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An investigation of the Distribution, Fractionation and Bioaccessibility of Potentially Toxic Elements in Urban Soils of Lagos, Nigeria

by

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Dedication

To the memory of my late grandmother Alhaja Sikiratu Aduke Famuyiwa who loved me unconditionally and have been calling me Dr Abimbola since I was age 5 because she wanted me to become a medical doctor but i lost interest while growing up, Mama I hope I did not do too badly with a PhD. You remain in my heart every day and may the Almighty God grant you eternal rest, amen.

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Abstract

Lagos is one of the fastest-developing metropolises in the world, with a population of 21 million, increasing by 2.8 % annually. The impact of this rapid development and industrialisation on levels of potentially toxic elements (PTE) in the city's soils is of concern, and requires investigation, because of possible effects on human health.

Soil samples were collected from different land-use types and socioeconomic areas in Lagos state in February and August of 2014 and returned to Scotland, UK. The microwave-assisted *aqua regia* digestion, the revised BCR sequential extraction, and the simplified bioaccessibility extraction test (SBET) were applied to the soils. The analytes Cr, Cu, Fe, Mn, Ni, Pb and Zn were determined in soil extracts and digests by ICP-MS.

Mean pseudototal PTE concentrations at locations remote from point sources of pollution were generally low, but soils taken from locations close to industrial activities such as foundries, dumpsites, and e-waste recycling sites were often highly contaminated. Principal component and cluster analysis identified Cr-Fe-Mn-Ni and Cu-Pb-Zn groupings. Correlation coefficient analysis further confirmed these relationships; grouping the lithogenic PTE (former) separately from ‘‘urban metals’’ (latter). Sequential extraction result indicated that Cr, Fe and Ni were mainly of geogenic origin, whilst the ‘urban metals’ Cu, Pb and Zn were in more labile forms of greater environmental concern. The SBET indicated that PTE uptake by a hypothetical 10 kg child with pica tendencies (consuming 10 g of soil per day) would greatly exceed tolerable daily intake (TDI) values for Cu, Pb and Zn at many locations. Finally, the last stage of the work revealed that, the exposure of PTE in PM_{10} fractions of Lagos urban soils to the general public may not likely pose any serious health effects considering inhalation pathway as the only route by which PTE enters into human body.

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1.0 Introduction

According to the world population prospects report (2015 revision) by United Nations (UN), the world population is expected to reach 8.5 billion by 2030 and 9.7 billion by 2050[1]. As at 2011, half of the world's population (3.6 billion) already lives in the urban areas and this figure have increased because as at the last projection in 2015, the world population now stand at 7.3 billion[2]. The 2015 statistics revealed that more than half of the world population growth will occur in Africa between now and year 2050. The overall world urban population which is expected to reach 67 % by 2050 suggests that, the urban environment will become the dominant human habitat for the first time in history (Figure 1.1). The impacts of increasing urbanization and industrialization have resulted into environmental degradation and its quality for human health[3]. Due to continued intense anthropogenic activities, pollutants such as potentially toxic elements (PTE) such as Cr, Cu, Pb, Zn etc. are released to the environment, especially into urban soils and dusts[4-6].

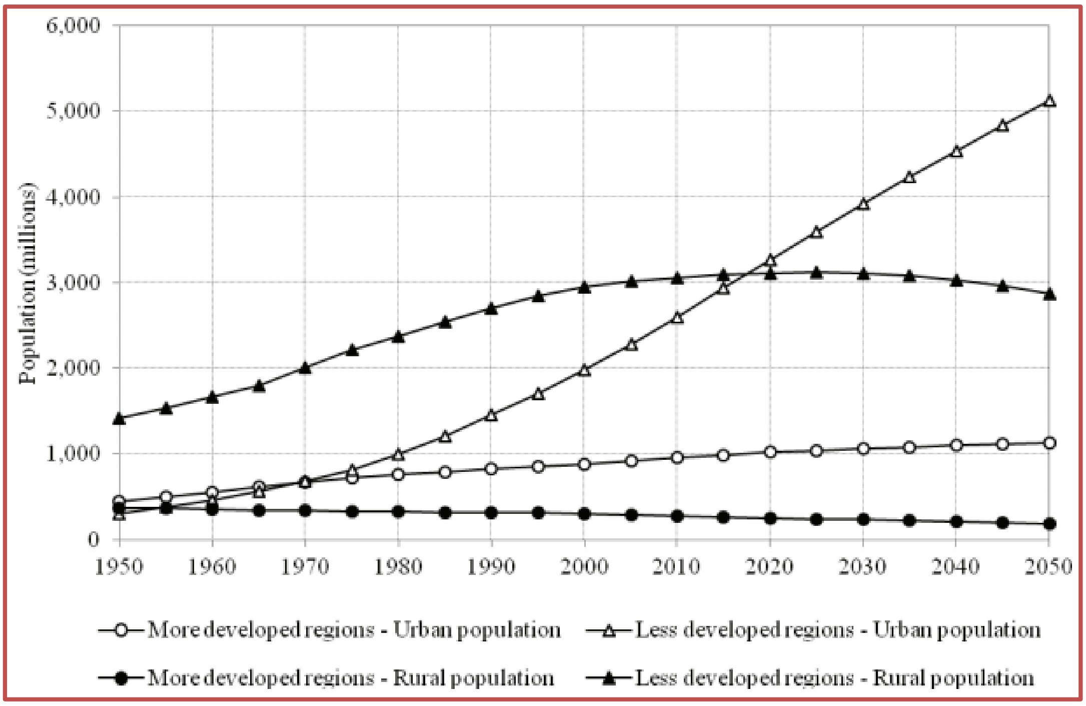


Figure 1.1: Urban and rural populations by development group (2010-2050)[2].

Over the last decades, high levels of PTE in urban soil have become a major issue. Numerous studies has been undertaken to investigate these sources, extent of pollution and the health risks these pollutants pose to human beings[7-17].

Potentially toxic elements are one of the most studied soil pollutants because of their non-biodegradability, accumulative nature and long residence time[3]. They become dangerous to human health when present in soil above certain concentrations and their close proximity to human populations can have direct influence on public health as PTE can enter human body via inhalation, ingestion and dermal contact[6, 18-22]. Children represent the most sensitive and vulnerable group due to their developing nervous systems and high absorption rate[23]. The exposure of children to PTE can increase significantly through their ingestion of soil and dust through frequent hand to mouth activities[24]. This is generally considered to be the main exposure route to PTE for children[18, 25]. High levels of PTE in urban soils can also indirectly affect public health and safety by influencing the properties of the atmosphere, hydrosphere and biosphere[20]. Human health has been suggested to be closely related to the quality of soil and to its degree of pollution[26]. Therefore, because of the growing concerns of PTE pollution in urban soils, there is need to investigate their concentrations, sources, transport, bioavailability and ultimately the associated human health risks.

1.1 Soil[27-30]

According to Soil Science Society of America, soil is defined as ''*a natural body comprised of solids (minerals and organic matter), liquid, and gases that occurs on the land surface, occupies space, and is characterised by one or both of the following: horizons, or layers, that are distinguishable from the initial material as a result of additions, losses, transfers, and transformations of energy and matter or the ability to support rooted plants in a natural environment. The upper limit of soil is the boundary between air, shallow water, live plants, or plant materials that have not begun to decompose. Areas are not considered to have soil if the surface is permanently covered by water too deep (typically more than 2.5 meters) for the growth of rooted plants*''. Soil performs several functions, such as being a media for the growth of all kinds of plants, modifies the atmosphere by emitting and absorbing gases (carbon dioxide, water, vapour etc.) and dust, provides habitat for animals, process and recycle nutrients , and serves as engineering media for construction.

Soil is the major source of trace elements to plants, acting as both micronutrients and pollutants. Its formation is based on major factors such as climate (temperature and moisture influence which speeds up weathering processes), organisms (organisms which speeds up the breakdown of large soil particles to smaller ones), relief or landscape (the shape of the land and the direction it faces influences how much sunlight gets to the soil and how much water it keeps), parent material (from which it is formed) and time (all the factors highlighted works together over time).

Soil can simply be categorised by size into three groups: sands (0.05 to 2 mm), silt (0.002 to 0.05 mm) and clay (less than 0.002 mm). Potentially toxic elements in soils can be of lithogenic (from parent material) and anthropogenic (from human activities) origins. Different rock types that serves as major lithogenic contribution of PTE in soils includes, black shale(have bituminous and oil shale, high organic matter and clay content), limestone (majorly contains calcium carbonate), ultramafic rocks (particularly notable for relatively high concentrations of Ni, Cr, Co and Ca), sedimentary ironstones (which have over 30 % of Fe oxides), and metalliferous ores.
Anthropogenic PTE sources includes atmospheric deposition of PTE emitted from different sources such as industrial emissions from smelters and foundries, coal electricity generating stations, traffic related emissions are released into the atmosphere and can be transported over large distances. Flooding and sediment deposition are also major sources of PTE contamination.
Other anthropogenic sources include; application of inorganic fertilisers, sewage sludge, livestock manures, and fungicides to agricultural soils.

1.1.2 Soil mineralogy and organic matter[29, 31, 32]

Inorganic components of soils represent more than 90 % of the solid components. Their properties such as size, surface area, charge can affect soil reactions and processes. The inorganic soil components include both primary and secondary minerals. Primary minerals represent the inorganic soil components which have not been chemically altered after deposition or its crystallization from molten lava.

Examples of primary minerals include quartz and feldspar. Other primary minerals that are present in soil in small quantities include pyroxenes, micas, amphiboles and olivines.

A secondary mineral represent a weathered primary mineral which has be altered structurally or results from the re-precipitation of product of weathering of a primary mineral e.g. aluminosilicate minerals such as kaolinite, montmorillonite, oxides such as gibbsite, goethite, amorphous materials such as imogolite and allophane. Others are sulphur and carbonate minerals.

Soil organic matter is the organic component of soils and it is composed of a mixture of decomposing or decomposed animal and plant residues and substances synthesized biologically or chemically from the breakdown products. It is typically present in the top 20 cm layer of most mineral soils. Soil organic matter or humus can vary from less than 1 % sandy soils to 90 % of peats. Major elemental composition include carbon (C, 50-60 %), oxygen (O, 30-40 %), and both hydrogen and nitrogen which are approximately about 5 %.

1.1.3 Urban soil

Urban soil is a material that has been manipulated, disturbed or transported by human activities in the urban environment. The physical, chemical, and biological properties are generally less favourable as a rooting medium for plants than soil found on the natural landscape[33]. Urban and industrial development have caused a major impact on environmental soil quality; these human activities have contributed to soil damage and lead to irreversible loss of ecological function and negative consequences for quality of human life[34].

Soils in urban areas are often significantly variable in their composition, which may be due to the wide variety of human influences. They characteristically contain higher loadings of contaminants than those from the rural settings due to the high density of anthropogenic activities in the urban areas[35]. In developed countries, the majority of people live and work in urban areas and developing countries in Asia and Africa are currently experiencing sporadic increase in rural urban migration.

Consequently, urban soils are the only type of soils which most people comes in contact with.

Urban soils are primarily a sink for PTE and also a significant source of atmospheric aerosol and street dust[36] and their accumulation of PTE over time not only downgrades soil quality but also poses risk to human health and the ecosystem in general[34]. Contamination of urban soils can cause river and groundwater pollution because of leaching processes of PTE in the soils[37]. Many studies have discussed the quality of urban soils and their PTE concentrations from different cities around the world.[6, 7, 9, 35, 37-41]. There have also been interests in the application of sequential extraction to urban soils to improve understanding of the processes in soil that controls the mobilization and retention of nutrient and toxic elements as well as their transport mechanism[35, 42-44]. Human bioaccessibility of PTE in urban soils and their health risk implications have also been investigated by many authors[7, 39, 45-48]. Because soil has been considered both as a source and a sink for pollution, it is vital to assess the environmental quality of urban areas to reduce and mitigate potential risks to ecosystems and human health[38].

1.2 Potentially toxic elements uses and health implications[29, 30, 32, 49]

There are ten major elements present in soil. They are Al, Ca, Fe, K, Mg, Mn, Na, P, Si, and Ti. The non-major elements in soil are typically found in concentrations less than 1000 mg/kg and are called trace elements[49]. Some of the elements found in soil are essential to living organisms but can be toxic if present in soil above critical levels. The fate and transport of these elements in soils largely depend on chemical forms in which they exist. These elements associates with soil particle by different mechanisms and certain changes in conditions will bring about their release into the environment. The reaction mechanisms involve both physical and chemical processes and they include: cation exchange, adsorption and desorption, co-precipitation, organic complexation[50, 51]. Chronic exposure of humans to these elements has been linked with developmental retardation, cancer, atherosclerosis and kidney damage. The PTE of interest in this study are Cr, Cu, Fe, Mn, Ni, Pb and Zn. Their chemistry, toxicity and health implications are discussed in detail below.

Chromium[30, 49, 50, 52]

Chromium is the seventh most abundant element on earth and is mined as chromite ($FeCr_2O_7$) ore. Chromium metal is grey, brittle and can be highly polished. Its use in alloys is because it resists attack by oxidation and corrosion. It increases hardness and resistance to mechanical wear in alloys. Chromium occurs in +3 and +6 oxidation states in the environment; although, Cr (III) is the most stable. Chromium (VI) can be reduced to Chromium (III) by soil organic matter, sulphide and ferrous ions under anaerobic conditions. Chromium (III) is the dominant form of Cr and its mobility is decreased by adsorption to clay and oxide minerals[53]. Chromium (IV) is the more toxic form and is also more mobile. Chromium is used principally for stainless steel, chrome plating, metallurgical and refractory purposes. In the chemical industry it is primarily used in pigments, metal finishing, leather tanning, wood preservatives, and manufacture of green tints for paints, varnishes, glazes and inks. The main sources of Cr pollution are considered to be from dyestuffs and leather tanning when wastes are discharged into streams, either in the liquid or solid form.

There is particular interest in sewage treatment plants from industrial and residential sources which discharge substantial amount of Cr. Chromium occurs as a trace element in food and water. It is essential micronutrient and its deficiency results in glucose intolerance, loss of weight, confusion and cardiovascular problem whereas high levels of Cr causes stomach ailments, respiratory problems, heart disease and cancer.

Copper[30, 49, 52]

Copper is one of the most crucial, essential elements to animals and plants. It has high abundance in the lithosphere ranking twenty sixth just behind zinc. Copper is often highly associated with organic matter (forms stable complex with ligands) and crystalline phases in soil which potentially indicates non-availability but becomes more mobile at low pH. Due to its versatility, Cu has wide range of numerous applications. It is used primarily in the manufacture of wire, brass, and bronze alloys.

It has also exhibited its relevance in electricity generation, transmission, conduction, and also in the fabrication of household articles, coins, art objects, ammunition, motor and electrical equipments.

It is an essential micronutrient required for the growth of both plants and animals. It helps in the production of haemoglobin in human and it is essential in seed production, disease resistance and water regulation. Deficiency in copper may cause anaemia, diarrhoea, demineralization of bones, especially malnutrition and malabsorption in infants. The acute and chronic toxicity of Cu in humans include congestion of nasal mucous membrane and pharynx, ulceration of nasal septum, metal fume fever, and stuffiness of the head.

Iron[30, 52]

Iron is the fourth most common element on the earth crust. It is lustrous, malleable, ductile and silver-grey metal. Iron is found in various oxides, such as the minerals haematite, magnetite and taconite. Iron is one of the most widely used metals. Iron (III) is the major oxidation state in iron minerals. Lowering of the pH and redox potential increases the amount of iron (II) in soil. This is more soluble and in turn increases its availability.

Its preferred use can be attributed to its combination of low cost and high tensile strength. It has a wide range of applications, spanning the food, automobile, maritime, manufacturing and steel industries. Iron is found in meat, whole meal products, vegetables and it is an essential part of haemoglobin in human red blood cells. Iron may cause conjunctivitis, haemotochromatis, and liver damage when in contact and remains in tissues. Its deficiency in humans which is a common problem is anaemia.

Manganese[29, 30, 49]

Manganese is one of the most abundant trace elements in the lithosphere. Manganese is important to industrial civilization, and also the maintenance of life within it. Its ores are widely distributed in diverse geological and climatic environments as oxides, hydroxides, and to a lesser extent carbonates and silicates.

The main forms of Mn in soils are Mn (II) which is soluble and exchangeable and insoluble forms are Mn (III) and (IV). The concentration of the soluble and exchangeable form of Mn occurs majorly by microbial oxidation of Mn (II) and chemical reduction of Mn oxides (by organic matter).

It is used principally in the metallurgical industry for the manufacture of steel and alloys. Its wide applications also extends to its use in the manufacture of dry cell batteries, pigment production, ceramic and glass. In agriculture it is used as fertilizer in the form of magnesium sulfate and also as fungicides in the treatment of seed. Potassium permanganate has long been used as an oxidizing catalyst in chemical processes, as disinfectant in medicine as well as in the purification of water. In humans, Mn (II) is involved in gene expression processes and stabilizes the DNA structure. However a symptom of Mn deficiency is uncommon in humans. Contents of it in human tissues especially in bones decreases with age which eventually results to osteoporosis, dermatitis, hypocholesterolaemia. Manganese deficiencies can generally results to skeletal deformities and testicular dysfunctions in human. Some hepatic dysfunction, iron deficiency and some kinds of vegetarian diet can promote chronic manganese toxicity to human beings.

Nickel[30, 49, 50]

Nickel belongs to the transition metal group 10 of the periodic table. It occurs in a number of oxidation states but only Ni (II) is stable over wide range of pH and redox conditions in the soil environment. Nickel is extracted from sulfides and oxides ores. Nickel typically exists in the environment at low levels but becomes dangerous when maximum tolerable limit is exceeded which is most cases is as a result of anthropogenic contribution. Nickel has recently become a serious pollutant released from the processing of metals and from the increased combustion of coal and oil. It has also been reported in some literature that some sewage sludge and phosphate fertilizers may be important sources of Ni in agriculture. Nickel steel alloys have been found to be resistant to corrosion and oxidation. These properties have increased their use in the manufacture of motor vehicles, armaments, aircrafts, catalysts and batteries. Elevated levels in humans lead to liver and kidney effects, neurological effects and lung cancer.

Lead[29, 30, 49, 50, 52]

Lead is ranked 36th element in terms of abundance in the earth crust. The abundance of Pb in sedimentary rock (shale) is 22 mg/kg and its mean concentration in uncontaminated soils around the world is 17 mg/kg. Ionic Pb, Pb oxides and hydroxides and Pb metal complexes are the general forms of Pb that are released into the environment. Lead (II) is the most reactive form of Pb, forming oxides and hydroxides. Lead phosphates and carbonates are formed when pH is above 6 and are the predominant insoluble forms of Pb. Lead sulfide is the most stable insoluble form of Pb in soils under reducing conditions. The behaviour of Pb in soil largely depends of the amount of organic matter. At pH above 4, Pb binds strongly to organic matter but is released when pH is lowered. In the absence of organic matter, Pb binds preferentially to clay and Fe minerals[54]. Lead is known to be a persistent pollutant that causes harmful effects to humans, animals and ecosystems. It is useful in the manufacturing of lead-acid batteries, bullet and shots, fusible alloys, radiation shield and also in building construction. Over the years, there have been several natural and anthropogenic sources of lead, but the dominant anthropogenic source has been its use as an antiknock motor vehicles addictive. There has been strict regulation, since the 1990s, of the use of lead in gasoline in the developed countries which in effect, has virtually eliminated its use and successive release to the environment. However it is still in use in several African countries like Nigeria. Lead is a non-essential element. In humans, absorbed Pb is distributed in blood, soft tissues, bones and teeth. The toxicity of lead has been known to cause severe health effects which include damage to the nervous systems, inhibition of heme formation, kidney damage, anaemia, and impaired mental development in young children.

Zinc[29, 30, 49]

Zn is an essential trace element for higher plants, animals and humans. The principal ores of Zn are composed of sphalerite and wuzite. Zinc ores typically contains several other elements such as Ag, Cd, Cu and Pb. Zinc is specifically adsorbed to oxyhydroxides and organic matter at oxidation state of +2 and undergoes ion exchange process at high concentrations. Zinc is widely used in industries mostly as corrosion protection on steel components and other metals.

Due to its versatile properties, it is an important component of alloys. Its usefulness spans many sectors of industry, (e.g., automobile, plastic, pesticides, rubber etc). Different compounds of zinc have also been documented to have medical and dental applications which are beneficial to animals and humans. It plays several fundamental functions in metabolic processes. Severe deficiency of zinc leads to frequent infections, diarrhea, delayed sexual and bone maturation, dysfunctional immune system, alopecia, and mental disturbance. The ingestion or inhalation of larger doses of zinc can result to chills, excessive sweating, weakness, and damage to the alimentary tracts.

1.3 Extraction of PTE from environmental solids[7, 29, 41, 49, 55]

The determination of PTE from environmental solids, such as soils may be carried out for variety of reasons. An extraction method employed in a particular work is often associated with the information required or the purpose of study. For instance, when data relating to baseline information that reflects the geological origins of soils is required or PTE concentration in metal rich soil like mining waste, total metal determination may be best suitable. Total metal determinations in soil are poor indicators of PTE mobility and bioavailabilty. However, single or multi-step extraction procedures gives a relevant assessment or the estimation of fraction of PTE content likely to be available to plant or be solubilised in the gastro intestinal tract of man in case of accidental soil ingestion. In order to measure the maximum potentially soluble or mobile contents of PTE in soil, pseudo-total digestion using strong acid is required. All these forms of PTE in soil can be determined either directly or indirectly.

1.3.1 Direct methods

These methods allow direct determination of PTE in soils without destroying the sample. Some of the direct methods include Instrument Neutron Activation Analysis (INAA), X-ray fluorescence spectrometry (XRF), Laser-induced Breakdown Spectroscopy (LIBS), Laser ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS).

One of the key advantages of direct methods, specifically XRF, is the availability of the instrument on the field (portable XRF instruments), therefore allowing rapid screening of sampling sites. Other general advantages of direct PTE determination in a sample matrix include relative insensitivity to sample form and there is no complexity in sample handling, thereby eliminating contamination and samples losses. Disadvantages includes requirements of highly trained personnel, specialist irradiation facilities for INAA, expensive instrument component parts and some of methods have less sensitivity for Cd, Cu and Zn compared to ICP-MS.

1.3.2 Indirect methods

For indirect methods of analysis, PTE of interest is leached into solution by digestion with appropriate reagents and measured using suitable analytical technique. The properties of reagent used to liberate PTE from soil are of vital importance; hence, a certain reagent is suitable for a particular soil component and therefore provides specific information. Some of different approaches used in indirect PTE determination are summarised below and shown diagrammatically in Figure 1.2 a and b:

Total Digestion[29, 56]

Total digestion is simply the determination of the total concentration(s) of PTE in soil. It is used to characterize soil as regards its fundamental elemental composition as derived from the parent geological material and anthropogenic inputs. Total digestion with HF is usually used when complete liberation of metals from environmental solids is required. One of the advantages of this approach is that, it has the ability to release silica-bound metals. Fusion is another approach for complete PTE dissolution in soil samples. This process typically involves heating a small sample (about 0.2 g) with lithium metaborate to about 1000 ^{o}C. The method is usually employed for samples that are difficult to bring into solution by other means e.g refractory minerals such as chromite[57]. The limitation of the total digestion method is that it gives no estimate of the potential mobility, bioavailability or toxicity of PTE.

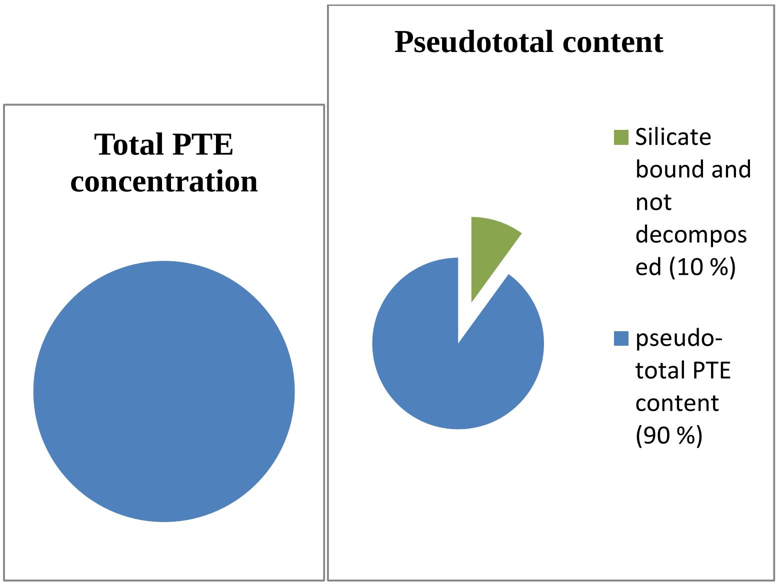


Figure 1.1 a: Pie charts representing total and pseudo-total PTE concentration[58]*.*

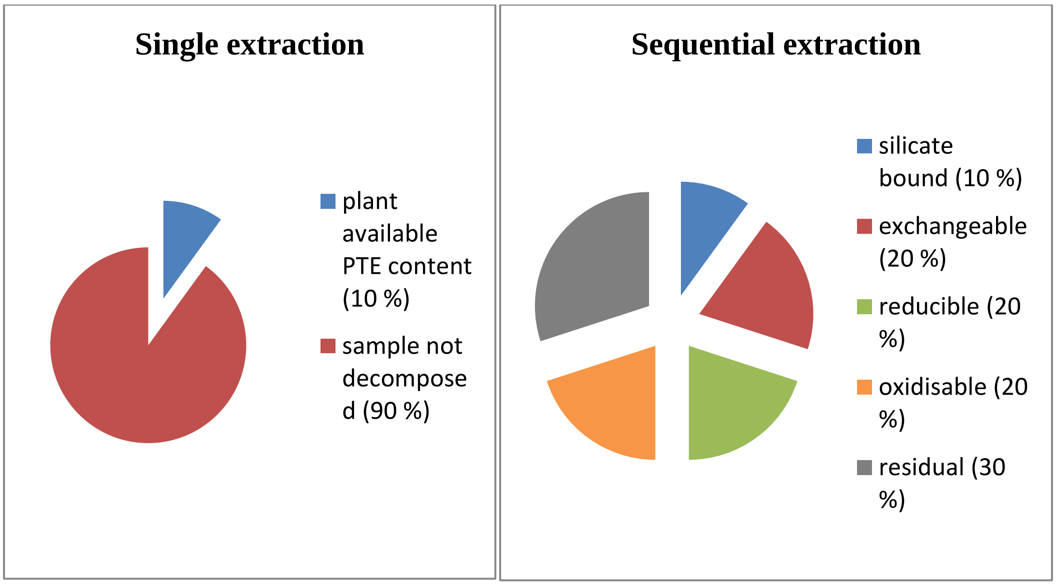


Figure 1.2b: Pie charts representing single and sequential PTE concentration[58]*.*

Pseudo-total Digestion[29, 30, 49, 56]

Pseudo-total digestion has been used predominantly for the assessment of soil pollution where most of the pollutant inputs are in forms not bound to silicate. It estimates hypothetical amount of PTE that can be mobilised and transported in an environment and capable of affecting a receptor. Strong acid digestion not involving hydrofluoric acid is usually sufficient to dissolve the PTE of interest. The most widely adopted and useful method is *aqua regia* digestion. *Aqua regia,* a mixture of hydrochloric and nitric acids in a ratio 3:1 have shown to be more effective for volatile elements As, Bi, Sb, Se, than digestion with nitric or hydrochloric acids alone[56].

Single Extraction[55, 59, 60]

In the assessment of the mobile fractions of PTE in soils, one of the most widely used approaches is single extraction. Many studies have demonstrated the suitability of these procedures to the prediction of plants uptake in soils[55, 59]. Single extractants release metals from particular soil phases with which they are associated or bound. Neutral salt solution like weak salt solutions of calcium chloride, sodium nitrate, and ammonium acetate has been used extensively in many studies. 0.1 M calcium chloride, 0.1 M sodium nitrate and 1 M ammonium nitrate have been adopted in the Netherlands, Switzerland and Germany, respectively, as standard national protocols for assessing potentially leachable trace element contents in soils[55]. Some of the other single extractants used are chelating reagents such as diethylene triaminepentaacetic acid (DTPA) and ethylene diamine tretra acetic acid[61-63].

Sequential extraction[42, 55]

This type of extraction involves the treatment of soil or sediment with series of reagents in order to partition the trace metal content into various phases. Series of reagents are added sequentially to the same substrate in order of increasing harshness in sequential extraction approach. Its major advantage over single extraction is that the phase specificity is improved, in that reagents have different chemical nature and the fact that the steps are performed in order of increasing vigour.

Information from this extraction process has been used to estimate mobility, bioavailability and toxicity of metals.

1.4 Potentially toxic elements in urban soils

The PTE content of urban soils around cities of the world have been widely published and is still very topical which may be because of the potential health risk it poses to public health. Urban soil quality has been investigated for many different parameters and in several different ways. For instance, studies on PTE concentration in roadside soils[64-66], parks[67], school playgrounds[22, 68, 69], sports ground[70], different particle size of urban soil[71], different land uses of a city[12, 72], comparative studies between rural and urban soils[73, 74], influence of large cities on PTE distribution[71], PTE concentration in urban soil at increasing depth[75], effect of compost application on PTE load[76] have been studied. Table 1.1 shows the average total PTE concentrations in previous urban soil studies across the world. Many studies have also employed different fractionation schemes to study PTE mobility and distribution in urban soils. Single extraction and bioaccessibility tests have been applied to urban soils to predict PTE availability in plants and potential bioavailability in humans[7, 77].

Literature on urban soil studies have shown that Cu, Pb and Zinc are the most studied PTE but Cd, Cr, Mn, and Ni are also widely reported. The anthropogenic contribution of PTE to urban soils has been attributed mainly to traffic and industrial sources[3, 36, 78]. The PTE most often suggested to be indicative of anthropogenic input are Cu, Pb and Zn[18, 76, 79, 80]. Chromium, Mn and Ni have been proposed to emanate mostly from lithogenic sources but some studies have linked them to anthropogenic sources[37, 81-84]. The Contaminated Land Exposure Assessment (CLEA) guidelines of the Environment Agency, UK and the Dutch intervention values were included in Table 1.1. These soil guideline values (SGVs) are generic assessment criteria that assess risks to human health from chronic exposure to contaminated soil. Concentrations less than these SGVs is thought not to be harmful and concentrations suggest the soil might be contaminated and potentially pose a human health.

Table 1.1 Average PTE concentrations of urban soils (mg/kg) from different cities across the world.

City	Cd	Cr	Cu	Mn	Ni	Pb	Zn	Reference
Aberdeen, Scotland	-	22	44	264	15	172	113	Paterson *et al.*[85].
Akure, Nigeria	-	-	-	-	7.24	18.1	-	Olorundare *et al.*[86]
Auby, France	-	60.5	71.7	-	36	1118	1340	Doauy *et al.*[87]
Bangkok, China	0.29	26	42	-	25	48	118	Wilcke *et al.*[80]
Berlin, Germany	0.5	18	19	-	5	41	101	Banat *et al.*[88]
Damascus, Syria	-	57	34	-	39	17	103	Moller *et al.*[89]
Glasgow, UK	-	45	85	-	35	307	199	Rodrigues *et al.*[90]
Gaborone, Botswana	1.6	72	36	-	48	112	248	Zhai *et al.*[91]
Hong Kong, China	0.36	18	16	-	4	88	103	Lee *et al.*[92]
Kowloon, China	0.62	23	23	-	12	95	125	Li *et al.*[78]
Ibadan, Nigeria	-	64	47	-	20	95	228	Odewande *et al.*[93]
Oslo, Norway	-	32.5	31.7	486	28.4	55.6	160	Tijhuis *et al.*[94]
Ottawa, Canada	-	44.8	13.19	-	16.3	64.6	114	Rasmussen *et al.*[95]
Naples, Italy	0.3	-	63	-	-	56	84	Angelone *et al.*[96]
Poznan, Poland	0.3	-	10	-	-	17	32	Grzebisz *et al.*[97]
Rock stock, Germany	-	48	35	-	30	83	100	Madrid *et a*l.[7]
Madrid, Spain	-	75	72	477	14	161	210	Madrid *et al.*[7]
Seville, Spain	-	39	68	471	22	137	145	Madrid *et al.*[77]
Tarragona, Spain	0.19	10.2	-	191	-	66	-	Nadal *et al.*[98]
Tallinn, Estonia	-	40	45	-	16	75	156	Bityukova *et al.*[26]
CLEA SGV[99]	-	200	-	-	200	450	-	Environment Agency, UK
Dutch SGV[100]	-	-	190	-	210	530	750	

CLEA: Contaminated Land Exposure Assessment, 2002; Soil guideline value (SGV).

Different approaches have been used to assess anthropogenic influence on urban soils. Anthropogenic contributions and anomalous PTE enrichments in urban soils have been estimated by enrichment factor (EF)[101-103], geo-accumulation index (Igeo)[86, 104, 105], contamination factor (CF) and potential ecological risk[15, 106].

The relationship between different variables such as pH, loss on ignition, cation exchange capacity and PTE in urban soils has also been investigated. Pearson correlation coefficients have been employed for this purpose and have also shown to indicate possible common sources of PTE[9, 103, 107-111]. Identification of common sources of PTE by multivariate statistical techniques such as principal component analysis (PCA) and cluster analysis (CA) have been used to assess anthropogenic influences and natural factors[15, 38, 105, 111-115]. Geographic information system (GIS) technology was used in some urban soils studies to examine PTE distribution and their relationship with urban geographical features such as traffic densities and land uses; this tool is becoming increasingly popular in the assessment of PTE in urban soils[3, 74, 92, 116-118]. Measurements of Pb isotopic ratios in order to investigate anthropogenic influence of Pb as against the non-geogenic contribution in urban soils have been reported[75, 119].

Human toxicity assessment models have been applied to PTE in urban soils to evaluate carcinogenic and non-carcinogenic risks via three exposure route: ingestion, inhalation and dermal contact[22, 81, 84, 102, 110, 120]. These models take into account different land uses, age, exposure pathways, and receptors.

In the investigation of PTE in urban soils, the traditional approach to soil surveys that are typically used in non-urban areas may not be applicable because of a number of problems such as high spatial variability of urban soil properties (chemical, physical and biological), fragmented distribution (exposed soil areas usually in variable sizes and randomly distributed which is usually a constraint to sampling design), inaccessibility to some area or premises such as protected government properties such as prisons, private property, construction areas. Rapid and unpredictable land use change is one of the major problems of soil survey in urban areas[121].

The measurement of different soil depths, non-uniform standard sampling strategy, different city or study coverage areas, disparity in industrialization history of study areas, different analyte of interest, different number of samples or composite samples in which average concentration of a particular study is based, and diverse environmental conditions of study areas makes quantitative comparisons between urban areas difficult.

The harmonization of urban area sampling design, prescribed sampling depth, minimum set of PTE to be investigated could make comparison between cities more holistic regardless of the geographical location, geological substrate and population size[121]. Generally, PTE concentrations in urban soils of less industrialized cities have been noted to be more likely influenced by geological inputs[90] and may not be comparable with general PTE pollution levels of European countries which has long history of industrialization that spans several decades [35], though much of PTE pollution in old industrial cities of Europe is historical rather than current, due to the decline in heavy industries and improvements in environmental protection.

1.5 Sequential extraction of PTE in soil[42, 55, 122-124]

Sequential extraction involves the use of series of reagents to chemically leach out metals in soil, sediments and other environmental samples. The underlying principle are that each reagent has a different chemical nature (e.g. a dilute acid, reducing or oxidizing agent) and that steps are performed in order of increasing “vigour”[55]. Sequential extraction may be traced back to a valuable work by Tessier *et al.*[125] in 1979, where a five stage extraction was carried out to provide information on potential impacts of sediments bound metals on water quality. In their work, accuracy was evaluated by comparing total trace metal concentrations with the sum of the individual fractions of the targeted soil phases, proved to be satisfactory[125]. The reagents used were selected based on their ability to remove analytes from specific, major sediment phases.

The use of sequential extraction has continued to increase after the method development by Tessier *et al*, particularly in the early 1990s. Quite a number of different extraction schemes have been developed to sequentially extract PTE in soils and sediments[126-134]. Thus, most of these procedures involve chemical partitioning into water soluble, exchangeable, reducible, oxidisable and residual extraction phases. Potentially toxic elements extracted in the water-soluble fraction of soils and sediments, are relatively mobile and thus may be potentially bioavailable. Undoubtedly, this fraction contains the most mobile and potentially the most available PTE.

This phase contains water soluble species made up of free ions and ions complexed with soluble organic matter and other constituents. De-ionized water at a certain soil-water ratio is used for the extraction of metals in this phase. This can be achieved by employing conventional laboratory procedures that include centrifugation, filtration, displacement or dialysis. Metals extracted in the exchangeable phase include weakly adsorbed metal species that are retained on the soil surface by relatively weak electrostatic interactions and those that can be released by ion-exchange processes[122]. Changes in the ionic composition, influencing adsorption-desorption reactions, or lowering the pH could cause remobilisation of this fraction. Metal ions in the exchangeable fraction are measures of those trace metals which are readily released into the environment and some of the reagents used are NH_4AOc and $MgCl_2$.

The acid soluble fraction contains metals which are precipitated or co-precipitated with carbonates. This fraction is sensitive to changes in pH and metal release is achieved through the dissolution of a fraction of the solid material at pH close to 2. The carbonate fraction is loosely bound phase and prone to changes in environmental conditions[122, 123]. Oxides of iron and manganese are excellent scavengers of metals. By controlling pH and redox potential, dissolution of some or all metal-oxide phases can be achieved. Hydroxylamine hydrochloride in nitric acid is usually employed in most sequential extraction schemes for isolation of this phase. The peculiarity of this reagent in leaching out metals bound to this fraction is that it contains a reducing agent and a ligand which is able to retain released ions in a soluble form[122]. Oxalic acid/ammonium oxalate buffer and Sodium citrate/sodium ditionite buffer (DCB) are other reagents that have been used for dissolving Fe oxides.

Potentially toxic metals may be associated through complexation or bioaccumulation processes with various forms of organic material such as living organisms, detritus or coatings on mineral particles. Degradation of organic matter under oxidizing conditions can lead to the releasing of soluble trace metals bound to this component. Trace metals bound to sulfides might also be extracted in this phase. However the PTE released in the oxidizable step are not considered to be very mobile and available because they are believed to be bound with stable high molecular weight humic substances that release small amounts of metals in a slow manner.

An oxidation process is usually employed in leaching out metals bound to this phase, as metals bound to organic matter and sulfides can easily be released under oxidizing conditions[42]. The most common reagent used for this purpose is hydrogen peroxide in acid medium. This reagent applied at 85ºC for several hours, has been applied in some sequential extraction schemes. Its preferred use in dissolving organic matter can be attributed to its compromise of completely attacking the organic matter with minimum alterations of silicates. The major setback displayed by hydrogen peroxide is metal readsorption in the residual fraction which requires for example an additional extraction stage with ammonium acetate at pH 2. Many schemes have adopted the use of H_2O_2/NH_4OAc in leaching out metals bound to the organic matter and sulfides and also preventing re-adsorption[122]. Reagents such as H_2O_2/ascorbic acid, sodium pyrophosphate have also been used.

The residual fraction usually consists mainly of primary and secondary minerals containing metals in the crystalline lattice. The extraction is carried out by digestion with strong acids such as $HClO_4$, HCl, HNO_3, HF and *aqua-regia*. The concentration of metals associated with this fraction has been estimated by some researchers as the difference between the total concentration and the sum of the fractions of metals extracted during previous steps.

The use of different protocols, with different number of steps, reagents and extraction conditions did not allow inter-laboratory comparison and validation of results worldwide. This lack of uniformity coupled with deficient suitable reference materials gave rise to the need for standardization. The Community Bureau of Reference of the Commission of the European Communities (BCR) launched a project to harmonise a three stage, sediment sequential extraction protocol. The project commenced with inter-laboratory trials and detailed description of the conditions of use at each step. Detailed instructions for preparation of extraction solutions were provided to avoid any difference that could impair the reproducibility and validation of the procedure.

The influence of several factors like pH, temperature, extraction time, and reagent type was also addressed. This scheme gave rise to the production and certification of a sediment reference material (CRM 601).

A problem of irreproducibility was, however reported. In particular step 2 of the inaugural BCR procedure. A revised protocol was recommended in the late 1990s after thorough re-evaluation of the original protocol. This improved version proposed by BCR integrates an *aqua regia* digestion of the residue from step 3. In the revised BCR protocol, it was recommended that the summation of all the four steps of the sequential extraction scheme be compared with the result of a separate pseudo-total *aqua-regia* digestion[123]. This was to serve as an internal control check for assessing the overall effectiveness of the scheme and element recoveries.

Sequential extraction schemes have been extensively criticised, mainly because of problems of re-adsorption and redistribution of analytes among phases during extraction, non-selectivity of reagents for target phases, incomplete extraction and formation of new mineral phases during extraction[42]. Despite these limitations, the sequential extraction technique remains a useful method in evaluating the relative importance of geochemical fractions that may be present in sample.

Sequential extraction has been applied to a wide variety of environmental samples ranging from sewage sludge amended soil[61], industrial contaminated soils[44], sediments[44], urban dust[135, 136], tunnel dust[137], urban particulates[43, 138-140]. Sequential extractions have been widely employed to study urban soils across the world. For example, it has been used to study PTE mobility and availability in urban soils from five European cities[35], urban soils from Guiyang city, China[141], soils collected from an industrial district in Weinan, China[142], urban vegetable garden soils[143], contaminated urban soils[144, 145], and urban refuse dump soils[146]. Because different sequential extraction schemes have been applied to urban soils in past work, comparison between results was difficult. However, some similarities were observed in the general trend and behaviour of PTE in previous urban soils studies irrespective of the scheme used. For example, Cr and Ni were mainly associated with the residual phase, the predominant phase for Cu was the oxidisable phase, Fe and Mn were mainly associated with the reducible and residual phase, Pb was mainly associated with the reducible phase, but Zn was identified as the most mobile PTE according to the literature because the significant amount of Zn species present in the exchangeable fractions.

Another issue which makes comparison between results difficult was the presentation and interpretation of data and this depends to some extent, on aim of the study and data processing conducted e.g comparison of a 3 stage protocol to a 7 or 8 step sequential extraction protocol or the disparity in the presentation of results in percentages or concentrations. This typically creates ambiguity in data interpretation and comparison.

1.6 Oral bioaccessibility of PTE

Soil guideline values (SGVs) such as CLEA and Dutch intervention values are often used with site specific risk assessment models. Land use, fate and transport of pollutants and pollutant toxicology are the main factors considered in the derivation of SGVs. The question of whether contaminated soils pose a risk to human health depends on the potential of contaminant getting to the human blood stream from the soil. The use of total or pseudo-total PTE concentrations as risk assessment criteria assumes 100 % availability of PTE in human blood steam and this overestimate the risk since only a fraction of it is actually available for absorption. Animal test results have demonstrated that, contaminant in a soil matrix may be absorbed to a lesser degree and show less toxic effects compared to the soluble salts of the contaminant in a food or liquid matrix[147, 148].

Human health risk assessment may be better assessed using bioaccessibility extraction tests. Bioaccessibility tests simulate the human gastro-intestinal tract especially of children, the target group most susceptible to accidental or deliberate ingestion of non-food substances. The extraction protocol estimates the actual fraction that is soluble and available for absorption into the blood stream. Absorption of ingested metals takes place mainly in the gastro intestinal tract and dissolution generally occurs in the acid stomach environment. Any test of human bioaccessibility of contaminants that have entered the gastro-intestinal tract by direct ingestion of soil must enable quantification of the dissolution under "realistic worst conditions". Bioaccessibility can be useful to "*confirm the presence of dangerous substances that pose a significant risk to human health*" as stated by the new European soil strategy[41].

Previous work has suggested that, bioaccesibility of soil contaminants depends on soil type[149] and contaminant properties[150, 151]. Therefore, it is impracticable to perform *in vivo studies* (measurement of bioavailability using animal models) for every soil type and every contaminated sites[151]. However, *in vitro* extraction models were developed based on the simulation of human physiology. The *in vitro* models are simple, cheap and fast to carry out. These models simulate human digestive system, from the mouth to gastric and intestinal conditions.

A number of bioaccessibility extraction procedures have been developed[151-153]. These include Physiological Based Extraction Technique (PBET)[154], Simplified Bioaccesibility Extraction Test (SBET)[155], the German Din model (DIN), In Vitro Digestion Model, (RIVM Netherlands), and Simulator of Human Intestinal Microbial Eco-systems of Infants, Belgium (SHIME)[151]. The majority of these protocols involve simulated gastric extractions using varying quantities of digestive juices and enzymes (pepsin, amylase, pancreatin etc). Hence, variability in procedures exists, such as digestive juice concentration, fasted verses non-fasted conditions, liquid-sample ratio, incuba''tion times in the mouth, stomach and intestine compartments, pH, centrifugation and filtration regimes[156].

The Physiological based extraction technique (PBET)[154], is one of the most popular schemes used in urban soil studies. It involves two stages, gastric and an intestinal phase, which successively simulates stomach and intestinal tract conditions. However, this protocol is relatively cumbersome to carry out and time consuming. The Simplified Bioaccessibility Extraction Test (SBET) was developed to simplify the process; taking into account only the stomach phase. The SBET has been used to determine bioaccessibility as well as to assess health risk factors in children and adults[7, 157-159]. Of the in- vivo methods that currently exist , the disparity of one or more of the experimental parameters have been identified as the cause of significant differences in bioaccessibility results[156].

The Bioaccessibility Research Group of Europe (BARGE) developed the unified bioaccessibility method (UBM), with the aim of producing a validated and standardised protocol which harmonises various extraction schemes for both regulatory and scientific acceptance.

Unified bioaccessibility method has proved to be successful in the inter-laboratory trial for the assessment of As, Cd and Pb. However, further validation of this approach was recommended because of the problem of inter-laboratory reproducibility[152]. Nevertheless, UBM has proved that it provides a robust tool for use in the risk assessment of PTE[45, 160]. The UBM procedure requires a large number of reagents compared to PBET and SBET and it is time consuming, therefore not suitable for large batches of samples.

1.6.1 Simplified Bioaccessibility Extraction Test[7, 151, 155, 158]

Simplified bioaccessibility extraction test is a simplified form of PBET extraction. The protocol was developed specifically for Pb bioaccessibility measurements in a series of young swine studies. This procedure was carried out by United State Environmental Protection Agency (USEPA) and the University of Missouri[155]. This *in-vitro* assay was found to correlate well ($R^2 = 0.83$, $p = .0001$) with relative bioavailability for Pb in juvenile swine model developed by USEPA[155]. According to Rawlins and Wragg[155] in 1999, it is thought likely to be adopted as a standard procedure. The test is carried out at 37°C for one hour using a 0.4 M glycine solution adjusted to pH of 1.5 with hydrochloric acid. A thermostated shaker is typically employed for constant agitation, to simulate a normal body temperature and movement within the stomach. It uses simple reagents in a single extraction test for a relatively short period of time, it is simple to perform and consequently ideal for large batches of samples[155]. Results from this protocol have been published in an inter-comparison method of bioaccessibility tests[151, 161], PTE studies in urban roadside soils[7, 158], arsenic enriched soils[157], urban park soils[162], urban soils[7, 77, 158, 163], contaminated urban soils[41, 164], urban street dusts[159].

1.7 Aims and objectives.

1. **To obtain information about the current PTE status of urban soils in Lagos as an example of a rapidly urbanising megacity in a developing country**.
    - To determine pseudototal concentrations of PTE (Cr, Cu, Fe, Mn, Ni, Pb and Zn) in soils collected away from known point sources as an indicator of ambient urban levels of contamination and also to assess if socio-economic areas influence PTE distribution in the soils.
    - To determine the pseudototal levels of PTE in soils collected close to known point sources as an indicator of the ‘’worst case scenario’’ of a possible PTE toxicity risks to human and ecological receptors.
    - To assess the variability of PTE between different land use types
    - To serve as a baseline for future urban soil studies in developing countries.
2. **To obtain information on potential mobility of PTE in Lagos urban soils to assess their likelihood of affecting other environmental media such as water and plants.**
    - To use the revised BCR protocol to determine PTE lability
3. **Human health risk assessment associated with the PTE measured in the soils and potentially resuspended soil fractions.**
    - Application of SBET to soil samples in order to predict the fraction available for absorption in the gastrointestinal tract of humans.
    - To assess the level of risk PTE in urban soil poses to children in the event of both deliberate and unintentional soil ingestion.
    - To examine the effectiveness of an optimised PM_{10} isolation method from soils and its adaptability to real test urban soil samples.
    - To revise the current SBET procedure by miniaturising sample mass and extractant volume and its adaptability to small amount of PM_{10} samples isolated from urban soils.
    - To assess PTE levels in potentially resuspended urban soil (PM_{10} fraction) and to appraise the incorporation of bioaccessibility results into the current inhalation human health risk assessment model (which

assumes 100 percent bioavailability of PTE in the blood stream of humans) thereby, the associated health risks to both children and adult receptors can be determined.

2 General experimental procedures

A pseudototal digestion was applied to Lagos urban soils to determine the PTE concentrations, so as to obtain information about the current levels of contamination. The revised BCR sequential extraction technique was used to partition PTE into various operationally defined phases to determine PTE lability and the SBET procedure was used for the estimation of PTE available for absorption in the gastro-intestinal tract of humans. Analytes (Cr, Cu, Fe, Mn, Ni, Pb and Zn) were quantified in digests and extracts by ICP-MS. Data handling was performed using Microsoft Excel 3.0 and Software environment; R version 3.1.0 was used to perform multivariate data analysis. The multivariate data analysis was conducted by Dr Piotr Gromski of the department of Chemistry, University of Glasgow. Details of each experimental procedure are extensively discussed later in this chapter.

2.1 Study sites and sampling

Study area[165-168]

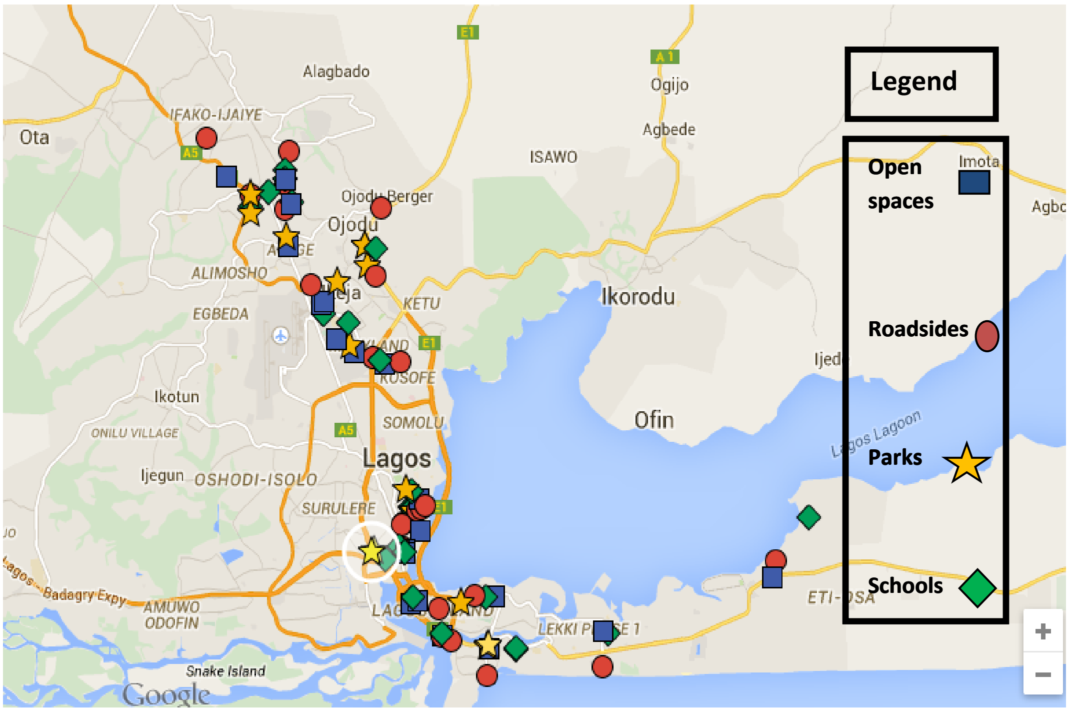
Lagos is Nigeria’s most populous city and seventh fastest growing city in the world[169]. Lagos State Government estimated the population of Lagos as 17.5 million during a parallel census conducted in 2006 with over 12 million people living in the urban areas. A more recent report estimated its population as 21 million, making Lagos the largest city in Africa[170].

Lagos centre is located at 6°35N and 3°45'E. It was formally annexed as British Lagos colony in 1861 and served as the capital of Nigeria from 1914 to 1991. Lagos state has an area of about 3600 km^2 of which 1700 km^2 is water body. Lagos is on a built up land area of about 18,558 hectares and made up of about 9,669 hectares of residential (52.1 %), commercial (1,021 hectares; 5.5 %), industrial (1,448 hectares; 7.8 %), institutional and special areas (2,784 hectares; 14 %), transportation (3,340 hectares; 18 %) and open spaces (520 hectares; 2.8 %)[166]. The rate of population growth is about 600,000 per annum with a population density of about 4,193 people/km^2. Most of the population live on the mainland while the rest of the population settled on the island. The island is separated from the mainland by Lagos harbour (the main channel draining the lagoon into the Atlantic Ocean).

Lagos experiences rainy and dry seasons with the latter accompanied by hot, dry and dusty winds. It represents the most industrialised area in Nigeria with over 60 % of total industrial activities [171]. Lagos state is made up of 20 local government areas (LGA). For the purpose of this study, five areas spread across four local government areas were selected; representing different socio-economic areas of Lagos (see Fig 2.1 a, b and c). The choice of sampling areas was characterised based on income earnings (high, medium and low) and population densities specific to each of the areas.

a

b


Legend
Open spaces
Roadsides
Parks
Schools
Ota
Alagbado
IFAKO-IJAIYE
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ISAWO
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Imota
ALIMOSHO
EGBEDA
Ikeja
KETU
KOSOFE
Ikorodu
Ijede
Ofin
Ikotun
ONILU VILLAGE
SOMOLU
Lagos
Ijegun
OSHODI-ISOLO
SURULERE
Lagos Lagoon
Lagos-Badagry Expy
AMUWO ODOFIN
LEKKI PHASE 1
ETI-OSA
Snake Island
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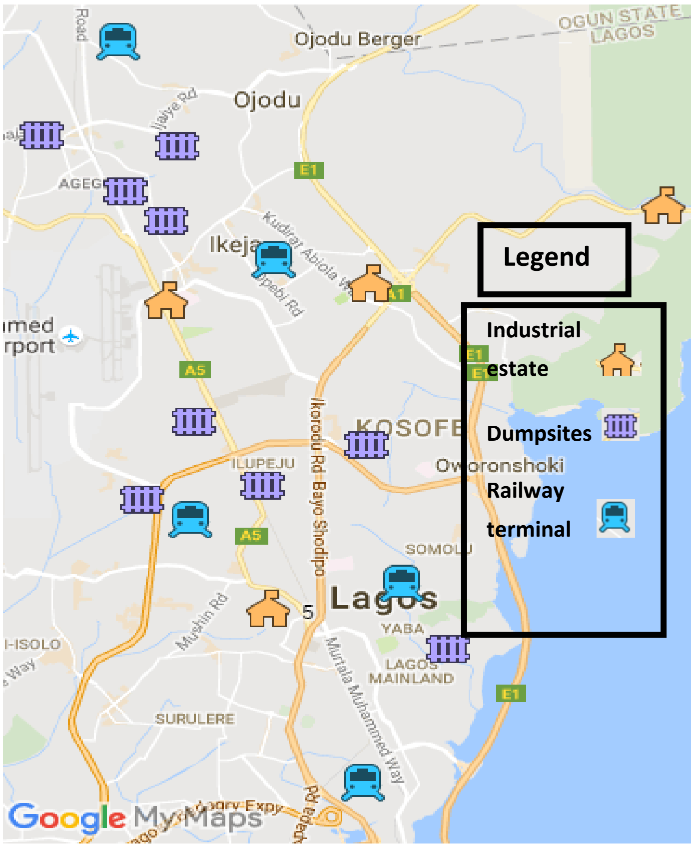
Legend
Industrial estate
Dumpsites
Railway terminal
Ojodu Berger
Ojodu
OGUN STATE
LAGOS
AGEGE
Ikeja
Kudirat Abiola Way
Opebi Rd
KOSOFE
ILUPEJU
Oworonshoki
SOMOLU
Ikorodu Rd-Bayo Shodipo
Lagos
YABA
LAGOS MAINLAND
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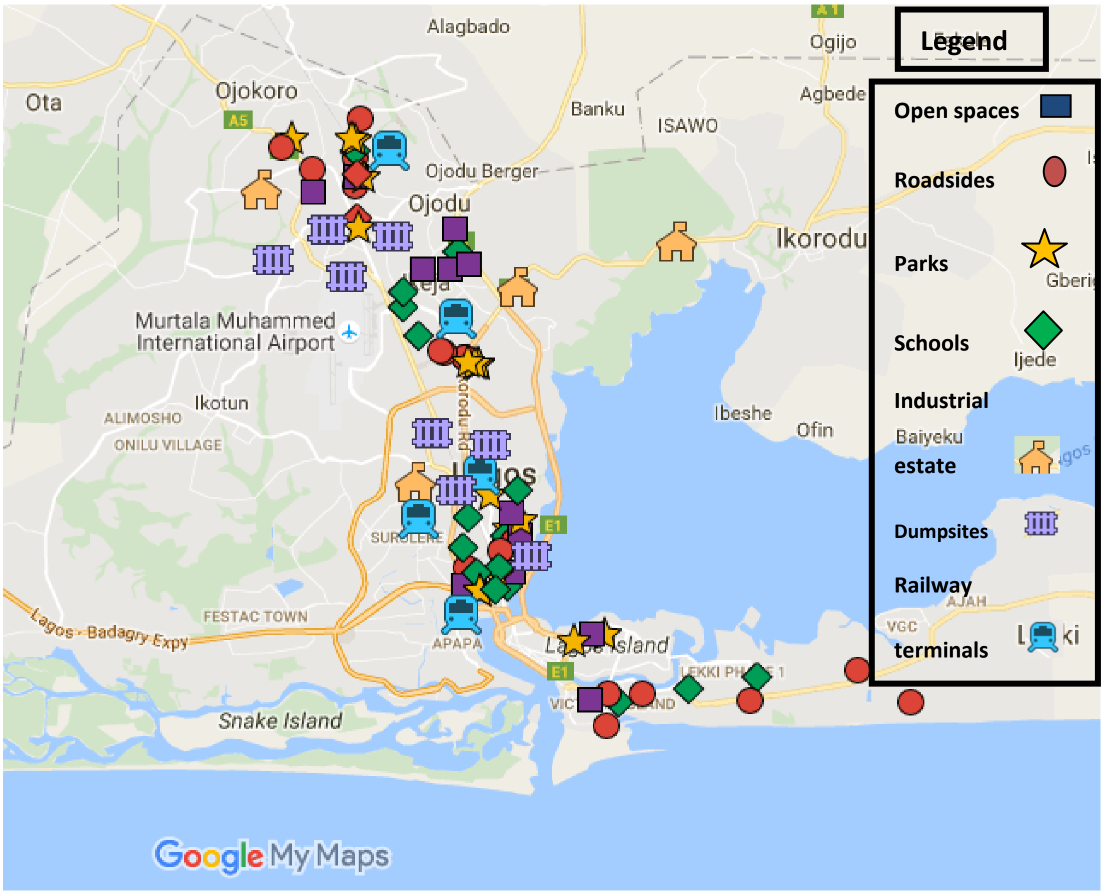


e

Fig 2.1 (a) Map of Nigeria showing federal capital territory, Abuja and Lagos state (b) Lagos state map; shaded areas are local government areas of interest in this study (c) Lagos map showing sampling points for soils collected away from potential point sources (d) Lagos map showing sampling points for soils collected close to point sources (e) An overaching Lagos map showing all sampling points.

Victoria Island (VI) represents the high income area. Ikeja (Ikj) the state capital, Ifako ijaiye (Ifk) and Lagos mainland (LM) represent the middle income areas. Makoko (Mak) represents the low income area. Figure 2.2 a, b and c shows a pictorial view of some of the areas studied.

Victoria Island[172] is an affluent area and lies within the boundary of Eti Osa local government area (LGA). This island serves as the business and the financial centre of Lagos with most of the Nigerian and international corporations located on the island. It is one of the most exclusive and expensive areas to live in Nigeria.

Victoria Island is the diplomatic centre of Nigeria with numerous foreign missions, embassies and consulates such as Russia, United Kingdom, USA, Brazil, Spain, etc. located there. It houses the upper class and basic social amenities are available in more than 80 % of the area.

a

b

c

Figure 2.2 (a) aerial view of VI showing good road networks and green areas (b) picture showing a Makoko slum littered with rubbish and plastics (c) one of the major roads within Ikeja.

Ikeja[173] LGA is the Lagos state capital and houses the government secretariat, Governor's and Lagos legislator's residential accommodations. Ikeja is a well-planned and quiet suburb which was initially built during the colonial era to house the upper class. The government residential area (GRA) within Ikeja is still home to a quite number of high ranking Nigerian government officials and their families. Ikeja is predominantly of residential area but over the years, it has developed into a major commercial and industrial area (co-located with the residential area). It is home to Nigeria's major airport (Muritala Mohammed Airport). To a large extent, most of the roads are paved and it has a lot of newly built green areas.

IfakoIjaiye[174] LGA is next to Ikeja and it is located between two industrial areas (Ikeja and Sango Otta). The industries sited at Ikeja, Oshodi and Sango Otta and its closeness to a neighbouring state (Ogun) makes Ifako Ijaiye a preferred residential area for workers. It is a Lagos suburb which has experienced a sporadic increase in population since the early 1990s. Ifako Ijaiye is known for high incidences of erosion and environmental degradation arising from quarrying activities.

Lagos mainland (LM) is a very old part of Lagos, perhaps the oldest part of Lagos since it houses Tinubu's square which is a site of historic significance in which the amalgamation ceremony that unified the northern and southern protectorates to form Nigeria in 1914 took place. Many of the houses within Lagos mainland area are old mainly because most of them were built during the colonial era. A large central business district area is located at the heart of LM and it also houses Lagos largest wholesale markets (Idumota, Oyingbo and Balogun markets). Nigeria's national museum, the oldest Anglican Church in Nigeria, the University of Lagos, Yaba College of Technology (the oldest higher education institution in Nigeria), the Federal college of Education and Nigeria rail way headquarters are all located within Lagos mainland LGA. Lagos mainland is a very significant and important area to Lagos residents since it serves as the main access route that connects Victoria Island (and the rest of Lagos Island) to other parts of Lagos. Lagos mainland area encompasses both medium and low socio-economic areas since places such as Makoko and Iwaya communities are under this LGA. Other parts of the LGA such as Akoka (University of Lagos area), Yaba, and Bariga may be categorised as areas for middle income earners.

Makoko[175, 176] is primarily a fishing village established in the 18th century and it is a small area within the boundaries of Lagos mainland LGA. Makoko is predominantly a slum and an ecologically vulnerable area prone to flooding and storm damage. The slum is easily visible from the bridge (third mainland bridge) that connects the rich island districts to other parts of Lagos. Most residents settle on hazardous and unbuildable terrains such as flood plains and over steep slopes. Residents also live in dumpsites with heaps of refuse all over the area and on margins of railways and highways. Basic infrastructures such as electricity, drinking or clean water, waste disposal system are non-existent in Makoko; consequently, residents are prone to several environmental and health hazards.

2.1.2 Sampling and site description

Soils from school playgrounds (SH), road sides (RD), open spaces (PO) (comprising bus stations, markets, relaxation centres etc.), ornamental gardens (OG) from all the above areas were sampled.

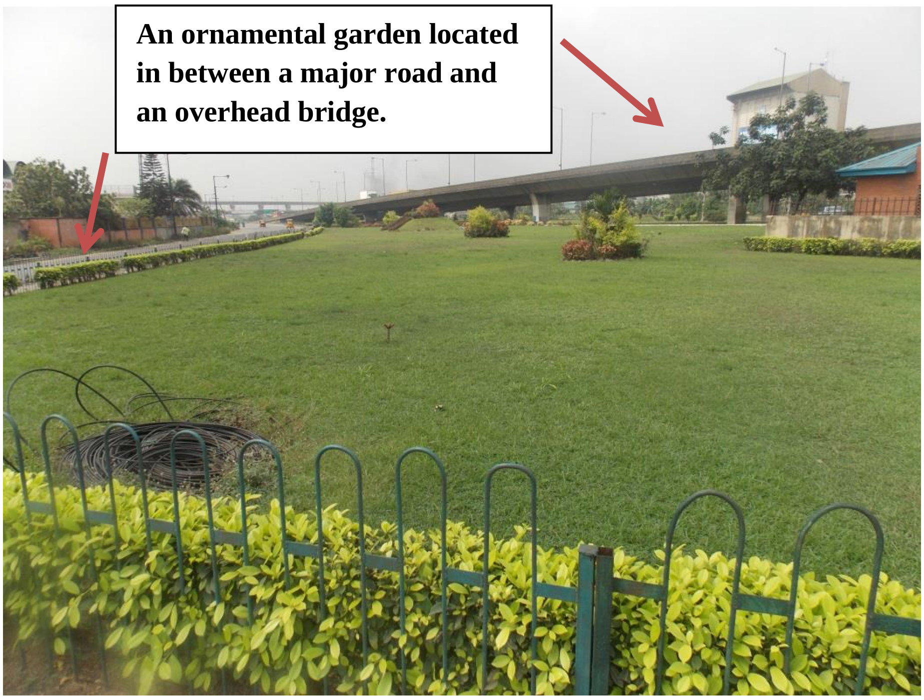
These land use types were sampled in all the areas highlighted above (VI, Ifako, Ikeja, Lagos mainland and Makoko). Sampling sites were selected away from known point sources of pollution. This was carried out in order to obtain a general overview of the current ambient levels of PTE in Lagos urban soils. A total of 91 composite samples were collected.

a

b


Makoko residents relaxing under a wooden shed.

c


An ornamental garden located in between a major road and an overhead bridge.

d

e

Figure 2.3 (a) picture showing children playing with soil in one of the schools sampled at Ikeja, (b) unpaved school playground at Lagos mainland (c) an open space at Makoko, where people frequently relax (d) picture of a park in Lagos mainland sited in between a major road and overhead bridge (e) one of the parks sampled at Victoria Island.

These comprise of 25, 25, 23 and 18 composites samples from SH, RD, PO and OG respectively. The sampling points in each of the locations were selected giving preference to where people frequently relax or spend time (see Fig 2.3 a, b, c, d and e). In the case of the school playgrounds, samples were collected at locations where children normally play. Soils were also collected from pedestrian walk-ways along the roadsides sampled. Thereafter, a total of 17 sampling sites were chosen close to potential point sources. There were 8 dump sites, 4 industrial estates sites and 5 train terminals making up a total of 33 composite soil samples. The sites chosen were identified giving preference to locations with reasonable proximities to those collected away from known point sources. Global positioning system device (Garmin GPSMap 60 Csx) was used in defining the locations.

Ikeja, Ogba, Ilupeju and Ikorodu industrial estates were sampled. Activities of the estates span production of cosmetics, food and beverages, aluminium sheets, plastics, paper, brewery and pharmaceuticals. Ikorodu industrial estate mainly consists of metal based industries producing iron rods, galvanized pipes and steel rolling mills. Ikeja, Ilupeju and Ogba industrial estates are co-located with residential layouts.

The distance separating the two land-use types is about 20 to 30 m. Residential areas typically occupy about 30 % of the total land space within the estates. Waste management of the estates is generally poor and most of the factories have no emission control monitoring systems installed.

The dump sites sampled were Owode, Ladipo, Computer Village, Katangua and Olusosun. Dasco, Nigerian and Grand Foundry companies dumpsites located within Ikeja were sampled. These dumpsites generally cover large expanses of land and have existed for more than two decades. Wastes in these dumpsites were mostly generated from domestic and industrial sources. Olusosun dumpsite covers about 42 hectares of land and it is the biggest dumpsite in Lagos. This dumpsite receives and processes about 2400 metric tonnes of solid wastes on a daily basis and it is maintained by Lagos State Waste Management Agency (LAWMA)[177]. Ikeja Computer Village dumpsite primarily consists of electronic waste (scraps from computer monitors, laptops, television sets, radio sets etc.) while Ladipo and Owode dumpsites comprise majorly of waste generated from scraps of automobiles spare parts. The wastes from the three foundries sampled mainly consist of steel and iron dust generated from the foundry factory sites, scrap metal, domestic and other industrial wastes. Generally, most of the sites sampled are open dumps with heaps of waste littered around with no proper demarcation, and they are less than 50 m from pathways alongside roads.

Railway terminals sampled were Agege, Alagomeji, Iddo, Ikeja, and Oshodi. These are major train terminals located in the metropolis and are accessible to users because of their closeness to residential settlements, workplaces, markets and schools. Figures 2.4 (a and b) and 2.5 (a, b and c) shows the pictures of some of the sampled locations.

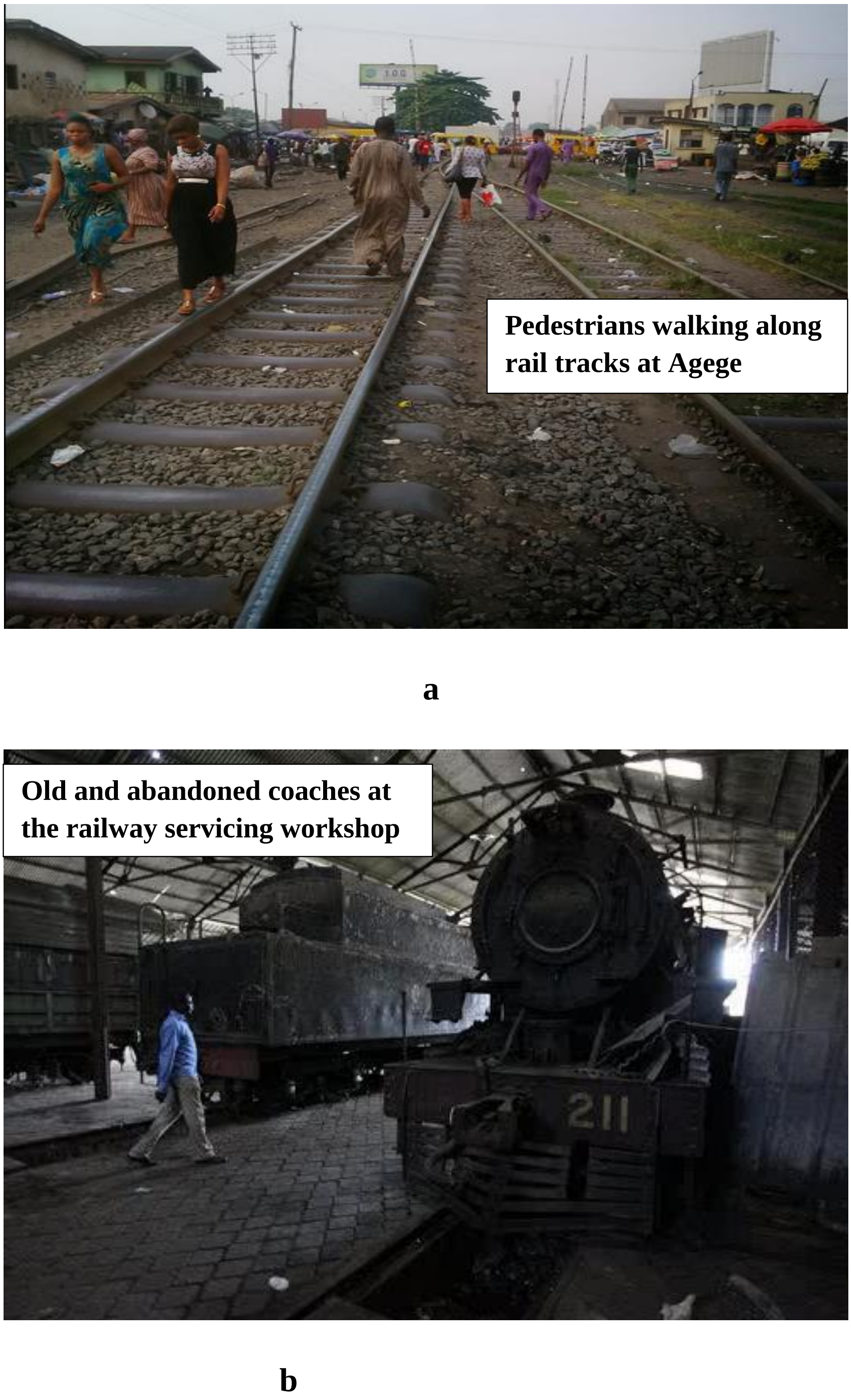
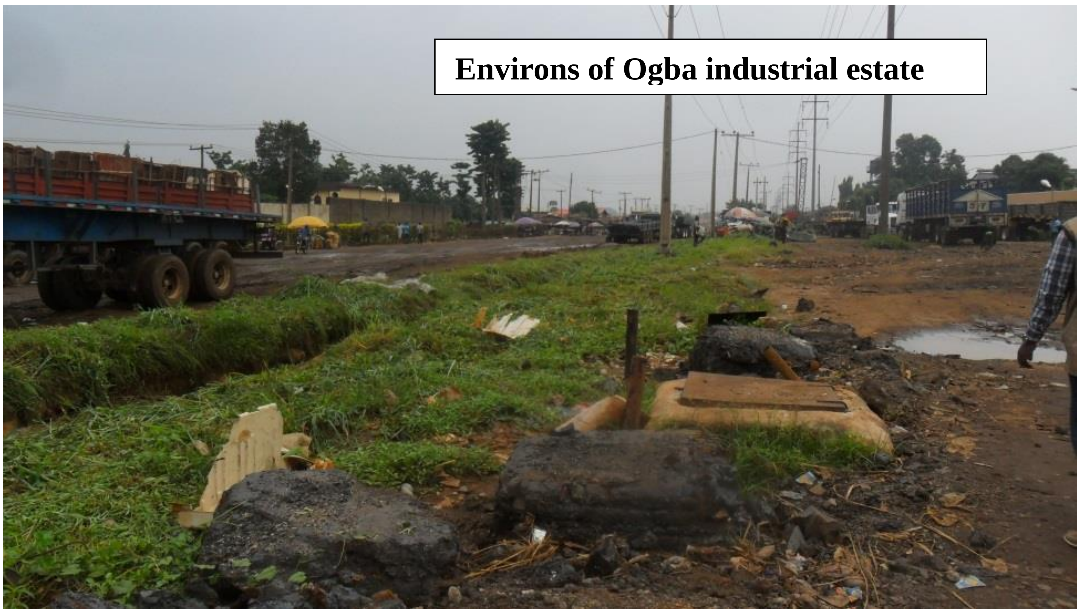


Figure 2.4 (a) People walking along the rail tracks around Agege terminus (b) Old and abandoned coaches at the Nigerian railway corporation workshop at iddo.



a

b

c

d

Figs 2.5 (a) A section of Ogba industrial estate environ (b) Heaps of abandoned metal scraps at Ikorodu industrial estate (c) a foundry factory site at Ikeja (d) a section of Olusosun dumpsite.

2.1.3 Soil samples studied for fractionation and bioaccessibility studies

A total of 20 soil samples were studied. Seven (7) soil samples were chosen from soils collected away from known point sources and thirteen (13) soil samples were chosen from those collected close to potential PTE point sources. Soils chosen were within reasonably close proximity, as determined using GPS coordinates (see Fig 2.1 e).

Soils collected away from known point sources were,

1. LM PO 1 = Lagos mainland open spaces 1
2. Ikj PO 3 = Ikeja open spaces 3
3. Ikj PO 5 = Ikeja open spaces 5
4. Ifk PO 5 = Ifako open spaces 5
5. Ifk PO 4 = Ifako open spaces 4
6. Ikj OM 1 = Ikeja ornamental garden 1
7. Ifk RD 2 = Ifako road 2

Soil collected close to known point sources were:

8. Ogba ind 2 = Ogba industrial estate 2
9. Ikj ind 2 = Ikeja industrial estate 2
10. Ikorodu 2 = Ikorodu industrial estate 2
11. Ikj along 2 = Ikeja along 2
12. Iddo 1 = Iddo railway terminal 1
13. Agege = Agege railway terminal
14. Owode 1 = Owode dumpsite 1
15. Owode 3 = Owode dumpsite 3
16. Dasco = Dasco dumpsite
17. Comp. village = Computer Village dumpsite
18. Ladipo 3 = Ladipo spare part market dumpsite
19. Katangua 1 = Katangua spare part market dumpsite
20. Grand Foundry = Grand Foundry dumpsite

2.2 Soil processing

In each of the sampling location (for both categories of soils sampled away and from known point sources) , composite surface soil samples (to a depth of 0-10 cm) which consisted of 4-8 sub-samples were obtained by drawing about a 2 m squared grid from a centre point and then taking random subsamples within the square. Grass, leaves, papers, polythene bags etc. present in the collected soil samples were gently discarded to remove soils attached to them. Wet soil samples were air dried for 3 days before storage. About 500 g of the bulked samples were taken at each location and kept in a sealed air tight polythene bag and labelled. Soil samples were kept for 6 days in the Lagos Ministry of Environment laboratory before being transported from Lagos, Nigeria to University of Strathclyde, Scotland, UK for further processing and analysis under Scottish Government soil import license (IMP/SOIL/24/2014).

The soil samples were thereafter air dried in the laboratory for 14 days and sieved through a 2 mm nylon mesh sieve before grinding and homogenization with mortar and pestle. Coning and quartering of individual soil sample was performed before sample digestion.

2.3 Extraction procedures

All glass and plastic-ware used were soaked in 5 % (*v/v*) nitric acid overnight (a general purpose grade supplied by Sigma Aldrich, UK), and then washed thoroughly with distilled water. This was necessary in order to reduce or eliminate any form of contamination from glass and plastic wares. Prior to analysis, all solutions were stored in polyethylene bottles at 4^{o}C.

2.3.1 Pseudototal digestion

Pseudototal digestion of soil samples was performed using a microwave digestion system (MARS Xpress, CEM Microwave Technology, Ltd, Buckingham, UK).The samples were digested with *aqua regia* which was prepared by mixing extra pure hydrochloric (HCl) and nitric (HNO_3) acids (Sigma-Aldrich, Gillingham, UK), in the ratio 3:1 (*v/v*).

A subsample (1.0 g) of soil was accurately weighed into a high pressure vessel and 20 mL of freshly prepared *aqua regia* was added. This was placed in the fume cupboard and allowed to stand overnight, allowing vigorous reactions to subside. The pressure vessels containing the sample mixture was placed in the MARS Xpress microwave digestion system and the digestion programme shown in Table 2.1 was applied. The pressure vessels and its contents were allowed to cool and the digested samples were filtered into 100 mL volumetric flasks, using Fisher brand filter papers (FB 59023) and were washed thoroughly using distilled water. Filtrates were made up to mark with distilled water to obtain 20 % *aqua regia* solution and these were further diluted as required. Replicate samples (n = 3) were digested along with procedural blanks.

Table 2.1 MARS Xpress microwave digestion program conditions for the extraction of PTEs using aqua regia.

Power• (>16 vessels)	1600 watts
Temperature	160 °C
Ramp time	10 mins
Holding time	20 mins

• 4 – 15 vessels (800 watts), < 4 vessels (400 watts)

2.3.2 BCR sequential extraction procedure[61]

2.3.2.1 Apparatus

A G.F.L 3040 mechanical end-over-end shaker (G.F.L, Burgwedel, Germany) was used in performing extractions at a speed of 23 rpm with the appropriate extractant solutions. Care was taken to minimise delay between the addition of extractant and shaking. The extracts were separated from sample residue using Allegra 21 centrifuge (Beckman Coulter Ltd, California, USA), at 3000 g for 20 minutes.

2.3.2.2 Reagents

2.3.2.2.1 Preparation of extraction solutions

Exchangeable phase extraction solution (acetic acid, 0.11 M)

0.43 M acetic acid was prepared by diluting 25 mL of glacial acetic acid, puriss grade (Sigma Aldrich, Gillingham, UK), to 1L with distilled water.

This solution was further diluted by taking 250 mL and making it up to 1L to obtain the corresponding and final concentration of 0.11 M acetic acid solution.

Reducible phase extraction solution (hydroxylamine hydrochloride, 0.5 M)

34.75 g of hydroxylamine chloride, analytical reagent grade (Fisher Scientific, Loughborough, UK), was dissolved in 400 mL distilled water. This solution was transferred to a 1L volumetric flask and a 25 mL aliquot of 2 M nitric acid was added. Distilled water was then used to make up the flask to mark. The solution was prepared the same day the extraction was carried out.

Oxidisable phase extraction solution (hydrogen peroxide, 8.8 M)

A 30 % hydrogen peroxide solution, puriss grade (Sigma-Aldrich, Gillingham UK), was used as supplied by the manufacturer, i.e. acid stabilised to pH 2-3.

Residual phase extraction solution (ammonium acetate, 1.0 M)

77.08 g of ammonium acetate, analytical reagent grade (Fisher Scientific, Loughborough, UK), was dissolved in 800 mL of distilled water. The pH of the solution was adjusted to 2.0 ± 0.1 with concentrated HNO_3 and made up to 1 L with distilled water.

Blanks

A procedural blank was prepared for each batch of extractions. 40 mL of 0.11 M acetic acid for exchangeable phase, 40 mL of 0.5 M hydroxylamine hydrochloride for reducible phase, and 50 mL of 1.0 M ammonium acetate for oxidisable phase, were added to the vessels without the sample and carried through the complete procedure and analysed at the end of each extraction step.

2.3.2.3 BCR sequential extraction procedure

Step 1: Exchangeable phase

Approximately 1 g of soil sample was weighed into a 100 mL centrifuge tube with 40 mL of solution A. This was placed on the shaker for 16 hours (overnight). The extract was separated from the residue by centrifuging at 3000g for 20 mins and the supernatant liquid was subsequently stored in a polyethylene bottle at 4^{o}C in a refrigerator prior to analysis. The residue was washed by adding 20 mL of distilled water and shaking for 15 mins. Following centrifugation, the supernatant was decanted and discarded.

Step 2: Reducible phase

40 mL of freshly prepared solution B was added to the washed residue from step 1 in the same centrifuge tube, the sample was then shaken, centrifuged and stored as earlier described in step 1.

Step 3: Oxidisable phase

10 mL of solution C was added slowly in small aliquots to avoid losses due to possible violent reaction, to the washed residue from step 2.

The centrifuge tube was loosely covered with its cap and sample was digested for 1 hour with occasional manual shaking. The digestion continued for another 1 hour at 85 ± 2^{o}C with occasional manual shaking for the first 30 minutes in a water bath and then the sample mixture was reduced in volume to about 3 mL by further heating the uncovered tube. Another 10 mL of solution C was added, and the covered samples were heated for a further 1 hour at 85^{o}C ± 2. Subsequently, the caps of the centrifuge tubes were removed and volume was reduced to about 1 mL, with care not to take to complete dryness. 50 mL of solution D was thereafter added to the cool moist residue and the mixture shaken for 16 hours (overnight). The sample was centrifuged and stored as described in step 1.

Step 4: Residual phase

20 ml of *aqua regia* was used to wash the residue from step 3 into a pressure vessel and digested using the procedure described in section 2.3.1.

2.3.2.4 Simple bioaccessibility extraction test procedure[178]

50 ml of 0.4 M glycine (Fisher Scientific, Loughborough, UK) adjusted to pH 1.5 with HCl was added to 0.5 g of soil sample. The mixture was then shaken using Stuart SI500 bench top orbital shaking incubator (Bibby Scientific, Staffordshire, UK) for 1 hour at 37 ^{o}C to mimic the stomach residence time in humans under fasting conditions. The sample mixtures were filtered through 0.45 µm cellulose acetate filters obtained from Sigma Aldrich, Gillingham UK. The filtrates were stored in the refrigerator prior to analysis.

2.3.2.5 Optimised PM_{10} isolation from soil samples.

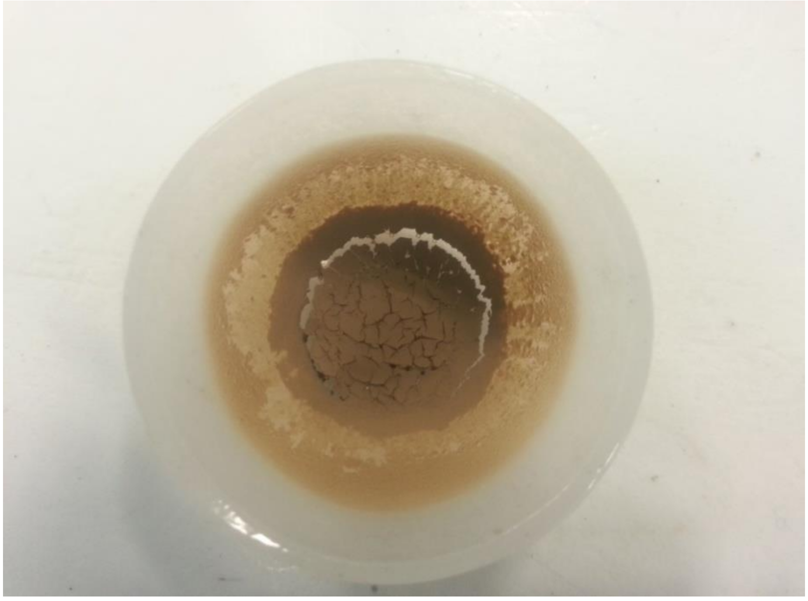
Particulate matter (< 10 µm) was isolated from the Lagos urban soil samples by optimising the wet method described by Ljung *et al*.[179]. The method was modified by adjusting the sample mass, volume of water used and a cheap and more affordable PM_{10} sieve was used. The soil samples were processed as described in section 2.2. Following the preliminary sample processing, the samples were sieved through a < 45 µm sieve and about 4 g of the samples were obtained for nine out of the Lagos urban soil samples studied.

Into a 250 mL beaker, approximately 4 g sample of < 45 µm soil fractions were suspended in 100 mL of deionised water and solution was mechanically dispersed with three 90 seconds repeat using a glass rod. The agitated suspension was left for 10 minutes and small aliquots of the suspension were poured at a time to about the top reservoir of the plastic vacuum filter. The filter was made of a 10 µm mesh sieve (typically used for the separation of zooplankton from culture water) and obtained from marine aqua farm, Cleveleys, Lancashire, UK. The filter was moistened with deionised water prior to pouring the suspension and additional 50 mL of deionised water was used in clearing the filter mesh in between pourings.

Approximately 150 mL of the filtrate was poured in centrifuge tubes (50 mL, Figure 2.6 a). The suspension was centrifuged for 10 minutes at 4000 rpm to obtain < 10 µm fraction. The supernatant (clear water) was decanted and kept for analysis. The residue (<10 µm suspension) was poured into clean washed crucible (uncovered) and placed in the oven at 30 ^{o}C for 4 days.

After removal from the oven, the dust sample (Figure 2.6 b) was scrapped out of the crucible using disposable plastic spatulas. The dust sample was weighed, grounded and stored in labelled plastic vial prior to SBET extraction.

a



b

Figure 2.6 (a) Aliquots of isolated PM_{10} fraction in suspension (b) isolated PM_{10} after removal from the oven.

2.3.2.6 Pseudototal digestion procedure for PM_{10} samples

The pseudototal PTE concentrations were determined by microwave assisted digestion using *aqua regia* as described in section 2.3.1. A reference material, BCR 143R (sewage sludge amended soil) was included in soil digestion batches, in order to assess digestion efficiency. In this work, the original pseudototal digestion procedure was miniaturised in that, the mass of sample and volumes of extractant for BCR 143R were scaled down to 50 mg (using a microbalance Mettler Toledo model XP2U, Leicester, UK) and 5 mL. This was necessary in order to assess the repeatability and validation of procedure for pseudototal PTE concentrations recovery in small mass of test PM_{10} samples.

2.3.2.7 Simplified bioaccessibility extraction procedure for PM_{10} samples

Details of the SBET extraction procedure employed for the inhalation bioaccessibility in PM_{10} fractions of Lagos urban soils is provided in section 2.3.2.4. This procedure was miniaturised to extract small mass of isolated PM_{10} samples.

About 10 mL of pH adjusted glycine was used in extracting approximately 0.1 g of test samples.

2.4 Analysis of extracts

Inductively coupled plasma mass spectrometry (ICP-MS model 7700x instrument, Agilent Technologies, UK) was used to determine PTE concentration in digests and extracts (operating conditions shown in Table 2.6). Mass Hunter Workstation software was used on the 7700x ICP-MS which was operated on Microsoft Windows 7 Professional. The software provided general instrument control, from automated start up checks following plasma ignition, through batch and queue method setup and sequencing, data acquisition, qualitative and quantitative data analysis and final report generation. Reagent matched multi element calibration standard solutions (Qmx Laboratories, Thaxted, Essex, UK) were prepared over the range of 0 – 1600 µg/L for PTE studied (Cr, Cu, Mn, Pb, Ni and Zn), except for Fe, where the calibration standards were prepared over the range of 0 – 100,000 µg/L. These were used to calibrate the instrument and to construct the calibration curves.

Table 2.6 ICP-MS Operating conditions

ICP-MS conditions	CCT mode
Power (W)	1550
Quadrupole bias (V)	-15
Octopole bias (V)	-18
Nebulizer gas flow (L/min)	0.89
Plasma gas flow (L/min)	15
Collision cell gas (L/min)	He (4.3)
Internal standard	^{115}In
Sample uptake rate (mL/min)	0.4

Indium (^{115}In) was chosen as the internal standard to correct variations in instrument drift and also to correct for changes in analyte sensitivity due to variations caused by matrix effects (non-spectral interferences). Blank samples were also analysed to check for contamination.

Before each batch of analytical runs, the instrument was tuned to verify mass resolution and sensitivity maximisation. The collision cell technology (CCT) mode was used for the determination of ^{52}Cr, ^{63}Cu, ^{56}Fe, ^{55}Mn, ^{60}Ni, ^{208}Pb and ^{64}Zn. During sample analysis, instrument consistency was checked intermittently by ensuring calibration standards were checked after every tenth sample measured. The calibration curves for the PTE determined gave a linear fit with the regression coefficient (R^2) of at least 0.999.

2.5 pH measurement[180]

About 1 g of each air-dried, sieved sample (< 2 mm) was weighed into a 50 mL centrifuge tubes, after which 5 mL of deionised water was added. The centrifuge tubes were then closed firmly and placed on the end-over-end mechanical shaker (G.F.L 3040, Burgwedel, Germany) for 1 h, and thereafter removed. This was allowed to stand for 2 h. The pH was then measured in the suspension after calibrating the pH meter [Metller Toledo (SevenGO^{TM}), Schwerzenbach, Swizerland] with pH 4 and 7 buffer solutions.

2.6 Loss on ignition determination[181]

Moisture content was determined in order to express the PTE concentrations on a dry weight (d.w) basis. Approximately 1.0 g of each sample (< 2 mm) was weighed into dry and pre-weighed crucible and placed in an oven (Memmert GMbH, Camlab Ltd., Cambridge, UK), at 110 ^{0}C for 24 hours. This was then removed and placed in the desiccator and allowed to cool. The crucible containing the sample was then weighed accurately and loss in weight was determined. The residues from the determination of moisture content were used to estimate the organic matter content of the samples.

The crucible and residue was placed in a muffle furnace (Box Furnace, Elite Thermal Systems Ltd., Market Harborough, UK) which was ramped at 10 °C per minutes and held at 550 °C for 8 h, then allowed to cool to about 110 °C. The crucibles containing the residue were transferred into the desiccator and allowed to cool again. The crucibles were weighed thereafter and the difference in mass obtained before and after ignition was used to estimate the % organic matter content using Equation 2.1.

$$\%\,LOI \;=\; \frac{dry\,weight - weight\,after\,combustion}{dry\,weight} \times 100$$

Equation 2.1

2.7 Data Handling

2.7.1 Detection limits

Detection limits (DL) is a measure of the minimum concentration of analyte that generates a signal which differs significantly from the background within a specified statistical confidence limit. The instrument detection limit was determined using equation 2.2.

$$DL \;=\; \frac{(3\;\times s)}{gradient\;of\;the\;calibration\;slope}$$

Equation 2.2

Where s, is the standard deviation of 10 replicate measurements of the lowest concentration of the standards, defined by equation 2.3

$$s = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n-1}}$$

Equation 2.3

Where x_i is an individual value, n is the number of replicate measurements and $\bar{x}$ is the mean as defined in equation 2.4

$$\bar{x} = \frac{\sum_{i=1}^{n} x_i}{n}$$

Equation 2.4

The procedural detection limits (DL_{pro}), the minimum analyte concentration that can be determined in an environmental substrate, allowing for the method of sample preparation, were calculated from instrument detection limits. Procedural detection limits were calculated according to Equation 2.5

$$DL_{pro} = \frac{DL \times volume\ of\ extractant\ \times dilution\ factor}{mass\ of\ sample}$$

Equation 2.5

2.7.2 Precision

This is the degree of agreement between different measurements carried out in the same manner on the sample. It can be expressed as the percentage relative standard deviation (% RSD) calculated using Equation 2.6

$$\text{RSD} = \frac{s}{\bar{x}} \times 100\%$$

Equation 2.6

2.7.3 Accuracy

The percentage accuracy of an analytical method expresses the closeness of a measured mean analyte concentration($\bar{x}$), to the target or certified value (μ), expressed as a percentage which is represented in Equation 2.7

$$Accuracy(\%) = \frac{\bar{x}-\mu}{\mu} \times 100$$ **Equation 2.7**

2.7.4 Calculation of concentration values

The analyte concentrations obtained from ICP-MS were measured in µg/L of solution, but in soil analysis, this is usually expressed in terms of mass of analyte per mass of dry soil. The concentration values of analyte in solution were converted to µg/g (which is the same as mg/kg) using Equation 2.8

$$Concentration\ (mg/kg) = \frac{concentration\ (\mu g/L)\ \times volume\ of\ extractant\ (mL)\ \times dilution\ factor}{mass\ of\ sample\ (dry\ weight) in\ g}$$

Equation 2.8

2.8 Statistics[182]

2.8.1 Pearson correlation coefficient

Pearson correlation coefficient (r) is a bivariate approach which measures the strength of the association between two variables. The strength of the relationship or association is usually denoted as correlation coefficient (r):

$$\frac{\sum_i[(\boldsymbol{x_i} - \boldsymbol{\overline{x}})(\boldsymbol{y_i} - \boldsymbol{\overline{y}})]}{\sqrt{\{[\sum_i(\boldsymbol{x_i} - \boldsymbol{\overline{x}})^2][\sum_i(\boldsymbol{y_i} - \boldsymbol{\overline{y}})^2]\}}}$$

Equation 2.9

The numerator in Equation 2.9 is called the covariance of the two variables x and y. The covariance measures their joint variation and in the case where, x and y are not related, their covariance will be close to zero. The correlation coefficient (r) is computed by dividing the covariance of x and y by the product of their standard deviations. The Pearson correlation coefficient (r) only takes values in the range of − 1 to + 1. When there is no linear combination between the two variables (x and y), the value of r is close to zero while -1 and +1 indicates perfect negative and positive correlation, respectively. The closer the value is to -1 and + 1, the stronger the correlation.

In this current study, correlation coefficient analysis was applied to the pseudototal concentrations data in order to test an hypothesis on the sources (anthropogenic against lithogenic) of PTE in soil samples and also the relationship between PTE and soil main properties such as pH and organic matter content. Calculations of correlations were also applied to PTE extracted from operationally defined phases (BCR) and SBET to evaluate the dependency of phase extracted PTE on pseudototal content; this evaluated the relationship between availability or bioaccessibility and pseudototal concentrations.

2.8.2 Principal component analysis[60, 182-184]

Principal component analysis is a multivariate statistical tool which describes a data set using a small number of abstract variables, usually called principal components (PCs). It reduces the dimensionality of a data set. Principal component analysis is concerned with the elucidation of covariance structure of a set of variables or it simply identifies the principal direction in which the data set varies. The PCA tool provides the most significant variables that show the source of variation with minimum loss of the original information. However, the PCs obtained from the original data must reflect its underlying structure, both in terms of retaining information about associated samples and also the relationship between different measurement variables (analytes). Strongly correlated variables in data sets are effectively combined to define a new PC; which allows all the data available to be defined by fewer variables and simplifies data handling and ease of interpretation.

Principal component one (PC1) typically explains the most significant or maximum variation, PC2 is orthogonal to PC1 and explain the next most significant variation and so on. Considering a large data set which has a large number of variables to compare, the choice of how many PCs which will adequately describe the data is somewhat arbitrary. However, eigen values are related to the amounts of variation captured by each PC i.e. each PC has an associated eigen value.

In the case where the eigen value becomes so low that is hardly describing any additional variance in the data, then it clear that there is already a sufficient number of PCs to describe the data set.

Owing to the fact that PC1 retains most of the explained variance, many variables can be summarized in few components, depending on the significance of eigen value in variance description.

The PCA produces arrays of ***scores*** and ***loadings*** matrixes. The scores of a PC represent patterns that exist in a data and thus indicate any relationships between samples or sampling sites (e.g. different land use types in soil sampling and analysis). The loadings of a PC provide information regarding relationships between analyte or analyte concentrations (e.g. PTE measured in soil samples). Hence, the reduced data set can be defined on a new set of axes to meet different criteria. The method usually employed is a varimax rotation (rotation of the PCs). This type of rotation involves changing the coordinates used in PCA such that it maximises the sum of the variances of the squared loadings (squared correlation between variables); thus the new squared correlation with factors, will either be large or near zero with few intermediates. This ultimately, produces a new scores and loadings data set. The main aim of a varimax rotation is to associate each variable to at most one factor which eventually allows for the results of PCA to be more simplified. Principal component analysis followed by varimax rotation can then be studied to provide information on relationships existing between variables in each factor loadings.

Principal component analysis followed by varimax rotation is usually employed to classify objects or variables reflecting similar characteristics or vice versa, identification of positive and negative correlations among variables which suggests mutual influence or possible common sources or opposite characteristics, or the influence of a particular variable on the PC (variables with high loadings having a huge influence on the PC or vice versa)[60]. In relation to soil studies, previous literatures have reported the use of PCA to identify possible common source of PTE in urban soils[90, 92, 112, 115, 184], agricultural soils[185], urban dust[5, 186, 187], urban particulate matter[43], and sediments[188].

Principal component analysis was used in this current study to classify soil samples with similar compositions reflecting anthropogenic or lithogenic influence. It was useful in providing a hypothetical position relating to where PTE emanated from in Lagos urban soils. This was conducted by grouping variables and samples into factors according to their respective composition thereby explaining the influence of each variable on a PC i.e. variables with high loadings on a PC reflects high influence or dominance or vice versa.

2.8.3 Cluster analysis[189-191]

Cluster analysis (CA) is a multivariate statistical technique which aims at classifying objects on the basis of a set of measured variables in an attempt to form ‘‘groups’’ or ‘‘clusters’’ such that, objects with similar characteristics are grouped together. The CA technique is divided into two:

(i) Hierarchical, which involves stepwise grouping of objects in an agglomerative (joining single objects successively to form larger groups) or divisive (starting from one group of cluster which comprises all objects and dividing it into successively smaller or homogenous clusters) approach.

(ii) Non-hierarchical cluster in which objects are not successively linked together but clusters are determined directly.

Agglomerative methods are more frequently used than divisive methods. Hierarchical cluster analysis (HCA) basically starts with a square matrix containing distances or dis (similarities) between objects.

The most common distance measured is ***Euclidean distance.*** Considering *y* variables $X_1, X_2, \ldots\ldots, X_Y$ measured on a sample of *n* objects, the observed data for object *i* can be denoted by $X_{i1}, X_{i2}, \ldots\ldots, X_{iy}$ and the observed data for object *w* by $X_{W1}, X_{W2} \ldots\ldots, X_{WY}$. The Euclidean distance between these two objects is given by Equation 2.10.

$$d_{iw} = \sqrt{(x_{i1} - x_{w1})^2 + (x_{i2} - x_{w2})^2 + \cdots + (x_{iy} - x_{wy})^2}$$

Equation 2.10

A typical algorithm employed for cluster analysis would first find the Euclidean distances between all possible pairs of points. However, different methods are used to determine which cluster should be joined at each point (single, average, complete, centroid and Ward’s method linkage). Ward’s linkage is mostly employed; this method combines all possible pairs of clusters and the sum of the squared distances of each member to the centroid (point with mean values of variables) is calculated. It is a minimum variance method i.e. the combination that gives the lowest sum of squares is chosen. In general, a tree-like structure called a ‘‘*dendrogram*’’ is often used to visualize hierarchical clustering. Typically, two sub-sets of data often exist, some of the data points very closely related to each other (subset A) and the other remaining data points which also possess similar characteristics (subset B). The distances between different groups of clusters are clearly shown at the y-axis (indicated by where successive splits or joints take place). The results of this technique have been used in previous literature to distinguish between sources of PTE[92, 187, 192], identify zones within different contaminated sites[193, 194], distinguish soils from different areas[194] and to better interpret PCA results[195].

Cluster analysis was employed in this study to group PTE of similar characteristics or behaviour. It was a useful tool in determining source characterization of PTE; predicting the possible emanating PTE sources in Lagos urban soils. Results of CA was compared and contrasted with PCA and correlation coefficient results to evaluate similarities or disparities in the outcome thereby a proper inference was made and part of the aims and objectives of the study was achieved. The PCA and CA were computed using the R program by Dr Piotr Gromski of the Department of Chemistry, University of Glasgow, UK.

2.9 Enrichment Factor (EF)

A common approach in assessing anthropogenic influence on soils is to calculate an enrichment factor (EF) for PTE concentrations above background values[196, 197]. Calculation of EF reduces PTE variability and it is valuable in comparing the extent of pollution in absolute terms[198]. It is an appropriate tool for plotting geochemical trends of PTE and other pollutants across large geographic areas[198, 199]. Enrichment factor is calculated by comparing measured PTE content with respect to a reference element[200]. Previously used reference elements include Al[201], Fe[202-204], Mn[205, 206], Sc[207], Ti[208] and Co[209]. These elements serve as conservative elements in geochemical normalization of PTE data in order to identify degree of anthropogenic contributions and anomalous enrichments in soils and sediments[101].

The EF is calculated using the equation below:

$$\boldsymbol{EF = \frac{x_a}{x_b} \Big/ \frac{y_a}{y_b}}$$

Equation 2.11

X_a is the concentration of PTE examined in the sample, X_b is the concentration of reference element in the sample, y_a is the background concentration of PTE examined and y_b is the background concentration of reference element. In this study, Fe was chosen as the reference element since its one of the most abundant element in the earth crust, other than Al[206], its geochemistry is similar to many PTE and its standard deviation of successive measurements in Lagos urban soils were generally good. Several other studies used Fe as a reference element[103, 104, 204, 210]. Since background levels of PTE have not been established in Nigeria, the background concentrations of Cr, Cu, Fe, Mn, Ni, Pb and Zn published by Turekian and Wedepohl[211] was used. The PTE values published by the authors were natural shale concentration values. Shale and world average soil or Earth's crust values are often used to provide background reference values for PTE[103]. Zhang and Liu[212] noted that EF values between 0.5 and 1.5 indicate PTE is entirely from natural origins whereas EF values greater than 1.5 suggests source/s are more likely to be anthropogenic.

Sutherland[213]empiricallysuggested five categories of degree of pollution based on enrichment factor :

1. EF < 2 no or minimal enrichment
2. EF = 2 - 5 moderate enrichment
3. EF = 5 – 20 significant enrichment
4. EF = 20 – 40 very high enrichment
5. EF > 40 extremely high enrichment

2.10 Geoaccumulation index

The index of geoaccumulation (Igeo) expresses the contamination levels of soils by comparing current PTE levels to that of non anthropogenically-influenced soils (e.g. background Earth's crust values). Geoaccumulation index is usually used to assess the degree of contamination in soils and it is expressed using Equation 2.12.

$$\boldsymbol{log_2} = \left(\boldsymbol{C_n} / \boldsymbol{1.5 B_n} \right)$$

Equation 2.12

Where C_n *is* the average concentration of PTE in the soil sample and B_n is the background geochemical Earth's crust value. The factor 1.5 is introduced in the relationship in order to compensate for possible variations in background values which may be attributed to various lithogenic effects. The following classification is given togeoaccumulation index:

1. Igeo< 0 practically unpolluted
2. Igeo 0-1 unpolluted to moderately polluted
3. Igeo 1-2 moderately polluted
4. Igeo 2-3 moderately to strongly polluted
5. Igeo 3-3 strongly polluted
6. Igeo 4-5 strongly to extremely polluted
7. Igeo> 5 extremely polluted.

A number of studies have also Igeo to assess the contamination degree of soils[11, 86, 102, 104]. Pollution assessment tools (EF and Igeo) were employed in this current study to assess the anthropogenic influence of PTE in the soils studied.

2.11 Safety

All work involving apparatus and chemical substances were conducted in a safe and controlled manner in accordance with experimental risk assessments. In this study, a number of substances were used which are classified as hazardous to health in relation to the ‘‘Control of Substances Hazardous to Health’’ regulations (Table 3-3). Due to their hazardous chemical properties, substances were handled with gloves and other personal protective equipment like safety glasses and laboratory coats were worn.

Chemicals were sealed and kept safe in acid or solvent cupboards as appropriate when not in use. Excess acids and digests were disposed off as highlighted in the relevant COSHH assessment.

Table 2.7 Hazardous substances associated with present work

Substance	**Very toxic**	**Toxic**	**Harmful**	**Corrosive**	**Irritant**	**Sensitizer**
Acetic acid		yes	yes	yes	yes	
Ammonium acetate		yes			yes	
Hydrochloric acid		yes	yes	yes	yes	
Hydrogen peroxide		yes	yes	yes	yes	
Hydroxylamine hydrochloride		yes	yes		yes	yes
Nitric acid	yes	yes	yes	yes		
Glycine			yes			
Multi-element standard solution				yes		

2.12 Conclusion

This chapter presents information about the study sites, strategies employed for soil sampling, the methods applied for sample preparation, PM_{10} isolation, microwave assisted digestion, BCR sequential extraction technique, oral bioaccessibility, ICP-MS analysis of digests and extracts, statistics employed for data analysis and pollution assessment tools used in assessing anthropogenic influence of PTE in soil samples.

Samples were collected away from potential point sources to assess the current PTE status in Lagos urban soils as an indicator of ambient urban levels of contamination and samples were also collected from potential contamination hotspots to evaluate PTE distribution in the two categories of soils and generally to assess the variability of PTE in different land uses. This allowed for comprehensive information and understanding of PTE contamination in Lagos soils. Details of site sampled and soil processing were highlighted in this chapter. Detailed maps showing the sampling sites were included in this chapter.

Method for soil pH and loss on ignition determination, step by step extraction procedures (pseudototal digestion, BCR sequential extraction and SBET) and the modified PM_{10} isolation method applied to soil samples were described in detail for reproducibility in future urban soil studies.

The ICP-MS equipment (ICP-MS model 7700x instrument, Agilent Technologies, UK) employed in this study complies with USEPA standard method 6020A[214]. The ICP-MS instrument was tuned to verify mass resolution and sensitivity maximisation and collision cell technology (CCT) mode was used for the determination of ^{52}Cr, ^{63}Cu, ^{56}Fe, ^{55}Mn, ^{60}Ni, ^{208}Pb and ^{64}Zn. The conditions at which the ICP-MS was operated are listed in Table 2.6.

Microsoft Excel 3.0 and R program were used for the evaluation of data generated in this study. The multivariate statistical analysis (PCA and CA) was conducted by Dr Piotr Gromski of the department of Chemistry, University of Glasgow.

The PCA and CA were used to distinguish PTE sources, relationship between samples and analytes from the data generated and this allowed part of the aims and objectives of the study to be achieved. The correlation coefficient analysis was useful in corroborating the inference deduced from the multivariate statistical analysis (chapter 3) and was also employed to BCR sequential and oral bioaccessiblity extraction data to evaluate the relationship between PTE and soil characteristics (pH and loss on ignition). It was was used to study relationship between PTE extracted at various operationally defined BCR extraction phases to respective pseudototal concentrations in order to predict environmental significance of PTE in soil samples to the environment.

The pollution assessment tools used in this study were EF and Igeo. These tools were employed to assess the anthropogenic influence of PTE in Lagos urban soils. The extent or degree of contamination was quantified using these tools and this allowed for increased understanding of the general pollution status of PTE in soil samples from different land uses. Information obtained would be useful to local authorities and assist with urban planning decisions and would also be relevant for future urban soil studies in developing countries.

3 Assessment of the current potentially toxic elements levels in urban soils of Lagos, Nigeria

3.1 Introduction

Over the last decades, increasing urban soil pollution has become a major issue in both developed and developing countries[15]. The consequence of increasing migration of people to urbanized areas results in high population density and anthropogenic activities. This has a resultant effect on the quality of soil[215, 216]. Soils in urban and suburban areas are frequently contaminated owing to various human activities which include coal combustion, vehicle emissions, municipal waste, and chemical industries amongst others[3, 112, 217]. Numerous studies have been undertaken to investigate PTE sources, the extent of resulting pollution and the health risks PTE pose to human beings in urban environments[7-9, 15, 21, 84, 91, 93, 184, 218-222]. Potentially toxic elements are of interest in urban environments because they are ubiquitous, toxic and persistent[186, 223]. The prolonged presence of PTE in urban soils and their close proximity to human populations can greatly amplify the exposure of the urban populations to metal contamination via inhalation, ingestion and dermal contact[18, 19, 21, 102, 162, 224]. Thus, trace metal contamination of the urban environment can have long term and far reaching environmental and health implications[81, 103, 184, 223]. Owing to the growing dominance of urban environments and potentially profound health implications of trace metal contamination there is a need to continually investigate the sources and behaviours of PTE. Although much has been done in developed countries in studying concentration, mobility and availability of metals in urban soils and dust, not much attention has been given to developing countries where there is a rapid increase in population growth, urbanization and industrialization[2]. Of particular concern is Lagos, Nigeria which has experienced an unprecedented sporadic increase in urban migration which may be due to the fact that it serves as the commercial capital of Nigeria[171].

The potential health implication of PTE is worrisome in a city like Lagos which is home to over 17 million people[171] and with high prevalence of vehicular traffic congestion because of few or non-availability of alternative means of transport or routes.

This leaves pedestrians and motorist on the road for hours and consequently being potentially exposed to harmful emissions from dust and poorly maintained vehicles. Evidence of PTE contamination have been reported for Lagos roadside soils[225], classroom dust[171], soils collected around vicinities of an auto-mechanic repair workshop [226].

Aside from industrial emissions, which are a major source of pollution in urban areas, inappropriately sited open dumps are common in many cities of developing countries[227]. Uncontrolled distribution, dumping and recycling of contaminated goods such as domestic and electronic wastes are common practices in developing countries such as Nigeria[228, 229]. Inadequate and improper disposal systems for toxic substances coupled with noncompliance or enforcement of environmental laws has worsened this problem over the years. Ultimately, these activities potentially endanger public health and are of serious environmental concern due to toxicological effect of pollutants such as PTE[177, 230]. Some attempts have been made to investigate PTE concentrations in top soils of industrial estates[231, 232] and dumpsites[177] but no data has been reported for PTE concentrations in soils of Lagos railway terminals. The increased concentrations of PTE in soils around areas of intense industrial activities have been reported in various studies[233-238] where high levels of PTE are derived from indiscriminate waste disposal, discharge of poorly treated effluents to the land and emissions of particulates to the atmosphere[232]. Fakayode *et al.*[232] reported PTE concentrations in top soils and their bioaccumulation in guinea grass around the Ikeja industrial estate of Lagos. Levels of PTE were found to be higher in soil and plants analysed than soils collected from remote (control sites), although concentration of PTEs were much less compared to levels reported around industrial areas of many developed countries.

Numerous attempts have been made to study PTE concentrations in soils collected from dumpsites across Nigeria. In Lagos metropolis, soils collected from electronic waste dismantling sites and dumpsites were investigated for PTE concentrations by Ofudge *et al.*[177]. Dust and soil samples were collected from e-waste dismantling sites and dumpsites respectively in December 2012 and March 2013.

Control samples were taken 1 km away from the sampling points to compare the level of PTE input generated by the e-waste disposal. High levels of PTE were recorded with significant influence from e-waste disposal and processing on the sites investigated. There were consistent higher concentrations of PTE compared to their respective control sites for both dismantling and dump sites. For instance, the range of Pb concentration measured in dumpsites soils ranged from 146 to 328 mg/kg against the average Pb concentration of 75 mg/kg measured in control samples. The authors also observed high level of correlation between the PTE pollution loads of dismantling and dump sites indicating a possible common source of pollution.

In a bid to investigate possible leaching of PTE from surface soils to groundwater, Laniyan *et al.*[239] studied PTE contamination in ground water collected around Olushosun municipal dumpsite in Lagos. Twenty ground water and leachate samples collected around the dumpsite were tested for possible PTE contamination revealing high levels of PTE, mean concentrations 1170, 485, 3370 and 16700 mg/kg for Cr, Pb, Zn and Fe respectively. In comparison to WHO permissible limits, these were extremely contaminated with all PTE analysed. Pollution assessment also showed extreme contamination for Pb and Fe in ground water samples analysed and that the degree of contamination reduced farther away from the dumpsite. Water in the study area was assessed as contaminated and unhealthy for human consumption.

Other evidences of pollution arising from PTE in dumpsites across Nigeria includes, high levels of PTE measured in plants found on major dumpsites in Umuahia, Abia state (South eastern Nigeria)[230]; high Ni contamination of soils (309 mg/kg) around waste dumpsites in Uyo, Akwa Ibom state (South southern Nigeria)[240]; higher concentration of Pb (92 mg/kg) in dumpsite soil of Oke-ogi, Iree (South western Nigeria) against the Pb concentration measured in control sample (11 mg/kg)[227].

For several decades anthropogenic contributions of PTE from transportation sources have been well documented by researchers. The majority of this focused on PTE pollution associated with automobiles or along roads. In contrast, relatively little is known about rail transport pollution perhaps because it was in the past it was thought of as being relatively insignificant[241].

However, pollution surveys in different cities across the world such as Naples, Olsztyn, Rome, and Sydney, showed that soil, air and plants around railway lines or their vicinities had more PTE contents than control areas[79, 242-245]. Liu *et al.*[246] reported high EF values for Cd (7.7) and Zn (3.7) in soils collected in the vicinity of

Chengdu-Kunming railway, Sichuan, China. No data is available regarding PTE pollution status of soils around railway station terminals and along rail tracks in Lagos, Nigeria. This would be of interest owing to the long history of rail transportation in Lagos, which dates back to 1912[247]. Therefore, a study of the general PTE pollution around Lagos train terminals and rail tracks may help to ascertain the level of potential health risk this poses to users and people who live close to railways.

The few literature available have shown that PTE contamination of Lagos soils is apparent and requires comprehensive investigation. However, general assessment of the PTE status of urban soils across Lagos has not been conducted. In developing countries such as Nigeria, the anthropogenic contribution of PTE to soils and its associated health impact may have been the likely causes of increasing respiratory diseases, premature mortality and morbidity[248, 249]. Health impacts are more pronounced due to lack of environmental law enforcement, inadequate pollution management, continued rural-urban migration which typically increases the growth of informal urban settlements, inefficient urban planning decisions, non-existent regulation on emission standards, and poorly maintained vehicles[106, 250].

Previous studies have focused on PTE concentration measurements but not much effort has been devoted to determining sources and distribution in various land uses. Moreover, there is still little or no understanding of the relationship between urban socio-economic areas and PTE distribution in urban soils. Part of the aims of this work is to conduct a comprehensive investigation of studying current PTE concentrations in urban soils of Lagos, as an example of a rapidly urbanising megacity in a developing country. This chapter is in three parts and the first section focused on soils that were purposely collected away from known contamination point sources and their distribution across different socio-economic areas was assessed in order to serve as an indicator of ambient urban levels of contamination.

Comparisons were made between PTE concentration measurements of this current study against similar studies that have taken similar approach, for example the European Union Urbsoil project[35,67]. Therefore, places where people frequently spend much time such as school playgrounds (SH), Ornamental gardens (OG), roadsides (RD) and open spaces (PO) were sampled. Multivariate statistical analysis techniques comprising principal component analysis, cluster analysis and correlation coefficient were employed in the study of PTE association and likely emanating sources.

The second part discusses the concentrations of PTE in soils located close to known point sources of PTE contamination. This separate study was conducted in order to determine what the highest level of PTE were in the urban soils at these sites and to determine the ‘’worst case scenario’’ of possible PTE toxicity risks to humans since an appreciable fraction of the Lagos population (most especially children who represent the most vulnerable group susceptible to PTE toxicity risk) live close to these point sources. This is in contrast to the well-studied situation in most developed countries because people in rapidly urbanising cities in the developing countries often live in residential structures co-located with dumpsites and industrial estates. It was therefore decided to investigate industrial estates, dumpsites and major railway terminals which would provide new information about the potential health risk at these locations.

One of the key objectives of this chapter was to test the hypothesis that land use may influence PTE distribution in urban soils of a rapidly urbanising megacity such as Lagos. Therefore, PTE variability in different land use types (School playgrounds, ornamental garden, roadsides, open spaces, industrial estates, dumpsites and railway stations) were investigated since PTE in soils collected at different locations may exert different impact on public health. The third part of this chapter discusses this and the general overview of PTE in urban soils of the study area.

Aim and objectives

To obtain information about current PTE status of urban soils of Lagos, Nigeria as an example of a rapidly urbanising megacity in a developing country. Specific objectives are:

- To determine pseudototal concentrations of PTE (Cr, Cu, Fe, Mn, Ni, Pb and Zn) in soils collected away from known point sources as an indicator of ambient urban levels of contamination and to also assess if socio economic area influences PTE levels in urban soils
- To determine the pseudototal levels of PTE in soils collected close to known point sources which serve as an indication of the ‘’worst case scenario’’ of a possible PTE toxicity risks to human and ecological receptors.
- To determine if different land use types influences PTE distribution
- To serve as a baseline for future urban soil studies in rapidly urbanising megacities of developing countries.

3.2 Experimental

Chapter 2 explained the general experimental procedures used. This section covers the aspects specific to this chapter.

3.2.1 Characterisation of soil

3.2.1.1 Soil pH and % loss on ignition

The soil pH, and % loss on ignition of soil samples were determined as described in sections 2.5 and 2.6 respectively.

3.3 Pseudototal digestion

The pseudototal PTE contents were determined by microwave assisted digestion of the samples using *aqua regia* as described in section 2.3.1. An in-house reference material, Glasgow URBSOIL reference material (URM)[251] was included in soil digestion batches, in order to assess the efficiency of the digestion. The digests were analysed using ICP-MS as described in section 2.4.

3.4 Detection limits

The detection limits of the instrument (DL) and the procedure (DL_{pro}) for Cr, Cu, Fe, Mn, Ni, Pb and Zn were calculated as described in section 2.6.1 using equations 2.3 and 2.6 respectively. Values are shown in table 3.1.

Table 3.1 Instrument detection limits (µg/L) and procedural detection limits (mg/kg, d.w) of PTE measured in samples (Pseudototal concentration).

PTE	DL (µg/L)	DL_{pro}(mg/kg)
Cr	0.07846	0.00784
Cu	0.0525	0.0525
Fe	3.309	0.330
Mn	0.02894	0.00289
Ni	0.0217	0.00217
Pb	0.02279	0.00227
Zn	1.125	0.112

3.5 Results and discussion of soils collected away from known point sources

3.5.1 pH and loss on ignition

The summary statistics for % LOI and pH measured from Lagos urban soils analysed are presented in Table 3.2 and appendix B. Soil pH measured in the soil samples ranged between 6.8 and 11. The ornamental garden soils were slightly alkaline with a mean pH value of 7.5. Soils collected from open spaces, roadside and school playgrounds all had a mean pH value of 8. The results indicate that the pH value for all soils analysed were near neutral or slightly alkaline with minimal variation between successive measurements. This is expected since the pH measurements of the soil samples are typical of urban soils which generally ranges between 7 and 8. The soil samples studied are probably calcareous (partly composed of $CaCO_3$) in nature and may explain the slight alkalinity observed in some of the samples. Loss on ignition measured in the soils were generally low (ranging from 0.02 to 2.7 %).

Most of the soil samples are sandy soils and they are known to contain low organic matter content

Table 3.2 statistics summary results of % LOI and pH

		SH (n = 25)	RD (n = 25)	PO (n = 23)	OG (n = 18)
% LOI	**Mean**	0.3	0.2	0.4	0.9
	Minimum	0.04	0.1	0.02	0.14
	Median	0.1	0.2	0.2	0.4
	Max	3	1	1	3
	SD	0.5	0.1	0.4	0.9
		SH (n = 25)	**RD (n = 25)**	**PO (n = 23)**	**OG (n = 18)**
pH	**Mean**	8	8	8	7.5
	Minimum	7	8	7	6.95
	Median	8	8	8	8
	Max	9	10	11	8
	SD	0.3	0.4	0.8	0.4

SH= school playgrounds, RD = roadsides, PO = open spaces, OG = ornamental gardens

3.5.2 Pseudototal content

3.5.2.1 Quality control[251]

The quality of the analysis was assessed using GLA-URM, which is an urban soil sample previously collected from Glasgow city during the EU URBSOIL project (contract EVK-CT-2001-00053). This soil was used as a secondary reference material in that project, thus the PTE concentration (n=34) is known. This was digested alongside soils in the current work to control batch-to-batch variation in sample digestion. The percentage relative standard deviation (% RSD) for pseudo-total PTE analysis were generally less than 10 % (n=27) and average PTE recoveries (%) were generally good. Table 3.3 shows found values in close agreement with the target values (± 10 % except for Cr and Ni which had mean recoveries of 130 and 117 % respectively).

Table 3.3 Recovery of Glasgow urban reference material[251]

URM	**mg/kg**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
n = 27	**Found values**	56	106	30200	449	57	383	190
n =34	**Target values**	43	111	30600	445	49	389	177
	STDEV	2	4	1460	21	3	15	11
	% RSD	4	4	5	5	5	4	6
	% recovery	130	96	99	101	117	99	107

3.5.2.2 School playgrounds

The mean concentrations and precision of results for pseudototal metal content in school playground soil samples are shown in appendix C. Table 3.4 shows the summary statistics of PTE concentrations measured in school playgrounds soils.

The concentrations of all PTE analysed were below the Dutch intervention and CLEA values. Chromium concentration ranged from 5 to 49 mg/kg with an average concentration of 20 mg/kg. The average Cr concentration of 20 mg/kg was four times less than the world mean urban soil concentration of 80 mg/kg (see Table 3.4). Previous studies have reported low Cr content in urban playground soils of Dhaka, Bangladesh[15], Madrid, Spain[22] and Naples, Italy[79]. Similarly, low concentrations of Cu and Ni were measured in the SH soils. About 84 and 96 % of the soil samples had Cu and Ni concentrations below 10 mg/kg respectively. Their low concentration suggests PTE (Cu and Ni) may be of mainly lithogenic origin in the SH soils. A previous study has also reported low concentrations of Cu and Ni in school playground soils of Uppsala, Sweden[252] (see Table 3.5). Massas *et al.*[108] reported higher concentrations of Cu and Ni in soils collected from children's playground in Athens, Greece and higher concentrations (than this study) of Cu and Ni were measured in playground soils of Dhaka, Bangladesh[15] (Table 3.5). Both studies blamed emissions or atmospheric depositions from heavy industries as the likely cause of elevated PTE concentrations reported.

Table 3.4 Summary statistics for Lagos school playground soils

n = 25; mg/kg	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Minimum	5	3	2230	44	2	6	22
Median	18	6	7300	117	4	12	61
Mean	20	8	7690	132	4	17	86
Max	49	27	19900	252	11	66	327
SD	12	6	3740	55	2	14	76
% RSD	23	22	19	22	17	22	23
Dutch intervention values[100]	380	190	-	-	210	530	720
Environment Agency, UK[99]	130	-	-	-	200	450	-
World mean urban soil concentrations[253]	80	39	22300	729	33	54.5	158

Table 3.5 Concentrations of potentially toxic elements in urban playground soils

Location	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Athens, Greece[108]	84	42	-	311	78	101	146
Bangkok, Thailand[80]	-	48	-	340	-	48	118
Cracow, Poland[69]	-	-	-	-	-	26	-
Dhaka, Bangladesh[15]	20	82	-	-	117	49	-
Madrid, Spain[22]	17	14	8522	249	-	22	50
Mexico city[254]	-	98	-	-	-	1189	742
Naples, Italy[79]	11	74	-	-	-	262	251
Palermo, Italy[37]	34	63	-	566	18	202	138
Uppsala, Sweden[252]	79.9	43	17000	312	82	110	174
Xuzhou, China[215]	78	38	-	543	34	43	144

Iron and Mn concentrations were evidently higher than other PTE and this is expected because they constitute a major part of soil minerals[49]; despite this, the average concentration of Fe (7690 mg/kg) and Mn (132 mg/kg) measured in SH soils were lower than the world mean urban soil concentrations of 22300 and 729 mg/kg for Fe and Mn respectively[253]. There was no indication of anthropogenic contribution of these PTE to the soils studied as their concentrations did not exceed typical soil concentrations[29]. The average concentration of Fe measured in SH soils of this study was comparable to mean concentration of Fe measured in Madrid school playground soils[22]. Other studies from Table 3.5 reported higher concentrations of Fe and Mn in urban playground soils of Bangkok, Thailand,[80], Palermo, Italy[37] and Xuzhou, China[215].

Lead concentrations in Lagos SH soils ranged between 6 and 66 mg/kg with an average concentration of 17 mg/kg. In comparison to CLEA and Dutch intervention values, the SH soils may be considered unpolluted with Pb (see Table 3.4). Relatively similar mean Pb concentrations were reported for Cracow, South Poland[69], Uppsala, Sweden[252] and Madrid, Spain [22]. Other studies reported higher Pb concentrations in playground soils of Naples, Italy [79], Athens, Greece[108], Mexico and City [254] (Table 3.5). Zinc concentrations followed a similar pattern to Pb. Although, Zn concentrations were higher than Pb and it ranged from 22 to 327 mg/kg with an average 86 mg/kg. It was observed that soils with higher Pb concentrations also had higher Zn concentrations which may suggest their possible emanation from a common source. In comparison to the Dutch intervention value for Zn (720 mg/kg), all the SH soils analysed may be considered unpolluted. The highest Zn concentration was measured in LM SH 1 (327 mg/kg) and this was found to be very much higher (and highly variable) than Zn concentration measured in other soil samples. There is no obvious point source near this location or any experimental error that might explain the high value except that the school is located about 100 metres away from a major road and a bus station. The contamination profile of Zn in urban playgrounds of Uppsala, Sweden and Madrid, Spain appeared to be similar to Lagos SH soils considering their respective average Zn concentration (Uppsala, Sweden, 84 mg/kg; Madrid, Spain, 78 mg/kg; Lagos, Nigeria, 86 mg/kg).

Higher Zn concentrations were measured in two schools in Makoko, Mak SH 3 and Mak SH 4 (185 and 298 mg/kg respectively) compared to other school playgrounds studied (with exception of LM SH 1). Higher Pb and Zn concentrations were apparent in these soils and the only likely explanation is the close proximity of an auto repair mechanic workshop cited within a 50 metre radius of the schools. Possible anthropogenic contributions of Pb and Zn from automobiles serviced at this workshop may have resulted in the higher concentrations of these PTE in the soil samples. A major road which connects the community to the expressway also passes between these schools and this may also have contributed to the elevated Pb and Zn measured in the soils.

The pseudototal concentrations of all PTE measured in Lagos SH soils were low and unlikely to cause any potential health hazard to school children. In order to further substantiate this hypothesis, enrichment factors (EF), and geo-accumulation indices (Igeo) were computed to assess the possible anthropogenic contributions of PTE to soils studied. Figure 3.1 and 3.2 shows the overall average EF and Igeo values respectively.

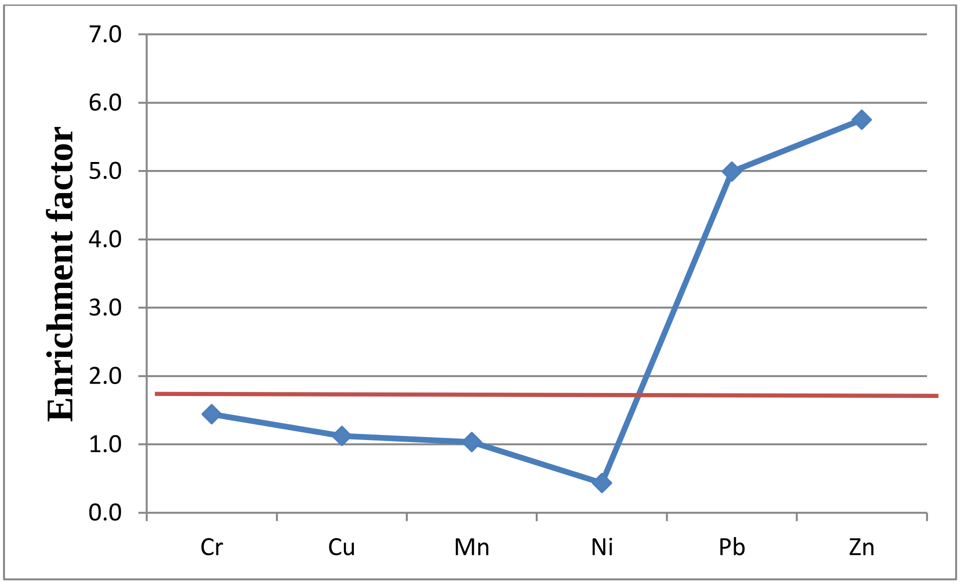


Figure 3.1 Mean enrichment factors of PTE measured in Lagos school playground soils. The bold horizontal line represents limit for minimal enrichment.

The individual EF and Igeo values for all PTEs are shown in appendix D and E respectively. The EF results show that Cr, Cu and Mn were not enriched or minimally enriched (average EF values of 1.4, 1.1 and 1 respectively) in Lagos SH soils.

Nickel had the lowest EF value in all the PTE analysed and this was also evident from the low average pseudototal concentrations of Ni measured in the soil samples and its EF value indicates no enrichment. Lead and Zn had higher mean EF values compared to other PTE studied. The PTE (Pb and Zn) showed moderate to significant enrichment (EF = 5 to 10). Lead had an average EF value of 5 and Zn had a higher EF value of 5.8. The EF results of Pb and Zn showed possible anthropogenic contributions to the soil samples. However, LM SH 1 which had the highest and Pb and Zn concentrations as expected recorded the highest EF value for Pb and Zn (10 and 18.8 respectively); which implies Pb and Zn were significantly enriched in the soil sample. The general EF value trend for all PTE is in the descending order of Zn > Pb > Cr > Cu > Mn > Ni. The geo-accumulation index of PTE in soil samples showed a very similar pattern to the EF values (See Fig 3.2); although lower values were observed in the case of Igeo values. Chromium, Cu, Fe, Mn and Ni Igeo values were less than 1, which implies no contamination for all soils samples studied.

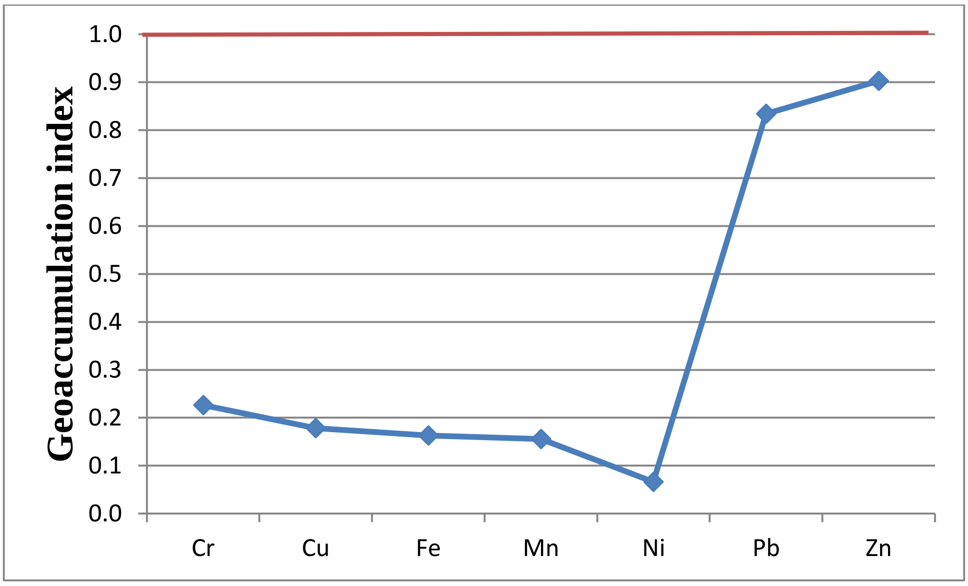


Figure 3.2 Mean geo-accumulation index of PTE measured in Lagos school playground soils. The bold horizontal line represents Igeo limit of contamination.

However, as seen in EF results, Pb and Zn showed higher Igeo values in comparison to other PTE studied. Despite this, most of the soils samples still did not exceed the Igeo of 1 which implies no contamination with the exception of LM SH 1, Mak SH 3 and 4 which showed moderate contamination. The general contamination (Igeo) trend for all PTE was in the descending order of Zn > Pb > Cr > Cu > Fe > Mn > Ni (similar to EF).

Correlation coefficient was also computed to study the relationship between PTE. Chromium was not significantly correlated with any other PTE but showed a relatively low positive correlation (above 0.4) with Fe, Mn and Ni (0.49, 0.46 and 0.47) and but showed very weak correlations (below 0.2) with Cu, Pb and Zn (0.15, 0.19 and 0.08); suggesting it has a stronger relationship with the first group. Manganese displayed a similar behaviour to Cr as it showed a better relationship with Ni, Fe and Cr compared to Cu, Pb and Zn (see Table 3.6).

Table 3.6 Correlation coefficient analysis of PTE in Lagos school playground soils @ 95 % confidence level; n = 25.

	Cr	Cu	Fe	Mn	Ni	Pb	Zn	% LOI	pH
Cr	1								
Cu	0.15	1							
Fe	0.49	**0.81**	1						
Mn	0.46	0.44	0.66	1					
Ni	0.47	**0.84**	**0.85**	0.62	1				
Pb	0.19	**0.92**	**0.80**	0.39	**0.76**	1			
Zn	0.08	**0.81**	0.61	0.29	0.69	**0.79**	1		
% LOI	0.42	-0.06	0.21	0.27	0.10	0.02	-0.09	1	
pH	0.04	0.21	0.25	0.001	0.24	0.19	0.29	0.07	1

This indicates a possible contribution (Cr and Mn) from common sources which may probably be lithogenic. Copper showed positive correlations with Fe (0.81), Ni (0.84), Pb (0.92) and Zn (0.81). Iron, Ni and Pb showed similar behaviour to Cu as the PTE correlated significantly with each other, these associations suggests contributions from both natural and anthropogenic sources. Zinc displayed a rather different trend by correlating significantly with only Cu and Pb (0.81 and 0.79). This indicates that Zn may have emanated predominantly from anthropogenic sources. The % LOI was weakly correlated with Cr, Fe, Mn and Ni (0.42, 0.21, 0.27 and 0.10 respectively) despite their low concentration measurements in SH soils. This relationship reflects a minimal influence of % LOI on lithogenic elements. From Table 3.6, it is evident that the relationship between Cu, Zn and % LOI were negative and insignificant (-0.06, -0.09). Low and insignificant correlation was observed between % LOI and Pb (0.02). These latter relationships suggest that % LOI did not have any influence on the concentrations of ‘‘typical urban metals’’[76] in SH soils. Soil pH appeared to have little influence on PTE concentrations in SH soils as the results of correlation coefficients showed weak relationships for Cu, Fe, Ni, Pb and Zn but insignificant relationship were observed for Cr and Mn.

3.5.2.3 Roadsides

The mean concentrations and precision (% RSD) of pseudototal PTE content in RD soil samples are shown in appendix C. Table 3.7 and 3.8 shows the summary statistics of the results in this current study and PTE concentration in urban roadside soils of previous studies respectively. The average concentration of Cr, Cu, Ni, Pb and Zn were generally within typical soil values[49] and well below the CLEA and Dutch intervention values. The world mean urban soil concentration values for Cu, Pb and Zn were exceeded for a few RD soil samples. World mean urban soil concentration for Cu (39 mg/kg) was exceeded in LM RD 1 (124 mg/kg), LM RD 4 (72 mg/kg), Ikj RD 5 (50 mg/kg) and Mak RD 1, 2 and 4 (50, 50 and 65 mg/kg respectively) soil samples. The average concentration of Cu in the Lagos RD soils studied was comparable to that reported for Cu in roadside soils of Beijing, China[255], and Ibadan, Nigeria (Table 3.8)[66]. Some cities in developed countries with a longer history of industrialization reported higher Cu concentration values in highway soils i.e. Istanbul, Turkey[64] and urban area soils in Kavala, Greece[65].

Table 3.7 Summary statistics for Lagos roadside soils

n = 25; mg/kg	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Minimum	5	3	3560	39	4	5	19
Median	24	18	11000	146	7	31	120
Mean	23	28	9840	141	7	32	121
Max	38	124	14200	213	19	66	403
SD	9	29	3090	42	3	18	76
% RSD	24	23	22	20	16	27	19
Dutch intervention values	380	190	-	-	210	530	720
Environment Agency, UK	130	-	-	-	200	450	-
World mean urban soil concentrations	80	39	22300	729	33	54.5	158

Table 3.8 Concentrations of potentially toxic elements in urban roadside soils

	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Beijing, China[255]	62	30	-	-	27	35	92
Galway, Ireland[70]	-	17	1700	650	22	41	82
Ibadan, Nigeria[66]	52	31	2613	196	39	307	-
Istanbul, Turkey	-	69	-	-	191	255	-
Jeddah, Saudi[256]	53	-	-	-	47	48	222
Kampala, Uganda[257]	-	-	-	-	-	45	149
Kavala, Greece[65]	232	172	-	-	68	389	355
Paris, France[258]	50	14	154	277	14	93	57
Shanghai, China[24]	26	23	-	-	31	71	103
York, England[259]	-	87	-	-	-	233	175

Lead concentration is of interest in RD soils of Lagos because the city experiences high traffic congestion on a daily basis. Lead has been identified by several authors as a traffic related PTE[255, 260, 261] and this has been corroborated in a number of studies. For example, the concentration of Pb in soils and plants collected from roadsides in Peshawar, Pakistan was found to be significantly higher than control samples which were collected away from roadsides[260]. A similar study by Olajire *et al.*[66] demonstrated a decrease in Pb concentration in roadside soils of Ibadan, Nigeria with increasing distance from the road. Another study[262] in Ljubljana, Slovenia reported similar observations for Pb in roadside soils along the Obrezje highway.

Average Pb concentrations in Lagos RD soils was 32 mg/kg and this is considered low in comparison to CLEA and Dutch intervention values for Pb (see Table 3.7). Olukanni *et al.*[225] reported mean concentration of Pb in urban roadside soils of Lagos to be in the range of 5.57 – 69.2 mg/kg, which was comparable to the range of Pb concentration measured in this study (5 – 66 mg/kg). The average concentration of Pb measured in RD soils of this study also falls in the typical range of 30 – 50 mg/kg for Pb concentration in urban soils of African cities proposed by Nriagu *et al.*[263]. In support of this premise, Pb concentration in roadside soils of Kampala city, Uganda was in the range of 30 – 65 mg/kg[257]. However, Pb concentration measured in roadside soils of Gaborone, Botswana contained a higher range of Pb concentration (53 - 222 mg/kg)[91].

The world mean urban soil concentration for Pb (54.5 mg/kg) was exceeded in Ifk RD1 and Mak RD 5 soils (64 and 66 mg/kg respectively). In comparison to Pb concentration measured in RD soils of this study, higher Pb concentrations were reported for other developing countries such as Dubai, UAE (range of 146 – 308 mg/kg)[261] and Dhaka city, Bangladesh (mean of 74 mg/kg)[264]. Previous studies of Pb concentration in roadside soils of highly industrialized cities such as Houdan and Versailles, France[258], Ljubljana, Slovenia[262], Kavala, Greece[65], Yorkshire, Northern England[259] also had Pb concentration in their respective roadside soils which exceeded the average concentration measured for this study.

Zinc concentration in the RD soils ranged from 19 to 403 mg/kg with an average concentration of 121 mg/kg. This is higher than the typical background value for Zn (10 – 100 mg/kg) in soils[29]. The average Zn concentration of 121 mg/kg of this study was less than world mean urban soil concentration for Zn (158 mg/kg)[253] and Dutch intervention value for Zn (720 mg/kg)[100]. There are indications of a possible anthropogenic contribution since the typical background concentration was slightly exceeded. This may be more evident considering the mean Zn concentrations in Makoko (193 mg/kg) and Lagos mainland (165 mg/kg) soils which were higher than the values of both the world mean urban soil concentration and typical background concentration values for Zn. Elevated Zn concentration in urban soils have been related to traffic sources, industrial emissions and abrasion of vehicle tyre in literatures[5, 65, 265]. In comparison with the mean Zn concentration for this study, lower Zn concentration were reported for roadside soils of Bejing, China, Galway, Ireland[70], Ibadan, Nigeria[66], and Yuaan, southwest China (84.7 mg/kg)[266]. However, previous works from Guney *et al.*[64] and Christoforidis *et al.*[65] reported higher Zn concentrations of 355 and 255 mg/kg for roadside soils of Istanbul Turkey and Kavala, Greece, respectively.

Generally, pseudototal concentration results for PTE measured in Lagos roadside soils indicated no contamination considering SGVs from CLEA and Dutch intervention values. Nevertheless, EF and Igeo were calculated for all PTE to assess the possible anthropogenic contributions of PTEs to roadside soils studied. Figure 3.3 and 3.4 shows the overall average EF and Igeo values respectively while appendix D and E shows the individual EF and Igeo values.

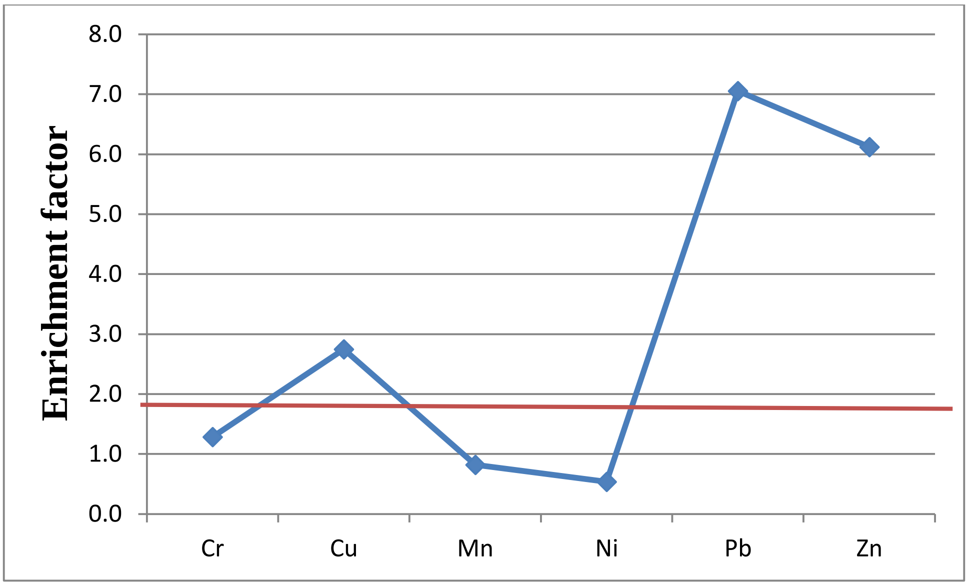


Figure 3.3 Mean enrichment factors of PTE measured in Lagos roadside soils. The bold horizontal line represents limit for minimal enrichment.

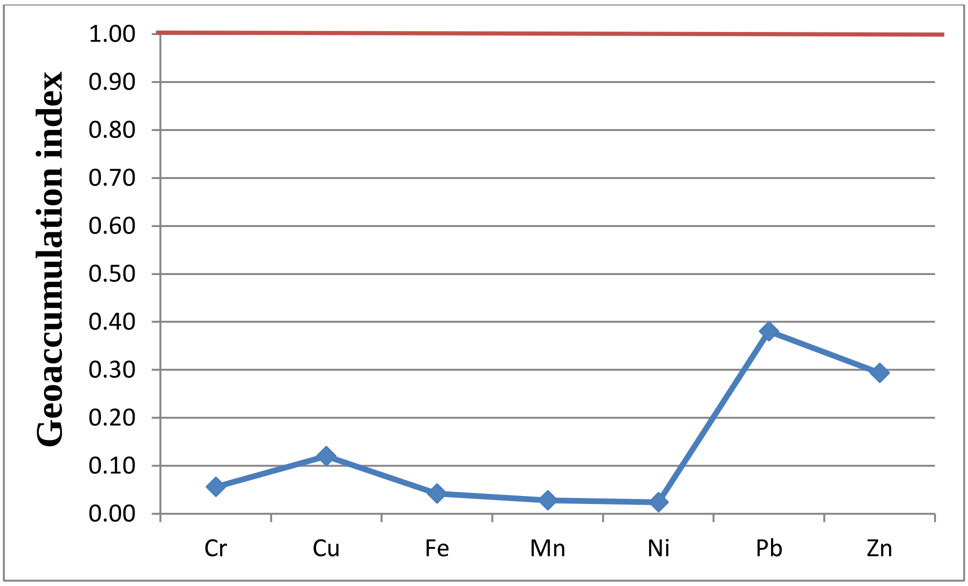


Figure 3.4 Mean geo-accumulation index of PTE measured in Lagos roadside soils**. **The bold horizontal line represents Igeo limit of contamination

The average EF values for Mn (0.8) and Ni (0.5) were both less than 1 which implies no enrichment. Chromium was found to be moderately enriched in RD soil samples with an average EF value of 1.3. Copper, Pb and Zn had average EF values greater than 2 indicating from moderate to significant enrichment. Copper had an average EF value of 2.7 signifying significant enrichment.

Lead EF values ranged from 2.1 to 16, which suggests moderate to significant enrichment. The average EF value for Pb was 7.1 and Zn also had average value of 6.1 (ranged between 1.3 – 18.2). It is evident that Pb and Zn were the mostly enriched PTE in Lagos roadside soils.

The general EF value trend for all PTE was in the descending order of Pb > Zn > Cu > Cr > Mn > Ni. Unlike EF value result for SH soils (where Zn was the most enriched PTE), Pb was the most enriched PTE in Lagos RD soils, followed by Zn and Cu. Possible anthropogenic contribution of the ‘‘typical urban metals’’ in RD soils is not unlikely since the three PTE all exceeded EF value of 2. The Igeo displayed the same pollution pattern as EF in the descending order of Pb > Zn > Cu > Cr > Fe > Mn > Ni. Manganese and Ni consistently displayed no or minimal enrichment in RD and school SH soils studied.

Little information was obtained from the results of correlation coefficient analysis (Table 3.9). Only a few groupings showed significant relationships. Chromium showed significant positive correlation with only Fe (0.51), suggesting a lithogenic relationship. Copper showed significant relationship with Fe, Ni and Zn. Iron correlated positively and significantly with Mn, Cu, Pb and Zn. Zinc showed similar behaviour to Cu by correlating significantly with Cu, Fe and Mn. Nickel only showed positive relationship to Cu (0.73).

Lead displayed positive relationship with Fe and Mn. Low correlation coefficient was observed between Cu, Mn, Ni, Zn and % LOI. Chromium, Fe and Pb were anti-correlated with % LOI (-0.26, -0.12, -0.05 respectively) and similarly, very weak relationship exists between Cu, Mn, Ni, Zn and % LOI. This suggests that organic matter content had minimal or no influence on the PTE concentrations in RD soils. Soil pH was negatively correlated with PTE concentrations and implies no significance.

Table 3.9 Correlation coefficient analysis of PTE in Lagos roadside soils @ 95 % confidence level; n = 25.

	Cr	*Cu*	*Fe*	*Mn*	*Ni*	*Pb*	*Zn*	*% LOI*	*pH*
Cr	1								
Cu	0.10	1							
Fe	**0.51**	**0.52**	1						
Mn	0.48	0.41	**0.81**	1					
Ni	0.35	**0.73**	0.45	0.26	1				
Pb	0.33	0.28	**0.67**	**0.57**	0.16	1			
Zn	0.02	**0.51**	**0.53**	**0.63**	0.25	0.35	1		
% LOI	-0.26	0.05	-0.12	0.08	0.24	-0.05	0.23	1	
pH	-0.20	-0.28	-0.13	-0.15	-0.27	-0.28	-0.41	-0.04	1

3.5.2.4 Open spaces

The descriptive statistics results for PTE concentrations in Lagos PO soils as well as the soil guideline values (CLEA and Dutch intervention values) are shown in Table 3.10 and the individual concentrations and % RSDs are shown in appendix C. The average PTE concentrations were within typical soil values[29]. Neither CLEA nor the Dutch intervention values were exceeded for Cr, Cu, Ni, Pb and Zn in all soil samples, with exception of Cu and Zn levels measured in Ifk PO 2. However, average Cu, Pb and Zn concentrations in PO soils were relatively comparable to the world mean urban soil concentrations (Table 3.10). This may be partly due to the fact that, Ifk PO 2 had very high concentrations compared to the PTE concentrations in other soil samples, particularly for Cu, Pb and Zn. This noticeable high variability is obvious in the value of % RSDs for Cu, Pb and Zn shown in Table 3.10 (267, 100 and 102 % respectively). Ifk PO 2 sample was collected from Agege market (Ifako Ijaiye area). A railway passes through the market and it is possible that abrasion of the track and rolling stock could be a route by which PTE were introduced to soils in the vicinity. Since open spaces soils are not usually regarded as a specific land use, results of this current study were compared with the average PTE concentrations measured in urban soils across the world (see Table 1.1)

Table 3.10 Summary statistics for Lagos open spaces soils

n = 23; mg/kg	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Minimum	5	3	2210	30	2	1	34
Median	22	18	10000	168	6	24	116
Mean	23	37	10600	170	7	40	147
Max	53	485	27500	430	19	139	757
SD	11	98	5360	91	4	41	151
% RSD	49	267	50	54	58	100	102
Dutch intervention values	380	190	-	-	210	530	720
Environment Agency, UK	130	-	-	-	200	450	-
World mean urban soil concentrations	80	39	22300	729	33	54.5	158

Mean concentrations of Cr (23 mg/kg) and Ni (7 mg/kg) of PO soils were comparable to those from other cities in Bangkok, Thailand [80], and Hong Kong, China [78]. Average Cu and Pb concentration in PO soils was found comparable to those from previous studies in developing countries such as Bangkok, Thailand [80], Beijing, China[72], Changchun, China [111] and Damascus, Syria[89] but lower than those from cities of developed countries such as Naples, Italy[79], Seoul, Korea [267], Madrid, Spain[76] with exception to Mexico City[268].

The average concentration of Zn in the PO soils (147 mg/kg) was higher than those from Changchun, China[111], Damascus, Syria[89], Bangkok, Thailand[80], Hong Kong and Beijing, China[72, 78] and as expected (as seen in the case of Cu and Pb), it was less than those from more highly industrialized cities such as Naples, Italy[79], Madrid, Spain[76], Seoul, Korea[267], Shanghai, China[24] and Mexico city[268] (Table 1-1). From the discussion above it is clearly obvious that cities with high concentrations of Cu concentration were also higher in Pb and Zn (Cu, Pb and Zn suggested as ‘‘typical urban metals’’[71, 76]). Figure 3.5 and 3.6 shows the average EF and Igeo values for all PTEs analysed. Results showed the average EF value of Cr, Cu, Mn, Ni, Pb and Zn were 1.1, 1.7, 0.9, 0.5, 7.6 and 5.9 respectively.

The PTE can be subdivided into 3 groups based on the average EF value results. The mean EF values for Mn and Ni were below 1 and can be categorized as no enrichment. Chromium and Cu both had mean values greater than 1 and ranged from 1.5 – 2, suggesting minimal enrichment. The mean EF values for Pb and Zn were greater than 5 (7.6 and 5.9 respectively), which indicates significant enrichment. This is consistent with EF value results of PTE in other land use types discussed earlier (school playgrounds, and roadsides). The average EF value of PTE in Lagos open spaces soils was in the descending order of Pb > Zn > Cu > Cr > Mn > Ni (a trend consistent with EF results for RD soils).

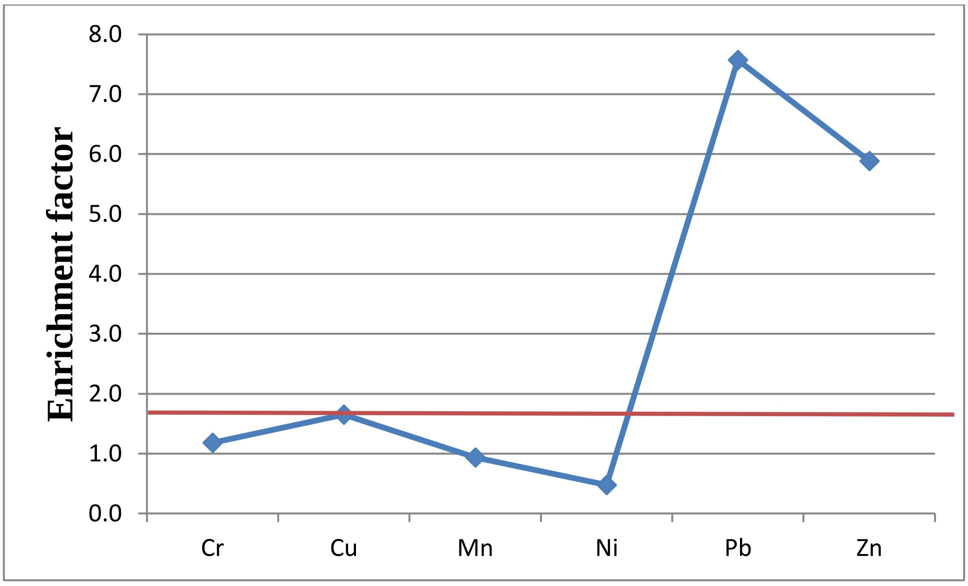


Figure 3.5 Mean enrichment factors of PTE measured in Lagos open spaces soils. The bold horizontal line represents limit for minimal enrichment.

The average Igeo values of Cr, Cu, Fe, Mn, Ni, Pb and Zn in Lagos PO soils were 0.05, 0.07, 0.04, 0.03, 0.2, 0.45 and 0.29 respectively, ranging from unpolluted to moderately polluted. The average Igeo value for PTE was in the descending order of Pb > Zn > Cu > Cr > Fe > Mn > Ni. This trend is consistent with results of average EF values of PTE.

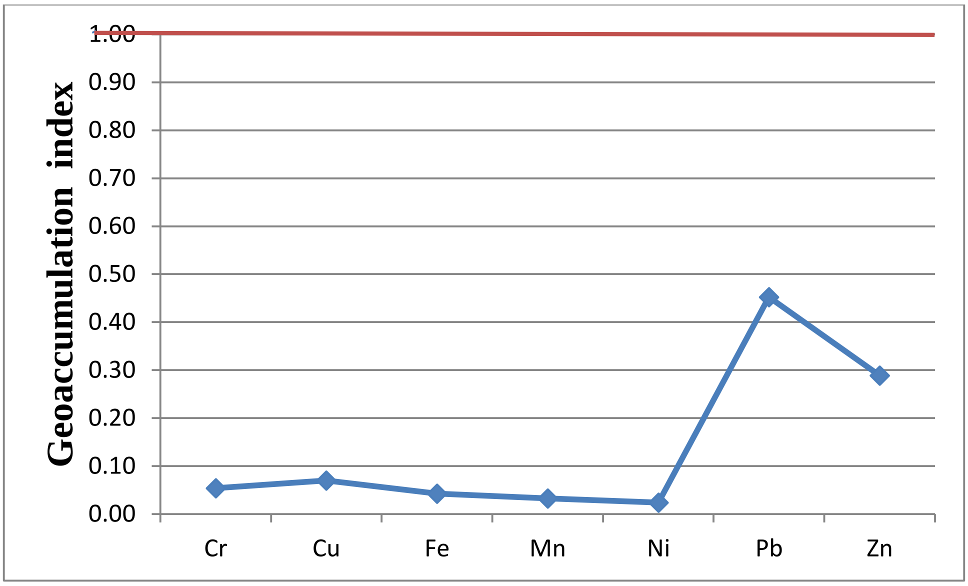


Figure 3.6 Mean geo-accumulation index of PTE measured in Lagos open spaces soils. The bold horizontal line represents Igeo limit of contamination

For all PTE in the land uses previously discussed, the average EF and Igeo values have shown a consistent trend. Lead and Zn (first group) may be categorised as mostly enriched PTE (probably from anthropogenic sources) in PO soils, followed by Cu and Cr (second group; suggesting contributions from mixed sources of both lithogenic and anthropogenic characteristics) and Fe, Mn and Ni (third group; suggesting significant contributions from lithogenic sources).

For the PO soils, 0.6 was chosen as a benchmark for significantly positive relationship between PTE. This is because the correlation results showed a sizable number of relationships between PTE greater than 0.5, unlike the correlation results of other land uses (see Table 3.11). Chromium and Ni showed a significant positive relationship with each other and also with Cu, Fe, Mn, suggesting they share common attributes. The relationships between PTE in this category suggest they originated predominantly from natural sources. Copper correlated positively with Fe, Ni and Zn. Iron and Pb showed similar behaviour to Cu, in that both PTE significantly correlated with Ni, and Zn.

Table 3.11 Correlation coefficient analysis of PTE in open spaces soils @ 95 % confidence level; n = 23.

	Cr	Cu	Fe	Mn	Ni	Pb	Zn	% LOI	pH
Cr	1								
Cu	**0.63**	1							
Fe	**0.82**	**0.82**	1						
Mn	**0.63**	0.40	0.52	1					
Ni	**0.67**	**0.68**	**0.76**	0.41	1				
Pb	0.45	0.58	**0.67**	0.25	**0.60**	1			
Zn	0.56	**0.81**	**0.83**	0.43	**0.59**	**0.68**	1		
% LOI	-0.01	0.16	0.14	-0.02	0.13	0.50	0.29	1	
pH	0.02	-0.12	0.14	-0.26	0.22	0.53	-0.05	0.19	1

As seen for other land uses discussed earlier, weak relationship exists between PTE and organic matter. Low positive correlations were observed for Cu, Fe, Ni and Zn but negative correlations for Cr and Mn. Unexpectedly, a relatively positive relationship was observed between organic matter, soil pH and Pb (0.50 and 0.53 respectively) and the probable reason for this could not be established because the range of measurements of these soil properties were reasonably similar to other land uses. Low and negative correlations were observed between pH and other PTE analysed and implies no siginificance.

3.5.2.5 Ornamental gardens

The summary statistics of PTE in Lagos OG soil samples are shown in Table 3.12 while the mean concentrations and precision results (% RSD) for pseudototal PTE content in each soil are shown in appendix C and PTE concentration in previous studies shown in Table 3.13. The high % RSD recorded for Cr, Pb and Zn (41, 42 and 42 % respectively) results from variability between sampled sites. Average levels of Cr, Cu, Fe, Mn, Ni, Pb and Zn were generally within typical soil values[29, 49]. The average PTE concentration in the soils were also well below the world mean urban soil concentrations[253].

Table 3.12 Summary statistics for Lagos ornamental garden soils

n = 18; mg/kg	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Minimum	14	10	8070	230	6	18	42
Median	25	17	11400	439	8	25	86
Mean	28	16	11900	439	9	29	97
Max	51	22	22200	557	16	57	198
SD	11	4	3550	96	2	12	41
% RSD	41	26	30	22	26	42	42
Dutch intervention values	380	190	-	-	210	530	720
Environment Agency, UK	130	-	-	-	200	450	-
World mean urban soil concentrations	80	39	22300	729	33	54.5	158

Table 3.13 Concentrations of potentially toxic elements in urban ornamental garden soils

	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Beijing, China[269]	-	71	-	-	22	66	88
Belgrade, Serbia[270]	103	45	29973	688	62	-	121
Glasgow, UK[67]	29	85	-	-	35	307	199
Hangzhou, China[11]	-	38	-	-	-	56	94
Ljubljana, Slovenia[67]	21	33	-	-	22	78	114
Pearl River, China[271]	-	26	-	134	7	134	201
Sevilla, Spain[67]	76	48	-	-	29	107	107
Shanghai, China[272]	77	45	-	-	31	55	199
Torino, Italy[67]	188	87	-	-	207	144	225
Uppsala, Sweden[67]	36	36	-	-	22	47	112

Average Cr and Cu concentrations in OG soils are not likely to cause any health effects since their presence in OG soils were well below the SGVs. Nickel concentrations in all soils analysed were below 10 mg/kg and much lower than Ni concentration in Earth's crust (58 mg/kg) and Earth's soils (40 mg/kg)[253]. A similar Ni concentration result (less than 10 mg/kg) was obtained by En-Qing *et al.* [271] for urban park soils of Pearl River Delta, China.

As observed in RD and SH soils earlier discussed, Pb and Zn seemed to consistently behave differently compared to other PTE analysed. Lead concentration ranged from 18 – 57 mg/kg with an average of 29 mg/kg. Levels of Pb measured in Lagos OG soils did not exceed the CLEA value of 450 mg/kg and Dutch intervention value of 530 mg/kg. Most of the ornamental gardens sampled were sited along major roads; therefore a small contribution from traffic sources may be apparent. The range of Pb concentration in OG soils in this study was higher than these measured in urban park soils of 3 cities in northern and southern Taiwan (11.5 – 42 mg/kg)[10] . It is lower than average Pb concentrations in more industrialized European cities such as Glasgow, UK, Ljubljana, Sevilla, Spain, Torino, Italy and Uppsala, Sweden[67] (see Table 3.13).

Zinc concentration ranged from 42 – 198 mg/kg (with an average of 97 mg/kg). Average Zn concentration of 97 mg/kg in OG soils exceeded natural background levels of Zn in soil (earth's crust; 83 mg/kg and earth's soil; 50 mg/kg). Considering the natural background levels of Zn in soils, Zn is possibly enriched in the soil samples studied and may be from traffic sources and industrial emissions[6, 65].The mean Zn concentration in OG soils of this study was similar to that in other studies Zn concentration measured in previous works such as urban parks of Beijing (87.6 mg/kg)[269],Hangzhou, China (93.64 mg/kg)[11] and Belgrade, Serbia (95 mg/kg)[270]. A study by Calace *et al*[273]. reported higher Zn concentration (range of 86 - 996 mg/kg) in urban parks of Rome, Italy higher than the average Zn concentration in OG soils of this study.

Enrichment factors and Igeo were calculated for all soil samples (Fig 3.7 and 3.8; appendix D and E respectively). The average EF value for Ni was 0.5 which signifies no enrichment and this is consistent with Ni EF results in SH, RD and PO soils.

The EF value for Ni is expected since the pseudototal concentrations measured in soil samples were less than 10 mg/kg and lower than the natural background levels. EF value for Cr and Cu were 1.2 and 1.5 respectively, which indicates minimal enrichment. Manganese and Zn had average EF values of 2.2 and 4.2 respectively; indicating moderate enrichment. The EF value for Zn ranged from 1.5-8.1; signifying minimal to significant enrichment. The mean EF value for Pb was 5.7 (significant enrichment) while the maximum EF value for Pb (10.9) was greater than 10 which shows the possibility of Pb originating mainly from anthropogenic sources[274, 275]. The order of average EF values was in the descending order Pb > Zn > Mn > Cu > Cr > Ni, which appeared similar to the descending order of the overall contamination degree of PTE in OG soils based on Igeo (Pb > Zn > Mn > Cu > Cr > Fe > Ni; see Figure 3.7 and 3.8).

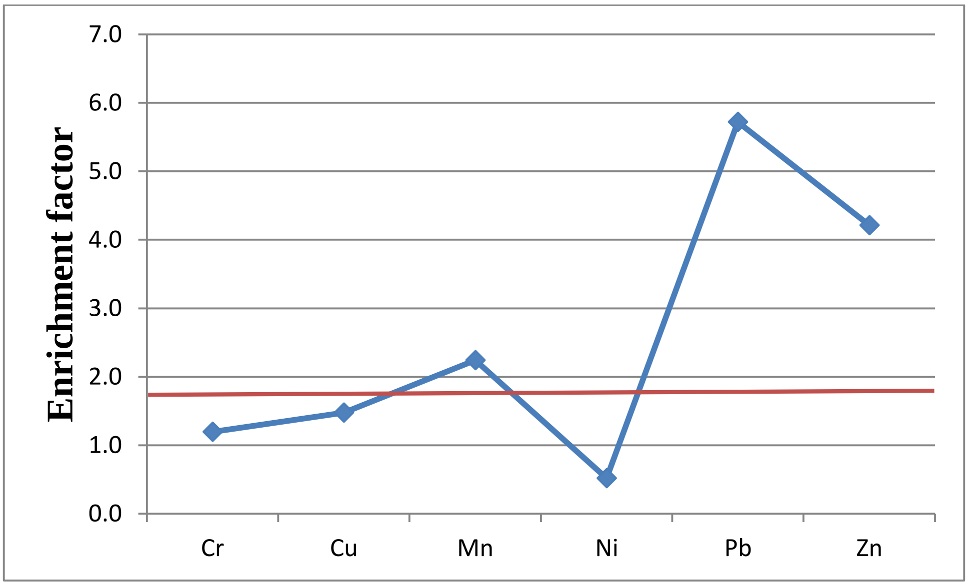


Figure 3.7 Mean enrichment factors of PTE measured in Lagos ornamental garden soils. The bold horizontal line represents limit for minimal enrichment.

From Table 3.14, correlation coefficient results showed the strong positive relationship between Cr, Fe and Ni (0.87, 0.83 and 0.93); suggesting these PTE emanated mainly from lithogenic sources. Manganese was anti-correlated with all other PTE. Reasons for this were unclear, perhaps the relatively higher Mn concentrations in the OG soil may be from fertilizers or other soil additives applied.

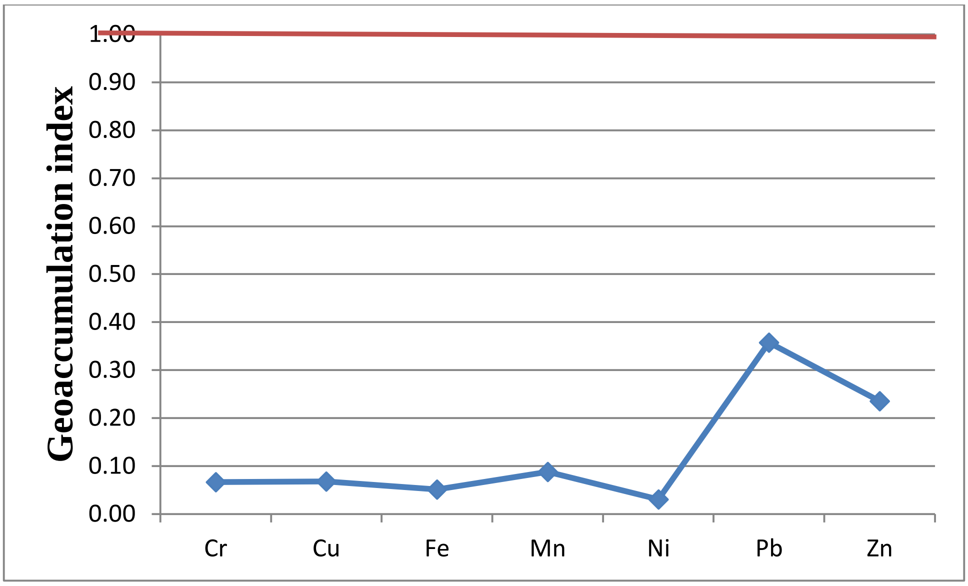


Figure 3.8 Mean geo-accumulation index of PTE measured in Lagos ornamental garden soils. The bold horizontal line represents Igeo limit of contamination

Table 3.14 Correlation coefficient analysis of PTE in Lagos ornamental garden soils @ 95 % confidence level; n = 18.

	Cr	Cu	Fe	Mn	Ni	Pb	Zn	% LOI	pH
Cr	1								
Cu	0.13	1							
Fe	**0.87**	0.06	1						
Mn	-0.29	-0.66	-0.37	1					
Ni	**0.83**	-0.13	**0.93**	-0.23	1				
Pb	0.32	0.23	0.63	-0.66	0.51	1			
Zn	0.08	0.27	0.41	-0.70	0.27	**0.89**	1		
% LOI	-0.02	-0.06	0.01	0.18	0.24	-0.09	-0.16	1	
pH	-0.18	-0.07	-0.27	0.06	-0.42	-0.12	0.15	0.10	1

Lagos ornamental gardens were built mainly in 2008[276]; therefore the possibility of urban anthropogenic contributions of Mn to the soils is unlikely. Copper was weakly correlated with other PTE, although higher positive correlations were recorded for Pb and Zn (0.4 and 0.39 respectively).

This may suggest Cu emanating from mixed sources of lithogenic and anthropogenic components. A very positive significant correlation was observed between Pb and Zn (0.89) and this suggest a strong possibility of both originating from common sources which are likely to be anthropogenic. Organic matter content and soil pH appeared to have no influence on PTE concentrations in OG soils. Very low concentration and negative correlation were observed for both soil properties against pseudototal concentrations.

3.5.2.6 Source characterization of PTE in soils collected away from known point sources.

3.5.2.6.1 Principal component analysis (variance and analyte loadings)

The relationships between PTE content in Lagos urban soils were investigated by principal component analysis (PCA). Results of varimax rotated loadings, communalities, eigen values and percentage variance of PTE in the urban soil samples are presented in Table 3.15

Table 3.15 Varimax rotated loadings, communalities, eigen values and percentage of explained variance for PTE in Lagos urban soil samples.

PTE	**Principal components**			**Communalities (h2)**
	1	2	3	
Cr	0.03	0.93	0.08	0.86
Cu	0.51	0.25	-0.68	0.78
Fe	0.6	0.71	0.17	0.88
Mn	0.15	0.35	0.83	0.83
Ni	0.48	0.73	0.06	0.77
Pb	0.8	0.25	0.01	0.71
Zn	0.89	0.1	-0.11	0.82
Eigen values	2.31	2.15	1.19	
% of variance	33.1	30.7	17	

Results showed PTE groupings in 3 components which accounts for 81% of the total data variation. The spatial illustration of the three rotated components is shown in Fig 3.9. The PC1 was dominated by Cu, Fe, Pb and Zn accounting for 33% of the total variance. Positive loading values in the first component suggest a common source of the PTE (Cu = 0.51, Fe = 0.6, Pb = 0.8, Zn = 0.89). According to several previous studies, association of these elements can be interpreted as indicative of an anthropogenic origin[74, 112, 113, 117, 277]. The primary source of Pb has been suggested as atmospheric which may have originated from vehicular emissions[24, 109, 218, 278, 279]. Copper and Zn have also been suggested to emanate from wear and tear of brake pads, anti-rust car primers, galvanized rims of automobiles[112, 117]. Other sources of Cu and Zn may also be linked to industrial emissions[105, 110]. Iron is known to be one of the major components of soil minerals [30, 49] but its inclusion in PC1 may suggest partial contributions from anthropogenic sources which may probably be industrial emissions from smelting, galvanizing or electroplating industries. The association of Fe with ‘‘typical urban metals’’ (Cu, Pb and Zn) may support the earlier assertion that the pseudo-total PTE concentrations of Cr, Ni, Fe and Mn may not be totally geogenic.

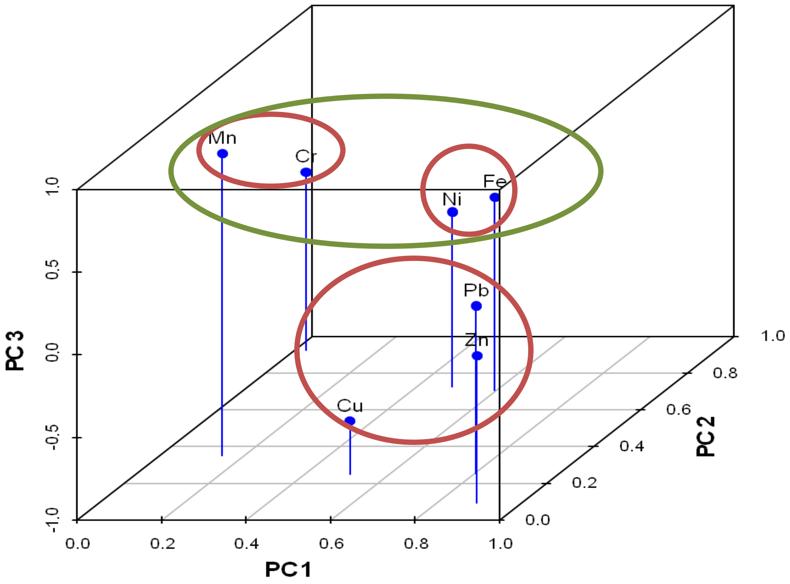


Figure 3.9 PCA results in three dimensional space: loadings of first three components (Conducted by Dr Piotr Gromski).

Iron has significant loading on both the first and second components (0.6 and 0.71 respectively), suggesting a mixed source of both natural and anthropogenic origin. The grouping of Cu, Pb and Zn indicates a strong possibility that these PTE may have emanated from anthropogenic sources. Several previous studies have reported this association[24, 37, 72, 108, 109, 118, 184, 216].

The second component explains 31% of the total variance and loads primarily on Cr, Fe and Ni (0.93, 0.71 and 0.73 respectively). The PTE grouping is in agreement with cluster analysis result which is discussed subsequently in section 3.5.2.6.2

Strong positive correlations and cluster groupings were observed between this set of PTE. Principal component 2 (Cr, Fe and Ni) may be of lithogenic origin. Chromium and Ni have been found in low concentrations in Lagos urban soils suggesting they may be from natural sources. Similar observations have been reported for other studies[37, 84, 106, 115, 187, 280].

The third PC explained 17 % of the total variation and was primarily loaded on Mn (0.83). Copper and Zinc were both negatively correlated with Mn (- 0.68 and – 0.11 respectively). Typical concentration of Mn in soil is 850 mg/kg[29] and those for Lagos urban soils were well below this. Copper and Zn as earlier noted were strongly associated with anthropogenic contributions to soils and their negative values in PC3 indicates non correlation with natural sources. The positive correlation of Mn with Cr (0.934), Fe (0.772), and Ni (0.776) may further support the assertion of natural contribution of Mn to the soils studied. Rodrigues *et al.*[90] reported a similar PCA result for Mn in their study of urban soil of two European cities. They ascribed Mn concentrations to geological inputs, although possible contribution from vehicular emissions was also cited.

3.5.2.6.2 Cluster Analysis

The dendogram is typically used to show the proximity and link between measured variables. The Lagos urban soils data of this current study was standardised by measuring Euclidean distances between PTE thereby showing similarities between variables.

Hierarchical clustering was applied to the standardised data using the Ward's method. Figure 3.10 shows three distinct clusters: (1) Cr-Fe-Ni; (2) Mn; (3) Cu-Pb-Zn. Cluster 1 and 2 are joined at a relatively higher point implying perhaps a common origin. This grouping appears to be consistent with results of PCA supporting a possible natural origin. This suggested natural origin of Cr and Ni may be further predicted by their low concentration values. Similarly, Cu, Pb and Zn were grouped together; which also confirms PCA and correlation coefficient results.

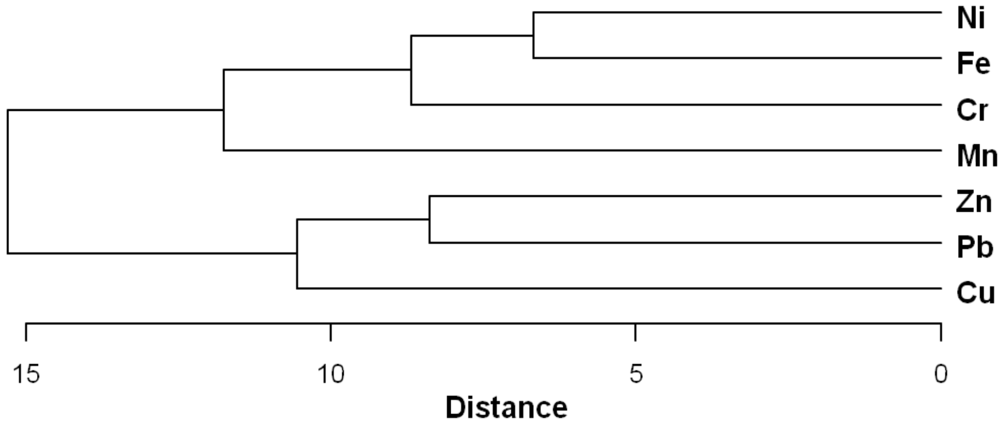


Figure 3.10 Dendogram results of hierarchical cluster analysis of PTE (Conducted by Dr Piotr Gromski).

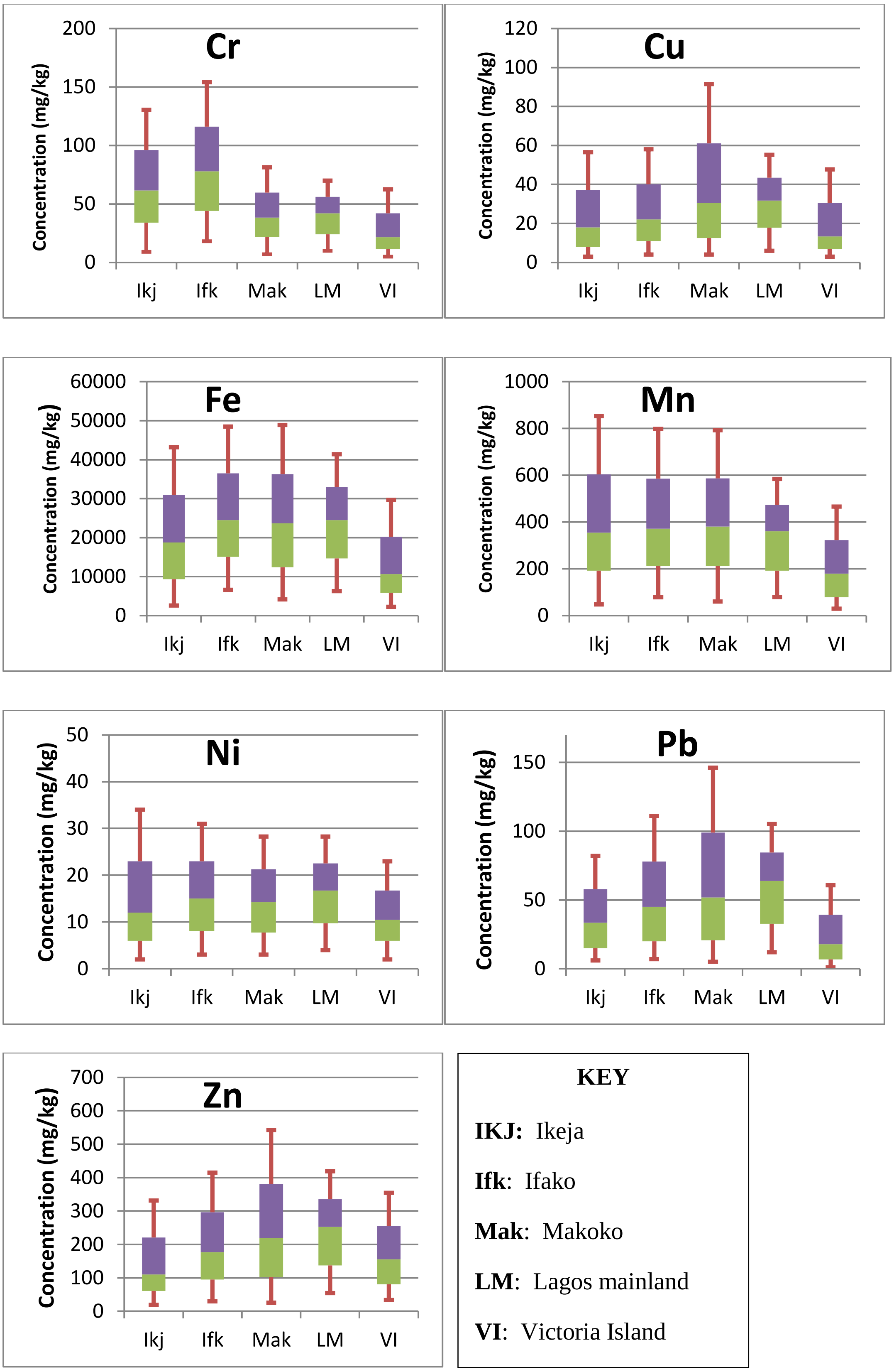
The clustering of Cu, Pb and Zn suggests urban anthropogenic origin and is reported in the literature[67, 74, 79].

3.5.2.6.3 Influence of socio-economic areas on PTE distribution in urban soils.

Box plots showing the contamination profile of PTE in different socio-economic areas in Lagos are shown in Fig 3.11. The areas sampled showed marked variations in PTE concentrations. Chromium and Mn consistently showed higher concentrations in soils from Ifako and Ikeja. High Mn concentration was also observed in Makoko soils and was found comparable to that of Ikeja and Ifako. Nickel concentration was highest in Lagos mainland soils and Ifako, Makoko, Ikeja soils appeared to have similar Ni contamination. Copper, Pb and Zn showed higher concentrations in Makoko and Lagos mainland soils.

Lagos mainland was the most contaminated area and this may be attributed to high traffic congestion coupled with location of three largest Lagos wholesale markets within this vicinity (Idumota, Oyingbo and Balogun markets). Lagos mainland is the oldest part of Lagos because the offices and residences of the colonial government are sited in this area; therefore, paints from old and dilapidated colonial buildings in this area may have also contributed to the elevated PTE concentration recorded in its soils. Lagos mainland and Makoko areas recorded close values for Cu, Pb and Zn. Makoko is a small part of Lagos mainland LGA so this may explain their close contamination profiles. For all PTE analysed (with exception to Zn), Victoria Island appears to be the least contaminated area. Average Zn level in VI soils was higher than Ikeja soils mainly because of a very high Zn concentration measured in VI RD 4which had a mean value of 728 mg/kg. Victoria Island area may have been less subjected to vehicular pollution from old and poorly maintained cars. Ikoyi (VI area) motor vehicle licensing office recorded the lowest figure of the total number of registered vehicles and motorcycles in Lagos for year 2011 (2,627 or 0.001 %, and 760 or 1.04 % respectively) [281]. This may be one of the reasons why PTE contents were lower in VI soils.

There have been growing concerns about vehicular pollution of soils in urban areas [3, 118]. Various degrees of vehicular pollution could have been the major factor influencing PTE distribution across the areas studied. Enrichment factors and Igeo values of PTE were calculated in order to have a better understanding of PTE enrichment in soils from the different socio-economic areas studied. From Figure 3.11, VI soils appeared to be consistently enriched with Cu, Pb and Zn than other socio-economic areas studied and this obviously did not give a true representation of the PTE status. The EF has showed showed its limitation as a pollution assessment tool for comparing variables such as PTE variability in different socio-economic areas, in an attempt to get a better understanding of PTE behaviour in soils. Figure 3.12 showed a better representation of PTE enrichment in the socio-economic areas but VI still appeared more contaminated with Pb and Zn than Ikeja.



KEY

IKJ: Ikeja

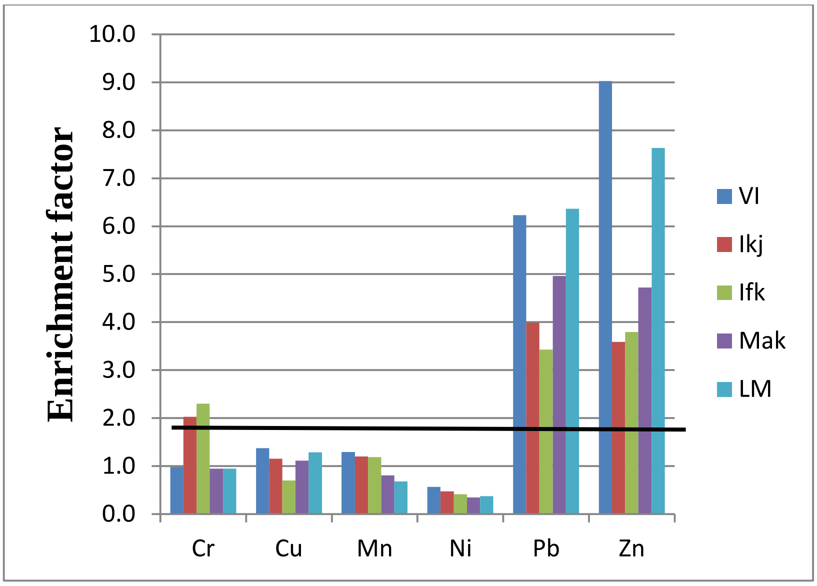
Ifk: Ifako

Mak: Makoko

LM: Lagos mainland

VI: Victoria Island

Figure 3.11 Box plots showing PTE distribution in different socio-economic areas of Lagos



KEY

VI: Victoria Island

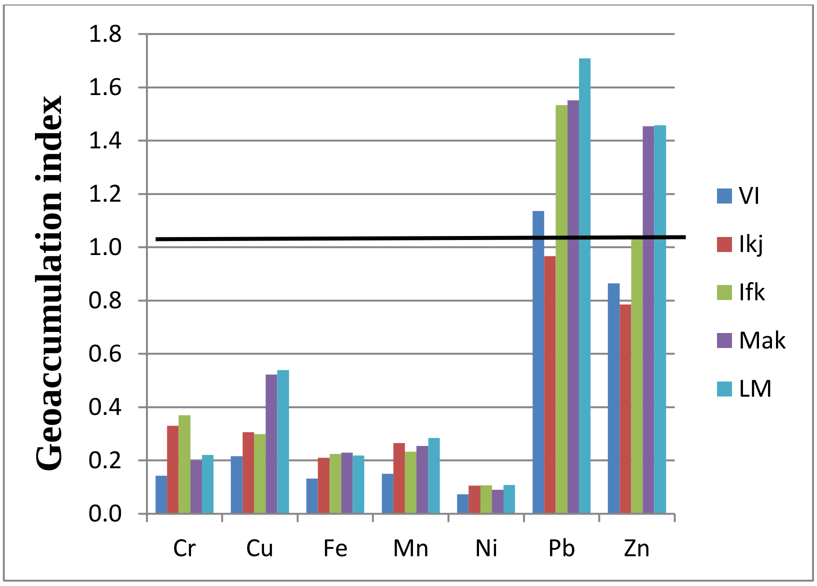
IKJ: Ikeja

Ifk: Ifako

Mak: Makoko

LM: Lagos Mainland

Figure 3.12 Enrichment factor values of PTE in soils from Lagos socio-economic areas. The bold horizontal line represents limit for minimal enrichment



KEY

VI: Victoria Island

IKJ: Ikeja

Ifk: Ifako

Mak: Makoko

LM: Lagos Mainland

Figure 3.13 Geoaccumulation index of PTE in soils from Lagos different socio-economic area. The bold horizontal line represents Igeo limit of contamination

Enrichment factor and Igeo analysis appeared to be only suitable for assessment of PTE enrichment in soils are not for evaluating PTE distribution in variables socio-economic areas.

Generally, concentrations of PTE decreased in the order of Lagos mainland > Makoko > Ifako > Ikeja > Victoria Island. The different socio-economic areas of Lagos studied seem to influence PTE distribution. Amongst many factors, population densities, traffic, location of industries, lack of legislation on PTE and non-enforcement of emission standards to properly check vehicular pollution might have influenced PTE concentration variations in the areas studied. Strong evidence of relationship between area-based socioeconomic conditions and urban neighbourhood environmental quality of Accra, Ghana have been reported[282]. The study noted that socio economic inequalities such as unemployment and income gaps could worsen the existing urban environmental quality and health. Similarly, urbanization and industrialization of large cities or urban areas have been demonstrated to clearly influence PTE distribution[35, 67, 71].

3.6 Results and discussion of PTE in soils collected from known point sources

Soil samples were collected from and close to known point sources because an appreciable number of the population live close to these sites. On site and laboratory sample preparation and processing were carried out as described in chapter 2.

3.6.1 pH and loss on ignition

The result of pH and % LOI for industrial estate, dump sites and train terminals soil samples are presented in appendix F. Soil pH measured in the soil samples ranged between 5.79 and 10.06. The dumpsite soil samples had the highest average pH value of 7.6 followed by the industrial estates soils (7.4) and train terminals soils (7.1). The pH of railway terminals, industrial estates and dump sites soil samples appeared to be near neutral. The pH values are typical of urban soils that are calcareous in nature. The % LOI values measured in the soils were generally low, ranging from 0.11 to 8.24. The low % LOI values in these soils are typical of soils in warm arid climates like Nigeria[283].

3.6.2 Pseudototal digestion

3.6.2.1 Quality Control[251]

Pseudo-total concentration of PTE in soil samples were determined by microwave assisted digestion as described in section 2.3.1. An in house reference material (GLA-URM) was included in every batch of soil sample digested and information about this reference material is provided in section 3.5.2.1. Table 3.16 shows the results of pseudototal concentration of PTE in the secondary reference material (GLA-URM), obtained during the 6 batches of digestion in this work and the target values indicative of each PTE concentration. Generally, the recoveries were 100 ± 5 % except for Cr. This indicates good accuracy of the analytical method and instrument employed.

Table 3.16 Results of pseudototal concentration of PTE in GLA-URM (mg/kg)

	Cr	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
Obtained values (n = 18)	57	109	29500	426	52	381	180
Target values (n = 34)	43	111	30600	445	49	389	177
% recovery	132	98	96	96	106	98	102

3.6.2.2 Industrial estates

The summary statistics of PTE concentrations in soils samples from Lagos industrial estates are presented in Table 3.17. Mean pseudototal concentrations and precision results for soil samples are presented in appendix C.

Chromium concentration ranged from 25 to 242 mg/kg for all the soil samples, with Ikorodu industrial estate soils having the highest concentration. The range is higher than Cr measured in soils of Patancheru industrial development in India[235] (5 to 150 mg/kg) and mean concentrations of three industrial estates in Akan, Iran[237] (11 to 80 mg/kg). Govil *et al.*[284] reported higher Cr concentration in soils of Katendan Industrial area, India (62 to 433 mg/kg). However, dumpsites of solid wastes were sampled in their work and this may account for the higher Cr concentration reported. Average Cr concentration for all the soil samples was 100 mg/kg (this study).

Table 3.17 Descriptive statistics of PTE concentrations in industrial estate soils

n = 10, mg/kg	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Minimum	25	25	10900	135	4	23	87
Mean	100	194	61000	1160	42	211	1230
Median	57	71	31500	406	16	160	382
Maximum	242	759	146000	3950	118	504	3560
SD	82	247	55000	1410	47	167	1450
% RSD	34	33	39	36	40	33	41
Dutch intervention values	380	190	-	-	210	530	720
Environment Agency, UK	130	-	-	-	230	450	-

This is lower than the UK Contaminated Land Exposure Assessment (CLEA) value for Cr (130 mg/kg) and Dutch intervention value (380 mg/kg) and therefore the sites sampled may be considered unpolluted. Individual soil concentration values for Cr were less than the SGVs with the exception of Ikorodu industrial estate.

The three individual composite samples collected from Ikorodu may be considered to be polluted by Cr since their respective concentration values exceeded CLEA value. Steel production, chrome plating and pigment manufacture are associated with Cr and its compounds. A number of metal processing industries are established at Ikorodu and this may possibly explain the source and high level of Cr. The average Cr concentration in Ikeja industrial estate soils was 111 mg/kg and this value exceeds the mean Cr concentration reported for the same estate by Fakayode *et al.*[232] in 2002 who reported an average concentration of 26 mg/kg and a range of 7.1 to 42 mg/kg. A build-up of Cr in the soils may have occurred over time.

Copper concentration ranged from 25 to 759 mg/kg with an average concentration of 194 mg/kg which is higher than the Dutch soil intervention value (190 mg/kg) and may be regarded as polluted. Other studies have reported lower average Cu concentrations in soils collected around industrial estates[233, 235, 236, 285].

Ilupeju industrial estate soils had the lowest Cu concentrations in comparison to others (25 and 33 mg/kg). However, soils collected close to a foundry site in the estate contained 137 mg/kg of Cu. Emissions from the nearby foundry may have contributed to the elevated Cu concentration in the soil sample (in comparison to the lower levels obtained for the other two samples). All the Ikorodu industrial estate soil samples exceeded the SGV for Cu (268, 492 and 759 mg/kg). Significant enrichment of Cu in soils of this estate is evident, and it may have emanated from smelter plants, foundries, steel production factories and chrome plating industries in the estate.

Average concentrations for Fe and Mn were 61,000 mg/kg and 1160 mg/kg respectively. These PTE are common components of soil. They form a substantial part of the elements present in the lithosphere[30]. Currently, there are no soil guideline values for Fe and Mn. Typical concentrations of Fe in soils ranges from 1000 to 100,000 mg/kg[30]. Pseudototal concentrations of Fe measured in industrial estates soils in this study were within typical soil concentrations with the exception of soils collected from Ikorodu industrial estate. The mean concentration of Fe in Ikorodu soils is 140,000 mg/kg. This value exceeds both typical concentrations for Fe in Earth’s soils and urban soils and may therefore suggest a possible anthropogenic contribution. Atmospheric emissions from steel, aluminium and galvanised pipe manufacturing factories may be responsible for the enrichment of the soil samples with Fe. Indiscriminate dumping of scrap metals and improper disposal of wastes from these factories may have also contributed.

The world mean concentration for Mn in soil is 850 mg/kg and it typically ranges from 10 to 9000 mg/kg[29, 30]. All soil samples analysed were within this range and therefore may be considered unpolluted. Concentrations of Ni in the industrial estates soil ranged from 4 to 118 mg/kg, with an average concentration of 42 mg/kg (Table 3.17, appendix C). The average Ni concentration is similar to that reported in literature for Otta (31 mg/kg) industrial estate in Nigeria[286]. Nickel concentrations in the soils analysed were generally low when compared with the SGVs and most of the soil samples may be considered unpolluted. Low concentration of Ni may indicate possible contribution from geogenic, rather than anthropogenic sources.

The highest Ni concentrations were recorded in Ikorodu soils with an average of 109 mg/kg. This is much higher than all other industrial estate soils analysed but lower than the CLEA soil guideline value for the UK (230 mg/kg) and the Dutch intervention value for Ni (210 mg/kg).

Lead concentration in top soils of industrial estates studied ranged from 23 to 504 mg/kg with mean of 211 mg/kg. This is higher than Pb concentration reported in previous studies for Arak industrial estate, Iran[237] (60 mg/kg), Chennai industrial estate, Southern India[234] (42 mg/kg), and Karak industrial estate, Jordan[238] (11.2 mg/kg). A previous study reported an average concentration of 2700 mg/kg for Pb measured in a soil litter horizon close to two Zn smelter plants at Palmerton, Pennsylvania, USA[287]. This value is several times higher than the average Pb concentration found in the current study and may be attributed to the long history of heavy industry manufacturing in USA cities compared to Nigeria. Another study by Yaylali-Abanuz[233] also reported higher Pb concentration (246 mg/kg) in soils collected from an industrial area of Gebze, Turkey.

The Pb concentration measured in Ogba 2 soil sample was 400 mg/kg and as observed for other PTE, Ikorodu soil samples had higher Pb concentrations in comparison to other samples analysed (388, 536 and 239 mg/kg). One of the Ikorodu soil samples (Ikorodu 2) exceeded the CLEA SGV for Pb (450 mg/kg). The Pb in these soil samples may be attributed to atmospheric deposition from industrial emissions. Sources of Pb in industrial areas are many but anthropogenic contributions from moving trucks and vehicles in industrial areas may be major contributors. Another possible significant source of Pb in these estates may be emissions from electricity power generators which in most cases are petrol driven. These petrol generators power industrial sites due to the erratic national grid power supply experienced in Nigeria and are normally in operation for several hours to keep the industries in continuous production.

Zinc concentration ranged from 86 to 3560 mg/kg with an average concentration of 1234 mg/kg for all the industrial estate soils investigated. The Ilupeju industrial estate soils had the lowest Zn concentrations with all 3 composite samples below the Dutch SGV and therefore can be regarded as unpolluted.

In common with Cr, Cu, Fe, Mn, Ni, and Pb, Zn concentrations were lower in Ilupeju in comparison to other industrial estates. Ikorodu soil samples had the highest concentrations for Zn with an average of 3290 mg/kg; the three composite samples exceeded 3000 mg/kg, four times higher than the Dutch intervention value of 750 mg/kg. Ikorodu soil samples may therefore be classified as polluted. The high Zn concentration may be attributed to emissions emanating from zinc smelting, steel production and metal foundry plants. Zinc ores typically contains several other elements such as Cd, Cu and Pb. This maybe the possible explanation for the elevated concentrations of Cu and Pb in some of the soils analysed. Ogba industrial estate soil sample 2 also had high Zn concentration of 1080 mg/kg. It was observed that this soil sample also had the highest Pb concentration in all the industrial estates soils studied with the exception of the Ikorodu 2 soil sample. Generally, Ikorodu was the most contaminated industrial estate followed by Ogba, Ikeja and Ilupeju in that order.

To further assess the level of PTE pollution in the soil samples, enrichment factor and geoaccumulation index were calculated. Average and individual EF values of PTE in industrial estate soils studied are presented in Figure 3.14. Chromium, Mn and Ni all had average EF values less than 1 which signifies no enrichment. A few individual samples exceeded the EF value of 1 for Cr and Mn, but were less than 1.5, which implies minimal enrichment. The EF value for Cu ranged from 1 to 9 with an average of 3. This suggests minimal to significant enrichment. Evidence of Cu enrichment was apparent in all of the industrial estate soils analysed as their respective EF values was greater than 1.5 except for Ikeja soil which had an EF of 1.23.

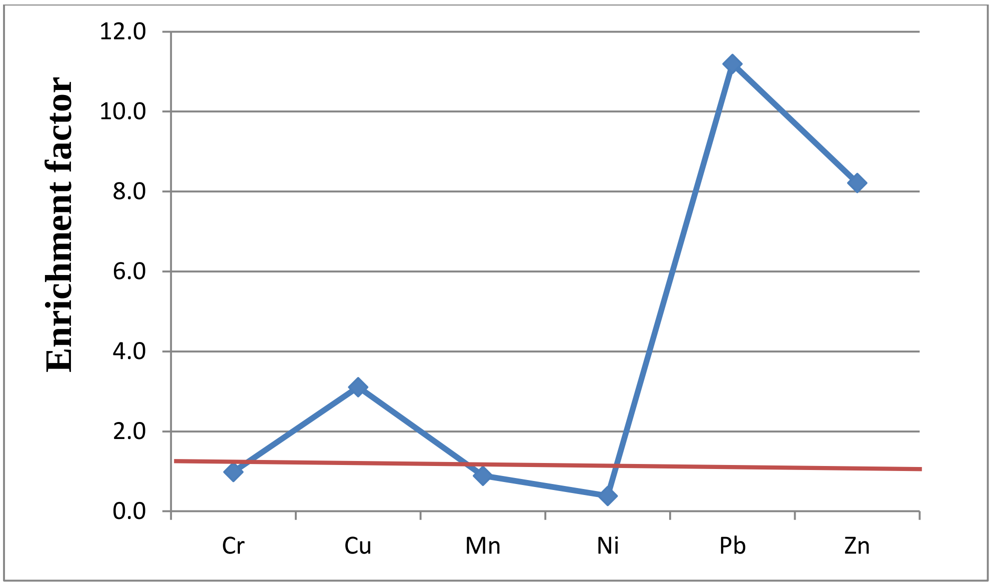


Figure 3.14 Enrichment factors of PTE measured in Lagos industrial estates soils. The bold horizontal line represents the limit for minimal enrichment.

Lead showed significant to very high enrichment as its EF value ranged from 4 to 33 with a mean value of 11. A very high enrichment value for Pb (EF = 33) was observed for Ogba 2 soil. From Figure 3.14 it is evident that Pb was the most significantly enriched PTE. Zinc was also significantly enriched in the soils. The EF ranged from 3 to 19 with an average of 8 and this indicates moderate to significant enrichment. The highest EF value for Zn (19) was recorded in Ogba 2 soil.

The soil sample had the highest enrichment value for Pb and Zn. The soil sample was collected close to a metal smelting and refining plant (Western Metal Products Company Limited). Emissions from smelting and refining processes and furnace effluent gases from this factory may be the primary contributor to Pb and Zn enrichment in the soil sample. Enrichment factor values of PTE generally decreased in the order of Pb > Zn > Cu > Mn > Cr > Ni.

Figure 3.15 shows the average Igeo values for each PTE. The geoaccumulation index calculation confirmed the EF results. From the EF and Igeo results, soil samples studied appeared to be more contaminated with the ‘‘typical urban metals’’ (Cu, Pb and Zn)[76] than other PTE analysed.

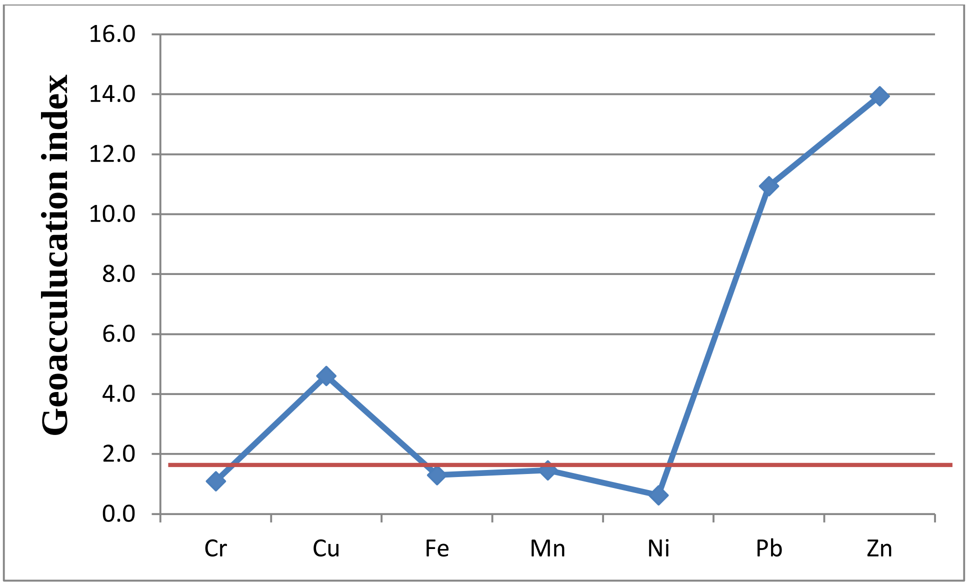


Figure 3.15 Geoaccumulation index of PTE measured in Lagos industrial estates soils. The bold horizontal line represents limit of contamination.

Copper displayed moderate to very high contamination. Only three out of the industrial estate soil samples showed low contamination. Lead and Zn showed moderate to very high contamination. About 70 and 40 % of the soil samples showed very high contamination for Pb and Zn, respectively. Chromium, Fe, Mn and Ni generally showed low contamination, but a few samples showed moderate contamination, as observed in the EF results.

The correlation coefficient results of PTE and soil properties are shown in Table 3.18. The relationship between all PTE showed significant positive correlations. This was expected since PTE analysed in most samples exceeded the SGVs, particularly the industrial estates and dumpsites soil samples. This suggests that PTE may have emanated majorly from anthropogenic sources. The relationship between % LOI and PTE concentrations appeared to be of little significance as the correlation coefficients showed low values which were less than 0.27. There was no relationship between soil pH and PTE concentrations as negative and insignificant correlations were observed for all PTE. This implies that PTE concentration measurements were independent of the soil properties.

Table 3.18 Correlation coefficient analysis of PTE in industrial estates soils @ 95 % confidence level; n = 10

	Cr	Cu	Fe	Mn	Ni	Pb	Zn	% LOI	pH
Cr	1								
Cu	0.76	1							
Fe	0.97	0.86	1						
Mn	0.93	0.73	0.95	1					
Ni	0.98	0.87	0.99	0.93	1				
Pb	0.63	0.77	0.70	0.60	0.72	1			
Zn	0.78	0.55	0.76	0.61	0.75	0.52	1		
% LOI	0.27	0.12	0.05	0.26	0.05	0.06	0.04	1	
pH	-0.14	-0.28	-0.24	-0.02	-0.13	-0.27	-0.35	-0.34	1

In summary, the industrial estate soil samples studied generally showed considerable pollution by all PTE analysed with some of the soils highly polluted with Cu, Pb and Zn. Ikorodu industrial estate appeared to be highly contaminated with all PTE analysed with exception to Ni. Ikeja and Ogba industrial estate showed moderate contamination with PTE and there were concerns about highly enriched Pb and Zn in the Ogba 2 soil sample. Ilupeju industrial estate soils may be considered unpolluted with PTE and this was the least contaminated among the industrial estates studied. The general PTE pollution of the industrial estates studied was in the order of Ikorodu > Ogba > Ikeja > Ilupeju.

3.6.2.3 Dump sites

The summary statistics of PTE concentrations in soils samples from dump sites are presented in Table 3.19. Mean pseudototal concentration and precision (% RSD) for each soil sample is presented in appendix C.

Table 3.19 Descriptive statistics of PTE concentrations in dumpsite soils

n = 16; mg/kg	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Minimum	19	9	10900	54	8	22	96
Mean	262	938	55600	1200	137	515	1070
Median	94	158	43100	685	45	154	515
Maximum	1830	11700	166000	6090	1040	4330	5600
Standard deviation	444	2880	43900	1470	257	1050	1510
% RSD	169	307	79	123	188	204	141
Dutch intervention values	380	190	-	-	210	530	720
Environment Agency, UK	130	-	-	-	230	450	-

Chromium concentrations in dumpsites soils samples ranged from 19 to 1830 mg/kg. The average Cr concentration for all the samples is 262 mg/kg and this was higher than the UK SGV for Cr (130 mg/kg) but lower than the Dutch soil intervention value of 380 mg/kg. The average concentration of Cr in the soil samples is higher than values reported for dumpsite soils in other studies of Nigerian cities (27 and 1.7 mg/kg)[177, 227, 240]. Chromium concentrations in Dasco (1830 mg/kg) and Grand Foundry (602 mg/kg) were higher than the SGVs by several times (CLEA and Dutch values). The foundry dumpsites as expected had the highest concentrations for Cr in comparison to the other dumpsites (see appendix C). The soils can be categorised as contaminated. One of the soil samples collected from the Owode motor spare part market dumpsite also had high concentration of Cr (290 mg/kg), which may be attributed to spilled engine oils, lubricants and more especially, continuous indiscriminate dumping of metal scraps. Due to high Cr contents in soils analysed, excavation of some of the dumpsites may be required.

The average concentration of Cu in dump site soils was 938 mg/kg, though a much lower median value of 158 mg/kg was observed and this is because of very high concentrations measured in Dasco soil (11700 mg/kg). By excluding this outlier, the average Cu concentration for other dumpsite soils is 218 mg/kg. This concentration is higher than the Dutch intervention value for Cu (190 mg/kg).

All the four soil samples collected from Owode motor spare part market were high in Cu (133, 182, 289, 470 mg/kg respectively). There are strong indications that high Cu content in these soils emanated from motor engine oil and automobile spare parts. The level of Cu in Kantangua dumpsite soils was 542 and 611 mg/kg respectively. These values are high and can be categorised as very contaminated when compared with Dutch SGV. Dasco foundry dumpsite soil had an unprecedented amount of Cu content (11,700 mg/kg) which is about 20 times higher than Katangua dumpsite soils, 40 times higher than other soils analysed and about 62 times higher than Dutch SGV for Cu. This may be categorised as an extremely contaminated soil.

The mean concentration of Fe and Mn measured in the dump site soils were 55, 000 mg/kg and 1200 mg/kg respectively. The concentrations ranged from 10900 to 166000 mg/kg and 54 to 6090 mg/kg for Fe and Mn, respectively. Soils of dumpsites associated with foundries were clearly higher in Fe and Mn concentrations than other dumpsite soil samples. Dasco and Nigerian foundry dumpsites soils had Fe concentrations of 142000 and 166000 mg/kg respectively; which are higher than the typical concentration ranges of Fe in soils (1000 to 100,000 mg/kg)[30]. The Computer Village dumpsite (a municipal dumpsite in Ikeja) which receives very large domestic, industrial and electronic waste also had high concentrations of Fe (99,800 mg/kg). Manganese concentrations were within typical soil concentrations for most soil samples except for the foundry sites. Grand Foundry dumpsites had the highest concentrations of Mn in its soils. The two samples collected from two different dumpsites (in and outside the factory premises) had 2330 and 6090 mg/kg of Mn. Other foundry dumpsites soil samples had high Mn concentrations (1530 and 1720 mg/kg). Cast iron products are commonly alloyed with Mn and foundry sites have been reported as major potential sites for exposure to Mn fumes and dusts from furnaces[288]. This may probably explain the high Mn concentrations recorded in the soil samples. There are strong indications that the high Fe and Mn contents of these soils may not be entirely of a geogenic origin since the concentrations exceed typical soil concentrations. Nickel concentration in dumpsites studied ranged from 8 to 1040 mg/kg with an average concentration of 137 mg/kg. Levels of Ni measured in these soils were generally low. Exceptions to this were soils from Owode 3 (224 mg/kg), Dasco (1040 mg/kg) and Grand foundry 2 (306 mg/kg).

These three soils exceeds the Dutch intervention value for Ni (210 mg/kg) while Dasco and Grand foundry soil sample both exceed the CLEA value of 230 mg/kg for Ni. These soils may be considered polluted with Ni.

Markedly variable Pb concentrations were observed in the dumpsite soils analysed, with concentration ranging from 22 to 4330 mg/kg and an average of 515 mg/kg, median 154 mg/kg. Lead levels were well below the SGVs for most of the dumpsite soils analysed. Dasco soil had the highest concentration for Pb (4330 mg/kg) as observed for most other PTE discussed. The two composite soils samples collected from Katangua market dumpsites exceed the 450 mg/kg CLEA SGV for Pb (450 and 802 mg/kg). A number of auto repair mechanic workshops are sited in this market and spent oil, spilled lubricants from auto spare parts, domestic waste and degraded metal scraps may account for the high Pb content in these soils.

Enriched Zn concentration was observed in some of the soil samples. The samples which had high concentrations of Pb also had elevated levels of Zn. The average concentration of Zn in the soils was 1070 mg/kg and this value exceeds the Dutch SGV for Zn (720 mg/kg).The two soils collected from Katangua market dump sites had the highest Zn concentration (3210 and 5610 mg/kg). These soils can be regarded as very contaminated because they were about four to seven times higher than the Dutch intervention value for Zn (750 mg/kg).Dasco soil as expected had high Zn concentration (2800 mg/kg) also contaminated. Zinc is an additive in the production of lubricating oil and vulcanization process[5, 265]. Atmospheric deposition from non-ferric metal industries[233] and possible leaching from galvanised materials within the environs of the dumpsites studied may also have contributed to high Zn levels in the soils. Strong positive relationships were observed between Cr, Cu, Fe, Ni, and Pb (see Table 3.20) and this shows possible common sources which most probably may be anthropogenic, because of the high level of PTE measured in the samples. Average and individual EF and Igeo values of PTE in dumpsite soils are presented in Figure 3.16, 3.17 respectively.

Chromium had an average EF value of 2. This shows that soil samples were moderately contaminated with Cr. The EF value ranged from 0.7 to 6, revealing no enrichment to minimal enrichment. Only Dasco and Grand Foundry 2 soil samples displayed significant Cr enrichment (5.8 and 6 respectively).

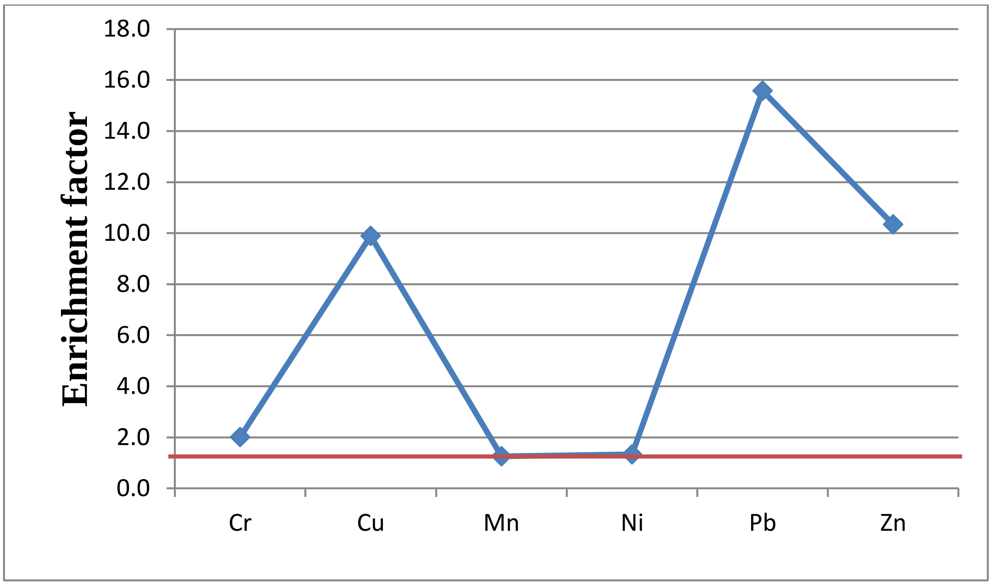


Figure 3.16 Enrichment factors of PTE measured in Lagos dumpsite soils. The bold horizontal line represents limit for minimal enrichment.

Copper had relatively high EF values with about 80 % of the dumpsite soils analysed having EF values greater than 2. This suggests that more than half of the soils analysed were considerably enriched with Cu. An unusual enrichment was observed for Dasco soil sample (EF = 74) and this is about 15 to 20 times higher in value than most of the dumpsite soils studied. This soil may be categorised as very enriched and contaminated with Cu and immediate excavation of the site may be necessary.

Manganese and Ni generally had low EF values. It is evident from Figure 3.16 that their average EF values were less than 1.5 (1.3 and 1.3 respectively). This indicates no or minimal enrichment of Mn and Ni in soils analysed. However, there were exceptions to this as the EF value for Mn in Grand Foundry soils were 3 and 6.4. These values were the highest EF values for Mn as also observed in their concentration values. Dasco and Grand Foundry 2 soils showed significant enrichment for Ni (EF of 4.4 and 4 respectively).

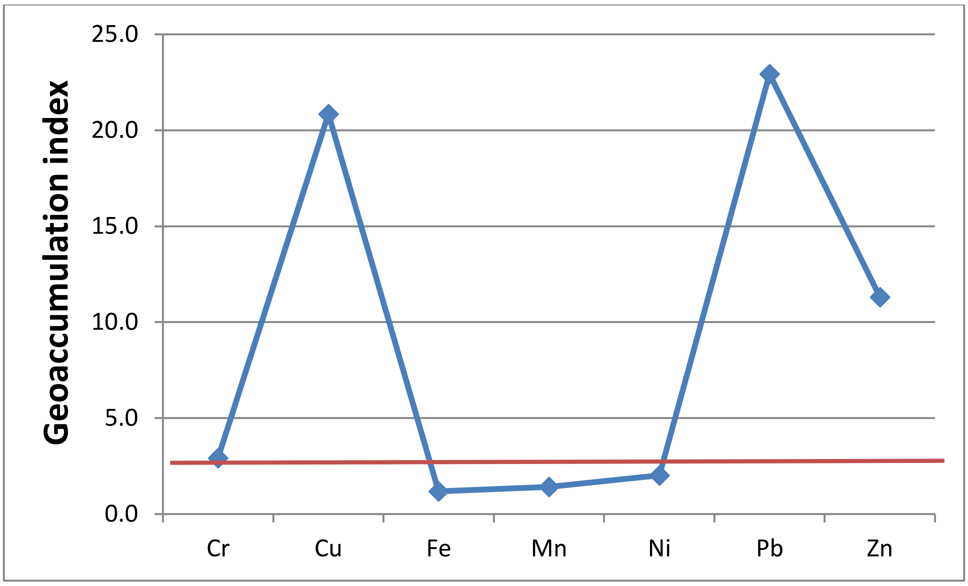


Figure 3.17 Geoaccumulation index of PTE measured in Lagos dumpsite soils. The bold horizontal line represents limit of contamination.

It is noticeable from Figure 3.16 that Pb enrichment is the most pronounced amongst PTE analysed. Enrichment factor values ranged from minimal to extremely high enrichment (1 to 61.7). Average EF value for Pb was 15.6, thus indicating significant enrichment. More than half of the soil samples had EF values greater than 5 (significant enrichment). Dasco soil had an unusual EF value of 61.7, indicating an extreme Pb contamination. Immediate excavation of the dumpsite may be required in order to avoid possible leaching of Pb into groundwater. Laniyan *et al.*[239] had reported Pb contamination of ground water around a municipal dumpsite in Lagos. Zinc had EF values which ranged from 1.5 to 48.4 (average value of 10.3). A larger percentage of the soils analysed revealed significant Zn enrichment with the exception of Katangua soil samples which showed very high Zn enrichment (EF value of 31.7 and 48.4). Generally, most of the dumpsites soils are contaminated with PTEs studied, particularly Dasco soil. Immediate excavation of most of the sites may be required. Enrichment factor values of PTE generally followed Pb > Zn > Cu > Cr > Mn > Ni.

The Igeo results showed very high contamination for the ‘‘typical urban metals’’ (Cu, Pb and Zn). Their respective average contamination factor values are greater than 10 (20.9, 22.9 and 11.3 for Cu, Pb and Zn respectively).

This supports the earlier conclusion from the EF value results that the dumpsite soil samples were very contaminated. Other PTE studied (Cr, Fe, Mn and Ni) showed moderate contamination as also seen in the EF results. The contamination factor results showed a slightly different PTE contamination pattern in comparison to the EF value results: Pb > Cu > Zn > Cr > Ni > Mn > Fe. However, weak statistical relationships were observed between Zn and other PTE (Table 3.20), reasons for this were unclear since very high concentrations exceeding SGV were observed for Zn.

Table 3.20 Correlation coefficient analysis of PTE in dumpsite soils @ 95 % confidence level; n = 16.

	Cr	*Cu*	*Fe*	*Mn*	*Ni*	*Pb*	*Zn*	*% LOI*	*pH*
Cr	1								
Cu	0.94	1							
Fe	0.75	0.68	1						
Mn	0.37	0.06	0.28	1					
Ni	0.97	0.94	0.70	0.29	1				
Pb	0.91	0.99	0.68	0.03	0.93	1			
Zn	0.27	0.35	0.29	0.03	0.31	0.46	1		
% LOI	-0.22	-0.28	-0.22	0.17	-0.26	-0.30	-0.10	1	
pH	-0.03	-0.18	-0.18	0.52	-0.09	-0.20	-0.17	0.73	1

Similarly, weak relationship exist between Mn and other PTE, but higher positive relationship were observed with geogenic PTE (Cr, Fe and Ni; 0.37, 0.28, 0.29 respectively) than anthropogenic PTE (Cu, Pb and Zn; 0.06, 0.03 and 0.03 respectively). This indicates that Mn in the soil samples were mainly of geogenic than anthropogenic origin. There was no relationship between % LOI and PTE concentrations. The % LOI was negatively correlated with PTE concentration and statistically insignificant. Similarly, there was no relationship between pH and PTE concentrations level. Manganese correlated positively with % LOI and pH. There was clear distinct behaviour as observed and discussed earlier and this may further support the suggestion of its possible emanation from geogenic sources.

3.6.2.4 Railway terminals

The summary statistics of PTE concentrations in railway terminal soil samples are presented in Table 3.21. Average pseudototal PTE concentration and precision (% RSD) for each soil sample is presented in appendix C. The average mean concentration of Cr in train terminals soils was 80 mg/kg and ranged from 43 to 128 mg/kg. Chromium concentrations in the soil samples were less than soil guideline values highlighted in Table 3.21. This indicates that soils collected in and around these railway terminals are not contaminated with Cr.

Copper concentrations ranged from 43 to 243 mg/kg with an average mean concentration of 123 mg/kg. This is the less than the Dutch soil intervention value for Cu (190 mg/kg) and so the soil samples may be considered unpolluted. The average Cu concentration of 123 mg/kg is higher than that in soils collected in and around train stations in other studies[246, 289]. Liu *et al.*[246] in their study found Cu levels to be 59.2 and 58.9 mg/kg in soils collected from flat and embankment sites of Chengdu-Kunming railway in Sichuan, China. Malawska *et al.*[289] reported a range of 24 to 115 mg/kg in Cu concentrations in soils collected from railway junction in Ilawa Glowna, Poland.

In the current study, Cu enrichment was observed in Agege train terminal soils with concentration of 243 mg/kg which is higher than the Dutch SGV for Cu. This soil sample may be categorized as contaminated since it exceeds SGV limit. Enriched Cu level observed in Agege soil may have originated from continuous ‘‘wear and tear’’ of rail tracks over the years. Iron and Mn levels in the samples were within typical concentrations for Fe and Mn in soils[30] (0.1 to 10 % and 350 to 9000 mg/kg respectively). Iron and Mn concentrations ranged from 26400 to 83600 mg/kg and 280 to 1200 mg/kg respectively (Table 3.21). Average concentrations of Fe and Mn in the samples were 57500 and 541 mg/kg, respectively. In comparison with this study, higher mean concentrations of Mn (676 mg/kg) were reported for soils collected in a vicinity of a train station in China[246]. However, Mazur *et al.*[245] reported 320 mg/kg as the highest concentration of Mn in soils collected near railway lines in Poland. This is lower than the average concentration of Mn in this study.

Table 3.21 Descriptive statistics of PTE concentrations in railway terminal soils

n = 7; mg/kg	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Minimum	43	43	26400	280	16	110	210
Mean	80	190	57500	542	28	206	614
Median	72	112	68300	413	29	182	511
Maximum	128	710	83600	1200	44	329	1220
Standard deviation	37	233	23900	310	10	90	438
% RSD	46	123	42	57	36	44	71
Dutch intervention values	380	190	-	-	210	530	720
Environment Agency, UK	130	-	-	-	230	450	-

Elevated concentrations of Mn in soils around railway areas have been attributed to wheel and rail track abrasion[246]. Anthropogenic contributions of Fe to some of the samples may be possible as Iddo and Ikeja train terminals soils were 2 times higher in Fe levels than soils collected from Agege, Alagomeji and Oshodi railway terminals. Iddo and Ikeja soils were evidently more enriched with Fe. Concentrations of Fe in soils collected around a railway junction in Ilawa Glowna, Poland (40000 and 56000 mg/kg) was reported to have exceeded Fe concentration at control sites by 75 to 95 times.

Nickel concentration in the soils was low, ranging from 16 to 44 mg/kg. Average Ni concentration in the soils was 28 mg/kg with a median value of 29 mg/kg. None of the soils investigated exceeded the soil guideline values. They may be categorized as uncontaminated. Similar to this work, another study has reported low Ni concentrations in soils collected around the vicinity of a railway in Olsztyn, Poland[245].

Lead concentrations ranged from 110 to 323 mg/kg across the train terminals studied with an average concentration of 205 mg/kg. In comparison with the CLEA and Dutch SGVs, the soil samples may be considered unpolluted but evidences of Pb enrichment may not be ruled out since the concentrations are about two to four times higher than typical background concentration for Pb in urban soils[253].

Wilkomirski *et al.*[241] reported high Pb concentrations in soils collected at railway sidings in Poland and values (448 and 494 mg/kg) that are higher than Pb concentrations in train terminal soils reported for the current study. However, lower Pb values than 206 mg/kg (this current study) were reported for soils collected around railway vicinities in other studies[245, 246]. Iddo soils (1 and 2) had 329 and 323 mg/kg Pb respectively. These values are apparently higher than Pb concentrations in other train terminals. Generally, lubrication oil leak, wagon decoration, discarded garbage and leaked cargo may be possible sources of elevated concentrations of Pb observed in these soil samples[290, 291].

Zinc concentrations varied across the train terminal soils studied with an average of 612 mg/kg and a range of 210 to 1220 mg/kg. The highest Zn concentrations were measured in Iddo 1 and Agege train terminal soils. These exceeded typical concentrations in urban soils (158 mg/kg)[253] by about 7 times and the concentrations also exceeded the Dutch SGV for Zn (720 mg/kg). Soils may thus be considered polluted by Zn. This is similar to results reported by Wilkomirski *et al*.[241] for Zn concentrations in soils collected around railway sidings (1264 and 1223 mg/kg). In their study, soil collected from platform areas had higher concentration of 1438 mg/kg. The average Zn concentration of 612 mg/kg is higher than concentrations from railway station soils of other studies[246, 289] (84 and 235 mg/kg). Zinc contamination of railway soils has been linked to spilled lubricants, leaked cargo, wheel and track abrasion[290, 291].

The average EF and Igeo values calculated for PTE are presented in Figure 3.18 and 3.19 respectively. Individual values are also presented in appendix F. Enrichment factors of Cr, Mn and Ni in the soil samples were generally low, in all cases less than 1 (0.8, 0.6 and 0.4 respectively). This indicates no enrichment and this also reflects the low concentrations of the PTE in the soil samples. Lead, Cu and Zn had higher EF values compared to Cr, Mn and Ni (Figure 3.18). This is similar to what was obtained for EF results in industrial estate and dumpsites soils. The average EF value for Cu is 2.9 and this indicates moderate enrichment. The range of Cu EF values is between 1.2 and 2.8, showing minimal to moderate enrichment.

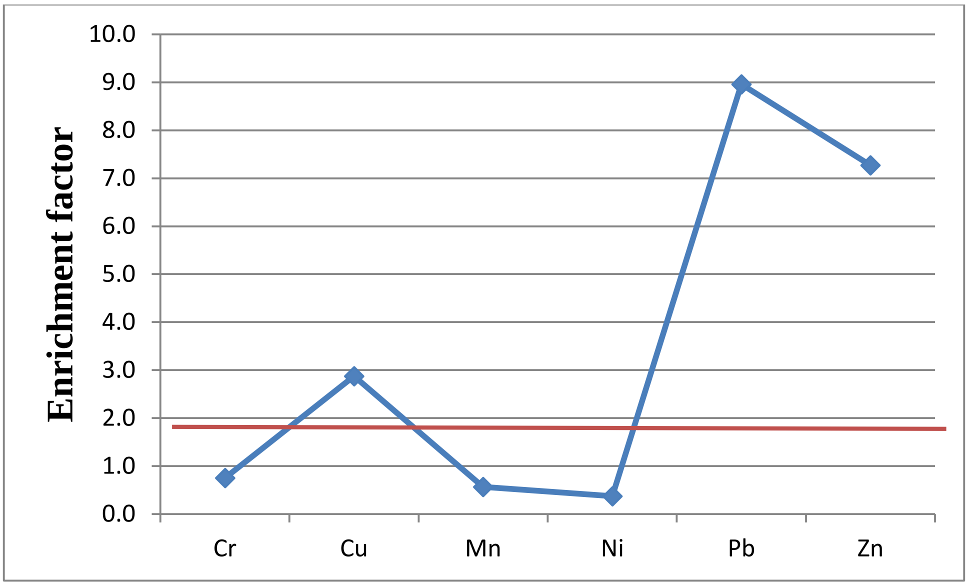


Figure 3.18 Enrichment factors of PTE measured in railway terminals. The bold horizontal line represents limit for minimal enrichment.

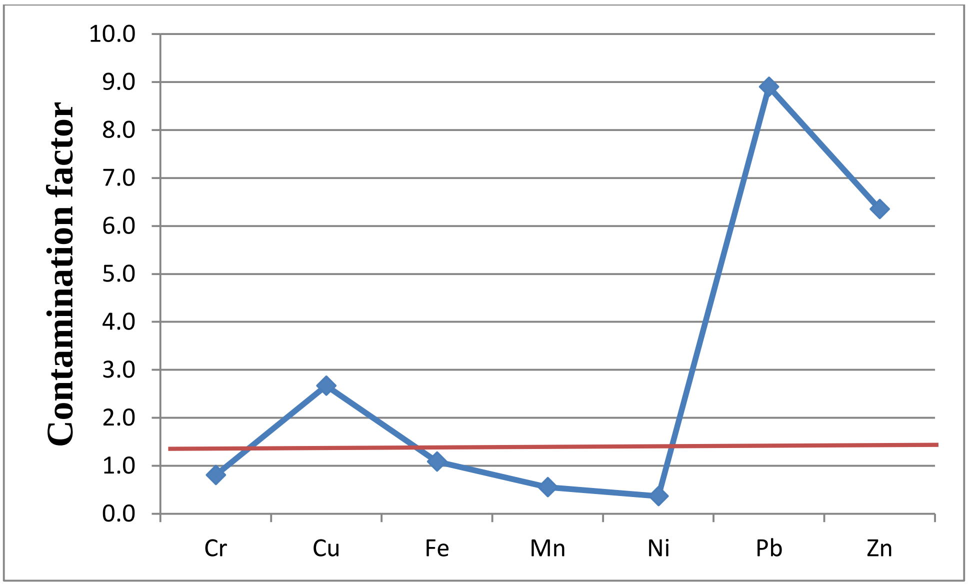


Figure 3.19 Geoaccumulation index of PTE measured in railway terminal soils. The bold horizontal line represents limit of contamination.

The only exception was Agege soil sample which had mean EF value of 7.1. Enrichment factor value for Pb ranged from 5.1 to 13.9 with an average of 9. This showed significant Pb enrichment in the soils analysed.

Zinc also showed significant enrichment in the soil analysed with an average EF value of 7.3 (range of 1.4 to 16.8). Agege train terminal soil had the highest EF value for Cu, Pb and Zn (7.1, 13.9 and 16.8 respectively).

Significant Cu, Pb and Zn enrichment observed for Agege terminal soil sample may be attributed to the frequent and busy train activities around the area. Agege is a densely populated area and the train station terminal and tracks were built across major roads. Continuous rail abrasion coupled with emissions from vehicles in the area could be the major sources of PTE in the soil samples collected in the vicinity. Enrichment factor of PTE in train terminal soils followed the order Pb > Cu > Zn > Cr > Mn > Ni. To a large extent, the Igeo results affirm the outcome of EF results. The PTE contamination trend followed the same order as EF; Pb > Zn > Cu > Cr > Mn > Ni. Table 3.20 shows the correlation coefficient results. Chromium and Fe showed negative correlation values with Cu and Zn and significant positive correlations with geogenic PTE, suggesting their main sources to be geogenic.

Table 3.20 Correlation coefficient analysis of PTE in railway terminal soils @ 95 % confidence level; n = 7.

	Cr	*Cu*	*Fe*	*Mn*	*Ni*	*Pb*	*Zn*	*% LOI*	*pH*
Cr	1								
Cu	-0.31	1							
Fe	0.94	-0.28	1						
Mn	0.16	-0.08	0.29	1					
Ni	0.51	-0.17	0.66	0.73	1				
Pb	0.22	0.18	0.47	0.70	0.89	1			
Zn	-0.10	0.67	-0.27	0.61	0.19	0.49	1		
% LOI	-0.13	0.19	-0.15	0.11	-0.10	0.15	0.16	1	
pH	0.01	-0.18	0.05	0.27	0.14	0.21	0.04	-0.34	1

Manganese, Ni and Pb showed similar behaviour in that, they were positively correlated with all PTE with exception to Mn-Cu (-0.08) and Ni-Cu (-0.17) and this is a likely indication that both PTE may have emanated from both geogenic and anthropogenic sources. Copper and Zn showed positive relationship between anthropogenic PTE and were negatively correlated with geogenic PTE suggesting their possible emanating sources to be mainly anthropogenic. Soil pH and % LOI showed low and negative correlations with PTE. These relationships indicate no significance.

3.7 General overview of PTE in Lagos urban soils and the impact of land use types on PTE distribution.

The values of pH and % LOI were discussed earlier in the chapter and their relationship with PTE concentrations were discussed for each land use. However, in order to get a clearer picture of the influence of these soil properties on PTE concentrations, linear regression showing the relationship between these variables was conducted. Soil properties (pH and organic matter) are important in determining the behaviour of PTE in soils. If the % LOI and pH are high in soils, PTE can become biologically inactive because colloids can bind them in forms that may not be available to plants or can cause reduced PTE lability. In the current study, the soil pH ranged from neutral to slightly alkaline and low organic matter content was obtained, therefore may be less significant. Figure 3.20 and 3.21, shows the relationships between the soil properties and PTE concentrations. Most of the soil samples analysed were near neutral except for few ones that were slightly alkaline. From Figure 3.20 and 3.21 it is apparent that the PTE concentrations measured in the soil were independent of the soil pH and % LOI. The values of R^2 for all PTE against pH were less than 0.15. Low organic matter content were measured in all of the soils. For all the samples analysed only three soils had % LOI above 5 % (Grand Foundry, Olusosun 1and 2; 5.06, 8.24, and 6.29 respectively). The low % LOI of the soils could explain the insignificant R^2 values obtained from Figure 3.21. The highest % LOI were found in soils collected from dumpsites, which may probably suggest that decayed or decaying plants debris and soil microorganisms or presence of vegetation at these sites may be responsible for the higher % LOI in comparison to other land uses.

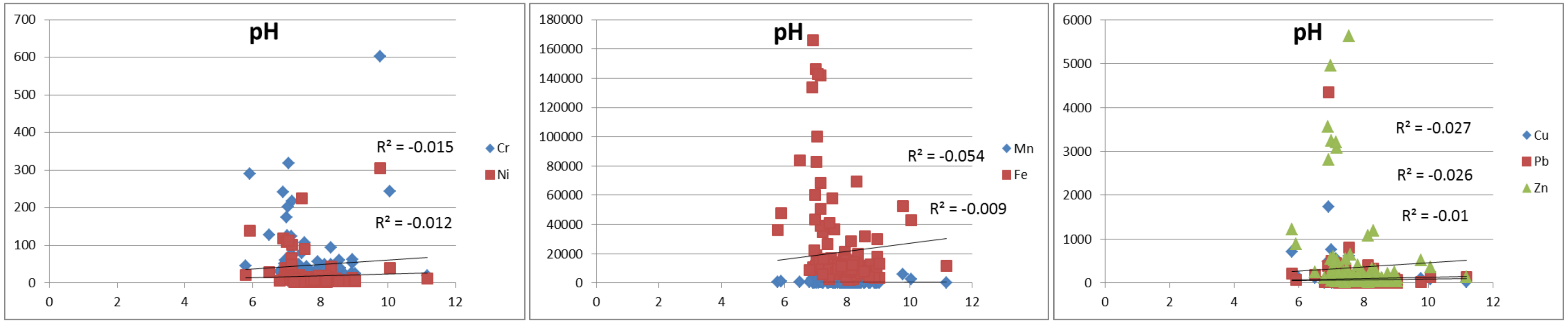


Figure 3.20 Linear regression relationships between PTE concentrations and pH for all soils studied.

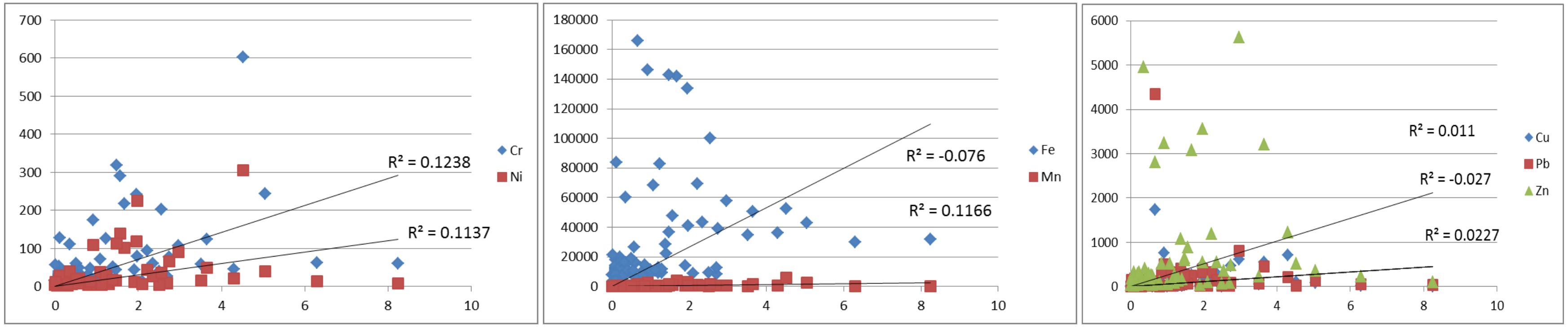


Figure 3.21 Linear regression relationships between PTE concentrations and % LOI for all soils studied

Vegetation was eroded in some of the school playgrounds and ornamental gardens sampled and since excessive trampling disrupts soil microorganism activities and their corresponding incorporation of litter into the soil, therefore the low % LOI measured at these sites were expected. The linear regression relationships between the soil properties (pH and % LOI) and PTE concentrations were insignificant and these were in agreement with correlation coefficient results for these variables in each of the land uses discussed earlier.

The overall mean concentrations of Cr, Cu, Fe, Mn, Ni, Pb and Zn in all the soil samples collected for this study (total of 124 samples) were 77, 198, 30600, 525, 34, 141 and 511 mg/kg respectively. The values were below the soil quality guideline values for Netherlands and the United Kingdom [292] with exception to Cu. The overall mean results of PTE levels in Lagos urban soils (this study) were compared to a previous study on PTE levels in Ibadan (capital of a neighbouring state to Lagos) [93] and Akure soils (capital of a South Western state)[86] . Results showed that PTE concentration were much higher in Lagos soils than those found in Ibadan and Akure soils (Table 1.1). A study conducted by Iwegbue[220] on the determination of PTE contents of soils collected from various land uses in Benin metropolis and Benin city (capital of a south southern state in Nigeria), revealed lower PTE concentrations compared to Lagos urban soils except for Pb. The overall mean levels of PTE concentrations in this study were found comparable to those found in large European cities whose main pollution sources include traffic and current or former heavy manufacturing industries. For instance, the levels of Cr, Cu, Mn, Ni and Pb in Lagos soils were comparable with those found in cities like Aberdeen[85], Naples[96], Palermo[37], Poznan, Poland[97], Tallinn[26], Seville[4], Madrid[76], Rostock[4] and Mexico city[268]. The very high PTE concentrations measured in the industrial estates and dumpsites were responsible for the comparable PTE concentrations observed. However, The average Pb concentration in Lagos soils were lower than that for Glasgow, UK[90] and Auby, France[87] soils. This may be attributed to the long histories of industrialization spanning several decades at these locations though it should be noted that much of PTE pollution in some old industrial cities of Europe is historical rather than current, due to the decline in heavy industries and improvements in environmental protection.

A previous study has likened the degree of PTE pollution in urban areas to time variation [269]. It is noteworthy to state that comparisons between these studies are somewhat relative and reported averages and ranges are all based on the methodology of a particular study. The non-uniformity of sampling strategies, study area, sampling locations (different land uses), number of samples, different sampling depth and extraction protocol can be a serious constraint in comparing published data. Because of the potential toxicity of PTE in urban soils and the threat to human health, there is need for harmonization of methodologies in study of the urban soil geochemistry of cities.

In terms of the influence of different land uses on PTE distribution (see Figure 3.22), as expected there was a clear distinction between the soils collected away from known point sources and those collected close to known point sources. The box plots showed Lagos soils varied widely in concentration, which reflects an array of lithogenic and anthropogenic impacts such as traffic emissions, industrial emissions, waste (domestic and electronic) disposal, soil transport and redistribution. The PTE concentrations were consistently higher for the second category of soils (IND, DS and TS) than the first category of soils (SH, RD, PO and OG). For IND, DS and TS, Chromium, Cu, Mn, Ni and Pb concentrations followed a consistent order of DS > IND > TS. This trend reflects strong influence from industrial activities and deposition of domestic, electronic, scrap metal, spent oil wastes on municipal dumpsites. Zinc was highest in IND followed by DS and TS in that order. Iron concentration followed the order IND > TS > DS. Industrial estate soils were obviously higher in Zn and Fe levels than the DS soils mainly because of the very high Zn and Fe concentrations in Ikorodu industrial estate soils. The concentrations of Zn and Fe measured in these soils were in multiple times higher than the SGV and typical soil concentrations. Atmospheric emissions from smelter plants, steel, aluminium and galvanised pipe manufacturing at this site may be responsible for the PTE enrichment in the soil samples. Indiscriminate dumping of scrap metals and improper disposal of wastes from these factories may have also contributed to the high levels of Fe and Zn in the soils.

For soils collected away from known point sources, PO presented the highest levels of Cu, Pb and Zn (37, 40 and 147 mg/kg respectively). This may be because most of the open spaces sampled were bus stations. The contributions of direct emissions from vehicles and refuse burning to soils at these vicinities were apparent. Traffic-related emissions have been identified as one of the main sources of Pb pollution in urban soils [24, 41, 65, 72, 121, 257, 269]. Lowest concentrations for Pb were measured in soils collected from school playgrounds. This may be expected as soils collected away from traffic and known point sources are likely to be less subject to PTE contamination [121]. Most of the SH soils sampled were located away from major roads and this reason may account for their lowest PTE concentrations in comparison to other land uses. Levels of Cu, Pb and Zn were higher in OG soils than SH. Reasons for higher PTE content here may include enrichment from organic amendments and closeness to traffic sources[12]. Influence of anthropogenic contribution to levels of PTE is likely because almost all of the parks and gardens sampled were located along major roads. Other studies have also reported PTE enrichment in urban park soils in relation to traffic sources[4, 269, 272]. Another reason may be the possible addition of organic amendments to the OG soils which may in turn have a considerable PTE content and consequently increasing the PTE contents of soils[12].

Concentrations of Cu, Pb and Zn followed a similar spatial distribution across the land use types studied (PO > RD > OG > SH). This pattern indicates strong influence from vehicular emissions coupled with other anthropogenic PTE sources. This is obviously in higher PTE concentrations measured in PO and RD soils; which are more likely to be susceptible to vehicular pollution. Chromium, Fe, Mn and Ni seems to be similarly influenced by land use as their median and mean values follow the same pattern OG > PO > RD > SH. The highest concentration for Cr, Fe, Mn and Ni were recorded in OG soils reflecting perhaps an influence from lithogenic sources. This may be likely since the creation of new parks and green areas in Lagos started 2008[276]. Generally, Cr and Ni levels in OG, PO, RD and SH presented low concentrations and this supports the earlier assertion that the primary source of these PTE in this category of land uses is probably of lithogenic origin.

For soils collected away from known point sources, the first group of PTE (Cu, Pb and Zn) were similarly influenced by anthropogenic inputs and this was evident in the decreasing concentrations of PTE measured in PO, RD, OG (land uses found along traffic axis and considerable proximities to industrial emissions) and SH soils (mostly located away from anthropogenic point sources).

The trend of Cr, Mn, and Ni pollution in all the land uses followed a consistent order of DS > IND > TS > OG > PO > RD > SH. For Cu and Pb the PTE variability in the land uses followed DS > IND > TS > PO > RD > OG > SH. Zinc distribution in the land uses followed IND > DS > TS > PO > RD > OG > SH and Fe distribution shows IND > TS > DS > OG > PO > RD > SH. It should be noted that SH consistently showed the lowest PTE concentrations for all the land uses, therefore it was the least polluted while DS was the most polluted. This current study has shown the variability and lack of uniformity of PTE distribution in the land uses studied and certainly attributed to different land use activities and disturbances ranging from duration and varied intensities of anthropogenic activities, geological characteristics of different soil types. This could alter environmental status of soil. Other studies have reported similar observations elsewhere noting the influence of land uses on PTE distribution in urban soils of cities in developing countries such as Akure, Nigeria[86], Benin, Nigeria[220], Dhaka, Bangladesh[15], Hoian, Vietnam[293], Hong Kong[294] and Beijing, China[72]. Figure 3.25 and 3.26 shows the variability of EF and Igeo values for each PTE across the land uses. The results reflect the varied anthropogenic influence of each PTE in the land uses. As expected the ‘’typical urban metals’’[76] had higher values than other PTE with Pb having the highest EF and Igeo values across all land uses followed by Zn and Cu in that order. In developed countries the variability of PTE content in different land use types may exert less impact because of the effective land use strategies, improvement in environmental control measures and the ban on leaded petrol. This premise may be supported by a previous work by Davidson *et al*[35], where authors noted that there was no relationship between PTE distribution and land use of five European cities. Similarly, Ljung *et al.*[295] reported no relationship between land uses and PTE distribution in urban soils of Uppsala, Sweden.

Economic development and industrialization which in turn will influence continued rural-urban migration are currently given greater emphasis than environmental protection in developing countries. Such high rate of growth in cites of developing countries has implications for the provision of urban infrastructural services which would prevent the continued increase in informal urban settlements and other existing problems such as traffic congestion, atmospheric, water and soil pollution, collapse of pubic service, proliferation of epidemic, and other negative environmental and socio-economic effects.

Unregulated urban residential layouts and poor urban planning decisions by local authorities have further worsened this problem. This is evident in some of the areas studied whereby houses are built directly behind dumpsites and some industrial estates co-located with residential settlements. This will apparently have a negative impact on environmental health. Another major problem at these cities is the poor or unavailability of spatial information. The sparse spatial data available are in forms of unscaled sketches, current and unclassified maps are at different scales and thereby these factors makes it difficult to share information efficiently between different sectors of the city. For the the rapidly urbanising megacities, the best environmental management practises that can mitigate against the current situation and consequences of increasing population growth are grossly inadequate and requires urgent attention. More research studies of this kind which can assist in urban planning decisions and policy making processes related to sustainable development that can accommodate present and future challenges at these cities is needed.

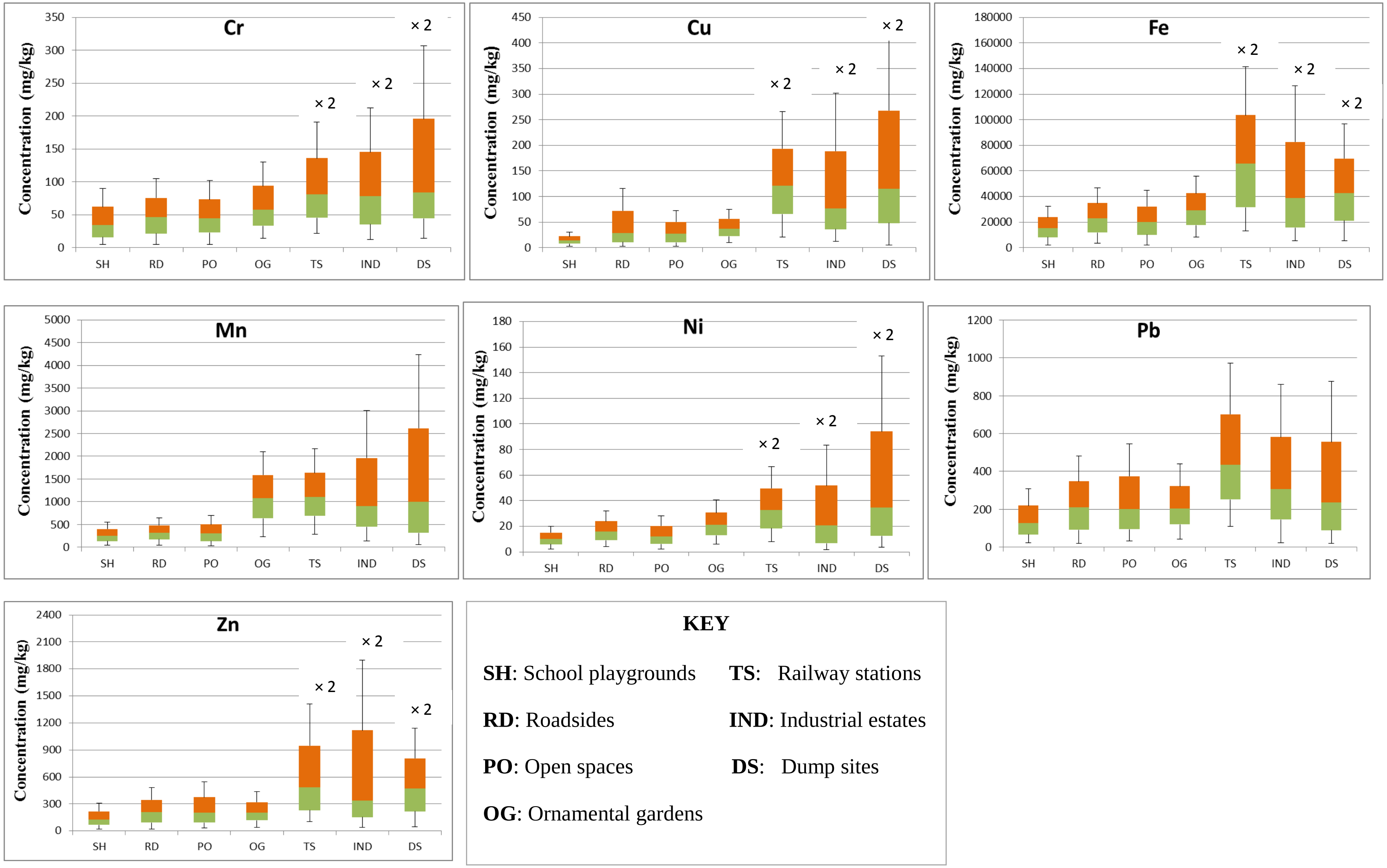
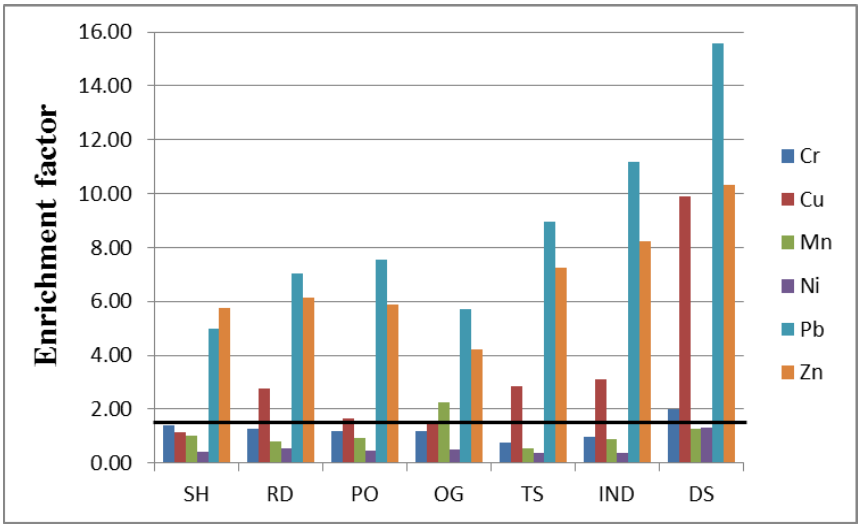


Figure 3.22: Box plots showing the variability of PTE concentrations in different land use types; Chromium, Cu, Fe, Ni and Zn plots for TS, IND and DS are ½ of actual concentrations.



KEY

SH: School playgrounds

RD: Roadsides

PO: Open spaces

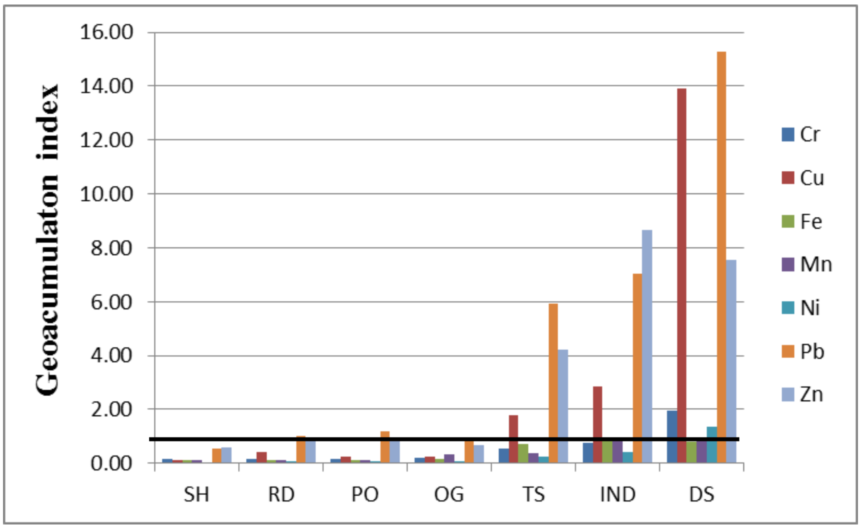
OG: Ornamental gardens

TS: Railway stations

IND: Industrial estates

DS: Dump sites

Figure 3.25: Enrichment factor showing the variability of PTE contamination in different land use types. The bold horizontal line represents limit for minimal enrichment.



KEY

SH: School playgrounds

RD: Roadsides

PO: Open spaces

OG: Ornamental gardens

TS: Railway stations

IND: Industrial estates

DS: Dump sites

Figure 3.26: Geoaccumulation index showing the variability of PTE contamination in different land use types. The bold horizontal line represents limit of contamination.

Generally, data from this current study have indicated that different land use types have specific inputs (anthropogenic and lithogenic) into the soil environment and have different variabilities in PTE contents and would exert different degrees of health impacts to humans. For instance, SH soils were consistently lower in PTE content compared to other land uses mainly because most of the schools sampled were located away from traffic sources or close to dumpsites. Roadside, PO and OG soils are located close to traffic and other anthropogenic sources and therefore were higher in PTE content than SH. Dumpsites receives daily load of municipal, electronic, medical and industrial wastes and industrial estate soils which have been impacted due to atmospheric emissions from factories were often more contaminated.

Therefore, these findings clearly demonstrate the need for setting up appropriate emission standards for vehicle and industries, as well as regulations and legislations on environmental issues which include effective solid waste management strategy and enforcement of environmental laws should be given close attention in order to reduce the impact of PTE pollution to the inhabitants of urban areas in developing countries.

3.8 Conclusions

The % LOI measured in the soils of this study were low. Soil pH ranged from neutral to slightly alkaline. Correlation coefficient and linear regression analysis between soil properties (pH and % LOI) and PTE concentrations were studied and result showed that the later was independent of the former. Negative correlations were generally obtained for the correlation coefficient relationships and R^2 values from linear regression results were low indicating no significance.

Pseudo-total acid digestion of urban soils of Lagos has shown that mean pseudototal PTE concentrations at locations remote from point sources of pollution were generally low and pose no risk, but soils taken from locations close to industrial activities such as foundries, dumpsites, and e-waste recycling sites were often highly contaminated.

Soils were collected away from known point sources as an indicator of ambient urban level of contamination and influence of socio-economic factors on PTE distribution and source characterization of PTE were investigated. Socio-economic areas (high, medium and low income areas) have been shown to influence the quality of Lagos urban soils. Potentially toxic elements accumulation in soils was in the order of VI < Ikeja < Ifako < Makoko < Lagos mainland. Vehicular pollution may have been an important factor because vehicle ownership in Lagos increased by 30 % in nine years (2002 to 2011)[281]. Most probable explanation for this could be the non-availability of other means of transportation coupled with the importation of used and poorly maintained vehicles. Victoria Island was the least contaminated area. Vehicular pollution arising from old vehicles may be less pronounced in this area. Ikeja and Ifako local government areas appear to have a similar contamination profile which maybe expected as they are next to each other.

Makoko and other parts of Lagos mainland local government had the highest PTE concentrations. This may be because strict adherence to environmental law and practises are not well established, especially in Makoko. Also, LM has a number of old establishments which date back several decades. Paint from these old buildings and the general dilapidation of most of these structures may have also contributed to the pollution load observed in this area.

Multivariate statistical analysis (principal component and cluster analysis) and correlation coefficients were applied to the pseudo-total PTE concentrations to determine the possible sources of PTE. Two major PTE groupings, one from lithogenic and one from anthropogenic sources, were identified. There was good agreement in the results of correlation coefficient analysis, PCA and CA confirming a predominantly lithogenic Cr-Fe-Mn-Ni association.

Similarly, the concentration of Cu, Pb and Zn appears to be controlled by anthropogenic inputs. Multivariate statistical analysis and concentrations of PTE in this work have provided new information about concentrations and possible origins of PTE in Lagos urban soils.

Potentially toxic elements levels in soils collected close to known point sources were higher than the SGVs indicating serious contamination levels. Based on comparison with soil guideline values for PTE, vicinities of Ogba and Ikorodu industrial estates were contaminated with PTE and Ilupeju and Ikeja industrial estate soils may be classified as unpolluted. Ikorodu industrial estate is recommended for immediate excavation as soils were extremely contaminated with PTE. As expected, most of the dumpsites studied were highly contaminated by PTE. Dasco soil appeared to be the most contaminated soil. Concentrations of PTE were about 6 to 20 times higher than the SGVs. According to environmental soil quality guideline criteria, concentrations of Cr, Cu, Pb and Zn in most of the dumpsites soils studied could be categorized as contaminated and extremely contaminated. Soils collected within and around train terminals appeared to be less subjected to PTE contamination in comparison with industrial estate and dumpsites soils. However, relatively high Pb and Zn concentrations were observed for Iddo and Agege terminal soil samples. This had been linked to possible contributions from wheel and track abrasion and high volumes of vehicles plying the vicinities.

The trend of Cr, Mn, and Ni pollution in all the land uses followed a consistent order of DS > IND > TS > OG > PO > RD > SH. For Cu and Pb the PTE variability in the land uses followed DS > IND > TS > PO > RD > OG > SH. Zinc distribution in the land uses followed IND > DS > TS > PO > RD > OG > SH and Fe distribution shows IND > TS > DS > OG > PO > RD > SH. School playground soils consistently showed less PTE concentrations for all the land uses, therefore it is the least polluted while DS was the most polluted. Dumpsites receives daily load of municipal, electronic, medical and industrial wastes and industrial estate soils which have been impacted due to atmospheric emissions from factories were often more contaminated.

As observed in the trend of PTE pollution in the land uses, soils collected from or close to potential point sources were more contaminated. There are indications that the higher concentrations of PTE measured in open spaces and roadside soils might have been influenced by vehicular pollution when compared with low PTE contents recorded in school playground soils. The school playground soils were generally less subjected to anthropogenic inputs probably because they are generally located farther away from emission sources such as roads and industries and this may have accounted for their low PTE contents. This current study has shown the variability and lack of uniformity of PTE distribution in the land uses studied and certainly attributed to different land use activities and disturbances ranging from duration and varied intensities of anthropogenic activities, geological characteristics of different soil types. This study has been able to demonstrate the possible influence of land use in the distribution of PTE in Lagos soil.

The ‘‘urban metals’’ (Cu, Pb and Zn) had the highest enrichment and contamination factor values in all the land uses studied and followed a pattern of Pb > Zn > Cu. Strong evidence was obtained that the high concentrations of these PTE in industrial estate soils, dumpsite soils and train terminal soils are of anthropogenic origin, since the concentrations were well above typical background levels and exceed the SGVs. Moderate to significant enrichment were also observed in SH, RD, PO and OG soils. Anthropogenic input of ‘‘typical urban metals’’ to the latter land uses was confirmed by PCA, CA and correlation coefficient analysis. Generally, minimal enrichment was observed for Cr, Fe, Mn and Ni, indicating no or low risk.

These findings clearly demonstrate the need for setting up appropriate emission standards for vehicles and industries, and for regular monitoring to be conducted to avoid risk to human health. Indiscriminate dumping of industrial waste, refuse and medical waste; continuous and uncontrolled emissions from industries and discharge of untreated effluents which are currently common practise in Nigeria and some other developing countries should be discouraged. Co-location of industrial and residential estates should also be discouraged and environmental guidelines must be strictly adhered in order to prevent possible health problems to inhabitants.

Considering the above highlighted summary of results and discussions, it is reasonable to conclude that, the aims and objectives of this current chapter have been achieved and can serve as a baseline for future urban soil studies relating to urbanised cities of developing countries.

4 Fractionation of PTE in urban soils of Lagos

4.1 Introduction

The potential risk PTE pose to humans was assessed in previous chapter by measuring ‘‘pseudototal’’ concentrations in Lagos urban soils. This gives information about potentially soluble or mobile contents of PTE not bound to silicates. Risk assessment to environment and human health were assessed based on comparison between PTE concentrations and threshold values for soil PTE pollution set by Environment Agency, UK and Department of Soil Protection, Netherlands. This form of evaluation was applied to soils collected both away from potential PTE point sources and in the vicinities of potential PTE point sources.

However, threshold values (SGVs) are based on the amount of PTE extracted from soil by employing strong acid digestion[41]. Such extractions tend to characterize the extent or total degree of pollution. Total or pseudo-total extraction over-estimates the risk of human exposure to PTE since only a fraction is actually available or bioavailable or bioaccessible. Mobility, availability and solubility of PTE determines their behaviour in the environment and this in turn depends on PTE binding to soil reactive sites, which is controlled by sorption, complexation and redox processes[30].

Weak extractions are used to predict or estimate the available, mobile or soluble fractions of PTE in soil[296]. These fractions may be categorized as ‘‘easily mobilisable’’. They can be determined to estimate the proportion that can become available for eventual uptake by plants and entry into the food chain[41]. To achieve this, extraction methods such as sequential extraction have been used to target element species in soil; or elements bound or associated with a particular phase or compound[55].

Sequential extraction involves the treatment of soil with a series of reagents to partition PTE content into various phases. Potentially toxic elements bound to particular soil phases are converted into soluble forms with the extractant employed for each step.

Several sequential extraction schemes have been developed and applied to different matrices[44, 59, 61, 125, 133, 134, 297-299]. The harmonised BCR sequential extraction technique has been employed in this work to study the chemical partitioning of PTE in urban soils of Lagos. Some attempts have been made to study PTE partitioning in industrial estate soils[300], agricultural soils[301], waste dumpsite soils[146], contaminated soils[144]and lagoon sediments[302, 303] from cities across Nigeria, little literature is available on Lagos urban soils and urban soils of rapidly urbanising cities or megacities in developing countries. While the limited literature available focused on a few PTE (mostly Cu, Pb and Zn) and one land use type; this study investigates a wide range of PTE (Cr, Cu, Fe, Mn, Ni, Pb and Zn) in soils collected from seven different land use types (dumpsites, train station terminal, industrial estates, open spaces, ornamental garden and roadside).

4.2 Aim and objective

To obtain information on potential mobility of PTE in Lagos urban soils to assess their likelihood of affecting other environmental media such as water and plants.

- Application of revised BCR sequential extraction protocol to measure PTE fractionation patterns and hence assess potential lability in Lagos urban soils.

The instrument detection limit for BCR sequential extraction measurements are within typical sensitivity values for ICP-MS measurements in soil samples (Table 4.1). The procedural detection limits values are fit for purpose as they are less than PTE concentration measurement in soil samples analysed.

Table 4.1 Instrument detection limits (µg/L) and procedural detection limits (mg/kg, d.w) of PTE measured in samples (BCR sequential extraction).

	Exchangeable		**Reducible**		**Oxidisable**		**Residual**	
	DL (ug/L)	DLpro (mg/kg)	DL (ug/L)	DLpro (mg/kg)	DL (ug/L)	DLpro (mg/kg)	DL (ug/L)	DLpro (mg/kg)
Cr	0.165	0.165	0.570	0.0570	0.217	0.0217	0.0624	0.0062
Cu	0.237	0.237	0.260	0.0260	0.747	0.0747	0.323	0.0323
Fe	0.650	0.650	2.68	0.268	6.27	0.627	0.216	0.0216
Mn	0.110	0.110	0.655	0.0655	0.169	0.0169	0.0525	0.0052
Ni	0.112	0.112	0.116	0.0116	0.087	0.0087	0.0389	0.0038
Pb	0.032	0.032	0.172	0.0172	0.474	0.0474	0.0080	0.0008
Zn	0.042	0.0426	0.758	0.0758	1.623	0.162	0.461	0.0461

4.3 Results and discussion

Quality Control

The quality of sequential extraction procedure employed in this work was assessed by extracting a certified reference material (BCR 701) in parallel with Lagos urban soils. This was necessary in order to evaluate batch-to-batch variations, accuracy and the methodology employed. Results of certified and obtained values are presented in Table 4.2. Agreements between the obtained and certified values were generally good. Recoveries of PTE in the exchangeable and reducible phases were 100 ± 10 % (except for Cr and Cu in exchangeable phase which had 88 and 85 % recovery respectively).

Table 4.2 Results of the analysis of certified reference material (BCR 701) for the extractable PTE contents (mg/kg)[304]

		Step 1	**Step 2**	**Step 3**	**Step 4**	**Sum**
Obtained	**Cr**	2.0 ± 1	45 ± 4	109 ± 9	80 ± 0.3	236
certified value		2.26 ± 0.16	45.7± 2.0	143 ± 7	62.5	253.46
% recovery		88	98	76	128	93
Obtained	**Cu**	42 ± 9	124 ± 15	39 ± 7	44 ± 3	249
certified value		49.3 ± 1.7	124 ± 3	55 ± 4	38.5	266.8
% recovery		85	100	71	114	93
Obtained	**Fe**	66 ± 8	370 ± 3	246 ± 43	21360 ± 81	22049
certified value						
Obtained	**Mn**	186 ± 25	5 ± 1	21 ± 0.1	261 ± 20	474
certified value						
Obtained	**Ni**	14 ± 9	25 ± 1	14 ± 0.2	40 ± 1	93
certified value		15.4 ± 0.9	26.6 ± 1.3	15 ± 0.9	41.4	98.7
% recovery		91	94	89	96	94
Obtained	**Pb**	3 ± 1	125 ± 8	3 ± 0.3	13 ± 2	144
certified value		3.18 ± 0.21	126 ± 3	9.3 ± 20	11	149.4
% recovery		94	99	32	122	97
Obtained	**Zn**	187 ± 25	104 ± 4	33 ± 1	118 ± 9	442
certified value		205 ± 6	114 ± 5	46 ± 4	95	460
% recovery		91	91	71	124	96

The standard deviation values (±) for the residual steps of the BCR 701 are not available in the production certificate.

The recoveries of PTE were poor in the oxidisable step compared to exchageable and reducible phases. An incomplete digestion of the step 2 residue (reducible phase) with hydrogen peroxide prior to the addition of ammonium acetate may have occurred. An unusual low Pb recovery was observed in the oxidisable phase (32 %). Sutherland[304] in 2010 reviewed measurement precision of BCR 701 in 10 years of sequential extraction analysis (2001 – 2010). He identified that reducible phase (step 2) is the most precisely measured for Pb, followed by exchangeable and oxidisable phases. Concerns relating to low Pb recovery (less than 50 %) of the certified Pb value in step 3 (oxidisable) in literature were highlighted, coupled with a high degree of imprecision associated with the measurement of Pb in step 3 in the BCR 701 certification process. These factors may have contributed to the poor Pb recovery in the oxidisable phase of BCR 701 measured in this work.

Recoveries of PTE in the residual phase ranged between 96 to 128 %; all PTE analysed had recoveries over 100 % except for Ni (96 %). Over extraction which is evident in the residual phase may be attributed to poor extraction efficiency in step 3 (oxidisable), which was mentioned earlier. In general, the sum of phases measured in BCR 701 and most of the Lagos urban soil analysed had good agreements with the pseudototal contents from the original sample (within ± 20 %). This suggests that the quality of the extraction was adequate.

Chromium

The average results and the RSD values for Cr measurement in the sequential extracts are presented in appendix F. Figure 4.1 and 4.2 shows Cr distribution in the various steps of the BCR extraction procedure. The precision for all phases were good as average RSDs for each step were generally less than 20 % (13 %, 9 %, 14% and 14 % for exchangeable, reducible, oxidisable and residual respectively). Average Cr recovery (sum of all phases extracted relative to pseudototal concentrations) for all samples ranged from 73 to 102 %. Exceptions to this were under extraction recorded in Owode 3 sample (66 %) and over extraction in Dasco soil sample (135 %). Figure 4.1 and 4.2 shows Cr to be predominantly associated with residual phase.

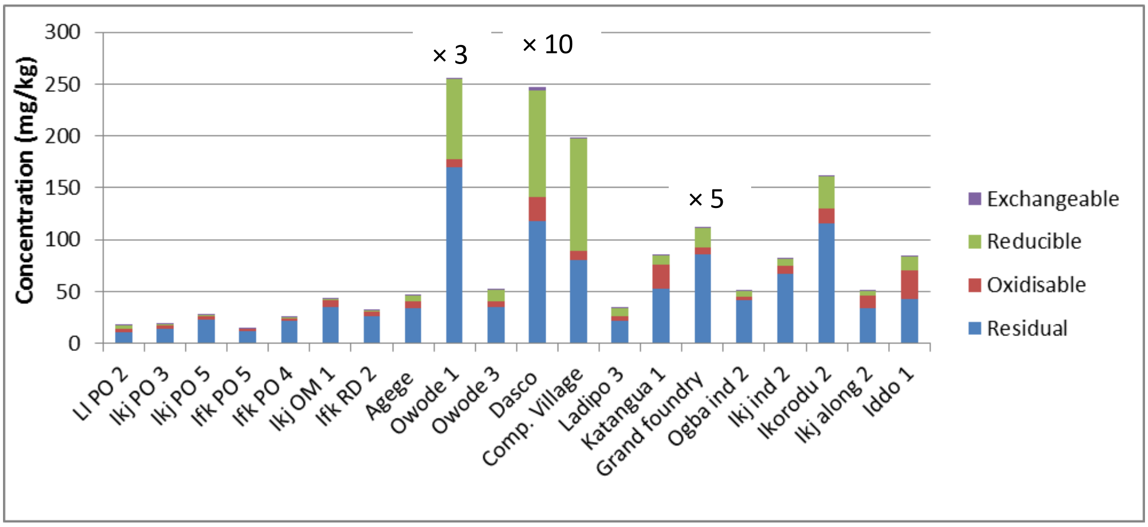


Figure 4.1 Mean concentration of Cr in the Lagos urban soil sequential extracts; actual concentrations of Dasco, Grand Foundry and Owode 3 soils are plotted at 1/10, 1/5 and 1/3 actual concentrations, respectively.

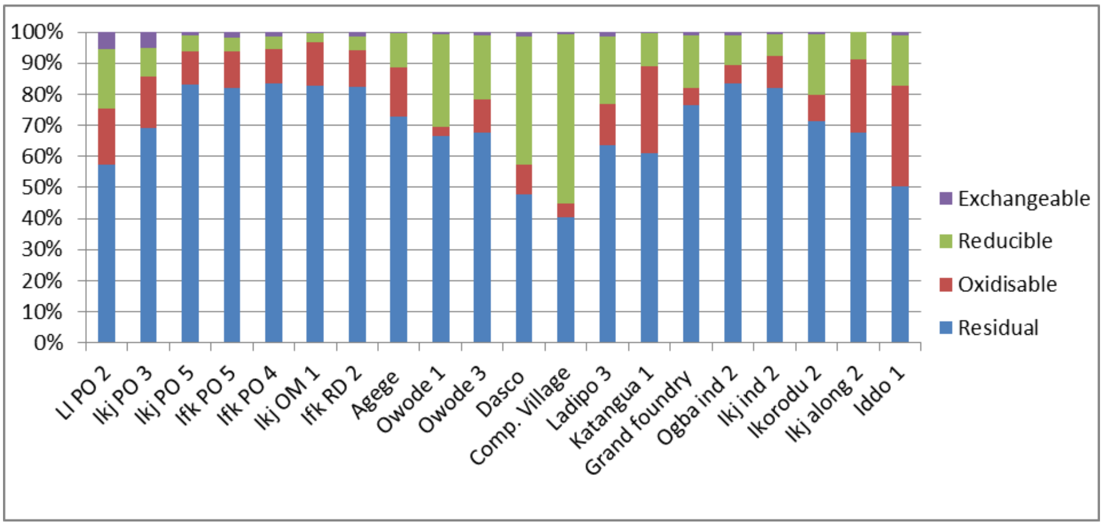


Fig 4.2 Percentage fractionation pattern of Cr in the soil samples

About 75 % of the samples studied had over 70 % of Cr content in the residual phase. This is in agreement with sequential extraction results of urban soils from other studies[142, 218]. Yongfeng *et al.*[141] found 92 % of Cr in the residual phase of urban soils of Guiyang city, China. Results of the current study are also similar to Cr behaviour in the urban soils of three European cities (Glasgow, Ljubljana and Torino)[35].

The high Cr content in the residual phase showed that element is strongly bound to minerals with preferential incorporation into silicate lattices of primary and secondary minerals[142]. This however suggests that mobilization of Cr is unlikely under normal environmental conditions and therefore poses no danger. Of concern however is one of the soil samples (Dasco soil) which had 41 % (1021 mg/kg) of its Cr content in the reducible phase. This is worrisome because the reducible phase Cr content was about four times the CLEA value for Cr (230 mg/kg). There is a high tendency of re-mobilization for Cr under reducible conditions in the soil.

Copper

Figure 4.3 and 4.4 shows the phase associations of Cu in the soil samples and appendix F reveals the data and % RSD values for measurements. The overall percentage RSDs of measurements were generally good (< 20 %) with the exception of a few soils which had % RSD values higher than 30 %. Ikj PO 5, Ifk PO 4 and Dasco soils had percentage RSDs of 36, 33 and 69 % in the residual phase while Katangua and Ifk PO 5 soils had percentage RSDs of 38 and 39 % in the reducible phase. The overall average % Cu recovery with respect to pseudototal concentrations was 89 %, although there were marked variations which ranged from 60 to 147 %. Copper was found mainly in the reducible phase accounting for about 45 % of the total extractable PTE. The association of Cu with iron and manganese oxides and hydroxides have been well documented in polluted urban soils, dusts and sediments in other studies[135, 143, 146, 218, 305-307]. An appreciable amount of Cu was found in the oxidisable phase which account for about 18 % of the extractable PTE content. This is in agreement with results obtained by Szolnoki *et al.*[143]. Authors reported 24 % of Cu in the oxidisable fraction of soils of urban vegetable gardens in Szeged, Hungary.

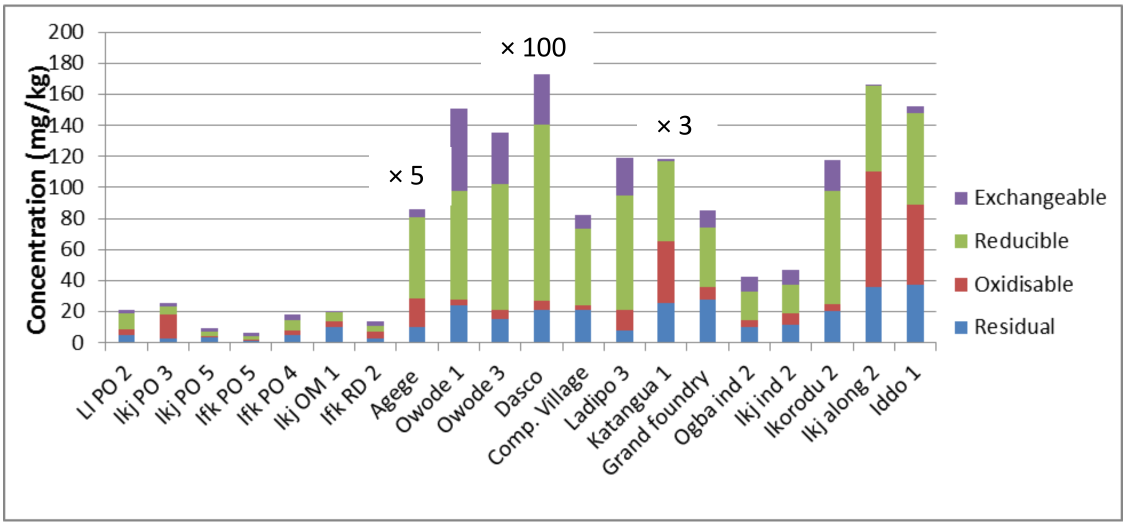


Fig 4.3 Mean concentration of Cu in the Lagos urban soil sequential extracts; actual concentrations of Dasco, Katangua and Agege soils are plotted at 1/100, 1/5 and 1/3 of actual concentrations respectively.

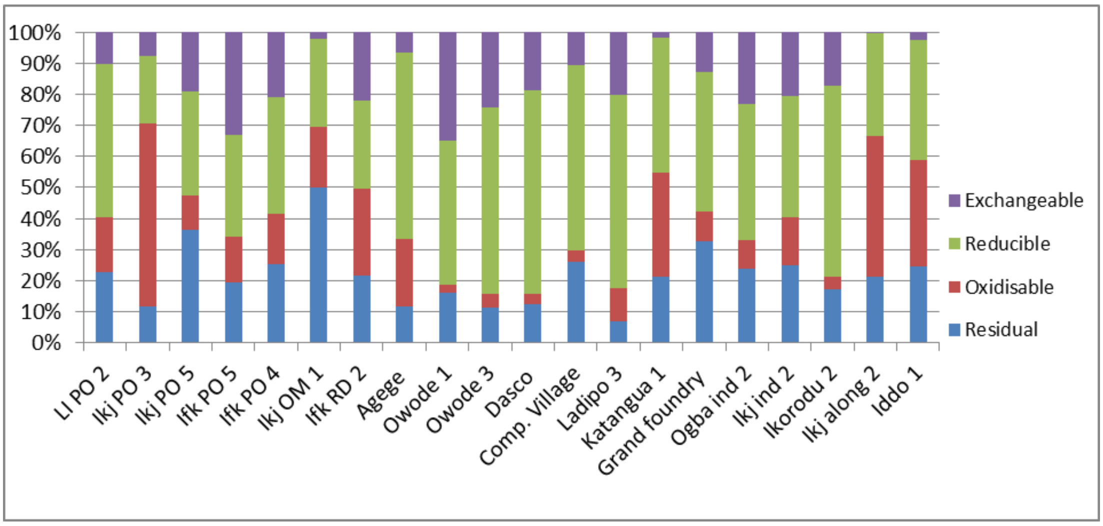


Fig 4.4 Percentage fractionation pattern of Cu in the soil samples

This indicates possible association between Cu and organic matter which under oxidising conditions in the environment may be degraded and complexed Cu may be released for mobilization[122]. The summation of Cu content in the non-residual phases of Ikorodu, Dasco and Katangua soils was 487, 15100 and 467 mg/kg, respectively, which is of concern.

These values are about 2 to 80 times higher than the Dutch intervention values (190 mg/kg)[100]. This indicates a serious potential health hazard to residents of the areas where the soils were collected. About 78 % of the total extractable Cu content for all soils studied were in the non-residual phase, thus indicating a high potential mobility of Cu under changing environmental conditions. Generally, the fraction size of Cu followed the order reducible > residual > oxidisable > exchangeable. This trend agrees with reports of Umoren *et al.*[146] and Zauyah *et al.*[308] for Cu partitioning in refuse dump soils and cultivated ultisols (red clay soils) respectively.

Iron

Figure 4.4 and 4.6 represents Fe distribution in the soils and appendix F presents the data and % RSD values for measurements. The % RSD values were generally good (< 20 %) with a few exceptions for reducible, oxidisable and residual phases.

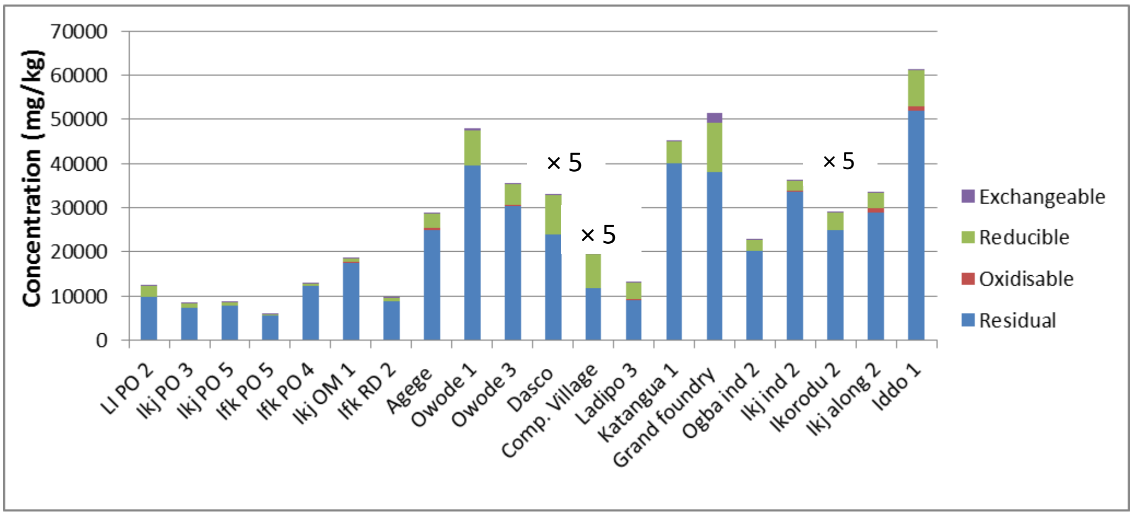


Fig 4.5 Mean concentration of Fe in the Lagos urban soil sequential extracts; actual concentrations of Dasco, Ikorodu 2 and Comp. Village soils are 1/5 of actual concentrations respectively.

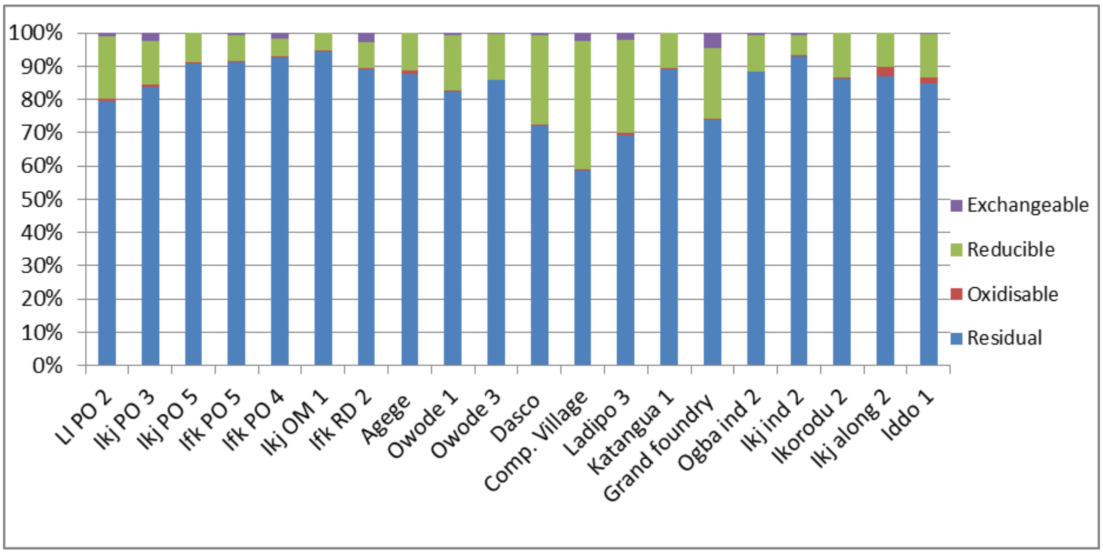


Fig 4.6 Percentage fractionation pattern of Fe in the soil samples

In contrast, the RSD for the exchangeable phase was generally poor, up to 89 % with an average of 33 %. Reasons for this were unclear. Overall mean recovery in respect to pseudototal concentrations was 87 %. About 98 % of total extractable Fe was present in the reducible and residual phases with 78 % associated with the residual phase as expected, because its minerals constitute a major structural component of soil. The reducible phase also had a significant amount of Fe which is about 14 % of the total extractable Fe. This is also expected since the reducible phase of the BCR protocol targets the release of PTE associated with iron and manganese oxyhydroxides. Results obtained in this current study are similar to reports of Fe behaviour in urban soils of five European cities[35], urban vegetable garden soil[145] and intertidal sediments[306]. The dominance of Fe distribution in the residual phase indicates that its release under changing environmental conditions is unlikely and thus suggests low mobility and bioavailability in the environment.

Manganese

Manganese partitioning is shown in Figure 4.7 and 4.8 and the % RSD values are shown in appendix F. The precision of Mn extractions were generally good (< 15 %) with a few exceptions in the exchangeable and oxidisable phases which exceeds 20 % but were less than 30 %. Manganese was found in all the four phases with residual and reducible phase dominating the distribution.

The reducible phase had the largest amount of extractable Mn with an average of about 38 %. This is expected and similar to earlier discussions on the significant amount of Fe found in the reducible phase. Manganese is one of the most abundant elements in the earth crust[306] and its noticeable presence in the reducible phase is predictable because the hydroxylamine-hydrochloride reagent employed in reducible phase of the sequential extraction principally targets Fe-Mn oxyhydroxides. The residual fraction also had a significant amount of Mn species (about 35 %). The general pattern of average Mn distribution was in the order of reducible > residual > exchangeable > oxidisable. This is similar to the study of Davidson *et al.*[35] who found the largest proportion of Mn in the reducible phase of urban soils from five European cities, with significant amounts of Mn in the exchangeable phase (24 %). Other studies also reported high mobility tendency of Mn which was related to its prevalence in the first three fractions (exchangeable, reducible and oxidisable phases)[187, 306, 309]. Non-residual phases account for about 65 % of Mn in this work and the element may be generally categorized as being considerably mobile. However, Grand Foundry, Ikorodu 2, Dasco and Computer Village soils with pseudototal concentrations of Mn above 1500 mg/kg (5719, 2625, 1567 and 1561 mg/kg respectively) had the largest proportion of Mn in the residual fraction (67, 55, 37 and 54 % respectively).

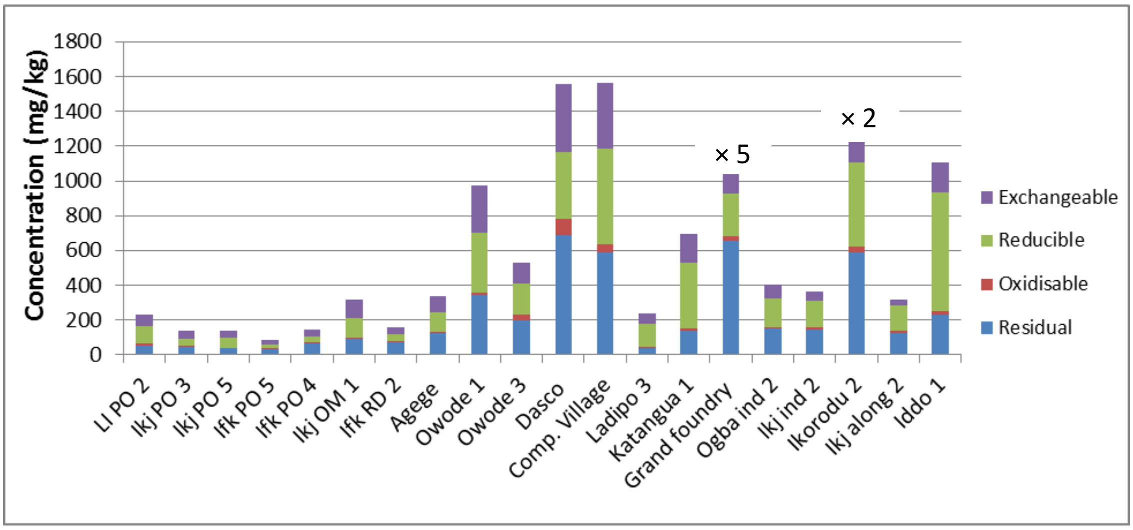


***Fig 4.7 Mean concentration of Mn in the Lagos urban soil sequential extracts; actual concentrations of Grand Foundry and Ikorodu 2 are 1/ 5 and 1/2 of actual concentrations respectively*.**

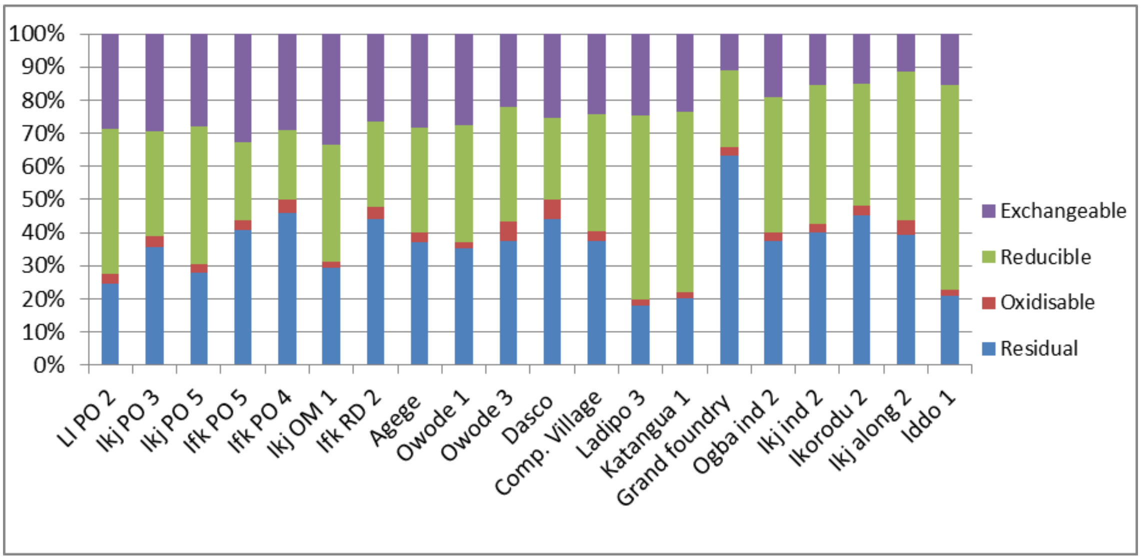


Fig 4.8 Percentage fractionation pattern of Mn in the soil samples

Therefore, mobility tendencies of Mn in this group of soils may be reduced. Manganese was partitioned almost uniformly between reducible, residual and exchangeable fractions (38, 35 and 24 % respectively). However, some of the soil samples had their predominant fraction in the reducible phase and some in the residual unlike Cr, Cu and Fe which had consistent patterns of distribution for the soils studied.

Nickel

The results of Ni measurements and RSD are presented in appendix F and Figure 4.9 and 4.10 shows the partitioning of Ni. The precision of Ni extractions were generally good (< 15 %) with exceptions from Dasco and Grand Foundry soils in step 4 (45 and 29 % respectively), Ifk PO 5 soil in step 3 (31 %), Ikj PO 5 in step 2 (22 %), and Ifk PO 4 and Ifk RD 2 in exchangeable phase (22 and 22 % respectively) which had RSDs greater than 20 %. The average recovery of sequential extraction measurements of Ni with respect to pseudototal concentrations was 91 %.

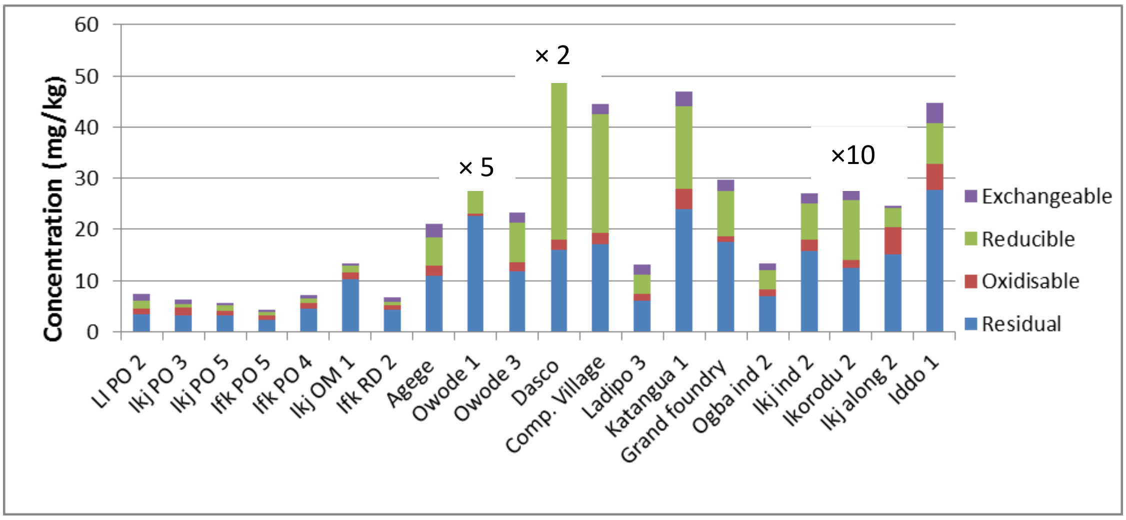


***Fig 4.9 Mean concentration of Ni in the Lagos urban soil sequential extracts; actual concentrations of Ikorodu 2, Owode 1 and Dasco are 1/10, 1/5 and ½ of actual concentrations respectively*.**

As seen for Cr and Fe, the distribution pattern of Ni between the phases followed a regular pattern with the residual phase being dominant (54 %) indicating low mobility. These three PTE were generally lithogenic and are associated with silicate matrix. This is in agreement with sequential extraction results of other studies which found the largest proportions of Ni in the residual phase of urban vegetable garden soils[143], urban soils[35], urban street dusts[40] and sediments[84]. Exceptions to Ni residual phase dominance were Dasco and Comp. village soils which had 57 and 56 % of Ni in the reducible phase. Apart from these two soils, studied soil samples followed a consistent pattern of residual > reducible > exchangeable > oxidisable. Nickel displayed similar behaviour to Cr in Comp. village and Dasco soils where a significant amount was found in the reducible phase. This indicates considerable environmental concern. 71 and 66 % of pseudototal PTE were present in labile forms; summing steps 1-3, Dasco soil was four times higher than the SGVs for Ni (CLEA and Dutch intervention values).

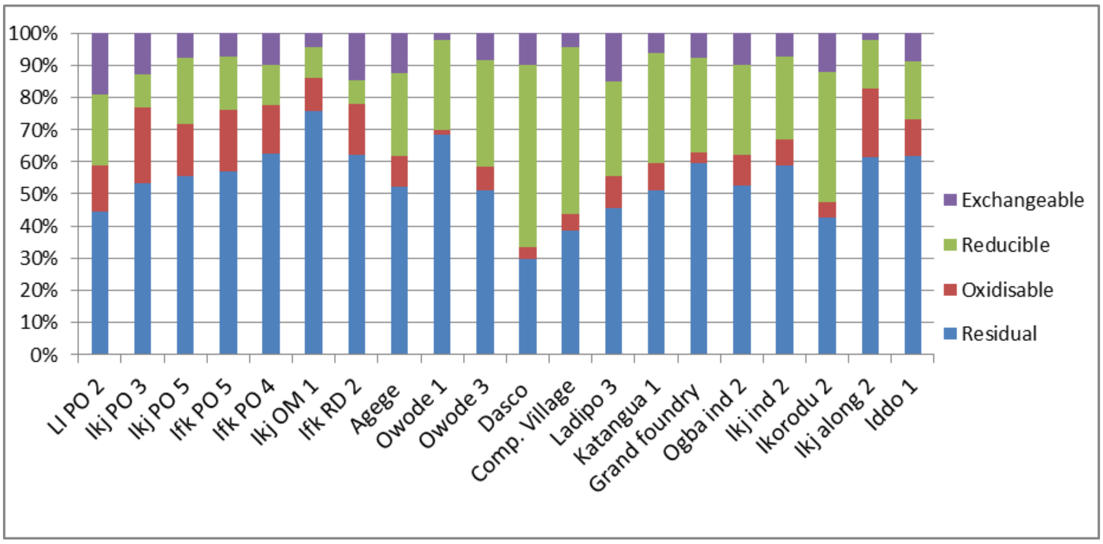


Fig 4.10 Percentage fractionation pattern of Ni in the soil samples

Changes in pH of soil samples can cause mobilization of the PTE which is a considerable risk to human health. As observed for Cr, Cu, Fe, Mn Ni, there are tendencies for higher PTE concentrations to be present in the mobile fractions, particularly in the reducible phase.

Generally, most of the soils had the highest proportion of Ni in the immobile form (step 4; residual phase) and the summation of Ni in the mobile fractions (except for Dasco soil) did not exceed the soil guideline values. Consequently, this element may not likely pose any environmental or health risk to inhabitants of these areas.

Lead

The mean results and % RSD values for Pb distribution in various fractions are shown in appendix F. Figure 4.11 and 4.12 shows the partitioning pattern of Pb in soils studied. Precision of Pb extractions were generally good (RSD < 20 %). A few exceptions occurred e.g. for Pb measurements in the residual phase of Ifk rd 2 (28 %), exchangeable phase in Katangua soils (28 %). Reducible phase measurement was the least reproducibly extracted phase for Pb in the samples as three soils exceeded RSD of 20 %. Ladipo, Ikorodu and Katangua soils had RSD values of 54, 25 and 22 % respectively. The reasons for the high RSD value in Ladipo soil were unclear but may be partly due to the in-homogeneity of Pb in soils.

The overall average Pb recovery with respect to pseudototal concentration was good (88 %). The distribution of various Pb fractions revealed that the largest proportion of Pb was associated with the reducible phase; accounting for about 64 % of the total extractable Pb. This indicates that Pb mainly occurred in the form bound to Fe-Mn oxides or sulfide minerals. Possibilities of Pb forming stable complexes with Fe-Mn oxides have been reported[122, 310]. In contrast, hydroxyl amine hydrochloride has also been demonstrated to dissolve sulfide minerals in sediments[311] and mining waste[312], therefore sulfide bound Pb in Lagos urban soils could have been extracted. Umoren *et al.*[146] found the largest percentage of extractable Pb (75 %) associated with the reducible fraction in their study of refuse dumps soils in Uyo metropolis, southern Nigeria. Similar observations were reported in previous studies for other urban areas[35, 80, 141, 299, 313]. Contradictory observations to the results of this current study were reported for PTE fractions in urban soils of Naples[79], Nanjing[218] and Jordan[88] urban areas. These authors reported that Pb associated mainly with the residual phase (77, 57 and 58 % respectively).

A large proportion of Pb was associated with reducible phase in Dasco and Katangua soils (89 and 77 % respectively) and this is of environmental concern. Their concentrations (2460 and 688 mg/kg) in this fraction pose a serious potential health risk if mobilised as they are about two to five times higher than the CLEA value for Pb (450 mg/kg). The potential exists for mobilization of Pb under reducing conditions such as changes in redox potential. Lead associated with the reducible phase can also be liberated by erosion processes of top soils and transported to a new environment such as road surfaces[314]. The sum of the first two fractions of Ikorodu soil (480 mg/kg, higher than CLEA's 450 mg/kg for Pb) is also a source of environmental concern because Pb present in the exchangeable phase is likely to be readily available to the environment (113 mg/kg) in addition to the possible mobilization of Pb in the reducible phase (367 mg/kg).

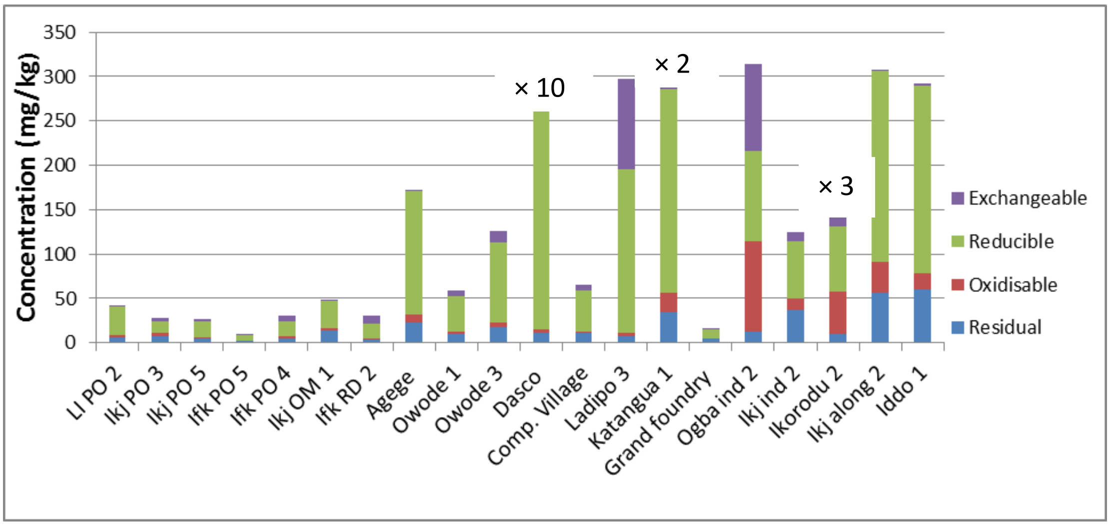


Fig 4.11 Mean concentration of Pb in the Lagos urban soil sequential extracts; Dasco, Ikorodu 2 and Katangua 1 soils are 1/10, 1/3 and ½ of actual concentrations respectively.

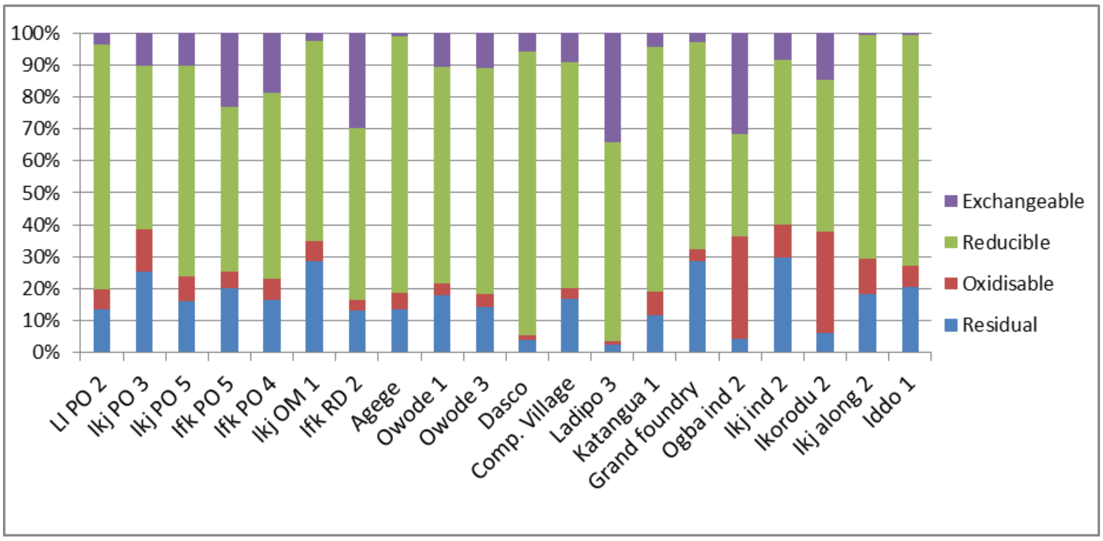


Fig 4.12 Percentage fractionation pattern of Pb in the soil samples

There was a similar pattern for Pb distribution between the fractions of the soil samples (reducible > residual > exchangeable > oxidisable). The exception to this was the Ogba ind 2 soil where Pb is almost evenly distributed between the first three fractions (32 % for step 3, 32 % for step 2 and 31 % for step 1). Appreciable amounts of Pb were also found in the exchangeable fractions of Ladipo 3, Ifk PO 5, Ifk PO 4 and Ifk RD 2 soil samples.

Zinc

Average results and RSD values for the measurement of Zn in the sequential extracts are shown in appendix F and Figure 4.13 and 4.14 shows the partitioning of Zn among the target phases for Lagos urban soils studied.

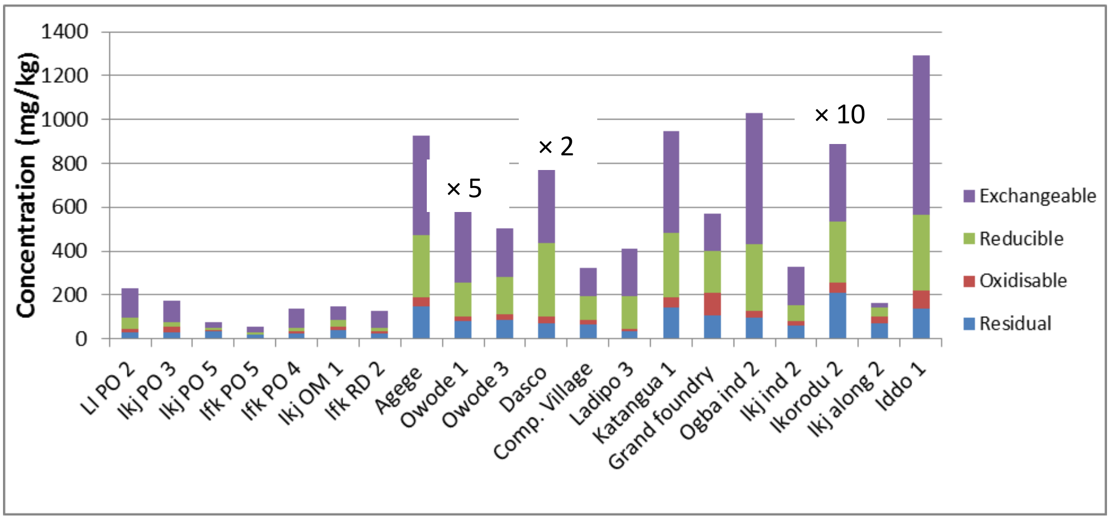


Fig 4.13 Mean concentration of Zn in the Lagos urban soil sequential extracts; Ikorodu 2, Owode 1 and Dasco are 1/10, 1/5 and ½ of actual concentrations respectively.

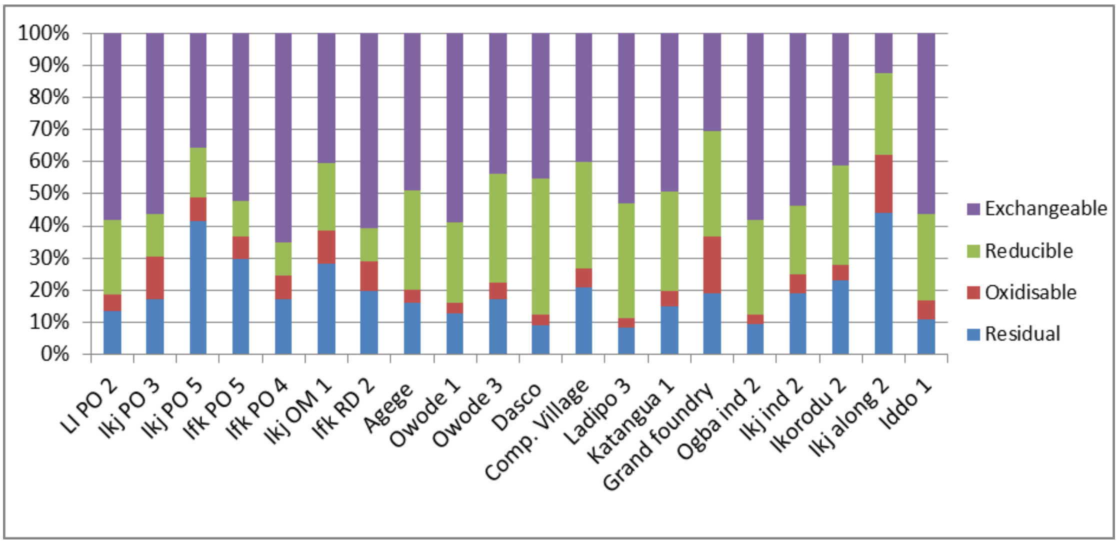


Fig 4.14 Percentage fractionation pattern of Zn in the soil samples

Precision of Zn extractions were generally good (average RSDs for each of the fraction measurements were less than 15 %).

However, high RSD values were observed in measurement of residual phase for Ikj PO 5 (36 %), reducible phase of Ogba ind 2 (37 %) and exchangeable phase of Iddo 1 (41 %). The overall average Zn recovery with respect to pseudototal concentration was 89 %. The greatest amount of Zn was associated with the exchangeable phase, averaging 48 %. The reducible phase was the next most important fraction with an average of 25 %, followed by the residual phase (20 %) and the oxidisable phase (7 %). The high Zn content in the exchangeable phase was similar to studies of three urban rivers and Lagos Lagoon sediments by Oyeyiola *et al.*[303] who found Zn strongly associated with the exchangeable phase (40 to 87 %). This may be typical of Lagos urban soils since considerable amounts are being washed away to adjoining rivers and the Lagos Lagoon[315]. Similar findings to this study were reported for soils and dusts collected in other urban areas by Chon *et al.*[316], Li *et al.*[40], Sutherland *et al.*[317], Umoren *et al.*[146] and Tokalioglu *et al.*[187]. Other studies reported a rather different observation as the residual phase was dominant in soils of Naples city, Italy and Honolulu, Hawaii[79, 314]. The reducible phase was considered to be the dominant phase for Zn in the study of urban vegetable garden soils in Szeged, Hungary[143] and urban soil and dusts in Hong Kong, China[265]. The variability of the dominant phases for Zn species as observed in literature, points out the heterogeneity of urban soil composition.

An average of about 80 % of extractable Zn was found in the labile fractions (sum of exchangeable, reducible and oxidisable fractions) making Zn the most mobile element among the PTE studied. This is environmentally significant and of concern since Zn concentration in urban soils has been suggested to be primarily controlled by anthropogenic sources[317]. The sum of the non-residual fractions in about half of the soils collected close to potential point sources exceeded 750 mg/kg (Dutch intervention value for Zn[100]). Dasco and Ikorodu soils were about two times higher in Zn concentration than the Dutch intervention value and Katangua soil was about four times higher. The concentration of Zn in these soils is worrisome and potential for mobility is high under changing environmental conditions. These soils have the potential to cause serious health risks humans.

4.4 Correlations between PTE in various fractions of the BCR sequential extraction and pseudototal concentrations.

Simple Pearson correlation coefficient between two variables was used to study the relationship between PTE extracted in the exchangeable phases and pseudototal concentrations and also between the sums of PTE extracted in the mobile phases (step 1-3; exchangeable, reducible and oxidisable) against pseudototal concentrations (at 95 % confidence level). Table 4.3 shows the correlation coefficient results.

Positive correlations were observed for Cr, Cu, Ni and Pb (0.57, 0.51, 0.62 and 0.59 respectively) where correlation coefficient values revealed that the amount of PTE extracted in the first fraction was dependent on its respective pseudototal content. Manganese and Zn displayed a different behaviour as the correlation coefficient showed higher dependence of extractable PTE in step 1 on pseudototal contents (0.88 and 0.94). This indicates that the higher their concentrations, the higher the PTE content available to be readily released to the environment. As discussed earlier, it is worrisome that subsets of the soils were polluted with Zn and the typical concentration of Mn in urban soils was exceeded in some of the soils; this is obviously of environmental concern. Iron extracted in exchangeable phase showed weak correlation with its pseudototal content (0.21) and this suggests little or no risk.

To evaluate the overall potential environmental risk, the relationship between the sum of PTE extracted in the non-residual phases and pseudototal contents was analysed. Chromium, Fe and Ni correlation coefficient values (0.84, 0.61 and 0.70) showed positive correlation with pseudototal contents but displayed less dependency compared to Cu, Mn, Pb and Zn (0.90, 0.94, 0.95 and 0.96 respectively). It is apparent from the sequential extraction results that Mn and the anthropogenic PTE were more mobile than elements likely to have a largely geogenic origin. Generally, the sum of PTE (Cr, Cu, Fe, Mn, Ni, Pb and Zn) extracted in the mobile fractions has showed to be highly dependent on their respective pseudototal contents. The significance of this in the soils studied indicates that the higher the pseudototal concentrations the higher the availability and the likelihood of causing toxicity risks to human and ecological receptors.

Table 4.3 Correlation coefficient relationship between BCR extractable PTE in exchangeable phase, **∑ step 1-3** ***and pseudototal concentrations (n = 20; at 95 % confidence level).***

PTE	**Exchangeable phase**	**∑ step 1-3 (Exchangeable + reducible + oxidisable fractions)**
Cr	0.57	0.85
Cu	0.51	0.91
Fe	0.21	0.61
Mn	0.88	0.95
Ni	0.62	0.71
Pb	0.59	0.96
Zn	0.94	0.97

4.5 Conclusion

The work in this chapter showed the successful application of the BCR sequential extraction protocol to study PTE (Cr, Cu, Fe, Mn, Ni, Pb and Zn) behaviour in Lagos urban soils. Information about mobility and possible human health risk was revealed. Generally, results of phase associations with PTE were in agreements with previous studies.

Sequential extraction results showed that Cr, Fe and Ni were predominantly associated with the residual fraction which implies less mobility and less environmental risk. Copper was found to be mainly associated with the reducible phase. Copper was identified to be considerably mobile taking into account its significant presence in other non residual phases (exchangeable, reducible and oxidisable). Of great environmental concern were some contaminated soils which had significant amounts of Cu present in the reducible phase and were many times higher than the Dutch intervention value. Copper may mobilize under reducing or changing environmental conditions. Lead was mainly associated with the reducible phase in some samples, and was twice the CLEA value of 450 mg/kg. The potential exist for mobilization under changing environmental conditions to pose significant risk to human health. The highest proportion of extractable Zn was found in the exchangeable phase making Zn the most mobile element among the PTE studied.

5 Application of bioaccessibility test to human health risk assessment of PTE in soil samples and PM_{10} isolated from soils.

5.1 Introduction

It is increasingly recognized that the human health risk associated with contaminated urban soils, resuspended inhalable soil fractions or dust is not related with the total or pseudototal PTE concentration but the biologically available portion of the contaminant[318]. Children are exposed to PTE via myriad of means which include ingestion of contaminated food or drink, dermal contact, inhalation of contaminated particulate matter in the ambient air, direct ingestion of soil in school playgrounds as well as urban gardens. Oral ingestion of soil can occur deliberately or accidentally. Deliberate soil ingestion is used for medicinal purposes as part of religious beliefs, often called geophagia[319] and deliberate consumption of soil or non-nutritive substances may occur in children between the age of 1 to 3 years old owing to their frequent hand to mouth activities, and this is typically termed as ‘‘pica behaviour’’. Children are the group of humans most susceptible to the adverse health effects arising from soil PTE pollution because of their small body size, developing nervous system and high exposure[252]. Many studies have employed various risk assessment model to evaluate the potential adverse effect PTE in soil may likely cause to human receptors and have considered the ingestion route as the main source of high blood metal level of children in some areas[7, 22, 103, 320]. These risk assessment models assumes 100 % bioavailability of the contaminant in the blood stream of human thereby overestimating the risk PTE may pose since only a fraction of the contaminant will be available for absorption in gastro-intestinal tract of humans. Therefore a realistic risk assessment based on toxicity of soluble doses of PTE from soils is needed to provide a more conservative approach to evaluate associated risks.

Inhalation of dust or particulate matter is an important route by which PTE gets into the human body. For some PTE such as As, Cd and Se, the inhalation contribution from soil re-suspended particulate matter is considered to be less than 1 %, while for other elements, such as Ni, the inhalation pathway is considered to be the most significant exposure pathway[321].

Particulate matter (PM_{10}) in ambient air is widely studied and related to human health and a fraction of it comes from re-suspended soil particles[322]. The PM_{10} is the fraction of suspended particulate matter usually monitored in the study of human health risk exposure[323]. This is because it represents the ambient particulate matter that gets into the respiratory tract of humans[120, 324]. The PM_{10} fraction has been linked with contaminant toxicity, respiratory symptoms, exacerbation of chronic respiratory and cardiovascular diseases, decreased lung function and mortality[120, 249, 323]. Studies carried out in the past revealed that the health effect of particles are dependent on it composition[325].

Potentially toxic elements are one of the most studied pollutants in PM_{10} fractions because of their ubiquitous, toxic and cumulative behaviour[21, 217].These PTE are primarily released via atmospheric emissions[263, 326]. They have been reported to preferentially bind to PM_{10} fraction[13, 120]. This may be because fine particulate matter has high specific area which absorbs PTE[3]. Mass contributions and loadings to ambient PM_{10} fractions in cities across the world have identified several sources including resuspended soil and dust[327-334]. A recent study has also indicated that the highest PM_{10} emission along US – Mexico border had originated from soil and debris on the side of unpaved road[335]. Similarly, the transport and resuspension of mobile fractions of urban soil and dusts particles have been suggested to contribute to PTE enrichment in low traffic urban areas in Toronto, Canada[336].

Fine fraction of soil particles (< 10 µm, PM_{10}) can be resuspended by air flows generated by wind or action of human feet, thereby contributing to the atmospheric particulate matter load. The PTE laden particulates remain suspended and transient in the atmosphere before being deposited on land and in water[3]. Considering the various potential human health risks associated with PTE in PM_{10} fraction of resuspended urban soils and dusts, there is a need to investigate their toxicity. Concerns about increasing concentrations of particulates in developing countries and its resultant effects such as premature mortality and morbidity related health issues have been noted[249, 337]. Several studies which include estimation, bioaccessibility and risk assessment of PTE in PM_{10}samples have been done in developed countries[330, 338-344].

Little previous research has focused on developing countries, even though they are more susceptible to health risks associated with PM_{10}[249], their concentrations are much higher than developed countries[249]. This may be largely due to the inefficient environmental management strategies, increasing urban population, and urban infrastructural deficit in many developing countries.

Attempts have been made in some developing countries such as China[345-347] and Brazil[337] to study health risks associated with PM_{10} in urban areas but literature is still sparse in this regard. Some attempts have also been made to study elemental concentrations in PM_{10} collected from Lagos Nigeria[348, 349]. However, these studies utilized respirable dust samplers and low volume Gent stacked filter for PM_{10} sampling. Potentially toxic elements were detected in the samples collected but none of the study reported PTE concentration in fugitive dusts or PM_{10} isolated from urban soil. Evidence of particle size distribution was also not reported in these studies. To this end, as the exposure to particulate matter is ubiquitous and involuntary, there is need to study significance of PM_{10} as it relates to human health of the general public.

In a bid to assess the risk associated with exposure to PTE, some studies have employed the use of *aqua regia* extractable PTE for the evaluation of potential amount of PTE ingested by human[7, 252], this method is considered unsuitable since only a fraction of the PTE is actually available for absorption into the blood stream of humans. Potentially toxic elements dissolution in the human digestive system may be determined by measuring the bioaccessibility, or the fraction that is soluble in the gastro intestinal tract and available for absorption into the blood stream[350].

Bioaccessibility testing can be used to ‘‘*confirm the presence of dangerous substances that pose a significant risk to human health*’’ as stated in the European soil strategy[41]. Various bioacessibility estimation protocols have been developed[151, 152, 154, 161]. These *in vitro* tests simulate the human gastro-intestinal tract especially of children, the target group most susceptible to accidental or deliberate ingestion of non-food substances such as soils[351]. Presently, there is no standard method for estimating bioaccessibility.

Of the *in vitro* methods that currently exist, the simple bioaccessibility extraction protocol (SBET) is the simplest, cheapest and the fastest to carry out. This procedure is a simplified form of PBET extraction[154] and was developed by USEPA for US laboratories to apply bioaccessibility testing regimes[352]. This method has undergone extensive validation by USEPA and it has been suggested to be the likely standard procedure for bioaccessibility testing[351].

The SBET has been employed in previous urban soil studies in developed countries to determine bioaccessible PTE concentrations and health risk assessments in children and adults[7, 157-159] but no information or literature is available on risk assessment of PTE in urban soils of Lagos and most developing countries using oral bioaccessibility testing. Part of the aims of this current study is to address this gap.

The SBET can also be applied to inhalable fraction of soil since the 2.5 – 10 µm particle size fractions are often deposited in the tracheal and bronchial region of the lower respiratory tract of humans and transported within a few hours by the mucociliary clearance[342, 353, 354]. This fraction reaches the gastro intestinal tract where it reacts with gastric juices thereby representing the available (bioaccessible) fraction, which is quantified for risk assessment studies. The SBET was chosen as the extraction protocol for soils and PM_{10} isolated from soil samples in the current study, because it is simple, fast, cheap and not cumbersome. Again, no studies of PTE bioaccessibility in PM_{10} fraction and associated human health risks appeared to have been carried out in Lagos and rapidly urbanising cities in developing countries. Therefore, the data from this current study would provide useful information for future studies aiming to estimate bioaccessible PTE concentrations arising from ingestion or inhalation of soil particles and hence their potential impacts on human receptors in the urban environment.

5.2 Aim and objectives

The aim of this chapter is to assess the human health risks associated with the PTE measured in the soils and potential resuspended soil fractions. Specific objectives include:

- Application of SBET to soil samples in order to predict the fraction available for absorption in the gastrointestinal tract of humans.
- To assess the level of risk PTE in urban soil poses to children in the event of both deliberate and unintentional soil ingestion.
- To examine the effectiveness of an optimised PM_{10} isolation method from soils and its adaptability to real test urban soil samples.
- To revise the current SBET procedure by miniaturising sample mass and extractant volume and its adaptability to small amount of PM_{10} samples isolated from urban soils.
- To assess PTE levels in potentially resuspended urban soil (PM_{10} fraction) and to appraise the incorporation of bioaccessibility results into the current inhalation human health risk assessment model (which assumes 100 percent bioavailability of PTE in the blood stream of humans) thereby, the associated health risks to both children and adult receptors can be determined.

5.3 Detection limits

The instrument detection limits for SBET extraction measurements are within typical sensitivity values for ICP-MS measurements (Table 5.1) and procedural detection limits calculated are less than concentrations of PTE in test samples.

Table 5.1 instrument detection limits (µg/L) and procedural detection limits (mg/kg, d.w) of PTE measured in samples (SBET extraction)

	DL (ug/L)	DLpro (mg/kg)
Cr	0.339	0.169
Cu	0.525	0.262
Fe	1.303	0.651
Mn	0.332	0.166
Ni	0.192	0.096
Pb	0.131	0.0656
Zn	1.42	0.711

5.4 Potentially toxic elements bioaccessiblity in soil and PM_{10} samples

This chapter is in two parts and the first section focused on the discussions relating to oral PTE bioaccessiblity in Lagos urban soils and assessment of associated risks to children. The second section discusses the effectiveness of optimised PM_{10} isolation method from soil samples, its applicability to real test samples and incorporation of bioaccessbility results to inhalation risk assessment model.

5.4.1 Oral PTE bioaccessibility estimation in Lagos urban soils

The SBET biocessibility extraction test was performed on the same set of Lagos urban soils as subjected to BCR sequential extraction (see section 2.1.3). The soils were further sieved to obtain < 250 μm size fraction because this represents the particle size which adheres to children's hands[178]. The estimation of potential health risks was calculated from the amount or concentration of PTE extracted by the SBET procedure. Table 5.2 shows the bioaccessible concentrations and percentage RSDs of PTE measured in soil samples and Table 5.3 shows the bioaccessible concentrations of PTE expressed as percentage of pseudototal concentrations (% BA) and was calculated using Equation 5.1. The % BA indicates the fraction of the pseudototal concentration which will be potentially bioaccessible or available in the human GIT.

$$\% BA = \frac{bioaccessible\ concentration}{pseudototal\ concentration} \times 100$$

Equation 5.1

The linear relationship between the two variables is expressed as correlation coefficients, shown in Table 5.4. The aim of the correlation coefficient computation was to assess the dependency of bioaccessible concentrations on pseudototal concentrations. This allowed for an inference to be made if higher pseudototal PTE concentrations in soil relates to amount of potentially bioaccessible PTE fraction in the human GIT. Discussions relating to Table 5.2, 5.3 and 5.4 are shown from page 161.

Table 5.2 *Bioaccessible PTE concentration in Lagos urban soils (n = 3; mg/kg).*

Location	Cr	% RSD	Cu	% RSD	Fe	% RSD	Mn	% RSD	Ni	% RSD	Pb	% RSD	Zn	% RSD
LM PO 2	3.55	4.68	14.5	14.6	665	6.00	111	4.98	2.82	5.38	37.3	7.11	218	19.4
Ikj PO 3	1.82	6.36	6.91	8.04	424	2.92	51.5	8.07	0.97	5.81	12.2	3.15	95.4	3.09
Ikj PO 5	0.99	15.3	7.29	13.2	244	17.4	64.0	5.28	1.04	2.00	21.2	12.2	15.7	40.5
Ifk PO 5	0.49	3.28	5.51	2.38	195	2.38	34.3	1.44	0.51	0.44	7.43	2.46	8.05	19.3
Ifk PO 4	0.74	17.1	10.1	17.4	276	13.6	50.0	10.0	0.77	2.2	25.2	11.4	95.5	4.97
Ikj OM 1	0.44	9.70	8.09	6.29	72	12.4	130	4.23	1.17	2.46	23.1	22.2	57.9	20.3
Ifk RD 2	0.54	10.9	8.03	12.4	225	8.00	40.1	9.73	0.56	6.43	11.5	9.35	47.3	10.6
Ogba ind 2	0.74	10.8	20.7	18.7	235	11.0	69.4	1.47	2.06	10.90	132	4.49	705	3.54
Ikeja ind 2	1.84	18.0	25.0	13.1	408	17.6	62.8	12.3	2.70	5.00	44.7	17.5	171	15.2
Ikorodu 2	3.35	10.2	218	15.1	984	8.34	507	16.3	25.5	1.37	256	15.0	1560	0.68
Ikeja along 2	1.05	17.1	45.6	13.0	105	19.4	65.5	19.7	1.79	1.00	140	21.2	23	29.3
Iddo 1	2.50	3.84	43.1	9.96	462	1.17	191	5.80	6.21	3.92	85.1	9.19	668	0.49
Agege	2.21	14.2	143	4.00	369	8.00	165	14.2	6.53	9.74	106	23.3	821	4.17
Owode 1	5.20	25.1	162	15.6	1540	21.6	440	9.96	8.75	22.1	46.2	22.3	926	4.12
Owode 3	1.51	18.6	67.5	10.9	612	11.0	134	12.4	4.01	10.2	76.4	7.36	270	0.69
Dasco	162	11.6	7290	7.92	5710	14.1	521	7.08	275	10.3	910	4.52	1690	4.83
Comp. Village	3.08	4.73	23.1	5.97	1990	8.31	478	4.34	3.54	1.56	31.1	3.78	209	14.1
Ladipo 3	1.94	9.66	115	12.8	1090	9.46	102	8.40	3.84	9.61	292	11.9	379	20.4
Katangua 1	4.45	3.27	186	9.33	512	7.37	347	3.17	9.14	8.56	392	4.53	4000	2.71
Grand Foundry	31.7	4.61	16.7	7.38	4380	8.16	743	1.42	15.4	9.26	7.97	10.3	350	4.50

Table 5.3 Bioaccessible concentrations of PTE expressed as percentages of pseudototal concentrations.

% BA	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
LM PO 2	16	60	5	48	37	43	91
Ikj PO 3	7	32	4	29	16	46	54
Ikj PO 5	3	70	2	30	13	87	16
Ifk Po 5	3	66	3	25	11	71	20
Ifk PO 4	2	35	2	25	4	62	58
Ikj OM 1	1	44	0.3	36	7	41	36
Ifk RD 2	1	40	2	25	7	40	36
Ogba ind 2	2	29	1	20	11	37	65
ikeja ind	2	35	1	14	7	31	40
Ikorodu	2	29	1	20	23	51	48
Ikeja along	1	41	0.1	16	6	77	10
Iddo	3	26	1	16	14	26	56
Agege	5	20	1	41	31	50	67
Owode	2	89	3	49	6	60	105
Owode	2	51	1	24	2	23	49
Dasco	9	62	3	34	26	21	60
Computer Village	2	28	2	30	10	31	59
Ladipo	4	101	7	39	37	93	74
Katangua	4	34	1	21	18	86	125
Grand foundry	5	16	8	12	5	37	67

Table 5.4 Correlation coefficient analysis of SBET and Pseudo total PTE concentrations (n = 20; @ 95 % confidence level)

PTE	SBET extractable PTE
Cr	0.98
Cu	1.00
Fe	0.60
Mn	0.67
Ni	0.96
Pb	0.92
Zn	0.89

Chromium

Average bioaccessible Cr concentrations (shown in Figure 5.1) were below 10 mg/kg with the exception of Dasco and Grand Foundry soils (162 and 32 mg/kg respectively). Their higher bioaccessible concentration may be attributed to the high pseudototal concentrations of the soils (1831 and 601 mg/kg respectively). Apart from Owode 1 which had 25 %, percentage RSDs for Cr measurement were less than 20 %. The % BA of Cr were generally low. It ranged from 1 to 16 % with an average of 4 %. The majority of soils analysed contained less than 5 % bioaccessible Cr indicating low bioaccessibility. Assessment based on pseudototal concentrations may have greatly over estimated the risk Cr poses in these soils since only a small fraction of it would be available for absorption in the gastro intestinal tract. Low Cr bioaccessibiity in the test may be corroborated with the sequential extraction results in chapter 4. A larger percentage of Cr contents (about 70 %) in the same set of soils were found in the residual phase indicating low availability.

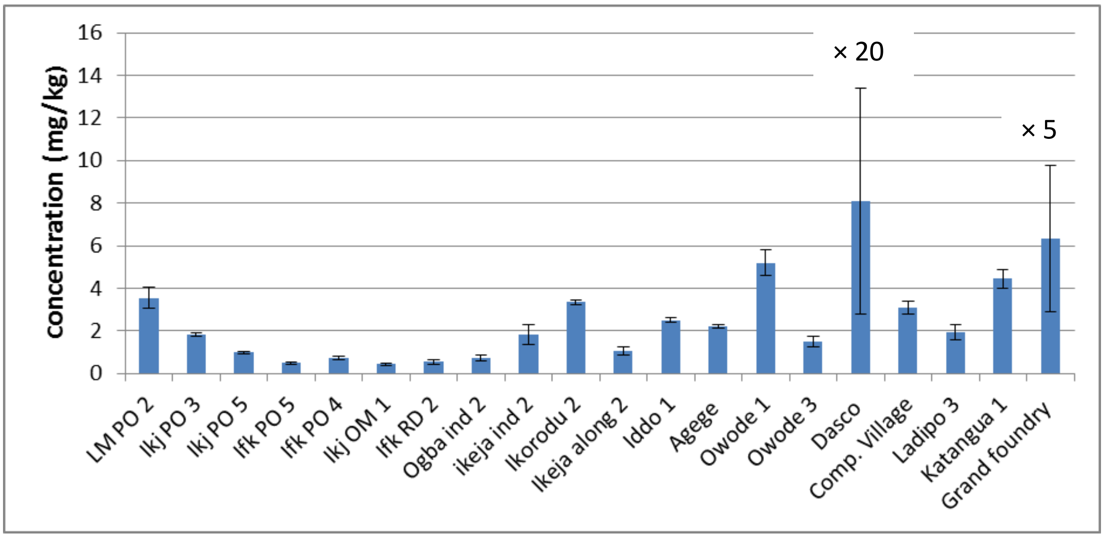


Figure 5.1 Bioaccessible concentrations of Cr in soils (mg/kg). Dasco and Grand Foundry's soils are plotted as 1/20 and 1/5 of actual concentrations, respectively.

The Cr bioaccessbility result of this study is similar to the findings by Sialleli *et al.*[48] who found that less than 3 % of the pseudototal Cr was bioaccessible in the stomach phase of PBET extraction of Glasgow soils. Other studies reported low Cr bioaccessibility in urban soils similar to this study; average of 5 % in Glasgow soils (UBM)[46], average of 4 % in urban playground soils of Sweden (RIVM)[355], average of 1.9 % for soils collected across Canada and USA (SBET)[163]. A good linear relationship between the bioaccessible and pseudototal Cr concentrations in the soils was indicated by a value the correlation coeffcient of 0.98 (see Table 5.4). This shows that the bioaccessible Cr content was highly related to the pseudototal concentrations.

Copper

Average bioaccessible concentrations of Cu are shown in Figure 5.2. Percentage RSDs for Cu measurement were less than 20 % . The % BA of Cu in the soils studied ranged from 16 and 89 % with an average of 46 %, thus Cu may be categorised as considerably bioaccessible. Copper lability in sequential extracts (chapter 4) showed that and average of 78 % of Cu was present in the non- residual phases and therefore support the assertion that Cu is considerably bioaccessible or available in the soil samples.

Of particular concern was the % BA measured in Dasco soil which suggests that 62 % of the pseudototal content (7290 mg/kg) of the soil would be available for absorption in the GIT of children. This is many times higher than the CLEA and Dutch SGVs suggesting high potential toxicity risks. Similar and highly variable Cu bioaccessibility was observed in both contaminated and uncontaminated soils. However, an exceptional Cu bioaccessibility was recorded in Ladipo 3 soil (101 %). This represents all Cu availability in the GIT, similar to a study of paddy soils collected fromthe Duckum Au-Ag mine, Korea where the maximum % BA was 102 %[356]. Copper have been identified to be highly bioaccessible in previous studies[162, 357]. Okorie *et al.*[358] in their study of PTE in soils collected from an urban recreational site in Newcastle upon Tyne, UK found bioaccessible Cu to range between 62 to 78 %.

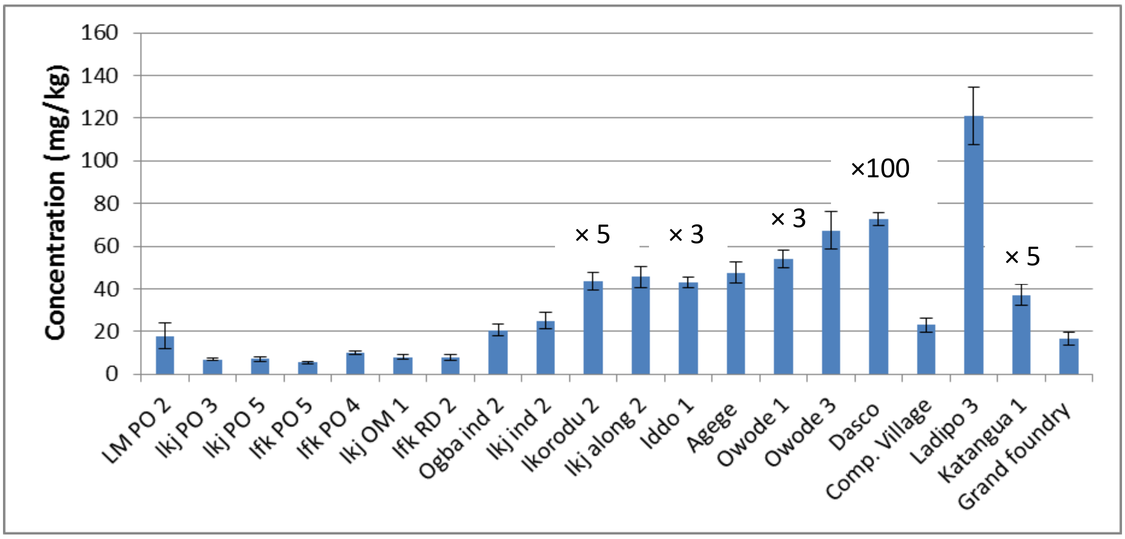


Figure 5.2 Bioaccessible concentrations of Cu in soils (mg/kg). Ikorodu 2, Agege, Owode 1, Dasco and Katangua's are plotted as 1/5, 1/3, 1/3, 1/100 and 1/5 of actual concentrations, respectively.

A highly significant positive correlation (see Table 5.4) was found between bioaccessible Cu and its corresponding pseudototal concentrations (1.00). This indicates that bioaccessible Cu was totally related to pseudototal concentrations, as also found by, Ettler *et al.*[164] who reported highly significant positive correlations between total and bioaccessible Cu concentrations (0.997) in soils collected around mining and smelting areas in the Zambian copper belt.

Iron

The average concentration of bioaccessible Fe in soils studied are represented in Figure 5.3 and Table 5.2. The percentage RSD apart from Owode 1 (21.6 %) for was less than 20. The % BA of Fe was between 0.1 and 8 %. A previous study[48] reported 10 % as the average % BA for Fe in Glasgow urban soils. Iron in comparison with other PTE measured in this work had the lowest average bioaccessible concentration value.

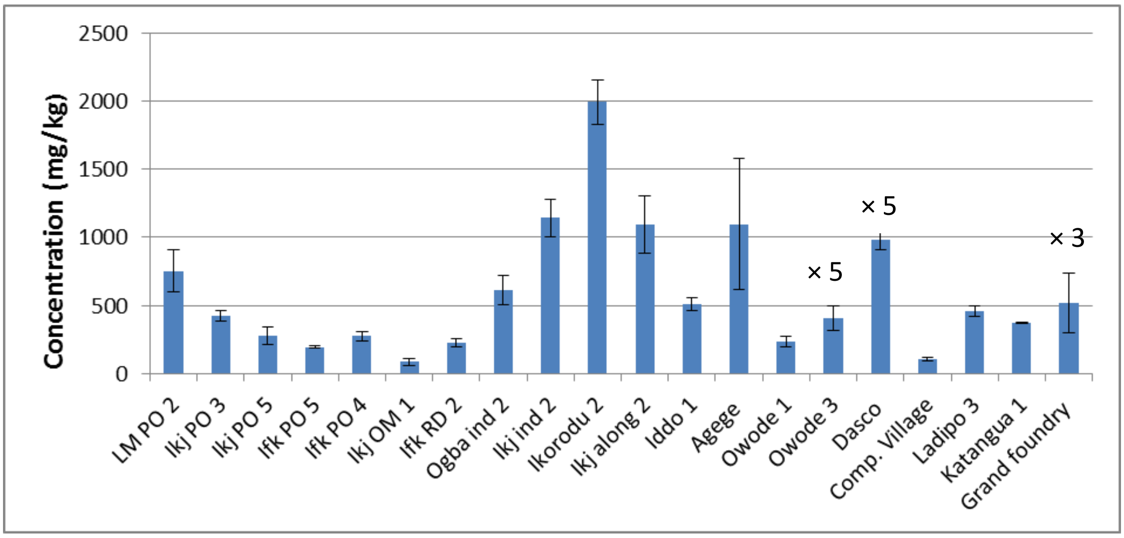


Figure 5.3 Bioaccessible concentrations of Fe in soils (mg/kg); Dasco, Owode 3 and Grand Foundry are plotted as 1/5, 1/5 and 1/3 of actual concentrations, respectively.

The % BA for all soils studied was less than 3 % with the exception of Grand Foundry and LM PO 2 soil samples which were 5 and 8 % respectively. The % BA results indicated that the dissolution or availability of Fe in the gastro intestinal tract of children may not be of concern since only a small fraction of the PTE would be available in the case of accidental soil ingestion. Iron showed low availability in sequential extraction results (chapter 4), having about 78 % of its content in the residual phase. Therefore the low bioaccessibility result confirms the low mobility or availability of Fe in the soil samples. A relatively weak statistical relationship of 0.60 (correlation coefficient) was observed between bioaccessible and pseudototal Fe concentrations (Table 5.4).

Manganese

The results of average concentrations of Mn and RSDs are presented in Table 5.2 with bioaccessible concentrations shown in Figure 5.4. The % RSD for Mn measurements were generally good (less than 10 %), indicating good precision of the bioaccessibility extractions. Manganese appeared to be more bioaccessible compared with Cr and Fe with percentages of bioaccessibility ranging between 12 to 49 %, average 28 %. Although the average % BA of soil samples were lower than sum of Mn extracted in the non-residual phases of sequential extraction measurements (65%) but bioaccessibility result still further indicates the considerable mobility of Mn in the soils.

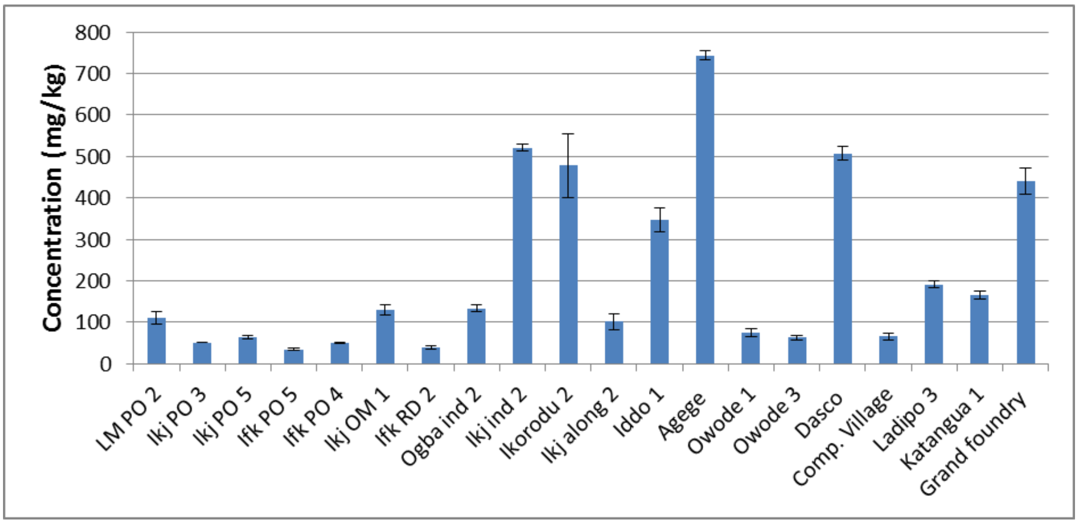


Figure 5.4 Bioaccessible concentrations of Mn in soils (mg/kg).

In a similar study elsewhere, the range of % BA of Mn in urban soils was reported as 12 to 41 % which appears similar to the % BA range for this study, although the relationship between pseudototal and bioaccessible Mn concentrations was lower (R = 0.67) [48].

Nickel

The RSDs for bioaccessible Ni measurements were generally less than 10 % indicating good precision of the extractions. Low bioaccessible Ni was noted in all the soils analysed (Figure 5.5), this is similar to Cr. All bioccessible Ni concentration were less than 10 mg/kg with exceptions of three soils which were 15, 25 and 275 mg/kg (Ikorodu 2, Grand Foundry and Dasco soils, respectively). Grand Foundry and Dasco soils also had highest pseudototal concentrations. This suggests that soil samples with high pseudototal PTE content may result in high bioaccessible concentration. A positive significant correlation between pseudototal and bioaccessible Ni concentrations further supports this claim (0.96). This is similar to correlation coefficient result for Cr (0.98) (Table 5.4).

The average % BA for Ni was 15 %. Similar observations to result of this study were reported for urban street dust of Nanjing, China[159] with average % BA for Ni at 15.7 %. Wang *et al.*[158] and Okorie*et al.*[358]reported % BA of Ni as 17 .7 % and 17.9 % (gastric phase of UBM) respectively. Luo *et al*.[162] in their study of health risk assessment of PTE in urban park soils reported relatively higher bioaccessible forms of Ni (average % BA of 26 %). Generally, Fe, Cr and Ni seem to be consistent in terms of their availability and statistical relationship between pseudototal and bioaccessible concentrations.

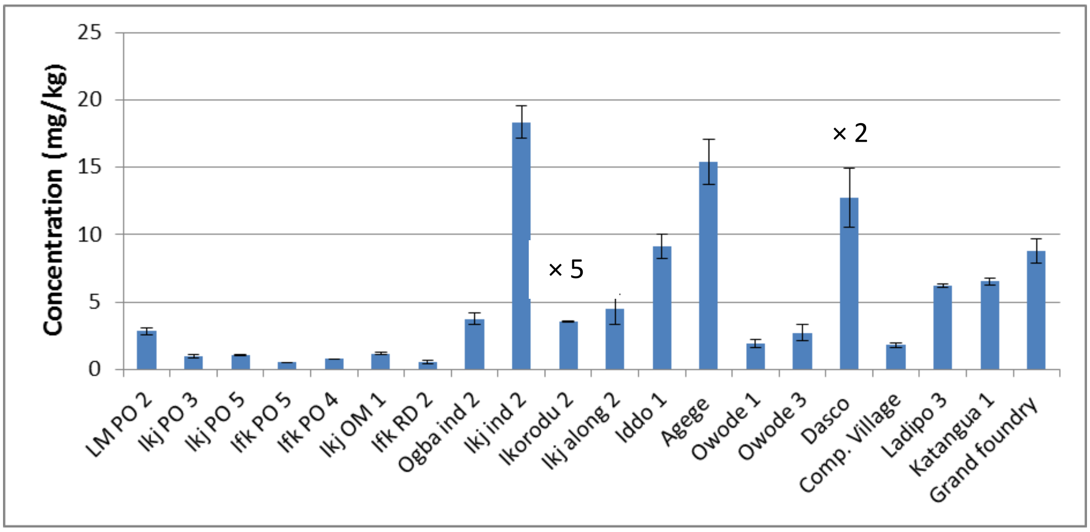


Figure 5.5 Bioaccessible concentrations of Ni in soils (mg/kg). Dasco and Ikorodu 2 are 1/15 and 1/2 of actual concentration respectively.

The low bioaccessibilities and predominant association with the residual phase in fractionation studies may further support the suggestion that the PTE might have mainly emanated from geogenic sources.

Lead

Bioaccessible Pb concentrations and RSDs are presented in Table 5.2 and Figure 5.6. The RSDs were generally less than 15 %. Bioaccessible Pb significantly and positively correlated with its pseudototal contents (R = 0.92) as with other PTE, however, Pb was more bioaccessible with % BA ranging between 21 to 93 %, average 51 %. Regardless of the mean bioaccessibility value of 51 % recorded for Pb in soils studied, potential risk associated with Pb toxicity in children and adult could have been exaggerated if pseudototal contents which assumes 100 % Pb availability was employed as the risk assessment criteria.

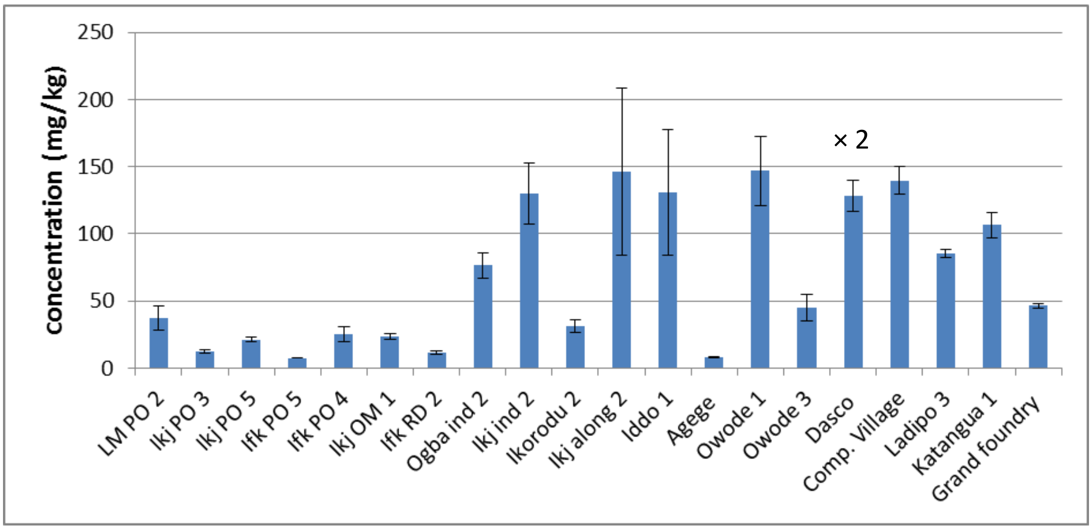


Figure 5.6 Bioaccessible concentrations of Pb in soils (mg/kg). Dasco is plotted as 1/2 of the actual concentration.

Other studies are in agreement e.g. Madrid *et al.*[7] reported 50 to 83 % and 39 to 73 % bioaccessible Pb for fine fractions of urban soils from Torino and Sevilla. Other studies reported median bioaccessible concentration of Pb in Swansea and London soils as 68 %[16],59 % average for bioaccessible forms of Pb in urban soils of Hong Kong China [357], average of 49 % in urban park soils of Xiamen, China[162].

High bioaccessibility in the gastric phase for Pb was also reported for other tests e.g. PBET and UBM. Okorie *et al.*[358] reported 53.1 % for bioaccessible forms of Pb measured in top soils collected from an urban recreational site in Newcastle upon Tyne, England (gastric phase of UBM), % BA of 62 % was reported for Pb in urban contaminated soils of Noyelles-Godault in Paris, France (gastric phase of UBM)[359], average of 32.98 % in Nothern Ireland soils (gastric UBM)[360], and a range of 21 to 44 % in Glasgow soils (gastric phase of PBET)[48].

The relatively high Pb bioaccessibility (% BA of 51 %) in soils of this current study may largely depend on pH (1.5), the simulated pH of stomach under fasting conditions. The effect of varying pH on Pb solubility was studied by Ruby *et al.*[154] who showed the amount of soluble Pb decreased to about 65 % in mine waste materials when pH was raised from 1.3 to 2.5[154]. Similarly, Yang *et al.*[361] also reported a decrease in Pb solubility from 81 % to 11 % when pH was adjusted from 1.5 to 4.0 in soils spiked with As and Pb[361]. The effect of gastric pH on Pb solubility may be relevant to risk assessments when the nutritional intake of the general populace of the study area is considered. Bosso *et al.*[362] suggested that children living under poor social and economic conditions (which imply irregular food intake or absence of breakfast) may be at higher risk of Pb solubility/dissolution in their stomach due to low pH associated with fasting conditions in an event of accidental or intentional soil ingestion. This situation may be typical of the majority of children living in Lagos, where the majority of the population lives inpoverty[363]. Perhaps, this factor should be noted as one of the major causes of increased Pb toxicity in children in the case of accidental ingestion of contaminated soils.

Zinc

Figure 5.7 and Table 5.3 shows the average bioaccessible Zn in soil samples analysed in the current study. The RSDs for Zn measurements were less than 20 % with the exception of IK PO 5 and Ikeja Along 2 which were 40 % and 29 % respectively. Owode 1 and Katangua soils were over-extracted by the SBET compared to pseudotototal digestion (105 and 125 % respectively). Bioaccessible Zn generally ranged from 10 to 125 % with an average of 57 %.This is in agreement with report of other studies[7, 158].

About 59 % bioaccessible Zn was reported for urban roadside soils[158], 60.1 % for urban street dusts[159], 47 % for contaminated urban soils (gastric phase of UBM)[359] and a range of 32 to 83 % for urban soils[7].

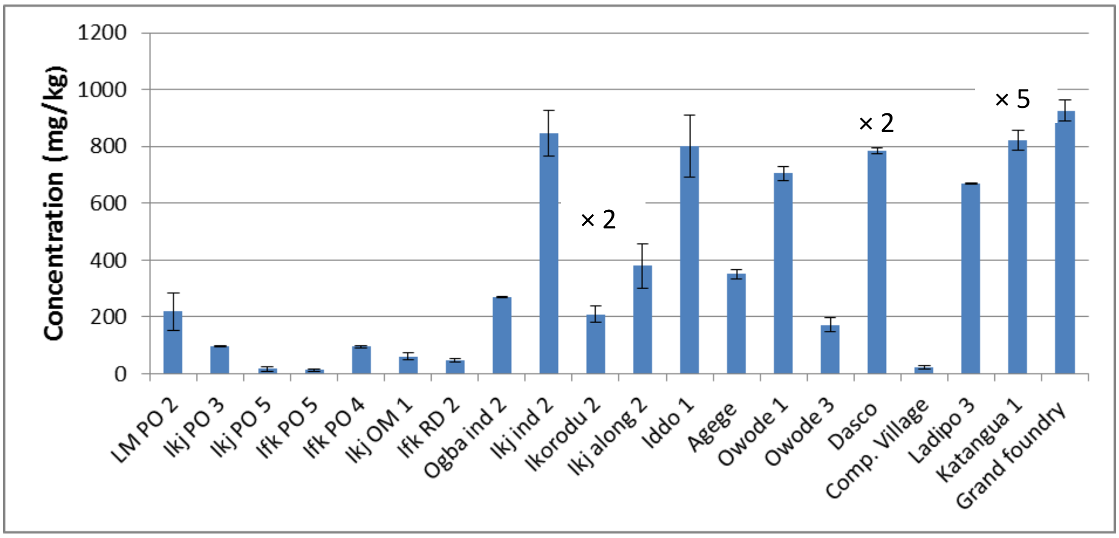


Figure 5.7 Bioaccessible concentrations of Zn in soils (mg/kg). Ikorodu 2, Dasco and Kantangua are plotted as 1/2, 1/2 and 1/5 of actual concentrations respectively

Zinc was the most bioacessible PTE in this current study. The overall PTE bioacessibility was in the order of Zn > Pb > Cu > Mn > Ni > Cr > Fe. This is similar to sequential extraction results in which ‘‘typical urban metals’’[76] (Cu, Pb and Zn) were more mobile than the geogenic PTEs, with the exception of Mn.

Lower bioaccessible concentrations of naturally occurring PTE versus anthropogenic PTE has previously been reported[158, 355, 360]. Correlation coefficient results showed positive linear relationship between bioaccessible and pseudototal Zn concentrations (R = 0.89). The relationships between pseudototal PTE contents (Cr, Cu, Fe, Mn, Ni, Pb and Zn) and their respective bioaccessible concentrations as revealed by correlation coefficients showed that the latter is largely dependent on the former. In support of this observation, Roussel *et al.*[359] noted in their study of Cd, Pb and Zn bioaccessibiltiy in urban contaminated soils that, ‘‘*as the total concentration increased, so did the bioccessible concentrations*’’. Reports of positive correlations from other studies also confirmed good linearity between the two variables[41, 48, 164, 364]. In contrast to this, Nathaniel *et al.*[365] published a report on Generic Assessment Criteria for Human Health Risk Assessment (2009) and noted that the relationship between pseudototal contents and its respective bioacessible fractions is not necessarily linear.

Okorie *et al.*[358] and Barsby *et al.*[360] also criticised the earlier assertion that increase in total concentration relates to increased bioaccessible concentrations.

The relationship between soil properties and PTE availability in urban soils

Due to PTE interactions with soil constituents, many soil physical and chemical properties can influence mobility or availability of PTE. Soil pH and organic matter are generally considered to control the bioavailability of PTE. Figure 5.8, 5.9 and 5.10 shows the relationships between soil pH, % LOI and PTE. Figure 5.8 specifically shows the relationship between oxidisable and SBET PTE against % LOI. This was conducted since the oxidisable phase of the revised BCR sequential extraction procedure targets the release of PTE associated with organic matter and similarly to investigate if organic matter influences the geochemistry of solubilised SBET PTE. The results from the figures below indicate insignificant relationships between these variables as values of R^2 were less than or equal to 0.07. There were also insignificant relationship between % LOI and pseudototal concentrations (see Figure 3.21). This may be the likely consequence of the very low % LOI values recorded in the soils and also low variability between samples. These results revealed that organic matter content does not influence PTE accumulation or geochemistry of PTE in Lagos urban soils. This is similar to the outcome of study by Finzgar *et al*[366] where no relationship was found between PTE (Pb and Zn) extracted in the oxidisable phase and organic matter content of soil. Organic matter minimizes PTE availability through adsorption processes and complexation mechanisms[78] but on the other hand, organic matter supplies organic chemicals to soil solution to serve as chelates and increase PTE availability to plants. However, the latter two mechanisms are less likely to be less important in the soils studied due to low organic matter content.

Furthermore, the sequential extraction results have revealed preferential incorporation of PTE in Fe-Mn and silicate minerals rather than organic matter as the reducible and residual fractions were the predominant phases in the revised BCR extraction for all the PTE studied (see chapter 4).

The oxidisable phase was the least phase for all PTE analysed with the exception of Cu which was higher than the exchangeable phase; this may show the significance of low organic matter content measured in the soils.

Many studies have suggested an association between soil organic matter content and PTE fixation in solid phase of soils[367, 368] but other studies found no association[369-371]. For instance, organic matter content in soil showed no correlation with Pb availability in a study[372], but showed positive associations with Pb and Zn availability in another study[357] and negative correlations with Cd availability in another study[373]. Rieuwerts *et al.*[374] suggested that the apparent contradiction of literature about the relationship between organic matter content of soils and different availabilities may be due to the tendency of PTE binding with organic components of both solid and solution phases of soil e.g. PTE can form a complex with low molecular weight organic constituents such as fulvic acids and also with solid phase organic matter as well as ligands which have varying affinities for adsorption onto the soil surface. This complexity coupled with the low organic matter content of the soils studied, may explain the lack of relationship between the variables.

Adsorption of PTE is generally acknowledged to be directly proportional to soil pH and PTE solubility tends to increase at lower pH and decrease at higher pH values. The association between PTE adsorption on exchangeable surface colloids and pH is partly due to the competition between the H^+ for adsorption sites at low pH resulting in decreased PTE adsorption. In the current study, no relationship was found between available PTE (SBET and non-residual fractions of sequential extraction and soil pH). Figure 5.9 shows the relationship between these variables and it was apparent that low and insignificant R^2 values were obtained.

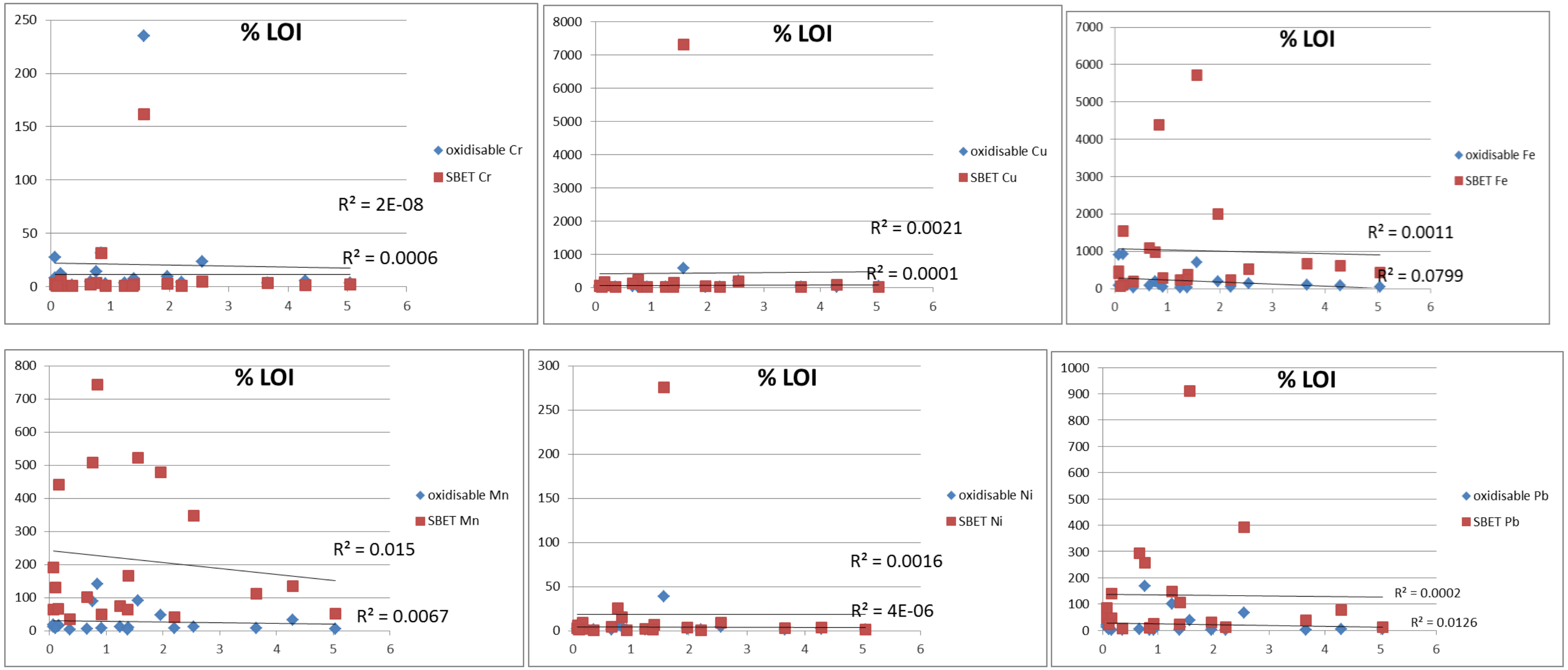
Other studies reported positive relationships between these variables[41, 357]. However, Lamb *et al*[375] in their study of PTE partitioning and bioaccessibility in uncontaminated and contaminated soils of New South Wales and South Australia found no relationship between available PTE and soil properties which includes soil pH. Similarly, De Miguel *et al.*[376] reported that soil pH does not influence bioaccessibility of PTE in Madrid urban playground soils. En-Qing *et al.*[271] also reported similar observation.

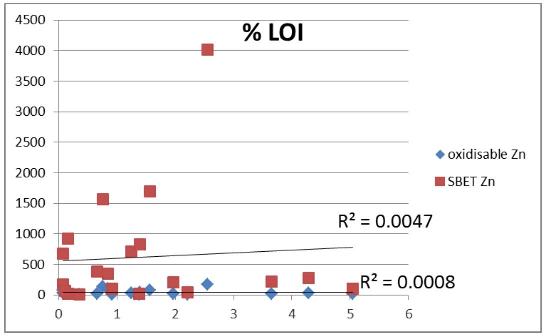
Gastric pH and chloride ion concentrations are co-variables in the human stomach and the pH dependent bioaccessible PTE forms stable chloro-complexes. Therefore, as a consequence and the differences in soil phase associations, different solubility patterns, affinities for digestive ligands displayed by various PTE, the precise pH dependence of bioaccessibility of PTE from soil in the GIT will be PTE specific[377]. The main variable controlling PTE solubility in the human GIT is the gastric pH and this has been severally confirmed in previous bioaccessibility studies[151, 154, 161, 355]. Ruby *et al.*[154] reported that the extent of Pb dissolution decreased by 65 % when stomach pH was increased from 1.3 to 2.5. Oomen *et al.*[151] noted that Pb bioaccessibility varied from 1-96 % depending on soil type and GIT pH. Yang *et al.*[361] found large gastric pH dependence of Pb bioaccessibility. The low pH (1.5) in the simulated human stomach is likely to desorb a very high percentage of adsorbed PTE and also cause H^+ induced dissolution of some solid phase fractions such as carbonates, labile mineral oxides, and sulfides i.e. in the absence of confounding variables, a low pH will increase the dissolution of PTE in soils. Perhaps, this may have been the major factor that influenced PTE bioaccessibility in soils investigated rather than the soil pH considering the near neutrality of the soils studied.

The available PTE fractions (SBET and non-residual fractions of SE) appeared to be positively and significantly related to the pseudototal concentrations (see Fig 5.10). The relationship between these variables is the only significant relationship observed and it implies that availability of PTE increases with increase in the pseudototal concentrations. Correlation coefficient (@ 95 % confidence level) results from Table 4.3, and 5.4 also confirm this observation. However, it is important to note that there was a clear distinct behaviour between the availability patterns of anthropogenic PTE compared to lithogenic PTE. This is evident from bioaccessible and sequential extraction results as anthropogenic PTE showed higher availabilities than the lithogenic PTE. Pollutants that originated from anthropogenic origin may enter the soil either in organically complexed form or as metal salts. In the latter case, metal cations adsorb on mineral or organic surfaces and tend to be more exchangeable than PTE of lithogenic origin[355] and this may explain the availability of Cu, Pb and Zn against Cr, Fe, Mn and Ni observed in this study.

However, the sorption of PTE in soil is a continuum of different processes which may occur at different rates and simultaneously. Ion exchange reactions are usually followed by slow reactions that are limited by ion diffusion. This rate limiting process can result in varying time scales for soil chemical reactions which may range from milliseconds to several years[31]. Increase in PTE sorption with time is likely attributed to surface precipitation in addition to intra and inter particle diffusion which may result into PTE forms that are not readily dissolved[378]. Because PTE that are mainly of lithogenic origins are typically preferentially bound to silicate matrices compared to those of anthropogenic origin, the lithogenic PTE are more likely to be less soluble in comparison to anthropogenic PTE. In addition, the rate of diffusion into pore spaces and particles decreases with increasing ionic diameter, which also supports the low bioaccessibility of Cr and Ni[355]. Another factor which may be responsible for the low bioaccessibility of some PTE is that, chloride complexes formed in the acidic solution used in simulating human stomach conditions carry negative charges and would be removed from solution fixing to the opposite charges developed by Fe oxides at this low pH and consequently lowering the bioaccessibility of some metal ions such as Cr[376].

Generally, PTE availability appeared to be strongly related to pseudototal concentrations for all PTE but not with organic matter content and soil pH but considerable further work is required in order to understand the intrinsic properties and interactions influencing PTE geochemistry in the study area. It is possible that the availability of PTE in the soils studied are partly controlled by other soil properties, processes and conditions not measured in this study which may include redox potential, cation exchange capacity, calcium carbonate content, presence of chelates and other miscellaneous factor such as microbial activity. Future studies can develop a predictive model e.g regression models predicting the influence of various soil properties on PTE geochemistry in the study area. Such models could be useful in the management of polluted soils. This study is the first of its kind in the area of study and there was no literature to compare with and more so the particular focus of this work was to apply the extraction schemes to soil samples in order to gain insight into present and future possibilities of PTE mobilisation and consequent potential environmental and human health risk effects and overall safety of the soil.



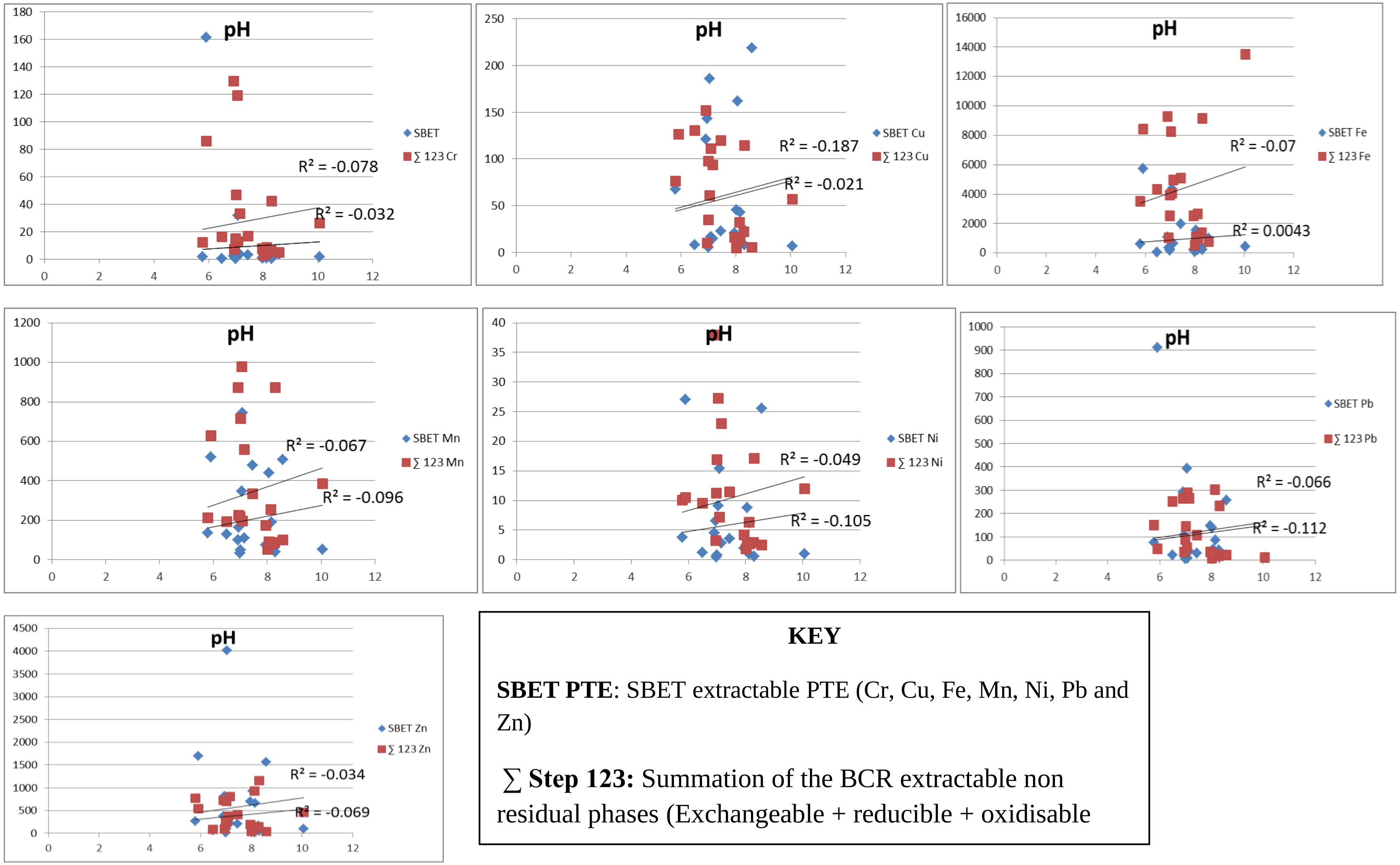


KEY

Oxidisable PTE: BCR extractable PTE (Cr, Cu, Fe, Mn, Ni, Pb and Zn) in the oxidisable phase

SBET PTE: SBET extractable PTE (Cr, Cu, Fe, Mn, Ni, Pb and Zn)

Figure 5.8 Linear regression relationships between oxidizable and SBET PTE (Cr, Cu, Fe, Mn, Ni, Pb and Zn) and % LOI.

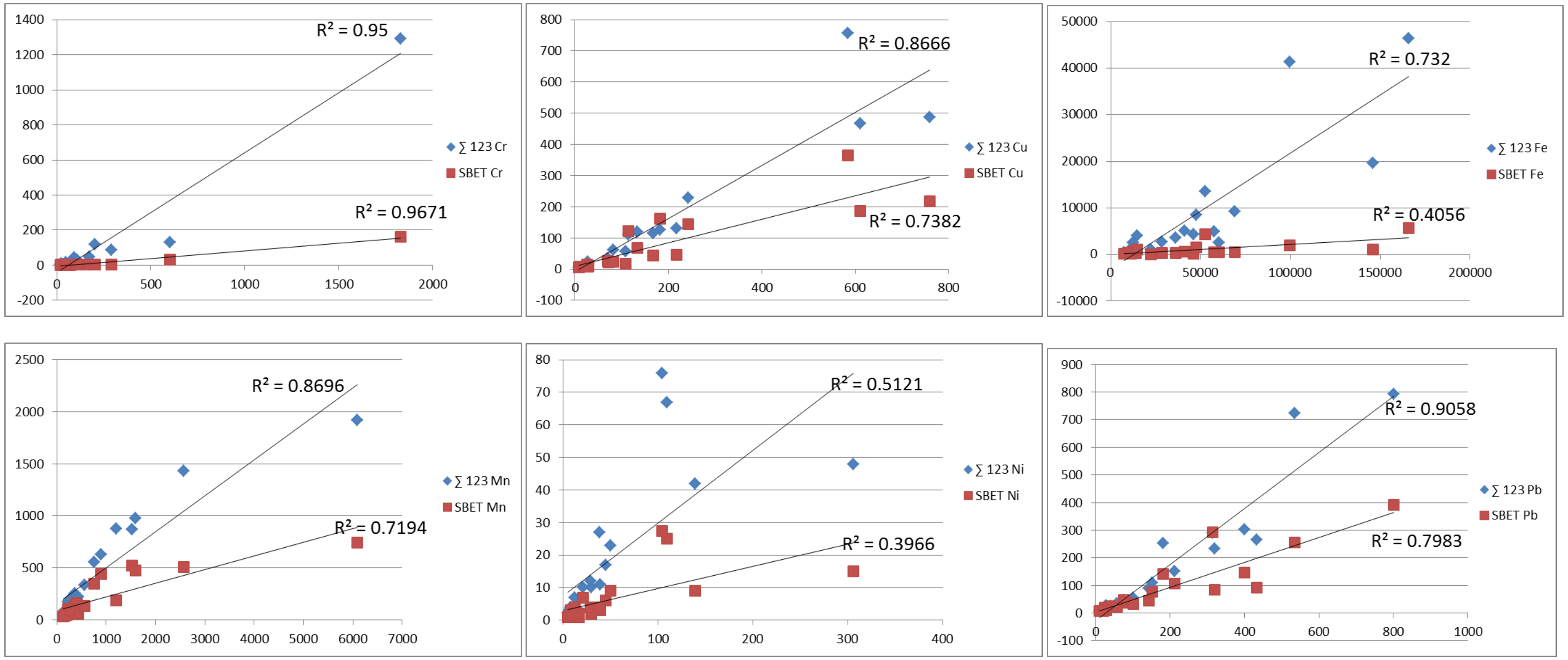


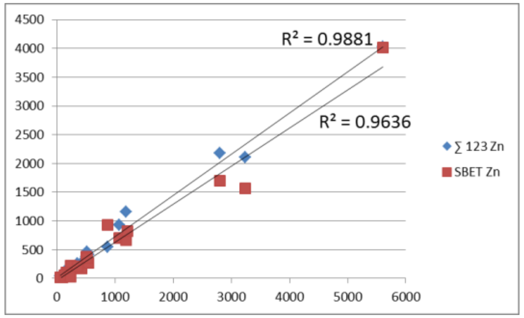
KEY

SBET PTE: SBET extractable PTE (Cr, Cu, Fe, Mn, Ni, Pb and Zn)

∑ Step 123: Summation of the BCR extractable non residual phases (Exchangeable + reducible + oxidisable

Figure 5.9: Linear regression relationship between non-residual fractions and SBET PTE (Cr, Cu, Fe, Mn, Ni, Pb and Zn) and soil pH.





KEY

SBET PTE: SBET extractable PTE (Cr, Cu, Fe, Mn, Ni, Pb and Zn)

∑ **Step 123:** Summation of the BCR extractable non residual phases (Exchangeable + reducible + oxidisable fractions)

Figure 5.10: Linear regression relationship between non-residual fractions and SBET PTE (Cr, Cu, Fe, Mn, Ni, Pb and Zn) and pseudototal concentration

Despite the inherent toxicity potentials of PTE, human require some essential PTE in varying amounts in the body for proper growth and general wellbeing. Chromium, Cu, Fe, Mn, Ni and Zn are essential PTE and Pb is a non-essential PTE. The essential PTE are obtained from food and pharmaceutical supplements through controlled and regulated exposure. The overdoses and deficiencies of the essential PTE can adversely affect human health. Inadvertent exposure to PTE from anthropogenic sources will certainly result in increased toxicity risk owing to overdoses from both essential and non-essential PTE. Non-essential PTE such as Pb tends to accumulate in the human body at a much higher rate compared to essential PTE and at continuous exposure; even at low concentrations may result to toxicity[379].

Inadvertent exposure to soils and potentially resuspended soil particles are calculated and compared tolerable daily intakes for PTE in subsequent discussions in order to assess the potential toxicity risks associated with ingestion or inhalation of these soil particles. Comparison of calculated toxicity risks will allow the estimation of contribution of PTE in soil particles to toxicity risk as an unconscious addition to recommended daily intakes for PTE that are typically accessed through food and pharmaceutical supplements.

Human health risk assessment

The following section assumes ingestion of soil by a child weighing 10 kg and Table 5.6 and 5.7 show calculated amounts of PTE (µg/kg) likely to be solubilized in the gastro intestinal tract assuming unintentional (100 mg) and intentional (10 g) soil ingestion by a child weighing 10 kg. A crude risk assessment was estimated by calculating amount of soil that a hypothetical child needed to ingest to reach a toxicologically significant level. The data was compared with tolerable daily intake (TDI) values calculated using the human-toxicity maximum permissible levels published by Baars *et al.*[380] and also values from Department for Environment, Food and Rural Affairs & Environment Agency, UK (DEFRA & EA) and Joint Food and Agriculture Organization/ World Health Organization Expert Committee on Food Additives (JECFA) (see toxicological data in Table 5.5)

It important to note that the estimations are unfeasible as they assume soil ingestion is the only pathway whereby PTE enters the human body. The calculated amounts are therefore only a guide to possible risk associated with PTE and the overall safety of soil.

Table 5.5 Toxicological data for PTE studied.

Element	Reference	Tolerable daily intake value	Tolerable daily intake for a 10 kg child (mg/day)
Cr	DEFRA & EA[381]	3 µg/kg bw/day	0.03
Cu	JECFA[382]	0.4 mg/kg bw/day	4
Fe	JECFA[382]	0.7 mg/kg bw/day	7
Mn	JECFA[382]	0.14 mg/kg bw/day	1.4
Ni	DEFRA & EA[381]	12 µg/kg bw/day	0.12
Pb	DEFRA & EA[381]	3.6 µg/kg bw/day	0.036
Zn	JECFA[382]	0.3 mg/kg bw/day	3

- µg ingested, per kg of an individual’s body weight, per day.
- mg ingested, per kg of an individual’s body weight, per day.

Table 5.6 Calculated amounts of PTE solubilised for conservative consumption of soil(100 mg) by a child weighing 10 kg, assuming soil ingestion is the only oral source of PTE intake (values calculated in µg/day according to Baars et al.[380]); the bold figures indicate exceeded TDI values.

n = 3	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
LM PO 2	0.4	2	75	11	0.3	4	22
Ikj PO 3	0.2	1	42	5	0.1	1	10
Ikj PO 5	0.1	1	28	6	0.1	2	2
Ifk PO 5	0.05	1	19	3	0.1	1	1
Ifk PO 4	0.1	1	28	5	0.1	3	10
Ikj OM 1	0.04	1	8	13	0.1	2	6
Ifk RD 2	0.1	1	22	4	0.1	1	5
Ogba ind 2	0.1	2	23	7	0.2	15	70
Ikeja ind 2	0.2	3	41	6	0.3	4	17
Ikorodu 2	0.3	22	98	51	3	26	157
Ikeja along 2	0.1	5	10	7	0.2	14	2
Iddo 1	0.3	4	46	19	1	9	67
Agege	0.2	14	37	17	1	11	82
Owode 1	0.5	16	155	44	1	5	93
Owode 3	0.2	7	61	13	0.4	8	27
Dasco	16.2	730	572	52	28	**91**	169
Comp. Village	0.3	2	199	48	0.4	3	21
Ladipo 3	0.2	12	109	10	0.4	29	38
Katangua 1	0.4	19	51	35	1	**39**	401
Grand Foundry	3.2	2	439	74	2	1	35
TDI (µg/day)	50	1400			500	36	5000

Table 5.7 Calculated amounts of PTE solubilised for soil pica tendencies/geophaghy (10 g) by child weighing 10 kg assuming soil ingestion is the only oral source of PTE intake (values calculated in µg/day according to Baars et al.[380]); the bold figures indicate exceeded TDI values.

n = 3	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
LM PO 2	36	150	7530	1100	28	**373**	2170
Ikj PO 3	18	69	4230	515	10	**122**	954
Ikj PO 5	10	73	2790	640	10	**212**	157
Ifk PO 5	5	55	1940	343	5	**74**	81
Ifk PO 4	7	101	2760	500	8	**252**	955
Ikj OM 1	4	81	847	1290	12	**231**	579
Ifk RD 2	5	80	2240	401	6	**115**	473
Ogba ind 2	7	207	2340	746	19	**1460**	**7040**
ikeja ind 2	18	250	4077	628	27	**447**	1714
Ikorodu 2	34	**2180**	9840	5060	255	**2560**	**15600**
Ikeja along 2	10	456	1040	655	18	**1390**	230
Iddo 1	25	431	4610	1910	62	**851**	**6680**
Agege	22	**1420**	3690	1650	65	**1060**	**8210**
Owode 1	**52**	**1610**	15400	4400	87	**462**	**9260**
Owode 3	15	675	6110	1340	38	**764**	2690
Dasco	**1610**	**72900**	57100	5210	**2750**	**9090**	**16900**
Comp. Village	31	231	19900	4770	35	**311**	2080
Ladipo 3	19	1209	10900	1010	45	**2920**	3790
Katangua 1	45	**1850**	5120	3470	91	**3910**	**40000**
Grand Foundry	**317**	167	43800	7430	154	**80**	3490
TDI (µg/day)	50	1400			500	36	5000

Table 5.8 Amounts of soil (g/day) that a 10 kg child would require to ingest to reach TDI values from Table 5.5 assuming soil ingestion is the only oral source of PTE intake.

n = 3	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
LM PO 2	8	276	11	13	43	1	14
Ikj PO 3	16	579	17	27	123	3	31
Ikj PO 5	30	549	29	22	115	2	192
Ifk PO 5	61	725	36	41	236	5	373
Ifk PO 4	41	397	25	28	155	1	31
Ikj OM 1	68	494	97	11	103	2	52
Ifk RD 2	55	498	31	35	215	3	63
Ogba ind 2	40	193	30	20	58	0.3	4
Ikeja ind 2	16	160	17	22	44	0.8	17
Ikorodu 2	9	18	7	3	5	0.1	2
Ikeja along	29	88	67	21	67	0.3	130
Iddo 1	12	93	15	7	19	0.4	4
Agege	14	28	19	8	18	0.3	4
Owode 1	6	25	5	3	14	0.8	3
Owode 3	20	59	11	10	30	0.5	11
Dasco	0.2	0.5	1	3	0.4	0.04	2
Comp. Village	10	174	4	3	34	1.2	14
Ladipo 3	15	35	6	14	31	0.1	8
Katangua 1	7	22	14	4	13	0.1	1
Grand Foundry	1	239	2	2	8	5	9

Human health risks assessment associated with Cr bioaccessibility showed that, on the assumption of non deliberate soil ingestion of 100 mg, none of the Lagos urban soils studied contained sufficient Cr to exceed the TDI of 50 µg/day (Baar's approach). However, three soil samples were capable of posing a significant health risk in the event the child ingested 10 g of soil a day. Owode 1 soil sample had value (52 µg/day) slightly exceeding the TDI for Cr (50 µg/day). The other two soils (Grand Foundryand Dasco) greatly exceeded the TDI value up to about 6 and 32 times respectively.For the toxicological evaluation based on TDI values from DEFRA & EA, the amount of soil that would be ingested to deliver the TDI for Cr of 0.03 mg/day was only 200 mg and 1 g for Dasco and Grand Foundry soils respectively (Table 5.8). These two soils may posea siginificant health risk to children suffering from geophaghy and soil pica tendencies.

The TDI for Cu (1400 µg/day; Baar's approach) was not exceeded assuming 100 mg of soil was ingested. Five soils from sampling campaign 2 (contaminated soils) exceeded the TDI for Cu many fold when 10 g of soil was assumed to be ingested (Table 5.7). Most worrisome was bioaccessible Cu in Dasco soil in which the TDI of 1400 µg/day was exceeded about 52 times. About 18 to 725 g of soil is needed to be ingested to deliver the TDI of 4 mg/day (based on JECFA values). As expected, the only exception was Dasco soil in which only 500 mg of soil is required to deliver the TDI of 4 mg/day.

With the average conservative soil ingestion of about 100 mg/day by a child, the majority of the soils appear to pose no risk of Fe toxicity. The soils which are likely to pose a risk were from Owode 1, Computer Village, and Grand Foundry since less than 5 g would deliver the TDI of 7 mg/day for Fe (JECFA values) in the case of deliberate soil ingestion. Of particular concern was Dasco soil in which only about 1 g of soil is required to deliver the TDI of Fe.

Eight of the contaminated soils samples posed Mn toxicity in the case of deliberate soil ingestion of 10 g/day (JECFA values). Less than three grams of Ikorodu 2, Owode 1, Dasco, Computer Village and Grand foundry soils samples were required to deliver a TDI of 1.4 mg/day. None of the uncontaminated soils is likely to pose a risk even in a worst case scenario of 10 g soil ingestion.

Considering the risk assessment proposed by Baars *et al.*[380] (TDI = 500 µg/day for Ni), none of the soils exceeded the TDI for unintentional soil ingestion (100 mg/day). For worst case scenarios of possible ingestion of 10 g/day, only one soil (Dasco) exceeded the TDI by five times (500 µg/day). Based on DEFRA& EA toxicological thresholds, the amount of soil needed to be ingested ranged between 13 and 236 g/day for most of the soil samples. These amounts appear unrealistic and therefore may pose no risk. Exceptions to this were Ikorodu 2, Grand Foundry and Dasco soils. Children with soil pica behaviour may be at risk in the case of deliberate ingestion of Ikorodu 2 and Grand Foundry soils since only about 5 g/day and 8 g/day respectively, will deliver the TDI. As observed for other PTE discussed, most worrisome was Dasco soil in which only about 400 mg of soil is needed to be ingested to deliver the TDI of 0.12 mg/day.

The assessment of Pb toxicity risk to human health revealed that, on the assumption of 100 mg/day soil ingested, the bulk of the soils studied pose no risks since the TDI of 36 µg/day for Pb was not exceeded (Baar's approach). The only exceptions were Dasco, and Katangua 1 soils which had values that exceeded the TDI (91 and 39 µg/day respectively). When the worst case scenario of soil pica behaviour was assumed (10g/day), all the soils studied (both contaminated and uncontaminated) exceeded the TDI of 36 µg/day for a child weighing 10 kg.

Based on DEFRA & EA toxicological value, less than 1 g of contaminated soil samples would deliver the TDI of 0.036 mg/day. The soil with the least toxicity risk out of the contaminated soils was Grand Foundry in which about 5 g is required to be ingested to reach the TDI. For Dasco soil, only about 40 mg of soil is required to deliver the TDI and this is worrisome considering the small quantity of soil needed. For Pbrisk assessment in the uncontaminated soils, less than 5 g of the soil samples would be required to deliver the TDI of 0.036 mg/day. On this basis, both the contaminated and uncontaminated soils appear to pose risk to children.

No significant health risk was associated with bioaccessible Zn concentrations in a case of unintentional soil ingestion. Calculated toxicological data for the soil samples were less than the TDI of 5000 µg/day.

On the assumption of 10 g/day soil ingestion, eight soils exceeded the TDI (Baar's approach) and therefore may pose a risk in children with soil pica behaviour. Based on DEFRA & EA toxicological data, seven out of the contaminated soils may pose risk to children because less than 5 g/day of soil samples would be needed to deliver the TDI. For the uncontaminated soils, about 31 to 372 g/day of soils is required to be ingested to reach the TDI of 3 mg/day. This appears unrealistic and therefore may pose no significant health risk.

5.4.2 Isolation and inhalation bioaccessibility of PM_{10} fraction of soil

5.4.2.1 Quality control and results of PM_{10} isolation method

Particulate matter was isolated from only nine out of the twenty soil samples fractionated in chapter 4. Their masses are presented in Table 5.9. Very small amounts were isolated, partly because of the unavailability of large enough samples from which to isolate PM_{10} and partly because of the lengthy time required to perform the isolation. The masses of PM_{10} were not adequate to conduct both pseudototal analysis and SBET extraction for all samples and so SBET was carried out for all, but only the two largest samples, Ifk RD 2 and Ifk PO 5 were subjected to pseudototal digestion.

Table 5.9 Masses of PM_{10} isolated from Lagos urban soil samples.

	Sample	**Amount of PM_{10} isolated**
1	Ikj OM1	0.109 g
2	Ifk RD 2	0.1959 g
3	Ifk PO 5	0.395 g
4	LM PO 2	0.0924 g
5	Agege	0.0980 g
6	Dasco	0.1002 g
7	Grand Foundry	0.0996 g
8	Ikeja Along	0.108 g
9	Katangua 1	0.101 g

To verify that PM_{10} had been isolated, test portions of Ifk PO 5 sample (which yielded approximately 0.4 g PM_{10}) was subjected to laser light scattering particle analyser (Malvern Mastersizer 2000, Malvern instrument LTD, Worcestershire, UK). Prior to the particle size analysis, about 0.1 g representative sample (PM_{10}) was dispersed in 25 mL of deaerated water in a capped centrifuge tube. The chart for the particle size distribution is presented in Figure 5.8.

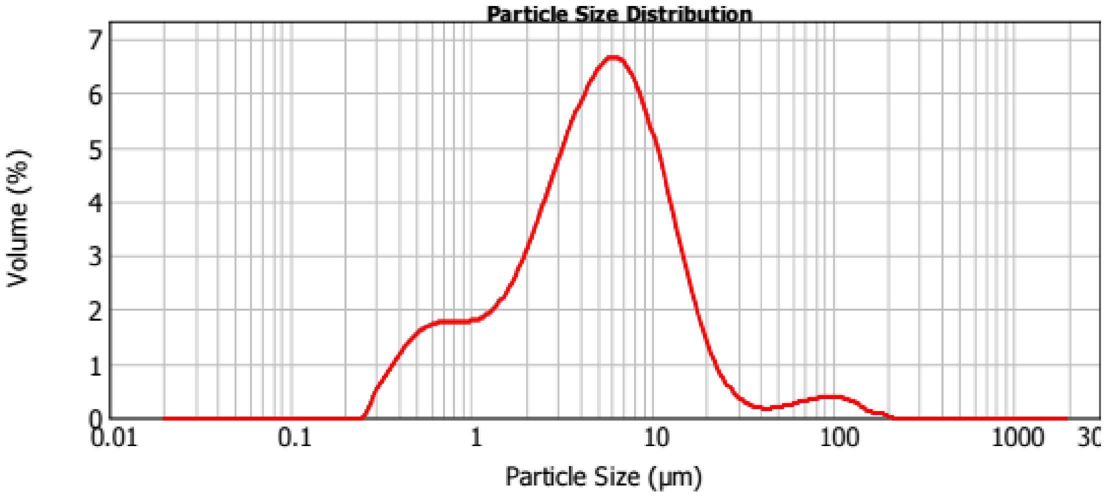


Figure 5.8 Particle size distribution chart for test soil sample (Ifk PO 5).

The mastersizer obscuration rate was 10.70 % and pump rate was 1300 rpm. The suspension was manually homogenised before pumping it through the laser light path. For the soil sample analysed, 83.4 % of the extracted particles were < 10 µm. This is similar to the result obtained by Boisa *et al.*[120] for soil and metallurgical waste samples (84.7 % and 97.3 % was obtained respectively). For this current study, about 17 % of the particles were larger than 10 µm. This may be due to agglomeration of fine particles to form flocs during centrifugation of dilute suspensions. The problems of water-based fine particulate suspensions and its corresponding agglomeration have been reported in similar studies[120, 383, 384].

Concern about the possible removal of PTE during water based isolation of the PM_{10} fraction was investigated by analysing test portions of decanted supernatants, which were obtained from suspension after the centrifugation process, by ICP-MS.

A summary of PTE losses during the wet isolation process of PM_{10} is presented in Table 5.10 and appendix G. Chromium was detected in Katangua and Dasco solutions but not in other samples. For Cu, Mn, Ni and Pb, less than 1 mg/kg was lost during PM_{10} isolation process. Iron and Zn losses were higher in comparison to other PTE studied but the average percentage losses (relative to the bioaccessible concentration) were 0.051 and 0.059 % respectively (see appendix H), which is almost negligible and this suggest high accuracy.

About 50 mg and 10 mg of Ifk PO 5 and Ifk RD 2 soils, respectively, were analysed in duplicate for pseudototal concentration analysis. Percentage PTE losses of water soluble components were calculated for these soils. Less than 0.5 % of PTE were lost during wet PM_{10} isolation for the soils (relative to pseudototal concentration; see appendix G). The only exception was 2.3 % of Zn lost in Ifk RD 2 PM_{10} sample. From Table 5.11 it is evident that wet based isolation method for PM_{10} appears suitable considering minimal losses of PTE.

Table 5.11 Summary of PTE losses during wet isolation of PM_{10} fraction from soil

mg/kg; n = 9	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Mean	0.25	0.52	17.28	0.88	0.09	0.05	9.73
Minimum	0.10	0.06	0.39	0.04	0.001	0.002	0.005
maximum	0.41	1.79	119	5.34	0.41	0.20	37.7

The result obtained for Cr losses in this current study is consistent with results of Boisa *et al.*[120] who noted Cr lost was below the detection limit of the ICP-MS. They also reported 2.0 % and 1.5 % as maximum % loss for Cu and Ni. Generally, % PTE lost during PM_{10} sampling for the current study is consistent with Ljung *et al.*[385] who reported that less than 1 % of pseudototal PTE concentration was lost during wet PM_{10} isolation.

5.4.2.2 Quality control of pseudototal analysis

The quality of the pseudototal PTE analysis was assessed using BCR 143R, which is a sewage sludge amended soil which was digested alongside PM_{10} samples. The RSD for pseudo-total PTE analysis was generally less than 10% (n = 3) and average (%) PTE recoveries were fit for purpose.

The percentage recoveries were 100 ± 3 % with the exception of Zn for which 110 % was obtained. Table 5.12 shows values in close agreement with the targets.

Table 5.12 Recovery of certified reference material (BCR 143R) used

(n =3); mg/kg	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
Obtained values	417	142	29000	883	297	173	1159
Certified values	426	-	-	858	296	174	1055
Recovery %	98	-	-	103	100	100	110
SD	31	8	1777	48	19	9	71
% RSD	8	5	6	5	6	5	6

- Certified values for Cu and Fe are not available in the production certificate

5.4.2.3 Quality control for SBET procedure

The quality control of the SBET procedure on the PM_{10} samples was assessed by extracting BGS 102 guidance material in parallel with the test samples. The only PTE with a target value in BGS 102 that is relevant to this work is Pb. This guidance material was validated for the UBM[152] procedure (simulates both the stomach and the intestinal compartments). The Pb target value in the stomach compartment phase of UBM procedure was compared to the Pb result for the SBET since no other certified reference material exists. Recovery of Pb from BGS 102 as extracted by the SBET agreed reasonably well with UBM for the simulated human stomach phase, regardless of the differences in chemical composition of the extracting solutions (121 %). The SBET and UBM procedures are performed at similar pH values of 1.5 and 1.2 respectively, at 37°C, which may explain the close agreement in results obtained.

Table 5.13 Recovery of Pb from BGS 102 using SBET [386]

	Cr	Cu	Fe	Mn	Ni	Pb	Zn
BGS 102 obtained	25	12	1240	1920	9	16	169
BGS 102 certified	-	-	-	-	-	12.9	-
% recovery						121	

- Certified values for Cr, Cu, Fe, Mn, Ni and Zn are not available in the BGS 102 production certificate

5.4.2.4 Pseudototal PTE concentrations in isolated PM_{10} fractions of two Lagos urban soil samples

Pseudototal digestion was performed on just two PM_{10} samples (Ifk PO 5 and Ifk RD 2). As stated earlier, this was because of inadequacy of amount of isolated PM_{10} fractions from the original soil samples. The pseudototal digestion was performed in duplicate using 50 mg and 10 mg of the isolated PM_{10} for Ifk PO 5 and Ifk RD 2 respectively. The PTE concentrations in the < 10 µm fractions were between 3 to 12 times of the 2 mm fractions previously reported in chapter 3 (see Table 5.14).

Table 5.14 Concentrations of PTE in PM_{10} and 2 mm fractions

	n = 2; mg/kg	Cr	Cu	Fe	Mn	Ni	Pb	Zn
IF PO 5	PM_{10} fraction	68.7	60.9	35100	701	27.1	123	365
	2 mm fraction	18.8	8.36	7460	135	4.49	10.4	61
IF RD 2	PM_{10} fraction	125	115	53300	434	55.2	199	977
	2 mm fraction	37.9	20.3	11000	159	7.59	28.7	132

From Table 5.14, it is apparent that enhancements in PTE concentrations in the smaller particle size fraction were greater for Cu, Pb and Zn (‘‘typical urban metals’’) than for Cr, Fe and Mn (lithogenic PTE) with the exception of Ni. This is in agreement with a previous study on the distribution and availability of trace metals in different particle size fractions of Hong Kong urban soils[347]. None of the PTE exceeded the SGVs (CLEA and Dutch intervention values) although noticeable elevated concentrations in the finer fractions were obvious. Only Zn in the Ifk RD 2 PM_{10} sample exceeded the Dutch intervention value of 750 mg/kg.

The result of this study has indicated that PTE concentrations tend to be higher in finer particle size fractions of urban soils. Ajmone-Marsan *et al.*[13]in their study of PTE concentrations of particle size fractions of soils from five European cities noted that over 50 % of PTE were accumulated in the < 10 µm fraction. Findings from other studies also support this assertion[347, 387]. If sufficient PM_{10} fraction of contaminated soils (samples collected from known point sources) had been obtained and analysed for PTE pseudototal content, it is likely they would have been unprecedented considering results from Table 5.14, particularly for foundry soils such as Dasco.

The result of the current study confirms the importance of PTE in finer fractions of soils studied in relation to elevated risks to human and ecological receptors, since resuspsension of urban soils have been suggested as a persistent source of Pb poisoning in children[17]. Future studies may have to be conducted on sufficient PM_{10} samples isolated from Lagos urban soils to ascertain the level of risks PTE poses to the general public.

5.4.2.5 Bioaccessible PTE in inhalable fraction (< 10 µm) of Lagos urban soils

The result of the bioaccessible PTE concentrations in the PM_{10} fractions of Lagos urban soils are presented in Table 5.15. Currently, there are no guideline values outlining toxicity risks or threshold levels based on bioaccessible concentrations and varying soil particle sizes, therefore, the most relevant assessment would be to compare bioaccessible PTE concentrations to SGVs which currently assumes 100 % bioavailability. However, this may not characterize the apparent toxicity risks the concentrations represent and therefore must be interpreted with caution, but nonetheless it was found relevant as screening values in which its exceedance may point out a possible risk to human receptors. A more relevant assessment which may be applicable in future studies would be to incorporate bioaccessible concentrations in the computation of SGVs, taking into account other factors such as soil type, particle size fraction, land use, age of receptor, nutritional intake, exposure pathway etc. Furthermore, to determine possible toxicity risks through inhalation, the average respiratory volume of ambient air in human receptor (adult or child) for the region or study area is needed to be determined or established and by doing this, the average daily intake value by the receptor can be calculated by multiplying the bioaccessible PTE concentration value in the PM_{10} sample by the average respiratory intake value.

The bioaccessibility results suggest significantly enhanced PTE concentration in < 10 µm fractions as the bioaccessible content of Cu, Pb and Zn in about 80 % of the samples exceeded the pseudototal concentrations in the 2 mm fraction reported in chapter 4 and 5. Bioaccessible Cu concentrations in three soils (Agege, Katangua 1 and Dasco) exceeded the Dutch SGV of 190 mg/kg. An exceptional value of bioaccessible Cu was observed in the Dasco sample (11200 mg/kg). This was about 59 times higher than the Dutch SGV for Cu. For Pb, Katangua and Dasco soils had bioaccessiblePb concentrations exceeding CLEA SGV of 450 mg/kg and Dutch SGV of 530 mg/kg (924 and 1720 mg/kg respectively).

Zinc may be considered the most bioaccessible PTE in the PM_{10} fractions as the Dutch SGV (750 mg/kg) was exceeded in more than half of the soils, including in Ikj OM 1 which is a sample from sampling campaign 1 (an urban background site). Bioccessible Zn in Katangua soil was about 12 times higher than the Dutch SGV for Zn. Table 5.15 shows the comparison between bioaccessible PTE in different fractions of Lagos urban soils (< 10 µm and < 250 µm fractions). A clear increment in the amount of bioaccessible PTE in the < 10 µm compared to the < 250 µm fraction was apparent. The increments were on average of 3 to 4 times for most PTE analysed, but about 9 times for bioaccessible Zn concentrations.

The % BA was calculated for bioaccessible and pseudototal PTE concentrations in the < 10 µm fractions of Ifk PO 5 and Ifk RD 2 (the two sites from which sufficient sample was obtained to perform both types of extraction). The so called ‘‘urban metals’’ were the most bioaccessible PTE in the PM_{10} fractions as also seen in results for the < 250 µm fractions of the Lagos urban soils. The higher abundance of bioaccessible forms of ‘‘anthropogenic PTE’’ (Cu, Pb and Zn) in PM_{10} fractions as against the lithogenic PTE (Cr, Fe, and Ni) has been reported in literature[7, 77, 347].

Table 5.15 Comparison between bioaccessible PTE concentrations in 250 µm and the < 10 µm fractions of Lagos urban soils

mg/kg	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
Agege (< 10 µm)	6	289	1080	361	15	240	1770
Agege (< 250 µm)	2	143	369	165	7	106	821
Grand foundry (< 10 µm)	79	45	11700	2100	44	44	1570
Grand foundry (< 250 µm)	32	17	4380	743	15	8	350
Ikeja along (< 10 µm)	2	82	240	135	4	253	197
Ikeja along (< 250 µm)	1	46	105	66	2	140	23
Katangua (< 10 µm)	15	447	1400	1063	27	924	8950
Katangua (< 250 µm)	4	186	512	347	9	392	4010
Dasco (< 10 µm)	425	11200	9550	934	585	1720	2560
Dasco (< 250 µm)	162	7290	5710	521	275	910	1690
IF PO 5 (< 10 µm)	4	29	1090	261	5	64	375
IF PO 5 (< 250 µm)	0.5	6	195	34	1	7	12
LI PO 2 (< 10 µm)	9	62	2060	328	7	89	668
LI PO 2 (< 250 µm)	3.6	15	665	111	3	37	218
IK OM 1 (< 10 µm)	2	22	397	233	4	56	907
Ikeja OM (< 250 µm)	0.4	8	72	130	1	23	60
IF RD 2 (< 10 µm)	4	40	1250	195	4	76	571
IF RD 2 (< 250 µm)	0.5	8	225	40	1	11	47

Table 5.16 Percentage bioaccessible PTE (% BA) concentrations in < 10 µm fractions

		Cr	Cu	Fe	Mn	Ni	Pb	Zn
Ifk PO 5	bioaccessible concentration	4	29	1094	261	5	64	375
	pseudotal concentration	69	61	35100	701	27	123	365
	% BA	6	48	3	37	18	52	103
Ifk RD 2	bioaccessible concentration	4	40	1257	195	4	76	571
	pseudotal concentration	125	115	53300	434	55	199	977
	% BA	3	34	2	45	8	38	58

Manganese showed an intermediate behaviour at Ifk PO 5, but high bioaccessibility at site Ifk RD 2. The general PTE availability trend followed the order Zn > Pb > Cu

> Mn > Ni > Cr > Fe. The same pattern was obtained for decreasing bioaccessible PTE in < 250 µm fractions.

Human health risk assessment

The health risk assessment equation used in estimating human exposure to airborne contaminants in this study was based on a method developed by United States Environmental protection Agency[388] and has been adopted as a risk assessment model for the inhalation pathway studies in previous work[102, 159, 221, 389-393].

Exposure to PTE in resuspended inhalable PM_{10} from Lagos urban soils by child and adult receptors was estimated by using equation 8.1:

$$D_{inh} = \left(\frac{C \times InhR \times EF \times ED}{PEF \times BW \times AT}\right)$$

Equation 5.2

Where C is the concentration of PTE in the PM_{10} fraction (mg/kg)

InhR is the inhalation rate and is taken as 7.6 m^3/day

EF is the exposure relative frequency (230 day/year for children and 180 days/year for adults).

ED is the exposure duration (3 years for children and 24 years for adults)

PEF is the particle emission factor and is taken as $1.36 \times 10^9/m^3/kg$

BW denotes body weight 18 kg for children and 70 kg for adults

AT is the averaging time and is represented as ED × 365 days for non-carcinogens and 70 × 365 days for carcinogens.

The average daily dose calculated for each PTE was then divided by the corresponding reference dose (RfD, mg/kg) to yield a hazard quotient (HQ) for non-cancer risk and for carcinogens, and then the dose was multiplied by the corresponding slope factors (SF, mg/kg) to produce a level of cancer risk.

The slope factor was used to estimate the risk associated with exposure to a potentially carcinogenic substance. In the current study, cancer risk was calculated for Cr and Ni because, among the PTE studied, only the SF for these PTE is available. The reference dose and slope factor values are presented in Table 5.17. Calculated risks are presented in Table 5.18, 5.19, 5.20 and 5.21. However, it should be noted that some of the toxicity values highlighted above for the inhalation risk calculation such as the exposure duration and the average weight of a child are based on US data may not totally represent the current study area where child weight will be lower due to differences in nutrition and exposure to soil derived dust will be greater due to differences in climate. Because data on Nigerian residents is not available, the protective default values of ED and BW (for children and adult) were considered as appropriate. Furthermore, the original USEPA model (Equation 5.2), assumes 100 % absorption efficiency (bioavailability in the blood stream of humans) for all PTE; in this regard, a large number of studies on PTE toxicity assessments are derived from this model which undoubtedly would have overestimated the toxicity risks going by bioaccessibility results in this current study, hence, the bioaccessible PTE obtained from the PM_{10} samples were incorporated into the model instead of the default total PTE concentration values in order to give a more reasonable quantitative risk estimate.

Table 5.17 The reference dose and slope factor values of PTE used in this study[159, 221, 390, 394]

	RfDinh (mg/kg)	SFinh
Cr	2.86E-05	4.20E+01
Cu	4.02E-02	
Fe	7.00E-01	
Mn	1.43E-05	
Ni	2.06E-02	8.40E-01
Pb	3.52E-03	
Zn	3.00E-01	

Table 5.18 Non-carcinogenic risks in children

Location	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Ifk PO 5	2.64×10^{-5}	1.34×10^{-7}	2.87×10^{-7}	3.35×10^{-3}	4.35×10^{-8}	3.33×10^{-6}	2.29×10^{-7}
LM PO 2	5.89×10^{-5}	2.86×10^{-7}	5.41×10^{-7}	4.21×10^{-3}	6.24×10^{-8}	4.66×10^{-6}	4.09×10^{-7}
Ikj OM 1	1.25×10^{-5}	1.01×10^{-7}	1.04×10^{-7}	2.99×10^{-3}	3.15×10^{-8}	2.94×10^{-6}	5.55×10^{-7}
Ifk RD 2	2.46×10^{-5}	1.81×10^{-7}	3.30×10^{-7}	2.51×10^{-3}	3.71×10^{-8}	3.95×10^{-6}	3.50×10^{-7}
Agege	4.01×10^{-5}	1.32×10^{-6}	2.84×10^{-7}	4.64×10^{-3}	1.34×10^{-7}	1.25×10^{-5}	1.09×10^{-6}
Grand Foundry	5.09×10^{-4}	2.07×10^{-7}	3.09×10^{-6}	2.70×10^{-2}	3.95×10^{-7}	2.27×10^{-6}	9.67×10^{-7}
Ikj Along	1.48×10^{-5}	3.76×10^{-7}	6.29×10^{-8}	1.73×10^{-3}	3.20×10^{-8}	1.32×10^{-5}	1.20×10^{-7}
Katangua 1	9.77×10^{-5}	2.04×10^{-6}	3.70×10^{-7}	1.37×10^{-2}	2.40×10^{-7}	4.82×10^{-5}	5.48×10^{-6}
Dasco	2.73×10^{-3}	5.15×10^{-5}	2.51×10^{-6}	1.20×10^{-2}	5.22×10^{-6}	8.99×10^{-5}	1.57×10^{-6}
Average	**3.9×10^{-4}**	**6.23×10^{-6}**	**8.4×10^{-7}**	**8.0×10^{-3}**	**6.9×10^{-7}**	**2.01×10^{-5}**	**1.20×10^{-6}**

Table 5.19 Non-carcinogenic risks in adults

Location	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Ifk PO 5	1.49×10^{-5}	7.57×10^{-8}	1.62×10^{-7}	1.89×10^{-3}	2.45×10^{-8}	1.88×10^{-6}	1.29×10^{-7}
LM PO 2	3.32×10^{-5}	1.61×10^{-7}	3.05×10^{-7}	2.37×10^{-3}	3.52×10^{-8}	2.63×10^{-6}	2.31×10^{-7}
Ikj OM 1	7.05×10^{-6}	5.68×10^{-8}	5.87×10^{-8}	1.69×10^{-3}	1.78×10^{-8}	1.66×10^{-6}	3.31×10^{-7}
Ifk RD 2	1.39×10^{-5}	1.02×10^{-7}	1.86×10^{-7}	1.42×10^{-3}	2.09×10^{-8}	2.22×10^{-6}	1.97×10^{-7}
Agege	2.26×10^{-5}	7.45×10^{-7}	1.60×10^{-7}	2.62×10^{-3}	7.58×10^{-8}	7.06×10^{-6}	6.14×10^{-7}
Grand Foundry	2.87×10^{-4}	1.17×10^{-7}	1.74×10^{-7}	1.52×10^{-2}	2.23×10^{-7}	1.28×10^{-6}	5.45×10^{-7}
Ikj Along	8.33×10^{-6}	2.12×10^{-7}	3.55×10^{-8}	9.78×10^{-4}	1.80×10^{-8}	7.43×10^{-6}	6.79×10^{-8}
Katangua 1	5.51×10^{-5}	1.15×10^{-6}	2.08×10^{-7}	7.70×10^{-3}	1.35×10^{-7}	2.72×10^{-5}	3.09×10^{-6}
Dasco	1.54×10^{-3}	2.90×10^{-5}	1.41×10^{-6}	6.77×10^{-3}	2.94×10^{-6}	5.07×10^{-5}	8.86×10^{-7}
Average	**2.22×10^{-4}**	**3.52×10^{-6}**	**4.7×10^{-7}**	**4.51×10^{-3}**	**3.9×10^{-7}**	**1.13×10^{-5}**	**6.8×10^{-7}**

Table 5.20 Carcinogenic risk in children

Location	Cr children	Ni children
Ifk PO 5	2.71×10^{-9}	5.31×10^{-11}
LM PO 2	6.07×10^{-9}	7.71×10^{-11}
Ikj OM 1	1.29×10^{-9}	3.89×10^{-11}
Ifk RD 2	2.53×10^{-9}	4.58×10^{-11}
Agege	4.13×10^{-9}	1.66×10^{-11}
Grand Foundry	5.24×10^{-8}	4.87×10^{-10}
Ikj Along	1.52×10^{-9}	3.95×10^{-11}
Katangua 1	1.01×10^{-8}	2.96×10^{-10}
Dasco	2.81×10^{-7}	6.45×10^{-9}
Average	**4.02×10^{-8}**	**8.50×10^{-10}**

Table 5.21 Carcinogenic risk in adults

Location	Cr adults	Ni adults
jIfk PO 5	6.12×10^{-9}	1.45×10^{-10}
LM PO 2	1.37×10^{-8}	2.08×10^{-10}
Ikj OM 1	2.91×10^{-9}	1.05×10^{-10}
Ifk RD 2	5.71×10^{-9}	1.24×10^{-10}
Agege	9.31×10^{-9}	4.49×10^{-10}
Grand Foundry	1.18×10^{-7}	1.32×10^{-9}
Ikj Along	3.43×10^{-9}	1.07×10^{-10}
Katangua 1	2.27×10^{-8}	8.01×10^{-10}
Dasco	6.34×10^{-7}	1.74×10^{-8}
Average	**9.07×10^{-8}**	**2.30×10^{-9}**

The term ‘‘carcinogenic risk’’ is a probability of an individual developing any kind of cancer from lifetime exposure to a carcinogenic substance or hazard. For regulatory purposes, the acceptable or tolerable risk is in the range of $10^{-6} – 10^{-4}$.

The results showed that Mn and Cr posed higher non-carcinogenic risks to the Lagos populace than the ‘‘urban metals’’ (Cu, Pb and Zn). For children, the average HQ for Mn was 8.0×10^{-3} and for Cr was 3.9×10^{-4}. Copper, Pb and Zn had average HQ values of 6.23×10^{-6}, 2.01×10^{-5} and 1.20×10^{-6} respectively. Iron and Ni presented the lowest values with averages of 8.41×10^{-7} and 6.88×10^{-7}. The non-carcinogenic effects of PTE in the PM_{10} samples followed a decreasing PTE order for children and adults: Mn > Cr > Cu > Pb > Zn > Fe > Ni. This is in agreement with the order found from resuspended dust sampled on building surfaces in Shandong, China[389], where crustal materials may be the most significant factor contributing to non-carcinogenic health effects in humans as Mn is mainly from lithogenic sources. Other studies have shown Cr to be a major contributor to non-carcinogenic effects in children exposed to classroom and street dust[40, 102]. The HQ values for the studied PTE were all lower than the safe level of 1, suggesting minimal adverse health risks. However, PM_{10} isolated from Dasco and Katangua 1 soils showed consistent higher HQ values for all PTE in comparison to other soils studied. This may be related to the high pseudototal and bioaccessible PTE concentrations measured in the test samples. Results of Dasco and Katangua test samples have shown that higher PTE concentration in urban soils corresponds to higher PTE concentration in PM_{10} fractions which in turn will result in higher susceptibility to non-carcinogenic risk. Therefore, there is need for continuous PTE monitoring in Lagos urban soils since resuspended soil particles or dust present in the ambient air may deposit PTE on food substances, drinks and indoor surfaces and appliances and this often results to health risks (cancer or non-cancer) to human receptors[40].

Previous studies on the human health risk of PTE in < PM_{10} fractions suggest ingestion and dermal contact pathways as the major routes of exposure, which result in human health risks [40, 159, 347, 389, 390, 392, 395]. Risks associated with accidental ingestion of soil by a child weighing 10 kg were considered in the first section of this chapter.

Considering the exposure frequency or the increased likelihood of soil/dust ingestion by children, the results of the current chapter suggest that the inhalation pathway could be less of a potential health risk to children.

The potential non-carcinogenic health risk for adults (due to the possible inhalation of PTE in PM_{10} fractions) was lower compared to the risk in children. The HQ values (for adults) are about one order of magnitude lower than the calculated values for children; although PTE followed the same decreasing order of non-carcinogenic effects as observed for children. This is consistent with results obtained for similar previous studies[40, 391].

For the potential carcinogenic risks in children and adults, only Cr and Ni were considered. The mean Cr and Ni cancer risk in children (average of 4.02×10^{-8} and 9.07×10^{-8} respectively) were lower than the international acceptable limits of 10^{-6} – 10^{-4}[389, 393] (see Table 5.20 and 5.21). The cancer risk assessment in adults presented higher values than in children but were also lower than the acceptable limits. Generally, this study has demonstrated that, exposure to PTE in PM_{10} fractions of Lagos resuspended soils may not pose any serious health effects to residents, considering only the inhalation pathway. However, the calculated non-cancer and cancer risk for the two receptor groups (children and adults), showed that children are more susceptible to non-cancer risk while adults are more vulnerable to cancer risks. These findings agree with other studies elsewhere[389, 393].

5.5 Conclusion

The work discussed in this chapter was in two parts, highlighting the oral bioaccessibility of PTE in soil and PM_{10} samples. The first part of the work showed the successful application of the SBET protocol to study PTE (Cr, Cu, Fe, Mn, Ni, Pb and Zn) behaviour in soil samples and information about the bioaccessibility of PTE in the soils and possible human health risk were revealed. Information from bioaccessibility data indicated pseudototal PTE concentrations to be a rather crude and inappropriate estimate of the fraction that is potentially available for absorption in the gastro intestinal tract of man.

However, bioacessible concentrations appeared to be strongly influenced by pseudototal concentrations considering the positive and significant correlations recorded between the two variables but not with soil pH and organic matter. Further work is required in future soil studies to understand the interactions, the mode of retention and release governing PTE dissolution in soils of the study area and ultimately in the human gastrointestinal tract.

Copper, Pb and Zn generally showed higher bioaccessibilty (% BA with respect to pseudototal concentrations) than Cr, Fe and Ni which may reflect an anthropogenic, as opposed to geogenic origin. Manganese showed intermediate behaviour. Chromium, Fe and Ni generally showed very low % BA of less than 5 %. Their presence in the immobile phase of sequential extraction (residual phase) may further explain their low bioaccessible concentrations. The % BA followed the order: Zn (57%) > Pb (51 %) > Cu (46 %) > Mn (28 %) > Ni (15%) > Cr (4%) > Fe (3%).

The obtained data and corresponding tolerable daily intakes calculated (based on Baar's *et al.*[380]approach) assuming a worst case scenario of 10 g/day indicates the presence of severe health risk related to soil ingestion especially for the contaminated soils. The calculated TDI indicated that all soils posed a risk of Pb toxicity, but only two soils exceeded the TDI for Pb for case of conservative consumption of 100 mg/day. More worrisome was one of the dumpsite soil samples (Dasco) in which only about 40 mg of soil was required to be ingested to deliver the TDI for a 10 kg child. The TDI for Zn was exceeded in almost half of the soils studied assuming soil pica tendencies (10 g/day). For all PTE studied, Pb appeared to be the PTE of greatest concern considering both typical and excessive soil intake by a child, and Dasco was the contaminated site of greatest concern. Discussions in this section highlighted the difficulty in comparing the results of this study with literature data since there are many parameter which include the size fraction investigated, extraction time, extraction fluid composition, therefore a standard internationally accepted bioaccessibility protocol and certified reference material is required to check accuracy and inefficiencies in the results.

Given the complexity of exposure criteria, and uncertainties in intake pathway in an urban environment, the risks assessment must be treated with caution but nevertheless has highlighted the PTE of greatest concern.

In the second section of this chapter, information was obtained from the isolation of < 10 µm particle size fraction of soil and the behavioural pattern of PTE in the potentially resuspended soils. A wet isolation method was optimised and adapted for the isolation of the PM_{10} fraction of real test urban soil samples. Particle size authentication was performed by analysing a test portion of an isolated PM_{10} fraction (Ifk PO 5) using a Malvern light scattering particle analyser and result showed that 84.3 % of the isolated particles were < 10 µm in diameter. The estimation of the percentage PTE losses (water soluble fraction) during PM_{10} isolation showed that less than 0.5 % of PTE was lost during wet PM_{10} isolation from the soils, with exception to Ifk RD 2 in which 2.3 % of Zn was lost. Operator time was also reduced by incorporating centrifugation in separating the suspension and the filtrate; this allowed several hours which is required for sedimentation process to be cut short. The isolation process optimised in this work appeared to be robust and adaptable. It can be utilised in future urban soil studies to isolate PM_{10} fraction from small sample mass in order to evaluate the contribution of resuspended soil fraction to particulate matter load. It will be particularly applicable to PM_{10} studies in developing countries where air sample monitoring stations are not available.

The SBET and pseudototal procedures were successfully modified and applied to PM_{10} isolated from test soil samples. The result of the miniaturised procedure was not affected by the reduced sample mass and extractant volume and there were consistencies in the % BA of the PTE analysed in the optimised and original procedure (< 250 µm). Despite the difference in particle size, the results obtained have demonstrated the robustness of SBET procedure. This was further confirmed in the general PTE availability trend in PM_{10} fractions which followed the order Zn > Pb > Cu > Mn > Ni > Cr > Fe and this matches the exact bioaccessibility PTE trend for the < 250 µm fraction.

The PTE contents of the two test samples subjected to pseudototal digestion (PM_{10} isolated from Ifk PO 5 and Ifk RD 2) revealed enrichment in the finer particles and this was in agreement with results obtained from the literature.

The SBET extractable Cu and Pb in two PM_{10} samples (Dasco and Katangua 1) exceeded the Dutch and CLEA soil guideline values for Cu and Pb. Similarly, bioaccessible Zn concentration in more than half of the PM_{10} samples exceeded the Dutch SGV for Zn. This was interpreted with caution since there are no guidelines values outlining toxicity risks associated with bioaccessible concentrations therefore comparison with established SGV gave an assessment or guide on how polluted the soils might be. Appropriate estimation method would have to include measurement of the air respiratory volume in the study area and incorporated into toxicity risk calculation. This would allow for better quantification in future studies.

Anthropogenic PTE (Cu, Pb and Zn) appeared to be more bioaccessible than lithogenic PTE (Cr, Fe and Ni) but Mn showed higher bioaccessibility than the lithogenic PTE group. This was similar to result of the non-residual fractions of BCR sequential extraction which strongly indicates the possible sources of these PTE in the urban environment.

Human health risks assessment of the inhalation pathway suggested that Mn and Cr posed higher non-carcinogenic risks than other PTE. Iron and Ni presented the lowest non-carcinogenic effects in PM_{10} samples and the general decreasing trend followed the order of Mn > Cr > Pb > Cu > Pb > Zn > Fe > Ni for children and adult receptors. Calculated non-cancer and cancer risks indicated that children are more susceptible to non-cancer risk while adults are more vulnerable to cancer risks. Generally, this study has shown that exposure to PTE in the PM_{10} fractions of resuspended soil is unlikely to pose any serious health effects to residents, considering the inhalation pathway as the only route by which PTE enters the human body. Owing to the aforementioned results and discussions, the aims and objectives of this chapter is achieved.

6 Conclusions and further work

6.1 Conclusions

The work carried out within the context of this thesis provides information about the current PTE status of urban soils in Lagos as an example of a rapidly urbanising megacity in a developing country. The potential mobility of PTE in urban soils and the human health risk assessment associated with the PTE measured in the soils and potentially resuspended soil fractions were investigated. *Aqua-regia* soluble PTE concentrations in Lagos urban soil samples were measured for Cr, Cu, Fe, Mn, Ni, Pb and Zn. Results showed that mean pseudototal PTE concentrations at locations remote from known point sources of pollution were generally low and pose no risk, but soils taken from locations close to industrial activities such as foundries, dumpsites, and e-waste recycling sites were often highly contaminated.

Socio-economic areas appear to influence the Lagos urban soils quality. Lagos mainland and Makoko areas were more polluted in comparison to Ikeja, Ifako and VI. Lagos mainland represents a mix of both low and middle income earners and Makoko which is a predominantly low income earning area is a small part of LM local government area. This may probably explain the similarities in the PTE pollution pattern of the areas. Higher PTE concentrations recorded in the areas may be because strict adherence to environmental law and practises are not well established. Ikeja and Ifako (middle income earning areas) have similar PTE contamination profiles. This may be expected since both LGA are next to each other. Victoria Island which represents the high income area and was the least polluted. Further studies are needed to investigate the variabilities of PTE distribution in different socio-economic areas of other cities or megacities of developing countries which will provide more literature for reference or comparison in this regard, since to my knowledge the current study is the first investigation of its kind. Such studies will provide more information about this topic and will assist in urban planning decisions.

Principal component analysis, cluster analysis and correlation coefficient identified two major PTE groupings in soils collected away from potential point sources. Copper, Pb and Mn association was confirmed by the multivariate statistical techniques (PCA and CA) and correlation coefficient analysis. This association can be regarded as the anthropogenic component which represents contribution of PTE from human activities. The association of Cr, Fe, Mn and Ni was also confirmed by PCA, CA and correlation coefficient analysis; this association appeared to be largely controlled by geogenic inputs. Various statistical analysis employed in this work have provided new information regarding possible origins of PTE in this category of Lagos urban soils.

Land uses appeared to have influenced PTE distribution in urban soils analysed in this current study. This study has demonstrated the variability and lack of uniformity of PTE distribution in the land uses studied and certainly attributed to different land use activities and disturbances ranging from duration and varied intensities of anthropogenic activities, geological characteristics of different soil types. The PTE concentrations in DS, TS and IND appeared to be strongly influenced by industrial activities and deposition of domestic, electronic, scrap metal, spent oil wastes on municipal dumpsites while SH, PO, RD and OG were influenced by contributions from both lithogenic and anthropogenic components. The anthropogenic influence on the latter land uses (SH, PO, RD and OG) was suggested to be largely controlled by traffic sources and considerable proximities to industrial emissions. The impact of land uses on PTE distribution pattern in urban soils of developing megacities such as Lagos will exert different degrees of health impacts to residents and economic development or industrialization which ultimately leads to rural-urban migration has been identified as the major factor worsening the situation. This obviously would lead to overstretch of urban infrastructures continuous increase of informal urban settlements or slum which would have associated health impacts to residents. Concerns about the co-location of the industrial estates with residential layout, siting of residential buildings directly behind or in front of dumpsites were noted. Regulations and legislations on environmental issues which include effective solid waste management strategy and enforcement of emission standards should be given close attention in order to reduce the impact of PTE pollution to the inhabitants of urban areas in developing countries.

The ‘‘urban metals’’ (Cu, Pb and Zn) had consistent higher enrichment factor, and geo-accumulation index values for all land uses studied in comparison to other PTE studied. The results of these pollution assessment tools strongly suggest that these PTE were enriched in Lagos urban soils and Pb was the PTE of greatest concern. However, there is need for proper SGV computation in Nigeria and other developing countries. This will allow for better comparison of PTE concentrations to the SGV related to the soil geochemistry of the study area. This would discourage the comparisons of PTE concentrations with SGVs computed by developed countries such as UK and Netherlands. Establishment of background concentrations by conducting national pollution surveys is required in most developing countries including Nigeria; this would provide better assessment of PTE pollution in future urban soil studies and would eliminate the substitution of background concentration values with rock shale values in the computation of pollution assessment tools such as EF and Igeo. The non-uniformity of sampling strategies, study area, sampling locations (different land uses), number of samples, different sampling depth and extraction protocol have been noted to be a serious constraint in comparing published data. Because of the potential toxicity of PTE in urban soils and the threat to human health, there is need for harmonization of methodologies in study of the urban soil geochemistry of cities.

The application of revised BCR sequential extraction to Lagos urban soils allowed further investigation of PTE fractionation and mobility. Results indicated that Cr, Fe and Ni were predominantly associated with the residual fraction implying less mobility and less environmental risk. Potentially toxic elements present mainly in the residual fractions were suggested to have originated from geogenic sources. This suggestion was confirmed in Cr, Fe and Ni fractionation patterns but contradicted for Mn. The highest amount of extractable Mn was found in the reducible phase followed by residual phase and significant amount of Mn species were also present in the exchangeable and oxidisable phases. Manganese was almost evenly distributed between the phases thereby displaying an intermediate behaviour of originating from mixed sources of natural and anthropogenic origins.

Copper and Pb were mainly associated with the reducible phase and can be categorised to be considerably mobile because of their significant presence in the non-residual fractions. Possibility exists that analytes may mobilize under changing environmental conditions. The highest proportion of Zn was found in the exchangeable phase making Zn the most mobile PTE studied.

Information from bioaccessibility studies revealed that risk assessment based on the comparison of pseudototal concentrations to SGVs would have overestimated the potential risks PTE poses. Results showed that less than 5 % (% BA with respect to pseudototal concentrations) of Cr, Fe and Ni were potentially available for absorption in the gastro intestinal tract of man. Copper, Pb and Zn (urban metals) showed higher bioaccessibilities compared to Cr, Fe and Ni which reflects anthropogenic, as opposed to geogenic origin. Manganese displayed an intermediate behaviour. There were good agreements in the results of mobility tendencies of PTE as shown by sequential extraction results and bioaccessibility results. Soil pH and % LOI appeared to have no influence on PTE accumulation in soil samples and dissolution in the human GIT and also not related to pseudototal concentrations. Negative correlation coefficient values and insignificant linear regression values were obtained for the relationships between extraction variables (pseudototal levels, bioaccessible concentrations, PTE extracted in the non-residual soil phases) and soil properties. These relationships apparently indicated no significance. It is important to note that findings may be limited since only two soil properties were measured and the application of regression models with larger number of samples and measurement of other soil properties such as cation exchange capacity, redox potential, calcium carbonate content and microbial activity in future studies would perhaps derive more robust and better prediction of the relationships between soil properties and PTE accessibility. The discussions in chapter 5 pointed out the difficulties in comparing results obtained in this study with literature data since literature is still sparse on bioaccessiblity of PTE in urban soils, particularly in developing countries and many parameters such as size fraction, compositions of fluid, bioaccesibility method, and extraction time differs.

Therefore, there is need for more work to be done on PTE bioaccessibility in urban soils most especially in developing countries, so also the harmonization of bioaccessibility method and establishment of reference materials to validate results and check reproducibility.

Risk assessment was estimated by calculating the amount of soil that a hypothetical child (weighing 10 kg) needs to ingest to reach a toxicologically significant level based on bioaccessible PTE concentrations. Obtained data showed Cr, Cu, Fe, Mn and Ni were not a significant health risk to children. However, all soils showed the tendency to pose Pb toxicity in the worst case scenario of deliberate soil ingestion (10 g/day). Two of the contaminated soils (sampling campaign 2) are likely to pose a risk in an event of conservative consumption of 100 mg/day. Dasco was the most contaminated as only 40 mg of soil is needed to deliver the TDI in a 10 kg child. Zinc was also a PTE of concern since the TDI was exceeded in about half of the soils studied assuming soil ingestion of 10 g/day.

The final part of the study focused on the isolation of < 10 µm fractions from soil samples (same set of soils studied for bioaccessibility and fractionation of PTE). This particle size is of great concern because it is easily carried by air flows generated from the action of human feet, traffic or wind and could be dangerous to general public since they constitute a significant portion of atmospheric air we breathe in as humans. In the current work, an existing wet isolation method developed by Ljung *et al*[179]. was optimised and adapted to real test urban soil samples. Cheap biological sieve, smaller sample and reduced extractant volume were employed in the current study. Operator time was reduced for the optimised procedure in this current study, by incorporating centrifugation in separating the suspension and the filtrate; this allowed several minutes which is required for sedimentation process to be cut short. The isolation process optimised in this work appeared to be robust and adaptable. Particle size authentication test on the isolated test portion (was not included in the original procedure) showed that over 80 % of the isolated particles were less than 10 µm. Less than 0.5 % of PTE were lost during PM_{10} isolation making the wet isolation suitable for PM generation for risk assessment studies. The optimised method can be utilised in future urban soil studies to isolate PM_{10} fraction from small sample mass in order to evaluate the contribution of resuspended soil fraction to particulate matter load. It would be particularly applicable to PM_{10} studies in developing countries where air sample monitoring stations are non-existent.

The SBET and pseudototal procedures were successfully modified and applied to PM_{10} isolated from test soil samples. The result of the miniaturised procedure was not affected by reduced sample mass and extractant volume as there were consistencies in the % BA of the PTE analysed in the optimised and original procedure (< 250 µm). Results obtained have demonstrated the robustness of SBET procedure. This was further confirmed in the general PTE availability trend in PM_{10} fractions which followed the order Zn > Pb > Cu > Mn > Ni > Cr > Fe and this followed the precise PTE bioaccessibility trend for the < 250 µm fraction.

Bioaccessible concentrations were incorporated to inhalation toxicity model for human health risk assessment which currently assumes a default of 100 % bioavailability. This was necessary considering the result of PTE bioaccessibility from soils which have given crucial evidences that pseudototal concentrations overestimate PTE toxicity risk to humans. Results arising from modified model showed that Mn and Cr were PTE of concern considering non-carcinogenic risk.

Calculated non-cancer and cancer risks indicated that children are more susceptible to non-cancer risk while adults are more vulnerable to cancer risks. However, it should be noted that the quantitative estimates of the inhalation risk modelling adopted in this study may be affected by some degree of uncertainties because of the assumptions of the default inhalation rate, exposure frequency and average body weight of child and adult by USEPA[396] that are yet to be established in Nigeria. This suggest that, the numerical outcome (carcinogenic and non-carcinogenic) obtained from this model should be interpreted with caution. The highlighted uncertainties nonetheless, the inhalation risk assessment employed has proven to be a useful tool to reveal the relevance of PTE concentrations and its associated potential toxicity risks in particulate matter. Considering the aforementioned observations and conclusions of experiments performed in this study, it is reasonable to conclude that the aims and objectives of this work have been achieved.

6.2 Key implications of this research study.

- Up until now, no scientific evidence is available in literature to determine if socio-economic areas of a developing megacity influences PTE distribution. This current study has been able to bridge the knowledge gap in this regard and will assist in urban planning decisions.
- Children have been noted to be more susceptible to PTE toxicity than adults therefore, ornamental gardens, and playgrounds where children normally play should be sited away from traffic sources since data from this current study have shown that land use types located away from traffic sources (leaded petrol is yet to be banned in many developing countries) are less likely to be subjected to anthropogenic inputs.
- Building of housing structures directly in-front or behind dumpsites and the co-location of residential and industrial estates which are still the usual common practises in many developing countries should be discouraged.
- The data from this current study highlighted the importance and requirement of further risk assessment studies employing fractionation and bioaccesibility if PTE concentrations in urban soils exceed the relevant established soil guideline values. To really predict the toxicity to human and ecological receptors, it is important to take PTE availability into consideration and this will provide a more realistic assessments of short to medium term risks.
- Data from this study showed that PTE availability was highly related to pseudototal concentrations i.e. the higher the PTE concentration in soil the higher its availability and consequently the likelihood of causing toxicity risks to receptors. This factor coupled with the high lability and bioaccessible nature of ‘‘typical urban metals’’ highlights the need for efficient and appropriate environmental management approaches that mitigate against their accumulation in urban soils and also limits the exposure of local populations to contaminated soils in urban areas.
- From risk assessment studies of this work, Pb was the PTE of greatest concern and capable of causing toxicity risks to children even at low concentrations and this pointed out the need for routine blood Pb surveillance in children living in contaminated areas of megacities of developing

countries, perhaps also for children living in urban areas of developed countries with historical urban soil Pb pollution.

- The cheap, fast and robust optimised PM_{10} isolation procedure employed in this work can be applied to future risk assessment studies to evaluate the contribution of potentially resuspended urban soil fractions to particulate matter load in urban areas particularly in most developing countries where air sampling monitoring stations are not available.
- The results from the miniaturised SBET procedure has proven this method to be robust and adaptable and it can be adopted as the internationally acceptable bioaccessibility procedure provided it is validated against *in vivo* studies for other PTE aside from Pb.
- Since bioaccessibility differs between soils and soil chemical parameters, this current study has contributed to the knowledge of the ongoing bioaccesibility research and procedure validation studies and potential risks to PTE in soils. It also provides useful information relating to the ongoing improvement of risk assessment criteria.
- There is need for proper environmental mitigation approaches such as the vegetation, road and side walk paving, and general improvement in urban infrastructural development in urban areas of most developing countries in order to limit resuspension of PM_{10} fractions from urban soils since data from this study has shown the preferential incorporation of PTE in smaller urban particulates; these actions will reduce potential risk PTE pose to humans through inhalation.
- A framework for integrated assessment of risks to ecological and human receptors should be developed taking into consideration the role of land use in PTE exposure to humans, exposure pathways, socio-economic factors such as nutritional intake, and PTE availability, this would facilitate more applicable guidelines for risk assessment processes and soil remediation.
- This work will be useful or can serve as a reference for future urban soil studies in other rapidly urbanising megacities of developing countries such as Karachi, Pakistan; Bangkok, Thailand; Dhaka, Bangladesh and Delhi, India

(they are part of the top ten rapidly urbanising megacities in the world) which have similar urban characteristics like Lagos, Nigeria.

The key overarching contribution of this work is that it advances knowledge on the effect of urbanisation and industrialisation on soil quality and the subsequent impact of urban soil pollution on human health, in a scenario not previously well-studied viz. a rapidly growing megacity in a developing country, where environmental regulation is (as yet) almost non-existent, and practices such as informal urban settlement mean a relatively high proportion of the population subsists on or close to contaminated land.

6.3 Future work

The findings of this study have revealed information about current PTE status of Lagos urban soils and have also indicated areas for future investigation. In order to increase the understanding of PTE concentrations in Lagos urban soils, the study areas could be further extended to all the 20 local government areas of Lagos thereby providing more information on the general soil PTE pollution status of the state and that can assist with urban planning decisions. Analyte variability in soils could also be further investigated to assess temporal or seasonal differences (e.g. wet and dry season typically experienced in Nigeria) of PTE concentrations.

The distribution of PTE with depth could be further studied to better assess PTE distribution and variation within individual sampling locations, particularly where elevated PTE concentrations were observed e.g. Dasco dumpsite and Ikorodu industrial estate and its environs.

Development of a predictive model which incorporates soil properties such as pH, organic matter, cation exchange capacity, calcium carbonate, microbial activity and PTE availability would be useful for the prediction and efficient management of polluted soils

Dusts have been noted to be enriched in PTE which can be accidentally ingested by children or can contribute significantly to the inhalable PTE load of ambient air[36].

Therefore, pseudototal PTE concentrations of street and indoor dusts of the areas covered in this current study and other areas in Lagos is of interest.

The isolation of substantial amount of PM_{10} fraction from contaminated soils would be of interest in order to gain more insights on potential PTE toxicity risks associated with the inhalable fraction of Lagos urban soils.

Since one of the anthropogenic contributions of PTE to Lagos urban soils is traffic, there is need to expand the range of PTE studied and platinum group elements such as palladium and rhodium which have been linked to catalytic converters of automobiles would be of interest. Isotopic information regarding the forms in which PTE exists in soils as well as source identification especially for Pb would be helpful. The investigation of organic pollutants along with PTE may also give a better understanding or stronger evidence of contamination and anthropogenic impact. The expansion of sequential extraction and bioaccessibility data of PTE in Lagos urban soils with respective to risk assessment might allow better decisions to be made on contaminated land. The is need for the development of a fit-for-purpose risk assessment in developing countries which incorporates the child body weight, exposure duration, age etc. This would provide a better quantitative estimate of the risks associated with PTE in urban particulates from the areas.

Appendix A: Theory of applied techniques

A-1 Introduction

This chapter describes in detail, the principle of operation and applicability of microwave-assisted digestion system and inductively coupled plasma mass spectrometry to environmental sample matrices. These techniques were the main instrumental techniques employed in this research work and were used in the determination of PTE (Cr, Cu, Fe, Mn, Ni, Pb and Zn) in urban soil sample digests and extracts.

A-2 Microwave-assisted digestion and its principle of operation[397-402]

A wide variety of complex samples such as soil, sediments and food stuffs in most cases must first be converted into liquid form prior to elemental analysis[403]. Analytical techniques employed for routine PTE determination such as inductively coupled plasma mass spectrometry (ICP–MS), ICP-OES and flame atomic absorption spectrometry (FAAS) use nebulization for sample introduction which makes it mandatory that solid state sample be converted to liquid form[404]. The term digestion or decomposition of matrices (organic and inorganic) involves the destruction of sample material to liberate metal/analyte content. The purpose of every digestion process is to dissolve the sample matrices, avoid element losses, minimise contamination risk, and reduce process times[399, 405, 406]. Conventional digestion procedures such as dry ashing (mostly for food, plant and biological samples), and wet digestion (e.g. conventional heating using burner, hot plate and sand bath) are often laborious and time consuming[399]. These methods are tedious and have high tendencies for contamination. Microwave heating offers many advantages over conventional digestion procedures. By employing microwave digestion, acid consumption, contamination and time are greatly reduced. Microwave digestion has been developed as a rapid and reproducible sample preparation method for a wide variety of matrices[398].

Microwave radiation is often used in the acceleration of sample preparation by applying it at the appropriate power, mode and specified time.

The principle of heating using microwave energy is based on its direct effect on molecules by ionic conduction and dipole rotation processes. In many applications, these two mechanisms take place concurrently. Ionic conduction refers to the electrophoretic migration of ions when an electromagnetic field is applied. Dipole rotation refers to realignment of dipoles under the influence of an applied electromagnetic field. For commercial microwave systems which use a frequency of 2450 MHz, dipoles align and randomize at 4.9×10^9 times per second and this results in forced molecular movement of ions. The sample solution under test causes resistance to the flow of these ions and this result in friction, thus heating the solution. The ability of a solvent to absorb microwave energy and transfer it in form of heat to other molecules depends on the dissipation factor (tan δ). The dissipation factor is given by equation A.1

$$\text{Tan } \delta = \varepsilon''/\varepsilon' \text{………………… Equation A.1}$$

Where ε'' is the dielectric loss which is a measure of the conversion efficiency of microwave energy into heat and ε' is the dielectric constant which designates the measure of the polarizability of a molecule in an electric field. Polar molecules and ionic solutions such as acids absorb microwave energy strongly because they have a permanent dipole moment (occurs when two or more atoms in a molecule have different substantial electronegativity) that is affected by microwaves and thus pass the heat to other molecules. Polar liquids which have high dissipation constants are ideal for solid sample digestion, transferring heat to a material after absorbing microwave energy. Non-polar solvents such as hexane or chloroform are not heated up when exposed to microwaves.

A magnetron is extensively used in microwave equipment as the main source of microwave radiation. Figure 2.1 shows a schematic representation of a magnetron. It incorporates both magnetic and electric fields in its operation. The applied magnetic field is usually constant and applied along the axis of the circular device.

The centre cathode is heated when power is supplied and this delivers energetic electrons which would, in the absence of the magnetic field, tends to move radially outward to the ring anode which surrounds it. By the process of thermionic emission, electrons are released at the centre hot cathode and they are moved towards the anode by an accelerating field. Magnetic force is exerted on these charges which is perpendicular to their initial radial motion. However, this is swept around the circle. As electrons sweep past the resonating cavities, a resonant high frequency is induced in the cavities.

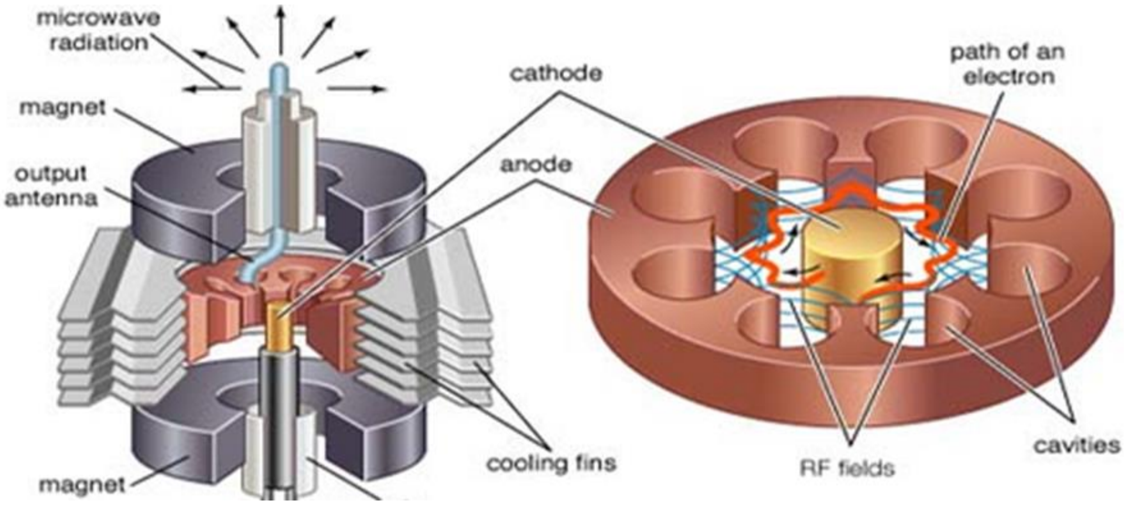


Figure A-1 : A schematic diagram of a magnetron[407]

A portion of the field is isolated with the antenna as microwave radiation and is harnessed accordingly for heating.

The application of microwave energy to sample digestion may be performed using two technologies[397]:

1. Closed vessels or pressurized microwave assisted extraction which is performed under controlled pressure and temperature.
2. Open vessels or focused microwave assisted extraction, performed under atmospheric pressure.

In the open system of microwave sample digestion (Fig 2.2), extraction is carried out under atmospheric pressure and as a consequence, the maximum possible temperature is determined by the boiling point of the solvent at that pressure.

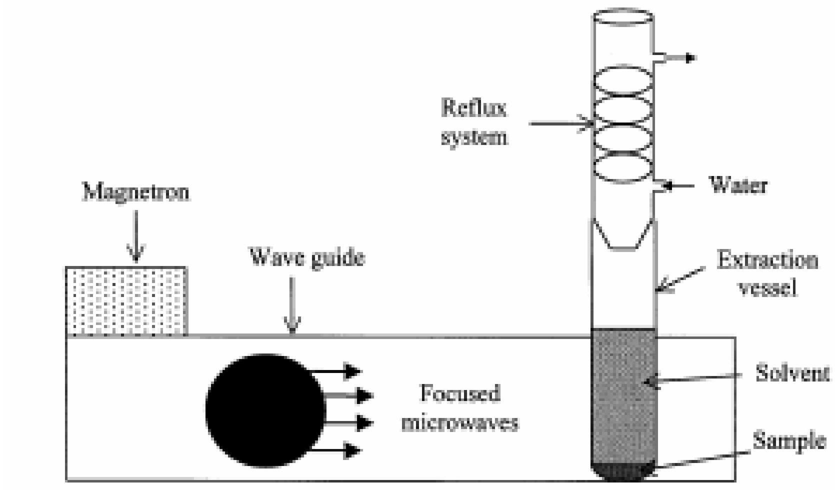
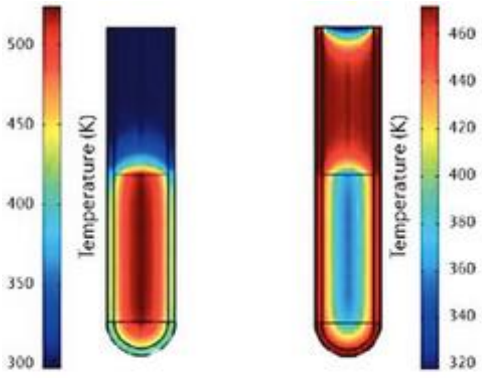


Figure A-2 Schematic representation of open microwave system[397]

The closed vessels system however offers advantage in this aspect in that, the material absorbs directly the microwave energy (see Figure 2.3 and 2.4) through the vessel which results in a more uniform distribution of heat throughout the absorbing material.



(I) (II)

Figure A-3 Heat distribution in digestion vessels, (I) microwave heating (II) conventional heating[408]

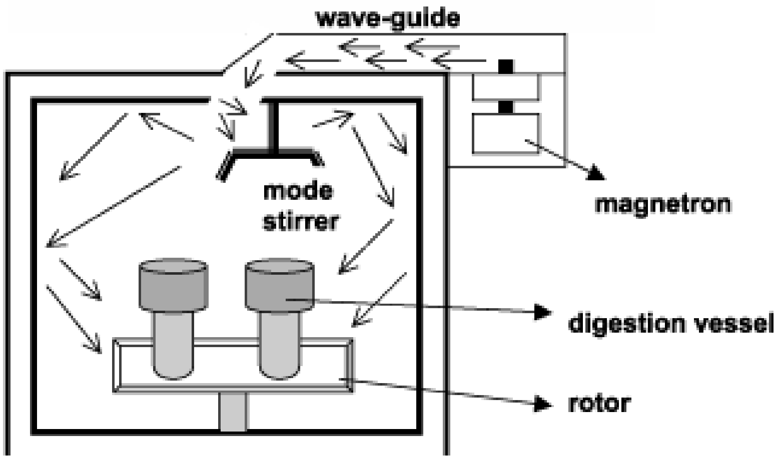


Figure A-4 Schematic representation of closed vessel system[409]

Thus, solvent can be heated above its boiling point at atmospheric pressure thus enhancing speed and efficiency of extraction. Other advantages of closed vessels systems are: loss of volatile substances is completely avoided; no heat loss to the environment; and less solvent is used. Microwave assisted digestion is used extensively in the field of analytical environmental chemistry. Over the years, it has been used for sample preparation, where it is applied mainly for the determination of metals employing nitric acid alone or a the mixture with hydrochloric acid as digestion agent[410]. Microwave digestion technique have been employed for the decomposition of a wide variety of sample matrices such as foods[411], biological samples[412], plant samples[413], fly ash samples[414], urban soil[15, 336], industrially contaminated soil[405], urban particulate matter[217, 415], sewage sludge[416]and sediments[303].

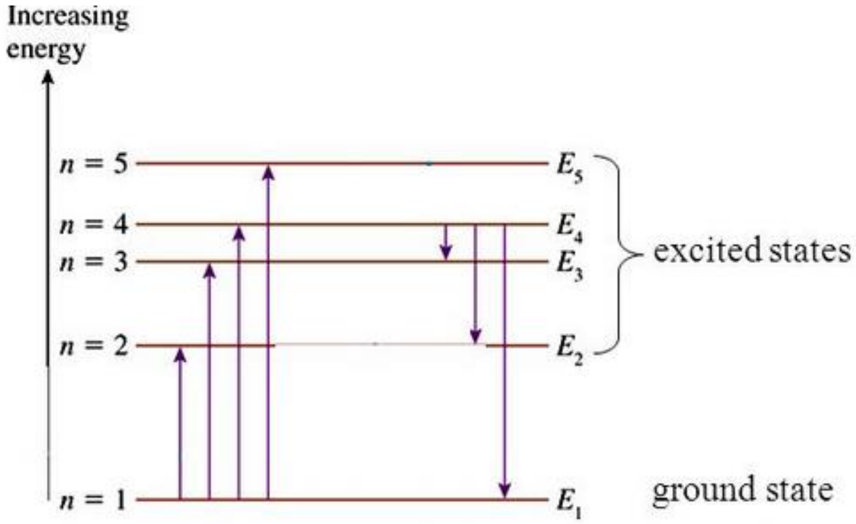
A-3Theory of atomic spectrometry

A.3.1 Introduction[404, 417]

Atomic spectrometry is widely used as a technique for the determination of trace elements in samples. This technique depends upon emission or absorption of electromagnetic radiation, which occurs from energy changes within an atomic system. The technique can be used for quantitative analysis.

The intensity of radiation absorbed or emitted by an atom represents the quantitative information while the qualitative information is given by the wavelength at which radiation is emitted or absorbed. Typical gaseous metal atoms remain in an unexcited state (ground state).

If these ground state atoms are supplied with sufficient energy, electrons are promoted to a higher energy level (excited state). This process is referred to as absorption. As the excited state is unstable, electrons returns back to a lower energy level (a more stable condition); this is referred to as emission. These processes are diagrammatically represented in Figure 2.5.



FigureA-5Energy level diagram showing energy transitions[418]

In the simplified energy level diagram, E_1 represents the ground state in which electrons of a given atom are at their lowest energy level and E_2, E_3,E_4 and E_5 represent higher or excited energy levels. The transition between two energy level e.g. from E_1 to E_2, denotes absorption of energy and the amount of energy absorbed is represented in equation A.2.

$\Delta E = E_2 – E_1 = hv= hc/\lambda$ ………………..**Equation 2.2**

Where c is the velocity of light, *h* is Planck's constant, and *v* is the frequency and λ is the wavelength of absorption. The transition from e.g. E_4 to E_1 corresponds to the emission of radiation of frequency *v*.

A.3.2 Inductively coupled plasma mass spectrometry[417, 419-424]

The inductively coupled plasma (ICP) is the most widely employed ionisation source for inorganic mass spectrometry. Inductively coupled plasmas are flame electrical discharges (either from direct current or radio frequency) that have modernized the practice of isotopic ratio and elemental analysis. Both electrical discharges produce plasma i.e. the direct current plasma (DCP) or the inductively coupled plasma (ICP). Microwave induced plasma (MIP) and glow discharge are also common plasma sources. Plasma sources operate at high temperatures typically between 7000 and 10 000 K. Plasma sources offers appreciable degree of ionization for many elements, simultaneous multi-element capability and excellent detection limits (0.1 – 100 ng/ml). The coupling of ICP and mass spectrometer offers greater sensitivity compared to optical emission and atomic absorption spectroscopy. In general, the ICP-MS technique involves the aspiration of sample solution into the plasma in the form of aerosol where desolvation, vaporisation, atomization, and excitation processes occurs.

A.3.3 Inductively coupled plasma (ion source)

The inductively coupled plasma torch (Figure 2.6) is typically an assembly of three concentric fused-silica tubes. These are frequently referred to as the outer, intermediate and the inner gas tubes. Each of the concentric fused-silica tubes has an entry point, with the intermediate glass tube (plasma) and the external one (coolant), tangentially arranged to each other. The inner tube consists of a capillary, through which sample aerosol is introduced into the nebulisation chamber. A coil of copper tubing is located around the outer glass tube, through which water is circulated for cooling. Power is inputted into the ICP by the copper coil. The input of power into the coil creates a magnetic field, which causes electrons to move in circular path. With argon gas flowing and the power on, some seed electrons and ions are produced in the argon gas by an electrical spark from a Tesla coil.

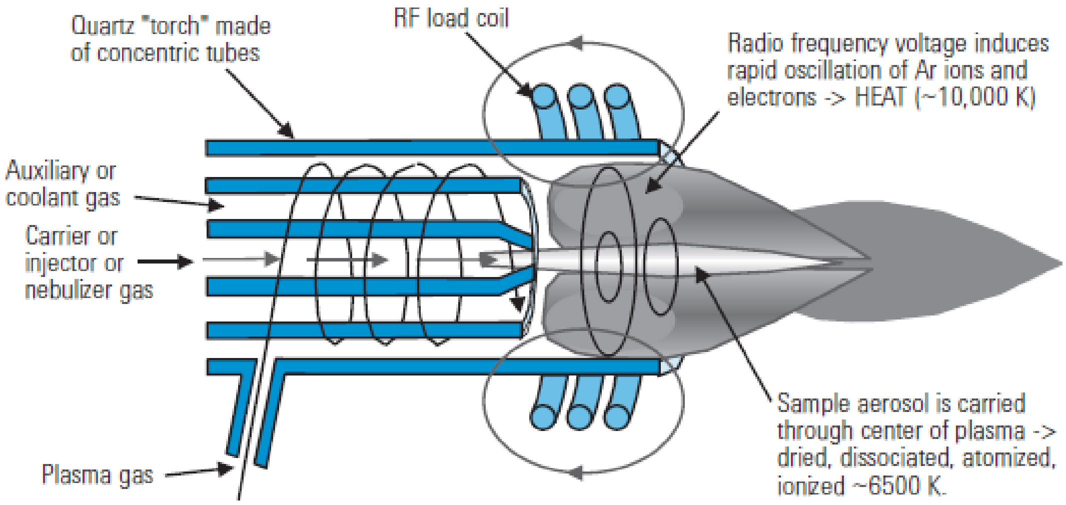


***Figure A-6 Schematic representation of plasma*[425]**

The electrons and ions are then accelerated by the magnetic field and collision with other argon atoms causes further ionisation and creates more electrons. Some of the high energy electrons and argon ions produced collide and recombine, giving off excess energy in the form of heat and radiation. At this point, intensely bright, brilliant white, high temperature plasma is formed. The sustenance of the ICP within the torch depends on the continuous supply of sufficient RF power. A high velocity sample aerosol, generated by the use of a nebulizer is introduced into the confines of the hot plasma gas, by switching on the carrier gas, which then punches a hole in the centre of the plasma, thereby creating a characteristic toroidal shape of ICP. The resultant ions produced from this process are subsequently channelled into mass spectrometer through the sampling interface.

A-3.4 Sample introduction

The efficient introduction of sample into the ICP is a very crucial process for the detection of elements of different concentrations. The combination of a nebulizer and spray chamber is the most common approach. The function of a nebulizer is to create an aerosol with uniformly small droplet size because only small droplets get into the ICP. The most common nebulizer in use today is pneumatic nebulizers.

In pneumatic nebulizers, low pressure and high velocity of argon gas breaks up the liquid into aerosol. The advantages of these nebulizers are excellent sensitivity and stability due to small orifices.

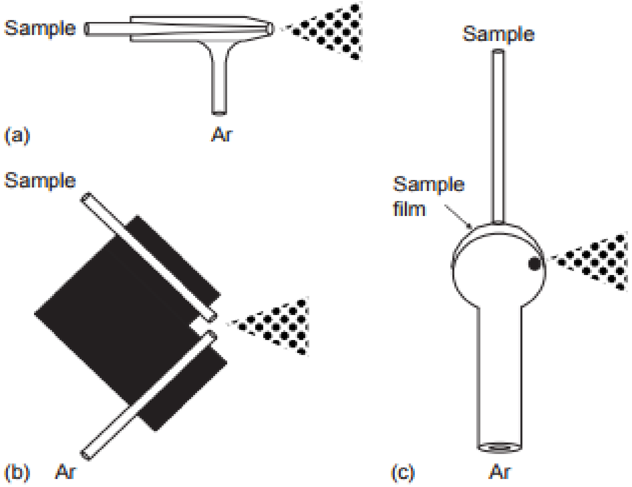


Figure A-7 Schematic diagrams of three types of pneumatic nebulisers; (a) the concentric nebuliser; (b) cross-flow nebuliser; and (c) the Babington nebuliser[424]

The three most common types of pneumatic nebulizers are concentric, Babington-type and micro-flow nebulizer. Early concentric nebulizers were plagued with clogging problem but advances in their designs have improved tolerance to dissolved solids. Concentric nebulizers are capable of operating at a flow rate down to 0.1 mL/min and self-aspirate (without external pumping). Therefore, aerosol formed offers high performance in terms of good precision, stable signal, low percentage relative standard deviation and rapid sample wash out.

The Babington-type nebulizer is designed for high solids applications since the sample capillary does not contain any restrictions to flow. This nebulizer is difficult to block because it does not accumulate salts associated with high dissolved solid samples. It is recommended for high matrix sample types or samples containing high particulate levels. Micro-flow nebulizers provide the best sensitivity of all pneumatic nebulizers.

Advantages of micro-flow nebulizers are high inertness and efficiency with corresponding high sensitivity. However, they suffer clogging problems from samples containing particulates. In order to avoid matrix interferences, a spray chamber (see Figure 2.8) is introduced prior to the plasma.

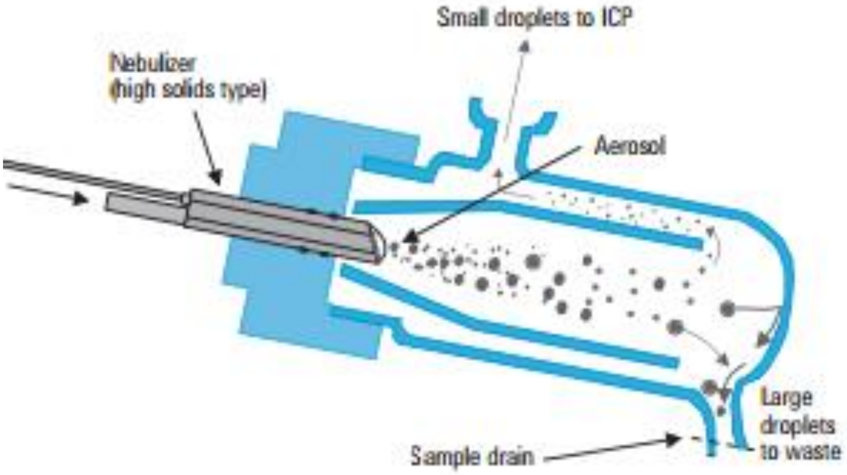


Figure A-8 Schematic diagram of a spray chamber separating small and large droplets[425]

The introduction of aerosol directly into ICP would either extinguish the ICP or lead to severe interference which may be caused as a result of lowering the temperature of the plasma. The main function of the spray chamber is to reduce the particle size of aerosol to an ideal size (typically about 10 µm). Spray chambers also smooth out any pulses that may occur during the process of nebulization. Only about 1 - 5 % of the sample introduced to the nebuliser is transported into the plasma, the remaining 95 - 99 % is drained as waste. Another function of a spray chamber is to remove solvent from aerosol, thereby improving the ionization efficiency.

A-2.5 Ion extraction interface

The interface couples the ICP source with the high vacuum mass spectrometer. After the process of ionisation, ions are brought into the mass spectrometer via the interface cones. This ion interface region of an ICP-MS (see Figure 2.9) transfers ions travelling in the argon sample stream of an extremely hot ICP, at atmospheric pressure (1-2 torr) into the low pressure region of the mass spectrometer (< $1\times10^{-}$

^{5}torr). This is achieved by an intermediate vacuum region formed by the two interface cones, the sampler and the skimmer. These two cones are metal disks (typically made of nickel because of its relative resistance to corrosion and high thermal conductivity) with a small sample hole in the centre. The main purpose of these cones is to function as a sampler in the centre portion of the ion beam coming from the ICP torch. The ions coming from both the plasma and plasma gas itself are drawn into the region of lower pressure through the small orifice of the sampling cone (≈ 1.0 mm). A moderate pressure is usually maintained at the region behind the sampling cone using a vacuum rotary pump (≈ 2.5 mbar). After passing through the sampling cone, a second cone (skimmer) is placed directly, closely enough to allow the central portion of the expanding jet of plasma gas and ions to pass through the smaller orifice of the second cone (an orifice diameter of ≈ 0.75 mm). Low pressure (≈ 10^{-4} mbar) is usually maintained behind the skimmer cone and the extracted ions are then focused by electrostatic lenses into the mass spectrometer.

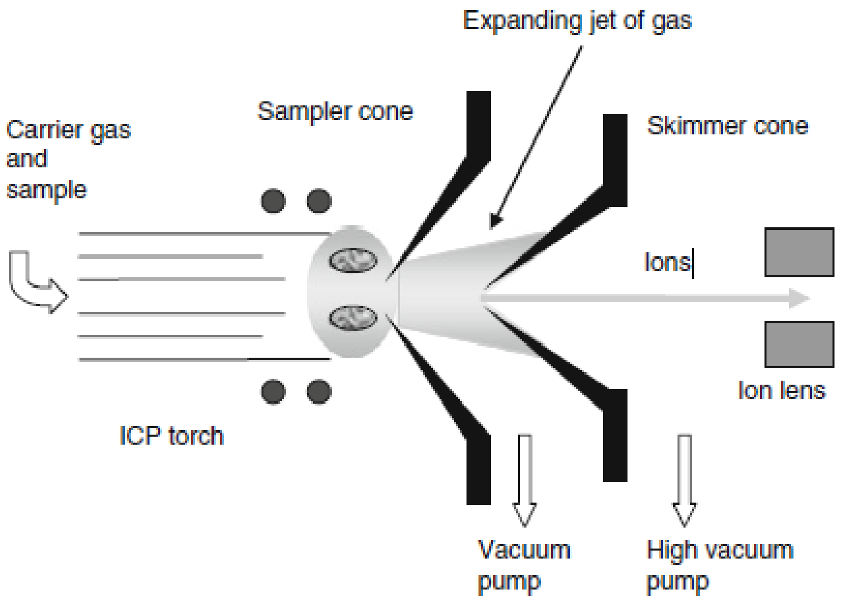


Figure A-9 Schematic diagram of the interface between the ICP and mass analyser[29]

A-3.6 Ion focussing and transmission

Ions from the ICP source are focused by electrostatic lenses in the system. These lenses have a dual function of focussing and transporting ions into the mass analyser. They are made of metal rings, each with a specific voltage. The lens stacks are usually located directly behind the skimmer cone in order to pull the ions from the interface region. Ions coming from the system are positively charged, as are the electrostatic lenses, which serve to gather the ion beam and subsequently focus it into the entrance slit of the mass spectrometer. A photon stop is usually incorporated into the lens stack in order to remove neutral species and photons from the ion beam. Applying a voltage to the photon stop will deflect ions around the disk, while stopping photons or neutral species that would otherwise be registered as additional ion counts by the detector. The removal of these species is important because they cause instability in signal and result in additional background noise. Different types of ICP-MS have different types of lenses. Each instrument designed, has a distinct ion optic system, specifically designed to work with the interface and mass spectrometer.

A-3.7 Ion separations and counting

For the quantification of each element, ions must be separated from the ion beam and counted. The mass spectrometer has the capability of separating ions, based on mass to charge ratio. The quadrupole mass filter (Figure 2.10) is one of the most widely employed mass analysers for this purpose. It consists of four metal rods (approximately 1 cm in diameter and 15 – 20 cm long) positioned parallel and equidistant from the central axis. Each rod is electrically connected to the rod directly opposite and voltages (D.C and A.C) are applied to both rod pairs.As ions entering the quadrupole travel through the central axis, the voltages applied to the rods cause the ions to oscillate. Extreme oscillations cause the ejection of ions from the stable transmission region, striking the quadrupole housing or the rods. Only ions of a single mass to charge ratio with stable oscillatory path are allowed to exit the quadrupole. Other ions are lost within the quadrupole analyser. On collision with the rods or quadrupole housing, they become neutralised.

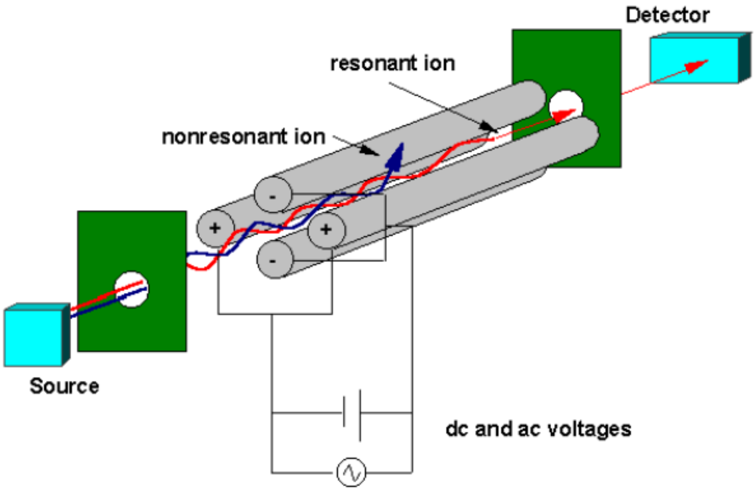


Fig A-10 Schematic diagram of a quadrupole mass filter[426]

The continuous dynode electron photomultiplier is a commonly employed detector in ICP-MS. It is similar in operation to the photomultiplier tube, with the exception of the absence of dynodes (electrodes in vacuum tubes that functions as electron multipliers through secondary emission). This device has an open tube with a wide entrance cone. Lead oxide semi conducting material is usually used to coat the inside of the tube. The high negative potential biased cone at the entrance attracts incoming positive ions emanating from the mass analyser and on impact, the positive ions causes one or more (secondary) electrons to be ejected. These ejected secondary electrons collide with the surface coating, causing further ejection of electrons inside the tube. Electrons multiply in this manner until all the electrons are collected towards the grounded collector within the tube (up to 10^8). This discrete electrical pulse of electrons is further amplified and recorded as a number of ion counts per second' (pulse counting) creating a mass spectrum. The spectrum produced provides the accurate qualitative representation of the sample.

The magnitude of each peak is directly proportional to the concentration of an element in a sample. Absolute concentration of each analyte is produced by comparing signal intensities from a sample with that generated by calibration standards

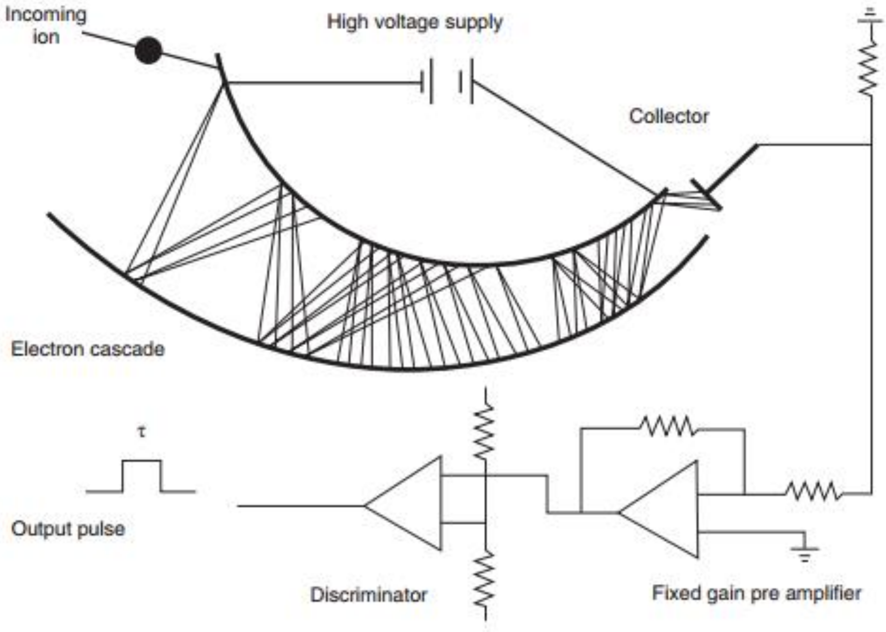


Fig A-11 Schematic diagram of a continuous dynode electron multiplier[427]

A-2.8 Interferences

Interferences that occur in ICP-MS can be broadly classified into spectral and non-spectral interferences. Spectral interferences usually occur as a result of overlap of atomic masses of different element and can be further subdivided into isobaric and molecular spectral interferences. Molecular interference may arise as a result of acid(s) used in preparing the sample or the argon plasma gas forming polyatomic species. The formation of oxides, hydroxides and doubly charged species can also occur. Non spectral interferences arise from problems associated with sample matrix which may cause decreased or loss of sensitivity.

Isobaric interferences

In spectroscopic interferences, isobaric overlap is considered the most problematic. This occurs when two elements on the periodic table have isotopes nominally of the same mass. An example of this type of interference is encountered when measuring Cr in a sediment sample. Chromium and iron both have an isotope of 54 amu (atomic mass unit). While the exact masses differs, (^{54}Fe = 53.939612 amu and ^{54}Cr = 53.938882 amu) the quadrupole mass analyser cannot resolve this. Ions counted at m/z = 54 may either be Fe or Cr.

Isobaric overlap can be avoided by selecting an alternative isotope since 70% of elements in the periodic table have more than one isotope. However this is not possible for all analytes. For example, in the determination of calcium there is interference from Ar ions, which have mass that coincide at atomic mass 40 (Ar, 99.6% abundant). The next most abundant isotope is ^{44}Ca which has abundance of just 2.08%. An alternative approach to suppress or eliminate this effect is to use collision/reaction cell technology. The collision or reaction cell is usually located behind the sample/skimmer cone arrangement before the mass analyser.

Molecular interferences

This type of interferences results due to the formation of polyatomic and doubly charged species. Polyatomic interference occurs when an element of interest is interfered by a polyatomic ion at the same mass. This may arise for the plasma gas or reagents used in sample preparation. A good example of a polyatomic interference is the formation of doubly charged species. If an ion changes from +1 to +2, the resultant mass/charge ratio will be halved. Typical examples are $^{138}Ba^{2+}$ interferes with $^{69}Ga^{+}$; and $^{208}Pb^{2+}$ interferes with $^{104}Ru^{+}$.

Interfering ions of this nature can be removed with recent advances in ICP-MS technology. Cold plasma has been developed to reduce interferences from argon. In cold plasma conditions, the ICP-MS operates in a low power state and at a high-central (injector) gas flow rates. The use of this technology has been found to reduce Ar^{+}, ArH^{+}, ArO^{+}, and Ar^{2+} species. By introducing collision gas (He), or a reactive gas (H_2), through the collision cell and/or reaction cell into the plasma as it flows through the interface, interfering ions as described above can be efficiently removed by collisional dissociations summarized below:

Charge exchange: this allows for the removal of the argon plasma gas ion interference and the resultant formation of unchanged argon plasma gas which is not then detected.

$$Ar^{+} + NH_3 \rightarrow NH_3^{+} + Ar$$

Proton transfer: invoves the neutralisation of the interfering species which results ina neutral argon plasma gas which is then not detected.

$$ArH^+ + H_2 \rightarrow H_3^+ + Ar$$

Hydrogen atom transfer: this results to an increase in the mass/charge ratio by one thereby making it impossible for the interfering species to interfere.

$$Ar^+ + H_2 \rightarrow ArH^+ + H$$

Adduct formation: this allows the mass/charge ratio to increase by addition e.g. ammonia, NH_3 increases the *amu* of analyte ion by 17 (N = 14, H = 1)

$$Ni^+ + NH_3 \rightarrow Ni^+NH_3$$

Sensitive measurements of greater accuracy can be achieved when reactive or collisions cells are deployed as analyte ions may not be affected byHe, H_2or NH_3.

Physical interference

Physical interferences may be attributed to differences in rates of sample nebulisation (viscosity effects), sample transportation into plasma, ion focussing and transmission through the interface. The differences between the instrument responses for the sample to that of the calibration standards may also results to this type of interference. Additionally, erratic and intermittent problems may arise owing to the blockage of the nebulizer. This usually happens when dissolved solids (e.g. NaCl) in the sample build up on the sample cone of the ICP-MS interface. Nevertheless, the use of high-solids nebulizer, aqueous dilution of sample matrix, use of internal standards, the method of standard additions and online coupling of chromatographic separation techniques to ICP-MS have all been demonstrated as possible remedies to these physical interferences.

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APPENDIX B

Table B-1   % LOI and pH from school playground and roadside soil samples

Location	% LOI	pH	Location	% LOI	pH
VI SH 1	0.04	8.05	**VI RD 1**	0.10	8.94
VI SH 2	0.11	8.22	**VI RD 2**	0.18	9.04
VI SH 3	0.07	8.70	**VI RD 3**	0.17	8.89
VI SH 4	0.05	7.98	**VI RD 4**	0.50	7.40
VI SH 5	0.07	8.31	**VI RD 5**	0.13	8.70
Ikj SH 1	0.21	7.65	**Ikj RD 1**	0.08	8.15
Ikj SH 2	0.15	7.77	**Ikj RD 2**	0.17	7.72
Ikj SH 3	0.07	7.43	**Ikj RD 3**	0.06	8.24
Ikj SH 4	0.21	7.23	**Ikj RD 4**	0.58	8.46
Ikj SH 5	0.77	7.90	**Ikj RD 5**	0.10	8.36
Ifk SH 1	2.54	8.22	**Ifk RD 1**	0.13	8.05
Ifk SH 2	0.13	8.31	**Ifk RD 2**	0.17	8.06
Ifk SH 3	0.08	7.94	**Ifk RD 3**	0.19	8.25
Ifk SH 4	0.27	7.85	**Ifk RD 4**	0.13	7.89
Ifk SH 5	0.07	8.58	**Ifk RD 5**	0.16	8.14
LM SH 1	0.14	8.27	**LM RD 1**	0.16	7.94
LM SH 2	0.09	8.13	**LM RD 2**	0.22	8.17
LM SH 3	0.12	8.24	**LM RD 3**	0.18	7.92
LM SH 4	0.11	7.97	**LM RD 4**	0.08	8.36
LM SH 5	0.09	8.42	**LM RD 5**	0.20	7.82
Mak SH 1	0.13	8.13	**Mak RD 1**	0.10	8.22
Mak SH 2	0.27	8.02	**Mak RD 2**	0.32	8.18
Mak SH 3	0.25	7.97	**Mak RD 3**	0.30	8.55
Mak SH 4	0.24	8.36	**Mak RD 4**	0.44	7.83
Mak SH 5	0.98	8.39	**Mak RD 5**	0.25	9.03

Table B-2 % LOI and pH from open spaces and ornamental garden soil samples

Location	% LOI	pH
LM PO 1	0.04	7.92
LM PO 2	1.25	7.96
LM PO 3	1.32	7.43
LM PO 4	0.63	7.24
LM PO 5	0.10	6.80
Ikj PO 1	0.21	8.13
Ikj PO 2	0.15	7.99
Ikj PO 3	0.07	8.28
Ikj PO 4	0.21	8.35
Ikj PO 5	0.77	8.58
Ifk PO 1	0.08	8.96
Ifk PO 2	1.40	7.55
Ifk PO 3	0.96	8.12
Ifk PO 4	0.08	8.15
Ifk PO 5	0.16	8.02
VI PO 1	0.17	8.11
V1 PO 2	0.09	8.20
VI PO 3	1.27	11.17
VI PO 4	0.10	8.74
Mak PO 1	0.002	8.91
Mak PO 2	0.16	8.42
Mak PO 3	0.33	8.02
Mak PO 4	0.11	8.74

Location	% LOI	pH
LM OG 1	0.31	7.84
LM OG 2	0.14	7.78
LM OG 3	0.14	8.10
LM OG 4	2.70	8.11
LM OG 5	0.63	7.92
Ikj OG 1	1.40	6.95
Ikj OG 2	0.35	7.03
Ikj OG 3	0.40	7.00
Ikj OG 4	1.94	7.12
Ikj OG 5	0.37	7.25
If OG 1	0.29	7.56
If OG 2	0.35	7.51
If OG 3	2.66	7.60
VI OG 1	0.35	7.70
VI OG 2	0.42	7.60
VI OG 3	0.32	7.40
Mak OG 1	2.13	8.02
Mak OG 2	1.23	7.18

Table B-3-1 % LOI and pH from industrial estates soil samples

Table B-2-1 % LOI and pH from dumpsite soil samples

Table B-3-3 % LOI and pH from railway terminals soil samples

1

Location	% LOI	Ph
Ogba 1	3.51	7.23
Ogba 2	1.38	8.13
Ogba 3	0.23	7.48
Ikeja	0.36	6.99
Ilupeju 1	0.02	7.93
Ilupeju 2	0.31	7.89
Ilupeju 3	1.12	7.63
Ikorodu 1	1.96	6.9
Ikorodu 2	0.92	7.01
Ikorodu 3	1.67	7.16

2

Location	% LOI	Ph
Owode 1	1.56	5.91
Owode 2	2.74	7.15
Owode 3	1.97	7.45
Owode 4	2.35	6.97
Dasco	0.67	6.91
Nig foundry	1.48	7.06
Comp. Village	2.55	7.05
Ladipo 1	0.56	6.91
Ladipo 2	0.50	7.02
Ladipo 3	0.85	7.09
Katangua 1	3.65	7.15
Kantagua 2	2.96	7.54
Grand foundry 1	5.04	10.06
Grand foundry 2	4.52	9.78
Olushosun 1	8.24	8.57
Olushosun 2	6.29	8.96

3

Location	% LOI	Ph
Ikeja Along	0.11	6.49
Oshodi	0.57	7.38
Iddo 1	2.21	8.31
Iddo 2	1.08	7.16
Iddo 3	1.23	7.03
Alagomeji	1.47	7.59
Agege	4.29	5.79

Table C-1   Average PTE concentrations and RSD in school playground soil samples (n = 3; mg/kg)

Location	Cr	% RSD	Cu	% RSD	Fe	% RSD	Mn	% RSD	Ni	% RSD	Pb	% RSD	Zn	% RSD
VI SH 1	4.52	3.86	3.14	12.4	2230	10.1	44.5	27.6	1.76	49.8	6.38	13.1	54.3	6.52
VI SH 2	11.3	13.6	5.58	24.6	6500	23.1	113	10.6	4.82	27.0	7.46	4.50	48.8	13.4
VI SH 3	7.68	3.04	8.42	11.3	4690	0.60	111	1.07	3.52	11.9	14.7	0.82	98.0	5.50
VI SH 4	7.34	6.29	3.82	17.2	3880	4.21	142	14.5	3.55	6.94	9.62	11.5	90.3	7.09
VI SH 5	10.0	10.6	7.32	33.0	4840	9.25	89.8	16.1	4.35	29.3	17.4	14.5	72.3	16.0
Ikj SH 1	21.0	10.4	5.87	8.33	6830	5.88	134	9.30	3.17	13.3	12.1	11.7	52.8	7.57
Ikj SH 2	28.4	5.56	4.65	19.7	5780	1.73	144	4.40	5.06	68.8	7.71	5.08	35.1	7.33
Ikj SH 3	9.16	8.53	5.49	79.5	2600	44.5	48.1	12.5	2.40	56.6	6.39	11.4	21.5	19.9
Ikj SH 4	24.7	6.77	4.69	7.62	5840	8.80	146	9.00	3.18	15.6	8.76	11.9	46.1	29.6
Ikj SH 5	27.2	25.1	6.82	3.12	7500	3.80	148	3.37	4.36	21.6	10.4	3.69	46.2	7.73
Ifk SH 1	39.3	0.52	5.05	1.74	9100	1.15	154	17.1	5.47	31.7	15.7	12.5	65.1	6.68
Ifk SH 2	49.4	1.39	4.67	12.2	7800	9.75	105	17.3	4.09	11.5	10.5	55.0	78.8	27.2
Ifk SH 3	18.3	12.1	4.21	25.5	6620	1.11	238	7.73	3.33	2.62	7.05	13.9	30.1	5.41
Ifk SH 4	31.4	2.8	7.56	20.4	8410	6.51	213	3.19	6.79	9.65	13.4	7.73	81.9	0.39
Ifk SH 5	38.9	7.53	5.07	26.0	8050	16.8	122	3.57	4.45	13.0	12.4	16.5	53.6	10.0
LM SH 1	14.1	27.4	13.6	11.1	8640	10.0	117	2.38	4.59	1.40	36.5	3.69	327	15.2
LM SH 2	19.0	4.45	6.99	10.2	10100	15.0	87.4	8.42	4.45	13.7	23.6	10.3	77.3	17.4
LM SH 3	13.3	13.0	5.58	0.06	6240	14.0	80.1	7.17	3.69	8.85	11.9	15.4	54.2	9.75
LM SH 4	12.5	22.1	6.68	44.9	7300	8.57	89.7	8.57	4.01	21.3	18.8	21.8	61.1	13.8
LM SH 5	10.3	5.49	13.0	23.5	6300	4.14	88.6	0.79	3.57	2.30	15.5	3.12	90.0	9.66
Mak SH 1	11.8	7.99	5.02	17.0	8400	3.12	114	1.88	3.62	9.89	8.20	6.19	26.3	0.48
Mak SH 2	17.3	9.00	8.98	26.9	7760	16.6	112	11.6	4.84	18.3	10.9	23.4	105	18.4
Mak SH 3	28.3	4.34	24.2	31.3	15400	4.08	193	2.32	8.37	3.53	65.6	7.00	185	0.53
Mak SH 4	30.7	3.60	27.4	7.35	19900	9.21	252	4.95	10.6	2.71	51.1	9.50	298	1.89
Mak SH 5	22.9	15.8	7.09	23.3	11300	5.62	218	19.0	4.28	3.03	15.1	33.9	44.7	10.1

Table C-2 Average PTE concentrations and RSD in roadside soil samples (n = 3; mg/kg)

Location	**Cr**	**% RSD**	**Cu**	**% RSD**	**Fe**	**% RSD**	**Mn**	**% RSD**	**Ni**	**% RSD**	**Pb**	**% RSD**	**Zn**	**% RSD**
VI RD 1	26.6	21.5	17.8	7.16	8280	11.3	106	4.00	6.96	28.1	11.7	5.44	104	8.79
VI RD 2	7.82	0.99	3.42	29.2	3560	5.77	74.1	1.54	3.53	17.4	4.87	4.91	39.7	0.004
VI RD 3	10.1	13.6	7.09	39.3	3650	28.9	49.8	16.0	5.11	44.4	6.56	14.8	66.9	13.3
VI RD 4	16.6	10.6	30.7	17.0	9060	8.58	150	17.2	5.42	20.5	26.4	18.2	728	32.2
VI RD 5	5.20	11.0	5.02	69.5	3900	27.7	39.1	25.7	4.27	39.3	5.18	6.37	39.4	13.9
Ikj RD 1	29.1	9.21	2.98	59.0	7170	22.7	132	6.98	3.92	18.6	6.32	6.23	18.6	21.5
Ikj RD 2	26.7	24.5	20.1	78.0	9870	4.04	165	49.0	6.35	40.4	21.7	67.7	109	53.7
Ikj RD 3	24.9	15.6	8.45	32.9	8450	9.60	144	5.39	4.71	7.21	31.8	90.9	60.4	7.70
Ikj RD 4	20.6	9.06	5.82	19.1	6560	8.67	113	7.11	10.8	10.4	17.5	58.8	44.3	8.71
Ikj RD 5	35.9	14.0	49.7	68.4	13000	7.27	159	3.27	10.5	13.0	24.9	18.0	158	12.4
Ifk RD 1	31.4	8.70	10.8	8.99	9470	5.11	132	7.51	5.64	16.3	64.4	6.28	105	18.9
Ifk RD 2	37.9	10.3	20.3	29.9	11000	15.1	159	10.9	7.57	10.1	28.7	18.7	132	12.7
Ifk RD 3	36.2	2.68	14.7	1.14	11800	5.01	164	6.61	8.03	9.4	32.7	15.0	122	0.15
Ifk RD 4	30.1	5.70	16.1	7.03	11900	11.1	155	10.0	6.50	1.83	26.4	15.3	119	4.55
Ifk RD 5	35.1	4.49	7.44	3.58	9080	6.90	140	6.82	4.98	1.77	54.1	13.0	75.4	12.9
LM RD 1	28.8	33.9	124	14.3	12600	11.8	139	5.42	18.7	10.8	39.8	18.0	133	6.58
LM RD 2	17.8	11.3	21.1	13.1	11000	7.54	143	10.8	6.07	19.3	53.6	3.11	213	16.4
LM RD 3	16.5	6.31	12.6	10.1	12500	9.01	147	5.17	6.73	7.18	32.9	46.4	141	15.1
LM RD 4	27.5	20.5	71.8	65.9	11700	2.82	189	24.8	7.12	13.2	48.4	12.9	180	5.49
LM RD 5	22.2	3.91	23.3	17.4	11500	2.29	213	4.07	8.11	26.0	38.5	8.53	158	6.04
Mak RD 1	19.5	8.95	49.6	18.9	14200	18.6	157	9.31	6.66	29.4	41.8	16.8	112	6.30
Mak RD 2	15.4	30.0	50.2	25.0	12000	25.1	168	8.36	5.77	11.3	46.5	23.6	132	7.85
Mak RD 3	13.1	20.0	41.1	47.2	7980	2.41	140	3.38	5.42	16.9	29.7	8.90	123	4.84
Mak RD 4	16.4	7.03	64.7	14.4	11000	3.04	202	5.27	7.76	16.6	29.7	7.03	403	16.9
Mak RD 5	23.6	25.4	18.0	18.7	13000	12.2	162	7.59	6.70	0.74	65.7	90.7	121	9.01

Table C-3 Average PTE concentrations and RSD in open spaces soil samples (n = 3; mg/kg)

Location	Cr	% RSD	Cu	% RSD	Fe	% RSD	Mn	% RSD	Ni	% RSD	Pb	% RSD	Zn	% RSD
VI PO 1	5.02	3.26	3.18	28.4	2210	41.8	29.5	44.0	2.00	13.7	3.12	7.25	33.9	9.8
V1 PO 2	4.54	7.28	3.14	54.9	2730	11.2	43.4	7.56	1.79	18.7	1.29	80.7	36.9	5.7
VI PO 3	19.9	10.6	16.7	6.21	11500	43.0	147	27.5	12.0	75.4	139	25.1	127	3.04
VI PO 4	18.5	29.5	6.08	30.8	10500	37.2	97	16.7	4.57	19.3	23.2	9.8	77.8	15.1
Ikj PO 1	24.1	15.0	4.97	15.3	6740	7.43	161	46.3	3.23	10.6	5.8	19.3	36.4	3.92
Ikj PO 2	25.9	19.7	26.7	86.5	8930	17.9	186	13.0	5.07	14.7	15.1	39.8	48.3	4.55
Ikj PO 3	24.7	6.13	21.9	11.3	11900	10.9	179	14.5	6.14	2.36	26.4	19.5	175	2.26
Ikj PO 4	33.5	8.54	21.2	53.1	12800	17.6	200	19.6	10.8	42.2	23.5	10.2	116	11.7
Ikj PO 5	30.4	7.79	10.4	22.5	10000	1.77	212	27.6	8.19	46.9	24.3	16.6	98.7	45.4
Ifk PO 1	53.3	23.2	32.9	16.2	17800	1.51	197	3.57	12.2	26.6	107	1.50	238	4.35
Ifk PO 2	40.2	1.63	485	50.7	27500	34.4	352	17.0	15.0	17.8	137	20.3	757	19.8
Ifk PO 3	22.4	6.64	6.81	39.3	8400	11.1	78.3	10.0	4.54	12.7	17.6	71.5	60.4	18.3
Ifk PO 4	34.3	6.14	28.5	42.1	14000	15.0	199	24.7	18.5	98.6	40.8	29.7	165	15.3
Ifk PO 5	18.8	4.65	8.36	13.2	7460	3.80	135	27.9	4.49	7.15	10.4	11.0	61.0	5.07
LM PO 1	12.0	11.2	19.6	39.0	8090	1.41	97.7	6.19	7.85	43.1	29.0	33.6	92.8	5.11
LM PO 2	22.4	9.29	25.2	16.6	12600	5.21	233	13.0	7.72	9.78	87.3	18.8	239	4.87
LM PO 3	18.0	6.71	23.4	17.2	9490	5.11	124	17.9	5.70	6.04	38.2	40.2	190	19.2
LM PO 4	29.5	5.95	43.2	7.00	16700	6.61	226	8.31	9.56	14.6	65.1	16.5	247	8.15
LM PO 5	30.1	8.25	11.1	5.00	8850	1.98	430	4.30	7.14	5.43	20.8	9.5	117	5.67
Mak PO 1	15.0	4.51	3.81	16.2	7910	6.60	168	6.93	4.20	6.52	4.8	38.2	35.8	6.98
Mak PO 2	20.4	31.5	19.0	17.5	11800	8.57	197	4.68	6.11	13.1	59.1	6.46	154	10.8
Mak PO 3	7.22	20.5	7.41	26.3	4130	25.3	60.2	27.3	2.88	25.2	16.2	75.2	66.3	28.3
Mak PO 4	20.7	17.4	18.1	12.8	12400	6.88	165	5.47	6.70	6.00	35.0	4.23	210	30.4

Table C-4 Average PTE concentrations and RSD in ornamental garden soil samples (n = 3; mg/kg)

Location	Cr	% RSD	Cu	% RSD	Fe	% RSD	Mn	% RSD	Ni	% RSD	Pb	% RSD	Zn	% RSD
VI OG 1	21.6	5.87	21.3	8.47	12100	2.79	230	29.1	8.12	10.1	56.0	12.1	198	16.5
VI OG 2	22.7	15.7	21.6	16.2	9500	15.4	323	31.9	7.29	34.4	36.0	16.5	142	31.8
VI OG 3	22.3	10.7	22.2	3.12	9600	4.47	403	5.08	6.48	6.65	20.9	2.07	85.2	3.20
Ikj OG 1	50.6	9.82	18.3	7.63	22200	7.69	359	11.6	16.5	5.64	56.9	0.98	165	5.40
Ikj OG 2	34.1	12.9	10.1	1.67	10300	12.0	508	7.59	8.18	10.9	19.4	6.97	45.5	18.3
Ikj OG 3	38.5	9.82	17.0	9.90	11900	7.69	430	11.6	8.81	5.64	17.9	0.98	50.3	5.40
Ikj OG 4	43.6	18.7	18.9	11.4	13800	16.5	515	10.8	10.5	14.2	18.8	1.53	42.4	32.3
Ikj OG 5	40.6	9.15	12.1	2.56	16000	8.56	433	9.72	10.6	5.62	31.4	9.09	122	8.37
If OG 1	37.2	16.9	21.4	6.02	14200	3.05	264	1.58	8.88	29.3	30.6	3.63	119	2.55
If OG 2	25.5	36.9	17.5	4.08	11800	4.52	495	16.3	8.48	15.8	23.6	34.1	73.3	13.9
If OG 3	26.1	5.66	16.7	2.10	12400	10.0	410	6.64	9.87	7.19	25.3	9.42	85.8	4.21
LM OG 1	13.8	9.05	10.4	5.11	8550	2.16	557	5.20	7.13	1.18	19.5	6.08	97.4	1.99
LM OG 2	15.7	3.58	12.3	5.15	8740	4.35	532	3.82	7.11	8.43	17.6	6.42	76.6	10.8
LM OG 3	20.7	6.11	11.8	9.52	10900	5.77	437	5.62	8.77	6.32	25.5	4.73	85.0	12.6
LM OG 4	17.0	10.4	14.1	2.52	8070	9.37	441	2.67	7.78	4.38	22.0	1.64	77.9	2.90
LM OG 5	35.3	14.0	16.0	4.38	15500	0.46	472	2.62	9.61	1.61	37.7	6.78	113	1.27
Mak OG 1	13.8	8.15	12.5	7.37	8550	5.95	557	0.90	7.13	10.3	19.5	4.30	97.4	2.35
Mak OG 2	16.4	7.87	13.3	1.14	9490	2.93	541	3.29	7.44	6.26	31.6	4.28	79.9	4.35

Table C-5   Average PTE concentrations and RSD in industrial estates soil samples (n = 3; mg/kg)

Location	Cr	% RSD	Cu	% RSD	Fe	% RSD	Mn	% RSD	Ni	% RSD	Pb	% RSD	Zn	% RSD
Ogba 1	58.3	34.5	52.0	21.1	34500	9.04	342	1.84	15.7	9.61	62.4	24.0	236	1.90
Ogba 2	49.2	22.3	71.1	4.95	28601	14.9	375	8.43	16.6	30.1	400	38.5	1080	11.3
Ogba 3	35.9	23.9	27.8	38.7	16700	9.93	534	104	6.50	18.2	166	13.1	331	31.3
Ikeja	111	15.9	70.5	11.50	60200	17.5	437	16.8	38.7	12.4	144	9.90	433	9.90
Ilupeju 1	56.4	68.9	33.0	39.6	21300	9.65	233	7.19	10.6	9.14	153	103	177	7.60
Ilupeju 2	31.9	10.0	137	153	16600	16.1	140	6.97	6.08	14.9	34.6	26.4	114	12.4
Ilupeju 3	25.1	16.6	25.0	61.1	10900	16.3	135	0.55	3.74	15.2	22.8	44.5	87	3.43
Ikorodu 1	242	23.7	492	45.9	133000	3.68	2870	7.43	118	3.72	388	16.7	3560	8.81
Ikorodu 2	175	6.77	759	53.4	146000	10.6	2570	12.1	109	8.14	536	6.84	3240	14.6
Ikorodu 3	218	16.7	268	25.9	141000	1.06	3950	3.20	101	8.50	239	9.38	3080	3.23

Table C-6 Average PTE concentrations and RSD in dumpsite soil samples (n = 3; mg/kg)

Location	**Cr**	**% RSD**	**Cu**	**% RSD**	**Fe**	**% RSD**	**Mn**	**% RSD**	**Ni**	**% RSD**	**Pb**	**% RSD**	**Zn**	**% RSD**
Owode 1	290	14.4	182	35.2	47600	8.01	899	3.84	139	17.5	76.5	4.85	880	23.0
Owode 2	77.0	15.7	470	17.8	38900	4.56	616	7.31	65.8	7.92	83.9	10.3	488	12.9
Owode 3	78.7	40.4	133	14.2	41000	6.64	566	10.4	28.7	28.6	153	18.9	546	1.09
Owode 4	59.6	17.0	289	58.9	43200	5.38	590	1.97	26.8	17.5	150	41.3	557	18.6
Dasco	1830	4.13	11700	15.2	166000	1.53	1530	4.02	1040	22.9	4330	22.5	2800	2.51
Nig foundry	319	11.8	323	9.18	142000	7.08	1720	7.17	112	9.41	257	3.58	594	7.25
Comp. Village	202	14.6	82	24.9	99800	4.25	1590	6.67	37.5	6.18	102	25.9	353	3.38
Ladipo 1	29.4	34.6	32	15.5	10900	14.9	86.8	12.0	8.34	49.4	25.2	8.08	117	3.21
Ladipo 2	59.5	27.3	268	53.5	18700	6.63	203	7.86	18.9	37.4	158	40.5	297	10.5
Ladipo 3	47.5	40.9	108	12.8	14700	6.90	261	28.9	12.0	10.2	315	14.4	511	43.5
Katangua 1	124	2.80	542	3.49	50300	6.74	1670	40.7	49.5	13.4	454	6.67	3210	5.85
Kantagua 2	108	12.0	611	25.0	57600	9.08	753	10.9	90.0	76.0	802	38.0	5610	6.44
Grand foundry 1	244	40.5	92.0	3.51	42900	6.90	2330	47.3	39.8	8.13	141	14.9	361	6.65
Grand foundry 2	602	8.74	108	19.2	52600	10.2	6090	28.7	306	103	21.6	34.0	520	3.87
Olushosun 1	60.0	6.48	9.37	5.40	31900	4.32	54.4	13.1	7.59	32.3	36.0	16.8	95.6	71.0
Olushosun 2	62.7	4.81	26.4	8.16	29900	7.89	257	78.5	12.8	4.24	45.9	2.71	222	6.42

Table C-7 Average PTE concentrations and RSD in railway terminals soil samples (n = 3; mg/kg)

Location	Cr	% RSD	Cu	% RSD	Fe	% RSD	Mn	% RSD	Ni	% RSD	Pb	% RSD	Zn	% RSD
Ikeja Along	128	12.41	112	6.14	83600	1.37	413	3.50	29.4	9.19	182	0.19	241	15.2
Oshodi	48.9	6.57	70.4	3.88	26400	2.84	280	8.27	21.7	5.00	110	19.5	260	15.2
Iddo 1	93.6	4.47	168	1.28	69000	1.14	1210	3.24	44.4	7.75	321	0.60	1190	2.94
Iddo 2	72.4	3.57	123	8.92	68300	10.4	546	8.63	37.9	8.31	323	6.25	511	4.24
Iddo 3	125.6	3.50	105	2.32	82800	3.54	413	0.59	28.7	1.35	174	2.04	210	1.12
Alagomeji	42.8	17.4	42.7	1.68	36500	7.71	525	6.16	15.5	1.51	111	4.04	653	39.6
Agege	46.2	6.14	243	7.00	36000	23.2	401	17.4	21.0	10.1	212	25.0	1220	23.2

APPENDIX D

Table D-1 Enrichment factor of PTE from school playground soil samples

Location	Cr	Cu	Mn	Ni	Pb	Zn
VI SH 1	1.06	1.47	1.10	0.55	6.73	12.1
VI SH 2	0.91	0.90	0.96	0.51	2.71	3.73
VI SH 3	0.86	1.88	1.32	0.52	7.41	10.4
VI SH 4	0.99	1.03	2.03	0.63	5.85	11.6
VI SH 5	1.08	1.58	1.03	0.62	8.45	7.40
Ikj SH 1	1.61	0.90	1.09	0.32	4.19	3.84
Ikj SH 2	2.57	0.84	1.38	0.61	3.14	3.01
Ikj SH 3	1.85	2.21	1.03	0.64	5.80	4.11
Ikj SH 4	2.21	0.84	1.39	0.38	3.54	3.92
Ikj SH 5	1.90	0.95	1.10	0.40	3.27	3.06
Ifk SH 1	2.27	0.58	0.94	0.42	4.06	3.55
Ifk SH 2	3.32	0.63	0.75	0.36	3.17	5.01
Ifk SH 3	1.45	0.67	1.99	0.35	2.51	2.26
Ifk SH 4	1.95	0.94	1.41	0.56	3.76	4.83
Ifk SH 5	2.53	0.66	0.84	0.38	3.63	3.31
LM SH 1	0.85	1.65	0.75	0.37	10.0	18.8
LM SH 2	0.99	0.73	0.48	0.31	5.50	3.80
LM SH 3	1.12	0.94	0.71	0.41	4.52	4.32
LM SH 4	0.90	0.96	0.68	0.38	6.06	4.16
LM SH 5	0.86	2.16	0.78	0.39	5.78	7.09
Mak SH 1	0.74	0.63	0.76	0.30	2.30	1.56
Mak SH 2	1.17	1.21	0.80	0.43	3.31	6.71
Mak SH 3	0.96	1.64	0.69	0.38	10.0	5.95
Mak SH 4	0.81	1.44	0.70	0.37	6.04	7.42
Mak SH 5	1.05	0.65	1.06	0.26	3.13	1.95
Minimum	0.08	0.58	0.48	0.26	2.30	1.56
Median	1.08	0.94	0.96	0.39	4.19	4.16
Mean	1.41	1.12	1.03	0.43	4.99	5.75
Max	3.32	2.21	2.03	0.64	10.0	18.8
SD	0.74	0.49	0.39	0.11	2.21	3.91

Table D-2 Enrichment factor of PTE from roadside soil samples

Location	Cr	Cu	Mn	Ni	Pb	Zn
VI RD 1	1.68	2.26	0.71	0.58	3.34	6.25
VI RD 2	1.15	1.01	1.16	0.69	3.23	5.53
VI RD 3	0.96	3.55	0.92	0.42	1.41	1.45
VI RD 4	1.45	2.03	0.76	0.97	4.23	9.09
VI RD 5	0.70	1.35	0.56	0.76	3.13	5.01
Ikj RD 1	2.13	0.44	1.02	0.38	2.08	1.29
Ikj RD 2	1.42	2.13	0.93	0.45	5.18	5.49
Ikj RD 3	1.55	1.05	0.95	0.39	8.89	3.55
Ikj RD 4	1.65	0.93	0.95	1.14	6.28	3.35
Ikj RD 5	1.44	3.98	0.67	0.56	4.49	6.01
Ifk RD 1	1.74	1.20	0.77	0.41	16.0	5.50
Ifk RD 2	1.79	1.91	0.80	0.47	6.08	5.91
Ifk RD 3	1.61	1.31	0.77	0.47	6.54	5.13
Ifk RD 4	1.32	1.40	0.72	0.38	5.19	4.92
Ifk RD 5	2.03	0.86	0.86	0.38	14.1	4.13
LM RD 1	1.19	10.23	0.61	1.02	7.42	5.21
LM RD 2	0.81	1.94	0.69	0.37	11.1	9.24
LM RD 3	0.69	1.06	0.65	0.37	6.19	5.57
LM RD 4	1.23	6.42	0.90	0.42	9.74	7.64
LM RD 5	1.00	2.11	1.02	0.49	7.86	6.80
Mak RD 1	0.72	3.65	0.61	0.32	6.92	3.92
Mak RD 2	0.67	4.39	0.78	0.33	9.14	5.48
Mak RD 3	0.86	5.40	0.97	0.47	8.77	7.64
Mak RD 4	0.78	6.15	1.02	0.49	6.36	18.2
Minimum	0.67	0.44	0.56	0.32	2.08	1.29
Median	1.05	1.44	2.17	0.56	5.43	4.20
Mean	1.29	2.75	0.82	0.54	7.05	6.12
Max	2.13	10.23	1.16	1.14	16.0	18.2
SD	0.45	2.39	0.16	0.23	3.42	3.17

Table D-3 Enrichment factor of PTE from open spaces soil samples

Location	Cr	Cu	Mn	Ni	Pb	Zn
VI PO 1	1.19	1.51	0.74	0.63	3.32	7.60
V1 PO 2	0.87	1.21	0.88	0.45	1.11	6.71
VI PO 3	0.90	1.52	0.71	0.72	28.4	5.45
VI PO 4	0.92	0.60	0.51	0.30	5.18	3.65
Ikj PO 1	1.87	0.77	1.32	0.33	2.04	2.68
Ikj PO 2	1.52	3.13	1.16	0.39	4.00	2.69
Ikj PO 3	1.08	1.92	0.83	0.36	5.19	7.24
Ikj PO 4	1.37	1.73	0.86	0.58	4.33	4.51
Ikj PO 5	1.59	1.08	1.17	0.57	5.72	4.89
Ifk PO 1	1.56	1.93	0.61	0.47	14.2	6.62
Ifk PO 3	1.39	0.85	0.52	0.37	4.92	3.56
Ifk PO 4	1.27	2.12	0.78	0.91	6.83	5.81
Ifk PO 5	1.32	1.17	1.00	0.42	3.30	4.06
LM PO 1	0.78	2.54	0.67	0.67	8.44	5.70
LM PO 2	0.93	2.09	1.02	0.42	16.3	9.38
LM PO 3	0.99	2.59	0.73	0.42	9.49	9.94
LM PO 4	0.93	2.71	0.75	0.40	9.19	7.35
LM PO 5	1.78	1.32	2.70	0.56	5.54	6.55
Mak PO 1	1.00	0.50	1.18	0.37	1.42	2.25
Mak PO 2	0.90	1.68	0.92	0.36	11.8	6.47
Mak PO 3	0.92	1.88	0.81	0.48	9.26	7.96
Mak PO 4	0.87	1.52	0.73	0.37	6.62	8.33
Minimum	0.78	0.50	0.51	0.30	1.11	2.25
Median	1.04	1.60	0.82	0.42	5.63	6.14
Mean	1.18	1.65	0.94	0.48	7.57	5.88
Max	1.87	3.13	2.70	0.91	28.4	9.94
SD	0.33	0.70	0.45	0.15	6.09	2.17

Table D-4   Enrichment factor of PTE from ornamental garden soil samples

Location	Cr	Cu	Mn	Ni	Pb	Zn
VI OG 1	0.95	1.81	1.05	0.46	10.9	8.11
VI OG 2	1.27	2.43	1.89	0.51	8.93	7.42
VI OG 3	1.20	2.40	2.33	0.43	5.16	4.40
Ikj OG 1	1.20	0.85	0.89	0.50	6.04	3.68
Ikj OG 2	1.72	1.01	2.72	0.54	4.32	2.16
Ikj OG 3	1.67	1.50	2.01	0.52	3.57	2.09
Ikj OG 4	1.67	1.44	2.06	0.55	3.24	1.51
Ikj OG 5	1.34	0.79	1.50	0.48	4.57	3.79
Ifk OG 1	1.37	1.55	1.03	0.44	5.15	4.16
Ifk OG 2	1.15	1.59	2.32	0.47	4.78	3.06
Ifk OG 3	1.09	1.43	1.83	0.56	4.74	3.43
LM OG 1	0.86	1.23	3.61	0.57	5.51	5.63
LM OG 2	0.96	1.44	3.38	0.56	4.86	4.37
LM OG 3	1.00	1.15	2.21	0.57	5.59	3.85
LM OG 4	1.10	1.82	3.03	0.69	6.43	4.80
LM OG 5	1.18	1.08	1.68	0.45	5.75	3.60
Mak OG 1	0.86	1.59	3.61	0.57	5.51	5.63
Mak OG 2	0.88	1.44	3.16	0.51	7.95	4.19
Minimum	0.86	0.79	0.89	0.43	3.24	1.51
Median	1.16	1.44	2.14	0.52	5.34	4.00
Mean	1.19	1.47	2.24	0.52	5.72	4.21
Max	1.72	2.43	3.61	0.69	10.9	8.11
SD	0.27	0.45	0.86	0.06	1.88	1.70

Table D-5 Enrichment factor of PTE from industrial estate soil samples

Location	Cr	Cu	Mn	Ni	Pb	Zn
Ogba 1	0.9	1.6	0.6	0.3	4.3	3.4
Ogba 2	0.9	2.6	0.7	0.4	33.0	18.8
Ogba 3	1.1	1.7	1.8	0.3	23.3	9.8
Ikeja	1.0	1.2	0.4	0.4	5.6	3.6
Ilupeju 1	1.4	1.6	0.6	0.3	17.0	4.1
Ilupeju 2	1.0	8.6	0.5	0.3	4.9	3.4
Ilupeju 3	1.2	2.4	0.7	0.2	4.9	3.9
Ikorodu 1	0.9	3.9	1.2	0.6	6.8	13.3
Ikorodu 2	0.6	5.5	1.0	0.5	8.1	11.0
Ikorodu 3	0.8	2.0	1.5	0.5	4.0	10.8
Minimum	0.6	1.2	0.4	0.2	4.0	3.4
Median	1.0	2.2	0.7	0.4	6.2	7.0
Mean	1.0	3.1	0.9	0.4	11.2	8.2
Max	1.4	8.6	1.8	0.6	33.0	18.8
SD	0.2	2.3	0.5	0.1	10.0	5.4

Table D-6 Enrichment factor of PTE from dumpsite soil samples

Location	Cr	Cu	Mn	Ni	Pb	Zn
Owode 1	3.2	4.0	1.0	2.0	3.8	9.2
Owode 2	1.0	12.7	0.9	1.2	5.1	6.2
Owode 3	1.0	3.4	0.8	3.8	19.0	6.6
Owode 4	0.7	7.0	0.8	0.4	8.2	6.4
Dasco	5.8	74.1	0.5	4.4	61.7	8.4
Nig foundry	1.2	2.4	0.7	0.5	4.2	2.1
Comp. Village	1.1	0.9	0.9	0.2	2.4	1.8
Ladipo 1	1.4	3.1	0.4	0.5	5.4	5.3
Ladipo 2	1.7	15.0	0.6	0.7	19.8	7.9
Ladipo 3	1.7	7.7	1.0	0.6	50.6	17.2
Katangua 1	1.3	11.3	1.8	0.7	21.3	31.7
Kantagua 2	1.0	11.1	0.7	1.1	32.8	48.4
Grand foundry 1	3.0	2.2	3.0	0.6	7.8	4.2
Grand foundry 2	6.0	2.2	6.4	4.0	1.0	4.9
Olushosun 1	1.0	0.3	0.1	0.2	2.7	1.5
Olushosun 2	1.1	0.9	0.5	0.3	3.6	3.7
Minimum	0.7	0.3	0.1	0.2	1.0	1.5
Median	1.2	3.7	0.8	0.7	6.6	6.3
Mean	2.0	9.9	1.3	1.3	15.6	10.3
Max	6.0	74.1	6.4	4.4	61.7	48.4
SD	1.7	17.8	1.5	1.4	18.3	12.6

Table D-7 Enrichment factor of PTE from dumpsite soil samples

Location	**Cr**	**Cu**	**Mn**	**Ni**	**Pb**	**Zn**
Ikeja Along	0.8	1.4	0.3	0.2	5.1	1.4
Oshodi	1.0	2.8	0.6	0.6	9.8	4.9
Iddo	0.7	1.9	0.5	0.3	8.8	4.3
Alagomeji	0.6	1.2	0.8	0.3	7.1	8.9
Agege	0.7	7.1	0.6	0.4	13.9	16.8
Minimum	0.6	1.2	0.3	0.2	5.1	1.4
Median	0.7	1.9	0.6	0.3	8.8	4.9
Mean	0.8	2.9	0.6	0.4	9.0	7.3
Max	1.0	7.1	0.8	0.6	13.9	16.8
SD	0.1	2.4	0.2	0.1	3.3	6.0

APPENDIX E

Table E-1 Geoaccumulation index of PTE from school playground soil samples

Location	Cr	Cu	Fe	Mn	Ni	Pb	Zn
VI SH 1	0.05	0.07	0.05	0.05	0.03	0.32	0.57
VI SH 2	0.13	0.12	0.14	0.13	0.07	0.37	0.51
VI SH 3	0.09	0.19	0.10	0.13	0.05	0.74	1.03
VI SH 4	0.08	0.08	0.08	0.17	0.05	0.48	0.95
VI SH 5	0.11	0.16	0.10	0.11	0.06	0.87	0.76
Ikj SH 1	0.23	0.13	0.14	0.16	0.05	0.6	0.6
Ikj SH 2	0.32	0.10	0.12	0.17	0.07	0.39	0.37
Ikj SH 3	0.10	0.12	0.06	0.06	0.04	0.32	0.23
Ikj SH 4	0.27	0.10	0.12	0.17	0.05	0.44	0.48
Ikj SH 5	0.30	0.15	0.16	0.17	0.06	0.52	0.49
Ifk SH 1	0.44	0.11	0.19	0.18	0.08	0.78	0.69
Ifk SH 2	0.55	0.10	0.17	0.12	0.06	0.52	0.83
Ifk SH 3	0.20	0.09	0.14	0.28	0.05	0.35	0.32
Ifk SH 4	0.35	0.17	0.18	0.25	0.10	0.67	0.86
Ifk SH 5	0.43	0.11	0.17	0.14	0.07	0.62	0.56
LM SH 1	0.16	0.30	0.18	0.14	0.07	1.82	3.45
LM SH 2	0.21	0.16	0.21	0.10	0.07	1.18	0.81
LM SH 3	0.15	0.12	0.13	0.09	0.05	0.60	0.57
LM SH 4	0.14	0.15	0.15	0.11	0.06	0.94	0.64
LM SH 5	0.11	0.29	0.13	0.10	0.05	0.77	0.95
Mak SH 1	0.13	0.11	0.18	0.13	0.05	0.41	0.28
Mak SH 2	0.19	0.20	0.16	0.13	0.07	0.54	1.10
Mak SH 3	0.31	0.54	0.33	0.23	0.12	3.28	1.95
Mak SH 4	0.34	0.61	0.42	0.30	0.16	2.55	3.14
Mak SH 5	0.25	0.16	0.24	0.26	0.06	0.75	0.47
Minimum	0.05	0.07	0.05	0.05	0.03	0.32	0.23
Median	0.20	0.13	0.15	0.14	0.06	0.61	0.64
Mean	0.23	0.18	0.16	0.16	0.07	0.83	0.90
Max	0.55	0.61	0.42	0.30	0.16	3.28	3.45
SD	0.13	0.13	0.08	0.06	0.03	0.71	0.80

Table E-2 Geoaccumulation index of PTE from roadside soil samples

Location	Cr	Cu	Fe	Mn	Ni	Pb	Zn
VI RD 1	0.30	0.40	0.18	0.13	0.10	0.59	1.10
VI RD 2	0.09	0.08	0.08	0.09	0.05	0.24	0.42
VI RD 3	0.11	0.16	0.08	0.06	0.08	0.33	0.70
VI RD 5	0.06	0.11	0.08	0.05	0.06	0.26	0.41
Ikj RD 1	0.32	0.07	0.15	0.16	0.06	0.32	0.20
Ikj RD 2	0.30	0.45	0.21	0.19	0.09	1.08	1.15
Ikj RD 3	0.28	0.19	0.18	0.17	0.07	1.59	0.64
Ikj RD 4	0.23	0.13	0.14	0.13	0.16	0.87	0.47
Ikj RD 5	0.40	1.10	0.28	0.19	0.15	1.24	1.67
Ifk RD 1	0.35	0.24	0.20	0.15	0.08	3.22	1.10
Ifk RD 2	0.42	0.45	0.24	0.19	0.11	1.43	1.39
Ifk RD 3	0.40	0.33	0.25	0.19	0.12	1.64	1.28
Ifk RD 4	0.33	0.36	0.25	0.18	0.10	1.32	1.25
Ifk RD 5	0.39	0.17	0.19	0.16	0.07	2.71	0.79
LM RD 1	0.32	2.75	0.27	0.16	0.28	1.99	1.40
LM RD 2	0.20	0.47	0.24	0.17	0.09	2.68	2.24
LM RD 3	0.18	0.28	0.27	0.17	0.10	1.65	1.48
LM RD 4	0.31	1.60	0.25	0.22	0.10	2.42	1.90
LM RD 5	0.25	0.52	0.25	0.25	0.12	1.93	1.67
Mak RD 1	0.22	1.10	0.30	0.18	0.10	2.09	1.18
Mak RD 2	0.17	1.12	0.25	0.20	0.08	2.32	1.39
Mak RD 3	0.15	0.91	0.17	0.16	0.08	1.48	1.29
Mak RD 4	0.18	1.44	0.23	0.24	0.11	1.49	4.24
Minimum	0.15	0.28	0.17	0.16	0.08	1.48	1.18
Median	0.20	1.10	0.25	0.18	0.10	1.99	1.48
Mean	0.22	1.13	0.25	0.20	0.12	2.00	1.87
Max	0.32	2.75	0.30	0.25	0.28	2.68	4.24
SD	0.06	0.75	0.04	0.03	0.06	0.42	0.95

Table E-3 Geoaccumulation index of PTE from open spaces soil samples

Location	Cr	Cu	Fe	Mn	Ni	Pb	Zn
VI PO 1	0.06	0.07	0.05	0.03	0.03	0.16	0.36
V1 PO 2	0.05	0.07	0.06	0.05	0.03	0.06	0.39
VI PO 3	0.22	0.37	0.24	0.17	0.18	6.95	1.33
VI PO 4	0.21	0.14	0.22	0.11	0.07	1.16	0.82
Ikj PO 1	0.27	0.11	0.14	0.19	0.05	0.29	0.38
Ikj PO 2	0.29	0.59	0.19	0.22	0.07	0.76	0.51
Ikj PO 3	0.27	0.49	0.25	0.21	0.09	1.32	1.84
Ikj PO 4	0.37	0.47	0.27	0.24	0.16	1.18	1.23
Ikj PO 5	0.34	0.23	0.21	0.25	0.12	1.21	1.04
Ifk PO 1	0.59	0.73	0.38	0.23	0.18	5.36	2.51
Ifk PO 3	0.25	0.15	0.18	0.09	0.07	0.88	0.64
Ifk PO 4	0.38	0.63	0.30	0.23	0.27	2.04	1.74
Ifk PO 5	0.21	0.19	0.16	0.16	0.07	0.52	0.64
LM PO 1	0.13	0.44	0.17	0.11	0.12	1.45	0.98
LM PO 2	0.25	0.56	0.27	0.27	0.11	4.36	2.51
LM PO 3	0.20	0.52	0.20	0.15	0.08	1.91	2.00
LM PO 4	0.33	0.96	0.35	0.27	0.14	3.25	2.60
LM PO 5	0.33	0.25	0.19	0.51	0.11	1.04	1.23
Mak PO 1	0.17	0.08	0.17	0.20	0.06	0.24	0.38
Mak PO 2	0.23	0.42	0.25	0.23	0.09	2.96	1.62
Mak PO 3	0.08	0.16	0.09	0.07	0.04	0.81	0.70
Mak PO 4	0.23	0.40	0.26	0.19	0.10	1.75	2.21
Minimum	0.08	0.08	0.09	0.07	0.04	0.24	0.38
Median	0.26	0.43	0.21	0.21	0.09	1.27	1.23
Mean	0.27	0.41	0.22	0.21	0.11	1.74	1.37
Max	0.59	0.96	0.38	0.51	0.27	5.36	2.60
SD	0.11	0.24	0.07	0.09	0.06	1.41	0.77

Table E-4 Geoaccumulation index of PTE from ornamental garden soil samples

Location	Cr	Cu	Fe	Mn	Ni	Pb	Zn
VI OM 1	0.24	0.47	0.26	0.27	0.12	2.80	2.08
VI OM 2	0.26	0.49	0.20	0.38	0.10	1.80	1.49
VI OM 3	0.24	0.49	0.20	0.47	0.09	1.05	0.89
Ikj OM 2	0.38	0.22	0.22	0.60	0.12	0.95	0.47
Ikj OM 3	0.42	0.38	0.25	0.51	0.13	0.90	0.53
Ikj OM 4	0.49	0.42	0.29	0.61	0.16	0.95	0.44
Ikj OM 5	0.46	0.27	0.34	0.51	0.16	1.55	1.28
Ifk OM 1	0.41	0.47	0.30	0.31	0.13	1.55	1.25
Ifk OM 2	0.29	0.40	0.25	0.58	0.12	1.20	0.77
Ifk OM 3	0.29	0.38	0.26	0.48	0.15	1.25	0.91
LM OM 1	0.16	0.22	0.18	0.66	0.10	1.00	1.02
LM OM 2	0.18	0.27	0.19	0.63	0.10	0.90	0.81
LM OM 3	0.23	0.27	0.23	0.51	0.13	1.30	0.89
LM OM 4	0.19	0.31	0.17	0.52	0.12	1.10	0.82
LM OM 5	0.39	0.36	0.33	0.56	0.15	1.90	1.19
Ikj OM 1	0.57	0.40	0.47	0.42	0.24	2.85	1.74
Mak OM 1	0.16	0.29	0.18	0.66	0.10	1.00	1.02
Mak OM 2	0.18	0.29	0.20	0.64	0.10	1.60	0.84
Minimum	0.16	0.22	0.17	0.42	0.10	0.90	0.81
Median	0.18	0.29	0.19	0.59	0.11	1.20	0.96
Mean	0.26	0.30	0.24	0.57	0.13	1.46	1.04
Max	0.57	0.40	0.47	0.66	0.24	2.85	1.74
SD	0.15	0.06	0.11	0.08	0.05	0.66	0.31

Table E-5 Geoaccumulation index of PTE from industrial estate soil samples

Location	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Ogba 1	0.65	1.16	0.73	0.40	0.23	3.12	2.49
Ogba 2	0.55	1.58	0.61	0.44	0.24	20.0	11.4
Ogba 3	0.40	0.62	0.36	0.63	0.10	8.29	3.49
Ilupeju 1	0.63	0.73	0.45	0.27	0.16	7.67	1.86
Ilupeju 2	0.35	3.05	0.35	0.16	0.09	1.73	1.20
Ilupeju 3	0.28	0.56	0.23	0.16	0.06	1.14	0.91
Ikorodu 1	2.69	10.9	2.83	3.38	1.73	19.4	37.5
Ikorodu 2	1.94	16.9	3.09	3.03	1.60	25.2	34.2
Ikorodu 3	2.42	5.96	3.00	4.66	1.48	12.0	32.4
Minimum	0.28	0.56	0.23	0.16	0.06	1.14	0.91
Median	0.63	1.58	0.61	0.44	0.23	8.29	3.49
Mean	1.10	4.61	1.30	1.46	0.63	10.9	13.9
Max	2.69	16.9	3.09	4.66	1.73	25.2	37.5
SD	0.96	5.74	1.27	1.73	0.73	8.78	15.9

Table E-6 Geoaccumulation index of PTE from dumpsite soil samples

Location	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Owode 1	3.22	4.04	1.01	1.06	2.04	3.82	9.26
Owode 2	0.86	10.4	0.83	0.73	0.97	4.20	5.14
Owode 3	0.87	2.96	0.87	0.67	3.29	16.6	5.75
Owode 4	0.66	6.42	0.92	0.69	0.39	7.50	5.87
Dasco	20.3	261	3.52	1.81	15.4	217	29.5
Nig foundry	3.55	7.18	3.03	2.03	1.64	12.9	6.25
Comp. Village	2.25	1.83	2.12	1.88	0.53	5.09	3.72
Ladipo 1	0.33	0.72	0.23	0.10	0.12	1.26	1.23
Ladipo 2	0.66	5.97	0.40	0.24	0.28	7.88	3.13
Ladipo 3	0.53	2.41	0.31	0.31	0.18	15.8	5.37
Katangua 1	1.38	12.0	1.07	1.97	0.73	22.7	33.8
Kantagua 2	1.20	13.6	1.22	0.89	1.32	40.1	59.2
Grand foundry 1	2.71	2.04	0.91	2.75	0.58	7.06	3.80
Grand foundry 2	6.69	2.40	1.12	7.17	4.50	1.08	5.47
Olushosun 1	0.67	0.21	0.68	0.06	0.11	1.80	1.01
Olushosun 2	0.70	0.59	0.63	0.30	0.19	2.30	2.34
Minimum	0.33	0.21	0.23	0.06	0.11	1.08	1.01
Median	1.04	3.50	0.91	0.81	0.66	7.28	5.42
Mean	2.91	20.9	1.18	1.42	2.02	22.9	11.3
Max	20.3	261	3.52	7.17	15.4	217	59.2
SD	4.93	64.1	0.93	1.74	3.78	52.7	15.9

Table E-7 Geoaccumulation index of PTE from railway terminals soil samples

Location	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Ikeja Along	1.42	2.48	1.77	0.49	0.43	9.11	2.54
Oshodi	0.54	1.57	0.56	0.33	0.32	5.50	2.74
Iddo	1.08	2.93	1.56	0.85	0.54	13.8	6.73
Alagomeji	0.48	0.95	0.77	0.62	0.23	5.54	6.87
Agege	0.51	5.40	0.76	0.47	0.31	10.6	12.9
Minimum	0.48	0.95	0.56	0.33	0.23	5.50	2.54
Median	0.54	2.48	0.77	0.49	0.32	9.11	6.73
Mean	0.81	2.67	1.09	0.55	0.37	8.90	6.35
Max	1.42	5.40	1.77	0.85	0.54	13.8	12.9
SD	0.42	1.71	0.54	0.20	0.12	3.51	4.20

APPENDIX F

Table F-1 Mean concentration of Cr in sequential extracts and pseudototal content (mg/kg) in Lagos urban soil samples

Location	**Step 1**	**% RSD**	**Step 2**	**% RSD**	**Step 3**	**% RSD**	**Step 4**	**% RSD**	**Sum**	**PT(*aqua regia*)**	**% Recovery**
LM PO 2	1.02	7.76	3.51	4.32	3.28	10.5	10.5	6.47	18.3	22.4	82
Ikj PO 3	0.97	34.0	1.81	29.7	3.25	5.52	13.5	6.81	19.5	24.7	79
Ikj PO 5	0.33	4.21	1.39	39.5	2.99	10.9	23.2	18.4	27.9	30.4	92
Ifk PO 5	0.28	2.84	0.66	2.59	1.69	5.13	12.2	6.53	14.8	18.8	79
Ifk PO 4	0.37	8.67	1.04	2.51	2.86	3.50	21.4	0.77	25.7	34.3	75
Ikj OM 1	0.09	13.2	1.33	9.27	5.91	2.76	35.3	12.5	42.6	51.0	84
Ifk RD 2	0.48	7.2	1.37	30.1	3.89	16.5	26.5	11.5	32.3	37.9	85
Ogba ind 2	0.45	9.74	4.83	9.43	3.11	3.92	42.0	22.7	50.4	49.2	102
ikeja ind 2	0.63	3.90	5.66	4.43	8.42	3.49	66.8	18.2	81.5	111	73
Ikorodu 2	1.27	17.3	31.7	14.7	13.9	16.5	116	14.7	162	175	93
Ikeja along 2	0.04	12.2	4.48	3.27	11.8	4.36	34.0	2.83	50.4	71.0	71
Iddo 1	1.00	2.51	13.5	9.09	27.7	11.2	42.6	8.94	84.9	93.6	91
Agege	0.15	2.50	5.08	5.60	7.16	1.37	33.3	12.5	45.7	46.2	99
Owode 1	1.35	18.0	76.6	19.1	7.97	6.79	170	21.5	256	290	88
Owode 3	0.58	1.38	10.7	8.94	5.42	4.88	35.0	5.07	51.6	78.7	66
Dasco	37.3	16.2	1020	4.92	235	11.0	1170	43.0	2470	1830	135
Comp. Village	1.09	45.1	109	8.61	9.15	1.37	80.0	4.73	199	202	98
Ladipo 3	0.47	9.04	7.58	50.9	4.54	7.66	22.0	14.3	34.6	47.5	73
Katangua 2	0.21	4.18	9.22	6.64	23.7	30.5	52.2	14.1	85.3	108	79
Grand Foundry	5.00	4.12	95.7	14.5	31.3	17.3	430	3.92	562	602	93

Table F-2 Mean concentration of Cu in sequential extracts and pseudototal content (mg/kg) in Lagos urban soil samples

Location	Step 1	% RSD	Step 2	% RSD	Step 3	% RSD	Step 4	% RSD	Sum	PT(*aqua regia*)	% Recovery
LM PO 2	2.18	9.37	10.3	20.4	3.67	12.2	4.76	19.5	20.9	25.2	83
Ikj PO 3	1.91	26.5	5.56	18.3	15.0	28.1	3.00	20.3	25.5	27.0	94
Ikj PO 5	1.71	4.3	3.00	28.0	1.00	10.0	3.27	36.2	11.1	10.4	87
Ifk PO 5	2.14	32.3	2.09	39.2	0.96	30.5	1.25	5.77	6.4	8.4	77
Ifk PO 4	3.90	24.7	6.93	6.83	6.02	7.1	4.69	32.9	18.5	28.5	65
Ikj OM 1	0.43	4.29	5.72	3.26	3.94	2.04	10	13.2	20.2	18.0	112
Ifk RD 2	3.07	47.6	4.00	10.2	3.94	0.01	3.04	8.18	14.0	20.3	70
Ogba ind 2	10.0	11.7	18.6	9.75	4.00	3.00	10.1	6.28	42.7	71.1	60
ikeja ind 2	9.6	0.17	18.3	9.80	7.16	31.4	11.7	11.0	46.7	70.5	66
Ikorodu 2	102	2.38	363	23.1	22.0	0.01	102	30.5	589	759	78
Ikeja along 2	0.77	18.1	54.8	13.0	75.0	2.81	35.5	1.98	166	218	76
Iddo 1	4.00	1.46	58.8	6.05	51.6	1.09	37.5	3.25	152	168	91
Agege	16.6	2.2	156	14.7	56.0	13.8	30.0	14.1	259	243	106
Owode 1	52.6	13.0	70.0	5.3	4.00	20.4	24.0	31.0	151	182	83
Owode 3	32.6	11.1	81.2	29.7	6.00	8.82	15.2	13.6	135	133	101
Dasco	3230	7.81	11300	11.3	579	24.1	2140	68.7	16700	11700	147
Comp. Village	8.69	18.0	49.0	11.6	2.93	14.0	21.4	12.1	82.1	82.4	100
Ladipo 3	24.0	9.0	74.0	7.6	13.0	12.5	8.00	8.92	119	114	110
Katangua 2	10.0	5.43	257	38.3	199	17.9	126	18.1	593	611	97
Grand Foundry	10.9	3.50	38.2	12.8	8.11	13.7	28	9.79	85.1	108	79

Table F-3 Mean concentration of Fe in sequential extracts and pseudototal content (mg/kg) in Lagos urban soil

Location	**Step 1**	**% RSD**	**Step 2**	**% RSD**	**Step 3**	**% RSD**	**Step 4**	**% RSD**	**Sum**	**PT(*aqua regia*)**	**% Recovery**
LM PO 2	106	49.6	2320	1.52	98.2	6.52	9790	15.3	12300	12600	98
Ikj PO 3	223	64.2	1120	14.6	49.1	7.67	7230	18.4	8620	11900	70
Ikj PO 5	5.93	0.89	748	8.10	36.3	28.3	7850	21.4	8640	10000	86
Ifk PO 5	39.0	1.37	463	6.56	22.0	37.6	5480	16.0	6000	7460	81
Ifk PO 4	231	88.9	683	27.2	41.0	5.23	12100	17.3	13000	14000	93
Ikj OM 1	2.93	40.4	949	12.7	71.5	1.37	17500	11.2	18500	22200	83
Ifk RD 2	285	92.1	740	22.0	41.1	18.7	8750	10.9	9810	11100	88
Ogba ind 2	141	33.4	2500	32.0	28.0	4.05	20200	25.1	22800	28600	80
ikeja ind 2	193	57.3	2270	17.9	79.1	5.10	33600	7.63	36100	60200	60
Ikorodu 2	113	59.5	19300	7.47	196	18.7	124000	8.01	143000	146000	99
Ikeja along 2	1.1	5.15	3420	2.04	914	5.74	29000	3.02	33300	46200	40
Iddo 1	97	44.4	8160	5.29	904	17.3	51900	7.71	61000	69000	88
Agege	6.5	10.8	3230	8.75	286	3.51	25000	9.94	28500	36000	79
Owode 1	298	30.1	8020	6.40	100	16.5	39400	0.43	47800	47600	101
Owode 3	158	5.86	4840	2.57	83.2	11.4	30500	5.91	35500	41000	87
Dasco	872	26.8	44700	40.1	697	23.5	119000	3.82	165000	166000	100
Comp. Village	2600	18.7	38500	6.64	139	52.4	58800	4.98	100000	99800	100
Ladipo 3	288	5.03	3690	35.4	75.3	1.35	9180	9.56	13200	14700	86
Katangua 2	1.8	31.8	4800	5.88	145	26.8	39900	16.8	44800	57600	78
Grand Foundry	2360	42.5	11000	17.6	145	31.2	38000	12.2	51500	52600	98

Table F-4 Mean concentration of Mn in sequential extracts and pseudototal content (mg/kg) in Lagos urban soil

Location	Step 1	% RSD	Step 2	% RSD	Step 3	% RSD	Step 4	% RSD	Sum	PT(*aqua regia*)	% Recovery
LM PO 2	65.6	0.47	101	4.65	7.10	8.45	56.2	11.3	230	233	99
Ikj PO 3	40.2	12.8	43.0	10.1	4.48	4.16	48.3	13.0	129	179	72
Ikj PO 5	39.7	1.81	58.8	6.91	3.28	6.72	39.6	9.63	141	212	67
Ifk PO 5	28.2	8.46	20.0	9.40	2.72	11.0	35.0	9.06	89	135	66
Ifk PO 4	43.1	9.26	31.0	3.19	6.00	52.8	68.2	12.1	157	199	79
Ikj OM 1	107	14.0	114	15.2	6.00	38.4	93.3	10.6	320	359	89
Ifk RD 2	42.0	8.35	41.1	14.8	6.00	32.6	70.2	22.9	161	159	101
Ogba ind 2	76.7	6.03	166	30.2	10.0	26.9	152	6.95	440	375	117
ikeja ind 2	56.1	12.6	153	0.20	10.6	15.4	146	10.1	365	437	84
Ikorodu 2	393	26.3	963	15.9	72.0	32.6	1180	19.4	2620	2570	102
Ikeja along 2	37.0	9.67	143	19.0	14.5	2.38	126	3.11	330	413	80
Iddo 1	169	25.1	687	4.36	17.3	8.33	232	5.80	1100	1210	91
Agege	95.6	3.88	107	2.40	9.6	10.0	126	8.22	338	401	84
Owode 1	269	19.6	344	6.01	16.3	8.70	345	5.58	974	899	108
Owode 3	118	2.67	183	7.00	32.1	10.5	198	10.3	531	566	94
Dasco	395	4.05	384	3.12	91.1	5.13	690	7.51	1560	1530	102
Comp. Village	382	27.7	550	1.74	46.3	12.2	588	6.21	1560	1590	98
Ladipo 3	58.6	3.83	132	17.4	5.00	13.8	42.4	11.5	238	261	91
Katangua 2	165	7.35	381	19.4	11.8	12.9	141	9.22	698	753	93
Grand Foundry	562	13.0	1210	11.0	140	24.0	3270	24.4	5710	6090	94

Table F-5 Mean concentration of Ni in sequential extracts and pseudototal content (mg/kg) in Lagos urban soil

Location	**Step 1**	**% RSD**	**Step 2**	**% RSD**	**Step 3**	**% RSD**	**Step 4**	**% RSD**	**Sum**	**PT(*aqua regia*)**	**% Recovery**
LM PO 2	1.44	15.7	1.65	6.70	1.07	9.41	3.33	6.50	7.49	7.72	97
Ikj PO 3	0.80	3.08	0.63	17.1	1.46	55.6	3.29	8.56	6.18	6.14	101
Ikj PO 5	0.43	4.76	1.18	19.8	0.91	12.3	3.15	11.8	5.67	8.19	69
Ifk PO 5	0.30	8.50	0.69	4.87	0.80	35.3	2.39	15.2	4.19	4.49	93
Ifk PO 4	0.71	22.1	0.88	3.83	1.07	2.25	4.44	10.5	7.10	8.00	89
Ikj OM 1	0.58	2.17	1.30	6.20	1.35	3.89	10.2	15.4	13.4	16.0	84
Ifk RD 2	1.00	21.8	0.49	15.5	1.06	2.84	4.50	5.60	6.76	7.57	89
Ogba ind 2	1.30	11.7	3.73	3.58	1.27	2.73	7.0	50.4	13.3	16.6	80
ikeja ind 2	2.00	0.59	7.00	4.82	2.20	3.47	15.9	4.41	27.1	38.7	70
Ikorodu 2	14.4	7.72	47.2	14.4	5.80	2.84	49.9	13.2	117	109	108
Ikeja along 2	0.57	4.71	3.66	1.53	5.27	1.98	15.2	3.50	24.7	29.4	84
Iddo 1	4.00	5.26	8.03	5.03	5.05	4.51	27.6	12.7	44.7	44.4	101
Agege	2.63	5.09	5.38	3.86	2.01	4.15	11.0	36.9	21.0	21.0	100
Owode 1	3.10	12.8	36.9	6.93	2.01	5.20	90.1	17.2	132	139	95
Owode 3	1.99	5.33	7.74	0.53	1.73	2.02	11.9	5.18	23.3	29.0	81
Dasco	106	11.9	614	10.1	38.5	8.51	321	44.7	1080	1040	103
Comp. Village	2.00	30.6	23.0	35.4	2.22	24.1	17.2	8.10	50.5	38.0	133
Ladipo 3	2.00	6.38	3.87	7.33	1.30	5.23	6.00	24.0	13.2	12.0	110
Katangua 2	2.92	6.97	16.0	3.50	4.02	14.5	24.0	28.9	45.0	49.5	91
Grand Foundry	8.95	17.4	35.0	11.6	4.11	7.41	70.5	2.90	119	306	39

Table F-6 Mean concentration of Pb in sequential extracts and pseudototal content (mg/kg) in Lagos urban soil

Location	Step 1	% RSD	Step 2	% RSD	Step 3	% RSD	Step 4	% RSD	Sum	PT(*aqua regia*)	% Recovery
LM PO 2	1.49	19.1	32.4	5.28	2.55	7.36	5.74	11.9	42.2	87.3	48
Ikj PO 3	2.78	15.8	14.0	6.57	3.66	22.9	6.87	3.24	25.0	26.4	95
Ikj PO 5	2.70	6.92	17.3	6.18	2.00	18.3	4.22	5.05	25.6	24.3	105
Ifk PO 5	2.39	2.99	5.3	9.51	0.53	26.3	2.08	13.4	10.3	10.4	99
Ifk PO 4	5.63	1.19	17.3	1.00	2.00	18.3	4.94	7.31	29.3	40.8	72
Ikj OM 1	1.29	10.8	30.1	2.10	3.03	10.5	13.69	11.2	48.1	57.0	84
Ifk RD 2	9.00	5.39	16.3	12.5	1.05	0.01	4.00	27.9	29.0	28.7	101
Ogba ind 2	99.0	12.5	101	10.1	102	18.4	13.0	0.88	315	400	79
ikeja ind 2	10.7	14.8	64.3	8.46	12.9	12.5	36.8	9.84	125	144	86
Ikorodu 2	113	12.6	367	24.9	244	0.01	47.0	0.26	771	536	144
Ikeja along 2	1.78	8.90	216	2.59	33.8	2.19	56.9	7.34	308	182	169
Iddo 1	2.00	15.7	211	2.43	18.5	9.64	60.2	3.68	292	321	91
Agege	1.91	6.40	139	7.14	9.00	29.7	23.4	8.20	175	212	82
Owode 1	6.32	11.6	39.8	3.66	2.23	25.2	10.5	8.23	58.9	76.5	77
Owode 3	14.0	16.2	89.1	2.72	5.25	19.8	18.0	17.6	124	153	81
Dasco	157	2.11	2460	8.38	39	6.88	113	1.93	2770	4330	64
Comp. Village	5.91	4.45	46.0	8.67	1.97	53.3	11.0	12.7	64.9	102	64
Ladipo 3	102	25.7	184	53.6	3.50	15.3	7.6	15.3	284	315	90
Katangua 2	39.0	27.5	688	22.0	66	5.41	104	8.02	984	802	123
Grand Foundry	0.49	13.8	10.3	3.77	0.61	2.26	4.53	6.86	15.9	21.6	74

Table F-7 Mean concentration of Zn in sequential extracts and pseudototal content (mg/kg) in Lagos urban soil

Location	Step 1	% RSD	Step 2	% RSD	Step 3	% RSD	Step 4	% RSD	Sum	PT(*aqua regia*)	% Recovery
LM PO 2	134	5.01	53.2	6.91	12.1	5.66	30.7	9.41	230	239	96
Ikj PO 3	97.7	12.6	23.0	9.40	23.2	5.91	29.8	24.7	171	175	98
Ikj PO 5	27.4	4.09	12.0	1.38	5.7	14.4	32.0	36.8	79.9	98.7	81
Ifk PO 5	29.8	18.0	6.2	15.3	4.0	8.38	17.0	10.6	57.0	61.0	94
Ifk PO 4	88.7	5.37	14.3	7.36	10.0	21.2	23.5	4.21	137	165	83
Ikj OM 1	59.0	1.47	30.2	4.05	15.1	6.94	41.1	6.94	145	165	88
Ifk RD 2	76.8	13.1	13.0	9.0	11.4	2.48	25.2	11.0	129	132	97
Ogba ind 2	600	7.85	302	36.7	30.8	21.4	98.0	4.91	1031	1080	95
ikeja ind 2	177	33.2	70.6	9.04	19.0	45.7	62.5	2.75	336	433	78
Ikorodu 2	1131	2.69	842	3.70	129	2.48	633	13.1	2730	3240	84
Ikeja along 2	20.1	5.65	41.3	0.89	28.8	18.8	71.6	6.21	162	241	67
Iddo 1	726	41.2	346	9.25	79.7	7.64	139	2.34	1290	1190	108
Agege	452	12.9	287	5.39	37.1	14.1	150	24.0	926	1220	76
Owode 1	368	20.0	154	13.2	21.5	1.65	80.0	21.3	624	880	71
Owode 3	220	12.2	171	7.02	25.1	9.64	86.9	2.38	502	546	92
Dasco	1080	6.39	1010	3.63	81.1	5.59	218	3.74	2390	2807	85
Comp. Village	130	18.5	108	10.6	19.1	7.46	67.3	9.02	325	353	92
Ladipo 3	218	15.4	147	13.7	12.9	6.81	34.2	18.3	412	511	81
Katangua 2	2320	8.45	1460	10.7	230	0.22	712	13.6	4730	5610	84
Grand Foundry	174	3.85	188	1.41	103	20.6	108	7.85	572	520	110

APPENDIX G

Table G-1 Percentage PTE losses in the PM_{10} samples.

n = 2; mg/kg	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
ik PO 5	ND	0.062	0.390	0.093	0.0059	0.0021	0.17
Mn PO 2	ND	0.514	1.263	0.079	0.033	0.087	4.08
IK OM1	ND	0.067	9.85	0.11	0.025	0.200	0.005
if RD 2	ND	ND	0.5953	0.0377	0.0007	0.0036	22.6
Agege	ND	ND	0.99	0.063	0.001	0.006	37.7
Grand Foundry	ND	0.44	0.404	ND	0.022	0.008	0.41
Katangua	0.098	0.64	5.92	0.397	0.258	0.059	1.10
ikeja along	ND	0.10	0.65	0.15	0.010	0.003	0.29
Dasco	0.41	1.79	119	5.34	0.409	0.094	15.6