In vitro BIOACCESSIBILITY FOR HEALTH RISK ASSESSMENT OF METAL CONTAMINATION IN URBAN DUST AND SOIL SAMPLES: A CHEMOMETRIC APPROACH

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FACULTY OF SCIENCE
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ABSTRACT

Anthropogenic activities in urban cities may pose a risk to human health and environment. For risk assessment studies, estimation of contaminants in environmental media is always depending on the concentration of metals determined in the matrices. Nevertheless, the metal fractions that are taken up by the human body via exposure routes are of topmost concern. The focus of this work is to assess these fractions of contaminants, through the application of a bioaccessibility protocol for health risk estimation via oral exposure. Therefore, arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), and lead (Pb) were determined in soil and urban dust samples using Inductively Coupled Plasma Mass Spectrometry technique (ICP-MS). The sampling location chosen in this study was Petaling Jaya and Sekinchan involving ninety-four urban dust and twenty-one soil samples. Total concentration of As, Cd, Cr, Cu, Ni and Pb were determined in urban dust using multivariate analysis. The result obtained shows that the concentrations of these metals in both urban dust and soils were found to be higher than their corresponding background values, indicating anthropogenic influence in the contamination of the metals. The enrichment factor (EF) analysis shows that all the metals have EF values greater than 1.5, suggesting anthropogenic influence. The multivariate analysis conducted revealed that anthropogenic activities, atmospheric deposition and wind could be the sources of the heavy metals (HMs) in the study area. The potential ecological risk assessment indicates that Cd was the main ecological risk factor in urban dust with the order Cd > Pb > Cu > As > Ni > Cr. The oral bioaccessibility of the heavy metal contaminants were determined in both dust and soil samples using a developed

Physiologically Based Extraction Test (PBET). The results obtained revealed that the contaminants were more solubilized in the gastric phase than of the intestinal phase for all the samples. Based on the results, more than 40% of the total concentration of the metals were solubilized in the gastrointestinal tract of soil, while the percentage increases up to 80% for urban dust. The result of the health risk assessment of the HMs via oral ingestion of dust and soil following Monte Carlo simulation (MC) analysis shows that for both children and adults who ingest urban dust and soil pose no significant possibility of non-carcinogenic effects, while adults could have carcinogenic consequences on ingestion of Cd in soil. Nevertheless, children are more vulnerable to non-carcinogenic risks, whereas, adults were more susceptible to cancer effects. Moreover, the risks estimation following ingestion of dust without bioaccessibility was higher than the risks accounting with bioaccessibility. This implies the importance of bioaccessibility in health risk assessment. The risks assessed without bioaccessibility seems to be overestimated. Therefore, bioaccessibility is an absolutely essential ingredient for accurate health risk evaluations of HMs exposure via oral ingestion of dust and soil.

Keywords: Health risk, *in vitro* bioaccessibility, heavy metals, pathways, Monte Carlo Simulation.

BIOACCESSIBILITY In vitro UNTUK PENILAIAN RISIKO KESIHATAN PENAMBAHAN LOGAM DALAM URBAN DUST DAN SAMPING SOIL: PENDEKATAN CHEMOMETRIC

ABSTRAK

Aktiviti antropogenik di bandar boleh menimbulkan risiko kepada kesihatan manusia dan alam sekitar. Untuk kajian penilaian risiko, anggaran pencemar dalam media alam sekitar sentiasa bergantung pada kepekatan logam yang ditentukan dalam matriks. Walau bagaimanapun, pecahan logam yang memasuki tubuh manusia melalui laluan pendedahan amat membimbangkan. Tumpuan kerja ini adalah untuk menilai pecahan kontaminan ini, melalui penggunaan protokol biokebolehcapaian untuk anggaran risiko kesihatan melalui pendedahan mulut. Oleh itu, arsenik (As), kadmium (Cd), kromium (Cr), tembaga (Cu), dan plumbum (Pb) dalam sampel tanah dan sampel habuk bandar ditentukan menggunakan teknik Spektrometri Plasma Berganding Aruhan−Spektrometri Jisim (ICP−MS). Lokasi pensampelan yang dipilih dalam kajian ini ialah Petaling Jaya dan Sekinchan yang melibatkan sembilan puluh empat habuk bandar dan dua puluh satu sampel tanah. Jumlah kepekatan As, Cd, Cr, Cu, Ni dan Pb ditentukan dalam habuk bandar bagi analisis multivariasi. Keputusan ini menunjukkan bahawa kepekatan logam ini dalam kedua-dua sampel habuk dan tanah bandar di dapati lebih tinggi daripada nilai yang diperolehi dari latarbelakang yang sama, yang menunjukkan pengaruh antropogenik dalam pencemaran logam. Analisis faktor pengkayaan (EF) menunjukkan bahawa semua logam mempunyai nilai EF lebih besar daripada 1.5, mencadangkan pengaruh antropogenik. Analisis multivariasi yang dijalankan menunjukkan bahawa aktiviti antropogenik, pemendapan atmosfera dan angin boleh menjadi sumber logam berat (HMs) di kawasan kajian. Penilaian risiko ekologi yang berpotensi menunjukkan bahawa Cd adalah faktor risiko utama dalam habuk bandar dengan turutan Cd > Pb > Cu > As > Ni > Cr. Biokebolehcapaian oral logam berat tercemar telah ditentukan dalam kedua-dua sampel tanah dan habuk menggunakan Ujian Pengekstrakan Berdasarkan Physiologically Based (PBET). Keputusan yang diperolehi menunjukkan bahawa bahan pencemar lebih mudah larut dalam fasa gastrik daripada fasa usus bagi semua sampel. Berdasarkan hasil ini, lebih daripada 40% dari jumlah kepekatan logam dalam tanah larut dalam saluran gastrointestinal, manakala peratusan meningkat hingga 80% bagi habuk bandar. Keputusan penilaian risiko kesihatan bagi HM secara penghadaman oral debu dan tanah menggunakan analisis simulasi Monte Carlo (MC) menunjukkan bahawa bagi kedua-dua kanak-kanak dan orang dewasa yang menghadamkan habuk dan tanah bandar tidak menimbulkan kesan yang signifikan terhadap kesan tidak karsinogenik, sementara orang dewasa boleh menyebabkan akibat karsinogenik bagi pengambilan Cd dalam sampel tanah. Walau bagaimanapun, kanak-kanak lebih terdedah kepada risiko tidak karsinogenik, sedangkan orang dewasa lebih mudah terdedah kepada kesan kanser. Lagipun, anggaran risiko setelah terdedah kepada habuk tanpa biokebolehcapaian adalah lebih tinggi berbanding dengan risiko yang melibatkan biokebolehcapaian. Ini membayangkan kepentingan biokebolehcapaian dalam penilaian risiko kesihatan. Risiko yang dinilai tanpa biokebolehcapaian nampaknya terlalu tinggi daripada jangkaan. Oleh itu, biokebolehcapaian adalah sesuatu yang sangat penting untuk penilaian risiko kesihatan yang tepat terhadap pendedahan HM melalui pengambilan secara oral sampel debu dan tanah bandar.

Kata kunci: Risiko kesihatan, bioaccessibility *in vitro*, logam berat, laluan, Simulasi Monte Carlo.

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Ibrahim Sani Shabanda

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LIST OF SYMBOLS AND ABBREVIATIONS

ABS	: Dermal absorption factor
ADD	: Average daily dose
ADI	: Average daily intake
AF	: Skin adhesion factor
AT	: Average time
BW	: Body weight
CA	: Correlation analysis
CF	: Conversion factor
COM	: Commercial
CR	: Cancer risk
ED	: Exposure duration
EF	: Exposure frequency
Er	: Potential ecological risk
FA	: Factor analysis
GBAF	: Gastric bioaccessibility fraction
GIBAF	: Gastrointestinal bioaccessibility fraction
GI	: Gastrointestinal
h	: Hour
HCA	: Hierarchical cluster analysis
HI	: Hazard index
HMs	: Heavy metals
HQ	: Hazard quotient

ICP-MS : Inductively coupled plasma mass spectrometry

IND : Industrial

IR : Ingestion rate

inhR : Inhalation rate

lnN : Log normal

LOD : Limit of detection

LTC : Life time cancer

MBPJ : Majlis Bandaraya Petaling Jaya

MC : Monte Carlo

MRLs : Minimal risk levels

N : Normal

NA : Not available

OMC : Organic matter content

PAHs : Polyaromatic hydrocarbons

PBET : Physiologically based extraction test

PCA : Principal Cluster analysis

PCs : Principal components

PEF : Particle emission factor

PJ : Petaling Jaya

PLM : Permissible limit

QC : Quality control

r : Correlation coefficient

RfD : Reference dose

RI : Potential ecological risk index

rpm : Revolution per minute

RSD : Residential

SA : Skin surface area

SD : Standard deviation

SF : Slope factor

SRM : Standard reference material

ST : Site

TF : Traffic

TCR : Total cancer risk

UK : United Kingdom

UPW : Ultrapure water

WHO : World health organization

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CHAPTER 1: INTRODUCTION

In an effort to explore and or improve life and environment, human beings have greatly changed the natural environment directly or indirectly. Lack of proper management of natural environment such as lands, soil, water, living and non-living things around disturbed the environmental settings and eventually could lead to negative effect on both humans and the environment. The land most especially urban soil which is the root of urban dusts has been as a result of modernization, urbanization and population increase subjected to various activities such as domestic, industrial, commercial, agricultural and traffic which eventually leads to a release of various pollutants among which are heavy metals. Human health can be associated to the quality of urban environment especially soil and air. In the recent years due to high rate of urbanization and modernization, the safety of urban soil and air has become a concern.

The status of urban environment depends upon its exposure to different factors. Therefore, the quality of urban environment depends on the rate of anthropogenic activities in it. Activities such as industrial, traffic, commercial, agricultural greatly influence and contaminate urban environment especially urban soil and dust with pollutants such as heavy metals. In many developing countries these activities are not properly regulated, as a result their comprehensive facts could be limited or unknown. Therefore, urban environment and lands should be well understood and evaluated for the contaminants. This is because the impact of these pollutants may be there for years creating human health risk at last.

Heavy metals extractions in soils and dusts have been employed for decades in order to identify the distribution and pollution of elemental metals in the environment. As the impact of heavy metals in the environmental media has become a great trouble for several years, thus there is an increase in the need to study the effects of the elemental pollution on human health. Heavy metals contamination in soil and dust can have an adverse effects both to human and environment. Dust has the capacity of transferring and spreading heavy metal contaminants suspended in it into the entire urban environment for many years, as such urban dusts and soil can be considered as a reservoir for heavy metals (Rajaram et al., 2014). Heavy metals in urban dusts could enter into humans' body through different exposure pathways. Therefore, it is necessary to assess the fraction of the metal contaminants in dusts that are mobilized and solubilized in the gastrointestinal tract and are available for absorption into human systemic so as to estimate the magnitude of the risks involved and identify the possible exposure routes of these metal contaminants into the human body. Bioaccessibility and health risk assessment is the basic tool to achieve this objective.

1.1 Heavy metals pollution in soil and dust

Dust particles especially urban dust are the main accumulators and primary paths for contaminants especially heavy metals into the environment. The amount of dust particles in urban cities could be a measure of its possible pollution and possible consequences on humans and the environment (Trujillo-González et al., 2016). Dusts are smaller particles components obtained from soil which settles on surfaces and objects including humans (Mohmand et al., 2015). Dust particles have compound sources in the environment which are made up of natural and artificial constituents (Al-Khashman, 2013). Rock and volcanic emissions, and plant residues are considered the natural components of dusts, while tyre wears, particles from vehicular exhausts, particles from break lining wear, construction activities, mining activities, wear of vehicular engine, motor vehicle parts corrosion, domestic discharge, burning of incinerators are considered parts of the anthropogenic sources (Harrison et al., 2017; Kamani et al., 2015). As a result of their smaller particles sizes when dusts are emitted from the point source, they become highly mobile and suspended in the air eventually coming in touch with objects and humans who are carrying out their daily activities and particularly children who play around with objects. Therefore, the effects of dust particles in urban towns could be great. In the recent decade, rapid urbanization, modernization and increased population in cities of the world are associated with significant emissions of pollutants such as heavy metals into urban environment such as soil and dusts, as a result of various human activities (Kamani et al., 2015). Heavy metals pollution has widely become a severe threat, in the recent years' pollution control and health risk prevention in urban environment, are among the main challenges facing the developing countries (Mohmand et al., 2015).

Cities that are located in tropical urban environments such as Petaling Jaya have been exposed to different kinds of soil and dust particles. Anthropogenic activities are widely known to be the primary cause of environmental pollution as a result of emissions from industries, traffic, municipal waste disposal and agricultural activities, and soil and dust within the city environments (Kamani et al., 2018; Yoshinaga et al., 2014). For instance Petaling Jaya, Malaysia is a city undergoing rapid development. In the recent years Malaysia is experiencing different forms of emissions such as traffic. Such emissions are due to wear and tear of road surfaces, tires, break lining and pads, motor vehicular pars corrosion, particles from vehicle exhaust and particles from engine combustion. This happens as a result of high number of motor vehicles and motorcycles with large traffic volume within the city (Abdelfatah et al., 2015). This has significantly add to high level of smaller particles in dust containing high amounts of heavy metals and other substance in the city.

Industrial activities such as manufacture of chemicals, automobile parts, electronic products, paints; construction works in urban cities, domestic discharges, resuspension of dusts within the city areas are mostly influenced by wind direction and seasonal activities in Petaling Jaya. As a result of increase in these activities and because there is no enforcement laws on the various emissions there will be significant contribution of high degree of particles and dusts containing high amount of these pollutant metals in the city. In order to minimize the health effects, therefore there is a need for continual checking of these pollutants from dust in urban cities, because such pollutants as heavy metals do not decompose as such the accumulation of the past and present discharge may escalate their concentration.

Agricultural soil is one of the accumulator of contaminants such as heavy metals. As a result of various human activities, pollutants discharged from their sources gets into water bodies and eventually into the food chain. Since that unprocessed water is commonly used for drinking and agricultural irrigation purposes especially in most developing countries, therefore, humans and environment could be at risk. In addition the application of manure which consists of different components in agriculture farms could be another potential pathways of contaminants getting into agricultural soils, application of fertilizer and chemicals such as herbicides and pesticides could also greatly contribute to the increase of contaminants concentrations of such heavy metals in soils and at last humans could suffer the consequences (Eqani et al., 2016). Therefore, it is evident that agricultural soils should continuously be checked for the safety of humans.

The amount of heavy metals in the urban environment especially in urban dust/soil depicts environmental pollution (Al-Khashman, 2013). The pollution of heavy metals in urban dusts/soil could lead to severe health risk effects to human as a result of resuspended dust particles originating from soil which contain significant amount of such toxic particles. Therefore, human population that work, walk and live in the city are exposed to the floating dust particles and could suffer health consequences (Han et al., 2017; Zheng et al., 2010). Human beings can be exposed to heavy metals in urban dusts through ingestion, inhalation and dermal contact that consequently leading to various health risks.

1.1.1 Pollution and human health risk

Urban dust/soil are heterogeneous mixture of derived particles from various sources, these particles contain metals at different levels of concentrations. Some of these metals such as As, Cd, Cr, and Pb are carcinogenic in nature and could induce health risk to human health (ATSDR, 2012). The contamination degree and the risks linked with heavy metals in urban dust/soil have in recent years attracted much concern (Men et al., 2018). In many urban cities, serious contamination of the urban environment is caused by heavy metals in urban dust/soil, and these metal contaminants are persistent and biologically accumulated (Zhang et al., 2017). Therefore, heavy metals are considered priority environmental contaminants.

In large urban cities, traffic is congested thus, more fuel is consumed as a result more toxic waste particles are escaped from the exhaust into the soil/dust and water bodies (Men et al., 2018; Rodrigues et al., 2018). Considerable amounts of heavy metals are also released into the urban dust/soil due to fuel combustion in factories (Bergthorson et al., 2015). These metals pollutants released from the source are transported to media such as urban soil, dust, water and vegetation and their fate could be ended in humans on exposure through exposure routes such as ingestion, inhalation and dermal contact (Cachada et al., 2016). In many cities the heavy metals found in those media are noted to cause environmental pollution (Rehman at al., 2018). Figure 1.1 shows the sources of these metals and how they get into the exposed populace via the exposure routes.

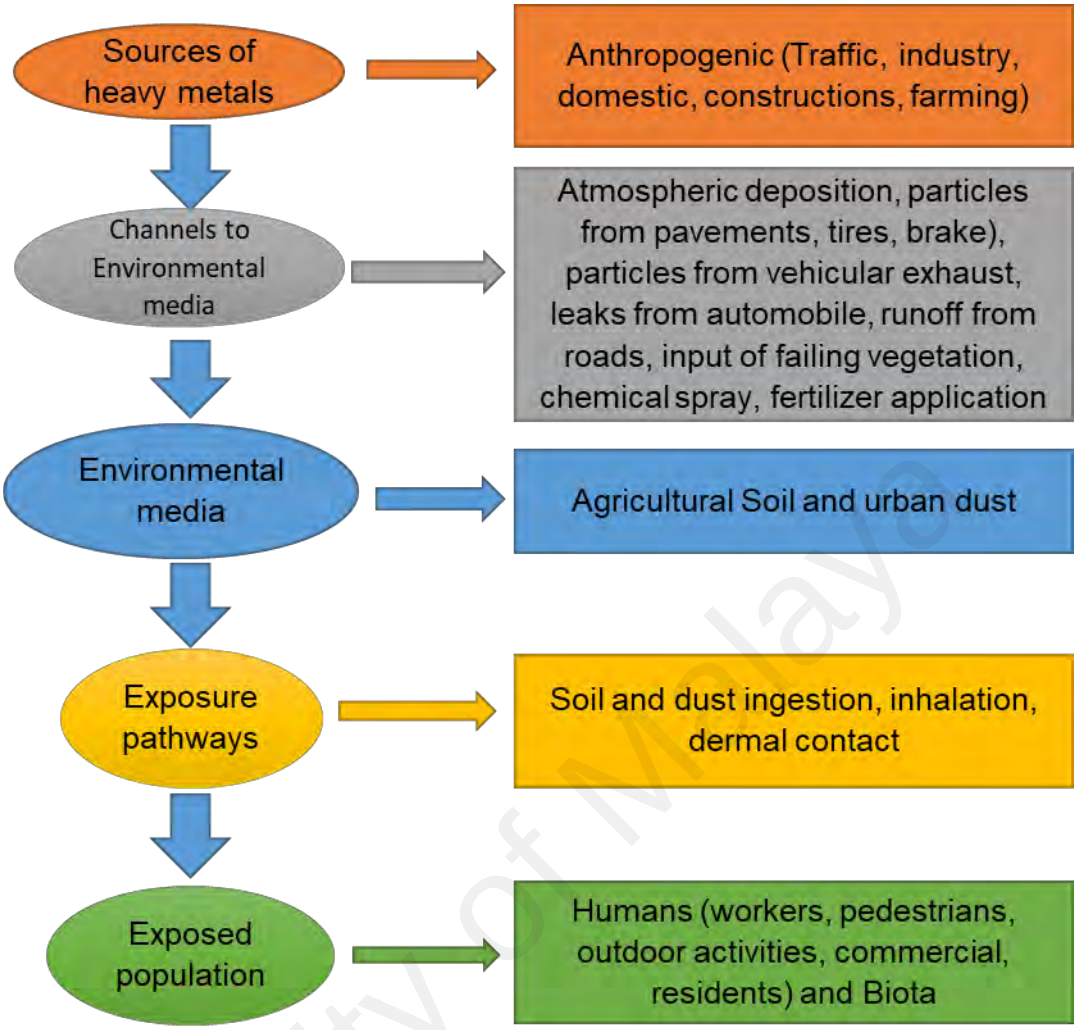


Figure 1.1: Flow of heavy metals contaminants from the sources to the exposed population through exposure pathways.

Exposure to these metal pollutants would cause bioaccumulation of these heavy metals into human tissues and organs thereby affecting the health of the victims. On the other hand, these toxic metals in soil/dust can be biomagnified into food chain, thereby creating health risk to the entire ecosystem. Accumulation of heavy metals in urban dust/soil has resulted to a significant increase in the human exposure to As, Cd, Cr and Pb (Rodrigues et al., 2013). Also, such exposure to such metals may possibly results to serious harmful consequences to humans but particularly children. Therefore, urban soil/dust are important components in urban environment that act as significant channel in transferring heavy metals into human body. The health effects of these toxic metals could be due to their non-biodegradable nature as such the body cannot be able to metabolize them, therefore they can easily be accumulated into body tissues for a long period of time and at the end become a threat to health by damaging the central nervous system, reproductive system and other related organs (Rastegari Mehr et al., 2016). Figure 1.2 shows the link between the sources, exposure, and risk consequences of heavy metals. On the other hand, the risk caused by heavy metals depends upon their solubility in the human intestinal system and their absorption in the body (Ali et al., 2017).

Similarly, heavy metals can enter into circulatory system and as a result of toxic and non-biodegradable nature they can be accumulated in fatty tissues containing fatty acids (Ali et al., 2017; Rodrigues et al., 2018; Zheng & Shi, 2017; Zhuang et al., 2014). Therefore, adults and children can be exposed to toxic substances especially heavy metals through different sources and exposure routes (ingestion, inhalation and dermal contact) but especially oral ingestion, causing health and economic problems most especially in the developing countries (Attina & Trasande, 2013; Neisi et al., 2016).

Chronic health effects could occur in children even at a very low level of exposure (Cao et al., 2014), expressing no safe level for exposure to some of these toxic metals. For instance brain disorder, spinal cord and nervous system happen to children at a low level Pb levels in children blood (Cao et al., 2016). Similarly, the effects of diabetes, heart disease and cancer occurred to children as a result of low level of exposure to heavy metals such as As, Cd among others (Ramirez-Andreotta et al., 2013). Therefore, there is a need to carefully and thoroughly analyze and confirm the level of these toxic metals, identify their sources in dusts and soils of urban environments, assess the risks involved so that measures will be taken to remediate the pollution.

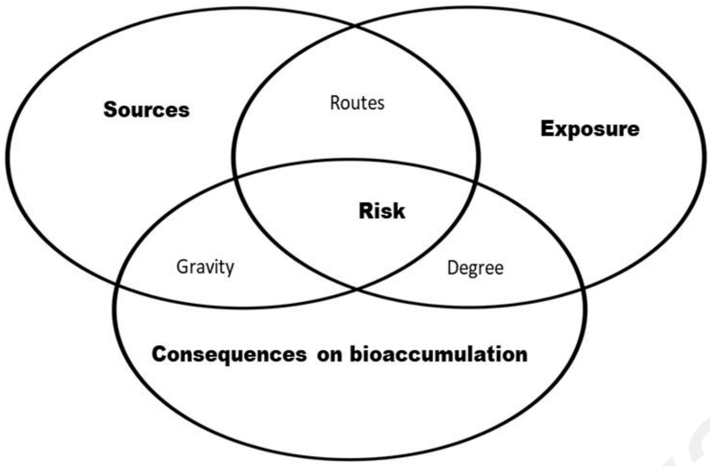


Figure 1.2: Shows the link between sources, exposure and consequences of heavy metals on bioaccumulation.

1.1.2 Oral Bioaccessibility

In general term, fraction of an orally administered dose that gets to the systemic circulation is referred to as oral bioavailability. Contaminants such as heavy metals in dusts/soil on ingestion by humans may be to a limited extent or fully be released from the dust/soil matrix into the gastrointestinal compartments during digestion process. The mobilized fraction of the contaminants is regarded to be the exact amount that is available for absorption. The amount of fraction of the toxicants that is mobilized and soluble in the gastrointestinal tract is known as bioaccessible (Ruby et al., 1999). Heavy metals which are extracted from the soil/dust samples using strong acid digestion known as total metal content. Such extraction overestimate the real metals contamination in an environment and the related risks. However, only a fraction of such contaminants is available and soluble to cause acute health risk when taken up by the body. Therefore, the use of a suitable test is required in order to assess their amount that is considered bioaccessible once in the body (Poggio et al., 2009). In this work, the Physiologically Based Extraction Test (PBET) has been chosen to simulate the mobilisation and absorption of toxic metals in the human gastrointestinal system from the ingested soil and dust. This protocol has been validated through the use of animals (Li et al., 2014; Ruby et al., 1993).

Oral bioaccessibility is therefore, defined as the amount of a fraction of heavy metals that is soluble in the gastrointestinal tract and is available for absorption into the blood stream (Elom et al., 2014b; Liu et al., 2016). The human bioaccessibility test of metal contaminants that got into gastrointestinal tract via ingestion of soil and dusts must allow the quantification of the dissolved toxic metals (Ettler et al., 2012). Similarly, the possible effects of these toxic metals on biota is usually fully understood through the bioaccessibility study of metals in soils and dusts. Therefore, human bioaccessibility test plays a very important role in that toxic substances that creates significant health risks to human is confirmed by it. To simulate the expected bioaccessibility of pollutants that gets into human system, the test is based on the characteristics of human digestion process, the pollutants and the geochemistry of the urban dust/soil.

1.1.3 Risk Assessment

Risk assessment is an organized process that requires variables with potential risks due to certain activity to be identified and evaluated based on their sources, routes and target (Wei et al., 2015). This is due to the fact that environmental pollution is usually associated with risks, therefore risk assessment is required in the studies that involved environmental pollution as the information is vital for regulated rules to be put in place by the concerned agencies involved in order to protect the health of the inhabitants (Zeng et al., 2016). Therefore, the foundation of risk analysis is associated with the environmental monitoring assessment of potential trends in the level of hazardous metals with reference to the international guide. Anthropogenic activities could be the sources of urban pollution and possible adverse effects on human and environment (Trujillo-González et al., 2016). Metal contamination as a result of various emissions in urban dusts could lead to health risk consequence as such their frequent evaluation is required (Han et al., 2017; Rastegari Mehr et al., 2016).

In risk assessment the main priority is given to metals such as Cd, As, Pb and Cr due to their extreme toxicity to humans and animals (Keil et al., 2015). This is because Cd is associated with cancer, kidney damage and hypertension (Wu et al., 2016). Also, exposure to As in dusts/soil causes cancer of skin, kidney, bladder, lungs and enlarged liver (Amos, 2017). Exposure to Pb in dusts/soil result to effect on central nervous system, reproductive system and malfunctioning of kidney (WHO, 2018). Cr(VI) is known to cause asthma, liver and kidney damage (Kamunda et al., 2016). Therefore, risk analysis of these metals in urban dusts/soils is necessary on the basis of their risk consequences to human health.

1.1.4 Human Health Risk Assessment

It involves the probable estimation of a severe human health consequences associated with exposure to toxic chemicals in a polluted environment by both children and adults. Even though the pollution characteristics of poisonous metals in environmental samples such as soil and dust are perceived hence, recognizing their environmental exposure risks serve as the primary preconditions for contamination prevention and control. However, important information are provided for the remediation plans to be established by the concerned legislatures. The human health risk process is usually conducted using the following basic steps: hazard identification, exposure assessment, toxicity estimation and risk characterization (USEPA, 2011). Therefore, this method is necessary as it could provide a clue for the environmental health safety that could help in decision making. The steps in health risk process is shown in Figure 1.3.

1.1.4.1 Hazard Identification

Hazard identification is the first step in health risk assessment that assumes the determination of the hazard of chemicals which could be present in the location and the medium of study. The classification of a chemical as the cause of the adverse health effect, carcinogenic and non-carcinogenic is therefore done based on the established procedure (IARC, 2012). The general concept of the hazard metals is mentioned in chapter two of this study.

1.1.4.2 Exposure Assessment

Exposure assessment is conducted in order to estimate the magnitude, frequency, and duration of human exposure to the toxic pollutants by individuals. It measures the degree of the absorbed toxic substances, assess the source of the chemical contaminants and identify the individual exposure routes. The intensity of the exposure could give a clue to the possible health consequence that an individual or population suffers by the contaminants. Therefore, in order to provide a reliable and quality data, an elaborate and an acceptable chemical analysis of the toxic substance is highly needed. Based on this fact, basic experimental process is followed in this study which comprised of standard reference materials so that right validation is obtained.

1.1.4.3 Toxicity (Dose-Response) Estimation

Toxicity estimation usually establishes the relationship of the effects on human population caused by the degree of exposure to chemical substance in the environment. The dose-response describes numerical estimation of exposure response based on the toxicity indices, this will help in identifying the toxicity and the risks involved to the concerned population. It is therefore a vital step in risk assessment. Major information is obtained from agencies that deals with toxicity of chemicals and diseases such as Agency for Toxic Substances, Diseases and Registry (ATSDR), and United States Environmental Protection Agency (USEPA). This is done for the successful estimation of the dose-response.

1.1.4.4 Risk Characterization

Risk characterization is the final step in human health risk assessment. It is therefore, reveal the intensity of the adverse health effect pose by a toxic chemical contaminant on a population in a given environment. The conclusion of a probable hazard caused by a chemical contaminant on the exposed population is done by comparing the obtained information from the exposure assessment and the dose-response estimation. The risks (cancer or non-cancer) caused by the toxic chemical is obtained through the use of site specific data and probability. In this study, carcinogenic risk (CR), total carcinogenic risk (TCR), hazard quotient (HQ) and hazard index (HI) were the terms used based on the USEPA format to define the potential carcinogenic and non-carcinogenic risks on exposure to toxic metal contaminant in the urban dusts.

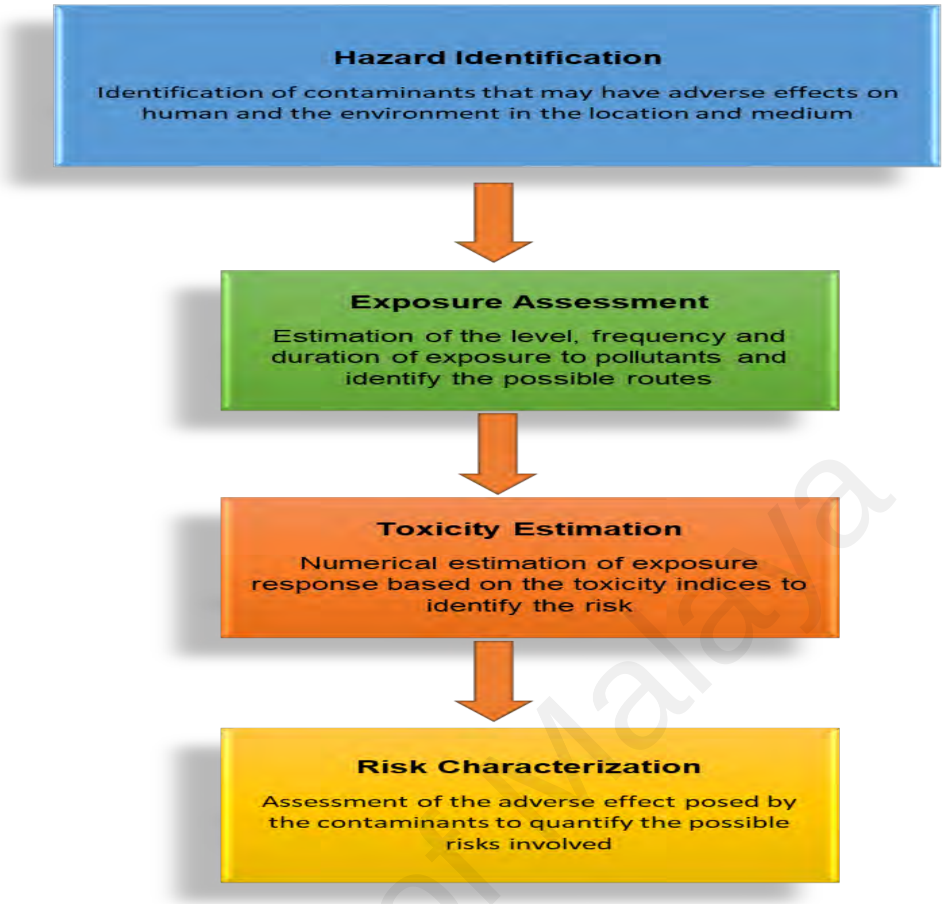


Figure 1.3: Steps involved in human risk assessment: Permission from Koki et al., 2018.

1.1.5 Chemometrics

In order to understand any chemical system analyzing chemical data statistically has become a solution to chemical problems for analytical chemists. The observations and characteristics of complex data is described through the use of multivariate statistical technique. For a successful outcome to be obtained, there is a need for the application of a particular statistical method based on the objective of a given assessment. Therefore, in the classification and monitoring of environmental data, chemometric is the ideal model.

It is observed that different natural and anthropogenic inputs basically cause a high variability in environmental data, and to identify and manage the pollution, repeated use of chemometric technique is required (Hussain et al., 2015). The application of multivariate method in the analysis of environmental data will ease the interpretation of the data and serve as a tool for extracting useful information as a result of analyzing a large raw data. Techniques such as Principal component analysis (PCA), Correlation analysis (CA), Hierarchical cluster analysis (HCA), and Factor analysis (FA) are the basic multivariate statistical analytical tools used in respect to urban dusts/soil data analysis (Cai et al., 2013; Keshavarzi et al., 2015; Saeedi et al., 2012; Soltani et al., 2015; Yongming et al., 2006).

However, Monte Carlo simulation analysis is another chemometric technique employed to simulate environmental data for probabilistic health risk analysis (Cao et al., 2016). Due to its robustness, Monte Carlo simulation technique has obtained increased recognition. Probabilistic risk assessment can be applied to generate uncertainties of parameters due to its inherent natural variability. Generally Monte Carlo simulation involves allocating a joint probabilistic distribution using randomly generated frameworks repeatedly so as to approximate the full scale of possible outcomes (Low et al., 2015). Therefore, its application is very much essential as it will provide a reasonable maximum exposure values which eventually will provide the probable extent of the risks involved.

1.1.6 Problem Statement and Limitation

Petaling Jaya is one of the busiest and densely populated cities in Malaysia and is experiencing a rapid development which includes increased population, modernization, urbanization, industrialization, modern agriculture, increased motor vehicles and congested traffic. Due to agricultural activities, Sekinchan is experiencing increase in population, modern agriculture which includes chemicals such as pesticides and fertilizer spray, the use farm machineries. Thus, these activities introduced toxic metallic contaminants such as heavy metals that not only can contaminate the urban environments, but also can transfer these heavy metals into human body through exposure to soil and dusts via different pathways. Therefore, there is possibility of health risk related to the exposure of metal contaminants through soil/dust by children and adult population.

Metals such as As, Cd, Cr and Pb are both carcinogenic and non-carcinogenic in nature, as such are considered to induce the associated health risks to humans on exposure (ATSDR, 2012; IARC, 2006; USEPA, 2004a). Based on these facts and the importance of human health risk to the inhabitants of Petaling Jaya, Malaysia, it is therefore, become necessary to embark on a full research to explore the effects these contaminants could cause. This is because, until now no research was carried out to examine and assess the well-being of the population in this area. In this regard, soil/dusts samples from Petaling Jaya and Sekinchan, Malaysia were collected to investigate contamination of heavy metals in the cities and subsequently developed a bioaccessibility method for human health risk estimation.

This research explores the variation of the contaminants level, sources of these contaminants, applied the bioaccessibility approach and employed a chemometric health risk approach using the Malaysian citizen body weight to estimate the actual risk involved. The results of health risk obtained with bioaccessibility fraction are compared with those accounting without bioaccessibility to find out the imperativeness of bioaccessibility on actual risk estimation instead of using the existing total metal content. Moreover, because health risk calculations comes up with certain uncertainties and variabilities, instead of direct calculation of health risk, chemometrics are included in this research in order to minimize these uncertainties and variability involved. Similarly on the calculation of the exposure daily dose and health risk, unlike the conservative approach of the USEPA, the point values assigned for body weight is a mean value of the

Malaysian citizens which is directly proportional to their diet and socio-economy status.

Similarly, the use of average exposure time for Malaysians which is equivalent to 74.69 years. Instead of a general assumptions, the risk assessment in this work is, therefore, less conservative and give the real situation on ground. Identifying the sources of these pollutant metals, the possible route of exposure and the actual risk involved on the citizens population. This would help the city council which administers Petaling Jaya city known as Majlis Bandaraya Petaling Jaya (MBPJ) map out strategies on how to reduce and prevent contamination in the air for the safety of its citizens.

1.2 Research Aims and Objectives

The aim of this research is to investigate heavy metals contamination in urban dusts and soils, by analyzing the heavy metals associated with (traffic, industrial, agricultural and commercial activities). Then the data collected will be used to assess the health risk associated with the exposure of selected heavy metals via urban dust and soil, by using the chemometric approach such as Monte Carlo Simulation analysis. This is done using the Malaysian body weight based on their diet and their average exposure time which is equivalent to the Malaysian average lifetime.

The study focuses on health risk prevention and pollution control as it will assess the health risk based on exposure to the metal contaminants and identify the sources of such contaminants in urban environment. Considering the importance of human health risk and Petaling Jaya being a developing city undergoing urbanization and modernization faced with various forms of human activities, and the possible health risk associated with exposure by the pedestrians, workers, recreational outdoor activities and people in the nearby residences, it is unfortunate that no research was ever carried out to identify and evaluate their safety. In an agricultural area such as Sekinchan excessive application of mineral fertilizers, pesticides and emissions from the farm machineries could influence the contamination of the soil by heavy metals which if not checked ultimately could reach a toxic level leading to risks for human health and the entire food chain. Thus, the objectives of this study are:

A) To determine the concentration and distribution of selected heavy metals in urban dusts/soil samples and identify their possible sources using multivariate analysis.
B) To assess the potential health risks posed by selected heavy metals through exposure to dust through various possible exposure routes, namely ingestion, inhalation and dermal.
C) To simulate the bioaccessible and total metal concentration data using Monte Carlo model for the estimation of the oral exposure and associated health risks to the population.

The findings would be useful to both inhabitants and the policy makers in managing urban contamination and promote future strategies to reduce health risks to urban residents.

1.3 The Significance of This Study

For a more comprehensive human health risk assessment, this study is considered important to estimate the health risk of soil and dust of smaller particle sizes < 125 µm and < 63 µm, respectively. This is because these particle fractions can easily be carried and be mobile by wind, traffic and on objects. Various activities significantly introduced and contribute these toxic particles on daily basis, therefore, pose a concern to urban environment. Inhabitants such as pedestrians, workers, those on outdoor activities, road users and those in the nearby residence could be at the risk of exposure to these fractions containing high amounts of heavy metals particularly children with more possibility of the particles adhere to hand or finger-to-mouth and object-mouth (Mingot et al., 2011; Ruby & Lowney, 2012). Based on this, and the search of literature much differences were found in *in vitro* protocols used in estimating health risk through oral ingestion. In order to make a contribution to bioaccessibility and health risk assessment of heavy metals via oral ingestion of urban dust and soil, the Physiologically Based Extraction Test method has been modified and utilized in this Ph.D. project. This approach differs from the previous studies (Cai et al., 2016; Li et al., 2015).

In this study, gastric pH of 1.55 which is related to children and adults fasting condition was employed, as low gastric pH facilitates the solubilization of metals from their bond minerals in the stomach phase. Also higher shaking incubation rate of about 120 rpm was employed. This speed allowed a maximum homogeneity of mixtures and prevents the soil or dust particles from settling at the walls and bottom of the extracting vessels for maximum output. On the other hand, for a clear and more realistic results associated with health risk estimation were identified via oral exposure to soil and dust.

This study has employed chemometric simulation approach and uses Monte Carlo simulation method to obtain a more precise risk estimation rather than deterministic approach. This is done because of the variability and uncertainties involved in health risk assessment. Similarly, all the health risk evaluation parameters were specifically selected for Malaysian citizens as the study involves exposure of individuals rather than adopting default body weight, average exposure time from USEPA and IRIS. The result of health risk evaluation for both cancer and non-cancer depends on the magnitude of the risk parameters. This makes the study specific and its findings very precise. Furthermore, different countries have dissimilar body weights, exposure rate, exposure duration and daily consumption due to differences in climate, dietary, anthropogenic, social and economic status (Eveleth & Tanner, 1976; Michaelsen, 2015). It is anticipated that this will contribute to the existing knowledge on bioaccessibility and human health risk assessment.

1.4 Thesis Outline

Chapter 1 presents a general introduction, problem statement, significance of research, aims and objectives of this research work.

Chapter 2 is concerning with the literature review on the development of bioaccessibility, risk assessment to exposure to toxic metal contaminants, and the multivariate statistical model.

Chapter 3 comprises methods and methodology for the bioaccessibility assay. The discussion about the instrumentation and analysis of dust/soil samples.

Chapter 4, this chapter discusses the obtained results of this work, the contamination with heavy metals in urban dust and their sources, the health risk of total metal in urban dust via ingestion, inhalation and dermal routes, the bioaccessibility of heavy metals urban dust/soil in stage I (gastric) and stage II (gastrointestinal), average daily dose of the bioaccessible metal fractions in urban dust/soil, simulated health risk of bioaccessibility, fractions of metals in urban dust/soil. Comparison of simulated health risk accounting with bioaccessibility and those accounting without bioaccessibility. It also contains the contribution and implication of bioaccessibility and health risk assessment study.

Chapter 5, represent the general conclusions and future perspectives from this work.

CHAPTER 2: LITERITURE REVIEW

2.1 Metal Bioaccessibility and Bioavailability in Association to Human Health

In the past decades total metal concentration was considered for human health risk assessment, but it has been found that total metal concentration overestimate the human health risks, because it assumes that the entire metal contaminants from the dust/soil can get into the bloodstream, considering ingestion to be the main exposure pathway to the contaminants (Paustenbach, 2000). Due to serious criticism regarding this matter increasing studies have revealed that health risks posed by metals in contaminated soil and dust to humans depends on the availability of the metal contaminants for uptake into the human bloodstream from the soil and dust (Ettler et al., 2012; Liu et al., 2016; Luo et al., 2012; Poggio et al., 2009).

Therefore, more emphasis has been put in place to find the real metal content that are actually available for uptake. Ruby et al (1999) defined bioavailability as a fraction of an administered dose in the gastrointestinal tract that can reach the bloodstream of human and ready for circulation depending on the various interactions such as chemical and biological. However, bioaccessibility is defined as the fraction of metal contaminant that is soluble in the gastrointestinal fluids and are assumed to be available for absorption into human system (Oomen et al., 2002; Ruby et al., 1999).

2.1.1 *In vivo* Bioaccessibility Extraction

To address this issue of conservative approach of assumption that all the metal concentrations in the dust and soil can enter human blood stream, a practical methodology of the use of animal species emerged. Animals were dosed with contaminant metals in soil and dust for a given period of time after which the blood, urine and the other organs of the animals were analyzed to measure the fraction of the metals contaminants that enters the systematic circulation of the animal body and pose toxic consequences (Ruby et al., 1992). This is known as *in vivo* assay. In view of this, various animals such as swine, rabbits, rats and monkeys were used since they are believed to have related gastrointestinal tract similar to humans and the results indicates only a fraction of these contaminants are absorbed into the animal bloodstream (Casteel et al., 1997; Davis et al., 1992; Dodds & Hsu, 1982; Freeman et al., 1996; Freeman et al., 1994; Freeman et al., 1995). However, Maddaloni et al., (1998); Ruby et al., (1999) discovered that physiologically there are differences between the animals used in the *in vivo* experiment and that of humans. Therefore, in respect to human health risk *in vivo* studies is not relevant. Similarly, the use of experimental animals is time consuming, expensive and infringing the animals right. Thus the solution to these problems should be sought out.

2.1.2 *In vitro* Bioaccessibility Extraction

The use of *in vitro* bioaccessibility modeling emerged as an alternative to the use of experimental animals in the evaluation of human health risk (Ruby et al., 1996; USEPA, 2007). This is a laboratory test that is designed to mimic the human gastrointestinal tract to predict the bioaccessibility of metals (DIN, 2000; Rodriguez et al., 1999). In this model soil/dust are incubated at low pH for a period of time to mimic human stomach condition. The pH is then increased to mimic the human intestinal condition. To simulate both the stomach and intestinal fluids, enzymes and organic acids are used. The methodology is considered to be easy, fast, and not costly, has no ethical implication by reducing the use of animals, provide accurate output in a short period of time, and large samples quantities can be evaluated (Chen et al., 2011; Jorge Mendoza et al., 2017; Juhasz et al., 2010; Omar et al., 2013; Oomen et al., 2002; Yang et al., 2012). However, even among the government agencies, it is becoming necessary to the use of bioaccessibility data in assessing the human health risks. For instance in Canada, a government agency known as Health

Canada is committed to research and funding of in respect to bioaccessibility contaminants (Organization et al., 2005).

Presently there are various *in vitro* models for risk assessment of variety of toxic metals in different exposure pathways ranging from simple step extraction test to a sequential extraction test involving many steps (Hack & Selenka, 1996; Hu et al., 2012; Juhasz et al., 2009; Li et al., 2014; Minekus et al., 1995; Molly et al., 1993; Oomen et al., 2002; Rotard et al., 1995; Ruby et al., 1992). Various *in vitro* models were reported such as simplified bioaccessibility extraction test (SBET) (Liu et al., 2016; Oomen et al., 2002; Wang et al., 2016), *in vitro* gastrointestinal method (IVG) (Schroder et al., 2004), simplified bioaccessibility research consortium (SBRC) (Juhasz et al., 2009), unified BARGE method (UBM) (Denys et al., 2012; Rosende et al., 2014; Wragg et al., 2011), physiologically based extraction test (PBET) (Ruby et al., 1996), dynamic computer-controlled gastrointestinal mode (TIM) (Barroso et al., 2015; Minekus et al., 1995), simulator of the human intestinal ecosystem (SHIME) (Molly et al., 1993; Possemiers et al., 2004), standardized German in vitro assay (DIN) (Minekus et al., 2014), relative bioaccessibility leaching procedure (RBALP) (Drexler & Brattin, 2007). On the other hand, various metals were tested such as As (Chi et al., 2018; Liu et al., 2016), Pb (Bi et al., 2015; Li et al., 2014), Cd (Li et al., 2016), Cr, Cu, Zn and other metals (Cai et al., 2016; Hu et al., 2011). However, some of these reported models have some limitations. For instance SBET, TIM, SHIME, DIN and RBALP only involve gastric stage, but the actual absorption of food only takes place in the intestine, not stomach. Furthermore, IVG employed 1 h for intestinal extraction. However, it takes 3−4 h for the completion of food digestion and absorption in the intestine. Moreover, SBRC uses glycine as the gastric enzyme, and glycine has strong affinity to some metal (e.g., Cd) which can reduce their solubility in the stomach. UBM involves mouth in its extraction stages, but food substances are only chewed in the mouth within little time, hence has no impact on absorption of food substances which takes place only in the intestine. For the sake of this study, we only focus on PBET oral *in vitro* bioaccessibility model.

2.1.3 Physiologically Bioaccessibility Extraction Test

Physiologically bioaccessibility extraction test (PBET) is an efficient model of toxicants extraction from the binding matrix planned to simulate biologically system of interest (Omar et al., 2013; Poggio et al., 2009; Ruby, 2004). It is a two stages extraction process, involving both stomach and intestine with the use of appropriate pH and enzymes that exactly mimics the human physiology. This model was validated for the bioaccessibility of toxic metals such as Pb and As using animal models (Ruby, 2004; Ruby et al., 1996). Hence, the relationship between bioaccessibility fraction, soil and dust properties was established through this model (Ruby et al., 1999).

This indicates that PBET technique could be employed in the assessment of human bioaccessibility fraction. Currently it is used in the estimation of human health risk for various toxic metals such as As, Cu Cr, Cd and Zn (Boros et al., 2017; Cheng et al., 2018; Li et al., 2017; Li et al., 2016; Morman et al., 2009; Praveena et al., 2014). Nevertheless, employment of this model in the assessment of human health risk in urban dust especially involving the use of chemometric such as Monte Carlo simulation, using the body weight parameter and average exposure time of the locals so as to get the real risk involve has not been explored.

This model has been considered in this study on the basis of these observations and also because it is a pragmatic method of evaluating the bioaccessibility of toxicants as such it represents the physiology of humans, it is easily applicable, it is robust, easy, fast, inexpensive, it can be applied to a large sample matrix and it can give a better insight which cannot be achieved in the whole animal studies (*in vivo*) (Omar et al., 2013). Mouth play a vital task of chewing and mastication of ingested materials with saliva moistening the food and helping to create food bolus for easy swallowing. Nevertheless, it is not regarded in the physiologically based extraction test, because ingested materials spend a very short time in the mouth, in addition, no absorption of substances takes place in the mouth.

2.2 Metal Bioaccessibility, Bioavailability and Dust/Soil Properties

Organic matter and pH are the soil and dust properties that influenced the bioavailability of heavy metals that are bound to soil and dust (Juhasz et al., 2007; Smith et al., 2014). Ions in soils and dusts are greatly controlled by pH. For instance the bioavailability cations were found to increase in the lower soil pH. The higher the soil pH, the lower the bioavailability of the cations (Das et al., 2013; Juhasz et al., 2009; Zovko & Romic, 2011). The organic matter has been observed to affect the mobility of certain metal ions from adsorption through the formation of soluble complexes and influence the adsorption of cations to negatively charged locations in the bioaccessibility of contaminated soils (Liu et al., 2016). Generally, lower soil/dust pH would increase the mobilization and solubilization of metals which would eventually leads to the metal contaminants to be more bioaccessible and bioavailable. While higher soil/dust pH would decrease the mobilization and solubility of metal contaminants leading to their being less bioaccessible and bioavailable. On the other hand, the higher organic matter content of soil/dust, the lower the metal contaminants are bioaccessible and bioavailable and vice versa.

2.3 Assessment of Human Health Risk from Exposure to Heavy Metals

There is a continual exposure to heavy metals contaminants by human, despite constant mobilization of the health effects these chemicals caused to humans and environment (Elom et al., 2014a). To minimize this, environmental regulatory agencies, institutions and organizations of the world such as World Health Organization (WHO), Agency for Toxic Substances Diseases and Registry (ATSDR), United State Environmental Protection Agency (USEPA), have developed and apply health risk evaluation protocol, thereby recommended research to be carried out in this aspect. This, therefore, depicts the importance of developing and application of health risk estimation procedures to environmental contamination, both locally and internationally. In addition, it is interesting to note that regulatory laws on environmental safety are been set based on the risk assessment studies, which also reiterates the vital part of risk assessment studies on environmental contaminants.

It has been discovered that the entire population in an environment face health consequences on exposure to environmental contaminants such as heavy metals (Rodrigues et al., 2018). Children population are particularly more risky on exposure than adults due to factors such as behavioral differences, changes in physiology, body metabolism and functions which makes them more sensitive and unsafe (Zeng et al., 2016). As a result, the variability in exposure to environmental pollutants between adults and children population is very large. According to literature any report on risk assessment can be regarded insufficient to protect human health except it has identified the distinctive exposure and risk on children (Cao et al., 2016). This, therefore, suggested the significance of children health care.

2.3.1 Exposure Routes

When there is an association between an organism and any chemical in the environment, an exposure has occurred. And the various avenue through which the contaminants gets into an exposed organism is termed to be exposure pathways (Li et al., 2015). Exposure to environmental chemical pollutants by population of organisms particularly humans occurred directly or indirectly. The direct form of exposure is where the heavy metals in an environmental media (soil, dust, water) from the source enters the human body through various channels, while the indirect form of exposure happens as a result of humans eating food grown in a contaminated soil and the pollutant metal eventually gets into the human body. The direct exposure can occur through three main pathways such as oral ingestion by gastrointestinal tract, inhalation by respiratory tract and dermal contact by skin.

2.3.1.1 Oral Ingestion Exposure to Dust and Soil by Gastrointestinal System

Any food consumed must be chewed, broken into pieces, digested, absorbed and the unwanted food is usually removed by the body. This process is known as digestion and the procedure is carried out in the human digestive tract. The human digestive system consists of the components such as mouth here food is broken into pieces by chewing and mixed with saliva, esophagus a tube where masticated food from the mouth passed into the stomach, stomach which serves as a container where food digestion starts, small intestine where further digestion of ingested food and absorption takes place and large intestine in which water and salt are absorbed and the removal of the unwanted food materials occurs, with liver, gallbladder and pancreas adding their components as digestive juices in the digestion process (Elom, 2012). Same procedure occurred when soil and dust are ingested and the poisonous metals which are soluble would be available for absorption into the circulatory system.

As a result of exposure by adults and children, soil and dust could incidentally be ingested. This happen through involuntary mouthing of hands, and objects, eating of falling food particles on which soil and dust particles quickly stick to. Another possible way of soil and dust oral ingestion occurs intentionally. This takes place in many parts of the world especially developing countries such as Africa and Asia, a behavior termed geophagy (Abrahams & Parsons, 1996; Kariuki et al., 2016; Owumi & Oyelere, 2015). This is a custom exercise by poor citizens where children and adults especially pregnant women consumed earthly substances such as clay and chalk with believe that it compliment mineral-deficient diet (Kawai et al., 2009). However, it has been established that geophagy takes place in urban settings (Mathee et al., 2014). Previous studies reported that a median amount of 28 g with a range of 8−108 g of soil is consumed daily by those who practice geophagy (Geissler et al., 1998). Even though it was discovered that out of the 28 g amount of soil ingested daily, the Fe content consumed as mineral was about 32−42%. However, not all soil ingested are rich in the assumed minerals and on top of it, geophagy could contribute significant risks of ingesting toxic metals such as Pb, Cd, As and Hg (Abrahams, 2012; Hunter-Adams, 2016), thus putting human health at stake. An *in vitro* bioaccessibility extraction test was conducted in the UK on sample of soil imported and was believed to have been consumed by Asian migrant pregnant women, 41-54% of mineral nutrient and a significant amounts of Ca, Cu and Mn was discovered in the soil samples (Abrahams et al., 2006). The metal analysis conducted on Calabash chalk soil mostly consumed by pregnant women in Nigeria revealed that it consisted of considerable amount of Pb that could possibly endanger the health of both women and their unborn babies (Dean et al., 2004). A recent study in South Africa revealed that high level of Pb was discovered among those who ingested clay materials (Mathee et al., 2014). In the United States, migrant women who practice geophagy were discovered to have elevated Pb content which could eventually affect their growing fetus in pregnancy (Alba et al., 2012). Similarly Lambert et al (2013) reported that exposure to poisonous metals via ingestion of soil by women during pregnancy could cause the damaging of the fetal neurological development.

Although geophagy may be regulated, nevertheless, the incidental ingestion of soil and dust by both population of adult and child in both city and rural areas could be difficult to regulate and this could pose health consequences to humans. This is because it depends on many factors such as weather conditions, the occupation of the urban dwellers activities in the urban cities, as well as the nature of the environmental or urban settings. Even though, dry and windy weather increased the amount of soil movement and dusts in urban cities, increase rate of various emissions increased the contents of contaminants in soil and dust and outdoor activities or work increase the risk of exposure. Nevertheless, wherever you live you hardly escape exposure to soil and dust especially in urban cities.

2.3.1.2 Dermal Absorption Exposure to Soil and Dust via Skin Contact

One of the important gate way to environmental chemicals getting into human body is through skin exposure. This is due to the fact that skin comes in contact with anything outside the body. It is established that dermal exposure to poisonous metals particularly at work place results into human health risks such as dermal lesions and skin cancer (Chen et al., 2015). This is because, there is a continual exposure and or interaction between the skin and the toxic substance. This could happen either by surface contact which involves the contaminants being transferred from the contaminated surfaces to the skin. Another form of workplace skin exposure is immersion where the skin is in direct contact with liquid or solid chemical substances and uptake of vapor through the skin (Fenske, 1993). For instance Lin et al. (2009) reported acute severe chromium poisoning after dermal exposure to Cr (VI) by a worker who washed a chromium electroplating tank. The authors noted that there is a significant consequences of transdermal exposure to Cr(VI) on human, as such should not be overlooked. It has been reported that dermal exposure by workers occur due to continuous wearing and removal of the gloves during the process of work (Cherrie et al., 2004). It has been noted that skin exposure to toxic metals can be significant across all occupational sectors such as agricultural, construction, manufacturing, painters and hairdressers (Delgado et al., 2004; Semple, 2004). In spite of the fact that occupational channel is found to greatly influence dermal exposure, nevertheless, skin exposure to soil and dust play a vital role in transferring of heavy metals into the human body. Both adults and children are exposed through various outdoor activities such as playing, walking.

2.3.1.3 Inhalation Exposure Pathway

The absence of air can be detriment to human life and even leads to death, this is because air, especially oxygen, is the primary vehicle for the entire metabolic activities in human body. Therefore, inhalation of air is vital to human. Air gets into the human body through the respiratory system. The respiratory system consists of organs such as pharynx, larynx, trachea, bronchi and lungs, grouped as upper and lower respiratory tract. The pharynx and larynx are part of upper respiratory tract, while the trachea, bronchi and lungs are found at the lower tract. As air is being breathed in through the nose it passes through the pharynx and into the larynx and at this region large inhaled particles are trapped for filtration (Bose-O’Reilly et al., 2018), while the inhaled particles moved to the lungs via the trachea and bronchi. At this part the inhaled particles can also be moved from the lungs to the oral cavity where with the aid of ciliated mucus lining. The particles that successfully reached the oral cavity can either be coughed out or swallowed.

The quality of air represents a healthy urban environment and life, but due to various human activities that leads to emission of various substances particularly heavy metals, the air in urban environment could be contaminated (Najmeddin et al., 2018). Human health is, therefore, threatened. As these contaminants particles are suspended in air in form of dust humans encounter them through breathing process as a result of any outdoor activities (Mohmand et al., 2015). As a result of undeveloped defense mechanism in children, therefore, they inhale more volume of air than adults due to a larger surface area of their lungs (Berhane et al., 2011; Salvi, 2007), children, could, therefore, be faced with more risks on inhalation exposure than adults. According to Krishna & Mohan, 2013, contamination of heavy metals in urban dusts increases with decrease in dust particle size. Even though dust particles of less than 10 μm could be more penetrative via inhalation exposure (Huang et al., 2016). However, high health risks is associated with particles of less than 63 μm, because they are inhalable particles where they could pass into the lungs and or be coughed from the larynx and be swallowed (Kennedy & Hinds, 2002; Soltani et al., 2015). It has been established that inhalable particles can be deposited in different places of the respiratory tract depending on their size, shape and chemical properties (Sturm, 2012).

2.4 Risk Assessment Techniques

Procedures established by the United State Environmental Protection Agency (USEPA), United State Department of Environment (USDOE) and the Agency for Toxic Substances, Diseases and Registry (ATSDR) are usually employed in the human health risk assessment of heavy metals in dust samples (ATSDR, 2007; USDOE, 2011; USEPA, 1989, 1991, 1997, 1999, 2002, 2008, 2011). These models involved the use of equations for the risk assessment due to exposure to toxic metals via ingestion, dermal contact and inhalation routes (equations 2.1, 2.2 and 2.3) (Alamdar et al., 2016; Cao et al., 2015; Cheng et al., 2018; Kamunda et al., 2016; Man et al., 2010; Mohmand et al., 2015; Praveena et al., 2015; Wei et al., 2015; Zheng et al., 2010). The risks involved were calculated based on the USEPA guidelines following (equations 2.4, 2.5, 2.6 and 2.7) (USEPA, 1989, 2001, 2002). In this study, the body weight of Malaysians is taken into consideration based on the Malaysian dietary guidelines (Anuar Zaini et al,. 2005; Azmi, 2009; Yang et al., 2017). This is due to the fact that weight of an individual depends on the dietary and socioeconomic status (Amarasinghe et al., 2009; Johnston & Lordan, 2014). The average body weight of an adult Malaysian is considered to be 62.70 ± 18.6 kg, while the average body weight of Malaysian child is estimated to be 32.6 ± 8.7 (Azmi, 2009; MOH, 2013). However, the exposed skin surface area for both adult and child are 5700 and 2800 cm^2/day, respectively (Sany et al., 2014). On the other hand, the Malaysian average exposure time (AT) is 27265 days which is equivalent to 74.69 years (DOSM, 2016). The exposure via ingestion, dermal and inhalation of toxic elements in dust are calculated using the following equations:

$$EXPing = \frac{Cdust \times IR \times ED}{BW \times AT} \tag{2.1}$$

$$EXPderm = \frac{Cdust \times SA \times EF \times ED \times AF \times ABS \times CF}{BW \times AT} \tag{2.2}$$

$$EXPinh = \frac{Cdust \times InhR \times EF \times ED}{PEF \times BW \times AT} \tag{2.3}$$

Where $EXP_{Ing,}$, EXP_{Derm} and EXP_{Inh} represent the exposure doses due to ingestion, dermal and inhalation contact; C_{dust} indicates the concentration of toxic metal represented in urban dust (mg/kg); IR is the dust ingestion rate (0.0001 and 0.0002 kg/day) for adult and child respectively (USEPA, 2002); ED represent exposure duration (30 and 7 years) for both adult and child (Koki et al., 2018); AT is the average exposure time for non-carcinogenic risk (10950, 2555 days) for adult and child respectively (Bortey-Sam et al., 2015); AT indicates the carcinogenic risk for both adult and child (27265 days) (DOSM, 2016); CF indicates the conversion factor (1×10^{-6} kg/mg) for both adult and child (USEPA, 2004); AF is the skin adhesion factor (0.07 and 0.2 mg/cm^2) for adult and child (USEPA, 2011); ABS represents dermal absorption factor (0.1 for both adult and child); SA indicates the skin surface area (5700 and 2800 cm^2) for adult and child, respectively (Sany et al., 2014); PEF denotes the particle emission factor (1.36×10^9 m^3/kg) for both adult and child (USEPA, 2002); InhR represents the dust inhalation rate (20 and 10 m^3/day) for adult and child, respectively (USEPA,2002) as shown in Table 2.1.

Previous studies that involved risk assessment in Malaysia majorly employed presumptive body weight in the risk estimation (Jamhari et al., 2014). Similar trend was adopted in the risk assessment due to exposure to urban soil (Praveena et al., 2014). However, for more accurate and reliable estimation of risks that involved exposure to toxic metals, this study has remodeled those existing approaches by employing the real Malaysian body weight and average exposure time in chemometric simulation. As errors in these parameters will cause large deviation in HRA, even when the concentration measured are accurate. Hence, involving the simulation analysis in the data and the use of the parameters for the citizens makes the output estimation of the risks precise. Therefore, this new approach in risk analysis is indicating a modification in the estimation of risks due to exposure to toxic metals in urban dust/soil in Malaysia.

Table 2.1: Risk assessment evaluation parameters for ingestion, inhalation and dermal exposure for total metal in urban dust.

Symbols	Units	Values for Adult	Values for Child	References
Cx	mg kg^{-1}	Please refer to table S3		This study
BW	kg	N(62.7, 18.6)	N(32.6, 8.7)	Azmi et al, (2009); Zaini et al, (2005)
ED	years	30	7	This study
EF	days $year^{-1}$	365	365	This study
IR	kg day^{-1}	0.0001	0.0002	USEPA (2002); DEA (2010)
IR inhalation	mg cm^{-2} day^{-1}	20	10	USEPA, (2002)
SA	cm^2 day^{-1}	5700	2800	Sany et al, (2014)
AF	mg cm^{-2}	0.07	0.2	USEPA (2011)
ABS	none	0.1	0.1	USEPA (2011)
PEF	m^3 kg^{-1}	1.36×10^9	1.36×10^9	USEPA (2002), DEA (2010)
CF	kg mg^{-1}	$1x10^{-6}$	$1x10^{-6}$	USEPA (2004)
AT Carcinogenic	days	27265	27265	DOSM (2016)
AT Non-Carcinogenic	days	10950	2555	Bortey−Sam et al, (2015)

2.4.1 Toxicity Assessment

The toxicity assessment as a result of exposure to hazard metals was computed for both carcinogenic and non-carcinogenic. The toxicity indices adopted by (USEPA, 1989) was applied, where the index as the slope factor (SF) was taken for cancer and reference dose (RfD) for non-carcinogenic. Each and every element has its SF and RfD values. The following equations are used for the toxicity estimation (USEPA, 1989):

$$CR = EXP \times SF \tag{2.4}$$

$$TCR = \sum \text{CRing} + CRderm + CRinh \tag{2.5}$$

Where CR = carcinogenic risk; EXP = exposure to the hazard contaminants in the dust through ingestion, dermal and inhalation routes; SF = slope factor, TCR = total carcinogenic risk for a lifetime of an individual. According to the USEPA (2002) guidelines, 1×10^{-6} to 1×10^{-4} is the permissible limits for carcinogenic risks. In contrast, the non-carcinogenic risk is represented in the following equations:

$$HQ = \frac{EXP}{RfD} \tag{2.6}$$

$$HI = \sum HQing + HQderm + HQinh \tag{2.7}$$

Where HQ = hazard quotient; RfD = reference dose (mg/kg/day); HI = hazard index. The tolerable value for HI is 1, if HI < 1 there is no possibility of non-carcinogenic risk, but if HI > 1 then there could be possibility of a non-carcinogenic risk to the community (USEPA, 2002). The values for SF and RfD are presented in Table 2.2.

Table 2.2: Slope factor (SF) and reference dose (RfD) values for health risk calculation (mg/kg/d).

Heavy metal	RfD oral	Dermal	Inhale	CSF oral	Dermal	Inhale	References
Pb	3.60×10^{-3}	NA	NA	8.500×10^{-3}	NA	1.20×10^{-5}	USDOE, (2011); WHO, (1993)
As	3.00×10^{-4}	1.23×10^{-4}	3.00×10^{-4}	1.50×10^{0}	3.66×10^{0}	1.51×10^{-1}	USEPA, (1999, 2011b)
Cd	5.00×10^{-4}	5.00×10^{-4}	5.70×10^{-5}	6.30×10^{0}	NA	6.30×10^{0}	DEA, (2010); USEPA, (1991, 2011b)
Cu	3.70×10^{-2}	3.70×10^{-2}	NA	NA	NA	NA	DEA, (2010); USEPA (2011)
Cr (III)	1.50×10^{0}	1.50×10^{0}	NA	NA	NA	NA	DEA, (2010); USEPA (2011b)
Cr (VI)	3.00×10^{-3}	3.00×10^{-3}	2.20×10^{-6}	5.00×10^{-1}	NA	8.40×10^{-2}	DEA, (2010); USEPA, (2011b)
Zn	3.00×10^{-1}	3.00×10^{-1}	NA	NA	NA	NA	DEA (2010); USEPA, (2011b)
Mn	2.40×10^{-2}	2.40×10^{-2}	1.43×10^{-3}	NA	NA	NA	DEA, (2010); USEPA, (2011b)

NA = not available.

2.5 Statistical Modelling

Statistical modelling is a technique applied to a given set of data in order to extract information on the relationship between variables. Statistical modelling technique such as chemometric emerged in the 1970s as computers were increasingly used for scientific exploration (Geladi & Esbensen, 1990). In the year 1971, Wold composed the term 'Chemometrics" (Wold, 1995). In the recent years, this technique is widely used for various applications in different fields such as analytical chemistry, industrially and academia (Wold et al., 1984). The choice and application of a suitable statistical model is mostly done for the purpose of presumptive test and the interpretation of data in order to get a logical assumption. Various tools such as descriptive statistics, plots and graphs can be used to evaluate the validity of the data so that the basic idea of the association between models variables would be obtained. There are numerous modelling and statistical analysis methods, however the objectives and the set of data of a work will determine the very one to apply.

2.5.1 Monte Carlo Simulation Model

The Monte Carlo simulation model is employed to achieve a forecast in statistical probability distribution in a situation where analytical solutions proved difficult or are not possible to be achieved, or on the other hand in a situation in which assumptions of specific regression are under suspicion of violation. A very large number of iterations are used for the repeated simulations with each repetition defined for the model by the values of the assumptive inputs so that statistical variables output of the system model could be obtained (Helton, 1993). The possible input variable values X (X_1, X_2, X_3,…, X_n) are sampled based on their distribution. Similarly the value for the output variable L is calculated through performance function L = f (X) at the samples input variable (Helton, 1993). There are three steps required when Monte Carlo simulation model is applied on dependent variables:

i. Random sampling on input variables X

ii. Evaluating model output L

iii. Statistical analysis on model output

The input variables are selected so as to create samples that represent distribution of the input variables. The sample representing the input variables will then be used for the simulation exercise. Similarly, the statistical analysis of the characteristic for the output variables (mean, variance, reliability) are performed after obtaining the samples of the output variable L.

Monte Carlo simulations were first introduced by David Hertz in 1964 in the application of corporate finance (Hertz, 1979). Later in 1977, Phelim Boyle initiated the use of simulation in predictive assessment (Boyle, 1977). It is later applied in other fields such as physics, chemistry and computer science (Binder et al., 1993; Vrugt et al., 2009) and in environmental pollution assessment (Burmaster & Anderson, 1994; Dominici et al., 2002; Kuik et al., 1993; Sun et al., 2017). In the recent years, Monte Carlo simulation model was successfully applied in the risk assessment of heavy metals on environmental samples (Koki et al., 2018; Low et al., 2015).

Similarly, in the most recent years Monte Carlo simulation model has been used in solving problems in respect to health risk assessment associated with heavy metals in soil and dust (Chabukdhara & Nema, 2013; Chen et al., 2015; Li et al., 2014; Othman et al., 2018; Qu et al., 2012; Qu et al., 2012; Wang et al, 2010). However, in the most recent times it is discovered that very few studies applied Monte Carlo simulation on health risk assessment of heavy metals in soil and dust based on bioaccessibility and bioavailability fractions (Cao et al., 2016; Cao et al., 2015). Therefore, this suggests that application of Monte Carlo simulation model using the citizens' parameters on the bioaccessiblility and bioavailability fraction is a new trend in health risk assessment of heavy metals in soil and dust.

2.5.2 Multivariate Statistical Technique

This model involves analysis of a set of data in order to discover the association between multiple observed variables (Tokalıoğlu & Kartal, 2006). Characterization of different environmental samples and classification of spatial data could be achieved through the use of multivariate statistical technique. In environmental studies, the commonly and widely applied multivariate statistical techniques are the principal component analysis (PCA), factor analysis (FA), hierarchical cluster analysis (HCA), and correlation analysis (CA) (Dong & Lee, 2009; Jamhari et al., 2014; Tahri et al., 2005), especially in respect to heavy metals in soil and dust (Al-Khashman, 2013; Chen et al., 2005; Han et al., 2014; Khan et al., 2017; Lee et al., 2006; Lu et al., 2010; Ordonez et al., 2003; Qiang et al., 2015; Yongming et al., 2006).

In PCA, smaller number of independent factors are majorly extracted from the reduced data set in order to analyze the association among metals as variables. The degree of the association between and among parameters is successfully explored by PCA and the related parameters are grouped into principal components (PCs). To explain the total variance of the variables involved in PCA, the eigen values greater than unity are considered. PCA extracts eigen values and eigen vectors from the square matrix sourced by multiplying the data matrix. This is done through the use of correlation matric in order to evaluate the anomalies caused by the overlap due to much data containing many variables (Chai et al., 2015; Franco-Uría etal., 2009; Li et al., 2017).

FA produced new class of variables called varimax factors through the varimax rotation of the significant principal components. The contributions on the variation by a variable is determined by the loadings of a parameter in the quadrant (left or right and positive or negative) (Dong et al., 2018; Khan et al., 2017). HCA measures similarities between locations and or classify metals in sites based on the similarities of their chemical properties and this is perfectly achieved through the use of Euclidean distance. In order to link the cluster or group of locations or parameters with similar distance and to isolate those clusters sited at large distance, an appropriate linkage algorithm (Ward's single, centroid or average) is employed (Facchinelli et al., 2001; Gu et al., 2012; Sun et al, 2010).

There is a need of a clear explanation in the interpretation of the clusters in order to justify the clustering type. CA is an effective statistical approach that indicates the relationships between toxic metals, toxic metals and dust physicochemical properties. It is also a functional tool to understand the controlling factors of metals, and on the other hand their possible sources. The degree of the relationship between the heavy metals is determined by the correlation coefficient (r). A correlation between metals with an r value of above 0.8 suggests a significant correlation, 0.6 – 0.8 indicates a strong correlation, 0.5 – 0.6 shows a moderately strong correlation, 0.4 − 0.5 suggest moderate correlation, 0.3 – 0.4 shows a fair correlation, and less than 3 suggests a poor correlation. While a negative r value indicates inverse correlation between two variables (Chan, 2003; Cheng et al., 2018; Franco-Uría et al., 2009).

2.6 Heavy Metals in Urban Dust/Soil and their Effects on Humans and the Environment

The concentration of heavy metals in soil and dust are supposed to be low because they occur naturally (Table 2.3). However, in the recent years due to rapid modernization, urbanization, industrialization and increase in population which has significantly increased the rate of anthropogenic activities in urban cities which significantly influenced the level of these toxic metals in soil and dust and eventually create a great concern (Abdullah et al., 2015; Hamad et al., 2014; Li et al., 2013). The anthropogenic activities that are the major sources of heavy metals pollutions into the urban environment in dust/soil, include emission from industries (coal combustion, chemical industries, automobile industries, electronic parts industries and auto repair shops), traffic emissions (vehicle exhaust particles, wear and tear of tires, particles from brake lining wear, wear of street surfaces and car components), agricultural (application of fertilizer and spray of chemicals), construction work, domestic emissions and atmospheric depositions (Dong et al., 2018; Faiz et al., 2009; Harrison et al., 2017; Qiang et al., 2015; Wei & Yang, 2010). Therefore, it has been found that human health is threatened due to the bioaccumulation, floating in air and long residence time of these metals in dusts on the basis of their non-biodegradable nature and toxicity (Mohmand et al., 2015; Rajaram et al., 2014; Sanderson et al., 2016; Zheng et al., 2010). Therefore in many countries of the world toxic metals pollution in respect to urban environment has received a total concern and attention.

Several previous studies have been conducted and report contamination of heavy metals such as Pb, As, Cd, Cu, Zn, Mn, Cr, and Ni among others in urban dusts/soil due to industrial, agricultural, traffic emissions and atmospheric deposition using total metal contents (Alamdar et al., 2016; Apeagyei et al., 2011; Christoforidis & Stamatis, 2009; Eqani et al., 2012; Han et al., 2014; Hu et al., 2012; Naderizadeh et al., 2016; Ripin et al., 2014; Yoshinaga et al., 2014).

Table 2.3: Soil and dust background concentration values of some selected heavy metals (mg/mg).

Metals	Background soil concentrations (mg/kg)	References
As	4 − 11.2	(CNEMC, 1990; Kabata-Pendias, 1992)
Cd	0.1 − 0.3	(Aloway, 1995), CNEMC, 1990
Cu	20 − 30	(Baker, 1995), CNEM, 1990
Cr	30 − 61	(McGrath, 1995),CNEMC, 1990
Ni	20 − 30	McGrath, 1995,CNEMC, 1990
Pb	26 − 50	(Davies, 1995), CNEMC, 1990
Zn	10 − 74.2	(Kiekens, 1995), 1995, CNEMC, 1990
Fe	ND	NA
Mn	ND	NA

CNEMC = China national environmental monitoring center, ND = not detected.

The contamination level of these toxic metals once exceeds the approved standard permissible limits in soil and dust, it could possibly lead to toxic consequences either directly or through food chain. However, not the entire ingested metal contaminants concentrations (total metal) are available for uptake into the human system. Therefore, there is an urgent need to find the exact fraction concentration of metal contaminant available for uptake and soluble ready for circulation in the human system (Bioaccessibility). Table 2.4 shows the approved standard permissible limits of heavy metals in dust and soils by Canadian Council of Ministers of the Environment for environmental quality guidelines based on the land use.

The primary consequences of heavy metals to human health could be associated to its toxicity and the exposure. However, the effect of toxicity and exposure to heavy metals in dust/soil such as As, Pb, Cd, Cr, and Ni among others to human health have been

Table 2.4 Canadian soil and dust approved guideline values (mg/kg) with respect to land use.

Metals	Agric	Resid/Park	Comm	Indus	References
As	12	12	12	12	CCME,1997
Cd	1.4	10	22	22	(CCME,1999)
Cu	63	63	91	91	CCME,1999
Cr	64	64	87	87	(CCME,1997)
Ni	45	45	89	89	(CCME,2015)
Pb	70	140	260	600	CCME,1999
Zn	200	200	360	360	CCME,1999
Fe	NA	NA	NA	NA	NA
Mn	NA	NA	NA	NA	NA

CCME = Canadian council of ministers of the environment, NA = not available, Agric = agricultural land, Resid/park = residential/park land, Comm = commercial, indus = industrial.

previously studied widely (Kamunda et al., 2016; Olawoyin et al., 2012; Wei et al., 2015; Keshavarzi et al., 2015). These studies suggest the consequences of metal contaminants in soil and dusts on humans, therefore, it is necessary to employ the right evaluation method in order to assess their bioaccessible fraction in the human body. But however, some of these studies such as Kamunda et al. (2016) and Wei et al. (2015) evaluated the toxicity of the metals and estimated the risks due to exposure to the metal contaminants in soil and dust based on total metal contents. Nevertheless, total metal content alone could provide inconclusive risks (Cai et al., 2016), because the risks induced to human health by these metals is dependent on their dissolution in the gastrointestinal tract. On the basis of this, the use of bioaccessibility and bioavailability fractions, is a choice of this study.

Hu et al, (2012) conducted a research on bioaccessibility and health risk of heavy metals in urban dusts of Nanjing, China. They reported high bioaccessibility of Cd, Zn, Pb, Mn and As from different functional areas and that children are more at risks in the city than adults population. Another study by Mohmand et al, (2015) reported human exposure to toxic metals via contaminated dusts in rural, urban and industrial areas of Punjab, Pakistan. Their results showed that significant concentration of heavy metals in urban areas, followed by industrial and then rural areas. The biaoaccumulation results revealed that dust/soil exposure is one of the major pathways of heavy metals getting into human body.

However, that children in urban and industrial areas of their study are vulnerable to risks of Cd and Pb. Moreover, in another study by Li et al, (2017) reported the total metal concentrations in urban dusts of Chengdu, China to be higher than the background values indicating anthropogenic influence. The bioaccessibility health risk assessment results showed that commercial and traffic areas of their study pose high concentration of bioaccessibility in the dusts indicating more risks to the inhabitants of those locations. However, to estimate the actual risks to human, Monte Carlo simulation analysis of the data have to be conducted rather than the deterministic method, which has not been observed by the previous research and is the method of choice in this study which makes it different from previous studies.

The following are heavy metals whose poisonous measure is dependent on their sources, forms, bioaccessibility and bioavailability (Hamad et al., 2014; Keshavarzi et al., 2015).

2.6.1 Arsenic (As)

As is classified as a metalloid having both metallic and non-metallic properties, but it is however referred to as a metal. As exists naturally in soil. It is distributed into the environment through the weathering of rocks and volcanic eruptions, and soil leaching. However, human activities such as industrial discharge, mining, agricultural, pigments, waste incineration, pharmaceutical, wood preservatives and traffic related activities significantly increased the level of As in the soil and dust. According to WHO, anthropogenic emissions of As into the atmosphere is very much higher than the natural source (WHO, 2001). When As reacts with carbon and hydrogen, it forms an organic compound but when it reacts with oxygen, chlorine and sulfur, it forms an inorganic compound. As occurs in either -3, +3, and/ or +5 valence states. Even though both the organic and inorganic forms of As are toxic, yet the inorganic As arsenite (+3) and arsenate (+5) are known to be more toxic and mobile in soil especially at low pH and is carcinogenic (ATSDR, 2007).

The arsenobetaine or arsenoribosides are the complex organometallic molecules which are non-toxic and are mostly found in aquatic environment (Sánchez-Rodas et al., 2007). Humans can be exposed to As in dusts/soil of urban environment through incidental ingestion, inhalation of dusts/soil and dermal contact, and for children by playing with contaminated sand or objects. Exposure to As and the acute toxicity of As can affect respiratory tract, skin, liver, gastrointestinal tract, cardiovascular and nervous system, consequently result to skin and lung cancer, neurotoxicity, and cardiovascular disease (Lu et al., 2009; NRC, 1999).

As compounds are known to cause cancer as such are classified by the USEPA as Group A human carcinogen (USEPA, 2004a). Other effects of long-term exposure to As includes diabetes, enlargement of liver, bone marrow depression and high blood pressure. Because of its toxicity, WHO could not recommend permissible level of its exposure due to inhalation, but only established a risk level of about 1.5×10^{-3} μg/ m^3 (WHO, 2001). The recommended permissible guidelines for As exposure with respect to land use is shown in Table 2.3. Health effect due to exposure to As has been reported by previous studies (Carrizales et al., 2006; Hu et al., 2012).

According to WHO, southeast Asia is a region which could suffer long-term effects of exposure to As because of the natural belt of arsenic-rich alluvium that has been deposited in the region million years ago a part from the anthropogenic addition and that dust/soil is one of the major possible means of exposure to As in that region (WHO, 2005). However, soils of Cornwall in the UK were one of the world's highest As concentrations as a result of that region once the world largest producer of As. It was a great concern to the population of Cornwall region because the exposure to As in the soil and dust resulted to skin cancer (Philipp et al., 1984).

2.6.2 Lead (Pb)

For decades, Pb has been found to have a negative effects on humans. It is ubiquitous and non-biodegradable (Faiz et al., 2009). Due to its toxicity WHO has define Pb as 1 of the 10 chemicals of major public health concern (WHO, 2018). Pb has been classified by the international agency for research on cancer (IARC) as a group B2 carcinogen, because it is suspected to be a human carcinogen (IARC, 2006). However, inorganic Pb compounds are probable human carcinogen as such are categorized in Group 2A (IARC, 2006). For instance, ingestion of Pb could affect the brain, kidney, reproductive system and nerve tissues, most especially when children are exposed to it. The consequences is retarded learning, growth and impaired hearing (Kamunda et al., 2016; WHO, 2018).

According to ATSDR (2007), bones are the reservoir of Pb on exposure, and that it was discovered that in human adults about 94% of the entire body, Pb load is located in bones and about 75% found in children. Even after the end of exposure the Pb from the accumulation point can be transferred to the different organs of human body thus incurring serious effects. Other researchers have reported that for each 10 µg/dL of blood Pb detected in children, their IQ is reduced by at least 1−3 points which if found in many individuals in a giving society could result to economic loss due to overall reduced intellectual performance (Morgan, 2013).

The effect of Pb exposure by pregnant women is retarded growth of the fetus and premature birth. Pb at high blood Pb has been reported to cause convulsion, comma and finally death. Exposure to Pb in urban dust can happen through incidental ingestion by playing or mouthing of objects. Pb occur naturally even though it is not abundant in nature. But human activities such as traffic, burning of fossil fuel and industrial emissions, mining activities, battery recycling, flaking of paints from building have increased the Pb content in the urban environment especially urban dusts/soils (Eqani et al., 2016; Laidlaw et al., 2014). Even though, leaded fuel has been banned for decades its long half-life in soil still exerts its effects, emissions from fossil fuels (Saint'Pierre et al., 2004).

Previous studies have reported Pb poisoning in dust and soils. In Zamfara, Nigeria, there was a significant Pb poisoning of blood Pb level > 45 µg/dL. The Pb contamination in dusts and soil was found due to a gold ore processing and it has caused the death of over 350 children (Lo et al., 2012; Plumlee et al., 2013; Tirima et al., 2016). According to Centers for Disease Control and Prevention, a child blood Pb level that is > 10 µg/dL is considered high, and they recommended that any child with a child blood level > 45 µg/dL should be giving an intensive medical care (CDC, 2002). Blood Pb concentrations of 5 µg/dL supposed to be the safe level (Madhavan et al., 1989), but however, even this blood Pb level has been found to be associated with decreased intelligence, behavioral difficulties and learning problems in children (WHO, 2018). Similarly significant contamination of soil and dusts with Pb from Pb-Zn mines in Kabwe, Zambia caused high blood Pb level in children from that region (Bose-O'Reilly et al., 2018; Yabe et al., 2015).

Also, WHO (WHO, 2018) reported that exposure to Pb contaminated soil and dusts from battery recycling has resulted to mass Pb poisoning and several deaths in young children in Nigeria, Senegal and other countries. Childhood Pb poisoning has been reported in inner cities of Australia due to exposure to Pb in soil dust (Laidlaw & Taylor, 2011). In Germany, elevated Pb content was reported in the soil which could lead to the pollution of the environment through dust arising from the soil (Rinklebe & Shaheen, 2014). In Poland, evidence showed that children living around Zn and Cu mills had elevated Pb levels in their blood when compared to children living where there are no industries (Jakubowski et al., 1996). Therefore, pollution of Pb in urban dust due to various human activities is a great concern to public health because of its toxic effects.

2.6.3 Cadmium (Cd)

Cd is found naturally in soils, however, anthropogenic activities influence its concentration in urban soil and dust. The possible sources of Cd in urban environment especially urban dusts/soils could include combustion of motor oil, automobile fuel, wear and tear of tire, metals coating, manufacture or disposal of batteries, automobile lubricants, pesticides and mineral fertilizers, mining and processing, municipal refuse, sewage sludge to land, construction and reconstruction activities (Al-Khashman, 2007; Han et al., 2014; Rout et al., 2013; UNEP, 2010). Exposure to Cd in dust particles beyond the acceptable limits of 3.00 mg/kg, could pose health consequences to humans because it has a significant toxic effect on human that could lead to cancer.

Table 2.3 shows the guidelines of Cd in urban soil and dusts of different urban land use. Exposure to Cd via urban dust could affect the kidney and other related human organs (Faiz et al., 2009). Previous studies reported high pollution degree of Cd in environmental samples (Ke et al., 2017; Shafie et al., 2014). Contamination of Cd in urban dusts have been reported by previous studies from Malaysia and different countries. For instance in road dusts of Kuala Lumpur city Centre, Malaysia, Cd was discovered to have an enrichment of a class extremely high enrichment (EF = 20−40) and was due to high anthropogenic input (Han et al., 2014; Kamani et al., 2018; Rout et al., 2013; Suryawanshi et al., 2016).

Similarly, in roadside dust of Delhi, India, Cd shows high contamination by the pollution index and potential ecological indices (Suryawanshi et al., 2016). On the other hand, spraying of phosphate fertilizer in farming activities in New Zealand has released a high concentration of Cd into the urban environment (Loganathan et al., 2003). Elevated concentration of Cd in the soil of Germany has been reported which could be as a result of atmospheric dusts (Rinklebe & Shaheen, 2014).

Cd is one of the metals classified as human carcinogens (Cancer, 1994, 2012; Sá et al., 2016). The USEPA Cancer Risk Assessment Validation Effort has classified Cd as Group B1 probable human carcinogen (Crave, 1986). The carcinogenic effect of Cd was first discovered in animals and later in humans (Huff et al., 2007). Cd exposure is associated with lung cancer (Beveridge et al., 2010), and possible prostate cancer (Goyer et al., 2004; Pan et al., 2010). However, research has shown that Cd is also associated with cancers of the breast, pancreas and urinary bladder (Huff et al., 2007). Schoeters et al. (2006) reported that elevated Cd exposure by pregnant women could possibly effect a child's motor skills and perception, and weakened immune system of children may be related to high level of Cd.

2.6.4 Nickel (Ni)

Ni occurs naturally in the earth crust and in combination with other elements such as oxygen and sulfur as oxides or sulfides. It is released into the atmosphere and soils through volcanic eruptions and wind-blown dusts (Cempel and Nikel, 2006). However, anthropogenic activities such as burning of residual and fuel oil, trash incinerator, coal burning, steel production, production of Ni alloy and application of some phosphate fertilizer have significantly increased the level of Ni in the urban environments especially the atmosphere (Iyaka, 2011; Rathor et al., 2014; Sreekanth et al., 2013). According to Cempel & Nikel, (2006) the toxicity effects of Ni comes as a results of its capacity to replace other metal ions in proteins or its ability to bind to cellular compounds. Exposure to Ni through dermal contact leads to the development of skin rashes which is associated to Ni induced hypersensitivity (USEPA, 1986; Russell and Lee, 2005), while inhalation exposure to Ni containing dusts could result to asthma and irritation of nasal membrane and nasal tumors (Iyaka, 2011).

Ni contamination due to atmospheric deposition in soils near a large Ni smelter in Ontario, Canada was reported (McIlveen & Negusanti, 1994). Similarly, in Germany Ni contamination has been reported in soil which could have resulted from dusts (Rinklebe & Shaheen, 2014). In Russia, contamination of soil and air with Ni was reported around Ni smelting operation which happened due to atmospheric deposition which is enriched with Cu and Ni waste products and consequently pollutes the atmosphere (Motuzova et al., 2014; Norseth, 1994). Taiwan reported Ni pollution in soil of about 420 ppm (Chen et al., 1999).

2.6.5 Chromium (Cr)

Cr exists in three stable oxidation states such as 0 which is elemental metal, +3 (trivalent) and +6 (hexavalent). It occurs naturally in soil and dust in form of Cr(III) and Cr(VI) and elemental metal Cr is derived by human activities (Organization, 1990). Cr(VI) in the air reacts with pollutants in dust particles to form Cr(III) (ATSDR, 2000). Human activities such as coal and oil combustion, chrome plating, cement-production plants, the wearing down of asbestos, wearing of vehicular mechanical parts, manufacture of chemicals, and different types of alloys, chrome plating, paints and pigments, manufacture of textile, production of high-fidelity magnetic audio tapes and tannery were identified to be the sources and add to the levels of Cr(VI) into the environment especially the air (Lu et al., 2017; Lu et al., 2010). As Cr(III) is required in low dose in human diet and its deficiency is associated with impaired fertility and glucose tolerance, diabetes and cardiovascular disease, Cr(VI) compounds on the other hand are toxic and carcinogenic, are even classified as Group A human carcinogen ATSDR, 2000; (EPA, 1998). In fact, Cr(VI) is known to be 100 times more toxic than Cr(III) (Saha et al., 2011). Exposure to Cr dose could result in adverse consequences to the liver, lung, kidney and small intestine (Cui et al., 2015; Gatto et al., 2010; Sudha et al., 2011; Stout et al., 2008). Health risk related to Cr exposure in soil/dust could possibly be associated with Cr(VI) as Cr(III) is less harmful; hence may pose no much risk (Saha et al., 2011; Sun et al., 2015; Tóth et al., 2016).

The major routes of exposure to Cr in urban dusts are ingestion, inhalation and dermal contact. Exposure to Cr in dust and soil above the permissible limits could result to human health effects such as lung cancer, asthma, nasal epithelial damage, liver and kidney damage, gastrointestinal and immune system effects and skin epithelial damage (Costa & Klein, 2006; Saha et al., 2011). In Guanajuato, Mexico, there was a report of Cr contamination in dusts due to Cr containing dust from a chromate factory, dusts from a landfill of chromate compounds and wastes from tannery (Armienta et al., 1996). Similarly, atmospheric deposition of dust from a Cr smelter was reported to have contain elevated concentration of Cr with an average content of about 2899 mg/kg in Burrel, Albania and exposure to these dusts could result to health consequence to the inhabitants of Burrel city (Shtiza et al., 2005).

2.6.6 Copper (Cu) and Zinc (Zn)

Metals such as Cu and Zn are essential elements for human health. They occur naturally in elemental form and minerals in soils. They can be found in plants, animals, foods and drinking water. Significant concentrations of these metals are found in urban dusts due to emissions from various human activities. Human activities such as traffic (lubricants and grease, wear of tire and brake pad, use of gasoline fuel, corrosion of metallic vehicular parts) and industrial other related anthropogenic activities are linked to the source of Cu and Zn in urban dusts (Kamani et al., 2015; Saeedi et al., 2012; Trujillo-González et al., 2016). Even though Cu and Zn are essential elements for human health, however, at elevated concentrations could pose health effect to human on long term exposure. Inhalation exposure to Cu in dusts could pose effects on the lungs with resulting symptoms such as cough, chills and muscles pain, it also could cause nausea and diarrhea by affecting gastrointestinal tract, and it affects the function of liver and kidney (ATSDR, 2004). The required recommended dietary intake of Cu 1.5−3.0, 0.7−2.5 and 0.4−0.7 mg/day for adults, children and infants, respectively (Faiz et al., 2009; Health and Welfare Canada, 1990). Zinc recommended dietary allowance are 11 and 8 mg/day for male and female, respectively (ATSDR 2005). However, the permissible limits of Cu and Zn concentrations in urban soils and dust based on land use is shown in Table 2.3.

Exposure to Zn could be through both dietary and non-dietary sources such as occupational and through urban soil/dusts. Ingestion exposure to high level of Zn could hinder the homeostasis of other essential elements in the body and damage pancreas (ATSDR, 2005; Faiz et al., 2009). Contamination of Cu and Zn in street dust in the Zn smelting district of Northeast China has been reported. The dust contamination was due to atmospheric deposition from the industrial activity in the region (Zheng et al., 2010). High mean concentration of Cu and Zn were reported in urban street dust of Birmingham, UK which was as a result of very high traffic activity in the city (Charlesworth et al., 2003).

Similarly, in Istanbul high concentration of Cu and Zn in street dust was reported due to high traffic related activities (Sezgin et al., 2004). It is evident that urban street and urban dusts contain high concentrations of Cu and Zn than the corresponding soil, and that much higher concentrations of these metals were usually found in urban dusts of more urbanized and industrialized centers. For instance, Cu level in urban dust of Cincinnati metropolis, Ohio in United State of America was reported to be in the range of 910–1883 mg/kg (Tong, 1990). Traffic and industrial emissions could, therefore, significantly influence the content of these metals in urban dusts which eventually could pose a threat to human health if not remediated.

2.6.7 Manganese (Mn) and Iron (Fe)

Mn and Fe are distributed abundantly in the earth crust. Their concentrations is usually higher than the other metals in soil and dust due to their abundance (Yongming et al., 2006). They occur in ores such as pyrolusite (MnO_2), hausmannite (Mn_3O_4), mangnite ($MnO(OH)$) for Mn, the ores of iron includes hematite (Fe_2O_3) and magnetite (Fe_3O_4), limonite ($FeO(OH)n(H_2O)$, siderite ($FeCO_3$) and goethite ($FeO(OH)$). They are essential elements found naturally in foods and drinking water (Aschner et al., 2007). However, anthropogenic activities increased the concentration level of these metals in the urban soils especially in urban dusts. Traffic activities such as combustion of engine, tear of the road surfaces, brake wear, diesel emissions significantly elevate iron content in urban dusts (Adachi & Tainosho, 2004; Reinard et al., 2007; Sanderson et al., 2016). Industrial and metallurgical processes also elevated the level of Fe in urban environments (Buonanno et al., 2011). Similarly, Mn is released into the urban environment especially urban dusts through automotive emissions such as industrial and traffic (Liu et al., 2014).

Even though Mn and Fe are among the least toxic elements, but at a very high concentrations, they could be toxic to human and organisms in the environment. Exposure to Fe in dust is found to have different health consequences on human such as inflammation and DNA damage through oxidative stress caused by the generation of free radicals and reactive oxygen species (Sanderson et al., 2016). Exposure to Mn for a long period of time could cause a syndrome similar to Parkinsonism as a results of toxicity effect on the nervous system (Guilarte, 2013; Lucchini et al., 2007). Previous studies have associated inhalation and oral exposure to high concentrations of Mn in dust with irritation of lungs that could lead to pneumonia, impairment of fertility, inflammation of the kidneys and kidney stone formation and urinary tract (ATSDR, 2012; Long et al., 2014; Roels et al., 2012)).

Similarly, exposure to high levels of Mn by children in the womb and early childhood stage may affect their brain development by decreasing their ability to learn and remember, cause difficulty in speech and walking (ATSDR, 2012; Bjørklund et al., 2017; Henn et al., 2012)). High blood Mn were reported on population exposed to Mn in dust in Mexico and the health consequences were increasing risks of deficient cognitive performance (Rodríguez-Agudelo et al., 2006; Santos-Burgoa et al., 2001). In another research reported on the effects of children exposure to high concentration of Mn in Mexico, the results shows that exposure to excessive Mn has a negative effects on children's memory and learning abilities (Hernández-Bonilla et al., 2011; Torres-Agustín et al., 2013). Similarly, in Brazil children exposed to elevated Mn in hair through dust were reported to have neurobehavioral impairments (Menezes-Filho et al., 2011). Mn exposure in dust was reported in Ohio, United State of America with elevated blood manganese of the population (Haynes et al., 2010). Considering the abundance of Mn in nature and the report findings by these previous studies, there is an urgent need for more and proper evaluation of the effects on exposure to Mn and Fe in urban dusts.

CHAPTER 3: METHODOLOGY

3.1 Materials

3.1.1 Reagents

In this study all the reagents used were of analytical grade. Prior to the digestion step all the plastic containers and glassware used were soaked in a 5% HNO_3 (v/v) for 24 h overnight and rinsed twice with ultrapure water (UPW) from Milli-Q purification system (Millipore 18.2 MΩ/cm resistivity Corporation, USA). All dilutions and preparation of solutions throughout this work were made using the UPW.

3.1.1.1 Reagents for Total Metal Digestion

For the total metal digestion, the following reagents were used: Concentrated suprapure HNO_3 (69% Merck, Germany), $HClO_4$ (60% Merck, Germany), 30% H_2O_2 (R & M Chemicals, UK). These acids were chosen based on the methods previously reported (Eqani et al., 2016; Hamad et al., 2014; Li, et al., 2016) EPA 3050B (SW846), (USEPA, 1996).

3.1.1.2 Reagents for Bioaccessibility Fraction Extraction

For the gastrointestinal solution preparation for the physiologically based extraction test, the following reagents were used, NaCl (Bendosen Lab. Chemicals), Malate (Merck, Canada), Lactic acid and Acetic acid (friendemann Schmidt Chemicals), Pepsin (Sigma-Aldrich), 12 M HCl (Merck, Germany), 1 M NaOH, Porcine bile extract (Acros Organics, Germany), Pancreatin (Sigma-Aldrich). These reagents were chosen to be used based on the previous reported methods (Ruby, et al., 1996).

3.1.1.3 Calibration Standards

In the preparation of a calibration standard, a 100 μg/L multi elemental calibration standard solution (XVI) for ICP Certipur® containing Cr, Cd, Fe, Zn, Ni, Mn, As, Cu and Pb from (Merck, Germany) was used.

3.1.1.4 Certified Reference Materials

In this study standard reference material Trace elements in soil containing Pb from paint (SRM 2586, USA) purchased from the National Institute of Science and Technology (NIST, USA) was used for the preparation of the quality control (QC) solutions.

3.2 Instrumentation

For the purpose of accuracy and reliability of the results in this study, all the instruments used were calibrated. Instruments such as inductively coupled plasma mass spectrometry (ICP-MS), pH meter, electronic analytical balance, centrifuge, incubator shaker, and muffle furnace oven were successfully used for the quantification of the metals and the urban soil/dust properties.

3.2.1 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

ICP-MS has found a global acceptance as one of the common spectroscopic techniques (Sastre et al., 2002) used for the assessment of metals in soil, dust and other environmental samples. Due to its high sensitivity, high detection power, capacity for multi element analysis in a very short moment of time, and low sample consumption, ICP-MS has become one of the widely accepted and used technique for trace metals analysis.

ICP-MS 7500ce (Agilent Scientific Technology Ltd, USA) was used in the determination of heavy metals in dust and soil samples of Petaling Jaya and Sekinchan, respectively. The Sample injection was performed by an auto- sampler (ICP-MS Auto –

sampler, ASX 500-Series) which was attached to a nebulizer and temperature controlled spray chamber (Figure 3.1). Table 3.1 shows the operating conditions of the instrument for the sensitive operation.

Table 3.1: ICP-MS 7500ce operating conditions.

Parameters	**Conditions**
ICP-MS	Agilent 7500ce
Auto sampler	ASX-500 series
Power	1550 W
Plasma gas flow rate	15 L/min
Auxiliary gas flow rate	0.75 L/min
Carrier gas flow	0.8-1.3 L/min
H_2 or He gas flow	3-5 L/min
Sample depth	6-8 mm

Figure 3.1: Inductively Coupled Plasma Mass Spectrometer (ICP-MS, Agilent 7500ce).

3.2.2 pH Meter

The determination of the acidity and alkalinity of the dust sample in this study was conducted using Mettler Toledo pH meter. The pH meter was calibrated with 3 buffer calibration solutions at pH 4.01, 7.00 and 9.21 prior to use. This pH meter consists of a sensitive sensor probe which is always dipped into a solution containing 4 M KCl after used in order to protect it and prevent its drying in accordance to the manufacturer's instruction. The instrument is shown in Figure 3.2.

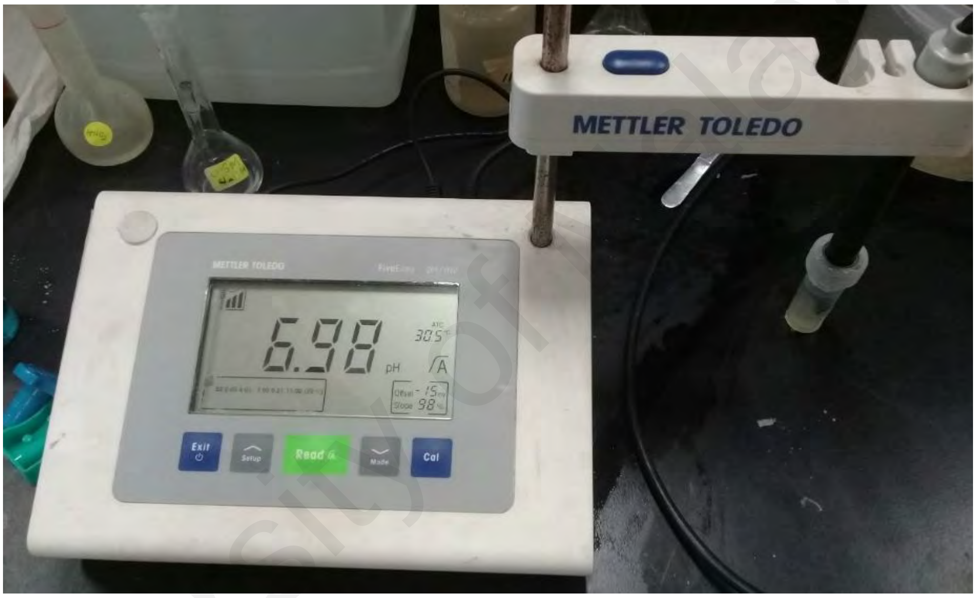


Figure 3.2: Mettler Toledo pH meter.

3.2.3 Electronic Analytical Balance

The electronic analytical balance allows an accurate measurement of mass of a substance. In this work, the (Mettler Toledo) electronic analytical balance was accurately calibrated into a gram (g) unit prior to the measurement. After which the mass of the soil/dust samples were accurately measured.

3.2.4 Centrifuge

Figure 3.3 shows the Kubota centrifuge. This instrument enable a correct centrifugation of the completed gastrointestinal extraction solution. This is done in order to allow a complete separation of the extract solution from all other residual particles even before the filtration. It consist of ten holes inside in a cycle into which 10 centrifuge tubes containing samples can be inserted for centrifugation. The instrument was calibrated based on the chosen speed of centrifugation and time. In this study, 3500 rpm speed was used at 10 min.

Figure 3.3: 4200 Kubota centrifuge (Kubota, Japan).

3.2.5 Shaking Incubator

The gastric and gastrointestinal solutions were successfully incubated based on the normal human body temperature of 37ºC and shaken based on the chosen speed using shaking incubator. The (Julabo SW 22) shaking incubator was successfully and accurately calibrated in this work at a temperature of 37°C at a shaking speed of 120 rpm and set at 1.10 h for gastric incubation and 3.45 h for intestinal incubation. Before the samples were placed in the incubator it was allowed first to reach the calibrated temperature after which the timer started reading the calibrated time for the extraction. The incubator is shown in figure 3.4.

Figure 3.4: Shaking Incubator (Julabo SW22).

3.2.6 Muffle Furnace

For the measurement of organic matter in the soil/dust samples in this study, muffle furnace was employed. The furnace was accurately calibrated at a temperature of about 600°C before the process began. The determination of organic matter contents was done through the loss of sample weight by ignition in the muffle furnace for 6 h. It burnt down all the organic matter contents in the soil/dust leaving only the inorganic contents.

3.3 Sampling Location

3.3.1 Petaling Jaya Study Area

Petaling Jaya (3.05°N, 101.39°E), commonly called PJ by the locals is one of the major city in Malaysia located in the Petaling district of Selangor. PJ is surrounded by Kuala Lumpur, the capital of Malaysia to the east about 10 km from the capital city centre, Sungai Buloh to the north, Shah Alam to the west and Bandar Kinrara to the south. Due to the rapid rural-urban migration as a result of its proximity to the Malaysian capital city, it has experienced a tremendous development in terms of population, modernization, structures, industries, commercial activities as well as traffic related activities. PJ has been the center for some federal government department due to its proximity to the capital city. Such as National Registration departments among others. Due to its uniqueness, PJ has become one of the major industrial and commercial cities in Malaysia with a densely traffic activities, including highways and road networks that in the day time can accommodate about 9650 vehicles per hour (Jamhari et al., 2014; Mohamad et al., 2015). But at present the situation could be twice what it used to be. Among the industrial activities in PJ include manufacture of automobile parts, industrial machineries, chemicals and electronic products, mechanical industries, pharmaceuticals, car protection and tire industries (Jamhari et al., 2014; Mohamad et al., 2015). Other activities include commercial and construction activities. Therefore, emissions from various sources could significantly influence the level of heavy metals in urban dust of PJ.

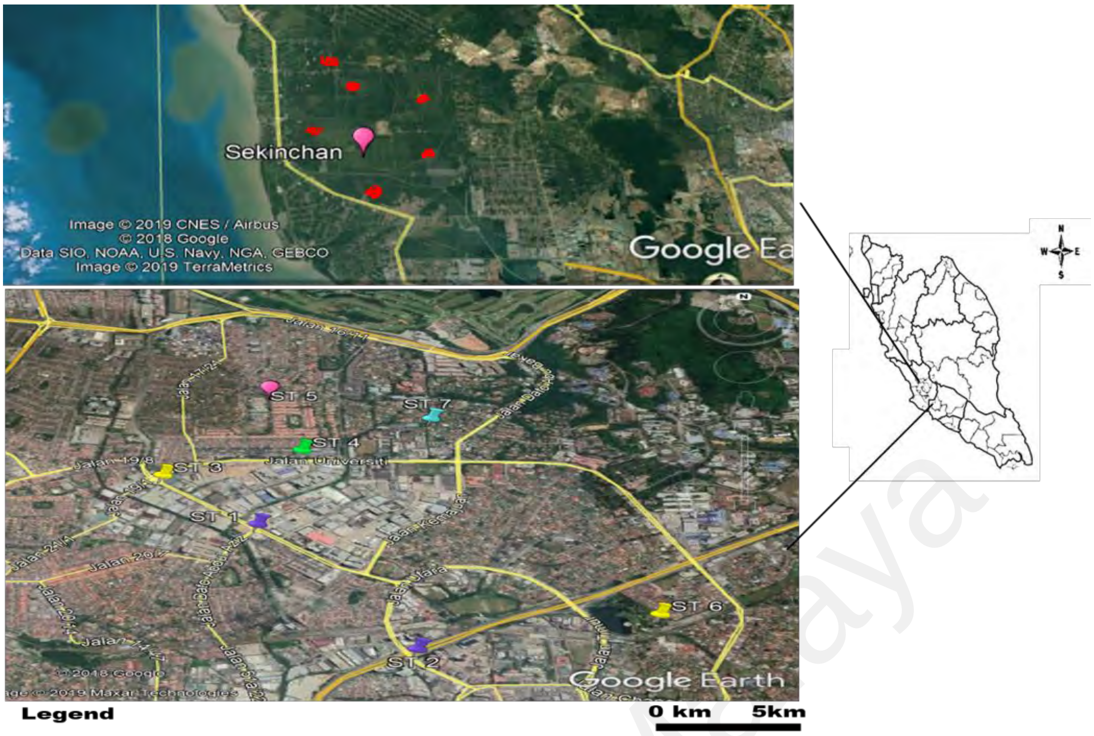
The climate in PJ is tropical rainforest which is warm with sunshine with an average temperature of 30°C, which makes the weather warm throughout the year. It has an average annual rainfall of about 3300 mm. it has no particular dry season except February, June, July and October which are considered the driest months. It has an average annual humidity of about 70%. The geology in PJ has various rocky types with a deposit of limestone around the Selangor state and the Malaysian Capital city Kuala Lumpur (Lai et al., 2018; Tan et al., 2006).

3.3.2 Sekinchan

Sekinchan (3.30.0° N, 101. 60 ° E) is a town in Sabak Bernam district of Selangor state, Malaysia. It is located at the west coast of Malaysia. It is a fishing as well as one of the major rice producing area in Malaysia. There is a rice industry as well as some rice millers which produced locally rice in Sekinchan. Therefore, the use of pesticides, application of fertilizers and machines used in the farms in addition to the rice industry and the millers could contribute to the influence of heavy metals in the area. Similarly, in the recent years, it became one of the fastest developed tourist attraction area. Because of the tourist attraction in addition to fishing, Sekinchan experienced more traffic which could eventually be another contributor to pollution of heavy metals in the area. It shared same climatic and weather condition with PJ.

3.4 Sampling of Soil and Dust Samples

Dust samples from PJ and soil samples from Sekinchan were collected. The first sampling was done in PJ in the month of February 2017 which was one of the months considered to have a minimum rainfall. The second phase of sampling was conducted in the month of October 2017 which also had low level of rainfall. The sampling was conducted in both PJ and Sekinchan on dry days, when it took some days without precipitate. Those days followed clear clouds and little windy weather condition. Composite samples were collected from different sites which included industrial, high traffic, commercial, residential and parks. The dust samples were collected using a clean plastic brush and a scoop based on the availability and the accessibility of the sites. Whereas, the soil samples were collected using a hand trowel as it was the surface soil of about (1−5 cm) that was sampled. The sampling was done based on the previous reported



Legend

Codes	Coordinates	Activities
ST 1	3°6'14.50"N ,101°38'54.50"E	Industrial/high traffic
ST 2	3°6'42.60"N, 101°37'58.60"E	Commercial/high traffic
ST 3	3°7'0.80"N, 101°37'47.70"E	Industrial/ traffic congestion
ST 4	3°7'27.50"N,101°37'51.90"E	Traffic/Commercial
ST 5	3°7'8.50"N, 101°38'7.60"E	Residential close to roads
ST 6	3°6'17.90"N, 101°39'1.40"E	Recreational centre
ST 7	3°7'27.50"N,101°37'51.90"E	Commercial
Sekinchan	3°10'14.65"N,101°21'18.69"E	Agricultural

Figure 3.5: Sampling Sites of Urban Dust at Petaling Jaya and Agricultural Soil at Sekinchan.

methods with some modification (Charlesworth et al., 2003; Charlesworth & Lees, 1999; Eqani et al.. 2016; Saeedi et al., 2012). The samples were then transferred into a zipped polyethylene bags with label for each, before they were transferred to the laboratory. Care was taken to clean thoroughly the plastic pan, brush and hand trowel during the sampling at each site in order to avoid cross contamination of samples in respect of sites. The samples were dried for 3 to 4 days in a clean closed hood at a room temperature of about 25°C.

The dried samples were then made to pass through stainless laboratory test sieve and fine particles of < 125 µm and < 63 µm of soil and dust, respectively, were collected. Soil and dust particles of < 250 µm were the fractions that likely adhere to human hands and fingers and can incidentally be ingested (Duggan et al., 1985; Li et al., 2015; Ruby & Lowney, 2012). According to USEPA, particles of soil and dust of < 250 µm are the most likely fractions ingested by children through hand-to-mouth activities (USEPA, 2007). However, finer particle sizes < 125 µm of soil and < 63 µm of dust are preferably adhere to human hands and fingers and can easily stick to clothing and human skin. These fractions can contain high amount of toxic metals (Cao et al., 2016). In addition, these fractions can easily float as dust in the air and being transported with finest particles and can remain as air borne particles for a long time (Li et al., 2017; Soltani et al., 2015). Therefore, in this study, particles of < 125 µm of soil and < 63 µm of dust size were used for the human risk exposure assessment.

3.5 Sample Preparation

3.5.1 Sample Preparation for Total Metal Concentration

Prior to the digestion step, all containers were soaked in a 5% HNO_3 (v/v) for 24 h overnight and rinsed twice with ultrapure water. The chemical preparation of the samples for total heavy metals was carried out based on the standard method EPA 3050B (SW846) (Saeedi et al., 2012; USEPA, 1996) using $HClO_4$, HNO_3 and H_2O_2. 10 mL of concentrated HNO_3 was added into a digestion vessels containing 1 g of dust sample each. The vessels were covered and the solutions were heated on a hot plate under hood. The temperature of the reaction mixture was made to be 95°C and was allowed to reflux for about 15 min without boiling. The sample was then allowed to cool. After which, 5 mL of concentrated HNO_3 was added into each vessel, covered and allowed the reaction mixture to reflux for 30 min. This step was repeated until all brown fumes that indicated an oxidation of the soil/dust samples were completely disappeared indicating complete reaction of the sample with HNO_3.

The heating of the mixture continued at 95°C for about 2 h and was allowed to cool. After cooling, 2 mL of ultrapure water and 3 mL of 30% H_2O_2 were added into each vessels containing mixture, covered. Heating and adding H_2O_2 continued until effervescence subsided and the general appearance of the mixture was unchanged and vessels were allowed to cool. After cooling, 5 mL of $HClO_4$ was added to each vessel, covered and heating continued for about 2 h or until the solution dried to about 5 mL. Then the mixture was cooled, diluted with ultrapure water after cooling and finally filtered into 50 mL volumetric flask using Whatman No1 filter paper. The volume made to 50 mL by adding 5% HNO_3. The total concentrations were determined using ICP-MS (Agilent, 7500ce). The blank solution and the SRM 2586 were prepared and analyzed following the same procedure. All analysis were conducted in triplicates and the results were expressed in ppb.

3.5.2 The *in vitro* Digestion Model Experimental Settings

This model has been designed to be simple, cheap and reproducible in order to reduce the use of animals due to ethical reasons, time consumption and cost. The ingestion matrix is the most delicate step in bioaccessibility as such this model should pay more attention to the oral bioavailability. This model is set to imitate human physiology (both child and adult) but especially children, as a result of their behavior of frequenting hand/finger-to-mouth and object-to-mouth (Calabrese, 1997). Secondly, to simulate a realistic situation which is between fasted and fed conditions, in accordance to the human digestion description and the uptake processes so that the highest bioaccessibility that may be possibly occurring should be estimated. The metals such as Pb, As, Cd, Cr, Cu and Zn are studied because of their presence in dusts and soils. The ingestion of these sample matrices is the primary pathway to these contaminants, and also due to their poisonous effects in humans.

The model represent the gastric and intestinal conditions as such both the gastric and intestinal fluids are based on human physiology and are added to the dust and soil matrix. A pH less than 2 should be adopted for the dissolution of dust and soil constituent and mobilization of metals in the stomach. In addition, the residence time for digestion and absorption should not be less than 240 minutes, a higher pH for the complete digestion and absorption of contaminants in the small intestine should be employed and the normal human body temperature of 37°C should be adopted. The bioaccessibility fraction is produced after the mobilization of the poisonous metals in the dust and soil by the digestive fluids. The experimental design is described as follows.

3.5.2.1 Digestive Compartments

Stomach and small intestine are considered following the model because the digestion and absorption of food is done in the stomach and small intestine, respectively (Elom et al., 2014b). Therefore, dissolution and absorption of all metals is done in these compartments as such their bioaccessibility is been estimated.

3.5.2.2 Solid to Juice Ratio

The ratio of the sample matrix: digestive fluids can influence the bioaccessibility outcome as a result of dissolution kinetic impacts. The small solid to liquid ratio may underestimate the bioaccessibility values because of the solubility issues coming as a result of diffusion-limited dissolution kinetics (Ruby et al., 1992). However, solid to liquid ratio of 1:37.50 (g/mL) was reported to show lower dissolution of Pb in gastric phase (Hamel et al., 1998; Li et al., 2016). Therefore, the solid to juice ratio in this model has been chosen to represent the bioaccessibility within the *in vivo* situation that will give a significant dissolution of metals in the gastric phase.

3.5.2.3 Digestive pH

One of the important factor that affect the dissolution of contaminants in *in vitro* digestive system is gastric pH. The gastric pH range of 1 to 4 is considered a fasting condition for children and pH 1.5 to 2.5 pH is considered fasting condition for adults. As a result of diluting effects by the ingested food contents, the pH 3 to 5 is considered a fed gastric condition (Ng et al., 2010). The gastric pH of 1.55 in this study has been selected in order to be in a realistic condition within the range of fasted child and adult. This is because both adults and children population are considered in this study.

In the literature, low gastric pH has been observed to increase the dissolution of metals in the stomach (Li et al., 2016; Ruby et al., 1992). This is because at low gastric pH, the metals that are electrostatically bonded with charged stomach surfaces are released (Ruby et al., 1992). Therefore, low pH of gastric is necessary for the quick mobilization and dissolution of metal contaminants in the assessment of metals toxicants, which influence the fraction that is potentially available for uptake.

In the human small intestine, pH varies from 4.5 to 7.5 as the absorption of materials takes place here. In the literature, most intestinal pH are set to be around 6.5 to 7.5 (Johnson, 2001; Sips et al., 2001), but some others also adjusting it to 5.5 (Oomen, 2000). In view of this and considering the composition of the intestinal contents and for the pH to be compared with the *in-vivo* condition, intestinal pH of 7.0 has been chosen in this study. In contrast, high intestinal juice pH in the small intestine will result to poor removal of some metals from the solution. This is due to the enhanced complexation and/ or absorption, re-adsorption of inorganic colloids, and precipitation (Roussel et al., 2010). However, some of the metals in the intestinal juice do exhibit high affinity for organic compounds or are engaged in competition for biding ions with main ions that were earlier released (Cai et al., 2016; De Miguel et al., 2012) As a result, the bioaccessibility values in the small intestine is found lower or similar to that in the stomach.

3.5.2.4 Chemical Composition of Gastric and Gastrointestinal Solutions

Chemical composition of gastric solution ranges from simple (glycine 0.4 M) to more complex solutions containing some organic and inorganic components. The base constituent in the *in vitro* gastric phase are pepsin and/ or glycine. Pepsin is chosen in this model because it is a digestive protease that breaks down proteins into peptides. Hence it may decrease the surface tension of the chime constituents, as such increasing the mobilization and solubility of the contaminants in the gastric phase (Tang et al., 2006). To modify the gastric condition into intestinal condition, bile and pancreatin were added. In *in vitro* bioaccessiblity models, bile and pancreatin stand to be the basic intestinal components. Bile facilitates the breaking down of toxicants and their mobilization in the small intestine (Ng et al., 2010). As a result of ethical issues, human bile could not be used in *in vitro* models (Cantafora et al., 1986). Therefore, bovine bile and porcine bile were an alternative used in this study. Even though chicken bile was used in some *in vitro* assays (Rotard et al., 1995), it was however, found to have different solubilizing effects. As such, could result to unexplainable bioaccessibility pattern. Moreover, the composition of human bile varied significantly with that of chicken bile. On this note, the use of chicken bile was therefore discouraged (Oomen et al., 2003). In this study, porcine bile has been chosen because of its related bile salt percentage with the human bile (Oomen et al., 2004).

In the simulated intestinal juice, pancreatin was added. Pancreatin which is secreted from the human pancreas, containing bicarbonate that neutralizes the small intestinal pH. It is also compose of digestive enzymes such as trypsin, amylase, protease, nucleases and lipase. As such, it facilitates the hydrolysis of starch, proteins, and triglycerides (Johnson, 2001).

3.5.2.5 Rate of Emptying of Stomach and Small Intestine

The stomach content complete emptying will take place within 60-120 minutes for adults. While for children, it takes within 54−68 minutes (Ruby et al., 1996). On this note, a stomach emptying time of 70 minutes was selected for this model so as to cover for both children and adults. The semifluid digested materials will move from the stomach into the small intestine. The emptying rate of chyme occurred here was reported to be within 180−300 minutes for adults, while 180−270 minutes for children (Ng et al., 2010). Based on these observation, a small intestine incubation time of 207 minutes was chosen for this model.

3.5.2.6 Incubation and Mixing

The extraction tubes containing both the gastric and intestinal constituents were placed in an incubation rotator, shaker, stirring, inert gas movement or peristaltic movement during the extraction process so as to mimic the gastric and gastrointestinal violent to obtain a constant mixing of the constituents. In order to get a total and homogenous mixture and more reproducible results, this model employed the horizontal rotation methods at a time at a speed rate of 120 rpm. This was done in order to hinder the dust particles settling to the bottom and walls of the tubes and to increase the contact between the sample and the fluid. The incubation temperature of 37°C was maintained in this model because physiologically it is the normal human body temperature. Further, activities of enzymes and other chemical processes in the human gastric and gastrointestinal compartments are affected by temperature.

3.5.2.7 Centrifugation and Filtration

The final process of the *in vitro* assay was the centrifugation of the chyme and the digested dust matrix and filtration. The separation process and the time taken may likely affect the bioaccessibility result. This was because the proper the sedimentation of the residual substances after centrifugation, the clearer the supernatant, then the easier the filtration and the more likely the solubilize bioaccesible metal fractions in the digested solutions. However, it has been observed by Oomen et al. (2002), that centrifugation time have no significant effect on the bioaccessibility results. But for the basis of practical, 10 minutes centrifugation time at a speed of 3500 rpm was considered in this model.

3.5.3 *In vitro* Bioaccessibility Fraction Assay

Pb, Cr, Cd, Cu and As bioaccessibility in urban dust and soil samples were measured for human health exposure assessment. The physiologically based extraction test following Juhasz model amended was adopted (Juhasz et al., 2010) in this study. The gastric solution for this model was prepared as follows: 8.78 g NaCl (Bendosen Lab. Chemicals), 0.5 g malate (Merck, Canada), 0.43 mL lactic acid (Friendemann Schmidt Chemicals), 0.5 mL acetic acid (Friendemann Schmidt Chemicals) and 1.25 g pepsin (Sigma-Aldrich) was added into a 1 L volumetric flask and was made to the mark using ultrapure water. The pH of the solution was then adjusted to 1.55 by addition of 12 M HCl solution (Merck, Germany).

1 g of the dust and soil samples were weighed into a 50 mL centrifuge tubes and 30 mL of the gastric solution was added into each centrifuge tube and then shaken for 70 min in an already programmed incubator shaker at 37°C temperature (normal human body temperature). The incubated samples were shaken using a horizontal rotator at about 120 rpm (adjusted). The increase of the shaking speed was to cause total interaction between

the fluids and the sample matrix particles and also to prevent the soil and dust particles from settling on the walls or bottom of the tubes. 10 mL of the gastric extract was taken and centrifuged at 3500 rpm for 10 min. The supernatant were filtered in a 0.25 µm Millipore filter and made to 30 mL using ultrapure water and finally sent for analysis using ICP-MS.

The gastric simulation condition of the remaining extract was then changed to intestinal condition by changing the pH to 7.0 through addition of 1 M NaOH solution in each tube. Similarly, to each tube 0.06 g porcine bile extract (Acros Organics, Germany), and 0.018 g pancreatin (Sigma-Aldrich) were added. The samples were again shaken for 207 min in the same incubator shaker at the same temperature and same shaking speed. Finally, the samples were centrifuged for 10 min at 3500 rpm (Kubota 4200, Japan) and then filtered through 0.25 µm Millipore filter and made to 35 mL with acidified ultrapure water. The extracts were then analyzed using ICP-MS (Agilent 7500ce) for the determination of Pb, As, Cr, Cd and Cu. The bioaccessibility of the hazard metals were calculated by dividing the gastrointestinal extractable content of the metals by the total metal content in dust samples as shown in the following equation:

$$\%\ bioaccessibility\ of\ metals\ (\%) = \frac{gastrointestinal\ extracted\ content}{Total\ metal\ content} \times 100 \quad (3.1)$$

Where the gastrointestinal extract and total metal content (mg/kg)

Prior to the analysis of the samples, calibration standards were prepared using the ICP multi element calibration standards (XVI Merck, Germany). Five calibration standards of 10, 30, 50, 75 and 100 ppb were prepared for the linear calibrations and dilutions were made using ultrapure water.

3.6 pH and Organic Matter of Soil/Dust

The pH of the soil/dust samples were measured following 1 h shaking of soil/dust suspension of (1:5 soil/dust: deionized water) using a rotatory agitator (Ettler et al., 2012). The pH of the suspension was measured using a pH meter (Mettler Toledo pH meter) after calibrating the pH meter using three buffer solutions at pH of 4.01, 7.0 and 9.21. However, the organic matter was determined on weight loss on ignition (Ben-Dor & Banin, 1989). The dust samples heated in an oven at 105°C for 12 h overnight, weighed after cooling and ignited at 600°C in a muffle furnace for 6 h and then cooled and weighed again (Liu et al., 2016). The organic matter was calculated using the following equation:

$$OM\ (\%) = \frac{W105 - W600}{W105} \times 100 \tag{3.2}$$

Where W_{105} represent the weight of dust after oven heated at 105°C and W_{600} is weight of the dust sample after ignition at 600°C.

3.7 Data Analysis

The distribution of the heavy metals in the sampling sites was determined through the descriptive statistics of the entire data set using MS Excel 2013. The entire results were expressed in $p < 0.05$ levels.

JMP Pro 12 was the statistical tool used in the multivariate analysis of the data set. The entire data set was subjected to various statistical analysis such as PCA, FA, HCA and CA in order to determine the variation of the metals concentration and their possible sources in the sampling sites.

Human health risk assessment due to exposure to toxic metals in urban dust of PJ was conducted through the three main route such as ingestion, dermal and inhalation routes using MS Excel 2013. Whereas, the health risk assessment due to exposure to both bioaccessible and total metal content in soil/dust was conducted through oral ingestion exposure route to urban dust and soil from PJ and Sekinchan. Similarly, the concentrations of the metals were simulated and estimated in the applicable fitted distributions using Monte Carlo algorithm. However, the exposure and the risks involved were estimated separately for children and adults having in view that there is a major difference in the behavior and physiology between children and adults.

3.8 Contamination Level Assessment

Various pollution estimation methods were employed to assess the level of heavy metal contamination in urban dusts. Such methods include enrichment factor (EF), ecological factor (Faiz et al., 2009; Kamani et al., 2018).

EF method is majorly used to find the origin of metal whether it is natural or anthropogenic. This is conducted based on the standardization of an element tested in respect to a reference element such as Al and Fe or Mn. These metals are considered as reference metals because of their abundance in the earth crust, as such normalization assumes that their anthropogenic sources to the atmosphere are minor (Kamani et al., 2015). The following equation was used for the computation of EF.

$$EF = \frac{Msample/Fesample}{Mref/Feref} \tag{3.3}$$

Where M_{sample} was the concentration of examined metals in the sample, M_{ref} indicate the background concentration of the examined metals, Fe_{sample} is the concentration of Fe in the sample, and Fe_{ref} is the background concentration of Fe. If EF < 1, the element is said to be natural; whereas if EF > 1, the element is enriched in the environment. The EF is classified into five categories and is shown as follows: EF between 0.5 and 1.5

demonstrates natural process is the source; EF > 1.5 represents anthropogenic activities; EF < 10 indicates less enrichment; 10 < EF < 100 advocates significant enrichment; and EF > 100 suggests severely enrichment (Al-Khashman, 2013).

Potential ecological risk index (RI) was employed to evaluate the degree of heavy metals contamination in environmental media. This technique was introduced by Hakanson and it is calculated according to the toxicity of toxic metals and the response of the environment (Hakanson, 1980). Equation 3.4 to 3.6 were used in the computation of RI as follows:

$$RI = \sum_{k=0}^{n} Er \tag{3.4}$$

$$Er = TiFi \tag{3.5}$$

$$Fi = \frac{Ci}{Bi} \tag{3.6}$$

Where Fi is the metal pollution factor, Ci represents the concentration of the metals in dust, Bi shows the metals background values, Er indicates the single elemental potential ecological risk factor, Ti is the metal toxic factor and it is represented as Cu = Pb = Ni = 5; As = 10; Cr = 2; Cd = 30, and RI is the sum of all four risk factors for metals in dust (Ke et al., 2017). The following order reveal the degree of metals contamination: If Er < 40, the metal contamination is low; and if Er = 40 – 80, it indicates moderate pollution; Er = 80 – 160 represents considerable pollution; but Er 160 – 320 denotes high contamination; Er ≥ 320 indicates very high pollution. Furthermore, if RI ≤ 50, then the metal contamination is low; 50 < RI ≤ 100, it suggests moderate pollution; 100 < RI ≤ 200 signifies considerable pollution; and RI > 200, is high contamination.

CHAPTER 4: RESULTS AND DISCUSSION

The discussion of the toxic heavy metals variation in urban dusts and agricultural soils in the studied research areas is included in this chapter. This chapter also contains the explanation of exposure estimation and health risk analysis of both the total and the bio-accessibility fractions of dusts and soils.

4.1 Method Verification for Elemental Analysis

The correlation coefficient (R^2) obtained for the linear calibration plots from the calibration standards was all very close to 1. The results obtained indicate the accuracy of the method as the recovery values of the metals were ranged between 81.40 to 120% as shown in Table 4.1. Recoveries between 80−120% suggest the satisfaction of any analytical procedure and the method precise (Khan et al., 2017).

4.2 Properties of Soil and Dust and Toxic Heavy Metals Concentrations

4.2.1 Properties of Dust and Soil

The dust and soil properties such as pH and organic matter (OM) were measured. The results show that generally the pH of the urban dusts and agricultural soil in the study areas is weakly acidic and weakly basic depending on the sites (Table 4.2). The organic matter contents of the agricultural soils were much higher than that of the urban dusts. This could be probably as a result of decomposed vegetation and accumulation of air driven particles mixed with agricultural soil resulted from the agricultural applications. Low pH increases the mobility and bioavailability of toxic heavy metals in soil and dust, and lower organic matter content increases the toxic heavy metal content in the environment as less accumulation of heavy metals occurred (Li et al., 2015; Yan et al., 2018). Therefore, both pH and organic matter could influence the concentration and mobility of toxic heavy metals in agricultural soil and urban dust.

Table 4.1: ICP-MS Recovery and limits of detection for metals in the Standard Reference Material.

Metals	Pb	Cu	Ni	As	Cr	Fe	Cd	Zn	Mn
SRM(certified) (mg/kg)	432±17	81 ± 0.00	75 ±0.00	8.7±1.50	301±45	51610±890	2.71±0.54	352 ±0.00	1000 ± 0.00
SRM (measured) (mg/kg)	403±1.60	76.14±0.8	76.2±1.9	7.47±0.64	294.75±0.62	42007±13.1	2.77±0.17	331.38 ±4.20	1201.3 ±9.86
Recovery (%)	93.00	94.00	101.60	85.91	98.00	81.40	102.20	94.14	120.00
LOD (µg/L)	1.03	0.008	0.055	0.029	0.02	1.89	0.002	0.07	0.03

LOD = Limits of detection, SRM = Standard reference material, Mean ± Standard deviation of three replicate

4.2.2 Toxic Heavy Metals Concentrations

The means and the standard deviations, minimum and maximum concentration of toxic heavy metals in urban dusts is revealed in Table 4.2. The results show a large standard deviation in the metals and this suggests a significant variation in the concentration of toxic heavy metals ($p < 0.05$) (Lu et al., 2010). The mean values of toxic heavy metals such as Pb, Cu, Cd, As, Ni and Cr were found to be higher than their corresponding background values (CNEMC, 1990). This depicts anthropogenic influence on the concentration of these toxic heavy metals in urban roadside dusts of Petaling Jaya.

The significant differences in the concentrations of the metals is thus; Pb (13.76–165.20 mg/kg), Cr (0.01−126.50 mg/kg), Cu (1.00−1101 mg/kg), Cd (0.0001–6.61 mg/kg), As (0.001−39.95 mg/kg), Ni (0.001−67.80 mg/kg) and Fe (5.00–9305 mg/kg). These variations in this study could be associated with much ongoing anthropogenic influence due to rapid urbanization, industrialization and increased population in the city (Makmom Abdullah et al., 2012). Activities such as repair and construction of roads, heavy traffic, biomass burning, spray of fertilizer and chemicals, and industrial emission are the possible link to the high concentration of these toxic heavy metals in the street dusts of this study.

However, the wind direction and seasonal activities could also possibly help in the spread of these toxic heavy metals in dusts form in the city (Han et al., 2014). Malaysia cities are known with significant increase in motor vehicles which brought about traffic congestion and consequently results to high number of particles in urban street dusts which contain high level of toxic heavy metals (Abdelfatah et al., 2015; Mohamad & Kiggundu, 2007). Human activities such as industrial and traffic emissions were found to significantly add to the toxic heavy metal content in urban roadside areas. For instance

Duong & Lee, (2011) discovered significant influence of industrial and busy traffic emissions on the heavy metals contamination in roadside dust of Korea.

In a related study Apeagyei et al. (2011); Pant & Harrison, (2013); Suryawanshi et al. (2016) reported traffic emissions such as vehicular exhaust, road tear, brake pad abrasion, and atmospheric depositions from industrial discharge and also domestic wastes could significantly add to the level of Pb, Cu, Cd, Cr, Ni and Fe in urban street dusts. Similarly, weathering of urban infrastructure may increase the concentration of Ni in urban environment, this is because Ni is used as an alloy in materials (Faiz et al., 2009). Fe is the major constituent of soil and the fourth most abundant element in the earth's crust. In Malaysia, hematite and weathering of rocks could be the natural sources of Fe (Shamshuddin & Anda, 2008), even though tear of road surfaces, combustion of vehicular engines could influence Fe concentration in urban road dust (Sanderson et al., 2016).

Table 4.2: Descriptive statistical summary for heavy metal concentration (mg /kg) and properties of dust/soil.

Metal	Maximum	Minimum	Median	Mean ± SD
Pb	165.2	13.76	90.33	87.29 ± 44.24
Cr	126.35	0.01	28.06	39.80 ± 39.90
Cu	1101	1	73.5	138.53 ± 211.90
Cd	6.61	1.00 × 10-4	1.31	1.88 ± 1.60
As	39.95	0.001	1.32	6.71 ± 10.32
Ni	67.8	0.001	9.3	15.82 ± 18.04
Fe	9305	5	3711.5	3841.56±271.50
pHd	10.12	6.91	8.01	8.35 ± 0.83
OMd	8.21	0.29	2.96	3.25 ± 2.19
pHs	8.31	4.96	6.65	6.57 ± 1.13
OMs	12.91	2.97	8.21	7.71 ± 2.88

Mean ± standard deviation for three replicates at 95% confidence limits, OMd = organic matter content for dust, OMs = organic matter for soil, pHd = pH for dust, pHs = pH for soil.

4.2.2.1 Enrichment Factor

Values for the metals enrichment in the sampling sites of Petaling Jaya are shown in Figure 4.1. The enrichment factor (EF) analysis was conducted to assess the contamination level of the toxic heavy metals in the study area. Values of EF that fall between 0.5 and 1.5 indicated natural processes and crustal materials to be the sources, whereas EF > 1.5 suggested anthropogenic influence to be the origin. On the other hand, EF < 10 proposed less enrichment, 10 < EF < 100 depicted significant enrichment, and severe enrichment was demonstrated when EF > 100.

The results as shown in Figure 4.1 indicates the enrichment of metals in sampling sites. Cu, Cd, Pb and As were found to be significantly enriched at the sites in this order: ST 2 > ST 1 > ST 4 > ST 3 > ST 5 > ST 6. This indicates that ST 2 has the highest enrichment of metal contaminants and ST 6 has the lowest enrichment. Generally all the sites suggests anthropogenic influence on the metals (EF > 1.5). Cu, Pb and Cd are richly found at all the sites except ST 6 which is a recreational park. Cr show high enrichment at ST 2 and ST 1, while As and Ni are highly enriched at ST 2. The significant enrichment of Cu, Cd and Pb at all sites could be attributed to high traffic volume due to commercial activity as most of the sites near hotels, commercial and industrial centers. Abrasion of brake lining and tire due to constant braking as a result of high traffic was reported to emit high volume of Cu, Cd and Pb in road dusts (Gietl et al., 2010; Thorpe and Harrison, 2008)). Similarly, corrosion of car components, lubricants and diesel could contribute to the influence of these metals in roadside dusts (Lu et al., 2010; Rashed, 2008).

Batteries, metal coating, mineral fertilizer and plastics could be linked to the Cd pollution in this study as there are more mechanic, electronic and plastic industries. The possible source of Cd in the urban environment could be motor oil combustion, mineral fertilizer, metal coating, batteries, automobile lubricants, burning of tire and plastic

(ATSDR, 2012; Rout et al., 2013). Previous studies noted high enrichment of Cd, Cu and Pb in road dust of Kuala Lumpur and the authors attributed the cause to be as a result of allocation of mineral fertilizer, high traffic volume and industrial emissions (Han et al., 2014). In a related study conducted on sediments in Selangor state, Malaysia high enrichment of these metals were reported as a result of human activities (Shafie et al., 2013). Therefore, anthropogenic activities may be the primary possible means that influence contamination of heavy metals in Peninsular Malaysian environment.

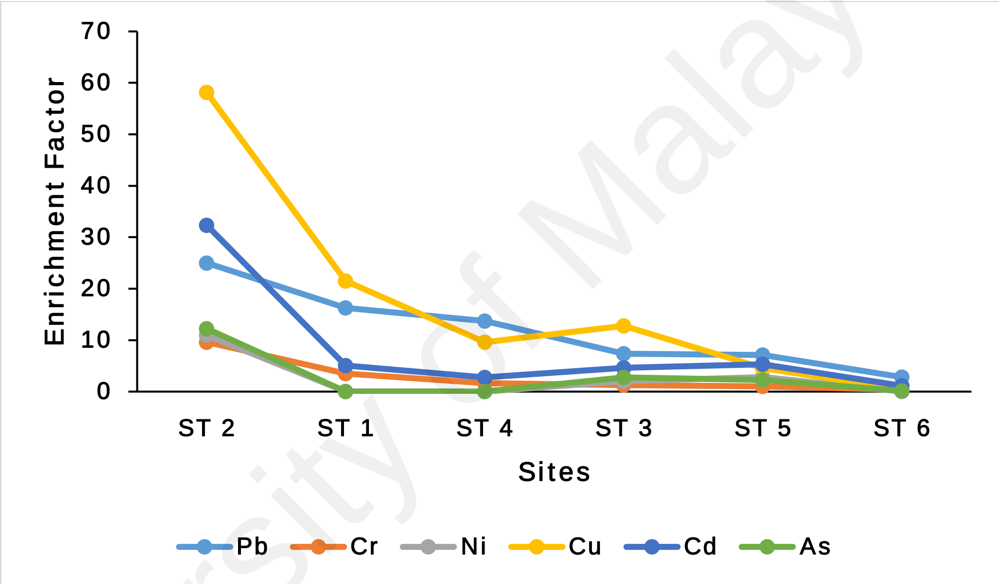


Figure 4.1: Enrichment factor of heavy toxic metals in roadside dust.

The moderate enrichment of Cd, Pb and Cu in ST 5, the residential areas could probably be due to domestic dirt dust, which composed of various kinds of materials containing heavy metals. In addition paints flickers from old buildings and used batteries could result to increase in heavy metals levels in residential areas if not properly disposed (Coalition, 2007). Residential areas located close to roads in urban cities are exposed to contamination of heavy metals as a result of floating of emitted particles containing metals in dust form. The residential areas in this study are close to roads therefore they should have heavy metals influence. The recreational park ST 6 has lower contamination of metals which could be attributed to low anthropogenic activities in the area.

4.2.2.2 Assessment of Potential Ecological Risks

This technique was employed to evaluate the degree of heavy metals pollution in the roadside dusts of this study. The results shown in Table 4.3 indicates that the degree of the single heavy metals pollution (Er) is in the order of Cd > Cu > As > Pb > Ni > Cr. When compared with other heavy metals, Cd shows the highest Er 288.46 at ST 2 site. Other heavy metals exhibited low Er in all the sites. High Er for Cd in street dust was reported by Kamani et al. (2018). The results imply that Cd might originate primarily from human activities. Mineral fertilizer, combustion of motor oil, pigments, metal coating, cement, batteries and plastics could be the main source of Cd in the environment particularly street dusts (ATSDR, 2012). Batteries, pigment and metal coating could possibly be the source of high Cd Er in ST 2. Generally, the mean potential ecological risk index (RI =193.93) for metals in the roadside dusts of this study was classified as considerably polluted. The RI for ST 2 and ST 3 sites which are traffic and industrial related was categorized as highly polluted and RI for ST 6 which is park related areas was classified as moderately polluted, while the RI for the remaining sites were considerably polluted. It was found that the two sites, i.e., ST 2 and ST 3 (33.3%) exhibited high potential ecological risk. A total of 3 sites, namely ST 1, ST 5 and ST 4 (50%) were found to show considerably potential ecological risk and the other site, ST 6 (16.7%) was found to show moderate ecological risk index RI. Therefore, generally the roadside dust of this study is considered to exhibit considerably potential ecological risk. In Delhi, India high potential ecological risk of heavy metals such as Cd, Pb and Cu in urban dusts to the industrial areas and those areas with high vehicular traffic emissions (Suryawanshi et al., 2016). Therefore, human activities influence high risks of toxic heavy metals in the urban environment.

Table 4.3: Potential ecological risk factor and ecological index.

Sites	Er						RI	Pollution degree
	Pb	Cr	Ni	Cu	Cd	As		
ST 1	27.11	1.69	0.17	29.77	119.23	1.88	179.86	considerable
ST 2	15.78	1.74	6.39	30.47	288.46	27.18	370.02	High
ST 3	17.06	0.86	4.31	24.68	151.92	22.74	221.7	High
ST 4	22.81	0.78	0.15	13.22	65.38	1.71	104.06	considerable
ST 5	14.59	0.61	5.41	7.85	153.85	16.15	198.46	considerable
ST 6	12.23	0.43	0.17	1.45	73.08	2.22	89.58	moderate
Mean	18.26	1.02	2.77	17.91	141.99	11.98	193.93	considerable

Er = potential ecological risks, RI = potential ecological risks index.

4.2.2.3 Principal Component and factor Analysis

PCA as a multivariate technique was applied into the data set in order to identify the loading distribution of the toxic heavy metals in the roadside dust of this study so that their sources could be identified. The most essential PCs with eigen values > 1 was shown to explain about 84.2% of total variation of the data set. On the extracted components, each station and variables loadings were observed by the PCA in biplots. The biplots represented a scattered plot with components 1 and 2 occupying the X and Y axes and the variables scores acting as coordinates. Sampling sites were clustered in the plot based on the similarity of contaminants. This parameters were represented in axes and the sampling sites as points. The length of the line and its closeness to the circle showed how well a parameter was represented in the plot. Variables whose arrows are longer are highly loaded whereas parameters that have shorter arrows are less loaded in the site.

The result as seen in Figure 4.2 shows that the two principal components PCs accounted for 68% of the total variance of the data. PC 1 accounted for 48% of the total variance and the heavy metal parameters Cr, Ni, Cu, Cd and As strongly correlated with each other as the angle between their vector arrows is small. The metals show scores and loadings at locations namely ST 2, ST 3, ST 4, and ST 1. This indicates that industrial, commercial and traffic activities could be the sources of these toxic heavy metals at those sites. PC 1 however is seen to have low loading of Pb at ST 1 and ST 4. This could possibly be due to atmospheric deposition where heavy metal pollutants, including particles, aerosol and gases are deposited from the atmosphere and are settled as dust/soil particles. According to Sany et al. (2013) related activities such as manufacture of chemicals, electronic, and automobile parts, corrosion of car components, wear and tear of brakes and pads add to these poisonous heavy metals in the urban environment. PC 2 accounted for 20% of the total variance, and it corresponds to Ni, As and Fe, with ST 3 and ST 2 loaded with Ni and As, while ST 6 and ST 5 sites loaded with Fe. This could be explained to be sourced from both crustal and traffic related discharges.

In addition to further explain the variances of the metal parameters in the data set, factor analysis was employed as shown in Table 4.4. The PCs were varimax rotated through the factor analysis development in order to reduce the contribution of those variables with less significance (Ma et al., 2016), the smaller independent factors were therefore extracted to analyze the relationships among the observed variables. Three factors with eigen values > 1 emerged after the varimax rotation of the PCs. Factor 1 explained 33.24% of the total variance and loaded highly with Ni, As and Cd. Factor 1 therefore, is evidenced by its heavy metal loading (Ni, As and Cd and belonging to PC 1 (Figure 4.2). This depicts that these heavy metals could have similar sources in the urban area of Petaling Jaya. Factor 2 shows 28.81% of the total variance that loaded significant ly with Cr and Cu and moderately loaded with Cd. Factor 2 is evidenced by agreeing with biplots (Figure 4.2). These heavy metals could probably originate from the same source which could be industrial and traffic related activities. Factor 3 explained 19.10% of the total variance and is significantly loaded with Pb. The source of Pb could possibly be from the precipitation of aerosol particles released by industrial and traffic activities as evidenced by the biplots in Figure 4.2. Due to the fact that the concentration level of heavy metals in this study was found higher than their corresponding background values as shown in Table 2.3 (in section 2), therefore this suggests various human activities to have influenced the heavy metal level.

Table 4.4: PCA varimax rotated for heavy metals in urban dust of Petaling Jaya.

Variable	Factor 1	Factor 2	Factor 3	Final Communality estimate
Pb	-0.12	0.01	**0.96**	0.93
Cr	0.12	**0.87**	0.21	0.82
Ni	**0.92**	0.05	-0.06	0.86
Cu	0.27	**0.87**	-0.11	0.84
Fe	-0.44	-0.52	-0.57	0.79
Cd	**0.74**	**0.42**	0.18	0.76
As	**0.79**	0.22	-0.06	0.68
Eigen Values	2.33	2.02	1.33	
Variability %	33.24	28.81	19.06	
Cumulative %	33.24	62.05	81.12	

PCA loading ≥ 0.40 are in bold.

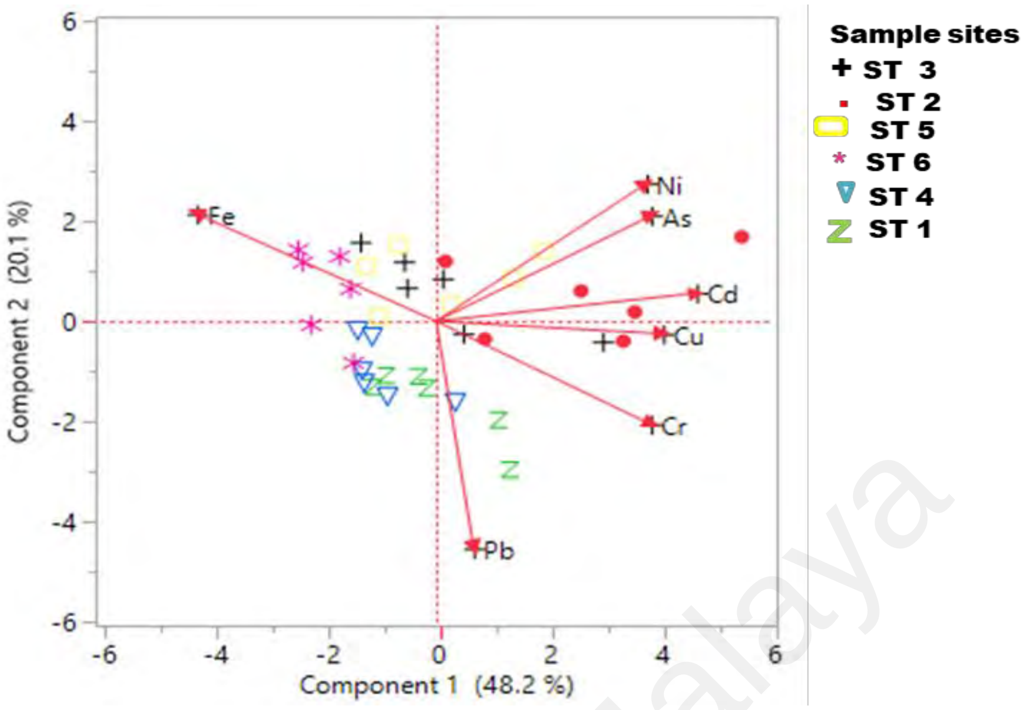


Figure 4.2: PCA biplots of urban dust in Petaling Jaya.

4.2.2.4 Hierarchical Cluster Analysis

In this multivariate statistical analysis method similar groups of sampling locations and or parameters are identified based on their characteristics. The two way cluster analysis is conducted in a way that sampling locations are clustered based on their pollution similarities, and the variables are also clustered based on their chemical relations (Figure 4.3). The outcome are observed in a most common effective flow chart which is dendrogram, where the sampling locations and the metals variables are linked on a wards' cluster by using Euclidean distance interval. This technique is employed to identify possible major sources of contamination as it correlates with the metal parameters. Three clusters were observed in this dendrogram as seen in Figure 4.3. The red color shows high concentration, whereas the blue color indicates low concentration of heavy metals at sampling sites. In the dendrogram, a decrease in concentration is indicated from red to blue. The distribution pattern of the heavy metals in the sites is in agreement with the

PCA implying that human activities could be their sources of contamination. ST 3 and ST 2 locations in Cluster 1 (C1) were more concentrated with Pb, Cr, Cd, As, Cu and Ni as a result of industrial and traffic influence around those sites. On the other hand, ST 1 and ST 4 in Cluster 3 (C3) were contaminated with Pb, Cr and Cu insinuating traffic and commercial influence. While, ST 6 and ST 5 revealed less concentration of all the studied heavy metals except for Fe. This might be due to less anthropogenic influence around those sites. Fe distribution is noted to be the main element originating from a crustal source (Lu et al., 2010).

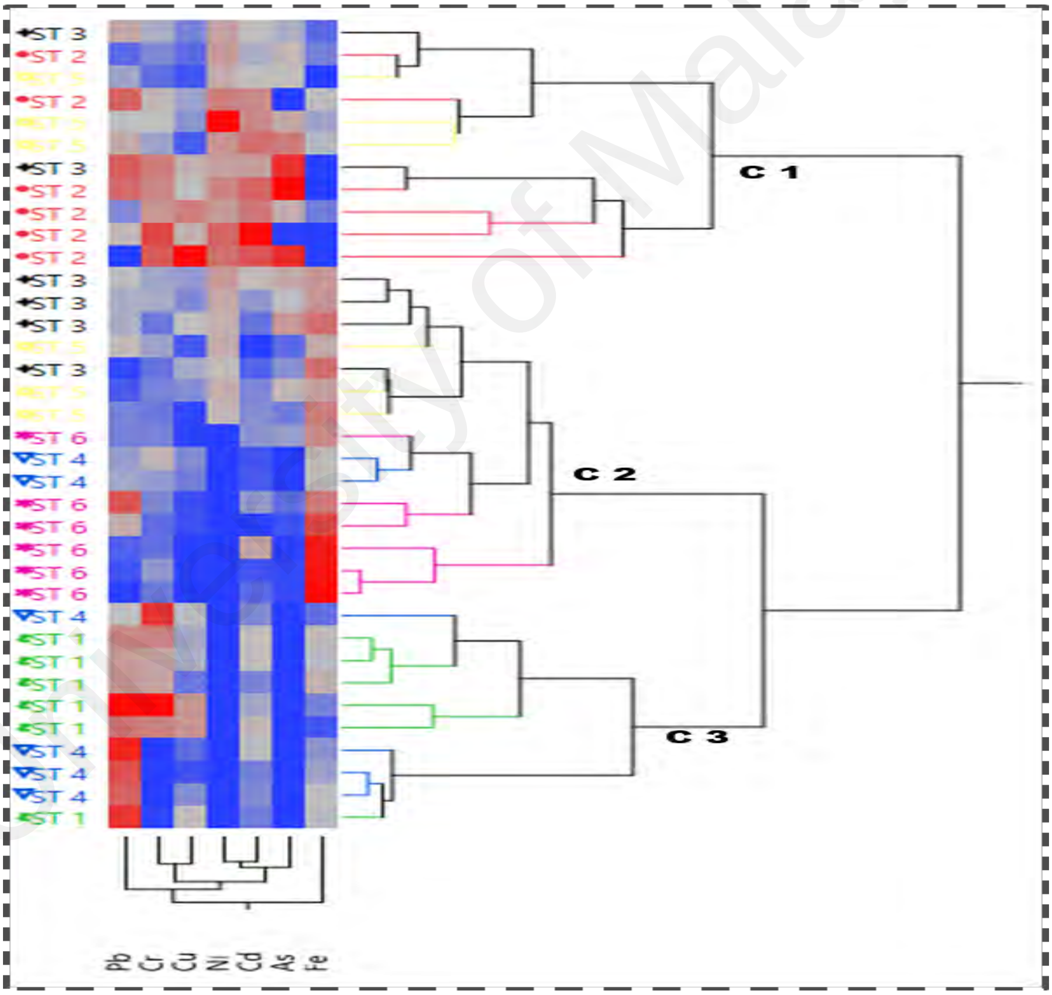


Figure 4.3: Dendrogram of the cluster analysis (C1, C2 and C3 = cluster 1, 2 and 3, respectively). Deep red colour shows high concentration, deep blue colour shows low concentration (decrease in concentration from deep red to deep blue).

4.2.2.5 Comparison of Toxic Heavy Metals Level in Petaling Jaya Urban Dust with Other Cities

The type of activities in an urban environment determined the level of heavy metals influence in that city. Therefore, it is interesting to compare the present level of heavy metals in this study with those reported for other cities of the world in the literature such as Al-Khashman, (2007); Christoforidis & Stamatis, (2009); Han et al. (2014); Lu et al. (2010); Ordonez et al. (2003); Rajaram et al. (2014); Robertson et al. (2003); Xia et al. (2011). These chosen cities are the major cities/capitals of the countries with related or higher industrial dynamics, some with larger population numbers compared to Petaling Jaya. The mean concentrations of all heavy metals reported in this study (Table 4.5) were found to be lower than the values reported from all cities except for Cu. This could be as a result of those cities been more industrialized and more populated that the chance of various sources of heavy metals emission into urban cities is high.

Take for example, the population of Amman in Jordan as of the time of study was about 2.5 million and their vehicle use leaded gasoline, Kavala in Greece has a port and petroleum refinery, Aviles in Spain has a port and is the third largest city, Manchester in UK is a very large industrialize city, Beijing, Delhi and Kuala Lumpur are the capital cities of China, India, and Malaysia, respectively, Baoji is the second largest industrious city in the Shaanxi province, Northwest China. The mean concentration of Cu in this study (Table 4.5) was slightly found lower as compared to other cities. Generally, each city has its own elemental composition characteristics, as such the observed variations and similarities may not reflect the real natural and anthropogenic differences among the different urban settings.

Table 4.5: Mean concentration of heavy metals in urban dust of Petaling Jaya compared to other cities of the world.

City	Fe	Pb	Cu	Cr	Ni	Cd	As	References
Aviles, Spain	42,200	514.00	183.00	ND	ND	22.30	ND	Ordonez et al. (2003)
Baoji	ND	433.20	123.20	126.70	48.83	ND	19.80	Lu et al. (2010)
Kavala	ND	301.00	124.00	196.00	58.00	0.20	13.70	Christoforidis (2009)
Manchester	ND	265.00	113.00	ND	ND	ND	ND	Robertsonetal.(2003)
Amman	7132	236.00	177.00	ND	88.00	11.20	ND	AlKhashman (2007)
Kuala Lumpur	10340	144.30	291.10	51.78	28.63	4.63	ND	Han et al. (2014)
Beijing	ND	135.10	212.30	102.10	40.32	0.591	ND	Xia et al. (2011)
Delhi	27047	128.00	168.70	170.80	37.20	ND	ND	Rajaram et al.(2014)
PJ	3841.60	87.29	138.40	39.80	15.85	1.88	6.71	This study

ND: not detected; generally concentration of metals is in the order of Fe > Pb > Cu > Cr > Ni > As > Cd

4.3 Health Risk Simulation Analysis on the Exposure to Heavy Metals on Urban Dust Through Ingestion, Inhalation and Dermal Pathways

Section 4.1 and 4.2 presented the metal distribution, the level of pollution, the sources of these heavy metal pollutants and evaluated the potential ecological risks due to the presence of metal pollutants in urban dust of this study. Section 2.3 of chapter 2 outlined the importance of risks assessment via multiple exposure pathways. The results and discussions of health risk assessment of heavy metals to humans via ingestion, inhalation and dermal exposure contact to urban dust is presented in this section.

Human health links intimately to soil and air quality. Soil and dust are reservoirs and sources of contamination with the potential of transferring pollutants into the food chain and eventually into human body (Mohmand et al., 2015). Human health and the quality of life are influenced with the dust containing pollutants such as heavy metals particularly in urban cities. Contamination of urban cities is, therefore, considered a significant threat to humans. Due to various forms of emissions and as a result of daily activities, humans could encounter these pollutants, either through ingestion, inhalation or dermal contact which eventually may result to adverse risk effects on human health. Health risk evaluation through these exposure pathways has, therefore, become crucial. Considering the importance of human health and the studied area to the citizens, and the possible health risk linked with exposure to the population who could possibly be engaged in working, walking, recreational activities and those in the nearby residences, it is unfortunate that no studies was carried out to discover and assess their safety. Therefore, this research was conducted as a means of potential health risk prevention and pollution control, which presently, are among the main challenges for the developing countries. This study however, employed the chemometric approach, such as PCA, HCA and Monte Carlo (MC) simulation, with these the health risk exposure assessment becomes more precise, which help accommodate the uncertainties arising from the calculation and exposure factors.

Prior to the MC simulation analysis, the concentration of the toxic heavy metals was fitted with appropriate distribution and assed for goodness of fit with Kolmogorov-Smirnov (K-S) using JMP Pro 12 a statistical software (Table 4.6). Equation 2.1 – Equation 2.3 (section 2) were used as input variables in the Monte Carlo simulation technique. This is done so that the estimation of probabilistic distribution of the heavy metals can be obtained. The normal distribution of body weight was acquired for child and adult from the Malaysian dietary guideline and Malaysia adult nutrition survey (Azmi, 2009; MOH, 2013; Mohammad, 2016). Using the locals' body weight will minimize potential error and give the exact risk situation associated to Malaysian and could be a light to the management to amend the existing law and or to plan ahead for future remedy of the risks due to heavy metals in the environment. The toxicity parameters for the heavy metals were derived from USEPA guidelines and international research findings. Furthermore, Microsoft Excel 2013 was used and 50 thousand iterations were employed to perform the simulation analysis. Separate exposure results were regarded for both adults and children, and were expressed in 75th and 95th percentiles of the simulated distributions and were considered as reasonable maximum exposures. Equations 2.4–2.5 and 2.6–2.7 (Section 2.4 of Chapter 2) were used for the estimation of cancer and non-cancer risks, respectively, associated with exposure to the heavy metal pollutants.

Table 4.6: Distribution of heavy metals in urban dust of Petaling Jaya.

Metals	Cluster 1	Cluster 2
Pb	lnN (4.99 ± 0.42)	lnN (3.95 ± 0.36)
Cr	lnN (3.97 ± 0.15)	lnN (2.99 ± 0.34)
Cu	lnN (5.18 ± 0.25)	lnN (3.72 ± 0.46)
Zn	lnN (6.13 ± 0.25)	lnN (4.95 ± 0.48)
Mn	lnN (5.42 ± 0.28)	lnN (5.28 ± 0.73)

The concentrations are in (mg kg^{-1}) at $p < 0.05$, lnN = Lognormal.

4.3.1 Correlation Analysis

The data set was subjected to Correlation analysis to identify the association of toxic heavy metals in dust of this study. This is done through the Pearson correlation coefficient matrix. It was observed that a significant correlation ($p < 0.01$) existed between Cr and Cu ($r = 0.94$), Cr and Zn ($r = 0.83$), Cu and Zn ($r = 0.75$), Pb and Cr ($r = 0.67$), Pb and Cu ($r = 0.60$), Pb and Zn ($r = 0.70$). Mn exhibited a poor correlation with all other heavy metals. This significant correlation between the hazard heavy metals suggests that these heavy metals have similar pollution source. This depicts that the heavy metals in dust of this study area could have interconnected anthropogenic origins.

Significant correlation of heavy metals is an evidence of heavy metals having similar chemical behavior (Wei & Yang, 2010). In this study, traffic related and industrial activities, and atmospheric deposition could be the sources of these heavy metal contaminants in the urban dust. Previous studies reported significant correlation between Cu, Pb, Cr and Zn in urban street dust of Tehran and associated the sources of these heavy metals to be industrial and traffic (Saeedi et al., 2012). The poor correlation of Mn with other heavy metals in this study demonstrates that Mn has a different pollution source probably crustal. Similarly, Saeedi et al. (2012) discovered Mn correlated poorly with other heavy metals in urban dust of their study. Mn in urban environment could be associated with the parent materials (Yan et al., 2018).

Dust pH and organic matter content are important factors influencing the concentration and distributions of heavy metals in urban environment. The correlation analysis for the physicochemical properties (Table 4.7) shows that pH correlated weakly with Cr, Cu, Zn and Pb ($r = 0.31$, 0.30, 0.30, and 0.20), respectively, while pH correlated poorly with Mn ($r = 0.12$). This implies that pH had not much influence on the distribution of toxic heavy metals. In a similar vein, organic matter content also had a little influence on the distribution of heavy metals in urban dust as it correlates weakly with Cu ($r = 0.30$) and Cr ($r = 0.30$), but poorly correlated with Pb ($r = 0.11$), Zn ($r = 0.20$) and negatively correlated with Mn ($r = -0.20$).

Table 4.7: Correlation analysis of heavy metals, pH and organic matter content in dust sample.

	Pb	**Cr**	**Cu**	**Zn**	**Mn**	**OMC**	**pH**
Pb	1						
Cr	0.67**	1					
Cu	0.60**	0.94**	1				
Zn	0.70**	0.83**	0.75**	1			
Mn	-0.06	0.002	0.03	-0.10	1		
OMC	0.11	0.30*	0.30*	0.20	-0.20	1	
pH	0.20	0.31*	0.30*	0.30*	0.12	0.11	1

Significant values at ** $p < 0.01$, * $p < 0.05$, OMC = organic matter content.

4.3.2 Exploratory Analysis

Heavy metals with low reference dose values such as Cr, Pb and Cu, Zn are considered as toxic heavy metals. They were basically regarded in the risk assessment for the cancer and the non-cancer risks, respectively. A 3D scatter plot of principal component (PC) is developed as shown in Fig. 4.4. It predicts that PC 1 and PC 2 show relationship among the observed parameters, and are responsible for the distribution of these heavy metals.

This is as a result of different human activities from the sampling locations such as 1, 2, 3, 4 and 7 which are traffic, industrial and commercial areas. This suggests that the PC1 score is responsible for the separation of samples in these sites from the other sites. The concentration of Pb, Cr, Cu and Zn could possibly be the important factor in this separation as a result of afore mentioned activities. This implies that the sites at PC1 and PC2 in the 3D scatter plot could cause risk on exposure to Pb, Cr, Cu, and Zn than the other sites. The samples in the residential and commercial areas such as sites 5, 6 and 7 were concentrated at the left hand side of the quadrant, implying both negative PC1 and PC2 were responsible. This predicted that negative PC1 and PC2 had less concentrations of all heavy metals, except Mn. More Mn concentration was observed at site 5 and 7 in PC2, suggesting that it was of a different source. Due to the rise in population densities, high volume of traffic, and industries urban environment are linked to high levels of heavy metals such as Cr, Pb, Zn, and Cu, while Mn could originate from natural source (Peng et al., 2013; Zhang et al., 2015).

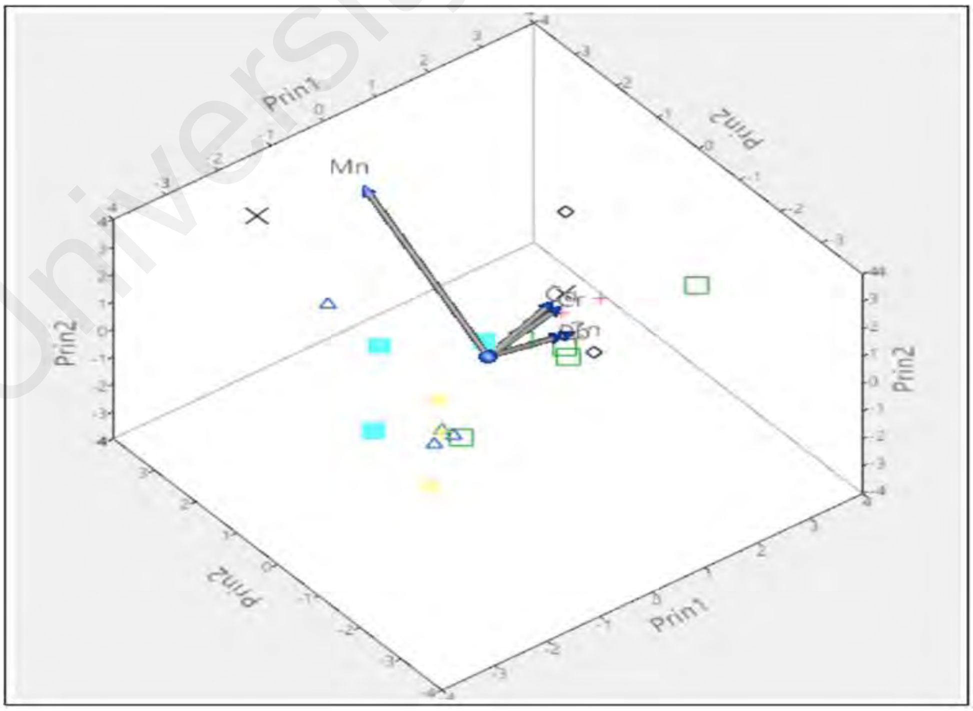


Figure 4.4: 3D scatter plot of PCA.

4.3.3 Exposure Assessment

Prior to the exposure assessment, the sites were divided according to the activities around using hierarchical cluster analysis (HCA). The conducted cluster analysis showed that the sampling sites were divided into two groups (Figure 4.5). The dendrogram shows sites which are related in one cluster. C1 is dominated by more variation of heavy metals concentrations at sites 1, 3 and 4 which are considered areas of congested traffic, industrial and commercial areas, whereas, C2 comprises low variation of heavy metals concentrations at sites 2, 5, 6 and 7 which are considered areas of residential, part of commercial and low traffic areas.

Exposure contribution assessment to toxic heavy metals for cancer and non-cancer risks have been applied in this study, for population of children and adults, to urban dusts. We employed this as a result of behavioral and physiological differences between children and adults. The contribution of exposures that caused the risks associated to heavy metals, probably due to the metal concentrations in the dust of the study area is shown in Table 4.8. The evaluation of the average daily intake (ADI) (mg/kg/day) for the ingestion, inhalation and dermal exposure pathways was done by the parameters in Equation 2.1 − 2.3 (chapter 2) using the Monte Carlo simulation approach.

4.3.3.1 Exposure Load of Heavy Metals for the Children and Adults Population

The concentration of heavy metals alone is not sufficient to estimate the hazard metals consequences on human health. Exposure and health risk evaluation are very much needed in order to assess the impact of the heavy metals on humans and environment.

The estimation of carcinogenic and non-carcinogenic exposure to toxic heavy metals in dusts for adults and children via ingestion, dermal contact, and inhalation routes was conducted and the exposure loads were estimated at 75^{th} and 95^{th} percentiles as shown in Table 4.8. The obtained results revealed that the ingestion exposure (ADI) to carcinogenic

Cr by children to be 1.39×10^{-4}, 2.03×10^{-4}, 1.06×10^{-4} and 1.57×10^{-4} mg/kg/day at 75^{th} and 95^{th} percentiles for Cluster 1 and Cluster 2, respectively. The degree of exposure to carcinogen Pb by children due to ingestion was also in the magnitude of 10^{-4} mg/kg/day. Nevertheless, the exposure amount of carcinogen Pb and Cr by adults through ingestion of dust at 75^{th} and 95^{th} percentiles was at the level of 10^{-6} mg/kg/day.

The amount of carcinogen Pb and Cr intake as a result of dermal contact exposure to urban dust by both children and adults at 75^{th} and 95^{th} percentiles was in the range of 10^{-7}–10^{-6} mg/kg/day. Furthermore, the amount of carcinogen Pb and Cr through inhalation exposure of urban dust by both children and adults population was in the magnitude of 10^{-10} mg/kg/day. This, therefore, indicated that children were more vulnerable to carcinogenic heavy metals exposure than adults because their exposure quantities were much higher than that of adults particularly on ingestion. The exposure level of carcinogen Pb was higher than that of Cr for all the three routes, perhaps due to the distribution contribution of Pb concentration in the study area. It was discovered that ingestion pathway was the primary exposure channel for the population of adults and children.

The ingestion exposure quantity of non-carcinogenic heavy metals, Pb, Cr, Cu, Zn and Mn in dusts by children in this study was in the range of 10^{-3} mg/kg/day, which was also found significantly higher than that of adults, which was in the magnitude of 10^{-6}–10^{-5} mg/kg/day. The dermal contact exposure to the aforementioned non-carcinogenic heavy metals for both population of adults and children was in the level of 10^{-6} and range of 10^{-7}–10^{-6} mg/kg/day whereas the inhalation exposure load of the same heavy metals for both adults and children of all percentiles were in the magnitude of 10^{-9} mg/kg/day.

In a general note, in this study, the ingestion exposure amounts for carcinogenic and non-carcinogenic heavy metals were observed to be that the children were more exposed than adults. This could likely be as a result of children having higher ingestion rate of contaminants in dust than adults (USEPA, 2002). Similarly, the frequency of hand-to-mouth behavior is higher in children, as such could deliberately ingest soil and dust that stick to their hands, objects or through outdoor play (Cao et al., 2014; Shi et al., 2011). To add more, the dermal and inhalation exposure amounts of heavy metal contaminants by adults were much higher than that of children. This possibly could be due to higher skin surface area and inhalation rate of adults than children (USEPA, 2002), as shown in Table 2.1 of chapter 2. The carcinogenic and non-carcinogenic amounts in C1 for all the exposure pathways were higher than that of C2 probably this could be due to the impact of human activities in the sites of C1 than those sites in C2.

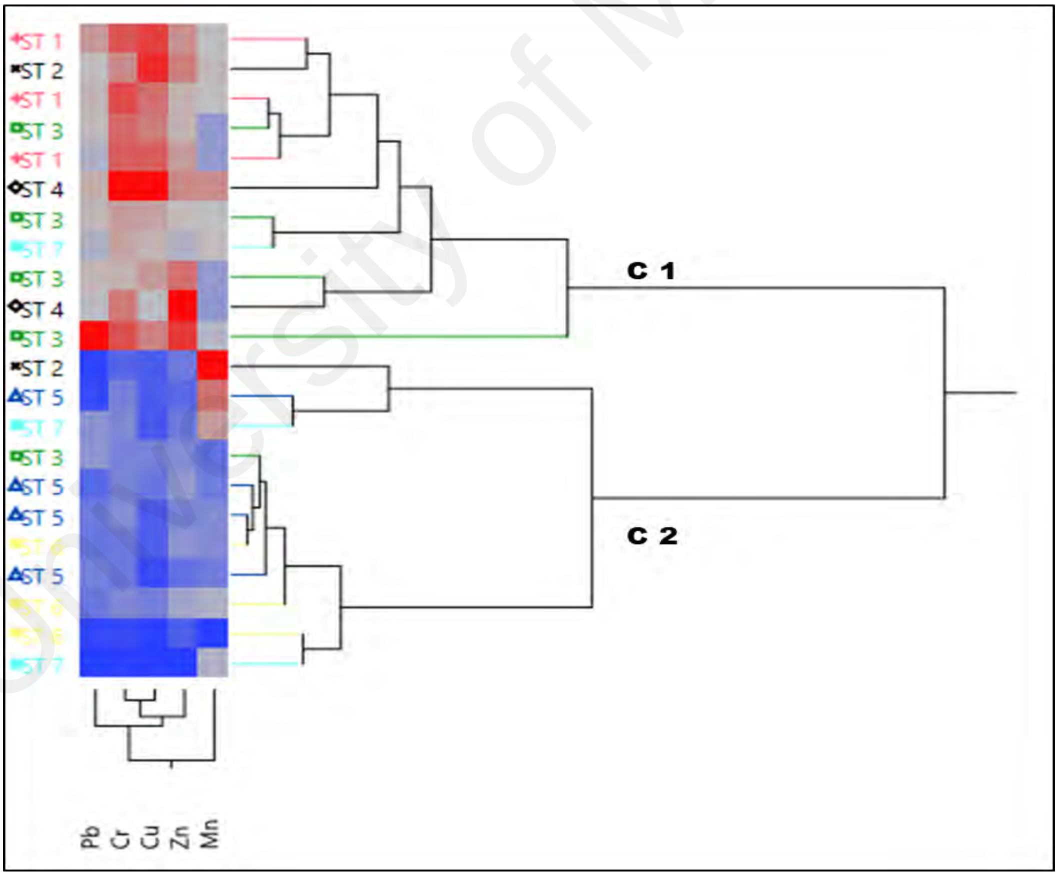


Figure 4.5: Two-way cluster analysis of urban dust in Petaling Jaya. In this figure red color represents high concentration of metals, blue color indicates lower concentration, and decrease in concentration is from red to blue color, ST = sampling site.

Table 4.8: Carcinogenic and non-carcinogenic average daily intake exposure for adults and children through three exposure routes estimated at 75th and 95th percentiles.

Carcinogenic Exposure								
Metals	Adult				Child			
	Cluster 1		Cluster 2		Cluster 1		Cluster 2	
	ADI (mg kg^{-1} day^{-1}) percentile				ADI (mg kg^{-1} day^{-1}) percentile			
	75th	95th	75th	95th	75th	95th	75th	95th
Ingestion								
Pb	4.02×10^{-6}	6.31×10^{-6}	3.18×10^{-6}	4.99×10^{-6}	1.76×10^{-4}	2.58×10^{-4}	1.40×10^{-4}	2.05×10^{-4}
Cr	3.18×10^{-6}	5.04×10^{-6}	2.42×10^{-6}	3.80×10^{-6}	1.39×10^{-4}	2.03×10^{-4}	1.06×10^{-4}	1.57×10^{-4}
Dermal								
Pb	1.60×10^{-6}	2.52×10^{-6}	1.27×10^{-7}	2.00×10^{-7}	9.87×10^{-7}	1.50×10^{-6}	7.82×10^{-7}	1.14×10^{-6}
Cr	1278×10^{-6}	1.98×10^{-6}	9.65×10^{-8}	1.51×10^{-7}	7.79×10^{-7}	1.14×10^{-6}	5.93×10^{-7}	8.71×10^{-7}
Inhale								
Pb	6.62×10^{-10}	9.62×10^{-10}	4.77×10^{-10}	7.65×10^{-10}	1.46×10^{-10}	1.99×10^{-10}	1.10×10^{-10}	1.58×10^{-10}
Cr	4.94×10^{-10}	7.75×10^{-10}	3.78×10^{-10}	5.87×10^{-10}	1.16×10^{-10}	1.72×10^{-10}	8.78×10^{-11}	1.20×10^{-10}
Non-carcinogenic Exposure								
Ingestion								
Pb	1.00×10^{-5}	1.57×10^{-5}	7.92×10^{-6}	1.24×10^{-5}	1.88×10^{-3}	2.76×10^{-3}	1.49×10^{-3}	2.19×10^{-3}
Cr	7.92×10^{-6}	1.24×10^{-5}	6.03×10^{-6}	9.50×10^{-6}	1.49×10^{-3}	2.17×10^{-3}	1.13×10^{-3}	1.67×10^{-3}
Cu	1.04×10^{-5}	1.62×10^{-5}	7.52×10^{-6}	1.18×10^{-5}	1.94×10^{-3}	2.84×10^{-3}	1.41×10^{-3}	2.09×10^{-3}
Zn	1.22×10^{-5}	1.91×10^{-5}	9.94×10^{-6}	1.56×10^{-5}	2.29×10^{-3}	3.36×10^{-3}	1.87×10^{-3}	2.75×10^{-3}
Mn	1.08×10^{-5}	1.70×10^{-5}	1.07×10^{-5}	1.68×10^{-5}	2.04×10^{-3}	2.98×10^{-3}	2.01×10^{-3}	2.96×10^{-3}

Table 4.8 Continued

Dermal								
Pb	3.99×10^{-6}	6.24×10^{-6}	3.16×10^{-6}	4.93×10^{-6}	1.04×10^{-6}	1.44×10^{-6}	8.34×10^{-7}	1.15×10^{-6}
Cr	3.16×10^{-6}	4.91×10^{-6}	2.40×10^{-6}	3.73×10^{-6}	8.33×10^{-7}	1.14×10^{-6}	6.34×10^{-7}	8.79×10^{-7}
Cu	4.12×10^{-6}	6.44×10^{-6}	2.99×10^{-6}	4.70×10^{-6}	1.09×10^{-6}	1.49×10^{-6}	7.91×10^{-7}	1.10×10^{-6}
Zn	4.88×10^{-6}	7.60×10^{-6}	3.96×10^{-6}	6.21×10^{-6}	1.29×10^{-6}	1.77×10^{-6}	1.04×10^{-6}	1.44×10^{-6}
Mn	4.32×10^{-6}	6.74×10^{-6}	4.26×10^{-6}	6.72×10^{-6}	1.13×10^{-6}	1.56×10^{-6}	1.12×10^{-6}	1.57×10^{-6}
Inhale								
Pb	1.54×10^{-9}	2.42×10^{-9}	1.21×10^{-9}	1.92×10^{-9}	1.45×10^{-9}	2.10×10^{-9}	1.10×10^{-9}	1.69×10^{-9}
Cr	1.21×10^{-9}	1.90×10^{-9}	9.39×10^{-10}	1.45×10^{-9}	1.13×10^{-9}	1.70×10^{-9}	9.28×10^{-10}	1.28×10^{-9}
Cu	1.58×10^{-9}	2.49×10^{-9}	1.15×10^{-9}	1.82×10^{-9}	1.60×10^{-9}	2.20×10^{-9}	1.07×10^{-9}	1.61×10^{-9}
Zn	1.91×10^{-9}	2.94×10^{-9}	1.42×10^{-9}	2.40×10^{-9}	1.90×10^{-9}	2.60×10^{-9}	1.44×10^{-9}	2.12×10^{-9}
Mn	1.69×10^{-9}	2.64×10^{-9}	1.67×10^{-9}	2.62×10^{-9}	1.68×10^{-9}	2.30×10^{-9}	1.66×10^{-9}	2.31×10^{-9}

ADI = Average daily intake

4.3.4 Health Risk Characterization via Three Pathways

4.3.4.1 Risks for Carcinogenic Heavy Metals on the Adults and Children Population

The carcinogenic and non-carcinogenic health risk estimation results are shown in Table 4.9. According to IARC (2012) USEPA (2011), Pb is regarded as carcinogenic and non-carcinogenic heavy metal; while Cu, Zn and Mn are considered non-carcinogenic heavy metals. The cancer risk was estimated for the lifetime exposure. Lifetime exposure is defined as the increased possibility of a human individual to develop cancer due to full exposure to the carcinogenic metals over a lifetime. The regulatory acceptable values for the cancer risks in accordance to the United State Environmental Protection Agency are ranged from 1×10^{-6} to 1×10^{-4} (USEPA, 2004a). Any value higher than this range is considered creating risk.

The result shows that the risk associated with children exposure to carcinogenic Pb via ingestion was 1.49×10^{-6}, 2.19×10^{-6}, 1.19×10^{-6} and 1.74×10^{-6} at 75th and 95th percentiles for Cluster 1 which comprises of industrial, traffic and part of commercial sites and Cluster 2, which comprises of residential and part of commercial sites, respectively. This suggests that heavy metals concentrations were higher in the sites in cluster 1 than those sites in cluster 2, which could be attributed to the industrial, traffic and commercial emissions influence in study sites in cluster 1. Previous studies reported that human activities contribute significantly to heavy metals pollution in dust of urban environment, which eventually contributes to risks to humans (Ali et al., 2017; Xu et al., 2016).

The carcinogenic risk caused by ingestion exposure to Pb in urban dust for children was found to be higher than that of adults at the sites in both clusters at 75th and 95th percentiles. This could possibly be due to lower body weight and higher ingestion rate of children when compared to that of adults (Table 2.1) in chapter 2. Children are significantly threatened by the exposure of poisonous heavy metals than adults that affect their brain and nervous system (Guney et al., 2014; Zheng and Shi, 2017). Similarly, according to Xue et al. (2010); Zhuang et al. (2014), children should be given close attention because they are prone to toxic heavy metals. Despite the fact that, cancer risk on ingestion of Pb in urban dust by adults and children at both percentiles were observed to be within or below the permissible limits of 1×10^{-6} to 1×10^{-4}, this proposes that in Petaling Jaya dust both adults and children did not pose consequences to cancer risk on ingestion exposure to Pb.

However, the highest cancer risk for children exposure to Pb in urban dust at 95th percentile of cluster 1 is noted to be 2.19×10^{-6}. Therefore, Pb in oral ingestion route could contribute to the total cancer risks of poisonous metals in sites with more anthropogenic impacts such as sites 1, 2, 3 and 4 in urban dusts. Anthropogenic emissions such as fugitive emissions from road dust, automobile brake lining, oil combustion, metal and electronic industries, manufacture or use of batteries and chemical processing were found to contribute to Pb content in the urban environment, especially atmospheric dust (Koki et al., 2017; Saeedi et al., 2012; Welling et al., 2015). There was no slope factor for Cr ingestion exposure as Cr is considered to be Cr(III) in this study. Therefore, its cancer risk was not calculated. The cancer risk as a result of dermal exposure to Pb and Cr was not calculated because Pb and Cr(III) have no toxicity indices on dermal exposure (Table 4.9).

Toxicity indices were shown in Table 2.2 in chapter 2. Furthermore, the carcinogenic risk due to inhalation exposure of adult to Pb in urban dust of this study is higher when compared to that of children at both percentiles of Cluster 1 and Cluster 2, particularly at 95th percentiles. This might be due to higher inhalation rate for adults (Table 2.1) in chapter 2. Therefore, adults could have possibility of been more vulnerable to cancer risk due to inhalation of Pb in urban dust. However, the cancer risk values on inhalation exposure of Pb in urban dust by both adults and children populations were found to be below the allowable range of 1×10^{-6} to 1×10^{-4}. This indicates no cancer effects on both populations due to inhalation exposure to urban dust. The cancer risk on inhalation exposure to Cr was not calculated. This is because there was no slope factor for inhalation exposure for Cr(III).

The trend in carcinogenic risk through pathways was in the following order, ingestion > dermal > inhalation. However, children were more vulnerable to the carcinogenic heavy metals than adults were particularly on ingestion exposure. This suggests ingestion exposure to be the dominant route for toxic heavy metals carcinogenic risk. On the other hand, cluster 1 comprising of industry, traffic and part of commercial sites for all the exposure pathways were identified to have higher carcinogenic values than those sites in C2. This could probably be due to more heavy metal distributions at those sites in C1 than C2.

Therefore, health risk of heavy metals could be attributed to heavy metal distributions in sites. The contribution of cancer risk to total cancer risk (TCR) because of exposure to Pb in urban dust by both populations in both clusters and percentiles are either within or below the permissible limits (Figure 4.6a), implying no risk posed. However, the values for children were higher especially at 95th percentiles in both clusters. Generally, this result suggests that Pb in urban dust of Petaling Jaya could pose no cancer risk to both populations, because the values were lower than the permissible limits.

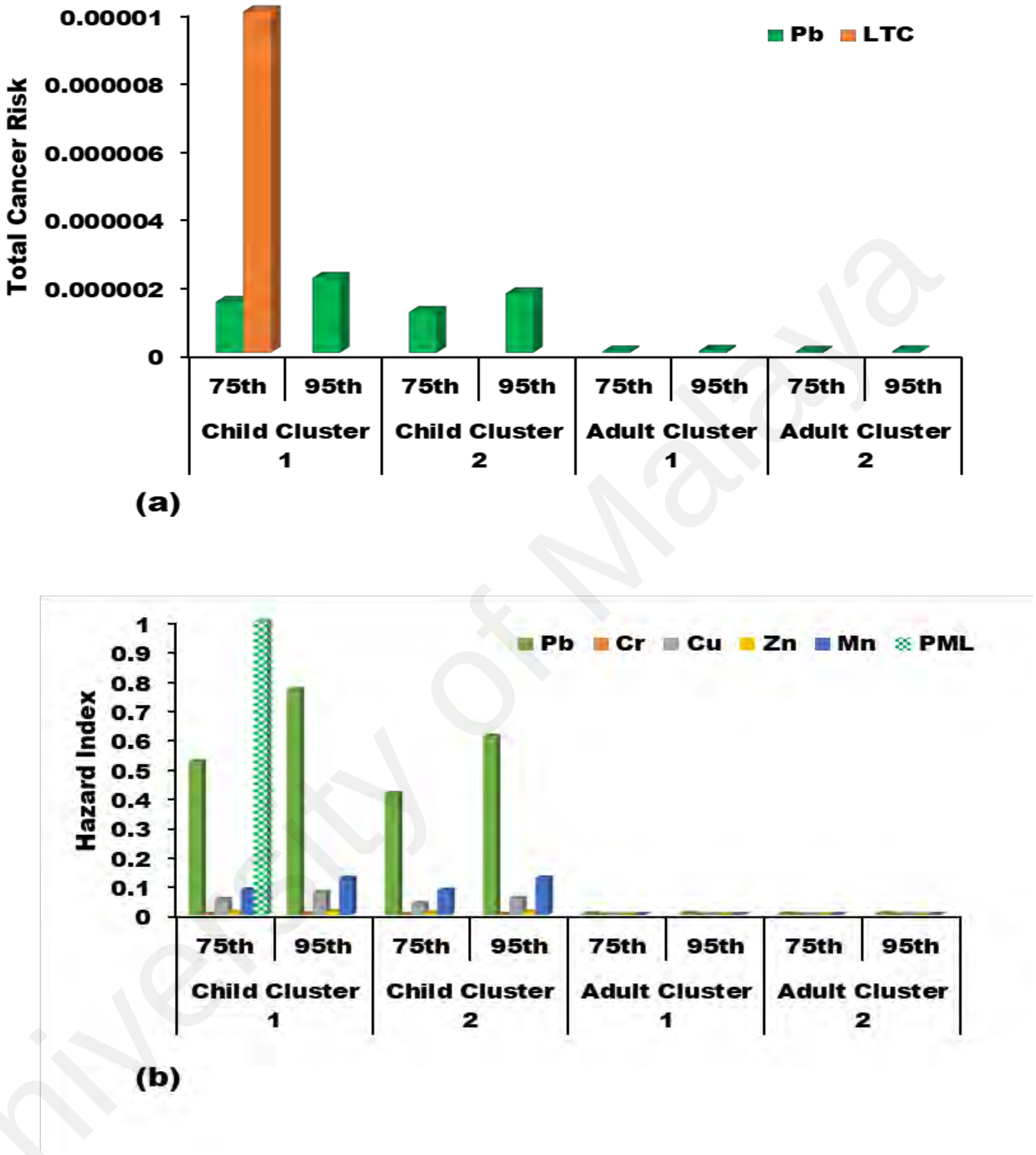


Figure 4.6: Total cancer risk (a) and hazard index (b) for both adults and children at 75th and 95th percentiles, LTC = Lifetime cancer limits, PLM = permissible limits.

4.3.4.2 Assessment of Risks for Non-Carcinogenic Heavy Metals for the Population of Children and Adults

The results of the non-carcinogenic risk for both children and adults are shown in Table 4.9. From the results, it was observed that the hazard quotient (HQ) caused due to ingestion exposure to Pb, Cu, Cr, Zn, and Mn by the population of children and adults in the samples at sites in both clusters, at 75th and 95th percentiles were noted to be less than the permissible limits of 1. This suggests that the non-cancerous hazard with respect to exposure to urban dust through ingestion route has no adverse health effects. The trend for hazard quotient due to ingestion exposure for the different heavy metals in sites at both cluster 1 and 2 was in the order of Pb > Mn > Cu > Zn > Cr. This rank order was the same in the case of both population of adults and children.

The health risk as a result of ingestion of urban dust was found to be higher in children than adults. The maximum risk due to hazard quotient as a result of ingestion of dust was noted to be for Pb. For children, the hazard quotient values for Pb at the sites in cluster 1 were 5.22×10^{-1} and 7.67×10^{-1} of 75th and 95th percentiles, respectively and for the sites in cluster 2 the hazard quotient values for Pb were 4.14×10^{-1} and 6.08×10^{-1} of 75th and 95th percentiles, respectively. Whereas, in the case of adults the values were 2.78×10^{-3}, 4.36×10^{-3}, 2.20×10^{-3} and 3.45×10^{-3} at the sites in both cluster 1 and 2 at 75th and 95th percentiles, respectively. This indicates that the non-carcinogenic risk for children due to ingestion was higher as compared to adults in both clusters.

The result was the same for the rest of the study heavy metals. The high hazard quotient value for Pb ingestion in urban dust by children at sites in cluster 1 in this study might be due to inputs from combustion of fuel, traffic related activities and industrial emissions. Emissions from the combustion of leaded gasoline and other related emissions from human activities have been reported to be the cause of highest hazard quotient values of Pb for children ingestion pathway in urban soil and dust (Cao et al., 2016; Luo et al., 2012). The higher hazard quotient values for children point out that children are more vulnerable to risk due to ingestion of urban dust as compared to adults. Previous researches reported that non-carcinogenic risk due to heavy metals exposure in urban dust was higher in children ingestion exposure (Ali et al., 2017; Liu et al., 2014).

The HQ dermal is the estimated hazard quotient for all the heavy metals via dermal exposure. The risk estimated indicates that the health risk was not significant in the case of dermal exposure to non-carcinogenic heavy metal contaminants in urban dust of this study. All the hazard quotient values on dermal contact to urban dust were less than 1. This shows that there is no possibility of adverse health effects. The hazard quotient due to dermal exposure to urban dust for all the sites in both cluster 1 and 2 are in the order Mn > Cu > Zn > Cr. This indicates that the high risk was as a result to Mn in urban dust of this study and the lowest was for Cr. The order was noted to be the same in case of both adults and children. It was noted that the hazard quotient for dermal exposure by adults for all the study heavy metals in the samples collected at sites in both clusters were higher when compared to children (Table 4.9). This might be due to higher surface area of the adult skin when compared to the children. The hazard quotient for Pb on dermal exposure was not estimated because there was no reference dose.

The risk assessment based on the inhalation exposure to urban dust showed that the health risk induced by Zn and Mn to both population on inhalation of dust was lower than the permissible limits of 1. Meaning there is no health consequences on inhalation of urban dust of this study to both adults and children. The order of the hazard quotient for inhalation exposure to the heavy metals in urban dust was Mn > Zn. The order was similar in the case of adults and children population. The adult population was more vulnerable to health risk on inhalation exposure to urban dust especially at the 95th percentile. The reason may be due to higher inhalation rate of adults as they have more exposure capacity and more intake of dust when compared to children (USEPA, 2002). There were no reference doses for inhalation exposure to Pb, Cr and Cu, as such their non-carcinogenic risk was not estimated (Table 4.9).

The contribution of quotient risks for individual heavy metals of the different exposure pathways to hazard risks is known as hazard index (HI). The hazard index for the different heavy metals for the ingestion, dermal contact and inhalation exposure at all sites in both clusters followed the rank order Pb > Mn > Cu > Zn > Cr. The order was same for the population of adults and children. The hazard index for all population was shown to be lower than the permissible limits of 1 (Figure 4.6b). This implies no health risk for both populations. However, the hazard index due to heavy metals exposure was discovered to be around 1–8 times higher in children when compared to adults (Figure 4.6b).

This high hazard index value for children implies that children are more likely to suffer health consequences due to heavy metals exposure (Bose-O'Reilly et al., 2018; Mielke et al., 2017). Previous studies reported hazard index values less than 1, which predicts no significant health risk but in case of children the risk was higher when compared to adults (Ali et al., 2017; Cao et al., 2015; Wei et al., 2015). In this study, the result revealed that generally the ingestion exposure was the significant route to both children and adults population for the hazard heavy metals in dust followed by dermal and the least inhalation, even though all the pathways posed no health risk to both populations.

Table 4.9: Carcinogenic and non-carcinogenic risks for child and adult through ingestion, dermal and inhalation pathways estimated at 75th and 95th percentiles.

Carcinogenic Risk								
Metals	Child				Adult			
	Cluster 1		Cluster 2		Cluster 1		Cluster 2	
	CR percentile				CR percentile			
	75th	95th	75th	95th	75th	95th	75th	95th
Ingestion								
Pb	1.49×10^{-6}	2.19×10^{-6}	1.19×10^{-6}	1.74×10^{-6}	3.42×10^{-8}	5.36×10^{-8}	2.70×10^{-8}	4.24×10^{-8}
Cr	NA	NA	NA	NA	NA	NA	NA	NA
Dermal								
Pb	NA	NA	NA	NA	NA	NA	NA	NA
Cr	NA	NA	NA	NA	NA	NA	NA	NA
Inhale								
Pb	1.75×10^{-15}	2.39×10^{-15}	1.32×10^{-15}	1.90×10^{-15}	7.94×10^{-15}	1.15×10^{-14}	5.72×10^{-15}	9.18×10^{-15}
Cr	NA	NA	NA	NA	NA	NA	NA	NA
Non-carcinogenic Risk (HQ)								
Ingestion								
Pb	5.22×10^{-1}	7.67×10^{-1}	4.14×10^{-1}	6.08×10^{-1}	2.78×10^{-3}	4.36×10^{-3}	2.20×10^{-3}	3.45×10^{-3}
Cr	9.93×10^{-4}	1.45×10^{-3}	7.53×10^{-4}	1.11×10^{-3}	5.28×10^{-6}	8.27×10^{-6}	4.02×10^{-6}	6.33×10^{-6}
Cu	5.24×10^{-2}	7.68×10^{-2}	3.81×10^{-2}	5.65×10^{-2}	2.81×10^{-4}	4.38×10^{-4}	2.03×10^{-4}	3.20×10^{-4}
Zn	7.63×10^{-3}	1.12×10^{-2}	6.23×10^{-3}	9.17×10^{-3}	4.07×10^{-5}	6.37×10^{-5}	3.31×10^{-5}	5.18×10^{-5}
Mn	8.50×10^{-2}	1.24×10^{-1}	8.38×10^{-2}	1.25×10^{-1}	4.50×10^{-4}	7.08×10^{-4}	4.46×10^{-4}	7.00×10^{-4}

Table 4.9 Continued

Dermal								
Pb	NA	NA	NA	NA	NA	NA	NA	NA
Cr	5.55×10^{-7}	7.60×10^{-7}	4.23×10^{-7}	4.86×10^{-7}	2.11×10^{-6}	3.27×10^{-6}	1.60×10^{-6}	2.49×10^{-6}
Cu	4.54×10^{-5}	6.20×10^{-5}	3.30×10^{-5}	5.58×10^{-5}	1.72×10^{-4}	2.68×10^{-4}	1.25×10^{-4}	1.96×10^{-4}
Zn	4.30×10^{-6}	5.90×10^{-6}	3.47×10^{-6}	4.80×10^{-6}	1.63×10^{-5}	2.53×10^{-5}	1.32×10^{-5}	2.07×10^{-5}
Mn	4.91×10^{-5}	6.78×10^{-5}	4.87×10^{-5}	6.83×10^{-5}	1.88×10^{-4}	2.93×10^{-4}	1.85×10^{-4}	2.92×10^{-4}
Inhale								
Pb	NA	NA	NA	NA	NA	NA	NA	NA
Cr	NA	NA	NA	NA	NA	NA	NA	NA
Cu	NA	NA	NA	NA	NA	NA	NA	NA
Zn	8.61×10^{-9}	1.28×10^{-8}	7.06×10^{-9}	1.04×10^{-8}	9.81×10^{-9}	1.60×10^{-8}	8.00×10^{-9}	1.28×10^{-8}
Mn	1.17×10^{-4}	1.61×10^{-4}	1.16×10^{-4}	1.62×10^{-4}	1.18×10^{-4}	1.85×10^{-4}	1.17×10^{-4}	1.83×10^{-4}

NA= Not available as a result of no toxicity indices, CR = Cncer risks, HQ = Hazard quotient.

4.4 Bioaccessibility and bioavailability of heavy metals in agricultural soils and urban dusts

The poisonous heavy metals emitted from various sources in urban soil and dust accumulate them hence, becoming the reservoir of these heavy metals. This study focused on the health effect associated with the exposure to these heavy metals by both population of adults and children, particularly children as a result of working, walking and playing.

The human health risk associated to exposure to these toxic heavy metals occur through oral ingestion of soil and dust which is noted to be the major exposure route by both populations. The ingestion exposure occur either intentional or by incidental ingestion which is the major channel due to frequent hand-to-mouth and object-to mouth behavior of children. Lack or non-proper hand wash and uncut fingernails could likely facilitate the risks on individual oral ingestion exposure to these heavy metals, most especially children. On the other hand, the amount of soil and dust ingested by individual could be another crucial aspect.

Previous studies reported that children have higher ingestion rate of soil and dusts than adults (Praveena et al., 2015; Wei et al., 2015). For instance daily soil and dust ingestion rates of children aged between 2 to 7 years and 6 to below 21 years was estimated to be in a range of 39 to 246 mg/day and 50 to 1000 mg/day, respectively, for different heavy metals (Davis et al., 1990; USEPA, 2008), whereas, that of adult was estimated to be between 10 to 100 mg/day (USEPA, 2002). Furthermore, soil and dust fraction size is another vital aspect that increases health implication. As discussed in section 3.4 of chapter 3, smaller particle fraction of soil and dust induced more risk than the bigger particles. Particles of < 125 μm of soil and < 63 μm of dust stick to human hands and fingers and clothing and objects. Therefore, these particle sizes of soil and dust can be used for the human health risk evaluation.

The need to use physiologically based approach to demonstrate human health risk estimation i.e., *in vitro* gastro-intestinal extraction is discussed in section 2.1 and the use of oral ingestion is discussed in section 2.3 of chapter 2. Oral bioaccessibility is the fraction of heavy metals that are solubilized from soil and dust in human gastrointestinal system via the action of digestive fluids and thereby are available for absorption into the circulatory system (Li et al., 2015). This research has employed the Physiologically Based Bioaccessibility Extraction Test (PBET). Moreover, this work paid much attention on five toxic heavy metals such as As, Cd, Cr, Cu and Pb due to their distribution and poisonous nature and effect on human.

The oral bioaccessibility of these heavy metals in agricultural soil and urban dust was determined and a chemometric approach was applied on the bioavailable extract fraction to assess the maximum possible health risk associated with both children and adult exposure. The application of PBET for oral bioaccessibility of Pb, As, Cd, Cu and Cr in agricultural soil and urban dusts of < 125 µm and < 63 µm fraction size, respectively, is very much limited. Similarly, using PBET on oral bioaccessibility for potential human health risk in agricultural soils of < 125 µm and urban dusts of < 63 µm with the application of chemometrics simulation technique incorporated with the local inhabitant's body weight and average exposure time is also limited. Therefore this research is very necessary.

4.4.1 Method Validation for *in vitro* Technique

For the purpose of accuracy and precision, all the heavy metals total concentration determined in the SRM in the bioaccessibility analysis were in good agreement with the certified values in the SRM. The results in Table 4.10 shows that the percentage recoveries of all the heavy metals fell between the ranges of 89.24% – 104%.

4.4.2 Oral Bioaccessibility of Toxic Heavy Metals in Urban Dust and Soil

Urban dusts/soils are known to accumulate large amount of heavy metals, as such the fraction amount of these toxic metals that is solubilized in the gastrointestinal tract and is made available for absorption (oral bioaccessible fraction) can be determined and be used as the basis of assessing health consequences on humans. The *in vitro* bioaccessibility which is physiologically based (PBET) was employed and the oral bioaccessibility of toxic heavy metals such as As, Cd, Cr, Cu and Pb were determined from the certified standard reference material (SRM 2586) and from the urban dusts of < 63 μm particle size, sampled from Petaling Jaya.

This is because it has been noted that accumulation of toxic metals in urban dusts is proportional to the particle size (Han et al., 2014). Dust particle size of < 63 μm could contain more of these heavy metals due to their large surface area, hence may have high health risk tendencies to human. The result of the SRM oral bioaccessibility, gastric and gastrointestinal is shown in Table 4.10. The result revealed high recoveries for the toxic heavy metals in the SRM ranging from 89–104%. This implies that the analytical method employed in the determination of these heavy metals is suitable. Hence the oral bioaccessibility of As, Cd, Cr, Cu and Pb in urban dust was assessed.

4.4.3 Total, Bioavailability and Percentage Bioaccessibility Fraction of Heavy Metals in Soil and Urban Dust

Table 4.11 shows statistical analysis of the variations in total metal content, bioavailability fraction and percentage bioaccessibility fraction in urban dust and soil.

Table 4. 10 Toxic heavy metals in certified standard reference materials on total, gastric and gastrointestinal bioaccessibility fractions.

Heavy Metals	**Cu**	**Pb**	**Cd**	**As**	**Cr**
Certified SRM (mg/kg)	81.00 ± 0.00	432 ± 17.00	2.71 ± 0.54	8.70 ± 1.50	301 ± 45.00
Determined Total (mg/kg) Mean ± SD	76.14 ± 5.28	403.00 ± 29.59	2.22 ± 0.17	6.23 ± 0.64	300.90 ± 10.57
In Vitro gastric and gastrointestinal extraction(mg/kg)					
Gastric fraction (Mean ± SD)	36.28 ± 0.77	230.97± 103.29	1.22 ± 0.16	3.68 ± 0.12	160.82 ± 0.97
GBAF (%)	47.64	57.31	55.04	59.08	53.45
Gastrointestinal fraction (Mean ± SD)	34.77 ± 3.57	188.07 ± 0.68	0.91 ± 0.01	2.39 ± 0.64	107.71 ± 0.17
GIBAF (%)	45.66	46.67	40.97	38.41	35.80
Total metal content (Gastric + Gastrointestinal) (mg/kg)	71.05	419.04	2.13	6.07	268.53
Total Recovery (%)	93.30	104.00	96.22	97.64	89.24

GBAF = gastric bioaccessibility fraction; GIBAF = gastrointestinal bioaccessibility fraction; $\%GBAF = \frac{Gastric\ fraction}{Total\ metal\ content} \times 100$; Mean ± SD (three replicates obtained at 95% confidence limit).

The results show that the total heavy metal content distribution in soil is in the order of Cu > Pb > Cr > As > Cd ranging, respectively 15.01 – 323.45 (133.94 ± 8.08) mg/kg, 10.48 – 262.70 (mean = 75.63 ± 6.91) mg/kg, 7.55 – 68.91 (mean = 30.39 ± 17.80) mg/kg, 1.27 – 53.75 (mean = 22.59 ± 16.76) mg/kg, and 0.27 – 2.23 (mean = 0.79 ± 0.58). The mean concentration variations of all heavy metals in soil except Cr were found to be higher as compared to the background values such as Cu (30.00 mg/kg), Pb (50.00 mg/kg), Cr (61.00 mg/kg), As (11.20 mg/kg) and Cd (0.30 mg/kg). The heavy metal concentrations in agricultural soil of this study could be as a result of fertilizer application, chemicals and contributions from the machines used in the farms. Previous studies reported distributions of heavy metals in agricultural soils (Juhasz et al., 2007; Wong et al., 2002) which was as a result of activities such as application of herbicides, pesticides and fertilizer.

On the other hand, the distribution of heavy metals concentration in urban dust varies with locations as industrial > traffic > commercial > residential for most of the study heavy metals except Cu which was higher in the traffic compared to other locations. Meaning industrial sites have higher heavy metals distribution and the lowest were the residential areas. The high concentrations of different heavy metals could be attributed to emissions by various anthropogenic activities and atmospheric depositions in the urban environment (Ali et al., 2017). In the industrial sites, the heavy metals distribution varied and followed the ranked trend Cu > Pb > As > Cr > Cd. The mean values of the heavy metals distribution in the industrial sites were 152. 57 ± 70.68, 142.97 ± 64.04, 30. 55 ± 18.41, 30.38 ± 5.59 and 1.02 ± 0.26 mg/kg, respectively, for Cu, Pb, As, Cr and Cd. Previous studies reported higher heavy metals distribution in industrial areas of urban environment due to industrial emissions (Yousaf et al., 2016).

In contrast, the distribution of heavy metals in the traffic areas was in the order of Cu > Pb > Cr > As > Cd. This implies that Cu has the highest concentration, and Cd the lowest in traffic areas. The order was almost same with industrial areas except for Cr that was found higher in traffic areas. The mean concentration of the heavy metals was 133.97 ± 119.00, 76.07 ± 25.49, 34.45 ± 11.63, 23.49 ±16.06 and 1.29 ±0.92 mg/kg, respectively, for Cu, Pb, Cr, As and Cd. This could be as a result of high number of vehicles that leads to congested traffic in the study area. Previous researches reported higher heavy metal concentration in traffic areas due to combustion of fuels, lubricants, deposition of vehicular particles such as exhaust, break lining and lubricating oil residues (Li et al., 2013; Yousaf et al., 2016).

On the other hand, in the commercial area the heavy metals distribution was Pb > Cu > Cr > As > Cd. Whereas, the residential area which was discovered to have the lowest concentration of the heavy metals showed variation of the mean heavy metals concentration to be Pb > Cu > As > Cr > Cd. Low concentrations of heavy metals in these areas could be as a result of low emissions due to low anthropogenic activities. However, the mean heavy metal content of all the heavy metals in dust at the industrial and traffic areas was noted to be higher than the corresponding background values from Chinese National Environmental Monitoring Center (CNEMC, 1990) (Table 2.2), except Cr that was lower (30.38 ± 5.59 and 34.45 ± 11.63 mg/kg) at the industrial and traffic areas, respectively.

As (8.94 ± 9.65 mg/kg) and Cr (10.29 ± 9.75 mg/kg) at the commercial areas was lower than the background values (11.20 mg/kg) As and (61.00 mg/kg) Cr. On the other hand, As (18.05 ± 6.84 mg/kg) and Cd (0.57 ± 0.24 mg/kg) in the residential areas was higher than the background values while all the other mean heavy metals concentration in the residential areas were lower. This suggests that human activities in urban areas influence heavy metal concentration distribution. Local background values from China were used (CNEMC, 1990) in this study because there is no data on the local soil background values in Malaysia, this has been confirmed by many published researches who used background values from different countries (Han et al., 2014; Ong et al., 2016; Ripin et al., 2014).

Heavy metals exposure that corresponding to health risk is influenced by land use types. On this critical note, the bioavailability fraction concentration of the heavy metals in this study were compared with soil guideline values so as to identify the contamination of these heavy metals in soil and dust. Soil guideline values are scientifically set general quality standards used in many countries to evaluate human health risks from soil contamination as a result of metal contaminants. These soil guideline values are expressed in the concentration threshold form in soil. The concentrations of metal contaminants in soil/dust which exceeds the soil guideline values suggests a potential risk to humans.

However, presently in Malaysia there is no available data on soil standards and guideline values developed for the assessment of heavy metals contamination level in soil and dust based on bioavailability of heavy metals concentration. This is confirmed by previous studies on health risk (Ghazali, 2010; Najib et al., 2012; Yuswir et al., 2015). This is not the case with countries such as United State of America (USA), Canada and Dutch who have developed guideline values of toxic heavy metals on the note of bioavailability of toxic heavy metals concentration for different land use types. Therefore, this study used the guideline values from different countries that were developed to monitor the functional properties of soil/dust for the environmental and human health protection (Table 2.4 and Table 4.12).

This is required so as to get a widely and meaningful view of the contamination. The result shows that the maximum bioavailability of As (19. 57 mg/kg) was higher than the Canadian soil guideline values (12.00 mg/kg) (CCME, 1997, 1999) for soil, the maximum values of Cd (0.63 mg/kg) have exceeded the tolerable daily intake (0.50 mg/kg). The maximum bioavailability concentration of Cu (167.33 mg/kg) in soil exceeded the Dutch target values (36.00 mg/kg), while the maximum bioavailability content of Pb and Cr (21.66 and 2.21 mg/kg), respectively, exceeded the California human health values (0.0035 and 0.00001 mg/kg) for Pb and Cr, respectively.

In the case of urban dust the maximum bioavailability values of Cd (0.64 mg/kg) in dust at the traffic areas have exceeded the tolerable daily intake (TDI) (0.50 mg/kg), whereas, Cd (0.39, 0.24 and 0.30 mg/kg) at the industrial, commercial and residential areas respectively, were found to be lower than the tolerable daily intake. Cu, Pb and Cr at their mean bioavailability values exceeded both the Dutch target Soil Guideline values and California Human Health SSLs values in dust. This trend was the same at all study sites. Anthropogenic inputs and atmospheric deposition have been reported to influence the heavy metals concentrations in locations in urban settings (Kamani et al., 2018; Rinklebe & Shaheen 2014). Therefore, our findings insinuate that areas with high activities such as industrial, traffic and commercial could contaminate soil and dust and significantly cause adverse health effects to humans. In this regard, health risk assessment on the bioavailability fraction concentration of heavy metals in this study is crucial.

The bioavailable and percentage bioaccessibility fraction concentration of the heavy metal contaminants are lower than the total metal content (Table 4.11). This is same in the agricultural soil and the urban dust of all study sites. For instance, the mean content of the total heavy metal contaminants in soil was 133.95 ± 88.08, 75.68 ± 62.91, 22.59 ± 16.76, 30.39 ± 17.84 and 0.79 ± 0.58 mg/kg for Cu, Pb, As, Cr and Cd, respectively. The mean heavy metal bioavailability fraction in soil was 33.19 ± 39.08, 5.29 ± 5.83, 4.44 ± 3.67, 1.15 ± 0.44 and 0.25 ± 0.17 mg/kg with respect to Cu, Pb, As, Cr and Cd, respectively.

While the heavy metal contaminants percentage bioaccessibility fraction was 31.88 ± 26.37, 8.55 ± 6.26, 27.61 ± 17.84, 5.04 ± 3.29 and 33.82 ± 16.37%, respectively, for Cu, Pb, As, Cr and Cd in soil. These differences followed the same trend in urban dust as shown in Table 4.11. This implies that bioavailable content and the bioaccessibility fraction is the actual amount of heavy metals in soil and dust that is ingested, solubilized and is available for absorption into the circulatory system. It is this fraction of the heavy metals that could express the precise risks involved in human. Therefore, the use of bioaccessibility protocol in human health risk assessment is indispensable.

Generally, the mean *in vitro* bioaccessibility and the mean % BAF of all the study heavy metals in both urban dust and soil in gastric phase were fund to be < 50% except Cu and As. Cu and As during the gastric phase were shown to be > 50% and during the gastrointestinal phase, the mean % bioaccessibility fraction of Cu was shown to be < 50%, whereas the remaining heavy metals also show < 50% bioaccessibility fraction in urban dust as seen in Table 4.13 and Table 4.14. This proposed that more than half of the Cu and As in urban dust could be available and less than half of the other heavy metals in urban dust could be available as a result of oral ingestion exposure. This therefore expresses the risk involved. Nevertheless, in the maximum *in vitro* % bioaccessibility fraction which is termed the worst case situation, 87 to 168% for all the study heavy metals in gastric phase of urban dust and 62 to 116% in gastric phase of urban soil *in vitro*

Table 4. 11: Total heavy metal content, bioavailable and % bioaccessible fractions in agricultural soil and urban dust.

Sites	TF		IND		COM		RSD		soil	
Total metal content (mg/kg)										
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Cu	133.97 ± 119.00	29.38 - 489.15	152.57 ± 70.68	25.77 - 256.5	31.53 ± 35.88	2.15 - 75.98	20.76 ± 14.05	4.88 - 38.61	113.95 ± 88.08	15.01 - 323.45
Pb	76.07 ± 25.49	49.74 - 124.6	142.97 ± 64.04	67.35 - 262.30	51.23 ± 46.99	7.49 - 129.5	38.09 ± 31.93	7.02 - 96.99	75.63 ± 62.91	10.48 262.70
AS	23.49 ± 16.06	7.69 - 55.89	30.55 ± 18.41	15.42 - 70.17	8.94 ± 9.65	0.89 - 24.09	18.05 ± 6.84	11.21- 30.26	22.59 ±16.76	1.27 - 53.75
Cr	34.45 ± 11.63	19.31 - 57.24	30.38 ± 5.59	19.85 - 39.45	10.29 ± 9.75	3.09 - 27.36	10.65 ± 7.38	3.46 - 23.37	30.39 ± 17.84	7.55 - 68.91
Cd	1.29 ± 0.92	0.68 - 4.03	1.02 ± 0.26	0.61 - 1.56	0.52 ± 0.22	0.22 - 0.84	0.57 ± 0.24	0.27 - 0.90	0.79 ± 0.58	0.27 - 2.23
Bioavailable fraction (mg/kg)										
Cu	44.91 ± 26.68	17.85 - 99.4	56.77 ± 34.20	6.47 - 108.7	8.77 ± 13.80	1.07 - 38.37	8.88 ± 5.23	2.59 - 15.61	33.19 ± 39.88	4.97 - 167.33
Pb	10.57 ± 8.05	9.03 - 35.15	16.29 ± 9.59	4.77 - 36.78	5.33 ± 2.13	3.00 - 8.67	6.48 ± 4.37	1.84 - 14.34	5.29 ± 5.83	0.36 - 21.66
As	7.99 ± 2.80	3.47 - 14.43	8.27 ± 3.69	4.54 - 18.32	4.53 ± 3.97	1.29 - 9.71	7.29 ± 2.45	4.78 - 10.19	4.44 ± 3.67	0.77 - 19.37
Cr	2.99 ± 1.19	1.08 - 4.84	1.98 ± 0.84	0.52 - 3.17	0.83 ± 0.58	0.35 - 1.69	1.07 ± 0.67	0.57 - 2.39	1.15 ± 0.44	0.53 - 2.21
Cd	0.42 ± 0.13	0.25 - 0.64	0.31 ± 0.05	0.24 - 0.39	0.21 ± 0.03	0.17 - 0.24	0.25 ± 0.04	0.19 - 0.30	0.25 ± 0.17	0.04 - 0.63
%BAF										
Cu	42.61 ± 21.66	18.96 - 73.46	37.31 ± 20.47	4.46 - 69.52	39.79 ± 20.41	3.57 - 51.34	46.30 ± 7.87	32.99 - 53.90	31.88 ± 26.37	4.84 - 121.41
Pb	25.28 ± 10.41	11.10 - 44.61	12.09 ± 6.48	4.44 - 25.00	17.75 ± 13.70	6.69 - 40.03	22.09 ± 10.06	5.36 - 31.20	8.55 ± 6.26	0.32 - 22.03
As	40.86 ± 14.18	19.24 - 61.81	29.73 ± 7.97	13.38 - 49.06	48.64 ± 8.47	40.29 - 61.32	41.68 ± 9.48	28.78 - 53.47	27.61 ± 17.84	7.83 - 60.83
Cr	9.14 ± 3.65	4.28 - 14.83	6.28 ± 2.06	2.62 - 9.44	9.48 ± 3.75	5.01 - 13.34	12.24 ± 5.54	4.57 - 18.28	5.04 ± 3.29	1.69 - 14.42
Cd	40.10 ± 19.84	7.90 - 86.47	31.17 ± 7.14	20.19 - 44.44	41.40 ± 12.38	27.77 - 54.86	43.91 ± 10.59	29.67 - 51.56	33.82 ± 16.37	8.05 - 67.24

% BAF = percentage bioaccessibility fraction, mean ± SD, TF = traffic, IND = industrial, COM = commercial, RSD = residential.

Table 4. 12 Soil Guideline values for different countries.

Metals	Cd	Cr	Cu	Pb	Reference
Dutch Soil Guidelines Target	0.8	100	36	85	VROM (2000)
Dutch Soil Guidelines Intervention	12	380	190	530	VROM (2000)
Tolerable Daily Intake (TDI)	0.5	0.0005	1400	36	Baars et al. (2001)
California Human Health SSLs Residential area	1.7	0.00001	0.003	0.015	CEPA (2005)
California Human Health SSLs Industrial area	7.5	0.00001	0.00038	0.0035	CEPA (2005)

Table 4.13 Summary of *in vitro* gastric bioaccessibility fraction of heavy metals in agricultural soil.

Metals	Cu	Pb	As	Cr	Cd
Gastric Bioaccessible fraction (%) in soil					
Maximum	108.63	70.26	62.75	116.21	68.81
Mean	58.31 ± 31.84	25.04 ± 25.96	38.76 ± 16.40	32.97 ± 24.81	38.75 ± 18.81
Median	53.45	11.33	37.49	26.95	37.43
Minimum	10.04	1.21	7.95	10.02	11.17
Gastric Bioaccessible fraction (mg/kg) in soil					
Maximum	98.86	56.15	22.52	11.85	0.25
Mean	45.97 ± 22.61	12.14 ± 13.66	7.21 ± 5.09	6.95 ± 1.77	0.21 ± 0.02
Median	45.00	8.11	6.08	6.61	0.22
Minimum	16.30	0.55	0.80	3.48	0.15

Mean ± SD, $Bioaccessibility\ \% = \frac{Bioavailability\ fraction}{Total\ metal\ content} \times 100$

Table 4. 14 Summary of *in vitro* gastric bioaccessibility fraction of heavy metals in urban dust.

Metals	Cu	Pb	As	Cr	Cd
Gastric bioaccessibility fraction (mg/kg) in urban dust					
Maximum	240.42	147.30	47.13	18.43	0.40
Mean	58.11 ± 64.49	30.20 ± 28.01	9.18 ± 9.59	10.10 ± 3.86	0.30 ± 0.06
Median	31.46	23.90	6.22	10.45	0.30
Minimum	1.98	1.47	0.8	0.63	0.20
Gastric Bioaccessibility fraction (%)					
Maximum	114.57	87.94	167.95	131.69	95.12
Mean	60.80 ± 3.46	37.25 ± 24.89	53.03 ± 41.59	48.65 ± 27.32	39.59 ± 20.19
Median	64.16	28.09	29.60	38.91	34.36
Minimum	3.85	6.05	8.86	17.91	6.39

Mean ± SD, $Bioaccessibility\ \% = \frac{Bioavailability\ fraction}{Total\ metal\ content} \times 100$

Table 4.15 Correlation coefficient between gastric bioaccessibility and total metal content in agricultural soil and urban dust.

Metal correlation coefficient	Cu (rvalue)	Pb (r value)	As (r value)	Cr (r value)	Cd (r value)
% GBAF & T in urban dust	-0.29*	-0.234	-0.391*	-0.67**	-0.682**
% GBAF & T in agricultural soil	-0.766**	-0.437*	-0.592**	-0.731**	-0.872**

*Significant at $p < 0.05$, **Significant at $p < 0.01$, % GBAF = percentage gastric bioaccessibility fraction, T = total metal content.

bioaccessibility could be available following ingestion exposure to urban dust which could eventually induce high impact on human health.

4.4.4 Bioaccessibility of Heavy Metals in Soil and Dust During Gastric Phase Extraction

The oral bioaccessibility of heavy metals in soil and dust for gastric and intestinal extraction is expressed in Figure 4.7. The result disclosed that there is a variation in the percentage bioaccessibility fraction of the heavy metals in both the gastric (stomach) and the gastrointestinal (intestinal) compartments. This bioaccessibility differences among the heavy metals could be explained by the occurrence of these heavy metals in different geochemical forms in the urban dusts and soil. The higher percentage gastric bioaccessibility fraction (% GBAF) of heavy metal contaminants in the stomach phase could possibly be due to solubilization / dissolution of these heavy metals from the mineral oxides, iron or carbonates and their adsorption in the lower gastric pH (Barrett et al., 2010; Li et al., 2016; Mercer & Tobiason, 2008).

This implies that out of the amount of heavy metals ingested from soil and dust, these percentage amounts are dissolved in the lower pH of the stomach and are available to be transported into the intestinal tract where the absorption of digested components take place. The bioaccessibility of the heavy metals in urban dust in the gastric phase for all locations is shown in Figure 4.8A-D as a box plot. The box plot showing the mean, median, box boundary (25th and 75th) percentiles and whiskers (2.5th and 90th) percentiles. It is observed that there was a significant difference in the percentage bioaccessibility fraction of the heavy metals across the sampling locations.

The mean and median % gastric bioaccessibility of the heavy metal contaminants across the sampling locations were as follows Pb = 37.68 ± 25.44, 32.10%, As = 61.26 ±

52.03, 26.63%, Cr = 41.66 ± 14.55, 38.53%, Cd = 36.34 ± 9.27, 34.89% and Cu = 60.97 ± 39.61, 59.08% at the industrial location. The mean and median gastric bioaccessibility at the traffic site was 35.52 ± 22.51, 26.05% for Pb, 39.03 ± 36.02, 26.05% for As, 37.58 ± 17.31, 35.65% for Cr, 23.60 ± 8.58, 25.65% for Cd and 47.97 ± 37.56, 29.66 for Cu. While at the commercial location, the gastric bioaccessibility fraction was 25.77 ± 16.91, 19.69% for Pb, 73.07 ± 26.89, 82.64% for As, 75.38 ± 35.19, 99.87% for Cr, 63.23 ± 20.09, 57.86% for Cd and For Cu it was 77.79 ± 20.54, 83.44%. And at the residential site the gastric bioaccessibility was 49.32 ± 33.56, 54.32 for Pb, 46.49 ± 32.88, 39.25% for As, 63.65 ± 40.76, 52.63% for Cr, 58.92 ± 22.72, 54.98% for Cd and 71.94 ± 27.60, 83.22% for Cu.

The percentage bioaccessibility fraction during the gastric phase of dusts was found to be higher than during the gastric phase of soil (Table 4.13 and Table 4.14). This suggests that heavy metals are more bioaccessible in urban dust than agricultural soil; probably this could be associated with sample matrix organic matter content and the concentration of heavy metals in the sample coming from different sources. The organic matter content of the agricultural soil was higher than those of urban dust. Previous studies reported that organic matter content had much effect in reducing the gastric bioaccessibility of heavy metals in agricultural soil (Cai et al., 2016; Liu et al., 2016). On the other hand, heavy metals of anthropogenic sources are reported to be mainly soluble in gastrointestinal compartment and would therefore be more bioaccessibile (Turner, 2011).

High reactivity of smaller particles of dust in aqueous environment could cause heavy metals to be more bioaccessible in dust (Ettler et al., 2012). Larger surface area of smaller dust particles could cause the dust particles to accumulate more of heavy metals than soil (Han et al., 2014), hence pose high-risk tendencies to human. Similarly, Juhasz et al.

(2011) reported decrease in gastric bioaccessibility of heavy metals with increase in soil particle size. Generally, the mean percentage gastric bioaccessibility fraction of the heavy metals in urban dust and agricultural soil, respectively was in the order of Cu > As > Cr > Cd > Pb and Cu > As > Cd > Cr > Pb. This shows that Cu was the highest bioaccessible heavy metal and Pb was the lowest. The order was same in the case of both urban dust and agricultural soil samples.

Previous study reported lower gastric bioaccessibility of Pb in agricultural soil, which was attributed to higher organic matter content of the soil (Cai et al., 2016). The maximum percentage bioaccessibility fraction during the gastric phase of some heavy metals such as Cu (114.5%) and As (131.69%) in urban dust and Cu (108.63) in soil are in excess of 100%, whereas Cd (95.12%) and Pb (87.94%) in urban dust were close to 100%. This could be as a result of using a lower pH of 1.55. Differences in gastric pH and sample matrix size fraction could lead to differences in the gastric percentage bioaccessibility fraction results by affecting the solubilization of the elements.

For instance, gastric bioaccessibility fraction of Pb was discovered to be between 0.85 to 60% using pH of 2.5 in soil fraction of 250 μm diameter using Physiologically based extraction test (Li et al., 2015), while 60 to 100% gastric percentage bioaccessibility of Cu and Pb were discovered in dust using pepsin (Turner & Simmonds, 2006). Similarly, Bi et al. (2015) noted a maximum gastric % BAF of 76% in urban dust of < 250 μm diameter using physiologically based extraction test with gastric pH of 1.5. Therefore, pH, sample fraction size, and the gastric juice are important factors contributing to the dissolution of heavy metal contaminants during gastric bioaccessibility.

The Pearson correlation analysis conducted on the total and gastric bioaccessibility data in urban dust and agricultural soil shows that the % gastric BAF was negatively correlated with the total heavy metal content (Table 4.15). For example, in urban dust Cu total and % BAF ($r = -0.290$, $p < 0.05$), Pb total and % BAF ($r = -0.234$), As total and % BAF ($r = -0.390$, $p < 0.0$), Cr total and % BAF ($r = -0.670$, $p < 0.01$), and Cd total with % BAF ($r = -0.681$, $p < 0.01$), whereas, the correlation in soil it is Cu total with % BAF ($r = -0.766$, $p < 0.01$), Pb total with % BAF ($r = -0.437$), As total and % BAF ($r = -0.592$, $p < 0.01$), Cr total and bioaccessible ($r = -0.731$, $p < 0.01$) and then Cd total with bioaccessible ($r = -0.872$, $p < 0.01$). This association between the total heavy metal and bioaccessible fraction of the heavy metals in this study is in agreement with the previous findings (Liu et al., 2016). This suggests that the total heavy metal is not a factor controlling the % bioaccessibility fraction of metal contaminants in urban dust and agricultural soil (Turner & Ip, 2007).

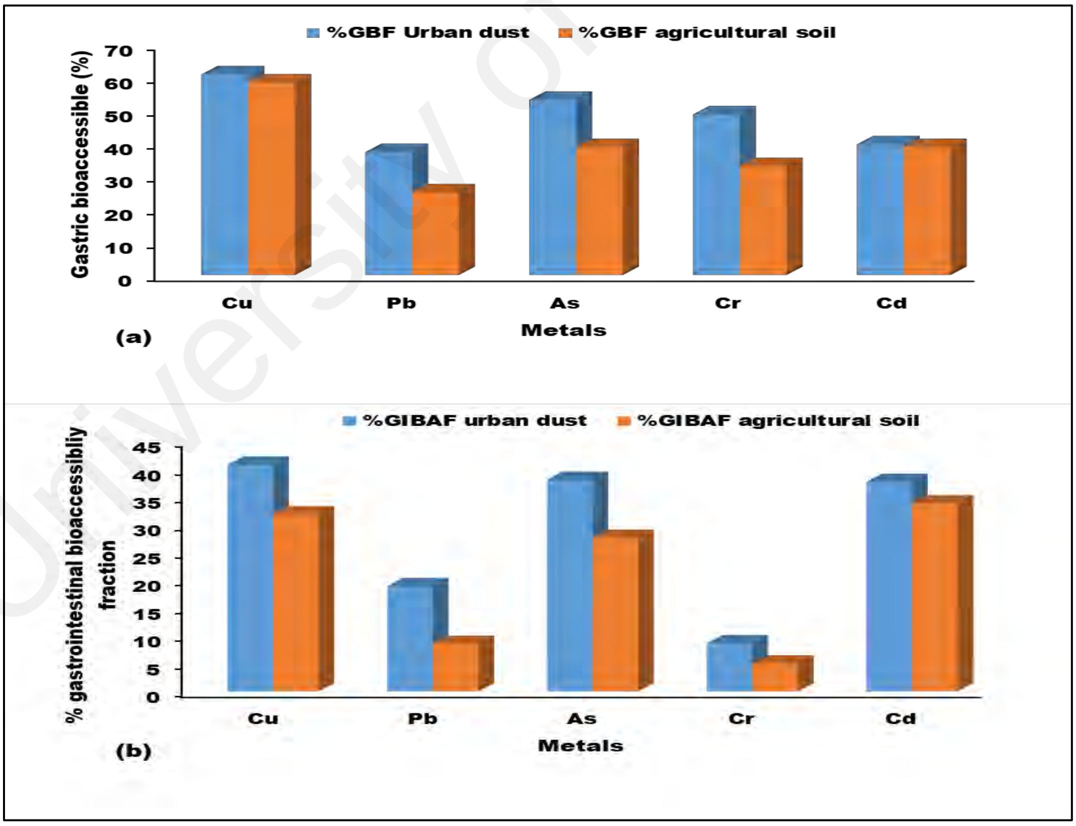


Figure 4.7: Differences in % bioaccessibility of heavy metals in soil and dust of (a) Gastric phase bioaccessibility fraction in agricultural soils and urban dusts, (b) Gastrointestinal phase bioaccessibility fraction in agricultural soils and urban dusts.

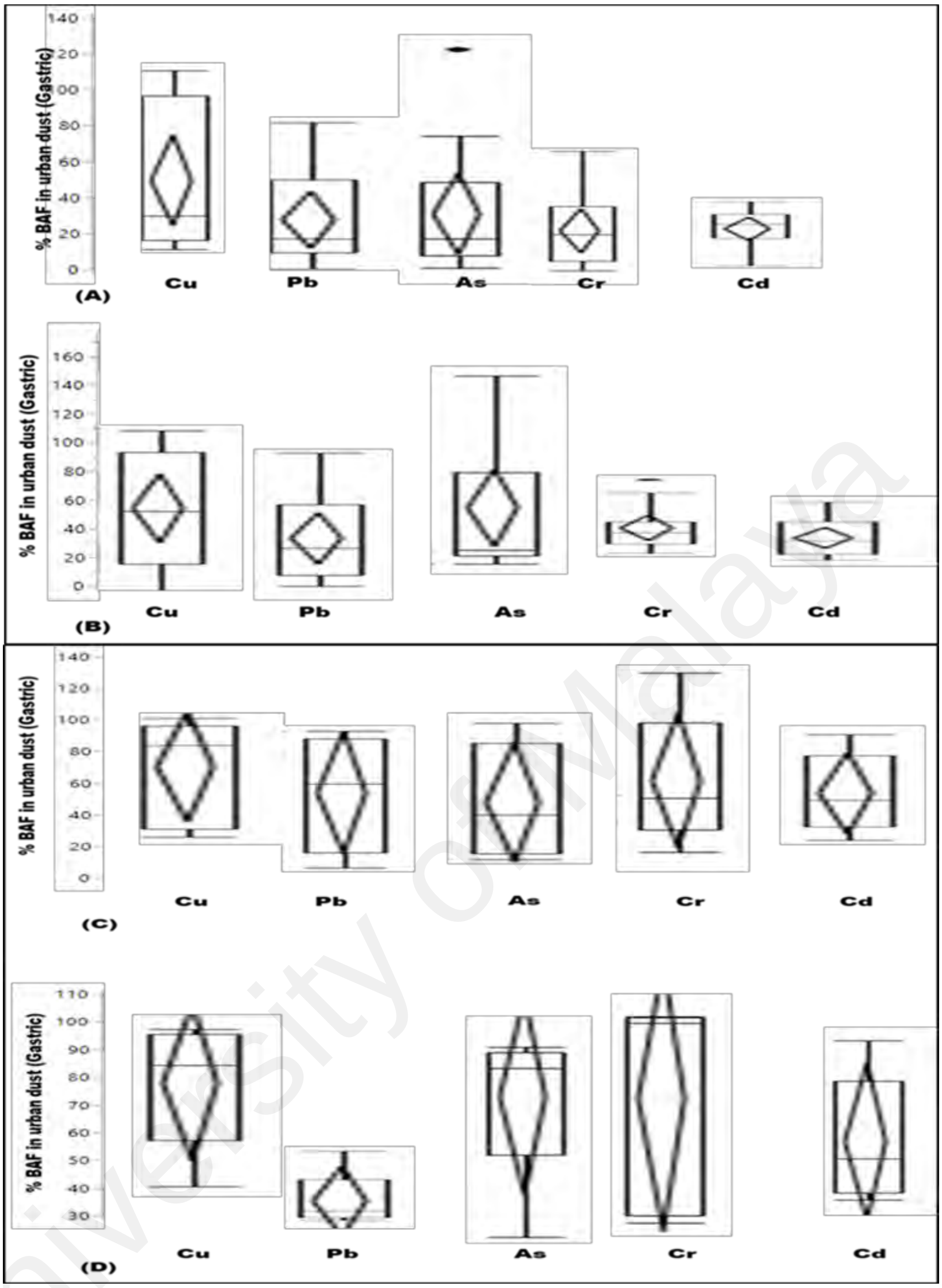


Figure 4.8: Box plots for heavy metals in urban dust of gastric phase (A) Traffic sites (B) industrial sites (C)Residential sites (D) Commercial sites revealing: median, mean, box borders (25th and 75th) percentiles and whiskers (2.5th and 90th) percentile, % BAF = percentage bioaccessibility fraction.

4.4.5 Bioaccessibility of Heavy Metals in Agricultural Soil and Urban Dust During Gastrointestinal Extraction

The percentage gastrointestinal bioaccessibility fraction (% GIBAF) of heavy metals in stage II, i.e., the gastrointestinal phase were identified to be lower when compared with those in the stomach for both agricultural soil and urban dust (Figure 4.7). For instance in urban dust, % BAF of Cu in the intestinal phase ranges between 3.57 to 73.46% with an average of 40.92%, Pb ranges between 4.44 to 44.61% with a mean of 18.94%, As was between 13.38 to 61.81% with an average of 38.06%, Cr rages between 2.62 to 18.28% with a mean of 8.67%, and Cd was between 7.90 to 86.47% averaging 37.69%, whereas, in agricultural soil 4.84 – 121.41 was the range for Cu averaging 31.88%, 0.32 – 22.03% for Pb with a mean of 8.55%, 7.83 – 60.83% for As with an average of 27.61%, 1.69 – 14.42% for Cr with a mean of 5.04%, and Cd ranges between 8.06 – 67.24% averaging 33.82%.

It is believed that the differences in the bioaccessibility fraction of gastric and gastrointestinal phases could be because of the chemical forms that bound them in the matrices (Elom et al., 2014b). The significant reduction in the % BAF of the heavy metals in agricultural soil and urban dust during the intestinal phase when compared to gastric phase could be mainly attributed to the increase in pH from 1.55 in the gastric phase to 7.0 in the intestinal phase. As a result, precipitation and sorption of heavy metals to mineral such as Fe leading to surface complexation in the intestinal tract (Li et al. 2015; 2016). In addition, at a higher intestinal pH of the urban dust and agricultural soil matrices and oxides of minerals might absorbed these heavy metal contaminants during the intestinal extraction thus, reducing the % fraction of the heavy metals (Bi et al., 2015; li et al., 2014; Mercer & Tobiason, 2008).

This implies that in a higher intestinal pH and an environment known to be rich in carbonate, toxic heavy metals may be stabilized in solution by complexation processes and by re-adsorption on the remaining soil particles and or by precipitation as relatively insoluble compounds. For instance Cd in *in vitro* bioaccessibility of agricultural soil during the gastro intestinal phase was found to be lower than that in the gastric phase, and this happen as a result of co-precipitation of Cd with Fe or absorbed onto Fe oxide to form ferrihydrite that has high affinity for Cd in a neutral pH (Li et al., 2016). On the other hand, As in an acidic pH of 1.55 was adsorbed onto Fe oxide in the stomach phase and / or the agricultural soil solid matrix absorbed the soluble As in the higher intestinal pH, as such reducing the bioaccessibility of As in the intestinal phase (Li et al., 2015).

The findings in this research are therefore, in agreement with previous findings (Bi et al., 2015; Juhasz et al., 2011; Li et al., 2016) that discovered higher bioaccessibility values of some heavy metals in gastric phase than intestinal compartments that was majorly attributed to change in pH. Similarly, the lower gastrointestinal bioaccessibility values were discovered by the studies involving animals known as *in vivo* study which was conducted to validate the physiologically based extraction test (Ruby et al., 1996). The maximum percentage bioaccessibility fraction during the intestinal extraction of Cu in agricultural soil was noted to be higher than during stomach extraction.

This could be due to the stabilization of Cu in higher pH of the intestine by complexation with some components such as malate ions from malic acid used in the bioaccessibility gastric solution as a digested sugar substitute, the presence of bile anions such as chemodeozycholate and hyodeoxycholate, and organic ligand available from the agricultural soil matrix. For instance, Cu in solution was noted to be kept at higher intestinal pH, by digestive enzymes used in gastric phase during comparison of methods in physiologically based extraction test (Li et al., 2013). Meaning, the solubility of Cu increases in the intestinal phase and / or remained constant. In spite that the maximum percentage bioaccessibility fraction of Cu in the gastrointestinal extraction is in line with previous literature (Boros et al., 2017), yet the difference was not significant because the average values of Cu during the gastric extraction were higher than in the intestinal extraction.

This implies that selection of a lower pH such as 1.55 in gastric phase had significant influence on Cu bioaccessibility. Therefore, in short a physiologically based extraction test bioaccessibility assay with lower pH is required for higher mobilization of heavy metals. The general mean and median % BAF during the intestinal extraction for heavy metals in agricultural soil and urban dust were respectively represented in Figure 4.9 and Figure 4.10 in a box plots. The box plots of the intestinal extraction in urban dusts of study locations are represented in Figure 4.11 A-D. The box plots indicates mean, median with the box border between 2^{th} and 75^{th} percentiles and the whiskers between 2.5^{th} and 90^{th} percentiles.

There seems to be variation in the bioaccessibility values in agricultural soil and urban dust. The results expressed that Cd was more bioaccessible in gastrointestinal extraction of agricultural soil followed by Cu, As, Pb and Cr. Cd was reported to be the highest bioaccessible metals (66.00%) and Cr the least (5.72%) in agricultural soil from Zhuzhou (Li, at al., 2013). Similarly, lowest bioaccessibility of Cr less than 10% was reported in urban garden soil that was attributed to soil organic matter and carbonate (Izquierdo, et al., 2015).

Whereas, in urban dust, Cu was more bioaccessible followed by As, Cd, Pb and Cr. This implies that Cu was more bioaccessible and Cr was the least in urban dust. Considering the bioaccessibility variation of heavy metals in the intestine at the various locations, the trend order in traffic areas was Cu > As > Cd > Pb > Cr. In the industrial areas it was Cu > Cd > As > Pb > Cr. This trend order was similar with the residential area. While the trend order at the commercial area was As > Cd > Cu > Pb > Cr. This shows that while Cu was more bioaccessible at all the locations except commercial area. Cr was the least bioaccessible at all the locations. As was more bioaccessible at commercial area. Cu in urban dust could be attributed to traffic and industrial activities (Ali et al., 2017), As can be associated to its use as a main ingredient in the manufacture of chemicals such as fungicides, herbicides and wood preservatives (Ratnaike, 2003). The results of this study when compared with others (Boros et al., 2017; Yuswir et al., 2015) who employed the use of PBET for oral bioaccessibility in soil and dust, revealed that the values in this study are higher than those reported, probably due to lower pH and smaller sample particle sizes.

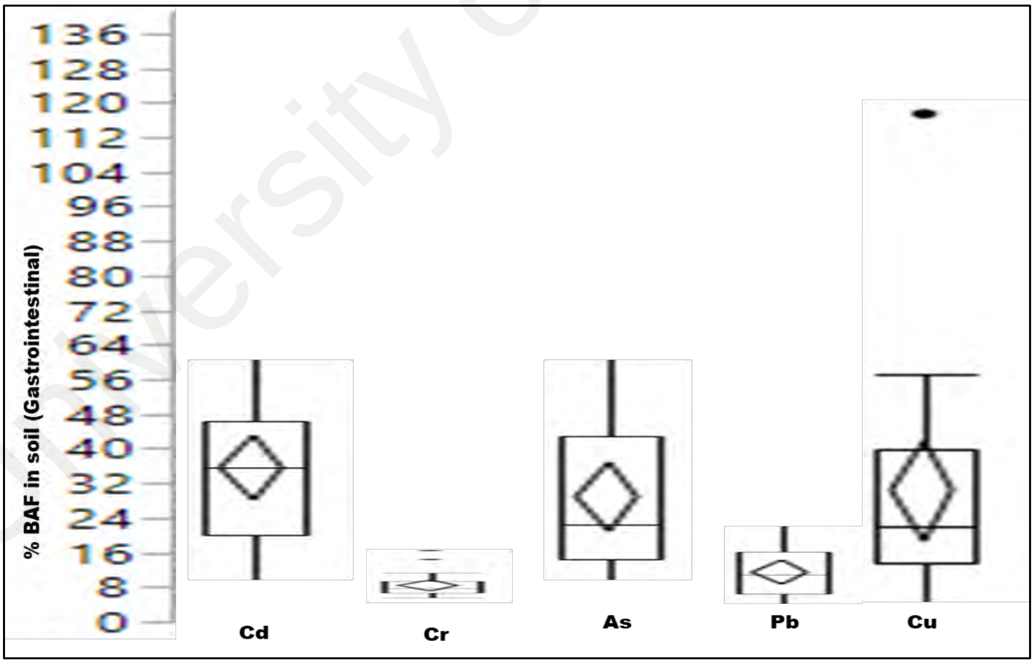


Figure 4.9 Box plot of heavy metals in agricultural soils of gastrointestinal phase indicating median, mean, box border (25th and 75th percentile and whiskers (2.5th and 90th) percentile, % BAF = percentage bioaccessibility fraction.

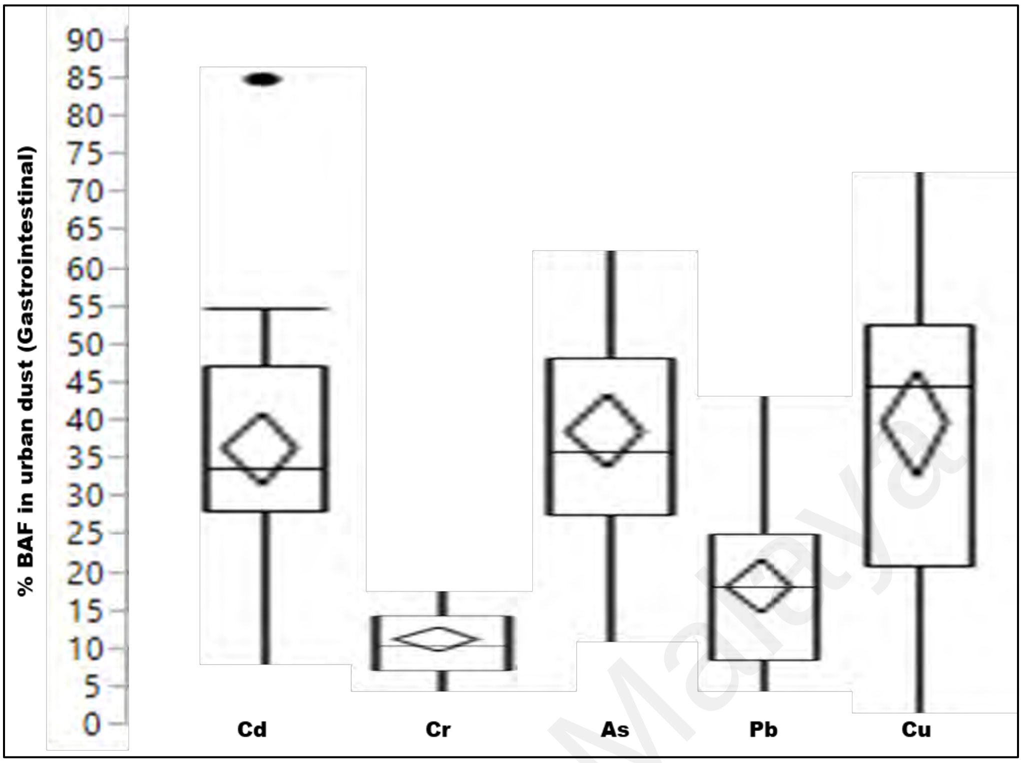


Figure 4.10 Box plot of general heavy metals in urban dusts of gastrointestinal phase indicating median, mean, box borders (25th and 75th) percentiles and whiskers (2.5th and 90th) percentile, % BAF = percentage bioaccessibility fraction.

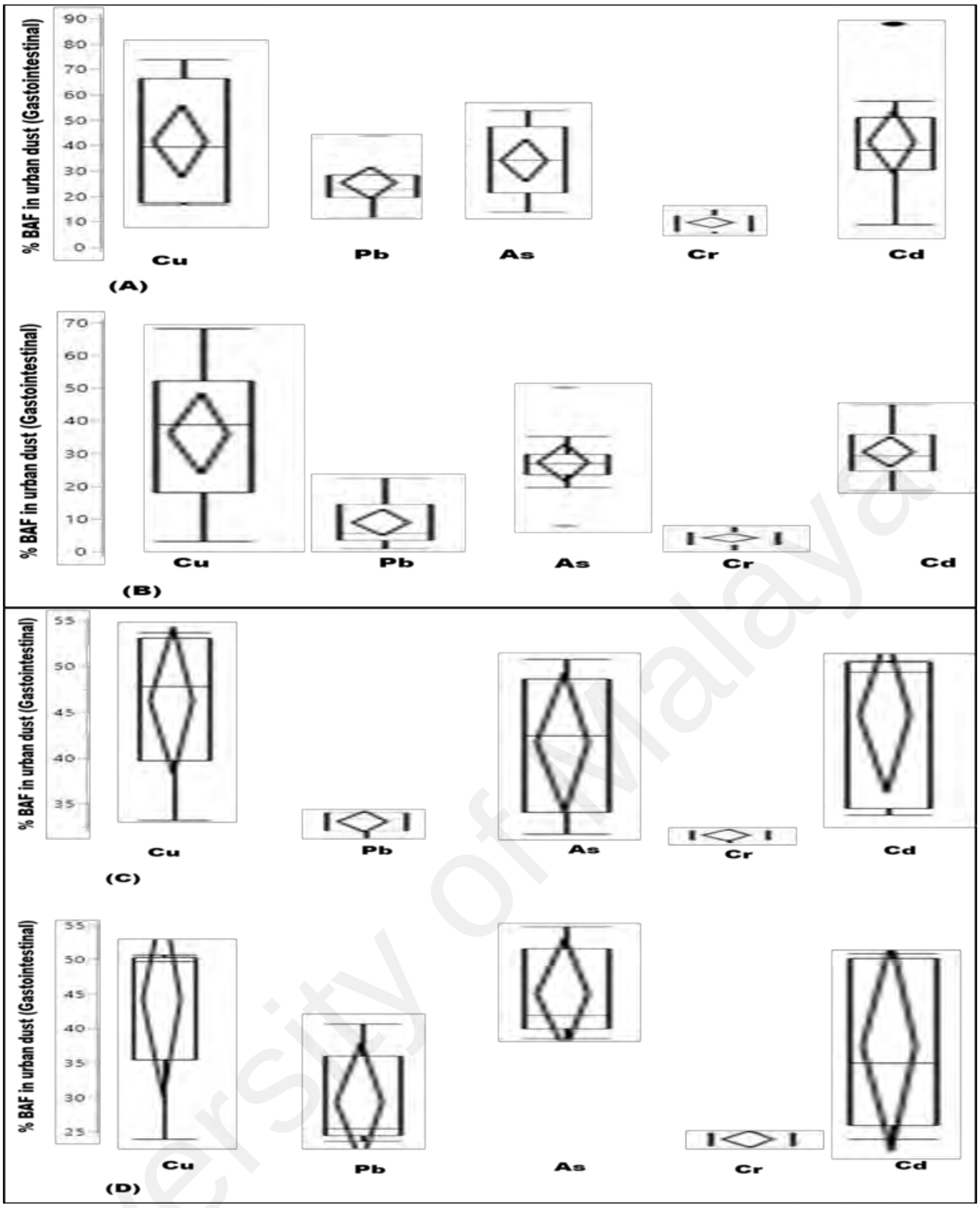


Figure 4.11: Box plots of heavy metals in urban dust of gastrointestinal phase at (A) Traffic sites (B) Industrial sites (C) Residential sites and (D) Commercial sites indicating: median, mean, box borders (25th and 75th) percentiles and whiskers (2.5th and 90th) percentile, % BAF = percentage bioaccessibility fraction.

Toxic heavy metals urban dusts originating from anthropogenic activities were discovered to solubilize in the gastrointestinal environment, as such could be bioaccessible (Ljung et al., 2007). Considering the variations noticed between the total heavy metal content, bioavailability concentrations and the bioaccessibility percentage, Pearson correlation analysis was employed on the data sets. The result of the correlation analysis conducted between total heavy metal, gastrointestinal bioavailable concentrations and % bioaccessibility of heavy metals in urban dust is shown in Table 4.16. This is done in order to investigate the associations of heavy metals as a result of differences discovered in the total content, bioavailability and % bioaccessibility in urban dust of this study.

The result advocates that in the bioavailable fraction extract, there is a better association in heavy metals in the intestinal phase (between gastrointestinal fraction and Total heavy metal) with r values ranging between 0.26 to 0.81 depending on element, whereas, the correlation between the gastrointestinal bioavailable fraction extract and total heavy metal in agricultural soil gave r values ranging from 0.27 to 0.79. The significant correlation between the gastrointestinal bioavailability of urban dust indicates that the total heavy metal content had more effect on the bioavailability fraction of heavy metals in the intestinal phase.

Meaning that the increase in total metal content would increase the bioavailability of the metals in the gastrointestinal tract. Similarly, same trend followed with % bioaccessibility fractions, but all are lower than the bioavailability fraction. The association between % gastrointestinal bioaccessibility fraction and total heavy metal show r values ranging between -0.43 to -0.68, while the correlation between gastrointestinal % bioaccessibility and total heavy metal in agricultural soil shows r value ranging between -0.14 to -0.68. This finding is in agreement with Liu et al. (2016); Turner & IP. (2007) who reported significant negative correlation between total metal concentration and % bioaccessibility fraction in urban soil and dust. Generally there was a better correlation in the bioavailability fractions than in the % bioaccessibility fractions. This significant variation in correlation of total heavy metal with bioavailability and %

bioaccessibility fractions suggests that total heavy metal content had significant influence on the bioavailability fraction then the % bioaccessibility fraction which could possibly be due to differences in the units (mg/kg for bioavailability fraction and % for bioaccessibility fraction).

Previous studies reported significant correlation between bioavailability and total heavy metal content, and that it could be as a result of decreasing sorption capacity at higher heavy metal contaminants levels in heavy metals enriched soil/dust (Das et al., 2013). Nevertheless, the significant correlations among heavy metals fraction extract, heavy metal % bioaccessibility fractions and total heavy metals in the intestinal phase are important in revealing risks associated to ingestion exposure route. Despite the interactions of metals between total, bioavailable and % bioaccessibility in the intestine, it is clear that the only proportion of the total metal content is available for absorption in the intestine as determined against the total heavy metal content.

Table 4.16: Correlation matrix of heavy metals in agricultural soil / urban dusts of different stages.

Bioavailability Fraction (mg/kg)			r values		
Metals	**Cu**	**Pb**	**As**	**Cr**	**Cd**
G I&T in Soil	0.59**	0.27*	0.57**	0.32*	0.79**
GI & T in Dust	0.75**	0.43*	0.81**	0.72**	0.26*
%BAF					
GI & T in Soil	-0.14	-0.33*	-0.63*	-0.68**	-0.26*
GI & T in Dust	-0.44*	-0.50**	-0.68**	-0.43*	-0.59**

*Significant at $p < 0.05$; **Significant at $p < 0.01$, BAF = bioaccessibility fraction, G = gastric, GI = gastrointestinal, T = total metal, r = correlation coefficient.

4.4.6 Correlation of pH, Organic Matter Content and Bioaccessibility of Heavy Metals in Agricultural Soil and Urban Dust of Gastric and Gastrointestinal Tract

Pearson correlation analysis was conducted for agricultural soil and urban dust bioaccessibility and the soil and dust physicochemical properties. Physicochemical properties such as soil/dust pH and OM are essential variables controlling the bioaccessibility of heavy metals in soil/dusts. The adsorption of heavy metal contaminants is influenced by the surface charge of soil/dust particles. Previous researchers established that bioaccessibility can be influenced by soil/dust properties and shown that the relationship between the soil/dust properties and bioaccessibility may be site specific (Das et al., 2013; Xia et al., 2016). The result in this study shows that soil pH and organic matter had effect on the *in vitro* bioaccessibility of heavy metals in the intestinal and gastric phase (Table 4.17).

Cu and Pb in the gastrointestinal phase had significant positive ($r = 0.42$ and 0.34) correlation with soil pH and negative correlation with soil OM, respectively ($r = -0.45–0.33$), $p < 0.01$. Cr had a significant negative correlation with soil pH ($r = -0.31$), whereas Cr and Cd had significant positive and negative correlation, respectively, with soil OM ($r = 0.20$ and -0.20), $p < 0.05$. Both the soil pH and OM had little effect on As bioaccessibility in intestinal phase ($r = -0.08$ and -0.15), respectively. The negative correlation between Cu, Pb and Cd bioaccessibility with soil organic matter indicates that decrease in soil organic matter would increase the bioavailability proportion of these metals in the gastrointestinal phase. While Cr bioaccessibility increases with decrease in soil pH.

This finding was consistent with (Liu et al., 2016) who also discovered no significant correlation between soil pH and OM with As bioaccessibility during intestinal phase. Poggio et al. (2009) reported the significant correlation between soil pH and Cu and Pb % bioaccessibility in the gastrointestinal phase. Note: detailed discussion on the effects of pH and OM on the bioaccessibility of toxic heavy metals in soil has been discussed in section 2.2 of chapter 2.

Table 4.17 Correlation coefficients (r-Pearson) obtained between soil/dust pH, organic matter content, and gastrointestinal bioaccessibility and bioavailability fractions.

Correlation	Cu	Pb	As	Cr	Cd
% GIBAF & pH in dust	0.03	-0.09	0.24	0.01	-0.40
% GIBAF & OM in dust	-0.13	-0.30	0.01	-0.30	-0.06
% GIBAF & pH in soil	0.42	0.34	-0.08	-0.31	0.08
% GIBAF & OM in soil	-0.45	-0.33	-0.15	0.20	0.20
Bioavailable concentration (mg/kg)					
GIBAF & pH in dust	0.17	0.18	0.03	0.40	0.05
GIBAF & OM in dust	0.25	0.15	0.08	0.14	0.17
GIBAF & pH in soil	0.37	0.26	-0.28	0.16	0.31
GIBAF & OM in soil	-0.52	-0.28	0.17	-0.27	-0.54
Gastric stage					
% GBAF & pH in dust	0.12	-0.23	0.21	-0.15	-0.49
% GBAF & OM in dust	-0.18	-0.19	0.01	-0.07	-0.24
% GBAF & pH in soil	-0.25	-0.02	-0.14	-0.24	-0.32
% GBAF & OM in soil	0.31	0.02	-0.25	0.18	0.52
Bioavailable concentration (mg/kg)					
GBAF & pH in dust	0.27	0.07	0.17	0.41	-0.35
GBAF & OM in dust	0.17	0.17	0.22	0.31	0.10
GBAF & pH in soil	-0.03	-0.10	-0.13	0.26	0.27
GBAF & OM in soil	-0.14	0.15	0.04	-0.24	-0.29

% GIBAF = percentage gastrointestinal bioaccessibility fraction, GIBAF = gastrointestinal bioavailability fraction, % GBAF = percentage gastric bioaccessibility fraction, GBAF = gastric bioavailability fraction, OM = organic matter content.

On the other hand, Pearson correlation analysis conducted in this study revealed that urban dust pH has significant effect ($r = -0.40$, $p < 0.01$) and ($r = 0.24$, $p < 0.05$) on Cd and As % gastrointestinal bioaccessibility, respectively. Meaning that the bioaccessibility of Cd in the gastrointestinal tract would increase as the pH of the urban dust decreases.

Likewise, organic matter of urban dust had significant effect on the % gastrointestinal bioaccessibility of Pb and Cr ($r = -0.30$), $p < 0.01$, whereas only little impact of organic matter was observed in Cu, As and Cd (Table 4.17). This indicates that decrease in organic matter of urban dust would increase the bioaccessibility of Pb and Cr in the gastrointestinal tract. In addition, Cu, Pb and Cr shows significant correlation with dust pH ($r = 0.20$, 0.20 and 0.40, respectively) in the gastrointestinal bioavailability extract, whereas, Cu, Pb, and Cd ($r = 0.37$, 0.26, and 0.31) show significant correlation with soil pH. The dust OM correlates significantly with Pb ($r = 0.30$), while soil OM correlate negatively with Cu and Cd ($r = -0.52$ and -0.54, $p < 0.01$) and Pb and Cr ($r = -0.30$, $p < 0.05$).

4.4.7 Association Between the Bioavailable Metals in the Gastrointestinal Phase

Multiple metal contaminants could possibly be ingested and during the absorption of these metals in the intestine there may be a synergistic and or antagonistic association. Thus, the bioaccessibility of the metals may increase or decrease (Xia et al., 2016). The result as shown in Table (4.18) revealed that in urban dust there is a positive link between As-Pb (0.45), Cr-Pb (0.58), Cd-Pb (0.69), Cr-As (0.61), Cd-As (0.57) and Cd-Cr (0.72) at the traffic site. At the industrial site Pb-Cu (0.82), Cr-Cu (0.48), As-Pb (0.46), C-Pb 90.41), Cd-As (0.54) and Cd-Cr (0.74). There was a positive interaction between Cr-Pb (0.94), As-Pb (0.48), Cd-Pb (0.59) and Cd-As (0.87), while negative correlation existed between Cr-Cu (-0.60) all at the residential site. As-Cu (0.55), As-Pb (0.53), Cr-Pb (0.69), Cr-As (0.95), Cd-Cu (0.50), Cd-As (0.66) and Cd-Cr (0.72) exhibited positive interaction at the commercial site.

Whereas, in the agricultural soil there was a positive association between Pb-Cu (0.84), Cr-Cu (0.76), Cd-Cu (0.74), Cr-Pb (0.76), Cd-Pb (0.73 and Cd-Cr (0.60). The positive interaction between metals indicates that an increase in one metal concentration would result to an increase in the concentration of the other metal. While the negative association suggests that an increase in one metal concentration would result to a decrease in the other metal and vice versa. It has been established that in the digestive system toxicity effects of metals results from their association with each other. This occurred during the absorption and distribution of these metals in the organisms (Bzorska & Moniuszko-Jakoniuk, 2001). Similarly, Obiakor et al. (2010) reported that cooperate action of metals could result to genotoxicity in organisms.

Table 4.18 Association between bioavailable metals in the gastrointestinal tract.

Traffic site	Cu GI	Pb GI	As GI	Cr GI	Cd GI
Cu GI	1				
Pb GI	0.21	1			
As GI	0.07	0.45*	1		
Cr GI	-0.17	0.58**	0.61**	1	
Cd GI	0.19	0.69**	0.57**	0.72**	1
Industrial site					
Cu GI	1				
Pb GI	0.82**	1			
As GI	0.11	0.46*	1		
Cr GI	0.48*	0.39	0.36	1	
Cd GI	0.29	0.41*	0.54**	0.74**	1
Residential site					
Cu GI	1				
Pb GI	-0.36	1			
As GI	0.27	0.48*	1		
Cr GI	-0.60**	0.94**	0.17	1	
Cd GI	0.23	0.59**	0.87**	0.30	1
Commercial site					
Cu GI	1				
Pb GI	-0.27	1			
As GI	0.55**	0.53**	1		
Cr GI	0.36	0.69**	0.95**	1	
Cd GI	0.50**	0.24	0.66**	0.72**	1
Agricultural soil					
Cu GI	1				
Pb GI	0.84**	1			
As GI	0.05	0.002	1		
Cr GI	0.76**	0.76**	0.02	1	
Cd GI	0.74**	0.73**	-0.04	0.60**	1

GI = gastrointestinal, **significant correlation P ≤ 0.01, * significant correlation p ≤ 0.05

4.5 Health Risk Assessment Based on the Bioavailability Faction of Heavy Metals in Agricultural Soil and Urban Dust

The gastric and gastrointestinal concentration extracts known as the bioavailability fractions were employed to assess the exposure to metals known as average daily intake. While the gastrointestinal proportion was used for the accurate estimation of health risks associated with ingestion of agricultural soils and urban dusts. This is because the gastrointestinal phase bioavailability of heavy metals is useful to measure the exact heavy metal contaminants that were absorbed in the gastrointestinal compartment of humans. As little or nothing is absorbed in the gastric (stomach) compartment. The metals that are solubilized could be absorbed and be transported across the intestinal wall into the circulatory system and be distributed to the different parts of the body were they can start exerting their toxicity.

In this study, in order to have more efficient result, the bioavailable data was subjected to simulation analysis using Monte Carlo Similar AR. Prior to the simulation analysis, the distribution of the data was conducted using JMP Pro 12 statistical software and the heavy metal contaminants were fitted with appropriate distributions and evaluated for goodness of fit through Kolmogorov's D and Shapiro-Wilk W Test, as detailed in section 4.3 of this study. In this study, the body weight of Malaysian locals was used as one of the parameters in Monte Carlo. This shows a new technique of health risk assessment in that local's body weight was used in chemometrics on the bioavailability data when compared with most of the health risks assessment employed using the general USEPA body weight of both children and adults as one of the parameters on ordinary calculations (Praveena et al., 2015; Yuswir et al., 2015) which may not possibly give the exact results of the situation on ground that will be of topmost benefit to the local population.

4.5.1 Estimation of Average Daily Intake of Heavy Metals from Agricultural Soil and Urban Dust

To assess the potential human health risk associated with exposure to agricultural soil and urban dust, which reflect the amount of heavy metals fraction in the sample matrices that an individual adult or child could ingest on exposure, in order to reach the estimated permissible daily intake. Both the gastric and gastrointestinal bioavailability content was treated for Monte Carlo (MC) simulation analysis so as to calculate the oral average daily dose (ADD). The agricultural soil and urban dust ingestion rate employed for children were 50 and 60 mg/day, respectively, whereas 30 and 40 mg/day of agricultural soil and urban dust for adults, respectively (USEPA, 2008) as shown in Table 4.19.

Children ingest more soils and dusts due to their general behavior of hand/fingers-to-mouth or object-to-mouth as well as their ability to play about for long. Therefore, the amount of soil and dust ingested could be equals to the exposure frequency. Because of the differences in the body weight, age and activity, children and adults are divided and the various contribution of soil and dust exposure was calculated separately. The result shows that the ADD for children was higher when compared to that of adults in both dust (Figure 4.12) and soil (Figure 4.13).

This could be as a result of children having higher ingestion rate than that of adults. It was observed that the ADD for all the study heavy metals with the exception of Cd at 90^{th} and 95^{th} were lower when compared with the minimal risk levels (MRLs) for oral exposure established by the Agency for Toxic Substances and Disease Registry (ATSDR, 2011). According to ATSDR, MRLs is defined as an estimate of daily human exposure to any chemical substance that is likely to be without an appreciable risk or adverse effects (carcinogenic or non-carcinogenic) over specified exposure duration. The MRLs for oral exposure of poisonous elements in (mg/kg/day) are: As = 0.0003; Cd = 0.00003; Cr = 0.0009; Cu = 0.01; Pb = 0.0003 (ATSDR, 2011).

The oral contributions of metals in gastric phase of soil for all metals were found to be lower at the 50^{th}, 75^{th}, 90^{th} and 95^{th} percentiles (Pb = 2.60×10^{-6}, 4.00×10^{-6}, 5.40×10^{-6}, 7.60×10^{-6}), As = (2.40×10^{-6}, 3.50×10^{-6}, 4.90×10^{-6}, 6.00×10^{-6}), Cr = (2.90×10^{-6}, 3.60×10^{-6}, 4.60×10^{-6}, 5.40×10^{-6}) as compared to the minimal risk level except for Cd (3.90×10^{-6}, 9.10×10^{-5}, 9.30×10^{-4} and 3.10×10^{-3}) which was higher. This trend was same for adults for soil and same trend for children and adults for urban dust. This high oral contribution of Cd might be as a result of its normal and Weibull fitted distribution in the dust and soil bioaccessibility contents, respectively.

In general, the soil and dust ingestion contribution were higher in the gastric fraction than in the gastrointestinal fraction (Figure 4.12 and Figure 4.13). This could possibly be due to high solubilization of the study heavy metals that occurred during the gastric extraction as a result of lower pH. However, the contribution of dust and soil ingestion for children was noted to be higher than the contribution for adults (Figure 4.12 and Figure 4.13) for all study heavy metals. This could be as a result of lower body weight of children as compared to that of adults. This finding suggests that ingestion of urban dust and agricultural soil could account for channel through which heavy metals can likely get into human body especially children. Therefore, in this study, estimation of risks involved is imperative.

Table 4. 19: Risk assessment evaluation parameters for oral ingestion of bioaccessibility and total metals in soil/dust.

Symbols	Units	Values for Adult	Values for Child	References
Cx	mg kg^{-1}	Please refer to table S3		This study
BW	Kg	N(62.7, 18.6)	N(32.6, 8.7)	Azmi et al, (2009); Zaini et al, (2005)
ED	years	30	7	This study
EF	days $year^{-1}$	365	365	This study
IRsoil	kg day^{-1}	0.00003	0.00005	USEPA (2008); DEA (2010)
IRdust	kg day^{-1}	0.00004	0.00006	USEPA,(2008)
CF	kg mg^{-1}	$1x10^{-6}$	$1x10^{-6}$	USEPA (2004)
AT Carcinogenic	days	LT×365	LT×365	USDOE (2011
LT	years	74.69	74.69	DOSM (2016)
AT Non-Carcinogenic	days	ED×365	ED×365	Bortey−Sam et al, (2015); USEPA (200

Cx = metal concentration, BW = body weight, ED = exposure duration, EF = exposure frequency, IRsoil = ingestion rate of soil, IRust = ingestion rate of dust, CF = conversion factor, AT= average exposure time, LT = lifetime.

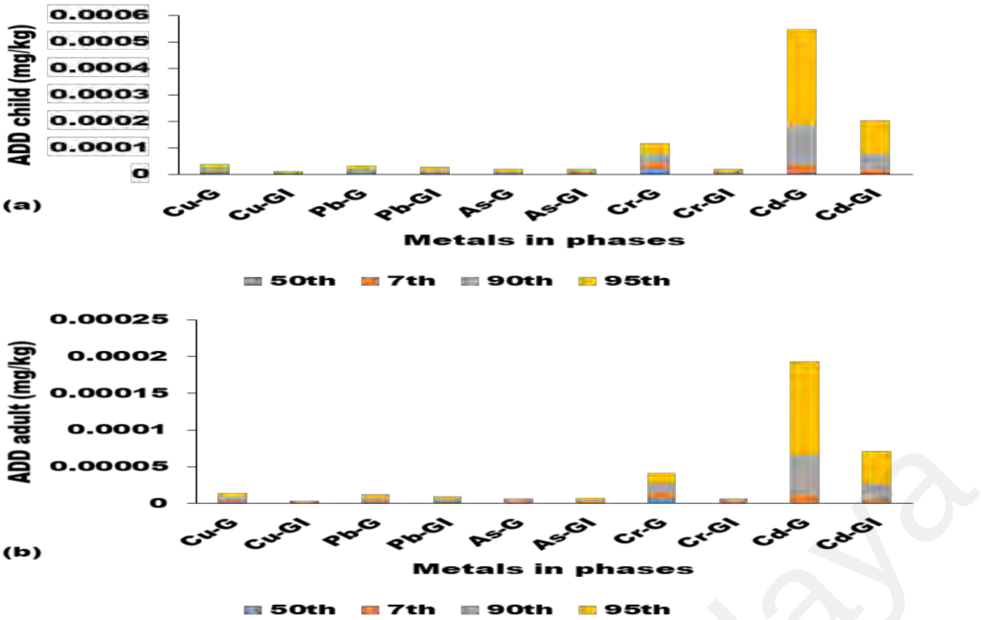


Figure 4.12: Average daily dose for child (a) and adult (b) in gastric (G) and gastrointestinal (GI) phases of urban dust.

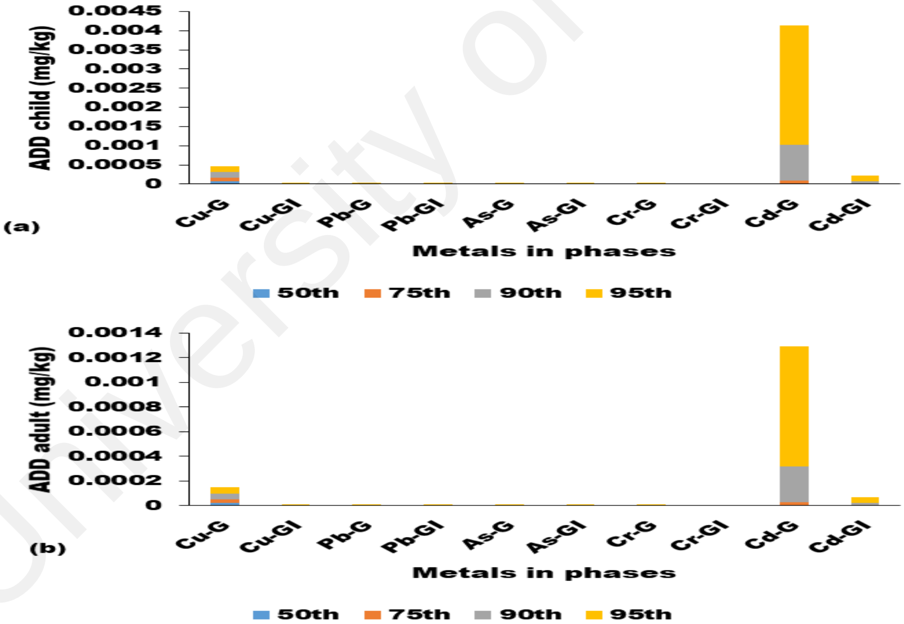


Figure 4.13: Average daily dose for child (a) and adult (b) in gastric (G) and gastrointestinal (GI) phases of agricultural soil.

4.5.2 Health Risk Estimation Based on Oral Bioaccessibility and Total Content of Heavy Metals in Soil/Dust

The hazard quotient (HQ) and the carcinogenic risk (CR) were calculated for the health risk assessment. According to USEPA, (1989) when HQ ≤ 1, there is no possibility of non-carcinogenic health effects, but when HQ ≥ 1, then non-carcinogenic consequences could likely occur. An individual is likely to develop cancer over a lifetime period as a result of exposure to carcinogenic elements, the tolerable value that represent carcinogenic risk is in the range of 1×10^{-6} to 1×10^{-4}. Any value higher than 1×10^{-4} is considered to have effect on human health.

4.5.3 Non-Carcinogenic Risk on Ingestion Exposure

The non-carcinogenic risks of heavy metals to the local adults and children were calculated based on the basis of the hazardous index average daily dose (ADD) obtained through the bioavailable fraction and the reference dose (RfD) values for each study element. Bioavailability is the fraction of heavy metals that is solubilized, reached the intestinal tract and is available to be absorbed into circulatory system. As the intestine plays a significant role in solubilization and absorption of heavy metals, therefore, gastrointestinal bioavailable fraction content of the heavy metals are considered in the risk estimation.

The hazard quotient for oral ingestion of urban dust and agricultural soil at 50th, 75th, 90th and 95th percentiles are shown in Table 4.20. The hazard quotient for both children and adults due to exposure to agricultural soil followed an increasing order Cr < Cu < Pb < As < Cd at 90th and 95th percentiles, while at 50th and 75th percentiles, As has higher quotient. This increasing order was the same for both adult and children. The hazard quotient for children at the 50th, 75th, 90th and 95th percentiles was 6.40×10^{-4}, 8.37×10^{-3}, 5.10×10^{-2}, 1.50×10^{-1} for Cd, 6.20×10^{-3}, 8.87×10^{-3}, 1.24×10^{-2}, 1.51×10^{-2} for

As, 2.98×10^{-4}, 5.50×10^{-4}, 9.56×10^{-4}, 1.35×10^{-3} for Pb, 1.22×10^{-4}, 1.62×10^{-4}, 2.14×10^{-4}, 2.57×10^{-4} for Cu and 9.18×10^{-6}, 3.06×10^{-5}, 9.00×10^{-5}, 1.71×10^{-4} for Cr.

While the hazard quotient for oral ingestion of agricultural soil by adults was 2.03×10^{-4}, 2.64×10^{-3}, 1.79×10^{-2}, 4.78×10^{-2} for Cd, 1.94×10^{-3}, 2.82×10^{-3}, 4.01×10^{-3}, 6.23×10^{-3} for As, 1.46×10^{-4}, 2.11×10^{-4}, 3.01×10^{-4}, 3.76×10^{-4} for Pb, 3.80×10^{-5}, 5.14×10^{-5}, 6.98×10^{-5}, 8.58×10^{-5} for Cu and 2.89×10^{-6}, 9.68×10^{-6}, 2.86×10^{-5}, 5.52×10^{-5} for Cr. From the result it was noted that the quotient for children was identified to exceed that of adults. This could probably be because of the higher ingestion rate of soil and dust for children than adults. Nevertheless, all the study heavy metals at all percentiles displayed HQ values below the permissible limits of 1.

Meaning that both populations may not have possibility for any health risk. The hazard quotient values for Cd at 95th percentile was noted to be 1.50×10^{-1} for children which was higher than adult. This indicates that increase in oral ingestion exposure to agricultural soil by children could lead to accumulation of Cd and eventually may lead to health effects. Adults are unlikely to have non-cancer risk on oral ingestion of soil. This high Cd value in agricultural soil of this study might be as a result of excess application of herbicides, mineral fertilizer and pesticides. Previous study reported high risk of oral ingestion exposure to Cd in agricultural soil (Eqani et al., 2016; Rehman et al., 2018). The result of this study was higher than those reported in the literature (Praveena et al., 2015), this could be as a result of smaller particle size of soil < 125 µm compared to 2 mm mesh.

The non-carcinogenic health risk estimated values for all study heavy metals for both population of children and adults on ingestion exposure to urban dust of different locations are shown in Table 4.20. In all the study locations (traffic, industrial, commerci al and residential), the hazard quotient for ingestion exposure showed no significant health risk for all the study heavy metals, which were below the permissible limits of 1. This implies that both population of children and adults could not possibly pose adverse non-carcinogenic health effects by any element pollutant on oral ingestion exposure to urban dusts at all the study locations.

The hazard quotient for oral ingestion of urban dust from the industrial area was in the ranked order As > Cr > Pb > Cd > Cu. This trend was the same in the case of both populations. The trend in the industrial area was discovered to be same as in the case of commercial area. The trend order was different in the case of traffic area. The order in traffic area was As > Pb > Cd > Cr > Cu whereas, in the residential area, the trend of heavy metals hazard quotient variation was As > Pb > Cr > Cd > Cu. In the case of traffic and residential areas, the trend was almost the same but was different in the residential area in the case of Cd which has a higher exposure in traffic area. In all the locations, the order was same for both adults and children.

Meaning that As has higher quotient value at all locations. The health risk due to oral ingestion of all study heavy metals in urban dust based on the bioavailability fraction was higher in the case of children when compared to that of adults. As was found to have the highest hazard quotient on oral ingestion of urban dust. The hazard quotient values for children exposure were 1.24×10^{-2}, 1.55×10^{-2}, 1.96×10^{-2} and 1.30×10^{-2} for industrial area; 1.24×10^{-2}, 1.55×10^{-2}, 1.96×10^{-2} and 2.33×10^{-2} for traffic area; 1.18×10^{-2}, 1.47×10^{-2}, 1.87×10^{-2} and 2.20×10^{-2} for commercial area and for residential area the values were 5.95×10^{-3}, 9.63×10^{-3}, 1.49×10^{-2} and 1.94×10^{-2} at 50^{th}, 75^{th}, 90^{th} and 95^{th} percentiles, respectively. Whereas, in the case of adults, the hazard quotient value for As was 4.29×10^{-3}, 5.49×10^{-3}, 7.18×10^{-3} and 8.67×10^{-3} for industrial area; 4.28×10^{-3}, 5.49×10^{-3}, 7.18×10^{-3} and 8.69×10^{-3} for traffic area; 4.09×10^{-3}, 5.24×10^{-3},

6.83×10^{-3} and 8.29×10^{-3} for the commercial area; 2.08×10^{-3}, 3.39×10^{-3}, 5.31×10^{-3} and 7.11×10^{-3} for residential areas at the 50th, 75th, 90th and 95th percentiles, respectively.

This predicts that health risk for children due to ingestion of As in dust was higher when compared to adults. The order of the increase in the quotient at the locations followed the order of traffic ≈ industrial > commercial > residential. In the urban dust, As could be associated with human activities such as combustion of coal and fuel, tanning, paints, vehicle emissions, pesticides manufacturing industries and fertilizers (Subhani et al., 2015). The source of As in urban dust of this study could be linked to vehicular emissions, pesticides and fertilizers and wind-blown dust from various sources. Oral Exposure to As particularly by children could cause diseases such as skin pigmentation and infertility (Alamdar et al., 2016). The HQ results for As on children in urban dust of this study were noted to be lower than those reported by Alamdar et al. (2016). This is expected because this study used the gastrointestinal bioavailable fraction of urban dust that is the precise fraction of heavy metals ready for absorption.

The hazard quotient on exposure to heavy metals in soil/dust accounting without bioaccessibility was shown to be higher with exception of Cd in agricultural soil when compared with those accounting with bioaccessibility. This happened for both children and adult population (Table 4.21) with the quotient of urban dust higher than that of agricultural soil. This could probably be as a result of concentration of total heavy metals in the soil/dust samples. The higher HQ of Cd in soil accounting with bioaccessibility when compared with HQ of Cd in soil accounting without bioaccessibility could be due to the differences in the fitted distribution of Cd as shown in Table 4.22 & Table 4.23. The quotient on exposure to HMs in total agricultural soil accounting by both children and adults followed the order of As > Pd > Cd > Cr > Cu at 50th and 75th percentiles, but at 90th and 95th percentiles, the order was As > Cd > Pb > Cr > Cu.

Whereas, the HQ for adult exposure to HMs in total soil at all percentiles followed As > Cr > Pb > Cd > Cu. On the other hand, the results of non-carcinogenic risk assessment of heavy metals in urban dust accounting without bioaccessibility at industrial, traffic, commercial and residential locations were also estimated. The hazard quotient for all the study heavy metals based on oral exposure showed that there was no health risk for both adult and children at all study locations. Which means the hazard quotient values in all cases were less than the permissible limits of 1.

The order of the heavy metals exposure in locations followed industrial > traffic > commercial > residential. In the industrial, commercial and residential areas, the quotient values of heavy metals for both children and adults at all percentiles were As > Pb > Cr > Cd > Cu, but at the traffic location the heavy metal quotient followed the order As > Cd > Cr > Pb > Cu. This predicts that the health risk of heavy metals accounting without bioaccessibility was also associated with oral ingestion of As in urban dust and the lowest was Cu. This trend was same at all the sampling locations and for both populations. This indicates that As, Pb and Cd are associated with anthropogenic activities (Ali et al., 2017), though their non-cancer risks were below the permissible limits at all study locations.

Generally, the health risk estimation result showed that the hazard quotient based on the oral ingestion exposure to heavy metals with bioavailability in urban soil, Cd ranked high, but in the case of urban dust, As ranked high. Whereas, the health risk based on oral ingestion of both agricultural soil and urban dust accounting without bioaccessibility showed that As ranked high. However, the risk associated with oral ingestion of soil accounting with and without bioaccessibility was discovered to be lower as compared to that of urban dust for both populations. This could be due to the high distribution of heavy metals in urban dust when compared to agricultural soil.

Table 4.20: Non-carcinogenic risks for oral ingestion of urban dust and agricultural soil for child and adult based on bioavailability fraction.

Child Hazard quotient						Adult Hazard quotient				
TF	**Cu**	**Pb**	**As**	**Cr**	**Cd**	**Cu**	**Pb**	**As**	**Cr**	**Cd**
50th	1.84×10^{-4}	1.30×10^{-3}	1.24×10^{-2}	5.88×10^{-4}	7.53×10^{-4}	6.36×10^{-5}	4.50×10^{-4}	4.28×10^{-3}	2.04×10^{-4}	2.62×10^{-4}
75th	2.28×10^{-4}	1.62×10^{-3}	1.55×10^{-2}	8.19×10^{-4}	9.98×10^{-4}	8.09×10^{-5}	5.73×10^{-4}	5.49×10^{-3}	2.90×10^{-4}	3.52×10^{-4}
90th	2.88×10^{-4}	2.05×10^{-3}	1.97×10^{-2}	1.12×10^{-3}	1.29×10^{-3}	1.06×10^{-4}	7.50×10^{-4}	7.18×10^{-3}	4.08×10^{-4}	4.69×10^{-4}
95th	3.38×10^{-4}	2.40×10^{-3}	2.33×10^{-2}	1.38×10^{-3}	1.53×10^{-3}	1.28×10^{-4}	9.13×10^{-4}	8.69×10^{-3}	5.05×10^{-4}	5.73×10^{-4}
IND										
50th	1.88×10^{-4}	1.19×10^{-3}	1.24×10^{-2}	1.21×10^{-3}	5.70×10^{-4}	6.49×10^{-5}	4.14×10^{-4}	4.29×10^{-3}	4.20×10^{-4}	1.98×10^{-4}
75th	2.38×10^{-4}	1.53×10^{-3}	1.55×10^{-2}	1.67×10^{-3}	7.58×10^{-4}	8.48×10^{-5}	5.42×10^{-4}	5.49×10^{-3}	5.84×10^{-4}	2.53×10^{-4}
90th	3.04×10^{-4}	1.97×10^{-3}	1.96×10^{-2}	2.21×10^{-3}	9.05×10^{-4}	1.11×10^{-4}	7.17×10^{-4}	7.18×10^{-3}	7.96×10^{-4}	3.29×10^{-4}
95th	3.60×10^{-4}	2.32×10^{-3}	2.30×10^{-2}	2.65×10^{-3}	1.06×10^{-3}	1.35×10^{-4}	8.71×10^{-4}	8.67×10^{-3}	9.79×10^{-4}	3.99×10^{-4}
COM										
50th	9.45×10^{-5}	7.43×10^{-4}	1.18×10^{-2}	8.82×10^{-4}	4.60×10^{-4}	3.29×10^{-5}	2.58×10^{-4}	4.09×10^{-3}	3.06×10^{-4}	1.59×10^{-4}
75th	1.28×10^{-4}	1.02×10^{-3}	1.47×10^{-2}	1.62×10^{-3}	5.74×10^{-4}	4.53×10^{-5}	3.58×10^{-4}	5.24×10^{-3}	5.67×10^{-4}	2.03×10^{-4}
90th	1.72×10^{-4}	1.37×10^{-3}	1.87×10^{-2}	2.57×10^{-3}	7.28×10^{-4}	6.17×10^{-5}	4.96×10^{-4}	6.83×10^{-3}	9.15×10^{-4}	2.66×10^{-4}
95th	2.07×10^{-4}	1.67×10^{-3}	2.20×10^{-2}	3.32×10^{-3}	8.55×10^{-4}	7.61×10^{-5}	6.14×10^{-4}	8.29×10^{-3}	1.19×10^{-3}	3.22×10^{-4}
RSD										
50th	5.46×10^{-5}	7.33×10^{-4}	5.95×10^{-3}	5.09×10^{-4}	3.87×10^{-4}	1.90×10^{-5}	2.55×10^{-4}	2.08×10^{-3}	1.77×10^{-4}	1.34×10^{-4}
75th	9.22×10^{-5}	9.37×10^{-4}	9.63×10^{-3}	7.88×10^{-4}	4.80×10^{-4}	3.23×10^{-5}	3.32×10^{-4}	3.39×10^{-3}	2.77×10^{-4}	1.71×10^{-4}
90th	1.49×10^{-4}	1.20×10^{-3}	1.49×10^{-2}	1.10×10^{-3}	6.06×10^{-4}	5.33×10^{-5}	4.39×10^{-4}	5.34×10^{-3}	3.94×10^{-4}	2.22×10^{-4}
95th	1.99×10^{-4}	1.42×10^{-3}	1.94×10^{-2}	1.34×10^{-3}	7.13×10^{-4}	7.21×10^{-5}	5.36×10^{-4}	7.11×10^{-3}	4.91×10^{-4}	2.69×10^{-4}
soil										
50th	1.22×10^{-4}	2.98×10^{-4}	6.20×10^{-3}	9.18×10^{-6}	6.40×10^{-4}	3.80×10^{-5}	1.46×10^{-4}	1.94×10^{-3}	2.89×10^{-6}	2.03×10^{-4}
75th	1.62×10^{-4}	5.50×10^{-4}	8.87×10^{-3}	3.06×10^{-5}	8.37×10^{-3}	5.14×10^{-5}	2.11×10^{-4}	2.82×10^{-3}	9.68×10^{-6}	2.64×10^{-3}
90th	2.14×10^{-4}	9.56×10^{-4}	1.24×10^{-2}	9.00×10^{-5}	5.51×10^{-2}	6.98×10^{-5}	3.01×10^{-4}	4.01×10^{-3}	2.86×10^{-5}	1.79×10^{-2}
95th	2.57×10^{-4}	1.35×10^{-3}	1.51×10^{-2}	1.71×10^{-4}	1.50×10^{-1}	8.58×10^{-5}	3.76×10^{-4}	6.23×10^{-3}	5.52×10^{-5}	4.78×10^{-2}

TF = traffic, IND = industrial, COM = commercial, RSD = residential.

Table 4.21: Non-carcinogenic risks for oral ingestion of urban dust/soil for child and adult based on total metal concentration.

Child Non-cancer risk (HQ)						**Adult Non-cancer risk (HQ)**				
TF	**Cu**	**Pb**	**As**	**Cr**	**Cd**	**Cu**	**Pb**	**As**	**Cr**	**Cd**
50th	2.31×10^{-4}	1.97×10^{-3}	1.81×10^{-2}	2.14×10^{-3}	2.37×10^{-3}	8.00×10^{-5}	6.83×10^{-4}	6.27×10^{-3}	7.40×10^{-4}	8.21×10^{-4}
75th	2.86×10^{-4}	2.42×10^{-3}	2.30×10^{-2}	2.64×10^{-3}	3.70×10^{-3}	1.02×10^{-4}	8.58×10^{-4}	8.13×10^{-3}	9.37×10^{-4}	1.30×10^{-3}
90th	3.62×10^{-4}	3.03×10^{-3}	2.93×10^{-2}	3.30×10^{-3}	5.17×10^{-3}	1.33×10^{-4}	1.11×10^{-4}	1.07×10^{-2}	1.21×10^{-3}	1.85×10^{-3}
95th	4.27×10^{-4}	3.60×10^{-3}	3.47×10^{-2}	3.90×10^{-3}	6.27×10^{-3}	1.61×10^{-4}	1.34×10^{-4}	1.30×10^{-2}	1.46×10^{-3}	2.30×10^{-3}
IND										
50th	2.42×10^{-4}	2.24×10^{-3}	2.01×10^{-2}	2.08×10^{-3}	1.90×10^{-3}	8.43×10^{-5}	7.80×10^{-4}	6.97×10^{-3}	7.20×10^{-4}	6.57×10^{-4}
75th	3.00×10^{-4}	2.50×10^{-3}	2.50×10^{-2}	2.54×10^{-3}	2.45×10^{-3}	1.06×10^{-4}	9.78×10^{-4}	8.87×10^{-3}	9.03×10^{-4}	8.63×10^{-4}
90th	3.78×10^{-4}	3.45×10^{-3}	3.16×10^{-2}	3.18×10^{-3}	3.13×10^{-3}	1.38×10^{-4}	1.27×10^{-3}	1.15×10^{-2}	1.17×10^{-3}	1.14×10^{-3}
95th	4.46×10^{-4}	4.05×10^{-3}	3.70×10^{-2}	3.73×10^{-3}	3.71×10^{-3}	1.68×10^{-4}	1.53×10^{-3}	1.40×10^{-2}	1.41×10^{-3}	1.39×10^{-3}
CO M										
50th	1.18×10^{-4}	1.61×10^{-3}	8.33×10^{-3}	1.21×10^{-3}	9.60×10^{-4}	4.08×10^{-5}	5.60×10^{-4}	2.89×10^{-3}	4.20×10^{-4}	3.32×10^{-4}
75th	1.75×10^{-4}	2.09×10^{-3}	1.34×10^{-2}	1.64×10^{-3}	1.33×10^{-3}	6.19×10^{-5}	7.43×10^{-4}	4.73×10^{-3}	5.80×10^{-4}	4.68×10^{-4}
90th	2.53×10^{-4}	2.73×10^{-3}	2.07×10^{-2}	2.20×10^{-3}	1.76×10^{-3}	9.14×10^{-5}	9.93×10^{-4}	7.43×10^{-3}	7.93×10^{-4}	6.40×10^{-4}
95th	3.19×10^{-4}	3.28×10^{-3}	2.71×10^{-2}	2.65×10^{-3}	2.11×10^{-3}	1.17×10^{-4}	1.21×10^{-3}	9.90×10^{-3}	9.73×10^{-4}	7.78×10^{-4}
RSD										
50th	1.35×10^{-4}	1.51×10^{-3}	1.74×10^{-2}	1.25×10^{-3}	1.05×10^{-3}	4.68×10^{-5}	5.25×10^{-4}	6.03×10^{-3}	4.37×10^{-4}	3.64×10^{-4}
75th	1.77×10^{-4}	1.95×10^{-3}	2.15×10^{-2}	1.67×10^{-3}	1.45×10^{-3}	6.27×10^{-5}	6.93×10^{-4}	7.63×10^{-3}	5.93×10^{-4}	5.07×10^{-4}
90th	2.32×10^{-4}	2.53×10^{-3}	2.69×10^{-2}	2.21×10^{-3}	1.91×10^{-3}	8.43×10^{-5}	9.18×10^{-4}	9.90×10^{-3}	8.07×10^{-4}	6.87×10^{-4}
95th	2.76×10^{-4}	3.00×10^{-3}	3.15×10^{-2}	2.65×10^{-3}	2.28×10^{-3}	1.03×10^{-4}	1.12×10^{-3}	1.20×10^{-2}	9.90×10^{-4}	8.46×10^{-4}
SOIL										
50th	1.83×10^{-4}	1.52×10^{-3}	1.37×10^{-2}	1.04×10^{-3}	1.21×10^{-3}	5.70×10^{-5}	4.75×10^{-4}	4.30×10^{-3}	5.13×10^{-4}	3.78×10^{-4}
75th	2.31×10^{-4}	1.94×10^{-3}	1.85×10^{-2}	1.40×10^{-3}	1.90×10^{-3}	7.38×10^{-5}	6.15×10^{-4}	5.90×10^{-3}	6.63×10^{-4}	5.99×10^{-4}
90th	2.95×10^{-4}	2.48×10^{-3}	2.46×10^{-2}	1.86×10^{-3}	2.67×10^{-3}	9.68×10^{-5}	8.15×10^{-4}	8.03×10^{-3}	8.70×10^{-4}	8.61×10^{-4}
95th	3.46×10^{-4}	2.98×10^{-3}	2.98×10^{-2}	2.22×10^{-3}	3.27×10^{-3}	1.18×10^{-4}	9.93×10^{-4}	9.90×10^{-3}	1.06×10^{-3}	1.07×10^{-3}

TF = traffic, IND = industrial, COM = commercial, RSD = residential.

Table 4.22: Fitted distribution of heavy metals in metal concentration without accounting for bioaccessibility (mg/kg).

Total metal content						
Sites	**Distribution**	**Cu**	**Pb**	**As**	**Cr**	**Cd**
TF	LogN	4.65 ± 0.67	4.28 ± 0.31	2.97 ± 0.59	3.49 ± 0.33	N(1.29 ± 0.92)
IND	LogN	4.88 ± 0.62	4.87 ± 0.42	3.28 ± 0.49	3.39 ± 0.18	N(1.03 ± 0.26)
COM	LogN	2.61 ± 1.43	3.56 ± 0.94	1.61 ± 1.16	2.04 ± 0.72	N(0.52 ± 0.23)
RSD	LogN	2.76 ± 0.80	3.33 ± 0.82	2.84 ± 0.33	2.10 ± 0.68	N(0.57 ± 0.24)
Soil	LogN	4.44 ± 0.81	3.99 ± 0.87	2.78 ± 0.93	3.24 ± 0.61	N(0.79 ± 0.58)

TF= traffic, IND = industrial, COM = commercial, LogN = lognormal, N = normal, at $p < 0.05$

Table 4.23: **Fitted distribution of heavy metals based on bioaccessibility content of metals in soil/dust (mg/kg).**

Sites	**Distribution**	**Cu**	**Pb**	**As**	**Cr**	**Cd**
TF	LogN	3.70 ± 0.52	2.83 ± 0.42	2.02± 0.34	1.01 ± 0.42	N(0.41 ± 0.13)
IND	LogN	3.80 ± 0.78	2.62 ± 0.60	2.03± 0.30	N(1.97 ± 0.84)	N(0.31 ± 0.05)
COM	LogN	1.97 ± 0.69	1.68 ± 0.63	1.93± 0.31	W(1.22 ± 1.90)	N(0.25 ± 0.04)
RSD	LogN	1.37 ± 1.12	1.61 ± 0.35	1.16± 0.83	N(0.83 ± 0.58)	N(0.21 ± 0.03)
Soil	LogN	3.01 ± 0.95	1.08 ± 1.11	1.30± 0.59	0.08 ± 0.36	W(0.27 ± 1.57)

TF= traffic, IND = industrial, COM = commercial, LogN = lognormal, N = normal, W = Weibull, $P < 0.05$.

4.5.4 Carcinogenic Risk of Bioavailable and Total Heavy Metal Contents via Oral Exposure of Agricultural Soil and Urban Dust

The result of cancer risk (CR) is revealed in Table 4.24. The result expressed the order of decrease of risks by elements on exposure to agricultural soil to be Cd > As > Cr > Pb. The results suggest that adults who ingested agricultural soil in the study site could have cancer effects by Cd (1.19×10^{-4}) at 95th percentile. For the 50th to 90th percentiles, the risks for adults were found to be within or below the tolerable limits. For children oral ingestion, the highest cancer risk (8.81×10^{-5}) was found to be within the acceptable limits at 95th percentiles, while at 50th to 90th percentiles, the risk was within or below the allowable limits range of $10^{-6} - 10^{-4}$. This indicates that the cancer risk for adults was higher as compared to that of children. The trend was same for all the other study heavy metals. Cd in soil is associated with application of mineral fertilizers and pigments (ATSDR, 2012). Cd have been proved to be a human carcinogenic agent therefore, oral exposure to Cd in agricultural soil and urban dust could cause damage to kidney, bone and reproductive system. The cancer risk for the remaining study heavy metals for both populations were below the permissible limits. Meaning that no possibility of cancer health risk.

The cancer risk for the heavy metals due to total metal contents in agricultural soil samples (Table 4.25) followed the same variation with the risk accounting for bioavailability content. However, the values of risks accounting without bioavailability were higher than those accounting with bioavailability except for Cd. This could be as a result differences in the goodness of fitted distribution of Cd (Weibull) fitted distribution accounting with bioaccessibility and (normal) fitted distribution accounting without bioaccessibility. The result showed that the cancer risk based on the ingestion of Cd and As in agricultural soil accounting without bioaccessibility was found to be higher than that of the remaining study heavy metals. The trend was the same for both populations.

The results of the cancer risk on oral ingestion of urban dust accounted with bioaccessibility showed that the health risk values were lower than the acceptable limit. Hence, suggesting that the carcinogenic risk from As, Cd, Pd, and Cr were negligible for all study heavy metals on both adults and children via oral exposure to urban dust. The cancer risk of Pb, As, Cr, and Cd for children in the traffic areas were 4.14×10^{-9}, 5.16×10^{-9}, 6.51×10^{-9}, 7.65×10^{-9}; 5.21×10^{-7}, 6.54×10^{-7}, 8.28×10^{-7}, 9.76×10^{-7}; 8.25×10^{-8}, 1.15×10^{-7}, 1.59×10^{-7}, 1.94×10^{-7} and 4.45×10^{-7}, 5.89×10^{-7}, 7.61×10^{-7}, 9.08×10^{-7} at 50th, 75th, 90th and 95th percentiles, respectively.

Whereas, the cancer risk for adults were 6.15×10^{-9}, 7.85×10^{-9}, 1.02×10^{-8}, 1.23×10^{-8}; 8.08×10^{-7}, 9.93×10^{-7}, 1.30×10^{-6}, 1.57×10^{-6}; 1.23×10^{-7}, 1.75×10^{-7}, 2.45×10^{-7}, 3.06×10^{-7} and 6.62×10^{-7}, 8.82×10^{-7}, 1.18×10^{-6}, 1.45×10^{-6} for Pb, As, Cr, and Cd at 50th, 75th, 90th and 95th percentiles, respectively. This indicates that there was no risk in both adults and children group. In case of industrial, commercial and residential areas, same results were found. This result was in agreement with previous study who reported insignificant cancer risk for heavy metals on oral ingestion of urban dusts, which is not likely to induce serious health consequences (Ali et al., 2017; Alamdar et al., 2016). The risk variation in urban dust for locations shows that for Pb, As and Cd are in the order of traffic > industrial > commercial > residential, whereas, Cr shows the order industrial > commercial > traffic > residential.

Considering the health risk for the total heavy metal content in urban dust, the results as seen in Table 4.25 show the variation of heavy metals with respect to sites are in the order Pb = industrial > traffic > commercial > residential and for As it is industrial > traffic > residential > commercial whereas, Cr and Cd are in the order traffic > industrial

> residential > commercial. This indicates that traffic and industrial activities seems to be the major contributors to heavy metals pollution and subsequent health risk in urban dust of this study.

In general, the health risk results for oral ingestion of both agricultural soil and urban dusts with bioaccessibility and without bioaccessibility shows that the cancer risk for the children was noted to be lower than that of adults. This implies that adults are more prone to cancer risk in both the urban dust and agricultural soil accounting for bioavailability and those without bioavailability (total heavy metal content). The higher carcinogenic risk of adults due to oral ingestion of soil as compared to children could be as a result of higher exposure duration of adults than children (Li et al., 2014). Koki et al. (2018) reported high cancer risk for adults compared to children as a result of oral exposure to pond water in Malaysia. Similarly, in Kuala Lumpur, Sulong et al. (2017) noted adult's cancer risk to be higher than that of children in haze period. Moreover, genetic alteration from parents to children has been noted to be much associated to causes of cancer in children more than risk of environmental factors (Moore, 2009). However, health risk on oral ingestion of some heavy metals in urban dust was discovered to be higher as compared to agricultural soil, suggesting urban environment to experience more human activities than agricultural soil.

4.6 The Criticality of Bioaccessibility in Health Risk Estimation

The bioavailability determined by the physiologically based extraction test technique and the total heavy metal contents were used in the evaluation of oral exposure risks (cancer risk and hazard quotient). The result showed that the risk values for the bioavailability fraction to be lower, making it to be more accurate than the risks values based on total heavy metal content. This is more pronounced in agricultural soil samples as result significantly lower heavy metals bioavailability in agricultural soil samples when compared with the urban dust samples as shown in Table 4.24 and 4.25. Moreover, the contribution of agricultural soil and urban dusts in different sampling sites differs due to the significant variation in the heavy metals' bioavailability in agricultural soil and the urban dust.

Comparing the risks simulated with bioavailability fraction and the risks with respect to total heavy metal content in both soil and dusts of different locations, the health risk results revealed that the cancer risk and non-carcinogenic risk values for both children and adults with total heavy metal content and the contributions of the sampling sites was higher than the risk accounting for heavy metals with bioavailability. Considering the significant differences between the risks accounting without bioaccessibility and the risks of heavy metals estimated with bioaccessibility values indicates the importance of bioaccessibility in health risk assessment of heavy metals in urban dust and agricultural soil. This suggests that the health risk determined without bioaccessibility could give excess risks than the precise risk that can be obtained using the bioavailability fraction. Therefore, bioaccessibility is an absolutely indispensable tool that is needed for the estimation of actual health risks for both population during oral ingestion exposure to urban dusts and agricultural soils.

Table 4.24: Carcinogenic risks for oral ingestion of urban dust and agricultural soil by children and adults based on bioavailability content.

CHILD						ADULT				
TF	**Cu**	**Pb**	**As**	**Cr**	**Cd**	**Cu**	**Pb**	**As**	**Cr**	**Cd**
50th	NA	4.14×10^{-9}	5.21×10^{-7}	8.23×10^{-8}	4.45×10^{-7}	NA	6.15×10^{-9}	8.08×10^{-7}	1.23×10^{-7}	6.62×10^{-7}
75th	NA	5.16×10^{-9}	6.54×10^{-7}	1.15×10^{-7}	5.89×10^{-7}	NA	7.85×10^{-9}	9.93×10^{-7}	1.75×10^{-7}	8.86×10^{-7}
90th	NA	6.51×10^{-9}	8.28×10^{-7}	1.59×10^{-7}	7.61×10^{-7}	NA	1.02×10^{-8}	1.30×10^{-6}	2.45×10^{-7}	1.18×10^{-6}
95th	NA	7.65×10^{-9}	9.76×10^{-7}	1.94×10^{-7}	9.08×10^{-7}	NA	1.23×10^{-8}	1.57×10^{-6}	3.06×10^{-7}	1.45×10^{-6}
IND										
50th	NA	3.8×10^{-9}	5.23×10^{-7}	1.70×10^{-7}	3.37×10^{-7}	NA	5.66×10^{-9}	7.79×10^{-7}	2.30×10^{-9}	5.01×10^{-7}
75th	NA	4.89×10^{-9}	6.54×10^{-7}	2.34×10^{-7}	4.20×10^{-7}	NA	7.39×10^{-9}	9.92×10^{-7}	3.54×10^{-7}	6.39×10^{-7}
90th	NA	6.25×10^{-9}	8.21×10^{-7}	3.11×10^{-7}	5.31×10^{-7}	NA	9.80×10^{-9}	1.29×10^{-6}	4.82×10^{-7}	8.32×10^{-7}
95th	NA	7.40×10^{-9}	9.66×10^{-7}	3.73×10^{-7}	6.24×10^{-7}	NA	1.19×10^{-8}	1.57×10^{-6}	5.92×10^{-7}	1.01×10^{-6}
COM										
50th	NA	2.36×10^{-9}	4.98×10^{-7}	1.24×10^{-7}	2.72×10^{-7}	NA	3.52×10^{-9}	7.40×10^{-7}	1.85×10^{-7}	4.03×10^{-7}
75th	NA	3.24×10^{-9}	6.23×10^{-7}	2.27×10^{-7}	3.40×10^{-7}	NA	4.91×10^{-9}	9.45×10^{-7}	3.40×10^{-7}	5.14×10^{-7}
90th	NA	4.40×10^{-9}	7.87×10^{-7}	3.60×10^{-7}	4.29×10^{-7}	NA	6.75×10^{-9}	1.23×10^{-6}	5.51×10^{-7}	6.72×10^{-7}
95th	NA	5.31×10^{-9}	9.23×10^{-7}	4.67×10^{-7}	5.02×10^{-7}	NA	8.45×10^{-9}	1.49×10^{-6}	7.30×10^{-7}	8.20×10^{-7}
RSD										
50th	NA	2.33×10^{-9}	2.53×10^{-7}	7.16×10^{-8}	2.28×10^{-7}	NA	3.48×10^{-9}	2.51×10^{-7}	1.06×10^{-7}	3.39×10^{-7}
75th	NA	2.99×10^{-9}	4.07×10^{-7}	1.11×10^{-7}	2.84×10^{-7}	NA	4.53×10^{-9}	6.15×10^{-7}	1.67×10^{-7}	4.32×10^{-7}
90th	NA	3.84×10^{-9}	6.3×10^{-7}	1.54×10^{-7}	3.57×10^{-7}	NA	5.97×10^{-9}	9.68×10^{-7}	2.35×10^{-7}	5.61×10^{-7}
95th	NA	4.55×10^{-9}	8.29×10^{-7}	1.88×10^{-7}	4.21×10^{-7}	NA	7.27×10^{-9}	1.29×10^{-6}	2.94×10^{-7}	6.79×10^{-7}
soil										
50th	NA	9.59×10^{-10}	2.61×10^{-7}	1.30×10^{-9}	3.80×10^{-7}	NA	1.28×10^{-9}	3.51×10^{-7}	1.75×10^{-9}	5.13×10^{-7}
75th	NA	1.74×10^{-9}	3.73×10^{-7}	4.32×10^{-9}	4.92×10^{-6}	NA	2.38×10^{-9}	5.09×10^{-7}	5.82×10^{-9}	6.72×10^{-6}
90th	NA	3.04×10^{-9}	5.23×10^{-7}	1.27×10^{-8}	3.30×10^{-5}	NA	4.21×10^{-9}	7.20×10^{-7}	1.71×10^{-8}	4.45×10^{-5}
95th	NA	4.28×10^{-9}	6.43×10^{-7}	2.43×10^{-8}	8.81×10^{-5}	NA	5.95×10^{-9}	9.10×10^{-7}	3.34×10^{-8}	1.19×10^{-4}

NA = not available, TF = traffic, IND = industrial, COM = commercial, RSD = residential.

Table 4.25: Carcinogenic risks for oral ingestion of agricultural soil and urban dust by children and adults based on the total heavy metal concentration.

CHILD RISK						**ADULT RISK**				
TF	**Cu**	**Pb**	**As**	**Cr**	**Cd**	**Cu**	**Pb**	**As**	**Cr**	**Cd**
50th	NA	6.28×10^{-9}	7.64×10^{-7}	3.01×10^{-7}	1.40×10^{-6}	NA	9.35×10^{-9}	1.13×10^{-6}	4.47×10^{-7}	2.08×10^{-6}
75th	NA	7.69×10^{-9}	9.67×10^{-7}	3.70×10^{-7}	2.19×10^{-6}	NA	1.17×10^{-8}	1.47×10^{-6}	5.65×10^{-7}	3.33×10^{-6}
90th	NA	9.61×10^{-9}	1.23×10^{-6}	4.64×10^{-7}	3.06×10^{-6}	NA	1.51×10^{-8}	1.94×10^{-6}	7.30×10^{-7}	4.81×10^{-6}
95th	NA	1.13×10^{-8}	1.46×10^{-5}	5.47×10^{-7}	3.66×10^{-6}	NA	1.83×10^{-8}	2.36×10^{-6}	8.85×10^{-7}	6.02×10^{-6}
IND										
50th	NA	7.14×10^{-9}	8.47×10^{-7}	2.92×10^{-7}	1.12×10^{-6}	NA	1.06×10^{-8}	1.26×10^{-6}	4.34×10^{-7}	1.66×10^{-6}
75th	NA	8.76×10^{-9}	1.06×10^{-6}	3.57×10^{-7}	1.44×10^{-6}	NA	1.33×10^{-8}	1.61×10^{-6}	5.45×10^{-7}	2.18×10^{-6}
90th	NA	1.10×10^{-8}	1.33×10^{-6}	4.47×10^{-7}	1.85×10^{-6}	NA	1.73×10^{-8}	2.10×10^{-6}	7.00×10^{-7}	2.88×10^{-6}
95th	NA	1.29×10^{-8}	1.57×10^{-6}	5.24×10^{-7}	2.19×10^{-6}	NA	2.09×10^{-8}	2.54×10^{-6}	8.50×10^{-7}	3.52×10^{-6}
COM										
50th	NA	5.12×10^{-9}	3.50×10^{-7}	1.69×10^{-7}	5.66×10^{-7}	NA	7.62×10^{-9}	5.22×10^{-7}	2.54×10^{-7}	8.38×10^{-7}
75th	NA	6.71×10^{-9}	5.64×10^{-7}	2.30×10^{-7}	7.84×10^{-7}	NA	1.01×10^{-8}	8.52×10^{-7}	3.48×10^{-7}	1.18×10^{-6}
90th	NA	8.76×10^{-9}	8.76×10^{-7}	3.09×10^{-7}	1.04×10^{-6}	NA	1.36×10^{-8}	1.34×10^{-6}	4.74×10^{-7}	1.63×10^{-6}
95th	NA	1.05×10^{-8}	1.15×10^{-6}	3.75×10^{-7}	1.25×10^{-6}	NA	1.65×10^{-8}	1.79×10^{-6}	5.90×10^{-7}	1.98×10^{-6}
RSD										
50th	NA	4.82×10^{-9}	7.34×10^{-7}	1.76×10^{-7}	6.22×10^{-7}	NA	7.17×10^{-9}	1.09×10^{-6}	2.62×10^{-7}	9.20×10^{-7}
75th	NA	6.21×10^{-9}	9.06×10^{-7}	2.36×10^{-7}	8.57×10^{-7}	NA	9.44×10^{-9}	1.38×10^{-6}	3.56×10^{-7}	1.29×10^{-6}
90th	NA	8.07×10^{-9}	1.14×10^{-6}	3.12×10^{-7}	1.13×10^{-6}	NA	1.26×10^{-9}	1.79×10^{-6}	4.86×10^{-7}	1.74×10^{-6}
95th	NA	9.61×10^{-9}	1.33×10^{-6}	3.76×10^{-7}	1.35×10^{-6}	NA	1.53×10^{-8}	2.16×10^{-6}	6.00×10^{-7}	2.13×10^{-6}
SOIL										
50th	NA	4.83×10^{-9}	5.81×10^{-7}	2.32×10^{-7}	7.12×10^{-7}	NA	6.46×10^{-9}	7.79×10^{-7}	3.10×10^{-7}	9.58×10^{-7}
75th	NA	6.18×10^{-9}	7.80×10^{-7}	2.92×10^{-7}	1.13×10^{-6}	NA	8.42×10^{-9}	1.06×10^{-6}	4.00×10^{-7}	1.52×10^{-6}
90th	NA	7.91×10^{-9}	1.04×10^{-6}	3.73×10^{-7}	1.58×10^{-6}	NA	9.86×10^{-9}	1.45×10^{-6}	5.25×10^{-7}	2.17×10^{-6}
95th	NA	9.44×10^{-9}	1.25×10^{-6}	4.39×10^{-7}	1.92×10^{-6}	NA	1.35×10^{-8}	1.79×10^{-6}	6.35×10^{-7}	2.69×10^{-6}

NA = not available, TF = traffic, IND = industrial, COM = commercial, RSD = residential.

4.7 The Contribution and Implication of Bioaccessibility and Health Risk Assessment Study

4.7.1 The Idea of Human Health Risk Evaluation

Generally human health risk evaluation aimed at searching the possibility that exposure to toxic substances could cause harmful consequences on human health and estimate the extent of the effect. Human health risk has various advantages such as its application to determine and estimate risk induced by contaminants in the environment. With it the production and use of chemicals in the environment are controlled. The use of leaded fuel was prohibited by many countries as a result of discovery of its effects on humans through the use of health risk assessment (Elom, 2012). The human health risk estimation has been showed to be a robust tool for distinguishing the toxic heavy metals and exposure pathways of most concern in urban environment (Wei et al., 2015).

It helps in identifying the root of chemical contaminants in the environment, the nature of health outcome that poses at a certain exposure duration. Human health risk expresses the factors that possibly exposed humans to the contaminants in the environment such as work, play, residence, taking a walk among others. It however, tries to show which category of human (i.e., age, gender, and health condition) is more liable to have more effects. Therefore, with these useful information, regulatory agencies in cities and countries will be able to assist in safeguarding the environment and its human health.

4.7.2 The Function of Bioaccessibility in Managing the Risk of the Environment

Various methodologies have been put to be practiced at both national and international levels to combat the contamination of environment so as to secure the health of human and environment. However, management of environmental contamination especially urban environment in many countries of the world is still a great challenge. Soil guideline value is one of the common risk assessment technique employed by various countries in environmental risk to manage land contamination (CCME, 1999; VROM, 2000). Even though, this approach has helped in revealing land contamination that could give clue to associated risks. Nevertheless, most developing countries including Malaysia have no developed guideline values and also for those countries that developed guideline values it is developed with presumption that the entire concentration of heavy metals in any soil/dust ingested is proportional to the amount that human body could absorb.

However, only a fraction of these concentrations is dissolved and available to be absorbed into the circulatory system (Ollson et al., 2009). Therefore, the total heavy metal concentration assumed by the soil guideline values could possibly exaggerate the risk therein. The solution to the existing dispute has led to the development of various *in vitro* bioaccessibility protocols that simulate the physiology of human digestive system. These assays were patterned to determine from ingested soil/dust the actual fraction of the heavy metals that has dissolved in the human gastrointestinal compartment and is available to be absorbed. Currently the attention of legislatures, health risk frameworks, and researchers have been turned towards applying bioaccessibility research based data and information to be the pivot for contaminated land assessment and human health risk assessment (Rodrigues et al., 2009). Among the assays design, one of which is the physiologically based extraction test that has been modified and used in this study.

4.7.3 The Implication of Human Health Risk in This Study

To investigate human health risk of heavy metals in soil/dust, this study has used a risk approach established by United State Environmental Agency (USEPA, 2011) for the human health risks assessment associated with environmental contamination. It assumes processes such as identification of the heavy metal contaminants and their sources in the environment, the pathway through which humans are exposed to these contaminants, and the potential risks induced by the heavy metals to humans. Following this procedure, the risks from the environmental samples are identified and estimated. Until the present, there have not been coherent methods and fitting variables for health risk assessment of the practical situation in Petaling Jaya. Heavy metals such as As, Cr, Cd, Cu, Pb, Mn, Ni and Zn were determined in urban dust and As, Cr, Cd, Cu and Pb were determined in agricultural soil. The concentrations of all the study heavy metals were higher than the background values. This implies that toxic heavy metals are influenced by human activities.

For the oral bioaccessibility risk assessment in soil and dust, it was discovered that both the carcinogenic risk values for adults are higher than those of children, even though, both are within or below the permissible limits of $1 \times 10^{-6} - 1 \times 10^{-4}$ with the exception of Cd in agricultural soil at 95th percentile which has a value slightly higher than 1×10^{-4}. This finding implies that there is no possibility of cancer risk from all the study heavy metals during oral exposure to soil/dust by adults and children except Cd. Though, adults are more liable to cancer risk than children. On the other hand, the non-carcinogenic risk values during exposure to heavy metals in soil/dust shows that the HQ values for children were higher than that of adults with values on exposure to urban dust higher than agricultural soil, although all the values are also below the permissible limits of 1.

The implication of this finding is that there is no likelihood of non-cancer risk on both populations, but children are more liable to non-cancer risk than adults. To add more, this implies that agricultural soil/dust are environmental media transferring heavy metals to humans either via work, traffic, or any outdoor activity and oral ingestion is the main exposure pathway through which hazardous heavy metals enters human body. Nevertheless, to minimize the possibility of risks based on accumulation of heavy metals, measures such as reducing the behavior of hand-to-mouth/object-to-mouth by children should be taken, encourage washing of hands by both children and adults at any time before eating.

Pica and geophagy either on account of behavior, tradition or means of nutrition due to poverty by children or adults should be discouraged and / or stopped. Washing of fruits and vegetables before eating should be encouraged. Seeing most of the heavy metals found at traffic and industrial areas. This findings would help the legislature as stated in the recommendation to strategies means of reducing emissions from these sources by enforcing laws and provide more free buses to minimize the use of private cars so as to reduce traffic congestion, sweeping of streets and pavements should be increased.

4.7.4 The Contribution of This Study to Bioaccessibility Method

The results of the bioaccessibility fraction on ingestion of urban dust and agricultural soil shows that on ingestion of these environmental matrices, high % of these heavy metals contaminants would dissolve in the human stomach and lower % in the intestine. This signifies that those % of heavy metal contaminants in the intestine would be available for absorption through the intestinal walls into the human blood stream. The higher % bioaccessibility of the heavy metals in both agricultural soil and urban dust in the stomach when compared with that in the intestinal phase is likely to be. This is because that at lower stomach pH the acid will enable the dissolution of the minerals that binds the metals; thus, the heavy metals are released and be more solubilized in the stomach.

In contrast, the lower bioaccessibility fraction of heavy metals in the intestine is as a result of absorption and precipitation of these heavy metal contaminants in the intestine. The distinctive feature of bioaccessibility in health risk assessment is its ability to give the exact risks associated with the oral consumption of the poisonous heavy metals. The traditional method of human health risk assessment assumed 100% intake of the poisonous heavy metals. However, the mean % bioaccessibility of poisonous element measured in this study were < 100%. Expressing higher dissolution of the heavy metals in the stomach phase and lower percentage in the intestinal phase, implying that it is not the whole amount of soils and dusts ingested that would be available for absorption in the intestine.

CHAPTER 5: CONCLUSION

5.1 Conclusion

The concentrations distributions, contamination, bioaccessibility and health risk assessment of heavy metals in urban dust / agricultural soil were investigated and assessed in this study. The concentrations of all the heavy metals in urban dust / agricultural soils were higher than the corresponding background values, and the bioavailability concentrations of all studied heavy metals were higher than Soil Guideline Values for land use of different countries, suggesting that this contamination could be due to anthropogenic inputs. The principal component and hierarchical cluster via exploratory analysis reveals the dominance of heavy metals at sites associated with high anthropogenic activities, indicating the significance of rapid urbanization and industrialization in the recent decades.

The assessment performed by enrichment factor indicates that Cd, Cu and Pb are significantly enriched, except at the residential and recreational park, whereas, Cr, As and Ni were moderately enriched. The ecological risk indicates the pollution levels of the heavy metals in urban dust to be Cd > Pb > Cu > As > Ni > Cr, with Cd the predominant element among them. The health risk assessment model with simulation analysis was employed to calculate human exposure to heavy metals in the urban dust via ingestion, inhalation and dermal exposure pathways. The results showed that ingestion, dermal and inhalation route posed no non-cancer health consequences on both adults and children population as a result of the values been lower than the permissible limits of 1. The hazard index for the different exposure pathways was in the order Pb > Mn > Cu > Zn > Cr, suggesting that Pb and Mn has the highest indexes, while the lowest in case of Cr.

To add more, the carcinogenic risk associated with ingestion and inhalation exposure to heavy metals in urban dust was showed to be negligible for both children and adults.

Implying these routes could pose no carcinogenic effects on both populations. However, the total cancer risk advocates no cancer risk for the heavy metals as the values was below the acceptable limits. On the other hand, the health risk based on cancer and non-cancer through the different exposure routes suggests that those sites at cluster 1 posed more risk as compared to those sites in cluster 2. This advocate's influence of more human activities on heavy metals distribution at those sites in cluster 1 when compared to those sites with less human activities in cluster 2. Among the three exposure pathways explored in this study, ingestion route was the dominant channel of exposure for all the population studied followed by dermal and inhalation. This proposed oral ingestion to be an important route in health risk analysis particularly on children population.

The human health risk assessment performed by bioaccessibility protocol shows that bioaccessibility protocol stand as an important ingredient, particularly in oral ingestion of chemicals through agricultural soils and urban dusts. The oral ingestion has become an important factor through which heavy metals enters human body especially children and also the fractions of soil/dust have become important components in heavy metal exposure. Health risk assessment on bioavailability data using ordinary calculations could not give a clear representation of the risk involved via ingestion of the sample matrices. However, attention was given to assessment of health risk on bioavailable data coupled with Monte Carlo simulation analysis especially involving the citizen's parameters which could represent the exact risks emerged as a result of oral ingestion exposure.

The bioaccessibility of stomach phase for all heavy metals was higher than that in intestinal phase probably as a result of differences in pH and the precipitation and complexation of minerals oxides in the higher pH of the intestinal phase. Similarly, the bioaccessibility of heavy metals in urban dusts was higher than those in the agricultural soils that could be due to urban dusts containing higher content of these heavy metals as a result of smaller particle size fraction than the agricultural soil. On the other hand, there was a significant correlation between the gastrointestinal phase of both bioavailability fraction and % bioaccessibility fraction in both agricultural soil and urban dust with total heavy metal content.

This indicates that gastrointestinal phase plays a vital role in health risk assessment of heavy metals in oral ingestion of soils and dusts. The mean bioaccessibility results shows that except for Cu and As in both gastric and gastrointestinal phase all heavy metals were < 50% bioaccessible indicating, except for Cu and As < 50% of all heavy metals, could be available for ingestion in agricultural soils and urban dusts which suggest probability of health risks. However, there could be a significant health risks on exposure to oral ingestion of heavy metals in agricultural soils and urban dusts considering the worst scenario of employing the maximum bioaccessibility fraction in both gastric and gastrointestinal phases in that they were > 50%. Demonstrating > 50% of these pollutants could be available during ingestion exposure to the sample matrices.

The simulated human health risk employed on the oral exposure to urban dust/soil indicates that the average daily dose of Cd was higher at 90^{th} and 95^{th} percentiles when compared with the minimal risk levels for oral exposure. The hazard quotient for oral ingestion of soil for all heavy metals were below the permissible limits of 1, but the hazard quotient for all heavy metals were higher for children than for adults in urban soil with the highest for Cd. The hazard quotient for heavy metals in urban dusts shows that As was the predominant element among the heavy metals even though all were below the tolerable limits. The HQ order for the sites are traffic ≈ industrial > commercial > residential.

The carcinogenic risk reveals that adults were more vulnerable to cancer risk than children with adult's cancer risk value for Cd slightly higher than the allowable limits at 95^{th} percentile. This implies that adults could have cancer risk for Cd on ingestion of agricultural soil. While the cancer risk for the other study heavy metals on agricultural soil exposure were below the permissible limits. The variation of health risk based on exposure to heavy metals via urban dust followed As > Cd > Cr > Pb with the values for adults higher than those of children. However, both the adults and children cancer risk values for oral ingestion of adults were within or below the tolerable limits.

On the other hand, the health risks associated with both cancer and non-cancer estimated for oral ingestion of heavy metals through dust/soil for both adults and children with respect to total heavy metal content was higher when compared with the risks accounting with bioaccessibility. Suggesting that risks accounting with bioaccessibility are low and accurate, thus, indicating the importance of bioaccessibility tool for health risk estimation of heavy metals in dust/soil. In short, this research will be really useful both for the residents to take protective measures and for the legislature to alleviate the heavy metals pollution of the urban environment.

Future Research Perspective

The bioaccessibility and health risk assessment of heavy metals in urban dust and agricultural soil was explored in this study area. However, the bioaccessibility and health risk of other contaminants such as polyaromatic hydrocarbons (PAHs) can be explored in the study area.

Arsenic toxicity is dependent on its valence states. Therefore its health implications may need further investigation.

The levels and the bioaccessibility of heavy metals contaminants in water bodies need to be investigated in addition to soil and dust. This is because unpurified water may be used for drinking and domestic activities by the poor inhabitants as the case may be for developing countries.

The collective metal-metal toxicity effects in gastrointestinal tract need further investigation.

Recommendations

Serious steps and strict measures should be taken by the authority's concern in addition to what is on to tackle toxic contamination triggered by various human activities as well as health relate risks associated with the traffic and industrial expansion as the city is developing rapidly. Soil and dust pollution in urban settings need a systematic approach of tackling it, such as proper control of the pollution sources and stern enforcement of environmental regulations.

Moreover, constant monitoring of the levels of these toxic heavy metals is needed in the urban environment.

The sweeping of the roadside areas in Petaling Jaya should be encouraged to continue and on regular basis and even expand it.

As motor vehicles are on the increase, traffic congestion can be reduced by further expanding the streets/roads through the construction of more flyovers in the city. Similarly, more free public buses should be provided and encouraged to be consistent so as to reduce the use of private vehicles.

Vulnerable populations particularly children should be given special attention. This can be done by controlling the soil and dust ingestion rate for children through reducing out-door playing time.

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LIST OF PUBLICATIONS AND PAPERS PRESENTED

PUBLICATIONS

1. **Shabanda, I. S.,** Koki, I. B., Farhana, A. R., Yook, H.L., Azizah, M., Abu Bakar, N. K. & Khor, S.M. (2019). Distribution of heavy metals in roadside dust of Petaling Jaya, Malaysia with multivariate and correlation analyses for source identification. *International Journal of Environmental Analytical Chemistry*. doi: 10.1080/03067319.2019.1661400.
2. **Shabanda, I. S.**, Koki, I. B., Low, K.H., Zain, S.M., Abu Bakar, N. K. & Khor, S.M. (2019). Daily exposure to toxic metals through urban road dust from industrial, commercial, heavy traffic, residential areas in Petaling Jaya, Malaysia: A health risk assessment. *Environmental Science and Pollution Research,* doi:10. 1007/s11356-019-06718-2.

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1. **Shabanda, I. S.**, Khor, S. M., Abu Bakar, N. K. (2018). Paper presented at the 7th International Graduate Conference on Engineering, Science and Humanities (IGCESH), 13-15 August 2018, Johor Bahru, Malaysia.
2. **Shabanda, I. S.**, Khor, S. M., Abu Bakar, N. K. (2019). Bioavailability and health risk of metals in urban dusts. Paper presented at the 3rd Asia International Multidisciplinary Conference (AIMC), 1-2 May 2019, Johor Bahru, Malaysia.
3. **Shabanda, I. S.**, Khor, S. M., Abu Bakar, N. K. (2019). Health risk assessment of heavy metals in urban soils and dusts of Petaling Jaya, Malaysia. Paper presented at the 3rd Asia International Multidisciplinary Conference (AIMC), 1-2 May 2019, Johor Bahru, Malaysia.
4. **Shabanda, I. S.**, Khor, S. M., Abu Bakar, N. K. (2019). Ecological risk assessment of heavy metals in traffic environment. Paper presented at the 2nd International Postgraduate Research Conference (IPRC), 7-8 December 2019, Universiti Sultan Zainal Abidin Kuala Terengganu, Malaysia.