A Comparative Study of Natural Rehabilitation at a Former Mine Waste Site in the Carnon Valley, Cornwall

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I certify that all material in this thesis which is not my own work has been identified and that no material has previously been submitted and approved for the award of a degree by this or any other University.

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Abstract

This study was carried out in the Carnon valley, which is located in Cornwall, south-west England. A river runs through the Carnon valley while former settlement ponds for processing tin and copper ore from the Wheal Jane mine are found on the floodplain. Tailings and waste rocks have accumulated on the floodplain to a height of about 6 meters.

The valley is physically divided by a country road into the Middle valley and the Lower valley. Plant growth on tailings in the Middle valley, where tailings heaps were bulldozed, is visibly different from plant growth in the tailings and coarse waste rock observed in the Lower valley. The Lower valley, which features hummocks and hollows, appears to be less rehabilitated than the Middle valley. However, flora diversity in the Lower valley is considerably higher compared to the Middle valley, where a relatively homogeneous vegetation coverage is dominated by a few species. Other noticeable differences between the Lower and Middle valleys are a relative consistent soil compaction and the absence of visible ponds in the Middle valley.

This research aims to identify the main drivers and limiting factors in the natural rehabilitation process and local biodiversity development in the middle and lower sections of the Carnon Valley. Through close year-round recording of natural plant species and colonies and habitat survey in the evolving terrain, it was attempted to correlate biota to progressive structural amelioration of the site. Species success was observed in relation to habitat evolution, restrictions imposed by residual toxicity of the former metal-mining terrain, advantages gained by artificial topographic diversity present on abandonment, and the stages reached in the dynamic progression of the combination of all of these features.

By observing and recording the outcome of natural revegetation and identifying the impacts of abiotic factors, recommendations are made about the significance of such abandoned mine-sites in relation to ecological conservation value of such former disturbed land, and derive proposals for its onward management. We conclude that, on the site, complex interwoven processes occur of which we observe the state at one moment in time. The volume of data collected in the Carnon Valley is probably greater than available for any other known mine site of comparable history and size. While the data enabled inference of important biotic progressions, this study suggests that the

approaches may be applied to other abandoned mine sites, especially for assessment of natural attenuation of residual toxic legacies and ways to engineer future biotic rehabilitation patterns. The potential development of abandoned mine sites to re-establish natural biodiversity is thus recommended, together with a strategy for monitoring of future rehabilitation progression.

The study consists of a field survey to record the present vegetation assemblage pattern, laboratory experiments to investigate soil features, data interpretation with statistical software, and evaluation of the interrelationship between emerging vegetation patterns and soil features.

Extensive field work was undertaken within a one-year period, observing the highly heterogeneous vegetation community in a state of succession towards natural rehabilitation. The study generated up-to-date, detailed insight into year-round biodiversity development, notably of species diversity and seasonal stages of its development. Both transect surveys and quadrat surveys were carried out to capture general and spatial vegetation distribution variances. Fifty-seven quadrats, deemed to be representative, are surveyed in terms of plant species present and physical and chemical properties of the soil. While the natural vegetation of areas surrounding the valley has already been mapped, it is possible to build a factually-based picture of the progression of on-site species-assembly in relation to taxa that are, or are not, present in the surrounding landscape's natural vegetation. This revealed that, out of a total of 87 species found in the valley, 9 are classified as very rare species in Cornwall. The presence of local rare species suggests the Carnon valley and other post-mining sites potentially have a significant ecological conservation value. This diversity and biotic taxonomic content of the former mine site highlights the importance of allowing natural biotic colonisation to continue in the wider interest of biodiversity conservation and utilisation of such sites as future biotic reserves.

Vegetation survey revealed a host of unusual species assemblage settling on the contaminated soil, which is especially true in the community around ditches. The significantly high species richness and presence of rare species in the ditch community indicates the potential of an edge effect, which has a benefit for biodiversity and may be applied in mine site rehabilitation. The prominent high species richness in the core area (excluding the ditch community) of the Lower valley (75 species compared to 18 species in the Middle valley) emphasizes the value of heterogeneity. Bulldozing and human disturbance proved to be effective to improve vegetation coverage, but failed to promote biodiversity recovery.

To investigate the effect of chemical contaminants on vegetation development, data is interpreted with ordination techniques such as redundancy analysis (RA) and principal component analysis (PCA). Both techniques indicate that arsenic and copper have a negative impact on vegetation development. Absorbed arsenic or phosphate exchangeable arsenic were found to be the most influential fractions of total arsenic in the soil which affect local species richness and biodiversity. Controlling arsenic fractionation is therefore an important strategy towards supporting vegetation recovery.

The thesis postulates that sites with mine waste have special conservation value and that an edge effect may exist -from observing relatively high species diversity in zones along ditches. Water availability has great influence in ditch community development, but is remains unclear how it interacts with other factors to contribute to biodiversity development.

The study shows the potential of natural rehabilitation, which should be considered as an option when planning for rehabilitation of former mine sites.

1.Introduction

1.1 Background

All the raw materials used to build up our civilisation are either grown, or are mined. As such, the mining industry plays an important role in the sustainable development of human society. Its products include fuels (coal, oil and natural gas), non-metallic materials and metallic materials.

The influences of the mining industry on human society can also be inferred from the way history is partitioned. Human history was divided into stone, bronze, iron and steel ages according to the material used to make artefacts. The primary material used to produce tools indicates that the advancement of science and technology promote mining development and vice versa. The fluctuation of market demand for mining products reflect expectations of economic development. The pricing of minerals futures is often taken as an indicator for economic growth.

With time passing, the demand for minerals is ever-increasing with the industrial revolution resulting in the gradual depletion of high-grade deposits near the surface. As a result, more waste rocks and mine tailings are generated because of the need to process lower grade ore. This would cause a dramatic increase in the scale of environmental impacts. Therefore, innovative solutions to mine site restoration is desired.

Current post-mining restoration practice evaluates project outcomes on the basis of quantitative metrics rather than potential ecological service quality. This may translate to unreasonable investment to ensure that a certain number of certain species can establish on a site. It is postulated that diverse rehabilitation pathways are a result of an uneven distribution of resources and resulting varied ecological stress (Bradshaw et al., 1982; Chapin et al., 1994). The complexity of physico-chemical features of mine sites and their interactions makes research to understand the dynamics of biodiversity development of post-mining sites a challenging project.

1.2 Motivation

Mining irrefutably has an impact on the environment, irrespect of whether extraction takes place from open cast or underground workings, , disturbance of the local ecological community is inevitable. In some cases, deposits are situated in areas with great ecological value. Extraction of such deposits may trigger controversy. In many jurisdictions, reinstatement of disturbed ecological communities is prescribed. However, the ecosystem function mechanism and role of environmental factors are not yet well understood. As a result, the outcome of the rehabilitation process may be jeopardised.

Restoration to the previous ecological state is a relative safe choice because it has a clear target and appeases public concerns. However, once a site has experienced dramatic changes in landscape and substrate physio-chemical features, continuous maintenance may become necessary to sustain the original vegetation community. Johnson (1996) argues that the altered abiotic conditions in mine sites create a habitat for some species which generally do not possess a competitive advantage in other places. It is thought that poor nutrient availability in mine site substrates will limit the establishment of fast growers and provide niches for those species which are out-competed elsewhere (Koerner, 2003). For example, poorly structured spoil tips with elevated metal concentrations are considered to be positive contributors to the preservation of biodiversity (Spalding, 1996). Over 25 per cent of moss and liverwort species in Cornwall are found in abandoned mine sites and some of these are marked as rare species in the UK (Spalding, 1996).

The conservation value of mine sites is increasingly being recognised and a number of sites in Cornwall are protected as Sites of Special Scientific Interest (SSSIs) and Special Areas of Conservation (SAC) (Spalding, 1996). However, there is limited scientific research into factors influencing rehabilitation in mine sites and how these can be managed to boost biodiversity conservation.

There are numerous studies investigating interactions between soil features and vegetation development. A number of these describe vegetation development in abandoned mine sites or land contaminated by mining activities (De Koe, 1994; Liu, 2005; Garcia-Salgado, 2011). However, there are only few studies which have looked into the impacts of substrate heterogeneity on vegetation species richness, diversity, and distribution patterns (Anawar et al., 2013). Heterogeneity in vegetation coverage, species composition and ground surface topology is readily observed at abandoned mine sites. A heterogeneous vegetation distribution can express either uneven allocation of resources, such as nutrients, seed banks etc., or ‘stressors’ such as soil toxicity (Bradshaw et al., 1982; Chapin et al., 1994). It is postulated that identifying and controlling the factors which nurture heterogeneous vegetation community can facilitate natural rehabilitation towards desired result and artificially increase local biodiversity.

With the advancement of knowledge, the benefit of natural progression of restoration is increasingly being realised. Nonogaki (2014) pointed out that a low germination rate is a self-protection mechanism to enable survival in abnormal climatic conditions. Lottermoser, Glass and Page (2011) found that arsenic contamination of a mine site in Cornwall did not hinder natural rehabilitation. It should be noted that the Earth's crust contains, on average, about 1.8 mg/kg of arsenic (Greenwood and Earnshaw, 1984). Arsenic is frequently found in mineral deposits and especially in sulphidic minerals (Morin and Calas, 2006). Arsenic contamination related to mining activities is observed in 74 countries (Figure 1). The highest levels of surface arsenic contamination are attributed to mining (Smedley and Kinniburgh, 2002).

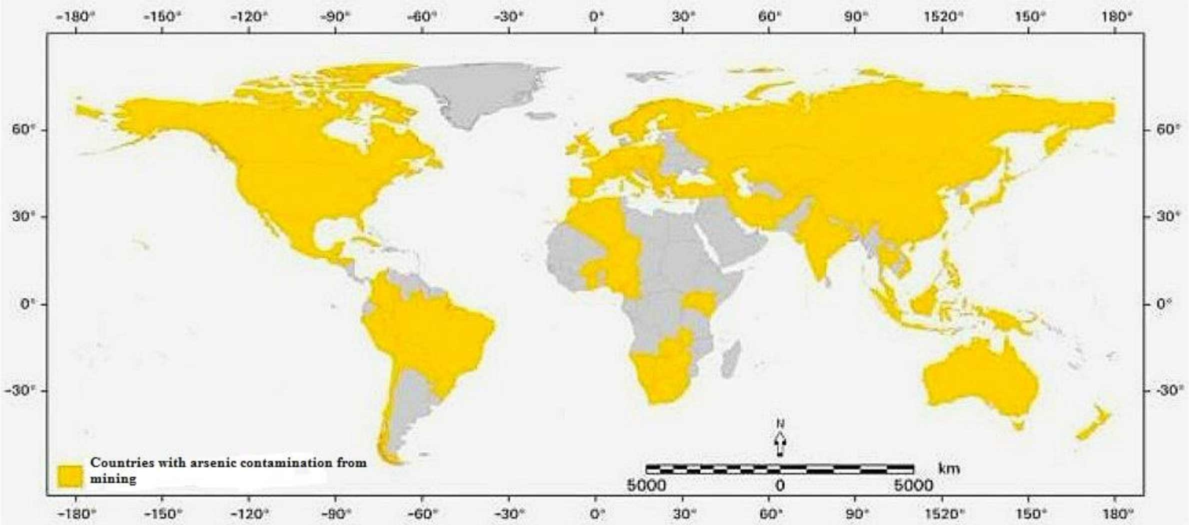


Figure 1: Countries contaminated by mining-related arsenic release (Murcott, 2012).

In natural conditions, arsenic is primarily associated with sulphide minerals (Alloway, 2012). Cornwall has a long history of intensive extraction of metals and many of these were mined from hydrothermal deposits rich in sulphide minerals. Therefore, high arsenic concentrations remained in mine spoils all over Cornwall and caused a number of incidents in the region. For example, a south-west England water aquifer was heavily contaminated by arsenic which was liberated during the rush for tin and cooper mining in this region (Barringer, 2013).

In the UK, the soil guideline value for arsenic in residential and allotment sites is set at 20mg/kg of arsenic in dry soil (DEFRA and EA, 2002a, 2002b). However, arsenic concentration in mine spoils in Cornwall can be well above 1000 mg/kg. The extent in which arsenic phytotoxicity affects vegetation recolonization is not always evident. It is suggested that soil quality outweigh high metal toxicity to vegetation development on mine tailing rehabilitation (Anawar et al., 2013). It would be interesting to conduct further research in a region with similar soil quality to evaluate the role of secondary factors, such as metal toxicity, in natural rehabilitation.

Naturally-colonised mine sites are ideal for investigating the driving and limiting factors of phytoremediation (Craw, 2007). A thorough site investigation could contribute to developing a methodology to support the planning and management of ecological restoration of areas contaminated with heavy metals. In general, reclaiming abandoned mine sites through phytoremediation is perceived to be attractive from an economic perspective (Chang et al., 2005).

Although a field study generates a comprehensive understanding of biotic and abiotic interactions and has great practical value, the number of comprehensive field studies is relatively small because the data complexity far exceeds that of data obtained from studies carried out in greenhouses. It is commonly assumed that knowledge about ecological restoration is not transferable to other sites due to intractable effects of different climatic and abiotic conditions. However, Wong and Bradshaw (2003) stated that, according to their experiences, it is possible to formulate generic rules which have practical value in all scenarios. This study aims to conduct a comprehensive field study of a research site, which effectively serves as an outdoor laboratory. It is anticipated that findings from this research could benefit practitioners elsewhere.

1.3 Scope of study

This research aims to evaluate the progress of natural rehabilitation on a site in Carnon valley, located in south west England. The site has served as settlement pond for tin and copper mining from the 19th century until 1991 (Moon et al., 1995). The evaluation work includes investigation of vegetation development, analysis of soil physicochemical properties, and statistical interpretation of data. Based on a literature review, a set of research methods was chosen consisting of field work, laboratory analyses, and statistical analysis.

Field work included a vegetation survey and soil sampling campaign, and was carried out from April 2013 to October 2013. The vegetation was surveyed repeatedly between April to October 2013 to identify plant species by their flower and fruit. Both transect and quadrats surveys were undertaken to monitor the species occurrence and frequency. The vegetation was recorded in 10 transects and 57 quadrats while soil sampling was carried out in all 57 quadrats.

Soil sampling focusses on top 20 cm of soil, which is deemed to be the most significant part for vegetation establishment. Two soil samples were drawn: from the top 10 cm and from the 10 to 20 cm horizon. The fieldwork generated a complete list of all species found on the site, as well as the frequency (abundance) of each species and the soil strength in each quadrat. Laboratory analyses served to measure soil electro-conductivity, pH, grain size distribution, mineralogical and elemental composition, and arsenic fractionation.

It was envisaged to revisit the site in 2014 to record changes in vegetation development. However, construction of a new parking lot covered 3 quadrats while foundation soil for this construction contaminated several adjacent quadrats. Due to the significant loss of site fidelity, the revisit was cancelled.

Correlations within the dataset acquired in 2013 were analysed with statistical tools. Vegetation development in the lower valley and middle valley was compared to establish divergence of natural rehabilitation in sites with similar history. To evaluate the significance of natural rehabilitation progress, vegetation data was also compared with a previous survey of flora in Cornwall.

Besides data collected first-hand, further ‘secondary’ data was also obtained from the Meteorological Office and the Environment Agency. This data contains information about temperature, precipitation, and Carnon river water quality in 2013. Evaluation of this data provides insight into variation of arsenic solubility and is analysed as a supplement in appendix E.

Vegetation establishment constitutes one aspect of ecological restoration. Fauna, lichens, and micro-organisms also are important components of ecological system. While natural rehabilitation potentially covers a wide range of subjects, it is impossible to cover every aspects in limited time. This research focusses on re-establishment of vegetation.

1.4 Aim

This study aims to investigate natural recolonisation and factors which impact on vegetation recolonisation in a mine site undergoing natural rehabilitation. This should provide insight into the progress of colonisation which has occurred. The significance of rehabilitation achieved is inferred from evaluation of a regional vegetation survey.

1.5 Objectives

The ecological significance of natural rehabilitation and the factors which potentially impact the process at a former mining site are evaluated through the following actions:

- Investigate vegetation development along transects.
- Investigate vegetation development and soil features in quadrats.
- Compare colonisation achievement in the core area (exclude ditch community) of the middle valley (flat topology) and the lower valley (undulating topology)
- Collect vegetation development information in the field.
- Analyse vegetation survey and substrate physico-chemical data to identify factors made major contribution to shape natural rehabilitation.
- Compare vegetation development in the investigated area with Cornwall flora survey.

1.6 Outline of thesis

This thesis consists of seven chapters: an introduction, literature review, study site description, methodology, results, discussion, and conclusion chapter. To maintain brevity, all supporting documents, to include a list of identified species, habitat similarity index, arsenic behaviour in adjacent river, and part of XRD analysis results, are given in an appendix.

The introductory chapter 1 provides the context and motivation for this study. Both the research question and a roadmap are given in this chapter.

The literature review in chapter 2 describes related research on vegetation development in primary succession, measurement of biodiversity, vegetation survey methods, previous reports of the impact of soil physical and chemical features on vegetation establishment and mobility of trace elements, and data process techniques.

Chapter 3 describes the study site in terms of its location, historical use, climate, and ground topography.

Chapter 4 provides a justification of the chosen methodology based on the literature review and the availability of techniques. Details of each technique employed in this research, as well as QA/QC aspects of data collection, are reported.

The results of all data activities, including the vegetation survey and soil properties, and the statistical analyses are presented in Chapter 5.

A detailed analysis and discussion of all aspects of natural rehabilitation of the Carnon valley follows in Chapter 6.

Chapter 7 gives the conclusion of the research, summarising the findings and assessing their potential application in mine site rehabilitation management. Suggestions for future research are made.

2 Literature review

2.1 Post-mining sites in a global context

The impacts of mining are controversial and negative influences on landscape include (adapted from Johnson et al., 1996):

- Lunar landscape with hummock and hollows,
- Barren land covered by regolith-like material and lack of soil,
- Random dumping and contaminated land vulnerable to erosion and extreme weather,
- Mixed waste rock and tailings mounds poor in nutrients and water retention capacity,
- Synthetic topography, with unstable and dramatic variation in topology.

Mine sites can simultaneously provide a series of ecological benefits (Maiti, 2012; Revuelta, 2017), including:

- Unique substrate features which contrast greatly from most surrounding areas. This can enable development of a unique ecological system.

- Shelter for tolerant species which often are out-competed elsewhere and are not found in the surrounding landscape.

- Opportunity to investigate the appearance of colonisation by such plants and their impacts on soil development.

- Opportunity to investigate unusual plant-mineral correlation and plant tolerances/mitigation mechanism (physical and chemical) displayed.

- Nursery for tolerant species which can be used in places with similar conditions for rapid colonisation.

- Understanding of the trade-off between biodiversity and coverage on such sites, and progressions of its vegetation assembly.

This points to the considerable scientific value of such sites in comparison with other habitats research and suggests that research into the ecological restoration process at mine sites can enhance our understanding of the evolutionary development of plants.

The level of contamination at abandoned mine site is determined by the nature of soil parent material (Garcia-Sanchez and Alvarez-Ayuso, 2003). The concentration of trace elements normally varies within an acceptable range but enrichment may be present in hot spots due to hydrothermal alteration or other reasons (Garcia-Sanchez and Alvarez-Ayuso, 2003). Arsenic contamination in mining areas was studied intensively world-wide and its concentration can vary from dozens (Romero, 2014) up to hundred thousand ppm (Wanat, 2014). The presence of arsenic is usually associated with a wide range of sulphide minerals (Morin, 2006). Arsenate is the dominant arsenic compound in soil and its solubility depends on the concentration of iron and manganese hydroxides, soil organics, acidity, and phosphate concentration (Moreno-Jimenez, 2010). Given sufficient time, a natural vegetation community may develop in soil with arsenic levels above 5500 ppm (Wanat, 2014).

With rising awareness of the role of plants in post-mining remediation, there are increasing numbers of studies which seek to identify hyper-accumulators and tolerant species for phytoextraction and phytostablisation purposes (Garcia-Salgado, 2011; Wanat, 2014). It is believed that arsenic-tolerant species are naturally available in the environment and that some native species can tolerate arsenic over a wide range of concentrations (Meharg and Hartley-Whitaker, 2002). Note that increasing arsenic concentration in soil is expected to reduce species richness (Steinhauser, 2009). Steinhauser (2009) observed the lowest biodiversity in soil which was richest in arsenic. Aziz (2010) stated that irrigating the rice field with arsenic-contaminated water reduced weed diversity.

Kuehnelt (2000) found Broad Buckler Fern (*Dryopteris dilate*) can tolerate - and take up - both inorganic and organic arsenic compounds. Macnair and Cumbes (1987) found that Yorkshire fog grass (*Holcus lanatus*) growing in arsenic-contaminated soil has developed an alternative phosphate uptake mechanism to deal with arsenic toxicity. This finding suggests that heavy metal contamination do not prevent the establishment of vegetation communities, in which plants develop unusual survival strategies.

Macnair (1987) states that metal tolerance gene is a low-frequency mutation of non-tolerant plants. The absence of some species in mine sites may indicate these are incapable of producing heavy metal-tolerant mutants. Ernst (2006) found that if plants are exposed to an elevated heavy metal concentration for a sufficiently long period of time, variation of metal tolerance within a taxonomic group, or even a species is possible. However, this phenomenon has not been sufficiently appreciated or studied (Ernst, 2006). The necessary length of time for a plant species to achieve metal toxicity tolerance varies. For example, colonial bent grass (*Agrostis capillaris*) can acquire the tolerance ability after only five years of exposure (Ernst, 1974). On the other hand, the rehabilitation time may not be decisive: Wanat (2014) observed only 7 species in a site abandoned 45 years ago.

Metal-enriched soils can facilitate mutation of the metal tolerant gene and conserve such genotypes permanently (McNeilly, 1968). In practice, native species are preferred due to their self-sustaining capacity and induced tolerance to local elevated trace elements (Bell, 2001). Remon (2005) stated that endemic species are sufficient for local phytostabilisation and can be used for effective restoration. However, most restoration projects use commercially-available cultivars which could limit plant diversity and resilience to extreme weather.

Some species accumulate arsenic in subsurface biomass as a strategy to limit arsenic toxicity. The common alder (*Alnus glutinosa*) is able to store arsenic up to levels of 370 mg per kg of dry mass (Cernansky, 2014). Dorrington (1983) records that blackberries (*Rubus fruticosus*) is a hyper-accumulator and accumulates arsenic and other heavy metals in fruits and other tissues. Note that this can lead to dissemination of arsenic toxicity through the food chain.

Negative effects of mining activities and abandoned land after excavation is generally recognised (Johnson et al., 1996). These effects inhibit vegetation development and create stress in ecological systems (Quainoo et al., 2016; Daniel, et al., 2015; Pandey et al., 2014). There are numerous reports of vegetation development in such sites; the findings are summarised in the Table 1. These studies have either focused on taxonomy, phytophysiology or soil contamination (Huang, 2004; Otones, 2011a; Otones, 2011b; Jankong, 2007; Ernst, 1996; Garg, 2011; Rascio, 2011; Tripathi, 2007; Hozhina, 2001; Schlmerdine, 2009). In some of the published studies of mine sites (Pratas, 2005; Chang et al., 2005; Craw et al., 2006; Garcia-Salgado, 2011), the species richness is lower than that of the Carnon valley, regardless of the site age or total arsenic concentration.

Many of the tolerant plant species found in the Carnon valley are present in other geographically distant locations. This indicates their potential for a mine site rehabilitation project (Petrik, 2009; Hejcman, 2012). Lottermoser et al. (2011) found *Calluna vulgaris* and *Ulex europaeus* can establish on substrate with elevated arsenic without accumulation of arsenic in their above-ground biomass. *Rumex obtusifolius* is a common weed species which prefers low pH and has great potential for phytoremediation of arsenic-contaminated soil (Hejcman, 2012). Several representative species in the Carnon valley including *Festica rubra, Potentilla anserine, Vicia cracca, Cirsium arvense, Senecio Jacobaea, Urtica dioica, Equisetum arvense, Ranunculus repens, Arenaria serpyllifolia,* and *Quercus robur*, also were found by Petrik (2009) in his research of sites contaminated by heavy metals include arsenic from an industrial source.

Tremlova (2016) and Feippi (2004) studied sites where the average arsenic concentration is significantly lower than in the Carnon Valley and observed more species. In a brownfield contaminated with anthropogenic sources of heavy metals, Gallagher (2008) found a correlation between soil metal concentration and the species composition of the vegetation assemblage. Other researchers found it is the physico-chemical features of the soil, rather than heavy metal concentration, which influences species diversity. In another spatial analysis of vegetation pattern and soil features, Tamas (2005) noted that the presence of vegetation is highly affected by soil pH value but not affected by total heavy metal load. This suggests that the heavy metal phytoavailability is more decisive than their concentration. However, Garcia-Salgado (2011) makes a controversial conclusion by stating that heterogeneous geochemical features do not necessarily induce a high species richness.

No previous study of an abandoned mine site integrates local plant diversity with variation in spatial abiotic factors has been found. The research reported in this thesis analyses the spatial distribution of factors with more comprehensive indicators and more intensive vegetation survey.

It is postulated that greenhouse experiments cannot explain the vegetation distribution on post-mining sites because the interaction between toxicity and environmental factors is missing in laboratory (Frouz, 2011). The study of natural rehabilitation process is a complex subject and only a few studies evaluated and reported the potential of indigenous species in post-mining remediation under field conditions (Marques, 2009). Herrick (2006) stated that plant community composition on its own cannot predict long term restoration development. Introduction of indicators about fundamental ecological system quality relating to substrate, water regime or biological aspects, can give a more reliable prediction of the success of the rehabilitation project in the long term. Therefore, the biodiversity index and similarity index are employed in this research.

Table 1: Literature review of world-wide mine site contamination and vegetation development.

Location	Tailing (T) or soil (S)	Arsenic Concentration (mg/kg)	Lead Concentration (mg/kg)	Copper Concentration (mg/kg)	Soil pH	Source	Species richness	Age	Ref.
Lower valley, Cornwall, UK	T	60-2964	30-586	65-1374	3.6-7.8	tin and copper mine	80	20 yrs (*)	This thesis (chapter 5), (*) Moon, 2009
Middle valley, Cornwall, UK	T	418-2789	133-374	408-1522	5.3-7.2	tin and copper mine	42	20 yrs	
Castelo Branco, Portugal	Mix T+S	11.1-651.1			3.3-5.2	stibium, tungsten, gold mining	16	-	Pratas, 2005
North Westland, New Zealand	T	12-15 % weight			3-7.5	gold mining	29	> 50 yrs	Craw et al., 2006

Cerro de Mercado, Durango Mexico	S	55-221	22.3-107		8.1-8.5	iron mining	-	operating	Morales 2015
Llallagua, Bolivia	T	29-4606	31-955	10-1362	2.5-5.2	tin mining	-	reprocessing	Romero, 2014
Pena del Hierro, SW Spain	T	46-1710	113-3455	11-1487	0.7-2	copper mine	-	40 yrs	Romero, 2006
Central Bohemia, Czech Republic	S	47-1120			4.3-5.9	gold mine	99	>70 yrs	Tremlova, 2016; Feippi, 2004
Salamanca, Spain	T	1200-1350	-	-	1.8	tungsten and tin mine	-	30 yrs	Murciego, 2011
Sierra de Guadarrama, Spain	S+T	35-6856		6.3-1863	3.8-5.9	pyrite mine	-	30 yrs	Garcia-Gomez, 2014
Chenzhou, China	S	145-1227	305-1443	110.08-221.4	4.7-8.2	lead/zinc mine	-	17 yrs	Liu, 2005

La Petite Faye, France	T	5465-119900	1299-21300		3.4-5.0	gold mine	7	45 yrs	Wanat, 2014
Monica mine, Spain	S	300-30000			4.3-5.3	silver/arsenic mine	10	>100 yrs	Garcia-Salgado, 2011
Duckum & Myoungbong, South Korean	T	6320-7340	12-26	916-974	3.7	gold mine	16	30 yrs	(Chang, Kim and Kim, 2005)
Queretaro, Mexico	T	183-14660	327-1754	149-459	2.1-8.35	Ag, Pb, Cu and Zn mine	10	recently	(Santos-Jallath et al., 2012)
Ouche, France	T	322-843		1.8-64	2.4-3.9	antimony mine	12	40 yrs	(Jana et al., 2012)
NE Portugal	S	2800-17000	940-2200	380-1800		gold and tungsten mine	2		(De Koe, 1994)

Sao Domingos, Portugal	T	260-7293			2.8-7.0	copper mine	24	50 yrs	(Anawar et al., 2013)
Salamanca, Spain	T	680-5330			4.4-4.9	tungsten mine	19	30 yrs	(Otones et al., 2011a; Otones et al., 2011b)

2.2. Measurement of vegetation community

2.2.1 Biodiversity

According to Page (1979), biodiversity sometimes shares the same meaning as ecological diversity. It describes the variation and complexity of the natural ecological system. Gaston (2004) states that biodiversity refers to the variation of flora and fauna species and also to the genotype and phenotype variation within individual species, the variation of habitat, community, ecosystem and their ecological functions. Ultimately, biodiversity has value for human society because of its potential to provide an ecological service (Benayas et al., 2009; Ren et al., 2016).

As a complex system, the ecological system functions as a whole. The combined activities of individual species provide ecological services that include water cycling, carbon sequestration, soil development, fuel generation, etc. (Bhardwaj et al., 2011; Jantz et al., 2015; Farley and Voinov, 2016). Individual services may depend on special features of single or multiple species such as the medical use of special herbs. For most ecological functions, the internal interaction mechanisms are not fully understood. It is believed that species richness and evenness are positively correlated with ecological system robustness (Wilmers, 2002). Therefore, richness and evenness are considered as the main factors in measuring habitat diversity (Güngör, 2011).

2.2.2. Species richness

Species richness is the number of different species found in an area, community or ecosystem (Colwell, 2009). It depends on geological, pedological, meteorological, landscape, and many other factors. Within the same ecosystem or under similar climate conditions, species richness is also not necessarily constant (Camill et al., 2004). Tropical rainforests and coral reefs are considered as the habitats which have the highest species richness (Adler, 2013; Moberg and Folke, 1999). Therefore, species richness is an indicator for long-term development of the vegetation assemblage. Although surveying for species richness is time-intensive, it is an important and useful measure.

A measure closely related to species richness, species abundance, has also been used as an indicator of biodiversity. By assigning different weights to species according to their abundance, one can distinguish dominant species and opportunists (Gaston and Spicer, 2004).

2.2.3. Simpson Biodiversity Index

Ever since the importance of biodiversity was realised, many assessment methods have been developed for specific applications, but none of these has gained widespread acceptance.

The BioDiversity Index, BDI, used in this research follows the definition proposed by Simpson (1949):

$$\text{BDI} = 1 - \frac{\sum_{i=1}^{T}\left(n_i\left(n_i - 1\right)\right)}{\sum_{i=1}^{T} n_i\left(\sum_{i=1}^{T} n_i - 1\right)}$$

where i = counter for species

n = number of plants of each species

T = number of species

BDI varies between 0 when one species dominates and 1 when the distribution of different species approaches absolute evenness. For any barren land or places where only one species is present, the BDI is assumed to be 0.

BDI expresses the dominance rather than the richness aspect of biodiversity (Colwell, 2009). In the ecological world, evenness in the distribution of species is important for the vegetation community because it indicates the stability of the plant community (Colwell, 2009). A community dominated by single species could possibly collapse through a single event such as an insect pest outbreak. Diversified ecological systems are more resilient to environmental change and have greater potential for self-regeneration (Peterson et al., 1998).

2.2.4. Similarity index

Comparison of vegetation assemblages in different plots is not adequately expressed by a biodiversity index. To assess habitat similarity or dissimilarity, a number of similarity indices have been proposed. Among these, the Sørensen similarity index (Sørensen, 1948; Magurran, 2004) is a relatively straightforward, easy-to-use index. Its calculation is based on the presence or absence of species in different sites. It only requires a limited amount of data as it is not necessary to input the number of individual plants. The Sørensen similarity index is defined as:

$$\text{Sørensen similarity index} = \frac{2C}{A+B}$$

where A and B represent the species richness in two different sites while C represents the number of common species found in both sites. The index varies between zero and unity. It is equal to zero when two plots do not share any species and unity when two plots have exactly the same species composition. Hereafter, the Sørensen similarity index is abbreviated as SSI and will be used to evaluate the level of auto-correlation.

2.3 Vegetation survey method

Given increased awareness of the importance of biodiversity, the need to evaluate and monitor local species richness and abundance is apparent. In restoration ecology, investigating the vegetation distribution patterns is a fundamental aspect of the design and management of rehabilitation projects (Zhang et al., 2006). In an ideal situation, all individual plants are recorded. Such exhaustive surveys are often not practical because of limitation of time, manpower, and other resource availability. Therefore, different survey methods have been developed to achieve different targets in different settings.

The success of vegetation survey relies, to a large extent, on decisions made prior to the starts of the field campaign (Smart and Grainger, 1974). The following aspects should be considered before developing a survey strategy and choosing the survey method (Kent and Coker, 1994):

- Objective of the survey: it defines the data which needs to be collected during field work.
- Data size of the study: it is defined by the features and size of the research site.
- Habitat type: it is decided by succession stages on the research site, vegetation cover, local climate, and other factors.

- Available resources: this includes equipment, skills, and labour available for the survey.

Making proper decisions about sampling techniques requires consideration of the size and shape of sampling unit, vegetation types, spatial arrangement of sampling sites, etc. (Smartt and Grainger, 1974; Goslee, 2006).

Survey methods adopt two main approaches: geometric and spatial arrangements. The geometric approach divides survey methods into plotless (point), transect (line) and quadrat (rectangular, square or circle) (Myers and Shelton, 1980). The spatial approach obtains samples vegetation according to subjective and objective methods. Objective methods are subdivided into random and systematic sampling.

The transect method records all plant passing through an imaginary line or belt across the investigation area. Transect or line surveys are widely applied because, unlike plotless or quadrat surveys, it does not require precise positioning. However, it does not work well when plant species are aggregated or there are few different species present (Buckland et al., 2007). While the transect method could effectively approximate land cover, it may underestimate species richness in heterogeneous communities unless high-density samples are taken (Goslee, 2006; Stohlgren, 2007).

The quadrat survey method is widely applied due to its high flexibility (Cox, 1990). A quadrat survey is suitable for gaining an understanding of the spatial distribution of plants. Its accuracy is limited by subjective decisions of the surveyor who decides whether plants located on the perimeter of a quadrat should be recorded or not (Cox, 1990). Traditionally, a quadrat is square although circular and rectangular quadrats have also been applied (Kent and Coker, 1994). The optimal size of a quadrat depends on the vegetation community under investigation. For example, when surveying woodland, the quadrat would be bigger than for grassland. The size and shape of a quadrat must be decided in accordance with vegetation type and desired accuracy, e.g. $1m^2$ quadrat is surveyed more thoroughly than 100 m^2 quadrat but this is inappropriate when investigating woodland with grown-up trees (Rice and Kelting, 1955; Leis, et al., 2003).

The quadrat method is especially popular in regions which have sparse vegetation cover or are difficult to access. While bias is introduced when surveying homogeneous vegetation communities (Hijbeek, et al., 2013), it is an efficient tool in species richness investigation (Leis, et al., 2003).

The sample stand method records plants in predetermined patches (Minnesota Department of Natural Resources, 2013). It requires intensive knowledge of the survey area to choose a representative patch of a community (Barbour et al., 1987). The representative species normally is the most abundant one. It is quick to accomplish, requires no mathematical calculation and can give almost an exhaustive list of all species presence.

With plotless (point) sampling, rods are randomly or systematically placed in the investigation area and all plants touching the rod are recorded (Barbour et al., 1987). The distance method is a variation of point sampling which measures the distance between two plants of the same species. It is normally used to evaluate the variation of limited number of landmark species (Buckland, 2004).

Different surveying methods serve different purposes: they can either work alone or in combination. The Line Point Intercept (LPI) method is a combination of the transect method with the point (plotless) method in which a rod is moved along a transect at equal distances and all plants touching the rod are recorded (Rochefort et al., 2013). LPI can improve survey efficiency when rough estimation is sufficient.

While it is possible to take samples on irregular spatial patterns, this will impact on the reliability of data obtained from vegetation surveys. In practice, a quadrat survey can be carried out with systematic, random and subjective spatial arrangement.

The photogrammetric survey method is becoming popular because it greatly reduces field work intensity and is suitable for rough estimation of vegetation assemblages on a landscape scale (Rieke-Zapp et al., 2009). Aerial photographs can be taken by aircraft, drones, satellite, or during field surveys. With the advancement of technology, photogrammetric survey is being combined with sensors which detect features at wavelengths outside the visible light spectrum (e.g. infrared spectrometry). Although aerial photogrammetry is convenient for periodically revisiting survey locations, it may fail to detect creeping plants underneath the taller plants. Neither may it be feasible for investigating the abundance of herbaceous species.

Upfront selection of sampling locations includes preferential/subjective, random and systematic designs. Preferential (judgemental) sampling requires investigators to make on site decisions. Therefore, it is more sensitive to vegetation variation and species richness, with a possible bias towards inclusion of relatively rare species and interesting types of vegetation (Hédl, 2007; Roleček et al., 2007). This method is especially efficient in small areas (Michalcová et al., 2011). It is less suitable for large land areas due to the time required for site visits and its reliance on the personal intuition of the surveyor (Hédl, 2007). Statistical analysis of preferentially sampled data is not recommended by some researchers (Chiarucci, 2007; Lájer, 2007), while others (e.g Økland, 2007) urge caution in the statistical interpretation of such data.

Systematic sampling is convenient for comparative study and require less background knowledge about the site but may overlook vegetation patterns when sampling sites resonance with regular vegetation variation pattern (Roleček et al., 2007; Finney, 1949).

The systematic sampling method may be less suitable for estimating vegetation variation than a random spatial arrangement of sampling points because the regular sampling pattern limits the smallest trackable vegetation pattern to the distance between samples (Smartt and Grainger, 1974).

Systematic sampling produces data that has the property of statistical independence. Lájer (2007) pointed out that independent observation is a prerequisite for statistical analysis of ecological data. However, Moore et al. (1970) stated that statistical representativity does not ensure ecological representativity, as required by ecology research. Økland (2007) reports that statistical and ecological analysis demand different types of data: statistical analysis requires that the sampling distance far exceeds the scale required for sensible observation of the ecological pattern to avoid the impact of autocorrelation. Økland (2007) concludes that statistical analysis is not necessarily a suitable tool in ecological research. Noss (1996) and Weber (1999) believe the application of strict statistical modelling will obscure field observation skills and diminish inductive and deductive traditions in ecological research.

While random and systematic sampling can characterise common landscape features efficiently (Økland, 2007), subjective or preferential sampling is historically preferred by ecologists because of its efficient resource utilisation and capability of detecting rare ecological communities (Roleček et al., 2007). In terms of scientific value for ecologists, vegetation communities containing rare species normally engender greater interest. Goslee (2006) adds that if ecological community attributes are determined by different surveying methods, these cannot be compared in a meaningful way. Since accumulated ecological data comes mainly from preferential sampling, following this method enables ecologists to track ecological system changes (Michalcová et al., 2011). As a result, statistical analysis has not been applied widely in ecological research.

The method of stratified random sampling has been developed to cater to the requirements of both statistical and ecological analysis. Roleček et al (2007) states “stratified random sampling starts with a priori definition of strata within which sampling sites are located randomly”. Although this method can achieve reasonable representativity of different vegetation types, it can only represent those environmental gradients which have been considered in stratification (Knollová et al., 2005; Firbank et al., 2003). Therefore, it is not suitable when ecologists explore relatively unknown environments. Stratified random sampling is particularly inefficient when fine-scale variation is present; this is especially true in land affected by anthropogenic disturbance (Roleček et al., 2007).

Besides the survey and sampling method, the timing of a vegetation survey also has great impact on the produced data (Halme and Kotiaho, 2012; Schultz et al., 2014). For example, plants are more readily detected in the flowering and fruit-bearing seasons. Since plants blossom and fruit in different time, vegetation surveys with high reliability can only be achieved by repeating surveys across the year (Schultz et al., 2014).

While vegetation communities can be studied at different resolution and scale, researchers have to balance accuracy and efficiency when developing an investigation strategy for each study (Leis, et al., 2003; Shuster, et al., 2005). The choice of surveying and sampling methods depends on investigation objectives and resource availability (Rochefort et al., 2013). It is suggested that two different methods should be used in parallel to minimise bias (Hijbeek, 2013).

2.4. Soil

While soil is a generic word for particulate matter found on the Earth's surface, the definition of soil is by no means universally accepted. An environmentalist may describe it quite differently than a soil scientist. The definition of USDA (2010) is among the most widely distributed which says "soil is a natural body comprised of solids (minerals and organic matter), liquid, and gases that occurs on the land surface, occupies space, and is characterised by one or both of the following: horizons, or layers, that are distinguishable from the initial material as a result of additions, losses, transfers, and transformations of energy and matter or the ability to support rooted plants in a natural environment". Some researchers may not fully agree with this definition, but it does give a comprehensive scope of what constitutes a soil. Without organic matter, loose material is not considered to be a soil. While it may take hundreds of years to produce soil from parent material under natural conditions, the process of soil formation can be accelerated (Amundson and Jenny 1991). The following observations describe aspects of soil which play an influential role in vegetation development.

Natural soil is a mixture of mineral particles, organic matter, water, gas and living organisms (Brady and Ray, 2002). It is not an inert material and experiences continuous change. Soil particles are all those particles with a diameter equal or less than 2 mm (USDA, 2010). Soil contains both inorganic and organic components. Organic soil materials derive from plants, algae, soil fauna, bacteria, fungi and other organisms. Water and gas fill voids and pores of soil, which normally account for half of soil volume (Schaetzl and Anderson, 2005).

The inorganic component of soil is produced through the weathering of rock. As parent material of soil, the mineral composition of rock decides the element composition and acidity of soil (Young and Stephen, 1965; Breemen and Buurman, 2003). Weathering involves both physical and biochemical process. Bastida (2008) believes biological parameters have enormous potential because they are sensitive to changes in soil condition and reflect the integrated features of soil for ecological colonisation. The primary biochemical agents are organisms include plants, animals and microbes (Amundson and Jenny 1991). They can support hydrolysis, complex formation, oxidation, reduction, and ion exchange (Casida, 1964; Venugopalan and Prasad, 1989). They are also the source of organics at an early soil formation stage. With the advancement of technology, human interaction with soil formation becomes more pronounced. For example, the mining industry breaks down rocks much faster than would be the case through natural processes.

Soil plays an important role in the biosphere by supporting plant growth and providing habitat for other living organisms, regulating hydrological systems, controlling element recycling in nature and as an engineering medium and building material (Brady and Weil, 2002). As the carrier of land ecological system, the carrying capacity or the quality of soil is critical. However, the well-established assessment framework focusses mainly on the assessment of agro-ecosystem. For natural ecosystems and decontaminated land, no consensus has been reached on the selection and application of methods.

On the other hand, plants established on soil also have impacts to the soil. Conifer trees can acidify soil by their leaf leachate (Howard, 1989). Plant litter can help to maintain or increase soil organic content, which is beneficial for soil development (Amundson and Jenny, 1991).

The following sections shall discuss the major soil features, which may influence rehabilitation process or limit vegetation reestablishment at a mine site.

2.5. Soil physical characterisation

Suitable techniques have been identified according to availability to measure all soil features which have direct but varying impact on vegetation development. In the following sections, advantages and disadvantages of widely adopted soil analysis techniques are described.

2.5.1 Soil particle size

Soil particle size is sometimes termed as soil texture which is often used as an indicator for soil properties such as moisture retention and hydraulic conductivity (Bittelli et al., 1999). Although more than 400 soil sizing techniques have been developed, these can be classified into classical and modern instrumentation methods (Syvitski, 1991; Loveland and Whalley, 2000). Loveland and Whalley (2000) have divided the methods further into nine groups as follows:

1. Direct measurement (ruler, caliper, microscope, etc.)
2. Sieving
3. Elutriation
4. Sedimentation (gravity, centrifugation)
5. Interaction with radiation (light, laser light, x-rays, neutrons)
6. Electrical properties
7. Optical properties
8. Gas adsorption
9. Permeability

Of these methods, sieving is the most common technique for particle sizing (Fan and Zhu, 1998). The recovery rate correlates positively with sieving time. At the same time, excessive mechanic wear could reduce particle size and there is no reliable method available to calculate the optimum sieving time (Fan and Zhu, 1998). Sieves contain round, square, or rectangular apertures to size particles. Although theoretically a sieving method can handle particles down to 5 µm, it is recommended that sieving is only employed for screening soil particles larger than 63 µm (Wanogho et al., 1987; Gee and Bauder, 1986).

Direct measurement through optical determination or microscopy is a method which measures individual particle sizes based on visualization (Fan and Zhu, 1998; Last and Smol 2001). It is labour-intensive and subjective judgement may be required to determine the size of irregular particles. Therefore, its industrial application is limited. Electrical properties such as resistance may also be used to measure particle size distribution. While the measurement is relatively fast, soil particles tend to clog the measuring tube and the method is incapable of handling aggregated soil grains (Last and Smol, 2001).

The sedimentation method normally measures the settlement time of particles as a function of their size (Fan and Zhu, 1998). For small particles, a centrifuge is used to accelerate the rate of sedimentation. The sedimentation method can only produce a rough estimate of particle size and particle density can affect the result. Some variants of the sedimentation method have been developed; these include the pipette and hydrometer methods (Gee and Bauder, 1986). The hydrometer method gives unreliable readings and the pipette method requires additional steps which introduce additional errors due to the loss of sample (Gee and Bauder, 1979). Application of these methods is further limited by subgroup resolution (Eshel et al., 2004) and their capacity to handle fine particles (Loveland and Whalley, 2000).

Compared with the classical sedimentation method, the Laser Diffraction (LD) method is quick and effortless (Wanogho et al., 1987). It uses forward diffraction of laser beam by particles to determine soil texture and has far better reproducibility than classical methods (Mudroch et al., 1997; Eshel et al., 2004). Based on measurement of a relatively small sample, LD can produce a continuous particle distribution curve which enables a comprehensive comparison (Eshel et al., 2004).

All particle size measurement techniques have their strengths and weaknesses and have to be chosen according to research objectives (Mudroch et al., 1997; Last and Smol, 2001; Goossens, 2008). It should be noted that classical methods normally give a mass-based particle distribution while LD is a volumetric method; this means their results are not comparable (Eshel et al., 2004). For current research, volume-based soil texture is appropriate because of the close relation between particle volume and surface area for fine particles. It should be noted that all particle size evaluation methods struggle with measurement of irregularly-shaped soil grains. As a result, the measured particle size is only an estimated value (Eshel et al., 2004). Furthermore, all methods measure only a relatively small mass of soil implies that the representativity of the measured particle size distribution is not guaranteed.

2.5.2 Soil compaction

As the name suggests, soil compaction refers to soil aggregates compacted into smaller volume, reducing soil porosity and increasing bulk density (Koolen and Kuipers, 1983). In nature, soil density increases with depth because of the gravitational pull of the soil mass above (Dedousis and Bartzanas, 2010).

Soil compaction limits vegetation root development due to increased physical resistance, reduced porosity and aeration (Dedousis and Bartzanas, 2010; Osman, 2013). The herbaceous species root system is less strong than shrubs and trees and therefore they are more sensitive to soil compaction. Godefroid (2004) found that forest herbaceous species are more sensitive to soil compaction than non-forest species. This could be due to forests typically having a higher biomass production and more litter falling under trees canopies, which could reduce the soil bulk density. It is also assumed that plant root penetration depth decreases with increasing soil compaction and seedlings growing in compacted soil are more vulnerable to drought (Skinner, 2009). Blouin (2004) observed that the reduced water availability is the main impact factor for seedling growth in compacted soil.

Compaction and reduced infiltration can impede groundwater refill and hence reduce water availability (Chong, 1986). The development of plant roots is also negatively affected by soil compaction. McSweeney (1984) found that plant rooting is less profuse when soil is compacted, which inhibits plant development and biomass production. Nawaz (2013) summarised soil compaction impacts on:

- Plants: compaction deforms plant roots, inhibits growth, delays germination and reduces germination rate.
- Biodiversity: compaction inhibits microorganism activity, reduces soil fauna and flora.

Ruthrof (2013) suggests ‘ripping’ can effectively improve plant root development and infiltration rate. This is important in regions which experience seasonal drought because longer and deeper root systems can capture more soil moisture. However, moderate soil compaction also can have positive impacts on woody species. Alameda (2009) found that controlled soil compaction can improve biomass production although it will reduce root development of some species. It is assumed that increased root-soil contact promotes uptake of nutrients (Alameda, 2009).

A technique for measurement of soil compaction was first developed by Proctor (1933) for civil engineering purposes. British Standard light compaction test is directly developed from the Proctor test (Head, 2006). A penetrometer is commonly used for soil strength measurement (Bengough et al., 2000). The American Association of Agricultural Engineers defined a penetrometer measurement unit called the Cone Index (CI), which is widely adopted (ASAE, 1969). Penetrometer readings can have considerable variation even the measurement is close enough (O’Sullivan et al., 1987; Carter and Gregorich, 2007). The difference between two readings can be up to 70% (Kogure et al., 1985). As a general rule, when tests are conducted at a distance greater than 1 m, the results are independent (O’Sullivan et al., 1987). Others state that the threshold for independent test results is 9 meters (Moolman and Van Huyssteen, 1989). Since all measurements in this research were done within a 1 m^2 quadrat, statistical independence within a quadrat is difficult to achieve. Furthermore, the presence of stones can cause sudden changes of readings and even damage force transducers. Unrepresentative values need to be identified and marked as outliers (Bengough et al., 2000).

There are two different types of penetrometers: the hand-push portable cone penetrometer and the motorised portable cone penetrometer. These two types of penetrometer were applied for testing at different depths while, for surface soil, the hand-push device is deemed sufficient.

2.6. Soil chemistry

The primary impact of soil on plant development is linked to chemical properties such as bioavailable ions. Eighteen chemical elements are considered to be essential for plants growth (Brady and Ray, 2002). The ability of soil to support these elements is called soil fertility. Nine of the eighteen elements are required in large amounts and they are called macronutrients; the remainder are denoted as micronutrients or trace elements (Brady and Ray, 2002). Some of the micronutrients such as copper and zinc would become toxic when they are available in excessive quantity (Verdejo et al., 2016). Other elements taken up by plants are not considered as essential. The focus of this research is to characterise the metal elements, which were released by mining activity into ground surface.

The metal elements can exist in soil in different forms; these are classified as (Hillel, 2008):

1. Bioavailable: exist in soil solution or in soluble form within active root zone.
2. Labile reserve: retained in the soil’s exchange complex and/or rapid decomposable organic matter.

3. Stable reserve: fixed in soil material or in slowly decomposable organic compounds (humus).

Normally, most metals are present as minerals and hence not bioavailable (stable reserve). They are released slowly through chemical weathering. Soil acidity, temperature and air exposure have different roles in the chemical weathering process and can alter minerals into different chemical compounds (Colman and Dethier, 1986).

The pH indicates soil acidity and is defined as the negative logarithm of the hydrogen ion concentration (Sørensen, 1909; Stewart, 1989). In most cases, a low pH is considered to limit soil productivity (Jing, 2011). Law (1984) states that bioavailable nutrient levels in soil depend on pH and can vary for different vegetation species. In acidic soil, ammonia is overwhelming and the ability of legume species to fix nitrogen is suppressed (Mohammadi et al., 2012). In New Zealand, Magesan (2012) found that *Ulex europaeus* can sequester up to 200 kg of nitrogen per year. The fixation efficiency depends on soil temperature, moisture, pH and nutrient availability. In the field, soil pH changes with the temperature, the ionic size and strength and solvent density variation (Stewart, 1989). pH is a temperature sensitive indicator. Hence all measurements have to be made under controlled conditions.

The soil acidity or alkalinity is a result of the weathering and leaching of parent material. Generally, when calcium, magnesium, potassium, and other alkali metals cation leach out and hydrogen, aluminium, iron and some heavy metal ions become the dominant exchangeable cations, the soil becomes acidic (Robert, 2006). Robert (2006) suggested the following pathways of soil acidification:

1. The dissolution of carbon dioxide in soil solution
2. The decomposition of organic matter
3. Nitrification process
4. Acid rain
5. The oxidation of iron pyrites

Acid soils are more frequently found in humid regions where extensive leaching may protonate clays (Onthong and Osaki, 2006). Soil acidity corresponds to the pH value of the solution present in the soil pores. This solution could have direct contact with plant roots, where many chemical reactions occur.

A low pH increases the solubility of many heavy metals in water, making these more accessible to plants (Kuo et al., 2006; Chen et al., 2010; Mosley et al., 2014). However, the solubility of arsenic may increase with reduced acidity, e.g. as a result of liming (Jones et al., 1997). It is also recognised that soil pH could change nutrients availability and acidic soil will result in nutrient deficiency in plants (Jing, 2011). Therefore, soil pH is an important indicator to characterise soil especially in contaminated land ecological restoration.

Mclean (1992) found that downward movement of heavy metals is rare unless the metal adsorption capacity of surface soil is exceeded or metals form more soluble compounds with organic ligands. Upward transport, on the other hand, is a continuous process due to the continuous dissolution of soluble heavy metal compounds and other nutrients in plant root zone (Kitano et al., 2009; Wang et al., 2014).

Electrical Conductivity (EC) is the capacity of soil to conduct or transmit electrical currents (Brady and Weil, 2002). EC is determined by the total amount of dissolvable ions in the soil; the main ions in soil solution include Na, Ca, Mg, SO_4, and Cl. Other ions such as K, HCO_3, CO_3, and NO_3 may also be present in low concentrations (Miller and Curtin, 2007). Therefore, EC is often used as an indicator of ionic strength of soil. Arshad and Martin (2002) pointed out that EC is a key indicator of soil quality due to the interdependence of nutrient availability and EC. Hence, EC sometimes is used to estimate nutrient availability in soil (Hartsock et al., 20000). Guretzky et al. (2004) found EC spatial variation can cause plant distribution heterogeneity.

2.6.1 Transformation of arsenic compounds

The main contaminant in Carnon Valley is arsenic in the form of arsenopyrite (FeAsS) (Basu, 2013). Arsenopyrite is known to be the major arsenic-bearing mineral out of Wheal Jane mine. It is also one of the minerals which is most resistant to dissolution (Basu, 2013). Gradual natural transformation affects arsenic phytoavailability and biological toxicity of the soil. Salzsauler (2005) stated that arsenopyrite in mine waste can be oxidised into scorodite, jarosite, and amorphous iron sulfo-arsenates.

Arsenopyrite is relatively stable under reducing conditions but its secondary products tend to be more stable in oxidising conditions. Therefore, disturbance of the environment, including capping of mine shafts, can increase the soluble concentration of arsenic in soil by introducing aeration. Robson (2013) found that any type of land re-working such as ploughing, will improve soil aeration and increase arsenopyrite oxidation. Arsenopyrite-bearing minerals in water or waterlogged conditions are relatively stable and not easily dissolved into the watercourse (Craw, 2003). Yu (2007) observed that oxidation and release of arsenic in water continues due to dissolved oxygen and temperature effect. Yu (2007) found that arsenic dissolution is relatively high when $pH<7$ or $pH>10$. Oxygen, Fe^{3+} and NO_3^- are potential electron acceptors in mine tailings during the oxidation process. NO_3^- is released through a mineralisation process of soil organic matter. While NO_3^- has a lower oxidative strength than oxygen and Fe^{3+}, the oxidation of arsenopyrite by NO^{3-} at similar concentrations is a slower process (Mihaljevic, 2010). The abundance of these molecules in soil determines the reaction equilibrium balance.

Salzsauler (2005) pointed out that iron oxyhydroxides can fix arsenic in most conditions. The absorption of arsenic as arsenate is more efficient at low pH value (Clara, 2002). As a main arsenic reservoir, iron hydroxide is stable in an oxidative atmosphere and insoluble under acidic (pH 4-6) conditions (Basu, 2013). Arsenate will be more soluble in neutral to basic soil solution and Basu (2013) found that arsenic can desorb from soil particles quickly in a reductive atmosphere. Mihaljevic (2010) found that arsenopyrite transformation behaviour is different under different vegetation covers. He suggested that this was influenced by variation of the organic mineralisation rate and the resulting production of nitrate and seepage conditions. While mineralisation is quicker in well-drained soil, nitrification and the amount and quality of litter can alter soil drainage. Hence forest soil may alter arsenopyrite into scorodite faster than soil in an unforested area. The formation of a passive layer on a weathered arsenopyrite surface will stop the oxidation-dissolution chain reaction when exposed for periods of time, reducing arsenic mobility by sequestration (Robson et al., 2013). Scorodite is a relatively stable compound within a wide range of pH values. Mihaljevic (2010) also stated that anaerobic conditions make arsenic less toxic and arsenic mobility increases in the dry season. Robson et al. (2013) found that periodically flooded regions will have relatively high arsenic in soil solution because arsenic compounds produced through oxidation in dry seasons can be easily dissolved under reductive conditions. Salzsauler (2005) reports that a change from oxidative to reductive state significantly increases arsenic solubility in soil solution from an arsenopyrite-bearing mine tailings dump. This indicates that constant soil moisture is important in preventing arsenic leaching. Furthermore, vegetation coverage is beneficial in improving the soil water storage capacity, which makes it is important to restore vegetation in contaminated areas.

A negative correlation between soil heavy metal and biomass of microorganisms and organic matter has been reported by Vasquez-Murrieta (2006). At the same time, however, microorganisms can detoxify arsenic-contaminated soil by transforming it into less toxic compounds (Pongratz, 1998).

2.6.2 Chemical characterization techniques

2.6.2.1 Electrical Conductivity

In situ (field) measurement of electrical conductivity (EC) can be achieved by a number of techniques:

- Wenner array
- four-electrode conductivity apparatus
- electromagnetic induction
- time domain reflectometry

Further information on these techniques can be found in Rhoades and Oster (1986), Brady and Weil (2002) and Rhoades (1990 and 1992). Field measurement techniques are widely applied due to their capacity of rapid survey. Measured EC values, correlating with the concentration of ions in solution, are affected by the moisture content and temperature of the soil (Reitemeier, 1954). While it is not possible to control such parameters during field measurements, laboratory analysis is required to obtain accurate data for scientific research purposes. Laboratory EC soil tests can be carried out on soil pastes or soils solutions with defined soil-to-water ratio (Conklin, 2014; Miller and Curtin, 2007). Because the analysis of soil paste requires more time and skill, the soil solution method is more popular (Miller and Curtin, 2007). Different soil preparation procedures have been employed for EC analysis. They differ from each other in terms of the drying temperature and duration of drying. Although the values of different testing methods differ, they are highly correlated with each other. In fact, when the operating temperature and soil-to-water ratio are specified, measurements can easily be converted into the standard electrical conductivity. However, the presence of sandy soil, organic soil and gypsum may cause errors when comparing EC values determined with different soil-to-water proportions (Robbins and Wiegand, 1990). Generally, the selection of measurement method is purely based on apparatus availability and the ease of application.

While EC is primarily applied to understand crop yield, there is little research linking conductivity with biotic effects of soil contamination (Kozlov et al., 2009). Research suggests that EC is indicative for trace element levels in metal contaminated land (Nagamori et al., 2007). However, its positive correlation with the concentration of both macronutrients and soluble pollutants make it is difficult to interpret unless there is supplementary data (Kozlov et al., 2009).

2.6.2.2 Soil pH

Soil pH testing methods commonly available for soil analysis include:

- indicator paper
- electric pH meter
- colorimetric (Kuhn’s method)
- Lovibond comparator

Indicator paper is the most cost-effective method which can narrow down pH value to 0.5 units (Head, 2006). It was the most common method before electrode pH meter is developed (Jones, 2001). Modern electric pH meters have an accuracy of 0.05 pH units or better (Head, 2006). Jones (2001) stated that electric pH meters are now the most common tool to measure soil acidity. It is, however, relatively expensive to operate and may require calibration between measurements. The colorimetric method is developed for field use and relies on subjective judgement of colour variation. The Lovibond comparator can reach accuracies of 0.2 pH units and was originally developed for groundwater (Head, 2006).

2.7 Soil mineralogy

Mineralogical analysis can be used to gain insight into the chemical character of soil. Hahm et al. (2014) established connections between bedrock type and vegetation succession and he suggested that the variation of element concentration and geochemistry could affect ecological evolution. The influence of substrate mineralogy on the type of vegetation has also been reported by Kruckeberg (2004) and Brady et al. (2005). Harris (2011) states that trace minerals have significant ecological impact, especially those minerals affect biogeochemical process. Alexander (2014) found that different soil mineralogy can affect the distribution and development of vegetation, corroborating an observation originally made by Whittaker (1960). Valente et al. (2012) suggest that subsurface mineralogy has a significant impact on revegetation efforts at a mine site. Soil at mine sites generally lacks macronutrients which will inhibit the development of vegetation (Spalding, 1996). On the other hand, plant root exudates could alter mineral compound availability in the rhizosphere by mobilising or immobilising minerals in the substrate (Dakora and Phillips, 2002).

The chemical composition of minerals in soil determines their solubility. While oxides are almost insoluble, sulphides are prone to be soluble and can generate acid mine drainage (Jambor et al., 2003). Wheal Jane was the largest producer of pyrite in this region because of the gossans and sulphidic lodes (Dines, 1956). The presence of sulphides can acidify soil solutions and further improve heavy metal mobility and biotoxicity. This is likely to stunt plant development.

2.8 Soil arsenic fractionation

The bioavailability and mobility of arsenic in soil rely on species of its compound and soil characteristics (Liu and Cai, 2007). Since the total arsenic concentration is not necessarily bioavailable, researchers have developed various Sequential Extraction Procedures (SEP) to evaluate arsenic partitioning. The Tessier method is the first internationally recognised method (Tessier et al., 1979; Arain et al., 2009). Davidson et al. (1999) and Tlustoš et al. (2005) found that arsenic fractionation in soil varies with the applied extraction scheme. SEPs such as BCR and Tessier (1979) do not accurately measure physicochemical forms of arsenic in arbitrary soils (Tlustoš et al., 2005). Due to poor reproducibility of SEPs, there is no universally-accepted calibration method nor representative standard materials for laboratory analysis (Nirel and Morel, 1990). Despite a number of attempts, Liu and Cai (2007) stated that little progress has been made in the validation of SEPs. The poor precision is due to fractionation of trace elements being highly sensitive to environmental factors such as soil pH, temperature, moisture content, contact time, solid-to-extractant volume ratio, and particle size while sample pretreatment can also lead to differences (Chowdhury et al., 1992; La Force, 2000; Gray and McLaren, 2003; Tlustoš et al., 2005). Mossop and Davidson (2003) observed that sequential extraction procedures operated by the same technician in the same lab can produce poorly comparable sequential extraction results. Single extraction procedures are also used to evaluate bioavailable arsenic but these neglect the other arsenic fractions in soil. As a result, the predictive capability of these methods, for example when the ambient conditions change, is strictly limited.

Despite the limitations of SEP, it is still the standard technique for studying arsenic mobility and behaviour (Liu and Cai, 2007). Some researchers compared 11 most widely-used SEPs for arsenic and found they all measure arsenic in the the following phases: easily-sorbed phase, Al-, Fe- and/or Mn-oxyhydroxide phase, and a residual phase (Hudson-Edwards et al., 2004). Other optional phases include water- or easily-soluble, acid volatile sulphide, organic matter, acid-soluble, Ca-associated, arsenic oxide and silicate, and As or Fe sulphide (Hudson-Edwards et al., 2004). Liu and Cai (2007) categorised them into three groups: classical SEPs, the BCR scheme, and three phase systems (mobile, mobilizable and residual). Due to the anionic behaviour similarity of arsenic and phosphorus and the higher charge density of phosphate, traditional SEPs feature various phosphate chemicals to extract arsenic from soil (Zhang and Selim, 2008; Carabante et al., 2010; Neupane et al., 2014). This arsenic fraction has a strong influence on vegetation development because it limits availability of phosphorus, a macro-nutrient. Keon et al. (2001), Wenzel et al. (2001), and Cai et al. (2002)

have specifically investigated the extraction of specifically adsorbed arsenic. Wenzel et al. (2001) devised a simplified SEP which partially overcomes the problem that some extraction agents are less selective or specific (Gruebel et al., 1988). Liu and Cai (2007) suggest Wenzel scheme is a reliable method.

2.8.1 Arsenic fractionation techniques

Arsenic phytotoxicity and phytoavailability are different for different arsenic compounds (Carbonell, 1998). Total arsenic in soil cannot describe edaphic toxicity for plants. Therefore, identifying the amount of arsenic in each soil fraction is very important. Its fractionation was defined depending on the potential liability of arsenic leaching into soil solution. After testing different extraction reagents and procedures, Wenzel (2001) developed a sequential extraction scheme specifically for soil arsenic fractionation. In the Wenzel scheme, arsenic is classified into the following categories:

1) Non specifically-bound
2) Specifically-bound
3) Amorphous hydrous oxide-bound
4) Crystalline hydrous oxide-bound
5) Residual phases

The first fraction represents dissolved arsenic but only accounts for a limited amount of total arsenic load in soil. The second fraction of arsenic minerals are adsorbed to soil grain surfaces and can be released when phosphate takes its place. Amorphous hydrous oxide binds considerable amount of arsenic and is, in some cases, the dominant pool of arsenic in soil. Kumpiene (2012) finds that plants can mobilise arsenic bound by poorly crystalline iron oxyhydroxides because their roots can exude oxalic acid and another organic compound which solubilise poorly crystalline ferrihydrite. Temperature, soil moisture, and soil pH also affect arsenic allocation to different fractions (La Force, 2000). Therefore, arsenic fractionation is not independent of seasonal fluctuation.

The Wenzel (2001) method is employed in this research with a minor modification. The detailed procedure is reported in the section 4.7 and appendix D. To get comparable results, soil sample are normally dried and sized to take out oversized grains and plant litter. The procedure has been criticised because soil drying can induce alteration of exchangeable fraction and the crystallisation of amorphous iron oxides (Bordas, 1998). To avoid this alteration, application of fresh soil has been recommended. In practice, soil moisture will increase soil aggregation and make sieving difficult. Soil moisture also makes it difficult to control sample weight. Bordas (1998) pointed out that air-dry samples are less susceptible to change than oven-dry samples.

The adsorption-desorption equilibrium is decided by the ratio of arsenic to hydrated amorphous Fe, Al and Mn oxyhydroxides, the percentage of clay minerals percentage, carbonates and sulphide minerals (Cullen,1989).

The pronounced adsorption ability of Fe, Al and Mn-oxyhydroxides (Wilkie and Hering, 1996; Bowell, 1994) has been well-studied. Their adsorption ability varies according to the change of pH because their surfaces will change from positively charged at low pH value to become negatively charged at high pH (Bowell, 1994). The turning point where surface charge alters from negative to positive varies from mineral to mineral. Arsenates are more easily absorbed by amorphous oxyhydroxides than crystalline minerals, especially under low pH (Magalhaes, 2002). This also can be inferred from the result of our sequential extraction scheme analysis.

2.9 Statistical analysis

Nature is a complicated system and the patterns of a vegetation community are normally driven by considerable biotic and abiotic processes which exhibit spatial and temporal variation (McGarigal et al., 2000; Jongman et al., 1995). The interactions and synergies between biotic and abiotic factors further complicate analysis of the system (McGarigal et al., 2000). As a result, ecological research normally is carried out in greenhouses or under controlled environment to avoid influences of unexpected factors. In a greenhouse, the impact of selected variables is tested while keeping other variables constant. Although this approach makes assessment relatively straightforward, the desire for more practical field investigation has driven the application of multivariate analysis techniques in ecology in past 20 years (Kent and Coker, 1996; Chahouki, 2012).

Commonly-used multivariate techniques for restoration ecology research in grassland include multivariate regression and ordination analysis (Liczner, 2014).

By reviewing 340 published restoration ecology papers, Liczner (2014) inferred that the increasing popularity of ordination techniques follows the pursuit of a better understanding of increased number of explanatory variables employed in ecological models.

Gauch (1982) noted that ordination analysis can faithfully describe the relationship between environment and species with a minimum of variable dimensions. It should be noted that a classification method such as cluster analysis can also be used to reduce the number of variable dimensions. However, classification uses stochastic data which makes it unsuitable for analysing environmental gradients (Chahouki, 2012). In contrast, ordination assumes that variables have gradually changing values. Fielding (2007) assumes that cluster analysis is normally used to generate hypotheses rather than test for significance because it could produce clusters with no physical significance. But Fielding (2007) suggests that cluster analysis can be beneficial when a researcher has a relatively poor knowledge of the data structure (Fielding, 2007). Therefore, a number of techniques have been used in this study.

2.9.1 Multivariate regression

Legendre and Legendre (2012) stated that the method of analysis is normally decided by availability rather than knowledge of variable properties and strength of methods. Hence, basic mathematical method such as linear regression is the most popular method in ecological literature (Liczner, 2014).

A multivariate regression model is a linear combination of products of variables and coefficients, plus an error term:

$$Y = a_1X_1 + a_2X_2 + a_3X_3 + \ldots + a_iX_i + \mathcal{E}$$

where Y is a dependent variable, a_i are coefficients, X are independent variables, and $\mathcal{E}$ is the noise (Zuur et al., 2007). A multivariate linear regression model uses the p-value to express statistical significance, or indicate which variable can best explain the data. While it establishes a linear relationship between environmental factors with single response variable, this does not necessarily describe the interrelationship among biotic response variables. The other disadvantage of multivariate linear regression is that it cannot visualise the relationship of all variables in a conventional single graph.

2.9.2 Ordination analysis

Ordination is a useful tool to visualise community data by plotting samples with similar features as a function of proximity in a low-dimensional space (Peet, 1980). The term ordination was introduced by Goodall in 1954 and originates from the German word ‘Ordnung’ used by Ramensky (1930) to describe this mathematical approach. Both constrained and unconstrained ordination methods have been developed.

Unconstrained ordination can reduce environmental variable complexity and characterise a group of environmental factors. Principal Component Analysis (PCA) is a commonly used ordination method which infers the significance of variables from their variance (Zuur et al., 2007). It was invented in 1901 by Karl Pearson (Dunn et al., 1987) and it is one of the earliest ordination techniques applied to ecological data (Chahouki, 2012). McGarigal et al., (2000) defined PCA as an “unconstrained ordination technique whose main purpose is to organise sampling entities along meaningful gradients based on the interrelationships among a large number of interdependent variables”. PCA creates a linear combination of new variables (scores) which describe maximum variation among individual entities (McGarigal et al., 2000). However, the variables which contribute most to environmental variation are not necessarily those which have most influence on the vegetation community. In the absence of a clear distinction between explanatory variables and response variables, PCA may not be a reliable method for predicting vegetation development. Zuur et al., (2007) stated that PCA is not suitable for ecological field study when there are many zeros present in the dataset, a common situation in field investigation. PCA will assume that two different variables with zeros are correlated with each other Zuur et al. (2007).

Chahouki (2012) stated that PCA is a tool to reveal the internal structure or patterns in a dataset which best explain variance in the data. Once a data pattern is found, reduction of data dimensions will not lead to loss of much information. However, it is very sensitive to the presence of outliers which can lead to large errors (Chahouki, 2012). Bakus (2007) stated that PCA is a poor method for community data evaluation because outliers are very difficult to identify in the presence of complex correlations in data pertaining to an ecological community.

Constrained ordination specifies a set of response variables which are explained by a corresponding set of environmental variables. The most common constrained ordination method is Redundancy Analysis (RDA), which starts with linear regression of the dependent variables and then uses PCA to further interpret the results (McGarigal et al., 2000). RDA produces axes which are not only a linear combination of the response variables, but also of the explanatory variables (Zuur et al., 2007). RDA is useful when gradients are short (Chahouki, 2012). Ter Braak and Šmilauer (2003) suggest that, when the gradient length is shorter than 3, RDA is a good choice for a constrained ordination method. Determination of the gradient length with the method suggested by Ter Braak and Šmilauer (2003) found RDA is a suitable for this investigation.

While explanation of PCA response variable in terms of explanatory variables may be cumbersome (Zuur et al., 2007), RDA is a more useful tool in the research or abiotic-biotic interactions. To infer a reliable RDA model, the number of explanatory variables has to be less than the number of valid observations (Zuur et al., 2007). The ordination technique cannot infer gradients if there is insufficient data available. However, this technique is useful to identify the environmental factors which contribute most to vegetation development from available data (Díez et al., 2003).

Bray and Curtis (1957) are among the pioneers to use indirect ordination technique. Kent and Coker (1996) believes that Bray-Curtis ordination is an effective ordination technique which produces comparable results to PCA. With increasing size of the dataset, however, it becomes more difficult to decide which pairs of data to plot along the axis. This potentially introduces inconsistency. With more advanced ordination techniques under development, polar ordination is less favoured but its simplicity still encourages its use (Malanson et al., 1993; Kent and Coker, 1996). Moral (1980) states that polar ordination can produce an ecologically-sound ordination result in multiple dimensions and is less sensitive to outliers than PCA. Other advantages of polar ordination include (Moral, 1980):

1. Mathematically direct and less vulnerable to distortion under beta diversity.
2. It is relatively robust to clustering, outliers, and noise.
3. It can disassociate entangled factors.

Moral (1980) also points out that drawbacks of polar ordination are inherited from its methodology when choosing the orientation of the axis. However, Kent and Coker (1996) argue that this selection only chooses the observation position and has no impact on the relative position of all values.

Multivariate linear regression and RDA are employed in this research to interpret natural rehabilitation development and vegetation reestablishment in the research site.

2.9.3 Cluster Analysis

The spatial distribution of vegetation is a cumulative response to environmental variables (Dray et al., 2012) and can be characterised with cluster analysis (Jacquez, 2008). Jacquez (2008) and Tan, Steinbach and Kumar (2005) state that cluster analysis can achieve two objectives in general: pattern recognition and hypothesis generation. James (1990) considers agglomerative hierarchical clustering to be the most suitable type of cluster analysis. These methods merge objects one-by-one according to their proximity (similarity) until the objects form a single group (Tan et al., 2005). Although cluster analysis can overinterpret clustering in continuous data, it is efficient for characterising taxonomy in ecological studies (James, 1990; Kent, 2011). The ordination method is more popular than cluster analysis in evaluating correlated measurements (James, 1990). However, the convenience of working with a few clusters rather than a great number of individual samples make cluster analysis a practical tool in ecological research (Wildi, 2013).

3 Study site

3.1 Cornwall

Cornwall is the only area in the United Kingdom which enjoys an sub-tropical oceanic climate being the most southern county in the UK and is located on the eastern edge of the North Atlantic Drift. The mild oceanic climate brings plenty of rainwater which is suitable for vegetation development. Temperate grassland, forest and sub-tropical species all can find their niche here. The dominant wind comes from the Atlantic Ocean, in a south-westerly direction.

The habitat in Cornwall is governed by its extended coastline bringing elevated precipitation. Its geographical location bestows a temperate climate and its unique geological history creates an unusual soil composition supporting plants rarely found elsewhere. There is also considerable variation of topography, leading to significant contrast in landscapes. Most of the vascular plants existing in Cornwall today are likely to have recolonised the region after the last Ice Age approximately seventeen thousand years ago (Colin, 1999). Since then, the natural landscape has been drastically altered by the local mining industry and development. Local soil is typically thin and poor (Leveridge, 1990).

Almost no natural biota can be found in Cornwall nowadays (French, 1999). The once extensive temperate rainforests were chopped to provide wood for supporting numerous mine tunnels below the surface. In its place, heathland and agriculture land dominate the local landscape. The mosaic distribution of mining legacy, agricultural land and semi-natural habitats subdivides the landscape into isolated patches and limits the chances for endangered species to develop.

The geology of south Cornwall is dominated by rocks of upper Devonian age, predominately the metamorphosis mudstones and subordinate sandstones of the Mylor Slate Formation (Leveridge, 1990).

3.2 Mining in Cornwall

Although the former wave of industrialisation left a legacy of contaminated land across Britain, no county is as severely affected as Cornwall. The county, which enjoys a reputation for its rich mineral reserves, used to be a major supplier of copper, lead and zinc in the UK (Dines, 1956). The mining spoils cover 4900 hectares of land in Cornwall, of which about 3900 hectares come from non-ferrous mining activities (Cornwall Council, 2011).

Although the last metalliferous mine in Cornwall was closed around twenty years ago, the influence of the mining industry is still clearly visible in the Cornish landscape. Some remediation work has been implemented around the outskirts of some towns to accommodate industrial estates and tourist facilities. However, much contaminated land is still left undisturbed due to the cost of remediation. There is no evidence of decreasing bioavailability or toxicity of trace elements over time and metal bioavailability and local toxicity levels are still high (Rainbow et al., 2011). The inherited biotoxicity distinguishes the local ecosystem from adjacent areas by its outstanding conservation value. A number of National Trust conservation sites in Cornwall, including Kenidjack, St. Agnes Head and Rinsey (French, 1999), used to be mined intensively. Ecological evolution is an expression of the species/ecosystem adaptive response to many factors including climate, geology, topography, competition, soil, and human activities.

As the deposits in Cornwall are relatively small-scale, the number of mines is large (up to several thousands) and these are scattered across the county. Subject to local variation, most former mining sites are characterised by a lunar landscape with low pH and a high trace metal concentration. The latter inhibits natural succession and retain pioneering vegetation community. Cobb et al. (2000) observes that physical and chemical properties of mine waste are heterogeneous. The potential impact of heterogeneous mine waste on vegetation development has been investigated by Steinhauser (2009). This research found that mine tailings from the same orebody can contain significant differences in pH, nutrient, carbonate content and mineralogical composition and that local species diversity is negatively correlated with arsenic concentration (Steinhauser, 2009). Therefore, spatial investigation of substrate physical and chemical features is necessary even the tailings originate from the same mine site. Uneven resource availability in micro-level promotes dramatic variation of in the structure of plant communities and leads to development of unique ecological systems across Cornwall. The vegetation communities in Cornwall distinguish themselves by associated species which normally do not grow together elsewhere. For example, heathland species are frequently found to co-exist with maritime plants, woodland species and disturbed land species. As a result, Cornwall has a unique ecological and cultural landscape which draws the attention of restoration ecologists (Whitbread-Abrutat, 1995).

Among all toxic elements, arsenic is of special concern as it occurs naturally at elevated concentrations in hydrothermally altered slate and rocks in Cornwall and in even higher concentrations at former mining sites (Camm, 2004). Arsenic was once widely applied as a pesticide, wood conservation agent, pigment, and for other industrial purposes. But in most mines, arsenic is considered to be an undesirable element which normally ends up in mine waste.

The majority of deposits in Cornwall have a relatively high sulphide content and arsenic is a common constituent of sulphide-bearing minerals (Craw and Bowell, 2014). Mining activities expose arsenic bearing minerals and the oxidation of sulphides could release arsenic into environment (Craw and Bowell, 2014). Smelters would vaporise arsenic followed by deposition in the local vicinity (Power, 2009). A combination of natural and anthropogenic factors makes arsenic levels in Cornish soil among the highest in Britain (Figure 2). Unsurprisingly, the environmental mobility and bioaccessibility of arsenic has been investigated in many studies (e.g. Camm et al., 2004; Slejkovec et al., 2010).

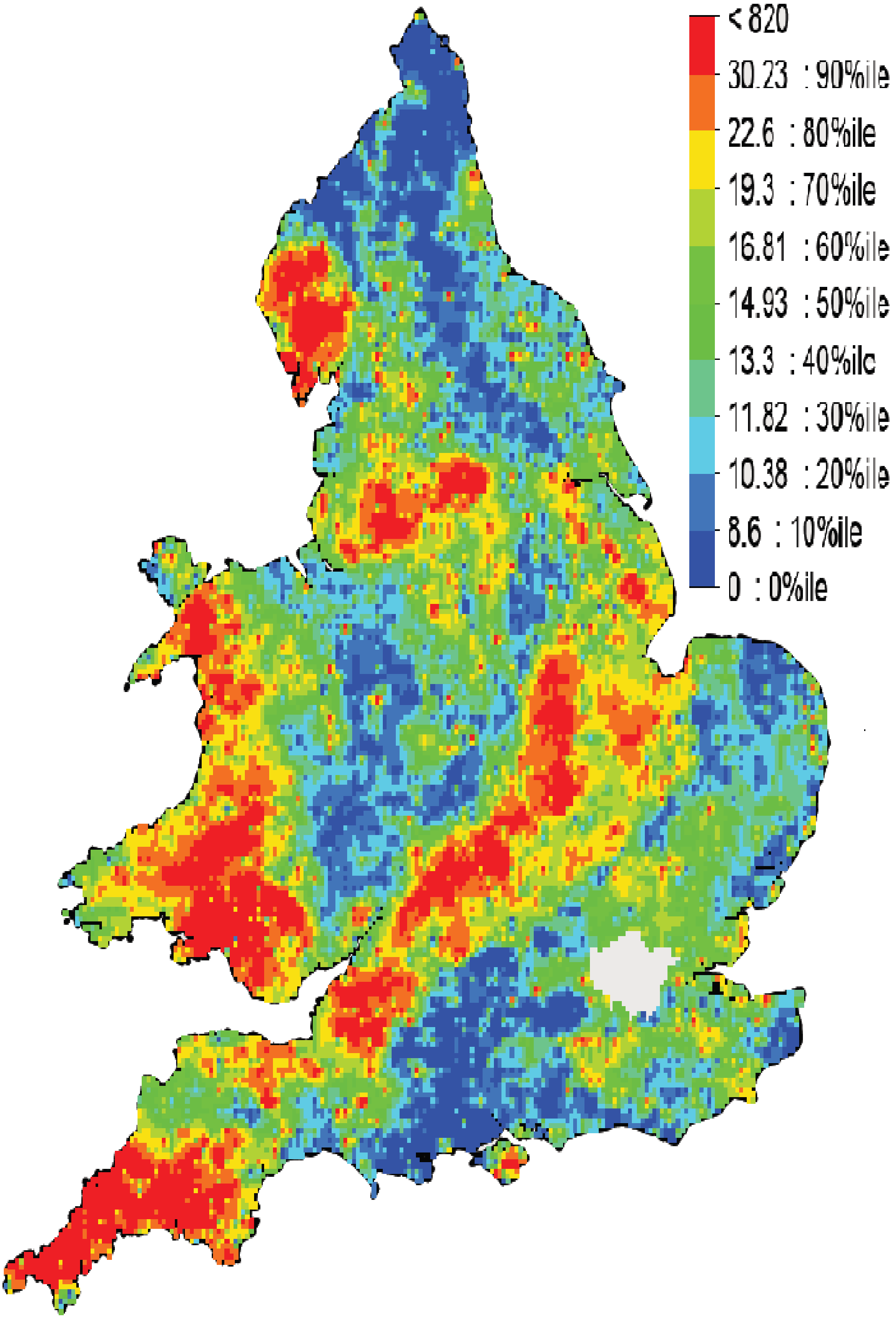


Figure 2: **Arsenic concentration (mg/kg) in England and Wales top-soil by percentile scale (Contains British Geological Survey materials © NERC [2012])**

According to Spalding (1996), among 700 prime wildlife sites in Cornwall, more than 20% are post mining sites and these sites are valuable for local ecological community. Typical habitat types found in post-mining sites in Cornwall include (adopted from Spalding et al., 1996):

1. Gorse shrubs
2. Willow and birch mixed forest;
3. Acid grassland
4. Heathland
5. Bare ground
6. Wetland
7. Wasteland or disturbed land
8. Open water

This research is conducted on one of the sites where a river valley has been used for tailing and waste rock disposal from the upstream Wheal Jane mine and several neighbouring small mines. The research is an attempt to understand ongoing local natural rehabilitation processes.

3.3. Carnon Valley

The Carnon river passes one of the major mining regions in Cornwall which has been mined for tin, copper, arsenic and other metals intensively from the 19th century till 1991 (Moon et al., 1995). The area adjacent to the Carnmenellis and Carn Marth granites is the most productive part of the Cornubian Orefield and Wheal Jane mine is one of the main producers. The B Lode subcrop of Wheal Jane deposit has a polymetallic composition. The Sn and Cu contamination of the Carnon Valley is a result of Sn placer deposits. (Moon, 2002).

Among all the mining legacy in Cornwall, Carnon Valley is well-known because of a water pollution accident due to flooding of the capped adit of the Wheal Jane mine in 1992 (Neal, 2005) which is located at upstream of the research site. The flood carried pollutants into the Falmouth estuary and forced authorities to take action. A passive water treatment facility was built in upstream of research site to reduce contaminants off-site migration.

The research area used to contain a number of settlement ponds (Figure 3) for Wheal Jane mine and accumulated mine waste since 1600's when mining activities started here (Burt, 1987; Camm, 1981). Therefore, the substrate composition is very similar to the mineral composition as in Wheal Jane processed ores. Wheal Jane mine was operational till 1991 and all mine spoils were dumped in the valley (Moon et al., 1995). Since then the site has been left largely untouched. It is an advantage for ecological research that the site was left unattended for such a long period of time. The duration is long enough to demonstrate divergent natural rehabilitation patterns when this research started in January 2013.

The Carnon Valley possesses a high variety of succession phases. Both autogenic succession (plants occupying emerged land from mine tailings) and allogenic succession, (gradual plants changes due to habitat change) can be found on site. This makes it possible to gather spatial data as an alternative for time series data to understand the vegetation community succession on a post-mining site.

Figure 3: Settlement ponds in Middle valley (Camm, 1981).

Like other areas of Cornwall, the mineralisation in Wheal Jane Mine also associates with a granite batholiths intrusion. The intrusion gives rise to local country rocks and has outcrops in some area in Cornwall and Devon (Dines, 1956). These country rocks known locally as killas and are composed of sandstones, shales, mudstones and conglomerates mostly. Killas are intruded by quartz-feldspar and porphyry dykes. Wheal Jane mine was developed within folded and faulted slates of Devonian age which are altered by epithermal to hydrothermal mineralisation process (Dineley, 1992; Herrington, 2011). When water follows faults down towards mantle, it will be heated up under high pressure. Minerals including sulphates and oxides are dissolved under high pressure and temperature. Hot solutions displaced by downwards cold water carry dissolved minerals upwards. On its way to the surface, the solution cools down. Depending on solubility, gravity, and critical solution temperatures, minerals are deposited in order of specific gravity.

The local mineralisation process is complex and experienced several rounds of hydrothermal deposition. In the Wheal Jane area several deposition processes overlap with each other. The deposited coarse quartz and cassiterite are remobilised under mechanical stresses and minerals are present in fine-grained form (Herrington, 2011). This also affects the mineral processing on site: extracted ores were ground into fine particles before separation through flotation. Therefore, the grain size in Carnon valley is very fine and prone to compaction. The compacted tailings are seasonally waterlogged and baked to form a hard pan.

The substrate accumulated over a long period of time in settlement ponds is compacted and stable. The high physical stability reduces dust dispersion and implies a highly compacted ground. Highly compacted soil makes it less easy for plant seeds to become resident and develop roots.

A survey of this area carried out by Geotechnics (1995) found that the depth of the dump is more than 5 metres and contains about 1.3 Mt tailings and waste rocks. Ever since, the vegetation coverage has increased steadily and shown different distribution pattern across the site.

The area borders are defined by road A39 and Grenna Lane. Coordinates of the south and north extents of the valley are 50°12’45.1141’’ north, 5°05’50.4556’’ west and 50°13’32.3359’’ north, 5°06’28.7613’’ west. It consists of two sections separated by the Old Carnon Hill road. We denote the southern section the Lower valley and the northern section the Middle valley (Figure 4). Different vegetation communities are developing in these two parts despite the common origin, and hence common mineralogy, of the surface materials found in the valley. Identifying the decisive factors for natural rehabilitation is important because this supports decision-making in target-oriented rehabilitation projects.

Figure 4 is an aerial view of the valley showing land defined by blue line as the Middle valley while land bounded by the orange line defines the Lower valley. To the north of the research site, adjacent to village Bissoe, is a water treatment facility constructed to process water from Wheal Jane mine. The valley is surrounded by private gardens and farmland. These are the main seedbanks for natural recolonisation.

Figure 4: Carnon Valley and its surrounding environment (orange circle is Lower valley and blue circle is Middle valley).

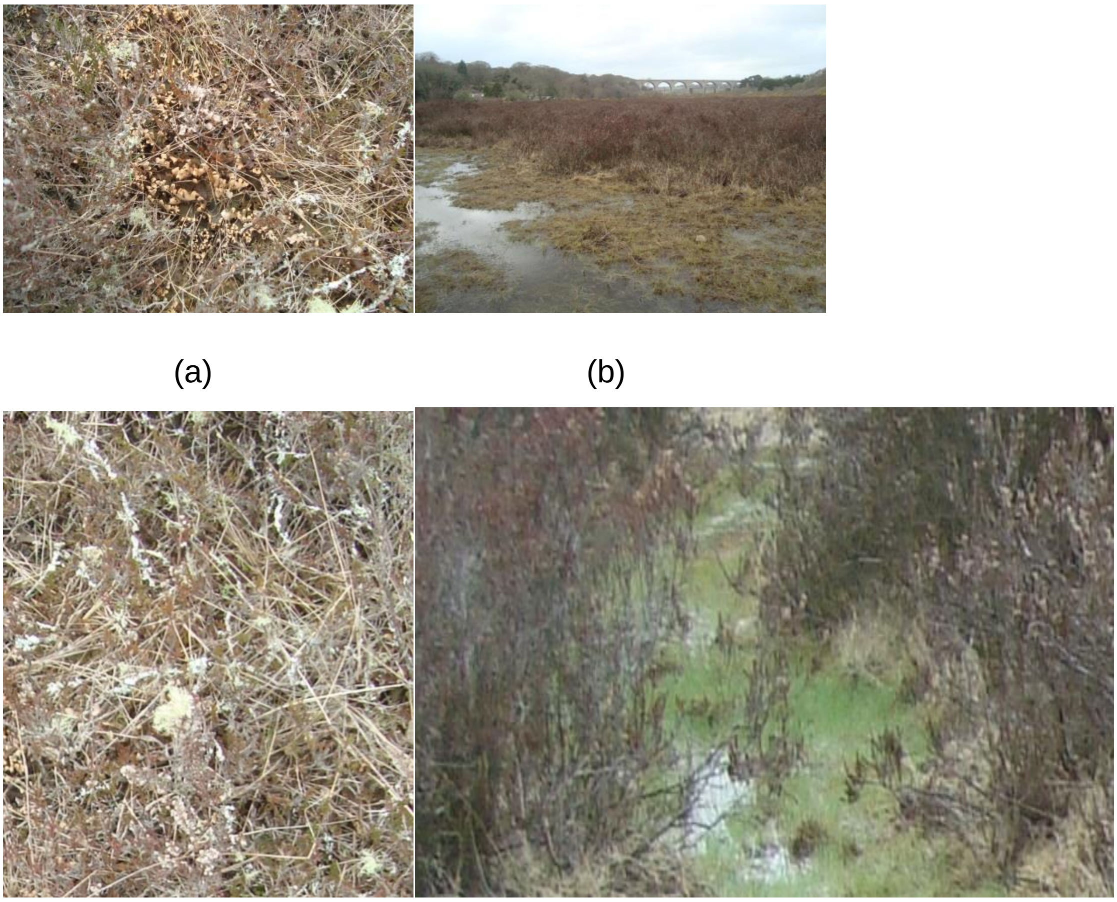
3.3.1 Microtopography and vegetation

Distinguishing features in middle and Lower valley include the contrast of land surface arrangement and vegetation coverage. Powlesland (2013) conducted a land survey of lower and Middle valley to illustrate the variation of local micro-topography in his dissertation. He used both Leica 1200 series Total Station and a differential GPS rover to measure land surface (Powlesland, 2013). GPS rover has been employed for quick measurement of mass flat area and total station was used to measure area with wavy surface. Both techniques rely on electromagnetic signal transmission. Therefore, the measurement can only achieve high accuracy when there are no barriers, such as vegetation, blocking or weakening signals. Unfortunately, dense gorse and mixed woodland in the research site make it is impossible to obtain accurate micro-topography data in some places. The acquired data was used in this research after further processing with Global Mapper 15 to produce a cross-sectional graph in which the result of the transect vegetation survey will be presented (chapter 5).

Being an artificial landscape, the topography in the Lower valley is more irregular than a natural landscape and this also applies to the vegetation community. Seasonal ponds, marsh, woodlands, heathland, ditches can all be found within the area spanning 7 hectares. In contrast to the Middle valley, where slopes are less than 5°, Lower valley slopes can be as steep as 25°.

Figure 5: Bird's eye view of Middle valley, showing ridges and furrows (taken by unmanned aerial vehicle in August 2013).

In the Middle valley, the land has been flattened and ploughed (Figure 5). A ridge and groove structure has been created on the surface. Furrows submerge under water, or are saturated with water, in winter while ridges rise above water surface most of the time (Figure 6 b and d). Common heather (*Calluna vulgaris*) dominant the ridges and red fescue (*Festuca rubra*) cover most of the grooves (Figure 6 d). Mosses and lichens also find their niche either on ground or on heather (Figure 6 a and c).



(a) (b)

(c) (d)

Figure 6: Picture of Middle valley vegetation. (a) lichen and *Festuca rubra* dominant in groove; (b) (c) lichen on *Calluna vulgaris* stem; (d) *Calluna vulgaris* on a ridge and *Festuca rubra* in a groove.

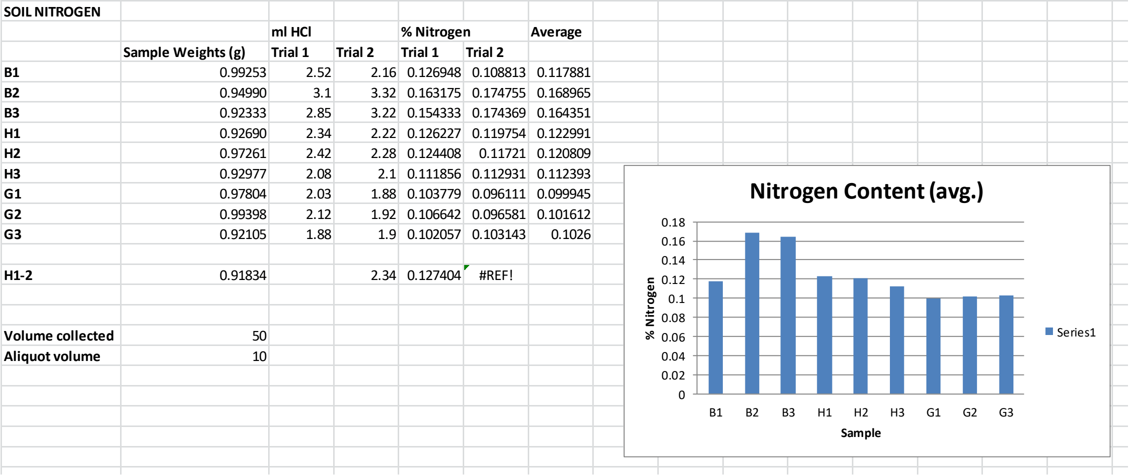
The uniform heather coverage in Middle valley demonstrates that self-sustained heathland can be established under natural process. Establishment of heathland proves the ecological value of a mine site and draws attention to alternative rehabilitation options.

In the southern section of the Middle valley, which has a low biodiversity index (BDI), *Calluna vulgaris* is one of the few species which can survive and tolerate the harsh environment. Moss extends over the ground like a blanket in some areas, preventing seeds from reaching and germinating in the ground. Further north in the Middle valley, there is a transition zone before common Gorse (*Ulex europaeus*) becomes the dominant species. Willow, birch, *Quercus robur*, heather, gorse and other few shrubs and grass species were identified in transition zone. Species richness in the transition zone is higher than in the heather- and gorse-dominated sections of the Middle valley.

At the west edge of the Middle valley, along the heather and gorse zone, some tree seedlings and herbaceous plants grow sparsely along a shallow ditch. The ditch accumulates water from the valley. Along the east edge of the valley, a gutter separates the tailings dump from country road. This gutter drain rainwater from the road and is about five time wider than the ditch along the west edge. There appears to be higher biomass production by trees grow along the gutter.

A study conducted on kaolin waste heaps 20 miles away from the research site found that common gorse can accumulate 700 kg of nitrogen per hectare in 10 years and *Rhododendron ponticum* and native woodland have replaced *Ulex europaeus* quickly (Dancer et al., 1977). This amount of nitrogen is considered to be the threshold level for establishment of woody species (Dancer et al.,1977) . Another pioneering species, *Calluna vulgaris*, is a species more tolerant to acidity, drought and erosion and could colonise more exposed places. At least 50 years will be required for *Calluna vulgaris* to accumulate the amount of nitrogen enough for other plants to survive (Dancer et al., 1977) . This data did not take background deposition into consideration. According to “Air pollution information system (www.apis.ac.uk)”, from 2010 to 2012, 21.28 kg of nitrogen settled down in Carnon Valley per hectare per year. If we assume that nitrogen deposition in this region remained constant since 1991, when dumping of tailings stopped, then the overall amount of nitrogen come from atmosphere is about 446 kg per hectare by the year 2013. A satellite map from Google Earth shows common gorse has established itself since 2001. This means that nitrogen levels in the common gorse-dominated area should be well above the threshold for woody species succession. However, in the Carnon Valley, the low nitrogen concentration in the substrate of research site (Table 2) indicates the nitrogen fixation activity by *Ulex europaeus* is minimal (Brenner, 2010), probably because of the biotoxicity, which limits nitrogen fixation through bacterial activity.

Table 2: Nitrogen content in common gorse dominated soil (Brenner, 2010).



SOIL NITROGEN						
		ml HCl		% Nitrogen		Average
	Sample Weights (g)	Trial 1	Trial 2	Trial 1	Trial 2	
B1	0.99253	2.52	2.16	0.126948	0.108813	0.117881
B2	0.94990	3.1	3.32	0.163175	0.174755	0.168965
B3	0.92333	2.85	3.22	0.154333	0.174369	0.164351
H1	0.92690	2.34	2.22	0.126227	0.119754	0.122991
H2	0.97261	2.42	2.28	0.124408	0.11721	0.120809
H3	0.92977	2.08	2.1	0.111856	0.112931	0.112393
G1	0.97804	2.03	1.88	0.103779	0.096111	0.099945
G2	0.99398	2.12	1.92	0.106642	0.096581	0.101612
G3	0.92105	1.88	1.9	0.102057	0.103143	0.1026
H1-2	0.91834		2.34	0.127404	#REF!	
Volume collected	50					
Aliquot volume	10					

3.3.2 Temperature

Climatic conditions, including temperature and precipitation, are determined by the geographical location of the site, expressed in geographical coordinates, elevation, etc.. The spread of life is to a greater extent determined by its ability to adapt to the local climate. Physiological functions of organisms can only work within a certain temperature range. The temperature on Earth is determined by the exposure to radiation from the sun, which decreases from equator towards the earth's poles. Hence, the range of temperature variation is influenced by geographical location which is characterised by altitude, latitude, topography and other factors. In general, species richness also drops in the same direction.

Soil temperature depends upon the atmospheric temperature. When the ambient temperature is high, the soil will be warmed up and vice versa. It is also affected by the presence of vegetation coverage, water content, exposure to wind, soil texture and soil depth (Keen and Russell, 1921; Lehnert, 2014). Temperature, which varies throughout the day, the seasons, and also across the year, enables atmospheric circulation and precipitation. These play an important role in shaping seasonal landscapes. The organic decomposition speed in soil is decided by soil temperature because microorganisms can grow and be active only within certain temperature range. Accelerated decomposition can release nutrients from minerals and organic compounds into bio-available forms, and microbial activity is negligible at temperatures below 5°C (Wood, 1989).

Soil temperature also has profound impacts on plant development. While seed germination depends on soil temperature, it is common practice to measure soil temperature before sowing. Most plants can germinate when soil temperatures are steady around 10˚C while only a few can establish at lower temperatures (Bierhuisen, 1974). According to the monthly record of water temperature in Carnon Valley in the last five years (Environment Agency), the surface water temperature varies between 9 and 18 ºC, around or above the temperature required for plant germination. Assuming that the surface soil has a similar temperature as the surface water, seed germination can take place throughout the year.

3.3.3 Precipitation

The Environmental Agency runs a gauge station upstream of the study site which records water levels in the Carnon river as well as precipitation. Over a period of six years (up to and including the period of study), data shows that on 60% of the days rainfall is at least 1 mm, on 36% of the days rainfall exceeds 10mm, and on 18% of the days more than 50mm precipitation is observed. This data is, however, not meaningful without considering the context as the significance of precipitation varies with the time of the year.

The local rate of evaporation is considerable. During the dormancy season, when daytime is shorter than night (September-March), the monthly evaporation rate is 30.89 mm. From 2008 to 2014, 61.58% of the days have precipitation less or equal to the evaporation rate in dormancy season (Met office communication). During the growing season (April-August), the monthly average evaporation rate is 79.41 mm and, from 2008 to 2014, 71.33% of the days have precipitation less or equal to the average evaporation rate (Cornwall Met office). Rainfall should be equal or greater than the evaporation rate to become meaningful for vegetation. Therefore, most of the time plants have to rely on deep roots to reach water unless they are close to other sources of water such as ponds. Analysis of the impact of precipitation and water temperature on water quality can be found in Appendix E.

4 Methodology

4.1 introduction

This chapter describes a research methodology which was developed on the basis of a set of clearly-defined objectives and understanding of the local context.

4.2 Vegetation survey

This research aims to develop knowledge about natural rehabilitation of a mine site. A surveying strategy was developed to characterize vegetation diversity, species richness and spatial distribution of vegetation community. As part of this study, specific transects and quadrats on the site were repeatedly surveyed from April 2013 to October 2013. Directed quadrat surveys provide data relating to spatial variation of vegetation patterns while directed transect surveys provide data which indicates variation of species density as a function of microtopography. While transects and quadrats provide complementary information, both surveying approaches are of interest.

Directed sampling relies on expert judgement and involves a degree of subjective decision-making. Establishing the location of quadrats and the orientation of transects traversing the site requires knowledge about the study site and phytotaxonomy. Bird’s eye view pictures of the site were taken from an Unmanned Aerial Vehicle (UAV) and used to aid the selection of quadrats and transects.

4.2.1 Quadrat survey

In this study, quadrats with fixed dimensions of 1 m x 1 m were surveyed. In the field, quadrats were always set with frames which were positioned in accordance with local vegetation variation identified during reconnaissance of the site (Figure 7 and 8). In the absence of historical vegetation data about the site, a chronological study of vegetation succession could not be carried out. However, mosaic habitat patterns were deemed to represent different stages of primary succession include herbaceous land, shrub land, woodland, etc. present on site. Therefore, preferential vegetation sampling provided data to describe the succession of vegetation under different levels of environmental stress. Altogether 57 quadrats were investigated. Of these, 32 were in the Lower valley and the remaining 25 were in the Middle valley. The number of quadrats was determined by the number of habitats with high biodiversity or containing species of interest, as identified during reconnaissance of the site. A certain redundancy, i.e. duplication of habitat in quadrats, was tolerated in order to obtain a more or less uniform coverage of the site.

Vegetation survey and soil sampling were carried out separately to reduce the duration of each round of the vegetation survey; the site was revisited every seven days from April to September. Maintaining this cycle is important for vegetation surveys because blooming, the most significant features of plants, may only last a few days.

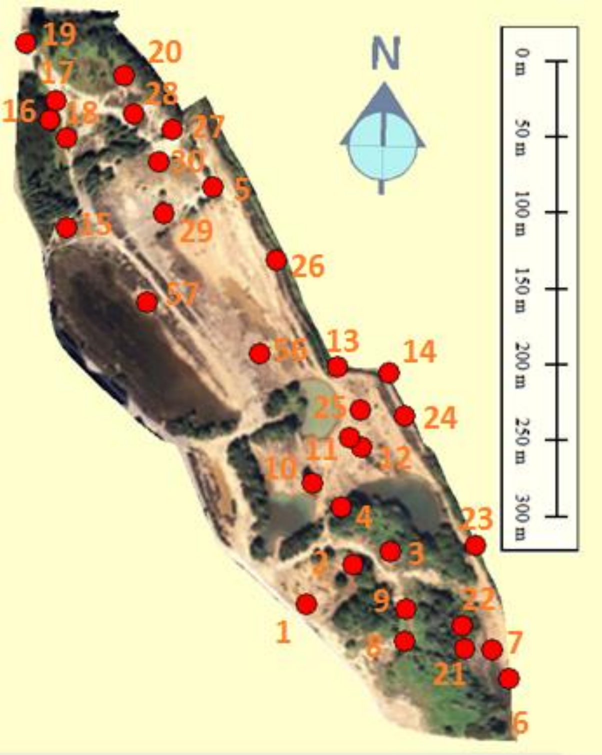


Figure 7: Location of investigated quadrats in the Lower valley.

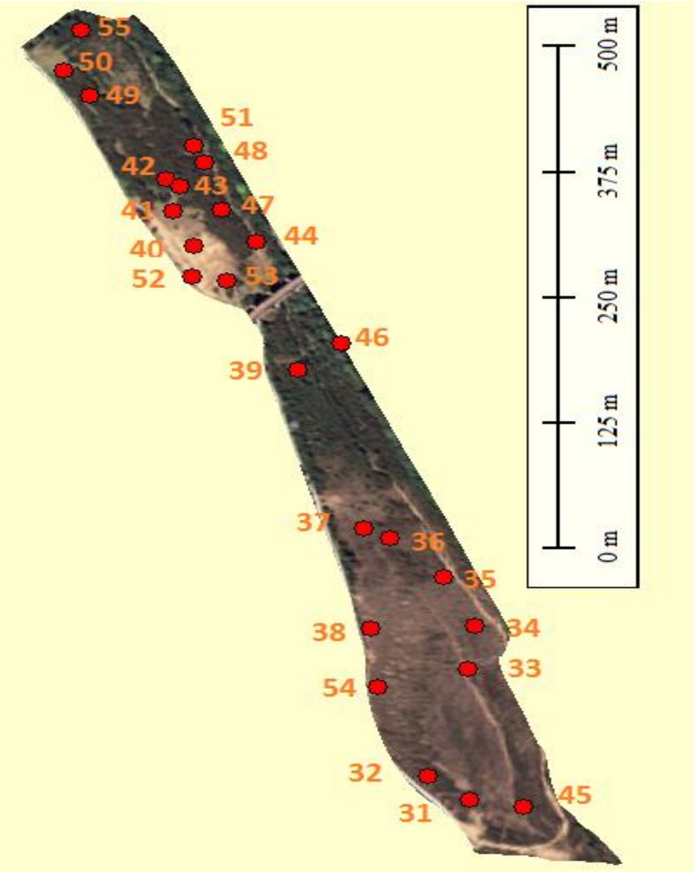


Figure 8: Location of investigated quadrats in the Middle valley.

4.2.2 Transect survey

During reconnaissance of the site, ten transects were chosen to cover strips of land which show variable topography. For each transect, a width of 3 metres was maintained. When a plant had at least half its biomass within a transect, it would be recorded. Since local vegetation communities were highly heterogeneous, the sub-division or sub-habitat concept was introduced in the transect survey. When surveying along a transect, the species composition was compared along one meter intervals and, if species variation was larger than 20% or the structural variation accounts for 20% land coverage or more, a new sub-habitat was defined.

The transect survey was carried out from April to October 2013. The location of the transects is given in Figure 9 and Figure 10. Five transects were chosen in the Lower and Middle valley which passed the most representative sub-habitat of the site. Transects started from the fence erected by the Environmental Agency at the western side to the gutter at the eastern side of the valley.

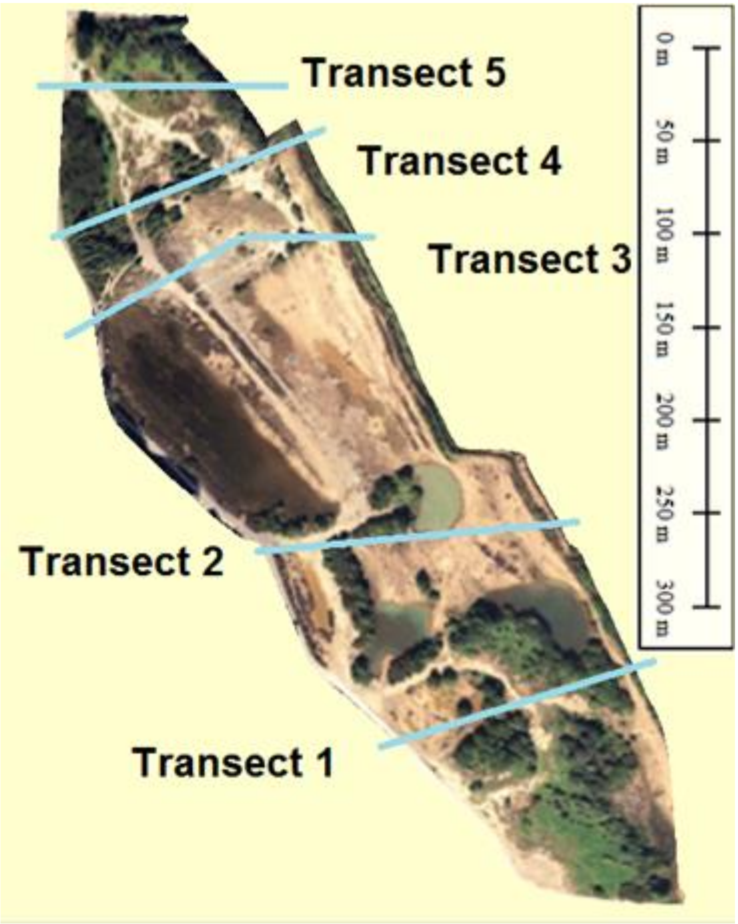


Figure 9: Transects in Lower valley.

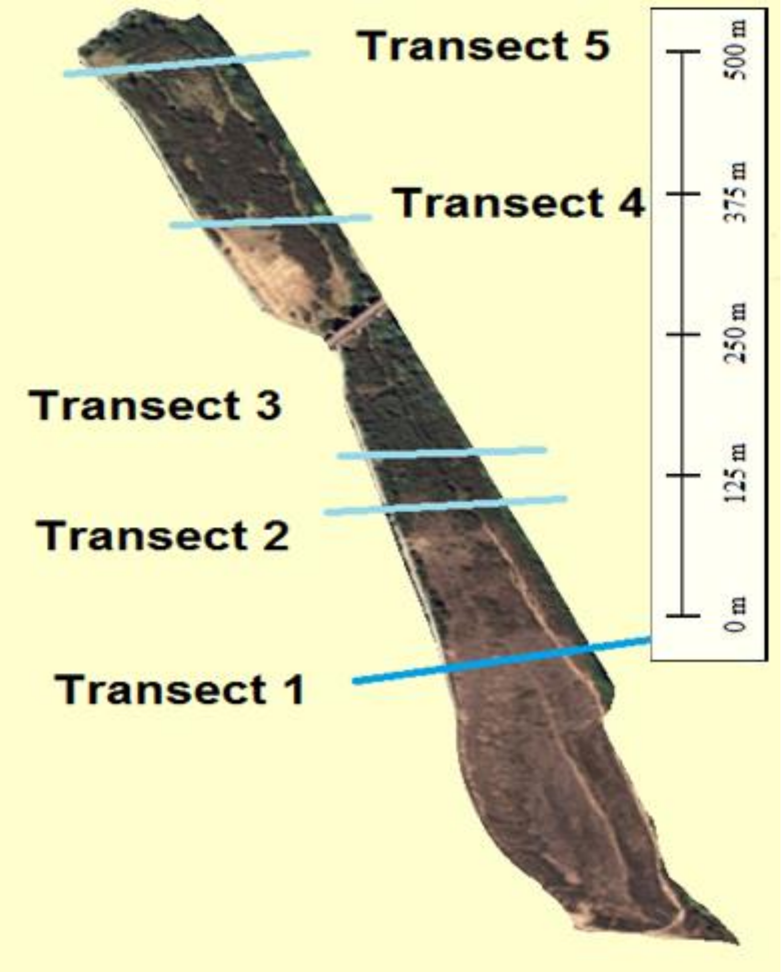


Figure 10: Transects in Middle valley.

An additional aim of the transect survey was to evaluate the existence of an edge effect triggered by variation in microtopography. Since transects pass through the most representative sections of the site, they could be used for comparative study of vegetation communities between edges and the core of different landforms.

4.3 Soil sampling

Soil samples were collected with a screw auger from all quadrats where the vegetation survey was carried out. It should be noted that barren land was considered to be a type of habitat but it was not sampled proportionally in the vegetation survey. Most of the barren land contained seasonal ponds which made soil sampling difficult. Barren land was subject to spare sampling since it would not add value to the research in terms of understanding vegetation-soil correlations.

Sampling and analysis focussed on the fraction of soil with particles smaller than 2 mm. Soil samples were analysed in the laboratory, with some tests requiring preparation of the material (e.g. drying and screening). The soil was sampled to a depth of 20 cm below the surface. This sampling depth was considered to be the most relevant for grass, shrubs and tree seedlings development.

In each quadrat, two layers of soil were sampled: a surface soil sample from the upper 10 cm, and a sub-surface soil sample, 10 to 20 cm deep. Soil samples from these layers were collected separately. At least four subsamples were taken to obtain a soil sample which is representative for a layer, i.e. at a given depth, in a quadrat. Before collecting a sample of the upper 10 cm of soil, plant litter was removed. Soils samples collected from the same quadrat were placed in a sealable PolyEthylene (PE) bag.

Testing of both surface soil and sub-surface soil layers was performed to study the effect of depth on ecology. While surface soil is important for seed germination and early root development, characterizing the condition of surface soil fostered understanding of all vegetation establishment, especially of herbaceous species. Characterization of subsurface soil, on the other hand, informed knowledge about the development of bush, shrubs, and trees. Comparison of data obtained from surface and subsurface soil samples provided insight into the direction of salt and ion movement. Because subsurface soil had been less exposed to air and other interferences, the impact of exterior influences on the surface soil could be discerned. In addition, correlating surface and sub-surface soil features with the vegetation community showed the influence of soil attributes on plant development.

With two representative soil samples from each of the 57 quadrats, altogether 114 samples were collected during the quadrat survey.

4.4 Soil: physical characterization

4.4.1 Soil compaction

Soil compaction was tested on site with a cone penetrator produced by Leonard Farnell. While the cone penetrator was neverbeen calibrated since purchase, it was used to qualitatively assess the relative value of soil compaction. The unit used to express soil strength is kPa and commonly denoted a Cone Index. In each of the chosen 57 quadrats, soil strength was tested at least three points in the top 20 cm of soil. For each test, five readings were recorded and averaged to produce a point value for soil compaction of each point. The average value of all compaction values at points within a quadrat was designated as the quadrat soil compaction value. It should be noted that, where soil was covered by plant litter, litter was always removed before conducting a test.

Soil compaction was heavily affected by moisture. To avoid the influence of moisture variation, soil compaction was measured within a period of three days when no precipitation was recorded (October 2013).

4.4.2 Soil particle size distribution

The soil particle size analysis was carried out with a Malvern Mastersizer which analyses laser diffraction scattering caused by suspended particles to measure the particle size distribution. This method produced quick results. Soil samples were oven-dried for 48 hours at 120 ˚C and analysed following CSM laboratory guidelines (CSM2317 Lab session 2b: sub-sieve sizing techniques):

1) Using a Jones riffle splitter, the sample size was reduced to 2.5 g of soil.

2) The material was placed in a 250 ml beaker and de-ionised water was added to the 200 ml gradation. Using an impellor, the sample was agitated within the beaker for one minute to ensure the solution was thoroughly mixed.

3) The pump arm was placed in the beaker and a solution was passed to the Malvern measurement unit.

4) Three replicate mesurements were made for each quadrat.

5) The equipment was flushed with deionised water between each measurement.

6) The process was repeated for a sample from each quadrat.

The equipment was maintained by technician from the producer to meet Whitehouse Scientific quality audit standards, which was based on measuring glass micron beads ranging in size between 15 – 150 μm. Three replicates were used for quality control. The result was processed by Malvern software to produce data displayed in a particle size distribution graph.

4.5 Soil chemical characterization

4.5.1 Electrical conductivity

Electrical conductivity is an indicator of available salt in soil solution. It has often been used to assess available nutrients in soil, including minerals and all nutrients demanded by plants (Radojevic, 1999). The analysis procedure here followed the Royal Society of Chemistry method (Radojevic, 1999).

While in situ measurements required that soil is moderately moist, an ex situ method was applied in this study. Soil samples were collected following the same procedure as in section 4.3. Both surface soil (0-10 cm) and substrate soil (10-20 cm) were analysed for electrical conductivity. This gave an indication of the profile affecting the rhizosphere of grasses and shrubs and the chance that seedlings of woody species could establish themselves.

A Jenway conductivity meter 4310 was used for measuring the electrical conductivity. Prior to measurement, the probe was calibrated with standard ORP solution for electrical conductivity meter before test. For each quadrat, two replicates and one blank sample (deionised water) was tested. The test was carried out at 20°C in an air-conditioned room. The measurement procedure was as follows:

1. 20 g of fresh soil was weighed, and plant litters were picked out before the soil was placed into a 50 ml glass beaker.
2. 20 ml deionised water was added into the beaker and stirred thoroughly with a glass rod before being left to settle down for 20 minutes.
3. The probe was immersed in the solution until the reading was stable.
4. Removing the probe and washed it with deionised water and immerse it into a 50 ml beaker filled with deionised water (blank sample).
5. The procedure was repeated to obtain the reading in replicate.

The probe was rinsed with deionised water between readings.

4.5.2 Soil pH

Soil samples were taken with a screw auger from each quadrat between 9 and 11 o'clock in mornings from 2nd September to 8th October 2013. Surface soil (depth 0-10cm) and subsurface soil (depth 10-20 cm) were collected separately in each quadrat. To obtain a representative sample for each depth in a quadrat, at least four soil subsamples were taken and mixed thoroughly. To minimise chemical changes (e.g. due to oxidation), all samples were placed in sealable PE bags and then stored in a dark backpack. All soil collected in the morning was tested within five hours in the afternoon.

The testing method followed the procedure proposed by Radojevic (1999). Note that the Stewart (1989) method required more processing of soil such as oven drying, which might trigger changes in chemical soil properties.

A glass bulb UNICAM 9455 pH/ISE meter was used. During the test air temperature in lab was moderated by air conditioner at 25°C. As part of QA/QC, the soil pH test meter was calibrated with Thermo Scientific pH buffer solution with pH value at 4.01 +/- 0.01, 7.00 +/- 0.01 and 10.01 +/- 0.02 at 25 ˚C each time before starting a test. The solution was certified by the National Institute of Standards and Technology (NIST). Due to the high consumption of soil in this test, only two replicates and one blank sample was tested. The pH was measured with the following procedure:

1. 20 g fresh soil was weighed and plant litter was removed.
2. the soil sample was placed in a 50 ml beaker and 20 ml of deionised water was added.
3. the soil was slurrified by stirring thoroughly with a glass rod before it was left to settle for 30 minutes.
4. a glass-bulb pH meter was immersed in he slurry until a stable reading could be taken.
5. the glass bulb was removed, rinsed with deionised water and then placed into 50 ml beaker filled with deionized water (blank sample).
6. the procedure was repeated to obtain the replicate reading for the sample.

4.5.3 Portable XRF

A portable XRF was used to take field measurements of metal concentrations during reconnaissance of the research site. Although portable XRF measurements are less accurate than a laboratory XRF, the data served to make a preliminary assessment.

The Thermo Scientific-produced Niton handheld XL2 XRF analyser provides a fast analysis of the elemental composition of soil. It was employed in the spatial soil survey for investigation of 25 quadrats in Middle valley and 32 in Lower valley. For each quadrat, one sample of surface soil (0-10 cm) and one sample of sub-surface soil (10-20 cm) were measured.

Portable XRF was used to test soil sample from each quadrat three times and Canmet STSD-2 stream sediment was used as the standard material for calibration.

4.5.4 Laboratory XRF

Both semi-quantitative analysis and major element X-ray fluorescence (XRF) analysis were carried out with a Bruker S4 Pioneer. Three composite samples of Lower valley soil were placed on a polyethylene membrane and dried in an oven for 72 hours at 40 ºC. Soil was sieved at 2 mm passing to remove plant litter and gravel. The material was then ground with a mortar and pestle for 5 minutes to make it finer, typically less than 50 µm. Soil samples were pressed into soil pellets for semi-quantitative analysis or fused glass beads for major element analysis.

The semi-quantitative analysis was not feasible because different programmes for XRF analysis applied to the same soil sample revealed big differences for same elements of the same soil sample. Further calibration is necessary to obtain reliable data.

When producing fused glass beads for major element analysis, the beads were prone to breakage during cooling. Out of every four beads, only one bead survived. Therefore, no replicates were made while equipment calibration was carried by the manufacturer of the XRF device regularly. The analysis result was used as indicative data and not used to derive any conclusive result.

4.6 Soil: mineralogical characterization

4.6.1 XRD

The bulk mineralogy was determined with X-ray diffraction (XRD). A Siemens D5000 diffraction meter was used, which has a detection limit of ~5%. While it can identify minerals with a crystalline structure, amorphous materials, that lack a crystalline structure, could not be measured. Output spectra were processed using EVA software. Because the concentration of arsenic falls below the detection limit of XRD, this test was used to understand the major minerals composition.

Three composite samples from the Lower valley soil were produced according to outcome of cluster analysis (section 5.7.3) and placed on a polyethylene membrane to be dried in an oven for 72 hours at 40 ºC. The soil was then sieved at 2 mm passing to pick out plant litter and gravel. The soil was ground with a mortar and pestle for 5 minutes to make it finer, typically less than 50 µm. Around 5 g of the ground soil was placed on a plastic holder and smoothed to remove all excessive soil and avoid contaminating the equipment. For each composite sample, two replicates were prepared for quality control purposes. The equipment was maintained and regularly calibrated by a CSM lab staff and producer technician. When all three composite soil samples were ready, these were put into automatic sample holders for analysis.

The results were analysed by EVA software to identify minerals according to recorded diffraction waves.

4.6.2 SEM

JEOL JSM-5400LV Scanning Electrical Microscope (SEM) was used in this analysis. Firstly, with the same soil composite samples used for XRD analysis, three blocks were prepared with epoxy by lab technician. Around 2 g of soil from each sample was added into blocks and allowed to solidify. The blocks were polished with diamond liquid to expose soil grains for SEM analysis. Before placing the blocks into the SEM, the material was coated with carbon to improve electrical conductivity. A slice of copper foil was attached to the block surface to form a bridge with the metallic block holder. No replicates were made for SEM analysis.

The low vacuum SEM (scanning electron microscope) uses an electron beam to irradiate the sample. The SEM equipped with backscatter/secondary detector to record electrons emitted from sample and X-ray EDS detector records X-rays to enable qualitative and semi-quantitative chemical analysis. This method was employed to identify species of arsenic compounds which is indicative about arsenic weathering product and their availability for plants uptake under reductive and oxidative conditions. The equipment has been maintained by the manufacturer's technician.

4.7 Arsenic fractionation

Fractionation is a method to precisely quantify trace metal of different physiochemical forms because their environmental behaviour is determined by how they present rather than total concentration (Tack and Verloo, 2006).

Arsenic in soil was fractionated by a sequential extraction scheme in which various reagents, degrees of acidity, and washing methods were used in a series of steps. For this study, the Wenzel scheme (Wenzel, 2001) was chosen because it was specifically designed for arsenic. Other methods, such as the BCR method, were deemed to target a wider spectrum of heavy metals to the detriment of the accuracy of arsenic fractionation.

The Wenzel scheme sequentially separated soil arsenic into the following five fractions (Wenzel, 2001):

1. Non-specific sorbed
2. Specific sorbed
3. Amorphous hydrous oxide-bound
4. Crystalline hydrous oxide-bound
5. Residue.

Further details of the Wenzel scheme are given in Appendix D.

ICP-MS was used to determine the arsenic concentration of extraction solutions collected during the fractionation tests. ICP-MS was calibrated with standard arsenic solution with 0, 1.6, 8, 40, 200 and 1000 ppb arsenic respectively. Canmet STSD-2 Stream sediment had been used as a reference material. The arsenic concentration in the solution of soil total arsenic and some fractions was more than one hundred times higher than standard solution. Underestimation of the arsenic concentration when preparing standard solutions subsequently produced a large error in the first round of analyses. The requirement to re-analyse the extraction solution demonstrated the importance of estimating the approximate composition of the analyte when undertaking chemical analyses.

For each composite soil sample, five replicates were run through the Wenzel scheme test and, at the same time, two replicates of each sample were taken for Aqua Regia digestion to assess total arsenic concentration. One blank sample was employed for each procedure as quality control measure.

During the second round of analyses, the original extraction solutions were diluted 500 times while the standard solution concentration was increased to 2000 ppb. The achieved analysis result were now similar to the portable XRF result. The recovery rate of the three composite soil samples was around 87% which was comparable with the result Wenzel (2001) achieved in his experiment (88%).

4.8 Statistical analysis of data

The selection of independent variables in multivariate regression analysis was based on their potential influence on vegetation development. For example, excessive amounts of native tin could have a negative impact on plant development (Dines, 1956). However, tin was present in Carnon valley at elevated levels in the form of the mineral cassiterite, which is an insoluble oxide. Hence, tin was excluded from the statistical analysis.

Besides metal concentrations in the soil, indicators deemed relevant to plant establishment include variables such as soil acidity, soil strength, and soil electrical conductivity. These would be considered in multivariate regression analysis.

Tabachnick and Fidell (2007) stated that the sample size must be seven times larger than the number of independent variables to successfully perform statistical analysis in ecological study. This was required to compensate for the loss of information due to high level of autocorrelation. However, field surveying is a time-consuming process, which undermines the effort to expand sample size.

Therefore, robust statistical analysis may be difficult to achieve. As a result, subjective judgement based on personal experience and knowledge about research site played an important role in the study.

Multivariate linear regression was performed on the complete dataset with SPSS, a recognised statistical interpretation package. SPSS can perform stepwise regression which, in view of complex interactions between variables in living systems, is not an appropriate method (Studenmund and Cassidy, 1987). In this study, the “enter” method was used which produced a result for all input variables.

To avoid multicollinearity, correlation analysis was used to distinguish highly correlated variables from independent variables. Iron was removed from the dataset of predictor variables because of its high correlation with arsenic (correlation coefficient > 0.9).

Redundancy Analysis (RDA) was carried out with Canaco for Windows 4.5 software, a popular package for ordination analysis of ecological data (Jiangshan, 2014). Lepš and Šmilauer (2003) stated there are two main modelling methods in ordination analysis: unimodal and linear models. To find out which method should be applied, Detrended Correspondence Analysis (DCA) was applied. If the length of the first axis is greater than 4, then one should use the unimodal model and, if the length is smaller than 3, one should go for the linear model (Lepš and Šmilauer, 2003). For values between 3 and 4, one can choose either of the two (Lepš and Šmilauer, 2003). DCA analysis indicated the length of the first axis is 0.4. Therefore, linear ordination methods, rather than unimodal methods, were used in this study.

A large number of cluster analysis methods aiming to characterise the structure of a dataset have been proposed (Gan et al., 2007; Everitt et al., 2011). Two main types of clustering techniques were identified: partitional and hierarchical methods. The former family of methods was represented by K-means cluster analysis (Khalid, 2011). K-means method required the researcher to specify the number of clusters upfront (Khalid, 2011). This requirement made application of K-means cluster analysis unsuitable for exploratory studies or situations where the number of clusters could not be discerned ion advance of the clustering process. Another weakness of K-means was its inability to handle clusters of diverse size and densities and its sensitivity to outliers (Tan et al., 2005). In

Hierarchical clustering was identified as the method of choice in ecological research (James, 1990). Given limited knowledge of the interaction between environmental factors and vegetation development, hierarchical cluster analysis had the advantage of presenting similarity relationships between groups at various levels, which enabled context-informed selection of cluster structures (Wildi, 2013). Hierarchical cluster analysis was carried out in SPSS 22.

Polar ordination analysis was performed with PC-Ord 5, an ecological statistical software package. The input matrix contained the Sørensen similarity index between all sub-habitats in the lower and Middle valley. The endpoint selection method used was variance regression.

4.9 Visualization of spatial distribution of variables

Global mapper 15 software was used to produce layers with digitised survey features of the study site. This Geological Information System (GIS) software used various interpolation methods to fill gaps between grid nodes, which corresponded to the central location of surveyed quadrats. Triangulation and minimum curvature were identified as the most common interpolation methods. These two methods were compared to establish which method is the most suitable for this research.

Before the advent of modern computers, triangulation was a commonly-used method for two-dimensional interpolation of property values (Kresic, 2007). Triangulation performs exact linear interpolation between three points located close to each other. With datapoints unevenly distributed in the study site, the method was considered to be inaccurate because resulting surfaces were not smooth and had angular planes, generating unrealistic triangular facets. Interpolation with the triangulation method was also constrained by boundary data points. For creating a map covering the exact area of interest in this study, additional sample points along the physical border of the area would have been required.

The minimum curvature method was developed by Briggs (1974) and adapted by Smith and Wessel (1990). This method produces a linear elastic plate to connect data points with minimum amount of bending. Minimum curvature honoured the original data as closely as possible and generated a smooth surface. Note that gradual transitions were obtained by defining a tension constraint to avoid oscillations.

Although it was recognized that the minimum curvature method is not an exact interpolation method, it produced a plausible interpolation between sampled locations. The surfaces produced with this method were rectangular in shape. Along the edge, the method assigned the value of the nearest sampling point, avoiding the necessity to sample along the border of the study site. Note that surfaces produced with minimum curvature method were cropped according to the real border of the study site.

5.Results

5.1. Vegetation survey

Vegetation surveys, consisting of quadrat and transect investigation, provide data and insight into local species richness and biodiversity. Additional observations of on site habitat are recorded as metadata during the seven-month long field work. To fully recognise the presence of rare species, all plants are not common in Cornwall are given additional attention.

5.1.1 Quadrat survey result

The research site is long and narrow. When walking along the central axis of the valley, most parts of the area can be seen. All different habitats or areas which display distinct vegetation are investigated.

Figure 11: Mosaic distribution of vegetation assemblage in the Lower valley (Powlesland, 2013).

In the Lower valley, the vegetation community is highly diversified with a mosaic distribution (Fig 11). There is no core zone or stable vegetation community on this part of the site. This indicates a pioneer succession process; quadrat dimensions should be relatively small to capture vegetation variation. In contrast, a homogeneous vegetation coverage is observed in the heath-dominated part of the Middle valley. *Calluna vulgaris, Betula pubescens* and *Salix atrocinerea* are the dominant species. In the dense, thorny gorse-dominated part of the Middle valley, a vegetation survey is difficult to carry out. While it appears that almost no plants can grow under dense gorse shrubs, species richness and abundance are estimated based on observation from a distance.

Table 3 lists the Simpson biodiversity index and species richness for each of the quadrate in the lower and Middle valley respectively. Note that quadrats need to contain at least 2 species when calculating the Simpson biodiversity index. Where this not the case, the Simpson biodiversity index is set to zero. This is relatively rare occurrence in a healthy ecosystem, but common in mine sites which are experiencing early stage rehabilitation.

Table 3: Vegetation surveys in lower and Middle valley quadrats

Lower valley			Middle valley		
Quadrat No.	Biodiversity index	Species richness	Quadrat No.	Biodiversity index	Species richness
1	0.591	5	33	0	1
2	0.552	4	34	0.342	2
3	0.823	12	35	0	1
4	0.421	6	36	0.609	6
5	0.763	9	37	0.591	4
6	0.858	14	38	0.698	6
7	0.032	3	39	0.704	7
8	0.831	10	40	0.462	3
9	0.801	13	41	0.867	4
10	0.801	8	42	0	1
11	0	0	43	0.59	6
12	0.279	4	44	0.677	8
13	0.734	7	45	0.54	2
14	0.778	7	46	0.295	7
15	0.638	4	47	0	1

16	0.79	15	48	0.581	4
17	0.818	19	49	0.572	3
18	0.928	7	50	0.344	4
19	0.821	13	51	0.686	6
20	0.684	11	52	0.615	8
21	0.816	10	53	0	0
22	0.836	10	54	0	1
23	0.758	6	55	0.639	4
24	0.592	6	56	0.335	2
25	0	1	57	0.756	6
26	0.218	4			
27	0.764	8			
28	0.813	10			
29	0.686	7			
30	0.669	9			
31	0.242	2			
32	0.516	2			

The spatial distribution of vegetation expresses the extent of natural rehabilitation which generally reflects resource availability. Data for the lower and Middle valleys in Table 3 confirms that the species richness is much higher in the Lower valley. This suggests that resources in the Lower valley are better matched to encourage biodiversity development.

5.1.2 Transect survey

Table 4 shows the number of species which were counted in transects passing through the Lower valley. Each transect is subdivided into sub-habitats, whose starting point is recorded when a significant change of at least 20 % in species composition is observed along the transect. All species are listed by their scientific name.

Table 4: Analysis of transects across the Lower valley

Sub-habitat number	**Length of sub-habitat (m)**	**Number of species**	**Species**
Transect 1: 50°12'52.013"N 5°5'57.735"W			
1.1	**27.9**	**8**	***Betula pubescens, Buddleja davidii, Calluna vulgaris, Cirsium arvense, Salix atrocinerea, Holcus lanatus, Myosotis arvensis, Festuca rubra***
1.2	**6.2**	**5**	***Salix atrocinerea, Festuca rubra, Agrostis tenuis, Betula pubescens, Calluna vulgaris***
1.3	**8.2**	**2**	***Scirpus setaceus, Festuca rubra***
1.4	**15.8**	**7**	***Salix atrocinerea, Betula pubescens, Rudus fruticosus, Ulex europaeus, Alnus glutinosa, Potentilla anserine, Cirsium arvense***
1.5	**8.01**	**2**	***Festuca rubra, Agrostis tenuis***
1.6	**7.4**	**9**	***Calluna vulgaris, Salix atrocinerea, Cirsium arvense, Rudus fruticosus, Anagallis tenella, Holcus lanatus, Anagallis arvensis, Stachys arvensis, Dipsacus fullonum***

1.7	**52.5**	**19**	***Salix aurita, Ulex europaeus, Salix atrocinerea, Rumex obtusifolius, Rudus fruticosus, Cirsium arvense, Urtica dioica, trifolium campestre, Primula Vulgaris, Acer pseudoplatanus, sorbus latifolia, Lythrum salicaria, Lotus Hispidus, Agrostis Tenuis, Potentilla anserine, Potentilla erecta, Equisetum arvense, Vicia cracca, Scirpus setaceus***
Transect 2 50°12'55.563''N 5°6'03.663''W--50°12'57.912''N 5°5'59.374''W			
2.1	**3.89**	**3**	***Betula pubescens, Ulex europaeus, Calluna vulgaris***
2.2	**8.96**	**11**	***Hedera helix, Dryopteris filix-mas, Athyrium filix-femina, Pteridium aquilinum, Hyacinthoides non-scripta, Rosa Canina, Lonicera peridlmenum, Quercus robur, Rudus fruticosus, Lotus corniculatus, Scirpus setaceus***
2.3	**10.76**	**8**	***Ulex europaeus, Buddleja davidii, Festuca rubra, Dryopteris filix-mas, Calluna vulgaris, Betula pubescens, Rudus fruticosus, Asplenium scolopendrium***
2.4	**13.79**	**6**	***Salix atrocinerea, Ulex europaeus, Betula pubescens, Potentilla anserina, Cirsium arvense, Scirpus setaceus***
2.5	**33.01**	**4**	***Festuca rubra, Calluna vulgaris, Veronica chamaedrys, Rumex acetosella***
2.6	**13.79**	**2**	***Carex pendula, Quercus robur***

2.7	**16.97**	**10**	***Betula pubescens, Buddleja davidii, Athyrium filix-femina, Dryopteris dilatata, Polystichum setiferum, Urtica dioica, Rumex obtusifolius, Circaea lutetiana, Hypericum calycinum, Narcissus ssp.***
2.8	**15.92**	**3**	***Calluna vulgaris, Festuca rubra, Agrostis tenuis***
2.9	**13.2**	**1**	***Calluna vulgaris***
2.10	**23.11**	**2**	***Quercus robur, Athyrium filix-femina***
Transect 3 50°12'57.602"N 5°6'4.905"W			
3.1	**4.38**	**15**	***Quercus robur, Holcus lanatus, Betula pubescens, Acer pseudoplatanus, Salix atrocinerea, Rudus fruticosus, Ulex europaeus, Calluna vulgaris, Vinca major, Teucrium scorodonia, Athyrium filix-femina, Ilex aquifolium, Silene dioica, Lonicera periclymenum, Rubus fruticosus***
3.2	**39.15**	**11**	***Festuca rubra, Salix atrocinerea, Rumex acetosa, Epilobium lanceolatum, Mercurialis perennis, Myosotis scorpioides, Lactuca virosa, Athyrium filix-femina, Rumex acetosella, Holcus lanatus, Rubus fruticosus***
3.3	**20.18**	**3**	***Holcus lanatus, Calluna vulgaris, Epilobium lanceolatum***
3.4	**18.97**	**5**	***Lotus corniculatus, Calluna vulgaris, Rubus fruticosus, Buddleja davidii, Myosotis scorpioides***

3.5	**37.57**	**6**	***Festuca rubra, Holcus lanatus, Calluna vulgaris, Rubus fruticosus, Urtica dioica, Lotus corniculatus***
3.6	**6.69**	**4**	***Calluna vulgaris, Ulex europaeus, Rubus fruticosus, Holcus lanatus,***
3.7	**10.09**	**8**	***Athyrium filixfemina, Rumex acetosella, Rubus fruticosus, Holcus lanatus, Ulex europaeus, Calluna, Scirpus setaceus, Dipsacus fullonum***
3.8	**10.46**	**14**	***Teucrium scorodonia, Athyrium filixfemina, Ilex aquifolium, Calluna vulgaris, Betula pubescens, Silene dioica, Rubus fruticosus, Lonicera periclymenum, Quercus robur, Hedera helix, Ulex europaeus, Salix atrocinerea, Lamium album, Holcus lanatus***
3.9	**8.63**	**2**	***Typha angustifolia, Lemna minor***
Transect 4 50°13'01.259"N 5°06'08.625"W			
4.1	**4.65**	**2**	***Calluna vulgaris, Scirpus setaceus***
4.2	**9.64**	**6**	***Betula pubescens, Calluna vulgaris, rhododendron, Salix atrocinerea, Scirpus setaceus, Ulex europaeus***
4.3	**33.76**	**4**	***Calluna vulgaris, Betula pubescens, Buddleja davidii, Rhododendron***
4.4	**5.15**	**1**	***Festuca rubra***
4.5	**9.11**	**5**	***Calluna vulgaris, Betula pubescens, rhododendron, Buddleja davidii, Senecio jacobaea***

4.6	**22.13**	**7**	***Betula pubescens, Calluna vulgaris, Rhododendron, Scirpus setaceus, Cortaderia selloana, Salix atrocinerea, Buddleja davidii***
4.7	**21.7**	**11**	***Calluna vulgaris, Betula pubescens, Buddleja davidii, Festuca rubra, Scirpus setaceus, Veronica serpyllifolia, Salix atrocinerea, Centaurium pulchellum, Bellis perennis, Arenaria serpyllifolia, Agrostis curtisii***
4.8	**21.99**	**7**	***Buddleja davidii, Betula pubescens, Scirpus setaceus, Calluna vulgaris, Cirsium arvense, Quercus robur, Holcus lanatus***
4.9	**5.29**	**6**	***Festuca rubra, Calluna vulgaris, Holcus lanatus, Myosotis arvensis, Centaurium pulchellum, Plantago coronopus***
4.10	**5.13**	**7**	***Betula pubescens, Calluna vulgaris, Festuca rubra, Buddleja davidii, Agrostis tenuis, Holcus lanatus, Agrostis setacea***
4.11	**14.32**	**8**	***Calluna vulgaris, Festuca rubra, Buddleja davidii, Betula pubescens, Holcus lanatus, Veronica chamaedrys, Polygonum aviculare, Silene dioica***
4.12	**5.87**	**12**	***Salix atrocinerea, Buddleja davidii, Asplenium scolopendrium, Rudus fruticosus, Betula pubescens, Scirpus setaceus, Urtica dioica, Holcus lanatus, Typha angustifolia, Hypericum calycinum, Athyrium filix-femina, Salix alba***
Transect 5 50°13'05.877''N 5°06'11.550''W			

5.1	**15.58**	**11**	***Ulex europaeus, Alnus glutinosa, Rhododendron, Cirsium arvense, Rudus fruticosus, Buddleja davidii, Athyrium filixfemina, Acer pseudoplatanus, Silene dioica, Primula vulgaris***
5.2	**11.82**	**12**	***Holcus lanatus, Agrostis tenuis, Agrostis setacea, Cirsium arvense, Betula pubescens, Calluna vulgaris, Scirpus setaceus, Rumex acetosella, Primula vulgaris, Lotus corniculatus, Carex arenaria, Epilobium palustre***
5.3	**14.28**	**10**	***Festuca rubra, Calluna vulgaris, Centaurium pulchellum, Senecio jacobaea, Rumex obtusifolius, Medicago sativa, Plantago coronopus, Reseda luteola, Epilobium palustre, Centaurium pulchellum***
5.4	**9.49**	**7**	***Ranunculus repens, Cirsium arvense, Urtica dioica, Salix atrocinerea, Salix aurita, Buddleja davidii, Rudus fruticosus***
5.5	**15.18**	**15**	***Calluna vulgaris, Agrostis tenuis, Agrostis setacea, Potentilla erecta (perennial), Holcus lanatus, Viola riviniana (perennial), Hypericum calycinum, Glechoma hederacea, Rumex acetosella (perennial), Centaurium pulchellum, Cerastium glomeratum, Cerastium semidecandrum, Arenaria serpyllifolia, Euphrasia nemorosa, Viola riviniana***
5.6	**20.69**	**10**	***Betula pubescens, Buddleja davidii, Salix atrocinerea, Rudus fruticosus, Cirsium arvense, Urtica dioica, Dryopteris filix-mas,***

			Hypericum calycinum, Glechoma hederacea

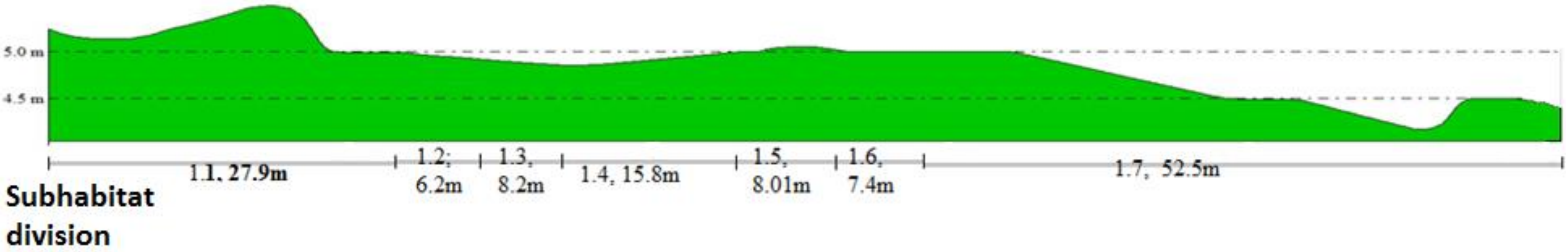
Noting the relatively high species density and large number of sub-habitats in each transect, Table 4 suggests that vegetation patterns in the Lower valley are very diverse.

Topographical variation in the Lower valley is more significant than in the Middle valley. To characterise the topography, a land survey was conducted from August to September 2013 (Powlesland, 2013). Topological data was collected by a Leica 1200 series Total Station and a differential GPS rover. All survey data is processed with AutoCAD 2010 to produce a ground surface topography map. This map is used as a Geological Information System (GIS) layer to overlay with Ordnance Survey maps of Carnon Valley downloaded from the DigiMap web site (2013). The cross-sections of five transects were captured in Global-Mapper 15 software and marked with sub-habitat.

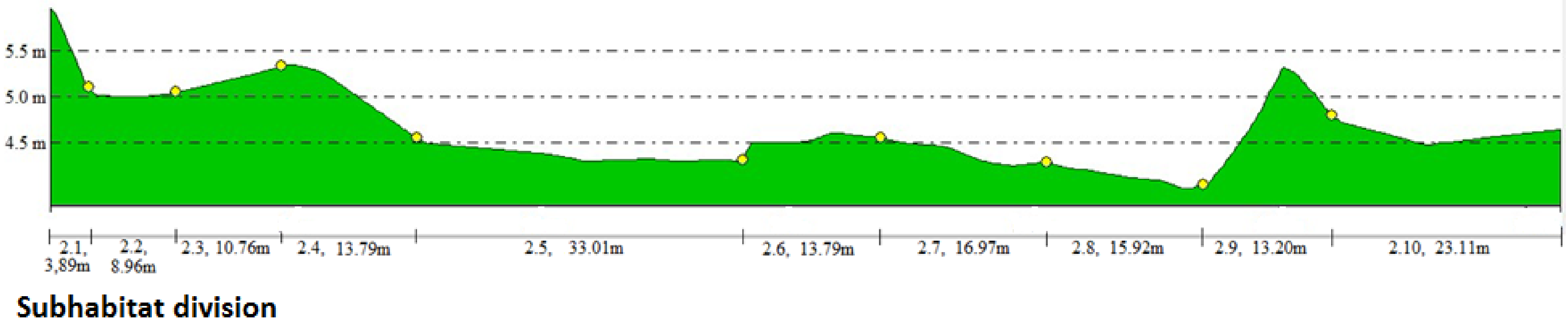
The elevation in Lower valley transects, as illustrated in Figure 12, varies by about 2 m. In contrast, differences in elevation created by ridges and furrows in the Middle valley are so small that these cannot be detected by surveying equipment. Therefore, a tape measure was used to identify the height differences between ridges and furrows. While local height differences were less than 7 cm, a gradual decrease in elevation is observed from north to south. This gradient helps to ensure that runoff of surface water and makes the northern section of the Middle valley relatively dry.

Not all Middle valley transects could be surveyed precisely because of dense gorse shrub coverage. Forests of the spiny shrub are impossible to penetrate. Vegetation survey for this area was carried out by lying down on ground surface to observe the undergrowth. The dense patches of gorse shrub in Middle valley reduce vegetation assemblage variation. Therefore, sub-habitats number is limited of each transects.

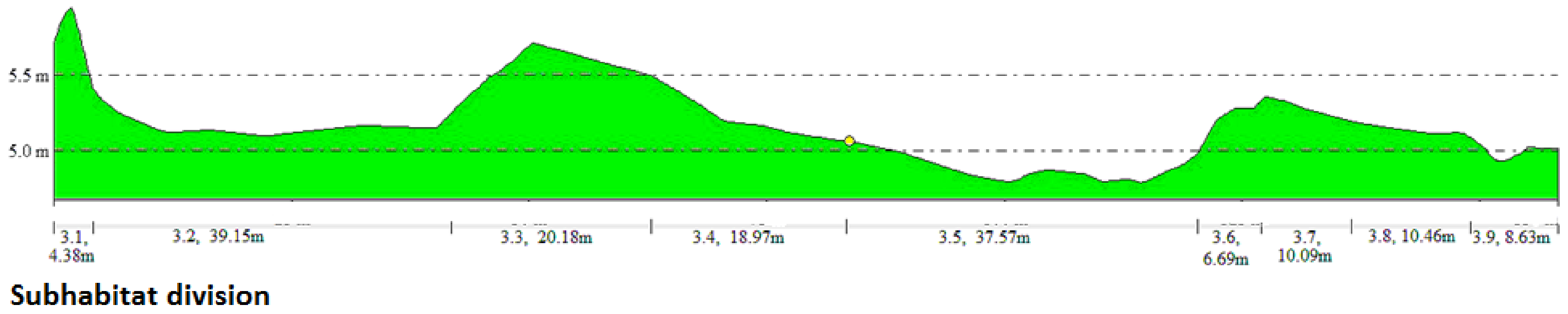
Closer inspection of Figure 12 suggests that there is no positive correlation between sub-habitat length and species richness. For example, transect 2 sub-habitat 7 (2.7) has 11 species and is 16.97 m long. Sub-habitat 2.5 is 33.01 m long but only 4 species are recorded. In the Middle valley, most transects only feature three sub-habitats, including two narrow edges along the western and eastern extent. Therefore, the distribution of sub-habitats is more likely to be an expression of micro-topography or variation of substrates.


5.0 m
4.5 m
1.1, 27.9m
1.2; 6.2m
1.3, 8.2m
1.4, 15.8m
1.5, 8.01m
1.6, 7.4m
1.7, 52.5m
Subhabitat division

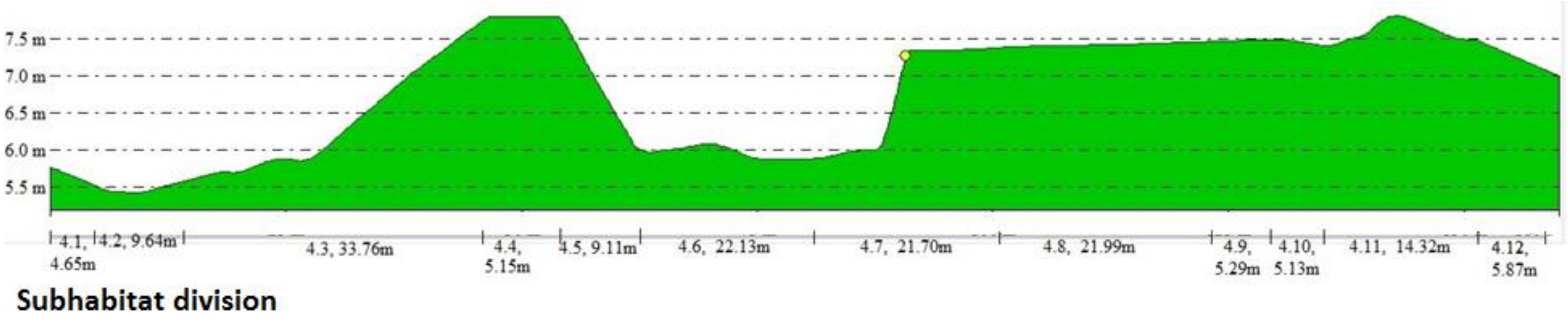
(A)


5.5 m
5.0 m
4.5 m
2.1, 3,89m
2.2, 8.96m
2.3, 10.76m
2.4, 13.79m
2.5, 33.01m
2.6, 13.79m
2.7, 16.97m
2.8, 15.92m
2.9, 13.20m
2.10, 23.11m
Subhabitat division

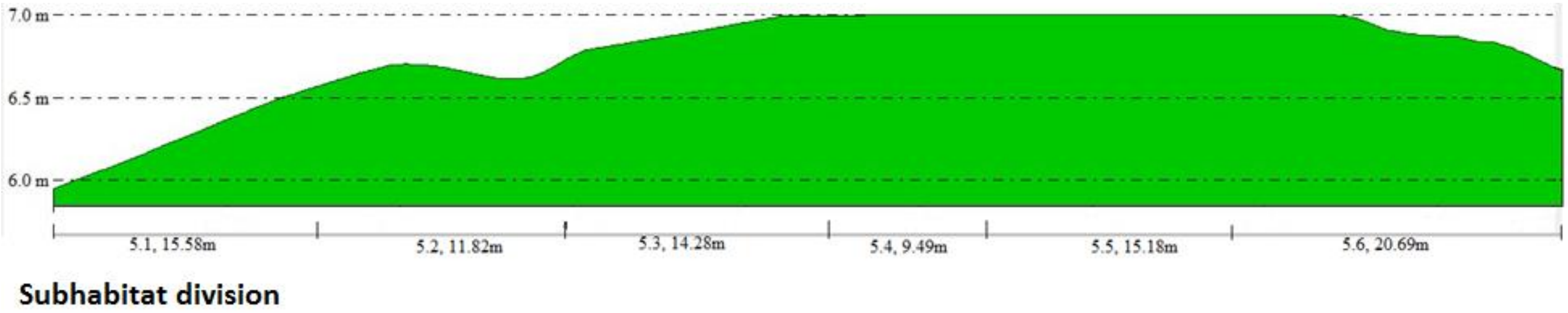
(B)


5.5 m
5.0 m
3.1, 4.38m
3.2, 39.15m
3.3, 20.18m
3.4, 18.97m
3.5, 37.57m
3.6, 6.69m
3.7, 10.09m
3.8, 10.46m
3.9, 8.63m
Subhabitat division

(C)


7.5 m
7.0 m
6.5 m
6.0 m
5.5 m
4.1, 4.65m
4.2, 9.64m
4.3, 33.76m
4.4, 5.15m
4.5, 9.11m
4.6, 22.13m
4.7, 21.70m
4.8, 21.99m
4.9, 5.29m
4.10, 5.13m
4.11, 14.32m
4.12, 5.87m
Subhabitat division

(D)



(E)

Figure 12: Transects in of Lower valley. (A) transect 1; (B) transect 2; (C) transect 3; (D) transect 4; (E) transect 5.

Ground surface patterns can influence the distribution of vegetation by affecting the distribution of water resources. Several centimetres of height difference can alter the flow direction of water and affect the moisture content of the soil. For example, *Calluna vulgaris* dominates relatively dry ridges while *Festuca rubra* mainly grows in furrows which contain perennial water. This indicates that different types of vegetation have different wetness preferences. Habitat preferences related to water availability are also observed for other species. For example, it can be seen that trees prefer relatively dry soil compared to *Calluna vulgaris* and grasses. The topography in the Lower valley creates a habitat for plants with a spectrum of water preferences.

The extent in which topography influences the sub-habitat distribution is difficult to assess because the gradient in soil wetness is difficult to quantify on a microscale. This is especially true when water is not a rare resource, as is the case in the Carnon valley. In literature, the role of topography on the distribution of vegetation has been discussed at landscape level, especially the impact of considerable elevation variation. However, no research on the influence of micro-topography has been found.

In Figure 12 (C), sub-habitat 3.2 is sited at an elevation above sub-habitat 3.5. It is intuitive to assume that sub-habitat 3.5 will be wetter. However, the opposite is the case. A settlement pond was built in sub-habitat 3.2 in which rainfall accumulates. The fine silty clay accumulated from historic processing operations covers the floor of the pond. On the other hand, sub-habitat 3.5 is low-hanging, flat ground connected to water channels which can drain water out quickly. As a result, sub-habitat 3.5 is wet for a much shorter period of time.

The species density is defined as the number of plant species found in each sub-habitat divided by the length of sub-habitat along a transect. The width of sub-habitat is not considered because the transect width was kept constant at 3 meters. Table 5 shows the species density of sub-habitats in the Lower valley.

Table 5: Species density in subhabitats within transects across the Lower valley

Sub-habitat	Length (m)	Number of species	Species density (M^{-1})	Classification
2.9	**13.2**	**1**	0.08	Low density
2.1	**23.11**	**2**	0.09	
4.3	**33.76**	**4**	0.12	
2.5	**33.01**	**4**	0.12	
2.6	**13.79**	**2**	0.15	
3.3	**20.18**	**3**	0.15	
3.5	**37.57**	**6**	0.16	
2.8	**15.92**	**3**	0.19	
4.4	**5.15**	**1**	0.19	
3.9	**8.63**	**2**	0.23	
1.3	**8.2**	**2**	0.24	
1.5	**8.01**	**2**	0.25	
3.4	**18.97**	**5**	0.26	
3.2	**39.15**	**11**	0.28	
1.1	**27.9**	**8**	0.29	
4.6	**22.13**	**7**	0.32	medium density
4.8	**21.99**	**7**	0.32	
1.7	**52.5**	**19**	0.36	
4.1	**4.65**	**2**	0.43	
2.4	**13.79**	**6**	0.44	
1.4	**15.8**	**7**	0.44	
5.6	**20.69**	**10**	0.48	
4.7	**21.7**	**11**	0.51	
4.5	**9.11**	**5**	0.55	
4.11	**14.32**	**8**	0.56	
2.7	**16.97**	**10**	0.59	
3.6	**6.69**	**4**	0.60	
4.2	**9.64**	**6**	0.62	
5.3	**14.28**	**10**	0.70	
5.1	**15.58**	**11**	0.71	

5.4	**9.49**	**7**	0.74	high density
2.3	**10.76**	**8**	0.74	
2.1	**3.89**	**3**	0.77	
3.7	**10.09**	**8**	0.79	
1.2	**6.2**	**5**	0.81	
5.5	**15.18**	**15**	0.99	
5.2	**11.82**	**12**	1.02	
4.9	**5.29**	**6**	1.13	
1.6	**7.4**	**9**	1.22	
2.2	**8.96**	**11**	1.23	
3.8	**10.46**	**14**	1.34	
4.1	**5.13**	**7**	1.36	
4.12	**5.87**	**12**	2.04	
3.1	**4.38**	**15**	3.42	

Table 5 shows that sub-habitat 1.7 has the biggest size and the highest species richness. However, in terms of species density, it only ranks 27th among all 44 sub-habitats in the Lower valley. Some contrary examples are also observed in table 5. Sub-habitat 4.3 is 33.76 metres long but only 4 species were established there. In sub-habitat 3.1, which is less than 5 metres long, 15 species find their niche here. In fact, the highest species density in Lower valley is found in this small patch of land. The species richness of each sub-habitat may be limited by seed availability or abiotic conditions of the habitat. This is especially true for contaminated land because it would have rather different features compare to the surrounding green field.

The origin of substrate in the Middle valley is from the same source as that in the Lower valley, but it was bulldozed in the 1990's. Different vegetation coverage has developed here, as shown in table 6.

Table 6: Analysis of transects across the Middle valley

Sub-habitat	Transect 1 50°13'12.642"N 5°06'16.679"W
1.1	*Salix atrocinerea, Calluna vulgaris, Holcus lanatus, Agrostis tenuis, Betula pubescens, Quercus robur, Festuca rubra, Ulex europaeus*
1.2	*Calluna vulgaris, Festuca rubra*
1.3	*Arum Maculatum, Athyrium filixfemina, Pteridium aquilinum, Hedera helix, Ulex europaeus, Calluna vulgaris, Salix atrocinerea, Festuca rubra, Rudus fruticosus*
Transect 2 50°13'16.96"N 5°06'15.077"W	
2.1	*Senecio jacobaea, Salix atrocinerea, Urtica dioica, Rudus fruticosus, Ulex europaeus, Calluna vulgaris, Betula pubescens, Holcus lanatus, lonicera periclymenum,*
2.2	*Festuca rubra, Ulex europaeus, Calluna vulgaris, Betula pubescens, Salix atrocinerea, rhododendron, Senecio jacobaea*
2.3	*Betula pubescens, Ulex europaeus, Salix atrocinerea, Urtica dioica, Rudus fruticosus, Hedera helix, Calluna vulgaris*
Transect 3 50°13'19.040"N 5°06'19.471"W	
3.1	*Festuca rubra, Plantago coronopus, Lythrum portula*
3.2	*Ulex europaeus, Rudus fruticosus, Agrostis Tenuis, Festuca rubra, Rhododendron, Holcus lanatus*
3.3	*Rudus fruticosus, Cirsium arvense, Scirpus setaceus, Agrostis tenuis, Holcus lanatus, Festuca rubra, taraxacum palustre,*
3.4	*Polypodium interjectum, Calluna vulgaris, Rudus fruticosus, Betula pubescens, Quercus robur, Hedera helix, Athyrium filix-femina, Asplenium scolopendrium, taraxacum palustre, Agrostis tenuis, Festuca rubra, Holcus lanatus*

Trabsect 4 50°13'25.447"N 5°06'22.224"W	
4.1	*Urtica dioica, Rudus fruticosus, Holcus Lanatus, Primula vulgaris, Rumex crispus, Dryopteris filix-mas, Lotus corniculatus, Silene dioica, Viola canina, Bellis perennis, Asplenium scolopendrium, vicia cracca, Agrostis tenuis, Agrostis curtisii, Ranunculus repens, Lonicera periclymenum, Veronica chamaedrys, Pteridium aquilinum, Lotus subbiflorus, Teucrium scorodonia, Rumex acetosa, taraxacum palustre,Rhododendron,Festuca rubra, Ulex europaeus*
4.2	*Ulex europaeus, Rudus fruticosus, Calluna vulgaris, Dryopteris filix-mas, Hedera helix, Festuca rubra, Acer pseudoplatanus, Betula pubescens, Scirpus setaceus*
4.3	*Betula pubescens, Calluna vulgaris, Scirpus setaceus, Salix atrocinerea, Festuca rubra, Athyrium filix-femina, Hedera helix, Rudus fruticosus*
Transect 5 50°13'30.2"N 5°06'30.5"W	
5.1	*Epilobium lanceolatum, Rudus fruticosus, Urtica dioica, Holcus lanatus, Buddleja davidii, Agrostis tenuis, Ulex europaeus, Asplenium scolopendrium, Betula pubescens, Dryopteris filix-mas, Veronica chamaedrys, Lotus corniculatus, Cirsium arvense, Salix atrocinerea, Scirpus setaceus, Festuca rubra*
5.2	*Ulex europaeus, Rudus fruticosus, Festuca rubra, Scirpus setaceus*
5.3	*Salix atrocinerea, Betula pubescens, Dryopteris filix-mas, Rudus fruticosus, Hedera helix, Holcus lanatus*

Table 6 shows that 4 out of 5 transects only have three sub-habitats, which includes two sub-habitats on both ends and an elongated sub-habitat across the whole valley. Compared to the Lower valley (Table 4), the number of sub-habitats in the Middle valley is much smaller. The number of species recorded in the

Middle valley is also much smaller than the number found in the Lower valley. At the western and eastern border of Middle valley, species richness is slightly higher than in the centre. The farms and private gardens on both sides of the valley are considered as the main seed-bank for valley rehabilitation. They are only separated from the mine spoils by a footpath to the west and traffic road to the east.

The average elevation of the Middle valley (Figure 13) is higher than the Lower valley. Surface water from Middle valley flows into the Carnon river directly through a roadside creek (Carnon river). Along the west-east orientation, there is around 80 centimetres drop from centre to both sides. The ground roughness is undetectable because the ridge and ravines are too small to be detected by the total station used to survey the topography.

In the relative flat centre of each transect, only a couple of species were recorded. The established species have a competitive advantage over others. In the case of *Calluna vulgaris*, its dominance is strengthened by its ability to acidify soil during its litter decomposition. An explanation why the Middle valley is only colonised by a few plant species is that conditions are too harsh for other species to survive. Although substrates in the lower and Middle valley are derived from the same parent material (Wheal Jane mine), redox condition are different. Note that the redox condition is determined by the water saturation rate of the soil and exposure to oxygen.

The soil moisture content appears to be significantly higher in the Middle valley, especially in the area dominated by *Calluna vulgaris*. The ridge and ravine structure in the Middle valley increase water retention and infiltration. Compared to the highly compacted soil in the Lower valley, the surface roughness in Middle valley is beneficial to trap seeds and support gemination when rehabilitation starts. Mosses and lichens develop carpets in wet areas which prevents new plants from germinating. Further north, close to the viaduct, the ridge and ravine structure disappears. The land here is relatively dry. Hence, *Calluna vulgaris* gives way to shrubs and trees. Under a dense crown of *Salix atrocinerea* and *Betula pubescens*, even *Festuca rubra* does not stand a chance. Only *Rudus fruticosus* can be seen occasionally

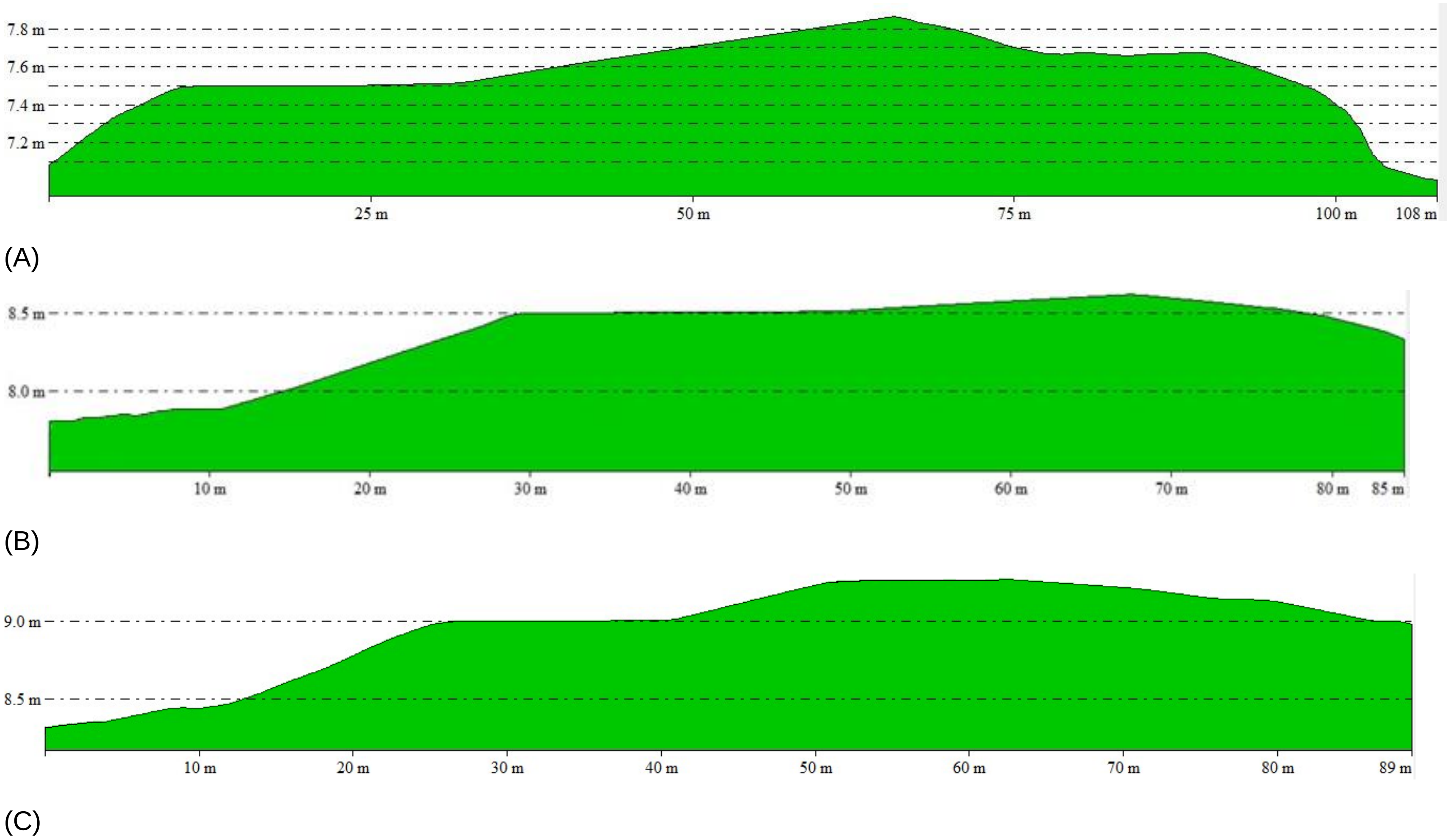


Figure 13: Transects in Middle valley, (A) transect 1; (B) transect 3; (C) transect 5.

The young forest disappears at the edge of viaduct where the ground is subsiding due to the soil settlement around the pylons of the viaduct. *Scirpus setaceus* takes advantage and shares this habitat with *Calluna vulgaris* and *Festuca rubra*. The area under the viaduct is seasonally flooded and dominated by bristle club rush (*Scirpus setaceus*). *Ulex europaeus* dominates the land to the north of viaduct. Under leggy *Ulex europaeus*, there are open spaces in which its seedlings were found. This regeneration phenomenon has not been previously documented in literature. It is generally assumed that, when *Ulex europaeus* matures, other fast-growing species will succeed because gorse shrubs can enrich nitrogen in soil. These higher levels of nitrogen make it easier for fast-growing species to establish. This phenomenon does not apply in the study site. Succession has only occurred in the northern border of the Middle valley, where an invasion of trees and herbaceous species is observed.

The transect survey demonstrates that habitat diversity and species richness in the Lower valley is much higher than in the Middle valley. Relative elevation is more important than absolute elevation because it plays an important role in water distribution. The presence of an edge effect was observed in some locations， especially along the ditches, but the causation is not conclusively in this study.

5.2.2.1 Habitat similarity

Generally, species numbers at a site follow a cyclical pattern. Newly-exposed ground would only contain a few pioneer species. With time passing, the soil condition improves by decomposition of plant litter, precipitation of nitrogen from the atmosphere, weathering of minerals, etc.. More species will then be able to colonise the site and fast-growing species will out-compete others and become dominant. The latter process will, in turn, reduce species richness.

Species composition of a habitat indicates the robustness of the habitat, ecological system maturity, and local land-use traditions. Plant establishment is a result of multiple complex interactions between these factors. In nature, most of the environmental factors are relatively stable. Therefore, the eco-system will have a highly similar structure across the landscape. Seemingly random patterns of vegetation colonisation and succession are an expression of an immature ecosystem. In restoration ecology, the species similarity between interested areas and reference sites can be used to evaluate rehabilitation development.

The sub-habitat vegetation survey gives details about species composition of each assemblage but struggles to describe the dramatic variation between them. The SSI (section 2.2.4) between sub-habitats of Middle and Lower valley transects is a valuable tool to describe the dynamics. The similarity indices of the middle valley are presented in table 7.

Table 7: Middle valley sub-habitat similarity indices

Sub-habitat	**1.1-1.2**				**1.2-1.3**	**1.1-1.3**
Similarity index	0.4	0.364	0.471			
Sub-habitat	**2.1-2.2**	**2.2-2.3**	**2.1-2.3**			
Similarity index	0.706	0.571	0.706			
Sub-habitat	**3.1-3.2**	**3.2-3.3**	**3.1-3.3**			
Similarity index	0.222	0.462	0.2	**3.3-3.4**	**3.1-3.4**	**3.2-3.4**
Sub-habitat	**4.1-4.2**	**4.2-4.3**	**4.1-4.3**	0.526	0.133	0.444
Similarity index	0.242	0.667	0.125			
Sub-habitat	**5.1-5.2**	**5.2-5.3**	**5.3-5.1**			
Similarity index	0.4	0.2	0.456			
transects	01/02	02/03	03/04			
Similarity index	0.64	0.533	0.49	04/05	01/03	01/04
transects	01/05	02/04	02/05	0.531	0.645	0.409
Similarity index	0.516	0.512	0.533	0.503		
Transect similarity index mean = 0.5365				0.556		

Although the overall number of species found in Middle valley is 42, each sub-habitat only has a few species in common. Transect 2 is an exception, crossing a transition zone between *Calluna vulgaris* and *Ulex europaeus* dominated area. The main plant community here consists of a mixture of trees and shrubs. This is possibly a result of viaduct renovation, which introduced new soil and construction materials.

Almost all similarity indices are bigger than 0.5 and the average Middle valley transect similarity index is 0.5365. This implies that more than half of the species are identical to those found in other transects. Consequently, the vegetation community in the Middle valley is relatively homogeneous, although the dominant species are different in each transect.

Table 8 shows that the similarity in Lower valley is lower: the average transect similarity index is 0.4476 and, along each transect, more than 10 sub-habitats are identified.

Table 8: Lower valley transect similarity indices

Transects	01~02	02~03	03~04	04~05	01~03
Similarity index	0.407	0.481	0.426	0.575	0.367
Transects	01~04	01~05	02~04	02~05	03~05
Similarity index	0.426	0.444	0.509	0.424	0.417

Similarity index mean = 0.4476

A complete similarity index of all sub-habitats of the study site, including the Lower valley and the Middle valley, is given in appendix B and C.

5.1.3 Additional observations on non-flowering plants present

Some interesting vegetation habitats were observed. Mosses covered nearly half the area of the Middle valley and developed carpets under *Calluna Vulgaris* stands. The moss carpet can prevent colonisation of other species because germinated seeds cannot reach the soil.

Lichens are found in waterlogged furrows in Middle valley where they are submerged by water in rainy season. The most common species is liver lichen. Its growth season is different from other plants. When furrows dry up in summer, lichens become dormant until furrows fill up with water again.

Ferns are shade-loving plants which like a humid substrate. Altogether seven fern species were found on site. Most of them settle down next to ponds or drainage ditch. Another common feature of their habitat is thick plant litters which improve water holding capacity and guarantee nutrients for their establishment. Heathland is a desired vegetation community because its special cultural landscape attribute. Ferns, especially horsetails occur in mine site will need much detail study.

5.2 Soil: physical characterisation

While soil acts as a substrate for all vegetation growth in the Carnon Valley, comprehensive characterisation of physical and chemical soil properties was carried out. Physical properties measured were soil compaction, and particle size distribution.

5.2.1 Soil compaction

Since the cone penetrator has never been calibrated, the measurement shall only be used to show the relatively changes. The variation in soil strength in the Lower valley (range: 30-200 kPa) is greater than in the Middle valley (range: 50-180 kPa) (Figure 14 and 15). The variation of individual quadrats, however, is slightly greater in the Middle valley. Note that readings in quadrats 17 and 18 of the Lower valley are missing, which is a result the high proportion of waste rocks preventing measurement.

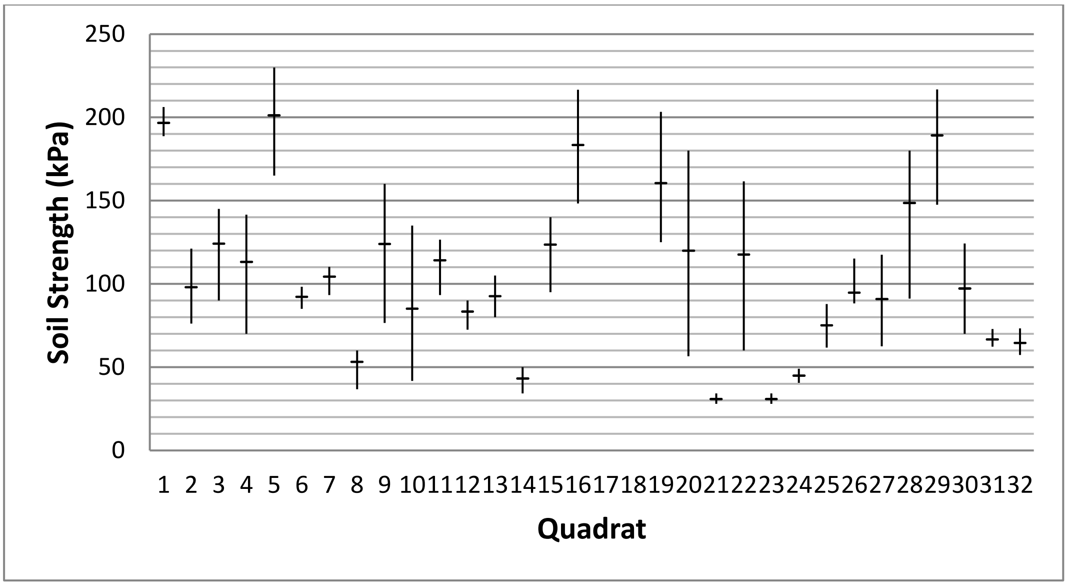


Figure 14: Soil strength in the Lower valley (with maximum and minimum value)

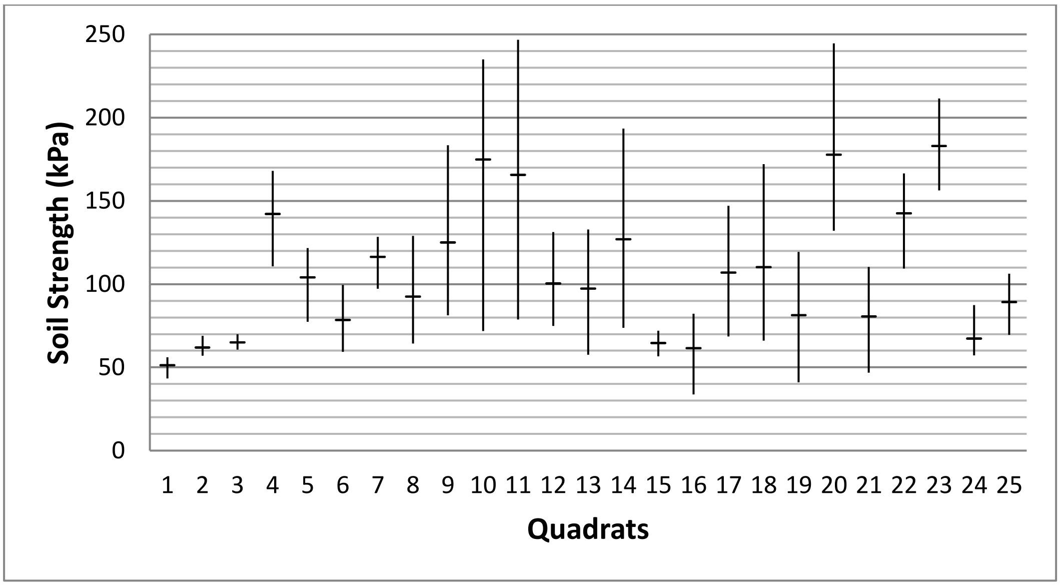


Figure 15: Soil strength of the Middle valley (with maximum and minimum value).

The average soil strength indicates the degree of soil compaction but does not provide a vertical soil strength profile. Based on indicative tests, soil compaction in the vegetated land in the Carnon Valley increases with increasing depth, an effect already noticeable in the top 20 cm of the soil. The soil strength in barren land in the Carnon Valley increases in a consistent manner with depth.

Analysis of the correlation between surface soil strength and species richness or biodiversity index reveals an absolute value of correlation coefficient between 0.1 and

0.3. This suggests that variation in soil strength is not correlated to vegetation development. The quadrats in the Lower valley with the highest species richness and biodiversity also exhibit the highest soil strength.

5.2.2 Particle size distribution

From visual observation and field tests, the particle size has a relatively narrow distribution. This observation was confirmed by soil particle size analysis in the laboratory. The difference between replicates is in second digit, which is beyond detection limit. Therefore, the error bar is not given here. The only significant variable in soil texture is the presence or absence of waste rocks which were sampled in his study. The sampling technique, a screw auger, cannot take oversized particles: when the auger takes particles out of ground, coarser waste rocks fall out and make samples incomplete. It should also be noted that particles with a diameter greater than 2 mm are not considered to be classified as soil (USDA, 2010). Therefore, these have to be manually removed before analysing soil for particle size.

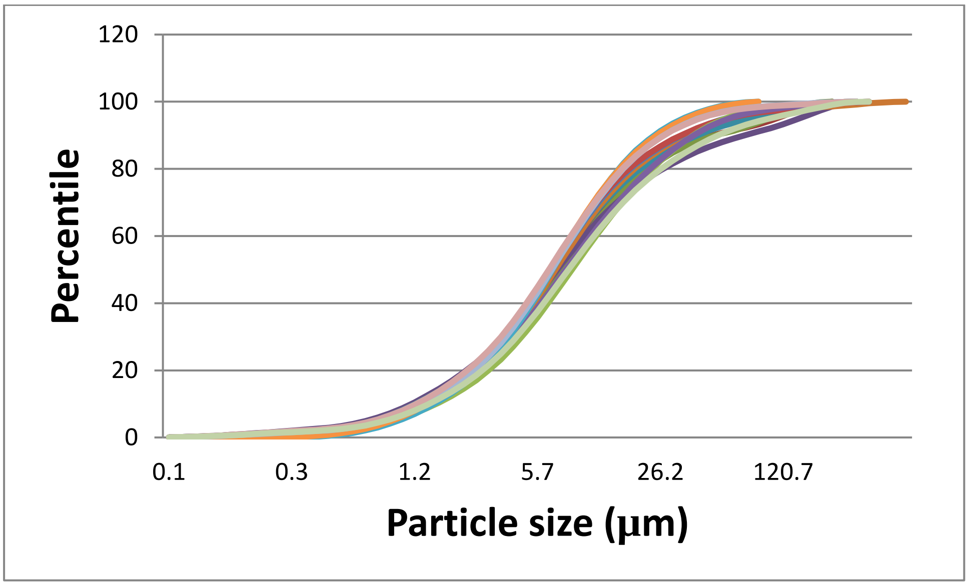


Figure 16: Cumulative particle size distribution of soil in Lower valley.

Figure 16 shows particle size distribution of soil samples from the Lower valley. This Figure indicates that more than 90% of soil solid diameter is equal or less than 50 µm and 70% soil particle diameter is equal or less than 20 µm, suggesting that the material is a typical clay (USDA, 2010). The average particle size of soil in the Middle valley is slightly larger though it is still classified as clayey soil (Figure 17). Clayey soil causes compaction and reduce water infiltration.

The legacy of waste rock tipping was observed in surface soil of the Lower valley. The presence of waste rock inhibited soil sampling in quadrats number 17 and 18. This observation is also supported in a report produced by Geotechnics (1995). With a correlation coefficient smaller than 0.3, no correlation between soil particle size and vegetation development can be established.

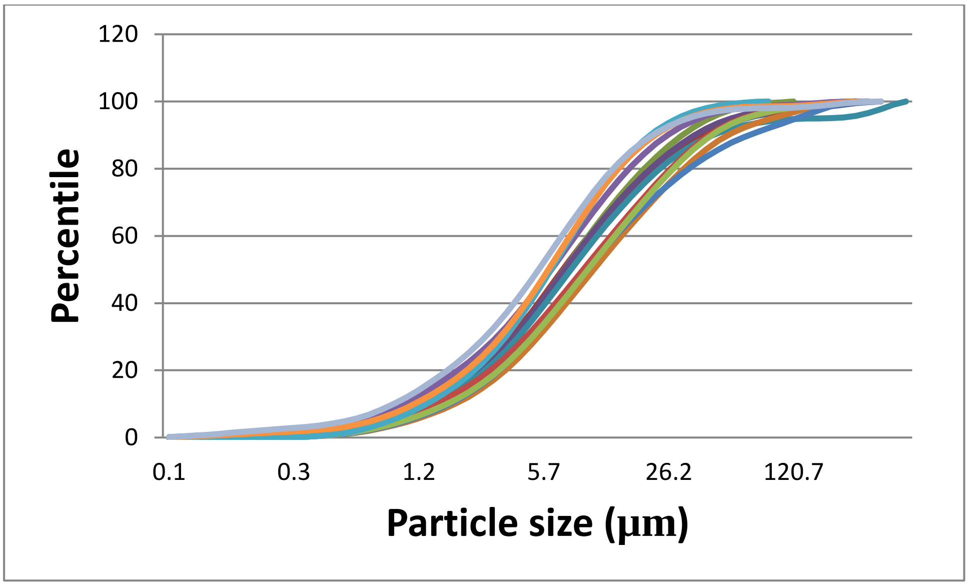


Figure 17: Particle size distribution of soil in Middle valley

5.3 Soil: chemical characterisation

5.3.1 Electrical conductivity

The electrical conductivity deviation value between duplicate soil samples are within 5%, which is less than ion meter detection limit. Therefore, the error bar not given in graph. The surface and subsurface soil electrical conductivity can be found in Figure 18 and 19. Soil electrical conductivity in surface and subsurface soil demonstrate similar variation tendency. It indicates substrate vertical correlation. Even though the substrates in the study area share common origin, the difference among quadrats is considerable. Surface soil has greater variation amplitude than subsurface soil and Lower valley electrical conductivity generally has greater variation range than the Middle valley. The dynamic soil chemistry in Lower valley may play a key role in vegetation succession in the valley. However, further investigation still needed to find out what role the salts and ions play in this process.

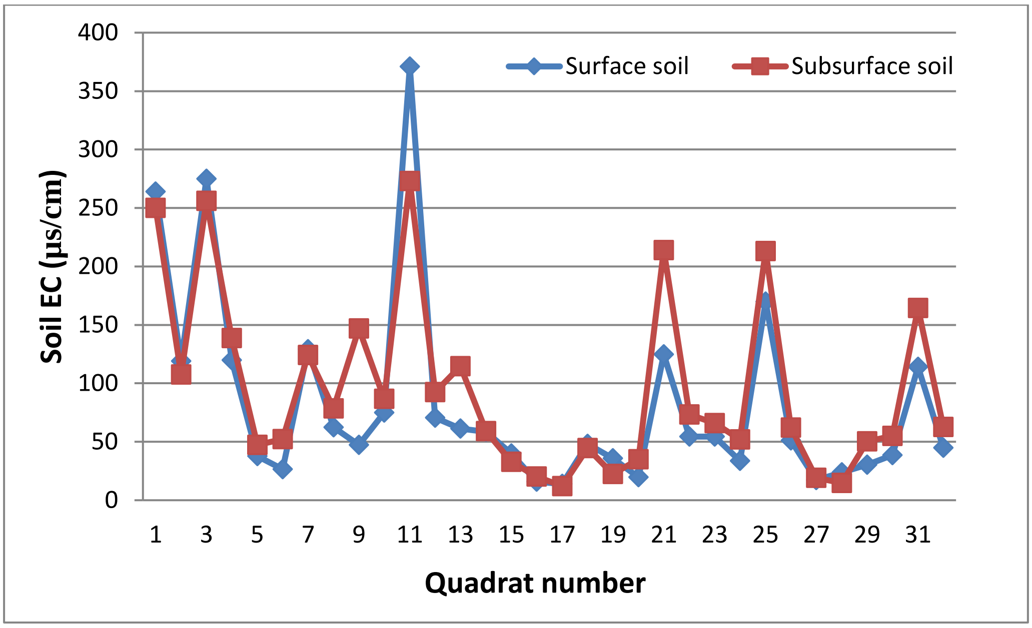


Figure 18: Lower valley soil: electrical conductivity.

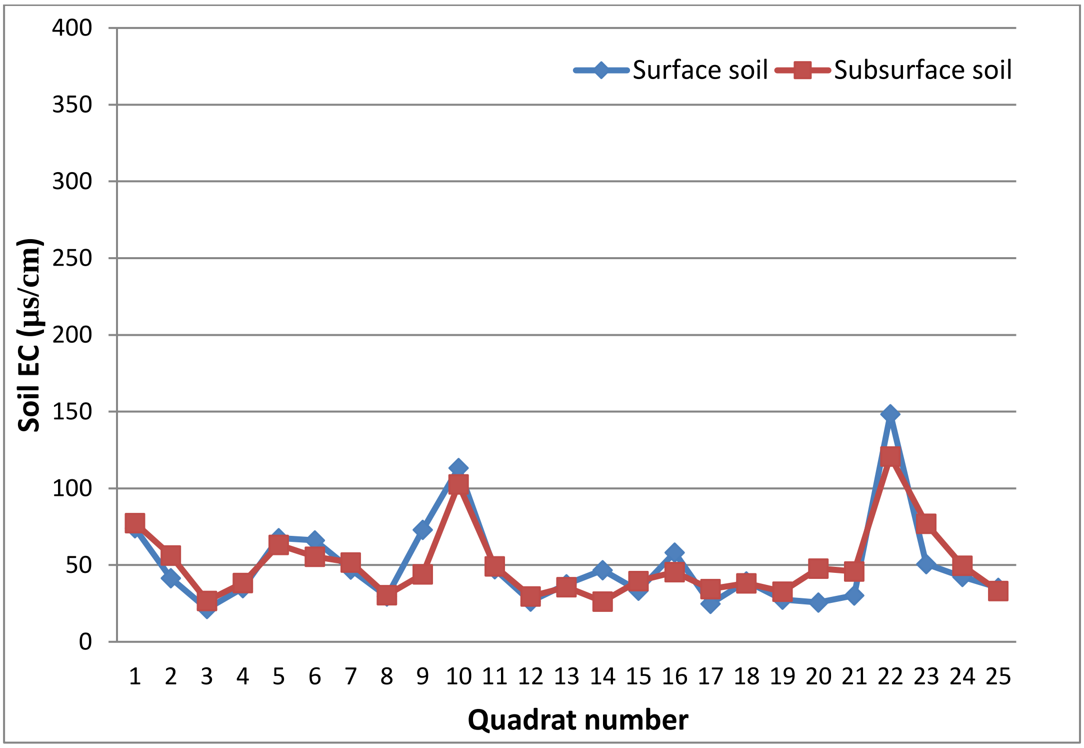


Figure 19: Middle valley soil: electrical conductivity.

5.3.2 Acidity

Figures 20 and 21 show the surface (0-10 cm) and subsurface soil (10-20 cm) acidity value for the Lower and the Middle valley respectively. The pH test of the replicates prepared from the Lower and Middle valley soil varies in the second digit, which is below pH meter detection limit. Therefore, the standard deviation and error bar are considered to be negligible. Subsurface soil has slightly wider variation range than surface soil. It maybe is a result of long term exposure. The soil acidity in the Middle valley is more level up when compare with the Lower valley. This difference is highly likely because of acidity relocation by surface runoff in the Lower valley. The hummock and hollows in the Lower valley may responsible for the soil acidity variation.

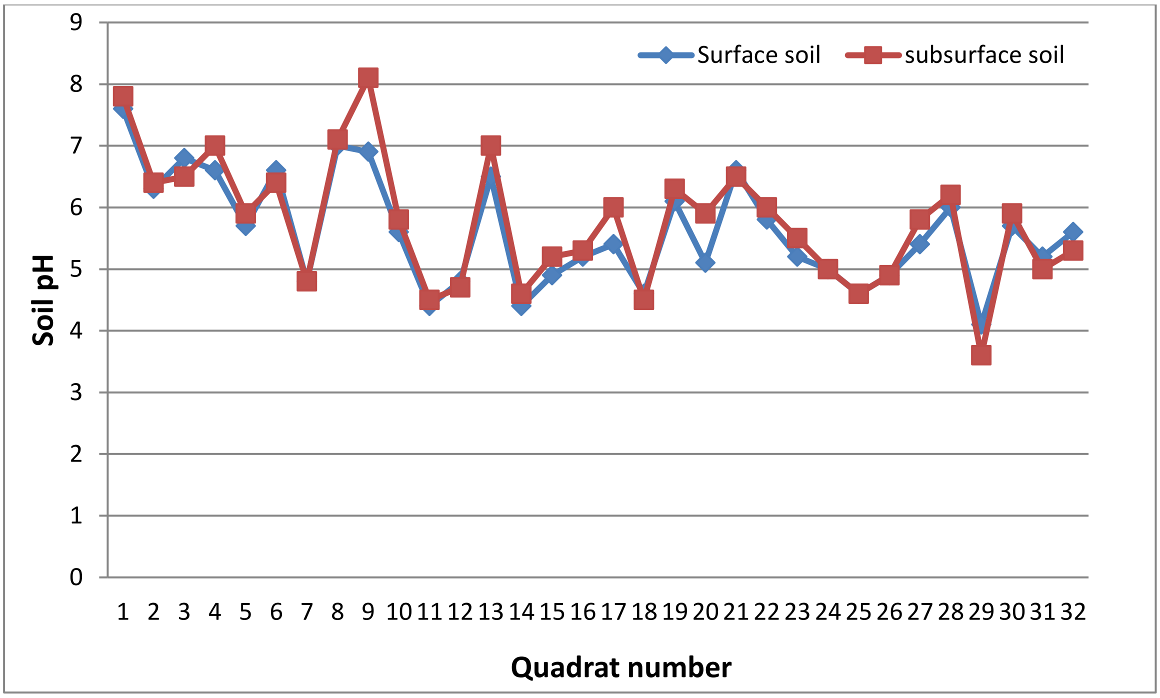


Figure 20: Soil acidity in the Lower valley.

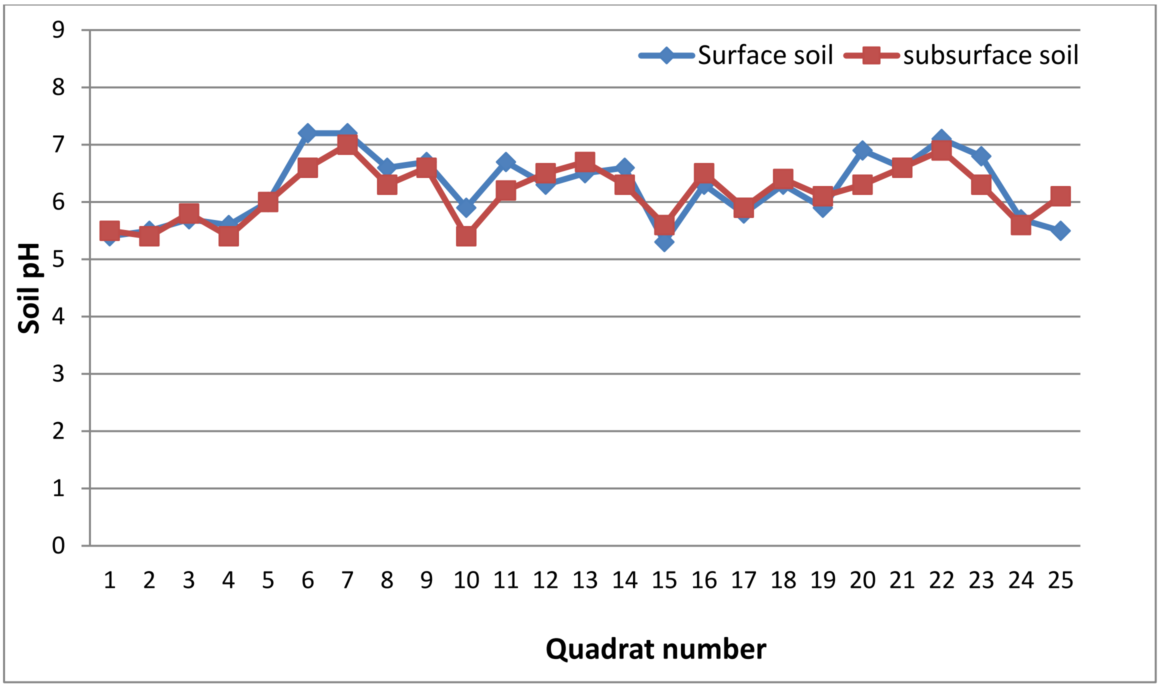


Figure 21: Soil acidity in the Middle valley.

5.3.3 Portable XRF

The metalliferous deposits around the Carnon Valley contain an array of heavy metals. Extraction was predominantly geared towards the recovery of tin which was present with an average grade of tin of 0.8% (Dominy, 1998). Processing of the ore produced enormous amounts of tailings, which contain traces of many metals. These tailings were disposed in the Carnon Valley.

There are 14 mineral elements consistently present in all soil samples collected from the valley. Even more elements were measured in soil samples using portable XRF. The following graphs (Figure 22 to 27) give three trace elements (arsenic, copper and lead) concentration in Lower valley and Middle valley, which are later indicated as the top three toxic elements to vegetation in RDA analysis (section 5.6.2). The graphs show a relatively large variation in arsenic and copper concentrations. The concentration of these elements varies considerably because they are present in relatively large mineral particles. The concentration measured with protable XRF can vary significantly depending on whether or not large grains are measured. Measuring replicates is very important to get relative accurate value of element soil concentration. It is also possible that considerable variation indicates uneven distribution of soil biotoxicity, which can create gradient of phytotoxicity which may generate different vegetation community. As with soil acidity and electrical conductivity, trace element concentrations in the Lower valley also vary across a greater range than in the Middle valley.

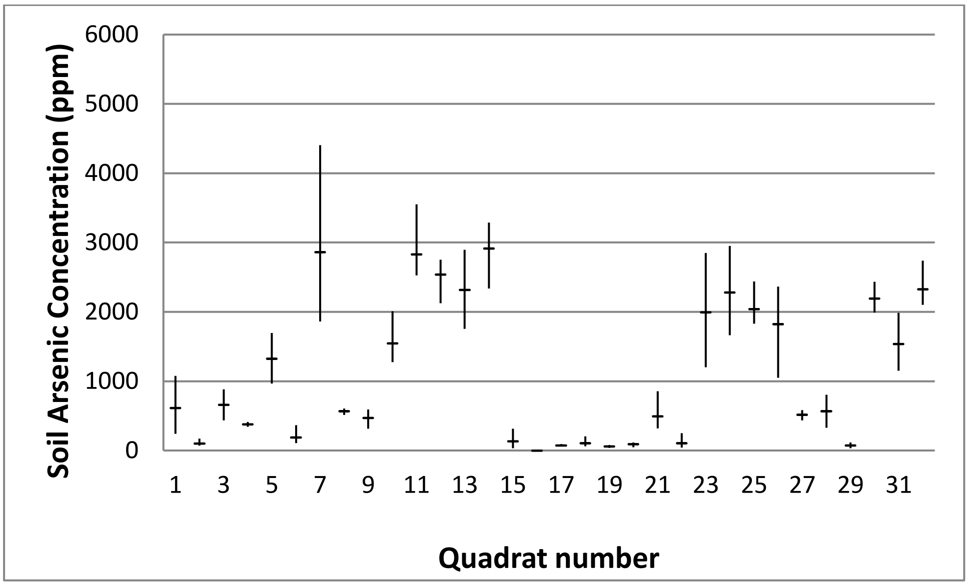


Figure 22: Arsenic concentration in the Lower valley.

Quadrats in the Lower valley display a greater fluctuation in arsenic concentration. This points to a higher phytotoxicity heterogeneity in the Lower valley substrate. The abnormally high value in the first quadrat of Middle valley is more likely to be an outlier.

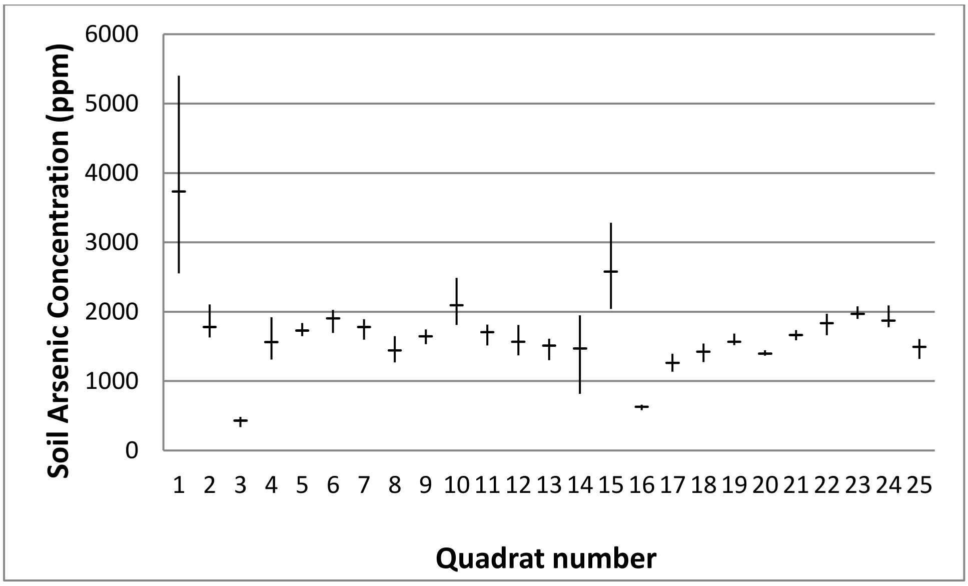


Figure 23: Arsenic concentration in the Middle valley.

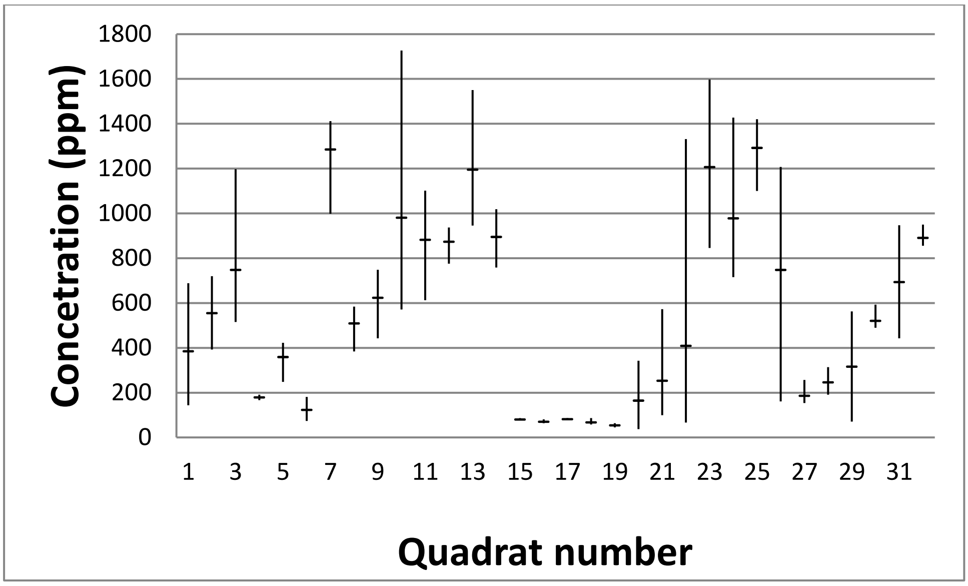


Figure 24: Copper concentration in the Lower valley.

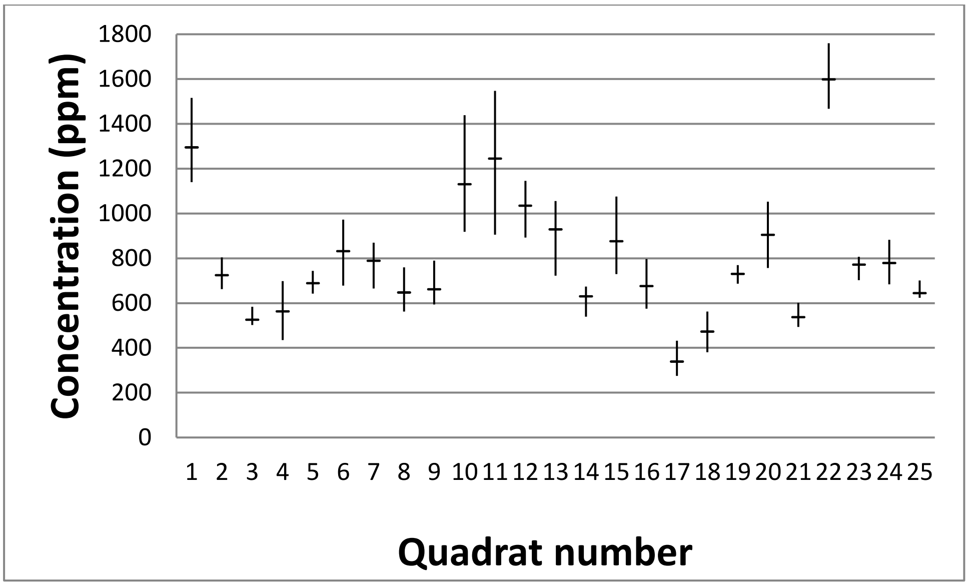


Figure 25: Copper concentration in the Middle valley

Although the highest copper concentration is found in Middle valley, there is less variability in copper concentration in Middle valley quadrats. There are several quadrats in Lower valley where the copper concentration is close to the detection limit, notably where the site has been used as waste rock tip location.

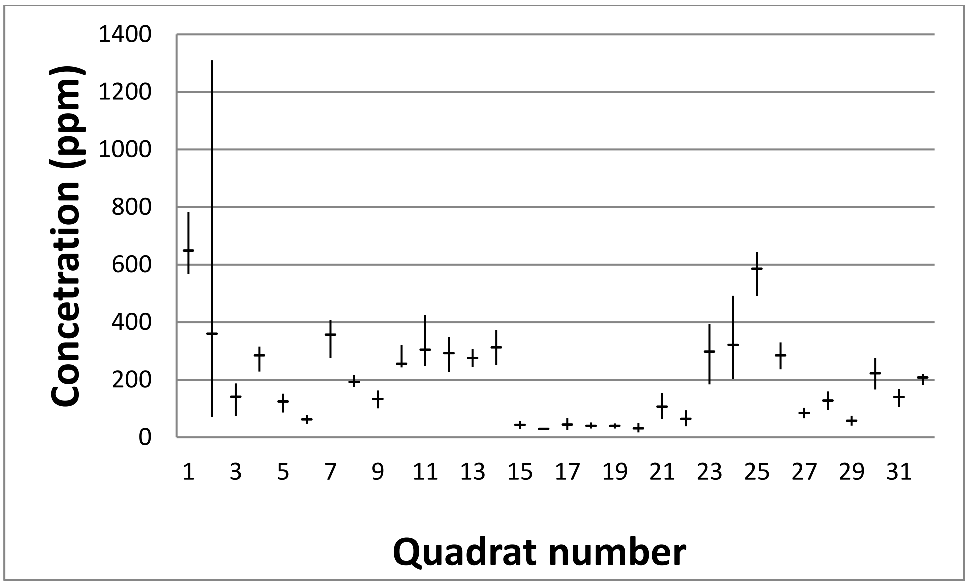


Figure 26: Lead concentration in the Lower valley

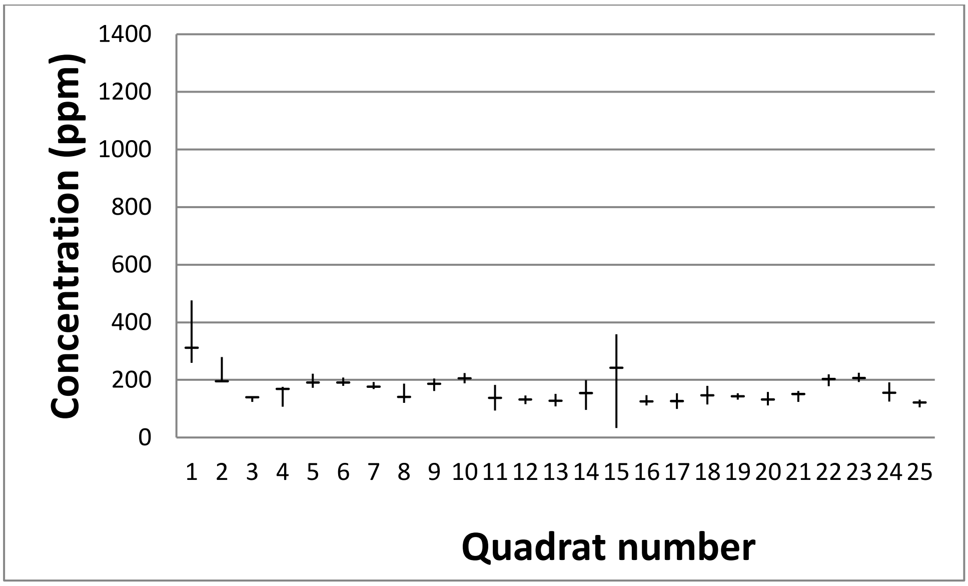


Figure 27: Lead concentration in the Middle valley

Comparison of Figures 26 and 27 shows that the distribution of lead is more homogeneous in the Middle valley than in the Lower valley.

Table 9 gives the concentrations range of arsenic, copper and lead in Lower and Middle valley substrates, as measured by portable XRF.

Table 9: Concentration range of heavy metals measured by portable XRF

Location	Elements	Concentration (ppm)
Lower Valley	Arsenic	31-4405
	Lead	17-1310
	Copper	37-1727
Middle Valley	Arsenic	337-5402
	Lead	33-476
	Copper	275-1760

According to the Soil Guideline Value (SGV) suggested by the UK Environment Agency (2009), arsenic in the valley is generally above acceptable levels. The concentration of lead in the Middle valley is deemed safe for residential land and, although the lead concentration in the Lower valley nearly triples, it is still safe for commercial use. No SGV for copper has been published (Table 10).

In the UK, no SGVs for wildlife have been defined. The SGVs developed by the US EPA for the protection of ecological receptors is termed Ecological Soil Screening Levels (Eco-SSLs) which relate plants, soil invertebrates, birds, and mammals (Table 11).

Table 10: UK Soil Guideline Values for relevant heavy metals (Environmental Agency, 2009; DEFRA and Environment Agency, 2002)

Element	Function of Land use	Soil Guideline Values (mg/kg)
Arsenic	Residential	32
	Commercial	640
	Allotment	43
Copper	Residential/Commercial agricultural	Not available
Lead	Residential	450
	Commercial	2330
	allotment	450

Table 11: Ecological Soil Screening Level (Eco-SSL) of arsenic, copper and lead (US EPA, 2005a; US EPA, 2005b; US EPA, 2007)

Name of Value	Arsenic (mg/kg)	Copper (mg/kg)	Lead (mg/kg)
Eco-SSL plants	18	70	120
Eco-SSL invertebrates	N/A	80	1700
Eco-SSL avian	43	28	11
Eco-SSL mammalian	46	30	56

The recommended Eco-SSL is lower than the corresponding SGV because it considers many sensitive species in each ecological group. It has been observed that, for different species, the capacity for heavy metal tolerance varies greatly. The United States EPA use the ECo-SSL solely as a reference value (US EPA, 2005a). Depending on the target species, exceeding Eco-SSL values does not necessarily make remediation mandatory. Since species composition varies from site-to-site, a generic Eco-SSL is impossible to determine. Therefore, the use of Eco-SSL will not be considered further in this study.

5.3.4 Laboratory XRF

The XRF analysis of a fused bead produced from a composite sample from the Lower valley is shown in Table 12. The composite sample represents a reference value for the average composition of the substrate in the Lower valley. It should be noted that it is difficult to create fused beads, which tended to crack during the cooling process. Therefore, only a limited dataset is available.

Table 12: XRF analysis result for the Lower valley.

Chemical compound	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O
Concentration	0.15%	1.44%	14.30%	65.90%	0.14%	0.08%	3.09%
Chemical compound	TiO_2	Cr_2O_3	MnO	Fe_2O_3	LOI	CaO	
Concentration	0.64%	0.01%	0.06%	6.45%	6.99%	0.11%	

XRF analysis provides inconclusive information because it was not possible to prepare intact fusion beads. However, results presented in Table 12 provides a general description about chemical composition of substrates in the valley.

According to XRF analysis, the phosphorus content in Carnon Valley soil is 0.6 g per kg and the potassium content is even higher. These both are available to vegetation in a soluble form which excludes these as growth-limiting factors. Soil acidity is a result of oxidation of sulphide. Aluminium oxide and ferric oxide account more than one fifth of matter in soil samples. These compounds have a high arsenic adsorption capacity. It should be noted that the high alkaline oxide content found in soil samples can reduce acidity.

5.4 Soil: mineralogical characterization

Since tailings and waste rocks originating from the Wheal Jane mine are the sole source of the Carnon valley substrate, mineralogical characterization can provide insight into mineral decomposition and biochemical processes within the rhizosphere, as well as indicating phytotoxicity. In this study, mineralogical characterization was performed with XRD.

SEM analysis gives details about trace elements and evidence of its decay. This is beneficial for understanding redox conditions which have an effect on arsenic bioavailability.

5.4.1 XRD

Appendix F shows the XRD measurement of three composite samples, suggesting they have similar parent material. Although XRD is not a very sensitive method and its detection limit is relatively high, it still is useful to obtain basic information about all macro-minerals in substrate and characterise parent material of soil. The minerals of the three composite soil samples are the same, though graphs are slightly different. The differences between two replicates is undetectable.

The minerals have been identified are: quartz, muscovite, biotite, clinochlore, kaolinite, anorthite, diaspore and schorl. A brief description about them is given as the following (Parker, 1994; Deer, 2013):

Schorl is commonly found in granites and metaporphic rocks. It is a compound of seven elements. Among them, boron is beneficial for plants and aluminium is toxic.

Chemical weathering can release these from schorl but, under ambient conditions, schorl is inert.

Quartz is quite stable under chemical weathering and can only be broken down through mechanical weathering into smaller grains. It is a typical constituent of granitic and granite pegmatite. It also accounts considerable part of sandstone, quartzite, hydrothermal metal deposits, and carbonate rocks. It is one of the most common minerals in the Earth’s crust and is not toxic to living organisms.

Muscovite is the most common member of mica group. It is a major constituent of phyllite, schist, gneiss, granite, granite pegmatite and aplite. It can be transformed from other minerals through hydrothermal processs authigenically.

Biotite usually includes all dark coloured mica found by geologists. This mineral can be found in wide range of rocks include igneous rocks, felsites lavas and porphyries metaporphic rocks. It is found commonly in association with chlorite and muscovite.

Clinochlore is a product of hydrothermal alteration of biotite, pyroxene and amphibole.

Anorthite is a member of the feldspar group. It is usually formed along metamorphic limestone or in alkali plutonic rocks and lava.

Diaspore is either formed by hydrothermal alteration of aluminous minerals or from hydrothermal mineral in alkali pegmatites.

Kaolinite is a clay mineral converted from aluminosilicates through weathering and hydrothermal process. It is commonly found in decomposed feldspar-bearing rocks.

Of the main elements in above mentioned minerals, only aluminium may have a negative effect on plants when dissolved at elevated concentrations in water. However, aluminium oxide is not soluble in water and Environment Agency report states that aluminium in the Carnon river water is below the detection limit or only present in small concentrations - several ppm - which pose no threat to vegetation.

Interpretation of an XRD spectrum requires more than three peaks of a single mineral to verify its presence. Though traces of arsenic mineral are found in XRD spectra, the presence of arsenic minerals cannot be confirmed.

While XRD analysis has a detection limit of 5%, it only provides insight into the predominant species of crystallized minerals, creating understanding of the context for biochemical p+rocesses in the substrate.

5.4.2 SEM

SEM analysis gives insight into trace compounds and evidence of their decay. Measuring in back-scatter mode with semi-quantitative EDS spectra, weathered arsenopyrite products were found (Figure 28 and Figure 29).

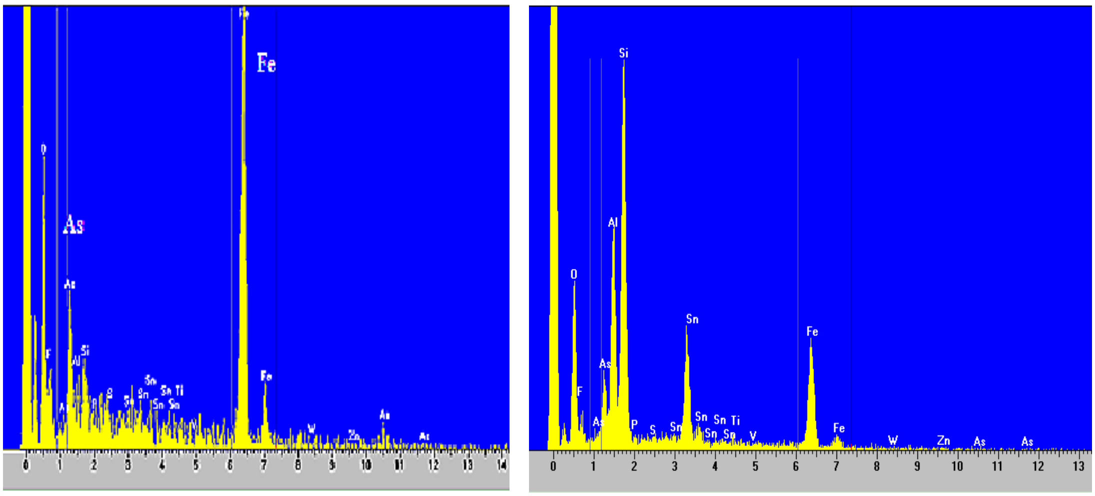


Figure 28: Semi-quantitative EDS spectra of arsenopyrite-weathered product (particle A in Figure 29).

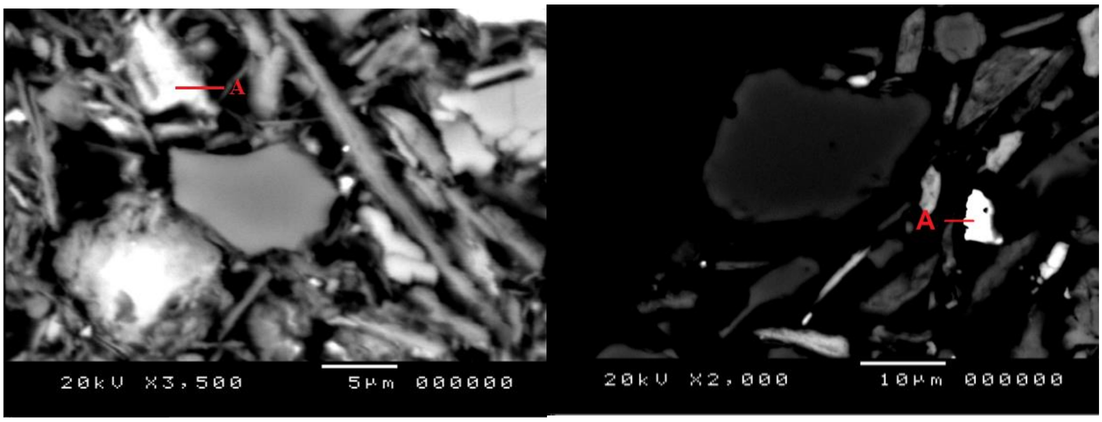


Figure 29: Backscattered Scanning Electron Microscopy (SEM) image showing arsenopyrite weathered product (A).

In different weathering stages, iron, sulphur and arsenic account for different proportions in the mineral. In a later stage, other elements may replace iron and arsenic to develop into new mineral species. That is why the intensity of the signature of each element can vary.

It is noted that arsenopyrite is the primary source of arsenic in the Carnon Valley. This mineral can break down or decay over time. To reduce soil toxicity, stabilisation of arsenopyrite and slowing down the weathering process hold the key to limiting dispersion of toxic arsenic in the environment.

SEM can verify that arsenopyrite is the primary form of arsenic mineral in the sample, but SEM cannot identify arsenopyrite weathering products.

5.5 Arsenic fractionation

The recovery rate of three composite soil samples is around 87% which is comparable with the result achieved by Wenzel (2001) in his experiment (88%). The three clusters used to produce composite soil sample for this analysis are derived from statistical analysis in section 5.7.3.

When checking the distribution of arsenic fractionation shown in Figure 30, it was found that the total arsenic content in each soil sample could be as high as 5000 ppm. However, the first fraction or readily bioavailable part is less than 7 ppm, which is well below the UK guideline value for garden soil (DEFRA and EA, 2002a, b). The remaining fractions contain concentrations of arsenic which are all above the Soil Guideline Value of 20 mg/kg of dry soil (DEFRA and EA, 2002a, b). The second fraction is extracted with ammonium dihydrogen phosphate solution and is denoted as the specifically-sorbed fraction. Like arsenic, phosphorus has five electrons in the outermost shell and is chemically similar in terms of valence and dissociation constants. If excessive exchangeable phosphate is present, then specifically-sorbed arsenic could be released from the soil. Since the atomic radius of phosphorus is smaller than that of arsenic, it has a stronger polarity. Therefore, phosphate is more prone to be bound by soil grains. This suggests that, when levels of specifically-sorbed arsenic in soil are high, plants on site may not able to obtain enough phosphorous nutrients.

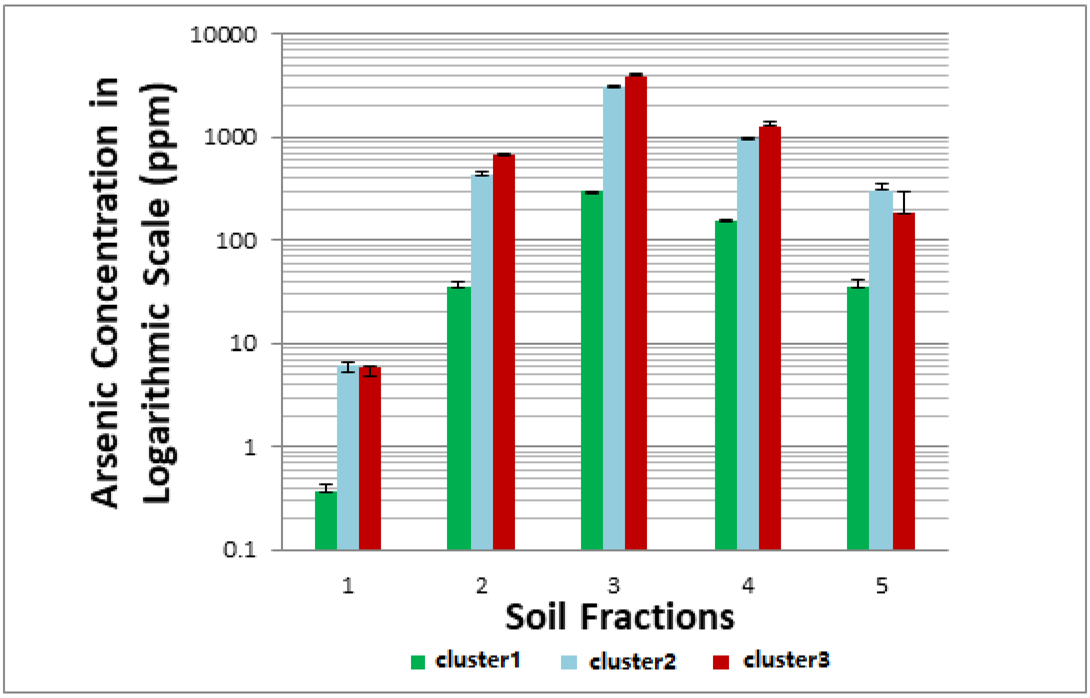


Figure 30: Comparison of arsenic concentration in five fractions of the three composite samples. (Series 1: quadrats with low total arsenic and high biodiversity index value; Seriesr 2: quadrats with high total arsenic and high biodiversity index value; Series 3: quadrats with high total arsenic and low biodiversity index value.)

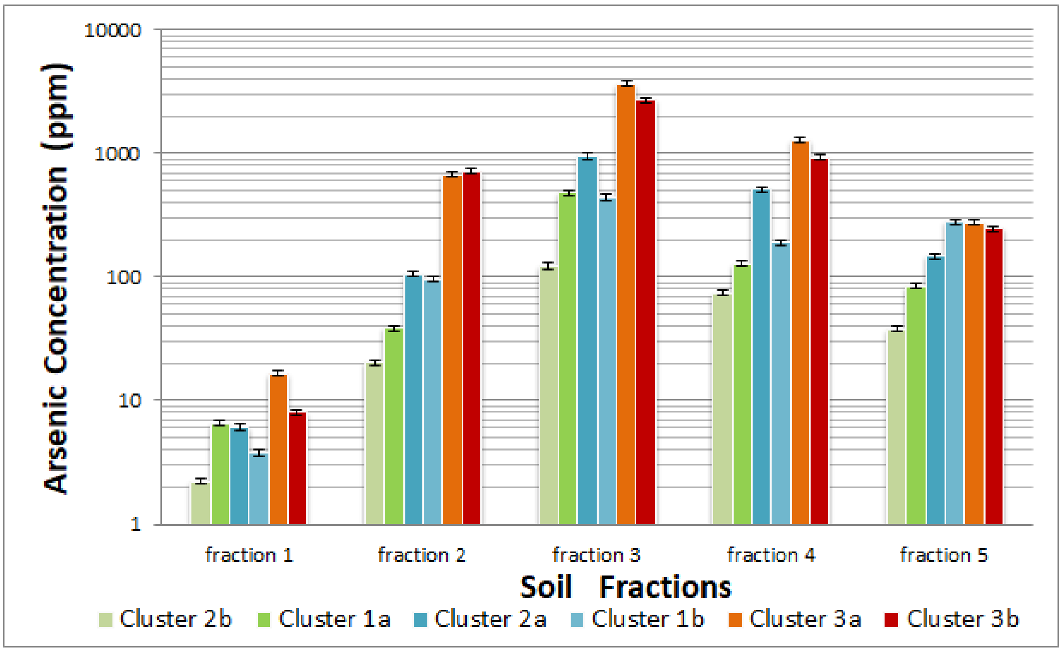


Figure 31: **Comparison of arsenic factionation of two quadrats from each of the three clusters.**

The concentration of arsenic of the second fraction is highest in the composite soil sample from quadrats with a high total arsenic which supports a low biodiversity (cluster 3). This suggests that the gradient in soil exchangeable arsenic concentration may determine the diversity of the re-established vegetation community. With increasing exchangeable arsenic concentration in soil, fewer plants can establish themselves. Therefore, a low biodiversity can be observed when excessive specifically-sorbed arsenic reaches a certain level (between 370 ppm and 600 ppm). When the threshold is reached, no vegetation can grow anymore.

The third fraction accounts for the biggest share of arsenic in all three composite samples and at least half the arsenic is found in this fraction. The fourth fraction takes second position in terms of arsenic content among all five fractions. The sum of these two fractions contribute more than 80% of arsenic in all three samples. Arsenic in these two fractions is less readily dissolved in soil water but acidification, variation of redox state and other factors may release them. The quadrats with low BDI have more soil arsenic stored in fractions 3 and 4. Local arsenic toxicity potentially can be more persistent than the other quadrats. The sequential extraction scheme proved that iron hydroxide has a strong capacity to stabilise arsenic, reducing arsenic availability in soil.

To further investigate the fractionation behaviour of quadrats in different cluster, two quadrats from each cluster have been randomly chosen to see whether they have followed the same fractionation pattern. While part of the site has been occupied by a new constructed parking lot, a complete test of all quadrats in the Lower valley is impossible. The result, as shown in Figure 31, is consistent with Figure 30. The two quadrats from the cluster with high total arsenic which supports a low biodiversity (cluster 3) have higher portion of arsenic present in the 2nd fraction.

5.6 Quality assurance and quality control

All laboratory analyses were carried out in Camborne School of Mine's laboratories. Therefore, the option of analysis techniques is limited by availability. Cone penetrator is the only equipment available for soil compaction measurement in field. Although the calibration of cone penetrator has never been done since it was purchased, it was still used for qualitative assessment in this research. The presence of a large quantity of waste rocks in the substrate creates a large standard deviation in the soil compaction measurements.

The Malvern Mastersizer, laboratory XRF, XRD and SEM are regularly calibrated by technicians from producers. Electrical conductivity meter and pH meter are calibrated with standard ORP solution and Thermo Scientific pH buffers respectively. Both portable XRF and ICP-MS were calibrated with Canmet STSD-2 Stream sediment by technicians.

Due to limits on available funding, composite soil samples were used for fractionation analysis. Efforts have been made to split quadrats reasonably by using cluster analysis (section 5.7.3).

During experimental campaigns, QA/QC is important. QA/QC samples should be included randomly among the actual samples prior to analysis. There are three types of QA/QC samples:

- duplicates – to identify reproducibility (these can be actual samples which are submitted twice for analysis)
- matrix-matched standards – to identify accuracy
- blanks – to identify noise

Analysis of QA/QC samples provides insight into the reliability of the sample analysis process. When QA/QC results are good, it enhances the confidence in analysis results prior to interpretation.

5.7 Statistical analysis

Of the 87 plant species found in research site, 14 of these have not been found in regions within a 2 km radius, while 28 species have been recorded in all the neighbouring eight tetrads (Table 13). Altogether 31 species, or 36% of all observed plants, were found in 2 or less tetrads around the research site. This indicates that a high percentage of vegetation growing on mine tailing in the research site is locally rare. In other words, rare plant species have propagated over a distance to reach the Carnon Valley. It is possible that these species are out-competed elsewhere or are selective in terms in terms of habitat.

The following sections will discuss statistical inference of driving factor(s) relating to vegetation development in the Carnon Valley.

Table 13:: Species occurence in tetrads surrounding the research site

Number of tetrads	0	1	2	3	4	5	6	7	8
Number of species observed in the research site	14	8	9	2	4	2	9	11	28
Percentage	16.09 %	9.20 %	10.34%	2.30 %	4.60 %	2.30 %	10.34 %	12.64 %	32.18 %

5.7.1 Multivariate linear regression

The species richness and biodiversity were considered as dependent variables and substrate features were used as predictors. Multivariate regression was carried out with SPSS 22. The results are sorted according to location (Lower valley, Middle valley) and acidity because pH has been considered as an influential factor on trace element solubility (Reddy et al., 1995).

Statistical significance (p value) of the multivariate analysis is presented in Table 14. The model is very significant for species richness when analysing the Carnon Valley as a whole. When analysing the Lower valley and Middle valley separately, the model behaves inconsistently. After categorising data according to soil acidity, the model becomes worthless (non-significant). The inconsistent values for statistical significance related to species richness and biodiversity indicate the analysis method cannot establish a sensible model to predict rehabilitation. Therefore, the regression model may not be a suitable tool for this study.

Table 14: Statistical significance (p value) of each model

	Species Richness	BioDiversity Index
Carnon Valley	0	0.697
Lower valley	0.026	0.188
Middle valley	0.6	0.076
Lower valley low pH soil	0.499	N/A
Lower valley high pH soil	0.753	0.248
Middle valley low pH soil	N/A	N/A
Middle valley high pH soil	0.538	0.215

5.7.2 Ordination techniques

5.7.2.1 RDA result

The redundancy analysis produced by CANOCO 4.5 is summarised in Table 15. It is clear that the third axis has the greatest eigenvalue, explaining the greatest variation between environmental variables. However, the third axis has almost no explanatory power relating to the species-environment correlation. This indicates that the majority of the variance is noise or irrelevant to vegetation development. The first axis explains 99.9% variance of species-environment relation which supports the understanding of the following RDA graph (Figure 32).

Table 15: Summary of RDA result.

Axis	1	2	3	4	Total variance
Eigenvalue of species data	0.449	0	0.547	0.003	1
Species-environment correlation	0.672	0.32	0	0	
Cumulative percentage variance of species data	44.9	45	99.7	100	
Cumulative percentage variance of species-environment data	99.9	100	100	100	
Sum of all eigenvalues					1
Sum of all canonical eigenvalues					0.45

The data is loaded into the software CanoDraw to derive a biplot graph describing the correlation between vegetation and environmental indicators.

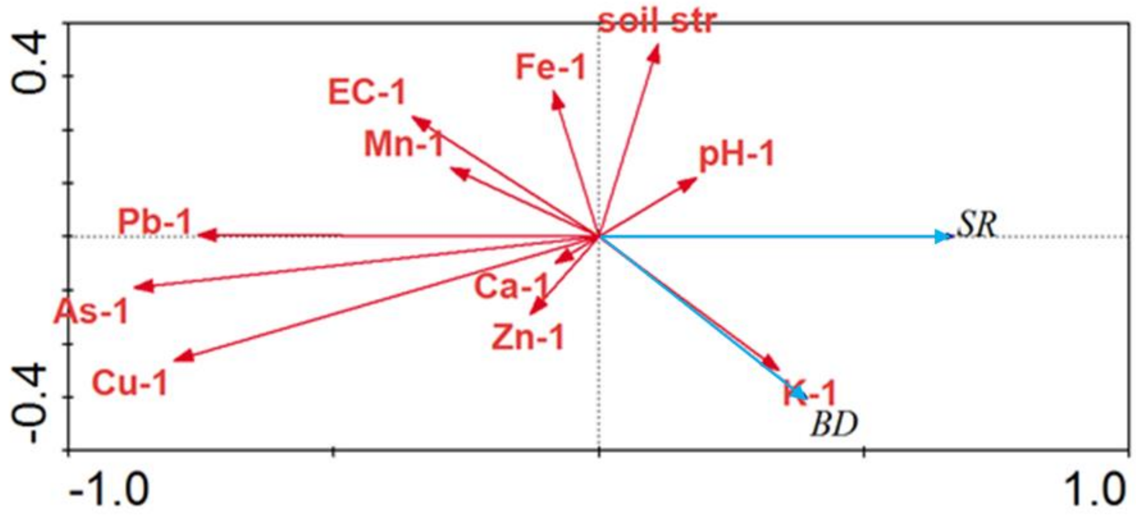


Figure 32: RDA biplot graph. Red arrows represent environmental variables and blue arrows represents species indicator variables.

Fundamental rules on how to interpret RDA graphs are given in the literature (Legendre and Legendre, 1998; Zuur et al., 2007):

- The length of each arrow is proportional to its strength.
- The further apart two arrows are from each other, the less these are correlated.

- Arrows representing species richness and local biodiversity point to the direction of greatest increase and the angle between them indicates the extent of their correlation.

Since the first axis represents 99.9% of the correlation between environmental factors and vegetation, the relation between environmental factors and vegetation development can be read by projecting all arrows onto the first axis.

Arsenic has only a slightly higher negative impact than lead and copper, though its concentration in local substrate is significantly higher. It is concluded that arsenic, copper, and lead are the top three negative factors of vegetation development and potassium has the greatest positive impact on vegetation development. A higher soil pH promotes vegetation development which is probably a result of reduced solubility of lead and copper in less acid soil.

To evaluate the behaviour of trace elements with variation of pH, the dataset has been categorised according to soil acidity. All quadrats are sorted into two subgroups by mean value of soil acidity above or below pH = 5.8.

With soil acidity decreasing, heavy metal becomes more detrimental and arsenic is less available in soil solution (Kuo et al., 2006). This phenomenon is supported in this research. Figure 33 give the interrelation between environmental variables and vegetation development under more acidic conditions. When the soil pH is below 5.8, copper has a stronger negative impact than arsenic and lead put slightly less stress on vegetation development than arsenic. When the soil pH value is above 5.8, then arsenic becomes the prominent limiting factor in vegetation reestablishment and copper and lead have an insignificant influence on vegetation development. Figure 34 is the RDA biplot of quadrats where the soil pH exceeds 5.8.

Electrical conductivity measurements also indicate that an increasing concentration of ions in soil solution in acidic soil has a stronger negative impact on vegetation development. The reverse impact of potassium in a low pH environment is also a notable point.

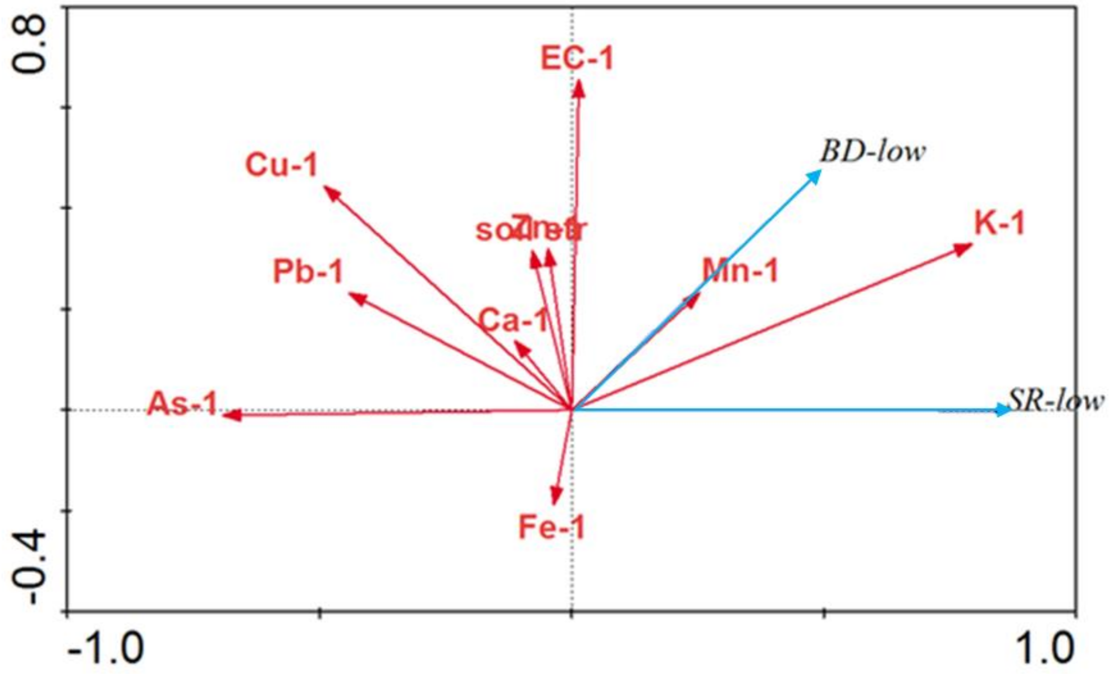


Figure 33: RDA biplot of low pH samples

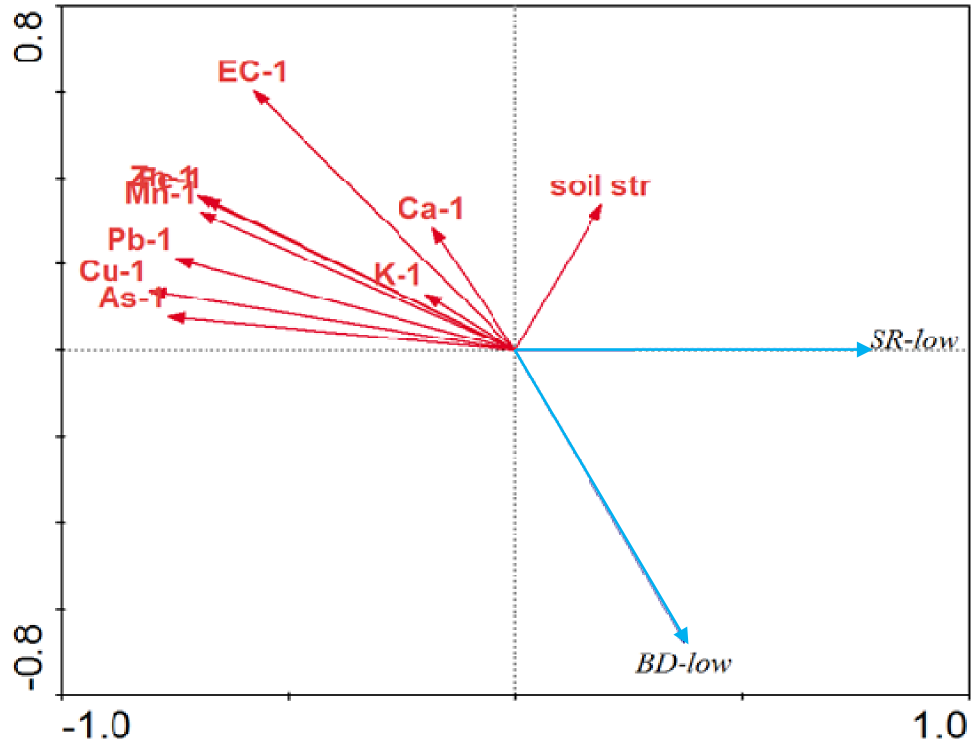


Figure 34: RDA biplot of high pH samples.

5.7.2.2 PCA result

PCA is an unconstrained ordination method which evaluates the contribution of each variable to local environmental features and the dynamics between all variables. It has limited explanatory power for vegetation development and sometimes requires normalization to achieve an unbiased result. In this study, the iron concentration is disproportionally large to the others variables. The weathering product of arsenopyrite can potentially chelate with iron hydroxide and is considered to be inert. Therefore, iron is removed in PCA analysis. The interpretation of PCA graph follows the same rules as for RDA.

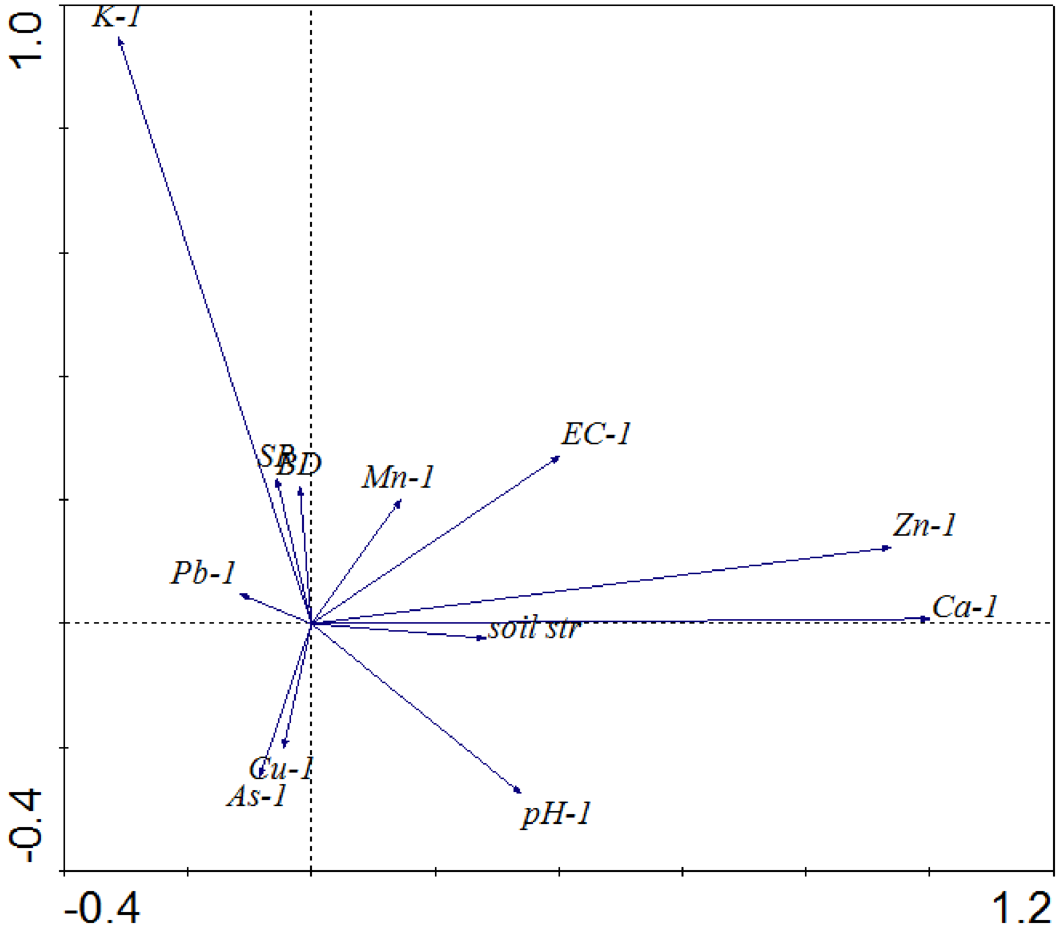


Figure 35: PCA loadings obtained from the two biggest eigenvectors

The most significant feature of Figure 35 is that potassium has positive effect on species richness and biodiversity index. Note that pH, copper and, arsenic have a negative effect on species richness and local biodiversity.

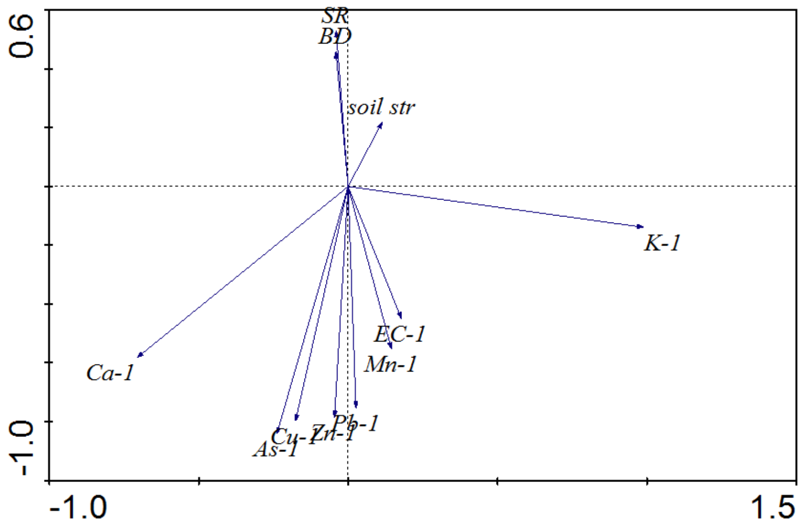


Figure 36: PCA graph of low pH samples

Figure 36 shows the results of PCA performed on quadrats with a pH below 5.8 (29 out of 57 quadrats). With the exception of the soil strength, all environmental factors (Figure 36) have a negative impact on species richness and biodiversity. Figure 37 shows that, when pH exceeds 5.8, only lead, copper, and arsenic have a negative impact on vegetation development (Figure 37).

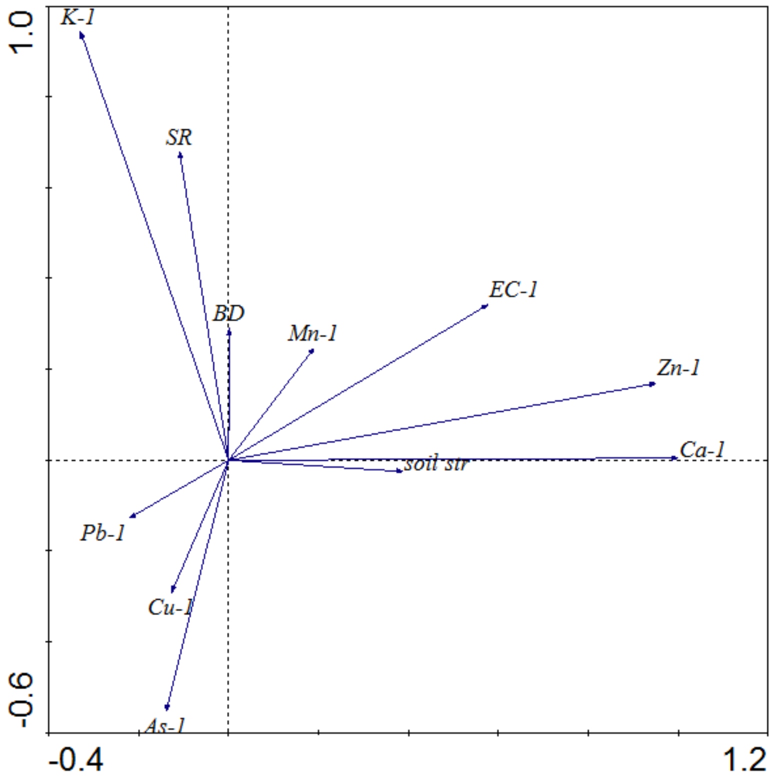
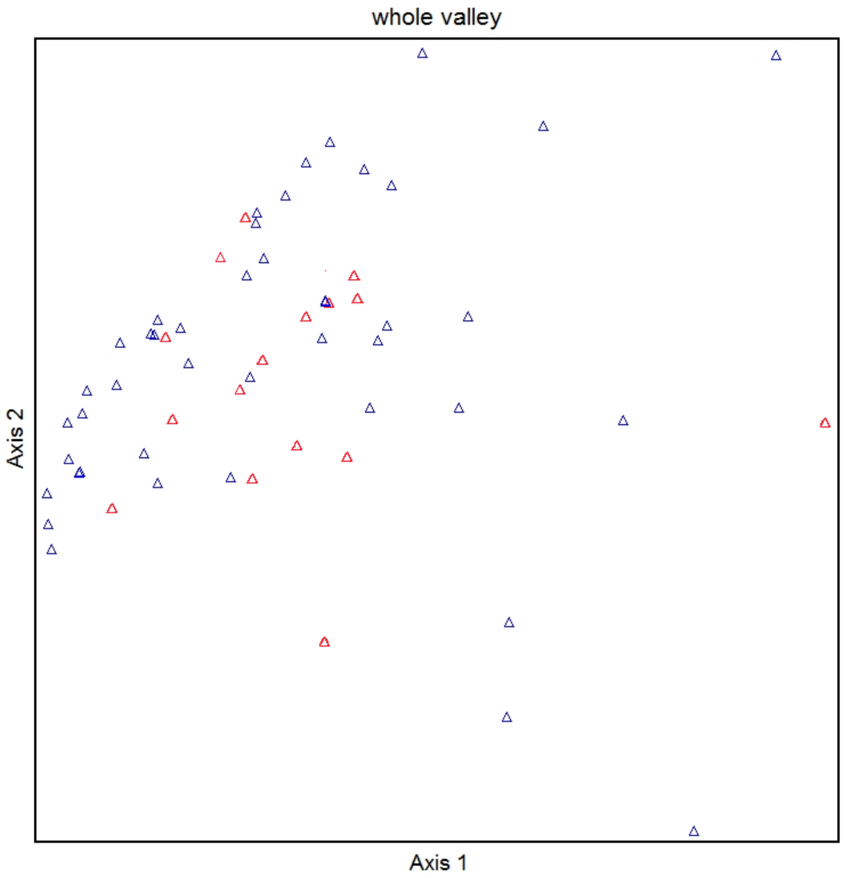


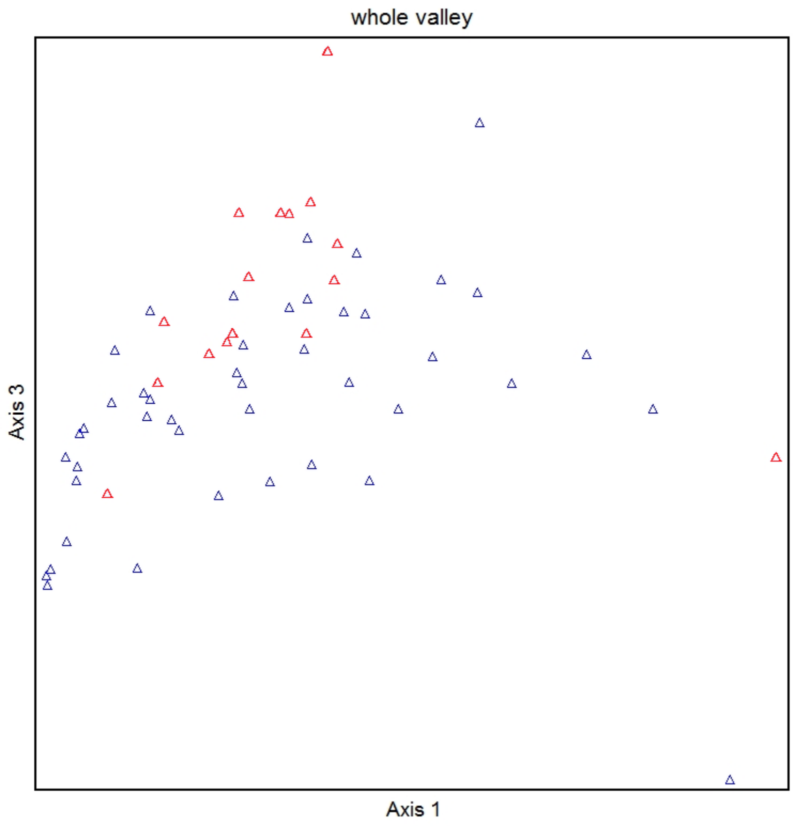
Figure 37: PCA graph of soil with high pH

5.7.2.3 Polar ordination result

Polar ordination analysis of sub-habitats similarity index produces a three-dimensional graph which is represented in Figure 38 with three two-dimensional graphs. These graphs indicate the relative position of all sub-habitats in the Lower and Middle valley. The three axes explain 41.09%, 26.73%, and 11.19% of the variance, and represent a total of 79.01% of the variance in the distance matrix. The sub-habitats in the Lower valley are more sparsely distributed than sub-habitats in the Middle valley. This corresponds to a high species richness and diversity of local ecological community.

The presence of outliers in Middle valley sub-habitats may come from human intervention or abnormality.





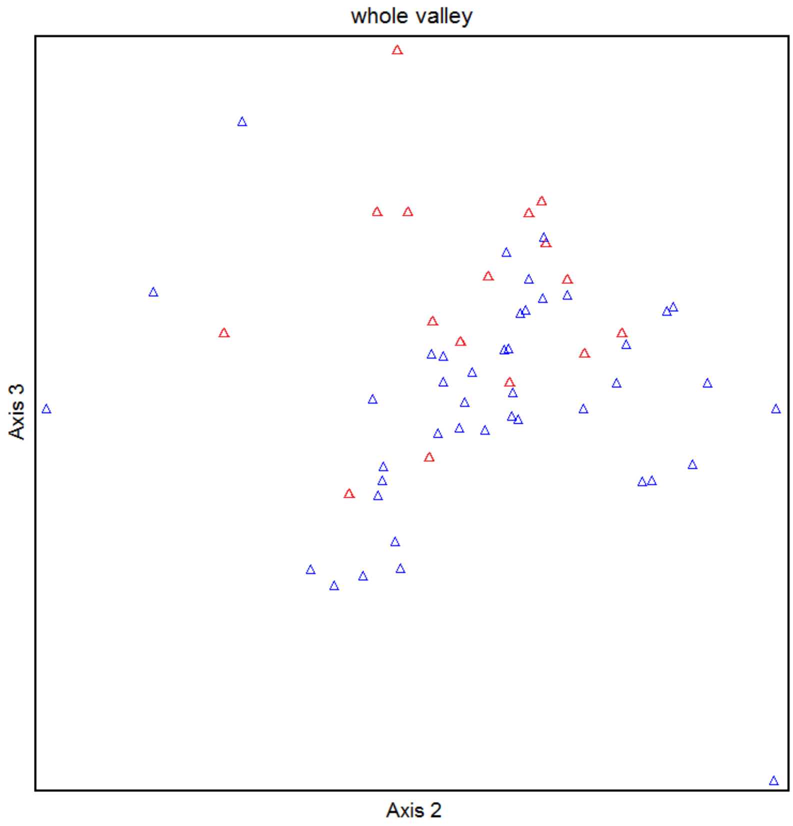


Figure 38: Polar ordination graph of Lower valley subhabitats (blue triangles) and Middle valley (red triangles) similarity index (Sørensen).

5.7.3 Cluster Analysis

In this study, hierarchical cluster analysis is performed by SPSS 22 to test a hypothesis about the vegetation pattern. Figure 39 is a scree plot of the agglomeration schedule coefficients which indicates how much the quadrats are clustered. The slope visualises the significance of the difference when successively merging clusters. The resulting dendrogram is presented in Figure 40. This graph shows that, all quadrats in the Lower valley can be classified into three clusters based on total soil arsenic and biodiversity index. The three clusters have the same membership as was observed by visual classification in the scatter graph (Figure 60).

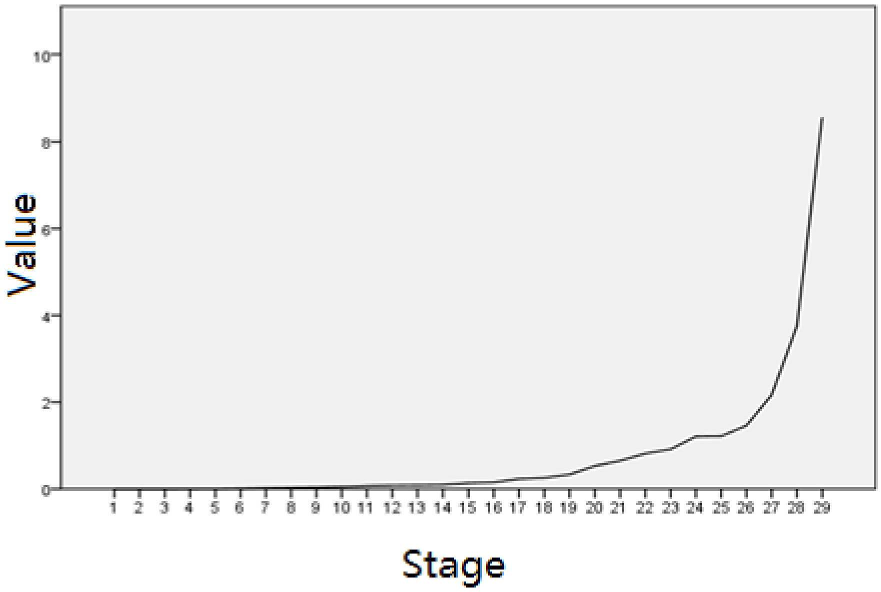


Figure 39: Agglomeration schedule coefficients of Lower valley quadrats cluster analysis, with total arsenic and local biodiversity index as variables.

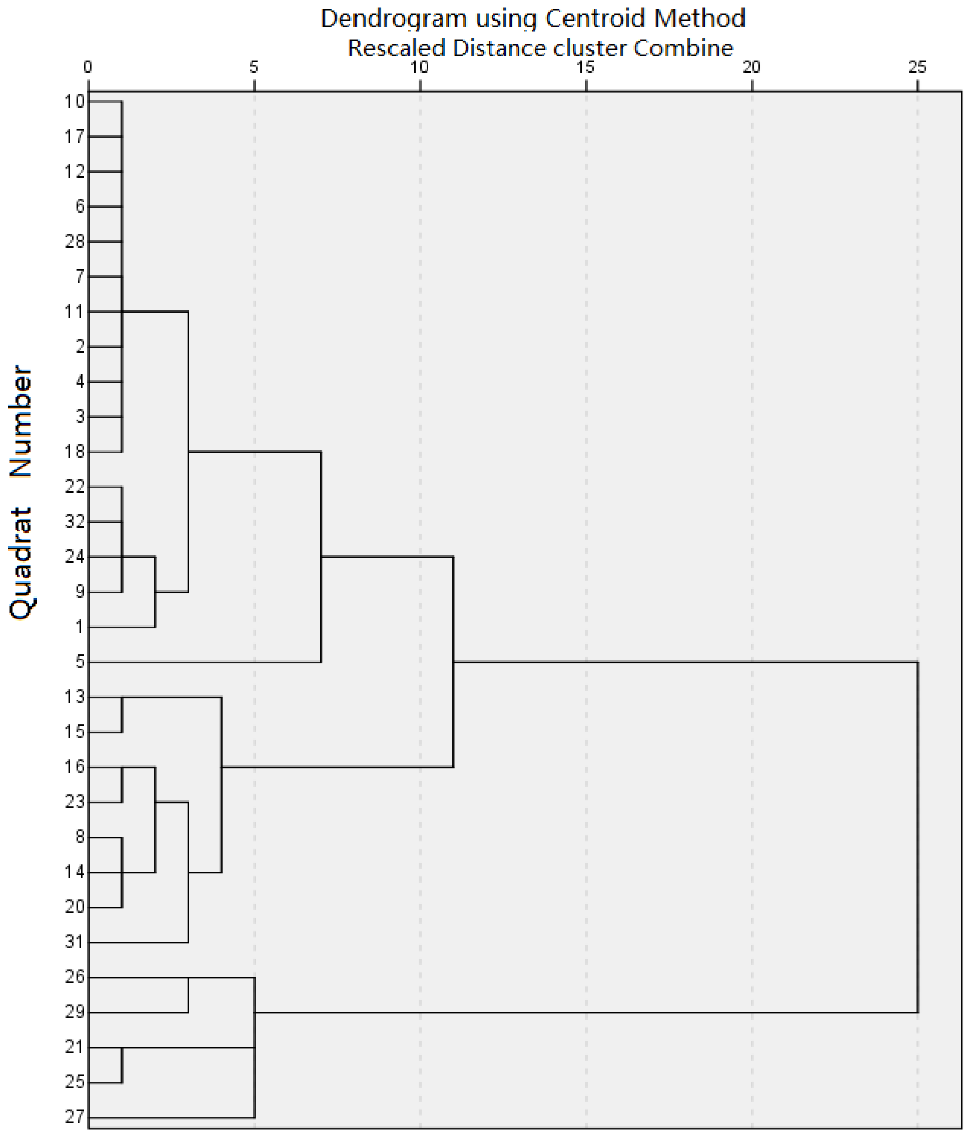


Figure 40: Dendrogram of Lower valley quadrats cluster analysis with total arsenic and biodiversity index as variables.

5.8 Visualisation of variables spatial distribution

Figure 41 and 42 show GIS layers produced with minimum curvature and triangulation interpolation. It could be easily seen that the layer in Figure 42 is smaller than real area. The other drawback of triangulation interpolation was its intensive data demand when a smooth transition through gradients is desired. Otherwise, the sharp angular shape in Figure 42 is inevitable.

Based on this analysis, the minimum curvature method was employed in this research to visualise survey results. Compared to graphical representation of statistical analysis, visualised data readily shows the spatial distribution of variables and their interrelationship, making it a useful analysis tool for communication purposes. It should be noted that the visualisation could not replace statistical analysis nor give additional scientific information.

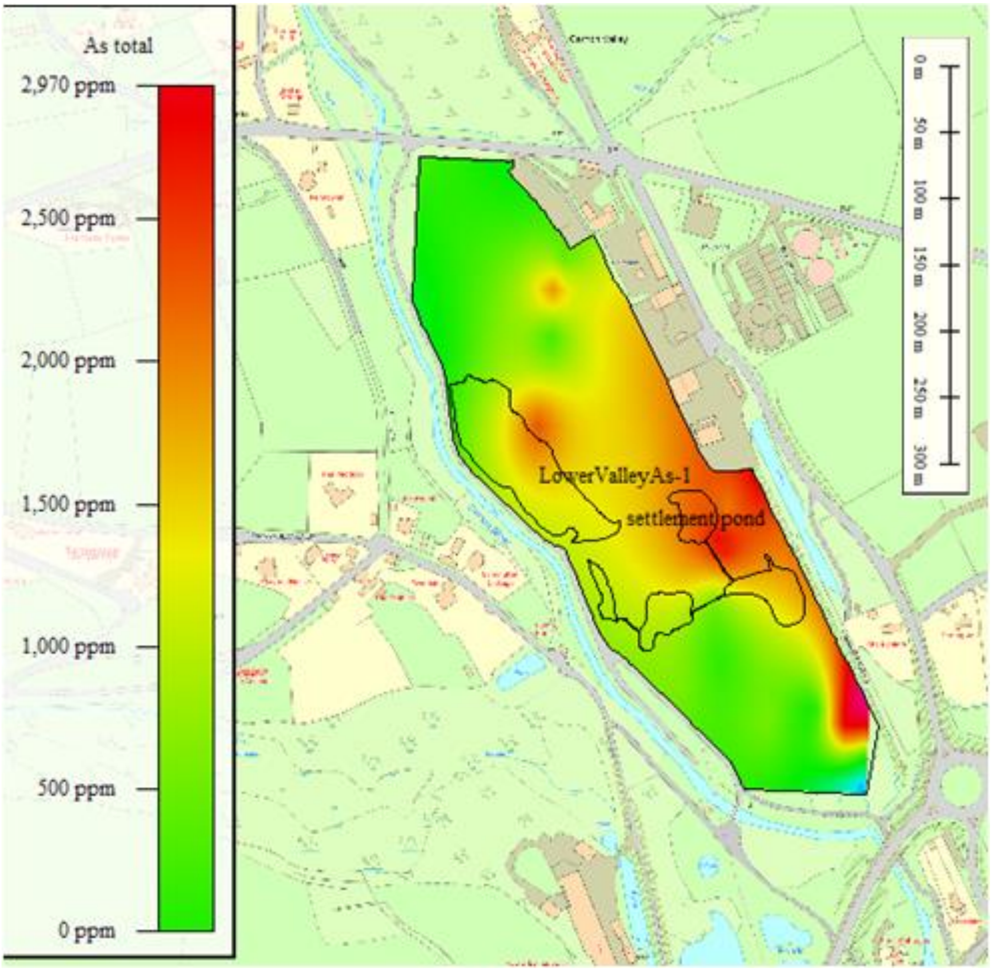


Figure 41: Minimum curvature interpolated arsenic concentration in Lower valley.

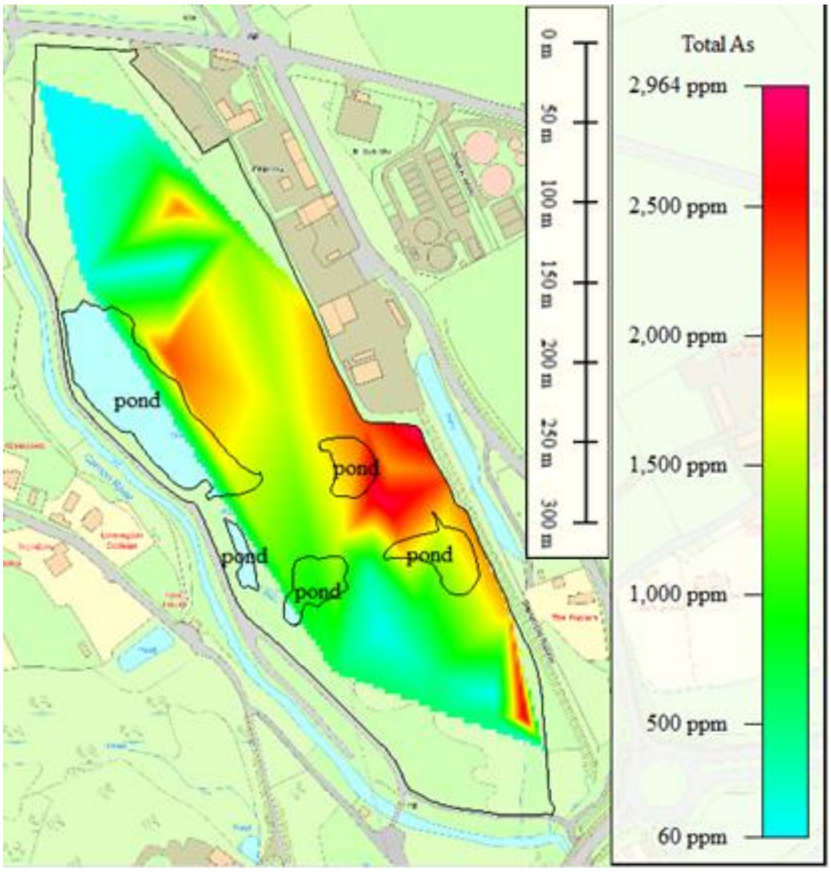
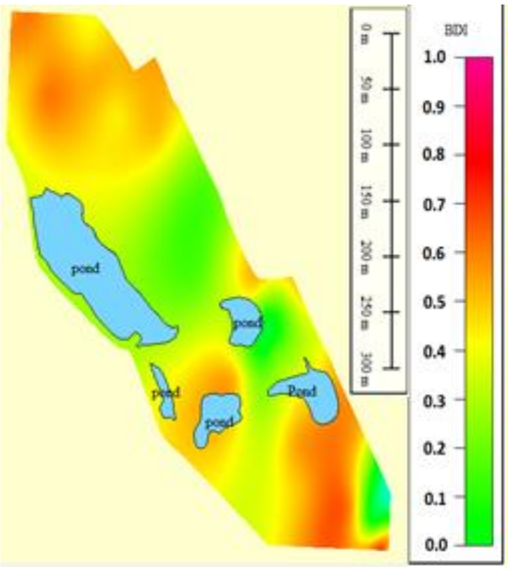
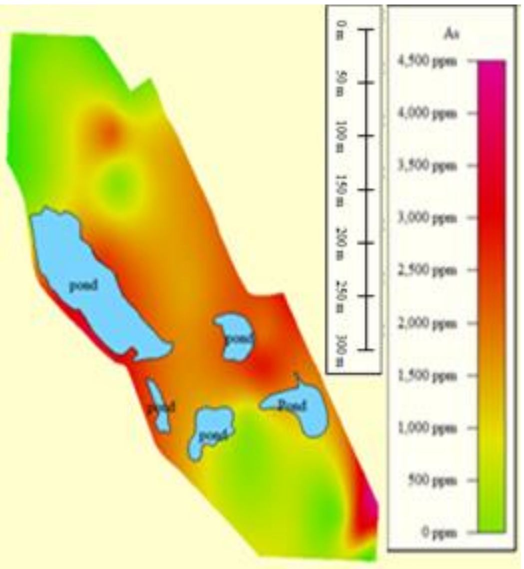


Figure 42: Triangulation-interpolated arsenic concentration in Lower valley.

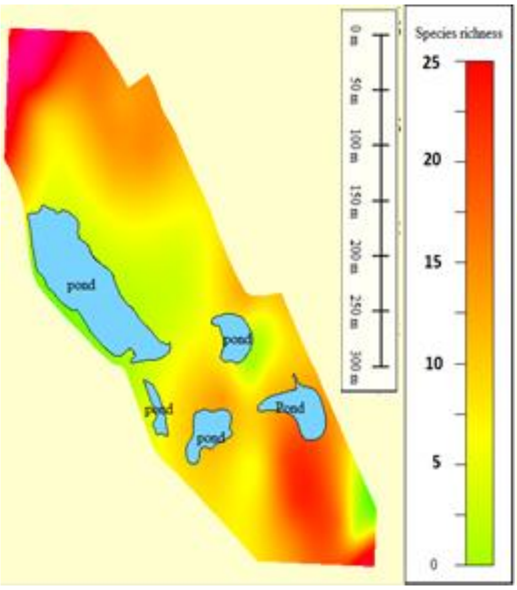
The following graphs present the spatial distribution of vegetation and investigated soil features.



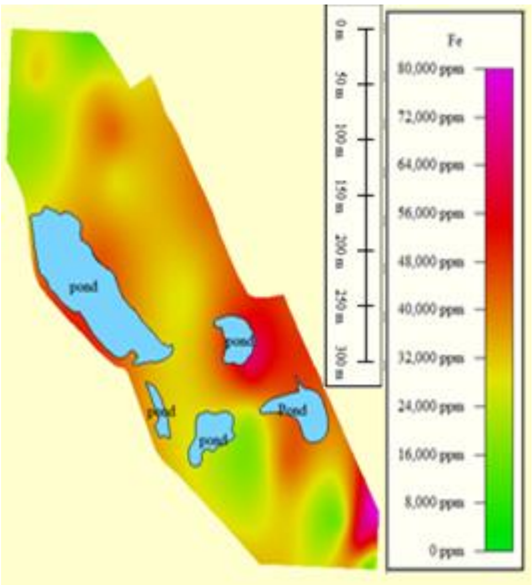
BDI



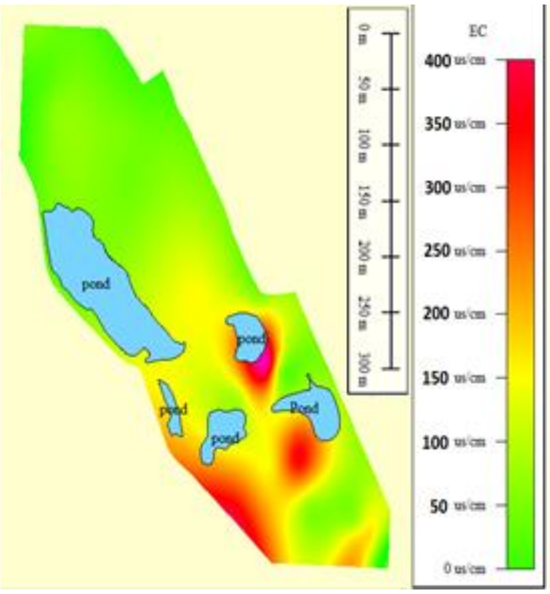
As



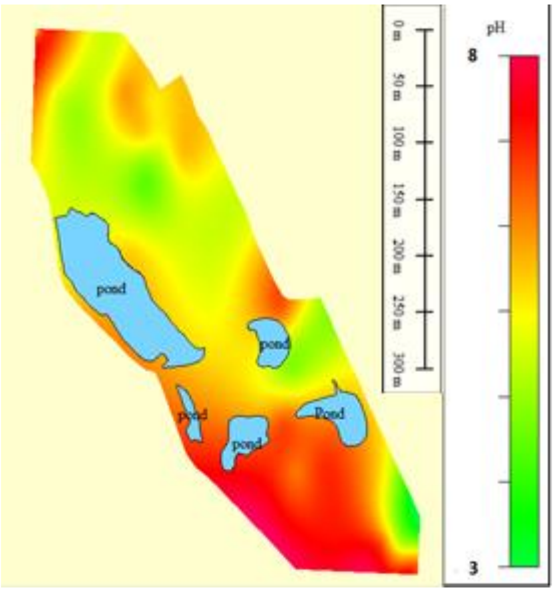
Species Richness



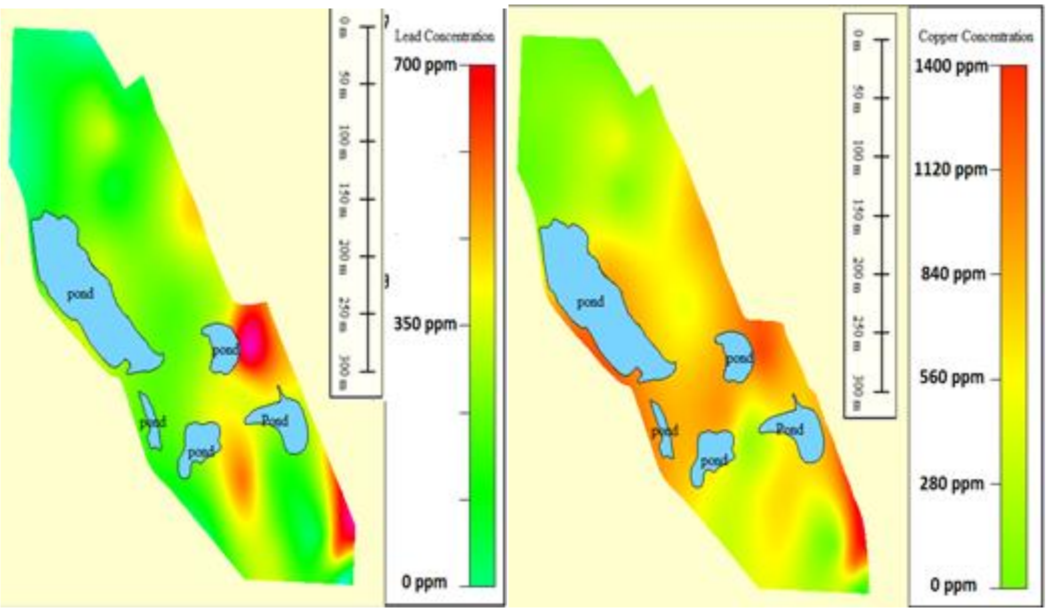
Fe



Electroconductivity



pH



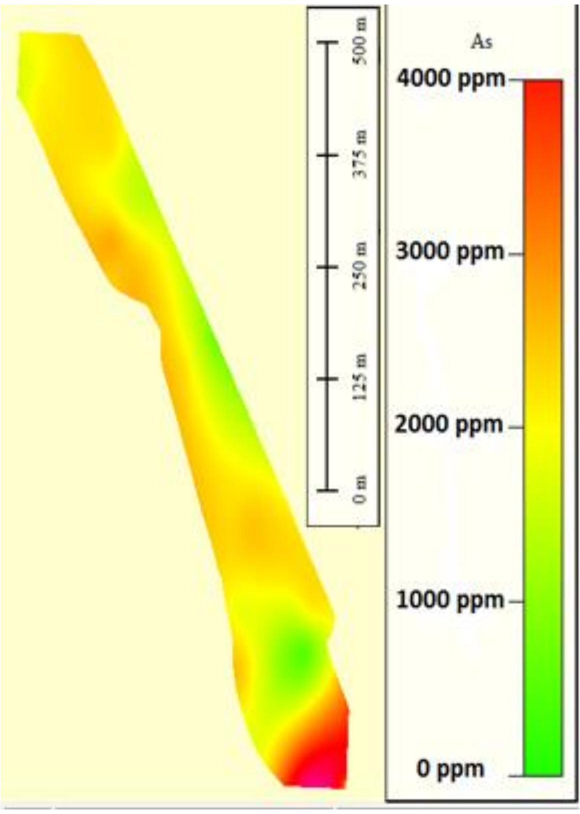
Pb Cu

Figure 43: Spatial distribution of some key features of soil and vegetation in the Lower valley.

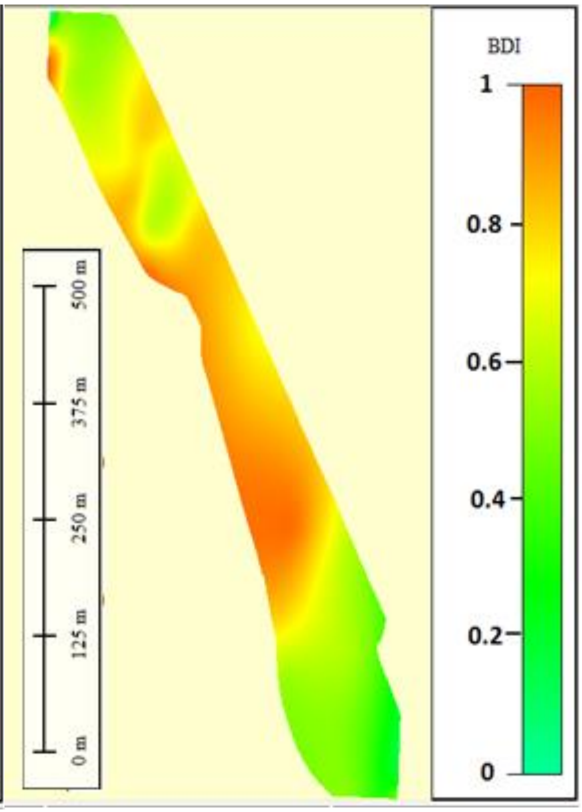
The spatial variability of the investigated variables is more pronounced in the Lower valley than in the Middle valley. Figure 43 shows that variables in the Lower valley exhibit a more heterogeneous distribution and greater variation range than the middle valley (Fig 44). As such, visualisation of variables supports characterisation of the current state of variables and complements data analysis for landscape study. It should be noted that the GIS layers is a tool of communication, which cannot be used for conclusive inference.

Table 16: Correlation coefficients of Lower valley chemical variables.

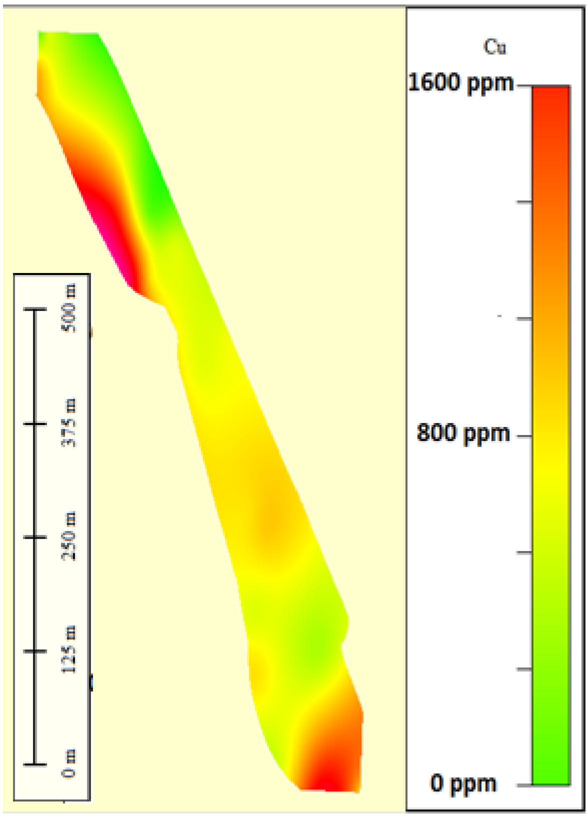
	As	Fe	Ba	Ca	K	Sn	Pb	Zn	Mn	Cu	SR	BD	EC	pH
As	1.00													
Fe	0.88	1.00												
Ba	0.01	0.16	1.00											
Ca	-0.11	-0.14	0.42	1.00										
K	-0.25	0.03	-0.11	-0.49	1.00									
Sn	0.93	0.82	0.11	0.06	-0.40	1.00								
Pb	0.70	0.71	-0.12	-0.14	-0.07	0.55	1.00							
Zn	-0.03	-0.02	0.42	0.95	-0.40	0.11	0.06	1.00						
Mn	0.49	0.68	0.29	0.14	-0.03	0.51	0.41	0.25	1.00					
Cu	0.83	0.82	-0.02	-0.07	-0.11	0.71	0.84	0.12	0.58	1.00				
SR	-0.58	-0.51	-0.01	-0.13	0.04	-0.56	-0.63	-0.18	-0.27	-0.56	1.00			
BD	-0.52	-0.56	0.04	-0.04	-0.03	-0.45	-0.66	-0.11	-0.25	-0.54	0.72	1.00		
EC	0.23	0.41	0.34	0.41	-0.05	0.34	0.33	0.52	0.55	0.33	-0.43	-0.32	1.00	
pH	-0.41	-0.38	0.16	0.44	-0.19	-0.30	-0.22	0.52	0.14	-0.18	0.38	0.34	0.15	1.00



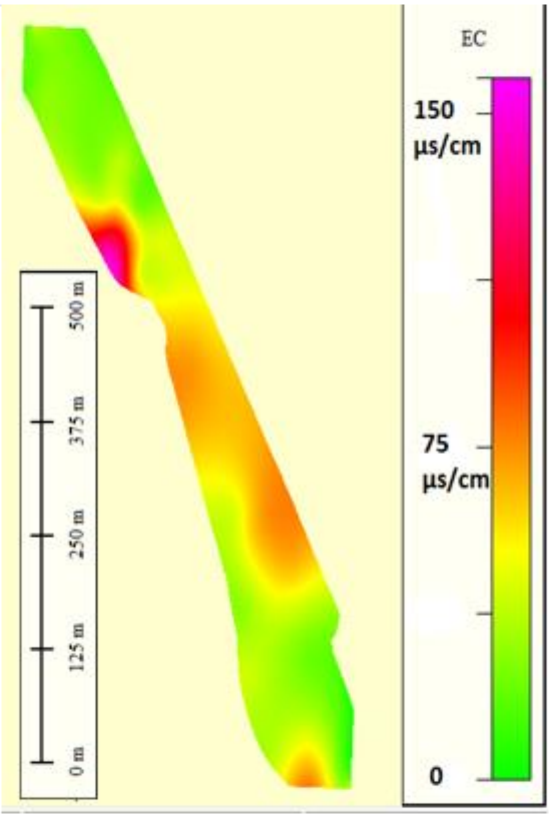
Arsenic



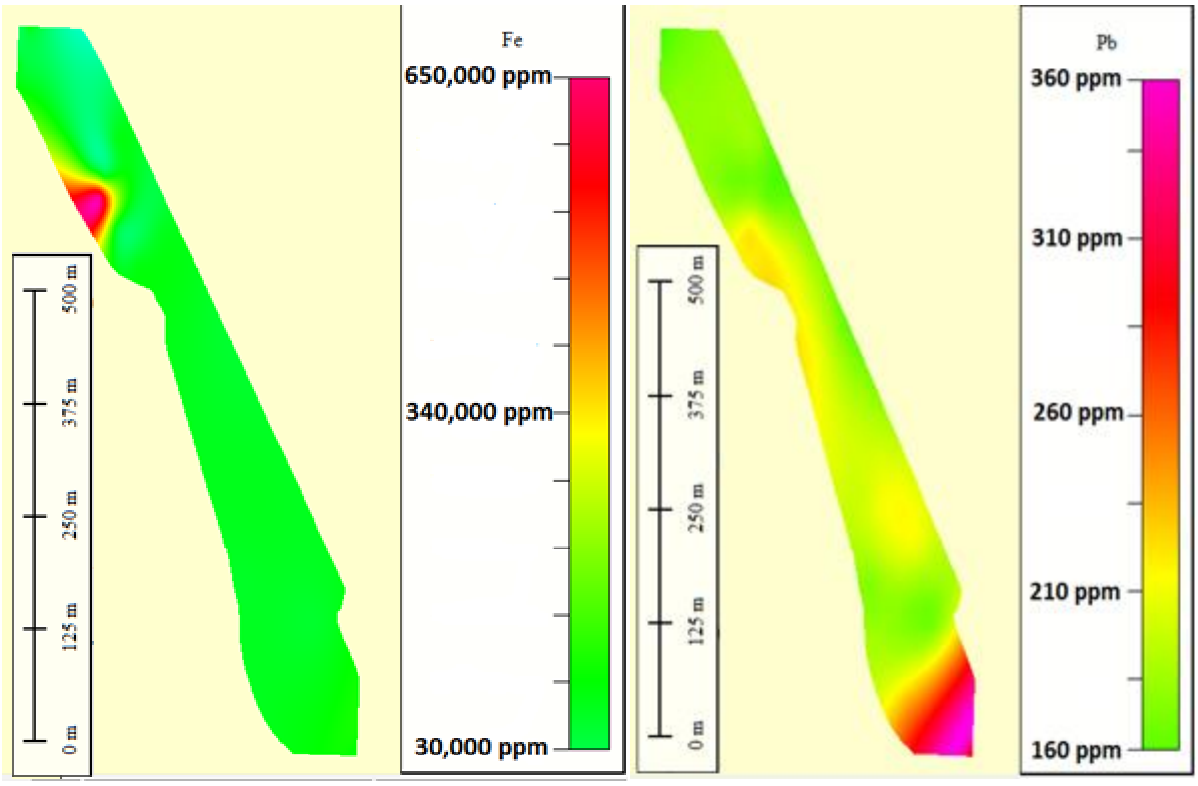
Biodiversity



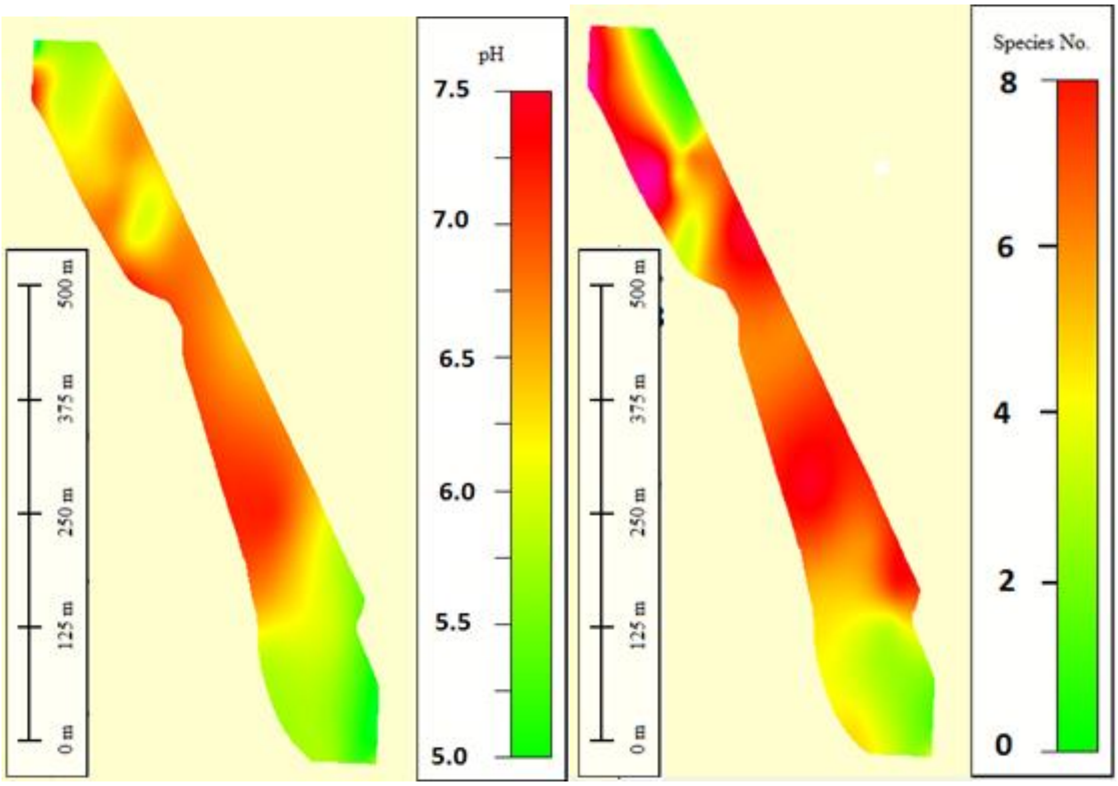
Cu



Electrical conductivity



Fe Pb



pH Species richness

Figure 44: Spatial distribution of some key features of soil and vegetation in the Middle valley.

Table 17: Correlation coefficients of Middle valley variables.

	As-1	Ba-1	Ca-1	Cu-1	Fe-1	K-1	Mn-1	Pb-1	Sn-1	Zn-1	EC-1	pH-1	SR	BD
As-1	1.00													
Ba-1	0.25	1.00												
Ca-1	-0.07	0.22	1.00											
Cu-1	0.54	0.35	0.46	1.00										
Fe-1	0.07	0.17	0.18	0.39	1.00									
K-1	0.65	0.39	-0.26	0.43	0.05	1.00								
Mn-1	0.47	0.36	0.01	0.47	0.10	0.54	1.00							
Pb-1	0.85	0.24	-0.24	0.43	-0.06	0.73	0.52	1.00						
Sn-1	0.52	0.06	0.13	0.46	0.24	0.32	0.70	0.35	1.00					
Zn-1	0.38	0.49	0.48	0.79	0.17	0.33	0.28	0.44	0.04	1.00				
EC-1	0.34	0.49	0.53	0.65	0.01	0.23	0.23	0.36	0.16	0.81	1.00			
pH-1	-0.20	0.37	0.44	0.20	0.16	-0.23	0.14	-0.32	0.13	0.27	0.25	1.00		
SR	-0.26	-0.07	0.25	-0.18	0.16	-0.40	-0.27	-0.49	0.04	-0.30	-0.38	0.42	1.00	
BD	0.32	-0.04	-0.34	0.37	-0.08	0.42	0.36	0.52	0.10	0.39	0.37	-0.37	-0.73	1.00

5.9 Local water quality

The Environment Agency carries out long-term monitoring project of the Carnon river quality. Near the study site, the Environment Agency maintains a gauge station to record precipitation and water flow data on a daily basis. Under the data open access policy, data was made available by the Environmental Agency for the period of January 1st, 2009 to September 30th, 2014. The influence of pH, temperature, and precipitation on river water quality were investigated. Although results do not necessarily represent the water quality at the study site, it provides a context about how trace elements may behave. Since the tailings in Carnon valley originate from the former mining operation at Wheal Jane, the whole area has the same mineralogical origin (Dines, 1956) and contaminant behaviour is expected to be similar.

The analysis indicates both copper and arsenic solubility are sensitive to water temperature change in winter (plants dormancy season) when water temperature is low. Further details please find in appendix E.

5.10 Precipitation

Based on four years of precipitation data (2009-2014) relating to the Carnon Valley, autocorrelation in rainfall is analysed by producing a semivariogram (Figure 45). The semivariogram curve levels off after approximately 21 days. This indicates a characteristic pattern in precipitation with a three weeks period.

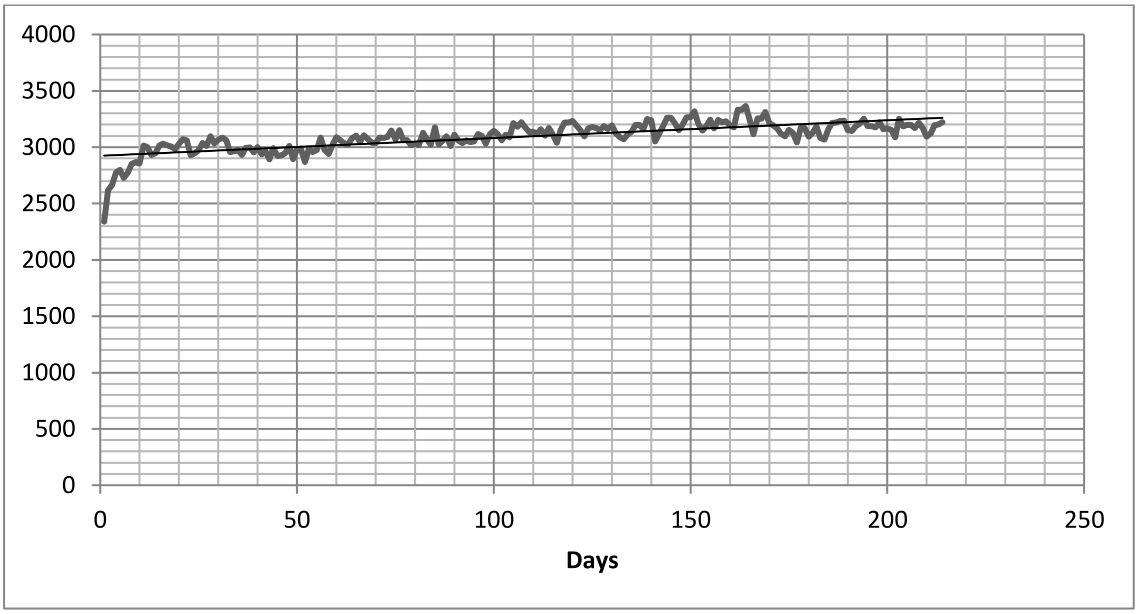


Figure 45: Semivariogram of Carnon river precipitation 2009-2014

6. Discussion

6.1 Flora development and comparison

6.1.1 Within-site comparison

The vegetation survey is used to support an overall comparison between the progress of colonisation which has occurred, in the same location from the same incoming biota on the same contaminated soil types, but differing in its topographic state at abandonment. While the middle valley has been flattened on abandonment by use of bull-dozing machinery, the lower valley features undulating areas which had been left with an overall hummock and hollow topographic structure with no bulldozing on abandonment. In the lower valley, materials were left as they had been dumped immediately before abandonment. This comparison is important, because we are unaware of any such comprehensive botanical somparison ever having been made between two such large but topographically contrasting areas, which otherwise share commonality in time-scale, biotic and climatic settings, and as this survey shows, ruling toxicity levels of the abandoned mine spoil in question. We are hence able to attribute biotic differences arising thus entirely to differences in physical sites structure (topography) present, as a valid and unique basis for comparison.

The comparison of colonisation achievement between the Middle valley (flat area) and the lower valley (undulating area) gives data a more within-site comparative basis, and thus a basis from which draw simple statistical comparisons. Since the ditch community along the study site eastern and western borders is affected by external factors accept intensively, they are excluded from the comparison. There are 12 species in the Lower valley and 24 species in the middle valley which have only been found in ditch community along study site borders. In other words, excluding the communities in the ditches, there are 75 species in the Lower valley and 18 species in the Middle valley.

The 12 species only found in the Lower valley ditch community are: *Acer pseudoplatanus, Equisetum arvense, Lemna minor, Lotus hispidus, Lythrum salicaria, Potentilla erecta, Salix alba, Sorbus latifolia, Trifolium campestre, Typha angustifolia, Vicia cracca*, and *Vinca major*. These species account for 14% of Lower valley species and nearly half (41 species) of the species found in the Lower valley (87 species) grow in ditch community.

The 24 species only found in the Middle valley ditch community are: *Agrostis curtisii, Arum maculatum, Asplenium scolopendrium, Athyrium filix-femina, Bellis perennis, Buddleja davidii, Epilobium lanceolatum, Ionicera periclymenum, Lotus corniculatus, Lotus subbiflorus, Lythrum portula, Planto coronopus, Polypodium interjectum, Primula vulgaris, Pteridium aquilinum, Quercus robur, Ranunculus repens, Rumex crispus, Silene dioica, Tenucrium scorodonia, Urtica dioica, Veronica chamaedrys, Vicia cracca*, and *Viola canina*. These species account 51% of all species found in the Middle valley. On the other hand, among all 42 species found in the Middle valley only 3 species were not present in ditch community. Although it is difficult to identify the factor which is more significant to promote species richness in ditch community. Better water availability and human disturbance are the two top candidates.

Among all of the species found in ditch community, there is one species present in ditch community only in the whole study site. It is *Vicia cracca*, a common species in roadside ditch.and disturbed land.

The species richness in the Lower valley and the Middle valley ditch communities is quite high. This makes it highly desirable to evaluate which factor, footpath or country road, contributes more to promote species richness. The footpath and country road ditches differentiate themselves from each other by users (automobile traffic in country road and dog walkers, bicycle riders and horsemen on footpaths) and surface treatment (asphalt paved county road and footpath is a dirt road). Therefore, the two ditches experience different degree of human disturbance and have different water-collecting areas. The two ditch communities are divided into two groups to identify which one has a higher species richness (Table 18). The species richness in ditch community along footpath and country road in the lower valley and middle valley are irregular. A reasonable inference cannot be made. Both in the Lower valley and the Middle valley, the ditch communities have a high species density, which potentially represents an edge effect because of water availability.

Table 18: Species number along footpath and country road in the Lower and Middle valley

Lower Valley Ditch		Middle Valley	
Footpath	Country road	Footpath	Country Road
21	30	35	19

6.1.1.1 Comparison of overall biodiversity progression

The comparison of floristic diversity occurring after the time scale of abandonment of the whole valley allows valid fundamental comparisons to be made between species components actually present on a flat areas compared with an undulating one. The survey basis is probabaly the most detailed ever achieved over two such large, adjacent areas which share a common history with the exception of the physical structure (flat versus undulating) in which the sites were left on abandonment.

Figure 46: Some pictures of the lower valley demonstrate the biodiversity richness.

Figure 47: Some pictures of the middle valley demonstrate the poor species richness.

Figure 46 and 47 demonstrates the additional biodiversity richness achieved between the areas of contrasting topographic structure, and allowfurther analysis. Hendrychová (2008) has stated that technical reclamation causes the loss of biodiversity, compared to what could be achieved by spontaneous natural rehabilitation. The biodiversity and species richness in the Middle valley may have been condemned by bulldozing.

6.1.1.2 Gain of drainage

The drainage available in the abandoned spoil surface and a medium for natural plant colonisation process is always fundamentally influenced by the availability of soil drainage profiles. We hence demonstrate that the greatest diversity of drainage profile diversity through the mosaic-pattern of the undulating topography produces areas of maximised biodiversity. This is especially significant for establishing vegetation in a region with such a high annual rainfall as west Cornwall. Highest drainage will thus be present on mounds, lowest drainage in depressions. In the deepest hollows, water accumulates for varying period, resulting in year-round standing-water ponds. Each of these have gradated biotic communities which are able to develop following these patterns. A factor enhancing the differences is the degree of natural compaction. In the undulating areas of the Lower valley, the vertical soil profile settlement has always been without un-natural compaction whereas, in the flat areas (Middle valley), application of pressure by machinery flattened the surface. This has un-naturally compacted the soil profile from the very beginning of abandonment in the Middle valley.

6.1.1.3 Gain of aspect availability

In addition to a gain of a mosaic of drainage patterns achieved in the Lower valley, is also an integrally associated gain in site-aspect due tio the undulations of the resulting site-structure. Such differences in aspect (including not only north-south but also east-west, and all intermediates) offers sites which hence are subject to different illumination patterns on a daily basis and which can influence the evaporation rate on a daily basis. This opens opportunities for a far wider range of biodiversity to successfully establish, from light-demanding (eg. many pioneer flowering-plant species) to more shade-tolerant species (eg ferns).

Such shade contrasts are expected to correlate with the greatest undulations in the topography, and will also tend to increase in degrees of contrast as vegetation establishes itself (especially upgrowth of more woody species). The latter add availability of further, deep shade on slopes with a more northern aspect compared to better illuminated south-facing slopes. These contrasts will be present in sites which have not suffered from excessive artificial compaction (see above) and contribute to their natural vegetation-availability.

6.1.1.4 Enhancement of site dynamism

All slopes are unstable when compared with entirely flat ground, and hence overall areas where topographic variation is maximised can be expected to display the most dynamic revegetation behaviour. This is reflected in patterns of developing erosion, which are always greatest on the steepest slopes and smallest on the flattest areas, especially where these have been additionally compressed. Slopes are positive for vegetation development, in that resulting erosion slopes open and re-open new sites for pioneer establishment, often integrally amongst already-establishing vegetation patches, which allow for new rounds of colonisation by pioneer species to begin again.

Such dynamism itself occurs as irregular patterns, adding additional mosaic-structure, imposed on all previously present, and thus further contributes, in the most undulating areas, to the richness of vegetation mosaics intimately arising, which have thus strong contrast to those of flatter areas which are much more devoid of such post-abandonment dynamic processes continuing.

6.1.1.5 Gain of multiple edge-effects

Much overlooked, but an inevitable consequence of the gain of patterning to resulting communities, is the gain not only in contrast between them, but also the increasing of gain in edge effects between them, which becomes increasingly greater with subsequent vegetation development, and hence with contrasts between areas. These are the total of contrasting margins achieved, and their intimacy with one another, and variety of communities which they separate, whose gain can be expected to be that of progressing in contrasts as vegetation communities develop. Hence, such edge effects themselves contribute significantly to the structural diversity of overall environment.

6.1.1.6 Principles concluding

Analysis of the differences resulting in biotic success in areas of such contrasting topography and which are overall similar in all other factors (see below) is an opportunity to demonstrate not just differences which are appearing on the Carnon Valley site, but especially of general principles which are much more widely applicable to other mine-sites in other areas, and the likely success and diversity of vegetation which can be expected to develop upon them.

These principles then have important outcomes in considering the types of bio-engineering required (however modest this may be), to achieve enhanced biodiversity success, if such future elements are to be considered as ultimate objectives of post-industrial mine-site usage.

These analyses demonstrate that bioengineering of mine site topography can be a basis and fundamental step towards enhancement of ultimate biodiversity, and that such routes can be a cost-effective approach to such ultimate site-enhancement benefit. Should it be appropriate, such initial bioengineering can also be integrated with construction of necessary access routes for use for further monitoring of progress of site-recovery, as objectives may demand.

Long-term gains are likely to be not just enhancement of the biodiversity itself, as estimated here through species sampling, but also longer term in gain within such biota of enhanced genetic diversity, especially of genotypes of plants of enhanced tolerance levels to unusual and especially toxic terrains, and thus as even seed-sources for future utilisation towards enhancement of colonisation achievement in future areas on contaminated mine-site abandonment.

6.1.2 Cornish flora comparison

Any inference about site ecology must be made with consideration of the local and regional context of the site. Cornwall is one of the most extensive biologically-monitored counties in Britain or anywhere in the world. Local ecologists have organised numerous field surveys to record species richness. The latest Cornwall flora survey was published in 1999 (French, 1999). This survey is used in this research to understand the significance of the rehabilitation in Carnon valley.

The Cornwall flora survey subdivides Cornwall into 2 km X 2 km tetrads and records all species present in each tetrad, regardless of their abundance (French, 1999). The species density of selected tetrads can be compared with the research site in the Carnon Valley, providing a better understanding of rehabilitation patterns. While the area of a tetrad is more than one hundred times larger than the Carnon Valley site – the middle and Lower valley covers about 15 hectares – a comparison of species densities is necessarily flawed. However, it does provide an indication of the conservation value of the Carnon Valley.

Considered in its entirety, the Cornwall flora survey indicates how common each species is in Cornwall. This helps to identify which species found in the Carnon Valley may be classified as locally rare.

6.1.3 Rare and unusual species present

The appearance frequency is defined as the number of tetrads in Cornwall in which a species is recorded, divided by the total number of tetrads. The appearance frequency of all species found in Carnon Valley was calculated; the result is presented in Figure 48.

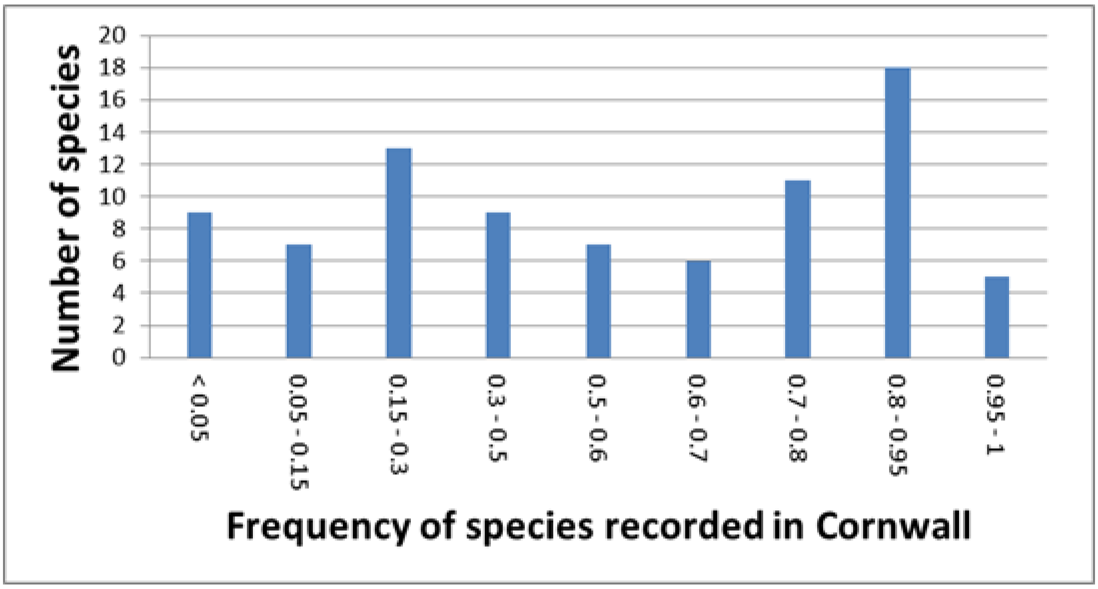


Figure 48: The appearance frequency of Carnon Valley species throughout Cornwall.

Species recorded in the Carnon Valley which are found in less than 5 % of the tetrads in Cornwall are considered to be locally rare species. The following rare species are observed in the Carnon Valley:

- Lucerne (*Medicago sativa)* was recorded in the Carnon Valley since 1979. French (1999) assumed it came from cultivation. Although it is not native to Cornwall (Bennallick, 2009), it poses no threat to the local habitat because it is not an aggressive species under local environmental conditions.
- Lesser Centaury (*Centaurium pulchellum*) is found occasionally in coastal areas and seems to prefer a salty habitat. It is also recorded in quarries, wastelands and mineralised soil (French, 1999). Therefore, it can be considered as a pioneer or tolerant species.
- Rose of Sharon (*Hypericum calycinum*) is a fugitive from gardens and found in wasteland, hedges and walls (French, 1999). It is an alien species but not aggressive.
- White Willow (*Salix alba*) spread into different part of Cornwall randomly and first recorded around Carnon Valley after 1979 (French, 1999). It is a native species but relatively rare. It is unknown whether it is out-competed elsewhere or habitat selective.
- Water Forget-me-not (*Myosotis scorpioides*) (French, 1999) is an alien species in Cornwall and easily confused with Creeping Forget-me-not

(*Myosotis secunda*), which is the most common forget-me-not found in waterlogged places in Cornwall. Bennallick (2009) pointed out it is a native or archaeophyte species.

- Little Mouse-ear (*Cerastium semidecandrum*) is a native species (Bennallick, 2009) which prefers a maritime habitat and is extremely rarely found inland (French, 1999).
- Heath Dog-violet (*Viola canina*) is a very rare species in the local area, though it is native to British Isles but in rapid decline (French, 1999; (Bennallick, 2009). It has been recorded in two sites and one of them was given Special Area Conservation (SAC) status. Therefore, its presence in the lower and middle valley indicate the significance of post mining natural rehabilitation for biodiversity conservation.
- Wild Lettuce or Great Lettuce (*Lactuca virosa*) has not been recorded after 1974. French (1999) believes it was introduced by shipping.
- Devon Whitebeam (*Sorbus devoniensis*) is a native species to Cornwall and Devon. It is a nationally-scarce tree but its habitat is not protected. French (1999) only found two records of this tree in Cornwall. Hedge cutting poses a threat to its distribution.

The composition of rare species is a mixture of alien and endemic species, herbaceous and woody plants. Some of them are known wasteland plants or prefer mineralised soil.

As a native species, Devon Whitebeam (*Sorbus devoniensis*) and Heath Dog-violet (*Viola canina*) are in decline and becoming rare in Cornwall. These may be less competitive or vulnerable to disturbance. Cornwall has the mildest climate in Britain and has been used as the first stop for introduced species. Therefore, native species are exposed to relative high competition while intensive mining activities also altered the local geochemical and ecological environment significantly. French (1999) has demonstrated this change by showing the differences of species occurrence between two flora surveys in Cornwall, in 1979 respectively 1999.

The presence of rare native species may also indicate local species are more tolerant to soil contamination. The phytotoxicity in Carnon Valley reduces competition and creates a refuge for tolerant species. Consequently, leaving a post-mining site to natural rehabilitation has significant value for ecological conservation and biodiversity.

Except for *Viola canina*, all rare species in the Carnon Valley were found only in the Lower valley. This suggests that the Lower valley has a higher conservation value and sets a good example on how to optimise species richness and biodiversity during a mine closure project.

While the Cornwall flora survey used 2 km x 2 km tetrads, it potentially did not attend to detail as much as the study of the much smaller Carnon Valley site. Therefore, the Red Data Book of Cornwall (Bennallick, 2009) is used as a quality control measure in this study.

6.2 Aerial overview of vegetation progression

The field survey carried out for this study only reflects vegetation structure in the year 2013. As such, it cannot reflect the succession of rehabilitation dynamic in the valley. Aerial photos taken by Google Earth (2013 and 2001) are used to give a coarse reflection of vegetation pattern development in the valley. Though coarse reflection from secondary data is not sufficient for scientific research and are not precisely dated, it is still beneficial for the understanding of natural rehabilitation progression in the valley.

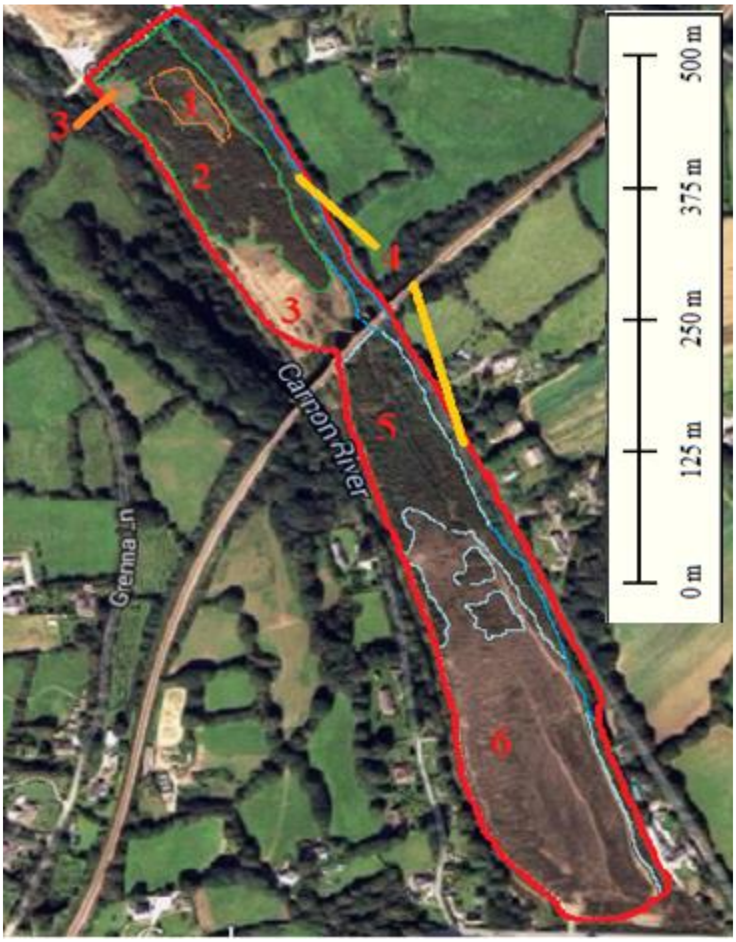
During the field survey in 2013, six habitat modes were identified in the Middle valley. These include the *Calluna vulgaris* dominated heathland, *Ulex europaeus* dominated shrub, and the transition zone between them where *Salix atrocinerea* is the dominant species. The vegetation assemblage can be clearly discerned in a bird's eye picture (Figure 49) and is numbered as zone 1 through to zone 6. Inside *Ulex europaeus* dominated shrub, leggy gorse starts to make space (Figure 49, zone 1) which suggests the onset of secondary succession. However, seedlings of *Ulex europaeus* are the only species to establish in these spaces. It should be noted that the life span of *Ulex europaeus* is about 25 to 30 years (Lee, 1986). While the age of gorse in the Carnon Valley is no more than 20 years (established after the Wheal Jane mine closed), it is postulated that the shorter life of gorse in the Carnon Valley is a result of increased environmental stress. The barren land (3) and *Ulex europaeus* regrowth underlines the colonisation barrier which still exists and indicates the potential for future colonisation.

Along the eastern edge of Middle valley, there is an elongated belt (4) which hosts a distinctly different vegetation community. Within this area, trees such as *Quercus robur*, willows and *Betula pubescens* are the dominant species. Ferns, ivy, *Rudus fruticosus* and other sciophilous plants also are common. This area is developed along a ditch which collects precipitation from the valley and neighbouring road. The edge along west side of the valley is dominated by herbaceous species and occasionally rhododendron, *Betula pubescens* and willows.

The well-developed plant community along the edges of Middle valley is possibly a result of the following factors:

1. Disturbance. Along the edges are a traffic road, a foot path, and a cycle path. The foot path has been used for dog walking, horse riding, jogging and other recreational activities. These activities could produce litters and disseminate seeds. Animal excretion will enrich soil nutrients and enhance microorganism activities which could reduce heavy metal solubility and inhibit vegetation uptake. Water ditches can improve water penetration into the soil and create a niche for hygrophilous plants. Note that a paved road adjacent to the ditch will add a large volume of precipitation to the ditch. Some researchers classify the ecological system developed around water ditches as a ‘ditch community’ (Armitage, 2003). Therefore, the rehabilitation pattern along the edges is not a typical mine site rehabilitation pattern. It is unlikely to impose the same intervention to a vast post-mining area to encourage natural rehabilitation. However, it does indicate the potential of edges in biodiversity improvement in mine site rehabilitation.
2. Distance. The study site is located in the bottom section of the Carnon Valley. Private gardens and farms are distributed along both sides of the valley slopes; these act as the main seed-bank for natural recolonisation. The site edges are closer to seed sources which give these an advantage in early stages of natural rehabilitation. Distance is especially important for species which are not dispersed by wind.

3. Toxicity. The edge of the middle valley is drainage ditch, which has extensive drainage of rainwater in most of the time. Therefore, bio-available toxicity maybe significantly reduced Hence, the substrate along the edge maybe is less detrimental to vegetation..



1. Gorse replaced by woody species.
2. Dense gorse
3. Barren land with sparse pioneer species
4. Shrub, woody species mixed with herbaceous species along ditch
5. Mixed woodland
6. Dominanted by common heather

Figure 49: Bird eye view of Middle valley in late succession stage (Google Earth, 2013). Numbered zones used for the convenience of succession comparison of Middle valley.

The two photos of Middle valley with a time gap (Figure 49 and Figure 50) show that the open space in zone 1 used to be covered by intense gorse shrubs. Zone 5 used to be occupied by *Calluna vulgaris* and has now turned into dense woodland. The advancement of woodland in southerly direction is evident and the barren land to the north separates gorse shrubs from the woodland.

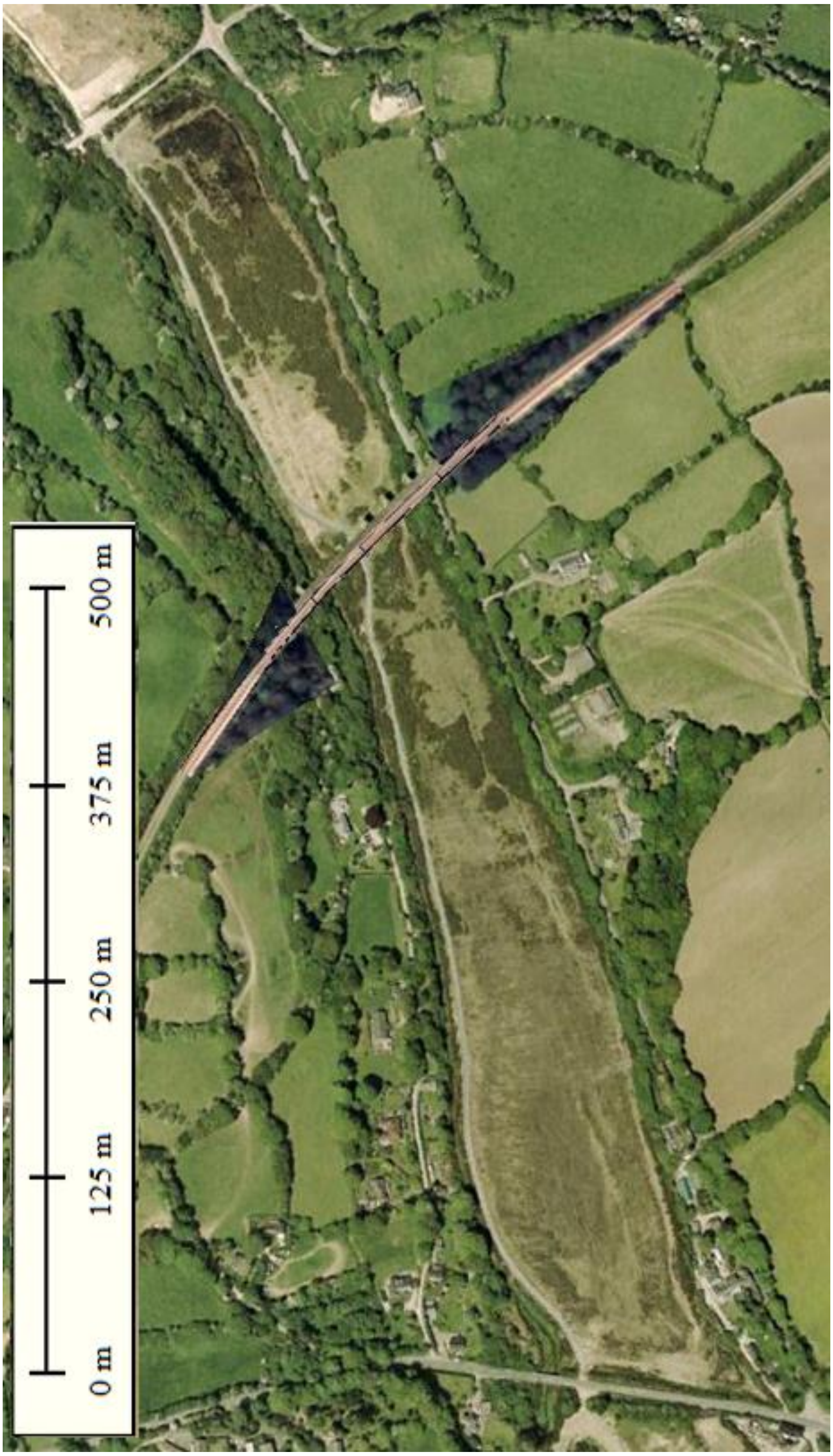


Figure 50: Bird view of Middle valley in early succession stage (Google Earth, 2001).

The field survey suggests that the Lower valley can be roughly divided into two parts: a northern part which is a little highland mainly made of waste rock tipping, and a southern part which has several former settlement ponds for mine tailings.

To understand the development of primary succession in the Lower valley, two photos from Google Earth are discussed (Figure 51 and Figure 52). Compared to the Middle valley, the plant community in the Lower valley is sparser. The area of barren land (zone 1) in the Lower valley is much bigger and decorated with some ponds (zone 2). There is no single species which dominates a large area in the Lower valley. A heathland (zone 3) plant community only established itself along the banks of ponds.

In the southern part of the Lower valley, mixed woodland (zone 4) is only found next to water ponds. The sparse plant community reflects the uneven availability of resources. The Lower valley may give more information on limiting factors for natural rehabilitation. Vegetation colonies have mainly developed along ditches or ponds, which reflects the importance of water availability for pioneering species during the rehabilitation process. As observed by Haghnazari et al. (2015), clayey soil may affect rehabilitation by regulating water distribution and infiltration, the uneven distribution of bioavailable heavy metals is another influencing factor. This uneven distribution may arise from geological processes, relocation by precipitation, or chemical transformation. The local micro-topography, or hummock-and-hollows structure, may have played an important role in relocating soluble toxicity through precipitation and runoff.

1. Barren land with acid grass species and heather.
2. Ponds
3. Dominated by heather
4. Shrub mixed with woody species

Figure 51: Aerial view of the Lower valley plant communities in a later stage of succession (Google Earth, uploaded in 2013). Numbers indicate different land coverage.

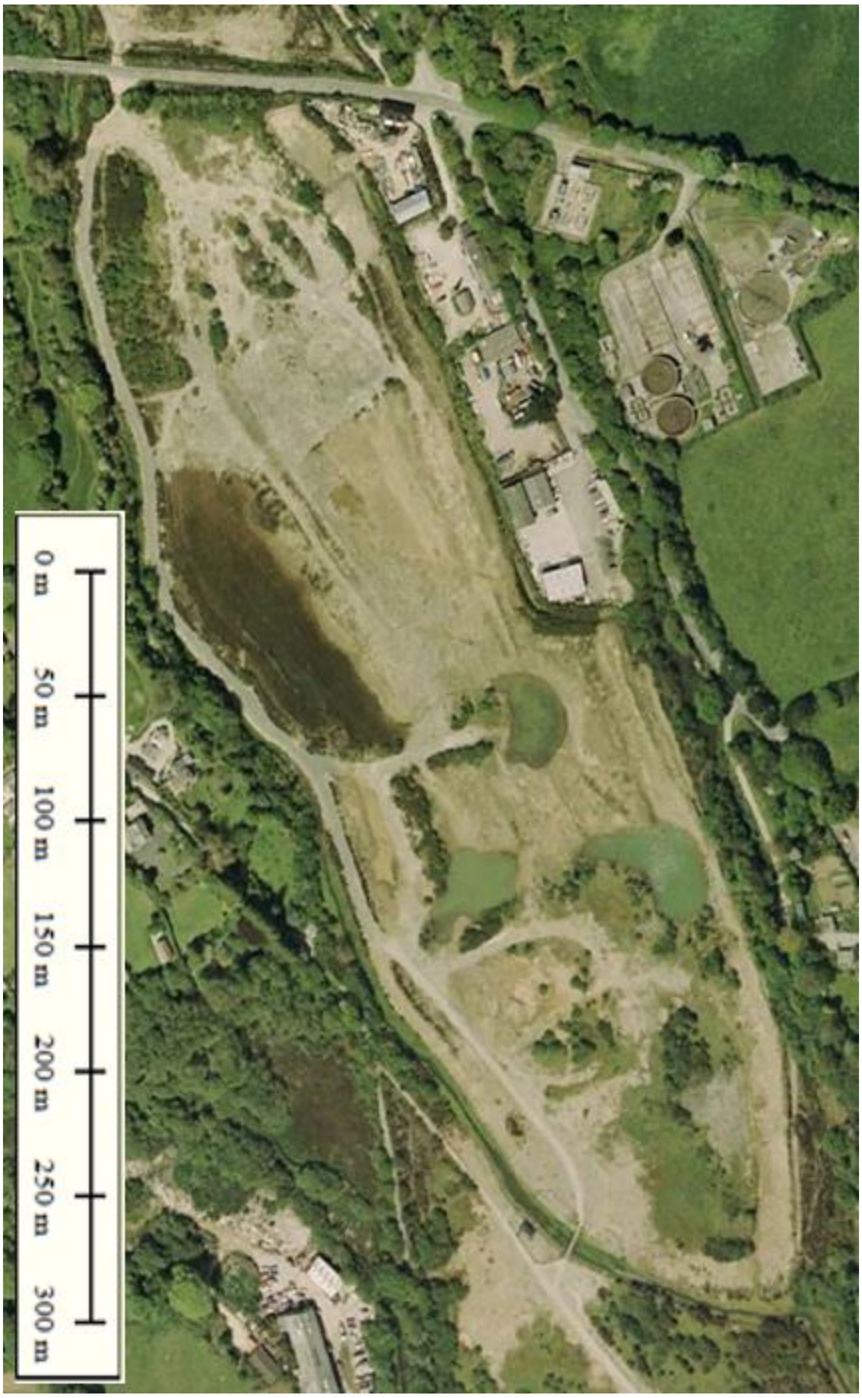


Figure 52: Aerial view of Lower valley plant communities in an early stage of succession (Google Earth, uploaded in 2001).

The findings show that two different vegetation cover patterns occur in the Carnon Valley. The first cover type is a mosaic distribution of plant patches with great contrast in plant structure and composition, as observed in the Lower valley. The second cover type is a homogeneous vegetation coverage with less diversity, as found in in the

Middle valley. Compared to the Middle valley, the species richness in the Lower valley is twice as high, although it is smaller in size (7.1 hectare versus 8 hectares of the Middle valley). Since the two sites are separated by a dual track road only, the difference in species richness is more likely to be due to habitat selection rather than physical barriers. Note that the main species richness in the Middle valley is only found along its egdes (section 6.1.1) implying that the actual homogeneity of species composition is even higher there than in the Lower valley.

It is difficult to provide a simple answer whether the rehabilitation mode of the Lower of Middle valley is better. It depends on subjective judgement and the objective of rehabilitation. When a target area is close to a community or prone to erosion, rapid vegetation establishment and high coverage is highly desired to reduce migration of pollution. In that case, the rehabilitation mode of the Middle valley is best. In contrast, nearly half of Lower valley is unvegetated.

If a highly diverse ecological community is attractive, lessons learnt from the Lower valley are more valuable. Even without excluding the barren ground and water pond in Lower valley, the species density in Lower valley is above average in Cornwall. While over 99% of Cornwall land area has less than 113 plant species per square kilometre, the Lower valley has 88 species in 7 hectares (=0.07 km^2).

These two rehabilitation patterns have practical value in different scenarios. A well-defined rehabilitation target should be defined to facilitate substrate preparation and enable human-induced natural rehabilitation to develop in the desired direction.

6.3 Influence of soil properties

Chemical analyses reveal that chemical soil properties in the two sampled layers of soil are different. However, differences as a function of deptyh are relatively small compared to the differences observed between quadrats.

Mineralogical analyses show that arsenopyrite is the main arsenic-bearing mineral which is experiencing different stages of weathering. While the grain size of arsenopyrite is in the order of µm, its weathered product is even smaller and below detection limit. Therefore, it was not possible to identify scorodite or other secondary minerals during SEM analysis. XRD analyses suggest all substrate have a common parent material because all minerals with 5% or higher concentration are the same species.

Since this area has been used as a settlement pond, the local substrate has a relatively homogenous fine texture. Size analysis showed that the majority of substrate particles is between 20 to 40 µm (section 5.2.2). Therefore, soil texture contributes little to a heterogeneous vegetation coverage pattern. As shown in Figures 53 and 54, soil strength and vegetation diversity are not linearly correlated in this study. This observation is supported by ordination analysis (section 5.6.2). For quadrats with high soil strength, species richness and biodiversity are only slightly lower.

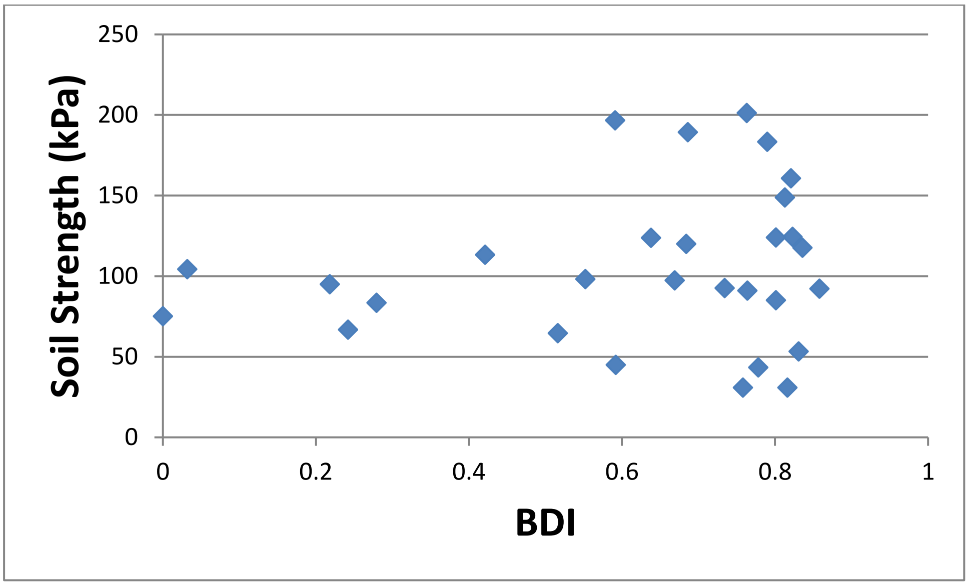


Figure 53: Correlation between soil strength and biodiversity index.

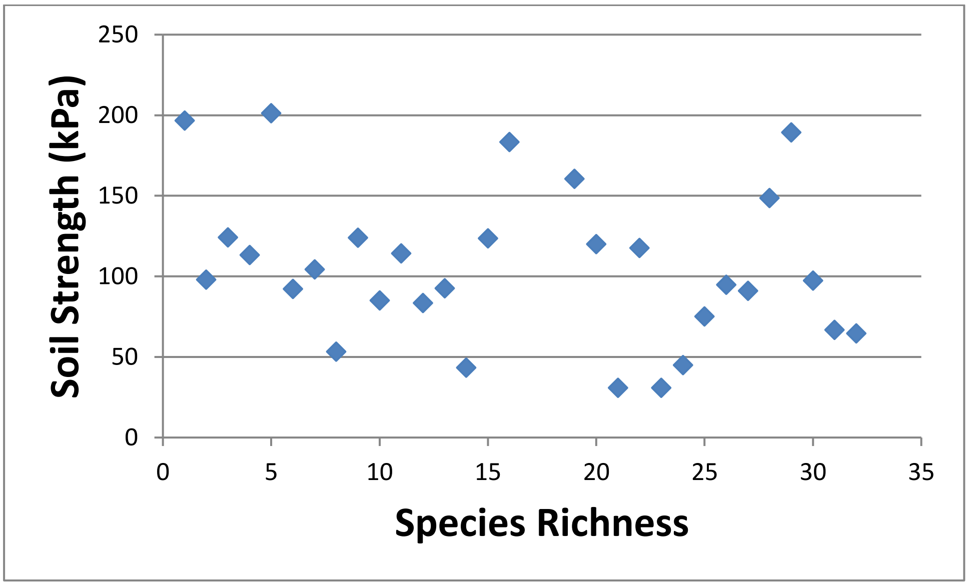


Figure 54: Correlation between average soil strength and species richness

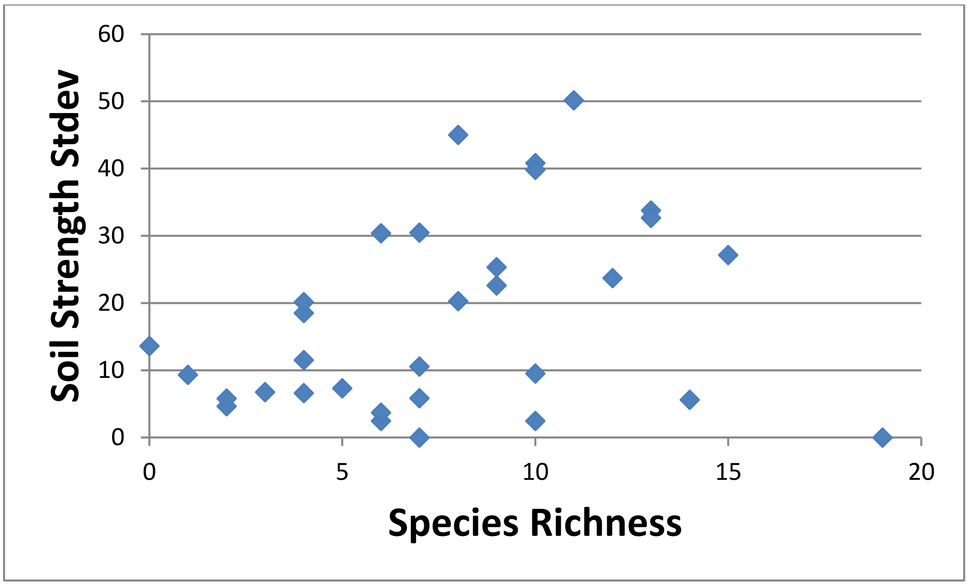


Figure 55: Correlation between soil strength standard deviation and species richness

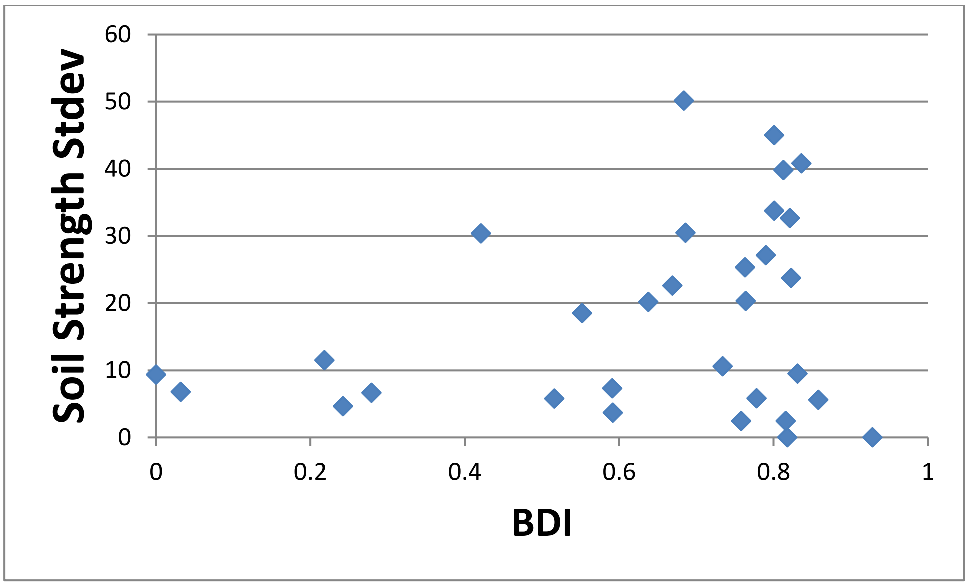


Figure 56: Correlation between soil strength standard deviation and biodiversity index

In some quadrats, the variation of soil strength is considerable. Therefore, the average soil strength in each quadrat does not necessarily correlate with vegetation development. To evaluate the impact of local soil strength on vegetation diversity, the standard deviation in soil strength is used (Figures 55 and 56). However, no evidence can be found that soil strength has direct impact on local vegetation development.

No clear impact of soil acidity on local biodiversity is observed in a scatter plot (Figure 57) but ordination analysis suggests its impact. It indicates the potential or ordination analysis in complex ecological study.

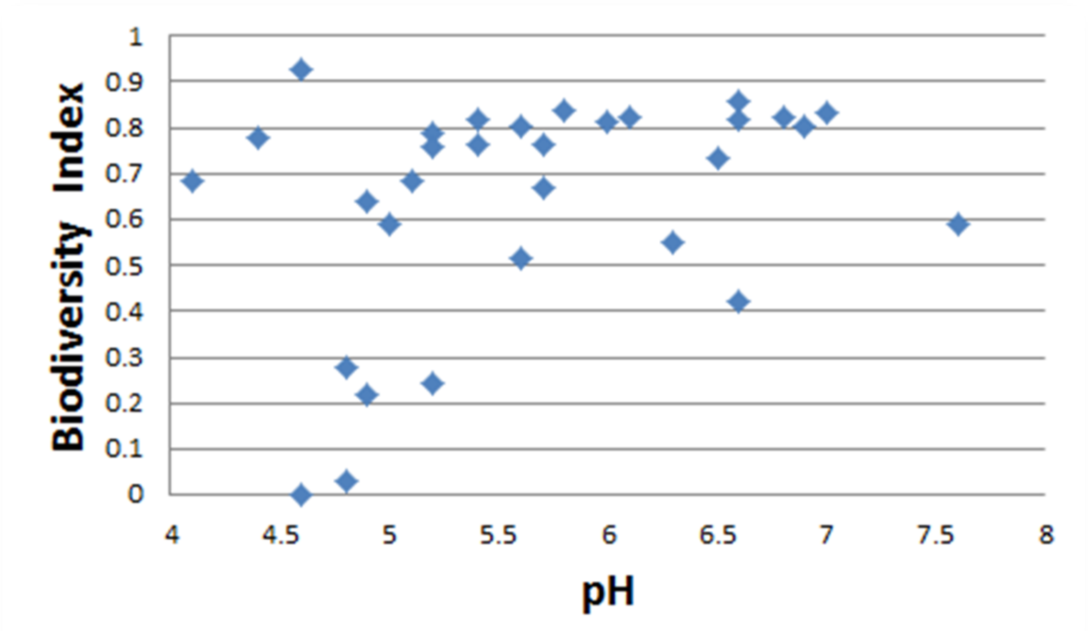


Figure 57: Influence of soil acidity on Simpson biodiversity index.

According to Skousen (1994), herbaceous species would recolonise a site provided that the pH is equal to, or exceeds, 5. The presence of high biodiversity in some quadrats with pH between 4 and 4.5 (Figure 57) indicates the presence of tolerant species in Carnon valley.

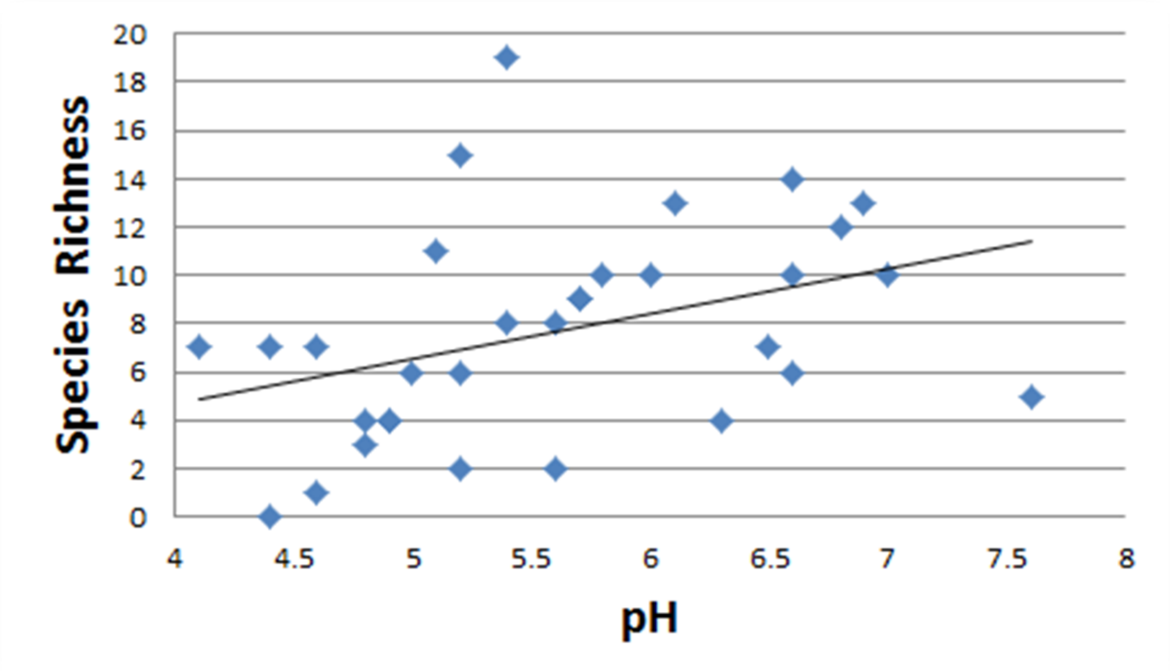


Figure 58: Influence of soil acidity on species richness in surveyed quadrats.

Figure 58 shows a small but positive effect of rising soil pH on local species richness. Since soil acdification is accompanied with increasing trace element bioavailability, the indistinct effect of increasing pH may represent a complex collective effect of reduced soil biotoxicity. This tendency can be observed more clear after ordination analysis reduce its complexity (section 5.6.2).

Correlation analysis shows that arsenic, copper, and lead are negatively correlated with indicators of vegetation development (Table 19). This observation is supported by RDA analysis (section 5.6.2). The weak correlation coefficient represent the uneven arsenic, copper, and lead bioavailability or synergistic effects across the valley.

Table 19: Correlation between element and habitat indicators

	Species richness	BDI
Arsenic	-0.58	-0.52
Copper	-0.56	-0.54
Lead	-0.63	-0.66

6.4 Impact of arsenic on vegetation

The only arsenic compound found in SEM analysis is arsenopyrite (FeAsS) at different stages of weathering. A high correlation coefficient (>0.9) is observed between iron and arsenic which supports the notion that these elements are co-deposited.

Plotting the species richness versus the total arsenic concentration in quadrats reveals two distinct clusters (Figure 59). Quadrats with higher arsenic concentration in the soil tend to have lower species richness (Cluster B).

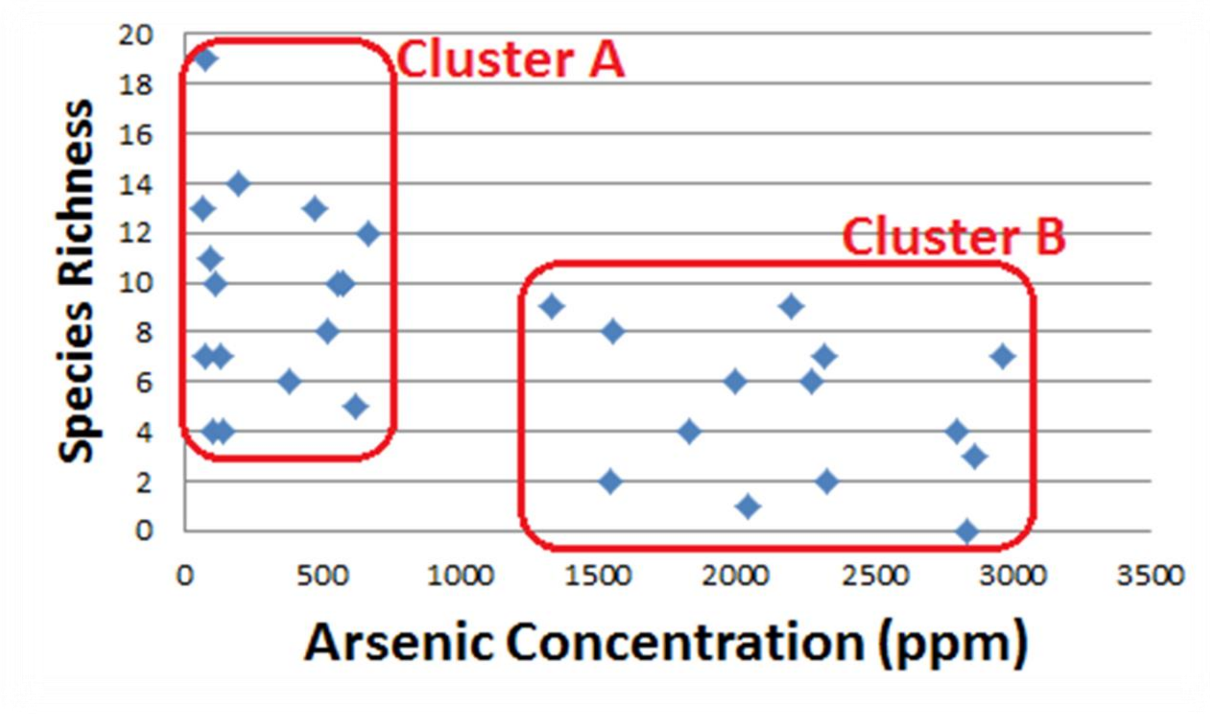


Figure 59: Clustering of quadrats according to species richness and arsenic concentration (ppm) in the Lower valley.

The Simpson biodiversity index in the 32 Lower valley quadrats varies between 0 and 0.93. This high variation in the makeup of the vegetation assemblage indicates an uneven distribution of resources and stressors. It demonstrates the unpredictability of the natural rehabilitation process and suggests that due care and effort is required to make a rehabilitation project successful. The key finding is that natural rehabilitation still is feasible in sites with up to 3000 ppm soil total arsenic.

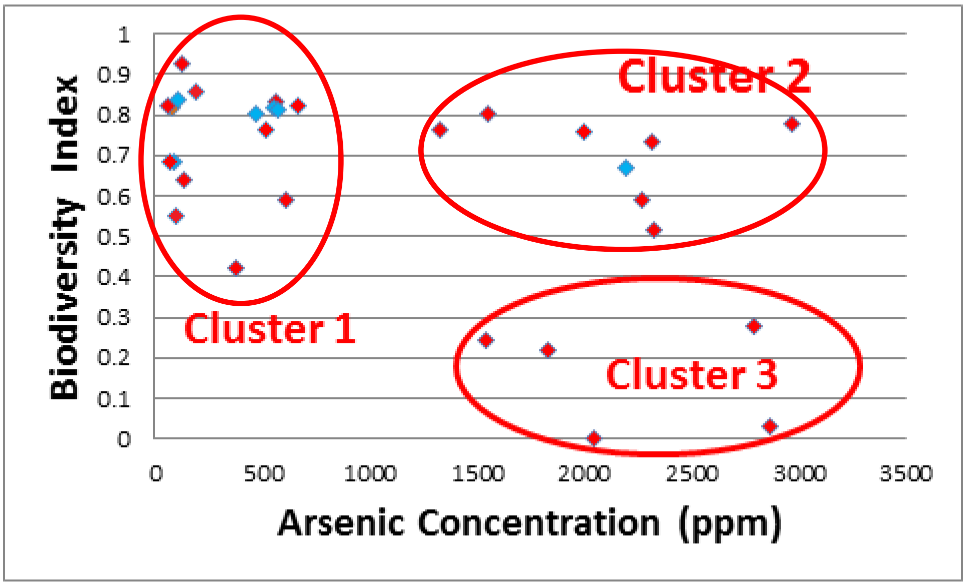


Figure: 60: Clustering of quadrats according to biodiversity index and arsenic concentration (ppm) in the Lower valley. Red dots represent quadrats which have been used for composite sample preparation.

Figure 60 shows the Simpson biodiversity index plotted against total arsenic concentration in a scatter graph. Compared to Figure 59, a third cluster is discerned:

- Cluster 1: quadrats with low total arsenic and high biodiversity index value;
- Cluster 2: quadrats with high total arsenic and high biodiversity index value;
- Cluster 3: quadrats with high total arsenic and low biodiversity index value.

The clustering behaviour is consistent with the cluster analysis result in section 5.7.3 and the composition of three cluster members are exactly the same as Fig 40 described. This suggests that arsenic toxicity may not solely depend on total arsenic in the soil. Little research has been carried out into the impact of arsenic fractionation on vegetation community and biodiversity development. Arsenic fractionation analysis is performed on composite soil samples, which are made up by soils originating from quadrats marked as red dots in Figure 60.

The repeated arsenic fractionation produced highly consistent data. The result of the arsenic fractionation measurement (section 5.5) indicates a correlation between arsenic phytoavailability and local biodiversity. Steinhauser et al. (2009) found that mine tailings from the same orebody can have a significantly different pH, nutrient base, carbonate content, and mineralogical composition. Therefore, variation of arsenic fractionation observed in Carnon valley soil may also be common in mine tailings. However, the observation that local species diversity correlates negatively with the total arsenic concentration in the soil (Steinhauser et al., 2009) does not apply in the Carnon Valley. While arsenic in soil clearly limits species richness, its fractionation has a more substantial impact on the development of the plant community assemblage.

According to Wenzel et al. (2001), the first fraction contains soluble arsenic and the second fraction is exchangeable arsenic which can reduce the availability of phosphorus to plants. In the Carnon Valley samples, the first fraction contains less than 10 ppm in all quadrats, posing no threat to plants. The concentration of arsenic in the second fraction displays significant differences across the Lower valley. The concentration of arsenic in the second fraction can be as high as 500 ppm; release of this fraction of arsenic will dramatically increase local phytotoxicity.

From a positive perspective, it can be argued that impact of arsenic on site biodiversity is an active selection of (a) species with unusually high tolerance levels for arsenic toxicity, and (b) species which are able to survive in less-closed vegetation structures. Such plants necessarily establish better in more open and less dense but stressed vegetation structures. Factors encountered on mine waste surfaces may promote the survival of unusual alliances of species and the strength of individual plants, including hybrids arising, can be strong. Once a species establishes itself, opportunities for further selection exist, with species preferentially surviving on apparently ‘stressed’ sites (i.e. mine-waste surfaces) themselves building up population numbers.

In addition, arriving ‘extremist’ plants which are rare or even unknown in surrounding areas, may not only thrive, but may themselves become further genotypically selected and build within-site population-levels, contributing to the presence of increasing population balances of unusual biodiversity elements of such apparently extremist sites.

Because of the flattening of the Middle valley, mixing has occurred and the soil arsenic concentration is relatively consistent across the site (Figures 61 and 62). Except for a couple of outliers, soil in all other quadrats in the Middle valley contain similar total arsenic concentration. However, the species richness and biodiversity still vary considerably. It is difficult to perform cluster analysis since the data covers the data space fairly uniformly.

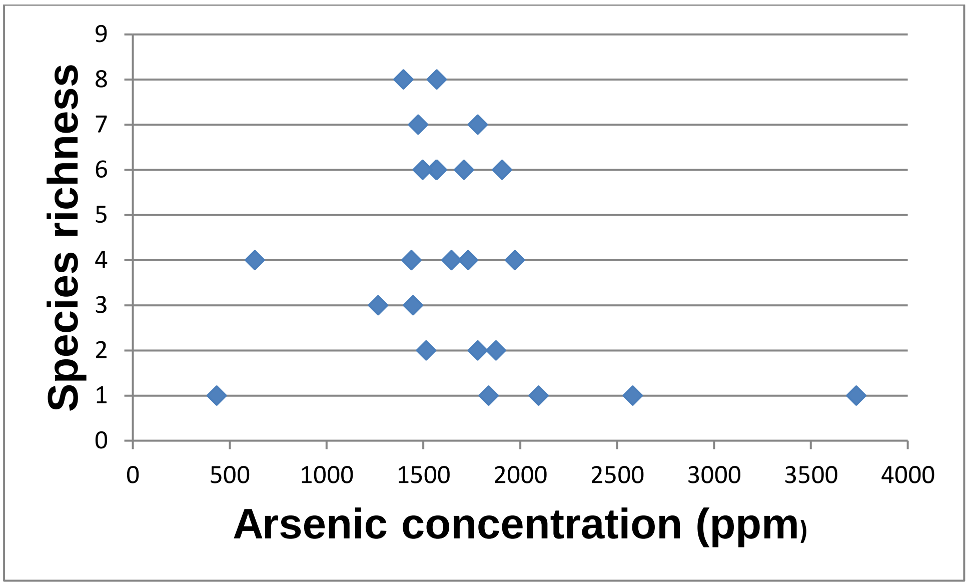


Figure 61: Influence of total arsenic concentration on the species richness in the Middle valley.

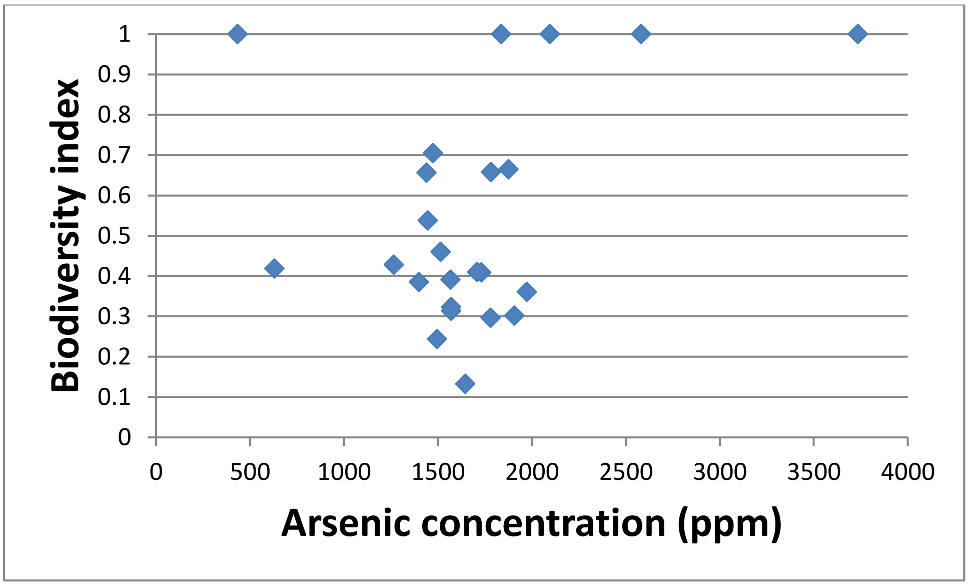


Figure 62: Influence of total arsenic concentration on Simpson biodiversity index in the Middle valley.

Some quadrats in the Middle valley show a biodiversity value of unity. As discussed previously (section 2.2.1), the biodiversity index used in this study evaluates the evenness of the species distribution rather the number of plants of each type.

Therefore, quadrats with biodiversity index equal to 1 do not necessarily have a high species richness.

6.5 Statistical analysis

It is postulated that ecological research can only be practical and relevant to society when knowledge is generated from the field rather than greenhouses. However, interpretation of field work studies pose a great challenge to data analysts due to environmental complexity. Due to the discrepancy between ecological and statistical representativity, ecologists are highly critical of the statistical methodology. During this research, SPSS 22, PAST 3 and Canoco 4.5 software was used to perform PCA analysis. It is found that processing the same dataset by these three software packages produces eigenvalues with up to 5% difference between them. Such variation is a reason for concern and affects the adoption of statistical methods in ecological research.

Although RDA was employed to successfully identify prominent factors influencing vegetation development in Carnon valley, autocorrelation between samples limits further analysis of the dataset. As inferred with XRD, the substrate in Carnon valley has a common origin which makes soil features dependent and highly correlated with each other. The correlation between element concentrations also limits the explanatory power of ordination analysis. According to portable XRF measurements, the total arsenic concentration in the substrate is much higher than the copper concentration in the substrate. However, RDA indicates that arsenic only has a slightly larger negative effect on plant development than copper. This may be due to copper having a higher phytotoxicity or a smaller fraction of arsenic being bioavailable.

Multivariate linear regression is a common tool to identify linear relationships between environmental factors and independent variables which are typically indicators for vegetation development. However, when several variables interact, the interpretation is complicated..

Two different methods of cluster analysis revealed a similar cluster structure which is consistent with the pattern given by scatter plot. Polar ordination supports the observation that Lower valley quadrat species structure is more dissimilar from each other than Middle valley.

6.6 Natural rehabilitation and their significance to mine closure

Natural rehabilitation on mine sites is sometimes termed as primary succession. Dobson (1997) defined primary succession as ecosystem development in a place where no previously developed soil exists, and he divided endemic ecosystem reconstruction into two aspects: biological and physical. Bradshaw (1996) assumes that restoration work includes both physical and chemical remediation aspects of habitat which define the species composition. Vegetation succession is influenced by variation in local abiotic conditions. Development of the local ecosystem can be predicted by taking environmental factors into consideration. However, the interaction between environmental factors and the process of vegetation changes is normally site-specific. This implies that knowledge distilled from other sites has to be put into a local context.

The process of primary succession is greatly affected by the properties of the overburden or surface layer and the topography (Bradshaw, 1997). It often is the case to witness natural soil heterogeneity as divergent as observed at a mining site. Natural heterogeneity in the physical and chemical properties of the substrate is mainly caused by differences in the - weathered - geological parent material (Frouz, 2011). Human intervention can introduce spatial variation into the properties of the substrate in accordance with site use, including the manner in which mine waste was spread and heaped. The spatial heterogeneity of the substrate can last for several decades, or even hundreds of years, after mining ceases. The resulting vegetation community which develops on a site partly expresses physicochemical variation of soil properties. Hence, understanding the history of the site, the evolution of substrate characteristics, and development of the vegetation community should inform the target-oriented mine planning of mine closure.

The arbitrary dumping of waste rock, overburden and tailings from a mining operation generates a surface with contrasting chemical and physical properties on a micro-scale. This micro-scale heterogeneity is not sustainable in the long run because substrate features tend to become more homogeneous under natural conditions (Pottier, 2009). On an intermediate time-scale, primary succession on a mine site could differ in structure and scale from what happens under natural conditions. Habitats developed on mine sites normally consist of small patches ranging between several metres to hundreds of meters in diameter. These patches are an expression of the so-called edge effect, a phenomenon which occurs at sharp transitions in topology and substrate. The edge effect is becoming more visible in the environment with increasing frequency and intensity of human interventions.

Powlesland (2013) investigated the hypothesis that local hummocks and hollows are an influential factor for edge development. The ability to test this hypothesis was restricted by the detection limit of currently available surveying methods. Dense vegetation coverage limits the operation of Zeiss total station and therefore leaves a blind spot in topography map. GPS rover typically has large errors in altitude. Therefore, no conclusions about the impact of micro-topography can be reached.

Although evidence for topography-induced variation of vegetation assemblage variation is missing, the existence of a toxicity gradient in the substrate is supported by arsenic fractionation data and statistical analysis. In the absence of historical data, it is not clear whether a gradient in arsenic phytoavailability is inherited or induced. The electrical conductivity of surface soil in the Carnon Valley varies over a greater range than in subsurface soil. Therefore, soil disturbance is assumed to play a vital role in surface substrate features. This emphasises that human intervention has a role in facilitating natural rehabilitation in the Carnon Valley, and mine sites in general.

6.7 Mine closure strategy

No two mine sites which are the same. Therefore, remediation or rehabilitation of each mine site should be considered in context on its own merits. A better understanding of environmental factors and their roles in rehabilitation would facilitate mine closure planning. Physical aspects that affect habitat development can be spontaneous or unmodifiable factors, and acquired or modifiable factors. Spontaneous factors are those aspects which are determined by ambient conditions such as climatic and geological settings. For ecological rehabilitation, spontaneous factors shall define the rehabilitation path when engineering options are not feasible or too costly

Substrates at mine sites are normally hostile to plants. Often imported topsoil is applied to accelerate vegetation development, a measure which is beneficial in the short term but its long-term benefit is uncertain. Isolating linings are applied to avoid contaminant migration but severing the bond between topsoil and substrate can trigger erosion and other problems. In contrast, natural rehabilitation is more viable in the long run as it relies on native, tolerant species.

Acquired factors such as the particle size distribution of mine waste are determined by extraction and processing techniques used by former mining operations. Mine waste normally consists of either tailings, which is very fine clayey silt, or waste rocks, which are pebble size or bigger. Mine waste dumped randomly can easily create an unfavourable particle size distribution, affecting water infiltration, soil compaction and exchangeable ions concentrations. Note that different plants have different preferences in terms of soil texture. A well-designed mine closure project should consider all acquired factors and attempt to optimise these accordingly. For example, a mix of waste rock and tailings may produce optimum soil strength and infiltration rate.

Therefore, rehabilitation target has to be set up at the very beginning of a mine operation plan or mine closure project, addressing the following questions:

1. What has to be restored or maintained?
2. What factors on site are limiting factors and to which extent can it could inhibit the rehabilitation process?
3. What aspects improve or reduce the effectiveness management of the restoration process?

The answer of the first question depends on the value of the land to the owner or local community. Varied land use demand different restoration objectives. The second question only can be answered when sufficient information is available about local environment and knowledge of biotic and abiotic factors in primary succession. The third question requires consideration of the trade-offs in ecological engineering.

Generally, land remediation may be achieved through the following actions:

1. Remove all tailings and replace with clean soil
2. Remove all tailings and allow waterlogging.
3. Clean all tailings and return to site.
4. Cover bulldozed tailings with clean soil.
5. Leave the site as it is but plant desired species.
6. Bulldoze tailings to create a flat surface.

7. Leave the site to spontaneous rehabilitation.

The first three options are costly and could cause secondary contamination. The fourth option is a popular option as it enables rapid establishment of vegetation. However, sourcing imported soil at cost combined with potential erosion create challenges for its application.

The 5th option has been applied in regions without strict law enforcement and often fail when plantation dies. The last two options are relatively low-cost and were applied to the site studied in this research. Advantages of these two rehabilitation options are:

1. Maximise biodiversity/species richness. (Lower valley)
2. Maximise stabilisation or minimise leaching of metals into environment. (Middle valley)
3. Maximise vegetation coverage of land. (Middle valley)
4. Provide recreational use (ponds, walking, biking). (Middle and Lower valley)
5. Improve aesthetic appearance of site. (Middle valley)

Natural remediation targets have been achieved through natural restoration process in Carnon valley. However, the process takes time and the unusual landscape and habitat types may be present for a prolonged period of time.

With population increasing and resource exhausting, human society is more actively engaging in land use alteration. Natural landscape is transferred into tourism, agriculture and other managed land use. Mining has been considered as one industry which can change landscape intensively. As part of the effort to improve industry image, many mine closure projects aim to restore mine site to the previous ecological system. However, this may prove to be irrational in view of cost and chance of long-term success.

This research highlights that natural rehabilitation is an option provided that a correct understanding of biodiversitty progression is in place. A discussion of gains from biodiversity progression, as observed in this study, is given in section 6.8.

6.8. Comparison of overall biodiversity progression

The survey described in this study is probably the most detailed ever undertaken over an area which, despite a common history, displays different physical structures (flat versus undulating) in adjacent sections. Comparison of species diversity present on flat and undulating areas after abandonment of the valley demonstrates the additional biodiversity richness, and enables further analyses.

6.8.1. Gain of an enhanced drainage mosaic

This research demonstrates that the mosaic pattern of the undulating topography offers the greatest diversity of drainage profiles and leads to areas of maximised biodiversity. This is especially significant for establishing vegetation in a region such as west Cornwall, which has a high annual rainfall. Highest drainage is present on mounds while the lowest drainage was observed in depressions. Water accumulates in depressions for varying period and, in the deepest and largest, year-round, standing-water ponds are formed. The differing degrees of drainage present allows for equally-gradated biotic communities to develop. Enhancing the effect of topology is that, in the undulating area (lower valley), the vertical soil profile settlement has always been through natural compression, wheras, in the flat area (middle valley), machinery was used to flatten the abandonned mine waste. The latter process saw application of pressure, causing man-made compaction of the soil.

6.8.2 Gain of aspect availability

In addition to the mosaic drainage patterns in the lower valley, the undulating topology also results in a gain in site aspect. Differences in aspect, including not only north-south but also east-west, and all intermediates, offer different illumination patterns on a daily basis and influence the rate of evaporation on a similar daily basis. Variation between the deepest shade on a more northern aspect and the better-illuminated more southern aspect shade contrasts tends to increase as vegetation itself establishes. This creates opportunities for a far wider-range of biodiversity to successfully establish, from light-demanding (e.g. many pioneer flowering-plant species) to more shade-tolerant species (e.g. ferns).

6.8.3 Gain of multiple edge effects

An inevitable consequence of patterns in plant communities is the formation of edge effects between zones of vegetations. Edge effects express the structure of contrasting margins and the variety of communities which they separate. The gain of edge effects is expected to be that progression in contrasts as vegetation communities develop. Such edge effects hence themselves come to add significance to the structural diversity of overall environment present.

6.8.4 Summary of discussion

Analysis of differences in biotic success in areas of contrasting topography studied in the Carnon Valley presented an opportunity to learn lessons which may be more widely applicable, specifically at other mine-sites and inform the likely success and diversity of vegetation which can be expected to develop upon them.

Engineering of mine-site toxicity gradients can provide a basis and fundamental step towards enhancement of ultimate biodiversity in a cost-effective manner. As objectives may demand, initial engineering can also be integrated with construction of necessary access pathways for further monitoring of site recovery progress.

Long-term gains are likely to include enhancement of the biodiversity, as estimated here through species sampling, and creation of biota of enhanced genetic diversity. Especially genotypes of plants with enhanced tolerance levels to unusual and especially toxic terraines are able to thrive. Hence, areas of abandonned and contaminated land can serve as seed resources for safeguarding of future biodiversity.

7 Conclusion and Recommendation

7.1 Conclusion

The surveys and investigations of the Carnon valley identified several influential factors of post-mining site natural rehabilitation. Analysis of the biodiversity and similarity indices suggest a greater variation in vegetation assemblage in the lower valley. This is ascribed to differences in resource availability and stress intensity. The smaller variances of soil electrical conductivity, pH and trace element concentration in the middle valley (section 5.3.1, 5.3.2 and 5.3.3) are deemed to result from bulldozing.

Cluster analysis and arsenic fractionation indicates there is a threshold at which arsenic starts to affect local biodiversity. Due to the impact of other environmental factors and varied tolerance capacity of different vegetations and vegetation communities, the threshold value for arsenic-toxicity to local biodiversity is possibly a variable within a certain range rather than a fixed value. As a result, the biodiversity index of the vegetation assemblage can serve as an important indicator of soil toxicity. The uneven distribution of arsenic or arsenic fractionation is deemed to be an important factor affecting natural vegetation development.

The impact of soil strength on vegetation development was suspected but not conclusively proven in this research. Neither the average soil compaction of each quadrat, nor the standard deviation variation range of soil compaction correlated strongly with vegetation development (section 6.3). This is considered to be a result of the obstruction of waste rock in soil compaction measurement. Similarly, the similarity in substrate grain texture prevented reaching a conclusion about its impact on vegetation recolonisation in Carnon valley (section 5.2.2).

RDA analysis indicates arsenic, copper, and lead are the most important limiting factors to vegetation development (sections 5.6.2 and 6.5). Clustering analysis reveals three different types of vegetation-soil interaction in rehabilitation process (section 5.6.3). This phenomenon has been partially explained by arsenic fractionation analysis.

The occurrence of locally rare species gives further evidence of the value of abandoned mine site in ecological conservation (section 6.1.3).

Different rehabilitation patterns can establish on a mine site with one type of substrate. This gives more options and challenges to planning for mine closure with an expected end-point. The high diversity in the Lower Carnon valley is correlated with substrate heterogeneity. Heavy metal, especially arsenic bioavailability plays a significant role in local biodiversity. The high ecological conservation value of Lower valley is associated with the presence of local rare species, which lends a unique perspective to mine site remediation.

The significantly high species richness and presence of rare species in the ditch community indicates the benefit of edge effect in mine site rehabilitation. The environmental factors which create such edges is not certain yet but water availability is among the most promising one. After excluding the ditch community, the poor species richness in bulldozed middle valley suggests the negative influence of human intervention to biodiversity in natural rehabilitation. (Section 6.1.1)

This research creates a foundation to develop strategies to manage rehabilitation of abandoned mine sites in the future.

7.2 Recommendation for further investigation

Currently there are no studies of a comparable scale in abandoned post-mining sites. Table 1 shows that, while many studies reported the general level of contamination and give exhaustive lists of adapted plant species, soil spatial heterogeneity did not correlate with local vegetation rehabilitation. Therefore, validating the practical value of findings from this research requires further investigation of other sites.

This research proved the great potential of field study and identified further areas of research:

- The hypothesis about micro-topography impact on bioavailable trace elements relocation has not been proven in the absence of surveying equipment capable of recording tiny differences in local topography. While the small variation in topography may vary substantially as a function of time, it may be worth investigating in future.
- The edge along drainage ditch proved to have a significant effect on biodiversity and species richness, but the influence of factors such as water availability, the interface with human activity, proximity to seed sources, and attenuated phyto-toxicity, in the development of the edge have not been identified. Further work is required to establish a comprehensive model .
- Improvement of soil nitrogen content through legume species is well known. However, the impact of heavy metal contaminated land on this mechanism is poorly researched. The presence of *Ulex europaeus* give the opportunity to look into the reaction of mycorrhiza to the gradient of toxicity.
- The RDA result of this research indicates copper and lead also has great impact on local species richness and biodiversity. Targeted sequential extraction scheme worth to be carried out to find out the relationship between the form of their presence and local natural restoration progress.

Recommendations given above for future research along with findings of this thesis will benefit the understanding of natural rehabilitation process and facilitate its wider application.

Reference

Adler, G.H. (2013). Rainforest ecosystems, animal diversity. Encyclopedia of Biodiversity, 2nd ed. Pp 304-312.

Agency for Toxic Substances and Disease Registry (2004). Toxicological profile for strontium, Atlanta, United States Department of Health and human services, Public health service.

Alameda, D. and Villar, R. (2009). Moderate soil compaction: Implication on growth and architecture in seedlings of 17 woody plant species. *Soil and Tillage Research* 103, pp. 325-331.

Alameda, D., Villar, R. and Iriondo, J.M. (2012). Spatial pattern of soil compaction: Trees' footprint on soil physical properties. *Forest Ecology and Management* (283), pp 128-137.

Alexander, E.B. (2014). Arid to humid serpentine soils, mineralogy, and vegetation across the Klamath Mountains, USA. *Catena*, 116, pp 114-122.

Alloway, B. (2012). Heavy metals in soils. Dordrecht: Springer.

Alpert, P. (2006). The advantage and disadvantages of being introduced. *Biological Invasions* 8, pp. 1523-1534.

Alvarez-Alvarez, P., Barrio-Anta, M., Camara-Obregon, A. and Bento, J.M.R.D.S. (2013). Ground vegetation as an indicator of site quality: effect of non-site factors on the productivity of newly established chestnut plantations in northwestern Spain. *Journal of Forest Research* 18(5), pp. 407-417.

American Society of Agricultural Engineers (ASAE) (1969). Soil cone penetrometer. In: Recommendation ASAE R313, Agricultural Engineering Yearbook. St. Joseph, MI: *American Society of Agricultural Engineers*, pp. 296 –297.

Amundson, R. and Jenny, H. (1991). The Place of Humans in the State Factor Theory of Ecosystems and Their Soils. *Soil Science,* 151(1), pp.99-109.

Anawar, H., Canha, N., Santa-Regina, I. and Freitas, M. (2013). Adaptation, tolerance, and evolution of plant species in a pyrite mine in response to contamination level and properties of mine tailings: sustainable rehabilitation. *Journal of Soils Sediments*, 13(4), pp.730-741.

Arain, M., Kazi, T., Jamali, M., Baig, J., Afridi, H., Jalbani, N. and Sarfraz, R. (2009). Comparison of Different Extraction Approaches for Heavy Metal Partitioning in Sediment Samples. *Pedosphere,* 19(4), pp.476-485.

Armitage, P.D., Szoszkiewicz, K., Blackburn, J.H. and Nesbitt, I. (2003). Ditch communities: a major contributor to floodplain biodiversity. *Aquatic Conservation: Marine and Freshwater Ecosystems* (13), pp165-185.

Arshad, M. and Martin, S. (2002). Identifying critical limits for soil quality indicators in agro-ecosystems. *Agriculture, Ecosystems & Environment*, 88(2), pp.153-160.

Aziz, A. and Ahmed, A. (2010). Effects of arsenic on diversity of rice field weeds. *Dhaka University Journal of Biological Science* 19(1), pp. 95-98.

Bakker, J.P., Marrs, R.H. and Pakeman, R.J. (2002). Long-term vegetation dynamics: Successional patterns and processes. Introduction. *Applied Vegetation Science* 5, pp. 2-6.

Barbour, M., Burk, J. and Pitts, W. (1980). *Terrestrial plant ecology*. Menlo Park, CA: Benjamin/Cummings Pub. Co.

Barringer, J.L. and Reilly, P.A., (2013). Current perspectives in contaminant hydrology and water resources sustainability, chapter 4: Arsenic in groundwater: A summary of sources and the biogeochemical and hydrogeologic factors affecting arsenic occurrence and mobility, pp 83-116, INTECH. U.S. Geological Survey, USA.

Basu, A. and Schreiber, M. E. (2013). Arsenic release from arsenopyrite weathering: Insights from sequential extraction and microscopic studies. *Journal of Hazardous Materials* 262, pp. 896-904.

Bell, L.C. (2001). Establishment of native ecosystem after mining—Australian experience across diverse biogeographic zones. *Ecological Engineering* (17), pp. 179-186.

Bellini, F. and Figà-Talamanca, G. (2005). Runs tests for assessing volatility forecastability in financial time series. *European Journal of Operational Research*, 163(1), pp.102-114.

Benayas, J.M.R., Newton, A.C. , Diaz, , Bullock, J.M. (2009). Enhancement of biodiversity and ecosystem services by ecological restoration: a meta-analysis. *Science*, 325, pp. 1121–1124.

Bengough, A.G., Campbell, D.J., and O'Sullivan, M.F. (2001). Penetrometer techniques in relation to soil compaction and root growth. In: Mullins, C.E. and Smith, K.A., *Soil and Environmental Analysis, Physical methods*. New York: Marcel Dekker.

Bennallick, I., Board, S., French, C., Gainey, P., Neil, C., Parslow, R., Spalding, A. and Tompsett, P. (editors) (2009). *Red data book for Cornwall and the isles of Scilly* (2nd Edition). Croceago Press.

Besseris, G. (2013). Robust quality controlling: SPC with box plots and runs test. *The TQM Journal*, 25(1), pp.89-102.

Bhardwaj, A.K., Jasrotia, P., Hamilton, S.K. and Robertson, G.P. (2011). Ecological management of intensively cropped agro-ecosystems improves soil quality with sustained productivity. *Agriculture, Ecosystems and Environment*, 140 (3-4), pp. 419-429.

Bierhuisen, J.F. and Wagenvoort, W.A. (1974). Some aspects of seed germination in vegetables. 1. The determination and application of heat sums and minimum temperature for germination. *Scientia Horticulturae*, 2, pp. 213-219.

Biodiversity reporting and information group, (2007). *Report on the species and habitat review*. jncc.defra.gov.uk/pdf/UKBAP_Species-HabitatsReview-2007.pdf, accessed on 14th. Aug. 2015.

Bittelli, M., Campbell, G. and Flury, M. (1999). Characterization of Particle-Size Distribution in Soils with a Fragmentation Model. *Soil Science Society of America Journal*, 63(4), p.782.

Blouin, V., Schmidt, M., Bulmer, C. and Krzic, M. (2004). Soil compaction and water content effects on lodge pole pine seedling growth in British Columbia. SuperSoil 2004: *Third Australian New Zealand Soils Conference*, University of Sydney, Australia.

Bonanomi, G., Legg, C. and Mazzoleni, S. (2005) Autoinhibition of germination and seeding establishment by leachate of *Calluna vulgaris* leaves and litter. *Community Ecology,* 6(2), pp.203-208.

Bordas, F., Bourg A.C.M.1998. A critical evaluation of sample pretreatment for storage of contaminated sediments to be investigated for the potential mobility of their heavy metal load. *Water Air Soil Pollution* 103 (1-4), pp. 137-149.

Bowell, R.J. (1994). Sorption of arsenic by iron oxides and oxyhydroxides in soils. *Applied Geochemistry* 9, pp. 279-286.

Bradshaw, A. (1997). Restoration of mined lands-using natural processes. *Ecological Engineering* 8, pp. 255-269.

Bradshaw, A., (2000). The use of natural processes in reclamation—advantages and difficulties. *Landscape and Urban Planning* 51, pp. 89-100.

Bradshaw, A.D. (1996). Underlying principles of restoration. *Canadian Journal of Fisheries and Aquatic Sciences* 53(Suppl. 1), pp. 3-9.

Bradshaw, A.D., Marrs, R.H. and Roberts, R.D., (1982). Succession, in ecology of quarries. *The importance of natural vegetation*, edited by Davis, B.N.K., Institute of Terrestrial Ecology Symposium. No. 11, pp. 47-52.

Brady KU, Kruckeberg AR, Bradshaw HD, Jr. (2005) Evolutionary ecology of plant adaptation to serpentine soils. Annu Rev Ecol Evol Syst 36(1):243–266.37.

Brady, N.C. and Weil, R.R. 2002. The Nature and Properties of Soils 13th edition. Pearson Education Inc.

Brenner, M, 2010, MSc dissertation thesis, Camborne School of Mines, University of Exeter.

British Geological Survey, Geology of Britain, http://www.bgs.ac.uk/makeamap/ accessed on 13th November, 2014.

Buckland, S. (2004). Advanced distance sampling. Oxford: Oxford University Press.

Buckland, S., Borchers, D., Johnston, A., Henrys, P. and Marques, T. (2007). Line Transect Methods for Plant Surveys. *Biometrics*, 63(4), pp.989-998.

Burke, I.C., Lauenroth, W.K., Vinton, M.A., Hook, P.B., Kelly, R.H., Epstein, H.E., Aguiar, M.R., Robles, M. D., Aguilera, M.O., Murphy, K.L., and Gill, R.A. (1998). Plant-soil interactions in temperate grasslands. *Biogeochemistry* 42, pp. 121-143.

Burt, R., Waite, P. and Burnley, R., (1987). The Cornish mines: metalliferous and associated minerals, 1845-1913, vol. 8 (Mineral statistics for the United Kingdom, 1845-1913). University of Exeter in association with the Northern Mine Research Society.

Cai, Y., Cabrera, J., Georgiadis, M. and Jayachandran, K. (2002). Assessment of arsenic mobility in the soils of some golf courses in South Florida. *Science of The Total Environment*, 291(1-3), pp.123-134.

Calow, P. (1998). The encyclopaedia of ecology and environmental management. Blackwell Science Ltd...

Cambridge, M. (1999). Rehabilitation of historic mineworkings in Europe. *Mine, Water and Environment proceeding*, IMWA Congress. Sevilla, Spain.

Camill, P., McKone, M., Sturges, S., Severud, W., Ellis, E., Limmer, J., Martin, C., Navratil, R., Purdie, A., Sandel, B., Talukder, S. and Trout, A. (2004). Community- and Ecosystem-Level Changes in a Species-Rich Tallgrass Prairie Restoration. *Ecological Applications*, 14(6), pp.1680-1694.

Camm, G.S., Glass, H.J., Bryce, D.W., Butcher, A.R., (2004). Characterisation of a mining-related arsenic-contaminated site, Cornwall, UK. *Journal of Geochemical Exploration*, 82, pp. 1-15.

Camm, G.S., Taylor, I., Hartwell, P. and Scarborough, B. (1981). Carnon Valley, Cornwall, a placer tin deposit. *British Geologist*, 7, pp. 65-71.

Carabante, I., Grahn, M., Holmgren, A. and Hedlund, J. (2010). In situ ATR–FTIR studies on the competitive adsorption of arsenate and phosphate on ferrihydrite. *Journal of Colloid and Interface Science*, 351(2), pp.523-531.

Carbonell, A.A., Aarabi, M.A., DeLaune, R.D., Gambrell, R.P. and Patrick Jr., W.H. (1998). Arsenic in wetland vegetation: Availability, phytotoxicity, uptake and effects on plant growth and nutrition. *The Science of the Total Environment* 217, pp. 189-199.

Carter, M.R. ad Gregorich, E.G. (2007). Soil Sampling and Methods of Analysis, 2nd Ed. CRC Press.

Casida, L. (1964). Anaerobic Microorganisms in the Soil. *Science*, 145(3629), pp.300-301.

Cernansky, S., Falt'an, V., Koli, M., Samelova, A., Rusnak, M., Hamada, R. and Zahumensky, V. (2014). Occurrence of arsenic and antimony in water, soil and vegetation near tailing impoundments in Pezinok, Slovakia. *Acta Environmentala Universitatis Comenianae (Bratislava)*, 22(2), pp.17-25.

Chang, P., Kim, J. and Kim, K. (2005). Concentrations of arsenic and heavy metals in vegetation at two abandoned mine tailings in South Korea. *Environmental Geochemistry Health*, 27(2), pp.109-119.

Chapin, F.S., Walker, L.R., Fastie, C.L. and Sharman, L.C., (1994). Mechanisms of primary succession following deglaciation at Glacier Bay, Alaska: *Ecological Monographs*., v. 64, pp. 149-175.

Chen, A., Lin, C., Lu, W., Ma, Y., Bai, Y., Chen, H. and Li, J. (2010). Chemical dynamics of acidity and heavy metals in a mine water-polluted soil during decontamination using clean water. *Journal of Hazardous Materials*, 175(1-3), pp.638-645.

Chen, M. and Ma L.Q. (2001). Comparison of three aqua regia digestion methods for twenty Florida soils. *Soil Science Society of America Journal* 65, pp. 491–499.

Chiarucci, A. (2007). To sample or not to sample? That is the question ... for the vegetation scientist. *Folia Geobotanica*, 42(2), pp.209-216.

Choi, Y.D, (2007). Restoration ecology to the future: A call for new paradigm. *Restoration Ecology*, 15(2) pp. 351-353.

Chong, S.K., Becker, M.A., Moore, S.M. and Weaver, G.T. (1986). Characterisation of reclaimed mined land with and without topsoil. *Journal of Environmental Quality* 15(2), pp. 157-160.

Chowdhury, A., McLaren, R., Swift, R. and Cameron, K. (1992). Effects of extraction period and soil.-solution ratio on the amount of zinc extracted from soils by different extractants. *Communications in Soil Science and Plant Analysis*, 23(13-14), pp.1451-1459.

Clarke, C.T. (1997). Role of soils in determining sites for lowland heathland reconstruction in England. *Restoration Ecology* 5(3), pp 256-264.

Colman, S.M. and Dethier, D.P. (1986). Rates of chemical weathering of rocks and minerals. Orlando: Academic Press.

Colwell, Robert K. (2009). Biodiversity: Concepts, Patterns and Measurement. In Simon A. Levin. *The Princeton Guide to Ecology*. Princeton: Princeton University Press. pp. 257–263.

Conklin, A.R. (2014). Introduction to soil chemistry: analysis and instrumentation, 2nd edition. John Wiley and Sons, Inc. Hoboken, New Jersey.

Cornwall Council, (2011). The ecological value of metalliferous mining sites. http://www.cornish-mining.org.uk at 28th, Aug. 2014.

Cottle, R. A. (2004). Linking Geology and Biodiversity. Peterborough: English Nature.

Cox, G. (1990). Laboratory manual of general ecology, 6th edition. Dubuque, Iowa: W.C. Brown.

Craw, D. and Bowell, R. (2014). The Characterization of Arsenic in Mine Waste. *Reviews in Mineralogy and Geochemistry*, 79(1), pp.473-505.

Craw, D., Falconer, D. and Youngson, J.H. (2003). Environmental arsenopyrite stability and dissolution: theory, experiment, and field observations. *Chemical Geology* 199, pp. 71-82.

Craw, D., Rufaut, C., Haffert, L. and Paterson, L. (2006). Plant Colonization and Arsenic Uptake on High Arsenic Mine Wastes, New Zealand. *Water, Air & Soil Pollut*ion, 179(1-4), pp.351-364.

Cullen, W.R. and Reimer, K.J. (1989). Arsenic speciation in the environment. *Chemical Reviews* 89(4), pp. 713-764.

Dakora, F.D. and Phillips, D.A. (2002). Root exudates as mediators of mineral acquisition in low-nutrient environments. *Plant and Soil*, 245(1), pp 35-47.

Dancer, W.S., Handley, J.F. and Bradshaw, A.D. (1977). Nitrogen accumulation in Kaolin mining wastes in Cornwall I. natural communities. *Plant and Soil*, 48, pp. 153-167.

Daniel, W.M., Infante, D.M., Hughes, R.M., Tsang, Y.P., Esselman, P.C., Wieferich, D., Herreman, K., Cooper, A.R., Wang, L., and Taylor, W.W. (2015). Characterizing coal and mineral mines as a regional source of stress to stream fish assemblages. *Ecological Indicators*, 50, pp. 50-61.

Darling, P. (2011). SME mining engineering handbook (3rd Edition), Society for Mining, Metallurgy, and Exploration (SME).

Davidson, C., Ferreira, P. and Ure, A. (1999). Some sources of variability in application of the three-stage sequential extraction procedure recommended by BCR to industrially-contaminated soil. *Fresenius' Journal of Analytical Chemistry*, 363(5-6), pp.446-451.

Dedousis, A.P. and Bartzanas, T. (2010). Soil Engineering, Soil Biology, 20, Springer-Verlag Berlin Heidelberg.

Deer, W.A., Howie, R.A. and Zussman, J., (2013). An Introduction to the Rock Forming Minerals, 3rd edition. The Mineralogical Society.

DEFRA and Environment Agency (2002) CLR 9 TOX5 Contaminants in Soils: Collation of Toxicological Data and Intake Values for Humans. Lead. DEFRA/EA, London.

De Koe, T. (1994). *Agrostis castellana* and *Agrostis delicatula* on heavy metal and arsenic enriched sites in NE Portugal. *Science of The Total Environment,* 145(1-2), pp.103-109.

Digimap Ordnance survey [Online], Available: http://edina.ac.uk/digimap [14, Sep. 2013].

Dineley, D.L. (1992). Chapter 5 Devonian. In: Duff, P. and Kenyon-Smith, A. Geology of England and Wales. London: Geological Society.

Dines, H.G., (1956). The Metalliferous Mining Region of South- west England. HMSO, London.

Dobson, A.P., Bradshaw, A.D. and Baker, A.J.M. (1997). Hopes for the future: Restoration ecology and conservation biology. *Science, New series*. 277(5325), pp. 515-522.

Dominy, S.C., Phelps, R.F.G., Sangster, C.J.S., Camm, G.S., (1998). Narrow Vein Mining Techniques in the United Kingdom. Underground Operators' Conference Proceedings.

Dorrington, V. and Pyatt, F. (1983). Some aspects of tissue accumulation and tolerance to available heavy metal ions by Rubus Fruticosus L., A Coloniser of spoil tips in S.W. England. *International Journal of Environmental Studies*, 20(3-4), pp.229-237.

Dray, S., Pélissier, R., Couteron, P., Fortin, M., Legendre, P., Peres-Neto, P., Bellier, E., Bivand, R., Blanchet, F., De Cáceres, M., Dufour, A., Heegaard, E., Jombart, T., Munoz, F., Oksanen, J., Thioulouse, J., Wagner, H. (2012). Community ecology in the age of multivariate multiscale spatial analysis. *Ecological Monographs*, 82(3), pp.257-275.

Elbarghouthi, S., Qasim, A. and Yassin, M. (2012). The Use of Runs Test in Amman Stock Exchange. *International Business Research*, 5(2).

Environment Agency (2009). Soil Guideline Values Report Series, http://www.environment-agency.gov.uk/research/planning/64015.aspx

Ernst, W.H.O. (1996). Bioavailability of heavy metals and decontamination of soils by plants. *Applied Geochemistry* 11, pp. 163-167.

Ernst, W.H.O. (2006). Evolution of metal tolerance in higher plants. *ForestSnow and Landscape Research*, 80(3). Pp.251-274.

Erst, W.H.O., Mathys, W., Janiesch, P. (1974). Aspekte von Schwermetallbelastungen in Westfalen. *Abhandlungen Landesmuseum Naturkunde zu Muenster in Westfalen*, 36, pp. 1-31.

Eshel, G., Levy, G., Mingelgrin, U. and Singer, M. (2004). Critical Evaluation of the Use of Laser Diffraction for Particle-Size Distribution Analysis. *Soil Science Society of America Journal,* 68(3), p.736.

Everitt, B., Landau, S., Leese, M. and Stahl, D. (2011). *Cluster analysis*. 5th ed. Chichester: John Wiley & Sons, Ltd.

Fan L.S. and Zhu, C. (1998). Size and Properties of Particles. In: Principles of Gas-Solid Flows. Cambridge Series in Chemical Engineering. Cambridge University Press. pp. 3-45.

Farley, J. and Voinov, A. (2016). Economics, socis-ecological resilience and ecosystem services. *Journal of Environmental Management*, in press.

Fielding, Alan (2007). *Cluster and Classification Techniques for the Biosciences*. Cambridge, UK: Cambridge University Press.

Filippi, M., Goliáš, V. and Pertold, Z. (2003). Arsenic in contaminated soils and anthropogenic deposits at the Mokrsko, Roudný, and Kašperské Hory gold deposits, Bohemian Massif (CZ). *Environmental Geology*, 45(5), pp.716-730.

Finney, D.J. (1948). Random and systematic sampling in timber surveys. *Forestry*, 22, pp. 64-99.

Firbank, L., Barr, C., Bunce, R., Furse, M., Haines-Young, R., Hornung, M., Howard, D., Sheail, J., Sier, A. and Smart, S. (2003). Assessing stock and change in land cover and biodiversity in GB: an introduction to Countryside Survey 2000. *Journal of Environmental Management*, 67(3), pp.207-218.

Force, M.J.L., Hansel, C.M. and Fendorf, S. (2000). Arsenic speciation, seasonal transformations, and co-distribution with iron in a mine waste-influenced Palustrine emergent wetland. *Environmental Science and Technology* 34, pp. 3937-3943.

French C. Murphy R. and Atkinson M. (1999). Flora of Cornwall. Wheal Seton Press, Camborne.

Frouz, J., Hrckova, K., Lana, J., Kristufek, V., Mudrak, O., Lukesova, A. and Mihaljevic, M. (2011). Can laboratory toxicity tests explain the pattern of field communities of algae, plants, and invertebrates along a toxicity gradient of post-mining sites? *Applied Soil Ecology* 51, pp. 114-121.

Frouz, J., Kalcik, J. and Velichova, V. (2011). Factors causing spatial heterogeneity in soil properties, plant cover, and soil fauna in a non-reclaimed post-mining site. *Ecological Engineering* 37, pp. 1910-1913.

Gallagher, F.J., Pechmann, I., Bogden, J.D., Grabosky, J. and Weis, P. (2008). Soil metal concentrations and vegetative assemblage structure in an urban brownfield. *Environmental Pollution* 153, pp. 351-361.

Gan, G., Ma, C. and Wu, J. (2007). *Data clustering*. 1st ed. Philadelphia, Pa.: SIAM, Society for Industrial and Applied Mathematics.

García-Gómez, C., Sánchez-Pardo, B., Esteban, E., Peñalosa, J. and Fernández, M. (2014). Risk assessment of an abandoned pyrite mine in Spain based on direct toxicity assays. *Science of The Total Environment*, 470-471, pp.390-399.

García-Salgado, S., García-Casillas, D., Quijano-Nieto, M. and Bonilla-Simón, M. (2011). Arsenic and Heavy Metal Uptake and Accumulation in Native Plant Species from Soils Polluted by Mining Activities. *Water, Air & Soil Pollution*, 223(2), pp.559-572.

Garcia-Sanchez, A. and Alvarez-Ayuso, E. (2003). Arsenic in soils and waters and its relation to geology and mining activities (Salamanca Province, Spain). *Journal of Geochemical Exploration*, 80(1), pp.69-79.

Garg, N. and Singla, P. (2011). Arsenic toxicity in crop plants: physiological effects and tolerance mechanisms. *Environmental Chemistry Letters* 9, pp. 303-321.

Garson, G. (2012). *Testing Statistical Assumptions*. 1st ed. Asheboro: G. David Garson and Statistical Associates Publishing.

Gaston, K. J. and Spicer, J. I. (2004). Biodiversity an introduction, 2nd edition. Blackwell Science Ltd.

Gee, G.W. and Bauder, J.W. (1986). Particle size analysis. In: Klute, A., Weaver, R., Sparks, D., Dane, J. and Topp, G. (1986). Methods of soil analysis. Madison, Wis.: Soil Science Society of America, pp. 383-411.

Geotechnics, (1995). Wheal Jane Minewater Study, Carnon Valley, Cornwall. Ground Investigation. Report for the National Rivers Authority, Southwestern Region. Geotechnics Ltd, Exeter.

Gieselman, T.M., Hodges, K.E. and Vellend, M. (2013). Human-induced edges alter grassland community composition. *Biological Conservation* 158, pp. 384-392.

Giljum, S., Polzin, C., Lutter, S. and Dittrich, M. (2011). Green Economies around the world? Implications of resource use for the environment and development. Sustainable Europe Research Institute.

Gimingham, C.H. (1975). An Introduction to heathland ecology. Oliver and Boyd, a division of Lomgman Group Ltd.

Godefroid, S. and Koedam, N. (2004). Interspecific variation in soil compaction sensitivity among forest floor species. *Biological Conservation* 119, pp. 207-217.

Godefroid, S. and Koedam, N. (2004). The impact of forest paths upon adjacent vegetation: effects of the path surfacing material on the species composition and soil compaction. *Biological Conservation* 119, pp. 405-419.

Golley, P. & Williams, R. (1995): Cornish Mineral Reference Manual. Endsleigh Publications (Truro).

Goossens, D. (2007). Techniques to measure grain-size distributions of loamy sediments: a comparative study of ten instruments for wet analysis. Sedimentology, 55, pp. 65-96.

Goslee, S. (2006). Behavior of Vegetation Sampling Methods in the Presence of Spatial Autocorrelation. *Plant Ecology*, 187(2), pp.203-212.

Gough, L., Osenberg, C.W., Gross, K.L., and Collins, S.L. (2000). Fertilisation effects on species density and primary productivity in herbaceous plant communities. *Oikos* 89, pp. 428-439.

Graaf, M.C.C.D., Bobbink, R., Smits, N.A.C., Diggelen, R.V., and Roelofs, J.G.M. (2009). Biodiversity, vegetation gradients and key biogeochemical process in the heathland landscape. *Biological Conservation* 142, pp. 2191-2201.

Gray, C. and McLaren, R. (2003). Effects of Air Drying or Sample Storage on Soil-Solution Properties of Biosolids-Amended Soil. *Communications in Soil Science and Plant Analysis*, 34(15-16), pp.2327-2338.

Greenwood, N. and Earnshaw, A. (1984). Chemistry of the elements. Oxford [Oxfordshire]: Pergamon Press.

Grime, J.P. (1977). Evidence for the existence of three primary strategies in plants and its relevance to ecological and evolutionary theory. *The American Naturalist*, 111(982), pp. 1169-1193.

Gruebel, K., Leckie, J. and Davis, J. (1988). The Feasibility of Using Sequential Extraction Techniques for Arsenic and Selenium in Soils and Sediments. *Soil Science Society of America Journal*, 52(2), p.390.

Güngör, Ş. (2011). Measuring plant species diversity in alpine zones: A case study at the Kazdaği National Park, in Turkey. *Archives of biological sciences (Beograd)*, 63(4), pp.1147-1156.

Guo, Q. and Berry, W.L. (1998). Species richness and biomass: Dissection of the hump-shaped relationships. *Ecology* 79(7), pp. 2555-2559.

Guo, X., Zhang, G., Gong, H., Wang, K. and Zhang, J. (2009). Development of plant communities after restoration of the Antaibao mining site, China. *Frontiers of Biology in China* 4(2), pp. 222-227.

Guretzky, J., Moore, K., Burras, C. and Brummer, E. (2004). Distribution of Legumes along Gradients of Slope and Soil Electrical Conductivity in Pastures. *Agronomy Journal*, 96(2), p.547.

Haghnazari, F., Shahgholi, H. and Feizi, M. (2015). Factors affecting the infiltration of agricultural soils: review. *International Journal of Agronomy and Agricultural Research,* 6(5), pp.21-35.

Hahm, W.J., Riebe, C.S., Lukens, C.E., and Araki, S. (2014). Bedrock composition regulates mountain ecosystems and landscape evolution. *Proceedings of the National Academy of Sciences*, 111(9), pp, 3338-3343.

Halme, P. and Kotiaho, J. (2011). The importance of timing and number of surveys in fungal biodiversity research. *Biodiversity and Conservation*, 21(1), pp.205-219.

Harris, W. (2011). Mineral distribution and weathering in the Greater Everglades: implication for restoration. *Critical Reviews in Environmental Science and Technology* 41. Sup1, pp 4-27.

Hartsock, N.J.; Mueller, T.G.; Thomas, G.W.; Barnhisel, R.I.; Wells, K.L.; Shearer, S.A. (2000). Soil electrical conductivity variability. In: Robert, P.C.; Rust, R.H.; Larson, W.E. (eds). *Proceedings of the 5th International Conference on Precision Agriculture*, Bloomington, 16–19 July 2000 [CD-room]. Center for Precision Agriculture, University of Minnesota, St Paul, American Society of Agronomy.

Head, K. (2006). Manual of Soil Laboratory Testing, volume 1: Soil Classification and Compaction Tests (3rd Edition), Dunbeath: Whittles Publishing.

Hédl, R. (2007). Is sampling subjectivity a distorting factor in surveys for vegetation diversity? *Folia Geobotanica*, 42(2), pp.191-198.

Hejcman, M., Vondrackova, S., Muellerova, V., Cervena, K., Tlustos, P. (2012) Effect of quick lime ad superphosphate additives on emergence and survival of Rumes obtusifolius seedlings in acid and alkaline soils contaminated by As, Cd, Pb, and Zn. *Plant Soil and Environment*, 58(12), pp. 561-567.

Hendrychová, M. (2008). Reclamation success in post-mining landscapes in the Czech Republic: A review of pedological and biological studies. *Journal of Landscape Studies*, 1, pp.63-78.

Herrick, J.E., Schuman, G.E. and Rango, A. (2006). Monitoring ecological processes for restoration projects. *Nature Conservation* (14), pp. 161-171.

Herrington, R. 2011. Chapter 3.1 Geological features and genetic models of mineral deposits, SME Mining Engineering Handbook, 3rd edition, Vol. one/edited by Darling, P. Society for Mining, Metallury, and Exploration (SME).

Hijbeek, R., Koedam, N., and Nabiul Islam Khan, M. (n.d.) (2013). An evaluation of plotless sampling using vegetation simulations and field data from a mangrove forest. *PLoS One*, 8 (6), pp. 1-10.

Hillel, D. (2008). Soil in the environment. Crucible of terrestrial life. Academic Press. Elsevier, Amsterdam.

Hinsinger P. (2001). Bioavailability of soil inorganic P in the rhizosphere as affected by root-induced chemical changes: a review. *Plant and Soil*, 237 (2), pp. 173–195.

Hook, P.B, and Burke, I.C. (2000). Biogeochemistry in a shortgrass landscape: control by topography, soil texture, and microclimate. *Ecology* 81(10), pp. 2686-2703.

Houdijk, A.L.F.M., Verbeek, P.J.M., Dijk, H.F.G.V., and Roelofs, J.G.M. (1993). Distribution and decline of endangered herbaceous heathland species in relation to the chemical composition of the soil. *Plant and Soil* ,148, pp. 137-143.

Houle, G. (1990). Species-Area Relationship During Primary Succession in Granite Outcrop Plant Communities. *American Journal of Botany*, 77(11), p.1433.

Howard, P.J. and Howard, D.M., 1989. Effects of trees on soil properties: a resampling of J.D. Ovington’s plot at Abbotswood. *Merlewood research and Development Paper*. No. 101, Institute of Terrestrial Ecology.

Hozhina, E.I., Khramov, A.A., Gerasimov, P.A. and Kumarkov, A.A. (2001). Uptake of heavy metals, arsenic, and antimony by aquatic plants in the vicinity of ore mining and processing industries. *Journal of Geochemical Exploration* 74, pp. 153-162.

Huang, Z.C., Chen, T.B., Lei, M. and Hu, T.D. (2004). Direct determination of arsenic species in arsenic hyperaccumulator Pteris vittata by EXAFS. *Acta Botanica Sinica*, 46(1), pp. 46-50.

Hudson-Edwards, K., Houghton, S. and Osborn, A. (2004). Extraction and analysis of arsenic in soils and sediments. *TrAC Trends in Analytical Chemistry*, 23(10-11), pp.745-752.

International Standard Organization, (2002). ISO 14688-1, Geotechnical investigation and testing -- Identification and classification of soil -- Part 1: Identification and description.

Iwara, A.I., Gani, B.S., Njar, G.N., and Deekor, T,N. (2011). Influence of soil physic-chemical properties on the distribution of woody tree/shrub species in south-southern Nigeria. *Journal of Agriculture Science* 2(2), pp. 69-75.

Jacquez, GM. (2008). Spatial Cluster analysis, chapter 22 In: The Handbook of Geographic Information Science, Fotheringham and Wilson, J. (Eds.) Blackwell Publishing, pp 395-416.

Jambor, J.L., Blowes, D.W. and Ritchie, A.I.M. (2003). Environmental Aspects of Mine Wastes. Ottawa, Mineralogical Association of Canada.

James, F. (1990). Multivariate Analysis In Ecology And Systematics: Panacea Or Pandora Box. *Annual Review of Ecology and Systematics*, 21(1), pp.129-166.

Jana, U., Chassany, V., Bertrand, G., Castrec-Rouelle, M., Aubry, E., Boudsocq, S., Laffray, D. and Repellin, A. (2012). Analysis of arsenic and antimony distribution within plants growing at an old mine site in Ouche (Cantal, France) and identification of species suitable for site revegetation. *Journal of Environmental Management*, 110, pp.188-193.

Jankong, P., Visoottiviseth, P. and Khokiattiwong, S. (2007). Enchanced phytoremediation of arsenic contaminated land. *Chemosphere* 68, pp. 1906-1912.

Jantz, S.M., Barker, B., Brooks, T.M., Chini, L.P., Huang, Q.Y., and Moore, R.M. (2015). Future habitat loss and extinctions driven by land-use change in biodiversity hotspots under four scenarios of climate-change mitigation. Conservation Biology, 29 (4), pp. 1122-1131.

Jochimsen, M. E. (2001). Vegetation development and species assemblages in a long-term reclaimation project on mine spoil. *Ecological Engineering* 17, pp. 187-198.

Johnson, N., Payton, P., Spalding, A. (1996). The conservation value of metalliferous mine sites in Cornwall, pp 31-41. Cornwall archaeological unit and Institute of Cornish studies.

Jones, J. (2001). Laboratory guide for conducting soil tests and plant analysis. Boca Raton: CRC Press.

Jongman, R., Braak, C. and Van Tongeren, O. (1995). Data analysis in community and landscape ecology. Cambridge: Cambridge University Press.

Keen, B., & Russell, E. (1921). The factors determining soil temperature. *The Journal of Agricultural Science*, 11(3), 211-239.

Kent, M. (2011). *Vegetation Description and Data Analysis*. 1st ed. Hoboken: John Wiley & Sons.

Kent, M. and Coker, P. (1996). Vegetation description and data analysis-A Practical Approach. Chichester, West Sussex, UK: John Wiley & Sons.

Keon, N., Swartz, C., Brabander, D., Harvey, C. and Hemond, H. (2001). Validation of an Arsenic Sequential Extraction Method for Evaluating Mobility in Sediments. *Environmental Science & Technology*, 35(16), pp.3396-3396.

Khalid, M. (2011). Cluster Analysis - A Standard Setting Technique in Measurement and Testing. *Journal of Applies Quantitative Methods*, 6(2).

Kitano, M., Urayama, K., Sakata, Y., Sonoda, Y., Ebihara, K., Sago, Y., Yoshikoshi, H., Araki, T., Yasutaka, D., Cho, H. and Kobayashi, T. (2009). Water and salt movement in soil driven by crop roots: a controlled column study. *Biologia*, 64 (3), pp. 474-477.

Knollová, I., Chytrý, M., Tichý, L. and Hájek, O. (2005). Stratified resampling of phytosociological databases: some strategies for obtaining more representative data sets for classification studies. *Journal of Vegetation Science*, 16(4), pp.479-486.

Koerner, C. 2003. Limitation and stress-always or never? *Journal of Vegetation Science*,14, pp. 141-143.

Kogure, K., Ohira, Y. and Yamaguchi, H. (1985). Basic study of probabilistic approach to prediction of soil trafficability — Statistical characteristics of cone index. *Journal of Terramechanics*, 22(3), pp.147-156.

Koolen, A. and Kuipers, H. (1983). *Agricultural soil mechanics*. Berlin: Springer-Verlag.

Kozlov, M., Zvereva, E. and Zverev, V. (2009). Impacts of point polluters on terrestrial biota. Dordrecht: Springer.

Kruckeberg AR (2004) Geology and Plant Life: The Effects of Landforms and Rock Types on Plants. University of Washington Press, Seattle.

Kuck, Peter H., and Magyar, Michael J. (2007) U.S. Geological Survey Open-File Report 2007-1257, p. 112.

Kuehnelt, D., Lintschinger, J. and Goessler, W. (2000). Arsenic compounds in terrestrial organisms. IV. Green plants and lichens from an old arsenic smelter site in Austria. *Appl. Organometal. Chem.*, 14(8), pp.411-420.

Kumpiene, J., Fitt, J.P., Mench, M. (2012). Arsenic fractionation in mine spoils 10 years after aided phytostabilition. *Environmental Polution* 166, pp. 82-88.

Kuo, S., Lai, M. and Lin, C. (2006). Influence of solution acidity and CaCl2 concentration on the removal of heavy metals from metal-contaminated rice soils. *Environmental Pollution*, 144(3), pp.918-925.

Last, W. and Smol, J. (2001). Tracking Environmnetal Change Using Lake Sediments Volume 2: Physical and Geochemical Methods. Kluwer Academic Publishers, Norwell, MA, USA.

Law, D. L. (1984). Mined-land rehabilitation. Van Nostrand Reinhold Company Inc.

Lee, W.G., Allen, R.B. and Johnson, P.N. (1986). Succession and dynamics of gorse (*Ulex europaeus* L.) communities in the dunedin ecological district South Island, New Zealand. *New Zealand Journal of Botany* 24, pp. 279-292.

Lehnert, M. (2014). FACTORS AFFECTING SOIL TEMPERATURE AS LIMITS OF SPATIAL INTERPRETATION AND SIMULATION OF SOIL TEMPERATURE. *Acta Universitatis Palackianae Olomucensis – Geographica,* 45(1), pp.5-21.

Leis, S. A., Engle, D. M., Leslie, D. M., Fehmi, J. S., & Kretzer, J. (2003). Comparison of Vegetation Sampling Procedures in a Disturbed Mixed-Grass Prairie. Proceedings of the Oklahoma Academy of Science. 83, 7-16.

Leveridge, B.E. Holder, M.T. and Goode, A.J.J. (1990). Geology of the country aroundFalmouth. Memoir of the British Geological Survey, Sheet 352 (England and Wales).

Liu, G. and Cai, Y. (2007). Arsenic speciation in soils: An analytical challenge for understanding arsenic biogeochemistry. In: Sarkar, D., Datta, R. and Hannigan, R. (ed.). Concepts and applications in environmental geochemistry. Amsterdam: Elsevier.

Liu, H., Probst, A. and Liao, B. (2005). Metal contamination of soils and crops affected by the Chenzhou lead/zinc mine spill (Hunan, China). *Science of The Total Environment*, 339(1-3), pp.153-166.

Lottermoser, B., Glass, H. and Page, C. (2011). Sustainable natural remediation of abandoned tailings by metal-excluding heather (*Calluna vulgaris*) and gorse (*Ulex europaeus*), Carnon Valley, Cornwall, UK. *Ecological Engineering*, 37(8), pp.1249-1253.

Loveland, P.J. and Whalley, W.R. (2000). Chapter 7 Particle Size Analysis. In: Smith, K. A., and Mullins, C. E.. Soil and Environmental analysis: physical methods. 2nd. Rev. New York, M. Dekker.

Macnair, M. and Cumbes, Q. (1987). Evidence That Arsenic Tolerance in *Holcus Lanatus* L. id Caused by an Altered Phosphate Uptake System. *New Phytologist*, 107(2), pp.387-394.

Macnair, M.R. (1987). Heavy metal tolerance in plants: a model evolutionary system. *Trends in Ecology and Evolution*, 2 pp. 354-359.

Magalhaes, M.C.F. (2002). Arsenic. An environmental problem limited by solubility. *Pure and Applied Chemistry*, 74(10), pp. 1843-1850.

Magesan, G.N., Wang, H. and Clinton, P.W. (2012). Nitrogen cycling in gorse-dominated ecosystems in New Zealand. *New Zealand Journal of Ecology* 36(1), pp. 21-28.

Magurran, A. (2004). Measuring biological diversity. Oxford, UK: Blackwell Publishing.

Maiti, S.K., (2012). Ecorestoration of the coalmine Degraded Lands. Springer Science and Business Media, pp122-127.

Makri, F., Psillakis, Z. and Arapis, A. (2015). Length of the minimum sequence containing repeats of success runs. *Statistics & Probability Letters*, 96, pp.28-37.

Malanson, G.P., Pavlik, C. and Ceilley, D. (1993). Introducing students to plant geography: polar ordination applied hanging gardens. *Journal of Geography*, 92(3); Periodicals Archive online, pp. 129-138.

Marques, A., Moreira, H., Rangel, A. and Castro, P. (2009). Arsenic, lead and nickel accumulation in Rubus ulmifolius growing in contaminated soil in Portugal. *Journal of Hazardous Materials*, 165(1-3), pp.174-179.

Marrs, R.H. (1993). Soil fertility and nature conservation in Europe: Theoretical considerations and practical management solutions. *Advances in Ecological Research* 24, pp. 241-300.

Mclean, J. E. and Bledsoe, B. E. (1992). Behaviour of Metals in Soil. Ground Water Issue. Office of research and development, and office of Solid Waste and Emergency Response. United States EPA. EPA/540/S-92/018.

McNeilly, T.S. (1968). Evolution in closely adjacent plant populations. III. *Agrostis tenuis* on a small copper mine. *Heredity*, 23, pp.99-108.

McSweeney, K. and Jansen, I.J. (1984). Soil structure and associated rooting behaviour in minesoils. *Soil Science Society of America Journal* 48, pp. 607-612.

Meharg, A. and Hartley-Whitaker, J. (2002). Arsenic uptake and metabolism in arsenic resistant and nonresistant plant species. *New Phytologist*, 154(1), pp.29-43.

Michalcová, D., Lvončík, S., Chytrý, M. and Hájek, O. (2011). Bias in vegetation databases? A comparison of stratified-random and preferential sampling. *Journal of Vegetation Science*, 22(2), pp.281-291.

Mihaljevic, M., Ettler, V., Sebek, O., Drahota, P., Strnad, L., Prochazka, R., Zeman, J. and Stracek, O. (2010). Alteration of arsenopyrite in soils under different vegetation covers. *Science of the Total Environment* 408, pp. 1286-1294.

Mikanova, O. (2006). Effects of heavy metals on some soil biological parameters. *Journal of Geochemical Exploration* 88, pp. 220-223.

Miller, J.J. and Curtin, D. (2007). Electrical Conductivity and Soluble Ions. In: Carter, M.R. and Gregorich, E.G. (eds). Soil Sampling and Methods of Analysis, 2nd edition. Canadian Society of Soil Sciece, CRC Press, pp. 161-173.

Miller, J.J. and Curtin, D. (2007). Chapter 15. Electrical Conductivity and Soluble ions in: Carter, M. and Gregorich, E. Soil sampling and methods of analysis. Boca Raton, FL: CRC Press.

Minnesota Department of Natural Resources. (2013). A handbook for collecting vegetation plot data in Minnesota: The relevé method. 2nd ed. Minnesota Biological Survey, Minnesota Natural Heritage and Nongame Research Program, and Ecological Land Classification Program. Biological Report 92. St. Paul: Minnesota Department of Natural Resources.

Moberg, F. and Folke, C. (1999). Ecological goods and services of coral reef systems. *Ecological Economics*, 29, pp. 215-233.

Mohammad, A. Z. C. (2013). Classification And Ordination Methods As A Tool For Analyzing Of Plant Communities. INTECH Open Access Publisher, 2013. Print.

Mohammadi, K., Sohrabi, Y., Heidari, G., Khalesro, S., Majidi, M. (2012). Effective factors on biological nitrogen fixation, *African Journal of Agricultural Research*, 7 (12), 1782-1788.

Moolman, J. and Van Huyssteen, L. (1989). A geostatistical analysis of the penetrometer soil strength of a deep ploughed soil. *Soil and Tillage Research*, 15(1-2), pp.11-24.

Moon C. J. (2002). Wheal Jane: soil geochemistry revisited. *Geoscience in south-west England*,10(3), pp. 336-342.

Moon, C.J., Whateley, M.K.G. and Evans, A.M.(Editors) (1995). Narrow vein deposits – Wheal Jane, Cornwall. Introduction to Mineral Exploration. Blackwell Science, Oxford, pp. 344-367.

Moore, J., Fitzsimons, S., Lambe, E. and White, J. (1970). A comparison and evaluation of some phytosociological techniques. *Plant Ecology*, 20(1-4), pp.1-20.

Moral, R.D. (1980). On selecting indirect ordination methods. *Vegetatio*, 42 (1), pp. 75-84.

Morales, N., Martínez, D., García-Meza, J., Labastida, I., Armienta, M., Razo, I. and Lara, R. (2014). Total and bioaccessible arsenic and lead in soils impacted by mining exploitation of Fe-oxide-rich ore deposit at Cerro de Mercado, Durango, Mexico. *Environmental Earth Sciences*, 73(7), pp. 3249-3261.

Moreno-Jiménez, E., Manzano, R., Esteban, E. and Peñalosa, J. (2009). The fate of arsenic in soils adjacent to an old mine site (Bustarviejo, Spain): mobility and transfer to native flora. *Journal of Soils and Sediments*, 10(2), pp.301-312.

Morin, G. and Calas, G. (2006). Arsenic in Soils, Mine Tailings, and Former Industrial Sites. Elements, 2(2), pp. 97-101.

Morin, G. and Calas, G. (2006). Arsenic in Soils, Mine Tailings, and Former Industrial Sites. *Elements*, 2(2), pp. 97-101.

Mosley, L., Fitzpatrick, R., Palmer, D., Leyden, E. and Shand, P. (2014). Changes in acidity and metal geochemistry in soils, groundwater, drain and river water in the Lower Murray River after a severe drought. *Science of The Total Environment,* 485-486, pp.281-291.

Mossop, K. and Davidson, C. (2003). Comparison of original and modified BCR sequential extraction procedures for the fractionation of copper, iron, lead, manganese and zinc in soils and sediments. Analytica Chimica Acta, 478(1), pp.111-118.

Mudroch, A., Azcue, J. and Mudroch, P. (1997). Manual of physico-chemical analysis of aquatic sediments. Boca Raton, Fla: CRC Lewis.

Murciego, A., Álvarez-Ayuso, E., Pellitero, E., Rodríguez, M., García-Sánchez, A., Tamayo, A., Rubio, J., Rubio, F. and Rubin, J. (2011). Study of arsenopyrite weathering products in mine wastes from abandoned tungsten and tin exploitations. Journal of Hazardous Materials, 186(1), pp.590-601.

Murcott, S. (2012). Arsenic Contamination in the World: An international Sourcebook. IWA Publishing.

Myers, L.W. and Shelton, R.L. (1980). Survey methods for ecosystem management. Wiley, New York.

Nagamori, M., Watanabe, Y., Hase, T., Kurata, Y., Ono, Y. and Kawamura, K. (2007). A simple and convenient empirical survey method with a soil electrical conductivity meter for incineration residue-derived soil contamination. J Mater Cycles Waste Manag, 9(1), pp.90-98.

Nawaz, M.F., Bourrie, G. and Trolard, F. (2013). Soil compaction impact and modelling. Areview. Agronomy for Sustainable Development 33, pp. 291-309.

Neal, C., Whitehead, P.G., Jeffery, H., Neal, M., (2005). The water quality of the River Carnon, west Cornwall, November 1992 to March 1994: The impacts of Wheal Jane discharges. *Science of the Total Environment*, Vol 338 (1-2), pp. 23-39.

Neupane, G., Donahoe, R. and Arai, Y. (2014). Kinetics of competitive adsorption/desorption of arsenate and phosphate at the ferrihydrite–water interface. *Chemical Geology*, 368, pp.31-38.

Nirel, P. and Morel, F. (1990). Pitfalls of sequential extractions. *Water Research*, 24(8), pp.1055-1056.

Nonogaki, H., (2014). Seed dormancy and germination—emerging mechanisms and new hypotheses. *Frontiers in Plant Science*, 5, pp. 1-14.

Noss, R. (1996). The Naturalists Are Dying off. *Conservation Biology*, 10(1), pp.1-3.

Økland, R. (2007). Wise use of statistical tools in ecological field studies. *Folia Geobotanica*, 42(2), pp.123-140.

Onthong, J. and Osaki, M. (2006). Adaptations of tropical plants to acid soils. *Tropics*, 15(4), pp.337-347.

Osman, K.T. (2013). Soils Principles, Properties and Management. Dordrecht: Springer.

O'Sullivan, M., Dickson, J. and Campbell, D. (1987). Interpretation and presentation of cone resistance data in tillage and traffic studies. J*ournal of Soil Science*, 38(1), pp.137-148.

Otones, V., Alvarez-Ayuso, E., Garcia-Sachez, A., Regina, I.S. and Murciego, A. (2011a). Mobility and phytoavailability of arsenic in an abandoned mining area. *Geoderma* 166, pp. 153-161.

Otones, V., Alvarez-Ayuso, E., Garcia-Sachez, A., Regina, I.S. and Murciego, A. (2011b). Arsenic distribution in soils and plants of an arsenic impacted former mining area. Environmental Pollution 159, pp. 2637-2647.

Owen, K.M. and Marrs, R.H. (2000). Acidifying arable soils for the restoration of acid grasslands. Applied Vegetation Science 3, pp. 105-116.

Page, C.N., (1979). Experimental aspects of fern ecology. The Experimental Biology of Ferns. London, Academic Press. Dyer, A.F. (ed.), pp. 551-579.

Page, C.N., (1998). Ferns, their habitats in the landscape of Britain and Ireland. London: Colins New Natures.

Page, C.N., (2006). Celtic hedge as refuges for plant iversity in predominantly agriculturalised landscape. In Leach, S.J., Page, C.N., Peytoureau, Y. and Sandford, M.N. (eds). Botanical Links in the Atlantic Arc. London: B.S.B.I. and English Nature.

Pandey, B., Agrawal, M., and Singh, S. (2014). Coal mining activities change plant community structure due to air pollution and soil degradation. *Ecotoxicology*, 23 (8), pp 1474-1483.

Papp, J. F., Corathers, L. A., Edelstein, D. L., Fenton, M. D., Kuck, P.H. and Magyar, M.J. (2007). Cr, Cu, Mo, Ni, and steel commodity price influences, Version 1.1. Reston, VA. U.S. Geological Survey Open-File Report 2007-1257, p19.

Park, M. (1980). Chapter 9: Method of sampling the plant community. In: Barbour, M., Burk, J. and Pawlesland, M. (2013). The effect of local topography on the regeneration of vegetation on an abandoned Cornish mine waste site. MSc. dissertation, University of Exeter, Camborne School of Mines.

Parker, S. (1994). *McGraw-Hill dictionary of geology and minerology*. New York: McGraw-Hill.

Pausas, J.G. and Austin, M.P. (2001). Patterns of plant species richness in relation to different environments: an appraisal. Journal of Vegetation Science 12, pp. 153-166.

Peterson, G., Allen, C. and Holling, C. (1998). Original Articles: Ecological Resilience, Biodiversity, and Scale. *Ecosystems*, 1(1), pp.6-18.

Pongratz, R. (1998). Arsenic speciation in environmental samples of contaminated soil. *The Science of the Total Environment* 224, pp.133-141.

Pottier, J., Bedecarrats, A. and Marrs, R.H. (2009). Analysing the spatial heterogeneity of emergent groups to assess ecological restoration. *Journal of Applied Ecology* 46, pp. 1248-1257.

Power, M.R., Pirrie, D., Camm, G.S., and Andersen, J.C.O. (2009). The mineralogy of efflorescence on As Calciner buildings in SW England. *Mineralogical Magazine* 73(1), pp. 27-42.

Powlesland, M.A., (2013). The Effect of Local Topography on the Regeneration of Vegetation on an Abandoned Cornish Mine Waste Site, (MSc. Dissertation). Camborne School of Mines, University of Exeter.

Prach, K., and Rehounkova, K. (2006). Vegetation succession over broad geographical scales: which factors determine the patterns? Preslia 78, pp. 469-480.

Pratas, J., Prasad, M., Freitas, H. and Conde, L. (2005). Plants growing in abandoned mines of Portugal are useful for biogeochemical exploration of arsenic, antimony, tungsten and mine reclamation. *Journal of Geochemical Exploration*, 85(3), pp.99-107.

Primack, R. B. (2010). Essentials of Conservation Biology, 5th edition. Sinauer Associates, Inc.. pp. 374-375.

Proctor, R.R., (1933). Fundamental Principles of Soil Compaction. Engineering News-Record, 11(9), pp. 245-248.

Quainoo, S., Seena, S., and Graca, M.A.S. (2016). Copper tolerant ecotypes of *Heliscus lugdunensis* differ in their ecological function and growth. *Science of The Total Environment*, 544, pp 168-175.

Radojevic, M. and Bashkin, V. N., 1999. Practical Environmental Analysis. Royal Society of Chemistry, UK.

Rainbow, P., Kriefman, S., Smith, B. and Luoma, S. (2011). Have the bioavailabilities of trace metals to a suite of biomonitors changed over three decades in SW England estuaries historically affected by mining? *Science of The Total Environment*, 409(8), pp.1589-1602.

Rascio, N. and Navari-Izzo, F. (2011). Heavy metal hyperaccumulating plants: How and why do they do it? And what makes them so interesting? *Plant Science* 180, pp. 169-181.

Reddy, K., Wang, L. and Gloss, S. (1995). Solubility and mobility of copper, zinc and lead in acidic environments. *Plant and Soil,* 171(1), pp.53-58.

Reitemeier, R. (1946). Effect of Moisture Content on the Dissolved and Exchangeable Ions of Soils of Arid Regions. *Soil Science*, 61(3), pp.195-214.

Remon, E., Bouchardon, J.-L., Cornier, B., Guy, B., Leclerc, J.-C. and Faure, O. (2005). Soil characteristics, heavy metal availability and vegetation recovery at a former metallurgical landfill: Implications in risk assessment and site restoration. Environmental Pollution 137, pp. 316-323.

Ren, Y., Lue, Y., and Fu, B. (2016). Quantifying the impacts of grassland restoration on biodiversity and ecosystem services in China: A meta-analysis. *Ecological Engineering*, 95, pp 542-550.

Revuelta, M. B., (2017). Mineral Resources: From Exploration to Sustainability Assessment. Springer International Publisher, pp576-579.

Rhoades JD & Oster JD (1986) Solute content In: Klute A (ed) Methods of Soil Analysis, Part 1. Physical and Mineralogical Methods, pp 985–1006. Madison, WI: American Society of Agronomy.

Rhoades, J. (1990). Determining soil salinity from measurements of electrical conductivity. Communications in Soil Science and Plant Analysis, 21(13-16), pp.1887-1926.

Rhoades, J.D. (1992). Instrumental field methods of salinity appraisal. In G.C. Topp et al., Eds. Advances in Measurement of Soil Physical Properties: Bringing Theory into Practice. SSSA Special Publication No. 30. ASA, CSSA, and SSSA, Madison, WI, pp. 231–248.

Rice, E. and Kelting, R. (1955). The Species--Area Curve. Ecology, 36(1), pp.7-11.

Richards, L. A. (ed.) (1954), Diagnosis and Improvement of Saline and Alkali Soils, USDA Handbook No. 60. Washington, D.C.: U.S. Department of Agriculture.

Rieke-Zapp, D., Rosenbauer, R. and Schlunegger, F. (2009). A photogrammetric surveying method for field applications. *The Photogrammetric Record,* 24(125), pp.5-22.

Robbins, C.W. and Wiegand, C.L. (1990). Field and Laboratory Measurements. In: Agricultural Salinity Assessment and Management. New York: American Society of Civil Engineers.

Robson, T.C., Braungardt, C.B., Keith-Roach, M.J., Rieuwerts, J. S. and Worsfold, P.J. 2013. Impact of arsenopyrite contamination on agriculture soils and crops. *Journal of Geochemical Exploration* 125, pp. 102-109.

Rochefort, L., Isselin-Nondedeu, F., Boudreau, S. and Poulin, M. (2013). Comparing survey methods for monitoring vegetation change through time in a restored peatland. *Wetlands Ecology and Management*, 21(1), pp.71-85.

Roleček, J., Chytrý, M., Hájek, M., Lvončík, S. and Tichý, L. (2007). Sampling design in large-scale vegetation studies: Do not sacrifice ecological thinking to statistical purism! *Folia Geobotanica*, 42(2), pp.199-208.

Romero, A., González, I. and Galán, E. (2006). Estimation of potential pollution of waste mining dumps at Peña del Hierro (Pyrite Belt, SW Spain) as a base for future mitigation actions. *Applied Geochemistry*, 21(7), pp.1093-1108.

Romero, F., Canet, C., Alfonso, P., Zambrana, R. and Soto, N. (2014). The role of cassiterite controlling arsenic mobility in an abandoned stanniferous tailings impoundment at Llallagua, Bolivia. *Science of The Total Environment*, 481, pp.100-107.

Ruthrof, K.X., Fontaine, J.B., Buiser, M., Matusick, G., McHenry, M.P. and Hardy, G.E. St. J. (2013). Linking restoration outcomes with mechanism: the role of site preparation, fertilisation and revegetation timing relative to soil density and water content. *Plant Ecology* 214, pp. 987-998.

Salzsauler, K.A., Sidenko, N.V. and Sherriff, B.L. (2005). Arsenic mobility in alteration products of sulphide-rich, arsenopyrite-bearing mine wastes, Snow Lake, Manitoba, Canada. *Applied Geochemistry* 20, pp. 2303-2314.

Santala, K.R. and Ryser, P. (2009) Influence of heavy-metal contamination on plant response to water availability in white birch, Betula papyrifera. *Environmental and Experimental Botany* 66, pp. 334-340.

Santos-Jallath, J., Castro-Rodríguez, A., Huezo-Casillas, J. and Torres-Bustillos, L. (2012). Arsenic and heavy metals in native plants at tailings impoundments in Queretaro, Mexico. Physics and Chemistry of the Earth, Parts A/B/C, 37-39, pp.10-17.

Satterthwaite, W.H., (2010). Competition for space can drive the evolution of dormancy in a temporally invariant environment. Plant Ecology, 208, pp. 167-185.

Schaetzl, R.J. and Anderson, S. (2005). Soils-Genesis and Geomorphology, Cambridge University Press, pp. 17.

Schultz, N., Reid, N., Lodge, G. and Hunter, J. (2014). Seasonal and interannual variation in vegetation composition: Implications for survey design and data interpretation. *Austral Ecology*, 39(7), pp.755-766.

Shelmerdine, P.A., Blacj, C.R., McGrath, S.P. and Young, S.D. (2009). Modelling phytoremediation by the hyperaccumulating fern, Pteris vittata, of soils historically contaminated with arsenic. *Environmental Pollution* 157, pp. 1589-1596.

Shuster, W., Herms, C., Frey, M., Doohan, D., and Cardina, J. (2005). Comparison of survey methods for an invasive plant at the subwatershed level. *Biological Invasions*. 7, 393-403.

Siegel, S. (1956). *Nonparametric Satistics for the Behavioral Sciences*. 1st ed. McGraw-Hill.

Simpson, E.H. (1949). Measurement of diversity. Nature 163, pp. 688-688.

Skinner, A.K., Lunt, I.D., Spooner, P. and McIntype, S. (2009). The effect of soil compaction on germination and early growth of Eucalyptus albens and an exotic annual grass. *Austral Ecology* 34, pp. 698-704.

Skousen, J.G., Johnson, C.D. and Garbutt, K. (1994). Land reclamation--Natural revegetation of 15 abandoned mine land sites in West Virginia. Journal of Environmental Quality 23, pp. 1224-1230.

Slejkovec, Z., Elteren, J., Glass, H., Jeran, Z. and Jacimovic, R. (2010). Speciation analysis to unravel the soil-to-plant transfer in highly arsenic-contaminated areas in Cornwall (UK). *International Journal of Environmental Analytical Chem*istry, 90(10), pp.784-796.

Smartt, P. and Grainger, J. (1974). Sampling for Vegetation Survey: Some Aspects of the Behaviour of Unrestricted, Restricted, and Stratified Techniques. *Journal of Biogeography*, 1(3), p.193.

Smedley, P. and Kinniburgh, D. (2002). A review of the source, behaviour and distribution of arsenic in natural waters. Applied Geochemistry, 17(5), pp.517-568.

Smith, R. L. and Smith, T. M. (2003). Elements of Ecology, 5th edition. Pearson Education, Inc.

Soil survey staff. (2010). Keys to soil taxonomy, 11th edition. USDA (The U.S. Department of Agriculture), Natural Resources Conservation Service.

Sørensen, S. P. L. (1909). Enzymstudien II: Uber die Messung und die Bedeutung der Wasserstoffionenkonzentration bei enzymatischen Prozessen. Biochemische Zeitschrift, 21, pp. 131-200.

Sørensen, T. (1948). A method of establishing groups of equal amplitude in plant sociology based on similarity of species and its application to analyses of the vegetation on Danish commons. *Kongelige Danske Videnskabernes Selskab*. **5** (4): 1–34.

Spitz, K. and Trudinger J.(Editors). (2009). Mining and the Environment : from ore to metal. CRC Press/Balkema, Taylor and Francis Group, London, UK.

Steinhauser G, Adlassnig W, Lendl T, Peroutka M, Weidinger M, Lichtscheidl I, Bichler M (2009) Metalloid contaminated microhabitats and their biodiversity at a former antimony mining site in Schlaining, Austria. *Open Environmental Sciences* 3: 26-41

Stewart, E. Allen, (1989). Chemical Analysis of Ecological Material, 2nd edition. Blackwell Scientific Publications, pp. 16.

Stohlgren, T. (2007). Measuring plant diversity. Oxford: Oxford University Press.

Surhone, L., Timpledon, M. and Marseken, S. (2010). Wald-Wolfowitz Runs Test: Wald-Wolfowitz Runs Test, Non-parametric Statistics, Statistical Hypothesis Testing, Independence, Probability Theory, Random Variable. 1st ed. Betascript Publishing.

Syvitski, J. (1991). Principles, methods, and application of particle size analysis. Cambridge: Cambridge University Press.

Tack, F. and Verloo, M. (1995). Chemical Speciation and Fractionation in Soil and Sediment Heavy Metal Analysis: A Review. *International Journal of Environmental Analytical Chemistry*, 59(2-4), pp.225-238.

Tamas, J. and Kovacs, E. (2005). Vegetation pattern and heavy metal accumulation at a mine tailing at Gyoengyoesoroszi, Hungary. *Verlag der Zeitschrift fuer Naturforschung* 60(3-4), pp. 362-367.

Tan, P., Steinbach, M. and Kumar, V. (2005). *Introduction to data mining. 1st ed. Boston: Pearson Addison Wesley.*

Tessier, A., Campbell, P. and Bisson, M. (1979). Sequential extraction procedures for the speciation of particulate trace metals. Analytical Chemistry, 51(7), pp.844-851.

The council of the European Communities, (1992). Council Directive 92/43/EEC, on the onservation of natural habitats and of wild fauna and flora.

Tlustoš, P., Száková, J., Stárková, A. and Pavlíková, D. (2005). A comparison of sequential extraction procedures for fractionation of arsenic, cadmium, lead, and zinc in soil. *Open Chemistry*, 3(4).

Townsend, C. R., Beron, M. and Harper, J.L. (2008). Essentials of Ecology, 3rd edition. Blackwell Publishing.

Tremlová, J., Vašíčková, I., Száková, J., Goessler, W., Steiner, O., Najmanová, J., Horáková, T. and Tlustoš, P. (2016). Arsenic compounds occurring in ruderal plant communities growing in arsenic contaminated soils. *Environmental and Experimental Botany*, 123, pp.108-115.

Tripathi, R.D., Srivastava, S., Mishra, S., Singh, N., Tuli, R., Gupta, D.K. and Maathuis, F.J.M. (2007). Arsenic hazards: strategies for tolerance and remediation by plants. *Trends in Biotechnology* 25(4), pp. 158-165.

United Nations Population Division (2012), World Population Prospects, the 2012 Revision.

US EPA 2005a. Ecological soil screening level for arsenic. Washington DC, US EPA. https://www.epa.gov/chemical-research/interim-ecological-soil-screening-leveldocuments (accessed January 2020).

US EPA 2005b. Ecological soil screening level for lead. Washington DC, US EPA. https://www.epa.gov/chemical-research/interim-ecological-soil-screening-leveldocuments (accessed January 2020).

US EPA 2007. Ecological soil screening level for copper. Washington DC, US EPA. https://www.epa.gov/chemical-research/interim-ecological-soil-screening-leveldocuments (accessed January 2020).

Valente, T., Gomes, P., Pamplona, J. and de la Torre, M.L. (2012). Natural stabilization of mine waste-dumps—evolution of the vegetation in distinctive geochemical and mineralogical environments. *Journal of Geochemical exploration,*123, pp 152-161.

Vasquez-Murrieta, M.S., Migueles-Garduno, I., Franco-Hernandez, O., Govaerts, B. and Dendooven, L. (2006). C and N mineralisation and microbial biomass in heavy-metal contaminated soil. European Journal of Soil Biology 42, pp. 89-98.

Venugopalan, M. and Prasad, R. (1989). Hydrolysis of ammonium polyphosphate in soils under aerobic and anaerobic conditions. *Biology and Fertility of Soils*, 8(4).

Verdejo, J., Ginocchio, R., Sauvé, S. and Neaman, A. (2016). Thresholds of copper toxicity to lettuce in field-collected agricultural soils exposed to copper mining activities in Chile. *Journal of soil science and plant nutrition,* 16 (1), pp. 154-158.

Vickers, H., Gillespie, M. and Gravina, A. (2012). Assessing the development of rehabilitated grasslands on post-mined landforms in north west Queensland, Australia. *Agriculture, Ecosystem and Environment* 163, pp. 72-84.

Wali, M.K. (1999). Ecological succession and the rehabilitation of disturbed terrestrial ecosystems. *Plant and Soil* 213, pp. 195-220.

Wanat, N., Joussein, E., Soubrand, M. and Lenain, J. (2014). Arsenic (As), antimony (Sb), and lead (Pb) availability from Au-mine Technosols: a case study of transfer to natural vegetation cover in temperate climates. Environment Geochem Health, 36(4), pp.783-795.

Wang, J., Bai, Z. and Yang, P. (2014). Simulation and prediction of ion transport in the reclamation of sodic soils with gypsum based on the support vector machine. *The Scientific World Journal*, 2014,pp 1-9.

Wanogho, S., Gettinby, G. and Caddy, B. (1987). Particle size distribution analysis of soils using laser diffraction. *Forensic Science International*, 33(2), pp.117-128.

Weber, T. (1999). A Plea for a Diversity of Scientific Styles in Ecology. Oikos, 84(3), p.526.

Weis, J.S. and Weis, P. (2004). Metal uptake, transport and release by wetland plants: implications for phytoremediation and restoration. *Environment International* 30, pp. 685-700.

Wenzel, W., Kirchbaumer, N., Prohaska, T., Stingeder, G., Lombi, E. and Adriano, D. (2001). Arsenic fractionation in soils using an improved sequential extraction procedure. *Analytica Chimica Acta*, 436(2), pp.309-323.

Whitbread-Abrutat, P.H., (1995). The improvement of tree establishment on metalliferous mine wastes, PhD thesis. Camborne, University of Exeter.

White, R. E., (2006). Principles and Practice of Soil Science, 4th edition. Blackwell Publishing, pp. 242-244.

Whittaker, R.H. (1960). Vegetation of the Siskiyou Mountains, Oregon and California. *Ecological Monographs*. 30, pp 279-338.

Wildi, O. (2013). *Data analysis in vegetation ecology*. 2nd ed. John Wiley & Sons.

Wilkie, J. A. and Hering, J. G. (1996). Adsorption of arsenic onto hydrous ferric oxides: effects of adsorbate/adsorbent ratios and co-occurring solutes. Colloids and surfaces A: Physicochemical and engineering aspects 107, pp. 97-110.

Willis, C.G., Baskin, C.C., Baskin, J.M., Auld,J.R., Venable, D.L., Cavender-Bares, J., Donohue, K., Casas, R.R.D. and The NESCent Germination Working Group, (2014). The evolution of seed dormancy: environmental cues, evolutionary hubs, and diversification of the seed plants. *New Phytologist*, 203 (1), pp.300-309.

Wilmers, C.C., Sinha, S. and Brede, M., (2002). Examing the effects of species richness on community stability: an assembly model approach. *OKIOS* 99, pp. 363-367.

Wong, M. and Bradshaw, A. (2002). The restoration and management of derelict land. New Jersey: World Scientific Publishing.

Wood, M. (1989). Soil biology. Blackie and Son Ltd.

Yu, Y.M., Zhu, Y.X., Gao, Z.M., Gammons, C.H. and Li, D.X. (2007). Rates of arsenopyrite oxidation by oxygen and Fe(III) at pH 1.8-12.6 and 15—45˚C. *Environmental Science and Technology,* 41, pp. 6460-6464.

Zelnik, I., Carni, A. (2013). Plant species diversity and composition of wet grasslands in relation to environmental factors. *Biodiversity and Conservation* 22, pp. 2179-2192.

Zhang, H. and Selim, H. (2008). Competitive sorption-desorption kinetics of arsenate and phosphate in soils. *Soil Science*, 173(1), pp.3-12.

Zhao, J., Dong, Y., Xie, X., Li, X., Zhang, X. and Shen, X. (2011). Effect of annual variation in soil pH on available soil nutrients in pear orchards, *Acta Ecologica Sinica* 31, pp. 212-216.

Zhou, L., Hou, J., Chan, G.C., and Sze, D.M., (2014). Arsenic trioxide for non-acute promyelocytic leukemia haematological malignancies: A new frontier, *Journal of blood disorders,* 1(4), pp 1018-1026.

Zhou, T. and Peng, S., (2008). Spatial scale types and measurement of edge effects in ecology. *ACTA Ecologica Sinica,* 28(7), pp. 3322-3333.

Appendix A: Species found in Carnon Valley

Common name	Scientific name	Middle valley	MV ditch	Lower valley	LV ditch
Bee nettle	*Lamium album*	0	0	1	0
Bigleaf periwinkle	*Vinca major*	0	0	1	1
Black alder/common alder	*Alnus glutinosa*	0	0	1	1
Bog pimpernel	*Anagallis tenella*	0	0	1	0
Bracken	*Pteridium aquilinum*	1	1	1	0
Bramble	*Rudus fruticosus*	1	1	1	1
Bristle leaved bent	*Agrostis setacea/* *Agrostis curtisii*	1	1	1	0
Broad buckler fern	*Dryopteris dilatata*	0	0	1	0
Broad leaved dock	*Rumex obtusifolius*	0	0	1	1
Buck's horn plantain/ minutina	*Plantago coronopus*	1	1	1	0
Buddleja	*Buddlesja davidii*	1	1	1	1
Bristle club-rush	*Scirpus setaceus*	1	1	1	1
Bulrush	*Typha angustifolia*	0	0	1	1
Common bent	*Agrostis tenuis*	1	1	1	1
Common daisy	*Bellis perennis*	1	1	1	0
Common dog-violet	*Viola riviniana*	0	0	1	0
Common eyebright	*Euphrasia nemorosa*	0	0	1	0
Common knotgrass	*Polygonum aviculare*	0	0	1	0
Common sorrel	*Rumex acetosa*	1	1	1	0
Creeping buttercup	*Ranunculus repens*	1	1	1	0
Curly dock	*Rumex crispus*	1	1	1	0
Tufted vetch	*Vicia cracca*	1	1	1	1
Daffodil	*Narcissus agg.*	0	0	1	0
Dog's mercury	*Mercurialis perennis*	0	0	1	0
Downy birch/moor birch	*Betula pubescens*	1	1	1	1
Common duckweed	*Lemna minor*	0	0	1	1

Dyer's rocket	*Reseda luteola*	0	0	1	0
Eared willow	*Salix aurita*	0	0	1	1
Encharter's nightshade	*Circaea lutetiana*	0	0	1	0
English Bluebell	*Hyacinthoides non-scripta*	0	0	1	0
English oak	*Quercus robur*	1	1	1	1
Field Forget-me-not	*Myosotis arvensis*	0	0	1	1
Field horsetail	*Equisetum arvense*	0	0	1	1
Germander speedwell	*Veronica chamaedrys*	1	1	1	0
Gorse	*Ulex europaeus*	1	1	1	1
Grey willow	*Salix atrocinerea*	1	1	1	1
Ground Ivy	*Glechoma hederacea*	0	0	1	1
Hart's tongue	*Asplenium scolopendrium*	1	1	1	1
Heath violet	*Viola canina*	1	1	1	0
Heather	*Calluna vulgaris*	1	1	1	1
Holly	*Ilex aquifolium*	0	0	1	1
Honeysuckle	*Lonicera periclymenum*	1	1	1	1
Ivy	*Hedera helix*	1	1	1	0
Lesser centaury	*Centaurium pulchellum*	0	0	1	0
Little mouse-ear	*Cerastium semidecandrum*	0	0	1	0
Lucerne	*Medicago sativa*	0	0	1	0
Male Fern	*Dryopteris filix-mas*	1	1	1	1
Marsh wilowherb	*Epilobium palustre*	0	0	1	0
Narrow leaved marsh dandelion	*Taraxacum palustre*	1	1	1	0
Common nettle	*Urtica dioica*	1	1	1	1
Pampas grass	*Cortaderia selloana*	0	0	1	0
Pendulous sedge/ hanging,drooping, weeping sedge	*Carex pendula*	0	0	1	0
Primrose	*Primula vulgaris*	1	1	1	1
Red campion	*Silene Dioica/Melandrium rubrum*	1	1	1	1

Rhododendron	*Ponticum ionicera*	1	1	1	1
Dog rose	*Rosa canina*	0	0	1	0
Sand sedge	*Carex arenaria*	0	0	1	0
Scarlet pimpernel	*Anagallis arvensis*	0	0	1	0
Shivas fern	*Polypodium interjectum*	1	1	1	0
Silverweed	*Potentilla anserine/Argentina anserina*	1	0	1	1
Spatulaleaf loosestrife	*Lythrum portula*	1	1	1	0
Spear-leaved willowherb	*Epilobium lanceolatum*	1	1	1	0
Sticky mouse-ear chickweed	*Cerastium glomeratum*	0	0	1	0
Sycamore	*Acer pseudoplatanus*	1	0	1	1
Teasel	*Dipsacus fullonum*	0	0	1	0
Creeping thistle	*Cirsium arvense*	1	1	1	1
Thyme-leaved sandwort	*Arenaria serpyllifolia*	0	0	1	0
Thyme-leaved speedwell	*Veronica serpyllifolia*	0	0	1	0
Water Forget-me-not	*Myosotis scorpioides*	0	0	1	0
Whitebeam	*Sorbus latifolia*	0	0	1	1
White willow	*Salix alba*	0	0	1	1
Wild lettuce	*Lactuca virosa*	0	0	1	0
Yorkshire fog	*Holcus lanatus*	1	1	1	1
Hop trefoil/low hop clover	*Trifolium campestre*	0	0	1	1
Purple loosestrife	*Lythrum salicaria*	0	0	1	1
Hairy Bird's-foot-trefoil	*Lotus Hispidus/Lotus subbiflorus*	1	1	1	1
Bird's-foot trefoil	*Lotus corniculatus*	1	1	1	0
Common tormentil	*Potentilla erecta*	0	0	1	1
Lady fern	*Athyrium filix-femina*	1	1	1	1

Festuca grass	*Festuca rubra*	1	1	1	1
Soft shield fern	*Polystichum setiferum*	0	0	1	0
Rose of Sharon	*Hypericum calycinum*	0	0	1	1
Ragwort benweed	*Senecio Jacobaea/ Jacobaea vulgaris*	1	1	1	0
Sheep's sorrel	*Rumex acetosella*	0	0	1	0
Slender centaury	*Centaurium pulchellum*	0	0	1	0
Stagger weed	*Stachys arvensis*	0	0	1	0
Wild Arum	*Arum maculatum*	1	1	0	0
Wood sage	*Teucrium scorodonia*	1	1	1	1
Sum		42	39	87	41

0—not found; 1-- found

Appendix B: Similarity indices between sub-habitats of each transect in the Lower valley

	1.1	1.2	1.3	1.4	1.5	1.6				
1.2	0.62									
1.3	0.2	0.29								
1.4	0.4	0.33	0							
1.5	0.2	0.4	0.5	0						
1.6	0.47	0.29	0	0.37	0					
1.7	0.07	0.17	0.1	0.38	0.1	0.21				

Average value: 0.24 Standard deviation: 0.55

	2.1	2.2	2.3	2.4	2.5	2.6	2.7	2.8	2.9	
2.2	0									
2.3	0.54	0.21								
2.4	0.44	0.12	0.28							
2.5	0.28	0	0.33	0						
2.6	0	0.15	0	0	0					
2.7	0.15	0.09	0.22	0.125	0	0				
2.8	0.33	0	0.36	0	0.57	0	0			
2.9	0.5	0	0.22	0	0.4	0	0	0.5		
2.10	0	0.31	0	0	0	0.5	0.17	0	0	

Average value: 0.15   Standard deviation: 0.19

	3.1	3.2	3.3	3.4	3.5	3.6	3.7	3.8
3.2	0.16							
3.3	0.23	0.28						
3.4	0.21	0.25	0.25					
3.5	0.3	0.35	0.44	0.54				
3.6	0.33	0.27	0.57	0.44	0.6			
3.7	0.45	0.42	0.36	0.31	0.43	0.67		
3.8	0.85	0.32	0.23	0.21	0.3	0.44	0.45	
3.9	0	0	0	0	0	0	0	0

Average value: 0.30   Standard deviation: 0.21

	4.1	4.2	4.3	4.4	4.5	4.6	4.7	4.8	4.9	4.10	4.11
4.2	0.5										
4.3	0.33	0.6									
4.4	0	0	0								
4.5	0.28	0.54	0.89	0							
4.6	0.44	0.77	0.73	0	0.67						
4.7	0.31	0.47	0.4	0.17	0.37	0.56					
4.8	0.44	0.46	0.54	0	0.5	0.57	0.44				

4.9	0.25	0.17	0.2	0.28	0.18	0.15	0.35	0.31			
4.10	0.22	0.31	0.54	0.25	0.5	0.43	0.44	0.57	0.46		
4.11	0.2	0.28	0.5	0.22	0.46	0.32	0.42	0.53	0.43	0.67	
4.12	0.14	0.33	0.25	0	0.23	0.53	0.35	0.42	0.11	0.31	0.3

Average value: 0.36   Standard deviation: 0.20

	5.1	5.2	5.3	5.4	5.5
5.2	0.18				
5.3	0	0.18			
5.4	0.35	0.1	0		
5.5	0	0.37	0.24	0	
5.6	0.31	0.19	0	0.37	0.17

Average value: 0.16   Standard deviation: 0.14

Appendix C: Similarity indices between sub-habitats of each transect in the Middle valley

Sub-habitat	**1.1-1.2**	**1.2-1.3**	**1.1-1.3**			
Similarity index	0.4	0.364	0.471			
Sub-habitat	**2.1-2.2**	**2.2-2.3**	**2.1-2.3**			
Similarity index	0.706	0.571	0.706			
Sub-habitat	**3.1-3.2**	**3.2-3.3**	**3.1-3.3**	**3.3-3.4**	**3.1-3.4**	**3.2-3.4**
Similarity index	0.222	0.462	0.2	0.526	0.133	0.444
Sub-habitat	**4.1-4.2**	**4.2-4.3**	**4.1-4.3**			
Similarity index	0.242	0.667	0.125			
Sub-habitat	**5.1-5.2**	**5.2-5.3**	**5.3-5.1**			
Similarity index	0.4	0.2	0.456			

Appendix D: Procedure for sequential extraction of arsenic fraction

Arsenic fractionation in soil was measured with a sequential extraction procedure adapted from Wenzel (2001). The procedure was a follows:

1. Sieve the soil using 2 mm mesh to remove oversize particles which are not considered to be part of soil.
2. The soil is placed on polyethylene sheet and dried in an oven for 72 hours at 40°C.
3. Weigh 1 g soil and put into 50 ml centrifugation tube and prepare 5 replicates for each composite soil sample. For each replicate, the operation procedures are described as follows:

   1) prepare 500 ml 0.05M $(NH_4)_2SO_4$ with deionised water; add 25ml of the solution into the centrifuge tube and then shake for 4 hours at 20 °C. The suspension is centrifuged for 15 minutesat 3000G before being filtered into PE bottles through a 0.45 μm cellulose nitrate membrane aided by vacuum pump; arsenic concentrations were determined later. Extracts which could not be analysed immediately were stored in the refrigerator (5°C). The residual soil kept in the centrifuge tube was used for the next step.

   2) prepare 500 ml 0.05 M $(NH_4)H_2PO_4$ with deionised water; add 25 ml of the solution into the centrifuge tube. The tubes were shaken for 16 hours at 20 °C before being centrifuged for 15 minutesat 3000G. The solution was filtered into PE bottles through a 0.45 μm cellulose nitrate membrane aided by vacuum pump; arsenic concentrations were determined later. Extracts which could not be analysed immediately were stored in the refrigerator (5°C). The residual soil kept in the centrifuge tube was used for the next step.

   3) prepare 500 ml 0.2 M ammonium oxalate and 0.2 M oxalic acid separately, then add oxalic acid solution to the ammonium oxalate solution until the pH equals 3.25 (monitor the pH and mix vigorously to maintain a homogeneous solution. Add 25 ml 0.2 M Ammonium oxalate buffer with pH 3.25 into the centrifuge tube and then shake for 4 hours in the dark at 20 °C. The suspension was centrifuged for 15 minutesat 3000G before being filtered into PE bottles

through a 0.45 μm cellulose nitrate membrane aided by vacuum pump; arsenic concentrations were determined later. Extracts which could not be analysed immediately were stored in the refrigerator (5◦C). The residual soil remaining in the centrifuge tube was used in the next step.

Place another 12.5 ml Ammonium oxalate buffer (0.2 M) with pH 3.25 into the centrifuge tube to shake for 10 minutes in the dark to wash the soil. The suspension was centrifuged for 15 minutes at 3000G before being filtered into PE bottles through a 0.45 μm cellulose nitrate membrane aided by vacuum pump; arsenic concentrations were determined later. Extracts which could not be analysed immediately were stored in the refrigerator (5◦C). The residual soil remaining in the centrifuge tube was used for the next step.

4) Add 25 ml ammonium oxalate buffer (0.2 M) and ascorbic acid (0.1M) with pH value at 3.25 (prepare 250 ml 0.1M ascorbic acid and 250 ml 0.2 M ammonium oxalate and put them together. Use 0.2 M oxalic acid to adjust the pH of the solution in the centrifuge tube until it reaches a value of 3.25. Put the tube into a water bath for 40 minutes around 90 ºC. Note that Wenzel suggests to heat the water bath for 30 minutes to 96 ºC. The longer time was used to compensate for the lower temperature, which was the maximum temperature reached by the water bath used in the laboratory. The tube was subsequently centrifuged for 15 minutes at 3000G. The solution was filtered into PE bottles through a 0.45 μm cellulose nitrate membrane aided by vacuum pump; arsenic concentrations were determined later. Extracts which could not be analysed immediately were stored in the refrigerator (5◦C). The residual soil was kept in the centrifuge tube and used for the next step.

Wash with 12.5 ml Ammonium oxalate (0.2M) with pH 3.25 which was prepared for procedure 3 for 10 minutes by shaking in the dark.
The solution was filtered into PE bottles thtrough a 0.45 μm cellulose nitrate membrane aided by vacuum pump; arsenic concentrations were determined later. Extracts which could not be analysed immediately were stored in the refrigerator (5◦C). The residual soil kept in the centrifugation tube and was used for the next step.

5) Aqua Regia digestion on hotplate, with 1 g of solid to 50 ml of acid, consisting of 3 parts of concentrated HCl and 1 part of concentrated HNO3. Wenzel used microwave digestion in his experiment but Chen (2001) stated that for arsenic, a hotplate aqua regia digestion is relatively more accurate. Arsenic is possibly more volatile and the high pressure in microwave can crush soil grains and expose more arsenic to acid solution. Since this test aim to find the different fractions of arsenic which are directly available to dissolve in soil solution under different physico-chemical condition, it was decided to use hot plate digestion method.

For each composite soil sample, two 1 g samples were scaled put into 50 ml PE tube for hot plate Aqua Regia digestion as reference to calculate recovery rate. A blank sample was processed with the same procedure to provide a background check for contamination.

After the digestion, the solution leaved still for 48 hours to settle down and then diluted 500 times for analysis.

Appendix E: Metal ion mobility analysis

The main limitation factor to rehabilitation in Carnon Valley is elevated metal ions and acidity. Soil is a storage bank of metal ions but they can only have impact on vegetation development when they dissolve in water. Hence, the mobility of metal ions is analysed.

During the research, the Environmental Agency made available data of the daily precipitation, water flow and water quality from January 1st, 2009 to September 30th, 2014. The precipitation and flow data was collected at a gauge station (Figure E1) on Carnon river right above the research site. Samples for testing water quality were taken from a point right at the downstream of the Lower valley (Figure E1).

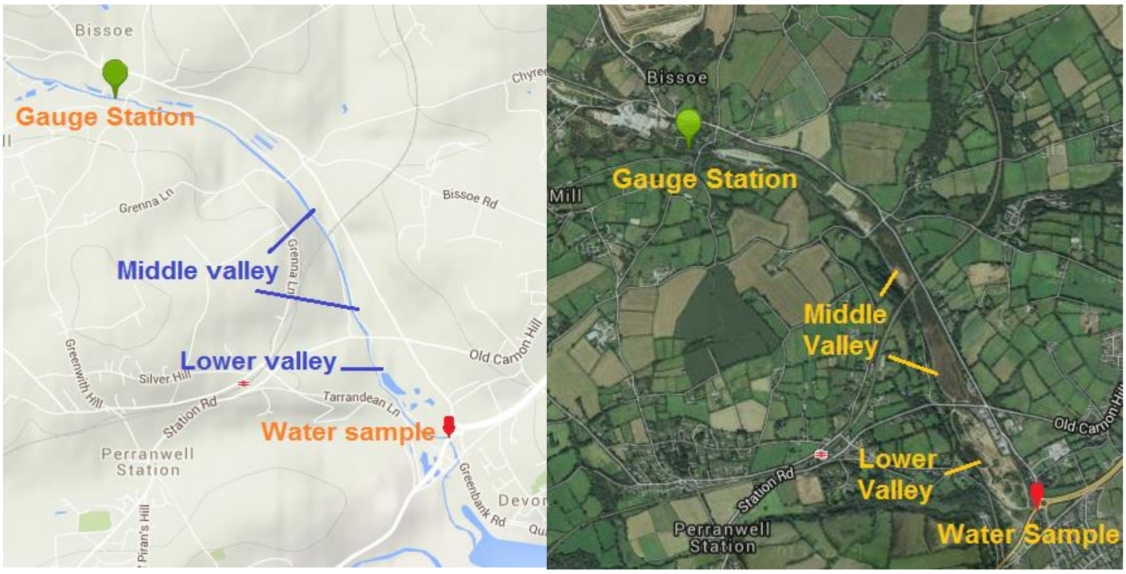


Figure E1: Location of Environmental Agency gauge station and water sampling.

Water quality data reflects the collective result of upstream processes which is not limited to the soil solution on site. However, all sampling is downstream of Wheal Jane mine and hence interpretation should provide relevant insights. Specifically, the analysis aims to create understanding of the fluctuation of the solubility of metals with rainfall and water flow.

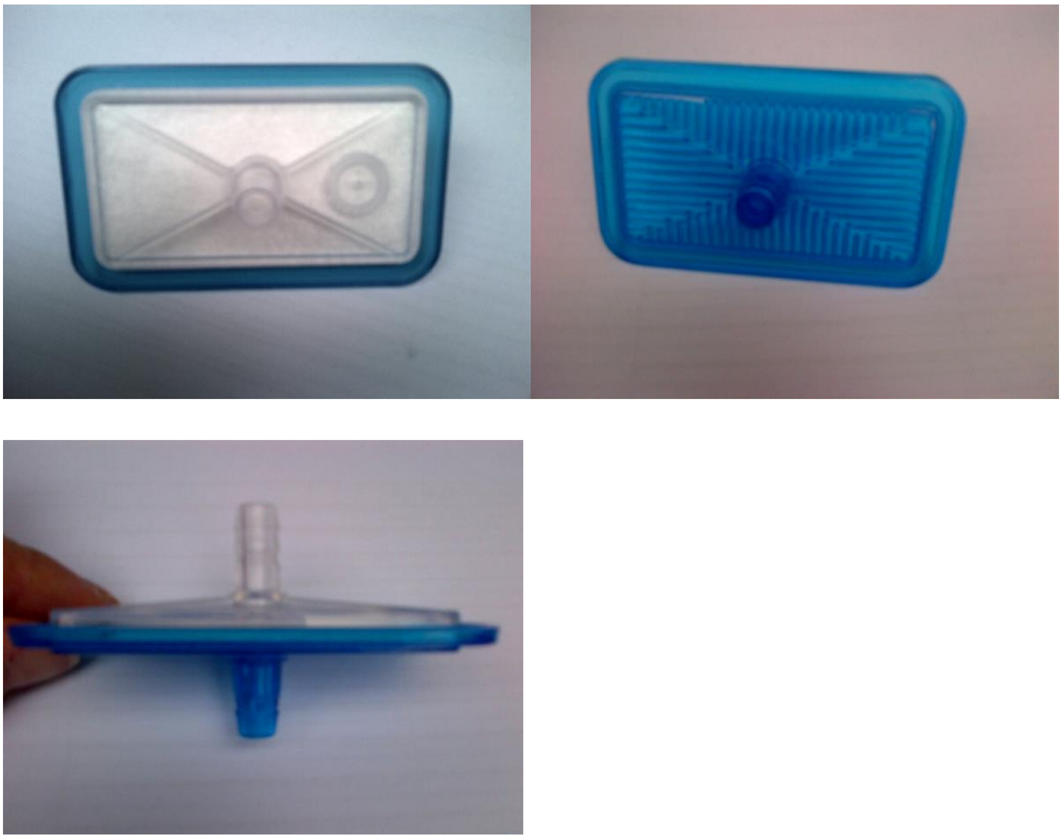


Figure E2: Disposable 0.45 micron filters used by the Environmental Agency to take water samples from Carnon River.

Although the two data sets were taken with different frequency the time frame was extensive. Firstly, the correlation between daily water flow and precipitation was analysed. This is used to verify whether a time-delay exist between precipitation and water flow variation in river. Based on a penetration test and soil texture analysis, compaction is relatively high and soil grain size ranges between 20 to 40 μm. The fine soil texture enables the development of a physical soil crust (or 'hard pan') which reduces water infiltration. It is expected that the low infiltration rate will make most of the rainfall run of the surface. Fast runoff may increase erosion: once physical soil crust cracks, more aggregates are carried away by runoff. This suggests that vegetation on the soil crust would reduce runoff and erosion, and improve infiltration.

The Environmental Agency has analysed water quality with and without filter and the differences are discussed in the following section. Filtration was initially carried out with single-use disposable 0.45 micron filters (Figure E2).

In Cornwall, days start to be longer than nights from the middle of March. This marks the beginning of the vegetation growing season. This season ends in September, ushering in the dormancy season. Therefore， the analysis considers both: annual variation in metal ions mobility and metal ions mobility in growing season and dormancy season.

E.1 Influence of precipitation on water quality

The correlation coefficient between the daily mean flow rate of the Carnon River and the daily rainfall is surprisingly low at 0.295. The absece of correlation between precipitation and river flow may be due to neglecting the minimum flow of the river which produces distortion in the data. Considering this region has high precipitation all around the year, soil moisture and minimum flow of the river is always high. A single rainfall event may not be strong enough to add significant change to river water flow to demonstrate the correlation between them. Secondly, precipitation is expected to influence the water flow but not the other way around. This one-way dependency is analysed with linear regression method in SPSS 21 software.

The p value is 0.000 which means there is less than 0.5‰ of the scenario outside of the confident interval. That means Carnon river water flow is strongly dependent on rainfall variation.

This result indicates that the pollutant concentration of the river may be spontaneously affected by the precipitation if soluble ions available in soil. The Environment Agency has tested a long list of heavy metals, pollutants and bio-chemical indicators. In this research only, those elements and properties with a relatively complete record were evaluated because it enables reliable evaluation. The most important water sample properties include heavy metal ions, temperature, electrical conductivity and pH value.

Solubility of metal ions is not only decided by their species: fractionation also plays an important role. A metal may have totally different availability in account of different valence or being part of different compounds. Minerals may experience different weathering processes under different climate and geochemical conditions, producing different secondary products. The analysis of metal ions in Carnon River aims to identify their solubility and mobility in a local context.

In this research, the metallic arsenic is of special interest. Its concentration in soil because local geological reason is elevated while its toxicity to people and ecological system is well-known.

The water pollutant test is carried on a regular but random basis. According to the Environmental Agency, the practice aims to have a good spread of data for each location and sampling is not biased towards particular times of the day or days of the week.

Precipitation in the Carnon Valley is measured automatically by gauge station on the river on a daily basis. To better understand how precipitation affects metallic ions solubility, it is necessary to consider the bigger picture. Therefore, precipitations in 7 days prior to water sampling are summed. The dependency of the metal concentration on rainfall is shown in Figure E3. The metal concentration used here is based on the annual analysis of unfiltered Carnon River water.

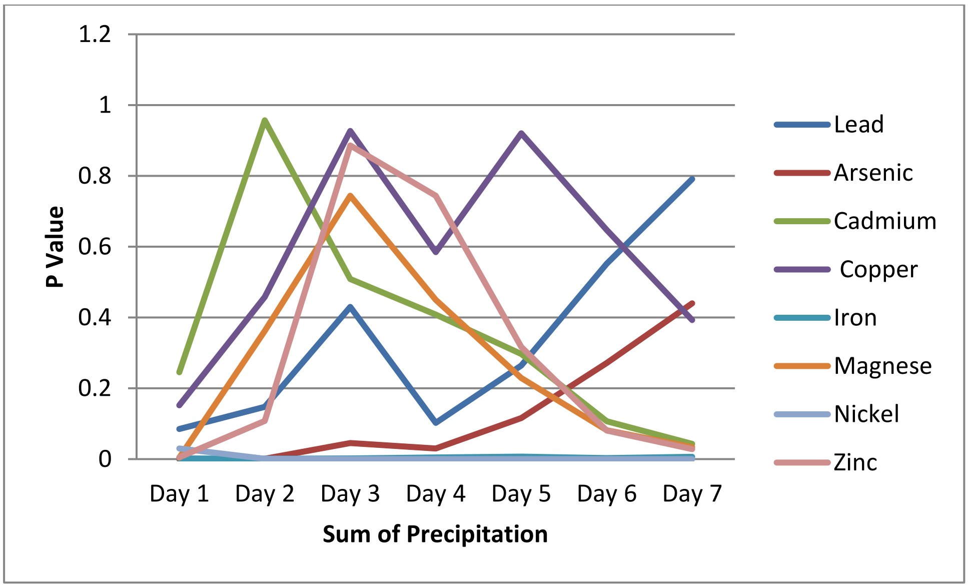


Figure E3: Dependence of unfiltered water quality on accumulated precipitation previous to water sampling time.

Rainfall and unfiltered pollutant concentration data were correlated using linear regression in SPSS 21 and. The result (Figure E3) for arsenic shows its presence in river water is affected by precipitation. When precipitation happens more than three days before, no correlation with the arsenic concentration in the river is observed. The trend of reduced dependence on accumulated rainfall is observed. Decreased arsenic concentration in the leachate implies that the more rainfall falls on soil or the longer the rainfall lasts, the more arsenic will be transported by water into the Carnon river but at a reduced concentration. When summingthe rainfall for more than 5 days prior to water sampling day, the effect of rainfall on adding additional arsenic in the river is less obvious.

The consistent association between arsenic and accumulated rainfall become more obvious. It indicates that the variation of arsenic concentration in the river can be predicted by measuring precipitation in five days prior to water sampling. Even the sum of six- or seven-days precipitation before water sampling time can still be used to estimate arsenic concentration in the river with acceptable error. The same correlation is also observed for iron. The curves for iron and arsenic overlap, suggesting that iron and arsenic are chemically associated in the soil.

While the concentration of cadmium is quite low (less than 2μg/l), it can be easily affected by minor condition variation. Cadmium solubility is known to fluctuate violently with precipitation. Therefore， it will not be considered in this research. The other tested elements are copper, zinc, lead, magnese and nickel. These elements did not show clear trend in this analysis. The association between rainfall and the pH value shows a strong relationship when considering precipitation over more than three days. This effect disappears when precipitation is summed more than five days.

Since soil aggregates in water samples can trigger abnormal spikes, further analysis was implemented based on filtered water samples. Collected water samples are filtered in the field using single use disposable 0.45 micron filters. Filtered water sample reduces random error made by solid mineral particles in water and can give accurate results about dissolved contaminants.

After filtration, lead is below the detection limit. There is no repeated test for pH value in filtered water. The association between other elements and rainfall is presented in Figure E4.

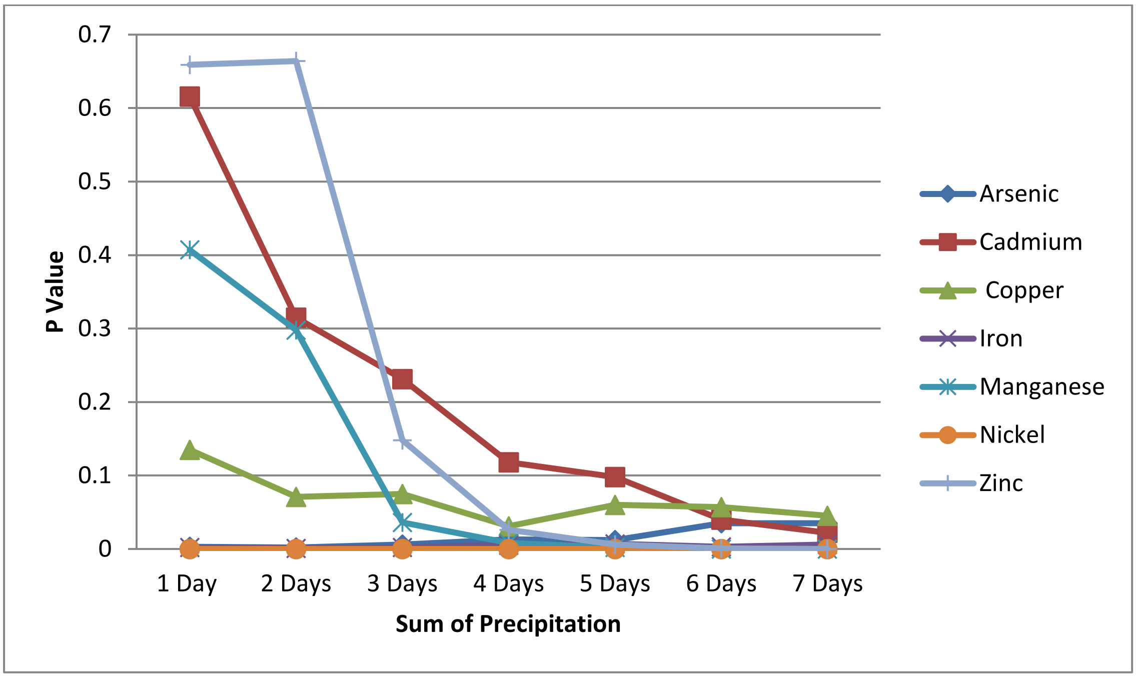


Figure E4: Dependence of filtered water quality on accumulated precipitation prior to water sampling time.

The solubility of the other four elements zinc, manganese, cadmium and copper show their solubility is a function of accumulated precipitation. Using the total rainfall in seven days prior to water sampling, a model to predict the concentration of these elements in filtered water was developed. It appears that manganese and zinc are more vulnerable to longer period precipitation condition or greater variation of rainfall. This may be because of random distribution of these elements has weakened the correlation between precipitation and dissolved elements or these elements are more concentrated in the subsurface than near the surface. The latter implies that the leaching process requires more water and is time-consuming.

Biotoxicity of heavy metals have different influences on vegetation development. During the growing season (April to August), plants are more sensitive to toxicity than in dormancy season (September to March). Therefore，the influences of summing up precipitation prior to water sampling time From 2008 to 2014, altogether 36 valid water quality data were recorded in growing season (1st April- 31st August). These will be analysed separately.

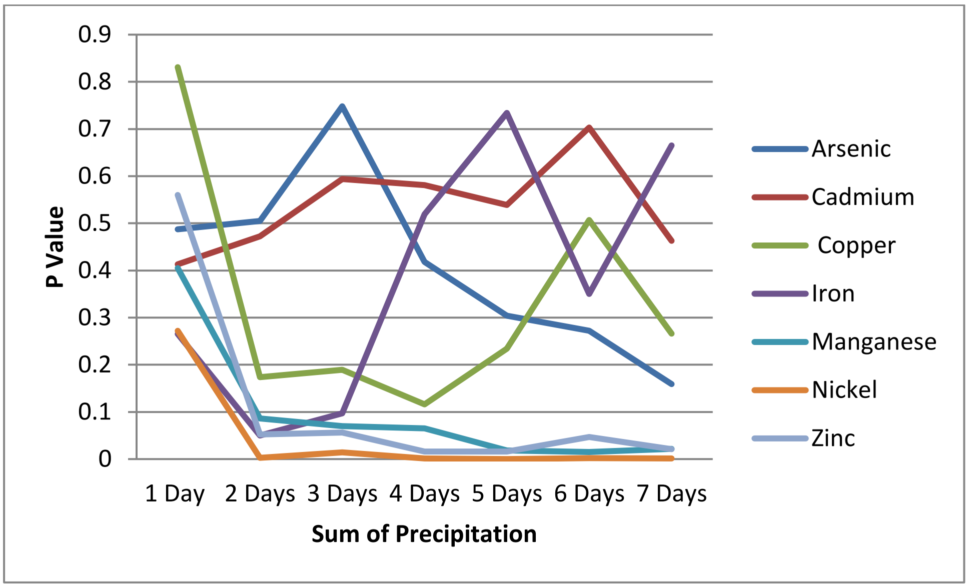


Figure E5: Dependence of filtered water quality on accumulated precipitation prior to water sampling time in growing season.

Figure E5 suggests that precipitation cannot be used to establish a model to predict water quality in growing season. Only nickel, zinc and manganese demonstrate relation with cumulative precipitation. The possible reason is effect rainfall can only be reached add up more than two days precipitation. Figure E5 shows that, when summing rainfall before water sampling, water quality varies as a function of precipitation. Even nickel, it shows spontaneous react to rainfall in previous analysis also is not sensitive anymore. This possibly because the reduce precipitation intensity and frequency make soil has greater capacity to absorb water which reduce runoff and leachate greatly. Reduced surface flow could not carry enough ions into river to show its influence.

The most interested elements, arsenic, does not relate its presence in river with rainfall variation. The site has been shut down for 20 years, it may have experienced certain period of harsh time before arsenic can be dissolved and wash away. To understand arsenic solubility variation over the site, a sequential extraction scheme experiment has been done. Its detail will be presented in chapter about arsenic later.

To compare heavy metal solubility in different seasons, a linear regression analysis for dormancy season also is developed (Figure E6). Figure E6 indicates that dissolved ions in Carnon River all depend on accumulated precipitation. Except manganese, zinc and copper, the concentration of elements in the river depends on precipitation and this correlation does not change with summing rainfall prior to water quality test. The copper concentration depends on precipitation when adding up more than two days precipitation. Apart from acidity, all the other water quality indices show a certain dependence on precipitation when a longer period rainfall is summed up.

The concerned element, arsenic, its concentration in river is more closely related with rain water in winter. Therefore, water relocation on site can divert arsenic greatly and affect vegetation development.

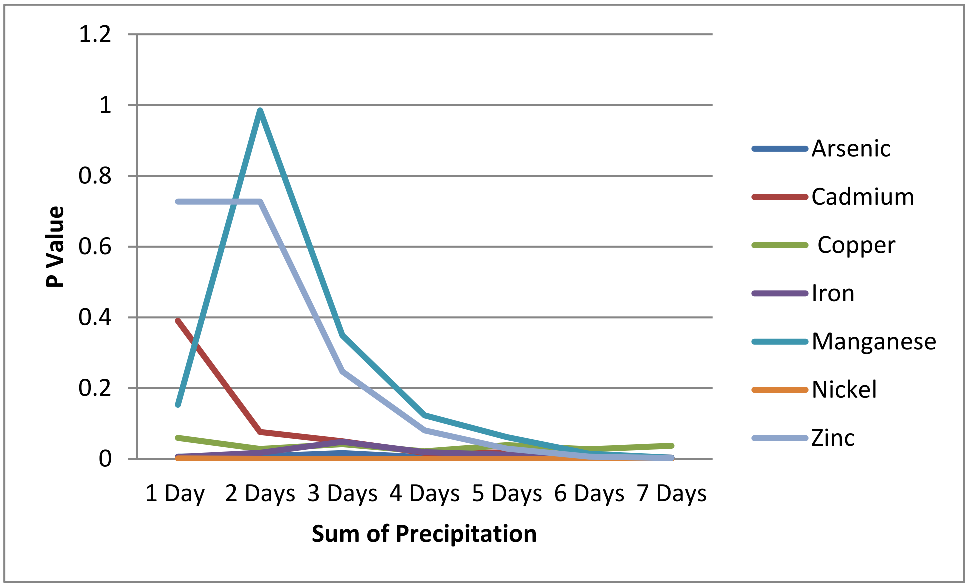


Figure E6: The dependence of filtered water quality on accumulated precipitation previous to water sampling time in dormancy season.

When analysis the influence of the accumulated precipitation prior to water sampling, it was assumed that the other indicators such as water temperature and water acidity were constant. Although their variation range is far smaller than rainfall, it is still interesting to explore their impact on metal ions solubility in the river. It is generally accepted that arsenic solubility is affected by acidity but no study on the impact of temperature variation has been found. In the following section, the impact of these two influencing factors is analysed separately and jointly.

While precipitation data is automatically recorded continuously in gauge station, water temperature and pH data have to be collected manually. Normally this is done when water sampling is taking place.

E.2 Impact of temperature and pH on solubility

Temperature affects solubility because raised temperature increases chaos within a system. Thermal energy is transformed into kinetic energy and enables solute molecules to get away from bonding force. Therefore, when specify solubility one needs to define the temperature. Water is the most common polar solvent in nature and has a good capacity to dissolve polar molecules such as metallic ions. Normally, water temperature has positive impact on solubility, but the extent varies for different solutes.

Cornwall has a temperate oceanic climate due to its proximity to the north Atlantic drift. Water temperature in the Carnon river fluctuated from 9.2 to 18 Celsius through the whole period from January 2009 to August 2014. During the growing season (April to August) and dormancy season (September to March), the temperature varies between 12 to 18 °C and 9.2 to 15.8°C respectively. The variation is quite limited. Whether it is significant to produce impact on solubility is investigated follows. Table E1 indicates how many per cent of the heavy metal variation scenarios can be predicted by water temperature through the level of significance, 1-p. Generally, when it is higher than 0.95 then the dependency is considered to be true.

Table E1: Impact of water temperature variation on metal ions solubility in Carnon river through the year during research period.

Property	Nickel	Electro-conductivity	Arsenic	Iron
1-P	0.779	1.000	0.998	0.306

Property	Copper	Zinc	Manganese	pH
1-P	0.998	0.007	1.000	0.765

Table E1 suggests that electroconductivity, arsenic, copper and manganese solubility are significantly affected by temperature variation. Electro-conductivity reflects the conductivity of water which depends on the ions concentration and degree of ionic “disorder”. Its high dependence on temperature is a proved rule. From the data above, zinc and iron are insensitive to temperature. This could be explained by several possibilities: a). The temperature variation is not significant enough to change their solubility or the temperature need to reach a threshold before affecting their solubility; b). The change of other influencing factors balance out the impacts of temperature change; c).Their solubility is stable and change in a rate below detection limit of analysing equipment; d). There are no spare mineral present for dissolution.

Based on the data, one can easily exclude options c) and d). Both zinc and iron concentration in the Carnon River fluctuate from several hundred ppb to over one thousand ppb, which implies that their solubility can change greatly and there are enough minerals available to dissolve. Investigating option a) is beyond the scope of this research. Some further analyses are made to find the interaction between temperature, pH value and extended wash out time duration.

Table E2: pH impact on metal ions solubility through the year

Property	Electro-conductivity	Zinc	Nickel	Arsenic
1-P	0.179	0.907	1.000	0.951
Property	Copper	Manganese	Iron	
P value	1.000	0.970	0.887	

Obviously electro-conductivity does not depend on pH while nickel is highly dependent on pH rather than temperature. Copper is more sensitive to acidity while arsenic and manganese, though responsive to both factors are more affected by temperature, though they are sensitive to both factors. The 1-P value for zinc and iron is not large enough to establish statistical significance.

Table E3: Joint impact of temperature and pH on ions solubility through the year

Property		Iron	Manganese	Copper	Arsenic
1-P	Temperature	0.484	1.000	1.000	0.997
	pH	0.950	0.941	1.000	0.986
Property		Nickel	Zinc	electroconductivity	
1-P	Temperature	0.606	0.275	1.000	
	pH	1.000	0.962	0.607	

Table E3 shows the results of multiple regressions with temperature and pH as variables. When water temperature and acidity change simultaneously, dissolved copper and arsenic are sensitive to both variables. Acidity is more influential to iron, nickel and zinc while manganese solubility varies with temperature. Electroconductivity shows the same tendency as copper and manganese, possibly because of the high conductivity of copper or because increased of molecule chaos in water.

Water acidity plays important role in chemical compound solubility. Sorption and desorption of heavy metal ions also are affected by soil solution pH. Its influence on ionic concentration are analysed by linear regression analysis.

E.3 Temperature dependence in summer

The influence of temperature and pH on metal ions solubility were analysed for growing season and dormancy season separately. Water pH is a dependent of temperature. Therefore, their impacts are analysed together.

Table E4: Joint effect of temperature and pH on metal ions solubility in growing season.

Metal ions		Iron	Manganese	Copper
1-P	Temperature	0.993	0.974	0.497
	pH	0.475	0.788	0.99
Metal ions		Nickel	Zinc	Arsenic
1-P	Temperature	0.036	0.356	0.075
	pH	0.918	0.972	0.881

Influencing factors for metal solubility is not limited to the three factors mentioned here. It will need further work to understand metalliferous mineral weathering process, edaphic physical features, biological impacts and other factors.

In table E5 it follows that precipitation has no impact over metal ions solubility in the river. To prove it, precipitation data for the sampling day was introduced as a regressor in linear regression to test its p value. The result supports the notion that no linear regression function can represent the relationship between ions solubility variation and precipitation.

Table E5: Joint effect of temperature, precipitation and pH on metal ions solubility in growing season.

Metal ions		Iron	Manganese	Copper
1-P	Temperature	0.995	0.97	0.484
	pH	0.398	0.758	0.989
	precipitation	0.836	0.528	0.104
Metal ions		Nickel	Zinc	Arsenic
1-P	Temperature	0.073	0.339	0.041
	pH	0.901	0.967	0.859
	precipitation	0.676	0.24	0.631

Table E6: Joint effect of temperature and pH on metal ions solubility in dormancy season.

Metal ions		Iron	Manganese	Copper
1-P	Temperature	0.94	0.999	0.999
	pH	0.881	0.784	1.000
Metal ions		Nickel	Zinc	Arsenic
1-P	Temperature	0.383	0.191	0.979
	pH	0.999	0.769	0.757

Comparison of table E5 and E6 reveals the difference of influencing factors impact on metal ions solubility. It seems temperature has more influence on ions solubility in the dormancy season than in the growing season. The solubility of copper and arsenic looks invariant to temperature in the growing season. It can be explained by two possibilities: a) less samples were available from the growing season (total 34) in comparison to the dormancy season (total 56); b) the relation between solubility and temperature is a nonlinear function. When it plateaus, it is difficult to identify the correlation.

Table E7: Joint effect of temperature, precipitation and pH on metal ions solubility in dormancy season.

Metal ions		Iron	Manganese	Copper
1-P	Temperature	0.874	0.998	0.998
	pH	0.723	0.881	0.999
	precipitation	0.97	0.864	0.626
Metal ions		Nickel	Zinc	Arsenic
1-P	Temperature	0.018	0.032	0.998
	pH	0.994	0.839	0.379
	precipitation	0.995	0.703	0.999

Table E7 suggests that, in the dormancy season, iron, nickel and arsenic, concentrations are affected by precipitation. Whether this is because of redox conditions change, data sufficiency, waterlogging effect or other reasons is not clear.

In the growing season, rainfall did not enhance or reduce metallic ions solubility. The leaching of arsenic was not related to any of temperature, pH and precipitation.

In Cornwall, a place with a mild climate, the different influence factors have impact in growing season and dormancy season. This suggests that the difference must be even bigger in other areas.

E.4 Origin of soluble metals

Noting the behaviour of metal ions in water, it is interesting to understand the origin of these ions. The source of water pollutants is identified with following method. Firstly, the correlation between metal ions is established by correlation analysis. Those absolute correlation values (CV) between 1 and 0.5 are highlighted with shadow background in Table 8.

The mineral concentration in surface soil and sub-surface soil measured with portable XRF are analysed for vertical correlation. The analysis result (Table 9) indicates Lower valley soil experience less disturbances: among 16 metallic ions, 14 demonstrate correlation (correlation coefficient>0.6). There are six elements which have correlation coefficients above 0.9. This result indicates that the top 20 cm soil comes from the same parent material. In the Middle valley metal concentration in the substrate demonstrates less correlation with depth (Table E8).

Table E8: Correlation analysis of metallic ions in Carnon River

	pH	Water Temp	Cond @ 25C	Cd	Zn-	Ni-	As-	Cu	Mn-	Fe	Rainfall	
pH	1.00	-0.14	0.03	-0.35	-0.18	-0.43	-0.22	-0.38	-0.26	-0.18	0.05	pH
Water Temp	-0.14	1.00	0.50	-0.31	-0.01	0.15	0.36	-0.36	0.55	-0.05	-0.03	Water Temp
Cond @ 25C	0.03	0.50	1.00	-0.15	0.08	0.25	0.33	-0.26	0.55	0.12	-0.14	Cond @ 25C
Cd	-0.35	-0.31	-0.15	1.00	0.73	0.51	-0.11	0.79	0.04	-0.05	-0.06	Cd
Zn-	-0.18	-0.01	0.08	0.73	1.00	0.62	-0.04	0.54	0.44	0.02	0.05	Zn-
Ni-	-0.43	0.15	0.25	0.51	0.62	1.00	0.31	0.51	0.43	0.39	-0.42	Ni-
As-	-0.22	0.36	0.33	-0.11	-0.04	0.31	1.00	-0.21	0.40	0.59	-0.32	As-
Cu	-0.38	-0.36	-0.26	0.79	0.54	0.51	-0.21	1.00	-0.12	-0.14	-0.16	Cu
Mn-	-0.26	0.55	0.55	0.04	0.44	0.43	0.40	-0.12	1.00	0.26	0.10	Mn-
Fe	-0.18	-0.05	0.12	-0.05	0.02	0.39	0.59	-0.14	0.26	1.00	-0.33	Fe
Rainfall	0.05	-0.03	-0.14	-0.06	0.05	-0.42	-0.32	-0.16	0.10	-0.33	1.00	Rainfall

Table E9: Correlation between surface soil and sub-surface soil mineral and chemical features in Lower valley.

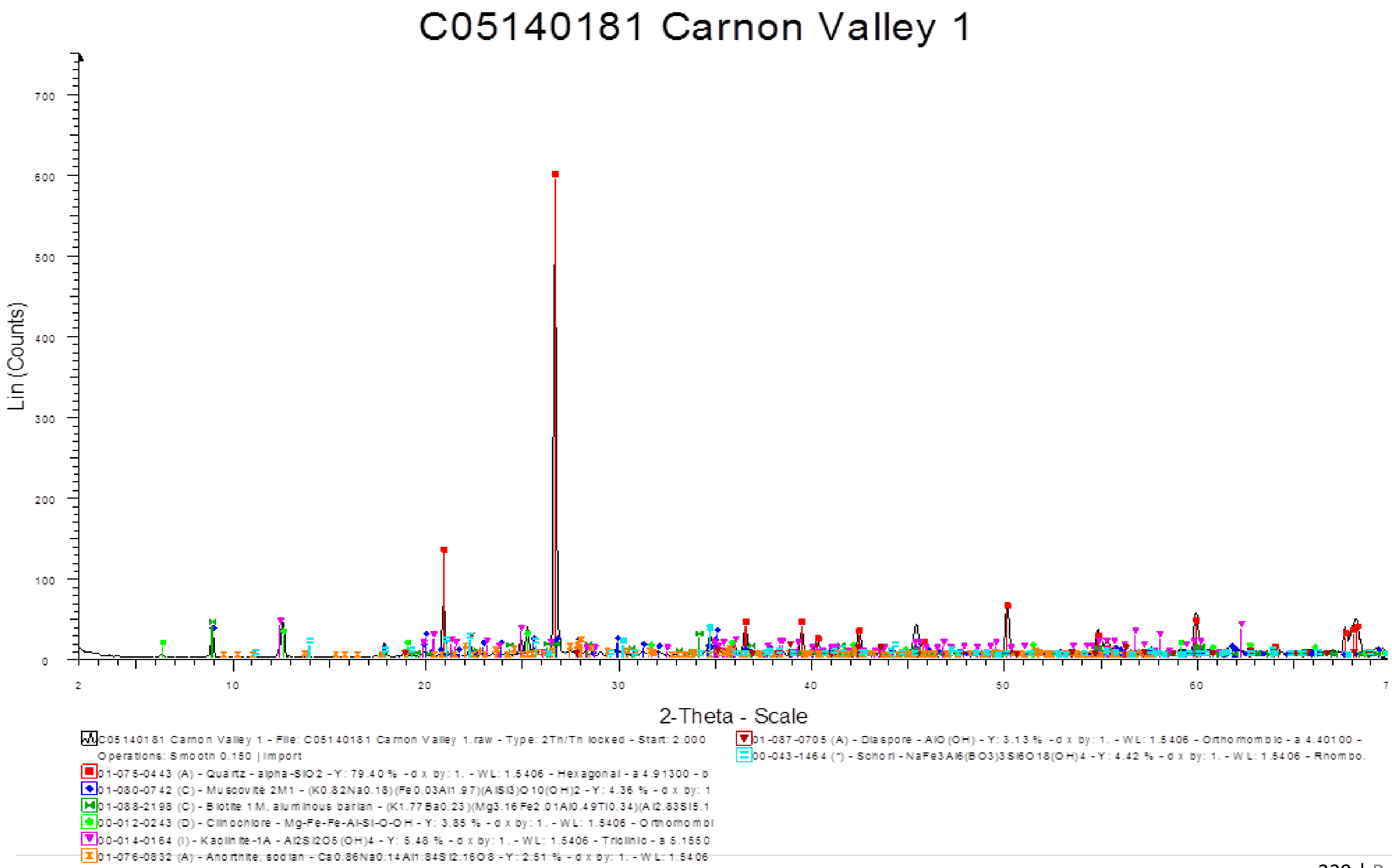
EC	**As**	**Fe**	**Sr**	**Zr**	**Ti**	**Zn**	**Mn**
0.91	0.91	0.87	1	0.74	0.78	0.97	0.77
K	**Ba**	**Sn**	**Pb**	**Cu**	**Ca**	**Rb**	**pH**
0.63	0.14	0.81	0.68	0.88	1	0.42	0.95

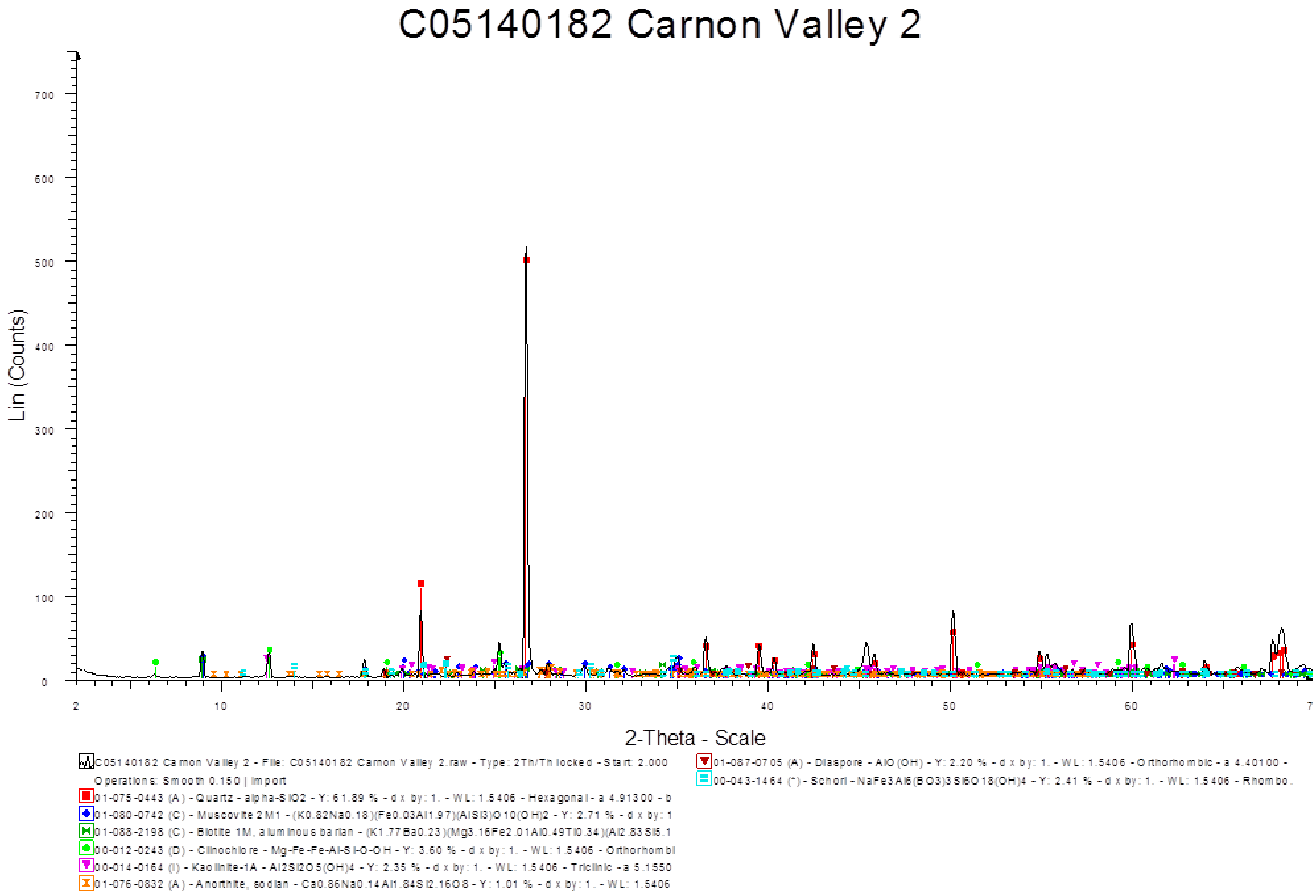
Table E10: Correlation between surface soil and sub-surface soil mineral and chemical features in Middle valley.

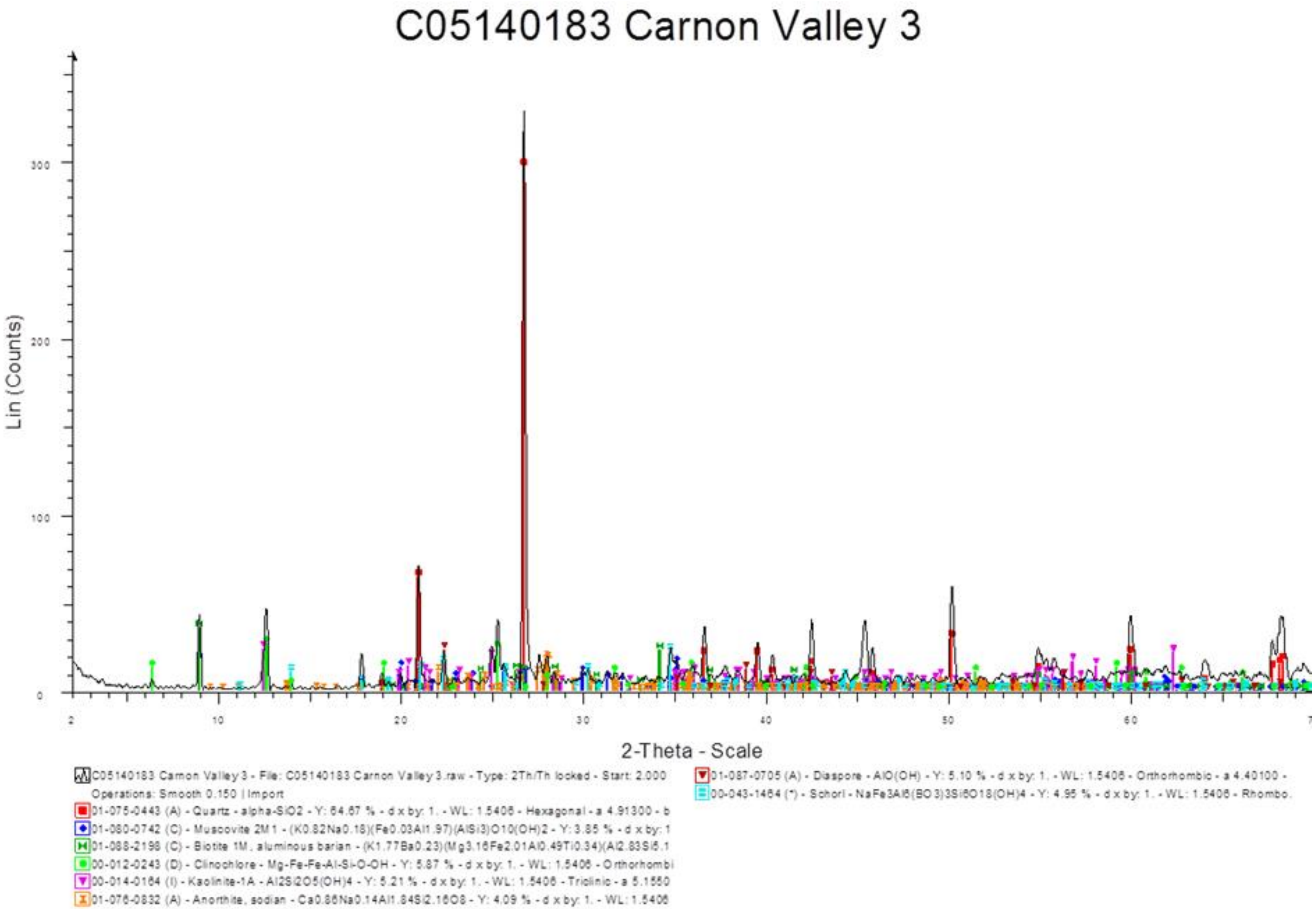
EC	**As**	**Fe**	**Sr**	**Zr**	**Ti**	**Zn**	**Mn**
0.89	0.79	0.14	0.57	0.28	0.70	0.54	0.33
K	**Ba**	**Sn**	**Pb**	**Cu**	**Ca**	**Rb**	**pH**
0.80	0.47	0.2	0.75	0.59	0.6	0.75	0.85

There are no correlation coefficients above 0.9 and five elements demonstrate no correlation (correlation coefficient <0.5). This indicates that the substrate in Middle valley experienced disturbance but still has highly vertical consistency. This result supports the hypothesis that ground work in Middle valley has delayed the rehabilitation process. Therefore， the habitat in Middle valley is more primitive

Appendix F: XRD analysis result of the Lower valley soil composite samples




C05140182 Carnon Valley 2
Lin (Counts)
700
600
500
400
300
200
100
0
2
10
20
30
40
50
60
7
2-Theta - Scale
C05140182 Carnon Valley 2 - File: C05140182 Carnon Valley 2.raw - Type: 2Th/Th locked - Start: 2.000
Operations: Smooth 0.150 | Import
01-075-0443 (A) - Quartz - alpha-SiO2 - Y: 61.89 % - d x by: 1. - WL: 1.5406 - Hexagonal - a 4.91300 - b
01-080-0742 (C) - Muscovite 2M1 - (K0.82Na0.18)(Fe0.03Al1.97)(AlSi3)O10(OH)2 - Y: 2.71 % - d x by: 1
01-088-2198 (C) - Biotite 1M, aluminous barian - (K1.77Ba0.23)(Mg3.16Fe2.01Al0.49Ti0.34)(Al2.83Si5.1
00-012-0243 (D) - Clinochlore - Mg-Fe-Fe-Al-Si-O-OH - Y: 3.60 % - d x by: 1. - WL: 1.5406 - Orthorhombi
00-014-0164 (I) - Kaolinite-1A - Al2Si2O5(OH)4 - Y: 2.35 % - d x by: 1. - WL: 1.5406 - Triclinic - a 5.1550
01-076-0832 (A) - Anorthite, sodian - Ca0.86Na0.14Al1.84Si2.16O8 - Y: 1.01 % - d x by: 1. - WL: 1.5406
01-087-0705 (A) - Diaspore - AlO(OH) - Y: 2.20 % - d x by: 1. - WL: 1.5406 - Orthorhombic - a 4.40100 -
00-043-1464 (*) - Schorl - NaFe3Al6(BO3)3Si6O18(OH)4 - Y: 2.41 % - d x by: 1. - WL: 1.5406 - Rhombo.


C05140183 Carnon Valley 3
Lin (Counts)
300
200
100
0
2
10
20
30
40
50
60
7
2-Theta - Scale
C05140183 Carnon Valley 3 - File: C05140183 Carnon Valley 3.raw - Type: 2Th/Th locked - Start: 2.000
Operations: Smooth 0.150 | Import
01-075-0443 (A) - Quartz - alpha-SiO2 - Y: 64.67 % - d x by: 1. - WL: 1.5406 - Hexagonal - a 4.91300 - b
01-080-0742 (C) - Muscovite 2M1 - (K0.82Na0.18)(Fe0.03Al1.97)(AlSi3)O10(OH)2 - Y: 3.85 % - d x by: 1
01-088-2198 (C) - Biotite 1M, aluminous barian - (K1.77Ba0.23)(Mg3.16Fe2.01Al0.49Ti0.34)(Al2.83Si5.1
00-012-0243 (D) - Clinochlore - Mg-Fe-Fe-Al-Si-O-OH - Y: 5.87 % - d x by: 1. - WL: 1.5406 - Orthorhombi
00-014-0164 (I) - Kaolinite-1A - Al2Si2O5(OH)4 - Y: 5.21 % - d x by: 1. - WL: 1.5406 - Triclinic - a 5.1550
01-076-0832 (A) - Anorthite, sodian - Ca0.86Na0.14Al1.84Si2.16O8 - Y: 4.09 % - d x by: 1. - WL: 1.5406
01-087-0705 (A) - Diaspore - AlO(OH) - Y: 5.10 % - d x by: 1. - WL: 1.5406 - Orthorhombic - a 4.40100 -
00-043-1464 (*) - Schorl - NaFe3Al6(BO3)3Si6O18(OH)4 - Y: 4.95 % - d x by: 1. - WL: 1.5406 - Rhombo.

Appendix G : Runs Test

The randomness of the distribution of species around the study area is investigated with the runs test. Runs are defined as the continued occurrence of the same state (Davis, 1986), here corresponding to the presence of species in neighbouring areas. This method can be traced back to Wald and Wolfowitz (1940) and is sometimes called Wald and Wolfowitz test. Runs test is used to find non-randomness of a series data (Besseris, 2013; Garson, 2012). In other words, it can be used to assess the independence of a set of binary variables (Elbarghouthi, Qasim and Yassin, 2012; Makri, Psillakis and Arapis, 2015). A run is a group of consecutive 0s or 1s in a Bernoulli sequence (Bellini and Figà-Talamanca, 2005). The number of runs R is the frequency of change. If hypothesis H_0 is true, then 0/1 has equal possibility to occur. When the number of total sample size N is decided, R always varies within a certain range (Siegel, 1956). If R is too small, this indicates the presence of clustering phenomenon and, if R is too large, then it is highly possible that the observations are affected by short-period perturbation of the system (Surhone, Timpledon and Marseken, 2010). In both extreme cases, the sequence is not randomly distributed.

There are two methods to evaluate the randomness in runs test: critical value table or calculation through a Z-test (Elbarghouthi, Qasim and Yassin, 2012). When the sample size is small, one can use critical value table, which gives a lower and higher boundary of R for valid randomness (Siegel, 1956). The table assumes a level of significance equal to 0.05.

The Z-test is used when the number of samples is of great number and samples approach normal distribution. Under this condition, the hypothesis can be evaluated by calculating a critical value. Since in this study sample size N=9 , a normal distribution cannot be proven (Siegel, 1956). While this affects the validity of Z score (Bellini and Figà-Talamanca, 2005), the discussion of runs test is described in an appendix.

The specific part of the adopted runs test is its circular sequence and there are only eight trials. The test is developed on a Cornish flora survey Atlas (French, Murphy and Atkinson, 1999). In this survey, a taxonomist divided Cornwall into squares (tetrads with dimensions 2 km x 2 km) and then surveyed the majority of each tetrad to record species present (French, Murphy and Atkinson, 1999). For each tetrad, there are eight tetrads which surround it. The arrangement of the squares is given in Figure G1:

1	2	3
8	Study site	4
7	6	5

Figure G1: Runs test sequence.

Data preparation for the runs test started from desktop work with the book "Flora of Cornwall" (French, Murphy and Atkinson, 1999) to identify presence and absence of each species recorded in study site in the eight tetrads around it. A macro programme was used to do the runs test to evaluate the randomness of the distribution of plant species.

The runs test result is summarised in table G1. The highest numbers of runs in this test is 5 which represent a low randomness of the species like those with 0 runs. For those species have 0 runs: this can represent two situations, either indicating a local dominant species or a locally rare species that has not been recorded in surrounding area.

Table G1: Runs test result

Runs	2	3	4	5	0
Number of species	6	23	5	11	42
Percentage	6.9%	26.44%	5.75%	12.64%	48.28%

Hypothesis test result is given in table 15. Its result returned as a logical value.

If h = 1, then runs test rejects the null hypothesis at the Alpha significance level.

If h = 0, then runs test fails to reject the null hypothesis at the Alpha significance level.

The result in runs test is based on the number of runs of consecutive values above or below the mean of x. Too few runs indicate a tendency of clustering. Too many runs indicate a high frequency of variation. It can be told from the table G2 that runs test uses a test statistic which is the difference between the number of runs and its mean, divided by its standard deviation. The test statistic is approximately normally distributed when the null hypothesis is true. Among 87 species found in Carnon valley 45 are ramdom occurred in land neighbouring study site. However, the short sequences of plants presence/missing are not sufficiently considered to be normal distribution. Therefore, the power of the test is limited. That is why Runs test is attached as appendix.

Table G2: Result of Runs test for all species occur in study site.

Scientific name	number of runs	n1 — number of tetrads where the species ispresent	n0 — number of tetrads where the species is not present	z — test statistic	Hypothesis test result
Lamium album	3	1	7	-0.5774	0
Vinca major	4	2	6	0	0
Alnus glutinosa	4	4	4	-0.3819	0
Anagallis tenella	3	2	6	-0.5401	0
Pteridium aquilinum	-	0	0	-	-
Rudus fruticosus	-	0	0	-	-
Agrostis setacea/Agrostis curtisii	3	7	1	-0.5774	0
Dryopteris dilatata	-	0	0	-	-

Rumex obtusifolius	-	0	0	-	-
Plantago coronopus	3	1	7	-0.5774	0
Buddleja davidii	5	6	2	0.5401	0
Scirpus (isolepis)setaceus	3	1	7	-0.5774	0
Typha latifolia	3	2	6	-0.5401	0
Agrostis capillaris	3	7	1	-0.5774	0
Bellis perennis	-	0	0	-	-
Viola riviniana	-	0	0	-	-
Euphrasia nemorosa	2	2	6	-1.6202	0
Polygonum aviculare	2	6	2	-1.6202	0
Rumex acetosa	-	0	0	-	-
Ranunculus repens	-	0	0	-	-
Vicia cracca	5	6	2	0.5401	0
Narcissus agg.	5	6	2	0.5401	0
Mercurialis perennis	3	1	7	-0.5774	0
Betula pubescens	2	6	2	-1.6202	0
Lemna minor	-	0	0	-	-

Reseda luteola	4	4	4	-0.3819	0
Salix aurita	3	2	6	-0.5401	0
Circaea lutetiana	3	7	1	-0.5774	0
Hyacinthoides non-scripta	-	0	0	-	-
quercus robur	3	1	7	-0.5774	0
Myosotis arvensis	4	2	6	0	0
Veronica Chamaedrys	-	0	0	-	-
Ulex europaeus	-	0	0	-	-
Salix cinerea	-	0	0	-	-
Glechoma hederacea	5	6	2	0.5401	0
Asplenium Scolopendrium	-	0	0	-	-
Viola canina	-	0	0	-	-
Calluna vulgaris	3	7	1	-0.5774	0
Ilex aquifolium	-	0	0	-	-
Lonicera periclymenum	-	0	0	-	-
Hedera Helix	-	0	0	-	-
Centaurium Pulchellum	-	0	0	-	-

Cerastium semidecandrum	-	0	0	-	-
Medicago Sativa	5	2	6	0.5401	0
Dryopteris filix-mas	-	0	0	-	-
Epilobium palustre	-	0	0	-	-
Dandelion taraxacum	-	0	0	-	-
Urtica dioica	-	0	0	-	-
Cortaderia selloana	-	0	0	-	-
Carex Pendula	2	6	2	-1.6202	0
Primula Vulgaris	3	7	1	-0.5774	0
Silene Dioica/Melandrium Rubrum	-	0	0	-	-
Rhododendron ponticum	3	7	1	-0.5774	0
Rosa Canina	5	5	3	-0.206	0
Carex arenaria	-	0	0	-	-
Anagallis arvensis	-	0	0	-	-
Polypodium interjectum	5	3	5	-0.206	0

Potentilla anserine/Argentina anserina	-	0	0	-	-
Lythrum portula	-	0	0	-	-
Epilobium lanceolatum	2	2	6	-1.6202	0
Cerastium glomeratum	3	7	1	-0.5774	0
Acer pseudoplatanus	-	0	0	-	-
Dipsacus fullonum	5	5	3	-0.206	0
cirsium arvense	-	0	0	-	-
Arenaria serpyllifolia	-	0	0	-	-
Veronica Serpyllifolia	3	7	1	-0.5774	0
Myosotis scorpioides	-	0	0	-	-
Sorbus Latifolia	-	0	0	-	-
salix alba	3	1	7	-0.5774	0
Lactuca virosa	-	0	0	-	-
Holcus Lanatus	-	0	0	-	-
Trifolium Campestre	5	2	6	0.5401	0
Lythrum Salicaria	3	1	7	-0.5774	0

Lotus Hispidus/Lotus subbiflorus	-	0	0	-	-
Lotus corniculatus	3	7	1	-0.5774	0
Potentilla Erecta	5	4	4	0	0
Athyrium Filix-femina	-	0	0	-	-
Festuca rubra	3	6	2	-0.5401	0
Polystichum setiferum	3	7	1	-0.5774	0
Hypericum Calycinum	2	1	7	-0.5774	0
Senecio Jacobaea/Jacobaea Vulgaris	-	0	0	-	-
Rumex Acetosella	4	6	2	0	0
Centaurium pulchellum	-	0	0	-	-
Stachys arvensis	3	3	5	-1.0299	0
Arum Maculatum	3	7	1	-0.5774	0
Teucrium scorodonia	-	0	0	-	-
Equisetum arvense	5	4	4	0	0

The runs test suggests that nearly half the species present in study site are distributed randomly in neighbouring areas. Their presence or absence is either a result of their habitat selection or competition. Therefore, mine tailings possibly plays a role as a habitat filter. Additionally, the occurrence of locally rare species give further evidence of the value of abandoned mine site in conservation.