# POTENTIAL INTAKE AND RISK CHARACTERIZATION OF HEAVY METALS DUE TO INGESTION OF SOILS FROM PARKS, PLAYGROUNDS AND PICNIC AREAS

**by**

**NURTEN DOĞAN**

**BS. in Environmental Engineering, Kocaeli University, 2007**

**Submitted to the Institute of Environmental Sciences in partial fulfillment of the requirements for the degree of**

**Master of Science**

**in**

**Environmental Technologies**

**Boğaziçi University**

**2010**

# ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to Prof. Dr. Turgut T. Onay and Prof. Dr. Gerald J. Zagury for their valuable, guidance, support, encouragement and patience during this study.

I would like to thank Assoc. Prof. Dr. Nadim Copty for being a member of my thesis jury and his valuable comments as well as in my education of Masters of Science.

Very special thanks go to Mr. Mert Güney for his great support and patience in my thesis study, worthy experience he shared with me, his kind and willing assistance in all issues and his invaluable friendship we delighted up to now.

I am also thankful to Mrs. Gülhan Özkösemen and Mr. Mehmet Ali Küçüker for their support and suggestions during my laboratory studies and measurements. I would like to thank all members of the Institute of Environmental Sciences for their worthy friendships.

I would also like to acknowledge Boğaziçi University Research Fund for financial support (Project No: 09Y103P).

Finally, I would like to sincerely thank to my family and my friends for their love, support, understanding and encouragement during this thesis.

# POTENTIAL INTAKE AND RISK CHARACTERIZATION OF HEAVY METALS DUE TO INGESTION OF SOILS FROM PARKS, PLAYGROUNDS AND PICNIC AREAS

Heavy metal pollution in soils near parks, playgrounds and picnic areas which in there are Chromated Copper Arsenate (CCA) treated wood structures is an important consideration since when children are playing in this sites, they may be exposed to harmful effects of heavy metal pollution.

The objectives of this study were to assess urban soil contamination by selected metals (As, Cd, Cr, Cu, Ni, Pb, and Zn) in 24 sites (127 soil samples) in Istanbul, Turkey, investigate relationships between soil contamination and site properties, characterize the risk for critically contaminated sites by taking oral metal bioaccessibility and two soil ingestion scenarios into account. Average metal concentrations were similar in the 17 playgrounds, 4 parks and 3 picnic areas sampled. Five out of 24 sites (all equipped with treated wood structures) had systematically higher contamination than background for As, Cd, Cu, Cr or Zn, and measured concentrations generally exceeded Turkish regulatory values. High Cu concentrations in these sites were attributed to the leaching from wood treated with Cu-containing preservatives other than chromated copper arsenate (CCA). Risk characterization for these sites showed that hazard index was below one in both involuntary soil ingestion and soil pica behaviour scenarios for all metals. However, probabilistic carcinogenic risk for As uptake exceeded $1\times10^{-6}$ in both scenarios. A sensitivity analysis showed that soil ingestion rate was the most important parameter affecting risk estimation. Risk from As uptake for children from soils of parks, playgrounds and picnic areas may be serious, especially if soil pica behaviour is present.

# PARK, OYUN VE PİKNİK ALANLARINDAKİ TOPRAKLARIN YUTULMASINA BAĞLI OLARAK AĞIR METALLERİN OLASI ALINIMI VE RİSK KARAKTERİZASYONU

Çocuklar, içerisinde kromlanmış bakır arsenat (Chromated Copper Arsenat-CCA) ile işlenmiş ahşap yapıların bulunduğu park, oyun ve piknik alanlarının yakınındaki topraklarda oynarlarken ağır metal kirliliğinin zararlı etkilerine maruz kalabilmeleri nedeniyle bu bölgelerdeki ağır metal kirliliği önemli bir husustur.

Bu çalışmanın amacı secilmiş metaller (As, Cd, Cr, Cu, Ni, Pb ve Zn) bakımından İstanbul'un 24 bölgesindeki kentsel toprakların kirliliğini değerlendirmek, toprak kirliliği ile bölge özellikleri arasındaki ilişkiyi incelemek, kritik olarak kirlenmiş bölgeler için metallerin oral biyolojik ulaşılabilirliği ve iki senaryoyu hesaba katarak riski karakterize etmektir. 17 oyun alanı, 4 park ve 3 piknik alanından alınan numunelerin ortalama metal konsantrasyonlarının benzerlik gösterdiği görülmüştür. 24 bölgeden tamamı işlenmiş ahşap ile donatılmış beş bölgenin As, Cd, Cu, Cr ve Zn bakımından sistematik olarak zemin değerlerinden daha yüksek kirlilik içerdiği ve ölçülen konsantrasyonların genellikle Toprak Kirliliği ve Kontrolü Yönetmeliği (TKKY) limit değerlerini aştığı tespit edilmiştir. Bu bölgelerdeki yüksek bakır konsantrasyonları, CCA'den başka bir bakır içeren ahşap koruyucudan kaynaklanan sızıntılara yorumlanmıştır. Bu bölgeler için risk karakterizasyonu tüm metaller için "toprak yeme alışkanlığı" ve "istemsiz toprak yeme" senaryoları için tehlike endeksi 1'in altında olduğunu göstermiştir; ancak As alımı için olası kansorojen risk değeri her iki senaryoda da $1\times10^{-6}$ limitini aşmıştır. Hassasiyet analizleri, toprak yutma oranının risk tahminini etkileyen en önemli değişken olduğunu göstermiştir. Özellikle toprak yeme alışkanlığı olan çocuklar için park, oyun ve piknik alanlarındaki topraklardan As alımı ile doğan risk ciddi olabilmektedir.

# TABLE OF CONTENTS

# LIST OF FIGURES

# LIST OF TABLES

# LIST OF SYMBOLS/ABBREVIATIONS

| Symbol/Abbreviations | Explanation | Units used |
|---|---|---|
| ACA | Ammoniacal Copper Arsenate | |
| ACC | Acid Copper Chromate | |
| ACZA | Ammoniacal Copper Zinc Arsenate | |
| Al | Aluminium | |
| As | Arsenic | |
| AT | Averaging time | days |
| ATSDR | Agency for Toxic Substances&Disease Registry | |
| B | Bioaccessibility | % |
| BDL | Below Detection Limit | |
| BW | Body weight | kg |
| C | Metal concentration of soil | ppm |
| CCA | Chromated Copper Arsenate | |
| Cd | Cadmium | |
| $CDI_{adjusted}$ | Adjusted metal daily intake | $\mu g.kg^{-1}.d^{-1}$ |
| $CDI_{metal}$ | Metal daily intake | $\mu g.kg^{-1}.d^{-1}$ |
| CF | Unit conversion factor | $10^{-3}$ |
| $C_{ICP}$ | Metal concentration found by ICP readings | ppm |
| Cl | Clor | |
| Cr | Chromium | |
| Cu | Copper | |
| ED | Exposure duration | yr |
| EF | Exposure frequency | $d.yr^{-1}$ |
| EPC | Exposure point concentration | $mg.kg^{-1}$ |
| Fe | Ferrous | |
| HI | Hazard index | |
| ICP-MS | Inductively Coupled Plasma-Mass Spectrometry | |

| Symbol/Abbreviations | Explanation | Units used |
|---|---|---|
| L | Loam | |
| $M_c$ | Mass of container | g |
| $M_{cds}$ | Mass of container and oven dry specimen | g |
| $M_{cms}$ | Mass of container and moist specimen | g |
| $M_s$ | Mass of oven dry specimen | g |
| $M_w$ | Mass of water | g |
| Mn | Manganese | |
| NC | Not Calculated | |
| Ni | Nickel | |
| Pb | Lead | |
| RDAs | Recommended Dietary Allowances | |
| RfD | Reference dose | $mg.kg^{-1}.d^{-1}$ |
| S | Sand | |
| SCL | Sandy clayey loam | |
| SF | Cancer slope factor | $(kg.d.mg^{-1})$ |
| SIR | Soil ingestion rate | $mg.d^{-1}$ |
| SL | Sandy loam | |
| SPSS | Statistical Package for the Social Sciences | |
| TKKY | Turkish Soil Pollution Control Regulation | |
| TOC | Total Organic Carbon | |
| USDA | United States Department of Agriculture | |
| USEPA | United States Environmental Protection Agency | |
| W | Water content | % |
| Zn | Zinc | |

# 1. INTRODUCTION

Since heavy metals may cause metal poisoning and results in chronic toxicity effects, heavy metal pollution is an issue of major concern. Heavy metal pollution in urban soils may originate from different sources such as high background soil concentrations (Teutsch et al., 2001), industry (Govil et al., 2008), traffic (Guney et al., 2009) or treated wood structures (Cookson, 2008). Parks, playgrounds, and picnic areas are locations where children are potentially exposed to heavy metal pollution as treated wood structures in these areas are the sources of heavy metal contamination.

Treated wood structures are used for numerous purposes in outdoor places. These structures are typically treated with preservatives to protect them against fungi and insect attacks. These preservatives contain arsenic (As), chromium (Cr), and copper (Cu) and other components which can leach from the wood with time due to climate conditions during service. As a result, nearby soils can get contaminated with As, Cr, and Cu depending on the type of preservative used. One of commonly used wood preservatives is Chromated Copper Arsenate (CCA) which is still utilized without restrictions in Turkey. However, it has been phased out from the United States and Canadian residential markets and publicly used facilities at the end of the 2003 (Zagury et al., 2008). The most common type of CCA (CCA-C) contains 47.5% $CrO_3$, 18.5% CuO and 34% $As_2O_5$ (w/w) (Balasoiu et al., 2001).

When treated wood structures are being used in a recreational activity (i.e.: a picnic bench or playground structures) ingestion of contaminated soil by children may cause metal poisoning, resulting in acute and chronic toxicity effects. When children play outdoors the fraction smaller than 250 microns adheres to their hands (Yamamoto et al., 2006) and they either unintentionally ingest soil by putting their dirty hands and objects in their mouths, or deliberately eat soil. Moya et al. (2004), suggest an average soil ingestion value of 137 $mg.d^{-1}$, where upper percentile values reach up to 1432 $mg.d^{-1}$ and reported children with soil pica behaviour may exhibit even higher amounts of soil ingestion. In 2008, the U.S.EPA (2008) proposed recommended ingestion values of 50

$mg.d^{-1}$ for soil, 100 $mg.d^{-1}$ for soil and dust (central tendency values) and 1 $g.d^{-1}$ for soil pica behaviour (upper percentile). The carcinogenic risk for children from playing in playgrounds was estimated to be close to the probability level of $1\times10^{-5}$ (De Miguel et al., 2007). Therefore it is important to quantify metal levels and to assess potential metal intake and risk.

Total concentration of a metal in a soil sample may not be a direct estimate of its toxicity for humans. When ingested, only the biologically absorbable fractions of metals represent a risk for human health. Oral bioavailability is defined as the fraction of a contaminant that reaches the systemic circulation from the gastrointestinal (GI) tract, and bioaccessibility is the fraction of the contaminant dissolved in the GI system which is potentially available for absorption (Ruby et al., 1999). Relative bioavailability (RBA) can be estimated by measuring bioaccessibility via in vitro tests. In vitro bioaccessibility tests are easy to perform and are a good estimator of bioavailability, especially if the test used is validated through comparison to the results of in vivo tests. Therefore, there is a need for extensive studies on risk characterization which assess children's metal uptake considering oral bioaccessibility following soil ingestion by children.

The objectives of this study are assessment of selected heavy metals (As, Cd, Cr, Cu, Pb, Ni, Zn) contamination, determination of the relationships between contamination levels and site properties, exposure assessment in soil samples collected from parks, playgrounds, and picnic areas, and characterizing the risk to children who might be exposed to these soils. The specific objectives of this work are discussed in Chapter 3.

# 2. THEORETICAL BACKGROUND AND LITERATURE REVIEW

## 2.1. Soil Definition

Soil is essentially a natural body of mineral and organic constituents. It is the interface at which all forces acting on the Earth's crust meet to produce a medium of unconsolidated material, acting as an environment for further changes and developments, keeping pace with the evolution of the global Earth system as a whole. It offers shelter and habitat for a countless number of organisms, provides an incubation and living medium for plants, while playing its role prefectly in the universal cycle of material flow between the four main geospheres (atmosphere, lithosphere, hydrosphere, and biosphere) (Mirsal, 2008). Soil is the end product of physical chemical weathering and erosion in combinations with biological actions on igneous rock and it is complex mixture of minerals, water, air, and organic matter (both dead and alive), forming at the surface of land (www.soils.org, 2010).

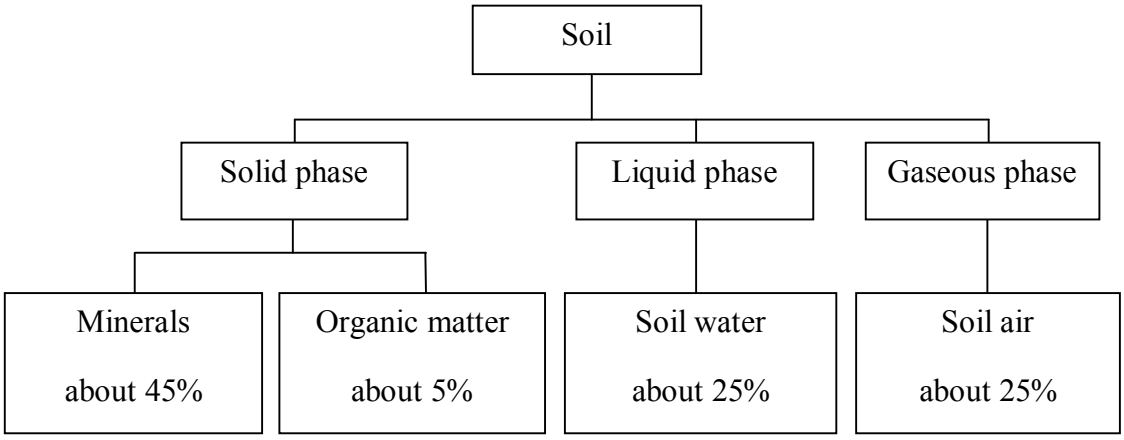


Figure 2.1. Composition by volume of an average soil.

The weathering of rocks and minerals results in a wide range in size of particles; from those easily seen with the unaided eye to those below the range of a high-powered microscope. The particles-size distribution determines the soil's texture. Soil texture is a term commonly used to designate the proportionate distribution of the different sizes of mineral particles in a soil. Size limits of soil separates in the USDA soil textural

classification system and textural triangle are shown in Table 2.1 and Figure 2.3 respectively.

Table 2.1. Size limits of soil separates in the USDA soil textural classification system (Brown, 2003).

| Name of soil separate | Diameter limits (mm) |
|---|---|
| Very coarse sand* | 2.00 - 1.00 |
| Coarse sand | 1.00 - 0.50 |
| Medium sand | 0.50 - 0.25 |
| Fine sand | 0.25 - 0.10 |
| Very fine sand | 0.10 - 0.05 |
| Silt | 0.05 - 0.002 |
| Clay | less than 0.002 |
| * Note that the sand separate is split into five sizes (very coarse sand, coarse sand, etc.). | |

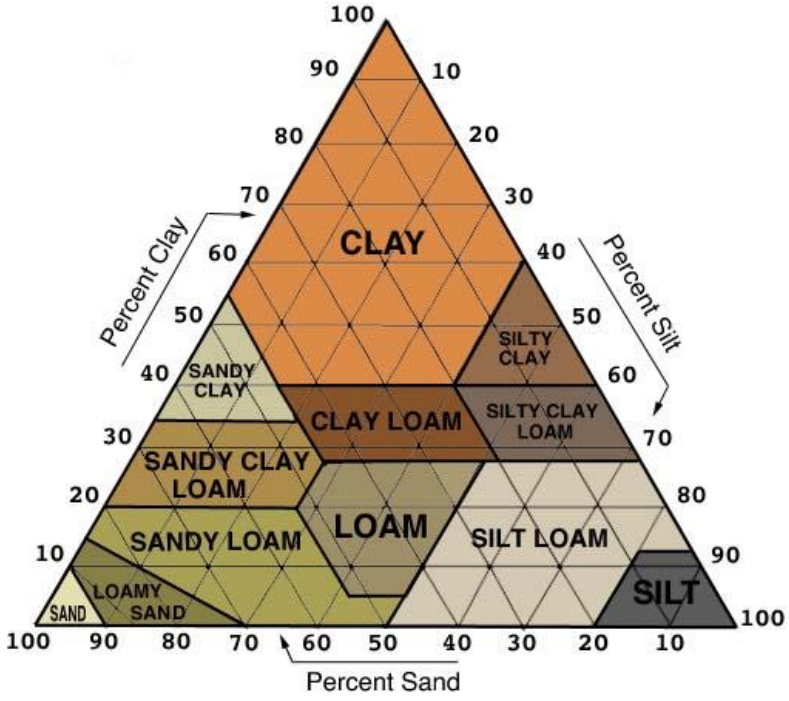


Figure 2.2. The textural triangle and limits of sand, silt, and clay

Sandy soils tend to be low in organic matter content and native fertility, low in ability to retain moisture and nutrients, low in cation exchange and buffer capacities, and rapidly permeable (i.e., they permit rapid movement of water and air). Finer-textured soils generally are more fertile, contain more organic matter, have higher cation exchange and buffer capacities, are better able to retain moisture and nutrients, and permit less rapid movement of air and water. When soils are so fine-textured as to be classified as clayey, however, they are likely to exhibit properties which are somewhat difficult to manage or overcome (Brown, 2003).

Parent materials have a wide ranging mineralogical composition and pH, and young soils inherit these properties from the parent material. Soil pH is a measure of the acidity or alkalinity in the soil. Many heavy metals become more water soluble under acidic conditions and can move downward with water through the soil, and in some cases move to aquifers, surface streams, or lakes (NRSC, 1999).

## 2.2. Soil Pollution by Heavy Metals

Soil pollution is the occurrence of pollutants in soil above a certain level causing a deterioration or loss of one or more soil functions. One of the major types of soil pollutants is heavy metals (Mirsal, 2008).

'Heavy metals' is a group name for the metals and semimetals with certain properties. Although there is no perfect and completely clear classification for the term, a metal is generally assumed as 'heavy metal' if it has a mass per unit volume of five times of water or more (Duffus, 2002). Other than the specific gravity classification widely accepted, there are numerous other definitions based on relative atomic mass, atomic number, chemical properties and toxicity.

Within the scope of this study, heavy metals are considered as substances with the following properties:

- Have common metal or metalloid properties
- Have high density in atomic form
- Mostly emitted by anthropogenic sources, but also found in the environment inherently
- Found both in element and substance forms in environment
- Have biologically toxic properties at exceeded specific levels

Heavy metals found in soils can be from natural sources (inherent concentrations from bedrock mineralogy) or from anthropogenic sources. Natural concentrations of heavy metals in soils depend primarily on the type and chemistry of the parent materials from which the soils are derived. However, anthropogenic inputs may lead to concentrations highly exceeding those from natural sources. While usually natural forms are present at relative low concentrations, in recent years a number of anthropogenic sources such as dumping of waste, smelter stacks, waste incineration, vehicle exhausts, fertilizers, agricultural waste, and sewage sludges have contributed to the increase of environmental metal concentrations (Granero and Domingo, 2002). Heavy metal concentrations in soils should not exceed certain limits. Maximum allowable concentrations specify the acceptable limits to protect human and ecological health. Allowable limits for selected heavy metals in soils and limit value for arsenic of remediated soils are given in the following Table 2.2.

Table 2.2. Limits for heavy metals in soils and limit value for arsenic of remediated soils (TKKY, 2005)

| Metals | Allowable limits ($mg.kg^{-1}$) | |
|---|---|---|
| | pH 5-6 | pH > 6 |
| Lead (Pb) | 50 | 300 |
| Cadmium (Cd) | 1 | 3 |
| Chromium (Cr) | 100 | 100 |
| Copper (Cu) | 50 | 140 |
| Nickel (Ni) | 30 | 75 |
| Zinc (Zn) | 150 | 300 |
| Pollutant | Limit values ($mg.kg^{-1}$) | |
| Arsenic (As) | 20 | |

### 2.2.1. Fate and Transport of Heavy Metals

When metals are introduced into soils, they may be distributed in one or more of the following forms (Sharma and Reddy, 2004):

- Dissolved in soil solution (pore water)
- Occupying exchange sites on inorganic soil constituents
- Adsorbed on inorganic soil constituents
- Associated with insoluble soil organic matter
- Precipitated as pure or mixed solids
- Present in the structure of minerals.

Heavy metals are accumulated in soils by adsorption mechanisms which is a major process (Bradl, 2004). Metal sorption is closely correlated with soil properties (Philips, 1999). The most important parameters controlling heavy metal adsorption and their distribution between soil and water are soil type, metal speciation, metal concentration, soil pH, solid to solution mass ratio, and contact time.

Arsenic (As) is a metallic grey redox active element that generally persists in either the +3 or +5 oxidation states within soils. Arsenic is ubiquitous in soils with natural background concentrations ranging from 0.1 to 40 $mg.kg^{-1}$ (Rodriguez et al., 1999). However, arsenic is usually found in the environment combined with other elements such as oxygen, chlorine, and sulfur. Arsenic combined with these elements is called inorganic arsenic. Arsenic combined with carbon and hydrogen is referred to as organic arsenic (ATSDR, 2007).

Copper (Cu) is a reddish metal which occurs in solids and solutions as a divalent cation. However, reduction of $Cu^{+2}$ (cuprous) to $Cu^{+3}$ (cupric) and $Cu^{0}$ (metallic copper) is possible under reducing conditions. In reduced soils, copper has very low mobility. Most of the colloidal materials of soils (oxides of Mn, Al, and Fe, silicate clays, humus) adsorb $Cu^{+2}$ strongly, and increasingly so as the pH is raised.

Chromium (Cr) exists in two possible oxidation states in soils; the trivalent chromium, Cr (III) and the hexavalent chromium, Cr (VI). Cr has different chemical properties from other metals. It is found in the environment in two ionic forms; chromate ($CrO_4^{-2}$) and dichromate ($Cr_2O_7^{-2}$) which are both negatively charged unlike most of the other metal ions. This unique difference affects the adsorption behaviour of Cr especially against negatively charged soil minerals such as clays, where adsorption and chemical complexation is rare due to the repellent forces between the chromates and clay particles (Güney, 2006).

Cadmium (Cd) may be adsorbed by clay minerals, carbonates or hydrous oxides of iron and manganese or may be precipitated as cadmium carbonate, hydroxide, and phosphate. Cd solubility is high and very little adsorption of Cd by soil colloids, hydrous oxides, and organic matter takes place. At pH values greater than 6, Cd is adsorbed by the soil solid phase or is precipitated. Cd forms soluble complexes with inorganic and organic ligands, in particular with Cl. The formation of these complexes will increase Cd mobility in soils (Güney, 2006).

Zinc (Zn) is bluish-white shiny metal which is readily adsorbed by clay minerals, carbonates, or hydrous oxides. Zinc occurs in the environment mainly in the +2 oxidation state. The greatest percent of the total Zn in polluted soils and sediments was associated with Fe and Mn oxides. Precipitation is not a major mechanism for Zn in soils because of the relatively high solubility of Zn compounds. In general, Zn adsorption increases with pH. In acidic sediments and soils, more zinc is available in ionic forms while in alkaline soils, the chemistry of zinc is dominated by interactions with organic ligands.

Lead (Pb) is redox stable divalent cation that has a high affinity for numerous soil materials. Migration of Pb in the environment is primarily dependent upon the solubility of the original Pb-bearing solids and their weathering products (Hettiaratchchi, 2004). In soluble form lead reacts with clays, phosphates, sulphates, carbonates, hydroxides. At pH values above 6, Pb is either adsorbed on clay surfaces or forms lead carbonate. Carbonate content in soils plays an important role in controlling Pb behaviour.

Nickel (Ni) is a hard, silvery-white metal when it is pure. The +2 oxidation state is the only stable form of nickel in soil environments. It does not form insoluble precipitates in unpolluted soils and retention for Ni is through adsorption mechanisms, which is a quite different characteristics from the other metals mentioned. Nickel may be adsorbed by clays, iron and manganese oxides, and organic matter. The formation of complexes of Ni with both inorganic and organic ligands will increase Ni mobility in soils (Güney, 2006).

### 2.2.2. Health Related Impacts of Heavy Metals in Soils

Arsenic is found naturally in the environment. Since children often play in the soil and put their hands in their mouths and sometimes intentionally eat soil, ingestion of contaminated soil may be an important source of arsenic exposure for children. Thus, children may be at a higher risk of exposure because of normal hand-to-mouth activity. Inorganic arsenic has been recognized as a human poison since ancient times, and large oral doses can result in death (ATSDR, 2007). Swallowing lower levels of inorganic arsenic, may result in experiencing irritation of stomach and intestines, with symptoms such as stomachache, nausea, vomiting, and diarrhea. Other effects resulting from swallowing inorganic arsenic include decreased production of red and white blood cells, which may cause fatigue, abnormal heart rhythm, blood-vessel damage resulting in bruising, and impaired nerve function causing a "pins and needles" sensation in hands and feet (ATSDR, 2007). Swallowing arsenic has also been reported to increase the risk of cancer in the liver, bladder, and lungs. Direct skin contact with high concentrations of inorganic arsenic compounds leads irritation of skin, with some redness and swelling (ATSDR, 2007). There is also some evidence that suggests that long-term exposure to inorganic arsenic in children may result in lower IQ scores and exposure to arsenic in early life may increase mortality in young adults. Almost no information is available on the effects of organic arsenic compounds in humans (ATSDR, 2007).

Copper is common in the environment. Soil generally contains between 2 and 250 ppm copper, although concentrations close to 17,000 ppm have been found near copper and brass production facilities (ATSDR, 2004). Copper is essential for good health.

However, exposure to higher doses can be harmful. Long-term exposure to copper dust can irritate nose, mouth, and eyes, and cause headaches, dizziness, nausea, and diarrhea. Intentionally high intakes of copper can cause liver and kidney damage and even death. We do not know if copper can cause cancer in humans. Exposure to high levels of copper will result in the same types of effects in children and adults. It is not known if these effects would occur at the same dose level in children and adults (ATSDR, 2004).

People can be exposed to chromium by ingestion soil as well as breathing air containing it or drinking water, bathing in water, and food containing chromium. Chromium (VI) compounds are more toxic than chromium (III) compounds. The most common health problem in people exposed to chromium involves the respiratory tract. These health effects include irritation of the lining of the nose, runny nose, and breathing problems (asthma, cough, shortness of breath, wheezing). People have also developed allergies to chromium compounds, which can cause breathing difficulties and skin rashes. Sperm damage and damage to the male reproductive system have also been seen in laboratory animals exposed to chromium (VI) (ATSDR, 2008). There are no studies that have looked at the effects of chromium exposure on children. It is likely that children would have the same health effects as adults. It is not known whether children would be more sensitive than adults to the effects of chromium (ATSDR, 2008).

Cadmium may cause kidney disease, irritation in stomach, vomiting and diarrhea and death. Exposure to lower levels of cadmium for a long time can also cause bones to become fragile and break easily. The health effects seen in children from exposure to toxic levels of cadmium are expected to be similar to the effects seen in adults (kidney and intestinal damage depending on the route of exposure) (ATSDR, 2008). EPA considers cadmium to be a probable human carcinogen (cancer-causing agent) and has classified it as a Group B1 carcinogen. Several occupational studies have reported an excess risk of lung cancer in humans from exposure to inhaled cadmium (USEPA, 2000). However, the evidence is limited rather than conclusive due to confounding factors. There is no information about Cd carcinogenety from exposure to ingested cadmium.

Zinc is an essential element needed by body in small amounts. The average daily zinc intake through the diet ranges from 5.2 to 16.2 milligrams. Taking too much zinc into the body through food, water, or dietary supplements can also affect health. The levels of zinc that produce adverse health effects are much higher than the Recommended Dietary Allowances (RDAs) for zinc which is 11 $mg.d^{-1}$ for men and 8 $mg.d^{-1}$ for women. If large doses of zinc (10-15 times higher than the RDA) are taken by mouth even for a short time, stomach cramps, nausea, and vomiting may occur. Ingesting high levels of zinc for several months may cause anemia, damage the pancreas, and decrease levels of high-density lipoprotein (HDL) cholesterol. Consuming too little zinc is at least as important a health problem as consuming too much zinc. Without enough zinc in the diet, people may experience loss of appetite, decreased sense of taste and smell, decreased immune function, slow wound healing, and skin sores (ATSDR, 2005). Too little zinc in the diet may also cause poorly developed sex organs and retarded growth in young men. If a pregnant woman does not get enough zinc, her babies may have birth defects. Zinc is essential for proper growth and development of young children. Mothers who did not have enough intake of zinc during pregnancy had a higher frequency of birth defects and gave birth to smaller children (lower birth weight) than mothers whose zinc levels were sufficient. Very young children who did not receive enough zinc in the diet were smaller, both in length and in body weight, than children who ate enough zinc. Little is known about whether children who eat too much zinc will react differently from adults who have ingested large amounts of zinc (ATSDR, 2005).

Lead is commonly found in soil especially near roadways, older houses, old orchards, mining areas, industrial sites, near power plants, incinerators, landfills, and hazardous waste sites. Skin contact with dust and dirt containing lead occurs every day. The main target for lead toxicity is the nervous system, both in adults and children. Lead exposure may also cause weakness in fingers, wrists, or ankles. In addition, lead exposure causes small increases in blood pressure, particularly in middle-aged and older people. Lead exposure may also cause anemia, brain and kidney damages, miscarriage, decreased sperm production, and death (ATSDR, 2007). Children are more vulnerable to lead poisoning than adults. Babies and children can swallow and breathe lead in dirt,

dust, or sand while they play on the floor or ground. Lead affects children in different ways depending on how much lead a child swallows. A child who swallows large amounts of lead may develop anemia, kidney damage, colic, muscle weakness, and brain damage, which ultimately can kill the child (ATSDR, 2007).

Nickel normally occurs at very low levels in the environment. Skin contact with soil can result in exposure. The most common harmful health effect of nickel in humans is an allergic reaction. Approximately 10-20% of the population is sensitive to nickel (ATSDR, 2005). The most common reaction is a skin rash. In some sensitized people, dermatitis (a type of skin rash) may develop. For example, hand eczema (another type of skin rash) is fairly common among people sensitized to nickel. The most serious harmful health effects from exposure to nickel, such as chronic bronchitis, reduced lung function, and cancer of the lung and nasal sinus. It is likely that the health effects seen in children exposed to nickel will be similar to the effects seen in adults. It isnot known whether children differ from adults in their susceptibility to nickel (ATSDR, 2005).

### 2.3. Exposure and Risk Assessment

Risk is defined as the probability of suffering harm or loss (LaGrega et al., 1994). Risk assessment is the attempt to measure the potential for harm. Hazard is different from risk; it is a descriptive term that characterizes the intrinsic ability of an event or a substance to cause harm. Hazard is one source of risk and is a function of the persistence, mobility, and toxicity of the contaminants (Watts and Teel, 2000).

The widely recognized risk assessment process consists of four-step (Watts and Teel, 2000).

- Hazard identification (source analysis; investigating the chemicals present at the site and their characteristics),
- Exposure assessment (pathway analysis; estimating the potential transport of the chemicals to receptors and levels of intake),

- Toxicity assessment (receptor analysis; determining numerical indices of toxicity for computing risk)
- Risk characterization (estimating the magnitude of risk, and the uncertainty of the estimate).

The first step in risk assessment is the evaluation of the identity and properties of the contaminants, their potential for release from the source, and their rate of release. Risk at a hazardous waste site is often dictated by a few contaminants and one or two pathways; these are the risk drivers. The most common practice in assessing the risks of Superfund sites is to screen the contaminants and pathways using surrogate analysis (Watts and Teel, 2000). The surrogate chemicals are selected on the basis of which compounds best represent the risk posed by the site:

- The most toxic, persistent, and mobile
- The most prevalent in terms of spatial distribution and concentration
- Those involved in the more significant exposures

Exposure is the contact of an organism with a toxic substance; exposure assessment is the estimation of the magnitude, frequency, duration, and route exposure. Development of exposure scenarios is important. The primary tasks of exposure assessment include:

- Identifying the populations that may be exposed,
- Identifying the possible exposure pathways,
- Estimating the concentrations to which the populations are exposed,
- Estimating chemical intakes.

The most important factor that influences toxicity is the dose. A second important factor is the time period of exposure. Toxicity is often classified by the number and/or the duration of exposures. Many chemicals that are acutely toxic are not chronically toxic, and vice versa. For chemicals that are both acutely and chronically toxic, the mechanisms of the two types of toxicity are often different. For example acute toxicity

of chloroform affects the central nervous system causing dizziness while its chronic toxicity results in liver damage and cancer (Watts and Teel, 2000). The lack of toxic response from zero dose to the threshold dose is the result of a biochemical or physiological defense that prevents the occurrence of toxicological effects. Toxicity first appears at the threshold dose. Non-carcinogens have thresholds below which they fail to induce any discernible adverse health effect. This threshold is defined as the reference dose (RfD). There is no threshold dose for carcinogen chemicals because even one molecule can initiate cancer. Dose-response relationships for carcinogens are conventionally reported as incidence of life time cancer versus dose. The slope, known as slope factor (SF), represents the carcinogenic potency for the chemical (LaGrega et al., 1994).

Risk characterization is the calculation of risk for all potential receptors that may be exposed to hazardous wastes. It includes calculating risk for different exposure routes to both noncarcinogenic and carcinogenic hazardous chemicals (Watts and Teel, 2000). In the exercises required for Superfund sites, both average and maximum exposure point concentrations are used to estimate risk. It should be noted that the use of a single, upper bound estimate of exposure point concentration in the calculation of potential risks is emphasized. This value is often taken to be 95% percentile upper confidence limit of the arithmetic mean. Use of this number generally provides a worst-case estimate of risk. Carcinogenic risk may be defined as the chronic daily intake dose (developed in the exposure assessment) multiplied by the carcinogenic slope factor (selected by the toxicity assessment). Non-carcinogenic risk is normally characterized in terms of a hazard index (HI). This index is simply the ratio of the estimated intake dose from exposure to the reference dose (RfD). A hazard index less than 1.0 is acceptable (LaGrega et al., 1994).

### 2.4. Studies on Heavy Metal Contaminated Sites near CCA-Treated Wood

Chemical preservatives can reduce damage by organisms such as fungi or insects and increase durability and life expectancy of wood. Wood preservatives can be broadly

divided into two categories: the 'organics' or oil-based preservatives (e.g., pentachlorophenol, creosote, copper naphthenate, and coal tars), and the 'inorganics' or waterborne preservatives (e.g., Chromated Copper Arsenate-CCA, ammoniacal copper arsenate-ACA, ammoniacal copper zinc arsenate-ACZA, and acid copper chromate-ACC). 'Hybrid' preservatives, such as ammoniacal copper quat-ACQ, which contain both organic (quat) and inorganic (CuO) components have also become available in recent years. Since the 1970s, inorganic wood preservatives have been more popular because of restrictions on usage and potentially serious environmental and health risks associated with exposure to organic preservatives (Rahman et al., 2004).

The water borne wood preservative CCA has been used extensively to treat wood since its development by Dr. Sonti Kamesam, in 1993. The roles of Cu and As in the CCA formulation are to inhibit fungi and insects, respectively, while Cr plays a key role in the 'fixation' process, which bind CCA components to wood. CCA is currently available in three different formulations (Types A, B, and C), each with different ratios of $CrO_3$, CuO, and $As_2O_5$ (Rahman et al., 2004). The most popular is type C, constituting 47.5% $CrO_3$, 18.5% CuO, and 35% $As_2O_5$ in USA. The other formulations, Types A and B constitute of 65.5% $CrO_3$, 18.1% CuO, and 16.4% $As_2O_5$, and 35.3% $CrO_3$, 19.6% CuO, and 45.1% $As_2O_5$, respectively. The formulations generally get better going from Type A to C (Chirenje et al., 2003).

In many studies like Chirenje et al. (2003) elevated As, Cr and Cu concentrations were observed in soils immediately surrounding CCA-treated wood utility poles, fences and decks, with the distance of greatest impact being within the first 0.3 m. The age of the structure seemed to determine the level of impact, with newer structures showing the greatest impact (Chirenje et al., 2003).

Also Cookson (2008) showed in preschool playgrounds soil there was arsenic content near CCA-treated pine structures in Melbourne, Australia. While the highest background arsenic content of topsoil and subsoil were 9.1 and 14.6 $mg.kg^{-1}$, respectively, arsenic contents near CCA-treated pine structures were 31.7 and 46.4 $mg.kg^{-1}$ for topsoil and subsoil respectively.

Heavy metal pollution in soils near CCA-treated wood structures has received significant attention especially related to its risk assessment. A study about risk assessment was conducted 'A Probabilistic Risk Assessment for Children Who Contact CCA-Treated Playsets and Decks' Final Report by USEPA (USEPA, 2008). This comprehensive report focuses on the non-dietary assessment of risks from CCA treated wood, specifically the potential health risks to children that may result from contact with CCA-treated wood playsets, decks and CCA-contaminated soil around these structures. It purposes to provide revisions to earlier reports. The risk assessment is revised using the latest toxicological endpoints for CCA.

'The Probabilistic Exposure Assessment' portion of this report was developed by Zartarian and his collegues. Zartarian and his collegues considered (2006) skin contact with, and nondietary ingestion of, arsenic in soil and wood residues for the population of children in the U.S. who frequently contact CCA-treated wood playsets and decks. Model analyses were conducted to assess the impact of potential mitigation strategies such as hand washing after play events. The results showed that predicted central values for lifetime annual average daily dose values for arsenic ranging from $10^{-6}$ to $10^{-5}$ $mg.kg^{-1}.d^{-1}$. Residue ingestion via hand-to-mouth contact was determined to be the most significant exposure route for the scenario in their study (Zartarian et al., 2006).

Since bioaccessibility is the key element of risk assessment, there are a number of studies in literature that focuses on determining bioaccessibility values of metals. Pouschat and Zagury reported that arsenic bioaccessibility ranged between 25 - 66.3 % (mean value 40.7 %) (Pouschat and Zagury, 2006). Also, Girouard and Zagury (2009) focused on bioaccessibility of arsenic. Arsenic bioaccessibility values ranged between 17 and 46.9 % (mean value 30.5 %). They stated that dissolved arsenic in the intestinal phase was exclusively under the form of arsenate As (V) and arsenic bioaceessibility increased when soil particles <90 μm.

Pouschat and Zagury (2008) investigated copper gastrointestinal bioaccessibility ranged between 19.4 – 89.4 % (mean value 54.1%), whereas chromium bioaccessibility varied from below detection (<0.3 %) to 32.9 % (mean value 8.5 %). Also the authors

calculated potential intakes of Cu and Cr from incidental ingestion of soil near CCA-treated utility poles. They concluded that Cr and Cu intake values were very low 0.03 $\mu g.kg^{-1}$ body weight.$d^{-1}$ and 2.5 $\mu g.kg^{-1}$ body weight.$d^{-1}$ respectively. These values are much lower than the dietary reference intakes and oral minimal risk levels for Cu and Cr.

# 3. THE OBJECTIVES OF THE WORK

Since there was a significant need for such a study in Turkey as no previous work has been done and there is a high potential of exposure to children since wood preservative (CCA) was used this research will be an original study filling an important gap. Moreover, exposure scenarios are more likely and repeatedly to occur than some studies in the literature since areas with preserved-wood structures within the scope of this study (picnic areas, playgrounds) are more accessible to children than the cases mentioned in the literature (i.e.: CCA-treated utility poles).

A preliminary research was conducted in parks of Istanbul to justify the need for the study mentioned above. Soil samples were collected near wood structures treated with preservatives from a total of seven locations. A total of 23 samples (including backgrounds) were analyzed for their As, Cr and Cu contents and results from contaminated soils were compared to the background concentrations. Results showed that in some locations, As, and Cu concentrations were much higher than background samples. Then 24 sampling sites were selected by visual inspection and 103 soil samples were taken for analysis as stated in 4.1. Analysis took 8 months and detailed procedures of analysis were explained in 4.2. According to analysis results 5 critically contaminated sites were chosen. Potential intake and risk calculations were done. Deatils about calculations were presented 'Results and Discussions' part.

The purpose of this study are; assessment of selected heavy metals (As, Cd, Cr, Cu, Pb, Ni, Zn) contamination in parks, playgrounds, and picnic areas which are situated throughout İstanbul, determination of the relationships between contamination levels and site properties (type of site, type of recreational structure, and soil properties), exposure assessment in soil samples collected from parks, playgrounds, and picnic areas, particularly near wood structures treated with wood preservatives in sites with high potential for incidental or deliberately ingestion of soil by children, characterizing the risk to children who might be exposed to these soils ,and doing sensitivity analyses by using different scenarios in order to see if there is a risk to children and its significance in worst case.

# 4. MATERIALS AND METHODS

## 4.1. Site Selection and Sampling Procedure

Soil samples were collected from 24 sites in the city of İstanbul which is the biggest city of Turkey in terms of population, industrial and commercial activities. Sampling sites were evenly distributed throughout the city. The sites were playgrounds, parks or picnic areas and were selected such that children have a high possibility to come in contact with nearby soil. Sampling sites with treated wood structures were selected due to the increased possibility of metal contamination from leaching, and playgrounds with metal or plastic structures were also included due to the possibility of contamination via other ways (high background concentrations or traffic-related metal deposition). Existence of treated wood structures was determined by visual inspection of wood for greenish brown color.

Seventeen playgrounds; ten playgrounds with treated wood structures, four playgrounds with metal structures, and three playgrounds with plastic structures, four parks with treated wood structures, and three picnic areas with treated wood structures were selected for this study. Site 02, 03, 05, 07, 10, 13, 14, 15, 16, 17, 19, 20, 21, 22, and 23 were located near the main arterials or secondary streets. Therefore they were under a potentially high impact of traffic activity. Sites 01, 08, 11,12, and 24 were exposed to moderate traffic activity since sites were not located near roads, distance was about 10 m. Sites 04, 06, 09, 18, and 19 were far away from roads so they were not impacted by the traffic.

To assess contamination levels and soil properties, soil samples were manually collected with a flat stainless steel sampling instrument which was covered by a plastic sheet in order to prevent cross contamination between samples from different locations in each sampling site. Surface soil samples were collected within a distance of 10 cm from the structures, and each sample consisted in 100-150 g of soil. The number of collected samples ranged between three and seven for each site, depending on the site

layout and characteristics. An additional representative sample was taken from each site to measure background metal levels in soil, and to determine the particle size distribution. A total of 24 background and 103 potentially contaminated soil samples were collected. Soil samples were placed in plastic zip-lock bags after sampling. Collected samples were air dried at room temperature, sieved (<2 mm), and then refrigerated at 4°C until analysis. All analyses on samples were completed within a few days after sampling.

Table 4.1. The list of sampling sites and their properties

| Number of the site | Name of the site | Type of recreational utility | Materials used |
|---|---|---|---|
| 01 | Ağaç Ev | Picnic area | Wood |
| 02 | Mevlana Park | Playground | Wood |
| 03 | Yunus Emre Park | Park | Wood |
| 04 | Emirgan Koru | Picnic Area | Wood |
| 05 | Mimar Sinan Park | Park | Wood |
| 06 | Belgrad Forest | Picnic Area | Wood |
| 07 | Tarabya Park | Playground | Wood |
| 08 | Ulus Park | Park | Wood |
| 09 | Koç University | Playground | Wood |
| 10 | Ataşehir Park 1 | Playground | Wood |
| 11 | Ataşehir Park 2 | Playground | Wood |
| 12 | Ataşehir Park 3 | Playground | Wood |
| 13 | Ataşehir Park 4 | Playground | Wood |
| 14 | Göksu Park 1 | Playground | Plastic |
| 15 | Göksu Park 2 | Playground | Metal |
| 16 | Kanlıca Park 1 | Playground | Plastic |
| 17 | Kanlıca Park 2 | Playground | Metal |
| 18 | Beykoz Koru | Playground | Plastic |
| 19 | Ünalan Park | Playground | Metal |
| 20 | Örnek Park 1 | Playground | Wood |
| 21 | Örnek Park 2 | Playground | Wood |
| 22 | Hisarüstü Park | Playground | Metal |
| 23 | Çengelköy Park | Park | Wood |
| 24 | Beylerbeyi Park | Playground | Wood |

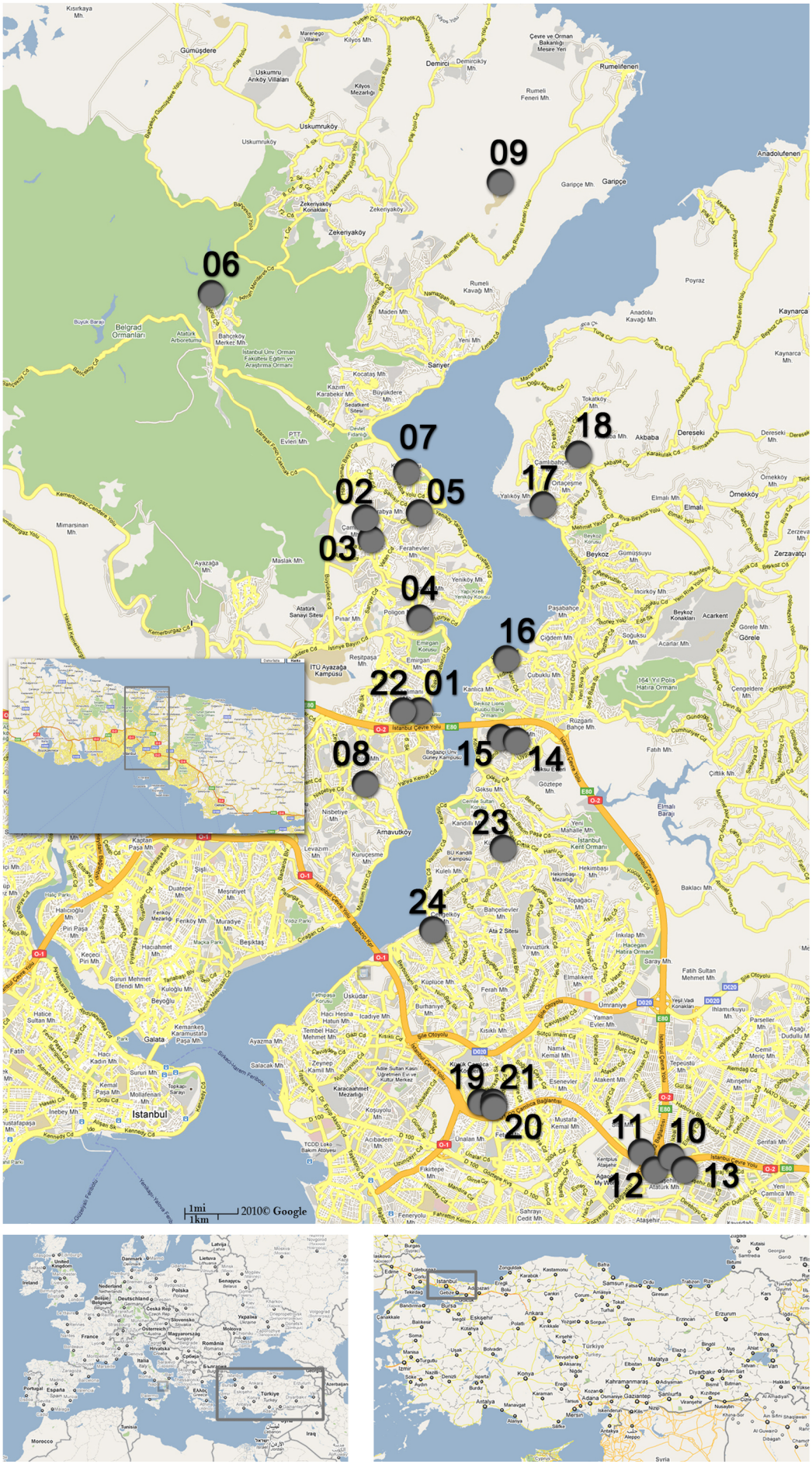


Figure 4.1. The map of sampling sites

## 4.2. Experimental Procedure

All experiments were performed in duplicates for each of the samples from all of the sampling sites.

### 4.2.1. pH

pH is one of the important parameters controlling heavy metal pollution in soils. For this study pH values of soil samples were measured according to ASTM D 4972 – 01 'Standard Test Method for pH of Soils' with a 1:2 soil to water ratio by using Hanna HI 221 microprocessor pH meter (ASTM, 2007).

This measurement determines the degree of acidity or alkalinity in soil materials suspended in water. For this method, begin with an air dried soil that has been sieved through a No. 10 sieve (2 mm holes) to remove the coarser soil fraction is important. Air drying the soil is necessary to accomplish sieving and to control the amount of water present at the time of measurement. Also the soil-water mixture should be at approximately room temperature (15 to 25°C) at the time of pH measurement (ASTM, 2007).

The detailed procedure for the pH measurement of the soil samples used during this study is as follows:

- Calibration of the testing equipment was done by using manufacturer's direction.
- For each sample, approximately 10 g of air dried soil weighed out and placed into a glass container, then approximately 10 mL of deionized water added and mixed thoroughly for 15 minutes by using shaker and let stand for 1 hour.
- When suspended particles settled after 1 hour, pHmeter's electrode was inserted to the aqueous medium and waited until constant pH value.
- Results were reported together with the temperature values of solution. There was no need to apply correction due to temperature since mixture is at approximately room temperature at the time of pH measurement.

### 4.2.2. Carbon Content

Total organic carbon (TOC) analysis was done according to DIN EN 13137 'Determination of total organic carbon (TOC) in waste, sludges and sediments' (European Committee for Standardization, 2001). In this procedure the carbonates present in sample are previously removed by treating the sample with acid. The carbon dioxide released by the following combustion step is measured.

In this study Method B (direct procedure) was applied by first soaking the sample in acid to remove inorganic carbon, and then determining the remaining carbon with Costech Instruments ECS 4010 elemental combustion system.

The detailed procedure followed for carbon content measurement of the soil samples is given below:

- For each sample, approximately 10 g of soil sample which was sieved through <2 mm before was taken as possible as homogeneous into oven treated ceramic crucible with constant weight.
- A few millimeter of $H_3PO_4$ was added in order to remove the inorganic carbon prior to the determination of the TOC. The sample was carefully treated with acid by adding acid slowly and avoiding foaming and splashing of the samples. Acid was added as little as possible but enough to soak the entire sample and to remove the inorganic carbon completely.
- Acid treated sample was taken into centrifuge vessels by washing deionized water and centrifuged by using Nüve NF 1200 centrifuge instrument at 6000 rpm for 5 minutes in order to wash out acid from samples. After centrifuge, sample was taken into owen at 105°C for 24 hours in order to remove moisture before combustion.
- When sample was dried, carbon content of sample was measured by elemental combustion system. According to procedure the combustion temperature has to be high enough to convert the organic carbon completely to carbon dioxide. The temperature range is between 900°C and 1500°C (European Committee for

Standardization, 2001). It was seen that during combustion temperature was 980ºC and appropriate to this range.

### 4.2.3. Metal Concentrations

Heavy metal concentrations of soil samples were determined for all of the sampling points within the scope of this study. Measurement of the pollutants becomes possible when all the desired metals are extracted from the soil media to aqueous phase. For this reason, to determine the heavy metal concentration of samples they were digested by strong acids in order to set metals free into a certain amount of liquid solution. During the digestion, organic part of the soil is completely destroyed, releasing the metal ions bound to it (Güney, 2006).

Total metal concentrations in soils were determined on filtered liquids extracts with Perkin Elmer instruments, Optima 2100 DV ICP-MS after microwave digestion based on EPA Method 3052 'Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices' (USEPA, 1996).

The detailed procedure for metal concentrations of the soil samples used during this study is as follows:

- For each sample, approximately 0.5 g soil sample was taken into vessel of microwave digestion which is made of teflon.
- 9 mL concentrated nitric acid ($HNO_3$), 3 mL concentrated hydrofluoric acid (HF), and 2 mL hydrogen peroxide ($H_2O_2$) were added to sample under a fume hood.
- Vessel's cap was closed and placed into microwave acid digestion instrument.
- Instrument was started.
- When acid digestion process was completed, extract was filtered through <0.45 µm into 50 mL volumetric flask under a fume hood.
- Metal concentration of sample was determined on filtered liquid extract with ICP-MS.

On sites where metal concentrations were found systemically higher than criteria of the Turkish Soil Pollution Control Regulation (TKKY, 2005), soil samples were sieved through <250 μm fraction since it represents the fraction more likely to adhere to children's hands (USEPA, 2008 and Ruby et al., 1996) and metal digestion procedure was repeated on the finer fraction.

A certified reference material (CRM 025-50) were analyzed in order to verify the accuracy and precision of the analytical procedure for metal determination. Certified metal concentrations for CRM 025-050 are 339 $mg.kg^{-1}$ for As, 369 $mg.kg^{-1}$ for Cd, 441 $mg.kg^{-1}$ for Cr, 7.8 $mg.kg^{-1}$ for Cu, 12.2 $mg.kg^{-1}$ for Ni, 1,447 $mg.kg^{-1}$ for Pb and 51.8 $mg.kg^{-1}$ for Zn. All metal concentrations obtained were consistent with the reference values (within the 95% prediction interval). Moreover, ten procedure blanks were tested during total metal determinations and metal concentrations were below-detection limits (50 $\mu g.L^{-1}$) for all metals.

### 4.2.4. Moisture Content

Gravimetric water content of the samples were measured by first having porcelain dishes with constant weight by oven treatment, then putting 10 g of soil sample to 104°C for 24 hours according to ASTM D 2216-05 'Standard Test Method for Laboratory Determination of Water (Moisture) Content of Soil and Rock by Mass'(ASTM, 2005).

The procedure followed is given in detail below:

- Dishes with a constant weight were weighed and their weight were recorded.
- For each sample, approximately 10 g of soil sample was weighed and taken into one of these dishes and total weight of dish and sample was recorded.
- Sample within the dish was placed and let stand in an oven at 105° for 24 hour in order to remove moisture.
- After drying of sample was completed sample within the dish was weighed again and the weight was recorded.

- Then water content of sample was calculated.

Moisture content was calculated according to formula 4.1 (ASTM, 2005):

$$W = \frac{M_{cms} - M_{cds}}{M_{cds} - M_c} x100 = \frac{M_w}{M_s} x100 \quad (4.1)$$

Where:

W: Water content, %

$M_{cms}$: Mass of container and moist specimen, g

$M_{cds}$: Mass of container and oven dry specimen, g

$M_c$: Mass of container, g

$M_w$: Mass of water ($M_w$=$M_{cms}$-$M_{cds}$), g

$M_s$: Mass of oven dry specimen ($M_s$=$M_{cds}$-$M_c$), g

A correction to the metal contents of soils was made according to the following equation (4.2) :

$$C = \frac{C_{ICP}}{W} \times 100 \quad (4.2)$$

Where:

C: Metal concentration of soil, ppm

$C_{ICP}$: Metal concentration found by ICP readings, ppm

W: Gravimetric water content, %

### 4.2.5. Texture Analysis

Particle size distribution was determined according to ASTM D 1140-00 'Standard Test Methods for Amount of Material in Soils Finer than No.200 (75μm) Sieve' (ASTM, 2006) and ASTM D 422-63 'Standard Test Method for Particle-Size Analysis of Soils' (ASTM, 2007).

Soil texture was identified using the United States Department of Agriculture (USDA) classification system (gravel > 2 mm, 2 mm > sand > 0.05 mm, 0.05 mm > silt > 0.002 mm and clay < 0.002 mm).

Texture analysis was done by İstanbul Metropolitan Municipality (İBB) since there was no required equipment for texture analysis in laboratory.

### 4.3. Bioaccessibility and Risk Assessment Calculations

Chemical daily intake for each heavy metal was calculated with equation 4.3 (U.S.EPA, 1989):

$$CDI_{metal} = \frac{EPC \text{ x } SIR \text{ x } EF \text{ x } ED}{BW \text{ x } AT} \text{ xCF} \qquad (4.3)$$

Where:

$CDI_{metal}$: Metal daily intake, $\mu g.kg^{-1}.d^{-1}$

EPC: Exposure point concentration, $mg.kg^{-1}$

SIR: Soil ingestion rate, $mg.d^{-1}$

EF: Exposure frequency, $d.yr^{-1}$

ED: Exposure duration, yr

BW: Body weight, kg

AT: Average time, days

CF: Unit conversion factor of $10^{-3}$

All parameters except exposure point concentrations (EPC) were taken from the literature or selected in accordance with the exposure scenarios. Exposure point concentrations (EPC) were calculated according to metal concentrations of samples.

Relative oral bioavailability (RBA) data can be used to provide a more accurate exposure assessment. In vitro methods are useful as rapid screening tools in assessing relative bioavailability of arsenic at contaminated sites and much cost prohibitive than

animal-based studies (Pouschat and Zagury, 2006). It was seen from Pouschat and Zagury's work (2006) that bioaccessibility values are in agreement with the RBA values stated in literature. Therefore, chemical daily intake (CDI) values were adjusted by using the equation 4.4 which is shown below (Basta et al., 2001).

$$CDI_{adjusted} = CDI_{metal} \text{ x } B \quad (4.4)$$

Where:

$CDI_{adjusted}$: Adjusted metal daily intake, $\mu g.kg^{-1}.d^{-1}$

B: Bioaccessibility, %

Carcinogenic risk was determined according to equation 4.5.

$$Risk = CDI_{adjusted} \text{ x } SF \quad (4.5)$$

Where:

Risk: Probability of carcinogenic effect (unitless)

SF: Cancer slope factor, $(mg.kg^{-1}.d^{-1})^{-1}$

Hazard index (HI) was calculated by using equation 4.6.

$$HI = \frac{CDI_{adjusted}}{RfD} \quad (4.6)$$

Where:

HI: Hazard index

RfD: Reference dose, $mg.kg^{-1}.d^{-1}$

Slope factor (SF) and reference dose (RfD) values were taken from literature.

Statistical evaluation of the data was performed using SPSS 11.5.

# 5. RESULTS AND DISCUSSION

## 5.1. Heavy Metal Pollution in Sampling Locations

In this study Arsenic (As), Cadmium (Cd), Cromium (Cr), Copper (Cu), Nickel (Ni), Lead (Pb) and Zinc (Zn) concentrations in sampling sites were measured. Concentration values of these metals are shown in the following table.

Table 5.1. Metal concentrations of soil samples (<2 mm)

| Site number | Detection limit ($mg.kg^{-1}$) | As | Cd | Cr | Cu | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|---|
| | | (average, $mg.kg^{-1}$ dry soil) | | | | | | |
| 01 | 5.7 | 6.3 | BDL | 50.6 | 93.4 | 33.1 | 11.1 | 72.6 |
| 02 | 6.1 | 6.1 | BDL | 140.6 | 301.9 | 31.2 | 21.2 | 127.0 |
| 03 | 5.4 | 6.7 | BDL | 52.6 | 26.9 | 42.5 | 11.0 | 88.8 |
| 04 | 5.5 | BDL | BDL | 71.4 | 68.9 | 46.7 | 44.9 | 111.4 |
| 05 | 5.8 | 8.9 | 6.1 | 32.7 | 228.3 | BDL | 13.9 | 205.5 |
| 06 | 5.9 | BDL | BDL | 30.2 | 31.3 | 14.7 | 35.9 | 33.3 |
| 07 | 5.5 | BDL | BDL | 35.7 | 24.6 | 17.5 | 6.6 | 22.1 |
| 08 | 5.7 | BDL | BDL | 91.2 | 42.5 | 25.6 | 18.7 | 68.2 |
| 09 | 5.2 | 12.6 | BDL | 36.3 | 35.9 | BDL | BDL | 19.1 |
| 10 | 5.3 | 6.5 | BDL | 185.9 | 230.1 | 20.1 | 13.9 | 182.1 |
| 11 | 5.1 | 6.8 | BDL | 16.1 | 13.0 | 8.9 | BDL | 13.6 |
| 12 | 5.2 | BDL | BDL | 15.3 | 12.4 | BDL | BDL | 13.7 |
| 13 | 5.4 | 8.8 | BDL | 157.8 | 223.4 | 26.1 | 22.0 | 173.8 |
| 14 | 5.6 | 8.2 | BDL | 24.5 | 9.3 | 7.3 | 6.3 | 26.8 |
| 15 | 5.3 | BDL | BDL | BDL | BDL | BDL | BDL | 43.8 |
| 16 | 5.2 | 11.4 | BDL | 33.7 | 17.8 | 6.8 | 7.3 | 38.9 |
| 17 | 5.2 | 5.9 | BDL | 15.8 | 8.2 | 14.2 | 5.6 | 22.0 |
| 18 | 5.4 | 6.5 | BDL | 13.4 | BDL | 8.6 | BDL | 16.5 |
| 19 | 5.3 | BDL | BDL | 15.1 | 11.2 | BDL | BDL | 42.7 |
| 20 | 5.5 | BDL | BDL | 22.0 | 25.5 | 19.1 | BDL | 33.4 |
| 21 | 5.4 | BDL | BDL | 27.7 | 74.3 | 7.0 | 6.5 | 28.6 |
| 22 | 5.4 | BDL | BDL | 24.1 | 22.1 | 18.2 | 10.9 | 64.4 |
| 23 | 5.3 | 8.9 | BDL | 68.0 | 71.9 | 21.3 | 38.4 | 102.3 |
| 24 | 6.0 | BDL | BDL | 24.6 | 21.7 | 18.3 | 18.3 | 46.8 |

BDL: Below Detection Limit

When metal concentrations of samples were considered in respect to Turkish Soil Pollution Control Regulation (TKKY) limit values, it was seen that there was no Ni and Pb pollution in samples, their values were always below the maximum allowable values. In addition, samples from Site 01, 02, 05, 08, 09, 10, 11, 12, 13, 14, 16, and 21 had concentrations of As, Cd, Cr, Cu or Zn, in at least one sample, above the maximum allowable values in Turkish regulations.

The detailed results of metal concentrations measurement in <2 mm fraction was written below:

- In Site 01, Cu concentration in one sample was above regulatory limits. Cd values of two samples out of six samples in this site were above regulatory limits.
- In Site 02, Cr and Cu values were higher than regulatory limits.
- In Site 05, one of the samples's As value exceeded the limit values. Two samples's Zn values and three samples's Cu values were above limits. Also in this site there was Cd pollution.
- In Site 08, Cr concentration in one samples was above the limit value.
- In Site 09, one of the samples's As value exceeded the limit values and Cd values of four samples's out of six samples were above regulatory limits.
- In Site 10, Cd and Zn values exceeded the limit values in one sample and there were Cr and Cu pollution.
- In Site 11, Cd value in one sample exceeded the limit value.
- In Site 12, two out of four samples's Cd values were above limits.
- In Site 13, Cd value exceeded the limit value and three out of four samples's Cr and Cu values were higher than regulatory limits.
- In Site 14, one of the samples's As value exceeded the limit value and two samples's out of four samples Cd values were above limit values.
- In Site 16, one of the samples's As value exceeded the limit value and two samples out of four samples Cd values were above limit values.
- In Site 21, one of the samples's Cu value exceeded the limit value.

Table 5.2. The list of polluted sites (<2 mm) and pollutant types

| Number of the site | Pollution |
|---|---|
| 01 | Cd, Cu |
| 02 | Cr, Cu |
| 05 | As, Cd, Cu, Zn |
| 08 | Cr |
| 09 | As, Cd |
| 10 | Cd, Cr, Cu, Zn |
| 11 | Cd |
| 12 | Cd |
| 13 | Cd, Cr, Cu |
| 14 | As, Cd |
| 16 | As, Cd |
| 21 | Cu |

Pollution levels in site 08, 09, 11, 14, 16, and 21 were not found critical since either measured concentrations did not exceed regulatory values or slightly exceeded them in only one or two sample. Also, Cd pollution in Site 12 and other sites except Site 05 was not considered as critical, since measured concentration slightly exceeded regulatory value and samples of this sites' average did not exceed regulatory value. Another important reason for not considering Cd pollution as critical was due to detection limit. It was about 5 $mg.kg^{-1}$ and above regulatory limit which is 3 $mg.kg^{-1}$. When considering a site as contaminated or not, detection limit was used instead of regulatory limit for Cd in this study. Therefore according to detection limit Cd pollution was significant only in Site 05.

In Sites 01, 02, 05, 10, and 13, metal concentrations systemically higher than the measured background values and they were considered as critically contaminated since their metal concentrations were close to or exceeded the regulatory values.

Contaminated sites (Site 01, 02, 05, 10, and 13) were further analyzed for metal concentrations in the <250 µm soil fraction since particles which have a size about <250 µm is more likely to adhere to children's hands (USEPA, 2008).

Table 5.3. The list of metal concentration values of soil samples (<250 µm)

| Site number | Detection limit ($mg.kg^{-1}$) | As | Cd | Cr | Cu | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|---|
| | | (average, $mg.kg^{-1}$ dry soil) | | | | | | |
| 01 | 5.7 | 12.6 | BDL | 43.0 | 222.7 | 75.1 | 48.6 | 136, |
| 02 | 6.1 | 4.7 | BDL | 120.2 | 371.7 | 36.3 | 33.9 | 117. |
| 05 | 5.8 | 5.3 | BDL | 47.0 | 524.1 | 52.3 | 100.0 | 497. |
| 10 | 5.3 | 4.4 | BDL | 194.1 | 254.7 | 25.7 | 22.9 | 209. |
| 13 | 5.4 | 10.4 | 5.5 | 175,7 | 251.8 | 31.8 | 27.4 | 184. |

BDL: Below Detection Limit

Table 5.4. The list of metal concentration values in background soils and near installed structures in selected sites with critical pollution

| Number of the site | Metal | Fraction | Background | Average | Maximum |
|---|---|---|---|---|---|
| Site 01 (n=6) | As | 2 mm | BDL | 6.3 | 12.1 |
| | Cu | 2 mm | 57.3 | 93.4 | 148 |
| | Ni | 2 mm | BDL | 33.1 | 64.2 |
| Site 02 (n=4) | Cr | 2 mm | 77.4 | 141 | 150 |
| | Cu | 2 mm | 63.7 | 302 | 348 |
| Site 05 (n=4) | As | 2 mm | BDL | 8.9 | 34.2 |
| | Cd | 2 mm | 5.8 | 6.1 | 7.0 |
| | Cu | 2 mm | 63.9 | 228 | 340 |
| | Pb | 2 mm | 76.0 | 13.9 | 40.3 |
| | Zn | 2 mm | 555 | 206 | 357 |
| Site 10 (n=4) | Cr | 2 mm | 89.3 | 186 | 203 |
| | Cu | 2 mm | 44.0 | 230 | 306 |
| | Zn | 2 mm | 77.1 | 182 | 182 |
| Site 13 (n=4) | As | 2 mm | BDL | 8.8 | 13.5 |
| | Cr | 2 mm | 54.6 | 158 | 246 |
| | Cu | 2 mm | 44.0 | 22 | 439 |

The detailed results of metal concentrations measurement in <250 µm fraction is:

- In Site 01 (picnic area), one sample of this site exceeded As limit. Also, Cu and Ni contamination was notable.
- In Site 02 (playground), Cu and Cr values were higher than regulatory values.

- In Site 05 (park), had one sample critically contaminated with Ni. There were Cu and Zn pollution.
- In Site 10 (playground), Cr and Cu values exceeded legal limits in four and three samples out of four samples respectively and one sample had Zn value above regulatory limits.
- In Site 13 (playground), Cr and Cu concentrations were above regulatory limits.

Some important results may be seen if metal concentrations in <2 mm and <250 µm fractions were compared like:

- In Site 01 (picnic area), when there was no As contamination in <2 mm, As contamination was seen in one of the sample in <250 µm. Cd pollution was not seen in finer fraction while in <2 mm fraction it was seen. In finer fraction Cu and Ni pollution was seen and the average concentrations of Cu and Ni in <250 µm fraction were 2 to 2.5 times higher than in <2 mm fraction.
- In Site 02 (playground), Cr and Cu values were higher than regulatory values in both of the fractions.
- In Site 05 (park), one of the sample's As value exceeded the limit values and there were Cd, Cu and Zn pollution significantly in <2 mm fraction. One sample was critically contaminated with Ni and there were Cu and Zn pollution in <250 µm and there were no Cd pollution.
- In Site 10 (playground), Cr and Cu values exceeded legal limits in four and three samples out of four samples respectively and one sample had Zn value above regulatory limits in both of the soil fractions.
- In Site 13 (playground), Cr and Cu pollution was seen in both of the soil fractions. In addition, Cd values in <250 µm fraction Cd pollution was also significant.

In summary, all of critically contaminated sites (Site 01, 02, 05, 10, and 13) were equipped with treated wood structures; however, high concentrations of As, Cr, and Cu concentrations were not attributed to the possible leaching from CCA-treated wood since their concentrations were not jointly higher in soils. High Cu concentrations in these sites may be due to the leaching of a Cu-containing wood preservative more likely

other than CCA such as ACQ or copper azole. High concentrations of other metals may be attributed to other sources such as contaminated backfill, atmospheric deposition or heterogeneity of samples.

### 5.2. Relationships Between Soil Parameters and Metal Pollution

In the selected sampling sites, coarse grained soils were common. Sand, sandy loam and sandy clayey loam soil classes were observed. Soil samples' pH values were between 5.50-8.53. pH values were at neutral values between 7.0-7.50 in most of the samples. Carbon contents of samples were ranged between 0.00-5.40. It was seen that carbon contents were generally lower in sandy soils and carbon contents values were increasing in accordance with silt and clay content.

Classification of soil pollution data according to the type of site as playgrounds, parks and picnic areas and the type of structure as wood, metal and plastic showed that As, Cd, Cu, Cr, or Zn pollution levels exceeded regulatory limits in nine playgrounds (Site 02, 08, 09, 10, 11, 12, 13, 14, 16, and 21) out of 17 in terms of maximum values and one playground (Site 12) out of these playgrounds, one park (Site 05) out of 4, and one picnic area (Site 01) out of 3 were exceeded regulatory values in terms of some samples.

Table 5.5. The list of soil types and sand, silt and clay contents, pH values and carbon content of soil samples

| Number of the site | Soil type | Sand | Silt | Clay | pH values | | Total Organic Carbon (TOC) |
|---|---|---|---|---|---|---|---|
| | | (%) | (%) | (%) | Min. | Max. | (%) |
| 01 | SCL | 52 | 25 | 23 | 6.56 | 7.80 | 1.40 |
| 02 | SL | 67 | 21 | 12 | 7.21 | 8.01 | 3.60 |
| 03 | SL | 63 | 28 | 9 | 6.73 | 7.40 | 3.25 |
| 04 | L | 51 | 31 | 18 | 5.50 | 6.93 | 5.40 |
| 05 | SL | 61 | 21 | 18 | 7.55 | 7.75 | 1.06 |
| 06 | SL | 67 | 21 | 12 | 5.93 | 7.14 | 2.36 |
| 07 | S | 91 | 5 | 4 | 7.54 | 8.03 | 0.08 |
| 08 | SCL | 54 | 26 | 20 | 7.13 | 7.80 | 1.43 |
| 09 | S | 97 | 1 | 2 | 7.77 | 8.53 | 0.02 |
| 10 | SCL | 51 | 27 | 22 | 6.45 | 7.34 | 2.70 |
| 11 | S | 98 | 1 | 1 | 7.69 | 7.93 | 0.00 |
| 12 | S | 98 | 1 | 1 | 7.02 | 7.93 | 0.01 |
| 13 | SCL | 55 | 23 | 22 | 6.48 | 7.37 | 2.38 |
| 14 | S | 93 | 4 | 3 | 7.20 | 7.79 | 0.33 |
| 15 | S | 97 | 1 | 2 | 7.43 | 7.77 | 0.10 |
| 16 | S | 91 | 5 | 4 | 7.45 | 8.22 | 0.42 |
| 17 | S | 96 | 3 | 1 | 7.62 | 8.03 | 0.11 |
| 18 | S | 95 | 4 | 1 | 7.44 | 7.72 | 0.26 |
| 19 | LS | 85 | 13 | 2 | 7.34 | 7.57 | 0.49 |
| 20 | S | 94 | 4 | 2 | 7.32 | 7.77 | 0.15 |
| 21 | S | 94 | 3 | 3 | 7.26 | 7.75 | 0.22 |
| 22 | S | 92 | 6 | 2 | 7.25 | 7.68 | 0.94 |
| 23 | SL | 69 | 18 | 13 | 7.66 | 8.03 | 1.25 |
| 24 | SCL | 50 | 24 | 26 | 7.40 | 7.80 | 1.90 |

S : Sand
SL: Sandy loam
SCL : Sandy clayey loam
L : Loam

The majority of the contaminated sites were playgrounds however, there is not enough data to conclude that the type of site affects pollution characteristics of the soils. There were 11 sites with elevated soil concentrations except Site 12. Nine of these sites were equipped with treated wood structures, and two of them with plastic structures.

When these sites were considered in order to find out that there was a relationship between contamination from CCA-treated wood structures and metal concentrations, except sites with plastic structures and Site 12, it may be concluded as follow:

- Cu contamination on six site (Site 01, 02, 05, 10, 13, and 21) may be attributed to the leaching from wood treated with Cu containing preservatives,
- Elevated As, Cr and Cu concentrations of samples in Site 08 may be attributed to leaching from CCA-treated wood,
- Elevated metal concentrations in individual samples of Site 09 may be thought due to the heterogeneity of the collected samples.

For the calculations of the concentration average and standard deviations, any concentration lower than the detection limit was taken equal to 3 $mg.kg^{-1}$ which is half of the detection limit.

Table 5.6. The list of average concentrations, standard deviations and maximum values for soil metal concentrations (< 2mm fraction) categorized by type of site and type of installed structure

| | | As | Cd | Cr | Cu | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|---|
| Playgrounds | Average | 6.1 | BDL | 46 | 60.0 | 13.6 | 8.4 | 53.0 |
| | St. Dev. | 6.7 | BDL | 56.3 | 100 | 9.4 | 7.6 | 58.4 |
| | Maximum | 42.8 | 11 | 246 | 439 | 37.1 | 37.4 | 305 |
| Parks | Average | 8.1 | BDL | 61.1 | 92.4 | 23.1 | 22.1 | 116 |
| | St. Dev. | 7.5 | BDL | 42.5 | 96.2 | 16.2 | 16.4 | 88.3 |
| | Maximum | 34.2 | 6.7 | 200 | 340 | 47.8 | 52.3 | 357 |
| Picnic areas | Average | BDL | BDL | 47.1 | 62 | 28.7 | 30 | 65.6 |
| | St. Dev. | BDL | BDL | 19.1 | 34.5 | 17.6 | 16.5 | 33.4 |
| | Maximum | 12.1 | BDL | 84.5 | 148 | 64.2 | 56.6 | 126 |

Table 5.7. The list of average concentrations, standard deviations and maximum values for soil metal concentrations (< 2mm fraction) categorized by type of installed structure

| | | As | Cd | Cr | Cu | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|---|
| Wood Structures | Average | 6.2 | BDL | 60.3 | 86.6 | 20.4 | 17.7 | 76.5 |
| | St. Dev. | 6.2 | BDL | 54 | 99.7 | 14.3 | 15.2 | 70.9 |
| | Maximum | 42.8 | 11 | 246 | 439 | 64.2 | 56.6 | 357 |
| Plastic Structures | Average | 9.1 | BDL | 23.8 | 10.5 | 10.5 | BDL | 27.4 |
| | St. Dev. | 9.8 | BDL | 10.7 | 9.5 | 7.5 | BDL | 12.6 |
| | Maximum | 31.3 | 6.80 | 40.1 | 38.6 | 23.2 | 12.8 | 56.9 |
| Metal Structures | Average | BDL | BDL | 14.5 | 11 | 10.3 | BDL | 43.2 |
| | St. Dev. | BDL | BDL | 8.8 | 8.9 | 7.7 | BDL | 30 |
| | Maximum | 7.10 | BDL | 32.4 | 37.2 | 24.7 | 17.1 | 116 |

Highest and mean concentrations of As near treated wood structures were comparable to the values which were reported by Cookson's study (2008) conducted in Melbourne, Australia and Ljung and colleagues' study in Uppsala, Sweden (2006). However, As concentrations in a park located in Seoul, South Korea with various 1 yr-old CCA-treated wood structures measured by Kim and his colleagues (2007) and in a playground located in Miami, Florida with treated wood structures conducted by Townsend et al. (2003) were higher than measured concentrations in this study. The values of mentioned studies were in the range of 15.0 to 79.8 $mg.kg^{-1}$ and 33.9 $mg.kg^{-1}$, respectively (Kim et al., 2007 and Townsend et al., 2003). Furthermore concentrations of metals in this study were not in agreement with the values which found near CCA-treated utility poles (Zagury et al., 2003 and Pouschat and Zagury, 2006-2008). Concentrations of metals in this study were in the order of Cu>Cr>As while stated order as Cu>As>Cr. There was a relationship between increased Cu concentrations in soil and the presence of treated wood structures, which indicates that Cu-containing wood preservatives other than CCA or a different type of CCA may be used in order to treat the structures in sampling sites of this study.

Correlation analysis was performed for metal average concentrations (As, Cd, Cr, Cu, Ni, Pb and Zn) in <2 mm and soil properties (pH, TOC, sand, silt and clay percentages) with data from the 17 sites equipped with treated wood structures. Pearson

correlation values between As – Cr (0.311) and As – Cu (0.438) showed no indication that As, Cr and Cu were originating from a common source, namely CCA-treated wood. In general metal concentrations were negatively correlated with pH and sand content, and were positively correlated with TOC values, silt and clay percentages. Cu and Cr concentrations were strongly related to each other (0.760), but weakly to As. This may be explained by the faster removal of As by leaching especially in sandy soils. Cu concentrations also were related to Ni, Pb and Zn. These relationships and further significant correlations between Cd – Cr, Ni – Pb and Zn – Cr were thought to exist due to another cofactor such as TOC or clay content, however, further investigation was needed to prove this. Significant As – clay correlation was reported in the literature for playground soils (Ljung et al., 2006), but in this study that correlation was weak (0.076).

Table 5.8. The list of minimum and maximum concentrations, standard deviations and mean values for soil metal concentrations and soil properties for wood structure installed sites (< 2mm fraction)

| | N | Minimum | Maximum | Mean | Std. Deviation |
|---|---|---|---|---|---|
| As | 17 | 0.00 | 12.60 | 4.21 | 4.35 |
| Cd | 17 | 0.00 | 6.10 | 0.36 | 1.48 |
| Cr | 17 | 15.30 | 185.90 | 6.28 | 52.19 |
| Cu | 17 | 12.40 | 301.90 | 89.77 | 93.59 |
| Ni | 17 | 0.00 | 46.70 | 19.53 | 13.95 |
| Pb | 17 | 0.00 | 44.90 | 15.43 | 13.84 |
| Zn | 17 | 13.60 | 205.50 | 79.00 | 62.72 |
| Sand | 17 | 50.00 | 98.00 | 71.29 | 19.26 |
| Silt | 17 | 1.00 | 31.00 | 16.47 | 11.10 |
| Clay | 17 | 1.00 | 26.00 | 12.23 | 8.83 |
| $pH_{min}$ | 17 | 5.50 | 7.77 | 7.01 | 0.65 |
| $pH_{max}$ | 17 | 6.93 | 8.53 | 7.72 | 0.38 |
| TOC | 17 | 0.00 | 5.40 | 1.60 | 1.54 |

Table 5.9. Correlation between soil metal content and soil properties for wood structure installed sites (< 2mm fraction) (N=17)

| | | As | Cd | Cr | Cu | Ni | Pb | Zn | Sand | Silt | Clay | pHmin | pHmax | TOC |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| As | Pearson Correlation | 1 | 0.277 | 0.311 | 0.438 | -0.108 | -0.086 | 0.449 | -0.063 | 0.050 | 0.076 | 0.285 | 0.333 | -0.026 |
| | Sig. (2-tailed) | . | 0.281 | 0.225 | 0.079 | 0.681 | 0.743 | 0.071 | 0.809 | 0.850 | 0.772 | 0.268 | 0.191 | 0.923 |
| Cd | Pearson Correlation | 0.277 | 1 | -0.146 | 0.381 | -0.361 | -0.029 | 0.520* | -0.138 | 0.105 | 0.168 | 0.214 | 0.017 | -0.090 |
| | Sig. (2-tailed) | 0.281 | . | 0.576 | 0.131 | 0.155 | 0.913 | 0.032 | 0.598 | 0.688 | 0.519 | 0.410 | 0.947 | 0.730 |
| Cr | Pearson Correlation | 0.311 | -0.146 | 1 | 0.760** | 0.418 | 0.326 | 0.714** | -0.555* | 0.544* | 0.527* | -0.343 | -0.298 | 0.542* |
| | Sig. (2-tailed) | 0.225 | 0.576 | . | 0.000 | 0.095 | 0.202 | 0.001 | 0.021 | 0.024 | 0.030 | 0.178 | 0.245 | 0.025 |
| Cu | Pearson Correlation | 0.438 | 0.381 | 0.760** | 1 | 0.122 | 0.207 | 0.845** | -0.434 | 0.401 | 0.443 | -0.121 | -0.136 | 0.398 |
| | Sig. (2-tailed) | 0.079 | 0.131 | 0.000 | . | 0.641 | 0.426 | 0.000 | 0.082 | 0.111 | 0.075 | 0.643 | 0.604 | 0.114 |
| Ni | Pearson Correlation | -0.108 | -0.361 | 0.418 | 0.122 | 1 | 0.531* | 0.282 | -622** | 0.721** | 0.452 | -0.592* | -0.545* | 0.791** |
| | Sig. (2-tailed) | 0.681 | 0.155 | 0.095 | 0.641 | . | 0.028 | 0.274 | 0.008 | 0.001 | 0.069 | 0.012 | 0.024 | 0.000 |
| Pb | Pearson Correlation | -0.086 | -0.029 | 0.326 | 0.207 | 0.531* | 1 | 0.400 | -649** | 0.691** | 0.548* | -0.581* | -0.578* | 0.735** |
| | Sig. (2-tailed) | 0.743 | 0.913 | 0.202 | 0.426 | 0.028 | . | 0.111 | 0.005 | 0.002 | 0.023 | 0.015 | 0.015 | 0.001 |
| Zn | Pearson Correlation | 0.449 | 0.520* | 0.714** | 0.845** | 0.282 | 0.400 | 1 | -677** | 0.661** | 0.645** | -0.270 | -0.390 | 0.537* |
| | Sig. (2-tailed) | 0.071 | 0.032 | 0.001 | 0.000 | 0.274 | 0.111 | . | 0.003 | 0.004 | 0.005 | 0.295 | 0.122 | 0.026 |

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

## 5.3. Risk Assessment

An exposure assessment was performed for critically contaminated sites (Site 01, 02, 05, 10, 13). Two scenarios were considered which were involuntary soil ingestion and soil pica behaviour. In accordance with the exposure assessment, the average metal daily intakes of metals calculated by considering contaminant source as soil, release mechanism as adherence of contaminated soil to hands and exposure route as ingestion. Risk characterization was done on chronic basis by calculating carcinogenic risk for As and hazard index values for As, Cd, Cr (III), Cu, and Zn. In order to calculate carcinogenic risk and hazard index values slope factors and reference dose values were taken from IRIS (Integrated Risk Information System) database (USEPA, 2009).

Cr (VI) ions which may be present in contaminated soil is easily reduced to Cr (III) under gastric conditions, therefore toxicological profile of Cr (III) was used instead of Cr (VI) (Pouschat and Zagury, 2008).

### 5.3.1. Chemical Daily Intake (CDI)

In this study, average chemical daily intakes of metals were calculated based on the equations presented Materials and Methods Section. Exposure point concentrations (EPC) in the involuntary scenario were taken as the average concentrations of metals in the <250 μm soil fraction while in the soil pica behaviour scenario they were taken as the average concentrations of metals in the <2 mm soil fraction for each critically contaminated site. The reason for using concentrations in different soil fractions was that while the children who have no soil pica behaviour ingest just soils which adhere their hands in <250 μm fraction, the children with soil pica behaviour ingest soils in <2 mm fraction. It was considered that a child between 2-6 years old since in these years soil eating behaviour is common. The soil ingestion rate (SIR) for involuntary soil ingestion scenario and soil pica behaviour scenario were 0.1 $g.d^{-1}$ and 1 $g.d^{-1}$ respectively (USEPA, 2008). Exposure frequency (EF) was selected as 180 $d.yr^{-1}$ for parks and playgrounds, and 50 $d.yr^{-1}$ for picnic areas. Body weight (BW) was taken as 18.6 kg for ages 3-6 (USEPA, 2008). Averaging time (AT) was taken as 70x365 days

which is considered as entire spanlife for assessing the carcinogenic risk of As, 5x365 days (from age 2 to 6) which is considered as total exposure duration (ED) for assessing non-carcinogenic risk.

After calculating average chemical daily intakes of metals, they were adjusted by using bioaccessibility values. Gastrointestinal average bioaccessibility values which were determined on the <250 µm fraction of As, Cr, and Cu for CCA-contaminated sandy soils with moderate to high organic content, were taken as 45.8% for As (range: 30.9-51.2%) (Girouard and Zagury, 2009), 19.4% for Cr (range: 9.9-32.9%) and 81.2% for Cu (range: 62.2-89.4%) (Pouschat and Zagury, 2008). An average bioaccessibility value on the <250 µm fraction of 27% Zn in residential soils is reported in the literature (Poggio et al., 2009) and it was used for this study. Bioaccessibility of Cd was assumed to be 59% as reported by Morman and co-workers and it was taken into account (Morman et al., 2009).

Table 5.10. Exposure assessment for As, Cd, Cr, Cu, and Zn in critically contaminated sites for children 2 – 6 years old

| | | Exposure Assessment | | | | | |
|---|---|---|---|---|---|---|---|
| | | Chemical daily intake ($\mu g.kg^{-1}.d^{-1}$) | | | | | |
| | | Carcinogenic | Non-carcinogenic | | | | |
| Loc. | Behaviour | As | As | Cd | Cr | Cu | Zn |
| 01 | Normal | 3.03E-04 | 4.25E-03 | * | 6.14E-03 | 1.33E-01 | 2.72E-02 |
| | Soil Pica | 1.53E-03 | 2.14E-02 | * | 7.23E-02 | 5.58E-01 | 1.44E-01 |
| 02 | Normal | * | * | * | 6.18E-02 | 8.00E-01 | 8.43E-02 |
| | Soil Pica | 5.31E-02 | 0.743 | * | 7.23E+00 | 6.50E+01 | 9.14E+00 |
| 05 | Normal | * | * | * | 2.42E-02 | 1.13E+00 | 3.56E-01 |
| | Soil Pica | 7.71E-02 | 1.08E+00 | 0.955 | 1.68E+00 | 4.91E+01 | 1.47E+01 |
| 10 | Normal | * | * | * | 9.98E-02 | 5.48E-01 | 1.50E-01 |
| | Soil Pica | 5.60E-02 | 0.784 | * | 9.56E+00 | 4.95E+01 | 1.30E+01 |
| 13 | Normal | 8.99E-04 | 1.26E-02 | 8.63E-03 | 9.04E-02 | 5.42E-01 | 1.32E-01 |
| | Soil Pica | 7.64E-02 | 1.07E+00 | * | 8.12E+00 | 4.81E+01 | 1.24E+01 |

*: Not calculated since average exposure point concentrations were below detection limit

Calculations for average chemical daily intake values for As, Cr and Cu yielded similar findings for involuntary soil ingestion scenario to the previous studies on CCA-treated wood poles (Pouschat and Zagury, 2006-2008). As seen in Table 5.10, chemical daily intake values for As were calculated. When As concentrations in the <250 μm soil fraction were above the detection limit in Site 01 and Site 13 out of the five critically contaminated sites, they were above the detection limit in all of the critically contaminated sites in <2 mm soil fraction. Cd concentrations were above detection limits in <2 mm fraction and <250 μm in Site 05 and 13 respectively. For these sites chemical daily intake values for Cd were calculated. Also Cr, Cu and Zn values were above detection limits in both of the soil fractions. Chemical daily intake values for Cr, Cu and Zn were calculated

### 5.3.2. Carcinogenic Risk

Carcinogenic risk of As was calculated by taking slope factor as 1.5 $kg.d.mg^{-1}$.

In terms of carcinogenic risk, the calculated chemical daily intake value for As in soil pica behaviour scenario exceeded $1\times10^{-6}$ in critically contaminated sites due to the high frequency and long duration of exposure, and relatively low bodyweight although As concentrations were below the Turkish regulatory values (20 $mg.kg^{-1}$).

However, risk values of the present study were higher than the study reported a risk of $4.9\times10^{-7}$ for children between 2 and 6 years old exposed to CCA-treated wood, using a reasonable maximum exposure value for ingestion, dermal and inhalation exposure pathways by Dube and his co-workers (2004). For soil pica behaviour, Ljung et al (2006) reported that tolerable daily intake values for As exceeded the acceptable level of 1 $\mu g.kg^{-1}.d^{-1}$ (assuming 10 $g.d^{-1}$ of ingestion, bioaccessibility was not taken into account) for each of the 25 playgrounds tested in Uppsala, Sweden. As daily background As exposure from other sources already poses a certain carcinogenic risk for children, additional risk exceeding $1\times10^{-6}$ under the scenario of soil pica behaviour for the children should be considered important.

Table 5.11. Carcinogenic risk vaules for As in critically contaminated sites for children 2 – 6 years old

| | | Carcinogenic Risk |
|---|---|---|
| Loc | Behaviour | As |
| 01 | Normal | 4.55E-07 |
| | Soil Pica | 2.29E-06 |
| 02 | Normal | * |
| | Soil Pica | 7.96E-06 |
| 05 | Normal | * |
| | Soil Pica | 1.16E-05 |
| 10 | Normal | * |
| | Soil Pica | 8.40E-06 |
| 13 | Normal | 1.35E-06 |
| | Soil Pica | 1.15E-05 |

*: Not calculated since average exposure point concentrations were below detection limit

### 5.3.3. Hazard Index (HI)

The toxic risk was calculated for each of the heavy metals considered in this study. Reference dose values were taken as 0.3 $\mu g.kg^{-1}.d^{-1}$ for As, 0.1 $\mu g.kg^{-1}$ for Cd, 1.5 $mg.kg^{-1}.d^{-1}$ for Cr(III), and 0.3 $mg.kg^{-1}.d^{-1}$ for Zn. Hazard index was not calculated for Cu since there is no reference dose value stated in the literature. Instead, a tolerable daily intake value of 140 $\mu g.kg^{-1}.d^{-1}$ (Baars et al., 2001) was used for the comparison with results.

Table 5.12. Hazard index values for As, Cd, Cr, Cu, and Zn in critically contaminated sites for children 2 – 6 years old

| | | Hazard Index | | | | |
|---|---|---|---|---|---|---|
| Loc | Behaviour | As | Cd | Cr | Cu | Zn |
| 01 | Normal | 0.014 | * | <0.001 | NC | <0.001 |
| | Soil Pica | 0.071 | * | <0.001 | NC | <0.001 |
| 02 | Normal | * | * | <0.001 | NC | <0.001 |
| | Soil Pica | 0.248 | * | <0.001 | NC | 0.003 |
| 05 | Normal | * | * | <0.001 | NC | 0.001 |
| | Soil Pica | 0.360 | 0.095 | <0.001 | NC | 0.005 |
| 10 | Normal | * | * | <0.001 | NC | 0.001 |
| | Soil Pica | 0.261 | * | 0.001 | NC | 0.004 |
| 13 | Normal | 0.042 | 0.009 | <0.001 | NC | <0.001 |
| | Soil Pica | 0.356 | * | 0.001 | NC | 0.004 |

*: Not calculated since average exposure point concentrations were below detection limit

NC: Reference dose is not available for Cu, tolerable daily intake is stated as 140 $mg.kg^{-1}.d^{-1}$ by Baars et al. (2001).

For the non-carcinogenic risk, hazard index values for As, Cd, Cr and Zn under both soil ingestion scenarios were less than one in the five critically contaminated sites. However, keeping in mind that background exposure for As from other sources is already 0.3 $\mu g.kg^{-1}.d^{-1}$, which is equal to reference dose used in HI calculations, additional arsenic uptake from playground soils always leads to a combined HI value larger than 1. For Cu, exposure values were well below the daily background exposure and tolerable daily intake. Therefore, toxic risk for these metals appears below dangerous levels even for soil pica behaviour.

### 5.3.4. Sensitivity Analysis

A sensitivity analysis was done with different soil ingestion rates, body weights, exposure frequencies and bioaccessibilities for selected heavy metals in this study. Sensitivity analysis is done within the limits of realistic values.

The soil ingestion rate is the factor with the highest uncertainty due to the significant limitations in methodologies used in ingestion studies such as bias in sample selection, poor representation of target populations in terms of race, ethnicity and socioeconomic situation, low reproducibility and limited or absent quality control and assurance (USEPA, 2008). Variations in ingestion rate findings inside a given study and between different studies are very high (in the order of $10^3$ in some cases) and individual observations exceeding 50 $g.d^{-1}$ have been reported in many studies (USEPA, 2008). Soil ingestion rate was selected as 10 $g.d^{-1}$ for soil pica behaviour as reported by USEPA and risk values calculated. Calculated carcinogenic risk values for As and hazard index values for selected heavy metals were tabulated as Table 5.13. It was seen that when soil ingestion rate increased, carcinogenic risk and hazard index values increased. As seen from the table carcinogenic risk of As was higher than $1x10^{-6}$ in all of the sites and hazard index of As was higher than one in Site 02, 05, 10, and 13. Hazard index values of Cd, Cr, Cu, and Zn was not higher than one.

Body weight is another important value which is dependant to many factors such as, females are likely to weigh less than males. According to EPA's handbook their corresponding average and $10^{th}$ percentile value is 13.8 and 11.0 kg for ages 2-3 (USEPA, 2008). Toddlers which are just learned to walk are exposed to risk due to their frequent hand to mouth activity behaviour. When body weights were considered as 11.0 kg and 13.8 kg chemical daily intake values and calculated risk were as shown below. It was seen that carcinogenic risk values were in the range of $1.03x10^{-5}$ and $7.69x10^{-7}$ when body weight was considered as 11.0 kg and $1.54x10^{-5}$and $6.13x10^{-7}$ when body weight was considered as 13.8 kg. Hazard index values of As which were calculated for these body weights were between 0.024 and 0.608 for body weight 11 kg and 0.019 and 0.485 for body weight 13.8 kg. The values of other heavy metals which were focused on this study were shown in the Table 5.14. It was seen that when body weight decreased, carcinogenic risk and hazard index values increased which demonstrated that children with low body weight are more sensitive than others. Carcinogenic risk of As in soil pica behaviour scenario was higher than $1x10^{-6}$ for all of the body weight values used in sensitivity analysis. Hazard index values of As, Cd, Cr, Cu, and Zn was not higher than one.

Table 5.13. Comparison of exposure assessment and risk characterization for different soil ingestion rate values

| | | | Exposure Assessment | | | | | | Risk Characterization | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Chemical daily intake ($\mu g.kg^{-1}.d^{-1}$) | | | | | | Carcinogenic Risk | Hazard Index | | | | |
| | | | Carcinogenic | Non-carcinogenic | | | | | | | | | | |
| Loc. | SIR ($g.d^{-1}$) | Behaviour | As | As | Cd | Cr | Cu | Zn | As | As | Cd | Cr | Cu | Zn |
| 01 | 0.1 | Normal | 3.03E-04 | 4.25E-03 | * | 6.14E-03 | 1.33E-01 | 2.72E-02 | 4.55E-07 | 0.014 | * | <0.001 | NC | <0.001 |
| | 1.0 | Soil Pica | 1.53E-03 | 2.14E-02 | * | 7.23E-02 | 5.58E-01 | 1.44E-01 | 2.29E-06 | 0.071 | * | <0.001 | NC | <0.001 |
| | 10 | Soil Pica | 1.53E-02 | 2.14E-01 | * | 7.23E-01 | 5.58E+00 | 1.44E+00 | 2.29E-05 | 0.714 | * | <0.001 | NC | 0.005 |
| 02 | 0.1 | Normal | * | * | * | 6.18E-02 | 8.00E-01 | 8.43E-02 | * | * | * | <0.001 | NC | <0.001 |
| | 1.0 | Soil Pica | 5.31E-02 | 0.743 | * | 7.23E+00 | 6.50E+01 | 9.14E+00 | 7.96E-05 | 2.476 | * | 0.005 | NC | 0.030 |
| | 10 | Soil Pica | 5.31E-03 | 0.074 | * | 7.23E-01 | 6.50E+00 | 9.14E-01 | 7.96E-06 | 0.248 | * | <0.001 | NC | 0.003 |
| 05 | 0.1 | Normal | * | * | * | 2.42E-02 | 1.13E+00 | 3.56E-01 | * | * | * | <0.001 | NC | 0.001 |
| | 1.0 | Soil Pica | 7.71E-02 | 1.08E+00 | 0.955 | 1.68E+00 | 4.91E+01 | 1.47E+01 | 1.16E-04 | 3.597 | 0.955 | 0.001 | NC | 0.049 |
| | 10 | Soil Pica | 7.71E-03 | 1.08E-01 | 0.095 | 1.68E-01 | 4.91E+00 | 1.47E+00 | 1.16E-05 | 0.360 | 0.095 | <0.001 | NC | 0.005 |
| 10 | 0.1 | Normal | * | * | * | 9.98E-02 | 5.48E-01 | 1.50E-01 | * | * | * | <0.001 | NC | 0.001 |
| | 1.0 | Soil Pica | 5.60E-02 | 0.784 | * | 9.56E+00 | 4.95E+01 | 1.30E+01 | 8.40E-05 | 2.615 | * | 0.006 | NC | 0.043 |
| | 10 | Soil Pica | 5.60E-03 | 0.078 | * | 9.56E-01 | 4.95E+00 | 1.30E+00 | 8.40E-06 | 0.261 | * | 0.001 | NC | 0.004 |
| 13 | 0.1 | Normal | 8.99E-04 | 1.26E-02 | 8.63E-03 | 9.04E-02 | 5.42E-01 | 1.32E-01 | 1.35E-06 | 0.042 | 0.009 | <0.001 | NC | <0.001 |
| | 1.0 | Soil Pica | 7.64E-02 | 1.07E+00 | * | 8.12E+00 | 4.81E+01 | 1.24E+01 | 1.15E-04 | 3.565 | * | 0.005 | NC | 0.041 |
| | 10 | Soil Pica | 7.64E-03 | 1.07E-01 | * | 8.12E-01 | 4.81E+00 | 1.24E+00 | 1.15E-05 | 0.356 | * | 0.001 | NC | 0.004 |

*: Not calculated since average exposure point concentrations were below detection limit

NC: Reference dose is not available for Cu, tolerable daily intake is stated as 140 $mg.kg^{-1}.d^{-1}$ by Baars et al. (2001).

Table 5.14. Comparison of exposure assessment and risk characterization for different body weight values

| | | | Exposure Assessment | | | | | | Risk | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Chemical Daily Intake (μg.kg$^{-1}$.d$^{-1}$) | | | | | | Carcinogenic Risk | Hazard Index | | | | |
| | | | Carcinogenic | Non-arcinogenic | | | | | | | | | | |
| Loc. | BW (kg) | Behaviour | As | As | Cd | Cr | Cu | Zn | As | As | Cd | Cr | Cu | Zn |
| 01 | 18.6 | Normal | 3.03E-04 | 4.25E-03 | * | 6.14E-03 | 1.33E-01 | 2.72E-02 | 4.55E-07 | 0.014 | * | <0.001 | NC | <0.001 |
| | | Soil Pica | 1.53E-03 | 2.14E-02 | * | 7.23E-02 | 5.58E-01 | 1.44E-01 | 2.29E-06 | 0.071 | * | <0.001 | NC | <0.001 |
| | 13.8 | Normal | 4.09E-04 | 5.72E-03 | * | 8.27E-03 | 1.79E-01 | 3.66E-02 | 6.13E-07 | 0.019 | * | <0.001 | NC | <0.001 |
| | | Soil Pica | 2.06E-03 | 2.89E-02 | * | 9.74E-02 | 7.53E-01 | 1.95E-01 | 3.09E-06 | 0.096 | * | <0.001 | NC | 0.001 |
| | 11 | Normal | 5.13E-04 | 7.18E-03 | * | 1.04E-02 | 2.25E-01 | 4.59E-02 | 7.69E-07 | 0.024 | * | <0.001 | NC | <0.001 |
| | | Soil Pica | 2.59E-03 | 3.62E-02 | * | 1.22E-01 | 9.44E-01 | 2.44E-01 | 3.88E-06 | 0.121 | * | <0.001 | NC | 0.001 |
| 02 | 18.6 | Normal | * | * | * | 6.18E-02 | 8.00E-01 | 8.43E-02 | * | * | * | <0.001 | NC | <0.001 |
| | | Soil Pica | 5.31E-03 | 0.074 | * | 7.23E-01 | 6.50E+00 | 9.14E-01 | 7.96E-06 | 0.248 | * | <0.001 | NC | 0.003 |
| | 13.8 | Normal | * | * | * | 8.34E-02 | 1.08E+00 | 1.14E-01 | * | * | * | <0.001 | NC | <0.001 |
| | | Soil Pica | 5.46E-03 | 0.076 | * | 9.75E-01 | 8.76E+00 | 1.23E+00 | 8.18E-06 | 0.255 | * | 0.001 | NC | 0.004 |
| | 11 | Normal | * | * | * | 1.05E-01 | 1.35E+00 | 1.43E-01 | * | * | * | <0.001 | NC | <0.001 |
| | | Soil Pica | 6.84E-03 | 0.096 | * | 1.22E+00 | 1.10E+01 | 1.55E+00 | 1.03E-05 | 0.319 | * | 0.001 | NC | 0.005 |
| 05 | 18.6 | Normal | * | * | * | 2.42E-02 | 1.13E+00 | 3.56E-01 | * | * | * | <0.001 | NC | 0.001 |
| | | Soil Pica | 7.71E-03 | 1.08E-01 | 0.095 | 1.68E-01 | 4.91E+00 | 1.47E+00 | 1.16E-05 | 0.360 | 0.095 | <0.001 | NC | 0.005 |
| | 13.8 | Normal | * | * | * | 3.26E-02 | 1.52E+00 | 4.80E-01 | * | * | * | <0.001 | NC | 0.002 |
| | | Soil Pica | 1.04E-02 | 1.45E-01 | 0.018 | 2.27E-01 | 6.62E+00 | 1.98E+00 | 1.56E-05 | 0.485 | 0.018 | <0.001 | NC | 0.007 |
| | 11 | Normal | * | * | * | 4.09E-02 | 1.91E+00 | 6.02E-01 | * | * | * | <0.001 | NC | 0.002 |
| | | Soil Pica | 1.30E-02 | 1.82E-01 | 0.023 | 2.84E-01 | 8.31E+00 | 2.49E+00 | 1.95E-05 | 0.608 | 0.023 | <0.001 | NC | 0.008 |
| 10 | 18.6 | Normal | * | * | * | 9.98E-02 | 5.48E-01 | 1.50E-01 | * | * | * | <0.001 | NC | 0.001 |
| | | Soil Pica | 5.60E-03 | 0.078 | * | 9.56E-01 | 4.95E+00 | 1.30E+00 | 8.40E-06 | 0.261 | * | 0.001 | NC | 0.004 |
| | 13.8 | Normal | * | * | * | 1.35E-01 | 7.39E-01 | 2.02E-01 | * | * | * | <0.001 | NC | 0.001 |
| | | Soil Pica | 5.12E-03 | 0.072 | * | 1.29E+00 | 6.68E+00 | 1.76E+00 | 7.68E-06 | 0.239 | * | 0.001 | NC | 0.006 |
| | 11 | Normal | * | * | * | 1.69E-01 | 9.27E-01 | 2.54E-01 | * | * | * | <0.001 | NC | 0.001 |
| | | Soil Pica | 6.43E-03 | 0.090 | * | 1.62E+00 | 8.38E+00 | 2.20E+00 | 9.64E-06 | 0.300 | * | 0.001 | NC | 0.007 |
| 13 | 18.6 | Normal | 8.99E-04 | 1.26E-02 | 8.63E-03 | 9.04E-02 | 5.42E-01 | 1.32E-01 | 1.35E-06 | 0.042 | 0.009 | <0.001 | NC | <0.001 |
| | | Soil Pica | 7.64E-03 | 1.07E-01 | * | 8.12E-01 | 4.81E+00 | 1.24E+00 | 1.15E-05 | 0.356 | * | 0.001 | NC | 0.004 |
| | 13.8 | Normal | 1.21E-03 | 1.70E-02 | 1.16E-02 | 1.22E-01 | 7.31E-01 | 1.78E-01 | 1.82E-06 | 0.057 | 0.012 | <0.001 | NC | 0.001 |
| | | Soil Pica | 1.03E-02 | 1.44E-01 | * | 1.09E+00 | 6.48E+00 | 1.68E+00 | 1.54E-05 | 0.480 | * | 0.001 | NC | 0.006 |
| | 11 | Normal | 1.52E-03 | 2.13E-02 | 1.46E-02 | 1.53E-01 | 9.17E-01 | 2.23E-01 | 2.28E-06 | 0.071 | 0.015 | <0.001 | NC | 0.001 |
| | | Soil Pica | 1.29E-02 | 1.81E-01 | * | 1.37E+00 | 8.13E+00 | 2.10E+00 | 1.94E-05 | 0.603 | * | 0.001 | NC | 0.007 |

*: Not calculated since average exposure point concentrations were below detection limit

NC: Reference dose is not available for Cu, tolerable daily intake is stated as 140 mg.kg$^{-1}$.d$^{-1}$ by Baars et al. (2001).

Exposure frequency was considered while sensitivity analysis. It was estimated as 250 $d.yr^{-1}$ for parks and playgrounds (assuming access for 5 $d.wk^{-1}$, 50 $wk.yr^{-1}$) instead of 180 $d.yr^{-1}$ increased maximum risk for As from $1.15\times10^{-5}$ to $1.59x10^{-5}$ and HI from 0.36 to 0.50. Similarly using an exposure frequency of 100 $d.yr^{-1}$ for picnic areas (assuming access for 2 $d.wk^{-1}$, 50 $wk.yr^{-1}$) instead of 50 $d.yr^{-1}$ revealed a carcinogenic risk of $2.29\times10^{-6}$ instead of $4.59\times10^{-6}$ and a HI of 0.07 instead of 0.14. Also hazard index values of other heavy metals were calculated and shown in the Table 5.15. Hazard index values of As, Cd, Cr, Cu, and Zn was not higher than one. When carcinogenic risk and hazard index values in this table was compared to our scenarious, it was seen that if exposure frequency increased carcinogenic risk and hazard index values were increased. However this increase in carcinogenic risk and hazard index values due to exposure frequency showed that exposure frequency had a limited effect on risk values.

Bioaccessibility of metals were also evaluated for sensitivity analysis since it can widely vary with different soil types and is influenced by particle size fraction (Ljung et al., 2007, Girouard and Zagury, 2009, Pouschat and Zagury, 2006, 2008). Maximum bioaccessibility values in literature were used in calculations. As risk values were taken as example. When As bioaccessibility was selected as 45.8% which was average value of Girouard and Zagury's study carcinogenic risk was between $1.15x10^{-5}$ and $4.55x10^{-7}$ and hazard index was between 0.01 and 0.36 and when As bioaccessibility was selected as 51.2% which was maximum value of Girouard and Zagury's study carcinogenic risk was between $1.28x10^{-5}$ and $5.08x10^{-7}$ and hazard index was between 0.01 and 0.40. Maximum bioaccessibility values from literature of other metals which were used in sensitivity analysis were 51.2% for As, 86% for Cd, 32.9 for Cr, 94.9 for Cu, and 40.4% for Zn. Risk values calculated by using these values were shown in the Table 5.16. As seen from table hazard index values of As, Cd, Cr, Cu, and Zn was not higher than one and carcinogenic risk of As and hazard index values of all of the metals were increased while bioaccessibility values increased.

Table 5.15. Comparison of exposure assessment and risk characterization for different exposure frequency values

| | | | Exposure Assessment | | | | | | Risk Characterization | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Chemical daily intake (µg.kg$^{-1}$.d$^{-1}$) | | | | | | Carcinogenic Risk | Hazard Index | | | | |
| | | | Carcinogenic | Non-carcinogenic | | | | | | | | | | |
| Loc. | EF (d.yr$^{-1}$) | Behaviour | As | As | Cd | Cr | Cu | Zn | As | As | Cd | Cr | Cu | Zn |
| 01 | 5 | Normal | 3.03E-04 | 4.25E-03 | * | 6.14E-03 | 1.33E-01 | 2.72E-02 | 4.55E-07 | 0.014 | * | <0.001 | NC | <0.001 |
| | | Soil Pica | 1.53E-03 | 2.14E-02 | * | 7.23E-02 | 5.58E-01 | 1.44E-01 | 2.29E-06 | 0.071 | * | <0.001 | NC | <0.001 |
| | 1 | Normal | 6.06E-04 | 8.49E-03 | * | 1.23E-02 | 2.66E-01 | 5.43E-02 | 9.10E-07 | 0.028 | * | <0.001 | NC | <0.001 |
| | | Soil Pica | 3.06E-03 | 4.28E-02 | * | 1.45E-01 | 1.12E+00 | 2.89E-01 | 4.59E-06 | 0.143 | * | <0.001 | NC | 0.001 |
| 02 | 1 | Normal | * | * | * | 6.18E-02 | 8.00E-01 | 8.43E-02 | * | * | * | <0.001 | NC | <0.001 |
| | | Soil Pica | 5.31E-03 | 0.074 | * | 7.23E-01 | 6.50E+00 | 9.14E-01 | 7.96E-06 | 0.248 | * | <0.001 | NC | 0.003 |
| | 2 | Normal | * | * | * | 8.59E-02 | 1.11E+00 | 1.17E-01 | * | * | * | <0.001 | NC | <0.001 |
| | | Soil Pica | 5.62E-03 | 0.079 | * | 1.00E+00 | 9.03E+00 | 1.27E+00 | 8.43E-06 | 0.262 | * | 0.001 | NC | 0.004 |
| 05 | 1 | Normal | * | * | * | 2.42E-02 | 1.13E+00 | 3.56E-01 | * | * | * | <0.001 | NC | 0.001 |
| | | Soil Pica | 7.71E-03 | 1.08E-01 | 0.095 | 1.68E-01 | 4.91E+00 | 1.47E+00 | 1.16E-05 | 0.360 | 0.095 | <0.001 | NC | 0.005 |
| | 2 | Normal | * | * | * | 3.36E-02 | 1.57E+00 | 4.94E-01 | * | * | * | <0.001 | NC | 0.002 |
| | | Soil Pica | 1.07E-02 | 1.50E-01 | 0.019 | 2.33E-01 | 6.83E+00 | 2.04E+00 | 1.61E-05 | 0.500 | 0.019 | <0.001 | NC | 0.007 |
| 10 | 1 | Normal | * | * | * | 9.98E-02 | 5.48E-01 | 1.50E-01 | * | * | * | <0.001 | NC | 0.001 |
| | | Soil Pica | 5.60E-03 | 0.078 | * | 9.56E-01 | 4.95E+00 | 1.30E+00 | 8.40E-06 | 0.261 | * | 0.001 | NC | 0.004 |
| | 2 | Normal | * | * | * | 1.39E-01 | 7.62E-01 | 2.09E-01 | * | * | * | <0.001 | NC | 0.001 |
| | | Soil Pica | 5.28E-03 | 0.074 | * | 1.33E+00 | 6.88E+00 | 1.81E+00 | 7.92E-06 | 0.246 | * | 0.001 | NC | 0.006 |
| 13 | 1 | Normal | 8.99E-04 | 1.26E-02 | 8.63E-03 | 9.04E-02 | 5.42E-01 | 1.32E-01 | 1.35E-06 | 0.042 | 0.009 | <0.001 | NC | <0.001 |
| | | Soil Pica | 7.64E-03 | 1.07E-01 | * | 8.12E-01 | 4.81E+00 | 1.24E+00 | 1.15E-05 | 0.356 | * | 0.001 | NC | 0.004 |
| | 2 | Normal | 1.25E-03 | 1.75E-02 | 1.20E-02 | 1.26E-01 | 7.53E-01 | 1.83E-01 | 1.87E-06 | 0.058 | 0.012 | <0.001 | NC | 0.001 |
| | | Soil Pica | 1.06E-02 | 1.49E-01 | * | 1.13E+00 | 6.68E+00 | 1.73E+00 | 1.59E-05 | 0.495 | * | 0.001 | NC | 0.006 |

*: Not calculated since average exposure point concentrations were below detection limit

NC: Reference dose is not available for Cu, tolerable daily intake is stated as 140 mg.kg$^{-1}$.d$^{-1}$ by Baars et al. (2001).

Table 5.16. Comparison of exposure assessment and risk characterization for different bioaccessibility values

| | | Exposure Assessment | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Chemical daily intake (µg.kg$^{-1}$.d$^{-1}$) | | | | | | | | | | | |
| | | Carcinogenic | | Non-carcinogenic | | | | | | | | | |
| | | As | | As | | Cd | | Cr | | Cu | | Zn | |
| | | B (%) | | B (%) | | | | | | | | | |
| Loc. | Behaviour | 45.8 | 51.2 | 45.8 | 51.2 | 59.0 | 86.0 | 19.4 | 32.9 | 81.2 | 94,4 | 27.0 | 40.4 |
| 01 | Normal | 3.03E-04 | 3.39E-04 | 4.25E-03 | 4.75E-03 | * | * | 6.14E-03 | 1.04E-02 | 1.33E-01 | 1.55E-01 | 2.72E-02 | 4.06E-02 |
| | Soil Pica | 1.53E-03 | 1.71E-03 | 2.14E-02 | 2.39E-02 | * | * | 7.23E-02 | 1.23E-01 | 5.58E-01 | 6.49E-01 | 1.44E-01 | 2.16E-01 |
| 02 | Normal | * | * | * | * | * | * | 6.18E-02 | 1.05E-01 | 8.00E-01 | 9.30E-01 | 8.43E-02 | 1.26E-01 |
| | Soil Pica | 5.31E-03 | 5.93E-03 | 0.074 | 0.083 | * | * | 7.23E-01 | 1.23E+00 | 6.50E+00 | 7.56E+00 | 9.14E-01 | 1.37E+00 |
| 05 | Normal | * | * | * | * | * | * | 2.42E-02 | 4.10E-02 | 1.13E+00 | 1.31E+00 | 3.56E-01 | 5.33E-01 |
| | Soil Pica | 7.71E-03 | 8.62E-03 | 1.08E-01 | 1.21E-01 | 0.095 | 0.139 | 1.68E-01 | 2.85E-01 | 4.91E+00 | 5.71E+00 | 1.47E+00 | 2.20E+00 |
| 10 | Normal | * | * | * | * | * | * | 9.98E-02 | 1.69E-01 | 5.48E-01 | 6.38E-01 | 1.50E-01 | 2.25E-01 |
| | Soil Pica | 5.60E-03 | 6.26E-03 | 0.078 | 0.088 | * | * | 9.56E-01 | 1.62E+00 | 4.95E+00 | 5.76E+00 | 1.30E+00 | 1.95E+00 |
| 13 | Normal | 8.99E-04 | 1.00E-03 | 1.26E-02 | 1.41E-02 | 8.63E-03 | 1.26E-02 | 9.04E-02 | 1.53E-01 | 5.42E-01 | 6.30E-01 | 1.32E-01 | 1.97E-01 |
| | Soil Pica | 7.64E-03 | 8.54E-03 | 1.07E-01 | 1.20E-01 | * | * | 8.12E-01 | 1.38E+00 | 4.81E+00 | 5.59E+00 | 1.24E+00 | 1.86E+00 |
| | | Risk Characterization | | | | | | | | | | | |
| | | Carcinogenic Risk | | Hazard Index | | | | | | | | | |
| | | As | | As | | Cd | | Cr | | Cu | | Zn | |
| | | B (%) | | B (%) | | | | | | | | | |
| Loc. | Behaviour | 45.8 | 51.2 | 45.8 | 51.2 | 59.0 | 86 | 19.4 | 32.9 | 81.2 | 94.4 | 27.0 | 40.4 |
| 01 | Normal | 4.55E-07 | 5.08E-07 | 0.014 | 0.016 | * | * | <0.001 | <0.001 | NC | NC | <0.001 | <0.001 |
| | Soil Pica | 2.29E-06 | 2.57E-06 | 0.071 | 0.080 | * | * | <0.001 | <0.001 | NC | NC | <0.001 | 0.001 |
| 02 | Normal | * | * | * | * | * | * | <0.001 | <0.001 | NC | NC | <0.001 | <0.001 |
| | Soil Pica | 7.96E-06 | 8.90E-06 | 0.248 | 0.277 | * | * | <0.001 | 0.001 | NC | NC | 0.003 | 0.005 |
| 05 | Normal | * | * | * | * | * | * | <0.001 | <0.001 | NC | NC | 0.001 | 0.002 |
| | Soil Pica | 1.16E-05 | 1.29E-05 | 0.360 | 0.402 | 0.095 | 0.139 | <0.001 | <0.001 | NC | NC | 0.005 | 0.007 |
| 10 | Normal | * | * | * | * | * | * | <0.001 | <0.001 | NC | NC | 0.001 | 0.001 |
| | Soil Pica | 8.40E-06 | 9.40E-06 | 0.261 | 0.292 | * | * | 0.001 | 0.001 | NC | NC | 0.004 | 0.007 |
| 13 | Normal | 1.35E-06 | 1.51E-06 | 0.042 | 0.047 | 0.009 | 0.013 | <0.001 | <0.001 | NC | NC | <0.001 | 0.001 |
| | Soil Pica | 1.15E-05 | 1.28E-05 | 0.356 | 0.399 | * | * | 0.001 | 0.001 | NC | NC | 0.004 | 0.006 |

*: Not calculated since average exposure point concentrations were below detection limit

NC: Reference dose is not available for Cu, tolerable daily intake is stated as 140 mg.kg$^{-1}$.d$^{-1}$ by Baars et al. (2001).

# 6. CONCLUSIONS

24 sites through out İstanbul were evaluated in this study. There was no Ni and Pb contamination in samples from these parks, playgrounds, and picnic areas. In 11 sites out of 24 sites with a concentration of As, Cd, Cr, Cu or Zn above Turkish regulations. The majority of the contaminated sites were playgrounds. In 5 sites (Site 01, 02, 05, 10, and 13) of 11 contaminated sites metal concentrations were systemically higher than the measured background values and they were considered as critically contaminated since their metal concentrations were close to or exceeded the regulatory values. The elevated Cu concentrations in soil samples from these five critically contaminated sites may be linked to leaching from wood treated with copper containing wood preservatives more likely other than CCA. Higher concentrations of As, Cr and Zn may be attributed to other contamination sources. Although average levels of metal concentrations were similar in playgrounds, parks and picnic areas, the latter is of less importance due to the lower possible exposure frequency to the soil.

In terms of carcinogenic risk, the calculated chemical daily intake value for As in soil pica behaviour scenario exceeded $1\times10^{-6}$ in critically contaminated sites due to high frequency and long duration of exposure, and relatively low bodyweight although As concentrations were below the Turkish regulatory values (20 $mg.kg^{-1}$).

For the non-carcinogenic risk, hazard index values for As, Cd, Cr and Zn under both soil ingestion scenarios were less than one in the five critically contaminated sites. It should be kept in mind that high background exposure of children to As leads to HI value larger than 1 and even low soil As concentrations in park and playground soils yield a significant additional risk for children.

The soil ingestion rate is the factor with the highest uncertainty due to the significant limitations in methodologies used in ingestion studies such as bias in sample selection, poor representation of target populations in terms of race, ethnicity and socioeconomic situation in sensitivity analysis. High soil ingestion rate values may

increase the risk and HI values to unacceptable levels. Body weight is another important value. It was seen that when body weight decreased, carcinogenic risk and hazard index values increased which demonstrated that children with low body weight are more sensitive than others. Effect of exposure duration and bioaccessibility of As on the risk values were lower compared to the effect of soil ingestion rate and body weight.

Under a conservative approach it can be concluded that, for children 2 – 6 years old who have soil pica behaviour there is a considerable risk in terms of As uptake when playing in soils from playgrounds, parks or picnic areas. If they have low body weight, risk may be more serious. Also 2-3 year old children with lower body weights who have frequent hand to mouth activity may be under risk to heavy metal pollution in soils near treated wood structures even if they do not have soil pica behaviour.

# 7. RECOMMENDATIONS

Accurate assessment of Cd concentrations and making judgement whether a site was contaminated or not was difficult due to the method detection limit. Detection limit for Cd was approximately 5 $mg.kg^{-1}$, and this was above regulatory limit value which is 3 $mg.kg^{-1}$. To overcome this problem, the detection limit has been used in the risk assessment study when a result below detection limit was obtained. Therefore, more sensitive analytical procedures are recommended for total metal determination in soils. A method detection limit of at least 1 $mg.kg^{-1}$ is needed for an accurate assessment of Cd contamination in urban soils.

When calculating chemical daily intake values since there is not bioaccessibility values in literature measured in <2 mm fraction, bioaccessibility values measured in <250 µm fraction from literature were used in the soil pica behaviour scenario. Studying bioaccessibility values of metals in <2mm soil fraction may be recommended as a further step to those experiments.

The soil ingestion rate is the factor with the highest uncertainty for sensitivity analysis and variations in ingestion rate findings inside a given study and between different studies are very high. Also bioaccessibility of metals widely vary with different soil types and is influenced by particle size fraction. Therefore, more accurate values for soil ingestion rates and bioaccessibility are needed to better assess the risk.

**REFERENCES**

Agency for Toxic Substances & Disease Registry (ATSDR), 2004. Public Health Statement for Copper, http://www.atsdr.cdc.gov/PHS/PHS.asp?id=204&tid=37 (accessed in April, 2010).

Agency for Toxic Substances & Disease Registry (ATSDR), 2005. Public Health Statement for Zinc, http://www.atsdr.cdc.gov/PHS/PHS.asp?id=300&tid=54 (accessed in April, 2010).

Agency for Toxic Substances & Disease Registry (ATSDR), 2005. Public Health Statement for Nickel, http://www.atsdr.cdc.gov/PHS/PHS.asp?id=243&tid=44 (accessed in April, 2010).

Agency for Toxic Substances & Disease Registry (ATSDR), 2007. Public Health Statement for Arsenic, http://www.atsdr.cdc.gov/toxprofiles/phs2.html (accessed in April, 2010).

Agency for Toxic Substances & Disease Registry (ATSDR), 2007. Public Health Statement for Lead, http://www.atsdr.cdc.gov/PHS/PHS.asp?id=92&tid=22 (accessed in April, 2010).

Agency for Toxic Substances & Disease Registry (ATSDR), 2008. Public Health Statement for Cadmium, http://www.atsdr.cdc.gov/PHS/PHS.asp?id=46&tid=15 (accessed in April, 2010).

Agency for Toxic Substances & Disease Registry (ATSDR), 2008. Public Health Statement for Chromium, http://www.atsdr.cdc.gov/PHS/PHS.asp?id=60&tid=17 (accessed in April, 2010).

Baars, A.J., Theelen, R.M.C., Janssen, P.J.C.M., Hesse, J.M., van Apeldoorn, M.E., Meijerink, M.C.M., Verdam, L., Zeilmaker, M.J., 2001. Re-evaluation of human-toxicological maximum permissible risk levels. RIVM, Bilthoven, Netherlands.

Balasoiu, C.F., Zagury, G.J. Deschênes, L., 2001. Partitioning and speciation of chromium, copper, and arsenic in CCA-contaminated soils: influence of soil composition. Science of the Total Environmental, 280, 239-255.

Basta, N.T., Rodriguez, R.R., Casteel, S.W., 2001. Bioavailability and risk of arsenic exposure by the soil ingestion pathway. In W. T. Frankenberger (Editor), Environmental Chemistry of Arsenic, 117, Marcel Dekker Inc., New York.

Brown, R.B., 2003. Florida Cooperative Extension Service, Institute of Food and Agricultural Sciences, University of Florida, http://edis.ifas.ufl.edu/ss169 (accessed in April, 2010).

Child-Specific Exposure Factors Handbook in N.C.f.E.A. Office of Research and Development, 2008. U.S:EPA, Washington Office (Editor), Washington, DC.

Chirenje, T., Ma, L.Q., Clark, C., Reeves, M., 2003. Cu, Cr and As distributionin soils adjacent to pressure-treated decks, fences and poles. Environmental Pollution, 124, 407-417.

Cookson, L.J., 2008. Influence of CCA-treated pine structures on the arsenic content of soils in preschool playgrounds near Melbourne, Australia. Forest Products Journal, 58, 94-99.

De Miguel, E., Iribarren, I., Chacón, E., Ordoñez, A., Charlesworth, S., 2007. Risk-based evaluation of the exposure of children to trace elements in playgrounds in Madrid (Spain). Chemosphere, 66, 505-513.

Dube, E.M., Boyce, C.P., Beck, B.D., Lewandowski, T., Schettler, S., 2004. Assessment of Potential Human Health Risks from Arsenic in CCA-Treated Wood. Human and Ecological Risk Assessment, 10, 1019-1067.

Duffus, J.H., 2002. Heavy Metals – A Meaningless Term? Pure and Applied Chemistry, 74, 5, 793-807.

Standard Test Method for pH of Soils, 2007. ASTM.

D. Norm, Determination of total organic carbon (TOC) in waste, sludges and sediments, 2001. European Committee for Standardization, Brussels.

Girouard, E., Zagury, G.J., 2009. Arsenic bioaccessibility in CCA-cotaminated soils: Influence of soil properties, arsenic fractionation, and particle-size fraction, Science of the Total Environment, 407, 2576-2585.

Govil, P., Sorlie, J., Murthy, N., Sujatha, D., Reddy, G., Rudolph-Lund, K., Krishna, A., Rama Mohan, K., 2008. Soil contamination of heavy metals in the Katedan Industrial Development Area, Hyderabad, India. Environmental Monitoring and Assessment, 140, 313-323.

Granero, S., Domingo, J.L., 2002. Levels of metals in soils of Alcala deHenares, Spain: Human health risks. Environmental International, 28, 159-164.

Güney, M., 2006. Heavy Metal Determination in Roadside Soils and Highway Dust From the Major Highways of İstanbul, M.S. Thesis, Boğaziçi University.

Güney, M., Onay, T., Copty, N., 2009. Impact of overland traffic on heavy metal levels in highway dust and soils of İstanbul, Turkey. Environmental Monitoring and Assessment, 164, 101-110.

Hettiarachchi, G.M., Pierzynski, G.M., 2002. Soil Lead Bioavailability and in Situ Remediation ofLead- Contaminated Soils: A Review. Environmental Progress, 23, 1, 78-93.

International Cannagraphic Magazine Forums, Evaluating your polts soils: Soil texture, https://www.icmag.com/ic/showthread.php?t=49474 (accessed in April, 2010).

Kim, H., Kim, D., Koo, J., Park, J., Jang, Y., 2007. Distribution and mobility of chromium, copper, and arsenic in soils collected near CCA-treated wood structures in Korea. Science Total Environment, 374, 273-281.

LaGrega, M.D., Buckingham, P.L., Evans, J.C., 1994. Hazardous Waste Management. McGraw-Hill, Inc., New York, UnitedStates of America.

Ljung, K., Selinus, O., Otabbong, E., Berglund, M., 2006. Metal and arsenic distribution in soil particle sizes relevant to soil ingestion by children, Applied Geochemistry, 21, 1613-1624.

Ljung, K., Oomen, A., Duits, M., Selinus, O., Berglund, M., 2007. Bioaccessibility of metals in urban playground soils. Journal of Environmental Science and Health. Part A, 42, 1241-1250.

Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices, 1996. U.S.EPA, 20.

Mirsal, İ.A., 2008. Soil Pollution Origin, Monitoring & Remediation (Second Edition). Springer-Verlag, Berlin Heidelberg.

Morman, S.A., Plumlee, G.S., Smith, D.B., 2009. Application of in vitro extraction studies to evaluate element bioaccessibility in soils from a transect across the United States and Canada. Applied Geochemistry, 24, 1454-1463.

Moya, J., Bearer, C.F., Etzel, R.A., 2004. Children's Behavior and Physiology and How It Affects Exposure to Environmental Contaminants. Pediatrics, 113, 996-1006.

Natural Resources Conservation Service (NRSC), 1998. Soil Quality Information Sheet, Soil Quality Indicators:pH, http://urbanext.illinois.edu/soil/sq_info/ph.pdf (accessed in April, 2010).

Poggio, L., Vrscaj, B., Schulin, R., Hepperle, E., Ajmone Marsan, F., 2009. Metals pollution and human bioaccessibility of topsoils in Grugliasco (Italy). Environ. Pollut., 157, 680-689.

Pouschat, P., Zagury, G.J., 2006. In Vitro Gastrointestinal Bioavailability of Arsenic in Soils Collected near CCA-Treated Utility Poles. Environmental Science&Technology, 40, 4317-4323

Pouschat, P., Zagury, G.J., 2008. Bioaccessibility of Chromium and Copper in Soils near CCA-Treated Wood Poles. Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management, 12, 216-223.

Rahman, F.A., Allan, D.L., Rosen, C.J., Sadowsky, M.J., 2004. Arsenic Availability from Chromated Copper Arsenate (CCA)-Treated Wood. Journal of Environmental Quality, 33, 173-180.

Risk Assessment Guidance for Superfund Volume I Human Health Evaluation Manual (Part A), 1989. U.S. EPA, in O.o.E.a.R. Response (Editor), Washington, D.C. 20450, 287.

Rodriguez, R.R., BastaStan N.T., Casteel, W., Pace, L.W., 1999. An In Vitro Gastrointestinal Method To Estimate Bioavailable Arsenic in Contaminated Soils and Solid Media. Environmental Science&Technology, 33, 642-649.

Ruby, M.V., Davis, A., Schoof, R., Eberle, S., Sellstone, C.M., 1996. Estimation of Lead and Arsenic Bioavailability Using a Physiologically Based Extraction Test. Environmental Science&Technology, 30, 422-430.

Ruby, M.V., Schoof, R., Brattin, W., Goldade, M., Post, G., Harnois, M., Mosby, D.E., Casteel, S.W., Berti, W., Carpenter, M., Edwards, D., Cragin, D., Chappell, W., 1999. Advances in Evaluating the Oral Bioavailability of Inorganics in Soil for Use in Human Health Risk Assessment. Environmental Science&Technology, 33, 3697-3705.

Sharma, H.D., Reddy, K.R., 2004. Geoenvironmental engineering: site remediation, waste containment and emerging waste management Technologies. John Wiley & Sons Inc., New York.

Soil Science Society of America, About Soils, https://www.soils.org/about-soils (accessed in April, 2010).

Standard Operating Procedure for an In Vitro Bioaccessibility Assay for Lead in Soil, 2008. U.S. EPA, Washington, DC.

Standard Test Method for Laboratory Determination of Water (Moisture) Content of Soil and Rock by Mass, 2005. ASTM.

Standard Test Methods for Amount of Material in Soils Finer than No.200 (75μm) Sieve, 2006. ASTM.

Standard Test Method for Particle-Size Analysis of Soils, 2007. ASTM.

Toprak Kirliliğinin Kontrolü Yönetmeliği (TKKY), 2005. In Turkish Ministry of Environment and Forestry (Editor), T.C. Resmi Gazete, 13, Ankara, Turkey.

Townsend, T., Solo-Gabriele, H., Tolaymat, T., Stook, K., Hosein, N., 2003. Chromium, Copper, and Arsenic Concentrations in Soil Underneath CCA-Treated Wood Structures. Soil Sediment Control, 12, 779-798.

Teutsch, N., Erel, Y., Halicz, L., Banin, A., 2001. Distribution of natural and anthropogenic lead in Mediterranean soils. Geochimica et Cosmochimica Acta, 65, 2853-2864.

United States Environmental Protection Agency Integrated Risk Information System (IRIS), 2009. http://www.epa.gov/ncea/iris/, U.S.EPA, Washington (accessed in April, 2010).

USEPA, 2008. A Probabilistic Risk Assessment for Children Who Contact CCA-Treated Playsets and Decks. A.D. Office of Pesticide Programs, Washington, DC.

USEPA, 2000. Technology Transfer Network Air toxics Web Site, Cadmium Compounds. http://www.epa.gov/ttn/atw/hlthef/cadmium.html (accessed in May, 2010)

Watts, R.J., Teel, A.L., 2000. Groundwater and Air Contamination: Risk, Toxicity, Exposure Assessment, Policy, and Regulation. Washington State University, Pullman,WA, USA.

Yamamoto, N., Takahashi, Y., Yoshinaga, J., Tanaka, A., Shibata, Y., 2006. Size Distributions of Soil Particles Adhered to Children's Hands. Archives of Environmental Contamination and Toxicology, 51, 157-163.

Zagury, G.J., Samson, R., Deschenes, L., 2003. Occurrence of Metals in Soil and Ground Water Near Chromated Copper Arsenate-Treated Utility Poles. Journal of Environmental Quality, 32, 507-514.

Zagury, G.J., Dobran, S., Estrela, S., Deschênes, L., 2008. Inorganic Arsenic Speciation in Soil and Groundwater Near In-Service Chromated Copper Arsenate-Treated Wood Poles. Environmental Toxicology and Chemistry, 27, 799-807.

Zartarian, V.G., Xue, J., Özkaynak, H., Dang, W., Glen, G., Smith, L., Stallings, C., 2006. A Probabilistic Arsenic Exposure Assessment for Children Who Contact CCA-Treated Playsets and Decks, Part 1: Model Methodology, Variability Results, and Model Evaluation. Risk Analysis, 26, 2.