HEAVY METAL DISTRIBUTION IN WRIGLEY HEAD, MOSTON BROOK, GREATER MANCHESTER,

NORTHWEST ENGLAND: IMPLICATIONS FOR RISK ASSESSMENT AND REMEDIATION

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DEDICATION

To late dad and mum!

ABSTRACT

Heavy metal contaminated sites pose potential environmental and health problems and represent a great barrier to the beneficial use of contaminated sites. Therefore, the study of heavy metal contamination is a vital knowledge gap which, when filled, will facilitate development of sound management strategies to minimise the adverse environmental impacts and ensure remediation of contaminated sites. Within the context of a study site in Greater Manchester, UK, desk and laboratory studies were conducted to: (a) evaluate the relationship between XRF and aqua regia/ICP-OES derived heavy metal data, (b) investigate the multiple sources of historical heavy metal contamination, (c) investigate small-scale spatial variation in heavy metal contamination across the study site, (d) assess heavy metal uptake by different herbaceous plant species, and (e) make recommendations to overcome the barrier of heavy metal contamination at the site. The results indicated that there was a strong relationship between the concentrations of heavy metals yielded by XRF and aqua regia/ICP-OES techniques across the study site and suggest that XRF is a rapid, cost effective and preferred technique for determination of targeted elements from the investigated soils compared to conventional aqua regia/ICP-OES technique. XRF technique demonstrated the capacity to measure the targeted elements from the investigated soils in relatively shorter times compared to conventional aqua regia/ICP-OES technique. The desk study revealed that the site suffers from multiple historical contamination and forms a legacy of potential source of unknown contaminants. This represents a big barrier to overcoming the challenges occasioned by historical contamination across the site. The site was heavily contaminated by multiple heavy metals at levels above UK and EU tolerable limits. There was a high spatial variation in heavy metal contamination across the site with Football Ground having relatively higher heavy metal contamination compared to the soils elsewhere around Wrigley Head. Based on the site conditions and levels of contamination at the site, revegetation of the site with plants and surface capping were suggested as feasible remediation options for the site. The study conducted to examine the uptake of heavy metals by herbaceous plants growing across the site suggests that metal uptake by the investigated plants was highly variable, leading to identification of some hyper-accumulating plants from the site. The findings obtained from this study have implications for environmental risk assessment and remediation of Wrigley Head, Moston Brook.

CHAPTER ONE

Introduction

1.1 Background and Significance

A significant proportion of soil in industrialised countries contains excessive levels of potentially toxic elements and substances such as oils, tars, waste metals, organic compounds, gases and mining materials considered as pollutants above their corresponding natural background values due to the increased industrial and human activities associated with urban soils (Hijmans et al., 2005; Sun et al., 2010). Among the potential toxic elements, heavy metals are the most dangerous environmental contaminants due to their non-degradable nature, potential toxicity to biota, and capacity to accumulate at all trophic levels of a food chain (Tawari-Fufeyin & Egborge, 1998; Enuneku et al., 2013). Human activities such as mining, metal smelting, pesticides and fertilizer applications for agricultural production, solid waste dumping, and electroplating are the major drivers of environmental contamination by heavy metals (Ogundiran & Osibanjo, 2009; Vargas-Machuca et al., 2021; Ota et al., 2021). For more than 200 years from the middle of the 18th century, there were high levels of heavy metals entering the environment and causing significant adverse effects to human health and to other species (Jarup, 2003). Over the past few years, there have been increasing global and public health concerns related to environmental contamination caused by heavy metals (Tchounwou et al., 2012).

Areas contaminated by heavy metals pose potential environmental, safety and economic difficulties to communities and governments in a number of countries. For example, a land contamination report published by the United Kingdom’s Department for Environment, Food and Rural Affairs (DEFRA) showed the extent of the problem – more than 100,000 contaminated sites in England and Wales – and that remediation requirements – about 5 – 20% of these sites may require to be remediated to minimise unacceptable risks to the environment and human health (DEFRA, 2012). These contaminated sites represent a potential barrier to land development for different beneficial land uses. Many of these sites are contaminated by heavy metals with about 80 percent of all the identified sites believed to be contaminated by metals and metalloids in England and Wales (Environment Agency, 2009). Similarly, the Environment Agency (2016) report on contaminated land in England showed that since the Part 2A regime (a requirement of the Environmental Protection Act, 1990) came into force in 2000, local authorities have spent at least £32 million carrying out inspections on more than 11,000 sites, leading to identification of more than 511 contaminated sites posing unacceptable risks to human health and require remediation. The detailed investigations conducted on these sites revealed that the most common substances responsible for contamination are heavy metals such as arsenic, lead and benzo(a)pyrene (Environment Agency, 2016).

Industrial activities that lasted for a period of more than 200 years in the Greater Manchester have left a legacy of contamination. Wrigley Head, Moston Brook with a history of dye works, brick works, print works and waste disposal to landfills which took place between 18th and 19th centuries (Groundwork Oldham & Rochdale, 2008) is one such site. One of the significant problems associated with this site is that contamination activities had taken place prior to the enactment of Pollution Control Act in 1974, which makes it practically impossible to identify the original nature of various contaminants buried at the site. It is known that the site is contaminated with heavy metals (Groundwork Oldham & Rochdale, 2008) and this, in turn, represents a significant barrier to the use of the site and may prevent it from being used for various beneficial ways.

Management and clean-up of contaminated sites has been a subject of public debate due to scientific and technical challenges heavy metal contamination presents (Jiang et al., 2015). The high number of contaminated sites across the UK and the cost implications of remediating these sites are putting a heavy financial burden on government and businesses (DEFRA, 2012). Therefore, the study of heavy metal contamination at the site is crucial for developing sound management strategies to minimise the adverse environmental impacts and ensure the beneficial use of sites. Many techniques have been developed for analysing heavy metals which raises questions about their usefulness. Hence this study begins with a comparison of two commonly used techniques before reporting on a case study of a site contaminated by multiple sources of heavy metals. The findings obtained from the present study could be relevant to local authority, land managers, or decision makers in adopting and developing effective strategies to manage the invstigated site.

1.2 Research Aims, Objectives and Research Questions

The overall goal of this research is to develop understanding of the small-scale spatial distribution of heavy metals across a site subjected to multiple sources of historical heavy metal contamination, the barriers to future uses of such sites and remediation options.

The study begins with a comparison of XRF and Aqua regia/ICP-OES techniques (Aim 1) in order to establish the most appropriate technique for the study of a site subjected to multiple sources of historical heavy metal contamination prior to presenting that case study (Aims 2 – 5).

Evaluation of analytical techniques

Aim 1. To evaluate the relationship between XRF and Aqua regia/ICP-OES Techniques.

> **Objective 1.1:** To compare the relationship between XRF and Aqua regia/ICP-OES heavy metal concentrations yielded by the two techniques.
>
> *Research question 1: Are they any relationship between XRF and aqua regia/ICP-OES heavy metal data at the study site?*
>
> *Research question 2: What are the implications of these techniques in terms of determining heavy metals at the study site?*
>
> *Research question 3: What are the implications of these data with regards to environmental risk assessment at the study site?*

Case Study of a site with multiple sources of historical heavy metal contamination

Aim 2. Preliminary investigation of multiple sources of historical heavy metal contamination.

> **Objective 2.1** To gather information on Wrigley Head, Moston Brook from historical maps, previous site reports, and a site visit.
>
> *Research question 4: What was the historical use of the investigated site?*
>
> *Research question 5: What are the types of contamination at the site?*

Aim 3. To investigate small-scale spatial variation in heavy metals across a site with multiple sources of historical contamination.

> **Objective 3.1:** To determine heavy metal concentrations and spatial variation across Wrigley Head.
>
> *Research question 6: What is the current heavy metal contamination status of the study site?*

Research question 7: What are the environmental implications of heavy metal contamination in the study site?

Aim 4. To elucidate the uptake of heavy metals by different naturally occurring herbaceous plant species in the study area.

Objective 4.1: To examine the uptake of heavy metals by different naturally occurring herbaceous plant species in the study area and identify potential hyper-accumulating plants.
Research question 8: Are heavy metals being absorbed by herbaceous plant species across the study site? If yes, how much heavy metals are being absorbed by plants?

Research question 9: Do these herbaceous plants at the study site have potential for phytoremediation?

Aim 5. To establish proposals to overcome the barrier of heavy metal contamination in sites with a legacy of multiple sources of heavy metal contamination.
Objective 5.1 To set out possible heavy metal mitigation strategies to inform future use of Wrigley Head, Moston Brook

1.3 Structure of the Thesis Report

A flowchart showing thesis organisation and the relationship between each chapter is presented in Figure 1.0.

Chapter 1 is an introductory chapter that sets out the research context, background, and significance. In this chapter, the research aims, objectives, and various research questions derived from the research aims and objectives are set out, and finally, this chapter is concluded with a statement describing the structure of the thesis and a flowchart explaining the thesis organisation and relationship between each chapter.

Chapter 2 contains a broad synthesis and critical discussion of relevant literature covering issues regarding contaminated soils in the UK and EU, heavy metals in soil and the adverse effects of heavy metals on human health and plants. Contained in this chapter is a description of various analytical techniques for determining heavy metals from soil and plant samples, and which of these techniques is a preferred candidate for determining heavy metals in the present study. In section 2.6, there is a critical discussion on the UK Regulatory Framework for investigating contaminated land including a framework presented in form of flowchart that explains the summary of the contaminated land investigation processes in Fig. 2.3. In addition, there is also a critical discussion on the sites with multiple sources of historical contamination. Similarly, there is also a description on the processes involved in the uptake and transfer of heavy metal in soil and plants, and followed by a section detailing the barriers associated with contaminated land. The last section of this chapter contains a critical discussion on the selected remediation practices for the case study site and this chapter is concluded with a summary of the literature review.

Chapter 3 contains details of the research approach taken and of the research methods. There is a critical discussion of the research philosophy underpinning the methodology adopted and the overview of the research methods used in the present study. There is also an overview of the standard framework for investigating contaminated land set out in Fig. 2.2 and the details of the modifications to the standard site investigation model set out in Fig. 3.1 relevant to this study. Similarly, there is a diagram (Fig. 3.2) presented in the form of research flow chart that draws together the research aims, field and laboratory methods and explains how each aim is related. Details of the methods used to obtain data on the comparisons of XRF and Aqua regia/ICP-OES heavy metal are set out in section 3.4. The case study of Moston Brook is described including the rationale for site selection, details of the desk study, the field observations, and the details of the field and laboratory methods that took place. The chapter is concluded with a statement on the quality control and assurance procedures observed in the current study.

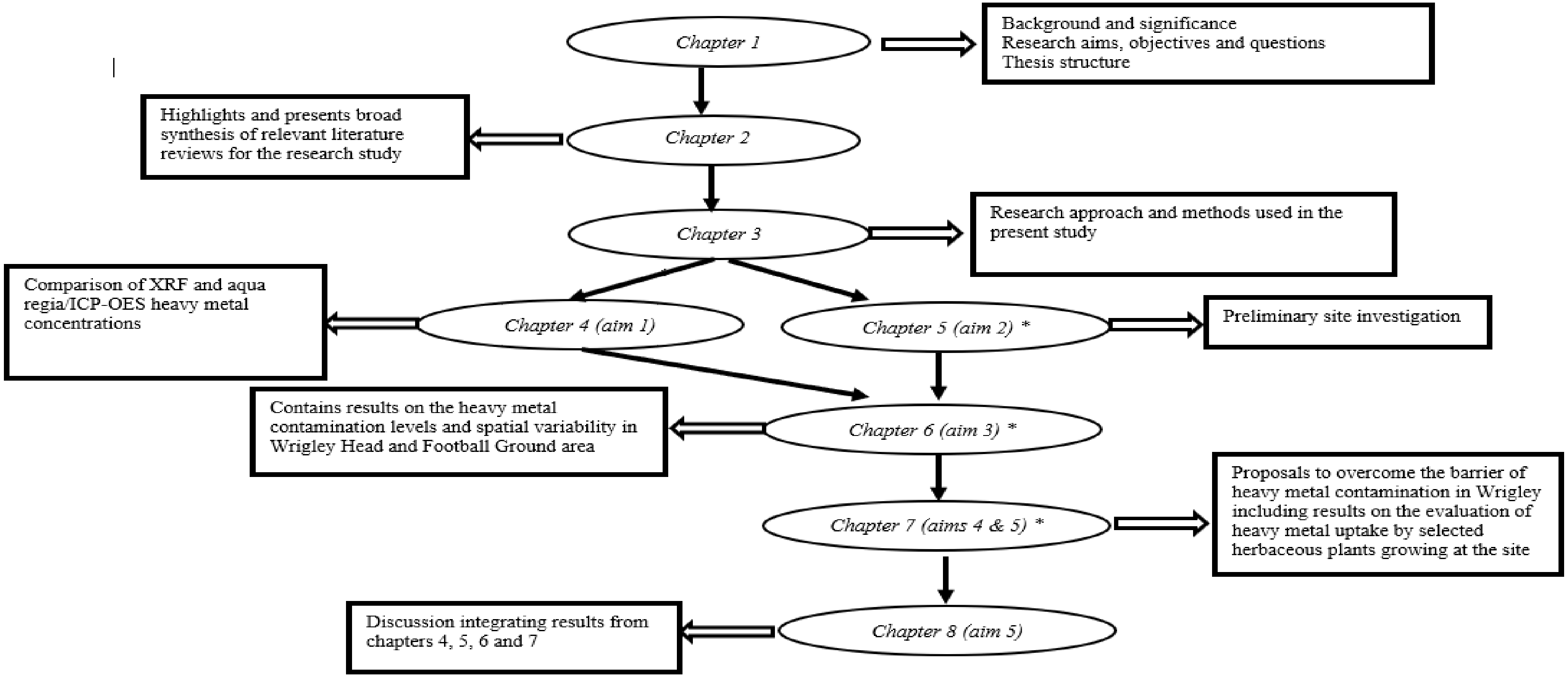
Chapter 4. In any site study, it is important to establish the appropriate analytical techniques for determining heavy metals in soil. In this instance both XRF and aqua regia/ICP-OES were used in the present study. The results obtained from these techniques can be strongly influenced by the methodology used or the exraction protocol implemented. Aqua regia digestion procedure determines the “pseudo-total concentrations” while XRF measures the total heavy metals from soil. Since this is the case, it is important to make a robust comparison to establish any relationship between the two techniques and/or differences in metal concentrations yielded by the two techniques and decide the better technique to use in the case study investigation. The goal addressed by the contents of this chapter was to compare the relationship between the concentrations of heavy metals yielded by the two analytical techniques and decide the appropriate technique for the case study investigation. The data in this chapter address aim 1 and research questions 1, 2 and 3. The main finding from this chapter shows that there is a strong relationship between XRF and aqua regia/ICP-OES heavy metal concentrations yielded by the two techniques. This relationship implies that the two techniques are good candidates for determining heavy metals from the investigated soils, however, XRF technique technically can effectively predict the targeted heavy metals from the investigated soils in a rapid, safe, and cost-effective manner compared to chemical methods such as aqua regia/ICP-OES. Therefore, XRF technique will be used in the research reported in the case study investigation reported in this thesis.

Chapter 5 – this is the first chapter reporting on the case study of Wrigley Head, Moston Brook a site with a legacy of multiple contamination sources. In this chapter, the findings from the preliminary study of Wrigley Head, based on historical maps, previous site reports, and a walk over visit, site photographs and desk study of site environmental context are presented. This chapter addresses aim 2 and research questions 4 and 5. The main findings that emerged from this chapter are that Wrigley Head was heavily contaminated by multiple contaminants from multiple historical industrial activities and that the contaminants are poorly reported. The lack of information on the nature and extent of contamination at the site is a major setback to overcoming the barriers occasioned by historical contamination at this and any similar site. The historical land uses of the site suggest that there may be a potential risk of contamination sources that may affect human and wildlife health.

Chapter 6 contains the results on the heavy metal contamination levels and spatial variability in Wrigley Head and Football Ground area. Contaminated sites often pose potential environmental, safety and represent a barrier to the beneficial use of contaminated land. Management and clean-up of heavy metal contaminated sites presents huge scientific and technical challenges due to heavy metals being potentially toxic and non-biodegradable and, thus present persistent challenges. Therefore, determining the levels of heavy metals at this and any other site is crucial for developing sound management strategies to minimise the potential adverse environmental impacts and to ensure the beneficial use of site. This chapter addresses Aim 3 and Research Questions 6 and 7. The main findings reported in this chapter suggest that the site is highly contaminated by heavy metals, and that, there is high spatial variations of heavy metals across the site. The concentrations of heavy metals obtained across the site were above the UK background and screening levels and EU tolerable limits for these regulated elements in soil – indicating the significant contributions of historical anthropogenic contamination across the site. The Football Ground area of the site – a bare area with near complete absence of vegetation – had relatively higher heavy metal concentrations compared to the soils elsewhere around Wrigley Head. The findings obtained have implications for site risk assessment, remediation and restoration.

Chapter 7 contains the results on the evaluation of mitigation scenarios for the contaminated land at Wrigley Head. Remediation options for overcoming the barrier of heavy metal contamination at the site are appraised. Included here are the results on the evaluation of heavy metal uptake by selected herbaceous plants growing at the site. This chapter addresses Aim 4 and Research Questions 8 and 9 and the overall recommendations for the site to address Aim 5. Knowledge of plant uptake of heavy metals is important for evaluating the potential of herbaceous plants for cleaning up of contaminated sites. The use of native plants is increasingly attracting significant research interest as a promising, cost-effective, and more practicable approach to clean up contaminated sites. The main findings from this chapter suggest that the uptake of heavy metals is highly variable among the investigated plants species. The findings also suggest that some investigated plant species may hold a promising potential for remediation of the historically investigated contaminated site. Overall, it is suggested that remediation options within the context of the site include revegetation with plants, blending/mixing the soil with soil amendment and surface capping.

Finally, *Chapter 8* is the discussion chapter that draws together and integrates results from chapters 4, 5, 6 and 7 to present the main findings, research implications, limitations of the current research and recommendations for future studies and ends with research contributions and conclusion.



*Chapters 5, 6 & 7 follow the modified site investigation scheme set out in Figure 3.1

Figure 1.0 A flowchart showing thesis organisation and relationship between each chapter

CHAPTER TWO

Literature Review

2.1 Contaminated Soil

Soil contamination is defined as the build-up in soils of toxic compounds, chemicals, salts, radioactive materials, or disease-causing agents beyond a certain threshold leading to the deterioration of natural, chemical, physical or biological soil properties, which have adverse effects on plant growth, human and animal health (Okrent, 1999). Soil contamination can be caused by a wide range of anthropogenic activities such as mining and smelting, combustion of fossil fuel, uncontrolled disposal of sewage and waste, fertiliser and pesticide application, traffic emissions, process and manufacturing industries, irrigation with contaminated water, waste incineration and other agricultural practices (Alloway, 1995; Kelly et al., 1996; Paterson et al., 1996; Mielke et al., 1999; De Kimpe & Morel, 2000; Wong et al., 2006; Poggio et al., 2009; Wei & Yang, 2010). Table 2.1 sets out the common examples of substances associated with a selected industrial activity.

Table 2.1. Some examples of common substances that may be derived from four industrial processes.

Industrial processes	**Potentially contaminating substances**
Oil refineries	These include substances such as cyanides, lubricating oil, fuel oil, organic acids, bitumen, alcohols, etc.
Lead works	These include substances such as cadmium sodium hydroxide, lead, arsenic, cadmium, sulphides, sulphates, chlorides, sulphuric acid, etc.
Textile and dye works	These include substances such as aluminium, cadmium, mercury, bromides, fluorides, ammonium salts, trichloroethene, polyvinyl chloride, etc.
Production of pesticides	These include substances such thallium dichloromethane, methanol, fluorobenzene, acetone, benzene, arsenic, copper sulphate, etc.

Source: Department of the Environment (1995)

Soils contaminated with various toxic elements pose a major environmental and human health risk across the world as well as having huge economic implications with respect to the cost of rehabilitation and restoration (Semenzin et al., 2007). It is not just the ex-industrial sites that may be contaminated; land that was previously located adjacent to the industrial, commercial, or agricultural activities may be affected by contamination coming from chemical substances and gas production from the ground (Public Health England [PHE], 2019).

The legacy of contamination is significant. A high proportion of soil in industrialised countries have been contaminated due to the industrial activities and have elevated levels of potentially toxic elements and compounds considered as pollutants above their corresponding natural background values (Hijmans et al., 2005; Sun et al., 2010). For example, in Europe, there is a widespread soil contamination due to over 200 years of industrialisation, which has created a legacy of contaminated sites. Mineral oil and heavy metals are the major contaminants accounting for up to 60% of soil contamination (Stolte et al., 2015). Presently, there are approximately 340,000 identified contaminated sites in Europe, only about 15 percent (51,000) of which have been remediated (Van Liedekerke et al., 2014) despite an estimated spending of six billion Euros (€6b) per year to put them into productive uses (Domínguez et al., 2009; Van Liedekerke et al., 2014). The high number of contaminated sites across Europe and the huge cost implications of remediating these sites are putting a heavy financial burden on governments and a search for more cost effective, economically, and sustainable remediation approach is being explored. For instance, in the 1980s, it was estimated that the cost of remediating all the identified contaminated sites in Holland would cost up to 50 billion Euros (Honders et al., 2003). By 1997, the Dutch government realised that the government was not financially sustainable to afford the cost of rehabilitating these sites, and consequently, adopted a more cost-effective risk-based management approach which is also practiced in the UK (CABERNET, 2003). The European Commission (EC) has also adopted a proposal for a Framework Directive (European Communities, 2006) that sets out common principles aimed at soil protection across the European.

2.2 Heavy Metals in Soil

The term “heavy metals” refer to a group of naturally occurring metallic elements that have relatively high density, atomic number or atomic mass and are toxic in low concentrations with atomic number greater than 20 (Ali & Khan, 2018). Metalloids are group of chemical elements that exhibit some properties of metals and some of non-metals (Dixon & Vasiliu, 2017). Examples of heavy metals and metalloids include arsenic, copper, manganese, zinc, cadmium, nickel, mercury, lead, cobalt, selenium, iron, molybdenum and chromium. Some of the heavy metals such as cobalt, manganese, iron, zinc, copper, nickel have been recognised to be essentially important for the normal growth, development and physiological functioning of the plants (Rascio & Navari-Izzo, 2011). These groups of metals are essentially required by plants for various biochemical processes; however, at excessive threshold levels, they become toxic to plants affecting their various physiological and biochemical functions (Kalinowska & Pawlik-Skowronska, 2010). On the other hand, heavy metals and metalloids such as arsenic, cadmium, mercury and lead have no biological roles in plant growth and metabolic processes and can be toxic even at the slightest concentrations (Rascio & Navari-Izzo, 2011). There is a group of elements referred as “priority heavy metal (loids)” due to their high level of toxicity and their implications on public health. These priority heavy metals and metalloids are shown in Table 2.2 contains.

Table 2.2. Priority Heavy Metals and Metalloids (Martin & Cowie, 2008).

Metal/metalloids	**Symbol**
Arsenic	As
Cadmium	Cd
Chromium	Cr
Copper	Cu
Lead	Pb
Mercury	Hg
Molybdenum	Mo
Nickel	Ni
Selenium	Se
Vanadium	V
Zinc	Zn

The origin of heavy metals in soil may be either natural from pedogenic sources or anthropogenic (Antoniadis et al., 2017). Naturally occurring soil-borne heavy metals are found mostly in soil parent materials in the form that is not available for uptake by plants (Bolan et al., 2014). The major contributor to pedogenic-associated heavy metals is weathering of soil parent materials, for example, igneous and sedimentary rocks. Both igneous and sedimentary rocks contain variable contents of heavy metals and metalloids particularly arsenic. A case in point is coal which is estimated to emit about 45,000 tons of arsenic yearly in comparison to anthropogenic activities that release about 50,000 tons of arsenic every year (Ferguson & Gavis, 1972; Mahimairaja et al., 2005). Compared with heavy metal originating from pedogenic sources, those from anthropogenic sources are more mobile and have higher bioavailability which makes them more available for uptake (Keeperman, 2000; Kaasalainen & Yli-Halla, 2003). Heavy metals in contaminated soil can originate from a variety of anthropogenic sources as shown in Figure 2.1.

Moreover, heavy metals can be released into the environment through atmospheric deposition because of acid rain (Nriagu, 1990). However, heavy metals emitted through anthropogenic processes have been found to be more available for uptake by various receptors in comparison to the naturally occurring heavy metals (Naidu & Bolan, 2008; Lamb et al., 2009). On the other hand, anthropogenic activities such as manufacturing, industrial activities, disposal of domestic and industrial waste materials, metal smelting, and irrigation with wastewater, fertilizer and pesticide applications have been directctly linked to be the major emitter of heavy metals in the environment (Bolan et al., 2014). Lasat (1999) reported that soil heavy metals can exist in different forms such as free metal ions; soluble metal complexes; metals bound to soil organic matter; metals bound to oxides, hydroxides, and carbonates and those found into silicate minerals structure.

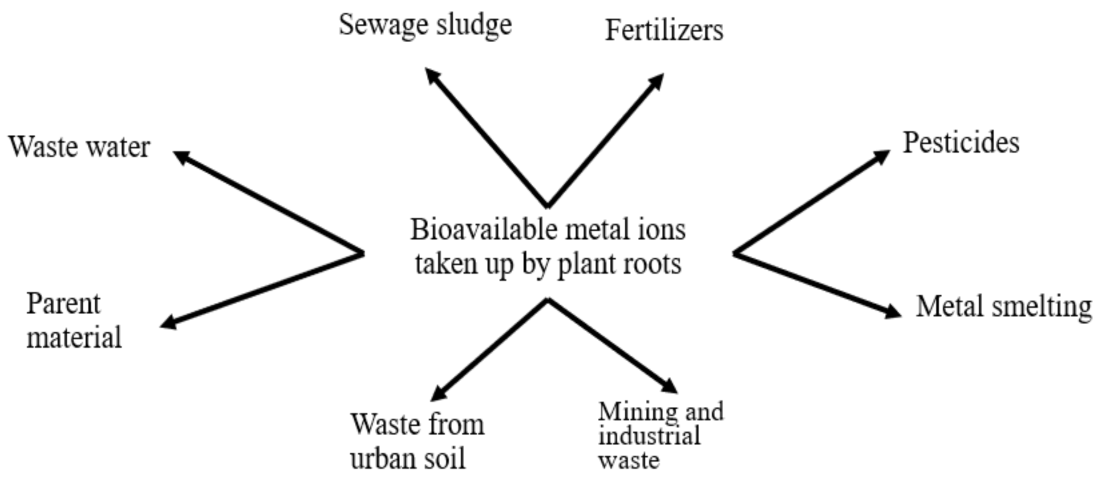


Figure 2.1. Major sources of heavy metals in soil (Modified from Mahar et al., 2016)

Soil is one of the key components of the terrestrial ecosystems and provides the required support and nutrients for the sustainability of plant life and important for degradation and transfer of biomass (Bradl, 2004). Soil is a very complex heterogeneous body consisting of solid, soluble and gaseous phases, minerals, organic matter and microorganisms interacting with each other and ions entering the soil system (Alloway, 2012). The mobility and availability of toxic elements in the environment is dependent on their chemical forms and speciation. The ecological toxicity of heavy metals in soil are closely dependent on the content and metal speciation in soil solid and liquid phases (Brümmer, 1986). Mobility of heavy metal is a term used to describe the potential migration of heavy metals in soil. In soil, heavy metals found mainly in six different geochemical forms, and these include: water soluble, exchangeable, carbonate bound, Fe – Mn oxide bound, organic matter bound and residual fractions (Tessier et al., 1979; Hickey & Kittrick, 1984; Ramos et al., 1994; Abollino et al., 2006). Except for the residual fraction, the sum of these fractions is referred to as non-residual fraction and these fractions tend to be more available compared to residual fraction (Hickey & Kittrick, 1984).

The relationship between heavy metals and soil components increases from water-soluble to residual, thereby making the water-soluble and the exchangeable fractions the most soluble and mobile forms of heavy metal in soil. In soil, heavy metals can occur in both solid and solution phases. Heavy metals occurring in solid phases are rarely mobile and less toxic while those found in solution phase have more potential to be mobilised and are toxic (Ogundiran & Osibanjo, 2009). Heavy metals can occur in soil in both solid and solution phases. In the solid phase, heavy metals are immobilised through adsorption on organic and inorganic components of the soil or through precipitation as pure solids (Ogundiran & Osibanjo, 2009). In solution phase, metals can exist as free metal ions, as soluble complexes with inorganic or organic ligands (McLean & Bledsoe, 1992). With a change in soil cation, pH or oxidation – reduction potential, heavy metals in solid phase may become mobile and thus, could be mobilised. Heavy metals in soil are subjected to numerous reaction processes, in which, their mobility, solubility and availability can be affected (Scokart et al., 1983). Heavy metal migration from soil to other media (for example, water and air) and consequently biological systems are strongly controlled by their different forms in which they exist in soil (Ogundiran & Osibanjo, 2009).

The occurrence and behaviour of heavy metals in soil differs, and their bioavailability greatly depends on the solubility of heavy metals in soil (Cristaldi et al., 2017). For example, arsenic is a metalloid and an abundant naturally occurring element in the earth's crust, oceans, lakes and rivers (Tchounwou et al., 2012). Arsenic contamination of the environment is caused by both natural phenomena and anthropogenic activities. Its mobility, bioavailability and toxicity are determined by its ionic form (Tchounwou et al., 2012; Cullen & Reimer, 1989). Chromium is comparatively abundant in earth's crust, rivers, lakes and marine (Sreeram & Ramasami, 2003). Cadmium mobility in soil occurs through both natural and anthropogenic sources and can form insoluble complexes with inorganic and organic compounds (Tchounwou et al., 2012; Crea et al., 2013). Zinc occurs naturally in soil, its mobility depends on soil parameters such as cation exchange capacity, pH and other chemical elements, but elevated concentrations of zinc in soil is mainly due to anthropogenic sources (Broadley et al., 2007; Cristaldi et al., 2017). Lead is a naturally occurring element mostly found in the lithosphere and its applications cut across agricultural, domestic and industrial sectors (Cristaldi et al., 2017). Lead is toxic to all organisms including humans and can persist for a long time in soil due to its low soluble nature in comparison to other elements (Hernberg, 2000). Nickel is widely distributed in soil and seawater and has wide range of applications in different industries and technology. Factors such as soil texture, organic matter, amounts of mineral crystals, pH, water and the presence of hydroxides greatly affect the retention of nickel in soil (United States Agency for Toxic Substances and Disease Registry [ATSDR], 2005). Copper is widely, naturally occurring element and has high application in anthropogenic activities. In both soil and sediment, this element readily bounds with inorganic and organic compounds and can be influenced by factors such as pH, redox potential and presence of anions (Van Sprang et al., 2005). Mercury is widespread and forms liquid at a room temperature. It exists in soil as organic and inorganic complexes and exhibits three forms: elemental, inorganic and organic mercury (Tchounwou et al., 2012). This element is potentially mobilised into the environment through volcanic respiration or thermal springs. Major anthropogenic sources causing mercury contamination are copper and zinc extractions, industrial burning of wastes, use of fertilisers in agriculture, fungicides, sewage sludge, use fossil fuels and wastes associated with various industrial processes (Pacyna et al., 2006).

The dynamic nature of heavy metals in soil is influenced by several factors such as physical and chemical processes and chemical reactions such as adsorption/desorption and precipitation/dissolution (Peng et al., 2018). These processes may influence the kinetic behaviour of heavy metals at any point in time and is strongly dependent on certain field conditions (Peng et al., 2018). Among the soil chemical processes, the reactivity and bioavailability of heavy metals in soil is greatly controlled by the adsorption/desorption reaction (Peng et al., 2018). In soil, metal ions are retained through sorption, precipitation and complexation reactions and can equally be removed from the soil through metal uptake by plants, solubilisation and volatilisation (Bolan et al., 2014). Although not all metals undergo volatilisation losses, some metals and metalloids especially mercury, arsenic and selenium tend to produce gaseous compounds (Mahimairaja et al., 2005; Bolan, et al., 2013). Sorption is the retention of charged metal/metalloid solute species by the surfaces of charged soil components (Bolan et al., 1999; Sparks, 2003). In soil, the most important metal pools exist as exchangeable fractions, metals bound to carbonates, metals bound to manganese and iron ox-hydroxides and those bound to mineral structures (Monterroso et al., 2014). The level of mobility as well as the rate at which heavy metals become available in soil is greatly determined by the equilibria that exist between the metal fractions in soil not the soil total metal concentration (Monterroso et al., 2014). Similarly, the soil parameters and the constituents of the soil solution control the dynamic equilibrium that exists between metals in solution and soil solid phase. When soil pH is greater than 6, the activity of free metal ions in soil solution tends to decrease due to soil surface charge on oxides of iron, aluminium, manganese, chelation by organic matter or through precipitation of metal hydroxides (Stahl & James, 1991; Mouta et al., 2008). In a similar way, the activity of metal ions in soil solution especially in natural acidic soils, has been found to decrease with an increase in soil pH which was a result of increase in the rate of cation exchange capacity (Naidu et al., 1997; Violante et al., 2010; Nigussie et al., 2012).

Mobilisation of heavy metals in soil can also be influenced by precipitation especially in high pH soil (Hong, et al., 2007). Precipitation is considered the major immobilisation process in soil with high pH and metal concentration in the presence of anions (Naidu et al., 1997; Ok, et al., 2010). Precipitation of phosphates/carbonates is the dominant mechanisms for the immobilisation of heavy metals in soil such as lead and copper especially at high soil metal concentration (Bolan et al., 2014). A study by McGowan et al. (2001) found that the presence of phosphorus in soil inhibited the dissolution of cadmium, lead and zinc. In a similar circumstance, the addition of liming materials in soil could enhance the retention of metals (Naidu et al., 2012). Bolan and Thiyagarajan (2001) reported that the increase observed in the retention of chromium (II) as a result of lime applied to the soil was due to an increase in soil pH.

Metals also undergo microbial oxidation/reduction in which case both their mobility and speciation could be affected (Bolan et al., 2014). Redox potential describes the overall reducing or oxidising condition of a system (Søndergaard, 2009). Under these systems, the redox processes are grouped into two stages: assimilatory and dissimilatory (Brock et al., 2003). Assimilatory reactions are reaction processes whereby the metal substrate plays a major role in the metabolic functioning of the organism, which acts as aterminal electron acceptor. Conversely, in dissimilatory reactions, the metal substrate plays no known role in the metabolic functioning of the species responsible for the reaction, in which redox reactions are indirectly initiated. Heavy metals and metalloids such as arsenic, mercury, selenium and chromium are greatly influenced by microbial oxidation/reduction reactions in soil, which in turn controls their speciation and mobility (Bolan et al., 2014). Heavy metals such as copper and mercury generally become less soluble when higher oxidation state prevails, however, the mobility and solubility of metalloids in soil, for instance, arsenic is controlled by their oxidative state and ionic form (Ross, 1994). Arsenic, a case in point, exists in different chemical forms in soil. Inorganic arsenic (arsenite (III)) has been found to be less mobile in the environment but has a greater toxic effect compared with inorganic arsenate (V). Although, both arsenite (III) and arsenate (V) have harmful effects on living receptors due to their potential to cause alteration of metabolic pathways (Caruso et al., 2001). Arsenite (III) readily binds to sulphur groups from enzymes and proteins and then to thiol groups from phytochelatins while arsenate (V) readily attaches to amino, or reduced nitrogen groups (Kumaresan & Riyazuddin, 2001).

Complexation reaction between heavy metals and inorganic and organic ligand ions is another chemical interaction that influences metal retention in soil (Bolan et al., 2014). In soil, there is a high affinity between organic components of soil constituents and heavy metals because ligands can chelate with heavy metals (Harter & Naidu, 1995; Bolan et al., 2011). All these interactions are predominantly governed by a wide range of factors such as the pH of the solution and ionic strength, dominant cation, the nature of the metal species, and inorganic and organic ligands present in the soil solution. When the soil pH increases, the carboxylic, phenolic, alcoholic and carbonyl functional groups that exist in organic matter tend to disassociate and as a result, the affinity of these ligands for metal ions is promoted. Thus, in this system, the degree of complexion that exists between metal ions and organic matter can vary as a result of influencing factors such as temperature, metal concentration and steric (spatial arrangement of atoms in a molecule) factors.

Heavy metals are released from the soil through desorption, solubilisation, complexation and chelation reactions (Bolan et al., 2014). The soil’s capacity to adsorb metal ions from aqueous solution is of significant importance and has implications for both agricultural problems relating to soil fertility and environmental issues such as remediation of heavy metal contaminated soils and disposal of waste (Bradl, 2004). The desorption and adsorption of heavy metals in soil greatly depends on soil organic matter (SOM), which plays a dominant role in controlling metal partitioning (Weng et al., 2001; Tipping et al., 2003; Cabaniss, 2009; Xiong et al., 2013). Desorption is a key mobilisation process through which heavy metal ions are released from soil surfaces while adsorption is the binding of metal ions on the surfaces of soil components. Adsorption is a key process controlling heavy metal accumulation in soil. In adsorption reaction, charged solute ion species and charged soil surface are attracted together by electrostatic force and/or through the specific bond formation. Charged solute retention by charged surfaces is grouped into specific and non-specific retention (Bolan et al., 1999). In non-specific adsorption, the charge on metal ions balances the charge on the soil particles through electrostatic attraction in the reaction process, whereas specific adsorption involves formation of chemical bond between metal ions and the sorption sites on the soil surface (Adriano et al., 2004). Therefore, knowledge of adsorption processes in soil is of significant importance for understanding the dynamic behaviour of heavy metals from a liquid mobile phase to the surface of a solid phase.

Among all the binding sites present in soil organic matter (SOM), the carboxylic and phenolic sites are recognised as two of the most important functional groups which control metal binding with binding sites formed through various combinations of sites that consist of distinct thermodynamic properties, such as proton and metal binding constant (Benedetti et al., 1995; Koopal et al., 2005; Carbonaro et al., 2011; Tipping et al., 2011). The binding of metals to various sites of SOM can cause different metal adsorption and desorption rates of heavy metals which may significantly affect the behaviour of metal ions in soil (Shi et al., 2008; Shi et al., 2013b). Inorganic colloid interface such as clay is the most important interfaces responsible for heavy metal adsorption in soil. In addition, organic colloidal matter provides heavy metal adsorption and desorption interfaces, for example, those of detrital origin and living organisms such as algae and bacteria (Kerndorff & Schnitzer,1980; Lion et al., 1982; Fein et al., 1999). Heavy metal adsorption onto these surfaces controls their concentration in solution which is also influenced by the presence of inorganic and organic ligands. These ligands can be found in contaminated soil and wastewater and can be of biological origin, for example, humic and fulvic acids (Schlautman & Morgan, 1994; Du et al., 1995) and anthropogenic origin such as Ethylenediaminetetraacetic acid (EDTA), polyphosphates, and others (Bowers & Huang, 1986; Szecsody et al., 1994; Zachara et al., 1995). The adsorption of heavy metals and their distribution between soil and water are governed by important factors such as type of soil, metal speciation and concentration, soil pH, the mass ratio of solid and solution, and contact time (Cavallaro & McBride, 1980; Martınez & Motto, 2000; Kent et al., 2000). Generally, with high soil pH condition, greater metal retention and lower solubility occurs (Barrow & Cox, 1992; Temminghoff et al., 1994; Yin et al., 1996). Other important soil components such as soil minerals, (e.g., iron and aluminium hydroxides) affect metal adsorption and desorption reactions in soil.

Addition of desorbing agents such as phosphate fertilizers to contaminated soils can significantly increase the solubility and availability of certain oxyanions such as selenite, arsenic (V) and chromium (VI) in soil (Davenport & Peryea, 1991; James et al., 1995; Alam, Tokunaga, et al., 2007; Zupančič et al., 2012). A study conducted by Seaman et al. (2001) found that an increased level of hydroxyapatite to a metal contaminated soil resulted in significant increases chromium (V1) and arsenic (V) concentrations found in soil solution. The resultant increase was attributed to increased competition for adsorption by $H_2PO_4^-$ ions with the oxyanions (Karczewska et al., 2009). Similarly, Bolan et al. (2015) found that phosphorus variedly affected arsenic mobility and bioavailability in soil and between soil system and solution culture.

2.3 Effects of Heavy Metals on Human Health and Plants

2.3.1 Human Health

The adverse effects of heavy metal contamination on human health have gained global attention. Over the last few decades, data revealing the effects of heavy metals, especially in urban soil on human health has drastically increased and this has attracted the attention of a wider public and media outfits (Duzgoren-Aydin, 2007; Sipter et al., 2008). Though, some heavy metals (e.g., iron and manganese) are essential for certain physiological and biochemical activities, elevated levels can have negative health effects. Most heavy metals generate free radicals which cause oxidative stress, damage to biological molecules (e.g., enzymes, proteins, lipids, and nucleic acids – damage to DNA can lead to carcinogenesis) at low levels. While some toxic effects are acute, others are chronic and may lead to damage of several organs including the brain, lungs, liver, and kidneys (Engwa et al., 2019). People living or working around the industrial sites which make use of these metals and their compounds or formal industrial sites where heavy metals have not been appropriately disposed stand a high risk of exposure to heavy metals. Generally, human exposure to heavy metals occurs through three major pathways, namely, ingestion, inhalation, or dermal contact (Martin & Griswold, 2009). Elevated levels of trace elements in soil have been reported in many studies to cause adverse human health effect due to close proximity to human activities and also because these metals can easily be transferred into human bodies from suspended dust or through direct contact (Madrid et al., 2002). Moreover, significant cases of adverse human health effects of soil metal contamination have been documented in many studies: Calderón et al. (2003) reported the adverse human health effects of heavy metals on children and pregnant women; the neurological effects of arsenic, lead and mercury from metal contaminated soil were also reported in many studies (Wasserman et al., 2004; Rothenberg & Rothenberg, 2005; Trasande et al., 2005).

2.3.2 Plants

Plants are important components of ecosystems and have the potential to uptake various contaminants from the surroundings such as heavy metals particularly through their roots and subsequent translocation to the leaves. Plants require some heavy metals as they constitute essential micronutrients for plants (Reeves & Baker, 2007). Some heavy metals such as copper, zinc, iron, nickel, cobalt, molybdenum and manganese are essentially required by plants for growth and development, however, at excessive concentrations; these elements can become toxic and cause impairment of plants' physiological and biochemical processes (Gangwar et al., 2010; Kalinowska & Pawlik-Skowronska, 2010; Chou et al., 2011; Thounaojam et al., 2012). As metals cannot be degraded, when they are taken up by plants at concentrations above the optimal levels, the resultant effect is the production of adverse phytotoxic effect directly or indirectly on the plants, and some of the direct phytotoxic effects induced by high metal concentration in plants may include hinderance of cytoplasmic enzymes and destruction of cellular structures due to oxidative stress (Van Assche & Clijsters, 1990; Jadia & Fulekar, 2009). Other resultant effects include low biomass production, chlorosis, inhibition of growth and photosynthesis, altered water balance and nutrient assimilation, and senescence leading ultimately to death (Singh et al., 2016).

However, there are other heavy metals that include cadmium, lead, arsenic and mercury that play no biological roles in plant growth, and these set of heavy metals can cause potential adverse effects on plants at the slightest concentration (Asati et al., 2016). Therefore, the phytotoxic effects of heavy metals differ among different heavy metals. Some heavy metals such as chromium, mercury, cadmium, nickel, arsenic and zinc have been shown to manifest their phytotoxic effects in different ways upon uptake in high concentrations by plants (Hossain et al., 2012). The phytotoxic effects of heavy metal contamination to plants have been a subject of concern to many environmental researchers globally particularly during the last decades because plants represent the major entry point through which the food chain is contaminated with heavy metals which could have a potentially adverse effect on human health (Amari et al., 2017). In addition, the effects of heavy metal contamination to plants have been associated with various adverse effects particularly at the biochemical level, to include impairment of enzymatic activities, membrane function and oxidative stress in plants (Romero-Puertas et al; 2007; Gajewska et al., 2009; Yan et al., 2010). In soil contaminated with heavy metals, various physiological functions of plants such as photosynthesis, plant-water relationships, uptake of nutrients, nitrogen metabolism can be evident (Alam, Hayat, et al., 2007; Gopal & Rizvi, 2008; Chen et al., 2009; Gajewska et al., 2009). Such phytotoxic effects result in altered metabolism, physiological and biochemical malfunctioning which cumulatively results in retarded plants growth and poor biomass development (Nagajyoti et al., 2010). Moreover, the adverse effects of heavy metals on the activities of the important soil microorganisms can indirectly affect the plants growth (Asati et al., 2016). High metal concentrations in soil may affect the activities of some important soil microorganisms, and consequently, result in a decrease in the number of beneficial microorganisms in the soil that perform vital soil functions. For example, soil organic matter may be decreased due a decrease in the number of beneficial soil microorganisms caused by heavy metal toxicity, and thus lead to a less fertility (Asati et al., 2016). In addition, soil enzyme activities may be affected due to a reduction in the number of beneficial soil microorganisms (Asati et al., 2016).

2.4 Selected Analytical Techniques for Determining Heavy Metals in Soil and Plants

The importance of accurately determining heavy metals from various environmental samples – soil, sediment, sewage sludge and similar other matrices, with the goal of better evaluating their potential toxic effects on the environment so as to develop and implement effective management strategies to reduce their potential adverse effects has long been receiving much research attention (Ure et al., 1993; Quevauviller et al., 1997). There are several well-established analytical techniques available for measuring heavy metal contents in soil. In this section, the techniques will be compared, and questions raised about their usage. These techniques have been widely used to measure the contents of heavy metal from different environmental samples such as soil, sediment and sludge. Although, the choice of techniques to be used is determined by the intent of the study, nature of samples to be analysed and the type of elements being examined (Soodan et al., 2014). Some of the widely used heavy metal analytical techniques and digestions methods are discussed in detail in this chapter.

2.4.1 Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

ICP-OES is considered as one of the most popular techniques employed for the determination of heavy metals from environmental samples (Soodan et al., 2014). This analytical technique provides robust, rapid and multi-element determination from digested solid samples in solutions. ICP-OES was first used in the analysis of heavy metals in 1965 by Greenfield and his colleagues. Since then, many researchers have employed the ICP-OES technique for the measurement of heavy metals from soil ecosystem. Today, the ICP-OES technique is recognised as one of the most vital tools in the field of heavy metal pollution analysis (Morrison & Talmi, 1970). In comparison to other spectroscopic techniques, ICP-OES has the capacity to perform simultaneous multi-elemental analysis of trace elements at part per billion (ppb) or part per million (ppm) level for a wide range of trace elements and limited volume of samples more particularly the biological samples (Soodan et al., 2014). Also, ICP-OES has the capacity to analyse large number of environmental samples within a limited timeframe and sample characterisation (Bettinelli et al., 2000). This technique can be assisted by acid digestion or microwave assisted acid digestion. High purity inorganic acids such as nitric are normally used for digestion. Sample digestions could be achieved by either using fusion or wet digestion procedures based on acid digestion with a heated mixture of mineral soils (Sastre et al., 2002). The use of microwave assisted acid digestion for ICP-OES helps to reduce the analysis time and minimise the risk of sample contamination (Greenfield et al., 1964; Scott et al., 1974). This analytical instrument is widely used for heavy metal analysis because of its good detection limits for trace elements, linearity in terms of calibration curves and its ability to reduce sensitive matrix effects to its lowest level (Bettinelli et al., 2000). However, the main limitations of ICP-OES in elemental analysis include continuous background emission, higher detection limits in comparison to ICP-MS, spectral overlaps, and sensitive matrix effects and high operational costs (Olesik, 2020). Moreover, ICP-OES is a destructive analytical procedure, and implies that after analysis, it not possible to recover the sample. Consequently, highly precious, or rare samples cannot be analysed through this analytical technique. In addition, this analytical technique is cumbersome and time consuming as it requires multiple steps involving performing crude analysis to obtain a fundamental knowledge of the elements that are present in the sample, selecting the best wavelength based on your knowledge, performing separation optimisation to limit overlap of signals from the various wavelengths and spectral interferences analysis and how to ensure elimination of spectral interferences from the read-out without necessarily eliminating target signals (Katakam & Aboul-Enein, 2020).

2.4.2 Inductively Coupled Plasma Mass Spectroscopy (ICP-MS)

The ICP-MS trace element analytical tool is designed for multi-elemental ultra-detection capability which makes it a good analytical technique in the field of trace element analysis. In recent years, the use of ICP-MS in speciation analysis has gained a wider application for ultra-sensitive detection of metals and metalloids from environmental samples (Rosen & Hieftje, 2004). This analytical technique has been widely employed for the analysis of trace metals in industries, environment, food beverages and clinical and biological materials (Truscott et al., 2001; Meisel et al., 2003; Taylor et al., 2003; Trandafir et al., 2012). This technique is mostly employed for wastewater analysis and analysis of samples from textile industries (Zeiner et al., 2007). This analytical technique employs difference in the mass to charge ratio of ionised atoms or molecules which enables it to separate atoms or molecules from each other. The exceptional feature of this technique is that it has good sensitivity and has the capability to provide simultaneous multi-elemental detection in comparison to other spectroscopic techniques (Soodan et al., 2014). Other features of this technique include low detection limits for greater number of trace elements, wide dynamic analytical range, simultaneous analysis of a range of trace elements, isotope composition, high sample throughput, low sample volume (Zeiner et al., 2007; Wilschefski & Baxter, 2019). It has been reported that ICP-MS can measure metal-containing species even when a specific element is scattered over a wide number of species (Chyla & Zyrnicki, 2000; Mataveli et al., 2010). Zhang et al. (2009) used this technique to measure metal contents from soils where different agricultural practices are in place in China North of Zhejiang Province. The main disadvantage of this analytical tool is the high cost of operation associated with purchasing of argon for the analysis and the presence of high salt contents in the digested solutions could affect the performance of the instrument through interferences in the measurements (Zeiner et al., 2007). Other limitations of this analytical technique include high cost of equipment, requires high level of trained personnel, multiple high purity gases are required and problem with interferences (Wilschefski & Baxter, 2019).

2.4.3 X-Ray Fluorescence Spectrometer (XRF)

The X-Ray fluorescence spectrometry technique has been widely used in many industries as well as environmental analysis and geological applications (Higueras et al., 2012; Congiu et al., 2013; Shuttleworth et al., 2014; Young et al., 2016; Menšík et al., 2021). XRF technique can perform a wide range of elemental analysis with high level of accuracy and can measure elemental concentrations of various trace elements in both solids and solution and can also detect trace elements even in complex matrices (Potts, et al., 1997).

This technique has been widely used for the measurement of heavy metals from the soil. XRF has the capacity for muti-elemental determination in soil. For instance, Cheng et al. (2013) employed this technique in the measurement of metal (zinc, copper and nickel) contents in sediment and soil contaminated with industrial waste pollution from agricultural area in Taiwan. Similarly, Bhuiyan et al. (2010) used this technique to measure the contents of manganese, zinc, lead, arsenic, iron, strontium and zirconium in soil contaminated by acid mine drainage and nearby agricultural soil in coal basin in Northern Bangladesh. XRF technique has been widely used in mapping of contaminants in contaminated areas especially in urban and mine-impacted areas (Mokhtari et al., 2015; Zissimos et al., 2018), and has generally been used in soil geochemical mapping (Martin et al., 2016).

Potts et al. (1997) reported that one of the exceptional features of XRF relies on its capacity to perform a wide range of elemental analysis with high level of accuracy. Also, this technique has the capacity of measuring the composition of matter as well as the elemental concentrations of various trace elements in both solids and solution and can also detect trace elements even in complex matrices. This technique can be used for measurement of metals in both field and laboratory. In situ measurement is achieved through the use of Field Portable X-ray Fluorescence which makes it possible to measure heavy metal contents directly from the soil as the instrument is pointed towards the soil and in that case, real time data can be obtained. This allows for more flexibility as large number of sampling points can be measured for heavy metal contents in comparison to other technique where samples are collected and subsequently prepared before analysis in the laboratory. In contrast, XRF technique based on laboratory requires sample collection and preparation before analysis could take place. As a result, a limited number of samples can be collected, prepared, and analysed when compared to Field Portable X-ray Fluorescence. Although, laboratory based XRF has been widely used because of good analytical precision and high accuracy of the data it produces (Melquiades & Appoloni, 2004).

XRF measures the accurate total elemental concentrations in solid soil samples (Reidinger et al., 2012), however, it has been reported that this technique may have low sensitive detection limits for most element especially in adverse conditions like the lab based analytical techniques (McComb et al., 2014). In addition, XRF technique is cost effective and offers the possibility for rapid, on-site determination of heavy metal concentrations compared to conventional laboratory methods that employ acid sample digestion (Kilbride et al., 2006).

XRF is a heavy metal analytical tool anchored on the fundamentals of physics: comprising of atom-reduction interactions (Soodan et al., 2014). It is a powerful analytical tool which is specially designed to produce high sensitivity in terms of trace element analysis (Gilfrich, 1990; Potts et al., 1997; Anjos et al., 2002).

XRF is a non-destructive analytical technique used mainly to measure the elemental composition of materials. As a non-destructive analytical technique, it makes it possible for the re-run of the samples in case of any experimental error (Zhu et al., 2011). In this analytical technique, the chemistry of a meterial is determined by measuring the fluorescent X-ray discharged from a material when the material is excited by an X-ray source (Ward et al., 2018). Thus, the target is excited by primary X-rays, thereby making it possible for the elements in the target material being analysed to fluoresce at their characteristic wavelengths or energy levels (Ward et al., 2018). The intensity of the fluorescent signal is directly linked to the concentration of the corresponding element in the target material being analysed. This analytical technique generates data based on the concentration of the inorganic elements contained in the material that is being analysed. Drying and grinding samples prior to analysis improves the accuracy of the results obtained by XRF (Padilla et al., 2019; Menšík et al., 2020). This is because soil samples ground to finest texture contains lower particles which provides higher accuracy because the incident angles are samaller (Menšík et al., 2021). Therefore, a sieved and ground soil samples provide more accurate XRF results when compared to unsieved soil samples (Laiho & Peramaki, 2005; Stockmann et al., 2016).

Several other factors such as sample homogeneity, spectral interferance elements, analytical drift, sample mineralogy, sample matrix and soil moisture are known to affect the quality and precision of results produced by XRF technique (Kalnicky & Singhvi, 2001; Laiho & Perämäki 2005; Binstock et al., 2008; Parsons et al., 2013; Weindorf et al., 2014; Ward et al., 2018). Spectral interference is a common phenomenon in heavy metal contaminated soil, and can affects the accuracy of results produced by XRF (Menšík et al., 2021). It has been found that during XRF analysis of iron and copper, iron tended to absorb copper X-rays, thus decreasing the copper intensity measured by XRF detector (United States Environmental Protection Agency [USEPA], 2007). This is just a common example of spectral interference that could affect the accuracy of results produced by XRF. Although, Hangen et al. (2019), argue that this is not always the case. The moisture content of the soil is the significant source of error in XRF results, particularly when the soil moisture content is above 20 % (Laiho & Perämäki 2005). The soil moisture content affects the results by absorbing the primary X-ray radiation coming from the source and as well as the characteristic X-rays of the analytes which causes characteristic X-rays to decrease exponentially (Ge et al., 2005). In addition, water increases the intensity of scattered X-rays in the fluorescence spectrum (Menšík et al., 2021). However, the magnitude of effect of soil moisture is dependent on the elements being examined (Schneider et al., 2016).

2.4.4 Heavy Metals/Sample Digestion Procedures.

There is a wide range of analytical tools for heavy metal determination from environmental samples. However, for spectroscopic analysis, samples need to be digested first: in which the samples solid matrix is decomposed in order to leach out the analytes into the acid solution so that the metals can be measured by ICPs (Prichard et al., 1996). In digestion of environmental samples, the most popular methods used to achieve this are conventional acid digestion procedures and microwave assisted acid digestion (Bettinelli et al., 2000). There are wide varieties of high purity inorganic acids that are used for both acid leaching and microwave assisted acid digestions. In every digestion procedure, the objective is to: (a) ensure complete dissolution of sample matrix so that the analytes will be leached into acid solution, (b) to minimise the risk of sample contamination as far as possible and prevent losses of elements, and (c) minimise amount of time used for handling and processing (Dean, 2003).

2.4.5 Conventional Acid Leaching Procedure

In conventional acid leaching procedure, open systems are used to extract solid matrix on a heating source in the presence of an acid or mixture of different extracting reagents/acids (Duyusen et al., 2010), in which different heating systems such as sand-bath, heating plate and aluminium blocks may be used (Sastre et al., 2002). Aqua regia (HNO_3+HCl) is one of the mostly used reagents for acid digestion of the environmental samples (ávan den Akker & Delft, 1991; Kalbitz, & Wennrich, 1998; Florian et al., 1998). The most widely used of aqua regia for acid heavy metal leaching stems from the fact that it has the capacity to achieve highest soluble acid fraction of metals (Kalbitz & Wennrich, 1998). However, the constraints associated with conventional leaching method are that the procedure is very laborious, time-consuming and there is high risk of sample contamination (Sastre et al., 2002). In addition, this procedure is associated with high loss of volatile elements such arsenic and mercury. Also, conventional acid leaching procedure is less efficient in terms producing controlled and reproducible results when compared to microwave assisted acid digestion (Lorentzen & Kingston, 1996).

2.4.6 Microwave Assisted Acid Digestion.

This digestion procedure is considered as the most suitable methods for digestion of matrixes that are very complex in nature such as soils, sediments and sludges particularly when the samples contain silicates, clay, oxides and organic materials (Sakan et al., 2011). The use of microwave assisted acid digestion and subsequent determination of trace elements concentration using spectroscopic analytical instruments is regarded as one of the most popular and versatile methods used for analysis of heavy metals from soil samples (Kowalewska, et al., 1998; Tam & Yao, 1999). This method is particularly very important because it allows samples to be digested in a relatively short period of time and the high recoveries especially for volatile elements (Bettinelli et al., 2000). Microwave assisted acid digestion has the potential to overcome the limitations of conventional acid leaching method because in microwave digestion, analysis time is relatively reduced. Also, the risk of sample contamination is minimised, less volume of acids is required which also enhances the safety of the operator (Bettinelli et al., 2000). These factors combined together help in improving the detection limits and total level of accuracy of the analytical methods. Apart from the above listed advantages, microwave assisted acid digestion is more efficient in terms of controllability and the reproducibility of the results when compared to conventional acid leaching procedure (Sandroni & Smith, 2002; Sastre et al., 2002). It also reduces the loss of volatile elements such as arsenic and mercury. There are various acid combinations that are used for microwave assisted sample digestion. The most common used acids are HNO_3/H_2SO_4 and HNO_3/HCl (Sandroni et al., 2003); HNO_3/HF; $HCLO_4/HNO_3$ (Nadkarni, 1984); $HF/HNO_3/HCl$ (Bettinelli et al., 2000). To achieve accurate and reproducible results in some cases, complete sample digestion may be necessary. HF has been recognised to play a pivotal role in terms of the amount of metal recovery of microwave assisted acid digestion of environmental samples (Melaku et al., 2005), because of its capacity to attack and break silicate minerals in comparison to other inorganic reagent combinations (Melaku et al., 2005). However, the limitations of this reagent are that they can damage glass wear and the ICP-OES torch (Melaku et al., 2005). The Environmental Protection Agency (EPA) recommends the use of microwave assisted procedure with nitric acid (Element, 2007). Nitric acid is a strong acid which has been identified to possess the capacity to achieve complete decomposition of metals. This reagent has been successfully used to leach out the trace elements from different environmental samples such as soils, sediments and sludges ((Element, 2007). In a similar way, this acid has also been used to achieve metal solubilisation from fly ashes, soils and plant samples.

Of these techniques XRF offers the possibility of rapid and cost-effective determination of heavy metals in soils. Compared with chemical analysis methods, XRF is non-destructive and offers the possibility for rapid, on-site determination of heavy metal concentration. However, XRF cannot distinguish between different oxides (it quantifies the total concentration of each element in a sample), and it cannot quantify levels lower that ppb or ppm. Hence, before embarking on the case study it is necessary to establish if XRF is a suitable candidate for analysing the heavy metals from the investigated soils. This was done by testing samples by both XRF and aqua regia extraction. Aqua regia is known to underestimate some metals (cobalt, cadmium, chromium and nickel) by up to 50% (Ščančar et al., 2000; Taraškevičius et al., 2013). The better of these two techniques for the case study area will then be used in the study to address Aims 3 and 4.

2.5 The UK Regulatory Framework for Investigating Contaminated Land

2.5.1 Overview

The UK has a considerable legacy of historical land contamination due to a long history of industrialisation and urbanisation involving a very wide range of substances, which created a legacy of elevated levels of various contaminants in the environment (DEFRA, 2012; Johnson et al., 2012). Contaminated land can be blight on communities and may pose unacceptable risks to people and the environment (Environment Agency, 2016). Preventing land from being contaminated by various substances remains the best way to safeguard land and ensure that future generations inherit land free from a legacy of contamination (Environment Agency, 2016). Some lands are associated with greater concentrations of contaminants, linked to different industrial use and disposal of waste. Although, in a few circumstances, there may be sufficient risk to health or environment for such land to be deemed contaminated land.

Today, the legislation regarding management of contaminated land differs among the four countries that made up the United Kingdom. The risks associated with historical contamination in relation to current land uses are dealt with under the Part 2A of the Environmental Protection Act in Wales, Scotland and England – though with differences in the underlying secondary legislation as set out in Statutory Guidance (Land Quality Management Limited, 2015). To deal with unacceptable risk to health and environment from contaminated land, a legal framework for assessing the potential risks from contaminated land was developed. The contaminated land regime under Part 2A of the Environmental Protection Act (EPA) 1990 provides as a basic framework and main policy measures for dealing with contaminated land in the UK (DEFRA, 2012). The Part 2A regime provides a risk-based framework for identifying and remediating contaminated land. This statutory guidance provides a means to identify and remediate contaminated land that presents a significant risk relating to health or environment especially where no other alternative solution is available (DEFRA, 2012). In other words, if land contamination is suspected, and cannot be addressed through any other means, for example, during development processes, then the Part 2A regime should be used to deal with the contamination. Part 2A of the Environmental Protection Act 1990 sets out a better way in which such land can be identified and remediated (Environment Agency, 2016). In addition, the statutory guidance describes how local authorities, and the Environment Agency should carry out and go about in deciding whether land is considered “contaminated land” in the legal sense of the term. This is also used alongside planning rules to make sure that land is made acceptable for use after redevelopment, and details on the provisions of remediation, such as the aims of remediation stated under Part 2A of the Environmental Protection Act 1990, and how regulators should go about implementing the regime to ensure that the requirements for remediation are reasonable (DEFRA, 2012). The major objectives of Part 2A regime are: (a) To identify and deal with unacceptable risks to human health and environment from contaminated land, (b) To make sure contaminated land is made suitable for its current use and (c) To ameliorate the challenges faced by individuals, companies and society from contaminated land and ensure that they are proportionate, manageable and in line with the principles of sustainable development. The Part 2A regime is one of several ways in which land contamination can be addressed. Other instances where land contamination can be managed include during the development or redevelopment of land under the planning system. In addition, land contamination can also be addressed during the building control or when the landowner takes independent action to deal with land contamination.

It is important to note that other legislative regimes such as Building Regulations, Environmental Permitting, Waste Regimes and Environmental Damage (Prevention and Remediation) may also apply and provide avenues to deal with land contamination. The Part 2A regime places a legal duty on the local authority to identify and deal with contaminated land. Enforcing authorities can only refer to Part 2A regime to identify and deal with land contamination if there are no other available solution within their reach. Under Part 2A regime, the starting point is that land is not contaminated unless there is reason to suggest that the land is contaminated. The Part 2A definition of contaminated land applies to only land where unacceptable risks are clearly identified following a risk assessment conducted in line with Part 2A regime.

2.5.2 Inspection Duties by the Local Authority

Under Part 2A, the local authority is expected to cause inspection to be carried out in his area from time to time with the goal of identifying contaminated land and also allowing

/permitting the authority to make a decision as to whether such land required to be designated as a special site (DEFRA, 2012). Under Part 2A regime, there are two types of inspection a local authority may carried out: (a) strategic inspection – an example may include gathering information in order to make assessment of land within the local authority's area with a view to identifying priority land for a more detailed investigation (b) a local authority may conduct a detailed inspection of particular land so that information on ground conditions can be obtained and to carry out the risk assessment in line with the Part 2A relevant to the land under inspection. When carrying out strategic inspection, the local authority must act in line with any guidance provided for this purpose by the Secretary of the State. Under this regime, local authority is expected to take a strategic approach in identifying contaminated land. The strategic approach adopted by the local authority must include the aims, objectives, description of the relevant aspects of the area, its approach to strategic and detailed inspections including remediation, how its approach reflects Part 2A regime in dealing with the contamination and priorities, which must reflect the local features of the areas under consideration. The local authority is charged with the responsibility of undertaking a strategic approach in conducting the inspection under the regime and in doing so, the approach adopted by the local authority should be rational, ordered and efficient and should reflect local conditions. Although, local authority strategic approach to land contamination may differ according to available resources, technical knowledge, size, population, and political control. The local authority is expected to set out its approach in the form of a written plan of action, that should be adopted formally and publish within the timeframe that will be decided by the authority. Depending, the authority may decide to have a separate action plan document and/or include its action plan as part of a wider document, which should be subject to a periodic review for it to be up to date and for the authority to make decision when the written action plan should be reviewed. In a situation, where a local authority identifies land with reasonable likelihood of significant contaminant linkage, inspection should be carried out on the land to gain sufficient information so that a decision will be made whether the land is contaminated in line with statutory guidance. The timeframe of the inspection is dependent on the authority's approach to undertaking the detailed inspection and before conducting the inspection, the local authority should contact the owner of the land prior to inspection.

In terms of carrying out a detailed land inspection under Part 2A, the local authority prioritises the areas of land deemed to pose the most serious risk to human health or environment. Where the local authority considers that, a reasonable likelihood of significant contaminant linkage exists in land, inspection should be conducted to gather sufficient information to be able to decide whether the land under consideration is contaminated. Consent must be obtained from the owner of the land prior to land inspection unless where this is not possible due to a specific reason (e.g., where it is not possible to identify the owner of the land or landowner cannot be found and where the landowner refuses access to local authority to inspect the land). In such circumstances, the authority should invoke the statutory powers of entry in as much as the local authority satisfied that a significant contaminant linkage exists on the land (DEFRA, 2012). The local authority may decide at any stage to stop any further inspection regarding the contaminant linkage based on the information obtained if it establishes that there is no longer a reasonable likelihood that a significant contaminant linkage exists on the land.

2.5.3 Risk Assessment Processes

In the risk assessment processes, the focal point is to understand the risks the land might present and the associated uncertainties, and this understanding is usually developed in the form of a “conceptual model” in practical sense. Through, a staged approach to risk assessment, risks understanding is developed, and this often requires a preliminary risk assessment based on desk-based study to be conducted; a visit to the site and walkover survey; a generic quantitative risk assessment; and more detailed quantitative risk assessment at different stages. Risk assessment processes normally proceed until it is possible for the local authority to decide that there is lack of sufficient evidence to suggest that the land under investigation might be contaminated to give reason for the land to be further inspected and assessed; and/or whether or not the land is contaminated land. In circumstances where there is reasonable evidence that an unacceptable risk exists on land, the risk assessment should proceed to the next stage. However, if the authority believes that there is no justifiable evidence that unacceptable risk to human and environment exist on such land, inspection duties by the local authority should stop at this stage.

In terms of conducting risk assessment on contaminated land under Part 2A regime, the focus of the local authority should be on land which might pose an unacceptable risk to human health and environment and in doing this, they should conduct the risk assessment in line with provisions of good practice guidance on risk assessment so that robust decision can be made in accordance with Part 2A and good practice guidance. The risk must be based on the current use of the land and risk assessments and on scientific information, authoritative, relevant to the risk assessment of contaminants under investigation and appropriate to make regulatory decisions in line with Part 2A and good practice guidance (DEFRA, 2012). In risk evaluation, the local authority disregards any receptors that are not likely to be present based on the current land use or other land that might be affected under Part 2A Regime. For a risk to relevantly exist, there must be one or more contaminant – pathway – receptor linkages. For land to relevantly meets definition of “contaminated land under Part 2A regime, there must be presence of all three elements of a contaminant linkage regarding specific land.

(a) “A contaminant is a substance which is in, on or under the land and which has the potential to cause significant harm to a relevant receptor, or to cause significant pollution of controlled waters” (DEFRA, 2012, p. 10).

(b) “A receptor is something that could be adversely affected by a contaminant; examples include a person, an organism, an ecosystem, property, or controlled waters” (DEFRA, 2012, p. 10).

(c) “A pathway is a route by which a receptor is or might be affected by a contaminant” (DEFRA, 2012, p. 10) (Figure 2.2)

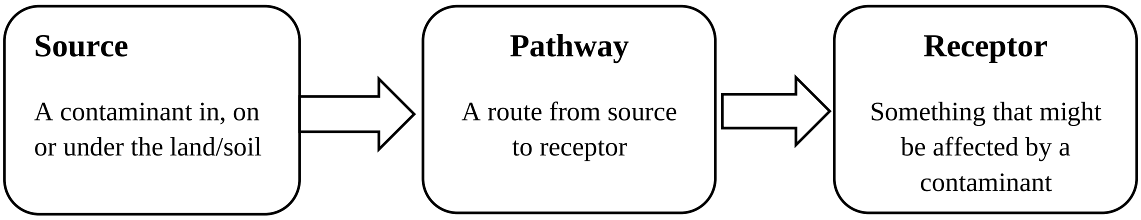


Figure 2.2. Source-Pathway-Receptor linkages

In other words, this means there must be presence of contaminant in, on or under the land in a form and amount that causes a risk, and one or more pathways that can cause significant harm to human health, environment or cause significant pollution of controlled water. The term “contaminant linkage” defines the integral relationship between a contaminant, a pathway and a receptor. These three elements must be present on the land for it to be qualified “potentially contaminated land” under Part 2A regime, including evidence of the actual presence of contaminants.

Where it is established that the contamination may pose significant risk, mitigation measures may be required to remove unacceptable risk and manage the risk. UK current guidance recommends a phased approach when conducting risk assessment on contaminated land, with regards to developing and updating a specific conceptual model (CSM) associated with the site (Land Quality Management Limited, 2015). This makes it possible to identify, characterise, evaluate all potential risks and, where it becomes necessary, to quantify in a logical and cost-effective stepwise process.

In phase 1, the first process of risk assessment usually begins with preliminary investigation, in which, a desk-top study and site reconnaissance visit/site walkover are undertaken. During the preliminary investigation, the initial conceptual model of the site under investigation is developed and this marks the first stage in any land contamination assessment. The initial conceptual site model is aimed at identifying all potential contaminant linkages associated with the site and based on a comprehensive desk-top review of all available documents which may include maps, aerial photographs, archived documents and past reports, regarding the site and a site visit (site reconnaissance visit) in order to inform the current condition of the site, any evidence on the site not documented and any potential challenge to further investigation. At the end of the phase 1 risk assessment, if the evidence suggests that significant risks may exist on the site, a phase 2 risk assessment is conducted.

The phase 2 risk assessment involves a more detailed risk assessment consisting of a site investigation which provides robust data on the soil types and the concentrations of contaminant among other factors, data interpretation and a quantitative assessment of the risk at the site (Land Quality Management Limited, 2015). Samples such as soil, groundwater, etc. may be collected from the site and taken to the laboratory for relevant analysis. These data are therefore, interpretated to establish if the contamination levels are likely to cause unacceptable risk. Where the initial CSM suggests that assumptions and uncertainties exist, a further assessment in the form of intrusive investigation may be required to collect relevant samples from the site for analysis, although, the nature and scope of investigations must be site-specific and inform by the findings from phase 1 risk assessment (Land Quality Management Limited, 2015). The potential risks identified in the initial CSM using the data from the site investigation will require further quantitative assessment, in order to confirm if the levels of contamination pose unacceptable risks and whether there is need for further assessment or remediation to be conducted. The quantitative risk assessment which uses mathematical algorithms is conducted to determine the levels of contamination a receptor may be exposed from such contaminated site under phase 2 risk assessment (Land Quality Management Limited 2015). This risk assessment helps to determine the actual significant risk posed by the contamination level present in such land. The nature of algorithms may vary depending on the receptor types being considered from each site. In summary, the phase 2 risk assessment should be a detailed report comprising of factual description of phase 1 site investigation, data assessment and the conclusions derived from the quantitative risk assessment. In addition, it should include information on updated CSM and conclusions stating clearly whether further investigations/site assessment or remediation is required.

Where the results suggest that unacceptable risk exist in such contaminate land, appropriate risk management action should be implemented. The management measures may include contaminant removal, encapsulation of the contaminants, treating the contaminants or breaking the contaminant linkages (The Cumbria Contaminated Land Officer Group, 2013). The risk management action should be targeted at breaking or removing the contaminant-pathway-receptor linkages from such contaminated land. The overall aim of risk management should be to eliminate the contaminant linkages present in such land or permanently break them to render them insignificant and reduce the unacceptable risk associated with them (DEFRA, 2012). The risk management adopted must be practicable and effective. The risk management practices adopted must conform with current good practice and guidance. Before any risk management action is carried out on the site, the risk management plan must be approved by the Local Planning Authority. An option appraisal is carried out with a view to identifying and evaluating feasible risk management actions (remedial options) for dealing with unacceptable risks to human health and environment from such contaminant site (DEFRA, 2012). All the identified feasible risk management actions should be combined into a scheme that can achieve the most desired result.

Where a site has been remediated following contamination, the developer is expected to submit a verification report and may be required to undertake post-completion monitoring. Verification in the context of remediation is defined as the process to demonstrate that risks posed by the contaminated land have been reduced to meet the criteria and objectives set out in the remediation based on the quantitative assessment of remediation performance (Environment Agency, 2010). This post-completion monitoring must be approved by the Local Planning Authority and the results obtained from the monitoring should also be submitted for review (The Cumbria Contaminated Land Officer Group, 2013). The essence of verification is to confirm that all the approved risk management actions regarding the contaminated site have been successfully implemented where appropriate. This ensures the risk management actions implemented with regard to the contamination has met the defined objective, usually to render the risks to human health and environment from such contaminated site insignificant. A framework for investigating contaminated sites is presented in the form of a flowchart in Figure 2.3.

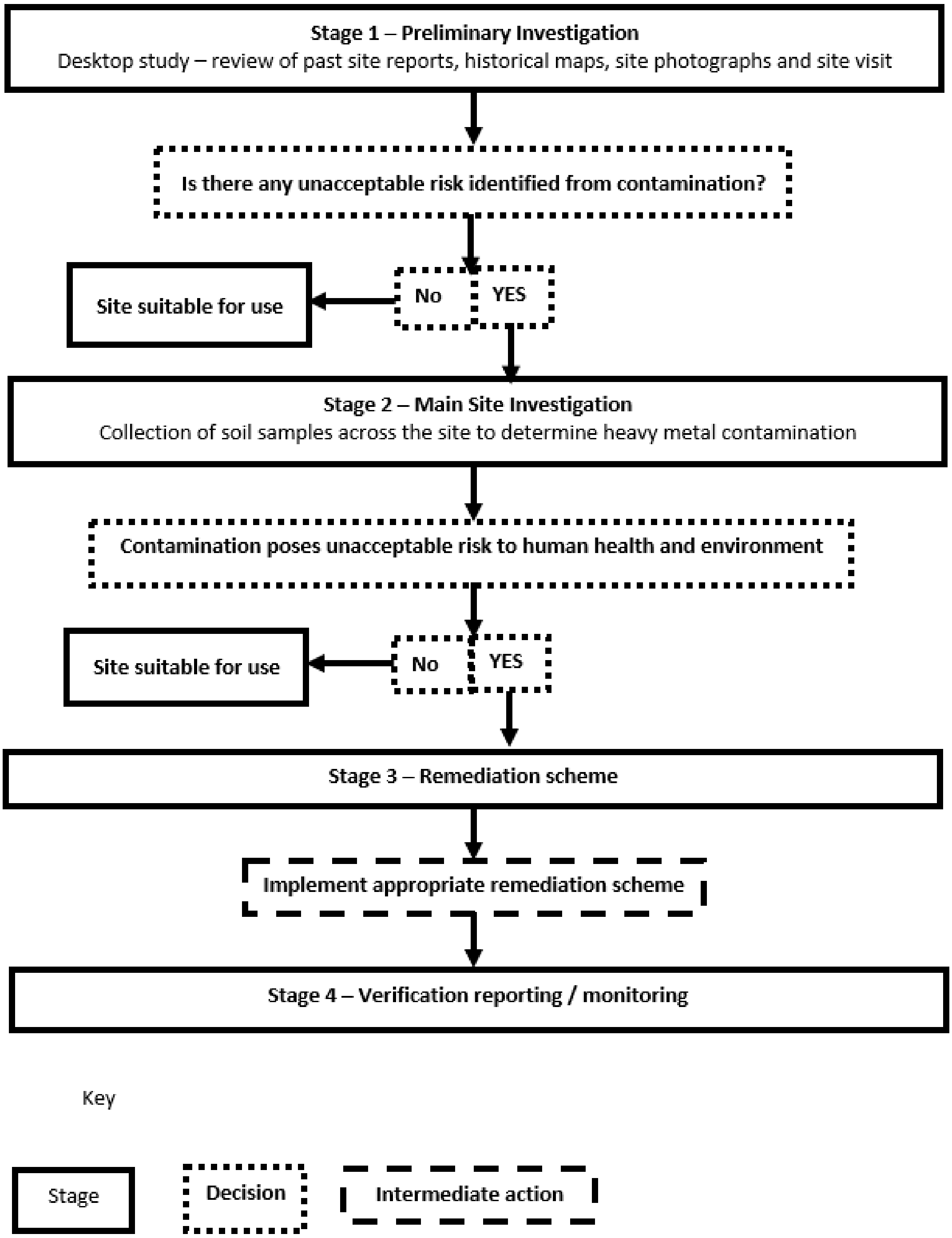


Figure 2.3. A flowchart showing the standard contaminated land risk assessment investigation procedure (Adapted from: The Cumbria Contaminated Land Officer Group, 2013)

2.5.4 Remediation of Contaminated Land (Risk Control)

Once it is established that land is contaminated, the enforcing authority must be clear on how the land should be remediated and must issue a remediation notice where appropriate for such remediation to be carried out. In the case of remediating the land, the enforcing authority may be the local authority that identified the contaminated land, or the Environment Agency, which oversees the responsibility once the contaminated land has been identified especially if the land is considered a "special site" (Table 2.3).

Table 2.3. Main responsibilities of Local Authority and Environment Agency under Part 2A regime.

Local Authorities Responsibilities	**Environment Agency Responsibilities**
• Responsible for Production and publication of an inspection strategy	• Disseminate relevant information held by the Agency to local authorities
• Carry out Inspection in their areas with the aim of identifying contaminated land	• Give advice to local authorities regarding remediation of contaminated land
• Responsible for consulting the Environment Agency regarding pollution of controlled waters	• Give advice to local authorities on how to recognise and deal with pollution of controlled waters
• Make sure land identified as contaminated land is remediated	• Carry out inspection on designated potential special sites for local authority
• Handover sites designated as special sites to the Environment Agency	• Ensure maintenance of a public register of regulatory action for special sites
• Ensure maintenance of a public register of regulatory action	• Develop a national report on the condition of contaminated land

Source: Environment Agency (2002)

The major criteria for designating a land as special sites, and various legal requirements for issuing remediation notices, are set out in the Contaminated Land (England) Regulations 2006 (DEFRA, 2012). The statutory guidance must be consulted in terms of: (a) deciding what remediation strategy/action should be included in the remediation notice (b) reassuring that remediation being carried out is appropriate, or will be, carried out without issuance of a notice; or (c) deciding what remediation action plan is going to be implemented. Enforcing authority is expected to ensure any remediation action carried must be practicable and effective. The major goal of the remediation should be to eliminate significant contaminant linkages that have been identified or permanently disturb/derange them so that they remain insignificant and reduce the risks below unacceptable level and/or take appropriate measures that would remedy the harm or pollution created by a significant contaminant linkage. In carrying out remediation of contaminated land, a range of treatment, assessment and monitoring actions may be involved, and in some cases, different remediation actions may be used in combination or consecutively to achieve the complete land remediation. For example, in cases where the main goal of remediation is to remove or disrupt significant contaminant linkages permanently, remediation action plan should involve demonstrable disruption or elimination of the significant contaminant linkage(s) responsible for the contamination of the land to reduce or eliminate unacceptable risks to receptors from such contaminated land. In addition, remediation may require assessment or monitoring actions as part of remediation. For example, assessment actions may be needed in terms of characterising and understanding the nature of significant contaminant linkage(s), which will help the authority to decide what remediation action, should be implemented. Assessment may also be required whilst carrying out other remediation actions, or after other remediation actions have been conducted (e.g., to see how effective other remediation measures are, or to explore further remediation actions). After remediation of contaminated land, further monitoring actions may be needed to assess whether the remediation that had been carried out has been successful or whether a further assessment or remedial action may be required.

2.5.5 Recovery of Cost of Remediation

The 'polluter pays' principle is an important principle of Part 2A regime, whereby the person who is responsible for the pollution then pays the cost of clean-up. The UK is committed to the polluter pays principle and Part 2A outlined the procedure for identifying who should pay for the cost of cleaning up a site deemed to be contaminated. Considering current land pollution incidents, the polluter pay principle may seem very reasonable; however, in terms of applying this principle retrospectively, it may be unfair to companies responsible for land contamination even though they followed acceptable practices and complied with all available regulations at the time (DoE, 1994; RICS, March 1994). According to the Environment Agency (2016), there are two classes of people responsible for the remediation of contaminated land as defined in the regulations: (i) Class A: those responsible for the pollution or deliberately permitted the pollution (ii) Class B: refers to a site owner or occupier and can only be liable if a Class A appropriate person responsible for a particular pollution cannot be traced or found.

In terms of deciding on whether to recover the cost of remediation and how much, the enforcing authority shall consider any hardship the recovery may cause the payer and shall refer to any guidance issued by the Secretary of State for the purposes of the recovering the remediation cost. In making decision for cost recovery, the enforcing authority shall ensure that the overall result is as fair and equitable as possible for all who may be involved in the cost recovery, including national and local taxpayers. Where possible, the 'polluter pays' principle should be applied with the target that the polluter should be responsible for the remediation cost. There may be other considerations the enforcing authority should have regard to when making decision for cost recovery; for example, different situations may arise due to variations in land history and ownerships and who is liable for remediation. Generally, the enforcing authority should recover all of its reasonable costs.

There may be circumstances where land is currently used for housing, in such scenarios; the best way for a potentially liable individual to deal with land contamination without recourse to payment is through the redevelopment processes. For example, land deemed to be potentially contaminated may be sold to developers subject to the relevant planning permission, which can be redeveloped, by the developer and restore the beneficial use of the land. Based on the proposed end use of land, there may be fiscal incentives such as the Contaminated Land Tax Credit and Landfill Tax Credit available for regeneration of land that suffered contamination. In some circumstances, where the land is being redeveloped and it is established that such landfalls within one of the 20% most deprived wards in the UK, potential buyers are exempt from Stamp Duty.

2.6 Sites with Multiple Sources of Historical Contamination

Like many other industrialised nations, UK has a legacy of contaminated sites due to different historical human activities (PHE, 2019). Over the last two centuries, urban characteristics in the UK have changed rapidly due to a legacy of historical industrial activities. In most cities and towns in the UK, industrial and manufacturing sectors grew tremendously in the late 18th and early 19th centuries, although, these activities started declining considerably during the 1970s and 1980s. These human-induced historical activities created a legacy of contamination in many urban areas. These contaminated sites may be associated with potentially harmful substances including oils, tars, waste metals, organic compounds, gases and mining materials that left over from or, introduced by the historical activities that took place at these sites (PHE, 2019). Although, it is recognised that all lands are associated with background levels of substances, including those that are present naturally and those that are as a result of various human induced activities (DEFRA, 2012). However, in some areas, the concentrations of these substances are higher due to a legacy of historical industrial land use and waste disposal to landfill, but in a few circumstances, there might be a potential risk to health or to the environment from these contaminated sites (PHE, 2019). In the legal sense, land is deemed “contaminated” if there is evidence to suggest it poses a sufficiently high risk to health or the environment and meets the criteria for Part 2A regime of the Environmental Protection Act 1990. This means that significant contamination linkages (i.e., source-pathway-receptor) must exists for the land to be considered as contaminated land. Thus, there has to be a “contaminant linkage” for harm to occur. Other terms, such as “land affected by contamination” or “land contamination” may also be used in a much broader sense to describe land where contaminants exist but not sufficient to cause significant harm or risk to public health to satisfy the criteria for legal definition of contaminated land (Yorkshire & Humberside Pollution Advisory Council, 2015).

There has been a wide variation on the previously published figures on the scope of land affected by contamination in the UK. In England, about 34 percent of land covers urban, semi-urban and industrial areas (Johnson et al., 2012). Another estimate is that there is between 50,000 and 300,000 hectares, totalling about 100,000 sites (Environment Agency, 2002). Up to 5,000 to 20,000 of these contaminated sites may be problematic and require remediation to remove unacceptable risk to human health or environment from these sites (Environment Agency, 2002). Presently in the UK, contaminated land is managed under Part 2A of the Environmental Protection Act 1990. Under this Act, contaminated land is defined under Section 78A (2) A as:

> Any land which appears to the local authority in whose area the land is situated to be in such a condition, by reason of substance in, on or under the land that, (i) significant harm is being caused or there is significant possibility of such harm being caused; or (ii) pollution of controlled waters is likely to be caused (DEFRA, 2012, p. 17).

If land contamination is not adequately tackled, it could cause harm to human health, property, to the ecological system and to human health through dermal contact, dust inhalation and soil ingestion (Abrahams, 2002; Siciliano et al., 2009) and also limit or preclude the land from being used for new development (Department for Communities & Local Government, 2014). Land contamination can affect the land quality, land use, surface and ground water and the contamination, if high enough, may represent a potential barrier to the future use of the site for residential, business, urban agriculture, greenspace and other purposes (Environment Agency, 2001). The strategic goal of UK soil protection policies is to reduce the inputs of heavy metals to soils (DEFRA, 2004) and the EU (European Commission, 2002). In June 2016, the UK government stated:

> More action required to protect UK soil health! Our industrial heritage means that hundreds of thousands of sites across the country are contaminated by chemicals, heavy metals, tar, asbestos and landfill. The Government’s ambition to manage the UK’s soil sustainably by 2030 will not be met unless further action is taken (House of Commons Environmental Audit Committee, 2016, para. 1).

Among the potentially toxic contaminants, heavy metal contamination is one of the most challenging environmental problems. This is due to the large number of sources and the properties of the heavy metals. They are toxic and non-biodegradable. Hence they bio-accumulate and bio-magnify and tend to have deleterious effects over many years (Pandey et al., 2003; Qing et al., 2015). In the UK, there is a widespread soil contamination associated mostly with metals and metalloids, and approximately 300,000 hectares of soil are believed to have been contaminated with toxic elements such as cadmium, arsenic and lead as a result of the UK's past industrial heritage (Environment Agency, 2009). Because the concentrations of heavy metals in soil may get to a level where they could become toxic and thus, may cause a potential risk to human health and environment. It has become necessary to control the concentrations of heavy metals in soil through effective legislations. Many countries have developed a guideline aimed at regulating the concentrations of heavy metals in soil and UK is not exception to this. In 1987, the UK government in conjunction with Interdepartmental

Committee on the Redevelopment of Contaminated Land (ICRCL) came up with the first guidance (Note 59/83) regarding the concentrations of heavy metals in soil which was published in 1983 and updated in 1987 respectively (ICRCL, 1983, 1987). This guidance was used for appraisal of the levels of metal contaminated soil for many years; however, this guidance was later withdrawn because it was out of date and needed to be modified to reflect the current law regarding heavy metal concentrations in soil (DEFRA, 2002a). Consequently, a new legislation called Note 70/90 was introduced in 1990 and, this law was aimed at amending the regulations on contaminated land so as to remove the adverse effects that are associated with contaminated land with regards to environment. The new regulation sets a standard trigger threshold value above which soil is considered “contaminated “and the concentrations of heavy metals in soil that are deemed to cause risk to health and environment. However, if the heavy metal concentrations in soil are below the trigger values, such soil is considered “uncontaminated” (ICRCL, 1990).

Following this, a new law called Environmental Protection Act 1990 came into effect in 2002 under Part 2A contaminated land (DEFRA, Environment Agency, 2002b). This law aims at identifying and dealing with unacceptable risk to human health and environment from contaminated land based on different land uses. Later on, the Contaminated Land Exposure Assessment Model (CLEA) software package was used to create the soil guideline values (SGVs) and thus, substituting the soil guideline values initially derived by ICRCL in Note 59/83. Soil Guideline Values (SGVs) are assessment criteria set up by the UK and primarily used to assess the risk to human health from exposure to contaminated soil (Environment Agency, 2009). As lands are used differently by different people, it affects who and how people might be affected by the contamination. Therefore, SGVs are derived based on different land use (e.g., allotments, commercial, residential etc). SGV represent 'trigger values' used specifically for screening-out areas associated with low risk with reference to land contamination. SGV give information about the representative levels of chemicals in soil below which the long-term health risks are likely to be low (Environment Agency, 2009).

Moreover, a report by DEFRA (2014) revealed that between 2000 and 2013, most sites posing a significant unacceptable risk to public health were contaminated by chemical substances such lead, chromium, nickel and hydrocarbons (persistence aromatic hydrocarbons). In England and Wales, about 80 percent of all the identified sites are contaminated with metals and metalloids (Environment Agency, 2009). Much of the contaminated sites are currently left derelict or underutilised, and this is mostly true for areas that experienced a long history of industrial heritage and as a result, suffered a drastic reduction in inward investment over the last few decades giving rise to large areas of potentially contaminated land where land value is too low for cost-effective remediation (Doick et al., 2006). Analyses of survey undertaken by Environment Agency in 2007 under Part 2A of the Environmental Protection Act 1990 showed that only 144 out of 746 identified contaminated sites had been remediated according to report (Environment Agency, 2009).

Greater Manchester was an historical hub of industrial activities and factories were discharging contaminants directly into the soil and rivers and along with other unsustainable waste disposal practices that have now left a legacy of potential contamination across the conurbation (Douglas et al., 2002; Groundwork Oldham & Rochdale, 2008; Manchester City Council Contaminated Land Strategy, 2011; Hurley et al., 2017). Manchester’s industrial heritage extensively focused on textile industries and other industrial and commercial activities such as paper and printing works, tanneries, saw mills, chemical plants, engineering works, and coal mines (Hurley et al., 2017). By the 19th century, increased industrial activities had led to the operation of many mills, works and factories that were discharging contaminants directly into the soil and rivers (Douglas et al., 2002). The uncontrollable release of contaminants from a variety of industrial sources over a long period resulted in large quantities of heavy metals across the Greater Manchester region. Early surveys found that high level of contaminants were deposited into river channels (Coates1862; Mersey and Irwell Joint Committee1892; Douglas et al., 2002). Lead and zinc salts were historically used in the textile production industry to soften and dye fabrics (Choudhury 2006). Hurley et al. (2017) reported that there was a positive relationship between high metal(loid) concentrations and areas with high densities of textile mills across the Manchester region.

These historical contaminations spanned through Wrigley Head, Moston Brook situated in the Greater Manchester, and had potentially contaminated the soil and groundwater beneath at this site (Groundwork Oldham & Rochdale, 2008). Moston Brook was regarded as an active part of the northern sector of ‘Cottonopolis’ during the 18th and

19th centuries (Groundwork Oldham & Rochdale, 2008). During this period, this area was predominantly associated with bleaching and dyeing works as an important finishing process of manufacturing cotton fabrics and Moston Brook was actively involved in these industrial and commercial processes. As a result of various industrial and commercial activity in the 18th, 19th and 20th centuries, Moston Brook was affected by the past industrial legacy and waste disposal to landfills which took place between these periods (Groundwork Oldham & Rochdale, 2008). Management and decontamination of these sites through appropriate remediation techniques has been a subject of public interest and presents clear scientific and technical setbacks because heavy metals cannot be degraded further into less toxic state unlike organic contaminants (Jiang et al., 2015). From the environmental point of view, these contaminated sites need to be remediated and rehabilitated to the highest possible standard irrespective of their potential costs to ensure their productive uses.

The review of the literature has identified a clear protocol to follow in terms of the assessment of contaminated land. However, the information contained within the literature tends to relate to a site as if it were homogeneous. In sites such as Wrigley Head, there have been multiple sources of contamination and the contamination across the site are not homogeneous. Small scale spatial variations need to be investigated in order to understand the contamination profile of sites such as this. Conducting such a study will be an important element of this research. The investigated site has a history of multiple sources of contamination and this, represents a significant barrier to the use of the site, and may further prevent the site from being used for various beneficial ways. In order to develop an understanding of the background context of the site regarding its historical use, a preliminary study was undertaken. Information was gathered through the historical maps, previous site reports and walkover surveys, site visit, and desk study of environmental context. This will help to develop an understanding of the site conditions as well as the types and nature of multiple contamination at the site and any evidence on the site not documented and any potential challenge to the present investigation. The preliminary study marks the first stage of any contaminated site investigation.

In addition, results from the preliminary study suggest that heavy metal contamination is one of the major historical contaminations associated with the investigated site

(Groundwork Oldham & Rochdale, 2008, Miller 2011). This represents a significant barrier to the use of the site looking at the challenges heavy metal contamination presents and may further prevent the site from being used for various beneficial ways. Thus, an investigation into heavy metal contamination and spatial variations across the site was conducted in order to understand heavy metal contamination profile at the site. The study of heavy metal contamination at the site is crucial for developing sound management strategies to minimise the potential environmental impacts and ensure the beneficial use of the case study site. In addition, the findings obtained from such a study have implications for site risk assessment, remediation and restoration.

2.7 Heavy Metal Uptake and Transfer in Soil and Plants.

Soil–plant transfer of trace elements is naturally a part of chemical element cycling and a very complex process facilitated by both natural and anthropogenic factors (Kabata-Pendias, 2004). The concentration and distribution of heavy metals and the extent of mobility and bioavailability of heavy metals in soil-plant systems is a complex process and could be influenced by a range of factors such as chemical, biological and environmental characteristics (Li & Thornton, 2001; Peijnenburg & Jager, 2003; Panuccio et al., 2009). Bioavailable fractions of metals in soil play a very crucial role because this fraction controls the form and extent of metal uptake by plants and equally determines the amount that would be transferred to above-ground biomass of plants (Naidu et al., 2003). The term "bioavailability" refers to the potential of receptor organisms to take up chemicals from food or from the abiotic environment to the level that the chemicals may become involved in the organism metabolic processes (National Research Council, 2003). Similarly, "bioavailable fraction" refers to the biologically available chemical fraction of heavy metals that can be taken up by an organism and can react with its metabolic process (Campbell et al., 1995), or it refers to the fraction of the total chemical element that can interact with a biological target (Vangronsveld & Cunningham, 1998). For bioavailability of heavy metal to occur in plants, heavy metals must make a contact with plant in what can be referred as "physical accessibility" and must be in mobile and chemically accessible form for absorption by plants' roots (Adriano et al., 2004). The mobility and uptake of heavy metals in the soil-plant system is affected by both soil and plant parameters that influence the processes taking place outside and inside of the plant body mainly by selective uptake and translocation procedures (Antoniadis et al., 2017). Mobility and bioavailability of heavy metals is generally dependent on geochemical, environmental and biological factors and as a result, accurate prediction of metal uptake by plants and the associated risks of metals should consider both biotic and abiotic factors influencing metal mobility and bioavailability in soil (Kabata-Pendias, 2004).

Studies have shown that metals such as manganese, iron, nickel, copper and zinc are essential for plant growth and metabolism (Fox & Guerinot, 1998), and act as co-factors for many enzymatic reactions taking place in plants. However, at excessive concentrations, these metals could be phytotoxic, which may be detrimental to plants physiological functions and development (Gangwar et al., 2014). On the other hand, metals such as mercury, lead, arsenic, and cadmium have been found to play no biological functions in the plants and as a result, these set of metals may be toxic to the plants even at low concentration (Gangwar et al., 2014). The problem associated with plant uptake of heavy metals is that plants are not able to distinguish non-essential metals and as result, during uptake, both essential and non-essential metals are taken up together by plants (Gangwar et al., 2014).

In view of these challenges associated with heavy metals, plants have developed specialised mechanisms that enable them to sense, transport and regulate essential elements within their physiological thresholds and to regulate the uptake and accumulation of non-essential elements within their system (Mendoza-Cozatl et al., 2011). For instance, studies have shown that metal transporters play a significant role in ensuring intracellular metal homeostasis within the plant system (Pilon et al., 2009). These transporter proteins help in mediating the uptake of heavy metals especially in root cells and regulate the movement of metals occurring between plant cells and their organs (Gangwar et al., 2014). These transporter proteins also play a very essential role in the detoxification of metals by mediating the metal transport from cytosol to the vacuolar compartment (Salt & Rauser, 1995; Rea et al., 1998). These metabolic processes help the plants to regulate the metal uptake within their system (Clemens, 2001). Similarly, plants have developed defensive mechanisms that enable them to control the uptake, accumulation and translocation of heavy metals; in which they are able to detoxify them by ignoring the free ionic forms found in cytoplasm (Rascio & Navari-Izzo, 2011). One of the defensive strategies adopted by plants to regulate the uptake and accumulation of dangerous metals is preventing the intake of these metals into their root cells in the rhizosphere through entrapment and then bind them to the exuded organic acids (Watanabe & Osaki, 2002) or to ionic groups found in the cell wall (Dalla Vecchia et al., 2005; Rascio et al., 2008). As result of this strategy, greater amounts of metals entering the plant roots are only restricted to the root cells only and further detoxified by complexation process with organic acids produced in the plants' root, amino acids or can be sequestered into plant vacuoles (Hall, 2002). This is a common defensive mechanism found in potential excluders. In the case of hyperaccumulating plants, they take up large amounts of metals with their roots, and then translocate them to aboveground biomass without any symptom of stress and phytotoxicity (Revees, 2006). This type of plant species tends to shade their leaves as a means of discarding these toxic metals particularly in the period of seasonal leaf drops (Kuzovkina et al., 2004). Some of the distinctive features of these plants are greater efficiency for metal uptake from soil; ability to translocate metals from root-to-shoot at very fast rate and the capacity of plant species to detoxify high amounts of metal (Rascio & Navari-Izzo, 2011). In soil, the most important metal pools exist as exchangeable fractions, metals bound to carbonates, metals bound to manganese and iron ox-hydroxides and those bound to mineral structures (Monterroso et al., 2014). The level of mobility, as well as the rate at which heavy metals become available in soil, is determined by the equilibria that exist between the above-mentioned fractions rather than the soil total metal concentration (Monterroso et al., 2014). Similarly, the soil parameters and the constituents of the soil solution control the dynamic equilibrium that exists between metals in solution and soil solid phase.

Soil-plant transfer of trace elements is a key step leading to the entry of potentially toxic elements into the food chain. Uptake and accumulation of toxic metals through soil-plant system has been identified as a major pathway through which humans are exposed to adverse effects of heavy metals (Liu et al., 2007). Once potential toxic elements gain entry into the food chain, they pass through several processes such as bioaccumulation, transformation, and bio-magnification and, thus, it is very difficult to remove heavy metals from living organisms (Widowati 2012). A high concentration of heavy metals in soil results in metal bioaccumulation in plants due to increase absorption (Muchuweti et al., 2006). Accumulation of toxic metals in soil and plants is an important environmental issue because these metals can be subsequently transmitted to human body and animals through food chain where they can cause potential toxic effects (Reeves & Chaney, 2008; Singh et al., 2010). Empirical models which are effective for both large scale and field applications taking into account plant features and soil factors have been successfully used to predict concentrations of heavy metals in plants (Ye et al., 2014). A study by Adams et al. (2004) predicted the concentrations of cadmium in wheat grain using cadmium concentration in wheat grain and pH. Similarly, Cao et al. (2014), successfully predicted heavy metal concentrations in rice grains using a combination of soil pH and EDTA extracted from cadmium, zinc, chromium, lead and copper concentrations. Furthermore, Warne et al. (2008) estimated the phytotoxic effects of heavy metals across different soil-crop systems using soil properties and found that this was one of the fundamental steps in improving risk assessment of heavy metals.

Plants possess the ability to influence heavy metal behaviour by transforming the fraction of metals to ensure that these metal ions become easier for them to be taken: a condition achieved through root exudations or by influencing the pH of the rhizosphere (Hinsinger et al., 2003). Plants may have various influences in terms of heavy metal uptake due to variation in plant species and in similar way; their responses to heavy metals may vary as well. For example, metal uptake and accumulation in plants have been found to differ among plant species and different uptake patterns have been observed in *Salix* species (Vandecasteele et al., 2004). Nguyen et al. (2009) reported that *Eleocharis acicularis* hyper-accumulated notable amount of lead in abandoned mine site. Similarly, Ranjeev et al. (2007) found that *Eichhornnia crassipes* accumulated high amounts of iron, manganese and copper in an industrial effluent contaminated site. Moreover, Yoon et al. (2006) found that various herbaceous plants examined from a contaminated site in Florida had the capacity to take up lead, copper and zinc. The extent of bioavailability of heavy metals is determined by the chemical and physiological conditions prevailing in the rhizosphere (Ovecka & Takac, 2014). Furthermore, plants are known to produce exudates from their roots which can influence the mobility and bioavailability of metals in soil. The presence of these organic acids may affect desorption, solubility and mobility of metals in soil (Schwab et al., 2005). Simple organic acids from plants have been identified to have the potential to enhance metal mobility in soil through reduction in soil pH of the rhizosphere and formation of stable complexes with metal ions and as a result influence the behaviour of these metals in soil-plant system (Renella et al., 2004). In addition, plant roots can initiate acidification of soil environment with protons expelled from the roots and, as result, mobilise heavy metals (Raskin et al., 1994).

An experiment conducted by Chen et al. (2016) on the characteristics of heavy metal transfer and their influencing factors in different soil–crop systems of the industrialisation region, China, revealed that soil pH and total organic matter were the major implicating factors controlling bioavailability and uptake of heavy metals from soil by rice plants. In this study, three different plant species: rice (*Oryza sativa*.), wheat (*Triticum*) and canola (*Brassica napus*) were used. The results showed that the transfer capacity of the investigated heavy metals from soil-rice plant was observed to be stronger in comparisons to other two plants studied. In a similar way, wheat demonstrated a strong capacity to translocate metals such as cadmium, zinc and cadmium from the root to above-ground parts while canola exhibited restricted effects on the uptake and translocation of copper and cadmium.

Generally, plants absorb a number of elements from soil, including essential elements required for growth and development and non-essential elements which have no known biological functions, and some non-essential elements such as mercury and lead can be potentially toxic at low concentrations (Peralta-Videa et al., 2009). In contaminated soil, heavy metals can be potentially absorbed by the plants, which may cause ecosystem disruption and adverse human health effects (El-Sikaily et al., 2004). Many studies have shown that uptake and accumulation of heavy metals by plants growing in contaminated soil represents a potential adverse human health effect due to subsequent contamination of food chain (Brun et al., 2001; Ginocchio et al., 2002). Similarly, uptake and accumulation of trace elements in aboveground plant tissues may also lead to increase in trace element accumulation in the topsoil due to leaves deposition and decomposition or can cause exposure pathways for metal accumulation in food chain (Unterbrunner et al., 2007). Plants can absorb both essential and non-essential elements from soil in response to concentration gradients caused by selective root uptake of ions, or through diffusion of elements in soil (Peralta-Videa et al., 2009). It has been observed that not all heavy metals in soil are available for plant uptake; however, plant uptake is determined by the form and the species of metal in soil solution. Heavy metals, which are available for plant uptake, are those that exist mostly in soluble fractions in soil solution or fractions of metals that can easily be solubilised by root exudates (Blaylock & Huang, 2000).

The uptake and transfer of heavy metals from root to shoot can be influenced by soil properties, plant species, microorganisms and types of metal (Yanai et al., 2006; Hinsinger & Courchesne, 2008). Plants have the capacity to mobilise heavy metals bound to the soil solid phase into soil solution and can accumulate these metal ions through their roots. Similarly, plants may exhibit varying capacities in terms of heavy metal accumulation and translocation depending on plant species in question and the prevailing environmental conditions (Weis & Weis, 2004; Sheoran & Sheoran, 2006). Baker (1981) categorically classified plants into three major categories in terms of their heavy metal uptake; (i) *excluders*: these are plants that grow in metal contaminated soil and maintain low shoot metal concentration level up to a critical soil value, above this level, the plants relative root-shoot accumulation may occur, (ii) *accumulators*: these group of plants concentrate metals in the above ground parts without any symptoms of phytotoxicity' and (iii) *indicators*: these plants regulate the uptake and transport of metals to the shoot so that internal concentration reflects external levels until toxicity may occur. Plant species that have the capacity to accumulate high amounts of metals at their above-ground tissues have implications for phytoremediation of heavy metal contaminated soils as these accumulated metals could be removed and disposed to appropriate places through harvesting (Dzantor & Beauchamp, 2002; Pilon-Smits, 2005). The quantity of trace elements taken up by plants in relation to the soil trace element concentration can be estimated by the concentration factor (CF), expressed as the ratio of trace element concentration in a plant to the concentration of trace element in soil (Noli & Tsamos, 2016).

In addition, uptake of bioavailable heavy metals, metal chelation and compartmentation in the root, transport of metals from root to shoot as well as the chelation and compartmentation of metals occurring in the leaves have been recognised as the basic processes associated with uptake of metals from the soil and translocation to plant tissue (Weis & Weis, 2004; Pilon-Smits, 2005; Colangelo & Guerinot, 2006). The rate at which plants potentially absorb metals from the root to shoot is controlled by metal bioavailability whereas soil pH, redox potential and organic matter contents have been linked to influence the rate at which metals are released unto soil solution (Pilon-Smits, 2005; Sposito, 2008;

Violante et al., 2010). Figure 2.3 shows the processes of heavy metal uptake and phytoextraction in soil.

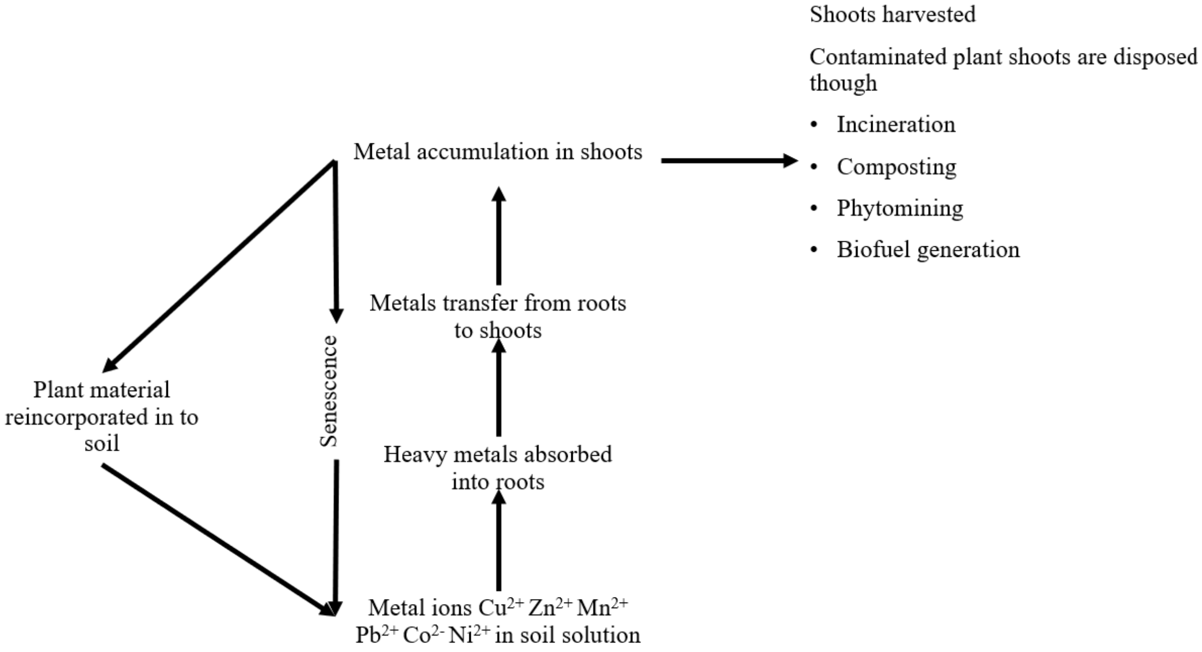


Figure 2.4. Schematic diagram illustrating the processes of heavy metal uptake from soil by plants (Modified from Favas et al., 2014).

Plants also possess the ability to influence heavy metal sequestration mechanisms through organic matter production, by creating an oxic environment in the plant's rhizosphere and by excretion of proton exudates (Mishra et al., 2017). Plant metal uptake and response could differ in a given soil-plant system (Kabata-Pendias, 2001). For plants to uptake heavy metals, there must be the presence of metal soluble species adjacent to the plant roots. Although, the rate at which plants tolerate heavy metals in soil is dependent on the balance between the rate of plant uptake and detoxification within plant system (McGregor, 1999). The soluble forms of metals and the rate at which metal ions are released will determine the rate and extent of uptake by plants and their level of toxicity to plants and animals (Cataldo & Wildung, 1978b). The accumulation of these toxic metals in both plant root and shoot increases as the available metal content in the soil increases. The uptake and translocation of heavy metals within the plant system can vary, for instance, it has been observed that lead tends to accumulate in plant roots rather than in the above ground biomass because of the high immobility associated with lead while other metals such as cadmium can easily accumulate in the aerial plant parts (Garbisu & Alkorta, 2001). Therefore, heavy metal uptake by plants could pose a potential risk to wild animals, grazing cattle and humans who eat the above ground portions of plants. To assess the environmental risk from the exposure to contaminated plant tissues in a contaminated site, it is necessary to understand the status of heavy metal in plant system.

Heavy metal contamination of soil and vegetable plants is one of the most challenging ecological problems particularly in developing industrialised countries (Gupta et al., 2019). Soil and vegetable contamination with heavy metals has become a burning issue due to metal accumulation and potential human health risks that are associated with it (Gupta et al., 2019). Crops have the capacity to take up heavy metals and retain them in their tissues and these metals can equally interact with roots through absorption processes in a given heavy metal contaminated soil; thereby increasing their adverse effects on both plants and animals (Rosselli et al., 2006). Vegetable plants consist large parts of human diets, which supply the body with essential nutrients such as carbohydrates, minerals, dietary fibre, proteins, vitamins and antioxidant (Slavin & Lloyd, 2012). Vegetable plants uptake metals from different sources mostly from metal contaminated soil and through atmospheric deposition of particulate matter and when these metals are taken up by vegetable plants, they are first absorbed in the root apoplast and subsequently distributed to other parts of the plants through diverse pathways where they impede plants growth by affecting the plant physiological, metabolic and biochemical processes (Sharma et al., 2007; Singh et al., 2016; Gupta et al., 2019). Excessive uptake and accumulation of heavy metals by vegetable plants are associated with two consequences, viz; contamination of harvested vegetable plants which has potential risk to human health and reduction of plant yield due to inhibition of metabolic activities of the plants (Singh et al., 2012).

The uptake and accumulation of heavy metals by crop plants and subsequent contamination of food chain represent a potential risk to human health (Jan et al., 2011) Analysis of plants comprising wild and cultivated plant species to determine heavy metals is one of the ways of evaluating risks of metal contaminated soil (Wenzel et al., 1993; Blaylock et al., 2003). Heavy metal contents in crop plants are evaluated by comparing metal concentrations in soil in relation to the concentrations in plants (Khan et al., 2010a; Li et al., 2012). Vegetables are susceptible to heavy metal contamination at elevated concentrations, particularly at large-scale irrigation involving wastewater and inorganic fertilizer applications significantly increase heavy metal contamination in food chain (Gil et al., 2004). Consumption of heavy metal contaminated vegetables may pose a significant risk to human health (Trebolazabala et al., 2017). Uptake and accumulation of heavy metals by vegetable crops can be influenced by a wide range of factors such as plant factors, physicochemical soil parameters, environmental factors, biotic factors, sampling seasons, geographical location and these factors often act concurrently and as a result make it difficult to specifically identify mechanism underpinning uptake of heavy metals by vegetable crops (Trebolazabala et al., 2017).

The uptake, accumulation and distribution of heavy metals in plants is an index of the bioavailable and mobile fractions of metals and not necessarily dependent on the total metal concentration in soil (Zeng et al., 2011). Heavy metal contamination have significantly adverse effects on plant growth and development (López-Millán et al., 2009); other potential toxic effects may include browning of the roots, alteration of mineral concentrations and photosynthesis in plants (López-Millán et al. 2009). At higher concentrations, metals move from roots to shoots of the plant (Rodríguez-Celma et al., 2010). Cobb et al. (2000) performed a laboratory experiment to evaluate the effect of mine waste on the uptake of arsenic, cadmium, lead and zinc by lettuce, radish, bean and tomato in contaminated mine waste soil and found that lettuce and radish accumulated significant levels of heavy metals compared to tomato and bean; implying that consumption of lettuce and radish cultivated in such a mining area could pose a greater risk to human health than beans and tomato. In addition, higher concentrations of lead in Chinese cabbage, lettuce, and Chinese leaf mustard due to substantial industrial contamination has been documented (Chang, Yu, et al., 2014). Furthermore, Osma et al. (2012) reported higher concentrations of cadmium, chromium, copper, nickel, lead and zinc from *Brassica oleraceae* var. *acephala*, and *Beta vulgaris* cultivated in an industrial area. (A better knowledge of the soil-plant metal transfer factors is necessary for adopting and implementing effective remediation approach for contaminated soil (Rai et al., 2019).

2.8 Barriers to Use Associated with Contaminated Land

Contaminated land is recognised as one of the major threats to use of soil resources in Europe (Duffield et al., 2000; Swartjes et al., 2008; Rodrigues et al., 2009). However, it is important to recognise that the presence of a contaminant in, on or under the land does not necessarily mean that a potential significant risk can be anticipated. What determines if a land poses an unacceptable risk to a receptor is when both a contaminant (a source) and a receptor, for example, groundwater, people or the wider environment, are established to be present at a site with a pathway linking both of them. In other words, this means that there must be presence of a significant contamination linkage (source – pathway – receptor) for a harm to occur in a contaminated land. In contaminated land, there may be a threat to human health, ecological receptors, water and property from the contamination (Bone et al., 2010; Fonge et al., 2011). Contaminated land has a significant implication for environmental justice, and within the local context, frequently represents unwanted land uses, and often areas where deprived/neglected communities that are disadvantaged or marginalised people live (Song et al., 2019). Contaminated land is a barrier for the beneficial land uses. When a parcel of land is contaminated, a large group of people such as stakeholders, developers, financiers, engineers, insurers, regulators, and the general public may be affected in different ways (Yorkshire & Humberside Pollution Advisory Council, 2015). Consequently, the inability to adequately tackle the contamination could cause potential risks to human health, property, and the wider environment**.**

Contaminated land may present risk to building, and thus, preclude developments on contaminated land. For example, building, building materials and services may be affected by the presence of contamination such as toxic substances, combustible materials, unstable fill materials and/or other compounds containing in, on or under the land (Environment Agency, 2001). In the course of development on contaminated land, a significant contaminant linkage may be created, and this may represent a potential risk to the new receptors that might be introduced, for instance, exposing residents to a contaminated site (Yorkshire & Humberside Pollution Advisory Council, 2015). There is also a likelihood that the presence of contaminants may affect the health of the residents who are using the building and are frequently exposed to the contaminated land through inhalation of contaminated dust, ingestion of contaminated soil or dermal contact with the contaminated soil materials. In addition, the presence of flammable contaminants such as gases particularly in confined spaces may cause fire risk to buildings in form of explosion (Manchester City Council, 2021). This underground fire explosion may trigger ground subsidence and eventually lead to the damage of the buildings' structures. Similarly, there might be a risk of chemical attack to buildings from the contamination. For example, a site contaminated by sulphate may attack concrete structures of buildings and building materials (Manchester City Council, 2021). In addition, the presence of acids, oils and tarry substances may trigger metal corrosion or cause plastic and rubber materials and other polymeric materials used in pipe work in building construction to be attacked (Manchester City Council, 2021). Moreover, contaminants such as heavy metals can affect the use of site for construction due to the contamination in soil being above the threshold levels, and as a result, may not be suitable for some land uses, for example, residential, allotments, commercial/industrial without subjecting the land for further investigations and likely remediation (Environment Agency, 2001).

Contaminated land may pose a risk to human health and environment through several pathways. Contaminated land presents a major barrier to potential use of urban soil for urban farming because most urban soil are below the stipulated standards for agricultural soil (Platt, 2012). There are many benefits derived from urban agriculture such as availability of inexpensive fresh foods and increased economic activities, increased biodiversity, enhanced nutrient cycling, storm water management, and improvement in air quality and local climate regulation (Platt, 2012; Camps-Calvet et al., 2016). Such benefits can be reduced or eliminated when land is contaminated with various toxic substances. Similarly, if the soil is used for growing crops, the contaminants may be taken up by plants which represents a potential risk to human health through food chain. Food crops grown in contaminated soil, for instance, soil contaminated with heavy metals and other contaminants (e.g., persistence organic pollutants) could take up heavy metals in the amounts above the legal tolerable limits and /or may pose a risk to human health (Manchester City Council, 2021). Consequently, the health of people could be affected by the contamination through consumption of contaminated vegetables grown in contaminated soil (Yorkshire & Humberside Pollution Advisory Council, 2015). The exposure pathways are through ingestion, inhalation, and skin contact. The contaminants absorbed by plants or contaminated with soil or dust may be ingested especially by young children playing on the contaminated soil or are contaminated with soil or dust (Manchester City Council, 2021). There may be also a risk of ingestion or inhalation from contaminated soil materials or dust by people using the contaminated site. In addition, soil contaminated with various substances such as oils, tars, corrosive materials may affect the skin when a physical contact is made with the contaminated soil materials (Manchester City Council, 2021). Furthermore, contaminants such as heavy metals can produce various toxic effects on plants such as inhibition of various physiological functions of plants, for example, photosynthesis, plant-water relationships, uptake of nutrients, nitrogen metabolism are well documented in many studies (Alam, Hayat, et al., 2007; Gopal & Rizvi, 2008; Chen et al., 2009; Gajewska et al., 2009). Such phytotoxic effects may result in altered metabolism, physiological and biochemical malfunctioning which cumulatively results in retarded plants growth and poor biomass development (Nagajyoti et al., 2010). This potentially may hamper efforts to revegetate the site with plants in the phytoremediation processes. Lastly, if the site is used for recreational activities such as open space or public parks, the contaminants may affect the health of the people using the site through exposure pathways.

2.9 Selected Remediation Techniques for Contaminated Land

Acute and diffuse soil contamination caused by organic and inorganic contaminants has generated concerns among the scientific community due to their adverse effects on public health and ecological system. Consequently, over the years, different remediation technologies such as physical remediation, chemical remediation and bioremediation have been adopted for the remediation of contaminated soil. Soil remediation involving in-situ and ex-site techniques have been used to decrease the potential risks that come with potentially toxic elements and improve the productivity of agricultural lands to ensure sustainable food security (Wang et al., 2015a; Beiyuan et al., 2017b). Many in-situ and ex-situ remediation techniques such as immobilisation, soil capping, soil washing, vitrification, phytoremediation have been developed to tackle the problem of soil contamination with potentially toxic elements (Beiyuan et al., 2017c; Beiyuan et al., 2018a; Liu et al., 2018). Different overall working principles and specific advantages and disadvantages characterised these soil remediation techniques. However, some of these techniques are not cost effective in terms of application or practicability and may require highly invasive treatments that can only be reasonably practiced *ex situ* which is associated with adverse consequences on the environment. Hence, the development of new techniques is necessary because of the constraints associated with the conventional remediation techniques. In this review, soil remediation practices including phytoremediation, soil amendments and soil capping are critically evaluated and discussed.

2.9.1 Phytoremediation

Phytoremediation – an aspect of bioremediation is recognised as the more promising and practicable option, a relatively recent technology with sustainable costs and environmentally friendly than conventional physicochemical techniques (Ali et al., 2013; Cristaldi et al., 2017). In the past 20 years, there have been increased research interest on the use of plants to remediate heavy metal contaminated sites. This plant-based approach is recognised an emerging remediation technology that is relatively cheaper, less destructive, more environmentally friendly, requires less work and is a safe alternative to conventional soil remediation (Chaney et al., 1997; Cristaldi et al., 2017). The major challenge associated with conventional remediation technologies such as soil washing is that most of them are not cost effective and probably not practicable (Pérez-Esteban et al., 2013). Phytoremediation is a plant-engineered technology that employs different plant species that have the potential to accumulate or degrade different contaminants in soil, and as such the biomass generated from plants during this process can be used in different beneficial purposes such as co-generation of energy and/production of biofuels, thus ensuring a considerable benefits to health, environment and cost management (Cristaldi et al., 2017). Phytoremediation technology aims to degrade, stabilise, remove, or volatilise contaminants from the environment, and thus, their potential adverse effects (Pandey & Bauddh, 2018). Phytoremediation is a vital remediation technology that can be used for reclamation of metal contaminated sites. This technology has already been used for many years (Baker et al., 1994; Chaney et al., 1997; Raskin et al., 1997; Gleba et al., 1999). There have been several advances in this area in recent years because of modern biotechnology as a phytoextraction and phytodegradation (Rajakaruna et al., 2006; Souza et al., 2014). Phytoremediation technology could be applied in terms of recovering of sites heavily contaminated by heavy metals.

Recently, phytoremediation technology has been used for decontamination of heavily polluted sites: for example, in Spain, phytoremediation involving the use of native plant species were used to clean up contaminated mining sites (Fernandez et al., 2017). Similarly, in Ukraine, phytoremediation involving the use of native sunflowers were successfully used in Chernobyl in Ukraine to decontaminate contaminated soil polluted by radioactive materials (Vinichuk et al., 2013). In Italy, this technique was successfully used to recover some heavily contaminated sites classified as Sites of National Interest (SIN) and high-risk sites which are predominantly located near industrial areas (Cristaldi et al., 2017). Phytoremediation technology employs the use of different green plants*;* herbs, (e.g., *Thlaspi caerulescens, Brassica juncea, Helianthus annuus),* energy plants (e.g., *Ricinus communis*) and woody plants (e.g., *Salix* spp*, Populus* spp) because these plants have been tested to have the potential to remove, uptake or render various environmental contaminants such as heavy metals harmless in soil or water (Tahir et al., 2016). Native green plants have been reported in many studies to have the potential to accumulate high amounts of trace elements and can play a vital role in effort to remediate metal contaminated sites (Sainger et al., 2011; Nawab et al., 2015).

However, mechanisms and effectiveness of phytoremediation technology are affected by several factors such as metal bioavailability, soil parameters, nature of plant species and contaminants species, level and nature of contamination (Berti & Cunningham, 2000; Sreelal & Jayanthi, 2017). In addition, the use of non-native (exotic) plant species for reclamation and restoration of contaminated sites may ecologically affect the community structure of such contaminated sites (Mahar et al., 2016). Hyperaccumulators are plants that can accumulate high metal in their aerial parts where they can be harvested without showing any phototoxic effects. These set of plant species are mostly used in the phytoremediation process, although low biomass production associated with hyperaccumulating plants seems to be a major limiting factor for their use in phytoremediation (Van Oosten & Maggio, 2015). The aerial parts of these plants when harvested can be disposed through incineration or composting (Rajakaruna et al., 2006; Sharma & Pandley, 2014) or can be used for production of renewal energies such as biofuels (Jiang et al., 2015). However, if the harvested plant biomass is not managed properly, contaminants may return to the environment and cause a secondary contamination. Therefore, efficient utilisation of and management of the harvested biomass is very critical to the success of cleaning up contaminated sites using plants. Phytoremediation technology is limited by slowness of the process and several plant species cannot be planted in strongly contaminated areas (Cristaldi et al., 2017).

More recently, there has been increased interest in phytoremediation involving the use of medicinal, bioenergy, aromatic, ornamental and metal hyperaccumulator plants because of numerous benefits associated with these plants (Sharma et al., 2021). The integrated approaches of using these plants species can offer numerous economic benefits in the long run such as timber production, biofuel production, as a decorative material and medicinal productions and numerous other benefits (Figure 2.4) (Sharma et al., 2021). For example, cost-effective bioenergy may be produced from their residual biomass which has an important role to play in terms of alleviating some environmental problems such as decrease emissions of greenhouse gases in the environment (Bauddh et al., 2017). Plants utilise the energy from the sun in the process of photosynthesis to fix carbon dioxide (CO_2). Bioenergy crops planted in a contaminated site can be a good of source of biomass. Because plant biomass is generally made up of lignin, hemicellulose, and cellulose at different percentages, it makes them suitable for use in the production of biofuels for heat, transportation, and electricity generation (Lebaka, 2013). Thus, the chemical energy deposited in these plants has a great potential for use in the generation of energy by way of direct combustion or after it has been converted to liquid biofuels (Vassilev et al., 2012).

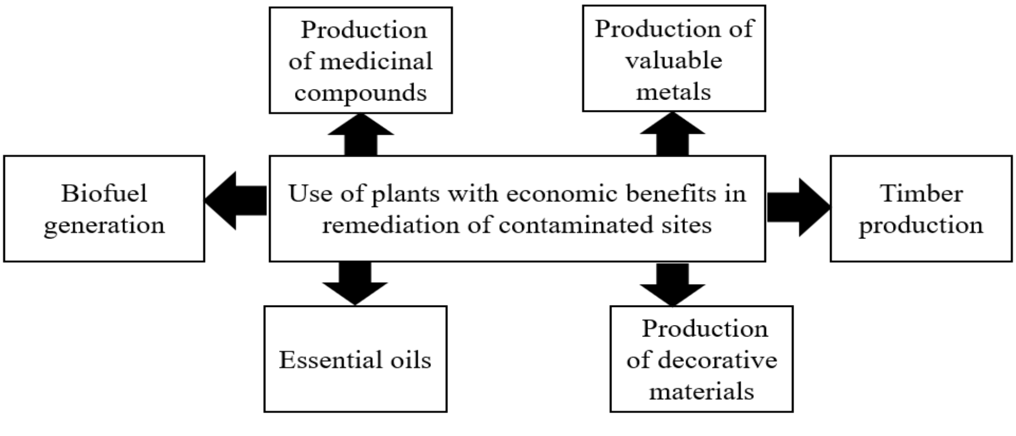


Figure 2.5. Schematic diagram illustrating phytoremediation of contaminated sites using plants with economic benefits. Source: Sharma et al. (2021).

Similarly, ornamental plants used in the remediation of contaminated sites can be utilised for decorative purposes, and the residual biomass produced after harvest can be a good of bioenergy generation (Sun et al., 2011; Xiao et al., 2015; Pande et al., 2019). Ornamental plants such as *Mirabilis jalapa* (four o'clock flower), *Calendula officinalis* (pot marigold) and *Althaea rosea* (common hollyhock) have been reported to adapt successfully and accumulated a substantial number of contaminants in contaminated soil (Liu et al., 2008; Peng et al., 2009; Sun et al., 2011; Xiao et al., 2015). Moreover, some medicinal and aromatic plants such as Vetiver (*Vetiveria zizanioides*), geranium mint *(Mentha* sp.), peppermint (*Mentha* sp.), industrial hemp (*Cannabis sativa*), Tulsi (*Ocimum basilicum*), and neem (*Azadirachta indica*), etc., have been proven to be effective in the remediation of contaminated sites (Jisha et al., 2017). In addition, it has been found that some aromatic plants in the families of Poaceae, Lamiaceae, Geraniaceae and Asteraceae tend to be promising candidates for phytoremediation of heavy metal contaminated sites because of their capacity to be used as hyperaccumulators, phytostabilisers and bio-monitors (Pandey et al., 2019). A lot of these plants can adapt in heavily metal contaminate sites and can be grown in such contaminated sites where food crops cannot be successfully grown (Pandey et al., 2019). As the aromatic plants growing in contaminated sites are accumulating heavy metals, the percentage of essential oils in aromatic plants also increases (Pandey et al., 2019). These oils can be potentially extracted, and the residual biomass of the plants can be used for generation of bioenergy by direct combustion or biomass gasification.

Most metals are potentially toxic to plants, animals, and humans, and cannot be degraded and, thus, need to be removed from the environment (Sharma et al., 2021). Some plants have the potential to accumulate high amounts of heavy metals in the aerial biomass compared to others. Such candidates with high metal accumulating capacity are called "hyperaccumulators" and are suitably used for used for phytoextraction (Sharma et al., 2021). Hyperaccumulators or plants with a high accumulating capacity and tolerance to metals, are often used for phytoextraction. Such a technology is used for in-situ treatment of heavy metal contaminated areas, and plant species that have high potential to accumulate, transfer and store heavy metals in their above-ground biomass harvestable parts (Mahar et al., 2016; Sreelal & Jayanthi, 2017). In addition, the plants used for this purpose must possess the ability to accumulate heavy metals under low contaminants concentrations, ability to uptake high concentrations of heavy metals, ability to accumulate various types of heavy metals and finally, the plants must be fast growing with large biomass and must be resistant to both pests and diseases. Metal hyperaccumulator plants able to produce high biomass can generate significantly more revenue because the harvested biomass can be utilised for various purposes (e.g., production of bioenergy and metal recovery) (Sharma et al., 2021).

Several studies have been conducted to examine the phytoextraction potential of some plant species for heavy metals in contaminated areas. A study by Kos et al. (2003) and Guo and Miao (2010) evaluated the phytoextraction potential of the perennial herbaceous plant *Arundo donax* in soil contaminated by cadmium and their results showed that *Arundo donax* accumulated 2.92 – 4.02 mg/kg of cadmium in leaves and 0.57 –1.42 mg/kg of cadmium in rhizomes respectively. Similarly, Fiorentino et al. (2013), repeated the tests using the same plant species; *Arundo donax* assisted by the fungal microorganism *Trichoderma harzianum* and found that the phytoextraction of cadmium in the leaves increased by 20% and (30%) in the rhizome. There has been increase interest recently to investigate the suitability of native plant species for remediation of metal contaminated soil as these plant species are often characterised by fast growth and large biomass and can withstand extreme environmental conditions compared to non-native plant species (Barbafieri et al., 2011). The use of native plants has been recognised as a promising and cost-effective option and more practicable approach to clean up contaminated sites compared to other remediation techniques (Perez-Esteban et al., 2013). The potential of native plant species to uptake high amounts of heavy metals have been reported in many studies, and these plant species can play a vital role in the effort to remediate metal contaminated soil (Sainger et al., 2011; Nawab et al., 2015). Therefore, assessment of heavy metal uptake by a range of native plant species at the investigated site has implication for identifying and selecting appropriate native plant species that have potential for cleaning up of the case study site.

2.9.2 Soil Amendments

There have been increased public awareness amongst the scientific group on the implications of contaminated soil on human health and ecosystem to develop new remediation techniques for clean-up of metal contaminated soil (Bolan et al., 2014). Interest in soil remediation research has increased recently among the scientific community in order to bring an urgent need for advancement in its applications and integrated understanding of the function of amendments in soil (Palansooriya et al., 2020). Among these soil remediation techniques, there is increasing recognition globally that application of soil amendments to immobilise heavy metals may be a promising option for remediation of heavy metal contaminated soil because of its efficacy, practicability and its commercial viability (Beiyuan et al., 2016; Wang et al., 2018d). Specifically, *in situ* remediation techniques such as application of organic and inorganic amendments to heavy metal contaminated soil have been recognised as very effective and cheap option for immobilisation of heavy metal availability and phytotoxicity (Friesl et al., 2003; Mench et al., 2006). *In situ* immobilisation involves application of amendments such as compost, biochar, lime, biosolids to soil in order to reduce the mobility and bioavailability of metals in soil. Over the last few decades, several soil amendments such as lime, apatite, ferrihydrite, fly ash, zeolite and red mud have been used for remediation of heavy metal contaminated soil (Gray et al., 2006; Qian et al., 2009; Janoš et al., 2010; Tica et al., 2011). Similarly, the mobility and bioavailability of heavy metals can be minimised through application of chemical and biological immobilising agents such as inorganic compounds (e.g., lime and phosphate) and organic compounds, such as biosolids (Park, et al., 2011). In many agricultural soil, different soil amendments comprising of organic and inorganic origins have been used to improve the soil/organic matter properties and have been used to alter the mobility of heavy metals in the environment (Garau et al., 2007).

Research on low-cost and eco-friendly materials such as soil amendments for remediation of heavy metal contaminated soil has received a significant attention leading to a great scientific interest on researching organic and inorganic soil amendments impacts on heavy metal mobility and bioavailability in contaminated soil (Palansooriya et al., 2020). Moreover, soil amendments are cheap, environmentally friendly, abundant, easily sourced, and biodegradable and have high sorption capacity for use in remediation of metal contaminated soil compared to other soil remediation techniques (Mahar et al., 2015). However, the success of soil amendments as a remediation option greatly depends on good knowledge and understanding of the nature of specific heavy metals, interactions between selected soil amendments with heavy metals, the right number of amendments to be used, heavy metals exposure pathways and potential adverse effects of heavy metals. In addition, a comprehensive assessment of all potential soil amendments and their ease of application and efficacy to specific heavy metals is a prerequisite for instructive evaluations of soil remediation's feasibility. Selecting appropriate immobilising agents can deliver cost-effective remediation techniques and contributes significantly to achieving “green and sustainable remediation” concepts because of their lower life cycle environmental footprints (Hou & Al-Tabbaa, 2014).

It has been found that different amendments may have varying capacities in mobilising heavy metals in soil. Under different soil conditions, an amendment may be effective in immobilising one heavy metal while the same amendment may be ineffective for another metal given other conditions or may even facilitate mobility of metals (González et al., 2012; Houben et al., 2012). Lime addition to heavy metal contaminated soil is a remediation technique that has been known to reduce the solubility and mobility of metal ions in the soil through increase in soil pH, facilitate precipitation of metal carbonates, oxides or hydroxides (Chlopecka & Adriano, 1996; Castaldi et al., 2005). The mobility and bioavailability of contaminants in the soil environment can be minimised by the soil stabilisation technique through addition of suitably immobilising agents. Adsorption of contaminants such as heavy metals on soil mineral surfaces, formation of fixed complexes with organic ligands, surface precipitation and exchange of ions in the soil environment have been recognised as the major mechanisms underpinning reduction in metal mobility and bioavailability in soil (Janoš et al., 2010). Heavy metal behaviour and their potential risk to human health is determined by the chemical nature and binding forms with the soil matrix, which influences their mobility, bioavailability and toxicity to various living components in the environment (Bacon & Davidson, 2008). In situ remediation techniques such as addition of organic and inorganic amendments are a promising option that reduces metal mobility and availability in soil environment through precipitation or increased sorption. The application of suitably soil amendments unto heavy metal contaminated soil may minimise the detrimental effects on various environmental receptors such as humans, water bodies, microorganisms, plants, and animals (Lombi et al., 2002). In addition, application of amendments to metal contaminated soil is not intended to alter the total concentration of metal in the soil but to restrict the mobility and bioavailability of metals by activating major immobilising processes such as complexation, precipitation, adsorption/sorption and redox reactions which results in reduction of labile pools of metals in soil (Adriano et al., 2004).

Furthermore, soil amendments should be cheap, abundant, easily sourced, and biodegradable and have high sorption capacity for use in remediation of metal contaminated sites (Mahar et al., 2015). The objective of in situ remediation is not to remove metal contents from the soil but to decrease or reduce their mobility and bioavailability potentials to minimise their toxic effects on plants, animals, humans and the environment (Dermont et al., 2008; Kumpiene et al., 2008; Radziemska, 2018). In situ stabilisation technology using amendments works by increasing the proportion of total metal contents within the soil phase through sorption or precipitation processes in order to reduce the soluble fractions of metal in solution phase (Basta et al., 2005). Soil amendments have been categorised into two viz; pH induced, and sorption induced amendments (Huang et al., 2018). pH induced amendments such as lime, dolomite, steel slag effects the metallic cations by reducing their availability in the soil through increase in soil pH and also cause removal of protons from the soil surface and as a result increase more sorption sites for metal adsorption (Al-Abed et al., 2006; O'Day & Vlassopoulos, 2010). In addition, it also produces OH^+ which acts by replacing or breaking off H^+ in soil solution thereby resulting in reduction of soil acidity to produce metal-containing precipitates (Dermont et al., 2008; Chang et al., 2013). Sorption induced amendments such as compost, clay, zeolite and iron compounds have various surface types that contain multidentate functional groups, and this group of amendments reduces the mobility and bioavailability of metals in contaminated soil through absorbing and forming stable complexes with metal ions (Bolan et al., 2014; Radziemska, 2018).

2.9.3 Surface Capping

Capping literally means placing a cover over a contaminated material such as landfill or contaminated soil to prevent leaching of contaminants to other areas. This method of treatment of contaminated sites have been widely used to restore small areas contaminated by heavy metals and organic pollutants (New Jersey Department of Environmental Protection, 2014). Surface capping is a simple, fast, and effective soil treatment method that has the potential to eliminate the potential risk of soil contamination (Liu et al., 2018). The purpose might include preventing contaminants from spreading to groundwater and/or preventing people and wild animals from coming into contact with the contaminants. In surface capping, the contaminated soil or material is usually covered with a low permeable material which can be clay or other capping materials. Physical barriers such as steel, concrete, asphalt, bentonite and grout walls may be used as capping materials to contain the contaminants vertically and horizontally across the site (Jankaite & Vasarevičius, 2005). The main purpose is not to destroy the contaminants but to isolate and keep the contaminants in a place to avoid spreading to other areas. This potentially helps to break the contaminant linkage and thus reduce the exposure to contaminants through skin contact or ingestion of contaminated soil and spread of contaminants to surface and groundwater (Liu et al., 2018). This treatment option is mostly used for highly contaminated sites and applicable to treatment of small, contaminated sites (e.g., area less than 2000sqm) (Liu et al., 2018). According to Ohio Environmental Protection Agency (2000), if a contaminated site has a land size greater than 2000sqm, it may be difficult to construct surface capping at such site. In the designing of capping for a contaminated site, the site-specific conditions and level of site contamination, contamination type and the current use of the site must be considered during planning and designing. In addition, factors such as hydrogeological features, availability of capping materials and the cost are considered in the planning process. Zhang et al. (2016) reported that the main benefits of capping remediation technology are that it is mostly inexpensive and interrupts the pathway between the contaminants and the receptor.

The literature review highlighted the importance of plant-based approach as a promising, cost effective and environmentally friendly remediation option to cleaning up contaminated sites. The aim of plant-based approach is to reduce the potential risk associated with contaminated sites by restricting the transfer of contaminants to ecosystems or humans (Robinson et al., 2009). Several authors have suggested that revegetation of contaminated soil is crucial to stabilising contaminants in soil (Arienzo et al., 2004; Ruttens et al., 2006). Vangronsveld et al. (1991, 1995) noted that revegetation of contaminated soil with plants will play a significant role in terms of stabilising contaminated sites and engender cover crop that will fend off the dispersion of metal-contaminated particles by water or wind erosion, and to minimise the mobility of heavy metals caused by rhizosphere-induced adsorption and precipitation processes. However, in heavily contaminated sites, this approach may prove difficult due to the high level of contamination which may inhibit the plant growth. Thus, establishing vegetation in such contaminated sites may not be feasible without some form of treatments such as incorporation of soil amendments. Under such condition, the way forward is to revegetate the site with the metal-tolerant plant ecotypes and treat the soil by adding metal-immobilising soil amendments (e.g., compost) and/or blending/mixing the soil with non-contaminated soil to improve the soil conditions and reduce the concentration of individual contaminants within the resultant mixture. The benefit of adding amendments and/or blending/mixing the soil is that it will help to revegetate contaminated sites by supporting the plants growth. In addition, the capping of contaminated soil is increasingly being recognised as a low-cost remediation technology for contaminated sites (Lee & Jones-Lee, 1997). Considering the small size of the bare area and levels of heavy metal contamination in the investigated site, surface capping is considered another feasible remediation option for overcoming the barriers and restoring the site. Liu et al. (2018) suggested that capping is mostly used for highly contaminated sites and applicable to treatment of small, contaminated sites. The main benefits of this remediation technology are that it is cost effective and interrupts the pathway between the contaminants and the receptor (Zhang et al., 2016). As these remediation approaches are identified as a promising and cost-effective options for cleaning contaminated soil as evidenced in the body of the literature review, and considering the levels of historical contamination at the investigated site, these remediation options are recommended in the present study for cleaning up of the case study site. Hence the final aim of this research is to investigate the feasibility of these remediation techniques in an area with multiple historical sources of heavy metal contamination.

2.10 Summary

The literature review has clearly demonstrated that there is a legacy of contaminated sites across the UK due to historical industrial activities. These sites are contaminated by various potentially toxic elements; however, majority of the sites were contaminated by heavy metals. Heavy metal contaminated sites are barriers for the beneficial use of these sites and could pose adverse effects on the ecological system, human health, animals, and other environmental receptors. Management and remediation of these contaminated sites pose scientific and technical challenges due to heavy metals being non-degradable and persistence long in the environment and coupled with the financial burden they put on government. Different remediation techniques have been developed over the years to address the problem of soil contamination, but some of these techniques are not technical feasible and coupled with high operational costs involved. Emerging remediation techniques such as the use of soil amendments to immobilise heavy metals, surface capping and phytoremediation are globally accepted as promising, practicable, environmentally friendly, and cost-effective option for remediation of metal contaminated sites. However, there are some challenges that confront the use of these approaches in cleaning up contaminated sites as highlighted in the body of the literature. To enhance the reliability and operational feasibility of these approaches in cleaning contaminated sites, these crucial challenges need to be addressed. More research works are needed to overcome these challenges, and in terms of selecting the feasible remediation approaches that will integrate the type and degree of site contamination, remediation goals, site characteristics, cost effectiveness, implementation time, and public acceptability for remediation of contaminated sites.

CHAPTER THREE

Research Approach and Methods

3.1 Overview

This chapter contains details of the approach taken and of the research methods used in the current study. The chapter begins with a setting out of the research philosophy underpinning the methodology adopted and overview of the research methods used in the present study. This is followed by the details of the modifications to the standard site investigation model relevant to this study and a diagram showing the overview of the relationship between the research aims and the field and laboratory methods and how each aim are related. In the next section (section 3.4) the rationale for the study site selection is set out. In the next section (section 3.5) of this chapter, the approaches used for the preliminary investigation set out. In sections 3.6 and 3.7, details of the field and laboratory methods used in the present study are set out. In section 3.8, a table showing the European Union heavy metal standards in soil is set out. The chapter is concluded with a statement on the quality control and assurance procedures observed in the current study.

3.2 Research Philosophy underpinning the Methodology

Within the research context, philosophy provides the general framework for theoretical thinking. There is a philosophical framework that underpins all research which is recognised as the building block of research (Grix, 2010; Heller, 2011). Within natural and social sciences, there are two important main branches of philosophy that exist, viz: ontology and epistemology (Moon & Blackman, 2014). Ontology is concerned with the nature of reality (Jonasson, 1991). In other words, it describes the assumptions we make about the physical world. While epistemology is concerned with the study of the nature of knowledge and thought (Jonasson, 1991). The interdisciplinary approach between the natural and social sciences is critical when it comes to understanding the contemporary ways the natural world is affected by social, political, institutional, and economic factors (Moon & Blackman, 2014).

Ontology is regarded as the first point of focus for the researcher. This branch of philosophy is concerned with the study of being or what exists in reality for people to know

(Marsh & Furlong, 2002; Grix, 2010; Hathcoat et al., 2019). In the natural sciences, ontology is regarded as an important philosophical branch because it helps researchers to demonstrate a degree of certainty regarding their research (Moon & Blackman, 2014). Ontology exists along a continuum: realism to relativism. Realism is the ontological position of positivism. Realism holds the views that object exist without the knower or researcher (Cohen et al., 2007). In other words, a discoverable reality exists without researcher (Pring, 2000a). This suggests, from an ontological viewpoint, that one single reality exists. For example, everything is either black or white. This ontological position assumes that reality is not moderated by our sense. In contrast, relativism holds the view that reality is a construct of human mind (Moon & Blackman, 2014). In other words, this means that reality is subjective and varies from individual to individual (Guba & Lincoln, 1994). This ontological position is concerned with the belief that knowledge is a product of the researcher because of their own experiences and the subjective nature of the concept (Jonassen, 1991). However, subjectivity has no room when it comes to the conventional quantitative natural science research, but in social sciences, it has a role to play. Relativism is the ontological position of interpretivism. This ontological position believes that our realities are being moderated by our senses, and in absence of human consciousness, the world seems meaningless. For example, what is perceived “black” by one person may be perceived “white” by another person or more usually “grey”. From the ontological point of view, it can be said that the research presented in this thesis is related to realism because the researcher’s main goal was to gain an understanding about one reality: to investigate small scale spatial heavy metal contamination levels in soil.

Epistemology deals with the study of the nature and forms of knowledge (Cohen et al., 2007). Epistemology is regarded as the fundamental building blocks that define research methodologies (Grix, 2010). Epistemological assumptions are based on how knowledge can be created, obtained and communicated. Moon and Blackman (2014) note that these epistemological positions influence how researchers conduct their work with a view to discovering knowledge. Similarly, Guba and Lincon (1994) note that epistemology asks pertinent question: for example, what type of relationship exists between the would-be knower and what can be known? The epistemological assumptions are categorised either as a ‘objectivism’ or ‘subjectivism’. Epistemological objectivism holds the views that through empirical methods and statistical analysis, knowledge about relationship or phenomena can be gained (Hathcoat et al., 2019). Objectivism is the epistemological position of positivists. The positivists conduct their work impartially in the world, and in the process discover full knowledge about an objective of reality. They believe that the researcher and what is researched are not dependent. Positivists seek methods to test reality through collection and analysis of evidence to explore the real-world claims (Patton, 2002). Grix (2010) maintains that an important aspect of epistemological objectivism is the assumption that theory can be used to create hypotheses; these hypotheses can be tested by observation, and thus allowing relationships to be validated. In contrast, epistemological subjectivism holds the views that knowledge is determined by how people perceive and understand reality (Moon & Blackman, 2014). The Interpretivists believe that subjective reality can be explained but, no phenomena or relationship can be proved with absolute certainty (Gummesson, 2003; Järvinen, 2016). This epistemological assumption tries to impose meaning and value on the world and interpret reality in the manner that makes sense to them (Pratt, 1998). Thus, this epistemological assumption does not support a natural science approach. Grix (2004) explains that the world does not exist without our knowledge of it. Regarding trees, Crotty (1998, p. 43) explains: “We need to realise that here that it is humans who have constructed it as a tree, assign it the name, and attributed the associations we make with trees.” A tree is not a tree without someone to call it a tree. The work reported here is primarily objectivism’, based on measurements of physical and chemical variables, though there is some ‘subjectivism’ where previous reports and historical maps are interpretated.

The importance of philosophical paradigms in research cannot be overemphasised because they indicate the assumptions made by the researchers as informed by their understanding and viewpoints about their research, and these assumptions greatly influence their choice of research methods (Moon & Blackman, 2014). In the case of inter-disciplinary research, different viewpoints are brought together with a view to generating a critical evaluation of what can be known, what can be learnt and how this knowledge can impact the way research is conducted (Moon & Blackman, 2014). In the present thesis, both quantitative and qualitative approaches were used in the investigation. Therefore, the research reported in this thesis is both deductive and inductive investigations involving quantitative and qualitative data based on hypothesis (research questions) in accordance with the objectivist and subjectivist viewpoints of the researcher. Similarly, the research philosophy adopted in the present thesis is based on ontological positivism and epistemological objectivism and subjectivism approach. This draws together the subjectivist epistemology of social science and the objectivist epistemology and positivist ontology of the natural sciences.

3.3 Overview of the Research Methods

Methods set out the specific techniques and procedures deployed in data collection and analysis (Crotty, 1998). Research methods tend to be discipline specific. There are different methods of investigating heavy metal contamination in contaminated soils. The choice of method in each investigation is designed to reflect the intent of the research being carried out. In this research project, the choice of the methods adopted was pre-empted by the aim of the investigation. The sampling strategy implemented in the present study was to provide information on heavy metals for near surface soils to a depth of 0 – 10 cm below ground level. Selecting appropriate method that fulfils the aim of the investigation is a key step towards obtaining unbiased and reliable results. In the present study, XRF and aqua regia/ICP-OES techniques were compared prior to the use of the preferred technique in a case study of a site contaminated by multiple historical sources. XRF emerged as the preferred technique.

The second part of the thesis is case study of Wrigley Head, Greater Manchester. Within the case study a mixed method approach comprising of quantitative methods (samples and laboratory methods) and qualitative methods (mixing chronologies, documentary analysis, and environmental context of the site) was adopted. In order to address the potential risks associated with contaminated sites and ensure these sites are suitable for various land use purposes, a standard framework for investigating contaminated sites has been developed. The standard framework for investigating contaminated sites begins with the preliminary investigation (stage 1) and ends with verification reporting/monitoring (stage 4) as shown in Figure 2.3. The standard framework used in the presented study originated from the Cumbria Contaminated Land Officer Group, 2013. However, in the present study, the framework adopted for site investigation was modified to suit the aims and objectives of the investigation. The framework used in the current study is shown in Figure 3.1. Stages 1 to 4 of the standard investigation framework are implemented when carrying out a holistic site investigation and risk assessment in contaminated sites. Therefore, it is outside the scope of the present study to conduct both site investigation and risk assessment at the site. This explains why the standard framework was modified to suit the aims and objectives of the present investigation.

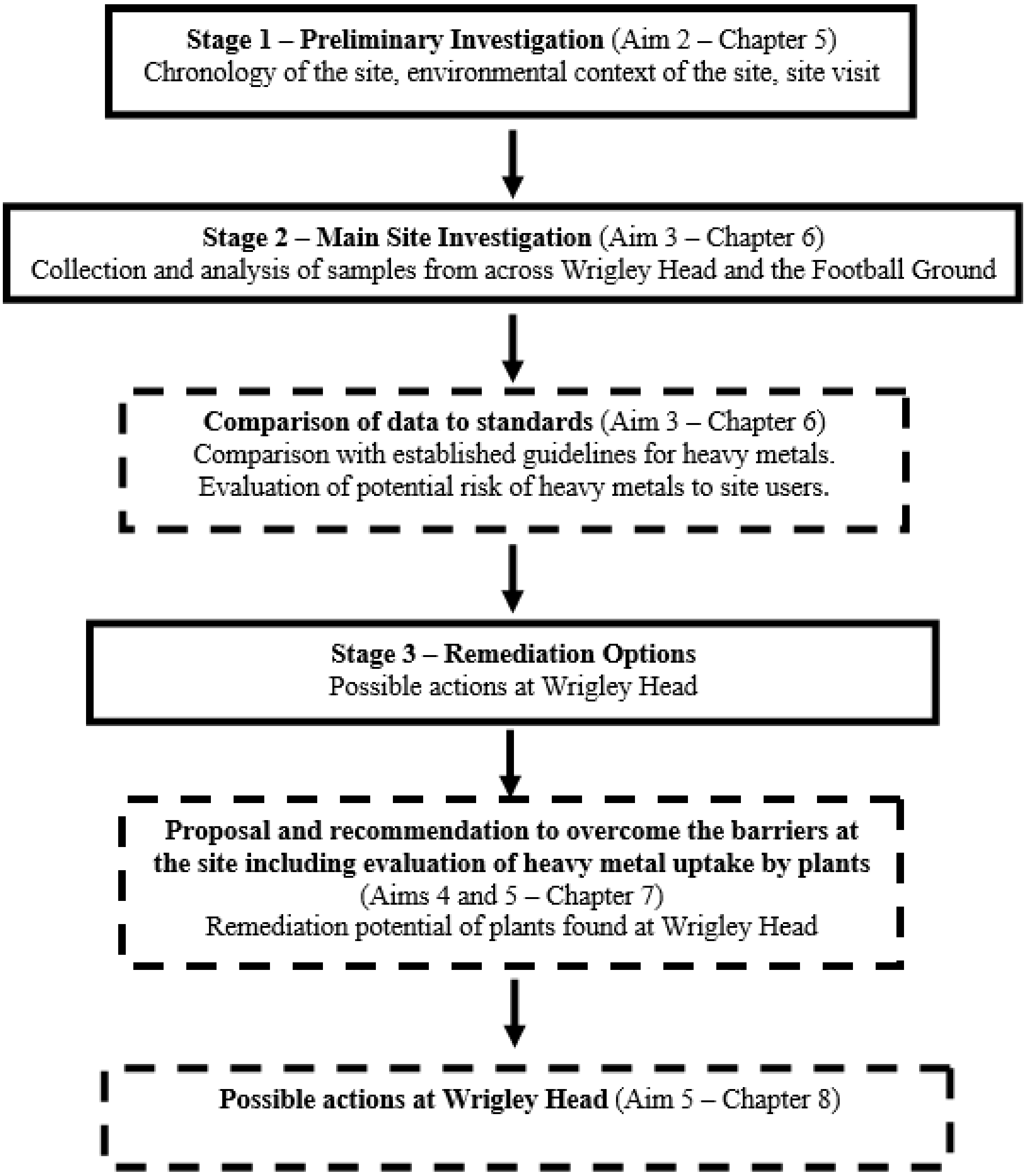


Figure 3.1. A modified framework used for site investigation in the present study

This justifies why the framework for site investigation was modified to suit the main aim of the present study and this explains why all the investigation stages involved in the standard framework were not carried out in the present study. Thus, in the present study, stage 1 of the standard framework for site investigation was carried out; part of stage 2 and 3 was also carried out while stage 4 was not carried out because it is not part of the study. Details of how the aims and the methods used are linked are set out in Figure 3.2.

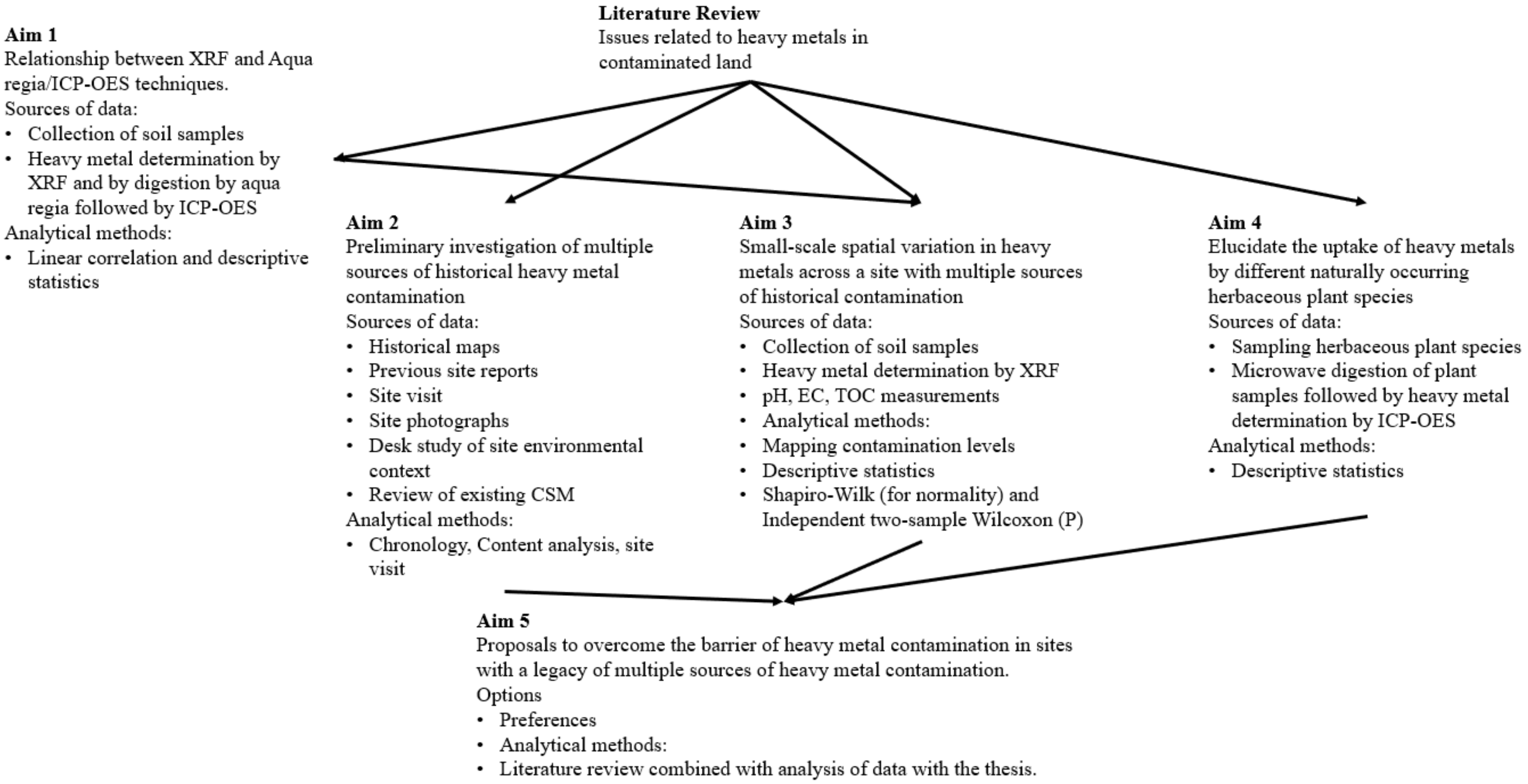


Figure 3.2. Research flow chart showing the research aims, field and laboratory methods and how each aim are related (CSM – Conceptual Site Model).

3.4 Comparisons of XRF and Aqua Regia/ICP-OES

The aim was to compare data from XRF and Aqua Regia/ICP-OES. Sixty-six (66) surface (0 – 10 cm) soil samples were collected using an auger soil sample from the Football Ground area of Wrigley Head, part of Moston Brook in East Manchester. Soil samples were stored in appropriately labelled laboratory polyethylene bags and then transported to the laboratory for analysis after collection. They were then analysed by both XRF and Aqua Regia/ICP-OES (Sections 3.8.1, 3.8.5 and 3.8.6). The data were then subject to correlation and regression analysis in Microsoft Excel.

3.5 CASE STUDY – The case study site

Contaminated land, resulting from industrial activities is a legacy of industrialisation found across the globe in industrial and post-industrial countries. Many of these sites are contaminated by heavy metals – the focus of this research. Heavy metal contaminated sites present clear scientific and technical setbacks because heavy metals cannot be degraded further into less toxic state unlike organic contaminants (Jiang et al., 2015). Therefore, significant risk arising from heavy metal contaminated sites must be adequately addressed to minimise their potential adverse effects on human health and environment. The present study aims to investigate small-scale spatial heavy metal contamination in Wrigley Head, Moston Brook. The outcome of this study could offer important information needed to assist the local authority and other relevant authorities in adopting and developing effective strategies to protect the site from potential risks and contaminations. In order to meet the research aims, it is necessary to identify a site that is representative of such sites across the globe.

Greater Manchester has a long history of industrial activities dating back to the 16th century and reaching a peak in the 19th and 20th centuries, and is regarded as the first centre of industrial heritage in the world (Manchester City Council, 2011). In the 19th century, for example, many mills, works and factories were discharging contaminants directly into the soil and rivers (Douglas et al., 2002) and along with other unsustainable waste disposal practices that have now left a legacy of potential contamination across the conurbation (Douglas et al., 2002; Manchester City Council, 2011). The historical industrial activities in cities such as Manchester has led to a legacy of contaminated sites across the region, and in certain cases, significant risks arising from these contaminated sites must be adequately addressed to minimise their potential adverse effects on human health and environment. One such site with historical contamination is Wrigley Head, Moston Brook (latitude: 53.515889°N; longitude: 002.155625°W) shown in Figures 3.3 and 3.4. A wide range of contaminants including heavy metals have been stored and buried at Wrigley Head, Moston Brook over time and there is a history of potential source of unknown contaminants at the site (Groundwork Oldham & Rochdale, 2008).

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Figure 3.3. Location of Wrigley Head, Moston Brook

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Figure 3.4. The different parts of Wrigley Head, Moston Brook

A preliminary site investigation showed that Wrigley Head, Moston Brook is contaminated with lead, copper nickel, zinc, arsenic, chromium, and cadmium and the level of contamination at the site has the potential to affect human health (Groundwork Oldham & Rochdale, 2008; Miller, 2011). Similar heavy metals have been reported from contaminated urban soil around the world. For example, Qing et al. (2015) reported heavy metals such as chromium, cadmium, lead, zinc, copper and nickel from urban soil of Anshan (a steel industrial city), Liaoning, Northeast China in a study conducted to assess heavy metal pollution and human health risk. Similarly, Wilcke et al. (1998) reported the contents of aluminium, cadmium, chromium, copper, iron, manganese, nickel, lead and zinc from urban soil in Bangkok, Thailand. Therefore, Wrigley Head, Moston Brook is a site that is representative of industrially contaminated areas around the globe.

This site is currently used as informal open space and serves as an important green asset to the local residents and the wider community. Similarly, there is a proposal jointly sponsored by Manchester City Council and Oldham Metropolitan Borough Council to make this site a ‘fantastic’ green asset for the local people and the wider community in the future. The site is suspected to have a peculiar problem because there is a history of unknown contaminants at this site and no validated records are held regarding these contaminants. This has further complicated the efforts to overcome the barriers associated with the site. Before this can occur, there is a need to investigate the level of heavy metal contamination across the site in order to provide relevant information from the findings to the local authorities regarding the level of site contamination and offer suggestions on how to overcome the barriers associated with metal contamination at the site. The contamination associated with this site is a great barrier for its beneficial and productive uses.

One option is to evaluate the uptake of heavy metals by herbaceous plant species across the site. It is suspected that heavy metals are being mobilised from the soil into plants and currently, it is not known how much heavy metals are being absorbed by these plant species and their phytoremediation potentials. Hence a survey of the plant species across the site was undertaken and the potential of these plant species for phytoremediation evaluated.

In addition, the choice of the case study site was based on the following considerations:

(a) Physical accessibility and suitability for field work – The case study site selection was greatly influenced by ease of access and suitability for field work. These factors were initially considered during site preliminary site visit in May 2015 before the final decision was made to choose the site for the current study.

(b) Safety – The safety of the research student using the study site was considered and appropriate safety measures were taken before the site was selected for the current study. One of the measures considered was to visit the site with a minimum of three persons each time the fieldwork is taking place at the site.

Also, part of the selection process of this study site was granting of a formal access request to carry out the field works at the site by the management of Wrigley Head, Moston Brook.

3.6 CASE STUDY– PRELIMINARY INVESTIGATION

3.6.1 Chronology

Combined historical maps from Digimap covering the period 1840s to 2020 with a site report prepared by Groundwork Oldham and Rochdale (2008) and a preliminary site investigation report prepared by Miller (2011) contained within those reports. The maps were annotated to highlight important changes and developments within from one map to the next. This was combined with the information from the two reports to illuminate the potential sources of contamination and when they occurred over the history of the site. The reports produced by Groundwork Oldham and Rochdale (2008) and Miller (2011) were used to produce a summary of the contamination that had occurred on the site. The conceptual site model was also examined for this site. These data were summarised in a narrative in appropriate tables.

3.6.2 Environmental context of the site

The environmental context of the site was examined by a desk study to drawing together data from the Greater Manchester Ecology Unit (2007), MAGIC (this source provides authoritative geographic information about the natural environment from across the UK government), Groundwork Oldham and Rochdale (2008) and Miller (2011), the UK government flood risk map, human health risk from contaminated land from DEFRA (2014). Data from these sources were combined to give a holistic overview of the setting of Wrigley Head within its local area and the risk to health that is presented by the site.

3.6.3 Site visit

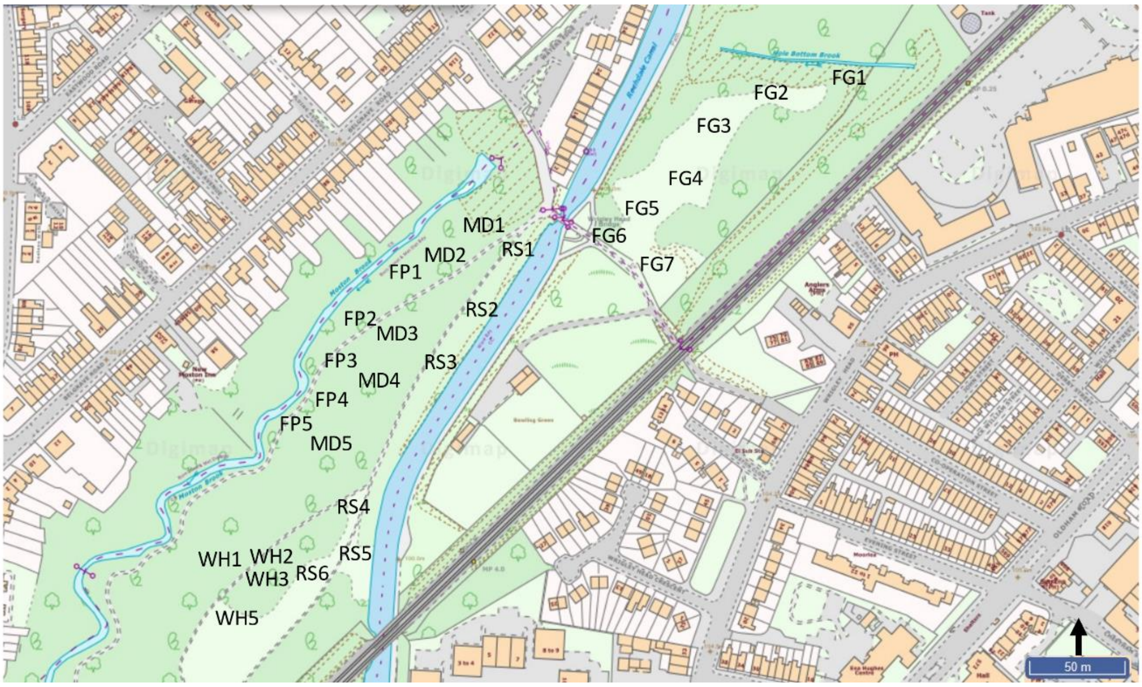
The site was visited at the beginning of this research in May 2015. The site was walked over, observations were made, and photographs taken. These data were then combined into a narrative describing the visible landscape of Wrigley Head and identifying features of interest for further investigation. The scope of investigation and site conditions was informed by the site visit and the desktop study. The site visit and review of a past desktop study which includes past site reports, site photographs and historical maps undertaken at the site gave the indication of the history of the site contamination. Past reports indicated that there are variations in the level of heavy metal contamination across the site. This justifies why several locations were chosen for evaluation of heavy metal contamination across the site.

3.7 CASE STUDY – FIELD METHODS

3.7.1 Field Method Relating to Detailed Investigation of the Soils around Wrigley Head and Uptake of Heavy Metals by Herbaceous Plants

The aim was to investigate heavy metal contamination levels and spatial variation across Wrigley Head and also to examine the uptake of heavy metals by different naturally occurring plant species across the site for their phytoremediation potentials. Twenty-seven herbaceous plant species (representing 26 dominant species) with their corresponding soils were collected in May 2015 across Wrigley Head. The plant species were collected during the growing season (spring) in May 2015. Five locations; Football Ground (FG), Floodplain (FP), Middle site (MD), Roadside (RS) and White Hills (WH) (Figure 3.6) within Wrigley Head site were selected for sampling due to variable levels of heavy metals across the site and to systematically evaluate heavy metal uptake by a range of herbaceous plant species across the site. Samples WH1 – 4 were collected from the central part of the “White Hills”; samples MD1 – 5 were collected from the area extending north from the central part of the “White Hills”; samples FP1 – 5 were collected from the floodplain of the study site; samples RS1 – 6 were collected from the soils along the road running parallel to the canal and samples FG1 –7 was collected from the “Football Ground”.

At each location, a minimum of four different but dominant plant species with their corresponding rhizospheric soils were collected at 0 – 10cm depth (topsoil) with the help of spade and a hand-held Global Positioning System was used to record the coordinates of each sampling locations. Soil samples were collected from topsoil (0 – 10cm) because plants absorb most of the heavy metals at this depth and metals tend to be more active and mobile within this depth especially where there is high presence of organic matter and large amount of biomass (Bradley & Cox, 1990; Adrian et al., 2004). The map showing where samples had been taken within Wrigley Head is shown in Figure 3.5.



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WH – White Hills, FP – Floodplain, MD – Middle site, RS – Roadside, FG – Football Ground

Figure 3.5. The Wrigley Head Moston Brook and the sampling points.

Due to rough terrains and accessibility issues surrounding the site, equal number of plant species and corresponding soil samples could not be practically sampled from each location. However, efforts were made to collect samples from the whole study area as much as possible as this will give a better representation of the area under investigation. A total of twenty-seven herbaceous plant species (representing 26 dominant species) with corresponding soils were collected from the site, stored in appropriately labelled polyethylene bags, and transported to the laboratory on the same day for further analysis. The data obtained were subject to descriptive statistics: median and range for soil, pH and EC data and median, minimum and minimum values for plant data. All data below the limit of detection (< LOD) of the analytical instruments used were treated by substitution method. This method has been widely used in environmental radioactivity data analyses (Wood et al., 2011). Croghan and Egeghy (2003), suggest that in statistical analyses, < LOD values commonly referred as “censored data” are often treated by substituting with a constant value, such as half the LOD, the LOD value divided by the square root of 2, or zero. In the present study, all the < LOD values were treated as zero during the data analyses.

3.7.2 Field Method Relating to the Detailed Investigation of the Football Ground Area of Wrigley Head, Moston Brook

The aim was to investigate heavy metal contamination levels and spatial variation in the Football Ground area, Wrigley Head, Moston Brook. High spatial variation in the distribution and contents of heavy metals is generally a unique characteristic of anthropogenically contaminated soil such as the investigated soils. Therefore, a detailed site investigation involving the collection and analysis of many soil samples is important. Soil samples were collected from 66 sampling locations across the bare and vegetated areas of Football Ground in June 2018. Sixty-six (66) surface soil samples were collected in order to ensure that the whole area under investigation is covered, and also based on the number of samples that can be practically processed in the laboratory. The sampling design adopted in this study was to provide a sampling scheme that would allow investigation of the variable heavy metal contamination levels across Football Ground area. The sampling procedures are described as follows: At each sampling location, an auger soil sample was collected at a depth of 0 – 10 cm with the aid of stainless-steel hand auger. A hand-held Global Positioning System was used to record the coordinates of each sampling point. A total of 66 soil samples were collected from the bare and vegetated areas of the study area – Football Ground. Soil samples were stored in appropriately labelled laboratory polyethylene bags and then transported to the laboratory for analysis after collection. Figure 3.6 showing the sampling points of the study area.

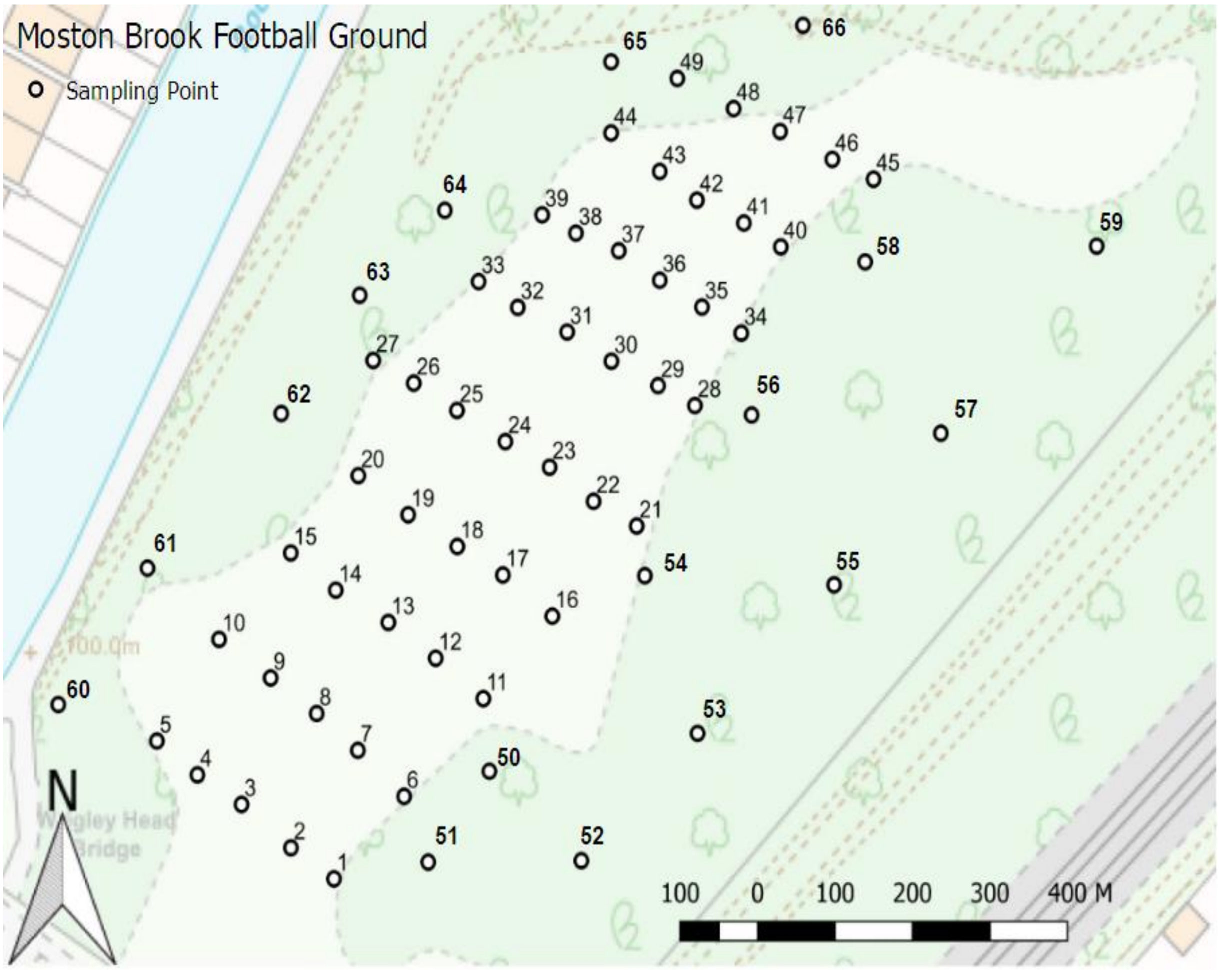

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Figure 3.6. Map showing the sampling points across the bare and vegetated areas

The data obtained from this study were subject to descriptive statistics: mean, median, minimum, and maximum values, range, coefficient of variation and online tests for the Shapiro-Wilk (for normality) and the Independent two-sample Wilcoxon (P). Grid maps were made, and linear regression analyses were performed in Microsoft Excel to compute linear correlation and regression graphs for XRF and aqua regia/ICP-OES heavy metal data. In addition, the heavy metal concentrations charts yielded by XRF and qua regia/ICP-OES were computed in Microsoft Excel. All <LOD values which were below the limit of detection (< LOD) of the XRF technique were treated as zero (substitution method) during the data analyses.

3.8 CASE STUDY – LABORATORY METHODS

3.8.1 Preliminary Soil and Plant Sample Preparations

The initial laboratory sample preparations are very critical and sample preparations should be done carefully in order to reduce sample contamination as much as possible. In the laboratory, the plants were carefully separated from the soils. The soil samples were contained in laboratory paper bags and oven-dried at 40 ˚C (Ha et al., 2019) until a constant weight was obtained, ground to pass a 2 mm stainless steel and stored sealable laboratory bags before analysis. For XRF analysis of soil heavy metals, a sub-soil sample was further ground to pass a 0.063 mm sieve.

For aqua regia heavy metal determination, the soil samples were contained in laboratory paper bags and oven-dried at 40 ˚C (Ha et al., 2019) until a constant weight was obtained, ground to pass a 2 mm stainless steel sieve in order to remove large debris, gravel-sized materials and other foreign materials and thereafter stored in sealable laboratory bags for the analysis.

The plant samples were washed with deionised water to remove all the soils attached to the roots, dried with a paper towel and air-dried for about two hours. The air-dried plant samples were then separated into roots, shoots, and the fresh biomass of both root and shoot portions were measured. The fresh plant parts were contained in paper bags and oven-dried at 65 °C for three days until a constant weight was obtained. The oven drying was necessary in order to eliminate the moisture content of the plants samples and prepare them for analysis. After oven-drying, the dry biomass of root and shoot portions was determined. Each of the dried plant samples was then ground using an electrical plant tissue pulveriser and stored in sealable laboratory bags prior to analysis.

3.8.2 Plant Species Identification

The twenty-seven fresh plant species were taken to Greater Manchester Ecology Unit for identification. Prior to identification, each of the plant samples was carefully transferred into appropriately labelled laboratory bags before taken to Greater Manchester Ecology Unit for identification. The plant species were identified by David Dutton of the Greater Manchester Ecology Unit.

3.8.3 Measurement of pH and Electrical Conductivity (EC)

Soil pH and EC were measured from soil-water suspension (1:5). In each case, 10 grams of oven dried soil sample was used for the measurements of the above chemical parameters. Ten grams of each dried soil sample was weighed into a clean bottle and 50 mL of deionised water was added to each of the bottle containing the soil and agitated for one hour with the aid of mechanical shaker before the soil parameters were measured. Prior to the measurements, the pH meter (HANNA instruments Woonsocket RI USA) and Electrical Conductivity Meter (METTLER TOLEDO SevenCompact Conductivity meter S230**)** were first calibrated according to manufacturers' instructions using respective buffer solutions (pH 4.0 and 7.0 respectively) and conductivity buffer solution to ensure accuracy and minimise experimental errors. Then the pH was measured by carefully inserting pH probe in respective soil-water suspensions, and measurements were taken when equilibrium point was reached. pH electrode was washed with deionised water in between samples to avoid cross contamination. Similarly, EC was measured with the aid of conductivity probe from soil-water suspension.

3.8.4 Total Organic Carbon Measurement

The total organic carbon determination from the soil sample was carried out in a commercial laboratory (i2 Analytical Ltd) in Watford, United Kingdom. In this method, organic matter within the soil samples was oxidized with potassium dichromate according to the Walkley and Black method. Organic matter was then determined by rapid dichromate oxidation of soil samples followed by manual titration. Five grams of dried homogenised soil sample, air dried at < 30°C, and crushed to produce a fine powder < 250 µm was oxidized with potassium dichromate and sulphuric acid, mixed gently and left for at least one hour. The extract was titrated with ferrous ammonium sulphate and organic matter calculated thereafter.

3.8.5 Heavy Metal Determination by XRF Technique

XRF technique was used to measure heavy metal contents in soil in the case study investigation. The XRF technique was considered as a preferred candidate for analysing the heavy metals in soils in the case study investigation due its potential to offer a rapid, easy and cost-effective determination of heavy metals and line with the goal of the site investigation.

In addition, XRF technique measures the total concentrations of heavy metals in soil in comparison to aqua regia method. Thus, the heavy metal data obtained by the XRF technique could give an overview of the total heavy metal contamination profile across the site. The data potentially could provide important information needed in defining and mapping out potential areas of serious contamination across the site.

In this procedure, a sample of soil was ground to pass a 0.063 mm sieve. The soil samples were ground to 0.063mm (fine-textured) so as to improve the accuracy of the results obtained. The samples were agitated for 5 minutes each by mechanical test sieve shaker. Then, 5g of each of the soil sample was transferred into an XRF sampling cup and a thin cling film material was used to cover the base of the cup prior to XRF analysis. During XRF analysis, the XRF analyser was placed on holding support and then connected to a laptop through which real time data of the analysis was obtained in a excel file. The instrument was calibrated by first analysing the 73308 standard reference material (Buffalo river sediment, NIST^{R}) prior to proper analysis which was done in duplicates to minimize experimental errors. The total concentrations of heavy metal in the soils were measured with X-ray fluorescence Spectrometer (Thermo Scientific Niton XL2 Gold Handheld XRF Analyser, Winchester, UK). To ensure accuracy and reliability of the results obtained, all analyses were performed in duplicates and analysis time was set at 240s (4 minutes) per sample. Figure 3.7 shows soil sample preparations in the laboratory for XRF analysis.

Figure 3.7. Laboratory soil sample preparations for XRF analysis

3.8.6 Heavy Metal Determination by Aqua regia/ICP-OES

Aqua regia digestion procedure was also used in the present study because of the need to determine the “pseudo-total concentrations” so as to make a robust comparison with the total heavy metals obtained by the XRF technique. The advantage is that this would help to critically discuss any relationship and/or differences in metal concentrations yielded by the two techniques. This was done by testing samples by both XRF and aqua regia/ICP-OES methods. The data obtained helped to decide which analytical technique is most suitable for analysing the heavy metals in the case study investigation. In addition, the concentrations determined by the aqua regia method are regarded as the harmful levels of heavy metals across the site, and could provide important data for environmental risk assessment of heavy metals at the site. This method involving the use aqua regia (HNO_3 + HCl) was used to determine soil heavy metal concentrations in a commercial laboratory located in Watford, United Kingdom. The procedure was carried out in a commercial laboratory (i2 Analytical Ltd) in Watford, United Kingdom. In this procedure, 1g of dried homogenised soil sample was added to 10 ml aqua regia (7.5 mL HCl + 2.5 mL HNO_3) and was digested under reflux at 115˚C for 1 hour and 15 minutes then made up to 50 mL using distilled deionised water; then filtered through Whatman no 1 hardened ashless filter papers. The extracts were then analysed for heavy metals by ICP-OES method.

3.9 Plant Samples Heavy Metal Determination

The concentrations of heavy metals in the plant tissues were determined by ICP-OES (Varian 720ES ICP-OES, Palo Alto, CA, USA). For each plant tissue sample, 0.5 g of the powdered sample was weighed and added into a microwave digestion tube, followed by adding 1 mL of 30% (m/m) H_2O_2 and 7 mL of concentrated HNO_3 solution. The tubes were fitted with bungers and closed appropriately with lids to prevent loss of volatile elements during digestion and placed into microwave carousel. The microwave digestion was done by firstly increasing the temperature linearly from 25 to 90 °C for 4 minutes; secondly, the temperature was maintained steadily at 90 °C for 2 minutes; thirdly, the temperature was increased linearly to 180 °C for over 6 minutes; and finally, the temperature was maintained at 180 °C for 10 minutes (Bressy et al., 2013). After cooling, the digested plant samples were filtered using Whatman filter papers (No. 42). The filtrates were then diluted to a final volume of 25 mL with deionised water. The diluted samples were stored at 4 °C in a refrigerator prior to analysis of heavy metals using ICP-OES. Figure 3.8 shows ICP-OES heavy metal analytical instrument.

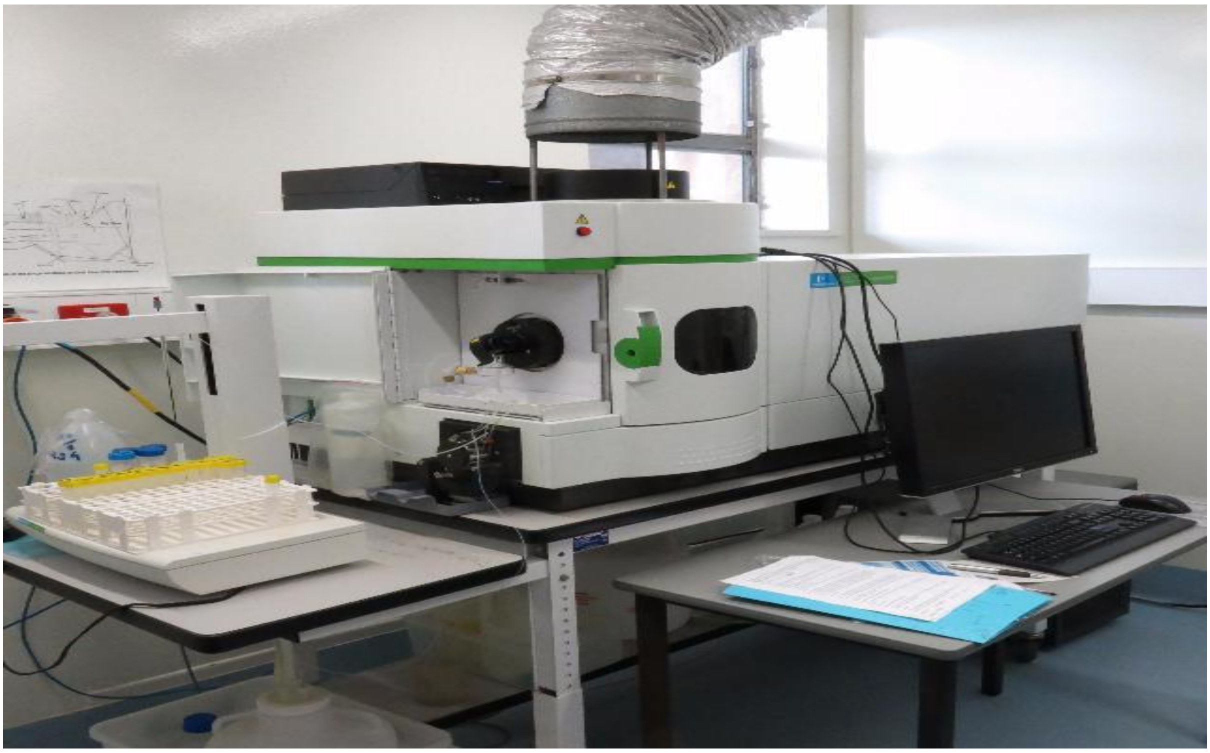


Figure 3.8. ICP-OES Analytical Equipment

3.10 Comparison of Heavy Metal Levels with Established Standards

The levels of heavy metals obtained across the site were compared to European Union Threshold and guideline values (Table 3.1). The European Union threshold and guideline values for heavy metals in soil is shown in Table 3.1. The levels of heavy metals across the site in the present study were compared to European Union Threshold and guideline values because it provides an appropriate representation of mean values used by different national systems within Europe (Finland Ministry of the Environment, 2007; van der Voet et al., 2013). In addition, the EU standards provide threshold and guideline values for all the heavy metals examined in the present study and this is considered to be appropriate. The EU European Union threshold and guideline values set out the values, that if these values are exceeded, then the area under investigation poses health/ ecological risks.

Table 3.1. European Union threshold and guideline values for heavy metals in soil.

Metals and metalloids	**Threshold value (mg/kg)**	**Lower guideline value (mg/kg)**	**Higher guideline value (mg/kg)**
Arsenic (As)	5	50 (e)	100 (e)
Cadmium (Cd)	1	10 (e)	20 (e)
Chromium (Cr)	100	200 (e)	300 (e)
Copper (Cu)	100	150	200
Lead (Pb)	60	200 (t)	750 (e)
Mercury (Hg)	0.5	2(e)	5(e)
Nickel (Ni)	50	100(e)	150 (e)
Zinc (Zn)	200	250 (e)	400(e)

Finland Ministry of the Environment (2007). The guideline values have been defined based on either ecological risks (e) or human risks (t)

3.11 Metal Uptake Calculations

In this study, heavy metal uptake from soils to roots and shoots were quantified using Bioaccumulation Factor (BF) and Translocation Factor (TF) using the following equations:

BF = [Heavy metal] plant root/ [Heavy metal] soil

TF = [Heavy metal] plant shoot/ [Heavy metal] plant root

Where, BF represents Bioaccumulation Factor and TF represents Translocation Factor.

3.12 Quality Control and Assurance

All the glassware used for the laboratory analyses were pre-cleaned and acid washed. All reagents and acids used during these analyses were of analytical standards and used without additional purification. Distilled water was used to wash the plant samples after initially washing in tap water while deionised water (18.2 Ω/cm) was used to prepare all the reagents. Reagent blanks were used as controls and multi-element standards were used to validate the analytical results.

CHAPTER 4

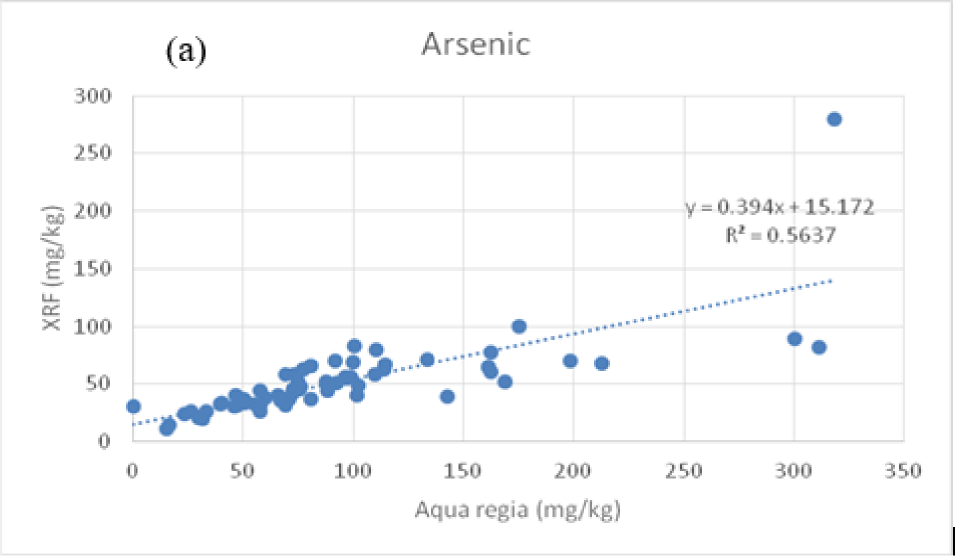
Comparison of XRF and Aqua regia Heavy Metal Concentrations

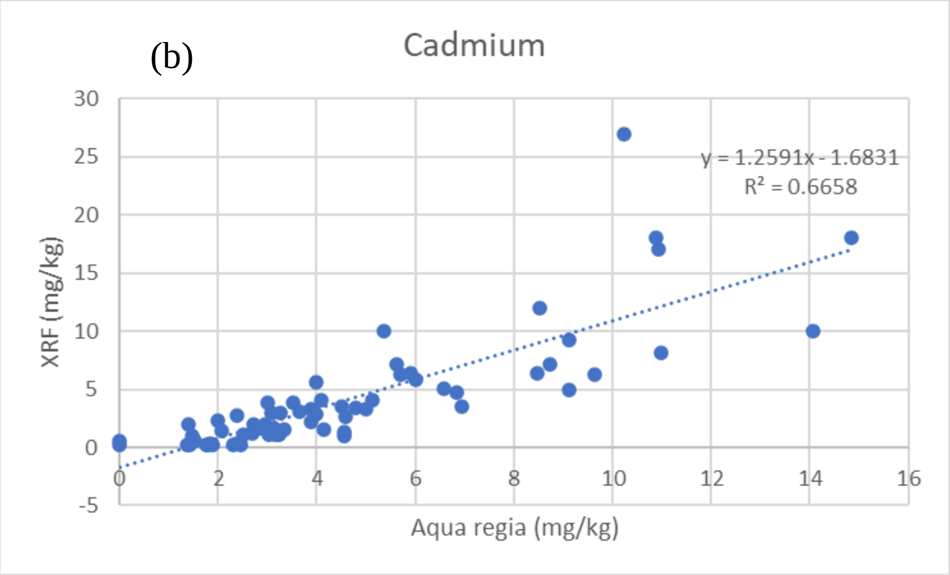
4.1 Overview

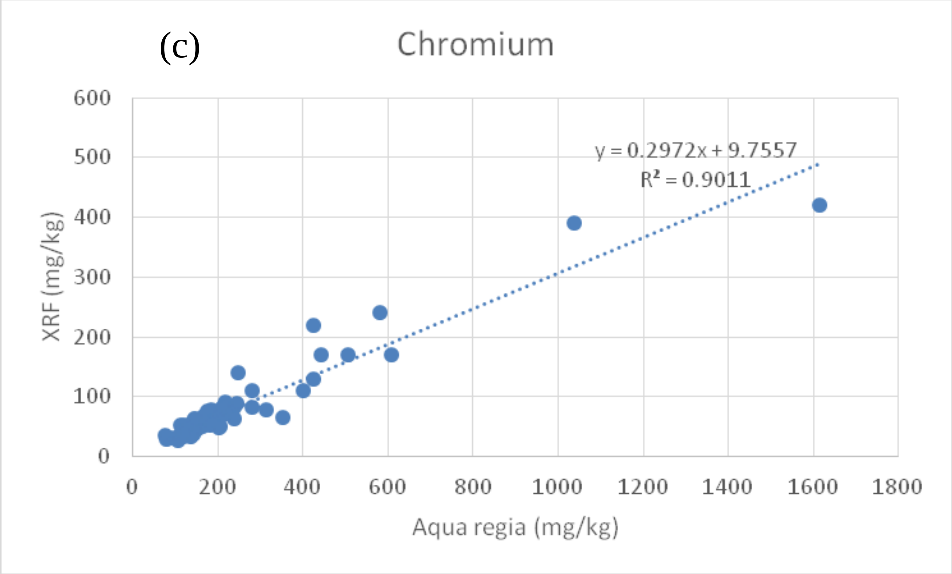
In this chapter, XRF and aqua regia/ ICP-OES heavy metal data are presented. The chapter starts with the presentation on the linear relationship between XRF and aqua regia/ICP-OES heavy metal data. This is followed by the presentation of the heavy metal concentrations yielded by XRF and aqua regia/ ICP-OES techniques across the sampling locations.

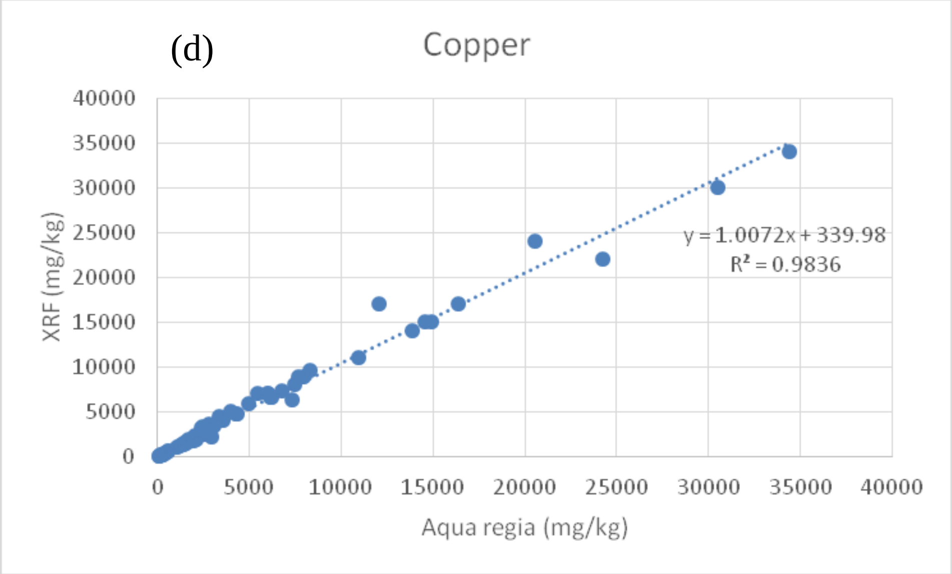
4.2 Relationship between XRF and Aqua regia Heavy Metal data

The results on the linear relationship between the XRF and aqua regia/ICP-OES heavy metal data in the Football Ground are shown in Figures 4.1




(b)
Cadmium
y = 1.2591x - 1.6831
R² = 0.6658
XRF (mg/kg)
30
25
20
15
10
5
0
-5
0
2
4
6
8
10
12
14
16
Aqua regia (mg/kg)


(c)
Chromium
y = 0.2972x + 9.7557
R² = 0.9011
XRF (mg/kg)
600
500
400
300
200
100
0
0
200
400
600
800
1000
1200
1400
1600
1800
Aqua regia (mg/kg)


(d)
Copper
y = 1.0072x + 339.98
R² = 0.9836
XRF (mg/kg)
40000
35000
30000
25000
20000
15000
10000
5000
0
0
5000
10000
15000
20000
25000
30000
35000
40000
Aqua regia (mg/kg)

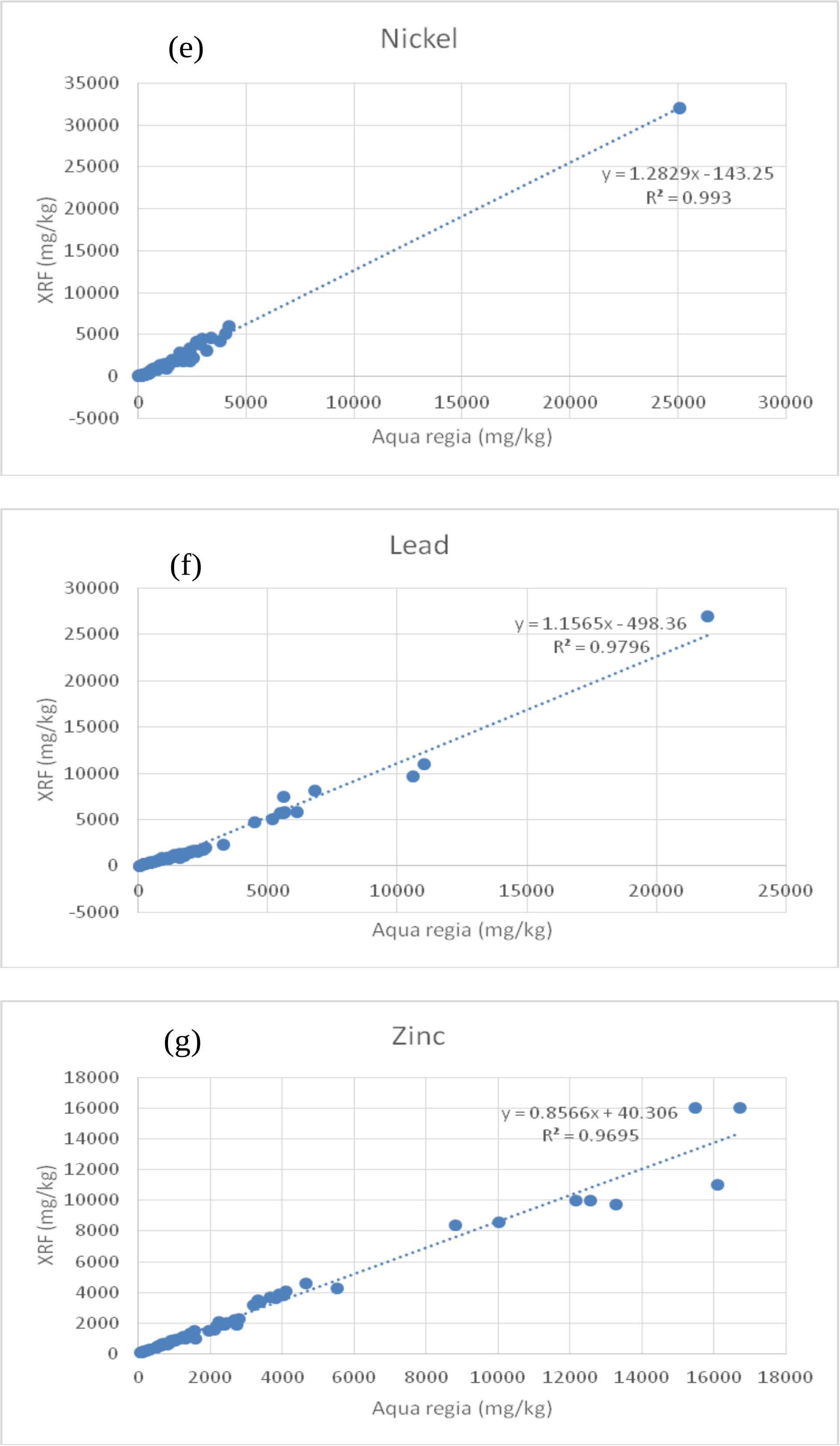


Figure 4.1. Linear correlation graphs of XRF versus aqua regia /ICP-OES heavy metal data

Data from the two extraction techniques were linearly correlated in order to explicitly understand any relationship between the heavy metal concentraions yielded by XRF and aqua regia/ICP-OES techniques in the present study. The data indicated that the correlation coefficients are generally high indicating a strong linear relationship between heavy metal data derived from XRF and those from aqua regia/ICP-OES in the present study (Figure 4.1). In other words, this means that heavy metal data obtained by XRF techniques strongly correlated to those obtained by aqua regia/ICP-OES digestion. Importantly, the relationship between the XRF and aqua regia /ICP-OES derived heavy metals was stronger among heavy metals especially chromium, copper, nickel, lead and zinc (Figures 4.1c, d, e, f and g) compared to arsenic and cadmium (Figures 4.1a and b). In other words, XRF and aqua regia /ICP-OES yielded a more satisfactory relationship for chromium, nickel, lead, copper, zinc and lead compared to arsenic and cadmium.

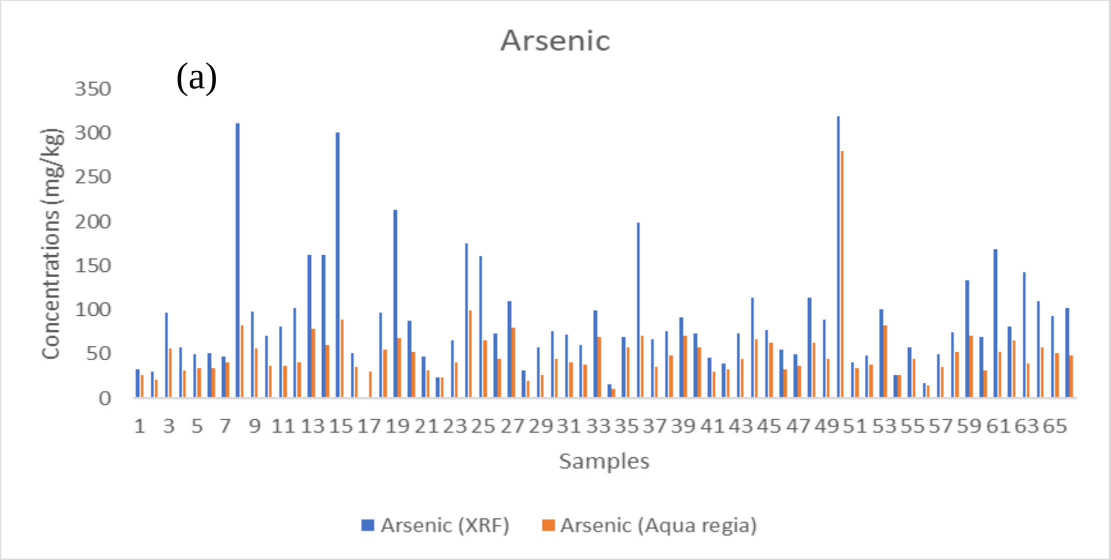
Among the XRF and aqua regia/ICP-OES heavy metal data, nickel showed the strongest correlation coefficient ($R^2 = 0.9930$) while arsenic and cadmium recorded the weakest correlation coefficient ($R^2 = 0.5637$ and 0.6658) respectively (Figures 4.1a, c and e) Similarly, strong correlation coefficients were also observed for chromium, copper, lead, and zinc derived from, XRF and aqua regia/ICP-OES techniques in the present study (Figures 4.1c, d, f and g). The linear regression lines represent the XRF and aqua regia/ICP-OES heavy metal data points on the correlation graphs. As can be seen, all the linear regression lines representing the heavy metal data points are perfectly straight lines (Figure 4.1). Most of the dots representing the data points for chromium, copper, nickel, lead and zinc fall on the linear regression lines (Figures 4.1c, d, e, f and g), while the data points for arsenic, and cadmium were slightly scattered around the linear regression lines on the correlation graphs (Figures 4.1a and b). This observation depicts the degree of relationship between XRF and aqua regia/ICP-OES heavy metal data across the area.

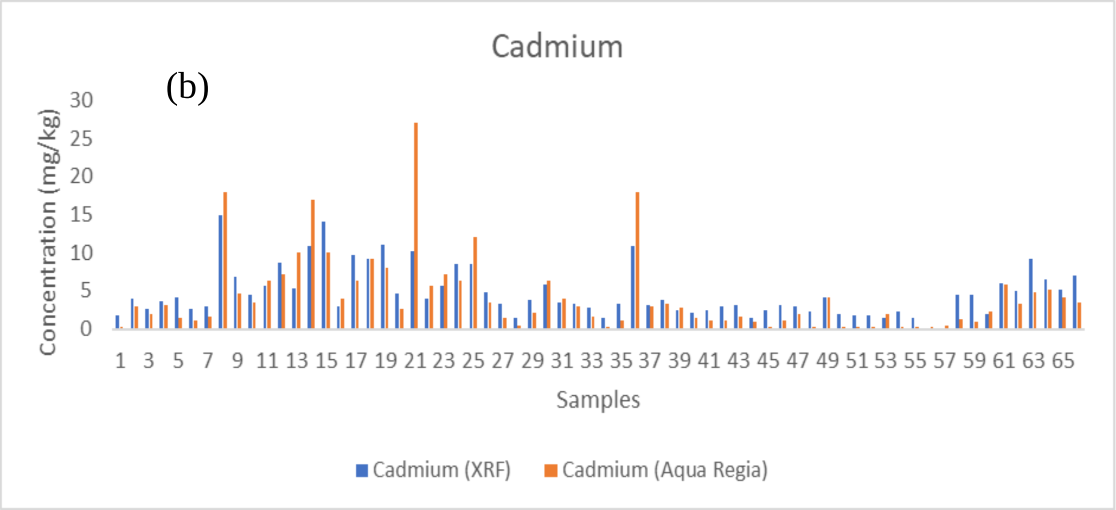
Similarly, the regression equations showed that the gradients representing heavy metal data points on the graphs were variable (Figure 4.1). All the gradients are positive values confirming the positive linear relationship between XRF and aqua regia heavy metal data (Figure 4.1). From the regression equations on the graphs, cadmium, copper, nickel and lead had gradients greater than 1 (Figures 4.1b, d, e and f). Similarly, arsenic, chromium, and zinc had gradients less than 1 (Figures 4.1a, c and g). The regression equations showed that the concentrations of heavy metals can be quantitively predicted by the two extraction techniques. Although, linear regressions are influenced by high values, the prediction of low concentrations by the linear regression can be affected.

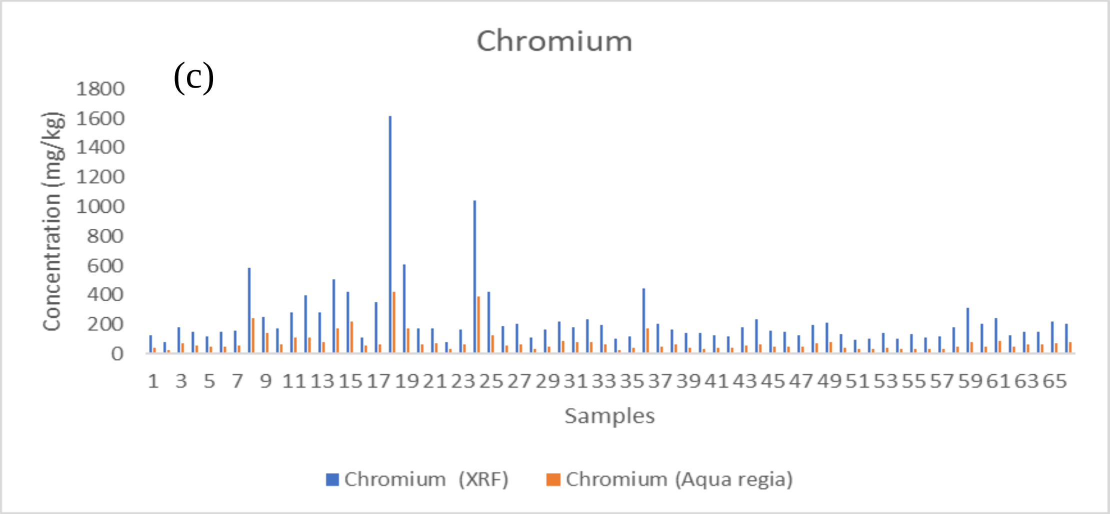
Summarily, there was a strong linear relationship between XRF and aqua regia /ICP-OES heavy metal data in the present study, however, there were some differences in terms of the overall heavy metals yielded by each extraction technique across the sampling locations.

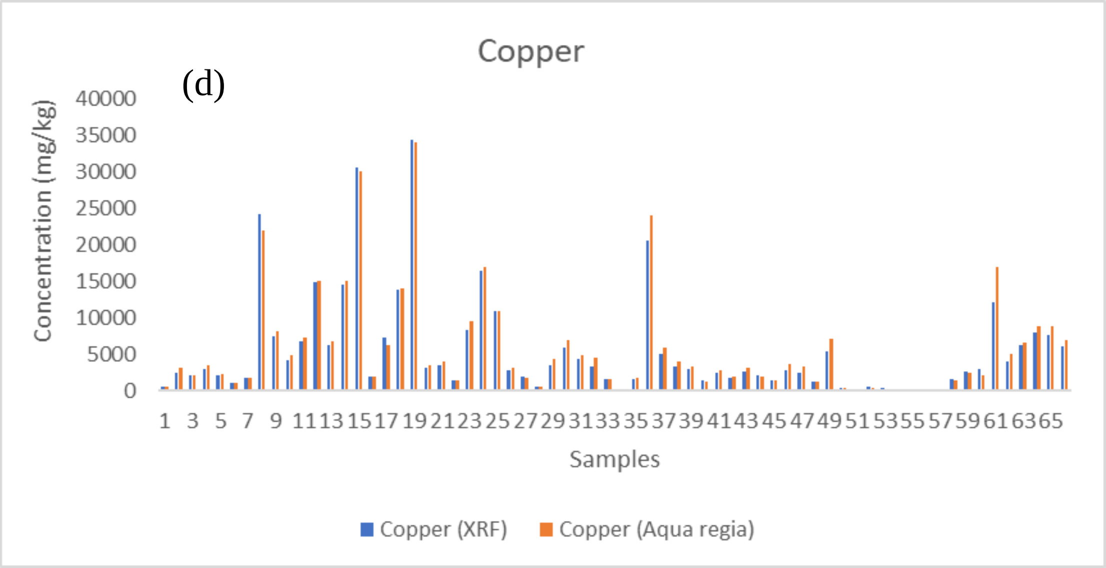
4.3. The Concentrations of Heavy Metal yielded by XRF and Aqua regia/ICP-OES

The concentrations of heavy metals yielded by XRF and aqua regia/ICP-OES techniques across the sampling locations are presented in Figure 4.2.




Cadmium
(b)
Concentration (mg/kg)
30
25
20
15
10
5
0
1 3 5 7 9 11 13 15 17 19 21 23 25 27 29 31 33 35 37 39 41 43 45 47 49 51 53 55 57 59 61 63 65
Samples
Cadmium (XRF)
Cadmium (Aqua Regia)


Chromium
(c)
Concentration (mg/kg)
1800
1600
1400
1200
1000
800
600
400
200
0
1 3 5 7 9 11 13 15 17 19 21 23 25 27 29 31 33 35 37 39 41 43 45 47 49 51 53 55 57 59 61 63 65
Samples
Chromium (XRF)
Chromium (Aqua regia)


Copper
(d)
Concentration (mg/kg)
40000
35000
30000
25000
20000
15000
10000
5000
0
1 3 5 7 9 11 13 15 17 19 21 23 25 27 29 31 33 35 37 39 41 43 45 47 49 51 53 55 57 59 61 63 65
Samples
Copper (XRF)
Copper (Aqua regia)

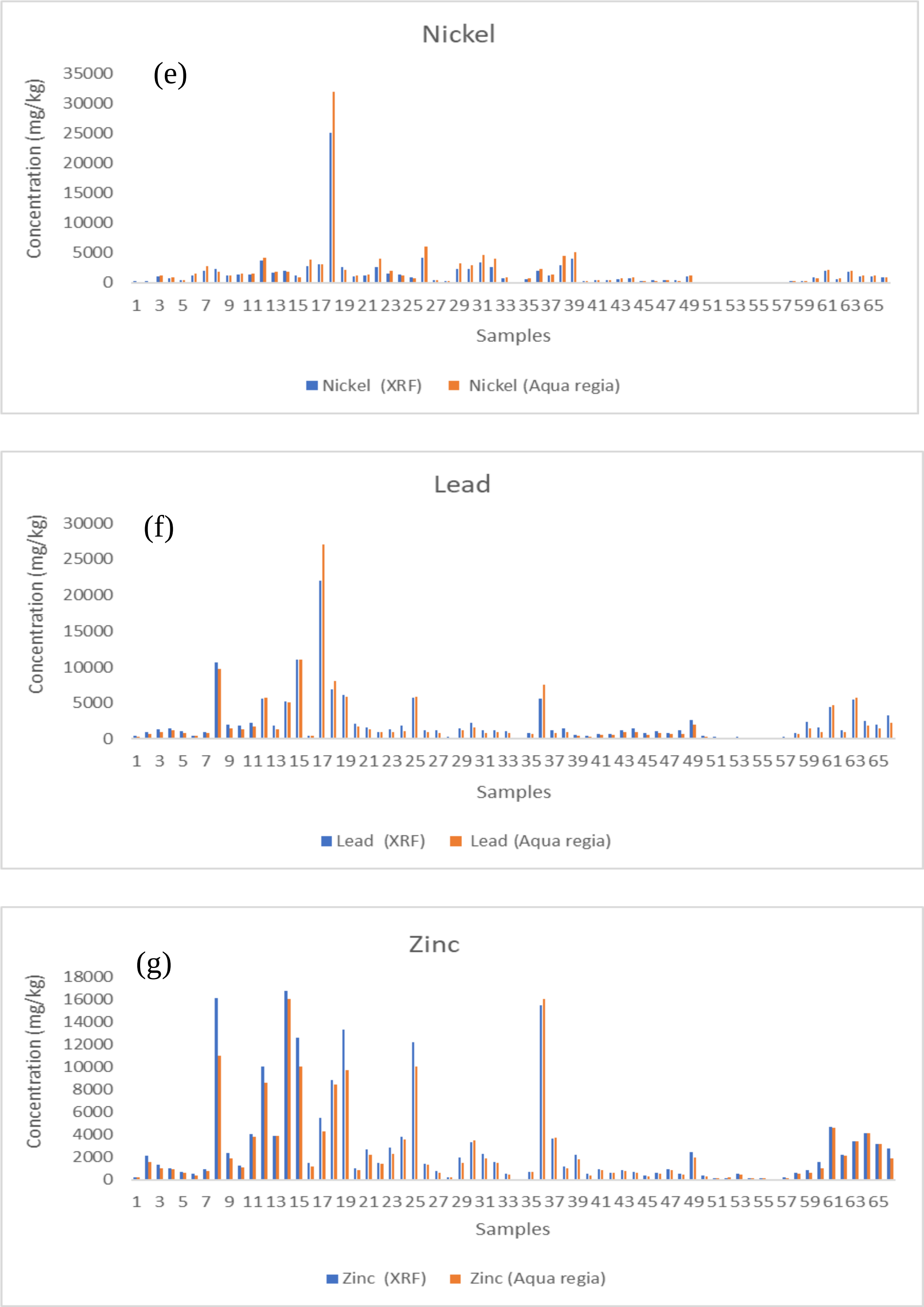


Figure 4.2. Heavy metal concentrations (arsenic, cadmium, chromium, copper, nickel, lead and zinc) yielded by XRF and Aqua regia/ICP-OES across the sampling locations.

Despite the strong correlations between XRF and aqua regia/ICP-OES heavy metal data in the present study, there were some differences in terms of the overall heavy metals yielded by each technique across the sampling locations (Figures 4.2a, b, c, d, e, f and g). The data showed that the differences between heavy metal data yielded by XRF and Aqua regia/ICP-OES in the present study were not systematic. In other words, this means that heavy metal concentrations yielded by the two techniques across the sampling locations were not regular. There was variability in the concentrations of heavy metals yielded by the two extraction techniques across the sampling locations which might be due to relatively high variation of heavy metals across the study site (Figures 4.2a, b, c, d, e, f and g). The results revealed that the concentrations of copper, lead, nickel and zinc (Figures 4.2d, e, f and g) yielded by XRF and aqua regia/ICP-OES techniques were relatively higher compared to arsenic, cadmium and chromium (Figures 4.2a, b and c). This could be due to relatively higher concentrations of copper, lead, nickel and zinc in the investigated soils compared to arsenic, cadmium and chromium. The results also revealed that some samples had a very low cadmium concentrations which were below the detection limits of the XRF technique (Figure 4.2b). In general, the data also showed that XRF technique yielded higher concentrations for arsenic, chromium and zinc while aqua regia/ICP-OES technique seemed to yield higher concentrations for cadmium, copper, nickel and lead across the sampling locations (Figures 4.2a, b, c, d, e, f and g).

Even though there were differences in the concentrations of heavy metals yielded by the two techniques across the sampling locations, the results suggest that the differences in the concentrations of heavy metals yielded by two extraction techniques in the present study were not remarkable. This is evidently demonstrated by the strong correlation between XRF and aqua regia/ICP-OES heavy metal data.

CHAPTER 5

Preliminary Investigation of Wrigley Head, Moston Brook

5.1 Overview

This chapter contains the results for the second aim of the research outlined in Chapter 1. The chapter begins with results of the desk-based study of Moston Brook and more specifically Wrigley Head and then moves on to detail the results of a site visit conducted.

5.2 Desk-based Study

5.2.1 Chronology

Results gathered from past site reports showed that in the 14th century, the area located around Moston Brook, Manchester was an open countryside with different farming settlements, for instance, Hardman Fold farm. Results from the past site reports revealed that at the beginning of the 16th century, washing and bleaching of linen and open seam coal mining were significant economic activity dominating this area (Groundwork Oldham & Rochdale, 2008). The finding obtained showed that during the 18th and 19th centuries, Moston Brook was regarded as an active part of the northern sector of ‘Cottonopolis’ (a pseudonym for Manchester) (Groundwork Oldham & Rochdale, 2008).

Communications into and out of the area were enhanced in 1804 by the opening of the Rochdale Canal (Figure 5.1). In1840, the first pit shaft was sunk at Moston Pit. A report obtained from WS Atkins (2002) showed that there were eight seams of coal at the site worked at the depths between 230 meters and 660 meters with the last coal activity operated in 1967 (Miller, 2011). These underground coal seams were presumed to be located towards the eastern end of the site with the geology revealing coal measures (Miller, 2011). However, presently, there is no evidence of underground mining around Moston Brook site (Miller, 2011).

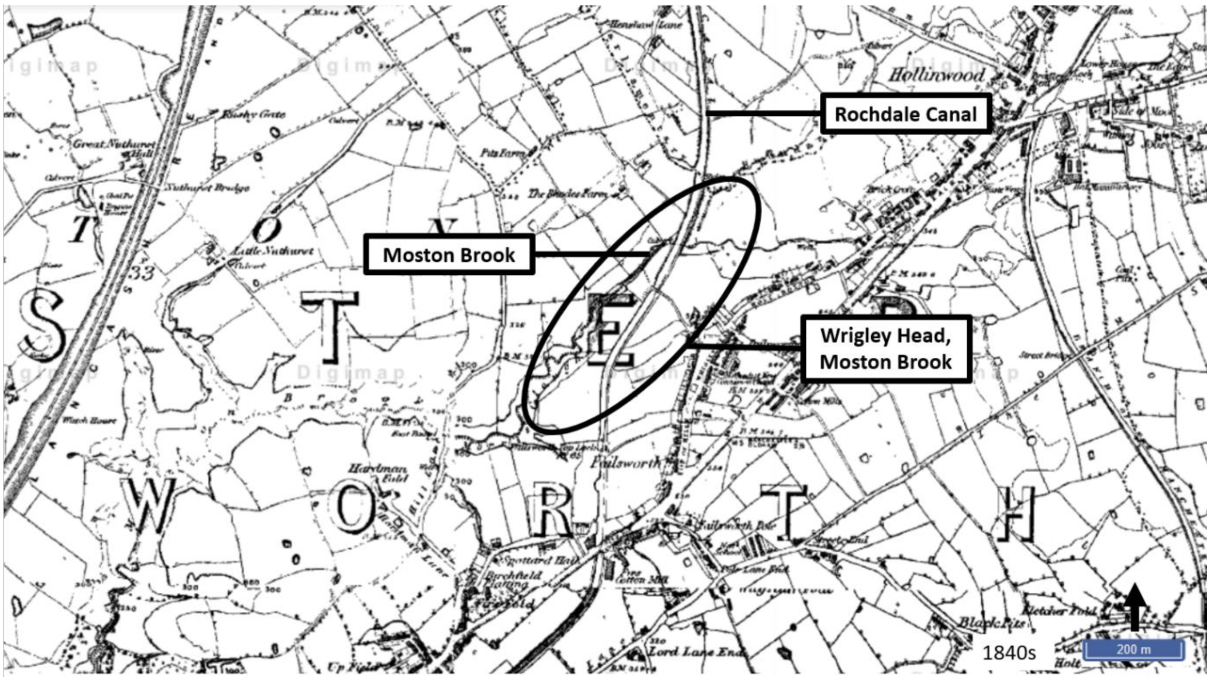


Figure 5.1 Historical map of the Wrigley Head, Moston Brook dated 1840s

The findings showed that the late 1840s saw the advent of the cotton and other industries in this area. There were several mills established from 1848 including Wrigley Head mill, Hope mill, Ridgefield mill and Moston Mill Print Works. The mills were linked to mill ponds and mill races and the Moston Brook that flows through the site (Groundwork Oldham & Rochdale, 2008). There were also tanneries, for example Failsworth tannery, and dye works, for example Spring Valley Dye Works, in this area (Figure 5.2). Communication into and out of the area was improved by the coming of the railway in 1880. In addition, information obtained from the historical maps showed that residential development such as Witch House, Failsworth Lodge and Ridgefield House had progressed in this area since the 18th century. In 1890s, the new housing development started to develop at the northern part of the Wrigley Head on the area currently known as Belgrave Road and this housing development progressively extended towards the Fairway. In addition, the results obtained from previous site reports showed that many farm settlements such as Bluestone farms were opened around Wrigley Head in 1890s (Figure 5.2) together with different industrial and economic activity being the major activity around Wrigley Head.

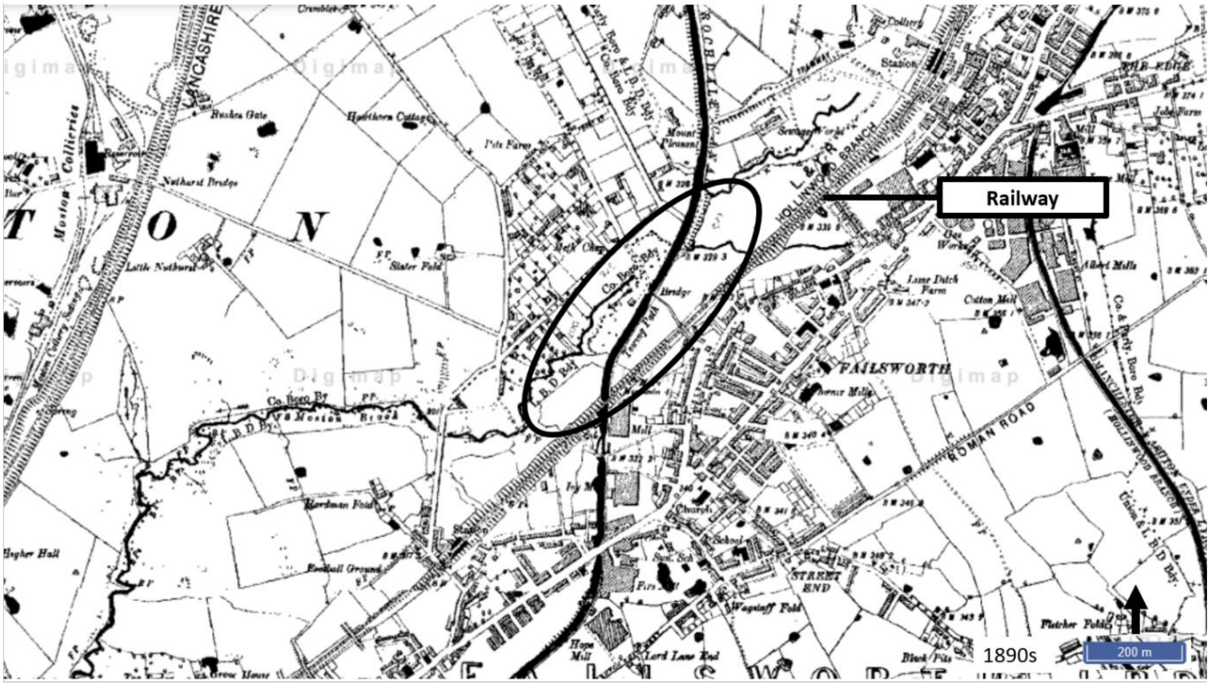


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Figure 5.2 Historical map of the Wrigley Head, Moston Brook dated 1890s

By 1910s, industrial and commercial activites such as Brick works, Springfield works, and Hope mill were the major industrial and commercial activities around Wrigley Head area (Figure 5.3). Having extracted clay for bricks many of the results holes were subsequently used as landfill sites. For example, the landfill site presently referred to as Hardman Fold was formally a large clay pit.

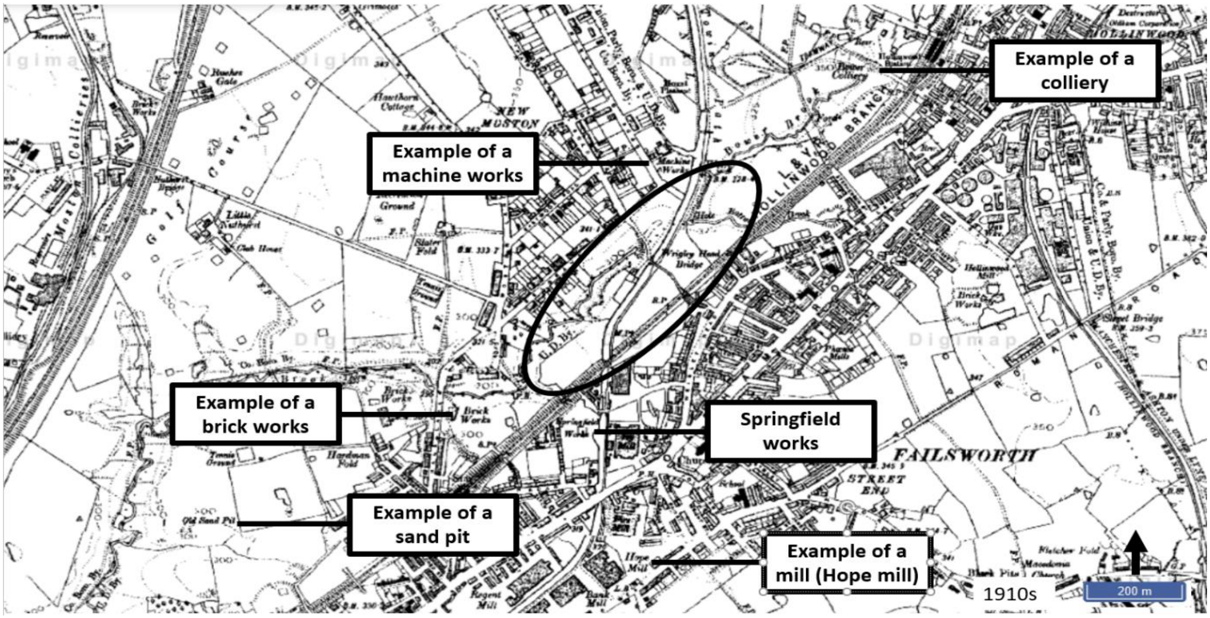

Figure 5.3 Historical map of the Wrigley Head, Moston Brook dated 1910s

Along with more housing the 1930s also saw an increase in recreational facilities in the area. For example, there were football pitches and bowling greens (Figure 5.4).

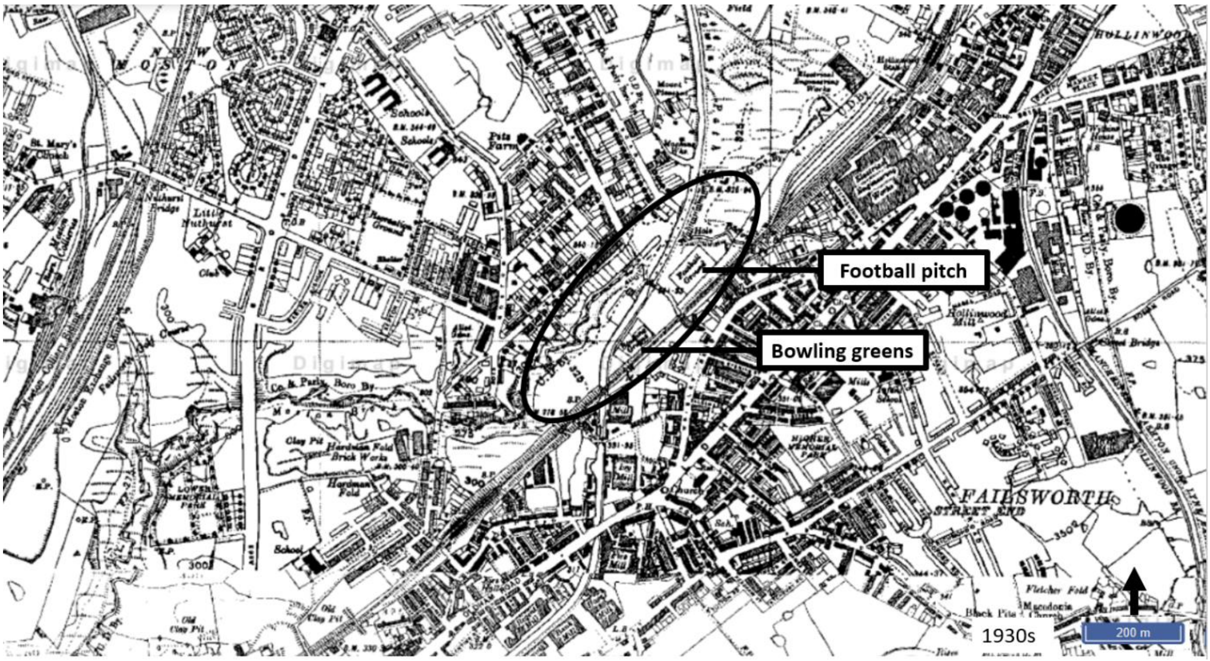

Figure 5.4 Historical map of the Wrigley Head, Moston Brook dated 1930s

By 1950s, many industrial and commercial activities appeared to have stopped in the area by 1950s leading to significant decrease in economic activities in the area. Taking advantage of the holes left after the extraction of sand and clay, several refuse heaps open around the Wrigley Head area (Figure 5.5).

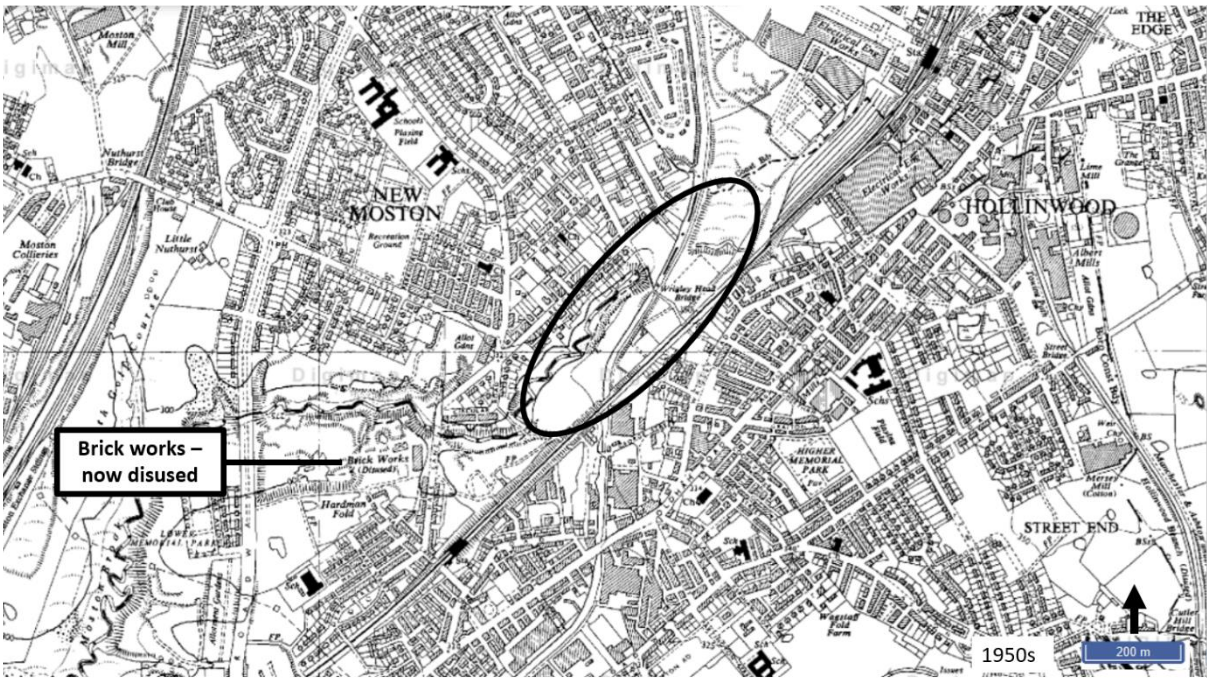

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Figure 5.5 Historical map of the Wrigley Head, Moston Brook dated 1950s

Tipping of refuse materials commenced around Wrigley Head before Environmental Pollution Act (1974). These refuse dumps became visible in ordnance survey maps as from 1949 onwards. Within this period, only a few industries were probably still operational as can be seen on the map (Figure 5.6). Between the 1970s and 1990s, many refuse dumpsites around Wrigley Head, Moston Brook area had been closed due to enforcement of Environmental Pollution Control Act 1974. This environmental legislation resulted in significant decrease in refuse heaps at the site and led to reprofiling of some of the open dumpsites in the early 1980s during the landscaping works.

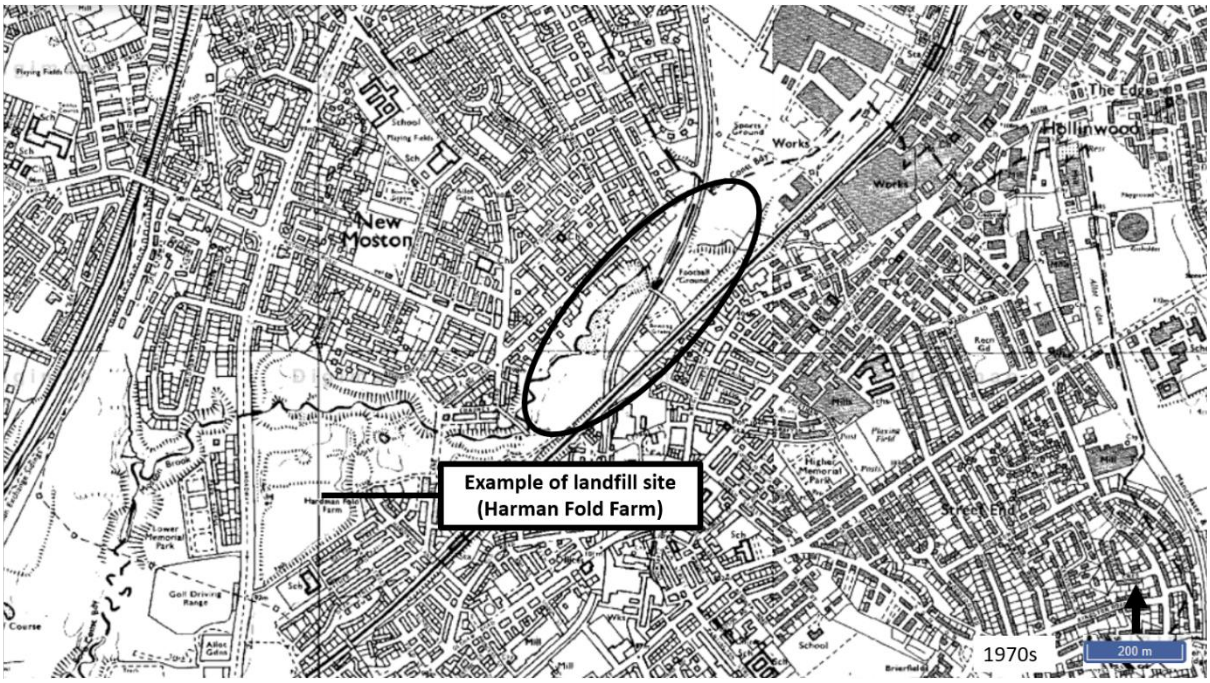


Figure 5.6 Historical map of the Wrigley Head, Moston Brook dated 1970s

One waste dump in the 1970s has left a legacy by way of its name. Known locally “White Hills” is thought to have been a dump of China Clay. It was certainly a clear landmark in the landscape (Figure 5.7)

Figure 5.7 "White Hills" beside the brook near Wrigley Head, here shown in 1970 (Source Alan Hampson, created 1 November 1970, Creative Commons - CCBY-SA 4.0).

Information gathered from a past site report showed that previous site walkover survey was carried out by MCC Contaminated Land Section (CLS) on 10 and 25 January 2011 at the site. The results revealed that there had been several historical landfill sites in the area (Miller, 2011). The sites are all formed of informal public open space along the Moston Brook river valley. The river banks are all steeply sloping and enclosed within steep banks (potentially formed of landfill material). In addition, the findings obtained from the previous walkover survey and site reports indicated that there had been fly tipping along the bank of Moston Brook. Tipping of waste started prior to implementation of Environmental Pollution Act 1974, which requires licensing of all controlled waste deposited onto land. The tipped waste consisted of heterogeneous materials and no validated information is held regarding the nature of waste materials buried in the soil. Records obtained from Manchester City Council showed that there had been thirteen historical landfill sites located around the Moston brook Area (Miller, 2011). A brief description of these landfill sites can be found in Table 5.1.

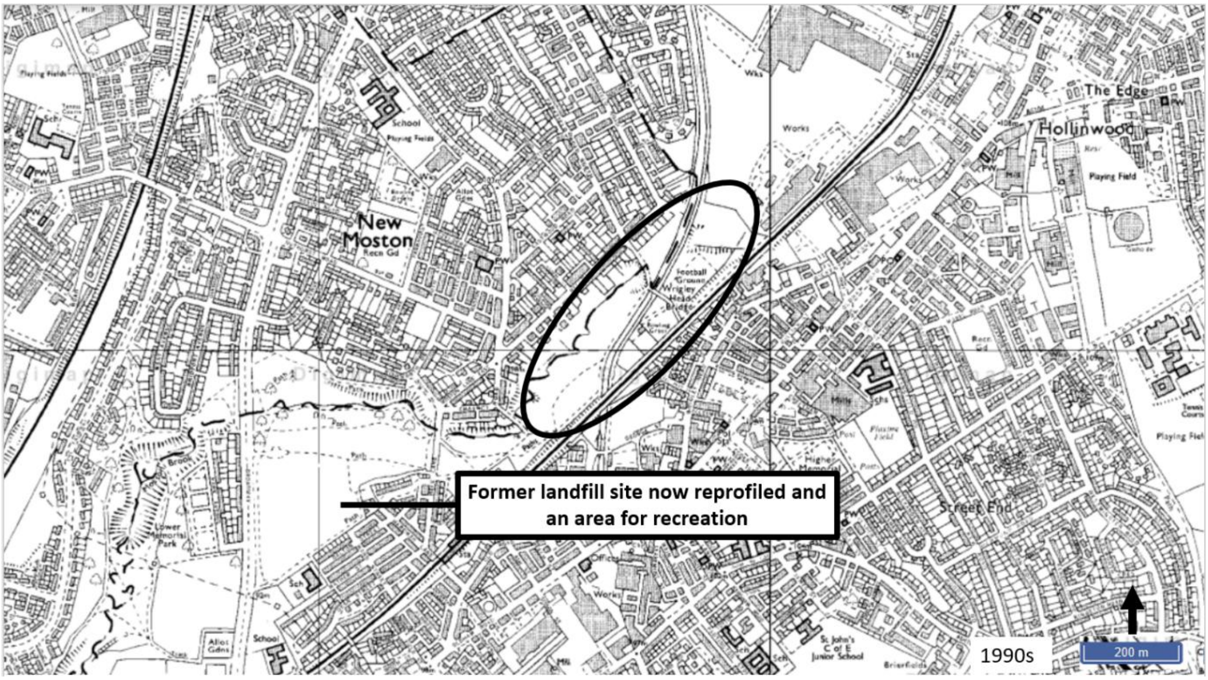
Table 5.1. Historically landfill sites located within and around Moston Brook

Landfill Site	**Details of Landfill Site**
“White Hills” Moston Brook	No validated data is held for this landfill site. Although, a walkover undertaken by Parsons Brinckerhoff in 2008 identified waste material near the soil surface
Reliance Street	There is a history of unknown fill material at this landfill site because this landfill was filled before the Control of Pollution Act 1974 which legally required licensing of all controlled wastes deposited onto land. Planning permission which was granted in 1979 for the landfill sites to be use as a waste disposal site
Belgrave Road	No validated information is held regarding this landfill site
Rear of Fairway	This landfill site operated before the Control of Pollution Act 197, and consequently, the exact nature of fill material is not known
Mill Lane/ Mill Street	No validated information is available for this landfill site
Rear of Romer Avenue	It is believed this landfill site was located in Oldham Metropolitan Borough Council and was used for tipping of domestic waste before the Control of Pollution Act 1974. Consequently, the exact nature of fill material was not known.
Morton Street	No validated information is held for this landfill site.
Moston Brook	No validated information is available for this landfill site
Moston Colliery	In 1966, an approval for planning permission was granted for private tipping of waste on the part of golf construction. Tipping of waste started at the landfill site before Control of Pollution Act 1974. Consequently, the exact nature of fill material was not known
Hole Bottom Clough	Tipped by Sheelin Construction for demolition and construction waste, generating maximum of 75,000 and less than 250,000 tonnes of waste in a year.
Joyce Street	An approval for waste management license was obtained in 1979 for the purpose of controlling waste disposable activities on site during the bulk fill stage of a landscape contract. Landfill gas monitoring is thought to have been carried out at this site, however, no information is available regarding the nature of fill material and outcome of gas monitoring.
Lancaster Sports Club	No documented information is available for this landfill site
Hardman Fold	No validated gas monitoring information available for this landfill site. Operated by GMWDA and tipping of waste started in 1979 but the site was restored in 1983. A passive venting system was installed at this site.

(Source: Miller, 2011)

Tipping of waste materials into landfill significantly contributed to the contamination of the area and this site forms a potential source of unknown contaminants. Most of the historical landfill sites had no documented records regarding them, which means that the nature of materials used for landfill and state of the landfill sites are not known. Evidence gathered from a previous site report also suggests that some of the landfills have been in use until recently before they were shut down and this was believed to have created a legacy of heavy metal contamination at the site (Groundwork Oldham & Rochdale, 2008). There are records of the Brook being visibly blue because of dye-works contamination discharging into the water.

During the 1980s, Manchester City Council's Education Department established an urban farm in the south-western edge of the Moston Brook, however, the farm closed in the early 1990. By the 1990s most industrial activities had ceased in the Wrigley Head area and the land was open space (Figure 5.8)



Former landfill site now reprofiled and an area for recreation

1990s

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Figure 5.8. Historical map of the Wrigley Head, Moston Brook dated back from 1990s

Today Moston Brook consists of four linked sites namely:

(a) Wrigley Head = 12.96 ha is a mosaic of broadleaved woodland and neutral grassland, and these sections are mostly used for informal recreational activities. Along the bank of the Brook is the mosaic of habitats that comprise marshy grassland, dominated by hard rush and hairy sledge. The Rochdale Canal, which runs through this area, is designated as a Site of Special Scientific Interest and Special Area of Conservation and provides an important link to recreational activities and maintains additional access to the site.

(b) Hardman Fold = 13.80 ha with meadows, woodland and a waterside walk

(c) Broadway Common = 26.11 ha incorporating Lower Failsworth Memorial Land. This is adjacent to Lower Memorial Park. Part of this land was purchased by public subscription after the First World War as open space for the residents of Failsworth. This is the site on which we plan to hold our annual Moston Brook Fun Day and other outdoor events; and

(d) Moston Fairway = 7.47 ha part of which is a Site of Biological Importance, is a Lancashire Wildlife Trust nature reserve and contains a remarkable piece of marsh in the otherwise urban environment. (Groundwork Oldham & Rochdale, 2008) (Figure 5.9).

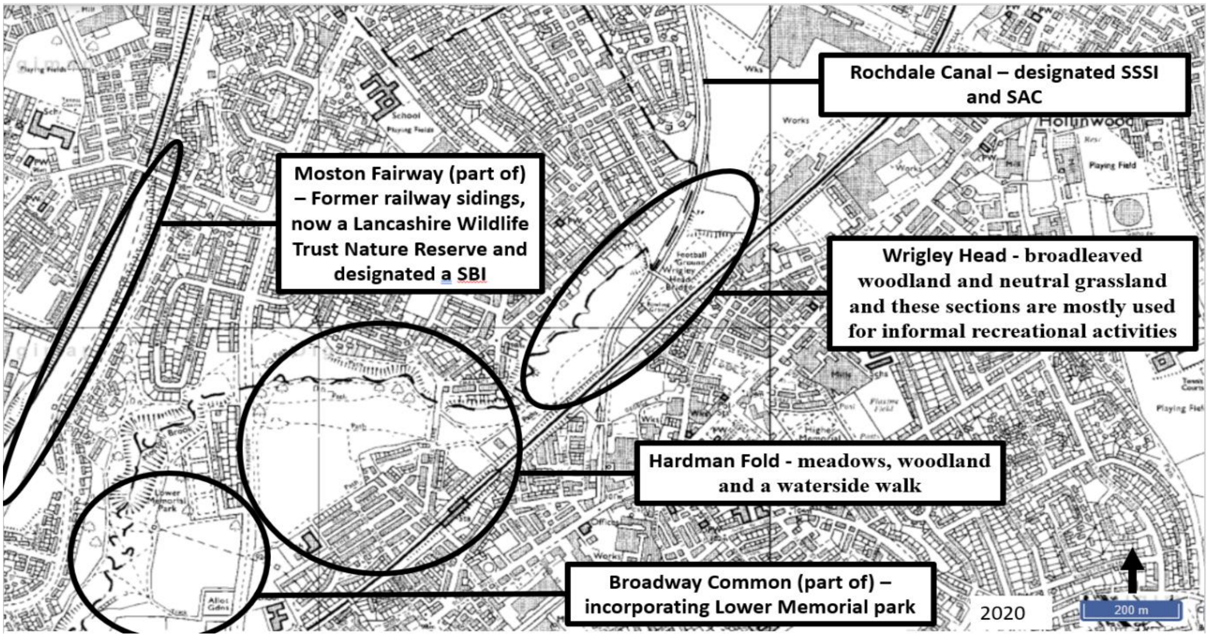

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Figure 5.9. Map of Moston Brook in 2021

5.2.2 Environmental Context of the Site.

Collectively this corridor creates a continuous linear greenspace that links with the wider Irk Valley green space network through Lightbowne Country Park and Newlands site at Moston Vale. It is an area dominated by deciduous woodland (Figure 5.10). In 2007, The Greater Manchester Ecology Unit conducted habitat survey of the Moston Brook corridor. The results obtained showed that Moston Brook corridor is bookended by the Rochdale Canal designated as both a Special Area of Conservation (SAC) and a Site of Special Scientific Interest (SSSI) – designated for being an important habitat for submerged aquatic plants and emergent vegetation, including extensive colonies of the nationally scarce SAC species floating water-plantain (*Luronium natans*) and supporting a diverse assemblage of aquatic flora, notably its assemblage of pondweeds, *Potamogeton* spp; the nine species of which found in the canal) and Moston Fairway Nature Reserve a Site of Biological Importance (SBI) which is a designated site of sub-regional nature conservation importance. The results obtained revealed that the important habitats identified in the corridor include lowland broad leaved woodland, marshy grassland, reed bed and lowland heath/acid grassland. Similarly, the important species identified included song thrush (*Turdus philomelos*), house sparrow (*Passer domesticus*), starling (*Sturnus vulgaris*), snipe (*Gallinago gallinago*) and kestrel (*Falco tinnunculus*) (Greater Manchester Ecology Unit, 2007).

Map removed due to copyright restrictions.

Map detail can be viewed at www.magic.gov.uk

Figure 5.10 Deciduous Woodland habitat at Wrigley Head (Source www.magic.gov.uk)

The results obtained from the previous reports indicated that an area located within Wrigley Head Bridge is popularly known as the Football Ground (Figure 5.17) due to various recreational activities such as football matches that took place in this area in the past and also used presently as informal open place for local people and visitors and a training ground for Alsatian dogs (Groundwork Oldham & Rochdale, 2008). This area is made up of a piece of fairly flat land bounded by native hedge trees, scrubland and the railway embankment. The trees enclosing the towpath prevent the Rochdale Canal from being visibly seen and extend further to Belgrave Road across the bridge. The surface is characterised by loose rocks that probably linked to past industrial land use. The area has open and exposed area suspected to be heavily contaminated with heavy metals at the centre and the eastern end and western edge are presently used as a BMX track and a dog training centre (Groundwork Oldham & Rochdale, 2008). This area is cut up by the ‘white stuff’ path and has been abandoned, with overgrown vegetation particularly along the edges. The remaining parts of Hole Bottom brook that contributes to Wrigley Head, Moston Brook can still be visibly seen on the northeastern end. This currently looks like a linear marsh land. The rough and unmanaged nature of the site is linked with an unsettling air to it (Groundwork Oldham & Rochdale, 2008). An area of contamination (locally known as “White Hills”) (Figure 5.17) is located between the Rochdale Canal and the brook with the soils consisting of pale-yellow materials. These hills were reprofiled during the landscaping works that were carried out in the early 1980s. Consequently, paths and steps were constructed, and the waterway edges were reinforced. In addition, some of the valley slopes were smoothed and drainage channels installed. British Rail carried out some planting to stabilise the embankments and fencing was also installed along the railway.

The results also indicated that Moston Brook watercourse flows from east to west through the site and defines the boundary between the Manchester City and Oldham Metropolitan Borough Councils, and this watercourse is regarded as a main river according to Environment Agency (Groundwork Oldham & Rochdale, 2008).

Figure 5.11 Degraded Moston waterways

The study site has a natural floodplain, and the magnitude of natural floodplain is shown on the flood map developed by Environment Agency (Miller, 2011). The Environment Agency flood map suggests that this site is prone to flooding from rivers and the likelihood of flooding each year is 1 in 100 (1%) or even greater (Miller, 2011).

Figure 5.12 Extent of flooding from Moston Brook (Source https://flood-warning-information.service.gov.uk/long-term-flood-risk/map)

Figure 5.13 Extent of flooding from surface water (source https://flood-warning-information.service.gov.uk/long-term-flood-risk/map).

Other extended areas of the study area are likely to be affected by a severe flooding. The Brook has a poor water quality due to a legacy of historical contamination (Groundwork Oldham & Rochdale, 2008) (Table 5.2).

Table 5.2. Environment Agency environmental quality standards for watercourses within 1000 metres of the site

Water course	Distance from the site	River quality (chemical)	River quality (biological)	Surface water abstractions
Moston Brook	Located on site	E	F	None identified

Source: Miller (2011)

Considering both the chemical and biological general quality assessment of the Brook water, Moston Brook is classed as Grade F (bad) by the Environment Agency.

Data obtained from the past report showed that there has been one significant documented environmental pollution incident at the study site since 2001 (Miller 2011).

Details of the pollution incident are shown in Table 5.3. In addition, the data obtained from the British Geological Survey (BGS0 and the Health Protection Agency (HPA) showed that the sites are not located within a Radon Affected Area (Miller 2011).

Table 5.3. Recorded pollution incidents located within 250 metres of the site

Date	Location	Pollution incident type	Pollutant
15th June, 1995	Moston Brook	Category 2 (significant incident)	Discharge of crude sewage into Moston Brook

Source: Miller (2011)

Three elements of contaminant linkage (contaminant – pathway – receptor) were identified at the site during the preliminary risk assessment of the site. These three elements of contaminant linkage must be present for harm to occur to a designated receptor at the site. Although, the nature and level of the risk at the site may be affected by the technical and scientific factors such as the surrounding land uses, soil nature and the underlying geology and hydrology (Miller, 2011). All these factors may affect contamination risk assessment at the site. These contaminants may impact negatively on designated receptors through several pathways. The history of the site is such that there are a number of potential sources of contamination at the sites. Tables 5.4, 5.5, 5.6 and 5.7 contain the onsite potential contaminant sources, offsite potential contaminants sources, major identified contaminant pathways and potential receptors for the investigated site and source – pathway – receptor linkage (Miller, 2011).

Table 5.4. On site potential sources of contaminants

Onsite	Potential Contaminants
• Infilled ponds • Landfill sites /heaps of refuse • Mill • Brickworks	• Ash Cinders • Asbestos • Metals • Phenols • Polycyclic Aromatic Hydrocarbons (PAHs) • Total Petroleum Hydrocarbons (TPHs) • Volatile Organic Compounds (VOCs) • Ground Gas • Leachable Contaminants • Semi Volatile Organic Compounds

Source: Miller (2011)

Table 5.5. Offsite potential sources of contaminants

Offsite	Potential Contaminants
• Railway lines and Goods Sheds • Infilled Excavated Areas • Refuse Destructor • Landfill Sites • Dye Works	• Metals • Asbestos • TPHs/PAHs • Leachable Contaminants • Ground Gas

Source: Miller (2011)

Table 5.6. Major identified contaminant pathways and potential receptors for Wrigley Head.

Potential contaminants pathways for the site	Identified Potential Receptors
• Human ingestion	• Humans (particularly those using the site in its present condition, ground workers in site development; using the site in its remediated/developed form
• Dermal contact	• Vegetation/plants
• Inhalation of contaminated soil/dust/water/food through uptake by plant roots.	• Land next to the site
• Controlled waters pollution through infiltration and percolation of leachable contaminants and movement of contaminated ground water.	• Controlled waters below and next to the site, Principal aquifer, Secondary A aquifer, the Moston Brook and Rochdale Canal.

Source: Miller (2011)

Table 5.7. Source – Pathway – Receptor linkage

Pollution Linkages		
Source	Pathway	Likely Receptors
• Gas emissions from made Ground (linked to former industrial use and landfilling)	• Vapour inhalation • Movement/migration through made Ground	• Site users (open space) • Nearby residential properties
• Soil contaminants such as metals, asbestos, PAHs, TPHs	• Ingestion/inhalation/direct contact with contaminated soil or dust	• Site users (open space)
	• Uptake by plants through roots	• Vegetation and potential vegetable planting
	• Leaching of contaminants within and off the site	• Site users • Moston Brook
• Particulates	• Ingestion/inhalation/direct contact with contaminated soil or dust	• Site users (open space)

Source: Miller (2011)

Results from the preliminary risk assessment and site investigation report conducted by Contaminated Land Section Manchester City Council showed that study area was contaminated by multiple contaminants especially arsenic and other heavy metals and total petroleum hydrocarbons (TPH) (Miller, 2011). The investigations consisted of soil and water chemical testing at these sites to determine the condition of the underlying sediments and the likelihood of any contamination at the site. The investigations included machine excavated trial pits and hand dug pits at a maximum depth of 1 metre below ground level. The findings of the report indicated that made ground was found across all the investigated sites because of anthropogenic historical industrial activities in the area. Material associated with “White Hills” site was observed during the excavation in parts of the “White Hills” located around the Wrigley Head. In addition, the results obtained from this report showed that elevated concentration of arsenic and total petroleum hydrocarbon (TPH), and elevated iron and ammonia in the surface water and in the Brook were found across the site (Miller, 2011) (Tables 5.8 and 5.9).

Table 5.8. Summary of elevated contaminants identified in soil in Wrigley Head

Contaminant	**Tier 1 Assessment Criteria (mg/kg)**	**Number of Exceedances**	**Sample Details**	**Maximum Concentration (mg/kg)**
Arsenic	32	8	Includes all the samples at various depths	800 (HP112)
Cadmium	10	1	HP112 at 0.1 mbgl	15
Lead	450	3	TP112 at 0.1 mbgl. TP112 at 1.0 mbgl. HP112 at 0.1 mbgl.	1970 (TP112, 0.1 mbgl)
TPH >C16-C24	8.48	2	HP111a at 0.1 mbgl. HP111a at 0.4 mbgl.	17.1 (HP111 a, 0.4 mbgl)
TPH >C24-C40	8.48	2	HP111a at 0.1 mbgl. HP111a at 0.4 mbgl	44.6(HP111 a, 0.4 mbgl)

Source: Miller (2011)

bgl = below ground level

m = metre

TP112, HP111, etc = sample labels

LOD = Limit of detection

TPH = Total Petroleum Hydrocarbon

Table 5.9. Summary of elevated ammonia and iron identified in controlled waters in Wrigley Head

Site	**Contaminant**	**Tier 1 Assessment Criteria (mg/L)**	**Number of Exceedances**	**Sample details**	**Maximum concentration (mg/L)**
Wrigley Head	Ammonia	0.015	3	Includes all sampled locations	0.24 (L111A)
	Iron	1	3	Includes all sampled locations	140 (L112)

Source: Miller (2011)

Therefore, Wrigley Head was found to pose a moderate risk to controlled water because of high levels of iron and ammonia in the surface water and the Moston Brook. The potential risk to human health from the contaminants identified within the materials at the site was assessed using a Generic Quantitative Risk Assessment where the levels of contaminants identified at the site were compared with appropriate Generic Assessment Criteria (GAC or Tier 1 Assessment Criteria). Soil Guideline Values (SGVs) and GACs were used to evaluate the potential risk of contaminants to human health at the site. SGVs are assessment criteria developed by the UK to assess the risk to human health from exposure to contaminated land (DEFRA, 2014). SGVs and GACs have been derived for a limited number of typical lands uses as defined within the Contaminated Land Exposure Assessment (CLEA) model (version 1.06). The human health risk assessment indicated that Wrigley Head was found to pose a high risk to human health due to significant level of arsenic above Tier 1 assessment criteria in the “White Hills” of the site. Table 5.10 shows the summary of environmental risk assessment for Wrigley Head.

Table 5.10. Wrigley Head Environmental Risk Assessment

Source	Targeted receptor	Siteuse	Exposure route	Probability	Consequence	Risk classification
1.Contaminated soil material	**Humans**	Current	**Ingestion.**	Likely	Medium	Moderate
		Developing	**Inhalation.**	**High Likelihood**	**Medium**	**High**
		Future	**Direct contact.**	Likely	Medium	Moderate
2. Samples from Surface Water	Humans	Current	Ingestion.	Low likelihood	Mild	Low
		Developing	Direct contact.	Likely	Medium	Moderate
		Future		Low likelihood	Mild	Low
	Controlled Waters	**Groundwater**	**Leaching. Direct contact**	**Likely**	**Medium**	**Moderate**
		Surface waters		**Likely**	**Medium**	**Moderate**
	Vegetation		Root uptake Direct contact	Likely	Medium	Moderate

Source: Adapted from Miller (2011)

Key

🟧	High risk
🟧	Moderate risk
🟨	Moderate/Low risk
🟩	Low risk
🟦	Very Low Risk

Current plans for Wrigley Head are to install an all-weather eco waterside path leaving the site much as it is. There is also a suggestion to use the site as a solar power farm (Ann Bates, Personal Communication).

5.2.3 Site Visit

The initial site visit was undertaken in May 2015 by Junhao Quin and Obinna Nworie in order to develop an understanding of the current conditions of Wrigley Head and to plan the field sampling strategy. Junhao Quin was a visiting PhD student from South China Agricultural University and Obinna Nworie was the main research student. Consent was obtained from the management of Moston Brook before the research work proceeded.

Field observation during the site visit showed that Wrigley Head was dominated by Rochdale Canal at the northwestern edge of the area and is predominantly flat area with the surrounding houses. The Rochdale canal is a linear waterway with a path along one of the sides. Moving towards the southern edge of the canal, the flat land appears to be larger, but the small area of the site occupied mostly by Hole Bottom Brook dramatically slopes down. There is an embankment which is very steep and inaccessible towards the northern edge of area which slopes steeply down from the surrounding backs of the houses. A close look at the southern edge of the area shows that the edge has a gentler slope and more accessible, and it is flat in the areas located near to the canal. Also, at the southern edge of the area, is the Manchester Oldham railway which runs at a higher level of the site separating it from the nearby houses, and at the same time providing an enclosure. Figures 5.14 and 5.13 show the pictures of Wrigley Head bridge and Rochdale Canal.

Figure 5.14 Wrigley Head Bridge

Figure 5.15 Rochdale canal

The field observation showed that the surface of the site is characterised by informal mud paths and boardwalks with fragmented areas of leachate accumulation and sits within a steep sloping river valley dominated by closed landfill sites. A look at the topography of the site indicates that the area has been altered because of historical human activity, and thus, the shape of the land in this area has changed considerably. The site visit shows that the site is currently used as informal public open space. Dog walkers appear to be the main users of the site and people accessing the footpaths to the adjoining main roads during the site visit. Figure 5.16 shows site users walking their dog across the site during the site visit.

Figure 5.16 Dog walkers at the site

Through visual observation and desktop survey, several areas across Wrigley Head Bridge were identified for sampling as can be seen in Figure 5.17, and these areas are Football Ground – bare and vegetated areas, middle of the site, floodplain areas, areas close to footpath and areas located around “White Hills”. The middle of the site covers area extending north from the central part of the “White Hills”. The roadside covers area along the road running parallel to the canal.

Figure 5.17 Aerial map of different parts of Wrigley Head, Moston selected for site investigation

The Football Ground is a former area for various recreational activities such as football matches and used presently as informal open space for local people and visitors and as informally used for BMX track and a training ground for Alsatian dogs as shown in Figures 5.18 and 5.19. This area is characterised by a piece of fairly flat land bounded by native hedge trees, scrubland and the railway embankment (Figure 5.19). The area is dissected by the ‘white stuff’ path and is neglected with overgrown vegetation along the edges. From carrying out a site visit the centre of the site was bare ground with very little vegetation and what looked like “slag’’ / iron works waste deposits protruding from the ground. The surface is characterised by loose rocks that probably linked to past industrial land use. The area appears to have a peculiar contamination issue due to the open bare area at the centre suspected to be heavily contaminated. No sign of fly tipping was seen at Football Ground.

Going towards the boundaries of this area, there were lots of self - seeded / unmanaged vegetation – grass, trees etc. The surrounding vegetated area is characterised by unmanaged dense vegetation comprising of different trees and grasses as can be seen in Figure 5.19. Presence of dry plant litters and other materials were found on the soil surface. These materials are believed to be plant leaves that had fallen off and decomposed alongside with other organic materials. The surrounding vegetated area covers both sides of the open bare ground of the Football Ground with a rough slope. Rochdale Canal – a Site of Special Scientific Interest and Special Area of Conservation runs through this area. The trees enclosing the surrounding area prevent the Rochdale Canal from being visibly seen.

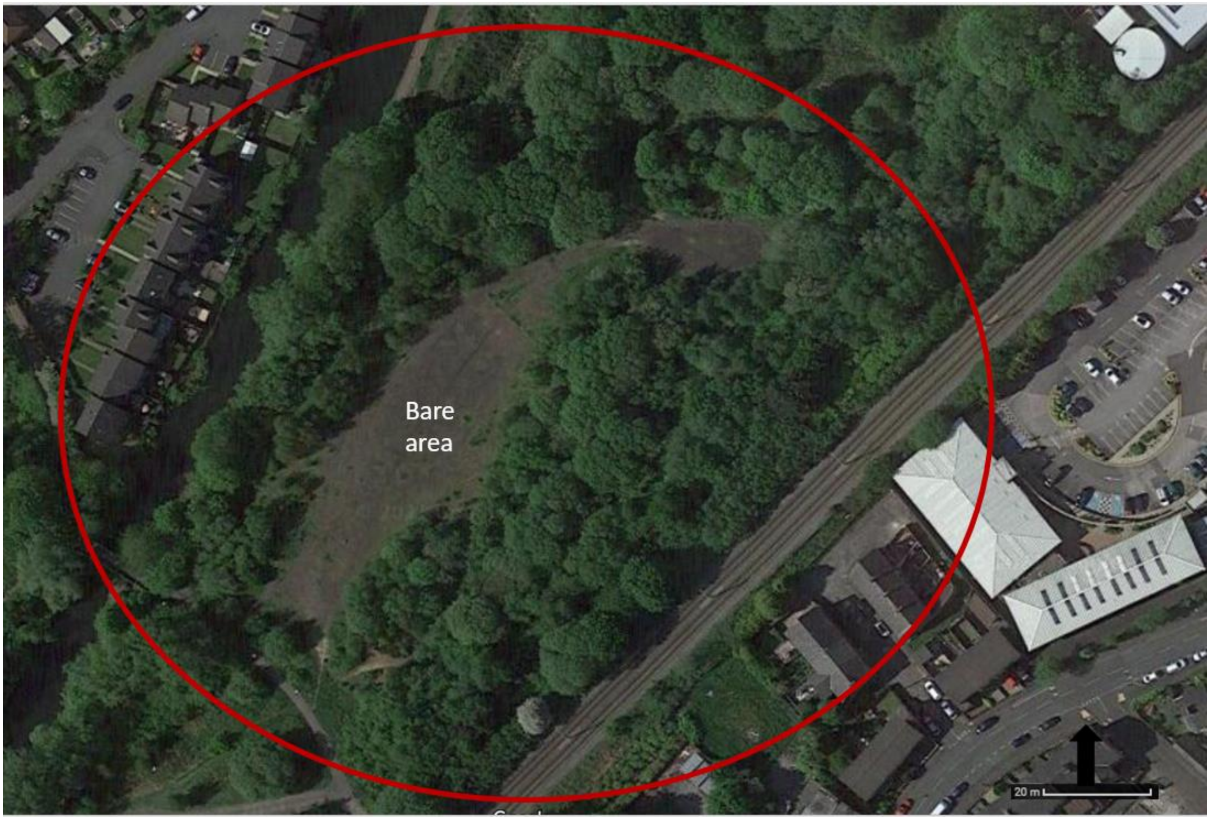

Figure 5.18 Aerial photograph showing the bare area of Football Ground with surrounding vegetation

Figure 5.19 Open and bare area of Football Ground including the surrounding vegetation

Several visual observations of the historical industrial activities in the area were made. Traces of historical industrial activities at the site were also observed. For example, traces of several mills that were operating at the site in the past such as the Mill Lane Bridge and the weir, probably linked to the Moston Mill race, and the pond north of the brook located on the path towards Williams Road are still visible in the area. However, evidence of other industrial activities such as print, dye and brick work that had taken place at the site in the past can be seen on the historical maps (See Figure 5.1) but are no longer visible at the site due to these industrial activities probably could have been altered by the waste disposal activities that dominated the study area after major industrial activities had ceased in the area.

Results obtained from the site visit showed that informal and improved pathways were constructed along the river corridor and boardwalks were also seen around the Wrigley Head. Figure 5.20 shows the informal footpath improvement along Wrigley Head.

Figure 5.20 Wrigley Head improved footpath

Figure 5.21 A constructed bench at the site for the local public

The area around Wrigley Head bridge is known by local residents as the White Stuff or the ‘White Hills’ in reference to the brickworks’ waste that formed steep and unstable hills alongside the brook. The “White Hills” (5.53 hectares) is located between the canal and the brook with the soils consisting of pale-yellow materials and is suspected to be heavily contaminated by arsenic and total petroleum hydrocarbon. This area is situated in the Failsworth West ward and covers an area of 5.53 hectares according to previous report (Miller, 2011). The area is bounded to the north by informal public open space and residential housing, to the east by public open space and the Rochdale Canal, to the south by a railway line and commercial premises and to the west by public open space (Hardman Fold). This area received a substantial number of wastes in the past and it is referred to as “White Hills” by the residents. During the visit, traces of materials associated with former landfill sites were observed particularly around the “White Hill” area of the site. Whitish materials were seen deposited in this area as can been seen in Figures 5.21 and 5.22. These whitish materials are believed to be china clay waste from historical cotton mills in Failsworth area (Miller, 2011) as can been seen in Figures 5.21 and 5.22. Although, it was also observed that these whitish materials have been covered by grassland and woodland, but traces of it are still visible on the surface

Figure 5.21 Material from the landfill locally known as the ‘white stuff’.

Figure 5.22 Badger sett on the slope bringing white material to the surface

CHAPTER 6

Heavy Metal Contamination levels across the Investigated Soils in the Study Area

6.1 Overview

This chapter contains the results from the study conducted to examine heavy metal contamination in the Wrigley Head area of Moston Brook. The chapter begins with a presentation of data on the soil pH and electrical conductivity (EC) of the investigated soils in Wrigley Head. This is followed by presentation of data on the concentrations and spatial distribution of heavy metals in the investigated soils around Wrigley Head. Also presented in this chapter are the results of correlation of heavy metals around Wrigley Head. In the next section, the data on soil heavy metal contamination in the Football Ground area of Wrigley Head are presented. It starts with presentation of data on soil pH, electrical conductivity, and the total organic carbon of the investigated soils. The final section contains a presentation of results on the concentrations of heavy metals obtained from bare and vegetated areas of the Football Ground including the spatial distribution of heavy metals in the investigated areas.

6.2 Heavy Metal Contamination in Wrigley Head, Moston Brook.

6.2.1 Soil pH and Electrical Conductivity in the Investigated Soils

The pH and EC of the investigated soils are presented in Table 6.1. Among the studied soils, pH ranged from 5.46 – 8.32 with a median value of 6.50. The pH was highly variable across the investigated locations, and the median value indicated a slightly acidic condition. The median EC value was 64.50 mS/cm with a range of 17.6 – 182 mS/cm. No clear spatial variation trend was observed. There was no close relationship ($R^2 = 0.26$, $n = 27$) between the pH and EC. The EC values observed for all the investigated soils suggest that the investigated soils are typically non-saline soils.

Table 6.1 pH and Electrical Conductivity of the investigated soils.

Location	**pH**	**EC (mS/cm)**
FG1	8.32	96.40
FG2	5.86	70.60
FG3	6.62	35.20
FG4	6.57	17.60
FG5	7.12	39.10
FG6	6.76	182.00
FG7	6.16	64.80
FP1	7.58	39.20
FP2	7.69	135.00
FP3	6.27	70.60
FP4	7.41	138.00
FP5	7.10	152.00
MD1	7.02	64.30
MD2	7.61	153.00
MD3	6.21	42.10
MD4	5.46	38.90
MD5	7.53	123.00
RS1	6.39	116.00
RS2	6.47	72.40
RS3	6.50	45.20
RS4	6.81	132.00
RS5	6.25	61.50
RS6	5.50	53.50
WH1	5.85	37.50
WH2	6.09	45.50
WH3	6.16	51.40
WH4	6.12	62.10
Median	6.50	64.50
Range	5.46 – 8.32	17.6 – 182.00

6.2.2 Total Concentration of Heavy Metals in Wrigley Head, Moston Brook

The results showing the concentrations of heavy metals in the investigated soils are presented in Table 6.2. The concentrations of various heavy metals in the investigated locations were spatially variable (Table 6.2). The concentrations of copper, lead and zinc were relatively higher in some locations compared to chromium, nickel and arsenic. There were a few locations with concurrent presence of copper, nickel, lead and zinc at very high concentration. These locations are potentially more contaminated compared to other locations

Table 6.2. Concentration (mg/kg) of heavy metals in the investigated soils.

Location	**Arsenic**	**Chromium**	**Copper**	**Nickel**	**Lead**	**Zinc**
FG1	69	155	2768	802	1492	1263
FG2	80	154	3348	920	1587	1026
FG3	770	223	59	< LOD [a]	649	89
FG4	12	47	197	55	114	186
FG5	39	121	1237	1075	891	1881
FG6	40	103	408	145	345	218
FG7	51	133	626	129	402	580
FP1	510	161	78	57	362	143
FP2	148	144	170	71	434	453
FP3	472	136	119	17	919	242
FP4	54	108	63	53	137	128
FP5	50	95	60	55	132	119
MD1	34	87	32	11	46	72
MD2	1132	126	38	< LOD	623	28
MD3	269	142	35	6	191	71
MD4	761	204	79	< LOD	690	89
MD5	215	126	57	11	253	121
RS1	350	165	78	24	337	174
RS2	451	172	52	22	330	95
RS3	88	177	2380	425	1316	1450
RS4	324	152	75	9	329	118
RS5	857	202	89	< LOD	597	92
RS6	688	217	88	< LOD	569	109
WH1	993	200	61	< LOD	1380	89
WH2	96	108	134	10	156	95
WH3	268	139	51	< LOD	257	107
WH4	125	117	54	17	148	98
Median	215	142	78	17	362	119
Range	12–1132	47–223	32–3348	< LOD –1075	46–1587	28–1881
UK soil range [b]	0.5 – 143	1.14 – 236	2.27 – 96.7	1.16 –216	2.6 – 713	2.63 – 442
UK soil median [b]	7.1	29.2	17.2	15.8	37.4	65.9
UK screening level [c]	79	21	–	–	630	–
UK background value [d]	33.40	81.00	64.20	28.50	99.50	129.00

[a] < LOD: a concentration less than the limit of detection of XRF; [b] Ross et al. (2007) (determination by ICP-MS after aqua regia extraction); [c] DEFRA (2014); [d]Ander et al. (2012) and Appleton et al. (2013).

Most of the locations had a concentration of chromium over 100 mg/kg. There were locations with arsenic concentration greater than 500 mg/kg while copper and nickel concentrations were below 100 mg/kg in most locations. This suggests that there is a significant low concentration of nickel in these locations compared to other locations. The concentrations of nickel were below analytical detection limits in seven locations. There was no clear trend in the distribution of heavy metals across the investigated locations. The median concentrations of arsenic chromium, copper, nickel, lead and zinc in the present study were higher than the UK median soil values. Similarly, all the median concentrations of heavy metals except zinc and nickel were higher than the UK background value. The results of this study showed that there are marked differences in the concentrations of heavy metals across the investigated locations. The findings of the present study that there were variable levels of heavy metal contamination across the investigated locations.

6.2.3 Spatial Distribution of Heavy Metals in Wrigley Head, Moston Brook

Figures 6.1 – 6.6 show the spatial distribution of heavy metals across the investigated locations in Wrigley Head. The heavy metal concentrations obtained from the investigated soils were compared to EU standards (Table 3.1) and plotted on a map of Wrigley Head, Moston Brook to illustrate the level of contamination and where any hotspots occurred (Figures 6.1 – 6.6). On the map, each heavy metal was plotted separately across the 27 locations where soil samples had been taken as shown in Figures 6.1 – 6.6. Figures 6.1 – 6.6 indicate the generally high level of heavy metal contamination across the Wrigley Head. Many samples returned results that were above the EU Threshold limits. These data also illustrate the high variability of heavy metals across the whole of Wrigley Head.

The map showing the concentrations of arsenic across the investigated locations in Wrigley Head is shown in Figure 6.1. Arsenic exhibited high spatial variability pattern across the investigated locations as can be seen in Figure 6.1. The data showed that there was no clear spatial trend in the distribution of arsenic across the investigated locations. Arsenic concentrations exceed the EU higher guideline value (100 mg/kg, See Table 3.1) in most sampling locations (Figure 6.1). These locations with high level of arsenic contamination are indicated on the map by a dark grey colour and located towards the southwest part of the site and the central part of the site. In other words, these locations can be regarded as the "hotspots" compared to other parts of the site. There were seven locations, indicated by medium grey shading that had arsenic concentrations that exceed EU lower guideline value (50 mg/kg, See Table 3.1). These locations extend towards the southwest, central and northern parts of the Wrigley Head as can be seen on the map (Figure 6.1). Among the investigated locations, only four locations had arsenic concentrations below EU threshold value (5 mg/kg, See Table 3.1), and these locations are indicated on the map by a light grey colour and suggest locations with the lowest arsenic contamination within the Wrigley Head.

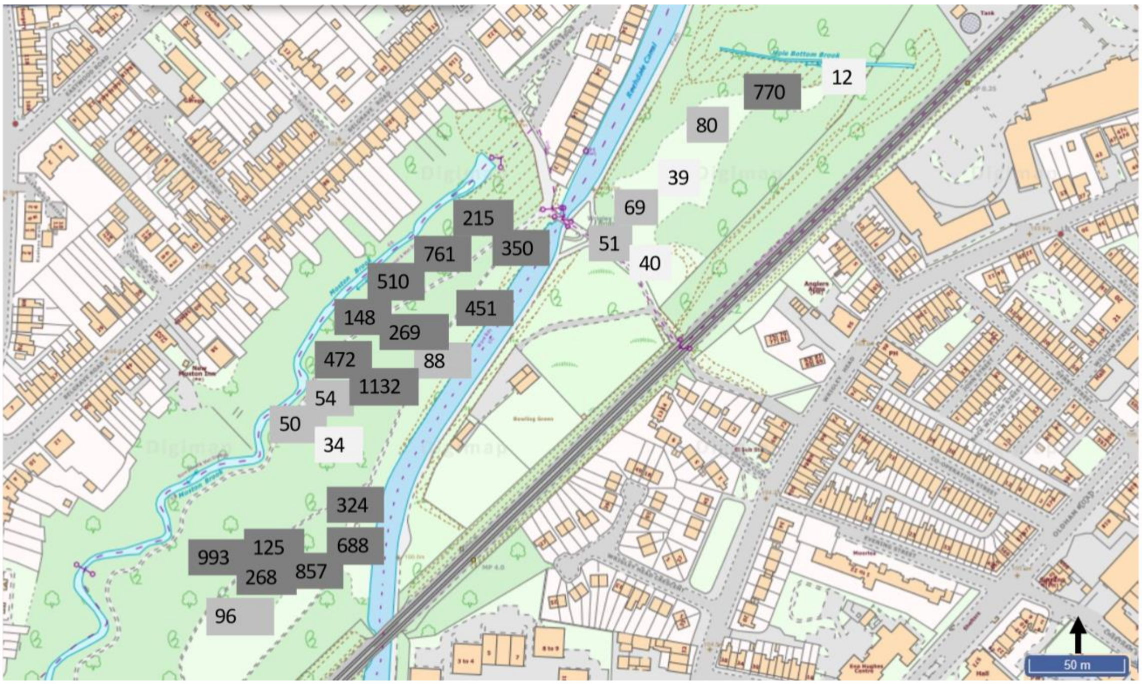

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Figure 6.1 Arsenic concentrations (mg/kg) (Shading: Light grey – value exceeds EU Threshold; medium grey – value exceed EU Lower Guideline; Dark grey- value exceeds EU Higher Guideline).

In addition, the map showing the concentrations of chromium across the investigated locations in Wrigley Head is shown in Figure 6.2. The chromium displayed low spatial variability across the investigated locations in comparison to other heavy metals. In most locations, the concentrations of chromium were below the EU higher guideline value (300 mg/kg, See Table 3.1). In other words, these data show that chromium concentrations exceed the EU threshold value (200 mg/kg, See Table 3.1) in most locations. These locations are shown on the map with a light grey colour. As can be seen on the map, there were a few locations indicated by a medium grey colour on the map scattered around the south west, central and northern parts of the Wrigley Head with chromium concentrations exceeding the EU lower guideline value (200 mg/kg, See Table 3.1). These locations potentially recorded the highest level of chromium contamination. However, there were a very few locations represented on the map by a white colour with chromium concentrations below the EU threshold value (100 mg/kg, See Table 3.1). These locations had the lowest chromium concentrations. There was no constant spatial distribution pattern of chromium observed across the investigated locations in the present study.

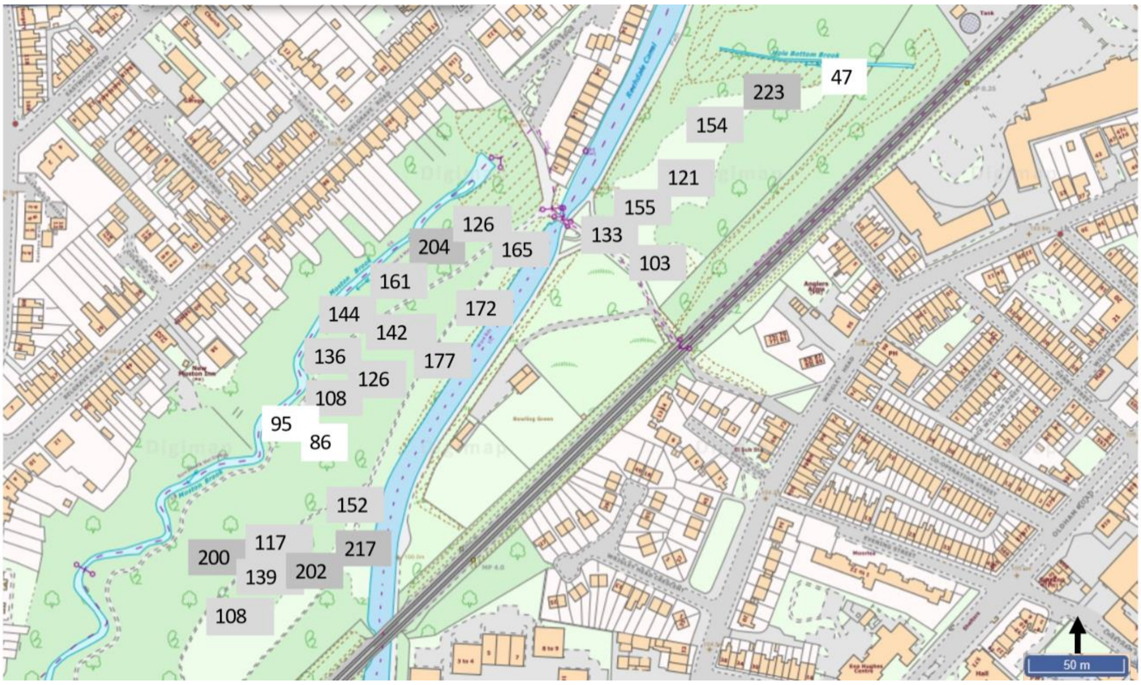

Figure 6.2 Chromium concentrations (mg/kg) (Shading: white – value below EU Threshold; Light grey – value exceeds EU Threshold; medium grey – value exceed EU Lower Guideline).

Copper showed relatively higher concentrations in locations in the northern part of the Wrigley Head compared to other locations of the site (Figure 6.3). Figure 6.3 shows a map containing copper concentrations across the investigated areas in Wrigley Head. Copper exhibited relatively high spatial variability and no clear spatial trend was observed across the investigated locations. Most of the locations had copper concentrations higher than the EU higher guideline value (200 mg/kg, See Table 3.1). These locations represent the highest copper contamination level among the investigated locations in the Wrigley Head, and are indicated on the map by a dark grey colour. Due to elevated copper concentrations observed in these locations, it can be regarded as the “hotspots”. Nevertheless, the data showed that most investigated locations had copper concentrations below the EU threshold value (100 mg/kg, See Table 3.1), and these locations are highlighted on the map by a white background. In other words, these locations recorded the lowest copper concentration, and they are scattered predominantly around the central and south west parts of the Wrigley Head are less contaminated with copper. The findings of this study suggest that a few locations around the northern part of the Wrigley Head are highly contaminated.

Figure 6.3 Copper concentrations (mg/kg) (Shading: white – value below EU Threshold; Light grey – value exceeds EU Threshold; medium grey – value exceeds EU Lower Guideline; Dark grey- value exceeds EU Higher Guideline).

Unlike arsenic, chromium, copper, lead and zinc, nickel concentrations recorded in the present study were below the analytical detection limits in most of the investigated locations (Figure 6.4). Figure 6.4 shows a map containing nickel concentrations across the investigated locations in Wrigley Head. Nickel concentrations recorded in most of the locations in the present study were below the EU threshold limit (50 mg/kg, See Table 3.1) for this regulated heavy metal. These are represented on the map by a white colour and indicate least contaminated locations. Moving towards the northern part as shown on the map, there were a few locations with concurrent elevated levels of nickel above the EU higher guideline value (150 mg/kg, See Table 3.1). These a few locations are represented on the map by a dark grey colour and potentially signify the highest nickel contamination level within the Wrigley Head. In addition, there were other areas with variable nickel concentrations scattered around the central part of the study area. These areas are indicated on the map by a light grey colour with nickel concentrations above the EU threshold limit (50 mg/kg, See Table 3.1). This highlights the variable level of nickel contamination in the present study. The data showed that nickel exhibited high spatial variability pattern in some investigated locations (Figure 6.4).

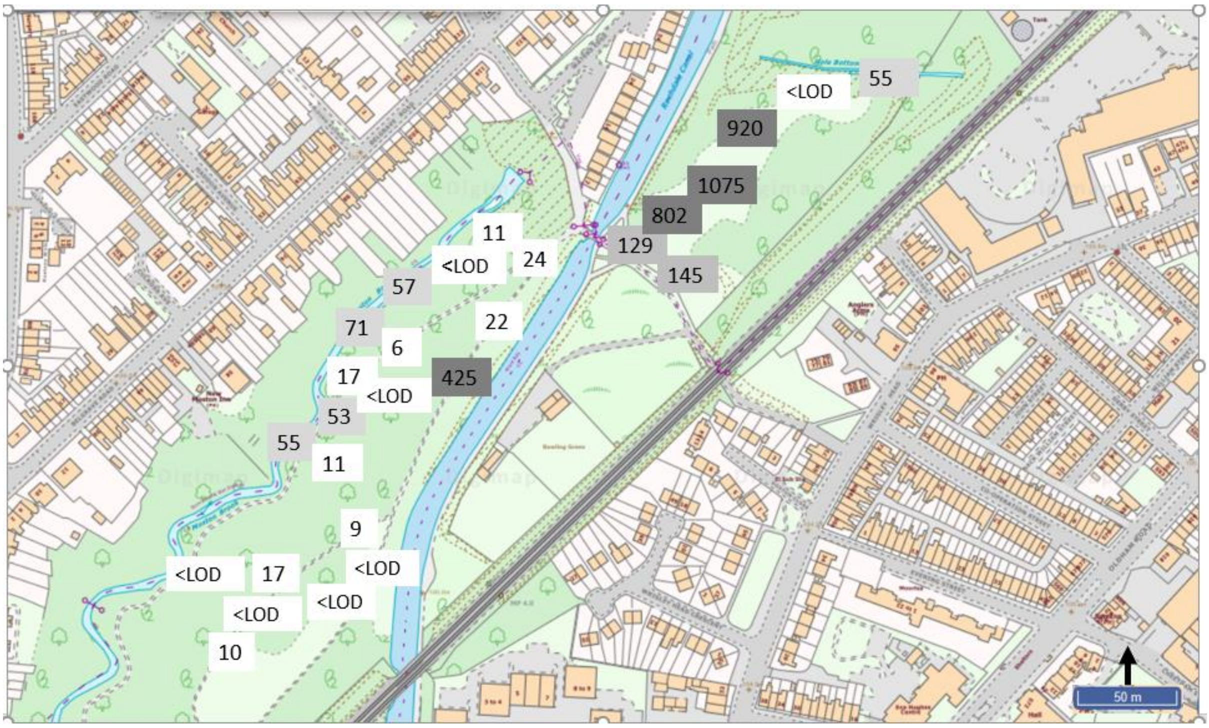

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Figure 6.4 Nickel concentrations (mg/kg) (Shading: white – value below EU Threshold; Light grey – value exceeds EU Threshold; medium grey – value exceed EU Lower Guideline; Dark grey- value exceeds EU Higher Guideline). < LOD: Less than limit of detection.

Moreover, the results showed that most locations had lead concentrations above the EU lower guideline value (200 mg/kg, See Table 3.1) (Figure 6.5). These locations are highlighted on the map by a medium grey colour and scattered around the south west to the central part of the site and extending towards the northern part of the Wrigley Head. Figure 6.5 shows a map containing lead concentrations across the investigated areas in Wrigley Head. In addition, there were a few other locations highlighted by a slight grey colour on the map scattered around the south western, central, and northern parts of Wrigley Head. The concentrations of lead obtained from these locations were below the EU threshold limit (60 mg/kg, See Table 3.1). Going north-east, there were five locations indicated on the map by a dark grey colour with concurrent elevated concentrations of lead above the EU higher guideline value (750 mg/kg, See Table 3.1). The concentrations of lead observed in the present study mostly exceed the EU lower guideline value and can be regarded as the "hotspots". Lead appears to exhibit moderate variability patterns across the investigated locations.

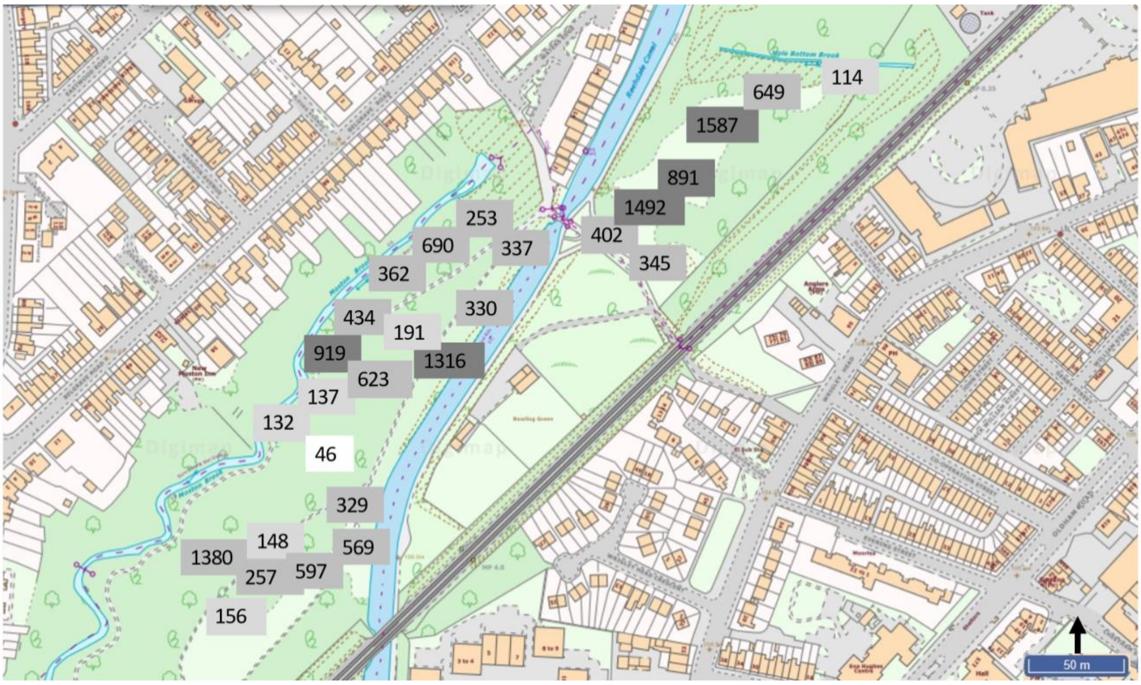

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Figure 6.5 Lead concentrations (mg/kg) (Shading: white – value below EU Threshold; Light grey – value exceeds EU Threshold; medium grey – value exceed EU Lower Guideline; Dark grey- value exceeds EU Higher Guideline)

Furthermore, zinc concentrations were spatially variable across the investigated locations (Figure 6.6). Figure 6.6 shows a map containing zinc concentrations across the investigated areas in Wrigley Head. The results indicated that zinc concentrations were below the EU threshold value (200 mg/kg, See Table 3.1) in most of the locations. Those locations with zinc concentrations below the EU threshold value are indicated on the map by a white shading. These locations can be regarded as potentially “least-contaminated” due to zinc concentrations being below the EU threshold value in these locations. On the other hand, there were locations north-east with elevated zinc concentrations above the EU higher guideline value (400 mg/kg, See Table 3.1). These are “hotspots” locations and are highlighted by a dark grey colour on the map and represent potentially the highest level of zinc contamination. These data suggest that zinc showed a similar contamination level with copper in the present study.

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Figure 6.6 Zinc concentrations (mg/kg) (Shading: white – value below EU Threshold; Light grey – value exceeds EU Threshold; medium grey – value exceed EU Lower Guideline; Dark grey- value exceeds EU Higher Guideline).

In summary, the results of the present study showed that heavy metals exhibited different spatial variability across the investigated locations. The locations around the northern part of the Wrigley Head appear to be more contaminated with copper, lead, zinc and nickel compared to locations around the central part of the site and south western part of the Wrigley Head. In addition, locations within the central part (RS, MD and FP) and south western part (White Hills) tend to be more contaminated with arsenic compared to the northern part of the site. Among the investigated elements, arsenic appears to represent the most serious risk due to its concentrations exceeding the EU limit in most locations compared to other elements in the present study.

6.3 Contamination in Football Ground area of Wrigley Head, Moston Brook

6.3.1 Soil pH and Electrical Conductivity in the Investigated Soils

The results on soil pH, electrical conductivity (EC) and total organic carbon in the present study are presented in Figures 6.7 – 6.9. The spatial variation in pH across the sampling locations in the bare and vegetated areas of the Football Ground indicated variability and showed no specific trend across the sampling locations. Figure 6.7 shows the spatial distribution in pH across the sampling locations in the bare and vegetated areas of the Football Ground.

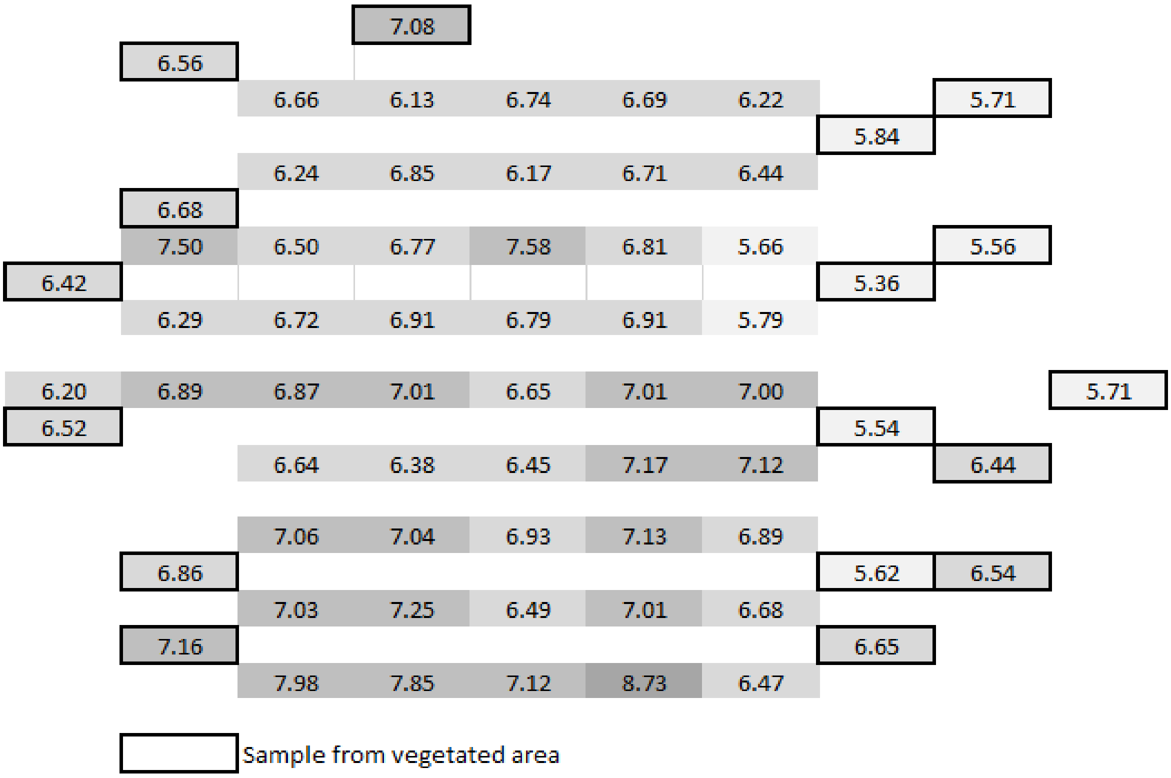


Figure 6.7 Grid map showing pH across the bare patch and vegetated area in the Football Ground (Dark grey shades – mild alkalinity; Medium grey shades – slightly acidic/near neutral pH; Light grey shades – moderately acidic).

The pH data obtained across the two investigated areas showed that there is a difference in soil pH in the bare and vegetated areas. The pH obtained across the bare patch tends to be higher and mostly indicates mild alkaline conditions compared to the vegetated area where the soil pH is generally lower and indicates slightly acidic conditions.

As shown in Figure 6.8, there is a difference in the EC observed in the bare and vegetated areas of the Football Ground. The spatial variation in EC across the sampling locations in the bare and vegetated areas did not follow any specific trend. There were a couple of sampling locations indicated by a dark grey colour with EC greater than 100 (mS/cm) in the bare area. These a few sampling locations recorded the highest EC level across the investigated locations. It is important to note that the EC recorded across the sampling locations in the vegetated area were below 100 (mS/cm). Although, the median EC recorded in the vegetated area tend to be slightly higher than that for the bare area. Nevertheless, the EC data suggest that the EC recorded in both the bare and vegetated areas of the Football Ground were generally below the optimum EC range (110 – 570 mS/cm) in soil. In other words, it shows that the EC recorded in the bare and vegetated areas can be considered low – an indication of non-saline soils.

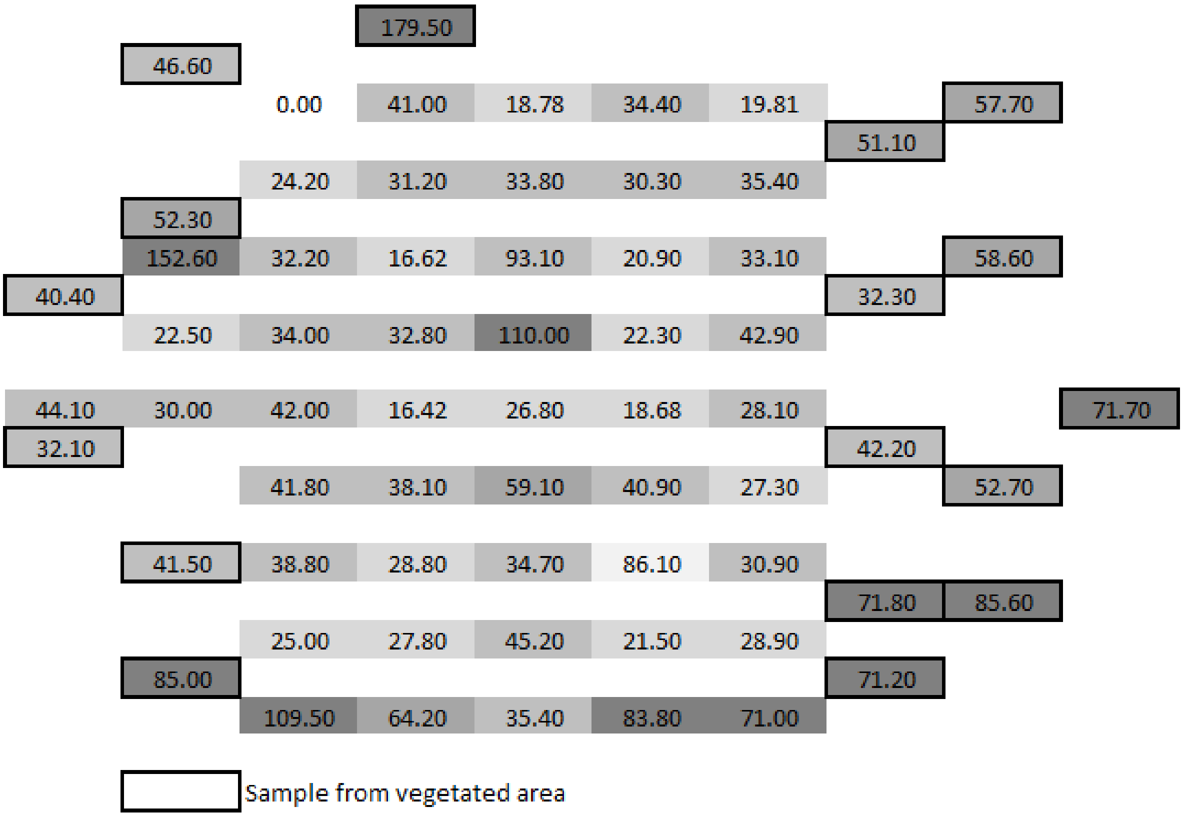


Figure 6.8 Grid map showing electrical conductivity (mS/cm) across the bare patch and vegetated area in the Football Ground (Shading darker shades – electrical conductivity)

The spatial variation in TOC in the bare and vegetated areas of the Football Ground is shown in Figure 6.9. Like pH and EC data, there is a variability in the spatial distribution of TOC across the bare and vegetated areas of the Football Ground. These data showed that the distribution of TOC across the sampling locations did not follow any specific trend. There is a difference in the TOC observed from the bare and vegetated areas of the Football Ground. The TOC recorded from the vegetated area tends to be higher compared to the bare area. This suggests that the TOC is higher in the vegetated area compared to the bare area as shown in Figure 6.9. These locations with what can be considered as “high TOC” are indicated on the map by a dark grey colour. There were also a very few sampling locations with the lowest TOC highlighted on the map with a light grey colour. These data showed that there is a remarkable difference in the TOC in the bare and vegetated areas of the Football Ground.

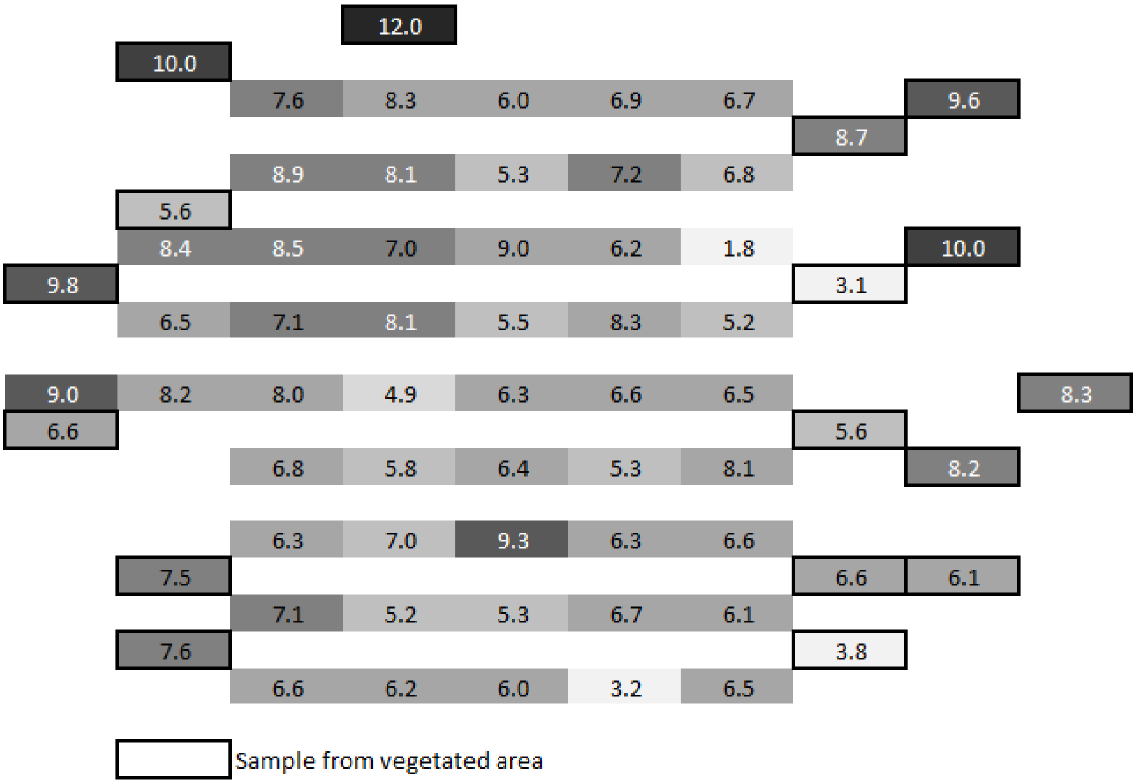


Figure 6.9. Grid map showing total organic carbon (%) across the bare patch in the Football Ground area

Analysis of results showed that the soil pH varied across the bare and vegetated areas of the Football Ground (Table 6.3). Generally, the soil pH tended to be higher in the bare area (non-vegetated) compared to vegetated area (Table 6.3). The median soil pH obtained from bare area was slightly higher than in the vegetated area (Table 6.3). In addition, the pH data showed that there was a low variability in soil pH across the two areas as indicated by the coefficient of variation (Table 6.3). Similarly, the coefficient of variation obtained in the bare area was slightly higher than the vegetated area.

Moreover, the results indicated that there was a difference in EC obtained in the bare and vegetated areas. As can be seen, the median EC was slightly higher in the vegetated area than in the bare area (Table 6.3). In addition, the coefficient of variation indicated that EC varied more widely across the bare area compared to the vegetated area. In addition, the EC data showed that the coefficient of variation obtained in the bare area was slightly higher than the vegetated area (Table 6.3). Furthermore, TOC results indicated that there was a variation in TOC across the bare and vegetated areas (Table 6.3). A difference in the median TOC was observed in bare and vegetated areas of the Football Ground. Generally, TOC tended to be higher in vegetated area in comparison to bare area (Table 6.3). In addition, the coefficient of variation which indicates a measure of relative dispersion of TOC across the two areas was higher in vegetated area compared to the bare area (Table 6.3). In other words, this means that TOC varied more widely in the vegetated area compared to the bare area.

6.3.2 Total Concentrations of Heavy Metals in the Football Ground

The median concentrations of the studied heavy metals in the bare and vegetated areas of the Football Ground are presented in Table 6.3. Shapiro-Wilk test indicates that heavy metals are not normally distributed. Furthermore, the concentration of heavy metals recorded in bare and vegetated areas were relatively higher than the normal background concentrations (Table 6.3). The results indicated a difference in the level of heavy metal contamination across the bare and vegetated areas of the Football Ground (Table 6.3). The medians and ranges for the concentrations of these heavy metals in the bare and vegetated areas are shown in Table 6.3. Importantly, independent two-sample Wilcoxon (P) test indicated that there is a major difference in heavy metal contamination level between bare and vegetated areas in the present study. The results revealed that the concentrations of most heavy metals were relatively higher in bare area compared to the vegetated area: the excepting being arsenic (Table 6.3). Copper, lead, nickel and zinc were found in elevated concentrations compared to arsenic, cadmium and chromium (Table 6.3). This suggests that copper, lead, nickel and zinc and potentially pose more serious contamination problem than arsenic, cadmium and chromium. Similarly, these data also revealed that the bare area is relatively more contaminated compared to the vegetated area. Relatively high concentrations were observed for all heavy metals in the bare area compared to vegetated areas with copper, nickel, lead and zinc having a very range of values. Heavy metals displayed a great degree of variability, indicated by large coefficient of variation (CV) in bare and vegetated areas (Table 6.3). Heavy metals obtained in the bare area displayed greater degree of variability compared to vegetated area (Table 6.3). Copper, nickel, lead and zinc recorded high coefficient of variation greater than 100% (CV > 100%) while arsenic, cadmium and chromium had coefficient of variation less than 100% (CV < 100%) in both bare and vegetated areas (Table 6.3).

Table 6.3 Heavy metal concentrations (mg/kg) of the investigated bare and vegetated areas of the Football Ground including soil pH, total organic carbon, electrical conductivity.

	Arsenic (mg/kg)	**Cadmium (mg/kg)**	**Chromium (mg/kg)**	**Copper (mg/kg)**	**Nickel (mg/kg)**	**Lead (mg/kg)**	**Zinc (mg/kg)**	**pH**	**EC (mS/cm)**	**TOC (%)**
Bare area										
Mean	90	5	264	6218	1972	2582	3487	6.79	57.05	6.44
Median	73	4	178	3044	1233	1257	1451	6.81	44.20	6.90
Max	311	15	1615	34374	25090	21990	16726	8.53	171.00	10.00
Min	< LOD	1	77	80	50	53	85	4.73	19.22	1.80
Range	311	14	1538	34295	25040	21937	16640	3.80	151.78	8.20
CV	70	66	98	121	178	143	130	10.16	58.87	27.26
Shapiro-Wilk	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001			
Vegetated area										
Mean	96	4	161	3131	587	1505	1472	6.25	63.08	7.59
Median	81	2	142	1574	321	877	632	6.44	52.70	7.60
Max	319	9	313	12040	1961	5493	4657	7.16	179.50	12.00
Min	17	< LOD	92	66	40	48	73	5.36	32.10	3.10
Range	302	9	221	11974	1922	5445	4584	1.80	147.40	8.90
CV	72	75	35	112	103	106	104	9.12	52.68	30.04
Shapiro-Wilk	0.0039	<0.001	0.0407	0.0134	0.0044	0.0046	0.0043			
Independent two-sample Wilcoxon (P)										
	0.6494	0.0111	2.50E-05	0.0423	0.0005	0.0113	0.0423			
UK soil range [a]	0.5 – 143	0.10 –1.80	1.14 – 236	2.27 – 96.7	1.16 –216	2.6 – 713	2.63 – 442			
UK soil median [a]	7.1	0.29	29.20	17.2	15.8	37.4	65.9			
UK screening level [b]	79	220	21	–	–	630	–			
UK BV [c]	33.4	0.74	81	64.2	28.5	99.5	129			

Max: Maximum; Min: Minimum; Std: Standard deviation; CV/%: Coefficient of variation; BV: Background value; [a] Ross et al. (2007) (determination by ICP-MS after aqua regia extraction); [b] DEFRA (2014); [c]Ander et al. (2012) and Appleton et al. (2013); < LOD; a concentration below the XRF limit of detection; Dash (–): No published screening values; Shapiro-Wilk – indicates normality – all the results show non-normal distribution.

6.3.3 Spatial Distribution of Heavy Metals in the Football Ground Area.

In the present study, the concentrations of heavy metals (arsenic, cadmium, chromium, copper, lead, nickel and zinc) were plotted on the grid maps and compared to the EU tolerable limits (Table 3.1 – Finland Ministry of the Environment, 2007). The EU tolerable limit values are guideline values, that if these values are exceeded, then the area under investigation poses health/ ecological risks. The grid maps showing the spatial distribution of heavy metals across the the sampling locations in the bare and vegeteted areas of the Football Ground are shown in Figures 6.10 – 6.16. The results of this study showed that there is a high variability in the spatial distribution of heavy metals across the sampling locations in the bare and vegetated areas of the Football Ground. Several locations with elevated concentrations of heavy metals were observed in the bare and vegetated areas. However, the concentrations of most heavy metals were relatively higher in the bare area compared to the vegetated area. In other words, these data suggest that the bare area may be potentially more contaminated compared to the vegetated area of the Football Ground. Copper, lead, nickel and zinc represent more serious contamination problem due to their elevated concentrations above acceptable threshold limits in most locations compared to arsenic, cadmium and chromium. Different colour shadings are used to illustrate the level of contamination across the sampling locations in the bare and vegetated areas and where any hotspots occurred. Dark grey colour – indicates areas metal concentration exceed the EU higher guideline value; Medium grey colour – indicates areas metal concentration exceed the EU lower guideline value; Light grey colour – indicates areas metal concentration exceed the EU higher threshold value and no shading – indicates area metal concentration below EU threshold value.

6.3.3.1 Arsenic (As)

The grid map showing arsenic concentrations (mg/kg) across the sampling locations in the bare and vegetated areas is shown in Figure 6.10. The concentrations of arsenic in the study area were compared to EU tolerable limits and the results showed that values observed in most of the sampling locations were higher than the EU tolerable limits for this regulated element in soil (Table 3.1, Figure 6.10). The data obtained revealed that there is a difference in the level of arsenic contamination between bare and vegetated areas of the Football Ground. Arsenic demonstrated a high spatial variability pattern across the investigated areas

(Figure 6.10). A couple of locations with elevated arsenic concentrations were observed in the bare and vegetated areas. Although, it appears that the level of arsenic contamination was generally higher in the vegetated area compared to the bare area of the Football Ground. These locations can be potentially referred to as the “hotspots” due to arsenic concentrations exceeding the EU higher guideline value (100 mg/kg, See Table 3.1) indicated on the map by a dark grey colour. Consequently, these locations represent potentially the highest arsenic contamination level in the bare and vegetated areas of the Football Ground.

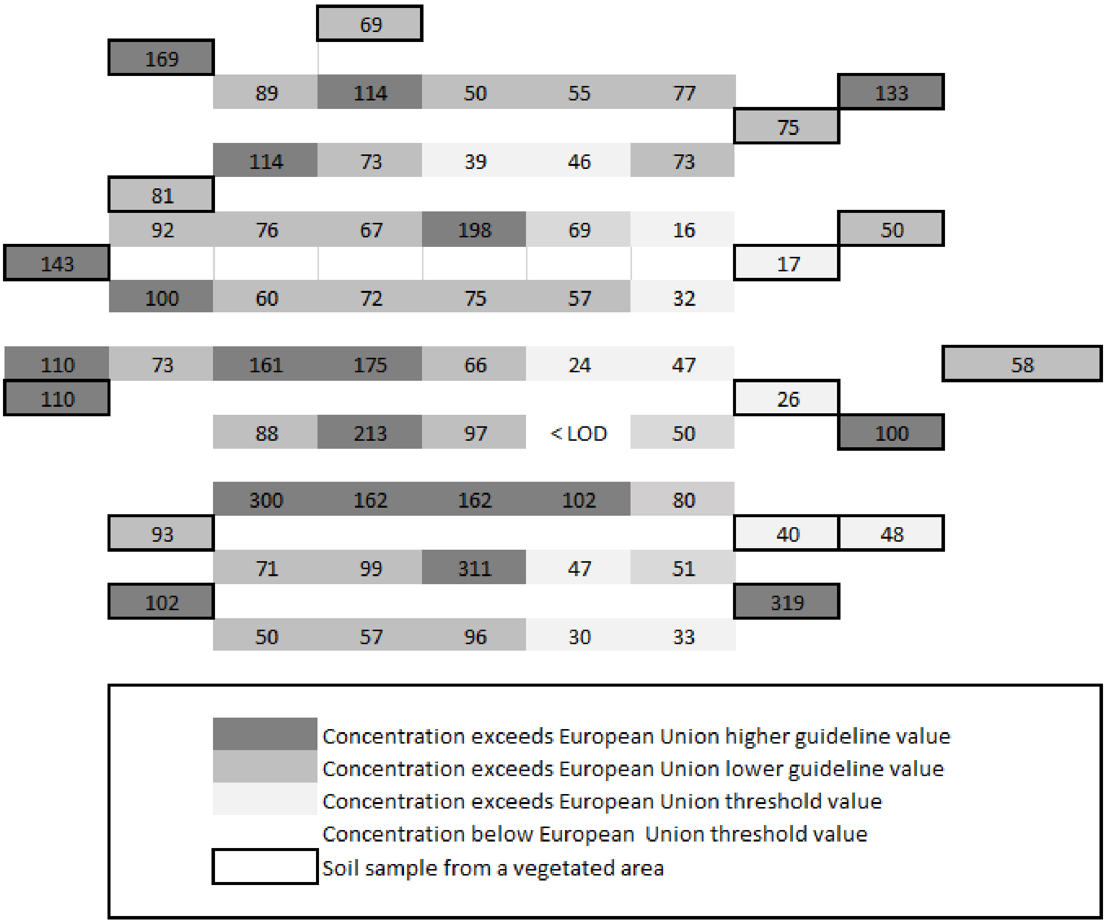
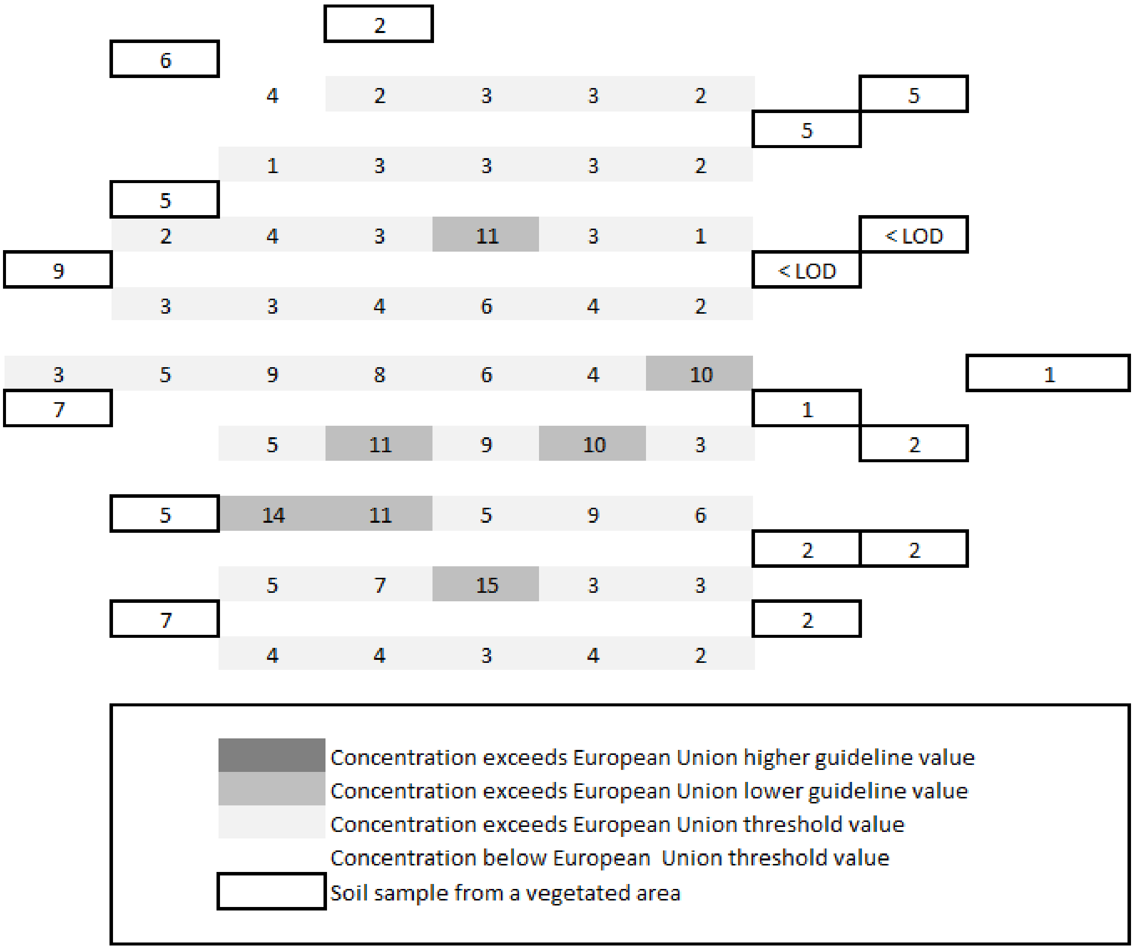


Figure 6.10 Grid map showing arsenic concentrations (mg/kg) in the bare and vegetated areas of the Football Ground. < LOD denotes a concentration less than the limit of detection of XRF.

6.3.3.2 Cadmium (Cd)

The grid map showing cadmium concentrations (mg/kg) across the sampling locations in the bare and vegetated areas is shown in Figure 6.11. Cadmium displayed a low spatial variability in the bare and vegetated areas. There was a remarkable difference between cadmium concentrations obtained from the bare and vegetated areas of the Football Ground. In the vegetated area, the results showed that admium concentration was below detection limits in all the sampling locations and suggests that these locations are non contaminated. Compared to the bare area, the concentrations of cadmium obtained across the sampling locations were very low relative to other heavy metals. These data further revealed that cadmium concentrations obtained in the bare area exceed the EU threshold value (1mg/kg, See Table 3.1).



▨ Concentration exceeds European Union higher guideline value
▨ Concentration exceeds European Union lower guideline value
▨ Concentration exceeds European Union threshold value
Concentration below European Union threshold value
☐ Soil sample from a vegetated area

Figure 6.11 Grid map showing cadmium concentrations (mg/kg) in the bare and vegetated areas of the Football Ground. < LOD denotes a concentration less than the limit of detection of XRF.

The data showed that a few sampling locations indicated by a medium grey colour exceed the EU lower guideline value (10 mg/kg, See Table 3.1) for this regulated metal. The results of the present study showed that the level of cadmium contamination was relatively low compared to other studied heavy metals.

6.3.3.3 Chromium (Cr)

Chromium concentrations in the study area were compared to EU tolerable limits (Table 3.1). The grid map showing chromium concentrations (mg/kg) across the sampling locations in the bare and vegetated areas is shown in Figure 6.12. However, these data reveal that chromium exhibited low spatial variability patterns across the investigated locations. Chromium concentrations observed in most of the sampling locations in bare and vegetated areas generally exceed the EU threshold value (100 mg/kg, See Table 3.1) for this regulated heavy metal in soil.

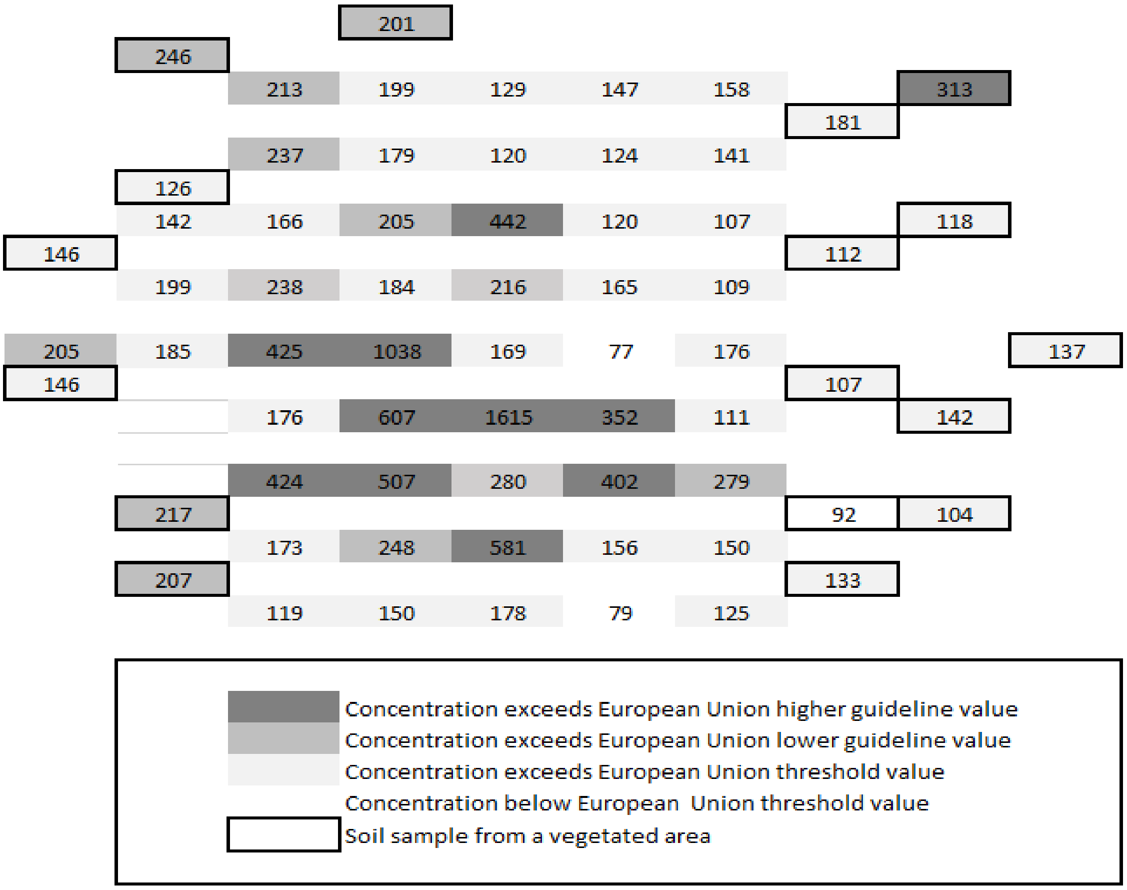


Figure 6.12 Grid map showing chromium concentrations (mg/kg) in bare and vegetated areas of the Football Ground.

These locations are indicated on the map by a light grey colour and depict areas of least contamination (Figure 6.12). These data further showed that there were sampling locations in the bare area with cadmium concentrations above the EU higher guideline value (300 mg/kg, See Table 3.1) as shown in Figure 6.12. These areas can be regarded as “hotspots” and are marked on the grip map by a dark grey colour and represent potentially the highest level of chromium contamination across the investigated areas. These data suggest that there is a variable levels of chromium contamination across the sampling locations in the bare and vegetated areas and chromium exceed the EU threshold value in most sampling locations.

6.3.3.4 Copper (Cu)

The grid map showing copper concentrations (mg/kg) across the sampling locations in the bare and vegetated areas is shown in Figure 6.13. Copper was considerably one of the most dominant heavy metals found in elevated concentration in the study area. Copper indicated a high spatial variability across the sampling locations in the bare and vegetated areas. There is a difference in copper concentrations in the bare and vegetated areas. Relatively elevated copper concentrations were found in the bare area compared to the vegetated area of the Football Ground. Compared to other studied heavy metals, copper is among heavy metals that represent potentially serious contamination in the study area. More importantly, it was also found that copper concentrations observed nearly in all the sampling locations in bare and vegetated areas greatly exceed the EU higher guideline value (200 mg/kg, See Table 3.1) for copper in soil. These “hotspots” are marked on the map with a dark grey colour and represent areas of most serious copper contamination. The result indicated that the bare area is relatively more contaminated compared to the vegetated area. These data show that there is a high level of copper contamination in the bare and vegetated areas that exceed the EU higher guideline value nearly all the locations.

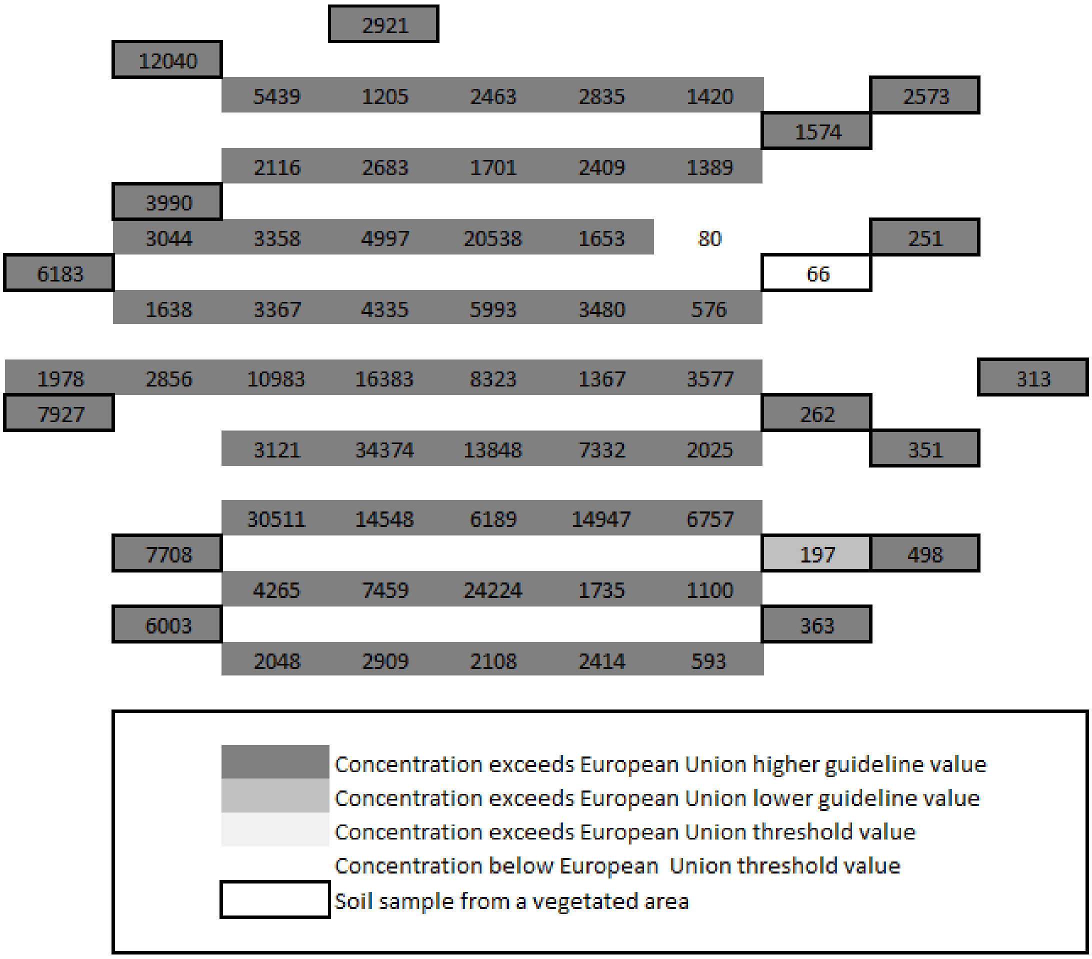


Figure 6.13. Grid map showing copper concentrations (mg/kg) in bare and vegetated areas of the Football Ground.

6.3.3.5 Lead (Pb)

The grid map showing lead concentrations (mg/kg) across the sampling locations in the bare and vegetated areas is shown in Figure 6.14. High lead spatial variability was observed across the sampling locations in the bare and vegetated areas. There is a marked difference in the concentrations of lead in the bare and vegetated areas of the Football Ground. These data showed that lead concentrations in the bare area were relatively higher compared to the vegetated area. In addition, it is important to note that nearly all the sampling locations in the bare area recorded lead concentrations above the EU higher guideline value (750 mg/kg, See Table 3.1) for this regulated heavy metal. This suggests that the bare area of the Football Ground is heavily contaminated. Although, the two areas can be regarded as “heavily contaminated”. These “hotpots” are indicated on the map by a dark grey colour and recorded lead concentrations above the EU higher guideline value. The results showed that there is a difference in the level of lead contamination between bare and vegetated areas of the Football Ground.

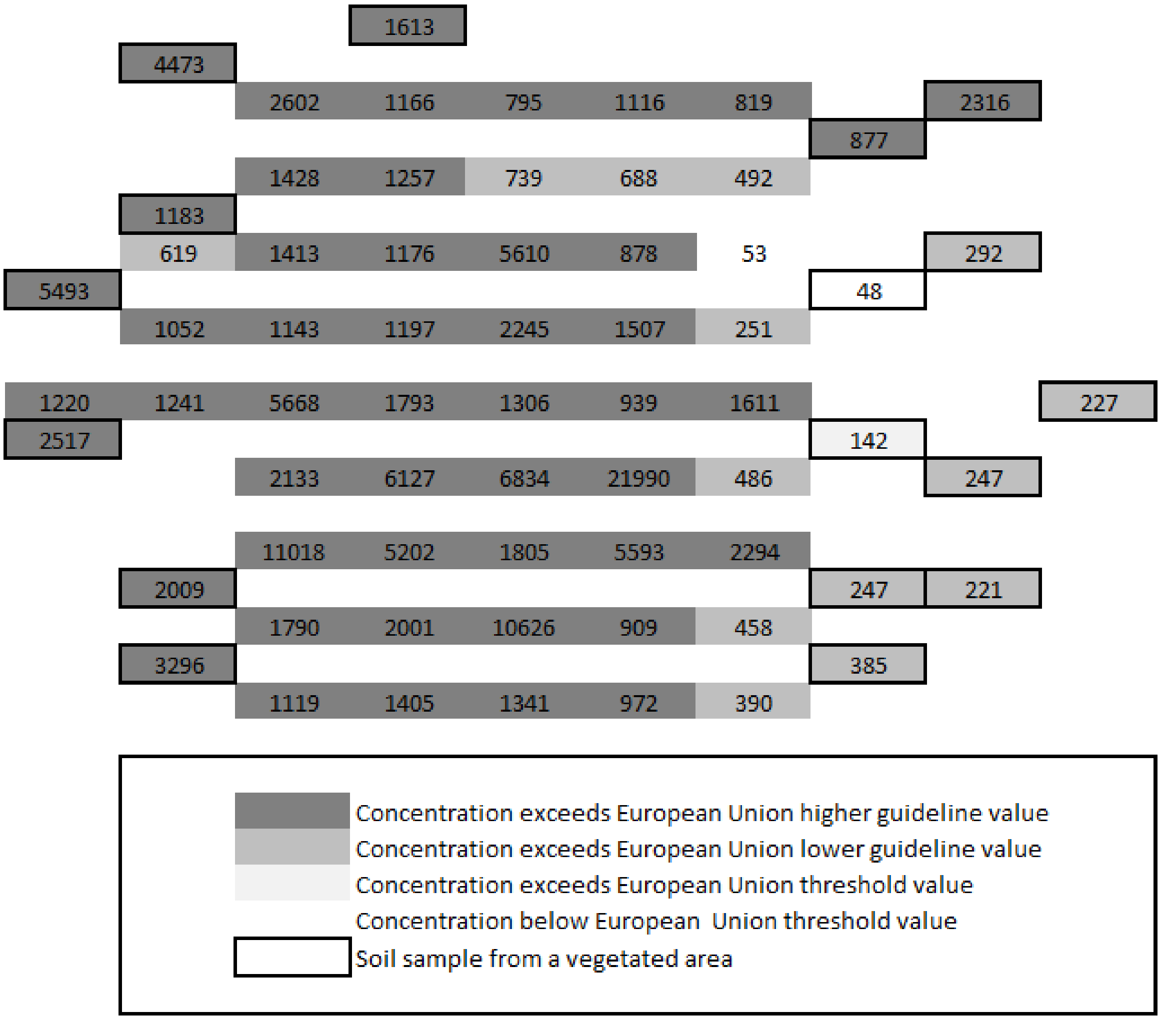


Figure 6.14. Grid map showing lead concentrations (mg/kg) in bare and vegetated areas of the Football Ground.

6.3.3.6 Nickel (Ni)

The grid map showing nickel concentrations (mg/kg) across the sampling locations in the bare and vegetated areas is shown in Figure 6.15. There is a difference in the spatial variability of nickel across the bare and vegetated areas of the Football Ground. Nickel concentrations were relatively higher in the bare area compared to the vegetated area;

although, nickel concentrations obtained in both areas mostly exceed the EU higher guideline value (150 mg/kg, See Table 3.1). These areas can be regarded as the “hotspots” and are indicated on the map by a dark grey colour. Even though, the level of nickel obtained in the two areas exceed the EU higher guideline value, these data suggest that the bare area is more contaminated compared to the vegetated area.

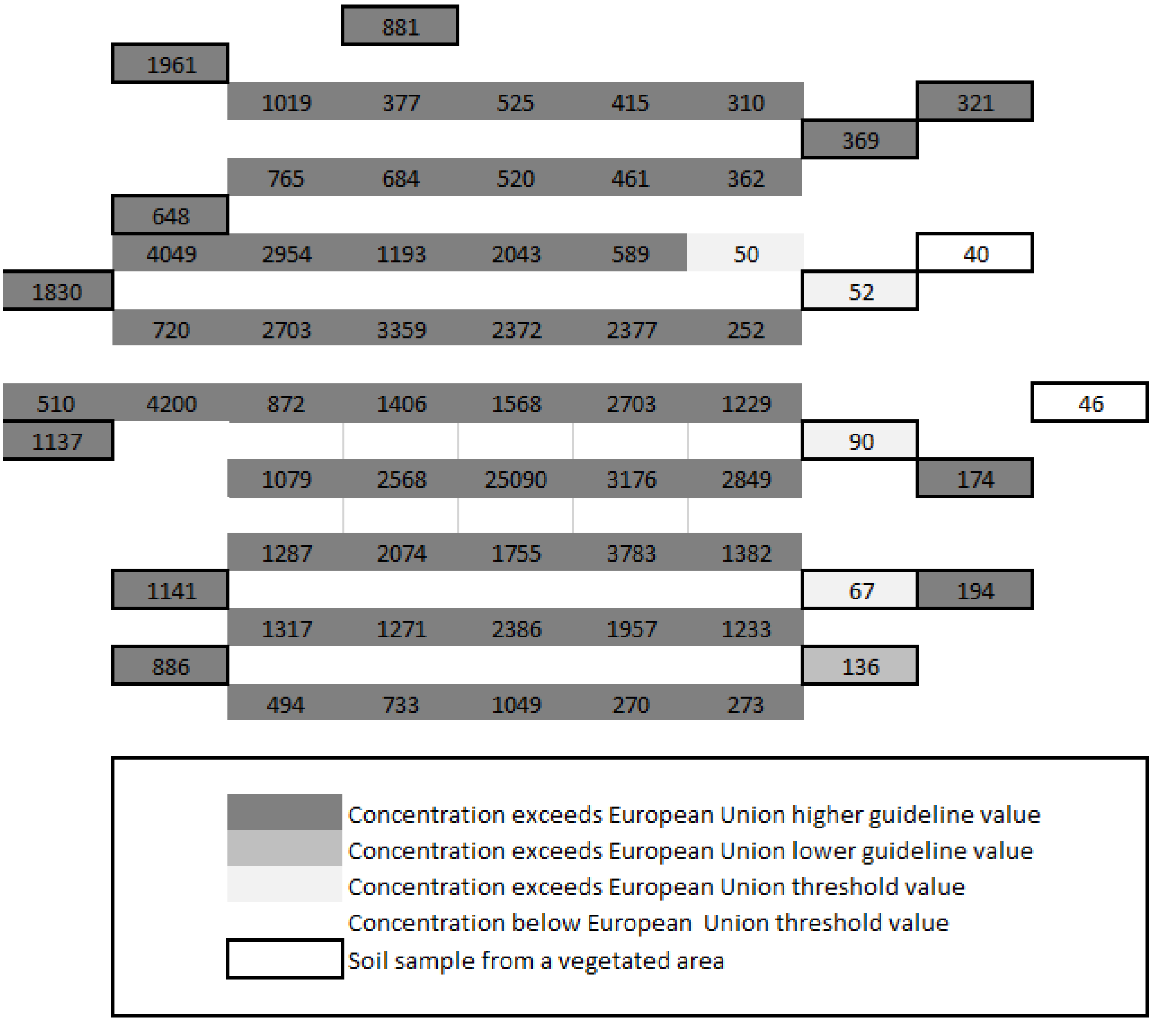


Figure 6.15. Grid map showing nickel concentrations (mg/kg) in bare and vegetated areas of the Football Ground.

These data show that the concentrations of nickel obtained in the bare and vegetated areas are generally high and both areas can be considered a “hotspot”.

6.3.3.7 Zinc (Zn)

The grid map showing zinc concentrations (mg/kg) across the sampling locations in the bare and vegetated areas is shown in Figure 6.16. Most sampling locations had zinc concentrations far above the EU higher guideline value (400 mg/kg) in the bare and vegetated areas of the Football Ground for this regulated heavy metal in the soil (Table 3.1, Figure 6.16). These areas can be regarded as the “hospots” and indicated on the map by a dark grey colour and represent areas of most serious contamination within the Football Ground.

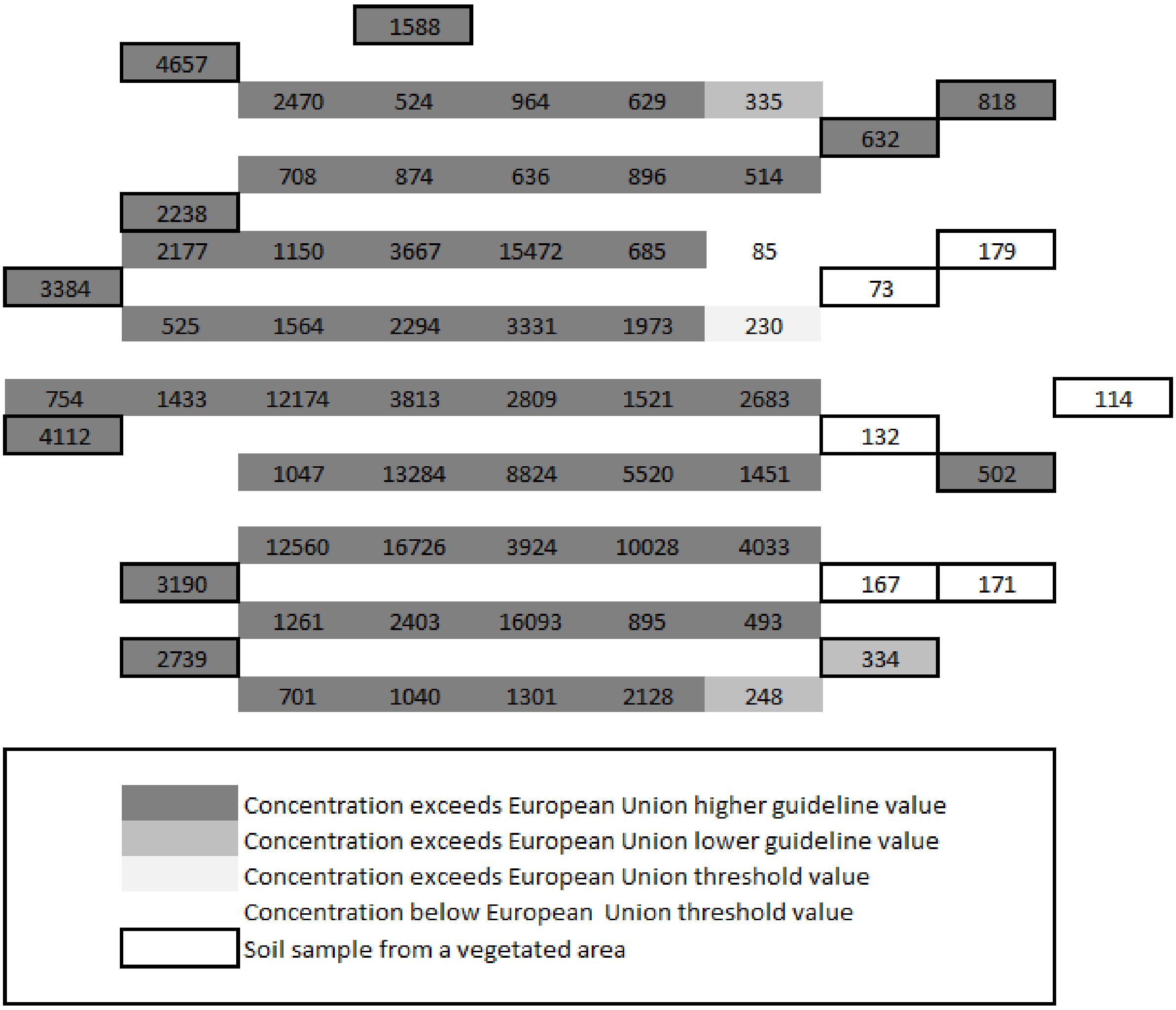


Figure 6.16. Grid map showing zinc concentrations (mg/kg) in bare and vegetated areas of the Football Ground.

Although, these data showed that there a few sampling locations in the bare area with very high levels of zinc relative to the vegetated area (Figure 6.16). It is important to note that a few sampling locations in the vegetated areas had zinc concentrations below the the EU threshold value (200 mg/kg, See Table 3.1). These areas are regarded as the "least contaminated" and highlighted on the map with white shading. Lastly, the results suggest that the bare area is heavily contaminated in comparison to the vegetated area, but both of them can be regarded as" a hospot" due to elevated zinc concentrations identfied in these areas.

Collectively Figures 6.10 – 6.16 demonstrate the high level of contamination across the Football Ground area and the variability across the area. There are no clear trends indicating specific hotspots, rather the whole area can be considered as a hotspot. This suggests that the bare area needs to be considered as one area and not one that is made of different parts.

CHAPTER 7

Remediation Options

7.1 Overview

There are barriers to the future use of this site which may be overcome by remediation. In this chapter those options are investigated. The first option is the use of plants. The results of a study conducted to examine heavy metal uptake by a range of native herbaceous plants growing across Wrigley Head, Moston Brook are presented. Also presented in this chapter are the results of the Bioaccumulation and Translocation factors of heavy metals among the investigated plant species across the site. The last section of this chapter contains a discussion on capping – another option that can be explored for overcoming the barrier within the context of the study site.

7.2 Overcoming the Barriers Associated with Wrigley Head, Moston Brook and Future use of the Site

The historical release of contaminants into the environment has created a legacy of contaminated sites throughout the world (Reible & Lampert, 2014). Increasing land degradation and decreasing land productivity due to potentially toxic element contamination has attracted growing interest in techniques for soil remediation among the wider scientific community (Palansooriya et al., 2020). Management and clean-up of contaminated sites has been a subject of public debate due to scientific and technical challenges heavy metal contamination presents (Jiang et al., 2015). This is the case for Wrigley Head, Moston Brook which has a legacy resulting from historical contamination from multiple sources, neglect and dereliction. The site is recognised as an important green asset for the local residents and community. Driven by the importance of this site to the local communities and to improve the physical environments, health and wellbeing, Manchester City Council and Oldham Metropolitan Borough Council, in 2008, jointly funded and commissioned Groundwork Oldham and Rochdale to undertake a feasibility study of the site with a view to drawing out the action plan and long-term aspiration plan for the site (Groundwork Oldham & Rochdale, 2008). Consultations with the local communities were undertaken and some of the ideas from the consultation workshops were included in the action plan for the site which included the importance of linking up the site with adjacent open spaces to create a 70-hectare corridor of open space (Groundwork Oldham & Rochdale, 2008). To realise funds to implement these action plans, the councils jointly established the Moston Brook Partnership. This eventually led to a bid for regional reclamation funding. However, the barriers associated with the site contamination are yet to be addressed, and this presents a big challenge to the beneficial use of the site for different purposes.

The results of the present investigation show that this site is highly contaminated with toxic heavy metals. The level of heavy metal contamination at the site may have the potential to cause health risk to the site users (Table 5.10). Cleaning up this site will significantly reduce the potential health risks to the local communities who are currently using the site in its present condition and encourage a health-promoting space alongside areas of high deprivation. It is possible that this site may have the potential to impact on local environments and the surrounding areas via erosion, surface run-off or leaching of contaminants through the soil profile. Thus, the remediation approaches targeted at overcoming the barriers associated with the site must consider the nature and level of contamination at the site, the desired end use and the technical feasibility and availability of funds for this project.

One of the options that should be considered for overcoming the barriers associated with bare soil is revegetation of the area with plant species in the phytoremediation process. This remediation technology makes use of the plants with the aim of degrading, stabilising, extracting, removing or volatising contaminants from the environment, and thus reduce the amount or toxicity of contaminants in the environment (Chakravarty et al., 2015; Jha et al., 2017; Ashraf et al., 2019). Such plant species can be sourced locally or elsewhere, and the site conditions must be suitable for plants growth. Arienzo et al. (2004) noted that the success of revegetating contaminated sites is measured by the degree of the plants’ tolerance to contaminants in the soil. In other words, this means that the plant species selected for the purpose of revegetation must be able to withstand the toxicity of the contaminants in the soil. The selection of appropriate plant species is crucial to the success of any phytomanagement (Burges et al., 2018). In addition, a plant’s suitability for revegetating the bare area can be evaluated based on the potential of a plant species to uptake heavy metals, size of biomass production, ability of the plants to adapt to the site conditions, growth rate changes in yield and basic metabolic processes. In other words, the plant species selected must be able to adapt to the soil conditions of the bare area, able to develop a vegetation cover in a short period and produce a high biomass.

It is also important to consider bioenergy, medicinal, aromatic and ornamental plants and metal hyperaccumulators for this purpose of revegetating the bare area. For example, there are many bioenergy plants such as *Populus spp.* (poplar), *Salix spp.* (willow), *Ricinus communis* (castor) and *Jatropha curcas* (jatropha) that have been successfully used to clean up contaminated soils with the economic benefit of biofuel generation using the harvested biomass (Chhetri et al., 2008; Yıldırım & Kasım, 2018; Hunce et al., 2019; Álvarez-Mateos et al., 2019). This is important because contaminants can return to the environment when the plants' biomass are not harvested and managed appropriately. Therefore, appropriate management and utilisation of the harvested biomass is critical for any successful clean up of contaminated site using plants. These plants can offer a lot of advantages because their harvested biomass can be used for cost effective bioenergy production, as a decorative material, for timber and medicinal productions and aromatic compound, and will produce economic benefits in the long run (Sharma et al., 2021). Bauddh et al. (2015) suggest that revegetating contaminated soil with plant that have ability to produce timber, medicinal and aromatic compounds, and valuable metals and high biomass have added benefit. In addition, a plant's suitability for revegetating the bare area can be evaluated based on the potential of a plant species to uptake heavy metals, size of biomass production, growth rate changes in yield and basic metabolic processes. In other words, the plant species selected must be able to adapt to the soil conditions of the bare area, able to develop a vegetation cover in a short period and produce a high biomass. The aim of plant-based approach is to reduce the potential risk associated with contaminated soils by restricting the transfer of contaminants to ecosystems or humans (Robinson et al., 2009). Several authors have suggested that revegetation of contaminated soil is crucial to stabilising the contaminants in the soil (Arienzo et al., 2004; Ruttens et al., 2006). The presence of vegetative cover has a lot to offer in terms of reducing the potential migration of contaminants particularly from bare area of the Football Ground to nearby watercourses or inhalation by receptor organisms. A similar observation was noted by Tordoff et al. (2000).

Although, revegetation of the bare soil may be challenging due to the high level of contamination which may inhibit the plant growth. The contamination level in this area may be such that establishing vegetation is not possible without some form of soil treatment due to the contaminants in the soil might cause direct toxicity to the vegetation through roots uptake. This was the case when contaminated soils were taken from the bare area and sow with lettuce (*Lactuca sativa*) and mustard (*Sinapis alba*) plants in the greenhouse (data not presented). The observation revealed that the test plants showed a poor growth, chlorosis, low biomass and eventually died off between 3 to 4 weeks which was likely due to the phytotoxic nature of the soil. Although, there might be some other soil related factors that also contributed to this. Similarly, the contaminated soils from the bare area were also mixed with garden soil with some soil amendments in the greenhouse, planted with lettuce (*Lactuca sativa*) and mustard (*Sinapis alba*) and the observation shows that the plants adapted and grew successful on the soil in the greenshous (data not presented, see appendix 1e). These observations suggest that revegetation of the bare soil may be possible with application of some soil amendments and/or blending/mixing the bare soil with non-contaminated soil to improve the soil conditions and reduce the concentration of individual contaminants within the resultant mixture. Amendments help to immobilise heavy metals in soil or encourage the plants establishment and growth (Barbosa & Fernando, 2018). Although, blending or mixing will not reduce the mass of contaminants in the soil but could reduce the rate of contaminants release into the environment and help to revegetate the bare area of the site by supporting the plants growth.

Arienzo et al. (2004) conducted a revegetation trial study in the greenhouse using *Lolium perenne* for revegetation of soil contaminated by copper, lead and zinc from a former ferrous metallurgical plant (Naples, South Italy) and the results showed an acceptable healthy vegetative cover can be feasible through this remediation approach and metals can be stabilised with slight variation of the more available metal forms. This remediation approach can offer some benefits in terms of reclamation and restoration of the bare area of the site. The revegetation will help to stabilise the bare area and encourage establishment of a cover crop that will potentially prevent the dispersion of metal contaminated dusts or particles through either wind or water erosion. Vangronsveld et al. (1991, 1995) noted that revegetation of contaminated soil with plants will play a significant role in terms of stabilising contaminated sites and engender cover crop that will fend off the dispersion of metal-contaminated particles by water or wind erosion, and to minimise the mobility of heavy metals caused by rhizosphere-induced adsorption and precipitation processes. Norland and Veith (1995) noted that stabilising contaminated soil through vegetation improves both chemical and biological properties of the contaminated soil through net increase in the amount of organic matter, nutrient levels and biological activity. These plants have the capacity to tolerate, detoxify and store high metal concentrations in their tissues. In addition, the roots of vegetation can offer some benefits in terms of stabilising the soil and thus reduce the surface water run-off of potentially contaminated materials being transported into surface water or nearby areas from the bare soil. Moreover, the biomass of the plants can be harvested and used for different purposes such as the production of bioenergy/biofuel or disposed through incineration or composting. There are several ways the contaminated plant biomas could be disposed without causing a secondary pollution to the environment. For example, during the incineration process, the contaminated plant biomass can be converted into heat and/or electricity during which two ashes are produced, namely, bottom ash and fly ash (Sharma et al., 2021). The bottom ash contains crucial elements needed by plants and a smaller number of heavy metals while the fly ash has significant number of heavy metals. The fly ash containing high number of heavy metals be treated with sodium hydroxide to allow for precipitation of heavy metals, and the recovered ash can be used as as soil conditioner (Kröppl & Lanzerstorfer, 2013). The benefit of establishing vegetation on the bare soil of the Football Ground will be the creation of a self-sustaining ecosystem that can support productive land use activities and also improve the aesthetic appearance of this area and may offer some economic benefits in the long-term. While revegetating the bare area of the site is a promising option to overcome the barriers associated with this area, Dadrasnia et al. (2013) argued that the success and applicability of this remediation option may be limited by several factors such as suitability of the site to support plants growth, depth and nature of contamination, soil parameters and the time requirement. Similarly, Doran (2009) highlighted low biomass and slow growth as limiting factors.

7.3 Concentrations of Heavy Metals in the investigated Plants across the Site

7.3.1 Roots

The concentrations of heavy metals in the roots of the investigated plant species are presented in Table 7.1. There was a big variation in the uptake of heavy metals by the selected plant species (Table 7.1).

Table 7.1. Concentrations (mg/kg) of heavy metals in the roots of the investigated plant species.

Plant Species	**Common Name**	**Arsenic**	**Chromium**	**Copper**	**Nickel**	**Lead**	**Zinc**
Agrostis stolonifera	Creeping bent	5.13	12.32	422.19	191.19	182.14	332.87
Artemisia vulgaris	Mugwort	1.86	1.79	81.61	105.46	10.26	190.32
Argrostis capillaries	Common bent	3.11	2.11	87.79	57.42	39.09	373.43
Chamerion angustifolium	Rosebay willowherb	1.39	2.15	18.87	6.21	2.79	53.20
Agrostis tenuis	Slender rush	3.48	10.01	731.24	316.65	256.33	558.28
Dactylis glomerata	Cocksfoot	2.17	10.01	77.06	28.04	27.32	180.49
Urtica dioica	Stinging nettle	2.07	6.67	61.31	16.01	15.13	124.39
Galium aparine	Cleavers	2.34	< LOD	24.90	1.27	8.37	55.90
Phalaris arundinacea	Reed canary grass	3.00	2.32	14.06	3.07	13.84	111.19
Heracleum sphondylium	Hogweed	2.10	0.18	8.81	22.10	18.70	54.70
Juncus inflexus	Hard rush	5.34	7.96	42.54	7.77	19.01	87.66
Impatiens glandulifera	Himalayan balsam	3.96	0.40	38.10	14.60	11.80	119.00
Plantago lanceolata	Ribowort plantain	1.49	1.79	23.82	2.56	4.04	119.93
Lolium multiflorum	Italian Rye grass	3.71	1.36	22.99	2.74	13.05	215.28
Juncus effusus	Soft rush	23.98	4.47	27.34	9.20	31.32	116.37
Chamerion angustifolium	Rosebay willowherb	4.99	2.41	12.55	5.48	15.92	49.66
Holcus lanatus	Yorkshire fog	7.92	0.73	40.4	9.62	7.37	173.00
Urtica dioica	Stinging nettle	51.90	3.59	71.92	12.32	40.60	416.68
Dactylis glomerata	Cocksfoot	57.30	45.74	42.24	11.85	67.55	81.68
Festuca pratensis	Meadow fescue	31.60	3.22	22.49	4.52	47.53	83.25
Glyceria maxima	Reed sweetgrass	27.50	4.03	104.45	6.39	35.59	279.74
Phleum pratense	Timothy grass	29.30	2.69	47.05	15.95	25.95	161.18
Lolium pratense	Ryegrass	96.90	34.94	51.37	16.72	100.9	147.86
Equisetum arvense	Field horsetail	39.70	2.29	52.77	5.07	82.89	81.62
Cynosurus cristatus	Crested dog’s tail	4.21	6.86	31.89	9.19	13.42	117.56
Filipendula ulmaria	Meadowsweet	3.99	3.90	54.42	7.06	19.29	141.13
Bistorta officinalis	Bistort	102.63	3.17	28.32	12.15	50.24	51.60
Median		4.21	3.17	42.24	9.62	19.29	119.93
Min		1.39	< LOD	8.81	1.27	2.79	49.66
Max		102.63	45.74	731.24	316.65	256.33	558.28

< LOD denotes a concentration below the limit of detection of ICP-OES analysis.

In other words, this means that the studied plant species demonstrated varying uptake potentials for heavy metals. Generally, the results revealed that the concentrations of heavy metals in the root portions of the investigated plant species were higher compared to the shoot portions (Tables 7.1 and 7.2). The results of the present study also revealed that the root-borne concentrations of copper and zinc were relatively higher compared to arsenic, chromium, nickel and lead (Table 7.1). Root-borne arsenic had a median concentration of 4.21 mg/kg with a range of 1.39 – 102.63 mg/kg across the investigated locations (Table 7.1). Among the investigated plant species, *Bistorta officinalis* and *Lolium pratense* accumulated relatively higher concentrations of arsenic in the root portion compared to other plant species (Table 7.1). Similarly, *Dactylis glomerata*, *Urtica dioica* and *Equisetum arvense* also showed higher potential to accumulate arsenic in their root portions (Table 7.1). In contrast, some plant species such as *Artemisia vulgaris, Chamerion angustifolium* and *Plantago lanceolata* showed a very low potential to accumulate arsenic in their root portions with arsenic concentrations (< 2 mg/kg) (Table 7.1).

Among the investigated plant species, root-borne chromium was generally low and ranged between UDL – 45.74 mg/kg with a median concentration of 3.17 mg/kg (Table 7.1). *Dactylis glomerata* showed the highest potential to accumulate chromium in the root portion while *Galium aparine* had no detectable chromium in the root. Most of the investigated plant species accumulated root-borne chromium less than (< 5 mg/kg) (Table 7.1). In addition, *Heracleum sphondylium, Impatiens glandulifera* and *Holcus lanatus* also showed very low root-borne chromium concentrations (< 1mg/kg). Root-borne copper varied from 8.81 – 731.24 mg/kg with a median concentration of 42.24 mg/kg (Table 7.1). *Agrostis tenuis* showed the highest potential to accumulate copper in the root (731.24 mg/kg) while *Heracleum sphondylium* recorded the lowest uptake potential with copper concentration of 8.81 mg/kg (Table 7.1). Similarly, the root-borne nickel varied from 1.27 – 316.65 mg/kg with a median concentration of 9.62 mg/kg for all the investigated plant species. *Agrostis tenuis* demonstrated the highest capacity to accumulate nickel in the root, followed by *Agrostis stolonifera* while the lowest uptake potential was observed for *Galium aparine* (Table 7.1). Root-borne lead varied from 2.79 – 256.33 mg/kg among the investigated plant species. The findings showed that the median concentration of root-borne lead was 19.29 mg/kg. *Agrostis tenuis* had the highest concentration of root-borne lead, followed by *Agrostis* *stolonifera* while the lowest concentration of root-borne lead was observed for *Chamerion angustifolium* (Table 7.1). Furthermore, root-borne zinc had a median concentration of 119.93 mg/kg and varied between 49.66 – 558.28 mg/kg among the investigated plant species. *Agrostis tenuis* had the highest concentration of root-borne zinc while the lowest concentration was observed in *Chamerion angustifolium* (Table 7.1). The results of this study showed that uptake of heavy metals by the investigated plant species differed considerably and *Agrostis tenuis* demonstrated the highest potential to accumulate most of the elements in the root compared to other plant species (Table 7.1).

7.3.2 Shoots

The concentrations of heavy metals in the shoot portions of the investigated plant species are shown in Table 7.2. Like the roots, heavy metal concentrations varied between the plant species. Generally, the shoot-borne concentrations of heavy metals were relatively lower compared to the root-borne concentrations. The shoot-borne concentrations of copper and zinc were relatively higher than arsenic, chromium, nickel and lead (Table 7.2). For arsenic, the shoot-borne concentrations varied from < LOD – 6.18 mg/kg with a median concentration of 0.65 mg/kg. The highest shoot-borne concentration of arsenic (6.18mg/kg) was observed for *Phleum pratense* while the lowest shoot-borne arsenic (< LOD) was found in *Dactylis glomerata* (Table 7.2). Most of the investigated plant species had very low arsenic concentrations in their shoots (< 1 mg/kg). The shoot-borne chromium ranged from 0.04 – 0.78 mg/kg with a median concentration of 0.35 mg/kg. *Bistorta officinalis* had the highest shoot-borne chromium (0.78 mg/kg) while *Chamerion angustifolium* recorded the lowest shoot-borne chromium (Table 7.2). The results showed that all the investigated plant species had a very low shoot-borne chromium (< 1 mg/kg). The shoot-borne copper ranged from 3.46 – 58.66 mg/kg with a median concentration of 8.50 mg/kg (Table 7.2).

Among the investigated plant species, *Agrostis tenuis* recorded the highest shoot-borne copper concentration (58.66 mg/kg) while the lowest (3.46 mg/kg) was observed for *Filipendula ulmaria* (Table 7.2). Most of the investigated plants showed a higher potential to uptake copper in their shoots compared to arsenic and chromium (Table 7.2). Similarly, the shoot-borne nickel had a median value of 2.0 mg/kg with concentration range of 0.75 – 52.75 mg/kg. *Agrostis tenuis* recorded the highest shoot-borne nickel (52.75 mg/kg) seconded by

Artemisia vulgaris and Agrostis stolonifera that recorded similar concentrations (24.06 mg/kg and 23.93 mg/kg) while *Galium aparine* recorded the lowest shoot-borne nickel concentration (0.75 mg/kg) (Table 7.2).

Table 7.2. Concentrations (mg/kg) of heavy metals in the shoots of the investigated plant species.

Plant Species	**Common Name**	**Arsenic**	**Chromium**	**Copper**	**Nickel**	**Lead**	**Zinc**
Agrostis stolonifera	Creeping bent	0.97	0.61	10.25	23.93	3.40	53.78
Artemisia vulgaris	Mugwort	1.71	0.26	12.34	24.06	2.02	188.52
Argrostis capillaries	Common bent	0.26	0.19	10.52	13.48	2.34	67.87
Chamerion angustifolium	Rosebay willowherb	0.67	0.04	8.50	2.56	0.16	39.82
Agrostis tenuis	Slender rush	1.34	0.71	58.66	52.75	27.84	147.39
Dactylis glomerata	Cocksfoot	< LOD	0.16	9.32	5.29	2.68	39.54
Urtica dioica	Stinging nettle	0.25	0.34	18.18	1.35	1.31	17.74
Galium aparine	Cleavers	0.38	0.11	4.43	0.75	1.09	25.73
Phalaris arundinacea	Reed canary grass	0.82	0.23	11.60	5.40	3.41	84.59
Heracleum sphondylium	Hogweed	0.34	0.35	6.69	1.63	2.25	56.76
Juncus inflexus	Hard rush	3.35	0.40	12.05	0.90	1.55	28.08
Impatiens glandulifera	Himalayan balsam	0.29	0.22	7.73	2.81	1.79	41.82
Plantago lanceolate	Ribowort plantain	0.41	0.27	4.79	1.09	1.17	19.66
Lolium multiflorum	Italian Rye grass	0.58	0.17	6.29	1.37	3.29	43.97
Juncus effuses	Soft rush	1.07	0.41	5.70	1.02	0.27	39.55
Chamerion angustifolium	Rosebay willowherb	0.70	0.42	7.22	0.99	1.35	32.39
Holcus lanatus	Yorkshire fog	0.63	0.69	4.24	0.98	1.18	14.48
Urtica dioica	Stinging nettle	0.31	0.20	10.44	1.42	2.02	22.29
Dactylis glomerata	Cocksfoot	1.50	0.30	5.70	1.85	2.49	21.35
Festuca pratensis	Meadow fescue	1.33	0.46	8.57	2.00	4.13	37.02
Glyceria maxima	Reed sweetgrass	2.62	0.38	7.06	1.12	1.26	25.46
Phleum pratense	Timothy grass	6.18	0.75	8.78	4.29	6.59	40.05
Lolium pratense	Ryegrass	0.18	0.33	4.88	2.55	1.67	26.26
Equisetum arvense	Field horsetail	0.65	0.60	10.71	1.32	3.57	50.87
Cynosurus cristatus	Crested dog's tail	0.36	0.56	5.20	3.69	1.63	35.27
Filipendula ulmaria	Meadowsweet	0.02	0.41	3.46	3.15	0.56	18.19
Bistorta officinalis	Bistort	1.00	0.78	8.76	3.52	0.58	63.41
Median		0.65	0.35	8.50	2.00	1.79	39.54
Min		< LOD	0.04	3.46	0.75	0.16	14.48
Max		6.18	0.78	58.66	52.75	27.84	188.52

< LOD denotes a concentration below the limit of detection of ICP-OES analysis.

For lead, the shoot-borne concentrations varied from 0.16 – 27.84 mg/kg with a median concentration of 1.79 mg/kg. Among the investigated plant species, the highest concentration of shoot-borne lead (27.84 mg/kg) was found for *Agrostis tenuis* while

Chamerion angustifolium had the lowest lead concentration (0.16 mg/kg) in the shoot (Table 7.2). For shoot-borne zinc, the concentrations ranged from 14.48 – 188.52 mg/kg with a median value of 39.54 mg/kg. *Artemisia vulgaris* recorded the highest zinc concentration (188.52 mg/kg) in the shoot, followed by *Agrostis tenuis (*147.39 mg/kg) while *Holcus lanatus* had the lowest zinc concentration (14.48 mg/kg) (Table 7.2). The present findings showed that the shoot-borne metal concentrations among the investigated plant species were highly variable and the shoot-borne metal concentrations were generally lower compared to the root-borne concentrations. Most of the investigated plant species showed higher potentials to uptake zinc, copper, and nickel compared to arsenic, chromium, and lead (Table 7.2).

7.4 Bioaccumulation of Heavy Metals among the investigated Plants

The bioaccumulation factor (BF) of heavy metals for the investigated plant species are presented in Table 7.3. The ability of plants to take heavy metals from soil can be quantified using the BF. In the present study, the BFs among the investigated plant species was highly variable (Table 7.3). Bioaccumulation factor of heavy metals in the present study was calculated as a ratio of heavy metal concentration in plant root to that in the soil according to Adams et al. (2004):

$$BF = Cplant\ root / Csoil \qquad (1)$$

Where $C_{plant\ root}$ and C_{soil} represent the concentration of a given heavy metal in plant root tissue and in the corresponding soil sample, respectively.

The results indicated that the BF of heavy metals was highly variable among different plant species across the site (Table 7.3). The results of the present study showed that the BF among the investigated plant species was generally less than one (BF < 1). This suggests that there is a generally low accumulation of heavy metals from the investigated soils to the roots of the investigated plant species. Among the investigated plants, the median BF values for arsenic, chromium, copper, nickel, lead and zinc were 0.04, 0.02, 0.58, 0.15, 0.08, 0.86 (Table 7.3). Some plant species showed unusual capacity to take certain heavy metals from the soils. Zinc had BF greater than 1 (BF > 1) for most of the plant species compared to other heavy metals, which is an indication of higher bioaccumulation potentials from soil to plant species. For arsenic, chromium and lead, their BF is less than 1 (BF < 1) indicating potentially relatively low bioaccumulation from soil to plant species (Table 7.3). For arsenic, *Bistorta officinalis* had much higher BF (0.82) as compared to other plant species. Three plant species had BF > 1 for copper: *Argrostis capillaries*, *Glyceria maxima* and *Filipendula ulmaria*.

Table 7.3 Bioaccumulation Factor of heavy metals for the investigated plant species.

Plant Species	Common Name	Arsenic	Chromium	Copper	Nickel	Lead	Zinc
Agrostis stolonifera	Creeping bent	0.07	0.08	0.15	0.24	0.12	0.26
Artemisia vulgaris	Mugwort	0.02	0.01	0.02	0.12	0.01	0.19
Argrostis capillaries	Common bent	0.00	0.01	1.48	0.00	0.06	4.18
Chamerion angustifolium	Rosebay willowherb	0.11	0.05	0.10	0.11	0.02	0.29
Agrostis tenuis	Slender rush	0.09	0.08	0.59	0.30	0.29	0.30
Dactylis glomerata	Cocksfoot	0.05	0.10	0.19	0.19	0.08	0.83
Urtica dioica	Stinging nettle	0.04	0.05	0.10	0.12	0.04	0.22
Galium aparine	Cleavers	0.01	0.00	0.32	0.02	0.02	0.39
Phalaris arundinacea	Reed canary grass	0.02	0.02	0.08	0.04	0.03	0.25
Heracleum sphondylium	Hogweed	0.00	0.00	0.07	1.31	0.02	0.23
Juncus inflexus	Hard rush	0.10	0.07	0.67	0.15	0.14	0.69
Impatiens glandulifera	Himalayan balsam	0.08	0.00	0.64	0.27	0.09	1.00
Plantago lanceolata	Ribowort plantain	0.04	0.02	0.75	0.23	0.09	1.67
Lolium multiflorum	Italian Rye grass	0.00	0.01	0.58	0.00	0.02	7.69
Juncus effusus	Soft rush	0.09	0.03	0.77	1.51	0.16	1.63
Chamerion angustifolium	Rosebay willowherb	0.01	0.01	0.16	0.00	0.02	0.56
Holcus lanatus	Yorkshire fog	0.04	0.01	0.71	0.89	0.03	1.43
Urtica dioica	Stinging nettle	0.15	0.02	0.93	0.51	0.12	2.39
Dactylis glomerata	Cocksfoot	0.13	0.27	0.81	0.54	0.21	0.86
Festuca pratensis	Meadow fescue	0.36	0.02	0.01	0.01	0.04	0.06
Glyceria maxima	Reed sweetgrass	0.09	0.03	1.39	0.69	0.11	2.36
Phleum pratense	Timothy grass	0.03	0.01	0.53	0.00	0.04	1.76
Lolium pratense	Ryegrass	0.14	0.16	0.58	0.00	0.18	1.36
Equisetum arvense	Field horsetail	0.04	0.01	0.86	0.00	0.06	0.92
Cynosurus cristatus	Crested dog’s tail	0.04	0.06	0.24	0.96	0.09	1.23
Filipendula ulmaria	Meadowsweet	0.01	0.03	1.07	0.00	0.08	1.32
Bistorta officinalis	Bistort	0.82	0.03	0.52	0.72	0.34	0.52
Median		0.04	0.02	0.58	0.15	0.08	0.86
Min		0.00	0.00	0.01	0.00	0.01	0.06
Max		0.82	0.27	1.48	1.51	0.34	7.69

For nickel, *Heracleum sphondylium* and *Juncus effuses* had the BF > 1 (Table 7.3). The median value of BF for zinc was close to 1, indicating strong uptake of zinc by plant roots. It is interesting to note that nearly half of the investigated plant species had a BF greater than 1 for zinc with *Lolium multiflorum* having a BF as high as 7.69.

7.5 Root-shoot Translocation

The translocation factor (TF) for the investigated plant species is given in Table 7.4. The TF is defined as the ratio of metal concentration in the shoot to that in the root (Zhang et al., 2002; Fayiga & Ma, 2006). The TF was calculated based on Gupta et al. (2008), Zhang et al. (2002) and Fayiga and Ma (2006) using the following relation:

$$TF = C_{\text{plant shoot}} / C_{\text{plant root}} \qquad (2)$$

Where, TF is the Translocation Factor, $C_{\text{plant shoot}}$ and $C_{\text{plant root}}$ represent respective heavy metal concentrations in the plant shoot and root.

In general, the TF among the investigated plant species varied considerably (Table 7.4). Most of the investigated plant species had TF less than one (TF< 1) for one heavy metal or the other; indicating low translocation capacity of heavy metals from belowground roots to aboveground shoots (Table 7.4). For all the investigated plant species, the median TF values for arsenic, chromium, copper, nickel, lead, and zinc were 0.10, 0.09, 0.19, 0.19, 0.09 and 0.26 respectively (Table 7.4). All the median TF values for all the heavy metals were less than one suggesting relatively low phytoavailability. The TF results indicated that most of the heavy metals were poorly translocated from the roots to shoots. Although, a few plant species had TF nearly or greater than 1 (TF > 1) at least for one heavy metal. Specifically, *Artemisia vulgaris* had TF nearly or greater than 1 for arsenic and zinc, *Phalaris arundinacea* for nickel, *Heracleum sphondylium* for chromium and zinc, and *Bistorta officinalis* for zinc (Table 7.4). Thus, the potential hyperaccumulators identified in the present study include *Artemisia vulgaris* for arsenic and zinc, *Phalaris arundinacea* for nickel, *Heracleum sphondylium* for chromium and zinc, and *Bistorta officinalis* for zinc. These plant species have implications for phytoremediation of historically contaminated sites.

Table 7.4. Translocation factor of heavy metals for the investigated plant species.

Plant Species	Common Name	Arsenic	Chromium	Copper	Nickel	Lead	Zinc
Agrostis stolonifera	Creeping bent	0.19	0.01	0.02	0.13	0.02	0.16
Artemisia vulgaris	Mugwort	0.92	0.15	0.15	0.22	0.20	0.99
Argrostis capillaries	Common bent	0.08	0.09	0.12	0.23	0.06	0.18
Chamerion angustifolium	Rosebay willowherb	0.48	0.02	0.44	0.41	0.05	0.74
Agrostis tenuis	Slender rush	0.39	0.07	0.08	0.16	0.11	0.26
Dactylis glomerata	Cocksfoot	0.00	0.02	0.12	0.19	0.10	0.22
Urtica dioica	Stinging nettle	0.12	0.05	0.30	0.08	0.09	0.14
Galium aparine	Cleavers	0.16	0.00	0.17	0.59	0.13	0.45
Phalaris arundinacea	Reed canary grass	0.27	0.10	0.83	1.76	0.25	0.76
Heracleum sphondylium	Hogweed	0.16	1.94	0.75	0.07	0.12	1.03
Juncus inflexus	Hard rush	0.63	0.05	0.28	0.12	0.08	0.32
Impatiens glandulifera	Himalayan balsam	0.07	0.54	0.20	0.19	0.15	0.34
Plantago lanceolate	Ribowort plantain	0.28	0.15	0.20	0.43	0.29	0.16
Lolium multiflorum	Italian Rye grass	0.56	0.13	0.28	0.50	0.25	0.20
Juncus effusus	Soft rush	0.04	0.09	0.21	0.11	0.01	0.34
Chamerion angustifolium	Rosebay willowherb	0.14	0.17	0.58	0.18	0.09	0.65
Holcus lanatus	Yorkshire fog	0.07	0.94	0.10	0.10	0.16	0.08
Urtica dioica	Stinging nettle	0.01	0.06	0.15	0.12	0.05	0.05
Dactylis glomerata	Cocksfoot	0.03	0.01	0.13	0.16	0.04	0.26
Festuca pratensis	Meadow fescue	0.04	0.12	0.38	0.44	0.09	0.44
Glyceria maxima	Reed sweetgrass	0.10	0.09	0.07	0.18	0.04	0.09
Phleum pratense	Timothy grass	0.21	0.28	0.19	0.27	0.25	0.25
Lolium pratense	Ryegrass	0.00	0.01	0.10	0.15	0.02	0.18
Equisetum arvense	Field horsetail	0.02	0.26	0.20	0.26	0.04	0.06
Cynosurus cristatus	Crested dog’s tail	0.09	0.08	0.16	0.40	0.12	0.30
Filipendula ulmaria	Meadowsweet	0.01	0.11	0.06	0.44	0.03	0.13
Bistorta officinalis	Bistort	0.01	0.25	0.31	0.29	0.01	1.22
Median		0.10	0.09	0.19	0.19	0.09	0.26
Min		0.00	0.00	0.02	0.07	0.01	0.05
Max		0.92	1.94	0.83	1.76	0.29	1.22

Compared to the normal levels of heavy metals in plants, the findings of this study show that the concentrations of arsenic and lead in the shoots of the investigated plant species generally exceed normal threshold levels in plants. While the concentrations of chromium, copper, nickel and zinc in the shoots of the investigated plants are generally within the normal level reported ranges for plants. Normal levels of heavy metals in plants are considered within the following ranges: 0.1 – 0.5 mg/kg for arsenic; 0.1 – 0.5 mg/kg for chromium; 5 – 30 mg/kg for copper; 30 – 300 mg/kg for manganese; 0.1 – 5 mg/kg for nickel, 0.1 – 0.5 mg/kg for lead and 27 – 150 mg/kg for zinc (Kabata Pendias, 1984; Kabata Pendias, 2010).

7.6 Other Remediation Options

Moreover, another feasible remediation option that should be considered is capping of the bare area of the site. This could help to overcome the barriers associated with contamination in the bare area by preventing the contaminated soil from being released unto the air and water. This means that uncontaminated soil must be brought in from elsewhere to use and cover the bare area for this remediation approach to be successful. The most important components of a capping system are the barrier (capping) layer and the drainage. The capping of contaminated soils is increasingly being recognised as a low-cost remediation technology for contaminated sites (Lee & Jones-Lee, 1997). A thick layer of dense clay soil with low permeability can be used as a cap barrier. In capping the bare area, consideration should be given to the contamination type, the site use, and the targeted receptors. It is important that any capping material that will be used is assessed on case-by-case basis in line with the above-mentioned factors. Although, capping the bare area will not destroy or remove contaminants from the soil, but will help to isolate and keep contaminants in place and potentially prevent the spread of contamination across the site. Capping the bare area could help to break the contaminant linkage, acts as a barrier to the underlying contamination and provides avenue for plant growth at the site. The main benefits of this remediation technology are that it is cost effective and interrupts the pathway between the contaminants and the receptor (Zhang et al., 2016). It is important that the design of the cap adopted for the site must reflect site specific conditions and consideration should be given to many factors such as local availability of capping materials, cost of capping materials, nature of contaminants, local climate, terrain, hydrogeology, and the proposed future use of the site. In addition, potentially significant long-term issues that may arise in the course of capping the bare area, for example, integrity of low permeability layer, groundwater contamination and funds availability to maintain the cap must be addressed in developing remediation design of the site (Lee & Jones-Lee, 1997). It should be clear where the non-contaminated soil for capping the bare area will be sourced from and whether the soil is sufficiently available for this purpose. Capping could help restore the bare area of the Football Ground, but this remediation option is only practicable when suitable capping material is available (Bradshaw, 2000).

CHAPTER 8

Discussion

8.1 Overview

The general discussion reported in this chapter draws together and integrates material from Chapters 4, 5, 6 and 7 of this thesis. The first part of the research presented in this thesis was to establish the feasibility of using XRF for analysis of heavy metals at the study site. Following this the findings of the second part of the research – the desk study and field visit, the heavy metal survey, and remediation opportunities – are discussed. This is followed by a discussion of the limitations of the current research and recommendations for future studies and ends with sections detailing the research contributions and conclusion of the work reported in this thesis.

8.2 XRF and Aqua regia/ICP-OES Heavy Metal data

One thing that is remarkable in the present study is that the concentrations of the targeted heavy metals obtained by XRF and aqua regia/ICP-OES techniques show a strong positive linear relationship (Figures 4.1a, b, c, d, e, f and g). In other words, this means that the correlation among heavy metal data obtained by the two techniques was highly satisfactory. It is also interesting to note that, there was a very good agreement between the two techniques, despite the difference between the matrices of the total sample digestion of aqua regia and the section of sample analysed using XRF (Figures 4.1a, b, c, d, e, f and g). The very good agreement between the techniques suggests that the section of sample analysed using XRF provides an appropriate representation of the total element concentrations within the investigated soils. These results indicated that XRF corroborated aqua regia/ICP-OES for quantitative prediction of specific heavy metals from the investigated soils, and suggests that XRF was a reliable, quick and cost-effective alternative to conventional aqua regia/ICP-OES analytical method, allowing the analysis of much larger samples in relatively shorter times from the investigated soils in the laboratory.

Among the heavy metals yielded by the two techniques, nickel had the strongest correlation while the correlations for arsenic and cadmium were the weakest (Figures 4.1a, b, c, d, e, f and g). The lower correlation coefficients observed for arsenic and cadmium in the present study may be explained by the low concentrations of these elements in the dataset (Figures 4.1a and b). Although, the prediction by the linear regression for arsenic and cadmium in the present study was good. Several studies have reported strong correlation between heavy metals yielded by XRF and those obtained by chemical methods such aqua as regia digestion (Ramsey et al., 1995; Somogyi et al., 1997; Laperche & Billaud, 2008; Radu & Diamond, 2009). Thus, the findings of the present study confirmed similar results that have been reported in many literature about the strong relationship between XRF and aqua regia/ICP-OES derived heavy metals from contaminated soils. The present findings are consistent with those of Kilbride et al. (2006).

Despite the data obtained by XRF and aqua regia/ICP-OES show a very strong linearity, there were differences in terms of the overall heavy metals yielded by each technique across the sampling locations (Figures 4.2a, b, c, d, e, f and g). The concentrations of heavy metals yielded by XRF and aqua regia/ICP-OES techniques were above the normal background value (Ander et al., 2012). The difference in terms of the heavy metals yielded by each technique across the sampling locations may be explained by several factors: XRF technique is regarded as a non-destructive technique and measures the total elemental concentrations in soil (Schneider et al., 2016). Similarly, XRF technique produces measurements based on the whole contents of the sample and matrix dependent egression volume (Ravansari & Lemke, 2018). In addition, it is important to recognise that XRF heavy metal data can be greatly affected by the sample matrix and other factors such as variability in soil total metal concentration, interfering elements, sample homogeneity and particle size. Several factors such as sample homogeneity, particle size, interfering elements and sample matrix can affect the quality and precision of results produced by XRF technique (Kalnicky & Singhvi, 2001; Laperche, 2005; Binstock et al., 2008). It is possible that heavy metal concentrations yielded by XRF technique in the present study might have been influenced by these factors. On the other hand, aqua regia/ICP-OES measures the “pseudo total concentration” of heavy metals from soil (Dos Santos & Alleoni, 2013). Aqua regia/ICP-OES derived heavy metals being independent from the sample matrix are more likely not to be influenced by the sample matrix effect.

Moreover, the concentrations of heavy metals yielded by XRF technique may also be explained by the fact that XRF measures the total concentration of element, irrespective of the amount bound to different soil matrices. This observation has been documented in many studies (Gałuszka et al., 2015; Sharma et al., 2015; Lemiere, 2018; Tighe et al., 2018). Similarly, the nature of extraction techniques used may also affect the results produced. Furthermore, there is a high variation of heavy metals across the investigated soils, and some of the investigated soils in the present study contain unusually high concentrations of heavy metals. High spatial variation in the distribution and contents of heavy metals is generally a unique characteristic of anthropogenically contaminated soil such as the investigated soils. It is likely that these factors played a role in terms of the overall heavy metal concentrations yielded by XRF and aqua regia/ICP-OES techniques across the sampling locations in the present study.

The much lower arsenic and chromium concentrations (Figure 4.2 a and c) obtained by aqua regia/ICP-OES than XRF technique suggests that these elements most likely bound to silicates in the investigated soils in comparison to copper, lead, nickel and zinc. Similar observation was documented by Fassbender and Seekamp (1976). Aqua regia/ICP-OES does not totally dissolve silicates; hence, the metal concentration extracted by this method is referred to as “pseudo-total concentration”. It is generally accepted that the concentration of heavy metals extracted by strong extractants such as (HF and $HClO_4$) or other acids combinations are regarded as the “real total concentration” due to the fact these acids can achieve total dissolution of heavy metals from the soil matrices (Taraškevičius et al., 2013). However, in some cases, the concentrations of toxic heavy metals such as mercury, zinc, lead, cadmium and copper obtained by aqua regia digestion do not show much difference when compared to concentrations obtained by HF and other acids combinations (Sastre et al., 2002). In the European Union, aqua regia/ICP-OES is the most used reagent for extracting metals from polluted soil (Gleyzes et al., 2002; Grotti et al., 2002; Quevauviller, 2002), and it is the standard method for certifying soil samples in Great Britain and France (Sakan et al., 2011).

While both techniques seemed to be suitable for predicting heavy metal concentrations in the investigated soils as demonstrated in the present study, the findings show that XRF technique represents easy and a cost-effective alternative to aqua regia/ICP-OES chemical method for determining heavy metals from the investigated site. Conventaional aqua regia/ICP-OES is very laborious, time-consuming, and associated with risk of sample contamination, high operational cost, and loss of volatile elements (Sastre et al., 2002). In addition, it is very time-consuming, especially when a large number of soil samples is involved. XRF has the advantage of measuring total elemental concentrations without any complicated sample pre-treatment (Somogyi et al., 1997) as shown in the present study. Similarly, XRF technique has demonstrated the capacity to measure the targeted elements from the investigated soils in relatively shorter times compared to conventional aqua regia/ICP-OES technique. Therefore, the findings of the present study suggest that XRF could be considered the preferred technique for potential determination of heavy metals from the investigated site due its capability to determine heavy metals in a rapid and cost-effective manner compared to aqua regia/ICP-OES. However, this will depend on the aim and intent of the investigation and the targeted heavy metals.

Summarily, the heavy metals yielded by XRF technique in the present study has implication for the purpose of rapid mapping and delimiting contaminated areas around Wrigley Head and Football Ground, Moston Brook since this represents the real total metal concentrations. This could help to define and map out potentially areas of serious contamination across the site considering the high spatial variability of heavy metal contamination in the study area. This is essentially important considering the present land use of the site so that appropriate strategies can be developed to minimize any potential adverse health effects on the site users. This data importantly could potentially provide relevant information that would assist the Local Authority to make decisions regarding the environmental risk assessment and remediation of the study site.

Moreover, the concentrations of heavy metals yielded by aqua regia/ICP-OES technique represent the harmful levels of heavy metals from the investigated soils. Aqua regia digestion is widely used to determine the toxic concentrations of chemical elements from the soils with the purpose of solving environmental problem relating to toxic element contamination (Soon & Abboud, 1993). Folarian et al. (1998) reported that aqua regia digestion is regarded as the more appropriate method for determining the concentrations of heavy metals that are potentially dangerous to the environment. In the context of the study site, the harmful levels of heavy metals yielded by aqua regia/ICP-OES can be used as a starting point for environmental monitoring of heavy metals in the study area because they give indication of worst-case scenario of possible long-term changes. These data potentially could provide relevant information to the local authority, decision/policy makers and/or environmental managers regarding the environmental risk assessment of the site targeted at minimising the potential risks of heavy metal contamination at the site.

8.3 Case Study – Desk and site visit studies

The desk and site visit results indicate there are contamination issues associated with the site (Figures 5.1 – 5.7). The results indicate the site has been heavily contaminated with multiple contaminants from various historical industrial and commercial activities alongside with uncontrollable disposal of waste into landfill sites operating within and adjacent to the site (Figures 5.1 – 5.7). Wastes of unknown types were buried in the landfill sites, and it is likely that this will produce leachates containing contaminates (Groundwork Oldham & Rochdale, 2008). The desk study shows that most of the landfill sites operated before the enactment of Environmental Pollution Act 1974 which legally requires licensing of all controlled wastes deposited onto land (Table 5.1). Consequently, the historical land use of the area led to contamination of the site and its controlled waters due to uncontrollable pollution from different sources. These historical land uses of the site suggest that there may be a potential risk of contamination sources that may affect human health, controlled waters, and vegetation (Groundwork Oldham & Rochdale, 2008) (Table 5.10). The contamination problem at this site was compounded due to there were no validated records on the nature and status of contaminants emitted at the site, and thus, this site forms a potential source of unknown contaminants (Table 5.1). This is a great setback and further complicates the efforts to overcome the barrier associated with the site.

The Football Ground is an open bare area with lack of vegetation (Figures 5.18 and 5.19). This area has a peculiar problem and is suspected to be heavily contaminated probably due to the legacies of past industrial activities and absence of vegetation in this area might be due to high level of contamination. This raises a further concern that the contamination issue in this area may be significant and may require a further investigation and risk assessment to understand their likely impact on the proposed future use of this area. In addition, the high level of contamination in this area could be a barrier to revegetate the area.

A previous preliminary risk assessment undertaken by Manchester City Council Contaminated Land Section in 2011 shows that Wrigley Head – the section of the site investigated presents a high risk to human health due to elevated arsenic associated with the landfill materials and total petroleum hydrocarbons and poses a moderate risk to controlled waters due to elevated iron and ammonia in the surface water and the brook (Miller, 2011) (Table 5.10). This suggests that the presence of elevated contaminants identified in the made ground at this site may cause potential significant risks to designated receptors such as vegetation, humans, and controlled waters (Table 5.10). The variable heterogeneous nature of historical landfill materials buried at this site are attributed to historical industrial activities that included mills, dye works and print works in the vicinity of this site (Miller, 2011), and it is important that this area be treated as “potentially contaminated”. Arsenic is a known carcinogen and prolonged exposure via inhalation of arsenic contaminated soil dust can cause numerous adverse health effects such as skin cancer, liver cancer, lung cancer, bladder cancer, dermal lesions, peripheral vascular diseases and peripheral neuropathy (Martin & Griswold, 2009; Patlolla et al., 2012; Tan et al., 2016). Similarly, lower-level arsenic exposure is associated with nausea and vomiting, poor production of red and white blood cells, abnormal heart function and damage to blood vessels (Martin & Griswold, 2009). Elevated ammonia is a landfill product produced during the decomposition of organic matter through the process of ammonification (Jackson & Jackson, 1996). The presence of ammonia identified in landfill water can be because of a mixed landfill material from different landfill sites as some of the landfill sites may contain some form of organic waste. This ammonia in the historical landfill sites and other industrial waste materials might have been transported to the brook through run off. This could explain the high level of ammonia identified in the surface water and the brook in the study area.

Although, in general, the findings of this report suggest that the site poses low and very low risks to current and future site users (Miller 2011). Low risk is defined as the likelihood that harm could occur to a designated receptor from an identified hazard, but it is likely that if this harm occurs, the harm would worst normally be mild. For the future users of the site, the risk is considered very low (Miller 2011). Very low risk indicates a low likelihood that harm could occur to a receptor, but if such harm occurs, the outcome is not likely to be severe. The risk to controlled waters is classified moderate risk (Miller 2011). Moderate Risk is defined as the likelihood that a designated receptor could be exposed to harm from an identified hazard, but it is relatively unlikely that the outcome of any such harm would be severe, or if harm occurs, the outcome of such harm would be relatively mild. For this risk type, further investigation is normally required to understand the risk and determine the potential liability. Some remedial works may be required in the longer term.

It is important to point out that the potential human health risk assessment from the contaminants to the current and future users of the site was assessed based on those contaminants are being beneath the paths and the potential to human contact to bare soil should the site users walk away from the path. It is also considered that the potential risk (moderate risk) of contaminants to the site workers especially during the construction of path may be higher because the site workers may come in a direct contact with the contaminants in the course of site path construction work developments (Miller 2011). However, significant contaminant linkage may be created at the site during any proposed future development which may impact negatively on the designated receptors particularly around the Wrigley Head. It is important that adequate risk mitigation strategies are implemented at the site against any proposed developments which may potentially affect human health. In addition, it is important that low risks identified at the preliminary risk assessment stage are incorporated in the remaining risk assessment process and to update the site risk assessment regularly in accordance with any proposed developments. The background study of the site reveals that there had been several historical industrial activities at the site, and consequently, the site could be potentially considered to hold some interesting industrial archaeology.

The site visit reveals that majority of this site is currently used as informal open space for the local people. The site is mainly used by dog walkers and people accessing the footpaths to the adjoining main roads (Figure 5.16). Evidence show that the site is affected by contamination, dereliction and neglect and has a polluted waterway (Figure 5.11, Table 5.2). The contaminations probably, in part, the result of there being several landfill sites at Moston Brook and the resultant historical leachate discharge from adjoining contaminated land as well as a few combined sewers overflows that discharge storm sewage directly into the Brook during heavy downpour (Groundwork Oldham & Rochdale, 2008; Manchester City Council, 2007) (Table 5.1). This leachate is suspected to be iron orche alongside some surface water sheen (Miller, 2011). A look at the topography of the site indicates that the area has been altered because of historical industrial activities, but evidence of industrial activities such as print, dye and brick works are no longer visible at the site due to these industrial activities probably could have been altered by the waste disposal activities that dominated the study area after major industrial activities stopped in the area. However, whitish materials associated with "White Hills" landfill were still visible at the site (Figures 5.21 and 5.22). These whitish materials are believed to be china clay waste from historical cotton mills in Failsworth area. There is an open bare area with lack of vegetation suspected to be heavily contaminated popularly known as Football Ground located around Wrigley Head Bridge (Figures 5.18 and 5.19). This area is a former area for various recreational activities such as football matches and used presently as a training ground for Alsatian dogs. The area surrounding bare area is characterised by unmanaged dense vegetation comprising of different trees and grasses (Figure 5.19). There also are some improvement works going on at the site such as construction of footpath around Wrigley Head (Figure 5.20). These improvement works are carried out to make the site more attractive to the local public. The site visit shows that the site is located close to residential area (Figure 5.17) and is recognised as an important green asset for the local residents and community.

8.4 Case Study – Heavy Metal Contamination in Wrigley Head and the Football Ground

8.4.1 Selected Chemical Properties across Wrigley Head and Football Ground Area.

In the present study, the data indicate that there was a high variability in soil pH across the investigated soils in the Wrigley Head generally and the Football Ground (Table 6.1 and Figure 6.7). Soil pH is one of the most measured parameters because it is regarded as a good indicator of a wide range of chemical properties (McLean, 1982). The soil pH data generally indicate that the pH of the investigated soils varied from slightly acidic (pH > 5) to mild alkaline (pH > 8) across the investigated soils (Table 6.1 and Figure 6.7). The variation in soil pH across the investigated soils in the Wrigley Head and Football Ground in the present study is most likely due to differences in soil characteristics and different industrial waste materials upon which the investigated soils were formed. It is important to note that the investigated soils are not of geological origins but was largely formed from solid industrial wastes transported from other locations. Generally, the findings of the present study show that the pH of the investigated soils are slightly acidic or alkaline in nature (Table 6.1 and Figure 6.7). In other words, this suggests that the investigated soils have circumneutral or less acidic pH conditions. The investigated soils were heavily contaminated as a result of the past industrial activities in the area linked with inputs of contaminants from various sources (Douglas et al., 2002; Groundwork Oldham & Rochdale, 2008; Manchester City Council Contaminated Land Strategy, 2011). Many studies have shown that industrial processes such as pulp and paper mills, dye works can generate substantial amounts of highly alkaline wastes rich in calcium (Jia et al., 2014; Morris et al., 2012; Royer-Tardif et al., 2019). Soil pH values ranging from 8.18 to 8.96 and 8.27 to 9.30 respectively have been reported from soils contaminated by textile and dyeing effluents (Malarkodi et al., 2007). Similary, Mohan and Jaya (2013) reported acidic and slightly acidic pH in the vicinity of an industrial area associated with industrial effluents. Therefore, most likely, the slightly acidic or alkaline pH conditions of the investigated soils are attributed to the nature of industrial effluents generated from the historical undustrial proceseses located within or adjacent to the site.

The implication of the circumneutral or less acidic pH of the investigated soils is that under these conditions mobility of heavy metals is limited to a great extent in the bulk soil. In heavy metal contaminated soil derived from other industrial processes such as the investigated soils with circumneutral or less acidic soil pH, most heavy metals tend to be absorbed in soils under these pH conditions, and thus result in a decrease in metal mobility (Lu et al., 2003; Banat et al., 2005; Waterlot et al., 2013). In other words, mobilisation of heavy metals from such metal contaminated soil may or may not take place, subject to specific environmental conditions, and it is likely that mobility of heavy metals (if any) from such metal contaminated soils, may be limited to certain periods of time when favourable environmental conditions prevail. Generally, cationic metals are mostly mobile under acidic soil condition (low pH) but with increasing pH, their mobility and bioavailability decrease in soil (Sauvé et al., 2000; Jung, 2008; Gebrekidan et al., 2013). Malik et al. (2010) found that higher pH might cause a decrease mobility and lower solubility of heavy metals in soil. In this study, the pH of the investigated soils is not sufficiently low to favour mobility of heavy metals from the bulk soil (Lu et al., 2003; Banat et al., 2005; Waterlot et al., 2013).

There was a variation in soil pH between the bare and vegetated areas of the Football Ground as indicated by the coefficient of variation (Figure 6.7). The findings show that soil pH was slightly higher in the bare area compared to the vegetated area (Figure 6.7). The slightly lower pH in the vegetated area is most probably due to the impact of vegetation in the study area over time. Soil pH can be impacted upon by the nature of vegetation and landuse and management. It is possible that the presence of vegetation in this area might have impacted on the soil pH over time. For instance, vegetation may impact on soil pH through release of organic acids synthesised in the plant roots. Low-molecular-weight organic acids (LMWOAs) are commonly produced in soils due to root exudation and the microbially mediated breakdown of components of soil organic matter (Strobel, 2001; Boddy et al., 2007). These LMWOAs may cause acidification of soil pH in the rhizosphere, and thus, result in a decrease in soil pH. It has been reported that LMWOAs can cause mobility and phytoavailability of heavy metals through acidification of the pH of the rhizosphere (Jones & Darrah, 1994; Schwab et al., 2008).

Similarly, EC varied widely across the investigated soils in Wrigley Head and Football Ground (Table 6.1and Figure 6.8). Soil EC is an important parameter that influences the mobility and bioavailability of heavy metals in soils. EC is a measure of salts in soils (salinity) and reflects an important indicator of soil health. Similarly, the EC data reveal that the investigated soils had low EC, which is an indication of non-saline soils. Most EC values observed in the present study area were below the recommended optimum levels (110 – 570 mS/cm) in Wrigley Head generally and the Football Ground (Table 6.1 and Figure 6.8). Additionally, it also possible that the spatial variation in EC across the investigated soils in the present study may be due to inherent factors such as climate, bulk density, soil structure, the timing of measurement, soil aggregation and water potential which collectively affects the EC of the studied soil. A study by Rhoades et al. (1976) found that soil texture, moisture content and cation exchange capacity are the major factors responsible for variation in electrical conductivity in non-saline soil. Under high soil EC condition, macro and micronutrients such as calcium, potassium, magnesium and sodium tend to increase, thereby competing with cationic heavy metals for sorption sites (Naidu et al., 1994; Du Laing et al., 2008). The implication of low EC is that more cationic heavy metals may be retained in the soil due to low competition between micro and macro elements such as calcium, potassium, magnesium, and sodium with cationic heavy metals for sorption sites. This low competition may eventually lead to a decrease in the mobility and bioavailability of heavy metals due to increase adsorption of heavy metals in soils thereby making it less available for plant uptake.

Furthermore, Total Organic Carbon (TOC) was eveluated in the bare and vegetated areas of the Football Ground in the present study (Table 6.3 and Figure 6.9).TOC refers to the amount of carbon in soil or in a geological formation. It is a component of soil organic matter derived primarily from plant and animal materials in soil at various stages of decomposition. In the present study, there was a remarkable difference in TOC in the bare and vegetated areas of the Football Ground (Figure 6.9). The slight decrease in TOC in the bare area could be due to absence of vegetation in this area (Figure 6.9). However, in the case of vegetated area, the slightly high TOC observed in this area suggests that the input of TOC derived from the historical industrial wastes has been impacted by the presence of vegetation over time. This suggests that the slightly higher organic carbon in the vegetated area is likely due to decomposition of organic litters partly derived from plant materials. This shows that the level of metal contamination and vegetation can affect the distribution of organic carbon in soil. Therefore, most likely, the spatial variation in TOC in the investigated soils are linked to combined factors resulting from various historical industrial activities associated with organic effluents and/or carbonaceous materials and the impact of vegetation over time. Somasundaram (2001) reported that the organic carbon content of the soil was strongly linked to the addition of high soluble organic matter through industrial waste materials.

Studies have shown that industrial processes such as pulp and paper mills, dye works, textile industries, paintworks, plastic works, bleaching works, can produce high amounts of organic and/or inorganic industrial effluents in soils (Deepali & Gangwar, 2010; Yaylali-Abanuz, 2011; Morris et al., 2012; Jia et al., 2014; Royer-Tardif et al., 2019). These historical industrial activities were reported to have taken place at the site (Groundwork Oldham & Rochdale, 2008; Miller, 2011), and might have contributed to the input of organic carbon at the site. Dondi et al. (1997) reported that effluents from a wide range of industrial processes contain high organic and/or carbonaceous material content which give them a high calorific value. This category of wastes is highly variable due to their different origins and different treatment processes. This could explain the spatial variation in TOC at the site. Other authors (Dahlgren et al 1997; Baker et al., 2007; Sinoga et al., 2012) have reported that several factors such as soil management, landuse, vegetation type, climatic factors, soil contamination, altitude, topography, weathering rate, microorganisms, internal drainage, rainfall, leaching intensity can affect the TOC in soils.

8.4.2 The Concentrations of Heavy Metals Across the Investigated Soils in Wrigley Head and Football Ground.

The concentrations of heavy metals obtained across the investigated soils in Wrigley Head are presented in Tables 6.2 and 6.3. There was a remarkable difference in the concentrations of heavy metals across the Wrigley Head (Tables 6.2 and 6.3). The concentrations of most heavy metals were relatively higher in the Football Ground area compared to the soils elsewhere around Wrigley Head (Tables 6.2 and 6.3). These metals were investigated because they are regarded as priority heavy metals which have implications on the ecosystem and human health (Tchounwou et al., 2012). Copper, lead, zinc, and nickel were the most dominating heavy metals across the investigated areas with elevated concentrations far above the background level (Tables 6.2 and 6.3). The findings of the present study suggest that the Football Ground is heavily contaminated compared to the investigated soils elsewhere in Wrigley Head (Tables 6.2 and 6.3).

The median concentrations of arsenic, copper, lead and zinc obtained across the investigated soils in Wrigley Head were higher than that in typical UK soils (Table 6.2), respectively while nickel had the median concentrations very similar to the respective UK-wide value (Ross et al., 2007) (Table 6.2). The median concentrations of arsenic, chromium, copper and lead are higher than the normal background value (Ander et al., 2012; Appleton et al., 2013) (Table 6.2). This reveals the significant contributions of anthropogenic contamination across the study area. The median concentrations of soil-borne arsenic and chromium all well exceeded the current UK screening levels for these two regulated soil elements (DEFRA, 2014) (Table 6.2). There were a few locations with concurrent presence of copper, nickel lead and zinc at very high concentration (FG1, FG2, FG4 and RS3) (Table 6.2). The concentration of lead in the investigated soils were within the range previously reported by others (McGrath, 1986; Alloway, 1995; Ross et al., 2007; Johnson et al., 2012) for British soils except in FG2, FG4, RS3 and WH1 locations where lead concentrations were above the reported concentration range; indicating elevated level of lead in these soils (Table 6.2). The concentration of arsenic in the investigated soils exceeded the upper limit of background arsenic level (74.4 mg/kg) in British soils (Johnson et al., 2012) except for the soils collected at FG1, FG4, FG5, FG6, FG7, FP4, FP5 and MD1 locations where the soil-borne arsenic was within the background arsenic range (Table 6.2). Chromium concentrations observed in the investigated soils are within the range reported in the literature for UK soils. Nickel concentrations in most of the investigated soils fall within the range reported for the British soils (Ross et al., 2007) and the world soils (0.2 – 45 mg/kg) (Kabata-Pendias, 2000) except for the soils collected from locations FG1, FG2, FG4 and RS3 where elevated nickel concentrations were observed (Table 6.2). Copper concentrations in the investigated soils varied widely and in most investigated soils; copper concentration was within the range reported for British soils (Archer & Hodgson, 1987; Ross et al., 2007; Johnson et al., 2012) except in FG1, FG2, FG4, FG6, FG7 and RS3 where elevated copper concentrations were observed (Table 6.2). The results indicate that copper was among the most dominating heavy metals in FG soils. Furthermore, zinc concentrations in most of the soils are in agreement with the range of soil-borne zinc reported for UK soils (Alloway, 1995; Ross et al., 2007) except in FG1, FG2, FG4, FG7, FP2 and RS3 soils where elevated concentrations of zinc were observed (Table 6.2). However, McGrath and Loveland (1992) did report extremely high zinc concentration (3648 mg/kg) for some UK soils.

In the Football Ground, the results of the present study show that the median concentrations of studied heavy metals varied considerably across the bare and vegetated areas (Table 6.3). The Football Ground area at Wrigley Head is notable for an area of bare soil. A detailed survey of the heavy metal content of the soil in that area was undertaken. The findings suggest that the study area was potentially contaminated by arsenic, cadmium, chromium, copper, lead, nickel and zinc respectively. Marked differences were also observed between the concentrations of heavy metals in the bare and vegetated areas of the Football Ground (Table 6.3). The summary data in Table 6.3 indicate the high levels of contamination across the Football Ground. Importantly the independent two-sample Wilcoxon (P) indicates a significant difference between the vegetated and bare areas (Table 6.3). The data obtained show that the bare area is potentially more contaminated compared to the vegetated area. This suggests that lack of vegetation in the bare area might be due to the high level and phytotoxic nature of the heavy metal contamination in this area. The elevated levels of heavy metal contamination in the bare area of the Football Ground might have affected the natural succession of vegetation in this area. Woch et al. (2016) found that high level of heavy metals in soil may be the major factor affecting the distribution of plant species in contaminated areas. Similarly, Vangronsveld et al. (1995b) reported that elevated contamination and poor soil conditions, for example, poor soil nutrients can result in a complete lack of natural vegetation in contaminated sites. Copper, zinc, lead and nickel potentially present the most serious contamination problem compared to cadmium, chromium and arsenic across the bare and vegetated areas. The relatively high concentrations of most heavy metals in the Football Ground suggest that this area is more contaminated compared to the soils elsewhere in Wrigley Head (Tables 6.2 and 6.3). Some soils were taken from the bare area and sow with lettuce (*Lactuca sativa*) and mustard (*Sinapis alba*) seeds in the greenhouse (data not presented). These plants did not grow indicating the phytotoxic nature of the contamination in the soil. The elevated levels of heavy metals in the Football Ground area reflect the strong influence of local anthropogenic inputs of heavy metals mainly from historical industrial activities and revealed the significant contribution of anthropogenic contamination.

High ranges in values were observed for copper, zinc, lead and nickel in the bare and vegetated areas of the Football Ground compared to cadmium, chromium and arsenic (Table 6.3). The ranges indicate that there is a marked difference in the distribution of heavy metals across the bare and vegetated areas of the Football Ground (Table 6.3). These data reveal that heavy metals tend to be more widely distributed across the bare area compared to the vegetated area. The large range for copper, zinc, lead and nickel suggests that the concentrations of these heavy metals varied widely across the study area compared to the concentrations of cadmium, chromium and arsenic (Table 6.3). Similarly, the coefficient of variation indicates the relative variability of heavy metals across the study site. In the present study, higher coefficient of variation was observed among heavy metals in the bare area compared to the vegetated area (Table 6.3). The concentrations of heavy metals in soil vary based on geological origins and anthropogenic activity. Numerous factors such as the processes of soil formation and the human-induced contamination activities control the relative abundance of heavy metals in soils (Li, Fan, et al., 2009). Copper, lead, nickel and zinc had high CV greater than 100% (CV > 100%) while arsenic, cadmium and chromium had low CV less than 100% (CV < 100%) in the bare and vegetated areas (Table 6.3). Nezhad et al. (2015) found that if coefficient of variation is less than or equal to 20% (CV ≤ 20%), it indicates low variability pattern; 21% < CV ≤ 50% is considered as moderate variability; 50% < CV ≤ 100% is considered high variability and CV > 100% is regarded as exceptionally high variability pattern. These results imply that, copper, lead nickel and zinc exhibit exceptionally high variability patterns across the study area while arsenic, cadmium and chromium displayed high variability across the study area. This observation suggests that copper, lead, nickel and zinc varied more widely across the investigated areas compared to arsenic, cadmium and chromium. In addition, Yongming et al. (2006) reported that heavy metals dominated by natural sources exhibit relatively low CV values while heavy metals affected by anthropogenic sources are quite high in CV values. High metal concentrations and large CV values observed for most of the heavy metals in the present study commonly suggest a strong anthropogenic influence. Thus, the findings show that copper, lead, nickel and zinc had a stronger anthropogenic influence compared to arsenic, cadmium and chromium. The differences in CV among heavy metals in the bare and vegetated areas highlight the degree of the influence of heavy metal contamination sources. Shapiro-Wilk test indicates that all heavy metals are not normally distributed (Table 6.3).

The median heavy metal concentrations obtained from bare and vegetated areas of the Football Ground in the present study greatly exceeded the normal background values reported for English soils (Table 6.3). Ander et al. (2012) reported that the normal background contamination level of arsenic for English soils was 33.4 mg/kg. Similarly, Ross et al. (2007) reported that normal background concentration of arsenic in urban soil of England ranges 6.64 to 26.8 mg/kg while in the UK urban soils, it varies between 1.75 and 32 mg/kg respectively. Furthermore, Barraclough (2007) reported that ambient background concentration of arsenic in UK soils is 10.09 mg/kg. However, in the present study, it was observed that the median concentrations of arsenic in the bare and vegetated areas were 73 mg/kg and 81 mg/kg respectively which were higher than the reported normal background values for English and UK soils (Table 6.3). Similarly, Ross et al. (2007) reported the normal background values of 0.44 mg/kg for cadmium, 34.3 mg/kg for chromium, 42.5 mg/kg for copper, 110 mg/kg for lead, 28.5 mg/kg for nickel and 121 mg/kg for zinc respectively in the UK urban soils. Moreover, Ander et al. (2012) reported that the normal background contamination level for cadmium, chromium, copper, lead and zinc in English soils were 0.74 mg/kg, 81.0 mg/kg, 64.2 mg/kg, 99.5 mg/kg and 129.0 mg/kg respectively. In the present study, the median concentrations of cadmium, chromium, copper, lead, and zinc obtained from bare and vegetated areas were 4 mg/kg and < LOD mg/kg, 178 mg/kg and 142 mg/kg, 3044 mg/kg and 1574 mg/kg, 1257 mg/kg and 877 mg/kg and 1451 mg/kg and 632 mg/kg respectively (Table 6.3). This reveals the significant contamination levels and suggests that heavy metal contamination in the study area is strongly linked to historical anthropogenic contaminations in the study area. The findings of present study corroborated with Reimann and Garrett (2005) who reported that in soils, heavy metal natural background concentrations are unlikely to still exist because of human-induced activities, and this is very true more especially for the UK that had a long episode of industrial activities. Futhermore, the median concentrations of arsenic, chromium and lead obtained from bare and vegetated areas of the Football Ground UK greatly exceeded the current UK screening levels for these regulated heavy metals (Table 6.3) (DEFRA, 2014). The UK screening levels for arsenic, cadmium, chromium and lead for public open space are 79 mg/kg, 220 mg/kg, 21 mg/kg and 630 mg/kg respectively (DEFRA, 2014). However, there was no published UK screening values for nickel, zinc and copper. The screening levels give information about the representative levels of chemicals in soil below which the long-term health risks are likely to be low. In other words, the screening levels indicate the concentration of a contaminant in soil under which a site is not considered “contaminated land” based on Part 2A definition by the Environmental Protection Act 1990 (DEFRA, 2014). It is important to recognise that exceeding the screening levels does not mean that remediation of the area is always necessary, in many cases, further investigations and risk evaluations may be required.

The unique characteristics of the investigated soils is that the soil is not of geological origins but was largely formed from solid industrial wastes transported from other locations within Manchester. The uncontrollable release of contaminants from a variety of industrial sources over a long period resulted in large quantities of heavy metals across the study area.

There are several explanations for the elevated concentrations of heavy metals in the study area. This could be explained by the legacy of historical industrial activities in the study area. Numerous studies have shown that industrial activities are one of the main drivers of anthropogenic sources of heavy metals in soils and can affect the soils directly or indirectly (Wong & Zhou, 1997; Sekhar et al., 2005; Wang et al., 2005). The high concentration of arsenic is mainly due to anthropogenic inputs of arsenic from historical landfill materials in the study area. According to Miller (2011) significant elevated arsenic concentrations in the study area is attributed to historical landfill and made ground materials that were previously buried at the site. This clearly demonstrated local anthropogenic contribution and revealed a significant level of arsenic contamination in the study area. Similarly, the high concentrations of several heavy metals in the investigated soils may be explained by several factors. Several industrial and commercial activities associated with emissions of heavy metals such as brickworks, bleaching and dye works, textile industries, mills, open seam coal mining, landfilling activities had taken place in the study area (Groundwork Oldham & Rochdale, 2008; Miller, 2011). In addition, Researchers (e.g., Romic & Romic 2003; Krishna & Govil 2005) reported that the accumulation of cadmium, lead, copper and zinc in the topsoil of urban area is mainly affected by anthropogenic activities. High copper concentration is known to be historically linked to blue and green dyes, especially a hotspot for the dyeing industry (Hurley et al., 2017). In addition, Deepali and Gangwar (2010) found that elevated concentrations of zinc and lead in soil and sediment is linked to industrial activities such as dye works, bleaching and pesticide application and textile production. High zinc concentration may be linked to former industrial waste tips in operation generated during the early twentieth century (Douglas et al., 2002). Similar observations have been reported in the vicinity of industrial areas around the world. In addition, Fishel (2014) reported that copper accumulation in soil is mainly due to anthropogenic emissions such as mining or industrial activities, agricultural use of products containing copper.

The decrease in heavy metal concentrations in the vegetated area may be due to the impact of vegetation. In metal contaminated soils, heavy metals can be potentially absorbed by the plants (El-Sikaily et al., 2004; Luo et al., 2012). Plants can remove, transfer, or stabilize heavy-metal soil contaminants to render them harmless (Baker et al, 1994). Plants have the potential to influence changes in heavy metal behaviour by transforming the fraction of metals to ensure that metal ions become available for uptake; a condition achieved through root exudations or by influencing the pH of the rhizosphere (Hinsinger et al., 2003). This, consequently, may affect desorption, solubility and mobility of metals in the soil. Due to acidic condition of the vegetated area, it is possible that the decrease in heavy metal concentration may be because of plant uptake due to changes in soil pH and complexation with organic acids in the rhizosphere. This may be the case in the present study as the soil pH of the vegetated area tends to be more acidic compared to the bare area (Figure 6.7). Also, the increase in the organic matter content derived from plant litters in the vegetated area may have contributed to increase adsorption and complexation of heavy metals in the vegetated area. Soil organic matter is an important parameter that gives good information about the potential sink of heavy metals in soil. Thus, the availability of organic constituents reduce the potential mobility of heavy metal in soils (Bradl, 2004).

Compared to the reported heavy metal concentrations in other urban soils, the data show that the concentrations of most heavy metals obtained in the bare and vegetated areas of the Football Ground including the Wrigley Head in the present study were relatively higher than the mean concentrations reported from Mexico City, Bangkok, Madrid and Beijing respectively (Table 8.1). Table 8.1 shows a comparison between the results of the present study with the reported concentrations of some heavy metals in some world urban soils. This comparison suggests that the investigated soils are heavily contaminated compared to the reported concentrations of some heavy metals in some urban soils around the world as presented in Table 8.1.

Table 8.1. Reported concentrations of some heavy metals (mg/kg) in some world urban soils.

Element	This study			Mexico[a]	Bangkok[b]	Madrid[c]	Beijing[d]
	Football Ground		Wrigley Head				
	bare	vegetated					
Arsenic	90	96	215	–	–	–	11.97
Cadmium	5	4	–	–	–	–	0.49
Chromium	264	161	142	117	26.4	74.7	63.57
Copper	6218	3131	78	100.8	41.7	71.7	35.49
Lead	2582	1505	362	140.5	47.8	161	36.43
Nickel	1972	587	17	39.8	24.8	14.1	27.12
Zinc	3487	1472	119	306.7	118	210	145.68

[a] Morton-Bermea et al. (2009) [b]; Wilcke et al. (1998); [c] De Miguel et al. (1998); [d] Liu et al. (2020); Dash (–) : No reported data.

The concentrations of all the studied heavy metals obtained across the investigated soils in Wrigley Head and the Football Ground area were also compared to the European Union (EU) threshold and guideline values. Table 3.1 shows the EU threshold and guideline values for heavy metals in soil. European countries have various ways of determining the potential risk levels of heavy metals in soil in relation to human health and the environment. In this regard, Finnish legislation is most recently used because it is internationally recognised as it provides an appropriate representation of mean values used by different national systems within Europe (Finland Ministry of the Environment, 2007; van der Voet et al., 2013), and are commonly referred as the ‘EU tolerable limits. The EU tolerable limit values are guideline values, that if these values are exceeded, then the area under investigation poses health/ ecological risks. The Finnish document sets out concentration levels for each heavy metal to identify the needs for soil contamination and remediation. It sets out the lower and higher guideline values that if exceeded, there may be a need for different remedial actions. Higher concentration levels are primarily determined by major land uses for examples, lands used for industrial or transport purposes and for other land uses. The threshold value applies for all land uses and suggests the area under investigation may require a further assessment. Higher guideline values are mostly used for industrial and transport sites and lower guideline values are used for all other land uses (Finland Ministry of the Environment, 2007).

The concentrations of heavy metals obtained from the investigated soils around Wrigley Head and the Football Ground exceeded the EU threshold and guideline values in most sampling locations (Figures 6.1 – 6.6 and 6.10 – 6.16). There was a remarkable difference in the concentrations of heavy metals obtained from the soils around Wrigley Head and the Football Ground. Nearly all the studied heavy metals exceeded the EU higher, lower and threshold values in the Football Ground area (Figures 6.10 – 6.16). This indicates the high level of contamination in the Football Ground area compared to areas around Wrigley Head. The high level of contamination in Football Ground may be due to high inputs of anthropogenic heavy metals related to historical industrial activities compared to Wrigley Head. In the light of this, the Football Ground area may require soil remediation in order to remove the unacceptable risks to human health and ecological components in the study area; however, this will be determined by present and future land use of this area. In the areas around Wrigley Head, the findings show that arsenic is potentially a major health concerns due to its concentrations being above the UK screening levels and EU threshold and guideline value in most sampling locations (Figures 6.1 – 6.6). The elevated arsenic concentration in this area may be attributed to the variable heterogeneous nature of historical waste materials and made ground associated with the former landfill sites (Miller, 2011). The concentrations of heavy metals exceeding the UK screening levels and EU tolerable limits may pose a potential risk to human health and environment.

High spatial variability in heavy metal concentrations was observed in the Football Ground compared to the areas around Wrigley Head (Figures 6.1 – 6.6 and 6.10 – 6.16). The data obtained show that there is a difference in the level of contamination between areas around Football Ground and soils around Wrigley Head (Figures 6.1 – 6.6 and 6.10 – 6.16). The findings show that the concentrations of heavy metals across the sites are highly spatial variable. The data show that the level of contamination in the Football Ground was potentially higher compared to the locations around Wrigley Head (Figures 6.1 – 6.6 and 6.10 – 6.16). Therefore, the whole area around Football Ground can be considered as a hotspot even though the level of contamination appears to be lower in the vegetated area of Football Ground (Figures 6.10 – 6.16). The spatial variability of heavy metals in the present study may be linked to different historical contaminations that had taken place in the study area. The investigated sites have a history of various industry activities in the area, which may have contributed to any contamination across the sites (Miller 2011). Similarly, Liu et al. (2020) reported that the spatial heterogeneity of heavy metals (chromium, copper, lead, nickel, zinc, mercury, arsenic and cadmium) may be linked to factors such as parent materials, soil formation, traffic and industrial activities. The spatial variablility of heavy metals across the sites has implication for understanding heavy metal contamination profile at the site and for the purpose of environmental risk assessment and remediation. This is essentially important in terms of establishing a basis for assessment of the potential risk of heavy metal contamination and human health as well as the decision making regarding appropriate remediation strategy.

The implications of the current findings are that the levels of heavy metal contamination in the study area may cause potential health risk if the site is continued to be used in its present condition considering the elevated concentrations of heavy metals in the study area above the UK screening levels and EU tolerable limits (Tables 6.2 and 6.3, Figures 6.1 – 6.6 and 6.10 – 6.16). The concentrations of heavy metals obtained across the sites were above the background value, UK and EU and acceptable limits (Tables 6.2 and 6.3, Figures 6.1 – 6.6 and 6.10 – 6.16). Heavy metal concentrations above these limits could pose a potential health risk and ecological disruption in the study area. The environmental implications of heavy metals in the study area may include inhalation of toxic dust, ingestion of toxic soils by site users, direct contact with the contaminated soil, inhibition of plant growth (barren land) due to high level of contamination and leaching of heavy metals to the surrounding areas. The proposed future use of the site will involve land disturbances, and in order to remove the potential health risk that may arise from land disturbances considering the elevated levels of heavy metals at the site above the stipulated threshold levels. Human health effects may occur through ingestion, inhalation or direct contact especially for site workers,visitors and the local residents that are using the site. The potential health risks to site users who are using the site in its present condition may occur through inhalation of toxic contaminated soil dusts in the event of windy conditions, ingestion of contaminated soils or direct contact with the contaminated soils. Human exposure to heavy metals occurs mainly through ingestion, inhalation, and dermal contact (Abrahams, 2002; Siciliano et al., 2009). In addition, the absence of a vegetative cover in the bare area could facilitate lateral dispersion of metal contaminated soil dusts which may impact on the health of the site users through exposure pathways. This may be the case since the site is currently used as informal green asset for the local residents and the wide community. Studies have shown that heavy metals in urban soils may potentially accumulate in the human body through these exposure routes (Davydova, 2005; Duruibe et al., 2007; Ljung et al., 2007). Heavy metals, due to their toxic, non-degradable nature and their persistence in the environment may cause potential risks to human health and environment (Ljung et al., 2007). The potential health risk of heavy metals from the investigated soils may be higher in the Football Ground particularly the bare area due to high level of contamination and absence of vegetation compared to locations within the Wrigley Head. However, the health effects will depend on the metal type, exposure route, frequency and exposure duration. In addition, the human health effects on the exposure to studied heavy metals in the study area are various and may differ between adult and children due to differences in their immune systems. A similar observation was reported by Brtnický et al. (2019) on the health effects of cadmium, copper, lead and zinc from a contaminated urban soil.

Although, it is also important to recognise that a high concentration of heavy metals in the environment does not necessarily mean that it is always sufficient to cause adverse health effects to living receptors (Peijnenburg et al., 2002; Lanno et al., 2004). The transfer of heavy metals from abiotic environments to living receptors depends on the biological characteristics of the targeted living receptors and heavy metal bioavailability which is greatly controlled by physico-chemical properties of both the contaminant and the environmental medium (van Gestel, 2008). Where a site has been previously contaminated, such as the investigated site, but it is no longer receiving inputs of heavy metals from anthropogenic activities, heavy metal bioavailability at such site may be expected to decrease due to various physico-chemical processes that immobilise metals in abiotic compartments such as soils (Lock & Janssen, 2003). Therefore, site remediation may be considered as an option based on the current and future land use at the site.

Furthermore, the level of contamination and possibly other toxins may hamper efforts to revegetate the bare area. The levels of contamination at the bare area may imply that establishing vegetation is not practicable on the site without some form of remediation. This may be because of direct toxicity to the vegetation through root uptake of contaminants. The phytotoxic effects of heavy metal contamination such as inhibition of various physiological functions of plants, for example, photosynthesis, plant-water relationships, uptake of nutrients, nitrogen metabolism are well documented in many studies (Alam, Hayat, et al., 2007; Gopal & Rizvi, 2008; Chen et al., 2009; Gajewska et al., 2009). Such phytotoxic effects may result in altered metabolism, physiological and biochemical malfunctioning which cumulatively results in retarded plants growth and poor biomass development (Nagajyoti et al., 2010). This phytotoxic effect was also confirmed when some soil samples were taken from the bare area and sow some vegetables plants, but the vegetable plants died off probably due to high level of heavy metal contamination (results not reported) (see appendix 1e). This phytotoxic effect could potentially prevent the effort to revegetate and restore the barren area in the phytoremediation process. However, when the contaminated soil was blended with garden soil with addition of some soil amendments in the greenhouse, the plants were able to adapt and grow successful on the soil in the greenshouse (appendix 1e). Apparently, plants grow better, faster, vigorous and adapt better in blended soils compared to the non-blended soils (results not reported). The trial studies indicate that it is possible that native plant species could adapt and grow well in the bare soil when the soil is blended and/or addition of some soil amendments in the revegetation process.

8.5 Case Study – Remediation Considerations

Soil contamination presents a major barrier to potential agriculture developments on urban areas because most urban soils are below the stipulated standards for agricultural soil (Platt, 2012). Over the last few years, there has been increase interest in urban agriculture development in several developed countries in an effort to boost community food security and serve as a design inspiration (Specht et al., 2013). However, one of the major challenges facing urban agriculture is that many urban soils are contaminated by heavy metal(loid)s to some level, and thus there may be high level of heavy metal(loid)s contamination associated with foods produced from these urban farms which can cause a potential health risk to the consumers. The availability of arable land in urban areas is limited, so potential urban farmers are often left with sites adjacent to, or previously used for industrial and commercial activities (Hurdle, 2008). Consequently, food crops cannot be grown on the contaminated soil because of the potential human health risks. The remediation options discussed in chapter 7 particularly soil capping when implemented at the site can create a land surface that can support vegetation and/or be used for other purposes such as growing food crops in raised beds. This area may be explored for community urban agriculture through installation of raised beds. Today, urban agriculture is recognised as an important emerging field due to its positive implications for urban food security, community development, and urban environmental conditions. There has been increased interest in backyard and community gardens over the past few years as people increasingly think about what food to eat, where it will come from, and how it will be transported to their local markets (Martinez et al., 2010).

Many people now live in urban areas. Approximately 50% of the world population now live in urban cities, and this figure is expected to increase to about 70% by 2050 (United Nations, 2008; United Nation Development Programme, 2013). In the United States, almost 250 million people now live in urban area (US Census Bureau, 2013). Similarly, in the UK, approximately 55.91 million are believed to live in urban areas (Clark, 2020). Therefore, these large percentage of people living in the urban areas today particularly in the UK stand to benefit from an urban agricultural development. There are numerous benefits individuals and society at large stand to enjoy from urban agriculture such as availability of inexpensive fresh foods and increased economic activity, and the governments and policymakers should consider how to address this menace of soil contamination which is a barrier to the potential use of contaminated urban soils for agricultural purposes (Platt, 2012). There are many other benefits associated with urban agriculture, and these include increased biodiversity, enhanced nutrient cycling, storm water management, and improvement in air quality and local climate regulation (Camps-Calvet et al., 2016). Contaminated lands located in urban areas such as the present investigated site have great potentials for urban agriculture if appropriate remediation strategies can be successfully implemented to ensure the level of heavy metals are below the permissible limits and deemed safe for humans.

8.5.1 Heavy Metal Concentrations in the Roots and Shoots of the investigated Plants

The concentrations of heavy metals in the roots and shoots of the investigated plant species are presented in Tables 7.1 and 7.2. For the investigated plant species, the concentrations of heavy metals in the root and shoot portions varied markedly from plant species to plant species (Tables 7.1 and 7.2). The median concentration of root-borne heavy metals among all the investigated plant species are in the following decreasing order: zinc > copper > lead > nickel > arsenic > chromium while the median shoot-borne concentrations are in the order of zinc > copper > nickel > lead > arsenic > chromium. The median heavy metal concentrations order suggests that zinc was absorbed in the highest concentration by the investigated plants while chromium was taken up in the lowest concentration. Generally, high metal concentrations were observed in the roots compared to the shoots (Tables 7.1 and 7.2). This suggests there is a higher bioaccumulation of heavy metals from soil to plant roots compared to the rate of metal translocation to the aerial shoots across the site.

Similarly, the variation in heavy metal uptake by the investigated plant species might be due to nature of plant species, soil characteristics, plant uptake capacity and plant physiology (Tables 7.1 and 7.2). A similar finding was reported by Rehman (2018). Studies have shown that plants have different metal uptake and detoxification capacities for heavy metals (Alloway et al., 1990). The present finding is consistent with Shukla et al., (2011), who reported that plants growing in metal contaminated media could uptake metal ions at varying capacities and that the uptake of heavy metals by plants is heavily controlled by their bioavailability which in turn is determined by both soil and plant factors. In addition, other factors such as soil metal concentrations, metal bioavailability, and presence of essential nutrients, plant root size and temperature have also been linked to influence heavy metal uptake and accumulation in plants (Yan et al., 2017).

Copper, nickel and zinc were taken up relatively in higher concentrations by plants compared to arsenic, chromium and lead in the present study (Tables 7.1 and 7.2). *Agrostis tenuis* showed a higher potential to accumulate most of the heavy metals in the root portion compared to other plant species (Table 7.1). Plant roots play a crucial role in uptake, accumulation, and translocation of heavy metals in plants. The high uptake of heavy metals by *Agrostis tenuis* specie have been noted by other authors: Dahmani-Muller et al. (2000) reported lead, copper and zinc concentrations of 471 mg/kg, 65 mg/kg and 2320 mg/kg respectively in the root portion of *Agrostis tenuis* species from the contaminated soils. This implies that *Agrostis tenuis* specie may be a promising excluder plant due to high metal concentrations found at the root portion but maintains shoot – root quotients less than 1. On the other hand, some plant species such as *Artemisia vulgaris*, *Chamerion angustifolium* and *Plantago lanceolata* showed a very low potential to accumulate arsenic in their root portions with arsenic concentrations (< 2 mg/kg) (Table 7.1). This indicates that these plant species have low bioaccumulation potentials for heavy metals.

Moreover, some plant species such as *Agrostis tenuis, Agrostis stolonifera, Argrostis capillaries, Glyceria maxima, Phleum pratense, Lolium pratense, Lolium multiflorum* relatively recorded high concentrations of heavy metals in their tissues compared to other investigated plant species (Table 7.2). The relatively high concentrations of heavy metals in these plant species suggests that they have higher uptake capacity compared to *Chamerion angustifolium, Heracleum sphondylium, Equisetum arvense* and *Galium aparine.* It has been previously reported that *Lolium multiflorum* could tolerate high concentrations of heavy metals in mine soil and has the capacity to phytoextract a range of heavy metals from soil (Liu et al., 2007). This observation is consistent with the findings by Weis and Weis (2004) and Sheoran and Sheoran (2006) who reported that plants may exhibit different capacities in terms of heavy metals accumulation and transfer which is dependent on plant species in question and the prevailing environmental conditions.

The generally low concentrations of heavy metals in the shoots in the present study suggests that there is a low transfer of heavy metals from the roots to shoots by the investigated plants across the sites. This probably could be attributed to the nature of plant species, different uptake potentials of the investigated plant species and bioavailable heavy metals in the investigated soils. On the other hand, it is possible that the low shoot translocation might be due to the sequestration of metals inside the root vacuoles of the plant species where metals are fixed as nontoxic elements. A similar finding was also observed by Shanker, Cervantes et al. (2005). Low chromium and lead concentrations observed in the shoots of the investigated plants may be attributed to the low solubility of these heavy metals in the investigated soils. It has been reported that some heavy metals particularly chromium and lead is associated with low solubility in soils and often demonstrates a particular barrier; even when they accumulate in the root, they are rarely translocated to above-ground biomass (Tiwari et al., 2011). The concentrations of lead in root and shoot portions of the investigated plant species in the present study were lower than the those reported by Dahmani-Muller et al. (2000) and Nguyen et al. (2009) from herbaceous plants growing in contaminated soils. In addition, copper, nickel, and zinc appeared to be mostly translocated to the aerial shoots compared to arsenic, chromium, and lead (Table 7.2). The higher copper and zinc in the shoot portions suggest that these metals are efficiently translocated from the roots to the aerial shoots compared to other heavy metals. The reason for this might be that copper and zinc are essential elements to plants and can be taken up by plants in higher concentrations than the non-essential elements such as arsenic, cadmium and lead. Similar findings were reported by Ai et al. (2018). Stefanowicz et al. (2016) reported that the zinc concentrations in the root portions of *Mycelis muralis* and *Mercurialis perennis* species were 752 mg/kg and 520 mg/kg respectively. The relatively higher concentrations of copper and zinc in the shoot portions suggest that these metals are efficiently taken up from the soil to the roots compared to other heavy metals.

By comparison with other available reports, it is evident that the levels of shoot-borne heavy metals in the investigated plant species tended to be higher than those reported by Misra and Mani (1991) and McLean et al. (1987) except for arsenic and chromium (Table 8.2).

Table 8.2. A comparison of shoot-borne heavy metals (mg/kg) between this study and other reports.

Element	**Misra and Mani (1991)**	**MacLean et al. (1987)**	**This Study**
Arsenic	0.02–7	-	0–6.18
Chromium	0.2–1	1.22	0.04–0.78
Copper	4.15	12.3	3.46–58.7
Nickel	1	4.08	0.75–52.8
Lead	1–13	1.54	0.16–27.8
Zinc	8–100	28.4	14.5–189

Dash (–) : No reported data

Furthermore, the BF and TF of the investigated plant species among the investigated plant species are highly variable and suggest low phytoavailability (Tables 7.3 and 7.4). The plants’ ability to uptake heavy metals from soils and transfer heavy metals from roots to aboveground parts can be quantified using BF and TF (Ghosh & Singh, 2005a; Gupta et al., 2008). Thus, BF and TF are important parameters used to assess plants’ suitability for phytoremediation. These parameters are very important indexes used in quantifying the distribution of heavy metal among different parts of the plant and help us to make decisions as to whether a given plant species can be suitably used as an accumulator in phytoremediation or phytostabilization processes in metal contaminated soils. Fitz and Wenzel (2002) reported that plants having bioaccumulation factor less than one (BF < 1) cannot be successfully used for the phytoextraction of trace element contaminated soils. Similarly, Zhao et al. (2007) reported that TF > 1 shows a very efficient capacity of a plant to translocate nutrients from below ground roots to above ground shoots, most likely due to efficient metal transport systems. Chanu and Gupta (2016) suggested that TF > 1 is a decisive factor for classifying plant species’ suitability for phytoremediation. TF > 1 is an indication that plants not only tolerate the contaminants but used it beneficially.

The variations in BF and TF among different plant species growing in contaminated soils in the present study are thought to be due to the differences in nature of plant species, plant uptake capacity and soil metal concentration. Rehman (2018) also reported similar findings. Uptake of heavy metals in plant species varies from metal to metal and species to species (Baker, 1981). Some plant species showed unusual capacity to take certain trace elements from the soils. Most investigated plant species had BF greater than 1 (BF < 1) for zinc compared to other heavy metals in this study (Table 7.3). In addition, zinc had a median BF value nearly 1 (0.86) suggesting higher uptake of zinc by the investigated plant roots compared to other heavy metals. Specifically, plant species: *Argrostis capillaries*, *Impatiens glandulifera, Plantago lanceolata, Juncus effuses, Holcus lanatus, Urtica dioica, Glyceria maxima, Phleum pratense, Lolium pratense, Cynosurus cristatus and Filipendula ulmaria* respectively had BF greater than 1 for zinc with *Lolium multiflorum* having a BF as high as 7.69. This suggests that these plant species can efficiently bioaccumulate zinc in contaminated soils. In other words, this means that these plant species are considered to have a great potential for phytostabilisation of zinc in contaminated sites. It has been previously reported that *Lolium multiflorum* could tolerate high concentrations of heavy metals in mine soil and can phytoextract a range of heavy metals from soil (Mugica-Alvarez et al., 2015).

There were three plant species that had BF > 1 for copper: *Argrostis capillaries, Glyceria maxima, Filipendula ulmaria* (Table 7.3). There were two plant species with BF >1 for nickel: *Heracleum sphondylium and Juncus effuses* had the BF > 1. In addition, *Dactylis glomerate* and *Bistorta officinalis* had the capacity to phytoextract a wide range of trace elements. This suggests that these plant species efficiently bioaccumulated selected heavy metals from the soil to the roots compared to other investigated plant species (Table 7.3). For arsenic, chromium, and lead, their BFs for most of the plant species were less than 0.1, indicating that these heavy metals have relatively low phyto-availability across the investigated soils (Table 7.3). A similar observation has been reported by Tiwari et al. (2011) The only exception is *Bistorta officinalis* had much higher BF for arsenic as compared to other plant species in the present study (Table 7.3). The BFs of heavy metals reported for the investigated plant species in the present study are similar to those previously reported for herbaceous plant species (Hao & Jiang, 2015; Stefanowicz et al., 2016).

Most of the TFs of the investigated plants were less than 1 indicating low translocation of heavy metals from the roots to the aerial shoots across the sites (Table 7.4). Although, zinc and nickel had TFs greater than 1 for one or two plant species (Table 7.4). Manganese, zinc and nickel are readily transported via the xylem to the shoot (Page & Feller, 2015). The high rate of root-shoot translocation for manganese, zinc, nickel and copper was also noted by other authors (Ximénez-Embún et al., 2002; Chandra et al., 2009; Page & Feller, 2015). Nevertheless, the TFs of the investigated plant species suggest that there is a general poor transfer of heavy metals from the roots to the aerial shoots across the sites (Table 7.4). The TFs reported in the present study are consistent with those previously reported by Hao and Jiang (2015) and Stefanowicz et al. (2016) for herbaceous plant species growing in contaminated soil. A few plant species had TFs near to or greater than 1 at least for heavy metals and therefore can be regarded as hyperaccumulating plants (Tangahu et al., 2011). Thus, the potential hyperaccumulators identified in the present study include *Artemisia vulgaris* for arsenic and zinc, *Phalaris arundinacea* for nickel, *Heracleum sphondylium* for chromium and zinc, and *Bistorta officinalis* for zinc. These plant species have implications for phytoremediation of historically contaminated sites. In the last few years, phytoremediation has been generally considered as a cost-effective approach to remediate metal or metalloid-contaminated soil (Cooper et al., 1999).

Compared to the normal levels of heavy metals in plants, the findings of this study show that the concentrations of arsenic and lead in the shoots of the investigated plant species generally exceed normal threshold levels in plants. While the concentrations of chromium, copper, nickel and zinc in the shoots of the investigated plants are generally within the normal level reported ranges for plants. Normal levels of heavy metals in plants are considered within the following ranges: 0.1 – 0.5 mg/kg for arsenic; 0.1 – 0.5 mg/kg for chromium; 5 – 30 mg/kg for copper; 30 – 300 mg/kg for manganese; 0.1 – 5 mg/kg for nickel, 0.1 – 0.5 mg/kg for lead and 27 – 150 mg/kg for zinc (Kabata-Pendias, 1984; Kabata-Pendias, 2010). The concentrations of heavy metals in plants above the normal threshold levels could induce toxicity in plants and could potentially affect the ecological system and health of animals feeding on them (Annenkov, 1982).

In summary, the findings of the present study imply that heavy metals are being taken up by the investigated plant species, and the uptake of heavy metals was highly variable across the site. Even though the investigated herbaceous plants do not have direct impacts on human health due to their non-human-consumable nature, however, the marked accumulation of some heavy metals by the investigated plant species in the study area suggests that there may be environmental implications associated with the metal uptake. The generally high concentration of heavy metals particularly arsenic and lead above the normal threshold limits in the investigated plant species may affect the ecosystem functioning in the affected areas. Therefore, it is recommended that a further study is conducted to fully understand the environmental implications of heavy metal uptake by native plant species across the site.

Uptake and translocation of heavy metal(loid)s from contaminated soil by plants is an essential part of cleaning up of contaminated land. Based on the BF and TF recorded in the present study, the findings suggest that native herbaceous plants may hold a promising potential for phytoremediation of heavy metal contaminated soil. The understanding of the potential of native herbaceous plants to absorb and transfer heavy metals from soil has important implication for screening the potential of native plants for phytoremediation of historically contaminated sites. Knowledge of plant tissue-borne heavy metal(loid)s is also needed for evaluating the potential of the herbaceous plants to be used for phytoremediation to clean up the contaminated soil. Moreover, their translocation patterns from roots to shoots in growing native plant species across the site has implication for biological monitoring of heavy metal contamination and as well as in the evaluation and selection of tolerant native plant species. This will potentially guide in the identification and selection of several native plant species that have the potential for remediation of heavy metal contaminated sites. Therefore, the phytoremediation potentials of the investigated native herbaceous plant species in the present study could provide useful information about their selective exploitation for phytoremediation of the Moston Brook historically contaminated site.

Despite the potential for bioremediation, capping of the bare area is also identified as another feasible option to mitigate heavy metal contamination so as to create opportunities for growing food crops through installation of raised beds and, thus, the barrier associated with the use of the site for urban agriculture may be overcome. Capping can mitigate the environmental and human health issues associated with the high levels of heavy metals identified in the area. It can prevent the generation of dust from the bare area which could be inhaled by people and animals and prevents uptake of heavy metals by food plants.

However, if capping is not technically or economically possible the route forward is via some activity which does not involve access by people – such as establishing a photovoltaic array or a solar farm at the site. However, significant contaminant linkages may be created during the installation of such infrastructure which may impact on the health of the workers at the site through inhalation of contaminated soil, ingestion, or physical contact with the contaminated soil materials during the establishment of solar farms. Therefore, it is important that proper assessment of potential health risks to the site workers is carried out and consequently implement the most appropriate risk reduction strategies prior to any development works at the site.

These recommendations when implemented will potentially contribute to the improvement of the future use of the Wrigley Head site. The site is recognised as an important green asset for the local community. Establishment of vegetation at the site will enhance nature/biodiversity and thus improves the physical environments, health and wellbeing. The benefit will be the creation of a self-sustaining ecosystem that can support productive land use activities of the site, and improves the aesthetic appearance of the area, and may offer some economic benefits in the long-term. In addition, there is a need to prohibit any activities which could cause soil and vegetation disturbances at the Wrigley Head area and to ensure regular update of the site risk assessment in accordance with any proposed developments.

8.6 Limitations and Recommendations for Future Study

The findings reported suggest that the contamination level at the site is high. In order to determine the actual potential risk posed by the site to the targeted receptors, it would have been beneficial to look at heavy metal bioavailability at the site, but this was outside the scope of this study. Therefore, it is recommended that future studies should investigate heavy metal bioavailability at the site to determine the actual potential adverse risks of heavy metals on the environment and human health at the site since heavy metal potential toxicity is greatly controlled by their bioavailability and mobility. There is increase recognition of the risk-based approach which relies on the influence of contaminants bioavailability and mobility when it comes to risk assessment of contaminated sites (Swartjes,1999; Fernández et al., 2005). This risk-based approach considers the influence of contaminants bioavailability rather than just relying on the *total concentration* in soil.

The data presented in chapter 7 were based on the evaluation of plant species across the site for their potential for phytoremediation. It is recommended that a future study should be conducted to examine multiple plants of similar species across the site to validate the results obtained from the present study. In addition, more works will be needed to explicitly understand the growth rate and biomass of these plant species as these parameters are important for them to be successfully used for revegetation.

8.7 Research Contributions and Conclusion

The findings reported in chapter 4 indicate that there is a strong relationship between the concentrations of heavy metals yielded by XRF and those of aqua regia/ICP-OES across the site. This means that XRF results obtained in the present study are similar to those of aqua regia/ICP-OES and suggests that both techniques can technically predict the concentrations of heavy metals from the investigated soils. While both analytical techniques proved to be suitable for predicting heavy metal concentrations in the investigated soils as demonstrated in the present study, XRF technique represents an easier and more cost-effective alternative to the aqua regia/ICP-OES chemical method for the analysis of heavy metals in the investigated site. One of the setbacks against the efforts being made to ensure continuous monitoring of the potential toxicity of heavy metals in contaminated areas with regards to the environment and human health is the high operational cost involved when analysing soil samples with conventional analytical technique such as aqua regia/ICP-OES for toxicity especially in large areas, such as agricultural areas, contaminated areas, alluvial areas with frequent flood threats (Shokr et al., 2016; Adimalla, 2020; Ren et al., 2020; Konstantinova et al., 2021). Determining heavy metals in soil using the rapid and cost-effective analytical techniques such as XRF without the need for soil digestion could be a major step forward especially in the event of rapid mapping and monitoring of heavy metal contaminants in the study site with regards to making decisions to minimise their potential for toxicity on the environment and human health. XRF technique has the potential to analyse a large number of soil samples in a relatively shorter times and in cost effective manner; thereby facilitating timely prediction of the potential toxicity of heavy metals so that appropriate management strategies can be developed to minimise their adverse effects. Therefore, seeking and validating rapid and cost-effective analytical techniques such as XRF which provides comparable accuracy to the standard laboratory methods for analysis of heavy metals in the investigated soils could be a promising alternative. The contribution of this findings has implication for selecting appropriate analytical techniques for potential heavy metal determination from the investigated site. The accurate determination of heavy metals from soils is important for evaluating their potential for toxicity, and to develop appropriate strategies to contain their adverse effects on human health and environment.

The case study results have been presented in four chapters. The desk and site visit results reported in chapter 5 indicate that Wrigley Head was heavily contaminated from multiple historical industrial and commercial sources along with the uncontrollable disposal of waste into landfill sites operating within and adjacent to the site. The contamination problem at this site was compounded due to there being no validated records on the nature and status of contaminants emitted at the site, and thus, this site is recognised to form a potential source of unknown contaminants. This is a great setback and further complicates the efforts to overcome the barrier associated with the site. The level of contamination at the site suggest that the contamination may be significant and there may be a potential risk of contamination sources that may affect human and wildlife health. Therefore, there is a need for further risk assessments to understand the likely impact of these contaminations on the preoposed use of the site. The current findings highlight the need to address the contamination issues at the site and ensure adequate environmental risk assessment at the site at a regular interval against any proposed developments.

The findings reported in chapter 6 indicate that there was a high variation of heavy metals across the sites and concentrations of heavy metals obtained across the sites were above the UK and EU background values and acceptable limits. The concentrations of most heavy metals were relatively higher in the Football Ground area compared to the soils elsewhere around Wrigley Head (Table 6.1). The high variability of heavy metals across the site reflects anthropogenically conmantinated nature of the site. The findings suggest that copper, zinc, lead and nickel pose more serious contamination problem particularly in the Football Ground compared to cadmium, chromium and arsenic. Importantly the independent two-sample Wilcoxon (P) indicates a significant difference between the vegetated and non-vegetated areas. The data obtained show that the bare area is potentially more contaminated compared to the vegetated area. This suggests that the lack of vegetation in the bare area could be due to the high level and phytotoxic nature of the heavy metal contamination. Given the rapid and extensive industrialisation observed historically in the study area, it is evident that historical anthropogenic contamination plays a major role in elevating heavy metal contamination in the study area. The current findings suggest that the level of heavy metal contamination in the study area may cause potential health and ecological disruptions if the site is continued to be used in its present condition considering the elevated concentrations of heavy metals in the study area above the UK screening values and EU tolerable limits.

Heavy metal contamination is a global issue of concern as shown by the plethora of contaminated sites around the world. Data on the level of potential toxic chemical elements in soil such as heavy metals is important to scientists, farmers, builders, miners, or environmental workers/managers. Potentially, Information on the level of heavy metal contamination across the investigated site is crucial to developing the effective policy to protect the site. Similarly, the current data obtained on heavy metal contamination profile across the site could offer important information needed to monitor and evaluate soil heavy metal contamination and ensure overall environmental quality of the site. Importantly, heavy metal data obtained by XRF can be used as a basis for the purpose of rapid mapping and delimiting contaminated areas around Wrigley Head and Football Ground, Moston Brook since this reflects the real total metal concentrations across the site. Such data could help to define and map out potentially areas of serious contamination across the site considering the high spatial variability of heavy metal contamination across the site. This is essentially important considering the present land use of the site so that appropriate strategies can be developed to minimise any potential adverse health effects on the site users.

Moreover, such data importantly could potentially provide relevant information that would assist the Local Authority, environmental scientists and/or site manager to make decisions regarding the environmental risk assessment and remediation of the study site. Similarly, the information regarding the sources, levels of contamination and hotspots of heavy metals across the site can be integrated in the site-specific environmental risk assessment model for assessment of the potential threat of heavy metals to the local environment and human health. Collectively, such data could potentially assist the local authority in adopting and developing effective and sound management strategies to protect the site from potential risks and contaminations.

Lastly, the findings reported in chapter 7 provide feasible remediation options for the investigated site. The thesis explores and appraises feasible and practictable remediation options and makes appropriate recommendations within the local context of the study site towards adressing the contamination problem at the site especially the bare area of Football Ground, Wrigley Head, Moston Brook urban green corridor. These suggested remediation options and recommendations offered by the present thesis, when implemented, could help to alleviate or overcome the barriers associated with the site, ensure its beneficial land uses and reduce the potential health risk associated with the site.

Similarly, the findings on the evaluation of heavy metal uptake by plants at the site indicate that heavy metals are being taken up by the native plant species across the site. This suggests that high concentrations of heavy metals in soil can lead to accumulation of heavy metal in plants through plant uptake, which has implication for the ecological system and human health. The present study has shown that the uptake of heavy metals by native herbaceous plants growing across the site is highly variable. This could be the case due to nature of the investigated plant species and variable levels of heavy metal contamination across the site. Although, the investigated plant species have no direct impacts on human health as they are not used as food, but the marked accumulation of heavy metal in the plant tissues suggests that there might be environmental implications of heavy metal uptake by plants across the site. Therefore, this aspect of the thesis brings an important opportunity for further research works to be conducted to fully understand the environmental implications of heavy metal uptake by plants across the site.

In addition, the study reported here also shows that native herbaceous plants may hold a promising potential for use in the remediation of historically contaminated sites. For example, the findings suggest that native plant species at the site such as *Artemisia vulgaris, Phalaris arundinacea, Heracleum sphondylium and Bistorta officinalis* are potential hyperaccumulators capable of accumulating one heavy metal or the other at the aerial parts. Similarly, *Agrostis tenuis* specie may be a promising excluder plant due to high metal concentrations absorbed at the root portion but maintains shoot – root quotients less than 1. This plant species may have a promising potential for phytostabilisation of heavy metal in contaminated sites. However, more research works are needed to examine multiple plants of similar species across the site to validate the results obtained from the present study.

The findings obtained from this chapter makes important contributions to knowledge in terms of identifying, screening, and exploiting the potentials of native plant species across the study site for remediation of the site. In other words, this aspect of the thesis provides an opportunity for more in-depth research to be conducted to assess the suitability and potential of native plant species for remediation of the investigated site. In addition, the present study also offers the opportunity to evaluate the environmental implications of heavy metal uptake by native plant species across the site.

List of Published Articles

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APPENDICES

Appendix 1a –Concentrations of heavy metal (loid) (mg/kg) obtained from the bare and vegetated areas of Football Ground area by aqua regia/ICP-OES method.

Sample ID	Arsenic	Cadmium	Chromium	Copper	Nickel	Lead	Zinc
1	26	0.3	39	600	220	300	220
2	21	2.9	29	3200	220	730	1600
3	56	2	70	2100	1200	1000	1000
4	32	3.1	55	3500	910	1200	910
5	34	1.5	52	2300	470	880	630
6	34	1.2	46	1100	1500	370	410
7	40	1.7	57	1800	2800	800	770
8	82	18	240	22000	1900	9700	11000
9	56	4.7	140	8100	1300	1400	1900
10	37	3.5	66	4800	1500	1300	1100
11	37	6.3	110	7300	1500	1700	3800
12	40	7.2	110	15000	4200	5700	8600
13	78	10	82	6700	1900	1300	3900
14	60	17	170	15000	1900	5100	16000
15	89	10	220	30000	1000	11000	10000
16	36	3.9	53	2000	3900	400	1200
17	30	6.3	65	6300	3100	27000	4300
18	55	9.2	420	14000	32000	8100	8400
19	68	8.1	170	34000	2200	5800	9700
20	52	2.6	63	3500	1200	1700	850
21	32	27	76	4100	1400	1300	2200
22	24	5.6	36	1400	4100	890	1400
23	40	7.2	62	9600	2000	1000	2300
24	100	6.4	390	17000	1300	1100	3600
25	65	12	130	11000	830	5800	10000
26	45	3.4	56	3200	6000	890	1300
27	80	1.5	67	1800	420	880	620
28	20	0.5	33	610	240	180	230
29	26	2.2	50	4300	3300	1200	1500
30	45	6.4	90	7000	3000	1600	3500
31	41	3.9	79	4800	4600	880	1900
32	38	3	82	4500	4100	900	1500
33	69	1.6	64	1600	860	810	460
34	11	0.2	26	79	45	42	91
35	58	1.1	45	1800	720	700	660
36	70	18	170	24000	2300	7500	16000
37	36	3	50	5900	1400	880	3700
38	48	3.3	67	4000	4500	1000	980
39	70	2.8	39	3400	5100	440	1800
40	58	1.4	37	1300	270	360	400
41	30	1.1	45	2800	390	530	860
42	33	1.1	44	1900	500	590	610
43	45	1.7	56	3100	810	950	770
44	67	1	64	1900	880	960	590
45	63	0.2	51	1500	260	620	300
46	33	1.1	52	3700	340	790	570
47	37	2	46	3300	480	640	860
48	63	0.2	70	1200	280	740	470
49	44	4.1	82	7100	1300	2000	2000
50	280	0.2	45	340	100	290	260
51	34	0.2	30	200	60	230	160
52	38	0.2	31	450	150	170	190
53	83	2	41	310	130	180	420
54	26	0.3	31	260	87	110	130
55	44	0.2	34	270	55	170	110

56	14	0.2	37	62	39	35	79
57	36	0.5	33	260	49	210	170
58	52	1.3	52	1500	330	660	540
59	71	1	78	2500	230	1500	630
60	32	2.3	48	2200	810	890	1000
61	52	5.8	89	17000	2200	4700	4600
62	66	3.3	52	5000	820	920	2100
63	39	4.9	64	6600	2000	5700	3400
64	58	5.1	64	8900	1300	1800	4100
65	51	4.1	72	8900	1300	1500	3200
66	49	3.5	81	7000	980	2300	1900

Appendix 1b – Concentrations (mg/kg) of heavy metal (loid) obtained from the bare and vegetated areas of Football Ground by XRF

Sample ID	Arsenic	Cadmium	Chromium	Copper	Nickel	Lead	Zinc
1	33	2	125	593	273	390	248
2	30	4	79	2414	270	972	2128
3	96	3	178	2108	1049	1341	1301
4	57	4	150	2909	733	1405	1040
5	50	4	119	2048	494	1119	701
6	51	3	150	1100	1233	458	493
7	47	3	156	1735	1957	909	895
8	311	15	581	24224	2386	10626	16093
9	99	7	248	7459	1271	2001	2403
10	71	5	173	4265	1317	1790	1261
11	80	6	279	6757	1382	2294	4033
12	102	9	402	14947	3783	5593	10028
13	162	5	280	6189	1755	1805	3924
14	162	11	507	14548	2074	5202	16726
15	300	14	424	30511	1287	11018	12560
16	50	3	111	2025	2849	486	1451
17	< LOD	10	352	7332	3176	21990	5520
18	97	9	1615	13848	25090	6834	8824
19	213	11	607	34374	2568	6127	13284
20	88	5	176	3121	1079	2133	1047
21	47	10	176	3577	1229	1611	2683
22	24	4	77	1367	2703	939	1521
23	66	6	169	8323	1568	1306	2809
24	175	8	1038	16383	1406	1793	3813
25	161	9	425	10983	872	5668	12174
26	73	5	185	2856	4200	1241	1433
27	110	3	205	1978	510	1220	754
28	32	2	109	576	252	251	230
29	57	4	165	3480	2377	1507	1973
30	75	6	216	5993	2372	2245	3331
31	72	4	184	4335	3359	1197	2294
32	60	3	238	3367	2703	1143	1564
33	100	3	199	1638	720	1052	525
34	16	1	107	80	50	53	85
35	69	3	120	1653	589	878	685
36	198	11	442	20538	2043	5610	15472
37	67	3	205	4997	1193	1176	3667
38	76	4	166	3358	2954	1413	1150
39	92	2	142	3044	4049	619	2177
40	73	2	141	1389	362	492	514
41	46	3	124	2409	461	688	896
42	39	3	120	1701	520	739	636
43	73	3	179	2683	684	1257	874
44	114	1	237	2116	765	1428	708
45	77	2	158	1420	310	819	335
46	55	3	147	2835	415	1116	629
47	50	3	129	2463	525	795	964
48	114	2	199	1205	377	1166	524
49	89	4	213	5439	1019	2602	2470
50	319	2	133	363	136	385	334
51	40	2	92	197	67	247	167
52	48	2	104	498	194	221	171
53	100	1	142	351	174	247	502
54	26	2	107	262	90	142	132
55	58	1	137	313	46	227	114
56	17	< LOD	112	66	52	48	73

57	50	< LOD	118	251	40	292	179
58	75	5	181	1574	369	877	632
59	133	5	313	2573	321	2316	818
60	69	2	201	2921	881	1613	1588
61	169	6	246	12040	1961	4473	4657
62	81	5	126	3990	648	1183	2238
63	143	9	146	6183	1830	5493	3384
64	110	7	146	7927	1137	2517	4112
65	93	5	217	7708	1141	2009	3190
66	102	7	207	6003	886	3296	2739

Appendix 1c – Concentrations (mg/kg) of heavy metal obtained across the investigated soils in Wrigley Head by XRF method

Location	Arsenic	Chromium	Copper	Nickel	Lead	Zinc
FG1	67	153	2769	812	1499	1277
	71	158	2768	791	1486	1249
Mean	69	155	2768	802	1492	1263
FG2	77	148	3378	915	1598	1032
	82	160	3319	926	1576	1021
Mean	80	154	3348	920	1587	1026
FG3	755	231	59	< LOD	644	87
	785	215	60	< LOD	653	92
Mean	770	223	59	< LOD	649	89
FG4	10	29	198	35	116	186
	14	65	196	75	112	185
Mean	12	47	197	55	114	186
FG5	37	132	1228	1046	900	1855
	40	109	1246	1104	881	1906
Mean	39	121	1237	1075	891	1881
FG6	39	104	402	144	346	213
	42	102	414	146	344	223
Mean	40	103	408	145	345	218
FG7	50	121	628	126	402	579
	52	145	624	132	402	581
Mean	51	133	626	129	402	580
FP1	500	165	77	59	362	143
	520	157	79	56	362	142
Mean	510	161	78	57	362	143
FP2	146	129	165	82	429	451
	151	158	176	60	439	455
Mean	148	144	170	71	434	453
FP3	476	135	116	8	922	242
	469	138	122	26	917	242
Mean	472	136	119	17	919	242
FP4	51	108	61	58	137	127
	57	108	66	49	137	128
Mean	54	108	63	53	137	128
FP5	49	94	62	55	134	119
	51	96	57	54	129	120
Mean	50	95	60	55	132	119
MD1	35	90	34	18	47	71
	33	85	29	4	46	72
Mean	34	87	32	11	46	72
MD2	1137	124	33	< LOD	614	29
	1128	127	43	< LOD	632	27
Mean	1132	126	38	< LOD	623	28
MD3	269	143	31	21	189	67
	270	140	39	9	193	76
Mean	269	142	35	6	191	71
MD4	765	204	75	< LOD	689	89
	756	203	83	< LOD	692	90
Mean	761	204	79	< LOD	690	89
MD5	213	124	57	31	250	120
	218	128	57	9	256	122
Mean	215	126	57	11	253	121
RS1	354	159	78	22	340	181

	346	171	77	26	333	168
Mean	350	165	78	24	337	174
RS2	448	172	51	29	334	94
	455	171	53	15	327	97
Mean	451	172	52	22	330	95
RS3	86	168	2384	431	1323	1461
	89	187	2376	420	1309	1440
Mean	88	177	2380	425	1316	1450
RS4	321	146	74	7	330	121
	327	159	77	11	328	116
Mean	324	152	75	9	329	118
RS5	860	216	93	< LOD	602	96
	854	189	85	< LOD	593	88
Mean	857	202	89	< LOD	597	92
RS6	692	219	87	< LOD	564	109
	683	216	89	< LOD	575	109
Mean	688	217	88	< LOD	569	109
WH1	1000	199	62	< LOD	1399	91
	986	200	61	< LOD	1360	87
Mean	993	200	61	< LOD	1380	89
WH2	96	108	135	11	158	94
	97	109	133	8	155	97
Mean	96	108	134	10	156	95
WH3	264	144	50	< LOD	256	101
	271	133	52	< LOD	259	113
Mean	268	139	51	< LOD	257	107
WH4	126	120	58	15	147	96
	124	114	50	19	149	101
Mean	125	117	54	17	148	98

n=2

Appendix 1d – Fresh and dry weights of the investigated herbaceous plant species.

Plant species	Shoot fresh weight (g)	Root fresh weight (g)	Shoot dry weight(g)	Root dry weight (g)
Agrostis stolonifera	13.01	85.42	3.71	23.17
Artemisia vulgaris	36.06	32.97	7.68	8.60
Argrostis capillaries	120.91	81.79	24.61	15.92
Chamerion angustifolium	64.43	11.31	8.65	1.77
Agrostis tenuis	31.41	21.96	9.05	5.68
Dactylis glomerata	57.87	36.08	8.89	5.01
Urtica dioica	100.40	30.78	20.83	4.89
Galium aparine	81.45	14.47	10.78	8.99
Phalaris arundinacea	107.40	5.65	19.68	1.62
Heracleum sphondylium	208.67	90.76	27.13	34.87
Juncus inflexus	41.63	23.60	10.54	4.71
Impatiens glandulifera	29.67	15.08	6.26	2.04
Plantago lanceolata	51.70	10.67	7.26	2.00
Lolium multiflorum	25.03	4.85	4.62	0.93
Juncus effusus	86.43	31.21	17.32	7.28
Chamerion angustifolium	116.84	6.51	15.85	1.13
Holcus lanatus	61.22	9.02	11.42	3.74
Urtica dioica	106.80	11.61	15.49	1.48
Dactylis glomerata	95.83	18.41	16.17	3.06
Festuca pratensis	73.43	18.86	14.83	4.03
Glyceria maxima	158.93	18.10	29.40	3.35
Phleum pratense	28.42	30.97	5.74	5.64
Lolium pratense	46.28	40.03	9.55	6.53
Equisetum arvense	36.08	3.05	7.06	0.69
Cynosurus cristatus	47.98	19.48	10.78	3.07
Filipendula ulmaria	100.64	4.60	15.14	0.71
Bistorta officinalis	62.61	20.68	6.49	6.36

Appendix 1e – Revegatation trial experiments in the greenhouse

Figure 1a. lettuce and mustard plants growing in blended contaminated soil in the greenhouse

Figure 1b. Mustard plants growing in non-blended contaminated soil in the greenhouse showing symptoms of metal toxicity