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SPATIAL ANALYSIS OF EXPOSURE TO SOIL HEAVY METALS, ORAL BIOACCESSIBILITY AND RISK ASSESSMENT IN HOUSTON, TEXAS

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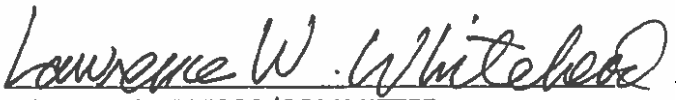

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by

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SPATIAL ANALYSIS OF EXPOSURE TO SOIL HEAVY METALS, ORAL BIOACCESSIBILITY AND RISK ASSESSMENT IN HOUSTON, TEXAS

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Abstract

Chronic exposure to heavy metals could lead to adverse health effects such as cancer, neurological development diseases and immunological diseases. The ingestion pathway has been considered the major exposure route for heavy metal contaminated soils. Heavy metals may be proportionally bioaccessible for the human body to absorb. There are no risk assessment studies done in Houston to evaluate health risks from exposure to heavy metals and no spatial analysis done yet. The aims of this dissertation are (1) to characterize 13 heavy metals: magnesium (Mg), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), lead (Pb), barium (Ba), and cadmium (Cd) in soils in Houston, Texas (TX), and evaluate spatial distribution maps of these metals; (2) to assess bioaccessibility of 13 metals (Pb, Cd, Cu, As, Cr, Zn, Ni, Mn, Ba, Co, Mg, Fe, and V) in soils; (3) to estimate human health risks of 10 toxic

metals (As, Ba, Cd, Cr, Cu, Mn, Ni, Pb, Zn, and V) using metal concentrations in soils and bioaccessibility concentrations, and to simulate cancer and non-cancer risks maps.

We sampled top soils at 96 locations in Houston, TX. We used microwaved-acid digestion system to prepare the soil samples and analyzed metal concentrations in soils by inductively coupled plasma mass spectrometry. Besides, we obtained Environmental Justice Screening and Mapping Tool Indexes to identify possible high exposure groups and emission sources of metals. We simulated heavy metal distribution by ordinary kriging in SAS software and ArcGIS software. Moreover, we used an in-vitro bioaccessibility method to obtain percent bioaccessibility fractions (%BAF) in gastric phase and gastro-intestinal phase. We assessed human health risks by using metal concentrations in soils and bioaccessibility results among five age groups, 0 to < 1 year old (infants), 1 to < 6 year old (toddlers), 6 to < 12 years old (children), 12 to < 18 years old (teenagers), and 18 to < 78 years old (adults), and estimated hazard index (HI) and cancer risks with SAS software and ArcGIS software for non-sampled area.

Ninety-six percent of samples had either one or more than one metal over Texas Commission on Environmental Quality (TCEQ) background values. Pb and Zn had more than 80% of samples over TCEQ background levels. We found that closer proximity to National Priority sites and Risk Management Plan sites had higher Ni, Cr, Ba, Cu, Pb and Zn in soils than further proximity. We also discovered environmental justice issues in Houston as minority and low income groups live in neighborhoods with high Ni, Cr, Ba, Cu, and Zn concentrations in soils. We found that most of the metals had decreasing %BAF from gastric

phase to gastro-intestinal phase, except Cu and V. The %BAF in gastric phase ranged from 1.22 % to 69.71 %. The %BAF in gastro-intestinal phase ranged from 0.22 % to 45.87%. For chronic non-cancer health effects, all hazard indexes among 5 age groups were under one (1). The infants group had the highest HI followed by toddlers group. Pb contributing 90% and As contributing 6% in HI when applying all three experimental results. Adults group's cancer risks were 1.02 in a million followed by toddlers group.

We suggested that future metal pollution studies interested to point sources in Houston should focus in East and South side. Other studies interested to traffic volume should have better study design to differentiate emission since Houston doesn't have zoning between industrial area and residential area. Furthermore, for exposure of young children, future studies should focus for soils in playgrounds, parks, or schools, especially around old downtown areas.

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CHAPRTER I. BACKGROUND

Literature Review

Anthropogenic Emissions of Metals

People living in urban areas are widely exposed to heavy metals from two major anthropogenic sources: (1) point sources such as petrochemical plants, metal production plants, old lead-painted houses, smelting plants, metals recycling plants, and municipal dumpsites; (2) non-point sources such as vehicle engine emissions, wear or abrasions of vehicle components, resuspension of urban polluted soils. Depending on the anthropogenic activities in the cities, each metal has unique emission profiles from various sources. Arsenic (As)- major sources of emissions include copper smelting, herbicide, pesticide, rodenticide use, waste incinerations, steel/glass production (Datta et al., 2007). Zinc (Zn) could be emitted from tire wear to road surface and copper (Cu) could be emitted from brake pad wear to road surfaces (Cai et al., 2016). Cadmium (Cd) could come from the production of alloys, pigments and batteries (Tchounwou et al., 2012). Chromium (Cr) release would include metal processing, stainless steel welding, leather tanning, anticorrosive agents in cooking systems and boilers (Tchounwou et al., 2012). Houston is the fourth-most-populous city in the United States with high traffic roadways and many industrial sources such as oil and gas, petrochemical industry, and other steel making industries. Fabricated metal products, machinery manufacturing, petroleum & coal products, and chemicals comprise of 64% of Houston manufacturing sectors (Greater Houston Partnership, 2017). Because there are a lot of potential metal emission sources in Houston, people living in Houston are likely exposed to various toxic heavy metals during their daily activities.

Metals Toxicity

Exposure to selected toxic metals could lead to detrimental health effects. Human toxicity of metals of interest is summarized in Table I-1 (pg. 3) (ATSDR, 2016; USEPA, 2016). There are two types of human toxicity among several metals: carcinogenicity and non-cancer health effects. First, carcinogenic heavy metals are summarized in Table I-1 (pg. 3). Lead (Pb) is classified as B2 probable human carcinogen by the United States Environmental Protection Agency (USEPA); that means Pb has sufficient animal bioassay but little or no human evidence. High exposure to Pb results in cardiovascular, neuro-developmental, and reproductive health effects. Cadmium (Cd) is classified as B1 probable human carcinogen by USEPA; that means Cd shows sufficient animal bioassay but limited human evidence. Further, exposure to elevated levels of Cd is associated with cardiovascular and neuro-developmental outcomes. Arsenic (As) is classified as a level A human carcinogen by USEPA; that means As shows adequate human data to demonstrate the causal association of the agent with human cancer. Exposure to As causes dermal, neurological, and respiratory health effects. Exposure to total chromium (Cr) may affect adverse immunological and respiratory effects. Hexavalent Cr (Cr^{6+}) is known as a human carcinogen by USEPA through inhalation route. Cobalt (Co) is reasonably anticipated to be a human carcinogen by Agency for Toxic Substances and Disease Registry (ATSDR), and it affects cardiovascular, developmental, and respiratory system.

Second, the following metals are not classified as human carcinogens but they are associated with other health effects. For instance, Zinc (Zn) is associated with blood forming and adverse outcomes for respiratory and gastrointestinal system. Nickel (Ni) in nickel refinery dust is classified as a human carcinogen by USEPA, and it affects cardiovascular and

Table I-1 Metals Toxicity Summary

Metal	Carcinogen	Cardiovascular	Developmental	Gastrointestinal	Musculoskeletal	Reproductive	Neurological	Respiratory	Skin	Immunological
Lead (Pb)	USEPA classified B2[a]	✓[b]	✓[b]	✓[b]	✓[b]	✓[b]	✓[b]			
Cadmium (Cd)	USEPA classified B1[a]	✓[b]	✓[b]	✓[b]			✓[b]	✓[b]		
Copper (Cu)	USEPA classified D[a]			✓[b]						
Arsenic (As)	USEPA classified A[a]			✓[b]			✓[b]	✓[b]	✓[b]	
Chromium (Cr)	Cr(VI) (inhalation) – USEPA classified A[a]							✓[b]		✓[b]
Zinc (Zn)	USEPA classified D[a]			✓[b]				✓[b]		
Nickel (Ni)	USEPA nickel refinery dust classified A[a]	✓[b]						✓[b]	✓[b]	✓[b]
Manganese (Mn)	USEPA classified D[a]	✓[b]					✓[b]	✓[b]		
Vanadium (V)	No data	✓[b]		✓[b]		✓[b]		✓[b]		
Barium (Ba)	No data	✓[b]		✓[b]		✓[b]				
Cobalt (Co)	ATSDR classified NTP[b]	✓[b]	✓[b]					✓[b]		

a: USEPA, 2016
b: ATSDR, 2016

immunological systems. Manganese (Mn) affects cardiovascular and immunological systems. Vanadium (V) may result in adverse cardiovascular, reproductive, and respiratory effects. Barium (Ba) affects cardiovascular, gastrointestinal and reproductive systems.

Characteristics of metals in soils in United States

Toxic heavy metals are ubiquitous in soils. The profiles and concentrations of toxic metals in soils are heterogeneous among different U.S. cities (Table I-2).

Table I-2 Metals concentrations in soils in US studies

Metal (mg/kg) / Location	Pueblo/CO[1]	Sacramento/ CA[2]	Spokane/ WA[3]	Anniston/ AL[4]	Baltimore/ MD[5]
Arsenic	12.9	8.9/7.5	7.9	6.9	2.5
Cadmium	2.6	0.5/0.3	0.3	0.7	0.2
Chromium	N/A	N/A	21.7	17.6	13.5
Copper	N/A	41.9/39.3	16.6	61.7	13.6
Lead	89.8	128.0/52.6	48.0	182.8	33.8
Nickel	N/A	N/A	N/A	12.0	9.7
Zinc	N/A	216.0/120.0	207.0	344.7	68.5

1 Diawara et al., 2006: means of 66 samples
2 Solt et al., 2015: means/medians of 91 samples
3 Nezat et al., 2017: geomatric means of 20 samples in residential area
4 Ha et al., 2014: means of 66 samples in less polluted area
5 (Pouyat et al., 2015): medians of 107 soil samples

For example, means of As were: 12.91 mg/kg in Pueblo, Colorado; 8.9 mg/kg in Sacramento, California; and 6.92 mg/kg in Anniston, Alabama (Diawara et al., 2006; Ha et al., 2014; Solt et al., 2015). Means of Cd were reported as: 2.60 mg/kg in Pueblo, Colorado; 0.49 mg/kg in Sacramento, California; and 0.68 mg/kg in Anniston, Atlanta (Diawara et al., 2006; Ha et al., 2014; Solt et al., 2015). Means of Pb were: 89.76 mg/kg in Pueblo, Colorado; 128 mg/kg in Sacramento, California; and 182.81 mg/kg in Anniston, Alabama (Diawara et al., 2006; Ha et al., 2014; Solt et al., 2015). Even though there were studies in the U.S., due to differences of contamination sources and traffic loading, it is difficult to extrapolate the metal contamination information to Houston.

Another interesting finding for metal characteristics in soil is that concentrations of metals are more elevated in urban soils than in rural soils. Lead concentrations in urban soils were 3 to 5 times higher than in suburban soils in several US cities (Datko-Williams et al., 2014). Davis et al. found that median Pb from all pooled urban sampling sites was 23 mg/kg compared with 13 mg/kg from rural sampling locations (Davis et al., 2014). Aelion et al. also found mean Pb in urban areas was 45 mg/kg and that in rural areas was 12 mg/kg, and metal concentrations of As, Ba, Cr, Cu, Pb, Mn, and Ni were statistically greater in the urban area than the rural area ($p<0.0001$)(Aelion et al., 2009). Although these studies did not examine the sources of metal emissions, the facts suggested that anthropogenic sources are major contributor in urban soils.

Houston is the 4th largest city in the U.S. in population, and has no formal separation between residential and industrial area. There are pollution sources like the oil and gas industry, chemical industry, metal fabrication industry and metal recycling facilities. A study done in Anniston, Alabama, had showed that Pb, Co, Cu, Mn, Zn, As were 1.2 to 2.2 times higher within 500 meters proximity to industrial facilities compared to further away (Ha et al., 2014). There is great potential that metals concentrations in soil in residential area would be elevated because of proximity to industrial activities.

Metal characteristics data in soil are limited in Houston. Table I-3 shows that U.S. Geological Survey (USGS) sampled soils of four suburban sites in Houston (Smith et al., 2013).

Table I-3 Metals concentrations in Houston in USGS survey (Smith et al., 2013)

Site ID/Metals Con. (mg/kg)	Latitude	Longitude	As	Ba	Cd	Cr	Cu	Mn	Ni	Pb	Zn
A	29.9504	-95.0364	3.7	209	0.1	43	16.2	97	12.1	16.7	53
B	29.943	-95.225	2	145	<0.1	11	6	69	5.4	11.8	28
C	29.9064	-95.1531	3.6	186	<0.1	20	10.2	135	8.3	21.4	38
D	29.776	-95.5575	4	237	0.1	15	7.9	209	8.8	20.2	29

Concentrations of metals were varied from site to site (Smith et al., 2013). Benipal et al. examined 19 sites around downtown Houston, and found that samples surrounding by

heavy automobile traffic had elevated metal concentrations (Benipal et al., 2017). Although these studies were done in Houston, they only cover less than 1 % of the city. There is a need to collect more soil samples and address the environmental health question. Eleven metals (Pb, Cd, Cu, As, Cr, Zn, Ni, Mn, V, Ba and Co) showed toxicity in human body as Table I-1 presented (pg. 3), and Mg and Fe are good indicators for soil minerals (Mayland and Sneva, 1983). Therefore, I propose to analyze the 13 metals in soil.

Application of In-Vitro Bioaccessibility Test

One of the potential exposure pathways for soil for adults and children is ingestion. According to USEPA, soil ingestion comes from various behaviors like, mouthing, contacting dirty hands, eating dropped food, consuming soil directly, and smoking cigarettes with adhered soil; soil ingestions is especially significant for children, for they tend to play on the ground, mouth objects or their hands (USEPA, 2017). There have been studies showing elevated blood-lead levels in children related to exposure inside and outside of residences with lead-contaminated soils (Solt et al., 2015). Furthermore, ingestion of soil is such a significant exposure for children that an estimated 87% of the total lead in blood in children is obtained from the soil/dust pathway (Carrizales et al., 2006).

While ingestion of soils contaminated with metals is possible, available environmental data for exposure assume that total ingested amounts of metal are absorbed, therefore neglecting the human gastrointestinal tract effect. Stomach and

intestine are the important digestion organs in the body and absorption mainly happens in the intestine. Because pH conditions and digestion reactions happen, metals might not be 100% accessible for absorption. To fill the gap, in-vitro bioaccessibility tests can provide dissolution information of metals in human digestion systems using materials mimicking saliva, gastric, and intestinal fluids. The bioaccessibility results represent how much metals are dissolved in our gastrointestinal systems and are ready to be absorbed in the intestines.

There are advantages using an in-vitro bioaccessibility test. First, bioaccessibility tests are less expensive and less time-consuming than in-vivo tests (bioavailability); no animal studies and no need to extrapolate animal studies results to human systems are required, with less uncertainty (Molina et al., 2013; Roussel et al., 2010). Second, total metal concentrations do not reflect the quantities that are available to the body in risk assessment (Roussel et al., 2010), so bioaccessibility test results are more realistic. In-vitro bioaccessibility is composed of two parts, gastric phase and gastric-intestinal phase. Because intestines are the main locations for absorption, gastric-intestinal phase is more representative than gastric phase when compared to in-vivo tests (Ellickson et al., 2001).

There are studies showing various metals bioaccessibility results in gastric-intestinal phase, which are summarized in Table I-4 (pg. 9) (Carrizales et al., 2006; Ellickson et al., 2001; Okorie et al., 2011; Pelfrêne et al., 2015; Roussel et al., 2010). Percentage bioaccessibility fractions (%BAF) in gastric-intestinal phase of As, Cd, Cr, Cu, Pb, Ni, Zi all showed lower amounts than total concentrations detected in the soil samples. In other

words, metals are not 100% accessible in the digestion systems. As a result, to assess metal exposure, applying in-vitro bioaccessibility tests is more accurate than just detecting concentrations in the soils when considering metal pollution in the cities or near industrial facilities. So far, no studies in Houston for metals bioaccessibility in soil have been conducted, and this project provided information of metals in-vitro bioaccessibility results in Houston.

Table I-4 %BAF of metals in gastric-intestinal phase

Metal/Ref	Okorie et al., 2011[1]	Roussel et al., 2010[2]	Carrizales et al., 2006[3]	Pelfrêne et al., 2015[4]
Arsenic	64		46	
Cadmium	96	31		43
Chromium	74			
Copper	78			
Lead	58	32	32	22
Nickel	71			
Zinc	62	23		10
Locations	Newcastle upon Tyne, UK	Noyelles-Godault, FR	San Luis Potosi, MX	Noyelles-Godault, FR

1 highest bioaccessibility from 19 soil samples
2 mean of 27 soil samples
3 median of 10 soil samples
4 mean of 502 soil samples

Risk assessment combining bioaccessibility test data

EPA suggested that soil ingestion rates are 20 mg/kg for infants 0 to <6 months, 30 mg/kg infants 6 months to <1 year, 40 mg/kg for children 1 to <6 years, 30 mg/kg for children 6 to <12 years, and 10 mg/kg for 12 years through adults for risk assessment (USEPA, 2017). Conventional risk assessment uses total concentrations of metal in soil. To assess the ingestion amount of metals from soils, using total concentrations in soils estimates potential dose; while using bioaccessibility tests estimates applied dose. Compared to total concentration risk contaminants in the body (Markus and McBratney, 2001), which provides closer estimation to the true biologically effective dose on the organ. Because only a fraction of total soil metal species is absorbed in human bodies, human health risk assessment with the data from bioavailability increases the accuracy of potential exposures and related risks (Saleem et al., 2014).

When using bioaccessibility test data, the health risks are expected to be lower than using total concentration data. Pelfrêne et al. conducted a study in France near 2 smelter plants. And they considered risk assessment for 3 metals (Cr, Pb and Zn); only uptake of metals by soils ingestion, and children (2-6 yr-old) were considered. Two scenarios were assessed, 100 % intake of metals, and based on %BAF in gastric and gastrointestinal phase. Bioaccessibility analyses provide a more realistic estimate of exposure than do total metal conc. HQ-GI is more physiologically based estimate of exposure than HQ-total (Pelfrêne et al., 2015). Summary of values are shown in Table I-5 (pg. 11).

Table I-5 Risk assessment of metals in soils

Location	Outcome[4]	Cadmium	Chromium	Cobalt	Copper	Lead	Nickel	Zinc
Beijing, China[1]	HQ (ingestion)	1.88×10^{-4} (7.29×10^{-5}, 3.99×10^{-4})	1.08×10^{-2} (7.26×10^{-3}, 2.11×10^{-2})	2.18×10^{-4} (1.63×10^{-4}, 2.56×10^{-4})	4.15×10^{-4} (2.12×10^{-4}, 7.16×10^{-4})	4.21×10^{-3} (2.93×10^{-3}, 8.12×10^{-3})	5.38×10^{-4} (3.23×10^{-4}, 8.15×10^{-4})	1.80×10^{-4} (7.75×10^{-5}, 3.17×10^{-4})
	Cancer Risk	1.1×10^{-11} (4.3×10^{-12}, 2.4×10^{-11})	1.3×10^{-8} (8.7×10^{-9}, 2.5×10^{-8})	4×10^{-10} (3×10^{-10}, 4.7×10^{-10})			8.5×10^{-11} (5.1×10^{-11}, 1.3×10^{-10})	
Northern France[2]	HQ (ingestion)	1.7×10^{-2} (1.0×10^{-3}, 2.06×10^{-1})				2.99 (4.6, 65.8)		5.64×10^{-3} (5.46×10^{-4}, 7.96×10^{-2})
	HQ-GI[3] (ingestion)	7×10^{-3} (1.0×10^{-4}, 7.9×10^{-2})				0.7 (0.02, 16.3)		9.55×10^{-4} (2.67×10^{-6}, 3.05×10^{-2})

1 Sun et al., 2016 means (range)

2 Pelfrêne et al., 2015 means (range)

3 HQ-GI: Hazard quotient in gastric-intestinal phase

4 HQ over 1 represents non-cancer risk is not safe, and cancer risk over one in a million is not safe.

However, only a few studies have conducted risk assessment with both total concentration data and the bioaccessibility test approach, and no studies in Houston have been identified. I proposed to conduct estimates of ingestion of soil for both adults and children with 4 scenarios; first is assuming adults and children absorb total concentrations with central tendency ingestion rates; second is assuming adults and children absorb %BAF in gastric-intestinal phase with central tendency ingestion rates; third is assuming adults and children absorb total concentration with upper tendency ingestion rates; and forth is assuming adults and children absorb %BAF in gastric-intestinal phase with upper tendency ingestion rates. I intend to establish hazard quotients of the 4 scenarios, and identify metals with high health risks in Houston.

Spatial Analysis

Geographic Information System (GIS) has been applied to metals in soils studies and is a useful tool to establish possible contamination area. In a study in Beijing, China, Sun et al. collected 46 soil samples to analyze 12 metals (Ba, Cd, Co, Cr, Cu, Li, Mo, Ni, Pb, Sr, V, Zn). They found Cu, Cd, Zn and Pb showed higher concentrations in the central part of the city through graduated graphics (Sun et al., 2016). GIS has the advantage of using graphics to present more clearly metal geographic distributions of concentrations.

There are advantages in analyzing data with spatial analysis, such as identifying patterns in the spatial distribution, allowing immediate appreciation of the change in the

contaminant with space, and interpolation of data saves costs of chemical analysis and time taken (Markus and McBratney, 2001). The kriging method in GIS is considered to be a more-advanced method than other interpolation methods (Ha et al., 2014), and has been used to characterize metals spatial distribution and relationships considering urban factors (Yesilonis et al., 2008). For example, Pb, Cu, Zn were found to be associated with anthropogenic sources and regional and local traffic (Davis et al., 2009; Ha et al., 2014; Wu et al., 2010; Yesilonis et al., 2008). Houston being the 4th most populated city in the U.S., is likely to have elevated Pb, Cu, and Zn in the soils.

On the other hand, risk assessment can also incorporate spatial analysis. Better understanding of spatial variation of risk assessment is also useful with the same reasons described above. Two studies done in China and France showed that spatial analyses are informative to provide health risk distributions (Pelfrêne et al., 2015; Sun et al., 2016). Nonetheless, geostatistics techniques for spatial interpolating data have not been comprehensively employed in standard risk assessment methodologies (Markus and McBratney, 2001).

No study using kriging method has been identified to establish metals concentrations in Houston. Prior data from USGS and one study done in downtown are not sufficient to interpolate un-sampled areas in Houston. Therefore, there is a need to conduct systematic sampling and establish spatial prediction in Houston, in order to give a bigger picture of spatial distribution of metals in Houston. Furthermore, utilizing the novelty of

bioaccessibility results in risk assessment, spatial analysis could be able to identify hot spots of health risks.

Public Health Significance

Soil is one of the media by which humans could have exposure to environmental hazards. Metals concentrations in soils are site specific, and it is hard to extrapolate metals concentrations. Characterizing local metals concentrations in soils is important, and using bioaccessibility tests is useful to give more accurate exposure estimation. Furthermore, by combining a GIS application and its spatial statistical methods, areas that need public health/environmental health interventions could be prioritized.

This project is intended to provide concentrations of metals in soils in Houston. The study also provides spatial distribution of metals concentrations in Houston to evaluate if there are violations of EPA standards, hot zones, or any special spatial distributions. Furthermore, the bioaccessibility tests of metals in soils could provide in-vitro information, which is more accurate to evaluate absorbed dose for the public than traditional methods. The risk assessments of metals in soils through the ingestion pathway could provide information for the authorities concerned. To conclude, the study fills the gap of exposure to metals in soils for the public in Houston.

Specific Aims

Exposure to toxic heavy metals is associated with the development of cancer and other adverse health effects in humans. People living in urban areas are exposed to elevated levels of toxic heavy metals from various industrial activities. Houston is home to 23 companies on the 500 most profitable U.S. industrial corporations (City of Houston, 2017). Due to no formal zoning in Houston, residents are in proximity to various sources of metal emissions (e.g., oil and gas industry, chemical industry, metal fabrication industry and metal recycling facilities) (Union of Concerned Scientists & Texas Environmental Justice Advocacy Services, 2016). Ingestion of metal is the important and direct exposure pathway at the point of contact on contaminated soils among three major routes of exposure (USEPA, 2017). Adults and children are estimated to ingest 10 to 30 mg/kg of soil through mouthing, contacting dirty hands, eating dropped food, and consuming soil directly (USEPA, 2017).

To understand the exposure and potential health risk of metal exposure from soil, it is essential to have information about the concentrations of metals in soil in Houston. While two studies have reported the concentrations of several heavy metals in Houston (Benipal et al., 2017; Smith et al., 2013), the results from these studies were not representative of metal concentrations in soil due to the limited number of samples. To evaluate metal exposures and to estimate potential health risks across Houston, it is important to characterize representative metal contamination across Houston.

Absorbed amounts of metals are related to bioaccessibility in human gastric and intestinal organs. An In-vitro bioaccessibility test is an easy and useful method to assess metal dissolution behaviors in gastric and intestinal phases. There is limited information. However, regarding the metals dissolution and accessibility in human digestion systems. Systematic soil sampling and metal analysis coupled with a bioaccessibility test is innovative to identify hot spot areas of metal contamination and to examine the heterogeneity of health risk across Houston. The overall objective of this study is to identify soil contamination hotspots and to assess health risks in Houston.

To achieve the objective, I proposed (1) to characterize 13 metals (lead (Pb), cadmium (Cd), copper (Cu), arsenic (As), chromium (Cr), zinc (Zn), nickel (Ni), manganese (Mn), barium (Ba), cobalt (Co), magnesium (Mg), iron (Fe), and Vanadium (V)) in soils from 96 different locations in Houston (Aim 1-1), and predict spatial distributions of 13 metals concentrations in soils (Aim 1-2); (2) to assess internal doses of 13 metals in human digestion systems (Aim 2); (3) to conduct risk assessment via oral ingestion of 10 metals (As, Ba, Cd, Cr, Cu, Mn, Ni, Pb, V, and Zn) (Aim 3-1), and to predict spatial distribution of them on human health risks (Aim 3-2).

Aim 1: To characterize 13 metals (Pb, Cd, Cu, As, Cr, Zn, Ni, Mn, Ba, Co, Mg, Fe, and V) in soil in Houston.

Aim 1-1: To characterize metals concentrations in soil sampling locations

Aim 1-2: To predict spatial variations of 13 metals

Aim 2: To evaluate bioaccessibility of 13 metals (Pb, Cd, Cu, As, Cr, Zn, Ni, Mn, Ba, Co, Mg, Fe, and V) in soils in Houston. I determined the dissolution of metals in gastric and intestinal phases using synthetic saliva, gastric, and intestinal fluids.

Aim 3: To assess human health risks of 11 metals (As, Ba, Cd, Cr, Cu, Mn, Ni, Pb, Zn, Co, and V) using total concentrations and bioaccessibility concentrations.

Aim 3-1: To assess oral route exposure of non-cancer health risks for 11 metals (As, Ba, Cd, Cr, Cu, Mn, Ni, Pb, Zn, Com and V) and cancer health risks for As in soils in Houston through total concentrations and bioaccessibility test results

Aim 3-2: To predict spatial distributions risk using 11 metal concentrations in soils and bioaccessibility tests in Houston

Hypothesis: Spatial distributions of human health risks are different as risks adjusted by bioaccessibility test

The study addresses the gap of exposure to metals in soils for the public, and identifies hot spot areas of metal contamination and high health risks area in Houston.

CHARPTER II. ENVIRONMENTAL HEALTH DISPARITY AND SPATIAL VARIATION OF HEAVY METALS IN SOILS IN HOUSTON, TEXAS

To be submitted to Environmental Science and Technology

Introduction

People living in urban areas are exposed to heavy metals primarily from two major anthropogenic sources: (1) point sources such as petrochemical plants, metal production plants, old lead-painted houses, smelting plants, metals recycling plants, and municipal dumpsites (Datta et al., 2007; Tchounwou et al., 2012); and (2) non-point sources such as vehicle engine emissions, wear or abrasions of vehicle components, resuspension of urban polluted soils (Cai et al., 2016). Due to various anthropogenic and natural sources of metals in urban areas, the profiles and concentrations of toxic metals in soils are heterogeneous among different U.S. cities. For example, lead (Pb) concentrations in soils widely vary in urban areas in the U.S- 89.76 mg/kg in Pueblo, Colorado, 128 mg/kg in Sacramento, California, and 182.81 mg/kg in Anniston, Alabama (Diawara et al., 2006; Ha et al., 2014; Solt et al., 2015).

Exposure to heavy metals could lead to adverse health effects, such as cancer (USEPA, 2016), cardiovascular health effects, neuro-developmental health effects, reproductive health effects, muscle soreness, and nausea (ATSDR, 2016; Plum et al., 2010). Among three potential exposure pathways (inhalation, ingestion, and dermal contact), ingestion of soil is an important exposure pathway for children as well as adults. Soil

ingestion comes from mouthing, contacting dirty hands, eating dropped food, consuming soil directly, and ingestion of resuspended dust or soils. Soil ingestion is especially significant for children since they tend to play on the ground with unique exposure pathways such as mouth objects (USEPA, 2017).

Houston is the fourth largest city in the U.S. The east side of Houston has more than 10 industrial plants and oil refinery plants along with the Ship Channel that allows active import and export activities of 1,000,000 containers, respectively (Port Houston, 2018; USEPA, 2018d). In contrast, the west side of Houston is mostly comprised of residential and commercial areas. Given the different land use, heavy metal concentrations in soils on the east side of Houston may be higher than those in the west side of Houston. Furthermore, people living in the east side of Houston have lower socioeconomic status, and higher percentage of minority and low-income households, which may raise potential environmental justice issues as they may be exposed to higher heavy metal concentrations in their residences than high-income neighborhoods (Nicole, 2018).

In 2017, Houston has 422 toxic registry inventory facilities and total 4.6 million pounds of toxic chemicals in on-site disposal (USEPA, 2018d). Most facilities are located in east or north east of Houston, 3 to 10 km away from the downtown area. Fabricated metal products, machinery manufacturing, and production of petroleum, and chemicals comprise of 64% of the Houston manufacturing sector (Greater Houston Partnership, 2017). According to US EPA Facility Registry Service (FRS), there are 999 facilities registered in

Houston, TX including metal finishing, fabricated metal product manufacturing, metal coating, metal heat treating, scrap metal, metal construction materials, metal gravitating, metal recycling, smelting, refinery and alloying metal facilities (USEPA, 2018c). Elevated levels of lead, cobalt, copper, zinc, manganese and arsenic were found in soils in Houston due to emission from industrialized plants and local traffic (Davis et al., 2009; Ha et al., 2014; Wu et al., 2010; Yesilonis et al., 2008). In addition, no formal zoning between residential and industrial areas in Houston may put residents at greater risk for exposure to toxic metals in soil in their neighborhoods because of proximity to industrial activities. After the unprecedented flood damage caused by Hurricane Harvey in August 2017, 14 superfund sites were identified for potential leakages of toxic chemicals including heavy metals (Ratnapradipa et al., 2018). To assess potential exposure to heavy metal in soils among Houstonians, the objectives of our study were to 1) characterize heavy metal distributions in Houston with a systemic grid sampling method, 2) assess the effects of environmental and sociodemographic factors on disproportionate exposures to heavy metals in residential areas, and 3) identify hot spot areas with elevated toxic heavy metals.

Materials and Methods

Study Area

Houston, Texas is encircled by two major freeways- Interstate 610 (I-610) and Beltway 8. Interstate 610 (I-610) is an urban freeway and within it is generally referred to as

“inside loop 610”. The area inside Loop 610 is 251 square kilometers, and Beltway 8 is outer loop of toll way which has 1124 square kilometers between Loop 610 and Beltway 8 (Walker and Shelton, 2016).

Our sampling areas included four US EPA superfund sites and eight Texas Commission on Environmental Quality (TCEQ) sites classified as metal-contaminated sites (Figure II-1)(TCEQ, 2017). Detailed sampling locations including latitude and longitude are in Appendix A (pg. 88). Detailed TCEQ and US EPA super fund sites are addressed as following:

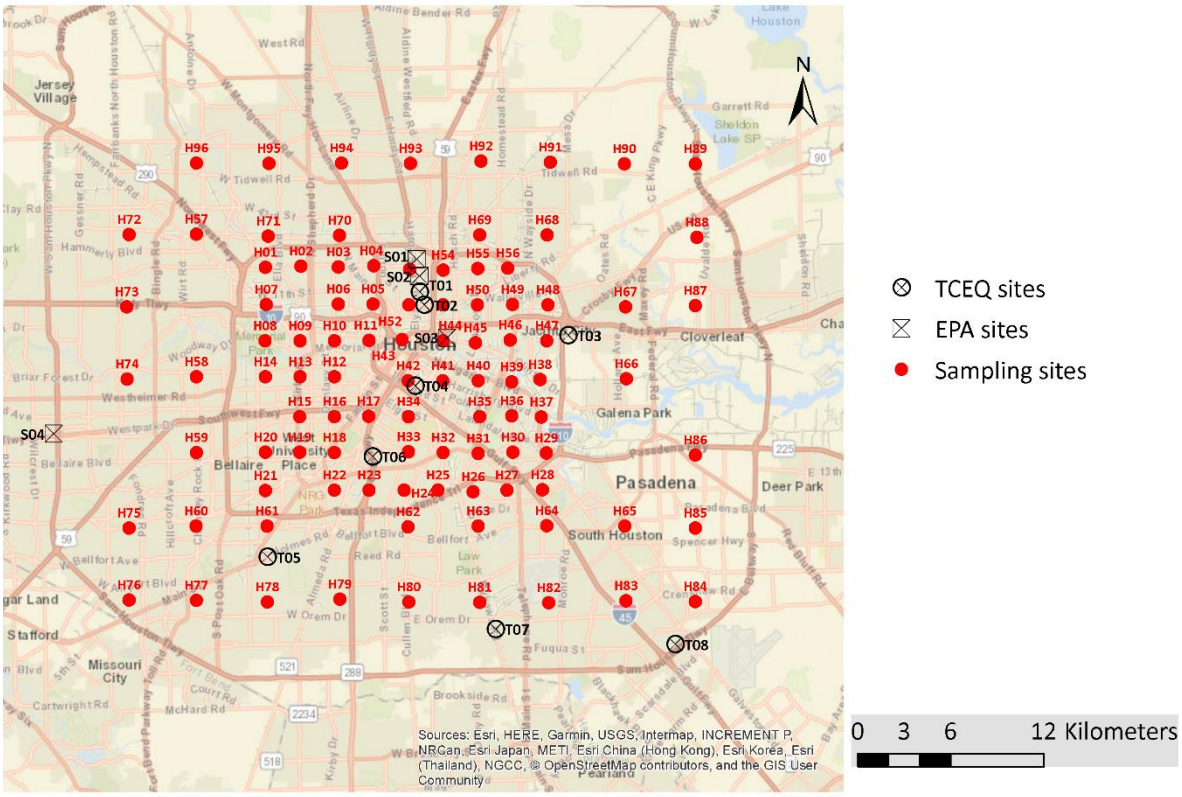


Figure II-1 Sampling locations in Houston

TCEQ site (T01) was a lead-acid battery recycling facility and soils were contaminated with Pb. TCEQ site (T02) was a scrap salvage facility, and soils were contaminated with Cu and iron (Fe). TCEQ site (T03) at the northeast corner of loop I-610 was a Magnesium Dross/Sludge Disposal Inactive Landfill, and soils were contaminated by barium (Ba), Pb and magnesium (Mg). TCEQ site (T04) was a as waste oil recycling facility; the soil was contaminated with chromium (Cr) and Pb. TCEQ site (T05) at the southwest corner of loop I-610 was a lead smelter and lead-acid battery recycling plant, and soils were contaminated by Pb, cadmium (Cd) and As. TCEQ site (T06) along highway 288 inside loop I-610 was a metal plating facility, and soils were contaminated with Cd, Cr, Pb and As. TCEQ site (T07) on the south of Houston was Gulf Metal Industries landfill site, and soils were contaminated with Ba, Cr, Pb and Zn. TCEQ site (T08) on southeast of Beltway 8 was a specialty chemical manufacturing plant, and soils was contaminated with Pb.

Two US EPA superfund (S01 and S02) sites used to be a wood-treating plant and a coal tar distillation plant, and soils were contaminated by arsenic (As), Cr, copper (Cu), Pb and zinc (Zn). US EPA site (S03) was once a metal casting foundry manufacturing large wheels, tracks and mining equipment; lead-contaminated soils were found. Four sites were up north of Interstate 59 and inside loop I-610. US EPA site (S04), west of Beltway 8, was a chemical plant, and soils were contaminated with As.

Soil sampling

Within the I-610 loop, we systemically collected 56 soil samples on a 2 kilometer-square grid. We collected additional 40 soil samples between Beltway 8 and I-610 on a 4 kilometer-square grid. If the sampling locations selected by grid squares were not accessible, those sites were excluded.

We collected top soil (0-5 cm) samples to represent recent contamination with the greatest possibility of ingestion (Aelion et al., 2014; Diawara et al., 2006). We collected soil samples using clean plastic shovels and put into 500 ml glass jars. At each sampling location, we documented latitude and longitude using Google map (Google LLC, Mountain View, CA), recorded sampling information and description of sampling locations and surrounding area. After completion of sampling on each day, we transported all the samples with ice packs in a cooler to the UTHealth School of Public Health Exposure Assessment laboratory. We stored soil samples in 4^{o}C refrigerators and analyzed within 6 months after sampling (USEPA, 2014).

To evaluate the effects of environmental factors and neighborhood characteristics of the sampling locations on heavy metal concentrations, we used the Environmental Justice (EJ) Screening and Mapping Tool (EJSCREEN) database, developed by US EPA. The EJ screening index provides environmental pollution and sociodemographic indicators in a chosen geographic area (USEPA, 2018a). To understand possible sources or neighborhood characteristics to metals at each sampling location, we used environmental EJSCREEN indexes by drawing a 2 kilometer buffer zone at each sampling location by its latitude and

longitude. Demographic indicators included percent low-income, percent minority, percent of less than high school education, percent of linguistic isolation, percent of individuals under age 5 and percent of individuals over age 64. Environmental indicators included traffic proximity and traffic volume, proximity to national priorities lists and proximity to risk management plan sites.

Metal Analysis

Soil samples were dried at room temperatures for a week and homogenized. We used Microwave system, MARS 6 (CEM Corporation, Matthews, North Carolina) to assist acid digestion. First, we cleaned 55 mL MARSXpress digesion vessels with element-free soap, rinsed with de-ionized water, and dried them at room temperature. When dried, we added 10 ml nitric acid (TraceMetal grade, Fisher Scientific, Hampton, NH) into each vessel and placed them into MARS 6 microwave digestion system (CEM Corporation, Matthews, NC) for cleaning the vessels. Ramp time for cleaning was 15 minutes to 150 Celsius degrees and hold for 10 minutes (CEM, 2015). After we completed the cleaning procedure, we discarded the acid solution to a waste bottle, cleaned the vessels with milliQ water (MilliporeSigma, St. Louis, MO) and dried them at room temperature for sample digestion.

We weighed one gram of sample and put it into the acid-cleaned 55 ml MARSXpress digestion vessels. We added 10 ml concentrated nitric acid into the vessels (TraceMetal grade, Fisher Scientific, Hampton, NH)(USEPA, 2018e). After adding concentrated nitric acid,

we waited 5 minutes and then capped each vessel tightly to place them into 40 sample trays (either 16 or 24 samples per run). A microwave temperature program was used following USEPA 3051A method (USEPA, 2018e). Ramp time was 5 minutes 30 seconds to 175 Celsius degrees and hold for 4 minutes and 30 seconds. After the samples were run, we transferred nitric acid solution into 50 ml digestion tubes and diluted to 50 ml by ultra pure element-free water (Aristar Ultra Water, VWR, Radnor, Pennsylvania). We filtered the samples by FilterMate with PTFE prefilter (0.45 μm PVDF)(Environmental Express, Charleston, SC). Each sample was prepared by using 1 ml from the 50 ml digestion tube and diluted to 10 ml by the ultra water for Inductively Coupled Plasma Mass Spectrometry (ICP/MS) analysis (USEPA, 1998).

We used an Inductively Coupled Plasma Mass Spectrometry (ICP/MS) 7500 series (Agilent Technologies, Santa Clara, CA) for the analysis of magnesium (Mg), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn) and arsenic (As). We ran the ICP/MS with both helium gas modes to decrease interferences. We analyzed cadmium (Cd), barium (Ba) and lead (Pb) with no gas mode. Acquisition time for each sample was 114 seconds with 3 times repetition. We added 50 ppb internal standard mix (AG-INTSTD-ASL-1, AccuStandard, New Haven, CT) to each sample for quality control and assurance. We tuned the ICP/MS before sample analysis. We constructed standard calibration curves for each metal: Mg and Fe ranging from 0 to 200,000 ppb and the rest of the metals ranging from 0 to 2000 ppb. R squares of standard calibration curves ranged

from 0.9997 to 1). We calculated method detection limits (MDL) of ICP/MS for each metal by using 1 ppb of analytes solution (n=10), and calculated the MDL for each metal as the following equation: $MDL = 2.821 \times Standard\ deviation$ (2.821=t value, degree of freedom= 9 and α value= 0.01)(USEPA, 2011a). The relative standard deviations of duplicate samples in every tenth sample were less than 10% of the mean between two paired measurements.

Data Analysis

We used SAS 9.4 (SAS Institute, Cary, NC) for statistical analysis. We conducted Spearman correlation to evaluate correlation among metals. We categorized 96 sampling locations by two groups (e.g., high vs. low) based on social and demographic indicators of EJSCREEN. We used median values as a cut point for each indicator. Among 96 sampling locations, two sampling sites (H48 and H79) did not have any EJSCREEN indexes because no people are within a 2 kilometer radius. Metal concentrations were not normally distributed, thus, we used the two-sided Wilcoxon Rank Sum Test with α=0.05 to test the differences of each metal between high and low groups for all EJ indexes.

To find hot spot areas with elevated levels of heavy metals, we conducted ordinary kriging estimation in Houston (-95.57, 29.59 to -95.11, 29.94, 161811 points) using ArcGIS 10.5.1 (Esri, Redlands, CA). The kriging method in Geographic Information System (GIS) is considered to be a more-advanced method than other interpolation methods (Ha et al.,

2014), and has been used to characterize metals spatial distribution and relationships considering urban factors (Yesilonis et al., 2008). We used the ordinary kriging method to interpolate non sampled areas in Houston. We used best fit variogram models of each metal to calculate weights for each interpolated locations. The ordinary kriging method assumes that the mean and variance of the values are constant across the spatial field. With the estimation results, we used ArcGIS software were used to visualize metal distribution in Houston and identify highly-polluted area. Metal concentrations were natural-log transformed in models and then transformed back to original values without natural-log transformation. To evaluate accuracy and precision of prediction models for each metal, we used the cross validation method. We separated data into a training dataset (16) and validation dataset (80) and repeated the procedure 6 times. We conducted the ordinary kriging models we selected for each metal with the validation dataset, and then compared the predicted data points with the training dataset. We calculated mean error (ME), mean standardized error (MS), average standard error (ASE), root mean square error (RMS), and root mean square standardized error (RMSS). If the prediction model is good, ASE should be close to 1, and RMS and RMSS should be close to 0.

Results and Discussion

Concentrations of Heavy Metals in Houston

Table II-1 Distribution of 13 metal compounds in 96 soil samples (mg/kg) in Houston, Texas

Metal	MDL	TCEQ background	Mean±SD	Min	10%	25%	Median	75%	90%	Max
As	0.10	5.9	2.92±2.35	0.38	1.25	1.71	2.51	3.33	4.92	17.29
Ba	0.037	300	120.93±99.80	27.18	49.65	66.01	93.59	133.14	199.90	714.17
Cd*	0.04	-	0.31±1.05	0.02	0.02	0.02	0.09	0.24	0.49	9.74
Co	0.03	7	3.14±2.03	0.35	1.20	1.83	2.78	3.70	5.15	12.14
Cr	0.02	30	11.49±9.29	1.89	4.51	6.27	8.49	13.55	20.76	58.84
Cu	0.04	15	58.20±357.29	1.98	6.63	9.51	13.19	23.22	58.28	3,515.20
Fe	2.88	15,000	6,403.12±,3300.90	1,231.57	3,254.91	4,093.51	5,391.94	7,952.83	10,775.07	18,297.19
Mg	4.00	-	2,494.11±4,576.47	322.74	581.31	902.10	1,705.17	2,574.55	3,658.97	41,252.79
Mn	0.03	300	220.63±165.82	24.43	102.33	115.52	176.52	250.36	366.86	910.80
Ni	0.05	10	8.00±5.52	1.63	3.42	4.51	7.00	9.81	14.53	41.57
Pb	0.02	15	60.18±98.31	3.61	10.35	20.20	34.95	68.60	116.33	855.86
V	0.03	50	11.71±6.00	4.13	6.51	7.72	10.24	13.17	20.76	58.84
Zn	0.08	30	279.76±1042.63	15.35	34.06	63.19	103.86	202.83	339.44	10,107.48

*57% detected (n=55 among 96 samples); values under MDL were adjusted to MDL/$\sqrt{2}$ and calculated following the same procedures as rest of the samples.
MDL: method detection limit
SD: standard deviation

All metals, except Cd (58% (n=56) detected), were detected in 96 soil samples. (Table II-1, pg. 28) The lowest mean concentration was Cd, 0.31 mg/kg (median=0.09 mg/kg), whereas the highest mean concentration was Fe, 6,403 mg/kg (median=5391 mg/kg). The relative standard deviations (RSDs) of Cd, Cu, Pb, and Zn were greater than 150% while the RSDs for the other metals were less than 100%. The spearman correlation coefficients between Ba, Cu, Cr, Ni, Pb and Zn ranged from 0.45 to 0.79 ($p<0.0001$). Tthe correlation between Pb and Zn was the highest (R=0.79).

The median concentrations of certain metals in our study were generally greater than background concentrations in Texas reported by Texas Commission on Environmental Quality (TCEQ). In our study, median of Pb (34.95 mg/kg) was two times greater than the background concentration (median=15 mg/kg); median of Zn (103.86 mg/kg) was three times greater than the background concentration (median=30 mg/kg)(TCEQ, 2018). The medians of the rest of the metals were lower than the TCEQ background concentrations.

We compared our results with previous studies conducted in urban areas in the United States (Pouyat et al., 2015; Solt et al., 2015). Like our study, these studies collected surface soil samples (depth of 10 cm or 5 cm). Median concentrations of Cd, Cr and Cu in this study were 0.30 to 0.97 times less than those in Baltimore, MD (Pouyat et al., 2015) or in Sacramento, CA (Solt et al., 2015). On the other hand, median concentrations of As, Zn and Pb were equal to or 1.52 times greater than those in Baltimore (Pouyat et al., 2015). Mean concentration of Zn in this study was 1.30 times larger than that in Sacramento (Solt

et al., 2015). The findings of this study suggest that elevated metals, especially Pb and Zn, are related to anthropogenic activities in Houston. Wang et al. found that As, Pb, Zn, Cd, Cr, and Cu were elevated in urban soils and associated to anthropogenic sources explained by 70% variance in principle component analysis (Wang et al., 2005).

Possible Environmental Determinants

We summarized EJSCREEN indexes (high vs. low) to assess the effects of environmental burdens and socioeconomic factors on metal concentrations of soils in our study locations. Detailed information about high and low EJSCREEN Indexes are shown in Appendix B (pg. 93). Environmental burdens include proximity to traffic, superfund sites and industrial plants. Socioeconomic factors include percentages of children, minority, low income groups, and education levels (Table II-2, pg. 31). The cutoff points for EJSCREEN indexes were median values of each parameter. For example, the median of traffic proximity and volume was 800 (daily traffic count/distance (meter) to road). If a location has an EJSCREEN index for traffic proximity and volume less than 800, we classified this location as 'low'; if equal to or greater than 800, we assigned this location as 'high'. Similarly, we calculated median values for all other parameters. The median proximity to National Priorities List sites was 0.16 (site count/km distance); median proximity to Risk Management Plan sites was 1.25 (facility count/km distance); median minority was 88.5;

Table II-2 Distribution of EJSCREEN indexes of 96 locations in Houston, Texas*

EJSCREEN Indexes	Mean	SD	Min	25%	50%	75%	Max
Traffic Proximity and Volume (daily traffic count/distance (meter) to road)	1,104.92	1,107.58	2.9	270	800	1,800	5,600
Proximity to National Priorities List Sites (site count/km distance)	0.32	0.42	0.045	0.11	0.16	0.33	2.3
Proximity to Risk Management Plan Sites (facility count/km distance)	1.71	1.51	0.088	0.72	1.25	2.5	9.8
Percent of Minority	76.08	26.23	14	58	88.5	96	100
Percent of low income	46.45	20.62	7	29	53	63	75
Percent of linguistic Isolation	13.44	11.55	0	4	9	22	54
Percent of less than high school education	26.95	17.48	1	10	29.5	43	56
Percent of age under 5	7.01	2.23	1	6	7	9	11
Percent of age over 64	10.76	4.06	3	8	10	13	25

*Two sampling sites don't have EJSCREEN indexes.

median low income households was 53; median of linguistics isolation was 9; median less than high school education was 29.5; median percent of age under 5 percent was 7; median percent of age over 64 was 10. We defined high risk group ≥ medians, whereas low risk group < medians using each environmental burden and socioeconomic parameters.

For proximity to National Priority List (NPL) sites, the sum of scores of Ba, Cr, Cu, Ni, Pb and Zn in close proximity to NPL sites were significantly greater than those with less proximity to NPL sites (Figure II-2a, pg. 33). However, the mean concentrations of Cu in the low group were higher than the high risk group. This resulted from extremely high values from the H90 site, where and the value was 30 times higher than the highest value in high risk group.

The sum scores of Ba, Cu, Pb and Zn at sampling locations with close proximity to Risk Management Plan (RMP) sites were significantly greater than those at sampling locations with less proximity to RMP sites (Figure II-2b, pg. 33). Similar to results of Cu from NPL sites, we observed that mean concentrations of Zn in the low risk group were higher than the high risk group due to an extreme outlier, 10,107 mg/kg at the H40 site. Mean concentrations of Cu in soils in high RMP sites were 7 times higher than low RMP sites. Copper is ubiquitous and widely used such as construction, machinery, energy, electronics, fungicide and in brakes to control heat transportation (Manno et al., 2006; Panagos et al., 2018).

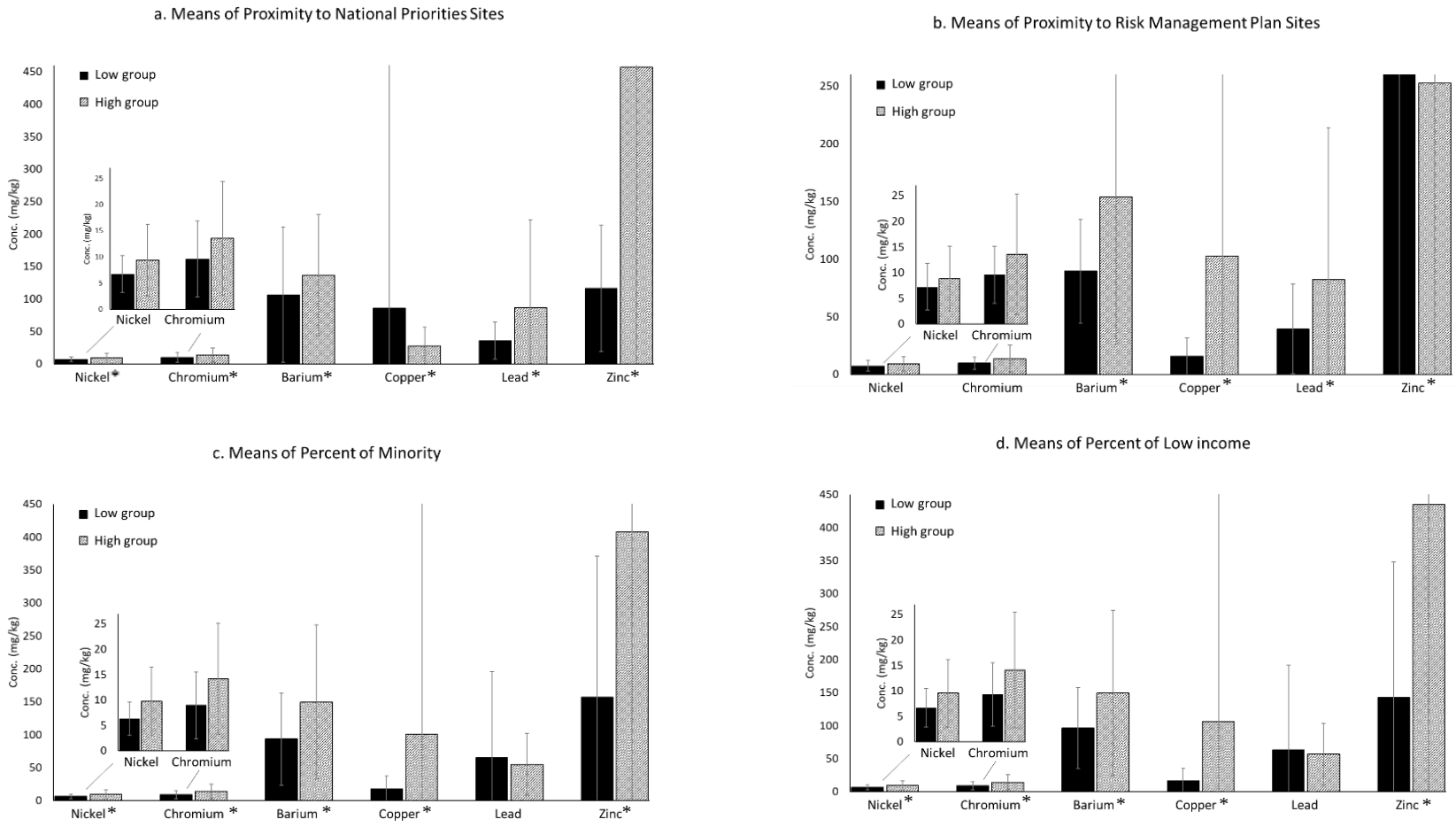


Figure II-2 Means of four EJSCREEN indexes in six metals of high and low groups

(* represents statistically significant, α=0.05). Error bars represent minimum and maximum concentrations of each metal; details in Appendix C, pg. 94.)

As previously described in Page 29, we found that Pb and Zn levels were 2-3 times higher than those in TCEQ background guidelines. Thus, it suggests that Pb and Zn in soils may be related to anthropogenic activities in Houston (Falahi-Ardakani, 1984). Figure II-2a (pg. 33) shows that close proximity to NPL sites resulted in Zn 4 times and Pb 2 times higher in High group than low group, respectively. Figure II-2b (pg. 33) also shows that Pb concentrations in high proximity to RMP were 2 times higher than low proximity to RMP. Lead is emitted from petrochemical refinery plants along with other heavy metals (Adeniyi and Afolabi, 2002). Industrial sources of Zn include smelter and refinery plants and paint sources (Diawara et al., 2006; Solt et al., 2015). The mean concentration of Ba in the high risk group was 1.28 times higher than those in the low risk group in NPL sites. And in RMP sites, mean concentrations of Ba in the high risk group was 1.72 times higher than those in the low risk group. Ba is widely-used in manufacturing of glass, ceramics, insecticides, fuel synthesis, and could be found in gasoline (Monaci and Bargagli, 1997).

The finding in this study addressed that people living close proximity to superfund sites and industrialized plants in Houston likely have greater heavy metals exposure to Ba, Cu, Pb and Zn. No zoning restriction (City of Houston, 2018c) may make people be more vulnerable to exposure to these elevated heavy metals.

Environmental Justice Indexes

We analyzed the odds ratio between minority and close proximity to industrial plants. Locations with high percentage of minority had 2.33 times higher odds (95%

confidence limits, [1.02, 5.27]) of living closer to industrial plants than locations with low percentage of minority. This findings suggests that minority groups have a higher chance exposure to heavy metals in soils.

Locations with a high percentage of minority (> 88.5%) showed significantly higher concentrations of Zn, Cu, Ba, Cr, and Ni than locations with a low percentage of minority (< 88.5%) (Figure II-2c, pg. 33). Concentrations of Ba, Cr, Cu, Ni and Zn were significantly higher in low-income neighborhoods than those in counterparts (Figure II-2d, pg. 33). Moreover, we found that concentrations of Ba, Cr, Cu, Ni and Mg are significantly higher in less education (high school diploma and less) neighborhoods than those in high education neighborhoods (Appendix C, pg. 94). Concentrations of Ba, Cr, Cu, Ni, and Zn are consistently high in minority and low income communities. Detailed information on nonparametric test of EJSCREEN indexes could be found in Appendix C (pg. 94).

Spatial distribution of metals

We used Ordinary Kriging method to estimate concentrations of 13 metals across Houston with their best fit semivariogram models of metals (Appendix D, pg. 103). We did 6 fold cross validation to test robustness of the spatial models (Appendix D, pg. 103). Among 13 metals, As, Ba, Mn, Fe and Mg prediction models were the closest to the measured metal concentrations in soils. Cadmium prediction model was the farthest from the measured Cd concentrations in soils, which may be due to losing sample size in non-

detectable locations. This is the first study in Houston using the ordinary kriging method to predict heavy metals distribution in soils. Most of the higher concentrations of metals were located in East Houston. The results were consistent with those from the effects of environmental and socioeconomic burdens as described previously.

Figure II-3 (pg. 37) shows that concentrations of Ba, Cr, Cu, Pb, and Zn were higher in older central downtown area or spreading out through the east of Houston. High Pb appearing in the old urban area in downtown could be related to traffic density and age of the area (Laidlaw and Filippelli, 2008; Mielke and Reagan, 1998; Solt et al., 2015). Miguel et al. conducted principle component analysis and identified elevated levels of Zn, Ba, Pb, and Cu associated with traffic sources (Miguel et al., 1997). Although we did not conduct source apportionment analysis in this study, we found that high correlation between Pb and Zn ($r=0.79$) may be related to vehicle traffic sources (Solt et al., 2015; Wang et al., 2005). Copper and Zn had several hot spots in Houston. For Cu, high concentrations were found east of inside loop 610 and in the northeast of Houston. We found a hot spot around the H90 site, between a bayou and a waste water treatment plant. The concentration of Zn was the highest at the H40 site, next to a Zinc dust plant. When we collected soil sample at the location, the soil was covered with silver powder like dusts (See Appendix E, pg. 104). These isolated high concentration locations may be impacted by nearby point source emission. We estimated for the rest of the metals (Appendix F, pg. 105). Concentrations of Cd and Ni were generally higher near the downtown of Houston whereas concentrations of other

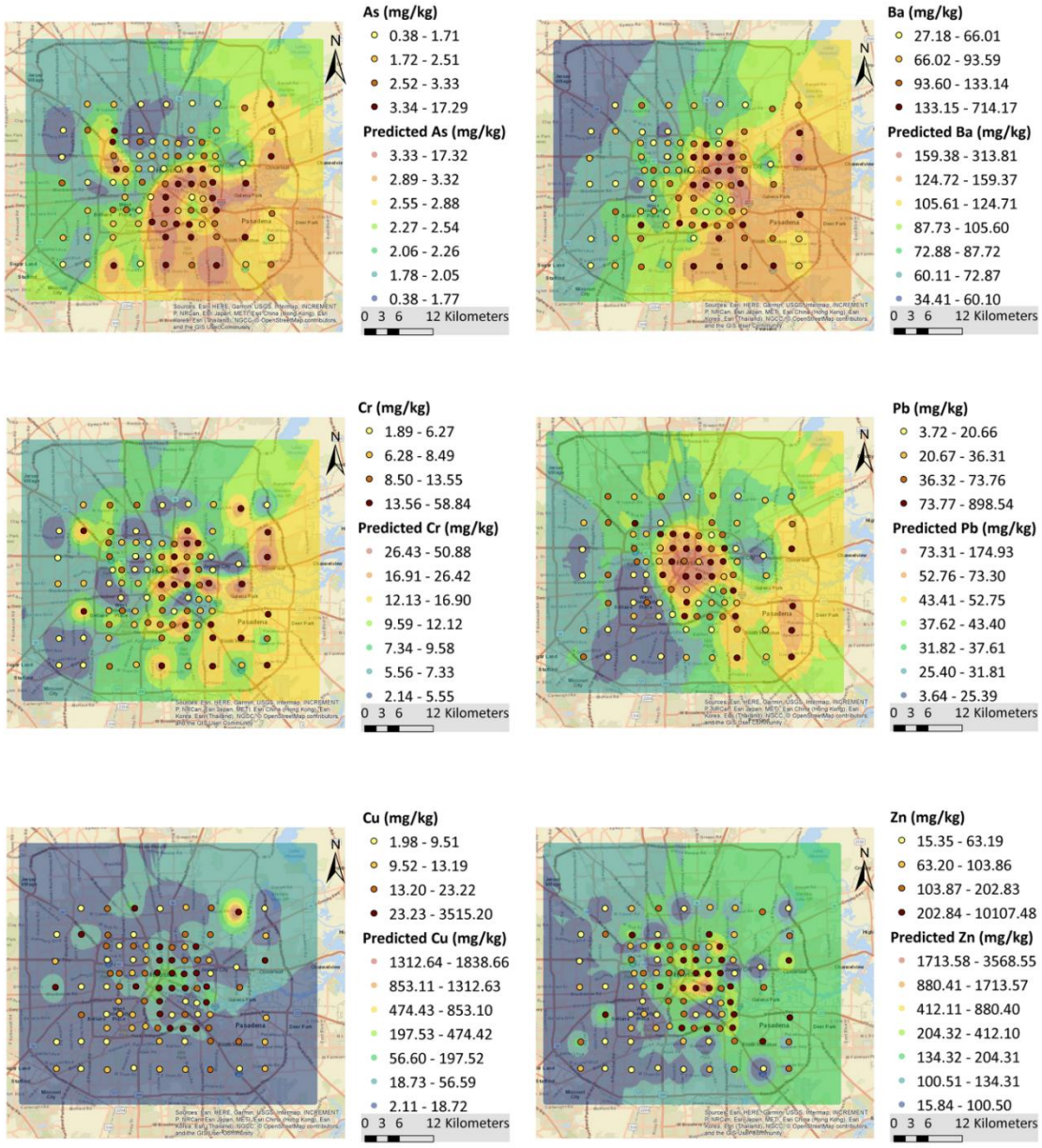


Figure II-3 Simulated 6 metals (As, Ba, Cr, Pb, Cu and Zn) Distribution in Houston, Texas

metals (As, V, Fe, Co, and Mn) were higher outside of Houston downtown (southeast of Houston between I-610 and Beltway 8). Overall the east side of Houston including

downtown neighborhoods has higher concentrations of these metals than the west side of Houston.

East Houston is considered to have more industrialized activities with high percent low income and minority neighborhood (Appendix G, pg. 106). Thus, people living in these disadvantaged community are more likely to be exposed to elevated levels of heavy metals. Whitworth et al. found 2-5 times higher concentrations of Ni, Zn, Ba As, Cd and Pb in blood samples among disadvantaged pregnant women in Houston compared with the average US population data (Whitworth et al., 2017). Further research on the association between heavy metals in soil and potential adverse health outcomes in those neighborhoods would provide useful information to identify environmental determinants of health.

A limitation of this study is that there are no specific sources of emission identified with heavy metals because we did not have the comprehensive emission data of traffic sources or industrial activities. However, EJSCREEN indexes provide community levels of risk factors such as proximity to road and traffic counts, density of industrial plants and superfund sites. These are the major anthropogenic sources that may be related to elevated metal concentrations in Houston. Elevated metal concentrations were frequently measured in vulnerable neighborhood such as high proportion of minority and low income communities.

CHARPTER III. APPLYING BIOACCESSIBILITY TESTS IN EXPOSURE ASSESSMENT OF HEAVY METAL INGESTION IN SOILS IN HOUSTON, TX

To be submitted to the Science of Total Environment

Introduction

Heavy metals such as lead (Pb), zinc (Zn) and copper (Cu) are ubiquitous in urban areas, in part, due to anthropogenic sources such as traffic and industrial activities (Nezat et al., 2017; Pouyat et al., 2015; Solt et al., 2015; Yesilonis et al., 2008). Exposure to toxic metals such as Pb and arsenic (As) could lead to detrimental health effects such as cancer, cardiovascular, developmental, and reproductive health effects (ATSDR, 2016; USEPA, 2016). For children in urban areas, the predominant exposure route of concern for heavy metals is oral ingestion (McGeer et al., 2004). According to USEPA, soil ingestion comes from various behaviors like, mouthing, contacting dirty hands, eating dropped food, and consuming soil directly (pica). Children's exposure to Pb is mostly from soil ingestion than other dietary sources (Carrizales et al., 2006; Glorennec et al., 2016). Soil ingestion is especially significant for children while they play on playground, via mouth objects or their hands (USEPA, 2017). Guney et al. sampled soils in parks and playgrounds in Turkey and found that children 2 to 6 years old have excess cancer risks (Guney et al., 2010). Another study reported that elevated blood-lead levels in children were related to exposure to lead-contaminated soils inside and outside of residences (Solt et al., 2015).

Exposure assessment using heavy metal concentrations in soils evaluated potential maximum metal exposure assuming heavy metals in soils were completely absorbed into the human body. The fraction of metals bioaccessible to the human body is dependent on physico-chemical characteristics of soils such as pH, dissolved organic carbon, and calcium ion in soils, and human metabolism (McGeer et al., 2004). Moreover, stomach and intestine play a role on absorption of metals. Many factors affect the adsorption of heavy metals in human body. These factors include the pH of human gastrointestinal tract, characteristics of ligands and different types of enzymes. Thus, it is not likely that ingested metals are 100% accessible to human body. To understand the fraction of heavy metals absorbed into the human gastrointestinal tract, in-vitro bioaccessibility tests can be applied using artificial solutions mimicking saliva, gastric, and intestinal fluids. The bioaccessibility test has been used to understand to what extent ingested metals are readily absorbed in human gastrointestinal systems (Mingot et al., 2011; Okorie et al., 2011; Wragg et al., 2011; Xia et al., 2016).

Houston, Texas (TX) has diverse metal-related industrial activities such as metal finishing, manufacturing, coating, construction materials, recycling, smelting, and alloying (USEPA, 2018c). Due to no formal zoning, many communities in Houston are in close proximity to these metal-related industrial complexes (City of Houston, 2018c). People living in Houston may be exposed to heavy metals in soils potentially emitted from these sources near their residential homes.

The purpose of this study is to (1) evaluate the bioaccessibility fractions of gastric and gastro-intestinal phases of magnesium (Mg), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), lead (Pb), barium (Ba) and cadmium (Cd) in soils in Houston, Texas, and (2) assess exposure doses based on both heavy metals concentrations in soils and bioaccessible values for five age groups: birth to < 1 year (infant), 1 year to < 6 years (toddlers), 6 year to < 12 years (children), 12 years to < 18 years (teenagers), and > 18 years old (adults).

Materials and Methods

Study area and soil sampling

Houston, TX is located at the center south of the United States, close to Gulf of Mexico. Houston is the 4th largest metropolitan city in the United States with 2.3 million population (City of Houston, 2018b) of which 44 percent are Hispanic, 25 percent White, 22 percent Black, and 6 percent Asian (US Census Bureau, 2018). Industrial activities in Houston include oil and gas exploration, petroleum refining, and production, manufacturing and distribution of petrochemicals (City of Houston, 2018a). In October, 2017, we collected 96 top soil (0 to 5 cm) samples with a systematic grid of either 2 km or 4 km in 1375 km^2 area using the sampling strategy described previously (Walker and Shelton, 2016). Detailed information about sampling locations and sampling methods are written in Chapter II materials and method section (Pages 20-23).

Trace metal analysis and in vitro oral bioaccessibility measurement

We analyzed concentrations of Mg, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Pb, and Cd in soils based on USEPA methods 3051A and 6020A (USEPA, 1998; USEPA, 2018e). After sample collection, we dried 96 soil samples at room temperatures and weighed 1 g for microwave assisted acid digestion (Microwave system, MARS 6, CEM Corporation, Matthews, North Carolina). Detailed sample preparation procedures are shown in chapter II materials and method section (Page 24). We analyzed the digested soil samples with Inductively Coupled Plasma Mass Spectrometry (ICP/MS) 7500 series (Agilent Technologies, Santa Clara, CA). We analyzed blanks, duplicated samples and spiked samples in every tenth sample. We obtained a method detection limit (MDL) of ICP/MS for all by using 1 ppb of analytes solution, except Fe and Mg in 100 ppb (n=10). We calculated the MDL for each metal as the following equation: MDL=2.821 × Standard deviation (2.821=t value, degree of freedom= 9 and α value= 0.01) (USEPA, 2011a).

We conducted in vitro oral bioaccessibility tests for Mg, V, Cr, Mn, Fe, Co, Ni, Cu, Zn and As using the Unified Bioaccessibility Method (UBM) (Wragg et al., 2009). We evaluated bioaccessibility of those metals in both gastric phase and gastro-intestinal phases. Detailed procedures of bioaccessibility tests are shown in Figure III-1 (pg. 44). We prepared simulated saliva fluids, gastric fluids, duodenal fluids and bile fluids a day before procedures. We checked individual pH of each fluid with pH papers (saliva: 6.0 – 7.0, gastric: 0.9 – 1.0, duodenal: 7.2 – 7.6, bile: 7.8 – 8.2) before we added soil samples into each fluid

solution. For simulation reaction, we first weighed 0.6 g dry soil with spatula from each sample and added the soils into two separate Erlenmeyer flasks, one for gastric phase and the other for gastro-intestinal phase. In gastric phase, we added 9.0 ml of simulated saliva fluid to each Erlenmeyer flask. We manually agitated each flask for 5 minutes. Then, we added 13.5 ml of simulated gastric fluid to each flask and placed them in an incubator (Precision Dubnoff Metabolic Shaker and Incubator, Waltham, MA) at 37 ± 2 ^{o}C for 1 hr. After the gastric reaction, we separated simulated solutions from soil with centrifugation (BD Clay Adams Compact II centrifuge, Hampton, NH) at 3000 rpm for 5 min. After centrifugation, we removed the supernatant and transferred 1.0 ml of supernatant into a 10 mL tube. We added additional 9.0 ml 0.1 M HNO_3 to the tube and stored them at < 4 ^{o}C before analysis. For gastro-intestinal phase, we followed the same steps as described in gastric phase and then added 27.0 ml of simulated duodenal fluid and 9.0 ml of simulated bile fluid to gastro-intestinal flask. Furthermore, we placed the samples in an incubator (Precision Dubnoff Metabolic Shaker and Incubator, Waltham, MA) shaking at 37 ± 2 ^{o}C for another 4 hr. After the gastro-intestinal reaction, we separated gastro-intestinal solution from soils with centrifuge (BD Clay Adams Compact II centrifuge, Hampton, NH) at 3000 rpm for 5 min. After centrifugation, we removed the supernatant and transferred 1.0 ml of supernatant into 10 mL tube. We added 9.0 ml 0.1 M HNO_3 into the tube and stored them at < 4 ^{o}C before analysis. We analyzed duplicated samples and spiked samples in every tenth sample and blank samples in every sixteenth sample. We also analyzed four standard

reference material 2710a (National Institute of Standards and Technology, Gaithersburg, MD) soils samples for quality control and assurance.

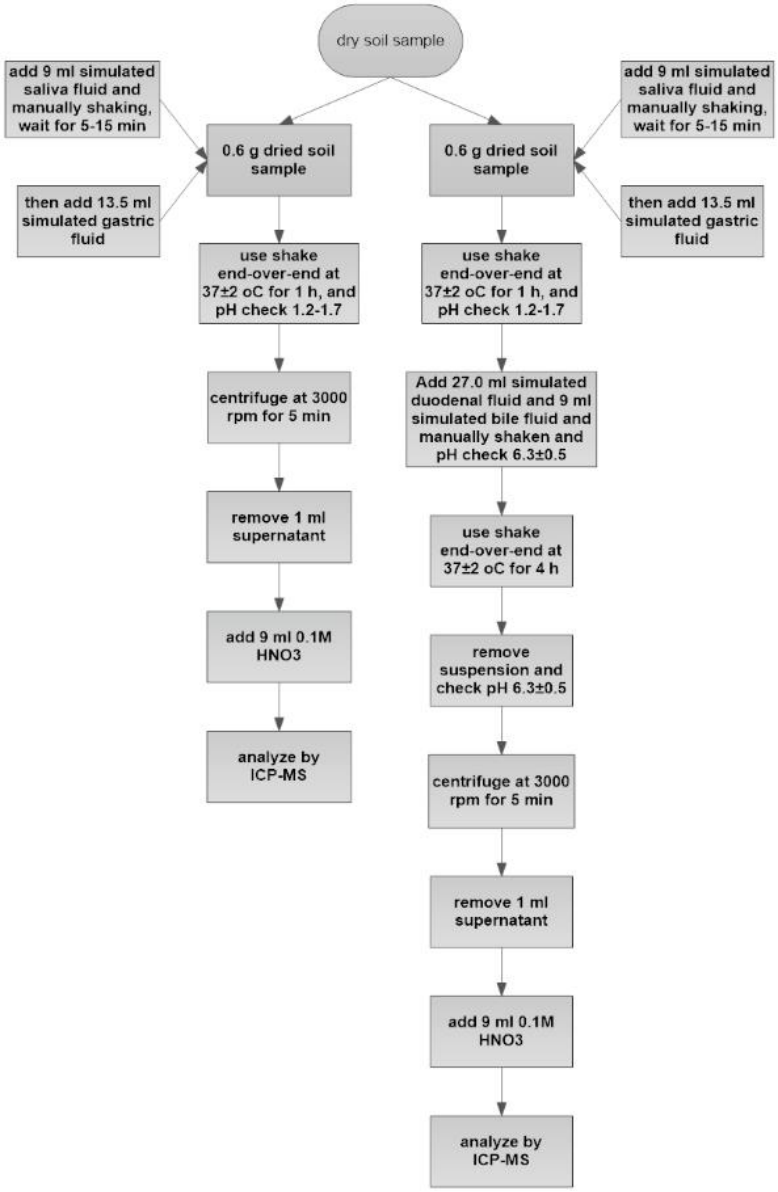


Figure III-1 In-vitro bioaccessibility procedures
(First and second columns from the left represent gastric phase; The third and fourth columns from the left represent gastrointestinal phase)

We used Inductively Coupled Plasma Mass Spectrometry (ICP/MS) 7500 series (Agilent Technologies, Santa Clara, CA) for the analysis of simulated digestive solution for magnesium (Mg), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn) and arsenic (As) in helium gas mode to decrease interferences. We analyzed cadmium (Cd), barium (Ba) and lead (Pb) with no gas mode. Acquisition time for each sample was 114 seconds with 3 times repetition. We added 50 ppb internal standard mix (AG-INTSTD-ASL-1, AccuStandard, New Haven, CT) to each sample for quality control and assurance. We tuned the ICP/MS before sample analysis. We constructed standard calibration curves for each metal: ranging from 0 to 2000 ppb. We obtained the calibration curve r square ranging from 0.9997 to 1. We calculated method detection limit (MDL) of ICP/MS for each metal by using 1 ppb of analytes solution (n=10), and calculated the MDL for each metal as the following equation: $\mathrm{MDL} = 2.821 \times \mathrm{standard\ deviation}$ (2.821=t value, degree of freedom= 9 and α value= 0.01) (USEPA, 2011a). The relative standard deviations of duplicate samples in every tenth sample were less than 10% of the mean between two paired measurements. The concentrations of in-vitro tests of each metal detected by ICP/MS were expressed as levels in mg per dry weight soil in kg (mg/kg). Data points under the limit of detection (LOD) were treated as LOD/√2. The LOD of each metal were presented in chapter II Table II-1 (pg. 28).

Data analysis

We calculated percentage bioaccessible fraction (% BAF) of gastric phase by dividing heavy metal concentrations in gastric phase samples to total concentrations in soils and multiplied by 100%. The % BAF of gastric phase of each metal was calculated by equation 1,

$$\%\ BAF_G = \frac{Conc._{bio-G}\ (\frac{mg}{kg})}{Conc._{soil}\ (\frac{mg}{kg})} \times 100\% \quad \text{(eq 1)}$$

where % BAF_G as bioaccessible fraction (% BAF) of gastric phase.

$Conc._{bio\text{-}G}$ as the concentration of the contaminant detected in ICP/MS in bioaccessible gastric phase,

$Conc._{soil}$ as the concentration of the contaminant detected in ICP/MS in soil.

For percentage bioaccessible fraction (% BAF) of gastro-intestinal phase, we divided heavy metal concentrations in gastro-intestinal phase samples to total concentrations in soils and multiplied by 100%. The % BAF of gastro-intestinal phase of each metal would be calculated by equation 2,

$$\%\ BAF_{GI} = \frac{Conc._{bio-GI}\ (\frac{mg}{kg})}{Conc._{soil}\ (\frac{mg}{kg})} \times 100\% \quad \text{(eq 2)}$$

where % BAF_{GI}= bioaccessible fraction (% BAF) of gastric-intestinal phase,

Conc.$_{bio\text{-}GI}$ as the concentration of the contaminant detected in ICP/MS in bioaccessible gastric-intestinal phase,

Conc.$_{soil}$ as the concentration of the contaminant detected in ICP/MS in soil.

After calculation we identified several outliers that %BAF of metals were greater than 3 standard deviations from the mean %BAF values of each metal. We excluded the extreme outliers beyond 3 standard deviations.

We performed multivariable linear regression analysis to analyze relationships between metals in soils and metals in in-vitro bioaccessibility tests. We used concentrations of each metal in gastric phase or in gastro-intestinal phase as dependent variables, and metal concentrations in soils as independent variables. The α-value in all the model analysis was 0.05. We selected significant independent variables by choosing step forward method for multivariable regression analysis. First, we conducted simple linear regression analysis for each dependent variable that had significant independent variables. Second we conducted multiple linear regression analysis with interaction terms for models with two independent variables.

Exposure assessment

We conducted average daily dose (ADD) exposure scenarios for five age groups: birth to < 1 year (infant), 1 year to < 6 years (toddlers), 6 year to < 12 years (children), 12 years to < 18 years (teenagers), and 18 years and above (adults). We estimated

Table III-1 Description of input parameters for the evaluation of exposure assessment

Parameter	Value	Unit	Reference
Exposure frequency (EF)	365	days/year	USEPA, 2011
Exposure duration (ED)	1 for 0 to < 1 year 5 for 1 to < 6 years 6 for 6 to < 12 years 6 for 12 to < 18 years 60 for 18 to < 78 years	years	USEPA, 2011
Ingestion rate (IngR)	30 for 0 to < 1 year 50 for 1 to < 6 years 50 for 6 to < 12 years 50 for 12 to < 18 years 22 for 18 to < 78 years	mg/day	USEPA, 2017
Body weight (BW)	8 for 0 to < 1 year 16.2 for 1 to < 6 years 36 for 6 to < 12 years 62 for 12 to < 18 years 81 for 18 to < 78 years	kg	USEPA, 2011
Averaging time (AT)	365 for 0 to < 1 year 1825 for 1 to < 6 years 2190 for 6 to < 12 years 2190 for 12 to < 18 years 21900 for 18 to < 78 years	days	USEPA, 2011

representative exposure assessment in equation 3 for each age group using exposure parameters from USEPA factors handbook as Table III-1 showed (USEPA, 2011b; USEPA, 2017).

$$ADD_{ing}\ (\frac{mg}{kg-day})$$

$$= \frac{Conc._{soil}\ \left(\frac{mg}{kg}\right) \times IngR\left(\frac{g}{day}\right) \times EF\left(\frac{day}{year}\right) \times ED(year) \times \frac{1kg}{1000g}}{BW\ (kg) \times AT(day)} \quad (eq\ 3)$$

Where, ingestion rates (IngR) for each age group were 30 mg/day (infant), 50 mg/day (toddlers), 50 mg/day (children), 50 mg/day (teenagers), and 22 mg/day (adults), respectively.

Exposure frequency (EF) for all the age groups was 365 days.

Exposure durations (ED) for each age group were 1 year (infant), 5 years (toddlers), 6 years (children), 6 years (teenagers), and 60 years (adults), respectively.

Body weights (BW) for each age group were 8 kg (infant), 16.2 kg (toddlers), 36 kg (children), 62 kg (teenagers), and 81 kg (adults), respectively.

Average time (AT) for each group were 365 days (infant), 1825 days (toddlers), 2190 days (children), 2190 days (teenagers), and 21900 days (adults), respectively.

Using Equation 3 (pg 48), we calculated daily potential dose and daily applied dose with bioaccessibility results for V, Cr, Mn, Co, Ni, Cu, Zn, As, Ba, Pb (USEPA, 2018b).

Results

Bioaccessibility Tests

Table III-2 (pg. 50) summarizes concentrations of heavy metals and %BAF. For gastric phase, we found that the highest mean %BAF was Ba (61.91 ± 23.89) but the lowest mean

Table III-2 Heavy metal concentrations and bioaccessibility results

Metal	Soil (mg/kg)		Gastric phase (%)[b]		Gastro-intestinal phase (%)[a,b]	G% + GI%[a,b]
	N	Mean±SD	N	Mean±SD	Mean±SD	Mean±SD
As	96	2.92±2.35	92	31.52±27.18	27.57±22.55	59.09±43.35
Ba	96	120.93±99.80	94	61.91±23.89	45.87±25.22	107.78±40.67
Co	96	3.14±2.03	94	34.32±21.40	12.69±16.72	47.02±32.83
Cr	96	11.49±9.29	96	2.08±2.64	0.70±1.21	2.78±3.00
Cu	96	58.20±357.29	95	14.29±15.44	36.88±26.35	51.18±35.87
Fe	96	6,403.12±3,300.90	96	1.22±1.11	0.22±0.43	1.44±1.39
Mg	96	2,494.11±4,576.47	96	42.46±19.06	55.12±25.31	98.58±43.24
Mn	96	220.63±165.82	95	54.53±22.11	41.66±22.10	96.19±41.18
Ni	96	8.00±5.52	94	25.29±17.13	12.80±14.44	38.10±25.95
Pb	96	60.18±98.31	94	39.97±21.53	27.03±24.41	67.01±40.34
V	96	11.71±6.00	96	13.97±11.38	13.25±12.56	27.22±22.65
Zn	96	279.76±1042.63	94	48.39±22.81	18.46±16.46	66.85±32.90

a: number of samples were the same as gastric phase samples

b: exclude values greater than 3 standard deviations (SD) from means

%BAF was Fe (1.22±1.11). We found the mean % BAF were greater than 50 for Ba and Mn whereas the mean %BAF for the rest of the metals were less than 50 (Zn, Mg, Pb, Co, As, Ni, Cu, V, Cr, and Fe). In gastro-intestinal phase, the highest mean %BAF was Mg (55.12 ± 25.31) whereas the lowest mean %BAF was Fe (0.22 ±0.43). All metals, except Cu and Mg showed higher %BAF in gastric phase than in gastro-intestinal phase.

The sum of %BAF by combining gastric phase and gastro-intestinal phases together (G% + GI%) was greater than 50 % for Ba, Mn, Pb, As, Cu, and Zn. The sum of % BAF was the highest for Ba (107.78±40.67) followed by Mg (98.58±43.24), Mn (96.19±41.18), and Pb (67.01±40.34). The sum of %BAF for V, Co, Cr, and Ni was less than 50%. The results confirmed that not all heavy metals were absorbed 100% in human digestion systems and each metal had its unique bioaccessibility fraction in either gastric phase or gastro-intestinal phase. Detailed distribution of concentrations of gastric phase, gastro-intestinal phase and %BAF are in Appendix H (pg. 107).

In our regression analysis, we observed that Pb concentrations in gastric phase were positively associated with Pb concentrations in soil (regression slope=0.37, p-value <0.001) but negatively associated with Zn concentrations in soil (regression slope= -0.03, p-value 0.0024) (Table III-3, pg. 52). The interaction between Pb and Zn in soils were significant but the effect size of interaction was small (regression slope= 0.0001, p-value 0.0209). Bioaccessibility of Pb in gastro-intestinal phase were also positively affected by Pb concentrations in soil (regression slope= 0.50, p-value <0.0001) but negatively associated

with Zn concentrations in soil (regression slope= -0.05, p value 0.0001). The effect of interaction between Pb and Zn was small (regression slope= -0.0002, p-value 0.0017).

Table III-3 Regression results of Pb, Zn, and Mn

(mg/kg)	Intercept	X1	X2	X1*X2	R^2	P-value
Pb-G	3.60	0.37 Pb[a]	-0.028 Zn[a]	0.00011 Pb * Zn[a]	0.68	<0.0001
Pb-GI	-3.86	0.50 Pb[a]	-0.045 Zn[a]	0.00019 Pb * Zn[a]	0.72	<0.0001
Zn-G	-11.64	0.63 Zn[a]	-0.38 Pb[a]	0.00072 Zn * Pb[a]	0.99	<0.0001
Zn-G	22.21[a]	0.67 Zn[a]	-0.64 Ba[a]	0.00010 Zn * Ba[a]	0.996	<0.0001
Mn-G	32.47[a]	0.31 Mn[a]	14.19 As[a]	-0.059 Mn * As[a]	0.30	<0.0001

a: p-value < 0.05

Bioaccessibility of Zn in gastric phase were significantly affected by both Zn and Pb in soil. Bioaccessibility of gastric phase was positively affected by Zn concentrations in soil (regression slope= 0.63, p value < 0.0001) but negatively affected by Pb concentrations in soil (regression slope= -0.38, p-value 0.0027). Another multivariable regression model showed that Zn concentrations in gastric phase were positively affected by Zn concentrations in soil (regression slope= 0.67, p value < 0.0001) but negatively associated with Ba concentrations in soil (regression slope= -0.64, p-value < 0.0001).

Mn concentrations in gastric phase were positively affected by both Mn concentrations in soil (regression slope= 0.31, p-value < 0.0001) and As concentrations in soil (regression slope= 14.19, p-value 0.0002). Although the effect size (regression slope)

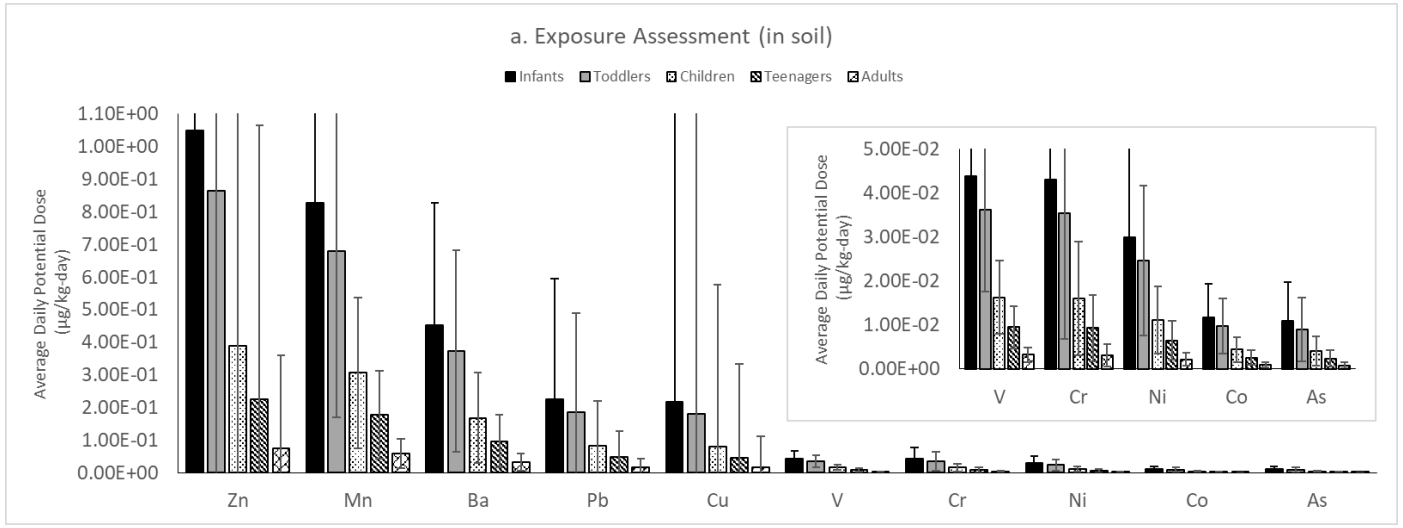
for As was about five time greater than that for Mn, the effect of As in soil on bioaccessibility of Mn was similar due to low As concentrations in soil (mean= 2.92 mg/kg) compared with Mn in soil (mean= 220.63 mg/kg).

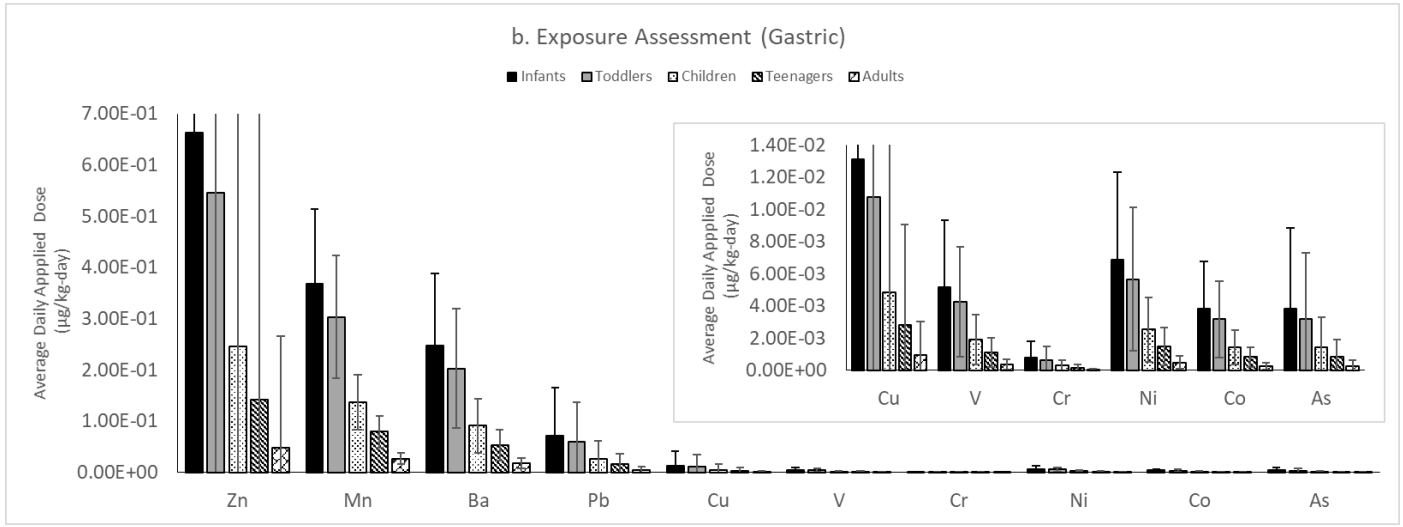
Exposure assessment for age groups

We assessed exposure doses of metals through ingestion for infants (0 to 1 year old), toddlers (1 to < 6 years old), children (6 to < 12 years old), teenagers (12 to < 18 years old), and adults (18 to < 78 years old) using 11 toxic metals (As, Ba, Co, Cu, Cr, Mn, Ni, Pb, V, and Zn) concentrations in soil, gastric phase concentrations, and gastro-intestinal concentrations from 96 sampling locations (Figure III-2, pg. 54).

Daily potential dose (metals in soil): In Figure III-2a (pg. 54), we found the mean average daily potential dose using metal concentrations in soil was highest in infants, followed by toddlers, children, teenagers and adults. The doses of all metals for infants and toddlers were approximately 10 times greater than that of adults and 2-5 times greater than for children and teenagers. Furthermore, the magnitude differences between the highest dose and the lowest dose were decreased as age increasing. Among all age groups, we found Zn in soil was the highest dose and As in soil was the lowest dose.

Daily applied dose: In Figure III-2b (pg. 54), we found the mean average daily applied doses of all metals concentrations in gastric phase were the highest in infants, followed by toddlers, children, teenagers, and adults. Among all age groups, the highest applied dose in


a. Exposure Assessment (in soil)
Infants
Toddlers
Children
Teenagers
Adults
Average Daily Potential Dose (µg/kg-day)
1.10E+00
1.00E+00
9.00E-01
8.00E-01
7.00E-01
6.00E-01
5.00E-01
4.00E-01
3.00E-01
2.00E-01
1.00E-01
0.00E+00
Zn
Mn
Ba
Pb
Cu
V
Cr
Ni
Co
As
Average Daily Potential Dose (µg/kg-day)
5.00E-02
4.00E-02
3.00E-02
2.00E-02
1.00E-02
0.00E+00
V
Cr
Ni
Co
As


b. Exposure Assessment (Gastric)
Infants
Toddlers
Children
Teenagers
Adults
Average Daily Appplied Dose (µg/kg-day)
7.00E-01
6.00E-01
5.00E-01
4.00E-01
3.00E-01
2.00E-01
1.00E-01
0.00E+00
Zn
Mn
Ba
Pb
Cu
V
Cr
Ni
Co
As
Average Daily Appplied Dose (µg/kg-day)
1.40E-02
1.20E-02
1.00E-02
8.00E-03
6.00E-03
4.00E-03
2.00E-03
0.00E+00
Cu
V
Cr
Ni
Co
As

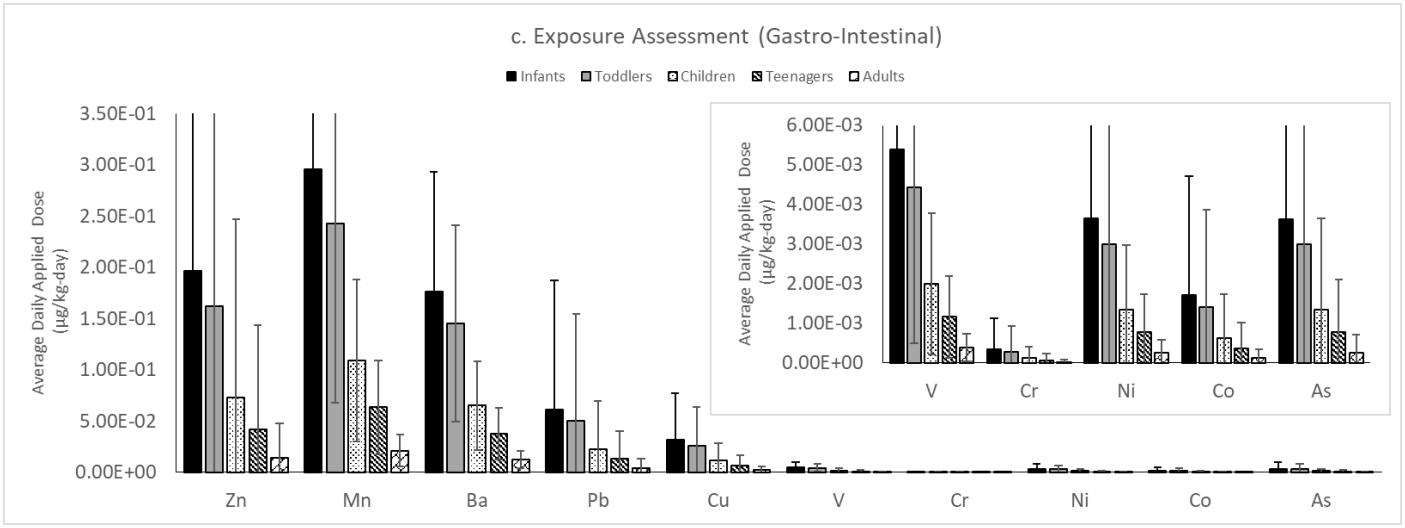


Figure III-2 Exposure assessment for 5 age groups integrating bioaccessibility results
(Error bars represent SD of each metal. Summary of descriptive analysis is in Appendix I, pg. 112)

gastric phase was Zn while the lowest applied dose was Cr. Figure III-2c (pg. 55) shows that the mean average daily applied dose in gastro-intestinal phase was also the highest in infants, followed by toddlers, children, teenagers and adults. Unlike the results from soils and gastric phase, the highest applied dose in gastro-intestinal phase was Mn and the lowest applied dose was Cr for all age groups.

Figure III-3 shows toddlers' estimated average daily dose (µg/mg-day) of metals. We found the estimated average daily dose in soils was the highest followed by gastric phase

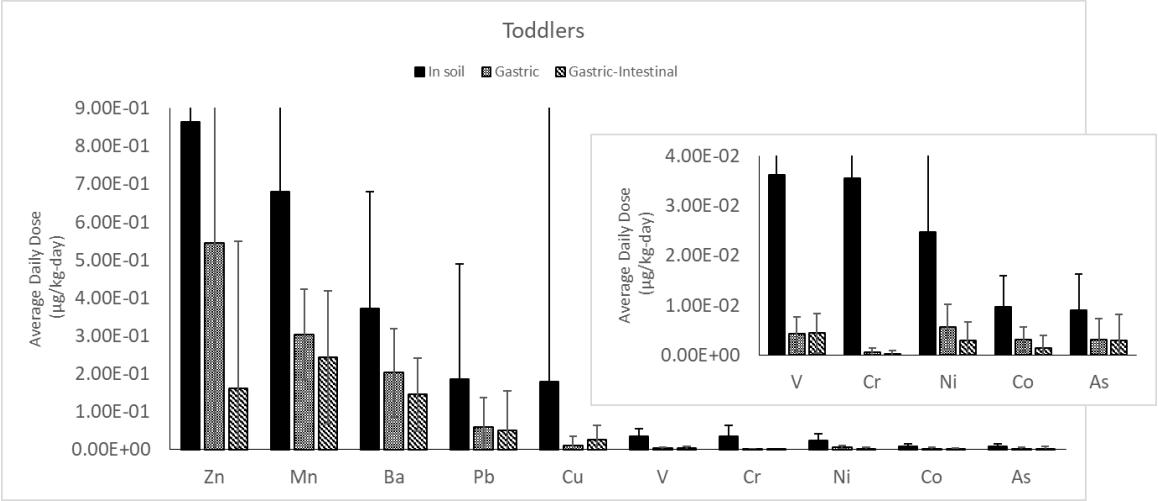


Figure III-3 Exposure assessment results for age 1 to < 6 years old
(Error bars represent SD of each metal. Summary of descriptive analysis is in Appendix I, pg. 112)

and gastro-intestinal phase for all metals, except Cu and V. Both Cu and V showed that the estimated average daily doses were the highest in soils followed by gastro-intestinal phase and gastric phase. For Zn, the dose in gastric phase was two times greater than that in gastro-intestinal phase. The estimated doses for Pb, V, Cr, and As between gastric phase

and gastro-intestinal phases were almost same. On the other hand, V and Cr showed 8 and 55 times differences of doses between soils, gastric, and gastro-intestinal phases. Copper was adsorbed about 2.4 times greater in gastro-intestinal phase than in gastric phase. Vanadium was adsorbed about 4% more in gastro-intestinal phase than in gastric phase. The estimated daily doses of metals for other age groups (data not shown) were the same trend as those for toddlers.

Discussion

Bioaccessibility tests results

We compared %BAF for selected heavy metals in gastro-intestinal phase with previous studies (Table III-4, pg. 60). These cited studies used the same in-vitro bioaccessibility UBM procedure that we used in this study. In our study, mean concentration of Pb in soil (60.18 mg/kg) was lower than studies conducted near Pb, Cu, and Zn smelters in the United Kingdom (Okorie et al., 2011) or coal mining activities in France (Pelfrêne et al., 2015; Roussel et al., 2010). Lead concentration in our study was 1.6 times greater than the study done in urban and rural areas of Northern Ireland (Barsby et al., 2012). Pb in soils are related to point sources such as smelters and mining activities (Tchounwou et al., 2012). Moreover, historical Pb emission in 1970's from Pb-added gasoline and Pb-based paint may still exist in soils even after long period of times (Datko-Williams et al., 2014; Yesilonis et al., 2008).

In our study, the mean %BAF of Pb in gastric phase (40%) was higher than that in gastro-intestinal phase (27%). The findings are consistent with previous studies (Pelfrêne et al., 2012; Pelfrêne et al., 2015; Roussel et al., 2010). We found that %BAF of Pb in gastric phase ranged from 40% to 60%, and %BAF of Pb in gastro-intestinal phase ranged from 15% to 30%.

Arsenic (As) is a classified human carcinogen by USEPA (USEPA, 2016). Major sources in urban area are copper smelting and gardening activities using herbicide, pesticide, rodenticide (Datta et al., 2007). In our study, the mean concentration of As in soils (2.92 mg/kg) was 3 to 300 times lower than the studies in urban and rural areas of Northern Ireland (Barsby et al., 2012) and in industrial areas in UK (Okorie et al., 2011). Compared to the extensive high As concentration in UK, our sampling locations were not close to Cu smelters. The %BAF of As in gastric phase and gastro-intestinal phase in our study were consistent around 30% and similar to the study done in Northern Ireland (Barsby et al., 2012).

Mean value of %BAF of Zn in gastric phase in our study (48%) was similar to a previous study done in France (47%) (Roussel et al., 2010). And mean value of %BAF of Zn in gastro-intestinal phase in our study (18%) was close to a previous study done in Northern Ireland (14%) (Barsby et al., 2012).

If metals have high %BAF, it means that they are highly accessible in stomach to be absorbed. The absorbed metals can be transport to organ or cell tissues and be

accumulated causing toxic effects. On the other hand, low %BAF indicates that metals are not readily accessible in the human digestion system. Means of %BAF Cr in our study in gastric phase (2.08%) and gastro-intestinal phase (0.70%) were similar to the results from a study in Northern Ireland (4% and 3%, respectively). Another study also reported that bioaccessibility of Cr was the lowest compared to other toxic metals (Barsby et al., 2012).

All metals, except Cu and Mg, showed that %BAFs in gastric phase were higher than in gastro-intestinal phase. Okorie et al. (2011) found %BAF of Cu in gastro-intestinal phase was approximately 3 times higher than those in gastric phase (Okorie et al., 2011). The high Cu %BAF in gastro-intestinal phase in our study may be influenced by different soil characteristics such as organic ligands in simulated digestion fluids (Cai et al., 2016).

The different %BAF of each metal in Table III-4 (pg. 60) suggests that metal bioaccessibility can be affected by soil characteristics and physio-chemical characteristics of metals. These characteristics include soil properties, organic matter in soils, other mineral compounds, such as $CaCO_3$. For example, Pb and Zn concentrations in soils were found positively related to Pb and Zn in bioaccessibility tests; while $CaCO_3$ may have negatively affected to Pb in gastric phase and Zn in both phases (Pelfrêne et al., 2012). Moreover, organic matter in soils may have a positive impact to Zn in both phases but negative impact to Pb in gastric phase; while sand and clay types were negative to Cu (Poggio et al., 2009). Lastly, interaction between metal species is also a possible factor to explain those variation of %BAF. In our study, we found that bioaccessibility of Pb was related to concentrations of

Table III-4 Percent bioaccessibility fractions in gastric phase (G) and gastro-intestinal (GI) phase

Reference	Okorie et al., 2011[1]			Roussel et al., 2010[2]			Barsby et al., 2012[3]			Pelfrêne et al., 2015[4]			This study		
Location	Newcastle upon Tyne, UK			Noyelles-Godault, FR			Northern Ireland, IE			Noyelles-Godault, FR			Houston, US		
Metal	Total (mg/kg)	G%	GI%	Total (mg/kg)	G%	GI%	Total (mg/kg)	G%	GI%	Total (mg/kg)	G%	GI%	Total (mg/kg)	G%	GI%
As	820	32	54	-	-	-	6.43	28	24	-	-	-	2.92	31.52	27.57
Ba	-	-	-	-	-	-	-	-	-	-	-	-	120.93	61.91	45.87
Co	-	-	-	-	-	-	12.03	23	8	-	-	-	3.14	34.32	12.69
Cr	163	29	49	-	-	-	46.10	4	3	-	-	-	11.49	2.08	0.70
Cu	240	22	68	-	-	-	38.25	31	28	-	-	-	58.20	14.29	36.88
Fe	-	-	-	-	-	-	-	-	-	-	-	-	6403.12	1.22	0.22
Mg	-	-	-	-	-	-	-	-	-	-	-	-	2494.11	42.46	55.12
Mn	-	-	-	-	-	-	-	-	-	-	-	-	220.63	54.53	41.66
Ni	67.8	25	42	-	-	-	41.19	11	5	-	-	-	8.00	25.29	12.80
Pb	11134	30	44	984	62	32	38.85	43	15	273	59	22	60.18	39.97	27.03
V	-	-	-	-	-	-	59.98	15	6	-	-	-	11.71	13.97	13.25
Zn	2816	33	50	1941	47	23	93.14	35	14	515	35	10	279.76	48.39	18.46

1 mean of 19 soil samples
2 mean of 27 soil samples
3 mean of 91 soil samples
4 mean of 502 soil samples

both Pb and Zn in soils. This results were consistent with previous studies (Pelfrêne et al., 2012; Roussel et al., 2010).

Exposure assessment

We found that average potential doses (calculated using concentrations of metals in soil) were greater than average applied doses (calculated using bioaccessible fraction from gastric phase and gastro-intestinal phase). All metals, except Cr and V, had over 30% bioaccessibility from each s gastric and gastro-intestinal phased to the human body. In in-vitro bioaccessibility tests, % BAFs of both Cr and V had less than 15% at each both gastric and gastro-intestinal phase, respectively.

We found that among all age groups, infants and toddlers had the highest average daily potential dose in Houston. Previous studies showed that young children were vulnerable to Pb exposure in soils. Glorennec et al. found that soil ingestion was the primary exposure route among all routes of exposures (respiratory exposure, dietary exposure, tap water exposure, dust exposure, and soil exposure) for children ages between 3 to 6 years old (Glorennec et al., 2016). Carrizales et al. also demonstrated that elevated levels of blood Pb in children were positively associated with Pb concentrations in soils (Carrizales et al., 2006).

A limitation of this study was that we did not use 'actual' exposure parameters for all ages living in real-world situations. As Houstonians are diverse in ethnicity and race with

different life styles and exposures to metals, soil ingestion among individuals may largely vary from the general parameters from the US EPA Exposure Factors Handbook (USEPA, 2017). However, using these parameters is useful to estimate representative central tendency in exposure to metals and daily dose estimates. Thus, the results in this study provide useful information to understand the overall exposure and dose among all age groups in Houston, TX.

Conclusions

In this study, we analyzed concentrations of 13 metals in soil, and their bioaccessibility using simulated digestion fluids. We assessed exposure doses of infants, toddlers, children, teenagers, and adults for 11 toxic metals among 13 metals. All metals, except Cu and Mg, were adsorbed more in gastric phase than gastro-intestinal phase. Barium (Ba), Mg, and Mn were almost 100% bioaccessible in digestion systems whereas Cr, Fe, and V showed less than 15% bioaccessibility. The exposure doses were highest in infants and toddlers among all age groups. The %BAFs in our study were specific for Houston soils and could be used for future studies regarding metal exposure from soils.

CHARPTER IV. RISK ASSESSMENT OF EXPOSURE TO HEAVY METAL IN SOILS IN HOUSTON, TX, INTEGRATING IN-VITRO BIOACCESSIBILITY TESTS AND SPATIAL ANALYSIS

To be submitted to Environmental Health Perspectives

Introduction

In the United States, heavy metal concentrations in soils such as lead (Pb), zinc (Zn), copper (Cu), and arsenic (As) were elevated in urban areas. Potential sources of these metals are associated with industrial activities (Davis et al., 2014) and high volume of traffic (Goldhaber et al., 2009; Solt et al., 2015). Houston, Texas has around 1,000 metal facilities, including finishing, manufacturing, coating, scrap metal, metal construction materials, recycling, smelting, refinery and alloying (USEPA, 2018c). These point emission sources emit toxic heavy metals in surrounding areas. Heavily trafficked roadways in Houston also generate other heavy metals like Pb and Cu from automobiles (Benipal et al., 2017).

Heavy metals emitted from these sources are eventually deposited on urban soils. Ingestion, especially to children, is one of the important exposure pathways of metal exposure in soil. According to the Unites States Environmental Protection Agency (USEPA) Exposure Handbook, young children (1 to < 6 years old) have higher ingestion rates than other age groups since they tend to play on the ground and to lick dirt or soil on mouth or their hands (USEPA, 2017). Chronic adverse health effects from exposure to heavy metal are cancers, developmental effects, neurological effects, and cardiovascular effects (ATSDR,

2016). As Houston has a lot of metal emission sources near residential areas, Houstonians are potentially at high risk of diseases related to heavy metal exposures (Hawley, 1985).

Evaluation of potential risk can be assessed using measured concentrations of metals in soil (potential dose) or bioaccessible fractions of metals that represent 'true' absorbed metals into human body (applied dose) (USEPA, 2018b). Conventional risk assessment using metal concentrations in soils provides maximum health risk whereas risk assessment using bioaccessibility test data provides improved risks close to the relatively 'true' biologically effective dose on the organ (Markus and McBratney, 2001). Because a fraction of soil metals can be absorbed in human bodies, human health risk assessment with the data using bioavailability has been suggested for a better understanding of potential exposures and related risks (Saleem et al., 2014). Assuming less than 100% bioaccessibility, the health risks using bioaccessibility data are expected to be lower than those using metal concentrations in soils. For instance, Pelfrêne et al (2015) assessed human health risks in exposure to cadmium (Cd), Pb and Zn in France near 2 smelter plants. The authors found that the hazard index (HI) using metal concentrations in soils was 0.46 whereas HIs using gastric phase and gastro-intestinal phases were 0.15, and 0.03, respectively (Pelfrêne et al., 2015).

Due to spatial differences of metal concentrations in urban areas, evaluating spatial heterogeneity of risk assessment is useful for a better understanding of risk disparities in local or regional scales (Pelfrêne et al., 2015; Sun et al., 2016). A recent study evaluated

spatial variations of risk assessment with both metal concentrations in soils and the bioaccessibility test in France (Pelfrêne et al., 2015). However, no study has been conducted with this novel spatial analysis along with bioaccessibility in Houston, TX.

The aim of the study is to examine cancer and non-cancer risks associated with exposure to (1) 11 toxic metals, arsenic (As), barium (Ba), Cd, chromium (Cr), cobalt (Co), Cu, manganese (Mn), nickel (Ni), Pb, vanadium (V), and Zn in soils in Houston, TX; (2) compare risk outcomes using metal concentrations in soils with risk estimates using bioaccessibility data; and (3) identify possible high risk neighborhood in Houston, TX using spatial analysis. To identify susceptible age groups, we also examined these health risks by five age groups, 0 to < 1 years old (infants), 1 to < 6 years old (toddlers), 6 to < 12 year old (children), 12 to < 18 years old (teenagers), and 18 to < 78 years old (adults).

Methods

Study Area and Soil Sampling

Houston is encircled by two major freeways, Beltway 8 and interstate 610. Interstate 610 is an urban freeway and within it is generally referred to as “inside loop 610”. The area inside Loop 610 is 97 square miles, and the area from loop 610 to Beltway 8 is 434 square miles (Walker and Shelton, 2016). We collected 96 soil samples in Houston, Texas from October 11th to October 25th, 2017. Within and around loop 610, we determined 56 soil sampling sites systematically by 2 kilometer-square grids. Between beltway 8, which is a

state highway system of 143 kilometers around Houston, and Loop 610, we determined 40 sampling sites by 4 kilometer-square grids.

Using a plastic shovel at each site, we collected top soil samples (0 to 5 cm depth) at all sampling locations and placed the samples into 500 ml glass bottles. We stored samples with ice packs in a cooler during field sampling efforts. After we completed the sampling, we transported the samples back to UTHealth Exposure Assessment Laboratory. Detailed information regarding soil sampling was in Chapter II materials and method section (pg. 20-23).

Heavy Metal Analysis

We dried soil samples at room temperatures for a week and homogenized them. We followed the USEPA 3051A acid-digestion method to extract metals from soils (USEPA 2018). We used a Microwave system, MARS 6 (CEM Corporation, Matthews, NC) for sample preparation. The detailed acid digestion procedure was in the chapter II materials and method section (pg. 24-26). After the completion of microwave assisted acid digestion of each sample, we produced the diluted solution by transforming 1 ml of digested samples into 50 ml digestion tubes with trace metal free ultra pure de-ionized water (50:1 dilution). Further, we transferred 1 ml aliquots from 50 ml digestion tubes into another 10 ml tubes and added metal free ultra pure water to make final solutions (overall dilution 500:1). The final solution was injected to an Inductively Coupled Plasma Mass Spectrometry (ICP/MS) analysis (USEPA, 1998). We analyzed 11 metals: vanadium (V), chromium (Cr), manganese

(Mn), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), cadmium (Cd), barium (Ba), and lead (Pb). We made calibration curves of each metal ranging from 0 to 2000 ppb; the calibration curve r square ranged from 0.9997 to 1. The method detection limit (MDL) of ICP/MS for each metal was obtained by using 1 ppb of analytes solution (n=10), and the MDL for each metal was calculated as the following equation: $MDL = 2.821 \times Standard\ deviation$ (2.821=t value, degree of freedom= 9 and α value= 0.01) (USEPA, 2011a).

In-Vitro Bioaccessibility Tests

We conducted in vitro oral bioaccessibility test of V, Cr, Mn, Co, Ni, Cu, Zn, Ba, Cd, and As with the Unified Bioaccessibility Methods (UBM) (Wragg et al., 2009). We examined bioaccessibility of 11 metals in both gastric phase and gastro-intestinal phase. We synthesized artificial saliva fluids, gastric fluids, duodenal fluids and bile fluids mimicking human intestinal solutions based on the UBM method. We evaluated bioaccessibility using artificial solutions to simulate heavy metal digestion in human bodies. The detailed procedure of bioaccessibility tests is described in the Chapter III materials and method section (pg. 41-44). After the completion of bioaccessibility test, the simulated aliquots were analyzed for heavy metals with ICP/MS. For quality control, we measured duplicate samples and spiked samples in every tenth sample. We also analyzed blank samples in every sixteenth sample. We analyzed four standard reference material 2710a (National Institute

of Standards and Technology, Gaithersburg, MD) soils samples following the same experimental procedures described above.

Risk assessment

Average daily dose (ADD): In this study, we assessed non-cancer and cancer risks to five age groups: 0 to < 1 year (infants), 1 year to < 6 year (toddlers), 6 years to < 12 years (children), 12 years to < 18 years (teenagers), and 18 to < 78 years (adults). First, we calculated average daily dose (ADD) using equation 1.

$$ADD\ (\frac{mg}{kg-day}) = \frac{Conc.\ \left(\frac{mg}{kg}\right) \times IngR\left(\frac{g}{day}\right) \times EF\left(\frac{day}{year}\right) \times ED(year) \times \frac{1kg}{1000g}}{BW\ (kg) \times AT(day)} \quad (1)$$

Where,

ADD is average daily dose, average exposures or doses over the period of exposure

IngR is ingestion rate.

EF is exposure frequency.

ED is exposure duration.

BW is body weight.

IngR is Ingestion rates of soil (mg/day) for the five age groups: we used 30, 50, 50, 50, and 22, respectively.

EF is exposure frequencies (days/year). For the five age groups we used 365 days.

ED is exposure durations (years). For the five age groups, we used 1, 5, 6, 6, and 60, respectively.

BW is body weight (kg). For five age groups, we used 8, 16.2, 36, 62, and 81, respectively.

AT is averaging time. For non-cancer risk assessment, average time (days) of chronic non-cancer risks assessment for the five age groups were 365, 1825, 2190, 2190, 21900, respectively. All the exposure parameters are imputed data from the USEPA exposure handbook (USEPA, 2011b).

For concentrations of metal, we calculated the 95% upper confidence limit (UCL) of mean concentration of each metal from soil, gastric phase, and gastro-intestinal phase, respectively. We used ProUCL 5.1.00 (US EPA Region 4, Atlanta, GA) to calculate 95th percentile upper confidence limits of mean values for each metal based on data distribution (normal, gamma, lognormal, or nonparametric).

Non-cancer risk assessment: We calculated the hazard quotient (HQ) for each individual metal and obtained the hazard index (HI) by summation of all HQ values. To assess the HI and HQ, we used the following equation 2.

$$HQ = \frac{ADD\ (\frac{mg}{kg-day})}{RfD\ (\frac{mg}{kg-day})} \quad (2)$$

In equation 2, HQ is the hazard quotient of the ingestion route from soil exposure. After obtaining average daily potential dose (ADD) from soil ingestion exposure calculated from equation 1, we divided the values with their relevant reference dose to calculate hazard quotient (HQ) of each metal. Reference dose is an estimate of a daily oral exposure for a duration to the human population that is likely to be without an appreciable risk of deleterious effects during a lifetime. Reference doses (Rfd) (mg/kg-day) of As, Ba, Co, Cu, Mn, Ni, and Zn are 0.0003, 0.2, 0.02, 0.04, 0.14, 0.02, and 0.3, respectively (USEPA, 2010; USEPA, 2016). Reference doses (mg/kg-day) of Cd is adapted from food exposure, and the value is 0.001 (USEPA, 2010). Reference doses (mg/kg-day) of Cr is adapted from trivalent chromium, and the value is 1.5 (USEPA, 2010). Reference doses (mg/kg-day) of V is adapted from vanadium pentoxide, and the value is 0.007. While Pb doesn't have a reference dose from USEPA, we adapted 0.0003 (mg/kg-day) associated with the decrease of 0.5 intelligent quotients (IQ) points (Pelfrêne et al., 2013). We summed the HQ of each metal to obtain the hazard index (HI). If HI is greater than one, we conclude the health risk is not safe.

Cancer risk assessment: We calculated cancer health risks using equation 4. Similar to non-cancer risk, we calculated the 95^{th} percentile UCL of the mean for As in soils, gastric phase, and gastro-intestinal phase. To calculate lifetime average daily potential dose (LADD), we used the parameters in equation 3. Average time (days) of cancer risks assessment for the

five age groups were 28,470 days. And the rest of the parameters are the same in the previous non-cancer risk assessment section.

$$LADD\ (\frac{mg}{kg-day}) = \frac{Conc.\ \left(\frac{mg}{kg}\right) \times IngR\left(\frac{g}{day}\right) \times EF\left(\frac{day}{year}\right) \times ED(year) \times \frac{1kg}{1000g}}{BW\ (kg) \times AT(day)} \quad (3)$$

$$Risk = LADD\ \left(\frac{mg}{kg-day}\right) \times SF\left(\frac{1}{\frac{mg}{kg-day}}\right) \quad (4)$$

Where, SF is slope factor = 1.5 $(mg/kg\text{-}day)^{-1}$ for As (USEPA, 2010).

We calculated cancer risk for each age group. If cancer health risk is greater than one in a million, we considered this as not safe.

Spatial analysis

We used ArcGIS 10.5.1 software (ESRI, Redlands, CA) and SAS 9.4 software (SAS Institute, Cary, NC) for spatial analysis. We recorded the longitude and latitude for each sampling location. For non-cancer risk at each sampling location, we used metal concentrations measured at each sampling site instead of UCL of means of metals. This allowed us to calculate HQ for individual metals at each sampling location. Similarly, we calculated HI for each sampling location by summing all HQs at each sampling site. For cancer risks, we transformed the data into 10E-05 scale for model estimation, then

transformed back to original scale. We used SAS 9.4 software to find the best fit semivariogram of cancer risk and HI. Using best fit semivariogram models, we predicted spatial variations of cancer risk and non-cancer risk in Houston, TX (-95.57, 29.59 to -95.11, 29.94, 161811 points). For HI model, we used spherical model with nugget, 1.1118, sill, 0.2123, and range (m), 0.000001, whereas for cancer risk model, we used spherical model with nugget 0.005041, sill 0.00000104, and range (m), 0.000001.

Results

Non-cancer risk

All metals, except Cd (N=56 detected), were detected in 96 soil samples. Due to high non-detectability of Cd, we did not include Cd for risk assessment. Figure IV-1 (pg. 73) shows 11 heavy metals in soils, gastric phase, and gastro-intestinal phase. In soils, Zn had the highest mean concentration (279.76 mg/kg), followed by Mn (220.63 mg/kg), Ba (120.93 mg/kg), Pb (60.18 mg/kg), Cu (58.20 mg/kg), V (11.71 mg/kg), Cr (11.49 mg/kg), Ni (8.00 mg/kg), Co (3.14 mg/kg), As (2.92 mg/kg), and Cd (0.31 mg/kg).

In gastric phase, Zn had the highest mean concentration (176.73 mg/kg), followed by Mn (98.28 mg/kg), Ba (65.80 mg/kg), Pb (19.28 mg/kg), Cu (3.50 mg/kg), Ni (1.84 mg/kg), V (1.38 mg/kg), As (1.03 mg/kg), Co (1.03 mg/kg), and Cr (0.21 mg/kg). In gastro-intestinal phase, Mn had the highest mean concentration (78.78 mg/kg), followed by Zn (52.51 mg/kg), Ba (47.06 mg/kg), Pb (16.41 mg/kg), Cu (8.42 mg/kg), V (1.44 mg/kg), Ni (0.97

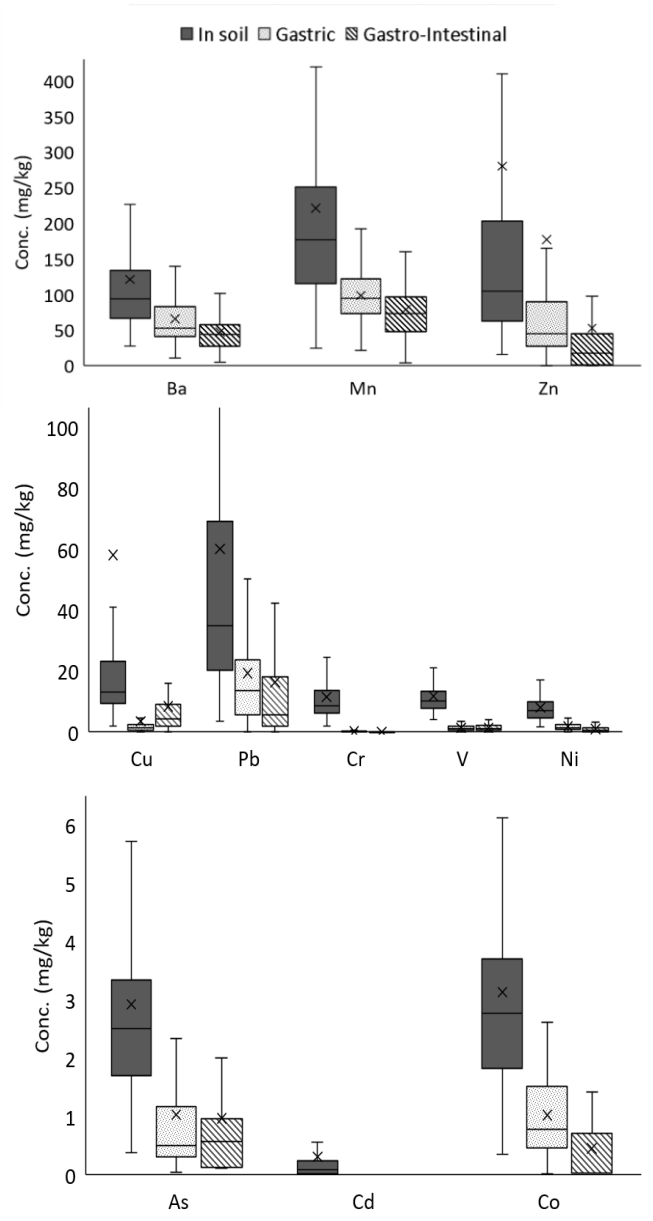


Figure IV-1 Boxplots of heavy metals in soils, gastric phase, and gastro-intestinal phase
(In boxplot, upper quartile, third quartile, median(-), first quartile, and lower quartile were plotted. X represents mean.)

Table IV-1 Upper confidence limits of each metal and risk assessment results of infants (0 to < 1 year old) group using metals in soils and bioaccessibility tests*

	In soil	G	GI
UCL (mg/kg)			
Pb	71.66	23.64	21.46
As	3.25	1.36	1.72
V	12.56	1.88	2.01
Mn	245.90	104.90	104.10
Cu	217.10	6.92	13.9
Zn	249.80	538.3	108.80
Ba	133.30	73.23	52.63
Ni	8.85	2.13	1.50
Co	3.48	1.38	0.82
Cr	12.84	0.33	0.19
Cd	0.78	N/A	N/A
Risk Assessment			
HI	0.98	0.33	0.30
Cancer	2.34E-07	9.81E-08	1.24E-07

*UCL is 95th percentile of means; G: gastric phase; GI: gastro-intestinal phase; detailed risk assessment results in Appendix J, pg. 113.

mg/kg), As (0.97 mg/kg), Co (0.46 mg/kg), and Cr (0.09 mg/kg). All the metals, except Cu, had a decreasing trend from soil to gastric phase, and to gastro-intestinal phase.

We summarized UCLs of means for each metal in soil, gastric phase, and gastro-intestinal phase (Table IV-1, pg. 74) (Detailed non-cancer risks are in Appendix J, pg. 113). Table IV-1 also includes risk assessment results for infant age group (0 to < 1 year old). Hazard index

(HI: sum of each metal HQ) of metal concentrations was 0.98, 0.33, and 0.30 in soils, gastric phase, and gastro-intestinal phase, respectively. All HI values were smaller than one (1) in the infant age group.

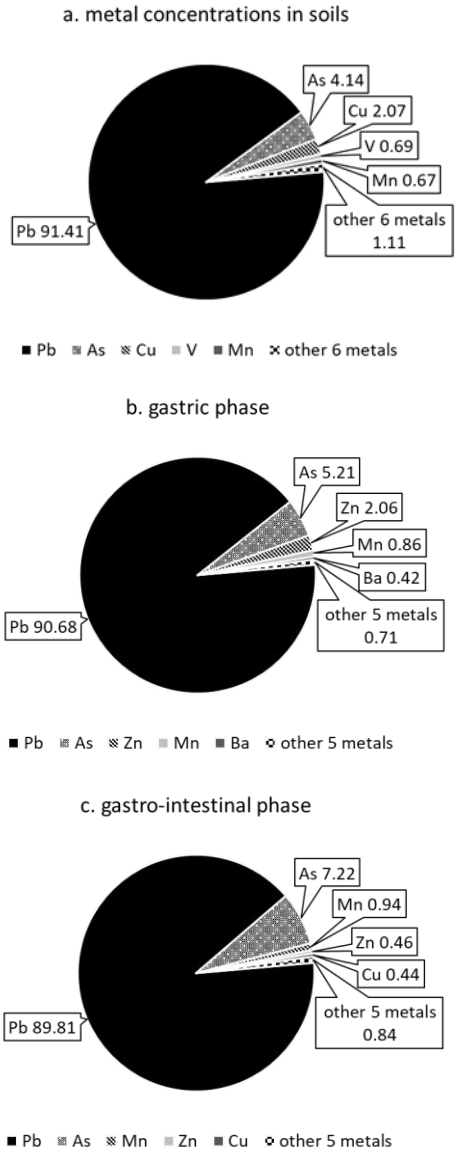


Figure IV-2 Contribution of each metal on HI results in total concentrations in soils, and bioaccessibility tests

We found that Pb contributed around 90% of total risk using potential dose (soil) and applied doses (both G and GI Phases) (Figure IV-2). Although concentrations of Pb were not the highest in all three media, the contribution of Pb for risk assessment was the highest (91.41%) in soils, followed by As (4.15%), Cu (2.07%), V (0.69%), Mn (0.67%), and the rest of the six metals (1.11%). Similarly, we found the contribution of Pb for risk assessment was the highest for gastric and gastric-intestinal phase. In gastric phase, the contribution of Pb was 90.68%, followed by As (5.12%), Zn (2.06%), Mn (0.86%), Ba (0.42%), and the rest of the five metals (0.71%). In gastro-intestinal phase, contribution of Pb was 89.81%, followed by As (7.22%), Mn (0.94%), Zn (0.46%), Cu (0.44%), and rest of the five metals (0.84%).

In Figure IV-3a (pg. 77), we compared non-cancer risks among five age groups. We found that adults (18 to 78 years old) showed the lowest non-cancer risk (HI=0.07) while infant (0 to < 1 year old) had the highest non-cancer risk (HI=0.98). As age groups became younger, the HI values increased. The exposure duration is longer for the adults group than for young children, but ingestion doses are higher in young children, and their body weights are less than adults. Therefore, young children showed higher HIs. Similarly, we found that non-cancer risks for infants were the highest (HI= 0.33 in gastric phase, 0.30 in gastro-intestinal phase) whereas those for adults were the lowest (HI= 0.02 in gastric phase, 0.02 in gastro-intestinal phase). Figure IV-3a (pg. 77) shows that the HIs using bioaccessibility tests

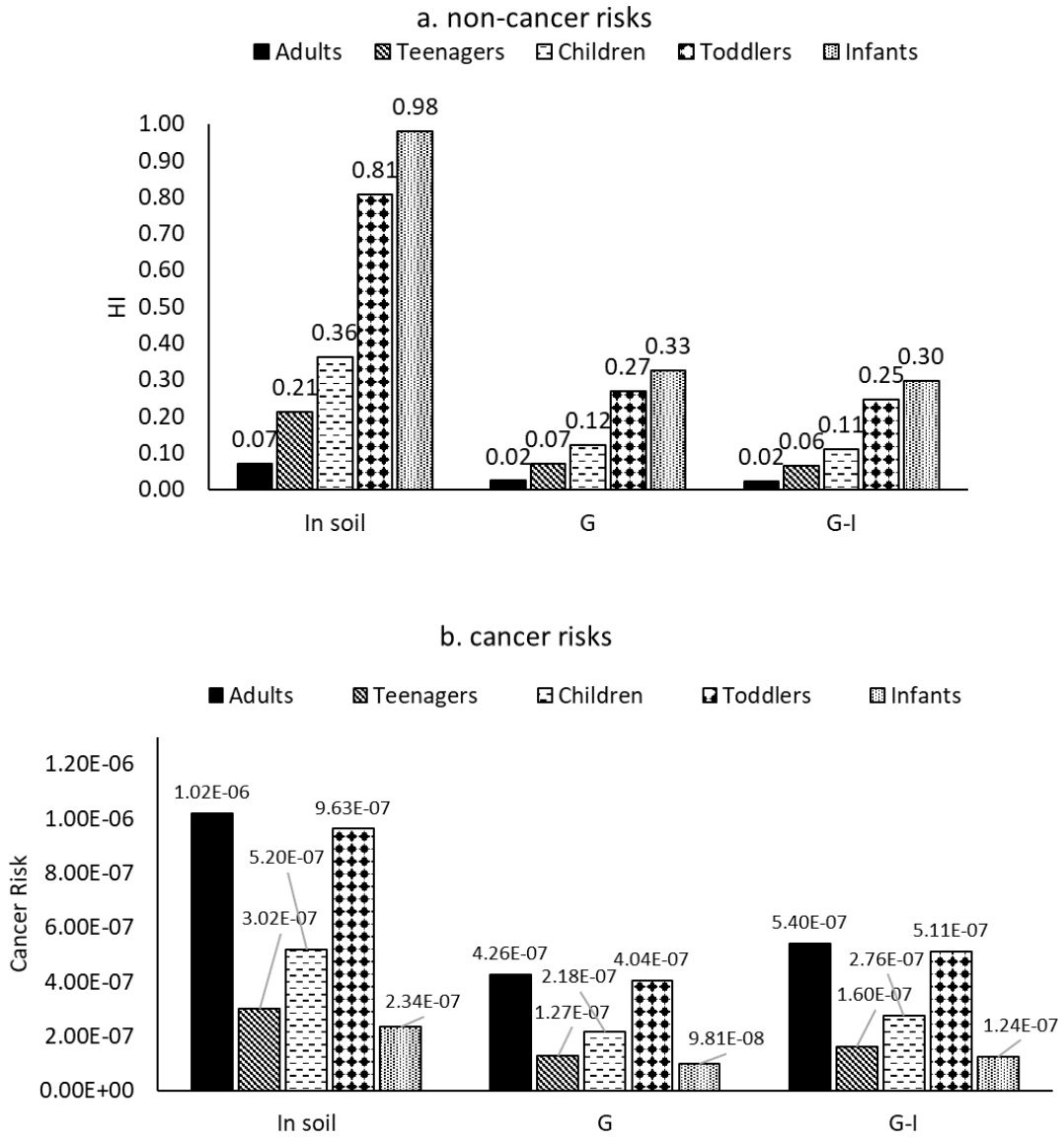


Figure IV-3 Risk assessment results among each age groups with metal concentrations in soils, and bioaccessibility tests

(*G: gastric phase; GI: gastro-intestinal phase; detailed information in Appendix J, pg. 113)

in both phases (the His in gastric phase were slightly higher than those in gastro-intestinal phase) are lower than those using metal concentrations in soils among all age groups.

Cancer Risk

Table IV-1 (pg. 74) summarizes that cancer risk of As concentration for infants group was 2.34E-07 in soil followed by gastric phase (9.81E-08) and gastro-intestinal phase (1.24E-07). Figure IV-3b (pg. 77) shows that cancer risks of As in soils were the highest in adult age group (18 to < 78 years) (1.02 E-06), followed by 1 to < 6 years (9.63 E-07), 6 to < 12 years (5.20E-07), 12 to < 18 years (3.02 E-07) and 0 to < 1 year (2.34 E-07). We found the same trend of cancer risks for both gastric phase and gastro-intestinal phase among five age groups. Thus, the cancer risks using bioaccessibility test were lower than those applying concentrations in soil.

Spatial Risk Assessment

We identified that 13 sampling sites had HI values greater than 1 (Figure IV-4, pg. 79). The locations with HI > 1 were between loop 610 and east of interstate 69 (US 59). The range of HIs was from 1.08 to 8.91. The lowest HI (0.05) was observed in the Memorial Park location, west side of Houston.

For cancer risk assessment (Figure IV-5, pg. 79), we found that 23 sites had cancer risks greater than 1 in a million. The range of cancer risks were between 1.02 in a million

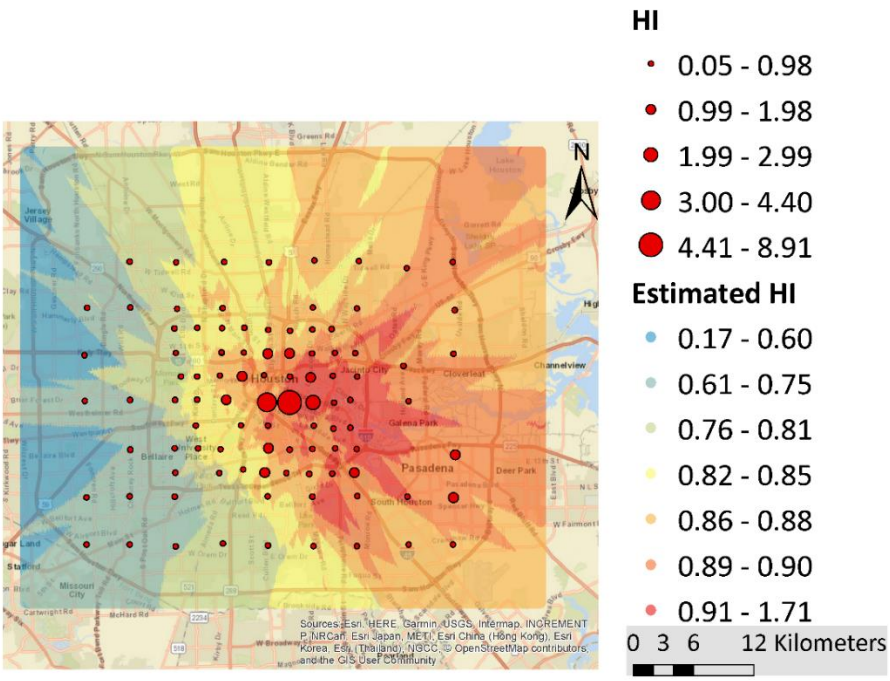


Figure IV-4 Spatial variation using HI of age group 1 to < 6 years old

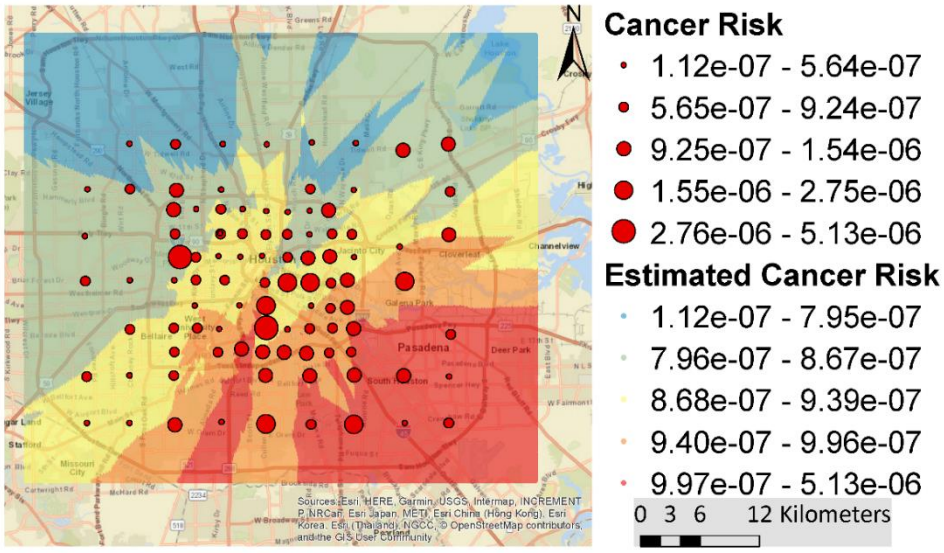


Figure IV-5 Spatial variation using cancer of age group 1 to < 6 years old

and 5.13 in a million. Twenty sites were in the east or south of Houston, but three sites were in memorial park area. The lowest cancer risk (0.11 in a million) was in a location in central north Houston, a little outside loop 610.

Discussion

We analyzed metal concentrations from 96 soil samples in Houston, TX. We also conducted bioaccessibility test to evaluate the potentially adsorbed amount of heavy metals from ingestion of soils. We estimated risks for cancer and non-cancer using metals concentrations in soil, gastric, and gastro-intestinal phases. We found that health risks applying bioaccessibility tests were lower than those from traditional risk assessment. In overall, the health risks using bioaccessible fraction of metals were less than 60% of health risks using metal concentrations of soils in this study.

Non-cancer risk

We found that non-cancer risks of HI were less than one (1) among all age groups. We observed that non-cancer risks were primarily attributed to Pb and As concentrations in soils and in gastric or gastro-intestinal phase. In our study, we found the contribution of both Pb and As were greater than 95% for non-cancer risk assessment. However, both Pb and As only comprised of less than 10 % of total metals in soil samples. This suggests that even relatively low concentrations of Pb and As in soils play a role for estimation of non-

cancer risks. Our study results are consistent with findings from a previous study. Pelfrêne et al., (2015) found that HQ of Pb in soil near smelter facilities in France contributed 99% of HIs among 3 metals (Pelfrêne et al., 2015). On the other hand, another study conducted in Beijing, China showed HQ of Pb (0.004) in soils but the contribution of Pb was about 20% of HIs among 9 metals (Sun et al., 2016). The major discrepancy of the results between this study and their study is partially related to high concentrations of other toxic metals (e.g., Cr and V) in soils in Beijing, China.

Children form a vulnerable age group for exposure to Pb. We compared risks of the toddlers group in this study to a previous study done in France assessing 3 to 6 years old. HQ of Pb in gastric phase in this study (0.74) was lower than mean HQ of gastric phase (1.83) in the other study. Moreover, the HQ of Pb in gastro-intestinal phase in this study (0.22) was lower than mean HQ of gastro-intestinal phase (0.70) (Pelfrêne et al., 2015). The authors used upper-end ingestion rate of soil which is 2 times greater than in this study, while the rest of the exposure parameters were similar to this study. Another reason for the differences of HQ may result from their mean Pb concentrations in soils were 4 times greater than our study (Pelfrêne et al., 2015).

Among all age groups, young children had the highest HQs for all metals in soil compared with other age groups. Pelfrêne et al. found that HQs of Cd and Pb in children (0 to 6 years old) were 6 to 100 times higher than those in adults (Pelfrêne et al., 2013). In our study, we found HQs of Cd and Pb in toddlers group (1 to < 6 years old) were about 11 times

higher than those in adults. Through spatial analysis, we found the east and south east of Houston are the most concerning areas (HI 1.08 to 8.91) because non-cancer risks were above 1.

Cancer risk

We observed that cancer risks were less than one in a million among all ages, except for age group 18 to < 78 years old (1.02 E-6). The age group 18 to < 78 years old had the highest cancer risk and the age group 1 to < 6 years old (9.63 E-7) showed the second highest. The differences among the age groups resulted from different exposure dose parameters such as ingestion rates, body weight, and exposure duration at each specific age group. Exposure duration in this study may have a major influence on cancer risks as the values varied from 1 to 60 years, and body weight also has influence as the values varied from 8 to 81 kg.

In spatial analysis, cancer risks at several locations were above one in a million. The areas are located in the south or east side of Houston. These locations are near the Texas Commission on Environmental Quality Superfund sites associated with As or other metals (TCEQ, 2017). However, we also found other areas that are not associated with TCEQ superfund site regulation. For example, the highest cancer risk (5.13E-6) was in Memorial Park. Arsenic could come from pesticide and herbicide use (Datta et al., 2007), and this might be the reason As was high in the park.

Although the cancer risks of the adult age group was slightly over safety values, the calculated cancer risk in our study was lower than previous studies conducted in home gardens (Ramirez-Andreotta et al., 2013) and near an antimony mining site (the cancer risks of As was 200 folds greater than this study (Li et al., 2014).) The calculated UCL (3.25 mg/kg) of As in this study was about two time lower than a study in New Orleans conducted after Hurricane Rita (GM 6.99 mg/kg) (Presley et al., 2010).

Cancer risks from soil exposure to As may not represent the whole exposure profile of As. There are other sources of As exposure. Arsenic in soils could migrate to water or accumulate in agricultural products such as rice (Chen et al., 2016; Rajpert et al., 2016). Although it is unlikely that people in Houston consume As via well water, As intake from food consumption is possibly higher than that from soil ingestion (O'Rourke et al., 1999). Another limitation is that we used USEPA exposure parameters for risk assessment. Although the exposure parameters were evaluated and provided by US EPA, these may not represent the representative exposure parameters for people in Houston with dynamic and different ethnicity.

Conclusion

In our study, we found that Pb and As were the most concerning metal hazards in Houston based on the risk assessment. Among five age groups, age group 1 to < 6 was the most vulnerable when considering both non-cancer risks and cancer risks. Several locations

had HI greater than 1 for non-cancer risks and greater than 1 in a million for cancer risks. The locations were mostly located at the east of and southeast of Houston. Non-cancer risks based on bioaccessibility tests were less than 40% of non-cancer risks using metal concentrations in soils. However, there were no significant differences of cancer risks calculated using 95^{th} UCL between As in soils and bioaccessibility of As in human artificial gastro-intestinal phase.

CHARPTER V. CONCLUSIONS

We collected 96 soil samples in Houston, Texas in October 2017. The purpose of this study was to characterize 13 metal concentrations in soils, to assess bioaccessibility, and to estimate risk assessment using metal concentrations in soils and bioaccessibility test. We quantified all metals except Cd from 96 soil samples. We found that mean concentrations of Cu, Pb, and Zn were greater than background levels suggested by TCEQ whereas the rest of the metals were lower than TCEQ background levels. We observed that more than 80% of sample locations were over TCEQ background levels for Pb and Zn. However, we found that approximately 10% of sampling locations were over TCEQ background levels for most of metals (e.g., Cu, Mn, Ni, As, Ba, Cr, and V). We assessed the impact of environmental and socioeconomic and demographic factors on metal concentrations in soils using EJSCREEN. We found that closer proximity to National Priority List (NPL) sites had higher concentrations of Ni, Cr, Ba, Pb and Zn in soils, compared to further distance to NPL sites. We observed that concentrations of Ni, Cr, Ba, Cu and Pb in soils were higher in close proximity to risk management plan sites, than further proximity. We also discovered elevated levels of these metals in neighborhood with high minority population and high percentage of low income groups. Furthermore, in simulated maps of 13 metals, high concentrations of metals were mostly in older downtown central area are toward East and South Houston where most of the industrial facilities and disadvantaged neighborhoods are.

In bioaccessibility tests, we found that all the metals had over 30% BAF in both gastric or gastro-intestinal phase, except Cr, Fe, Ni, and V. We found that Cu and Mg had higher %BAF in gastro-intestinal phase than in gastric phase. When applying bioaccessibility tests in calculating exposure doses, they are all lower than using metal concentrations in soils. In our exposure assessment results, we found that infants (age 0 to 1 year old) and toddlers (age 1 to 6 year old) had the highest exposure compared to other age groups. Among 11 toxic metals, we observed that Zn, Mn, Ba, and Pb were contributed to high exposure dose. In the risk assessment, we found that Pb and As contributed 95% in HI for non-cancer risk assessment. Infants and toddlers age groups had the highest HI among other age groups. HI for all age groups were less than 1. On the other hand, cancer risk of As in adults group (age 18 years old to < 78 years old) was slightly higher than one in a million followed by the toddlers group. The health risk assessment in this study suggested that when considering health risks of soil exposure through the ingestion pathways, the toddlers group was the most concerned. Lastly, from the estimated spatial map of non-cancer health risks, high HI areas were in the old central Houston and the east side of Houston. In estimated mapping of cancer health risks, we found that most sampling sites in the south east of Houston showed cancer risks greater than one in a million.

The strength in this study is that this is the first study to examine the impact of environmental disparities in metal exposure in soils, bioaccessibility and spatial analysis for risk assessment in Houston. We systematically collected soil samples in Houston for better

understanding of spatial variation of metals in soils, so metal concentrations in soils were representative. The estimated spatial maps of metals and health risks pointed out several hot spots and potential areas for public health concerns, which could be useful to future research. Our study also supports that young children are the greatest concern in health risks when considering soil ingestion of toxic metals.

The limitation in this study is that the exposure parameters we used were for the general population in the U.S., thus, risk assessment results may not be specifically representative for the Houston population. We did not measure soil characteristics such as pH or soil types. These characteristics are known to affect bioaccessibility of metals in human body. So, we were not able to explain the effects of the factors on variations in bioaccessibility tests. Lastly, the simulated digestion fluids were not from humans. Therefore, %BAF may not sufficiently represent human digestion systems.

We recommend that future metal pollution studies interested to point sources in Houston should focus in East and South of Houston. To protect young children from metal exposures in soils, future study should focus on soils in playgrounds, parks, or schools in those locations, especially around the old downtown area.

APPENDICES

Appendix A. Sampling location with geocoordinates

Site ID	Latitude	Longitude	Location
H01	29.802738	-95.437064	between Nauts Ct and Watercrest Dr, Lazybrook Dr and W 18th St
H02	29.8033	-95.416447	between Neall St and N Durham Dr, W 19th St and W 20th St
H03	29.803032	-95.394885	between E 20th St and E 18th St, Cortlandt St and Arlington St
H04	29.803557	-95.374189	between W Cavalcade St, Cordell St and Archer St
H05	29.78435	-95.374821	between Byrne St and Teetshorn St, Beauchamp St and Florence St
H06	29.784329	-95.394747	between E 8th St and E 7th St, Cortlandt St and Arlington St
H07	29.784243	-95.436462	between Eureka St and Kansas St, Hempstead Hwy
H08	29.766057	-95.437178	in Memorial Park (up north of memorial drive and S picni Ln intersection
H09	29.766044	-95.41697	between Gibson St and Feagan St, Detering St and Reinicke St
H10	29.765989	-95.397076	between Willia St and Memorial Dr, Park Trail Ln and Waugh Dr
H11	29.76614	-95.376906	between Kane St and Lubbock St, Sabine St and Silver St
H12	29.747989	-95.397046	between Michigan St and Maryland St, Commonwealth St and Yupon St

Site ID	Latitude	Longitude	Location
H13	29.74801	-95.417027	between San Felipe St and Brazoria St, Revere St and Argonne St
H14	29.747973	-95.437049	between Chevy Chase Dr and Olypia Dr, Timber Ln and Willowick Rd
H15	29.727961	-95.417153	2502 North Blvd
H16	29.728024	-95.397121	1324 North Blvd
H17	29.728084	-95.377116	4622 Almeda Rd
H18	29.709998	-95.396975	1301 Moursund St
H19	29.710107	-95.417138	Between Goldsmith St and Southgate Blvd, Kirby Dr and Morningside Dr
H20	29.71	-95.437062	between Farber St and Elmora St, Edloe St and Auden St
H21	29.690973	-95.437047	3801 GlenArbor Dr
H22	29.690999	-95.396975	Uthousing Phase 1 (near Recreation Center)
H23	29.691069	-95.377072	3360 Alice St
H24	29.691028	-95.356623	between Yellowstone Blvd and Ward St, England St and Sidney St
H25	29.691049	-95.336965	between Perry St and Cosby St, Beekman Rd and Martin Luther King Blvd
H26	29.690342	-95.316848	6317 Sunnycrest Ave
H27	29.690994	-95.297037	7315 Southway Dr
H28	29.691277	-95.276633	8118 Hartford St
H29	29.70977	-95.274229	1809 Roosevelt St
H30	29.710003	-95.293827	7036 Japonica St
H31	29.709581	-95.313716	Telephone Rd and Brays Bayou Greenway Trail
H32	29.709962	-95.334172	5277 Old Spanish Trail

Site ID	Latitude	Longitude	Location
H33	29.710351	-95.354098	3831 N MacGregor Way
H34	29.727956	-95.354084	3355 Simmons St
H35	29.727835	-95.312924	6451 Jefferson St
H36	29.728282	-95.294296	Mason Park
H37	29.72776	-95.277241	Near Port Of Houston
H38	29.746636	-95.277871	8411 Clinton Dr
H39	29.745313	-95.294394	7128 Avenue Q
H40	29.74601	-95.313878	211 N Greenwood St
H41	29.74588	-95.334245	4101 Wilmer St
H42	29.746025	-95.354477	1401 St Charles St
H43	29.766645	-95.357833	Championship Park
H44	29.766009	-95.334081	304 Baron St
H45	29.765044	-95.31531	1038b Lockwood Dr
H46	29.766399	-95.29536	7321 Karnes St
H47	29.765962	-95.274018	8511 Tilgham St
H48	29.78393	-95.273419	531 Portwall St
H49	29.784162	-95.293923	7402 Texarkana St
H50	29.783981	-95.314357	2413 Sam Wilson St
H51	29.783948	-95.334196	2402 Bringhurst St
H52	29.784007	-95.353982	2417 Champman St
H53	29.801848	-95.353479	4605 Terry St
H54	29.801486	-95.333995	3419 Coal St
H55	29.802122	-95.31413	5514 Bunte St
H56	29.802486	-95.296684	4730 Darien St
H57	29.819457	-95.476842	5906 W 34th St

Site ID	Latitude	Longitude	Location
H58	29.74799	-95.476963	between Terwilliger way, Willers way and Chimney Rock Rd
H59	29.709853	-95.477007	6500 Chimney Rock Rd
H60	29.67298	-95.477219	between Queensloch Dr and Rutherglenn Dr, Braesmont Dr and Chimney Rock Rd
H61	29.673132	-95.436148	Willow Meadows/W Bellfort Ave
H62	29.672721	-95.354355	4810 Red Bud St
H63	29.672957	-95.313845	6309 Hogue St
H64	29.673254	-95.274054	7902 Glen Prairie St
H65	29.672975	-95.228962	2503 Leprechaun St
H66	29.747014	-95.228035	Galena Park
H67	29.783008	-95.228377	2322 John Ralston Rd
H68	29.818981	-95.273951	6114 Wedgefield St
H69	29.819121	-95.312945	5325 Bennington St
H70	29.818823	-95.394078	414 E 36th St
H71	29.8185	-95.435305	2008 Lou Ellen Ln
H72	29.819226	-95.516035	9108 Friendship Rd
H73	29.783027	-95.517373	960 Piney Point Rd
H74	29.74678	-95.517115	120 Radney Rd
H75	29.672067	-95.516034	7818 Braesview Dr
H76	29.635902	-95.516014	11701 N Willow Cir
H77	29.635782	-95.476996	6210 Greenwick Ln
H78	29.634967	-95.435929	Brentwood Park
H79	29.636335	-95.393976	Central Southwest Mowery Rd
H80	29.63506	-95.353937	11514 Greenshire Dr
H81	29.634784	-95.312975	6541 Madden Ln

Site ID	Latitude	Longitude	Location
H82	29.634576	-95.272967	8217 Braniff St
H83	29.635468	-95.228183	10418 Barada St
H84	29.635126	-95.18802	5055 W Circle Park St
H85	29.672065	-95.188046	1610 Everglade Dr
H86	29.708651	-95.188021	211 Tilden Dr
H87	29.783501	-95.187978	13358 Joliet St
H88	29.817893	-95.18708	6499 Pineview Dr
H89	29.854713	-95.187986	9007 E Sam Houston Pkwy N
H90	29.854723	-95.229091	10601 Tidwell Rd
H91	29.855409	-95.271994	8342 Sterlingshire St
H92	29.856086	-95.3121	5904 Parker Rd
H93	29.854938	-95.353001	9839 Burden St
H94	29.854965	-95.39295	413 Rosamond St
H95	29.854814	-95.434966	1678 De Soto St
H96	29.854983	-95.476966	6200 N Houston Rosslyn Rd

Appendix B. EJSCREEN Indexes by high/low groups

EJ Indexes	High Group N mean±SD (range)	Low Group* N mean±SD (range)
Traffic Proximity and Volume (daily traffic count/distance (meter) to road)	46 1948.04±1027.83 (810-5600)	50 296.93±231.08 (2.9-800)
Proximity to National Priorities List Sites (site count/km distance)	46 0.55±0.51 (0.17-2.30)	50 0.11±0.03 (0.045-0.16)
Proximity to Risk Management Plan Sites (facility count/km distance)	47 2.72±1.56 (1.3-9.8)	49 0.71±0.34 (0.088-1.20)
Percent of Minority	47 95.79±3.00 (89-100)	49 56.36±24.26 (14-88)
Percent of low income	45 63.64±6.28 (54-75)	51 30.65±15.99 (7-53)
Percent of linguistic Isolation	44 23.52±9.23 (10-54)	52 4.56±2.61 (0-9)
Percent of less than high school education	47 42.00±8.64 (30-56)	49 11.89±8.93 (1-29)
Percent of age under 5	38 9.16±1.10 (8-11)	58 5.55±1.49 (1-7)
Percent of age over 64	44 14.16±3.12 (11-25)	52 7.76±1.78 (3-10)

N=96

*= plus 2 missing counted in the low group.

Appendix C. Nonparametric results by high/low groups

Metals (mg/kg)	Traffic Proximity and Volume (daily traffic count/distance (meter) to road)		p value[a]
	High group >800 (46)	Low group ≤800 (50)	
	Mean±SD (range)	Mean±SD (range)	
As	2.82±2.57 (0.38-19.29)	3.02±2.14 (0.60-12.53)	0.51
Ba	115.79±80.95 (27.18-399.00)	126.66±115.09 (28.94-714.17)	0.94
Cd	0.28±0.46 (0.02-2.32)	0.34±1.39 (0.02-9.74)	**0.03**
Cr	9.98±6.41 (1.89-39.13)	12.89±11.21 (3.22-58.84)	0.38
Cu	26.44±27.87 (1.98-131.26)	87.42±494.93 (2.07-3515.20)	0.16
Mn	203.93±165.17 (56.10-910.80)	235.99±166.59 (24.43-846.51)	0.16
Ni	7.95±6.16 (2.54-41.57)	8.05±4.92 (1.63-24.14)	0.67
Pb	57.54±65.20 (4.66-400.46)	62.62±121.75 (3.61-855.86)	0.53
Zn	166.90±149.97 (20.31-832.58)	383.59±1436.66 (15.35-10107.48)	0.46
Co	2.86±1.54 (0.35-7.46)	3.39±2.38 (0.37-12.14)	0.36
Mg	3027.94±6396.92 (322.74-41252.79)	200.98±1584.95 (337.28-10133.96)	0.84
Fe	5966.54±2925.49 (1231.57-14494.88)	6804.77±3594.64 (1929.40-18297.19)	0.28
V	11.75±5.79 (4.13-37.16)	11.68±6.25 (5.19-35.51)	0.68

a=two sided Wilcoxon p-value α=0.05 (bold font)

Metals (mg/kg)	Proximity to National Priorities List Sites (site count/km distance)		p value[a]
	High group >0.16 (46)	Low group ≤0.16 (50)	
	Mean±SD (range)	Mean±SD (range)	
As	2.89±1.81 (0.38-9.28)	2.96±2.77 (0.60-17.29)	0.50
Ba	136.81±93.48 (27.18-419.01)	106.33±104.08 (28.94-714.17)	**0.02**
Cd	0.51±1.49 (0.02-9.74)	0.13±0.15 (0.02-0.63)	0.17
Cr	13.58±10.79 (2.61-58.84)	9.58±7.26 (1.89-43.71)	**0.01**
Cu	27.95±28.47 (1.98-131.26)	86.03±495.07 (2.07-3515.20)	**0.02**
Mn	228.84±150.94 (69.59-910.80)	213.07±179.62 (24.43-862.47)	0.09
Ni	9.39±6.83 (2.77-41.57)	6.72±3.57 (1.63-17.88)	**0.04**
Pb	86.70±135.07 (4.77-855.86)	35.79±28.80 (3.61-119.27)	**0.004**
Zn	457.24±1490.91 (20.31-10107.48)	116.48±97.31 (15.35-473.21)	**0.006**
Co	3.03±1.30 (0.35-5.68)	3.24±2.53 (0.37-12.14)	0.43
Mg	2797.37±5889.53 (486.48-41252.79)	2215.11±2930.04 (322.74-18699.82)	0.19
Fe	7026.15±3550.44 (1231.57-16532.78)	5830.02±2974.69 (1424.97-18297.19)	0.10
V	11.95±5.93 (5.26-37.16)	11.49±6.11 (4.13-35.51)	0.51

a=two sided Wilcoxon p-value α=0.05 (bold font)

Metals (mg/kg)	Proximity to Risk Management Plan Sites (facility count/km distance)		p value[a]
	High group >1.25 (47)	Low group ≤1.25 (49)	
	Mean±SD (range)	Mean±SD (range)	
As	2.82±1.57 (0.60-9.28)	3.03±2.92 (0.38-17.29)	0.43
Ba	153.68±127.74 (31.96-714.17)	89.52±44.95 (27.18-236.83)	**0.002**
Cd	0.31±0.54 (0.02-2.32)	0.32±1.38 (0.02-9.74)	0.22
Cr	13.55±11.74 (1.89-58.84)	9.52±5.54 (2.61-25.37)	0.11
Cu	102.55±509.34 (6.04-3515.20)	15.66±15.99 (1.98-92.77)	**0.002**
Mn	235.77±174.97 (24.43-910.80)	206.10±156.97 (59.37-862.47)	0.08
Ni	8.82±6.31 (1.63-41.57)	7.22±4.57 (2.06-24.14)	0.08
Pb	81.92±132.02 (4.66-855.86)	39.33±38.98 (3.61-194.05)	**0.003**
Zn	252.34±325.27 (23.10-1874.38)	306.06±1431.32 (15.35-10107.48)	**0.001**
Co	3.08±1.38 (0.37-6.56)	3.19±2.51 (0.35-12.14)	0.21
Mg	1947.20±1327.51 (343.79-6914.30)	3018.70±6260.12 (211.74-41252.79)	0.95
Fe	6979.29±3519.68 (1424.97-16532.78)	5850.46±3009.34 (1231.57-18297.19)	0.09
V	12.04±5.52 (4.13-32.35)	11.40±6.46 (5.78-37.16)	0.19

a=two sided Wilcoxon p-value α=0.05 (bold font)

Metals (mg/kg)	Percent of Minority		p value[a]
	High group >88.5 (47)	Low group ≤88.5 (49)	
	Mean±SD (range)	Mean±SD (range)	
As	3.10±1.82 (0.77-9.28)	2.75±2.77 (0.38-17.29)	**0.046**
Ba	149.53±117.44 (31.96-714.17)	93.50±70.20 (27.18-419.01)	**0.0005**
Cd	0.39±1.45 (0.02-9.74)	0.24±0.40 (0.02-2.16)	0.07
Cr	14.17±10.90 (1.89-58.84)	8.93±6.59 (2.61-43.71)	**0.001**
Cu	100.93±509.46 (2.91-3515.20)	17.22±20.30 (1.98-131.26)	**0.007**
Mn	268.37±194.77 (56.10-910.80)	174.84±117.01 (24.43-846.51)	**0.005**
Ni	9.73±6.75 (2.06-41.57)	3.34±3.31 (1.63-17.88)	**0.0019**
Pb	54.94±46.87 (4.66-194.05)	65.21±130.28 (3.61-855.86)	0.30
Zn	407.73±1471.21 (23.10-10107.48)	157.02±214.06 (15.35-1201.67)	**0.032**
Co	3.60±2.43 (0.60-12.14)	2.69±1.44 (0.35-7.46)	**0.044**
Mg	2514.54±2736.75 (337.28-18699.82)	2474.52±5854.34 (322.74-41252.79)	**0.02**
Fe	7406.67±3825.32 (1424.97-18297.19)	5440.53±2368.46 (1231.57-13660.82)	**0.007**
V	12.47±5.96 (4.13-35.51)	10.98±6.00 (5.19-37.16)	**0.0499**

a=two sided Wilcoxon p-value α=0.05 (bold font)

Metals (mg/kg)	Percent of Low income		p value[a]
	High group >53 (45)	Low group ≤53 (51)	
	Mean±SD (range)	Mean±SD (range)	
As	2.80±2.53 (0.38-9.28)	3.04±2.90 (0.60-17.29)	0.35
Ba	149.06±125.36 (27.18-714.17)	96.11±61.29 (28.94-419.01)	**0.02**
Cd	0.42±1.48 (0.02-9.74)	0.22±0.40 (0.02-2.16)	0.68
Cr	14.05±11.40 (2.61-58.84)	9.24±6.23 (1.89-34.98)	**0.005**
Cu	105.66±520.44 (1.98-3515.20)	16.32±19.30 (2.07-131.26)	**0.002**
Mn	256.93±210.07 (59.37-910.80)	188.59±105.71 (24.43-563.96)	0.18
Ni	9.52±6.69 (2.06-41.57)	6.66±3.82 (1.63-21.71)	**0.007**
Pb	56.84±46.77 (4.77-194.05)	63.13±128.15 (3.61-855.86)	0.09
Zn	435.20±1500.94 (20.31-10107.48)	142.61±205.03 (15.35-1201.67)	**0.002**
Co	3.13±1.75 (0.35-10.01)	3.14±2.26 (0.37-12.14)	0.57
Mg	3210.77±6395.24 (337.28-41252.79)	1861.77±1712.44 (322.74-10133.96)	0.08
Fe	6945.69±3401.65 (1231.57-16532.78)	5924.38±3165.59 (1424.97-18297.19)	0.07
V	12.42±6.45 (5.26-37.16)	11.08±5.56 (4.13-35.51)	0.15

a=two sided Wilcoxon p-value α=0.05 (bold font)

Metals (mg/kg)	Percent of linguistic Isolation		p value[a]
	High group >9 (44)	Low group ≤9 (52)	
	Mean±SD (range)	Mean±SD (range)	
As	2.65±1.37 (0.38-6.27)	3.16±2.93 (0.71-17.29)	0.90
Ba	148.96±133.27 (27.18-714.17)	97.21±48.26 (28.94-236.83)	0.06
Cd	0.45±1.52 (0.02-9.74)	0.19±0.28 (0.02-1.80)	0.33
Cr	13.05±11.57 (1.89-58.84)	10.18±6.65 (3.22-40.33)	0.38
Cu	102.97±526.83 (1.98-3515.20)	20.32±24.08 (2.07-131.26)	0.39
Mn	231.54±186.50 (24.43-910.80)	211.39±147.31 (59.37-862.47)	0.82
Ni	9.19±6.89 (1.63-41.57)	7.00±3.80 (2.54-21.71)	0.10
Pb	72.35±129.22 (4.66-855.86)	49.89±60.76 (3.61-400.46)	0.27
Zn	415.00±1508.59 (20.31-10107.48)	165.33±277.46 (15.35-1874.38)	0.12
Co	2.96±1.41 (0.35-6.56)	3.29±2.44 (0.60-12.14)	0.90
Mg	3317.29±6500.68 (343.79-41252.79)	1797.57±1517.96 (322.74-10133.96)	0.11
Fe	6718.51±3459.47 (1231.57-16532.78)	6136.25±3169.76 (1929.40-18297.19)	0.27
V	12.04±6.52 (4.13-37.16)	11.43±5.57 (5.26-35.51)	0.63

a=two sided Wilcoxon p-value α=0.05

Metals (mg/kg)	Percent of less than high school education		p value[a]
	High group >29.5 (47)	Low group ≤29.5 (49)	
	Mean±SD (range)	Mean±SD (range)	
As	2.77±1.63 (0.38-8.73)	3.07±2.88 (0.71-17.29)	0.90
Ba	152.42±129.72 (27.18-714.17)	90.72±41.06 (28.94-236.83)	**0.01**
Cd	0.43±1.47 (0.02-9.74)	0.20±0.29 (0.02-1.80)	0.15
Cr	14.01±11.87 (1.89-58.84)	9.08±4.87 (3.22-25.37)	**0.03**
Cu	101.47±509.41 (1.98-3515.20)	16.70±19.20 (2.07-131.26)	**0.02**
Mn	233.91±180.41 (24.43-910.80)	207.89±151.28 (59.37-862.47)	0.36
Ni	9.56±6.97 (1.63-41.57)	6.50±3.01 (2.54-15.15)	**0.02**
Pb	72.40±124.72 (4.66-855.86)	48.47±62.75 (3.61-400.46)	0.06
Zn	435.46±1474.94 (20.31-10107.48)	130.42±142.19 (15.35-832.58)	**0.02**
Co	3.00±1.46 (0.35-6.56)	3.27±2.46 (0.67-12.14)	0.72
Mg	3262.19±6290.39 (343.79-41252.79)	1757.39±1549.14 (322.74-10133.96)	**0.05**
Fe	6788.90±3552.25 (1231.57-16532.78)	6033.09±3030.96 (1929.40-18297.19)	0.24
V	11.96±6.41 (4.13-37.16)	11.47±5.63 (5.78-35.51)	0.63

a=two sided Wilcoxon p-value α=0.05 (bold font)

Metals (mg/kg)	Percent of age under 5		p value[a]
	High group >7 (38)	Low group ≤7 (58)	
	Mean±SD (range)	Mean±SD (range)	
As	3.78±1.15 (0.95-6.27)	3.02±2.88 (0.38-17.29)	0.19
Ba	126.80±81.48 (31.96-399.00)	117.09±110.70 (27.18-714.17)	0.13
Cd	0.46±1.61 (0.02-9.74)	0.22±0.37 (0.02-2.16)	0.19
Cr	12.58±9.27 (1.89-43.71)	10.78±9.32 (2.61-58.84)	0.10
Cu	115.80±566.95 (2.91-3515.20)	20.46±21.00 (1.98-131.26)	0.93
Mn	247.51±196.08 (56.10-910.80)	203.01±141.67 (24.43-862.47)	0.31
Ni	9.33±7.11 (2.06-41.57)	7.13±4.00 (1.63-21.71)	0.12
Pb	53.24±43.65 (4.66-194.05)	64.73±121.73 (3.61-855.86)	0.42
Zn	422.46±1618.56 (21.77-10107.48)	186.27±297.98 (15.35-1874.38)	0.37
Co	3.19±1.67 (0.93-10.01)	3.10±2.24 (0.35-12.14)	0.42
Mg	2542.63±2977.47 (501.70-18699.82)	2462.32±5399.03 (322.74-41252.79)	0.08
Fe	6993.41±3146.87 (1424.97-14494.88)	6016.38±3357.62 (1231.57-18297.19)	0.06
V	12.12±5.36 (4.13-32.35)	11.45±6.41 (5.19-37.16)	0.16

a=two sided Wilcoxon p-value α=0.05

Metals (mg/kg)	Percent of age over 64		p value[a]
	High group >10 (44)	Low group ≤10 (52)	
	Mean±SD (range)	Mean±SD (range)	
As	3.09±2.60 (0.38-17.29)	2.79±2.13 (0.60-12.53)	0.37
Ba	125.46±124.45 (27.18-714.17)	117.10±73.92 (31.96-399.00)	0.31
Cd	0.38±1.48 (0.02-9.74)	0.25±0.45 (0.02-2.32)	0.74
Cr	11.55±10.00 (2.61-58.84)	11.45±8.75 (1.89-43.71)	0.98
Cu	19.75±18.26 (1.98-92.77)	90.74±484.92 (2.91-3515.20)	0.93
Mn	219.09±162.64 (59.37-862.47)	221.93±170.03 (24.43-910.80)	0.89
Ni	7.72±4.41 (2.54-24.14)	8.23±6.34 (1.63-41.57)	0.97
Pb	63.68±128.45 (3.61-855.86)	57.22±63.82 (4.66-400.46)	0.61
Zn	413.41±1528.98 (15.35-10107.48)	166.68±159.47 (21.77-832.58)	0.73
Co	3.20±2.36 (0.35-12.14)	3.08±1.72 (0.37-11.65)	0.47
Mg	2731.04±6167.05 (322.74-41252.79)	2293.64±2618.66 (343.79-18699.82)	0.24
Fe	6246.40±3656.75 (1231.57-18297.19)	6535.73±3088.23 (1424.97-14494.88)	0.48
V	11.50±6.55 (5.26-37.16)	11.89±5.55 (4.13-32.35)	0.41

a=two sided Wilcoxon p-value α=0.05

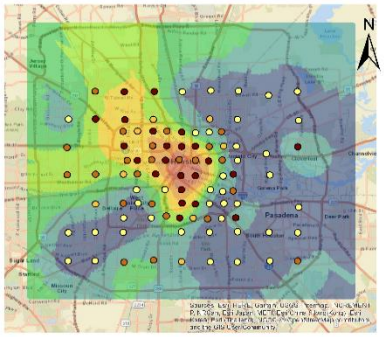
Appendix D. Ordinary kriging results and cross validation

	Variogram model				Cross Validation*				
	Coorelation function	Nugget	Sill	Range (m)	ME	MS	ASE	RMS	RMSS
As	Gaussian	0.243	0.1242	0.02786	-0.020	-0.038	0.581	0.596	1.062
Ba	Gaussian	0.07852	2.1769	1.1036	0.080	0.155	0.578	0.549	0.981
	Exponential		0.1931	0.01608					
	Gaussian		0.06854	0.000001					
Zn	Spherical	0.2442	0.8272	0.02835	-0.140	-0.131	1.037	1.032	1.022
	Spherical		0.002604	0.000001					
	Spherical		0.002133	0.000001					
Cu	Gaussian	0.06542	7.6567	0.9673	-0.010	-0.326	0.769	1.105	3.054
	Gaussian		0.6964	0.02458					
	Spherical		0.03738	0.000001					
Cr	Gaussian	0	296.59	10.3696	0.009	-0.057	0.548	0.618	1.478
	Gaussian		0.3262	0.01841					
	Exponential		0.02630	0.000001					
Cd	Spherical	1.1811	0.000001	30.2728	-0.193	-0.122	1.529	1.400	0.938
	Spherical		0.7672	0.07630					
	Gaussian		0.5169	0.000001					
Co	Gaussian	0.2315	1.0551	0.5538	0.020	0.469	0.549	0.567	1.016
	Spherical		0.1454	0.1972					
Mn	Gaussian	0.2430	336.90	9.4562	0.021	0.041	0.522	0.555	1.083
	Gaussian		0.07191	0.1136					
	Spherical		0.00000197	0.000001					
Ni	Gaussian	0	7.8842	1.9964	0.005	-0.003	0.524	0.476	0.933
	Exponential		0.2812	0.009737					
	Gaussian		0.000001	0.000001					
Pb	Spherical	0.6614	0.3052	0.06033	-0.076	-0.075	0.960	0.912	0.962
	Exponential		0.000001	3.2646					
V	Gaussian	0.000013	78.4892	9.8506	-0.002	-0.003	0.387	0.432	1.128
	Spherical		0.04660	0.1291					
	Exponential		0.1209	0.00001					
Mg	Spherical	0.03501	0.01188	0.01806	-0.010	-0.013	0.790	0.815	1.053
	Gaussian		0.4922	0.000001					
	Spherical		0.1190	0.1096					
Fe	Exponential	0.05991	0.1501	0.01304	-0.002	-0.011	0.458	0.496	1.098
	Gaussian		0.1224	0.1741					
	Gaussian		0.000917	0.000001					

*ME: mean error; MS: mean standardized error; ASE: average standard error; RMS: root mean square error; RMSS: root mean square standardized error

Appendix E. H40 Site Photo

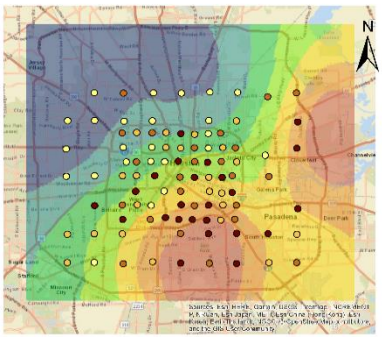
Appendix F. Simulated 7 metals (Cd, Co, Mn, Ni, Fe, V and Mg) distribution in Houston, Texas



Cd (mg/kg)
- 0.03
- 0.04 - 0.09
- 0.10 - 0.24
- 0.25 - 9.74

Predicted Cd (mg/kg)
- 0.34 - 0.89
- 0.23 - 0.33
- 0.16 - 0.22
- 0.11 - 0.15
- 0.09 - 0.10
- 0.06 - 0.08
- 0.02 - 0.05

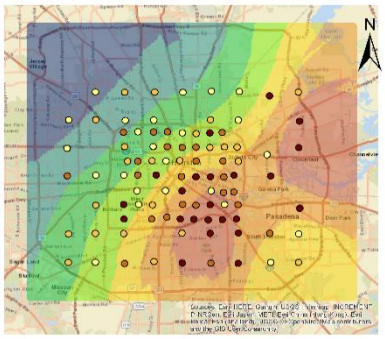
0 3 6 12 Kilometers



Co (mg/kg)
- 0.35 - 1.83
- 1.84 - 2.78
- 2.79 - 3.70
- 3.71 - 12.14

Predicted Co (mg/kg)
- 4.06 - 12.13
- 3.61 - 4.05
- 3.10 - 3.60
- 2.53 - 3.09
- 1.99 - 2.52
- 1.50 - 1.98
- 0.35 - 1.49

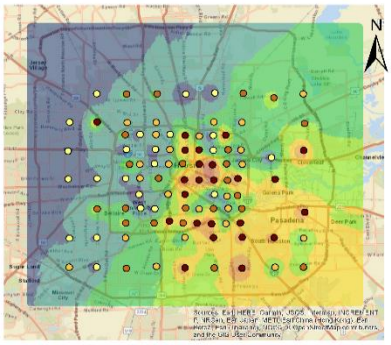
0 3 6 12 Kilometers



Mn (mg/kg)
- 24.43 - 115.52
- 115.53 - 176.52
- 176.53 - 250.36
- 250.37 - 910.80

Predicted Mn (mg/kg)
- 244.15 - 862.63
- 214.29 - 244.14
- 182.04 - 214.28
- 150.22 - 182.03
- 120.92 - 150.21
- 91.08 - 120.91
- 56.65 - 91.07

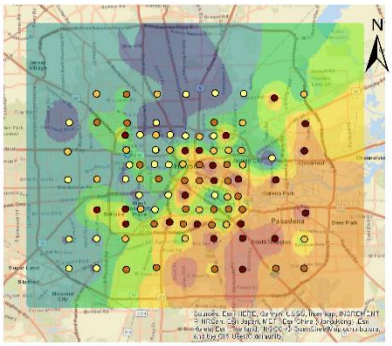
0 3 6 12 Kilometers



Ni (mg/kg)
- 1.63 - 4.51
- 4.52 - 7.00
- 7.01 - 9.81
- 9.82 - 41.57

Predicted Ni (mg/kg)
- 15.68 - 39.15
- 10.76 - 15.67
- 8.82 - 10.75
- 7.42 - 8.81
- 5.93 - 7.41
- 4.56 - 5.92
- 1.69 - 4.55

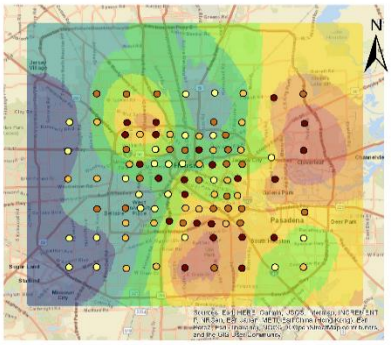
0 3 6 12 Kilometers



Fe (mg/kg)
- 1231.57 - 4093.51
- 4093.52 - 5391.94
- 5391.95 - 7952.83
- 7952.84 - 18297.19

Predicted Fe (mg/kg)
- 8365.82 - 17987.72
- 7315.13 - 8365.81
- 6419.49 - 7315.12
- 5559.51 - 6419.48
- 4726.57 - 5559.50
- 4017.11 - 4726.56
- 1266.27 - 4017.10

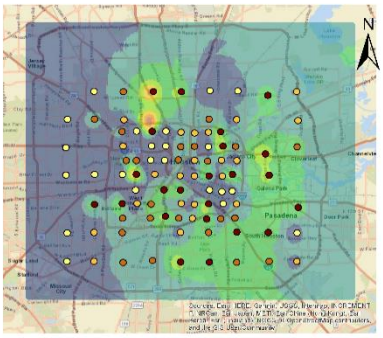
0 3 6 12 Kilometers



V (mg/kg)
- 4.13 - 7.72
- 7.73 - 10.24
- 10.25 - 13.17
- 13.18 - 37.16

Predicted V (mg/kg)
- 13.63 - 15.61
- 12.53 - 13.62
- 11.54 - 12.52
- 10.49 - 11.53
- 9.45 - 10.48
- 8.47 - 9.44
- 7.40 - 8.46

0 3 6 12 Kilometers

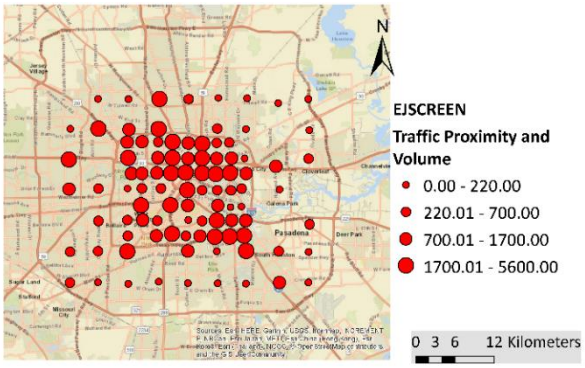


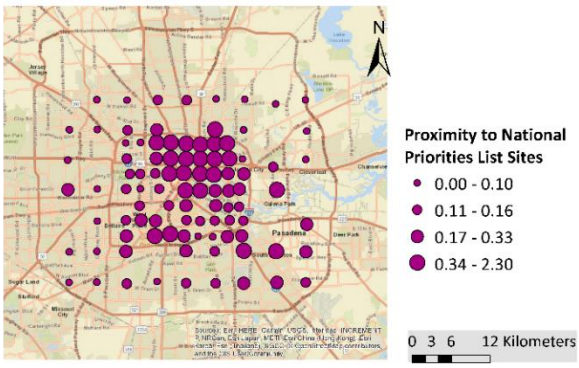
Mg (mg/kg)
- 322.74 - 902.10
- 902.11 - 1705.17
- 1705.18 - 2574.55
- 2574.56 - 41252.79

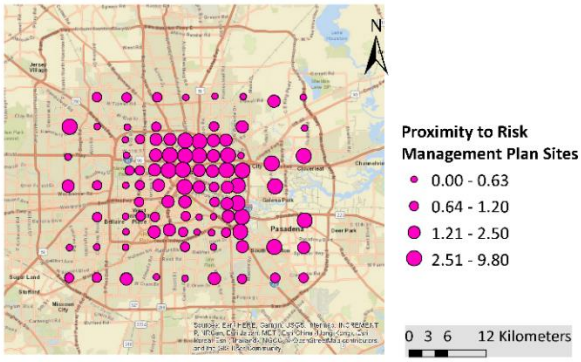
Predicted Mg (mg/kg)
- 19024.22 - 38854.48
- 10048.27 - 19024.21
- 5198.79 - 10048.26
- 2854.31 - 5198.78
- 2001.20 - 2854.30
- 1513.59 - 2001.19
- 331.83 - 1513.58

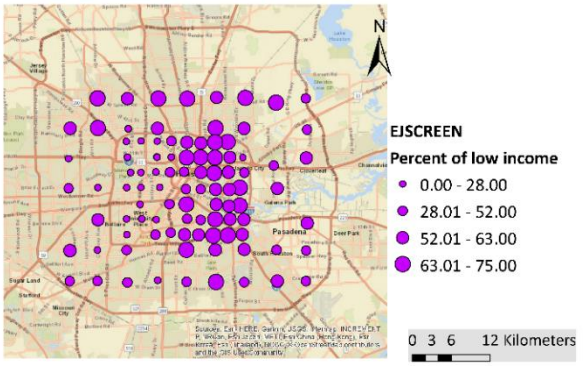
0 3 6 12 Kilometers

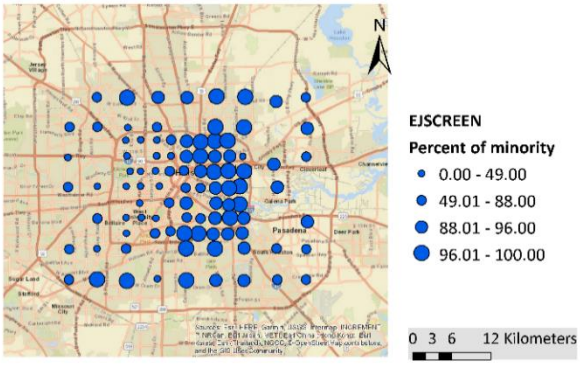
Appendix G. EJSCREEN indexes distribution of 94 sampling sites in Houston, TX











Appendix H. Distribution of bioaccessibility results in mg/kg and %BAF

Metal Concentrations in Gastric Phase											
Metal (mg/kg)	N	Mean±SD	Min	5%	10%	25%	50%	75%	90%	95%	Max
As	92*	1.03±1.34	0.04	0.11	0.15	0.31	0.50	1.16	2.59	3.63	9.32
Ba	94*	65.80±37.86	10.57	25.09	29.49	41.37	52.72	81.35	116.56	147.04	186.45
Co	94*	1.03±0.77	0.01	0.01	0.19	0.46	0.79	1.51	2.24	2.47	3.44
Cr	96	0.21±0.27	0.01	0.01	0.01	0.01	0.12	0.31	0.50	0.73	1.71
Cu	95*	3.50±7.75	0.02	0.02	0.02	0.60	1.47	2.49	4.71	19.05	55.17
Fe	96	63.71±43.15	1.27	1.27	1.27	27.13	55.00	111.81	115.12	129.88	150.72
Mg	96	751.12±644.17	117.56	202.41	246.69	349.47	620.20	935.78	1,306.09	1,881.01	4,698.19
Mn	95*	98.28±38.73	21.42	36.33	50.77	72.85	94.82	121.72	141.89	177.48	209.60
Ni	94*	1.84±1.44	0.02	0.19	0.51	0.85	1.34	2.51	4.24	5.14	5.97
Pb	94*	19.28±25.01	0.01	0.24	2.63	5.96	13.53	23.40	41.45	50.28	204.01
V	96	1.38±1.11	0.01	0.04	0.14	0.62	1.10	1.92	2.91	3.63	5.30
Zn	94*	176.73±804.19	0.04	3.20	11.71	26.99	45.00	89.82	162.43	392.16	7,640.75

* exclude values greater than 3 SD from means

Metal Concentrations in Gastro-Intestinal Phase											
Metal (mg/kg)	N	Mean±SD	Min	5%	10%	25%	50%	75%	90%	95%	Max
As	92*	0.97±1.65	0.12	0.12	0.12	0.16	0.57	0.94	1.85	3.42	13.50
Ba	94*	47.06±31.10	4.40	10.29	13.52	26.71	43.90	57.26	87.25	101.10	202.60
Co	94*	0.46±0.80	0.03	0.03	0.03	0.03	0.03	0.71	1.28	1.86	6.06
Cr	96	0.09±0.21	0.03	0.03	0.03	0.03	0.03	0.03	0.13	0.80	1.05
Cu	95*	8.42±12.26	0.05	0.32	0.77	1.96	4.26	9.02	16.06	38.89	66.84
Fe	96	11.64±23.46	3.30	3.30	3.30	3.30	3.30	3.30	41.81	61.44	160.65
Mg	96	1,009.31±940.36	130.95	259.25	311.17	461.03	804.11	1,241.41	1,647.71	2,407.72	6,810.91
Mn	95*	78.78±56.71	3.81	9.25	17.91	47.50	72.90	96.80	130.91	179.24	446.22
Ni	94*	0.97±1.17	0.06	0.06	0.06	0.06	0.50	1.43	2.48	3.24	6.79
Pb	94*	16.41±33.54	0.03	0.03	0.43	1.90	5.78	17.92	46.96	59.33	278.75
V	96	1.44±1.28	0.03	0.03	0.03	0.58	1.14	2.12	3.27	3.54	7.48
Zn	94*	52.51±125.30	0.10	0.10	0.10	1.35	17.85	44.39	74.29	235.66	774.42

* exclude values greater than 3 SD from means

%BAF In Gastric Phase											
Metal	N	Mean±SD	Min	5%	10%	25%	50%	75%	90%	95%	Max
As	92*	31.52±27.18	2.09	7.70	9.28	13.72	21.71	42.84	69.81	88.88	144.88
Ba	94*	61.91±23.89	12.01	22.63	31.47	45.19	62.54	75.62	85.11	106.68	136.73
Co	94*	34.32±21.40	0.10	0.65	6.82	19.95	31.54	43.71	60.56	77.33	97.56
Cr	96	2.08±2.64	0.05	0.07	0.11	0.25	1.48	2.76	4.80	5.72	19.55
Cu	95*	14.29±15.44	0.05	0.09	0.19	4.43	10.23	19.91	30.63	44.91	90.85
Fe	96	1.22±1.11	0.01	0.01	0.04	0.57	1.01	1.72	2.51	2.56	7.91
Mg	96	42.46±19.06	1.98	15.51	17.90	27.02	42.29	57.74	66.01	73.11	90.42
Mn	95*	54.53±22.11	8.50	18.47	22.40	38.63	54.56	70.08	79.69	92.47	111.44
Ni	94*	25.29±17.13	0.23	4.04	6.72	13.81	23.55	31.97	43.17	71.19	91.89
Pb	94*	39.97±21.53	0.05	0.38	8.20	28.06	39.27	55.63	66.20	72.62	95.55
V	96	13.97±11.38	0.04	0.20	0.97	5.17	13.04	17.16	28.70	42.75	51.31
Zn	94*	48.39±22.81	0.01	4.08	13.48	35.65	50.84	63.66	75.49	86.36	101.82

* exclude values greater than 3 SD from means

%BAF In Gastro-Intestinal Phase											
Metal	N	Mean±SD	Min	5%	10%	25%	50%	75%	90%	95%	Max
As	92*	27.57±22.55	4.21	5.42	6.65	9.64	21.61	35.79	57.96	74.25	111.09
Ba	94*	45.87±25.22	3.41	12.25	15.97	25.34	40.79	63.90	83.93	86.93	105.07
Co	94*	12.69±16.72	0.25	0.66	0.85	1.24	2.92	21.98	30.91	43.96	87.34
Cr	96	0.70±1.21	0.04	0.13	0.18	0.26	0.36	0.54	1.35	2.41	7.32
Cu	95*	36.88±26.35	0.35	1.57	5.69	15.89	32.28	56.83	73.31	85.77	111.59
Fe	96	0.22±0.43	0.02	0.03	0.03	0.05	0.07	0.10	0.71	0.93	2.27
Mg	96	55.12±25.31	2.62	18.84	23.72	37.32	53.09	75.33	86.30	94.97	128.76
Mn	95*	41.66±22.10	2.54	6.90	9.24	23.22	43.01	60.43	69.06	73.95	93.38
Ni	94*	12.80±14.44	0.15	0.59	0.83	1.27	10.23	21.33	30.26	38.09	79.15
Pb	94*	27.03±24.41	0.13	0.27	1.11	6.82	17.80	47.95	62.35	72.08	89.73
V	96	13.25±12.56	0.09	0.36	0.54	4.41	10.63	16.10	30.95	97.70	70.22
Zn	94*	18.46±16.46	0.05	0.11	0.21	1.57	18.09	29.85	42.42	45.80	62.78

* exclude values greater than 3 SD from means

%BAF Together In Both Gastric and Gastro-Intestinal Phase											
Metal	N	Mean±SD	Min	5%	10%	25%	50%	75%	90%	95%	Max
As	92*	59.09±43.35	7.51	13.55	16.12	25.97	43.96	81.50	116.09	156.40	217.30
Ba	94*	107.78±40.67	23.83	41.17	49.55	81.99	109.93	139.10	163.01	170.80	176.44
Co	94*	47.02±32.83	0.35	2.35	12.76	22.57	40.76	65.83	92.44	116.70	183.22
Cr	96	2.78±3.00	0.16	0.24	0.35	0.66	1.96	3.78	5.57	8.27	19.85
Cu	95*	51.18±35.87	0.53	4.38	10.21	21.39	41.91	73.56	104.07	116.90	164.15
Fe	96	1.44±1.39	0.025	0.053	0.092	0.62	1.13	1.99	2.63	3.95	10.18
Mg	96	98.58±43.24	4.60	34.57	42.40	64.24	97.28	128.15	150.00	165.80	214.76
Mn	95*	96.19±41.18	11.51	32.46	38.60	60.62	98.39	125.77	148.08	168.02	185.85
Ni	94*	38.10±25.95	0.82	4.31	10.22	18.53	32.80	50.86	70.24	92.95	133.31
Pb	94*	67.01±40.34	0.18	0.31	11.13	36.63	63.00	93.70	123.16	138.64	160.99
V	96	27.22±22.65	1.26	3.12	4.87	12.37	22.08	33.52	54.82	79.68	119.94
Zn	94*	66.85±32.90	0.33	0.61	19.91	45.30	71.18	90.86	105.53	117.75	160.13

* exclude values greater than 3 SD from means

Appendix I. Exposure doses from ingestion of soil and from bioaccessibility results

(µg/kg-day)*	Pb	As	V	Mn	Cu	Zn	Ba	Ni	Co	Cr
Infants										
ADD	2.26E-01 ±3.69E-01	1.10E-02 ±8.81E-03	4.39E-02 ±2.25E-02	8.27E-01 ±6.22E-01	2.18E-01 ±1.34E+00	1.05E+00 ±3.91E+00	4.53E-01 ±3.74E-01	3.00E-02 ±2.07E-02	1.18E-02 ±7.61E-03	4.31E-02 ±3.49E-02
ADD-G	7.23E-02 ±9.38E-02	3.87E-03 ±5.01E-03	5.19E-03 ±4.17E-03	3.69E-01 ±1.45E-01	1.31E-02 ±2.91E-02	6.63E-01 ±3.02E+00	2.47E-01 ±1.42E-01	6.90E-03 ±5.40E-03	3.86E-03 ±2.90E-03	7.86E-04 ±1.00E-03
ADD-GI	6.16E-02 ±1.26E-01	3.64E-03 ±6.21E-03	5.40E-03 ±4.80E-03	2.95E-01 ±2.13E-01	3.16E-02 ±4.60E-02	1.97E-01 ±4.70E-01	1.76E-01 ±1.17E-01	3.65E-03 ±4.40E-03	1.72E-03 ±2.99E-03	3.41E-04 ±7.93E-04
Toddlers										
ADD	1.86E-01 ±3.03E-01	9.03E-03 ±7.25E-03	3.62E-02 ±1.85E-02	6.81E-01 ±5.12E-01	1.80E-01 ±1.10E+00	8.63E-01 ±3.22E+00	3.73E-01 ±3.08E-01	2.47E-02 ±1.70E-02	9.68E-03 ±6.26E-03	3.55E-02 ±2.87E-02
ADD-G	5.95E-02 ±7.72E-02	3.18E-03 ±4.12E-03	4.27E-03 ±3.43E-03	3.03E-01 ±1.20E-01	1.08E-02 ±2.39E-02	5.45E-01 ±2.48E+00	2.03E-01 ±1.17E-01	5.68E-03 ±4.45E-03	3.18E-03 ±2.39E-03	6.47E-04 ±8.25E-04
ADD-GI	5.07E-02 ±1.04E-01	2.99E-03 ±5.11E-03	4.45E-03 ±3.95E-03	2.43E-01 ±1.75E-01	2.60E-02 ±3.79E-02	1.62E-01 ±3.87E-01	1.45E-01 ±9.60E-02	3.01E-03 ±3.62E-03	1.41E-03 ±2.46E-03	2.81E-04 ±6.53E-04
Children										
ADD	8.36E-02 ±1.37E-01	4.06E-03 ±3.26E-03	1.63E-02 ±8.33E-03	3.06E-01 ±2.30E-01	8.08E-02 ±4.96E-01	3.89E-01 ±1.45E+00	1.68E-01 ±1.39E-01	1.11E-02 ±7.66E-03	4.35E-03 ±2.82E-03	1.60E-02 ±1.29E-02
ADD-G	2.68E-02 ±3.47E-02	1.43E-03 ±1.85E-03	1.92E-03 ±1.54E-03	1.37E-01 ±5.38E-02	4.86E-03 ±1.08E-02	2.45E-01 ±1.12E+00	9.14E-02 ±5.26E-02	2.55E-03 ±2.00E-03	1.43E-03 ±1.07E-03	2.91E-04 ±3.71E-04
ADD-GI	2.28E-02 ±4.66E-02	1.35E-03 ±2.30E-03	2.00E-03 ±1.78E-03	1.09E-01 ±7.88E-02	1.17E-02 ±1.70E-02	7.29E-02 ±1.74E-01	6.54E-02 ±4.32E-02	1.35E-03 ±1.63E-03	6.36E-04 ±1.11E-03	1.26E-04 ±2.94E-04
Teenagers										
ADD	4.85E-02 ±7.93E-02	2.36E-03 ±1.89E-03	9.44E-03 ±4.84E-03	1.78E-01 ±1.34E-01	4.69E-02 ±2.88E-01	2.26E-01 ±8.41E-01	9.75E-02 ±8.05E-02	6.45E-03 ±4.45E-03	2.53E-03 ±1.64E-03	9.27E-03 ±7.50E-03
ADD-G	1.56E-02 ±2.02E-02	8.31E-04 ±1.08E-03	1.12E-03 ±8.97E-04	7.93E-02 ±3.12E-02	2.82E-03 ±6.25E-03	1.43E-01 ±6.49E-01	5.31E-02 ±3.05E-02	1.48E-03 ±1.16E-03	8.31E-04 ±6.24E-04	1.69E-04 ±2.16E-04
ADD-GI	1.32E-02 ±2.71E-02	7.82E-04 ±1.33E-03	1.16E-03 ±1.03E-03	6.35E-02 ±4.57E-02	6.79E-03 ±9.89E-03	4.24E-02 ±1.01E-01	3.80E-02 ±2.51E-02	7.86E-04 ±9.47E-04	3.70E-04 ±6.44E-04	7.34E-05 ±1.71E-04
Adults										
ADD	1.64E-02 ±2.67E-02	7.94E-04 ±6.38E-04	3.18E-03 ±1.63E-03	5.99E-02 ±4.50E-02	1.58E-02 ±9.70E-02	7.60E-02 ±2.83E-01	3.29E-02 ±2.71E-02	2.17E-03 ±1.50E-03	8.52E-04 ±5.51E-04	3.12E-03 ±2.52E-03
ADD-G	5.18E-03 ±6.78E-03	2.80E-04 ±3.63E-04	3.76E-04 ±3.02E-04	2.67E-02 ±1.05E-02	9.50E-04 ±2.10E-03	4.80E-02 ±2.18E-01	1.79E-02 ±1.03E-02	4.99E-04 ±3.91E-04	2.80E-04 ±2.10E-04	5.69E-05 ±7.26E-05
ADD-GI	5.18E-03 ±6.78E-03	2.80E-04 ±3.63E-04	3.76E-04 ±3.02E-04	2.67E-02 ±1.05E-02	9.50E-04 ±2.10E-03	4.80E-02 ±2.18E-01	1.79E-02 ±1.03E-02	4.99E-04 ±3.91E-04	2.80E-04 ±2.10E-04	5.69E-05 ±7.26E-05

*mean±SD; ADD: average daily dose; ADD-G: average daily dose in gastric phase; ADD-GI: average daily dose in gastro-intestinal phase

Appendix J. Health risk distribution among age groups using UCL and bioaccessibility tests*

	HQs In Age Groups										
	Pb	As	V	Mn	Cu	Zn	Ba	Ni	Co	Cr	Cd
Infants											
HQ	8.96E-01	4.06E-02	6.73E-03	6.59E-03	2.04E-02	3.12E-03	2.50E-03	1.66E-03	6.52E-04	3.21E-05	2.93E-03
HQ-G	2.96E-01	1.70E-02	1.01E-03	2.81E-03	6.53E-04	6.73E-03	1.37E-03	3.99E-04	2.58E-04	8.23E-07	N/A
HQ-GI	2.68E-01	2.15E-02	1.08E-03	2.79E-03	1.30E-03	1.36E-03	9.87E-04	2.82E-04	1.53E-04	4.63E-07	N/A
Toddlers											
HQ	7.37E-01	3.34E-02	5.54E-03	5.42E-03	1.68E-02	2.57E-03	2.06E-03	1.37E-03	5.37E-04	2.64E-05	2.41E-03
HQ-G	2.43E-01	1.40E-02	8.28E-04	2.31E-03	5.37E-04	5.54E-03	1.13E-03	3.29E-04	2.13E-04	6.77E-07	N/A
HQ-GI	2.21E-01	1.77E-02	8.86E-04	2.29E-03	1.07E-03	1.12E-03	8.12E-04	2.32E-04	1.26E-04	3.81E-07	N/A
Children											
HQ	3.32E-01	1.50E-02	2.49E-03	2.44E-03	7.54E-03	1.16E-03	9.26E-04	6.15E-04	2.42E-04	1.19E-05	1.08E-03
HQ-G	1.09E-01	6.30E-03	3.73E-04	1.04E-03	2.42E-04	2.49E-03	5.09E-04	1.48E-04	9.57E-05	3.05E-07	N/A
HQ-GI	9.94E-02	7.97E-03	3.99E-04	1.03E-03	4.83E-04	5.04E-04	3.65E-04	1.04E-04	5.67E-05	1.71E-07	N/A
Teenagers											
HQ	1.93E-01	8.73E-03	1.45E-03	1.42E-03	4.38E-03	6.72E-04	5.38E-04	3.57E-04	1.40E-04	6.90E-06	6.29E-04
HQ-G	6.35E-02	3.66E-03	2.16E-04	6.04E-04	1.40E-04	1.45E-03	2.95E-04	8.58E-05	5.56E-05	1.77E-07	N/A
HQ-GI	5.77E-02	4.63E-03	2.32E-04	6.00E-04	2.80E-04	2.92E-04	2.12E-04	6.06E-05	3.29E-05	9.95E-08	N/A
Adults											
HQ	6.49E-02	2.94E-03	4.87E-04	4.77E-04	1.47E-03	2.26E-04	1.81E-04	1.20E-04	4.72E-05	2.32E-06	2.12E-04
HQ-G	2.14E-02	1.23E-03	7.29E-05	2.04E-04	4.73E-05	4.87E-04	9.94E-05	2.89E-05	1.87E-05	5.96E-08	N/A
HQ-GI	1.94E-02	1.56E-03	7.80E-05	2.02E-04	9.44E-05	9.85E-05	7.15E-05	2.04E-05	1.11E-05	3.35E-08	N/A

*infants: 0 to < 1 year old; toddlers: 1 to 6 years old; children: 6 to < 12 years old; teenagers: 12 to < 18 years old; adults: 18 to < 78 years old; HQ: hazard quotient; HQ-G: hazard quotient in gastric phase; HQ-GI: hazard quotient in gastro-intestinal phase

Health Risks Assessment		
Age Groups	HI	Cancer Risk
Infants		
In soil	9.81E-01	2.34E-07
G phase	3.26E-01	9.81E-08
GI phase	2.98E-01	1.24E-07
Toddlers		
In soil	8.07E-01	9.63E-07
G phase	2.68E-01	4.04E-07
GI phase	2.45E-01	5.11E-07
Children		
In soil	3.63E-01	5.20E-07
G phase	1.21E-01	2.18E-07
GI phase	1.10E-01	2.76E-07
Teenagers		
In soil	2.11E-01	3.02E-07
G phase	7.00E-02	1.27E-07
GI phase	6.40E-02	1.60E-07
Adults		
In soil	7.10E-02	1.02E-06
G phase	2.36E-02	4.26E-07
GI phase	2.16E-02	5.40E-07

*infants: 0 to < 1 year old; toddlers: 1 to 6 years old; children: 6 to < 12 years old; teenagers: 12 to < 18 years old; adults: 18 to < 78 years old; G: gastric phase; GI: gastro-intestinal phase

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