METALLIFEROUS POLLUTION IN AN ARCHAEOLOGICALLY IMPORTANT SITE ON ANGLESEY, NORTH WALES, UK

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ABSTRACT

Parys Mountain is situated on Anglesey, North Wales, UK and since the Bronze Age, has been exploited for the metal rich ores that exist there due to its diverse geology. The site is approximately $3km^2$ in area and is archaeologically important because of a significant industrial past of which many remnants of buildings still stand. Artefacts from the Roman and Bronze Age have also been discovered in the area. At one time the mine was the World's largest producer of copper and saw the greatest amount of productivity between 1768 and 1802. This was followed by a gradual to decline in production during the first part of the 1900's. Prolonged anthropogenic activity at Parys Mountain has left the area composed of spoil tips, paths, precipitation ponds and large depressions. There is low plant and animal biodiversity and population numbers are low; however some plant heavy metal ecotypes have managed to establish here successfully. Vegetation cover is between 20-30%, dominated by *Calluna vulgaris*. The extensive mining and ore processing that took place has produced a mosaic of contamination across the site and prolonged erosion and weathering of these tips has led to mobilisation and consequently has increased the bioavailability of copper, lead and zinc in the substrate. Plants inhabiting the area are exposed to these elevated concentrations of essential and non-essential metals and some species have subsequently bioaccumulated these through different absorption routes, whereas others have mechanisms to prevent excess uptake. Analysis of animal samples has revealed markedly elevated concentrations of copper, lead and zinc and from this, it is apparent that movement of these elements through the trophic levels occurs. In a number of plants and animals, partitioning of

metals occurs in different tissues of the organism which may be one of many mechanisms utilised to cope with such contaminated environmental conditions.

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CONTENTS

LIST OF FIGURES

LIST OF TABLES

1.0 AIMS

The objective of this research is to assess the extent of heavy metal contamination of an archaeologically important metalliferous site in Anglesey, UK and to identify the movement of these metals through trophic levels. To achieve this, substrate, vegetation and animal samples collected from the site will be analysed for copper (Cu), lead (Pb) and zinc (Zn). From the results of this analysis, the extent of bioaccumulation in the species present on Parys Mountain will be identified and the degree of movement through trophic levels discussed. Selected plant and animal species will be evaluated to ascertain whether tissue partitioning is evident. Control samples from local uncontaminated site will also be analysed to help determine the extent of contamination.

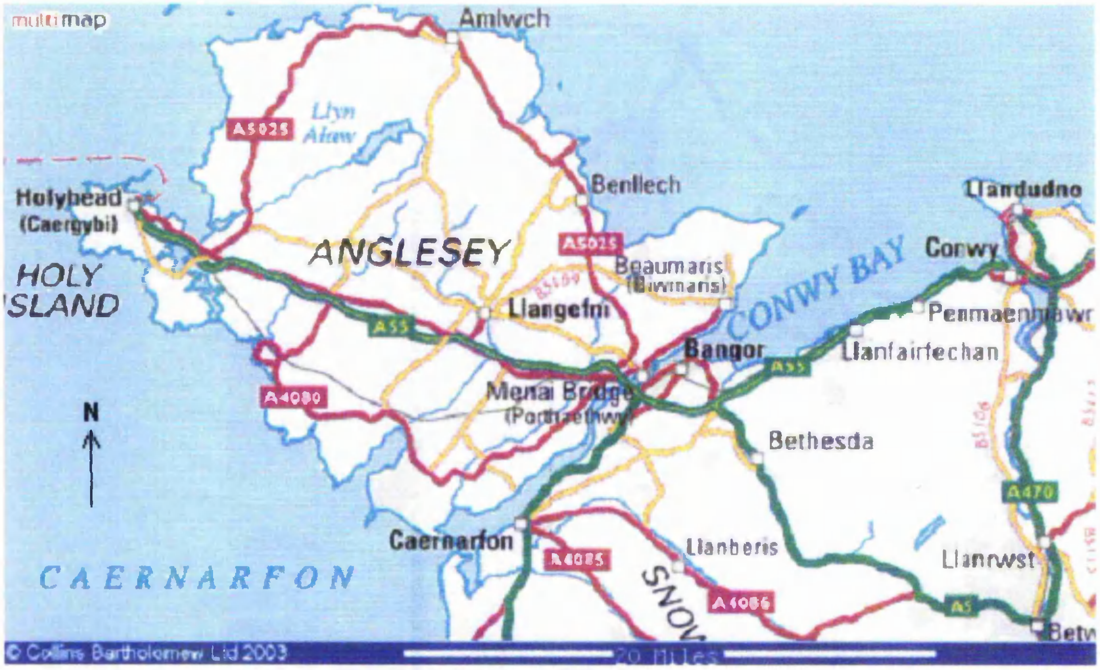
2.0 INTRODUCTION

2.1 Parys Mountain

2.1.1 Study Area

Parys Mountain is on the north coast of Anglesey (see Fig. 1.0), Wales with an elevation of approximately 230m (Timberlake and Jenkins, 1997). It covers an area of around 3 km^2 and is located south of Amlwch (see Fig. 1.1). It is dominated by spoil tips, ponds and abandoned, deep opencast mines. The mines are managed by the Conservation Council for Wales (CCW) and Almwch Industrial Heritage Trust (AIHT), a volunteer group with a great interest in the site.

Figure 1.0: A Map of Anglesey



Source: www.multimap.com

Figure 1.1: Parys Mountain

Source: www.multimap.com

The control site Mynydd Bodafon (SH473853) is approximately 12km south-east of Parys Mountain and has an elevation of 178m. The ecology of the control site is very similar to that of Parys Mountain but has greater vegetation cover and biodiversity. There has been no known contamination of the control site and any wind blown contaminants would be limited as the prevailing wind on Anglesey is from the south-west.

2.1.2 Ecology of Parys Mountain

The vegetation on Parys Mountain is typical of a lowland heath where the climate is temperate with moderately small variation in seasonal temperature and precipitation. Webb (1986) states that where heath is present the coolest mean temperature in the winter never falls below 0°C and never rises above 8°C whereas in the summer months the mean temperature range is between 19°C and 22°C in areas.

Calluna vulgaris or its common name 'Ling', is dominant on most types of European heath and remains so because of moist air related to oceanic or sub-oceanic climates. Tansley (1965) comments that heaths are a plagioclimax and maintained in this state because trees and other shrubs are unable to colonise due to grazing, high winds and fire. However, on Parys Mountain the absence of higher plants may be due to elevated metal concentrations and poor soil structure.

Pioneer plant species that exist on typical heaths are algae, lichens and mosses for example, *Cystococcus humicola*, *Cladonia* spp. and *Sphagnum* spp.. Parys Mountain is no exception to this. Herbaceous species that will generally colonise are *Rumex acetosella* and *Galium saxatile* however these are not found in great abundance on Parys Mountain. Grasses such as *Festuca ovina* and *Agrostis tenuis* are commonly found on heath and these exist on Parys Mountain. Finally, *Calluna vulgaris* which is the dominant species, covers the ground layer and out competes many ground species for light. In a typical heath situation *Vaccinium myrtillus* which can survive fire and *Erica cinerea* which germinates quickly can become co-dominant in some stands (Tansley, 1965) although on Parys Mountain this has not occurred. On Parys Mountain there are few tree species although common invaders such as *Prunus spinosa, Quercus* spp., *Fagus sylvatica* and *Betula* spp. are not present.

Insects are the most commonly found fauna on Parys Mountain but the biodiversity and population numbers are limited. Webb (1986) reports that invertebrate numbers are limited on heath as the flora species from which they feed are very sensitive to herbivore damage due to unfertile soils. Gimmingham (1972) supports this view and mentions that there are a large number of herbivorous taxonomic groups found on heaths but they are small in biomass.

The invertebrates found on Parys Mountain largely belong to the orders Hymenoptera, Coleoptera, Lepidoptera, Odonata, Diptera, Araneida and Gastropoda. Herbivorous vertebrates found on heaths include *Lepus capenis* (Brown Hare), *Oryctoglagus cuniculus* (Rabbit) and *Cervus elaphus* (Red Deer) although evidence and sightings suggests that Parys Mountain only supports rabbit populations mainly feeding on *Calluna vulgaris* (Goodall, 1979). Insectivorous fauna common on heath include lizards, *Sorex araneus* (common shrew) and birds although none of these inhabit Parys Mountain in great numbers, if at all. However, *Buteo buteo* (Buzzard) and *Falco tinnunculus* (Kestrel) are often seen in the area. The most common predator is *Vulpes vulpes* (Fox) which feeds on rabbits and other carrion. Although the foxes feeding range will not be limited to Parys Mountain, their presence is evident by faeces found around the site.

2.1.3 Overview

The anthropogenic activities on Parys Mountain have caused widespread environmental damage. The excavation of ore and tipping of mine spoils and slag have altered the topography, ecology and hydrology leading to extensive, heavy metal pollution in the area. To date there has been little published work to assess the impact of these activities. This current research programme looks at the transport and fate of copper, lead and zinc in the pedosphere and movement of these elements through the trophic levels.

2.1.4 Geology and Mineralogy

The geology of the Parys Mountain area is a combination of Ordovician volcanic rocks and Silurian graptolitic shales which cover a basement of metamorphic Precambrian rock (Jenkins *et al.*, 2000; Barber and Max, 1979; Swallow, 1990). The structure of the volcanic rocks forms a folded isoclinal syncline (Challinor and Bates, 1973).

Work by Tennant published in Jenkins *et al.* (2000) refers to the detailed rhyolite chemostratigraphy and that Acadian tectonism resulted in a steep dip to the north, reverse faulting/thrusting and north/south faulting (see Fig. 1.3). This geological mass runs for 6 km ENE-WSW.

The Ordovician and Silurian volcano-sedimentary rocks and deposits host a sulphide mineralisation which is associated with the polymetallic mineral deposits known as a Volcanic Massive Sulphide (VMS) (Southwood, 1984; Barrett *et al.*, 2001).

Fletcher *et al.* (1993) and Pointon and Ixer (1980), suggested that the origin of the mineralisation was from a synergistic exhalative origin, in other words it was precipitated from a hydrothermal marine environment. Mineralisation is present in two forms; the first is in veins, lenses and disseminations of mainly pyrite and chalcopyrite in the upper part and Silurian bases. The second is present as lenses close to the bottom of the volcanic sequence. These two descriptions are given by Fletcher *et al.* (1993) and Challinor and Bates (1973), who comment on three mineral groups found at Parys Mountain. The first mineral group is a combination of iron and copper pyrites enclosed within the silicified rock and as scatterings of crystals. The second is of mineralised veins forming more distinct fissures with a combination of quartz, iron pyrites, copper pyrites, galena and sphalerite (zinc blende). This formed after the first type. The final type of mineral assemblage is a group of vague ore bodies that are called bluestone. These are heavy and granular with a dark-bluish appearance and include sphalerite and galena as the dominant components with some copper and iron pyrite also present.

Before extraction the main ores that could be found in great abundance on Parys Mountain were chalcopyrite ($CuFeS_2$), galena (PbS) and sphalerite (ZnS) as well as pyrite (FeS_2) (Pointon and Ixer, 1980; Barrett *et al.*, 2001). These minerals still exist on Parys Mountain but in much lesser quantities than before because of mineral wealth exploitation. Pyrite and chalcopyrite are the most profuse respectively of all four and there are many other ores and gangue minerals present in trace amounts too. The ore deposit complex known as Kuroko is still extremely diverse and rare.

As a result there are number of Sites of Special Scientific Interest (SSSI) which exhibit important geological features. Rare minerals that exist are Pisanite [$(Fe_2+Cu)SO_4.7H_2O$], Antlerite [$Cu_3(SO_4)(OH)_4$], Basaluminite [$Al_4(SO_4)(OH)10.5H_2O$] and Anglesite, a lead sulphate. The weathering of the ore products is responsible for the array of colours on the mountain (see Fig. 1.2). The main Fe^{3+} oxides create the red and yellow shades but 'Blue Stone' (galena) is also noticeable.

Figure 1.2: Parys Mountain, Illustrating the 'patchwork' of colours

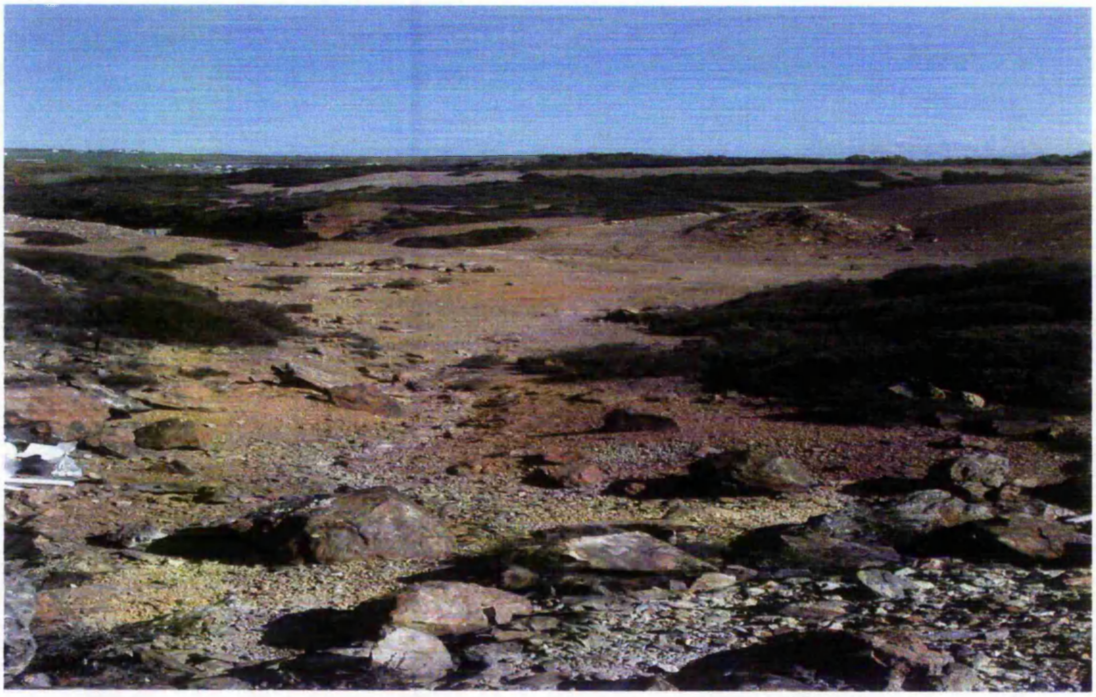
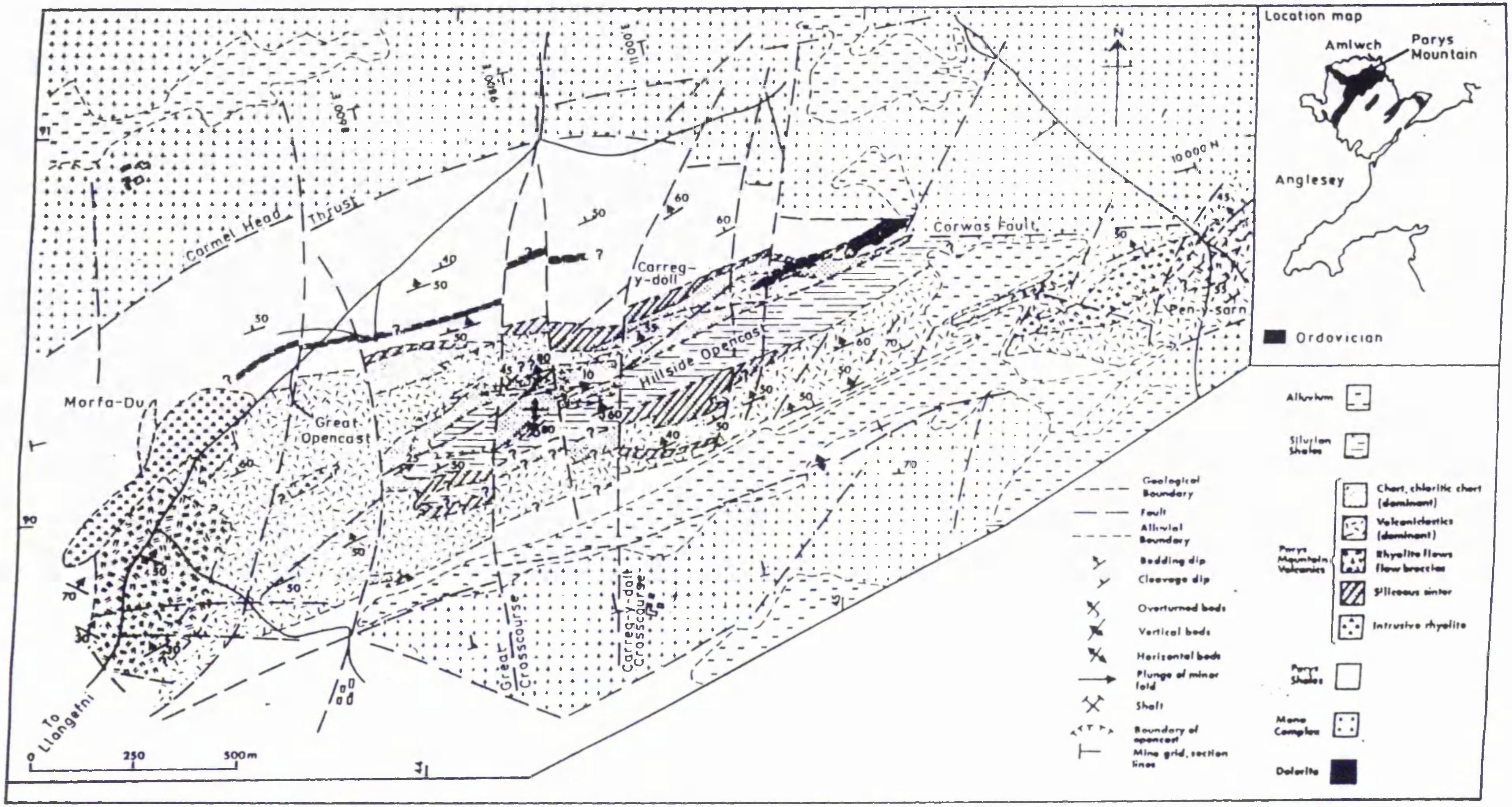


Figure 1.3: Geological map of Parys Mountain (Source: Pointon and Ixer, (1980))



A survey was carried out in 1990 by the Robertson Group to try and establish the amount of reserves left on Parys Mountain. They claim to have found a reserve of 6.45Mt of which 2.34% was copper, 2.60% was lead and 5.35% was zinc (Barret *et al.*, 2001). Swallow (1990), argues that the initial estimated resources at Parys Mountain were 6.3 Mt but after re-evaluation was thought to be more in the region of 4.8 Mt, with a 1.49% copper, 3.03% lead and 5.94% zinc grading. Work by Barrett *et al.* (2001) analysed rhyolite, shale and mafic rock types for heavy metals concentrations (see table 1.0).

Table 1.0: Concentration ranges of copper, lead and zinc in three different rock types from Parys Mountain (mg/kg)

	copper	lead	zinc
Rhyolite	9 – 1659	2 – 132	3 – 118
Shale	24 – 4747	1 – 140	19 – 178
Mafic	93 – 1799	3 – 78	22 – 213

Pointon and Ixer (1980), have recorded percentage contents of Cu, Zn, Pb, Fe, S and SiO_2 in samples of Bluestone and Pyrite-Chalcopyrite ores. Bluestone is composed predominately of zinc (30%) followed by the sequence, S > SiO_2 > Pb > Fe > Cu. Pyrite-Chalcopyrite is composed in the order; SiO_2 > S > Fe > Cu > Zn.

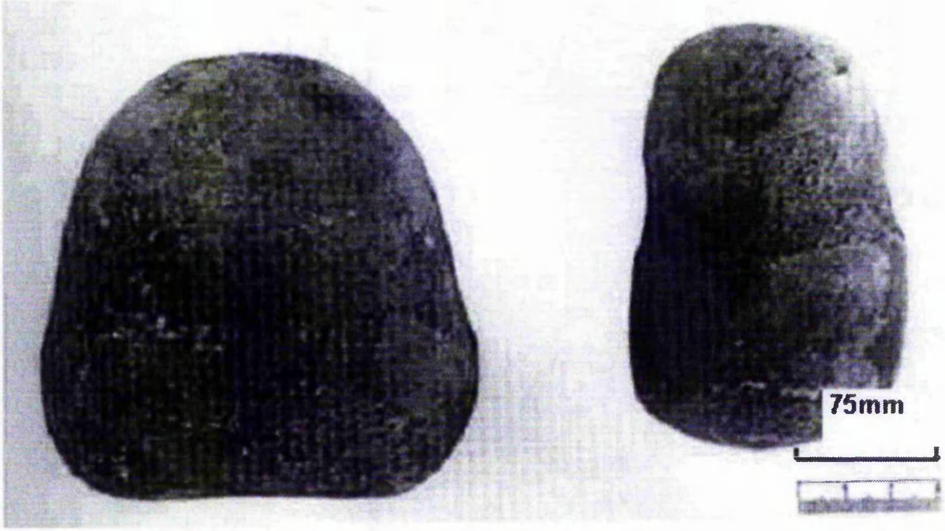
The minerals found here are sulphides and have the anion S_2- present (O'Donoghue, 1982). Unlike sulphates which have an oxygen atom present, they are formed in anaerobic conditions usually submerged under water. Bonding between sulphur is common and this is evident on Parys Mountain as most ores are sulphides. This bond is usually covalent rather than ionic and the sulphides themselves have comparatively high densities but are not relatively hard.

2.1.5 Ancient History and Archaeology of Parys Mountain

Parys Mountain has a long history as an industrially important site. For millennia it has provided civilisations with resources to make and produce many products that have altered and enhanced their way of life. The metal produced from here was a much valued commodity and undoubtedly used in trading.

There are few artefacts providing evidence for ancient activity on Parys Mountain. However, utilisation of the ore resource on the mountain dates back some 4000 years to the Bronze Age (Parkman *et al.*, 1996). This evidence of activity on the mountain came when a foreign, large quartzite pebble was found underground (Hope, 1994). This 'Maul' (see Fig. 1.4) like several others, was found on the north side of the mountain amongst the older spoil heaps (Royal Commission, 1937). It was used like a hammer to crush and grind the brittle ore to a fine powder which could then be easily smelted. Each Maul was found with worn-in grooves which the four fingers and thumb of the user had created during use.

Figure 1.4: A Maul used for crushing ore in the Bronze Age



Source: www.parysmountain.co.uk

There is also evidence that fire setting was used on Parys Mountain. This technique uses fire to heat the surface of the rock which is then quickly cooled by dousing the ore surface with water causing it to crack and weaken. The ore can then be easily picked or smashed away from the face. The findings instigated excavation work to carbon-date some materials found in these ancient workings. Fragments of wood found in the roof of an underground chamber at Parys Mountain has been dated at 4120 – 3400 BP (2120 - 1400 years BC) (Timberlake and Jenkins, 1997).

Bronze Age Man would have excavated from the surface because of limited technology and techniques known to them. There is evidence that bell pits were used. This is where the ore is excavated from a small area on the surface and then dug from around the side walls of the initial hole to form a ‘bell’ shape.

Owing to the lack of stability, these holes were abandoned quite quickly and another one would be started elsewhere. The decline in activity would probably have been because of the reduction of easily workable seams.

Hope (1994), explains that the crushed and roasted ore would have been smelted using charcoal in a primitive smelter. He also describes how Edwin Cockshutt, an acknowledged authority on the history of Parys Mountain, allegedly discovered what he thought to be a smelter. However, Hope argues that it was in fact a kiln used for the roasting of ores to improve their quality. Unfortunately the alleged kiln or smelter has never been found. The kiln was described as a gulley packed with ore and covered by large stones, sealed with earth and clay. A long, sloping chimney stood at both ends and the lower end had been packed with kindling. This appears similar to the process of calcination that was used later in the history of Parys Mountain.

Workers in the 19th century found copper ingots and cakes with Roman inscriptions on Parys Mountain and in the vicinity (Royal Commission, 1937; Barrett *et al.*, 2001). Hope (1994), noted that these copper 'bun' ingots were found on the western flank of the mountain (see Fig. 1.5). This is the only existing evidence for the Romans ever abstracting ore from Parys Mountain. Rowlands (1966), states that there is evidence of Romans working outcrops in other parts of the country but not from Parys Mountain, although when they left Britain, all large scale mining of metal ores ceased.

Figure 1.5: Copper 'cake' found at Parys Mountain

Source: www.parysmountain.co.uk

More recent archaeology on Parys Mountain is in the form of several above-ground structures in various states of ruin around the site. Four of these have been listed by the Welsh Heritage Agency (CADW). They are the Pearl Engine House, the Windmill, the Great Opencast and the Precipitation Ponds (see Fig 1.6) (web: copperkingdom.fsnet.co.uk, 2001).

Figure 1.6: Pearl Engine House and Windmill

Source: www.parysmountain.co.uk

The site has also been considered for a nomination as a World Heritage Site and has been designated a 'Historic Landscape' in Wales. There are many other features on the mountain that were once vital for the working of the mine in years past. Other engine houses on Parys Mountain include the Marquis and Calciner. There are also remnants of the Mona and Parys mine yards which served as the onsite offices and other facilities. The most prominent structure is the 19th century windmill that was used to power a number of technologies. Kilns and furnaces still remain but require detailed excavation and many may exist under the tonnes of spoil on Parys Mountain. The network of underground tunnels and shafts are also important but many shafts have been filled. A local group called Parys Underground Group (PUG) have been excavating and reconstructing these workings and offer the public expeditions to the extensive network of tunnels to appreciate the geology. Finally the spoil itself is important as an archaeological relic. It is strong evidence of the mining activity that has taken place over time and illustrates the diverse geological composition at Parys Mountain.

2.1.6 Modern History

From the Middle Ages up until the 16th Century, the Crown had a monopoly on all gold and silver mines. This acted as a disincentive to mining companies because copper and other base metals are often found alongside silver and gold (Rowlands, 1966).

It was not until 1406 when Robert Parys the younger was given an area of land and appointed tax collector to the people of Anglesey for acknowledgement of his loyalty to Henry IV during the revolt that the area came to be known as Parys Mountain. Before this time it was known as 'Mynydd Trysglwyn' translated by Rowlands (1966), as 'grove of trees with lichen on their trunks'. The actual translation is 'Mountain with a grove of bushes' (Pyatt, *pers comm*, 2003).

It was a matter of national defence and economics that breathed life into the mining industry on Parys Mountain, but a lack of technical expertise in Henry VIII's staff that halted any development (Donald, 1955). When Elizabeth I came to the throne she initiated the 'Company of the Mines Royal' in 1564 which established the British copper industry, yet, it was initially Mary Tudor who had previously in 1557 tried to regenerate the defunct British copper industry (Hope, 1994). Eventually experts and industrialists were employed from Germany and were given exclusive rights to mine because of their experience on the Continent.

Mining stopped during the Civil War (1642-1650) (O'Gorman, 1997), and never recovered to its original scale owing to acts passed around the 1690's breaking up the Mines Royal monopoly.

Charles Roe from the Macclesfield Copper Company took over the workings in 1763 (Harris, 1964), and up to this point was close to abandoning any further exploration until the discovery of a workable vein in 1768 called the Great Golden Venture Lode. It was discovered by Rowland Puw (Swallow, 1990) under the exploratory direction of John Roose, and until this time the true mineral wealth of Parys Mountain had not been fully realised. The discovery suddenly caused disputes over the previously thought, invaluable pastoral land.

Thomas Williams was a local lawyer and dealt with the legal battle between the two owners of the land (Harris, 1964). On one side was the Mona Mine (eastern side) owned by Sir Nicholas Bayly, a descendent of the Marquess of Anglesey, and the other, Parys Mine, owned by a Rev. Edward Hughes, and previously owned by the uncle of Hughes's wife, William Lewis.

Thomas Williams established the area under the Parys Mine Company in 1774 and introduced warehouses and smelters along with other essential logistical and processing installations.

The Mona Mine expired from a 21 year lease in 1785 and only the obvious and easily accessible ore-rich parts of the mine had been excavated. Thomas Williams became a partner in the new 'Old' Mona Mine Company which doubled his power (Harris, 1964), and he invested a great deal of money in both mines.

The 1780s represented the most productive decade the mines had seen. This was mainly due to the demand for copper by the navy which it utilised on the hulls of ships (Harris, 1964). At this time the mine was producing 44,000 tons (44,704t) per annum. According to other sources the mines produced between 5,000 and 10,000 tons per quarter (20,000-40,000t per annum) (Rowlands, 1966). The production was so great that Great Britain was producing three quarters of the Worlds' copper by the end of the eighteenth century (Mikesell, 1979).

Down and Stocks (1977), also state that at the beginning of the 19th Century Parys Mountain was the largest copper mine in the world with a production in excess of 9000t per annum of approximately 6% grade ore. Southwood (1984), has said that Parys Mountain produced 3,050t per annum of metallic copper at the height of production (approximately 50,800t of ore at 6%).

The ore was transported from Parys Mountain to the port by pack horse or horse drawn sleds, in loads of approximately 495kg (Hope, 1994). Generally there was poor infrastructure in the area with no major roads, so one was built from Parys Mountain to the port using spoil from the mine. At the port, bins were built so the ore could be stored and loaded on to ships.

Production at Parys Mountain dropped dramatically after Thomas Williams' death in 1802. The existence of workable veins had diminished and the market for copper had declined. In 1808 it was recorded that only 120 men were still employed at the mine. For the rest of the 19th century, ownership and leases changed hands many times and under different guises, but the mines have never reached the prosperity they once saw. The mines continued to produce copper from the precipitation ponds but there was a great decrease in demand and consequently in price.

In the early 1900s a Mr. T.F. Evans ran the mines until receivership in 1921. Then from 1928, the mines were owned by a private company until 1955 when the first modern exploration techniques were used by Anglesey Mining Exploration Ltd.

Several more companies have carried out exploration surveys over the site but the most recent was the sinking of The Morris Shaft by The Anglesey Mining Company who now currently hold the mineral rights.

2.1.7 Extraction and Processing of Ore

At the peak of its industrial activity, the town Amlwch had a population of over 1200 who were all were employed to work at Parys Mountain or its associated businesses in the town. Many different methods of ore preparation and refining were being carried out on the mountain, but one of the most labour intensive was to grade and prepare the ore for smelting. The primary reason for this was to reduce transportation costs. Many by-products of these refining techniques, such as sulphur and ochre also became economically important to Parys Mountain. These different processes shaped the mountain, with different activities forming a mosaic of spoil tips, paths, buildings and ponds.

Mining

There were three major types of mining employed at Parys Mountain. The earliest methods were surface workings involving shallow shafts very similar to bell pits. Open pit mining started as demand grew and surface deposits became scarcer and in this case, gunpowder was used to blast the ore and break it up (Harris, 1964). Drift mines were also implemented in some areas but in the early 19th Century deep shaft mines were utilised. Mining engineers from Cornwall were used for their expertise and some shafts were sunk to depths of 300m (Swallow, 1990). Shafts were also sunk so that the mountain could be drained for the metal rich waters.

The ore was lifted to the surface from the open cast pits and deep shafts by ‘whimseys’. These were horse powered rope and pulley systems that lifted buckets of ore and water.

Eventually many shafts collapsed and lives were lost so opencast mining started up again and miners would use rope and pulley systems to lift or descend miners up and down the open cast walls to work the face.

Copper Ladies

One of the first processes on the mountain was crushing and grading the ore that had been mined, this was the role of the ‘Copper Ladies’. Women and boys were never employed to work underground but were employed to work on the surface preparing the ore for smelting. The work of the Copper Ladies was observed by Faraday in a visit in 1819 and again by Griffith Owen in 1897.

They record seeing women breaking the ore up into pieces using a hammer called a 'knockstone'. The women wore a type of iron glove which protected their fingers holding the ore in place.

They sorted the 'walnut' sized pieces of ore (Jenkins, 2000) into piles according to quality which were then taken away by boys employed at the mine for further processing. Owen (1897), also describes long timber sheds in an area known as Charlotte Yard in which the women sat on long benches to work. Faraday (1819), records that the women were paid for piece work in which the quality and quantity of their work determined their pay. Griffith (1897), on the other hand states that they were paid 12 pence for a 12 hour day.

Calcination

After the ore had been broken up and sorted into grades it was smelted to remove any impurities. This would result in large amounts of sulphur dioxide being released into the atmosphere with potentially detrimental effects to the environment. Sulphur dioxide is known to cause respiratory problems in humans and animals as it is an irritant to the lungs (Spiro and Stigliani, 1996). When plants are exposed to excess levels it causes chlorosis, leaf shedding, reduced productivity and a decrease in species diversity (Harrison, 1990). This mainly is caused by the oxidation of sulphur dioxide to create sulphuric acid where it has much more of a profound effect on organisms it comes into contact with. Grattan and Pyatt (1994), noted that pollutants are concentrated when dews, frosts or fogs take place leading to necrosis of the leaf.

It was realised that the sulphur produced from the smelting had market potential and so calcining or 'roasting' of the ore took place. Rowlands (1966), describes that the high grade ore was smelted immediately but the lower grade ores were burnt in kilns near the sea at first and later in kilns on the mountain itself. An area now referred to as the Brimstone Yard on the northern side of the mountain is where most of the calcining took place and evidence of the process still exists there today.

The ore was stacked in rows varying between 20 to 50 yards (approximately 18 to 46 metres) in length as noted by Bingley in 1978, 70 feet (21 metres) by Lentin in 1800 and 35 feet (11 metres) by Faraday in 1819.

All three described that the width varied from 10 to 20 feet (3 to 6 metres) and the height from 4 to 10 feet (1 to 3 metres) high. These piles formed a rectangle with ore heaped on top to form a pitch roof like structure. Large pieces of ore were externally placed to form a crude wall and clay was used to seal any gaps. The ends would then be lit using coal and the ore left to burn with the sulphur rich gas condensing in a flue. Here they would intermittently be cleared of sulphur deposits while the ore was burning (Harris, 1964). This process would take many months but it was a highly economical way of producing sulphur and partially refining the ore. The enriched ore remains were one quarter of the original ore before it was calcined (Rowlands, 1966). This refined product was melted in large copper pans, moulded, washed and sent to Amlwch or elsewhere to be smelted.

Another calcination method used a vertical, conical brick structure supported with iron straps on the exterior. This method, first used on Anglesey, was 23 feet (approximately 8m) high. Below the cone there was a deep chamber which was filled with ore and a basement chamber, lower down, where the ore was ignited again using coal. The kiln was built near to a hill or wall where the flue, which acts as the condenser, could be built to a high level. The ore was ignited and left to burn, although at regular intervals more ore could be added through a series of holes which were also used for ventilation. This would push the older calcined ore down into the basement chamber where it was collected and taken to be smelted. This method of calcining ore was more continuous than the previous and required less attention and coal. When Lentin documented this process there were 45 furnaces on Anglesey with more planned for the future.

Smelting

James Treweek developed smelting at both Amlwch and Parys Mountain which at one point became an independent activity of the mining industry. As more ore was imported from other places across the UK and abroad, the smelting facilities at Amlwch and Parys Mountain began to rival the larger and more established facilities in Swansea (Rowlands, 1966). In 1820 the Mona and Parys mines had sixteen and nine separate smelters respectively and in 1851 James Treweek died which, combined with the increased availability of coal to other smelting works in South Wales, brought a gradual decline of smelting on Anglesey.

Precipitation Ponds

Some of the most distinct features on Parys Mountain are the precipitation ponds which are shallow rectangular pits, lined with bricks, stone and more recently wood. The water that had percolated through the mountain was originally lifted by ‘bucket and whimsey’ from the deep shafts but later, a steam engine patented by Watt in 1775 was employed which also prevented flooding. As the water drained through the mountain came into contact with sulphides which would react with the water and oxygen to produce a strong acid solution (see equation below) (Nemerow, 1978). This would in turn release metal cations into solution.

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4$$

This metal rich water would then be pumped in to the first pond where scrap iron would be added to precipitate out the copper. A by-product of this is ferric hydroxide (ochre) which was used as a pigment for house and artists’ paints (Hope, 1994). The water would be channelled through a series of ponds containing iron until all the available copper had been dropped out of solution. The pits would then be drained once every three months and the sediment in the ponds collected. The copper content of which was approximately 80-90% in the first pond but would steadily decline in subsequent ponds. The average 20-30% copper content ‘cake’ would be dried, baked and smelted into pure copper (Rowlands, 1966). However, Harris (1964), argues that the roasted copper cake would produce 50% pure copper. The use of the ponds for precipitation of copper continued until the 1950s (Pointon and Ixer, 1980), long after mining had ceased at Parys Mountain.

2.1.8 Occupational Health

With exposure to such high heavy metal levels for extended periods and for many years, the health of workers at Parys Mountain would have suffered. This long term exposure would have led to bioaccumulation of heavy metals through inhalation of air-borne particulates and ingestion through hand to mouth action and following poor hygiene practices. As the majority of food was imported with little being produced locally, ingestion of heavy metals through food would not have been significant. It is not known whether the water supply was contaminated or not.

As a measure to reduce inhalation of dust, the Copper Ladies wore scarves around their faces (Hope, 1994), but this would only have had a limited effect over a long period of time. The general toxicological health problems associated with exposure to high copper concentrations are nausea, vomiting, convulsions, diarrhoea, coma, Wilson's disease and subsequently, death (Pyatt and Grattan, 2001). Exposure to elevated lead concentrations can cause loss of appetite, constipation, abdominal pains, motor nerve paralysis, fatigue, anaemia, head aches, brain damage and Parkinson's disease (Pyatt and Grattan, 2001). However, the welfare of the miners and other workers was clearly paramount to Nicholas Bayly who paid a local apothecary to provide medical attention to all (Hope, 1994).

2.2 Environmental Impacts and Pollution

2.2.1 Impacts of Mining and Smelting

The mining and processing of ore has many environmental impacts but the extent of these is dependant on the level of management. There was no management plan on Parys Mountain during its working life. Consideration for the environment was not a priority mainly because the impacts were not understood. Parys Mountain was primarily an opencast mine which suffers the greatest effects of any type of mining (Down and Stocks, 1977). Open cast mining typically yields the least amount of ore and therefore extensive areas are worked with methods such as direct stripping of the overburden to excavate the ore from the ground. This causes major scarring of the landscape and the Great Opencast at Parys Mountain is a prime example of this.

The largest environmental impact of metalliferous mining is the waste from excavation. This 'spoil' is low grade, economically unviable ore or rock, collectively known as Gangue (Lawrence *et al.*, 1998). Spoil is a product of sorting the metal rich ores from the unusable ore and usually accumulates near to the area of production unless it is commercially viable to move it further away. Contained within this waste are 'tailings', finely milled particles with heavy metals associated with them derived from the ore separation process (Alloway, 1995). The tips on Parys Mountain still contain considerable amounts of heavy metals and in some cases were 're-worked' by the miners at Parys Mountain, as the higher grade ores became increasingly scarce. Spoil tips were then left open to the effects of weathering and erosion with little management or land remediation.

These erosional processes by wind and rain are the catalyst of which these heavy metals disperse through the terrestrial, atmospheric and hydrological systems (Timberlake and Jenkins, 1997).

Table 1.1: Dispersion of heavy metals from naturally high geochemical content, highlighting the role anthropogenic metal mining in relation to natural processes.

AGENT	HOST DEPOSIT	FORM OF HEAVY METAL
ICE	Glacial till, melt water and flow movement deposits.	Detrital ore/secondary minerals.
WATER – natural (with or without anthropogenic contribution during mining and processing)	Derived clay-like deposits. fluvial lacustrine estuarine marine	Stable detrital ores/secondary minerals. Unstable minerals – dissolution with or without redeposition/absorption in situ on clay minerals, Fe/Mn deposits. Organic fraction – original (transported) or adsorbed downstream.
WIND – natural (with or without anthropogenic contribution from dust or smelting)	In situ – peats and organic top soils. Transported – organic deposits/muds.	Particulate (fine sand – silt) ore/secondary minerals. Aerosols (particularly for the relatively volatile metals copper, lead, Sn & zinc).
PEOPLE – in situ and traded	Mining spoil, ore-processing and smelting slags. Habitation deposits.	Ore/secondary/slag minerals, (adsorption e.g. on charcoal) Metal artefacts, etc.

(Modified from Timberlake and Jenkins, (1997))

Pollution to watercourses and bodies from mining and processing of ores is inevitable where the climate is typically wet. Particulates of waste ore are released in great amounts into drainage systems in the surrounding area and will then settle out as sediment in the watercourse or will be translocated further from the source.

Another impact to the aquatic environment is Acid Mine Drainage (AMD). This occurs in contact with water of heavy metals associated with sulphur rich ores and spoil. AMD is the product of oxidation of pyrite and other sulphidic minerals which can also be aided by acidophilic bacteria (Walton and Johnson, 1992). AMD has a very low pH and this inevitably impacts on receiving water courses.

Afon Goch is a receiving watercourse from Parys Mountain and work by Walton and Johnson, (1992); Parkman *et al.*, (1996) and Boult *et al.*, (1994), have reported pH values as low as 2. The AMD also causes the precipitation of ochre in to the stream, this sludge is high in heavy metals and contamination can remain in situ for many years or directly affect alluvial soils during flooding.

Terrestrial pollution from direct contact with metal-rich spoils can occur when contaminated dust and particles are transported by wind and water to uncontaminated areas. Flooding of rivers with metal rich alluvial deposits can contaminate terrestrial areas as they remain in situ after the water level has dropped (Nriagu *et al.*, 1998). Detrital grains of ore can be wind blown and disperse from these sources causing contamination over a large vicinity but predominantly in the direction of the prevailing wind direction. In a temperate environment these metal ions are associated with sulphides which are unstable and can be mobilised in soils through oxidation. This leads to transportation of metals by water in the matrix of the soil where the cations will adhere to clay minerals, iron and manganese deposits or organic matter (Timberlake and Jenkins, 1997).

Therefore, accumulation of metals is possible in soils where any of these three components exist in the topsoil. Another effect that these chalcophile metals can have is acidification of the soil unless there is a large buffering capacity (Alloway, 1995).

Different types of ore processing activities on Parys Mountain included calcination, roasting, sorting, precipitation and smelting and whether these occur nearby or at distance from the source of excavation, there will be environmental impacts. The impacts of calcination have been discussed earlier and are similar to those connected with smelting. Smelting is an extraction process where the ore is melted into its elemental form with the addition of an oxidising agent (Lawrence *et al.*, 1998). This takes place at high temperatures and is preceded by roasting or calcination to remove sulphur and other impurities. Smelting causes the release of massive amounts of sulphur dioxide which is dependant on the original sulphide content. Along with sulphur dioxide, metals in the ore, including copper, lead and zinc, are vaporised and these aerosols are spread over a wide area particularly if the wind speed is particularly high. These emissions are a potential source of surface water and terrestrial contamination (Nriagu, 1984), that can lead to soil acidification and toxification (Nriagu *et al.*, 1998).

The sorting and grading of ore produces considerable amounts of contaminated fine particles and dust. This increase in surface area of the waste would have enhanced the amount of cations released, to then be mobilised through the effects of weathering. This is similar to the contamination issues with finely ground tailings of modern ore processing.

The precipitation of copper from the acidic waters that had percolated through the mountain was actually of some benefit. Not only would heavy metals be stripped out of the water and the ochre removed, but the water would be less acidic before entering a receiving watercourse. However, this is no longer practiced and therefore highly acidic water drains directly from Parys Mountain into the catchment.

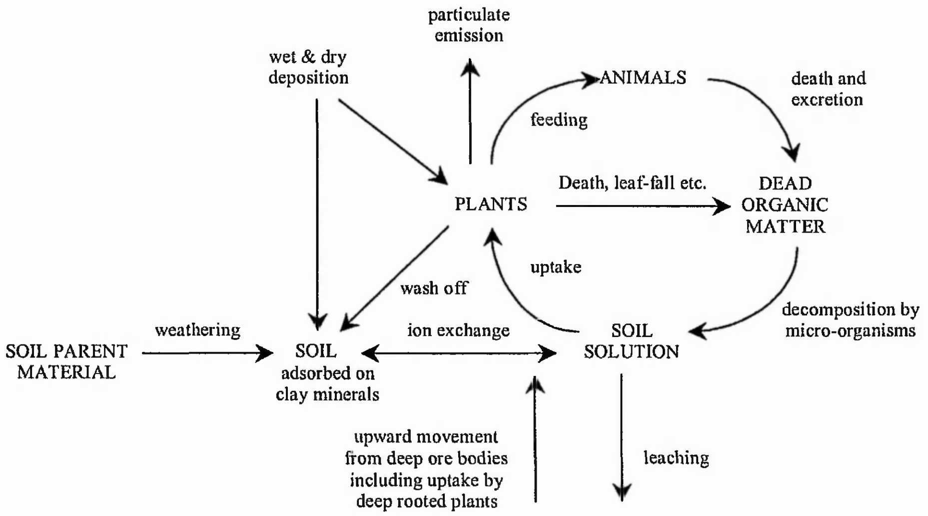
Redundant mining areas are vulnerable to dereliction by acidification and toxification after commercial mining activities stop at a site (Downs and Stocks, 1977), unless a well managed remediation or revegetation programme is implemented. On Parys Mountain there is an immediate requirement for such action as erosional processes continue to mobilise heavy metals. These may be transported by wind to adjacent pastoral land which grazing sheep could take up through ingestion leading to bioaccumulation.

2.3 Heavy Metals

2.3.1 Heavy Metals in the Ecosystem

Fig. 1.7 illustrates the sources and fates of heavy metals in a natural, biogeochemical cycle. Mining and processing of ores increase the availability of metal cations to this ongoing system and in turn they can accumulate at each stage. The metals analysed from the samples collected at Parys Mountain, will hopefully allow an understanding to the extent of metal pollution at this site.

Figure 1.7: The biogeochemical processes of heavy metals



(Modified from Martin and Coughtrey, 1982)

2.3.2 Uptake, Bioaccumulation and Partitioning in Plants

Plants and animals require several trace elements to function but the speciation of metals and the exact amount required varies between species. The phytoavailability or bioavailability of metals is dependent on various soil factors such as pH, clay, organic matter content and the presence of the Fe and Mn oxides (Adriano, 1986).

The more bioavailable they are the more likely plants are able to take up excess elements. The sensitivity to these elements varies between species with some species being more tolerant than others. These tolerant species often have mechanisms to cope with such high soil concentrations and avoid phytotoxicity. These may include control at the root-soil interface, immobilisation within the cell walls and transportation and compartmentalisation (partitioning) within the plant (Harborne, 1993).

In soils with both excess and 'normal' metal concentrations some plants have the ability to bioaccumulate heavy metals. Bioaccumulation is the ability of an organism to continue to concentrate an element or compound throughout its lifetime (Nriagu, 1979). This means that the tissue concentration within the plant will continually increase over time and will usually be higher than that of the surrounding environment.

Once in the plants system, the extent of transport within the plant again varies between species. In plants trace elements are not uniformerly distributed (Adriano, 1986) and some species are known to transport metals into the upper parts whereas others store or partition heavy metals in the roots. This is interesting because if metals within a plant accumulate specifically in leaves there will be a greater impact to herbivores which select leaves as food. Adriano (1986), comments that the ultimate concentration in a specific tissue is related to the flux and period of transpirational water lost through evapotranspiration.

Although the age of the organism also affects the concentration of the trace elements, seasonal changes in plants may have a more significant effect with the loss of vegetative matter containing a significant amount of metals. There has been little research in partitioning historically; however, it is becoming an area of great interest.

2.3.3 Heavy Metals in Animals

Plants can be looked upon as intermediates between the heavy metals in soils and substrates, and animals (Adriano, 1986). The main routes of uptake into animals are direct ingestion of elements, ingestion of contaminated food, and inhalation. Factors that will affect the severity of uptake will be whether they are omnivores, herbivores or carnivores. Their feeding range as a large range may lessen the body burden and type of feeding behaviour, for example ground feeding increases contact with the contaminated surface (Smith and Rongstad, 1982). Direct ingestion of food covered with atmospherically deposited metal-rich dust may expose the consumer to the most severe level of contamination. In many cases more than one element will be taken up and antagonistic and synergistic interactions between metals may affect the rate of intake.

Once in the system, the mobility and accumulation of the metal depends on the animal's homeostatic mechanisms (Smith and Rongstad, 1982). It is also apparent that essential elements are regulated more effectively than those that are not. Lead is a non-essential element but may well accumulate with age (Storm *et al.*, 1994). As for partitioning of elements there is some discussion to what extent this occurs although this varies between species.

2.3.4 Copper

Copper is present naturally in the environment in two major forms. The first, as concentrated mineral deposits and the second, more widely dispersed in sediments, soils and rocks (Nriagu, 1979). Copper is found in forms of sulphides, sulphosalts, and carbonates and as native metals but the most abundant sulphide of copper is chalcopyrite ($CuFeS_2$), which has a typical copper content of 34%. Other common ores of copper are cuprite and bornite. Present day major uses of copper include electric cable and pipes for plumbing and heating systems.

Copper occurs as Cu^+ or Cu^{2+} but in soil it occurs only as the latter (Nriagu, 1979; Friberg, 1979). Sulphides of copper are almost always in the +1 oxidation state and like other metals, copper in soil can originate from many sources including weathering of parent material or from anthropogenic sources. Environmental levels of copper vary significantly; however, work by Nriagu (1979), Lonergoran *et al.* (1981) and Cox (1995), have determined the mean concentration in the Earth's crust as 24-55 mg/kg, 70 mg/kg and 50mg/kg respectively.

Nriagu (1979), suggests that the average UK concentration of copper in soils is 20 mg/kg. However, in the same publication he quotes ranges of between 1-50 mg/kg and 2-200 mg/kg in world soils. Friberg (1979), states the soil range of copper is between 2 –100 mg/kg, whilst Alloway (1995), suggests a range of 20-30 mg/kg total copper in soils is more likely.

Copper in soil behaves similarly to that of zinc where it adheres to organic matter, iron and manganese oxides (Owen, 1982). This makes it one of the least mobile metals. The pH of the soil and the proportion and composition of organic matter can affect the ratio to which copper is distributed between organic matter, iron and manganese oxides. A large proportion of total copper in soils is not available for plant uptake but the amount of copper in soil solution decreases with pH increase because of stronger copper absorption. Higher concentrations of copper in the uppermost horizons of a soil indicate contamination but the level and distribution of copper in the soil profile is usually dependant on the soil type and parent material (Alloway, 1995).

Copper is an essential element to both plant and animal life (Friberg, 1979), in plants, copper plays a significant role in photosynthesis and respiration (Nriagu, 1979). Alloway (1995), suggests that plant matter may have a typical range of between 1-30 mg/kg copper. Work by Bech *et al.* (1997), reports that concentrations in leaves from a polluted mine in Peru can be as high as 614 mg/kg whereas Ye *et al.* (1998), states that *Phragmites australis* can accumulate levels of up to 230 in the roots and 59 mg/kg in stems. Copper concentrations in animals can also vary greatly. Work by Storm et al. (1994), has shown that rabbits can have concentrations of 17.8 mg/kg in kidney tissue and 6.7 mg/kg in bone in a non polluted area whereas deer can have 29.3 mg/kg and 16.5 mg/kg respectively in a polluted contaminated area.

Copper uptake in plants is pH dependant and the available form of copper to plants in acidic soils is $[Cu(H_2O)_6]^{2+}$ and in neutral and alkaline soils is $Cu(OH)_20$ (Alloway, 1995). The transport and localisation process of copper within the plant is controlled by the nitrogen metabolism. Evidence suggests that the largest proportion of copper is likely to be found in the roots and is not transferred to above ground parts. Phytotoxicity and accumulation of copper vary between species and it is impossible to quote concentrations of copper at which these occur. However at a soil pH of ≤ 6 phytotoxicity is known to occur. Duffus (1980), states there is no evidence to support that copper biomagnification occurs in plants or animals and therefore any toxic effects on organisms are due to one off events or immediate exposure.

2.3.5 Lead

The utilisation of lead has occurred for many thousands of years because of its low melting point and ease with which it can be worked (Harrison and Laxen, 1981). It has played a vital role in the building of civilisations and the Romans were an early major civilisation to use it. However, this use eventually subsided after the decline of the Empire (Waldron, 1980). It was first used for water pipes, cisterns, pewter and also as a sweetener in wine.

All these utilisations contributed to epidemics of lead poisoning even after the decline of the Roman Empire because lead has a slow excretion and therefore accumulates, specifically in bones (Duffus, 1980). Some modern uses of lead include batteries, ammunition and as an 'anti-knocking' additive in petrol, though this is now on the decline since the introduction of unleaded petrol (Fergusson, 1990).

Lead mainly occurs naturally as the ores galena (PbS), cerussite ($PbCO_3$) and anglesite ($PbSO_4$), but there are many other known lead minerals (Fergusson, 1990). It occurs in sphalerite and chalcopyrite too which were the two main ores once present in vast quantities at Parys Mountain.

Lead is bivalent and is classified as a chalcophile as well as a lithophile (Nriagu, 1978). The oxidation states Pb(II) and Pb(IV) are relatively stable but it is lead, in it its bivalent form that is the most important in its behaviour in the environment (Alloway, 1995).

The natural average values of lead in the Earth's crust are reported to be 15 mg/kg (Waldron, 1980); 13 mg/kg (Fergusson, 1990); 16 mg/kg (Nriagu, 1978) and 14mg/kg (Cox, 1995).

Due to atmospheric deposition of lead from anthropogenic sources such as tetraethyl lead fuel additives in car emissions, fossil fuels and lead smelting, concentrations of lead in the environment worldwide have risen (Waldron, 1980). Natural sources of lead in soil primarily originate from the parent material but some may also come from volcano fallout in the atmosphere (Nriagu, 1978). Agricultural wastes, fertilisers and sewage sludges have all increased lead concentrations in soils over several centuries (Alloway, 1995).

Nriagu (1978), states that average uncontaminated concentration in English soils is 14 mg/kg, whereas in Wales it is 42 mg/kg. Nriagu (1978), also commented that work by Swaine (1955), gave a range of lead in soil between 2 – 200 mg/kg and Friberg (1979), also reports a range of between 2 – 200 mg/kg with a mean of 16 mg/kg. Alloway (1995), quotes work by Ure and Berrow (1982), who reported an uncontaminated soil lead concentration of 29 mg/kg but because of the anthropogenic source increase of contamination Alloway (1995), suggests a soil lead concentration range of 30 – 100mg/kg. In contrast Cox (1995), suggests a range of 1 – 30mg/kg for anthropogenically polluted soils.

It is not known if lead is an essential element for life and there are many conflicting views as to whether lead is bioavailable to plants. Friberg (1979), states that the amount of lead taken up by plants is not influenced by the concentration in the soil. There have been instances where soils with hundreds of mg/kg of lead, have plants colonising with much lower tissue concentrations. The phytotoxicity of lead is extremely low and so higher concentrations would not affect the health of the plant. On the contrary Alloway (1995), claims that there is a positive correlation in the amount of lead in a soil and the concentration of that in the plant but only a small proportion of lead in the soil is available for uptake. However, the mobility and therefore bioavailability does increase with a decrease in Cation Exchange Capacity (CEC), organic content and lowering of pH in the soil (Harrison and Laxen, 1981). Any bioavailable lead is almost always taken up in the roots (Duffus, 1980), but lead that atmospherically deposits on aerial parts of plants will be stored in these tissues with little or no translocation (Waldron, 1980).

Generally there is agreement that the bioavailability of lead is low but the susceptibility and capacity of bioaccumulation varies from species to species with some plants being more tolerant in soils with a high concentration. Grass samples collected from around a polluted lead mine were analysed by Sanchez *et al.* (1999), and recorded to have concentrations between 412 mg/kg and 3,329 mg/kg in the roots but only between 43 mg/kg and 1,436 mg/kg in leaves and shoots.

Lead is widely known to be toxic to animals with detrimental health effects occurring with increased body burdens. Pyatt *et al.* (2000), analysed goats grazing in areas highly polluted with lead in Jordan and discovered varying concentrations in different bones, hair and faeces. Faeces were recorded at 590 mg/kg and hair at 326 mg/kg, however, bone samples varied from between 192 mg/kg to 405 mg/kg.

2.3.6 Zinc

The main ore of zinc is sphalerite or 'zinc blende' (Nriagu, 1980). Others include Zincite and Smithsonite. Sphalerite is a sulphide and has a yellowish or brown appearance and has an approximate zinc content of 67%. It too, was, and still is one of the main ores present at Parys Mountain.

Uses for zinc include use in batteries, galvanising other metals and in the textile industry. Previously in history the Romans mixed zinc ore with copper to form Bronze (Friberg, 1979). The most common forms of zinc are Zn and Zn^{2+} although other ionic forms are found in the environment.

Zinc concentrations in the Earth's crust have been reported to be between 65 and 80 mg/kg (Nriagu, 1980), 40 mg/kg (Friberg, 1979) and 80 mg/kg (Alloway, 1995). Nriagu (1980), also commented that basic, acid and sedimentary rocks had concentrations of 130, 60 and 80 mg/kg respectively. Zinc levels in soils differ from region to region and again one major factor of this is the amount present in the parent rock and other natural sources. Again anthropogenic sources such as mining, smelting, burning coal and applying sewage sludges to land have increased the amount of zinc in the environment and more specifically soils. Nriagu (1980), indicates a range from 40 to 58 mg/kg and Friberg (1979), and Alloway (1995), report a range between 10 – 300 mg/kg. Bech *et al.* (1997), recorded a range of 56 to 772 mg/kg in soils contaminated from a copper mine in Northern Peru.

Zinc is essential to plant growth and so is found naturally to some degree of concentration in most soils where plants colonise. Zinc is easily fixed to Al, Fe hydroxides, clays and organic matter. Zinc in aquatic environments also binds with the same solid components as mentioned previously and consequently sediments in streams and rivers can become rich in zinc (Nriagu, 1980). However, a sudden change in surrounding conditions can alter the chemistry and these cations can be released. Zinc is generally considered to be one of the most soluble of all trace metals and for zinc to become bioavailable for plants to take it up, it must be in the soluble form (Alloway, 1995). Phytotoxicity of zinc occurs at high concentrations and is rarely seen in specimens other than those close to pollution sources (Friberg, 1979). Sanchez *et al.* (1999), has carried out some work on concentrations of zinc in grass from a polluted site.

These are in excess of 1,730 mg/kg in roots and 1,189 mg/ kg in leaves and shoots. Recent work by Stoltz and Greger (2002), discovered concentrations of *Salix* spp. growing in soils with 14,500 mg/kg were 1,130, 852 and 566 mg/kg in leaf, stem and root respectively.

Solubility and availability of zinc is dependant on five main factors. The first is pH and because it is well documented that zinc becomes more mobile and highly available in acidic conditions an increase in pH reduces the amount available to plants. Phosphorus can precipitate zinc in soil but there are arguments to whether suggest this either increases or reduces the amount of zinc availability to plants and if this relationship is active in the soil or just in the plant alone. Fixation reactions can immobilise zinc and therefore decrease its bioavailability. Temperature and moisture play a significant role in zinc solubility and uptake. Because temperature is usually associated with where the plant exists the effects from this will be varied between species. However, moisture contents of soil especially if waterlogged can decrease the amount of uptake by plants combined with the breakdown of iron oxides that are associated with zinc (Nriagu, 1980). Finally living material and organisms have a controlling factor of zinc availability and solubility. Plant roots produce chelates, reducing compounds, and H^+ ions that can all have an influence on the fate of zinc and microbes in the soil immobilise zinc but in return release it during their decomposition.

Zinc is also an essential element for animals but can be toxic in excess (Cox, 1995) although the level required causing toxicity is much higher than that of other elements. Storm *et al.* (1994), recorded concentrations of kidney between 147 mg/kg from a control site and 338 mg/kg from a polluted site. Whereas Dip *et al.* (2001), recorded concentrations of zinc in the kidneys of foxes of 9.5 mg/kg and 58.5 mg/kg over an urban area of 26km^2.

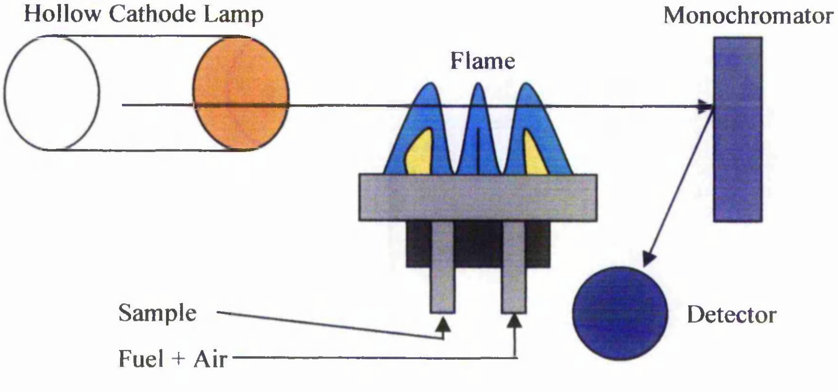
2.3.7 Determination of Metals

There are several methods that can be employed in the determination of heavy metals in environmental samples. For this study Flame Atomic Absorption Spectrophotometry (FAAS) will be used. This is a widely recognised method and has been in use since the 1960s. FAAS is relatively free of interferences and is useful where the sample is solubilised or already in a solution medium (Ebdon, 1982).

A flame atomic absorption spectrophotometer consists of four parts (see figure 1.8). The first is a hollow cathode lamp that emits the radiation through the flame to the diffraction grating monochromator. Usually a different hollow cathode lamp is used for each specific element that is to be determined but multi element lamps are available. Radiation levels are monitored by a photomultiplier detector.

The intensity of radiation passing through the flame is compared with a reference beam, the difference being due to metal atoms in the flame. The absorbance recovered is related to metal atom concentrations.

Figure 1.8: Flame Atomic Absorption Spectrophotometer



The ions of the metal analyte present in solution are aspirated with the acetylene fuel/air mixture via a nebuliser and transported into the flame. A flame temperature of 2600°C converts the ions to ground state atoms. These absorb energy (appropriate wavelength) for excitation. See Planck Equation below.

$$E = \frac{hc}{\lambda}$$

The absorbed energy corresponds to the concentration of atoms in the flame and therefore to the ion concentration in solution given a stable reproducible nebuliser/flame system.

The relationship between the amount of radiation absorbed and the concentration is known as Beer's Law Relationship (Manahan, 1994). This is shown below

$A = \varepsilon c p$

Where,

A = absorbance

c = concentration

p = path length of the sample (flame)

ε = is a constant which reflects the quantum efficiency of the excitation process

The absorbance is detected and then expressed as an absorbance figure which can be calculated in concentration terms by first running a set of known calibration standards and blanks through the machine and plotting a calibration graph. It is important that certified reference material and constant checks are made throughout analysis to ensure that there has been no drift from the response of the machine, i.e. absorbance/concentration value.

3.0 METHODS

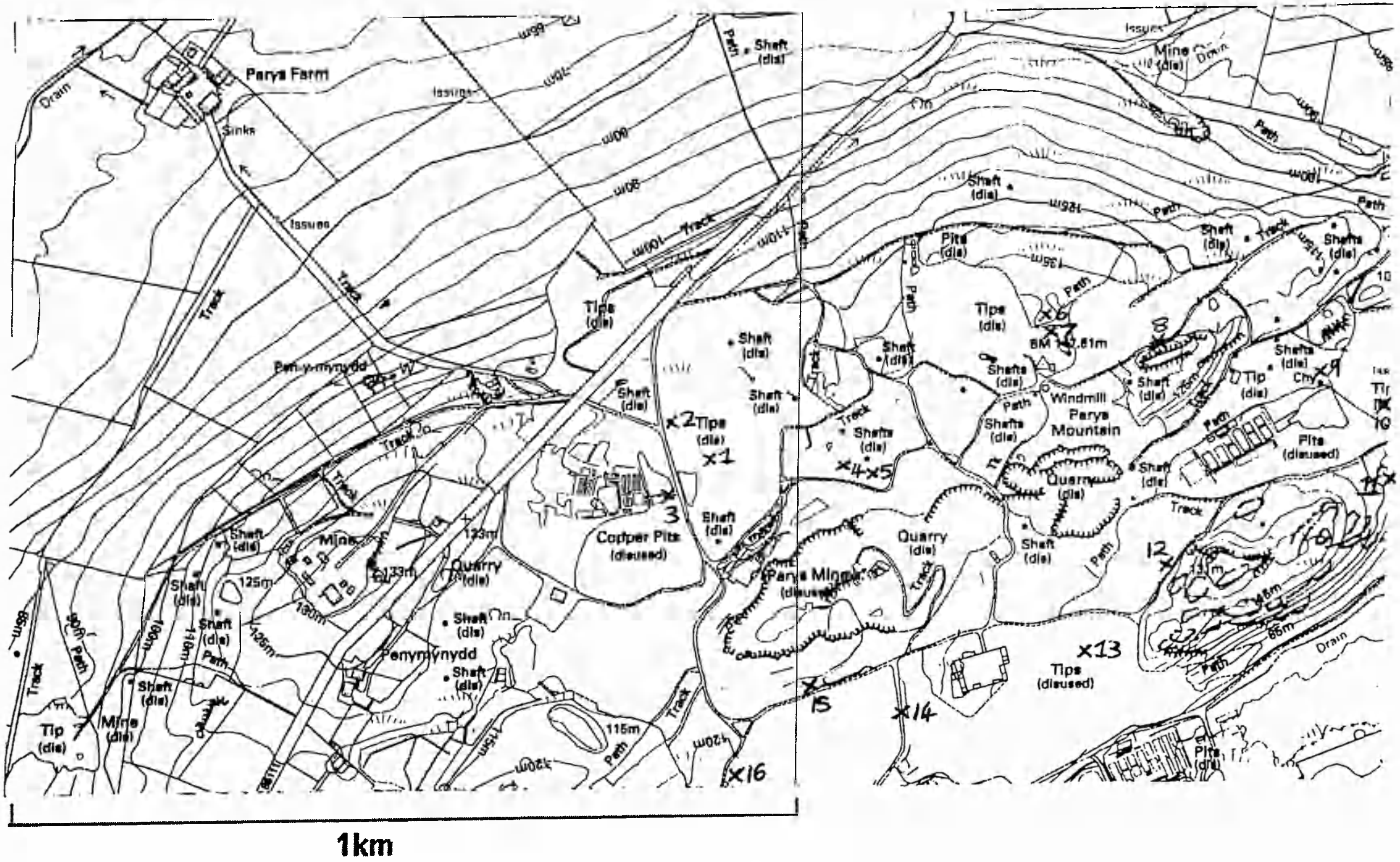
3.1 Sample Details

3.1.1 Sample Sites Utilised

Table 2.0: Sample site numbers, names and national grid references

Site Number	Site Name	Grid Reference	Materials Present	Refer to Page
1	Maria's Shaft Tip	SH43859053	Rocky area	47
2	Maria's Shaft Area	SH43859055	Rocky area	47
3	Copper Pits	SH43849047	Heavily silted area	47
4	Calcination Area	SH44079039	Fine purple/pink substrate	47
5	Calcination Pit	SH44089040	Very fine white and pink dust	47
6	Oxen Quarry	SH44329061	Boggy area with deep organic layer	48
7	Above Oxen Quarry	SH44339057	Large pieces of ore bound with loose spoil	48
8	Rocky Outcrop	SH44489055	Compacted spoil	48
9	Chimney	SH44689051	Compacted spoil	48
10	Mona Adit	SH44789049	Running water with compacted spoil around	49
11	Pond	SH44799040	Silt substrate with some large pieces of spoil	49
12	Gulley	SH44479027	Compacted spoil eroded away	49
13	Mona Mine Yard Tip	SH44359016	Large pieces of spoil bound with clay like substrate	49
14	Mona Mine Yard	SH44159012	Compacted spoil	50
15	Twll Drwg Path	SH44069015	Very compacted and eroded spoil	50
16	South-West Tip	SH44079015	Loose spoil predominately rocky	50
X	Control Site - Mynydd Bodafon	SH473853	Well defined soil with organic content	50

Figure 2.0: Map of sample points (Source: Ordnance Survey)



3.1.2 Site Descriptions

Site 1: This is a large spoil tip to the east of Maria's shaft. It is a steep sided tip that has a flat area at the top but falls away steeply to the south-east. This area had approximately 10% vegetation cover.

Site 2: This area is a strip of spoil close to the shaft that has been filled in with spoil and larger stones around the area to form a plateau. This area had approximately 30% vegetation cover.

Site 3: This pond was fairly shallow where the sample was taken from with a sloping bank.

Site 4: This was an area where calcination had taken place. The spoil was a dark red colour that was devoid of any organic matter. This area had approximately 5% vegetation cover.

Site 5: There was evidence of a wall that surrounded this pit. The spoil in this area was quite fine with distinct differences in colour from white to the dark red as observed at site 4. This area had no vegetation cover.

Site 6: This area is on the north side of Parys Mountain approximately north west of the windmill. It is a hollow that has become a wetland bog with an established community of wetland species of plant. There is thick *Calluna vulgaris* cover with a dense layer of *Sphagnum spp.* in the understorey. This area had approximately 95% vegetation cover.

Site 7: Overlooking the Oxen Quarry to the south is a steep sided spoil tip which is approximately 140m above sea level. This is made up of large pieces of spoil typically from 300mm to dust on the slope of the tip dipping into Oxen Quarry. This did not have any vegetation established due to extremely good drainage and lack of soil type substrate. On the top area, another plateau, the substrate was more compact with regular stands of *Calluna vulgaris.* This area had approximately 75% vegetation cover.

Site 8: This area was between a track and a rocky outcrop, north-east of the windmill past Charlottes Yard. There were areas of very short intensely grazed grass with a large amount of *Oryctoglagus cuniculus* faeces. This area had approximately 40% vegetation cover.

Site 9: This area is dominated by grasses and close to the chimney on the eastern side of Parys Mountain. This area had approximately 10% vegetation cover.

Site 10: Mona Adit is to the east of the mountain and issues from the direction of the Great Opencast. The spoil tip to the west of the direction Mona Adit issues is a very steep sided tip. The tip forms a crescent shape at the top where the substrate is quite fine but loose. This crescent focuses onto a plateau where water drains. This has become an area with a significant deposit of very fine silt that is periodically dried in times of dry weather. From this plateau a gulley has been carved out by erosion from periodic drainage. This area had approximately 10% vegetation cover.

Site 11: A row of pitfall traps were set up along the west side of this pond and vegetation samples also taken. The pond is shallow and is approximately 90 metres above sea level. On the Western edge of the pond, *Calluna vulgaris* has established together with some lichens. This area had approximately 80% vegetation cover.

Site 12: This gulley was a damp area that has formed between a spoil tip and a compacted path. The area had sporadically established vegetation but mainly grasses. This area had approximately 50% vegetation cover.

Site 13: This tip is on the south side of the site and falls away gradually to the North-West. It is a fairly barren area with several erosional gulleys and depressions. Samples were taken 10 metres apart starting at the highest point in the south-west and continuing north-west. This area had approximately 20% vegetation cover.

Site 14: This area is a path directly west of the Mona Mine yard with approximately 75% vegetation cover.

Site 15: This was a ditch beside a path on the south side of the site with approximately 30% vegetation cover.

Site 16: This spoil tip is on the south-west side of the mountain and consists of many different spoil colours including grey, orange and red. There were also a few stands of *Calluna vulgaris* dotted about and samples were taken of these. This area had approximately 15% vegetation cover.

Site X: This is the control site that is dominated by *Calluna vulgaris* and is similar in altitude to Parys Mountain. This area had approximately 90% vegetation cover.

3.2 Sample Collection and Preparation

3.2.1 Vegetation

All vegetation samples were taken using secateurs, a knife and a trowel. Samples were stored in a sterile sample tube or polythene bag immediately on collection. These samples were then air dried in the laboratory as soon as possible. After they were dry any residual dirt was removed and then washed with deionised water. These samples were again air dried and where relevant, were dissected with a sterile scalpel as required for the investigation.

3.2.2 Substrates

The core samples were taken using an auger and immediately wrapped in aluminium foil and sealed in a plastic bag. The cores were then frozen when returned to the laboratory and different sections of the core were removed as required. These subsamples were gently defrosted and air dried ready for the extraction procedure.

All surface substrate samples were collected using a stainless steel trowel. The trowel was rinsed and wiped dry between each sample. Samples were placed in sterile plastic sample tubes from collection and sealed tightly. These were air dried at the first opportunity and then transferred to new sterile sample pots.

3.2.3 Animal and Insects

All faecal and skeletal samples were also collected using a sterile trowel and placed in sterile sample pots immediately. Again, the trowel was rinsed and wiped dry before use each time. These samples were air dried back in laboratory as soon as possible after collection. The skeletal samples were cleaned of any dirt, rinsed with distilled water and again air dried.

Most of the insects were captured using pitfall. The pitfall taps were sterile plastic cups buried at ground level, filled with a minimal amount of 30% alcohol solution and covered with a cardboard cover with suitable space for insects to get under. The animals that were caught were killed and preserved using a minimal amount of 30% alcohol solution. Some insects were caught opportunistically and they were killed and stored identically to the pitfall caught specimens. Once in the laboratory the insects were rinsed using demineralised water and then frozen. The relevant samples were later dissected while frozen and put into new sterile sample pots to defrost before the extraction.

One limitation of using pitfall traps is that only ground insects or those inhabiting vegetation that come in to contact with the ground will be caught. However this ensures that the majority of specimens are feeding in this area and provide more confidence when discussing the exposure levels the insects have endured in relation to the substrate contamination levels.

3.3 Sample Extractions

3.3.1 Total Metal Extraction Method (US EPA)

The method of analysis follows that as described in Radofevic, M., and Bashkin, V.N. (1999). Practical Environmental Analysis. Cambridge: Royal Society of Chemistry.

All glass and plasticware was thoroughly washed with 10% nitric acid solution and rinsed with demineralised water before use throughout the whole extraction process.

1) A sub sample from the original was taken and placed on a clean watch glass and dried in an oven at 105°c for three hours.
2) The dried samples were ground in a pestle and mortar into a fine powder or into the smallest particle size possible. The pestle and mortar was washed and dried with demineralised water and ethanol in between samples to prevent cross contamination.
3) The dried and ground samples were weighed on a watch glass using a balance. Approximately 1 gram of the sample was weighed and recorded. However for some samples this was considerably less than 1 gram due to the nature of the sample and also because of the rarity and abundance at the site of investigation for others.
4) The sample was placed in a 75mL beaker and 5mL of 1:1 nitric acid and demineralised water solution was added. This was shaken and heated on a hotplate for 15 minutes. After this period the solution was left to cool and then 2.5mL of concentrated nitric acid was added and again heated for a further 30 minutes.

5) Next, another 2.5mL of concentrated nitric was pipetted and heated vigorously until approximately 5mL of solution remained in the beaker.
6) 1mL of demineralised water was pipetted into the beaker and left to cool, after which 1.5mL of 30% hydrogen peroxide was added and then heated again.
7) After 5 minutes of heating, the solution was again left to cool and a further 1mL of hydrogen peroxide was added. This step was continued until the effervescence in the beaker ceased.
8) After effervescence had subsided, 5mL of demineralised water and 2.5mL of concentrated hydrochloric acid was pipetted. This solution was heated for 15 minutes without boiling.
9) Again, the solution was allowed to cool and the contents of the beaker were filtered into a sterile graduated container through a Whatman 541 filter paper in a funnel.
10) The beaker was rinsed with demineralised water and the excess poured through the filter paper. Once all the solution had been filtered the solution was made up to the 25mL mark with demineralised water. The container was sealed and stored in a refrigerator until analysis.

3.3.2 Bioavailable Metal Extraction Method

The method of analysis modified from that as described in Lakanen, E., and Ervio, R., (1971). A Comparison of Eight Extractants for the Determination of Plant Available Micronutrients in Soils. *Ann. Agric. Fenn.* 125. Pp.223-232

All glass and plasticware was thoroughly washed with 10% nitric acid solution and rinsed with demineralised water before use, throughout the whole extraction procedure.

1) 500mL of 0.02M Acid Ammonium Acetate solution was made up using 19.72g of 0.5M Ammonium Acetate and dissolved into 14.4mL of 0.5M Acetic Acid. This was shaken and 3.72g of 0.002M EDTA was dissolved into the solution to which demineralised water was added to reach 500mL.
2) A subsample from the main sample was taken and placed on a clean watch glass and dried in an oven at 105°c for three hours.
3) The dried samples were ground in a pestle and mortar into a fine powder or into smallest particle size possible. The pestle and mortar was washed and dried with demineralised water and ethanol in between samples to prevent cross contamination.
4) The dried and ground samples were weighed on a watch glass using a balance. Approximately 1 gram of the sample was weighed. The weight of each sample was recorded. Because of the amount of original sample remaining there was enough for 1 gram all samples.

5) The sample was placed in a sterile graduated container and 10mL of the reagent was pipetted. The lid was replaced and the sample solution was shaken every 20 minutes.

6) After 1 hour, the sample was centrifuged at 1500rpm for 5 minutes using an MSE Mistral 2000 centrifuge.

7) The supernatant was then carefully poured, avoiding any solids carry over, into another sterile graduated container and made up to the 15mL mark with demineralised water.

8) All sample containers were marked and stored in a refrigerator until analysis.

For the purposes of statistical confidence six replicates of the same sample were extracted and analysed. This was carried out on three samples; two of these were using the total extraction method on a substrate and plant sample and the other the bioavailable extraction method on a substrate. These were all analysed and the results and statistics are presented in section 4.2.

3.4 Analysis

3.4.1 Standards

All glassware used in the calibration and throughout analysis was first washed in 10% nitric acid solution and rinsed with demineralised water. To calibrate the spectrophotometer a standard (Standard A) was made up with certified stock solutions from Fisher, Loughborough and BDH, Poole. The stock solutions contained 1000mg/L ± 0.05mg/L each of copper, lead and zinc respectively. 10mL of each was taken and pipetted into a 100mL flask; this was topped up with demineralised water to the mark for a 100mg/L concentration standard and was labelled Standard A. A series of varying concentrations, called Standard Bs, to be used to calibrate the spectrophotometer were made up from Standard A in 50mL flasks (see table 2.1). Two concentrations, 0.5mg/L and 8 mg/L were duplicated and called ‘a’ and ‘b’ respectively.

Table 2.1: Calibration standard dilution details

Standard B (mg/L)	**Amount of Standard A Used (mL)**
0.5a	0.25
0.5b	0.25
1	0.5
2	1
3	1.5
5	2.5
8a	4
8b	4
10	5
20	10

To check the validity of the calibration standards a Certified Reference Solution (CRS) was made up using the Marshall Calibration Standard Solution. A concentration of 10mg/L was made up by taking 0.5mL of 100mg/L Standard and adding 5mL of demineralised water.

3.4.2 Spectrophotometer Set Up and Calibration

A Perkin Elmer Flame Atomic Absorption Spectrophotometer was used for the analysis of all sample extractants and was configured following the instructions from the manufacturer. An integration time setting of 1 second was set to gain a more stable absorbance reading. See table 2.2 for each elements settings for the flame atomic absorption spectrophotometer below.

Table 2.2: Varying element spectrophotometer settings

Element	**Wavelength (nm)**	**Light Source**	**Flame**	**Split Setting (nm)**
Copper	524.8	Hollow Cathode Lamp	Air Acetylene, Oxidising, Lean & Blue	0.7
Lead	283.3	Hollow Cathode Lamp	Air Acetylene, Oxidising, Lean & Blue	0.7
Zinc	213.9	Hollow Cathode Lamp	Air Acetylene, Oxidising, Lean & Blue	0.7

To calibrate the spectrophotometer the standards including a blank (demineralised water), were analysed and the absorbance figure noted for each element. The blank and replicates 0.5 a/b and 8 a/b were analysed six times to confirm the precision of the machine. A graph was drawn from the calibration results to establish the linear range of the element. Mean averages of both the six replicate standards were used as absorbance figure for the calibration graphs. The CRS was also cross checked with the calibration results before analysis was carried out for accuracy. With the linear range known for each element a maximum allowable absorbance figure was determined so the samples could be screened.

The spectrophotometer and calibration procedure was repeated identically in both analysis sessions 1 (2nd and 3rd of September 2003) and 2 (6th January 2004). In both sessions different sets of calibration standards (Standard B's) were made up and used from the original Standard A.

3.4.3 Analysis

The analysis involved a certain amount of preliminary screening. This was to identify any samples that were above the maximum allowable absorbance that would not fall in the linear range of the calibration graph. If one was identified then it was put to one side for dilution and repeat analysis. Between each sample the intake capillary tubing for the spectrophotometer was dipped in demineralised water and wiped dry. This demineralised wash water was changed every ten samples. The sample was analysed until the absorbance figure stabilised.

To check the accuracy and consistency of the machine, batches of ten samples were 'bracketed' together. Before analysis, a blank was analysed and the spectrophotometer zeroed. One Standard B was used to cross check the absorbance reading and also the CRS was analysed at the start and again at the end of the analysis session. At the end of each 'bracket' (10 samples) the blank was analysed and again cross referenced with the known Standard B. A tolerance of 10% either side of the original known absorbance was given otherwise the batch would be repeated. The spectrophotometer was the zeroed again using the blank.

3.4.4 Example Calculation

Below is an example calculation used to determine the concentration in mg/kg of the samples from the measured absorbance of the sample solution.

Site 1, *Calluna vulgaris* Root (Top) copper concentration = 42 mg/kg.

Session 1, copper linear calibration graph equation (See appendices): $y = mx + c$

Mass of sample = 0.1240g

Absorbance measured (y) = 0.015

Where, $y = 0.0291x + 0.009$

Therefore,

$$\text{mg/L} = \frac{(y - c)}{m}$$

$$\text{mg/L} = \frac{(0.015-0.009)}{0.0291}$$

$$\text{mg/L} = 0.2062$$

Where,

$$\text{Copper concentration (mg/kg)} = \frac{(x * (25\text{mL} / 1000))}{\text{Mass (g)}} * 1000$$

$$\text{Copper concentration (mg/kg)} = \frac{(0.2062 * (25\text{mL}/1000))}{0.1240\text{g}} *1000$$

$$\text{Copper concentration (mg/kg)} = \frac{0.005515}{0.1240\text{g}} * 1000$$

Therefore, Copper concentration (mg/kg) = 42

The calculation steps have been added accordingly for samples that required additional dilution so that the measured absorbance was in the linear range.

4.0 RESULTS AND STATISTICS

4.1 Results

The Limit of Detection (LOD) for copper = 0.01mg/L, lead = 0.5mg/L and zinc = 0.018mg/L.

Consequently the Limit of Quantification (LOQ) for copper = 0.1mg/kg, lead = 0.04mg/kg and zinc = 0.3mg/kg

4.1.1 Total Metal Results

Table 3.0: Site 1, Maria's Shaft Tip Results

Sample	Cu mg/kg	Pb mg/kg	Zn mg/kg
Surface spoil (Top)	15	2295	13
Festuca spp. (Top)	36	4	47
Calluna vulgaris Root (Top)	42	292	49
Calluna vulgaris Stem (Top)	<LOQ	<LOQ	11
Calluna vulgaris Leaves (Top)	<LOQ	71	26
Surface spoil (Middle)	25	1309	8
Calluna vulgaris Root (Middle)	65	405	24
Calluna vulgaris Stem (Middle)	<LOQ	<LOQ	7
Calluna vulgaris Leaves (Middle)	<LOQ	314	20
Surface spoil (Bottom)	24	823	26
Sphagnum spp. (Bottom)	360	165	115
Calluna vulgaris Root (Bottom)	58	2867	11
Calluna vulgaris Stem (Bottom)	<LOQ	<LOQ	9
Calluna vulgaris Leaves (Bottom)	<LOQ	<LOQ	5
Oryctoglagus cuniculus Bone	159	85	272

Top = Top of spoil tip
Middle = Halfway down slope of tip
Bottom = Bottom of tip

Table 3.1: Site 2, Maria's Shaft Area

Sample	**Cu mg/kg**	**Pb mg/kg**	**Zn mg/kg**
Surface spoil	230	563	32
Soil	10	1227	10
Calcination spoil	45	18712	18
Sphagnum spp.	426	1401	150
Stereocaulon vesuvianum A	18	983	66
Stereocaulon vesuvianum B	80	2531	31
Parmelia physodes	143	551	56
Trifolium spp.	<LOQ	<LOQ	12
Calluna vulgaris Root A	14	2599	12
Calluna vulgaris Stem A	21	4310	17
Calluna vulgaris Leaves A	3	884	7
Calluna vulgaris Root B	17	2008	18
Calluna vulgaris Stem B	2	1538	4
Calluna vulgaris Leaves B	13	1701	9
Cicindella campestris Head and Thorax	<LOQ	<LOQ	187
Cicindella campestris Legs	<LOQ	<LOQ	<LOQ
Cicindella campestris Abdomen	<LOQ	<LOQ	212
Amara famliaris	<LOQ	<LOQ	<LOQ
Oryctoglagus cuniculus faeces	77	642	145
Vulpes vulpes faeces	76	296	128

Table 3.2: Site 3, Copper Pits

Sample	Cu mg/kg	Pb mg/kg	Zn mg/kg
Sediment	16	9994	16
Ulothrix spp.	94	31678	44

Table 3.3: Site 4, Calcination Area

Sample	Cu mg/kg	Pb mg/kg	Zn mg/kg
Surface Spoil	45	2701	36
Agrostis tenuis	14	3760	31
Hieracium pilosella	255	1426	238
Oryctoglagus cuniculus faeces	96	39	204
Vulpes vulpes faeces	49	<LOQ	75

Table 3.4: Site 5, Calcination Pit

Sample	Cu mg/kg	Pb mg/kg	Zn mg/kg
Calcined Surface Spoil (centre)	28	639	1
Calcined Surface Spoil (+1m from centre)	29	3013	31

Table 3.5: Site 6, Oxen Quarry

Sample	Cu mg/kg	Pb mg/kg	Zn mg/kg
Substrate A 0mm	35	1150	17
Substrate A 50mm	62	8636	1025
Substrate A 100mm	59	4959	52
Substrate B 0mm	78	524	26
Substrate B 50mm	86	9450	50
Substrate B 100mm	49	3556	19
Substrate C 0mm	37	456	6
Substrate C 50mm	15	7363	7
Substrate C 100mm	36	2971	35
Soil	24	11075	11
Cladonia impexa A	28	81	80
Cladonia impexa B	6	62	28
Sphagnum spp.	11	50	21
Polytrichum commune	10	62	31
Juncus spp. Stem	<LOQ	<LOQ	72
Juncus spp. Flowers	<LOQ	<LOQ	45
Juncus spp. Leaves	8	<LOQ	97
Calluna vulgaris Root	5	78	29
Calluna vulgaris Stem	<LOQ	43	8
Calluna vulgaris Leaves	5	3	14
Salix spp. Root	1	700	24
Salix spp. Stem A	<LOQ	54	487
Salix spp. Stem B	<LOQ	38	605
Salix spp. Bark	31	9	640
Salix spp. Buds	<LOQ	<LOQ	727
Salix spp. Leaves	<LOQ	<LOQ	810
Cicindella campestris Head and Thorax	<LOQ	<LOQ	<LOQ
Cicindella campestris Legs	<LOQ	<LOQ	<LOQ
Cicindella campestris Abdomen	<LOQ	<LOQ	<LOQ
Silpha atrata Head and Thorax	<LOQ	51	<LOQ
Silpha atrata Legs	<LOQ	<LOQ	<LOQ
Silpha atrata Abdomen	<LOQ	13	22
Opilio spp.	<LOQ	<LOQ	<LOQ
Tachypodoiulus niger	424	28	371
Pterostichus oblongopunctatus	<LOQ	<LOQ	<LOQ
Pterostichus oblongopunctatus	<LOQ	<LOQ	<LOQ
Philonthus laminatus (female)	<LOQ	95	<LOQ
Philonthus laminatus (male)	<LOQ	<LOQ	<LOQ

Table 3.6: Site 7, Above Oxen Quarry

Sample	Cu mg/kg	Pb mg/kg	Zn mg/kg
Surface spoil A	66	534	27
Surface spoil B	2524	185	32
Calluna vulgaris Root	49	133	24
Calluna vulgaris Stem	<LOQ	206	<LOQ
Calluna vulgaris Leaves	10	4	10
Calluna vulgaris Flowers and Leaves	3	<LOQ	20

Table 3.7: Site 8, Rocky Outcrop

Sample	Cu mg/kg	Pb mg/kg	Zn mg/kg
Oryctoglagus cuniculus faeces	41	52	105

Table 3.8: Site 9, Chimney

Sample	Cu mg/kg	Pb mg/kg	Zn mg/kg
Festuca spp.	281	2107	37
Oryctoglagus cuniculus faeces	36	189	122

Table 3.9: Site 10, Mona Adit

Sample	Cu mg/kg	Pb mg/kg	Zn mg/kg
Surface spoil	2	7645	3
Calluna vulgaris Root	<LOQ	2106	10
Calluna vulgaris Stem	3	852	20
Calluna vulgaris Leaves	23	543	31
Surface spoil	20	5428	17
Calluna vulgaris Root	30	2121	22
Calluna vulgaris Stem	75	488	58
Calluna vulgaris Leaves	<LOQ	78	9
Surface spoil	3	28953	1
Vulpes vulpes faeces	15	62	59

Table 3.10: Site 11, Pond

Sample	Cu mg/kg	Pb mg/kg	Zn mg/kg
Surface spoil	2	1266	24
Cladonia impexa	2	214	42
Sphagnum spp.	14	335	45
Calluna vulgaris Root	<LOQ	<LOQ	15
Calluna vulgaris Stem	<LOQ	3	6
Calluna vulgaris Leaves	<LOQ	135	36
Arion spp.	<LOQ	<LOQ	<LOQ
Rilaena triangularis	746	442	8706

Table 3.11: Site 12, Gulley

Sample	Cu mg/kg	Pb mg/kg	Zn mg/kg
Soil (O horizon)	22	668	20
Peltigera spp.	28	269	263
Deschampsia spp.	19	439	233

Table 3.12: Site 13, Mona Mine Yard Tip

Sample	Cu mg/kg	Pb mg/kg	Zn mg/kg
Surface spoil	8	8850	15
Calluna vulgaris	<LOQ	843	3
Surface spoil	9	10351	5
Calluna vulgaris	3	1109	7
Surface spoil	10	3002	20
Calluna vulgaris	9	203	40
Surface spoil	38	4233	33
Calluna vulgaris	<LOQ	1100	0

Table 3.13: Site 14, Mona Mine Yard

Sample	Cu mg/kg	Pb mg/kg	Zn mg/kg
Oryctoglagus cuniculus Bone	8	469	730

Table 3.14: Site 15, Twll Drwg Path

Sample	Cu mg/kg	Pb mg/kg	Zn mg/kg
Peltigera spp.	46	277	77

Table 3.15: Site 16, South-West Tip

Sample	**Cu mg/kg**	**Pb mg/kg**	**Zn mg/kg**
Red surface spoil	<LOQ	7677	14
Grey surface spoil	13	13412	4
Orange surface spoil	37	3710	12
Calluna vulgaris Root	<LOQ	1448	1
Calluna vulgaris Stem	<LOQ	388	28
Calluna vulgaris Leaves	61	460	57

Table 3.16: Site X, Control Site - Mynydd Bodafon

Sample	**Cu mg/kg**	**Pb mg/kg**	**Zn mg/kg**
Surface soil	7	44	38
Sphagnum spp.	<LOQ	48	20
Cladonia impexa	<LOQ	32	18
Stereocaulon vesuvianum	<LOQ	39	22
Polytrichum commune	<LOQ	33	21
Trifolium spp.	<LOQ	35	17
Young *Calluna vulgaris* Root	<LOQ	<LOQ	14
Young *Calluna vulgaris* Stem	2	<LOQ	11
Young *Calluna vulgaris* Leaves	<LOQ	<LOQ	25
Old *Calluna vulgaris* Root	<LOQ	<LOQ	22
Old *Calluna vulgaris* Stem	<LOQ	<LOQ	12
Old *Calluna vulgaris* Leaves	4	<LOQ	29

4.1.2 Bioavailable Metal Results

LOQ = Limit of Quantification

Table 3.17: Site 1, Maria's Shaft Tip Results

Sample	Cu mg/kg	Pb mg/kg	Zn mg/kg
Surface spoil	6	4	1
Surface spoil	6	12	<LOQ
Surface spoil	6	8	5

Table 3.18: Site 2, Maria's Shaft Area

Sample	Cu mg/kg	Pb mg/kg	Zn mg/kg
Surface spoil	66	32	11
Soil	46	7	45

Table 3.19: Site 3, Copper Pits

Sample	Cu mg/kg	Pb mg/kg	Zn mg/kg
Sediment	20	26	28

Table 3.20: Site 4, Calcination Area

Sample	Cu mg/kg	Pb mg/kg	Zn mg/kg
Surface soil	34	15	30

Table 3.21: Site 5, Calcination Pit

Sample	Cu mg/kg	Pb mg/kg	Zn mg/kg
Calcined surface spoil (centre)	6	25	3
Calcined surface spoil (+1m from centre)	14	42	4

Table 3.22: Site 6, Oxen Quarry

Sample	Cu mg/kg	Pb mg/kg	Zn mg/kg
Soil (O horizon)	1026	144	125

Table 3.23: Site 7, Above Oxen Quarry

Sample	Cu mg/kg	Pb mg/kg	Zn mg/kg
Surface spoil A	18	1	<LOQ
Surface spoil B	14	2	<LOQ

Table 3.24: Site 10, Mona Adit

Sample	Cu mg/kg	Pb mg/kg	Zn mg/kg
Surface spoil	7	116	<LOQ
Surface spoil	8	4	4
Surface spoil	28	4	31

Table 3.25: Site 11, Pond

Sample	Cu mg/kg	Pb mg/kg	Zn mg/kg
Surface spoil	83	118	59

Table 3.26: Site 12, Gulley

Sample	Cu mg/kg	Pb mg/kg	Zn mg/kg
Soil (O horizon)	46	13	24

Table 3.27: Site 13, Mona Mine Yard Tip

Sample	Cu mg/kg	Pb mg/kg	Zn mg/kg
Surface spoil	13	99	<LOQ
Surface spoil	42	83	<LOQ
Surface spoil	16	51	<LOQ
Surface spoil	157	109	<LOQ

Table 3.28: Site 16, South-West Tip

Sample	Cu mg/kg	Pb mg/kg	Zn mg/kg
Red surface spoil	2	73	<LOQ
Grey surface spoil	3	44	<LOQ
Orange surface spoil	4	3	5

4.2 Statistics

4.2.1 Total Metal Results Statistics

Table 3.29: Vegetation replicate sample results - mean average, standard deviation and precision

Sample	Cu mg/kg	Pb mg/kg	Zn mg/kg
Calluna vulgaris Leaves Replicate 1	209	248	57
Calluna vulgaris Leaves Replicate 2	238	265	43
Calluna vulgaris Leaves Replicate 3	213	231	61
Calluna vulgaris Leaves Replicate 4	208	255	54
Calluna vulgaris Leaves Replicate 5	192	221	77
Calluna vulgaris Leaves Replicate 6	199	235	55
Mean Average	**210**	**243**	**58**
Standard Deviation	**15.59**	**16.23**	**11.14**
Relative Standard Deviation %	**7.43**	**6.69**	**19.18**
Precision %	**21.91**	**18.13**	**31.00**

Table 3.30: Substrate replicate sample results - mean average, standard deviation and precision

Sample	Cu mg/kg	Pb mg/kg	Zn mg/kg
Orange surface spoil Replicate 1	604	497	241
Orange surface spoil Replicate 2	534	582	228
Orange surface spoil Replicate 3	450	372	158
Orange surface spoil Replicate 4	520	434	251
Orange surface spoil Replicate 5	447	513	177
Orange surface spoil Replicate 6	526	445	207
Average	**514**	**474**	**210**
Standard Deviation	**58.68**	**73.05**	**36.74**
Relative Standard Deviation %	**11.43**	**15.41**	**17.46**
Precision %	**30.57**	**44.31**	**44.20**

4.2.2 Bioavailable Metal Results Statistics

Table 3.31: Substrate replicate sample results - mean average, standard deviation and precision

Sample	Cu mg/kg	Pb mg/kg	Zn mg/kg
Calcination spoil Replicate 1	5	298	<LOQ
Calcination spoil Replicate 2	6	324	<LOQ
Calcination spoil Replicate 3	6	359	<LOQ
Calcination spoil Replicate 4	5	299	<LOQ
Calcination spoil Replicate 5	6	348	<LOQ
Calcination spoil Replicate 6	6	312	<LOQ
Average	**6**	**323**	**<LOQ**
Standard Deviation	**0.18**	**25.46**	**<LOQ**
Relative Standard Deviation %	**3.20**	**7.87**	**<LOQ**
Precision %	**17.69**	**18.87**	**<LOQ**

For each set of data from tables 3.29 to 3.31 the mean average, standard deviation, relative deviation and precision has been calculated. The relative standard deviation is expressed as a percentage of the standard deviation coefficient, with standard deviation being a calculation of variance around a mean average. This is an indicator of reproducibility of analysis with a lower figure being favourable. The precision is also a measure of reproducibility for replicate analyses with again a lower percentage figure representing greater confidence in the method.

4.2.3 Analytical Accuracy

Table 3.32: Copper measurement accuracy

	Session 1	**Session 2**
Equation	y = 0.0291x + 0.009	y = 0.0467x + 0.0068
M	0.0291	0.0467
C	0.009	0.0068
Checked CRF Abs	0.323	0.4765
Calibrated CRF Abs	0.321	0.463
Checked CRF mg/l	10.79	10.06
Calibrated CRF mg/l	10.72	9.77
% Accuracy (Abs)	**99.38**	**97.08**
% Accuracy (mg/l)	**99.36**	**97.04**

Table 3.33: Lead measurement accuracy

	Session 1	**Session 2**
Equation	y = 0.0056x + 0.0019	y = 0.0096x - 0.0008
m	0.0056	0.0096
c	0.0019	0.0008
Checked CRF Abs	0.064	0.1015
Calibrated CRF Abs	0.060	0.100
Checked CRF mg/l	11.09	10.49
Calibrated CRF mg/l	10.38	10.33
% Accuracy (Abs)	**93.33**	**98.50**
% Accuracy (mg/l)	**93.12**	**98.49**

Table 3.34: Zinc measurement accuracy

	Session 1	**Session 2**
Equation	y = 0.0913x + 0.0128	y = 0.1481x + 0.0276
m	0.0913	0.1481
c	0.0128	0.0276
Checked CRF Abs	0.684	0.786
Calibrated CRF Abs	0.685	0.785
Checked CRF mg/l	7.35	5.12
Calibrated CRF mg/l	7.36	5.11
% Accuracy (Abs)	**99.85**	**99.87**
% Accuracy (mg/l)	**99.85**	**99.87**

5.0 DISCUSSION

The spoil tips and areas around Parys Mountain on Anglesey, North Wales, U.K contain a variety of cations including copper, lead and zinc. The distribution of these cations is not homogenous but heterogeneous; there are some areas where the levels of cations are markedly enhanced and Fig. 3.0 – 3.2 illustrates this. In just a small area it is apparent that lead decreases in concentrations further down the tip whereas both copper and zinc combined actually increase or remain approximately the same. The error bars that can be seen on all figures throughout this section are derived from the precision as a percentage as calculated on pages 70 and 71.

Figure 3.0: Spoil copper concentrations down the side of a tip at Maria's Shaft Tip (Site No.1)

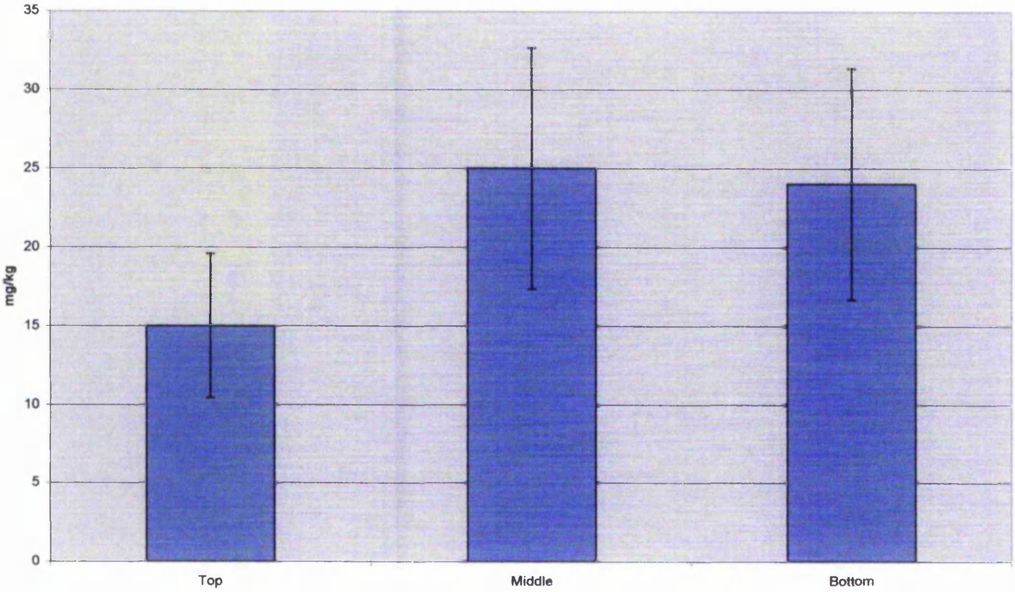


Figure 3.1: Spoil lead concentrations down the side of a tip at Maria's Shaft Tip (Site No.1)

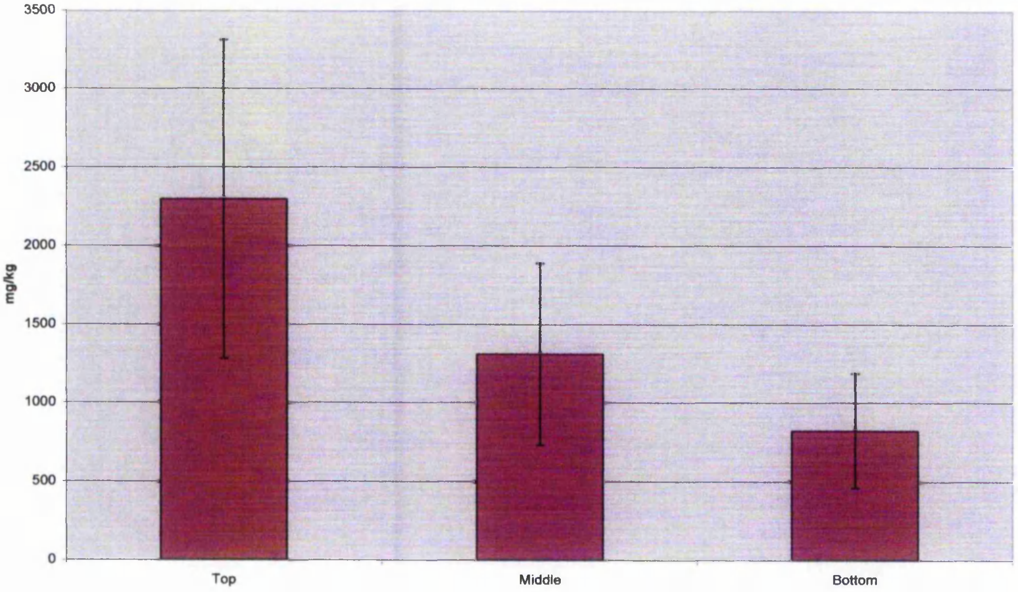
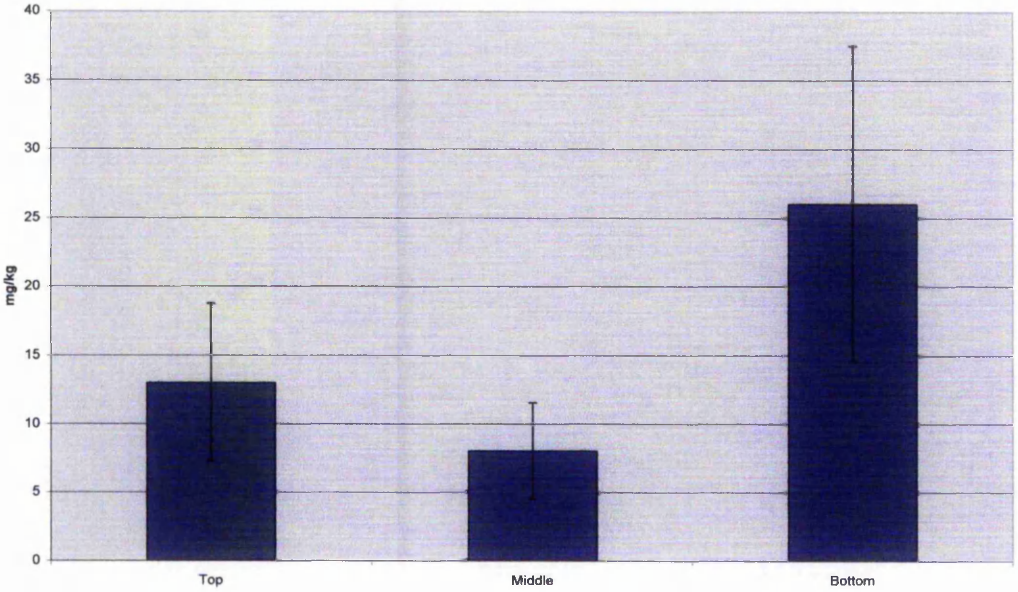


Figure 3.2: Spoil zinc concentrations down the side of a tip at Maria's Shaft Tip (Site No.1)



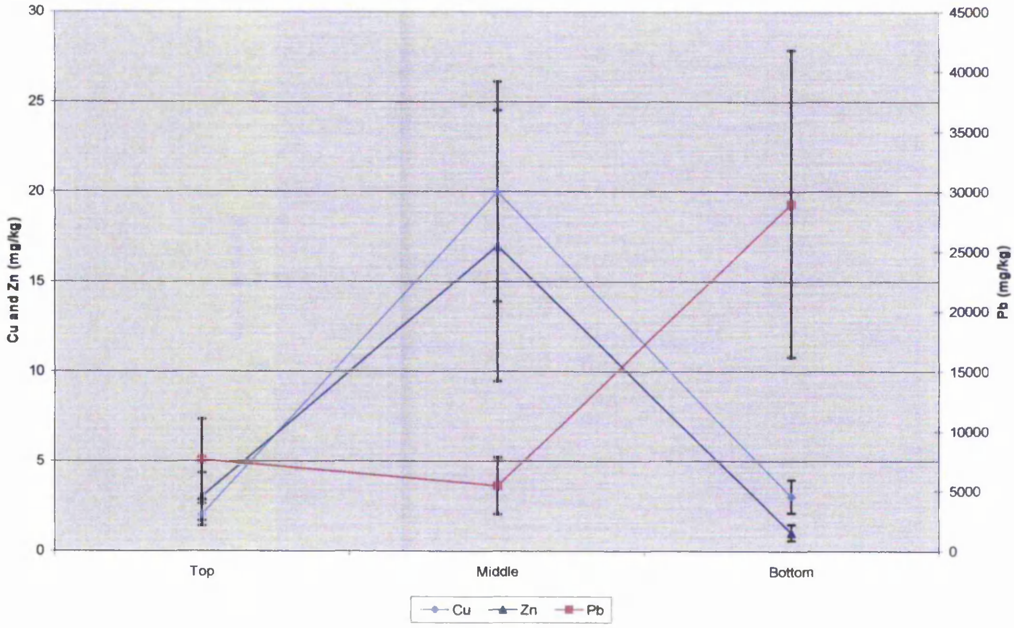
Some 3500 years of weathering at Parys Mountain (Jenkins *et al.*, 2000), will have led to a complex dispersion of these elements and a mosaic distribution has formed. Various agents have been responsible for this dispersion including atmospheric erosion, sheet and gulley erosion, leaching and mechanical disturbance.

Many of the minerals on Parys Mountain are sulphides which release cations into solution as they are unstable and mobilise heavy metal associated particulates in temperate weathering environments (Timberlake and Jenkins, 1997).Wind causes heavy metal particulates to be blown and distributed over a wide area with previously uncontaminated areas eventually becoming contaminated. The degree to which these particulates are dispersed is controlled by the velocity and direction of the wind and particle size (Pyatt, 2001). Stronger winds will increase the dispersion and the area that will consequently be affected is determined by prevailing wind direction which on Parys Mountain is from the south-west. The distribution distance of smaller particulates is greater than larger particles that from the original pollution source (Pyatt, 1973), but particle density will also affect distance of dispersion.

Precipitation causes sheet and gulley erosion by water draining from the mountain. In areas where the spoil is loose and un-bound, particulates can be readily eroded. Translocation of metal ions to other areas on the mountain and the concentration of metals in sediments and areas where any suspended particles settle and consolidate are major effects of this. Fig. 3.3 shows an example of this increase in heavy metals through erosion, transport and deposition.

Both copper and zinc are relatively low in concentrations at the top of this particular spoil tip where sheet erosion is evident down the steep side of the tip. The topography and other evidence suggests that the water drains on to a plateau (middle) where a layer of fine silt has deposited over time and dried out during a period of dry weather. An additional factor could possibly be gravity as observed by Dinelli and Tateo (2001). This theory would suggest that the increase of copper and zinc in this area is due to deposition and gradual accumulation of heavy metals. In the same area, water appears to have cut a gulley into the compacted spoil. This continually eroded area seems to decrease in copper and zinc and this may be due to the recurrent washing and erosion of the spoil. Lead in this area is exceptionally high in comparison to other areas on Parys Mountain and does not exhibit the same behaviour as copper and zinc at this site.

Figure 3.3: Spoil copper, lead and zinc concentrations in an area of sheet and gulley erosion (Site10, Mona Adit)



Leaching of metal ions also takes place on Parys Mountain and this is enhanced by the acidic nature of the environment. Acid Mine Drainage (AMD) occurs when large scale exposures of previously buried sulphide ores react with water (Boult *et al.*, 1993). This reaction produces sulphuric acid and creates a highly acidic environment, which in turn mobilises metal cations and increases the pollution potential. Parys Mountain falls partly in the catchment of a stream called Afon Goch (literally meaning 'Red River') that has recorded to have had a pH of 2.3 (Boult *et al.*, 1993) and ≤2.45 (Walton and Johnson, 1992), the terrestrial environment has been monitored to have a pH of ≤2 (Timberlake and Jenkins, 1997).

Finally, mechanical disturbance from mining and the associated processes on the mountain have led to a wider dispersion of cations. Throughout the working life of the mine, ore has been excavated, graded and processed. Each of these stages would have released significant amounts of dust and particulates into the atmosphere. Charlotte's Yard was once the site where the Copper Ladies would crush the ore in to walnut-sized pieces ready to be further processed. Smelting also took place on the mountain and this would release copper, lead and zinc as aerosols as they are easily vaporised (Timberlake and Jenkins, 1997), and create metal rich slags that would be potential sources for pollution. Tips to the north west of the site were re-worked during in the 1930s (Summers, *pers comm*, 2002) due to scarcity of ore and improvements in recovery methods. This would have had a large potential to re-release cations into the surrounding environment from this source. Evidence implies that areas around Oxen Quarry could be Roman spoil tips and would therefore be some of the oldest on Parys Mountain (Summers, *pers comm*, 2002).

It is possible to suggest that these older tips are now less contaminated than newer tips due to the length of time they have endured weathering, erosion and leaching of cations. However, Table 4.0 shows a comparison between surface spoil levels of copper, lead and zinc between Oxen Quarry, the supposedly older tip and a newer tip, Mona Mine Yard. It provides evidence that even the older tips on Parys Mountain still have high concentrations of copper, lead and zinc and this could be due the dynamic nature of spoil tips (Pyatt, 2000), and the constant relocation and deposition of elements on the surface from other sources on Parys Mountain.

Table 4.0: Surface spoil concentrations of copper, lead and zinc from different age spoil tips on Parys Mountain (mg/kg)

Older Tip (Site 7)				**Newer Tip (Site 13)**			
	copper	**lead**	**zinc**		**copper**	**lead**	**zinc**
Spoil A	66	534	27	**Spoil A**	8	8,850	15
Spoil B	2,524	185	32	**Spoil B**	9	10,351	5
				Spoil C	10	3,002	20
				Spoil D	38	4,233	33

(Refer to site map on page 46 for site locations)

The extent of contamination around Parys Mountain is variable but is comparable to other heavy metal mine areas. Arias *et al.* (1998), has noted copper levels in soil surrounding mine spoil in Spain between 34.9 and 249.2 mg/kg. Whereas Dinelli and Tateo (2001), have studied an abandoned copper mine in Italy and have found surface spoils (<2mm depth) to have copper concentrations over 5,000 mg/kg and zinc levels above 140 mg/kg. Pyatt *et al.* (2000), has observed levels of copper of 11,961 mg/kg and lead of 15,025mg/kg in spoils from Jordan.

The highest recorded levels of copper, lead and zinc in surface spoil from Parys Mountain are 2,524, 18,712 and 1,025 mg/kg respectively.

The study of Parys Mountain has revealed much about the long term fate of heavy metals and similar work has been undertaken by F.B. Pyatt concentrating on the legacy of pollution left behind by ancient mining activities in Jordan and Cyprus. Pyatt (2000); Pyatt *et al.* (2000 & 2000), and Pyatt and Grattan (2001), have all recognised that inevitably heavy metals find a route into living organisms and are subsequently transported through the trophic levels. However, the speed of movement through the trophic levels can often be quick but can also be prolonged.

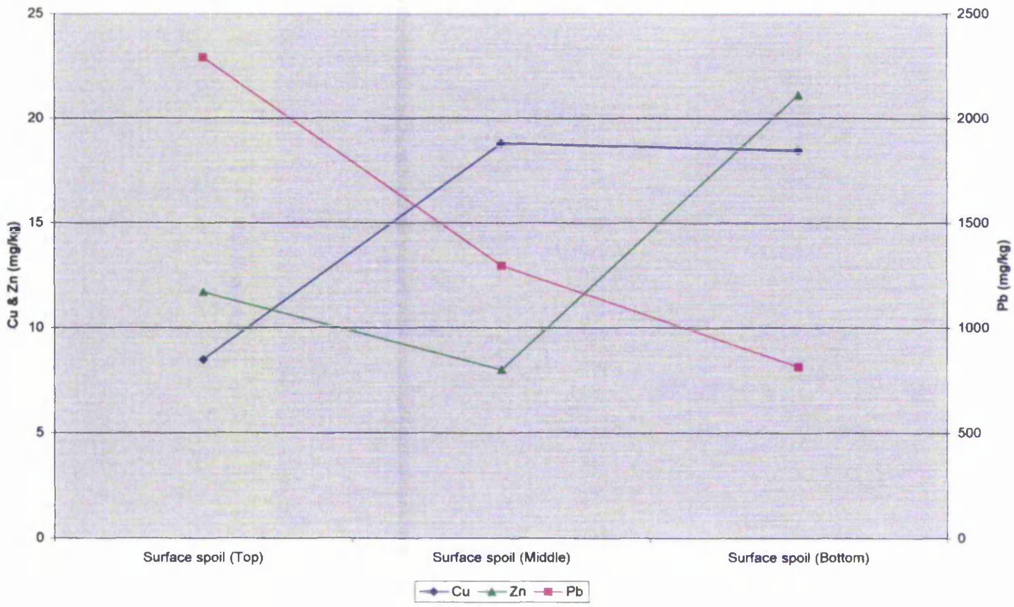
The most common route of heavy metals entering trophic levels, especially in areas where human activity has long ceased, is through the pollutant-plant interface. Bioavailability is the degree to which plants and other organisms can readily uptake these cations. Copper, lead and zinc all have varied bioavailability and bioavailable metals exist on Parys Mountain as it is entirely covered by mine spoil, except where there are precipitation ponds (Walton and Johnson, 1992). However, the analysis in this investigation suggests that bioavailable metals are more significant in certain areas of Parys Mountain. It is closely related to the extent to which the metal cations are available in solution rather than that of total metal concentrations (Romkens *et al.*, 1999), as discussed up until this point. The various factors affecting the bioavailability in soils and spoils are clay content, organic matter content and finally pH (Pendersen and Elmegaard, 2000).

An increase in pH, organic matter or clay content will reduce the amount of bioavailable metals by adsorbing them and rendering them unavailable for uptake (McBride, 1994). The area is well known for its low pH, low organic matter and clay content in the substrate and therefore this leads to mobilisation of metals by dissolution and an increase in the concentration of bioavailable metals.

In this study there are many samples of substrate that have greater bioavailable metal concentrations than total concentrations. The spoil samples from Parys Mountain may still contain particles with high metal concentration associated with them and therefore cause anomalies in results. From the data it seems that lead > copper > zinc when comparing the mean average difference in total versus bioavailable metal concentrations. However, copper and zinc are relatively similar in the mean average difference between total and bioavailable concentrations.

Fig. 3.4 illustrates the large difference between the lead total and bioavailable concentrations and it can be assumed that the ratio of total to bioavailable of lead is high whereas copper and zinc have low ratios and this may have a direct affect on the amount of metals taken up by organisms on Parys Mountain. The concentrations of total copper, lead and zinc also are in the same order where lead > copper > zinc. The average for soils and spoils on Parys Mountain are 5,800, 155 and 25 mg/kg respectively.

Figure 3.4: Difference between total and bioavailable copper, lead and zinc concentrations in three different spoils from the same site (mg/kg) (Site 1, Above Maria's Shaft)



It may be suggested from the evidence, that the ratio of bioavailable metals compared to total metals varies between different sites and substrates. As discussed previously this is affected by the composition and properties of the substrate and may be worth in any further work including analysis for organic matter, aluminosilicates (clay) and pH to try to identify what extent these factors have in reducing or increasing the amount of bioavailable metals.

The ecology of Parys Mountain is heathland and animal and plant species found here are typical of this (Tansley, 1965). Plant species collected from around the area were *Calluna vulgaris*, *Salix* spp., *Agrostis tenuis*, *Festuca* spp., *Deschampsia* spp., *Hieracium pilosella*, *Trifolium* spp., *Juncus* spp., *Sphagnum* spp., *Polytrichum commune*, *Peltigera* spp., *Cladonia impexa*, *Parmelia physodes*, *and Stereocaulon vesuvianum*. Animal species that exist in the area are a diverse insect population and rabbit and fox populations.

The plants are important as they are agents for stabilising the spoil tip environment. The biomass cover per unit area is approximately 20-30%, less than that of similar unpolluted sites and it is felt that species invasion should be encouraged to improve stabilisation. Hence, damage caused by trampling should be limited. There is also evidence of significant fly tipping occurrences on areas of Parys Mountain and this has led to compaction by heavy vehicles. Some of the fly tipping material contains top soil from other, unpolluted areas and this allows other species, not native to Parys Mountain, to colonise and establish.

It is apparent that some organisms contain exceptionally high values of heavy metals whereas the opposite is also true. The most abundant species on Parys Mountain is *Calluna vulgaris* and it appears to be heavy metal tolerant because of the high concentrations found within the plant and surrounding environment. Fig. 3.5, 3.6 and 3.7 show the results of several root, stem and leaf concentrations of copper, lead and zinc from *Calluna vulgaris* samples taken from around the site.

The copper, lead and zinc concentrations in *Calluna vulgaris* range from the less than Limit of Quantification <0.01(LOQ) to 75 mg/kg, <0.04(LOQ) to 4,310 mg/kg and <0.03 (LOQ) to 58 mg/kg respectively. The control specimens contained less than the LOQ in the root for copper and below 4 mg/kg for all other parts. There was less than the LOQ for lead in the control specimen but interestingly, the amount of zinc compared similarly to a specimen in a known polluted area. From the copper and lead data it would suggest that Parys Mountain is highly contaminated in places and the plants are affected with high concentrations of metals in the vicinity of the mine (Bech *et al.*, 1997). This proves that there exists a mosaic of various concentrations of copper, lead and zinc.

Figure 3.5: *Calluna vulgaris* root, stem and leaf copper concentrations

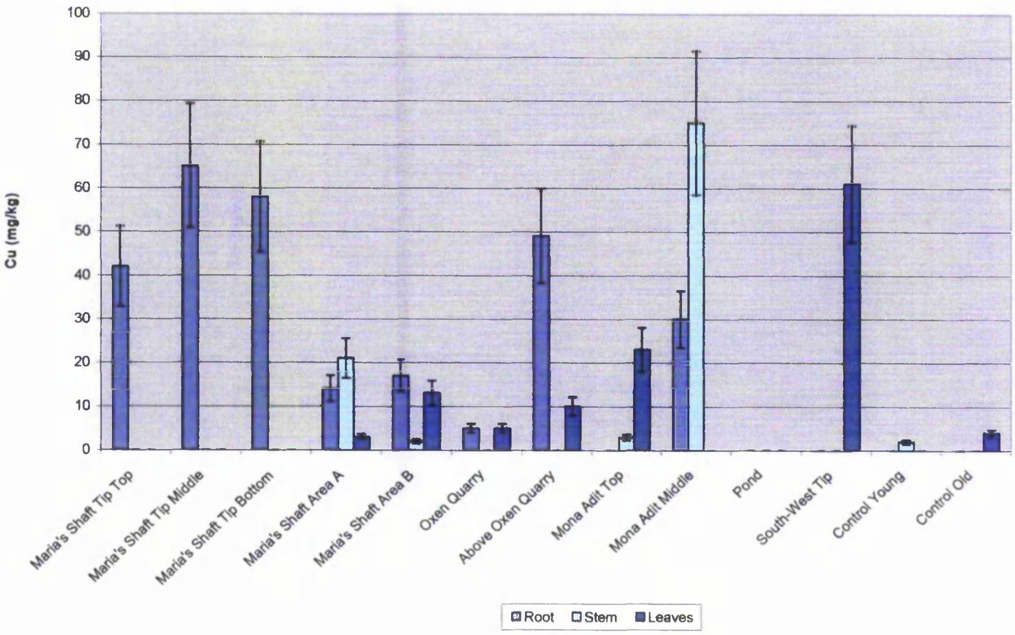


Figure 3.6: *Calluna vulgaris* root, stem and leaf lead concentrations

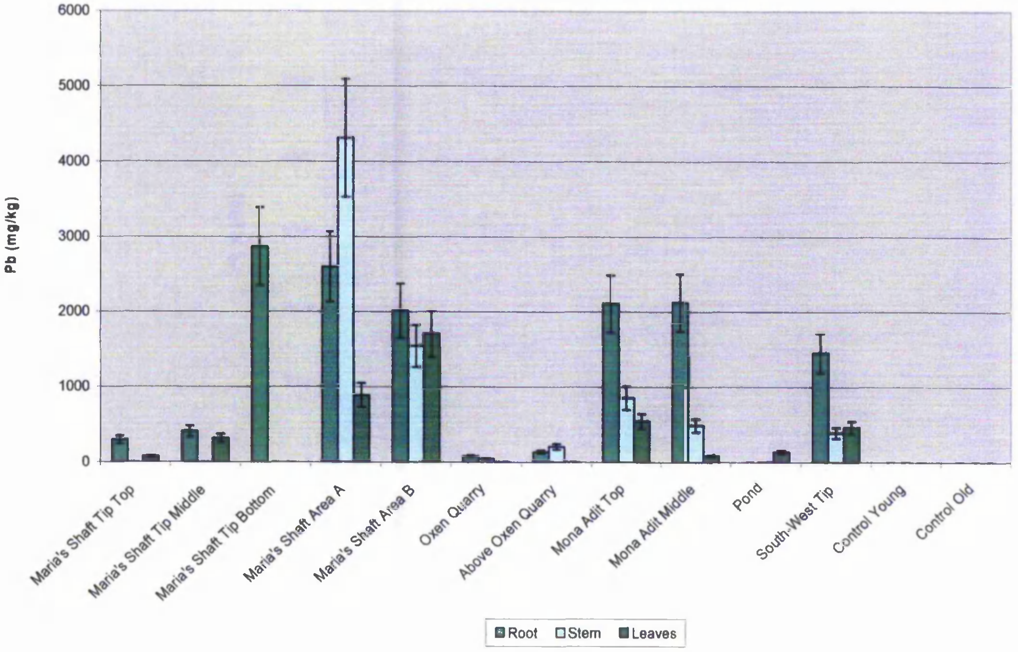


Figure 3.7: *Calluna vulgaris* root, stem and leaf zinc concentrations

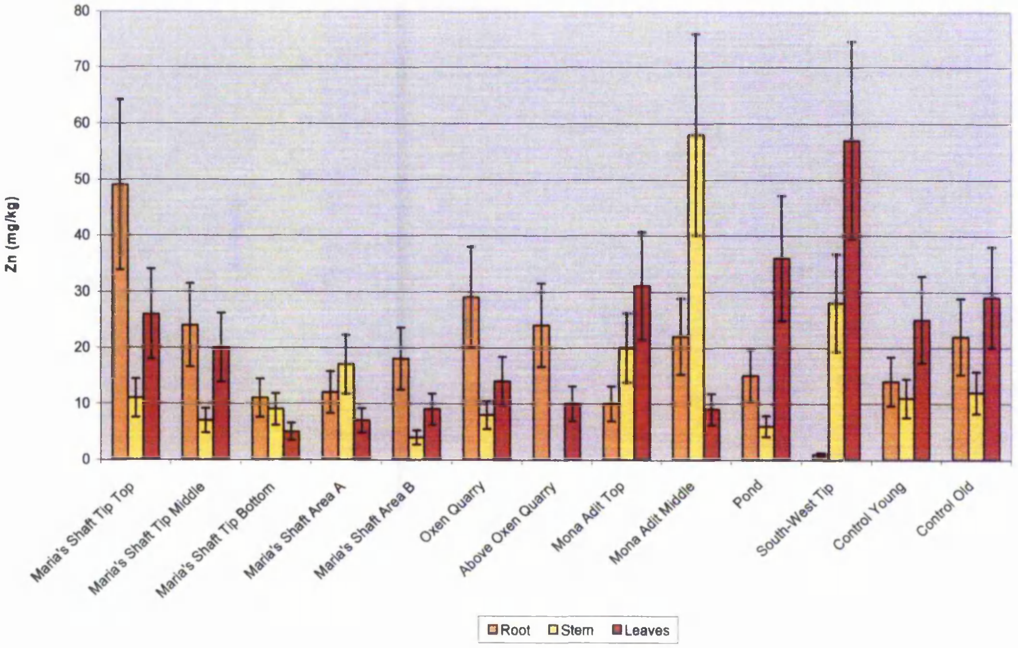


Fig. 3.5, 3.6 and 3.7 can also be used to illustrate heavy metal partitioning in organisms and the data reveals compartmentalisation of the metals has occurred within particular tissues of the plant. The primary path of cations into plants is through the root. Work by Bech *et al.* (1997), has assumed that metal ions can be taken up by the roots of vegetation and transported elsewhere in the plant. Atmospheric deposition of metals on to leaves serves as another route but Kruckeberg and Wu (1991), comment that a common mechanism that plants use is to store copper in the roots to stop translocation to other parts, specifically high proportions of this are immobilised in the cell wall. The findings suggest *Calluna vulgaris* stores excess copper and lead in the roots to prevent phytotoxicity because some of the root samples have higher concentrations than those of other tissues. Conversely it is also possible that the specimens with the higher leaf concentrations are using this as a method to excrete excess metals through leaf abscission. The zinc results are more conclusive, illustrating a better relationship compared to copper and lead where greatest concentrations are predominantly found in the order root > leaf > stem. This proves that *Calluna vulgaris* may use the same mechanisms for zinc tissue regulation as for copper and lead and thus the stem serves as a route to transport the metals from the roots to the leaves. It also demonstrates that plants can exhibit multiple-tolerance to more than one metal utilising the same mechanisms (Robb and Pierpoint, 1983). The main difference is that copper and zinc are essential for plants (Friberg, 1975), whereas there is still discussion to whether lead is essential and this is exemplified by the concentrations of <LOQ in the control samples of *Calluna vulgaris*.

It is apparent from the results that other species on Parys Mountain have similar tolerance to such high cation concentrations. Studies by Ye *et al.* (2003), states that a number of wetland plants have the ability to tolerate increased metal concentrations in the environment. This may explain the presence of *Juncus* spp. in the Oxen Quarry site (See Table 4.1). The surface concentrations of copper, lead and zinc are highly elevated compared to the amount actually found in the plants tissues. This would imply that the plant has a mechanism for selecting or reducing the amount of cations it takes up at the soil-root interface.

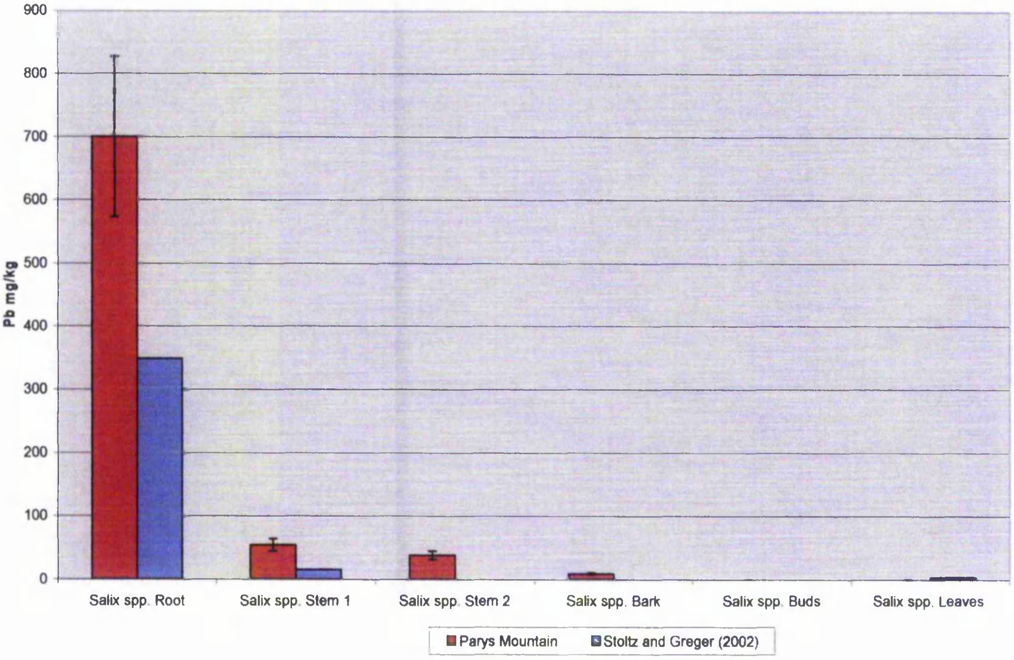
Table 4.1: Surface substrate and *Juncus spp.* copper, lead and zinc concentrations in different tissues (mg/kg) (Site 6, Oxen Quarry)

	copper	**lead**	**zinc**
Substrate A 0mm	35	1150	17
Substrate B 0mm	78	524	26
Substrate C 0mm	37	456	6
Juncus spp. Stem	<LOQ	<LOQ	72
Juncus spp. Flowers	<LOQ	<LOQ	45
Juncus spp. Leaves	8	<LOQ	97

Salix spp. is also found in Oxen Quarry, however, the specimen had established in a drier area with an absence of a defined organic layer whereas *Juncus* spp. is not present. This defined organic layer may have also decreased the amount of bioavailable metals. Fig. 3.8 demonstrates that *Salix spp.* may use a mechanism of compartmentalisation similar to that of the *Calluna vulgaris.*

Again the primary route for cations is through the root. The possibility of foliar uptake through deposition of metal rich dusts seems unlikely because of the ultra low concentrations found in the leaf and bark tissues. Stolz and Greger (2002), studied *Salix* spp. in areas of submerged mine tailings similar to those found at Parys Mountain and their work confirms this trend towards bioaccumulation and partitioning of lead in the root. Copper and zinc do not demonstrate the same behaviour as lead and this may be because they are essential elements for plants and are relatively low in concentration in the surrounding substrate, between 15-86 mg/kg for copper and 17 and 52 mg/kg for zinc, however, there is zinc anomaly of 1,025 mg/kg for this set of results. This compares to the higher substrate concentration range for lead of between 456 – 11,075 mg/kg.

Figure 3.8: Lead concentrations in different *Salix* spp. tissues from Oxen Quarry (Site 6) and work by Stoltz and Greger (2002)



Some species on Parys Mountain do show evidence of foliar uptake, for example the lichen *Peltigera spp.*, with large flat areas is prone to intercept particulates which have been wind eroded and subsequently transported. There is an abundance of lichen and moss on Parys Mountain and some areas have been classed as lichen heath SSSI's. Mosses and lichens rely mainly on atmospheric deposition for nutrients and do not shed parts as often as higher plants, therefore they bioaccumulate metals in greater concentrations than that of the surrounding environment (Bargagli *et al.*, 2002). Lichens are well known for their sensitivity to pollution especially sulphur dioxide in the atmosphere and have long been used as biomonitors (Moriarty, 1983). Biomonitors are chosen with specific characteristics in mind such as accumulation of pollutants without mortality, limited mobility and limited genetic variability to ensure a representative observation (Pyatt, *pers comm*, 2003). Because of this it can be suggested that the lichens on Parys Mountain provide a good indication of the level of contamination of cations but their presence and biodiversity is indicative of good air quality. However, Nash (1975), noted toxicity in lichens where soil levels of zinc exceeded 5,000 mg/kg. No samples of substrate analysed in this study exceeded this level and so possibly explaining the large biodiversity of lichens that exist on Parys Mountain.

Figure 3.9: *Cladonia impexa* copper, lead and zinc concentrations from around Parys Mountain

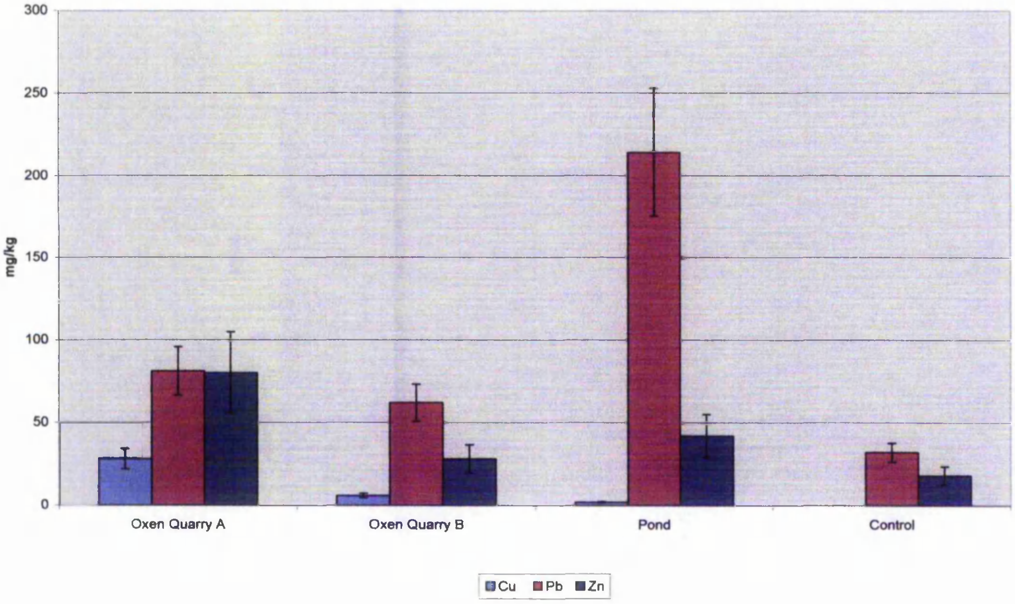
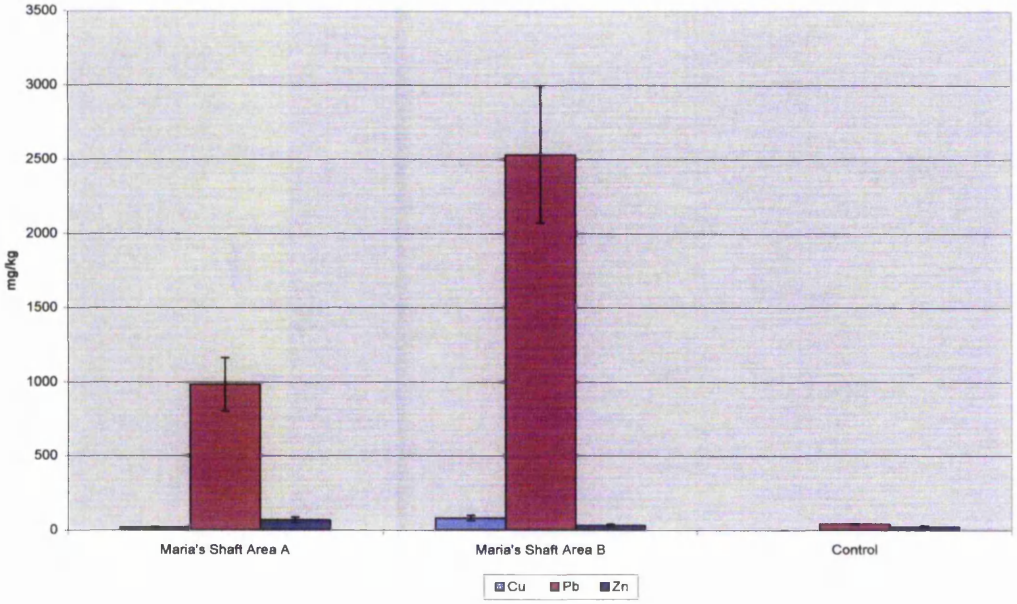


Figure 3.10: *Stereocaulon vesuvianum* copper, lead and zinc concentrations from around Parys Mountain



Analysis of the fruticose lichen *Cladonia impexa* and *Stereocaulon vesuvianum* for copper, lead and zinc show various concentrations around the site and in each case lead is the highest concentration. Copper and zinc are also present but the zinc concentration is generally higher than that of copper. Again this data provides further evidence that the contamination around Parys Mountain is non-uniform. Bargagli *et al.* (2002), comment that in contaminated areas in Italy, amounts of copper and zinc in *Parmelia* spp. are significantly related. The single sample of *Parmelia physodes* from Parys Mountain has concentrations of copper, lead and zinc of 143, 551 and 56 mg/kg respectively and does not reaffirm this relationship.

Mosses too can be used as biomonitors for assessing the extent of pollution and are often used for geographical patterns (Gerdol *et al.*, 2002). Generally they are more tolerant to atmospheric pollution than lichens and therefore in areas with poor air quality could be used as biomonitors. The areas of Maria's Shaft area is identified by the analysis of *Sphagnum* spp. as the most polluted (see Fig. 3.11). It is exposed and is not particularly abundant in vegetation in which *Sphagnum spp*. colonises, especially under stands of *Calluna vulgaris*. This may increase the amount of exposure of *Sphagnum* spp. to wet and dry atmospheric deposition and thus the opportunity to accumulate cations by direct contact through the foliar route. The Oxen Quarry and Pond samples show less amounts of copper, lead and zinc. These areas are sheltered by the nature of the sites topography and increased density of *Calluna vulgaris* and other vegetation. This may act as an intercept of deposition and therefore reduce the amount of exposure to heavy metals.

As a result, such a site where the extent of pollution is known to be varied and above 'normal' levels, it would be difficult to use mosses as a biomonitor. Bargagli *et al.* (2002), discuss that mosses and lichens cannot be used 'interchangeably' as biomonitors in areas with extensive natural and anthropogenic contamination. But they do note that the geochemical characteristics of an area have a greater affect on the elemental concentrations of mosses compared to that of lichens. Saxena *et al.* (2003), comment that *Sphagnum* spp. is a hyperaccumulator of lead and the amount of lead found in *Sphagnum* spp. when analysed can be closely related to the surrounding substrate and atmospheric concentrations the specimen has been exposed to. Saxena *et al.* (2003), also state that *Sphagnum* spp. may be used as a phytoremediator, however, the author expresses that in a commercial environment this would not be feasible. In terms of this study, evidence suggests that mosses in particular *Sphagnum* spp., do bioaccumulate metals and in comparison to the control specimen highlight there are excessive levels of heavy metals in the area. Because of the ability of *Sphagnum* spp. it may be a pathway of cations getting into the trophic levels.

The grass species present on Parys Mountain are *Agrostis tenuis*, *Festuca* spp., and *Deschampsia* spp.. These are also found in adjacent podsolised areas and the control site where there is no known contamination. Both *Agrostis tenuis* and *Festuca* spp. are widely recognised as heavy metal tolerant species (Romkens *et al.*, 1999; Boon *et al.*, 1998 and Harborne, 1993) and can colonise successfully in areas of excessive heavy metal substrate concentrations.

Figure 3.11: *Sphagnum* spp. copper, lead and zinc concentrations from around Parys Mountain

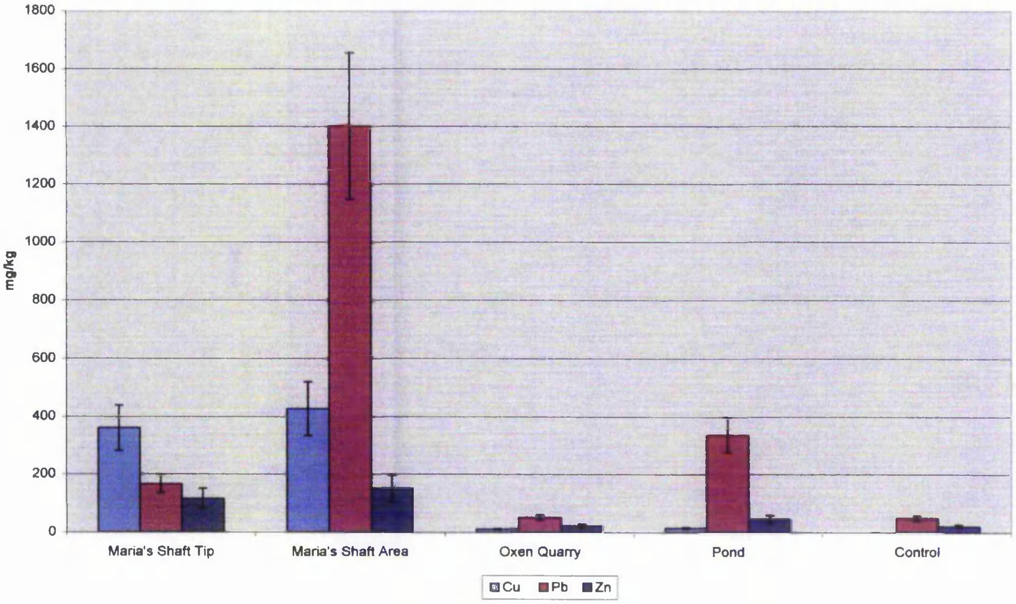


Table 4.2: Grass specimen and total and bioavailable substrate analysis for copper, lead and zinc at three sites on Parys Mountain (mg/kg)

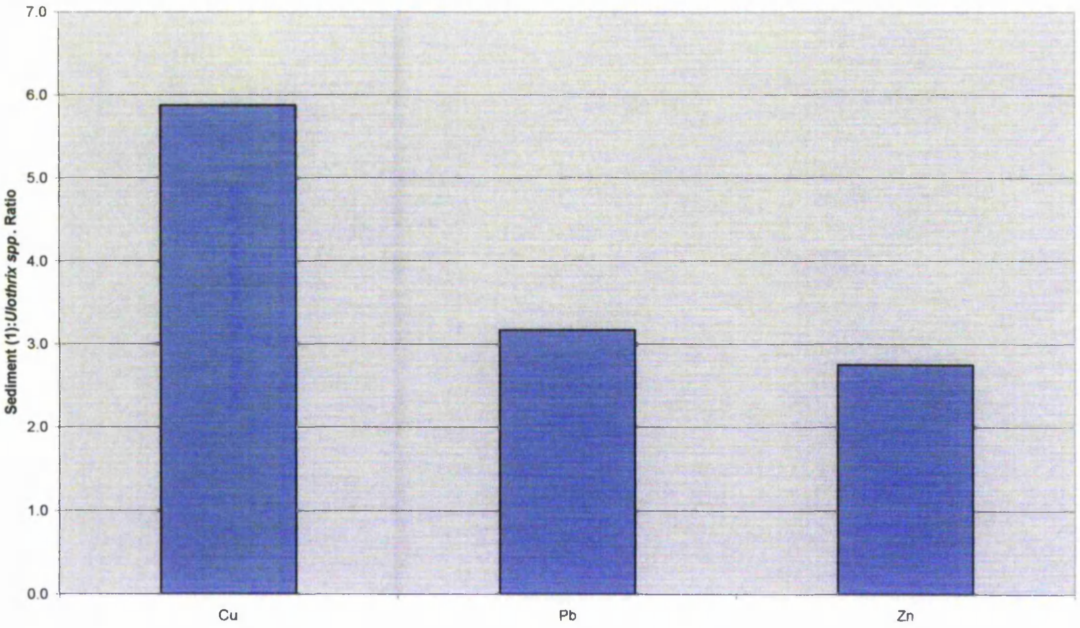
Species	Site	copper	lead	zinc
Surface Spoil Total	Maria's Shaft Tip (Top) (Site 1)	15	2,295	13
Surface Spoil Bioavailable		6	4	1
Festuca spp.		36	4	47
Festuca spp.	Chimney (Site 9)	281	2,107	37
Surface Spoil Total	Calcination Area (Site 4)	45	2,701	36
Surface Spoil Bioavailable		34	15	30
Agrostis tenuis		14	3,760	31
Surface Soil Total	Gulley (Site 12)	22	668	20
Surface Soil Bioavailable		46	13	24
Deschampsia spp.		19	439	233

Table 4.2 shows the various concentrations of copper, lead and zinc in the three species of grass found on Parys Mountain. Also displayed are the total and bioavailable concentrations of metals in the substrate that the specimen was growing in. As common with other vegetation samples that have been analysed, lead is the most prevalent with the exception of the Site 1 *Festuca* spp. sample. Already discussed previously are that the copper and zinc bioavailable metal results for Site 12 exceed the total concentration. This has been concluded because of the separate extractions between total and bioavailable. Generally there are mixed scenarios where plant concentrations exceed substrate concentrations or are similar. It would be expected where there is a greater proportion of bioavailable metals that the accumulation in the grass would be significantly increased, however this is not the case. One factor affecting this may be the ability of the plants to control absorption of cations. Harborne (1993) explains that tolerant ecotypes may have the ability to change the nature of the cations by chelation and other biochemical changes to deal with the excess metals at the root-soil interface. Either way, the metals contained within the grasses is now in a form that is readily bioavailable through ingestion for any animals that feed on it.

It is conclusive that vegetation on Parys Mountain varies extensively in elemental concentrations. Specimens with excessively high concentrations of cations do not show any anatomical or physical defects. From this it is feasible to state that plants which colonise Parys Mountain include heavy metal ecotypes.

High heavy metal concentrations appear to limit the species diversity in general and Pyatt *et al.* (1993), noted a similar situation in a polluted stream in Betws-y-Coed, North Wales. The only algae able to withstand such conditions were *Ulothrix* spp. and *Spirogyra* spp.. They observed the same bioaccumulation potential of *Ulothrix* spp. as in this study. However, the ratio between spoil and *Ulothrix* spp. concentrations were 93 and 24 times greater for lead and zinc respectively. As can be seen from Fig 3.12 this is not as high for the sediment to *Ulothrix* spp. ratio, possibly because the elements are more mobile in the precipitation ponds than that of spoil above the water level and therefore have gradually reduced in concentration since commercial use of the precipitation ponds ceased in the 1950s. The lead concentrations found in the *Ulothrix* spp. sample are extremely elevated with copper, lead and zinc at 94, 31,678 and 44 mg/kg respectively. This may suggest that this is a hyperaccumulator species of this specific element. Pyatt et al. (1993), also found a similar scenario where lead concentrations in surface-washed *Ulothrix* spp. to be 133,350 mg/kg compared to the much lower 10,514 mg/kg zinc concentration. Looking closely at this data it appears that washing of the algae removes a considerable amount of metal as the concentrations are 159 mg/kg for lead and 3.65 mg/kg for zinc. It may be possible to comment on this evidence that the organism has the ability to partition elements but can also be selective on absorption.

Figure 3.12: Sediment to *Ulothrix* spp. bioaccumulation ratio of copper, lead and zinc



Twelve invertebrates in total were caught in pitfall traps and opportunistically, with *Cicindella campestris*, *Pterostichus oblongopunctatus* and *Philonthus laminatus* only slightly being the most abundant. The remaining species caught were *Amara famliaris*, *Silpha atrata*, *Opilio* spp., *Tachypodoiulus niger*, *Arion* spp. and *Rilaena triangularis*. This general lack of variety and greater relative abundancy were due to the paucity of food, toxicity of the environment and lack of appropriate habitats. The results for the invertebrates show there is minimal bioaccumulation but exceptions do occur. For example *Tachypodoiulus niger* and *Rilaena triangularis* are the only two insects to have any significant levels of copper, lead and zinc. These may be consumed by foxes or birds and so biomagnification could possibly take place. Invertebrates come in very close contact directly or indirectly with the soil or spoil (Heikens *et al.*, 2001), therefore this may closely influence the amount of metals absorbed and accumulated.

Lock *et al.* (2001), reviewed the effects of metal contamination on Carabid beetles and concluded that the amount of uptake of zinc and lead was affected by the amount present in the prey, which are usually soft bodied larvae. Nevertheless Carabids do have the ability to adapt to these high surrounding concentrations by excretion. This is common in other insects and therefore may point to the low levels of metals found in the specimens of this study. Both Heikens *et al.* (2001) and Storm *et al.* (1994), state that species of invertebrate that decompose organic matter near the soil compartment will have higher metal concentrations compared to that of insects that feed on vegetation. Generally, Coleoptera had low concentrations when compared to Isopods and Diplopoda. This may suggest why *Tachypodoiulus niger* contained significant levels of copper, lead and zinc. Work by Marigomez *et al.*, (1998) analysed slugs, *Arion ater* from Parys Mountain for copper and zinc and found that they had a whole body concentration of between 104 – 193 mg/kg and 54 – 74 mg/kg respectively. From the one specimen found on Parys Mountain in this study there showed to be levels below the LOQ, this maybe because it was found in an area where the concentration of metals was low or as concluded by Marigomez *et al.* (1998), the slugs can adapt to inhabit these areas by modifying cell and tissue organisation of their digestive gland and therefore inhibit uptake of heavy metals.

Invertebrates were dissected to investigate the partitioning of elements in different tissues. *Cicindella campestris* head and thorax (187 mg/kg) and abdomen (212 mg/kg) contained zinc but only in 50% of the specimens caught.

This would suggest that either the digestive tract of *Cicindella campestris* had contained contaminated food or that this is where the bioaccumulation occurs in the soft internal body tissues of the beetle. *Silpha atrata* was also dissected into head and thorax, legs and abdomen and a similar pattern occurred. This time lead was found in the head and thorax (51 mg/kg) and abdomen (13 mg/kg); however there was 22 mg/kg of zinc also present in the abdomen. It is then possible that bioaccumulation of metals may occur in beetles, in particular zinc and lead. It is difficult to conclude anymore because of the limited amount of data which is a consequence of the low biomass of the organisms present in this often toxic environment.

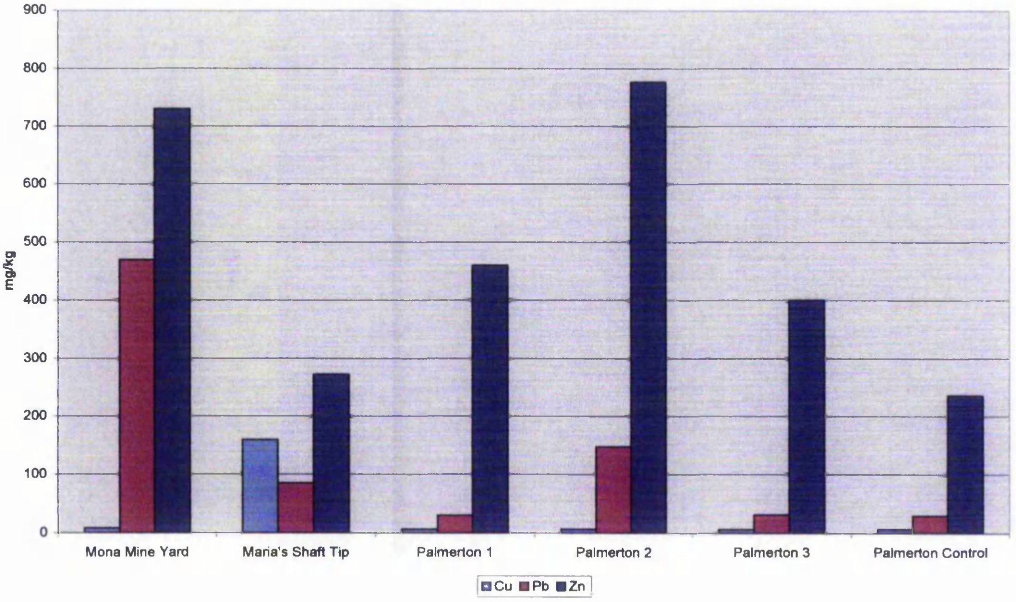
There is evidence of bioaccumulation higher up the trophic levels. Consumers, primarily rabbit not only vary in their skeletal content but also in their faeces. This may be related to age, diet or area to which the consumer had been feeding in (Smith and Rongstad, 1982). The faecal analysis (see Table 4.3) shows massive transient bioaccumulation of various elements.

Table 4.3: Rabbit faeces copper, lead and zinc concentrations (mg/kg)

Site	**copper**	**lead**	**zinc**
Maria's Shaft Area	77	642	145
Calcination Area	96	39	204
Rocky Outcrop	41	52	105
Chimney	36	189	122

The deposition of faeces is important as elements are returned to the pedosphere and subsequently recycled by vegetation and consumers. Furthermore, rural foxes have a fairly large geographic range (Dip *et al.*, 2001) and will not only be feeding around Parys Mountain but will be depositing faeces in unpolluted areas where there is potential to cause an effect. However, this is thought to be minimal. The movement of cations through the food chain is hard to quantify in species that feed over large areas as grazing adjacent unpolluted areas would diminish their copper, lead and zinc body burdens. When collecting the samples it was evident that rabbits and foxes had been feeding in the area by the presence of grazed grass, skeletal material that had been scavenged upon and faeces. Animal biodiversity is limited on Parys Mountain with sightings of rabbits and foxes being infrequent. This trend has also been noted by Storm *et al.* (1994), in a heavily polluted area near the Palmerton zinc smelter. However, enough samples of skeletons and faeces were collected and analysed to gain an insight to the extent of contamination.

Figure 3.13: Rabbit bone concentrations of copper, lead and zinc from Parys Mountain and work by Storm *et al.* (1994), from sites around a zinc Smelter in Palmerton



The above shows a comparison of the skeletal concentrations of rabbits from similarly polluted sites. The two Parys Mountain bone samples exhibit much higher concentrations of lead than that of Palmerton Control. The copper concentrations are in fact extremely similar to those of the Control at some sites whereas the zinc levels are highly elevated at Mona Mine Yard but not at Maria's Shaft Tip. Storm *et al.* (1994), notes that rabbits are likely to ingest soil particles due to grazing vegetation close to the ground. This may be a more direct and significant source of metals to the rabbits than the vegetation. However, the amount of accumulation in the rabbits will depend on the bioavailability and speciation of the cations once in the alimentary tract (Milton and Johnson, 1999). This bioaccumulation exceeds the normal levels as seen in control specimen skeletons, therefore it is likely that the concentration of metals in other tissues would also be elevated.

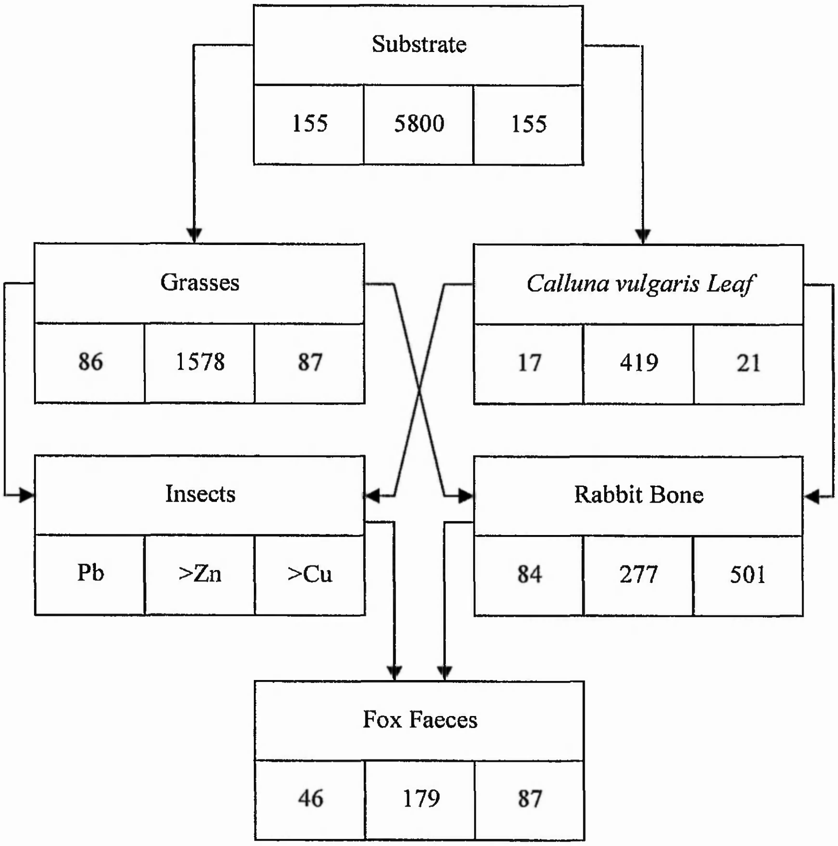
These cations would then be passed on to predators such as fox who would consume other tissues such as skin, muscle and other organs. This can be seen by the level of metals found in fox faeces in the table below.

Table 4.4: Fox faeces copper, lead and zinc concentrations (mg/kg)

Site	copper	lead	zinc
Maria's Shaft Area	76	296	128
Calcination Area	49	<LOQ	75
Mona Adit	15	62	59

As previously stated, the accumulation of metals through the food chain is not precise (Scharenberg and Ebeling, 1996). However, the transient bioaccumulation of metals in the faeces shows that there is a large possibility that absorption of a proportion of the ingested elements contaminated material could occur. In work focusing on the metal concentrations in urban, suburban and rural foxes, Dip *et al.* (2001), suggest that the fox may be used as a biomonitor. This is not because of its range, as this varies between urban and rural, but more importantly because of the ability of the fox to take up elements into tissues such as the kidneys and liver. This therefore shows a pathway for cations to travel through the trophic levels from the substrate to producers and on to consumers. Fig. 3.14 illustrates some of the bioaccumulation and translocation of heavy metals that occurs on Parys Mountain.

Figure 3.14: Food Web and relative copper, lead and zinc mean concentration averages (mg/kg)



After 3000 years or more of disturbance, with high concentrations of toxic elements in the soil, the author considers that these will affect the environment and the organisms they are in, for some considerable time. Humans may be affected by heavy metals and routes into the body include; inhalation of metal particles, contamination of food and direct ingestion. Health effects for humans of such intake of metals can include nausea, vomiting, convulsions, diarrhoea, coma, Wilson's disease, loss of appetite, constipation, abdominal pains, motor nerve paralysis, fatigue, anaemia, head aches, brain damage, Parkinson's disease and death (Pyatt and Grattan, 2001).

The author expresses slight concern that areas adjacent to Parys Mountain are being used for grazing by livestock. These areas could become contaminated by particulates that are transported and mobilised by both wind and water. Permission to collect samples of vegetation or fauna in the area was impossible to obtain.

6.0 CONCLUSIONS

From this study it is possible to conclude that the extent of heavy metal pollution around Parys Mountain is extremely varied. A mosaic of contamination exists with some areas containing exceptionally elevated levels of heavy metals. This patchwork of pollution is a consequence of centuries of anthropogenic activity exploiting the mines resources and has created a long term pollution focus from which the effects have continued over a prolonged period. Erosional processes have assisted this variance in concentrations as sheet and gulley erosion are particularly evident and there is no doubt that wind has caused wide-spread distribution of elements around the site and its proximity. The different age of the spoil tips did not seem to contribute to the degree of contamination as they are dynamic features where metals are constantly being eroded and redistributed around the site.

Mobilisation of cations to a bioavailable form occurs through several erosional processes and the harsh acidic environment only assists this. Once in the bioavailable form, metals are readily taken up by many species of plant. These heavy metal ecotypes have established and inhabited in this heavily polluted environment with no obvious physiological or anatomical defects. Adaptations to be able to exist in these conditions include limiting uptake at the root-soil interface and also translocation and partitioning within the plants system. Parys Mountain is inhabited by heathland community species but when compared to other, similar, non-polluted areas it is apparent that a low biodiversity exists and associated low population numbers for both plants and animals.

Concentrations of copper, lead and zinc vary significantly between species of plant and depending on plant structure. The routes in to the organisms system may well differ. Some plants with defined roots appear to absorb cations through this pathway such as *Salix* spp. where the higher concentrations of metals tended to occur. This method of partitioning was also observed in *Calluna vulgaris* roots taken from different areas around the site where copper and lead was generally higher than in other tissues. This could indicate that excess cations are partitioned and prevented from being stored elsewhere in the plant. However, zinc behaved very differently and in some tissues had lower concentrations than the uncontaminated control samples. *Juncus* spp. appeared to prevent the cations from entering at all, even when the substrate it was growing in had heavy metal concentrations in excess of normal levels found in the control site. Lichens and mosses may have been affected more by atmospheric deposition of elements rather than in the substrate. This work reinforces the suitability of using lichens and mosses as biomonitors as they readily bioaccumulated excess levels of metals from the surrounding environment.

This research has shown that the movement of metals through the trophic levels possible and evidence indicates that it occurs on Parys Mountain. Once in the plants system the movement of metals through the trophic levels is accelerated. Species in the area such as *Calluna vulgaris* and *Agrostis* spp. have the ability in some instances to bioaccumulate metals to higher concentrations than that of the surrounding environment.

These are grazed upon by herbivorous animals such as rabbits and therefore partitioning becomes important as excess cations have the potential to be stored in leaf material which is selectively consumed, and therefore rate of metal uptake is enhanced. In conjunction, deposition of metal rich dusts on food and feeding behaviour where the food is close to the source of contamination will alter the speed of bioaccumulation within the consumer. The feeding range of an animal such as a rabbit or fox may also vary the quantity and speed at which metals are bioaccumulated as a large range may reduce the body burden when occurs away from the contaminated site. Predators of these herbivorous consumers will also be vulnerable to excessive metal uptake as they feed on organisms inhabiting Parys Mountain. Analysis of fox faeces confirmed that large amounts of transient metals were being consumed by the animal and therefore a proportion of the metals will find a route in to the organism where they will be stored, with possible detrimental health effects.

Parys Mountain will continue to be a source of contamination for the foreseeable future with constant erosion, distribution and deposition of heavy metals. Subsequently, the area affected by this contamination will continue to increase in size. Land close to Parys Mountain is used for pastoral grassland. This may serve as a route in to the human food chain and therefore a possible threat to human health. To prevent this, a careful remediation strategy would need to be implemented to reduce the rate at which metals are being mobilised and released in to the environment.

However, due to the historical, archaeological and biological importance of this site and its geological diversity, it is unlikely that this will ever happen.

Further Work

From this study certain aspects need to be investigated further. Below are the most interesting issues.

1. Carry out a study into the windborne dispersion of contamination from Parys Mountain.
2. Compare the bioaccumulation and tissue speciation in *Calluna vulgaris* from Parys Mountain compared to other polluted and non-polluted sites.
3. Further investigation looking at various biomonitor species and their suitability to be used on Parys Mountain and elsewhere.

7.0 REFERENCES

Arias, M., Nunez, A., Barral, M.T., and Diaz-Fierros, F. (1998). Pollution potential of copper mine spoil used for road making. *The Science of the Total Environment*. 221, 111-116

Barber, A.J., and Max, M.D. (1979). A new look at the Mona Complex (Anglesey, North Wales). *Journal of the Geological Society*. 136, 407-432

Bargagli, R., Monaci, F., Borghini, F., Bravi, F., and Agnorelli, C. (2002). Mosses and lichens as biomonitors of trace metals. A comparison study on *Hypnum cupressiforme* and *Parmelia caperata* in a former mining district in Italy. *Environmental Pollution*. 116, 279-287

Barrett, T.J., MacLean, W.H., and Tennant, S.C. (2001). Volcanic Sequence and Alteration at the Parys Mountain Volcanic-Hosted Massive Sulfide Deposit, Wales, and United Kingdom: Applications of Immobile Element Lithogeochemistry. *Environmental Geology*. 96, 1279-1305

Bech, J., Poschenrieder, C., Llugany, M., Barcelo, J., Tume, P., Tobias, F.J., Barranzuela, J.L., and Vasquez, E.R. (1997). Arsenic and heavy metal contamination of soil and vegetation around a copper mine in Northern Peru. *The Science of the Total Environment*. 203, 83-91

Boon, G.T., Bouwman, L.A., Bloem, J., and Romkens, P.F.A.M. (1998). Effects of a copper-tolerant grass (*Agrostis capillaries*) on the ecosystem of a copper-contaminated arable soil. *Environmental Toxicology*. 17(10), 1964-1971

Boult, S., Collins, D.N., White, K.N., and Curtis, C.D. (1994). Metal Transport in a Stream Polluted by Acid Mine Drainage - The Afon Goch, Anglesey, UK. *Environmental Pollution*. 84, 279-284

Cottenie. A., Camerlynck, R., Verloo, M., and Dhaese, A. (1979). Fractionation and determination of trace elements in plants, soils and sediments. *Pure and Applied Chemistry*. 52, 45-53

Dinelli, E., and Tateo, F. (2001). Factors controlling heavy-metal mining areas: the case of Vigonzano (Northern Italy), a Fe-Cu sulfide deposit associated with ophiolitic rocks. *Environmental Geology*. 40, 1138-1150

Dip, R., Stieger, C., Deplazes, P., Hegglin, D., Muller, U., Dafflon, O., Koch, H., and Naegeli, H. (2001). Comparison of Heavy Metal Concentrations in Tissues of Red Foxes from Adjacent Urban, Suburban and Rural Areas. *Journal of Environmental Contamination and Toxicology*. 40, 551-556

Fletcher, C.J.N., Swainbank, I.G., and Colman, T.B. (1993). Metallogenic evolution in Wales: Constraints from lead isotope modelling. *Journal of the Geological Society*. 150, 77-82

Gerdol, R., Bragazza, L., and Marchesini, R. (2002). Element concentrations in the forest moss *Hylocomium splendens*: variation associated with altitude, net primary production and soil chemistry. *Environmental Pollution.* 116, 129-135

Grattan, J.P., and Pyatt, F.B. (1994). Acid damage to vegetation following the Laki fissure eruption in 1783 – an historical review. *The Science of the Total Environment.* 151, 241-247

Heikens, A., Peijnenburg, W.J.G.M., and Hendriks, A.J. (2000). Bioaccumulation of heavy metals in terrestrial invertebrates. *Environmental Pollution.* 113, 385-393

Jenkins, D.A., Johnson, D.B., and Freeman, C. (2000). Mynydd Parys Cu-Pb-Zn Mines: mineralogy, microbiology and acid mine drainage. Environmental Mineralogy: Microbial Interactions, Anthropogenic Influences, Contaminated Land and Waste Management. *The Mineralogical Society of Great Britain and Ireland.* 9, 161-179

Nash, T.H., III. (1975). Influence of Effluents from a Zinc Factory on Lichens. *Ecol. Monogr.* 45, 183-198

Lakanen, E., and Ervio, R. (1971). A Comparison of Eight Extractants for the Determination of Plant Available Micronutrients in Soils. *Ann. Agric. Fenn.* 125, 223-232

Lock, K., Desender, K., and Janssen, C.R. (2001). Effects of metal contamination on the activity and diversity of carabid beetles in an ancient Pb-Zn mining area at Plombiers (Belgium). *Entomologia Experimentalis et Applicata.* 99, 355-360

Kruckeberg, A.L., and Wu. L. (1991). Copper tolerance and copper accumulation of herbaceous plants colonizing inactive California copper mines. *Ecotoxicology and Environmental Safety.* 23, 307-319

Marigomez, I., Kortabitarte, M., and Dussart, G.B.J. (1998). Tissue-Level Biomarkers in Sentinel Slugs as Cost-Effective Tools to Assess Metal Pollution in Soils. *Archives of Environmental Contamination and Toxicology.* 34, 167-176

Milton, A., and Johnson, M. (1999). Biomonitoring of contaminated mine tailings through age accumulation of trace metals in the bank vole (*Clethrionomys glareolus*). *Journal of Environmental Monitoring.* 1, Pp.219-225

Nriagu, J.O., Wong, H.K.T., Lawson, G., and Daniel, P. (1998). Saturation of Ecosystems with Toxic Metals in Sudbury Basin, Ontario, Canada. *Science of the Total Environment.* 223, 99-117

Parkman, R.H., Curtis, C.D., Vaughan, D.J., and Charnock, J.M. (1996). Metal fixation and mobilisation in the sediments of the Afon Goch estuary – Dulas Bay, Anglesey. *Applied Geochemistry.* 11, 203-210

Pendersen, M.B., Kjaer, C., and Elmegaard, N. (2000). Toxicity and bioaccumulation of copper to Black Bindweed (*Fallopia convolvulus*) in relation to bioavailability and the age of soil contamination. *Archives of Environmental Contamination and Toxicology*. 39, 431-439

Pointon, C.R., and Ixer, R.A. (1980). Parys Mountain Mineral Deposit, Anglesey, Wales: Geology and Ore Mineralogy. *The Institution of Mining and Metallurgy: Section B*. 89, B143-B155

Pyatt, F.B. (1973). Some aspects of plant contamination by airborne particulate matter. International Journal of Environmental Studies. 5, 212-220

Pyatt, F.B. (2000). Copper and lead bioaccumulation by *Acacia retinoides* and *Eucalyptus torquata* in sites contaminated as a consequence of extensive ancient mining activities in Cyprus. *Ecotoxicology and Environmental Safety*. 50, 60-64

Pyatt, F.B., Barker, G.W., Birch, P., Gilbertson, D.D., Grattan, J.P., and Mattingly, D.J. (2000). King Solomon's Miners-Starvation and Bioaccumulation? An Environmental Archaeological Investigation in Southern Jordan. *Ecotoxicology and Environmental Safety*. 43, 305-308

Pyatt, F.B., Gilmore, G., Grattan, J.P., Hunt, C.O., and McLaren, S. (2000). An Imperial Legacy? An Exploration of the Environmental Impact of Ancient Metal Mining and Smelting in Southern Jordan. *Journal of Archaeological Sciences*. 27, 771-778

Pyatt, F.B., and Grattan, J.P. (2001). Some consequences of ancient mining activities on the health of ancient and modern human populations. *Journal of Public Health Medicine*. 23(3), 235-236

Pyatt, F.B., Pyatt, A. J., and Mould, N. (1993). Accumulation of Lead and Zinc from a Metalliferous Spoil Tip Stream by the Algae *Ulothrix sp*. And *Spirogyra Sp*.. *International Journal of Environmental Studies*. 45, 57-59

Romkens, P.F.A.M., Bouwman, L.A., and Boon, G.T. (1999). Effect of plant growth on copper solubility and speciation in soil solution samples. *Environmental Pollution*. 106, 315-321

Saxena, A., Saxena, D.K., and Srivastava, H.S. (2003). The Influence of Glutathione on Physiological Effects of Lead and its Accumulation in Moss *Sphagnum Squarrosum*. *Water, Air and Soil Pollution*. 143, 351-361

Scharenberg, W, and Ebeling, E. (1996). Distribution of heavy metals in a woodland food web. *Bulletin of Environmental Contamination and Toxicology*. 56, 389-396

Smith, G.J., and Rongstad, O.J. (1982). Small mammal heavy metal concentrations from mined and control sites. *Environmental Pollution (Series A)*. 28, 121-134

Southwood, M.J. (1984). Basaltic Lavas at Parys Mountain, Anglesey: Trace-Element Geochemistry, Tectonic Setting and Exploration Implications. *The Institution of Mining and Metallurgy: Section B.* 93, B51-B54

Stoltz, E., and Greger, M. (2002). Accumulation properties of As, Cd, Cu, Pb and Zn by four wetland plants species growing on submerged mine tailings. *Environmental and Experimental Botany.* 47, 271-280

Storm, G.L., Fosmire, G.J., and Bellis, E.D. (1994). Heavy Metals in the Environment: Persistence of Metals in Soils and Selected Vertebrates in the Vicinity of the Palmerton Zinc Smelters. *Journal of Environmental Quality.* 23, 508-514

Swallow, M. (1990). Parys Mountain: A Mine in Prospect. *Mining Magazine.* November, 334-336

Timberlake, S., and Jenkins, D. (1997). Prehistoric Mining: Geochemical Evidence from Sediment Cores at Mynydd Parys, Anglesey. *Archaeological Sciences.* 193-199

Walton, K.C., and Johnson, D.B. (1992). Microbiological and Chemical Characteristics of an Acidic Stream Draining a Disused Copper Mine. *Environmental Pollution.* 76, 169-175

Ye, Z.H., Baker, A.J.M., Wong, M.H., and Willis, A.J. (2003). Copper Tolerance, Uptake and Accumulation by *Phragmites australis*. *Chemosphere.* 53, 795-800

8.0 BIBLIOGRAPHY

Adriano, D.C. (1986). Trace Elements in the Terrestrial Environment. New York: Springer-Verlag

Alloway, B.J. (1995). Heavy Metals in Soils, 2nd Edition. Suffolk: Blackie Academic and Professional.

Bingley, Rev. E. (1798). A Tour Round North Wales Performed During the Summer of 1798. London: 1801

Challinor, J., and Bates, D.E.B. (1973). Geology Explained in North Wales.Newton Abbot: David & Charles.

Cox, P.A. (1995). The Elements of Earth: Inorganic Chemistry of the Environment. Oxford: Oxford University Press.

Donald, M.B. (1955). Elizabethan Copper: The History of the Company of Mines Royal 1568-1605. West Yorkshire: Michael Moon.

Down, C.G. and Stocks, J., (1977). Environmental Impact of Mining. London: Applied Science Publishers Ltd.

Duffus, J.H. (1980). Environmental Toxicology. London: Edward Arnold

Ebdon, L. (1982). An Introduction to Atomic Absorption Spectroscopy. London: Hayden and Son Ltd.

Faraday, M. (1819). Tour in Wales (ed Dafydd Tomos) Gwasg Gee

Fergusson, J.E., (1990). The Heavy Elements: Chemistry, Environmental Impact and Health Effects. Oxford: Pergamon Press.

Friberg, L., Nordberg, G.F., and Vouk, V.B., (1979). Handbook on the Toxicology of Metals. Amsterdam: Elsevier/North-Holland Biomedical Press.

Gimingham, C.H., (1972). Ecology of Heathland. London: Chapman and Hall.

Goodall, D.W., (1979). Ecosystems of the World 9A: Heathlands and Related Shrublands. Amsterdam: Elsevier Scientific Publishing Company.

Griffith, O., (1897). Mynydd Parys. Caernarfon

Harborne, J.B. (1993). Introduction to Ecological Biochemistry, Fourth Edition. Cambridge: Academic Press Ltd.

Harris, J.R., (1964). The Copper King: A Biography of Thomas Williams of Llanidan. Liverpool: Liverpool University Press.

Harrison, R.M. (1999). Understanding our Environment: An Introduction to Environmental Chemistry and Pollution, Third Edition. Cambridge: Royal Society of Chemistry.

Harrison, R.M. and Laxen, D.P. (1981). Lead Pollution, Causes and Control. Cambridge: Chapman and Hall.

Hope, B., (1994). A Curious Place: The industrial History of Amlwch (1550 – 1950). Anglesey: Watch House Books.

Lawrence, E., Jackson, R.W. and Jackson, J.M. (1998). Longman Dictionary of Environmental Science. Harlow: Addison Wesley Longman Ltd.

Lentin, G.L. (1800). Briefe uber die Insel Anglesea, vorzuglich uber das dasige Kupfer-Bergwerk und die dazu Gehorigen Schmelzwerke und Fabriken. Leipzig: 1800

Lonergoran, J.F., Robson, A.D., and Graham, R.D. (1981). Copper in Soils and Plants. London: Academic Press.

Manahan, S.E. (1994). Environmental Chemistry. Boca Raton: CRC Press Inc.

Martin, M.H., and Coughtrey, P.J. (1982). Biological Monitoring of Heavy Metal Pollution, Land and Air. London: Applied Science.

McBride, M.B. (1994). Environmental Chemistry of Soils. New York: Oxford University Press.

Mikesell, R.F. (1979). The World Copper Industry, Structure and Economic Analysis. London: John Hopkins Press Ltd.

Moriarty, F. (1983). Ecotoxicology: The Study of Pollutants in Ecosystems. Orlando: Academic Press, Inc.

Nemerow, N.L. (1978). Industrial Water Pollution: Origins, Characteristics and Treatment. California: Addison-Wesley Publishing Company

Nriagu, J.O. (1978). The Biogeochemistry of Lead in the Environment: Part A. Ecological Cycles. Amsterdam: Elsevier/North-Holland Biomedical Press.

Nriagu, J.O. (1979). Copper in the Environment, Part 1: Ecological Cycling. New York: John Wiley and Sons, Inc.

Nriagu, J.O. (1980). Zinc in the Environment, Part 1: Ecological Cycling. New York: John Wiley and Sons, Inc.

Nriagu, J.O. (1984). Environmental Impacts of Smelters. New York: John Wiley and Sons, Inc.

O'Donoghue, M. (1982). Beginner's Guide to Minerals. Sevenoaks: Newnes Technical Books.

O'Gorman, F. (1997). The Long Eighteenth Century: British Political and Social History 1688-1832. London: Arnold Publishing.

Owen JR, C.A. (1982). Biological aspects of copper: occurrence, assay, and interrelationships. New Jersey: Noyes Publications.

Radofevic, M., and Bashkin, V.N. (1999). Practical Environmental Analysis. Cambridge: Royal Society of Chemistry.

Robb, D.A., and Pierpoint, W.S. (1983). Metals and Micronutrients, Uptake and Utilisation by Plants. London: Academic Press.

Rowlands, J. (1966). Copper Mountain. Denbigh: Gee and Son Ltd.

Royal Commission, (1937). Anglesey: A Survey and Inventory by the Royal Commission on Ancient and Historical Monuments in Wales and Monmouthshire. London: Her Majesty's Stationery Office.

Smith, R.L. and Smith, T.M. (1998). Elements of Ecology: Fourth Edition. California: Benjamin Cummings.

Spiro, T.G. and Stigliani, W.M. (1996). Chemistry of the Environment. New Jersey: Prentice-Hall, Inc.

Tansley, A.G. (1965). The British Islands and their Vegetation: Volume II. Cambridge: University Press.

Waldron, H.A. (1980). Metals in the Environment. London: Academic Press Inc.

Waugh, D., (1997). Geography: An Integrated Approach. Ontario: Nelson.

Webb, N.R. (1986). Heathlands: A Natural History of Britain's Lowland Heaths. London: Collins.

9.0 WEB REFERENCES

Date	**Subject**	**Address**
21/10/01	Archaeology	http//www.copperkingdom.fsnet.co.uk
17/05/03	Bronze Age Artefacts	http://www.parysmountain.co.uk/
17/05/03	Roman Artefacts	http://www.parysmountain.co.uk/

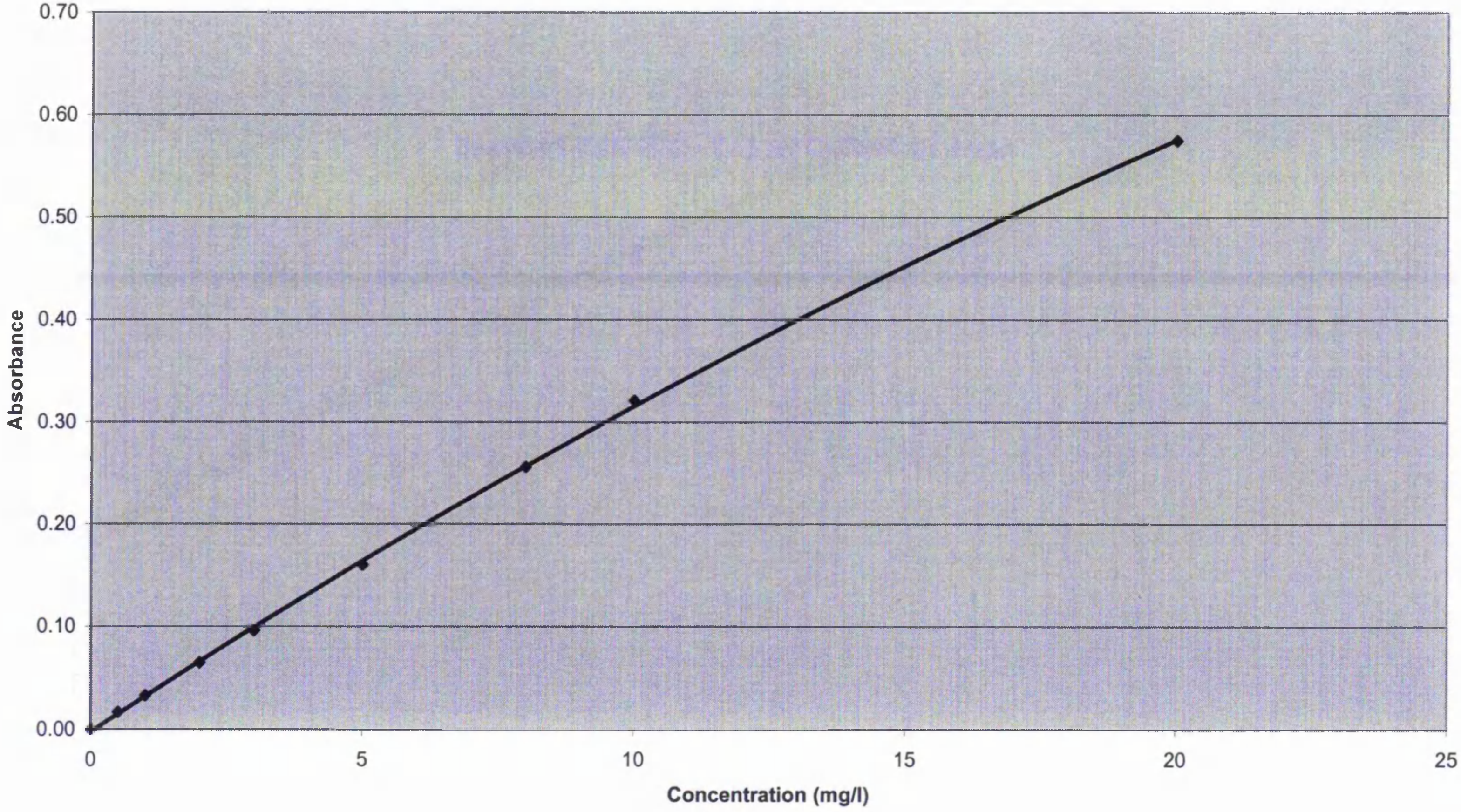
APPENDICES

Copper Calibration Standards Absorbance Figures

CALIBRATION			
Session 1		Session 2	
mg/l	Abs	mg/l	Abs
0	0.00	0	0.00
0.5	0.017	0.5	0.025
1	0.033	1	0.051
2	0.065	2	0.104
3	0.096	3	0.155
5	0.160	5	0.249
8	0.256	8	0.385
10	0.321	10	0.463
20	0.575	20	0.800

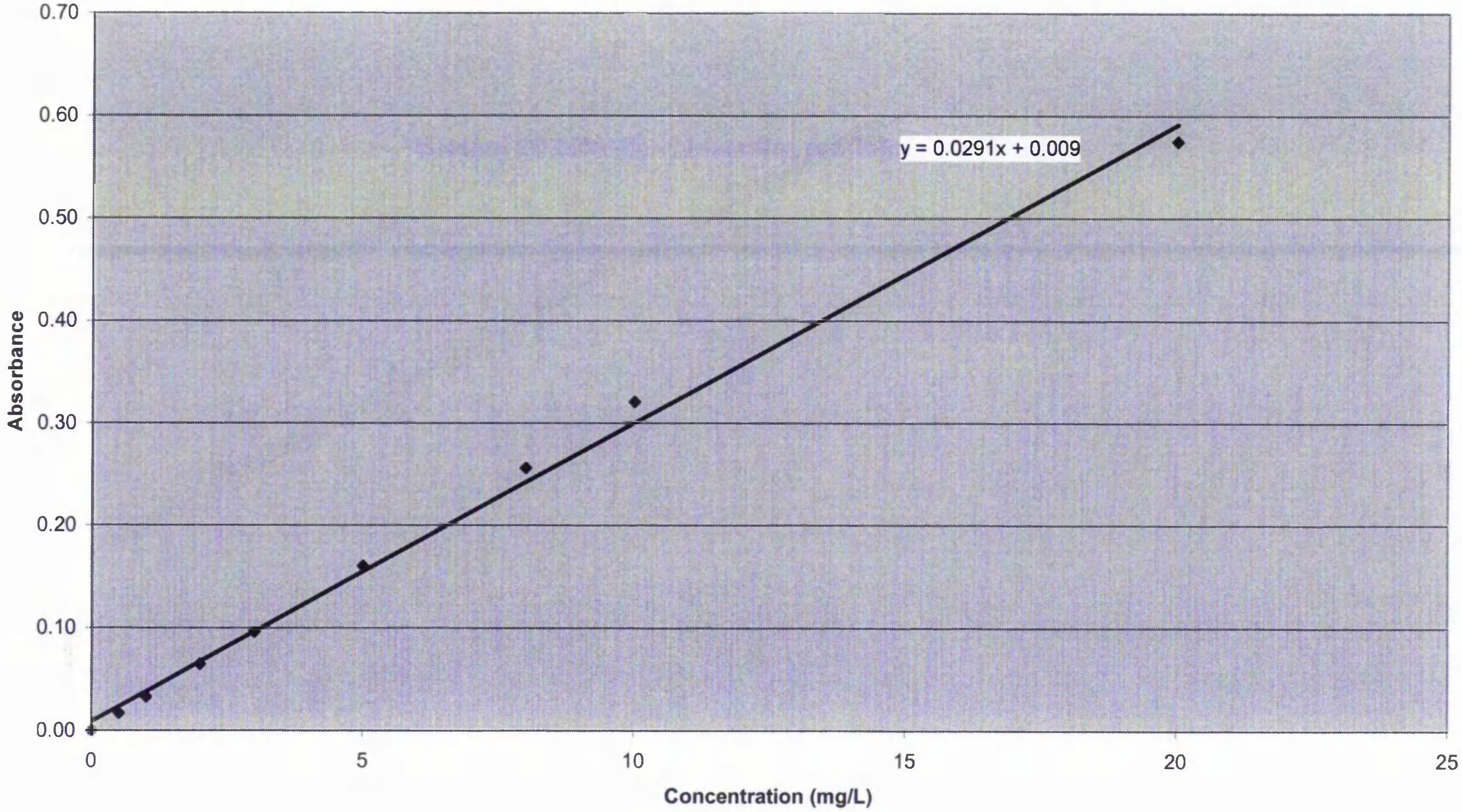
Copper Calibration Replicate Absorbance Figures

REPLICATES							
	Session 1						
Standard	**1**	**2**	**3**	**4**	**5**	**6**	**Average**
Blank	0.000	0.000	0.000	0.000	0.000	0.000	**0.000**
0.5A	0.015	0.015	0.016	0.017	0.016	0.016	**0.016**
0.5B	0.016	0.016	0.016	0.017	0.017	0.017	**0.017**
8A	0.254	0.253	0.254	0.256	0.254	0.255	**0.254**
8B	0.259	0.257	0.26	0.257	0.259	0.259	**0.259**
	Session 2						
Standard	**1**	**2**	**3**	**4**	**5**	**6**	**Average**
Blank	0.000	0.000	0.000	0.000	0.000	-0.001	**0.000**
0.5A	0.024	0.024	0.024	0.025	0.024	0.024	**0.024**
0.5B	0.025	0.025	0.025	0.026	0.026	0.026	**0.026**
8A	0.386	0.386	0.387	0.385	0.388	0.386	**0.386**
8B	0.386	0.379	0.380	0.380	0.382	0.382	**0.382**

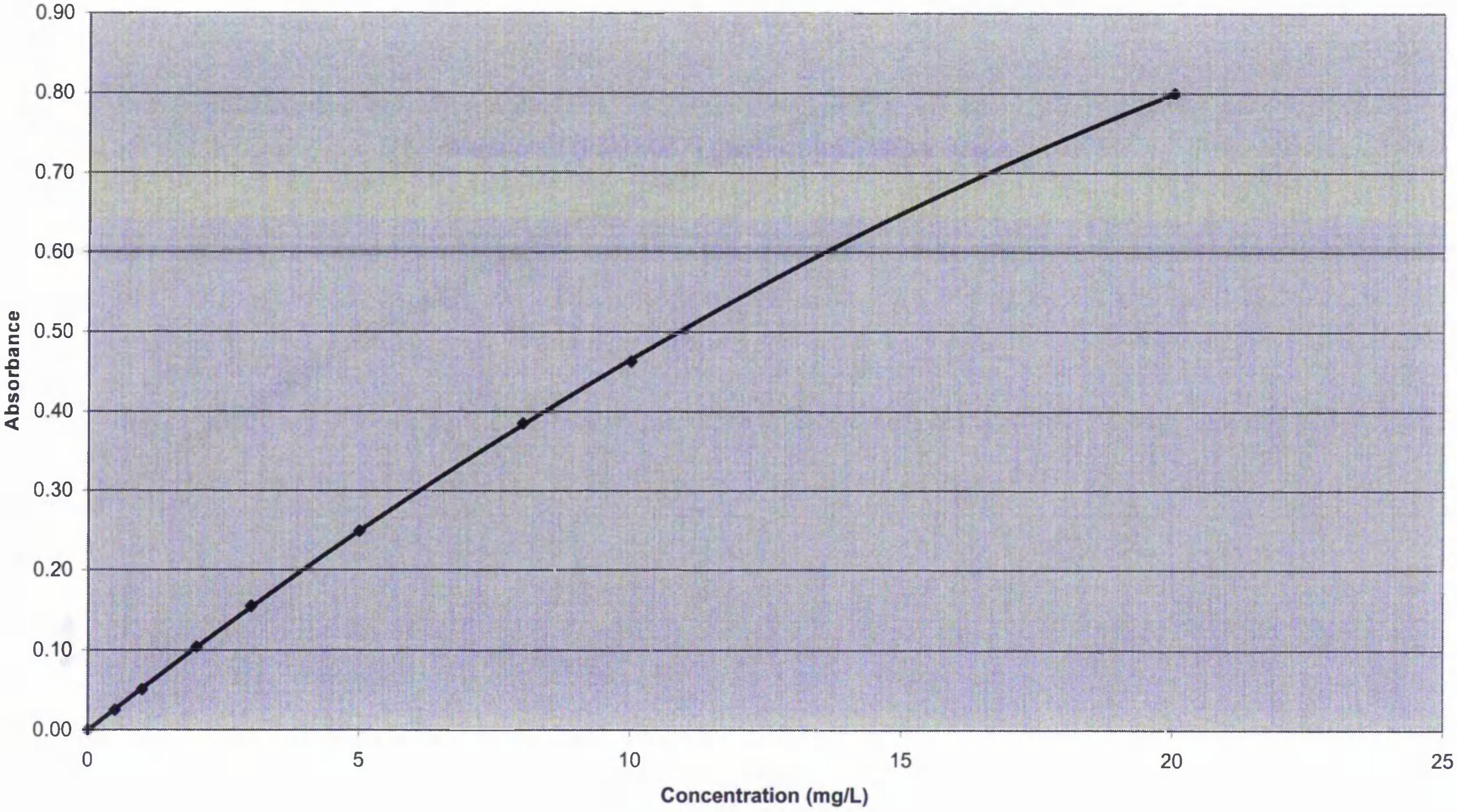


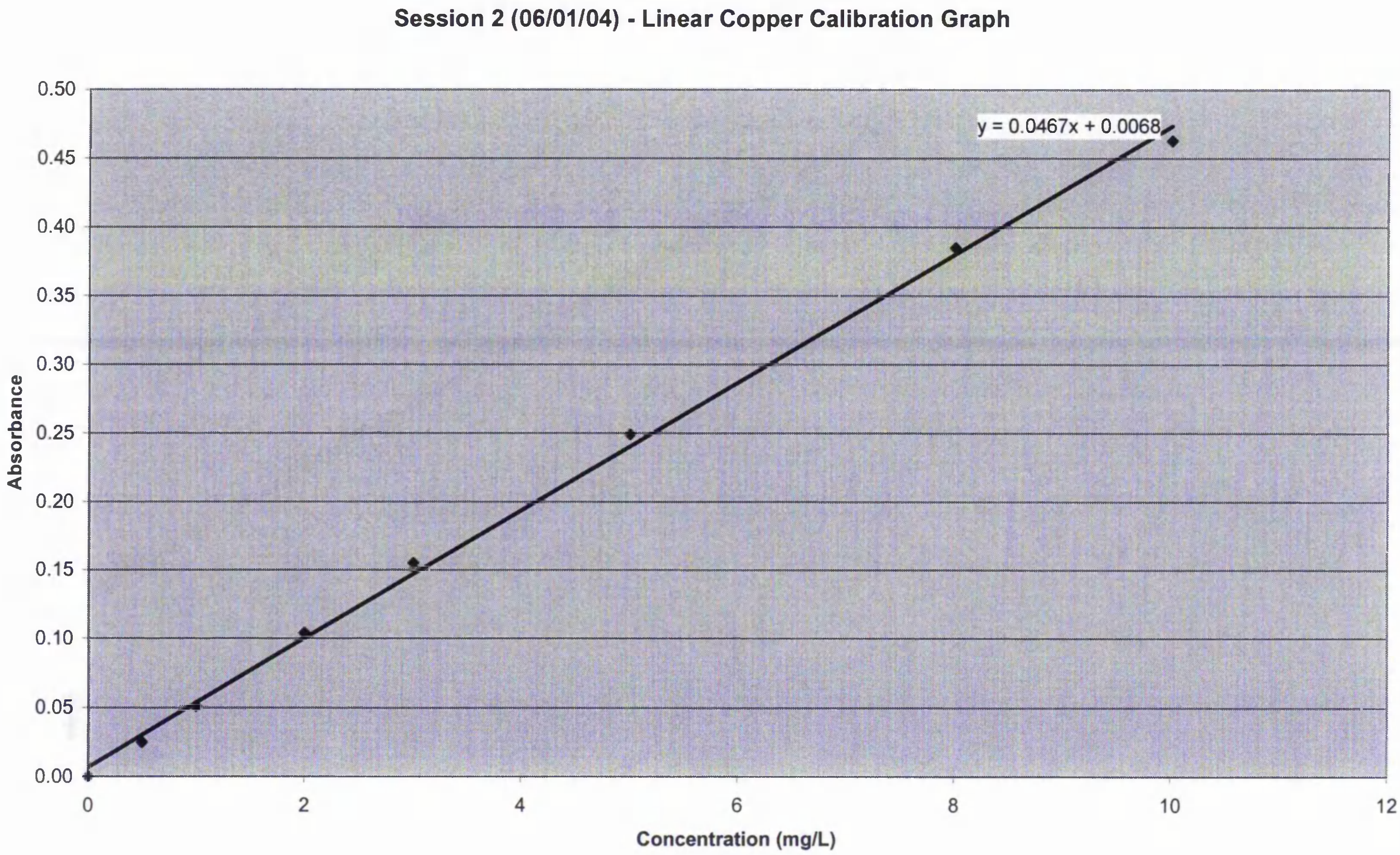
Session 1 (03/09/03) - Copper Calibration Graph

Session 1 (03/09/03) - Linear Copper Calibration Graph



Session 2 (06/01/04) - Copper Calibration Graph





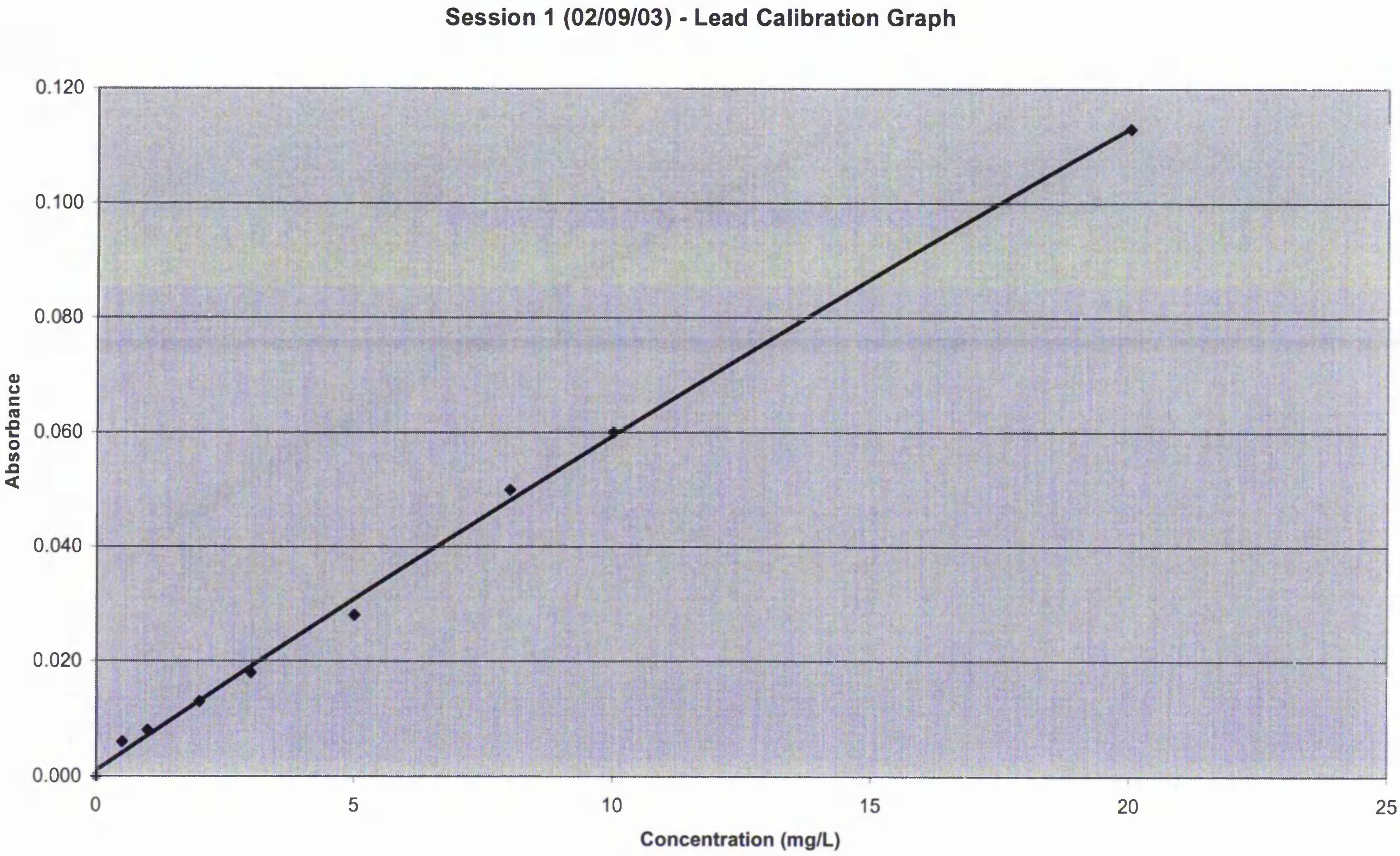
Session 2 (06/01/04) - Linear Copper Calibration Graph

Lead Calibration Standards Absorbance Figures

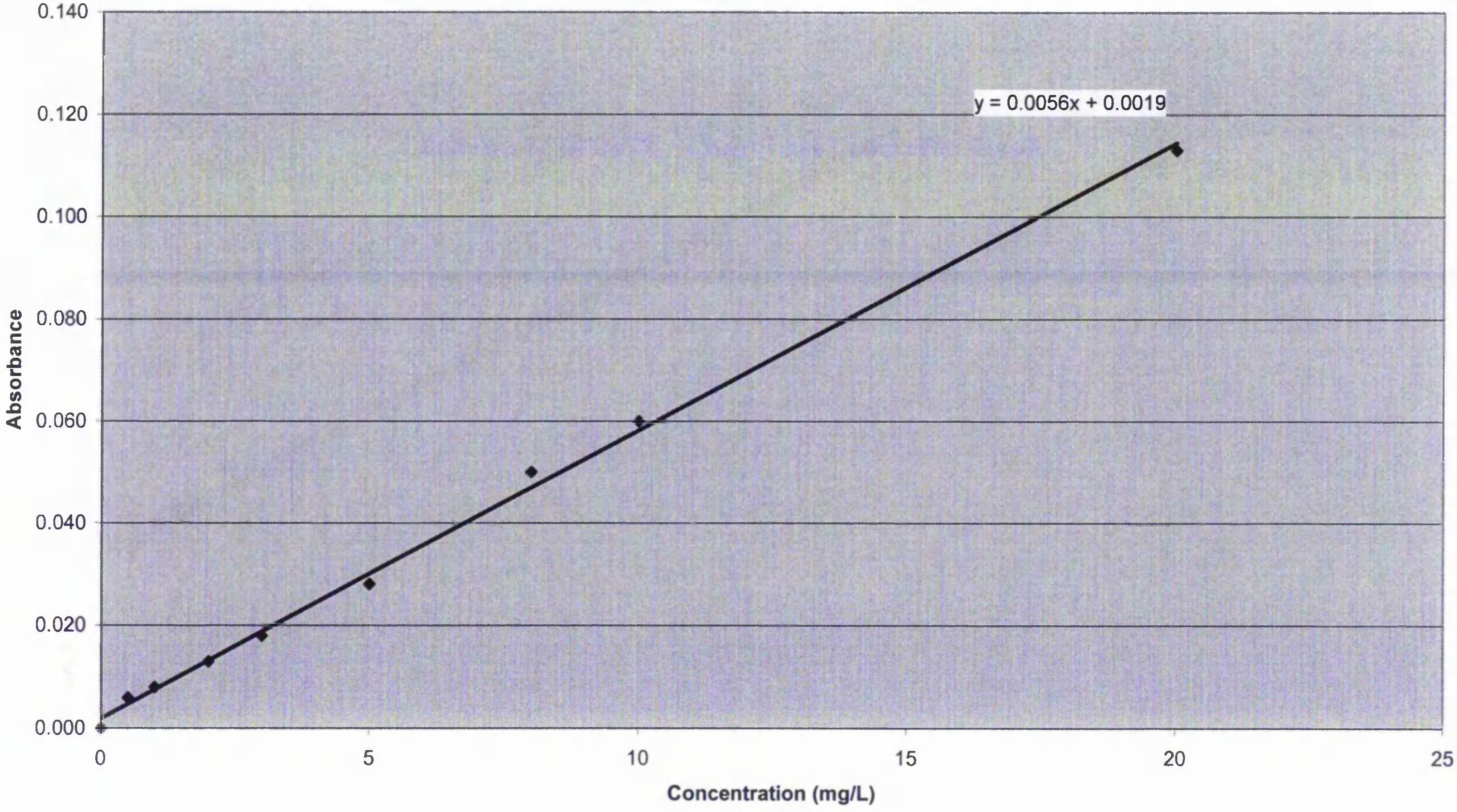
CALIBRATION			
Session 1		Session 2	
mg/l	Abs	mg/l	Abs
0	0.000	0	0.000
0.5	0.006	0.5	0.003
1	0.008	1	0.007
2	0.013	2	0.018
3	0.018	3	0.028
5	0.028	5	0.048
8	0.050	8	0.077
10	0.060	10	0.098
20	0.113	20	0.190

Copper Calibration Replicate Absorbance Figures

REPLICATES							
	Session 1						
Standard	**1**	**2**	**3**	**4**	**5**	**6**	**Average**
Blank	0.003	0.002	0.003	0.003	0.002	0.002	**0.003**
0.5A	0.005	0.006	0.006	0.006	0.006	0.007	**0.006**
0.5B	0.005	0.005	0.006	0.006	0.007	0.007	**0.006**
8A	0.051	0.051	0.051	0.051	0.05	0.05	**0.051**
8B	0.053	0.053	0.054	0.054	0.055	0.055	**0.054**
	Session 2						
Standard	**1**	**2**	**3**	**4**	**5**	**6**	**Average**
Blank	0.000	0.000	0.000	0.000	0.000	-0.001	**0.000**
0.5A	0.003	0.003	0.003	0.003	0.003	0.003	**0.003**
0.5B	0.002	0.002	0.002	0.002	0.003	0.003	**0.002**
8A	0.077	0.077	0.077	0.078	0.077	0.078	**0.077**
8B	0.077	0.076	0.077	0.077	0.078	0.077	**0.077**

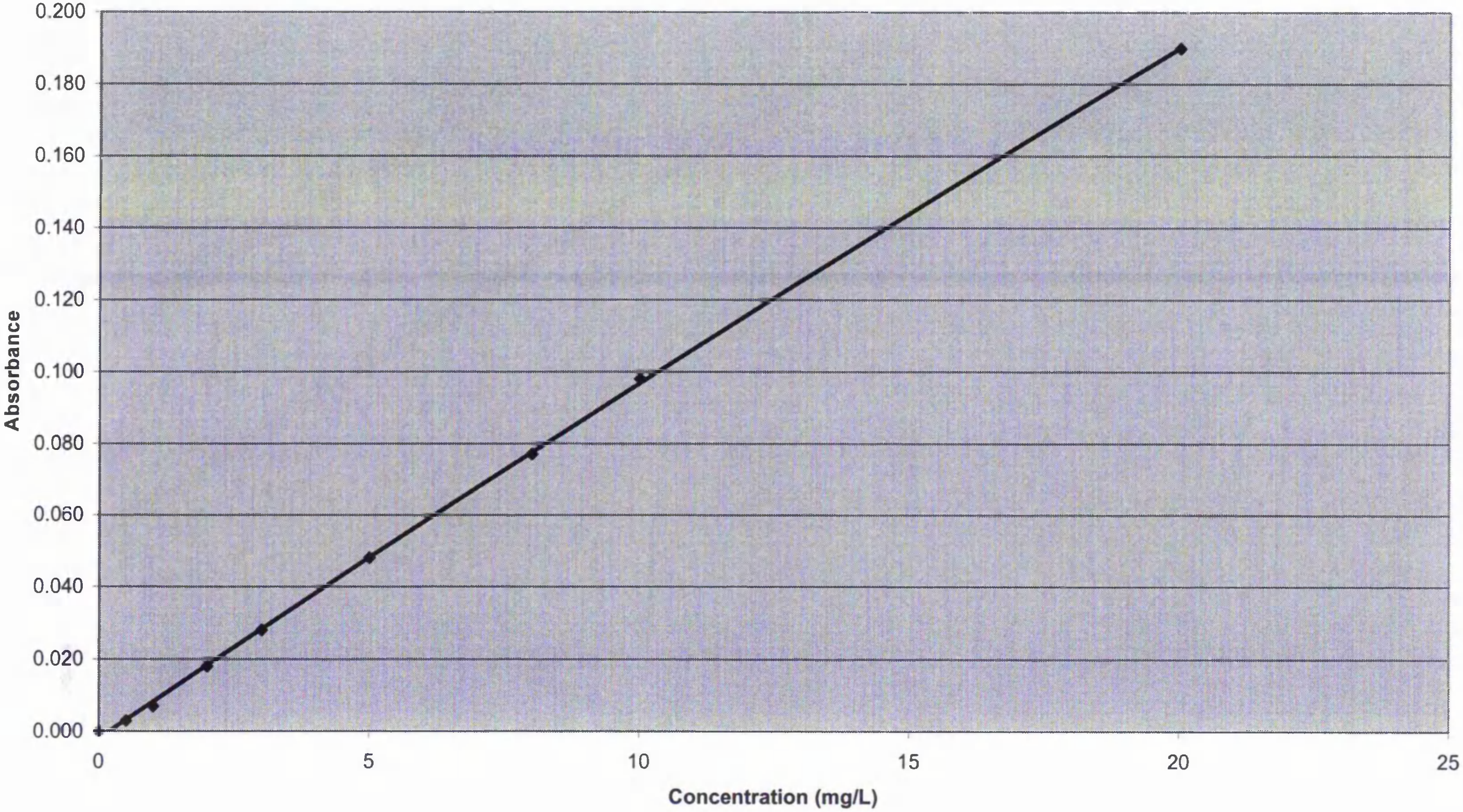


Session 1 (02/09/03) - Lead Calibration Graph
0.120
0.100
0.080
0.060
0.040
0.020
0.000
Absorbance
0
5
10
15
20
25
Concentration (mg/L)

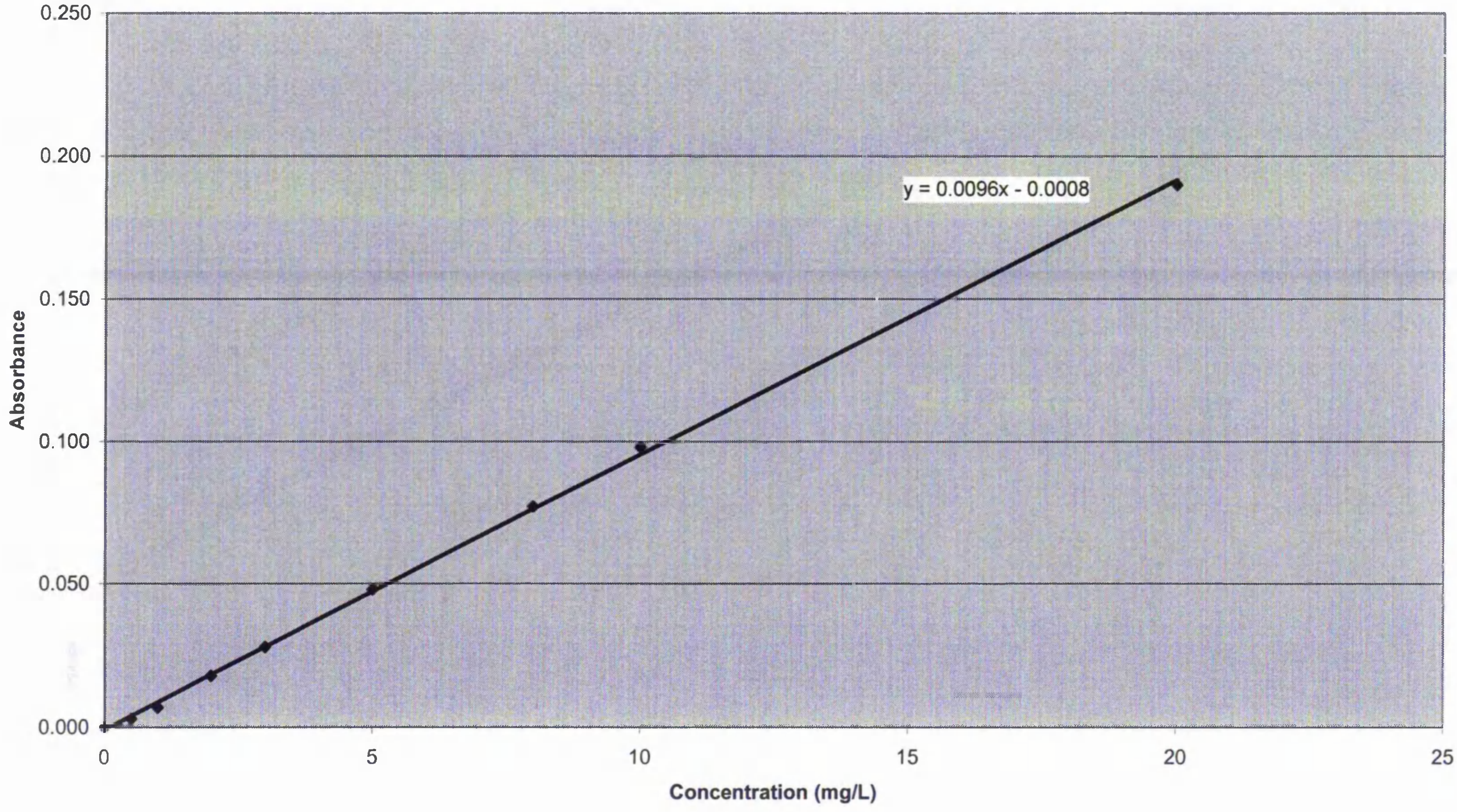


Session 1 (02/09/03) - Linear Lead Calibration Graph

Session 2 (06/01/04) - Lead Calibration Graph



Session 2 (06/01/04) - Linear Lead Calibration Graph



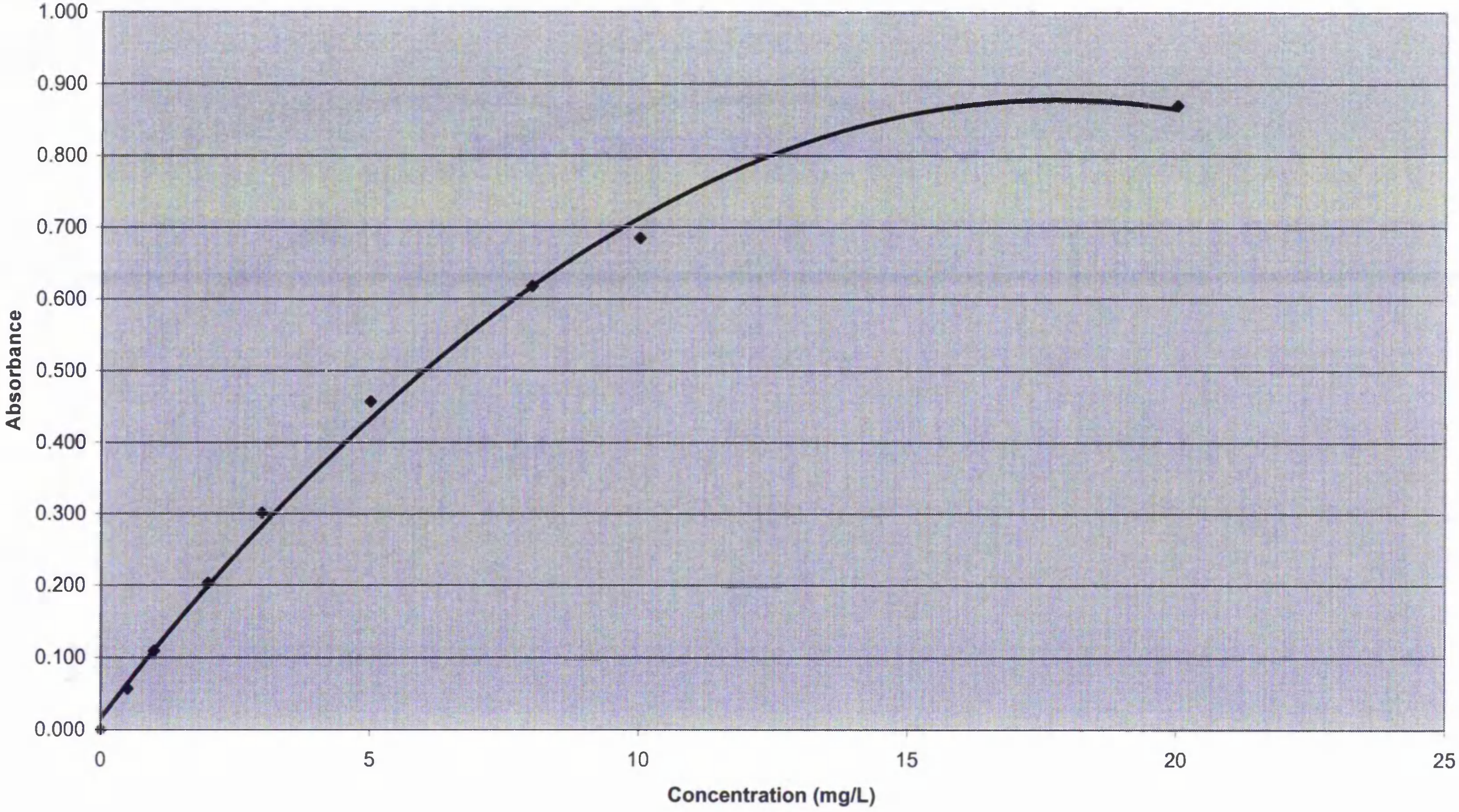
Zinc Calibration Standards Absorbance Figures

CALIBRATION			
Session 1		Session 2	
mg/l	Abs	mg/l	Abs
0	0.000	0	0.00
0.5	0.057	0.5	0.113
1	0.109	1	0.194
2	0.203	2	0.342
3	0.301	3	0.452
5	0.457	5	0.609
8	0.618	8	0.746
10	0.685	10	0.785
20	0.870	20	0.896

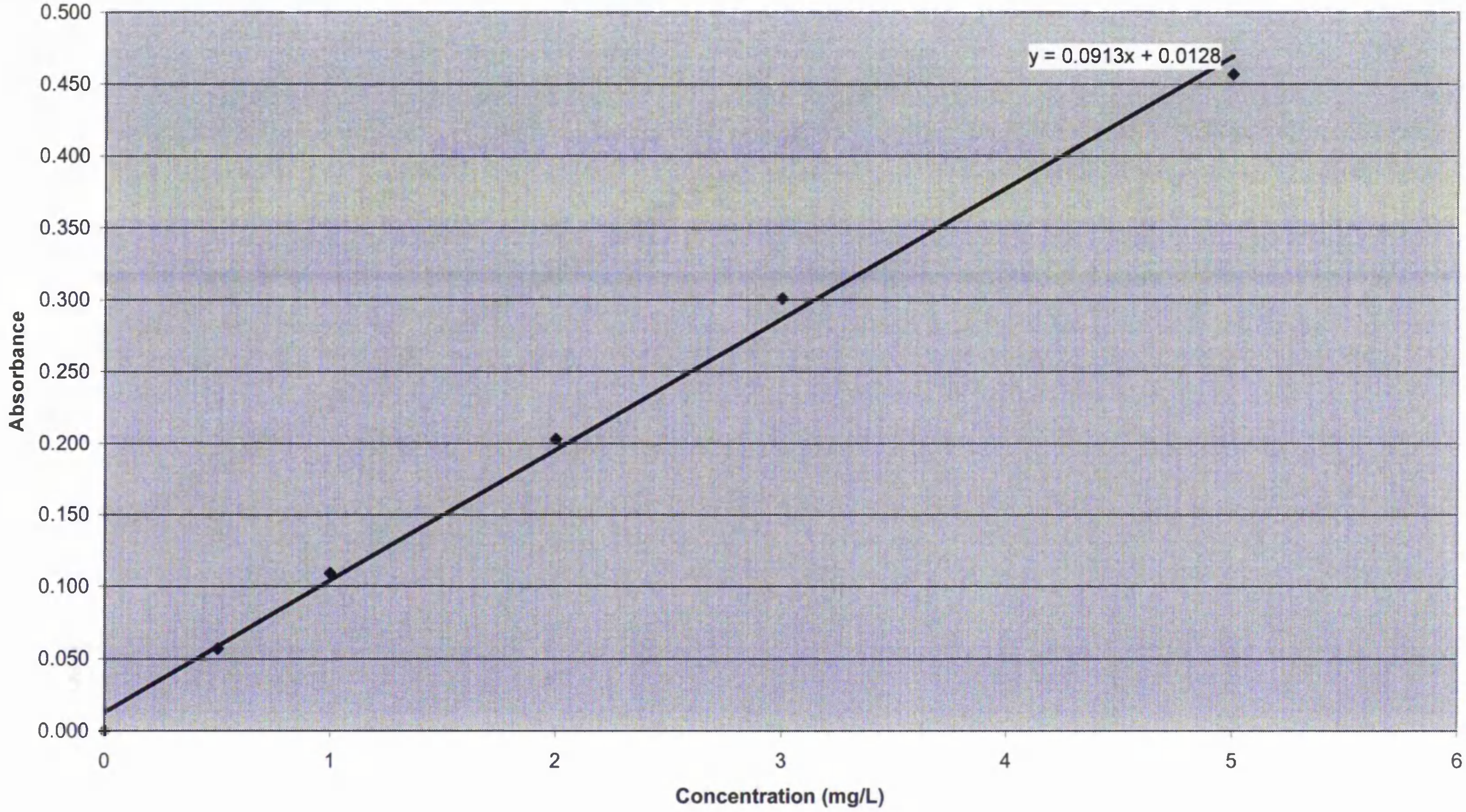
Zinc Calibration Replicate Absorbance Figures

REPLICATES							
	Session 1						
Standard	**1**	**2**	**3**	**4**	**5**	**6**	**Average**
Blank	0.003	0.002	0.003	0.003	0.002	0.002	**0.003**
0.5A	0.005	0.006	0.006	0.006	0.006	0.007	**0.006**
0.5B	0.005	0.005	0.006	0.006	0.007	0.007	**0.006**
8A	0.051	0.051	0.051	0.051	0.05	0.05	**0.051**
8B	0.053	0.053	0.054	0.054	0.055	0.055	**0.054**
	Session 2						
Standard	**1**	**2**	**3**	**4**	**5**	**6**	**Average**
Blank	0.000	0.000	0.000	0.000	0.000	-0.001	**0.000**
0.5A	0.003	0.003	0.003	0.003	0.003	0.003	**0.003**
0.5B	0.002	0.002	0.002	0.002	0.003	0.003	**0.002**
8A	0.077	0.077	0.077	0.078	0.077	0.078	**0.077**
8B	0.077	0.076	0.077	0.077	0.078	0.077	**0.077**

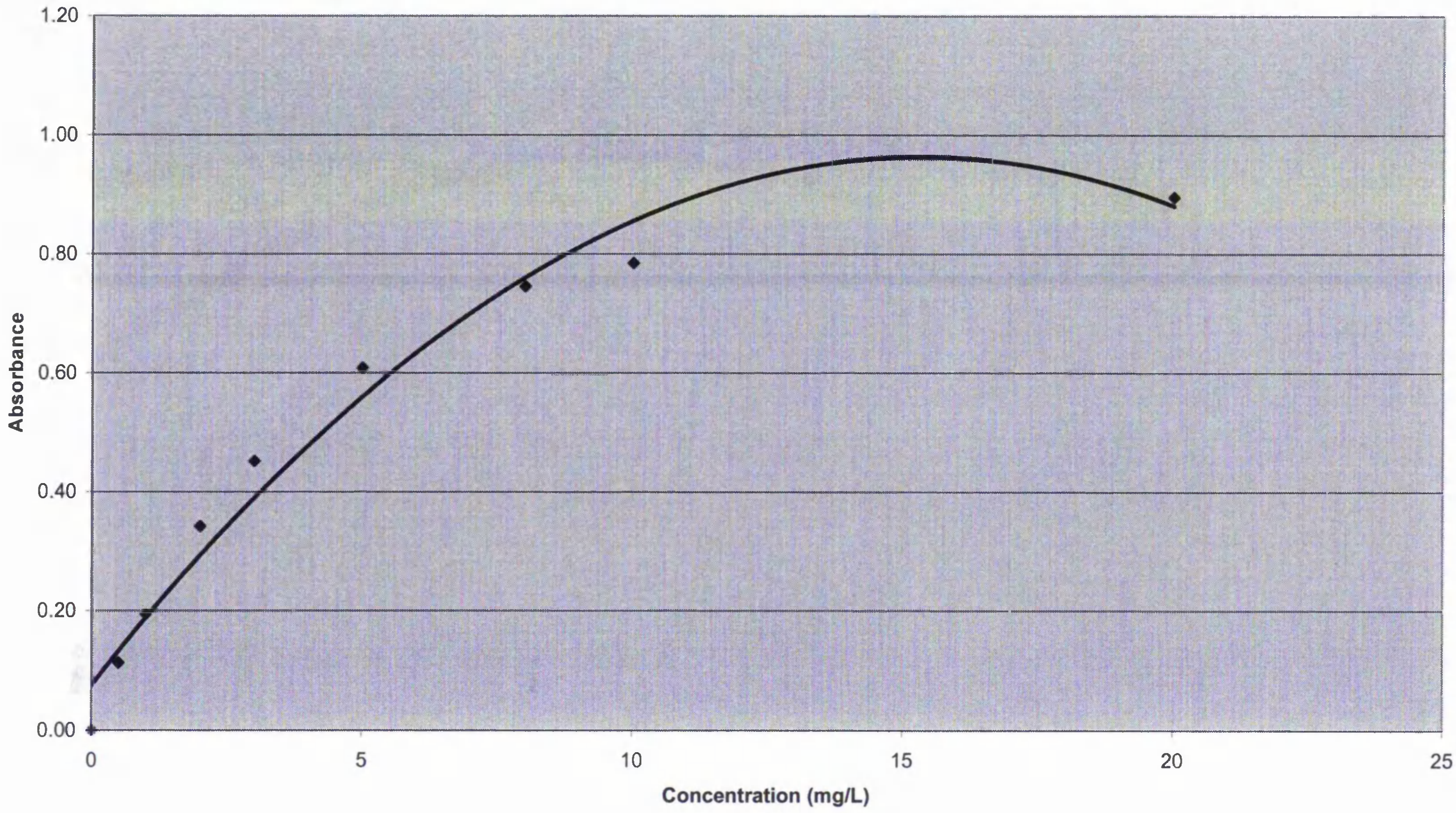
Session 1 (03/09/03) - Zinc Calibration Graph



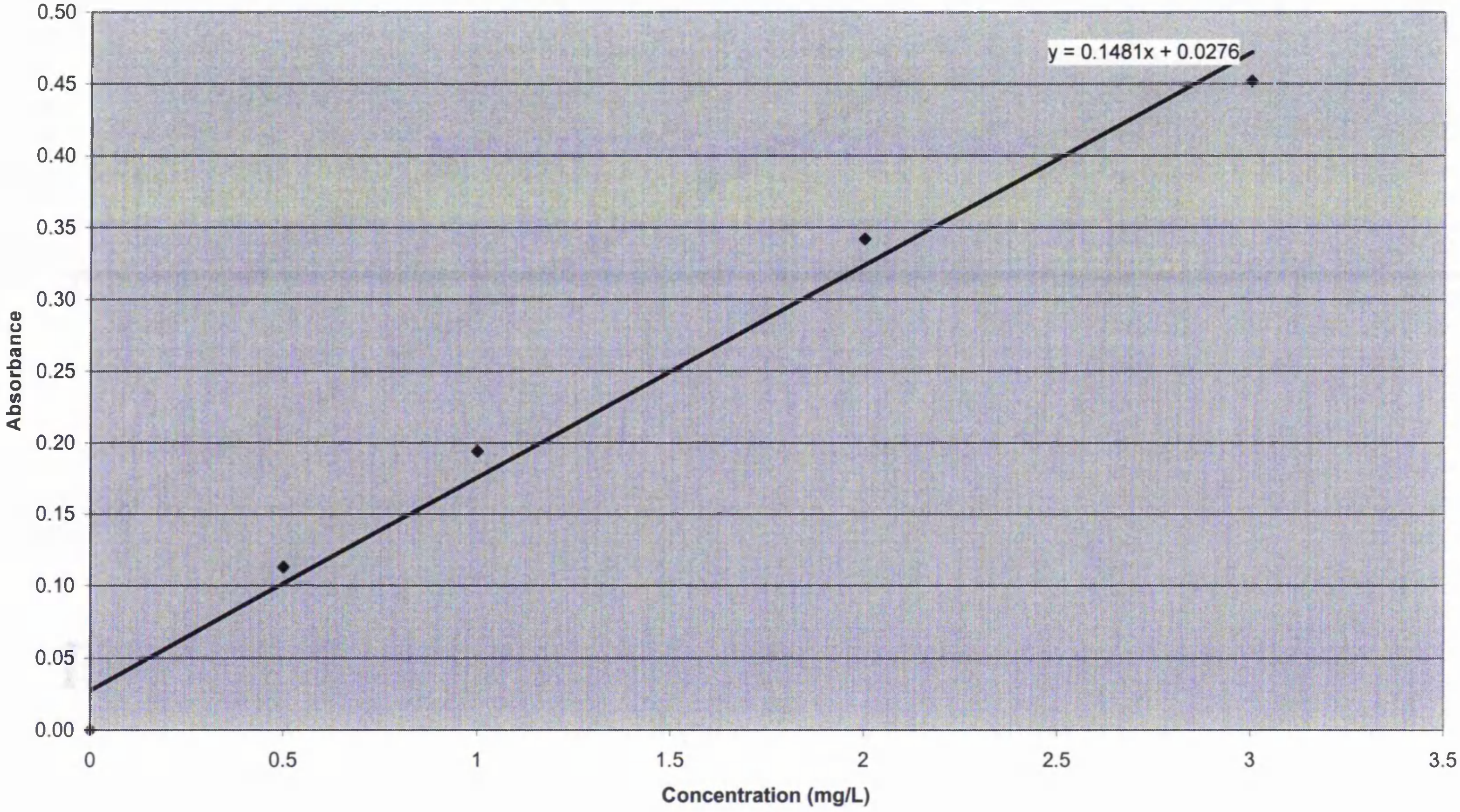
Session 1 (03/09/03) - Linear Zinc Calibration Graph



Session 2 (06/01/04) - Zinc Calibration Graph



Session 2 (06/01/04) - Linear Zinc Calibration Graph



Total Extraction Sample Names, Codes, Mass and Measured Absorbance

Sample	Code	Mass (g)		Abs	
			Cu	Pb	Zn
Calluna vulgaris Root	A1A	0.1240	0.015	0.010	0.035
Calluna vulgaris Stem	A1B	0.6130	0.009	0.004	0.038
Calluna vulgaris Leaves	A1C	0.3855	0.009	0.008	0.050
Surface spoil	A1D	0.8773	0.024	0.047	0.055
Calluna vulgaris Root	A2A	0.3321	0.034	0.032	0.042
Calluna vulgaris Stem	A2B	0.5851	0.005	0.007	0.028
Calluna vulgaris Leaves	A2C	0.3443	0.007	0.026	0.038
Surface spoil	A2D	0.9584	0.037	0.030	0.041
Calluna vulgaris Root	A3A	0.5309	0.045	0.036	0.034
Calluna vulgaris Stem	A3B	0.4670	0.004	0.004	0.028
Calluna vulgaris Leaves	A3C	0.5371	0.003	0.006	0.022
Surface spoil	A3D	1.0365	0.038	0.021	0.113
Sphagnum spp.	A4	0.9230	0.396	0.036	0.400
Bone (*Oryctoglagus cuniculus*)	A5	0.3720	0.078	0.009	0.383
Festuca spp.	A6	0.2092	0.021	0.004	0.086
Surface spoil	B1	0.9040	0.251	0.116	0.120
Sphagnum spp.	B2	0.1150	0.066	0.038	0.076
Stereocaulon vesuvianum	B3	0.1412	0.012	0.033	0.047
Parmelia physodes	B4	0.5032	0.093	0.064	0.115
Oryctoglagus cuniculus faeces	B5A	0.5010	0.054	0.074	0.279
Vulpes vulpes faeces	B6	0.9682	0.095	0.066	0.466
Calcination spoil	B7	0.9555	0.059	0.082	0.074
Soil	B8	0.9493	0.020	0.028	0.046
Stereocaulon vesuvianum	B9	1.0778	0.109	0.063	0.133
Trifolium spp.	B10	0.8257	0.008	0.006	0.048
Calluna vulgaris Root	B11A	0.5685	0.018	0.035	0.038
Calluna vulgaris Stem	B11B	0.4154	0.019	0.042	0.038
Calluna vulgaris Leaves	B11C	0.9643	0.012	0.021	0.036
Calluna vulgaris Root	B12A	0.2468	0.014	0.013	0.029
Calluna vulgaris Stem	B12B	0.4672	0.010	0.018	0.020
Calluna vulgaris Leaves	B12C	1.0525	0.025	0.042	0.048
Calluna vulgaris Leaves Replicate 1	B12Ci	0.5167	0.209	0.050	0.045
Calluna vulgaris Leaves Replicate 2	B12Cii	0.5218	0.200	0.045	0.041
Calluna vulgaris Leaves Replicate 3	B12Ciii	0.5085	0.209	0.046	0.046
Calluna vulgaris Leaves Replicate 4	B12Civ	0.5089	0.190	0.047	0.044
Calluna vulgaris Leaves Replicate 5	B12Cv	0.5324	0.198	0.046	0.052
Calluna vulgaris Leaves Replicate 6	B12Cvi	0.5000	0.193	0.046	0.044
Vulpes vulpes faeces	C1	0.4907	0.037	0.006	0.148
Oryctoglagus cuniculus faeces	C2	0.9282	0.174	0.140	0.140
Agrostis tenuis	C3	0.3693	0.015	0.033	0.054
Hieracium pilosella	C4	0.1788	0.062	0.059	0.168
Surface Soil	C5	0.9274	0.058	0.058	0.136
Oryctoglagus cuniculus faeces	D1	1.0001	0.010	0.060	0.098

Festuca spp.	D2	0.2006	0.017	0.013	0.128
Calluna vulgaris Root	E1A	0.6331	0.013	0.013	0.080
Calluna vulgaris Stem	E1B	0.7289	0.006	0.009	0.035
Calluna vulgaris Leaves	E1C	0.6095	0.012	0.007	0.078
Salix spp. Root	E2A	0.7077	0.010	0.013	0.076
Salix spp. Stem	E2B	0.8334	0.003	0.012	0.161
Salix spp. Bark	E2C	0.2779	0.023	0.010	0.133
Salix spp. Buds	E2D	0.1039	0.005	0.002	0.442
Juncus spp. Stem	E3A	0.3735	0.007	0.005	0.111
Juncus spp. Flowers	E3B	0.3381	0.006	0.002	0.068
Juncus spp. Leaves	E3C	0.2273	0.011	0.005	0.093
Sphagnum spp.	E4	0.6400	0.017	0.009	0.061
Polytrichum commune	E5	0.5126	0.015	0.009	0.070
Cladonia spp.	E6	0.5855	0.013	0.010	0.057
Cladonia spp.	E7	0.3608	0.005	0.002	0.032
Substrate 0mm	E8A	1.0907	0.053	0.030	0.080
Substrate 50mm	E8B	1.2433	0.099	0.050	0.478
Substrate 100mm	E8C	1.0542	0.081	0.119	0.213
Substrate 0mm	E9A	1.0299	0.102	0.014	0.111
Substrate 50mm	E9B	1.0180	0.111	0.045	0.197
Substrate 100mm	E9C	1.0685	0.070	0.087	0.086
Substrate 0mm	E10A	0.9882	0.051	0.012	0.033
Substrate 50mm	E10B	0.9125	0.025	0.032	0.035
Substrate 100mm	E10C	1.0682	0.054	0.073	0.148
Soil (O horizon)	E12	0.9493	0.035	0.049	0.052
Cladonia spp.	E13	0.3363	0.020	0.008	0.111
Cladonia spp.	E14	0.7952	0.015	0.013	0.094
Salix spp. Stem	E15A	0.7252	0.003	0.008	0.173
Salix spp. Leaves	E15B	0.7004	0.002	0.005	0.220
Calluna vulgaris Root	F1A	0.6075	0.044	0.020	0.067
Calluna vulgaris Stem	F1B	0.9120	0.007	0.044	0.007
Calluna vulgaris Leaves	F1C	0.4779	0.016	0.009	0.057
Surface spoil	F2	1.0952	0.093	0.015	0.119
Surface spoil	F3	0.9190	0.279	0.040	0.119
Calluna vulgaris Flowers and Leaves	F4	0.8970	0.012	0.007	0.079
Oryctoglagus cuniculus faeces	G1	0.9540	0.055	0.013	0.380
Erica tetralix Stem	G2A	0.3058	0.005	0.003	0.046
Erica tetralix Flowers	G2B	0.2431	0.005	0.004	0.099
Erica tetralix Leaves	G2C	0.3427	0.010	0.005	0.210
Surface soil	G3	9394.0000	0.160	0.091	0.530
Oryctoglagus cuniculus faeces	H1	0.7343	0.040	0.033	0.340
Festuca spp.	H2	0.5531	0.190	0.028	0.088
Calluna vulgaris Root	I1A	0.5532	0.006	0.028	0.032
Calluna vulgaris Stem	I1B	0.2887	0.010	0.057	0.034
Calluna vulgaris Leaves	I1C	0.8482	0.032	0.105	0.108

Surface spoil	I2	0.9372	0.011	0.034	0.022
Calluna vulgaris Root	I3A	0.9284	0.041	0.046	0.089
Calluna vulgaris Stem	I3B	0.4672	0.050	0.053	0.111
Calluna vulgaris Leaves	I3C	0.6926	0.007	0.014	0.036
Surface spoil	I4	0.9499	0.031	0.025	0.072
Vulpes vulpes faeces	I5	0.6506	0.020	0.011	0.154
Surface spoil	I6	1.0061	0.013	0.028	0.015
Cladonia spp.	J1	0.4407	0.010	0.023	0.080
Sphagnum spp.	J2	0.5340	0.018	0.042	0.100
Calluna vulgaris Root	J3A	0.1913	0.004	0.007	0.023
Calluna vulgaris Stem	J3B	0.7328	0.006	0.008	0.053
Calluna vulgaris Leaves	J3C	0.3012	0.009	0.011	0.046
Surface spoil	J4	0.7791	0.011	0.024	0.081
Deschampsia spp.	K1	1.0598	0.032	0.106	0.103
Soil (O horizon)	K2	1.1426	0.038	0.019	0.095
Peltigra spp.	K3	0.3666	0.021	0.024	0.365
Calluna vulgaris	L1A	1.0112	0.005	0.021	0.023
Surface spoil	L1D	0.9105	0.017	0.038	0.063
Calluna vulgaris	L2A	1.0914	0.013	0.029	0.040
Surface spoil	L2D	0.9510	0.019	0.046	0.029
Calluna vulgaris	L3A	1.0337	0.020	0.049	0.165
Surface spoil	L3D	0.9086	0.020	0.063	0.078
Calluna vulgaris	L4A	1.0099	0.004	0.027	0.014
Surface spoil	L4D	0.9923	0.053	0.096	0.132
Oryctoglagus cuniculus Bone	M1	0.9048	0.017	0.097	0.254
Ulothrix spp.	N1	0.6983	0.085	0.101	0.126
Sediment	N2	0.9180	0.026	0.043	0.065
Calcined Surface Spoil (centre)	O1	1.0553	0.043	0.017	0.018
Calcined Surface Spoil (+1m from centre)	O2	1.0090	0.043	0.070	0.126
Peltigra spp.	P1	0.5005	0.036	0.033	0.153
Red surface spoil	Q1	0.9042	0.007	0.033	0.058
Grey surface spoil	Q2	1.0002	0.024	0.062	0.026
Orange surface spoil	Q3	0.9157	0.048	0.078	0.052
Orange surface spoil Replicate 1	Q3i	1.0020	0.101	0.160	0.147
Orange surface spoil Replicate 2	Q3ii	1.0223	0.084	0.174	0.132
Orange surface spoil Replicate 3	Q3iii	1.0020	0.077	0.120	0.106
Orange surface spoil Replicate 4	Q3iv	0.9690	0.088	0.140	0.152
Orange surface spoil Replicate 5	Q3v	1.0291	0.070	0.150	0.107
Orange surface spoil Replicate 6	Q3vi	0.9970	0.081	0.130	0.120
Calluna vulgaris Root	Q4A	0.8357	0.008	0.029	0.015
Calluna vulgaris Stem	Q4B	0.4265	0.009	0.039	0.056
Calluna vulgaris Leaves	Q4C	0.9415	0.076	0.099	0.209

Young *Calluna Vulgaris* Root	X1A	0.9148	0.005	0.006	0.060
Young *Calluna Vulgaris* Stem	X1B	1.0988	0.012	0.003	0.058
Young *Calluna vulgaris* Leaves	X1C	1.0834	0.007	0.003	0.111
Old *Calluna vulgaris* Root	X2A	0.9897	0.007	0.004	0.091
Old *Calluna vulgaris* Stem	X2B	1.0803	0.006	0.005	0.061
Old *Calluna vulgaris* Leaves	X2C	1.0633	0.014	0.005	0.127
Stereocaulon vesuvianum	X3	0.9349	0.007	0.010	0.087
Polytrichum commune	X4	0.9541	0.006	0.009	0.085
Trifolium spp.	X5	0.9149	0.007	0.009	0.068
Surface soil	X6	1.0298	0.017	0.012	0.154
Sphagnum spp.	X7	0.6605	0.003	0.009	0.060
Cladonia impexa	X9	0.8601	0.005	0.008	0.068
Cicindella campestris Head and Thorax	ZE1i	0.0084	0.002	0.002	0.005
Cicindella campestris Legs	ZE1ii	0.0036	0.003	0.001	0.010
Cicindella campestris Abdomen	ZE1iii	0.0115	0.003	0.002	0.016
Silpha atrata Head and Thorax	ZE2i	0.0113	0.003	0.003	0.017
Silpha atrata Legs	ZE2ii	0.0079	0.002	0.002	0.016
Silpha atrata Abdomen	ZE2iii	0.0640	0.005	0.004	0.036
Opilio spp.	ZE3	0.0002	0.006	0.002	0.011
Tachypodoiulus niger	ZE4	0.0293	0.030	0.004	0.092
Pterostichus oblongopunctatus	ZE5	0.0124	0.001	0.002	0.024
Pterostichus oblongopunctatus	ZE6	0.0110	0.002	0.001	0.013
Philonthus laminatus (female)	ZE7	0.0060	0.004	0.003	0.019
Philonthus laminatus (male)	ZE8	0.0052	0.002	0.002	0.019
Cicindella campestris Head and Thorax	ZF1i	0.0103	0.002	0.001	0.039
Cicindella campestris Legs	ZF1ii	0.0037	0.002	0.001	0.016
Cicindella campestris Abdomen	ZF1iii	0.0186	0.003	0.001	0.051
Amara famliaris	ZF4	0.0073	0.002	0.002	0.015
Arion spp.	ZJ1	0.0850	0.002	0.001	0.025
Rilaena triangularis	ZJ2	0.0066	0.016	0.012	0.368

Bioavailable Extraction Sample Names, Codes, Mass and Measured Absorbance

					Abs	
Sample	**Code**	**Mass (g)**		**Cu**	**Pb**	**Zn**
Surface spoil	A1D	0.9925		0.026	0.026	0.042
Surface spoil	A2D	0.9802		0.026	0.076	0.024
Surface spoil	A3D	0.9920		0.024	0.050	0.080
Surface spoil	B1	0.9953		0.212	0.204	0.135
Calcination spoil Replicate 1	B7i	1.0066		0.024	0.193	0.008
Calcination spoil Replicate 2	B7ii	1.0489		0.026	0.218	0.011
Calcination spoil Replicate 3	B7iii	0.9756		0.024	0.225	0.009
Calcination spoil Replicate 4	B7iv	1.0102		0.024	0.194	0.004
Calcination spoil Replicate 5	B7v	0.9930		0.024	0.222	0.007
Calcination spoil Replicate 6	B7vi	1.0524		0.026	0.211	0.010
Surface soil	B8	1.0049		0.150	0.049	0.475
Surface soil	C5	0.9721		0.111	0.096	0.319
Soil (O horizon)	E12	0.9903		0.323	0.092	0.150
Surface spoil	F2	0.9938		0.062	0.008	0.018
Surface spoil	F3	1.0527		0.054	0.011	0.019
Surface spoil	J4	0.9921		0.264	0.076	0.085
Soil (O horizon)	K2	0.9958		0.149	0.084	0.266
Surface spoil	L1D	1.0139		0.049	0.065	0.012
Surface spoil	L2D	1.0050		0.139	0.054	0.011
Surface spoil	L3D	1.0243		0.059	0.034	0.008
Surface spoil	L4D	1.0074	*17ml	0.056	0.071	0.012
Sediment	N2	1.0277	*20ml	0.072	0.174	0.310
Calcined surface spoil (centre)	O1	1.0104	*20ml	0.027	0.164	0.056
Calcined surface spoil (+1m from centre)	O2	1.0190		0.052	0.275	0.063
Red surface spoil	Q1	1.0051		0.014	0.048	0.007
Grey surface spoil	Q2	0.9953		0.016	0.029	0.010
Orange surface spoil	Q3	1.0083		0.018	0.018	0.082
Surface spoil	I2	1.0012		0.029	0.075	0.008
Surface spoil	I4	0.9910		0.030	0.026	0.068
Surface spoil	I6	0.9958		0.094	0.024	0.333
Surface soil	G3	0.9508		0.159	0.094	0.092