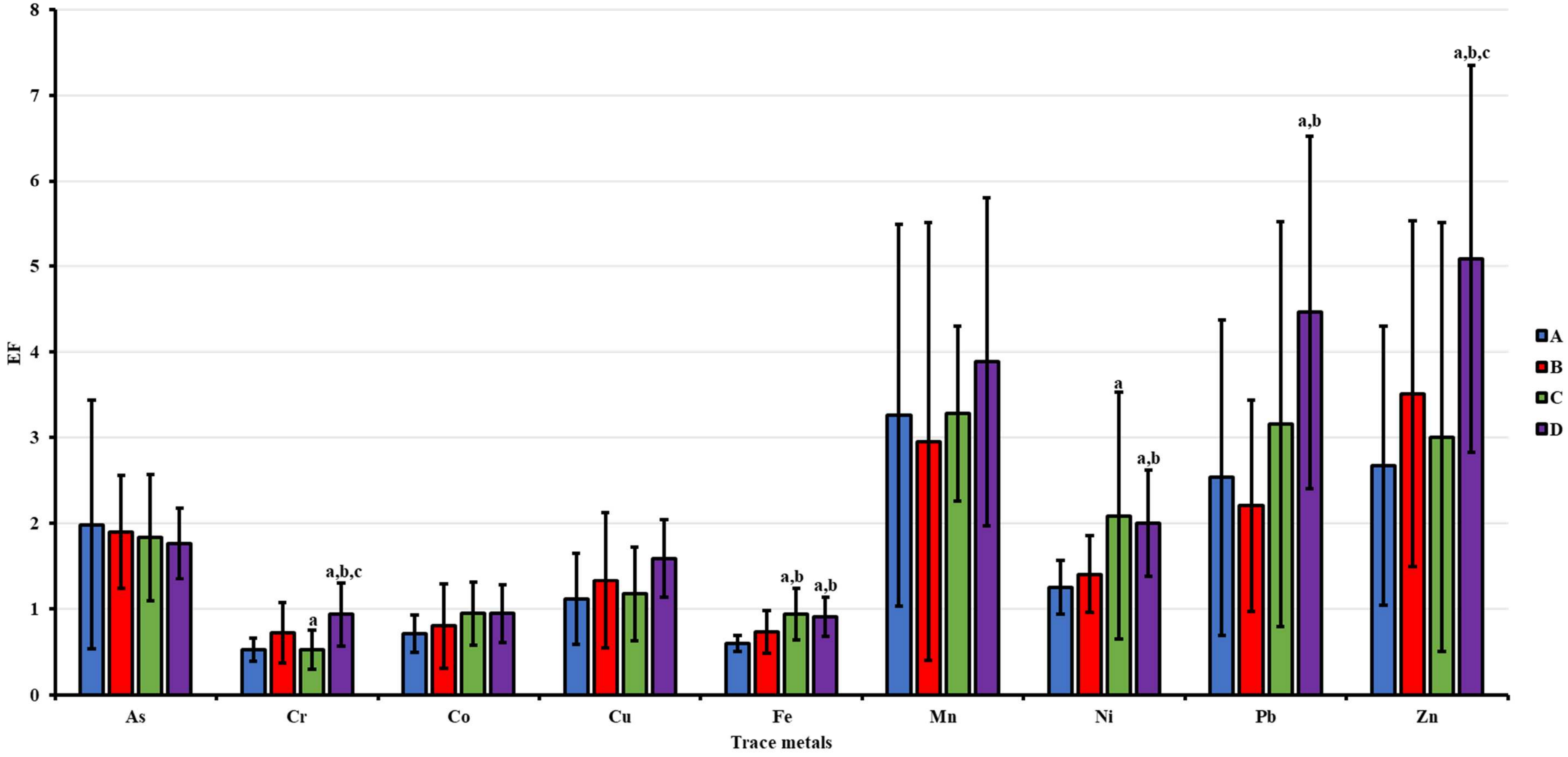

Figure 14 Al Enrichment factors (EF) of trace metals in urban soils

Mean values of EF
Errors bars represent ± SD
a, b, and c refer to the difference at significance level of 0.05 ($p < 0.05$) with Group A, B, and C, respectively.

Analysis of the Geo-accumulation factors (Igeo)

The Igeo analysis reveals that all urban soils are unpolluted by Al, As, Cr, Co, Cu, Fe, Ni, and Pb, with the lowest Igeo values portray by *Group A*; and the highest found in *Group D* (See details in Table 19 and Figure 15). The negative values of Al, As, Cr, Co, Cu, Fe, Ni, and Pb Igeo presented in Figure 4.6 are due to the deficient to minimal enrichment (Table 4.8). The values of the Mn Igeo (<1) imply that the soils have low levels of Mn or are moderately contaminated by this metal. The soils in *Group B* and *Group C* are moderately polluted by Zn (0<Igeo<1). The soils in *Group D* are moderately contaminated by Pb and Zn with the Igeo values fluctuating between 1 < Igeo <2.

Table 19 Geo-accumulation factors of trace metals

	A	**B**	**C**	**D**
Al	-1.27±0.33	-1.19±0.64	-0.92±0.43	-0.96±0.47
As	-0.48± 0.77	-0.39±0.63	-0.16±0.74	-0.25±0.67
Cr	-2.25±0.46	-1.85±0.72	-1.93±0.61	-1.18±0.86
Co	-2.05±0.89	-1.79±1.02	-1.09±0.76	-1.15±0.97
Cu	-1.28±0.60	-0.99±0.73	-0.81±0.69	-0.36±0.64
Fe	-1.38±0.44	-0.85±0.94	-0.22±0.72	-0.28±0.80
Mn	0.24±1.28	0.06±0.84	0.74±0.74	0.82±1.05
Ni	-1.16±0.72	-0.51±0.84	-0.09±0.88	-0.06±0.85
Pb	-0.34±0.77	-0.19±0.58	0.36±1.16	1.15±0.67
Zn	-0.20±0.73	0.51±0.82	0.29±0.94	1.15±0.67

Mean values of Igeo± SD

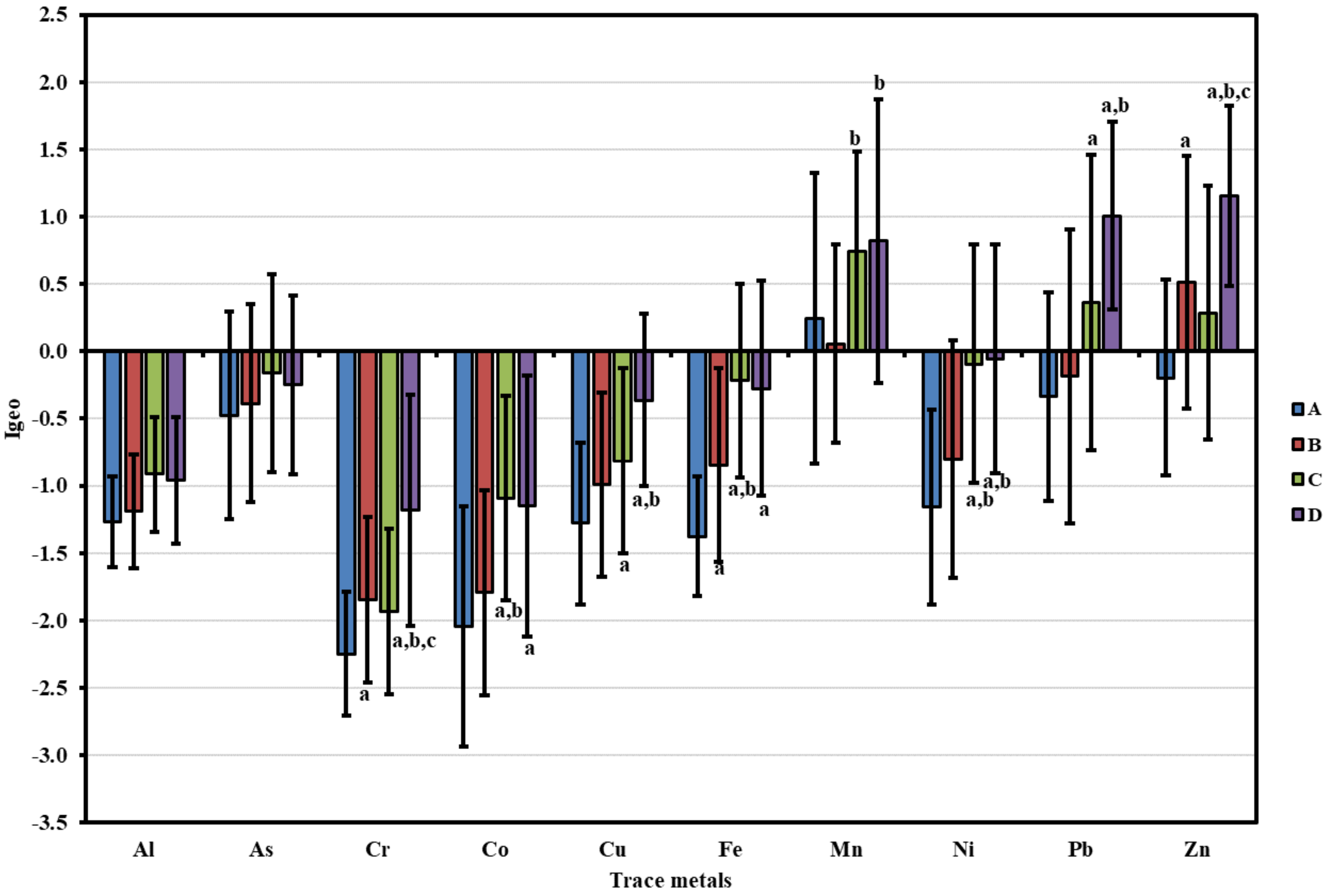

Figure 15 Geo-accumulation Indices (Igeo) of metals in urban soils

Mean values of Igeo. Errors bars represent ± SD

a, b, c and refer to the difference at significance level of 0.05 ($p < 0.05$) with Group A, B, and C, respectively.

Comparison of the EF and the Igeo

The correlation coefficients (R values) represented in Figure 16, Figure 17 and Figure 18 show a strong positive correlation between Igeos and EFs. The correlation coefficients are high for trace elements including Co (0.87), Fe (0.87), Mn (0.87), Ni (0.84), Cr (0.84), Pb (0.83), Zn (0.82) and As (0.64). The pollution assessment indicates that overall, the contamination of the soils is negligible for As, Co, Cr, Fe and Ni. These metal concentrations are likely due to natural processes. The soils in *Group A* are the least impacted by anthropogenic activities and those in *Group D* are the most impacted, though the trace metals enrichment is very moderate, especially for Mn, Pb and Zn. Since Pb and Zn are known as urban metals and usually exceed background concentration in cities, their obtained concentrations are not surprising. However, because the soil contains elevated amounts of Mn, Mn concentration should not have been impacted by human activities. Thus, the moderate enrichment of this element indicates that besides natural processes, additional potent contributors of Mn exist such as smelting emissions (Wang & Zhang, 2018).

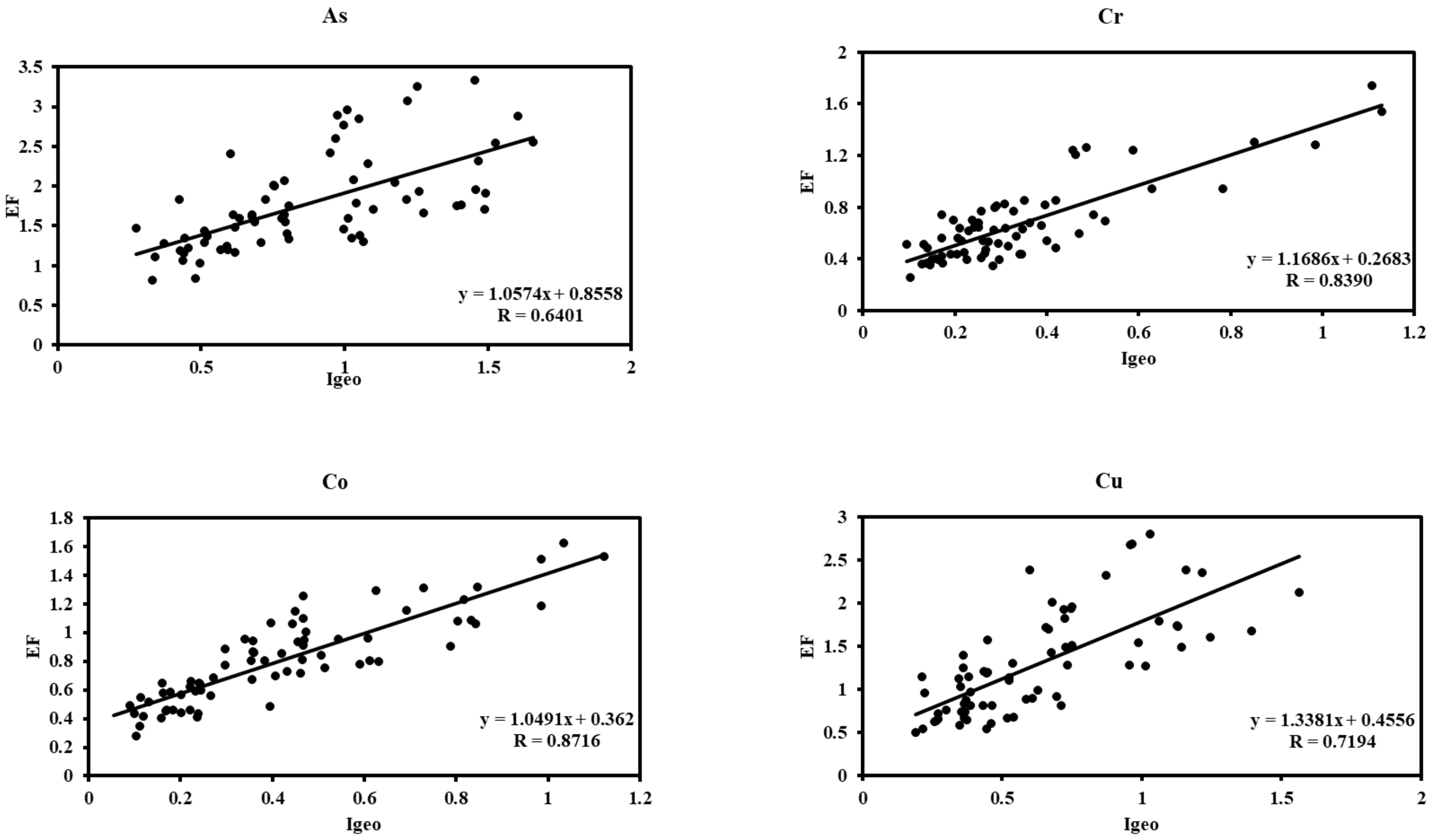

Figure 16 Correlation graphs of As, Cr, Co and Cu EF vs Igeo
The EF values were plotted against the Igeo values. The solid line represents the regression line.
R represents the coefficient of correlation.

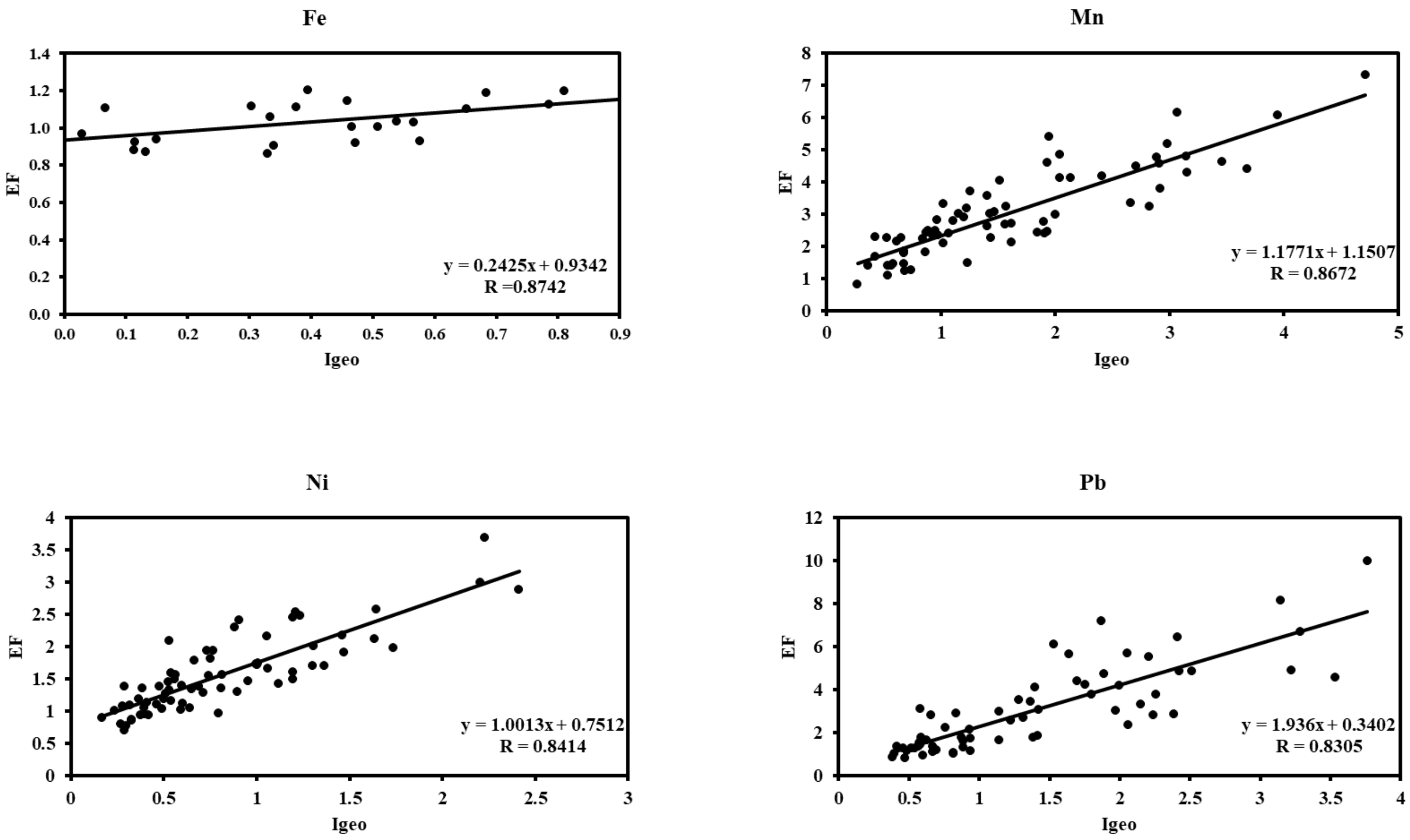

Figure 17 Correlation graphs of Fe, Mn, Pb, and Ni EF vs Igeo
The EF values were plotted against the Igeo values. The solid line represents the regression line.
R represents the coefficient of correlation.

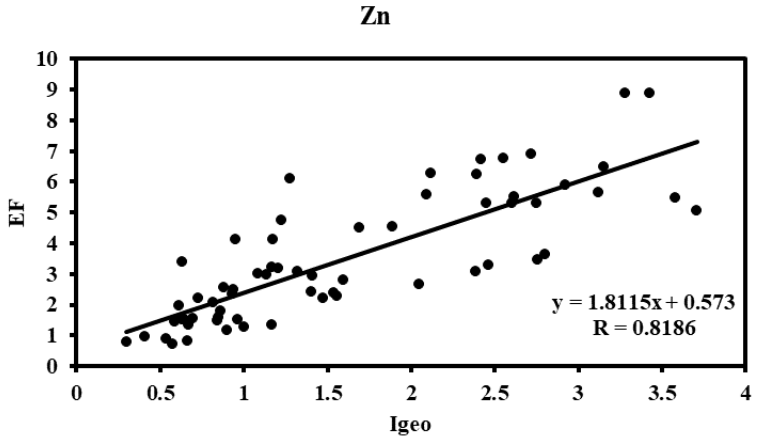

Figure 18 Correlation graph Zn EF vs Igeo
The EF values were plotted against the Igeo values. The solid line represents the regression line.
R represents the coefficient of correlation.

Analysis of the Toxic Units

Table 20 Reference values used in Toxic Units calculations

	% Al	As	Cd	Co	Cu	Total Cr	Cr III	Cr VI	% Fe	Mg	Mn	Ni	Pb	Zn
EPA[1]	7.70	0.39	71	23	3,100	NA	120,000	0.30	5.50	NA	1,800	1,600	400	23,000
NY[2]	NA	16	4.30	NA	270	NA	180	110	NA	NA	2,000	140	400	10,000
CA[3]	NA	0.11	91	NA	NA	NA	NA	0.30	NA	NA	NA	15,000	80	NA
TX[4]	6.50	24	52	680	1,300	33,000	33,000	120	NA	NA	3,900	840	500	9,900
WHO[5]	NA	NA	3	NA	30	100	NA	NA	NA	NA	NA	80	100	300

[1] USEPA Soils Screening Levels (SSLs)
[2] New York State Department of Environmental Conservation Soil Cleanup Objectives (SCOs)
[3] California Screening Levels for Residential Soil
[4] Texas Risk Reduction Program (TRRP)
[5] (WHO, 1996) (Ogundele et al., 2015)
NA Not Applicable

Table 21 Sum of Toxic Units (∑TU)

	TX	NY	WHO	EPA	CA
A	0.59±0.26	0.77±0.35	0.62±0.26	6.70±3.49	22.7±12.0
B	0.66±0.34	0.91±0.44	0.84±0.41	6.91±2.78	23.2±9.31
C	0.84±0.37	1.18±0.49	1.05±0.61	9.02±4.08	28.6±12.0
D	0.84±0.31	2.74±1.45	4.33±2.06	8.96±4.38	28.4±15.0

To determine the possible acute toxicity of the trace elements in the urban soils, the toxic units were calculated from references provided by various organizations (Table 20). The EPA's thresholds for residential soils were employed to estimate the sum of Toxic Units for EPA. Soils Screening Levels (SSLs) were established by EPA to organize the cleanup of superfund sites intended for upcoming land use as residential. They are a tool employed by EPA to standardize and speed up the assessment and remediation of contaminated soil at sites on the National Priorities List (NPL), where future residential land use is expected. SSLs are guidelines values and aim to focus resources for site evaluation and cleanup where they are most needed. Under the Superfund program, soils contaminants below the SSLs do not need to take any supplementary action. However, these soils must still comply with any standards or screening levels under states or local programs. States or local programs may be more stringent than EPA's thresholds and require cleaning actions. The sum of the TU (∑TU) obtained were compared to soil screening levels of the states of TX, NY, and CA. USEPA's thresholds were also compared to those of an international organization, World Organization Health (WHO) (See Table 21 and Figure 19 for details).

The ∑TU for trace elements in different urban surface soils are represented in Table 4.12 and Figure 4.7. Using TX references, no ∑TU surpassed 1 even though values obtained in *Group D* and *Group C* were significantly higher than values in A and B ($p<0.05$). The ∑TU derived from NY state indicates that Group A and Group B's soils do not require cleaning (∑TU <1), contrary to Group C and Group D, which may necessitate clean up. Likewise, following WHO's recommendations, soils in *Group A* and *Group B* do not demand cleaning up, but soils in *C* and *D* may require it.

Using EPA's screening levels, the ∑TUs exceed 1 in all groups, ranging from 6.7 to 9.02. These values are high, and according to EPA, all these soils may necessitate clean-up. The values reached using California references are remarkably high, ranging from 22.7 to 28.6. California ∑TU are 34 to 39-fold, 29.5 to 35-fold, and 3.2 to 3.4-fold the ∑TU of the states of TX, NY, and EPA, respectively. The ∑TU obtained are 2.1 to 10.8 times higher than WHO. These results clearly indicate that the state of CA is more stringent than the states of TX and NY and even more than the regulatory agencies USEPA and WHO.

In general, the ∑TUs for the studied metals for the soils in *Group C* and *D* are significantly elevated than the other soils. The ∑TUs are in the similar trends of metal concentrations in soils and the EFs and Igeos.

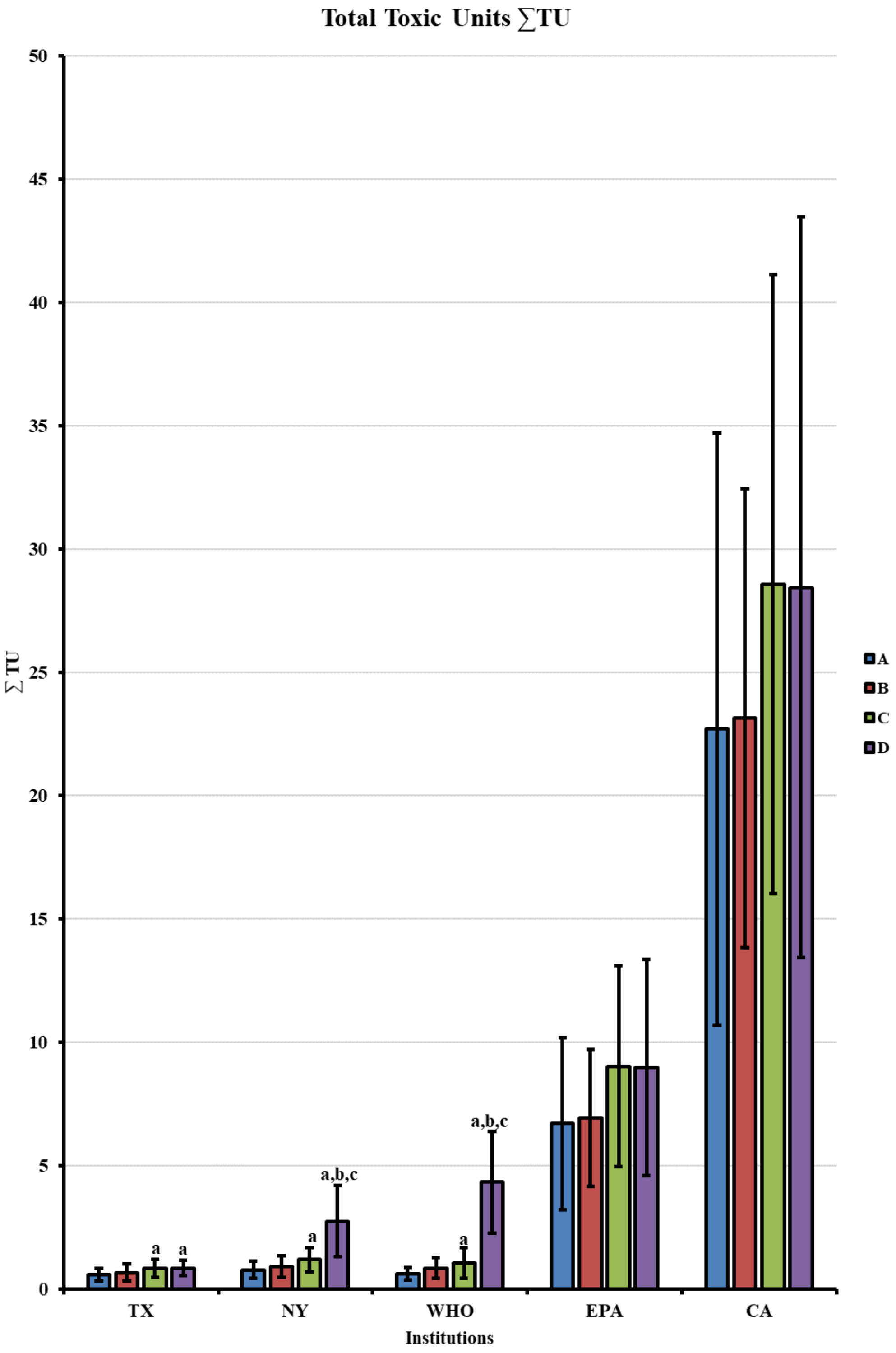

Figure 19 Sum of Toxic Units of the urban soils according to different institutions

CHAPTER 5

SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

In this study, two analytical methods ICP-MS and XRF, were used to obtain the concentration of 12 trace metals in Al, As, Cu, Co, Cd, Cr, Fe, Mg, Mn, Ni, Zn, and Pb in Houston MSA. Data revealed that ICP-MS analysis (preceded by nitric acid digestion) underestimated Al, Cu, Cr, and Fe. XRF did not detect Ni, Mg, and Cd, and it underestimated Pb, Zn, and Mn. The results indicate that both techniques have their advantages and drawbacks. ICP-MS is highly sensitive and provides analysis of metals at ultra-level concentrations. However, it requires extensive sample preparation and measured concentrations of metals strongly depend on the acid used in the sample pretreatment steps. The second one is rapid, low cost, and does not require exhausting sample preparation. However, low-level concentration of elements in the soil are undetectable. Also, due to the sample matrix used in calibration, accuracy can be a problem. In lieu of these instrumental capabilities this study shows that both techniques are reliable and depending on the analyte of interest and the degree of accuracy targeted, both can be used. The two analytical methods can be combined to measure trace elements in soils. This study highlights the necessity of a multi-technique approach on trace analysis of environmental samples.

Soil samples from 4 income groups across the Houston Metropolitan Area were analyzed for trace metals to examine the impacts of anthropogenic activities on Houston's surface soil pollution and explore the relationship between soil trace metal concentrations and economic status (annual income) of surrounding communities. The mean concentrations of trace metals in Houston Metropolitan soils vary between 1.67%, 0.99%, 0.18%, 201 mg/kg, 138 mg/kg, 39.0 mg/kg, 12.6 mg/kg, 10.1 mg/kg, 8.01 mg/kg, 3.51 mg/kg, 3.07 mg/kg, and 0.23 mg/kg, for Al, Fe, Mg, Mn, Zn, Pb, Cu, Cr, Ni, Co, As and Cd, respectively. Except for Pb and Zn, metal concentrations were below their equivalent TCQE background concentrations. When compared to urban soils in the US and the world, they are found to be in the same range. This shows that overall urban soils in Houston MSA follow the same overall trend as worldwide soils. The analysis of the soils per income group and emissions range shows that the soils located in Middle/High income without industrial emissions display the lowest concentrations of trace metals. These concentrations are below the TCQE background levels, and the Houston MSA' s mean concentrations. The soils of this income group are likely not impacted by anthropogenic activities. Therefore, concentrations of these soils can be used as background concentrations in Houston Metropolitan for future studies. The highest concentrations of trace metals were obtained in low-income communities, with values more often exceeding the TCQE background levels and Houston average concentrations. Even in low-income neighborhoods without industry reporting to TRI, trace metal concentrations are significantly higher in the soils. A further look at the EF and Igeo indexes indicates that surface soils in affluent neighborhoods are minimally affected by anthropogenic activities. Whereas the EF and Igeo values suggest that the concentrations of trace metals in low-income neighborhoods are due to moderate anthropogenic contamination of the soils. This study reveals that TRI data are not a good indicator of pollution. Thus, some industries that not required to report to TRI may still cause substantial contamination in low-income communities.

This study also looks at the values of the sum of TU values. Toxic units were estimated based on different regulations, including state regulations (TX, NY, and CA), federal (EPA), and international (WHO) guidelines. This study found that the state of California is very stringent compared to the other states, including TX and NY, even more than the national regulatory agency, EPA, and the international agency WHO. On the contrary, the state of Texas has the least stringent regulations. Under TX regulations, none of the soils of the income groups requires clean-up. However, under NY, CA, EPA, and WHO, soils located in "low-income without industrial emissions" and ‘‘low income with industrial emissions require clean up. This investigation underlines the importance of harmonizing federal and national regulations regarding the environment, so all socio-economic groups can be protected.

The hypothesis of this study was that “anthropogenic trace metal contamination in surface soils negatively correlate with income”. This hypothesis is accepted because the highest concentrations of trace metals in surface soils, along with the highest values of enrichment factors, geo-accumulation indices, and sum of toxic units, are recorded in low-income neighborhoods without and with industrial emissions.

This study enhances the scarce literature regarding trace metals concentrations in Houston surface soils and can serve as reference values for future environmental studies. This study helps better understand trace metals sources in soils by distinguishing between natural origin and anthropogenic input by using adequate and appropriate data. It also contributes to distributive EJ by revealing that low-income communities living in the proximity of industrial facilities face significantly higher exposure to surface soils trace metals. This study shows that closeness to industrial facilities is likely to be a crucial factor for the health risk of children living in economically disadvantaged communities. Thus, this study can be used to enhance policymaking decisions in Houston MSA.

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