HUMAN HEALTH RISK ASSESSMENT OF POTENTIALLY TOXIC ELEMENTS (PTEs) FROM ENVIRONMENTAL MATRICES

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Declaration

I declare that the work contained in this thesis has not been submitted for any other award and that it is all my own original work. I also confirm that this research fully acknowledges opinions, ideas and contributions from the work of others.

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Abstract

In assessing human health risk of potentially toxic elements (PTEs), it is not the concentration of PTEs in the environmental matrices that is of greatest concern but the fraction that is absorbed into the body via the exposure pathways. The determination of this fraction (i.e. the bioaccessible fraction) through the application of bioaccessibility protocols is the focus of this work. The study investigated human health risk of PTEs (As, Cd, Cr, Cu, Pb, Mn, Ni and Zn) from oral ingestion of soil / dust, inhalation of urban street dust and air-borne dust (PM_{10}).

To assess health risk via oral ingestion of soil and dust, total PTEs were determined in twenty nine soil samples collected from children's playing fields and ninety urban street dusts collected from six cities. Analysis of total PTE content in these samples via ICP-MS revealed high Pb concentrations (> 450 mg/kg) in 3 playground soils and 32 urban street dusts. Detailed quantitative risk assessment (DQRA) carried out in the playgrounds showed that no significant possibility of significant harm exist in the playgrounds. The concentration of Pb from a particular dust sample based on 50 mg/day ingestion rate that a child might possibly ingest to reach the estimated tolerable daily intake was calculated and it exceeded the tolerable daily intake for oral ingestion in 4 cities. The bioaccessible PTEs were determined both in the soil and dust samples using the Unified BARGE method and the result showed that in all the samples, the PTEs solubilised more in the gastric phase than in the intestinal phase.

A new method has been developed; simulated epithelial lung fluid (SELF) and was used to assess the respiratory bioaccessibility of Pb from inhalable urban dust (<10 μm). Low bioaccessibility (<10 %) was recorded in all the samples analysed.

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Chapter one: Human Health and the environment

1.1 Introduction

Everything that surrounds us may collectively be termed as the environment. The land on which we build houses, the soil we grow our fruits and vegetables, the air and dust we breathe, the water we drink and all general living and non-living things that are necessary for day to day life. These environmental components constitute life support to humans but mismanagement of these precious resources can result in loss of natural value as well as physical degradation (1). Humans in an attempt to improve life on earth and exercise control over their environment have already modified the natural environment and it is expected that such modification will continue. Such changes disturb the natural environmental balance (2). In addition, the modification of these natural resources into built environment (secondary environment) due to technological advancement without strategic planning could lead to degradation particularly in countries where such modification is not regulated. Environmental degradation could be disastrous more especially in the countryside areas where people live close to rivers and oceans. The soil, particularly urban soils have undergone the greatest modification than other environmental components and because of its importance, it is of common interest to individuals, government and the general public. Globally, soil has been subjected to domestic, commercial and industrial activities and each of them have resulted in the release of contaminants (3).

Historical industrial activities since the mid-nineteenth century with little or no environmental impact consideration have resulted in significant legacies of soil contamination (4-5). Such industrial activities include; mining, smelting, lead-works,

chemical production, foundries, incineration, transportation and illegal waste disposal practises particularly in developing countries. These various activities release chemicals which contribute greatly to soil contamination. Although most of these activities are either banned or regulated in many developed countries, however, detailed information of past activities may be often limited or unknown; hence proper identification and assessment of contaminated sites may be complicated. Moreover, their environmental impact and legacies may remain for decades thereby putting human health at risk. The mining industry is amongst the highest contributor that has caused significant pollution of soil, dusts, air and water (6). The large quantities of mine waste and tailings generated by mining are of great environmental and health concerns internationally. In the UK, historical industrial activities have been extensively reported, for example, a former lead mine in the Tamar valley district of west Devon and east Cornwall (7), Derbyshire mine (8), Tyndrum mine, central Scotland (9), mine and smelter wastes in S.W. England (10), St. Anthony lead Works, Newcastle upon Tyne (11). There is increasing awareness (12-13) that abandoned industrial sites harbour contaminants and since some of these contaminants particularly metals are immobile in soil, their accumulations occur over time which may result in elevated concentration. Such scenarios could be a potential threat to human health and the environment. It has been estimated that in England and Wales, over 100,000 contaminated sites might still exist, and out of these, 5 – 20 % are estimated to pose a 'significant possibility of significant harm' (14). A global inventory of natural and anthropogenic metal emissions, transportation, deposition and environmental effects are well documented (15-17). Studies (18-19) have shown that as a result of these various activities, river channels and flood plains (fluvial environments) in many countries of the world have become a principal route for the

dispersal of environmental contaminants as well as an important sink. Due to prompted major land development programmes and rapid urbanization, most of these derelict lands have been re-developed to day-care centres, schools, recreation parks and residential homes thereby exposing humans directly or indirectly to environmental contaminants.

In addition, dust is an environmental component that has been found to house contaminants particularly urban dust. Dust is derived from soil, and represents the small particles that have settled onto humans, outdoor objects and surfaces due to either wet or dry deposition. It consists basically of natural and anthropogenic components (20). The natural components include plant residue, fragmented rock and volcanic release while the anthropogenic constituents include vehicular exhausts particles, lubricating oil residues, tyre wears, engine coating wears, brake lining wear particles, heating systems, municipal waste incineration, constructions, renovations, mining and extraction processes, smelting, corrosion of galvanised metal components and building deterioration (21-23). Dust particles released from contaminated sites travel long distances and could be in constant contact with humans due to outdoor activities. This is because these dust particles have light weight. They are known to be fine solid particles (24) and settle out under their own weight but could also remain suspended for some time in the atmosphere depending on its particle size (24). Of particular concern are children (<6 years) and specifically those who may practice ‘pica’ (the habit of mouthing non-food substances and repetitive hand/finger sucking) (25). Thus, urban dust is a repository of environmental contaminants.

Air pollution is a term commonly used to describe a heterogeneous mixture of toxic substances that are naturally or artificially introduced into the air. Such substances

could come from various sources but in the urban settings, air pollution is derived basically from fossil fuel combustion (e.g. for energy generation, industrial processes and transportation) (26); in addition, the combustion of solid fuel, such as, coal and wood for domestic purposes are additional contributors in developing countries (27). Particulate matter is one air pollutant that has always attracted great attention because of its size, chemical composition and reactivity (28). Air pollution can pose more health risk than pollution from other environmental matrices because inhalation is involuntary and once the pollutants are in the air, human exposure cannot be avoided especially for people who spend a longer time in outdoor activities. Air pollution results in serious effects on people's health particularly people categorised as high-risks groups such as infants, children, pregnant women and the elderly. Environmental and health effects of air pollution have been widely reported (29-32) to include, smog, heart infection, heart failure, lung cancer, irritation of the upper respiratory tract, asthma, neurological and psychological disorder, fever, lung fibrosis, damage to the central nervous system, chronic bronchitis, inflammation and reduced lung capacity. Air pollution is seen as a global challenge. In the UK, it has been reported that air pollution reduces the life expectancy of everyone in the UK by an average of 7 – 8 months (33). Furthermore, a recent report (34) has revealed that the inability of UK government to meet up with EU standards on air pollution since 2005 is jeopardising the health of people and is reported to be costing the nation £8.5 – 20 bn yearly. Though environmental contaminants abound, studies (35-36) have shown that potentially toxic elements (PTEs) are contaminants that are ubiquitous in the environment due to former or current emissions. It has also been suggested (37-38) that there is a need to constantly monitor their concentrations globally because of environmental and health implications.

1.2 Potentially toxic elements (PTEs) in environmental matrices and health risk.

The presence of PTEs in environmental matrices (soil, dusts and air) of the urban environment represents significant health risks to humans and the ecosystem in general. It is also important to note that when these PTEs are emitted from their various point sources, a great percentage enter the water bodies (39). The presence of PTEs in water poses a serious threat to humans particularly in developing countries where people drink untreated water. The use of untreated water for irrigation purposes is also common in some parts of the world. This is a potential pathway through which these PTEs could easily enter the food chain. The presence of PTEs in the environment raises health concern because these elements can be toxic, ubiquitous and cannot be degraded to non-toxic forms by any known method and as a result remain in the environment for decades. Humans are exposed to these PTEs via oral ingestion, inhalation or dermal absorption (40-41). Some of these PTEs: chromium (Cr), copper, (Cu), manganese (Mn), nickel (Ni) and zinc (Zn) are beneficial to organisms at low concentrations (42), but arsenic (As), cadmium (Cd) and lead (Pb) have no known health benefit at any concentration (43-45). The presence of these PTEs in environmental matrices might have irreversible adverse effects on humans particularly children due to their pica behaviour, physiology unique exposures and special vulnerabilities (46), which put them at a higher risk because immature organs tend to be more susceptible to PTEs than other contaminants (47). It has been reported (48) that the absorption rate of lead (Pb) from environmental matrices by children is 40 % higher than adults. Children are exposed to PTEs in their homes, streets, roads, churches, shops, schools, recreation parks, picnic areas and playground. These PTEs released from their different point sources are carried by wind into the air, water and soil. This makes it possible for

humans to come into constant contact with the elements. Exposure to these PTEs could cause potentially adverse effects, carcinogenesis and development of numerous health effects including: Skin and internal cancer, DNA damage, neurological effects and alterations to endocrine system (49-51). Due to these adverse effects, there are a good number of studies that have investigated source identification (52-53), fractionation and spatial distribution (54-55) as well as bioavailability and bioaccessibility (56-57) of PTEs in the environment. Most of these studies have focussed on the assessment of human health risk via oral ingestion. In this research, apart from assessing human health risk via oral ingestion by employing the physiologically based extraction test (Unified BARGE Method (UBM)), a robust *in vitro* method has been developed and was applied to assess human health risk associated with inhalation of urban dusts (i.e. inhalation bioaccessibility).

1.2.1 An overview of PTEs commonly found in Environmental matrices.

The following elements: arsenic, cadmium, chromium, copper, lead, manganese, nickel and zinc have been listed as PTEs (58-59). Their toxicity levels depend on sources, forms, bioaccessibility, bioavailability (60) as well as underlying human health and conditioning factors such as sanitary conditions.

Arsenic (As)

The US Environmental Protection Agency (EPA) (61) has classified arsenic as the number one toxin (62) and its sources in the environment are: weathering of volcanic rocks, mining and smelting, waste incineration, combustion of coal and petroleum, the use of As-based wood preservatives, herbicides and pesticides. Basically the toxicity of As to humans depends on its chemical form (inorganic or organic) and oxidation state, with the inorganic forms being more toxic than the organic forms

(63). Most studies on arsenic (64-65) centre on arsenite As (III) and arsenate As (V) and have observed that As (III) is more toxic than As (V). Soil / dust ingestion and inhalation of industrial emissions are important exposure pathways. Such exposures results in adverse human health effects including: skin lesions, melanosis (change of pigmentation), cough, chest pain, hypertension and cardiovascular complications (66-67).

Cadmium (Cd)

It has been reported that Cd level in most soil is relatively low (0.2 – 0.78 mg/kg) (68) and hardly occurs in the pure state but is usually associated with sulphide ores of Cu, Pb and Zn. The greatest percentage of Cd in the environment comes from anthropogenic sources including: incineration of urban waste, atmospheric deposition, metallurgical activities, and the use of fertilizer for improvement of land for agricultural practices as well as smelting of non-ferrous metal ores (69). Cadmium is also used in a number of industrial processes including; welding, electroplating, production of nickel-cadmium batteries used in mobile phones and production of iron, steel and cement. Exposure to Cd is basically through inhalation of polluted air and ingestion of earth materials (70). High concentration of Cd if available in any environmental scenario represents a significant risk to humans due to its toxicity. Gastrointestinal human health effects include: abdominal pain, vomiting and diarrhoea, it is also associated with respiratory malfunctioning and renal disorder (71).

Chromium (Cr)

Chromium occurs naturally in soil as mineral chromite, $FeCr_2O_4$ and could be emitted into the environment via mining processes. Anthropogenic emissions comes from the

use of chromium compounds for metal plating, corrosion inhibitor, plating, wood preservatives, metal finishing, leather tanning, and stainless steel cookware (72). Chromium is also used to make dyes and pigments for paints, make refractory bricks for furnace and as an additive to inhibit corrosion. In the soil, it exists basically in two oxidation states, Cr (III) and Cr (VI) and its effects both on the environment and humans depend on the oxidation state. Chromium (VI) is about 300 times more toxic than Cr (III) (73). The health effects include: damage to nose and throat lining, anaemia, pulmonary disorder, skin and mucous irritation. These effects are observed in people who ingest earth materials (soil, dust and food) containing Cr, inhaled air containing Cr or its compounds or those dermal absorbed. In terms of solubility, Cr (VI) is more soluble in soil and its mobility in the soil and dust is more when compared to Cr (III) (74). Ingested hexavalent chromium is easily converted to trivalent chromium in the stomach (75).

Copper (Cu)

Copper has been extensively used in the industrial production of plumbing materials, electric wires, cables and coins because of its unique properties including high thermal and electrical conductivity, low corrosion, alloying ability, and malleability (76). In the agricultural sector, it is used in the manufacturing of fertilizers and fungicides (77). Emissions are basically from Cu smelters, incineration of waste, fly ash from coal–burning power stations, fallout from volcanic activities, combustion of wood products and fossil fuels. Ingestion of food containing Cu, soil and dust is one of the significant exposure pathways. Approximately 30 – 50 % of ingested Cu is in the form of Cu (II) and is absorbed in the small intestine with a smaller quantity in the stomach (78). Copper dusts and fumes could also enter the body via inhalation. Its toxicity results in acute gastrointestinal symptoms, damage to the brain, renal

tubules and liver complications (79). However, excess Cu in humans is mostly controlled due to decreased absorption or increased excretion (80).

Lead (Pb)

Lead is ubiquitous and persistent in the environment particularly in an urban setting and has no biological role in humans (81). Even with the use of unleaded fuel by many countries of the world, Pb pollution is still a threat to human population particularly those who live in the cities where there are more release of Pb in the environment. It is important to note that in countries where leaded fuel is still in use, the combustion of such fuel in different engines is a potential pathway through which Pb could be released into the environment. Historically, Pb has occurred through emissions from metal mining, smelting and processing as well as via the application of sewage sludge to soils, Pb battery manufacture, waste disposal and incineration. Lead is also a component of paints, ceramics and pipes used for water supply (82). Lead could enter the human body either through ingestion or inhalation and affects the development of nervous system and other major organs like the heart, intestine, kidneys and reproductive system (83). In the human body it also causes anaemia, renal and DNA damage (84).

Manganese (Mn)

Manganese is one of the most commonly used elements. It is used for: ceramics, dyes, dry-cell battery, pigments, steel and iron making. It is also used in fungicides and as an antiknock agent in petrol (85). Emission of Mn into the urban environmental is from metallurgical and chemical industries, combustion of coal and petrol. When emitted, it could enter the human body through inhalation of polluted air. Mn is an essential element (micro nutrient) needed in the human body for bone

formation and development; however, an excess dose could lead to DNA damage and chromosome abnormality particularly in adults (86).

Nickel (Ni)

Nickel has a wide distribution in the environment due to its industrial and commercial applications and, as such, the human population may be exposed to this PTE in soil, dusts, air and water (87). Nickel and its compounds are used in the production of stainless steel and alloys of high temperature and corrosion resistance. In the food industries, Ni is used as a catalyst and pigment (88). People who either work in these industries or use the products may be exposed to Ni. It is commonly emitted into the environment through incineration of waste and sewage, combustion of coal and fuel oil. In terms of health risks, inhalation is the primary route of exposure, though ingestion of soil / dusts could also be a pathway. It has been noted that its adverse effects is mainly in the respiratory system (the nasopharyngeal, tracheobronchial, and the pulmonary) and the immune system (87).

Zinc (Zn)

Zinc is one of the micro nutrients required by the human body for cell growth, development and proper functioning of the immune system (89). The principal use of Zn is for the galvanization of other metals to prevent corrosion but in the long run the galvanised materials release Zn in the environment. It is also used in the manufacture of dry cell batteries and dyeing fabrics (90). The pharmaceutical industry uses Zn compounds in the production of antidandruff shampoos. These shampoos after use on the hair are released into the environment. In addition, Oral ingestion of soil, dust and food is a significant exposure route of Zn. Gastrointestinal health effects of high zinc concentration are vomiting, diarrhea and abdominal

cramps while Zn that entered the human via the respiratory tract cause chest pain, cough and irritation (91-92).

1.2.2 Predominant forms of PTEs in soil and dust.

PTEs accumulate in environmental matrices in various geochemical forms and the forms of these PTEs are fundamental in assessing their risks to humans. This is because the toxicity of these elements does not depend only on their total concentration but also on their chemical forms, distribution, mobility, bioaccessibility, bioavailability and transformation (93). The predominant forms of these cations are: particulate-associated, exchangeable, carbonate associated, Fe-Mn associated, hydroxides and residual forms (94). The solid phase partitioning is influenced by soil pH, organic matter and the presence of oxidizing or reducing agents (95). The release of PTE from an environmental matrix during chemical extraction processes depends on the strength of the reagent.

1.3 Land contamination risk management in the UK

There is an increasing use of risk management to deal with land contamination globally. Over the years, land contamination risk management policies in the UK have focussed on identification and removal of unacceptable risks to human health and the environment, through the use of a risk - based approach. The current risk-based approach in the UK applies to managing historic and abandoned contaminated land for both on-going and changes in land use, through two principal regimes – Part IIA of the Environmental Protection Act 1990 and the Planning process (the Town and Country Planning Act 1990 and Town and Country Planning Act (Scotland) 1997). Although these two regimes are two separate systems, they interact effectively. The planning process is charged with the responsibility of

ensuring that land is safe, fit for its purpose and should not cause significant harm in its proposed use. The regime can also manage land known to contain hazardous chemicals particularly when change of use is being considered.

The implementation of Part IIA started in England and Scotland in 2000 and in Wales in 2001, respectively; with the responsibility of ensuring that land does not cause significant harm in its current use. Part IIA provides the basis for the identification, assessment and possible clean-up of 'contaminated land' that represent significant risks to human health and the environment. Under this Act, contaminated land is any land which appears to the local authority in whose area it is situated to be in such a condition, by reason of substances in, on or under the land, that – significant harm is being caused or there is a significant possibility of such harm being caused; or significant pollution of the water environment is being caused; or there is a significant possibility of such pollution being caused (96). According to the statutory mandate, concerned local authorities are expected to: investigate their areas to identify contaminated sites, compile and serve notifications of contaminated land, decide whether sites should be tagged as 'special sites' and hand over such to the Environment Agency, serve notification notices where applicable, assess best remediation techniques, contact authorised regulatory agencies and maintain up-to-date register of contaminated land (97).

Based on this act, the UK Environment Agency (EA) and the Department of Food and Rural Affairs (DEFRA) (98) developed risk-based approaches for assessing human health risks from contaminated sites. The starting point in the assessment is the ability to effectively identify the linkages between the (a) source (substances in environmental matrices which is a threat to the receptor), (b) pathway (a link between the source and the receptor which could be any of the pathways; oral

ingestion, inhalation, dermal contact) and (c) receptor (humans and ecosystem that are at risk). This concept of pollutant linkages helps to identify and assess the level of risk prevalent in a given environmental media; moreover, all the three elements (source-pathway-receptor) of the pollutant linkage must be complete for a risk to exist. If any of these components are absent, there can be no risk and the land is designated as 'uncontaminated'. The next step in the risk assessment involves the use of Soil Guideline Values (SGVs). Soil guideline values are scientifically based generic assessment criteria used to evaluate long-term risks to human health from chemical contamination in soil, example, PTEs. These values are given in the form of concentration thresholds of contaminants in soil and act as a check to contamination levels in a site. Contaminants concentration levels below the SGVs implies minimal or no health risks associated with but exceedence signifies risks to human health. The implications of exceeding the SGVs could range from the need for further and more detailed investigations to the necessity of site remediation. These SGVs were calculated using the non-statutory Contaminated Land Exposure Assessment model (CLEA) and were modelled for three land scenarios: (a) residential, (b) allotment and (c) commercial/ industrial. The CLEA model is a scientifically based frame work used to assess human health risks from contaminated sites. The model is an exposure assessment criterion that uses generic assumptions about the fate and mobility of chemicals in the environment, and a generic conceptual model for site conditions and human behaviour to estimate exposure to soil contaminants. In principle, the model allows determined contaminant exposure concentrations to be compared with certified toxicological or Health Criteria Values (HCVs). The CLEA model used to derive SGVs assumed that a contaminant is released from soil and is taken up by humans in the same

proportion just as the model which was used to establish the oral HCV (99); in practice this assumption, may not be true since HCVs were established using animate materials other than humans or where the environmental matrix of exposure used to derive the HCV is not soil.

In using SGVs to assess human health risks of contaminant from soils implies that all the PTEs that entered the human body via exposure routes is bioavailable (worst-case scenario), however, this could be seen as an over estimation because these PTEs occur in different geochemical forms and are bound to the soil components while some occur naturally in insoluble forms. Thus, the bioavailability of these PTEs to humans may not be total (100%). For a better understanding of the internal dose and health risks associated with oral soil ingestion, it is fundamental to consider their oral bioaccessibility. Among the elements being considered in this study, only SGVs for Ni, As, Cd has been published (100) for the different land-uses (residential, allotment and commercial/industrial). The SGVs for Pb has been withdrawn. In addition, Generic Assessment Criteria (GAC) has also been published (101) to augment for some of the elements not listed by SGVs.

1.4 Conclusion

This introductory chapter highlighted that the natural environment provides support to humans, but the quest to improve on the living standard and also overcome environmental challenges has resulted in the release of contaminants into the environment, particularly PTEs, which are known to be ubiquitous, non-degradable and toxic. Of all the environmental matrices (soil, water and air), soil is the most affected either due to past or current human activities. Hence, humans are at the risk of adverse health effects due the presence of PTEs in environmental matrices. It is in

the light of this challenge that the UK Environment Agency and the Department of Food and Rural Affairs (DEFRA) developed risk-based approaches for assessing human health risks from contaminated sites. This approach is based on CLEA model which assumes that the bioavailability of PTEs to humans is total (i.e. 100%). However, bioaccessibility studies (102-103) are investigating on how to improve the way risk is currently being assessed.

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Chapter Two: Human health risk assessment from exposure to potentially toxic elements (PTEs)

2.1 Introduction

Humans are still being exposed to elevated concentrations of PTEs despite increased awareness of their environmental and health consequences. This represents a potential health risk to exposed populations. The consistent exposure of humans to environmental PTEs as a result of accidental or intentional release of these contaminants has attracted the attention of international and local institutions, organisations and agencies such as World Health Organisation (WHO), the Organisation of Economic Cooperation and Development (OECD), European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC), the US Environmental Protection Agency (EPA) and England Department for Food, Environment and Rural Affairs (DEFRA) to the development and implementation of human health risk assessment and encourage studies in that direction. Hence, the use of risk assessment as a strategy for dealing with environmental pollution is gaining international recognition.

Human health risk assessment is the characterization of the potential adverse health effects of human exposure to environmental contaminants (1). This process involves the determination of the likelihood that human exposure to toxic chemicals could result in adverse effects on human health and quantitatively estimate consequences. Risk assessment is useful in the determination of the significance of contamination in a site and the level of clean-up required for the intended use of the site. As a result, regulatory decision issues are based on risk assessment studies. Although health implications of environmental contaminants affect everyone but children are more prone to health effects than adult because of differences in metabolism, behaviour,

diet, physiological changes and functions. Each of these factors which changes at different stages of development affect the way in which children are exposed and react to environmental contaminants. Therefore, children's exposure to environmental contaminants differs widely from that of an adult because of their sensitivity and vulnerability to PTEs, moreover, their exposure starts at conception and during breast feeding as infants (1). It has been noted that due to the importance of children's healthcare, no guidance document on risk assessment that did not recognise children's unique exposures and special vulnerability can be considered adequate to protect human health (2).

2.2 Exposure pathways.

Exposure could be defined as the contact in both space and time of an agent (chemical, physical or biological) and a target organism or a receptor (e.g. humans) such that they come together and interact (3). Human exposure to multiple routes can occur simultaneously or at different times. The term ''exposure pathway'' refers to the channel an environmental contaminant (example, PTE) takes from its source to exposed populations. It forms a link between environmental release and the potentially exposed populations. Risk assessments involve investigating and exploring the various components making up the linkage. The exposure pathway consists of five components; these are as shown in Figure 2.1 (3). Figure 2.1 illustrates the relationship that exists between the contaminant, source and the receptor. Humans are exposed to environmental PTEs indirectly or directly. Indirect exposure occurs, for example, through the food chain where plants grown on contaminated soil take up PTEs and pass on to animals and humans through three major routes: gastrointestinal tract (oral ingestion), respiratory tract (inhalation) and

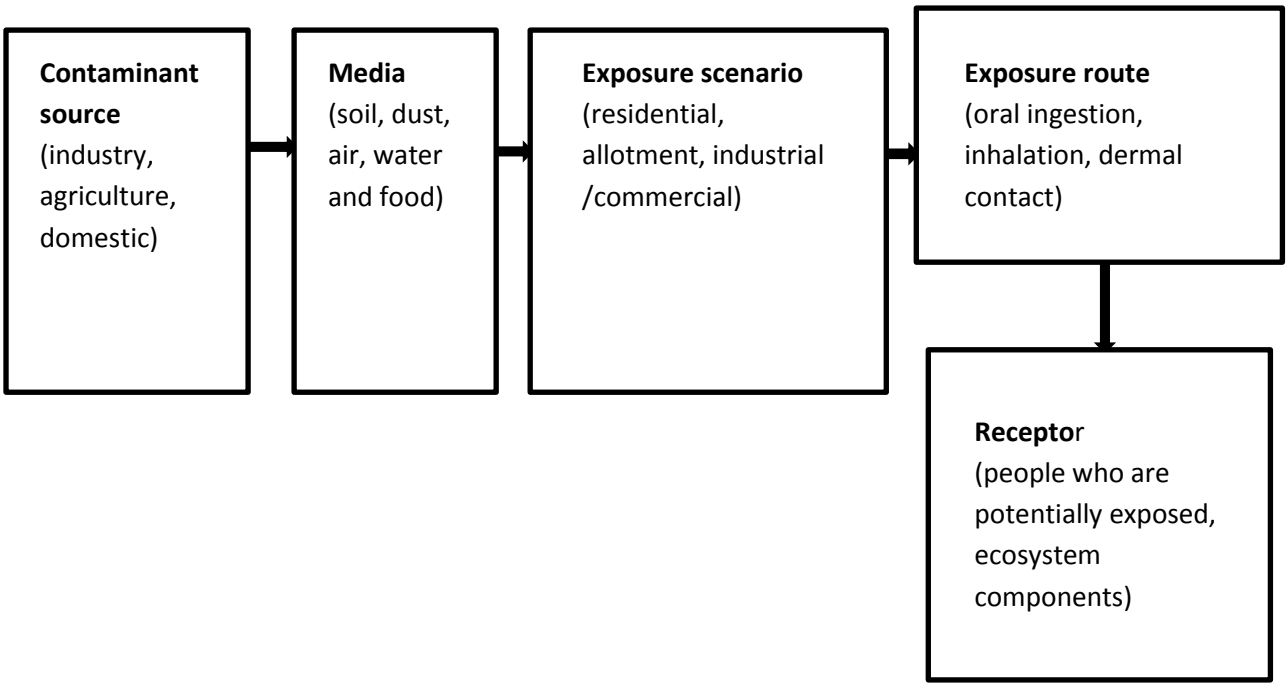

Figure 2.1: The five components of exposure pathway (3)

absorption through the skin (dermal absorption). These major routes are discussed below.

2.2.1 Oral ingestion of soil and dust (gastrointestinal tract)

The human digestive system is responsible for food and material intake, food break down, energy and nutrient release, and waste removal**.** In order to have a better understanding of oral ingestion of soil and dust, the medical physiology of the human digestive system which includes the gastrointestinal tract and accessory organs have been presented (Figure 2.2) (4). The organs of the gastrointestinal tract include the mouth, oesophagus, stomach, small intestine and large intestine (colon) while the accessory digestive organs include the teeth, tongue, salivary glands, Liver, gallbladder, and pancreas (4). Food and other materials enter through the mouth. The mouth helps to change the food and other ingested materials mechanically by biting and chewing and this increases their surface area. Saliva present in the mouth lubricates the food enabling it to be swallowed. Digestion of carbohydrate starts in the mouth. The oesophagus is a passage where masticated food moves from the

mouth to the stomach by rhythmical muscular contraction (peristalsis). The stomach acts as a reservoir where food is temporary stored in order to be churned over and mixed with enzymes and hydrochloric acid. Digestion of protein starts here. The stomach also transports food into the small intestine. The small intestine digests food further and absorbs food products. Absorption of water and salt take place in the large intestine (colon). The seven stage processes that summarises the digestion of ingested food and other related materials are; ingestion, mastication, deglutition, digestion, absorption, peristalsis and defecation (5). Numerous digestive juices (enzymes) play a key role in the overall digestion processes (6). Ingested soil and dust would also pass through these processes and release their content (example, PTEs) for absorption into the body system.

Oral ingestion of soil and dust occurs deliberately or involuntarily. It is common among all the exposed population. Due to the pervasive nature of soil particularly dust, it is constantly in contact with the skin, clothes and any other objects not specially protected. It has been noted (7) that every exposed population particularly in the urban environment would possibly ingest a small quantity of soil. This easily happens because soil and dust adhering to our body, especially the fingers, may be unintentionally ingested due to hand-to-mouth activity. Moreover, fruits and vegetables are grown in soil and if not properly washed would lead to unintentional soil ingestion. Eating of dropped foods could also lead to soil ingestion. Children with a natural tendency to explore their environment particularly during the summer/dry season are mostly vulnerable and easily associated with soil ingestion. Soil ingestion in children resulting as a result of hand-to-mouth behaviour is more pronounced among the age group 18 – 24 months; however, children above this age group also

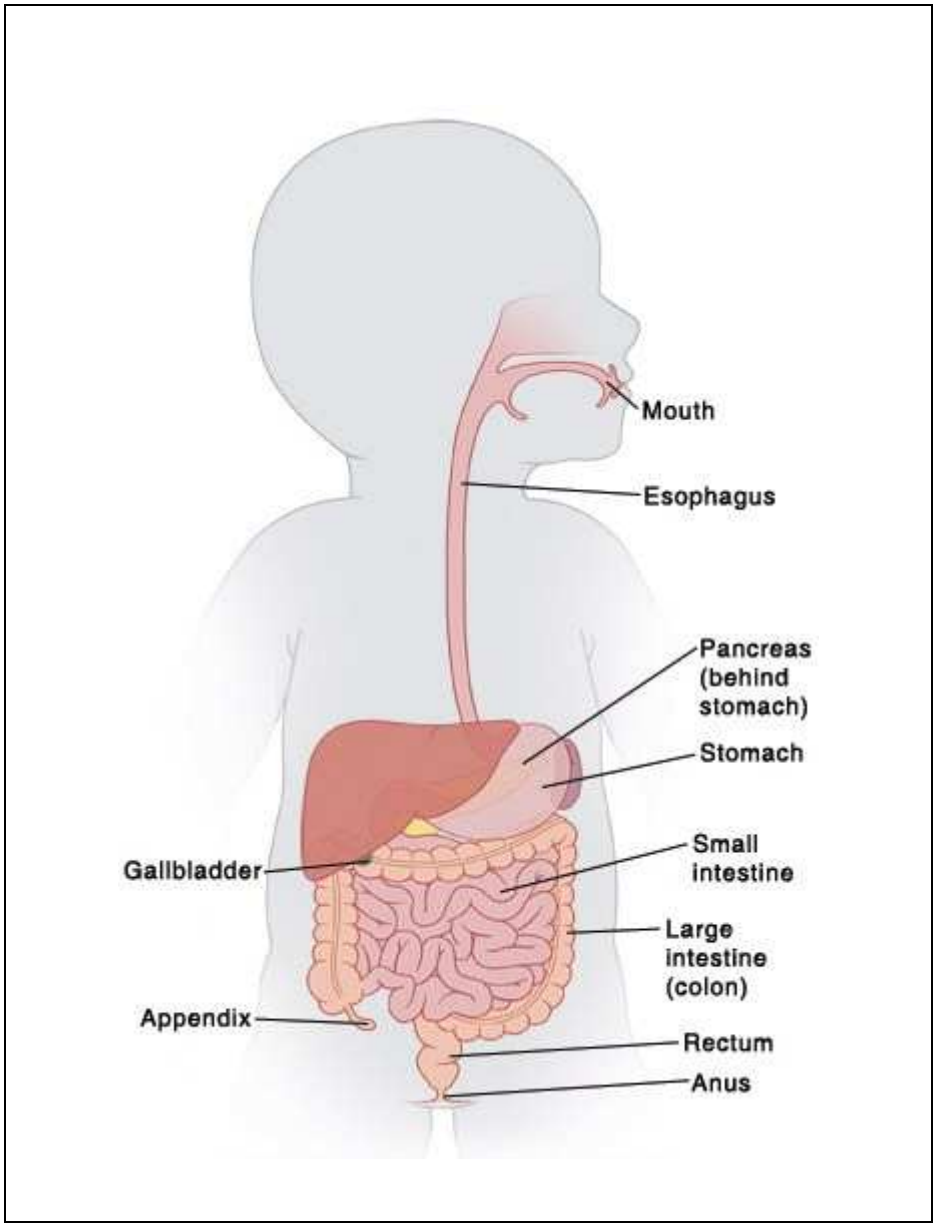

Figure 2.2: Anatomy of the human digestive system, child (4)

ingest soil particularly among the poor and rural dwellers. The consistent ingestion of non-food materials (such as: fingernails, pencils, paint chips, coal, coal, cigaretteends and faeces) above this age gap is referred to as ‘pica’ and has been considered to be developmentally inappropriate when the habit continues for over a month (8). Pica behaviour is not limited to children only, as adults with mental disability also ingest non-nutritive earth materials other than edible earth materials particularly in the developed world. Pica is more pronounced in children because of

their interest in outdoor activities but decrease as they grow and become more conscious of themselves and the environment. A study (9) has shown that 'pica behaviour' in children decreases with age due to developmental and societal factors. The investigation (9) revealed that children above 12 years ingest 10 % of soil and dust ingested by children 1 – 6 years old, while children 6 – 12 years of age ingest 25 % of soil relative to that consumed by children 1 – 6 years. Soil particle size fraction plays a key role in hand-to-mouth behavioural attitude in children. It has been noted (10) that the smaller particle size fraction (e.g. < 125 μm) that easily adheres to the hands are the type that are easily ingested via pica. Geophagy is a type of pica; it has been defined as the deliberate and regular ingestion of large amount of soil (clay) and other earth materials (11). It is practised in many countries of the world and it is not limited to any particular religion, age group, sex, race or any region. However, it has been noted (10) that geophagy is more pronounced in some geographical regions, such as, South America, Asia and Africa and that the practice is more prevalent among rural dwellers, low income earners, poverty-stricken population and most importantly pregnant women. In some of these societies, soils are available in the market and shops for purchases. The explanation to why people practise geophagy has been widely investigated (12-13). Pregnant women particularly in Africa are known to ingest different kinds of soil as a way of satisfying a compulsive physiological urge and also to overcome constant spitting and the symptoms of early morning vomiting. A study (12) that investigated soil ingestion among pregnant women in Africa (Kenya) revealed that out of 275 pregnant women, 154 deliberately ingested soil. It was also believed among geoghagists that the regular and deliberate consumption of soil could help supply the body with adequate nutrients particularly iron, but unfortunately, not all soils that are deliberately ingested

are rich in minerals. An *in vitro* investigation of five different geophagic materials sampled from four countries – India, Tanzania, Turkey and Uganda revealed though these materials were rich in minerals nutrients (Cu, Fe, Zn) needed by the human body, but observed that geophagy can possibly reduce the absorption of these bioavailable minerals (13). Some Asian pregnant women living in the UK ingest an imported soil (sikor) as a source of iron (14). A physiological based extraction test (PBET) that was used to examine these earth materials sourced from Birmingham and London, respectively revealed that with the amount of soil consumed, one of the sample can provide 41 – 54 % of Fe required by a 15 – 18 year old female, with the other sample providing up to 90 – 119 %. But the authors found out that high intake of this material by pregnant women could lead to risk of lead toxicity which would unavoidably affect the unborn child. A more recent study (15) on this earth material (sikor), commonly ingested by Bangladeshi pregnant women both at home and abroad (UK), revealed that the arsenic level in the sample ranged between 38 – 13.1 mg/kg, cadmium ranged between 0.09 – 0.4 mg/kg and the lead level between 21 – 267 mg/kg. The authors explained that the health implications of their findings was that based on median consumption values, oral ingestion of 50 g of sikor is equivalent to ingesting 370 µg of As and 1235 µg of Pb, respectively. Calabash chalk (locally called 'Nzu' in Nigeria) is a multi-cultural earth material widely eaten by some pregnant women in Nigeria and other African countries. The elemental analysis of this material revealed a substantial amount of lead which could pose a health risk to these pregnant women and the developing foetus (16).

Unintentional oral ingestion of soil and dust is inevitable; however, weather conditions, state of the environment and people's occupation would determine the amount of soil and dust that end up in the gastrointestinal tract. Dry weather

conditions help in the generation and dispersal of these environmental matrices. Moreover, where we work and spend quality time is very important. People whose work could lead to the emission of soil or dust are more exposed than office workers. However, irrespective of where we live, work or spend our leisure time, we are unavoidably exposed to soil and dust especially in the urban environment. Indirect exposure to oral ingestion of soil and dust has been the focus of much current research due to its health risks. The relationship between soil lead concentrations and children's blood lead levels was examined for a four-year period 1992 -1996 in Syracuse, New York, USA (17). The study analysed 194 soil samples collected from three locations (street, recreation parks and residential lots). The mean concentration of lead in these samples was found to be in the range 20 – 800 mg/kg with samples with smaller particle size fraction (< 85 μm) having more lead than samples with larger particle size fraction (2 mm). Also, out of 12,000 individual children (< 6 years) who were involuntarily exposed to these soils, 3,375 children had blood lead levels greater than the level of concern 10 μg dL^{-1}.

Oral ingestion of soil and dust via pica or geophagy might not be regular but involuntary ingestion is regular and unintentional. However, any form of soil and dust ingestion could lead to potential health implications. Ingested soil and dust will normally solubilise in the gastrointestinal tract just in the same way food taken will undergo digestion to release energy. Digestive juices solubilise ingested soil thereby making PTEs bioavailable (available for absorption into the blood stream). Oral ingestion more especially geophagy could lead to mineral nutrient imbalance in the body system because most elements bound by solid phase partitioning are released in the acidic medium of the human stomach, and where large amount of soil has been ingested, mineral nutrient release would be enormous. It has been reported

that people who ingest large amounts of soil could have a direct supply of mineral nutrients such as Ca, Cu, Fe, Mg, Mn and Zn, but the study also observed that this could lead to mineral nutrient imbalance in the body due to a high intake of soil (18). Oral ingestion is also an entry point for parasites that are easily associated with earth materials. It also contributes to iron depletion and low haemoglobin among pregnant women (12). Dental infection and injury, blockage of the large intestine and phosphorous intoxication have been associated with soil ingestion (19). Two studies (20-21) which examined the influence of blood lead level on the ability and academic attainment of children discovered that even children's exposure to low lead levels could have a significant negative impact in early academic excellence. Environmental arsenic exposure of 414 children (< 6 years) around a former copper smelter site was investigated (22) through urine test and elevated excretion of arsenic was obtained. Thus, oral ingestion of soil and dusts (directly or indirectly) is a potentially route through which these PTEs enter our body.

2.2.2 Inhalation of soil and dust (respiratory tract)

Humans can survive without food and water for days but denial from inhaling air for a few minutes will amount to death because continuous inhalation of air is required in order to maintain the proper functioning of the various activities taking place in the body system (23). Thus, the respiratory tract is an essential system in our bodies. Air (oxygen) is needed by all the body organs enter through this system and carbon dioxide released from body metabolism is removed as waste products through the same tract. Deposition and clearance of materials are complex processes which definitely occur during inhalation. These inhaled particles are initially deposited in the extracellular airway lining fluid and can be cleared from the lung either by dissolution or mechanical transport (24). Thus, a brief discussion of the medical physiology of

the human respiratory tract would be indispensable for a clearer understanding of the inhalation of dust particles (< 10 μm).

Figure 2.3 shows the anatomy of the human respiratory tract (25); the major regions of the human respiratory tract have been classified as the nasopharynx, tracheobronchial, and the pulmonary (26-27). However, it has been noted (26) that the exact names and classification vary according to different authors and sources. According to this classification, the nasopharynx which consists of the nose, pharynx and larynx extends from the nose to the larynx. This region filters out large inhaled particles (> 10 μm) (28). The tracheobronchial consists of the trachea, bronchi, and bronchioles. This region is responsible for the movement of inhaled particles from the deep part of the lung to the oral cavity with the help of ciliated mucus linings. Particles moved to the oral cavity can either be swallowed or coughed out. The epithelial lining fluids located within the nasopharynx and tracheobronchial region form an interface between the respiratory epithelial cells and the outer environment. It thus constitutes a 'first line of defence' against inhaled toxic gases, such as SO_2, O_3, NO_2, and tobacco smoke. Constitutes of the epithelial lining fluid may detoxify these pollutants to protect the underlying respiratory tract lining fluids cells (29 -30). This is a significant way through which the epithelial lining fluids reduces the burden of oxidants that reach the epithelial cells. The pulmonary region is comprised of many structures including the respiratory bronchioles, alveolar ducts and sacs, and alveoli. This is the key functional area of the lung because it is the site for gas exchange. Besides, macrophages (large cells) present in the pulmonary region which help in particle removal. The characteristics (particle size, mass and forms) of inhaled solid particles, their solubility in lung fluids and extent to which they can be removed by various clearing mechanisms together determine the depth to which

they can be transported in the human respiratory system (31). The human health risk associated with human exposure to airborne pollutants depends on the type and concentration of the pollutants, duration of exposure, dose, inhalation rate and age of the individual concerned (27). Clearing of deposited solid particles from the respiratory tract is an integral part of natural human body's immune system. However, clearing of dissolved particles is by dissolution

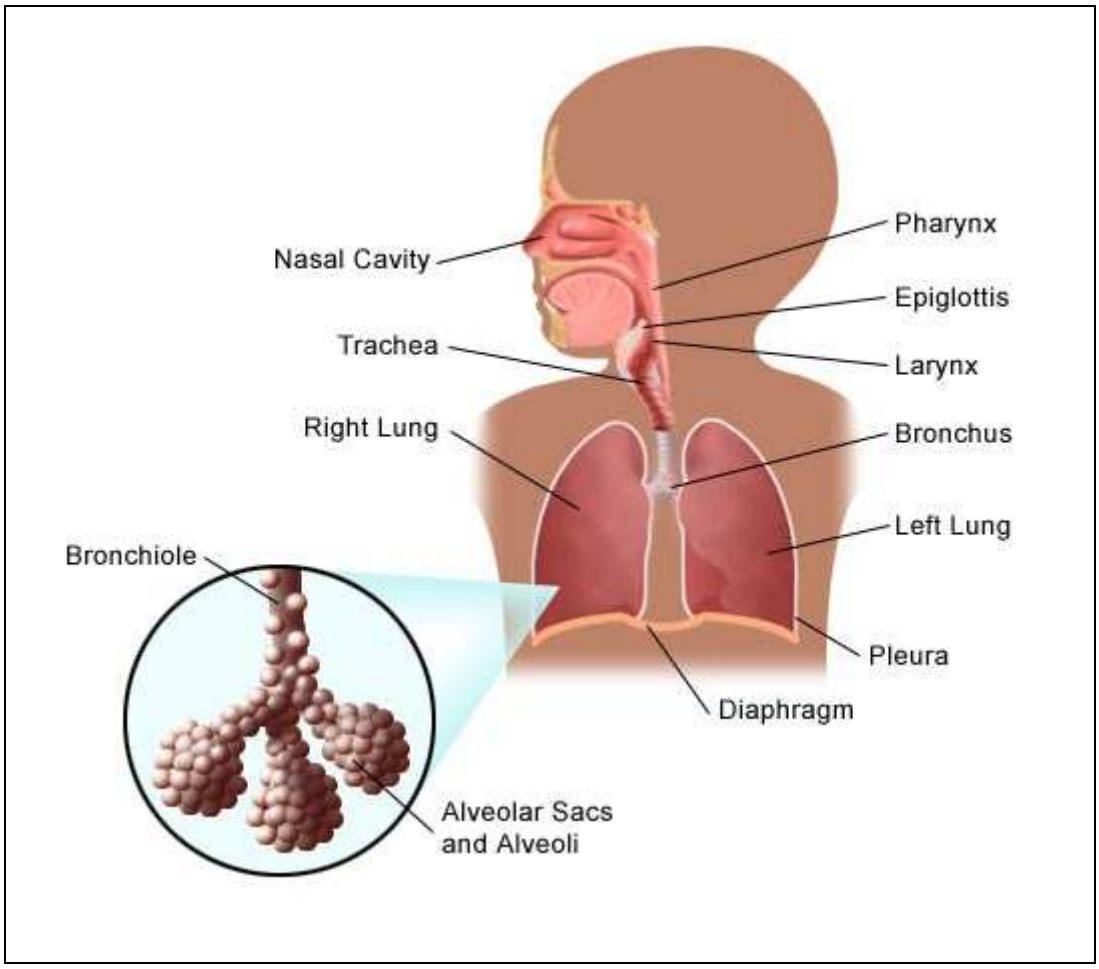

Figure 2.3 Anatomy of the human respiratory tract, child (24).

in the lung fluids, but since not all dissolved materials could possibly be removed, some are relatively and effectively absorbed through the thin epithelium contained in

the alveolar and are then transported to the blood stream through the capillaries (32).

Inhalation is a significant exposure route that needs to be considered in human health risk assessment considering the fact that people breathe continuously in homes, offices, playgrounds, recreation centres, construction sites, mining sites, exploration areas and virtually everywhere that life exists. Although quality air is a key requirement for the proper functioning of the human respiratory system but unfortunately, the air that we breathe are associated with environmental contaminants such as PTEs resulting from natural and anthropogenic activities. Human activities that pollute the air have been on the increase due to industrialization and man's consistent quest to improve the quality of life particularly in the developing countries where there is no regulated air monitoring. Despite decrease in environmental exposure to PTEs due to technological advancement and the elimination of processes and materials that pollute the air by authorised agencies particularly in the developed world, these contaminants are still present in environmental matrices and are still been carried from point sources to another by means of long-range atmospheric transport. Thus, the air we breathe might not be as clean as we assume, thereby exposing the body to potential risk (particularly children). Inhalation rates in children differ from that of adults because children have higher oxygen consumption rates (i.e. in terms of daily volume intake because they go through an intense anabolic process) compared with adults (33). Moreover, since they are still in the growing stage, their lungs have a larger surface area per unit of body weight than adults, hence a child breathes in about twice the quantity of air that an adult breathes in order to ensure proper cooling of the lung (34-35).

Studies have shown that urban street dust contributes significantly to urban environmental PTEs pollution (36- 39). Other studies on urban street dust that investigated the levels of PTEs in different particle size fractions revealed that PTE concentrations increase as the particle size decreases (40-41). With respect to human health risk from inhalation of urban dust and air particulate matter from the various emission sources, the fine particles (PM_{10}) represents a potential threat to the human population particularly the urban inhabitants (42). This is because; these mobile fine particles can be easily resuspended by human feet, traffic and wind erosion making their inhalation easier (43). Studies on PTEs in airborne particulate matter have shown that there is a strong correlation between inhaled particles (< 10 μm) and adverse health effects (44-46). The World Health Organisation (WHO) has revealed that 4 – 8 % of people that die annually are linked to air pollution (47). Moreover, it has been noted (48) that a greater percentage of adverse health effects resulting from inhalation of polluted urban dust come from the soluble fraction particularly metal ions rather than the insoluble components of the materials. These respiratory health effects including respiratory infections, cardiovascular disease, lung cancer, asthma, neurological and psychological disorder, fever, lung fibrosis, damage to the central nervous system and chronic bronchitis are more pronounced in children than in adults (49). This is because they are more often in contact with soil than adults and so are more potentially exposed per kg of body weight, besides, their developing fragile respiratory pathway are incapable of detoxifying inhaled pollutants (43). This also explains why lower doses (per kg weight) and extended time intervals are normally recommended for most drugs for children (50).

2.2.3 Dermal absorption (skin)

In human health risk assessment, this exposure route has often been neglected

when compared to the oral and inhalation routes but this is an important exposure route in human health risk assessment because the human skin comes in contact with different types of substances made from all kinds of materials. Dermal exposure is more significant in the workplace where the skin is constantly exposed to various hazardous substances. In manual machining of car or other components for example, the human skin is at risk because this involves the use of a range of milling, drilling, grinding and lathe machinery. In a study (51) that investigated the dermal exposure of electroplating fluids and metal working fluids in the UK, it was observed that humans are dermally exposed to toxic chemicals because electroplating industries use many toxic chemicals at a very high temperature in dipping baths. These dipping baths are known to contain potentially toxic metals in solution, such as, chromic acid which contains Cr (VI), nickel chloride, nickel sulphate, copper sulphate, copper cyanide and zinc hydroxide. Dermal exposure occurs in this industry because items are loaded into and out of the baths manually. Though in workplaces, gloves and other protective wears are worn but an investigation (52) that studied 'gloves and dermal exposure to chemicals: proposals for evaluating workplace effectiveness', noted that the constant removal and replacement of gloves while at work could lead to dermal exposure. The study also revealed that wearing of gloves could reduce an individual's sensitivity to toxic chemicals because less care is taken once gloves are worn. It is also important to mention that breaks, wounds or any opening in the skin (particularly the hands) due to physical and chemical damage could provide a direct access for toxic substances to human tissues and blood stream. This is potentially more prevalent in different occupational settings. A review (53) of field studies on absorption of chemicals through compromised skin reported high-risk exposure in various occupational scenarios including health care,

metal machining, food preparation, offset printing, hairdressing and cleaning. Metal objects that come into repetitive contact with the broken skin can release metallic ions that might gain access into the body and cause allergy. Research (54) that investigated the *in vitro* absorption of metal powder through intact and damaged human skin found that the concentrations of Cr and Ni were significantly higher in damaged skin than in intact skin.

Human environmental dermal exposure to toxic substances and metal-working fluids makes the skin come in contact and react to gases, liquids and solids which could cause a variety of adverse health effects including: skin sensitization, irritations, burns, degradation, cell dehydration, skin lesions, chapping, dryness, blisters, skin scars and hand eczema (55-56). Contact allergy is a global public health challenge (57). PTEs (Cu, Ni, and Zn) exposure is the most prevalent cause of contact allergy in the human population. Nickel-induced contact dermatitis is the most common allergy to man-made products. Nickel comes in contact with humans during production, use, recycling, or disposal and it is used in the making of products such as coins, keys, spectacle frames, suspenders, handles, tools, watches, buttons, ear piercing earring and other jewelleries which are in daily use. The constant use of these products releases Ni onto the human skin either through friction or corrosion of this metal that is in contact with human sweat (58). Investigations have revealed that Ni release from coins is the main cause of contact allergy (59-63). Although this exposure route is more significant in the occupational scenario, PTEs could as well enter the human body via environmental matrices. Children are dermally exposed during sporting and other outdoor activities because they come in contact with soil and dust particularly when playing on fields not fully covered with grass. Also Adults who work as diggers when laying pipes for water, gas, electricity and other related

activities are at risk of dermal exposure. In addition, in countries where agricultural practices are not mechanised, farmers are also dermally exposed to PTEs.

2.3 Protocols for assessing human health risk from PTEs

In vivo and *in vitro* experiments are useful when assessing human health risk from environmental matrices. While *in vivo* involves the use of animal models in risk assessment, the latter mimics the human body system (exposure routes) through the use of laboratory reagents. However, due to ethical issues, humans cannot be used for the purpose of research, also the use of animal models as surrogates for humans is also being phasing out because of ethical considerations, high cost, time consuming, low yield, labour-intensive experimental protocols (64), moreover, results obtained from such investigations cannot be used to represent the real human body system because of the differences in physiology (65-67). On the other hand, *in vitro* experiments have been designed to overcome these challenges and are more reproducible than *in vivo* studies. *In vitro* experiments focus on the bioaccessibility measurement. It has been noted that accurate *in vitro* (bioaccessibility) results have the potential to make a significant impact on risk assessment practice, more so, since bioaccessibility is one of the potential factors limiting the bioavailable fraction (the fraction of the contaminant that reaches the systemic circulation); bioaccessibility is a useful tool to measure for risk assessment purposes (68). Apart from assessing health risks via *in vitro* experiments, in the pharmaceutical industry, *in vitro* studies have proved to be better than *in vivo* studies in assessing product bioequivalence (BE) of immediate release (IR) of solid oral dosage forms (69). Two *in vitro* protocols used to assess human health risk from exposure to PTEs are discussed below.

2.3.1 The use of oral bioaccessibility

In order to accurately estimate the human health risk from exposure to soil and dust, it is important to study ingestion by investigating the oral bioaccessibility of PTEs using a standard protocol (e.g. the physiologically based extraction test (PBET)). In this research the Unified Barge Method (UBM), has been used (70). This protocol has been developed to simulate the dissolution and subsequent absorption of PTEs in the human gastrointestinal tract when soil or dust is ingested. The physiological based extraction test (PBET) has been used in a number of studies to evaluate the oral bioaccessibility of PTEs in urban dust (71-72), contaminated urban soil (73-74) and uncontaminated soils such as urban playground, recreation parks, roadsides, open spaces and picnic areas (75-78). The oral bioaccessibility is the fraction of the PTEs that are soluble or released from the soil or dust in the human gastrointestinal tract by digestive juices and are available for intestinal absorption (64). This bioaccessible fraction represents the amount of PTE that is potentially available to be transported across the intestinal walls and transferred to the blood. Hence, bioaccessibility is a useful tool in assessing human health risk from soil and dust ingestion.

Figure 2.2 shows the medical physiology of the gastrointestinal tract which oral bioaccessibility tends to mimic, with, the physiological based extraction test (PBET) simulating the stomach and intestines. Even though the mouth plays a key role of chewing ingested materials with saliva. However, the short time lag that these materials stay in the mouth means that it is not considered in the PBET protocol, moreover, no absorption of nutrients occurs from the mouth (79).

2.3.2 The use inhalation bioaccessibility

Lung bioaccessibility has been defined as the fraction of PTEs that are soluble in a simulated lung fluid environment and are available for absorption into the bloodstream, thus by implication the inhalation bioaccessible fraction represents an estimated amount of PTE potentially available (bioavailable fraction) for absorption into the blood stream (80). It has been suggested that for a more holistic human health risk assessment, in addition to oral bioaccessibility, the inhalation bioaccessible fraction needs to be fully exploited (81-82). However, despite the importance of bioaccessibility in human health risk assessment via the inhalation route, regulatory agencies in Europe and UK have not accepted or recognised any protocol for assessing the health risk from PTEs. It is in the light of this challenge that this research work has developed a simulated epithelium lung fluid which was used to assess the bioaccessibility of PTE (Pb) in inhaled dust particles (<10 μm). This robust protocol has been carefully formulated to truly represent the human epithelial lining fluids. Figure 2.3 shows the medical physiology of the human respiratory system. Previous studies on lung bioaccessibility have used either Gamble's solution or modified Gamble's solution to evaluate the bioaccessibility of PTEs (83-84). However, it was observed that there were discrepancies in terms of chemical compositions and experimental conditions. As at the time of this research, there is no study in the literature that has investigated lung bioaccessibility of any PTE in urban street dust.

2.4 Aims and objectives of the research.

An outline of the research is shown in Figure 2.4 which focused on soils from 12 primary schools, 90 urban street/road dusts from six urban cities and urban airborne

particulate (PM_{10}) sampled over a period of one year.

The study was designed to achieve the following aims:

- To determine the total concentration of PTEs (aqua regia) in soil collected from school playground and use oral bioaccessibility (UBM protocol) to assess their bioaccessible fraction (chapter 3).
- To determine the total concentration of PTEs (aqua regia) in urban/street dusts and evaluate their oral bioaccessibility (UBM protocol) (chapter 4).
- To develop a robust *in vitro* method that would be used to evaluate the lung bioaccessibility of PTEs in urban dust. (chapter 5)
- To apply the developed simulated epithelial lung fluid (SELF) to assess the bioaccessible Pb in urban dust (<10 µm) (chapter 6).
- To evaluate inhalable PTEs in PM_{10} through the use of XRF (chapter 6).

2.5 Conclusion

Despite concerted efforts by both government and non-governmental agencies to control contaminants emission and distribution, PTEs still abounds in the environment and their ever presence and interactions with humans in the environment implies that their entrance into the human body is inevitable. Thus, PTEs could enter the human body via oral ingestion, inhalation as well as dermal absorption of environmental matrices.

In order to accurately assess human health risk from PTEs, it is paramount to consider the bioaccessible fraction of these PTEs not just their total elemental concentrations in different environmental matrices. This is achieved through the use of *in vitro* experiments (bioaccessibility protocols). Oral bioaccesibility tends to mimic

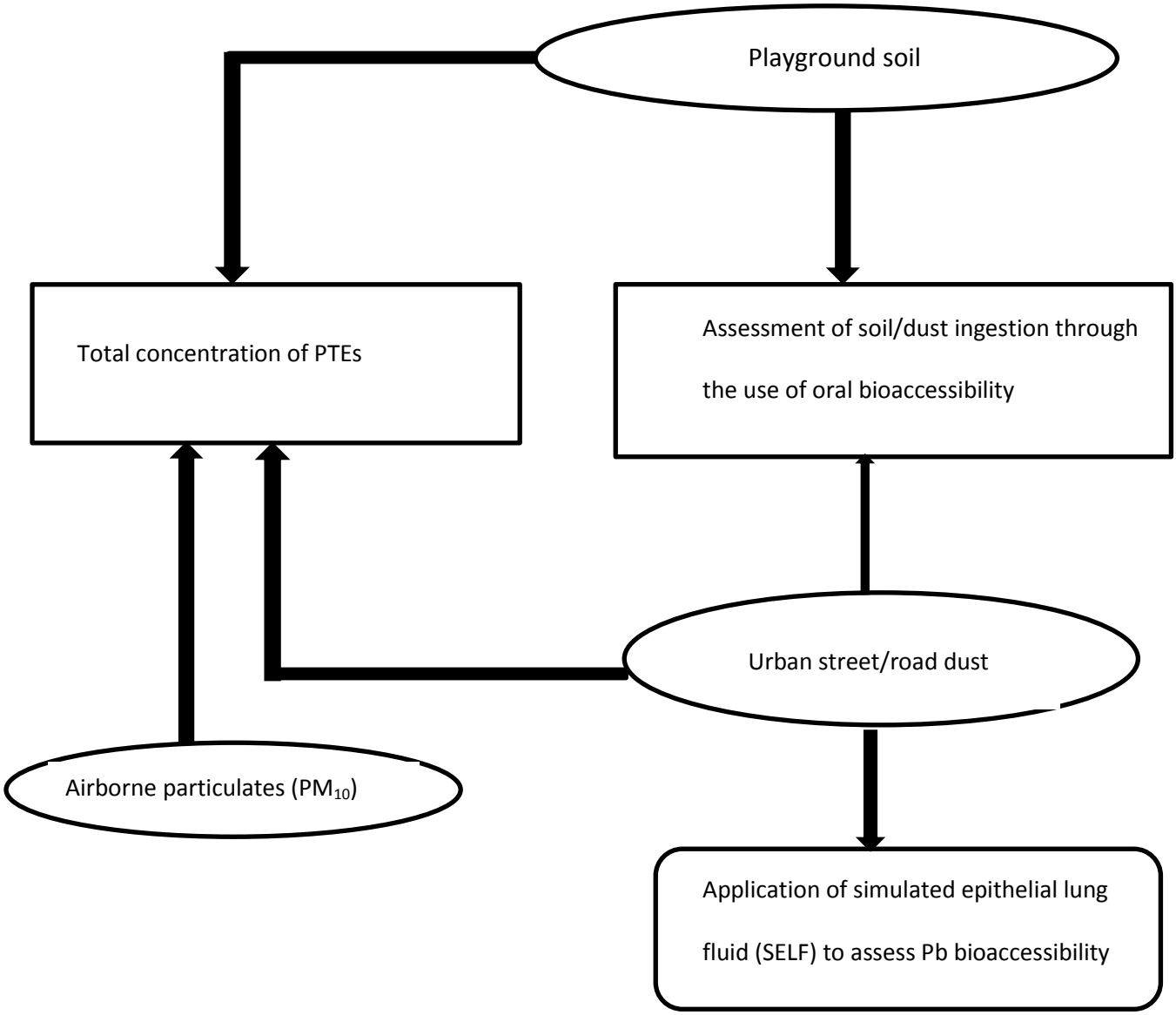

Figure 2.4: Overview of the research.

the human digestive system, thus, it is a useful tool when estimating the human health risk from ingestion of soil and dust while health risk from inhalation of these environmental matrices could be assessed via the use of simulated epithelial lung fluid.

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Section A: Human health risk assessment via oral bioaccessibility

Chapter three: Oral bioaccessibility of PTEs in playground soils: Potential risk to children's health.

3.1 Introduction

Soil provides an important link between humans and the various components that make up the environment; however, soil also acts as a sink to various PTEs released from various sources. These PTEs are known to be site-specific (1-2). Of concern in this work is the potential impact on children as a result of exposure to soil during the course of recreational activity within the School playground.

The dominant health risk to children is via intentional and unintentional ingestion of soil as a primary result of hand-to-mouth contact. Intentional ingestion may occur due to the pica tendencies of the child; however, unintentional ingestion is more likely to be due to the physical disturbance of the soil by the child resulting in increased contact. The potential increase in health risk is associated with a lack of hand washing and the consequent removal of surface contamination, as well as debris, from beneath finger nails. An important aspect in the retention of surface contamination is the soil particle size and its potential for adherence to hands and subsequent unintentional ingestion. Various studies have investigated soil particle adherence to children's hands and concluded that finer soil particles (definitely < 2 mm and most likely < 63 μm) adhere more readily (3-4).

In addition, as well as the soil particle size consideration must be given to the 'typical' amount of soil that a child may ingest based on pica tendencies or unintentionally. Various studies have investigated soil ingestion by children. For example, soil ingestion by young children has been investigated (5) by measuring the titanium, aluminium and acid-soluble residue in soil and faeces in different

environmental situations. They concluded, based on their study groups, that in the day-centre care group the ingestion rate was from 0 to 90 mg/day whereas for the camping group, the rate was between 30 and 200 mg/day. Similarly, an estimated mean soil ingestion rates, for up to an 8 day period, gave a mean intake of 208 mg/day or less for 95% of the children studied (n = 64) (6). Using soil tracer studies, based on aluminium, silicon and titanium soil ingestion rates, the estimated daily soil ingestion rates were 181, 184 and 1,834 mg/day based on Al, Si and Ti, respectively for children aged between 1-3 years (n = 59) (7). A similar soil tracer study using the same elements for children in the age group 2 to 7 years (n = 104) estimated the average daily soil ingestion rates as 39, 82 and 246 mg/day for Al, Si and Ti, respectively (8). Subsequently, it has been concluded (9) that a child (aged between 1 to < 6 years as well as between 6 and < 21 years) may ingest 50 mg/day soil (including outdoor settled dust) or up to 1,000 mg/day if the child had pica tendencies.

In the UK, the non-statutory Contaminated Land Exposure Assessment (CLEA) Model (10), which is a scientifically based framework, is used to assess human health risks from a range of sites, including residential, allotments and industrial. The model allows determined PTE exposure concentrations to be compared with toxicological or Health Criteria Values (HCVs), to obtain Soil Guideline Values (SGVs) and these SGVs depend exclusively on the site and contaminants (11). SGVs are used to assess human health risks from PTE contamination in soils. These values are assigned as intervention values and PTE exposure concentrations above these values represent a significant human health risk (12). The CLEA model used to derive SGVs assumes that a PTE is released from soil and is taken up by humans in the same proportion (just as the model which was used to establish the

HCVs) (12). In using SGVs to assess the human health risk from soils implies that all the PTEs that entered the human body via oral ingestion/inhalation are bioavailable. However, this could be seen as an over estimation because these PTEs occur in different geochemical (mineralogical) forms and are bound to soil components while others occur naturally in insoluble forms. Thus, the bioavailability of PTEs to humans may be <100%. The most appropriate approach in establishing a health risk assessment would be to use humans (or anatomically related animals). However, it is unethical to use humans in this type of study and also undesirable to use animals; the National Centre for the Replacement, Refinement and Reductions of Animals in Research (NC3Rs) seeks to reduce the use of animals in experimentation by applying alternative non-animal approaches.

One such alternative approach to estimate the human health risk from exposure to soils via oral ingestion i.e. the oral bioaccessibility of PTEs uses *in vitro* gastro-intestinal extraction. In this work, the Unified Bioaccessibility Method (UBM) has been used (13-14). The oral bioaccessibility is the fraction of the PTEs that are soluble or released from the soil in the human gastrointestinal tract by digestive juices and hence are available for intestinal absorption (15). This protocol has been developed to simulate the dissolution and subsequent absorption of PTEs in the human gastrointestinal tract when soil is ingested. A range of *in vitro* gastro-intestinal extraction protocols have been used in a number of studies to evaluate the oral bioaccessibility of PTEs in contaminated urban soil (16-17) and uncontaminated soils such as urban playground, recreation parks, roadsides, open spaces and picnic areas (18-21).

This study proposes to investigate the risk to children from soils found in the playground of primary and middle schools in the north east region of England,

covering the age range 4-13 years; in this region first schools operate for children in the age range 4-9 years, primary schools from 4-11 years, and middle schools from 9-13 years. The study will focus on eight PTEs, As, Cd, Cr, Cu, Pb, Mn, Ni and Zn. Total PTEs levels will be investigated across 12 schools and compared to data from playgrounds (and recreational parks) across the world. The PTEs soil levels will be assessed using the estimated maximum tolerable daily oral intake based on a soil ingestion rate of 50 mg/day. Finally, the potential health risk will be assessed using oral bioaccessibility to estimate the maximum absorption possible if the soil was ingested and its implications to children.

3.2 Experimental

3.2.1 Sample collection and preparation

Twenty nine soil samples were collected from the playing fields of twelve primary and middle schools in N.E. England (Figure 3.1). In order to collect the samples, the covering grass was carefully removed with the aid of a shovel, and soil samples collected by digging a square hole measuring approximately 15 cm^2. Samples were collected at a depth of 5 -10 cm. The samples were placed inside labelled bags and sealed. The samples were then oven dried at a temperature of 35 °C for two days, and then gently disaggregated before sieving. The soil samples were sieved using a < 125 μm nylon sieve to remove extraneous matter such as small pieces of brick, stones, and other debris. Finally, the < 125 μm soil samples were stored in plastic containers prior to analysis.

3.2.2 Instrument and reagents

All chemicals used were certified analytical grade. Concentrated hydrochloric acid

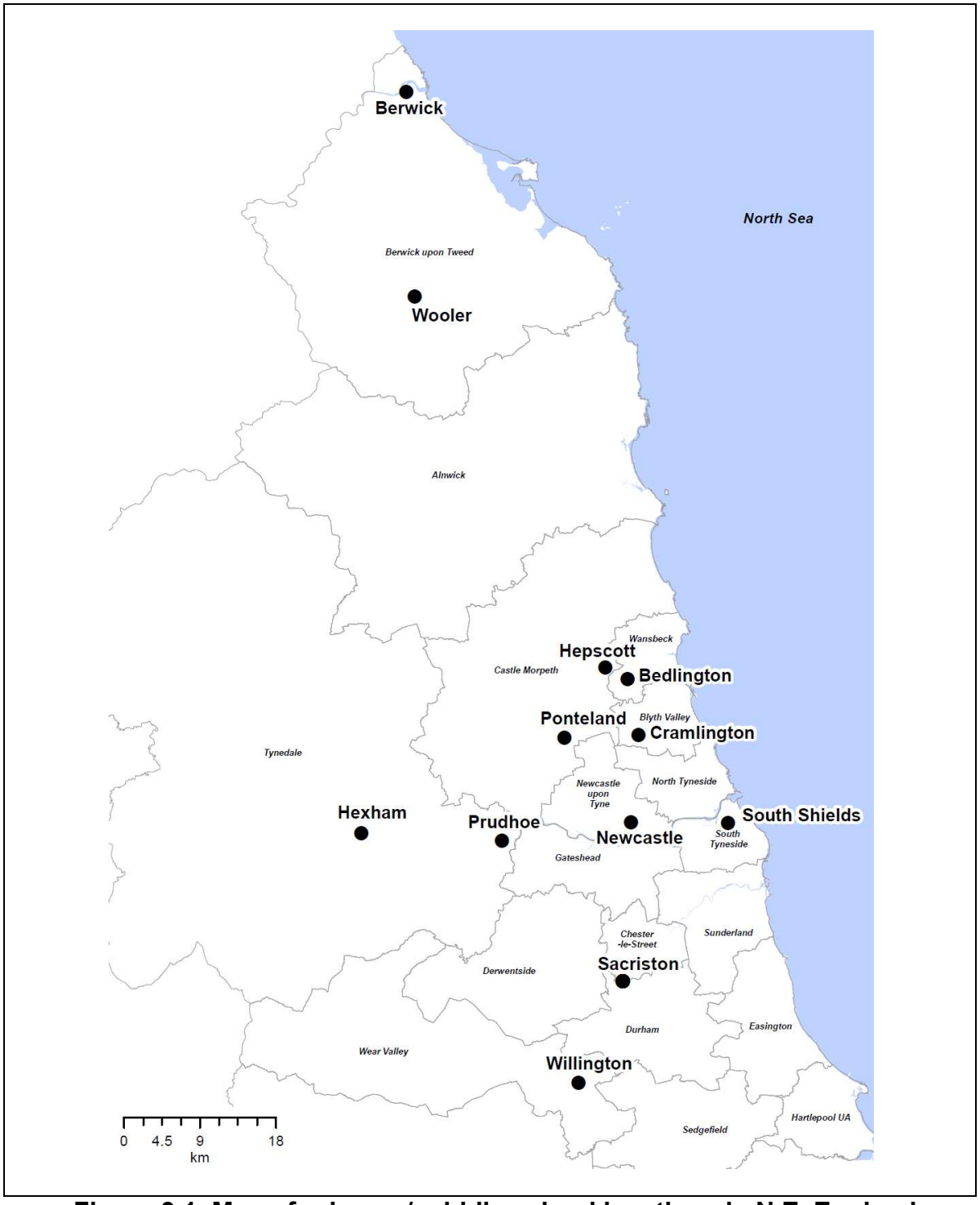

Figure 3.1. Map of primary / middle school locations in N.E. England

Legend: Bedlington Primary School, Bedlington, Northumberland; Longridge Towers School, Berwick upon Tweed, Northumberland; Cramlington Learning Village, Cramlington, Northumberland; Hepscott County Primary School, Hepscott, Northumberland; Sele First School, Hexham, Northumberland; Central Newcastle High School, Newcastle upon Tyne; Ponteland First School, Ponteland, Northumberland; Adderlane County First School, Prudhoe, Northumberland; Fyndoune Community College, Findon Hill, Sacriston, Co. Durham; Mortimer Community College, South Shields, Tyne and Wear; Willington Primary School, Willington, Crook, Co. Durham; Glendale Community Middle School, Wooler, Northumberland.

(HCl) was supplied by Fisher Scientific Ltd. (Loughborough, UK). Sodium hydrogen phosphate (NaH_2PO_4) and potassium hydrogen phosphate (NaH_2PO_4), α-amalyse (bacillus species), lipase (pig) and bile salts (bovine) were obtained from from Sigma-Aldrich Co. (Gillingham, UK). Sodium chloride (NaCl), potassium thiocyanate (KSCN), anhydrous sodium sulphate (Na_2SO_4), potassium chloride (KCl), calcium chloride ($CaCl_2.2H_2O$), ammonium chloride (NH_4Cl), sodium bicarbonate ($NaHCO_3$), magnesium chloride ($MgCl_2.6H_2O$), sodium hydroxide (NaOH), hydrochloric acid (HCl), 30% hydrogen peroxide, urea, uric acid, anhydrous D+ glucose, D-Glucosamine hydrochloride, pepsin (pig), bovine serum albumin (BSA), pancreatin (pig) and concentrated nitric acid (69% HNO_3) were all obtained from Merck (Poole, UK). Mucin (pig) was obtained from Carl Roth GmbH (Karlsruhe, Germany) while D-glucuronic acid was obtained from Fluka Chemicals Ltd. (Gillingham, UK)). A multi-element standard for As, Cd, Cr, Cu, Pb, Mn, Ni and Zn and internal standard solution containing Indium (In), scandium (Sc) and terbium (Tb) were obtained from SPEXCerPrep (Middlesex, UK). Ultra-pure water of conductivity 18.2MΩ-cm was produced by a direct Q^{TM} Millipore system (Molsheim, France). Two certified reference materials (BCR 143R, sewage sludge amended soil, and SRM 2711, Montana soil) were purchased from LGC-Promochem (Teddington, UK) while a guidance material (BGS 102) was obtained from British Geological Survey (Keyworth, UK). Sample digestions were carried out using a start D multiprep 42 high throughput rotor microwave system (Milestone Microwave Laboratory Systems) supplied by Analityx Ltd. (Peterlee, UK) while sample measurement was carried out using an ICP-MS X series II (Thermo Electron Corporation, Cheshire, UK).

3.2.3 Preparation of reagents for *in vitro* extraction test

The *in vitro* extraction test employed in this work is based on the Unified

Unified Bioaccessibility Method (UBM) (13).

To prepare the simulated saliva fluid, 145 mg of amylase, 50.0 mg mucin and 15.0 mg uric acid was added into a 2L HDPE screw top bottle. Also, 896 mg of KCl, 888 mg NaH_2PO_4, 200mg KSCN, 570 mg Na_2SO_4, 298 mg NaCl and 1.80 mL of 1.0 M HCl was added into a 500 mL volume plastic container and made to the mark with water (inorganic saliva component). To prepare the organic saliva component, 200 mg of urea was added to 500 mL container and made up to the mark with water. Both container (inorganic and organic phases) were simultaneously poured into the 2 L HDPE screw top container; the solution (simulated saliva fluid) was thoroughly mixed to a homogenous state. The pH of the simulated saliva fluid was measured and it was at 6.5 ± 0.5.

In preparing the simulated gastric fluid, 1000 mg of bovine serum albumin, 3000 mg mucin and 1000 mg pepsin was added into a 2 L HDPE screw top bottle. Then, 824 mg of KCl, 266 mg $Na_2H_2PO_4$, 400 mg $CaCl_2$, 306 mg NH_4Cl, 2752 mg NaCl and 8.30 mL of 37% HCl were added into a 500 mL volume container and made up to the mark with water (inorganic gastric component). To prepare the organic gastric component; 650 mg glucose, 20.0 mg glucuronic acid, 85.0 mg urea and 330 mg glucosamine hydrochloride was added into a 500 mL volume container and made up to the mark with water. The inorganic and organic components were simultaneously poured into the 2 L HDPE screw top bottle and the resulting simulated gastric fluid was thoroughly mixed. The pH was measured and found to be within the range of 0.9 – 1.0, also the final pH of mixed saliva (1 mL) and gastric phase (1.5 mL) was checked and found to be within specification 1.2 – 1.4.

Simulated duodenal fluid was prepared by first adding 200 mg of $CaCl_2$, 100 mg bovine serum albumin, 300 mg pancreatin and 500 mg lipase to a 2 L HDPE screw top container. To prepare the inorganic duodenal components, 564 mg of KCl, 80 mg KH_2PO_4, 50.0 mg $MgCl_2$, 5607 mg $NaHCO_3$, 7012 mg NaCl and 180 µL of 37% HCl was added into a 500 mL volume container and made up to the mark with water. The organic duodenal component was prepared by adding 100 mg urea to 500 mL volume container and made to the mark with water. Both the inorganic and organic duodenal components were simultaneously poured into the 2 L HDPE screw top bottle, and the simulated duodenal fluid was thoroughly mixed. The pH was measured and found to be at 7.4 ± 0.2.

To prepare the simulated bile fluid, 222 mg of $CaCl_2$, 1800 mg bovine serum albumin and 600 mg bile were added to a 2 L HDPE screw top bottle. The inorganic bile components was prepared by adding 376 mg of KCl, 5785 mg $NaHCO_3$, 5259 mg NaCl and 180 µL of 37% HCl to a 500 mL volume container and made up to the mark with water. Also the organic bile components was prepared by adding 250 mg urea to 500 mL volume container and made up to the mark with water. These two separate bile components (inorganic and organic) were poured to the 2 L HDPE screw top bottle and thoroughly mixed. The resulting simulated bile fluid was allowed to stand for one hour at room temperature to ensure complete dissolution of all reagents. The pH was measured and found to be at 8.0 ± 0.2. The final pH of the mixed saliva (1.0 mL), gastric (1.5 mL), duodenal (3.0 mL) and bile (1.0 mL) fluid was measured and found to be at 6.3 ± 0.5.

3.2.4 Sample preparation using Unified Bioaccessibility method (UBM)

‘Gastric’ Extraction

0.6 g of the soil samples, two certified reference materials (BCR 143 and SRM 2711) and a guidance material (BGS 102) were accurately weighed in triplicate and placed into a 50 mL screw cap sarstedt tube, 9 mL of simulated saliva fluid was carefully added and the resulting mixture was manually shaken. After 5 – 15 mins, 13.5 mL of simulated gastric was added. The extraction vessels were placed in an end-over-end shaker maintained at a temperature of 37 ± 2 ^{0}C for 1 h. At the end of 1 h, the pH of each of the soil suspension was measured and were all found to be at the range of 1.2 – 1.7. The solutions were collected and centrifuged at 3000 rpm for 5 mins. 1.0 mL of the supernatant was pipetted into a labelled centrifuge tube and 9.0 mL of 0.1 M HNO_3 was added. The prepared extract was kept at < 4 ^{0}C prior to the measurement of the bioaccessible PTE content using ICP-MS.

'Gastric + Intestinal' Extraction

0.6 g of the soil samples, two certified reference materials (BCR 143 and SRM 2711) and a guidance material (BGS 102) were accurately weighed in triplicate and placed into a 50 mL screw cap sarstedt, 9 mL of simulated saliva fluid was carefully added and the resulting mixture was manually shaken. After 5 – 15 mins, 13.5 mL of simulated gastric was added. The extraction vessels were placed in an end-over-end shaker maintained at a temperature of 37 ± 2 ^{0}C for 1 h. At the end of 1 h, the pH of each of the soil suspension was measured and were all found to be at the range of 1.2 – 1.7. Having achieved the required pH at this stage, 27.0 mL of simulated duodenal fluid and 9.0 mL of simulated bile fluid were added to the mixture in the Sarstedt tube, capped and manually shaken to ensure mixing of the components.

The pH of the resultant suspensions was adjusted to 6.3 ± 0.5 with the drop wise addition of 37% HCl, 1 M or 10 M NaOH as required. The extraction tubes were

placed in an end-over-end shaker maintained at 37 ^{0}C ± 2 and allowed to shake for 4 h. Then the soil suspensions were removed from the shaker, pH measured and were found to be at 6.3 ± 0.5. These were centrifuged at 300 rpm for 5 mins, 1.0 mL of the supernatant was pipetted into a labelled centrifuge tube and 9.0 mL of 0.1 M HNO_3 was added. The prepared extract was kept in the fridge (at < 4 ^{0}C) prior to analysis using ICP-MS.

3.2.5 Microwave digestion protocol

0.5 g of the each sample and the certified reference / guidance materials were accurately weighed into a 65 ml PFA (a perfluoralkoxy resin) microwave vessel pre-cleaned with concentrated acid. An acid mixture (aqua regia) of 13 ml (HCl: HNO_3, 3: 1 v/v) was carefully added into the PFA vessels and sealed with a TFM cover. The solution was gently swirled to homogenize the sample with the reagents; the vessels were then introduced into the safety shield of the rotor body and then placed in the polypropylene rotor of the microwave oven. All the vessels containing samples were properly arranged prior to starting the microwave digestion process. The microwave oven was operated at a temperature of 160^{0}C, power of 750 watts, extraction time of 40 mins and a ventilation (cooling time) of 30 mins. After cooling, the digested samples were filtered using a whatman filter paper (grade 41, pore size 20 µm) into 50 ml volumetric flask. The filtrate was diluted to the mark with ultrapure water of resistivity 18.2 MΩ-cm at 25^{0}C. It was then transferred into a 50 ml Sarstedt tube and stored in the refrigerator (< 4 ^{0}C) prior to PTE content determination using ICP-MS.

3.2.6 Inductively coupled plasma mass spectrometry (ICP-MS) protocol / Quality control

Samples to be analysed by ICP-MS were prepared in triplicate by measuring 1 ml of either the filtrate, certified reference material / guidance material (CRMs) or blank into a 10 ml Sarstedt tube; this was followed by addition of 30 µl of mixed internal standard (In, Sc and Tb) and 9 ml of water (1% HNO_3). The use of the CRM / guidance material was to assess the precision and accuracy of the methodology whilst reagent blanks were included to check contamination. Eight calibration standards over the range 0-400 ppb were prepared from a 100 ppm multi-element standard with mixed internal standard; this was used to calibrate the instrument and also to construct the calibration curves. The instrument was tuned to verify mass resolution and maximise sensitivity. This was done in both standard mode and Collision Cell Technology (CCT) mode. On that basis ^{75}As, ^{52}Cr, ^{63}Cu, ^{55}Mn, ^{60}Ni and ^{66}Zn were determined using CCT mode whereas ^{111}Cd and ^{208}Pb were determined using standard mode. During sample analysis, calibration standards were determined after every tenth sample to check for instrument consistency. Calibration curves for PTEs based on a concentration range of 0-400 ppb with 8 calibration data points were done on ICP-MS and the regression coefficient (R^2) obtained for both modes was 0.999 (linear graph). The detection limit are as follows: As (0.1 µg/L), Cd (0.1 µg/L), Cr (0.3 µg/L), Cu (0.2 µg/L), Pb (0.1 µg/L), Mn (0.2µg/L), Ni (0.2 µg/L) and Zn (4 µg/L). Table 3.1 gives the operating conditions of ICP-MS.

3.3 Results and discussion

3.3.1 Total PTE content in playground soils

The total PTE concentration determined in the CRMs showed excellent agreement for all the elements in terms of accuracy and precision (Table 3.2). The % accuracy ranged from 90 to 100.

Table 3.1: Operating conditions of ICP-MS

ICP-MS parameters	Standard Mode	CCT Mode
Nebulizer gas flow (L/min)	0.83	0.83
Forward Power (W)	1400	1400
Cool gas flow (L/min)	13.0	13.0
Dwell time per isotope (ms)	10	10
Collision cell gas (L/min)	NA	4.75 (7%H_2/93%He)
Quadrupole bias (V)	-1.0	-14.0
Hexapole bias (V)	0.0	-16.0
Internal standards	^{45}Sc, ^{115}In and ^{159}Tb	^{45}Sc, ^{115}In and ^{159}Tb
Isotopes monitored	^{111}Cd, ^{208}Pb,	^{52}Cr, Mn^{55}, Ni^{55}, ^{63}Cu, ^{66}Zn, ^{75}AS.

NA = not applicable; CCT = collision cell technology

Cadmium was not detected in the playground soils. A box plot (Figure 3.2) showing median, mean, box boundary (25th and 75th percentile) and whiskers (10th and 95th percentile) has been used to show the mean concentration distribution of As, Cr, Cu, Pb, Mn, Ni and Pb, whilst their mean values as well as results from other studies are shown in Table 3.3. The concentration of As in the playground soil ranged from 7.3 to 22.8 mg/kg. The mean concentration of Cr across the playground soil ranged from 41.9 mg/kg to 93.4 mg/kg. Copper was found to vary from 10.3 to 600 mg/kg. The concentration of Pb in playground soil samples, in this study, varied considerably (Table 3.3). The Pb concentration varied over the range 56.2 to 1270 mg/kg with notably high concentrations recorded at Hexham (1270 mg/kg): location 5, as well as Berwick upon Tweed (684 mg/kg): location 2, and Newcastle upon Tyne (671

mg/kg): location 6. Manganese concentrations varied from 278 to 1084 mg/kg, the concentrations of Ni in playground soil ranged from 30.4 to 81.2 mg/kg and mean Zn concentration varied from 112 to 934 mg/kg. It can be seen from Table 3.3 that the result obtained from this study is similar to worldwide PTE levels found in the following range: As (5.1 – 11 mg/kg); Cr (3.01 – 188 mg/kg); Cu (7.4 -87 mg/kg); Pb (20 – 307 mg/kg); Mn (92 – 612 mg/kg); Ni (5.30 – 207 mg/kg) and Zn (46 – 225 mg/kg).

One way to assess the environmental health impact is to compare these PTEs levels with soil guideline values. Soil guideline values (SGVs) are scientifically based generic quality standards adopted in many countries to assess human health risks from soil contamination due to the presence of pollutants. With respect to these PTEs, the SGVs are in the form of concentration thresholds in soil of which exceedance may signify a potential risk to humans. In the UK, apart from SGVs, Generic Assessment Criteria (GAC) have been published and are used alongside SGVs. SGVs/GAC (residential soil-use) from different countries of the world including England (UK) have been presented (Table 3.4) for the purpose of comparison. It is observed that no international agreement is possible on the threshold concentrations for the PTEs above which the element could cause significant harm to humans. With respect to the mean concentrations of these elements (Table 3.3), It is observed that As (mean concentration = 14.1 ± 5.4 mg/kg) does not exceed the 32 mg/kg SGV (England) in any location. The lower threshold SGV in use in Canada (12 mg/kg) and Norway (8 mg/kg) would cause concern. The mean concentration of Cr obtained in this study is 62.2 ± 15.9 mg/kg. With respect to England and South Africa where GAC / SGVs were differentiated into Cr III and VI (Table 3.4), if the mean concentration represents Cr III, then it is lower than

Table 3.2: PTEs in certified reference / guidance materials: total, stage related bioaccessible and residual fractions.

Elements	Certified Reference / Guidance Material values, (n = 3)			Total (mg/kg)	*In-vitro* gastro-intestinal extraction (mg/kg)						
	SRM 2711 (mg/kg)	BCR 143R (mg/kg)	BGS 102 (mg/kg)		Stage I (Gastric digest)		Stage II (Gastric + Intestinal)		Stage III (Residual digest)	Total PTE content (stage II + III)	
				Mean ± SD; (n = 3)	Mean ± SD; (n = 3)	% BAF	Mean ± SD (n = 3)	% BAF	Mean ± SD; (n = 3)	Mean (n = 3)	% Total Recovery
Cr	N/A	-	-	42 ± 2	23 ± 0.2	54.8	16 ± 0.5	38.1	28 ± 0.1	44.0	105
	-	426 ± 12	-	422 ± 11	201 ± 9	47.6	150 ± 3	35.5	232 ± 9	382	89.7
Mn	638 ± 28	-	-	632 ± 10	388 ± 8	61.4	275 ± 12	43.5	350 ± 19	625	98.9
	-	856 ± 11	-	850 ± 7	251 ± 6	29.5	173 ± 5	20.4	559 ± 11	732	86.1
Ni	20.6 ± 1.1	-	-	19.7 ± 0.4	12.8 ± 0.1	65.0	8.1 ± 0.4	41.1	11.2 ± 1	19.3	98.0
	-	296 ± 4	-	292 ± 8	130 ± 2	44.5	101 ± 7	34.6	190 ± 1	291	99.6
Cu	114 ± 2	-	-	111 ± 1	63.2 ± 0.4	56.9	43.3 ± 0.7	39.0	62.9 ± 0.2	106	95.7
	-	N/A	-	13.8 ± 1	6.11 ± 0.4	44.3	3.81 ± 0.7	27.6	7.17 ± 0.8	11.0	79.6

Zn	350.4 ± 4.8	-	-	342 ± 6.1	218 ± 1.3	63.7	154 ± 0.6	45.0	181 ± 7.3	335	98.0
	-	1063 ± 16	-	1060 ± 20	507 ± 10	47.8	403 ± 13	38.0	563 ± 10	966	91.1
As	105 ± 1.8	-	-	98 ± 2.6	58.5 ± 0.7	55.7	46.8 ± 0.2	44.6	57.4 ± 2.3	104	99.0
	-	N/A	-	13.8 ± 1	6.11 ± 0.4	44.3	3.81 ± 0.7	27.6	7.17 ± 0.8	11.0	80
	-	-	5.4 ± 1.2#	N/A	4.1 ± 0.1	N/A	3.8 ± 0.8	N/A	N/A	N/A	N/A
Pb	1162 ± 31	-	-	1143 ± 24	604 ± 11	52.0	476 ± 14	41.0	680 ± 8	1156	99.5
	-	174 ± 5	-	171 ± 4	73.4 ± 5	42.9	50.2 ± 3	29.4	116 ± 6	166	97
	-	-	13 ± 6*	N/A	9 ± 3	N/A	6 ± 1	N/A	N/A	N/A	N/A

N/A = not applicable; * Certified for stage 1 (gastric digest) only; # Certified for stage 2 (gastric + intestinal digest) only

$$\% \text{ BAF} = \frac{C_{\text{Bioaccessibility}}}{C_{\text{total content}}} \times 100$$

Where $C_{\text{Bioaccessibility}}$ – PTE concentration (mg/kg) in the certified reference / guidance materials obtained via the application of physiological based extraction test and $C_{\text{total content}}$ - PTE total content (mg/kg) in certified reference/guidance materials obtained via microwave digestion protocol.

% Residual: residual fraction calculated as a fraction of the total content.

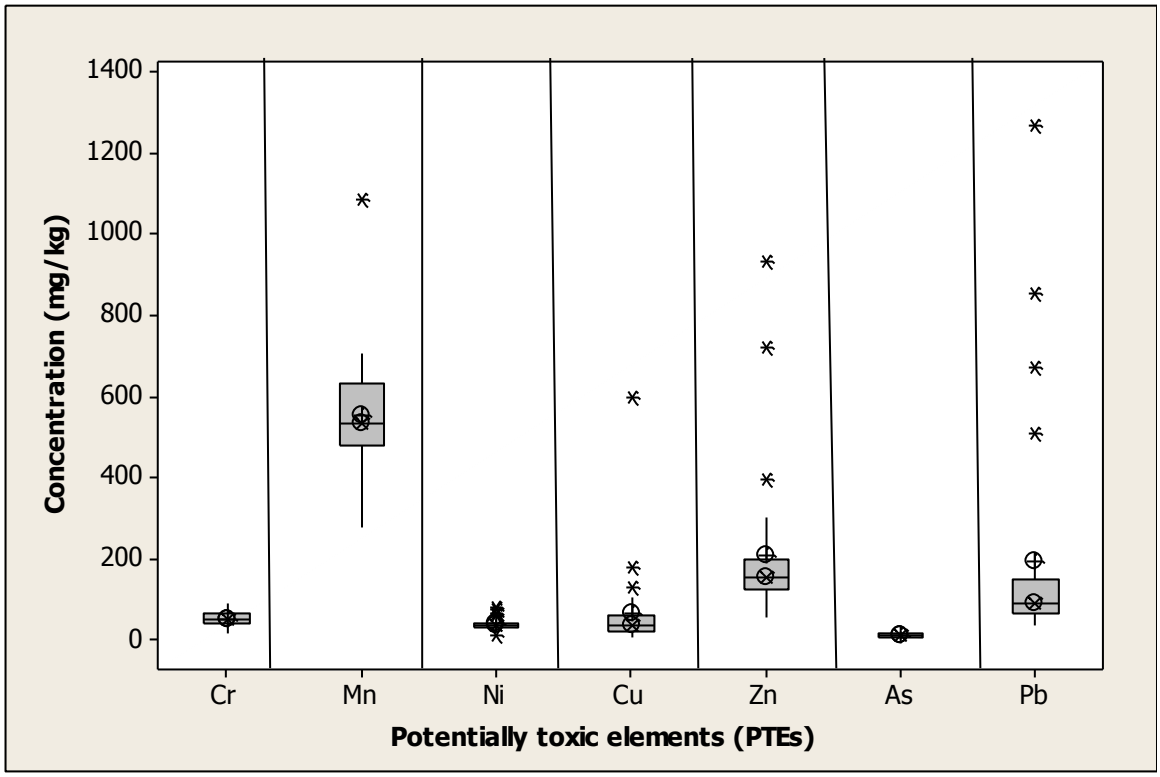

Figure 3.2: **Box plot for the total concentration of As, Cr, Ni, Cu, Pb, Mn and Zn in playground soil**

England's GAC value (3000 mg/ kg) and South African SGVs (96,000 mg/kg). If however, the concentration represents Cr VI, then it exceeds both England's GAC value (4.3 mg/kg) and South African's SGVs (13 mg/kg). The mean concentration of Cu (107 ± 104 mg/kg) obtained from the playground soils is lower than England's GAC value (2330 mg/kg) as well as SGVs from five countries but higher than Canadian SGV (63 mg/kg). Lead mean concentration (298 ± 380 mg/kg) resulting from this investigation is misleading due to the high Pb concentrations found in three locations (Berwick upon Tweed, Hexham and Newcastle upon Tyne). Lead concentrations for all other sample locations (Table 3.3) are well within the SGVs, except the values from Canada (140 mg/kg) and Norway (60 mg/kg). Table 3.4 shows that only Australia and South Africa have SGVs for Mn and the mean

Table 3.3: Mean concentration of PTEs from playground soil and recreation parks in several cities of the world (mg/kg) with the range values (minimum – maximum)

City (country) / Reference / No of samples / site	Cr	Mn	Ni	Cu	Zn	As	Pb
Bendlington (UK) / current study / 1 / playground soil	61.9 ± 0.8	480 ± 25	67.2 ± 1	31.1 ± 0.1	301 ± 8	10.2 ± 0.8	108 ± 0.1
Berwick upon Tweed (UK) / current study / 2 / playground soil	47.9 ± 18.7 (34.6 - 61.1)	447 ± 493 (400-493)	32.3 ± 3.5 (29.8-34.7)	33.5 ± 25.9 (15.2-51.8)	151 ± 60.8 (108-194)	7.26 ± 9.31 (5.21-9.31)	684 ± 243 (512-856)
Cramlington (UK) / current study / 1 / playground soil	52.4 ± 0.6	536 ± 33	42.3 ± 1	178 ± 5	215 ± 11	22.1 ± 0.2	213 ± 2
Hepscott (UK) / current study / 1 / playground soil	41.9 ± 2	511 ± 34	31.5 ± 0.4	17.9 ± 0.3	184 ± 12	12.4 ± 0.6	84.5 ± 0.1
Hexham (UK) / current study / 1 / playground soil	77.1 ± 1	1084 ± 60	63.5 ± 4	600 ± 12	934 ± 31	17.6 ± 0.3	1270 ± 5
Newcastle upon Tyne (UK) / current study / 1 / playground soil	93.4 ± 2	582 ± 31	81.2 ± 0.1	132 ± 5	721 ± 18	22.8 ± 1	671 ± 2

Ponteland (UK) / current study /1 / playground soil	76.4 ± 1	521 ± 20	76.9 ± 3	105 ± 4	398 ± 11	21.3 ± 0.4	169 ± 0.6
Prudhoe (UK) / current study / 1 / playground soil	55.8 ± 2	590 ± 33	30.4 ± 0.8	37.6 ± 8	155 ± 0.7	9.88 ± 0.1	61.7 ± 0.2
Sacriston (UK) / current study / 17 / playground soil	48.9 ± 18.4 (17.4-87.4)	540 ± 104 (286-684)	34.1 ± 9.3 (11.2-53.1)	38.0 ± 21.3 (9.11-78.1)	143 ± 38.7 (55.1-211)	13.8 ± 4.1 (4.89-19.2)	83.9 ± 36.8 36.4 – 185
South Shields (UK) / current study / 1 / playground soil	75.9 ± 1	278 ± 17	41.1 ± 0.2	31.4 ± 0.3	112 ± 1	10.4 ± 0.7	56.2 ± 0.1
Willington (UK) / current study / 1 / playground soil	67.6 ± 1	706 ± 40	37.3 ± 0.1	10.3 ± 0.1	178 ± 4	11.8 ± 1	74.6 ± 0.2
Wooler (UK) /current study / 1/ playground soil	47.4 ± 2	652 ± 45	43.9 ± 0.6	63.2 ± 0.2	191 ± 6	10.1 ± 0.1	95.6 ± 0.6
Mean values ± SD (n = 12)	**62.2 ± 15.9**	**577 ± 192**	**48.5 ± 18.5**	**107 ± 164**	**307 ± 260**	**14.1 ± 5.4**	**298 ± 380**
Other studies: Europe							
Glasgow (UK) / 22 / 14 / recreation park	29 ± 4.0 (24-34)	N/A	35 ± 9.0 (21-53)	85 ± 23 (24-113)	199 ± 81 (102-377)	N/A	307 ± 146 (98-676)
Glasgow (UK) / 22 / 14 / recreation park	45 ± 27 (21-131)	N/A	29 ± 10 (18-53)	62 ± 20 (24-113)	122 ± 65 (67-305)	N/A	194 ± 71 (114-414)

Various urban cities (UK) / 23 / 87 / playground soil	34.3 ± 21.6 (9.1 – 122)	502 ± 368 (98.3 – 2,100)	28.5 ± 21.9 (7.07 – 102)	42.5 ± 36.6 (8.27 – 181)	121.5 ± 89.9 (35.1 – 521)	11.0 ± 6.95 (1.75 – 32)	110 ± 80.9 (8.6 – 387)
Various rural areas (UK) / 23 / 366 / playground soil	34.41 ± 29.77 (1.14 – 236)	612 ± 938 (10 – 12,200)	21.1 ± 24.1 (1.16 ± 2.16)	20.64 ± 15.3 (2.27 – 96.7)	81.3 ± 576 (2.63 – 442)	10.9 ± 17.2 (0.5 – 143)	52.6 ± 66.8 (2.6 – 713)
Seville (Spain) /24 / 35 / playground soil	42.8 ± 8.8 (42.0-67.3)	480 ± 108 (335-893)	23.5 ± 4.1 (16.4-32.3	64.6 ± 74.8 (11.4-374)	107 ± 82 (25.8-450)	N/A	161 ± 184 (14.1-791)
Seville (Spain) /25 / 22 / playground soil	3.01 (0.18-4.85)	368 (222-765)	21.6 (12.1-46.7)	56.8 (14.1-198)	121 (38.8-288)	N/A	146 (23.4-702)
Murcia City (Spain) / 26 / 12 / playground soil	216 ± 2.2	N/A	13.5 ± 11	9.3 ± 1.0	26.9 ± 2.1	N/A	28.3 ± 2.2
Sevilla (Spain) /24 / 32 / playground soil	36 ± 7.0 (21-51)	N/A	29 ± 4.0 (21-37)	48 ± 10.9 (30-72)	107 ± 28.9 (73-191)	N/A	47 ± 24 (7.0-116)
Tuscany (Italy) /27 / NA / playground soil	N/A	N/A	59.03 ± 19.2 (27.5-112)	84.96 ± 70.79	127.65 ± 72.49	N/A	218.58 ± 217.05
Torino (Italy) / 28 / 5 / playground soil	116	N/A	127	57	106	N/A	57
Torino (Italy) / 28 / 25 / playground soil	188 ± 41 (150-288)	N/A	207 ± 43 (158-315)	87 ± 20 (44-123)	225 ± 57 (116-317)	N/A	144 ± 50 (68-257)
Stockholm (Sweden) / 29 / 8 / playground soil	35.0 ± 16 (10.0-66.0)	N/A	17.4 ± 7.2 (7.4-31.0)	30.0 ± 11 (15.0-45.0)	144 ± 147 (35.0-502)	5.1 ± 2.3 (1.9-8.9)	30.0 ± 13 (13-49)

Uppsala (Sweden) / 24 / 25 / playground soil	36 ± 10 (12-56)	N/A	22 ± 7.0 (7.0-34)	36 ± 17 (8.0-90)	112 ± 36 (27-193)	N/A	47 ± 24 (7.0-116)
Athens (Greece) /30 / 70 / playground soil	79.9 ± 19.3 (38.2-140.5)	311.6 ± 11.4 (125-490.5)	81.5 ± 25.8 (33.5-170.3)	43.4 ± 11.4 (21.9-85.9)	174.3 ± 97.0 (71.0-676.5)	N/A	110.3 ± 35.8 (59.7-289.6)
Belgrade (Serbia) / 31 / 15 / recreation park	N/A	417.6 (282-689)	N/A	46.3 (8.8-251)	174.2 (63.2-691.1)	N/A	298.6 (5- 785.7)
Aveiro (Portugal) / 24 / 26 / playground soil	10 ± 2.0 (6.0-15)	N/A	11 ± 6.0 (6.0-28)	18 ± 11 (8.0-61)	46 ± 15 (18-82)	N/A	20 ± 7.0 (7.0-38)
Ljubljana (Slovenia) / 24 / 25 / playground soil	21 ± 6.0 (13-33)	N/A	22 ± 6.0 (15-43)	33 ± 12 (21-78	114 ± 42 (84-300)	N/A	78 ± 37 (39-225)
Other studies: Asia							
Hong Kong (China) /32 / 594 / playground soil	N/A	N/A	N/A	24.8 ± 12.0 (5.12-190)	168 ± 74.8 (38.7-435)	N/A	93.4 ± 37.3 (5.27-404)
Hong Kong (China) /33 / 9 / recreation park	21.8 ± 6.7 (13.7-47.6)	N/A	5.30 ± 2.0 (1.77-9.62)	6.37 ± 4.02 (1.99-20.2)	46.8 ± 21.5 (25.3-136)	N/A	39.6 ± 23.3 (11.2-124)
Beijing (China) /34 / 9 / playground soil	59.11 ± 6.61	N/A	24.98 ± 3.64	30.80 ± 8.96	82.92 ± 8.96	N/A	34.76 ± 5.22
Islam Shahr (Iran) /35 / 25 / recreation park	75 ± 11.2 (60.3-87)	N/A	N/A	34 ± 2.8 (29.6-42.2)	105 ± 19.6 (78.2-192.7)	N/A	29 ± 13.4 (19.6-62)
Dungun (Malaysia) / 36 / 7 / playground soil	N/A	92 ± 31	N/A	7.4 ± 7.9 (0.5-20)	56 ± 43 (9.8-130)	N/A	59 ± 11 (0-74)

Table 3.4: Global Soil Guideline Values (residential soil-use) for potentially toxic elements.

Country / References	Elements (mg/kg dry weight)						
	Cr	Mn	Ni	Cu	Zn	As	Pb
Australia[37]	100	1500	600	1000	7000	100	300
Canada[38]	64	N/A	50	63	200	12	140
England[11,39]	Cr III 3000[39] Cr VI 4.3[39]	N/A	130[11]	2330[39]	3750[39]	32[11]	450[11]
Germany[40]	400	N/A	140	N/A	N/A	50	400
Netherlands[41]	380	N/A	210	190	720	55.0	530
Norway[42]	50	N/A	60	100	200	8	60
South Africa[43]	Cr III 9600 Cr VI 13	1500	1200	2300	19000	48	230

N/A = not available

concentration (577 ± 192 mg/kg) obtained in this work is lower than any of the values. The low mean concentration of Ni (48.5 ± 18.5 mg/kg) obtained from the playground soils is lower than worldwide SGVs (Table 3.4), while Zn mean concentration (307 ± 260 mg/kg) is lower than England's GAC value (3750 mg/kg) as well as SGVs from Australia, Netherlands and South Africa but higher than 200 mg/kg in use in Canada and Norway respectively.

3.3.2 Oral bioaccessibility of PTEs in playground soils

Though the total concentration results discussed above could be used in assessing human health risks from soil ingestion, they do not reflect the fraction of the PTEs that is released from its matrix under gastrointestinal conditions. To assess the oral bioaccessibility methodology both certified reference materials and a guidance material were subjected to the extraction protocol (Table 3.2). The oral bioaccessible fraction (% BAF) can be obtained by determining the concentration of the PTEs released from the playground soil (mg/kg) through *in vitro* gastrointestinal extraction and comparing it with the total PTE concentration (mg/kg). To allow the worst case scenario to be evaluated, the maximum concentration of the PTEs released in either the stage 1 (gastric only) or stage 2 (gastric + intestinal) phase is used. It is seen (Table 3.2) that in the case of the guidance material (BGS 102) reasonable results are obtained; in the case of Pb the guidance value ± SD incorporates the measured value in stage 1 (gastric digest only), similarly for As the guidance value ± SD incorporates the measured value in stage 2 (gastric + intestinal). In the case of the CRMs, while the oral bioaccessibility methodology can be applied it is not certified for the protocol. Nevertheless the use of the CRM allows a mass balance approach to be adopted that allows the overall system methodology to be assessed. The high recoveries for the PTEs in the CRMs (80 % and above for all elements) illustrates

the appropriateness of the analytical methodology in determining these two elements. In the light of this, the oral bioaccessibility of these PTEs in the playground soil was evaluated. Detailed information on total, stage I, stage II and stage III *in vitro* gastrointestinal extraction with standard deviations have been tabulated and are given in appendix A. Therefore, the actual range of concentrations (minimium, median and maximum) of PTEs obtained from the *in vitro* gastrointestinal extraction is given in Table 3.5A - C. Representation of bioaccessible concentration results in terms of minimium, median and maximum gives a better understanding and it has been noted (44) that reporting bioaccessibility results only in terms of % BAF conceals the exact concentration of the PTE in the extract. Thus, the actual range has been presented (Table 3.5A – C) for all the stages. Figure 3.3 shows a box plot of % BAF against individual PTE with respect to gastric and intestinal stages, the box plot showed the mean, median, box boundary (25th and 75th) percentile and whiskers (10th and 90th) percentile, it can be seen that the % BAF in both stages varied across the elements, though this study did not investigate the different forms in which these elements occurred in the playgrounds, the difference in their bioaccessibility suggest that these elements occurred in different chemical forms. In the gastric stage, the bioaccessible fraction for all the elements were >45% whereas in the intestinal phase, % BAF across the elements were found to be <40% except for Cu. It should be noted that % BAF obtained in both phases were lower than 100 % assumed in the CLEA model. The result showed that all the elements showed higher bioaccessibility in the gastric phase than in the second stage. This result is expected because the solubilisation of these PTEs is higher in the more acidic environment (gastric phase) than in the higher pH medium (intestinal phase) where re-adsorption and precipitation occurs (45). The results of this study are in are in

Table 3.5A: Summary of gastric bioaccessibility of PTEs in soil collected from playground soils: stage I

Elements	*In-vitro* gastrointestinal extraction (Stage I)					
	Gastric digest (mg/kg)			Gastric digest (% BAF)		
	Minimum	Median	Maximum	Minimum	Median	Maximum
Cr	7.15	24.8	45.3	38.8	46.6	59.3
Mn	106	265	676	31.7	48.9	62.4
Ni	4.33	15.8	40.1	35.5	42.8	49.4
Cu	5.20	20.4	324	39.8	53.3	54.0
Zn	26.9	76.3	416	34.9	39.8	44.5
As	2.11	6.57	11.9	31.9	46.3	53.8
Pb	15.8	38.7	589	38.0	40.6	46.4

BAF %: Bioaccessible fraction, calculated as a fraction of the total concentration

Table 3.5B: Summary of gastrointestinal bioaccessibility of PTEs in soil collected from playground soils: Stage II

Elements	*In-vitro* gastrointestinal extraction (Stage II)					
	Gastric + intestinal digest (mg/kg)			Gastric + intestinal digest (% BAF)		
	Minimum	Median	Maximum	Minimum	Median	Maximum
Cr	3.12	20.3	34.6	17.9	34.5	37.0
Mn	62.9	172	386	20.9	31.4	35.6
Ni	3.01	11.7	30.4	23.6	31.2	37.4
Cu	2.76	13.8	221	25.9	30.1	36.8
Zn	20.5	50.1	376	26.2	32.8	40.3
As	1.24	4.12	7.26	20.3	30.3	32.9
Pb	11.7	30.3	370	17.9	24.6	29.1

BAF %: Bioaccessible fraction, calculated as a fraction of the total concentration

Table 3.5C: Summary of residual fraction of PTEs in soil collected from playground soils: Stage III

Elements	Residual digest (mg/kg)		
	Minimum	Median	Maximum
Cr	8.12	27.8	51.2
Mn	159	309	675
Ni	6.07	19.6	43.8
Cu	4.10	20.3	346
Zn	28.1	94.6	528
As	2.62	7.93	12.6
Pb	20.4	42.1	768

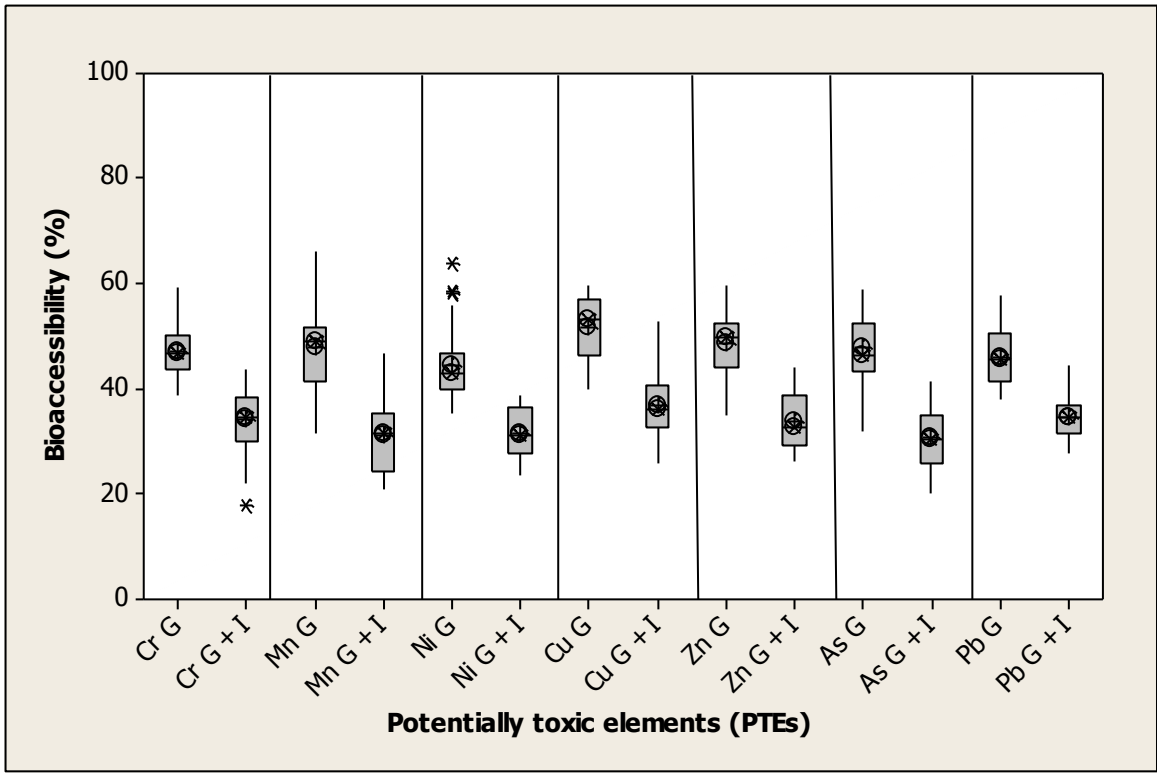

Figure 3.3: **Box plot for oral bioaccessibility of As, Cr, Ni, Cu, Pb, Mn and Zn in playground soil.**

agreement with other published data (16, 20, 45) that investigated the oral bioaccessibility of PTEs in soils where the highest amounts were found in the gastric phase for most of the elements. In addition, the *in vivo* study (46) that validated UBM employed in this investigation showed higher level of correlations between the UBM stage I (gastric extraction) and the *in vivo* data than with stage II (gastrointestinal extraction) results.

For a better understanding of bioaccesibility results, it was considered necessary to explore the relationship and potential differences between total elemental concentrations as well as the extraction stages (gastric and gastrointestinal stages). To investigate the relationship between total, gastric (stage I) and gastrointestinal stage (stage) concentrations, correlation analysis was carried out and the results showed that with respect to total concentration and stage I, total concentration and stage II, stage I and stage II concentrations, the correlation coefficient (r) was found

to range from 0.834 to 0.998 and p-value < 0.05 across the PTEs. Table 3.6 shows the results for Pb and appendix B for other PTEs. The result implies that the concentrations of these PTEs at the various stages correlated significantly meaning a linear relationship and that increase in one stage invariably affects the other. On the other hand, the correlation analysis between total concentration and stage I, total concentration and stage II, stage I and stage II bioaccesible fractions (% BAF) showed that r ranged from 0.089 to 0.642 and p > 0.05 across the PTEs. Table 3.6 shows the results for Pb and appendix B for other PTEs. The results showed that the % BAF stages showed a weaker correlation when compared to the concentration stages. Also a t test analysis was carried out in order to examine if there is any significant differences between stage I and II concentrations as well as stage I and II % BAF. The t test analysis across the PTEs (appendix C) shows that there are significant differences (P < 0.05) between the various stages.

Table 3.6: Inter-stage correlation analysis of Pb in playground soil.

Concentration stage						% BAF stage					
T & G		T & GI		G & GI		T & G		T & GI		G & GI	
r value	p value	r value	p value	r value	p value	r value	pvalue	r value	p value	r value	p value
0.997	**0.000**	**0.984**	**0.000**	**0.978**	**0.000**	**0.180**	**0.349**	**0.158**	**0.414**	**0.116**	**0.548**

r = correlation coefficient, T = total concentration, G = gastric stage,
GI = gastrointestinal stage.

To further assess the environmental health risk to children in playgrounds, another approach was adopted. This approach assesses the maximum potential daily intake (DI) from soil that a child could possibility ingest in order to reach the tolerable daily intake (TDI, for oral ingestion for metals (47-50). Due to the carcinogenic nature of As, a TDI would be inappropriate therefore an oral index dose (ID_{oral}) has been proposed of 0.3 µg kg^{-1} bw day^{-1} for As (51**)**. It was observed that none of the PTEs exceeded the TDI in any of the playground locations. However, it is noted that at one

location (Hexham) Pb maximum estimated daily intake was determined to be 3.4 μg kg^{-1} bw day^{-1} which is quite close to the TDI (3.6 μg kg^{-1} bw day^{-1}) (Table 3.7). The TDI range in terms of minimum, medium and maximum has been calculated and shown as footnotes (Table 3.7). Furthermore, for a more holistic human health risk assessment, the maximum bioaccessible estimated daily intake based on 50 mg/day ingestion for both stage I and stage II has been calculated. Table 3.7 shows the results for Pb whereas the results for the other PTEs are shown in appendix D. Lead values in Table 3.7 ranged from 0.07 to 1.57 μg kg^{-1}bw day^{-1} (stage I) and 0.05 to 0.59 μg kg^{-1}bw day^{-1} (stage II) . It is observed that the values of the PTEs across the sites were lower than TDI_{oral} for Pb (3.6 μg kg^{-1}bw day^{-1}) and as such does not represent threat to human health. However, due to health effects of Pb in the human body the highest concentration (1.57 μg kg^{-1}bw day^{-1}) observed in location 5 (Hexham) stage I should not be neglected. Additionally, it was appropriate to introduce a realistic exposure frequency for a child in the playgrounds. Based on an estimated 5 hours exposure per week over a 38 week term time it was determined that the exposure frequency was 0.021 day^{-1}. By applying this approach it was determined that both the PTE levels were considerably below the TDI and ID_{oral} respectively. Lead values ranged from 3.17 to 71.7 ng kg^{-1}bw day^{-1}. Table 3.7 shows these values for Pb and other PTEs are shown in appendix D**.** Based on the soil and dust ingestion rate of 50 mg/day recommended by the US EPA (9) for children between the age bracket of 3 – 6 years to exceed the (TDI_{oral} or ID_{oral} for As), a child would need to consume on daily basis a calculated amount of soil per PTE. This has been presented in Table 3.7 for Pb and in appendix D for other PTEs. This has been presented in Table 3.7 for Pb and in appendix D for other PTEs. Though for all the PTEs, the values obtained are significantly higher than 50 mg/day but with respect to

Table 3.7: Maximum Pb estimated daily oral intake from playground soils

Location (N.E. England)	Maximum estimated daily intake (µg kg^{-1}bw day^{-1}) based on 50 mg/day ingestion[@]	Maximum estimated daily intake (µg kg^{-1}bw day^{-1}) based on 50 mg/day ingestion and bioaccessibility[+] (Gastric only)	Maximum estimated daily intake (µg kg^{-1}bw day^{-1}) based on 50 mg/day ingestion and bioaccessibility[+] (Gastric + intestine)	Maximum estimated daily intake (ng kg^{-1}bw day^{-1}) based on 50 mg/day ingestion and an estimated annual exposure frequency[≠]	Amount of soil that could be consumed by a child[C] in order to exceed the guidelines (mg/day)
Bedlington	0.30	0.12	0.11	6.10	620
Berwick upon Tweed	1.84	0.96	0.59	38.6	98
Cramlington	0.57	0.26	0.24	12.0	316
Hepscott	0.23	0.09	0.08	4.78	783
Hexham	3.41	1.57	0.10	71.7	53
Newcastle upon Tyne	1.80	0.92	0.51	37.9	100
Ponteland	0.45	0.22	0.13	9.50	400
Prudhoe	0.17	0.08	0.05	3.48	1059
Sacriston	0.23	0.11	0.09	4.74	783
South Shields	0.15	0.07	0.06	3.17	1191
Willington	0.20	0.10	0.07	4.21	900
Wooler	0.26	0.13	0.13	5.40	692

TDI Range[@]: Berwick upon Tweed; (n = 2): Minimum = 0.01, Median = 0.04 Maximum = 0.82, where n = number of samples. Sacriston (n = 17): Minimum = 0.14, Median = 0.08, Maximum = 0.7, **other sites**, n = 1.

@ the maximum estimated daily intake (DI) was calculated using the formula DI= [EC x SIR] / BW (47-49), where DI = daily intake (µg kg bw^{-1} day^{-1}) as determined in < 125 µm fraction of the soil sample with the highest concentration; EC = Exposure concentration of the PTEs in < 125 µm (µg/g); SIR = soil ingestion rate (0.05 g day^{-1}) (9); and BW = body weight (18.6 kg for a 3-6 year old child) (48). In order to calculate the maximum estimated daily intake and bioaccessibility, the above equation was modified to DI= [EC x SIR X B] / BW where B is the bioaccessible fraction determined using Unified BARGE Method.

+ based on the maximum bioaccessible concentration using either 'gastric' or 'gastric + 'intestinal' phase

≠ the maximum estimated daily intake (DI) and estimated annual exposure frequency was calculated using the formula DI= [EC x SIR x EF] / BW, where DI = daily intake (ng kg^{-1}bw day^{-1}as determined in <125 µm fraction of the soil sample with the highest concentration; EC = Exposure concentration of As or Pb in <125 µm (µg/g); SIR = soil ingestion rate (0.05 g day^{-1}) (5); EF = Exposure frequency = 0.021 day^{-1} (estimated to be 5 hours a week for 38 weeks (term time) i.e. 190 hours per year or 7.9 days per year); and BW = body weight (18.6 kg for a 3-6 year old child) (48).

c child aged 3 - 6 years.

TDI_{oral} for Cr = 150 µg kg^{-1}bw day^{-1} (39)

TDI_{oral} for Mn = N/A

TDI_{oral} for Ni = 12 µg kg^{-1}bw day^{-1} (50)

TDI_{oral} for Cu = 160 µg kg^{-1}bw day^{-1} (39)

TDI_{oral} for Zn = 600 µg kg^{-1}bw day^{-1} (39)

ID_{oral} for As = 0.3 µg kg^{-1}bw day^{-1} (51)

TDI_{oral} for Pb = 3.6 µg kg^{-1}bw day^{-1} (52).

lead, some concern is required for Hexham (53 mg/kg) (Table 3.7) which was similar to the US EPA recommended soil ingestion rate.

Due to high Pb concentrations found in three sites, a detailed quantitative risk assessment (DQRA) was undertaken in the playgrounds in order to generate site-specific assessment criteria (SSAC) for Pb using CLEA model (53). This was done by incorporating information on land use; receptor, exposure frequency and determined bioaccessibility (worse-case scenario) in the CLEA model (v 1.06 software). This software allows default values to be altered with assessor's values in order to generate the SSAC. Table 3.8 summarises the input parameters altered in order to generate the SSAC. In the context of CLEA model (v 1.06 software), exposure frequency (EF) means the number of days per year in which a 24 hour (daily) exposure is taken into consideration. In this study, it is assumed that children could be in contact with soil during outdoor activities. Thus, while school may be open 30 hours a week, it is likely that children will be in playground for 15 minutes pre-school; 15 minutes mid-morning break and 30 minutes lunch break (i.e. maximum time in playground is 1 hour a day). Primary and middle schools in the UK open 9am – 3pm, Monday – Friday. Calculated holidays when children are out of the premises; 3 weeks for Christmas break, 3 weeks for Easter break and 8 weeks for long vacation, i.e., 14 weeks holidays in a year. 52 weeks in a year - 14 weeks holidays = 38 weeks term time. Therefore, exposure frequency for children (3 - 6 years) has been estimated to be 5 hours a week for 38 weeks i.e. 190 hours a year or 7.9 days / year. CLEA model (v 1.06 software) does not contain the physico-chemical data base for Pb because the SGV for Pb has been withdrawn. However, toxicological and physico-chemical data base for Pb has been compiled (54) and was used to calculate the SSAC. This was found to 16,449 mg/kg. The CLEA model

assumes that contaminant availability to receptors is total (100%), however, this could be an over estimate. Thus, the bioaccessibility SSAC was derived by altering

Table 3.8: CLEA model (v 1.06 database) for calculating Site specific assessment criteria (SSAC)

Input parameters	Default	Adopted value	Justification
Exposure frequency in days (direct ingestion, outdoor dermal contact and inhalation of dust and vapour)	365	7.9	Based on calculated hours that children spend on the playground
Occupancy period outdoor (h/day)	1.0	1.0	Calculated to be 1 h / day for 365 days year
Bioaccessibility	1.0	0.46	Determined highest % BAF (worst-case scenario)

the bioaccessibility default value of 1.0 to 0.46 (% BAF, worst-case scenario) and was found to be 8773 mg/kg. These values are seen to be higher than the highest Pb concentration (1272 mg/kg) (worst-case scenario). Therefore, the results show that significant possibility of significant harm does not exist in the sites since the highest Pb concentration in the playground is lower than both the SSAC and the bioaccessibility derived SSAC.

3.4 Conclusion

The PTEs do not exceed their respective ID_{oral} and TDI in any playground location; the exception is location 5 for Pb. However, further evidence on the lower health risk to children exposed to these playground sites is evident. The majority of samples from the different locations were taken from soil beneath a grass surface covering, the exception was site 9 which included eight soils from raised beds and five soils from greenhouses, as well as, four soils from fields. In reality children during

morning/afternoon breaks and lunchtime are unlikely to be exposed to any great extent to the risk of unintentional ingestion of soil. As sporting activity may be restricted and controlled in the grassy parts of the playground due to prevailing weather conditions, lack of opportunity, and restricted time in breaks the risks associated with exposure from this activity is limited. Precautions, such as, good personal hygiene i.e. washing of hands after contact with the grass and soil will further limit potential exposure and minimise the possibility of hand-to-mouth ingestion from these sites. It is not advisable however to convert playground locations where high Pb content was found into gardens for the growing of fruits and vegetables as this would increase the exposure risk to children.

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Chapter four: Potentially toxic elements (PTEs) in urban street dusts and implications for human health risk.

4.1 Introduction

Urban street dust is a mixed mineral-organic medium, typically comprising a significant soil component and containing a range of PTEs deposited either through natural or anthropogenic activities (1). A potential threat to human health due to elevated concentrations of PTEs in urban street dust is now well recognised (2-3) and concerns have been expressed about the immediate or prolonged long-term adverse effects on human health and ecosystems in general (4-5). Dusts can be seen to pose more risk to human health when compared to other environmental matrices like soil; this is due to its pervasive and omnipresent nature (6). Dust refers to minute solid particles (7) emitted into the air from various sources and which are found to have settled onto outdoor objects and surfaces due to either wet or dry deposition (8). The multi-component composition of urban street dusts as well as their inherent continuous intra-interactions means urban dust does not remain deposited onto a particular surface for long periods but it is easily re-mobilised into the air where it contributes a significant quantity of PTEs (9-11). In addition, processes like precipitation will mobilise dusts so that they become an important component of suspended and dissolved particles in urban street run-off (12); the presence of PTEs in urban street dusts can have an adverse effect on air and water quality (13).

According to many studies (14-17), the two main basic sources of urban street dust and consequently of the PTEs found within, are deposition of suspended particles (atmospheric aerosol) and displaced soil and biogenic materials (e.g. tree leaves, debris and other plant matter) that can be easily mobilised as dust mainly by moving

vehicles. Emissions from a multitude of anthropogenic sources (e.g. vehicular exhausts particles, petrol combustion residues, lubricating oil residues, tyre wear, engine coating wear, brake lining wear particles, heating systems, municipal waste incineration, construction, renovations, mining and extraction processes, smelting, corrosion of galvanised metal components and building deterioration) can also contribute greatly to urban dust compositions (18-23). The PTEs commonly associated with these emissions include; Arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), manganese (Mn), nickel (Ni), lead (Pb), and zinc (Zn). For example, lead is emitted from the deterioration of older buildings because lead oxide was used as a blocking and colouring agent in the manufacture of paints that were used for both interior and exterior purposes (24). Also, the presence of zinc in urban dusts can be traced to the use of zinc oxide during paint production for pigmentation and improved film strength as well as better spreading quality and ability to withstand adverse conditions (25). The sources of arsenic in urban dusts can be attributable to its use as a basic ingredient in the manufacture of fungicides, pesticides and herbicides as well as wood preservatives (26). Most of these PTEs are widely used in the manufacturing of vehicular components (27-30) and they are in turn released into the urban environment due to the aging process as well as friction which occurs constantly between the various surfaces. The selected PTEs are of interest because they are ubiquitous and potentially harmful to humans.

Urban dusts with their complicated composition could cause potentially adverse effects to humans since they can easily enter the human body through different exposure pathways (i.e. indirect and direct). An indirect pathway could occur as a result of the association of dust particles with consumed food (e.g. eating outdoors, insufficiently washed foodstuffs from urban allotments) as well as access to the food

chain via contaminant uptake by edible plants followed by consumption by animals and humans (31-32). Direct exposure can occur via inhalation, absorption through the skin (dermal) and oral ingestion (33-35). In this regard, children have the greatest risk considering their outdoor activities and their continual habit of finger sucking and mouthing of non-food substances (36-38). Moreover, children exhibit a higher absorption of PTEs than adults due to their less developed digestive systems (39-40). The increased accumulation and degradation-resistance of PTEs in urban dusts have alerted serious concerns amongst environmental researchers, governmental and non-governmental regulatory agencies resulting in numerous research outputs on urban dusts. However, most studies have centred on PTE content, fractionation, source identification and contamination assessment (41-43) as well as particle-size and spatial distribution (44-45). On the other hand, there is little information (46-47) on the human health risk assessment via the ingestion pathway (i.e. oral bioaccessibility) of urban dust. Since elevated PTE concentrations in dust represent a potentially significant risk to human health, it is important to study their potential for release within the human gastro-intestinal environment (i.e. oral bioaccessibility). This research assessed the oral bioaccessibilty of As, Cd, Cr, Cu, Mn, Ni, Pb and Zn in urban street dust of five cities in the UK and one city in Nigeria using the *in vitro* gastrointestinal extraction, based on the Unified Barge Method (UBM).

4.2 Experimental

4.2.1 Sampling and preparation

Fifteen urban street dusts were collected from each of the five different cities in the UK: Durham, Edinburgh, Liverpool, Newcastle upon Tyne and Sunderland. The

samples were all collected in the summer of 2010. Newcastle upon Tyne samples Figure 4.1) were collected on the 27th and 28th May, Durham samples (Figure 4.2) on the 15th June, Liverpool samples (Figure 4.3) on the 5th June, Edinburgh samples (Figure 4.4) on the 12th June and Sunderland samples (Figure 4.5) on the 31st May. In addition, fifteen urban street dust samples (Figure 4.6) were collected from Abakaliki, Ebonyi State, Nigeria on 30th January, 2011. The sampling days were selected due to the lack of precipitation i.e. were dry and sunny. All sampled sites were selected randomly but with due regard to the volume of traffic and the location of pedestrians i.e. central city locations were selected which featured, if possible, pedestrian walkways. Detailed site descriptions are shown in appendix E. Dust samples were collected using a plastic dustpan and brush (48-49). Different dustpans and brushes were used at each site; gloves were worn to avoid cross contamination. Collected samples were transferred to self-sealing bags (Kraft bag) for transport to the laboratory. The sampling procedure was maintained for all sites to minimise sampling variability and maintain sample integrity. The samples were dried at a temperature of 35 °C for 48 hours. The dust samples were then sieved using a < 125 μm nylon sieve to remove unnecessary matter such as small pieces of building material and other debris. The < 125 μm dust samples collected after sieving were weighed (their mass recorded) and stored in sealed plastic containers. All procedures were carried out without contact with metal objects / utensils to avoid potential cross-contamination of the samples. [It is noted that while plastics also contain metals that could potentially cross-contaminate samples their use was considered to minimise this source when compared to metal objects].

Figure 4.1: Newcastle upon Tyne sampling locations (1 – 15)

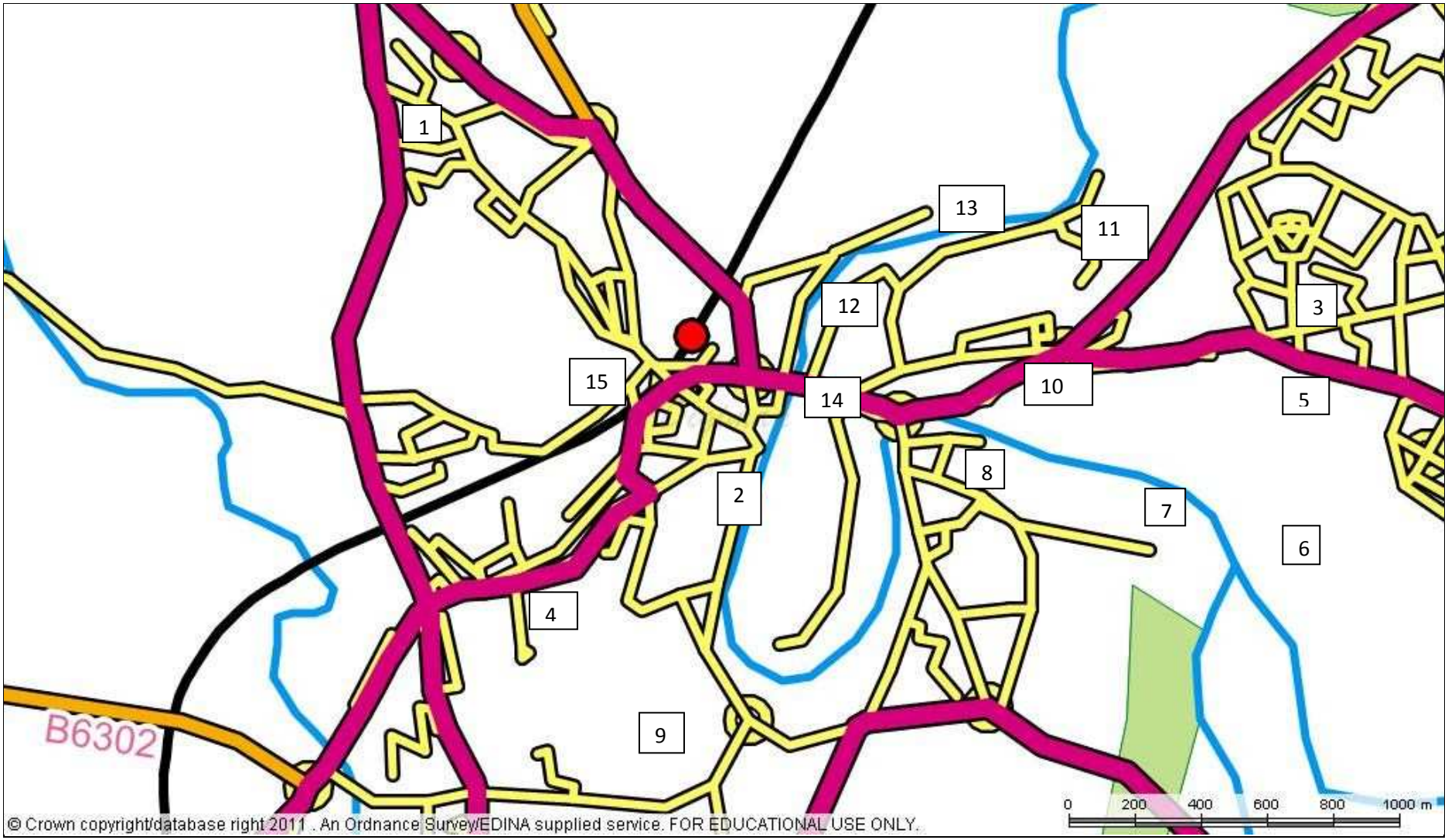

Figure 4.2: Durham sampling locations (1 – 15)

Figure 4.3: Liverpool sampling locations (1 – 15)

Figure 4.4: Edinburgh sampling locations (1 – 15)

Figure 4.5: Sunderland sampling locations (1 – 15)

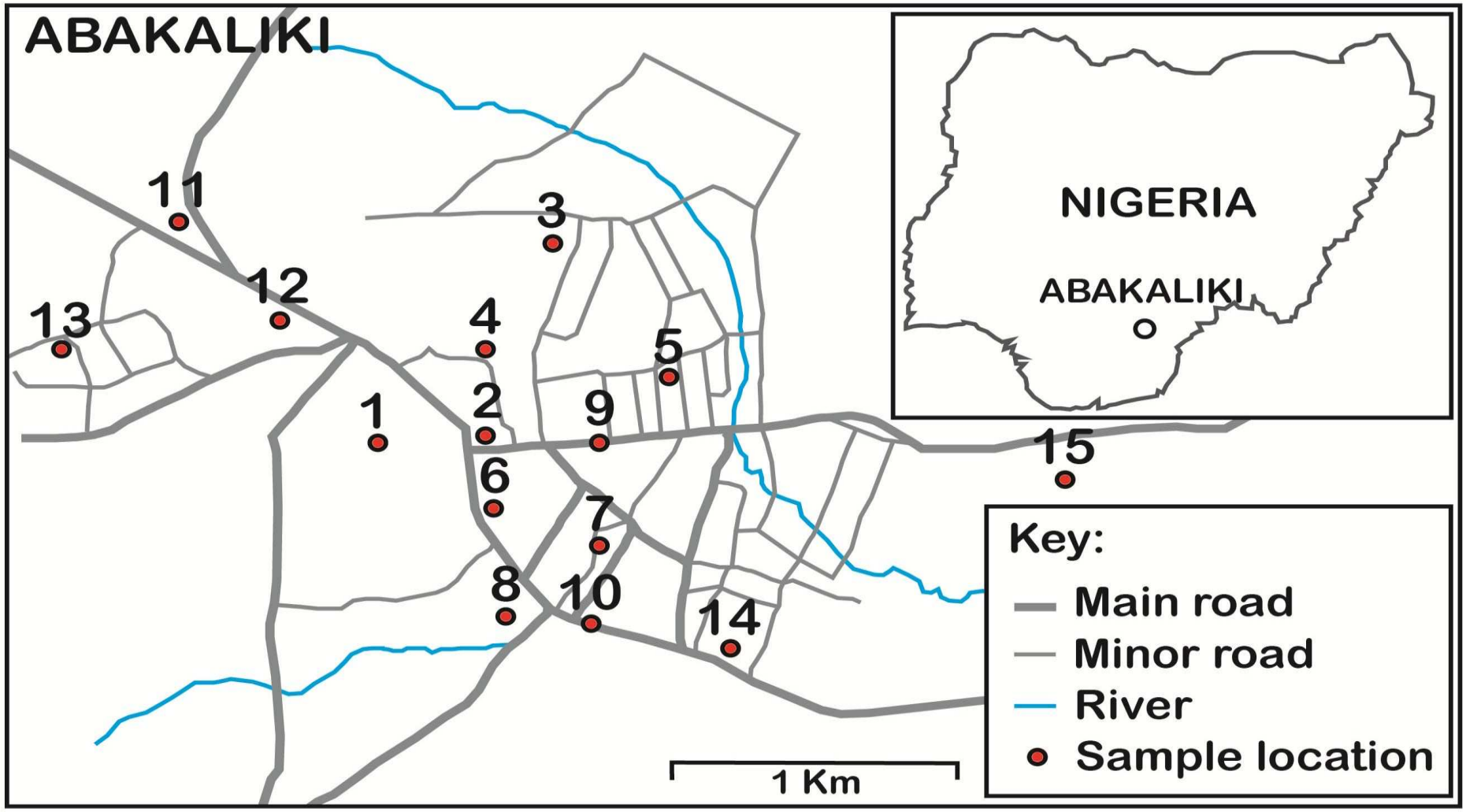

Figure 4.6: Abakaliki sampling locations (1 – 15)

4.2.2 Instrument and Reagents

Instrument and reagents analogous to section 3.2.2

4.2.3 Sample extraction using UBM

Extraction method same as section 3.2.3 and 3.2.4

4.2.4 Microwave digestion protocol

Digestion protocol analogous to section 3.2.5

4.2.5 ICP-MS protocol

ICP-MS protocol already outlined in section 3.2.6

4.3 Results and Discussion

4.3.1 Quality control

Calibration curves for PTEs based on a concentration range of 0-400 ppb with 8 calibration data points were done on the ICP-MS and the regression coefficients (R^2) obtained for each PTE, irrespective of operating mode, were > 0.999. To check the quality control of the method employed in this work, two CRMs (BGS 102 and BCR 143R) were used; BCR 143R allowed a quality check on determination of PTE total concentration (Table 4.1) while BGS 102 allowed a quality check on oral bioaccessibility determination (Table 4.2). However, due to the limited number of PTEs (As and Pb) determined using BGS 102, the CRM (BCR 143R) was also subjected to oral bioaccessibility testing using the UBM. The results obtained for both total and oral bioaccessible PTE determination were not different with certificate values (Tables 4.1 and 4.2). Excellent results were obtained for the total

Table 4.1: Certified value, total concentration, stage related bioaccessible and residual fractions of PTEs in BCR 143R

Elements	Certified value (mg/kg)	Total content (mg/kg)	*In-vitro* gastro-intestinal extraction (mg/kg)						
			Stage I (Gastric digest)		Stage II (Gastric + Intestinal)		Stage III (Residual digest)	Total PTE content II + III	
		Mean ± SD; (n = 3)	Mean ± SD; (n = 3)	% BAF	Mean ± SD	% BAF	Mean ± SD; (n = 3)	Mean (n = 3)	% Total Recovery
Cr	426 ± 12	424 ± 11	162 ± 3	38.2	124 ± 5	29.2	267 ± 6	391	92.2
Mn	858 ± 11	853 ± 11	181 ± 12	21.1	119 ± 4	13.9	564 ± 9	683	79.8
Ni	296 ± 4	297 ± 6	124 ± 4	41.8	96.7 ± 2	32.6	186 ± 3	283	95.3
Cu	NA	147 ± 3	61.3 ± 1	41.7	33.7 ± 4	22.9	106 ± 2	140	95.0
Zn	1063 ± 16	1058 ± 14	481 ± 6	45.5	354 ±7	33.5	619 ± 13	973	91.9
As	NA	14.3 ± 0.5	5.73 ± 0.1	40.1	3.42 ± 0.1	23.9	8.03 ± 0.2	11.5	80.1
Cd	72.0 ± 1.8	72.0 ± 2.0	38.2 ± 1.1	53.1	28.4 ± 1.5	39.4	40.9 ± 1.3	69.3	96.3
Pb	174 ± 5	173 ± 2	69.8 ± 2	40.3	42.7 ± 1	24.7	101 ±3	144	83.2

% BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}}$ X 100

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiological based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration; **NA**: not available.

Table 4.2: Certified values and measured stage related bioaccessible fractions of PTEs in BGS 102

Elements	Certified value (mg/kg)		Measured value (mg/kg) (n = 7)*	
	Stage I (Gastric digest)	Stage II (Gastric + Intestinal)	Stage I (Gastric digest)	Stage II (Gastric + Intestinal)
As	NA	5.4 ± 2.4	3.03 ± 0.7	3.34 ± 1.2
Pb	13 ± 6	NA	8.0 ± 4.0	5.18 ± 4

NA: not available.
* repeat extracts generated over a period of 2 weeks and measured on 7 different occasions.

PTE determination compared to certificate values (Table 4.1), with adequate results (> 60% recovery) for the oral bioaccessible PTE determination (Table 4.2). The % accuracy was found to be in the range of 99 – 101.

4.3.2 Total PTEs concentrations in urban street dust

The total concentrations of As, Cd, Cr, Cu, Mn, Ni, Pb and Zn were determined from the < 125 µm particle size fraction of all the urban dusts collected from the six cities. The < 125 µm particle size fraction was used to determine the PTE content instead of the < 250 µm commonly used in assessing PTE levels in soil and dusts because it has been shown that the PTE concentration in urban dusts increases with decreasing particle size (13, 50). Lower particle size fractions have an increased surface area for the deposition of the PTEs and so the < 125 µm represents the particle size fraction with a potentially higher risk to human health. Box plots showing the median, mean, box boundary (25^{th} and 75^{th} percentile) and whiskers (10^{th} and 90^{th} percentile) have been used to present the results obtained (Figures 4.7 - 4.14).

The results indicate that the total concentrations of PTEs in urban dusts vary from location to location. For example, the highest concentration of Cr (i.e. 187 mg/kg) was recorded in Durham (site 2) (Figure 4.9), while the highest concentration of Mn (i.e. 1607 mg/kg) was observed in Liverpool (site 13) (Figure 4.11)). Figure 4.14 shows that the highest concentration of Zn (i.e. 4646 mg/kg) was observed in Newcastle upon Tyne. The overall concentrations of As across all locations studied were found to be low (i.e. all median values between 4 – 8 mg/kg); Figure 4.7 shows that the highest concentration (i.e. 15.9 mg/kg) was obtained from a dust sample collected in Liverpool. Figures 4.8 and 4.13 show that the highest concentrations of

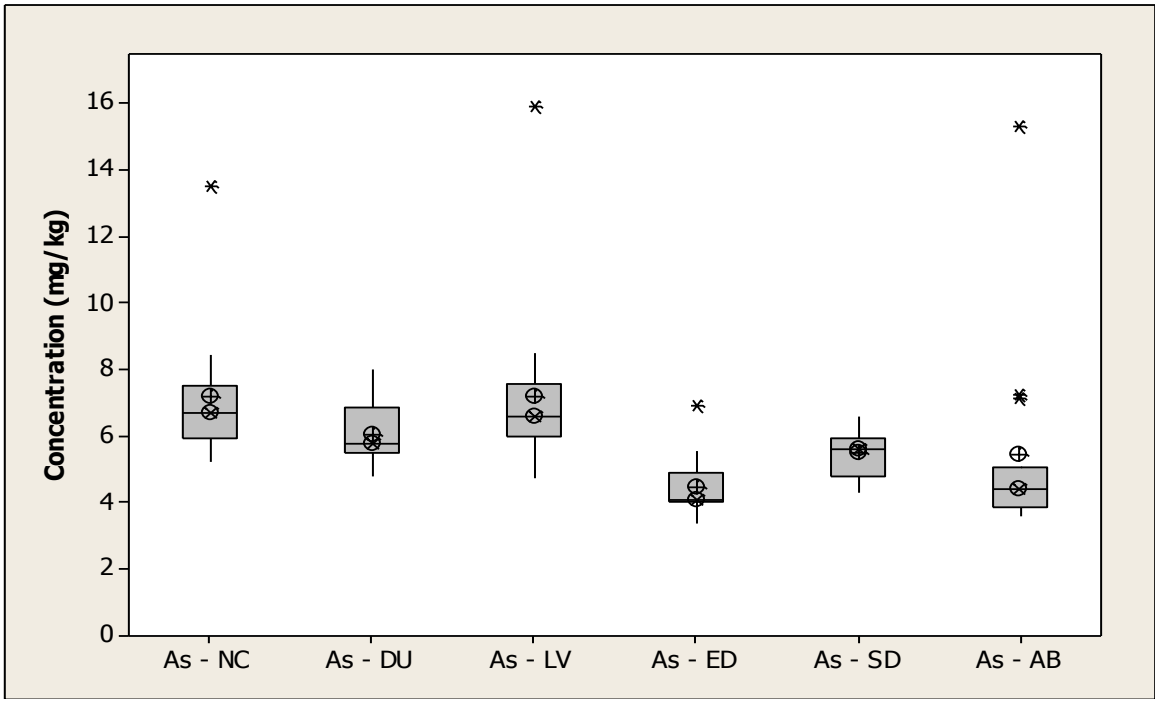

Figure 4.7: **Box plot of arsenic in urban street dusts showing: median, mean, box boundary (25th and 75th) percentile and whiskers (10th and 90th) percentile. (NC – Newcastle; DU – Durham; LV – Liverpool; ED – Edinburgh; SD – Sunderland; AB – Abakaliki).**

Cd (i.e. 3.62 mg/kg) and Pb (i.e. 2228 mg/kg) were observed at sites in Newcastle upon Tyne and Sunderland, respectively. In addition, it can be seen that most dust samples collected from the five UK locations gave higher concentrations of PTEs compared to the samples collected from Abakaliki, Nigeria (with the exception of Mn). The lower concentration of PTEs in urban dusts from Abakaliki, Nigeria may be expected; Abakaliki is a new city and all the street / road dusts sampled were from relatively newly constructed locations (i.e. less than 5 years old). Among the eight elements determined in the six cities, high concentrations of Pb were observed at all sites (Figure 4.13). High Pb levels in the urban environment potentially represent a risk due to the toxicity of lead. As a result of this, discussion will now be focussed on Pb levels in the six cities. In Newcastle upon Tyne, the Pb concentration varied between 94 and 1636 mg/kg with a mean concentration of 558 mg/kg.

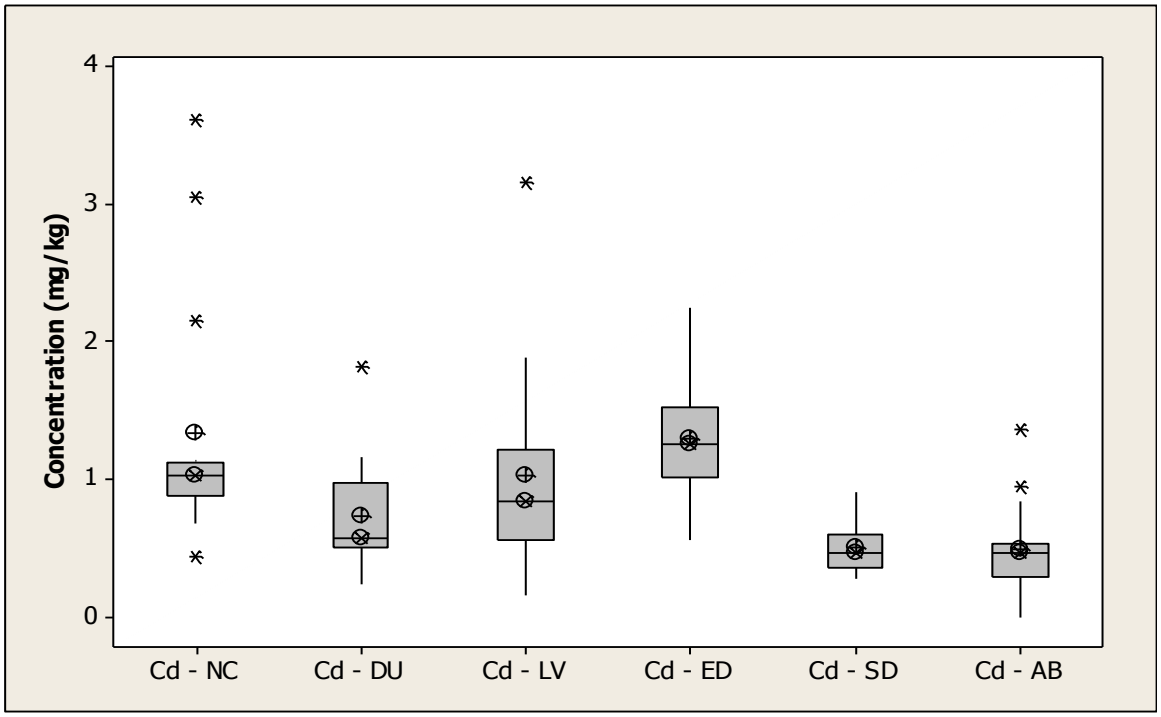

Figure 4.8: **Box plot of cadmium in urban street dusts showing: median, mean, box boundary (25th and 75th) percentile and whiskers (10th and 90th) percentile. (NC – Newcastle; DU – Durham; LV – Liverpool; ED – Edinburgh; SD – Sunderland; AB – Abakaliki).**

The highest Pb level in this city was obtained from site 3 (i.e. 1636 mg/kg) i.e. Grey Street (by the Monument) and the Theatre Royal both areas are close to each other and the centre of the pedestrianized heart of the city centre. In Durham, the concentration varied between 109 and 2119 mg/kg with a mean concentration of 446 mg/kg; Saddler Street, a busy street with vehicles and pedestrians gave the highest concentration of 2119 mg/kg. In Liverpool, the concentration varied between 109 and 915 mg/kg with a mean concentration of 362 mg/kg. In Liverpool, the highest concentration of Pb (i.e. 915 mg/kg) was found at sampling site 9 i.e. Brown Low Hill Road. In Edinburgh, the concentration varied from 76 to 1273 mg/kg with a mean concentration of 443 mg/kg while sampling point 9 (i.e. the Palace of Hollywood house, by the Scottish Parliament) gave the highest concentration at 1273 mg/kg. The concentration range of Pb in Sunderland was found to vary between 88 - 2228 mg/kg with a mean.

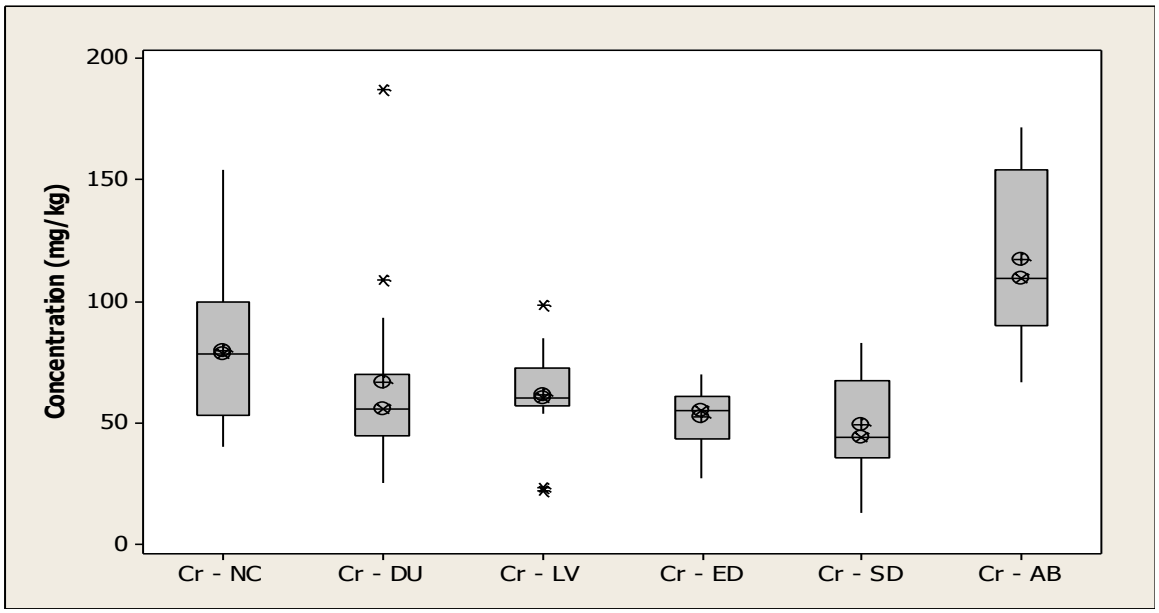

Figure 4.9: **Box plot of chromium in urban street dusts showing: median, mean, box boundary (25th and 75th) percentile and whiskers (10th and 90th) percentile. (NC – Newcastle; DU – Durham; LV – Liverpool; ED – Edinburgh; SD – Sunderland; AB – Abakaliki).**

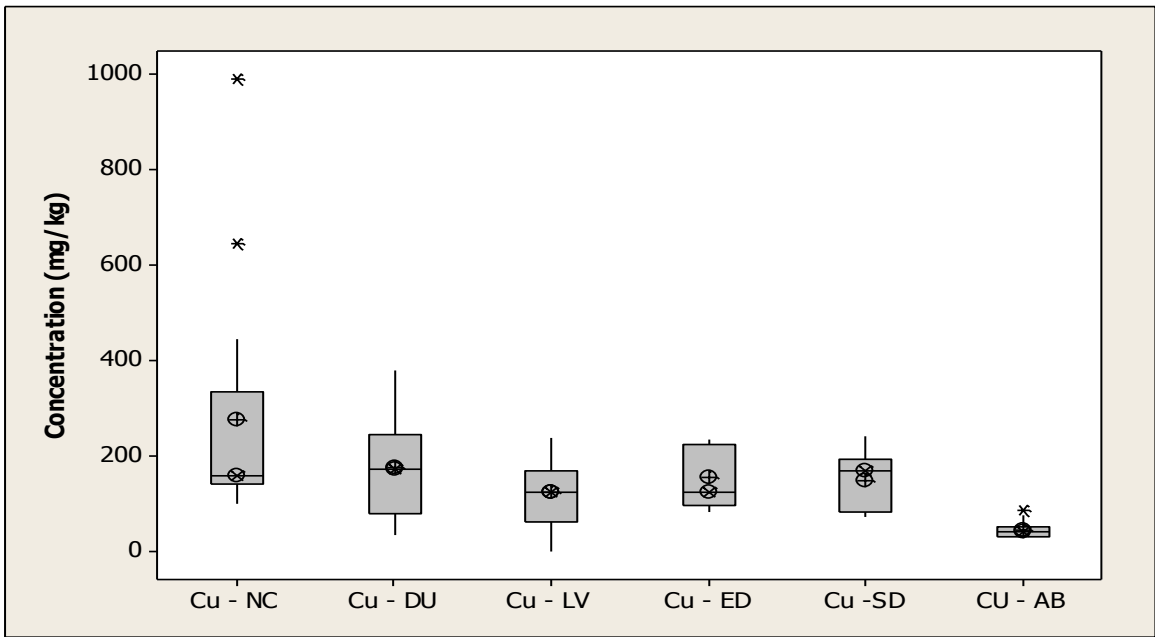

Figure 4.10: **Box plot of copper in urban street dusts showing: median, mean, box boundary (25th and 75th) percentile and whiskers (10th and 90th) percentile. (NC – Newcastle; DU – Durham; LV – Liverpool; ED – Edinburgh; SD – Sunderland; AB – Abakaliki).**

Note: the value of one of the copper values in Liverpool (site 2: Elliot Park Street) was very high (2222 mg/kg) compared to the other results. To allow the data to be clearly viewed on the one box plot it was removed from this display.

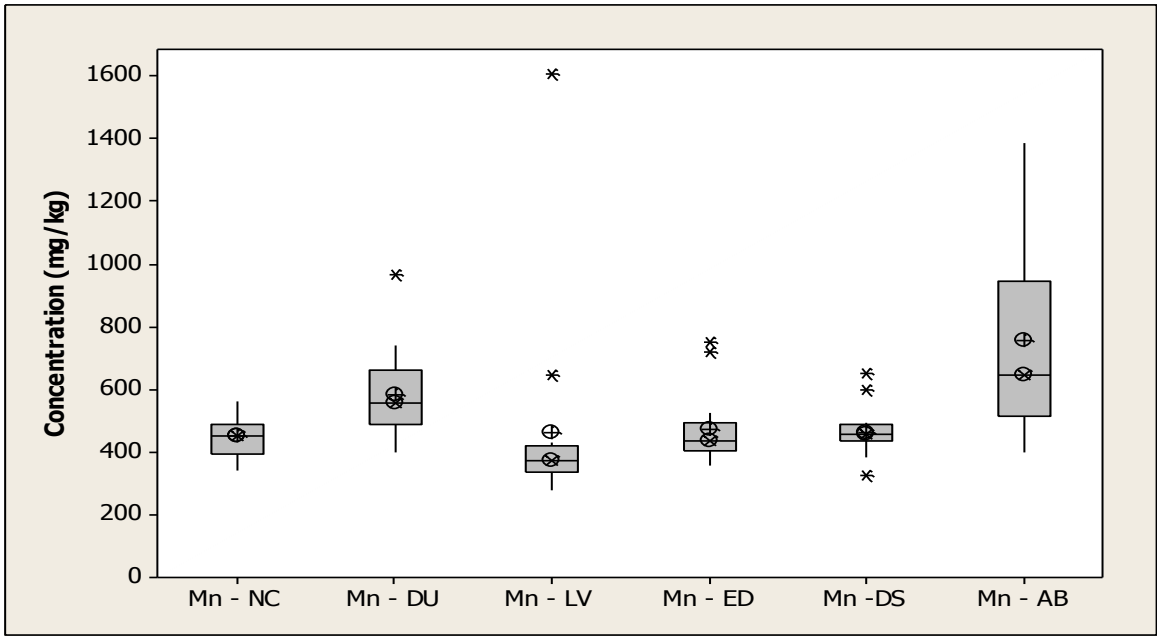

Figure 4.11: Box plot of manganese in urban street dusts showing: median, mean, box boundary (25th and 75th) percentile and whiskers (10th and 90th) percentile. (NC – Newcastle; DU – Durham; LV – Liverpool; ED – Edinburgh; SD – Sunderland; AB – Abakaliki).

concentration of 407 mg/kg. The highest Pb concentration (2228 mg/kg) was observed at sampling point 8 i.e. High Street West In Abakaliki, Nigeria Pb levels ranged from 55 to 1815 mg/kg with a mean concentration of 306 mg/kg; the highest Pb level (1815 mg/kg) was found at site 7 i.e. Vanco junction.

A characteristic feature that was common to all sites investigated and especially those found to contain high Pb concentrations was their proximity to a high population density i.e. their central location within or close to pedestrianized areas. For detailed site description see appendix E. In contrast, the background concentration of Pb in soils has typically been recorded in the range of 0.5 – 138 mg/kg (51). The total concentration of Pb obtained in all the sites mentioned are above background Pb levels in soil suggesting that the increased Pb level might

have occurred as a result of either anthropogenic activities or accumulation within the fine dust particles found at street-level. Although direct comparison of results from different studies are complicated due to the variation in sampling methods, the

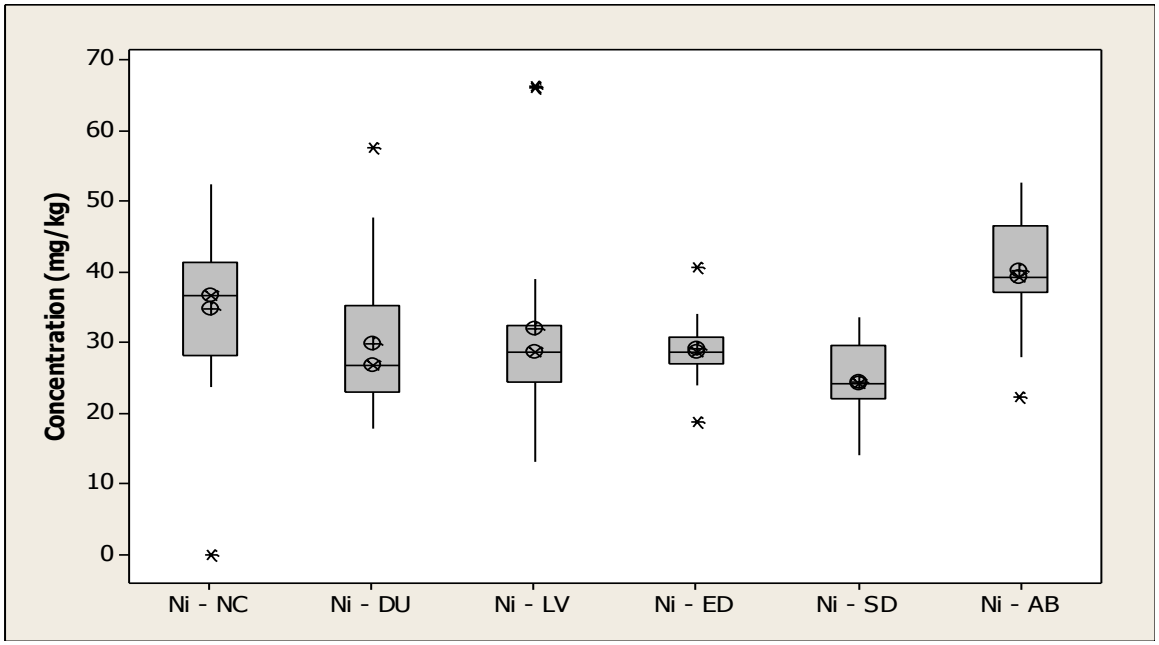

Figure 4.12: Box plot of nickel in urban street dusts showing: median, mean, box boundary (25th and 75th) percentile and whiskers (10th and 90th) percentile. (NC – Newcastle; DU – Durham; LV – Liverpool; ED – Edinburgh; SD – Sunderland; AB – Abakaliki).

Note: the value of one of the nickel values in Newcastle (site 10: Newcastle University, Robinson Library) was very high (1289 mg/kg) compared to the other results. To allow the data to be clearly viewed on the one box plot it was removed from this display.

different sample preparation methodologies, the variety of particle size fractions adopted as well as the digestion and sample analysis protocols, the mean results obtained in this study were not different from results obtained from other studies in different cities worldwide (Table 4.3) whose mean range levels are as follows: As(0.69 – 23 mg/kg); Cd (0.2 – 5 mg/kg); Cr(5.4 – 324 mg/kg); Cu(11.6 – 534 mg/kg); Pb(20.37 – 1927 mg/kg); Mn(59 – 914); Ni(1.7 – 129.7 mg/kg) and Zn(65.1

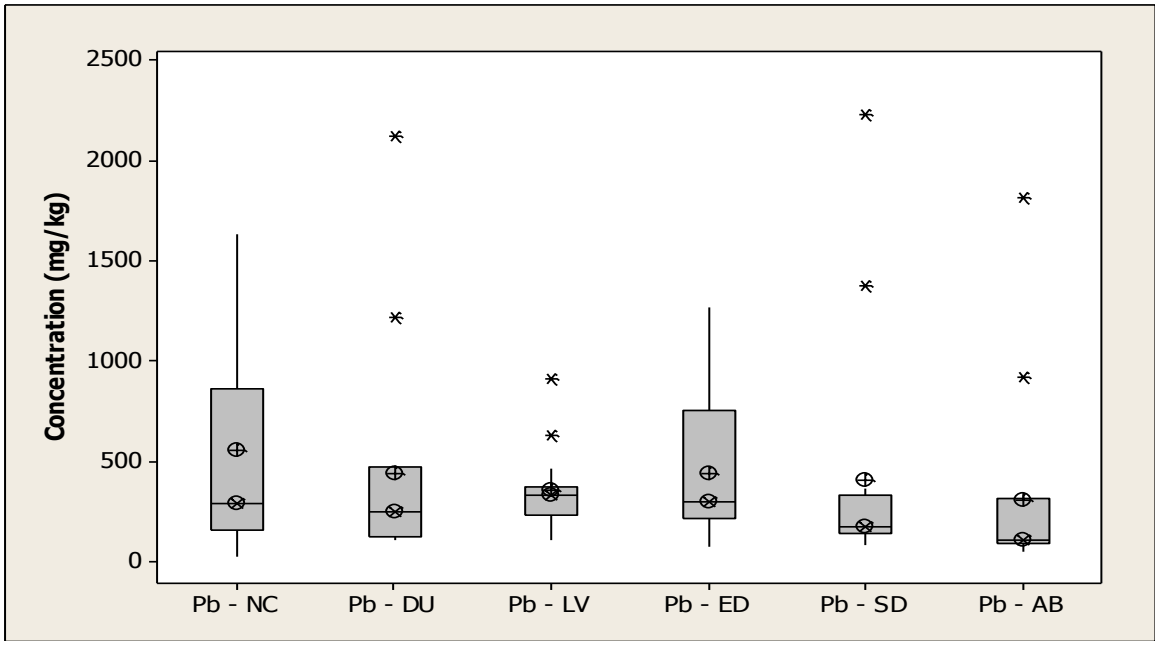

Figure 4.13: **Box plot of lead in urban street dusts showing: median, mean, box boundary (25th and 75th) percentile and whiskers (10th and 90th) percentile. (NC – Newcastle; DU – Durham; LV – Liverpool; ED – Edinburgh; SD – Sunderland; AB – Abakaliki).**

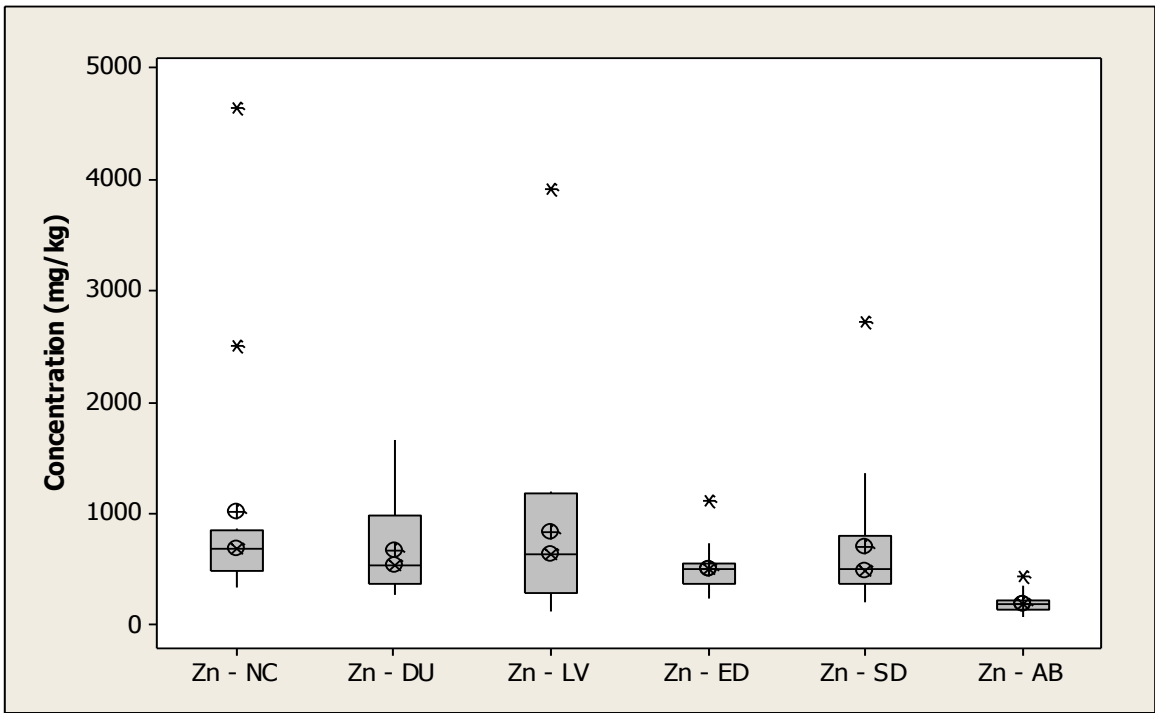

Figure 4.14: **Box plot of zinc in urban street dusts showing: median, mean, box boundary (25th and 75th) percentile and whiskers (10th and 90th) percentile. (NC – Newcastle; DU – Durham; LV – Liverpool; ED – Edinburgh; SD – Sunderland; AB – Abakaliki).**

Table 4.3: Mean concentration of PTEs in several cities of the world (mg/kg) with the range values (minimum – maximum)

City (country) / Reference / No of samples	Cr	Mn	Ni	Cu	Zn	As	Cd	Pb
Newcastle (UK) / current study / 15	80.0 ± 30.6 (40.4-154)	454 ± 68.2 (344-562)	121 ± 323 (23.8-1289)	277 ± 246 (100-989)	1012 ± 11.3 (338-4646)	7.20 ± 1.94 (5.24-13.5)	1.33 ± 0.89 (0.442-3.62)	558 ± 556 (27.9-1636)
Durham (UK) / current study / 15	66.7 ± 39.3 (25.9-187)	581 ± 140 (400-963)	30.0 ± 10.9 (17.8-57.6)	174 ± 109 (34.6-379)	668 ± 400 (268-1661)	6.04 ± 0.99 (4.79-8.03)	0.740 ± 0.4 (0.244-1.82)	446 ± 540 (109-2119)
Liverpool UK) / current study / 15	61.8 ± 19.8 (22.7-98.6)	464 ± 327 (279-1607)	32.1 ± 15.4 (13.1-66.5)	271 ± 543 (53.3-2222)	842 ± 929 (125-3920)	7.21 ± 2.6 (4.72-8.52)	0.843 ± 0.74 (0.154-3.16)	362 ± 197 (109-915)
Edinburgh (UK) / current study / 15	52.5 ± 12.4 (27.2-70.1)	475 ± 115 (356-753)	29.1 ± 4.87 (18.9-40.8)	155 ± 63 (82.6-235)	508 ± 217 (236-1119)	1.31 ± 0.87 (3.38-6.94)	1.26 ± 0.42 (0.563-2.25)	443 ± 346 (76.4-1273)
Sunderland (UK) / current study / 15	49.4 ± 20 (13.5-83.1)	463 ± 78.7 (325-649)	24.5 ± 5.19 (14.1-33.7)	149 ± 58.7 (71.5 -242)	707 ± 630 (212-2726)	5.51 ± 0.68 (4.31-6.58)	0.471 ± 0.17 (0.284-0.906)	407 ± 593 (88.3-2228)
Abakaliki (Nigeria) / current study / 15	118 ± 34.3 (66.8- 172)	754 ± 284 (397-1389)	40.2 ± 8.66 (22.3-52.7)	45.5 ± 18 (25.4-86.6)	193 ± 98.3 (69.1-434)	5.43 ± 2.95 (3.59-15.3)	0.489 ± 0.35 (0.288-1.36)	306 ± 471 (55.5-1815)

Other studies: Europe								
Lancaster (UK) / 52 / NA	NA	NA	27	138	562	NA	3.5	1740
London (UK) / 53 / NA	NA	NA	NA	155	680	NA	NA	1030
Coventry (UK) / 54 / 49	NA	NA	129.7 ± 8.7 (6.18-233.5)	226.4 ± 25.7 (49.3-815.0)	385.7 ± 65 (93.0-3038)	NA	0.9 ± 0.27 (0.0-8.9)	47.1 ± 8.4 (0.0-199.4)
Birmingham (UK) / 54 /49	NA	NA	41.1 ± 9.2 (0.0-636)	467 ± 99 (16-6688)	534 ± 47 (81-3165)	NA	1.62 ± 0.23 (0.0-13.1)	48.0 ± 2.9 (0.0-146)
Gela (Italy) / 55 / 8 / NA	79	527	47	109	185	8.8	NA	60
Kavala (Greece) / 56 / 96	232.4 ± 245 (50-692)	NA	67.9 ± 48.2 (25-269)	172.4 ± 87.6 (58-508)	354.8 ± 115 (200-558)	13.7 ± 9.8 (0-85)	0.2 ± 0.07 (0-1.2)	386.9 ± 245 (75-2500
Oslo (Norway) / 57 / 16	NA	833 ± 16	41± 1	123 ± 13	412 ± 61	NA	1.4 ± 0.2	180 ± 14
Madrid (Norway) / 57 / 16	61 ± 7	362 ± 13	44 ± 5	188 ± 24	476 ± 13	NA	NA	1927 ± 508
Yozgat (Turkey) / 58 / 45	28.5 ± 4.0 (23.2-31.7)	560 ± 92 (472-655)	40.4 ± 6.0 (33.5-44.5)	36.2 ± 5.2 (32.0-42.0)	NA	NA	2.31 ± 0.56 (1.67-2.67)	56.0 ± 7.0 (47.0-62.6)

Kayseri (Turkey) / 59 / 29	29.0 ± 13.0 (17.2-81.2)	237 ± 86.6 (127-419)	44.9 ± 35.3) (16.1-217)	36.9 ± 24.3 (11.8-144)	112 ± 122 (32.6-733)	NA	2.53 ± 2.49 (0.98-14.6)	74.8 ± 53.8 (27.9-312)
Other studies: North America								
Ottawa (Canada) / 60 / 45	43.3 (14.7-71.7)	431.5 (145.1-618)	15.2 (344-951)	65.84 (4.79-249.8)	112.5 (28.7-302.5)	1.3 (0.0-2.9)	0.37 (0.08-1.12)	39.05 (12.63-122)
Massachusetts, (USA) / 61 / 85	95 ± 74 (0-530)	456 ± 197 (89-1191)	NA	105 ± 204 (0-2130)	240 ±217 (35-1208)	NA	NA	73 ± 181 (0-1639)
Florida (USA) / 62 / 200	17.9 ± 59.6 (<1.34-552)	NA	8.69 ± 7.83 (<1.72-69.3)	16.5 ± 31.5 (<1.84-3721)	65.1 ± 86.5 (4.3-80)	0.69 ± 1.2 (<0.5-13.6)	NA	18.3 ± 32.5 (<1.43-386)
Hermosillo (Mexico) / 63 / 25	11.15	NA	4.70	26.34	387.98	NA	4.24	36.15
Other studies: Africa								
Gwagwalada (Nigeria) / 64 / 75	NA	96 ± 9.3	NA	97 ± 7.3	79 ± 7.2	NA	3.9 ± 0.1	210 ± 16.4
Mubi, Adamawa (Nigeria) / 65 / 10	5.40 ± 1.97	NA	NA	11.63 ± 1.99	102.2 ± 3.07	NA	NA	20.37 ± 1.97
Luanda (Angola) / 66 /	26 ± 4.4	258 ± 92	10 ± 3.3	42 ± 15	317 ± 177	5 ± 0.92	1.1 ± 0.47	351 ± 237

92	(17-37)	(157-728)	(6.2-32)	(18-118)	(142-1412)	(3.5-7.8)	(0.7-4)	(74-1856)
Other studies: Asia								
Singapore / 67 / NA	85.7 ± 11.4	NA	53.1 ± 18.5	246.9 ± 53.5	274.7 ± 55.1	NA	0.71 ± 0.3	68.6 ± 25.9
Ulsan (Korea) / 13 / 12	NA	NA	72.3 ± 20.9	139 ± 30	174 ± 3	NA	1.2 ± 0.4	136 ± 37
Ulsan (Korea) / 50 / 12	NA	NA	13.4 ± 2.9	89.8 ± 50.6	129 ± 15	NA	1.33 ± 0.98	92.1 ± 12.3
Taejon (Korea) / 68 / 81	NA	NA	NA	47 (17 -226)	214 (67-495)	NA	NA	52 (13-161)
Dhahran (Saudi Arabia) / 69 / 5	56.0 ± 19	231 ± 19	33.9 ± 6.2	104.2 ± 87.1	356 ± 186	5.01 ± 3.62	1.04 ± 0.36	40.3 ± 34.9
Calcutta (India) / 70 / 12	54 ± 3.4	619 ± 35	42 ± 2.3	44 ± 2.1	159 ± 6	23 ± 1.9	3.12 ± 0.32	536 ± 39
Dhanbad and Bokaro, (India) / 71 / 13	57 ± 28 (24-124)	NA	24 ± 12 (12-57)	26 ± 10 (13-48)	78 ± 27 (44-123)	NA	NA	48 ± 29 (17-128)
Dhaka (Bangladesh) / 72 /33	99 ± 16.9	NA	23 ± 4.22	22 ± 9.04	97 ± 28.8	5 ± 0.88	NA	35 ± 7.78
Islamabad (Pakistan) / 73 / 13	NA	NA	23 ± 6 (10-30)	52 ± 18 (30-80)	116 ± 35 (64.3-169)	NA	5.0 ± 1.0 (4.5-6.8)	104 ± 29 (60-150)
Aqaba (Jordan) / 74 / 140	20 ± 2.4	59 ± 1.5	51 ± 5.5	26 ± 4.5	114 ± 4.1	NA	2.0 ± 0.1	138 ± 6.2

Mutah (Jordan) / 75 / 24	NA	136 ± 39 (56-246)	1.70 ± 3.0 (1.0-11.3)	69 ± 39 (15-474)	132 ± 88 (65-351)	NA	1.33 ± 0.99 (1.3-3.6)	143 ± 109 (26-368)
Xi'an (China) / 76 / 65	167.28 ± 195.69 (28-853)	687 ± 192 (414-1318)	NA NA	94.98 ± 130.18 (20-1071)	421.46 ± 456.03 (80-2112)	10.62 ± 3.46 (5.95- 20)	NA NA	230.52 ± 431.02 (29-3060)
Urumqi (China) / 77 /42	56.27 ± 12.79	914.11 ± 94.46	43.23 ± 8.45	112.49 ± 46.12	407.76 ± 115.72	NA	1.19 ± 0.83	61.05 ± 14.13
Beijing, (China) / 78 / 25	85.6 ± 6.9	552 ± 60	NA	42 ± 8	214 ± 30	NA	1.2 ± 0.3	61 ± 17
Shanghai, (China) / 78 /25	242 ± 121	904 ± 218	NA	141 ± 56	699 ± 359	NA	0.9 ± 0.6	148 ± 58
Hong Kong (China) / 78 / 25	324 ± 136	639 ± 119	NA	534 ± 214	4024 ± 1278	NA	1.8 ± 1.6	240 ± 73
Baoji, (China) / 79 / NA	NA	804 ± 369 (545-2336)	48.8 ± 30.0 (33.3-219.3)	123 ± 43 (78-260)	715 ± 369 (385-1778)	NA	NA	408 ±295 (141-1847)
Nanjing (China) / 80 / 35	126 ± 47 (0.44-2.19)	646 ± 169 (382-1294)	55.9 ± 42.6 (24.5-268)	123 ± 54 (28.7-272)	394 ± 162 (140-798)	13.4 ± 1.7 (10.2-18.5)	1.10 ± 0.46 (0.44-2.19)	103 ± 48 (37.3-204)

NA = not available

– 4024 mg/kg). Mean Pb concentrations obtained in this study were found to be higher than the mean concentration from 34 cities while results from Lancaster (UK), London (UK) and Madrid (Spain) were ≥ 2x higher. The general similarity of results across all the cities suggests that the sources of PTEs in the urban street dust could be traced to common urban sources.

4.3.3 Estimation of daily intake of potentially toxic elements from urban street dust

In order to estimate the human health risk associated with exposure to urban dust, the concentration of PTE from a particular sample that a child (as the most sensitive receptor) could ingest to reach the estimated tolerable daily intake (TDI, for oral ingestion) was calculated (81-82). The calculated TDI for Pb is shown in Table 4.4 whilst that of other PTEs are shown in appendix F. Due to the carcinogenic nature of As, a TDI would be inappropriate therefore an oral index dose (ID_{oral}) has been proposed of 0.3 μg kg^{-1} bw day^{-1} for As (86). With respect to the maximum PTE daily intake (μg kg^{-1} bw day^{-1}), Pb exceeded the tolerable daily intake for oral ingestion (Table 4.4) for samples collected from Newcastle, Durham, Sunderland and Abakaliki. Other PTEs were found to be lower than the TDI_{oral} or ID_{oral} for As. Formula and details of calculations are shown as footnotes to Table 4.4. Also it was appropriate to introduce a realistic exposure frequency for a child. It was estimated that a child could be involved in outdoor activities for 1 hour a day (i.e. 7 hours a week). Based on an estimated exposure duration of 7 hours a week for 52 weeks (i.e. 364 hours in a year or 15.2 days /year), it was determined that the exposure frequency was 0.041. By applying this approach it was determined that the PTE concentrations (ng kg^{-1} bw day^{-1}) were considerably below the TDI and ID_{oral} respectively (Table 4.4 shows Pb values and appendix F shows values for other

Table 4.4: Maximum Pb estimated daily oral intake from urban street dust

Cities / country	Maximum estimated daily intake (µg kg^{-1} bw day^{-1}) based on 50 mg/day ingestion[@]	Maximum estimated daily intake (µg kg^{-1} bw day^{-1}) based on 50 mg/day ingestion and bioaccessibility[X] (gastric only)	Maximum estimated daily intake (µg kg^{-1} bw day^{-1}) based on 50 mg/day ingestion and bioaccessibility[X] (gastric + intestinal)	Maximum estimated daily intake rate (mg/kg) based on dustiness[”]	Maximum estimated daily intake (µg kg^{-1} bw day^{-1}) based on 50 mg/day ingestion and an estimated annual exposure frequency[+]	Amount of dust that could be consumed by a child[C] in order to exceed the guidelines (mg/day)
Newcastle upon Tyne, UK	4.40	2.37	2.02	0.03	180	40.9
Durham, UK	5.70	3.19	2.39	N/A	234	31.6
Liverpool, UK	2.46	1.06	0.91	0.08	101	73.2
Edinburgh, UK	3.42	1.92	1.61	0.03	140	52.6
Sunderland, UK	5.99	2.29	1.76	N/A	246	30.1
Abakaliki, Nigeria	4.88	2.54	1.90	N/A	200	36.9

N/A = Not available

[@] the maximum estimated daily intake (DI) was calculated using the formula DI= [EC x SDIR] / BW (81-82), where DI = daily intake (µg kg^{-1} bw day^{-1}) as determined in <125 µm fraction of the dust sample with the highest concentration; EC = Exposure concentration of the PTEs in <125 µm (µg/g); SDIR = soil + dust ingestion rate (0.05 g day^{-1}) (83); and BW = body weight (18.6 kg for a 3-6 year old child) (81). The maximum estimated daily intake and bioaccessibility was calculated by modifying the above equation to DI= [EC x SDIR X B] / BW where B is the bioccessibility fraction determined using Unified BARGE Method.

X based on the maximum bioaccessible concentration using the gastric phase.

“based on a determined air quality measurement (PM_{10}) in Newcastle City Centre, Liverpool and Edinburgh on the sampled days between the hours of 10.00 and 17.00 (http://uk-air.defra.gov.uk/data).

[+] the maximum estimated daily intake (DI) and estimated annual exposure frequency was calculated using the formula DI= [EC x SDIR x EF] / BW, where DI = daily intake (ng kg^{-1} bw day^{-1}as determined in <125 µm fraction of the dust sample with the highest

concentration; EC = Exposure concentration of PTEs in <125 µm (µg/g); SDIR = soil + dust ingestion rate (0.05 g day^{-1}) (83); EF = Exposure frequency = 0.041day^{-1} (estimated to be 7 hours a day, i.e. a child is likely to be involved in outdoor activities between the hours of 10.00 and 17.00 hours) for 52 weeks i.e. 364 hours per year or 15.2 days per year); and BW = body weight (18.6 kg for a 3-6 year old child) (81).

c child aged 3 - 6 years

TDI_{oral} for Cr = 150 µg kg^{-1} bw day^{-1} (84)

TDI_{oral} for Mn = N/A

TDI_{oral} for Ni = 12 µg kg^{-1} bw day^{-1} (85)

TDI_{oral} for Cu = 160 µg kg^{-1} bw day^{-1} (84)

TDI_{oral} for Zn = 600 µg kg^{-1} bw day^{-1} (84)

ID_{oral} for As = 0.3 µg kg^{-1} bw day^{-1} (86)

TDI_{oral} for Pb = 3.6 µg kg^{-1} bw day^{-1} (88)

PTEs). Formula and details of calculations are shown as footnotes to Table 4.4. Besides, the amount of dust per PTE that a child (age 3 – 6) would need to consume per day in order to exceed the soil / dust ingestion rate of 50 mg / day (83) was calculated. In this case, the amount of dust per PTE varied across the cities in proportion to the PTE concentrations. In the case of Pb, it was observed (Table 4.4) that the amount of dust that a child might need to consume was lower than recommended daily ingestion of 50 mg in Newcastle (40.9 mg /day), Durham (31.6 mg / day), Sunderland (30.1 mg / day) and Abakaliki (36.9 mg / day). The implication of this findings is that dust ingestion particularly in the cities represents potential pathway through which Pb could enter the human body especially children. However, further risk assessment via the application of bioaccessibility protocol is evident.

4.3.4 Bioaccessibility of PTEs in urban street dusts

Bioaccessibility results can indicate the amount of PTEs which can be absorbed into the body through the oral ingestion pathway; this is fundamental in assessing risks to humans particularly with respect to elevated Pb levels found in all the cities. The oral bioaccessibility of the PTEs from 90 urban street dusts, collected from six cities, as well as 2 certified reference materials (BGS Guidance Material 102 and BCR 143R) were determined using the *in vitro* gastrointestinal extraction procedure (UBM). The bioaccessible fraction (% BAF) was determined both in the 2 certified reference materials (BGS Guidance Material 102 and BCR 143R). In addition, to show the actual concentration of the PTE in the extract, minimum, median and maximum values (appendix G) have been used to present the results obtained from the *in vitro* gastrointestinal extraction of the urban street dust samples. However, the % BAF is shown only for the maximum determined PTE concentration for each extraction stage thereby representing the worst case scenario. Detailed information on stage I,

stage II and stage III *in vitro* gastrointestinal extraction, along with their respective standard deviation, are shown in appendix H. From the results, it was observed that the stage I (gastric) fraction gave a higher % BAF for all the 8 elements analysed from the 90 urban dust samples when compared to the stage II (gastric + intestinal) fraction. The reasons as to why higher PTEs bioaccessibility was obtained in stage I (gastric phase) had been given in the previous chapter (see 3.3.2). This study is in line with many current findings where higher PTEs bioaccessibility have been reported in the gastric phase (89-91). To this end, the % BAF of each element (gastric only) was plotted (Figures 4.15 – 4.22) for all the cities investigated; the results, shown as box plots, show the mean, median, box boundary (25th and 75th) percentile and whiskers (10th and 90th) percentile. In the case of Cd, only the bioaccessible fraction in three cities (Figure 4.16) was represented because Cd was below detection in most of the sites. It is seen that there is a wide variation in the % BAF of all the PTEs across the cities. The range of % BAF across the six cities is as follows: 12.3 - 62.8 % (Cr); 28.5 - 62.6 % (Mn); 7.30 - 50.8 % (Ni); 14.1 – 54.9 % (Cu); 25.1 – 55.1 % (Zn); 18.5 – 53.5 % (As); 32.2 – 59.8 % (Cd) and 24.5 – 56.2 % (Pb). The mean % BAF, across all cities / sites, irrespective of element was determined to be 40 ± 10%.

The bioaccessibility values achieved in this work could be as a result of the source(s) of these PTEs in the urban dust; it has been reported that PTEs of anthropogenic origin are typically more soluble in the gastrointestinal tract and therefore more bioaccessible (92). Although this study did not investigate the solid phase partitioning of these PTEs in dust, it is believed that the differences observed in their bioaccessibility are as a result of the chemical forms in which they are bound in the street dust (92).

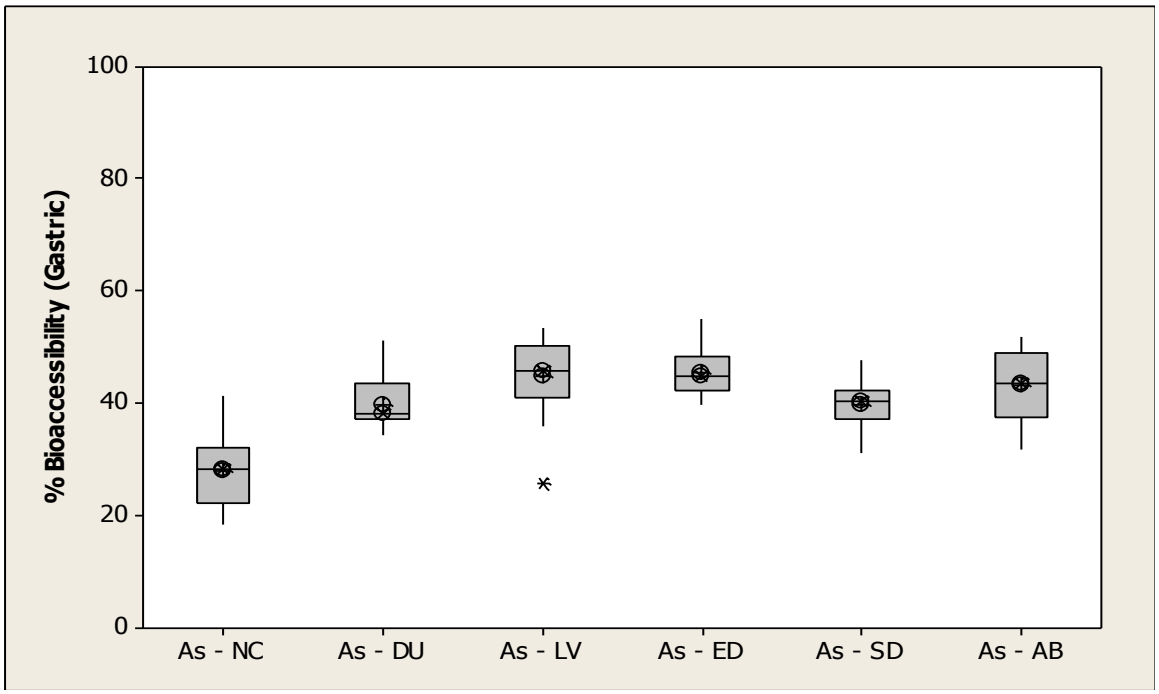

Figure 4.15: Box plot for the oral bioaccessibility (gastric only) of arsenic in urban street dust: indicating mean, median, box boundary (25th and 75th) percentile and whiskers (10th and 90th) percentile.

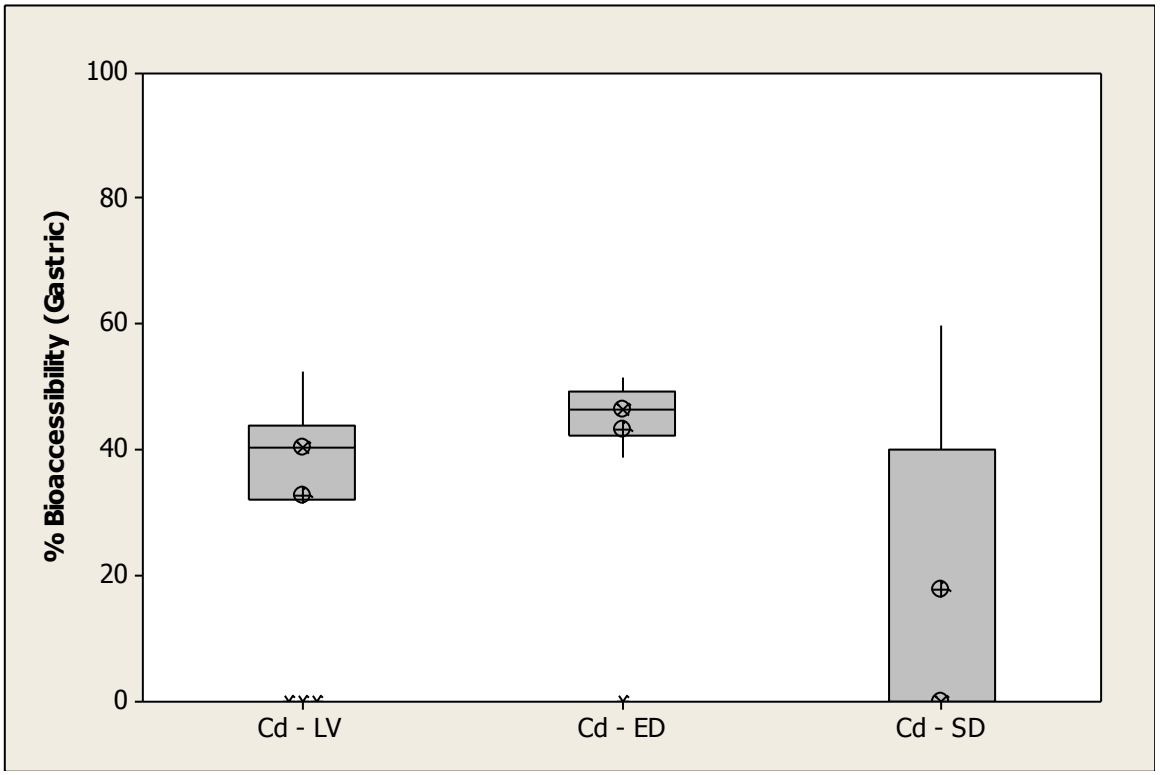

Figure 4.16: Box plot for the oral bioaccessibility (gastric only) of cadmium urban street dust: indicating mean, median, box boundary (25th and 75th) percentile and whiskers (10th and 90th) percentile.

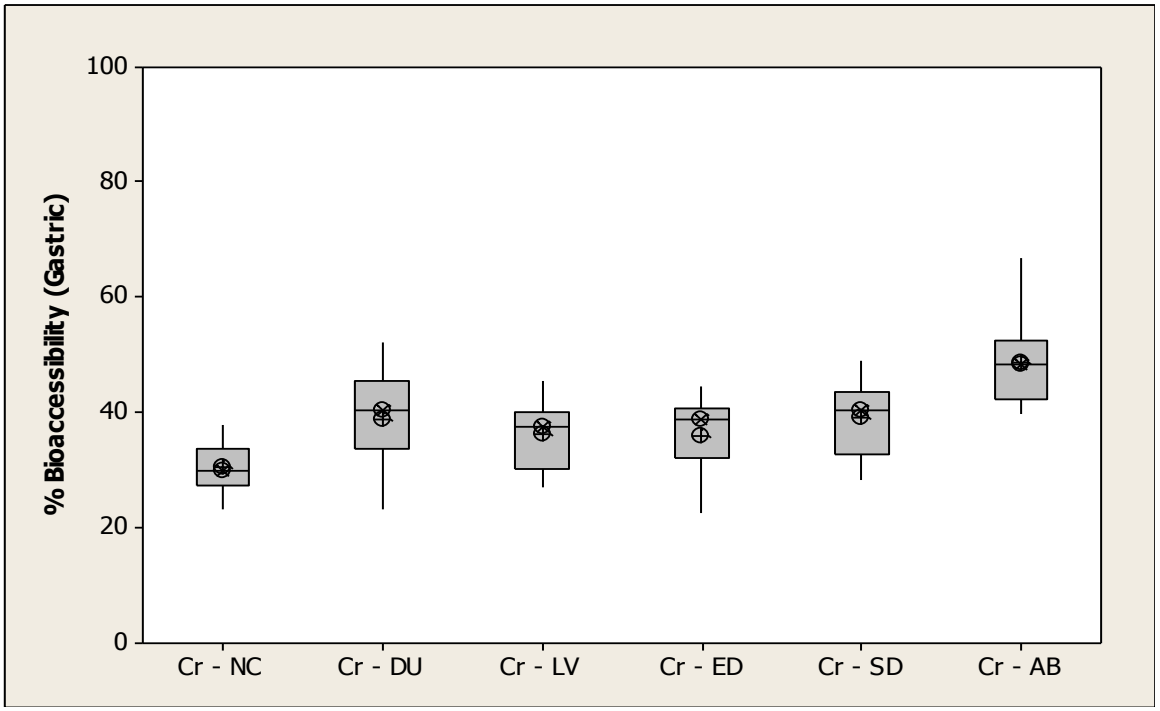

Figure 4.17: Box plot for the oral bioaccessibility (gastric only) of chromium in urban street dust: indicating mean, median, box boundary (25th and 75th) percentile and whiskers (10th and 90th) percentile.

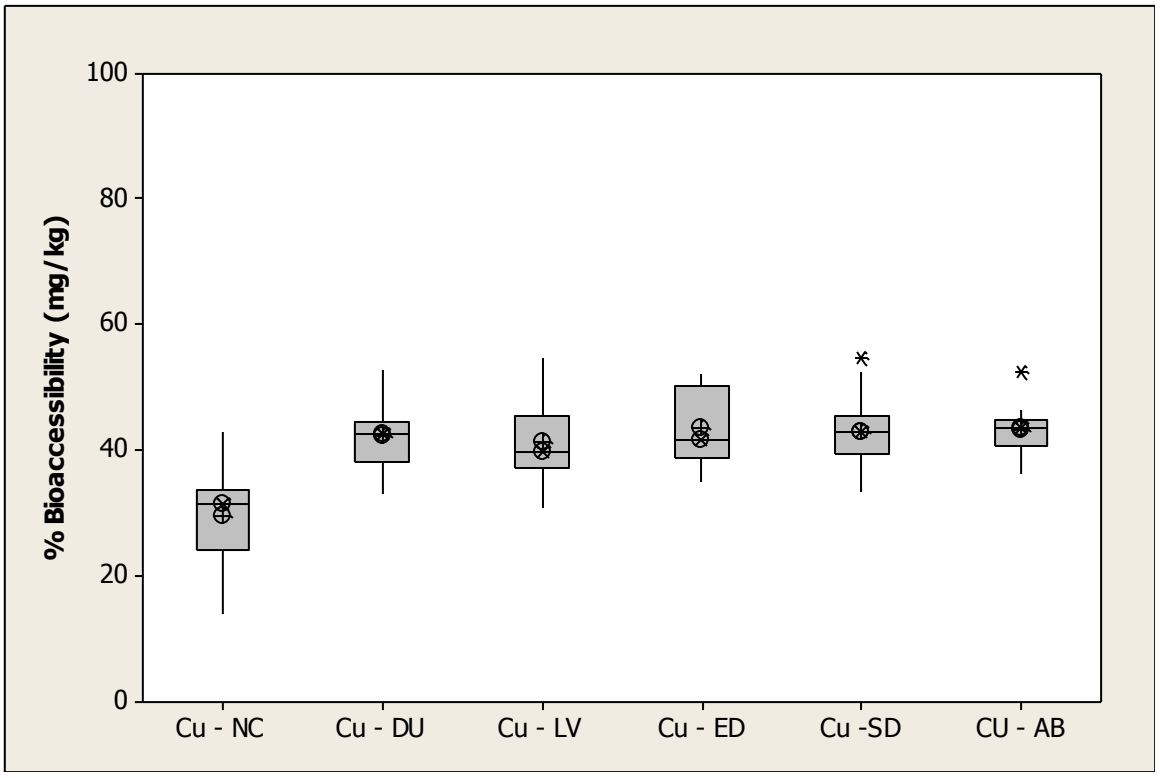

Figure 4.18: Box plot for the oral bioaccessibility (gastric only) of copper in urban street dust: indicating mean, median, box boundary (25th and 75th) percentile and whiskers (10th and 90th) percentile.

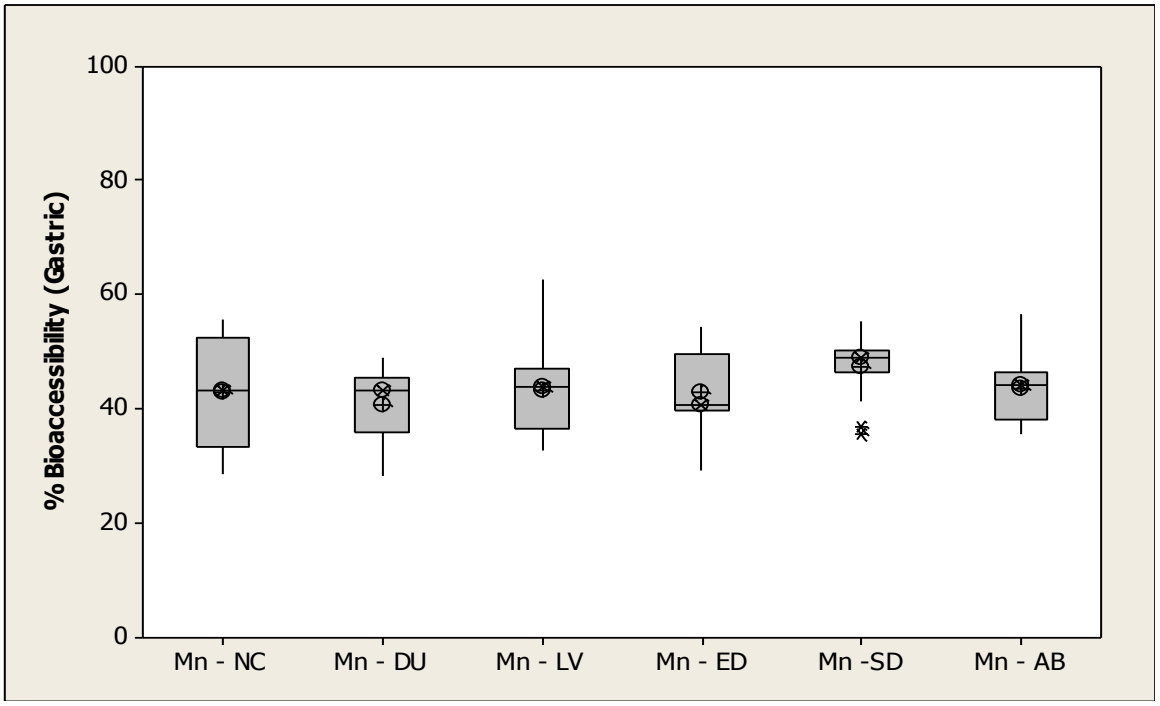

Figure 4.19: Box plot for the oral bioaccessibility (gastric only) of manganese in urban street dust: indicating mean, median, box boundary (25th and 75th) percentile and whiskers (10th and 90th) percentile.

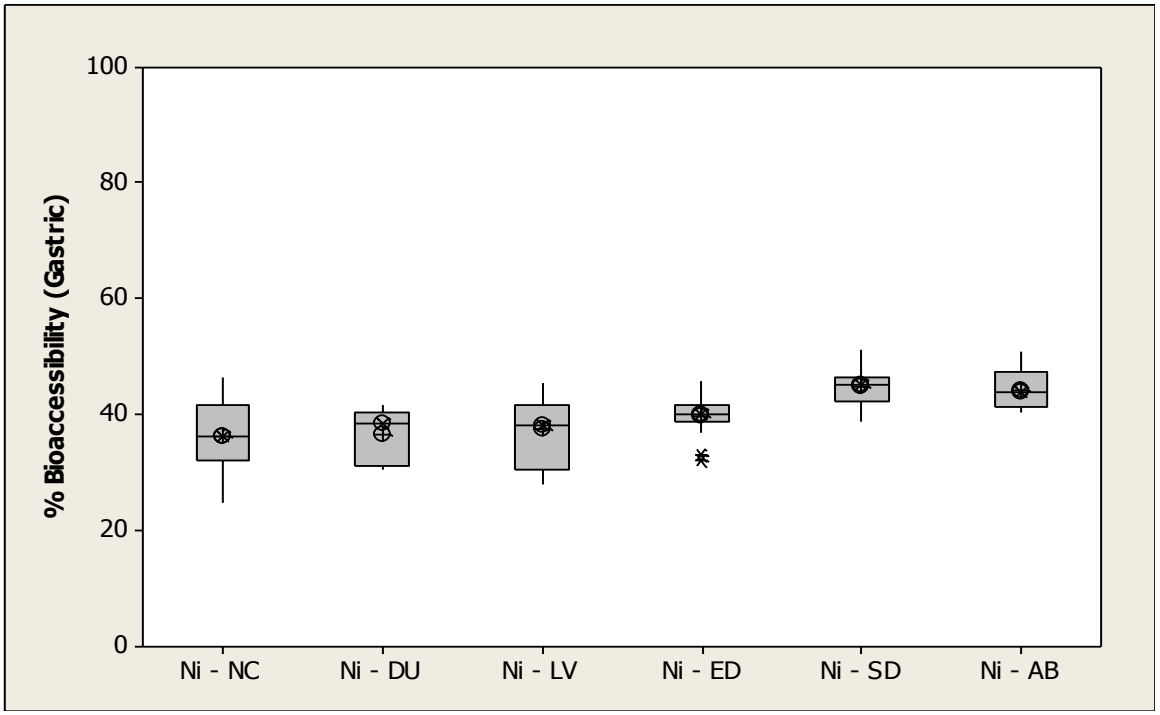

Figure 4.20: Box plot for the oral bioaccessibility (gastric only) of nickel in urban street dust: indicating mean, median, box boundary (25th and 75th) percentile and whiskers (10th and 90th) percentile.

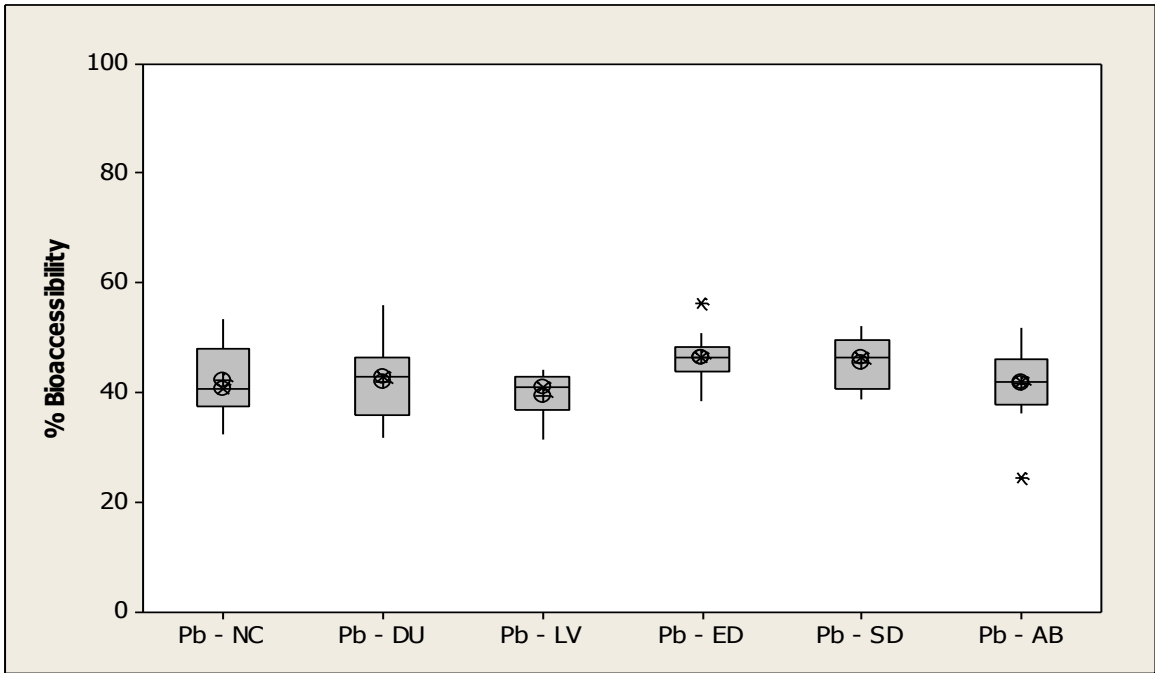

Figure 4.21: Box plot for the oral bioaccessibility (gastric only) of lead in urban street dust: indicating mean, median, box boundary (25th and 75th) percentile and whiskers (10th and 90th) percentile

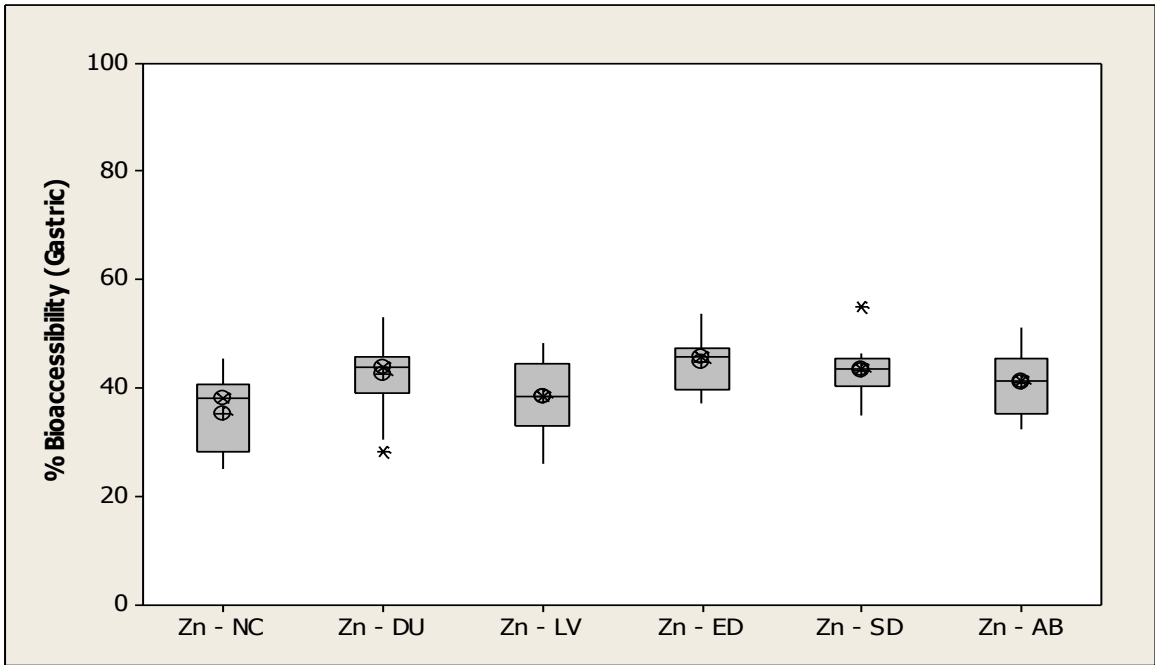

Figure 4.22: Box plot for the oral bioaccessibility (gastric only) of zinc in urban street dust: indicating mean, median, box boundary (25th and 75th) percentile and whiskers (10th and 90th) percentile.

Key: NC = Newcastle upon Tyne, UK; DU = Durham, UK; LV = Liverpool, UK; ED = Edinburgh, UK; SD = Sunderland, UK; and, AB = Abakaliki, Nigeria.

Considering the differences observed between total elemental concentrations, bioaccessible concentrations and percentage bioaccessibility (% BAF), the relationship between total elemental concentrations and the bioaccessibility stages were investigated via correlation analysis. The results (Table 4.5A for Pb) and appendix I for other elements, revealed that the concentration stages (total concentration and gastric, total concentration and gastrointestinal as well as gastric and gastrointestinal correlated significantly across the eight PTEs (correlation coefficient (r) > 0.812 and $p < 0.05$). Lower correlation was however observed in the bioaccessibility stages (total concentration and gastric, total concentration and gastrointestinal, gastric and gastrointestinal) (Table 4.5B for Pb) and appendix I for other PTEs. In this case, r varied from -0.015 to 0.874 and $p > 0.05$. In the same vein, to be able to ascertain the difference between stage I and II concentrations as well as their % BAF, a t test analysis was carried out. The result showed that with respect to all the PTEs, no significant differences in the concentration stages ($p > 0.05$) was observed whilst the bioaccessibility stages were statistically different from each other ($p < 0.05$) (Table 4.6 for Pb) and appendix J for other PTEs.

Furthermore, the maximum bioaccessible PTE concentration based on the ingestion rate of 50 mg/day ingestion rate (83) were determined for both gastric and gastrointestinal stages. Results for Pb (gastric only) in terms of μg kg^{-1} bw day^{-1}; are as follows: 2.37 μg kg^{-1} bw day^{-1}Newcastle); 3.19 μg kg^{-1} bw day^{-1} (Durham); 1.06 μg kg^{-1} bw day^{-1} (Liverpool); 1.92 μg kg^{-1} bw day^{-1} (Edinburgh); 2.29 μg kg^{-1} bw day^{-1} (Sunderland) and 2.54 μg kg^{-1} bw day^{-1} (Abakaliki). The results for other PTEs are shown in appendix F. It is noted from the results that based on an unintentional consumption of 50 mg soil / dust / day, the bioaccessible concentration for all the PTEs is below the guideline values across the cities, and as such does not represent

Table 4.5A: Correlation analysis of Pb in all cities (Concentration phase)

Elements	Correlation value	p-value	Stage
Newcastle upon Tyne, UK	0.983	0.000	T & G
	0.958	0.000	T &GI
	0.961	0.000	G & GI
Durham, UK	0.990	0.000	T & G
	0.989	0.000	T &GI
	0.993	0.000	G & GI
Liverpool, UK	0.975	0.000	T & G
	0.964	0.000	T &GI
	0.992	0.000	G & GI
Edinburgh, UK	0.995	0.000	T & G
	0.990	0.000	T &GI
	0.992	0.000	G & GI
Sunderland, UK	0.991	0.000	T & G
	0.998	0.000	T &GI
	0.991	0.000	G & GI
Abakaliki, Nigeria	0.991	0.000	T & G
	0.998	0.000	T &GI
	0.991	0.000	G & GI

T = Total concentration, G = Gastric phase, GI = gastric + intestine phase

.

Table 4.5B: Correlation analysis of Pb in all cities (% BAF phase)

Elements	Correlation value	p-value	Stage
Newcastle upon Tyne, UK	-0.167	0.553	T & G
	-0.418	0.121	T &GI
	0.874	0.000	G & GI
Durham, UK	-0.246	0.377	T & G
	-0.120	0.669	T &GI
	0.914	0.000	G & GI
Liverpool, UK	-0.031	0.914	T & G
	-0.019	0.947	T &GI
	0.853	0.000	G & GI
Edinburgh, UK	0.207	0.459	T & G
	0.521	0.046	T &GI
	0.838	0.000	G & GI
Sunderland, UK	-0.175	0.532	T & G
	-0.385	0.157	T &GI
	0.640	0.010	G & GI
Abakaliki, Nigeria	-0.015	0.958	T & G
	-0.074	0.793	T &GI
	0.552	0.033	G & GI

T = Total concentration, G = Gastric phase, GI = gastric + intestine phase

Table 4.6: T test analysis of Pb in all cities

Cities	Concentration stage (G & GI)		% BAF stage (G & GI)	
	t-value	**p-value**	**t-value**	**p-value**
Newcastle upon Tyne	0.695	0.493	3.243	0.003
Durham	0.286	0.776	2.961	0.006
Liverpool	0.896	0.378	4.375	0.0002
Edinburgh	0.497	0.622	4.467	0.0001
Sunderland	0.526	0.603	6.551	0.0005
Abakaliki	0.288	0.775	2.880	0.008

G = Gastric phase, GI = gastric + intestine phase

a significant risk to human health. However, it is not expected that a child would ingest (even one with pica behaviour) 50 mg of urban dust during a one hour per day visit (throughout the year) to these city centres. This study has shown however that a child would only need to ingest the following amounts of urban dust in order to exceed the Pb TDI, particularly in the specific locations identified i.e. 40.9 mg dust / day (Newcastle); 31.6 mg dust / day (Durham); 30.1 mg dust / day (Sunderland) and 36.9 mg dust / day (Abakaliki) (Table 4.4).

4.3.5 Adjustment to estimated daily ingestion rate based on known 'dustiness'

The calculated results have been based on a daily ingestion rate of 50 mg / day (83). However it is believed that this is an overestimate in the context of urban street dust ingestion. It is therefore suggested that the realistic assessment of human health risk should be based on the actual determined air borne particulate matter. Using the following methodology it is possible to estimate the known risk to a child on a specific date. The common particle size fraction measured in air borne particulate matter is 10 μm; this particular particle size fraction has the potential to easily enter the human body either through oral (mouth) or inhalation (nose / mouth) pathways (93). In the UK, daily air quality data is published (http://uk-air.defra.gov.uk/data) providing experimental values for selected cities including Newcastle upon Tyne, Liverpool and Edinburgh. Unfortunately no data exists for Durham and Sunderland based on this

source of air quality data; similarly no values are known for Abakaliki (Nigeria). As the sampling took place during summer 2010 (27 – 28th May in Newcastle upon Tyne); 5th June in Liverpool; and, 12th June in Edinburgh) it is reasonable to estimate that a child would be exposed to urban dust, and hence risk from oral ingestion, between 10.00 and 17.00 hours on these specific dates. The determined average experimental data (10 μm particle size, PM_{10}) available on these dates, for the selected 7 hours of exposure, are: 8 μg / m^3 in Newcastle upon Tyne; 38 μg / m^3 in Liverpool; and, 9 μg / m^3 in Edinburgh. If we assume that a child would occupy an active area of 1 m^3 (based on an estimate of hand- to-mouth distances) at any one time it is possible to calculate the amount of dust ingested based on the experimental data of: 8 μg per day (0.008 mg per day); 38 μg per day (0.038 mg per day) and 9 μg per day (0.009 mg per day) for Newcastle upon Tyne, Liverpool and Edinburgh, respectively. The results are shown in Table 4.4 for Pb and appendix F for other PTEs. It is observed that all PTEs were found to be considerably below the TDI_{oral} (or the oral Index dose for As) across the cities.

4.4 Conclusion

Results from the six cities indicate that Pb exceeded the TDI in Newcastle, Durham, Sunderland and Abakaliki in terms of total concentration whereas the bioaccessible fractions were low for all elements across the cities. Bioaccessibility results can indicate the amount of PTEs which are available for absorption into the body through the oral ingestion pathway and this is fundamental in assessing risks to humans particularly with respect to the elevated Pb found in some of the cities studied. Whilst there is a wide variation in the % BAF across all of the PTEs, the typically high observed bioaccessibility (range: 19% – 63%) could be as a result of the predominant sources (anthropogenic) of these PTEs in the urban dust since PTEs

from anthropogenic origin are typically reported to be more soluble in the gastrointestinal tract and therefore more bioaccessible (92).

Given the complexity of modelling exposure and intake pathway (ingestion / inhalation / dermal sorption), particularly in an urban environment, the risk assessments must be treated with caution, but they do highlight the PTE of most concern. Furthermore, whilst it is not expected that a child would ingest 50 mg (accepted soil + dust ingestion rate) (83) of urban dust during a daily visit to the city centres of these cities, the study shows that a child only needs to ingest less than 42 mg dust / day in order to exceed the Pb TDI in three cities. This, coupled with the typically high % bioaccessibility highlights the need for regular monitoring of PTE levels in the urban environment and of robust environmental management practices, including regular street sweeping. With the gradual move from leaded to unleaded petrol a number of studies have observed a reduction in Pb concentration in urban street dusts over recent decades (e.g. 36, 54, 57), however despite this decline monitoring of Pb and other PTEs as part of atmospheric monitoring programs remains warranted along with environmental policies (i.e. Air Quality Management Zones) to target a reduction in human exposure to PTEs in the urban environment.

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Section B: Human health risk assessment via inhalation bioaccessibility

Chapter five: Development of simulated epithelial lung fluid (SELF) to assess lead bioaccessibility from inhaled particulate matter (PM_{10}).

5.1 Introduction

In vitro experiments are aimed at simulating fluids that represent the natural physiological fluids which could be used in assessing health risk from inhaled environmental contaminants. The probability of inhalation depends on the particle size fraction, air movement within the exposure routes, and breathing rate. Inhalable particulate (< 10 μm) matter could be inhaled through the nose or the mouth and the fate of inhaled particulates depends on the nature of the physiological fluids and physiochemical properties of the particulates. The (< 10 μm) inhalable particle size fraction penetrates, deposits and is retained up-to different compartments of the human respiratory tract with the larger components commonly found in the nasopharynx and tracheobronchial region whilst the finer (< 1-2 μm) particles gets deposited in the deepest region (alveolar) (1-3).

To be able to formulate fluids that would truly represent the respiratory tract, all the chemical components (organic and inorganic) must be included; therefore, an understanding of the respiratory compartments and their functions, as well as the chemical compositions is fundamental. Basically, the respiratory system is comprised of three compartments; the nasopharynx, tracheobronchial, and the pulmonary (4-5). Classification of the respiratory system into different compartments gives a clearer understanding of the processes involved in particle inhalation, deposition and removal. The medical physiology and details of the various compartments had earlier been presented in chapter two (Figure 2.3) The nasopharynx protects the lower lung against inhaled particle through the natural structural design of the airflow which allows only the fine particles to pass through

this region; particles retained in this region can be removed from the respiratory tract by sneezing or blowing through the nose. In the tracheobronchial, the ciliated mucus linings help to transport particle-laden out of the respiratory tract to the oral cavity where it can either be swallowed or expectorated (coughed out). The epithelial lining fluids located within the nasopharynx and tracheobronchial region form an interface between the respiratory epithelial cells and the outer environment (6). The pulmonary region contains alveolar macrophages which are cells capable of removing inhaled particulates through phagocytosis (engulfing of particles). However, not all inhaled particulates are removed as soluble parts dissolve in lung fluids.

During the process of clearing inhaled solid particles, oxidants such as oxygen, ozone and nitrogen (IV) oxide are produced and these oxidants cause injury to the neighbouring cells (7). But studies (8-10) have shown that the epithelial lining fluid of the respiratory tract contain adequate concentrations of antioxidants (i.e. albumin, ascorbic acid, glutathione and uric acid) that could neutralise the damaging effects of these oxidants and help to maintain its integrity. Investigations (11-13) have also revealed that pulmonary surfactant (i.e. cysteine, dipalmitoylphosphatldylcholine (DPPC), glycine and mucin) being synthesised by the alveolar cells helps to provide mechanical stability by reducing the surface tension of the alveolar air-liquid surface. In addition to the presence of organic components in the epithelial lining fluid of the human lung, available *in vivo* data (14-15) have shown that inorganic components are present in the lung fluids. In formulating a new simulated epithelial lining fluid for this method development, all the organic and inorganic chemical components that are found to be present in the human epithelial lining fluid need to be correctly represented. It is expected that in mimicking the epithelial lining fluids located within the nasopharynx and tracheobronchial regions of the human respiratory system, all

the chemical components that are present must be fully represented so as to have solutions that truly resemble respiratory fluids. In addition, this protocol has also simulated pH and temperature similar to the human natural environment. This approach is recommendable for every *in vitro* experiment simulating the respiratory system because the solubility of inhaled particles does not depend only on its characteristics but also on the solvent characteristics.

The understanding of the composition of extracellular fluid (ECF), which is often referred to as body fluid physiology, was pioneered by James Gamble who introduced physiology into clinical practice. Gamble and his colleague (Darrow) (16) were the first to investigate the chemical anatomy and physiology of the extracellular fluids. Their research revealed that the extracellular fluids (blood plasma and interstitial fluid) consist of cations (sodium ions, potassium ions, calcium ions and magnesium ions), anions (carbonate ions, chloride ion, phosphate ions and sulphate ions) and organic components (cysteine and citrate). Table 5.1 shows these reagents and their concentrations and the combination of these reagents were referred to as Gamble's solution (17-18).

Table 5.1: Chemical composition of Gamble's solution

Reagents	Molar concentration
Ammonium chloride (NH_4Cl)	0.010
Calcium chloride ($CaCl_2$)	0.0002
Cysteine ($C_3H_7NO_2S$)	0.001
Glycine (H_2NCH_2COOH)	0.006
Sodium chloride (NaCl)	0.116
Sodium citrate dihydrate ($C_6H_5Na_3O_7$)	0.0002
Sodium dihydrate phosphate (NaH_2PO_4)	0.0012
Sodium hydrogen carbonate ($NaHCO_3$)	0.027

In an attempt to improve on this pioneer work, many authors have modified the original Gamble solution in order to simulate lung fluids that would truly represent the

natural human fluids. Such modification was basically in terms of the name of the fluid and chemical components (type and amount). An overview of such works in terms of name and reagents include; Serum ultra-filtrate simulant (19) which differed from Gamble's solution by having sulphuric acid (H_2SO_4), diethylenetriaminepentacetic acid (DPTA) and alkylbenzyldimethylammonium chloride (ABAC). Artificial alveolar fluid (20) differed from the original Gamble's solution by addition of sodium sulphate (Na_2SO_4), sodium tartrate dehydrate ($C_4H_4O_6Na_2.2H_2O$), sodium lactate ($C_3H_5NaO_3$) and sodium pyruvate ($C_3H_3O_3Na$) Modified Gamble's solution (21) differed with sodium sulphate (Na_2SO_4), sodium tartrate dehydrate ($C_4H_4O_6Na_2.2H_2O$), sodium lactate ($C_3H_5NaO_3$) and sodium pyruvate ($C_3H_3O_3Na$). Simulated lung fluid (22) differed from the original Gamble's solution with magnesium chloride hexahydrate ($MgCl_2.6H_2O$), sodium sulphate (Na_2SO_4), sodium tartrate dehydrate ($C_4H_4O_6Na_2.2H_2O$), sodium lactate ($C_3H_5NaO_3$) and sodium pyruvate ($C_3H_3O_3Na$). These formulations have been used to investigate the lung bioaccessibility of diverse elements from environmental matrices.

A thorough examination of these studies would reveal wide discrepancies in terms of chemical composition. It is on these premises that this research was undertaken to bridge the gap between published works and the natural chemical composition of the human epithelial lung fluids. This holistic approach has distinguished this research from other studies as none of the chemical compositions in the literature included all the antioxidants and surfactant-proteins present in the human epithelial lining fluid.

5.2 Experimental.

5.2.1 Instrument and reagents

All chemicals used in the analysis were certified analytical grade. Concentration nitric

acid (HNO_3) and concentrated hydrochloric acid (HCl) were supplied by Fisher Scientific UK Ltd. (Loughborough, Leicestershire). Sodium hydrogen phosphate (NaH_2PO_4) and potassium hydrogen phosphate ($NaHPO_4$) were purchased from Sigma-Aldrich Co. (Gillingham, UK). Sodium chloride (NaCl), anhydrous sodium sulphate (Na_2SO_4), potassium chloride (KCl), calcium chloride ($CaCl_2.2H_2O$), sodium bicarbonate ($NaHCO_3$), magnesium chloride ($MgCl_2.6H_2O$), sodium hydroxide (NaOH), uric acid, bovine serum albumin (BSA) and concentrated nitric acid (69% HNO_3) were all obtained from Merck (Poole, UK), Mucin (pig) was obtained from Carl Roth, GmbH (Karlsruhe, Germany). Ascorbic acid, glutathione, cysteine, dipalmitoylphosphatidylcholine (DPPC), and glycine were obtained from Sigma-Aldrich Co. (Gillingham, UK). A multi-element standard containing Pb and other trace elements and internal standard solution containing indium (In), scandium (Sc) and terbium (Tb) were obtained from SPEXCerPrep (Middlesex, UK). Ultra-pure water of conductivity 18.2MΩ-cm was produced by a direct Q^{TM} Millipore system (Molsheim, France). Certified reference materials: BCR 038 (fly ash from pulverised coal with a particle size fraction of < 10 μm), BCR 143R (sewage sludge amended soil with a particle size fraction of < 90 μm), BCR 176R (a fly ash with a particle size fraction of < 105 μm), and BCR 723 (a road dust with a particle size fraction of < 105 μm) was purchased from LGC-Promochem (London, UK), while BGS Guidance Material 102 (naturally contaminated soil from North Lincolnshire with a particle size fraction of < 40 μm) was obtained from British Geological Survey (Keyworth, UK). The soil sampled used for the preliminary method development had been previously used (23). The soil sample (< 250 μm) was ball milled. Sample digestions were carried out using a start D multiprep 42 high throughput rotor microwave system (Milestone Microwave Laboratory Systems) supplied by Analityx Ltd. (Peterlee, UK)

while sample measurement was carried out using an ICP-MS X series II (Thermo Electron Corporation, Cheshire, UK).

5.2.2 Preparation of simulated epithelial lung fluid (SELF) for *in vitro* extraction test

In order to avoid cross contamination and to ensure reliability and reproducibility of results, all vessels used for the preparation of simulated epithelial lung fluids and bioaccessibility extraction protocol were soaked in an acid bath containing 10 % HNO_3 for 24 hours and rinsed with ultrapure water. Chemical components needed to prepare 1000 ml of simulated epithelial lung fluid were prepared in two phases (inorganic and organic). To prepare the inorganic phase (500 ml), 6020 mg NaCl, 256 mg $CaCl_2$, 150 mg $NaHPO_4$, 2700 mg $NaHCO_3$, 298 mg KCl, 200 mg $MgCl_2$ and 72 mg Na_2SO_4 were accurately weighed into a 500 ml HDPE screw top bottle containing ultra-pure water with the water level maintained at the mark and thoroughly mixed. To prepare the organic phase (500 ml), 18 mg ascorbic acid, 16 mg uric acid and 30 mg glutathione were also accurately weighed into a 500 ml HDPE screw top bottle containing ultra-pure water with the water level maintained at the mark, the resulting solution was thoroughly mixed. The inorganic and organic components were simultaneously poured into a 2 L HDPE screw top bottle containing additional constituents; 260 mg albumin, 122 mg cysteine, 100 mg DPPC, 376 mg glycine and 500 mg mucin, this was thoroughly mixed until all the components dissolved. The pH was measured and found to be 7.8; this was adjusted to 7.4 ± 0.2 by adding about 0.2 ml HCl.

5.2.3 Sample preparation and bioaccessibility extraction protocol for preliminary method development.

0.3 g of the soil sample was accurately weighed into a labelled 50 ml screw-cap Sarstedt tubes (extraction tube). The water bath was switched on for 2 hours prior to

the commencement of the bioaccessibility extraction with the temperature set at 37 ^{0}C ± 2. The prepared simulated epithelial lung fluid was warmed in a water bath for 2 hours maintained at a temperature of 37 ^{0}C ± 2 to simulate the human body temperature. After 2 hours, the pH was checked and found to be 7.4. A calibrated Gilson pipette was used to measure 20 ml of the fluids which was added to the each of the extraction tubes containing the samples. The tubes were firmly capped and manually shaken. This was followed by shaking the mixture on an end-over-end rotator maintained at 37 ^{0}C ± 0.2 for 0, 0.5, 1, 2, 3, 4, 5, 6, 10, 12, 24, 48, 60, 70, 80, 96, 170 hours. The resulting solution was then centrifuged at 3000 rpm for 10 min. Then 1 ml of the supernatant was pipetted into 10 ml Sarstedt tube previously holding 9 ml of 0.1 M HNO_3 and 30 µl of mixed internal standard (indium, scadium and terbium). The sample was stored at < 4 ^{0}C prior to ICP-MS analysis. Then the residual component was air dried for 48 hours, gently disaggregated, reweighed and subjected to an acid digestion protocol.

5.2.4 Sample preparation and bioaccessibility extraction protocol for certified reference / guidance materials and a soil sample used in the method validation.

0.3 g of five certified reference / guidance materials and one soil sample were accurately weighed into labelled 50 ml screw-cap Sarstedt tube in triplicate. The bioaccessibility extraction protocol described was followed and samples extracted for 96 hours, the resulting solution was then centrifuged at 3000 rpm for 10 min. Then 1 ml of the supernatant was pipetted into 10 ml tube previously holding 9 ml of 0.1 M HNO_3 and 30 µl of a mixture of internal standard (In, Sc and Tb). The sample was stored at < 4 ^{0}C prior to ICP-MS analysis.

5.2.5 Protocol for total Pb determination via microwave digestion system

0.5 g of the each sample and the certified reference / guidance materials were accurately weighed into a 65 ml PFA (a perfluoroalkoxy resin) microwave vessel pre-cleaned with concentrated acid. Aqua regia of 13 ml (HCl: HNO_3, 3: 1 v/v) was carefully added into the PFA vessels and sealed with a TFM cover. The solution was gently swirled to homogenize the sample with the reagents; the vessels were then introduced into the safety shield of the rotor body and then placed in the polypropylene rotor of the microwave oven. All the vessels containing samples were properly arranged prior to starting the microwave digestion process. The microwave oven was operated at a temperature of 160^0C, power of 750 watts, extraction time of 40 mins and a ventilation (cooling time) of 30 mins. After cooling, the digested samples were filtered using a Whatman filter paper (grade 41, pore size 20 µm) into 50 ml volumetric flask. The filtrate was diluted to the mark with ultrapure water of resistivity 18.2 MΩ-cm at 25^0C. It was then transferred into a 50 ml Sarstedt tube and stored in the refrigerator (< 4 ^{0}C) prior to Pb content determination using ICP-MS.

5.2.6 ICP-MS analytical quality control

Samples to be analysed using the ICP-MS was prepared in triplicate by measuring 1 ml of either the filtrate, certified reference materials (CRMs) or blank into a 10 ml sarstedt tube; this was followed by addition of 30 µl of a mixture of internal standards (In, Sc and Tb)) and 9 ml of water (1% HNO_3). The use of CRMs and sample preparation in triplicate was used to assess precision and accuracy of the methodology whilst reagent blanks were included to check for potential contamination from extraction tubes and reagents. Calibration standards of 0-400 ppb (0, 20, 40, 60, 80, 100, 200 and 400 ppb) were prepared from the 100 ppm of

the stock solution with internal standard; this was used to calibrate the instrument and also construct the calibration graph. The instrument was tuned to verify mass resolution and maximise sensitivity in the standard mode. The instrument was re-calibrated with a particular calibration standard (100 ppb) after every ten samples to ensure instrument consistency and precision. A calibration curve for Pb based on the concentration range was done and the correlation coefficient (R^2) was 0.999. The Pb concentrations in both the total digestion blanks and the simulated epithelium lung fluid blanks were not detected. ICP-MS operating conditions for total Pb determination are shown in Table 5.2.

Table 5.2: ICP-MS operating conditions for total Pb determination

ICP-MS parameters	Standard Mode
Nebulizer gas flow (L/min)	0.83
Forward Power (W)	1400
Cool gas flow (L/min)	13.0
Dwell time per isotope (ms)	10
Collision cell gas (L/min)	NA
Quadrupole bias (V)	-1.0
Hexapole bias (V)	0.0
Internal standards	^{45}Sc, ^{115}In and ^{159}Tb
Isotope monitored	^{208}Pb,

NA = not applicable

5.3 Results and discussions

5.3.1. Total Pb content in the certified reference / guidance materials and soil sample.

Total Pb content in the certified reference / guidance materials and the soil sample have been presented in Table 5.3. Based on triplicate determination on nine different occasions, the results obtained shows that there is good agreement between measured total Pb and certified values across the reference / guidance materials.

This shows excellent accuracy and precision. In order to confirm the robustness of this analytical method, the mass balance recoveries were calculated and % total recoveries ranged from 91.1 % to 101 (Table 5.3). Mass balance results show that Pb loss or gain in all the experimental stages were insignificant indicating that the analytical protocols employed are robust.

5.3.2. Preliminary method development

The residence time of inhaled particulate matter (PM_{10}) in the respiratory tract varies, depending on the characteristic of the material and the health state of the individual concerned. It is expected that the longer the residence time the higher the chances of dissolution. The extraction-time employed in mimicking the lung should be synonymous with particulate matter residence time in the lung. This will allow *in-vitro* experiments to fully explore the extraction profile of a particulate matter in the lung with time. A study (24) that investigated the determination of the regional deposition of aerosol particles in the human respiratory tract revealed that the time required for the removal of deposited materials in the lower lung is longer than that required for the removal of materials deposited in the upper respiratory tract. It has also been suggested that the residence time of materials deposited in the lower lung by sedimentation and diffusion are removed slowly, with clearance time amounting to days (25). A study (26) on the effect of lung structure on mucociliary clearance on the particle retention in human and rat lungs observed that about 10 to 15% of initially deposited particles in the human bronchial tree were still present after 24 hours. Furthermore, a recent study (27) on Pb bioaccessibility via inhalation pathway noted that a minimum extraction time of 100 hours is conservative to obtain maximum Pb bioaccessibility.

Table 5.3: Lead in certified / guidance materials and soil sample: total content, inhalation bioaccessible fraction and residual digest.

Sample	Certified Reference /Guidance Material values (mg/kg)	Measured Total content (mg/kg)	*In-vitro* lung extraction (mg/kg)				
			Stage I (Bioaccessible Pb)		Stage II (Residual digest)	Total Pb content (Stage I + II)	
		Mean ± SD; (n = 3)	Mean ± SD; (n = 3)	% BAF	Mean ± SD; (n = 3)	Mean (n = 3)	% Total Recovery
BCR 038	262 ± 11	252 ± 3[+]	0.8 ± 0.06	0.317	252 ± 20	253	100
BCR 143R	174 ± 5	172 ± 3[+]	14.4 ± 2.2	8.37	160 ± 2	174	101
BCR 176R	5000 ± 500	5024 ± 51[+]	190 ± 31	3.78	4876 ± 311	5066	101
BCR 723	866 ± 16	851 ± 21[+]	33.8 ± 3	3.97	832 ± 18	866	100
BGS 102	79.4 ± 1.4	70.2 ± 3.4[+]	3.5 ± 0.2	4.96	68.8 ± 0.6	72.3	91.1
Ball milled soil	NA	2953 ± 97[#]	31.4 ± 3.6	1.06	2920 ± 86	2951	99.9

NA = not applicable; + n = 9 (mean values for nine successive occasions); # n = 6 (mean values for six successive occasions)

% BAF: $\% \text{ BAF} = \frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – Pb concentration (mg/kg) in the certified reference / guidance materials obtained via the application of simulated epithelial lung fluid and $C_{total\ content}$ - Pb total content (mg/kg) in certified reference/guidance materials obtained via microwave digestion protocol.

% Residual: residual fraction calculated as a fraction of the total content.

The study also reported that an *in vitro* experiment needs to be able to evaluate reasonable long residence times, in order to be able to track the gradual pattern of the extraction profile of the environmental contaminant in the lung with time

In order to ascertain the optimal extraction-time suitable for this method, various extraction times; 0, 0.5, 1, 2, 3, 4, 5, 6, 10, 12, 24, 48, 60, 70, 80, 96 and 170 hours were investigated. The extraction profile showed that the bioaccessible Pb increased with time from 0 hours to 96 hours and plateaued (Figure 5.1). A gradual increase was observed 30 minutes after the start of the experiment and continued until 96 hours. The results demonstrate that the bioaccessible lead in the soil sample increased from 13.6 mg / kg at 0.5 hour to 28.6 mg / kg at 96 hours (4 days) and then plateaued subsequently to 27.8 mg / kg after 170 hours (7 days) (appendix K), justifying that the minimum optimal- extraction time for this method is 96 hours (Figure 5.1).

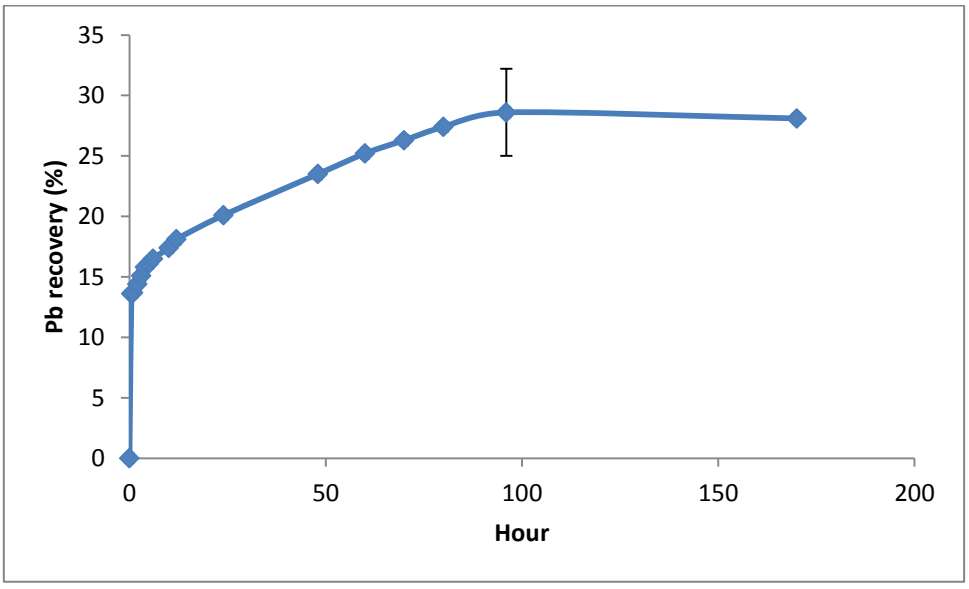

Figure 5.1: **Lead recovery**

In this investigation, exposure duration of 96 hours (4 days) has proved to be adequate to detect relatively maximum Pb bioaccessibility. Moreover, this technique

is anticipated to provide a maximum bioaccessible Pb and this is also, a precautionary protocol for risk assessment.

5.3.3. Lead bioaccessibility in the certified reference / guidance materials

The % bioaccessible Pb fraction (% BAF) was calculated by dividing the bioaccessible Pb with the total Pb content measured and then multiplied by 100. The bioaccessible Pb fractions obtained in the reference / guidance materials are as follows: BCR 038 (0.32 %), BCR 143R (8.4%), BCR 176R (3.4%), BCR 723 (4.0%), and BGS 102 (5.0 %). This indicated that the bioaccessible fraction varies across the reference / guidance materials with each one showing different bioaccessibility. The explanation to the variation of Pb bioaccessibility in these reference / guidance materials could be due to specific combination of chemical, biological, and environmental factors which influence bioaccessibility, particularly differences in their sources, particle size fractions and geochemical forms. However, it is seen that in all cases the inhalation bioaccessibility is low. This is not surprising because Pb found in environmental matrices predominantly shows low solubility, hence its continual accumulation in the environment (28-29). The lowest bioaccessibility (0.32 %) was observed in BCR 038 whilst the highest bioaccessible lead (8.4 %) was observed in BCR 143R.

However, of paramount concern with respect to bioaccessibility are the geochemical forms of Pb in these materials. The ubiquitous elemental- sequestering properties of different environmental matrices may significantly lower the bioaccessibility of Pb upon leaching and it is expected that Pb in these materials exists in several geochemical forms (oxides, sulphates, carbonates) and its bioaccessibility in the simulated epithelium lung fluid would differ significantly. Moreover, Pb tends to bind

to these environmental matrices in different degrees; hence, bioaccessibility would vary accordingly. The influence of solid phase partitioning on bioaccessibility of Pb has been relatively studied. A study (30) on bioaccessibility of Pb in high carbonate soils reported that Pb bioaccessibility was significantly low and different among soil samples analysed. An investigation (31) of Pb release from smelter and mine waste impacted materials under simulated conditions and relation to speciation observed that Pb released from the materials were generally low.

Studies on the bioaccessibility of Pb in simulated lung fluids are relatively few. Even with the available ones, comparison of results is complicated due to differences in chemical compositions and experimental conditions such as; extraction time, pH and leaching volume. In terms of the chemical composition, it has been assumed (32) that the addition of organic components, particularly protein would adversely affect experimental results due to poor dissolution and dispersion. Based on this assumption, most of the previous studies using simulated lung fluids have omitted one organic component or the other but the primary aim of simulating biological fluids is to be able to represent real physiological fluids and the omission of any biological component would mean deviation from natural biological fluids. Moreover, it has been noted (33) that such omission would amount to underestimating the true respiratory bioaccessibility. This research deviated from all the previous studies by incorporating proteins, antioxidants, surfactants and other components in an attempt to simulate lung fluids that truly represent biological fluids. Notwithstanding limited research in lung bioaccessibility and the wide variation in terms of chemical composition, this study has been compared with other studies. The optimal extraction time of 96 hours determined in this work is similar to the 100 hour extraction time recommended from a previous study (27) that investigated the

bioaccessibility of Pb from Welsh mine waste using a respiratory uptake test. The study investigated various extraction times ranging from 2 to 630 hours and observed that an extraction time of 100 hours would give a reasonable, conservative estimate of Pb bioaccessibility via this exposure pathway. In terms of Pb bioaccessibility, the result from this work is in the range 1 % to 23 %, this is higher than bioaccessibility results (0.32% to 8.4 %) obtained in this current study. An investigation into the development of an *in vitro* method to estimate lung bioaccessibility of metals from atmospheric particles (33) used four certified reference materials to validate the method development; the study noted that bioaccessibility result is both speciation and element dependent. It was observed that Pb bioaccesibility was as low as 3.3 % while Zn bioaccessibility was as high as 95.2 %, Pb bioaccessibility result obtained in this study particularly BCR 038 (1.3 %) is slightly higher than the bioaccessibility of Pb in BCR 038 (0.32 %) obtained in the current research.

5.4. Conclusion

Although the bioaccessible Pb was low across the certified / guidance materials, an optimal extraction time of 96 hours attained using simulated epithelium lung fluid is able to give a reasonable Pb bioaccessibility that would be used to assess human health risk via inhalation scenario. At the time of this study, there is no in vivo data for method validation but the mass balance approach employed shows that the analytical method is robust and reliable. In vivo data for method validation is declining due to ethical issues, moreover, it is also believed that animal physiology and anatomy differs from that of humans.

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Chapter Six: Bioaccessibility of Pb in urban dusts following extraction with simulated epithelium lung fluid.

6.1. Introduction

There are strict regulations in many developed countries on the use and release of lead into the environment, particularly, the use of lead in petrol as an anti-knock additive (1-2). However, this is not the case with most developing countries of the world where leaded petrol is still in use (3). Even in countries where Pb is no longer used in petrol, the previous use is an indication that a significant amount of Pb is present in the environment because Pb is persistent, corrosion-resistant and cannot be easily degraded by any known chemical means thereby making the local environment unhealthy. Over the years the emphasis has been on leaded fuel (4-6), but there are many other activities that release Pb into the environment particularly in the urban setting. Lead is one element that has always remained with humans because it has been in use particularly in industry since the beginning of the 19^{th} century (7). Though Pb could occur naturally in urban dust, the major processes that enable Pb to be found in urban dust include: industrial activities (such as metal mining, smelting and processing), the use of Pb in lead-acid batteries, pigments, alloys, lead wool, chemical manufacturing, cables, solders, plumbing components, food cans, coal combustion, lead based paint, and industrial waste (8-12). From the sources outlined, it is obvious that most Pb deposited and retained in urban dust is as a result of anthropogenic activities. This implies that the urban population are at a higher risk because studies have shown (13-15) that the Pb retained in soil / dust, as a result of anthropogenic activity occurs in a highly bio-available, exchangeable and carbonate forms, whereas, Pb retained as a result of natural occurrence is speciated in residual or non-bioavailable forms (16-17). Urban dust represents a significant

health risk to humans due to its small and ubiquitous nature. Direct exposure to urban dust through inhalation is expected as people have to breath continuously, move, interact and carry out their daily activities. Thus, the respiratory tract is a potentially significant pathway through which urban dusts could easily enter the human body. Though the human respiratory system is naturally equipped with coordinated mechanisms to provide protection against inhaled particulates not all inhaled dusts are expelled; in addition, there is a significant possibility that the soluble fraction would be dissolved by interstitial lung fluids. In assessing risk to humans, particle size is a very important parameter. The particle size of urban dusts and its associated chemical composition determine their characteristic behaviour in the human respiratory system. The particle size fraction considered potentially significant in this study is the < 10 μm as it represents the easily inhalable fraction. This particle size fraction is of concern because the degree of respiratory penetration depends on particle size, < 10 μm can penetrate up to the tracheobronchial region of the human lung (18). Moreover, it has been shown that the PTE concentration in urban dusts increases with decreasing particle size fraction (19-20). Thus, lower particle size fractions have increased surface area for the deposition of the PTEs and so the < 10 μm represents a higher risk to human health.

Children (3 - 6 years) are the target focus for exposure and risk assessment because of their distinctive behaviour and curiosity to actively explore their environment; thus leaded dust and paint chips could cling to their hands, clothes, shoes, toys, pets, and other objects in their possessions thereby keeping them in constant touch with dust and increasing their chances of inhaling dust (21-22). So this age group are most likely to be exposed to Pb through inhalation. Also, their physiological intake of lead is higher than those in adults (23), and since they are undergoing rapid development,

their sensitive systems (e.g., respiratory and digestive systems) are more vulnerable than adults to adverse health effects of lead (25-27).

Lead is toxic and the continuous exposure to this element remains a potential public health problem which could result in many health effects and death. It competes with calcium in the body at cellular sites and prevents calcium from entering into cells (26). A survey (27) of metals in UK dusts has shown that most of the dusts collected from many cities had widespread Pb contamination ranging from 172 to 9600 µg/g and it has been reported (28) in China that 80% of children exposed to urban dust had an excessive blood lead level. In addition, it was observed that dust levels best predicts children's blood lead levels (29). In South Africa, a study (30) has revealed that children's blood lead levels in urban settings of developing countries were higher than those of children in most developed nations. In Kingston (Jamaica) the blood samples of children were collected and analysed for Pb levels and it was discovered that 43 % of the children had an elevated blood Pb level of ≥75 µg/dl (31). This value is 7 times higher than 10 µg/dl chosen in 1991 by US Centres for Disease Control and Prevention (CDC) as an initial screening for Pb in children's blood (32). Recent studies (33-34) have shown that blood Pb levels found to be less than 10 µg/dl in children could result in significant health effects. In Jos (Nigeria) 218 children were screened for blood lead level and 70% of them had blood Pb level above 10 µg/dl (35). Also in India, a survey of seven cities revealed that 53% of children had blood Pb levels > 10 µg/dl (36). Lead poisoning is dangerous not only to children but also to the adult population. It was reported (37-39) that Pb poisoning occurred in Zamfara State (north-west of Nigeria) in 2010. The epidemic which was reported as the worst of such an occurrence in modern history killed 400 children (< 6 years) and made about 3,500 children seriously sick with symptoms including lethargy,

abdominal pain, vomiting, constipation and headaches. The epidemic was caused by illegal gold miners who in the process of extracting gold released substantive amount of lead into the air, road/street, homes, playgrounds and water. The report (39) also stated that these miners being ignorant of its health implications, did not put on protective gear and also had direct contact with their family members and friends on their return from the mining sites. The children were exposed to Pb poisoning among other routes through inhalation of polluted air and dust. Pb is a potent and pervasive contaminant and has the characteristics of aborting the effectiveness of virtually all organs including, the central and peripheral nervous system, the respiratory tract, the gastrointestinal tract, the liver, muscles, bones, teeth and the heart (40-41).

Since dusts have proved to be a repository of Pb, it is fundamental that urban dusts be scrutinized for Pb concentration and bioaccessibility, indeed lead is one of the priority contaminants listed by Bioaccessibility Research Group of Europe (BARGE) that its bioaccessibility via ingestion should be studied as it could be used for human health risk assessment and policy making. Therefore, to have a full-body and holistic human health risk assessment, it is imperative to evaluate the bioaccessible Pb from urban street dusts through the inhalation pathway in addition to the ingestion scenario by employing a simulated epithelial lung fluid. Urban dusts for this investigation were collected from five cities in the UK and one city in Nigeria. (Details of site descriptions had been presented in appendix E)

6.2. Experimental

6.2.1. Sample collection and preparation

Ninety street / road dusts were previously collected from six urban cities. However, based on earlier findings of high Pb content in some sites (chapter four), twenty

three samples were selected for this work. Four samples were selected from Newcastle upon Tyne, UK; Grey Street (N1), Cathedral Church (N2), Central Station (under the arch) (N3) and Clayton Street (N4). Four samples were selected from Durham, UK; Durham University (D1), Durham Cathedral (D2), Saddler Street (D3), and Penny Ferry Bridge (D4). Five samples were selected from Liverpool, UK; London Road (L1), Pembroke Place (L2), Brown Low Hill Road (L3), Royal Hospital (L4) and Prescott Street (L5). In Edinburgh, UK, five samples selected include; George Street (E1), Princess Street (E2), Leith Walk Street (E3), Nicolson Street (E4) and Saint John's Street (E5). In Sunderland, UK, three selected samples were collected from; High Street West (S1), Royal Theatre (S2) and Bridges Shopping Complex (S3). In Abakaliki, Nigeria, two samples selected were collected from; Abakpa Motor Park (A1) and Vanco Round About ((A2). These samples were placed in labelled self-sealing bag (kraft bags) and sealed properly. They were oven dried at a temperature of 35 ^{0}C for two days, manually disaggregated and all extraneous particles removed before sieving into < 125 μm particle size fraction. The < 125 μm dusts samples were then manually sieved using < 10 μm nylon sieve and the < 10 μm dusts samples obtained were stored in Sarstedt plastic tubes prior to extraction.

To further assess human health risk from urban dust, air-borne dust (PM_{10}) was collected by using two high volume air samplers mounted in an area located within the premises of University of Northumbria at Newcastle (Ellison Yard), UK. The Tecora Echo samplers (Ecotech Pty Ltd, Australia) are ultra-high volume particulate samplers equipped with an impactor cutoff of 10 μm and have high flow rate of 200 L / min. Prior to every sampling, the Munktell micro-quartz filter papers with diameter of 102 mm were conditioned in a desiccator for 24 hours at a constant temperature of 20 ^{0}C ± 1, weighed, mass recorded and then fitted into the sampler (samples were

collected in pairs). Each sampling was carried out for 100 hours and constant air flow was maintained. After each run, the filter papers were removed and transported to the laboratory. Again, the filters were conditioned in a desiccator for 24 hours at a constant temperature of 20 ^{0}C ± 1, reweighed and mass recorded. The filters were re-packaged ready for the determination of the total concentration of Pb. A total of 13 duplicate samples were collected over a period of one year (March 2011 to April 2012).

6.2.2 Instrument and reagents

All chemicals used in the analysis were certified analytical grade. Concentrated nitric acid (HNO_3) and concentrated hydrochloric acid (HCl) were supplied by Fisher Scientific UK Ltd. (Loughborough, Leicestershire). Sodium hydrogen phosphate (NaH_2PO_4) and potassium hydrogen phosphate ($NaHPO_4$) were purchased from Sigma-Aldrich Co. (Gillingham, UK). Sodium chloride (NaCl), anhydrous sodium sulphate (Na_2SO_4), potassium chloride (KCl), calcium chloride ($CaCl_2.2H_2O$), sodium bicarbonate ($NaHCO_3$), magnesium chloride ($MgCl_2.6H_2O$), sodium hydroxide (NaOH), uric acid, bovine serum albumin (BSA) and concentrated nitric acid (69% HNO_3) were all obtained from Merck (Poole, England), Mucin (pig) was obtained from Carl Roth, GmbH (Karlsruhe, Germany). Ascorbic acid, glutathione, cysteine, dipalmitoylphosphatidylcholine (DPPC), and glycine were obtained from Sigma-Aldrich Co. (Gillingham, UK). A multi-element standard containing Pb and other trace elements and internal standard solution containing indium (In), scandium (Sc) and terbium (Tb) were obtained from SPEXCerPrep (Middlesex, UK). Ultra-pure water of conductivity 18.2MΩ-cm was produced by a direct Q^{TM} Millipore system (Molsheim, France). Certified reference materials; BCR 038, BCR 143R, BCR 176R, and BCR 723 were obtained from LGC-Promochem (London, UK), while BGS

Guidance Material 102 was obtained from British Geological Survey (Keyworth, UK). Sample digestions were carried out using a start D multiprep 42 high throughput rotor microwave system (Milestone Microwave Laboratory Systems) supplied by Analityx Ltd. (Peterlee, UK). Measurement of urban street dust samples was carried out by using an ICP-MS X series II (Thermo Electron Corporation, Cheshire, UK) while Pb content in air-borne dust was determined via energy dispersive X-ray fluorescence (EDXRF) spectroscopy (Spectro Analytical X-Lab 2000).

6.2.3 Preparation of simulated epithelial lung fluid (SELF) for *in vitro* extraction test

In order to avoid cross contamination and to ensure reliability and reproducibility of results, all vessels used for the preparation of simulated epithelial lung fluids and bioaccessibility extraction protocol were soaked in an acid bath containing 10 % HNO_3 for 24 hours and rinsed with ultrapure water. Chemical components needed to prepare 1000 ml of simulated epithelial lung fluid were prepared in two phases (inorganic and organic). To prepare the inorganic phase (500 ml): 6020 mg NaCl, 256 mg $CaCl_2$, 150 mg $NaHPO_4$, 2700 mg $NaHCO_3$, 298 mg KCl, 200 mg $MgCl_2$ and 72 mg Na_2SO_4 were accurately weighed into 500 ml HDPE screw top bottle containing ultra-pure water with the water level maintained at the mark and thoroughly mixed. To prepare the organic phase (500 ml): 18 mg ascorbic acid, 16 mg uric acid and 30 mg glutathione were also accurately weighed into 500 ml HDPE screw top bottle containing ultra-pure water with the water level maintained at the mark, the resulting solution was thoroughly mixed. The inorganic and organic components were simultaneously poured into a 2 L HDPE screw top bottle containing additional constituents; 260 mg albumin, 122 mg cysteine, 100 mg DPPC, 376 mg glycine and 500 mg mucin, this was thoroughly mixed until all the

components dissolved. The pH was measured and found to be 7.8; this was adjusted to 7.4 ± 0.2 by adding 0.2 ml HCl.

6.2.4 Sample preparation and bioaccessibility extraction protocol

0.3 g of five certified reference / guidance materials (in triplicate) and twenty three urban dust samples (in duplicate) were accurately weighed into labelled 50 ml screw-cap Sarstedt tubes (extraction tubes). The water bath was switched on for 2 hours prior to the commencement of the bioaccessibility extraction with the temperature set at 37 ^{0}C ± 2. The prepared simulated epithelial lung fluid was warmed in a water bath for 2 hours maintained at a temperature of 37 ^{0}C ± 2. After 2 hours, the pH was checked and found to be 7.4. A calibrated Gilson pipette was used to measure 20 ml of the fluids and added to the each of the extraction tubes containing the samples. The tubes were firmly capped and manually shaken. This was followed by shaking the mixture on an end-over-end rotator maintained at 37 ^{0}C ± 0.2 for 96 hours. The resulting solution was then centrifuged at 3000 rpm for 10 min. 1 ml of the supernatant was pipetted into 10 ml Sarstedt tube previously holding 9 ml of 0.1 M HNO_3 and 30 µl internal standard. The sample was stored at < 4 ^{0}C prior to ICP-MS analysis.

6.2.5 Microwave digestion protocol

Digestion protocol analogous with section **5.2.5**

6.2.6 Protocol for total Pb content determination via XRF

Air-borne dust samples were analysed *in situ* on filter paper using energy dispersive X-ray fluorescence (EDXRF) spectroscopy on a Spectro Analytical X-Lab 2000 instrument fitted with a Gresham Si(Li) detector. Samples were prepared for analysis

by cutting 2.6cm diameter circles from the collection filter papers and sandwiching between two layers of prolene film; this was then assembled to make a standard powder cuvette (including lid), with the filter held tight between the prolene layers. Blank filter material was prepared for analysis in the same way. Each sample was analysed using the Filters programme of the instrument, comprising the following programme of targets: Compton/secondary molybdenum, 40 keV tube voltage, 200 s measurement time; Barkla scatter, aluminium oxide, 50 keV, 200 s; Barkla scatter, HOPG, 15 keV, 200 s. Verification of the Pb concentrations was carried out by measuring the blank corrected concentrations for a SRM 2783 filter standard. The standard was supplied as a polycarbonate filter membrane filter loaded with 31.83 ng/cm^2 Pb which had been deposited on the filter as $PM_{2.5}$ fraction airborne particulate matter; a blank filter was also supplied. This allowed a correction factor to be determined (1.022), which was applied to the measured concentrations.

6.2.7 ICP-MS protocol / Quality control

Samples to be analysed using the ICP-MS was prepared in triplicate by measuring 1 ml of either the filtrate and the blank into a 10 ml sarstedt tube; this was followed by addition of 30 µl of mixed internal standards (indium, scandium and terbium) and 9 ml of water (1% HNO_3). The certified reference /guidance materials and sample preparation in triplicate was used to assess precision and accuracy of the methodology whilst reagent blanks were included to check contamination. Calibration standards of 0-400 ppb (0, 20, 40, 60, 80, 100, 200 and 400 ppb) were prepared from the 100 ppm of the multi-element mixture with internal standard; this was used to calibrate the instrument and also construct the calibration graph. The instrument was tuned to verify mass resolution and maximise sensitivity in the standard mode. The instrument was re-calibrated with a particular calibration

standard after every ten samples to ensure instrument consistency and precision. A calibration curve for Pb based on the concentration range was done and the correlation coefficient (R^2) was 0.999. Pb concentrations in both the total digestion blanks and the simulated epithelium lung fluid blanks were not detected. ICP-MS operating conditions are shown in Table 6.1.

6.3 Results and discussion.

6.3.1 Total Pb content in the certified reference / guidance materials.

The robustness of the analytical procedure (i.e. digestion protocol using microwave oven and sample analysis via ICP-MS) was tested using five certified reference

Table 6.1: ICP-MS operating conditions

ICP-MS parameters	Standard Mode
Nebulizer gas flow (L/min)	0.83
Forward Power (W)	1400
Cool gas flow (L/min)	13.0
Dwell time per isotope (ms)	10
Collision cell gas (L/min)	NA
Quadrupole bias (V)	-1.0
Hexapole bias (V)	0.0
Internal standards	^{45}Sc, ^{115}In and ^{159}Tb
Isotope monitored	^{208}Pb,

NA = not applicable; CCT mode = collision cell technology

/guidance materials. Measured total Pb content after six successive occasions are shown in Table 6.2. It can be seen that measured total Pb content were not different from the certified values. The deviation is in a very close range of not more than ±

10. The closeness of the measured value to the certified reference material /guidance materials and excellent % recovery is an indication that the protocol is both accurate and reproducible.

6.3.2 Total Pb content in urban street dusts.

The mean total concentrations of Pb in urban dusts (< 10 μm) of six cities are shown in appendix H. In the city of Newcastle upon Tyne, Pb concentrations range from 772 mg/kg to 1778 mg/kg. The mean concentration of Pb in urban dusts of Durham ranges from 534 mg/kg to 2435 mg/kg. In Liverpool, the Pb levels were observed to be in the range of 452 mg/kg – 1408 mg/kg. Samples collected from Edinburgh, recorded mean concentrations that varied from 472 mg/kg to 1248 mg/kg. In Sunderland, it was found that the mean levels ranges from 535 mg/kg to 2357 mg/kg. Total Pb content in dust samples collected from Abakaliki were found to vary from 1138 mg/kg to 2002 mg/kg. It can be seen that the mean Pb concentrations varied widely across the cities with the dust sample collected from Durham (Saddler Street) recording the highest Pb level (2435 mg/kg) and the sample collected from Liverpool (Prescott Street) showing the lowest Pb mean concentration (452 mg/kg). The mean concentrations of Pb in the urban dusts of all the cities were observed to be much higher than Pb levels commonly found in the urban dust samples (47 – 181 mg/kg) (42-43). The difference in Pb levels of dusts samples in these cities suggests that the various emission sources differ significantly across the cities.

6.3.3 Relationship between air-borne urban dust and settled urban dust.

To be able to compare the results from air-borne dust (PM_{10}) and settled dust (< 10 μm) and for better understanding of their health implications via inhalation, it was considered necessary to explore the relationship between the two environmental

Table 6.2 Lead in certified / guidance materials: total content, bioaccessible fraction and residual digest.

Sample	Certified Reference /Guidance Material values (mg/kg)	Measured Total content (mg/kg)	*In-vitro* lung bioaccessibility (mg/kg)				
			Stage I (Bioaccessible Pb)		Stage II (Residual digest)	Total Pb content (Stage I + II)	
		Mean ± SD; (n = 3)	Mean ± SD; (n = 3)	% BAF	Mean ± SD; (n = 3)	Mean (n = 3)	% Total Recovery
BCR 038	262 ± 11	258 ± 2[+]	0.85 ± 0.01	0.329	254 ± 10	255	98.8
BCR 143R	174 ± 5	173 ± 6[+]	15.3 ± 2.2	8.84	158 ± 2	173	96.6
BCR 176R	5000 ± 500	5009 ± 17[+]	206 ± 26	4.31	4860 ± 31	5066	101
BCR 723	866 ± 16	860 ± 12[+]	34.7 ± 2	4.03	820 ± 10	855	98.7
BGS 102	79.4 ± 1.4	76.1 ± 1.6[+]	4.3 ± 0.5	5.65	70.1 ± 0.2	74.4	93.7

+ n = 6 (3 samples each run 6 times): % BAF: stage related bioaccessibility, calculated as a fraction of the total content : %

Residual: residual fraction calculated as a fraction of the total content

matrices. With respect to human health risk assessment, the relationship between them is basically in terms of sources, physical and chemical characteristics as well as toxicological mechanisms in exposed populations (38). These particulates are sourced from any type of earth-moving activity, or combustion activities, whether from business, industry or individual and their characteristics vary greatly and depend on many factors, such as climate, season and type of urban or industrial pollution (39). Of greatest concern is the fact that they both contain PTEs such as Pb. Air-borne dust consists mainly of tiny solid particles that float in the air we breathe. It has the potential to travel great distances from point sources before settling on any available surface. The settled dust is created by particles with enough sedimentation ability and short retention time in the atmosphere. Although the retention time in the atmosphere is not prolonged, it can be inhaled before settling and after settling, dust particles could be mobilised into the atmosphere and float with air and so could be inhaled by exposed people. Dust mobilisation is particularly significant in the summer or dry season (drier environment) and more prevalent in the developing countries where most roads / streets are not tarred. A recent study (44) that investigated the concentration of Pb and Zn in air-borne dust (PM_{10}) and settled dust described both environmental matrices as 'mobile toxic components' with the potential to contaminate the air, soil and ground water. The study highlighted that studies on sources, composition, distribution and health impacts of air-borne dust and settled dust are necessary for their risk assessment to atmospheric quality, ecology and human health particularly in a populated urban environment. In the light of these potential caveats and for holistic human health risk assessment via inhalation pathway, it was considered necessary to calculate the

inhalable Pb content and bioaccessible Pb inhaled per day in air-borne dust (PM_{10}) as well urban street dust (< 10 µm).

6.3.4 Amount of Pb inhaled per day via inhalation of urban street dust

One way to estimate Pb dose per day is to establish PM_{10} annual daily mean from air quality archive data (45) over representative years. This was calculated for 11 years (2000 to 2011) in three UK cities (Newcastle upon Tyne, Edinburgh and Liverpool) (Table 6.3); no data was available for Durham, Sunderland and Abakaliki. The annual daily mean was found to be 17.7 ± 2.4 µg/m^3. It has been established that the

Table 6.3: PM_{10} annual daily mean (µg/m^3) in three UK cities calculated from air quality archive data (41)

Year	Newcastle upon Tyne (µg/m^3)	Edinburgh (µg/m^3)	Liverpool (µg/m^3)
2011	19.8	15.2	16.3
2010	14.7	14.5	16.9
2009	14.6	17.5	16.6
2008	18	15.2	14.8
2007	14.9	17.2	17.4
2008	19.8	20	21.7
2006	16.9	18.5	20.1
2005	17.4	18.6	24
2004	21.8	NA	16.2
2003	18.1	NA	NA
2002	17.3	NA	NA
2001	17.1	NA	NA
2000	19.8	NA	NA

volume of air that a child (3 - 6 years) inhales in a day is 8.3 m^3/day (46), thus, total street dust (< 10 µm) that a child could possibly inhale per day is 147 µg and based on the body weight of a child (47), the total Pb inhaled per day was then calculated. The results are shown in Table 6.4 with footnotes showing details of calculations. Total Pb inhaled per day based on a child's body weight varied across the cities in proportion to total Pb concentrations in the dust samples. In Newcastle, it varied from

0.61 to 1.41 μg kg^{-1}bw day^{-1}. In Durham, it ranged from 0.41 to 1.93 μg kg^{-1}bw day^{-1}. The Liverpool result is in the range of 0.35 to 1.11 μg kg^{-1}bw day^{-1}, Edinburgh ranges from 0.37 to 0.99 μg kg^{-1}bw day^{-1}. Sunderland samples ranged from 0.42 to 1.87

Table 6.4: Total Pb inhaled per day via inhalation of urban street dust (< 10μm)

Sample sites	Total Pb content in urban dust (% w/w)	Total Pb inhaled per day (μg/day)	Total Pb inhaled per day based on a child's body weight (μg kg^{-1}bw day^{-1})
N1	0.178	26.2	1.41
N2	0.177	26.0	1.40
N3	0.077	11.3	0.61
N4	0.163	24.0	1.29
D1	0.128	18.8	1.01
D2	0.085	12.5	0.67
D3	0.244	35.9	1.93
D4	0.053	7.8	0.41
L1	0.084	12.3	0.66
L2	0.065	9.6	0.52
L3	0.141	20.7	1.11
L4	0.050	7.4	0.40
L5	0.045	6.6	0.35
E1	0.047	6.9	0.37
E2	0.059	8.7	0.47
E3	0.108	15.9	0.85
E4	0.049	7.2	0.39
E5	0.125	18.4	0.99
S1	0.236	34.7	1.87
S2	0.054	7.9	0.42
S3	0.207	30.4	1.63
A1	0.2002	29.4	1.58
A2	0.1138	16.7	0.90

(N = Newcastle, D = Durham, L = Liverpool, E = Edinburgh, S = Sunderland, A = Abakaliki). Total dust inhaled = volume of air inhaled (8.3 m^3) X annual daily mean (17.7 ± 2.4 μg/m^3) ≡ 147 μg. Total Pb inhaled per day = total Pb content in urban dust X 147 μg. Total Pb inhaled per day based on a child's body weight (μg/day kg^{-1}bw) = Total Pb inhaled per day / body weight (18.6 kg)

μg kg^{-1}bw day^{-1} and Abakaliki ranged from 0.9 to 1.58 μg kg^{-1}bw day^{-1} . From the results, the least amount of Pb (0.35 μg kg^{-1}bw day^{-1}) that a child could possibly inhale was observed in the dust sample collected from Prescott Street (site 5,

Liverpool) and the highest amount (1.93 μg kg^{-1}bw day^{-1}) was obtained in the dust sample collected from Saddler Street (Durham). In order to assess human health risk from the inhalation of urban street dust, these results were compared with Pb tolerable daily intake for inhalation pathway (TDI_{inh}) estimated to be 0.07 μg kg^{-1}bw day^{-1} (48) and it was observed that even the least inhalable Pb per day (0.35 μg kg^{-1}bw day^{-1}) was five times higher than than TDI_{inh}. The health implication of this finding is that children (3 – 6 years) who indulge in outdoor activities particularly for a long time could be at risk. However, further risk assessment through the application of bioaccessibility protocols would be undertaken. These results are line with previous finding (see 4.3.2) where all the sites investigated were found to contain high Pb levels.

6.3.5 Total Pb content in air-borne dust and daily inhalable amount

To further assess human health risk associated with inhalation of urban dust, it was considered necessary to determine Pb levels in air-borne dust. Although, it was not possible to evaluate Pb levels in air-borne dust of the six cities investigated, Pb concentrations in air-borne dust (PM_{10}) collected in the city of Newcastle upon Tyne for a period of one year (March 2011 to April 2012) was determined. A scanning electron microscopy (SEM) has been used to capture the quartz filter paper before and after sample collection. Figure 6.1 shows the configuration of the fibres of the filter before sample collection. The image of one of the filters after sample collection (Figure 6.2) shows the distribution of PM_{10} on the filter. It can be seen that the configuration of the fibres of the filter allowed small air-borne particulates to be trapped below the surface of the filter. It is observed that these fine particles collected formed clumps and are unevenly distributed on the fibres of the filters.

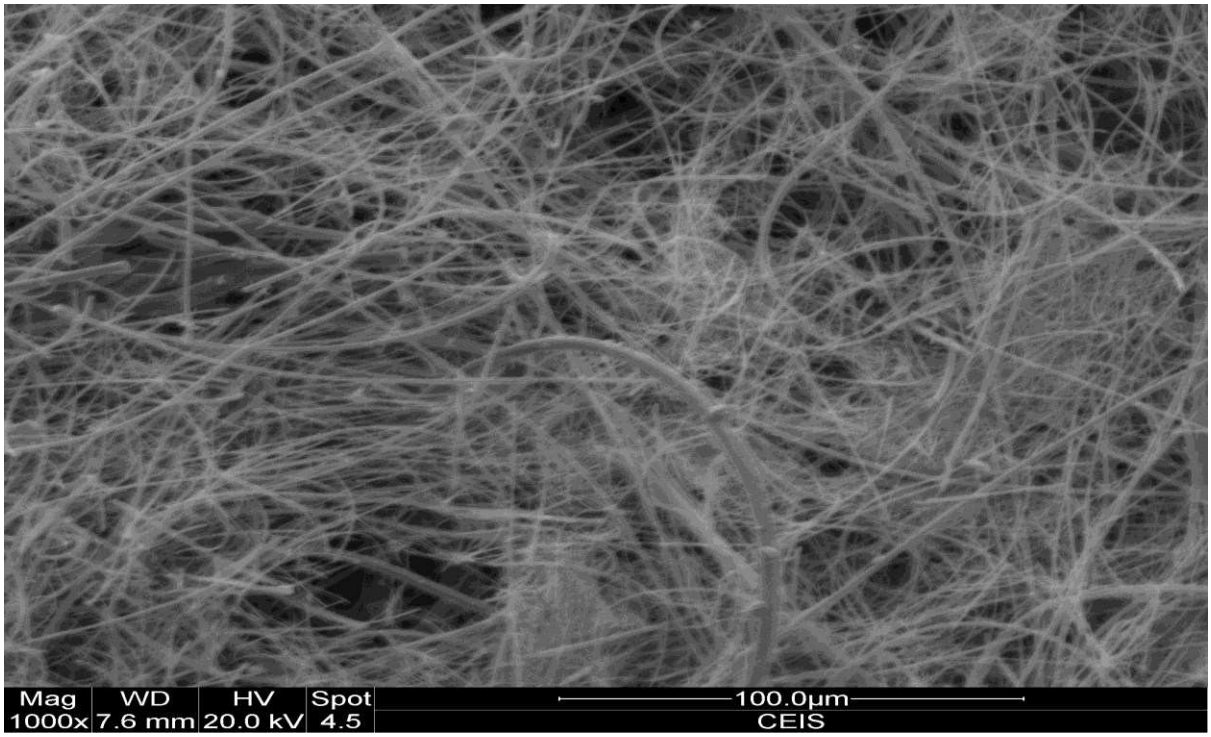

Figure 6.1: SEM image of quartz filter paper before sample collection

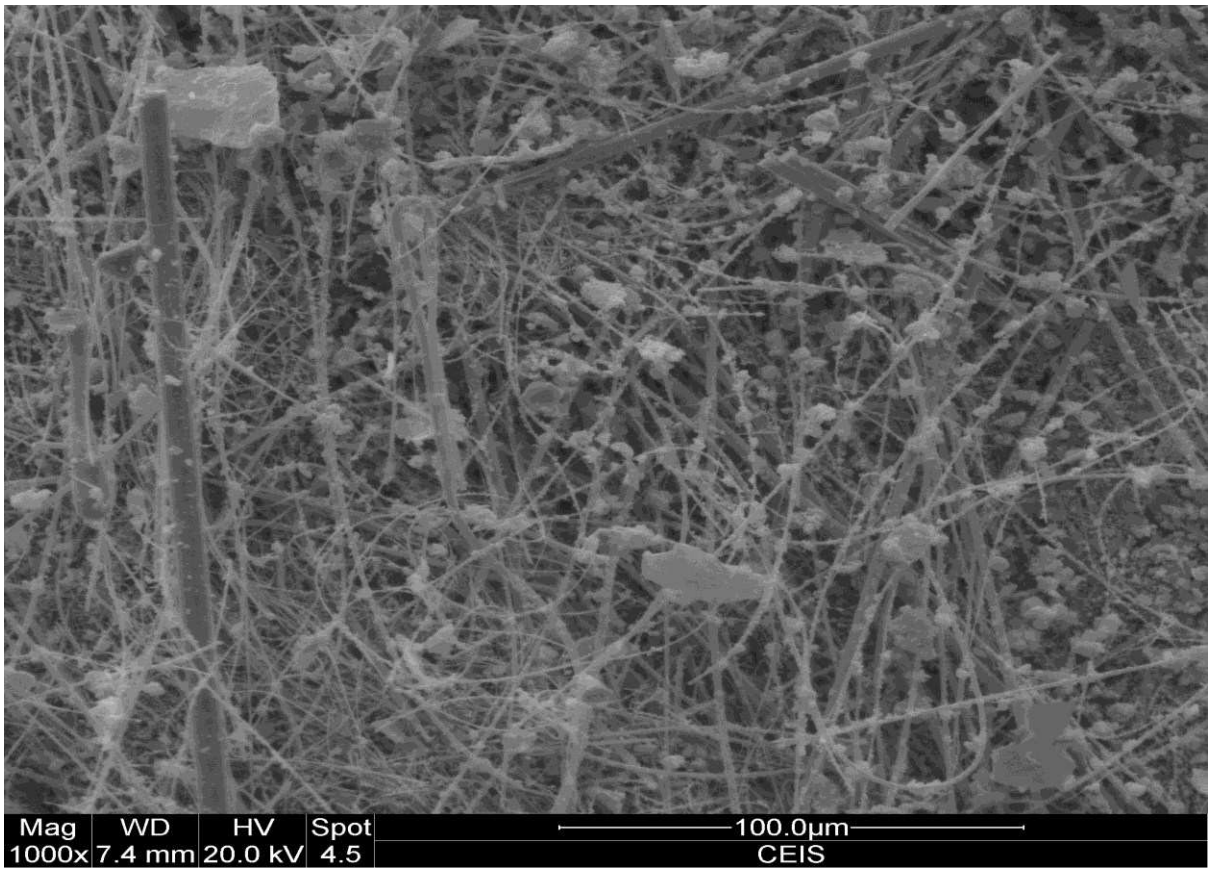

Figure 6.2: SEM image of quartz filter paper showing collected air-borne dust

The concentrations of Pb in the PM_{10} collected on the filters were measured using EDXRF. It is observed that Pb concentrations varied widely across the year. Based on 100 hours sampling duration, total Pb content varied from 3.1 to 1060 µg/g and based on daily calculation, it was found to be in range of 0.74 – 254 µg/g (appendix M). It was observed that the highest concentrations of Pb were observed in the samples collected in November 2011 and it is believed that construction works within the neighbourhood at the period of the sampling contributed to the increase.

To accurately assess human health risk associated with inhalation of air-borne dust, the amount of Pb that a child could inhale on daily exposure need to be calculated. Therefore, PM_{10} annual daily mean based on the weight of the sample and the sample flow rate was calculated and found to be 4.2 ± 4.1 µg/m^3. Since a child inhales 8.3 $m^3$of air per day, total air-borne dust (PM_{10}) that a child could possibly inhale per day is 34.9 µg. The total Pb inhaled per day was then calculated based on the total Pb content in the air-borne dust and a child's body weight. The results are shown in Table 6.5 and details of calculation given as footnotes. Total Pb inhaled per day via inhalation of PM_{10} was found to be relatively low and also in the same range (Table 6.5) over the sampled period with the exception of sample T (0.05 µg kg^{-1}bw day^{-1}) collected in November 2011. Similarity of results signifies common sources of Pb within the sampled area. The investigation also revealed that calculated daily inhalable Pb were all below TDI_{inh} for Pb (0.07 µg kg^{-1}bw day^{-1}), however, it has been stated (49) that it is not feasible to determine a threshold concentration below which there are no adverse health effects of inhaled PM_{10} to the exposed population, particularly when associated with Pb. The examination of total Pb per day via inhalation of urban street dust and air-borne dust (PM_{10}) has revealed that there is more health risk associated with inhalation of street dust than airborne dust. These

Table 6.5: Total Pb inhaled per day via inhalation of air-borne dust (PM_{10})

Sample number	Total Pb content in air-borne dust (% w/w)	Total Pb inhaled per day (µg/day)	Total Pb inhaled per day based on a child's body weight (µg kg^{-1}bw day^{-1})
A	0.011	0.37	0.02
B	0.004	0.12	0.006
C	0.003	0.11	0.006
D	0.002	0.09	0.005
E	0.001	0.02	0.001
F	0.001	0.04	0.002
G	0.002	0.05	0.003
H	0.001	0.05	0.003
I	0.002	0.07	0.004
J	0.005	0.18	0.01
K	0.001	0.04	0.002
L	0.001	0.02	0.001
M	0.001	0.02	0.001
N	0.001	0.03	0.002
O	0.002	0.01	0.0005
P	0.003	0.01	0.0005
Q	0.001	0.06	0.003
R	0.011	0.38	0.02
S	0.008	0.29	0.02
T	0.025	0.89	0.05
U	0.001	0.04	0.002
V	0.001	0.05	0.003
W	0.0002	0.01	0.0005
X	0.0001	0.01	0.0005
Y	0.001	0.03	0.002
Z	0.001	0.02	0.001

Total PM_{10} inhaled = volume of air inhaled (8.3 m^3) X annual daily mean (4.2 ± 4.1 µg/m^3) ≡ 34.9 µg. Total Pb inhaled per day = total Pb PM_{10} X 34.9 µg. Total Pb inhaled per day based on a child's body weight (µg/day kg^{-1}bw) = Total Pb inhaled per day / body weight (18.6 kg)

significant differences are expected for obvious reasons; firstly, the PM10 annual daily mean obtained from air quality archive data was 17.7 ± 2.4 µg/m^3 and the PM_{10} annual daily mean calculated from sampled air-borne dust was 4.2 ± 1.1 µg/m^3. PM_{10} annual daily mean obtained in this study differed from the PM_{10} annual daily mean obtained from the air quality archive data primarily due to difference in sampling locations. For example, in Newcastle city, PM_{10} monitoring centre is located at the civic centre (Figure 6.3).

Figure 6.3: Air quality monitoring station, Newcastle upon Tyne centre

This sampling location is surrounded with busy roads and it is expected that high percentage of PM_{10} would be emitted from vehicles plying the roads. On the other hand, air-borne dust sampling used in this study was carried out in an enclosed Ellison yard located within the premises of Northumbria University (Figure 6.4). The sampling site was located far away from busy roads. Incidentally these two values were the basis upon which daily inhalable Pb was calculated, hence the differences In addition, higher Pb inhaled per day via inhalation of urban street dust is expected because it has been reported that Pb accumulates in dust samples (17). It is to be noted from the study that inhalation of Pb in the urban environment is inevitable. Therefore, considering the toxic nature of Pb, implies that even the least amount of Pb could pose a potential threat to a child's health especially when exposed over a

Figure 6.4: Tecora Echo high volume PM10 sampler.

long period of time bearing in mind that inhalation occurs involuntarily and continuously. Moreover, it has been noted that any amount of Pb that reaches the absorbing surface is completely absorbed (50). Children with an inadequate feeding habit are more susceptible to Pb because their bodies would readily absorb more Pb if required nutrients particularly calcium, are lacking (26).

6.3.6 Pb bioaccessibility in simulated epithelial lung fluid (SELF)

A knowledge of total lead content and total Pb inhalable per day have helped in assessing human health risk from inhalation of urban dusts. However, for a more holistic approach, this study has investigated the bioaccessibility of Pb in urban street dust through the use of simulated epithelium lung fluid. As at the time of this study, no certified reference material was available for this protocol; however, five certified reference / guidance materials were used to assess the accuracy and robustness of the bioaccessibility protocols. The % bioaccessible Pb fraction (% BAF) was calculated by dividing the bioaccessible Pb with the total Pb content measured and then multiplied by 100 (Table 6.1). Pb bioaccesibility in these materials include BCR 038 (0.33 %), BCR 143R (8.8 %), BCR 176R (4.3 %), BCR 723 (4.0%), and BGS 102 (5.7 %). It can be seen that bioaccessibility of Pb in these samples following extraction with simulated epithelium lung fluid is generally low, it is to be noted that these samples sourced from different soil types must have occurred in different geochemical forms, thus, explaining the variation in the bioaccesibility results. However, certified and guidance materials analysis are for quality control checks. In this regard, the accuracy and robustness of this analytical technique was tested by calculating the mass balance of the certified reference / guidance materials. The results (Table 6.1) show excellent % recovery. The % total recovery ranged from 93.7 to 101. Having assessed the analytical protocol, the simulated epithelium lung fluid was used to extract the bioaccessible Pb from the twenty three street dust samples collected from six cities (see 6.2.1). Details of total Pb content, bioaccessible concentrations, % (BAF), residual digest, total residual and % total recovery are presented in appendix L. The % bioaccessible Pb fraction (% BAF) in the urban dusts samples was calculated in the same way as described for the

certified / guidance materials. As envisaged, the Pb bioaccessibility varied across the cities and were found to be generally low. In Newcastle upon Tyne samples, % bioaccessible fraction ranges from 1.18 to 3.20. In Durham, it is in the range of 3.16 to 6.76. Liverpool dusts samples released % BAF that ranges from 2.95 to 8.75, % BAF in samples collected from Edinburgh ranges from 3.29 to 7.65, Sunderland samples ranged from 1.38 to 4.24 while % bioaccessible Pb in dust samples of Abakaliki ranges from 1.51 to 2.14. The result shows highest % BAF (8.75) was recorded in Liverpool whereas the lowest % BAF (1.38) was observed in Sunderland. However, presenting bioaccessibility results only in terms of % BAF conceals the exact concentration of the PTE in the extract (51). In the light of this, a summary of stage related bioaccessible Pb and residual fraction in dusts samples from the six cities in terms of; minimum, median, maximum (% BAF) and maximum (% residual) has been presented in Table 6.6. In this case, the maximum (stage 1) represents the highest determined bioaccessible concentration (i.e. worst case scenario). Lead bioaccessibility in certified reference / guidance materials and urban street dust following extraction with simulated epithelial lung fluid produced similar results. In either of the environmental matrices, bioaccessibles Pb was found to be < 10 %. This is expected considering the pH (7.4 ± 0.2) of the epithelial linings of the tracheobronchial region which was mimicked and maintained throughout the extraction time. This pH represents a neutral environment which would normally release less metal in solutions when compared to the lower alveolar region of the human lung with a pH of 4.5 (acidic medium) (52). Moreover, it has been reported (52-53) that Pb bioaccessibility in environmental matrices following extraction with simulated fluid is generally low as it occurs in different geochemical forms and these forms exercise control over elemental mobility and bioaccessibility.

Table 6.6: summary of stage related bioaccessible Pb and residual fraction in urban dusts from 6 cities

Cities / No of samples	*In-vitro* epithelial lung fluid extraction (mg/kg), n = 2 (duplicates)					
	Stage I (Bioaccessible Pb)			Stage II (Residual digest)		
	Minimum	Median	Maximum (% BAF)	Minimum	Median	Maximum (% Residual)
Newcastle, 4	20.9	26.9	37.4 (2.3)	685	1637	1702 (96.4)
Durham, 4	31.7	48.8	112 (4.6)	472	918	2218 (91.9)
Liverpool, 5	16.1	38.2	65.9 (4.7)	398	533	1291 (91.7)
Edinburgh, 5	19.2	36.1	60.8 (4.9)	421	537	1174 (94.1)
Sunderland, 3	22.7	28.7	37.1 (1.6)	487	1984	2309 (98.0)
Abakaliki, 2	24.3	27.3	30.2 (1.5)	1094	1487	1879 (93.9)

% BAF: stage related bioaccessibility for the dust sample releasing the highest stage concentration, calculated as a fraction of that sample's total content for stage 1; **% Residual**: residual fraction calculated as a fraction of the total content for the sample releasing the highest residual concentration.

Moreover, Pb is a stable divalent cation that exhibits high affinity for different dusts components and such characteristics could possibly impart a significant control on its dispersal, enhance sequestration and decrease bioaccessibility (54).

Comparing lung bioaccessibility results is in a way difficult and complicated due to wide variation in experimental parameters and conditions, particularly; solvent type, chemical composition and extraction time. Currently, there is no study in the literature that has investigated the respiratory bioaccessibility of Pb in urban dusts. With respect to respiratory bioaccessibility of Pb in other environmental matrices, a study (55) that investigated the bioaccessibility of Pb from Welsh mine waste observed bioaccessible Pb to be in the range of 15% and 41%, while the mass balance ranged from 89.8% to 98.1%. The bioaccessible Pb in this study is higher that the results obtained in the current study. The difference in these results could be due differences in the chemical compositions of the fluids and extraction time.

In terms of mass balance, calculated mass balance in the current study from certified reference / guidance materials which ranges from 93.7% to 101% is slightly higher that the result from the study being considered. The mass balance ranged from 89.8 to 95.7 %. Another study (56) that examined the bioaccessibility of a range of elements including Pb from four certified reference materials using water and Gamble solution (simulated lung fluid) for extraction revealed that simulated lung fluids released more bioaccessible fraction than water. Bioaccessible Pb from the Gamble solution was found to range from 1.3% to 24.6% and calculated mass balance was found to range from 73 to 117 % across the certified reference materials. While % bioaccessible Pb in this study was higher than the result obtained in the current study, the mass balance recoveries compared favourably as both studies demonstrated that there is little Pb loss throughout the analytical procedures.

The investigation demonstrated the need of employing simulated lung fluids which closely resembles the human respiratory tract in studies of this nature instead of using water which does not contain the chemicals found in the lung.

A correlation analysis between total concentration of Pb in urban dust samples (< 10 μm) and bioaccessible concentration showed that the relationship strength between the two variables is very high (Table 6.7); correlation coefficient (r) was found to be > 0.800 across the cities and $p < 0.05$. On the other hand, the correlation analysis between total Pb concentration and bioaccessible fraction as well as bioaccessible concentration and bioaccesible fraction showed weak correlation (Table 6.7). In addition, no significant difference was observed between the bioaccesible concentration and bioaccessible fraction following a t test analysis of the data sets ($p > 0.05$) (Table 6.8).

Table 6.7: Correlation analysis of Pb in urban dust samples

Elements	r value	p-value	Stage
Newcastle upon Tyne, UK	0.850	0.001	TC & BC
	-0.919	0.081	TC & BAF
	0.253	0.747	BC & BAF
Durham, UK	0.916	0.004	TC & BC
	-0.488	0.512	TC & BAF
	-0.096	0.904	BC & BAF
Liverpool, UK	0.834	0.001	TC & BC
	-0.325	0.594	TC & BAF
	0.511	0.378	BC & BAF
Edinburgh, UK	0.808	0.008	TC & BC
	-0.448	0.449	TC & BAF
	0.143	0.818	BC & BAF
Sunderland, UK	0.890	0.002	TC & BC
	-0.979	0.130	TC & BAF
	-0.778	0.432	BC & BAF
Abakaliki, Nigeria	1.000	0.000	TC & BC
	-1.000	0.600	TC & BAF
	-1.000	0.100	BC & BAF

TC = Total concentration, BC = Bioaccessible concentration, BAF = Bioaccessible fraction.

Table 6.8: t test analysis of bioaccessible concentration and bioaccessible fraction

Cities	t-value	p-value
Newcastle upon Tyne	7.334	0.005
Durham	3.061	0.004
Liverpool	3.671	0.021
Edinburgh	4.472	0.011
Sunderland	6.337	0.024
Abakaliki	8.569	0.013

6.3.7 Bioaccesible Pb inhaled per day via inhalation of urban of street dust (< 10 µm)

It will be recalled (**see 6.3.3**) that the amount of Pb inhaled per day calculated from total Pb content in the street dust samples exceeded Pb tolerable daily intake (TDI_{inh}) and based on this, it was considered necessary to calculate the amount of Pb that a child could inhale per day from the determined bioaccessible Pb concentration in the urban street dust samples. The calculated values across the cities for the twenty three samples are shown in Table 6.9. The result shows closeness and similarity of values across the sites and all calculated bioaccessible Pb inhaled per day were found to be lower than TDI_{inh} (0.07 µg kg^{-1}bw day^{-1}) except the result obtained from the dust sample collected from Saddler Street (Durham) which was found to be 0.09 µg kg^{-1}bw day^{-1}. By implication, it is seen that low risk exists for children in these sites via inhalation of urban street dust. However, it is not advisable to allow children play in these areas longer than necessary to avoid Pb accumulation in the respiratory tract.

Table 6.9: Bioaccessible Pb inhaled per day via inhalation of urban of street dust (< 10 µm)

Sample sites	bioaccessible Pb in urban dust (% w/w)	Bioaccessible Pb inhaled per day (µg/day)	Bioaccessible Pb inhaled per day based on a child's body weight (µg kg^{-1}bw day^{-1})
N1	0.0021	0.31	0.02
N2	0.0029	0.42	0.02
N3	0.0025	0.37	0.02
N4	0.0037	0.55	0.03
D1	0.0040	0.59	0.03
D2	0.0057	0.85	0.05
D3	0.0112	1.65	0.09
D4	0.0032	0.46	0.02
L1	0.0025	0.36	0.02
L2	0.0057	0.84	0.05
L3	0.0066	0.97	0.05
L4	0.0016	0.24	0.01
L5	0.0038	0.56	0.03
E1	0.0036	0.53	0.02
E2	0.0019	0.29	0.02
E3	0.0039	0.58	0.03
E4	0.0027	0.40	0.02
E5	0.0061	0.90	0.05
S1	0.0037	0.54	0.03
S2	0.0023	0.33	0.02
S3	0.0029	0.42	0.02
A1	0.0030	0.44	0.02
A2	0.0024	0.36	0.02

Total dust inhaled = volume of air inhaled (8.3 m^3) X annual daily mean (17.7 ± 2.4 µg/m^3) ≡ 147 µg. Total Pb inhaled per day = total Pb content in urban dust X 147 µg. Bioaccesible Pb inhaled per day based on a child's body weight (µg/day kg^{-1}bw) = Bioaccesible Pb inhaled per day / body weight (18.6 kg)

6.4 Conclusion

Determination of total Pb content in the urban street dust samples (< 10 µm) and total Pb content in urban air-borne dust (PM_{10}) revealed that street dust samples contain more Pb than air-borne dust. The difference Pb levels in these environmental matrices could be due to Pb accumulation in street dust samples as it has been reported that Pb accumulates in street dust (13) over a period of time. In order to assess the health risk associated from inhalation of these environmental matrices,

the amount of Pb that a child could inhale per day was calculated from both results and it was observed that in the case of street dust, inhalable Pb per day from all sites exceeded (TDI_{inh}) (0.07 μg kg^{-1}bw day^{-1}). On the other hand, the amount of Pb that can be inhaled per day calculated from total Pb in air-borne dust were all found to be lower than TDI_{inh}.

To further assess human health risk from this study, bioaccessibility of Pb in urban dusts following extraction with simulated epithelium lung fluid was evaluated. Bioaccessible Pb varied across the samples and was generally low (< 10 %). Also the amount of Pb that a child could inhale per day from the determined bioaccessible Pb concentration in the urban street dust samples were calculated and only one sample out of the twenty three dust samples exceeded TDI_{inh}. The study has shown the significant role that bioaccessibility plays in risk assessment

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Chapter seven: Implications of the study.

7.1 The concept of human health risk assessment

The objective of human health risk assessment is to explore the likelihood that exposure to a toxic chemical will have an adverse effect on human health and to quantitatively estimate the nature of the effect now (or in the future). Human health risk assessment is not only useful in evaluating health effects from environmental contaminants but also a significant tool in the control of chemicals that are brought to the market. For example, the concept of human health assessment was the reason behind the ban on the sale and use of leaded fuel in many countries of the world (1-2). Risk assessment is used to estimate and evaluate the risk posed by environmental contamination (3). It has the potential to demonstrate whether a brownfield site is safe for its intended use despite the presence of environmental contaminants.

The concept of human health risk assessment is to attempt to answer the following questions: what are the sources of environmental contaminants; what type of health effect can they cause; is there a threshold above which there is an adverse health effect or below which there is no adverse health effect; which contaminant poses the greatest health risk; which contaminant are people exposed to and at what levels and for how long; are some people more likely to be exposed because of factors, such as where they live, work, undertake recreation; what they eat and finally, are some people more likely to be susceptible to environmental contaminants because of factors, such as, age, genetics, a pre-existing health condition, ethnic practices and gender. A holistic research based approach attempts to answers these

questions and assist environmental policy makers to understand the possible human health risk from environmental contaminants.

7.2 The role of bioaccessibility in environmental risk management

Environmental contamination management, particularly the management of soil from historic activities, still remains a challenge in most countries of the world. This is despite several national and international strategies that have been established to remediate contaminated sites and reduce human health risk emanating from such sites. Such strategies include: license for the operation of industrial plants and machine; control on the application of sewage sludge to land; a ban on waste disposal via landfill; and, regulation on the spreading of bio-solids in the environment (4). Risk assessment protocols that are currently used in environmental risk management of land contamination in many countries are based on generic assessment criteria (including the use of soil guideline values (SGVs)) and detailed quantitative risk assessment (the use of site specific assessment criteria (SSAC)). Both are very useful tools as they are able to demonstrate whether risk is evident as well as whether remediation is needed (or not). However, in developing SGVs in many countries (e.g. England) (5), it is assumed that the total concentration of potentially toxic elements in ingested soil (intake dose) is equal to that absorbed by the human body. Such an assumption does not consider the internal exposure (i.e. uptake dose) which represents the fraction of the ingested amount that is able to reach the blood stream. Therefore, this could be seen as an over estimation of the risk associated with oral ingestion of soil based on the principle of PTEs sequestration within various heterogeneous soil matrices (a scenario whereby the total elemental content present in the ingested soil is not readily accessible for absorption and transformation). However, the quest to obviate this challenge has

given rise to the development of several bioaccessibility (*in vitro*) methods simulating the physiology of the human digestive system with the overall intention of assessing the extent of mobilization of contaminants from ingested soil during digestion. These oral bioaccessibility protocols have been designed to determine the exact amount of PTE that is able to solubilise in the human gastrointestinal tract from ingested soil. This fraction is considered to represent the maximum amount of PTE available for intestinal absorption, that is, transported across the intestinal wall and transferred into the blood stream. In addition, it is important to note that PTEs that are not released from ingested soil matrix or released but not absorbed can spread through the body by the systemic circulation, and may exert systemic toxicity (6). Research based data and information on PTEs bioaccessibility from diverse range of bioaccessibility methods have attracted the attention of environmental regulators, legislators, health assessors and researchers (7), making bioaccessibility information a decision-support tool for human health risk and contaminated land assessment. Some of the bioaccessibility models that have been used to assess PTEs release from ingested soil include: the physiologically based extraction test (PBET), simplified bioaccessibility extraction test (SBET) and *in vitro* gastrointestinal method (IVG) (8). Initiatives aiming to bring together research on these models in European countries are being undertaken by Bioaccessibility Research Group of Europe (BARGE) (8). This body has carried out an inter-laboratory trial of a proposed harmonised *in vitro* physiologically based ingestion bioaccessibility procedure for soils called the Unified bioaccessibility Method (UBM) (9). This method has been used in this research. Since the oral bioaccessibility method is able to quantify the amount of PTE from ingested soil and dust, it can be seen as a conservative approach for environmental risk management. In addition to oral bioaccessibility,

health assessors are in the process of developing robust methods for assessing the human health risk via inhalation bioaccessibility and dermal absorption. While the bioaccessibility method is gaining credence in the field of human health risk assessment, it is yet to be accepted or recommended by government regulatory agencies, such as, the Department for Environment Food and Rural Affairs, UK (DEFRA) and the United States Environmental Protection Agency (US EPA). The major challenge facing the use of the bioaccessibility approach, as a tool for assessing human risk, is method validation via *in vivo* methods. However, the UBM has recently been validated (10) for four PTEs (antimony, arsenic, cadmium and lead) using a juvenile swine model. The authors believed that for UBM to be accepted by regulatory bodies as a tool for risk assessment, *in vivo* bioaccessibility results as well as *in vivo* bioavailability results must correlate. The result from the study showed that using benchmark criteria for assessing the fitness for purpose, the UBM met criteria on repeatability.

7.3 Human health risk implications of the study areas

This research has applied a risk-based approach to investigate the human health risk of PTEs from soil and dust. This was based on the UK EA and DEFRA risk-based approach for assessing human health risks from contaminated sites (11). This approach explores the likelihood, presence and significance of environmental contaminant linkages, which then reveals the relationship between a contaminant source, pathway, and receptor. This concept of pollutant linkages (source-pathway-receptor) helps to identify and assess the level of risk prevalent in a given environmental media; moreover, all three elements (source-pathway-receptor) of the pollutant linkage must be complete for a risk to exist.

The examination of children's playground field in the North East of England revealed the presence of seven PTEs (As, Cr, Cu, Pb, Mn, Ni and Zn) in the soil samples. Of greatest concern with respect to human health risk is the high lead content observed in three locations. At the time of this research, no international soil guideline values (SGVs) exist, however, for a more holistic human health risk assessment of high Pb levels, it was considered necessary to compare these results with SGVs from seven countries including England. It was observed that Pb concentrations recorded in these sites exceeded the SGVs from these seven countries. These high Pb present in children's playing field could enter their body via oral ingestion of soil. Children might not wash their hands properly after sporting or other outdoor activities and they could put their hands directly into the mouth, thereby introducing PTEs in their body. To further assess the risk, a detailed quantitative risk assessment (DQRA) was carried out in order to generate site specific assessment criteria (SSAC). This was found to be 16,449 mg/kg Pb which is about twelve times higher than 1270 mg/kg (representing the worse-case scenario from the study). The implication of this finding is that there is no significant possibility of significant harm (SPSH) in those sites. However, precautions, such as, good personal hygiene i.e. washing of hands after contact with the grass and soil will further limit potential exposure and minimise the possibility of hand-to-mouth ingestion. It is not advisable however to convert playground locations where high Pb content was found into gardens for the growing of fruits and vegetables as this would introduce Pb into the food chain thereby increasing the exposure risk to children particularly if such fruits and vegetables have the potential for Pb uptake.

Lead is one element that has attracted a lot of attention because of its toxicity, yet it is ubiquitous in environmental matrices particularly in the urban environment. The

ubiquitous nature of Pb was proven in this research as the determination of eight PTEs in ninety urban street dusts collected from six cities showed remarkable high concentrations of Pb (> 450 mg/kg) in thirty two sites across all study sites. With respect to the concentration of PTEs from a particular sample that a child (as the most sensitive receptor) could ingest to reach the estimated tolerable daily intake (TDI, for oral ingestion), it was observed that Pb exceeded the tolerable daily intake (3.6 μg kg^{-1} bw day^{-1}) (12) for oral ingestion for samples collected from Newcastle, Durham, Sunderland and Abakaliki. Given the complexity of modelling exposure and intake pathway (ingestion / inhalation / dermal sorption), particularly in an urban environment, the risk assessments must be treated with caution, but they do highlight the PTE of most concern. Furthermore, whilst it is not expected that a child would ingest 50 mg (accepted soil + dust ingestion rate) (13) of urban dust per day, the study shows that a child only needs to ingest < 38 mg dust / day in order to exceed the Pb TDI in Newcastle, Durham and Abakaliki. The implications of this finding is that urban dust is an environmental media through which these high Pb content could enter the human body particularly those who either live, work or undertake recreation within and around the locations. However, the entry route is also influenced by the sample particle size. Dust particles found to be < 10 μm could enter the human body during inhalation as dust easily mobilises with air particularly during the summer (dry season), on the other hand, dust particles with larger particle size fraction (e.g. < 125 μm) could enter the human body via intentional dust ingestion (e.g. children with pica behaviour) and unintentional dust ingestion (e.g. when fruits, vegetables, or dropped foods that are not properly washed are eaten).

When Pb enters the human body, it causes adverse effects. Its effects depend basically on the concentration as well as the age and health state of the individual

concerned. Children have been the focus of human health risk studies with respect to high lead content in environmental matrices, and its effects on them are well documented (14-15). In addition to adverse health effects, a study (16) has shown that there is a very strong association between preschool blood Pb and the subsequent crime rate trends over several decades in the USA and some European countries. A recent report (17) has labelled Pb as 'America's real criminal element'. This is because high crime rates in the US as well as other abnormal behavioural activities have been linked to high Pb content in children's bodies. The report noted that when differences in atmospheric Pb density between big and small cities went away, so did the difference in murder rates.

In view of the findings in this research, it is expected that children should not be unnecessarily exposed to urban dust particularly in those locations where high Pb content was recorded. The research further highlights the need for regular monitoring of PTE levels in the urban environment and of robust environmental management practices including constant street sweeping. Adequate personal hygiene such as washing of hands regularly is necessary precautionary measures.

7.4 Contribution of the study to bioaccessibility approach

Although this study employed the UBM in assessing human health risk associated with oral ingestion of soil from playground soil and oral ingestion of urban street dust, it however deviated from previous studies (18-19) by using a different particle size fraction. Previous studies (18-19) on oral bioaccessibility of PTEs in soil and dust used < 250 μm, as recommended by UBM, but it has been reported (20) that the elemental concentration of PTEs increase with decreasing particle size fraction, and moreover, the amount of soil and dust involuntarily ingested depends on the

adherence of soil / dust to the skin (21), thus, finer matrices tend to adhere more efficiently to human hands (22). In the light of these findings, this research used the < 125 µm particle size fraction instead of the < 250 µm to determine the bioaccessibility of PTEs in soil and dust. However, results obtained (in terms of bioaccessible fraction in the gastric and intestinal phases, respectively) were similar to results from previous studies (18-19) despite the difference in particle size. It further shows the robustness of the UBM. Bioaccessibility results from the children's field showed that should the playground soil be ingested, 55 ± 4 % of Pb would solubilise in the human stomach and 42 ± 5 % in the intestinal. With respect to the dust samples, 47 ± 5 % of Pb would be released in the human stomach while 36 ± 2 % would be released in the intestinal phase. The implication of the bioaccessibility results is that 42 ± 5 % of Pb from ingested soil and 36 ± 2 % of Pb from ingested dust are available for absorption in the human blood stream via the intestinal phase. The % Pb released in the stomach though might not be absorbed but should not be neglected as Pb could cause adverse effects in any part of body (14). Lead bioaccessibility results as well as that of other PTEs were found to be higher in the stomach phase than in the intestinal phase. This is expected because PTEs solubilises more at a lower pH of the stomach phase as the hydrochloric acid present in the stomach will allow the dissolution of labile mineral oxides, sulphides and carbonates that release these PTEs (23). The lower % BAF of these PTEs recorded in the intestinal phase is due to the fact that absorption, re-adsorption and precipitation of nutrients and other constituents (e.g., PTEs) take place in the intestine (24). Interestingly, the % BAF obtained in all cases are < 100 % assumed by the model used to derive SGVs. This highlights the unique role that bioaccesibility plays in human health risk assessment as it brings out the true picture of the actual

risk, hence its potential use as a conservative measure of human health risk assessment.

In addition to oral ingestion of soil and urban dust and for a more holistic human health risk assessment, it was considered necessary in this research to assess the potential health risk of urban dust with smaller particle size fraction (<10 μm). This particle size is of great concern because it can easily be carried by air flows generated by wind, traffic or human feet. Hence, they are quite mobile in the environment particularly in the urban environment with more people and vehicles and as a result they contribute significantly to the atmospheric air that we breathe daily (21). In the light of this, a literature survey of past and current *in vitro* methods used in assessing human health risk via inhalation bioaccessibility was carried out and it revealed wide discrepancies in terms of the chemical composition used to simulate the respiratory tract. In the order to make a significant input in the field of bioaccessibility and to further assess human health risk of Pb via inhalation of urban dust, a new method (simulated epithelia lung fluid) was developed for assessing Pb bioaccessibility in environmental matrices. The approach mimicked the tracheobronchial region of the human respiratory tract. It has been reported (25) that the <10 μm is the particle size that can easily be found in this region of the human respiratory tract. The unique feature of this new method is that the simulated fluid contains: proteins, surfactant, antioxidants and inorganic components found in the tracheobronchial region of the human respiratory tract. Previously reported works (26-27) on lung fluids omitted one or more of these components. It is expected that human health assessors would find the new method useful and that the result from this research would contribute significantly to the existing knowledge on bioaccessibility protocols and human health risk assessment in general.

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Chapter 8 Conclusion and future challenges

8.1 Conclusion

This study evaluated human health risk associated with oral ingestion of soil / dust and inhalation of urban street dust and air-borne dust. To estimate risk from oral ingestion of soil and dust, total content and oral bioaccessibility of 8 PTEs (As, Cd, Cr, Cu, Pb, Mn, Ni and Zn) were investigated in 29 soil samples collected from 12 children playgrounds and 90 urban street dusts collected from six cities. The results from playground soils revealed that total Pb content observed in three sites were higher than the UK SGVs. Human health risk was further assessed by investigating the oral bioaccessibility of these PTEs via the application of physiologically based extraction test (Unified BARGE method). The bioaccessibility results showed that all the PTEs were more bioaccessible in the gastric phase than in the intestinal phase. The result in gastric phase ranged from (44.5% - 62.4%). This implies than these PTEs mobilise more in the gastric phase, Besides, for a more holistic assessment of the potential maximum bioaccessible concentration, maximum estimated daily intake based on 50 mg/day ingestion and bioaccessibility has been calculated and it was observed that the values of the PTEs across the sites were relatively low and as such does not represent threat to human health. The study shows that it is not advisable however to convert playground locations where high Pb content was found into gardens for the growing of fruits and vegetables as this would increase the exposure risk to children.

Intentional or unintentional oral ingestion of urban street dust could be a potential pathway through which PTEs enter the human body. This is because the analysis of 90 urban street dusts collected from six cities revealed the presence of all the eight

PTEs and of particular concern was the high Pb concentrations recorded in 32 sites. These values were found to exceed the UK SGVs (450 mg/kg). Though exceedance does not necessarily represent health risk but it is important to note that children with either pica behaviour or people who practice geophagy could be at risk. With respect to the maximum PTE daily intake (μg kg^{-1} bw day^{-1}), Pb exceeded the tolerable daily intake for oral ingestion for samples collected from Newcastle, Durham, Sunderland and Abakaliki. Physiological based extraction test (UBM) results showed that these PTEs found in urban street dust mobilised more in the gastric phase than in the intestinal phase. In addition, air-borne dust collected for one year in the city of Newcastle upon Tyne was analysed for Pb concentration using EDXRF and the result revealed that there is more risk associated with inhalation of urban street dust (< 10 μm) than inhalation of air-borne dust (PM_{10}) with respect to Pb total content in these environmental matrices.

A new analytical procedure was developed (SELF) and has been used to evaluate the bioaccesibility of Pb in inhalable urban street dust (< 10 μm) where high Pb content was recorded (> 450 mg/kg). Though low bioaccessibility (< 10 %) was obtained in all cases but the new method has proved to be a useful tool in assessing human health risk via inhalation of urban dust. it is expected that this analytical method (SELF) would bridge the gap among lung fluids currently being used for the extraction of PTEs from environmental matrices.

The use of these analytical methods; Physiologically based extraction test (PBET) (UBM) and simulated epithelial lung fluids (SELF) has shown the significant role that bioaccessibility protocols play in human health risk assessment.

8.2 Future challenges

Environmental contaminant enter the human body via three exposure pathways; oral ingestion, inhalation and dermal absorption. This research investigated oral injgestion and inhalation pathways, *in-vitro* method that would be used to evaluate the dermal absorption pathway need to be developed.

Results from this study have shown that both total elemental composition and bioaccessible fraction in soil and dusts differed significantly rather than a uniform distribution across soil/dust samples. Therefore, investigating the mineralogical compositions of these environmental matrices would give a better understanding of the leaching mechanism and the bioaccessibility of the PTEs. In addition, for a better understanding of the environmental and health effects of these PTEs, it is worthwhile examining their speciation, particularly As and Cr, since their toxicity depends on the oxidation state.

It has been reported (chapter six) that Pb poisoning occurred in Zamfara State (north-west of Nigeria) which killed 400 children (< 6 years) and made about 3,500 children seriously sick. This incidence occurred as a result of illegal gold mining. An investigation of the contamination level of Pb and other PTEs in soil, street dust and house dust within the mining site need to be carried out in order to ascertain human health risk of the site. This will involve the determination of the elemental concentration, its bioaccessility (oral and inhalation) in soil and dust within the area, particularly areas such as playground soil where children spend quality time. Quantitative risk assessment of the site also needs to be undertaken. The mine tailings need to be investigated in terms of total elemental concentration, bioaccessibility (oral and inhalation). Also the contamination level and distribution of

Pb in vegetables and crops planted within the vicinity need to be thoroughly examined. The result of such a study would be useful in educating the rural dwellers and curtail future occurrence.

In order to have a broader knowledge of our environment with respect to health risk from contaminants, other chemicals known to have adverse effects on humans also need to be studied. One of such contaminants is platinum group elements (PGEs) (palladium (Pd), platinum (Pt), iridium (Ir), osmium (Os), rhodium (Rh) and ruthenium (Ru). These elements are widely used in various areas particularly in the manufacture of catalytic converters and as such are ubiquitous in the environment especially urban settlement. Thus, the determination of the total content of PGEs in urban soil and dust, its oral bioaccessibility viaUBM and its lung bioaccessibility through the use of simulated epithelial lung fluid need to be carried out.

In addition to soil and dust, it is necessary to investigate the levels of these environmental contaminants in water bodies particularly in developing countries where their emission is not regulated and moreover, rural dwellers and low income earners use untreated water for drinking and domestic purposes.

APPENDIX A

Total content, stage related bioaccessible and residual fractions of PTEs in playground soils.

A1: Total content, stage related bioaccessible and residual fractions of chromium (Cr) in soil collected from playground soils.

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	76.4 ± 1	45.3 ± 1	59.3	20.3 ± 0.5	26.8	43.7 ± 2	64.0	83.8
2	61.9 ± 0.8	30.7 ± 0.4	49.6	25.1 ± 0.1	40.5	36.3 ± 1	61.4	99.2
3	55.8 ± 2	29.6 ± 0.1	53.0	21.4 ± 2	38.4	26.2 ± 2	47.6	85.3
4	93.4 ± 2	43.3 ± 0.2	46.4	34.6 ± 0.3	37.0	51.2 ± 3	85.8	91.9
5	77.1 ± 1	33.6 ± 0.6	43.6	24.5 ± 0.1	31.8	39.6 ± 2	64.1	83.1
6	41.9 ± 2	17.4 ± 0.1	41.5	12.4 ± 0.3	29.4	28.3 ± 1	40.7	97.1
7	47.4 ± 2	23.8 ± 0.3	50.2	15.3 ± 0.1	32.3	30.7 ± 1	46.0	97.0

8	67.6 ± 1	34.1 ± 3	50.4	25.9 ± 0.6	38.3	34.4 ± 2	60.3	89.2
9	75.9 ± 1	31.2 ± 0.7	41.1	23.2 ± 0.7	30.6	44.7 ± 3	67.9	89.5
10	52.4 ± 0.6	24.3 ± 0.1	46.3	18.1 ± 0.5	34.5	23.1 ± 1	41.2	78.6
11-1	61.1 ± 0.3	34.7 ± 0.3	56.8	26.7 ± 0.3	43.7	24.7 ± 0.7	51.4	84.1
11-2	34.6 ± 0.2	15.4 ± 0.1	44.5	10.1 ± 0.4	29.1	12.8 ± 0.6	22.9	66.2
12-1	51.4 ± 0.3	27.6 ± 0.3	53.7	20.9 ± 2	40.7	27.5 ± 1	48.4	94.2
12-2	67.3 ± 0.1	34.4 ± 0.1	51.1	27.7 ± 0.1	41.2	33.2 ± 0.1	60.9	90.4
12-3	53.2 ± 1	24.8 ± 0.9	46.6	22.4 ± 0.9	42.1	28.2 ± 0.3	50.6	95.1
12-4	46.4 ± 0.4	23.6 ± 0.1	50.9	16.9 ± 0.2	36.4	27.8 ± 1	44.7	96.3
12-5	87.4 ± 0.3	40.2 ± 0.6	45.9	26.7 ± 3	30.5	46.1 ± 0.6	72.8	83.3
12-6	49.6 ± 0.4	22.7 ± 0.1	45.7	16.6 ± 1	33.5	27.2 ± 0.1	43.8	88.3
12-7	57.5 ± 1	28.2 ± 0.1	49.0	21.3 ± 0.5	37.0	30.2 ± 0.7	51.5	89.6
12-8	38.8 ± 0.2	16.9 ± 0.2	43.6	12.6 ± 0.1	32.5	23.7 ± 2	36.3	93.5
12-9	41.4 ± 0.1	19.5 ± 0.3	47.1	12.4 ± 1	29.9	23.2 ± 0.9	35.6	85.9
12-10	17.4 ± 0.2	7.15 ± 0.1	41.1	3.12 ± 0.2	17.9	8.56 ± 0.1	11.7	67.1
12-11	23.8 ± 0.1	9.23 ± 0.5	38.8	5.21 ± 0.1	21.9	16.2 ± 0.3	21.4	89.9
12-12	38.2 ± 1	17.5 ± 0.3	45.8	10.2 ± 0.3	26.7	26.5 ± 2	36.7	96.1

12-13	21.9 ± 0.2	10.7 ± 0.2	48.8	8.22 ± 0.1	37.5	8.33 ± 0.2	16.6	75.6
12-14	56.8 ± 0.1	26.8 ± 0.4	47.2	20.3 ± 0.5	35.7	33.3 ± 1	53.6	94.4
12-15	52.3 ± 0.2	22.9 ± 0.1	43.9	17.9 ± 0.1	34.2	26.2 ± 0.4	44.1	84.3
12-16	51.1 ± 0.6	24.6 ± 0.4	48.1	21.4 ± 0.4	41.9	26.3 ± 0.6	47.7	93.3
12-17	76.8 ± 2	32.1 ± 0.2	41.8	27.2 ± 0.1	35.4	43.8 ± 2	71.0	92.4

% BAF: % BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in the certified reference / guidance materials obtained via the application of physiological based extraction test and $C_{total\ content}$ - PTE total content (mg/kg) in soil samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total.

A2: Total content, stage related bioaccessible and residual fractions of manganese (Mn) in soil collected playground soils.

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	521 ± 20	255 ± 22	48.9	183 ± 15	35.1	309 ± 29	492	94.4
2	480 ± 25	289 ± 31	60.2	172 ± 13	35.8	243 ± 27	415	86.5
3	590 ± 33	305 ± 89	51.7	182 ± 11	30.8	349 ± 33	531	90.0
4	582 ± 31	375 ± 24	64.4	166 ± 12	28.5	364 ± 34	530	91.1
5	1084 ± 60	676 ± 24	62.4	386 ± 27	35.6	675 ± 76	1061	97.9
6	511 ± 34	265 ± 11	51.9	202 ± 15	39.5	291 ± 22	493	96.4
7	652 ± 45	233 ± 33	35.7	196 ± 13	30.1	340 ± 27	536	82.2
8	706 ± 40	320 ± 82	45.3	193 ± 14	27.3	331 ± 28	524	74.2
9	278 ± 17	130 ± 15	46.8	90.4 ± 7	32.5	172 ± 13	262	94.4

10	536 ± 33	285 ± 22	53.2	163 ± 10	30.4	301 ± 24	464	86.6
11-1	493 ± 31	273 ± 26	55.4	109 ± 6	22.1	230 ± 17	339	68.8
11-2	400 ± 17	264 ± 29	66.0	164 ± 10	41.0	204 ± 17	368	92.0
12-1	507 ± 15	256 ± 11	50.5	237 ± 13	46.7	243 ± 17	480	94.7
12-2	653 ± 38	301 ± 16	46.1	270 ± 24	41.3	363 ± 43	633	96.9
12-3	635 ± 27	323 ± 21	50.9	133 ± 10	20.9	474 ± 44	607	95.6
12-4	527 ± 39	241 ± 14	45.7	120 ± 9	22.8	336 ± 23	456	86.5
12-5	631 ± 41	311 ± 24	49.3	217 ± 18	34.4	361 ± 37	578	91.6
12-6	478 ± 33	219 ± 11	45.8	162 ± 8	33.9	273 ± 28	435	91.0
12-7	553 ± 12	274 ± 18	49.5	187 ± 10	33.8	301 ± 29	488	88.2
12-8	626 ± 41	317 ± 13	50.6	231 ± 17	36.9	320 ± 27	551	88.0
12-9	432 ± 34	169 ± 23	39.1	104 ± 4	24.1	302 ± 24	406	93.9
12-10	648 ± 32	264 ± 11	40.7	210 ± 13	32.4	385 ± 33	595	91.8
12-11	498 ± 28	158 ± 9	31.7	114 ± 3	22.9	340 ± 26	454	91.1
12-12	438 ± 24	143 ± 8	32.6	106 ± 8	24.2	310 ± 29	416	94.9
12-13	286 ± 16	106 ± 2	37.1	62.9 ± 3	21.9	159 ± 9	223	77.5
12-14	684 ± 20	327 ± 31	47.8	215 ± 14	31.4	370 ± 33	585	85.5

12-15	454 ± 29	193 ± 9	42.5	132 ± 4	29.1	246 ± 29	378	83.3
12-16	538 ± 32	278 ± 12	51.7	174 ± 9	32.3	225 ± 29	399	74.2
12-17	597 ± 54	232 ± 9	38.8	148 ± 11	24.8	276 ± 35	424	71.0

% BAF: % BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in the certified reference / guidance materials obtained via the application of physiological based extraction test and $C_{total\ content}$ - PTE total content (mg/kg) in soil samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total.

A3: Total content, stage related bioaccessible and residual fractions of nickel (Ni) in soil collected from playground soils.

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	76.9 ± 3	31.5 ± 0.3	40.9	22.7 ± 0.1	29.5	43.8 ± 2	66.5	86.5
2	67.2 ± 1	30.4 ± 1	45.2	21.6 ± 0.3	32.1	31.2 ± 1	52.8	78.6
3	30.4 ± 0.8	11.9 ± 0.1	39.1	8.76 ± 0.1	28.8	16.7 ± 0.5	25.5	83.8
4	81.2 ± 0.1	40.1 ± 2	49.4	30.4 ± 0.1	37.4	43.5 ± 1	73.9	91.0
5	63.5 ± 4	28.3 ± 0.4	44.7	21.9 ± 0.5	34.5	33.2 ± 2	55.1	86.8
6	31.5 ± 0.4	12.2 ± 0.6	38.7	8.21 ± 0.6	26.1	18.3 ± 0.8	26.5	84.2
7	43.9 ± 0.6	17.3 ± 0.4	39.4	12.9 ± 0.1	29.4	19.2 ± 1	32.1	73.1
8	37.3 ± 0.1	18.4 ± 0.2	49.3	10.5 ± 0.4	28.1	21.2 ± 1	31.7	84.9
9	41.1 ± 0.2	17.7 ± 2	43.1	15.7 ± 2	38.2	19.4 ± 0.8	35.1	85.4

10	42.3 ± 1	19.4 ± 0.4	45.9	13.2 ± 1	31.2	20.2 ± 0.7	33.4	78.9
11-1	34.7 ± 0.3	15.8 ± 0.6	45.5	11.8 ± 0.4	34.0	18.1 ± 0.7	29.9	86.2
11-2	29.8 ± 0.1	12.3 ± 0.1	41.3	9.11 ± 0.2	30.6	14.4 ± 2	23.5	78.9
12-1	24.3 ± 1	10.1 ± 0.7	41.6	6.92 ± 0.1	28.5	13.8 ± 1	20.7	85.3
12-2	36.8 ± 0.3	14.8 ± 0.5	40.2	11.7 ± 0.7	31.8	22.8 ± 0.4	34.5	93.8
12-3	43.3 ± 0.2	18.9 ± 0.2	43.6	10.3 ± 0.3	23.8	26.6 ± 0.1	36.9	85.2
12-4	28.7 ± 0.4	13.7 ± 2	47.7	7.83 ± 0.6	27.3	17.2 ± 0.8	25.0	87.2
12-5	53.1 ± 2	33.8 ± 1	63.7	20.5 ± 0.2	38.6	29.3 ± 1	49.8	93.9
12-6	46.8 ± 0.3	27.4 ± 0.3	58.5	17.6 ±1	37.6	25.3 ± 0.4	42.9	91.7
12-7	32.3 ± 0.1	11.8 ± 0.1	36.5	8.12 ± 0.1	25.1	18.2 ± 0.9	26.3	81.5
12-8	40.4 ± 0.5	17.3 ± 0.4	42.8	15.3 ± 3	37.9	21.4 ± 0.2	36.7	90.8
12-9	37.3 ± 0.1	14.9 ± 0.5	39.9	10.4 ± 0.3	27.9	19.6 ± 0.7	30.0	80.4
12-10	31.9 ± 0.3	12.7 ± 0.2	39.8	8.25 ± 0.1	25.9	21.8 ± 0.1	30.1	94.2
12-11	33.1 ± 0.1	14.2 ± 0.4	42.9	11.3 ± 0.9	34.1	17.2 ± 0.2	28.5	86.1
12-12	28.4 ± 0.2	16.5 ± 0.5	58.1	10.2 ± 0.2	35.9	16.2 ± 0.7	26.4	92.9
12-13	11.2 ± 0.1	4.33 ± 0.1	38.7	3.01 ± 0.1	26.9	6.07 ± 0.3	9.08	81.1
12-14	32.7 ± 0.3	13.7 ± 0.1	41.9	12.1 ± 2	37.0	19.6 ± 0.1	31.7	96.9

12-15	29.8 ± 0.1	10.6 ± 0.6	35.5	7.04 ± 0.9	23.6	18.4 ± 0.8	25.4	85.2
12-16	32.5 ± 0.2	13.8 ± 0.2	42.5	12.2 ± 0.1	37.5	18.7 ± 0.3	30.9	95.1
12-17	37.3 ± 0.1	20.9 ± 0.1	56.0	13.2 ± 0.4	35.4	23.4 ± 0.8	36.6	98.1

% BAF: % BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in the certified reference / guidance materials obtained via the application of physiological based extraction test and $C_{total\ content}$ - PTE total content (mg/kg) in soil samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total.

A4: Total content, stage related bioaccessible and residual fractions of copper (Cu) in soil collected from playground soils.

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	105 ± 4	41.8 ± 1	39.8	34.8 ± 0.6	33.1	46.4 ±3	81.2	77.3
2	31.1 ± 0.1	13.9 ± 0.1	44.7	10.4 ± 0.1	33.4	14.5 ± 2	24.9	80.1
3	37.6 ± 8	20.4 ± 3	54.3	15.3 ± 0.6	40.7	13.4 ± 3	28.7	76.3
4	132 ± 5	75.9 ± 1	57.5	42.1 ± 7	31.9	87.6 ± 4	130	98.3
5	600 ± 12	324 ± 9	54.0	221 ± 13	36.8	346 ± 13	567	94.5
6	17.9 ± 0.3	7.61 ± 0.1	42.5	6.14 ± 0.7	34.3	9.02 ± 1	15.2	84.9
7	63.2 ± 0.2	31.6 ± 0.6	50.0	27.6 ± 0.3	43.7	31.8 ± 2	59.4	93.9

8	10.3 ± 0.1	6.11 ± 0.1	59.3	3.13 ± 0.4	30.4	4.11 ± 0.6	7.24	70.3
9	31.4 ± 0.3	18.7 ± 0.2	59.6	14.2 ± 0.1	45.2	15.8 ± 0.2	30.0	95.5
10	178 ± 5	105 ± 0.1	58.9	93.9 ± 4	52.7	51.3 ± 3	145	81.6
11-1	51.8 ± 0.1	24.3 ± 0.6	46.9	20.8 ± 0.2	40.2	27.3 ± 6	48.1	92.9
11-2	15.2 ± 1	6.05 ± 0.3	39.8	5.74 ± 0.1	37.8	7.03 ± 0.1	13.1	86.1
12-1	10.4 ± 0.1	6.13 ± 0.1	58.9	4.17 ± 0.4	40.1	4.11 ± 1	8.28	79.6
12-2	53.6 ± 0.4	22.1 ± 0.5	41.2	18.6 ± 0.1	34.7	30.6 ± 3	49.2	91.8
12-3	78.1 ± 0.2	43.9 ± 5	56.2	24.1 ± 2	30.9	46.3 ± 0.1	70.4	90.1
12-4	9.11 ± 0.5	5.21 ± 0.1	57.2	2.76 ± 0.1	30.3	4.64 ± 0.3	7.40	81.2
12-5	18.7 ± 0.3	10.4 ± 0.7	55.6	6.11 ± 0.5	32.7	10.7 ± 2	16.8	89.9
12-6	38.9 ± 0.1	20.5 ± 3	52.7	12.6 ± 0.1	32.4	22.8 ± 0.3	35.4	91.0
12-7	32.3 ± 1	17.4 ± 0.4	53.9	13.7 ± 0.6	42.4	17.1 ± 0.1	30.8	95.4
12-8	61.9 ± 0.6	30.4 ± 0.2	49.1	28.3 ± 0.1	45.7	29.8 ± 0.4	58.1	93.9
12-9	19.7 ± 0.1	10.1 ± 0.6	51.2	6.42 ± 0.5	32.9	10.2 ± 1	16.6	84.4
12-10	40.3 ± 0.2	22.9 ± 2	56.8	15.7 ± 0.4	38.9	23.6 ± 1	39.3	97.5
12-11	38.3 ± 0.1	20.4 ± 1	53.3	13.8 ± 0.8	36.0	22.7 ± 2	36.5	95.3
12-12	71.6 ± 0.2	37.6 ± 3	52.5	30.9 ± 0.2	43.2	38.6 ± 3	69.5	97.1

12-13	64.9 ± 2	30.9 ± 0.6	47.6	23.5 ± 0.1	36.2	36.1 ± 2	59.6	91.8
12-14	23.4 ± 0.3	13.7 ± 0.1	58.5	6.71 ± 0.4	28.3	12.6 ± 2	19.3	82.5
12-15	21.4 ± 0.1	9.81 ± 0.2	45.8	5.56 ± 0.1	25.9	13.1 ± 1	18.7	87.2
12-16	26.1 ± 0.1	11.7 ± 0.4	44.8	10.7 ± 0.8	40.9	12.2 ± 0.1	22.9	87.7
12-17	36.8 ± 1	20.7 ± 3	56.3	13.3 ± 0.1	36.1	20.3 ± 1	33.6	91.3

% BAF: % BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in the certified reference / guidance materials obtained via the application of physiological based extraction test and $C_{total\ content}$ - PTE total content (mg/kg) in soil samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total.

A5: Total content, stage related bioaccessible and residual fractions of zinc (Zn) in soil collected from playground soils.

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	398 ± 11	149 ± 6	37.4	105 ± 7	26.4	279 ± 13	384	96.4
2	301 ± 8	105 ± 6	34.9	87.5 ± 0.3	29.1	165 ± 10	253	83.9
3	155 ± 0.7	86.3 ± 0.4	55.8	61.9 ± 0.1	39.9	73.6 ± 4	136	87.4
4	721 ± 18	408 ± 25	56.9	318 ± 18	44.1	320 ± 18	638	88.5
5	934 ± 31	416 ± 20	44.5	376 ± 9	40.3	528 ± 40	904	96.8
6	184 ± 12	91.3 ± 9	49.6	67.4 ± 0.3	36.7	101 ± 6	168	91.5
7	191 ± 6	87.9 ± 0.4	46.0	60.9 ± 0.1	31.9	111 ± 8	172	90.0

8	178 ± 4	90.1 ± 2	50.6	68.5 ± 4	38.5	100 ± 6	169	94.6
9	112 ± 1	56.8 ± 0.7	50.7	33.1 ± 1	29.6	63.4 ± 3	96.5	86.2
10	215 ± 11	107 ± 5	49.8	89.4 ± 0.5	41.6	114 ± 10	203	94.6
11-1	194 ± 5	103 ± 0.5	53.1	65.8 ± 0.2	33.9	93.6 ± 6	159	82.2
11-2	108 ± 3	61.6 ± 0.3	57.0	42.7 ± 0.1	39.5	57.9 ± 4	101	93.1
12-1	128 ± 6	76.3 ± 0.2	59.6	50.1 ± 4	39.1	70.2 ± 0.5	120	93.8
12-2	172 ± 3	83.1 ± 0.4	48.3	56.8 ± 0.2	33.0	106 ± 0.1	163	94.7
12-3	194 ± 6	111 ± 1	57.2	63.6 ± 0.1	32.8	127 ± 0.6	191	98.2
12-4	155 ± 4	64.2 ± 0.5	41.4	42.7 ± 0.4	27.5	94.6 ± 0.4	137	88.6
12-5	203 ± 10	101 ± 1	49.8	80.2 ± 0.1	39.5	117 ± 0.5	197	97.1
12-6	147 ± 7	62.5 ± 0.3	42.5	42.5 ± 0.2	28.9	102 ± 0.3	145	98.2
12-7	113 ± 4	47.8 ± 0.1	48.9	31.6 ± 0.3	27.9	72.6 ± 0.2	104	92.2
12-8	156 ± 2	67.9 ± 0.6	43.5	40.8 ± 0.1	26.2	101 ± 1	142	90.9
12-9	102 ± 6	54.3 ± 0.1	53.2	39.5 ± 0.4	38.7	48.2 ± 0.2	87.7	85.9
12-10	211 ± 9	110 ± 0.6	52.1	64.7 ± 0.1	30.7	138 ± 8	203	96.1
12-11	128 ± 12	51.8 ± 0.4	40.5	38.4 ± 0.4	30.0	75.8 ± 0.5	114	89.2
12-12	118 ± 5	60.2 ± 0.6	51.0	41.3 ± 0.1	35.0	67.1 ± 0.3	108	91.9

12-13	55.1 ± 1	26.9 ± 1	48.8	20.5 ± 0.1	37.2	28.1 ± 0.2	48.6	88.2
12-14	148 ± 5	62.8 ± 0.2	42.4	43.1 ± 0.3	29.1	75.2 ± 0.3	118	80.0
12-15	145 ± 3	74.7 ± 0.1	51.5	41.7 ± 0.2	28.8	90.4 ± 0.4	132	91.1
12-16	121 ± 4	61.2 ± 0.3	50.6	37.6 ± 0.1	31.1	77.4 ± 0.3	115	95.0
12-17	132 ± 1	62.5 ± 0.1	47.3	40.5 ± 3	30.7	73.4 ± 0.2	114	86.2

% BAF: % BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in the certified reference / guidance materials obtained via the application of physiological based extraction test and $C_{total\ content}$ - PTE total content (mg/kg) in soil samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total.

A6: Total content, stage related bioaccessible and residual fractions of arsenic (As) in soil collected from playground soils.

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	21.3 ± 0.4	8.13 ± 0.1	38.2	5.16 ± 0.3	24.2	12.3 ± 0.6	17.5	82.0
2	10.2 ± 0.8	5.64 ± 0.3	55.3	3.43 ± 0.5	33.6	6.02 ± 0.7	9.45	92.6
3	9.88 ± 0.1	3.13 ± 0.1	31.9	2.01 ± 0.7	20.3	5.68 ± 0.3	7.69	77.8
4	22.8 ± 1	9.44 ± 0.6	41.4	6.71 ± 0.1	29.4	12.4 ± 1	19.1	83.8
5	17.6 ± 0.3	7.45 ± 0.2	42.3	4.28 ± 0.4	24.3	11.5 ± 0.2	15.8	89.7
6	12.4 ± 0.6	6.17 ± 0.1	49.8	4.46 ± 0.1	35.9	5.56 ± 0.4	10.0	80.8
7	10.1 ± 0.1	5.87 ± 0.9	58.1	4.11 ± 0.6	40.7	5.33 ± 0.3	9.44	93.5
8	11.8 ± 1	6.23 ± 0.3	52.7	3.46 ± 0.1	29.3	6.42 ± 0.2	9.88	83.7
9	10.4 ± 0.7	4.81 ± 0.1	46.3	2.94 ± 0.6	28.3	6.37 ± 0.3	9.31	89.5

10	22.1 ± 0.2	11.9 ± 0.6	53.8	7.26 ± 0.5	32.9	12.1 ± 0.1	19.4	87.8
11-1	9.31 ± 0.6	4.74 ± 0.1	50.9	3.10 ± 0.2	33.3	6.11 ± 0.4	9.21	98.9
11-2	5.21 ± 0.1	2.11 ± 0.3	40.5	1.93 ± 0.1	37.0	2.63 ± 0.3	4.56	87.5
12-1	8.55 ± 0.7	4.11 ± 0.1	48.1	2.24 ± 0.4	26.1	4.92 ± 0.2	7.16	83.7
12-2	14.5 ± 0.1	7.13 ± 0.2	49.2	4.32 ± 0.9	29.8	9.21 ± 0.7	13.5	93.1
12-3	15.2 ± 0.4	6.57 ± 0.1	43.2	3.82 ± 0.1	25.1	10.4 ± 0.3	14.2	93.4
12-4	10.6 ± 0.1	6.16 ± 0.6	58.1	3.32 ± 0.6	31.3	6.22 ± 0.1	9.54	90.0
12-5	19.2 ± 0.6	7.64 ± 0.3	39.8	4.12 ± 0.1	21.5	12.6 ± 0.2	16.7	87.1
12-6	17.4 ± 0.1	7.89 ± 0.1	45.3	5.27 ± 0.5	30.3	10.2 ± 0.6	15.5	88.9
12-7	16.7 ± 0.2	9.82 ± 0.6	58.8	6.92 ± 0.1	41.4	8.54 ± 0.8	15.5	92.6
12-8	16.6 ± 0.1	7.65 ± 0.1	46.1	5.13 ± 0.6	30.9	9.63 ± 0.6	14.7	88.9
12-9	12.2 ± 0.6	6.31 ± 0.6	51.7	3.40 ± 0.2	27.9	7.93 ± 0.1	11.3	92.9
12-10	6.11 ± 0.2	3.21 ± 0.3	52.5	2.14 ± 0.6	35.0	3.56 ± 0.2	5.70	93.9
12-11	16.6 ± 0.1	7.65 ± 0.4	46.1	5.13 ± 0.1	30.9	9.46 ± 1	14.6	87.9
12-12	15.6 ± 0.3	7.13 ± 0.1	45.7	4.32 ± 0.8	27.7	9.14 ± 0.3	13.5	86.3
12-13	4.89 ± 0.1	2.13 ± 0.1	43.6	1.24 ± 0.2	25.4	2.62 ± 0.6	3.87	79.1
12-14	14.5 ± 0.2	6.71 ± 0.5	46.3	5.66 ± 0.7	39.0	8.33 ± 0.1	14.0	96.5

12-15	12.7 ± 0.6	6.32 ± 0.1	49.7	3.21 ± 0.3	25.3	6.93 ± 0.1	10.1	79.8
12-16	15.5 ± 0.1	8.41 ± 0.4	54.2	5.63 ± 0.7	36.3	7.11 ± 1	12.7	82.2
12-17	17.7 ± 0.3	7.86 ± 0.9	44.4	6.17 ± 0.2	34.9	9.14 ± 0.4	15.3	86.5

% BAF: % BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in the certified reference / guidance materials obtained via the application of physiological based extraction test and $C_{total\ content}$ - PTE total content (mg/kg) in soil samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total.

A7: Total content, stage related bioaccessible and residual fractions of lead (Pb) in soil collected from playground soils.

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	169 ± 0.6	83.3 ± 0.4	49.3	49.6 ± 0.2	29.3	85.8 ± 0.1	135	80.1
2	108 ± 0.1	45.3 ± 2	41.9	39.7 ± 0.7	36.8	51.6 ± 0.6	91.3	84.5
3	61.7 ± 0.2	28.7 ± 0.1	46.5	22.6 ± 0.5	36.6	33.1 ± 0.7	55.7	90.3
4	671 ± 2	345 ± 15	51.4	187 ± 9	27.9	328 ± 18	515	76.8
5	1270 ± 5	589 ± 23	46.4	370 ± 10	29.1	768 ± 34	1138	89.6
6	84.5 ± 0.1	40.9 ± 0.7	48.4	32.7 ± 0.4	38.7	42.1 ± 0.9	74.8	88.5
7	95.6 ± 0.6	38.7 ± 0.2	40.5	31.6 ± 0.1	33.1	50.2 ± 0.5	81.8	85.6
8	74.6 ± 0.2	30.4 ± 0.1	40.8	27.6 ± 0.2	36.9	36.2 ± 0.1	63.8	85.5
9	56.2 ± 0.1	28.8 ± 0.1	51.2	20.6 ± 0.8	36.7	30.2 ± 0.1	50.7	90.2

10	213 ± 2	98.7 ± 2	46.3	88.6 ± 0.3	41.6	103 ± 2	192	89.9
11-1	856 ± 4	442 ± 9	51.6	326 ± 0.1	38.1	422 ± 4	748	87.4
11-2	512 ± 1	231 ± 4	45.1	211 ± 12	41.2	242 ± 1	453	88.5
12-1	67.2 ± 0.3	35.9 ± 0.2	53.4	24.6 ± 0.1	36.6	32.2 ± 0.3	56.8	84.5
12-2	98.3 ± 0.2	43.9 ± 0.4	44.7	30.3 ± 0.3	30.8	44.3 ± 0.2	74.6	75.9
12-3	185 ± 0.1	81.4 ± 2	44.0	63.9 ± 0.1	34.5	105 ± 0.1	169	91.3
12-4	97.3 ± 0.2	38.7 ± 0.3	39.8	34.7 ± 0.9	35.7	47.3 ± 0.2	82.0	84.3
12-5	116 ± 0.6	46.8 ± 0.1	40.3	32.9 ± 0.1	28.4	56 ± 0.6	88.9	76.6
12-6	131 ± 0.9	59.8 ± 0.6	45.6	43.8 ± 0.5	33.4	80.1 ± 0.9	124	94.6
12-7	100 ± 0.6	57.9 ± 0.3	57.9	34.6 ± 0.2	34.6	51.3 ± 0.6	85.9	85.9
12-8	89.4 ± 0.1	36.5 ± 0.1	40.8	30.3 ± 0.1	33.9	39.4 ± 0.1	69.7	78.0
12-9	62.3 ± 0.3	30.9 ± 0.3	49.6	27.6 ± 0.3	44.3	32.3 ± 0.3	59.9	96.1
12-10	73.4 ± 0.1	27.9 ± 0.2	38.0	25.1 ± 0.4	34.2	33.4 ± 0.1	58.5	79.7
12-11	78.6 ± 0.3	34.8 ± 0.1	44.3	22.3 ± 0.1	28.4	38.6 ± 0.3	60.9	77.5
12-12	69.8 ± 0.2	35.9 ± 0.8	51.4	21.4 ± 0.4	30.7	39.8 ± 0.2	61.2	87.7
12-13	36.4 ± 0.3	16.8 ± 0.9	46.2	11.7 ± 0.8	32.1	20.4 ± 0.3	32.1	88.2
12-14	81.2 ± 0.1	36.9 ± 0.1	45.4	28.3 ± 0.1	34.9	41.2 ± 0.1	69.5	85.6

12-15	50.8 ± 0.3	26.5 ± 0.2	52.2	18.7 ± 0.4	36.8	30.8 ± 0.3	49.5	97.4
12-16	40.9 ± 0.1	15.8 ± 0.5	38.6	13.9 ± 0.2	34.0	20.9 ± 0.1	34.8	85.1
12-17	48.2 ± 0.4	21.4 ± 0.3	44.4	16.9 ± 0.6	35.1	28.2 ± 0.4	45.1	93.6

% BAF: % BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in the certified reference / guidance materials obtained via the application of physiological based extraction test and $C_{total\ content}$ - PTE total content (mg/kg) in soil samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total.

Appendix B

B1: Inter-stage correlation analysis of PTEs in playground soil (concentration phase)

Elements	Correlation value	P-value	Stage (mg /kg)
Cr	0.955	0.000	T & G
	0.925	0.001	T &GI
	0.910	0.000	G & GI
Mn	0.887	0.000	T & G
	0.841	0.000	T &GI
	0.834	0.000	G & GI
Ni	0.937	0.000	T & G
	0.950	0.000	T &GI
	0.957	0.000	G & GI
Cu	0.998	0.000	T & G
	0.990	0.000	T &GI
	0.992	0.000	G & GI
Zn	0.980	0.000	T & G
	0.964	0.000	T &GI
	0.993	0.000	G & GI
AS	0.918	0.000	T & G
	0.926	0.000	T &GI
	0.987	0.000	G & GI
Pb	0.997	0.000	T & G
	0.984	0.000	T &GI
	0.976	0.000	G & GI

T = Total concentration, G = Gastric phase, GI = gastric + intestine

B2: Inter-stage correlation analysis of PTEs in playground soil (% BAF phase)

Elements	Correlation value	P-value	Stage (% BAF)
Cr	0.252	0.188	T & G
	0.367	0.050	T &GI
	0.525	0.003	G & GI
Mn	0.251	0.188	T & G
	0.156	0.419	T &GI
	0.458	0.013	G & GI
Ni	0.264	0.166	T & G
	0.333	0.077	T &GI
	0.597	0.001	G & GI
Cu	0.089	0.645	T & G
	0.137	0.480	T &GI
	0.206	0.585	G & GI
Zn	0.116	0.550	T & G
	0.334	0.077	T &GI

	0.621	0.000	G & GI
AS	0.170	0.378	T & G
	0.121	0.531	T &GI
	0.642	0.000	G & GI
Pb	0.180	0.349	T & G
	0.158	0.414	T &GI
	0.116	0.548	G & GI

T = Total concentration, G = Gastric phase, GI = gastric + intestine

Appendix C: Inter-stage t test analysis of PTEs in playground soil

Elements	Concentration stage (G & GI)		% BAF stage (G & GI)	
	T-value	P-value	T-value	P-value
Cr	3.131	0.004	9.215	0.0001
Mn	4.268	0.0009	8.314	0.0004
Ni	2.808	0.007	8.370	0.0044
Cu	0.707	0.482	9.241	0.0007
Zn	1.229	0.224	10.2	0.0028
As	4.609	0.0003	10.89	0.00024
Pb	0.859	0.0002	9.607	0.0002

G = Gastric phase, GI = gastric + intestine

Appendix D

D1: Maximum PTE estimated daily oral intake from soil (Bedlington)

Element	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1})@ based on 50 mg/day ingestion≠	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1})@ based on 50 mg/day ingestion and bioaccessibility≠ (Gastric only)	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1})@ based on 50 mg/day ingestion and bioaccessibility≠ (Gastric + intestine)	Maximum estimated daily intake (ng kg_{bw}^{-1} day^{-1})+ based on 50 mg/day ingestion and an estimated annual exposure frequency	Amount of soil that could be consumed by a child[C] in order to exceed the guidelines (mg/day)	TDI_{oral} µg kg_{bw}^{-1} day^{-1}
Cr	0.17	0.05	0.04	3.49	45073	150[a]
Mn	1.29	0.77	0.46	27.1	N/A	N/A
Ni	0.18	0.08	0.06	3.80	3321	12[b]
Cu	0.08	0.04	0.03	1.76	95691	160[a]
Zn	0.81	0.28	0.23	17.0	37076	600[a]
As	0.03	0.02	0.01	0.58	500	0.3[c]
Pb	0.30	0.12	0.11	6.10	620	3.6[d]

@ the maximum estimated daily intake (DI) was calculated using the formula DI= [EC x SIR] / BW (47-49), where DI = daily intake (µg kg bw^{-1} day^{-1}) as determined in < 125 µm fraction of the soil sample with the highest concentration; EC = Exposure concentration of the PTEs in < 125 µm (µg/g); SIR = soil ingestion rate (0.05 g day^{-1}) (9); and BW = body weight (18.6 kg for a 3-6 year old child) (48). In order to calculate the maximum estimated daily intake and bioaccessibility, the above equation was modified to DI= [EC x SIR X B] / BW where B is the bioaccessible fraction determined using Unified BARGE Method.

+ based on the maximum bioaccessible concentration using either ‘gastric’ or ‘gastric + ‘intestinal’ phase

≠ the maximum estimated daily intake (DI) and estimated annual exposure frequency was calculated using the formula DI= [EC x SIR x EF] / BW, where DI = daily intake (ng kg^{-1}bw day^{-1}as determined in <125 µm fraction of the soil sample with the highest concentration; EC = Exposure concentration of As or Pb in <125 µm (µg/g); SIR = soil ingestion rate (0.05 g day^{-1}) (5); EF = Exposure frequency = 0.021 day^{-1} (estimated to be 5 hours a week for 38 weeks (term time) i.e. 190 hours per year or 7.9 days per year); and BW = body weight (18.6 kg for a 3-6 year old child) **(**48).

c child aged 3 - 6 years.

TDI_{oral} for Cr = 150 µg kg^{-1}bw day^{-1} (39)

TDI_{oral} for Mn = N/A

TDI_{oral} for Ni = 12 µg kg^{-1}bw day^{-1} (50)

TDI_{oral} for Cu = 160 µg kg^{-1}bw day^{-1} (39)

TDI_{oral} for Zn = 600 µg kg^{-1}bw day^{-1} (39)

ID_{oral} for As = 0.3 µg kg^{-1}bw day^{-1} (51)

TDI_{oral} for Pb = 3.6 µg kg^{-1}bw day^{-1} (52)

D2: Maximum PTE estimated daily oral intake from soil (Berwick upon Tweed)

Element	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1})@ based on 50 mg/day ingestion≠	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1})@ based on 50 mg/day ingestion and bioaccessibility≠ (Gastric only)	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1})@ based on 50 mg/day ingestion and bioaccessibility≠ (Gastric + intestine)	Maximum estimated daily intake (ng kg_{bw}^{-1} day^{-1})+ based on 50 mg/day ingestion and an estimated annual exposure frequency	Amount of soil that could be consumed by a child[C] in order to exceed the guidelines (mg/day)	TDI_{oral} µg kg_{bw}^{-1} day^{-1}
Cr	0.13	0.07	0.03	2.70	58246	150[a]
Mn	1.21	0.79	0.38	25.2	N/A	N/A
Ni	0.09	0.04	0.02	1.82	6910	12[b]
Cu	0.09	0.04	0.02	1.89	88835	160[a]
Zn	0.41	0.24	0.11	8.52	73907	600[a]
As	0.02	0.01	0.00	0.41	750	0.3[c]
Pb	1.84	0.96	0.59	38.6	98	3.6[d]

@ the maximum estimated daily intake (DI) was calculated using the formula DI= [EC x SIR] / BW (47-49), where DI = daily intake (µg kg bw^{-1} day^{-1}) as determined in < 125 µm fraction of the soil sample with the highest concentration; EC = Exposure concentration of the PTEs in < 125 µm (µg/g); SIR = soil ingestion rate (0.05 g day^{-1}) (9); and BW = body weight (18.6 kg for a 3-6 year old child) (48). In order to calculate the maximum estimated daily intake and bioaccessibility, the above equation was modified to DI= [EC x SIR X B] / BW where B is the bioaccessible fraction determined using Unified BARGE Method.

+ based on the maximum bioaccessible concentration using either 'gastric' or 'gastric + 'intestinal' phase

≠ the maximum estimated daily intake (DI) and estimated annual exposure frequency was calculated using the formula DI= [EC x SIR x EF] / BW, where DI = daily intake (ng kg^{-1}bw day^{-1}as determined in <125 µm fraction of the soil sample with the highest concentration; EC = Exposure concentration of As or Pb in <125 µm (µg/g); SIR = soil ingestion rate (0.05 g day^{-1}) (5); EF =

Exposure frequency = 0.021 day^{-1} (estimated to be 5 hours a week for 38 weeks (term time) i.e. 190 hours per year or 7.9 days per year); and BW = body weight (18.6 kg for a 3-6 year old child) **(**48).

c child aged 3 - 6 years.

TDI_{oral} for Cr = 150 µg kg^{-1}bw day^{-1} (39)

TDI_{oral} for Mn = N/A

TDI_{oral} for Ni = 12 µg kg^{-1}bw day^{-1} (50)

TDI_{oral} for Cu = 160 µg kg^{-1}bw day^{-1} (39)

TDI_{oral} for Zn = 600 µg kg^{-1}bw day^{-1} (39)

ID_{oral} for As = 0.3 µg kg^{-1}bw day^{-1} (51)

TDI_{oral} for Pb = 3.6 µg kg^{-1}bw day^{-1} (52)

D3: Maximum PTE estimated daily oral intake from soil (Cramlington)

Element	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1})@ based on 50 mg/day ingestion≠	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1})@ based on 50 mg/day ingestion and bioaccessibility≠ (Gastric only)	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1})@ based on 50 mg/day ingestion and bioaccessibility≠ (Gastric + intestine)	Maximum estimated daily intake (ng kg_{bw}^{-1} day^{-1})+ based on 50 mg/day ingestion and an estimated annual exposure frequency	Amount of soil that could be consumed by a child[C] in order to exceed the guidelines (mg/day)	TDI_{oral} µg kg_{bw}^{-1} day^{-1}
Cr	0.14	0.06	0.05	2.96	53244	150[a]
Mn	1.44	0.76	0.43	30.3	N/A	N/A
Ni	0.11	0.05	0.04	2.39	5276	12[b]
Cu	0.48	0.28	0.25	10.0	16719	160[a]
Zn	0.58	0.29	0.24	12.1	51906	600[a]
As	0.06	0.03	0.02	1.25	250	0.3[c]
Pb	0.57	0.26	0.24	12.0	316	3.6[d]

@ the maximum estimated daily intake (DI) was calculated using the formula DI= [EC x SIR] / BW (47-49), where DI = daily intake (µg kg bw^{-1} day^{-1}) as determined in < 125 µm fraction of the soil sample with the highest concentration; EC = Exposure concentration of the PTEs in < 125 µm (µg/g); SIR = soil ingestion rate (0.05 g day^{-1}) (9); and BW = body weight (18.6 kg for a 3-6 year old child) (48). In order to calculate the maximum estimated daily intake and bioaccessibility, the above equation was modified to DI= [EC x SIR X B] / BW where B is the bioaccessible fraction determined using Unified BARGE Method.

+ based on the maximum bioaccessible concentration using either 'gastric' or 'gastric + 'intestinal' phase

≠ the maximum estimated daily intake (DI) and estimated annual exposure frequency was calculated using the formula DI= [EC x SIR x EF] / BW, where DI = daily intake (ng kg^{-1}bw day^{-1}as determined in <125 µm fraction of the soil sample with the highest concentration; EC = Exposure concentration of As or Pb in <125 µm (µg/g); SIR = soil ingestion rate (0.05 g day^{-1}) (5); EF =

Exposure frequency = 0.021 day^{-1} (estimated to be 5 hours a week for 38 weeks (term time) i.e. 190 hours per year or 7.9 days per year); and BW = body weight (18.6 kg for a 3-6 year old child) **(**48).

c child aged 3 - 6 years.

TDI_{oral} for Cr = 150 µg kg^{-1}bw day^{-1} (39)

TDI_{oral} for Mn = N/A

TDI_{oral} for Ni = 12 µg kg^{-1}bw day^{-1} (50)

TDI_{oral} for Cu = 160 µg kg^{-1}bw day^{-1} (39)

TDI_{oral} for Zn = 600 µg kg^{-1}bw day^{-1} (39)

ID_{oral} for As = 0.3 µg kg^{-1}bw day^{-1} (51)

TDI_{oral} for Pb = 3.6 µg kg^{-1}bw day^{-1} (52)

D4: Maximum PTE estimated daily oral intake from soil (Hepscott)

Element	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1})@ based on 50 mg/day ingestion≠	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1})@ based on 50 mg/day ingestion and bioaccessibility≠ (Gastric only)	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1})@ based on 50 mg/day ingestion and bioaccessibility≠ (Gastric + intestine)	Maximum estimated daily intake (ng kg_{bw}^{-1} day^{-1})+ based on 50 mg/day ingestion and an estimated annual exposure frequency	Amount of soil that could be consumed by a child[C] in order to exceed the guidelines (mg/day)	TDI_{oral} µg kg_{bw}^{-1} day^{-1}
Cr	0.11	0.05	0.03	2.37	66587	150[a]
Mn	1.37	0.71	0.41	28.8	N/A	N/A
Ni	0.08	0.03	0.03	1.78	7086	12[b]
Cu	0.05	0.02	0.02	1.01	166257	160[a]
Zn	0.49	0.25	0.14	10.4	60652	600[a]
As	0.03	0.02	0.01	0.7	500	0.3[c]
Pb	0.23	0.09	0.08	4.78	783	3.6[d]

@ the maximum estimated daily intake (DI) was calculated using the formula DI= [EC x SIR] / BW (47-49), where DI = daily intake (µg kg bw^{-1} day^{-1}) as determined in < 125 µm fraction of the soil sample with the highest concentration; EC = Exposure concentration of the PTEs in < 125 µm (µg/g); SIR = soil ingestion rate (0.05 g day^{-1}) (9); and BW = body weight (18.6 kg for a 3-6 year old child) (48). In order to calculate the maximum estimated daily intake and bioaccessibility, the above equation was modified to DI= [EC x SIR X B] / BW where B is the bioaccessible fraction determined using Unified BARGE Method.

+ based on the maximum bioaccessible concentration using either 'gastric' or 'gastric + 'intestinal' phase

≠ the maximum estimated daily intake (DI) and estimated annual exposure frequency was calculated using the formula DI= [EC x SIR x EF] / BW, where DI = daily intake (ng kg^{-1}bw day^{-1}as determined in <125 µm fraction of the soil sample with the highest concentration; EC = Exposure concentration of As or Pb in <125 µm (µg/g); SIR = soil ingestion rate (0.05 g day^{-1}) (5); EF =

Exposure frequency = 0.021 day^{-1} (estimated to be 5 hours a week for 38 weeks (term time) i.e. 190 hours per year or 7.9 days per year); and BW = body weight (18.6 kg for a 3-6 year old child) **(**48).

c child aged 3 - 6 years.

TDI_{oral} for Cr = 150 µg kg^{-1}bw day^{-1} (39)

TDI_{oral} for Mn = N/A

TDI_{oral} for Ni = 12 µg kg^{-1}bw day^{-1} (50)

TDI_{oral} for Cu = 160 µg kg^{-1}bw day^{-1} (39)

TDI_{oral} for Zn = 600 µg kg^{-1}bw day^{-1} (39)

ID_{oral} for As = 0.3 µg kg^{-1}bw day^{-1} (51)

TDI_{oral} for Pb = 3.6 µg kg^{-1}bw day^{-1} (52)

D5: Maximum PTE estimated daily oral intake from soil (Hexham)

Element	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1})@ based on 50 mg/day ingestion≠	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1})@ based on 50 mg/day ingestion and bioaccessibility≠ (Gastric only)	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1})@ based on 50 mg/day ingestion and bioaccessibility≠ (Gastric + intestine)	Maximum estimated daily intake (ng kg_{bw}^{-1} day^{-1})+ based on 50 mg/day ingestion and an estimated annual exposure frequency	Amount of soil that could be consumed by a child[C] in order to exceed the guidelines (mg/day)	TDI_{oral} µg kg_{bw}^{-1} day^{-1}
Cr	0.21	0.01	0.07	4.35	36186	150[a]
Mn	2.91	1.81	1.00	61.2	N/A	N/A
Ni	0.17	0.08	0.06	3.59	3515	12[b]
Cu	1.61	0.87	0.60	33.9	4960	160[a]
Zn	2.51	1.13	1.00	52.7	11949	600[a]
As	0.05	0.012	0.01	0.99	300	0.3[c]
Pb	3.41	1.57	0.10	71.7	53	3.6[d]

@ the maximum estimated daily intake (DI) was calculated using the formula DI= [EC x SIR] / BW (47-49), where DI = daily intake (µg kg bw^{-1} day^{-1}) as determined in < 125 µm fraction of the soil sample with the highest concentration; EC = Exposure concentration of the PTEs in < 125 µm (µg/g); SIR = soil ingestion rate (0.05 g day^{-1}) (9); and BW = body weight (18.6 kg for a 3-6 year old child) (48). In order to calculate the maximum estimated daily intake and bioaccessibility, the above equation was modified to DI= [EC x SIR X B] / BW where B is the bioaccessible fraction determined using Unified BARGE Method.

+ based on the maximum bioaccessible concentration using either 'gastric' or 'gastric + 'intestinal' phase

≠ the maximum estimated daily intake (DI) and estimated annual exposure frequency was calculated using the formula DI= [EC x SIR x EF] / BW, where DI = daily intake (ng kg^{-1}bw day^{-1}as determined in <125 µm fraction of the soil sample with the highest concentration; EC = Exposure concentration of As or Pb in <125 µm (µg/g); SIR = soil ingestion rate (0.05 g day^{-1}) (5); EF =

Exposure frequency = 0.021 day^{-1} (estimated to be 5 hours a week for 38 weeks (term time) i.e. 190 hours per year or 7.9 days per year); and BW = body weight (18.6 kg for a 3-6 year old child) **(**48).

c child aged 3 - 6 years.

TDI_{oral} for Cr = 150 µg kg^{-1}bw day^{-1} (39)

TDI_{oral} for Mn = N/A

TDI_{oral} for Ni = 12 µg kg^{-1}bw day^{-1} (50)

TDI_{oral} for Cu = 160 µg kg^{-1}bw day^{-1} (39)

TDI_{oral} for Zn = 600 µg kg^{-1}bw day^{-1} (39)

ID_{oral} for As = 0.3 µg kg^{-1}bw day^{-1} (51)

TDI_{oral} for Pb = 3.6 µg kg^{-1}bw day^{-1} (52)

D6: Maximum PTE estimated daily oral intake from soil (Newcastle upon Tyne)

Element	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1})[@] based on 50 mg/day ingestion[≠]	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1})[@] based on 50 mg/day ingestion and bioaccessibility[≠] (Gastric only)	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1})[@] based on 50 mg/day ingestion and bioaccessibility[≠] (Gastric + intestine)	Maximum estimated daily intake (ng kg_{bw}^{-1} day^{-1})[+] based on 50 mg/day ingestion and an estimated annual exposure frequency	Amount of soil that could be consumed by a child[C] in order to exceed the guidelines (mg/day)	TDI_{oral} µg kg_{bw}^{-1} day^{-1}
Cr	0.25	0.12	0.09	5.27	29872	150[a]
Mn	1.56	1.00	0.45	32.9	N/A	N/A
Ni	0.22	0.11	0.08	4.58	27489	12[b]
Cu	0.35	0.21	0.11	7.45	22545	160[a]
Zn	1.94	1.10	0.86	40.7	15479	600[a]
As	0.06	0.03	0.02	1.29	250	0.3[c]
Pb	1.80	0.92	0.51	37.9	100	3.6[d]

[@] the maximum estimated daily intake (DI) was calculated using the formula DI= [EC x SIR] / BW (47-49), where DI = daily intake (µg kg bw^{-1} day^{-1}) as determined in < 125 µm fraction of the soil sample with the highest concentration; EC = Exposure concentration of the PTEs in < 125 µm (µg/g); SIR = soil ingestion rate (0.05 g day^{-1}) (9); and BW = body weight (18.6 kg for a 3-6 year old child) (48). In order to calculate the maximum estimated daily intake and bioaccessibility, the above equation was modified to DI= [EC x SIR X B] / BW where B is the bioaccessible fraction determined using Unified BARGE Method.

+ based on the maximum bioaccessible concentration using either 'gastric' or 'gastric + 'intestinal' phase

[≠] the maximum estimated daily intake (DI) and estimated annual exposure frequency was calculated using the formula DI= [EC x SIR x EF] / BW, where DI = daily intake (ng kg^{-1}bw day^{-1}as determined in <125 µm fraction of the soil sample with the highest concentration; EC = Exposure concentration of As or Pb in <125 µm (µg/g); SIR = soil ingestion rate (0.05 g day^{-1}) (5); EF =

Exposure frequency = 0.021 day^{-1} (estimated to be 5 hours a week for 38 weeks (term time) i.e. 190 hours per year or 7.9 days per year); and BW = body weight (18.6 kg for a 3-6 year old child) **(**48).

c child aged 3 - 6 years.

TDI_{oral} for Cr = 150 µg kg^{-1}bw day^{-1} (39)

TDI_{oral} for Mn = N/A

TDI_{oral} for Ni = 12 µg kg^{-1}bw day^{-1} (50)

TDI_{oral} for Cu = 160 µg kg^{-1}bw day^{-1} (39)

TDI_{oral} for Zn = 600 µg kg^{-1}bw day^{-1} (39)

ID_{oral} for As = 0.3 µg kg^{-1}bw day^{-1} (51)

TDI_{oral} for Pb = 3.6 µg kg^{-1}bw day^{-1} (52)

D7: Maximum PTE estimated daily oral intake from soil (Ponteland)

Element	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1})@ based on 50 mg/day ingestion≠	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1})@ based on 50 mg/day ingestion and bioaccessibility≠ (Gastric only)	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1})@ based on 50 mg/day ingestion and bioaccessibility≠ (Gastric + intestine)	Maximum estimated daily intake (ng kg_{bw}^{-1} day^{-1})+ based on 50 mg/day ingestion and an estimated annual exposure frequency	Amount of soil that could be consumed by a child[C] in order to exceed the guidelines (mg/day)	TDI_{oral} µg kg_{bw}^{-1} day^{-1}
Cr	0.21	0.12	0.06	4.31	36518	150[a]
Mn	1.40	0.69	0.49	29.4	N/A	N/A
Ni	0.21	0.08	0.06	4.34	2902	12[b]
Cu	0.28	0.11	0.09	5.93	28343	160[a]
Zn	1.07	0.40	0.28	22.5	28040	600[a]
As	0.06	0.02	0.01	1.20	20	0.3[c]
Pb	0.45	0.22	0.13	9.50	400	3.6[d]

@ the maximum estimated daily intake (DI) was calculated using the formula DI= [EC x SIR] / BW (47-49), where DI = daily intake (µg kg bw^{-1} day^{-1}) as determined in < 125 µm fraction of the soil sample with the highest concentration; EC = Exposure concentration of the PTEs in < 125 µm (µg/g); SIR = soil ingestion rate (0.05 g day^{-1}) (9); and BW = body weight (18.6 kg for a 3-6 year old child) (48). In order to calculate the maximum estimated daily intake and bioaccessibility, the above equation was modified to DI= [EC x SIR X B] / BW where B is the bioaccessible fraction determined using Unified BARGE Method.

+ based on the maximum bioaccessible concentration using either 'gastric' or 'gastric + 'intestinal' phase

≠ the maximum estimated daily intake (DI) and estimated annual exposure frequency was calculated using the formula DI= [EC x SIR x EF] / BW, where DI = daily intake (ng kg^{-1}bw day^{-1}as determined in <125 µm fraction of the soil sample with the highest concentration; EC = Exposure concentration of As or Pb in <125 µm (µg/g); SIR = soil ingestion rate (0.05 g day^{-1}) (5); EF =

Exposure frequency = 0.021 day^{-1} (estimated to be 5 hours a week for 38 weeks (term time) i.e. 190 hours per year or 7.9 days per year); and BW = body weight (18.6 kg for a 3-6 year old child) **(**48).

c child aged 3 - 6 years.

TDI_{oral} for Cr = 150 µg kg^{-1}bw day^{-1} (39)

TDI_{oral} for Mn = N/A

TDI_{oral} for Ni = 12 µg kg^{-1}bw day^{-1} (50)

TDI_{oral} for Cu = 160 µg kg^{-1}bw day^{-1} (39)

TDI_{oral} for Zn = 600 µg kg^{-1}bw day^{-1} (39)

ID_{oral} for As = 0.3 µg kg^{-1}bw day^{-1} (51)

TDI_{oral} for Pb = 3.6 µg kg^{-1}bw day^{-1} (52)

D8: Maximum PTE estimated daily oral intake from soil (Prudhoe)

Element	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1})@ based on 50 mg/day ingestion≠	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1})@ based on 50 mg/day ingestion and bioaccessibility≠ (Gastric only)	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1})@ based on 50 mg/day ingestion and bioaccessibility≠ (Gastric + intestine)	Maximum estimated daily intake (ng kg_{bw}^{-1} day^{-1})+ based on 50 mg/day ingestion and an estimated annual exposure frequency	Amount of soil that could be consumed by a child[C] in order to exceed the guidelines (mg/day)	TDI_{oral} µg kg_{bw}^{-1} day^{-1}
Cr	0.15	0.09	0.06	3.15	50000	150[a]
Mn	1.57	0.78	0.56	33.3	N/A	N/A
Ni	0.08	0.03	0.02	1.72	7342	12[b]
Cu	0.10	0.04	0.03	2.12	79149	160[a]
Zn	0.42	0.15	0.11	8.75	72000	600[a]
As	0.03	0.01	0.01	0.56	500	0.3[c]
Pb	0.17	0.08	0.047	3.48	1059	3.6[d]

@ the maximum estimated daily intake (DI) was calculated using the formula DI= [EC x SIR] / BW (47-49), where DI = daily intake (µg kg bw^{-1} day^{-1}) as determined in < 125 µm fraction of the soil sample with the highest concentration; EC = Exposure concentration of the PTEs in < 125 µm (µg/g); SIR = soil ingestion rate (0.05 g day^{-1}) (9); and BW = body weight (18.6 kg for a 3-6 year old child) (48). In order to calculate the maximum estimated daily intake and bioaccessibility, the above equation was modified to DI= [EC x SIR X B] / BW where B is the bioaccessible fraction determined using Unified BARGE Method.

+ based on the maximum bioaccessible concentration using either 'gastric' or 'gastric + 'intestinal' phase

≠ the maximum estimated daily intake (DI) and estimated annual exposure frequency was calculated using the formula DI= [EC x SIR x EF] / BW, where DI = daily intake (ng kg^{-1}bw day^{-1}as determined in <125 µm fraction of the soil sample with the highest concentration; EC = Exposure concentration of As or Pb in <125 µm (µg/g); SIR = soil ingestion rate (0.05 g day^{-1}) (5); EF =

Exposure frequency = 0.021 day^{-1} (estimated to be 5 hours a week for 38 weeks (term time) i.e. 190 hours per year or 7.9 days per year); and BW = body weight (18.6 kg for a 3-6 year old child) **(**48).

c child aged 3 - 6 years.

TDI_{oral} for Cr = 150 µg kg^{-1}bw day^{-1} (39)

TDI_{oral} for Mn = N/A

TDI_{oral} for Ni = 12 µg kg^{-1}bw day^{-1} (50)

TDI_{oral} for Cu = 160 µg kg^{-1}bw day^{-1} (39)

TDI_{oral} for Zn = 600 µg kg^{-1}bw day^{-1} (39)

ID_{oral} for As = 0.3 µg kg^{-1}bw day^{-1} (51)

TDI_{oral} for Pb = 3.6 µg kg^{-1}bw day^{-1} (52)

D9: Maximum PTE estimated daily oral intake from soil (Sacriston)

Element	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1})@ based on 50 mg/day ingestion≠	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1})@ based on 50 mg/day ingestion and bioaccessibility≠ (Gastric only)	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1})@ based on 50 mg/day ingestion and bioaccessibility≠ (Gastric + intestine)	Maximum estimated daily intake (ng kg_{bw}^{-1} day^{-1})+ based on 50 mg/day ingestion and an estimated annual exposure frequency	Amount of soil that could be consumed by a child[C] in order to exceed the guidelines (mg/day)	TDI_{oral} µg kg_{bw}^{-1} day^{-1}
Cr	0.13	0.08	0.05	2.76	57055	150[a]
Mn	1.45	0.71	0.49	30.5	N/A	N/A
Ni	0.09	0.04	0.03	1.93	6545	12[b]
Cu	0.10	0.04	0.03	2.15	78316	160[a]
Zn	0.38	0.14	0.11	8.07	78042	600[a]
As	0.04	0.01	0.01	0.78	375	0.3[c]
Pb	0.23	0.11	0.09	4.74	783	3.6[d]

@ the maximum estimated daily intake (DI) was calculated using the formula DI= [EC x SIR] / BW (47-49), where DI = daily intake (µg kg bw^{-1} day^{-1}) as determined in < 125 µm fraction of the soil sample with the highest concentration; EC = Exposure concentration of the PTEs in < 125 µm (µg/g); SIR = soil ingestion rate (0.05 g day^{-1}) (9); and BW = body weight (18.6 kg for a 3-6 year old child) (48). In order to calculate the maximum estimated daily intake and bioaccessibility, the above equation was modified to DI= [EC x SIR X B] / BW where B is the bioaccessible fraction determined using Unified BARGE Method.

+ based on the maximum bioaccessible concentration using either 'gastric' or 'gastric + 'intestinal' phase

≠ the maximum estimated daily intake (DI) and estimated annual exposure frequency was calculated using the formula DI= [EC x SIR x EF] / BW, where DI = daily intake (ng kg^{-1}bw day^{-1}as determined in <125 µm fraction of the soil sample with the highest concentration; EC = Exposure concentration of As or Pb in <125 µm (µg/g); SIR = soil ingestion rate (0.05 g day^{-1}) (5); EF =

Exposure frequency = 0.021 day^{-1} (estimated to be 5 hours a week for 38 weeks (term time) i.e. 190 hours per year or 7.9 days per year); and BW = body weight (18.6 kg for a 3-6 year old child) **(**48).

c child aged 3 - 6 years.

TDI_{oral} for Cr = 150 µg kg^{-1}bw day^{-1} (39)

TDI_{oral} for Mn = N/A

TDI_{oral} for Ni = 12 µg kg^{-1}bw day^{-1} (50)

TDI_{oral} for Cu = 160 µg kg^{-1}bw day^{-1} (39)

TDI_{oral} for Zn = 600 µg kg^{-1}bw day^{-1} (39)

ID_{oral} for As = 0.3 µg kg^{-1}bw day^{-1} (51)

TDI_{oral} for Pb = 3.6 µg kg^{-1}bw day^{-1} (52)

D10: Maximum PTE estimated daily oral intake from soil (South Shield)

Element	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1})@ based on 50 mg/day ingestion≠	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1})@ based on 50 mg/day ingestion and bioaccessibility≠ (Gastric only)	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1})@ based on 50 mg/day ingestion and bioaccessibility≠ (Gastric + intestine)	Maximum estimated daily intake (ng kg_{bw}^{-1} day^{-1})+ based on 50 mg/day ingestion and an estimated annual exposure frequency	Amount of soil that could be consumed by a child[C] in order to exceed the guidelines (mg/day)	TDI_{oral} µg kg_{bw}^{-1} day^{-1}
Cr	0.20	0.12	0.06	4.28	36759	150[a]
Mn	0.75	0.37	0.27	15.7	N/A	N/A
Ni	0.11	0.05	0.04	2.32	5431	12[b]
Cu	0.08	0.03	0.04	1.78	94777	160[a]
Zn	0.30	0.11	0.09	6.32	99643	600[a]
As	0.03	0.01	0.01	0.59	537	0.3[c]
Pb	0.15	0.07	0.06	3.17	1191	3.6[d]

@ the maximum estimated daily intake (DI) was calculated using the formula DI= [EC x SIR] / BW (47-49), where DI = daily intake (µg kg bw^{-1} day^{-1}) as determined in < 125 µm fraction of the soil sample with the highest concentration; EC = Exposure concentration of the PTEs in < 125 µm (µg/g); SIR = soil ingestion rate (0.05 g day^{-1}) (9); and BW = body weight (18.6 kg for a 3-6 year old child) (48). In order to calculate the maximum estimated daily intake and bioaccessibility, the above equation was modified to DI= [EC x SIR X B] / BW where B is the bioaccessible fraction determined using Unified BARGE Method.

+ based on the maximum bioaccessible concentration using either 'gastric' or 'gastric + 'intestinal' phase

≠ the maximum estimated daily intake (DI) and estimated annual exposure frequency was calculated using the formula DI= [EC x SIR x EF] / BW, where DI = daily intake (ng kg^{-1}bw day^{-1}as determined in <125 µm fraction of the soil sample with the highest concentration; EC = Exposure concentration of As or Pb in <125 µm (µg/g); SIR = soil ingestion rate (0.05 g day^{-1}) (5); EF =

Exposure frequency = 0.021 day^{-1} (estimated to be 5 hours a week for 38 weeks (term time) i.e. 190 hours per year or 7.9 days per year); and BW = body weight (18.6 kg for a 3-6 year old child) **(**48).

c child aged 3 - 6 years.

TDI_{oral} for Cr = 150 µg kg^{-1}bw day^{-1} (39)

TDI_{oral} for Mn = N/A

TDI_{oral} for Ni = 12 µg kg^{-1}bw day^{-1} (50)

TDI_{oral} for Cu = 160 µg kg^{-1}bw day^{-1} (39)

TDI_{oral} for Zn = 600 µg kg^{-1}bw day^{-1} (39)

ID_{oral} for As = 0.3 µg kg^{-1}bw day^{-1} (51)

TDI_{oral} for Pb = 3.6 µg kg^{-1}bw day^{-1} (52)

D11: Maximum PTE estimated daily oral intake from soil (Willington)

Element	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1})@ based on 50 mg/day ingestion≠	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1})@ based on 50 mg/day ingestion and bioaccessibility≠ (Gastric only)	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1})@ based on 50 mg/day ingestion and bioaccessibility≠ (Gastric + intestine)	Maximum estimated daily intake (ng kg_{bw}^{-1} day^{-1})+ based on 50 mg/day ingestion and an estimated annual exposure frequency	Amount of soil that could be consumed by a child[C] in order to exceed the guidelines (mg/day)	TDI_{oral} µg kg_{bw}^{-1} day^{-1}
Cr	0.18	0.11	0.07	3.82	41272	150[a]
Mn	1.90	0.93	0.51	39.6	N/A	N/A
Ni	0.10	0.04	0.03	2.11	5984	12[b]
Cu	0.02	0.01	0.01	0.59	288932	160[a]
Zn	0.49	0.18	0.19	10.0	62697	600[a]
As	0.03	0.01	0.01	0.67	500	0.3[c]
Pb	0.20	0.10	0.07	4.21	900	3.6[d]

@ the maximum estimated daily intake (DI) was calculated using the formula DI= [EC x SIR] / BW (47-49), where DI = daily intake (µg kg bw^{-1} day^{-1}) as determined in < 125 µm fraction of the soil sample with the highest concentration; EC = Exposure concentration of the PTEs in < 125 µm (µg/g); SIR = soil ingestion rate (0.05 g day^{-1}) (9); and BW = body weight (18.6 kg for a 3-6 year old child) (48). In order to calculate the maximum estimated daily intake and bioaccessibility, the above equation was modified to DI= [EC x SIR X B] / BW where B is the bioaccessible fraction determined using Unified BARGE Method.

+ based on the maximum bioaccessible concentration using either 'gastric' or 'gastric + 'intestinal' phase

≠ the maximum estimated daily intake (DI) and estimated annual exposure frequency was calculated using the formula DI= [EC x SIR x EF] / BW, where DI = daily intake (ng kg^{-1}bw day^{-1}as determined in <125 µm fraction of the soil sample with the highest concentration; EC = Exposure concentration of As or Pb in <125 µm (µg/g); SIR = soil ingestion rate (0.05 g day^{-1}) (5); EF =

Exposure frequency = 0.021 day^{-1} (estimated to be 5 hours a week for 38 weeks (term time) i.e. 190 hours per year or 7.9 days per year); and BW = body weight (18.6 kg for a 3-6 year old child) **(**48).

c child aged 3 - 6 years.

TDI_{oral} for Cr = 150 µg kg^{-1}bw day^{-1} (39)

TDI_{oral} for Mn = N/A

TDI_{oral} for Ni = 12 µg kg^{-1}bw day^{-1} (50)

TDI_{oral} for Cu = 160 µg kg^{-1}bw day^{-1} (39)

TDI_{oral} for Zn = 600 µg kg^{-1}bw day^{-1} (39)

ID_{oral} for As = 0.3 µg kg^{-1}bw day^{-1} (51)

TDI_{oral} for Pb = 3.6 µg kg^{-1}bw day^{-1} (52)

D12: Maximum PTE estimated daily oral intake from soil (Wooler)

Element	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1})[@] based on 50 mg/day ingestion[≠]	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1})[@] based on 50 mg/day ingestion and bioaccessibility[≠] (Gastric only)	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1})[@] based on 50 mg/day ingestion and bioaccessibility[≠] (Gastric + intestine)	Maximum estimated daily intake (ng kg_{bw}^{-1} day^{-1})[+] based on 50 mg/day ingestion and an estimated annual exposure frequency	Amount of soil that could be consumed by a child[C] in order to exceed the guidelines (mg/day)	TDI_{oral} µg kg_{bw}^{-1} day^{-1}
Cr	0.13	0.08	0.08	2.68	5900	150[a]
Mn	1.75	0.86	0.86	36.8	N/A	N/A
Ni	0.12	0.05	0.05	2.48	5080	12[b]
Cu	0.17	0.07	0.07	3.57	4700	160[a]
Zn	0.51	0.19	0.19	10.9	5800	600[a]
As	0.03	0.01	0.01	0.57	500	0.3[c]
Pb	0.26	0.13	0.13	5.40	692	3.6[d]

[@] the maximum estimated daily intake (DI) was calculated using the formula DI= [EC x SIR] / BW (47-49), where DI = daily intake (µg kg bw^{-1} day^{-1}) as determined in < 125 µm fraction of the soil sample with the highest concentration; EC = Exposure concentration of the PTEs in < 125 µm (µg/g); SIR = soil ingestion rate (0.05 g day^{-1}) (9); and BW = body weight (18.6 kg for a 3-6 year old child) (48). In order to calculate the maximum estimated daily intake and bioaccessibility, the above equation was modified to DI= [EC x SIR X B] / BW where B is the bioaccessible fraction determined using Unified BARGE Method.

+ based on the maximum bioaccessible concentration using either 'gastric' or 'gastric + 'intestinal' phase

[≠] the maximum estimated daily intake (DI) and estimated annual exposure frequency was calculated using the formula DI= [EC x SIR x EF] / BW, where DI = daily intake (ng kg^{-1}bw day^{-1}as determined in <125 µm fraction of the soil sample with the highest concentration; EC = Exposure concentration of As or Pb in <125 µm (µg/g); SIR = soil ingestion rate (0.05 g day^{-1}) (5); EF =

Exposure frequency = 0.021 day^{-1} (estimated to be 5 hours a week for 38 weeks (term time) i.e. 190 hours per year or 7.9 days per year); and BW = body weight (18.6 kg for a 3-6 year old child) **(**48).

c child aged 3 - 6 years.

TDI_{oral} for Cr = 150 µg kg^{-1}bw day^{-1} (39)

TDI_{oral} for Mn = N/A

TDI_{oral} for Ni = 12 µg kg^{-1}bw day^{-1} (50)

TDI_{oral} for Cu = 160 µg kg^{-1}bw day^{-1} (39)

TDI_{oral} for Zn = 600 µg kg^{-1}bw day^{-1} (39)

ID_{oral} for As = 0.3 µg kg^{-1}bw day^{-1} (51)

TDI_{oral} for Pb = 3.6 µg kg^{-1}bw day^{-1} (52)

Appendix E

Site description of urban street dust sampling in six cities.

E1: Newcastle upon Tyne sampling: location, description and receptors.

Site No.	Location / British National Grid (BNG)	Description/sources	Key receptors
1	Outside Ellison Building, Northumbria University (BNG: 425153, 564720)	Sample was collected at the edges of the building. The front of the building was carefully swept and sample collected. Environmental matrices: street dust, wear from shoes and car tyres, cigarette ends, particles from pencil sharpening and litter from droppings.	Students and university staff who cluster around the building. Pedestrians and cyclists.
2	Prudhoe Chase, outside Eldon Square (Northumberland Street). (BNG: 425119, 564804)	Vehicle restricted area except those on essential duties. Densely populated by pedestrians. Busy at all times because of large number of shops and restaurants. Sample was collected at the base of buildings and on the steps leading to Eldon square. Matrix: street dust, cigarette ends, rubbish from pedestrians, shops and restaurants.	Pedestrians and newspaper vendors. Workers and customers in shops. People who sit outside especially with food and drink; children.
3	Grey Street, by monument and Theatre Royal. (BNG: 424743, 564370).	Sample was taken from the edges of the buildings on the street including the various entrances to major shops and restaurants. Environmental matrices: street dust, litter, airborne particulates from industries, shoe and tyre wear material.	Pedestrians, people sitting within the area on seats provided (especially during the summer months).
4	Bigg Market. (BNG: 424619, 564575).	Sample was taken from the edges of the buildings within the area and also entrances to shops. Environmental matrices: street dust, litter from shops, cigarette ends and weathered materials.	People that shop and work within the market areas.

5	Outside Saint Nicholas Cathedral. (BNG: 424915, 564017)	Sample was collected at the entrance of the cathedral, edges of the building and the steps leading to the building. Environmental matrices: plant waste from flowers within the premises, animal waste from dogs, street dust, vehicular emissions and decayed paints from buildings and vehicles.	People going into and out of the church. Pedestrians who walk on the busy roads adjacent to the cathedral, drivers and cyclists.
6	Central railway station (under the arch) (BNG: 424621, 563569)	Sample was collected from the edges of the arch. Environmental matrices: Street dust, vehicular emissions, cigarette litters, emissions from inside of the railway station, decayed paints from buildings and vehicles.	Taxi drivers waiting for passengers under the arch. Security staff within the station. Pedestrians moving in and out of the station.
7	Clayton Street. (BNG: 424777, 563788).	Sample was collected along the street by sweeping, also at the edges of the building located along the street. Environmental matrices: street dust, vehicular and motorcycle emissions, cigarette ends.	Bicycle and motorcycle riders. Pedestrians and people in open shops.
8	Outside Grainger Market (end of Clayton Street). (BNG: 424719, 564159)	Sample was collected at the edges of the building located outside the building. Environmental matrices: street dust, cigarette ends and litter.	Pedestrians, people shopping and selling in the market.
9	Civic Centre (adjacent to St. Mary's Place). (BNG: 424954, 565050)	Sample was collected at the bus stop close to the entrance of the civic centre, steps at the entrance and at the edges of the building. Environmental matrices: street dust, sediments, vehicular emissions, shoe and tyre wears, air borne particulates from industries.	People working and visitors to the civic centre, drivers, passengers at the bus stop, cyclists and

			school children.
10	Newcastle University (outside of Robinson library). (BNG: 425163, 564921)	Sample was taken at the edges of the library building. Environmental matrices: street dust, litter, cigarette ends, decayed paints from houses and the arch, tyre and shoe wear material.	Students and other people that enter the library. Cyclists and pedestrians.
11	Outside Royal Victoria Infirmary. (BNG: 424368, 565132)	Sample was collected at the edges of the walls of the hospital, entrance of the hospital and bus stop close to the hospital. Environmental matrix: vehicular emissions, street dust and tyre wear.	Pedestrians, motorcyclists and cyclists.
12	Haymarket bus station (outside Marks and Spencer). (BNG: 424845, 565291).	Sample was collected inside the bus station where passengers sit and wait for buses, the entrance leading to Marks and Spencer within the station was also sampled. In addition, samples were also taken at various points were buses park for loading. Environmental matrices: street dust, cigarette ends, litter and vehicular emissions.	Bus drivers, passengers waiting for buses, pedestrians, buyers and sellers in the shops within the premises.
13	Outside St. James Park. (BNG: 424202, 564549)	Sample was collected at the edges of the building and the edges of the steps leading to the entrance of the stadium. Environmental matrices: street dust, tyre and shoe wear, cigarette ends, litter, vehicular emissions and airborne particulates from industries.	Football fans, dog walkers, and people using the outside of the stadium for recreation purposes as well as pedestrians.
14	Leazes Park Road (BNG: 424223, 564807)	Sample was taken at the entrance of the shops on the street and at the edges of the buildings on the street. Environmental matrices: street dust, cigarette ends and litter.	Pedestrians, drivers, cyclists and school children.
15	Stowell Street (“China Town”). (BNG: 424059,	Sample was collected at the edges of the building, entrance of the China town and shops on the street. Environmental	Pedestrians on the street and cyclists.

	564940).	matrices: street dust, urban rubbish and cigarette end.	

E2: Durham sampling: location, description and receptors.

Site No	Location / British National Grid (BNG)	Description / sources	Key receptors
1	Outside of Durham railway station. (BNG: 426995, 542733)	Sample was taken along the steps outside of the station. The steps are busy with pedestrians entering and leaving the station. Environmental matrix: sediment, detritus of plants and animals, dust particles and shoe wears.	Pedestrians who use the steps as a walk way.
2	Outside Gates Shopping Centre. (BNG: 427284, 542396)	Sample was taken from edges of the building. Environmental matrix: street dust, litter and cigarette ends.	Pedestrians, drivers and cyclists.
3	Millennium Place (Gala Theatre and Cinema). (BNG: 427668, 542937)	Vehicle restricted area except authorised ones. Busy with activities, like completion among school children, shows and seminars. The site is close to a road with vehicular traffic. Environmental matrix:	People who use the site for different activities.
4	Bus Station (North Road). (BNG: 426983, 542534)	Sample was taken from the edges of the road leading to the bus station and at the bus station. Environmental matrix: dust particles, tyre and shoe wears.	Passengers, drivers and people living close to the station.
5	New Elvet. (BNG: 427284, 542396)	Sample was collected from the edges of the road. Environmental matrix: dust particles.	Pedestrians.

6	Durham University (Elvet Riverside). (BNG: 427200, 542253)	Sample was collected from the corners of the building located along a busy vehicular traffic. Environmental matrix: vehicular emissions, street dust, tyre and shoe wear.	Students / university workers and pedestrians.
7	Elvet Street (behind Durham Cathedral and Castle Heritage Centre). (BNG: 427227, 542113)	Sample was taken from the edges of the road. Environmental matrix: street dust, vehicular emissions and decayed plant materials.	Pedestrians, cyclist and drivers.
8	Bow Lane (Bow Banks). (BNG: 427227, 542113)	Sample was taken along the lane and at edges of the buildings. Environmental matrix: street dust, litter and cigarette end.	Pedestrians
9	Durham Cathedral / University Library. (BNG: 427359, 542034).	The open space in the site is used for relaxation with a lot of people using either the cathedral or the library. Sample was taken from the edges of the building and at car park. Environmental matrix: vehicular emissions, dust particles and litter.	People that use the open space for recreation purposes as well as people that use the library and cathedral.
10	Saddler Street. (BNG: 427456, 542687).	Sample was taken from the corners of the road. Environmental matrix: street dust.	Pedestrians, drivers and cyclist.
11	Freeman's Premier Inn. (BNG: 427611, 542968).	Busy with vehicular traffic. Sample was taken from the edges of the road. Environmental matrix: vehicular emissions and street dust.	Pedestrians and people that use the premier inn.
12	Millburn Gate House (The Passport Office). (BNG:	Sample was taken from the edge of the road and buildings. Environmental matrix: vehicular emissions and street	People that work in the passport office, visitors to the office and

	427432, 542947)	dust.	pedestrians.
13	Penny Ferry Bridge. (BNG: 427752, 543019)	Sample was taken at the edge close the road. Environmental matrix: street dust.	Pedestrians.
14	Leazes Road. (BNG: 427320, 543002)	Busy with vehicular traffic and pedestrians. Sample was taken from the edge of the road and at bus stops. Environmental matrix: vehicular emission, street dust, litter and cigarette end.	People queuing at the bus stops, pedestrians, drivers and cyclist.
15	Framwelgate Road. (BNG: 426987, 542988)	Busy with vehicular traffic and pedestrians. Sample was taken at bus stops and at traffic light spots. Environmental matrix: street dust, tyre and shoe wears.	Pedestrians and other road users.

E3: **Liverpool sampling: location, description and receptors**.

Site no	**Location / British National Grid (BNG)**	**Description / sources**	**Key receptors**
1	Lime Street (railway station). (BNG: 335114, 390492)	High traffic and populated pedestrians. Sample was taken outside railway station and at the edges of the pavement, steps as well as the edges of the building. Environmental matrix: dust particles, litter, vehicular emissions and cigarette end.	Pedestrians and people who use the pavement outside the station as a recreation centre.
2	Elliot Park Street (St. John's market). (BNG: 334895, 390357)	Vehicle restricted area except those on essential duties. Sample was taken from the edges of the buildings within the park also at the edges of the seat out. Environmental matrix: dust particles, cigarette end and litter.	People that use the park for recreation purposes, advertisers as well as people that work and shop in the

			market.
3	Outside of Queen Square Centre (by Queen Street). (BNG: 334803, 390511)	The centre is located on a busy street with high traffic. Sample was collected at the edge of the building, entrance of shops, edge of pavements and inside of phone boot. Environmental matrix: dust particles, litter, vehicular emissions and cigarette end.	Pedestrians, people that use the centre for recreation purposes, drivers and cyclists.
4	London Road. (BNG: 335079, 390717).	Sample was collected along the edges of the busy road and at the corners of the building on the street. Environmental matrix: dust particles blown to the edges of the road vehicular emissions, litter and cigarette end.	Newspaper vendors, pedestrians, drivers and cyclists.
5	Norton Street (National Express). (BNG: 335263, 390826).	Sample was taken at bus stops and at the edges of the road. Environmental matrix: street dust, litter, plant materials and animal droppings.	Staff of national express, passengers and pedestrians.
6	Stafford Street. (BNG: 335487, 390962)	The street is characterised with shops, residential houses and offices. Sample was taken from the edges of the buildings. Environmental matrix: dust particles, cigarette end and litter.	Residents, pedestrians as well as people that work and shop along the street.
7	Pembroke Place (Liverpool School of Tropical Medicine). (BNG: 336853, 391002)	High traffic and densely populated pedestrians. Sample was taken from corners of the road and edges of buildings. Environmental matrix: street dust, vehicular emissions, litter and cigarette end.	Students, pedestrians, drivers and cyclists.

8	Dover Street. (BNG: 337399, 391544)	High traffic with a lot of people. Sample was taken from the corners of the road and buildings. Environmental matrix: dust particles, sediments and vehicular inputs.	Pedestrians, drivers, residents and cyclists.
9	Brown Low Hill Road. (BNG: 335356, 390079)	Sample was taken at the edge of the busy road. Environmental matrix: dust particles suspended at the edge of the road. Litter and cigarette end.	Pedestrians, drivers and cyclists.
10	Oxford Road (University of Liverpool). (BNG: 335356, 390079)	High traffic with a lot people especially students. Sample was taken from corners of the road. Environmental matrix: vehicular emissions, street dust and litter.	Students queuing for buses and taxis, pedestrians and drivers.
11	Myrtle Street (Liverpool Community College, Theatre Centre). (BNG: 336096, 389840)	Busy street with people and traffic. Sample was taken from corners of the road. Environmental matrix: street dust and litter.	Pedestrians, cyclists and people that use the theatre.
12	Falkner Street. (BNG: 335522, 38916).	Sample was taken from the edge of buildings and doorways. Environmental matrix: street dust and litter.	Pedestrians and cyclists.
13	Royal Liverpool University Hospital. (BNG:	Sample was collected at edges of the buildings and corners of pathways. Environmental matrix; plant material, dust particles', cigarette end and litter.	Patients, workers and visitors to the hospital.

	337280, 391816)		
14	Prescot Street. (BNG: 337033, 391995)	High traffic with many pedestrians. Sample was collected at corners of the road and at the edge of the buildings. Environmental matrix: street dust, litter and cigarette end.	Pedestrians, drivers and cyclist.
15	Epsworth Road. (BNG: 337241, 391983).	High traffic with less people. Environmental matrix: vehicular emissions, dust particles blown to the edge of the road, animal droppings, sediments and cigarette end.	People who queue at the bus stop, pedestrians and cyclists.

E4: Edinburgh sampling: location, description and receptors.

Site No	**Location / British National Grid (BNG)**	**Description/sources**	**Key receptors**
1	Outside of Waverley Railway Station. (BNG: 325751, 673787)	Outside of the station is busy with vehicular traffic with seat out for relaxation and a lot of shops. Sample was taken from the edges of the seat out and at steps on the entrance of the station. Environmental matrix: street dust, vehicular emissions and 'rubbish' (cigarette ends, litter, plant and animal waste).	People who use the seat out as a recreation place, pedestrians, and passengers who use the station.
2	George Street. (BNG: 325148, 674232)	Sample was collected at the edges of the building. Environmental matrix: street dust, tyre wear and shoe wear.	Pedestrians, cyclists, taxi and bus drivers.
3	Hanover Street. (BNG:	Busy with vehicular traffic. Sample was taken from the edges of the building and	Pedestrians and people that work

	324816, 673633)	entrance of the shops along the street. Environmental matrix: dust particles blown to the edges of the roads.	and shop on the street.
4	Princess Street. (BNG: 325005, 673655)	Very busy street with heavy vehicular traffic, pedestrians, shops and office. There is recreation park adjacent the street. Sample was collected at bus stops and edges of building. Environmental matrix: vehicular emissions, street dust, litter and cigarette ends.	People that use the recreation park for relaxation; pedestrians, cyclists and people that queue at the bus stop.
5	Leith Walk Street. (BNG: 327609, 675882)	Sample was taken from the edges of the building along the street. Environmental matrix: dust particles blown the edges of the building.	Cyclists, drivers and pedestrians.
6	Richmond Street. (BNG: 326794, 682560)	Sample was taken from the corners of the road and at the edges of the building. Environmental matrix: street dust.	Pedestrians and people that shop and work along the street.
7	St. Leonard Street. (BNG: 326559, 672733)	Sample was collected at the edges of the building along the street. Environmental matrix: dust particles blown to the edges of buildings.	Pedestrians and drivers.
8	Nicholson Street. (BNG: 326596, 672583).	Busy with vehicular traffic and pedestrians. Sample was collected from the edges of the building and at bus stop. Environmental matrix: street dust and 'rubbish' (litter, cigarette end, plant and animal waste).	People waiting at bus stop and pedestrians.
9	Holyrood Palace (Scottish Parliament). (BNG: 327040, 763603)	Sample was collected from edges of the road leading to queen's residence, opposite Scottish parliament. Environmental matrix: street dust.	People that use the outside of the parliament for relaxation and pedestrians.
10	University of Edinburgh	Sample was collected outside of the sports centre from rectangular seating	Students and other people who

	(outside of Sports Centre). (BNG: 325882, 672835)	area. Environmental matrix: dust particles, detritus of plants and animals.	use the place as a relaxation centre.
11	London Road. (BNG: 328032, 676125)	Busy with vehicular traffic and pedestrians. Sample was taken from the edges of the road and at bus stop. Environmental matrix: vehicular emissions, street dust, shoe wears and tyre wears.	Pedestrians, drivers, cyclists and people who queue at the bus stop.
12	Omni leisure cinema and entertainment complex. (BNG: 327899, 674721)	Sample was collected from the edges of the building within the complex. Environmental matrix: litter, cigarette end and street dust.	People who use both the inside and outside of the building for recreation and relaxation purposes.
13	St. John's Street. (BNG: 326469, 674721)	Sample was collected at the corners of the building located on the road. Environmental matrix: dust particles and vehicular emissions.	Pedestrians and other road users.
14	Carlton Road. (BNG: 326477, 674228)	Sample was taken from the edges of the road and also at bus stops.	Pedestrians, cyclists and drivers.
15	Market Street. (BNG: 325376, 674249)	Busy with vehicular traffic, pedestrians, shops and offices. Environmental matrix: street dust, tyre and shoe wears and urban 'rubbish' (urban inputs, litter and cigarette end).	Pedestrians, people that work in the offices as well as people in the shop.

E5: Sunderland sampling: location, description and receptors.

Site no	Location / British National Grid (BNG)	Description / sources	Key receptors
1	Outside of central railway station. (BNG: 440301, 557792)	Sample was collected at the edges of the buildings, entrance to station and shops. Environmental matrix: street dust, vehicular emissions, urban inputs and cigarette end.	Pedestrians, taxi drivers and cleaners that work on station daily.
2	Park Lane. (bus station). (BNG: 440470, 557898)	Sample was taken at the edges of the walls were passengers seat and wait for bus as well as the entrance to the shops located within the station. Environmental matrix: tyre and shoe wears, vehicular emissions, street dust, litter and cigarette end.	Passengers waiting for bus, bus drivers and pedestrians.
3	Bridge Street. (BNG: 440349, 557583).	Sample was collected at edges of the building, entrance to shops and on the street road. Matrix: street dust and litter.	Pedestrians and cyclists. People who sell and buy in the shops located on the street.
4	Empire Theatre. (BNG: 439201, 557064)	Sample was taken from the edges of the building and along the busy road. Environmental matrix: street dust, vehicular emissions and litter.	Pedestrians, cyclists and people that use the theatre for different purposes.
5	Sunderland Civic Centre. (BNG: 439545, 556541)	Sample was taken from the front of the building and at the edge of the buildings. (A sample was also collected from the car park). Environmental matrix: street dust, litter, vehicular emissions and cigarette end.	Car owners who park at the car park and people who work at the civic centre.
6	Durham Road / Derby Street. (BNG: 438965,	Sample was taken from the end edges of the road. Environmental matrix: street dust blown to the end of	Pedestrians, people who queue at the bus stop

	556710).	the road by high traffic.	waiting for buses and cyclist.
7	Murray Library (University of Sunderland). (BNG: 439150, 556861)	Sample was collected at the edges of the building; entrance of the building and at the edges of the high traffic road adjacent the library. Environmental matrix: street dust, vehicular emissions, litter and cigarette end.	People that work and read in the library. Pedestrians, cyclists and people queuing on bus stop close to the library.
8	High Street West. (BNG: 440068, 557104)	Sample was collected from the edges of buildings, entrance to shops and edges of the road. Environmental matrix: street dust, vehicular emissions from high volume traffic, tyre and shoe wears.	Pedestrians, newspaper vendors, bus and taxi drivers as well as cyclists.
9	Benedict's Building, University of Sunderland. (BNG: 439005, 556684).	Sample was collected at the edges round the building and at the edges of the steps within the premises. Environmental matrix: street dust, litter and cigarette head.	Students and workers within the premises. Users of the busy road behind the building.
10	West Street. (BNG: 43529, 537054)	Sample was taken at the edge of street and the corners of the building along the street. Environmental matrix: street dust blown to the edges of the road and corners of the building.	Taxi and bus drivers as well as pedestrians.
11	Station Street. (BNG: 439999, 556998)	Busy street with vehicular traffic. Sample was taken from edges of the building along the street. Environmental matrix: street dust, tyre and shoe wear, sediment and litter.	Pedestrians, motorcycle riders and cyclists.
12	Outside of Theatre Royal. (BNG: 438743, 556705).	Sample was collected at the entrance of the building and at the edges of the building too. Environmental matrix: vehicular emissions, street dust, litter	Users of the theatre and pedestrians.

		and cigarette end.	
13	Chester Road. (BNG: 438735, 556683).	High vehicular traffic and quite a lot of shops / offices along the road. Sample was collected at the edges of the road and also at edges of the buildings along the road. Environmental matrix: dust particles blown to edges of the busy road.	Drivers, pedestrians, cyclists and people that work in the shops / offices along the road.
14	Bridges Shopping Centre. (BNG: 439605, 556596)	Vehicle restricted area except those on essential duties. Busy shopping complex. Sample was collected at the edges of the seat out within the centre and also at the edges of the buildings. Environmental matrix: street dust, litter and cigarette end.	People, who use the shopping complex as a recreation centre, and people who work and shop in the centre.
15	Fawcett Street. (BNG: 440050, 537104)	Sample was taken from the edges of the buildings located along the street. Environmental matrix: dust particles and litter.	Pedestrians and motorists.

E6: Nigeria sampling: location, description and receptors.

Site no	Location	Description / sources	Key receptors
1	Outside of Government House (and by officer's mes)s.	High traffic (vehicles and motor cycle) and populated pedestrians and hawkers. Sample was collected along the road particularly at the edges. Environmental matrices: Dust particles, tyre wears and rubbish.	People that relax at the open place inside officer's mess, hawkers, motorist, motor cycle riders and pedestrians.
2	Outside of the Cathedral Methodist church (opposite Ebonyi Hotel).	Busy during day time with vehicles, bicycle and motor as well as pedestrians. Sample was taken at the bus stop and the edges of the church walls. Environmental matrices: Litter, vehicular emissions and road dust.	People at the bus stop, police standing at the roundabout monitoring traffic and motor cycle riders.
3	Outside of the Federal Medical Centre (FMC).	The outside of the FMC is populated with motor cycle riders waiting for passengers and hawkers. Environmental matrices: Plant materials, animal droppings, dust particles and cigarette ends.	Hospital staff, patients, hawkers and motorcycle riders.
4	Outside of the Independent National Electoral Commission (INEC)	The outside of the INEC office is on a busy location due to the presence of many other offices. Sample was collected along the road very close to the office. Environmental matrices: plant materials, road dust and vehicular emissions.	Staff working in the various offices, motor cycle riders and hawkers.
5	Awolowo Street	Densely populated street. Sample was collected at the edges of the street and beside abandoned parked vehicles. Environmental matrices: corroded materials from abandoned vehicle, street dust and cigarette end.	Residents, pedestrians and children that play on the street.
6	Outside of the Abakpa Main Market (Abacha	The Abacha roundabout is busy all day due the presence of motor cycle riders waiting for passengers, vehicles as	Motor cycle riders, shop attendants and

	roundabout).	well as people leaving and entering the market. Sample was taken at the motor cycle stand and in front of the shops. Environmental matrices: Dust particles and rubbish.	people that shop in the market.
7	Abakpa Motor Park	The motor park located at one the end of Abakpa market is densely populated with people including; drivers, passengers and hawkers. Environmental matrices: Urban dust particles, decayed plant materials and animal droppings.	Drivers, passengers, people that work at the park as well as residents living close to the park.
8	Vanco roundabout	High traffic and populated pedestrians. Sample was collected along the edges of the road. Environmental matrices: road dust, vehicular emissions and rubbish.	Hawkers, drivers, pedestrians, shop attendants as well police standing at the junction to monitor traffic.
9	Water Works Road / Ukwansi Street	Busy road with high traffic. Sample was collected at the entrance to Ukwansi street. Environmental matrices: vehicular emissions, dust particles and cigarette ends	Hawkers, drivers, motor cycle riders as well as cyclists.
10	Ogoja Road (opposite United Bank of Africa, UBA)	High traffic with a lot of people. Sample was collected at the edges of the road. Environmental matrices: Urban dust, vehicular emissions and decayed plant materials.	All road users and residents within the vicinity.
11	0utside of Old Kpirikpiri Market	The outside of Kpirikpiri Market is characterised with people selling at open shops, hawkers and high traffic. Sample was collected at the edges of the road. Environmental matrices: Dust particles blown to the edge of the road, litter and vehicular emissions.	People that sell within the vicinity, hawkers, motor cycle riders, pedestrians as well as cyclists.
12	Obodo Park (opposite Fati Lami Park)	At present, obodo park is a temporary motor park but has high traffic and densely populated pedestrians.	People relaxing at the recreation park and all road

		Sample was taken along the road. Environmental matrices: Road dust and urban rubbish.	users.
13	Unity Square (opposite Government Secretariat)	Unity square is an event centre for the government, NGO's and individuals. Sample was taken from the outside of the square. Environmental matrices: dust particles, decayed plant materials and cigarette ends.	People that use the place at one time on the other. Staff of the secretariat and road users.
14	Outside of St. Theresa's Catholic Church (opposite Bank PHB).	High traffic and populated pedestrians. Sample was taken at the edge of the church walls. Environmental matrices: Urban dust blown to the edges of the walls, vehicular emissions and urban rubbish.	People that worship in the church, road cleaners and all road users.
15	Ebonyi State University Abakaliki (CAS campus).	The university community is densely populated with both staff and students of the school as well as high traffic. Sample was collected at the gate leading to the pre-degree school. Environmental matrices: dust particles, animal droppings and sediments.	Staff and students of the university as well as visitors.

Appendix F

F1: Maximum PTE estimated daily oral intake from urban dust (Newcastle upon Tyne, UK)

Element	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1})[@] based on 50 mg/day ingestion[≠]	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1}) based on 50 mg/day ingestion and bioaccessibility[X]	0.008 mg/day ingestion[„]	Maximum estimated daily intake (ng kg_{bw}^{-1} day^{-1})[+] based on 50 mg/day ingestion and an estimated annual exposure frequency[≠]	Amount of dust that could be consumed by a child[C] in order to exceed the guidelines (mg/day)	TDI_{oral} µg kg_{bw}^{-1} day^{-1}
Cr	0.41	0.16	0.00	17.0	18117	150[a]
Mn	1.51	0.85	0.01	61.9	NA	N/A
Ni	3.46	1.63	0.02	142	173	12[b]
Cu	2.66	1.14	0.02	109	3009	160[a]
Zn	12.5	5.37	0.08	512	2402	600[a]
As	0.04	0.01	0.00	1.49	413	0.3[c]
Cd	0.01	0.00	0.00	0.40	18497	0.36[d]
Pb	4.40	2.37	0.03	180	40.9	3.6[e]

[@] the maximum estimated daily intake (DI) was calculated using the formula DI= [EC x SDIR] / BW (79-81), where DI = daily intake (µg kg_{bw}^{-1} day^{-1}) as determined in <125 µm fraction of the dust sample with the highest concentration; EC = Exposure concentration of the PTEs in <125 µm (µg/g); SDIR = soil + dust ingestion rate (0.05 g day^{-1}) (82); and BW = body weight (18.6 kg for a 3-6 year old child) (80). The maximum estimated daily intake and bioaccessibility was calculated by modifying the above equation to DI= [EC x SDIR X B] / BW where B is the bioavailibaility fraction determined using Unified BARGE Method.

X based on the maximum bioaccessible concentration using the gastric phase.

“ based on a determined air quality measurement in Newcastle City Centre between 27 – 28 May, 2010 between the hours of 10.00 and 17.00 hours of 8 μg/m^3 air particulate matter (PM10) (http://uk-air.defra.gov.uk/data); and ingestion rate of 8 μg has been assumed as the child is likely to occupy an active volume of 1 m^3.

[+] the maximum estimated daily intake (DI) and estimated annual exposure frequency was calculated using the formula DI= [EC x SDIR x EF] / BW, where DI = daily intake (ng kg_{bw}^{-1} day^{-1}) as determined in <125 μm fraction of the dust sample with the highest concentration; EC = Exposure concentration of PTEs in <125 μm (μg/g); SDIR = soil + dust ingestion rate (0.05 g day^{-1}) (82); EF = Exposure frequency = 0.041 (estimated to be 7 hours a day, i.e. a child is likely to be involved in outdoor activities between the hours of 10.00 and 17.00 hours) for 52 weeks i.e. 364 hours per year or 15.2 days per year); and BW = body weight (18.6 kg for a 3-6 year old child) (80).

c child aged 1 and < 6 years

(a) (83)
(b) (84)
(c) (85)
(d) (86)
(e) (87)

F2: Maximum PTE estimated daily oral intake from urban dust (Durham, UK)

Element	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1})[@] based on 50 mg/day ingestion[≠]	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1}) based on 50 mg/day ingestion and bioaccessibility[X]	Maximum estimated daily intake (ng kg_{bw}^{-1} day^{-1})[+] based on 50 mg/day ingestion and an estimated annual exposure frequency[≠]	Amount of dust that could be consumed by a child[C] in order to exceed the guidelines (mg/day)	TDI_{oral} µg kg_{bw}^{-1} day^{-1}
Cr	0.50	0.26	20.6	14920	150[a]
Mn	2.60	1.28	107	NA	N/A
Ni	0.15	0.07	6.35	3875	12[b]
Cu	1.02	0.54	41.8	7852	160[a]
Zn	4.47	2.37	183	6719	600[a]
As	0.02	0.01	0.89	695	0.3[c]
Cd	0.00	0.00	0.20	36791	0.36[d]
Pb	5.70	3.19	234	31.6	3.6[e]

[@] the maximum estimated daily intake (DI) was calculated using the formula DI= [EC x SDIR] / BW (79-81), where DI = daily intake (µg kg_{bw}^{-1} day^{-1}) as determined in <125 µm fraction of the dust sample with the highest concentration; EC = Exposure concentration of the PTEs in <125 µm (µg/g); SDIR = soil + dust ingestion rate (0.05 g day^{-1}) (82); and BW = body weight (18.6 kg for a 3-6 year old child) (80). The maximum estimated daily intake and bioaccessibility was calculated by modifying the above equation to DI= [EC x SDIR X B] / BW where B is the bioavailibaility fraction determined using Unified BARGE Method.

X based on the maximum bioaccessible concentration using the gastric phase.

[+] the maximum estimated daily intake (DI) and estimated annual exposure frequency was calculated using the formula DI= [EC x SDIR x EF] / BW, where DI = daily intake (ng kg_{bw}^{-1} day^{-1}) as determined in <125 µm fraction of the dust sample with the highest concentration; EC = Exposure concentration of PTEs in <125 µm (µg/g); SDIR = soil + dust ingestion rate (0.05 g day^{-1}) (82); EF =

Exposure frequency = 0.041 (estimated to be 7 hours a day, i.e. a child is likely to be involved in outdoor activities between the hours of 10.00 and 17.00 hours) for 52 weeks i.e. 364 hours per year or 15.2 days per year); and BW = body weight (18.6 kg for a 3-6 year old child) (80).

c child aged 1 and < 6 years

(a) (83)
(b) (84)
(c) (85)
(d) (86)
(e) (87)

F3: Maximum PTE estimated daily oral intake from urban dust (Liverpool, UK)

Element	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1})[@] based on 50 mg/day ingestion[≠]	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1}) based on 50 mg/day ingestion and bioaccessibility[X]	0.038 mg/day ingestion[”]	Maximum estimated daily intake (ng kg_{bw}^{-1} day^{-1})[+] based on 50 mg/day ingestion and an estimated annual exposure frequency[≠]	Amount of dust that could be consumed by a child[C] in order to exceed the guidelines (mg/day)	TDI_{oral} µg kg_{bw}^{-1} day^{-1}
Cr	0.27	0.12	0.01	10.9	28296	150[a]
Mn	4.32	2.72	0.13	177	NA	N/A
Ni	0.19	0.08	0.01	7.33	3356	12[b]
Cu	6.00	2.93	0.19	245	1339	160[a]
Zn	10.5	5.06	0.33	432	2846	600[a]
As	0.04	0.02	0.00	1.75	351	0.3[c]
Cd	0.01	0.00	0.00	0.35	21190	0.36[d]
Pb	2.46	1.06	0.08	101	73.2	3.6[e]

[@] the maximum estimated daily intake (DI) was calculated using the formula DI= [EC x SDIR] / BW (79-81), where DI = daily intake (µg kg_{bw}^{-1} day^{-1}) as determined in <125 µm fraction of the dust sample with the highest concentration; EC = Exposure concentration of the PTEs in <125 µm (µg/g); SDIR = soil + dust ingestion rate (0.05 g day^{-1}) (82); and BW = body weight (18.6 kg for a 3-6 year old child) (80). The maximum estimated daily intake and bioaccessibility was calculated by modifying the above equation to DI= [EC x SDIR X B] / BW where B is the bioavailibaility fraction determined using Unified BARGE Method.

X based on the maximum bioaccessible concentration using the gastric phase.

“ based on a determined air quality measurement in Liverpool on June 5, 2010 between the hours of 10.00 and 17.00 hours of 38 µg/m^3 air particulate matter (PM10) (http://uk-air.defra.gov.uk/data); and ingestion rate of 38 µg has been assumed as the child is likely to occupy an active volume of 1 m^3.

[+] the maximum estimated daily intake (DI) and estimated annual exposure frequency was calculated using the formula DI= [EC x SDIR x EF] / BW, where DI = daily intake (ng kg_{bw}^{-1} day^{-1}) as determined in <125 μm fraction of the dust sample with the highest concentration; EC = Exposure concentration of PTEs in <125 μm (μg/g); SDIR = soil + dust ingestion rate (0.05 g day^{-1}) (82); EF = Exposure frequency = 0.041 (estimated to be 7 hours a day, i.e. a child is likely to be involved in outdoor activities between the hours of 10.00 and 17.00 hours) for 52 weeks i.e. 364 hours per year or 15.2 days per year); and BW = body weight (18.6 kg for a 3-6 year old child) (80).

c child aged 1 and < 6 years

(a) (83)
(b) (84)
(c) (85)
(d) (86)
(e) (87)

F4: Maximum PTE estimated daily oral intake from urban dust (Edinburgh, UK)

Element	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1})[@] based on 50 mg/day ingestion[≠]	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1}) based on 50 mg/day ingestion and bioaccessibility[X]	0.009 mg/day ingestion[”]	Maximum estimated daily intake (ng kg_{bw}^{-1} day^{-1})[+] based on 50 mg/day ingestion and an estimated annual exposure frequency[≠]	Amount of dust that could be consumed by a child[C] in order to exceed the guidelines (mg/day)	TDI_{oral} µg kg_{bw}^{-1} day^{-1}
Cr	0.19	0.08	0.00	7.73	39800	150[a]
Mn	2.02	1.11	0.02	83.0	NA	N/A
Ni	0.11	0.05	0.00	4.50	5471	12[b]
Cu	0.63	0.33	0.00	25.9	12664	160[a]
Zn	3.01	1.62	0.02	123	9973	600[a]
As	0.02	0.01	0.0	0.76	804	0.3[c]
Cd	0.00	0.00	0.00	0.25	29760	0.36[d]
Pb	3.42	1.92	0.03	140	52.6	3.6[e]

[@] the maximum estimated daily intake (DI) was calculated using the formula DI= [EC x SDIR] / BW (79-81), where DI = daily intake (µg kg_{bw}^{-1} day^{-1}) as determined in <125 µm fraction of the dust sample with the highest concentration; EC = Exposure concentration of the PTEs in <125 µm (µg/g); SDIR = soil + dust ingestion rate (0.05 g day^{-1}) (82); and BW = body weight (18.6 kg for a 3-6 year old child) (80). The maximum estimated daily intake and bioaccessibility was calculated by modifying the above equation to DI= [EC x SDIR X B] / BW where B is the bioavailibaility fraction determined using Unified BARGE Method.

X based on the maximum bioaccessible concentration using the gastric phase

“ based on a determined air quality measurement in Edinburgh on June 12, 2010 between the hours of 10.00 and 17.00 hours of 9 µg/m^3 air particulate matter (PM10) (http://uk-air.defra.gov.uk/data); and ingestion rate of 38 µg has been assumed as the child is likely to occupy an active volume of 1 m^3.

[+] the maximum estimated daily intake (DI) and estimated annual exposure frequency was calculated using the formula DI= [EC x SDIR x EF] / BW, where DI = daily intake (ng kg_{bw}^{-1} day^{-1}) as determined in <125 µm fraction of the dust sample with the highest concentration; EC = Exposure concentration of PTEs in <125 µm (µg/g); SDIR = soil + dust ingestion rate (0.05 g day^{-1}) (82); EF = Exposure frequency = 0.041 (estimated to be 7 hours a day, i.e. a child is likely to be involved in outdoor activities between the hours of 10.00 and 17.00 hours) for 52 weeks i.e. 364 hours per year or 15.2 days per year); and BW = body weight (18.6 kg for a 3-6 year old child) (80).

c child aged 1 and < 6 years

(a) (83)
(b) (84)
(c) (85)
(d) (86)
(e) (87)

F5: Maximum PTE estimated daily oral intake from urban dust (Sunderland, UK)

Element	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1})[@] based on 50 mg/day ingestion[≠]	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1}) based on 50 mg/day ingestion and bioaccessibility[X]	Maximum estimated daily intake (ng kg_{bw}^{-1} day^{-1})[+] based on 50 mg/day ingestion and an estimated annual exposure frequency[≠]	Amount of dust that could be consumed by a child[C] in order to exceed the guidelines (mg/day)	TDI_{oral} µg kg_{bw}^{-1} day^{-1}
Cr	0.22	0.20	9.16	33574	150[a]
Mn	1.74	0.79	71.5	NA	N/A
Ni	0.09	1.76	3.71	6623	12[b]
Cu	0.65	1.46	26.7	12297	160[a]
Zn	7.33	6.87	300	4094	600[a]
As	0.02	0.02	0.73	848	0.3[c]
Cd	0.00	0.00	0.10	73907	0.36[d]
Pb	5.99	2.29	246	30.1	3.6[e]

[@] the maximum estimated daily intake (DI) was calculated using the formula DI= [EC x SDIR] / BW (79-81), where DI = daily intake (µg kg_{bw}^{-1} day^{-1}) as determined in <125 µm fraction of the dust sample with the highest concentration; EC = Exposure concentration of the PTEs in <125 µm (µg/g); SDIR = soil + dust ingestion rate (0.05 g day^{-1}) (82); and BW = body weight (18.6 kg for a 3-6 year old child) (80). The maximum estimated daily intake and bioaccessibility was calculated by modifying the above equation to DI= [EC x SDIR X B] / BW where B is the bioavailibaility fraction determined using Unified BARGE Method.

X based on the maximum bioaccessible concentration using the gastric phase.

[+] the maximum estimated daily intake (DI) and estimated annual exposure frequency was calculated using the formula DI= [EC x SDIR x EF] / BW, where DI = daily intake (ng kg_{bw}^{-1} day^{-1}) as determined in <125 µm fraction of the dust sample with the highest concentration; EC = Exposure concentration of PTEs in <125 µm (µg/g); SDIR = soil + dust ingestion rate (0.05 g day^{-1}) (82); EF = Exposure frequency = 0.041 (estimated to be 7 hours a day, i.e. a child is likely to be involved in outdoor activities between the

hours of 10.00 and 17.00 hours) for 52 weeks i.e. 364 hours per year or 15.2 days per year); and BW = body weight (18.6 kg for a 3-6 year old child) (80).

c child aged 1 and < 6 years

(a) (83)
(b) (84)
(c) (85)
(d) (86)
(e) (87)

F6: Maximum PTE estimated daily oral intake from urban dust (Abakaliki, Nigeria)

Element	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1})[@] based on 50 mg/day ingestion[≠]	Maximum estimated daily intake (µg kg_{bw}^{-1} day^{-1}) based on 50 mg/day ingestion and bioaccessibility[X]	Maximum estimated daily intake (ng kg_{bw}^{-1} day^{-1})[+] based on 50 mg/day ingestion and an estimated annual exposure frequency[≠]	Amount of dust that could be consumed by a child[C] in order to exceed the guidelines (mg/day)	TDI_{oral} µg kg_{bw}^{-1} day^{-1}
Cr	0.46	0.29	19.0	16221	150[a]
Mn	3.73	2.13	153	NA	N/A
Ni	0.14	0.07	5.81	4235	12[b]
Cu	0.23	0.12	9.54	34365	160[a]
Zn	1.17	0.60	47.8	25714	600[a]
As	0.04	0.02	1.67	365	0.3[c]
Cd	0.00	0.00	0.15	49235	0.36[d]
Pb	4.88	2.54	200	36.9	3.6[e]

[@] the maximum estimated daily intake (DI) was calculated using the formula DI= [EC x SDIR] / BW (79-81), where DI = daily intake (µg kg_{bw}^{-1} day^{-1}) as determined in <125 µm fraction of the dust sample with the highest concentration; EC = Exposure concentration of the PTEs in <125 µm (µg/g); SDIR = soil + dust ingestion rate (0.05 g day^{-1}) (82); and BW = body weight (18.6 kg for a 3-6 year old child) (80). The maximum estimated daily intake and bioaccessibility was calculated by modifying the above equation to DI= [EC x SDIR X B] / BW where B is the bioavailibaility fraction determined using Unified BARGE Method.

X based on the maximum bioaccessible concentration using the gastric phase

[+] the maximum estimated daily intake (DI) and estimated annual exposure frequency was calculated using the formula DI= [EC x SDIR x EF] / BW, where DI = daily intake (ng kg_{bw}^{-1} day^{-1}) as determined in <125 µm fraction of the dust sample with the highest concentration; EC = Exposure concentration of PTEs in <125 µm (µg/g); SDIR = soil + dust ingestion rate (0.05 g day^{-1}) (82); EF = Exposure frequency = 0.041 (estimated to be 7 hours a day, i.e. a child is likely to be involved in outdoor activities between the

hours of 10.00 and 17.00 hours) for 52 weeks i.e. 364 hours per year or 15.2 days per year); and BW = body weight (18.6 kg for a 3-6 year old child) (80).

c child aged 1 and < 6 years

(a) (83)
(b) (84)
(c) (85)
(d) (86)
(e) (87)

Appendix G

Summary of stage related bioaccessibility and residual fraction of PTES in urban street dusts showing minimum, median and maximum.

G1: Summary of stage related bioaccessibility and residual fraction of PTEs in urban street dust of Newcastle, UK

Element	In-vitro gastrointestinal extraction mg/kg								
	Stage I (Gastric digest)			Stage II (Gastric + Intestinal digest)			Stage III (Residual digest)		
	Minimum	Median	Maximum (% BAF)	Minimum	Median	Maximum (% BAF)	Minimum	Median	Maximum (% Residual)
Cr	12.2	23.1	40.1 (26.0)	10.1	19.6	34.3 (22.3)	25.4	46.3	90.6 (58.8)
Mn	100	192	291 (53.1)	71.5	124	201 (36.6)	186	298	370 (65.8)
Ni	7.30	12.9	320 (24.8)	6.60	11.3	296 (22.9)	11.1	17.7	597 (46.4)
Cu	30.1	49.2	301 (30.4)	25.8	41.3	286 (28.9)	61.8	81.3	632 (63.9)
Zn	98.4	232	1865 (40.1)	79.3	211	1530 (32.9)	149	333	2820 (60.7)
As	1.21	2.11	3.71 (27.5)	0.891	1.56	2.61 (19.3)	2.31	3.67	6.51 (4.99)
Cd	0.120	0.345	1.21 (33.4)	ND	0.302	1.11 (30.6)	0.211	0.623	2.10 (58.0)
Pb	9.10	121	736 (45.1)	8.1	109	534 (32.6)	14.5	143	934 (61.3)

% BAF: stage related bioaccessibility for the dust sample releasing the highest stage concentration, calculated as a fraction of that sample's total for both gastric and intestinal; **% Residual**: residual fraction calculated as a fraction of the total for the sample releasing the highest residual concentration; **ND**: not detected

G2: Summary of stage related bioaccessibility and residual fraction of PTEs in urban street dust of Durham, UK

Element	In-vitro gastrointestinal extraction mg/kg								
	Stage I (Gastric digest)			Stage II (Gastric + Intestinal digest)			Stage III (Residual digest)		
	Minimum	Median	Maximum (% BAF)	Minimum	Median	Maximum (% BAF)	Minimum	Median	Maximum (% Residual)
Cr	6.11	21.6	60.6 (32.4)	4.97	19.4	51.3 (27.4)	8.19	30.3	94.5 (50.5)
Mn	145	240	350 (36.1)	104	201	256 (26.4)	218	308	452 (46.7)
Ni	5.12	9.64	21.4 (37.2)	2.97	7.92	18.8 (32.6)	7.59	12.7	302 (52.4)
Cu	11.5	77.5	160 (42.2)	10.3	68.9	145 (38.3)	10.3	81.1	181 (47.8)
Zn	89.4	221	810 (48.9)	89.4	194	786 (47.3)	131	237	865 (52.1)
As	1.89	2.21	4.11 (51.2)	1.52	1.83	3.09 (38.5)	2.21	2.93	4.82 (60.0)
Cd	ND	0.252	0.587 (50.1)	ND	0.223	0.532 (29.2)	ND	0.281	0.832 (45.7)
Pb	42.3	118	845 (39.9)	38.7	102	803 (37.9)	59.1	141	1227 (57.9)

% BAF: stage related bioaccessibility for the dust sample releasing the highest stage concentration, calculated as a fraction of that sample's total for both gastric and intestinal; **% Residual**: residual fraction calculated as a fraction of the total for the sample releasing the highest residual concentration**. ND**: not detected.

G3: Summary of stage related bioaccessibility and residual fraction of PTEs in urban street dust of Liverpool, UK

Element	In-vitro gastrointestinal extraction mg/kg								
	Stage I (Gastric digest)			Stage II (Gastric + Intestinal digest)			Stage III (Residual digest)		
	Minimum	Median	Maximum (% BAF)	Minimum	Median	Maximum (% BAF)	Minimum	Median	Maximum (% Residual)
Cr	6.61	23.2	38.6 (45.4)	6.02	21.1	32.2 (37.8)	7.81	29.4	45.2 (45.8)
Mn	102	163	625 (38.9)	97.3	124	408 (25.4)	145	199	812 (50.5)
Ni	5.21	10.8	29.4 (44.5)	4.01	10.6	26.8 (40.3)	7.15	15.5	37.8 (56.8)
Cu	17.2	55.2	842 (37.9)	13.6	40.6	734 (33.1)	28.1	71.4	1200 (54.0)
Zn	41.0	232	1843 (47.1)	35.7	200	1425 (36.4)	54.0	347	2230 (56.8)
As	1.54	3.09	5.69 (35.9)	1.03	2.43	3.46 (40.6)	2.51	3.42	8.71 (54.8)
Cd	ND	0.384	1.18 (37.3)	ND	0.278	0.962 (30.4)	ND	0.432	1.53 (48.4)
Pb	34.2	143	374 (40.9)	28.7	121	293 (32.0)	43.2	153	412 (45.0)

% BAF: stage related bioaccessibility for the dust sample releasing the highest stage concentration, calculated as a fraction of that sample's total for both gastric and intestinal; **% Residual**: residual fraction calculated as a fraction of the total for the sample releasing the highest residual concentration; **ND**: not detected

G4: Summary of stage related bioaccessibility and residual fraction of PTEs in urban street dust of Edingurgh

Element	In-vitro gastrointestinal extraction mg/kg								
	Stage I (Gastric digest)			Stage II (Gastric + Intestinal digest)			Stage III (Residual digest)		
	Minimum	Median	Maximum (% BAF)	Minimum	Median	Maximum (% BAF)	Minimum	Median	Maximum (% Residual)
Cr	6.17	18.7	27.7 (39.5)	8.12	17.7	23.6 (38.5)	14.1	25.1	38.6 (55.5)
Mn	143	205	272 (36.1)	116	138	226 (30.0)	8.85	14.4	19.5 (57.2)
Ni	7.48	11.6	14.3 (14.9)	5.33	9.15	12.1 (29.7)	8.85	14.4	19.5 (57.2)
Cu	31.6	52.1	121 (51.5)	26.7	40.1	92.1 (40.8)	38.6	64.6	129 (54.9)
Zn	104	225	488 (43.6)	81.4	189	376 (33.6)	126	251	543 (48.5)
As	1.46	2.01	2.84 (40.9)	1.19	1.68	2.41 (34.7)	1.64	2.12	3.12 (44.9)
Cd	ND	0.618	0.871 (38.7)	ND	0.427	0.643 (42.3)	ND	0.683	1.06 (471)
Pb	29.5	136	617 (48.5)	21.1	108	584 (45.9)	39.6	154	643 (50.5)

% BAF: stage related bioaccessibility for the dust sample releasing the highest stage concentration, calculated as a fraction of that sample's total for both gastric and intestinal**; % Residual**: residual fraction calculated as a fraction of the total for the sample releasing the highest residual concentration; **ND**: not detected

G5: Summary of stage related bioaccessibility and residual fraction of PTEs in urban street dust of Sunderland

Element	In-vitro gastrointestinal extraction mg/kg								
	Stage I (Gastric digest)			Stage II (Gastric + Intestinal digest)			Stage III (Residual digest)		
	Minimum	Median	Maximum (% BAF)	Minimum	Median	Maximum (% BAF)	Minimum	Median	Maximum (% Residual)
Cr	4.11	19.3	33.7 (40.6)	3.12	14.2	28.9 (39.5)	5.14	23.4	48.9 (58.8)
Mn	163	218	287 (47.9)	136	173	241 (40.2)	173	247	346 (53.3)
Ni	6.41	11.2	15.6 (46.3)	4.75	9.67	13.8 (40.9)	7.33	13.6	17.6 (52.2)
Cu	29.4	64.2	102 (52.6)	23.6	51.4	72.8 (37.5)	32.9	81.7	126 (52.1)
Zn	98.5	218	1186 (43.5)	84.6	182	956 (35.1)	117	241	1397 (51.2)
As	1.64	2.21	2.84 (46.8)	1.21	1.68	2.24 (34.8)	1.96	2.34	3.32 (50.4)
Cd	ND	0.287	0.345 (38.1)	ND	0.221	0.305 (33.7)	ND	0.316	0.412 (45.5)
Pb	45.4	83.1	895 (40.2)	35.8	69.3	687 (30.8)	42.3	91.4	1211 (54.4)

% BAF: stage related bioaccessibility for the dust sample releasing the highest stage concentration, calculated as a fraction of that sample's total for both gastric and intestinal; **% Residual**: residual fraction calculated as a fraction of the total for the sample releasing the highest residual concentration; **ND**: not detected

G6: Summary of stage related bioaccessibility and residual fraction of PTEs in urban street dust of Abakaliki, Ebonyi State, Nigeria.

Element	In-vitro gastrointestinal extraction mg/kg								
	Stage I (Gastric digest)			Stage II (Gastric + Intestinal digest)			Stage III (Residual digest)		
	Minimum	Median	Maximum (% BAF)	Minimum	Median	Maximum (% BAF)	Minimum	Median	Maximum (% Residual)
Cr	28.3	52.2	108 (62.8)	27.4	46.4	59.4 (36.2)	31.3	61.4	120 (69.8)
Mn	176	285	538 (44.2)	143	221	422 (34.6)	216	368	715 (58.7)
Ni	10.6	18.3	23.1 (43.8)	7.11	14.7	19.3 (36.6)	13.4	21.5	34.2 (66.3)
Cu	10.4	17.4	40.1 (46.3)	8.54	14.3	34.3 (39.6)	13.7	22.5	46.9 (54.2)
Zn	28.6	73.4	186 (42.9)	23.7	54.8	107 (30.1)	32.1	97.4	235 (54.1)
As	1.16	2.11	7.94 (51.9)	1.01	1.68	5.13 (33.5)	1.25	2.31	9.28 (60.7)
Cd	ND	0.386	0.536 (39.4)	ND	0.181	0.345 (41.1)	ND	0.421	0.712 (52.4)
Pb	20.4	48.4	785 (43.3)	17.8	43.7	624 (34.4)	22.4	61.6	983 (54.2)

% BAF: stage related bioaccessibility for the dust sample releasing the highest stage concentration, calculated as a fraction of that sample's total for both gastric and intestinal; **% Residual**: residual fraction calculated as a fraction of the total for the sample releasing the highest residual concentration; **ND:** not detected

Appendix H

Summary of stage related bioaccessibility and residual fraction of PTES in urban street dusts showing total content, stage I, stage II, stage III and % total recovery in urban street dust samples.

H1: Total content, stage related bioaccessible and residual fractions of arsenic (As) in urban dust of Newcastle upon Tyne

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	6.53 ± 0.1	1.21 ± 0.1	18.5	0.891 ± 0.1	13.6	3.67 ± 0.6	4.56	69.8
2	6.53 ± 0.1	2.11 ± 0.2	32.3	1.03 ± 0.3	15.7	4.12 ± 0.3	5.15	78.9
3	5.85 ± 0.2	1.66 ± 0.1	28.3	1.18 ± 0.3	20.2	2.98 ± 0.3	4.16	71.1
4	6.91 ± 0.1	1.71 ± 0.1	24.7	1.17 ± 0.2	16.9	3.12 ± 0.1	4.29	62.1
5	7.29 ± 0.2	1.62 ± 0.1	22.2	1.27 ± 0.3	17.4	4.11 ± 0.6	5.38	73.8

6	6.71 ± 0.2	1.27 ± 0.4	18.9	1.86 ± 0.1	27.7	3.83 ± 0.3	5.69	84.7
7	7.45 ± 0.1	2.31 ± 0.1	31.0	1.91 ± 0.2	25.6	4.11 ± 0.3	6.42	86.2
8	13.5 ± 0.2	3.71 ± 0.3	27.5	2.61 ± 0.1	19.3	6.51 ± 0.2	9.12	67.6
9	8.43 ± 0.1	2.17 ± 0.1	25.7	1.81 ± 0.2	21.5	5.13 ± 0.1	6.94	82.3
10	5.24 ± 0.1	2.17 ± 0.4	41.4	1.91 ± 0.2	36.5	2.53 ± 0.1	4.44	87.7
11	5.83 ± 0.3	1.21 ± 0.1	20.7	1.11 ± 0.1	19.1	2.31 ± 0.1	3.52	60.4
12	7.91 ± 0.2	2.34 ± 0.1	29.6	1.56 ± 0.2	19.7	3.42 ± 0.3	4.98	62.9
13	5.92 ± 0.2	1.75 ± 0.1	29.6	1.02 ± 0.1	17.1	2.64 ± 0.2	3.66	61.8
14	6.41 ± 0.1	2.21 ± 0.3	34.5	2.12 ± 0.6	33.1	3.49 ± 0.1	5.61	87.6
15	7.54 ± 0.2	2.75 ± 0.6	36.5	2.23 ± 0.4	29.6	4.21 ± 0.3	6.44	85.4

% BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration

H2: Total content, stage related bioaccessible and residual fractions of cadmium (Cd) in urban dust of Newcastle upon Tyne

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% Total Recovery
1	1.05 ± 0.02	ND	ND	ND	ND	ND	ND	ND
2	3.06 ± 0.03	1.06 ± 0.3	34.6	0.832 ± 0.4	27.2	1.76 ± 0.4	2.59 ± 0.8	84.7
3	1.13 ± 0.01	ND	ND	ND	ND	ND	ND	ND
4	3.62 ± 0.01	1.21 ± 0.3	33.4	1.11 ± 0.1	30.6	2.10 ± 0.4	3.21 ± 0.5	88.6
5	1.06 ± 0.02	ND	ND	ND	ND	ND	ND	ND
6	1.02 ±	ND	ND	ND	ND	ND	ND	ND

	0.01							
7	1.08 ± 0.01	ND	ND	ND	ND	ND	ND	ND
8	2.15 ± 0.02	0.701 ± 0.2	32.6	0.522 ± 0.1	24.3	1.13 ± 0.1	1.65 ± 0.2	78.8
9	1.03 ± 0.01	ND	ND	ND	ND	ND	ND	ND
10	0.442 ± 0.1	ND	ND	ND	ND	ND	ND	ND
11	0.878 ± 0.1	ND	ND	ND	ND	ND	ND	ND
12	0.687 ± 0.1	ND	ND	ND	ND	ND	ND	ND
13	1.01 ± 0.01	ND	ND	ND	ND	ND	ND	ND
14	1.02 ± 0.01	ND	ND	ND	ND	ND	ND	ND
15	0.765 ± 0.1	ND	ND	ND	ND	ND	ND	ND

% BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Residual: residual fraction calculated as a fraction of the total concentration.

ND: Not detected.

H3: Total content, stage related bioaccessible and residual fractions of chromium (Cr) in urban dust of Newcastle upon Tyne

Sites	Total content (mg/kg)	*In-vitro* gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	53.7 ± 0.5	16.2 ± 0.1	30.2	11.3 ± 0.1	21.1	36.6 ± 0.2	47.9	89.2
2	70.8 ± 0.5	22.4 ± 0.7	31.6	17.8 ± 1.1	25.1	43.1 ± 2.1	60.9	86.1
3	81.1 ± 1	30.8 ± 1.2	38.0	24.6 ± 1.4	30.3	55.7 ± 1.4	80.3	99.0
4	106 ± 0.9	37.6 ± 0.3	35.5	31.2 ± 0.6	29.4	62.3 ± 2.1	93.5	88.2
5	100 ± 1	36.7 ± 1.2	36.8	30.4 ± 1.1	30.4	61.2 ± 1.3	91.6	91.6
6	98.3 ± 2	29.3 ± 0.4	29.8	24.6 ± 0.3	25.0	58.7 ± 1.1	83.3	84.7
7	104 ± 1	30.1 ± 1	28.9	28.1 ± 0.6	27.0	55.6 ± 1.1	85.7	82.4
8	43.4 ± 0.7	12.2 ± 0.1	28.1	10.1 ± 0.3	23.3	25.4 ± 0.2	35.5	81.2
9	98.4 ± 0.8	33.1 ± 0.3	33.6	27.4 ± 0.4	27.8	58.7 ± 0.3	86.1	87.5

10	154 ± 1	40.1 ± 1.1	26.0	34.3 ± 0.8	22.3	90.6 ± 1	125	81.1
11	55.5 ± 1	14.3 ± 0.8	25.8	10.9 ± 0.7	19.6	35.8 ± 1.2	46.7	84.1
12	59.9 ± 0.7	16.5 ± 1.1	27.5	13.4 ± 0.3	22.4	41.4 ± 1.1	54.8	91.5
13	53.1 ± 1	12.3 ± 0.2	23.1	10.2 ± 0.3	19.2	36.3 ± 1	46.5	89.8
14	78.8 ± 1	23.1 ± 1.2	29.3	19.6 ± 0.7	24.9	46.3 ± 1	65.9	83.6
15	40.4 ± 1	13.5 ± 0.5	33.4	11.1 ± 0.4	27.4	29.8 ± 1	40.9	101

% BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

H4: Total content, stage related bioaccessible and residual fractions of copper (Cu) in urban dust of Newcastle upon Tyne

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	159 ± 1	38.3 ± 0.7	24.1	35.8 ± 0.6	22.5	89.4 ± 1	125	78.7
2	445 ± 3	142 ± 2	31.9	135 ± 5	30.3	286 ± 7	421	94.6
3	145 ± 1	45.9 ± 1	31.6	41.3 ± 0.7	28.4	76.8 ± 2	118	81.4
4	166 ± 1	53.8 ± 1	32.4	52.9 ± 0.1	31.9	81.3 ± 0.4	134	80.8
5	146 ± 2	49.2 ± 0.8	33.7	39.1 ± 2	26.8	71 .6 ± 0.5	110	75.8
6	334 ± 4	122 ± 4	36.5	119 ± 1	35.6	213 ± 6	332	99.4
7	989 ± 8	301 ± 2	30.4	286 ± 4	28.9	632 ± 10	918	92.8
8	140 ± 0.6	32.2 ± 1	23.0	25.8 ± 0.4	18.4	63.7 ± 0.1	89.5	63.9
9	644 ± 10	118 ± 2	18.3	90.1 ± 2	13.9	425 ± 4	515	79.9

10	283 ± 2	40.1 ± 0.6	14.1	37.3 ± 0.1	13.1	121 ± 1	158	55.9
11	147 ± 1	46.1 ± 0.2	31.4	35.4 ± 0.3	24.1	67.9 ± 1	103	70.1
12	210 ± 1	90.4 ± 1	43.1	79.3 ± 0.7	37.8	100 ± 2	179	85.2
13	100 ± 0.8	30.1 ± 1	30.1	28.4 ± 1	28.4	62.3 ± 2	90.7	90.7
14	133 ± 1	50.5 ± 2	37.9	47.7 ± 1	35.9	76 .7 ± 1	124	93.5
15	111 ± 1	30.4 ± 0.4	27.4	26.7 ± 2	24.1	61.8 ± 2	88.5	79.7

% BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

H5: Total content, stage related bioaccessible and residual fractions of manganese (Mn) in urban dust of Newcastle upon Tyne

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	562 ± 12	186 ± 11	33.1	120 ± 4	21.3	370 ± 3	490	87.2
2	490 ± 10	258 ± 17	52.6	186 ± 9	37.9	298 ± 4	484	98.8
3	549 ± 13	291 ± 14	53.1	201 ± 6	36.6	335 ± 8	536	97.6
4	349 ± 3	189 ± 11	54.2	112 ± 5	32.1	230 ± 4	342	97.9
5	368 ± 6	149 ± 9	40.5	71.5 ± 5	19.5	211 ± 1	283	76.7
6	545 ± 13	238 ± 21	43.7	180 ± 6	33.1	305 ± 5	485	88.9
7	448 ± 9	223 ± 17	49.8	118 ± 6	26.3	331 ± 1	449	100
8	393 ± 12	206 ± 14	52.4	121 ± 4	30.7	233 ± 6	354	90.1
9	344 ± 7	100 ± 2	29.1	76.2 ± 2	22.1	186 ± 3	262	76.2

10	463 ± 9	192 ± 5	41.5	130 ± 3	28.1	289 ± 7	419	90.4
11	454 ± 9	151 ± 6	33.3	121 ± 2	26.7	249 ± 4	370	81.5
12	475 ± 9	137 ± 9	28.8	124 ± 6	26.1	301 ± 6	425	89.5
13	451 ± 15	160 ± 10	35.5	129 ± 2	28.6	310 ± 4	439	97.3
14	472 ± 11	204 ± 13	43.2	153 ± 4	32.4	335 ± 6	488	103
15	448 ± 10	249 ± 3	55.6	130 ± 3	29.1	268 ± 4	398	88.8

$$\% \text{ BAF} = \frac{C_{\text{Bioaccessibility}}}{C_{\text{total content}}} \times 100$$

Where $C_{\text{Bioaccessibility}}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{\text{total content}}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

H6: **Total content, stage related bioaccessible and residual fractions of nickel (Ni) in urban dust of Newcastle upon Tyne**

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	39.8 ± 0.6	12.9 ± 0.2	30.1	10.4 ± 1	26.1	21.2 ± 0.2	31.6	79.4
2	31.9 ± 0.2	12.2 ± 0.8	38.2	10.1 ± 0.3	31.7	17.7 ± 2	27.8	87.1
3	40.2 ± 0.7	16.4 ± 0.2	40.8	14.3 ± 0.1	35.6	21.5 ± 0.3	35.8	89.1
4	52.5 ± 0.3	18.3 ± 0.3	34.9	16.2 ± 0.1	30.9	24.6 ± 0.1	40.8	77.7
5	28.4 ± 0.5	12.1 ± 0.1	42.6	11.3 ± 0.3	39.9	16.6 ± 0.2	27.9	98.2
6	41.5 ± 0.5	17.4 ± 0.4	41.9	15.3 ± 0.7	36.9	24.1 ± 0.3	39.4	94.9
7	50.9 ± 0.5	21.2 ± 0.1	41.6	18.4 ± 0.3	36.1	27.8 ± 0.1	46.2	90.8
8	50.3 ± 0.4	23.4 ± 0.3	46.5	20.3 ± 0.6	40.3	29.1 ± 0.3	49.4	98.2
9	39.3 ± 0.4	12.6 ± 0.3	32.1	10.6 ± 0.2	26.9	16.7 ± 0.3	27.3	69.5

10	1287 ± 13	320 ± 5	24.8	296 ± 6	22.9	597 ± 13	893	69.4
11	28.3 ± 0.4	9.4 ± 0.1	33.2	7.9 ± 0.2	27.9	15.3 ± 0.3	23.2	81.9
12	30.9 ± 0.4	11.1 ± 0.1	35.9	10.3 ± 0.6	33.3	14.9 ± 0.7	25.2	81.6
13	23.8 ± 0.6	7.3 ± 0.4	30.6	6.6 ± 0.1	27.7	11.1 ± 0.2	17.7	74.4
14	36.7 ± 0.1	13.3 ± 0.7	36.2	11.4 ± 0.4	31.1	16.3 ± 0.4	27.7	75.5
15	28.1 ± 0.6	10.2 ± 0.3	36.3	8.7 ± 0.1	30.9	13.4 ± 0.2	22.1	78.6

% BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

H7: Total content, stage related bioaccessible and residual fractions of lead (Pb) in urban dust of Newcastle upon Tyne

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	167 ± 1	89.4 ± 0.2	53.5	76.1 ± 6	45.6	100 ± 2	176	105
2	565 ± 5	231 ± 1	40.9	176 ± 3	31.1	331 ± 4	507	89.7
3	1636 ± 12	736 ± 4	45.1	534 ± 12	32.6	921 ± 13	1455	88.9
4	868 ± 4	352 ± 3	40.6	322 ± 4	37.1	411 ± 4	733	84.4
5	1523 ± 7	500 ± 6	32.8	320 ± 2	21.1	934 ± 12	1254	82.3
6	761 ± 4	286 ± 4	37.5	221 ± 5	29.1	432 ± 10	653	85.8
7	1410 ± 11	622 ± 5	44.1	512 ± 4	36.3	771 ± 6	1283	90.9
8	237 ± 3	114 ± 1	48.1	83.6 ± 2	35.3	132 ± 2	216	90.9
9	79.6 ± 0.6	32.1 ± 0.2	40.3	27.7 ± 0.1	34.8	40.1 ± 0.3	67.8	85.2

10	27.9 ± 0.1	9.09 ± 0.4	32.6	8.11 ± 0.6	29.1	14.5 ± 0.4	22.6	81.1
11	294 ± 4	120 ± 4	40.8	109 ± 5	37.1	146 ± 9	255 ± 14	86.7
12	94.1 ± 0.7	32.3 ± 2	34.3	28.7 ± 0.2	30.5	40.2 ± 3	68.9 ± 3.2	73.2
13	163 ± 0.8	84.6 ± 0.5	51.9	67.3 ± 0.1	41.3	88.7 ± 0.4	156 ± 0.5	95.7
14	289 ± 1	121 ± 3	41.9	103 ± 4	35.6	143 ± 0.3	246 ± 4.3	85.1
15	256 ± 2	133 ± 1	51.9	113 ± 2	44.1	138 ± 3	251 ± 5	98.1

$$\% \text{ BAF} = \frac{C_{\text{Bioaccessibility}}}{C_{\text{total content}}} \times 100$$

Where $C_{\text{Bioaccessibility}}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of simulated physiologically based extraction test and $C_{\text{total content}}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

H8: Total content, stage related bioaccessible and residual fractions of zinc (Zn) in urban dust of Newcastle upon Tyne

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	468 ± 9	201 ± 11	42.9	146 ± 4	31.2	312 ± 5	458	97.7
2	4646 ± 148	1865 ± 28	40.1	1530 ± 19	32.9	2820 ± 34	4350	93.6
3	715 ± 12	301 ± 15	42.1	286 ± 6	40.0	333 ± 5	619	86.6
4	685 ± 3	312 ± 9	45.5	269 ± 4	39.3	338 ± 6	607	88.6
5	648 ± 5	233 ± 6	35.9	243 ± 9	37.5	286 ± 11	529	81.6
6	851 ± 18	336 ± 12	39.5	286 ±9	33.6	562 ± 16	848	99.6
7	2507 ± 28	964 ± 14	38.5	841 ± 11	33.5	1350 ± 19	2191	87.4
8	870 ± 13	232 ± 1	26.7	211 ± 4	25.3	438 ± 3	649	75.6

9	511 ± 21	209 ± 4	40.9	186 ± 3	36.4	312 ± 12	498	97.4
10	366 ± 7	101 ± 1	27.6	89.8 ± 2	24.5	156 ± 2	246	67.1
11	338 ± 4	98.4 ± 2	29.1	79.3 ± 1	23.4	149 ± 1	228	67.5
12	746 ± 11	229 ± 7	30.7	200 ± 3	26.8	412 ± 6	612	82
13	486 ± 7	186 ± 4	38.3	153 ± 2	31.5	301 ± 7	454	93.4
14	861 ± 10	243 ± 6	28.2	217 ± 4	25.2	612 ± 1	829	96.2
15	483 ± 3	121 ± 0.7	25.1	143 ± 0.6	29.6	289 ± 1	432	89.4

$$\% \text{ BAF} = \frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: residual fraction calculated as a fraction of the total concentration.

H9: **Total content, stage related bioaccessible and residual fractions of arsenic (As) in urban dust of Durham**

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	4.79 ± 0.1	2.11 ± 0.2	44.1	1.52 ± 0.3	31.7	3.11 ± 0.1	4.63	96.7
2	5.81 ± 0.2	2.49 ± 0.3	42.9	1.81 ± 0.1	31.2	3.62 ± 1	5.43	93.5
3	4.89 ± 0.2	1.93 ± 0.1	39.5	1.67 ± 0.4	34.2	2.41 ± 0.4	4.08	83.4
4	4.98 ± 0.1	1.87 ±0.4	37.6	1.52 ± 0.3	30.5	2.67 ± 0.3	4.19	84.1
5	5.84 ± 0.3	2.03 ± 0.1	34.7	1.88 ± 0.1	32.2	2.21 ± 0.4	4.09	70.1
6	5.68 ± 0.1	2.12 ± 0.3	37.3	2.09 ± 0.6	36.8	2.32 ± 0.1	4.41	77.6
7	6.89 ± 0.1	3.11 ± 0.1	45.1	2.64 ± 0.2	38.3	4.17 ± 0.5	6.81	98.8
8	5.62 ± 0.1	2.27 ± 0.3	40.4	1.73 ± 0.1	30.9	2.93 ± 0.3	4.66	82.9
9	7.21 ± 0.2	3.14 ± 0.3	43.6	2.73 ± 0.2	37.9	3.76 ± 0.6	6.49	90.1

10	8.03 ± 0.3	4.11 ± 0.2	51.2	3.09 ± 0.2	38.5	4.82 ± 1	7.91	98.5
11	5.76 ± 0.2	2.17 ± 0.2	37.7	1.79 ± 0.6	31.8	2.34 ± 0.1	4.13	71.7
12	6.13 ± 0.1	2.32 ± 0.1	37.8	2.07 ± 0.2	33.7	3.11 ± 0.2	5.18	84.5
13	7.69 ± 0.2	2.67 ± 0.4	34.7	2.14 ± 0.6	27.8	3.87 ± 0.1	6.01	78.2
14	5.77 ± 0.2	2.21 ± 0.3	38.3	1.83 ± 0.2	31.7	2.66 ± 0.2	4.49	77.8
15	5.48 ± 0.1	1.89 ± 0.1	34.4	1.54 ± 0.6	28.1	2.34 ± 0.3	3.88	70.8

$$\% \text{ BAF} = \frac{C_{\text{Bioaccessibility}}}{C_{\text{total content}}} \times 100$$

Where $C_{\text{Bioaccessibility}}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{\text{total content}}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

H10: Total content, stage related bioaccessible and residual fractions of cadmium (Cd) in urban dust of Durham

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	0.489 ± 0.04	ND	ND	ND	ND	ND	ND	ND
2	0.523 ± 0.04	0.247 ± 0.02	47.2	0.233 ± 0.01	44.6	0.281 ± 0.07	0.514	98.3
3	0.605 ± 0.02	0.252 ± 0.02	41.7	0.239 ± 0.04	39.5	0.325 ± 0.1	0.464	93.2
4	0.571 ± 0.02	0.184 ± 0.07	32.2	0.176 ± 0.03	30.8	0.236 ± 0.06	0.412	72.2
5	1.82 ± 0.03	0.573 ± 0.05	31.5	0.532 ± 0.01	29.2	0.832 ± 0.2	1.36	74.9
6	0.746 ± 0.01	0.304 ± 0.01	40.8	0.276 ± 0.04	36.9	0.355 ± 0.03	0.659	88.3

7	0.411 ± 0.03	0.156 ± 0.06	37.9	0.123 ± 0.02	29.9	0.209 ± 0.01	0.332	80.8
8	0.556 ± 0.02	0.161 ± 0.02	28.9	0.147 ± 0.01	26.4	0.221 ± 0.04	0.368	66.2
9	0.981 ± 0.03	0.405 ± 0.03	41.2	0.316 ± 0.04	32.2	0.432 ± 0.02	0.748	76.2
10	0.882 ± 0.04	0.431 ± 0.01	33.6	0.297 ± 0.02	33.6	0.422 ± 0.02	0.719	81.5
11	0.552 ± 0.02	0.203 ± 0.01	36.8	0.171 ± 0.02	30.9	0.213 ± 0.02	0.384	69.6
12	1.17 ± 0.01	0.587 ± 0.01	50.1	0.403 ± 0.01	34.4	0.634 ± 0.2	1.04	88.6
13	1.05 ± 0.02	0.347 ± 0.03	33.1	0.223 ± 0.02	21.2	0.456 ± 0.01	0.679	64.6
14	0.505 ± 0.03	0.253 ± 0.02	50.1	0.176 ± 0.01	34.9	0.271 ± 0.02	0.447	88.5
15	0.244 ± 0.02	ND	ND	ND	ND	ND	ND	ND

% BAF: % BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.
% Total Recovery: total recovery fraction calculated as a fraction of the total concentration. **ND**: Not detected.

H11: Total content, stage related bioaccessible and residual fractions of chromium (Cr) in urban dust of Durham

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	56.1 ± 0.6	23.1 ± 0.3	41.2	21.2 ± 0.1	37.7	30.3 ± 0.5	51.2	91.8
2	187 ± 2	60.6 ± 2	32.4	51.3 ± 0.1	27.4	94.5 ± 1	146	77.9
3	64.4 ± 0.6	29.2 ± 0.1	45.3	26.1 ± 0.3	40.5	33.6 ± 0.3	59.7	92.7
4	53.4 ± 0.8	21.6 ± 0.5	40.4	19.4 ± 0.3	36.3	26.2 ± 0.2	45.6	87.1
5	70.3 ± 0.8	36.6 ± 1	52.1	29.5 ± 2	41.9	41.3 ± 2	70.8	101
6	57.4 ± 0.9	19.3 ± 0.2	33.6	17.3 ± 2	30.1	25.9 ± 0.3	43.2	75.5
7	56.8 ± 0.9	20.1 ± 0.6	35.4	19.2 ± 0.1	33.8	30.3 ± 0.9	49.5	87.1
8	34.7 ± 0.4	12.9 ± 0.4	37.2	9.21 ± 1	26.5	17.1 ± 1	26.3	75.8
9	53.2 ± 0.8	25.4 ± 0.5	47.7	22.1 ± 0.3	41.5	31.3 ± 0.8	53.4	100

10	50.2 ± 1.2	17.8 ± 0.3	35.5	14.4 ± 0.2	28.7	21.2 ± 1	35.6	70.9
11	44.1 ± 1	10.2 ± 0.1	23.1	8.87 ± 0.6	20.1	14.7 ± 0.6	23.6	53.6
12	45.1 ± 0.8	19.6 ± 0.3	43.5	17.8 ± 0.4	39.5	23.3 ± 0.3	41.1	91.1
13	25.9 ± 0.5	6.11 ± 0.2	23.6	4.97 ± 0.5	19.2	8.19 ± 0.2	13.2	50.8
14	93.3 ± 1	43.6 ± 0.4	46.7	39.7 ±1	42.5	51.5 ± 2	91.2	97.7
15	109 ± 2	49.5 ± 0.3	45.4	38.3 ± 0.2	35.1	67.9 ± 0.4	106	97.4

% BAF: = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

H12: Total content, stage related bioaccessible and residual fractions of copper (Cu) in urban dust of Durham

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	65.9 ± 0.8	29.3 ± 0.1	44.5	22.5 ± 0.7	34.1	36.4 ± 0.2	58.9	89.4
2	379 ± 6	160 ± 4	42.2	145 ± 10	38.3	181 ± 4	326	86.1
3	171 ± 2	77.5 ± 1	45.3	68.9 ± 6	40.3	87.5 ± 8	156	91.5
4	225 ± 2	119 ± 3	52.9	98.7 ± 2	43.9	121 ± 1	210	97.6
5	244 ± 2	103 ± 2	42.2	87.4 ± 3	35.8	128 ± 7	215	88.3
6	216 ± 3	98.9 ± 2	45.8	84.3 ± 2	85.2	111 ± 4	195	90.4
7	274 ± 2	121 ± 3	44.2	102 ± 7	37.2	132 ± 3	234	85.4
8	44.5 ± 1	19.6 ± 3	44.1	18.4 ± 1	41.3	21.3 ± 2	39.7	89.2
9	83.5 ± 1	31.3 ± 2	37.5	26.4 ± 1	31.6	37.5 ± 1	63.9	76.5

10	133 ± 2	49.3 ± 1	37.1	44.3 ± 2	33.3	54.8 ± 4	99.1	74.5
11	78.8 ± 2	30.2 ± 1	38.3	27.9 ± 3	35.4	34.7 ± 2	62.6	97.3
12	87.2 ± 1	34 .7 ± 2	39.8	31.1 ± 3	35.6	40.4 ± 3	71.5	81.9
13	34.6 ± 0.6	11.5 ± 0.3	33.2	10.3 ± 0.7	29.8	13.2 ± 0.1	23.5	67.9
14	342 ± 2	146 ± 9	42.7	132 ± 5	38.6	174 ± 6	306	89.5
15	227 ± 3	98.4 ± 2	43.3	81.1 ± 2	35.7	114 ± 1	195	85.9

% BAF: $= \frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

H13: Total content, stage related bioaccessible and residual fractions of manganese (Mn) in urban dust of Durham

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	558 ± 13	245 ± 6	43.9	211 ± 4	37.8	342 ± 8	553	99.1
2	689 ± 18	240 ± 11	34.8	223 ± 9	32.4	352 ± 13	575	83.5
3	442 ± 7	217 ± 6	49.1	188 ± 4	42.5	232 ± 7	420	95.1
4	582 ± 15	266 ± 4	45.7	239 ± 11	41.1	308 ± 7	547	94.1
5	489 ± 11	214 ± 2	43.8	194 ± 3	39.7	277 ± 7	471	96.3
6	522 ± 6	223 ± 2	42.7	201 ± 7	38.5	273 ± 5	474	90.8
7	510 ± 11	240 ± 2	47.1	228 ± 7	44.8	281 ± 14	509	99.8
8	400 ± 7	145 ± 3	36.3	104 ± 3	26.1	218 ± 6	322	80.5
9	572 ± 13	247 ± 7	43.2	168 ± 9	29.3	370 ± 9	538	94.1

10	483 ± 11	182 ± 4	37.8	131 ± 3	27.1	261 ± 5	392	81.2
11	572 ± 15	163 ± 5	28.5	124 ± 11	21.6	236 ± 5	360	62.9
12	741 ± 21	237 ± 6	31.9	191 ± 2	25.8	359 ± 8	550	74.2
13	968 ± 30	350 ± 9	36.1	256 ± 14	26.4	452 ± 13	708	73.1
14	660 ± 12	303 ± 4	45.9	232 ± 7	35.2	341 ± 8	573	86.8
15	533 ± 16	241 ± 4	45.2	211 ± 3	39.6	331 ± 8	542	101

$$\textbf{\% BAF} = \frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

H14: Total content, stage related bioaccessible and residual fractions of nickel (Ni) in urban dust of Durham

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	37.1 ± 0.3	14.3 ± 0.6	38.5	10.4 ± 0.4	28.1	22.9 ± 0.9	33.3	89.8
2	47.7 ± 0.6	14.9 ± 0.1	31.2	12.2 ± 0.1	25.6	18.1 ± 0.1	30.3	63.5
3	25.8 ± 0.3	10.4 ± 1	40.3	8.91 ± 0.2	34.5	13.2 ± 0.2	22.1	85.7
4	23.1 ± 0.3	9.64 ± 0.2	41.7	7.92 ± 1	34.3	12.7 ± 0.1	20.6	89.3
5	28.8 ± 0.4	11.2 ± 3	38.9	8.11 ± 0.2	28.2	13.3 ± 0.6	21.4	74.3
6	26.9 ± 0.5	8.21 ± 0.2	30.5	6.92 ± 0.3	25.7	10.1 ± 0.1	17.1	63.6
7	26.1 ± 0.4	9.11 ± 0.3	34.9	7.75 ± 0.2	29.7	12.2 ± 0.1	19.9	76.4
8	17.9 ± 0.2	7.21 ± 0.2	40.3	5.14 ± 0.1	28.7	9.22 ± 0.4	14.4	80.2
9	31.3 ± 0.6	9.68 ± 1	30.9	8.36 ± 0.2	26.7	14.3 ± 0.2	22.7	72.3

10	28.2 ± 0.7	9.32 ± 0.5	38.5	7.64 ± 0.7	27.1	12.5 ± 0.1	20.1	71.4
11	26.3 ± 0.7	7.22 ± 0.2	31.2	5.42 ± 0.4	20.6	11.1 ± 0.9	16.5	62.8
12	20.2 ± 0.4	5.12 ± 0.1	40.3	3.46 ± 0.7	17.1	8.63 ± 0.4	12.1	59.9
13	17.8 ± 0.4	5.23 ± 0.4	41.7	2.97 ± 0.1	16.6	7.59 ± 1	10.6	59.1
14	35.4 ± 0.5	14.2 ± 0.3	38.9	12.6 ± 0.2	35.6	18.9 ± 0.4	31.5	88.9
15	57.6 ± 0.7	21.4 ± 0.6	30.5	18.8 ± 0.1	32.6	30.2 ± 2	49.2	85.1

% BAF: $= \frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

H15: Total content, stage related bioaccessible and residual fractions of lead (Pb) in urban dust of Durham

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	129 ± 1	42.3 ± 1	32.7	38.7 ± 1	30.1	59.4 ± 2	98.1	76.1
2	123 ± 1	43.7 ± 2	35.5	41.1 ± 2	33.4	60.1 ± 4	101	82.1
3	228 ± 1	84.7 ± 1	37.1	76.6 ± 3	33.5	109 ± 2	186	81.4
4	130 ± 0.8	55.8 ± 2	42.9	45.8 ± 2	35.2	67.1 ± 4	113	86.8
5	372 ± 4	160 ± 3	43.1	132 ± 1	35.5	197 ± 2	329	88.4
6	252 ± 3	118 ± 2	46.8	102 ± 2	40.5	141 ± 1	243	96.4
7	1221 ± 17	387 ± 12	31.7	347 ± 8	28.4	531 ± 9	878	71.9
8	336 ± 8	167 ± 2	49.7	133 ± 7	39.8	172 ± 5	305	90.8
9	473 ± 22	220 ± 11	46.5	182 ± 6	38.5	245 ± 4	427	90.3

10	2119 ± 42	845 ± 10	39.9	803 ± 14	37.9	1227 ± 13	2030	95.8
11	190 ± 8	73.7 ± 3	38.8	68.9 ± 2	36.3	87.7 ± 3	157	82.4
12	362 ± 8	167 ± 2	46.1	134 ± 4	37.1	184 ± 4	318	87.8
13	485 ± 8	174 ± 2	35.9	150 ± 5	30.9	214 ± 7	364	75.1
14	156 ± 6	87.7 ± 3	56.2	64.9 ± 1	41.6	85.9 ± 2	151	96.7
15	109 ± 3	50.3 ± 1	46.1	43.3 ± 3	39.7	59.1 ± 5	102	93.9

% BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

H16: Total content, stage related bioaccessible and residual fractions of zinc (Zn) in urban dust of Durham

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	316 ± 4	166 ± 4	52.5	123 ± 4	38.9	187 ± 6	310	98.1
2	979 ± 14	382 ± 9	39.1	366 ± 6	37.4	461 ± 11	827	84.4
3	422 ± 3	225 ± 2	53.3	194 ± 4	45.9	237 ± 4	431	102
4	424 ± 6	186 ± 2	43.9	167 ± 1	39.4	227 ± 3	394	92.9
5	1661 ± 20	810 ± 8	48.9	786 ± 12	47.3	865 ± 7	1651	99.4
6	567 ± 20	212 ± 2	37.7	197 ± 4	34.7	236 ± 4	433	76.4
7	714 ± 7	322 ± 3	45.1	286 ± 2	40.1	418 ± 3	704	98.6
8	268 ± 3	123 ± 2	45.9	104 ± 1	38.9	143 ± 4	247	92.2

9	373 ± 9	171 ± 4	45.8	151 ± 2	40.4	210 ± 8	361	96.9
10	543 ± 11	221 ± 7	40.7	193 ± 3	35.5	287 ± 12	480	88.4
11	1114 ± 27	342 ± 13	30.7	312 ± 6	28.1	607 ± 8	919	82.5
12	361 ± 6	102 ± 1	28.3	89.4 ± 2	24.8	131 ± 3	220	61.1
13	368 ± 9	148 ± 5	40.2	129 ± 7	35.1	164 ± 3	293	79.6
14	1166 ± 12	521 ± 4	44.6	497 ± 5	42.6	649 ± 9	1146	98.3
15	748 ± 15	321 ± 2	42.9	288 ± 5	38.5	359 ± 3	680	86.5

% BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

H17: Total content, stage related bioaccessible and residual fractions of arsenic (As) in urban dust of Liverpool

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	5.97 ± 0.2	1.54 ± 0.1	25.8	1.03 ± 0.2	17.3	2.72 ± 0.3	3.75	62.8
2	7.59 ± 0.3	3.12 ± 0.4	41.1	2.86 ± 0.1	37.7	3.42 ± 0.1	6.28	82.7
3	6.68 ± 0.3	3.01 ± 0.4	45.1	2.83 ± 0.2	42.4	3.48 ± 0.2	6.31	94.5
4	8.43 ± 0.2	3.47 ± 0.1	41.1	3.12 ± 0.1	37.0	4.93 ± 0.2	8.05	94.4
5	8.52 ± 0.2	4.54 ± 0.4	53.3	3.46 ± 0.6	40.6	4.73 ± 0.7	8.19	96.1
6	5.33 ± 0.2	2.63 ± 0.3	49.3	2.19 ± 0.3	41.1	3.08 ± 0.2	5.27	98.9
7	6.64 ± 0.2	3.34 ± 0.3	50.3	2.38 ± 0.1	35.8	3.76 ± 0.2	6.14	92.5
8	6.12 ± 0.3	2.49 ± 0.1	40.7	1.81 ± 0.9	29.6	2.87 ± 0.7	4.68	76.5
9	6.97 ± 0.3	3.58 ± 0.4	51.4	2.21 ± 0.2	31.7	4.11 ± 0.3	6.32	90.7

10	6.39 ± 0.2	3.42 ± 0.5	53.5	2.91 ± 0.1	45.5	3.19 ± 0.3	6.10	95.5
11	5.75 ± 0.4	2.64 ± 0.1	45.9	2.19 ± 0.4	38.1	2.84 ± 0.2	5.03	87.5
12	15.9 ± 0.3	5.69 ± 0.3	35.9	3.42 ± 0.2	21.5	8.71 ± 0.6	12.1	76.3
13	4.72 ± 0.08	2.21 ± 0.4	46.8	1.54 ± 0.7	32.6	2.51 ± 0.3	4.05	85.8
14	6.61 ± 0.3	2.88 ± 0.3	43.6	2.43 ± 0.1	36.8	3.24 ± 0.1	5.67	85.8
15	6.46 ± 0.3	3.09 ± 0.1	47.8	2.63 ± 0.4	40.7	3.54 ± 0.5	6.17	95.5

% BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

H18: Total content, stage related bioaccessible and residual fractions of cadmium (Cd) in urban dust of Liverpool

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	1.29 ± 0.05	0.521 ± 0.01	40.4	0.369 ± 0.03	28.6	0.711 ± 0.02	1.08	83.7
2	3.16 ± 0.06	1.18 ± 0.2	37.3	0.962 ± 0.04	30.4	1.53 ± 0.1	2.49	78.9
3	0.556 ± 0.02	0.233 ± 0.03	41.9	0.212 ± 0.02	38.1	0.321 ± 0.02	0.533	95.9
4	1.17 ± 0.06	0.615 ± 0.1	52.6	0.432 ± 0.02	36.9	0.721 ± 0.01	1.15	98.5
5	0.843 ± 0.02	0.389 ± 0.05	46.1	0.321 ± 0.01	38.1	0.432 ± 0.03	0.753	89.3
6	1.89 ± 0.05	0.623 ± 0.02	32.9	0.465 ± 0.1	24.6	0.681 ± 0.1	1.15	60.6
7	0.729 ± 0.04	0.312 ± 0.06	42.8	0.265 ± 0.02	36.4	0.347 ± 0.02	0.612	83.9

8	0.461 ± 0.02	ND	ND	ND	N D	ND	ND	ND
9	0.665 ± 0.03	0.226 ± 0.02	33.9	0.176 ± 0.02	26.5	0.287 ± 0.01	0.463	69.6
10	0.972 ± 0.03	0.427 ± 0.01	43.9	0.338 ± 0.01	97.5	0.527 ± 0.03	0.865	88.9
11	0.713 ± 0.02	0.317 ± 0.02	44.5	0.278 ± 0.01	38.9	0.361 ± 0.01	0.639	89.6
12	1.19 ± 0.01	0.384 ± 0.02	32.2	0.246 ± 0.01	20.7	0.516 ± 0.03	0.762	64.1
13	0.332 ± 0.1	ND	ND	ND	ND	ND	ND	ND
14	1.22 ± 0.02	0.512 ± 0.03	41.9	0.331 ± 0.02	27.1	0.521 ± 0.1	0.852	69.8
15	0.154 ± 0.03	ND	ND	ND	ND	ND	ND	ND

% BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

ND: Not detected.

H19: Total content, stage related bioaccessible and residual fractions of chromium (Cr) in urban dust of Liverpool

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	98.6 ± 2	37.2 ± 3	37.5	31.5 ± 2	31.9	45.2 ± 1	74.1	75.1
2	85.1 ± 1	38.6 ± 1	45.4	32.2 ± 3	37.8	43.2 ± 2	75.4	88.6
3	60.8 ± 0.4	23.4 ± 3	38.5	21.1 ± 1	34.7	26.1 ± 1	47.2	77.6
4	57.5 ± 1	16.7 ± 0.3	29.1	15.3 ± 0.1	26.6	24.6 ± 0.2	39.9	69.4
5	79.9 ± 0.9	24.3 ± 0.1	30.4	22.1 ± 0.2	27.6	30.9 ± 0.4	55.2	69.1
6	22.7 ± 0.4	6.61 ± 0.3	29.1	6.02 ± 0.7	26.5	7.81 ± 0.1	13.8	60.9
7	63.1 ± 1	23.2 ± 1	27.2	19.6 ± 0.1	31.1	40.3 ± 0.4	59.9	94.9
8	73.1 ± 0.9	27.1 ± 1	37.1	25.5 ± 2	34.8	33.3 ± 2	58.8	80.4
9	54.3 ± 0.5	19.3 ± 0.2	35.5	17.8 ± 0.6	32.8	21.3 ± 0.3	39.1	72.0

10	57.5 ± 1	22.1 ± 1	38.4	20.4 ± 2	35.5	27.4 ± 2	47.7	82.9
11	58.6 ± 0.7	23.2 ± 0.1	39.6	21.1 ± 0.7	36.1	25.1 ± 0.3	46.2	78.8
12	23.7 ± 0.4	10.1 ± 0.3	42.6	7.12 ± 0.3	30.1	14.4 ± 0.2	21.5	90.8
13	65.3 ± 0.9	26.2 ± 0.1	40.1	22.7 ± 0.2	34.8	33.5 ± 0.8	56.2	86.1
14	59.9 ± 0.6	24.3 ± 0.3	40.6	22.5 ± 0.4	37.6	31.3 ± 0.7	53.8	89.8
15	67.2 ± 0.9	22.6 ± 0.1	33.6	20.5 ± 0.2	30.1	29.4 ± 0.2	49.9	74.3

% BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

H20: Total content, stage related bioaccessible and residual fractions of copper (Cu) in urban dust of Liverpool

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	62.1 ± 2	30.6 ± 2	49.3	21.2 ± 1	34.1	34.9 ± 1	56.1	90.3
2	2222 ± 23	842 ± 12	37.9	734 ± 20	33.1	1200 ± 18	1934	87.1
3	98.1 ± 0.7	34.3 ± 2	34.9	29.6 ± 0.2	30.2	37.8 ± 1	67.4	68.7
4	214 ± 3	117 ± 4	54.7	106 ± 9	49.5	121 ± 7	227	106
5	239 ± 3	103 ± 43.1	43.1	74.7 ± 3	31.3	146 ± 4	221	92.3
6	55.7 ± 0.7	17.2 ± 0.3	30.8	13.6 ± 1	24.4	28.1 ± 2	41.7	74.9
7	190 ± 3	91.1 ± 4	47.9	70.1 ± 4	36.9	118 ± 1	188	98.9
8	53.3 ± 0.5	21.3 ± 1	39.7	14.3 ± 0.5	26.9	28.5 ± 3	42.8	80.3
9	159 ± 2	67.4 ± 4	42.4	58.5 ± 5	50.5	80.3 ± 4	134	87.3

10	124 ± 2	46.3 ± 1	37.3	37.8 ± 2	30.4	71.4 ± 2	109	88.1
11	130 ± 0.8	55.2 ± 0.6	42.3	40.6 ± 1	31.2	69.4 ± 3	110	84.6
12	106 ± 1	42.3 ± 0.1	39.9	34.4 ± 0.2	32.5	53.8 ± 1	88.2	83.2
13	76.2 ± 0.6	26.9 ± 0.4	35.3	21.1 ± 0.3	27.7	30.6 ± 0.3	51.7	67.8
14	169 ± 1	76.8 ± 0.9	45.4	61.3 ± 0.6	36.3	93.5 ± 2	155	91.6
15	168 ± 2	64.2 ± 0.7	38.2	58.6 ± 2	34.9	88.7 ± 3	147	87.7

% BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

H21: Total content, stage related bioaccessible and residual fractions of manganese (Mn) in urban dust of Liverpool

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	348 ± 9	218 ± 9	62.6	116 ± 5	33.3	171 ± 2	287	82.6
2	403 ± 7	188 ± 2	46.6	108 ± 4	26.8	189 ± 6	297	73.7
3	329 ± 6	163 ± 8	49.5	143 ± 2	43.5	169 ± 2	312	94.8
4	374 ± 7	165 ± 6	44.1	124 ± 4	33.2	199 ± 2	323	86.4
5	409 ± 7	134 ± 3	32.8	129 ± 2	31.5	223 ± 2	352	86.1
6	336 ± 8	139 ± 5	41.5	124 ± 3	36.9	206 ± 3	330	92.2
7	382 ± 12	133 ± 3	34.8	124 ± 2	32.4	168 ± 3	292	76.4
8	345 ± 8	158 ± 3	45.8	121 ± 3	35.1	145 ± 1	265	77.1

9	346 ± 7	117 ± 3	33.8	97.6 ± 4	28.2	209 ± 4	307	88.6
10	303 ± 9	133 ± 2	43.9	113 ± 1	37.3	174 ± 4	287	94.7
11	644 ± 8	267 ± 7	41.5	178 ± 4	27.6	311 ± 5	489	75.9
12	279 ± 5	102 ± 0.8	36.6	97.3 ± 2	34.9	168 ± 5	265	95.1
13	1607 ± 22	625 ± 14	38.9	408 ± 11	25.4	812 ± 22	1220	75.9
14	432 ± 9	204 ± 3	47.2	119 ± 4	27.5	300 ± 5	419	96.9
15	419 ± 7	210 ± 6	50.1	154 ± 8	36.8	243 ± 7	397	94.7

% BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

H22: Total content, stage related bioaccessible and residual fractions of nickel (Ni) in urban dust of Liverpool

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	66.1 ± 0.9	29.4 ± 2	44.5	26.2 ± 1	39.6	34.9 ± 1	61.1	92.4
2	66.5 ± 0.7	27.6 ± 1	41.5	26.8 ± 2	40.3	37.8 ± 3	64.6	97.1
3	22.2 ± 0.5	6.76 ± 0.1	30.6	4.61 ± 0.2	20.8	12.1 ± 0.5	16.7	75.2
4	27.1 ± 0.3	8.11 ± 0.2	29.9	5.13 ± 0.3	13.2	15.3 ± 0.3	20.4	75.6
5	32.4 ± 0.7	9.12 ± 0.3	28.1	5.38 ± 0.1	16.7	20.3 ± 0.4	25.7	79.2
6	13.1 ± 0.3	5.21 ± 0.7	39.7	4.01 ± 0.9	30.6	7.15 ± 0.1	11.2	85.1
7	28.8 ± 0.3	9.43 ± 0.6	32.7	8.23 ± 0.5	28.6	16.4 ± 0.3	16.7	57.9
8	39.2 ± 0.4	11.8 ± 0.3	30.1	10.6 ± 0.9	27.1	21.6 ± 0.6	32.2	82.1
9	24.5 ± 0.3	9.87 ± 0.4	40.2	7.49 ± 0.8	30.6	13.7 ± 1	21.2	86.5

10	32.5 ± 0.7	12.3 ± 0.5	37.8	10.4 ± 0.3	32.0	18.4 ± 0.6	28.8	88.6
11	28.8 ± 0.4	13.1 ± 0.4	45.5	11.2 ± 0.2	38.9	14.5 ± 0.1	25.7	89.2
12	26.9 ± 0.4	11.2 ± 0.2	41.6	9.74 ± 0.1	36.2	14.7 ± 0.3	24.4	90.8
13	14.4 ± 0.2	5.23 ± 0.1	36.3	3.32 ± 0.7	23.1	7.19 ± 0.4	10.5	72.3
14	31.4 ± 0.5	14.3 ± 0.4	45.5	10.2 ±0.5	32.5	17.3 ± 0.5	27.5	87.6
15	28.2 ± 0.5	10.8 ± 0.2	38.3	8.65 ± 0.3	30.7	15.5 ± 0.3	24.2	85.6

% BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentartion.

H23: Total content, stage related bioaccessible and residual fractions of lead (Pb) in urban dust of Liverpool

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	233 ± 13	101 ± 4	43.3	86.9 ± 6	37.3	116 ± 1	203	87.1
2	468 ± 16	151 ± 3	32.2	132 ± 2	28.2	170 ± 2	302	64.5
3	109 ± 4	34.2 ± 1	31.4	28.7 ± 3	26.3	43.2 ± 1	71.9	65.9
4	629 ± 14	206 ± 3	32.8	186 ± 2	29.6	247 ± 4	433	68.8
5	185 ± 4	68.4 ± 1	36.9	58.9 ± 1	31.2	87.6 ± 3	147	79.2
6	271 ± 7	113 ± 3	41.7	89.5 ± 1	33.1	132 ± 2	222	81.9
7	344 ± 11	143 ± 4	41.6	128 ± 9	37.2	168 ± 1	296	86.0
8	362 ± 12	154 ± 5	42.5	134 ± 2	37.0	181 ± 4	315	87.1
9	915 ± 31	374 ± 19	40.9	293 ± 4	32.0	412 ± 11	705	77.0

10	327 ± 5	124 ± 4	37.9	109 ± 3	33.3	149 ± 4	258	78.9
11	334 ± 3	134 ± 6	40.1	118 ± 2	35.3	153 ± 6	271	81.1
12	349 ±4	150 ± 1	42.9	121 ± 4	34.7	149 ± 3	270	77.4
13	374 ± 3	162 ±2	43.3	134 ± 2	35.8	180 ± 3	314	83.9
14	333 ± 2	148 ± 2	44.4	124 ± 3	37.2	154 ± 6	278	83.5
15	192 ± 2	78.8 ± 2	41.0	56.7 ± 1	29.5	87.8 ± 1	145	75

% BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

H24: Total content, stage related bioaccessible and residual fractions of zinc (Zn) in urban dust of Liverpool

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	244 ± 8	118 ± 4	48.4	82.2 ± 2	33.7	157 ± 8	239	97.9
2	3920 ± 26	1843 ± 21	47.1	1425 ± 13	36.4	2230 ± 31	3655	93.2
3	135 ± 3	43.6 ± 2	32.3	51.3 ± 1	38.0	63.4 ± 5	115	84.9
4	1195 ± 17	311 ± 17	26.1	276 ± 4	23.1	607 ± 22	883	73.9
5	635 ± 8	232 ± 3	36.5	200 ± 12	31.5	352 ± 3	552	86.9
6	425 ± 8	168 ± 8	39.5	132 ± 12	31.1	236 ± 5	368	86.6
7	755 ± 12	291 ± 3	38.5	230 ± 17	30.5	404 ± 10	634	83.9
8	125 ± 4	40.8 ± 2	32.6	35.7 ± 2	28.9	53.8 ± 3	89.5	71.6
9	430 ± 9	168 ± 6	39.1	143 ± 4	33.3	246 ± 13	389	90.5

10	1183 ± 20	421 ± 5	35.5	308 ± 11	26.1	663 ± 6	971	82.1
11	1201 ± 14	398 ± 23	33.1	284 ± 7	23.6	622 ± 2	906	75.4
12	722 ± 9	321 ± 4	44.5	276 ± 8	38.2	347 ± 9	623	86.3
13	286 ± 3	123 ± b3	43.0	112 ± 5	39.2	138 ± 6	250	87.4
14	897 ± 26	330 ± 12	36.8	281 ± 8	31.3	411 ± 6	692	77.1
15	476 ± 6	212 ± 2	44.5	186 ± 4	39.1	269 ± 7	455	95.5

% BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

H25: Total content, stage related bioaccessible and residual fractions of arsenic (As) in urban dust of Edinburgh

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	6.94 ± 0.3	2.84 ± 0.1	40.9	2.41 ± 0.2	34.7	3.12 ± 0.1	5.53	79.7
2	4.05 ± 0.1	1.87 ± 0.4	46.2	1.57 ± 0.1	38.8	2.12 ± 0.6	3.67	91.1
3	4.88 ± 0.2	2.07 ± 0.3	42.4	1.84 ± 0.7	37.7	2.39 ± 0.1	4.23	86.6
4	4.91 ± 0.1	2.17 ± 0.8	44.2	1.68 ± 0.3	34.2	2.31 ± 0.7	3.99	81.3
5	3.95 ± 0.1	1.74 ± 0.3	44	1.32 ± 0.1	33.4	2.11 ± 0.1	3.43	86.9
6	4.66 ± 0.2	1.86 ± 0.1	39.9	1.66 ± 0.2	35.6	2.06 ± 0.5	3.72	55.4
7	4.02 ± 0.1	2.22 ± 0.6	55.2	1.82 ± 0.4	45.3	2.12 ± 0.1	3.94	98.0
8	4.37 ± 0.2	2.01 ± 0.1	45.9	1.76 ± 0.2	40.3	2.23 ± 0.5	3.99	91.3
9	5.56 ± 0.2	2.68 ± 0.9	48.2	2.31 ± 0.2	41.5	3.11 ± 0.6	5.42	97.5

10	4.01 ± 0.2	1.94 ± 0.1	48.4	1.73 ± 0.4	43.1	2.09 ± 0.3	3.82	92.3
11	4.08 ± 0.1	2.03 ± 0.6	49.8	1.61 ± 0.1	39.5	2.13 ± 0.4	3.74	91.4
12	4.09 ± 0.1	1.84 ± 0.2	44.9	1.57 ± 0.7	38.4	2.04 ± 0.3	3.61	88.3
13	4.29 ± 0.2	2.13 ± 0.1	49.7	1.84 ± 0.2	42.9	2.25 ± 0.5	4.09	95.3
14	3.38 ± 0.1	1.46 ± 0.6	43.2	1.19 ± 0.8	35.2	1.64 ± 0.1	2.83	83.7
15	3.83 ± 0.1	1.57 ± 0.2	40.9	1.26 ± 0.7	32.9	1.86 ± 0.3	3.12	81.5

% BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

H26: Total content, stage related bioaccessible and residual fractions of cadmium (Cd) in urban dust of Edinburgh

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	2.25 ± 0.03	0.871 ± 0.03	38.7	0.521 ± 0.04	23.2	1.06 ± 0.01	1.58	70.2
2	1.81 ± 0.05	0.842 ± 0.01	46.5	0.618 ± 0.06	34.4	0.911 ± 0.04	1.53	84.5
3	1.59 ± 0.03	0.786 ± 0.01	49.4	0.462 ± 0.02	29.1	0.875 ± 0.1	1.34	84.3
4	1.51 ± 0.04	0.633 ± 0.04	41.9	0.462 ± 0.05	30.6	0.764 ± 0.04	1.23	81.2
5	1.48 ± 0.02	0.625 ± 0.02	42.2	0.431 ± 0.01	29.1	0.874 ± 0.01	1.31	88.2
6	0.881 ± 0.01	0.411 ± 0.01	46.7	0.281 ± 0.02	31.9	0.521 ± 0.01	0.802	91.0
7	1.23 ± 0.03	0.618 ± 0.03	50.2	0.414 ± 0.07	33.7	0.762 ± 0.02	1.18	95.6
8	1.26 ± 0.02	0.623 ± 0.01	49.4	0.427 ± 0.03	33.9	0.683 ± 0.04	1.11	88.1
9	0.806 ±	0.412 ± 0.01	51.1	0.307 ± 0.01	38.1	0.411 ± 0.03	0.718	89.1

	0.01							
10	1.14 ± 0.03	0.518 ± 0.01	45.4	0.402 ± 0.03	35.3	0.632 ±.002	1.03	90.7
11	1.31 ± 0.02	0.603 ± 0.05	46.1	0.544 ± 0.01	41.5	0.639 ± 0.1	1.18	90.3
12	1.52 ± 0.03	0.786 ± 0.01	51.7	0.643 ± 0.03	42.3	0.812 ± 0.02	1.46	95.7
13	1.15 ± 0.02	0.543 ± 0.04	47.2	0.397 ± 0.02	34.5	0.521 ± 0.04	0.918	79.8
14	1.02 ± 0.02	0.443 ± 0.03	43.4	0.401 ± 0.01	39.3	0.513 ± 0.03	0.914	89.6
15	0.563 ± 0.04	ND	ND	ND	ND	ND	ND	ND

% BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

ND: Not detected.

H27: Total content, stage related bioaccessible and residual fractions of chromium (Cr) in urban dust of Edinburgh

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	62 3 ± 0.8	24.1 ± 0.2	38.7	18.9 ± 1	30.3	32.4 ± 0.2	51.3	82.3
2	59.6 ± 0.7	25.6 ± 0.5	42.9	20.2 ± 0.3	33.8	30.4 ± 0.1	50.6	84.9
3	48.5 ± 0.8	19.5 ± 0.2	40.2	14.6 ± 0.1	30.1	25.1 ± 0.8	39.7	81.9
4	39.8 ± 0.4	16.4 ± 0.2	41.2	12.5 ± 0.4	31.4	24.8 ± 0.5	37.3	93.7
5	27.4 ± 0.5	6.17 ± 0.3	22.5	8.12 ± 0.1	29.6	14.1 ± 0.2	22.2	81.1
6	45.9 ± 0.7	15.6 ± 0.4	33.9	18.2 ± 0.1	39.7	20.4 ± 0.1	38.6	84.1
7	55.2 ± 0.7	13.4 ± 0.6	24.3	20.7 ± 0.6	37.5	25.7 ± 0.2	46.4	84.0
8	61.3 ± 0.5	19.8 ± 0.2	32.3	23.6 ± 0.2	38.5	32.9 ± 0.1	56.5	92.2
9	59.7 ± 0.8	18.7 ± 0.2	31.3	14.9 ± 0.3	24.9	24.2 ± 0.2	40.5	67.9

10	60.2 ± 0.8	19.9 ± 0.4	33.1	17.7 ± 0.2	29.4	29.8 ± 1	47.5	78.9
11	70.1 ± 1	27.7 ± 0.1	39.5	21.1 ± 0.3	30.1	34.7 ± 0.3	55.8	79.6
12	43.7 ± 0.6	17.8 ± 0.2	40.7	15.3 ± 0.1	35.1	19.6 ± 0.2	34.9	79.7
13	69.6 ± 0.8	27.4 ± 0.1	39.4	22.3 ± 0.6	32.0	38.6 ± 0.1	60.9	87.5
14	36.3 ± 0.4	16.2 ± 0.4	44.6	13.4 ± 0.4	36.9	16.6 ± 0.2	32.8	90.4
15	47.8 ± 0.5	16.6 ± 0.3	34.7	14.4 ± 0.2	30.1	22.1 ± 0.4	36.5	76.4

% BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

H28: Total content, stage related bioaccessible and residual fractions of copper (Cu) in urban dust of Edinburgh

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	226 ± 3	118 ± 2	52.2	92.1 ± 0.3	40.8	122 ± 2	214	94.7
2	224 ± 2	103 ± 1	45.9	87.9 ± 0.2	39.2	117 ± 3	205	91.5
3	235 ±3	121 ± 2	51.5	89.7 ± 0.1	38.2	129 ± 4	219	93.1
4	107 ± 0.9	44.8 ± 1	41.8	33.7 ± 0.2	31.5	53.7 ± 0.4	87.4	81.6
5	91.9 ± 1	35.8 ± 0.2	38.9	30.6 ± 0.1	33.3	41.1 ± 0.2	71.7	78.1
6	82.6 ± 1	31.6 ± 0.1	38.3	26.7 ± 0.3	32.3	38.6 ± 0.1	65.3	79.1
7	124 ± 1	43.6 ± 0.4	35.2	33.8 ± 0.1	27.3	55.1 ± 0.2	88.9	71.7
8	219 ± 1	104 ± 3	47.5	86.4 ± 1	39.5	123 ± 2	209	95.6
9	95.5 ± 1	39.2 ± 2	41.1	29.6 ± 1	30.9	51.3 ± 2	80.9	84.7

10	161 ± 2	65.7 ± 2	40.8	54.7 ± 2	33.9	75.6 ± 1	130	80.9
11	221 ± 3	111 ± 4	50.2	87.5± 2	39.6	122 ± 2	210	94.7
12	97.9 ± 1	34.2 ± 1	34.9	26.8 ± 1	27.5	42.3 ± 2	69.1	70.6
13	227 ± 2	97.8 ± 1	43.1	78.9 ± 2	34.8	116 ± 3	195	85.8
14	80.5 ± 1	40.9 ± 2	50.8	32.8 ± 3	40.7	38.7 ± 1	71.5	88.8
15	125 ± 2	52.1 ± 2	41.7	40.1 ± 3	32.1	64.6 ± 2	105	83.8

% BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

H29: Total content, stage related bioaccessible and residual fractions of manganese (Mn) in urban dust of Edinburgh

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	526 ± 18	237 ± 4	45.1	219 ± 11	41.6	301 ± 17	520	98.8
2	425 ± 10	231 ± 4	54.4	176 ± 6	41.1	254 ± 3	430	101
3	492 ± 14	237 ± 3	48.2	167 ± 10	33.9	285 ± 6	452	91.9
4	753 ± 10	272 ± 6	36.1	226 ± 8	30.0	441 ± 12	667	88.6
5	356 ± 6	145 ± 4	40.7	117 ± 6	32.8	180 ± 6	297	83.4
6	427 ± 14	218 ± 12	51.1	179 ± 8	41.9	242 ± 11	421	98.6
7	407 ± 8	202 ± 6	49.6	142 ± 5	34.9	230 ± 4	372	91.4
8	415 ± 7	165 ± 2	39.8	131 ± 3	31.6	229 ± 3	360	86.7
9	465 ± 17	234 ± 7	50.3	126 ± 6	27.1	289 ± 9	415	89.2

10	402 ± 7	164 ± 6	40.7	116 ± 4	28.9	239 ± 5	356	88.5
11	441 ± 13	205 ± 11	46.5	138 ± 9	31.3	284 ± 3	422	95.7
12	718 ± 18	221 ± 4	30.8	162 ± 8	22.6	378 ± 10	540	75.2
13	435 ± 8	174 ± 8	40.0	123 ± 3	28.3	271 ± 4	394	90.2
14	487 ± 10	143 ± 4	29.4	118 ± 2	24.2	264 ± 7	382	78.4
15	371 ± 5	148 ± 3	39.9	120 ± 4	32.3	178 ± 4	298	80.3

% BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

H30: Total content, stage related bioaccessible and residual fractions of nickel (Ni) in urban dust of Edinburgh

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	40.8 ± 0.5	14.2 ± 0.1	38.8	12.1 ± 0.4	29.7	17.8 ± 0.2	29.9	73.3
2	28.7 ± 0.3	11.6 ± 0.3	40.4	8.95 ± 0.1	31.1	15.6 ± 0.4	24.6	85.7
3	30.5 ± 0.5	10.1 ± 0.1	33.1	7.89 ± 0.3	25.9	14.4 ± 0.2	22.3	73.1
4	29.8 ± 0.3	9.56 ± 0.3	32.1	8.03 ± 0.2	26.9	13.4 ± 0.1	21.4	71.9
5	24.1 ± 0.4	10.3 ± 0.1	42.7	7.12 ± 0.4	29.5	14.3 ± 0.1	21.4	88.9
6	27.1 ± 0.3	11.1 ± 0.4	40.9	9.15 ± 0.2	33.8	13.3 ± 0.9	22.4	82.7
7	29.6 ± 0.4	12.2 ± 0.5	41.2	10.4 ± 0.3	35.1	15.7 ± 0.1	26.1	88.2
8	34.1 ± 0.3	14.3 ± 0.1	41.9	10.9 ± 0.2	31.9	19.5 ± 0.4	30.4	89.1
9	28.5 ± 0.2	11.9 ± 0.3	41.8	8.72 ± 0.2	30.6	13.2 ±0.1	21.9	76.9

10	32.2 ± 0.3	12.9 ± 0.3	40.1	10.2 ± 0.5	31.7	14.7 ± 1	24.9	77.3
11	28.6 ± 0.4	13.1 ± 0.1	45.8	11.3 ± 0.2	39.5	16.4 ± 0.3	27.7	96.9
12	24.6 ± 0.3	9.11 ± 0.5	37.0	7.54 ± 0.1	30.6	11.4 ± 0.1	18.9	76.9
13	28.1 ± 0.4	11.3 ± 0.2	40.2	9.32 ± 0.3	33.2	13.7 ± 0.2	23.1	81.9
14	18.9 ± 0.3	7.48 ± 0.1	39.6	5.33 ± 0.1	28.2	8.85 ± 0.2	14.2	75.1
15	30.9 ± 0.3	12.4 ± 0.2	40.1	9.33 ± 0.3	30.2	16.3 ± 0.2	25.6	82.9

% BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

H31: Total content, stage related bioaccessible and residual fractions of lead (Pb) in urban dust of Edinburgh

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	341 ± 2	150 ± 4	43.9	123 ± 1	36.1	173 ± 3	296	86.8
2	249 ± 7	119 ± 1	47.5	87.9 ± 2	35.3	143 ± 1	231	92.7
3	299 ± 2	135 ± 3	45.2	107 ± 2	35.8	139 ± 3	246	82.2
4	368 ± 1	143 ± 1	38.9	122 ± 3	33.2	154 ± 2	276	75.0
5	775 ± 3	337 ± 4	43.5	283 ± 1	36.5	342 ± 6	625	80.6
6	222 ± 1	103 ± 5	46.4	89.6 ± 0.1	40.4	114 ± 3	204	91.7
7	215 ± 0.6	121 ± 4	56.3	101 ± 0.8	46.9	113 ± 1	214	99.5
8	760 ± 2	361 ± 4	47.5	341 ± 8	44.9	378 ± 2	719	94.6
9	1273 ± 16	617 ± 12	48.5	584 ± 10	45.9	643 ± 21	1227	96.4

10	305 ± 2	136 ± 1	44.6	108 ± 2	35.4	156 ± 2	264	86.6
11	309 ± 2	158 ± 2	51.1	127 ± 7	41.1	172 ± 3	299	96.8
12	222 ± 1	106 ± 1	47.7	89.7 ± 0.7	40.4	119 ± 1	209	94.0
13	1012 ± 6	513 ± 3	50.7	423 ± 3	41.8	571 ± 8	994	98.2
14	76.4 ± 1	29.5 ± 0.2	38.6	21.1 ± 0.1	27.6	39.6 ± 0.7	60.7	79.5
15	214 ± 2	97.2 ± 1	45.4	72.5 ± 1	33.9	121 ± 2	194	90.4

% BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

H32: Total content, stage related bioaccessible and residual fractions of zinc (Zn) in urban dust of Edinburgh

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	1119 ± 19	488 ± 7	43.6	376 ± 20	33.6	543 ± 9	919	82.1
2	415 ± 8	223 ± 6	53.7	166 ± 3	40.1	251 ± 5	417	100
3	742 ± 18	276 ± 8	37.2	243 ± 7	32.7	445 ± 15	688	92.7
4	542 ± 5	282 ± 4	52.1	211 ± 13	38.9	301 ± 9	512	94.5
5	389 ± 5	153 ± 1	39.3	136 ± 3	34.9	176 ± 2	312	80.2
6	236 ± 6	109 ± 2	46.2	98.7 ± 1	41.8	126 ± 3	225	95.2
7	545 ± 7	234 ± 6	42.9	202 ±10	37.1	281 ± 6	483	88.6
8	563 ± 6	225 ± 7	39.9	189 ± 6	33.6	251 ± 10	440	78.2
9	640 ± 8	321 ± 12	50.2	290 ± 8	45.3	343 ± 11	633	98.9

10	368 ± 5	151 ± 6	41.0	134 ± 2	36.4	164 ± 2	298	80.9
11	502 ± 10	238 ± 2	47.4	207 ± 5	41.2	243 ± 5	450	89.6
12	422 ± 5	196 ± 4	46.4	167 ± 1	39.6	241 ± 4	408	96.7
13	529 ± 6	243 ± 5	45.9	211 ± 4	39.9	287 ± 10	498	94.1
14	263 ± 4	104 ± 2	39.5	81.4 ± 1	30.9	128 ± 4	209	79.6
15	350 ± 4	164 ± 3	46.9	149 ± 8	42.6	186 ± 3	335	95.7

% BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

H33: Total content Pseudo-total, stage related bioaccessible and residual fractions of arsenic (As) in urban dust of Sunderland

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	5.62 ± 0.1	1.76 ± 0.3	31.3	1.23 ± 0.5	21.9	2.04 ± 0.1	3.27	58.2
2	5.03 ± 0.2	1.89 ± 0.1	37.6	1.56 ± 0.4	31.0	2.32 ± 0.3	3.88	77.1
3	4.31 ± 0.8	1.64 ± 0.2	38.1	1.21 ± 0.1	28.1	1.96 ± 0.3	3.17	73.5
4	5.71 ± 0.1	2.42 ± 0.1	42.4	1.73 ± 0.3	30.3	2.64 ± 0.1	4.37	76.5
5	6.07 ± 0.2	2.84 ± 0.2	46.8	2.12 ± 0.5	34.9	3.14 ± 0.5	5.26	86.7
6	6.44 ± 0.2	2.63 ± 0.2	40.8	2.24 ± 0.1	34.8	3.14 ± 0.3	5.38	83.5
7	4.76 ± 0.2	1.96 ± 0.3	41.2	1.54 ± 0.1	32.4	2.31 ± 0.3	3.85	80.9
8	5.81 ± 0.1	2.34 ± 0.1	40.3	1.69 ± 0.5	29.1	2.47 ± 0.1	4.16	71.6
9	4.61 ± 0.2	2.21 ± 0.2	47.9	1.46 ± 0.1	31.7	2.32 ± 0.2	3.78	81.9

10	5.51 ± 0.1	1.83 ± 0.5	33.2	1.28 ± 0.1	23.2	2.27 ± 0.3	3.55	64.4
11	6.58 ± 0.2	2.65 ± 0.2	40.3	2.19 ± 0.3	33.3	3.32 ± 0.1	5.51	83.6
12	5.95 ± 0.2	2.21 ± 0.1	37.1	1.68 ± 0.1	28.2	2.34 ± 0.3	4.02	67.6
13	4.79 ± 0.1	1.86 ± 0.2	38.9	1.35 ± 0.1	28.2	2.17 ± 0.1	3.52	73.5
14	5.94 ± 0.1	2.21 ± 0.1	37.2	1.89 ± 0.1	31.8	2.61 ± 0.3	45.0	75.8
15	5.51 ± 0.1	2.34 ± 0.3	42.5	1.77 ± 0.2	32.1	2.34 ± 0.1	4.11	74.6

% BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

H34: Total content, stage related bioaccessible and residual fractions of cadmium (Cd) in urban dust of Sunderland

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	0.701 ± 0.02	0.287 ± 0.01	40.9	0.243 ± 0.03	34.7	0.331 ± 0.1	0.574	81.9
2	0.354 ± 0.02	ND	ND	ND	ND	ND	ND	ND
3	0.284 ± 0.01	ND	ND	ND	ND	ND	ND	ND
4	0.422 ± 0.01	ND	ND	ND	ND	ND	ND	ND
5	0.906 ± 0.5	0.345 ± 0.02	38.1	0.305 ± 0.01	33.7	0.412 ± 0.02	0.717	79.1
6	0.572 ± 0.02	0.342 ± 0.02	59.8	0.221 ± 0.01	38.7	0.312 ± 0.01	0.533	93.2
7	0.541 ± 0.03	0.212 ± 0.02	39.2	0.186 ± 0.03	34.4	0.231 ± 0.02	0.417	77.1
8	0.605 ± 0.03	0.243 ± 0.03	40.2	0.196 ± 0.01	32.4	0.316 ± 0.02	0.512	84.6
9	0.406 ± 0.01	ND	ND	ND	ND	ND	ND	ND
10	0.471 ± 0.01	ND	ND	ND	ND	ND	ND	ND

11	0.433 ± 0.02	ND	ND	ND	ND	ND	ND	ND
12	0.581 ± 0.03	ND	ND	ND	ND	ND	ND	ND
13	0.342 ± 0.01	ND	ND	ND	ND	ND	ND	ND
14	0.621 ± 0.02	0.292 ± 0.01	47.0	0.234 ± 0.03	37.7	0.374 ± 0.01	0.608	97.9
15	0.342 ± 0.01	ND	ND	ND	ND	ND	ND	ND

% BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

ND: Not detected

H35: Total content, stage related bioaccessible and residual fractions of chromium (Cr) in urban dust of Sunderland

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	41.9 ± 0.6	18.3 ± 0.5	43.7	13.3 ± 0.6	31.7	19.4 ± 0.1	32.7	78.1
2	67.7 ± 0.8	32.1 ± 0.3	47.4	26.3 ± 0.2	38.8	36.3 ± 0.4	62.6	92.5
3	44.5 ± 0.6	21.7 ± 0.2	48.9	17.9 ± 0.1	40.2	23.4 ± 0.1	41.3	92.8
4	83.1 ± 0.4	33.7 ± 0.1	40.6	24.7 ± 0.2	29.7	48.9 ± 0.3	73.6	88.6
5	13.5 ± 0.3	4.11 ± 0.3	30.4	3.12 ± 0.1	23.1	5.14 ± 0.1	8.26	61.2
6	73.1 ± 0.7	31.8 ± 0.1	43.5	28.9 ± 0.3	39.5	41.1 ± 0.2	70.0	95.8
7	19.6 ± 0.5	7.13 ± 0.2	36.4	6.77 ± 0.2	34.5	8.21 ± 0.1	14.9	76.4
8	53.9 ± 0.6	19.3 ± 0.3	35.8	15.6 ± 0.1	28.9	26.6 ± 0.4	42.2	78.7
9	35.9 ± 0.4	10.2 ± 0.2	28.4	13.7 ± 0.4	38.2	19.4 ± 0.3	33.1	92.2

10	67.5 ± 0.8	24.7 ± 0.1	36.6	19.2 ± 0.3	28.4	30.3 ± 0.3	49.5	73.3
11	64.3 ± 0.9	21.1 ± 0.3	32.9	18.7 ± 0.1	29.1	24.7 ± 0.1	43.4	67.5
12	62.1 ± 0.8	19.4 ± 0.6	31.2	14.2 ± 0.2	22.9	31.1 ± 0.2	45.3	72.9
13	37.3 ± 0.8	16.2 ± 0.1	43.4	11.3 ± 0.1	30.3	17.4 ± 0.1	28.7	76.9
14	40.9 ± 0.6	16.7 ± 0.3	40.8	13.3 ± 0.2	32.5	18.4 ± 0.3	31.7	77.5
15	35.5 ± 0.7	16.4 ± 0.1	46.2	11.9 ± 0.3	33.5	17.7 ± 0.2	29.6	83.4

% BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

H36: Total content, stage related bioaccessible and residual fractions of copper (Cu) in urban dust of Sunderland

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	207 ± 1	96.2 ± 2	46.5	67.4 ± 2	32.6	123 ± 2	190	91.9
2	194 ± 2	102 ± 1	52.6	72.8 ± 1	37.5	116 ± 3	189	97.3
3	115 ± 2	63.1 ± 2	54.9	38.5 ± 2	33.5	71.8 ± 2	110	95.9
4	226 ± 0.4	86.4 ± 1	38.2	61.7 ± 2	27.3	103 ± 1	165	72.9
5	74.4 ± 1	30.2 ± 0.3	40.6	25.3 ± 1	34.0	32.9 ± 0.3	58.2	78.2
6	172 ± 0.4	76.9 ± 0.1	44.7	54.6 ± 0.5	31.7	81.7 ± 1	136	79.2
7	72.5 ± 0.6	32.5 ± 0.6	44.8	28.7 ± 0.1	39.6	37.1 ± 0.2	65.8	90.8

8	169 ± 1	76.9 ± 0.1	45.5	51.4 ± 0.5	30.4	85.7 ± 2	137	81.1
9	71.5 ± 1	29.4 ± 0.1	41.1	23.8 ± 0.6	33.2	34.7 ± 1	58.5	81.8
10	192 ± 2	64.2 ± 2	33.4	56.9 ± 0.2	29.6	85.7 ± 2	143	74.3
11	174 ± 1	74.9 ± 1	43.0	54.8 ± 1	31.5	87.9 ± 0.2	143	82.0
12	242 ± 4	87.2 ± 2	36.0	65.8 ± 3	27.2	126 ± 3	192	79.3
13	80.7 ± 0.7	31.8 ± 0.6	39.4	23.6 ± 0.1	29.2	43.2 ± 0.2	66.8	82.8
14	124 ± 1	53.8 ± 0.1	43.4	43.8 ± 0.4	35.3	62.1 ± 0.4	106	85.4
15	117 ± 1	46.3 ± 1	39.6	37.9 ± 0.2	32.4	57.3 ± 2	95.2	81.4

% BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

H37: Total content, stage related bioaccessible and residual fractions of manganese (Mn) in urban dust of Sunderland

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	476 ± 9	234 ± 5	49.2	173 ± 3	36.3	284 ± 7	457	96.0
2	457 ± 8	231 ± 3	50.1	183 ± 7	40.1	247 ± 11	430	94.1
3	399 ± 6	187 ± 3	46.9	164 ± 2	41.1	204 ± 9	368	92.2
4	649 ± 17	232 ± 13	35.7	217 ± 7	33.4	346 ± 11	563	86.7
5	434 ± 7	218 ± 2	50.2	173 ±2	39.7	224 ± 1	397	91.5
6	599 ± 9	287 ± 4	47.9	241 ± 4	40.2	321 ± 6	562	93.8
7	382 ± 6	189 ± 4	49.5	152 ±3	39.8	217 ± 8	369	96.6
8	435 ± 8	202 ± 5	46.4	178 ± 3	40.0	234 ± 6	412	94.7
9	325 ± 8	163 ± 6	50.2	143 ± 4	44.0	173 ± 6	316	97.2

10	456 ± 8	253 ± 2	55.5	176 ± 8	38.6	279 ± 11	455	99.7
11	493 ± 7	183 ± 6	37.1	147 ± 2	29.8	220 ± 4	367	74.4
12	452 ± 8	218 ± 7	48.2	136 ± 3	30.1	279 ± 7	415	91.8
13	491 ± 7	246 ± 6	50.1	209 ± 9	42.6	260 ± 7	469	95.5
14	455 ± 8	189 ± 10	41.5	157 ± 3	34.5	216 ± 6	373	81.9
15	448 ± 11	234 ± 5	52.2	155 ± 9	34.6	272 ± 6	427	95.3

% BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

H38: Total content, stage related bioaccessible and residual fractions of nickel (Ni) in urban dust of Sunderland

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	22.1 ± 0.3	9.74 ± 0.1	44.1	6.23 ± 0.4	28.1	12.8 ± 0.1	19.0	86.1
2	29.6 ± 0.2	14.6 ± 0.3	49.3	10.6 ± 0.1	35.8	17.1 ± 0.6	27.7	93.6
3	17.3 ± 0.3	7.13 ± 0.2	41.2	6.14 ± 0.6	35.5	7.95 ± 0.3	14.1	81.4
4	33.7 ± 0.1	15.6 ± 0.1	46.3	13.8 ± 0.2	40.9	17.6 ± 0.7	31.4	93.2
5	25.1 ± 0.3	11.6 ± 0.3	46.2	9.87 ± 0.6	39.3	13.7 ± 0.1	23.4	93.2
6	29.7 ± 0.3	13.3 ± 0.1	44.9	11.5 ± 0.1	38.7	15.6 ± 0.3	27.1	90.9
7	22.9 ± 0.2	10.7 ± 0.2	46.7	8.76 ± 0.5	38.3	12.3 ± 0.3	21.1	91.9
8	24.3 ± 0.1	10.3 ± 0.1	42.4	9.83 ± 0.1	40.6	13.6 ± 0.2	23.4	96.4
9	19.2 ± 0.3	7.43 ± 0.1	38.7	5.98 ± 0.5	31.1	8.21 ± 0.3	14.19	73.9

10	27.5 ± 0.3	14.1 ± 0.2	51.3	12.8 ± 0.3	46.5	15.7 ± 0.4	28.5	103
11	29.7 ± 0.5	11.5 ±0.5	38.7	9.86 ± 0.3	33.1	13.7 ± 0.1	23.6	79.3
12	24.1 ± 0.5	11.2 ± 0.2	46.5	9.67 ± 0.1	40.1	12.9 ± 0.2	22.6	93.7
13	14.1 ± 0.3	6.41 ± 0.3	45.5	4.75 ± 0.4	33.7	7.33 ± 0.4	12.1	85.7
14	26.1 ± 0.4	11.8 ±0.3	45.2	9.23 ± 0.1	35.4	13.6 ± 0.2	22.8	87.5
15	22.7 ± 0.4	10.1 ± 0.1	44.5	9.23 ± 0.2	40.7	12.6 ± 0.1	21.8	96.2

% BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

H39: Total content, stage related bioaccessible and residual fractions of lead (Pb) in urban dust of Sunderland

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	199 ± 1	98.7 ± 1	49.6	76.2 ± 1	38.3	121 ± 2	192	99.1
2	146 ± 1	63.1 ± 2	43.2	54.6 ±	37.4	83.3 ± 2	138	94.5
3	368 ± 3	143 ± 4	38.9	127 ± 2	34.5	172 ± 1	299	81.3
4	147 ± 2	76.8 ± 1	52.2	55.4 ± 1	37.7	74.1 ± 2	130	88.1
5	167 ± 1	68.3 ± 2	40.8	46.2 ± 2	27.7	87.2 ± 1	133	79.8
6	145 ± 0.9	61.1 ± 0.1	42.1	46.3 ± 1	31.9	74.4 ± 0.1	121	83.2
7	179 ± 1	83.1 ± 0.2	46.4	69.3 ± 0.6	38.7	91.4 ± 2	161	89.8
8	2228 ± 16	895 ± 12	40.2	687 ± 9	30.8	1211 ± 20	1900	85.3
9	88.3 ± 0.6	45.4 ± 0.2	51.4	35.8 ± 1	40.1	42.3 ± 0.2	78.1	88.3

10	226 ± 1	89.3 ± 2	39.5	76.3 ± 0.3	33.8	124 ± 1	200	88.6
11	222 ± 1	104 ± 1	46.8	88.3 ± 0.1	39.8	118 ± 2	206	92.9
12	338 ± 3	145 ± 2	42.9	118 ± 1	34.9	168 ± 4	286	84.6
13	138 ± 0.8	67.3 ± 1	48.8	54.3 ± 0.4	39.3	75.8 ± 0.1	130	94.3
14	1374 ± 10	674 ± 3	49.1	465 ± 11	33.8	762 ± 8	1227	89.3
15	135 ± 0.3	67.8 ± 2	50.2	46.4 ± 4	34.3	76.9 ± 0.2	123	91.3

% BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

H40: Total content, stage related bioaccessible and residual fractions of zinc (Zn) in urban dust of Sunderland

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	1369 ± 18	543 ± 11	39.7	430 ± 7	31.4	762 ± 17	1192	87.1
2	636 ± 7	263 ± 5	41.4	193 ± 4	30.3	345 ± 6	538	84.6
3	327 ± 4	128 ± 3	39.1	104 ± 1	31.8	164 ± 3	268	81.9
4	803 ± 7	442 ± 2	55.1	342 ± 10	42.6	452 ± 6	794	98.9
5	379 ± 3	162 ± 7	42.7	129 ± 3	34.0	189 ± 3	318	83.9
6	921 ± 10	321 ± 3	34.9	263 ± 7	28.6	486 ± 5	749	81.3
7	649 ± 9	284 ± 3	43.6	237 ± 2	83.5	349 ± 4	586	90.3
8	2726 ± 33	1186 ± 21	43.5	956 ± 11	35.1	1397 ± 27	2353	86.3
9	385 ± 6	173 ± 3	44.9	141 ± 6	36.6	164 ± 2	305	79.2

10	514 ± 6	208 ± 6	40.5	176 ± 2	34.2	234 ± 3	410	79.8
11	479 ± 4	218 ± 2	45.5	182 ± 4	37.9	241 ± 2	423	88.3
12	339 ± 5	154 ± 4	45.4	137 ± 2	40.4	167 ± 3	304	89.7
13	212 ± 2	98.5 ± 1	46.5	84.6 ± 2	39.9	117 ± 2	202	95.1
14	498 ± 5	221 ± 4	44.4	203 ± 6	40.8	248 ± 3	451	90.6
15	374 ± 6	154 ± 3	41.2	132 ± 2	35.3	169 ± 2	301	80.5

% BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

H41: Total content, stage related bioaccessible and residual fractions of arsenic (As) in urban dust of Abakaliki, Nigeria

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	4.22 ± 0.2	1.84 ± 0.3	43.6	1.42 ± 0.2	33.6	2.13 ± 0.1	3.55	84.1
2	5.07 ± 0.3	2.45 ± 0.1	48.3	1.84 ± 0.3	36.3	2.87 ± 0.2	4.71	92.7
3	4.29 ± 0.3	2.04 ± 0.2	47.6	1.61 ± 0.2	37.5	2.31 ± 0.3	3.92	91.3
4	3.63 ± 0.2	1.16 ± 0.1	31.9	1.01 ± 0.5	27.8	1.25 ± 0.2	2.26	62.3
5	4.88 ± 0.3	2.23 ± 0.3	45.7	1.87 ± 0.2	38.7	2.52 ± 0.1	4.39	89.9
6	4.97 ± 0.2	2.11 ± 0.7	42.5	1.76 ± 0.3	35.4	2.47 ± 0.3	4.23	85.1
7	3.59 ± 0.3	1.34 ± 0.2	37.3	1.03 ± 0.1	28.7	1.43 ± 0.1	2.46	68.5
8	3.89 ± 0.2	1.39 ± 0.1	35.7	1.12 ± 0.2	28.8	1.63 ± 0.2	2.75	70.7
9	15.3 ± 0.6	7.94 ± 0.1	51.9	5.13 ± 0.1	33.5	9.28 ± 1	14.4	94.2

10	4.39 ± 0.1	2.18 ± 0.1	49.7	1.68 ± 0.5	38.3	2.26 ± 0.1	3.94	89.7
11	4.81 ± 0.2	2.01 ± 0.4	41.8	1.56 ± 0.1	32.4	2.27 ± 0.3	3.83	79.6
12	3.66 ± 0.2	1.38 ± 0.2	37.7	1.16 ± 0.4	31.7	1.85 ± 0.2	3.01	82.2
13	4.43 ± 0.4	2.17 ± 0.2	48.9	1.75 ± 0.3	39.5	2.31 ± 0.1	4.06	91.6
14	7.12 ± 0.4	2.74 ± 0.4	38.5	2.31 ± 0.1	32.4	3.32 ± 0.3	5.63	79.1
15	7.27 ± 0.5	3.68 ± 0.2	50.6	3.01 ± 0.4	41.4	4.11 ± 1	7.12	97.9

% BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

H42: Total content, stage related bioaccessible and residual fractions of cadmium (Cd) in urban dust of Abakaliki, Nigeria

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	0.371 ± 0.01	ND	ND	ND	ND	ND	ND	ND
2	0.532 ± 0.02	0.221 ± 0.02	41.5	0.181 ± 0.02	34.0	0.231 ± 0.01	0.412	77.4
3	0.471 ± 0.03	ND	ND	ND	ND	ND	ND	ND
4	0.293 ± 0.01	ND	ND	ND	ND	ND	ND	ND
5	ND	ND	ND	ND	ND	ND	ND	ND
6	0.839 ± 0.02	0.386 ± 0.02	46.0	0.345 ± 0.01	41.1	0.421 ± 0.02	0.766	91.3
7	1.36 ± 0.02	0.536 ± 0.04	39.4	0.362 ± 0.01	26.6	0.712 ± 0.01	1.07	78.9
8	0.955 ± 0.01	0.425 ± 0.01	44.5	0.328 ± 0.02	34.3	0.489 ± 0.05	0.817	85.5
9	0.491 ± 0.02	ND	ND	ND	ND	ND	ND	ND
10	0.422 ± 0.03	ND	ND	ND	ND	ND	ND	ND

11	0.288 ± 0.01	ND	ND	ND	ND	ND	ND	ND
12	0.325 ± 0.01	ND	ND	ND	ND	ND	ND	ND
13	ND	ND	ND	ND	ND	ND	ND	ND
14	0.533 ± 0.01	0.217 ± 0.2	40.7	0.165 ± 0.2	30.9	0.233 ± 0.01	0.398	74.7
15	0.463 ± 0.01	ND	ND	ND	ND	ND	ND	ND

% BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

ND: Not detected.

H43: Total content, stage related bioaccessible and residual fractions of chromium (Cr) in urban dust of Abakaliki, Nigeria

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	166 ± 6	87.3 ± 1	52.6	43.1 ± 0.2	25.9	114 ± 0.3	157	94.6
2	128 ± 5	64.3 ± 3	50.2	47.2 ± 0.1	36.9	83.1 ± 0.1	110	86.2
3	172 ± 6	108 ± 4	62.8	51.1 ± 2	29.7	120 ± 3	171	99.4
4	164 ± 4	89.4 ±3	54.5	59.4 ± 1	36.2	93.6 ± 3	153	93.3
5	154 ± 5	61.3 ± 5	39.8	51.9 ± 2	33.7	75.8 ± 1	128	82.9
6	93.5 ± 3	41.2 ± 3	44.1	32.4 ± 1	34.7	53.2 ± 0.3	85.6	91.6
7	77.4 ± 3	31.5 ± 0.1	40.7	27.4 ± 0.3	35.4	38.3 ± 0.2	65.7	84.9
8	81.2 ± 2	39.3 ± 0.2	48.4	30.5 ± 1	37.6	48.3 ± 0.1	78.8	97.0
9	104 ± 3	52.2 ± 2	50.1	37.8 ± 3	36.3	61.4 ± 4	99.2	05.4

10	101 ± 4	46.4 ± 2	45.9	33.2 ± 2	32.9	50.3 ± 2	83.5	82.7
11	127 ± 3	51.6 ± 1	40.6	41.6 ± 3	32.8	63.8 ± 2	105	82.9
12	110 ± 3	53.7 ± 4	48.8	39.7 ± 0.2	36.1	60.4 ± 3	100	91.0
13	130 ± 2	58.4 ± 3	44.9	43.5 ± 3	33.5	72.1 ± 1	116	88.9
14	90.6 ± 3	30.6 ± 1	66.9	27.8 ± 0.6	30.6	38.9 ± 2	66.7	73.6
15	66.8 ± 3	28.3 ± 0.5	42.4	23.8 ± 0.1	35.6	31.3 ± 3	55.1	82.4

% BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

H44: Total content, stage related bioaccessible and residual fractions of copper (Cu) in urban dust of Abakaliki, Nigeria

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	39.3 ± 1	17.4 ± 0.1	44.3	12.8 ± 0.7	32.6	21.5 ± 0.2	34.3	87.3
2	45.7 ± 0.9	18.2 ± 0.4	39.8	15.3 ± 0.1	33.5	25.3 ± 0.3	40.6	88.8
3	38.4 ± 0.9	16.7 ± 0.1	43.5	13.5 ± 0.3	35.2	19.4 ± 2	32.9	85.7
4	37.6 ± 1	15.8 ± 0.3	42.0	14.7 ± 0.2	39.1	20.6 ± 0.3	35.3	93.9
5	28.3 ± 0.4	12.3 ± 0.1	43.5	10.2 ± 0.3	36.0	17.6 ± 0.1	27.8	98.2
6	75.9 ± 1	32.1 ± 1	42.3	26.3 ± 0.1	34.7	40.3 ± 2	66.6	87.7
7	42.5 ± 0.7	19.7 ± 0.3	46.4	15.6 ± 0.4	36.7	24.7 ± 0.1	40.3	94.8
8	86.6 ± 0.7	40.1 ± 2	46.3	34.3 ± 0.2	39.6	46.9 ± 3	81.2	93.8
9	67.7 ± 0.4	35.6 ± 2	52.6	26.8 ± 1	39.6	38.5 ± 0.1	65.3	96.5

10	50.6 ± 0.6	21.8 ± 1	43.1	17.6 ± 0.3	34.8	28.9 ± 2	46.5	91.9
11	45.6 ± 0.5	16.6 ± 0.1	36.4	14.3 ± 0.4	31.4	24.9 ± 0.2	39.2	85.9
12	31.8 ± 0.3	14.2 ± 0.3	44.7	10.3 ± 0.5	32.4	18.3 ± 0.2	28.6	89.9
13	25.4 ± 0.3	10.4 ± 0.1	40.9	8.54 ± 0.1	33.6	13.7 ± 0.1	22.2	87.6
14	39.7 ± 1	17.8 ± 0.2	44.8	13.4 ± 0.4	33.7	22.5 ± 0.1	35.9	90.4
15	27.6 ± 0.4	10.7 ± 0.1	38.8	8.71 ± 0.1	31.6	14.1 ± 0.3	22.8	82.6

% BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

H45: Total content, stage related bioaccessible and residual fractions of manganese (Mn) in urban dust of Abakaliki, Nigeria

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	1003 ± 45	387 ± 4	38.6	323 ± 10	32.2	480 ± 19	803	80.1
2	945 ± 63	537 ± 11	56.8	353 ± 15	37.4	584 ± 28	937	99.1
3	1218 ± 68	538 ± 23	44.2	422 ± 12	34.6	715 ± 33	1137	93.3
4	873 ± 40	375 ± 9	42.9	284 ± 6	32.5	489 ± 21	773	88.5
5	492 ± 30	176 ± 7	35.8	143 ± 3	29.1	220 ± 8	363	73.8
6	640 ± 39	241 ± 6	37.7	203 ± 4	31.7	353 ± 8	556	86.9
7	770 ± 48	285 ± 7	37.0	221 ± 10	28.7	403 ± 6	624	81.1
8	596 ± 32	276 ± 5	46.3	217 ± 7	36.4	324 ± 7	541	90.8

9	1389 ± 87	532 ± 12	38.3	421 ± 8	30.3	643 ± 24	1064	76.6
10	648 ± 42	322 ± 6	49.7	236 ± 4	36.4	374 ± 6	610	94.1
11	758 ± 44	321 ± 4	42.3	285 ± 3	37.6	368 ± 4	653	86.1
12	514 ± 31	236 ± 5	45.9	186 ± 8	36.1	287 ± 6	473	92.0
13	503 ± 28	234 ±3	46.5	215 ± 4	42.3	279 ± 3	494	98.2
14	569 ± 39	264 ± 5	46.4	217 ± 3	38.1	303 ± 7	520	91.4
15	397 ± 26	184 ± 3	46.3	143 ± 2	36.0	216 ± 3	359	90.4

% BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

H46: **Total content, stage related bioaccessible and residual fractions of nickel (Ni) in urban dust of Abakaliki, Nigeria**

Sites	Pseudo-total (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	46.7 ± 1	21.6 ± 2	46.3	17.9 ± 1	38.3	24.2 ± 1	42.1	90.1
2	52.7 ± 1	23.1 ± 0.3	43.8	19.3 ± 0.3	36.6	30.6 ± 0.3	49.9	94.6
3	52.3 ± 2	21.3 ± 1	40.7	16.3 ± 0.2	31.2	26.8 ± 0.1	43.1	82.4
4	41.5 ± 0.8	18.3 ± 0.3	44.1	15.7 ± 1	37.8	23.4 ± 2	39.1	94.2
5	38.8 ± 0.9	16.2 ± 0.1	41.8	13.5 ± 0.4	34.8	20.3 ± 1	33.8	87.1
6	39.4 ± 0.8	17.3 ± 0.2	43.9	14.7 ± 0.1	37.3	22.8 ± 0.2	37.5	95.2
7	38.4 ± 0.7	15.7 ± 1	40.9	13.3 ± 0.1	34.6	18.4 ± 0.1	31.7	82.6
8	38.9 ± 0.8	18.7 ± 1	48.1	13.6 ± 0.4	34.9	21.3 ± 0.3	34.9	89.7
9	40.1 ± 0.8	19.2 ± 0.3	47.9	15.6 ± 0.1	38.9	21.5 ± 0.2	37.1	92.5

10	43.1 ± 1	18.3 ± 0.2	42.5	14.7 ± 0.3	34.1	26.1 ± 0.6	40.8	94.7
11	51.6 ± 1	21.3 ± 0.4	41.3	15.1 ± 0.2	29.3	34.2 ± 0.1	49.3	95.5
12	28.1 ± 0.3	12.7 ± 0.1	45.2	10.4 ± 0.5	37.0	15.7 ± 0.2	26.1	92.9
13	37.2 ± 0.6	18.9 ± 1	50.8	14.7 ± 2	39.5	20.5 ± 2	35.2	94.6
14	31.1 ± 0.7	12.6 ± 0.3	40.5	9.09 ± 0.4	29.2	17.6 ± 0.3	26.7	85.8
15	22.3 ± 0.6	10.6 ± 0.6	47.5	7.11 ± 0.1	31.9	13.4 ± 0.8	20.5	91.9

% BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

H47: Total content, stage related bioaccessible and residual fractions of lead (Pb) in urban dust of Abakaliki, Nigeria

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	114 ± 0.6	58.7 ± 2	51.5	43.7 ± 1	38.3	67.3 ± 1	111	97.3
2	236 ± 1	104 ± 3	44.1	98.3 ± 0.5	41.7	126 ± 2	224	95.0
3	112 ± 0.5	48.4 ± 2	43.2	38.7 ± 0.2	34.6	56.2 ± 1	94.9	84.7
4	92.8 ± 0.3	47.8 ± 2	50.6	36.3 ± 0.2	39.1	51.2 ± 2	87.5	94.3
5	98.1 ± 0.6	37.9 ± 0.1	38.6	28.4 ± 0.2	28.9	46.3 ± 1	74.7	76.1
6	338 ± 1	123 ± 2	36.4	110 ± 1	32.5	162 ± 2	272	80.5
7	1815 ± 11	785 ± 23	43.3	624 ± 9	34.4	983 ± 11	1607	88.5
8	925 ± 3	361 ± 4	39.0	332 ± 3	35.9	463 ± 6	795	85.9
9	121 ± 0.3	62.8 ±5	51.9	51.2 ± 2	42.3	63.7 ± 2	115	94.9

10	318 ± 2	134 ± 3	42.1	117 ± 1	36.7	151 ± 2	268	84.3
11	65.9 ± 0.3	30.4 ± 1	46.1	26.8 ± 2	40.7	36.8 ± 1	63.6	96.5
12	113 ± 0.2	46.7 ± 2	41.3	34.6 ± 0.3	30.6	61.2 ± 2	95.8	84.8
13	63.5 ± 0.1	23.4 ± 0.2	36.9	21.3 ± 0.1	33.5	27.4 ± 0.2	48.7	76.7
14	129 ± 0.3	31.6 ± 0.1	24.5	46.2 ± 0.2	35.8	61.6 ± 0.1	108	83.6
15	55.5 ± 0.2	20.4 ± 0.4	37.8	17.8 ± 0.1	32.1	22.4 ± 0.3	40.2	72.4

% BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

H48: Total content, stage related bioaccessible and residual fractions of zinc (Zn) in urban dust of Abakaliki, Nigeria

Sites	Total content (mg/kg)	In-vitro gastro-intestinal extraction, mg/kg						
		Stage I (Gastric digest)		Stage II (Gastric + Intestinal digest)		Stage III (Residual digest)	Total PTE content II + III	
	Mean ± SD ; (n = 3)	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	% BAF	Mean ± SD ; (n = 3)	Mean (n = 3)	% Total Recovery
1	137 ± 5	44.6 ± 2	32.6	38.6 ± 1	28.2	70.1 ± 1	109	79.3
2	192 ± 7	76.9 ± 4	40.0	57.8 ± 3	30.1	102 ± 4	160	83.2
3	226 ± 8	77.3 ± 2	34.2	55.8 ± 2	24.7	128 ± 3	184	81.3
4	142 ± 5	47.8 ± 3	33.7	38.9 ± 1	27.4	76.9 ± 2	116	81.5
5	73.3 ± 2	32.6 ± 0.1	44.5	28.8 ± 0.4	39.3	40.1 ± 0.4	68.9	93.9
6	356 ± 11	126 ± 3	35.4	107 ± 0.3	30.1	186 ± 5	293	82.3
7	434 ± 13	186 ± 4	42.9	151 ± 3	34.8	235 ± 6	286	88.9
8	244 ± 6	118 ± 4	48.4	95.4 ±2	39.1	130 ±2	225	92.3
9	210 ± 6	86.8 ± 1	41.3	72.2 ± 3	34.4	122 ± 2	184	92.5

10	188 ± 6	73.4 ± 1	39.0	59.4 ± 3	31.6	97.4 ± 2	157	83.4
11	199 ± 6	102 ± 4	51.3	65.3 ± 4	32.8	121 ± 3	186	93.6
12	107 ± 2	50.5 ± 2	45.6	31.4 ± 2	29.3	52.7 ± 2	84.1	78.6
13	69.1 ± 2	28.6 ± 1	41.4	23.7 ± 2	34.3	32.1 ± 2	55.8	80.8
14	177 ± 6	68.6 ± 3	38.8	53.8 ± 1	30.4	89.6 ± 2	143	81.0
15	134 ± 0.4	65.7 ± 2	49.0	52.1 ± 2	38.8	76.2 ± 3	128	95.7

% BAF = $\frac{C_{Bioaccessibility}}{C_{total\ content}} \times 100$

Where $C_{Bioaccessibility}$ – PTE concentration (mg/kg) in urban dust samples obtained via the application of physiologically based extraction test and $C_{total\ content}$ -PTE total content (mg/kg) in urban dust samples obtained via microwave digestion protocol.

% Total Recovery: total recovery fraction calculated as a fraction of the total concentration.

Appendix I

I1: Correlation analysis – Concentration phase (Newcastle upon Tyne)

Elements	Correlation value	P-value	Stage (mg /kg)
Cr	0.929	0.000	T & G
	0.943	0.000	T &GI
	0.993	0.000	G & GI
Mn	0.555	0.032	T & G
	0.752	0.001	T &GI
	0.812	0.000	G & GI
Ni	0.999	0.000	T & G
	1.000	0.000	T &GI
	0.999	0.000	G & GI
Cu	0.939	0.000	T & G
	0.984	0.000	T &GI
	0.923	0.000	G & GI
Zn	0.995	0.000	T & G
	0.934	0.000	T &GI
	0.954	0.000	G & GI
As	0.774	0.001	T & G
	0.607	0.016	T &GI
	0.772	0.001	G & GI
Cd	0.995	0.061	T & G
	0.994	0.067	T &GI
	0.945	0.061	G & GI
Pb	0.983	0.000	T & G
	0.958	0.000	T &GI
	0.961	0.000	G & GI

T = Total concentration, G = Gastric phase, GI = gastric + intestine

I2: Correlation analysis - % BAF phase (Newcastle upon Tyne)

Elements	Correlation value	P-value	Stage (% BAF)
Cr	0.154	0.583	T & G
	0.340	0.215	T &GI
	0.917	0.000	G & GI
Mn	-0.012	0.967	T & G
	0.342	0.212	T &GI
	0.655	0.008	G & GI
Ni	-0.550	0.034	T & G
	-0.476	0.073	T &GI
	0.973	0.000	G & GI
Cu	-0.174	0.534	T & G
	-0.111	0.693	T &GI
	0.957	0.000	G & GI
Zn	0.237	0.394	T & G
	0.141	0.616	T &GI
	0.826	0.00	G & GI
As	-0.093	0.741	T & G
	-0.175	0.534	T &GI
	0.639	0.010	G & GI
Cd	0.519	0.653	T & G
	0.983	0.116	T &GI
	0.355	0.769	G & GI
Pb	-0.167	0.553	T & G
	-0.418	0.121	T &GI
	0.874	0.000	G & GI

T = Total concentration, G = Gastric phase, GI = gastric + intestine

I3: Correlation analysis – Concentration phase (Durham)

Elements	Correlation value	P-value	Stage (mg /kg)
Cr	0.929	0.000	T & G
	0.924	0.000	T &GI
	0.945	0.000	G & GI
Mn	0.773	0.001	T & G
	0.572	0.026	T &GI
	0.882	0.000	G & GI
Ni	0.944	0.000	T & G
	0.962	0.000	T &GI
	0.943	0.000	G & GI
Cu	0.990	0.000	T & G
	0.984	0.000	T &GI
	0.954	0.000	G & GI
Zn	0.961	0.000	T & G
	0.962	0.000	T &GI
	0.952	0.000	G & GI
As	0.875	0.000	T & G
	0.886	0.000	T &GI
	0.936	0.000	G & GI
Cd	0.979	0.004	T & G
	0.982	0.003	T &GI
	0.976	0.001	G & GI
Pb	0.990	0.000	T & G
	0.989	0.000	T &GI
	0.993	0.000	G & GI

T = Total concentration, G = Gastric phase, GI = gastric + intestine

I4: Correlation analysis - % BAF phase (Durham)

Elements	Correlation value	P-value	Stage (% BAF)
Cr	0.139	0.622	T & G
	0.115	0.684	T &GI
	0.943	0.000	G & GI
Mn	-0.380	0.163	T & G
	-0.359	0.189	T &GI
	0.888	0.000	G & GI
Ni	-0.589	0.021	T & G
	0.361	0.186	T &GI
	0.054	0.848	G & GI
Cu	0.424	0.115	T & G
	0.223	0.425	T &GI
	0.443	0.098	G & GI
Zn	-0.048	0.866	T & G
	0.273	0.325	T &GI
	0.903	0.000	G & GI
As	0.393	0.147	T & G
	0.397	0.143	T &GI
	0.674	0.006	G & GI
Cd	-0.607	0.278	T & G
	-0.644	0.241	T &GI
	0.992	0.001	G & GI
Pb	-0.246	0.377	T & G
	-0.120	0.669	T &GI
	0.914	0.000	G & GI

T = Total concentration, G = Gastric phase, GI = gastric + intestine

I5: Correlation analysis – Concentration phase (Liverpool)

Elements	Correlation value	P-value	Stage (mg /kg)
Cr	0.936	0.000	T & G
	0.948	0.000	T &GI
	0.374	0.170	G & GI
Mn	0.975	0.001	T & G
	0.983	0.026	T &GI
	0.968	0.000	G & GI
Ni	0.963	0.000	T & G
	0.967	0.000	T &GI
	0.982	0.000	G & GI
Cu	0.999	0.000	T & G
	0.998	0.000	T &GI
	1.000	0.000	G & GI
Zn	0.986	0.000	T & G
	0.986	0.000	T &GI
	0.990	0.000	G & GI
As	0.866	0.000	T & G
	0.634	0.011	T &GI
	0.849	0.000	G & GI
Cd	0.973	0.000	T & G
	0.974	0.003	T &GI
	0.990	0.000	G & GI
Pb	0.975	0.000	T & G
	0.964	0.000	T &GI
	0.992	0.000	G & GI

T = Total concentration, G = Gastric phase, GI = gastric + intestine

I6: Correlation analysis - % BAF phase (Liverpool)

Elements	Correlation value	P-value	Stage (% BAF)
Cr	0.523	0.032	T & G
	0.424	0.000	T &GI
	0.760	0.012	G & GI
Mn	-0.160	0.569	T & G
	-0.520	0.047	T &GI
	0.284	0.305	G & GI
Ni	0.269	0.332	T & G
	0.502	0.057	T &GI
	0.860	0.041	G & GI
Cu	-0.092	0.745	T & G
	0.030	0.915	T &GI
	0.688	0.005	G & GI
Zn	0.199	0.476	T & G
	-0.072	0.799	T &GI
	0.700	0.004	G & GI
As	-0.273	0.325	T & G
	-0.377	0.167	T &GI
	0.797	0.000	G & GI
Cd	-0.521	0.230	T & G
	-0.633	0.127	T &GI
	0.786	0.036	G & GI
Pb	-0.031	0.914	T & G
	-0.019	0.947	T &GI
	0.853	0.000	G & GI

T = Total concentration, G = Gastric phase, GI = gastric + intestine

I7: Correlation analysis – Concentration phase (Edinburgh)

Elements	Correlation value	P-value	Stage (mg /kg)
Cr	0.848	0.000	T & G
	0.862	0.000	T &GI
	0.801	0.100	G & GI
Mn	0.637	0.011	T & G
	0.783	0.026	T &GI
	0.668	0.000	G & GI
Ni	0.822	0.000	T & G
	0.772	0.000	T &GI
	0.862	0.000	G & GI
Cu	0.981	0.000	T & G
	0.952	0.000	T &GI
	0.964	0.000	G & GI
Zn	0.964	0.000	T & G
	0.921	0.000	T &GI
	0.945	0.000	G & GI
As	0.882	0.000	T & G
	0.712	0.000	T &GI
	0.810	0.000	G & GI
Cd	0.943	0.000	T & G
	0.988	0.001	T &GI
	0.961	0.000	G & GI
Pb	0.995	0.000	T & G
	0.990	0.000	T &GI
	0.992	0.000	G & GI

T = Total concentration, G = Gastric phase, GI = gastric + intestine

I8: Correlation analysis - % BAF phase (Edinburgh)

Elements	Correlation value	P-value	Stage (% BAF)
Cr	0.150	0.593	T & G
	-0.151	0.590	T &GI
	0.049	0.862	G & GI
Mn	-0.454	0.089	T & G
	0.021	0.001	T &GI
	0.736	0.002	G & GI
Ni	-0.087	0.757	T & G
	0.035	0.901	T &GI
	0.772	0.001	G & GI
Cu	0.631	0.012	T & G
	0.630	0.012	T &GI
	0.937	0.000	G & GI
Zn	-0.072	0.799	T & G
	-0.234	0.401	T &GI
	0.779	0.001	G & GI
As	0.266	0.338	T & G
	-0.121	0.666	T &GI
	0.868	0.000	G & GI
Cd	-0.574	0.178	T & G
	-0.623	0.135	T &GI
	0.715	0.071	G & GI
Pb	0.207	0.459	T & G
	0.521	0.046	T &GI
	0.838	0.000	G & GI

T = Total concentration, G = Gastric phase, GI = gastric + intestine

I9: Correlation analysis – Concentration phase (Sunderland)

Elements	Correlation value	P-value	Stage (mg /kg)
Cr	0.742	0.000	T & G
	0.861	0.000	T &GI
	0.602	0.100	G & GI
Mn	0.537	0.011	T & G
	0.781	0.026	T &GI
	0.560	0.000	G & GI
Ni	0.632	0.000	T & G
	0.871	0.000	T &GI
	0.888	0.000	G & GI
Cu	0.990	0.000	T & G
	0.911	0.000	T &GI
	0.921	0.000	G & GI
Zn	0.946	0.000	T & G
	0.809	0.000	T &GI
	0.945	0.000	G & GI
As	0.882	0.000	T & G
	0.712	0.000	T &GI
	0.810	0.000	G & GI
Cd	0.862	0.000	T & G
	0.851	0.001	T &GI
	0.653	0.000	G & GI
Pb	0.991	0.000	T & G
	0.998	0.000	T &GI
	0.991	0.000	G & GI

T = Total concentration, G = Gastric phase, GI = gastric + intestine

I10: Correlation analysis - % BAF phase (Sunderland)

Elements	Correlation value	P-value	Stage (% BAF)
Cr	0.188	0.502	T & G
	0.069	0.807	T &GI
	0.567	0.028	G & GI
Mn	-0.506	0.055	T & G
	-0.382	0.160	T &GI
	0.548	0.034	G & GI
Ni	0.305	0.270	T & G
	0.396	0.144	T &GI
	0.592	0.020	G & GI
Cu	-0.124	0.660	T & G
	-0.513	0.050	T &GI
	0.596	0.019	G & GI
Zn	-0.238	0.394	T & G
	-0.408	0.131	T &GI
	0.640	0.010	G & GI
As	-0.043	0.880	T & G
	0.264	0.343	T &GI
	0.780	0.001	G & GI
Cd	-0.472	0.687	T & G
	-0.545	0.633	T &GI
	0.996	0.054	G & GI
Pb	-0.175	0.532	T & G
	-0.385	0.157	T &GI
	0.640	0.010	G & GI

T = Total concentration, G = Gastric phase, GI = gastric + intestine

I11: Correlation analysis – Concentration phase (Abakaliki)

Elements	Correlation value	P-value	Stage (mg /kg)
Cr	0.812	0.000	T & G
	0.923	0.000	T &GI
	0.711	0.100	G & GI
Mn	0.642	0.011	T & G
	0.722	0.026	T &GI
	0.632	0.000	G & GI
Ni	0.763	0.000	T & G
	0.772	0.000	T &GI
	0.812	0.000	G & GI
Cu	0.962	0.000	T & G
	0.928	0.000	T &GI
	0.812	0.000	G & GI
Zn	0.972	0.000	T & G
	0.912	0.000	T &GI
	0.912	0.000	G & GI
As	0.855	0.000	T & G
	0.773	0.000	T &GI
	0.923	0.000	G & GI
Cd	0.732	0.000	T & G
	0.831	0.001	T &GI
	0.789	0.000	G & GI
Pb	0.991	0.000	T & G
	0.998	0.000	T &GI
	0.991	0.000	G & GI

T = Total concentration, G = Gastric phase, GI = gastric + intestine

I12: Correlation analysis - % BAF phase (Abakaliki)

Elements	Correlation value	P-value	Stage (% BAF)
Cr	0.288	0.299	T & G
	-0.491	0.063	T &GI
	-0.405	0.134	G & GI
Mn	-0.140	0.620	T & G
	-0.349	0.202	T &GI
	0.749	0.001	G & GI
Ni	0.231	0.023	T & G
	0.365	0.124	T &GI
	0.153	0.084	G & GI
Cu	0.408	0.131	T & G
	0.535	0.040	T &GI
	0.673	0.006	G & GI
Zn	-0.523	0.001	T & G
	-0.321	0.100	T &GI
	0.023	0.431	G & GI
As	0.489	0.065	T & G
	0.129	0.646	T &GI
	0.853	0.000	G & GI
Cd	-1.000	0.003	T & G
	-0.963	0.175	T &GI
	0.964	0.171	G & GI
Pb	-0.015	0.958	T & G
	-0.074	0.793	T &GI
	0.552	0.033	G & GI

T = Total concentration, G = Gastric phase, GI = gastric + intestine

Appendix J

J1: T test analysis of Newcastle upon Tyne dust samples

Elements	Concentration stage (G & GI)		% BAF stage (G & GI)	
	T-value	P-value	T-value	P-value
Cr	1.227	0.229	3.770	0.0008
Mn	3.956	0.0006	5.115	0.00003
Ni	0.119	0.905	2.265	0.0313
Cu	0.288	0.775	1.117	0.274
Zn	0.325	0.747	1.785	0.085
As	2.00	0.054	2.420	0.022
Cd	1.038	0.408	2.829	0.216
Pb	0.695	0.493	3.243	0.003

G = Gastric phase, GI = gastric + intestine.

J2: T test analysis of Durham dust samples

Elements	Concentration stage (G & GI)		% BAF stage (G & GI)	
	T-value	P-value	T-value	P-value
Cr	0.735	0.468	1.854	0.074
Mn	2.341	0.026	2.815	0.008
Ni	1.351	0.187	4.823	0.0005
Cu	0.588	0.561	0.687	0.501
Zn	0.367	0.716	2.043	0.051
As	2.135	0.042	4.621	0.0001
Cd	0.666	0.514	1.281	0.218
Pb	0.286	0.776	2.961	0.006

G = Gastric phase, GI = gastric + intestine

J3: T test analysis of Liverpool dust samples

Elements	Concentration stage (G & GI)		% BAF stage (G & GI)	
	T-value	P-value	T-value	P-value
Cr	0.929	0.360	2.223	0.035
Mn	1.401	0.174	4.479	0.0002
Ni	0.827	0.415	3.113	0.004
Cu	0.246	0.807	2.933	0.006
Zn	0.471	0.641	2.953	0.006
As	2.314	0.029	3.487	0.0016
Cd	0.798	0.441	2.777	0.016
Pb	0.896	0.378	4.375	0.0002

G = Gastric phase, GI = gastric + intestine

J4: T test analysis of Edinburgh dust samples

Elements	Concentration stage (G & GI)		% BAF stage (G & GI)	
	T-value	P-value	T-value	P-value
Cr	1.059	0.299	1.674	0.106
Mn	3.489	0.001	4.386	0.0001
Ni	3.519	0.001	6.820	0.0002
Cu	1.226	0.231	4.609	0.0008
Zn	1.162	0.255	4.160	0.0003
As	2.531	0.017	5.031	0.0005
Cd	3.489	0.002	7.151	0.0002
Pb	0.497	0.622	4.467	0.0001

G = Gastric phase, GI = gastric + intestine

J5: T test analysis of Sunderland dust samples

Elements	Concentration stage (G & GI)		% BAF stage (G & GI)	
	T-value	P-value	T-value	P-value
Cr	1.251	0.222	3.184	0.003
Mn	3.904	0.0005	5.450	0.0009
Ni	1.893	0.068	5.093	0.0002
Cu	2.098	0.046	6.139	0.0002
Zn	0.628	0.535	1.237	0.232
As	4.120	0.0003	6.454	0.00006
Cd	1.344	0.227	1.779	0.173
Pb	0.526	0.603	6.551	0.0005

G = Gastric phase, GI = gastric + intestine

J6: T test analysis of Abakaliki dust samples

Elements	Concentration stage (G & GI)		% BAF stage (G & GI)	
	T-value	P-value	T-value	P-value
Cr	2.574	0.018	6.819	0.0002
Mn	1.767	0.089	5.152	0.0001
Ni	2.933	0.006	7.806	0.0002
Cu	1.268	0.215	6.908	0.0002
Zn	1.228	0.229	4.695	0.0007
As	1.114	0.276	4.704	0.0008
Cd	2.261	0.152	2.004	0.139
Pb	0.288	0.775	2.880	0.008

G = Gastric phase, GI = gastric + intestine

Appendix K

% Pb recovery at varying time interval

hours	Pb recovery (%)
0	0
0.5	13.6
1	13.7
2	14.4
3	15.1
4	15.8
5	16.1
6	16.5
10	17.4
12	18.1
24	20.1
48	23.5
60	25.2
70	26.3
80	27.4
96	28.6
170	28.1

Appendix L

Lead in urban dust samples (<10 µm): total content, bioaccessible concentrations, % (BAF), residual digest, total residual and % total recovery.

Sample	Total content (mg/kg)	*In-vitro* epithelial lung fluid extraction extraction (mg/kg)				
		Stage I (Bioaccessible Pb)		Stage II (Residual digest)	Total Pb content (Stage I + II)	
	Mean ± SD; (n = 3)	Mean ± SD; (n = 2)	% BAF	Mean ± SD; (n = 2)	Mean (n = 2)	% Total Recovery
N1	1778 ± 22	20.9 ± 0.5	1.18	1690 ± 10	1711	96.2
N2	1766 ± 17	28.7 ± 1	1.62	1702 ± 22	1731	98.0
N3	772 ± 1	25.1 ± 0.1	3.24	685 ± 9	710	92.0
N4	1627 ± 16	37.4 ± 0.2	2.30	1584 ± 16	1621	99.7
D1	1279 ± 19	40.4 ± 0.3	3.16	1152 ± 6	1192	93.2
D2	846 ± 3	57.2 ± 0.6	6.76	684 ± 11	741	87.6
D3	2435 ± 13	112 ± 1	4.60	2218 ± 7	2330	95.7
D4	534 ± 8	31.7 ± 0.2	5.94	472 ± 4	504	94.3

L1	837 ± 6	24.7 ± 0.1	2.95	719 ± 3	744	88.9
L2	646 ± 4	56.5 ± 0.2	8.75	533 ± 9	590	91.3
L3	1408 ± 9	65.9 ± 0.4	4.68	1291 ± 12	1357	96.4
L4	495 ± 5	16.1 ± 0.8	3.25	451 ± 2	467	94.4
L5	452 ± 5	38.2 ± 0.4	8.45	398 ± 6	436	96.5
E1	472 ± 4	36.1 ± 0.1	7.65	421 ± 3	457	96.8
E2	586 ± 5	19.2 ± 1	3.29	537 ± 5	556	94.9
E3	1082 ± 14	39.4 ± 0.8	3.64	1028 ± 17	1067	98.7
E4	486 ± 15	27.3 ± 1	5.62	435 ± 3	462	95.1
E5	1248 ± 45	60.8 ± 2	4.87	1174 ± 29	1235	98.9
S1	2357 ± 22	37.1 ± 0.6	1.57	2309 ± 19	2346	99.5
S2	535 ± 20	22.7 ± 0.1	4.24	487 ± 3	510	95.3
S3	2073 ± 42	28.7 ± 0.4	1.38	1984 ± 6	2013	97.1
A1	2002 ± 6	30.2 ± 0.1	1.51	1879 ± 5	1909	95.4
A2	1138 ± 5	24.3 ± 0.6	2.14	1094 ± 12	1118	98.3

N = Newcastle sampled sites; D = Durham sampled sites; L = Liverpool sampled sites; E = Edinburgh sampled sites; S = Sunderland sampled sites; A = Abakaliki sampled sites

% BAF: stage related bioaccessibility, calculated as a function of the pseudo-total;

% Residual: residual fraction calculated as a function of the pseudo-total.

Appendix M

Total Pb content in air-borne dust

Sampled date	Sample name	Pb level (µg/g) for 100 hrs	Pb level (µg/g) for 24 hrs was obtained from 100hrs sampling
21/03/2011	A	462	111
21/03/2011	B	148	35.4
12/04/2011	C	135	32.5
12/04/2011	D	102	24.4
03/05/2011	E	21.9	5.26
03/05/2011	F	42.6	10.2
23/05/2011	G	63.9	15.3
23/05/2011	H	55.1	13.2
13/06/2011	I	78.2	18.8
13/06/2011	J	212	50.8
04/07/2011	K	42.3	10.2
04/07/2011	L	27.7	6.65
17/08/2011	M	23.7	5.69
17/08/2011	N	30.1	7.22
05/09/2011	O	12.0	2.88
05/09/2011	P	13.5	3.24
07/11/2011	Q	58.6	14.1
07/11/2011	R	447	107
28/11/2011	S	348	83.6
28/11/2011	T	1060	254
30/01/2012	U	52.2	12.5
30/01/2012	V	58.5	14.0
01/02/2012	W	7.2	1.73
01/02/2012	X	3.1	0.74
12/03/2012	Y	41.6	9.98
12/03/2012	Z	19.4	4.66