Plymouth University
Department of Geographical Sciences

Heavy metals in soils: Investigation into an urban area of Bristol

By Rebecca Beighton

Student Number: 10267617

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The content of this dissertation is entirely the work of the author

Signed…………………………………..Date………………………

Cover photograph: Chimney at Troopers Hill, Bristol.

Abstract

The following study examines the spatial variation of soil characteristics along with the management of land on Troopers Hill, Nature reserve Bristol. Identifying if levels are distributed evenly by looking at indicators of change, i.e. Topography, profile, habitat, pH or to identify if soil leaching has occurred in relation to the concentration of the following heavy metals copper (Cu), zinc (Zn), lead (Pb), arsenic (As), aluminium (Al) and manganese (Mn). In addition accessing the impact of past industrial activity on the soil quality. Methods used included stratified, systematic sampling to collect a total of 80 samples from three transects 0-15cm and four deep soil profiles 0-40cm. The pH for six samples were analysed in the field, GPS readings and photographs were also taken. Samples were analysed in the laboratory for concentrations of Cu, Mn, As, Al, Zn and Pb using acid digestion followed by an ICP-OES Varian 725-ES.The study indicates the soil pH to be extreme acidic in nature affecting mobilisation of metals and there ability to leach through the soil profile. There is spatial variation of heavy metal concentrations and contamination of Cu and As on Troopers Hill is concentrated around the copper chimney. The study concludes metal contamination and soil leaching varies spatially across Troopers Hill due to the following soil characteristics; pH, geology, habitat, topography and profile and anthropogenic influences from industry. No costly remediation of the site is needed as As levels are not entering the food chain and Cu is not at phytoxic levels. Future research would benefit from looking at the bioavailability of metal concentrations in plants and their rate of uptake along with concentrations of Cr, Cd, Ni, Se.

Contents

References

Appendix

Acknowledgments

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Chapter 1.0 Introduction

1.1 Key issues and debates

Soil is a complex amalgam, a non-renewable natural resource because it cannot be re-created except within the context of geological timescales. It can be simply defined as the unconsolidated mineral or organic material on the immediate surface of the Earth that serves as a natural medium for the growth of land plants (Alloway, 1994). Other definitions state it to be a reactor, transformer and integrator of material and energy from other natural resources (solar radiation, atmosphere, surface and subsurface waters, biological resources), a medium for biomass production; storage of water, nutrients and heat, natural filter and a medium of past and present human activities (Nortcliff 2002, Schaetzl & Anderson 2005,Blum 2005). It is a basic component of ecosystems and is one of the most vulnerable to contamination and degradation through accidental or deliberate mismanagement (Herbert *et al*, 1995). English soils are dynamic and can vary from a few centimetres to a metre or more in depth. They are very young in a world context however represent about 10,000 years of ecological processes and human modification (Natural England, 2012). Soil functions can be grouped according to the principal purposes as either agricultural, environmental, landscape or urban in nature. In the soil protection strategy (European Commission, 2006) the main key functions are identified as:-

-Biomass production

- Storing, filtering and transforming nutrients, substances and water

- Biodiversity pool such as habitats, species and genes

- Physical and cultural environment for humans and human activities

- Source of raw materials

- Acting as carbon pool

- Archive of geological and archaeological heritage

Anthropogenic (human) activities essentially inadequate agricultural and forestry practices, tourism, urban and industrial sprawl are named as the main impacting factors that prevent the soil from performing to its full capacity leading to soil degradation. Soil degradation can cause decline in soil fertility, carbon and biodiversity; lower water retention capacity, disrupt gas and nutrient cycles and reduce degradation of contaminants particularly metals (Schaetzl & Anderson, 2005). Major developments of soil conservation policies have been taking place in the European Union with governments adopting a more active role in identifying and dealing with contaminated land, since the introduction of the Environmental Protection Acts of 1990, overseen by organisations like Defra.

Contaminated land can be defined as ‘the introduction or presence of alien substances or energy’ these substances or energy however are not always liable to cause damage or harm (Cairney, 1998, 11). The act was updated for the first time in April 2012 where policies have become more orientated in applying measures to find and deal with existing contaminated land alongside the prevention of more being created. These measures include policy and legislation on pollution, waste, water and chemicals (Defra, 2012). In particular chemical soil pollution is one of the underlying issues proposed to present day management of land. England has a known heritage of chemical contaminants in soil due to its prevalent industrial past. In addition The European Commission proposed a ‘Strategy for Soil Protection’ after recognising soil degradation needed to be managed in Europe based on the findings by academics (Le Bas & Jamagne 1996, Snakin et al 1996, Heinecke et al. 1998, Blum 2003, Jones et al. 2005). Enforced conservation polices provided a framework to ensure sustainable soil use and conservation planning for the future.

1.2 Study Aims

The main purpose of this work is to investigate the spatial variation of soil characteristics along with the management of land on Troopers Hill, Nature reserve Bristol.

Objectives

1) To look at the spatial variation of soil characteristics, to identify if levels are distributed evenly across the nature reserve by looking at indicators of change, i.e. Topography, profile, habitat, pH or to identify if soil leaching has occurred.

2) To identify levels of the heavy metals concentrations; copper (Cu), zinc (Zn), lead (Pb), arsenic (As), aluminium (Al) and manganese (Mn) in the topsoil (15cm) of Troopers Hill in order to assess the impact of past industrial activity on their quality. To see if the site is identified as contaminated on the basis of existing UK Soil Guideline Values and published ambient background values for English Soils.

3) From this to identify if a potential reclamation of the area is needed in order for the public to continue using the area as a nature reserve, and place for allotments sites, with reference to the present day management policies.

1.3 Literature Review

1.3.1 Context

Geography is a widely debated discipline with emphasis commonly placed on the interaction of the two sub-disciplines, human and physical geography. It is one of few subjects that can be seen to bridge the social sciences (human geography) with the natural sciences (physical geography). A key difference between the two includes the method of investigation. The 'scientific method' adopted by this study is an integral part of the empiricist approach of studying physical geography. This investigation more specifically puts focus on a reductionist approach, by only sampling a small area of Bristol i.e. Troopers Hill this gives opportunity for in depth analysis to be conducted. Field work and learning through experience are central to how we acquire individual geographic knowledge (Trudgill & Roy, 2003).

On a wider geographical context physical geography can allow us to become increasingly aware of the impact of natural and human induced environmental change on landscapes and the biosphere. In turn this allows geographers to monitor the effects humans have on the natural environment (Peterson et al, 2009) therefore the report will try to integrate both human and physical factors. Soil science and the study of soils (Pedology and edaphology) is an important sub-discipline of physical geography to study, as soils are a major component of the Earth's ecosystem (Holden, 2008). Increasing concerns over soil pollution have highlighted the importance of monitoring levels of heavy metals present in soils and the environment. Soil protection and sustainability of agricultural production have moved to the forefront of concern within the discipline, becoming increasingly important topics for discussion and research (Alloway, 1994). The study by Nicholson *et al*, 2000 focuses on the sources of heavy metals (Zn, Cu, Ni, Pb, Cd, Cr, As and Hg) and their inputs to agricultural soils in England and Wales. Their work will help develop strategies to reduce heavy metal inputs to agricultural land by focusing policies on protection of soils from long-term heavy metal accumulation. Studies like this show change over time as a central theme to geography.

Troopers Hill is an excellent site for investigation into heavy metals as it falls into a geographic location, the South West of England, which has been neglected in literature, with limited samples being taken on site for Giusti's study (2011). There is very little empirical research into spatial distribution of heavy metals in urban soils in Bristol. Therefore, the proposed dissertation seeks to begin to fill in this gap in current understanding by undertaking research into the spatial distribution of heavy metals in soils on Troopers Hill Nature Reserve, Bristol. Wider studies in Britain of heavy metals in ecosystems like the study by Kelly and Thorton, (1996) of the influence of anthropogenic activity on the heavy metal content of soils in traditionally industrial and non-industrial areas of

Britain have indicated that many areas near urban complexes, metalliferous mines or major road systems contain anomalously high concentrations of some of the following elements Pb, Cd, Hg, Cu, As. With this in mind the site Troopers Hill Would be an interesting area to carry out investigations on as it is located on a hill side overlooking the River Avon between the surrounding roads Crews Hole and A431, Air Balloon road.

The proposed dissertation project is relevant to geography as it seeks to understand the theory of 'space' which is seen in relation to material events and natural processes looking in particular at the soil characteristics and management of the land (Johnson et al, 2000). The results may account for the composition of vegetation and wildlife diversity within the nature reserve which in wider context may reflect how the space is used by man, in the case of Troopers Hill it is used predominantly for recreation as it is now a listed nature reserve.

The study by the Environmental agency, 2002 investigates the bio-accessibility of As this is supported by other studies on Arsenic contamination in Cornwall (Camm *et al*, 2004). The proportion of environmental problems caused by soil has increased becoming evident from the large-scale deterioration of forests, regional difficulties with groundwater reclamation, from problems surrounding abandoned landfills and from forms of soil degradation including erosion, urbanisation, salinization and desertification. Among these soil pollution is largely due to the activities of man and industrialisation (Kabata-Pendias, 2011). Metals are natural components of soils although since the start of industrialisation and the 200 years that have followed, extensive changes in the global budget of vital chemicals of the earth's surface soils have occurred, challenging the regulatory systems which have taken millions of years to evolve. For example the percentage of annual concentration output for an element in unpolluted soils is particularly high for Pb, Hg, Cu, Cd and Zn, namely 10 to 30 times higher than for Fe or Mn (Forstner, 1995).

Soil is essentially a non-renewable resource with possible high rate of degradation and extremely slow rate of regeneration processes. Degradation deteriorates soil quality by partially or entirely damaging one or more of its functions (Blum 1988). Degradation processes occurring in Europe are widely studied (Batjes and Bridges 1993, EC 2006c, EEA 2000, Kirkby et al. 2004, van Lynden 1997, 2000) and incorporated to soil protection policies on national (Kraemer et al. 1999) and European levels (EC 2006a,b). The focus of policy actions is the reduction of risk of soil degradation. Risk of soil degradation depends on soil and terrain properties which make the soil inherently receptive of degradation. Van Camp et al. (2004) provide substantial knowledge towards identifying and describing hazards (threats) to soil. The work of Eckelman et al. (2006) summarizes the risk assessment methodologies applicable for soil degradation studies (Annex I.) and applies the concept of threats to represent the hazards endangering the functioning of soils. Arsenic in UK Soils. Direct degradation threats to soils are manifold, among which erosion, salinisation, compaction, loss of organic matter, landslides, contamination and sealing have major impact on soil in Europe, therefore are in the focus of the Strategy.

1.3.2 Heavy Metals, Pollution and Contamination

Nearly all of earth's organisms require certain metals in order to maintain health and biological functions, with around 15 of these elements found naturally in rocks and soils, normally in very small amounts. Of these the following are required by humans for nutrition: copper (Cu), zinc (Zn), iron (Fe), cobalt (Co), manganese (Mn), molybdenum (Mo) however in large amounts these become carcinogenic or toxic, affecting, among others, the central nervous system (manganese, mercury, lead, arsenic), the kidneys or liver (mercury, lead, cadmium, copper) or skin, bones, or teeth (nickel, cadmium, copper, chromium) (Freedman and Hutchinson 1981, 1). The most widespread human deficiency in a heavy metal is zinc, for which over two billion humans, mostly in developing countries, suffer from inadequate amounts of zinc in their diet (Prasad, 2003). In Europe there are eleven elements of highest concern these are arsenic, cadmium, cobalt, chromium, copper, mercury, manganese, nickel, lead, tin, and thallium, the emissions of which are regulated in waste incinerators (Alloway, 1994).

Only a small proportion of metals found in the periodic table are listed as 'heavy metals' with a number of different definitions existing to define them. However emphasis is more commonly placed on pollution and toxicity aspects rather than its reference as a collective name for a group of elements of considerable economic and environmental importance. Heavy metals or trace metals is the term applied to a large group of trace elements which are both industrially and biologically important. 'Heavy metals' is the most widely used term for the large group of elements with an atomic density greater than 6g/cm^3 (Phipps, 1981). The normal abundance of an element is commonly referred to by geochemists as 'background', this varies according to the geology and soil type of an area, with initial hydrological processes (including land runoff and throughflow) provide the initial transportation of heavy metals. Ideally heavy metal concentrations and movements limited by natural environmental conditions would pose for a more sustainable environment. However human (anthropogenic) influences have impacted significantly causing environmental implications most commonly pollution and contamination of subsurface soils and groundwaters. It's important to understand metal concentrations found in groundwater are largely governed by the interactions with surrounding soils and geological materials. Soil mechanisms influence the partitioning of metals between solid and solution phases thereby affecting the leachability of metals in contaminated soils, with the major effect being the increase in solubility of heavy metal ions (Herbert *et al*, 1995) This leads to say the study and monitoring of heavy metals in soils is important when investigating the wider context of groundwater pollution especially when reviewing agricultural production as all trace elements are toxic to living organisms when present in excess.

Pollution is an easier term to define, the definition given by Holdgate, (1979) is widely accepted, referencing pollution as ‘the introduction by man into the environment of substances or energy liable to cause hazards to human health, harm to living resources and ecological systems, damage to structures or amenity or interference with legitimate uses of the environment’ essentially any chemical can become a pollutant in soil if present at a high enough concentration. The urban and suburban soils of former or present industrialised regions of the world are known to have accumulated a wide range of contaminants, particularly heavy metals. In the UK and in other EU countries, the soil of many gardens, allotments and parks were found to be contaminated with heavy metals and polycyclic aromatic hydrocarbons (Culbard et al, 1988; Prasad and Nazareth 2000; Alloway 2004; Hursthouse et al 2004). Limited information on soil chemistry is available for the southwest of England. The work carried out by Gisusti, 2011 is one of the few studies on Heavy metals on urban soils in the South West. The research was carried out to assess whether any allotment and park soil in Bristol could be defined as ‘Contaminated’. Results showed potentially contaminated sites included Troopers Hill Nature Reserve, where high levels of copper were found. A table from the World Resources Institute, (1992) shows that more Cu pollution is produced than any other metals listed, but Zn is the highest in terms of global emissions to soil. Evidently it will be beneficial to analyse the levels of these metals on Troopers Hill. Of the two Zn is generally considered a much lower toxicological risk to humans and animals however recent evidence suggests that it’s dispersion into the environment and accumulation in soils may cause soil fertility implications due to its toxicity to some soil microorganisms. Previous studies involving extraction of heavy metals from contaminated land include the on undertaken by Ellis et al (1939) which demonstrated the treatment of soil contaminated with cadmium, chromium, copper, lead and nickel using acid (EDTA), hydroxylamine hydrochloride and citrate buffer. The EDTA chelated and solubilised all of the metals, with the results of the three combined agents it removed nearly 100% of the lead and cadmium, 73% of the copper, 52% of the chromium and 23% of the nickel from the soil.

1.3.3 Heavy Metal Sources

Heavy metals can be sourced from both natural and anthropogenic influences; in some areas anthropogenic inputs are proportionately greater than those from natural sources with some academics (Ahmad, 2005, Holdgate, 1979, Alloway, 1994) proposing it’s often the by-products of mining, manufacturing, disposing of industrial metals and domestic waste that accounts for almost all environmental pollution. It’s without argument higher levels of heavy metals are found in urban landscapes and industrial sites which far exceed natural levels these can be sourced from a diverse range of origins from roadside vehicle pollution to runoff from contaminated land associated with industries. Heavy metal pollutants can localise and lay dormant; unlike organic pollutants they do not decay posing a different approach for remediation. Currently plants or microorganisms are tentatively used to aid removal of heavy metals like mercury from soils. Plants exhibiting hyper accumulation can be used to remove metals through the process of concentrating them into their bio matter. An impending concern associated with the persistence of heavy metals is the potential for bioaccumulation and biomagnification to become more prevalent to some organisms than would otherwise occur naturally (Hogan 2010).

Thornton (1981) lists there to be seven principal categories for sources of metal contamination with almost all but one being anthropogenic in cause, they are as follows:

1. *Natural sources, such as surface mineralisation, volcanic out-gassings, spontaneous combustions of forest fires.*
2. *The use of metal containing agricultural sprays or soil amendments.*
3. *The disposal of wastes from mines or mills.*
4. *Emissions from large industrial sources, such as metal smelters and refineries.*
5. *Emissions from municipal incinerators.*
6. *Emissions from moving sources, principally automobiles.*
7. *Other relatively minor sources of terrestrial contamination, such as smaller scale industries that process metals.*

The soil is both a natural source of metals and also a sink for metal contaminants metals with the quantities depending often on the lithology of the surrounding rock and soils. One of its many roles is to act as a filter protecting the groundwater from inputs of potentially harmful metals. Heavy metals do occur naturally in soils, usually at relatively low concentrations as a result of weathering and other pedogenic processes acting on the rock fragments at which the soils develop (soil parent material). In addition atmospheric inputs, precipitation, provide another natural source as heavy metals enter the aquatic environment. Therefore concentrations of heavy metals in soils can vary on different scales locally, regionally and globally due to the geology of the rocks containing different mineralogical and elemental compositions (Alloway, 1994).

Soil contamination has the potential to disrupt the delicate balance of physical, chemical and biological processes which soil fertility depends upon. Pollution of heavy metals compounds in soils can inhibit microbial enzyme activity subsequently reducing the diversity of populations of soil flora and fauna (Forstner,1995) The transfer of metals to humans can result from consuming contaminated plants and animals in addition there are specific concerns for the ability of contaminated material to enter into ground and surface water systems. There are a number of environmental indicators used to measure the quality of water and sediments however it has proven more difficult to develop generic soil guidelines for groundwater protection this is due to the key variables (length and thickness of soil and bedrock, depth to water table, source protection zone etc.) being highly site specific (Ferguson and Denner, 1996). However the World Health Organisation (1993) is confident in issuing some recommended maximum concentrations of a number of elements to ensure safe clean drinking water.

Table 1. European and International standards for drinking water (World Health organisation, 1993)

Element	European standards (mg/l)	International Standards (mg/l)
Arsenic (As)	<0.05	<0.005
Lead (Pb)	<0.1	<0.1
Copper (Cu)	<0.05	0.05-1.5
Manganese (Mn)	<0.05	0.1-1.0
Zinc (Zn)	<5	5.00-15.0
Aluminium (Al)	<0.1	0.1-0.2

1.3.4 Environmental Quality Standards

Preventing heavy metal pollution is critical because cleaning contaminated soils is extremely expensive and difficult to achieve. Soil Guideline Values (SGV) and supporting technical guidance are intended to assist professionals in the assessment of long-term risk to health from human exposure to chemical contamination in soil. There are different SGV according to land-use (residential, allotments, commercial) because people use land differently and this affects who and how people may be exposed to soil contamination. Environmental quality standards in England are building on the ‘First Soil Action plan for England (2004-2006) where the focus has become orientated towards the role of soils adapting to climate change and preventing pollution and dealing with historic contamination (Defra, 2012).

Table 2: Guideline values used to classify contaminated soils mg/kg (HMSO, 1991):

Metal	concentration	Residential	Parkland	Industrial

There has been concern both in the UK and elsewhere that soil guidelines are frequently misused or misunderstood public confidence in environmental policy and risk management requires confidence in regulations set.

1.3.5 Soil Quality and Sustainability

Environmental quality standards help to ensure soil quality is monitored and sustained to prevent soil degradation as soil functions are both spatially and temporally changing. Soil quality is the ability of soil to provide ecosystem and society services through its capacities to perform its functions and respond to external influences (Kabata-Pendias, 2011). The level a soil can perform its identified functions depends on its physical, biological and chemical characteristics also referred to as internal characteristics. The performance is further conditioned by natural (e.g. slope steepness) and/or anthropogenic (e.g. artificial drainage) factors referred to as external factors. Internal characteristics and external factors are time dependant with human activity directly or indirectly transforming the performance characteristics of soils most prevalently, thus limiting or enhancing the capacity of the soil to function. Essentially long term human impacts by land use change (amelioration/restoration degradation) on the ecological conditions of soil as well as the seasonal fluctuations of drainage, cultivation, and irrigation, nutrient management etc. modify material and energy flows. These alter pedogenic processes when these processes are controlled; soil-use and soil quality remains sustainable long term (Alloway, 1994, Holdgate 1979). Soil quality is evaluated by Soil Functional Ability (SFA). In order to evaluate soil quality, soil functions and response properties must be assessed taking into account influential factors (climate, hydrology etc.).

Soil quality assessment is considered one of the main criteria for planning and practicing sustainable soil-use. It’s important to ensure the quality of soils do not degrade by promoting management practices that aid the sustainability of them achieved through ensuring the material and energy flow associated with soil processes are controlled and positively influenced. A sustainable soil is referred to as ‘the use of soil as a natural resource on a way that does not exert any negative effects that are irreparable under rational conditions either on the soil itself or any other systems of the environment’ (Tóth, 2004).

Chapter 2.0 Study Area

2.1 Introduction to Troopers Hill

Troopers Hill is a picturesque nature reserve overlooking the River Avon, situated in St George, east Bristol, between the A431 Air Balloon Road and Crews Hole Road (see plate 2.0). These roads are linked by Troopers Hill Road, from which there are four pedestrian entrances on to the site (see Figure 1). Troopers Hill is located only three miles from the city centre (Bristol City Council, 2012).

Figure 1: The location of Troopers Hill Nature Reserve in South West England, Bristol. Source Ordnance Survey maps, 2012

The unique area of acid grassland and heathland was designated as a nature reserve by Bristol City Council in June 1995 in recognition of the wide range of wildlife present on the hill (Bristol, City Council, 2012). Troopers Hill has won the prestigious Green Flag Award every year since 2007, recognition and reward for being one of the best green spaces in the country (Friends of Troopers Hill, 2012). The area has had a history of multifunctional land use initially being used for industrial activities with the most prominent feature being the Grade 2 listed chimney at the top of the hill which may date from as early as the eighteenth century. Since the closure of industry its main purpose has turned to recreational use where a number of seasonal events regularly occur for public enjoyment.

Plate 2.0

Plate 2.0: View looking up main slope on Troopers Hill, capturing the old copper chimney and the heath and grassland vegetation. Source: Photograph taken by author 2012.

Troopers Hill's colourful history has shaped the terrain present today, essentially a large open area of acid heathland littered with a number of bare rock faces and steep sloped sides. There are multiple areas across the hill where the bare rock can be seen, ranging from smooth, sloping surfaces to fractured, and angled cross sections of strata. The gully area subjected to quarrying reflects the angled multi coloured and broken layers of rocks that form steep terrain. The top of Troopers Hill forms a small plateau which falls away in steep slopes on three sides. These slopes were originally formed by the River Avon now found to the south running under Troopers Hill Road. The summit of Troopers Hill reaches about 70metres above sea level a reflection of the steep slope height with the lowest elevation point 50m found at the bottom of the hill, its orientation towards the south west. The Hill gives view across Bristol to the younger Mendips Dundry Hill, seen to the southwest, composed of Jurassic Age Rocks (Friends of Troopers Hill, 2012).

2.2 Geology

Along with the effects of climate, relief, organisms and time, the underlying geology or 'parent material' has a very strong influence on the development of English soils. Bristol particularly has a varied geology (see figure 2) and in a geological timescale the valley Bristol lies in and the adjacent slopes across the River Avon from Troopers Hill are dated to the Triassic age. Troopers Hill geology is unusual in Bristol as much of the city lies on carboniferous limestone, but Troopers Hill is dominated by sandstone of the Pennant Measures. It has been officially recognised as a Regionally Important Geological and Geomorphological Site (RIGS) (also known as Local Geological sites) in April 2010 (Bristol City Council, 2012). The formation of Troopers Hill can be dated to the end of the Carboniferous age, 290 million years ago. This is where upheaval of the earth’s crust caused areas of rocks to break and fold, Troopers Hill is on an arm of one of these folds, as the rocks dip to the south at an angle of 30 degrees (Kellaway, 1969. The hills geology is composed of sandstone of the pennant measures that can be dated back to 300 million years old, a comparison to the slopes in the west forming the downs made up of carboniferous Limestone. Pennant measures are sedimentary rocks formed in tropical swamps some 300 million years ago they are mostly sandstones, mudstones, shales and clays with occasional coal seams they belong to the Upper Coal Measures of the Carboniferous Period. Over time the coal measures were formed as vegetation decomposed and was compressed by the weight of later sediments. The clayey soil, in which the plants grew, turned into bands of clay lying alongside the coal seams. Through weathering processes the rocks contributed inorganic mineral grains to the soils and thus exhibited control on the soil texture leaving the area to become covered by sands and fine gravels as rivers changed their course and finally disappeared (Natural England, 2012).

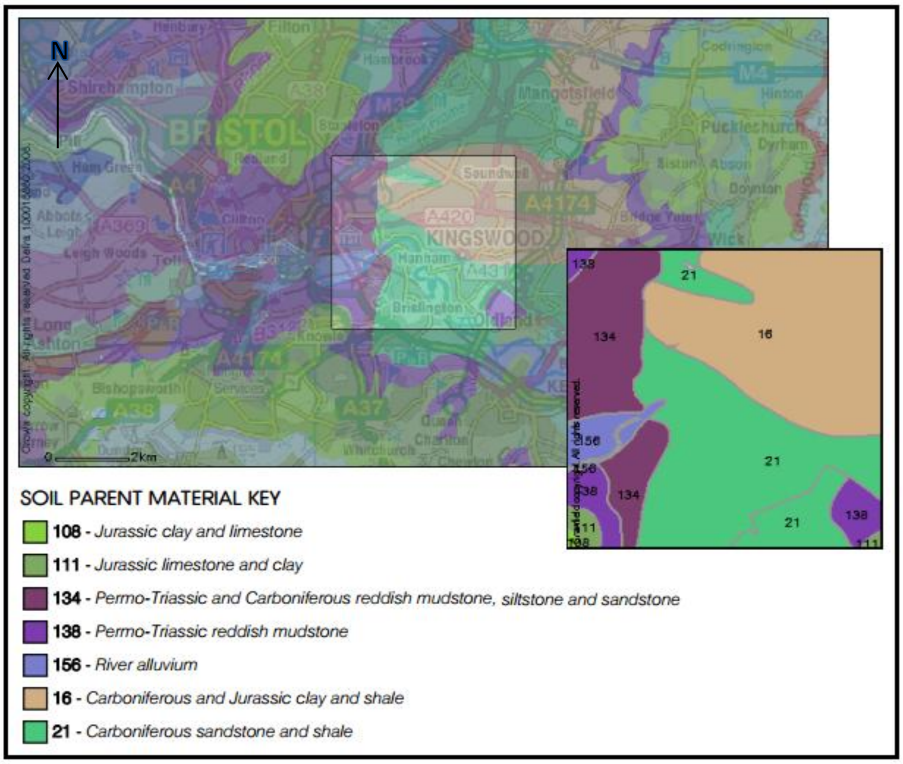


Figure: 2 .Soil Parent Material of Bristol with close reference to Troopers Hill area which lies in the main carboniferous sandstone and shale area. Source: Generated from the Natural Soil resource institute, 2012)

2.3 Soil Characteristics

Bristol is built up of a diverse range of soil types, many of these have been overbuilt as the city of Bristol developed, (see figure 3), (South West Observatory, 2012)). On Troopers Hill the combination of underlying sandstone and presence of past industry (quarrying, mining, and copper and lead smelting works) on site has left the area with acidic soils, a rarity in Bristol. These soils have encouraged a wealth of plants to flourish, found nowhere else in the City. Figure three shows Troopers Hill to just fall into the band of soils referred to as Neath (541h) association (see figure 4). These soils are described as permeable and well drained, fine loamy brown soils with clay loam upper horizons containing fine sandstone and siltstone fragments which increase in number downwards, as the soils pass into rubbly Head or fractured bedrock; over sandstone this soil type accounts for 1.6% of soils found in England and Wales. More specifically Troopers Hill falls into the subcategory of Neath Soils, called Neath- Nh which are medium loamy material over lithoskeletal sandstone, this subsoil type accounts for 31% of the total Neath soils (Landis Org, 2012).

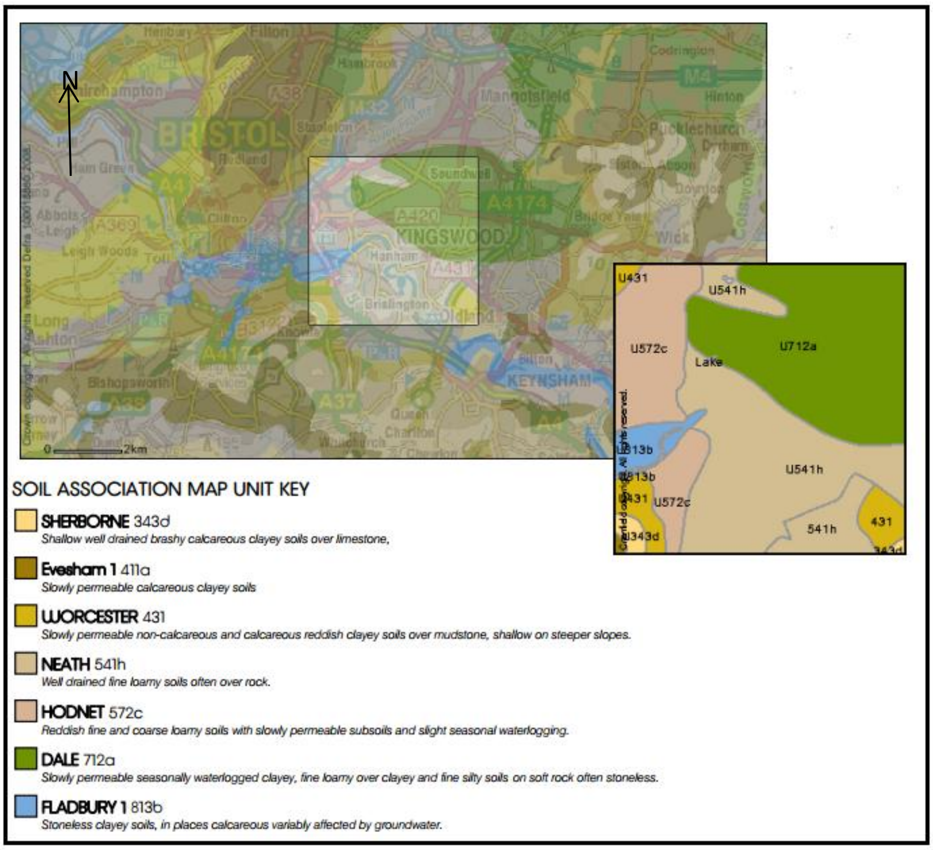


Figure: 3 Map of east Bristol depicting the different soils. Source: Generated from the Natural Soil resource institute, 2012.

Figure three shows the soil associations for Troopers Hill and surrounding area of Bristol. Soil associations represent a group of soil series (soil types) typically found occurring together in the landscape (Avery, 1973; 1980; Clayden and Hollis, 1984). They may occur in a number of geographical locations around the country where the environmental conditions are comparable. Soil associations have codes as well as textual names, thus code '541h' refers to the 'Neath' association. Where a code is prefixed with 'U', the area is predominantly urbanised (e.g. 'U571v').

The topsoil texture (see appendix) (upper 30cm) of Troopers hill is classified as loamy. Loamy soils have a mix of sand, silt and clay-sized particles and are intermediate in character (Avery, 1973). Soil fertility is dependent on soil type, soils that are very acid like those on Troopers Hill have low numbers of soil-living organisms and are classified as having low soil fertility. They support heathland and acid woodland habitats because of this, evident of Troopers Hill, as the Nature Reserve area has heathland vegetation, and the area adjacent has woodland. Soil fertility can be altered by land management especially through the application of manures, lime and mineral fertilisers (Kabata – Pendias, 2011).

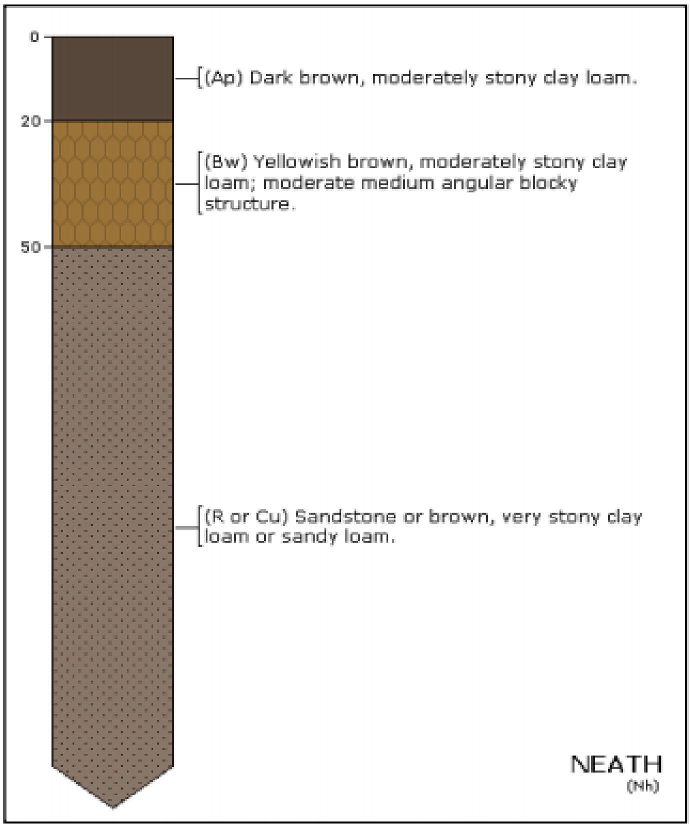


Figure 4: shows the typical soil profile structure of Neath (Nh soils) soils found on Troopers Hill. Source: Natural Soil resource institute, 2012)

For the project most samples came from the top 0-15cm of soil however not all samples were dark brown in colour some were a reddish brown and could have been altered by the presence of pollution. The potential of soil leaching on Troopers Hill is an environmental concern as leaching can contribute to groundwater contamination. Leaching occurs through water dissolving chemicals (and other nutrients) as it percolates through the soil carrying them into the underground water supply. The leaching potential of pollutants in an area is described by the Ground Water Protection Policy (see figure 5), (Hollis, 1991; Palmer et al, 1995). Troopers Hill falls into the I1 intermediate category, where soils have intermediate leaching potential, which have a moderate ability to attenuate a wide range of diffuse source pollutants but in which it is possible that some non-absorbed diffuse source pollutants and liquid discharges could penetrate the soil layer (Natural Soil resource institute, 2012).

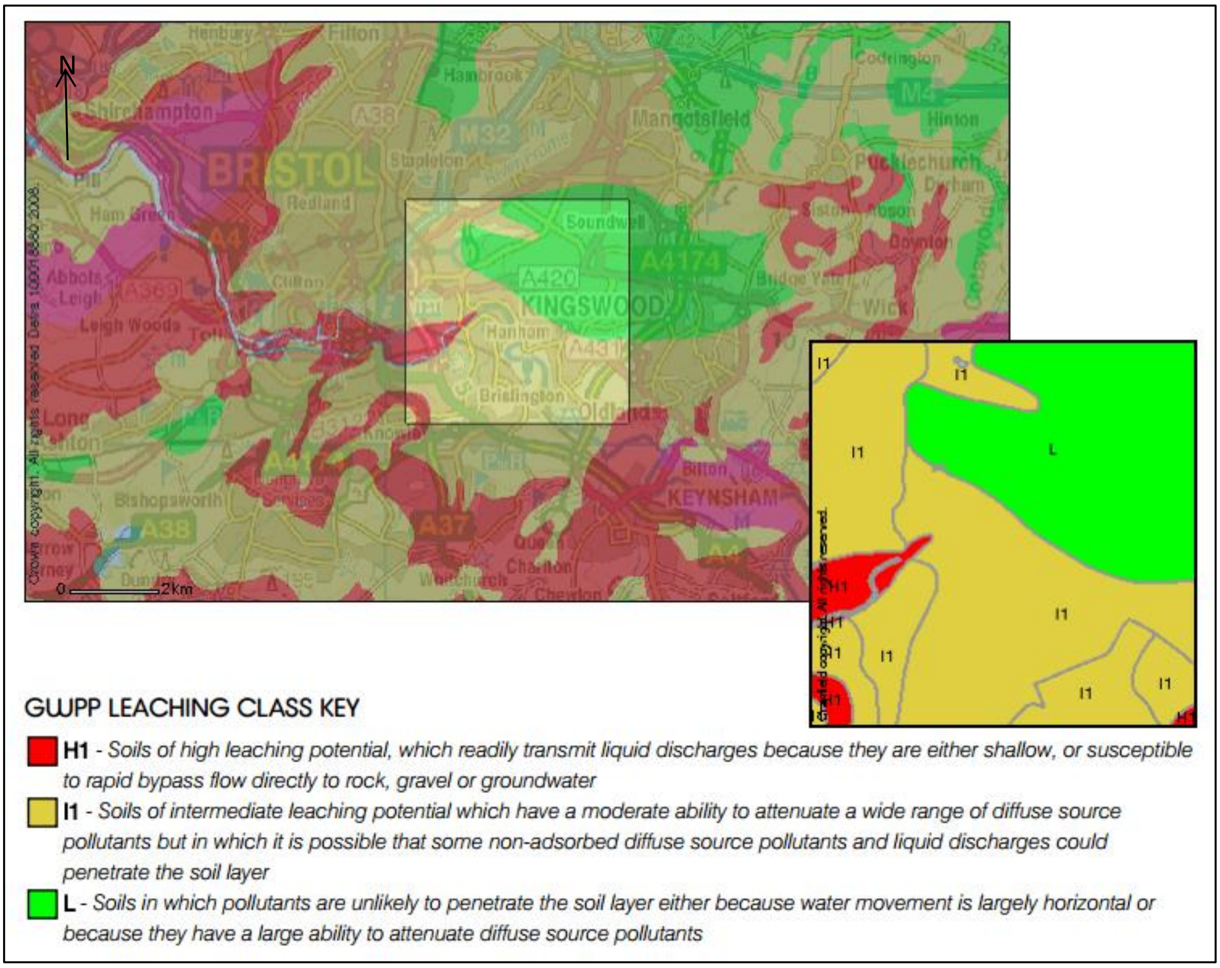


Figure 5: displays the Ground Water Protection Policy for the leaching potential of Soils in Troopers Hill and surrounding areas. Source: Generated from the Natural Soil resource institute, 2012.

2.4 History: Past Industries

Troopers Hill has a colourful history of past land uses initially the hill during the 1600s was part of a large royal hunting forest. In the late 1700s, the chimney at the top of the hill was used for copper smelting. Following this in the 1800s, coal and fireclay were mined from the hill. The square chimney at the foot of the hill (the junction of Troopers Hill Road and Crews Hole Road) is the remains of the engine house previously used by the coal mine (see plate 2.1). The area was also subject to quarrying of the sandstone during the 1800 and 1900s (Stephenson *et al*, 2003). As industry flourished in Bristol the sites steep slopes and tipped quarry waste discouraged builders from developing the site, this prompted the council to buy it for recreational use by local residents (BristolGov, 2012).

Plate 2.1

Plate 2.1 Mining Chimney at the foot of Troopers Hill. Source: Photograph taken by author, 2012.

Copper smelting

The copper smelting industry in Crews Hole was established in the 18th century. Copper ore was brought via boat mainly from Cornwall and North Devon, coal was locally sourced. Copper produced was mainly used with zinc ore from the Mendips in the manufacture of bras at Baptist Mills and other sites in Bristol. Around 1710 a copper smelting works, known as Cupolas, was established by the Bristol Brass and Wire Company, in the area between the River Avon and where the Bull Inn now stands this became the main industry in the vicinity of the hill (Stephenson *et al*, 2003, Cornwell *et al,* 2009). It’s though lead smelting occurred on this site between 1796 and 1820. The chimney on Troopers Hill is thought to have been built in the 1790s but most definitely before 1826 (where it was recorded in a photo). Stone & Tinson took over the use of the chimney by the end of the 1800s continuing to use it until the time of the First World War, for the chemical works that took over the site of the copper smelter (Acton- Campbell., 2006).

Plate 2.2

Plate 2.2: View of Copper Smelting industry at the foot of Troopers Hill, which can be seen in the background. Source: Acton- Campbell., 2006.

Pennant Sandstone quarrying

The shape of Troopers Hill is owed to the quarrying of pennant sandstone used as a stone building material throughout Bristol. The 1890 Ordnance Survey map showed the largest quarry area referred to as the gully to be in the centre of the hill. Comparison of this map which the 1904 Ordnance survey clearly shows a large proportion of rock to be removed between the dates, the area was worked until the end of the 19th century (see plate 2.3). The humps between the gully and Troopers Hill Road are tipped waste from the quarry. This left multi-coloured rock faces in the gully exposed on the south facing side of the hill. Both chimneys on the hill were probably built using on site pennant sandstone. In addition the 1890 map shows evidence of an old quarry on the south west side of the hill and one adjacent to the colliery engine house at the bottom of Troopers Hill Road (Acton- Campbell., 2006, Cornwell *et al*, 2009).

Plate 2.3

Plate 2.3: View of the gully on Troopers Hill the largest quarried area on the hillside. Source: Photograph taken by author, 2012.

Mining

Copper and lead smelting continued in Crews Hole during the early 19th century (although on a smaller scale to that experienced in the 18th century) allowing Troopers Hill to turn its attention to coal and fireclay mining, until its closure in 1904 when the last fireclay mines were abandoned (Acton-Campbell., 2006). Coal dating back to the Carboniferous age was mined from under the hillside, the mine shaft was located behind the engine house, with a second shaft located further up Troopers Hill Road, an area now covered in bramble its assumed it was filled in after the colliery closed; evidence of black patches on the hill from either spoil or extraction can be seen today. Two seams of clay were mined; the five feet thick Dibb clay and the deeper six feet thick Buff clay found below the coal seams and were used to make the bricks to line furnaces, perhaps accounting for the lean of the chimney at the top of the hill (Cornwell, 2003, Cornwell *et al*, 2009).

(See Appendix A Troopers Hill: Area time line for more information on the Hills use.).

2.5 Biodiversity and habitat of Troopers Hill

The combination of underlying sandstone and presence of past industry on the site has left Troopers Hill with acidic soils which has encouraged a wealth of plants to flourish, that are found nowhere else in the city (Friends of Troopers Hill, 2012).

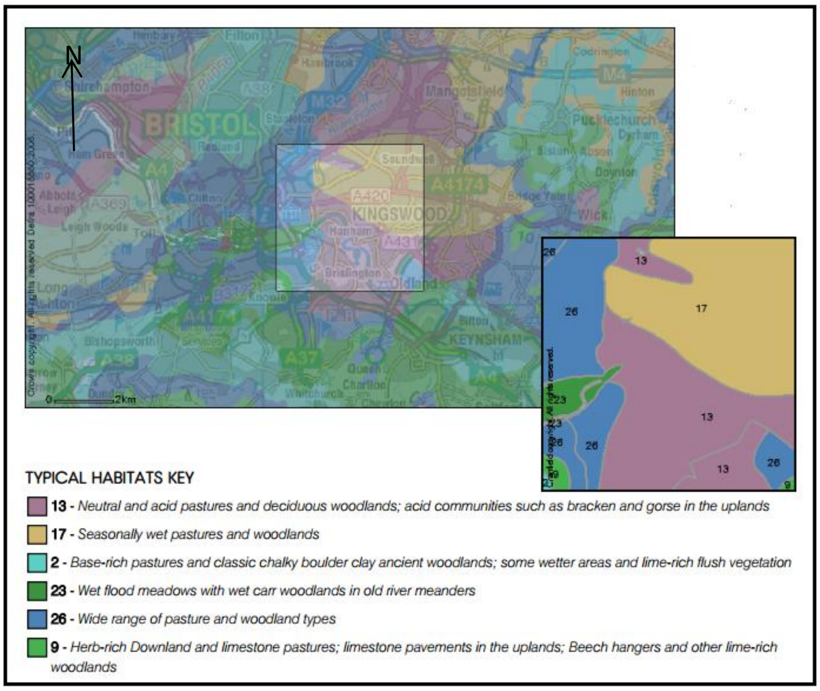


Figure 6: Map of the typical Habitats of Troopers Hill and surrounding areas. Source: Generated through the Natural Soils resource institute, 2012).

The map shows the broad habitat associated with the Neath soil type found on Troopers Hill to consist of neutral and acid pastures, deciduous woodlands, acid communities such as bracken and gorse in the uplands (area 13). This habitat is present due to the close relationship between vegetation and underlying soil as only plants that tolerate the acid soils survive. Key plants found include: grassland fungi such as waxcap; Ling and bell heather; hawtorn, silver birch, oak, apple trees, broom, bracken and gorse. In addition soil fertility; pH, drainage and texture are important factors in determining the type of habitat established in the area. Elevation above sea level and the orientation of a hillslope can affect the species present as heathland and grassland dominate the steeper slopes of the hill as woodland and shrub do the lower richer soils (see plate 2.5) (Kabata – Pendias, 2011).

This map does not take into account the recent land management or any urban development, but provides the likely natural habitats assuming good management has been carried out; this is true of

Troopers Hill. There is no threat to Troopers Hill from development however the heathland and grassland needs protection from the spread of shrub and woodland adjacent. Along with vegetation the Hill is important in terms of wildlife as it is home to a high number of rare invertebrates and endangered species that live there, e.g. mining bees (Nomada Guttulata were found in 2000) and bee flies nest in the areas of erosion on the hill (Friends of Troopers Hill, 2012).

Plate 2.4

Plate 2.4: North east view reflecting the diversity of vegetation found on Troopers Hill. Source: Photograph taken by author, 2012.

2.6 Research Methodology

2.6.1 Sample site design

The studies research objectives along with availability of resources were the main drivers for the sampling design as they involved looking at the spatial variation of soil characteristics, to identify if levels were distributed evenly across the nature reserve by looking at indicators of change, i.e. Topography, profile, habitat or to identify if soil leaching has occurred. In addition it was important to take into consideration the location of past industries on the site with regards to trace metals. To incorporate all factors sample site locations were chosen with a stratified method in statistics. Stratified sampling is a method of sampling from a population when subpopulations within an overall population vary, it is advantageous to sample each subpopulation (stratum) independently (Clifford and Valentine, 2003). Therefore at each location a probability based sampling method was used, this method aims to reduce bias and produce representative samples, they were identified and systematically acquired by the use of a (proportionate) repetitive sampling interval. Despite many types of existing sampling designs (reviewed in Gilbert 1987;Mulla and McBratney 2000) only two main types (random and systematic) are commonly used in the soil and earth sciences. Sampling of the area was necessary as it was not viable or practical to obtain information from the entire population.

2.6.2 Collection of Samples

The following methodology was implemented on Troopers Hill to collect the soil samples in summer 2012: initially a 1m auger was used to extract the soil samples from the area (originally chosen to ensure a uniform volume of soil is taken through the profile); however difficulties were experienced when using this method. The soil texture was too dense to push the auger in with ease, when a sample was finally extracted it was crumbly and half missing. Therefore a new method was adopted and each sample was hand dug to a depth of 0-15cm (the recommended depth for chemical analysis, Carter and Gregorich, 2008 and depth used by Giusti, 2011) for the three transects and 0-40cm (to see if downward leaching had occurred) for the four deeper samples. A total of 67 sites were sampled adding up to (80 samples), one transect was taken across the top of Troopers Hill (transect 1: site 5-22) at 500cm intervals, another along the quarry gully (transect 2: 23-45) at 500cm intervals and finally a third was taken down the hill (transect 3: 45-67) from the chimney entrance to foot of the hill by the mine shaft. These samples were taken at 1000cm intervals. In addition to the transects four deeper sample sites were taken from 1) Top of the hill from the front of the chimney 2) foot of the hill by the mine shaft 3) west side of the hill and 4) east side of the hill mid- way up. The following number of samples was chosen in order to obtain a representative characterisation of the area. A good sample aims to provide an unbiased and precise estimate of the parameter of interest. In addition GPS readings and photographs were taken at each site along with others for general overview and analysis (see figure 7).

In addition pH analysis of 6 soil samples (see figure 7 and table 5 for locations) was conducted in the field using a pH test kit by shaking 1 part soil in 5 parts water by hand and inserting a pH probe into suspension these were then recorded (Carter and Gregorich, 2008).

2.6.3 Laboratory preparation and Analysis of soil samples

Initial laboratory preparation saw the soil samples taken into the lab and dried in individual labelled trays using the fan assisted oven at 35°C over night. Following each sample was grinded with a pestle and mortar and sieved (with the aid of an extractor fan). Samples were then weighed to 100mg ±10mg and were subject to microwave assisted digestion using a mix of diluted hydrochloric acid and nitric acids. These are employed to extract the metals from the environmental samples. The method has been found to equate to techniques using full strength aqua-regia digests (Hassan *et al*, 2007) (see appendix B). The extraction was followed by the use of an ICP-OES (Varian 725-ES) to analyse the extracts for the following metals Al, As, Cu, Mn, Pb and Zn. After every 10th sample a blank solution containing

2% acid was used to ensure sufficient standards on the ICP. (In the Optical Emission Spectroscopy technique, atoms in a sample are excited by energy that comes from a spark formed between sample and electrode), (Conklin, 2005).

2.6.4 Data analysis and presentation

In quantitative research the main benefit of extensive sampling is that inferential statistics can be applied to aid statements about the soil population on Troopers Hill. The following statistics were applied to the data; a normality test to see if the data was normally distributed, followed by a parametric test (student T test) to show significance of data values in a given population. Data was presented mainly in the form of bar charts and correlation plots. This allows a quick comparison of all data from all sites without the need of lengthy tables.

2.6.5 Calibration methods/ data

Today's soil test laboratory analyses are the result of years of verification and a chemical procedure applied to a given soil should yield reported values within ±10% depending on the test. However to verify overall precision of results (i.e. both sampling and analysis) field replicate samples need to be analysed. Field replicate samples are two or more portions of a sample collected as closely as possible at the same point in time and space to be considered identical (Gilbert, 1987). For the study these were chosen randomly and a double sample was collected for two sites (site 21 and 46). In addition all equipment used was calibrated beforehand to ensure biases were not obtained and all samples were controlled under laboratory conditions. For the ICP-OES to ensure quality control a blank sample was run, (results were negligible), along with three standard samples of known element amount. These were used for quality control checks after every 10th sample; all came back as acceptable values.

2.6.6 Limitations of Methodologies

To all studies there are limitations they can include the introduction of biases by faulty or misused measurement devices and miscalibration of equipment, this was minimised where possible. Doing certified reference materials for my study would have ensured controls or standards of all my results and measuring pH in the lab as well as the field would have allowed for comparison providing a truer figure. Nitric acids used for digesting the metals will not always extract full concentrations so lower numbers of metals (about 5-10% error) should be accounted for, if concentrations appear low. In addition there was inadequate lab time to carry out a specific column leaching technique: this technique provides a very good simulation of the solubility of trace elements and pH. It is one of the best extraction procedures best suited to estimate metal mobility under field conditions this would have been highly valuable for the study (Carter and Gregorich, 2008).

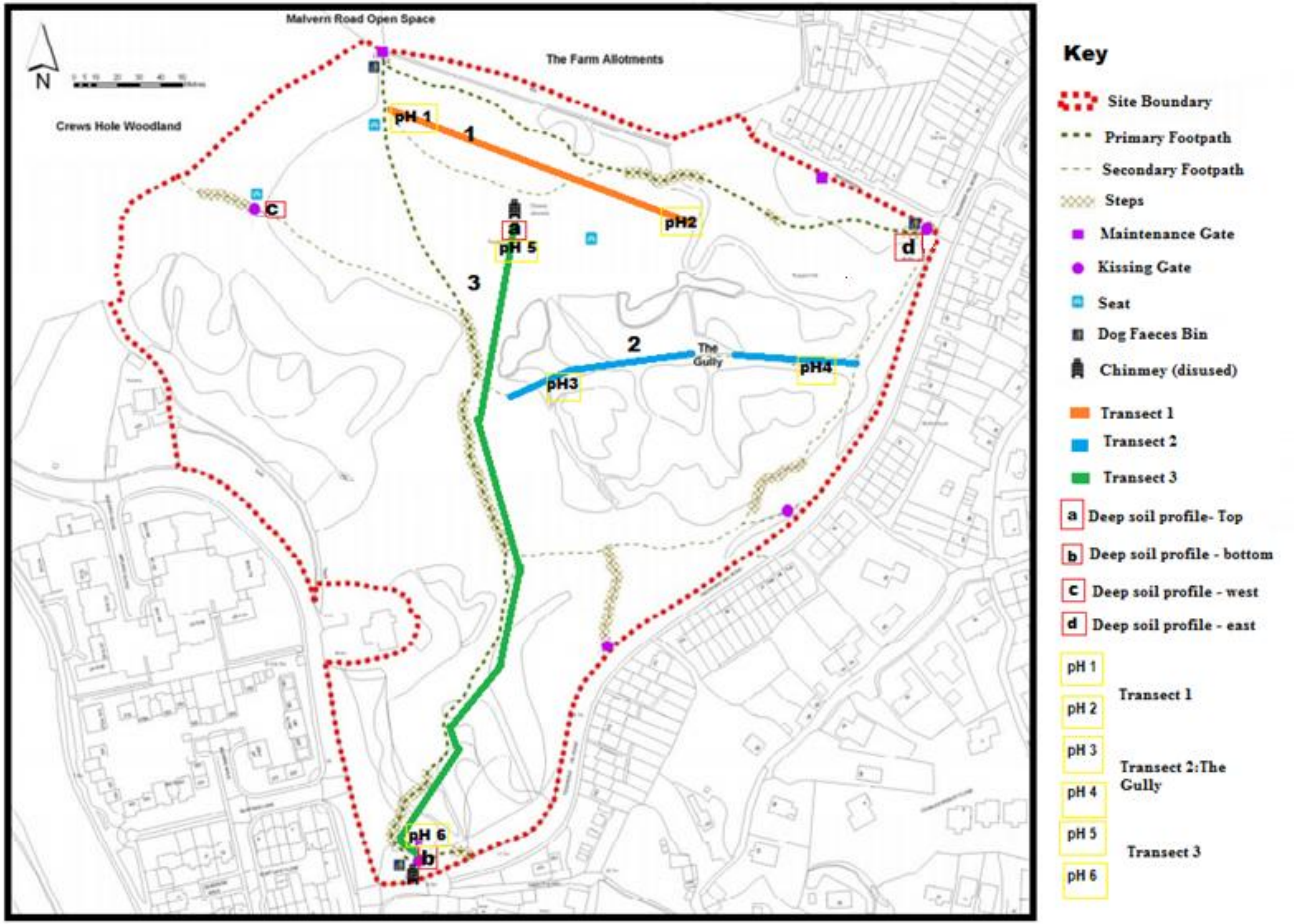


Figure 7: Study Site map of Troopers Hill showing sample sites. Source: Base map from Friends of Troopers Hill

Chapter 3.0 Results and Analysis

3.1 pH results

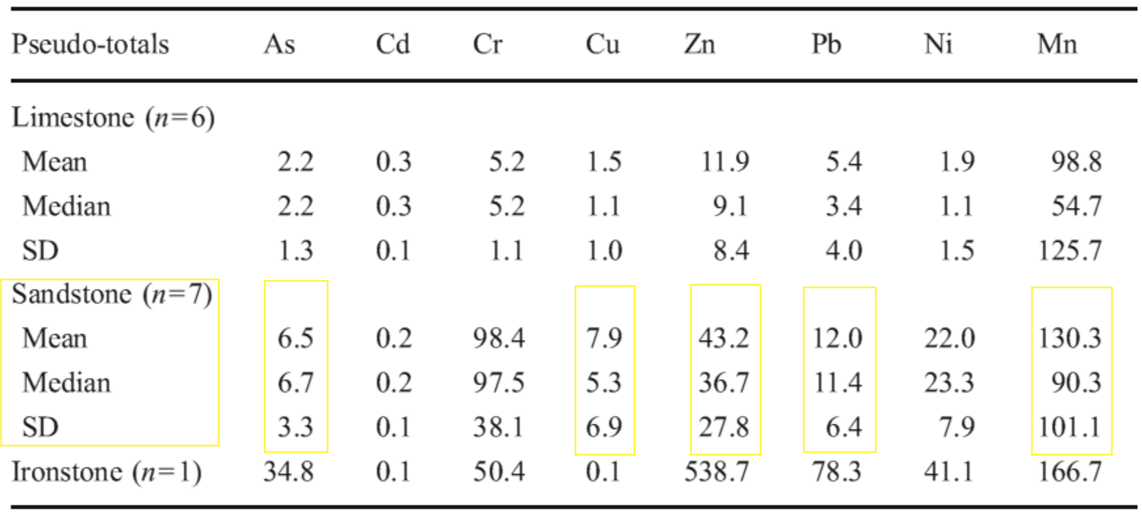
Table 3: pH values from six sites across Troopers Hill.

pH sample Number	GPS Reading	Area	pH value	Statistics for all samples	English ambient background value (UK SHS, 2007)
1	N.51°.45606° W.002°.53412°	Transect 1:Top of hill west	4.4	Mean=4.1	pH =5.9
2	N.51°.45635° W.002°.53525°	Transect 1: east	4.6	Median =4.05	
3	N.51°.45553° W.002°.53465°	Transect 2:Gully	3.9	St Dev =0.358	
4	N.51°.45556° W002°.53319°	Transect 2:Gully	4.1		
5	N.51°.27.337 W.002°.32.019	Transect 3:Top	3.6		
6	N.51°.27.185° W.002°.32.059°	Transect 3:Bottom	4.0		

Table 3 shows Troopers Hill pH readings to be classed as acidic in nature, with a mean value of 4.1 and a standard deviation from this of 0.358. This is significantly low so values collected are consistent to the mean. The lowest pH value 3.6 was recorded for sample 5 at the top of transect 3. This area is in very close proximity to the copper smelter building (approx. 500cm). The highest pH value 4.6 was found at the top of Troopers hill to the east on transect 1. All values are significantly lower than the proposed English Ambient back ground value 5.9 (UK soils 2007).

3.2 Background heavy metal values in Bristol soils

Table 4:'Pseudo- total' and 'near total' heavy metals (values in mg/kg,) in rocks for areas of Limestone, Sandstone and Ironstone in Bristol (Giusti,2011).

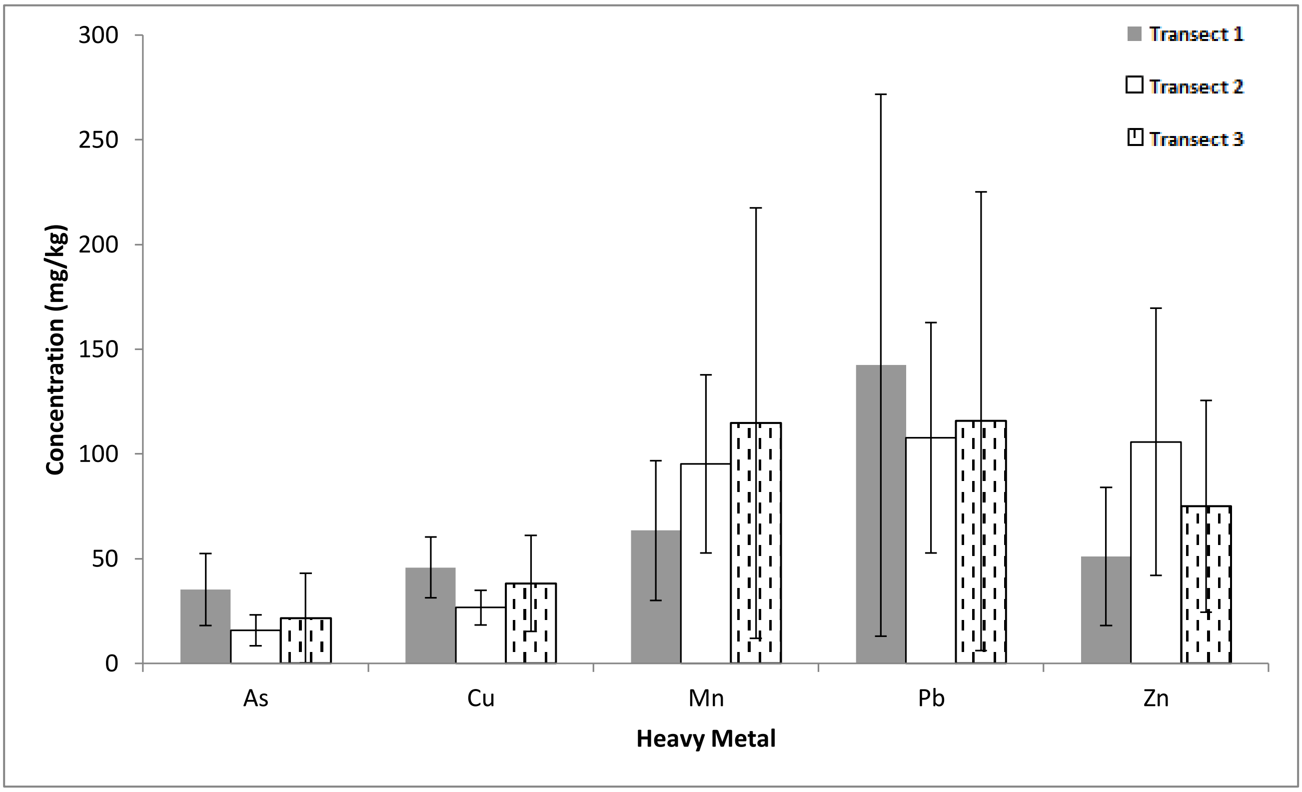


Pseudo-totals	As	Cd	Cr	Cu	Zn	Pb	Ni	Mn
Limestone (*n*=6)								
Mean	2.2	0.3	5.2	1.5	11.9	5.4	1.9	98.8
Median	2.2	0.3	5.2	1.1	9.1	3.4	1.1	54.7
SD	1.3	0.1	1.1	1.0	8.4	4.0	1.5	125.7
Sandstone (*n*=7)								
Mean	6.5	0.2	98.4	7.9	43.2	12.0	22.0	130.3
Median	6.7	0.2	97.5	5.3	36.7	11.4	23.3	90.3
SD	3.3	0.1	38.1	6.9	27.8	6.4	7.9	101.1
Ironstone (*n*=1)	34.8	0.1	50.4	0.1	538.7	78.3	41.1	166.7

As parent material and weathering processes are responsible for the natural geochemical characteristics of soils it's important to know the range of background heavy metal values in soils. These were adopted from Giusti, (2011), Table T1 as secondary data. Parent material for Troopers Hill is sandstone; values highlighted in yellow are the metals that were analysed in this study.

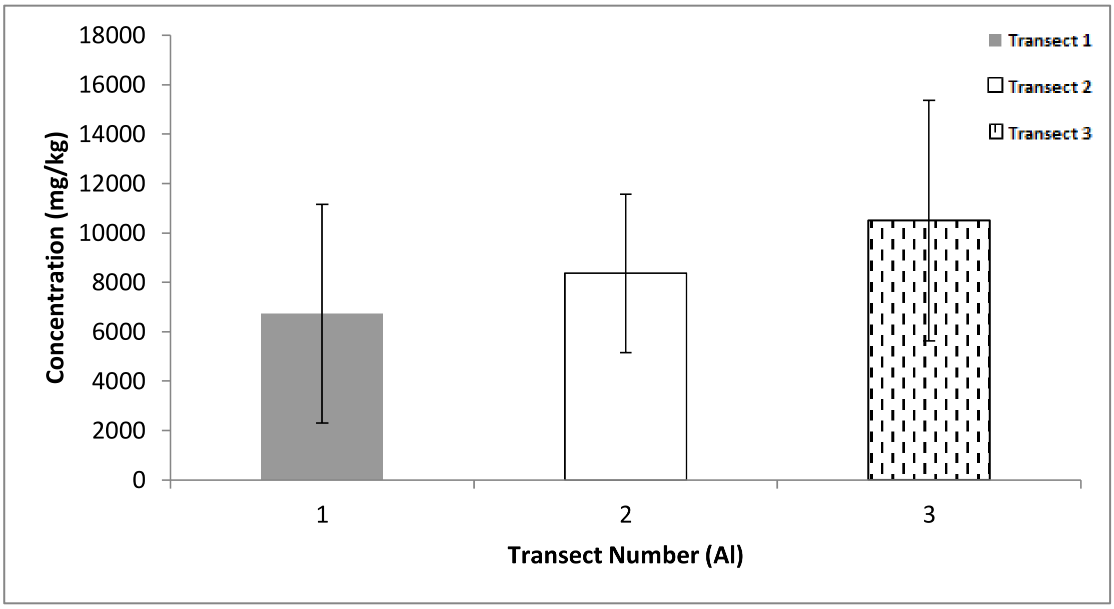
3.3: Heavy metal results from Transects

Figure 8: Mean concentration of metals from transects 1, 2 and 3 on Troopers Hill. Error bars represent 1standard deviation of results from 19 samples from Transect, 23 from Transect 2 and 22 from Transect 3.



As and Cu were found in lower concentrations to Mn, Pb and Zn. The lowest overall value was found of As in transect 2 (0.87mg/kg) and the highest of Pb in transect 1 (280mg/kg). As and Cu were found in lower concentration in transect 2 and higher in 1 and 3. Mn was found in lowest in transect 1 and highest in 3. Pb was found highest in 1 and lowest in 2. Zn was found lowest in 1 and was the only element to be found highest in 3. Mean concentration values for 64 samples were as follow: As 23.56; Cu 36.29, Mn 92.51, Pb 120.7 and Zn 78.97.

Figure 9: Mean concentration of Al mg/kg from transect 1, 2 and 3 on Troopers Hill. Error bars represent 1 standard deviation from the mean.



Al had to be put onto a separate graph to the other elements due to a significantly higher change in the scale of element concentration. The mean concentration value of Al for the 64 transect samples was 8614mg/kg., the highest mean of all elements analysed. The lowest Al value was found in transect 1 (2611mg/kg) and with the mean value for the transect also below that for the 80 samples (6730mg/kg) and the highest in transect 3 (20120mg/kg).

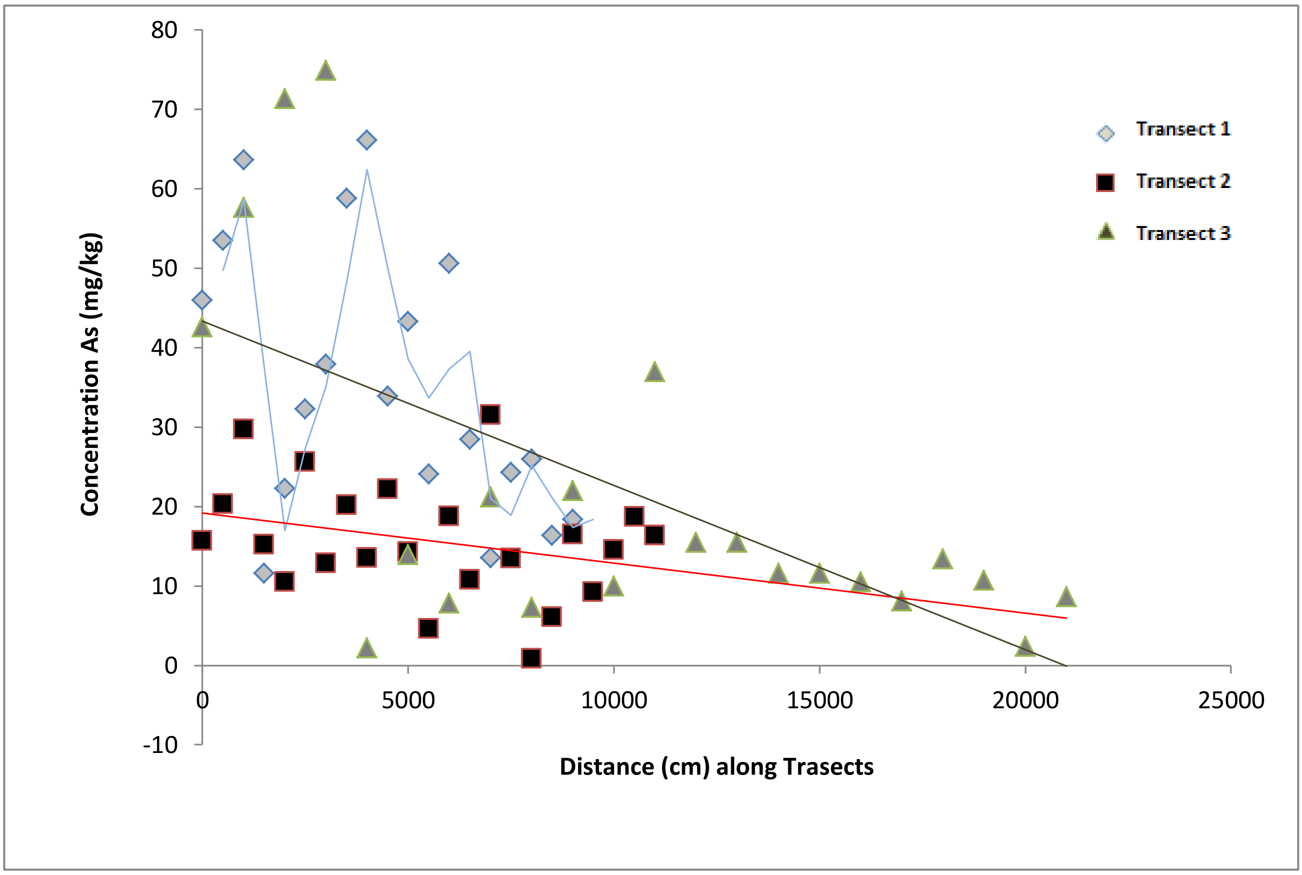
Table 5:.Showing the median values of elements on Troopers Hill against, Giusti, 2011 Troopers Hill results, the English ambient background values, Ambient background values in limestone rocks Bristol and suggested concentrations for UK soils. All units in mg/kg and number in bracket equates to number of samples (Environment Agency, SHS 2007), (ICRCL, 2002).

Metal	Median: Transects 1-3 (64)	Median: Deep soil profiles (16)	Median: Giusti study 2011 (9) Troopers Hill	English ambient background value UK soils (SHS, 2007)	Ambient value in Limestone rocks Bristol	UK Soil value mg/kg
As	16.44	30	35.9	8.32	6.7	32
Cu	32.09	49.28	43.1	17.4	5.3	130
Zn	61.60	119.6	47.7	79.5	36.7	300
Pb	93.8	110.2	221.0	40	11.4	450
Mn	81.06	156	128.4	450	90.3	N/A
Al	8107	13097	N/A	5-10% of sediment	N/A	50,000

Inferential statistics

A normality (Kolmogoror- smirnov) test was run on the samples to see if they were evenly distributed. Results showed P value of <0.010 which shows they had not deviated from expected distribution. A Student T test could be applied; results carried out on the 64 transect samples allowed for a Null hypothesis: there is no significant difference between the sample mean and the population mean to be accepted to 95% confidence levels for all six elements.

Figure 10: Concentration of As for transects 1, 2 and 3.



Transect 1 (blue line of best fit) is at the top of Troopers Hill and shows the most variation in results with some of the highest values of As found in this area. The pattern is not linear in nature however after a distance of 5000cm all values reduce in concentration (see figure 11 for clearer picture). Transect 2 (red line of best fit), the gully, has on average the lowest values of all the transects with the highest at only 32mg/kg. The values do display a weak negative correlation as they mostly decrease with distance (see figure 12). Transect 3 is the longest transect and reaches from the top to the bottom of Troopers Hill. This transect has the steepest negative correlation, having the highest and some of the lowest values of As (see figure 13).

Figure 11: Concentration of As along transect 1 Top of Hill west-east.

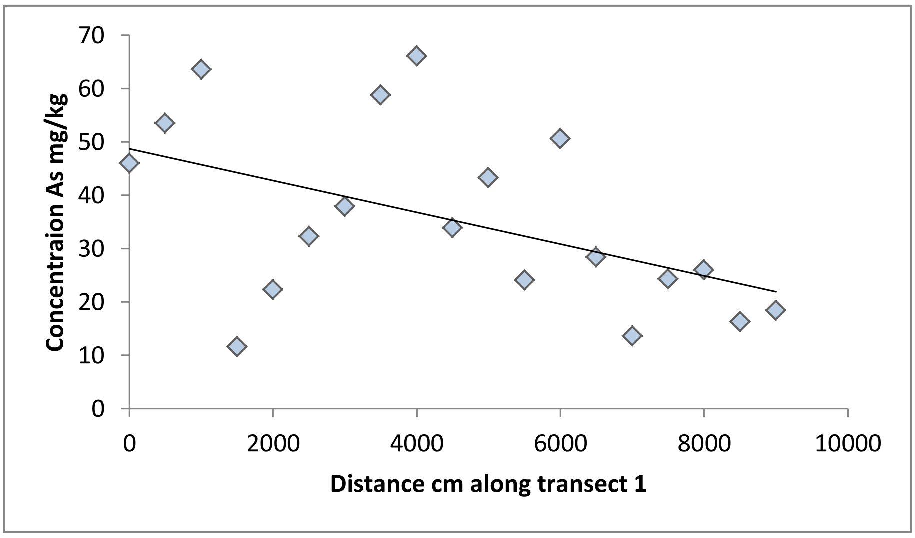


Figure 12: Concentration of As along transect 2, the Gully.

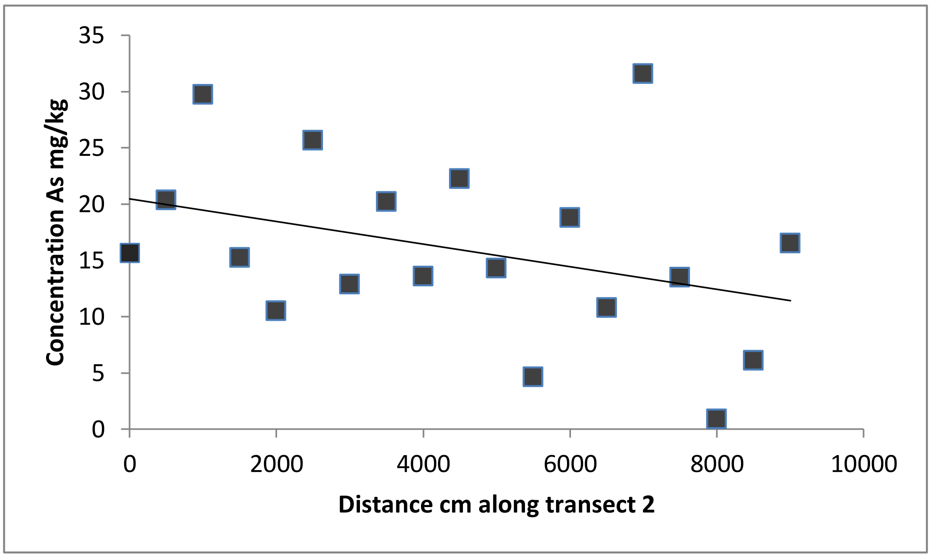


Figure 13: Concentration of As along transect 3, Top-Bottom of Hill.

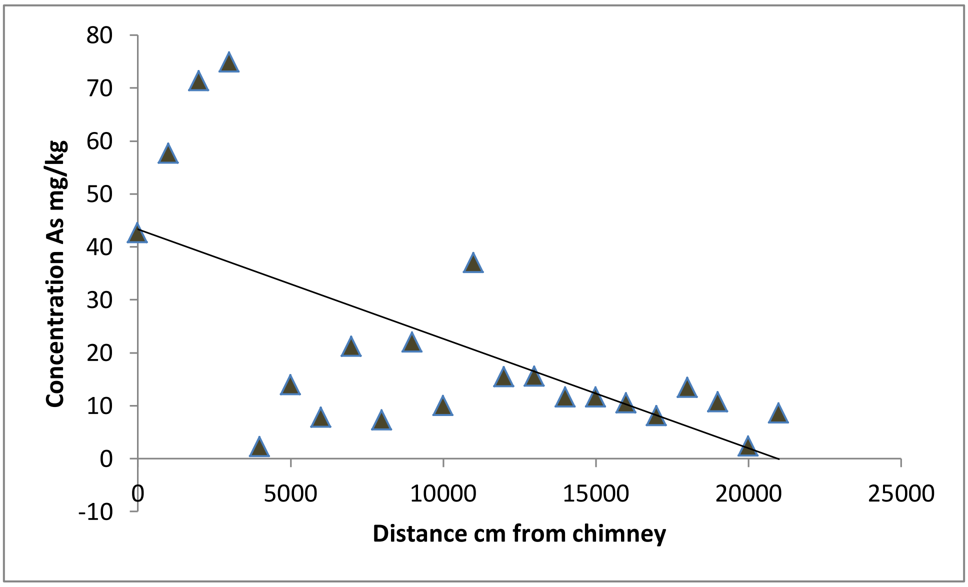
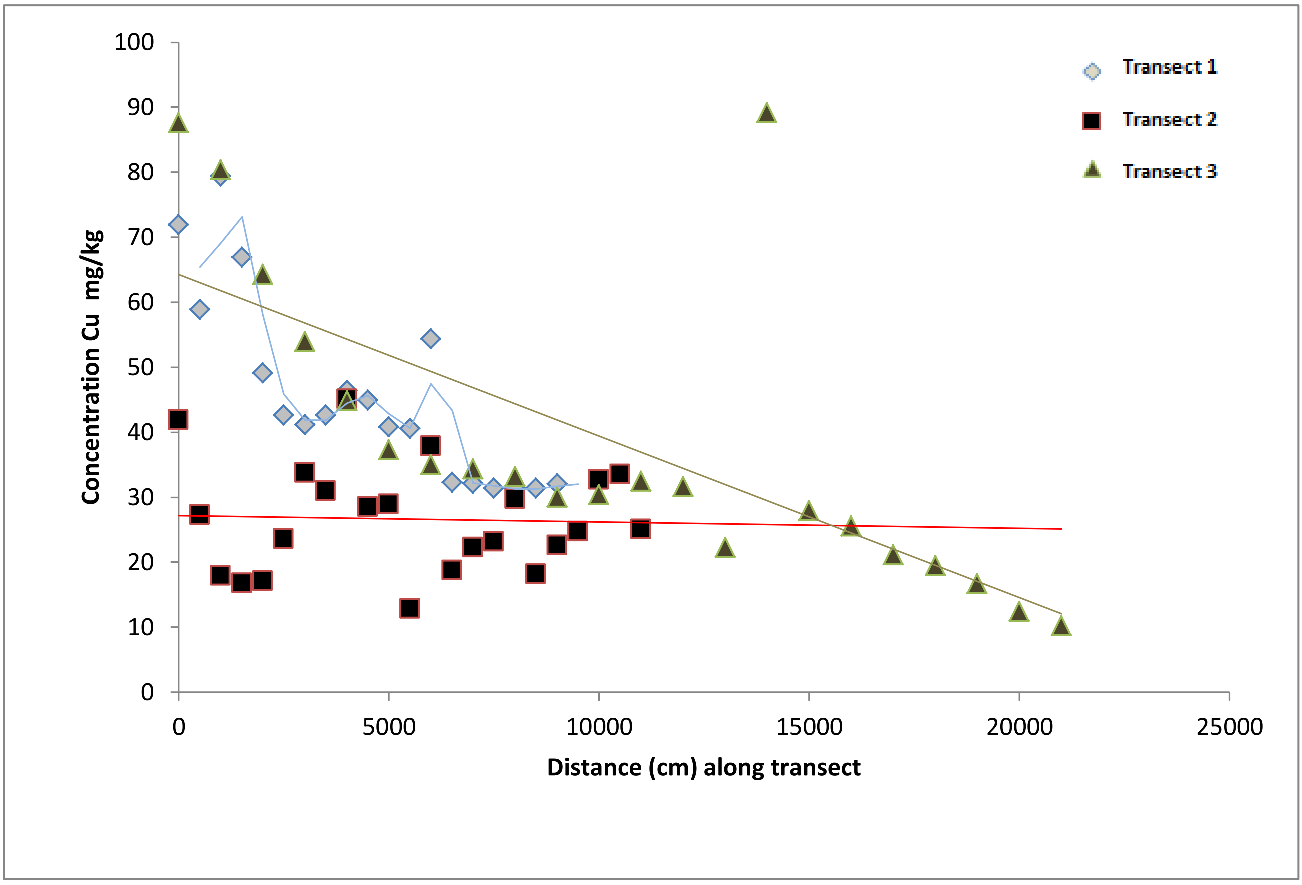


Figure 14: Concentration of Cu from transects 1, 2 and 3.



The start of transect 1 shows some of the highest total values of Cu, these reduce in an inconsistent pattern with distance and start to level off at about a distance of 6600cm. In location terms transect 1 shows Cu values reducing on site from west to east this pattern can be seen more clearly in figure 15 where is shows a strong negative correlation for the transect.

Transect 2 shows no correlation between concentration and distance for Cu. The highest concentrations are however found towards the more western side of the Gully, these are on a much lower scale to those found in transect 1 and 3. Figure 16 shows the highest concentration is about 45mg/kg and the lowest about 12mg/kg.

Transect 3 has a negative correlation as the concentration of Cu reduces as the distance from the chimney increases. The highest overall values of Cu on Troopers Hill are found at 0cm and 500cm from the chimney with the lowest found at the bottom of the hill over 20200cm (202m) away. However there is an anomaly at about 15000cm where the concentration of Cu is as high as the values at the top of the hill about 90mg/kg. see figure 17.

Figure 15: Concentration of Cu along transect 1 Top of Hill west-east.

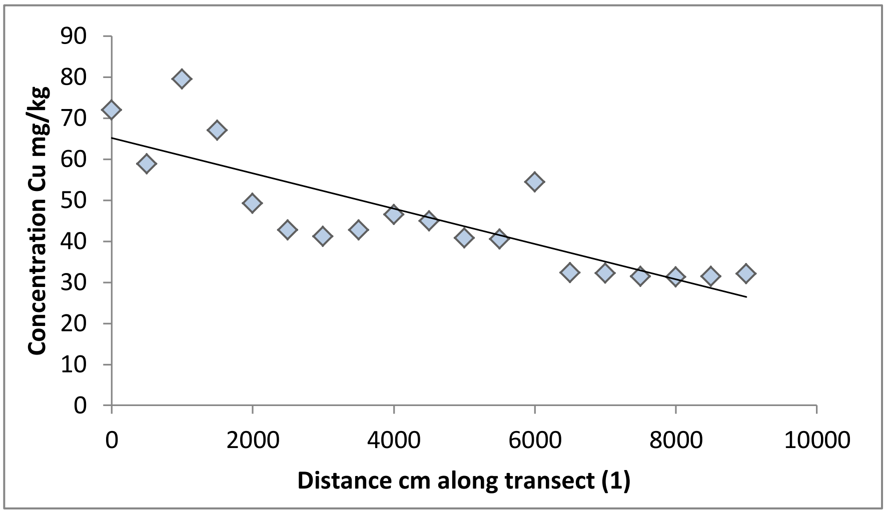


Figure 16: Concentration of Cu along transect 2, the Gully.

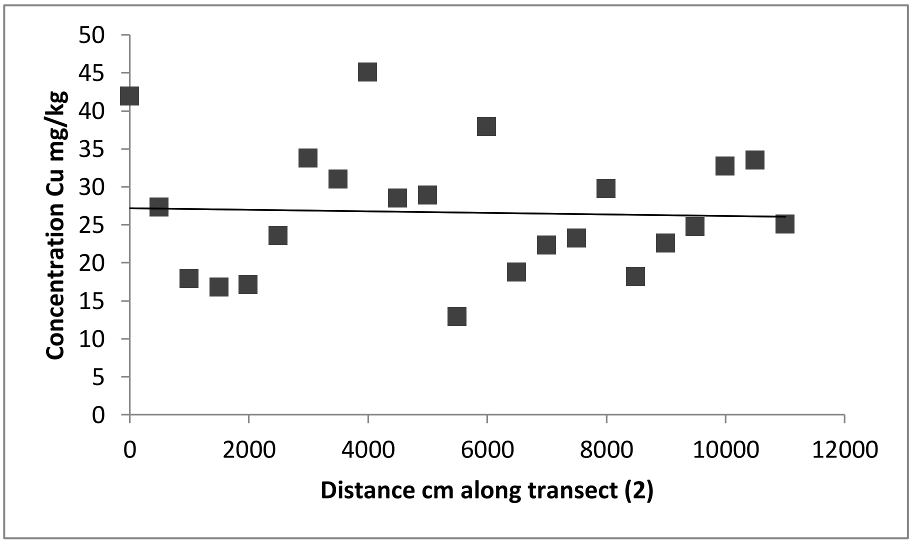


Figure 17: Concentration of Cu along transect 3, Top-Bottom of Hill.

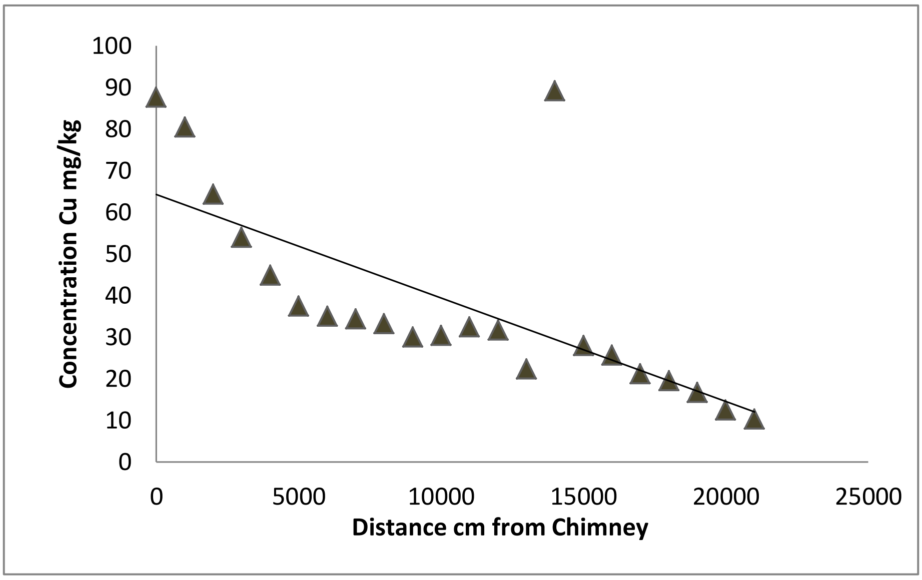
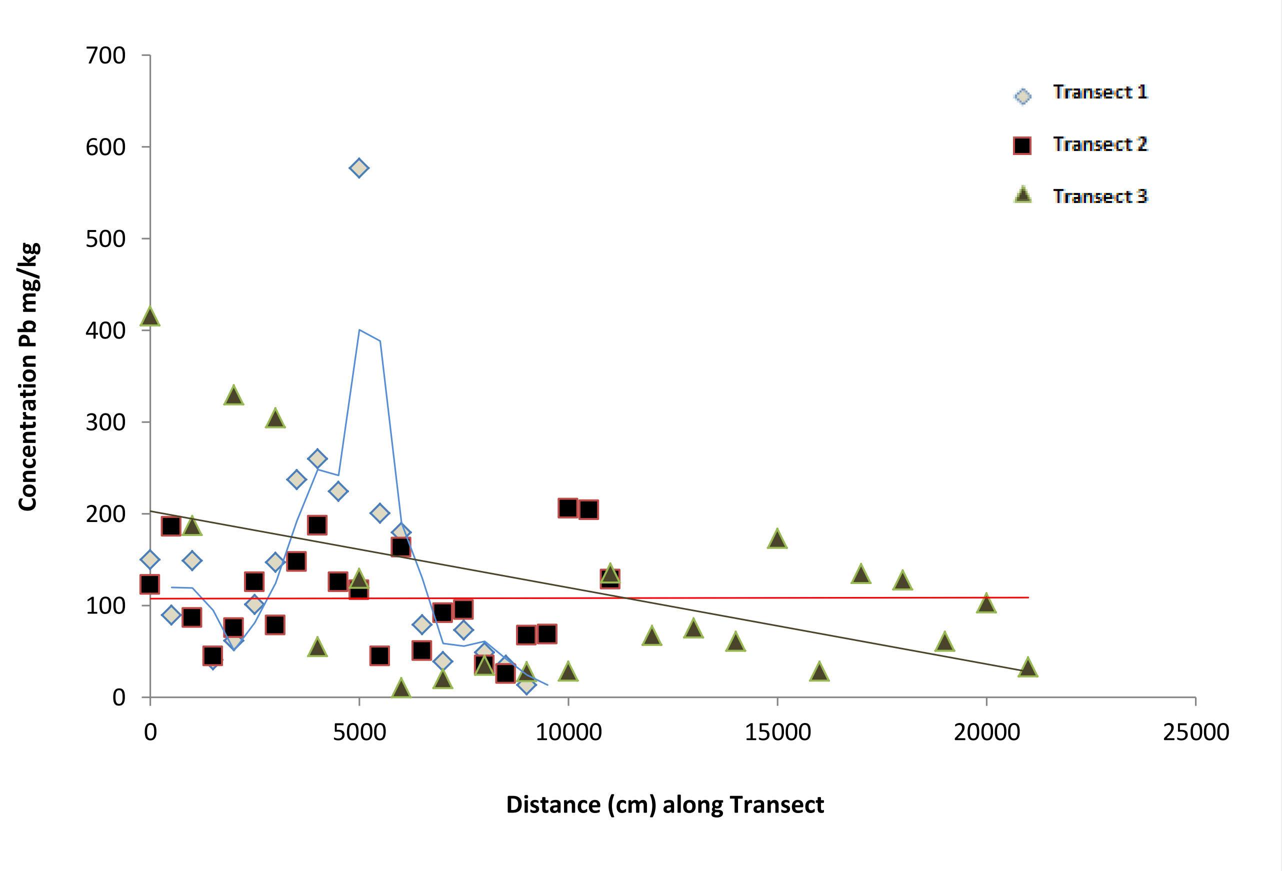


Figure 18: Concentration of Pb from transects 1, 2 and 3.



Transect 1 shows a changing pattern, with concentrations rising steeply from about 2000cm and peaking at about 5000cm at 590mg/kg. Concentrations then rapidly decrease with the lowest figures found orientated towards the east of the hill. Most values are below 200mg/kg in concentration see figure 19.

Transect 2 has the lowest values of the three transects with all values bellow 20mg/kg. There is no linear correlation between concentration and distance for Pb however there is a 'waved pattern of results' with values changing from high to low as distance increases.

Transect 3 has the highest concentrations of Pb of the three transects, these are found within the first 3000cm of the chimney with the highest value at 430mg/kg.. Between 5000cm – 10000cm the concentration of Pb vastly reduces to less than 50mg/kg, if these concentrations were higher and close to the line there would be a negative correlation. The concentration then picks up after 10000cm distance and is varied in concentrations close to either side of the line of best fit.

Figure 19: Concentration of Pb along transect 1 Top of Hill west-east.

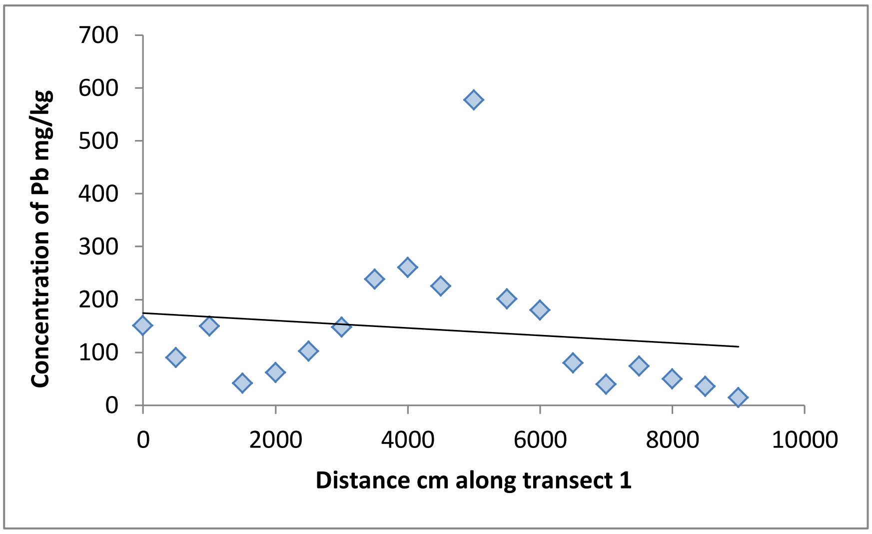


Figure 20: Concentration of Pb along transect 2, the Gully.

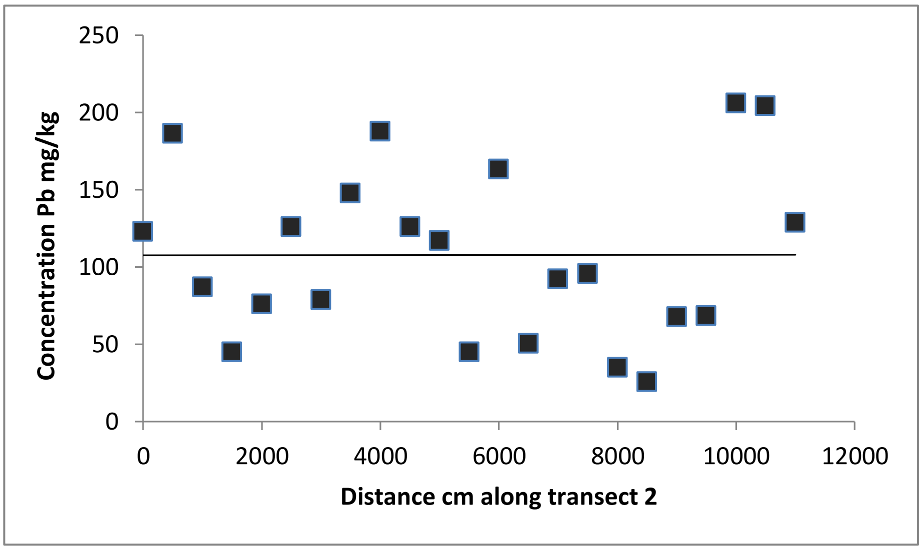


Figure 21: Concentration of Pb along transect 3, Top-Bottom of Hill.

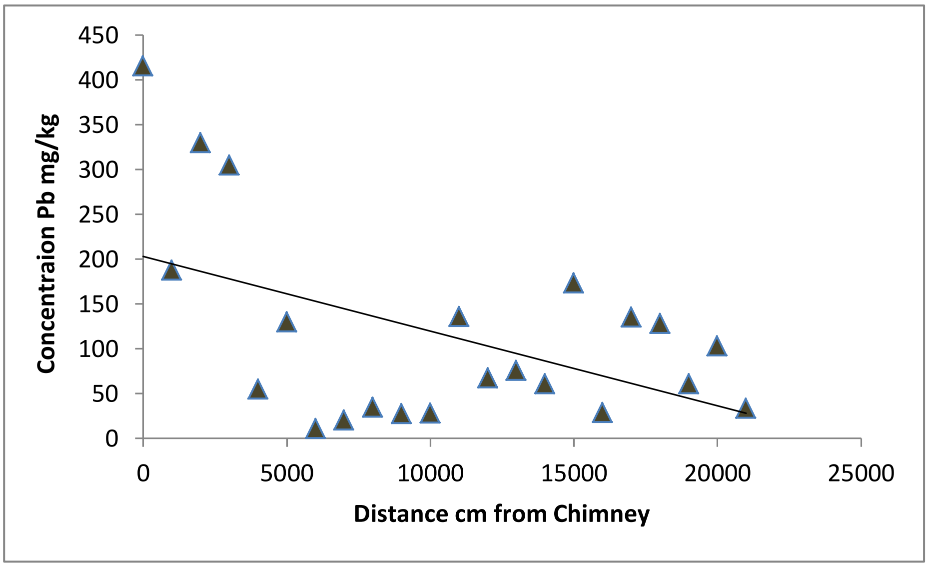
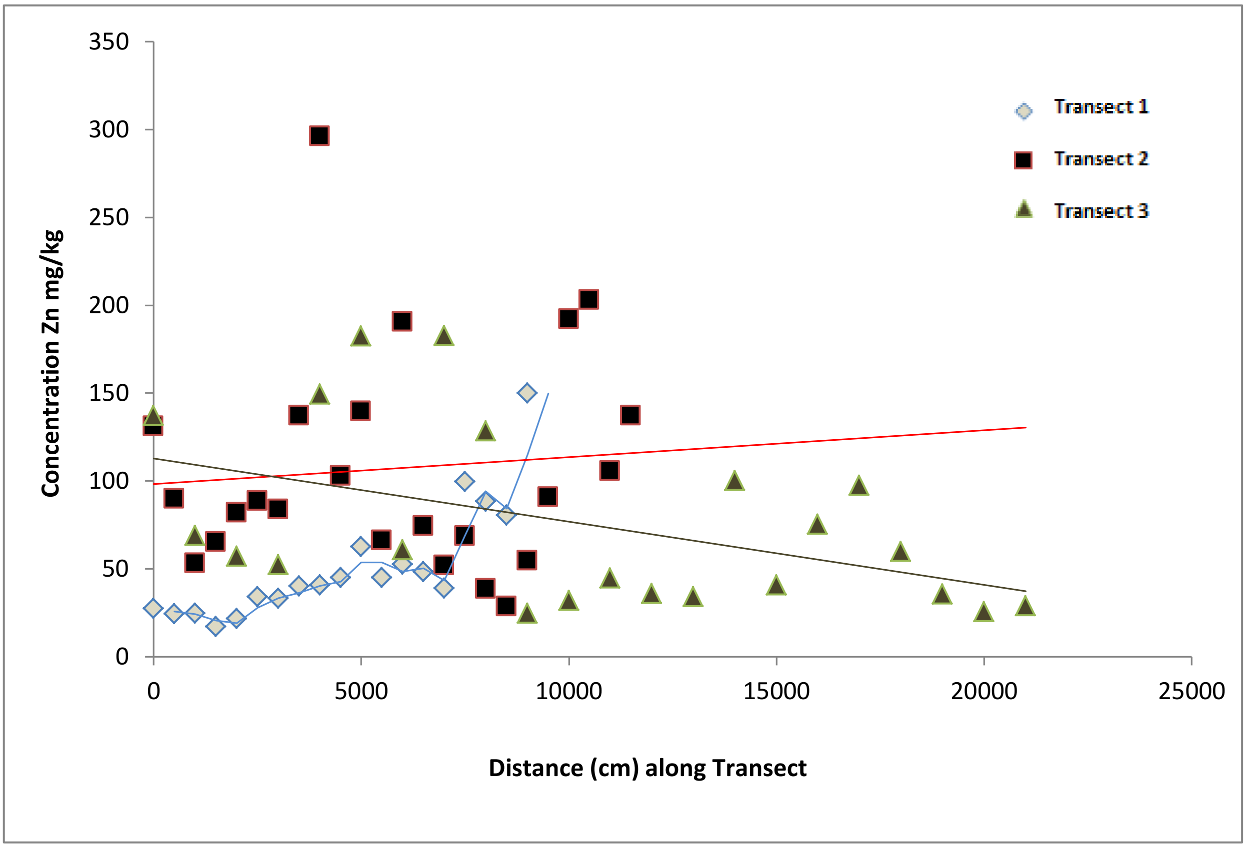


Figure 22: Concentration of Zn from transects 1, 2 and 3.



Transect 1 shows a positive correlation for Zn concentrations increasing evenly in concentration from 20mg/kg to 140mg/kg along the transect for most points. In terms of orientation the concentration increases from west to east on the site. This transect has the strongest correlation of the three see figure 23.

Transect 2 shows a slight increase in concentration and distance along the transect this equates to a very weak positive correlation; this can be seen easier in figure 24. Concentrations of Zn are on average higher than the other transects with the highest value found at 4000cm at 300mg/kg.

Transect 3 has a more negative correlation as concentration decreases as distance increases. After about 7000cm the concentration of Zn drops by about 100mg/kg this gradually increases and then drops again towards the end of the transect see figure 25.

Figure 23: Concentration of Zn along transect 1 Top of Hill west-east.

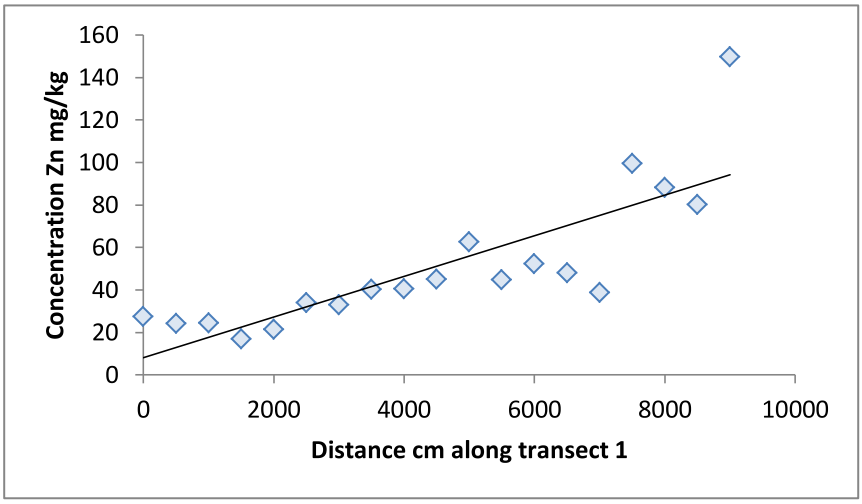


Figure 24: Concentration of Zn along transect 2, the Gully.

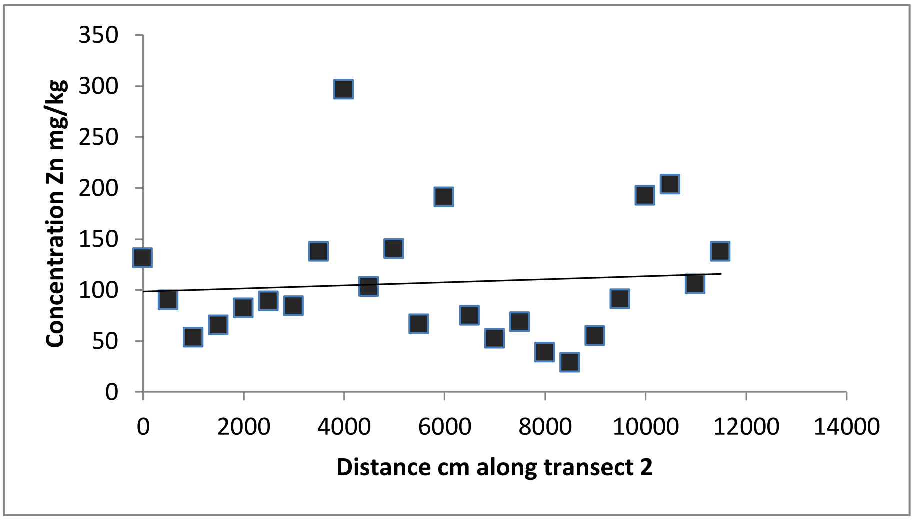


Figure 25: Concentration of Zn along transect 3, Top-Bottom of Hill.

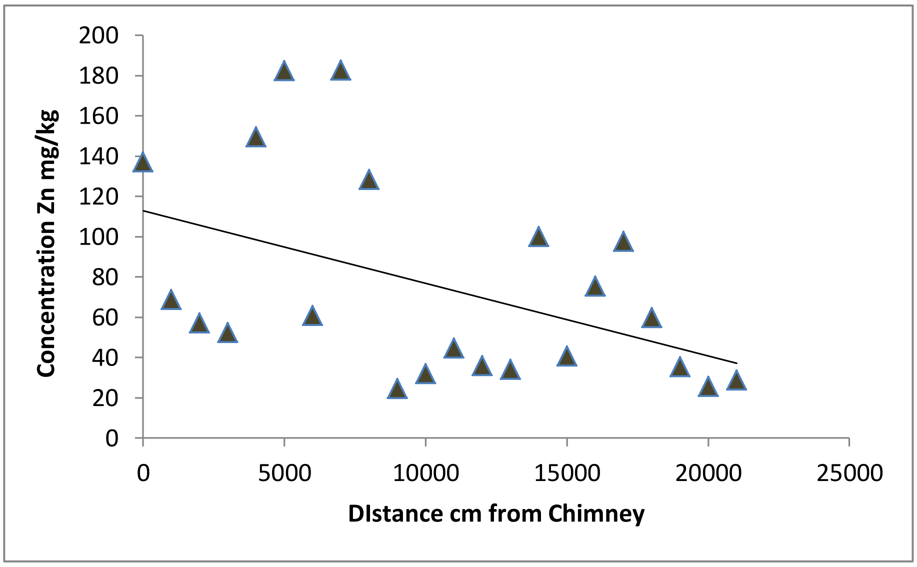
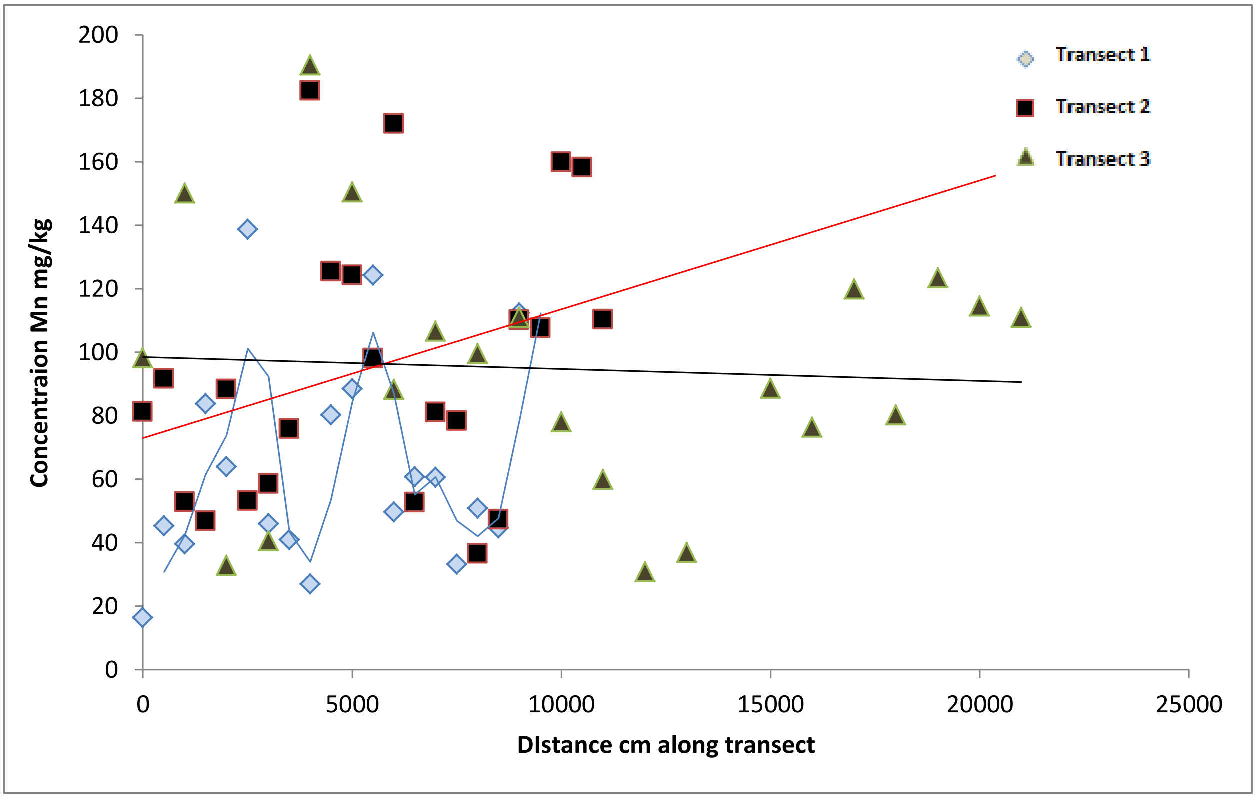


Figure 26: Concentration of Mn from transects 1, 2 and 3.



Transect 1 shows large fluctuations in the concentration of Mn along the transect, it is in a more waved pattern of high followed by low concentrations. There is no apparent correlation between concentration and distance. Some of the lowest concentrations of the three transects are found along transect 1 see figure 27.

Transect 2 shows a similar pattern to transect one, see figure 28 however concentrations fluctuate at a higher scale the highest value was 180mg/kg at 4000cm.

Transect 3 shows a fairly stable concentration along transect 3, with concentrations dipping around 10000cm and picking up around 15000cm. At the start and end of the transect concentrations are around the same about 100mg/kg, There is an anomaly just before 15000cm where the concentration of Mn rises significantly to about 500mg/kg see figure 29 (this point had to be taken off figure 26 due to the large change in scale bar when included).

Figure 27: Concentration of Mn along transect 1 Top of Hill west-east.

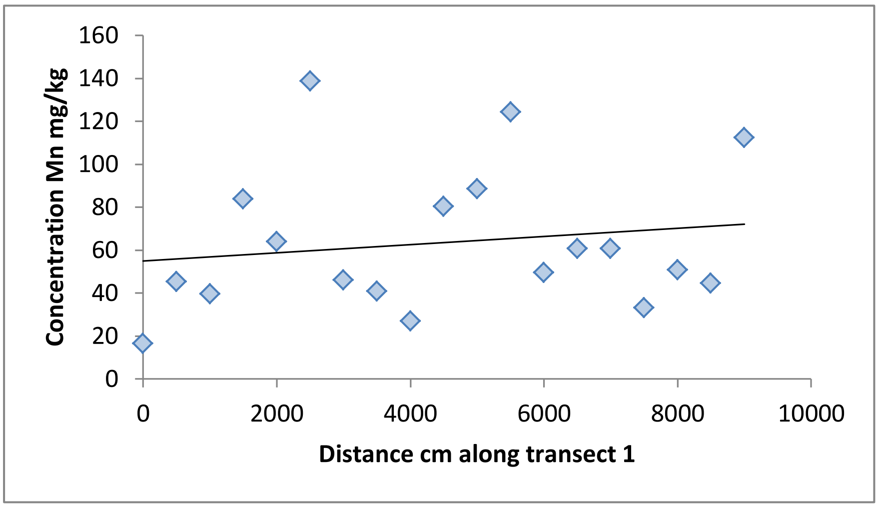


Figure 28: Concentration of Mn along transect 2, the Gully.

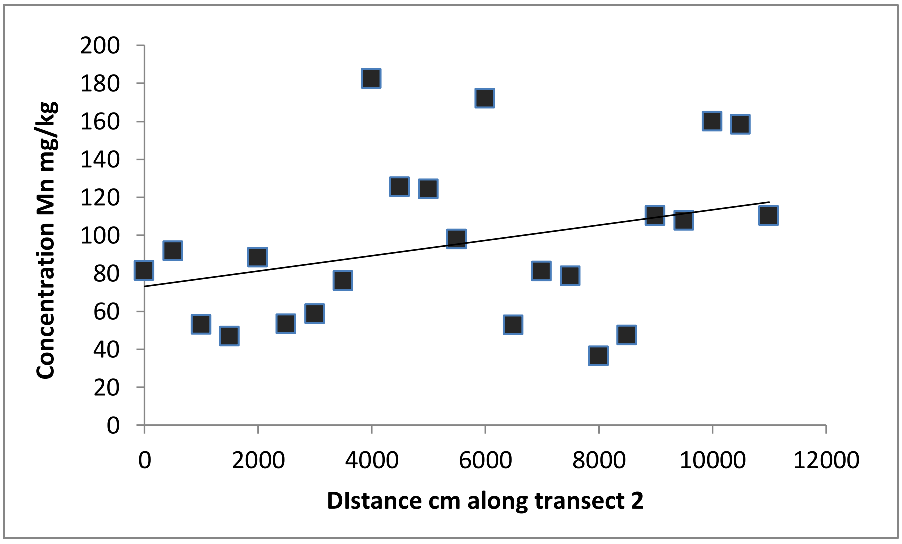


Figure 29: Concentration of Mn along transect 3, Top-Bottom of Hill.

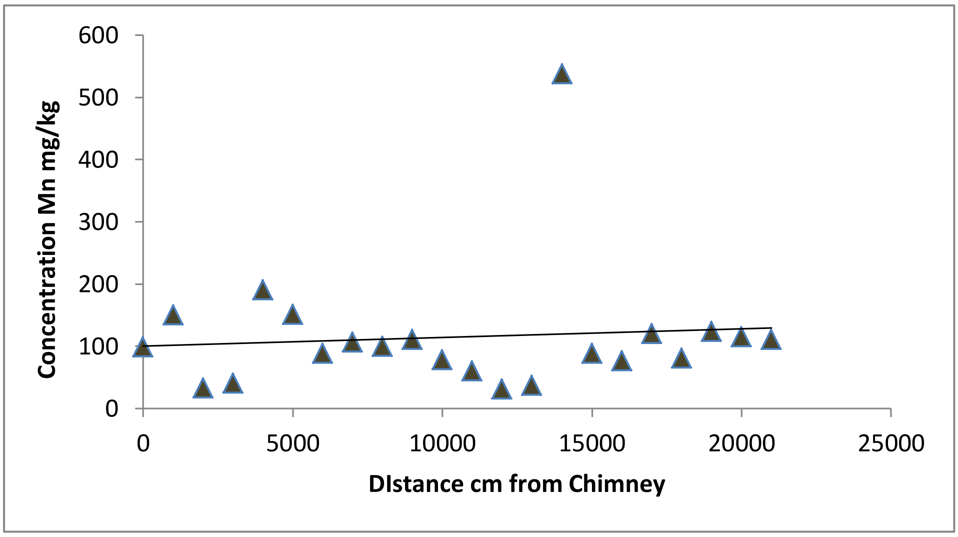
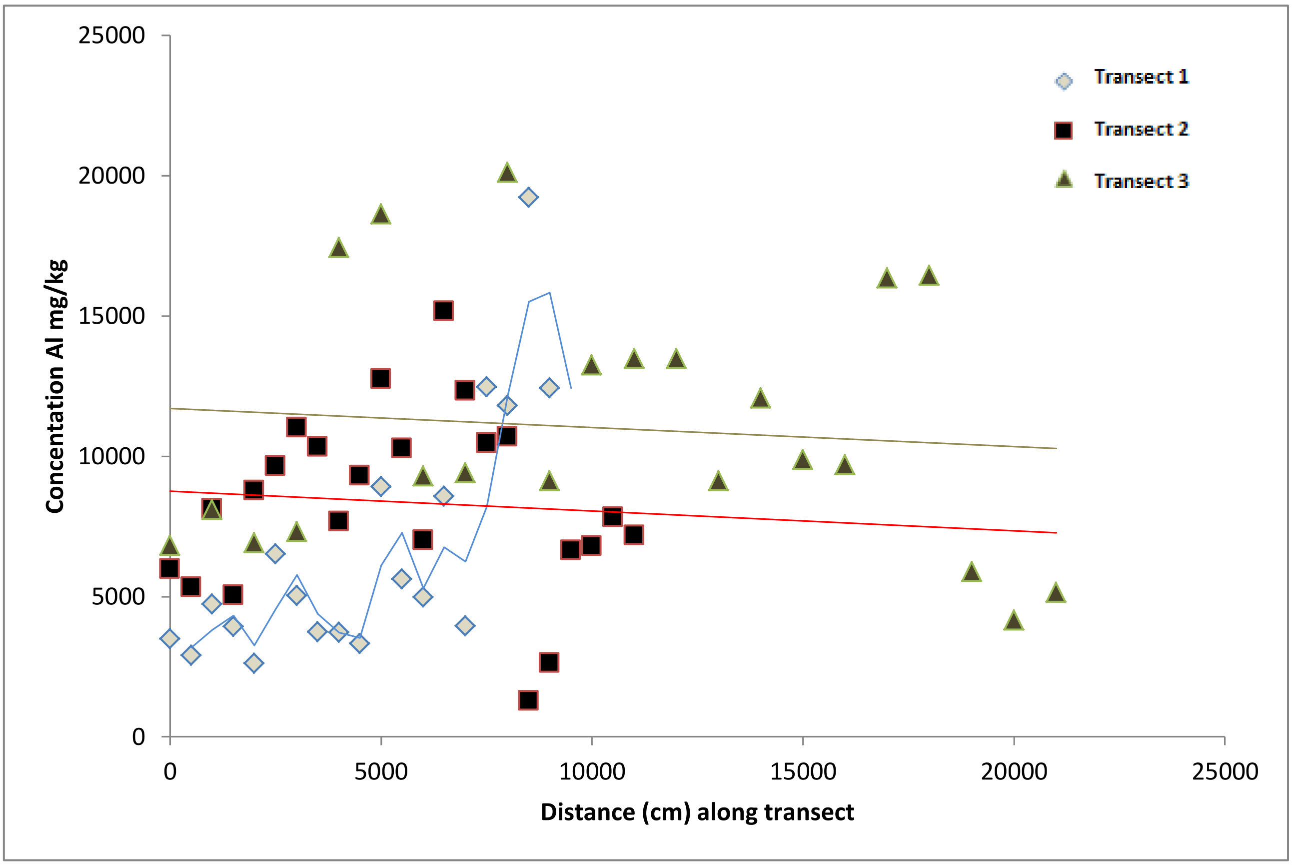


Figure 30: Concentration of Al from transects 1, 2 and 3.



Transect 1shows a positive correlation for Al concentrations increasing in concentration from about 4900mg/kg to 10,000mg/kg. In terms of orientation the concentration increases from west to east on the site. This transect has the strongest correlation of the three see figure 31.

Transect 2 has the highest consistent values of Al with most values over 9000mg/kg. There is no correlation between distance and concentration. The lowest values for all three transects are found towards the end of transect 2 and are less than 2000mg/kg.

Transect 3 has the highest values of Al reaching over 20,000mg/kg these are found around the distances 5000cm -10000cm. There is no correlation between the two variables, the lowest values are found at the beginning and end of the transect,

Figure 31: Concentration of Al along transect 1 Top of Hill west-east.

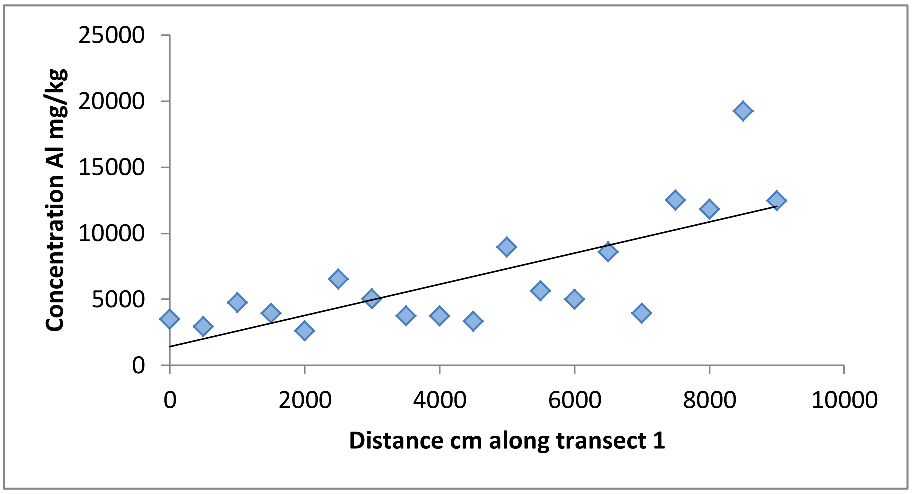


Figure 32: Concentration of Al along transect 2, the Gully.

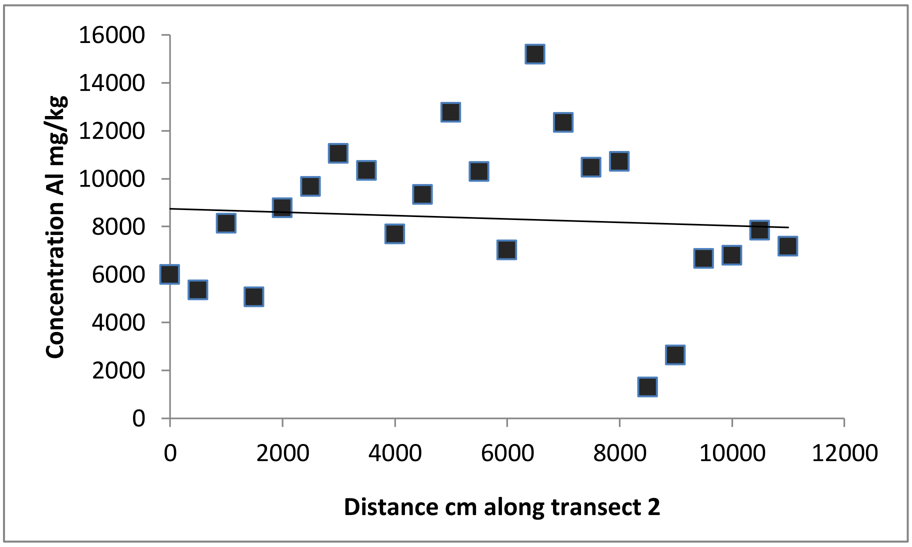
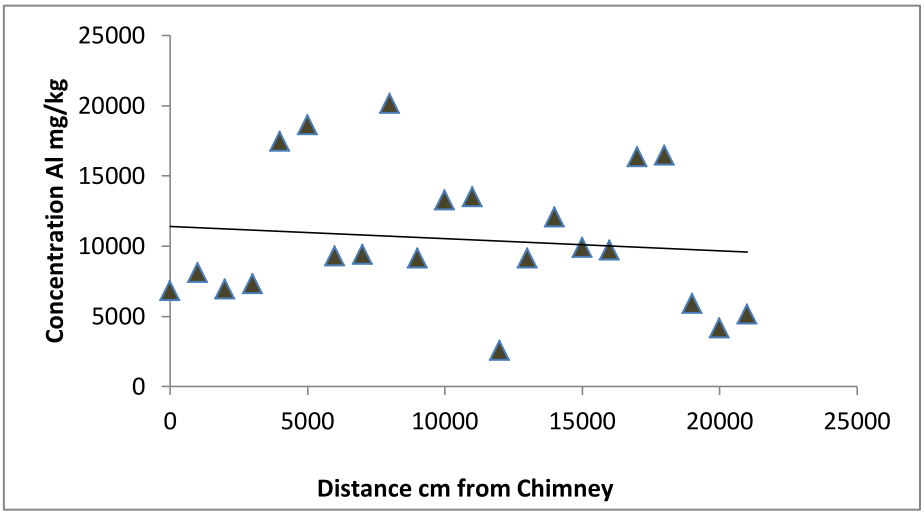
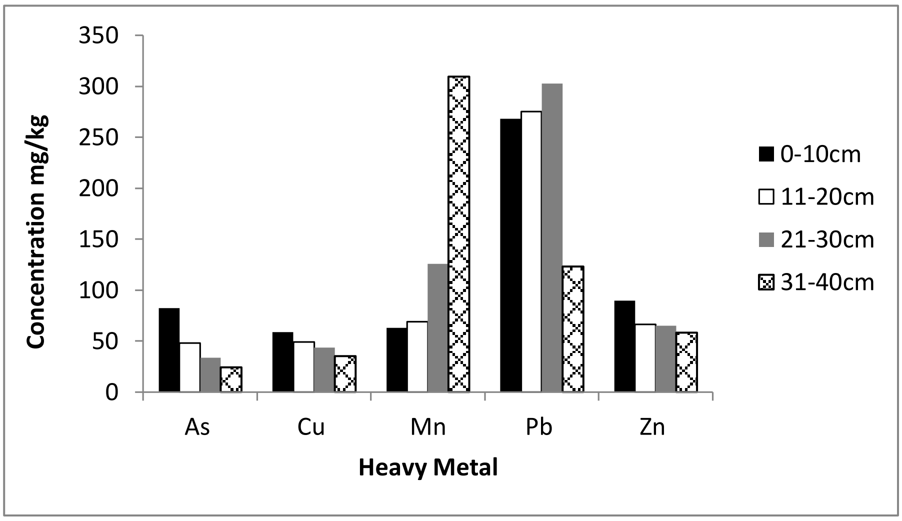


Figure 33: Concentration of Al along transect 3, Top-Bottom of Hill.



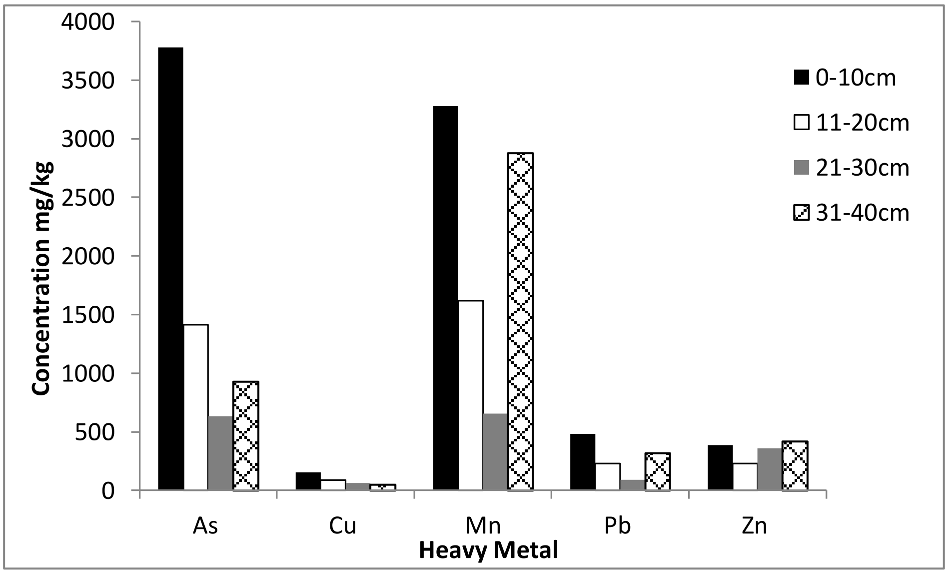
3.4 Deep soil profile results

Figure 34: Site A deep soil profile 0-40cm, top of transect 3 by chimney.



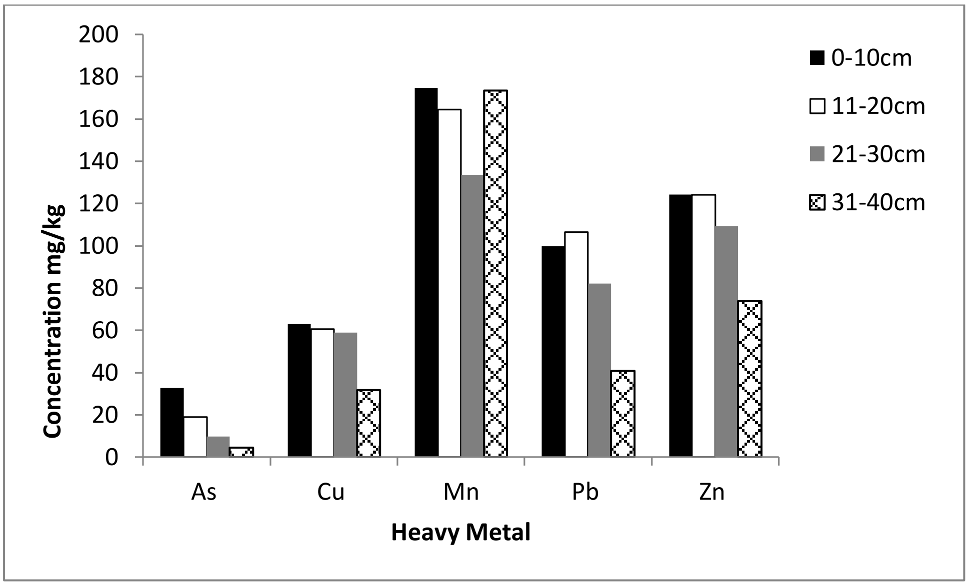
Of the five elements As, Cu and Zn decrease throughout the soil profile (see figure 38 for Al). Whilst Mn increases through the profile, Pb also increases but drops by almost half at 31-40cm. Mn and Pb were found in the highest concentrations.

Figure 35: Site B deep soil profile 0-40cm foot of hill behind mine shaft



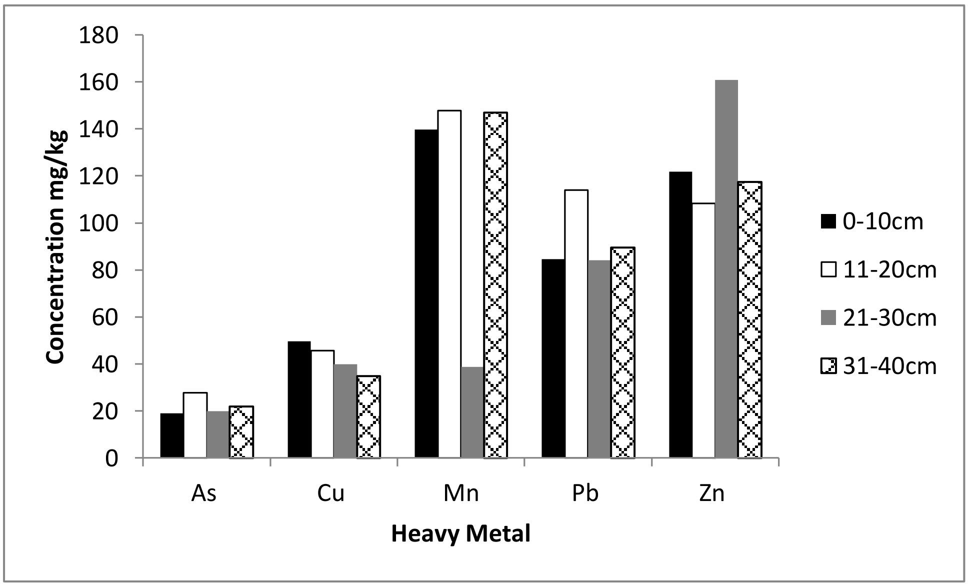
Elements at site B were found in the highest concentrations of all four sites. As is particularly high compared to other elements, but does decrease through the soil profile, only increasing slightly at 31-40cm, Mn follows a similar pattern but increase significantly at 31-40cm along with Pb. Cu decreases throughout, Zn stays about the same only dropping at 11-20cm (see figure 38 for Al)

Figure 36: Site C deep soil profile 0-40cm west side of hill.



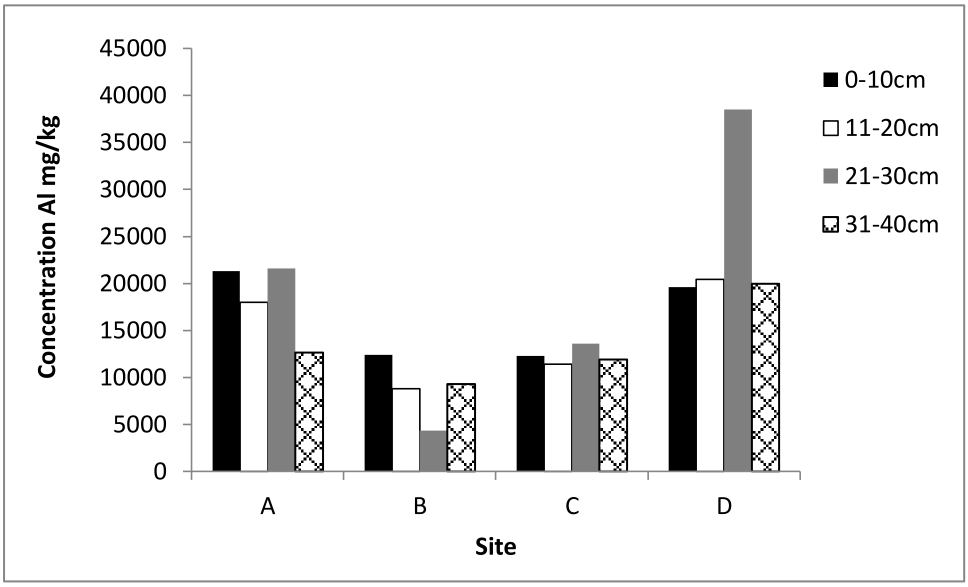
Elements As, Cu and Zn decrease throughout the soil profile. Mn decreases then rises at 31-40cm, whilst Pb rises at 11-20cm then decreases throughout the rest of the profile. Mn and Zn were found in the highest concentrations (see figure 38 for Al).

Figure 37: Site D deep soil profile 0-40cm east side of hill.



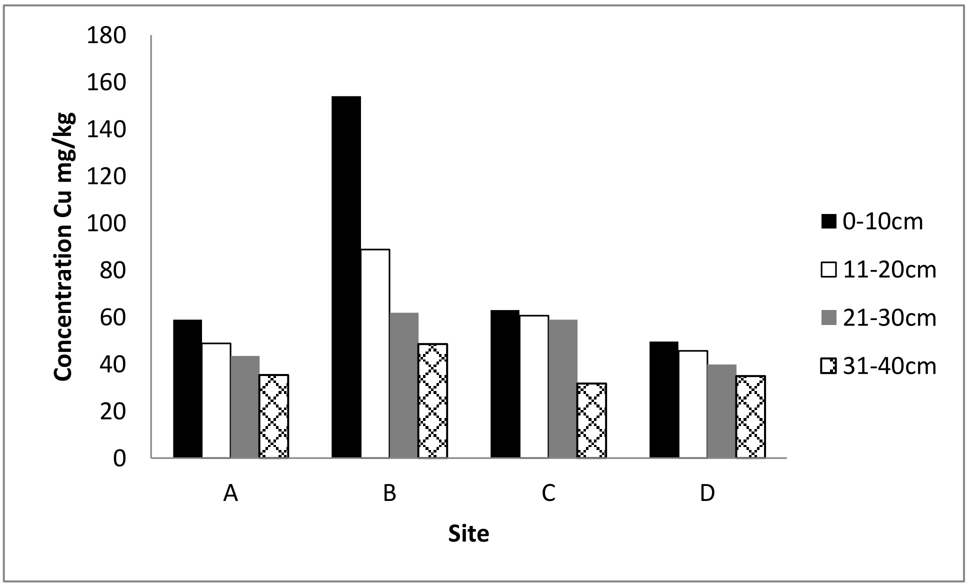
Elements were found in the lowest concentrations at this site. Cu is the only element to decrease throughout the entire profile. As remains around the same concentration fluctuating slightly. Mn and Pb increase in concentration with the exception of 21-30cm sample which decreases. Zn decreases in concentration with the exception of 21-30cm which increases and is the highest concentration found at site D (see figure 38 for Al).

Figure 38: Al deep soil profile 0-40cm for Site A-D



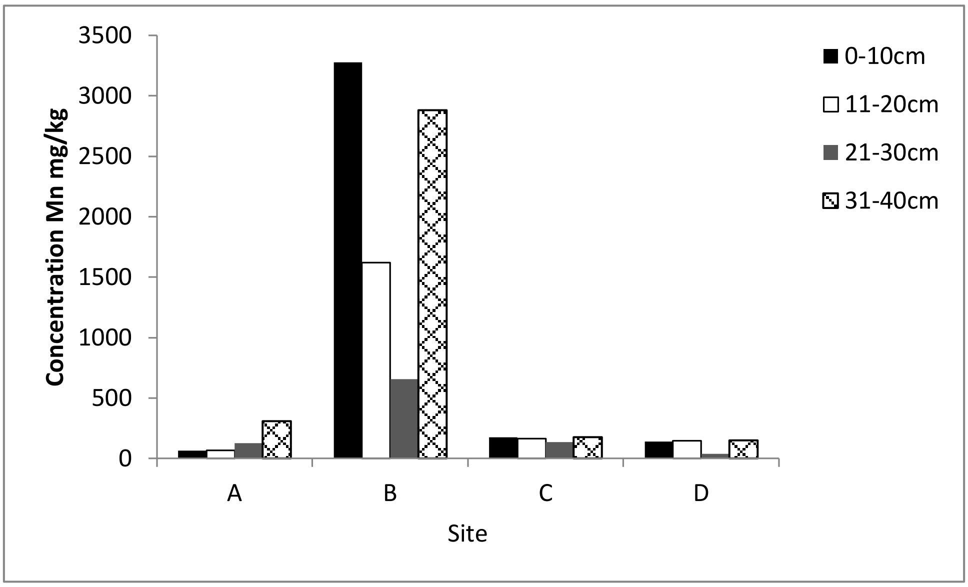
Al is found in highest concentrations at site D where 21-30cm was abnormally high in concentration compared to the other samples reaching 40000mg/kg however site A has similar values for other samples. Concentration decreases in site B increasing only at 31-40cm. Concentration for site C remains almost stable at around 12500mg/kg.

Figure 39: Cu deep soil profile 0-40cm for Site A-D



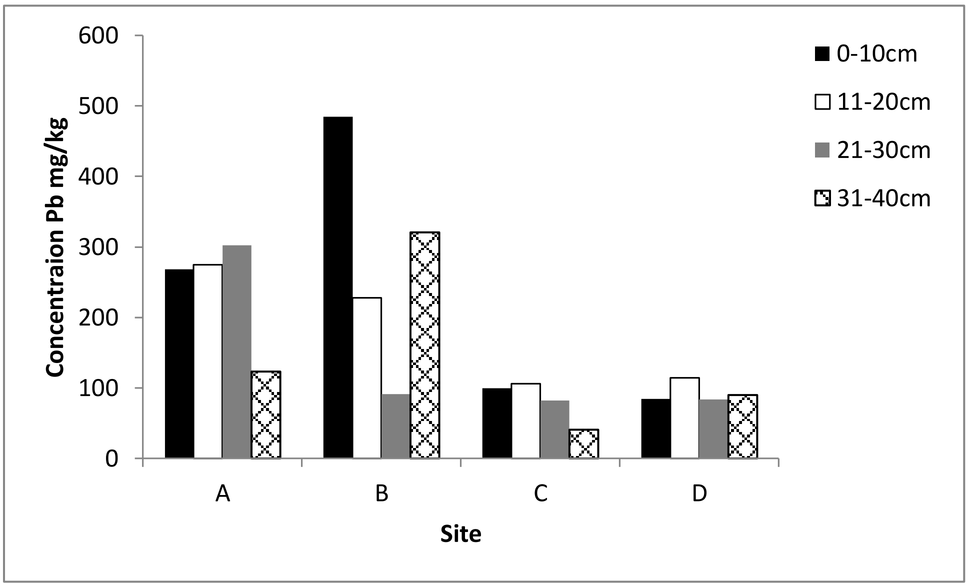
Cu decreases throughout the entire soil profile at all sites. It is found in highest concentration at site B 0-10cm where it reaches 150mg/kg. Sites A, C and D have similar values of Cu for 0-10cm around 60mg/kg.

Figure 40: Mn deep soil profile 0-40cm for Site A-D



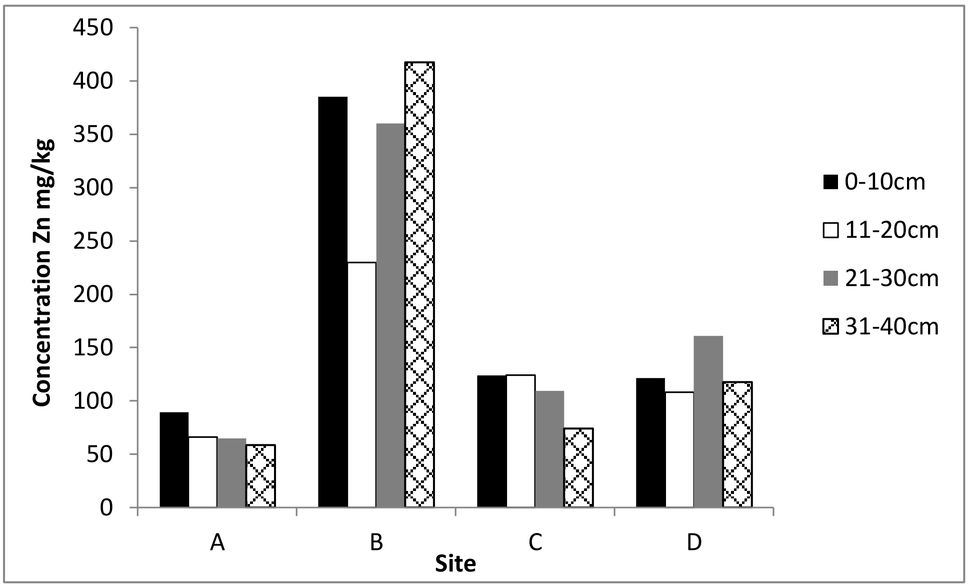
The graphs scale bar for Mn is skewed by the very high values found at site B. Lowest values are present at site A which increase through the profile. Site C and D have similar values.

Figure 41: Pb deep soil profile 0-40cm for Site A-D



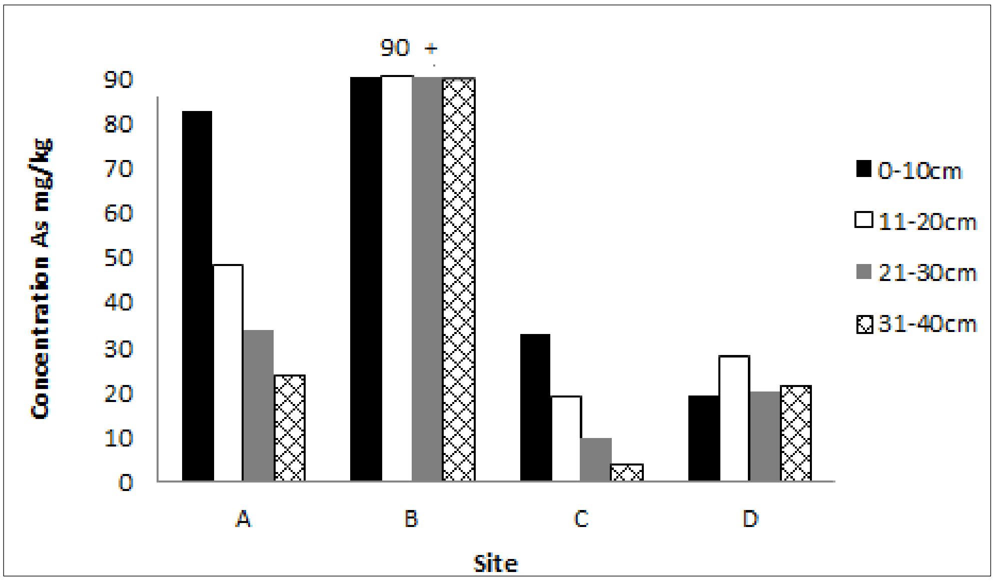
Site A and B have the highest values with site B 0-10cm being significantly higher. Site C and D have similar values but a different pattern with concentrations mostly decreasing,

Figure 42: Zn deep soil profile 0-40cm for Site A-D



Site A and C have concentration values that decrease through the soil profile, these site are also have the lowest concentration values, Site B has the highest concentration of Zn which stays around 350-400mg/kg only decreasing significantly at 11-20cm. Concentrations in site D are relatively stable with slight fluctuations, with the exception of 21-30cm which increases more.

Figure 43: As deep soil profile 0-40cm for Site A-D



Through site A and C the concentration of As decreases with depth, site A has almost double the staring concentration as C. Site B has larger concentrations than the scale bar (these were as follows 0-10cm 3781mg/kg, 11-20cm 1412mg/kg, 21-31cm 633mg/kg and 31-40cm 930mg/kg). Site D has consistent levels with the exception of 11-20cm which increases.

Chapter 4.0 Discussion, Analysis and Interpretation

4.1 Metals polluting Troopers Hill against soil guide line values.

Metal contamination and soil leaching varies spatially across Troopers Hill due to the following soil characteristics; pH, geology, habitat, topography and profile and anthropogenic influences from industry.

Results show the median value for As concentration on Troopers Hill (64 samples, transects 1-3) as 16.44mg/kg this is an acceptable concentration for As against the recommended soil guideline values for 2007 as a value over 32 is classed as polluted (see table 5), (Environment Agency SHS, 2007). Spatially however the results show a different picture, transect 2 the Gully is shown to have no results over 32mg/kg and has no As pollution (see figure 12). This is not the case for transect 1 and 3, transect 1 has a total of nine sites over 32mg/kg all within the first 6000cm of the transect and in close proximity to the copper smelter chimney, with the highest levels reaching 68mg/kg (see figure 10). Transect 3 has five sites over 32mg/kg and classed as polluted, it can be stated all As pollution (with the exception of one site on transect 3) is found within a 7 meter radius of the cooper smelter chimney, with higher levels the closer in proximity, with levels immediately outside the chimney reaching as high as 75mg/kg (see figure 13). These results are supported by Giusti's (2011) median value of As pollution on Troopers Hill 35.9 being above guideline values (see table 5).

Results for Cu show the median value as 32.09mg/kg (64 samples, transects 1-3) this is lower than results obtained by Giusti (2011) 43.1mg/kg for Troopers Hill however he conducted a smaller study with only nine samples (see table 5), (Environment Agency SHS, 2007). This is an acceptable concentration against the recommended soil guideline values for 2007 as a value for Cu has to be over 130mg/kg to be toxic to humans both copper and zinc contaminants are phytoxic but not normally hazards to health (ICRCL, 2002). Phytoxic effects are more common in acid soils Cu has to reach a value of 130mg/kg and Zn 300mg/kg to cause phytoxic effects. This is why the guideline values are higher than expected. However any value for Cu over 17.4mg/kg the English ambient background values for UK soils is classed as polluted. Ambient background values are levels of what occur naturally and any other value over this is anthropogenic in cause and therefore pollution. By this any Cu value over 17.4mg/kg can be viewed as high in concentration and would suggest that 44/64 sites on the transects are polluted. Spatially pollution levels can be seen to be highest in a 14m radius of the copper smelter chimney (see figure 14).

Normally acid soils increase Cu uptake, however this area had no vegetation accounting for the higher levels found. Copper is the most immobile micronutrient this could account for the highest levels being found in places with minimal vegetation and why there are high levels in the Gully despite it being further away than a 14m radius to the copper smelter chimney with higher levels the closer in proximity, with levels immediately outside the chimney reaching as high as 89mg/kg (See figure 16), (Holdgate,1979). Giusti's (2011) study also supports that levels of Cu on Troopers Hill are high as the median value for the study came out as 43.1mg/kg. There is no known naturally high source of Cu around Troopers Hill so the pollution levels must be the result anthropogenic causes i.e. the copper industry established in the 18th century and more recent pollution from Brass Manufactured with copper and zinc from the Mendip Hills (Bristol City Council, 2012).

Zn results showed the median value as 61.6 mg/kg (64 samples, transects 1-3) this is an acceptable concentration for Zn against the recommended soil guideline values for 2007 as a value over 300mg/kg is classed as polluted at this value like Cu phytoxic effects occur (see table 5), (Environment Agency SHS, 2007, ICRCL, 2002). Concentrations of Zn are shown to increase from west to east from 20-140mg/kg across Troopers Hill as displayed by transect 1 (see figure 23). This is further supported that Zn is found in higher concentrations on the east of the site as on average highest concentrations were found in the Gully 300mg/kg was the highest concentration found which is on the borderline for contamination (see figure 24). Zinc is primarily added to the soil through the weathering of rocks (Ahmad *et al*, 2005) and therefore the Gully previously used for quarrying is the most weathered area on the hillside. In a study by Alloway, 2004 it was emphasised that both garden and agricultural soils in England and Wales have a higher mean of Zn and Pb when compared to other countries like Germany. These higher levels have been attributed to contamination from metal mining and the application of sewage sludge. In addition urban soils which Troopers Hill is classes as tend to have higher concentrations of Zn present than agricultural ones. Most often high Zn levels will reduce Cu (Allen *et al*, 1995) this is evident on Troopers Hill. On Transect 1 concentration of Cu reduces towards the east as Zn increases, Cu is found in lowest concentrations in the Gully on average this is where the highest Zn levels are.

Pb is naturally low in sandstone geology, this could account for the low median 93.8mg/kg found (64 samples, transects 1-3). This is an acceptable concentration against the recommended soil guideline values for 2007 as a value for Pb has to be over 450mg/kg to be classed as contaminated (see table 5), (Environment Agency SHS, 2007). Pb varies spatially over Troopers Hill with one value over the UK soil guidelines, this is located midway along transect 1 590mg/kg (see figure19). This high value could be accounted for by its location in a ditch with little vegetation. The Gully has lowest levels of Pb some as little as 20mg/kg lower than the English ambient background value. Whilst transect 3 has the highest concentrations found in a 3meter radios of the smelter chimney (see figure 21). These high levels cannot be accounted for naturally and are the result of pollution from onsite metal smelting.

Plants grown in acid soils can experience a variety of symptoms including aluminium (Al), hydrogen (H), and/or manganese (Mn) toxicity (Phipps, 1981). However lower levels of Al, median

8107mg/kg, are found than expected as sediments often contain 5-10% Al 50,000-100,000mg/kg (see table 5), (Environment Agency SHS, 2007). Lower Al levels in soils could be accounted for as they increase in solubility at low pH Al when dissolved becomes Al^{3+} and is toxic to plants (see figure 30). Al is not a plant nutrient and is not actively taken up, instead enters the roots through osmosis. Al toxicity is one of the most widespread problems in acid soils as it damages root cell membranes. Some plants have adapted to deal with Al toxicity this is investigated in the study by (Watanabe and Osaki, 2002). Highly weathered soils are often characterized by having high concentrations of Fe and Al oxides, the Gully has higher levels of Al than the top of the hill because of this, levels are variable downhill higher in areas of more exposed rock (see figure 32).

Acidic soils are drier and less compact in nature this affects the availability of Mn in the soils making the concentrations lower, this is reflected in the median value (64 samples, transect 1-3) 81.06mg/kg, Giusti's (2011) also found low levels of Mn 128.4mg/kg (see table 5), (Environment Agency SHS, 2007). A value much lower than the ambient background one for English soils of 450mg/kg. However manganese, like aluminium becomes increasingly soluble as pH drops, and can account for the low concentration found in the soils on Troopers Hill. A common side effect of low pH (usually 5.6 and below) is manganese toxicity symptoms, usually the crinkling or cupping of leaves (Phipps, 1981).

4.2 pH influence on found metal concentrations

Soil conservation services class a pH ranging from 4.5-5.0 as very strong acidic and from 3.5-4.4 as extreme acidic soils. Table 3 shows Troopers Hill pH readings to be classed as extreme acidic in nature, as the mean value is 4.1 this is significantly lower than the ambient background value for English soils which puts the idealistic baseline pH of English soils at 5.9, this pH is ideal for nutrient stability. When it falls below this level the major plant nutrients required for growth (N, P, K, S, Ca, and Mg) become significantly less this can be seen in the study by Marschner, (1988) however many plants have adapted to thrive at pH values outside this range. This is seen in the case of Troopers Hill which is home to a large range of plant species most abundantly, bracken, gorse, broom, bell heather; hawtorn, silver birch, oak (see section 2.5) This habitat is present due to the close relationship between vegetation and underlying soil as only plants that tolerate the acid soils survive. The main plants species found on the hillside are ones consistently found with acidic soils (Price, 2003), backing up the data's reliability.

Soils under a pH of 5.0 encounter problems with the mobilization of heavy metals so they are more likely to be held in the top layers of acidic soils like those on Troopers Hill (see section 4.4). Instead of leaching through soils they are taken up in greater concentrations by plants (Vernet, 1991). Increasing studies have been undertaken on the bioavailability of metals in plants and their effectiveness in decontaminating soils as a more natural remediation method for polluted soils (Ernest 1996, Gupta and Sinha 2008). Troopers Hill could consider this method for management of areas with highest pollution levels arsenic however this would be less effective for copper as unlike other heavy metals, such as cadmium, lead, and mercury, it is not readily bioaccumulated (Fernandes and Henriques, 1991).

In addition soil pH is considered an important variable in soils as it controls chemical processes. Metal concentration is also affected by pH this is particularly the case for the following metals Cu, Fe, Mn and Zn which are sensitive to pH change (see figure 44), (Whiting *et al*, 2009). Highest pH values on Troopers Hill 4.6 and 4.4 are found at the top of the hill along transect 1. It is thought levels are highest here due to it being the furthest area of the reserve from the past mining activity which is the industry with the most changing effect on pH. It is also in close proximity about 300 meters from the Farm Allotment area where the pH of the soils have been treated (see figure 7) Giusti, 2011 recorded the pH there as between 6.5 and 6.8 for ten samples some micronutrients could have leached across. The recorded pH readings will have also been influenced by internal sources these include the parent material (sandstone for Troopers Hill, see figure 2 and table 4) and weathering processes which are responsible for the natural geochemical characteristics of soils. Sandstone rocks have a naturally higher concentration of the following metals As, Cr (very high naturally) and Cu compared to Limestone geology. However these are not as high as ambient levels found in soils forming over Jurassic ironstones e.g. the East Midlands of England which have elevated levels of arsenic pollution, areas of Northern Ireland also experience similar porblems as As, Cr, Ni concentrations exceed the Soil Guideline Values (SGV) due to parent material there excepted range is between 0.9-271mg.kg for As (Corridan, 1974), (The Gully located about mid-way up the hillside and has a lower pH range (3.9, 4.1) than transect 1 this could be the influence of internal sources i.e shallower soils with more parent rock exposure, as this area was subject to quarrying (Acton- Campbell., 2006, Cornwell *et al*, 2009). The lowest pH values were found along transect three, 3.6 was recorded for sample 5 at the top the transect (see table 3). This area is in very close proximity to the copper smelter building (approx. 500cm) where the highest concentrations of Cu pollution were found. As Cu is a micronutrient it is also naturally increased in acidic soils and could influence concentration levels. An increase in soil pH would help reduce the toxic effects of Cu pollution in this area along with increasing the Nitrogen, Zinc and Phosphorus concentrations; this is supported by Allen *et al*, 1995 and Quint *et al*, 1996.

There are external and internal sources of acidity in soils. External sources are added to the soils often through anthropogenic causes i.e. deposition of industrial pollutants, over time Troopers Hill has been exposed to air pollution from industries in Crews Hole road (chemical works) as well as the ones present on the Hill, copper and lead smelting, quarrying and mining (see section 2.4). In addition acid soils are also commonly found in areas of high rainfall this can be seen as an influencing factor effecting pH on Troopers Hill as its location in the Southwest of England experiences high rainfall for several months of the year. The excess rainfall leaches base cation from the soil, increasing the percentage of Al^{3+} (Aluminium) and H (Hydrogen) the increased Al can be toxic for plants in high concentrations. Furthermore rainwater naturally is slightly acidic pH of 5.7 in nature due to it reacting with CO_2 in the atmosphere forming carbonic acid (Ahmad *et al*, 2005). The pH reading 4.0 at the foot of the hill was the second lowest (see table 3) of the site this is most probably due to the largely acidic conditions that can form in soils near mine spoils due to the oxidation of pyrite (Allen *et al*, 1995). Troopers Hill pH is mainly attributed to natural causes but has been amplified over time through external anthropogenic sources most influentially by the presence of industries in the area.

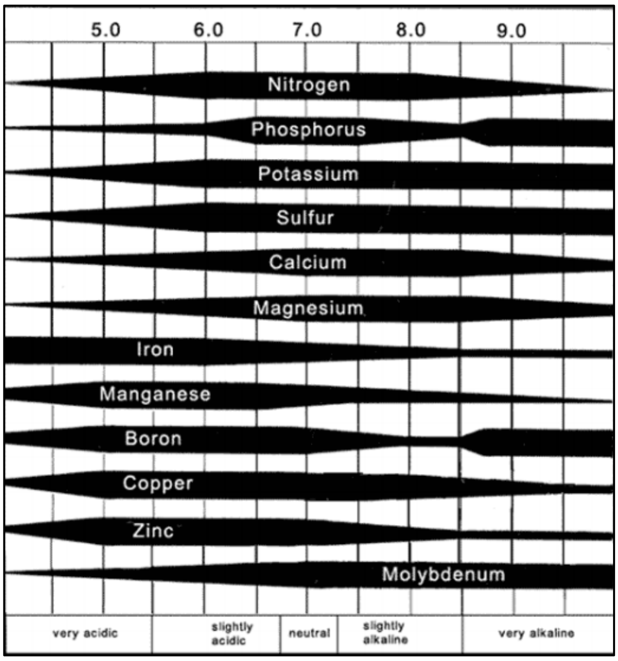


Figure 44: Nutrient availability in relation to pH (Whiting *et al*, 2009).

The capability of soils to store large amounts of cation acids makes it increasingly hard to get rid of and neutralise them once they have reached full capacity and all alkalinity is consumed. Therefore it is important in terms of management to monitor the pH levels on Troopers Hill to ensure they do not deteriorate. Currently there is no specific soil management act in Troopers Hill management policy, 2012. If this was the case changes in water chemistry to the river Avon (the areas catchment basin) could exert early warning signs to take measures for the fast reduction of acid deposition on Troopers Hill. Giusti's study in 2011 confirmed that sediment samples from the river Avon do not show evidence of contamination. If soil pH was in need of increase this could be achieved through a liming process, ground agricultural limestone is a method most frequently used, with soils high in clay like those on Troopers Hill requiring less lime than ones low in clay to make the same pH change (Vernet, 1991).

4.3 Topographies influence on metal concentrations

Results from the three transects (see figure 10-33) show topography to have a direct influence on heavy metal concentrations, as it affects the speed at which water flows across the surface. Transect 3 (see figure 7) is taken along a steep slope, typically a steep slope will promote fast surface runoff and reduce chances for water to infiltrate the ground and dissolve the metals this factor could account for the highest concentrations of most metals being found at the top of the hill. In addition the influence of the acidic soils makes heavy metals typically less mobile (Allen *et al*, 1995).

In comparison transect 2 the Gully is an exposed like valley area, water characteristically in valleys and flat areas flows more slowly across the surface allowing more time for it to seep into the soil profile (Ahmad *et al*, 2005). Metal concentrations in this area were found to be most consistent (see figures 12, 16, 20, 24, 28). Metal concentrations for Cu and As could be lowest in the top soils of this area due to more exposed bedrock allowing metals to leach through the soil profile at a faster rate. As there is no natural Cu or As sources levels are not re-added to the soils once they are leached (Alloway, 2004). In contrast Zn, Mn and Al are found in highest values in the Gully but this could be due to concentrations being constantly toped up or increased naturally by rock weathering.

Transet 1 (see figure 7) is also across a flat topography however spatially metal concentrations are most influenced by the transects proximity to the copper smelter chimney. Metal concentrations in As an Cu which have been identified in polluting levels near the chimney reduce the further east across the hillside you are (see figures 10,14,18,26 and 30).

4.4 Soil leaching influence on metal concentrations

The deep soil profiles have higher medians values (see table 5) because they are from a smaller sample group and are the sum of higher concentrations accumulated over time. Metal concentrations are spatially different through the soils profile. Leaching is the movement of contaminants, such as water-soluble metals or fertilizers, carried by water downward through permeable soils. Soils under a pH of 5.0 encounter problems with the mobilization of heavy metals so they are more likely to be held in the top layers of acidic soils like those on Troopers Hill (see section 4.3) (Ahmad *et al*, 2005).

Overall site results (see figures 34-38) show metals in order of slowest to quickest solubility as follows: Cu is presented as being the slowest metal to leach as it has not increased in concentration through any of the profiles. As leaching has occurred in profile D found at the foot of the hill. Pb and Zn have leached in most profiles to either a minimum depth of 11-20cm and in some cases to 40cm. Pb and Zn are catonic metals which characteristically have a higher retention capacity in alkaline soils and are leached quicker the more acidic the soil becomes (Quint *et al*, 1996). Pb and Cd are found in higher concentrations in waters near acid soils and could be elevated in the River Avon, because Pb has leached through the soils to groundwater levels at faster rates than other nutrients it is found in lower concentrations in the soil off Troopers Hill. Al and Mn are the quickest and most mobile of the heavy metals this is because contaminant mobalisation is primarily controlled by contents of Fe, Al and Mn oxides in the soil. Al and Mn are found most abundantly in site A which has experienced the most leaching from the metals (Ahmad *et al*, 2005).

In addition topography will affect the rate at which pollutants are leached through the soils, areas with thinner more exposed rock surface will hold higher levels of metal concentrations than areas covered in vegetation as plants will take up a certain percentage of metals for nutrients (Marschner, 1988). Soil texture will also effect levels, soils at site B (see figure 35) located by the mine shaft have high levels of clay. Clay holds more water absorbing more chemicals from it, this slows the downward movement of chemicals, shown at site B which has the least amount of metals leached and the highest concentrations of metals found in the topsoil 0-10cm. Characteristically this soil texture also reduces the chance of groundwater contamination (Allen *et al*, 1995). The areas bedrock will also affect the leachability rates (see figure 5 and section 2.3).

4.5 Is reclamation needed on Troopers Hill?

Based on concentrations of metals found, Troopers Hill does not need costly reclamation through processes like solidification/stabilization or soil washing/acid extraction the process most commonly used primarily to recycle arsenic from industrial wastes containing high concentrations from metals refining and smelting operations. Only attention to the immediate area around the copper smelter chimney could be lowed as this is where the highest concentrations and pollution of As and Cu were found. The higher As levels around the chimney could be reduced by the bioacessibility of plants or by adding ammonia, this causes the soil to become more alkaline and cause the metals to become more mobile, this technique was used in a study by Ottosen *et al*, (2000) to reduce both levels of Cu and As. However it is not advised to have large levels of pollutions leaching through the soils as this could eventually affect groundwater levels becoming more toxic to humans if drinking water is contaminated.

Despite levels of arsenic and copper being classed as polluting in some areas on Troopers Hill they are not at risk of causing harm to humans. Levels of Cu have to be 130mg/kg to cause phytotoxic effects and arsenic has to be able to enter the food chain (Vernet, 1991). If the area had been used for residential purposes levels of Cu and As would have to of been lowered and soil pH increased. Land use effects soil guideline values and the council's choice to manage the area as a nature reserve has been most successful in preserving the unique soils without need for remediation which could alter its unique characteristics and vegetation. There current management plan (2012) proposes their vision is to enhance the use of the site for recreation by the local community while protecting its natural beauty, rich bio-diversity, history and geology. To conserve and where possible enhance the geological features of the site where this does not conflict with important biological interest ad to quality of acidic grassland and heath habitats, including its associated bare earth for the benefit of species diversity (Parks and Estates, 2012).

4.6 Future Research

Troopers Hill would benefit from future research to firstly add reliability to data already collected in this study and by Giusti, 2011. Secondly it would be highly beneficial to look at the bioavailability of metal concentrations in plants and their rate of uptake along with concentrations of Cr (Chromium), Cd, (cadmium) Ni (nickel) Se (selenium) and Fe (Iron).

Chapter 5.0 Conclusion

Troopers Hill has been an excellent site for investigation into heavy metals as it falls into a geographic location, the South West of England, which has been neglected in literature, with only previous limited samples being taken on site for Giusti's study (2011). There is very little empirical research into spatial distribution of heavy metals in urban soils in Bristol. This study can conclude metal contamination and soil leaching varies spatially across Troopers Hill due to the following: soil characteristics, pH, geology, habitat, topography, profile and anthropogenic influences from industry.

The Spatial distribution of metals varies across Troopers Hill Cu and As were the only metals to be found in higher concentrations than were recommended by UK soil guidelines and ambient background values. All As pollution (with the exception of one site on transect 3) is found within a 7 meter radius of the cooper smelter chimney, with higher levels the closer in proximity, with levels immediately outside the chimney reaching as high as 75mg/kg. Cu over a value over 17.4mg/kg can be viewed as high in concentration and would suggest that 44/64 sites on the transects are polluted. Spatially pollution levels can be seen to be highest in a 14m radius of the copper smelter chimney. There is no known naturally high source of Cu around Troopers Hill so the pollution levels must be the result anthropogenic causes from industry i.e. the copper industry established in the 18th century and more recent pollution from Brass Manufactured with copper and zinc from the Mendip Hills. In addition the highest concentrations of Pb were found in 3meter radios of the smelter chimney these high levels cannot be accounted for naturally and are the result of pollution from onsite metal smelting. In comparison concentrations of Zn, Al and Mn are shown to increase most prominently from west to east found in highest concentrations in the Gully and lowest around the copper chimney. These metals are not added to the soils through anthropogenic processes instead there concentrations on the hill are dominated by natural sources, weathering, geology and pH.

The pH on Troopers Hill (4.1) is classed as extreme acidic in nature and is significantly lower than the ambient background value for English soils at 5.9 the ideal pH for nutrient stability. However many plants have adapted to thrive at pH values outside this range and is evident on Troopers Hill home to a large range of plant species most abundantly, bracken, gorse, broom, bell heather; hawtorn, silver birch, oak. This habitat is present due to the close relationship between vegetation and underlying soil as only plants that tolerate the acid soils survive. Troopers Hill has experienced problems with the mobilization of heavy metals linked to its low pH, causing levels to be held in the top layers instead of leaching through the profile. This allows for plants to take up the metals in higher concentrations. Metals studied that are most influenced by pH change are Cu, Mn and Zn. In addition the pH of Troopers Hill is also influenced by natural causes, the underlying sandstone geology and weathering processes the Gully has a lower pH than the top of the hillside which wasn't subject to quarrying.

Lowest pH found on site was approximately 500cm from the copper smelter chimney. External sources are added to the areas soils through anthropogenic deposition of industrial pollutants from industries in Crews Hole road (chemical works) as well as the ones present on the Hill, copper and lead smelting, quarrying and mining.

Soil leaching has occurred as metal concentrations are spatially different through the soils profiles this is closley linked to pH, as soils under a pH of 5.0 encounter problems with the mobilization of heavy metals so they are more likely to be held in the top layers of acidic soils like those on Troopers Hill (Ahmad *et al*, 2005). Overall site results show metals in order of slowest to quickest solubility as follows: Cu, As, Pb, Zn Al and Mn.

Based on the concentrations of metals found no costly remediation of the site is needed as levels of Cu have to be 130mg/kg to cause phytotoxic effects and arsenic has to be able to enter the food chain (Vernet, 1991). If levels were treated only attention to the immediate area around the copper smelter chimney would be of priority, levels could either be reduced using low impact natural methods of the bioacessibility of plants by planting vegetation around the area or by more artificial methods of adding ammonia to increase pH. Land use effects soil guideline values and the council's choice to manage the area as a nature reserve instead of using it for residential land has been most successful in preserving the unique soils without need for remediation which could alter its unique characteristics and vegetation.

The study involved a reliable number of samples to validate concentrations on Troopers Hill however for more accurate results repeating the same study or extending it on a wider scale would further validate the data collected. Calculating the upper and lower quartile percentages of metal concentrations for the site would be highly valuable also when applying management guidelines for the area. Future research would benefit from looking at the bioavailability of metal concentrations in plants and their rate of uptake along with concentrations of Cr, Cd, Ni, Se.

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Appendix

A) Troopers Hill Area - Timeline

2007 New Management Plan adopted. Troopers Hill LNR awarded a Green Flag for the first time.

2006

2005 Centenary of Air Balloon School

2004 Management and Action Plan launched, Awards for All Lottery Grant awarded

2003 Formation of Friends of Troopers Hill

2002

2000

1995 Troopers Hill Designated as Local Nature Reserve 22nd June

1994 Start of photographic monitoring

1991 Resurfacing of paths, erection of perimeter fence

1990

1987 Crews Hole Methodist Church closed

1982 Tar Works site cleared

1981 Tar Works closed

1980

1976 St George Church demolished

1974

1970 1970 1 April Ownership of Bristol & West Tar Distillers passed to British Steel

1968 Flood to 6 inches below 1894/1960 level 10 July

1962

1960 1960 Flood to 1894 record level 5 Dec

1956 14th Sept Freehold of Troopers Hill purchased by Bristol City Council for £600

1952

1950

1948

1940

1936 21st April Joseph John Ballard (owner of Troopers Hill) dies

1932 24th March Allotments including Troopers Hill Field purchased by BCC for £3,165

1930

1924

1924

1920 1920 30th Sept Freehold of Troopers Hill offered for sale by auction (20 acres or thereabouts)

1910

1908

1905 Little St Aidan's and adjoining school closed - bought by the Tar Works

1904

Bull Inn rebuilt in new location

1900 1900 William Butler dies 6 October

1897 St George becomes part of the City and County of Bristol

1896

1894 River flood 15 Nov

1890

1889 William Butler retires

1886

Troopers Hill Area - Timeline

End of Wildspace! Project, launch of Nature in the City led by Sally Oldfield.

LNRO appointed funded by Wildspace! through English Nature and the Lottery

Sublimed naphthaline plant closed as explosion risk after Flixborough

Southwestern Gas Board become sole owner of Bristol & West Tar Distillers

Formation of Bristol & West Tar Distillers - Southwestern Gas Board own 25%

3rd April Troopers Hill sold by J W Ballard to Frank Viner for £600

5th Sept Troopers Hill sold by B E Somers to Joseph John Ballard for £515

Stone & Timsons Muriate of Ammonia Works closed - incorporated into Tar Works

Troopers Hill Fireclay mine closed

Conham Chemical Works closed - incorporated into Tar Works

Troopers Hill Fireclay mine employs 9 underground workers

Troopers Hill leased to Bristol Fireclay Co by Elizabeth Somers1880 1880 OS map uses name of Troopers Hill, this name was authorised by 3 local residents

1878

1873 St George Local Board formed

1870

1863 Tar Works Fire - Works sold to William Butler

1860

1853 Crews Hole Methodist Church built

1850

1845 'Troopers Hill' shown on Tithe Map   Troopers Hill coal mine closed by this date

1843 Crews Hole Tar Works established by IKB with local financiers and William Butler as mgr

1841 GWR opened from Bristol to Paddington

1840 1840

1838

1835 Construction of the Great Western Railway starts

1833

1831 Bristol Riots 31st October

1830 1830 First recorded use of name 'Troopers Hill' on the first OS map

1828 Brass Company sells Crews Hole abandoned site for £1,880

1826

1820

1819 Crews Hole Pottery closes

1813

1812

1810 1810 Kennet and Avon canal completed linking Bristol to the Thames

1809

Construction of Floating Harbour and Feeder Canal

1804 Troopers Hill colliery established at about this time?

1800 1800

Troopers Hill Chimney built?

1790

1784 St George civil parish formed

1780 1780

1777

1774

1770

1766 Crews Hole bottle glasshouse advertised for sale occupied by William King & Co

Black Castle built using copper slag blocks from Crews Hole by William Reeve

1760

1758

1754 49 copper smelting furnaces reported at Crews Hole

1752 3 March St George Church foundation stone laid

1751 Ecclesiastical parish of St George created

1750

Manufacture of copper slag blocks started to dispose of this waste material

1742 49 Copper Furnaces

First record of Troopers Hill Fireclay mine.   22 Dec Fire destroys St George Church

Lander's Electoral Map shows 'Truebody's Hill'   GWR opened from Bristol to Bath

Patent for preserving timber with creosote by John Bethell

Scenes in our Parish by a Country Parson's Daughter (Elizabeth Emra) published in NY

Drawing commissioned by GW Braikenridge shows Troopers Hill Chimney

'Truebody's Hill' offered for sale.

Anthony Ammat builds Crews Hole Pottery (it was beside the river opposite Lamb Hill)

Revd John Emra becomes vicar of St George (to 1842)

Sale of glassworks (the glassworks was near the bottom of Strawberry Hill)

Crews Hole and Conham Copper Works leased by Elton and Tyndall?

Copper Smelting moved to Warmley and Crews Hole site leased to various businesses

William King, glassmaker dies

William Reeve bankrupt, Arnos Vale and Black Castle sold

25 March Sir Abraham Elton sells 'Harris's Hill alias Truebody's Hill' to Brass Company1740

1738

1730

1728 River Avon Navigation opened from Bristol to Bath

1725 Crews Hole producing 150T copper/year from 24 furnaces employing 33 men

1720

1712 Crews Hole Copper Works established by Bristol Brass & Wire Company

1710

1704

1702

1700

1698

1690

1682

1680

1670

1660

1650

1645

1643 Civil War - Royalist's Capture of Bristol, 26 July

1640

1630

1620

1610 1610

1600

George Whitefield and John Wesley preach at Hanham Mount

'Harris's Hill alias Truebody's Hill' purchased by Abraham Elton from Lancelot Dobson

Baptist Mills Brass Works establised (now under M32 J2)

Copper works established at Conham owned by Abraham Elton

20th Aug Br Edward Terrill ordered banks like a gallery to be cut above Crews Hole

Civil War - Prince Rupert forced to surrender Bristol to Parliament, 10 Setember

Map of Kingswood showing Harris Hill

B)

Metals analysis of environmental samples using microwave-assisted acid digestion and ICP-MS

Microwave-assisted digestion of soil and sediment samples using a mix of diluted hydrochloric and nitric acids is employed to extract the metals from environmental samples. The method has been found to equate to techniques using full strength aqua-regia digests. ICP-MS is used to analyse the extracts for metals.

Reagents

'Trace' analytical grade HCl, sg 1.18

'Trace' analytical grade NHO_3, sg 1.42

Ultra-pure water (≤0.3μScm^{-1})

Reagent A: *A mixture of 5.55% HNO_3 and 16.75% HCl (v/v)*

For 500ml (39.475 98.55)

To about 600ml pure water in a volumetric flask add 78.95g HNO_3 and 197.1g HCl. Make up to 1 litre with pure water.

Reagent B: *Standards base matrix*

Dilute the above acid reagent 1:7.666, ie. 130.4ml acid reagent diluted to 1 litre with pure water.

Method

- All glassware and plasticware must be thoroughly washed in 3% HNO_3, rinsed in ultra-pure water and dried before use.
- Carefully measure 100 ± 10mg sample into a Teflon microwave tube and record the exact weight.
- Add 3ml of acid Reagent A.
- A CRM sample and a blank sample should be run with each batch of analysis
- Tighten lid on the tube and place in the rack in the microwave.
- Run the microwave protocol given below.
- After the samples have cooled, dilute further with 20ml pure water.
- Centrifuge these extracts at 3000rpm for 10 minutes.
- Decant off the supernatant liquid and store for analysis on the ICP-MS instrument.
- Prepare a set of standards using Reagent B as the diluent.

Microwave Protocol (*CEM MARS Xpress*)

Maximum Power:	1600W 100%
Ramp time:	5.5 minutes
Temperature:	175°C
Hold time:	15 minutes
Cooling time:	30 minutes

References

Hassan, N.M., Rasmussen, P.E., Dabek-Zlotorzynska, E., Celo, V., & Chen, H.. 2007 Analysis of Environmental Samples Using Microwave-Assisted Acid Digestion and Inductively Coupled Plasma Mass Spectrometry: Maximizing Total Element Recoveries. *Water Air Soil Pollution, **178**, 323-334.*