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BIOACCESSIBILITY STUDIES OF POTENTIAL TOXIC ELEMENTS (PTEs) IN MEDICINAL PLANTS FROM DIFFERENT LOCATIONS IN ACCRA METROPOLIS, GHANA

BY

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DECLARATION

I, ROSE TAWIAH, do hereby declare that I have personally, under supervision, undertaken this research herein submitted.

Signed: …… Date: ……

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I declare that I have supervised the student in undertaking this project submitted herein and confirm that the student has my permission for presentation and assessment.

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ABSTRACT

Medicinal plants represent an important class of various traditional medicines. Over the years, their usage in primary health care intervention has increased in both developed and developing nations. Nowadays herbs are known to be the storehouses of most potential toxic elements (PTEs). In Ghana, most studies on PTEs have focused on only single environmental compartment to characterize medicinal plant contamination. In the present study, an integrated sampling programme that relates PTEs in herbal plants to natural/pristine (Botanical Garden) and anthropogenic (University of Ghana [UG] Campus and Tema Motorway [TM]) environments was carried out in Accra Metropolis. Fifty-six (56) herbal plants (with 20 different species) were collected from the natural and human impacted localities with their corresponding soils. Concentrations of nine (9) PTEs (Ni, As, Cd, Pb, Zn, Fe, Cu, Mn and Cr) were determined after acid digestion of both plant and soil samples. Metal fractionation through a modified three-step European Bureau of References (BCR) extraction procedure and Simple Bioaccessibility Extraction Test (SBET) were employed to evaluate the mobility, bioavailability and bioassessibility of the PTEs. The study revealed a high degree of ethnobotanical novelty of plants at the various sampling locations of which many Ghanaians use as traditional folk medicine. Analysis of the plants yielded 18 genera and 15 families. *Euphorbiaceace, caesalpinaceae*, *phyllanthaceace* and *solanaceae*, each had 2 medicinal plant species (13.33%). The remaining families gave single plant species (6.67%). The physicochemical parameters and PTEs found in the medicinal plants varied greatly among the different environments. The wide variations in PTEs concentrations in the analyzed herbs were attributed to differences in the plant metal uptake and translocation capabilities.

Medicinal plants harvested from Botanical Garden had the least metal contamination (57.27%) whereas UG Campus and TM were 70.00% and 86.67% respectively far greater than WHO/FDA international specifications. Fe had the highest concentration among all the 9 PTEs investigated in the medicinal plants followed by Mn and Zn. Soils collected from the various locations on which the herbs were picked were found to contain all the PTEs (Cu, Mn, Cd, Pb, Zn, Cr, Ni, and Fe) studied except As. Comparing the overall mean concentrations with EU soil quality guidelines for urban soils, only Cr exceeded the limit (0.3 ppm). However, the assessment of contamination levels of the soils through pollution and geoaccumulation indices indicated considerable to very high degree of pollution with the maximum value found at site M5 (Tema Motorway). Fractional concentrations of PTEs in the soils through BCR chemical extraction procedure showed different soil-specific patterns for the various availabilities (mobilizable, potentially and effectively bioavailability) with Pb being the least mobile. On the other hand, oral bioaccessibility of the studied PTEs showed variations among the medicinal plants with Fe registering the highest bioaccessible fraction (97.391%) in *phyllantus amarus*, at UG Campus. Hazard Index (HI) values for all PTEs studied in the medicinal plants indicated no significant risk of non-carcinogenic effects to both adults and children.

DEDICATION

This work is dedicated to the Most High God for His mercies

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LIST OF ABBREVIATION

AAS	Atomic Absorption Spectrophotometer
ADI	Average Daily Intake
BAF	Bioaccumulation Factor
BCR	European Bureau of References
CSRPM	Centre for Scientific Research into Plant Medicine
EPA	Environmental Protection Agency
EC	Electrical conductivity
Igeo	Geoaccumulation Index
EDQM	European Directorate for the Quality of Medicines in Healthcare,
GACP	Good Agricultural and Collection Practices
OM	Organic Matter
WHO	World Health Organization
WAHO	West African Health Organization
P_i	Pollution Index
P_{deg}	Degree of pollution
UG	University of Ghana
PTEs	Potential Toxic Element
SBET	Simple Bioaccessibility Extraction Test
Std. dev	Standard Deviation
HQ	Hazard Quotient
USEPA	United States of America, Environmental Protection Agency
FDA	Food and Drug Administration
CFDA	China Food and Drug Administration
Ppm	Part per million

CHAPTER ONE

INTRODUCTION

1.1 Background

Medicinal plants and their galenic forms are widely imbibed as home remedies as well as raw materials for the pharmaceutical industry. Usually they comprise of highly active pharmacological constituents like phytochemicals, minerals and trace metals (Dghaim *et al.*, 2015). Their use in therapeutics or as dietary supplements dates back from antiquity, but has increased substantially in recent years (Woods, 1999). Today, there has been two-fold increase in the demand for medicinal plants on the global market. This is as a result of increasing cost and distrust of Western medicine which have promoted medicinal plants patronage, in both the developed and developing nations (Edeoga *et al.*, 2005). It is estimated that one-third of Americans use some form of alternative medicine, spending close to $ 13.17 billion a year (Eisenberg *et al*., 1993). Also about 27 million South Africans depend on some medicinal plants for their primary health care needs. Additionally, studies also indicate that significantly higher number of patients in South Africa consult traditional healers for potentially life threatening conditions. Thus, the general reliance of these populations on medicinal plants is believed to be because of their: affordability, inadequate health facilities and healthcare professionals, anticipated lower side effects than synthetic drugs, general accessibility, extensive local knowledge and expertise among the local folks (Mulholland, 2004; Mander and Breton, 1996).

Further the World Health Organization (WHO) has indicated that within the last fifteen years, the demand for medicinal plants has reached about $14 billion annually and could reach five (5) trillion by 2050 (Akerele, 1992). Hence it is not surprising that, over 70-80% of the world's population

living in rural areas relies on non-conventional medicine for treatment of their ailments in Africa; the corresponding figure is 65 % in India (Khan *et al*., 2008).

Herbal medicine as the name implies concerns plant derived materials found in nature and are used with or without processing for treatment of sicknesses. Different plant parts are utilized in the formulation of herbal medicines which include the leaves, roots, barks, fruits and seeds. Accordingly, there is growing concern over the safety and toxicity of natural herbs in the environments because of their huge therapeutic benefits. Besides, there is widespread misconception that natural herbs and plants are inherently safe; nonetheless, there are large volumes of reports on incidences of toxicity and adverse effects linked to the use of herbal plants in different parts of the world (e.g. Dghaim *et al*., 2015; Ernst. E., 2002). The toxicity of herbal plants may be related to contaminants such as pesticides, potential toxic elements (PTEs)/heavy metals (HMs) and chemical toxins. In general, the various environmental activities (e.g transport, mining, storage, agriculture, etc) and their resulting contaminants in reference to soil, water and air can significantly affect the properties of the herbal plants and their formulations. Some of these metals are very vital for the normal biological processes of plants and animals when they are in their right quantities (Ernst, 2002). On the other hand, plants serve as a bridge in the transfer of PTEs/HMs from contaminated soil to humans and also are able to accumulate PTEs in elevated concentrations (bioaccumulation). However, when the metal concentrations are either too low or too high, there is the tendency for them to become toxic with their attending numerous health hazards. Metals like Zn, Cu, Fe, Mn, and Cr are essential elements (good for biological and physiological processes) whereas for example, mercury (Hg), thallium (Th) and lead (Pb) have the potentials to cause toxicity and are known to affect the central nervous, cardiovascular, respiratory, gastrointestinal, renal, dermatologic, immunological and haemapoietic systems (Baby

et al.,, 2010; Hedberg *et a*l., 2010; Rao *et al*., 2011). Hence, medicinal plants can pose a health risk due to the presence of HMs or PTEs and their speciation to humans (Chojnacka *et al*., 2005 and references therein). In this regard, dietary intake of PTEs via herbal medicines can decrease immunological defences, cardiac dysfunction, fetal malformation, impaired psychosocial and neurological behaviour, gastrointestinal cancer and many others in consumers (Dghaim *et al*. 2015). Studies of poisoning and toxic effects of trace metals in medicinal herbs from Asia, Europe and the United States, revealed that these plants are store houses (Kaličanin *et al*., 2014; Caldas and Machado, 2004; Kakosy and Hudak, 1996). Consequently due to their potential toxicity, persistent and irreversible property, PTEs like Cd, As, Hg, Pb, Ni and Cr have been listed as priority pollutants by United States Environmental Protection Agency (USEPA) (Rahimi *et al*., 2012). Apparently, in recent times, the toxicity of PTEs on human health and the environment has attracted great attention which require effective pollution control strategies.

1.2 Bioavailability of PTEs in soils to plants

Nowadays with rapid urbanization and industrialization, PTEs strongly enrich urban soils. Thus plants uptake is one of the principal pathways by which PTEs/HMs from soils enter the food chain. Plants are very sensitive to environmental conditions; hence they can store HMs in their harvestable parts which in turn affect the overall elemental composition of the plant on uptake. The uptake, accumulation and concentration of HMs in plants are influenced by atmospheric depositions (resulting from traffic emissions, metal mining and smelting operations), concentration and bioavailability of HMs in soil (through agricultural excipients like pesticides and sewage sludge), the nature of soil where herbs are grown (pH and organic matter concentration), individual plant performance (degree of maturity of the plant, time of harvest) and manufacturing conditions

of herbal drugs (eg. grinding weights, lead-releasing containers and manufacturing utensils) (Kulhari *et al*., 2013; Zia *et al.*,, 2011 and references therein). Different HMs have different transmitting rates from soil to-plant, based on transfer coefficients of metals viz: Cd, Tl and Zn are readily taken up by plants because of higher transfer coefficient, whereas Cu, Co, Cr and Pb are stably bound to the soil structures and show minimum transfer to plants from soil due to lower transfer coefficient (Kloke, 1984). Some metals (Mg, Mn and Zn) play a vital role in proper growth and development of the plant being directly or indirectly involved in various biological functions of enzyme activation and molecular metabolism. Very little information is available about potential influence of metals on pharmacological activity of natural drugs obtained from medicinal plants. Metal mediated hazardous impacts can be direct or indirect via binding of metals with pharmacologically active substances or by manipulating the pharmacokinetics (Weber, 2003). Consumption of raw herbal drugs from medicinal plants, grown in polluted sites can cause serious consequences on human health indicated earlier. For getting desirable therapeutic benefits, quality of these herbal products must be ensured in terms of metal contamination. Therefore, there is an urgent need for quick assessment of these heavy metals in medicinal plants to control the level of contaminants therein. Additionally, equally important is chemical speciation of PTEs which can provide comprehensive understanding of the source, occurrence, physicochemical and biological availability, mobility potential of these elements in herbal plants. Even though there are large variations among different plant species in terms of metal accumulation ability, most medicinal plants have the ability to accumulate heavy metals when grown under natural conditions hence their use in phytoremediation. Their bioaccumulation can have mid-term and long term health risks to both consumers and the ecosystem since these metals are not biodegradable. In cognizance of this, strict periodical surveillance of these contaminants is highly imperative. Studies of

HMs/PTEs contents in medicinal plants abound in the Ghanaian literature (Amponsah and Nooni, 2013; Annan *et al*., 2010; Okwu, 2004; Ernst, 2002). However, most of the related research works pertains to phytochemical screening, total metal content determination and contamination assessment (Nkansah *et al*., 2016; Annan *et al*., 2013; Sarpong *et al*., 2012) but no attention has been paid to the bioaccessibility, systematic incorporated occurrence, source, bioavailable fractions (fate) and pollution control of PTEs.

The relationships of limited significance are to be found between the total metal concentrations and their biological effects (uptake or toxicity) in plants because only a small portion of the metal content in the plant is bioaccessible (Madrid and Biasioli, 2008). Therefore, to account for more realistic exposures of PTEs to biota, detailed risk assessments of medicinal plant contamination should include the metal bioaccessible fractions. The control factors of metal speciation, their distribution in various forms from different sources must also be taken into account (Madrid *et al*., 2006). Thus the primary aim of the present study is to ascertain systematically the occurrence, source, fate, bioaccessibility and risk of some PTEs available for absorption by selected medicinal plants popularly used in Ghana, which to the best of my knowledge has not yet been reported.

1.3 Problem Statement/Justification

In Accra Metropolis, waste management has been a major challenge with the increasing rural urban migration coupled with inadequate sanitary facilities. Domestic and industrial wastes containing heavy metals are improperly disposed of` resulting in their contamination of the soil. Consequently, these metals are absorbed and/or adsorbed into the tissues of plants including the medicinal plants. The plants may be eaten by the key industry animals which may be subsequently consumed by man through direct ingestion. Through this process, the PTEs or HMs get into the

various system of man where they can be toxic with short and long term effects. According to Inoue (2013), Hg exposure to man can induce catastrophic health concerns involving serious neurological disorders. In Ghana, Hg is widely used in small-scale mining in almost all the ten regions of the country. These metals and other amalgams are washed down to riverine systems and are also very volatile and have long transport property and may eventually get to man along the food chain. The result is high toxicity which may manifest in kidney and other organ failures, neurological and reproductive disorders whose effect may vary from adults to neonates.

Unfortunately, the cultivation, harvesting, preparation and marketing of medicinal plants in different forms of various plant medicines (commonly called herbal medicine) is not comprehensively regulated. Therefore, herbal medicine practitioners normally harvest their medicinal plants from anywhere in the Accra Metropolis including heavily contaminated soils and landfill sites. Consequently, there is the fear that these metals could be major contaminants/pollutants in these medicinal plants and hence their safety is questionable.

The toxicity and non-biodegradable nature of PTEs have created the necessity for their control and monitoring in the environment. While the scientific literature regarding bioavailability and accessibility of PTEs abound in the literature in the developed nations (e.g. Koch *et al*., 2011; Kulkarni *et al.*, 2007; Leśniewicz *et al*., 2006) this is not the case in most third world nations including Ghana. Accordingly, there is no information available on the bioaccessibility evaluation of PTEs by the Ghanaian populace. This implies that studies into PTEs contamination of herbal remedies with regard to available elements in consumers is very imperative in Ghana. Thus, results from this study would provide information on the bioavailable and bioaccessible forms of the selected PTEs as well as consumer risk assessment data that could be used to take preventive

actions to minimize consumer health risks. It would also serve as baseline upon which annual or other long-term monitoring studies would be compared with. More so, with such data herbal practitioners' can be assured of compliance handling processes and ease development of regulatory policies as well.

1.4. Hypothesis

H_0: Medicinal plants collected from human activity oriented sites in Accra Metropolis are contaminated with PTEs

H_1: Medicinal plants collected from the wild in Accra Metropolis are not contaminated with PTEs

1.5 Objectives of the Research

1.5.1 Main Objective

The main objective of the study was to ascertain systematically the occurrence, source, fate, bioaccessibility and risk of PTEs available for absorption by the selected medicinal plants popularly used in Ghana

1.5.2 Specific Objectives

The specific objectives are:

1. To collect herbal plants from various localities in Accra Metropolis and their respective soils (pristine versus anthropogenically impacted environments).
2. To measure the concentrations of PTEs- Cd, As, Pb, Ni, Mn, Fe Cu and Cr in the sampled plants as well as the soils from the different environments.
3. To compare the source, mobility and effective bioavailability of PTEs to the plants through chemical extractions.

4. To evaluate human bioaccessibility of PTEs (the potential uptake of PTEs in the medicinal plants by consumers).
5. To investigate the relationships between various PTEs and the physicochemical properties in the soils
6. To assess potential health risks associated with PTEs via medicinal plants intake.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

Potential toxic elements (PTEs) of geogenic origin mostly occur within background levels in soils with their presence usually attributed to weathering of parent rocks and paedogenesis (Khan *et al.*, 2014, 2015). Nonetheless, rapid urbanization and industrialization have led to a drastic upsurge in the concentration of several PTEs in the ecosystem (Olowoyo *et al.*, 2012). Medicinal herbs have the propensity to accumulate PTEs in their tissues especially when they are cultivated on polluted environmental media such as roadsides and industrial areas due to their ability to tolerate potentially toxic ions in the environment (Başgel and Erdemoğlu, 2006). The adverse effects of PTEs/heavy metals (HMs) on human health have been known for a long time. Nevertheless, exposure to PTEs continues and even now is on the increase in some areas (Kaushik *et al*., 2009; Järup, 2003). Moreover, their high prevalence in the environment in the form of residues are able to reach medicinal plants where they are assimilated (Sarma *et al.*, 2012) .

Additional sources of these elements to plants are through rainfall, atmospheric dusts and plant protection agents, which could be adsorbed through the leaf. Plants take-up these heavy metals leading to a rise in certain toxic elements entering the food chain, hence understanding the bioavailable forms of the elements and their bioaccessibility to humans as well as the fate of such elements on organisms, is of considerable interest (Poggio *et al.*, 2008).

2.2. Plants as sources of medicine or food supplements

The use of medicinal plants in therapeutics or as dietary supplements dates back beyond recorded history but has increased substantially in the last decades (Khan *et al*., 2014). Majority of the world's population in one way or the other depend on herbal medicines for various health ailments due to the immense benefits they have (Annan *et al*., 2013). Most people are of the belief that medicinal plants are natural and thus safer than allopathic drugs (Ayitey-Smith, 1989). Several plants have been used by traditional herbalists to treat many illnesses. In his book, Kokwaro, (993) extensively illustrated how various plants in East Africa are used for treatment of human diseases by different communities within the region. Some medicinal plants are used to treat fever, indigestion, ulcers, asthma and malaria. For instance, the extract of some medicinal plants like fresh juice of onion is used to reduce both acute and chronic pain as well as irritation (Nasri *et al*., 2012). On the other hand, in India with her rich heritage, medicinal plants are used in traditional healing systems such as the Ayurveda, Siddha, and Unani systems, besides folklore practices. Ayurveda is perhaps, the most ancient of all medicinal traditions and is probably older than the Chinese traditional medicine where this practice is also pronounced. It is also considered to be the origin of non-orthodox medicine. Well known Ayurvedic medicinal plants include *Azadirachta indica* (Neem), *Centella asiatica* spp (Gotu kola), *Cinnamomum camphora* (Camphor), *Elettaria cardamomum* (ela or cardamomum), *Rauwolfia serpentina* (Indian snake root), *Santalum album* (San-dalwood), *Terminalia species* (Myrobolan) and *Withania somnifera* (Aswargandha).

In Ghana, herbal medicine has been and still being used to treat all kinds of ailments, for example, bruises, malaria, fever, sexual and reproductive health issues, menstrual irregularities, skin disorders and preparations that can manage AIDS in people living with HIV and other complex ailments. Traditional medicine in Ghana dates back to the time of the first settlers, not forgetting

the pioneering efforts of Dr. Oku Ampofo who was a Ghanaian allopathic medical practitioner. The government of Ghana set up the Centre for Scientific Research into Plant Medicine (CSRPM) in 1975 as a consequence of his efforts. Through Dr. Oku Ampofo's efforts, the Centre for Scientific Research into Plant Medicine was in 1981 designated as a WHO collaborating Centre for Traditional Medicine, the first in Africa. CSRPM runs clinic to treat patients, produces herbal medicines and leads in research and testing of herbal medicines from all over the country.

In an effort to promote and perpetuate the use of medicinal plants, the Tepa Medicinal Farm was established. It hosts a lot of Medicinal Plants with immense qualities, ranging from insecticidal, antihypertensive, antimicrobial to antibacterial, to mention a few. The interest in herbal medicine has increased with setting up of homeopathic clinics across the country by private companies or individuals. There are a number of clinics which operate with herbal medicine alone. These clinics have gained much approval from the general public and are continually being patronized.

2.3 Potential toxic elements accumulation by medicinal plants

Trace element plays a key role in biological, chemical, metabolic and enzymatic reactions in the living cells of plants, animals and human beings (Sarpong *et al.*, 2012). Plants are sensitive to environmental conditions and they accumulate these PTEs in their harvestable parts (via root uptake, foliar adsorption and deposition of specific elements in leaves) and the intensity of this uptake process changes the overall elemental composition. Thus the accumulation of heavy metals in edible and medicinal plants needs thorough investigation to prevent elevated concentrations of heavy metals reaching the users. The release of PTEs through human activities into the environment has increased over the years and the excess of these metals in the environment has been reported to be extremely dangerous to human health (Oluwoye *et al.*, 2010). According to

Rahimi et al. (2012), poisoning associated with the presence of toxic metals in medicinal plants has been reported in Asia and Europe. Heavy metal origin and content as well as their possible interaction with soil properties are priority objectives in environmental monitoring (Qishlaqi and Moore, 2007). This is due to the fact that apart from the sources of heavy metals, the physicochemical properties of soil such as soil pH and organic matter content may also affect their concentrations ((Logan *et al.,* 1997; Qishlaqi and Farid Moore, 2007). A study conducted by Gregor, (2004) revealed that accumulation of metals by both roots and leaves increases with increasing available metal concentration in the external medium.

Numerous medicinal plants have the ability to accumulate PTEs/HMs when grown even under natural conditions. *Helichrysum candolleanum, H. buek (Asteraceae)* and *Blepharis diversispina (Nees)* are also known to tolerate high concentrations of metals (Nkoane *et al.*, 2005). The levels of HMs in 27 medicinal plant species collected from their natural habitat in Ghana were studied in order to evaluate their health implications (Annan *et al.*, 2010). Cadmium (Cd) was present in all samples and some species, especially *Ocimum canum (Lamiaceae), Clausena anisata* (Rutaceae) and *Rauwolfi*a *vomitoria* (Apocynaceae) had levels of iron (Fe) which could cause Fe toxicity. Despite the popular use of the above mentioned African medicinal plant species, current evaluation of the bioaccessible forms of PTEs uptake by these species with regards to how much is bioavailable to the individual is not considered. Further, there is a widespread misconception that harvesting of medicinal plants from the wild, as opposed to collection from human activity oriented sites was safer. Nonetheless many agro-chemicals contain HMs/PTEs such as Cd and Pb which enter the soil due to fertiliser impurities thus heavy metal contamination in soils is often caused by repeated use of metal-enriched fertilisers (He *et al*., 2004). As a result, soil and water sources (both

primary and secondary) need to be monitored periodically under Good Agricultural and Collection Practices (GACP) but this is not the case in most developing countries like Ghana.

2.4 Potential toxic elements in medicinal plants and plant-based products

Numerous studies have been conducted worldwide to determine heavy metal levels in medicinal plants and plant-based products (e.g. Nkansah et al., 2016; Sarpong et al., 2012; Bempah *et al.*, 2012; Annan et al., 2010; Maharia y, 2010). Investigation by both developed and developing countries have shown high levels of PTEs in products available to the public (Denholm, 2010; Garvey *et al*., 2001). Examination of PTEs content in traditional Asian herbal remedies purchased in the United States, Vietnam and China revealed that majority of the products had detectable levels of HMs, with nearly 74% containing amounts greater than current recommended public health guidelines (Garvey et al., 2001). Also, high levels of toxic metals can occur in medicinal preparations when they are used as ingredients, as in the case of Pb and Hg in some Chinese, Mexican and Indian herbal medicines (Caldas and Machado, 2004). The occurrence of high levels of Cd, Hg and Pb in five medicinal plants including *Allium sativum* from randomly selected herbal farms and local markets in south India, revealed that the samples analysed contained toxic levels of Cd (33%) whereas 40% showed toxic levels of lead. However, none of the samples contained detectable As. Besides, Oluwoye (2012) demonstrated that significantly higher levels of trace metal contents were present in two popularly used different plant species (*Datura stramonium* and *Amaranthus spinosus)* from a waste dump site in Pretoria, South Africa.

Sarpong *et al* (2012) on assessment of herbal remedies used in Ghana showed that medicinal plants parts harvested from a wide range of undisclosed locations by plant gatherers and sold at the Kumasi Central Market, had multiple metal contamination. Arsenic and Zn were detected in all

samples and high Pb and Cd contents were recorded in some plant species. In a similar work by Annan *et al*. (2010), high levels of Zn, Cu and Cd were present in all the plant species examined. The concentrations of Zn, Cu, Mn and Cd were within their respective maximum permissible levels. However, some species, especially *Ocimum canum*, *Clausena anisata* and *Rauwolfia vomitoria* had levels of Fe higher than the maximum permissible level of 1000 µg/day which could lead to Fe toxicity. The results also highlighted the differences in contents of minerals in *Lippia multiflora* obtained from different locations in Ghana. Contaminated raw materials could lead to unwholesome herbal products which can adversely affect the health of consumers. The only way to ensure consumer safety is to periodically sample plants from the various harvesting sites and popular markets. However, this is complicated because plants of the same species are habitually collected from various sources and are added together in one storage container. Nonetheless, it is highly essential that medicinal plants are constantly tested for metal contamination and their bioavailable forms as these plants are used as starting material for numerous herbal products. Moreover, such an assessment is necessary for determining the effectiveness of medicinal plants in treating various diseases. The broad use of traditional medicine by rural communities due to the accessibility and affordability of herbal medicine has also necessitated a further research into the bioavailability and translocation pattern of trace metals by some medicinal plants grown in the urban areas (Ebrahim et al., 2012).

2.5 Impacts of potential toxic elements in humans

Medicinal plants have been shown to be both a rich source of essential metal ions and non-essential metals. Poisonings from traditional medicinal products containing trace or HMs are well documented (Kaličanin *et al.*, 2014; Benninger *et al.*, 1999). Consumption of raw herbal drugs

from medicinal plants, grown in polluted sites can cause serious consequences on human health. Toxic effects of heavy metals are due to their hindrance of the regular body biochemistry in normal metabolic processes (Kulhari *et al.*, 2013; Ernst, 2002).

According to Inoue (2013), many metals in trace or minute quantities have proved vital for normal body functions, for example, Fe in oxygen transport by the haemoglobin of the red blood cells, Mn and Se in antioxidant system and Zn in keratin metabolism. When the required normal concentration of these metals in the body is exceeded, toxicity occurs. Thus some metals like As, Hg, Pb and Tl are known to be very toxic (Dghaim et al. 2015). High concentration of As impacts on the nervous, cardiovascular, respiratory, gastrointestinal, hepatic, renal, haemapoietic, immunological and dermatological systems. Mercury exposure including exposure to short alkyl-Hg, elemental Hg as well as inorganic Hg salts induce acute neurological disorder (Moore, 2004).

Sarpong et al. (2012) demonstrated that Pb causes neurological disorders, anaemia, kidney damage, miscarriage, lower sperm count and hepatotoxicity in higher concentrations. The severity of Pb exposure in adult is less than that associated with hyperactivity in neonates and it has been experimentally deduced that these PTEs produce behavioural changes by altering the brain transmitters metabolism particularly catecholamines. Most of accumulated Pb is sequestered in the bone and teeth (Todd *et al*., 1996) thereby causing brittle bones and weakness in the wrist and fingers. Lead stored in bones can re-enter the blood stream during periods of increased bone mineral cycling. Mobilized Pb can be re-deposited in the soft tissues of the body and can cause musculoskeletal, renal and developmental defects (Maharia et al., 2010). These metals exert their devastating toxic effects on biological defence by damaging it. Acute or chronic exposure to Cd causes respiratory distress, lung and breast cancers, haemorrhagic injuries and cardiovascular

disorders (Bempah *et al.*, 2012). Cadmium intake due to the ingestion of environmentally contaminated plants has been related to potential risk of postmenopausal breast cancer (Bempah *et al.*, 2012).

Nickel has been reported to cause contact dermatitis, nasal, sinus and lung cancers, kidney disorders, chronic bronchitis, acute respiratory distress syndrome and pulmonary fibrosis. Chromium on the other hand, is known to cause nephrotoxicity, nasal and lung ulcers, skin ulcers, hypersensitivity reactions and "chrome holes" of the skin (Maharia et al., 2010). Excess Fe leaches out of storage sites and moves into the blood stream then to the brain where it destroys neurons, leading to neurodegenerative diseases and neurological dysfunction, with Alzheimer's symptoms (Thompson and Orvig, 2003). Recent investigation by a London-based toxicology unit recorded over a period of 5 years (1991–1995) 12 cases of poisoning with Pb, As or Hg. Metals have been implicated in many pathological conditions. These pathological conditions may be the result of deficiency or overload. For instance, Cu accumulations to toxic levels in the body tissues have been implicated in Wilson's disease which manifests as neurological or psychiatric symptom and liver disease (Subramanian *et al.*, 2002).

2.6 Chemical Extraction Schemes

PTEs are widespread in the soil as a result of geo-climatic conditions and environmental pollution. (Kaličanin *et al.*, 2014; Radulescu *et al.*, 2013; Saper *et al.*, 2004; Bin *et al*, 2001). Most metals present in soils can interact differently with the different fractions of soils depending on the chemical forms and phase associations. Total metal analysis may provide information concerning possible enrichment of PTEs/HMs in soils but it is often assumed that PTEs with different forms have different bioavailability and toxicity to plants and animals and the procedure does not provide

enough information regarding the chemical nature or phase association and bioavailability of a particular element. Thus determining content of PTEs in soils is not sufficient to assess the environmental impact of contaminated soil (Salmons and Forstner, 1980). This is because it is the chemical species or form that determines the mobility and bioavailability of PTEs in soil and other environmental compartments such as biota and plants (Koch et al. 2011). Therefore, to account for a more realistic exposure of PTES to biota (humans), detailed risk assessment of medicinal plants contamination should include a study of the mobility, effectiveness, bioavailability and potentially bioavailable metal fractions. However, very little information is available on PTEs in herbal plants of Ghana in this regard. Nowadays, the bioavailable forms of trace metals in herbs have become an important consideration for many researchers (Nolan *et al.,* 2003). When the possible biological effects of trace metals in medicinal plants need to be evaluated, additional studies are required. Various methods have been proposed to stimulate and quantify metal reactivity as well as the phytochemical and biologically available pools of metals in soil. One of the most popular surrogates for measuring metal bioavailability is chemical extraction by means of various mild to strong oxidising agents, resulting in operationally defined specific metal fractions (Madrid *et al,* 2008 ; Luo *et al.,* 2006). Conceptually, chemical extraction procedures selectively extract metals bound by specific soil fractions with little interference on the other soil components. Consequently, the process can provide important information on which PTEs are mobile and/or could possibly be taken up by plants and also predict the fate of heavy metals in the urban environment. Several sequential extraction procedures (Oome *et al*., 2003; Rauret *et al*., 1999) have been proposed with the most widely accepted method proposed by Tessier *et a*l, (1979). However, the extraction procedures are not standard and the outcomes of different experiments are not always comparable due to lack of uniformity in the procedures. Thus in the late 1980s, the Standards, Measurements

and Testing Programme, (formerly the Bureau of References (BCR), through the European Commission, organised a project for studying mobility and availability of metals in soils which reached a compromised between analysis time and the amount of information obtained to promote uniformity.

The modified three-step sequential extraction procedure proposed by the European Bureau of References (BCR) is one of the useful sequential extraction procedures and it has been successfully used in metal fractionation in soils and sediments (Oomen *et a*l 2003; Rauret *et a*l., 2002).

In this study, chemical extraction study protocol proposed by BCR (Ure *et al,* 1992) will be use to determine the mobility, effectiveness, bioavailability and potentially bioavailable (operationally define) solid phase distribution of PTEs in soils on which the selected medicinal plants were sampled.

2.8 In vitro bioaccessibility of PTEs in medicinal plants

Total metal concentrations alone may lead to an overestimate of potential toxicity unless bioaccessibility is considered. The fraction of a contaminant which solubilizes in an in -vitro system and available for absorption is referred to as *in vitro* bioaccessibility and is a good indicator of relative bioavailability (RBA) of a toxicant in a biological system, especially if the test used is validated in comparison to the results of *in vivo* tests (Hedberg *et al.*, 2010; Ruby *et al.*, 1999). The actual fraction of an ingested contaminant that is absorbed through the gastro-intestinal wall into the circulatory system is known as the bioavailability. *In vitro* methods were widely used to evaluate bioaccessibility of minerals and trace elements from different sort of herbal plants or food products (Koch *et al.*, 2011).

Studies which compare bioavailability (in- vivo) and bioaccessibility (*in vitro*) have indicated bioaccessibility could be used as a determinant of bioavailability (Ruby *et al*., 1999). Since *in vivo* studies are time consuming, costly and relatively complicated, *in vitro* extraction test using stimulated body fluids have been used to model bioaccessibility of toxicants (Oomen *et al.*, 2002). The *in vitro* bioaccessibility functions on the principle that metal solubilisation in an intestinal fluid can be a useful determinant of metal bioavailability in a biological system. The method determines the extent of metal solubilisation in an extraction solvent that mimic gastric fluid. *In vitro* bioaccessibility tests are easy to perform and in most cases, the toxicity of the ingested dose depends on the degree to which it is distributed to internal target organs and as such bioaccessibility data can be used to provide realistic information on potential health effects associated with ingestion of contaminated medicinal plants. Although bioaccessibility is not a direct measure of bioavailability, it is considered a reasonable predictor since solubilisation is a necessary step in the systemic absorption process. Thus, poorly soluble forms of PTEs, with low bioaccessibility may also have low bioavailability. Bioavailability data can be used to provide more realistic information on potential health effects from herbal plant ingestion, modify generic traditional medicine quality guidelines using site specific data and help prioritize sites based on contaminants exposure scenario. Even a relatively small adjustment in oral bioavailability can have significant impacts on estimated risks and clean up goals (US EPA, 2008). The simple bioaccessibility extraction test (SBET) which is a simplified form of the physiologically base extraction tests (PBET) has been successfully developed and validated to estimate the oral bioaccessibility of metals in medicinal plants. Protocols for various organic and inorganic chemicals are available in the literature and the specific test used for a substance may vary depending on the substance being tested (Ruby, 2004). A typical PBET for metals involves incubating the plant sample in a low-pH

solution for an allotted period that mimics the time the contaminant would spend in the stomach. The pH of the solution is then increased and the sample incubated for another period of time to mimic the time spent in the small intestine. Enzymes and bile acids may be added to the solution to mimic gastric and small- intestine fluids. After the final incubation period, the PTEs fractions that dissolved are measured to determine the bioaccessibility (Ruby, 2004). The in vitro digestion procedure takes into account various parameters in order to best simulate plant ingestion with regard to human's physiology. The model is made up of two compartments (stomach and small intestine) and takes into consideration human body temperature, plant-to-fluid and digestive juice ratios, pH and transit times in the different compartments, chemical composition of the digestive juices and the mixing that occurs in the human body.

2.9 Analytical Methods for Metal Analysis in Medicinal Plants

As it has already been stated, non-conventional medicine has a very large patronage (herbal medicine). However, owing to their nature and sources, herbal medicines can be contaminated with toxic heavy metals which may impose serious threats on the health of consumers. It is critical to analyse source materials for PTEs/HMs in order to ensure that their concentrations meet the related standards or regulations limiting their concentrations in herbal medicines. In this section, different analytical methods for analysis of PTEs in herbal medicines have been discussed.

A variety of analytical techniques, have been employed to examine product extracts as well as clinical samples in case reports involving suspected heavy metal toxicity, in order to screen for heavy metal contamination (Perharic *et al.*, 1994). These techniques include the Atomic Absorption Spectroscopy (AAS), Atomic Fluorescence Spectroscopy (AFS), Graphite Furnace Atomic Absorption Spectroscopy (GFAAS), Hydride Generation Atomic Absorption

Spectroscopy (HGAAS), Inductively Coupled Plasma-Emission Spectrometry (ICP-AES), Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), X−ray fluorescence (XRF), Electron Microprobe (EM), Flame Photometer (FP) , Instrumental Neutron Activation Analysis (INAA), High-Performance Liquid Chromatography (HPLC), Differential Pulse Polarography, Disposable Electrochemical Sensors, and Anodic Stripping Voltammetry (ASV).

These instruments accurately measure elements in environmental sample to parts per billion (ppb) concentrations i.e. µg L^{-1} and µg Kg^{-1} liquid and solid samples respectively. Before any element is determined with any of these instruments, pre-treatment with acidic extraction or acidic oxidation digestion and in some cases chelation may be required. The significance of pre-treatment is that all elemental species is converted into the inorganic form for easier detection and measurement. These laboratory assays and instruments measure elements accurately but they are expensive to operate and maintain. They are also bulky, requiring fully equipped and staffed laboratories to maintain and operate. Below is the list of the different instruments and their functions:

INAA provides a chemical matrix including REEs (rare earth elements), which are important in determining the uniformity of the consumed material and in particular the clay minerals (where the bulk of the REEs reside). FP uses flame atomic emission and a filter to quantify Li, Na, K and Ca in liquid samples.

AAS is a technique in which the absorption of light by free gaseous atoms in a flame or furnace is used to measure the concentration of atoms. AFS, a technique in which electronic transitions of atoms in a flame, furnace, or plasma are excited by light, which on return to the ground state, give off part of this energy as fluorescence.

HPLC detects based on the polarity or lipophilicity concentrations. As ions, metals lack the quality of lipophilicity. However, metals can be chelated to an appropriate agent that can confer on the metal ion the quality it lacks and subsequently separated and analyzed by UV at an optimum wavelength. Yang *et al* (2004) also reports of applying this technique to measure Cu, Zn, and Ni in Chinese herbal medicine.

XRF and ICP‑MS also provide a chemical composition of sample. The EM is particularly important in the analysis of thin sections where the chemical composition of mineral grains and matrix material is necessary. In some cases, micro transects can be established to analyse variations in particular chemical elements including Na, Al, Mg, Si, P, S, K, Ca, Ti, Mn, Fe and Ba, with P, S, K, Fe and Ca being of particular importance to geophagy (Mahaney *et al*., 2005). The energy dispersive XRF also known as the non‑destructive method which offers direct can be used to analysed power herbal medicine.

2.10 Bioaccessibility studies of medicinal plants in Ghana

Studies that ascertain heavy metal contaminations in medicinal plants are well documented in the Ghanaian literature (e.g. Annan et al., 2013; 2010; Nkansah et al., 2016**;** Sarpong et al., 2012). It is evident that, no bioaccessibility research has been carried on the medicinal plants in Ghana to determine bioavailable forms of PTEs and the likely health implications. Since there is paucity of data available on bioaccessibility of medicinal plants in Ghana, it is imperative that studies are carried out on medicinal plants found in the Accra Metropolis to bridge the knowledge gap. This dissertation is structured as:

- ✓ **Chapter 3** describes the methodology of the study. Captures the study site, the digestion process, the PTEs analysis, bioaccessibility or bioavailability evaluation and the assessment tools used for risk analysis.
- ✓ **Chapter 4** presents results of analysis; evaluates results using the statistical tools and discusses these results to expose the effects that may be posed to the consumer whiles presenting a long-term data for comparative and further studies.
- ✓ **Chapter 5** provides a general conclusion and emphasizes the major findings of this study, as well as recommendations for further studies.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Description of the Study Area

Accra Metropolis is located in the Greater Accra Region with total land size of 1.4% of Ghana, and serves as the capital city of Ghana, Fig. 1. It lies on latitude 5°46'-5°28N and longitude 0°24' W-0°2'E. The Metropolis is located along the southern coast of the region and had an estimated population of 2.27 million as at 2012 (Akrong *et al*,. 2012). The Metropolis consists of ten (10) Sub Metropolitan Districts made up of 72 communities. The Metropolitan Area lies in the dry equatorial climatic zone. It experiences two rainy seasons. The first begins in May and ends in mid-July while the second season begins in mid-August and ends in October. The average annual rainfall is about 730 mm which is the lowest in the country. There is very little variation in temperature throughout the year. The mean monthly temperature ranges from 24.7°C in August (the coolest) to 33°C in March (the hottest) with an annual average of 26.8°C (Akrong *et al.*, 2012; Dickson, 2001).

In the Metropolis, there are several diversified medicinal plants. Some of which are found in pristine environments, whereas several of these plants are located in the human impacted areas including those sited close to major roads, drainage systems, industrial zones, residential areas, construction and dumping sites. These medicinal plants are used for various sickness and diseases by many of the inhabitants. Thus samples of herbal plants were selected and collected from three geographical locations of distinct activity (Fig 3.1), pristine environment and two anthropogenic impacted locations, described below.

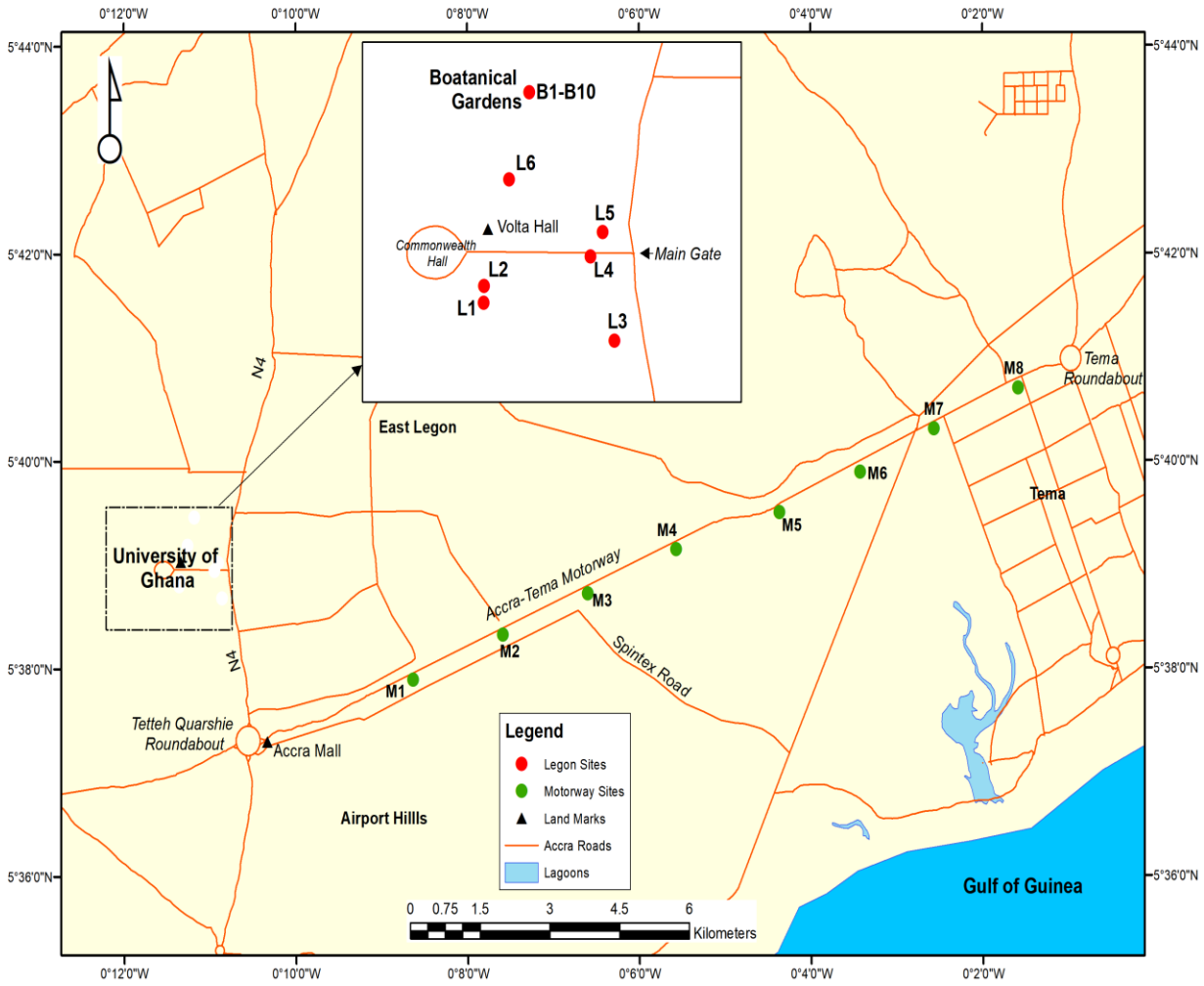

Figure 3.1: Map showing the geographic areas of the sampling sites within Accra Metropolis.

Tema Motorway (TM): This site stretches from the Tetteh Quarshie Interchange to the Ashiaman Roundabout which is well known for its high dense vehicular movement with emission of harmful gases into the atmosphere. Construction firms, vegetable farms and several processing companies and institutions engaged in activities that emit waste into the environment are found along this road. Many hawkers do sell food stuffs at the two toll booths at the entrance and exit of this major highway respectively, Table 3.1.

University of Ghana (UG) campus: University of Ghana, Legon is situated about 12 kilometres (7.5 miles) north-east of the city center in the Accra Metropolis, lying between latitude: 5° 38' 59.99" N and longitude**: 0**° 10' 60.00" E. The University is also very close to the major Madina highway leading to Aburi and other adjoining towns. Generally, there are several human activities in and around the campus (see Table 3.1).

The Botanical Garden (BG): This is a pristine environment, and is the hub of many plant species for both medicinal and non-medicinal use; which is sited inside in the University of Ghana. The Botanical Garden was chosen to serve as reference to compare with the anthropogenic impacted sites: Tema Motorway (TM) and UG campus. This would afford the opportunity to evaluate the differences if any between levels and distribution of PTEs in the medicinal plants from the virgin and human impacted areas respectively.

All the samples of the medicinal plants and their corresponding soils on which they grow were collected from the three distinct activity oriented areas. The activities in these selected locations which impact the plants health are defined in Table 3.1.

3.2 Containers and cleaning process

New Pyrex glass volumetric flasks were used. The flasks were rinsed with de-ionized (DI) water after a wash in a warm liquid soap solution. These were then immersed in 10 % HNO_3 at room temperature for three days. Flasks were again rinsed three times with DI-water, and then immersed in 50 % HNO_3 bath at 90 ºC for 24 hours. Flasks were further rinsed with DI-water several times and placed overnight in a clean oven at 60 ºC. The flasks were then removed from the oven and allowed to cool-down and double bagged in re-sealable new polyethylene bags and stored.

Table 3.1: Description of sites where herbal plants were collected: Pristine verses Human activity impacted areas**.**

Tema Motorway (TM)

Sites	M1	M2	M3	M4	M5	M6	M7	M8
Human Activity	Sited 3 metres away from the toll booth: refuse burning and dumping, defecating, vehicular emissions and littering of food wastes from hawkers Atmospheric particulate depositions	Sited 250 metres away from the toll booth: vehicular exhausts; constructional works; burning sites; and atmospheric particulate depositions	Refuse dumping site, farming activities, manures, agrochemical usage, atmospheric particulate depositions, vehicular emissions	Lakeside estate: refuse dump and atmospheric particulate emissions, wastewater from residential areas, vehicular emissions	Light industrial area-close to a pond used for irrigation: farming activities; fertilizers and pesticides; dumping site and motor vehicle exhausts	Around Fouta Industrial area-water logged: Farming activities; use of agrochemicals; ongoing constructions, dusty area and a dumping site.	Around Sherkina Herbal center-untreated wastewater from residential area; water logged; dumping site; constructional sites and vehicular emissions.	Around Ashiaman roundabout: vehicular emissions and littering of food wastes from hawker, constructional sites and refuse burning.
Herbs	*Hyptis sp* (flower & fruits) *Cassia occidentalis* *Euphorbia* sp *Phyllantus* sp	*Passiflora suberosa* *Lamiaceae sp* *Caltropis procera*	*Zanthoxylum sp* *Phyllanthus niruri* *Azadirachta indica* (neem) *Euphobia hirta* (Green variety)	*Physalis angulata* *Calotropis procera* *Ricinus communis* (castor oil)	*Ricinus communis* *Euphorbia hirta* (red variety) *Desmodium styracifolium* *Hyptis sp*	*Euphorbia hectare* (red) *Hyptis sp* *Sesame sp*	*Lamiaceae* *Calotropis procera*	*Calotropis procera* *Cassia occidentalis* *Euphorbia* sp *Phyllantus* sp

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UG CAMPUS

Sites	L1	L2	L3	L4	L5	L6
Human Activity	Legon Hall car park: close to a beauty salon; discharge of untreated wastewater from salon; refuse dumping; and vehicular emissions from major roads.	Legon Hall kitchen: indiscriminate disposal of untreated wastewater from the kitchen; vehicular emissions; atmospheric	Around Bush Canteen: dumping site; farming activities-agrochemicals; constructional sites; littering of food wastes from hawkers and vendors;	Around Jones Quartey Building (JQB): atmospheric particulate depositions; near construction sites and	Old Law Building: atmospheric particulate depositions; refuse dump and burning sites; vehicular exhausts and near	New N Block Building: very near to vehicular emissions; refuse dumping and burning sites; close to constructional sites; and atmospheric

		fall out and close to power generators.	close to heavy traffic vehicular emissions and atmospheric particulate depositions	electric power generators	construction sites	particulate depositions
Herbs	*Euphorbia hirta* *Dissotis sp* *Desmodium sp*	*Alternathera pungens* *Lantana camara* *Phyllantus amarus*	*Desmodium adscendens* *Cassia occidentalis* (flowers and fruits) *Cassia occidentalis* (physiological stage) *Euphorbia sp* *Ricinus sp*	*Cassia occidentalis* (physiological stage)	*Desmodium sp* *Phyllantus sp*	*Desmodium sp* *Euphorbia sp* *Euphorbia hirta* *Ricinus sp* (flowers and fruits)

BOTANICAL GARDEN
Pristine Environment

Sites	**BG 1**	**BG 2**	**BG 3**	**BG 4**	**BG 5**	**BG 6**	**BG 7**	**BG 8**	**BG 9**	**BG 10**
Human Activity	None	None	None	None	None	None	None	None	None	None
Herbs	*Desmodium sp*	*Lantana camara*	*Azadirachta indica* (neem) *Desmodium adscendens*	*Cassia alata*	*Cymbopogon citratus* (Lemon Grass)	*Solanum torvum*	*Euphorbia hirta*	*Phyllantus sp*	*Physalis angulata*	*Ricinus communis* (castor oil) *Passiflora suberosa* *Ricinus sp*

3.3 Reagents

All chemicals used were of trace metal free grade. Ultrapure water from a Millipore Milli-Q system (18 MΩ cm resistivity) was always used. Pure concentrated acids HCl (36%) were obtained from Fisher Co. (Denver, USA), $HClO_4$ (70%) and H_2SO_4 (60%) from Acros (New Jersey, USA) and HNO_3 (69%, Suprapure) from Fluka (Munich, Germany) were utilized. On the other hand, extractant solutions were prepared according to the following procedure:

Solution A (glacial acetic acid, 0.11 mol l^{-1}): 25 ml of glacial acetic acid (Fluka, ACS reagent, ≥ 99.8%) was added to about 500 ml of deionized water and made up to 1000 ml. Two hundred and fifty (250) ml of this solution (acetic acid 0.44 mol l^{-1}) was diluted to 1000 ml to obtain a 0.11mol l^{-1} acetic acid solution.

Solution B (0.01M volume of $CaCl_2$,): 0.022g of calcium chloride (Fluka, Puriss. p.a., for AAS, ≥ 99.0%) was dissolved in 20 ml distilled water; this solution was acidified with 5 ml of 2 mol l^{-1} HNO_3 solution.

Solution C (0.01M 0.1M triethanoalmine): the triethanoalmine buffer solution (Fluka, Trace Select Ultra, 30%) was used as supplied by the manufacturer.

Solution D (Diethylenetriaminepentaacetic acid (DTPA), 0.005 mol l^{-1}): 0.100g of DTPA (Carlo Erba (Chaussee du Vexin, France) ACS reagent, ≥ 97%) was dissolved in 30 ml deionized water. The solution was acidified with concentrated HNO_3 to pH 2 ± 0.1 and made up to 50 ml.

3. 4. Sample Collection and Preparation

3.4.1. Medicinal plants sampling

A total of 57 traditional herbs consisting of 20 different species employed in the treatment of various ailments (Table 3.1) were sampled beginning September 2017 to October 2017 from two different anthropogenic environmental settings and one pristine area within the Metropolis. Each medicinal plant was collected into previously cleaned plant press kit and authenticated at the Ghana Herbarium in the Department of Plant and Environmental Biology, University of Ghana, Legon. Collected samples were cleaned and air-dried in a chamber. The dried samples were blended and stored in a pre-cleaned polyethylene zip lock bags until digestion and analysis.

3.4.2. Soil Sampling

Composite soils (about 1 kg) each was taken at the different sites where the medicinal plants were obtained. The soil was scooped out at a depth of 0-10 cm, using an auger into acid-cleaned polypropylene sampling bags and then stored on ice before delivery to the laboratory. The ultraclean free– metal sampling protocol described by Gill and Fitzgerald (1985) was employed. All mixed samples collected were air dried at room temperature, ground gently with agate pestle and mortar, sieved with 150 μm mesh nylon sieve for homogenization, and then placed in plain self – sealing polyethylene bags until analysis.

3.5 SAMPLE ANALYSIS

3.5.1 Physicochemical parameters

Soil properties: pH, organic matter (OM), soil colour and electrical conductivity (EC) were determined based on the sample fraction 150 µm to obtain basic information about the soil conditions on which the traditional plants were obtained.

3.5 1.1 Colour determination: The Munsell soil colour chart was used to determine the actual colours of the soil samples.

3.5.1.2 Soil pH and Electrical conductivity (EC)

Electrical conductivity (EC) and pH were measured in a soil-deionized water suspension (soil: water, 1:2.5 (w/v) by a calibrated pH meter (Mettler Toledo MP 220) and conductivity meter (Phywe 13701.93) respectively (ISO, 2002a). The conductivity meter was calibrated using a 0.01M KCl solution with corresponding conductivity of 1411 µs/cm at 25℃. Specifically, the pH and EC of each sample were measured by placing 10 g of soil into a 50 mL beaker and adding 25 mL of water. The sample particulates were allowed to settle for 1 hour and then the pH and EC of the supernatant solution were measured.

3.5.2. Organic matter (OM) Determination

Samples were analysed for organic matter (OM) by loss on ignition (LOI) method. Approximately 2 g of the sample was weighed directly into a crucible and placed in a pre- heated oven at 105^{o}C overnight. The samples were removed and cooled to room temperature in a desiccator before being reweighed again. The weight loss was used in calculating the moisture content (MC). The samples

were then placed back into the furnace, and heated to 550ºC, for two hours (Allen *et al.*, 1974), allowed to cool overnight and reweighed to determine the organic matter content.

3.5.3 Total PTEs concentration in medicinal plants

Approximately 3g of each blended plant material was placed into a 100 ml Pyrex volumetric flask and 25ml of HNO_3 and H_2SO_4 (3:7) added. The mixtures were allowed to cool overnight after which they were heated on a hot plate at 110 °C in a fume chamber for about 6 hours until the production of reddish-brown fumes ceased and the solution turned colourless or pale yellowish. The completely digested samples were allowed to cool at room temperature, then deionized water added up to the 100 ml mark and filtered. The concentrations of the selected PTEs: Cd, As, Cr, Cu, Zn, Ni, Pb, Mn and Fe, in the final solutions were then determined with an atomic absorption spectrometer (AAS, Hitachi 180–30, Japan).

3.5.3.1 Total PTEs concentration in soils

One gram of each sieved soil sample (< 105 µm) was digested with 25 ml of HNO_3 and H_2SO_4 (3:7 mixture) on a hot plate at 110ºC for about 6 hours until the solutions turned colourless. This was then diluted to a 100 ml volume, filtered and analyzed for total metal concentrations. The instrumental detection limits in soils were: Cd (0.0008), Cr (0.0.003), As (0.03), Cu (0.0015), Zn (0.0015), Ni (0.006), Mn (0.0015), Pb (0.0015), and Fe (0.005) (all in mg kg^{-1}) respectively.

3.5.4 Chemical extraction procedure for PTEs in soils

The environmental availability of trace elements (Cd, As, Cr, Cu, Zn, Ni, Pb, Mn and Fe) in soils was assessed using the widely adopted extraction methods of acetic acid (Pueyo *et al.*, 2003;

Davidson *et al.,* 1998), $CaCl_2$ (Alvarenga *et al.*,2008) and diethylenetriaminepentaacetic acid (DTPA) (Poggio *et al.,* 2009). The metal fractions were operationally denoted as mobilizable (F1), effectively bioavailable (F2 i.e. actual biological uptake or absorption) and potentially bioavailable (F3, the pool that could be released and absorbed). Since acetic acid is used as the extractant in the sequential extraction procedure proposed by BCR, the first step of modified BCR speciation procedure was applied to assess the mobilizable metals in soils (Rauret *et al.,* 2000). The $CaCl_2$ extraction procedure was further applied to reflect the mobile or effectively bioavailable PTEs. Finally, the DTPA method was employed for the potentially bioavailable pool of PTEs (Table 3.2), a 2 g sample was used. The extraction was performed by shaking with an end-over-end shaker at 30 rpm (Ciceri *et al.,* 2008). Extractant volumes were also increased to maintain a constant solid: solution ratio, since it is known that this can affect the results obtained (Rauret et al., 1999). The PTE recovery was calculated by comparison of the sum of all fractions with the total PTE for each sample.

Step 1: 40 ml volume of acetic acid (0.11 $moll^{-1}$) was added to 2g of dry sieved soil in a 200 ml polypropylene wide–mouth bottle. The bottle was shaken for 16 hrs, (overnight) at 25^0C temperature on an end over end shaker operating at 30 rpm. No delay occurred between the addition of the extractant solution and the beginning of the shaking. The extractant was separated from the solid residue by filtration using cellulose acetate paper into a polyethylene container and stored at 4℃ until analyses for metals. The residue was washed with 40 ml of deionized water by shaking for 15 min and the washings discarded, taking care not to discard any of the solid residue.

Step 2: 20 ml of 0.01M volume of $CaCl_2$ (adjusted to pH 2 with nitric acid) was added to 2.0 g of soil. The extraction procedure was performed as described in step 1 for 3h at 25℃.

Step 3: 2.0 g of soil in 20 ml volume of 0.005M DTPA + 0.01M $CaCl_2$ + 0.1M triethanoalmine (TEA) at pH 7.3 shaken for 2h at 25℃ and the extract separated as described in step 1.

Table 3.2: Summary of chemical extraction procedure

Steps	**Reagents**	**Extraction conditions** (nominal target phases)
1	Acetic acid (0.11 mol l^{-1})	Mobilizable and acid-soluble PTEs (F1)
2	Calcium chloride (0.01 mol l^{-1}) adjusted to pH 2	Effectively bioavailable PTEs (F2)
3	0.005M DTPA + 0.01M $CaCl_2$ + 0.01M triethanoalmine adjusted to pH 7.3 with HNO_3	Potentially bioavailable pool of PTEs (F3)

3.5.5 Simple Bioaccessibility Extraction Test (SBET)

To determine PTE bioaccessibility for humans, a modification (Yang et al., 2003) of the original Physiologically Based Extraction Test (PBET), described by Ruby et al. (1996) and Ruby (2004) was employed. This determination consists of two sequential processes namely a gastric and intestinal digestion, with each phase carried out employing simulated human conditions (enzymes, pH and temperature). Using this method, the reported bioaccessibility is a measure of the amount of the ingested element that is soluble due to simulated human gastric functions and has the potential to cross the intestinal wall. The extraction process is as follows:

- **Phase One**: Approximately 10 g (accurately weighed) of the plant sample was placed into a 50 ml Sarstedt tube and treated with 80 ml of pepsin (1% (wt/vol) in saline

(154 $mmoll^{-1}$). The pH of the solution was adjusted to 1.8 with dilute HCl. The mixture was shaken at 100 rpm in a thermostatic bath maintained at 37℃ for 4 h. After 4 h, a portion of the supernatant (60 ml) was sampled using a disposable syringe and filtered.

- **Phase Two**: The pH of the remaining extract of the previous phase was adjusted to 2.5 with 2M HCl. To the gastric digest residue, 60 ml of mixed solution of pancreatin (3% (wt/vol) and amylase (1% (wt/vol) in saline and 7.5 ml of bile salts (0.15% (wt/vol) in saline were added. The sample pH was adjusted to 7 with saturated $NaHCO_3$. The plant–solution ratio was maintained at a constant. The suspension was shaken at 100 rpm in a thermostatic bath maintained at 37℃ for 4 h. After 4 h, a portion of the supernatant (60 ml) was sampled using a disposable syringe and filtered. All extracts (gastric and intestinal) were analysed by an atomic absorption spectrometer (ASS) (Hitachi 180–30, Japan).

3.6. Quality assurance and quality control

Appropriate procedures and precautions were taken to ensure reliability of the results. Deionized water was used throughout the study. Twenty percent HNO_3 was used to clean glassware and HDPE bottles and the reagents were of trace metal grade. Standards were prepared for each metal from their stock solution to calibrate the AAS instrument. Replicate analyses were done with reagent blanks and standards after every ten (10) sample measurement to ensure precision and accuracy of the analytical results. For validation of the analytical procedure, standard reference materials (SRM) were obtained from the International Soil-Analytical Exchange for soil (ISE sample 999) and the National Institute of Standard and Technology (NIST) for plant (SRM-1570). The recovery rates ranged from 90-110% for all elements.

3.7. DATA ANALYSIS

3.7.1. Pollution Assessment

In order to assess the degree of soil pollution (P_{deg}) with a particular PTE, the single-factor pollution index (P*i*) was calculated as the ratio between the measured PTE content (C*i*) in soil and its reference value (S*i*), according to (Cao *et al.*, 2013): a reference element is the one characterized by low occurrence variability. The most common reference elements are Sc, Mn, Ti, Al and Fe (Sutherland, 2000; Pacyna, 1990). This work uses the reference values of Taylor and Mclennan (1995) as well as the shale values for iron and manganese. Pollution index is used to differentiate PTEs originating from human activities and those of natural sources. This is determined by the relation:

$Pi = Ci/Si$

The P*i* classifies the following pollution levels: $Pi \leq 1.0$, clean (safe); $1.0 < Pi \leq 2.0$, slightly polluted; $2.0 < Pi \leq 4.0$, moderately polluted; $4.0 < Pi \leq 6.0$, heavily polluted, and $Pi > 6.0$, extremely polluted.

The sum of the pollution factors of all the elements in the sample gives the degree of pllution as indicated in the equation below:

$$P_{deg} = \sum Pi$$

Four categories have been defined for the degree of pollution as follows: <8 low degree of pollution 8-16 moderate degree of pollution, 16-32 considerable degree of pollution and >32 very high degree of pollution.

3.7.2. Index of geoaccumulation (Igeo)

The index geoaccumulation (Igeo) was originally used with bottom sediment by Müller (1969) (1969). It can also be applied to the assessment of soil contamination. This contamination assessment index has been cited by many researchers in environmental studies (Guo *et al*.,2014; Abrahim *et al.*, 2008; Loska *et al.*, 2004) and is defined by the equation:

$$\text{Igeo} = \log_2 \frac{Cn}{1.5\ Bn}$$

where Cn is the measured concentration of the metal ions in soil (mg/kg), Bn is the geochemical background value (Taylor and McLennan, 1995) of the corresponding metal (mg/kg), the coefficient 1.5 is used to detect very small anthropogenic influences (Loska et al., 2004). Müller (1979) proposed seven sediment quality classes associated with the geoaccumulation index as shown in Table 3.3

Table 3.3: Classes of the Geoaccumulation Index used to define sediment quality

Igeo value	Igeo Class	Quality of Sediment
< 0	0	Unpolluted
0-1	1	From unpolluted to moderately polluted
1-2	2	Moderately polluted
2-3	3	From moderately to strongly polluted
3-4	4	Strongly polluted
4-5	5	From strongly to extremely polluted
> 5	6	Extremely polluted

(Müller, 1979)

3.7.3. Bioaccumulation Factor (BAF)

PTEs concentrations of soils to plants were calculated on dried weight basis. The transfer factor (TF) expressed the ability of the herbal plant to accumulate a particular PTE with respect to its concentration in the soil. The factor was calculated as,

$$BAF = \frac{C_{plant}}{C_{soil}}$$

where,

C_{plant} is the PTE concentration in plants and C_{soil} is the toxic element concentration in soils (Zhuang *et al.*, 2009).

3.7.4. In Vitro Bioaccessibility

The in vitro bioaccessibility was calculated as a percentage of the total fraction measured by nitric-sulphuric acid digestion using the formula:

$$Bioaccessibility\ (\%) = \frac{C_{gid}}{C_t}\ \text{X}\ 100$$

where C_{gid} (in mg/kg of sample) denotes the concentration of the PTE determined in the supernatant resulted from gastro-intestinal digestion, while C_t is the total content of this element determined in the medicinal plant.

3.7.5. Risk Assessment of PTEs

Estimated Daily Intake (EDI)

The average daily intake (EDI) estimated how much of the element was consumed daily and depended on both the element concentration in medicinal plant and the quantity consumed of the respective traditional plant (US EPA, 2007;1986). EDI was calculated in mg/kg/day as:

$$EDI = \frac{C_{plant} \times IR_{plant}}{BW}$$

where,

C_{plant} is the element concentration in medicinal plant (mg/kg, dry weight basis), IR_{plant} is the ingestion rate or the daily average consumption of medicinal plant (2000mg/day for children and 4000mg/day [dry weight] for adults) based on a previous study (Kuranchie, 2012) . BW is the body weight of the exposed individual (kg). The BW of an adult Ghanaian was estimated as 70 kg and 40 kg for children (10-17yrs) (Ministry of Health, Ghana)

Hazard Index (HI)

The health risks from consumption of a particular medicinal plant by the consumers were assessed based on the hazard index (HI). The HI expressed the non-carcinogenic risks or the level of human exposure associated with the consumption of plant material. If the HI value was less than 1, the exposed population was unlikely to experience obvious adverse effects during life time (WHO, 2003).

$$HI = \frac{EDI}{RfD}$$

where, EDI (mg/kg) is the average daily intake of PTE and RfD is the oral reference dose (mg/kg); which is regarded as an estimation of daily exposure of the human population that is likely to be without an appreciable risk of deleterious effects during a lifetime (US EPA, 2014).

3.7.6. Statistical analysis and data treatment

A statistical analysis was carried out using SPSS 20 (SPSS Inc. Relationships between various variables were determined using the Pearson correlation coefficients (r). Regression models were performed by stepwise selection with a significance level of $p < 0.05$ for variables to remain in the predictive equations. Other statistical analyses including mean, standard error (SE), maximum, minimum and coefficient of variation (CV), and step - wise linear regressions were carried out in SPSS 20.0 and Microsoft excel. Independent T-test was also performed using SPSS 20.0.

CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.1. Ethno-botanical Studies

The use of medicinal plants has increased lately among the Ghanaian population as a result of their essential phytochemicals and elements needed by man to fight against certain diseases (gonorrhoea, helminthiasis, hypertension, diabetes, jaundice, etc). However, there is a global concern for their use because of reports of acute and chronic intoxication, as herbal plants could be contaminated with PTEs resulting from the intensified anthropogenic activities, a threat to the urban environment and human life. Several of these products are taken in raw or administered as herbal concoction or other modes. However national surveillance to check for quality, safety or standard of these class of products is lacking. Thus the traditional herbal medicine is mostly unchecked. Accordingly, there is the need for continuous and regular monitoring programmes that would ensure that the levels of these toxic metals in traditional medicinal plants do comply with existing regulations to safeguard the health of the consuming populace. In this study, a total of 56 medicinal plants were collected from the listed geographical locations and analysed (Table 3.1, in Chapter 3)

Table 4.1 summarizes the information obtained from studies into the indications and actions of these medicinal plants through extensive literature survey. In all, 20 different species belonging to 18 families were identified. The table also includes the mode of preparation and the relative importance of species known locally. The part of the medicinal plants used in the preparation was mostly leaves with bark being the least. Analysis of these species yielded 18 genera and 15 families (Table 4.2). *Euphorbiaceae, Caesalpinaceae, Phyllanthaceae, Solanaceae,* and *Passifloraceae,* each had 2 medicinal plant species (13.33%). The remaining families gave single plants (6.67%).

Table 4.2 further gives statistical distribution of the plant species from the selected locations in Greater Accra. On the whole, the study revealed a high degree of ethnobotanical novelty of plants at the various sampling locations of which many Ghanaians use as traditional folk medicine.

Table 4.1. Ethno-medicinal plants used in the study

Plants	Family	Local Name (Asante Twi)	Parts Used	Mode of preparation	Route of ADM	Ailment Treated
***Alternanthera pungens* Linn.**	Amaranthaceae	Nkassenkasee	Leaves Roots Whole plant	Decoction Paste	External Internal	Rheumatism, dysentry, dystocia, rectal prolapse, dysmenorrhea.
***Azadirachta indica* A. Juss**	Meliaceae	Gyedua	Leaves Seeds Stem-bark Root-bark	Infusion, Decoction Tincture Powder	External Internal	Ringworm, fever, hepatitis, jaundice, lumbago, malaria, intestinal helminthiasis, wounds, pharyngitis.
***Cassia/Senna alata* Linn.**	Caesalpinaceae	Osempi, Duawusu	Young leaflets	Infusion, Decoction Tincture Powder	Internal External	Constipation, eczema, gonorrhoea, ringworm, dermtitis, shingles.
***Cassia/ Senna occidentalis* Linn.**	Caesalpinaceae	Mmofra borode, Ananse borode	Seeds Whole plant Roots Leaves Flowers Stem	Decoction Tincture Infusion Powder	Internal External	Ringworm, jaundice, edema, angina peetoris, dracontiasis, wounds, fever, helminthiasis, hypertension.
***Calotropis procera* Ait. f.**	Apocynaceae	Mpatu-asa	Stalk stem roots leaves flowers	Infusion, Decoction Tincture Powder	Internal External	Boil, parotitis, conjuctivitis, ringworm, aphthous ulcer, dracontiasis, diarrhoea, skin ulcers, abdominal pain, toothache, lactation failure, migraine, dystocia, catarrh, female infertility, sinusitis, snake bite, dermatitis, constipation, sickle cell anaemia.
***Cymbopogon citratus*(D.C) Stapf**	Poeceae	Ti-ahaban	Leaves	Decoction, Infusion, Tincture	Internal	Fever, asthma, catarrhal, cholera, diarrhoea.

***Desmodium adscendens* (Sw.) DC**	Fabaceae	Akwamfunu Nkatenkate Ananse nkatee	Aerial parts	Decoction Infusion Tincture Capsule	Internal	Asthma, abdominal colic, cramps.
***Dissotis rotundifolia* (Sm) Triana**	Melastomataceae	Boreada, Borekere	Leave Aerial parts Roots	Decoction Powder Tincture	Internal	Abdominal pain, asthma, colds, cough, rheumatism.
***Euphorbia hirta* Linn.**	Euphorbiaceae	Animakoa	Leaves	Decoction, Infusion liquid extract Tincture	Internal	Asthma, bronchitis, catarrh, diarrhoea
***Hyptis suaveolens* Poit.**	Lamiaceae		Leaves	Decoction	Internal	Filariasis
***Lantana camara* Linn.**	Verbenaceae	Anansedokono	Leaves	Decoction Juice liquid extract	Internal External	Fever, Jaundice, wound, bronchial trouble, purgative.
***Phyllanthus fraternus* Brunel &Roux.**	Phyllanthaceae	Awommaa-guwakyi	Leaves	Decoction Infusion Tincture Liquid extract	Internal	Diabetes, Hypertension, liver cancer, hepatitis, kidney stones.
***sPhyllanthus niruri Var amarus*(Schum .et Thnn.)**	Phyllanthaceae	Awomma-guwakyi	Whole plant	Decoction	Internal	Abdominal pains, snake bite, dystocia
***Passiflora foetida* Linn.**	Passifloraceae		Leaves	Liquid extract	External	Wound
Passiflora incarnata	Passifloraceae		Leaves Roots	Infusion Powder Liquid extract	Internal	Nervous unsuety, insomnia, hysteria, epilepsy.
***Physalis angulata* Linn.**	Solanaceae	Tutotuto Totototo	Shoot Leaves	Decoction	Internal	Edema, female infertility, palpitation.

***Ricinus communis* Linn.**	Euphorbiaceae	Adedenkruma	Seeds Roots Leaves Friuts	Decoction Liquid extract	Internal	Keratoderma, dermatitis, constipation, headache, lumbago, rheumatism, gleurisy, sciatica.
Sesamum indicum	Pedaliaceae	Sesame	Seed	Chewing	Internal	Food supplement
***Solanum torvum* Swartz**	Solanaceae	Asama-ntorewa, Bedura	Fruits	Fresh fruit Powder Tincture	Internal	Anaemia, coughs, splenomegaly, stomach ache
***Zanthonxylum zanthoxyloides* (Lam.)Watern**	Rutaceae	Okanto Yea	Root Stem Bark	Decoction Tincture Liquid extract	Internal	Arterial hypertension, fevers, fibrositis, impotence, oedema, sickle cell, small pox.

ADM = administration

Table 4.2: The statistical distribution of the plant species from the selected locations in Accra Metropolis

Plants	Family	Frequencies		
		TM	UG Campus	Botanical Garden
***Alternanthera pungens* Linn.**	Amaranthaceae	0	1	0
***Azadirachta indica* A. Juss**	Meliaceae	1	0	1
***Cassia/Senna alata* Linn.**	Caesalpinaceae	1	0	1
***Cassia/ Senna occidentalis* Linn.**	Caesalpinaceae	0	3	0
***Calotropis procera* Ait. f.**	Apocynaceae	3	0	0
***Cymbopogon citratus*(D.C)**	Poeceae	0	0	1
***Desmodium adscendens* (Sw.) DC**	Papilonaceae	1	4	2
***Dissotis rotundifolia*(Sm) Triana**	Melastomataceae	0	1	1
***Euphorbia hirta* Linn.**	Euphorbiaceae	4	4	1
***Hyptis suaveolens* Poit.**	Lamiaceae	3	0	0
***Lantana camara* Linn**	Verbenaceae	0	1	1
***Phyllanthus niruri Var amarus*(Schum.et Thnn.)**	Phyllanthaceae	1	1	0
***Passiflora foetida* Linn.**	Passifloraceae	1	0	0
Passiflora incarnate	Passifloraceae			
***Physalis angulata* Linn.**	Solanaceae	1	0	0
***Ricinus communis* Linn.**	Euphorbiaceae	3	3	0
Sesamum indicum	Pedaliaceae	1	0	0
***Solanum torvum* Swartz**	Solanaceae	0	0	1
***Zanthonxylum zanthoxyloides* (Lam.)Watern**	Rutaceae	1	0	0

TM = Tema Motorway; UG = University of Ghana

4.2. Physicochemical parameters of soils

Soil colour, pH, conductivity and organic matter content values of the soils are summarized in Table 4.3. The results demonstrate varied distinct measurements depending on the environmental setting and its prevailing human activity (UG Campus and Tema Motorway [TM]) versus the virgin Botanical Garden (pristine environment). The pH of the soils in all the 3 studied locations ranged from acidic (6.30) to slightly alkaline (8.20) in nature.

Most of the soil samples from all the sites contained moderate to high amounts of soluble salts corresponding to greater electrical conductivity, generally larger than 200 μScm^{-1} (Table 4.3) except sites 2 (189 μScm^{-1}) and 3 (122 μScm^{-1}) (BG) and 2 (109 μScm^{-1}) (TM) which had lower dissolved salts. Organic matter (OM) contents varied among the sites. Tema Motorway and UG soils were richer in OM averaging (17.42%) to (11.9%) respectively compared to Botanical Garden (6.63%). Soil hues for the sampling sites fell into the dull orange, brownish black, dull brown, black and reddish brown respectively. The soils in the Botanical Garden were mainly brownish apart from Site 1 whereas the Tema Motorway and UG campus gave different colourations, Table 4.3. The brown and reddish brown colours suggest the presence of iron oxides and hydroxides which are common products of tropical weathering (Wilson, 2003).

Table 4.3: Selected physical characteristics of the soils from the study areas

Sample Locations	Sampling Sites	Colour Notation	Colour	pH	EC	% OM
Botanical Garden	1	10YR/8/8	Reddish orange	7.44	275	10.77
	2	5YR/4/8	Brown	7.30	189	4.15
	3	7.5YR/4/6	Brown	6.90	122	9.15
	4	7.5YR/4/3	Brown	7.70	216	9.09
	5	7.5YR/4/4	Brown	7.37	242	6.12
	6	7.5YR/4/6	Brown	7.87	455	3.70
	7	7.5YR/4/4	Brown	7.10	301	4.11
	8	7.5YR/5/4	Dull brown	7.35	275	6.67
	9	7.5YR/5/4	Dull brown	7.38	507	4.41
	10	7.5YR/4/4	Brown	8.20	271	8.11
UG-Campus	1	10YR/3/2	Brownish black	7.82	654	20.10
	2	7.5YR/2/1	Black	7.86	391	16.32
	3	5YR/4/4	Dull reddish brown	8.17	250	8.47
	4	5YR/4/8	Reddish brown	7.65	285	7.72
	5	5YR/4/8	Reddish brown	7.40	222	8.39
	6	7.5YR/4/6	Brown	8.03	364	10.26
Tema Motorway	1	5YR/5/6	Bright reddish brown	7.85	342	8.64
	2	7.5YR/7/4	Dull orange	7.57	109	42.52
	3	10YR/4/3	Dull yellowish brown	7.46	347	9.40
	4	10YR/1.7/1	Black	7.39	274	15.41
	5	10YR/4/4	Brown	7.41	343	37.71
	6	10YR/3/2	Brownish black	8.02	252	13.18
	7	7.5YR/7.5/6/4	Dull orange	7.99	214	4.36
	8	7. 5YR/3/4	Dark brown	7.64	312	8.14

4.3 Concentrations of PTEs in soil samples

The basic descriptive statistics of potential toxic elements (PTEs) (Pb, Cr, Cu, Ni, As, Cd, Fe, Mn and Zn) in the soils sampled from the three (3) varied environments where medicinal plants were collected are presented in Table 4.4. The studied PTEs with the exception of As were found in all the 3 compartments and differed from not detected to very high concentrations. All the soils examined in these locations showed signs of PTEs contamination with the higher

concentrations being observed at TM and UG campus sites. The overall mean concentrations of all the PTEs studied except Fe and Pb were of the order TM > UG > Botanical Garden. For example, the mean values of Cr, Cu, Mn, Zn and Ni (67.33±0.19, 28.90±1.87, 187.52±3.06, 317.95±5.05, 55.20±1.17) mg/kg for Tema Motorway and UG Campus (32.96±1.56, 12.94±0.64, 168.51±3.52, 57.18±2.24, 56.38±0.54) mg/kg were significantly higher than that of the Botanical Garden (16.52±0.57, 10.69±0.25, 59.69±2.92, 23.84±0.24, 13.46±0.13) mg/kg respectively, suggestive of anthropogenic point source contamination (e.g. vehicular emissions, burning of garbage, wastewater disposal, farming, industrial emissions or discharges, etc). On the other hand, the exceptional elevated levels of Fe are attributable to the geology which was not surprising as the brown colour of the soils measured at Botanical Garden demonstrated that. Lead (Pb) was also greater at TM compared to UG Campus and Botanical Garden. Perhaps this was be due to environmental persistency of Pb as a result of the past usage of lead in fuel or emanate from burning activities popular along this stretch of road. It might also come from the several on-going constructional works applying Pb as solder. Besides, the greater Pb levels observed at UG campus and the Botanical Garden could be linked to historic use of Pb arrowheads for hunting by early dwellers on the land. Moreover, the absence of As suggested the geology of the study area was not rich in this toxic element. Likewise, the mean levels of Cd were almost the same in all the areas showing no significant difference, implying geological influence with little anthropogenic contribution. Additionally, comparing the overall mean concentrations with EU (2002) soil quality guidelines for urban soils, only Cr exceeded the limit. Correspondingly, all Cr concentrations measured at each sampling site in the three geographical locations were far above the EU recommendation except few sites (3, 5, 6, and 8) at Botanical Garden. Similarly, Zn and Ni, were the only PTEs whose mean values at UG Campus and TM were higher than the EU recommendation. Cadmium mean level at TM was also far greater than the EU specification

Table 4.4: Overall mean concentrations of PTEs (mean ±SD, mg/kg) in the soils

LOCATIONS	Sites	Name of sites	Cr	Cd	Cu	Fe	Mn	Ni	Pb	Zn	As
	B1		24.7±0.49	2.35±0.31	5.77±0.04	86000.00 ±0.12	53.10 ±1.04	6.15±0.10	16.85±0.38	38.90±0.78	ND
	B2		35.55±0.27	1.87±0.11	23.57± 0.26	16905.00 ±0.19	76.10±1.12	6.35±0.13	26.75±0.44	16.50±0.01	ND
	B3		4.60 ± 0.32	1.31±0.05	23.35± 0.06	20575.00± 0.41	79.95±0.04	14.59±0.15	12.31±0.07	1.62±0.02	ND
	B4		22.86±0.22	1.30±0.25	5.20±0.04	7653.15± 0.49	57.00±0.10	8.66± 0.19	8.30± 0.03	46.43±0.04	ND
Botanical	B5	Pristine	8.22 ± 0.20	0.59±0.31	17.72±0.02	26325.89±0.80	79.50± 0.07	25.35±0.15	28.32±0.31	9.90±0.04	ND
Garden	B6	Environment	8.32± 0.07	1.82±0.08	5.14± 0.03	11514.85±2.53	74.86± 0.12	12.00±0.20	30.82±0.84	2.18±0.03	ND
	B7		14.21±0.28	1.00±0.24	8.05±0.03	8386.36±1.27	27.05± 0.97	24.65±0.56	43.50±0.33	15.05±0.02	ND
	B8		2.36± 0.37	1.28±0.19	4.68±0.06	14575.00±0.50	88.52±0.05	12.61±0.14	25.02±0.05	5.02±0.14	ND
	B9		21.00±0.26	1.79±0.07	7.05±0.06	6359.61±1.30	28.80± 0.88	10.03±0.27	27.65±0.23	82.85±0.18	ND
	B10		23.41±0.24	0.99±0.01	6.39±0.08	16194.31±2.46	31.99±0.10	14.24±0.11	18.20±0.26	19.95±0.03	ND
Mean			**16.52±0.57**	**1.43±0.71**	**10.69±0.25**	**21448.92±2.61**	**59.69± 2.92**	**13.46±0.13**	**23.77±0.63**	**23.84±0.24**	**ND**
Max.			**35.55±0.27**	**2.35±0.31**	**23.57± 0.06**	**86000.00±0.12**	**88.52±0.05**	**25.35±0.15**	**43.50±0.33**	**82.85±0.18**	**ND**
Min.			**2.36±0.37**	**0.59±0.31**	**4.68±0.06**	**6359.61±1.30**	**27.05± 0.97**	**6.15±0.10**	**8.30± 0.03**	**1.62±0.02**	**ND**
	L1	Legon hall car park	41.99±0.27	1.60±0.03	6.81±0.10	15635.32± 2.67	103.23±0.03	47.46±0.10	13.03±0.30	319.60±0.11	ND
	L2	Legon hall kitchen	22.27±0.28	1.92±0.02	33.89±0.09	13353.20±1.11	191.63±0.18	36.95±0.33	16.65±0.10	314.09±0.26	ND
UG Campus	L3	Bush canteen	32.38±0.29	2.57±0.32	17.67±0.14	10612.38±2.42	153.42± 0.05	65.45±0.04	27.57±0.18	157.04±0.38	ND
	L4	Jones Quartey Building	40.49±0.56	3.27±0.26	4.88±0.07	17749.76± 1.41	266.17± 0.22	67.66±0.27	10.34±0.19	38.66±0.24	ND
	L5	Old law building	15.00±0.11	3.24±0.58	8.77±0 10	24601.47± 3.37	115.02±0.52	64.31±0.51	25.10±0.05	70.29±0.31	ND
	L6	New ‘N’ Block	45.60±0.17	4.55±0.15	5.59±0.26	19340.10±0.47	181.56±0.07	56.44±0.37	23.12±0.35	43.42±0.06	ND
Mean			**32.96±1.56**	**2.86±0.17**	**12.94±0.64**	**16882.04± 1.62**	**168.51±3.52**	**56.38±0.54**	**19.30±0.59**	**157.18±2.24**	**ND**
Max.			**45.60±0.17**	**4.55±0.15**	**33.89±0.09**	**24601.47± 3.37**	**266.17± 0.22**	**67.66±0.27**	**27.57±0.18**	**319.60±0.11**	**ND**
Min.			**15.00±0.11**	**1.60±0.03**	**4.88±0.07**	**10612.38± 2.42**	**103.23±0.03**	**36.95±0.33**	**10.34±0.19**	**38.66±0.24**	**ND**

	M1	50m away from the tollbooth	68.81±0.21	4.75 ± 0.25	17.88±0.03	2530.54± 4.28	120.64± 0.17	16.80±0.13	38.92±0.30	64.60±2.12	ND
	M2	250m away from the tollbooth	57.16±0.21	3.30±0.59	34.64±0.05	18273.42± 3.14	321.67±0.34	45.51±0.30	40.82±0.39	92.35±0.12	ND
Tema											
Motorway	M3	Dumping site	70.30±0.46	4.26±0.11	26.68±0.12	2616.83± 2.32	134.88±0.58	76.44±0.37	40.19±0.83	367.78±0.59	ND
	M4	Lakeside estate	56.28±0.17	3.11±0.12	26.36±0.17	2322.37±5.60	189.96±0.23	76.67±0.25	74.96±0.47	243.90±0.15	ND
	M5	Light industrial area	28.58±0.13	4.82±0.42	91.45±0.87	22000± 3.77	124.35±0.22	59.90±0.33	41.65±0.87	980.00±0.17	ND
	M6	Around Fouta factory	134.25±0.7	4.40±0.16	10.90±0.41	26014.93±7.25	126.54±0.50	59.65±0.12	69.20±0.20	466.32±0.08	ND
	M7	Around Sherkina Herbal Center	91.30±0.45	3.75±0.08	22.70±0.06	26283.50± 5.39	181.15±0.25	79.10±0.17	4.50± 0.33	228.05±0.05	ND
	M8	150m away the Ashiaman roundabout	31.86±0.20	2.58±0.48	0.62 ± 0.01	11250.95± 8.47	300.95±0.06	27.52±0.06	32.62±0.11	100.52 ±1.01	ND
Mean			**67.33±0.19**	**3.87±0.28**	**28.90±1.87**	**12488.12± 8.47**	**187.52±3.06**	**55.20±1.17**	**42.86±0.11**	**317.95±5.05**	**ND**
Max.			**134.25±0.7**	**4.82±0.42**	**91.45±0.87**	**26283.50± 5.39**	**321.67±0.34**	**79.10±0.17**	**74.96±0.47**	**980.00±0.17**	**ND**
Min.			**28.58±0.21**	**2.58±0.48**	**10.90±0.41**	**11250.95± 8.47**	**120.64± 0.17**	**16.80±0.13**	**4.50± 0.33**	**64.60±2.12**	**ND**
EU, 2002			**10.00**	**3.00**	**100.00**	**50000.00**	**2000.00**	**50.00**	**100.00**	**300.00**	**20.00**

4.4 Source of Potential Toxic Elements (PTEs) – Correlation Coefficient Analysis

Tables 4.5 summarizes the correlation factors or coefficients *(R)* for the total concentration of PTEs and physiochemical parameters in soil samples. Values for the individual locations are presented in the Appendix A. Significant two tailed tests demonstrated statistically significant differences in the mean concentrations measured between some of the PTEs with 95% confidence. The correlation matrix amongst investigated PTEs (Table 4.5) points to:

(i) very poor or weaker correlations amongst the PTEs with other metals demonstrating that these metals did not originate from similar sources and were mutually independent. The PTEs with stronger correlations meant they might have come from common source.

(ii) statistically significant and strong positive correlation was found between Cu and Zn (0.788) and Ni and Cr. Thus, metals in each combination either were emanating from the same source or were emitted at similar concentrations.

(iii) the lack of correlation between organic matter (%OM) and all the analysed PTEs except Cu and Zn suggest a significant fraction of the metals of interest were associated with fine inorganic particles. According to McCauley *et al.* (2009), OM plays a vital role in determining the availability of metals because it is involved in supplying organic chemicals to the soil solution, which may serve as chelates and increase metal availability to plants.

(iv) PTEs did not have any correlation with pH and EC indicating that, these parameters had no impact on the metals.

Table 4.5: Overall mean Pearson correlation for soil data collected during the study period. (For all the 3 different locations).

	Cr	Cd	Cu	Fe	Mn	Ni	Pb	Zn	pH	EC	MC	OM
Cr	1.000											
Cd	0.616**	1.000										
Cu	0.449*	0.403	1.000									
Fe	-0.110	-0.014	-0.044	1.000								
Mn	0.423*	0.476*	0.155	-0.136	1.000							
Ni	0.723**	0.641**	0.312	-0.015	0.541**	1.000						
Pb	0.516**	0.373	0.244	-0.243	0.129	0.278	1.000					
Zn	0.578**	0.539**	0.788**	-0.032	0.140	0.509*	0.352	1.000				
pH	0.202	0.355	0.009	-0.066	0.208	0.284	-0.072	0.278	1.000			
EC	-0.048	-0.024	-0.123	-0.186	-0.194	-0.022	-0.053	0.226	0.258	1.000		
MC	.0035	-0.271	0.127	0.006	-0.068	-0.116	0.207	0.009	-0.149	-0.038	1.000	
OM	0.399	0.362	0.692**	0.061	0.440*	0.284	0.263	0.599**	0.119	-0.056	0.092	1.000

*$p < 0.05$; ** $p < 0.01$

4.5 Assessment of Contamination Level of the Soils

The anthropogenic input of PTEs was computerized by comparing the concentration with the background values. Since there are no data on background levels for soils available in Ghana, the mean shale value was used in this study (Turekian and Wedepohl, 1961). The overall contamination levels PTEs in soils in the study area was assessed based on the pollution index and the degree of pollution (P_{deg}); and the results are presented in Table 4.6. In general, the elements Cu, Mn, Ni and Cr recorded values less than one (1) for almost all the sites in the Botanical Garden indicating minimal anthropogenic impact of these PTEs. However, Fe (site B1), Pb (most sites) and Zn (site B9) showed values greater than 1 suggesting slight pollution of these sites. For Tema Motorway and UG campus, the results varied from slight pollution with Ni, Zn, Pb and Cr, to extremely pollution with Cd (Table 4.6). On the whole, the pollution index results were in agreement with the Igeo index model. The P_{deg} for the mean metal contents in the soil for the different areas was 17.1591, 34.453, 49.074 for Botanical Garden, UG campus and Tema Motorway respectively which indicated considerable to very high degree of pollution (Hakanson, 1980). The maximum value of the pollution degree denoted very high pollution was found at site M5(TM). Site 5 (Botanical Garden) was the least polluted with metals (P_{deg} = 9.40). The soil from this particular area was observed to have been minimally impacted by human activities. It was observed that Cd contributed most to the degree of pollution index of the soil, 81%. Zinc accounted for 22.18%, and Pb, 15.06%. The remaining metals negligibly influenced the soil contamination, not exceeding 10% and decreased in the following order: Ni> Fe > Cr Mn > Cd> Cu> Mn

Table 4.6: Mean values of pollution index (Pi) and degree of pollution (Pdeg) of soils

LOCATIONS	Sites	Cr	Cd	Cu	Fe[a]	Mn[b]	Ni	Pb	Zn	As	P_{deg}
	B1	0.358	23.500	0.148	1.822	0.062	0.112	0.991	0.581	-	27.574
	B2	0.515	18.700	0.604	0.358	0.090	0.115	1.574	0.246	-	22.202
	B3	0.067	13.100	0.599	0.436	0.094	0.265	0.724	0.024	-	15.245
	B4	0.331	13.000	0.133	0.162	0.067	0.157	0.488	0.693	-	15.031
Botanical	B5	0.119	5.900	0.454	0.558	0.094	0.461	1.666	0.148	-	9.400
Garden	B6	0.121	18.200	0.131	0.244	0.088	0.229	1.813	0.033	-	20.859
	B7	0.206	10.000	0.206	0.178	0.032	0.448	2.559	0.225	-	13.629
	B8	0.034	12.800	0.120	0.309	0.104	0.455	1.472	0.075	-	13.854
	B9	0.304	17.900	0.181	0.135	0.034	0.182	1.626	1.237	-	21.599
	B10	0.339	9.900	0.164	0.343	0.038	0.259	1.071	0.298	-	12.412
Mean		**0.239**	**14.300**	**0.274**	**0.455**	**0.070**	**0.268**	**1.398**	**0.356**	**-**	**17.1591**
	L1	0.609	16.000	0.175	0.331	0.121	0.863	0.766	4.761	-	23.626
	L2	0.323	19.200	0.869	0.283	0.225	0.672	0.979	4.688	-	27.239
	L3	0.469	25.700	0.453	0.225	0.180	1.190	1.622	2.344	-	32.183
UG Campus	L4	0.587	32.700	0.125	0.376	0.313	1.230	0.608	0.577	-	36.516
	L5	0.217	32.400	0.225	0.521	0.135	1.169	1.476	1.049	-	37.192
	L6	0.661	45.500	0.143	0.410	0.214	1.026	1.360	0.648	-	49.962
Mean		**0.478**	**28.583**	**0.332**	**0.358**	**0.198**	**1.025**	**1.135**	**2.345**	**-**	**34.453**
	M1	0.414	47.500	0.458	0.054	0.142	0.305	2.289	0.964	-	52.126
	M2	0.828	33.000	0.888	0.387	0.378	0.827	2.401	1.378	-	39.709
	M3	1.019	42.600	0.684	0.055	0.159	1.390	2.364	5.489	-	53.76
Tema	M4	1.946	31.100	0.676	0.049	0.223	1.394	4.409	3.640	-	43.437
Motorway	M5	0.167	48.200	2.345	0.440	0.146	1.089	2.450	14.620	-	69.457
	M6	0.997	44.000	0.279	0.520	0.149	1.085	4.071	6.960	-	58.061
	M7	1.323	37.500	0.582	0.526	0.214	1.438	0.265	3.404	-	45.252
	M8	0.462	25.800	0.016	0.238	0.354	0.500	1.919	1.500	-	30.789
Mean		**0.895**	**38.713**	**0.741**	**0.284**	**0.222**	**1.004**	**2.521**	**4.744**	**-**	**49.074**

Reference Values: Taylor and McLennan (2004); Fe* (50000) and Mn* (850) Turekian and Wedepohl, 1961

4.5.1 Geoaccumulation index (Igeo)

The pollution levels of these metals in the environment expressed in terms of geoaccumulation indices indicate that the medicinal plant soils are moderately to extremely polluted with Cd (Table 4.7) which is in agreement with high P_i values. In general, the results revealed that the samples are uncontaminated with respect to Ni, Fe, Cr, Mn and Cu. Pb gave *Igeo* values in the range of -0.2503 to 1.566 at Tema Motorway collection sites with the highest value found from at site M5. This showed that site M5 was moderately polluted with Pb which was confirmed by the high P_{deg} value for the same site.

Table 4.7: Average geoaccumulation index of soils

LOCATIONS	Sites	Cr	Cd	Cu	Fe	Mn	Ni	Pb	Zn	As
	B1	-2.067	3.970	-3.342	0.197	-4.587	-3.746	-0.598	-1.369	-
	B2	-1.542	3.640	-1.311	-2.149	-4.066	-3.790	0.069	-2.607	-
	B3	-4.492	3.127	-1.325	-1.866	-3.995	-2.499	-1.051	-5.955	-
	B4	-2.179	3.115	-3.492	-3.293	-4.483	-3.252	-1.619	-1.114	-
Botanical	B5	-3.654	1.976	-1.723	-1.510	-4.003	-1.702	0.151	-3.344	-
Garden	B6	-3.637	3.601	-3.509	-2.703	-4.090	-2.781	0.273	-5.527	-
	B7	-2.865	2.737	-2.861	-3.161	-5.559	-1.743	0.771	-2.739	-
	B8	-5.455	3.093	-3.644	-2.363	-3.848	-2.710	-0.027	-4.323	-
	B9	-2.304	3.577	-3.053	-3.468	-5.468	-3.040	0.117	0.279	-
	B10	-2.144	2.722	-3.195	-2.211	-5.317	-2.534	-0.487	-2.333	-
Mean		**-3.034**	**3.156**	**-2.746**	**-2.253**	**-4.542**	**-2.780**	**-0.240**	**-2.903**	-
	L1	-1.302	3.415	-3.103	-2.262	-3.627	-0.797	-0.969	1.669	-
	L2	-2.216	3.678	-0.788	-2.490	-2.734	-1.159	-0.615	1.644	-
	L3	-1.676	4.099	-1.727	-2.821	-3.055	-0.334	0.113	0.644	-
UG Campus	L4	-1.354	4.446	-3.583	-2.079	-2.260	-0.286	-1.302	-1.378	-
	L5	-2.787	4.433	-2.738	-1.608	-3.471	-0.359	0.023	-0.516	-
	L6	-1.183	4.923	-3.388	-1.955	-2.812	-0.548	-0.141	-1.21	-
Mean		**-1.753**	**4.166**	**-2.555**	**-2.203**	**-2.993**	**-0.581**	**-0.482**	**0.142**	-
	M1	-1.857	4.985	-1.710	-4.889	-3.402	-2.296	0.610	-0.638	-
	M2	-0.857	4.459	-0.756	-2.037	-1.987	-0.858	0.679	-0.122	-
	M3	-0.558	4.828	-1.133	-4.841	-3.241	-0.110	0.656	1.872	-
Tema	M4	0.376	4.374	-1.150	-5.013	-2.747	-0.106	0.708	1.279	-
Motorway	M5	-0.363	5.006	0.644	-1.759	-3.358	-0.462	1.566	3.286	-
	M6	-0.589	4.874	-2.424	-1.528	-3.333	0.468	1.440	2.214	-
	M7	-0.181	4.644	-1.366	-1.513	-2.815	-0.061	-2.503	1.182	-
	M8	-1.700	4.104	-6.560	-2.737	-2.083	-1.584	0.355	0.00	-
Mean		**-0.716**	**4.659**	**-1.807**	**-3.034**	**-2.871**	**-0.626**	**0.439**	**1.134**	-

4.6 Concentration of PTEs in the medicinal plants

The environment (atmosphere, water and soil) is continuously being polluted with chemicals and PTEs due to dynamic development of industries and motorization along with extensive use of agrochemicals and incineration activities which occur mostly in developing nations. In turn, these pollutants and PTEs reach plants growing in polluted areas, through wet and dry depositions which subsequently enter the food chain on consumption of plant parts and/or extracts. Hence humans could be at risk of adverse health effects. The results of analysis of nine PTEs (Cd, Pb, Cu, Zn, Fe, Mn, Ni, Cr and As) carried out on the various parts of fifty six (56) medicinal plants comprising of 20 species are summarized in Tables 4.8, 4.9 and 4.10 respectively. PTEs were detected in almost all the medicinal plants examined from the three different geographical locations. The concentrations of PTEs varied significantly among plant species as well as in the same plant species collected from different geographical locations. Likewise, the PTEs concentrations also differed in various plants collected from the same location. Fe had the highest metal concentration in the medicinal plants among all the nine elements investigated, followed by Mn and Zn. The medicinal plant *Calotropis procera* (fruits) was the richest in Fe (874.42mg/kg) and Mn (185.82mg/kg) at site M4 (Tema Motorway) than any other plant studied while the largest Zn (84.39mg/kg) was found in *Euphorbia hirta* (green) at L6 (UG campus). In addition, in spite of the very high Pb content found in all the soil samples except Botanical Garden, Pb in the herbal plants was low as Pb is known to bind effectively with organic matter in soil limiting uptake by the plants (Intawongse and Dean, 2006). Thus Pb was detected in only few medicinal plant species (22%) whilst majority were below its detection limit of 0.500, representing 78%. Cadmium (Cd) on the other hand, was found in all of the plant species in most of the geographical locations studied; the highest concentration of Cd occurred in *Euphorbia hirta* (red) harvested 50m away from the Tema Motorway tollbooth (M1) (9.357 mg/kg). In all cases, Cd level exceeded the permissible limit 0.3ppm, set globally

Table 4.8: Total PTEs (mg/kg dry weight) in the medicinal plants from the Botanical Garden

Site No	Name of Plants	Parts	Cd	Pb	Cu	Zn	Fe	Mn	Ni	Cr	As
B1	*Desmodium styracifolium*	Leaves	0.972	<0.500	0.458	38.592	56.761	62.746	4.813	5.634	1.747
B2	*Lantana camara*	seeds	0.327	< 0.500	1.569	10.765	40.200	74.100	7.329	6.953	3.754
B3	*Azadirachta indica*	Leaves	0.821	< 0.500	2.443	25.012	22.256	32.679	8.082	10.079	0.867
	Desmodium adscendens	Leaves	1.706	< 0.500	0.956	8.722	26.151	15.278	6.040	15.909	0.297
B4	*Cassia alata*	Leaves	2.347	< 0.500	0.119	32.509	8.740	9.504	13.031	4.024	1.255
B5	*Cymbopogon citratus*	Fruits	2.040	< 0.500	1.568	14.022	285.92	10.269	7.000	6.236	0.516
B6	*Solanum torvum*	Fruits	2.361	< 0.500	5.649	18.950	296.578	10.515	10.694	4.638	0.127
B7	*Euphorbia hirta (red)*	Fruits	0.478	< 0.500	1.773	27.150	15.618	14.606	5.890	0.598	0.591
B8	*Phyllantus fraternus*	Leaves	0.793	< 0.500	0.916	38.048	19.004	2.897	10.515	0.079	1.194
B9	*Physalis angulata*	Leaves	3.672	< 0.500	0.793	20.866	458.370	68.483	9.719	21.625	0.182
	Ricinus communis	Seeds	4.663	< 0.500	0.325	35.562	309.520	24.040	3.102	7.729	1.199
B10	*Passiflora suberosa*	Fruits	2.720	< 0.500	12.452	19.960	14.023	40.478	12.948	6.135	0.557
	Ricinus communis	Leaves	2.441	< 0.500	0.893	22.402	199.134	6.575	29.040	16.436	0.631
Min			**0.327**	**< 0.500**	**0.119**	**8.722**	**8.740**	**9.504**	**3.102**	**0.079**	**0.127**
Max			**4.663**	**< 0.500**	**5.649**	**38.592**	**458.370**	**74.100**	**29.040**	**16.436**	**3.754**

Table 4.9: PTEs concentrations (mg/kg dry weight) in medicinal plant samples from University of Ghana Campus

Site No.	*Name of Plants*	Parts	Cd	Pb	Cu	Zn	Fe	Mn	Ni	Cr	As
LI	*Euphorbia hirta (green)*	Leaves	2.244	<0.500	0.946	52.441	144.441	54.409	11.142	32.200	0.750
	Dissotis rotundifolia	Leaves	3.449	<0.500	1.693	25.039	26.181	106.024	37.992	26.969	1.151
	Desmodium adscendens	Leaves	9.150	<0.500	32.750	22.658	116.723	28.777	15.796	26.789	0.679
L2	*Alternathera pungens*	Leaves	3.672	<0.500	1.537	23.359	209.805	53.984	13.164	29.332	0.728
	Lantana camara	Leaves	0.547	<0.500	1.944	56.984	24.921	28.809	52.738	5.595	1.312
	Phyllantus amarus	Leaves	0.957	<0.500	9.078	15.293	67.983	58.589	19.707	4.789	1.547
L3	*Desmodium adscendens*	Leaves	0.772	<0.500	0.916	24.631	19.004	24.263	45.000	7.968	1.408
	Cassia occidentalis	Seeds	0.376	2.469	8.036	29.724	22.829	132.908	32.519	39.562	2.115
	Ricinus communis	Leaves	0.434	1.679	11.063	29.602	21.102	37.131	39.721	8.622	2.018
	Euphorbia hirta (red)	Leaves	1.752	<0.500	2.956	24.781	28.959	35.671	42.470	5.268	0.579
L4	*Cassia occidentalis*	Flowers	1.364	3.437	1.240	50.853	15.388	31.279	19.079	14.341	4.904
L5	*Phyllantus amarus*	Leaves	6.756	<0.500	14.567	15.679	16.332	25.579	30.368	12.076	1.068
	Cassia Occidentalis	Seeds	1.441	<0.500	5.039	35.827	30.239	27.569	30.598	10.079	1.354
	Desmodium styracifolium	Leaves	7.512	<0.500	1.268	14.804	27.790	60.049	23.905	0.256	0.876
	Hyptis suaveolens	Leaves	8.643	<0.500	7.789	31.685	83.669	92.261	16.171	6.853	1.864
L6	*Desmodium adscendens*	Leaves	5.648	<0.500	7.309	20.589	109.814	25.693	23.150	23.458	1.568
	Euphorbia hirta (green)	Leaves	3.778	<0.500	0.537	84.389	296.107	30.496	10.716	24.767	0.588
	Ricinus communis	Seeds	1.015	<0.500	7.300	27.604	34.829	21.179	16.236	56.238	2.645
Min.			**0.376**	**<0.500**	**0.537**	**14.804**	**15.388**	**21.179**	**10.716**	**0.256**	**0.579**
Max.			**9.150**	**3.437**	**32.750**	**84.389**	**296.107**	**132.908**	**52.738**	**56.238**	**4.904**

Table 3.10: PTEs concentrations (mg/kg dry weight) in medicinal plant samples from Tema Motorway

Site No.	Name of Plants	Parts	Cd	Pb	Cu	Zn	Fe	Mn	Ni	Cr	As
	Hyptis suaveolens	Leaves	4.480	0.726	3.648	5.440	30.200	53.680	20.476	14.956	0.253
M1	*Cassia occidentalis*	Leaves	7.512	8.794	7.469	58.150	209.878	60.048	16.171	1.428	0.467
	Euphorbia hirta (red)	Leaves	9.357	0.653	8.908	40.579	271.579	47.789	15.952	1.379	3.579
	Phyllantus amarus	Leaves	7.925	<0.500	10.478	31.905	180.112	35.693	14.854	1.012	1.568
	Passiflora suberosa	Fruits	2.550	<0.500	5.936	64.502	184.382	23.864	12.350	0.358	0.298
M2	*Lantana camara*	Leaves	5.872	<0.500	8.088	30.200	18.840	44.360	9.975	17.960	1.860
	Phyllantus niruri	Leaves	3.642	<0.500	4.684	43.967	60.579	25.659	10.568	13.459	2.459
	Zanthoxylum zanthoxyloides	Fruits	3.680	<0.500	2.492	35.879	269.920	47.417	6.096	12.623	0.441
	Phyllanthus amarus	Leaves	2.353	<0.500	5.320	54.700	681.490	46.825	9.020	10.823	2.400
M3	*Euphobia hirta* (green)	Fruits	1.318	<0.500	4.457	45.07	24.921	142.283	19.069	1.625	1.981
	Azadirachta indica	Leaves	0.976	<0.500	3.458	20.458	76.894	54.532	8.983	6.679	1.548
	Physalis angulata	Leaves	3.356	0.957	3.468	30.537	54.689	89.581	7.493	12.489	1.267
M4	*Calotropis procera*	Fruits	2.271	0.735	2.836	21.793	874.423	185.817	20.200	25.733	0.359
	Ricinus communis	Leaves	1.627	<0.500	3.521	46.454	311.066	137.400	17.381	19.156	0.662
	Phyllantus niruri	Leaves	4.621	<0.500	3.735	31.587	411.167	68.412	20.837	66.928	0.906
	Euphorbia hirta (green)	Fruits	0.977	<0.500	14.241	20.338	45.564	45.940	19.398	17.632	3.195
M5	*Desmodium styracifolium*	Leaves	2.369	<0.500	8.589	18.569	257.789	40.489	15.679	30.793	1.569
	Hyptis suaveolens	Leaves	2.047	<0.500	0.254	33.804	554.016	43.819	11.054	15.472	0.825
	Euphorbia hirta (red)	Fruits	2.008	<0.500	2.638	20.866	412.125	68.535	8.583	18.618	0.782

M6	*Hyptis suaveolens*	Leaves	1.450	<0.500	12.704	26.732	50.000	106.226	56.653	42.685	3.168
	Sesamum indicum	seeds	0.789	<0.500	4.679	20.458	68.659	79.379	46.789	30.467	2.436
M7	*Calotropis procera*	Fruits	1.268	<0.500	4.693	16.459	278.459	58.539	4.597	5.593	1.056
	Cassia occidentalis	Seeds	1.457	0.839	4.679	1.659	24.693	20.696	34.670	4.679	1.00
M8	*Euphorbia hirta (red)*	Leaves	1.168	0.956	3.689	1.569	79.368	26.459	30.479	3.587	1.459
	Phyllantus amarus	leaves	0.937	0.467	1.547	1.548	239.459	37.692	20.369	15.457	3.479
Min			**0.789**	**<0.500**	**0.254**	**1.548**	**24.693**	**20.696**	**4.597**	**0.358**	**0.253**
Max			**9.357**	**8.794**	**14.241**	**64.502**	**874.423**	**185.817**	**56.653**	**66.928**	**3.579**

for raw herbal materials (Table 4.11), suggesting that toxicity could arise from short term usage of these plants. This could possibly be due to its accumulation in the soil resulting from the teeming vehicular exhaust fumes.

Surprisingly As, which was not detected in initial soil assessment was established in all the plants with varied concentrations from the 3 studied areas presupposing that As was deposited on the flowers, leaves, seeds and fruits through atmospheric transport of particulates as well as wet and dry precipitations. Arsenic levels in all plant samples from the different geographical locations ranged from 0.127 to 4.904 mg/kg (Tables 4.8-4.10). The greatest, 4.90mg/kg was registered in *Cassia occidentalis* (flowers) at site L3 in UG Campus and the minimum (0.127mg/kg in *Solanum torvum*) found at Botanical Garden at site B6. All As values were within the allowable limit, though As is not used in any biochemical process in living organisms. It only accumulates in the kidneys and excessive exposure renders infertility and miscarriages in women. Additionally, the PTEs Cu, Ni and Cr were all detected in minimal quantities in the 3 locations (Botanical Garden, UG Campus and TM) with the largest concentrations established in *Desmodium adscendens* leaves (32.75mg/kg, L1), *Hyptis suaveolens* leaves (56.65mg/kg, M6) and *Phyllantus niruri* (66.93mg/kg, M5) respectively. The lower concentrations of Cu in all the plants, like Pb was the result of its strong adsorption onto soil particles rich in carbonate minerals, and manganese oxides reducing its availability to plants (Intawongse and Dean, 2006). On the whole, the PTEs uptake by the herbs collected from the UG campus and TM were higher than those from Botanical Garden which was obvious considering the various human activities that occur at these sites demonstrated in the higher quantities of metals recovered in the soils. Medicinal plants harvested from Botanical Garden recorded the least metal contamination (57.27%) whereas UG Campus and TM had 70.00% and 86.67% greater than WHO/FDA guidelines, Table 4.11 (indicates the overall range of

PTEs from the 3 studied areas). In all, the few herbs in which Pb was detected, only *Cassia occidentalis* (seeds – 2.47mg/kg, L3; leaves – 3.44mg/kg, L4) exceeded the regulatory limit (Table 4.11), whereas the PTEs Mn, Fe and Cu were within the limit comparatively. Nonetheless, for the PTEs (Zn, Ni and Cr) found in the medicinal plants, majority of them were greater than recommended limit required for raw herbs particularly those harvested from the TM and UG Campus.

Table 4.11: PTEs concentrations in medicinal plants compared with selected regulatory limits

This Study		**Regulatory limits** (ppm)				
Metal	Concentration (mg/kg) Range	WHO/FDA[a]	FAO/WHO[b]	EDQM[c]	CFDA[d]	Health Canada
Cd	<0.008 -9.357	0.3	-	1	0.3	0.3
Pb	< 0.500 -8.794	2	2	5	5	10
Cu	0.119 -32.750	150	3	-	-	-
Zn	1.548 -84.389	-	27.4	-	-	-
Fe	8.74 -874.423	1000	-	-	-	-
Mn	9.504 - 185.817	1200	1200	-	-	-
Ni	3.102 -56.653	30.00	10	-	-	-
Cr	0.079 - 66.928	2.00	2	-	-	-
As	0.127 -4.904	5.00	5	-	-	-

WHO; World Health Organization, FDA; Food and Drug Administration (USA), EDQM; European Directorate for the Quality of Medicines in Healthcare, CFDA; China Food and Drug Administration

4.7: Bioaccumulation Factor (BAF) of PTEs from Soils to Medicinal Plants

The bioaccumulation factor (BAF) which evaluates the potential capability of plants to transfer metals from the soil to their edible tissues is presented in Tables 4.12-14. This factor is one of the key components controlling human exposure to metals through the food chain. BAF depends on

several factors such as the soil pH, organic matter, metal availability, soil particle size and plant species (Gebrekidan *et al.*, 2013). BAF was calculated for Cr, Cd, Ni, Cu, Fe, Mn, Pb (only few sites) and Zn while As in the soil showed no corresponding transfer in the herbal plants. In general, the BAF of PTEs through soils to the medicinal plants varied with respect to the medicinal plants; also the individual PTE differed considerably in uptake from each other whereas the mean bioaccumulation factors for Cd, Fe, Mn, Zn and Cr were higher in Botanical Garden plants than the anthropogenic impacted sites: Tema Motorway (TM) and University of Ghana (UG) campus. The variations probably arose from the diverse metal concentrations in the soil and their uptake by the different plant species. Nonetheless, Cr, Cd and Zn showed comparably higher BAF of above 1.0 corroborating the evidence of their higher solubility in soils and their transfer to aerial parts of herbal plants (Intawongse and Dean, 2006). Further, some soil characteristics, for example, the pH, moisture, organic matter, etc., play very vital roles in the transfer of metals from soils to plants (McBride, 2003) which could account for the observed BAFs. In addition, the absence of BAF for Pb and As, confirms the fact that these elements are known to be less soluble in the soil system, which support their strong adsorption on the soil matrix (Intawongse and Dean, 2006). More so these metals also tend to form a tough barrier to prevent translocation from roots to edible parts of the herbal plants. Overall, the values of BAF showed that medicinal herbs from the pristine environment like Botanical Garden had higher BAF compared to that from UG and TM where human activities were greater.

Table 4.12: Bioaccumulation factor (BAF) of PTEs in medicinal plants collected from Botanical Garden

Site No	Name of Plants	Cr	Cd	Pb	Cu	Zn	Fe	Mn	Ni	As
B1	*Desmodium styracifolium*	0.228	0.414	NA	0.079	0.992	0.080	1.182	0.068	NA
B2	*Lantana camara*	0.196	0.175	NA	0.067	0.652	0.102	0.974	0.105	NA
B3	*Azadirachta indica*	2.191	NA	NA	0.105	15.440	0.007	0.409	0.017	NA
	Desmodium adscendens	3.458	1.302	NA	0.041	5.384	0.008	0.191	0.040	NA
B4	*Cassia alata*	0.176	1.805	NA	0.023	3.284	0.007	0.166	0.042	NA
B5	*Cymbopogon citratus*	0.248	3.458	NA	0.088	6.432	0.014	0.129	0.107	NA
B6	*Solanum torvum*	0.557	1.297	NA	1.099	1.259	0.873	0.140	6.235	NA
B7	*Euphorbia hirta (red)*	0.006	0.478	NA	0.220	1.004	0.219	0.540	0.406	NA
B8	*Phyllantus fraternus*	9.163	0.620	NA	0.196	7.579	0.026	0.033	0.783	NA
B9	*Physalis angulata*	0.175	2.051	NA	0.112	0.252	0.447	2.378	0.188	NA
B10	*Ricinus communis*	0.330	4.710	NA	0.051	1.783	0.029	0.751	0.038	NA
	Passiflora suberosa	0.262	2.747	NA	1.949	1.001	1.948	1.265	1.540	NA
	Ricinus communis	0.702	2.466	NA	0.140	1.123	0.124	0.206	0.604	NA
Mean		**1.361**	**1.794**	**-**	**0.321**	**3.553**	**0.299**	**0.643**	**0.782**	**-**

Table 4.13: Bioaccumulation factor (BAF) of PTEs in medicinal plants collected from UG Campus

Site No	Name of Plants	Cd	Pb	Cu	Zn	Fe	Mn	Ni	Cr	As
L1	*Euphorbia hirta (green)*	1.403	NA	0.202	0.164	0.009	0.527	0.235	0.767	NA
	Dissotis rotundifolia	2.156	NA	0.362	0.078	0.002	1.027	0.801	0.642	NA
L2	*Desmodium adscendens*	6.998	NA	6.998	0.071	0.007	0.279	0.333	0.638	NA
	Alternathera pungens	0.045	NA	0.045	0.074	0.016	0.282	0.356	1.317	NA
	Lantana camara	0.057	NA	0.057	0.181	0.002	0.150	1.427	0.251	NA
	Phyllantus amarus	0.268	NA	0.268	0.049	0.005	0.306	0.533	0.215	NA
L3	*Desmodium adscendens*	0.052	NA	0.052	0.157	0.002	0.158	0.688	0.246	NA
	Cassia occidentalis	0.455	0.089	0.455	0.189	0.000	0.866	0.497	1.222	NA
	Ricinus communis	0.626	0.061	0.626	0.188	0.002	0.242	0.607	0.266	NA
	Euphorbia hirta (red)	0.167	NA	0.167	0.158	0.003	0.233	0.649	0.163	NA
L4	*Cassia occidentalis*	0.254	0.339	0.254	1.315	0.001	0.118	0.282	0.354	NA
L5	*Phyllantus amarus*	2.085	NA	1.661	0.223	0.001	0.222	0.472	0.672	NA
	Cassia Occidentalis	0.445	NA	1.149	0.392	0.001	0.240	0.476	0.672	NA
	Desmodium styracifolium	2.319	NA	0.031	0.211	0.001	0.802	0.372	0.017	NA
	Hyptis suaveolens	2.668	NA	0.888	0.451	0.003	0.727	0.251	0.457	NA
L6	*Desmodium adscendens*	0.582	NA	1.308	0.474	0.006	0.142	0.410	0.514	NA
	Euphorbia hirta (green)	0.830	NA	0.096	1.944	0.015	0.168	0.190	0.543	NA
	Ricinus communis	0.223	NA	1.306	0.636	0.002	0.117	0.288	1.233	NA
Mean		**1.202**	**0.163**	**0.885**	**0.386**	**0.004**	**0.367**	**0.493**	**0.566**	**-**

Table 4.14: Bioaccumulation factor (BAF) of PTEs in medicinal plants collected Tema Motorway

Site No	Name of Plants	Cd	Pb	Cu	Zn	Fe	Mn	Ni	Cr	As
M1	*Hyptis suaveolens*	0.943	0.019	0.204	0.084	0.012	0.445	1.219	0.217	NA
	Cassia occidentalis	1.581	0.226	0.418	0.900	0.083	0.498	0.963	0.021	NA
	Euphorbia hirta (red)	1.970	0.017	0.498	0.628	0.107	0.396	0.950	0.020	NA
	Phyllantus amarus	1.668	NA	0.586	0.494	0.071	0.296	0.884	0.015	NA
M2	*Passiflora suberosa*	0.773	NA	0.171	0.698	0.010	0.074	0.271	0.006	NA
	Lantana camara	1.779	NA	0.233	0.327	0.001	0.138	0.219	0.314	NA
	Phyllantus niruri	1.104	NA	0.135	0.476	0.003	0.080	0.232	0.235	NA
M3	*Zanthoxylum zanthoxyloides*	0.864	NA	0.093	0.098	0.023	0.352	0.080	0.180	NA
	Phyllanthus amarus	0.552	NA	0.199	0.149	0.260	0.347	0.118	0.154	NA
	Euphobia hirta (green)	0.309	NA	0.167	0.123	0.010	1.055	0.249	0.023	NA
	Azadirachta indica	0.229	NA	0.130	0.056	0.029	0.404	0.118	0.095	NA
M4	*Physalis angulata*	1.079	0.013	0.132	0.125	0.024	0.472	0.098	0.093	NA
	Calotropis procera	0.730	0.010	0.108	0.089	0.377	0.978	0.263	0.192	NA
	Ricinus communis	0.523	NA	0.134	0.190	0.134	0.723	0.227	0.143	NA
M5	*Phyllantus niruri*	0.959	NA	0.041	0.032	0.019	0.550	0.348	2.342	NA
	Euphorbia hirta (green)	0.203	NA	0.156	0.021	0.002	0.369	0.324	0.617	NA
	Desmodium styracifolium	0.491	NA	0.094	0.019	0.012	0.326	0.262	1.077	NA
	Hyptis suaveolens	0.425	NA	0.003	0.034	0.025	0.352	0.185	0.541	NA
M6	*Euphorbia hirta (*red*)*	0.456	NA	0.242	0.045	0.016	0.542	0.144	0.139	NA
	Hyptis suaveolens	0.330	NA	1.166	0.057	0.002	0.839	0.950	0.318	NA
	Sesamum indicum	0.179	NA	0.429	0.044	0.003	0.543	0.784	0.227	NA
M7	*Calotropis procera*	0.338	NA	0.207	0.072	0.011	0.438	0.740	0.061	NA
	Cassia occidentalis	0.389	0.186	0.206	0.007	0.001	0.323	0.262	0.051	NA
M8	*Euphorbia hirta* (red)	0.453	0.029	5.950	0.016	0.007	0.069	0.961	0.113	NA
	Phyllantus amarus	0.363	0.014	2.495	0.015	0.021	0.125	1.370	0.485	NA
Mean		**0.748**	**0.064**	**0.568**	**0.192**	**0.050**	**0.429**	**0.489**	**0.307**	**NA**

4.8 Chemical fractionation Profile

It is known that the change of PTE enrichment relates to their chemical forms in soils. Thus, it is important to evaluate the bioavailability and mobility of PTEs to understand their chemical behaviour and fate in soils. In this work, the proportion of each chemical fractionation of nine PTEs (Cd, As, Cr, Cu, Zn, Ni, Pb, Mn and Fe) in 24 composite soils were examined. The study of sequential extractions focused only on the first three phases since the interest was in only the available fractions and not that of the residual. The extractions were performed for all the different human impacted environments and the averages determined; the raw data for each sampling sites are displayed in the Appendix (B).

4. 8.1 Total extracted amounts

The distribution patterns of the fractions differ from element to element as well as the different environments. The total recovery rates of all the elements except Fe and Cr, ∑ (steps 1–3), were between 56.33% and 406.50% of the corresponding total concentrations (Table 4.15). This is an acceptable agreement considering the large variability of soils, especially in densely populated areas (Mossop and Davidson, 2003). The total soil content for each of the eight elements studied has been compared with the sum of the amounts obtained from the three steps of the chemical extraction procedure (Table 4.15). The accumulated amounts from the chemical extraction were in good agreement with the total content in the samples for Pb, Ni and Cu for all the different environments.

Table 4.15: Comparison between the total PTEs content and the amounts measured from the three steps of the chemical extraction procedure.

Elements	Total content [a] (mg/kg)	Chemical extraction[b] (mg kg^{-1} dry weight)				Recovery [c] (%)
		STEP 1	STEP 2	STEP 3	TOTAL	
		Botanical Garden				
Pb	23.77±0.63	2.01 (1.34)	15.75 (3.57)	12.70 (4.67)	30.47(45.67)	128.15
Mn	59.69± 2.92	55.91 (23.56)	17.61 (45.76)	54.85 (20.45)	184.26 (29.35)	309.99
Cr	16.52±0.57	3.72 (45.29)	1.21(1.65)	4.38 (23.64)	9.31(43.68)	56.33
Cd	1.43±0.71	2.07 (1.57)	2.08 (0.95)	1.66 (0.96)	5.81 (1.56)	406.50
Fe	21448.92±2.61	367.87 (45.45)	54.07 (23.67)	148.86(7.69)	570.79 (32.58)	2.66
Cu	10.69±0.25	3.55 (1.02)	3.96 (0.87)	3.11 (1.45)	10.61 (1.43)	99.24
Zn	23.84±0.24	7.49(1.37)	1.27 (1.08)	4.97(1.99)	13.73 (4.67)	57.61
Ni	13.46±0.13	7.93 (4.98)	9.56 (2.69)	10.29 (4.67)	27.77 (1.58)	206.29
		UG Campus				
Pb	19.30±0.59	9.96 (1.57)	24.36 (12.78)	14.04 (6.47)	48.36 (32.68)	250.53
Mn	168.51±3.52	82.39 (97.34)	6.86 (37.69)	60.15 (32.56)	149.39 (103.67)	88.65
Cr	32.96±1.56	6.37 (4.67)	7.23(2.49)	14.17 (6.29)	27.77 (5.32)	84.28
Cd	2.86±0.17	3.70 (23.69)	2.40 (1.37)	2.54 (1.59)	8.64 (1.59)	302.14
Fe	16882.04± 1.62	7.79 (12.59)	7.15 (18.69)	31.87 (14.65)	46.82 (23.68)	0.28

Cu	12.94±0.64	12.50 (26.79)	6.62 (10.45)	2.75 (3.69)	21.87 (25.67)	169.09
Zn	157.18±2.24	40.18 (23.69)	15.59 (45.79)	56.38 (56.87)	116.15 (34.78)	73.89
Ni	56.38±0.54	13.23 (20.56)	24.47 (1.47)	18.13 (56.78)	55.83 (34.69)	99.03
			Tema Motorway			
Pb	42.86±0.11	12.05 (67.35)	19.61(39.37)	23.02 (96.74)	54.68 (49.39)	127.59
Mn	187.52±3.06	86.97 (121)	13.33 (48.56)	94.77 (48.67)	195.08 (69.69)	104.03
Cr	70.34±0.19	4.13(1.34)	6.02(2.46)	6.51(3.67)	16.65(3.67)	21.61
Cd	1.26±0.17	5.69 (37.35)	3.27 (68.45)	4.20 (93.57)	13.16 (53.78)	339.84
Fe	12488.12± 8.47	1.58 (38.35)	7.74 (29.47)	27.14 (64.32)	36.46 (42.57)	0.26
Cu	28.90±1.87	8.57 (38.94)	6.86 (47.34)	19.57 (64.57)	34.99 (53.26)	121.05
Zn	317.95±5.05	56.20 (67.34)	6.02(1.56)	54.02 (34.65)	116.24(21.34)	37.32
Ni	55.20±1.17	11.66 (52.69)	25.74 (53.34)	17.65 (68.39)	55.06 (89.47)	99.74

[a] Values reported are averages for 24 determinations.

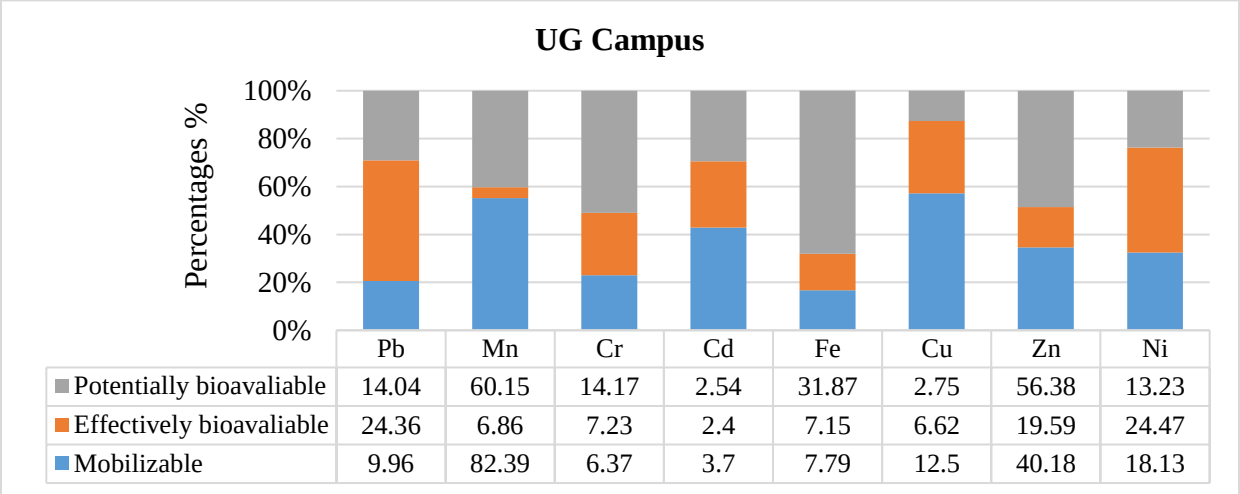
[b] Values reported are averages for 24 determinations. Values in parentheses are % R.S.D. for n = 24 measurements

[c] Recovery = (sum of three steps/ total) × 100

The possibility of contamination by the reagents or by the material used has been ruled out after analyzing all extraction solutions and performing the procedure without sample (blank). The gap was not due to a matrix effect because results obtained with a calibration curve were the same as those determined with a standard addition method. Contrary to Fe, Zn and Cr, the opposite trend was observed for Mn and Cd. For these elements, the difference between the total content in soil and the cumulated concentration measured after sequential extraction is even more significant. The differences could be attributed to the loss of samples during filtration at each stage of the extraction.

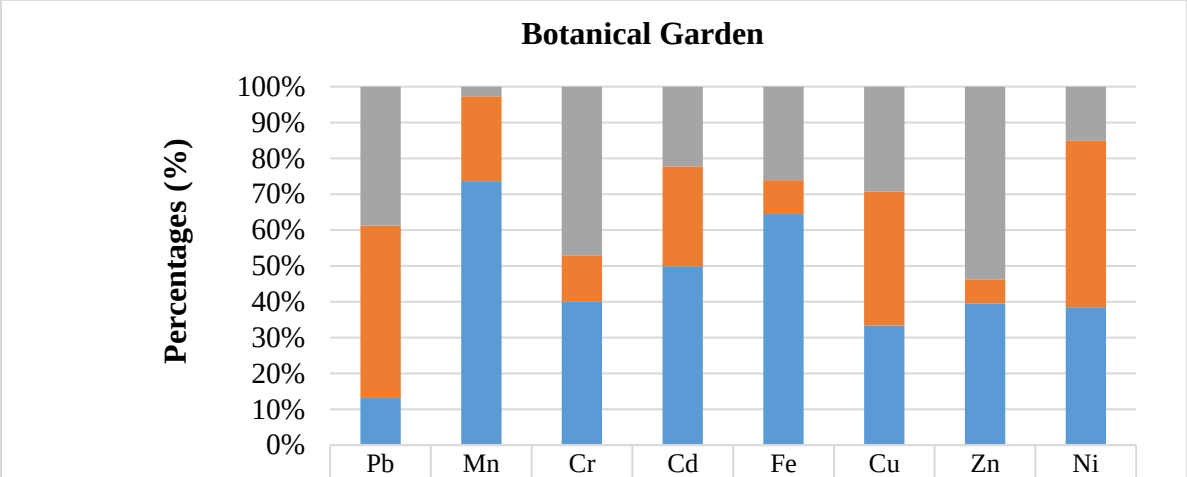
4.8.2 Chemical partitioning of PTEs in the soils

The average extraction results for the PTEs are presented in Fig. 4.1-4.3. The results, expressed as percentages of the total concentrations (mg kg^{-1}) of the elements determined in each step, (Table 4.15). The ranges of environmental availabilities varied widely among the different geographical locations and from element to element.



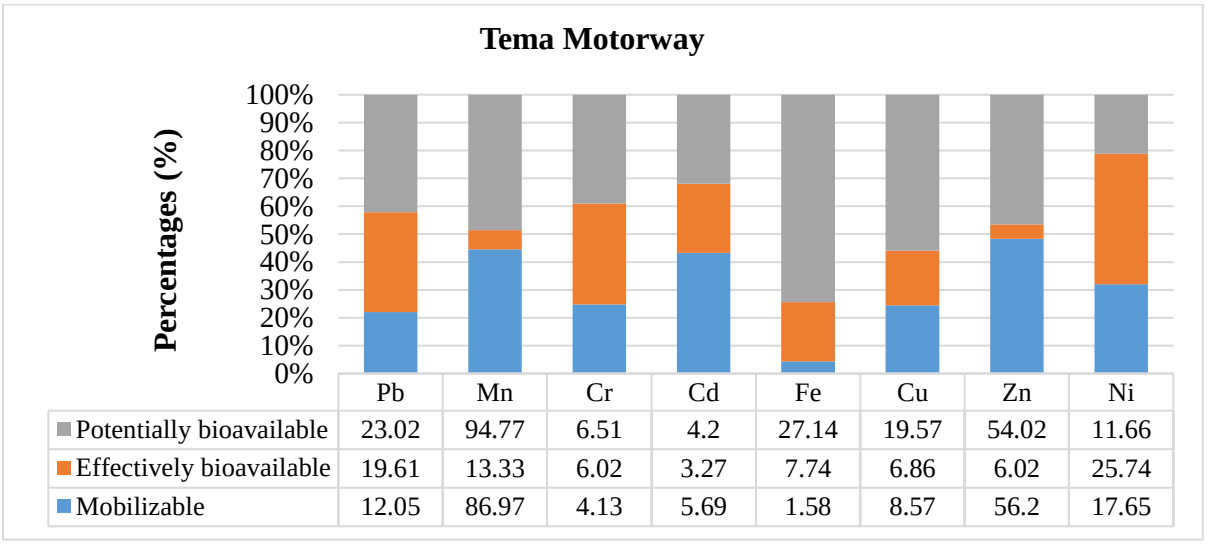
	Pb	Mn	Cr	Cd	Fe	Cu	Zn	Ni
Potentially bioavaliable	14.04	60.15	14.17	2.54	31.87	2.75	56.38	13.23
Effectively bioavaliable	24.36	6.86	7.23	2.4	7.15	6.62	19.59	24.47
Mobilizable	9.96	82.39	6.37	3.7	7.79	12.5	40.18	18.13

Figure 4.1: Fractionation of PTEs through chemical extraction. 100% indicates the ∑ of steps 1 - 3 of the extraction. The concentrations are expressed in mg/kg



	Pb	Mn	Cr	Cd	Fe	Cu	Zn	Ni
Potentially bioavailable	12.7	2.01	4.38	1.66	148.86	3.11	10.2	3.11
Effectively bioavaliable	15.75	17.61	1.21	2.08	54.07	3.96	1.27	9.56
Mobilizable	4.3	54.85	3.72	3.72	367.87	3.55	7.49	7.93

Figure 4.2: Fractionation of PTEs through chemical extraction. 100% indicates the ∑ of steps 1 - 3 of the extraction. The concentrations are expressed in mg/kg



	Pb	Mn	Cr	Cd	Fe	Cu	Zn	Ni
Potentially bioavailable	23.02	94.77	6.51	4.2	27.14	19.57	54.02	11.66
Effectively bioavailable	19.61	13.33	6.02	3.27	7.74	6.86	6.02	25.74
Mobilizable	12.05	86.97	4.13	5.69	1.58	8.57	56.2	17.65

Figure 4.3: Fractionation of PTEs through chemical extraction. 100% indicates the ∑ of steps 1 - 3 of the extraction. The concentrations are expressed in mg/kg

Lead

The acetic acid fraction (mobile phase) contained relatively low amount of Pb in almost all the different locations as shown in Fig.s 4.4-4.6 compared to the other two fractions indicating. Except for the soils at TM site M1, the following order of mobility (greatest to least mobile): Potentially bioavailable > Effectively bioavailable > Mobilizable were observed. Metals of natural origin are mainly bound to Fe-Mn Oxides and, therefore, have low mobility and bioavailability in soil (Wali et al., 2008). Fe-Mn oxides are effective scavengers for Pb (Tessier et al., 1979; Rath et al., 2009) and the dominant association of this element with the potentially bioavailable fraction may be a result of Pb adsorption onto colloids of Fe-Mn oxides (Rath *et al.*, 2009; Banerjee, 2003). High percentage (77%) contribution of Pb in non-residual fractions is an indicator of anthropogenic source for this metal in the samples such as industry and vehicular emissions. Site M5 (TM) showed the highest non-residual content of Pb among all 24 samples, which was located near to a highly traffic density zone and confirms the contribution of traffic to the contamination of the soil.

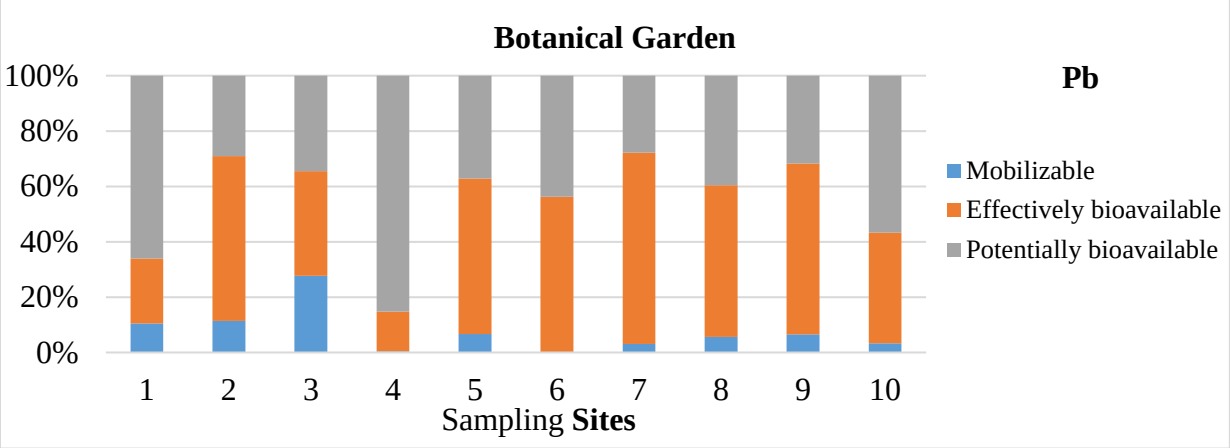


Figure 4.4: Pb fraction after performing a 3 - step chemical extraction.

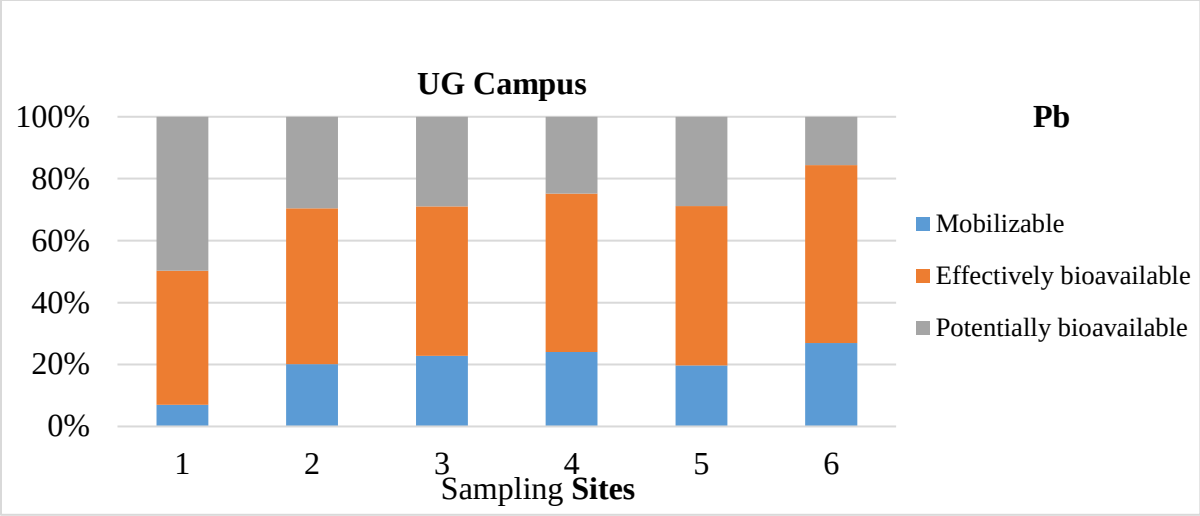


Figure 4.5: Pb fraction after performing a 3 - step chemical extraction

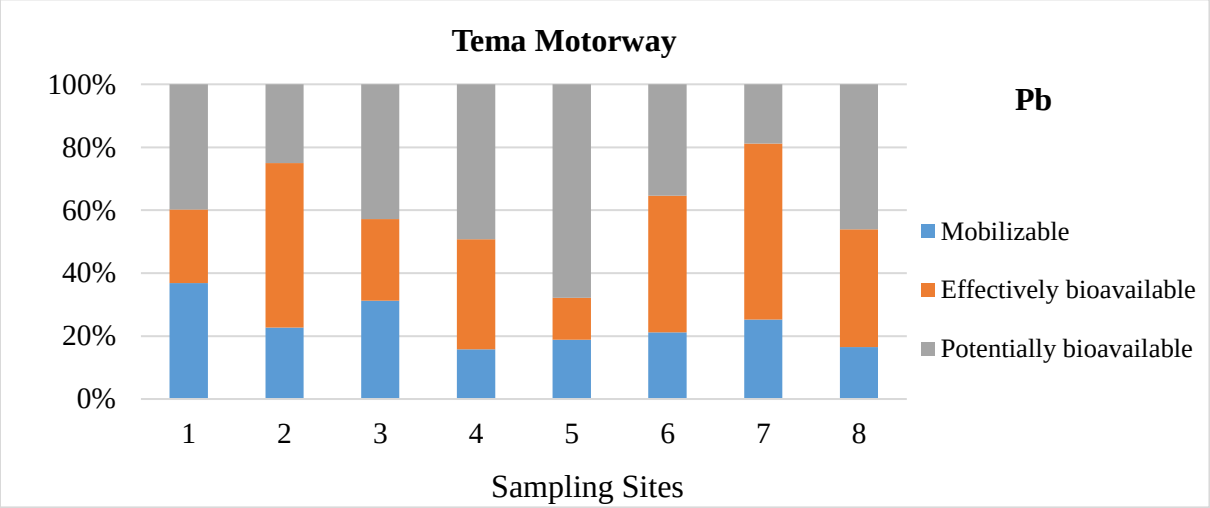


Figure 4.6: Pb fraction after performing a 3-step chemical extraction.

Zinc

Zinc was mostly concentrated in the mobilizable (acid soluble) fraction, although a significant amount was also present in the potentially bioavailable (Fe-Mn oxides) fraction for the various locations (Fig. 4.7) Zn bound to the carbonate bound (effectively bioavailable) fractions is found to be negligible, with exception for sites B1, B4, B7 and L1 that had significant values. The very high concentration of Zn in the mobilizable indicated high mobility of Zn in the soils where these medicinal plants were harvested. This agrees with the general pattern of association of Zn (Li and Thornton 2001). Sites B9, B10, L2, L3, L4, L5 M1, M3, and M5 had considerable amount of Zn bound to the potentially bioavailable (F2); for all the other sites, the F2 fraction is not much significant with respect to Zn.

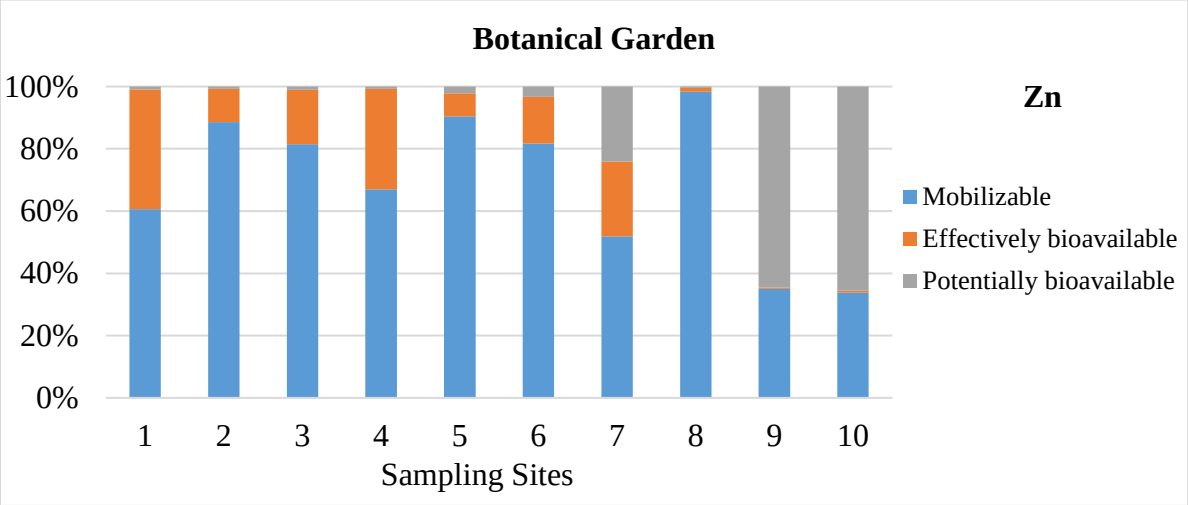


Figure 4.7: Zn fraction after performing a 3-step chemical extraction

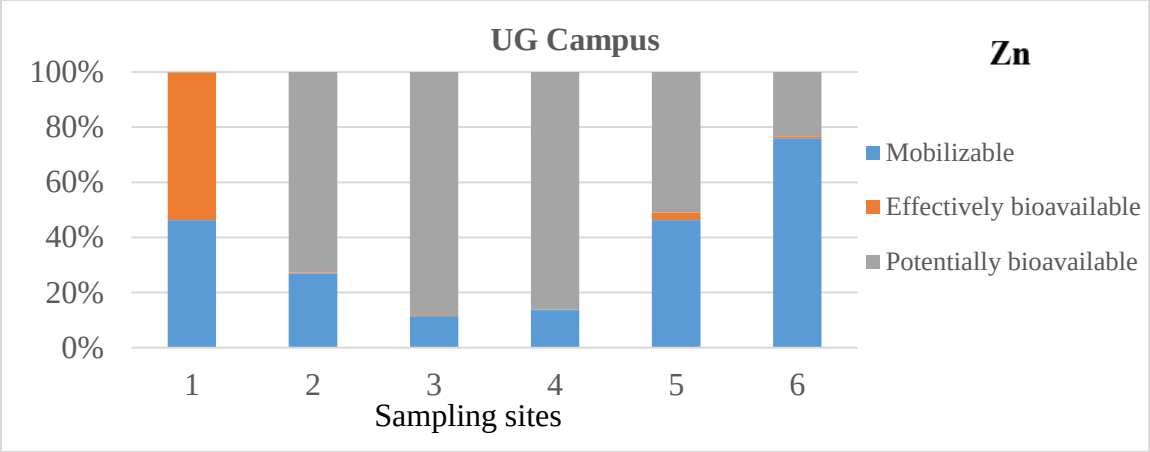


Figure 4.8: Zn fraction after performing a 3-step chemical extraction

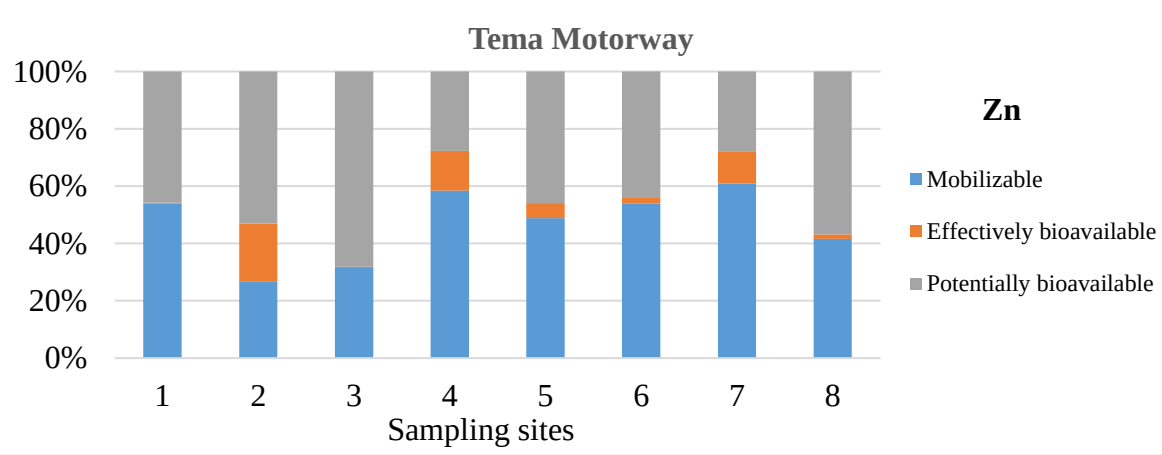


Figure 4.9: Zn fraction after performing a 3 -step chemical extraction

Chromium

The fractionation profile of Cr indicates that major portion of Cr is associated with the potentially bioavailable fraction (F3) in most of the sites within the study areas, but sites B4, B9, L2, L6 as well as most sites within the TM did not conform to this (Fig. 4.10-4.12). Considerable amount of Cr is also found in association with the two fractions, mobilizable (F1) and effectively bioavailable (F2). Cr in these two fractions is labile and may enter into the food chain (Jain et al. 2007) through water and other supporting systems. At sites B5, B8, B10, M1 and M3, Cr bound to F2 is negligible; at sites B6 and B9, the carbonate fraction (F2) is very small; F1 fractions have Cr in greater amounts except at sites L5 and M4. The average Cr content (in percentage) distribution among the different geographical location is in the order F3 (36%) > F1 (22%) > F1 (2%) and F3 > F2 (16%) > F1 (8%) for Botanical Garden and UG campus respectively. Similar trend was also seen for that of Tema Motorway as in the case of UG Campus (Fig. 7).

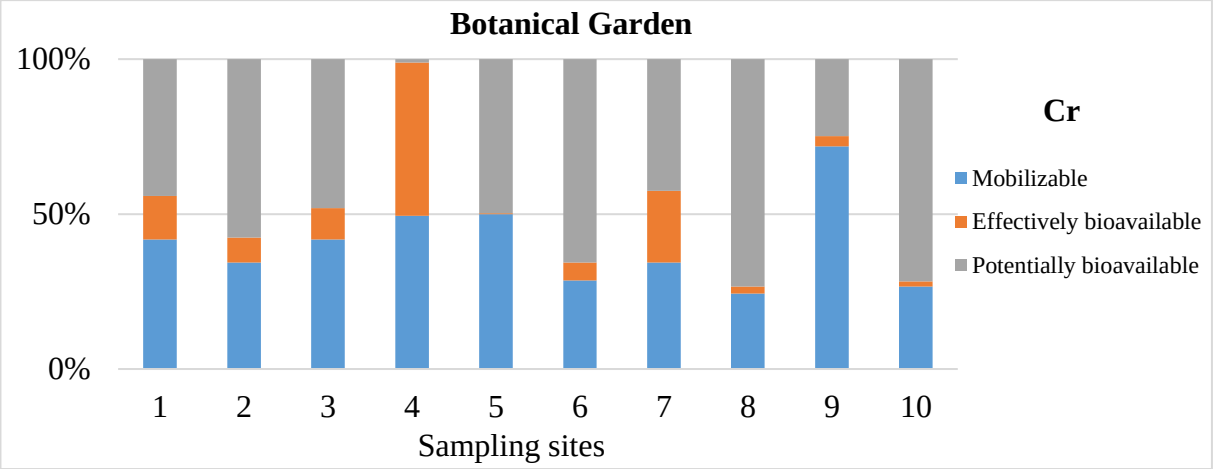


Figure 4.10: Cr fraction after performing a 3-step chemical extraction

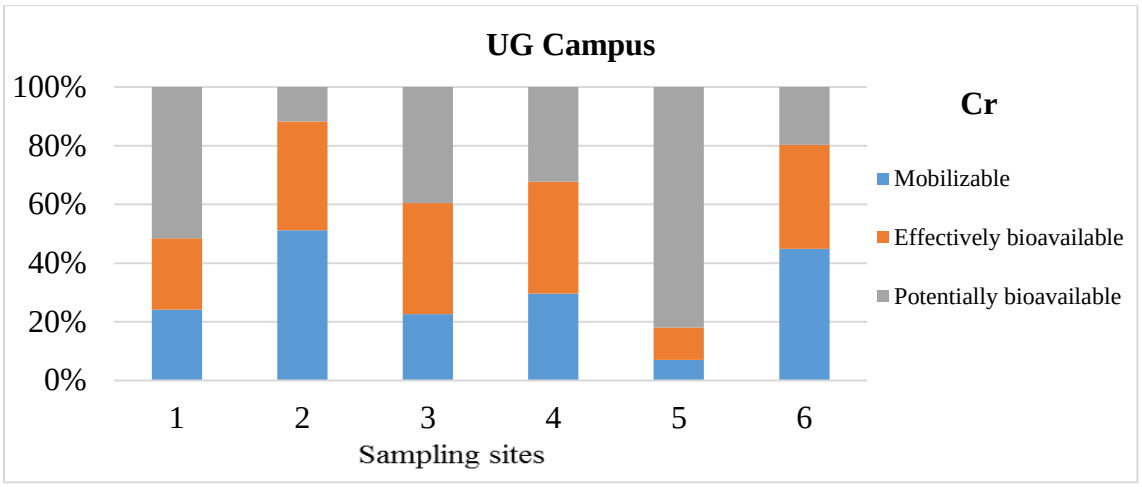


Figure 4.11: Cr fraction after performing a 3-step chemical extraction

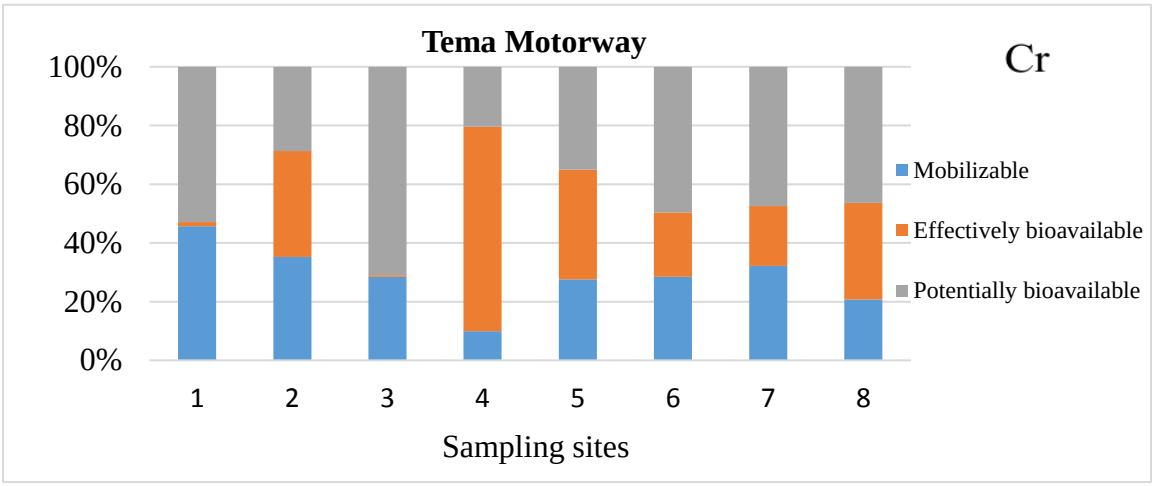


Figure 4.12: Cr fraction after performing a 3-step chemical extraction

Manganese

Manganese is present mostly in the mobilizable fraction (F1), particularly at sites B1, B2, B6, B9, L2, L6, M1, and M3 with the content as high as 228.32% at M6. The potentially bioavailable fraction (F3) account for about 4% of the total Mn in the soil, and this fraction has a very similar presence at the other two environments. Mn bound to the effectively bioavailable phase (F2) constitutes about 6% with sites 4, 8, and 31 having slightly higher value. Therefore, the appreciable content (~34%) of Mn associated with the acid soluble sample phase (fraction 1) shows that its availability is susceptible to pH or ionic composition changes in all the different environments (Petit and Rucandio, 1999). This further demonstrates a combination of some natural and some anthropogenic sources of Mn in the environment.

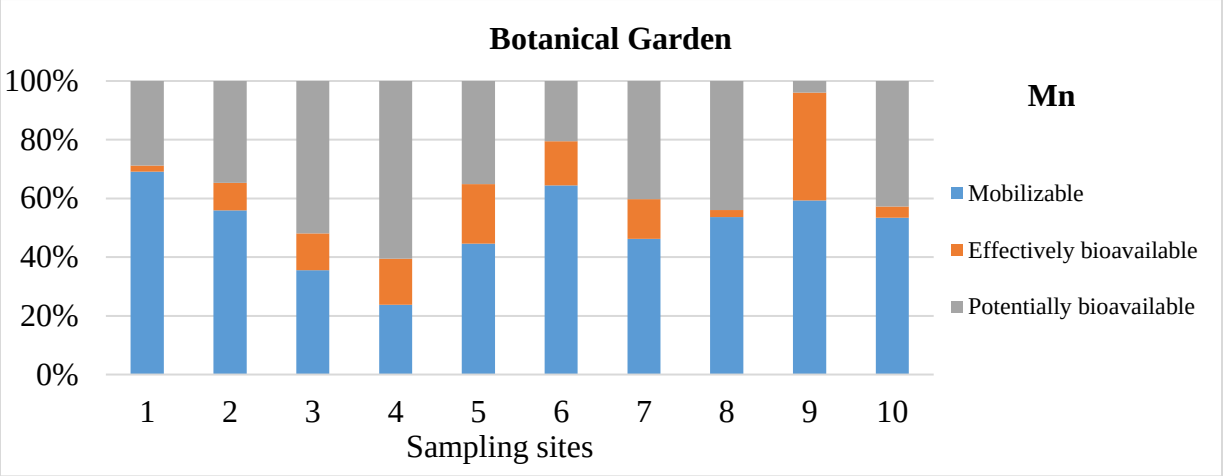


Figure 4.13: Mn fraction after performing a 3- step sequential extraction

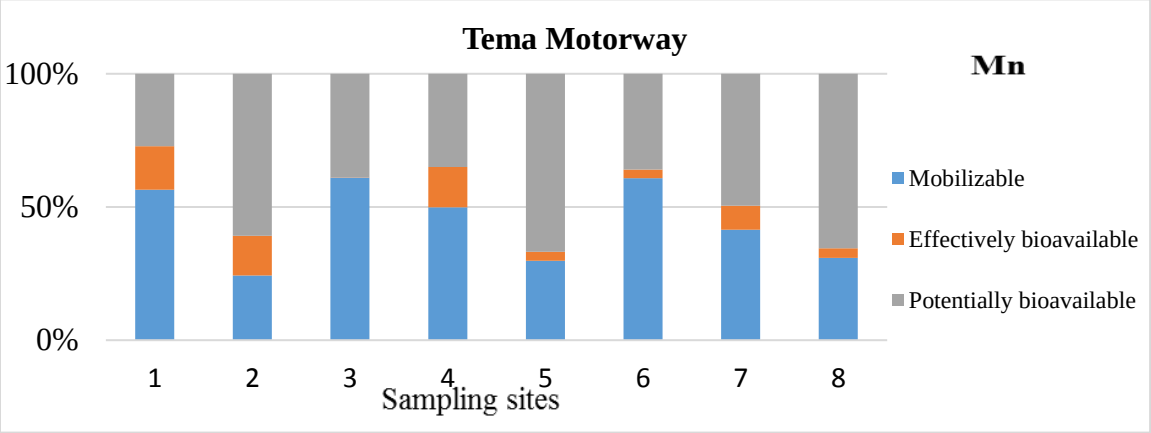


Figure 4.14: Mn fraction after performing a 3- step sequential extraction

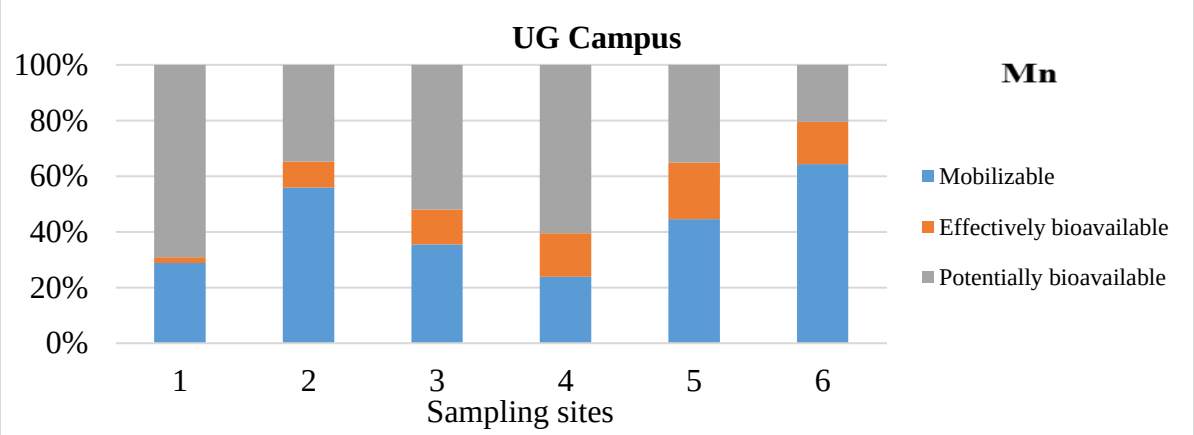


Figure 4.15: Mn fraction after performing a 3- step sequential extraction

Cadmium

The Cd speciation varied widely among all the soil samples from the various locations, while the mobilizable (F1) had more or less equal presence as in all the samples with the exception of L2 (Fig. 4.16). The effectively bioavailable (F2) had significant presence at sites B7 and B9, followed by the sites L4 and M1. The potentially bioavailable fraction (F3) was conspicuous by its large presence at sites B5, L2, and M6, while in other sites, its presence was small and more or less similar. When the sum of all the average Cd fractionation steps of the three different environments

were compared (Table. 5), it was seen that the Tema Motorway sites constituted more than 333%, while the other fractions were in the order of carbonate fraction (F2, 21%), exchangeable fraction (F1, 14%). The results indicated that considerable amount of Cd could be mobile under suitable environmental conditions and might become bioavailable. Similar results have been found earlier by other workers, and it was found that Cd did not form stable complexes with organic matter (Sposito and Lund, 1982). It is known that Cd associated with fractions other than the residual is easily taken up by plants growing in Cd-enriched soils (Olajire *et al.*, 2003). This underlines the need for frequent examination of Cd levels in soils on which herbal plants are cultivated.

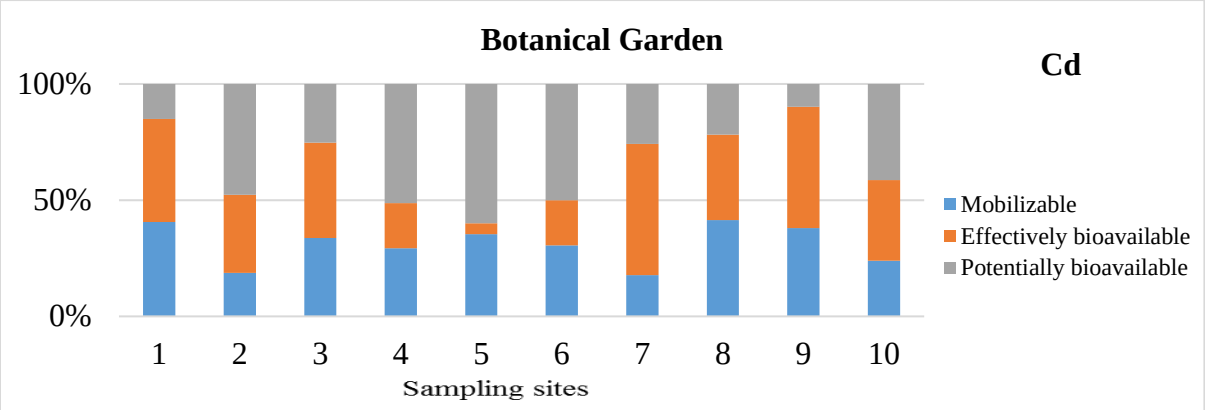


Figure 4.16: Cd fraction after performing a 3- step sequential extraction

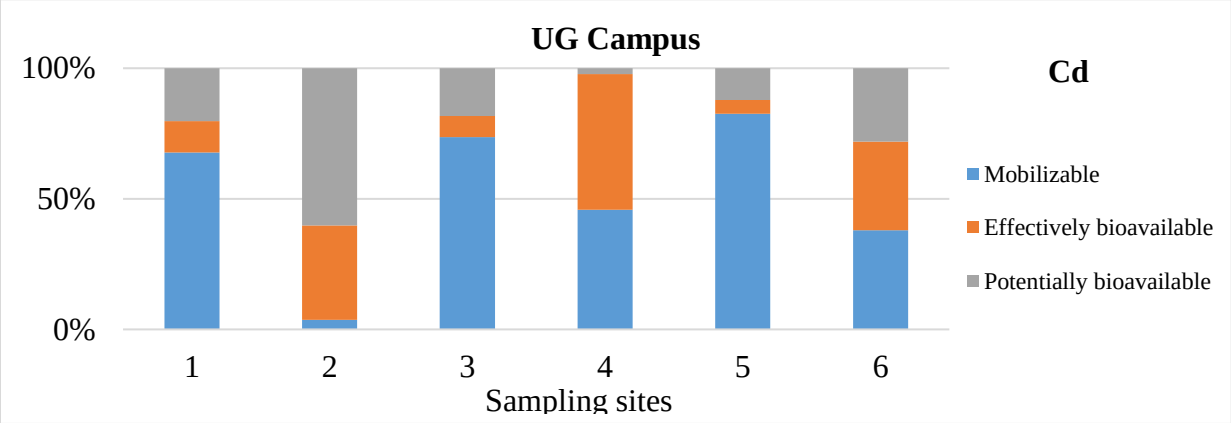


Figure 4.17: Cd fraction after performing a 3- step sequential extraction

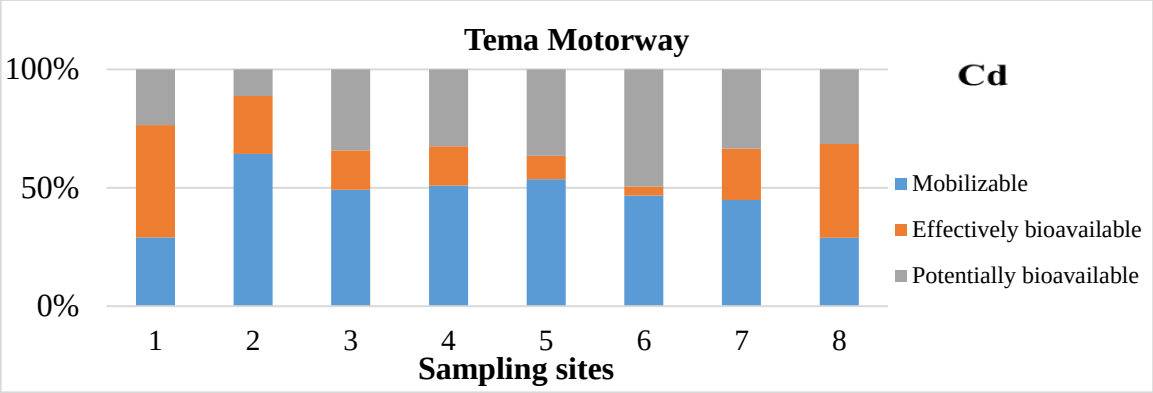


Figure 4.18: Cd fraction after performing a 3- step sequential extraction

Nickel

The average fractionation pattern of Ni in the medicinal plant soil samples showed this order: effectively bioavailable > mobilizable > potentially bioavailable (Fig 4.) for all the geographical locations. This meant a large proportion of nickel, could be extracted in the first two fractions (F1 and F2), and since these fractions represented the proportion of the PTEs that could be easily mobilized by changes in environmental conditions such as pH, redox potential, salinity, etc. (Huang et al. 2007; Jain et al. 2007), this is of serious concern. The dominant proportion of Ni was in the effectively bioavailable phase except in Site B1, B2 and B8 which showed otherwise (Fig 4.). Varied patterns of Ni partitioning in soils are reported in the literature. For example, Martin et al. (1999) and Davutluoglu *et al*. (2011) found that nickel was mainly associated with F2 fraction in sediments. In contrast, very high percentage of Ni in residual fraction has also been reported by Adamo *et al*. (1996), Ma and Rao (1997) in soils. Thus a combination of anthropogenic and natural origins could be considered for Ni in medicinal plant soil samples of the study area.

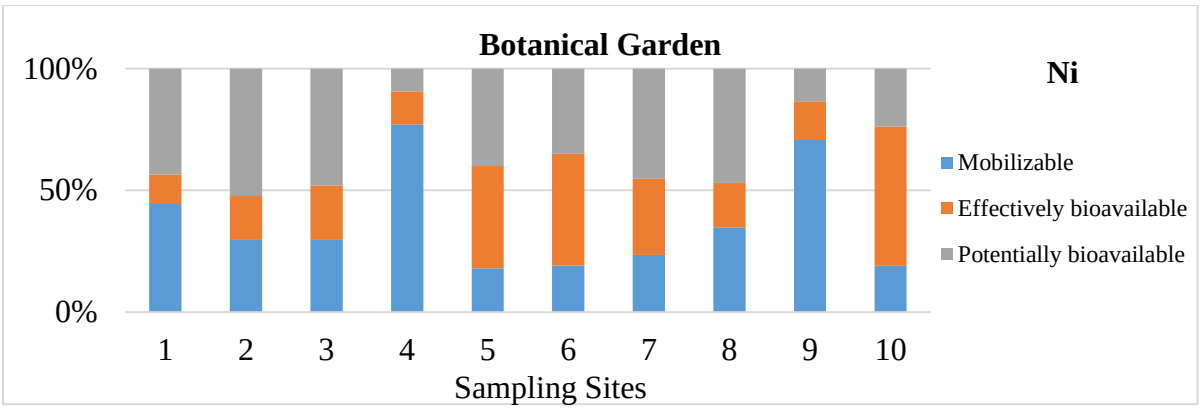


Figure 4.19: Ni fraction after performing a 3- step sequential extraction

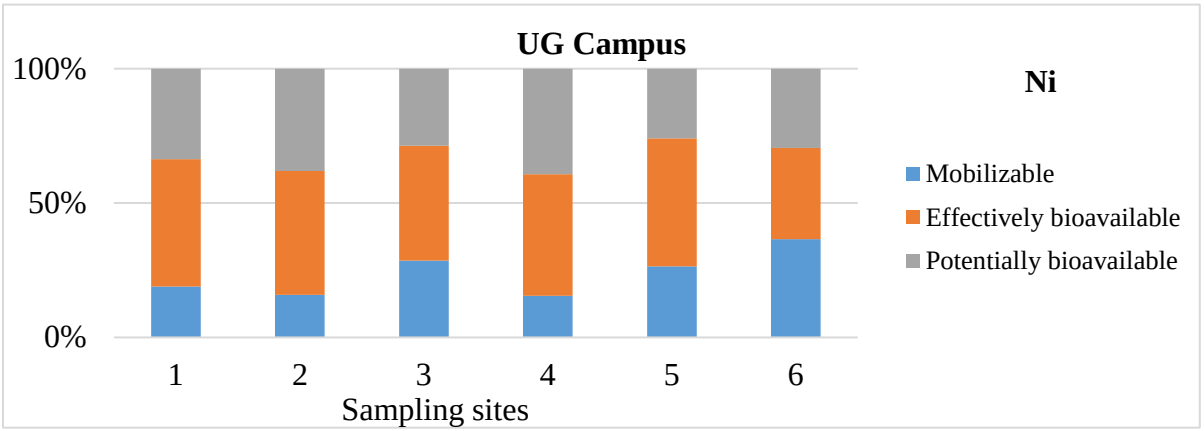


Figure 4.20: Ni fraction after performing a 3- step sequential extraction

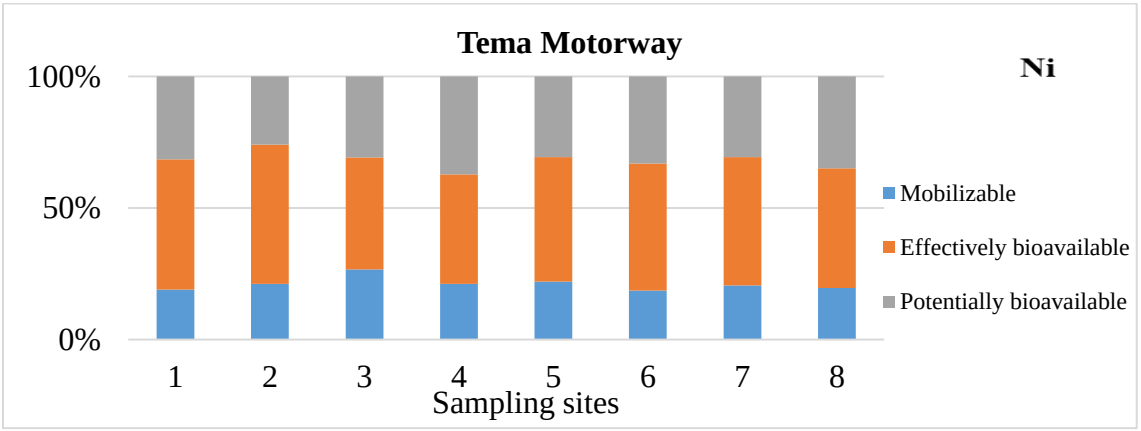


Figure 4. 21: Ni fraction after performing a 3- step sequential extraction

Copper

The distribution of various fractions associated with Cu showed that most of Cu was found to be bound to the mobilizable and effectively bioavailable phases (F1 and F2) (Fig.). Thus, Cu was likely to leach easily to the surrounding water column. The tendency of Cu to be associated with the effectively bioavailable fraction (organic matter and sulfides) has been widely reported by other researchers ((Imperato *et al.*, 2003; Fergusson and Ryan 1984; Harrison et al. 1981). This is attributed to the strong correlation between copper and organic matter in soil samples(Huang *et al.*, 2007). The potentially bioavailable fraction (*F3)* also has a considerable amount of Cu in a few number of sites especially M7 while for the others, this fraction is either very small or negligible. This indicates high mobility of Cu in the geographical locations.

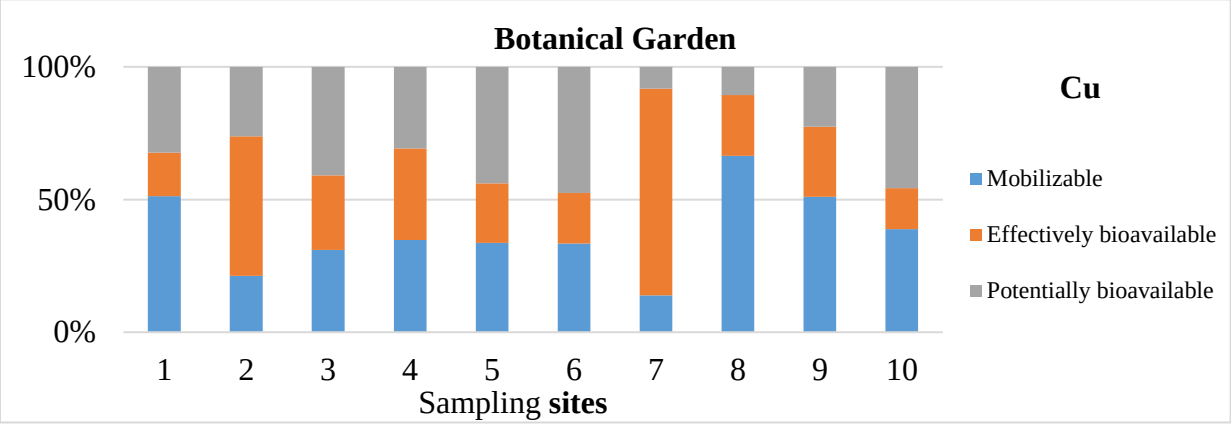


Figure 4.22: Cu after performing a 3- step sequential extraction

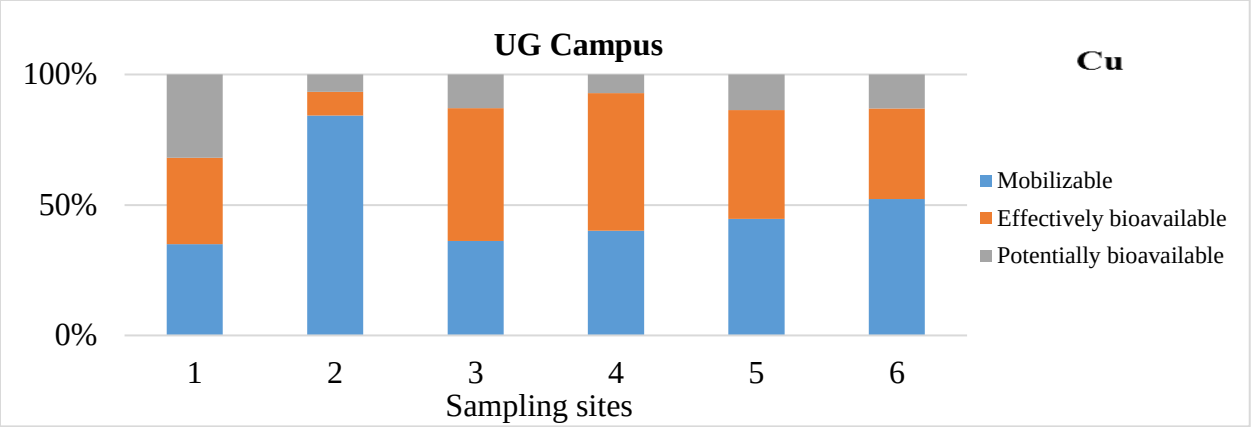


Figure 2.23: Cu fraction after performing a 3- step sequential extraction

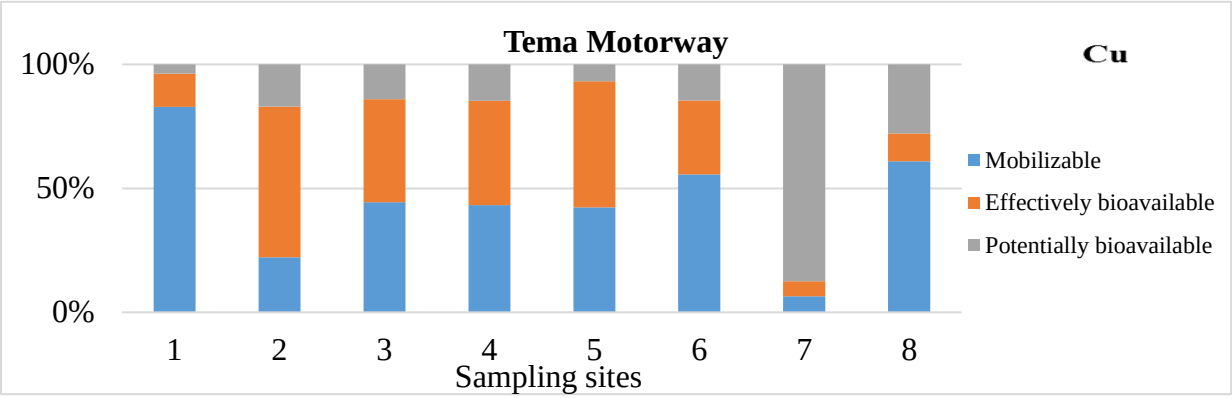


Figure 4.24: Cu fraction after performing a 3- step sequential extraction

Iron

Most of the Fe was held in the potentially bioavailable fraction at majority of the sites. Similar results have been reported by Kierczak *et al*. (2008); Martin *et al*. (1999); Davutluoglu *et al*. (2011) and at contaminated soil and sediment in the Pearl River Estuary in China (Yang *et al*., 2012; Yu, *et al*.,, 2010). A significant association of Fe with the residual fraction can be explained by the link to more resistant mineralogical phases, such as crystalline iron oxide and residual silicate phases.

The mobilizable fraction of Fe was maximum at Site B1 and the effectively bioavailable fraction which is the second dominant fraction ranged from 0.913% at Site B7 to 300.638% at Site B1. As stated earlier, minerals in the bioavailable fraction are strongly bonded to metals and do not represent an environmental risk as in the case of Ni (Wali *et al*., 2014).

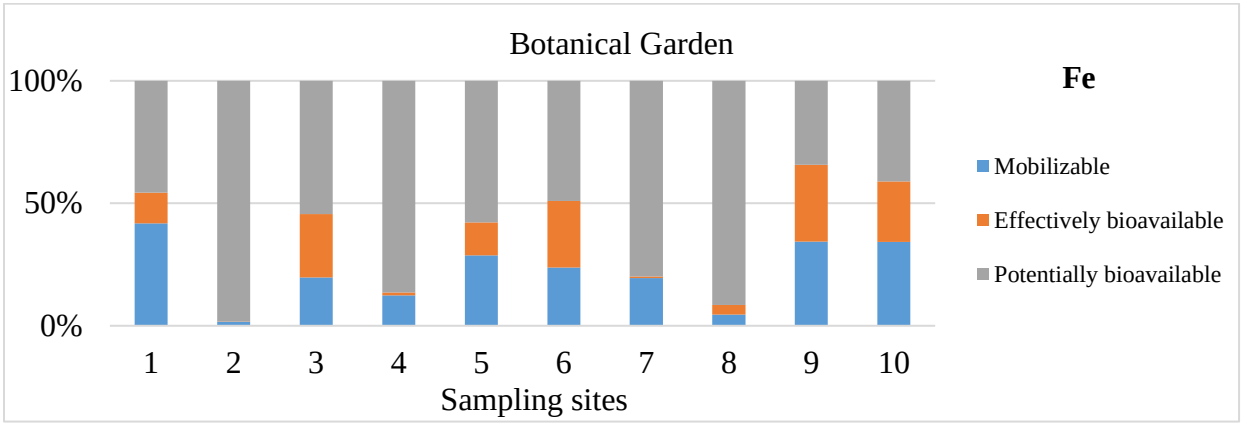


Figure 4.25: Fe fraction after performing a 3- step sequential extraction

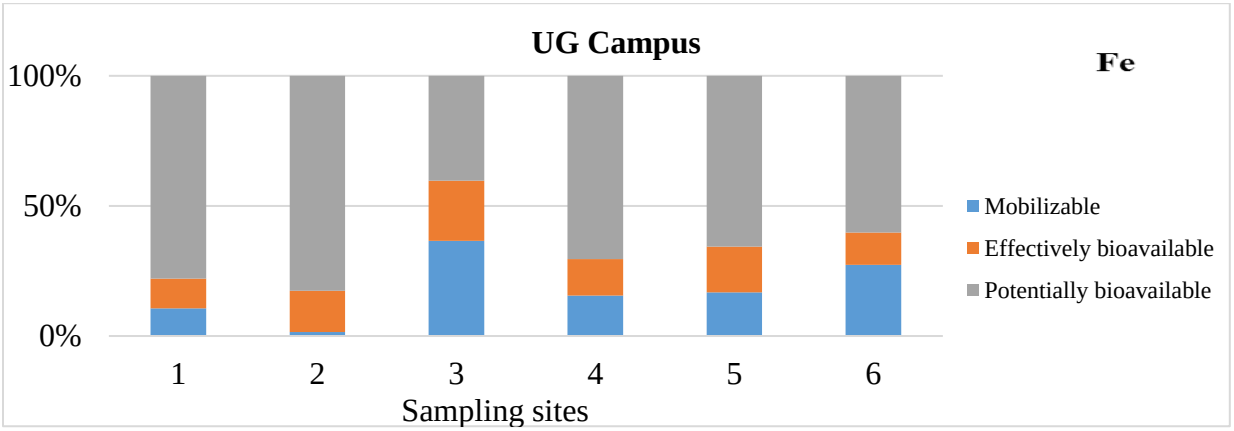


Figure 4.26: Fe fraction after performing a 3 - step sequential extraction

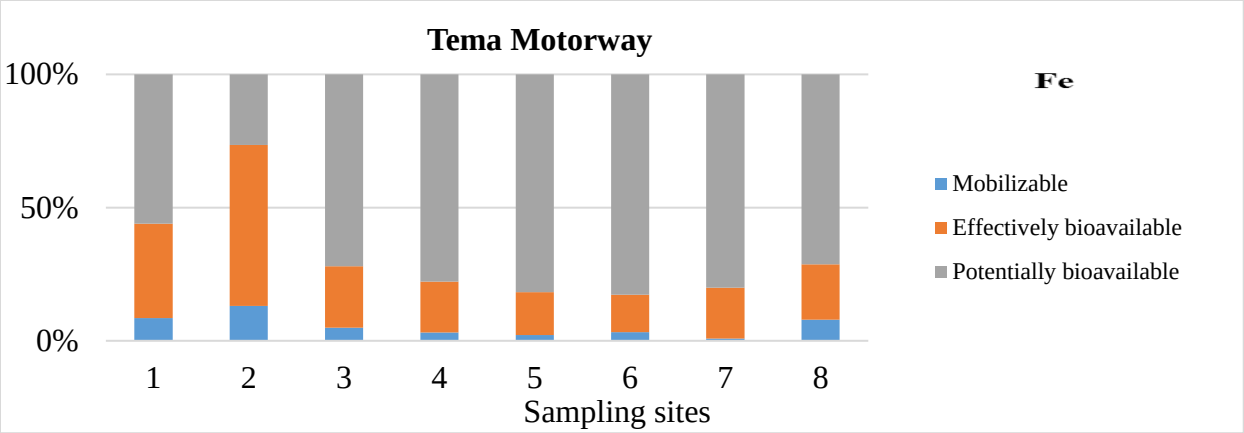


Figure 4.27: Fe fraction after performing a 3 - step sequential extraction

4.9. Bioaccessibility of PTES in the Selected Medicinal Plants

To ascertain the oral bioaccessibility of PTEs in the medicinal herbs, the parts of the herb used were extracted by using an *in vitro* gastrointestinal extraction procedure. This methodology was made up of 2 processes which stimulate human digestion. Phase 1 mimics extraction in *acidic stomach* using gastric fluid (pepsin), followed by phase 2 which is also the extraction in the neutral small intestinal fluid (pancreatin, amylase and bile salts). The SBET test results obtained indicated the amount of PTEs which could be absorbed via ingestion of the medicinal plants. Bioaccessibility for each phase was expressed as the percentage of the element content extracted by SBET with respect to its total concentration in the selected plant species:

$$\%\ \text{Bioaccessibility} = \frac{(\text{mg leached by extraction fluid per kg of plant})}{(\text{total concentration in plant;mg/kg})} \times 100$$

Tables 4.16 and 4.17 show the 2-part, acid –alkaline percent SBET system that represents the stomach and small intestine of the human digestion system respectively. Total element content (mg/kg) of the plants, quantity of metals dissolved by the simulated gastric fluid leach (mg/kg) for both stomach and small intestine compartment are given in Appendix C. PTEs concentrations in

each phase varied over a wide range in the studied medicinal plants. The results also revealed ability of most PTEs being easily available for absorption into the systemic circulation of humans. This could be linked to the differences arising from the composition and pH (gastric pH = 1.5 and intestinal pH = 7) of the two compartments in addition to the chemical constituents of the herbal plant itself like polyphenols and phytates that inhibit bioaccessiblity. More so under *in vitro* conditions, factors such as sorption and precipitation reactions in the medium as well as residence time also affect the solubility of PTEs. (Bolan *et al.*, 2017; Rasmussen *et al.*, 2013).

The bioaccessible fractions of PTEs in the medicinal plant species ranged from 2.526-97.391% in the gastric phase and 0.198-74.227% in the intestinal phase. In addition, the human bioaccessible fractions showed that the concentrations of most of the studied PTEs (As, Cu, Mn, Zn, Fe and Pb) were higher in the first stage (stomach compartment) of the extraction than the second stage. This was expected since most metals hydrolyse at low pH to increase solubilisation and precipitation as the pH is raised (Luo *et al.*, 2012). This was the situation for Pb human bioaccessible fraction as it was not detected for almost all the medicinal plants in all the phases except in Ricinus communis (L3) and physalis angulata (M4). The lower concentrations of Cr in the second stage was attributed to its high adsorption at high pH and the low affinity of the element to the pancreatin enzyme in the remaining extract as demonstrated by Martell and Smith (1982). Likewise, the higher concentrations of Fe, Cu, Mn, Zn and As in the first stage was due to the H^+ concentration and complex ion formation with Cl^- which controls dissolution of most elements in the stomach. The numbers for Zn was in close agreement with Lesniewicz et al. (2006) in vitro bioaccessibility studies of metals in Polish plant based medicines using HCl and pepsin digestion methods establishing Zn varied in the range of 40-80%. However bioaccessibility fractions by Cámara *et al.* (2005) were higher than this study. The other remaining elements: Ni and Cd showed

bioaccessible fractional values of less than 50 for the intestinal phase indicating low to moderate bioaccessibility.

Overall, Fe displayed the highest bioaccessibility (97.391%) in the medicinal plant (*phyllantus amarus*, in the stomach compartment) collected form UG Campus whiles Ni was the least in *lantana camara* (0.198 in the intestinal phase). The greater % bioaccessibilty of Fe in *phyllantus amarus* indicated the potential of this plant as a dietary source of Fe to the users. There was no distinct difference in the bioaccessible PTEs concentration of the herbal plants sampled from the diverse geographical locations. Thus, the PTE bioaccessibility of the medicinal plants varies with each PTE and also the plant species as well as the part being used, but does not necessarily depend on the location from which the plants are collected.

Table 4.16: Bioaccessibility of PTEs (as a percentage of SBET)-Stomach Compartment

Site No.	Name of Plants	Parts	Fe	Cu	Ni	Mn	Zn	Cd	Cr	As	Pb
B1	*Desmodium styracifolium*	Leaves	66.754	66.812	13.459	78.882	78.923	37.840	63.330	73.039	NC
B3	*Azadirachta indica*	Leaves	70.444	67.499	18.065	83.782	73.709	NC	66.257	65.629	NC
B4	*Cassia alata*	Leaves	68.534	78.908	23.976	69.118	24.813	27.660	50.114	95.133	NC
B5	*Cymbopogon citratus*	Leaves	31.252	88.749	55.710	56.096	76.786	17.450	12.974	93.226	NC
B6	*Solanum torvum*	Fruits	36.007	89.101	31.155	95.102	88.039	43.767	5.750	91.382	NC
B8	*Phyllantus fraternus*	Leaves	55.609	59.716	13.847	50.362	53.764	29.887	31.266	83.752	NC
B10	*Ricinus communis*	Leaves	84.200	75.924	18.065	81.808	88.684	55.674	56.197	54.834	NC
L1	*Dissotis rotundifolia*	Leaves	63.296	84.761	4.865	20.093	82.015	21.228	27.479	90.250	NC
L1	*Desmodium adscendens*	Leaves	60.940	32.315	12.292	28.119	77.243	17.764	51.640	77.169	NC
L2	*Alternathera pungens*	Leaves	13.822	66.467	2.822	16.169	54.124	8.053	6.867	88.383	NC
L2	*Lantana camara*	Leaves	92.177	55.813	17.514	70.242	16.120	73.126	54.130	92.814	NC
L3	*Ricinus communis*	Leaves	66.528	64.259	8.831	31.104	41.257	23.066	68.659	54.256	78.261
L5	*Cassia occidentalis*	Seeds	84.407	60.389	24.168	66.582	85.052	75.708	42.805	79.342	NC
L5	*Hyptis suaveolens*	Leaves	68.824	74.670	3.934	8.530	48.629	24.956	31.485	61.142	NC
L5	*Phyllantus amarus*	Leaves	97.391	63.066	9.066	10.764	60.686	12.036	25.398	96.794	NC
M2	*Passiflora suberosa*	Fruits	30.088	86.119	6.255	84.797	83.897	2.754	51.676	90.255	NC
M3	*Azadirachta indica*	Leaves	56.803	72.884	18.814	9.696	76.721	30.177	37.378	83.461	NC
M3	*Zanthoxylum zanthoxyloides*	Fruits	59.405	53.892	4.640	74.093	42.456	16.304	19.239	78.596	NC
M4	*Physalis angulata*	Leaves	74.921	84.631	44.049	77.844	60.205	10.881	36.324	85.666	87.983
M5	*Phyllantus niruri*	Leaves	70.709	76.948	16.727	52.242	87.970	6.884	6.613	86.140	NC
M5	*Euphorbia hirta (green)*	Fruits	76.569	84.090	3.882	14.661	55.442	91.262	63.172	84.795	NC
M6	*Sesamum indicum*	seeds	22.746	76.625	2.526	9.295	78.101	14.063	4.980	83.962	NC
M7	*Calotropis procera*	Fruits	19.233	69.700	48.479	33.897	77.248	36.052	95.977	88.564	NC
Min			**2.826**	**32.315**	**2.526**	**8.530**	**16.120**	**2.754**	**4.980**	**54.256**	**NC**
Max.			**97.391**	**89.101**	**55.710**	**95.102**	**88.684**	**91.262**	**95.977**	**96.794**	**87.983**

Table 4.17: Bioaccessibility of PTEs (as a percentage of SBET)-Small Intestinal Compartment

Site No.	Name of Plants	Parts	Fe	Cu	Ni	Mn	Zn	Cd	Cr	As	Pb
B1	*Desmodium styracifolium*	Leaves	27.093	27.729	9.073	18.116	12.409	16.245	8.129	38.861	NC
B3	*Azadirachta indica*	Leaves	24.573	23.209	9.515	19.765	33.816	NC	21.080	14.418	NC
B4	*Cassia alata*	Leaves	41.120	252.698	10.727	36.024	38.833	18.244	19.607	16.839	NC
B5	*Cymbopogon citratus*	Leaves	15.812	52.149	29.889	34.745	74.086	9.122	23.361	47.540	NC
B6	*Solanum torvum*	Fruits	7.547	36.860	2.338	30.889	44.679	20.472	31.436	50.919	NC
B8	*Phyllantus fraternus*	Leaves	18.191	25.972	6.448	13.462	24.275	21.160	21.380	28.960	NC
B10	*Ricinus communis*	Leaves	26.901	17.324	19.555	17.764	28.832	14.256	8.262	26.466	NC
L1	*Dissotis rotundifolia*	Leaves	42.197	52.823	4.099	9.654	40.880	10.355	13.071	35.295	NC
L1	*Desmodium adscendens*	Leaves	20.313	13.152	12.080	27.505	31.112	5.020	13.322	5.739	NC
L2	*Alternathera pungens*	Leaves	57.360	11.525	0.467	18.974	18.347	25.677	5.016	29.239	NC
L2	*Lantana camara*	Leaves	34.486	1.421	0.198	30.553	7.772	33.951	19.150	17.146	NC
L3	*Ricinus communis*	Leaves	44.352	12.652	3.764	18.215	24.063	14.828	38.982	15.606	47.469
L5	*Cassia occidentalis*	Seeds	38.956	35.495	6.863	37.107	5.862	21.396	9.213	23.718	NC
L5	*Hyptis suaveolens*	Leaves	41.294	12.963	6.552	16.431	29.247	18.237	9.907	16.198	NC
L5	*Phyllantus amarus*	Leaves	38.956	2.448	1.762	26.268	60.686	9.713	23.153	20.819	NC
M2	*Passiflora suberosa*	Fruits	6.018	34.355	11.827	41.227	4.812	19.277	3.799	49.841	NC
M3	*Azadirachta indica*	Leaves	24.314	64.489	10.835	11.034	43.876	10.059	38.431	44.228	NC
M3	*Zanthoxylum zanthoxyloides*	Fruits	2.826	11.695	20.318	17.611	40.814	14.363	6.111	44.768	NC
M4	*Physalis angulata*	Leaves	22.476	62.095	25.679	16.705	2.553	17.577	2.238	23.146	56.322
M5	*Phyllantus niruri*	Leaves	14.142	55.843	6.459	8.936	17.712	19.455	4.381	33.753	NC
M5	*Euphorbia hirta (green)*	Fruits	45.941	11.424	5.785	23.947	5.517	14.040	4.435	9.600	NC
M6	*Sesamum indicum*	seeds	15.164	52.842	5.801	12.039	47.999	35.157	15.460	12.720	NC
M7	*Calotropis procera*	Fruits	3.847	59.014	40.150	12.740	45.313	14.646	40.926	30.114	NC
Min.			**2.826**	**1.421**	**0.198**	**8.936**	**2.553**	**5.020**	**2.238**	**5.739**	**NC**
Max.			**45.941**	**64.489**	**40.150**	**41.227**	**74.086**	**35.157**	**40.926**	**50.919**	**56.322**

4.10. Health Risk Assessment

Health risk estimations were calculated based on an integration of chemical analysis data, (which comprises bioaccessible concentrations obtained for the stomach phase) and medicinal plants consumption assumptions. Only bioaccessible concentrations of the stomach phase were used in the risk calculation since the gastric phase results were always higher which is consistent with standard risk assessment practice. The study used the default: (a) hypothetical body weights of 40-kg for children (10-17yrs) and 70-kg for adults upon consultation with medics within the Ministry of Health, Ghana; and (b) maximum absorption rate of 100 % and bioavailability rate of 100%. Consumption rate of herbs (2000mg/day for children and 4000mg/day [dry weight] for adults) were based on a previous study of herbal teas consumed in Ghana where it was established that Ghanaian children and adults consume 1 and 2 tea bags per (100-250) ml per day respectively (Kuranchie, 2012). The average weight of tea bag was found to be 2000 mg/tea bag. Similarly, the herbs understudy, were all found to be present as tea bags on the Ghanaian as well as the international markets having maximum average weight of 2000 mg/tea bag. Most of these herbs are all administered as tea bags or other forms. And since dry herbs were prepared for this study it was imperative to assume consumption rate based on tea bag weight to make easier computations.

In order to quantify the health risk from ingesting the selected medicinal plants by children and adults, the estimated dose and hazard index (HI) were calculated and the results are summarized in Tables 4.18-4.22. The health risk values of PTEs to adult and children through individual plants were less than 1, posing no threat to the local consumers of these plants. This results were in agreement with findings of Muhammad *et al*. (2016) who carried out a similar study in Pakistan, where HI for single wild plants were less than one. Although the estimated risks of PTEs in

medicinal plants were low and proved no obvious adverse effect in humans, however, the long term consumption considering the larger concentrations of elemental total PTEs obtained in the medicinal plants could pose serious health implications to consumers.

Table 4.18: Health risk assessment of Cr and Cd in medicinal plants

		Cr						Cd					
			***Adults** (above 18yrs)*		***Children** (10-17yrs)*				***Adults*** (above 18yrs)		***Children*** (10-17yrs)		
Site #.	**Name of Plants**	**R_fD**	**EDI**	**HI**	**EDI**	**HI**	**Risk**	**R_fD**	**EDI**	**HI**	**EDI**	**HI**	**Risk**
B1	*Desmodium styracifolium*	1.5	2.04E-04	1.36E-04	1.78E-04	1.19E-04	No	0.001	2.12E-05	2.10E-02	1.84E-05	1.84E-02	No
B3	*Azadirachta indica*	1.5	3.82E-04	2.54E-04	3.34E-04	2.23E-04	No	0.001	7.43E-05	2.61E-02	2.28E-05	2.28E-02	No
B4	*Cassia alata*	1.5	1.15E-04	7.68E-05	1.01E-04	6.72E-05	No	0.001	6.78E-06	3.71E-02	3.25E-05	3.25E-02	No
B5	*Cymbopogon citratus*	1.5	2.61E-04	1.74E-04	2.28E-04	1.52E-04	No	0.001	3.48E-05	2.03E-02	1.78E-05	1.78E-02	No
B6	*Solanum torvum*	1.5	1.41E-04	9.41E-05	1.23E-04	8.23E-05	No	0.001	1.02E-05	5.90E-02	5.17E-05	5.17E-02	No
B8	*Phyllantus fraternus*	1.5	1.41E-06	9.41E-07	1.24E-06	8.23E-07	No	0.001	1.02E-09	1.35E-02	1.19E-05	1.19E-02	No
B10	*Ricinus communis*	1.5	5.28E-04	3.52E-04	4.62E-04	3.08E-04	No	0.001	0.000142	7.77E-02	6.80E-05	6.80E-02	No
L1	*Dissotis rotundifolia*	1.5	4.23E-04	2.82E-04	3.71E-04	2.47E-04	No	0.001	9.15E-05	4.18E-02	3.66E-05	3.66E-02	No
L1	*Desmodium adscendens*	1.5	7.91E-04	5.27E-04	6.92E-04	4.61E-04	No	0.001	0.000319	9.29E-02	8.13E-05	8.13E-02	No
L2	*Alternathera pungens*	1.5	1.16E-03	7.76E-04	1.02E-03	6.79E-04	No	0.001	0.000691	1.69E-02	1.48E-05	1.48E-02	No
L2	*Lantana camara*	1.5	1.73E-04	1.15E-04	1.51E-04	1.01E-04	No	0.001	1.53E-05	2.29E-02	2.00E-05	2.00E-02	No
L3	*Ricinus communis*	1.5	3.38E-04	2.26E-04	2.96E-04	1.97E-04	No	0.001	5.84E-05	2.21E-02	1.94E-05	1.94E-02	No
L5	*Cassia occidentalis*	1.5	2.47E-04	1.64E-04	2.16E-04	1.44E-04	No	0.001	3.1E-05	1.88E-02	1.64E-05	1.64E-02	No
L5	*Hyptis suaveolens*	1.5	1.23E-04	8.22E-05	1.08E-04	7.19E-05	No	0.001	7.76E-06	2.05E-02	1.80E-05	1.80E-02	No
L5	*Phyllantus amarus*	1.5	1.75E-04	1.17E-04	1.53E-04	1.02E-04	No	0.001	1.57E-05	4.65E-02	4.07E-05	4.07E-02	No
M2	*Passiflora suberosa*	1.5	1.06E-05	7.05E-06	9.25E-06	6.17E-06	No	0.001	5.7E-08	4.01E-03	3.51E-06	3.51E-03	No
M3	*Azadirachta indica*	1.5	4.83E-04	3.22E-04	4.23E-04	2.82E-04	No	0.001	0.000119	3.43E-02	3.00E-05	3.00E-02	No
M3	*Zanthoxylum zanthoxyloides*	1.5	4.83E-04	3.22E-04	4.23E-04	2.82E-04	No	0.001	0.000119	3.43E-02	3.00E-05	3.00E-02	No
M4	*Physalis angulata*	1.5	2.59E-04	1.73E-04	2.27E-04	1.51E-04	No	0.001	3.43E-05	3.69E-02	3.23E-05	3.23E-02	No
M5	*Phyllantus niruri*	1.5	2.55E-03	1.70E-03	2.23E-03	1.49E-03	No	0.001	0.003327	1.82E-02	1.59E-05	1.59E-02	No
M5	*Euphorbia hirta*	1.5	6.36E-04	4.24E-04	5.57E-04	3.71E-04	No	0.001	0.000207	5.10E-02	4.46E-05	4.46E-02	No
M6	*Sesamum indicum*	1.5	1.11E-03	7.37E-04	9.67E-04	6.45E-04	No	0.001	0.000624	6.34E-03	5.55E-06	5.55E-03	No
M7	*Calotropis procera*	1.5	3.07E-04	2.04E-04	2.68E-04	1.79E-04	No	0.001	4.8E-05	2.61E-02	2.29E-05	2.29E-02	No

Table 4.19: Health risk assessment of Cu and Fe in medicinal plants

			Cu						Fe				
			Adults (above 18yrs)		***Children*** (10-17yrs)				***Adults*** (above 18yrs)		***Children*** (10-17yrs)		
Site #.	**Name of Plants**	**R_fD**	**EDI**	**HI**	**EDI**	**HI**	**Risk**	**R_fD**	**EDI**	**HI**	**EDI**	**HI**	**Risk**
B1	*Desmodium styracifolium*	2	1.75E-05	8.74E-06	1.53E-05	7.65E-06	No	0.5	2.17E-03	4.33E-03	1.89E-03	3.79E-03	No
B3	*Azadirachta indica*	2	9.42E-05	4.71E-05	8.25E-05	4.12E-05	No	0.5	8.96E-04	1.79E-03	7.84E-04	1.57E-03	No
B4	*Cassia alata*	2	5.37E-06	2.68E-06	4.70E-06	2.35E-06	No	0.5	3.42E-04	6.85E-04	2.99E-04	5.99E-04	No
B5	*Cymbopogon citratus*	2	7.95E-05	3.98E-05	6.96E-05	3.48E-05	No	0.5	2.58E-03	5.17E-03	2.26E-03	4.52E-03	No
B6	*Solanum torvum*	2	2.88E-04	1.44E-04	2.52E-04	1.26E-04	No	0.5	1.28E-03	2.56E-03	1.12E-03	2.24E-03	No
B8	*Phyllantus fraternus*	2	3.13E-05	1.56E-05	2.74E-05	1.37E-05	No	0.5	6.04E-04	1.21E-03	5.28E-04	1.06E-03	No
B10	*Ricinus communis*	2	3.87E-05	1.94E-05	3.39E-05	1.70E-05	No	0.5	9.58E-03	1.92E-02	8.38E-03	1.68E-02	No
L1	*Dissotis rotundifolia*	2	8.20E-05	4.10E-05	7.18E-05	3.59E-05	No	0.5	9.47E-04	1.89E-03	8.29E-04	1.66E-03	No
L1	*Desmodium adscendens*	2	6.05E-04	3.02E-04	5.29E-04	2.65E-04	No	0.5	4.06E-03	8.13E-03	3.56E-03	7.11E-03	No
L2	*Alternathera pungens*	2	5.84E-05	2.92E-05	5.11E-05	2.55E-05	No	0.5	1.66E-03	3.31E-03	1.45E-03	2.90E-03	No
L2	*Lantana camara*	2	6.20E-05	3.10E-05	5.43E-05	2.71E-05	No	0.5	1.31E-03	2.63E-03	1.15E-03	2.30E-03	No
L3	*Ricinus communis*	2	4.06E-04	2.03E-04	3.55E-04	1.78E-04	No	0.5	8.02E-04	1.60E-03	7.02E-04	1.40E-03	No
L5	*Cassia occidentalis*	2	1.74E-04	8.69E-05	1.52E-04	7.61E-05	No	0.5	1.46E-03	2.92E-03	1.28E-03	2.55E-03	No
L5	*Hyptis suaveolens*	2	3.32E-04	1.66E-04	2.91E-04	1.45E-04	No	0.5	3.29E-03	6.58E-03	2.88E-03	5.76E-03	No
L5	*Phyllantus amarus*	2	5.25E-04	2.62E-04	4.59E-04	2.30E-04	No	0.5	9.09E-04	1.82E-03	7.95E-04	1.59E-03	No
M2	*Passiflora suberosa*	2	2.92E-04	1.46E-04	2.56E-04	1.28E-04	No	0.5	3.17E-03	6.34E-03	2.77E-03	5.55E-03	No
M3	*Azadirachta indica*	2	7.67E-05	3.84E-05	6.72E-05	3.36E-05	No	0.5	9.16E-03	1.83E-02	8.02E-03	1.60E-02	No
M3	*Zanthoxylum zanthoxyloides*	2	7.67E-05	3.84E-05	6.72E-05	3.36E-05	No	0.5	9.16E-03	1.83E-02	8.02E-03	1.60E-02	No
M4	*Physalis angulata*	2	1.68E-04	8.39E-05	1.47E-04	7.34E-05	No	0.5	2.34E-03	4.68E-03	2.05E-03	4.10E-03	No
M5	*Phyllantus niruri*	2	1.64E-04	8.21E-05	1.44E-04	7.19E-05	No	0.5	1.66E-02	3.32E-02	1.45E-02	2.91E-02	No
M5	*Euphorbia hirta*	2	6.84E-04	3.42E-04	5.99E-04	2.99E-04	No	0.5	1.99E-03	3.99E-03	1.74E-03	3.49E-03	No
M6	*Sesamum indicum*	2	2.05E-04	1.02E-04	1.79E-04	8.96E-05	No	0.5	8.92E-04	1.78E-03	7.81E-04	1.56E-03	No
M7	*Calotropis procera*	2	1.87E-04	9.35E-05	1.64E-04	8.18E-05	No	0.5	3.06E-03	6.12E-03	2.68E-03	5.36E-03	No

Table 4.20: Health risk Assessment of Mn and Ni in medicinal plants

			Mn						Ni				
			Adults *(above 18yrs)*		***Children*** *(10-17yrs)*				***Adults*** *(above 18yrs)*		***Children*** *(10-17yrs)*		
Site #.	**Name of Plants**	**R_fD**	**EDI**	**HI**	**EDI**	**HI**	**Risk**	**R_fD**	**EDI**	**HI**	**EDI**	**HI**	**Risk**
B1	*Desmodium styracifolium*	5	2.83E-03	5.66E-04	2.47E-03	4.95E-04	No	0.02	3.70E-05	1.85E-03	3.24E-05	1.62E-03	No
B3	*Azadirachta indica*	5	1.56E-03	3.13E-04	1.37E-03	2.74E-04	No	0.02	2.04E-04	1.02E-02	1.78E-04	8.92E-03	No
B4	*Cassia alata*	5	3.75E-04	7.51E-05	3.28E-04	6.57E-05	No	0.02	1.79E-04	8.93E-03	1.56E-04	7.81E-03	No
B5	*Cymbopogon citratus*	5	3.29E-04	6.58E-05	2.88E-04	5.76E-05	No	0.02	2.23E-04	1.11E-02	1.95E-04	9.75E-03	No
B6	*Solanum torvum*	5	9.00E-04	1.80E-04	7.88E-04	1.58E-04	No	0.02	1.90E-04	9.52E-03	1.67E-04	8.33E-03	No
B8	*Phyllantus fraternus*	5	8.34E-05	1.67E-05	7.30E-05	1.46E-05	No	0.02	8.32E-05	4.16E-03	7.28E-05	3.64E-03	No
B10	*Ricinus communis*	5	3.07E-04	6.15E-05	2.69E-04	5.38E-05	No	0.02	3.00E-04	1.50E-02	2.62E-04	1.31E-02	No
L1	*Dissotis rotundifolia*	5	1.22E-03	2.43E-04	1.07E-03	2.13E-04	No	0.02	1.06E-04	5.28E-03	9.24E-05	4.62E-03	No
L1	*Desmodium adscendens*	5	4.62E-04	9.25E-05	4.05E-04	8.09E-05	No	0.02	1.11E-04	5.55E-03	9.71E-05	4.85E-03	No
L2	*Alternathera pungens*	5	4.99E-04	9.98E-05	4.36E-04	8.73E-05	No	0.02	2.12E-05	1.06E-03	1.86E-05	9.29E-04	No
L2	*Lantana camara*	5	1.16E-03	2.31E-04	1.01E-03	2.02E-04	No	0.02	2.78E-05	1.39E-03	2.43E-05	1.21E-03	No
L3	*Ricinus communis*	5	6.60E-04	1.32E-04	5.77E-04	1.15E-04	No	0.02	2.00E-04	1.00E-02	1.75E-04	8.77E-03	No
L5	*Cassia occidentalis*	5	1.05E-03	2.10E-04	9.18E-04	1.84E-04	No	0.02	1.06E-05	5.31E-04	9.29E-06	4.64E-04	No
L5	*Hyptis suaveolens*	5	4.50E-04	8.99E-05	3.93E-04	7.87E-05	No	0.02	3.64E-05	1.82E-03	3.18E-05	1.59E-03	No
L5	*Phyllantus amarus*	5	1.57E-04	3.15E-05	1.38E-04	2.75E-05	No	0.02	1.57E-04	7.87E-03	1.38E-04	6.88E-03	No
M2	*Passiflora suberosa*	5	1.16E-03	2.31E-04	1.01E-03	2.02E-04	No	0.02	4.41E-05	2.21E-03	3.86E-05	1.93E-03	No
M3	*Azadirachta indica*	5	2.01E-03	4.01E-04	1.76E-03	3.51E-04	No	0.02	1.62E-05	8.08E-04	1.41E-05	7.07E-04	No
M3	*Zanthoxylum zanthoxyloides*	5	2.01E-03	4.01E-04	1.76E-03	3.51E-04	No	0.02	1.62E-05	8.08E-04	1.41E-05	7.07E-04	No
M4	*Physalis angulata*	5	3.98E-03	7.97E-04	3.49E-03	6.97E-04	No	0.02	1.89E-04	9.43E-03	1.65E-04	8.25E-03	No
M5	*Phyllantus niruri*	5	2.04E-03	4.08E-04	1.79E-03	3.57E-04	No	0.02	1.99E-04	9.96E-03	1.74E-04	8.71E-03	No
M5	*Euphorbia hirta*	5	3.85E-04	7.70E-05	3.37E-04	6.74E-05	No	0.02	4.30E-05	2.15E-03	3.77E-05	1.88E-03	No
M6	*Sesamum indicum*	5	4.22E-04	8.43E-05	3.69E-04	7.38E-05	No	0.02	6.75E-05	3.38E-03	5.91E-05	2.95E-03	No
M7	*Calotropis procera*	5	1.13E-03	2.27E-04	9.92E-04	1.98E-04	No	0.02	1.27E-04	6.37E-03	1.11E-04	5.57E-03	No

Table 4.21: Health risk assessment of Zn and As in medicinal plants

		Zn						As					
			Adults *(above 18yrs)*		***Children*** *(10-17yrs)*				***Adults*** *(above 18yrs)*		***Children*** *(10-17yrs)*		
Site #	**Name of Plants**	**R_fD**	**EDI**	**HI**	**EDI**	**HI**	**Risk**	**R_fD**	**EDI**	**HI**	**EDI**	**HI**	Risk
B1	*Desmodium styracifolium*	15	1.74E-03	1.16E-04	1.52E-03	1.02E-04	No	0.007	7.29E-05	1.04E-02	6.38E-05	9.11E-03	No
B3	*Azadirachta indica*	15	1.05E-03	7.02E-05	9.22E-04	6.15E-05	No	0.007	3.25E-05	4.64E-03	2.85E-05	4.06E-03	No
B4	*Cassia alata*	15	4.61E-04	3.07E-05	4.03E-04	2.69E-05	No	0.007	6.82E-05	9.75E-03	5.97E-05	8.53E-03	No
B5	*Cymbopogon citratus*	15	6.15E-04	4.10E-05	5.38E-04	3.59E-05	No	0.007	2.75E-05	3.93E-03	2.41E-05	3.44E-03	No
B6	*Solanum torvum*	15	9.53E-04	6.36E-05	8.34E-04	5.56E-05	No	0.007	6.63E-06	9.47E-04	5.80E-06	8.29E-04	No
B8	*Phyllantus fraternus*	15	1.17E-03	7.79E-05	1.02E-03	6.82E-05	No	0.007	5.71E-05	8.16E-03	5.00E-05	7.14E-03	No
B10	*Ricinus communis*	15	1.14E-03	7.57E-05	9.93E-04	6.62E-05	No	0.007	1.98E-05	2.82E-03	1.73E-05	2.47E-03	No
L1	*Dissotis rotundifolia*	15	1.17E-03	7.82E-05	1.03E-03	6.85E-05	No	0.007	5.94E-05	8.48E-03	5.19E-05	7.42E-03	No
L1	*Desmodium adscendens*	15	1.00E-03	6.67E-05	8.75E-04	5.83E-05	No	0.007	2.99E-05	4.28E-03	2.62E-05	3.74E-03	No
L2	*Alternathera pungens*	15	7.22E-04	4.82E-05	6.32E-04	4.21E-05	No	0.007	3.68E-05	5.25E-03	3.22E-05	4.60E-03	No
L2	*Lantana camara*	15	5.25E-04	3.50E-05	4.59E-04	3.06E-05	No	0.007	6.96E-05	9.94E-03	6.09E-05	8.70E-03	No
L3	*Ricinus communis*	15	6.98E-04	4.65E-05	6.11E-04	4.07E-05	No	0.007	6.26E-05	8.94E-03	5.47E-05	7.82E-03	No
L5	*Cassia occidentalis*	15	1.74E-03	1.16E-04	1.52E-03	1.02E-04	No	0.007	6.14E-05	8.77E-03	5.37E-05	7.67E-03	No
L5	*Hyptis suaveolens*	15	8.80E-04	5.87E-05	7.70E-04	5.14E-05	No	0.007	6.51E-05	9.30E-03	5.70E-05	8.14E-03	No
L5	*Phyllantus amarus*	15	5.44E-04	3.62E-05	4.76E-04	3.17E-05	No	0.007	5.91E-05	8.44E-03	5.17E-05	7.38E-03	No
M2	*Passiflora suberosa*	15	3.09E-03	2.06E-04	2.71E-03	1.80E-04	No	0.007	1.54E-05	2.20E-03	1.34E-05	1.92E-03	No
M3	*Azadirachta indica*	15	4.96E-04	3.31E-05	4.34E-04	2.90E-05	No	0.007	1.98E-05	2.83E-03	1.73E-05	2.48E-03	No
M3	*Zanthoxylum zanthoxyloides*	15	4.96E-04	3.31E-05	4.34E-04	2.90E-05	No	0.007	1.98E-05	2.83E-03	1.73E-05	2.48E-03	No
M4	*Physalis angulata*	15	1.05E-03	7.00E-05	9.19E-04	6.13E-05	No	0.007	6.20E-05	8.86E-03	5.43E-05	7.75E-03	No
M5	*Phyllantus niruri*	15	1.59E-03	1.06E-04	1.39E-03	9.26E-05	No	0.007	5.20E-05	7.43E-03	4.55E-05	6.50E-03	No
M5	*Euphorbia hirta*	15	6.44E-04	4.30E-05	5.64E-04	3.76E-05	No	0.007	1.55E-04	2.21E-02	1.35E-04	1.94E-02	No
M6	*Sesamum indicum*	15	9.13E-04	6.09E-05	7.99E-04	5.33E-05	No	0.007	1.17E-04	1.67E-02	1.02E-04	1.46E-02	No
M7	*Calotropis procera*	15	7.27E-04	4.84E-05	6.36E-04	4.24E-05	No	0.007	5.34E-05	7.63E-03	4.68E-05	6.68E-03	No

Table 4. 22: Health risk assessment of Pb in medicinal plants

			Pb				
			Adults *(above 18yrs)*		***Children*** *(10-17yrs)*		
Site No.	**Name of Plants**	**R_fD**	**EDI**	**HI**	**EDI**	**HI**	**Risk**
B1	*Desmodium styracifolium*	5	NA	NA	NA	NA	No
B3	*Azadirachta indica*	5	NA	NA	NA	NA	No
B4	*Cassia alata*	5	NA	NA	NA	NA	No
B5	*Cymbopogon citratus*	5	NA	NA	NA	NA	No
B6	*Solanum torvum*	5	NA	NA	NA	NA	No
B8	*Phyllantus fraternus*	5	NA	NA	NA	NA	No
B10	*Ricinus communis*	5	NA	NA	NA	NA	No
L1	*Dissotis rotundifolia*	5	NA	NA	NA	NA	No
L1	*Desmodium adscendens*	5	NA	NA	NA	NA	No
L2	*Alternathera pungens*	5	NA	NA	NA	NA	No
L2	*Lantana camara*	5	NA	NA	NA	NA	No
L3	*Ricinus communis*	5	7.51E-05	1.88E-02	6.57E-05	1.64E-02	No
L5	*Cassia occidentalis*	5	NA	NA	NA	NA	No
L5	*Hyptis suaveolens*	5	NA	NA	NA	NA	No
L5	*Phyllantus amarus*	5	NA	NA	NA	NA	No
M2	*Passiflora suberosa*	5	NA	NA	NA	NA	No
M3	*Azadirachta indica*	5	NA	NA	NA	NA	No
M3	*Zanthoxylum zanthoxyloides*	5	NA	NA	NA	NA	No
M4	*Physalis angulate*	5	4.81E-05	1.20E-02	4.21E-05	0.010525	No
M5	*Phyllantus niruri*	5	NA	NA	NA	NA	No
M5	*Euphorbia hirta*	5	NA	NA	NA	NA	No
M6	*Sesamum indicum*	5	NA	NA	NA	NA	No
M7	*Calotropis procera*	5	NA	NA	NA	NA	No

R_fD:=Reference dose (mg/kg/day), EDI=Estimated daily intake (mg/kg/day), HI= Hazard index

CHAPTER FIVE

5.1 CONCLUSIONS

- On the whole, the study revealed a high degree of ethnobotanical novelty of plants at the various sampling locations of which many Ghanaians use as traditional folk medicine. The parts of the medicinal plants used in the preparation were mainly leaves and decoction was the chief mode of preparation.
- PTEs were detected in almost all the 56 medicinal plants examined from the three different geographical locations in the Accra Metropolis.
- The study has shown that same species of medicinal plants, growing in either the pristine (Botanical Garden) or anthropogenic impacted environments (TM and UG Campus) accumulate different levels of PTEs.
- The concentrations of PTEs varied significantly among plant species as well as in the same plant species collected from different geographical locations with most exceeding the international accepted permissible levels.
- Medicinal plants harvested from Botanical Garden had the least metal contamination (57.27%) whereas UG Campus and TM were 70.00% and 86.67% greater than international guideline values.
- The wide variations in PTEs concentrations in the analysed herbs could be attributed to differences in the plant metal uptake and translocation capabilities
- Fe had the highest metal concentration in the medicinal plants among all the nine elements investigated, followed by Mn and Zn.

- Soils collected from the various locations on which the herbs were harvested in the Metropolis were found to contain all the PTEs (Cu, Mn, Cd, Pb, Zn, Cr, Ni, and Fe) studied except As.
- All the soils examined in these locations showed signs of PTEs contamination with the higher concentrations being observed at TM and UG campus sites suggestive of anthropogenic point source contributions. Comparing the overall mean concentrations of these PTEs with EU soil quality guidelines for urban soils, only Cr exceeded the limit
- Significant correlation was recorded for Cu and Zn; and Ni and Cr indicating that these metals were emanating from common source
- The P_{deg} calculated for the mean metal contents in the soil for the different areas gave considerable to very high degree of pollution with the maximum value found at site 5 (TM) Further, geoaccumulation indices revealed that the medicinal plant soils are moderately to extremely polluted with Cd indicating anthropogenic contributions in the enrichment of this PTE in the environment.
- Fraction concentrations of PTEs in the medicinal plant soils via BCR chemical extraction procedure showed different soil-specific patterns for the various availabilities (mobilizable, potentially and effectively bioavailability) with Pb being the least mobile.
- The study also demonstrated that ingested medicinal plants have the propensity to release PTEs when they come in contact with digestive fluids regardless of the metal and plant type. PTEs were mostly retained in the stomach with Fe registering the highest bioaccessible fraction (97.391%) in *phyllantus amarus*, collected form UG Campus
- Hazard Index values for all PTEs studied indicated no significant risk of non-carcinogenic effects to both children and adults.

5.2 RECOMMENDATIONS

The following recommendations are made to further the extent of knowledge of PTEs in medicinal plants.

- There is the need for nation-wide ethnobotanical study on medicinal plants usage in order to establish prevalence at national level and guideline values
- PTEs were found in medicinal plants sampled from Accra Metropolis. It would be interesting if continuous and regular monitoring programmes for PTEs in herbal plants in the other regions are done in order to safeguard the health of consumers against metal toxicities.
- Medicinal plants, used for herbal formulation, should be collected from areas not contaminated with PTEs.
- Additionally, the government should ensure that some educational and management programmes are organized for the traditional medicine practitioners to ensure compliance of quality and safety measures.

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APPENDICES

APPENDIX A

Pearson correlations for soil data collected during the study period for Botanical Gardens

	Cr	Cd	Cu	Fe	Mn	Ni	Pb	Zn	pH	EC	MC	OM
Cr	1.000											
Cd	.439	1.000										
Cu	.070	-.141	1.000									
Fe	.190	.496	-.042	1.000								
Mn	-.422	-.008	.438	.061	1.000							
Ni	-.540	-.824**	.131	-.276	-.087	1.000						
Pb	-.145	-.158	-.063	-.269	-.219	.544	1.000					
Zn	.494	.359	-.346	.043	-.612	-.395	-.164	1.000				
pH	.194	-.016	-.602	-.080	-.181	-.238	-.192	.062	1.000			
EC	-.039	.293	-.602	-.180	-.415	-.063	.466	.477	.331	1.000		
MC	.397	-.013	.570	-.043	.042	.102	.461	-.189	-.443	-.318	1.000	
OM	.025	.084	-.074	.609	.061	-.278	-.827**	.061	.061	-.533	-.410	1.000

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

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

a. Listwise N=10

Pearson correlations for soil data collected during the study period for UG Campus

	Cr	Cd	Cu	Fe	Mn	Ni	Pb	Zn	pH	EC	MC	OM
Cr	1.000											
Cd	.254	1.000										
Cu	-.528	-.508	1.000									
Fe	-.239	.541	-.556	1.000								
Mn	.287	.336	.046	-.139	1.000							
Ni	.089	.536	-.637	.318	.188	1.000						
Pb	-.370	.348	.107	.069	-.441	.303	1.000					
Zn	-.124	-.895*	.603	-.565	-.397	-.827*	-.288	1.000				
pH	.500	-.009	.264	-.779	.052	-.172	.281	.218	1.000			
EC	.455	-.527	-.059	-.235	-.357	-.647	-.536	.709	.159	1.000		
MC	-.010	-.196	.761	-.482	.155	-.828*	-.055	.536	.494	.266	1.000	
OM	.127	-.705	.301	-.312	-.410	-.859*	-.452	.900*	.117	.921**	.483	1.000

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

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

a. Listwise N=6

Pearson correlations for soil data collected during the study period for Tema Motorway

	Cr	Cd	Cu	Fe	Mn	Ni	Pb	Zn	pH	EC	MC	OM
Cr	1.000											
Cd	-.113	1.000										
Cu	.284	.480	1.000									
Fe	.041	.131	.243	1.000								
Mn	-.201	-.853**	-.284	.047	1.000							
Ni	.846**	.025	.248	.211	-.275	1.000						
Pb	.344	.023	-.016	-.275	-.181	.079	1.000					
Zn	.304	.566	.813*	.394	-.532	.383	.168	1.000				
pH	-.273	.489	-.001	.715*	-.378	-.147	-.328	.219	1.000			
EC	-.136	.412	.136	-.471	-.618	-.127	.089	.363	-.037	1.000		
MC	.626	-.209	.097	.124	.109	.421	.797*	.179	-.297	-.422	1.000	
OM	.059	.084	.705	.280	.291	-.041	.181	.403	-.183	-.408	.413	1.000

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

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

a. Listwise N=8

APPENDIX B

Comparison between the total PTEs content and the amount measured from the 3 steps chemical extraction procedure for all sites.

LOCATIONS	SITES	PTEs	Total content (mg kg-1)	Sequential extraction scheme				Recovery (%)
				STEP 1	STEP 2	STEP 3	TOTAL	
BG	B1	Pb	16.85	1.66998	3.737575	10.53678	15.94433	94.62512757
		Mn	53.1	2.266402	32.74354	78.48907	113.499	213.7457739
		Cr	24.7	6.441352	2.166998	6.799205	15.40755	62.37876385
		Cd	2.35	1.520875	1.662028	0.564612	3.747515	159.4687196
		Fe	86000	1000.497	300.6382	1090.702	2391.837	2.781205789
		Cu	5.77	5.085487	1.630219	3.212724	9.928429	172.069834
		Zn	38.9	3.419483	2.166998	0.050895	5.637376	14.4919685
		Ni	6.15	5.964215	1.630219	5.84493	13.43936	218.5262409
	B2	Pb	26.75	4.776699	24.81553	12.1165	41.70874	155.9205154
		Mn	76.1	81.39806	13.49515	50.52427	145.4175	191.0873531
		Cr	35.55	2.640777	0.621359	4.427184	7.68932	21.62959322
		Cd	1.87	0.349515	0.631068	0.893204	1.873786	100.2024817
		Fe	16905	2000.35	2.252427	36.07767	2038.68	12.05962503
		Cu	23.57	3.32233	8.213592	4.079612	15.61553	66.25173517
		Zn	16.5	5.165049	0.621359	0.045437	5.831845	35.34451309
		Ni	6.35	3.320388	2.019417	5.854369	11.19417	176.2862167
	B3	Pb	12.31	3.812375	5.209581	4.750499	13.77246	111.8802201
		Mn	79.95	14.37325	5.065868	21.01796	40.45709	50.60298415
		Cr	4.6	3.952096	0.958084	4.550898	9.461078	205.6756053

	Cd	1.31	5.10978	6.227545	3.832335	15.16966	1157.989365
	Fe	20575	106.3673	50.51098	38.48303	195.3613	0.949508031
	Cu	23.35	5.10978	4.630739	6.750499	16.49102	70.6253446
	Zn	1.62	4.471058	0.958084	0.056287	5.485429	338.6067371
	Ni	14.59	7.60479	5.708583	12.27545	25.58882	175.386034
B4	Pb	8.3	0.059406	2.089109	12.437	14.58551	175.7290946
	Mn	57	12.09901	7.960396	30.71287	50.77228	89.07417057
	Cr	22.86	4.376238	4.376238	0.09604	8.848515	38.70741405
	Cd	1.3	1.108911	0.732673	1.940594	3.782178	290.936786
	Fe	7653.15	11.60396	1.168317	81.06931	93.84158	1.226182476
	Cu	5.2	3.110891	3.10099	2.754455	8.966337	172.4295506
	Zn	46.43	9.089109	4.376238	0.09604	13.56139	29.20824066
	Ni	8.66	8.514851	1.50495	1.039604	11.05941	127.7067661
B5	Pb	28.32	2.86	24.32	16.05941	43.23941	152.6815182
	Mn	79.5	40	18.2	31.52	89.72	112.8553459
	Cr	8.22	3.5	0.02	3.48	7	85.15815085
	Cd	0.59	0.92	0.12	1.56	2.6	440.6779661
	Fe	26325.89	201.02	100.18	47.06	348.26	1.322880252
	Cu	17.72	2.294	1.536	2.992	6.822	38.49887133
	Zn	9.9	8.24	0.674	0.1986	9.1126	92.04646465
	Ni	25.35	8.86	20.62	19.6	49.08	193.6094675
B6	Pb	30.82	0.05814	20.25194	15.8	36.11008	117.1644306
	Mn	74.86	82.42248	19.32171	26.24031	127.9845	170.9651297
	Cr	8.32	3.275194	0.668605	7.51938	11.46318	137.7785853
	Cd	1.82	0.957364	0.612403	1.569767	3.139535	172.5019167
	Fe	11514.85	109.3411	60.24031	53.0814	222.6628	1.933701183
	Cu	5.14	2.48062	1.414729	3.534884	7.430233	144.5570537
	Zn	2.18	3.662791	0.668605	0.15	4.481395	205.568594

	Ni	12	8.139535	19.37984	14.82558	42.34496 0	352.874677
B7	Pb	43.5	0.703422	15.47529	6.24031	22.41902	51.53797081
	Mn	27.05	211.597	61.95817	184.1065	457.6616	1691.909785
	Cr	14.21	4.087452	2.756654	5.057034	11.90114	83.7518697
	Cd	1	0.315589	1.003802	0.460076	1.779468	177.9467681
	Fe	8386.36	29.08745	0.912548	118.9544	148.9544	1.776150471
	Cu	8.05	2.545627	14.29658	1.511407	18.35361	227.9951822
	Zn	15.05	5.95057	2.756654	2.756654	11.46388	76.17194902
	Ni	24.65	10.70342	14.29658	20.64639	45.64639	185.1780439
B8	Pb	25.02	2.459	23.68321	17.11027	43.25247	172.8715918
	Mn	88.52	120.4389	5.28626	98.81679	224.542	253.6624319
	Cr	2.36	1.431298	0.133588	4.312977	5.877863	249.0619744
	Cd	1.28	9.293893	8.282443	4.885496	22.46183	1754.83063
	Fe	14575	200.5	8.854962	9.923664	219.2786	1.504484569
	Cu	4.68	4.65458	1.603053	0.744275	7.001908	149.6134273
	Zn	5.02	10.53435	0.133588	0.043893	10.71183	213.3831088
	Ni	12.61	8.091603	4.236641	10.91603	23.24427	184.3320762
B9	Pb	27.65	2.557252	24.04339	12.36641	38.96706	140.9296804
	Mn	28.8	15.64103	9.704142	1.043393	26.38856	91.62694499
	Cr	21	5.424063	0.25641	1.873767	7.554241	35.97257443
	Cd	1.79	0.698225	0.960552	0.18146	1.840237	102.8065188
	Fe	6359.61	7.830375	7.140039	7.830375	22.80079	0.358524956
	Cu	7.05	3.544379	1.828402	1.568047	6.940828	98.4514667
	Zn	82.85	9.433962	0.132075	17.39623	26.96226	32.5434691
	Ni	10.03	10.17751	2.284024	1.934911	14.39645	143.5338954
B10	Pb	18.2	1.157791	13.86792	19.62525	34.65096	190.3899011
	Mn	31.99	32.45283	2.35283	25.98113	60.78679	190.0181071

		Cr	23.41	2.09434	0.132075	5.641509	7.867925	33.60924617
		Cd	0.99	0.415094	0.603774	0.716981	1.735849	175.3382885
		Fe	16194.31	12.11321	8.754717	14.56604	35.43396	0.218805014
		Cu	6.39	3.320755	1.320755	3.915094	8.556604	133.9061623
		Zn	19.95	14.89152	0.25641	28.93491	44.08284	220.9666177
		Ni	14.24	7.924528	23.88679	9.924528	41.73585	293.0888276
UG Campus	L1	Pb	13.03	2.457	15.1581	17.41107	35.02617	268.8117418
		Mn	103.23	74.32806	2.964427	53.18182	130.4743	126.3918515
		Cr	41.99	8.537549	8.616601	18.28063	35.43478	84.38862255
		Cd	1.6	0.889328	0.525692	2.964427	4.379447	273.715415
		Fe	15635.32	5.337302	5.770751	39.16996	50.27801	0.321566895
		Cu	6.81	6.146245	5.837945	5.612648	17.59684	258.397033
		Zn	319.6	99.38735	115.1976	0.466403	215.0514	67.2876669
		Ni	47.46	11.2253	28.00395	19.86166	59.09091	124.5067617
	L2	Pb	16.65	12.01581	30.03914	17.67123	59.72618	358.7158084
		Mn	191.63	56.65362	12.77886	74.79452	144.227	75.26327082
		Cr	22.27	8.121331	5.890411	1.8591	15.87084	71.26556573
		Cd	1.92	0.181996	1.778865	2.964427	4.925288	256.5254132
		Fe	13353.2	0.811808	8.238748	43.0137	52.06425	0.389900955
		Cu	33.89	41.32485	4.481409	3.248532	49.05479	144.7471069
		Zn	314.09	48.8454	0.643836	132.2896	181.7789	57.87476996
		Ni	36.95	9.960861	29.06067	23.99217	63.0137	170.53775
	L3	Pb	27.57	12.62231	26.78	16.02	55.42231	201.0239724
		Mn	153.42	87.12	7.02	55.22	149.36	97.35366966
		Cr	32.38	6.82	11.4	11.92	30.14	93.08214947
		Cd	2.57	4.9	0.5347	1.22	6.6547	258.9377432
		Fe	10612.38	12.57198	7.9	13.84	34.31198	0.323320282
		Cu	17.67	6.98	9.82	2.5	19.3	109.2246746
		Zn	157.04	7.3	0.216	56.1	63.616	40.50942435

		Ni	65.45	15.98	23.84	16.02	55.84	85.31703591
	L4	Pb	10.34	12.72	26.98259	13.13346	52.83605	510.9869841
		Mn	266.17	104.3133	9.090909	56.0735	169.4778	63.6727491
		Cr	40.49	5.89942	7.62089	6.421663	19.94197	49.2516002
		Cd	3.27	4.796905	5.435203	0.234	10.46611	320.0644745
		Fe	17749.76	9.471624	8.568665	42.88201	60.9223	0.343228873
		Cu	4.88	5.957447	7.814313	1.06383	14.83559	304.0079906
		Zn	38.66	18.78143	0.17795	118.2205	137.1799	354.8367407
		Ni	67.66	7.2147	21.02515	18.25919	46.49903	68.72455348
	L5	Pb	25.1	9.439072	24.70476	13.86667	48.0105	191.276893
		Mn	115.02	87.2381	8.514286	50.59273	146.3451	127.2344942
		Cr	15	3.828571	5.942857	44.3619	54.13333	360.8888889
		Cd	3.24	4.914286	0.314286	0.725338	5.95391	183.7626518
		Fe	24601.47	6.679174	7.028571	26.15679	39.86453	0.162041267
		Cu	8.77	7.828571	7.295238	2.380952	17.50476	199.5981973
		Zn	70.29	13.46667	0.83619	14.8381	29.14095	41.45817667
		Ni	64.31	14.20952	25.54286	13.86667	53.61905	83.37590984
	L6	Pb	23.12	10.53333	22.46654	6.118547	39.11842	169.1973156
		Mn	181.56	84.66539	0.764818	71.00952	156.4397	86.16420695
		Cr	45.6	4.99044	3.938815	2.198853	11.12811	24.40374358
		Cd	4.55	6.500956	5.81262	4.819048	17.13262	376.541168
		Fe	19340.1	11.88825	5.41109	26.15679	43.45612	0.224694413
		Cu	5.59	6.760994	4.493308	1.6826	12.9369	231.4293826
		Zn	43.42	53.30784	0.439771	16.36711	70.11472	161.4802459
		Ni	56.44	20.80306	19.33078	16.80688	56.94073	100.8871839
TM	M1	Pb	38.92	12.52183	7.936508	13.49206	33.9504	87.23123542
		Mn	120.64	63.19444	18.21429	30.39683	111.8056	92.67701886

	Cr	68.81	5.166052	0.15873	5.972222	11.297	16.41767772
	Cd	4.75	5.238095	8.531746	4.246032	18.01587	379.2815372
	Fe	2530.54	1.821782	7.619048	12.02381	21.46464	0.848223672
	Cu	17.88	10.98413	1.765873	0.498155	13.24815	74.09482652
	Zn	64.6	60.07937	0.15873	50.99206	111.2302	172.1829083
	Ni	16.8	8.095238	21.09127	13.45238	42.63889	253.8029101
M2	Pb	40.82	9.52583	21.99262	10.51661	42.03506	102.9766177
	Mn	321.67	40.73801	24.9262	102.0295	167.6937	52.13222462
	Cr	57.16	5.166052	5.313653	4.206642	14.68635	25.69339899
	Cd	3.3	6.125461	2.339483	1.064576	9.52952	288.7733423
	Fe	18273.42	1.634103	7.564576	3.321033	12.51971	0.068513239
	Cu	34.64	2.691882	7.380074	2.072937	12.14489	35.06031287
	Zn	40.82	6.99262	5.313653	13.92989	26.23616	64.27281323
	Ni	45.51	10	24.9262	12.19557	47.12177	103.541576
M3	Pb	40.19	12.57198	10.44146	17.23608	40.24952	100.1480969
	Mn	134.88	91.09405	0.24952	57.94626	149.2898	110.6834425
	Cr	70.3	3.723608	0.076775	9.289827	13.09021	18.62049948
	Cd	4.26	6.238004	2.117083	4.337812	12.6929	297.9553585
	Fe	2616.83	1.140316	5.335893	16.69866	23.17487	0.885608356
	Cu	26.68	7.888676	7.389635	2.502935	17.78125	66.64635068
	Zn	367.78	50.08061	0.076775	107.3512	157.5086	42.82686313
	Ni	76.44	15.54702	24.79846	17.90787	58.25336	76.20795254
M4	Pb	74.96	11.27202	24.91194	35.04892	71.23288	95.02785047
	Mn	189.96	84.40313	25.59687	59.2955	169.2955	89.12165668
	Cr	134.25	3.561644	25.04892	7.338552	35.94912	26.77774255
	Cd	3.11	3.933464	1.277886	2.502935	7.714286	248.0477722
	Fe	2322.37	1.41683	8.53229	34.83366	44.78278	1.928322311
	Cu	26.36	9.726027	9.491194	3.302064	22.51928	85.42976072

	Zn	243.9	105.7926	25.04892	50.25245	181.0939	74.24925521
	Ni	76.67	13.03327	25.59687	22.95499	61.58513	80.3249344
M5	Pb	41.65	12.49531	8.855535	45.06567	66.41651	159.4634101
	Mn	124.35	83.02064	9.249531	186.2852	278.5553	224.0091251
	Cr	28.58	5.478424	7.410882	6.941839	19.83114	69.38818917
	Cd	4.82	6.791745	1.249531	4.634146	12.67542	262.975563
	Fe	22000	1.192	8.855535	45.06567	55.1132	0.250514549
	Cu	91.45	7.711069	9.268293	1.233141	18.2125	19.91525725
	Zn	980	69.24953	7.410882	65.12195	141.7824	14.46758816
	Ni	59.9	12.49531	26.82927	17.42964	56.75422	94.74828279
M6	Pb	69.2	11.88825	24.27746	19.82659	55.99229	80.91371802
	Mn	126.54	228.3237	12.40848	134.9133	375.6455	296.8590739
	Cr	134.25	3.506744	2.697495	6.1079	12.31214	9.171053056
	Cd	4.4	6.705202	0.537572	7.109827	14.3526	326.1954808
	Fe	26014.93	1.547389	6.608863	39.03661	47.19286	0.181406834
	Cu	10.9	17.7842	9.518304	4.637624	31.94013	293.0287026
	Zn	466.32	77.64933	2.697495	63.39114	63.39114	63.3911368
	Ni	59.65	10.5973	27.55299	18.88247	57.03276	95.61233076
M7	Pb	4.5	14.65347	32.45545	10.9505	58.05941	1290.209021
	Mn	181.15	38.21782	8.336634	45.66337	92.21782	50.90688478
	Cr	91.3	2.930693	1.861386	4.316832	9.108911	9.976901305
	Cd	3.75	4.792079	2.336634	3.564356	10.69307	285.1485149
	Fe	26283.5	0.361905	8.336634	34.89109	43.58963	0.165844075
	Cu	22.7	10.39604	9.782178	141.6696	161.8478	712.9861005
	Zn	228.05	30.69307	5.577265	14.15842	50.42875	22.11302337
	Ni	79.1	12.0198	28.45545	17.86139	58.33663	73.75048504
M8	Pb	32.62	11.49201	26.00355	32.0071	69.50266	213.0676404

Mn	300.95	66.80284	7.655417	141.6696	216.1279	71.81521393
Cr	31.86	3.516874	5.577265	7.868561	16.9627	53.24136793
Cd	2.58	5.666075	7.744227	6.16341	19.57371	758.6710177
Fe	11250.95	3.499044	9.076377	31.2611	43.83652	0.38962507
Cu	0.62	1.34103	0.246892	0.612648	2.20057	354.9306562
Zn	100.52	49.07638	1.861386	66.9627	117.9005	117.2905516
Ni	27.52	11.49201	26.69627	20.53286	58.72114	213.3762237
Ni	55.19875	11.65999	25.74335	17.65215	55.05549	99.7404591

APPENDIX C

Bioaccessible concentration of PTEs -Stomach Compartment

Site No.	Name of Plants	Parts	Fe	Cu	Ni	Mn	Zn	Cd	Cr	As	Pb
B1	*Desmodium styracifolium*	Leaves	37.890	0.306	0.648	49.495	30.458	0.368	3.568	1.276	ND
B3	*Azadirachta indica*	Leaves	15.678	1.649	3.569	27.379	18.436	0.456	6.678	0.569	ND
B4	*Cassia alata*	Leaves	5.990	0.094	3.124	6.569	8.066	0.649	2.017	1.194	ND
B5	*Cymbopogon citratus*	Leaves	45.210	1.392	3.900	5.761	10.767	0.356	4.568	0.481	ND
B6	*Solanum torvum*	Fruits	22.383	5.033	3.332	15.750	16.683	1.033	2.469	0.116	ND
B8	*Phyllantus fraternus*	Leaves	10.568	0.547	1.456	1.459	20.456	0.237	0.025	1.000	ND
B10	*Ricinus communis*	Leaves	167.670	0.678	5.246	5.379	19.867	1.359	9.237	0.346	ND
L1	*Dissotis rotundifolia*	Leaves	16.571	1.435	1.848	21.304	20.536	0.732	7.411	1.039	ND
L1	*Desmodium adscendens*	Leaves	71.131	10.583	1.942	8.092	17.502	1.625	13.834	0.524	ND
L2	*Alternathera pungens*	Leaves	29.000	1.022	0.371	8.729	12.643	0.296	20.358	0.643	ND
L2	*Lantana camara*	Leaves	22.971	1.085	0.486	20.236	9.186	0.400	3.029	1.218	ND
L3	*Ricinus communis*	Leaves	14.039	7.109	3.508	11.549	12.213	0.387	5.920	1.095	1.314
L5	*Cassia occidentalis*	Seeds	25.524	3.043	0.186	18.356	30.471	0.329	4.314	1.074	ND
L5	*Hyptis suaveolens*	Leaves	57.584	5.816	0.636	7.870	15.408	0.360	2.158	1.140	ND
L5	*Phyllantus amarus*	Leaves	15.906	9.187	2.753	2.753	9.515	0.813	3.067	1.034	ND
M2	*Passiflora suberosa*	Fruits	55.478	5.112	0.772	20.236	54.115	0.070	0.185	0.269	ND
M3	*Azadirachta indica*	Leaves	160.347	1.343	0.283	35.129	8.686	0.600	8.459	0.347	ND
M3	*Zanthoxylum zanthoxyloides*	Fruits	160.347	1.343	0.283	35.129	8.686	0.600	8.459	0.347	ND
M4	*Physalis angulata*	Leaves	40.974	2.935	3.301	69.733	18.385	0.646	4.537	1.085	0.842
M5	*Phyllantus niruri*	Leaves	290.733	2.874	3.485	35.740	27.787	0.318	44.678	0.910	ND
M5	*Euphorbia hirta*	Fruits	34.888	11.975	0.753	6.735	11.276	0.892	11.139	2.709	ND
M6	*Sesamum indicum*	seeds	15.617	3.585	1.182	7.379	15.978	0.111	19.347	2.045	ND
M7	*Calotropis procera*	Fruits	53.557	3.271	2.229	19.843	12.714	0.457	5.368	0.935	ND

Bioaccessible concentration of PTEs –Small intestinal Compartment

Site No.	Name of Plants	Parts	Fe	Cu	Ni	Mn	Zn	Cd	Cr	As	Pb
B1	*Desmodium styracifolium*	Leaves	15.378	0.127	0.437	11.367	4.789	0.158	0.458	0.679	ND
B3	*Azadirachta indica*	Leaves	5.469	0.567	0.769	6.459	8.458	NA	2.125	0.125	ND
B4	*Cassia alata*	Leaves	3.594	0.024	1.398	3.424	12.624	0.428	0.789	0.211	ND
B5	*Cymbopogon citratus*	Leaves	45.210	0.818	2.092	3.568	6.689	0.186	1.457	0.245	ND
B6	*Solanum torvum*	Fruits	22.383	2.082	0.250	3.248	8.467	0.483	1.458	0.065	ND
B8	*Phyllantus fraternus*	Leaves	3.457	0.238	0.678	0.390	9.236	0.168	0.017	0.346	ND
B10	*Ricinus communis*	Leaves	53.569	0.155	5.679	1.168	6.459	0.348	1.358	0.167	ND
L1	*Dissotis rotundifolia*	Leaves	11.048	0.894	1.557	10.236	10.236	0.357	3.525	0.406	ND
L1	*Desmodium adscendens*	Leaves	23.710	4.307	1.908	7.915	7.049	0.459	3.569	0.039	ND
L2	*Alternathera pungens*	Leaves	29.000	0.177	0.061	10.243	4.286	0.943	1.471	0.213	ND
L2	*Lantana camara*	Leaves	10.347	0.028	0.104	8.802	4.429	0.186	1.071	0.225	ND
L3	*Ricinus communis*	Leaves	9.359	1.400	1.495	6.763	7.123	0.249	3.361	0.315	0.797
L5	*Cassia occidentalis*	Seeds	15.314	1.789	2.100	10.230	2.100	0.093	0.929	0.321	ND
L5	*Hyptis suaveolens*	Leaves	34.550	1.010	1.059	15.159	9.267	0.263	0.679	0.302	ND
L5	*Phyllantus amarus*	Leaves	6.362	0.357	0.535	6.719	6.689	0.656	2.796	0.222	ND
M2	*Passiflora suberosa*	Fruits	11.096	2.039	1.461	9.838	3.104	0.492	0.014	0.149	ND
M3	*Azadirachta indica*	Leaves	18.696	2.230	0.973	6.017	8.976	0.098	2.567	0.195	ND
M3	*Zanthoxylum zanthoxyloides*	Fruits	7.629	0.291	1.239	8.350	8.350	0.529	0.771	0.197	ND
M4	*Physalis angulata*	Leaves	40.974	2.153	1.924	14.965	0.779	0.590	0.279	0.293	0.539
M5	*Phyllantus niruri*	Leaves	58.147	2.086	1.346	6.113	5.595	0.899	2.932	0.356	ND
M5	*Euphorbia hirta*	Fruits	20.933	1.627	1.122	11.001	1.122	0.137	0.782	0.307	ND
M6	*Sesamum indicum*	seeds	10.411	2.472	2.714	9.556	9.820	0.277	4.710	0.310	ND
M7	*Calotropis procera*	Fruits	10.711	2.770	1.846	7.458	7.458	0.186	2.289	0.318	ND