DOCTOR OF PHILOSOPHY

Effect of slate quarrying on the Barlwyd catchment and remediation strategies

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Effect of slate quarrying on the Barlwyd catchment and remediation strategies

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Coleg
Cymraeg
Cenedlaethol

Declaration

I hereby declare that this thesis is the results of my own investigations, except where otherwise stated. All other sources are acknowledged by bibliographic references. This work has not previously been accepted in substance for any degree and is not being concurrently submitted in candidature for any degree unless, as agreed by the University, for approved dual awards.

Yr wyf drwy hyn yn datgan mai canlyniad fy ymchwil fy hun yw'r thesis hwn, ac eithrio lle nodir yn wahanol. Caiff ffynonellau eraill eu cydnabod gan droednodiadau yn rhoi cyfeiriadau eglur. Nid yw sylwedd y gwaith hwn wedi cael ei dderbyn o'r blaen ar gyfer unrhyw radd, ac nid yw'n cael ei gyflwyno ar yr un pryd mewn ymgeisiaeth am unrhyw radd oni bai ei fod, fel y cytunwyd gan y Brifysgol, am gymwysterau deuol cymeradwy.

Summary

Mining has serious environmental impacts including effects on water quality. Slate quarrying is neglected as with regards environmental impacts in the literature. Specifically, the geochemical effect of slate quarrying on water is an under-researched field. The effects of climate change may have future impacts with regards mining perhaps worsening any effects. Two metals which are of prime importance in this dynamic are Aluminium (Al) and Copper (Cu), which are found to be the most enriched in the river Barlwyd, they are also the most toxic to aquatic life. This thesis explores the geochemistry, hydrology, sediment effects and remediation in the Ffestiniog area, an area synonymous with historical and current slate mining.

The first aim was to quantify the temporal and spatial pollution of Al/Cu from slate quarrying on the rivers Barlwyd and Bowydd in line with the European Water Framework (EWFD) guidelines. This involved a yearlong study which was completed to establish a baseline. Samples were taken at 20 different sites throughout the year during different weather conditions. On the Bowydd concentrations of Al were 0.0015-0.8698 mg/L. Sample concentrations ranged for the Barlwyd ranged between 0.020 mg/L at B1 and 21.2656 mg/L at B12 and were spatially dependent. pH ranged between 3.4 at B12 and 7.62 at B1. Turbidity was negligible. Geochemical parameters were correlated to metal concentrations. This demonstrated that slate quarrying influences river water quality. This effect is most pronounced in the summer months when metal sample water concentrations are at their peak, as the water is more concentrated due to water availability. Geographically, Al and Cu were found to be enriched in the river Barlwyd and in the river Bowydd near sources of slate pollution/slate tips. Al/Cu also showed a temporal pattern of expression in this riverine environment, with higher concentrations in summer months when there was less rainfall. Al and Cu concentrations found by this research place the river in this area are poor status as with regards to the EWFD and are outside guidelines. Geochemical parameters also showed extreme tendencies, with low pH and high electroconductivities, outside recommended guidelines. Flux illustrated heavy loads on the river,

explaining the poverty of aquatic life found in the river. It is concluded that slate mining has a significant impact on the river water quality.

Chapter 4 in this study aimed to establish the influence of storm-driven hydrological change on Al/Cu concentrations and associated aqueous geochemistry of the of the Afon Barlwyd. Samples collected from 20 sites during storm events, showed an initial increase in Al and Cu concentrations (Site B4 0.319 mg/L and Cu 20.2 μg/L, Site B12 8.563 mg/L and 216.64, Site B14 0.0265- 0.0544 mg/L, 1.7523-2.72) and increase in pH to circa neutral levels over the course of the storm. This is evidence of a flushing effect, and as the storm progresses there is a physical dilution. Concentration: time relationships during the storm events demonstrated a clockwise hysteresis relationship, indicating that it could be as Doty and Carter (1965) claim that that the material decreases because of hydrological processes, or as Novotny (1980) suggests that the decrease in rainfall levels in the storm retreat means there is less polluted material carried into the water channel. Eh/pH relationships indicate that the speciation of Cu and Al are found in free ion states, suggesting it is more toxic to aquatic life. The key overall conclusion is that storms have a negative effect on aquatic life in the river as a flush of material causes toxicity from quarrying activity.

The aim of Chapter 5 was to estimate the sorption/desorption of the metals Al/Cu from sediment into the dissolved water fraction. The end goal was to work towards establishing better guidelines for the EWFD, by estimating the relative contribution of slate quarrying sediment to the Al/Cu load in the river. To examine the effect of sediment on the river water in the Barlwyd, sediment – aquatic phase exchange experiments modelling natural conditions were conducted. The study showed ambiguous results between sites and temperature and there was no overall clear pattern as there could sometimes be absorption and sometimes be desorption. This study indicated that sediment was not enough to explain the levels of metals in the water. Sediment analysis using TxRF revealed that the rock was rich in Al, and Cu, and laser ablation showed and that it was enriched in clay particles. To explain the

results, it is concluded that a pH dependent mechanism is responsible for the dissolution of minerals, and this could be due to clay presence in the rock.

The final aim was to evaluate two methods of remediation, biochar and zerovalent iron on removal of Al/Cu from samples of slate quarrying affected river water. Modelled lab trials with microcosms revealed that biochar was effective at removal of Cu but not as effective at removal of Al. Percentage removal of Al ranged from 44-97% biochar and 34-86.9% with FeO. The removal of Cu with biochar was not as efficient as with biochar with 44-76.9% removal. Percentage removal of Cu with FeO was 63-97 %. It is concluded that again the pH of the river water may play a crucial part in the mechanism of removal. It is demonstrated that viable remediation options could include the use of Biochar and FeO in the future.

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Abbreviations

AAS – Atomic Absorption Spectroscopy

Ag – Silver

Al – Al

ANC – Acid Neutralising Capability

As – Arsenic

ATR – Attenuated total reflectance

BLM – Biotic Ligand Model

BMWP – Biological Monitoring Working Party

C – Carbon

Ca – Calcium

CaO – Calcium oxide

Cd – Cadmium

Co_3 – Carbonate

Cr – Chromium

Cu – Cu

DNA – Deoxyribonucleic Acid

DO – Dissolved Oxygen

DOC – Dissolved Organic Carbon

EC – Electroconductivity

EU – European Union

EC – Electroconductivity

EQS – Environmental Quality Standard

ESA – Ecosystem Services Approach

EWFD – European Water Framework Directive

Fe – Iron

FITR – Fourier transform infrared spectroscopy

GDP – Gross Domestic Product

Hg- Mercury

ICP-MS – Inductively Coupled mass Spectroscopy

IPCC - Intergovernmental Panel on Climate Change

K – Potassium

Mg – Magnesium

Mn – Manganese

MOFF – Metallic Organic Framework

Na – Sodium

Ni – Nickel

NRW – Natural Resources Wales

NTU – Nephelometric Turbidity Unit

nZVI – Nanozerovalent Iron

OH - Hydroxide

ORP – Oxidative Reductive Potential

Pb – Lead

Se – Selenium

SEPA – Scottish Environmental Protection Agency

SQG – Sediment Quality Guidelines

SSC – Suspended-Sediment Concentration

TC – Total Carbon

TOC – Total Organic Carbon

TXRF – Total X-ray Florescence

WHO – World Health Organisation

XPS – X-ray photoelectron spectroscopy

XRD – X-ray Diffraction

ZIF – Zeolitic imidazolate framework

ZVI – Zerovalent Iron

CHAPTER 1 – LITERATURE REVIEW

1.1 Abstract

‘We never *know* the worth of *water* 'til *the well* is *dry*’ (Fuller, 1732). The significance of this quote is important given the industrial and technological developments that have occurred in the last century. These developments have led to conflicting interests in protecting water supplies. These conflicts of interests between economy, society and the environment are the trials of our time. Water is the fundamental element which underpins life. It is vital to all forms of life in the ecosystem. When we think of how much water comprises some organisms – up to 90%, its necessity seems quantifiably obvious. The protection of water supplies from threats to water supply is important, to not only man’s survival but also to the ecosphere. Historic mining has had negative environmental impacts which include water pollution (Karmakar, 2012; Macklin and Lewin, 1989; Macklin, 1986; Aspinall and Macklin, 1985; Harding and Whitton, 1978; Hudson-Edwards et al., 1997; Dennis et al., 2003; Brewer et al., 2005; Dennis, 2005; Lewin et al., 1983; Pirrie et al., 2002; Rawlins et al., 2003; Cave et al., 2005). This is true on a local and global scale. The catchment of the river Barlwyd in Blaenau Ffestiniog, Wales, runs through an active slate mine. As a result, there is water pollution that is either derived from the fine slate sediment which is postulated to be created by the weight of the slag heaps crushing slate below, or from the slate cutting process. Previous research shows high levels of Al (Al) and Cu (Cu) present in the water, and a low pH. This combination means a high bioavailability of metal and hence toxicity. This has implications for freshwater ecosystem services. Examining the problem in detail raises several questions. Firstly, where does the pollution derive? Secondly what is the scale of the problem, chemically, spatially and temporally? A field of which little is known is the toxicity of sediments, this will be examined in greater depth, by looking into the sorption and desorption of Al and Cu from sediment generated by the quarry. The last topic addressed prior to experimental work is remediation using biochar and zerovalent ion. One of the issues of our time, climate change, is addressed in the context of storm driven discharge and water quality, outlining

potential impacts for the future. Given the scope of the problem and the global production of slate the importance of these issues cannot be underestimated, both on a local and global scale.

1.2 Water security, health, and ecosystems

1.2.1 Defining the problem - water scarcity as a global challenge

Two thirds of the Earth are covered by water (Ball, 2000). A problem predicted by many political forecasters was that during this century shortages of water are going to cause political tension that may lead to social or military conflict. UNESCO states that current disputes happen principally in the Middle East (disputes stemming from the Euphrates and Tigris Rivers among Turkey, Syria, and Iraq; and the Jordan River conflict among Israel, Lebanon, Jordan and the State of Palestine), in Africa (Nile River-related conflicts among Egypt, Ethiopia, and Sudan), as well as in Central Asia (the Aral Sea conflict among Kazakhstan, Uzbekistan, Turkmenistan, Tajikistan and Kyrgyzstan) and south America (Bolivia) (UNESCO, 2013).

Globally, the drive for development has impacted natural resources such as water. 'The river runs black' summarises the impact that the economical drive for growth has had on China (Economy, 2005). In China more than three-quarters of the river water flowing through urban areas is not fit for drinking, or fishing (Economy, 2005). Levels of lead in the water in one part of the Guangdong province, where circuit boards had been processed and burned, were 2,400 times the guideline level set by the World Health organisation (Economy, 2005). This is one of the deep and complicated problems water resources are facing across the world.

In terms of actual supply, despite being covered by water, most of the water on Earth is too salty to be used (Ball, 2000). Only 3.5% of the planet's total surface water is fresh. A fraction, 0.01%, is in a form suitable for human use (Ball, 2000), half of which is inaccessible. However, water resources are

renewable, refreshed and recycled by the hydrological cycle. The negative aspect is that water is a finite resource; the amount of water in the system is limited.

As far as health is concerned this lack of water resource has detrimental effects on human health. Ball (2000) says that '80% of all diseases and one third of all deaths in developing nations are caused by contaminated water' (see Figure 2.1 – WHO, 2018, online source). This emphasises the importance of water to humanity. By 2025, the World Health Organisation estimates that half of the world's population will be living in water-stressed areas (WHO, 2017).

Figure 1.1 – Deaths from unsafe water, sanitation and hygiene.

(WHO, 2018)

<u>1.2.2 Ecosystem services - water provides a service</u>

It is estimated that 40% of human deaths are caused by environmental degradation (Pimental et al., 2007). It is thus clear that healthy ecosystems are thus crucial to the survival of humanity. Ecosystems have infrequently been given rights to water allocation and have suffered greatly from pollution

(Petts, 1996). Recent policy has integrated ecology and economy including payments for ecosystem services (Farley and Costanza, 2010). Ecosystem services views nature as capital value. In 1997 the economic value of 77 ecosystem services for 16 biomes was estimated to be in the range of $16-54 trillion ($10^{12}$) per year with an average of $33 trillion per year (Costanza et al., 1997). Global production per year was $38 trillion a year (Constanza et al., 1997). Ecosystem service approach (EA) has 12 principles which are pinned on fundamental values of human wellbeing and natural resources (Secretariat of the convention on biological diversity, 2004). The Ecosystems approach is important in securing a healthy natural environment and is a more holistic approach than that which has been applied previously. There have been several scoping surveys which demonstrate the benefit of the EA (NRW, 2014). The European Union has adopted these principles in a new environment strategy in 2011, owing to the 2010 biodiversity targets. The Environment (Wales) Act 2016 puts the ecosystem approach into statute through a set of principles, which are based on the 12 principles of the Convention on Biological Diversity. The Wales Environment Act (2016) focuses on the need to adopt a new, more integrated approach to managing our natural resources to achieve long-term sustainability.

Further environmental protection in Wales is the Wellbeing of Future Generations Act (2015), which requires public bodies in Wales to think about the long-term impact of their decisions, and to work better with people, communities, and each other and to prevent persistent problems such as poverty, health inequalities and climate change. In terms of water quality, indicators are a more resilient, healthier, equal Wales, of cohesive communities, of vibrant culture and thriving Welsh language, and a globally responsible Wales.

To emphasise the importance of the environment, the economic value of the natural environment can be assessed. A study in 2001, by Natural Resources Wales and the National Trust identified that the environment adds 9% to the total Welsh GDP. It was shown that the environment directly supplies £8.8 billion worth of goods and services, 1in 6 jobs and wages worth £1.8 billion (Natural Resources Wales and the National Trust, 2001).

There are many services provided by ecosystems, one of which is cultural values, which are easy to estimate. The UK National Ecosystem Assessment Technical Report (2011) notes that an average of £753 million per year is delivered to Wales though tourism, with the wider economic value of tourism estimated at 4.2 billion in 2007 and creating around 78,000 jobs. Examples of this include angling which is valued at over £100 million to the Welsh economy.

Biodiversity is an important aspect of ecosystem services. The General Assembly of the United Nations (2010) notes that biodiversity 'underpins ecosystem functioning and the provision of ecosystem services' (Meetings of the 65th Session). Every organism within an ecosystem has an important role to play and is connected to every other organism via a complicated network of interactions. Since ecological aspects interact, a direct impact on one aspect of the environment may catalyse other impacts elsewhere in a web (Constanza, 1997). The impact that pollution has on biodiversity, emphasises the value of biodiversity. Services provided by freshwater are summarised below in Table 1.1, which relates environment to economy (Aylward et al., 2005). Natural ecosystems have intricated and resilient mechanisms that filter and replenish freshwater resources and sustain marine environments. Since aquatic ecosystems are affected by pollution, ecosystem services are thereby affected, and thus so is our global capital. A link can be made between the importance of ecosystem services and the importance of researching into pollution and its effects on ecosystems.

Table 1.1 – Freshwater ecosystem services

Provisioning services	Regulatory services	Cultural services	Supporting services
Water consumption	Maintaining water quality	Recreation	Nutrient cycling, primary production
Water – non consumptive use	Buffering of flood flows, erosion control, flood control infrastructure	Tourism	Predator-prey relationship
Aquatic organisms for food and medicines		Aesthetic value	

Modified from Aylward et al., 2005.

1.2.3 What if we lose our ecosystems? The effect of pollution

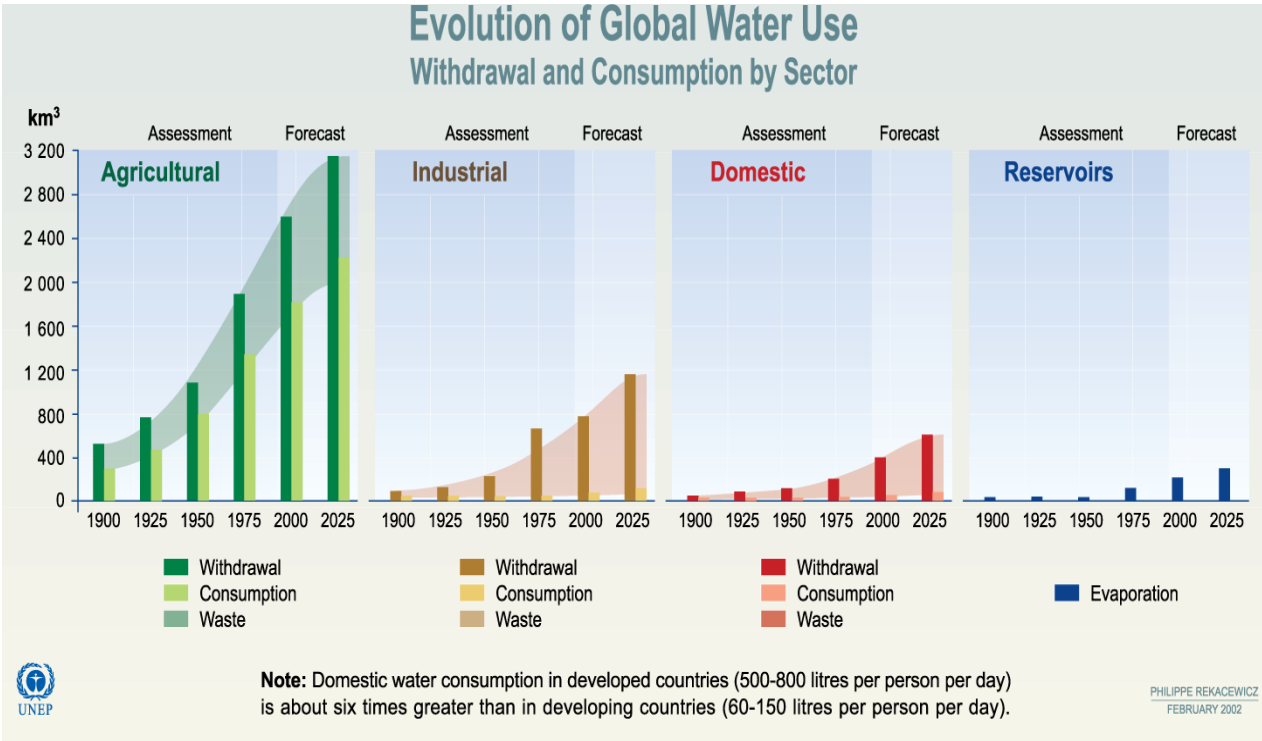
Public awareness surrounding pollution has increased significantly over the past 50 years. Pollution has been found to have significant effects on human health, agriculture and on natural ecosystems (Schwarzenbach et al, 2010; Conway and Pretty, 2013; Woodwell, 1970). Given estimations of ecosystem service values mentioned previously, the financial implications of pollution are quite significant (NRW and the National Trust, 2001). Despite this, ecosystems have also demonstrated how resilient they can be, and how nature can adapt to meet the challenges produced by pollution (Serengil et al., 2011; Schwarzenbach et al., 2010).

In terms of financial implications, costs can include depreciation of resources, lost productivity, and the cost of remediation (Pimental, 2007). Long term effects have not been sufficiently investigated and may go without being noticed, for these reasons environmental monitoring has become increasingly important. 40% of human deaths can be attributed to water, air and soil pollution (Pimentel et al., 2007). Environmental pollution and world population growth are contributing to malnutrition of 3.7 billion people worldwide and make them more susceptible to disease (Pimentel et al., 2007).

The increase in population is largely responsible for the extent of pollution globally (Commoner et al., 1971). Pollution can be described as caused by population, affluence, and technology (Meadows et al., 1992).

There was rapid expansion of the population after the Second World War which saw a doubling in population. The world population in 2013 stood at 7.2 billion and was projected to increase by 1 billion over the next 11 years and reach 9.6 billion by 2050 (UN, 2013). With this rise in population there will be an increased demand for resources and increased levels of pollution as a result. A greater demand for resources within affluent countries will lead to more pollution e.g., in the mining, transport and smelting of materials. Polluting activities associated with mining include the creating of metal products, their corrosion and disposing of products (Alloway and Ayres, 1996).

The rise in population has thus put increased pressure on water supplies. It was estimated in 1996 that humans were using over half the accessible fresh water (UN, 1996). Between 1950 and 1990 global water demand tripled and is still rising. Following these trends global water supply demand may exceed the total available supply by 2030 (see Figure 1.2) (UN, 2015).



Source: Igor A. Shiklomanov, State Hydrological Institute (SHI, St. Petersburg) and United Nations Educational,Scientific and Cultural Organisation (UNESCO, Paris), 1999.

Figure 1.2 – Evolution of global water use.

Bijani and Hayati (2011).

1.2.4 The technological revolution and a boom in mining

Anthropogenic effects on the environment have been considerable since the industrial revolution. With the introduction of improved technology and the "green revolution" in the 20th Century, man's demand on planetary resources has increased. This is largely due to an economy which depends on growth and the correlation between economic growth and demand on resources can be correlated, both showing an upward trend (Everett et al., 2010). The environmental impact of mining is wide reaching. Mining can cause erosion, formation of sinkholes, contamination of soil, loss of biodiversity, groundwater and surface water pollution, and can affect health of local population (Matschullat and Gutzmer, 2012). Of interest is the effect that mining has on water quality, and its consequent effect on ecosystems. The literature pertaining to metal mining is extensive. The literature associated with slate mining is more limited and thus the picture must be inferred. There is an

extensive history of metal mining which dates back over 4,000 years to the Bronze Age (Pattrick and Polya, 1993; Ixer & Budd, 1998). In terms of the extent of water pollution, the EU river basin characterisation exercise in 2005 estimated that 453 rivers in seven of the 11 river basin districts were in danger of being polluted by abandoned mines (which included coal mines and metal mines) (Jarvis et al, 2008).

Metals are of environmental concern as they cannot be degraded chemically or bacteriologically into simpler constituents. In this thesis Al and Cu are focused on owing to their risk ranked toxic effect on the environment (Donnachie et al., 2014) and their prevalence in the study area as demonstrated in previous studies in certain areas to exceed recommended concentrations by 54 and 12 times respectively (Buss et al., 2013).

1.2.5 Legislation and water

General legislation which applies to Wales, is the Wales Environment Act (2016) which includes the impacts of climate change and the Wellbeing of Future Generations Act (2015) which requires bodies to consider the long-term impact of their decisions which again would include the effects of climate change on society. These apply to water quality and land management in the instance of the river Barlwyd.

More recent legislation in Europe is holistic as it combines chemical and ecological measures of waterbody health. The European Water Framework directive (EWFD) aims to bring about good ecological and chemical status to all river basins in the EU by 2021 (Europa, 2014). Good ecological status is measured by the abundance of aquatic flora fish and fauna, the availability of nutrients and other conditions such as salinity, temperature and pollution by chemical pollutants. The EWFD aims to restore the quality of surface and ground waters by a river basin management plan, which includes interventions for restoring and maintain ‘good status’, using the most economical choice. The EWFD’s ecological assessment of rivers at the beginning of the legislation in England and Wales

showed that 26% were good or better, 60% were moderate, 12% were poor and 2% were bad quality (Europa, 2014). There are two assessment criteria, chemical and ecological status.

Natural Resources Wales are responsible for implementation and the monitoring which goes hand in hand with the EWFD in Wales. As the water framework directive spans a considerable amount of time there is an emphasis on the gradual decrease in waste. NRW take on the 17 different waterbodies, pollution legislation, and are the authority on regulating and waste disposal.

The Water Resources Act (1991) is responsible for the governance of discharges from quarries and mines in England and Wales. The law is part of the Integrated Pollution Prevention and Control which became legal after the environmental protection law (1990).

The European Water Framework directive has stipulated specific guidelines for certain substances Inventories of 33 dangerous substances known as "priority substances" were selected and for these Environmental Quality Standards (EQS's) were elucidated (Europa, 2014) EQS are guidelines for the chemical status of receiving waters (Chon et al., 2010). They are determined from assessment of their risk to ecosystems and to the aquatic systems at European levels. Following article 16 of the EWFD, these substances are categorised into two classes: priority substances and priority hazardous substances. It is necessary for priority substances to be controlled for progressive reduction of discharges emissions and losses, whilst it is imperative that priority hazardous substances are removed or phased out of discharges, emissions and losses by 2020 (Chon et al., 2010).

1.2.6 Metals of focus - Al and Cu

In terms of the metals upon which this research focuses, Al does not have specific Environmental Quality Standards (EQS) guidelines as it is difficult to estimate Al concentration due to the different forms of Al. There is not enough information to establish a reliable standard for Al (UKTAG, 2012). The UK Technical Advisory Group (UKTAG) has commissioned a study to establish (EQSs) for

substances falling under Annex VIII of the European Water Framework Directive (EWFD). The EWFD proposes predicted no-effect concentrations (PNECs) for Al using specific methodology outlined in Annex V of the Directive. EQS for Al have been proposed previously but never rigidly adopted by the EWFD. This is because the interaction between water and Al is complex (Bass et al., 2008). The EQS of the Al is assessed by NRW (Natural Resources Wales) at the non-statutory EQS of 10 µg/L set by SEPA (SEPA, 2010), and a higher 75.5 µg/L value considered more representative of the local environment based on data available from the geochemical atlas of Europe (Buss et al., 2013).

Cu is a priority substance under the water framework directive and the EQS is dependent on the $CaCO_3$ concentration. In the study region which this research focuses on the $CaCO_3$ annual mean concentration of the Barlwyd is variable (0-50, 50-100, 100-250 and >250 µg/L) and thus the EQS is 1µg/L bioavailable, and 1-28 µg/L dissolved (UKTAG., 2013).

Standards on acidification in rivers have been developed by the UKTAG taskforce. These standards are based on pH and 'acid neutralising capacity' (ANC) (UKTAG, 2012). pH can act as a twin to 'labile Al' and is thought to be responsible for the toxicity to biological communities at low pH (UKTAG, 2012). A longer-term measurement of acidification is ANC (UKTAG, 2012). Current recommendations for pH standards are set at the annual 5 - 10 percentile for acidification. UKTAG (2012) proposed new standards based on annual mean values (see Table 1.2).

Table 1.2 – Acidification values for WFD guidelines.

Boundary	WFD-A (Wales)	WFD-A (Scot-C)	WFD-A (Scot-H)	Fish (Fry)
High/Good	6.54	6.06	5.1	6.6
Good/Medium	5.95	5.58	4.55	5.9
Medium/Poor	5.44	4.90	4.22	5.3
Poor/Bad	4.89	4.50	4.03	-

1.2.6.1 Effects of metals on health

There are several factors which affect a metals bioavailability and its potential to have impacts on health, but the most important is its chemical form (Wang, 1987). To be bioavailable the metal is usually in a free ionic state (Gensemer and Playle, 1999; Wang, 1987; Worms et al., 2006). Factors such as pH, dissolved oxygen, turbidity, or temperature are factors which may determine whether a metal is in its free ionic form. A model that describes cellular control of metals is shown in Figure 1.3.

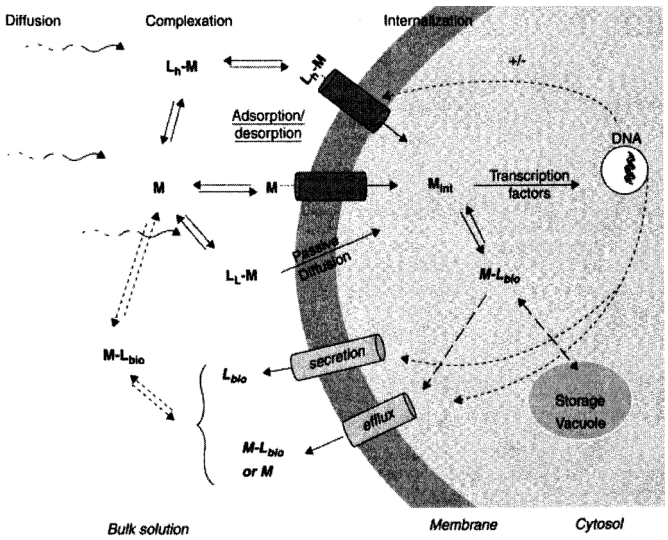


Figure 1.3 – The control of inflow and outflow of metals in a cell

(Worms et al., 2006)

1.2.6.2 Al's effects on health

One of the most common elements found in the earth's crust is Al. The abundance of Al in the crust is ~ 8.23% by weight, three times less than the 28.15% silicon (Si) in the earth's crust (Middag et al., 2015). Al is found mainly in Aluminosilicate minerals, most commonly as feldspars in metamorphic and igneous rocks and as clay minerals in well-weathered soils. Al forms polymorphs and hydrated species (Seiler et al., 1994). Al can form sulphides and oxides. It can form octahedral complexes with a variety of neutral ligands and with fluoride ions. It can form ionic salts, complexes and covalent compounds. These have a minimal effect on biological systems (Seiler et al., 1994). Despite being the

third commonest crystal element on the planet, Al has no known biological role (Williams, 1999). It is suggested that the reason for this is the low solubility in the circumneutral and anaerobic atmosphere in the early evolutionary world (Gensemer and Playle, 1999). Al was thereby not included in the evolution of life. This means that in nearly every case Al is toxic (Gensemer and Playle, 1999; Ganrot, 1986). Possible reasons for Al toxicity include binding to phosphate groups associated with DNA (Martin, 1986; Karlik et al., 1980) and additional organo-phosphate compounds (Karsch et al., 1987). It has been suggested that in plants Al may also alter Calcium ions (Ca^{2+}) toxicity due to a high binding affinity with the protein calmodulin (Haug & Foy, 1984). Exposure to Al can occur in a diverse manner of ways, including food, water, antacids as well as the inhalation of dust and fumes. Al intake can be between 370-550 pmol/day (Alfrey, 1987). Bioavailability of Al in humans is poorly understood (Srinivasan et al., 1999; Slanina et al., 1984, 1985, 1986) showed that Al uptake was enhanced by citrate. This has led scientists to believe that low molecular weight, neutral complexes of A1 may be absorbed within the gastrointestinal system ultimately leading to toxic effects (Martin, 1986). Due to its atomic size and electric charge (0.051 nm and 3^{+}, respectively), it is sometimes a competitive inhibitor of a few essential elements of similar nature e.g., magnesium (0.066 nm, 2^{+}), calcium (0.099 nm, 2^{+}), and iron (0.064 nm, 3^{+}). When the pH is equivalent to that of the human body, Al forms a barely soluble $Al(OH)_3$ that can be dissolved without difficulty, by small changes in the acidity of the media (Edwards, 2006).

Al tends to accumulate principally in bone and brain tissue, but it can also accumulate in the liver and spleen (Garnot, 1989). Some bone disorders have been linked with Al exposure e.g., osteomalacia (Klein, 2019). Al is also associated with Alzheimer's as high concentrations of Al have been found in brain tissue (Klatzo et al., 1965; Terry and Pena, 1965). There is no common consensus on the link between Al and Alzheimer's (Zatta, 1993; Zatta et al., 2003). In terms of Al and its effects on humans its mechanism is complex. The principal route for entry into the body is through the digestive and respiratory systems. Al interferes with numerous essential metals and metalloids by altering bioavailability. Al ions can compete with zinc (Zn), iron (Fe), chromium (Cr) and calcium (Ca) (Metwally and Mazhar, 2007). In lysosomes of the brain, kidneys and liver Al replaces phosphates

(Krewski et al., 2007). In bones Al replaces Calcium, and in the plasma, Al can form compounds with transferrin (Krewski et al., 2007). Evidence of the neurotoxicity of Al cations (Al^{3+}) includes: the link between chronic Al exposure and the development of Alzheimer's Disease; the association of Al adjuvants in the development of autoimmune syndrome induced by adjuvants (ASIA); and epidemiological evidence pointing to an association between the use of Al adjuvants and autism spectrum disorder (Morris et al., 2017).

1.2.6.3 Characteristics and health effects of Cu

In terms of character Cu is a rosy, pink coloured transition metal of atomic weight of 63.54 and atomic no 29 (Royal Society of Chemistry, 2021). Cu is both malleable and ductile and is an excellent conductor of heat and electricity (Royal Society of Chemistry, 2021). In ionic form Cu is found in either Cu^{1+} or Cu^{2+} form. In the lithosphere it is found in trace quantities in metallic form and is primarily found as Cu compounds in ores including Cu pyrites ($CuFeS_2$) and Malachite ($CuCO_3Cu(OH)_2$) (Artiola., 2005). Cu has long been used in metallic form and is made by reducing malachite ore by heating with Carbon (Conway and Pretty., 2021).

1.2.6.4 Effects of Cu on ecology

The toxicity of Cu is rarely of concern in mammals, the primary concern for Cu in drinking water supplies is its taste. Cu is detoxified in the liver and kidney, and as it readily binds organic matter is excreted readily (Chen et al., 2020)

The environmental impacts to aquatic systems of both Al and Cu are of major concern. The sensitivity of fish and crustaceans to Cu is 10 to 100 times higher than mammals and algae are up to 1,000 times more sensitive (Foster and Wittman, 1979; Hodson et al., 1970). In the environment, Cu is frequently accompanied by a low pH and is not usually the sole metallic compound (Wright and Wellbourn, 2002).

Aquatic systems receive Cu from many inputs, the atmosphere, agricultural run-off, deliberate additions of Cu Sulphate ($CuSO_4$) to control algal blooms and direct discharge from industrial processes (Flemming and Trevors, 1989; Georgopoulos et al., 2001). Cu solubility is largely pH dependent with dissolved Cu higher at acidic/neutral pH. Cu also tends to form strong complexes with organic ligands, and this can decrease its biological availability (Janssen et al., 2003).

Strong organometallic complexes are formed in soil and sediment also and its availability is normally decreased by complexation (Tack and Verloo, 1995). In aquatic systems, Cu tends to leave the water column and accumulates in sediments, thus sediments can be of particular concern in estuarine sediments (Flemming and Trevors., 1989; Bryan and Langston, 1992). This however is dependent on pH.

1.2.6.5 Effects of Al on ecology

Al is released from rocks and soils by weathering; however, this Al stays mostly in an insoluble form. Metals such as Al interact as shown in Figure 1.4. Chemical speciation of Al is mostly decided by pH as shown in Figure 1.5. An increase in acidity results in the release of Al from soils and rocks into soil solution by dissolution of Al hydroxides and by desorption of Al which is bound to the exterior of soil organic matter. Al which is dissolved can move with the soil solution via runoff into rivers (Wright and Welbourn, 2002). Al is not accurately described as toxic, as it is not biologically available in terms of being taken up by specific biological mechanisms, however it does have an effect by clogging membranous surfaces in fish (Poleo, 1995). Al is considered a contaminant when the pH decreases below a certain point, as this makes the form bioavailable and not found as a precipitate.

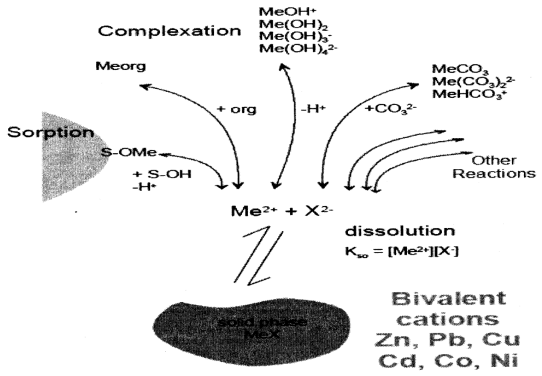


Figure 1.4 – A simple model showing pathways for metals following dissolution

(IFU, 2010)

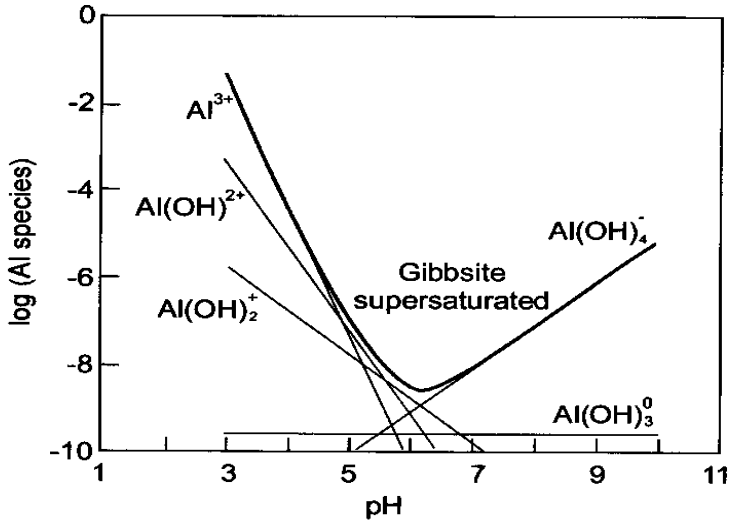


Figure 1.5 – Dissolved Al species activity in equilibrium with Gibbsite ($AlOH_3$) at 25°C.

The diagram represents the species of Al that would be present in dilute aqueous solutions at pH 3-10. The sum of individual species activity is represented by the heavy line (Wright and Wellbourn, 2002)

The loss of vegetation and riparian ecosystems is a direct consequence of mining (Parsons, 1977; McKnight and Feder, 1984). In terms of Al's effect on fish, equilibrium is a key factor. Metals in too high concentrations can be harmful to fish and can kill benthic organisms. Precipitation of Al on gill membranes of fish and as a result asphyxiation may result in fish death (Poleo, 1995). Al was thought not to be a biologically useful element as it was thought to be introduced after life was formed, hence it has no apparent function in living organisms (Exley, 2013). Research on the toxic effects of Al date

back as far as the 1970's (Dickson, 1978; Schofield., 1977). The forms which are shown to have toxic effects are the cationic forms. These have been demonstrated to be regulated by hydrogen ions, ionic strength, organic matter and temperature.

Al in streams is normally between 60 µg/L and 300 µg/L with an average of 64 µg/L (Wright and Wellbourn, 2002). Al levels are generally low in aquatic ecosystems where temperature, pH and redox potential are constant and organic and inorganic contaminants in the water are stable. The biogeochemical cycle for Al is outlined in Figure 1.6. Environmental conditions can cause sorption-desorption and water sediment equilibria to shift thus increasing bioavailability (Brusseau, & Chorover, 2019; Violante et al., 2010). Al mobilisation due to weathering is mainly associated with pH (Bache., 1988).

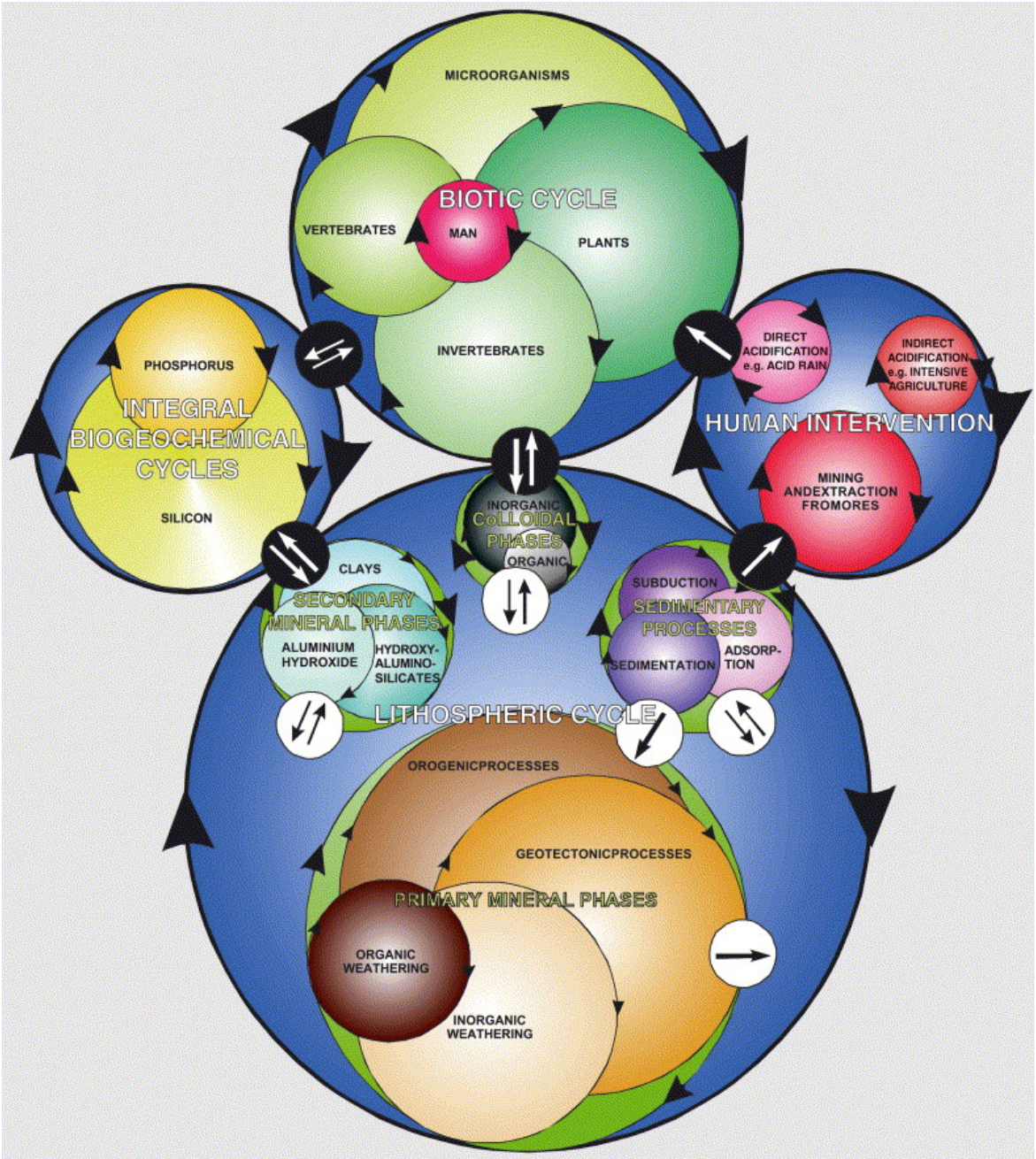


Figure 1.6 – The biogeochemical cycle for Al.

(Exley, 2003)

In terms of the environment, Al has been shown to be a problem in cases of acid rain. Tam and Williams (1986) show that there is competition by Al from calcium sites under acidic conditions. Remedial action is shown not to be effective as reversing the pH will not return the original chemical status quo (Tam and Williams, 1986). Acid rain discharged a large quantity of Al into natural waters as it mobilised Al from soil stores.

In environments such as the Barlwyd where the pH is acidic, the predominant form of Al is Al^{3+} (Gensemmer and Playle, 2010) In neutral conditions the Al $(OH)_3$ is the predominant form. Al is amphoteric, meaning Al reacts with mineral acids and strong alkalis (Rennie and Law, 2016). Al can enter the environment through anthropogenic sources (EA) e.g., wastewater treatment. Al has a high reactivity, with a high charge radius of Al ion forming hydroxide complexes. Al's speciation is dependent on pH, alkalinity, temperature, DOC, DIC and anion presence. Al is usually a hydroxide. Organic and inorganic ligands compete for complexation with the hydroxide ion. The most toxicological species is the inorganic monomeric form of Al. In reference to the river Barlwyd low pH's below 5.5 have been recorded, whereby the species Al^{3+}, [AlFAl (OH) x and $AlSO_4$ exist (Buss et al., 2013; Evans et al., 2011). At pH's of 6-7 which also exist further downstream in the river Barlwyd, solubility declines and insoluble Al $(OH)_3$ persists. This is particularly relevant to fish, as Al $(OH)_3$ precipitates onto fish gills. In algae Al interferes with intracellular phosphorus metabolism or glucose metabolism early in the glycolytic pathway (EA report, SCO40038/SR1, 2007). Algae are the most sensitive to Al toxicity long term (EA report, SCO40038/SR1, (2007).

The damaging effects of Al were first described in 1896 by Zimmerman (Zimmerman, 1896; Peiffer et al., 1997). Zimmerman (1896) goes on to report that three brooks contain white precipitates which are poisonous to fish and some plants.

In a detailed study Kennish (1998) looks at the effects of heavy metals on aquatic organisms. In his study he notes that high concentrations of heavy metals can have several effects on fish and other benthic organisms. These include 1) A change in histology and morphology in the tissues, 2)

physiological changes such as the inhibition of growth and development and cyclical changes which impede on the fish's ability to swim. 3) Biochemical changes such as enzyme activation and chemistry of the blood 4) Behavioural changes 5) Reproductive changes (Kennish, 1998). Despite this many aquatic organisms can control the concentration of heavy metals in their tissues e.g., fish and crustaceans can excrete essential metals such as Cu, Zn and Fe that exceeds biological need. When heavy metals are in excess it is much harder for them to be controlled in biological systems (Gemmel and Connel, 1984). It is such that heavy metals have a negative long-term effect on benthic organisms. A pH between 6.5 and 8.2 is optimum for aquatic organisms.

In terms of the specific effects of Al, $Al(OH)^{2+}$ and $Al(OH)_2$ enter the organism through the gills, cross cell membranes and reduce the activity of numerous enzymes, and following polymerisation is deposited on the gills. This prevents ion exchange and impairs respiration in fish (Exley et al., 1991; Poleo, 1995)

Al sensitivity is much more prevalent in plants than in mammal and lower organisms. In its ionic form, Al is especially phytotoxic at pH's lower than 4.5 (Parker et al., 1988). As Al interferes with phosphorus metabolism, plants suffering from Al deficiency are akin to those suffering from phosphorus deficiency (Roy et al., 1988). Al also interferes with Ca uptake (Ericsson et al., 1995).

It is also postulated that high level predators such as passerine birds could be ingesting Al via food sources such as invertebrates (Nyholm and Myhrberg 1977; Nyholm 1981). It is important to emphasise that the effects of Al can't be uncoupled from the effects of acidification (Buckler et al., 1987). Research in relation to Al and Cu should thus be an important topic of research with regards to bioavailability to aquatic life.

1.2.6.6 Additional caveats - metal interactions

Since the metals Al and Cu are not the sole metals found in the Barlwyd at higher concentrations than the EWFD, it is important to consider the effect of mixtures of metals. These are not considered for the purpose of this project as they are not the most prevalent or toxic metals and owing to the volume of work which would be required. Mixtures of metals present a complex and diverse problem to the ecosphere. Since different organisms are affected differently by different metals owing to their biology, the toxicity of metal mixtures to organisms is dependent upon which metals are present (Wang, 1987). Heavy metal interactions can be synergistic, antagonistic, non-interactive or additive (Wang, 1987). In the case of Cu, the effects of combining with Mn and Ni on algae – the primary producer is synergistic, and in freshwater fish the only metal which is synergistic is Zn. Interestingly the effect of combining Pb with Cu is antagonistic. Most effects with more than two heavy metals are synergistic.

Al also displays the same complexity of interactions. Hutchinson and Sprague (1986) show that a mixture of metals has a synergistic effect on ecology (Hutchinson & Sprague, 1989). Al alone displayed an acute toxicity at a concentration of 95 µg/L at a pH of 5.8. In the presence of 5 µg/L of Zn and 2 µg/L of Cu, the threshold of toxicity was 29 µg/L of Al. Other mixtures of metals containing low concentrations of Mn, Fe, Ni, and Pb did not show the same effect. DOC exerts the same effects on these metal mixtures as on one metal alone (Gensemer and Playle, 1999).

1.3 Effects on ecosystems particular to the river of study - the Barlwyd

In terms of aquatic life, there is anecdotal evidence presented by Pryce and Janes (2009) that the Atlantic salmon *Salmo salar L.* and brown trout *Salmo trutta* L. were no longer living in the river Barlwyd, although they were still found about 3 or 4 miles downstream in the Dwyryd. Salmon and brown trout were also found in the two Barlwyd lakes up until ca. 2004, but the larger lake was then drained for dam repairs.

Pryce and Janes (2009) note that the Pant-yr-Afon discharge channel was covered in milky white deposit, while the bed of the river is brown/red. The Llechwedd/Greaves discharge amongst others was also noted to leave a milky/white deposit on the discharge channel bed. Large waterfalls and boulders further downstream are suggested to be a factor in preventing fish migration upstream.

Existing data from Natural Resources Wales was analysed by Pryce and Janes (2009). This data included water quality and biological results. Water quality results showed fluctuations in pH both between and within monitoring locations. The biological data was composed of macro invertebrate samples from 24 locations on the river Barlwyd, 10 on the river Goedol and 3 on the river Dwyryd, and fish survey results from the Afon Barlwyd and Afon Goedol (Evans, 2011).

Macro invertebrates can be an indicator of water quality (Canfield et al., 1994; Kiffney & Clements, 1993). Biological Monitoring Working Party (BMWP) scores are assessed by the sensitivity of some species to pollution with those who are more sensitive gaining higher scores, thereby weighting the biological quality by the effects of biological quality. The summary presented by Pryce and Janes (2009) shows that sites upstream of the quarry illustrate good water quality, whilst those downstream show moderate or poor water quality. Samples on the Goedol and Dwyryd rivers showed either good or very good water quality. This indicates that the problem is localised to the Barlwyd and does not extend significantly downstream. The data was limited however, as each location had been sampled only once in a 28-year period.

Fish surveys showed that the Barlwyd was graded as F (fishless) for salmon and trout, except in one site in 1987 which was graded as D for trout. This shows that fish are mostly absent from the river. The data from the Goedol demonstrated that one site was fishless, whilst other sites were either D or E (Evans, 2011). These ecological data establish the need to do further research to establish the chemistry of the river.

Morphology of the river is also an important influence on the degree of pollution the river contributes (Ciszweski, 2004). A riverbed which comprises of noncohesive material is easily modified into various bed forms. The factors which govern the dimensions and number of bed forms in a particular river reach are on channel gradient, sediment supply from bank and bed erosion or from tributaries and on water discharge (Ciszweski, 2004). However, the morphology of the portion of river in the Barlwyd is largely modified, consisting of slate terraced platforms upstream and lose pebble downstream. There are no bars in the polluted portion of the stream. The terraced platforms may result in faster flow owing to decreased bed resistance. It is likely that the sediment contributed is dissolved as it does not impact downstream. The highest concentrations of metals occur at higher gradient where there is higher current velocity in the Barlwyd. This is consistent with the findings that a reversed sequence of metal concentrations can be observed in channels receiving effluents from polymetallic ore mines (Cisweski, 1998). Usually, in perennial rivers, augmented concentrations are found in zones with slow flow and the lowest ones are in a thalweg zone (Cisweski, 2004). Furthermore, during low water stages there are instances of higher metal concentrations in pools than in sand bars reworked in riffles (Cizweski, 2004). Floods and discharges higher than average cause erosion and redeposition of fine strongly polluted sediments (Cizweski, 2004).

1.4 Context of slate mining

The pollution found in the Barlwyd may or may not be linked with slate mining and the cutting process or weathering of the slate tips. It is therefore important to establish the scale of the problem, to aid with remediation efforts in the long term. The story of how slate quarrying became an important focus of economic activity is thus important to understand.

The history of slate mining in Blaenau Ffestiniog can be traced to the opening of the train line between 1833 and 1836. More business came to the town of Blaenau Ffestiniog when J.W. Greaves opened Llechwedd quarry.

Locally there are four areas which are renowned for their historic slate production, Dinorwig/Llanberis, Dyffryn Nantlle, Bethesda and Blaenau Ffestiniog. At the peak of the slate mining in Meirionnydd, there were 29 slate mines that produced over 166,000 tons of slate and employed over 5,000 of workers (Department for Environment, 1995). Later technological developments brought about a cut in the work force towards the end of the 19th Century. The arrival of the second World War was largely responsible for this with the curtailing of exports to Germany. Surviving today is the Llechwedd quarry and the Ffestiniog quarry, that supply a limited number of slates, which is ever decreasing (Thomas, 2010).

The problem with slate mining is the production of waste. For each ton of slate produced there are three tons of waste produced (Thomas, 2010). Given that the world estimated production of slate is 4 million tonnes, it is easy to see the extent of the problem (Thomas, 2010). The problem is a worldwide problem but is especially relevant to Spain as 90% of Europe's slates are derived from Spain (European Association of Mining Industries). It is important to recognize the environmental impacts which arise because of slate mining and mineral mining (Hilson 2002; Gray, 1997; Salmons, 1995). Specifically, the waste in Blaenau Ffestiniog is quantified by Natural Resources Wales as amounting to 185 tonnes of waste between Gloddfa Ganol and Llechwedd (Thomas, 2010).

As the pollution is thought to derive from the slate mine, the composition of minerals in slate which are contributing to this pollution is important (see Table 1.3). As the slate is weathered and affected by biological pathways, the minerals which form the slate are released into the surrounding environment. Welsh slate was formed during the Cambrian-Ordovician geological era, over 450 million years ago. In the Ffestiniog area the slate was formed during the Ordovician period, and is described as blue slate (Attewell & Taylor, 1969).

Table 1.3 – The composition of blue slate

Mineral	%
Quartz	41.2
Albite	9.7
Mica	30.5
Chlorite	7.4
Hematite	6.9
Calcite	1.1
Pyrite	2.4
Rutile	0.8
Total	100

(Attewell and Taylor, 1969)

Quartz is evidently the principal element in slate, which is principally composed of SiO_2, however Atewell and Taylor (1969) demonstrate that there are several additional impurities found in quartz (see Table 1.4). Al comprises 22.1% of quartz and this is where the Al identified in the river water is derived. The other element this thesis focuses on, Cu, is also found in Spanish roofing slates in the region of 4.2-60.9 ppm and is a trace element in slate (Cárdenes et al, 2013). This explains the relatively lower levels of Cu in slate.

Table 1.4 – Composition of quartz in blue slate

Composite	%
SiO_2	62.0
Al_2O_3	22.1
Fe_2O_3	7.0
FeO	7.0
Na_2O	1.5
K_2O	3.3
CaO	0.6
MgO	2.4
MnO	2.4
CO_2	H/G
P_2O_5	0.07
C	-
H_2O	H/G
TiO_2	0.84
S	0.04
Total	**100.01**

(Attewell and Taylor, 1969)

Another mineral found in blue slate is mica, which also contains Al. The most common form of mica is muscovite or potassium mica $KAl_2SiAlO_{10}(OH,F)_2$ (Lide, 1998), but there are various other forms which can contain elements which form complexes e.g., iron, magnesium, lithium etc. (Thomas, 2010).

The remaining minerals which comprise slate are all complexes of different elements except hematite (Fe_2O_3) and pyrite (FeS_2). Weathering releases these elements to react with the surrounding environment.

The link between mining and the presence of heavy metals means that the further study of the classification, transport and availability of these pollutants in river basins is key **(**Johnson et al*.,* 2005; Farag et al*.,* 2007). The chemical and physical characteristics of rivers our awareness of erosion processes and transport in rivers are important information to those which govern water resources (Evans, 2011). To mitigate anthropogenic problems in the most efficient and sustainable way thorough data about pollutant transport and characteristics is needed. It is these processes which govern and decide pollutant supply the river channel (Salomons, 1995; Zonta et al., 2005). The characteristics which are important are the variation in sediment supply, heavy metals organic matter, and radionuclides over time and space (Smith et al., 2003).

1.5 Geochemistry of slate and riverine environments

Metals are found in water in three different forms: a colloidal form, particulate or soluble. Particulate and colloidal metals can take several chemical forms; 1) hydroxides, oxides silicates or sulphates or 2) absorbed to clay, silica or organic matter. Metals that are soluble are chelates or organo-metallic complexes (Vink et al., 1999). Solubility of metals is governed mainly by the pH of the water, the types and concentrations of the ligands that the metals adsorb onto, and the oxidation state of the metal and the redox conditions of the system (Vink et al., 1999).

In terms of slate quarries, rivers running through mining areas are frequently acidic. The acidity is derived from peatlands upstream (Urban et al., 1989). This acidity increases the competition for binding sites between metals and hydrogen ions and the solubility of carbonate complexes, and releases metal ions into the water column (Foster and Charlesworth, 1998). When the pH in water decreases and creates more acidic conditions, metal ions dissociate. This results in the solubility of the metals increasing. In line with this, water with a low pH contains a considerable number of heavy metals, which are detrimental to fish and benthic organisms (Evans, 2011). Furthermore, water from quarries contains a considerable amount of raw material from slate waste – primarily slate dust. This causes high turbidity, which prevents oxygen from reaching the water (Evans, 2011). The dust is high in content of sulphates, heavy metals, and Al. Mance (1987) reports that it is slate waste which is derived from quarrying in slate mines which is to blame for most cases which are associated with metal pollution in river catchments.

A problem known as acid mine drainage is described by Lund et al. (1987). Oxidising sulphide minerals especially pyrite is the principal process in speeding up metal release from minerals as well as in creating acid waters at mine sites. The slate turns into fine dust through industrial processes. This increases the surface area and exposes the rock to oxygen and water thereby increasing reactivity. Lund et al. (1987) suggest that there is a biological process, catalysed by the bacterium *Thiobacillus ferroxidans* which creates acidic waters. This is particularly true of pyrite:

$$FeS_2 + 15O_2 + 14H_2O_{(l)} \longrightarrow 4Fe(OH)_{3(s)} + 8H_2SO_{4(l)} \qquad \text{Equation 1}$$

The high level of SO_4^{2-} found in the waters confirms this reaction. The increase in weathering reaction rates leads to more metals and acids being released from the rock into surface and ground water. Peiffer et al. (1997) suggest another mechanism which could explain the release of Al into water with the production of H_2SO_4 – through the dissolution of mica (muscovite).

KAl_2 [(OH_2) Si3AlO10] + H^+ + $9H_2O$ $\longrightarrow$ 3Al (OH_3) + $3H_4SiO_4$ + K^+

Equation 2

When Al^{3+} is a weaker acid than Fe^{3+}, protons from pyrite oxidation will redissolve Al (OH_3) and the following equation will result:

$KAl_2[OH_2)/Si_3AlO_{10}]$ + $6.25H_2O$+ 9.375 O_2+ $2.5FeS_2$ $\rightarrow$ 2.5FeOOH + $3Al^{3+}$+$5SO4^{2-}$ + $3H_4SiO_4$ + K^+

Equation 3 (Peiffer et al., 1997)

This could explain the high Al content in the acidic waters of the River Barlwyd.

DOC is also an important aspect of this with Cu showing differing levels of binding to DOC levels according to pH and different levels of binding according to form of ion and kind of metal (Meador et al., 1991) Therefore, this is an important area of research to examine DOC about the Barlwyd and both Al and Cu.

1.6 Historical research on the effect of mining and slate mining on water quality

There is an abundance of literature which links the effect of mining on water quality. This work focuses principally on recognising sources of pollutants such as heavy metals, and acid in natural waters (Cohen and Gorman, 1991; Church et al., 1994; Navarro et al., 2008). Some studies attempt to establish the processes which are responsible for/contribute to the increases in metal concentrations, turbidity and acidity levels in rivers that flow through metal mines (Chapman et al., 1983; Salomons, 1995; Zonta et al., 2005; Evans 2011). Several short- and long-term studies have been carried out, which examine heavy metals, pH and turbidity to explore spatial, physical and chemical parameters, transport processes and river fluxes. (Bradley and Lewin, 1982; Davis et al., 1991; Smolders et al. 2003; Evans, 2011). Chemical data are essential to understand load and turbidity in polluted rivers to

develop a comprehensive understanding of the effects of trace elements on water quality (Horowitz et al., 1989; Evans 2011).

Peiffer et al., (1997) shows that pollution in rivers because of mining is a great problem in the river Rebach, Germany. Specifically, there are high levels of Al and acid as result of seepage of the slate waste. As a result of further anthropogenic activity such as farming and urbanisation a white precipitate of Al hydroxide is formed. Byrne (2009) show that acidification happens following the release of concentrated efflorescent minerals on the surface of quarry waste, and as a result pollutants such as Al and Cu are dissolved and transferred to the river (Evans, 2011).

1.7 Sediment processes and the aquatic environment

In catchments affected by metal mining up to 90 per cent of the metals are associated with sediment rather than in aqueous forms (EA, 2008). Contaminants in metal form are primarily mobilised and transported downstream and deposited by river processes (EA, 2008). Therefore, there may be a bank of stored sediments downstream which could be remobilised into the water column later. These sediments may be causing damage to aquatic ecosystems in surface waters (EA, 2008).

The nature of sediment is imperative to the health of an aquatic system (Davoren et al., 2005). Assessment of sediments to prevent the impairment of water bodies is not sufficiently considered (White, 2008; Tueros et al., 2009), although previous studies suggest that sediments need to be considered as a source of pollutants in planning water quality research (Horowitz , 1991; Chon et al., 2010). Pollutants such as pesticides organophosphates and metals accrue in sediments, and should they be suspended in overlying waters, can cause toxicity to aquatic life (Burton & Johnston, 2010; Winkels et al., 1998; Zoppini et al., 2014). Sediments can be both a sink and as a source of pollution (Hollert et al., 2000). The total concentration of metals is not sufficient to estimate the real potentially toxicity and the general status of freshwater systems because of a higher number of variables such as metal bioavailability, interactions between different metals and the effects of mixtures of metals that

may also play a key role in the biological effects of these elements (López-Doval et al., 2012; Vazquez-Roig et al., 2013). The daughter Directive (2008/105/EC) of the WFD (Europa, 2014), stipulates that the long-term trend analysis for monitoring variation in concentrations of priority substances in sediments affected by anthropogenic activities is required in addition to the monitoring of water quality (Brils, 2008). For the catchment management approach, sediment quality must be considered (Brils, 2008; Tueros et al., 2009). This will aid to monitor anthropogenic pressure and prevent any deterioration. The purpose of sediment monitoring guidelines is to assess long-term trends in impacts of anthropogenic pressures and to ensure no deterioration limit is reached and that comparable data are collected (Brils, 2008). When ecological criteria of the EWFD fail, a check on the sediment quality may be required (Brils, 2008). This requires sediment-quality assessment approaches (cause-impact analysis) that can be linked to the WFD. SedNet recommends that sediment quality is assessed by the following criteria 1) persistence; 2) bioaccumulation/adsorption; 3) toxicity; 4) relevance at the large scale (river basin); 5) high fluxes (tendency to increase concentrations/fluxes on a long-term basis); 6) addition or replacement of pollutants will be based on the results of present and future monitoring programmes and on the results achieved by research and technological development projects where the identification of new or emerging contaminants takes place (Brils, 2008).

Interest in the determination of the real bioavailability of metals in aquatic systems, both in water and in sediment, has grown during the last decades (Alcorlo et al., 2006; Ankley et al., 1994). In terms of sediment toxicity, recently new approaches have been undertaken to estimate short- and long-term toxicity to biota. De Castro-Catala et al. (2015) carried out a sediment toxicity risk assessment in four rivers of the Iberian Peninsula. The risk assessment looked at chemical, toxicological and ecological parameters. The results demonstrated acute toxicity in most of the samples. Long-term tests showed lethal and sub-lethal effects. The chemistry of the sediments demonstrated that organophosphates and metals were primarily responsible for the toxicity (De Castro-Català et al., 2015).

1.7.1 The importance of the hyporheic zone to sediment interactions

Particularly relevant to sediment water interactions is the hyporheic zone. The hyporheic zone is the interface between streams and underlying shallow groundwater systems or subsurface water. Within this distinct biogeochemical environment important transformations occur that can impact the chemical makeup of both the overlying surface water and underlying ground water systems. This interface is important to the entire river's ecology. Several models have been developed to quantify the transport of chemicals between water and underlain sediments associated with the hyporheic zone. Hyporheic exchange is known to influence metals speciation (Bourg and Bertin, 1993; von Gunten and Lienert, 1993; Fuller and Harvey, 2000; Palumbo-Roe et al., 2012; Boano et al., 2014) and metabolism of organic carbon (Grimm and Fisher, 1984; Kim et al., 1995; Conant et al., 2004; Battin et al., 2008; Boano et al., 2014). Several solutes of concern, including heavy metals, radionuclides, and many organic contaminants are surface active and become associated with sediments by adsorption and precipitation processes (Stumm and Morgan, 1996; Schwarzenbach et al., 2002; Boano et al., 2014). Because mineral surfaces are negatively charged, multivalent metals are particularly likely to sorb to hyporheic sediments, and most hyporheic sorption models have been developed to assess transport of metals. Furthermore, when there are reduced groundwaters discharge into rivers, which is relevant to the Barlwyd catchment, oxidation of iron and manganese produces rapid precipitation, which results is an extensive accumulation of highly reactive solid phases within the hyporheic zone. Organic contaminants also usually sorb to organic carbon in sediments (Schwarzenbach et al., 2002; Boano et al., 2014), however, the behaviour of organic contaminants in the hyporheic zone has been investigated much less than metals—primarily because the early USGS studies focused specifically on metals. Biofilm coatings of benthic and hyporheic sediments contain abundant organic matter in the form of cells and extracellular polymeric materials, providing diverse reaction sites for binding both organic and inorganic contaminants (Flemming, 1995; Headley et al., 1998; Gadd, 2009; Boano et al., 2014). Important drivers of hyporheic exchange are gradient, temperature, solute concentration, geomorphology of the river (Boano et al., 2014). In terms of

sediment heterogeneity in grain size is an important factor in exchange (Boano et al., 2014). A variety of models have been suggested for hyporheic exchange, which include sediment.

The transient storage model (TSM) was the first popular model for hyporheic exchange (Hays, 1966; Thackston and Schnelle, 1970; Valentine and Wood, 1979; Bencala and Walters, 1983; Jackman et al., 1984; Kim et al., 1992; Wörman, 2000; Bencala et al., 2011; Boano et al., 2014). The multirate mass transfer model (MRMT) was the first model used to represent wide ranges of storage timescales in rivers (Haggerty et al., 2000; Haggerty and Reeves, 2002; Boano et al., 2014). Another model developed to describe hyporheic exchange was the advective storage path model. This model by Wörman et al. (2002) was the first study to explicitly link in-stream transport with residence time distributions predicted by physically based models (Boano et al., 2014). This study proposed the advective storage path model (ASP) as a special case of the MRMT model when hyporheic exchange of solutes is governed by purely advective processes. The continuous time random walk (CTRW) approach is a general model describing the outcome of motion represented as a random walk with a continuous distribution of travel times (Montroll and Weiss, 1965; Scher and Lax, 1973; Scher and Montroll, 1975; Margolin et al., 2003; Berkowitz et al., 2006; Boano et al., 2014). As described previously, random walks have long been used to represent mixing and transport processes (Einstein, 1905, 1906; Smoluchowski, 1916; Boano et al., 2014), and the classical ADE is the asymptotic outcome of a particular type of random walk (Brownian motion with drift) (Taylor, 1954; Fischer et al., 1979; Boano et al., 2014). Random walks provide a good description of transport in fluids because of the underlying thermally induced mixing motion of molecules in the fluid, and often adequately represent larger-scale fluid mixing processes, such as dispersion and turbulent diffusion. The solute transport in rivers (STIR) model provides a means to integrate individual process solutions into a comprehensive probabilistic framework through a multicompartment convolution method (Marion and Zaramella, 2005; Marion et al., 2008; Boano et al., 2014). An important factor to consider in this instance is the hyporheic exchange of fine suspended particles. This has primarily been studied in the laboratory but has recently been investigated in the field, and novel transport models for reach-scale particle dynamics are being

developed (Boano et al., 2014). Historically, removal of suspended particles from streams was assumed to occur only by gravitational settling, and particles without a considerable settling velocity were assumed to be composed of "wash load" that would be carried indefinitely in suspension and not interact with streambed sediment (Vanoni, 1975; Boano et al., 2014). These fine particles include colloids, normally described as particles with diameters of less than 10 µm and larger organic particles and flocs (10–100 µm) that have low settling velocity. Early models of hyporheic exchange of metals and nutrients engaging with a suspended particulate component also judged that particle deposition to the bed would be controlled by settling (e.g., Newbold et al., 2005; Kimball et al., 1994; Boano et al., 2014). Despite this assumption, Packman and Brooks (1995) and Huettel et al. (1996) independently determined that very fine suspended particles can be carried into bed sediments by advection and thereafter be deposited within pore space (Boano et al., 2014). Packman et al. (2000a, 2000b) devised a model for deposition of fine suspended particles driven by bedform-induced hyporheic exchange and demonstrated that it could be utilised for the deposition of clay particles in a sand bed (Boano et al., 2014). Several factors were involved in this model namely settling onto the streambed surface and settling and filtration within the hyporheic zone (Boano et al., 2014). Ren and Packman (2004) analysed the coupled hyporheic exchange of fine particles and sorbing solutes. This was based on an equilibrium nonlinear sorption model modelled on the Freundlich isotherm coupled with the advective pumping and particle filtration models. Over a long period of time, fine particle deposition in streambeds provides feedback on hyporheic exchange by accumulating within pore space and thus diminishing the porosity and permeability of the sediments (Brunke, 1999; Packman and MacKay, 2003; Boano et al., 2014). Thus the hyporheic zone is of importance to sediment in rivers. In the river Barlwyd the importance of groundwater is not negligible as the Harlech dome consists of bedrock, and there is no groundwater.

Many essential questions remain unanswered about the mechanisms of hyporheic exchange and how surface-groundwater interactions influence solute transport, microbial activity, and biogeochemical transformations at the scale of entire watersheds (Boano et al., 2014). The importance of stream-aquifer exchange for the ecological processes of fluvial ecosystems suggests that there is an

opportunity to preserve and restore channel properties that enhance exchange to improve the ecological status of streams (e.g., channel morphology, stream sinuosity, and sediment hydraulic conductivity) (Hester and Gooseff, 2010; Ward et al., 2011, O'Connor et al., 2010; Kasahara and Hill, 2007a, 2007b; Boulton, 2007; Lautz and Fanelli, 2008; Kasahara et al., 2009; Lawrence et al., 2013, Boano et al., 2014).

Many studies were performed to develop sediment quality guidelines (SQGs) (Burton, 2002; Di Toro et al., 1991), which were used as screening levels for regulatory action to prevent sediment contamination. In addition, some indices, factors and other approaches were developed to evaluate the chemical quality and biological toxicity of sediments. They included a pollution index (1982), an enrichment factor (Reimans and de Caritat, 2005), a geoaccumulation index (Chatterjee et al., 2007) and species sensitivity distributions (Leung et al., 2005) However, SQGs and other values mentioned above can neither quantify pollutants released into overlying waters nor assess the potential role of sediments in the deterioration of water quality. Several equations have been developed to estimate the transport of suspended solids and sediment particles in aquatic systems (White, 2008). However, these equations have not explained the movement of chemicals generated during the transport. More details on strategies for the monitoring and classification of sediments not only to improve and/or maintain their chemical and ecological status but also to provide information for the determination of control measures should be included in river basin management.

Chon et al. 2012 used a modified aquivalence mass balance approach which considered natural and anthropogenic influences on water bodies to estimate metal transport from sediments to overlying waters. The results showed that the aquivalence for surface sediments, was more susceptible to changes in parameter values than the aquivalence for water column (Chon et al., 2012). In particular, the sediment deposition and the sediment resuspension rates were parameters causing significant variations in surface sediments demonstrated that sediments could be significant sources of metal emissions in river catchments. In terms of further work Chon et al. (2012) states that sediment contribution needs to be assessed to provide data that could be used to develop control measures of

pollution in river catchments. This provides direct justification for the work that we carry out in this thesis.

Metals can persist in the sediments for a long period where they may be remobilised into the environment downstream (EA, 2008). Physicochemical reactions such as accumulation and sorption cause sedimentation of these substances to organic materials or suspended solids. Sediments are a separate potential source of metals. Metals are desorbed from sediments when the mineralogy of the water increases, when there is a decrease in redox potential, or when there is a decrease in pH (Foster and Charlesworth, 1998). Suspension initiates the release of entrapped soluble materials and oxidation of solid compounds in sediments (Foster and Charlesworth, 1998).

It is water chemistry which is responsible for the sorption and desorption of sediment. Adsorption releases the metals from the water column and stores them in the substrate (Evans, 2011). Desorption returns the metals to the water column where they are recirculated (Evans, 2011). When the minerality increases, there is a competition between metals and cations. Often water ions are outcompeted and are released into the water column. A reduction in redox potential which happens in water which is oxygen deprived, there is a change in the complexation of metals and the metal ions are released to the water. This acidic, metal rich water can have downstream effects a great distance from the original source. In some instances, metals may persist in high concentrations for a lengthy time, even in quarries which are closed (Evans, 2011; Merrington and Alloway,1994; Rösner, 1998; Parsons et al., 2001).

In terms of the type of sediment, in general sediment which is composed of sand and silt holds higher concentrations of metals in comparison to quartz feldspar and sediment which is abundant of carbonates (Perin et al., 1997). The effects of anoxic sediment resuspension on dissolved metal concentrations in river and sea water were studied by Simpson et al. (1998). It was shown that emission levels of dissolved Cu and Ni adsorbed to the surface of sulphides increases with a rise in resuspension time. It has also been demonstrated that sediments can chemically react with overlying waters releasing metals in solution (Eggleton and Thomas, 2004).

Mobilisation of heavy metals from sediments to the water column can occur via changes in pH. This can happen either by dissolving unstable metal compounds, precipitating heavy metals by the preferential absorption onto suspended particle surface, or through the creation of insoluble metal sulphides (Mwashote, 2003; Souza et al; 1986; Mohan, 1997; Kim et al., 1998). A summary of the processes involved in sediment chemistry exchange is summarised in a model in Figure 2.7. In terms of sediments there are several avenues of research direction that could be taken: (1) What happens to contaminants in undisturbed sediments not understood, (2) Kinetic processes that govern metal release during changes in redox potential need to be investigated further (3) there is limited data available on the release of organometallic compounds from sediments during re-suspension (4) the bioavailability is not well comprehended (Eggleton and Thomas, 2004).

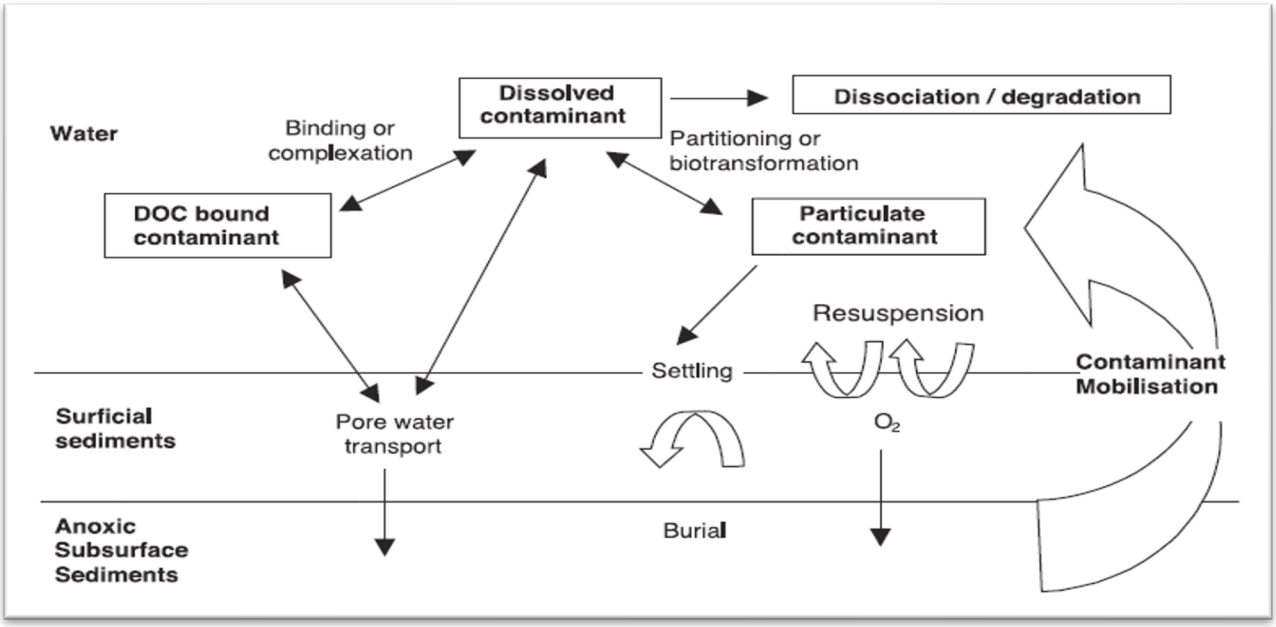


Figure 1.7 – Model of the processes involved in sediment exchange chemistry

(Eggleton and Thomas, 2004)

In terms of gaps in the literature, there is little research done which examines at the effect of the slate sediment created by the cutting process on water bodies. Further research could help determine the

mechanism and the degree to which slate sediment is toxic to water bodies, and help establish sediment quality guidelines, as well as source additional funding for remediating strategies.

1.8 Remediation of aquatic systems

Several remediation options have been explored in the literature already, including liming, bioremediation and phytoremediation as well as chemical remediation (Byrne et al., 2012). This research will focus on chemical remediation using biochar and the zerovalent ion FeO. The use of FeO and biochar and FeO have been extensively researched but not directly applied to this pollution source, or Al specifically (Gonçalves, 2016; Ahmad et al., 2014; Duwiejuah, 2020; Ullah et al., 2020). These are all to be used with a view to adsorbing metals.

1.8.1 Biochar

Biochar is a stable carbon rich by-product synthesised through pyrolysis/carbonisation of plant and animal biomass. It originates from Amerindian population in the Amazon region, where dark earth was created through slash and char techniques (Lehmann, 2009; Lehmann and Joseph, 2009). Biochar is known to be an excellent soil addition for soil fertility and sustainability. It has thus become renowned as a significant tool of environmental management. The precise definition of biochar is variable, but Lehman and Joseph (2009) define biochar as “a carbon rich product when biomass such as wood, manure or leaves is heated in a closed container with little or unavailable air" (Lehmann and Joseph, 2009). Biochar can also be defined by its end use. Biochar char use has diversified into several roles in terms of environmental management: (i) soil improvement (ii) waste management (iii) climate change mitigation and (iv) energy production.

1.8.1.1 Remediation of heavy metals with biochar

Studies examining heavy metal removal and advanced spectroscopic techniques have been applied to establish the absorption capacity and binding mechanisms in aqueous media (Ippolito et al., 2012).

Lima et al., (2010), looked at 8 different biochar's derived from broiler litter, alfalfa stems, switch grass, corn cobs, corn stover, guayule bagasse, guayule shrubs and soybean straw with their activated counterparts for their ability to adsorb Cu^{2+}, Cd^{2+}, Ni^{2+}+ and Zn^{2+} from water. They concluded activated biochars were the best metal adsorbents because they have a higher surface area and easy access to their functional groups. It was shown that Cu had a greater affinity to biochar's in comparison to other divalent metals. This could be because of the formation of surface complexes between Cu^{2+} and active functional groups (- COOH) and (–OH) on the biochar's (Tong et al., 2011) Further evidence gained from spectroscopic absorption predicted that Cu^{2+} sorption onto the biochar is pH dependent (Ippolito et al., 2012b). A conclusion was reached that Cu^{2+} is sorbed to the organic functional groups of biochar at pH 6 or &, Whereas azurite ($Ca_3(Co_3)_2(OH)_2$) and tenorite (CaO) precipitate within the biochar at pH 8 and 9 (Ippolito., 2012b). Another consideration is the atomic/ ionic size of the metal. In general, the smaller the ionic radius of the metal the greater the adsorption capacity due to the enhanced penetration into biochar pores (Ko et al., 2004; Ngah and Hanafiah, 2008).

The mechanism for ion exchange with regards to metals is explained in Figure 2.8. Lu et al. (2012). describes the mechanism for Pb^{2+} 1) metal exchange with K^{+} and Na^{+} which is principally due to the electrostatic outer-sphere complexation; (2) exchange with Ca^{+} and Mg^{2+}, for which o to co-precipitation and inner-sphere complexation with complexed humic matter and mineral oxides of SDBC is mainly responsible; (3) another mechanism is surface complexation with free carboxyl functional groups; (4) surface complexation with free hydroxyl functional groups, and (5) several other mechanisms which can include inner-sphere complexation with free hydroxyl groups of mineral oxides and other surface precipitation,

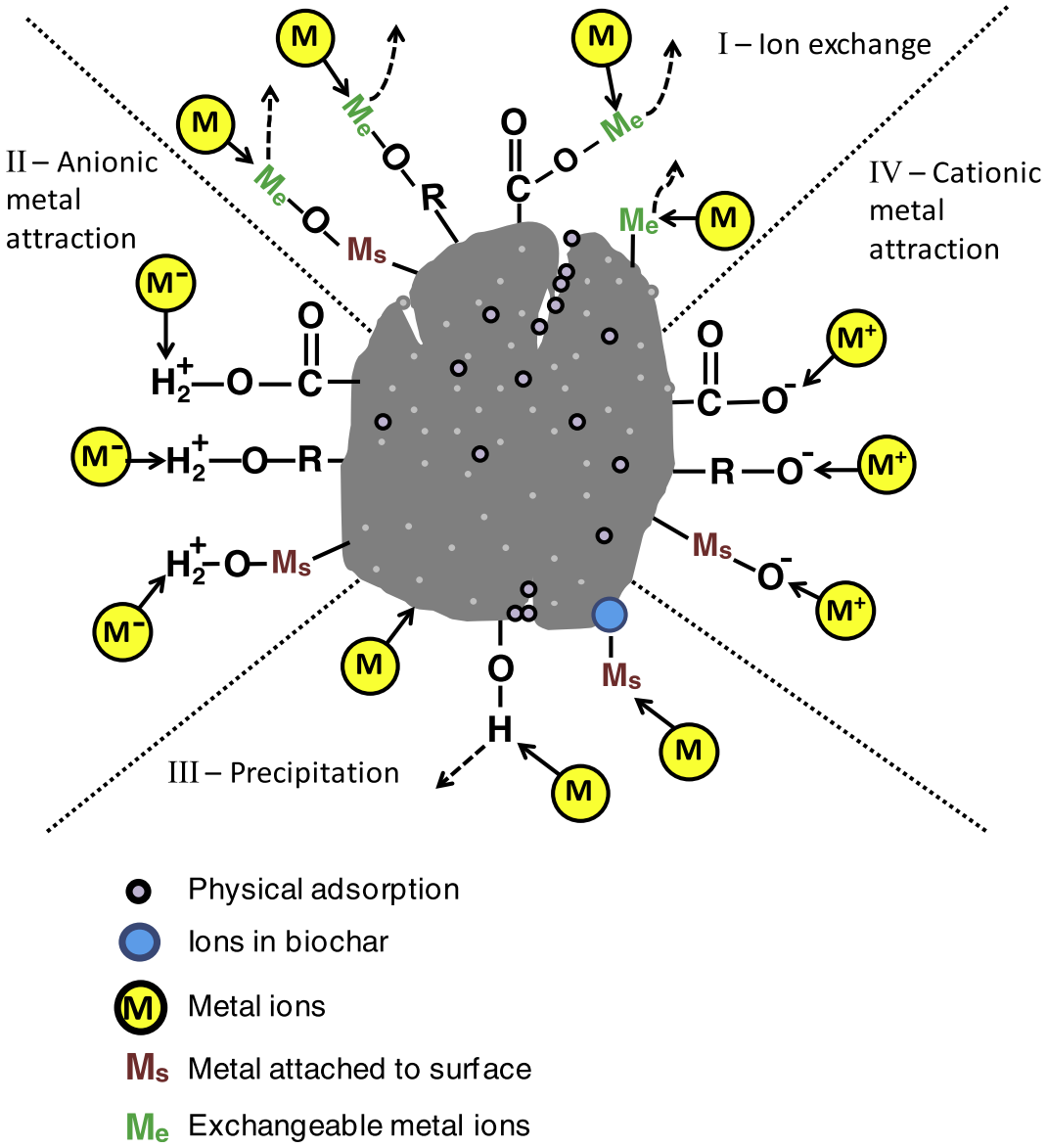


Figure 1.8 – Mechanism of metal binding to biochar (Smith et al., 2015)

Biochars can also be modified to enhance their adsorption efficiency. The method used by Yang and Jiang (2014) is amino modification. The adsorption capacity of the biochar and bed capacity are 5 and 8 times the pristine biochar respectively. XPS and ATRFIT showed there was high complexation after absorption as with compared to before amino modification and gives it high pH stability and ion selectivity.

1.8.2 Zerovalent iron

Heavy metal contamination is a major problem. As Cu is a metal which is toxic to life (Xu et al., 2012), and has a high tendency for bioaccumulation at relatively low concentrations. The removal of heavy metals by zerovalent ions has thus been an intense topic of research. Laboratory studies indicated that zerovalent iron could effectively remove a range of heavy metals, including Pb^{2+}, Hg^{2+}, Cd^{2+}, Cu^{2+} (Xu et al., 2012).

When zerovalent ion Fe^{O} is placed in aqueous media it is oxidised to Fe^{2+}(fast process), and Fe^{2+} (slower process). The preferred oxidant in natural waters is dissolved oxygen. The presence of dissolved oxygen leads to rapid corrosion and can be represented by equation (1). Consequently Fe^{2+} may be oxidised to Fe^{3+} by dissolved O_2. The H_2O_2 created can be reduced to water by an additional two-electron transfer from ZVI (Eq. (2)). Moreover, the combination of H_2O_2 and Fe^{2+} (known as Fenton reaction) can produce hydroxyl radicals ($^{\bullet}OH$) which possess strong oxidizing capability towards a variety of organic compounds (Eq. (3)). Under anaerobic conditions corrosion could also happen by utilising water as an oxidant and creating molecular hydrogen (Tosco et al., 2014).

$Fe^{o} + O_2 + 2H^{+} \longrightarrow Fe^{2+} + H_2O_2$ (1)

$Fe^{O} + H_2O_2 + 2H^{+} \longrightarrow Fe^{2+} + 2H_2O$ (2)

$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + {}^{*}OH + OH^{-}$ (3)

pH has a strong effect on redox reactions happening at the surface of the ZVI (Zerovalent iron) surface by accelerating corrosion at low pH and passivating the surface of the iron at high pH by formation of iron hydroxides (O'Carroll et al., 2013). The release of OH- ions in solution is enabled by oxidation, which consequently increases the pH of the system (>8.0) (O'Carroll et al., 2013). The effect of pH on metal removal by nZVI depends on the oxidation state of the metal and the removal mechanism. Passivation of the nZVI surface at high pH hinders electron transfer from the Fe^{o} core

thus diminishing the removal of metal contaminants by reductive precipitation (O'Carroll et al., 2013). It was shown that Se^{VI} removal by nZVI decreased from 91% to 11% with increase from pH from 3.5 to 11 (Mondal et al., 2004). Some metals are immobilised via precipitation by hydrolysing as metal hydroxides at high pH (e.g. Cd, Zn, Co, Cu.) More research is needed to study the effect of pH as metal removal by nZVI to determine the specific impact on each removal mechanisms is needed (Carroll *et al*., 2013). In the case of a combination of nZVI/ZVIAl, when the ratio of w/v ratio are lower (0.2-0.5 w/v), corrosion is favoured at a prevailing near neutral pH. Thus iron longevity/efficiency can differ for micro and nano-iron particles under the same field conditions (Han *et al*., 2016).

Zerovalent iron shell characteristics may be affected by pH. The extent to which pH affects the formation of the oxide layer is not fully understood. Liu and Lowry (2006) propose different Fe-oxides phases may exist on RNIP's (Reactive Nanoscale Iron Particles) at different pH's. However, Song and Carraway (2005) suggest that Fe^{BH} is less passivated than microscale nZVI as they observed a smaller effect of pH on the reaction rate constant for nanoscale nZVI than microscale nZVI.

In batch experiments used by Karabelli et al. (2008), in terms of Cu^{2+} specifically, Cu^{2+} has an E_0 which is much more positive than that of Fe^0 thus removal of metal ions is thought to be actualised by surface mediated reductive precipitation in comparison. The Cu^{2+} cations are only a little more electropositive than Fe^0. The removal is mainly realised via the adsorption with partial chemical reduction The findings of Karabelli et al. (2008) confirm the primary uptake mechanism is of redox type. The redox reactions, balanced by the standard redox method in acidic media, are represented below:

$$Fe^0 + Cu^{2+} \rightarrow Fe^{2+} + Cu^0$$

$$Fe^{2+} + 2Cu^{2+} + H_2O \rightarrow Fe + Cu_2O + 2H^+$$

Karabelli et al. (2008) conducted batch experiments under various conditions that indicated that nZVI

had fast kinetics and superior uptake ability toward Cu^{2+} ions over the range of concentrations 10.0-200.0 mg/L. The sorbent was seen underwent serious oxidation upon contact with aqueous solution. However, high removal capabilities were still obtained in repetitive applications at lower concentrations. XPS and XRD investigations suggested that Cu^{2+} is reduced to Cu^{+} (in the form of CuO) and, to a lesser 2 extent, to metallic Cu, Cu^{0}.

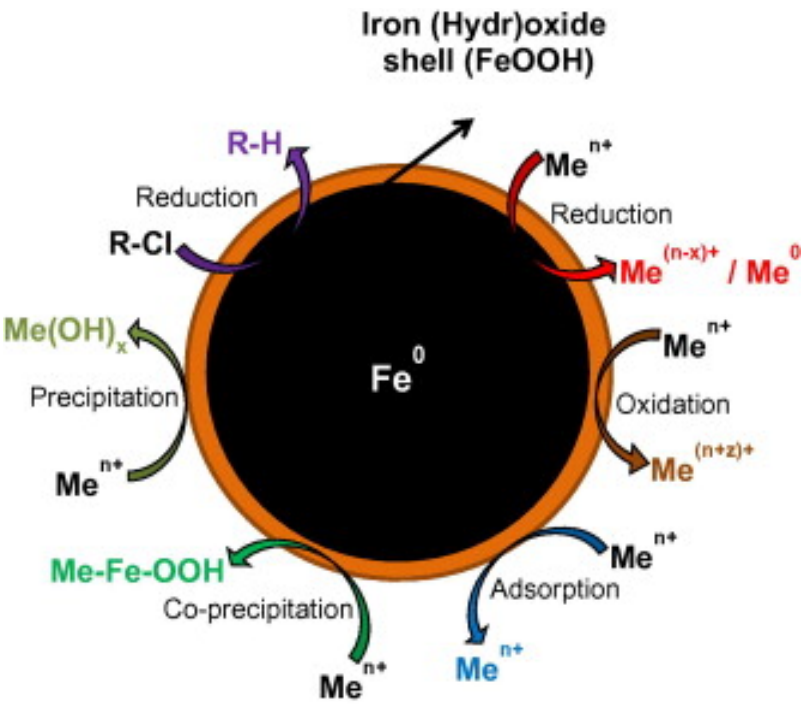


Figure 1.9 – Mechanisms of zerovalent iron exchange

(O'Caroll et al., 2013)

1.9 DOC and the biotic ligand model

The BLM (Biotic Ligand Model) consists of three primary components; thermodynamic speciation calculations which determine the equilibrium of dissolved species and complexed forms, the interaction of these species with the physiology of organisms, the uptake of metal by their partner biological receptors and metal toxicity (Smith et al., 2015). A further component is added in one case and that is the prediction of site-specific water quality criteria based on defined ecological or

toxicological effects (UESPA, 2007). This has been used by the US Environmental Protection Agency in the 2007 revised aquatic life ambient freshwater quality criteria for Cu. The BLM is a one metal one organism consideration. Ag, Ni, Pb and Zn are also available. There are many other BLMs under development, Niyogi and Wood (2004) describe 15 different BLM's. Cu is the most well developed (Di Torro et al., 2001; Santore et al., 2001). In this context i.e., mining sites there are several challenges in implementing the BLM at mined and mineralised sites (Smith et al., 2015). One of these challenges are historically incomplete datasets for BLM input parameters, especially DOC. Another point is that DOC fractionation is a concern in Fe and Al rich systems. In addition, DOC shows differences in quality that results in variations in metal binding affinities and resulting metal toxicity predictions that are temporally and spatially dependent. Additional influences on metal bioavailability such as multiple metal toxicity, dietary metal toxicity and competition among organisms or metals. Furthermore, a tolerance to metal toxicity has been observed for aquatic organisms living in areas with elevated metal concentrations.

In terms of Al toxicity (Kroglund et al., 2002) shows that Total Organic Carbon (TOC) can affect Al mobilisation and speciation. Increases in organic matter could lead to reductions in Al related toxicity but can also result in increased concentrations of cationic Al as total Al is increased and pH is reduced.

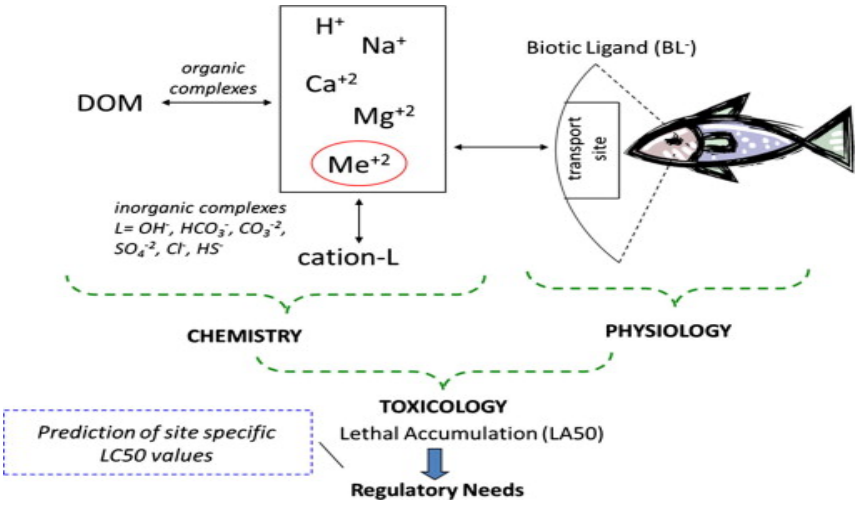


Figure 1.10 –The biotic ligand model (Smith et al., 2015)

Major cations such as CO_3 and SO_4 can out compete the metal for biotic ligands. Chemical conditions such as temperature, pH and concentration of cations and ligands can have an impact. Dissolved organic matter can be instrumental as it binds metals more strongly than the biotic ligand and inhibits metal binding with the biotic ligand or reaching the site of toxic action. Another important factor is the presence of metal sulphide complexes. In terms of compiling a biotic ligand model, the solution compositions are input and the organism of interest, the mode of operation is added, and the program checks that all input concentrations fall within the range for which the BLM has been calibrated. Of interest to this research, is that the model only considers dissolved equilibria and does not consider mineral precipitation or other interactions.

Total Al is an unsuitable way of describing Al toxicity. It is necessary to estimate Al speciation. Yet there has been no biotic ligand model formulated for Al owing to the difficulty of measuring Al and the complexity of Al speciation, and the availability of data sets such as DOC. This remains a gap in the literature and the addition of a DOC dataset will improve things generally.

1.10 Climate change

In the 2007 IPCC conference, there was a consensus among policy makers and scientists that human-induced global climate change is now occurring (IPCC, 2007). The magnitude of this climate change is unknown and is currently being predicted by climate models.

Increased river flows will increase sediment loads and may influence the morphology of rivers. The IPCC predict that in the effects of climate change will include drier summers and more intense and frequent storm periods during the winter (IPCC, 2015). This will have an impact on the levels of sediment transport and may potentially affect water quality and soil. Specific predictions about the effect on this on the biosphere have been made. It is anticipated that a rise in temperature will lead to a rise in river water temperatures (Jiminez Cisneros, 2014). River water temperature is a function of atmospheric temperature and is also affected by wind and solar radiation. An increase in air

temperature will not translate into a direct equivalent in water temperature, the increase will be slightly less (Kaczmarek et al., 1996). Although an increase in wastewater treatment in both developed and developing countries is expected in the future, point-source discharges of nutrients, heavy metals and organic substances will probably increase in developing countries (Bates et al., 2008). Flooding and heavy rainfall may cause contamination of water with chemicals, heavy metals or other hazardous substances, either from storage or from chemicals already in the environment (e.g., pesticides) (Bates et al., 2008). Moore et al. (1997) predict an increase in bioaccumulation due to water temperature increase in the New England/Mid-Atlantic region, possibly bio magnification, although the spring snowmelt period may be improved. It is also postulated that there may be an increase in rates of microbial degradation of toxins, reducing concentration in the environment. Predicted decreases of DOC may worsen toxicity of some metals by decreasing metal biding ligands, thereby increasing metal bioavailability. Furthermore DO (dissolved oxygen) is lower in warmer water. An increase in temperature will lead to a decrease in water quality in most water bodies by increasing oxygen consumption by biological activities and decreasing the saturation concentration of DO (Kramer, 1987). Fish expend energy on perfusion regarding oxygen uptake, this usually occurs with ventilation and locomotion (Kramer, 1987). It is seen that costs of these activities and predation risks vary with oxygen availability. Furthermore, the risk of predation, will change with oxygen availability and the type of behavioural response shown. The primary categories of biological activity affected would be (1) changes in activity, (2) increased use of air breathing, (3) increased use of aquatic surface respiration, and (4) vertical or horizontal habitat changes. To add to this increase in water temperatures may affect chemical reaction kinetics, which in turn will lead to deteriorations in water quality and ecological status (Kramer, 1987).

Recent research shows what may occur during storm conditions and during dry periods (Byrne et al., 2020; Foulds et al., 2014). Metals are shown to accumulate during dry periods in rivers (Dagenhart, 1980; Maest et al., 2004; Miller and Miller, 2007; Nordstrom, 2009), and then during the early part of storm periods there is a pronounced discharge of metals known as “first flush” (Younger and Blachare, 2004). This is often thought to be caused by the dissolution and flushing of soluble salts.

Nordstrom (2009) reviews acid rock drainage in the context of climate change. The underlying processes are thought to be pyrite oxidation and host rock dissolution. In the US the period for summers is lengthening (Nordstrom, 2009) and rainstorms are less frequent and more intense.

At Iron Mountain, California, the negative effects on the water quality of the Sacramento river were documented as long ago as 1905 (Haywood, 1905). The effect of Cu toxicity on anadromous fish from the Sacramento river was observed, and "Freshets" or rapid flushing events from rainstorms, were postulated to be the principal reason behind large fish mortality, which was estimated at around 100,000 fish per storm event.

The 'first flush' is a phenomenon which has been recorded by several researchers. Durum (1953) showed that there was a rise in the levels of chloride after spring snowmelt in the Saline River, Kansas which was due to the dissolution of salts found along the riverbanks. Hendrickson and Krieger (1960, 1964) found annual increases in sulphate concentrations for some springs in Kentucky that were thought to be caused by increased recharge dissolving sulphate salts such as gypsum. Gunnerson (1967) realised that there were seasonal changes in solute concentration associated with flow for the Columbia river basin. A seasonal increase in flow showed flushing of salts. In weekly sampling campaigns Edwards (1973) found that nitrate, sulphate, sodium, potassium and chloride concentrations frequently increased with increasing discharge especially at the start of the autumn wet season. This is owing to the accumulation of soluble weathering products being flushed from the soil. This has been called the 'flushing effect' by many authors. (Edwards, 1973; Walling, 1974; Walling and Foster, 1975; Kennedy, 1971, 1978).

Following a review of data at three different mine sites; Iron mountain, CA, Contrary Creek, VA, and Questa NM all in the US, Nordstrom (2009), conclude that although the mechanisms of metal transport during snowmelt, dry spells and rainstorm events are not clear, (1) that trends show a sudden rise in the concentration of acid and metals during the rising limb of the discharge for early rainstorms in the wet season. (2) long term patterns show that metal concentrations of acid drainage rise during

dry periods in the summer (3) that these trends are predicted to be augmented with the estimated trends in weather patterns of climate change for the western US.

Recent data in Wales from the 2012 floods suggests that flooding can significantly increase the number of metals found in soils. Foulds et al. (2014) showed higher concentrations of Pb in flood sediments - up to x 82 higher which led to cattle death on the floodplain (Foulds et al., 2014). A geomorphological approach was needed to understand the metal flux in these fluvial systems.

Data from the Barlwyd river from previous MSc projects shows an increase in both pH and dissolved metals in the quarry outlets, and diffuse pollution was found at another site thought to be affected by slate tips. Evans (2011) found the pH to be as low as 4.73 and 4.32 for certain parts. This study also showed the effect of storms on the Barlwyd river. pH was found to decrease and showed an anticlockwise pattern of hysteresis. This was also a pattern observed by Nordstrom (2009). This is thought to be because the storm water washes through slate piles and hydrological processes cause the dissolution of soluble minerals. Turbidity was found to increase during storms from 12.13 NTU to 81.2 NTU in the Llechwedd site. This is due to water washing fine slate sediments. Turbidity decreased after peak levels possibly owing to the depletion of fine materials (Williams, 1989). Or as Wood (1977) suggests, it could be material that was deposited during a previous storm which is then remobilised during a second storm. Furthermore, Wood's research (1977) shows that turbidity has a clockwise hysteresis and metal concentrations increase during storms. The increase in runoff means an increase in hydrological processes which results in more acidic conditions. Acidic conditions in the river increase competition for binding sites between metals and hydrogen ions and dissolve metal ions in the water column (Foster and Charlesworth, 1998).

Climate change has also been shown to affect sediment. Climate change affects the extent to which sediments are resuspended and directly exposed in water bodies (Chon et al., 2012; White, 2008; Taylor and Owens, 2009). There has been much research on sediment water interactions using tracers

(Guan et al., 2017). However, the quantification between the exchange between water and sediments in the context of slate mining remains unresearched.

1.11 Hysteresis patterns, discharge, and turbidity

Climate change is established as an important aspect of storm hydrology and metals. Blake et al. (2003) discovered that during a storm period its uncommon for metals concentrations and discharge to correlate with one another directly. It can be seen on occasion that there is a delay between metal concentrations and high discharge, thus the transfer of metals into the main channel is non-coinciding. One can study the relationship by looking at the relationship during a hydrologically significant storm by analysing and comparing the values of discharge and concentrations over time. Differences are seen between the ascending and descending limb. The relationship can then be clarified between discharge and metal concentrations. Hysteresis is defined by five different classifications: a single valued line, clockwise loop, a counter-clockwise loop, a single-valued line with a loop, and a figure of eight (Williams, 1989; Evans 2011). Metal concentrations during storm flow is a complex process (Blake et al., 2003). There is often a complicated relationship between pH, turbidity, metal concentration and discharge during high flow. Blake et al., (2003) emphasise this during a storm period.

As an important focus of storm sampling is the hysteresis relationship between discharge/concentration. The simplest form of hysteresis is single-valued (Evans, 2011). This in simple terms means that the ascending arm is equal to the descending arm for discharges of the same value. This rule usually follows when there is a constant supply of material throughout a storm period (Wood, 1977; Evans, 2011). The supply of material can range from being torrential to very low.

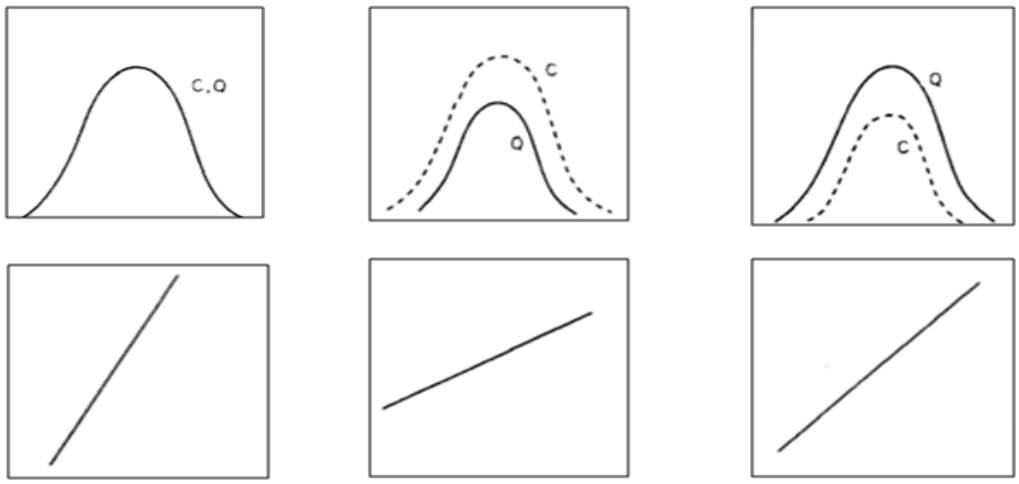


Figure 1.11 – Single-valued hysteresis where concentrations and discharge are coincident

The top diagrams compare the levels of discharge (Q) and Concentration (C) during a storm. The bottom diagrams reflect the hysteresis relationships which are created. (Williams, 1989).

If the peak concentrations precede peak discharge, and the concentrations on the ascending limb as compared to the descending limb are higher the relationship is described as a clockwise relationship. Graphically it could be shown that the values on the ascending limb are relatively high, but the values on the descending limb are much lower. Peart and Walling (1988) state that this is the commonest form of hysteresis between concentrations and discharge during a storm. This is like a flush phenomenon where the material is likely to be flushed out of a catchment early in the storm (Evans, 2011). This means the raw material is transferred to the river whilst the discharge is increasing (Evans, 2011). Clockwise hysteresis is more common at the beginning of a storm (Sidle and Campbell, 1985). There is a conflict in the literature about what causes this. On one hand, Doty and Carter (1965) claim that the clockwise hysteresis shows that the material decreases because of hydrological processes, whereas Novotny (1980) suggests that the decrease in rainfall levels in the storm retreat means there is less polluted material carried into the water channel.

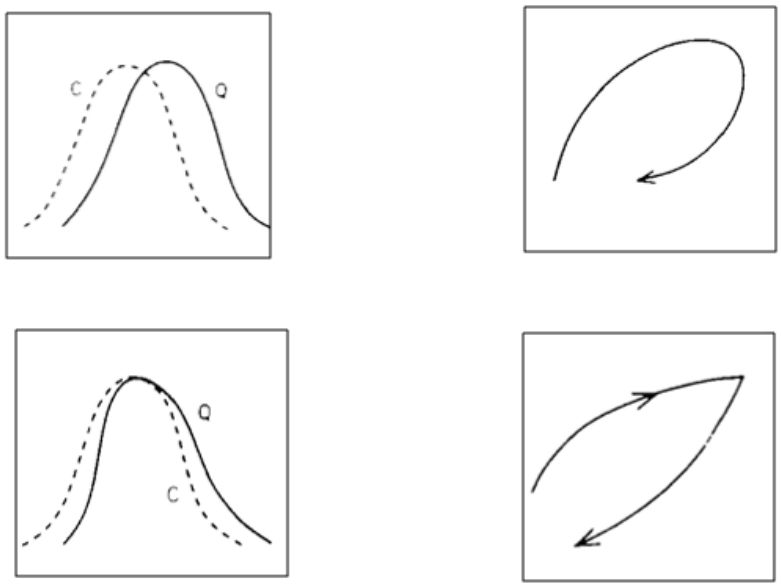


Figure 1.12 – Clockwise hysteresis where peak levels of concentration (C) precede peak levels of discharge (Q) (Williams, 1989)

Clockwise hysteresis can mean that its hydrological and physical processes on the surface of the earth which are responsible for the higher concentrations in the river system. Hysteresis circles are used to denote erosion processes of water as well as sources of pollutant material in the river basin (Seeger et al., 2004). This effect can be explained by a vacuum in the sediment supply locally before discharge levels peak (Slattery et al., 2002; Lefrançois et al., 2007). In contrast Steegan et al. (2000) suggests that the process does not denote a vacuum and exhaustion of sources of pollutant material, but instead is connected to sources of materials from higher slopes which are further away, and that this is the notable feature of the effect of the clockwise (Klein, 1984; Goodwin et al., 2003; Evans, 2011). Additional analysis includes a higher incidence of rain at the beginning of a storm which means a lower level of erosive force at the beginning of the storms and inputs into the main channel after the discharge has peaked (Wood, 1977; Baca, 2002; Evans 2011). Therefore, Rodríguez-Blanco (2009) states that analyses of hysteresis loops are not a reliable way of recognising the source of materials. It is requisite thus to come across exact information about the different sources of sediment sources and erosion processes in the catchment of the river basin (Evans, 2011).

In some cases, the peak discharge precedes the concentration peak. This is known as counter-clockwise hysteresis. Graphically, the data on the descending limb will be lower than the ascending limb. This is a very common hysteresis (Heidel, 1956; Evans, 2011). It is explained if the pollutant source is far from the monitoring station, thus the time it takes to transport the material is much longer. This pause increases further along the river especially in unusual rivers where there is a variety of influences stopping the movement of materials. Lakes are a good example of this. Axelsson (1967) shows that there was a delay of some days in peak levels of turbidity in the river Rapaalven, Sweden, due to the influence of the Laitaure lake. This relationship could also be because of increasing erosion during the storm period. After studying several small rivers in Huang He, China, Kung and Chiang (1977) discovered that heavy rainfall during a storm leads to erosion of particulate material after peak levels of water have peaked, which means that peak levels of turbidity are seen later. The relationship between concentrations of heavy metals and discharge during periods of heavy flow were studied by Zonta et al. (2005) on the bay of the river Dese, the main input to the lagoon in Venice. The study aimed to look at the effect of flow on the chemical attributes of the water column in addition to the transport of polluted particles and pollutants into the basin of the river. The study was based on uninterrupted water records of discharge and measurements of the chemistry of the water across the vertical section. The water samples were collected to analyse the concentrations of heavy metals (As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Zn). The study shows that discharge and concentrations of heavy metals increase at the same time and that the hysteresis between discharge and concentration is counter-clockwise. An increase is seen in the concentrations of Fe, Cu, Pb, Ni and Zn.

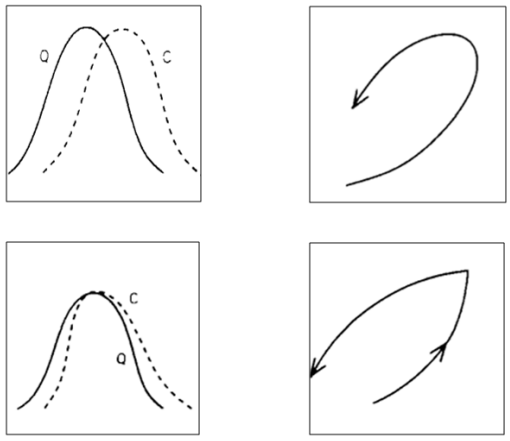


Figure 1.13 – Counter-clockwise hysteresis where peak levels of discharge (Q) precede peak concentrations (C) (Williams, 1989)

There can also be a single valued and loop hysteresis (Williams, 1989) (Figure 2.4**)**. This hysteresis combines all three, hysteresis. The factors which create this are thus equal to the factors which cause those classifications. The single line on the low discharges at the start and end of the hydrograph denote that the concentrations vary according to discharge.

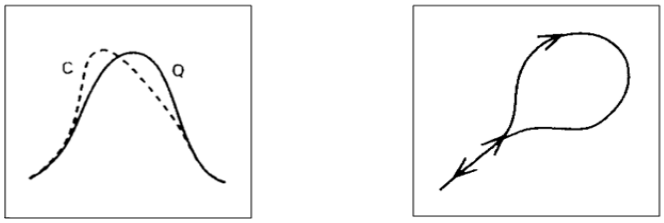


Figure 1.14 – Single valued line and loop where concentrations (C) and discharge are uncoincidental. The loop on the higher discharges means that levels of metals and discharge do not coincide in the middle of the hydrograph (Williams, 1989).

The peak levels of concentrations are seen before or after the peak levels of concentration. The availability of particulate material and pollutants in the supply medium, and the ability of the river to transport material influence the concentration peak timing (D'Agostino et al., 1994).

The last type of hysteresis relationship is described as the figure of eight. This relationship combines elements of the clockwise loop and the counter-clockwise loop (Williams, 1989). In this instance, the two ascending arms commence at the same time. But the concentrations increase on a much higher scale than the discharge, thus it peaks first. This produces the expected clockwise loop expected; thus, it peaks first. This creates the clockwise loop expected but only on the highest discharges. The availability of after peak levels is high enough so that concentrations diminish at a slow rate with time as compared with discharge. This means that the comparison of concentrations/discharge for a specific discharge is higher for the ascending arm with comparison to the descending arm. This hysteresis is given relatively little attention in the literature. Despite this the relationship is recorded by Bobrovitskaya (1967) and Arnborg et al. (1967).

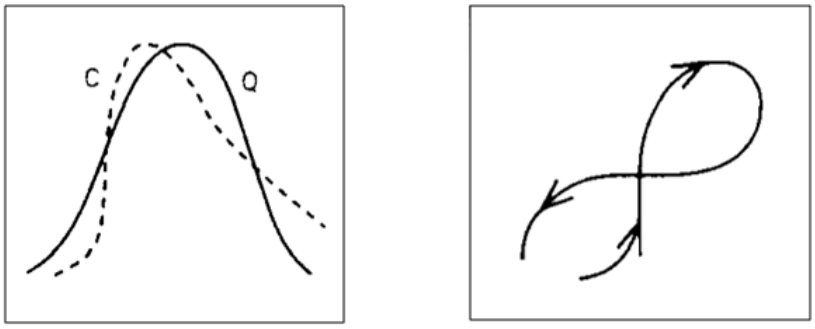


Figure 1.15 – Figure of 8 hysteresis

This hysteresis combines a clockwise figure of 8 and the anticlockwise hysteresis (Williams, 1989).

Thus, the relationship between discharge and concentrations of metals and turbidity is a complicated one. These include the density of rainfall along the basin, rate and density of water. It is problematic according to some that recognising supplies of sediment according to their sediment source is problematic. This is because different processes can lead to similar hysteresis loops. It is a gap in research that an appropriate relationship is established between pollutant supplies and a spatial distribution along the river. This would make analysis of the pollutants/discharge much easier (Steegen et al., 2002; Evans et al., 2011).

The problem is complex in terms of remediation strategies. Quantification and investigation of the dynamics of pollution preclude remediation strategies. These include identification of the source of the problem, magnitude, and mechanics of the chemistry underlying the problem.

This thesis adds to existing knowledge on the effects of slate mining in terms of identifying the source of the problem, chemistry of water in the catchment and sedimentology of catchment. Looking to the future these are estimated according to climate change predictions made by the IPCC with regards to water temperatures.

Solutions will need to be a balance between social economic and environmental factors as defined by Brutland's model for sustainable development. The problem in this case is the balance between the economy and the environment where the cost of remediation is unsustainable for the slate mining business itself. Remediation efforts may thus necessitate a source of governmental funding once the problem has been analysed. The main solution currently is integrated water resource management, protecting water from contamination from household to global level.

1.12 Conclusions

Several knowledge gaps and research challenges are thus identified in this literature review:

- Firstly, there is a need to identify in the academic literature the impact of slate mining tips/sediment on water quality on a temporal and spatial scale. A long-term study quantifying the metals Al and Cu in the Barlwyd is recommended as they are the most prevalent and risk-ranked toxic metals.
- The importance of DOC needs to be established as there are no previous data sets in the river Barlwyd for this. There is identified a lack of data concerning DOC for models such as the BLM.
- Having identified the impact of climate change on rivers, temporal changes are significantly important areas for research, both on a long term and short-term scale. It is important to

evaluate the effects of extreme weather; storms and dry periods, which can be identified in a long-term study. It is therefore important to gather information on the rainfall and flow regimes.

- Storm hydrology is another key factor which will influence the Barlwyd and slate mines globally. An analysis of the presence/absence of a flushing effect would be of interest globally and specifically to the Barlwyd. Furthermore, the sources may be discovered in view of hysteresis patterns. This is of relevance to future climate change predictors.
- Sediment chemistry could be of high importance as it is postulated to be an aspect of mining that is hypothesised to cause metal pollution. A study could focus on the exchange of metals between the sediment and the water fraction and its contribution to pollution. This could lead to an improvement in sediment quality guidelines. A portion of this research could involve quantifying the metal content of the sediment and particle size.
- Lastly, remediation strategies using FeO, and biochar are investigated as potential options for ameliorating water quality and could be applied to the chemistry of this river, with removal of Al with FeO/Biochar being trialled for the first time. This could be of international significance and could be applied not only to improving river quality associated with slate mining, but also to other types of wastewater effluents rich in Cu/Al.

1.13 Research aims

Based on the conclusions from the literature review, the following research aims were decided upon:

- Chapter 3 – To establish if there is a relationship between water chemistry and slate quarrying across different streamflows.

- Chapter 4 – To study the storm-driven high discharge geochemical response of the river Barlwyd in terms of pollution.

- Chapter 5 – To quantify the sorption/desorption of the metals Al and Cu from sediment into the dissolved water fraction by estimating the relative contribution of sediment to the Al/Cu load in the river.

- Chapter 6 – To evaluate two methods of remediation, biochar and zerovalent iron on removal of Al/Cu from samples of slate quarrying affected river water.

CHAPTER 2 – STUDY SITE

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Figure 2.1 – General pictures of the study site

2.1 General

Over the last 150 years the River Barlwyd has been seriously affected by slate quarrying in the Goedol catchment (see Figures 2.1-2.3), although to date, there has been little research undertaken into the impact of this on water quality, and any attempts to remediate the problem are near non-existent. The origin of the River Barlwyd is situated in the north-east of Blaenau Ffestiniog at a height of approximately 425m above sea level. The river flows through two quarries: the Ffestiniog quarry to the west and the Llechwedd quarry to the east, crossing the A470 and flowing through Blaenau Ffestiniog, before joining the Goedol adjacent to the Tan-y-grisiau reservoir. There are two hydro-electric generation schemes running in the valley, namely on the Barlwyd and the Bowydd, and the water from the Barlwyd hydro runs into Pant-yr-afon. Water diverted from both the Barlwyd and Bowydd runs into an outlet lake and is released to generate energy via hydroelectric. Llyn Newydd and Llyn Bowydd have streams that run through the slate tips in Maen Offeren and later through the town. The river runs down a steep incline into before joining the River Goedol at grid reference SH695438. The rivers are then joined by the Afon Cynfal which flows from the east forming the River Dwyryd. The River Dwyryd ultimately joins the Irish sea in Porthmadog.

Figure 2.2 – Blaenau Ffestiniog view, it is evident by eye how much the catchment has been affected by quarrying

By User:Stemonitis - Self-photographed, CC BY-SA 2.5 [https://commons.wikimedia.org/w/index.php?curid=627734]

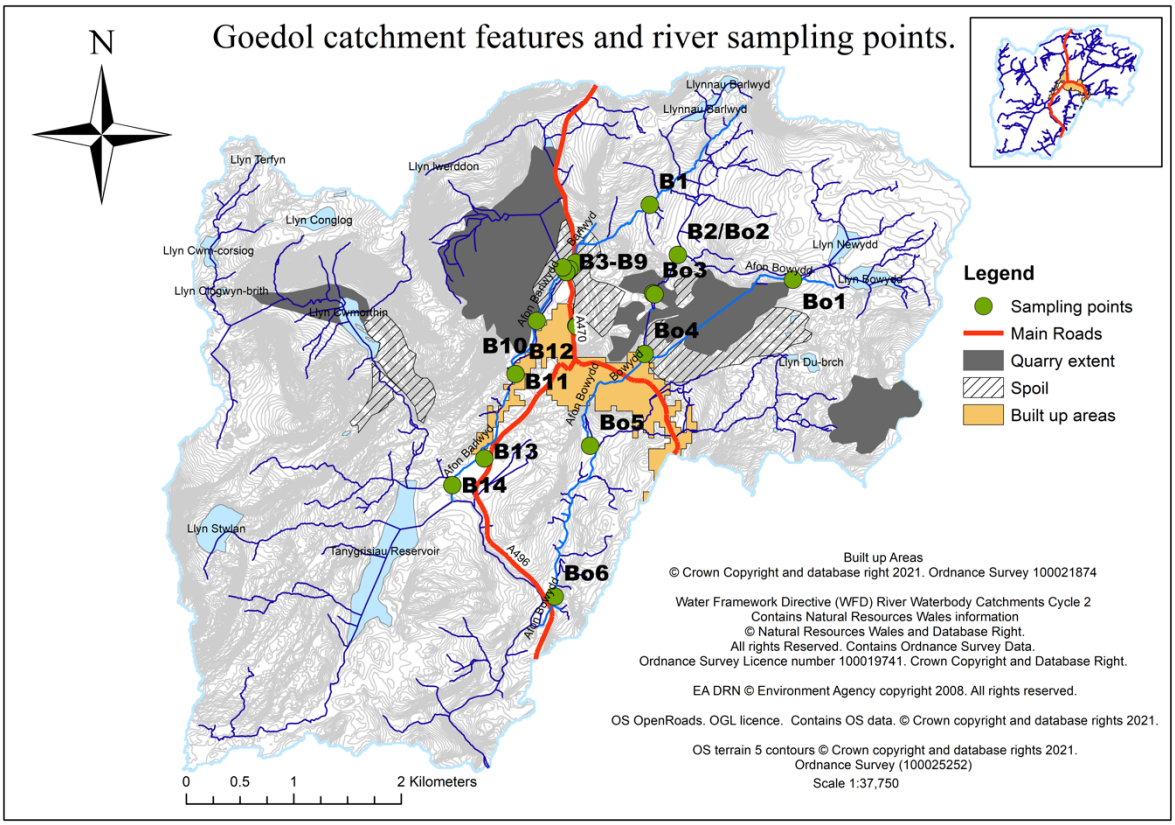


Figure 2.3 – Map showing the river Barlwyd/Bowydd rivers gradient, quarry/spoil, built up areas and main roads in the EWFD Goedol catchment.

2.2 General discharge conditions (range and mean flow)

There is no general flow data from the River Barlwyd. Estimates of total daily flow for rivers in the Barlwyd catchment are as follows: the Afon Goedol (SH 68912 42337), 1.90 m^3/s, Afon Cynfal (SH 68827 41523); 1.09 m^3/s, Afon Teigl (SH 69077 42284), - 0.795 m^3/s (NRW, 2020). Note that these are natural estimates and do not account for any artificial influences within the catchment (i.e., abstractions, discharges etc.).

2.3 Channel planform geomorphology

The channel planform geomorphology of the Barlwyd is of a sinuous river. Due to the high gradient at the source of the river and erosive potential of the river there are no bars in the channel form of the sampling site. The channel begins to widen substantially at Tan-y-grisiau Bridge where there is a substantial increase in flow as the catchment becomes larger. The bedrock is artificially modified, being terraced with slate at several points, but the bedrock further down is comprised of smaller coarse bed material. It is of a straight planform in the uplands. Further down where it joins the Dwyryd it becomes a meandering gravel bed river. This channel is active channel with a wide floodplain. As the gradient becomes gentler the erosive energy becomes less in the valley and it begins to deposit sediment. As the planform is altered in the upper reaches the riffles which are characteristic for forming spawning gravels for fish are altered, and the ground for supporting the invertebrates, especially the aquatic larval stage of insects is negatively impacted (Cordone and Kelley, 1961). Coarse sediment is generally found in the mountainous area, and finer better sorted sediment is found downstream in the Dwyryd. As there is a large amount of fine dust deposited in the Barlwyd, the pores between the gravels may become blocked with fine sediment and the river may become 'compacted' and the potential for spawning may be reduced (Kondolf, 2000). The diminishment in coarse particles which are often clustered together may result in an over loose bed

which may be unstable and form in an active reach where sediment transport may occur for a higher percentage of the time. Bars form lower down in the valley and form where the flow rate is lower.

2.4 Geology

The catchments of both the River Bowydd and Barlwyd end along the eastern and Northern sides of the Harlech Dome, a Caledonian fold that has a complex geological structure (Figures 2.4 -2.7). The dome is comprised of rocks from the Palaeozoic era (Matley and Wilson, 1946). The rocks which comprise the root of the dome are rocks of the Pre-Cambrian era, whilst the flanking rocks are a composition of volcanic rocks from the Ordovician era. The stratigraphy and Cambrian and Ordovician rock structure are a composition of four intrusive igneous rocks: Tan-y-grisiau microgranite microgranodiorite and quartz-latite, dolerite, with multiple intrusions including dolerites, diorites, quartz-latites and rhyolites, and the Tan-y-grisiau microgranite (Dewey and Eastwood, 1925; Dewey and Smith, 1922; Foster-Smith, 1977a, b). The dolerites occur as sills or sill-like bodies and are extensively altered. They are probably late Ordovician in age and are younger than the diorites (Lynas, 1973). The diorites, porphyritic, usually occur Cambrian rocks. Quartz-latites and rhyolites, however, form sills or large intrusive bodies within the Ordovician succession. The quartz-latites tend to intrude older rocks than do the rhyolites. Both types are commonly strongly auto brecciated. The diorites, quartz-latites and rhyolites are all quartz and calcite gangue on the Sarn Helen Fault. Affected by the regional cleavage recorded (Bromley, 1965; Evans, 2011). The surface geology is comprised of quartz latite, acid vitric tuff, and siltstone and mudstone.

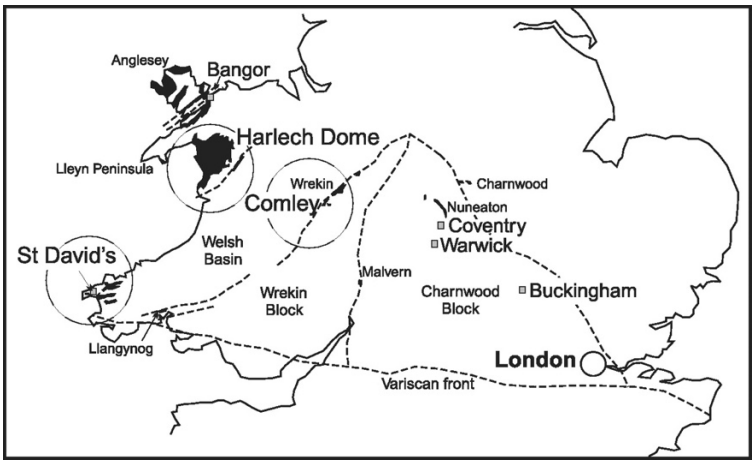


Figure 2.4 – Land map showing location of the Harlech dome (Waldron et al., 2011)

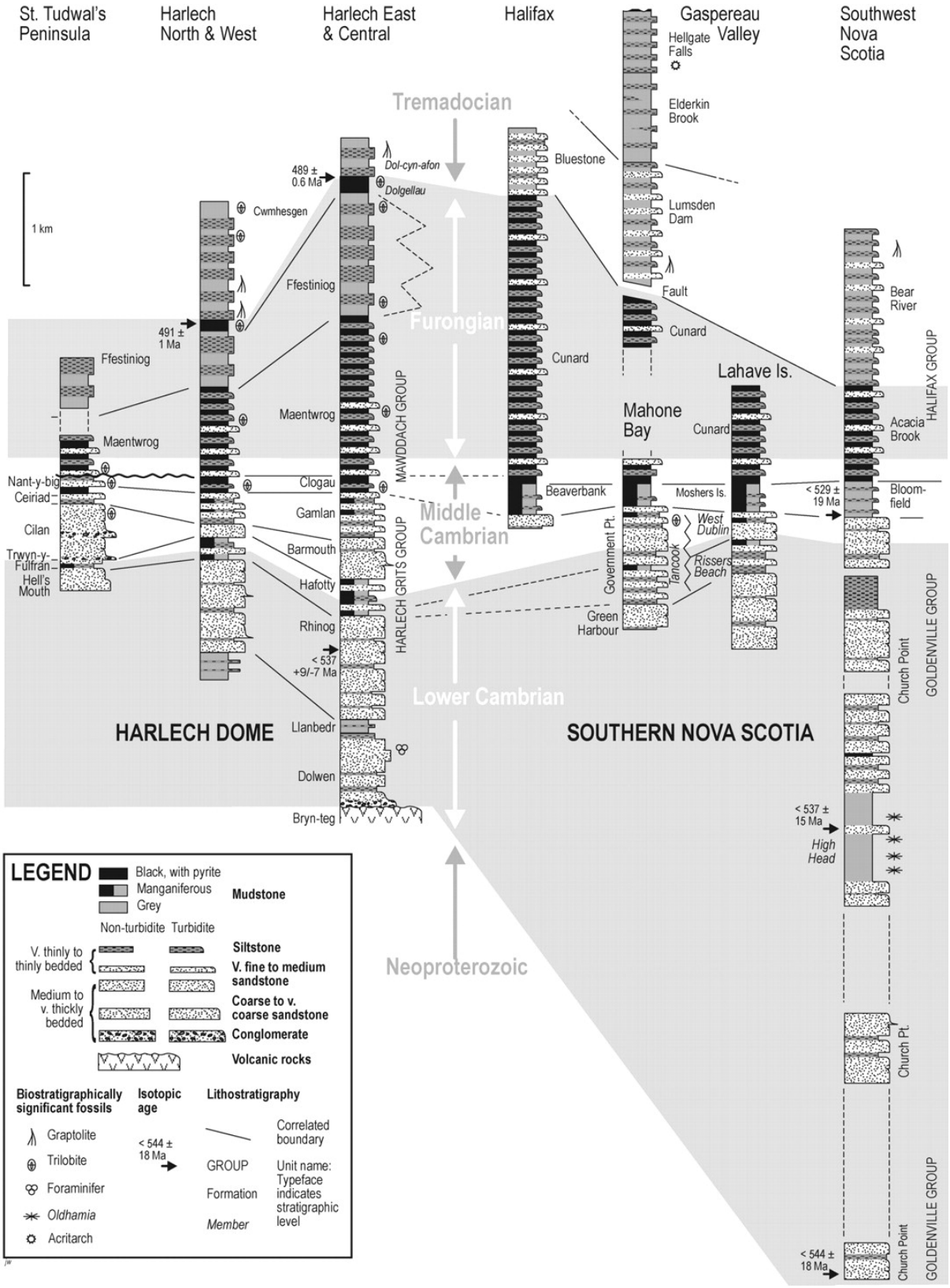
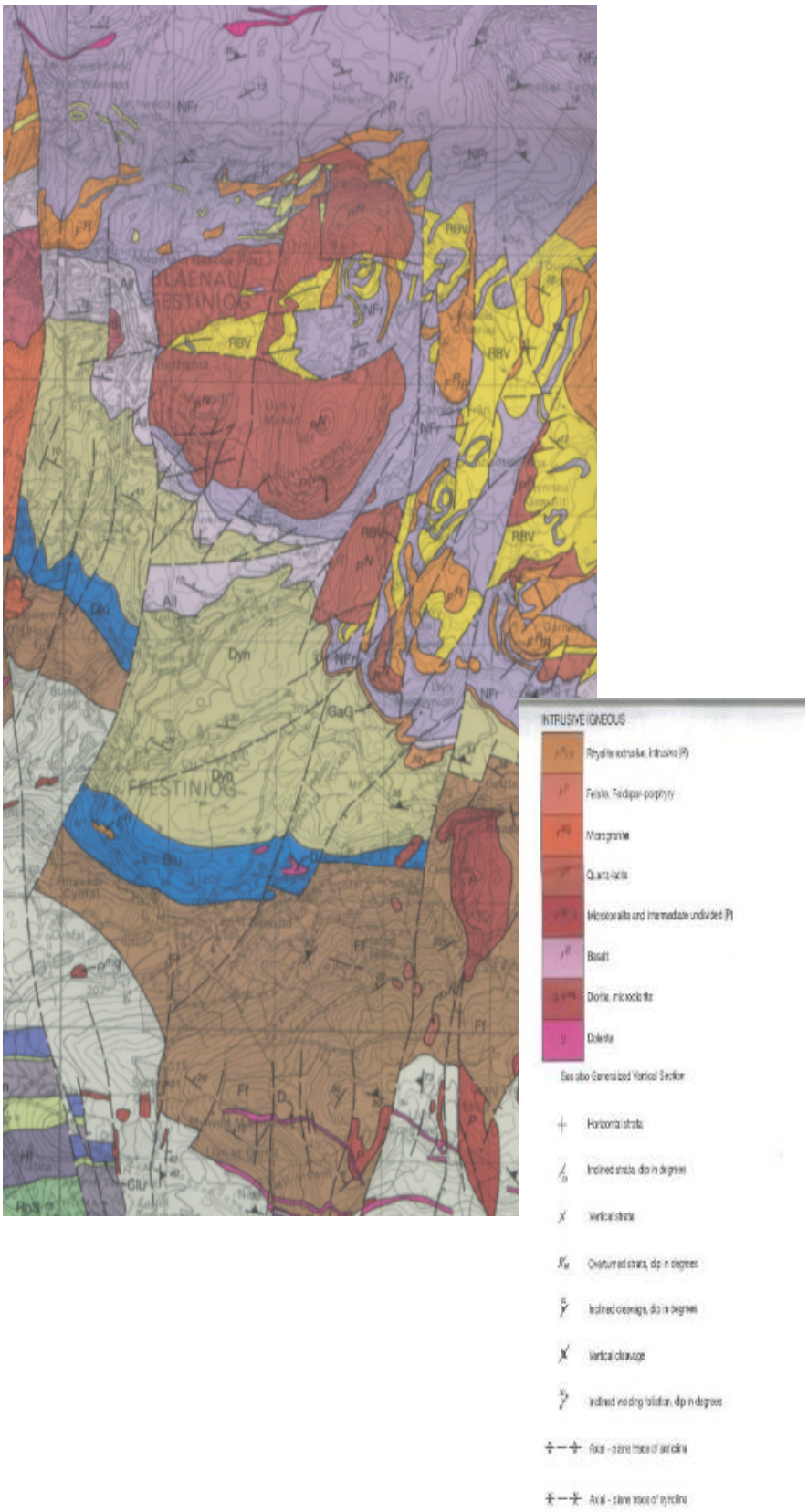


Figure 2.5 – Lithostragraphy of the Harlech dome (Waldron et al., 2011)



© Ordnance survey geological maps

Figure 2.6 – Surface geology for the Harlech dome

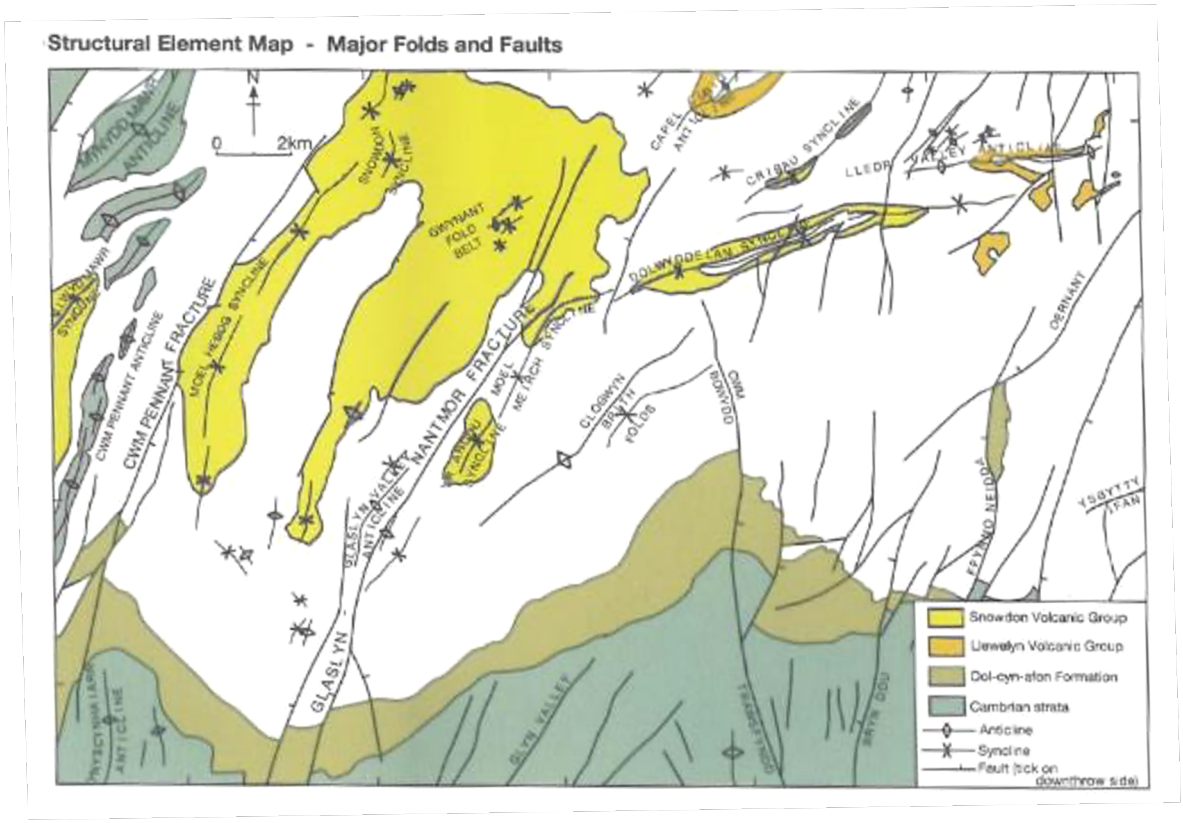


Figure 2.7 Structural element map – major folds and faults of the Harlech dome

2.5 Catchment topography and channel gradient

The upper reaches of the catchment for the river Barlwyd are characterised by mountainous terrain and steep slopes (see Figure 2.8). The lower reaches are characterised by a wide, yet deep valley. The catchment collects from the surrounding mountains which exceed 950m at the upstream extents of the

catchment. The river Barlwyd travels underground through the quarry and a tunnel and comes out at Pant-yr-afon in a waterfall, where the river becomes steeper.

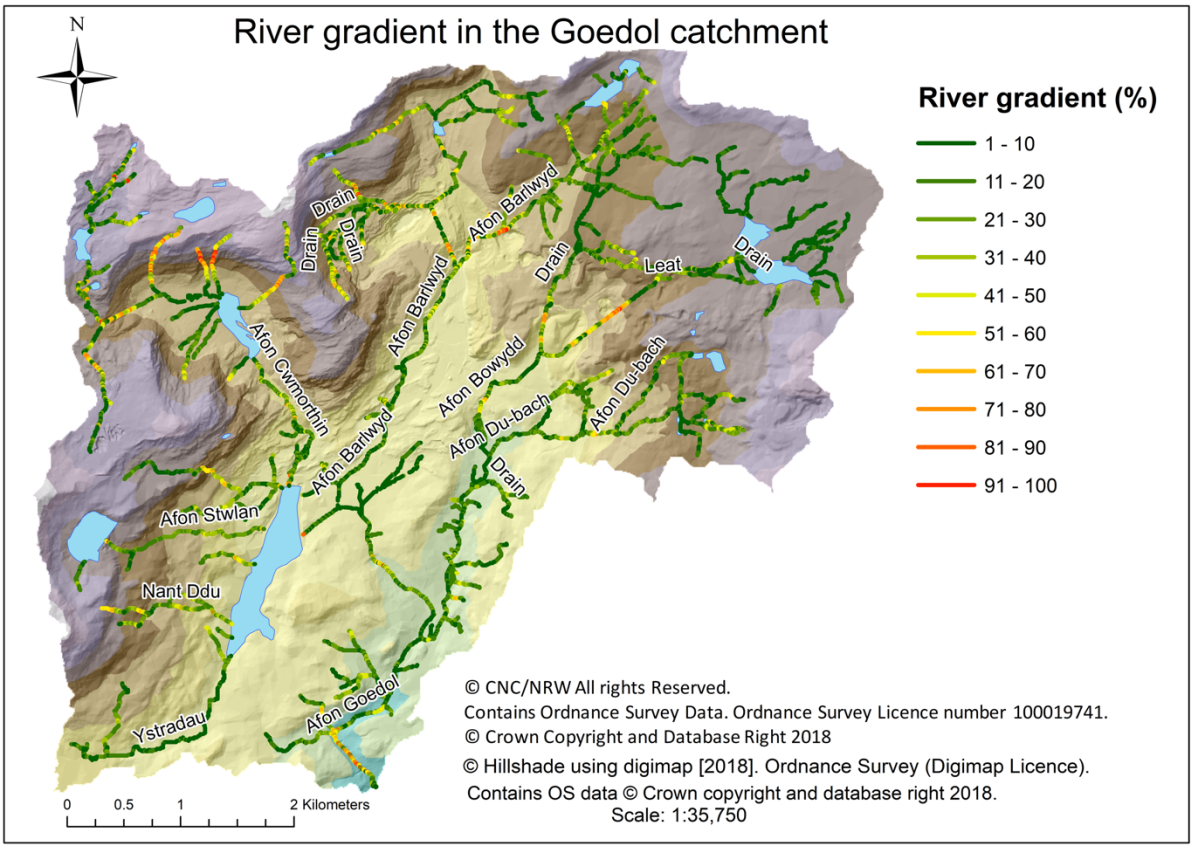


Figure 2.8 – Stream gradient for the Barlwyd and Bowydd.

In the upland part of the catchment the average annual rainfall is 2808 mm/year (1999-2018). Around the lower parts in Porthmadog on the Dwyryd this figure is much lower 1387.5 mm/year (1999-2019). The combination of abundant rainfall and rapid run off caused by topography and geology results in quick responses from the channels after heavy rainfall.

2.6 Sediment load

The River Barlwyd and other upstream tributaries contribute mostly fine particle dust from the quarry and a coarser bedload downstream. Many downstream tributaries produce coarser sediment, which is carried largely in the bedload (NRW, 2020).

2.7 History of study site

The earliest known use of slate was during the Roman period, for example in roof tiles at Segontium in Caernarfon, and at Roman forts at Caer Llugwy between Capel Curing and the Conwy valley. Slate was later used to roof the eight towers of Conwy castle also between 1283-87. Alongside an increase in the UK population from 8.8 million in 1801 to 29.9 million in 1881, the demand for slate roofing rose (Gwynedd Archives). Transport became easier along the canals, and the railways developed including private railways to the coast. This led to the development of ports like Porthmadog. The amount of slate carried from Ffestiniog to Porthmadog rose from 4,275 tons in 1836 to 12,426 tons in 1882 (Gwynedd Archives). A journalistic description described Ffestiniog in 1873 as 'a city of slate' with the mud on the roads even being 'a blue slaty colour' (Gwynedd Archives). The parish of Ffestiniog had a population of 11,274 in 1881 compared to only 732 in 1801. Further afield from Blaenau, there were additional quarries such as Nantlle, Dinorwic, and in Llanberis. and Bethesda (see Figure 2.9) (Gwynedd Archives).

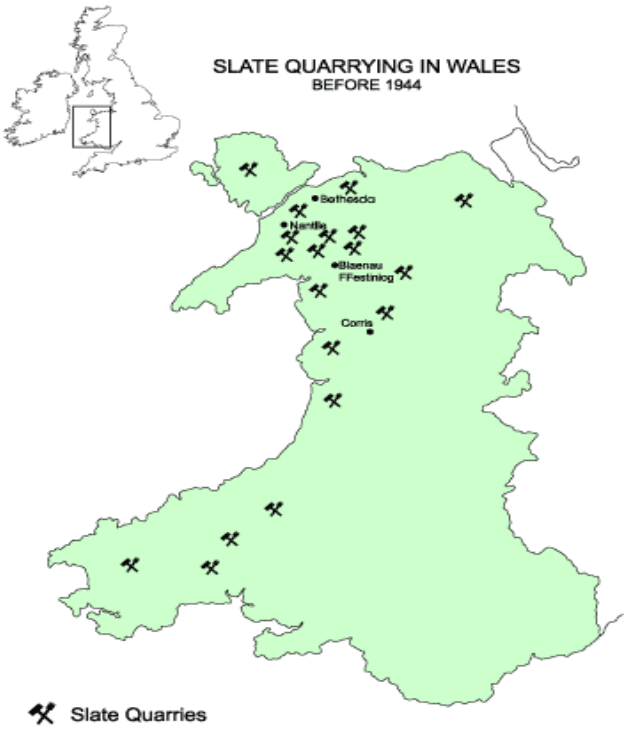


Figure 2.9 – Map of major slate quarries in Wales before 1944 (Gwynedd archives)

Several quarries were opened in and around Blaenau Ffestiniog including Bowydd, Foty, and Maenofferen, Llechwedd and Gloddfa Ganol/Oakley. A severe depression later led to reduced demand for slates in the 1880s, and prices did not rise again until the First World War. As shown in Figure 2.10 there was a dramatic decline in slate exports from 1889 and in 1918 the quantity of exported slates in general fell significantly from 79,912 tons to 1,592 tons. By 1906-08, Welsh slate was piling up at the quaysides at Porthmadog, Caernarfon and Felinheli.

The First World War brought about the closure of quarries, some going down to a three-day week and unemployment soaring. In 1917 slate quarrying was declared a non-essential industry. The production of slates in 1912 was 364,000 tons compared to 271,000 tons in 1935. Roofing tile production 1935 was estimated at 1,200,000 tons.

When the Second World War broke out in 1939 and there was strict control on new building work; demand for slate fell yet again. Around 4,600 men had left the industry by 1940, with a considerable

number of workers joining the armed forces. The diminishing number of employees reflects the speed of this decline. In 1939, there were 7,589. By 1945, there were 3,520, and by 1972 it was less than 1,000. Despite an order given by the British government that all slate produced could go to the repair of war-damaged houses, there was a lack of skilled labour, particularly rock men and miners.

Compared to cheaper roofing materials slate was expensive, thus poorer quality materials became more popular. Despite advances in machinery the decline in the industry has continued with very little production. In Blaenau Ffestiniog particularly, there has been a lack of slate to mine, with the blue vein resources exhausted. Production is currently based on the cutting of old slate already mined and not of new rock. Other sites in North Wales show a similar pattern.

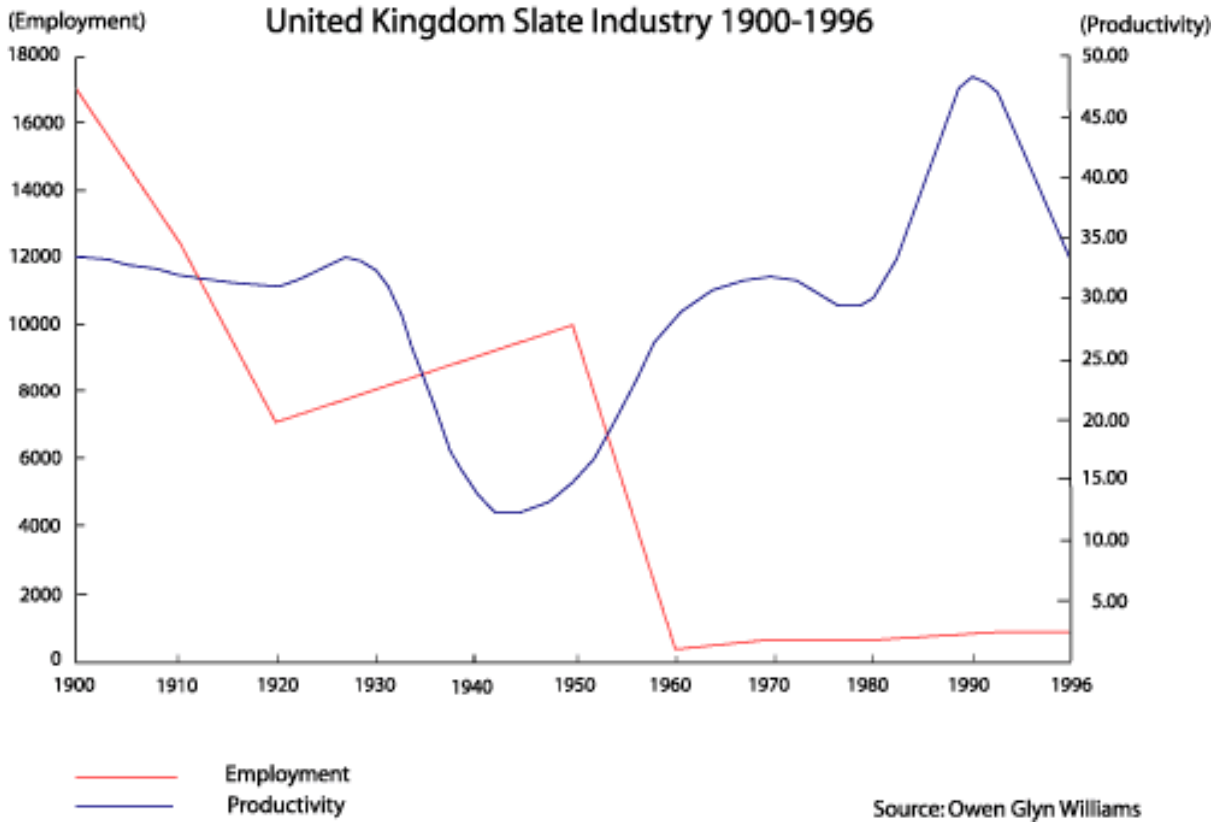


Figure 2.10 – Employment and productivity in Slate quarrying (Gwynedd archives)

2.8 Previous research on the river Barlwyd

Previous research on the river Barlwyd consists of data from Natural Resources Wales and MSc projects from Bangor University. In the first study in 1996, Natural Resources Wales sampled several streams in the quarry and further along the river (NRW, 1996). There were 21 sampling stations. The sampling was for 6 months over the winter and revealed higher levels of some metals than the standard British standard for sensitive aquatic life. Levels of Al were found to be higher in some points. In Gloddfa Ganol, for instance, the water was found to contain 0.133 mg/L of solubilised Al. In general Bray (1996) found all sampling points to be high in some form of metal. The pH was also found to be acidic in most cases. The worst point in terms of chemistry was found to be Llwyn-y-gell, having a detrimental effect on the river Barlwyd.

The data from an MSc project by Thomas (2010) shows a low pH, in some cases as low as 4.73 or 4.32 for some parts of the river. This pH is not consistent with NRW's guidelines for pH suitability for aquatic life of between 5 and 9. pH's as high as 6 have been reported to cause fish mortality, and this is the reason for the lack of wildlife in the Barlwyd (Barry et al., 2000).

Turbidity was not found to be a factor which affected wildlife in Evans's (2011) study with levels of turbidity being considerably lower than the upper limit for wildlife of 50 NTU. However, there was one reading of 81.2 next to site 2 in the study. In Pryce and Janes's (2009) opinion the effluents from the Llechwedd and Ffestiniog quarries contained a large quantity of fine material, which is mostly slate dust (Pryce and Janes, 2009).

An MSc project by Maleko (2010) examined the impact of slate quarrying on macro invertebrate communities. The study looked at three rivers, the Afon Barlwyd, Afon Ogwen, and the Afon Arddu as a control river. In the river Barlwyd ten sites were selected during June and July 2010, with three control sites upstream of the town and the quarries. BMWP scores were found to decrease from ca. 50 upstream of the quarries, to <5 downstream, these increased to ca.13 at the furthermost downstream

point. Chemical sampling by Maleko (2010) showed that the Afon Barlwyd had the highest observed pH (ca 6.68) but also the highest conductivity, turbidity Al concentration and sulphate concentration.

A thesis by Cutts (2010) examined the effects of suspended sediment on the biodiversity and chemical properties of the river. Cutts looked at three rivers for his study, the Afon Barlwyd, the river Arddu and the river Ogwen. Downstream of the quarries the river Barlwyd showed an increase in conductivity, metals, and sulphate. No relationship was found between the concentration of suspended solids and biodiversity indices of macro invertebrate samples.

The levels of heavy metals found in these instances were higher than recommended limits and this is interrelated to low pH. This is comparable to Aykol et al. (2003), who notes an increase in concentrations of pH next to sites which are in receipt of quarry discharges.

2.9 Reports on the river Barlwyd

2.9.1 Hydrological pathways

Looking at hydrological pathways indicates hydrological connections between a road drain the Llechwedd quarry and an unconsented discharge at Pant-yr-Afon and a culvert near the Llechwedd site was indicated as being connected to the Pant-yr-Afon discharge and the consented Llechwedd discharge.

Buss (2013) concludes in a report on the hydrological connectivity that it cannot be demonstrated that there is connection from Floor 7 to the Ael-y-Bryn stream. This conflicts with anecdotal reports that the pollution in the river Barlwyd began when the new cutting process began and suggests that the pollution is historic.

Buss (2013) suggests that the white suspended solids in Ael-y-Bryn that arise during rainfall are not slate dust. It is considered possible that this is an alumina/aluminosilicate precipitate that arises naturally from mixing rainwater with the high Al waters that perennially arise from the slate tip.

Previous research between 25th May and 2nd October 2012 indicates that approximately 1,800 kg was transported in the Ael-y-Bryn stream into the river Barlwyd. This equates to the discharge of approximately 5 tonnes of Al per year, from the dissolution of about 15 tonnes of slate from the tip. Cu was also calculated as 195 kg/year (Buss et al., 2013).

2.9.2 Dye Tracer reports

Bray reported that the Llechwedd quarry was having a 'clear deleterious effect on water quality in neighbouring water courses' and this included the River Barlwyd (Bray, 1996). Following this study an investigation was undertaken in 1996/1997.

The study looked at hydrological connections between the quarrying process and the slate dust laden effluent in the river Barlwyd. A rhodamine dye tracer test was carried out at locations high in slate dust. These tracer tests indicated a connection between these sources of slate dust. A similar connection was found between these sources and the Llwyn-y-Gell stream which enters the River Barlwyd further downstream of the site.

In the Llechwedd quarry, the main source of the pollution is thought to be at floor 7. Following the 1996/1997 study some pollution prevention was undertaken (RRC, 2009). Later studies by Bray (1998a and 1998b) showed that the connection between the sources at floor 7 and the Pant-yr-Afon remained.

In June 1998, a culvert was uncovered at the Llechwedd site, which was conveying water containing slate dust (RRC, 2009). Further dye tracer tests revealed that the culvert was hydrologically connected with unconsented discharges into the River Barlwyd at Pant-yr-Afon.

2.10 Land use around study site

The slate industry has formed the town of Blaenau Ffestiniog (Figure 2.11), without which, it may not have existed. Before the industrial revolution it was a remote, rural area. The industrial revolution brought about a transformation of the area into the Blaenau Ffestiniog that exists today. The tips of slate waste are a feature of the town, and the bustling industrial town centre of Blaenau Ffestiniog was one of the biggest towns in Meirionnydd. The agricultural centre remains in the area and the river flows adjacent to the industrial town on its journey to the sea.

The upper reaches are mainly acid grassland and bog, and heather, as shown in Figure 2.12. Reaches further down are surrounded by inland rock. There is a surrounding urban areas adjacent to the quarry. Downstream form this land use consists of heather grassland, improved grassland. The river Bowydd is then supported by broadleaved woodland and coniferous woodland.

© Google images 2017
Figure 2.11 – aerial photo of quarry from above

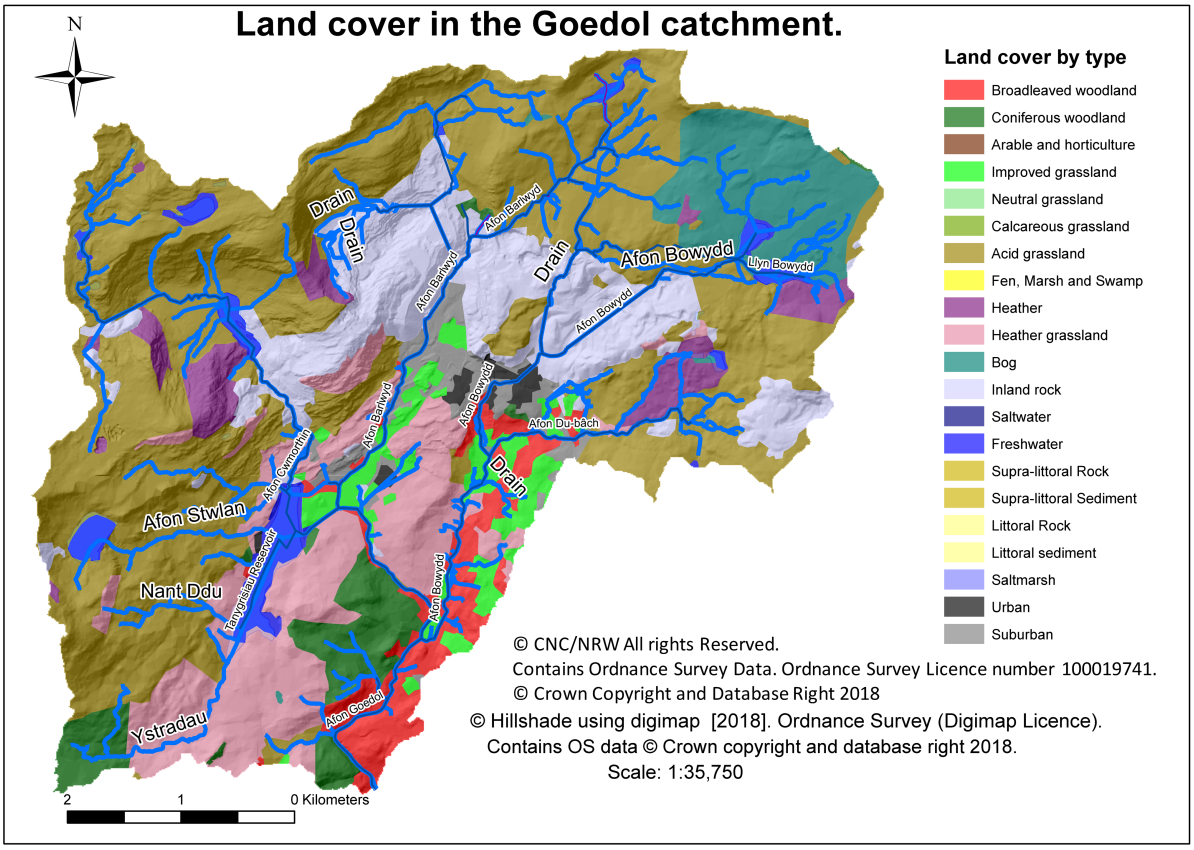


Figure 2.12 – The Goedol catchment and land cover types.

Land use around the quarry has altered significantly, with regards to recent developments at the quarry. Initially quarrying has been the focus, but as resources have declined, there has been a diversification to tourism as an industry with numerous outdoor adventure industries being promoted: Zip World – which claims to be the longest zipwire in the world, and the underground zipwire adventures that run through slate caverns; Bounce Below – an underground trampoline; a historic quarry tour, as well as 'Stiniog Adventures, which comprises a mountain bike track. The quarry also has used the rivers running through it to generate electricity by hydro power, with two hydroelectric existing on site. During the year of water sampling undertaken as part of the fieldwork for this research project, slate cutting was intermittent, with mainly old slate being cut during the summer of 2015, when the roads were used by the quarrying company and Zipworld, which led to the compacting of slate, creating fine dust that potentially could run off into the river following rainfall.

2.11 The river and its wildlife

The river has been terraced and straightened considerably because of quarrying activities; thus, the flow pathway of the river is not entirely natural. This may influence the fish life and macroinvertebrate diversity and abundance. It was previously reported that the Barlwyd lakes used to contain fish (Pryce and Janes, 2009), however the largest lake was emptied in 2003.

Figure 2.13– Pollution from slate quarrying as seen by eye

The slate tips around the quarry are particularly problematic. During heavy rainfall, runoff from the slate tips causes transport of metals into the river and peaty water from the mountains creates acidic conditions (Pryce and Janes, 2009; Evans, 2011). The tips have also left a lasting impact on the landscape, thereby being an aesthetic problem. Furthermore, the sediment created in the quarrying process affects wildlife, this can be seen by eye as a fine silt (Figure 3.13), which can affect spawning and DO in the river. In terms of NRW guidelines the load of dissolved Al should not be above 60 mg/L and the pH of the water should be between 5 and 9 (NRW, 2015).

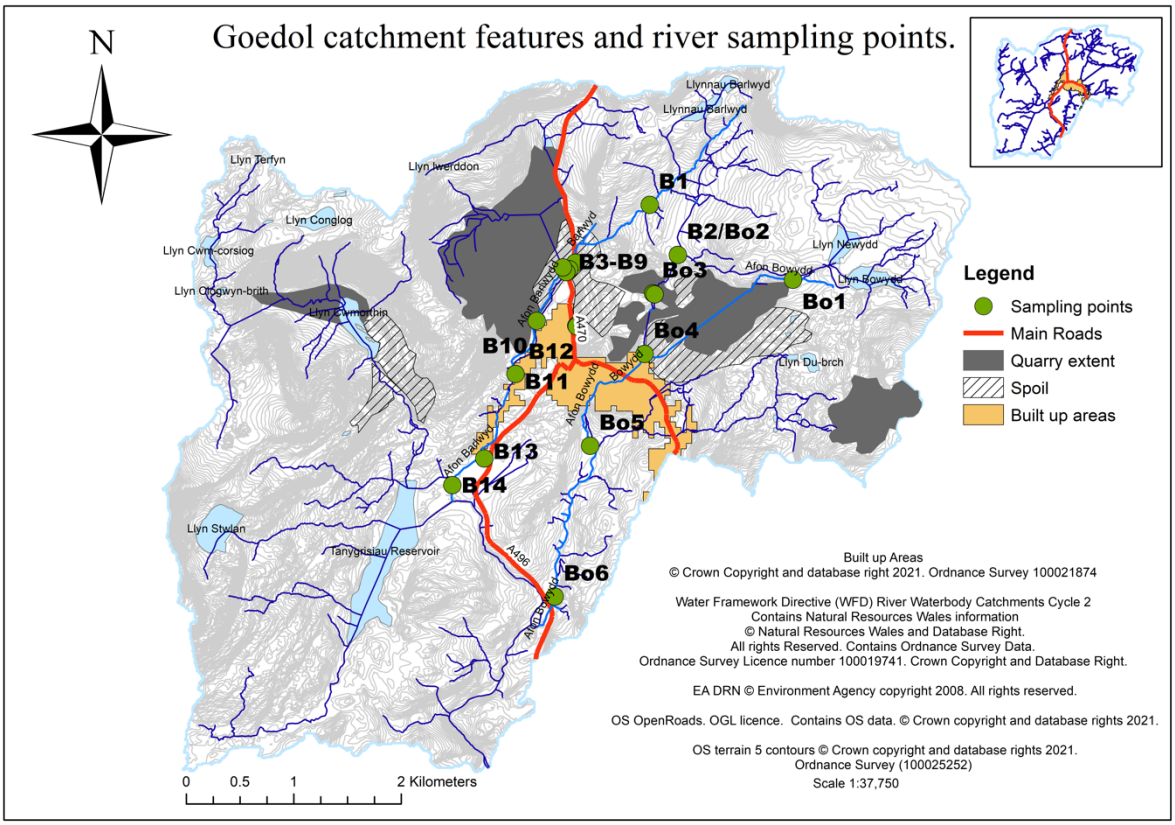


Figure 2.14 – OS map showing sites along the Barlwyd to the west (annotation = B) and Bowydd (annotated Bo)

2.12 Key point and diffuse pollution sources.

A key point source of pollution in the catchment is at site B4 in the Barlwyd (see Figure 2.14), where there is a consented discharge of water from the Llechwedd quarry. River water is used in the cutting process and then goes into a chambered settling tank, where sediment settles out before the water is then returned to the river at B4. This water is disposed in a downward shaft about 490m of length, which forms the discharge in Pant-yr-afon (SH6972 4688). B8 is another diffuse source of potential pollution, with rainwater coming from the A487 road and coming through a pipe to Pant-yr-afon but filtered from across the quarry. The final key point, B12- Ael-y-Bryn is a diffuse source of pollution which has previously been found to be contaminated by metal pollution by Buss et al, (2013). It is postulated that it filters through the slate tips. The gorse (*Ulex*) and rhododendron (*Rhododendron*

ponticum) flourish around the tips and prevent the growth of other plants. Thus, the environment is unsuitable for sustaining a healthy biodiversity and river life.

2.13 Site selection

Twenty study sites were chosen for this project: a total of 14 on the Barlwyd and 6 on the Bowydd (Figure 2.15, Figure 2.16, Figure 2.17). On the Bowydd (see Figure 2.14), a control river to test whether quarrying affects the river, 6 sites were selected owing to ease of access. Site Bo1 (SH717414) was selected due to its proximity to the source and is deemed a control site. Bo2 (SH707344) is associated with the hydro water and is also deemed a control site. Bo3 (SH707344) runs through the quarry, with the potential to demonstrate how water is affected as it runs through the quarry. Bo4 (SH704214) is situated at the foot of a slate tip, and it is anticipated that the tips affect the quality of water in this region of the tip. Bo5 (SH699704) is a site which is downstream of Bo4 and will show the effect downstream of quarrying. A final downstream site at Bo6 (SH694254) is used as measure of downstream diminishment of pollution.

(a)

(b)

(c)

(d)

(e)

Figure 2.15 – Sites on the Bowydd (a)-(e)

Bo1 – Bo6, site Bo3 was abandoned due to lack of flow from the hydro overflow lake. (a) Bo1 is a source control site, (b) Bo2 is a site flowing by a slate tip, (c) Bo4 flows through slate tips, (d) Bo5 is a site in the valley, and (e) Bo6 is a site downstream.

(a) B1

(b) B2

(c) B3

(d) B4

(e) B5

(e) B6*

(g) B7

(h) B8

(i) B9

(j) B10

(k) B11

(j) B12

(m) B13

(n) B14

Figure 2.16 – The river Barlwyd sites 1-14

*A wide variety of different river geomorphology and anthropogenic modifications exist in this river. *B6 is a hydro site which receives water from both the Barlwyd and Bowydd.*

With regards to the Barlwyd, some study sites were selected as controls at the source, at mixing points, diffuse pollution and downstream of described pollution (see Figure 3.15). Two sites were selected upstream, one close to the source at location – B1 (SH701914), and another which flow into the hydro holding lake at Flags Lake – B2 (SH704834), which act as controls. Further downstream at Pant-yr-afon, a site that is historically affected by pollution, and where the environmental degradation begins, 7 sites were selected. B3 (SH695284) which is upstream of where it has been historically shown that the pollution begins (Pryce and Janes 2009), B4 (SH696604) which is the consented point pollution discharge from the Llechwedd quarry, and B5 (SH696604), which was located on the River Barlwyd downstream of the discharge. Further downstream, the hydro-electric which receives upstream water from the Barlwyd and Bowydd, discharges its powering water at site B6 (SH696604), with site B7 downstream as a mixing point (SH696604), B8- (SH696604) is a diffuse pollution source of runoff from the A487, while B9- (SH696604) is its respective downstream mixing point.

The other quarry that is suspected to affect the river is Gloddfa Ganol or Oakley and is located to the west of the river. Site B10 (SH696604) was located here, where discharge water runs through an underground tunnel in the quarry and was previously reported to be polluted (Bray et al., 1997). To gauge the sum respective contribution of these sources of pollution a sample was taken at B11 (SH694463), a mixing point for Gloddfa Ganol. Ael-y-Bryn, a historically major contributor of pollution was selected as a site at B12 (SH694514). Further downstream where pollution was previously reported to end, also as a mixing point a site was selected at B13 (SH689544). Finally, to gather downstream effects as a control, another site selected was B14 (SH685204), in Tan-y-grisiau next to the reservoir.

As slate is hard and relatively impervious surface, and roads are found adjacent to pollution and are B8 shows a high level of metals from the road runoff. Furthermore, the domination of the land use by the quarry has meant that the natural plant life that would normally be found in the land has gone. Takase and Sato, (1994) studied the process of retention in catchments of different land uses (see Hong et al., 2007). They found that initial soil moisture deficit has a great effect on the rainfall

retention of storm runoff. Furthermore, the lack of trees or foliage for percolation also impact the catchment. There is also a reduction in soil and plant cover in the catchment owing to the slate tips. As plants use large amounts of water in transpiration, they are responsible for flood control by reducing the amount of water that otherwise would flow downstream (Alberti, 2008). The slate tips, roads and urban environment reverse all these functions by reducing the amount of riparian vegetation. Hydrological processes interweave with biological and geomorphic processes in complex ways by formulating and sustaining aquatic habitats for a multitude of species. These processes are created by interactions between soil, vegetation dynamics, and nutrient cycling. Urbanisation affects the unique set of conditions which aquatic species have adapted to changes nutrient fluxes as well as contributing pollution. Urbanisation affects these interactions by changing both land cover and nutrient fluxes, and particularly by replacing wetlands that provide essential habitat for both fish and wildlife (Alberti, 2008). The effect that the impervious surface has on the amount, quality, and timing of flow depends on several factors: climate, morphology, geology, vegetation, and land use (Dunne and Leopold, 1978; Ziemer and Lisle, 1998; Booth and Jackson, 1997; Alberti, 2008). As a result of impervious surfaces, streams become “flashier” as their flow changes more quickly and more often (Konrad, 2000; Konrad and Booth, 2002; Booth et al., 2004). Riparian areas also act as critical transition zones between upland and aquatic environments, maintaining streambed stability. Hydrological functions are crucial for aquatic ecosystems including salmon, creating shelter for wildlife, and providing nutrients for macroinvertebrates. Urban and industrial modification of the landscape structure and processes changes proportions of impervious surfaces so that up to 55% of rainwater may drain off, as water is delivered to streams rapidly, frequently, and in large volumes (Alberti, 2008).

CHAPTER 3 – RESULTS AND DISCUSSION: QUANTIFICATION OF THE GEOCHEMICAL DYNAMICS OF THE RIVER BARLWYD AND BOWYDD – ESTABLISHING A BASELINE FOR RIVER CHEMISTRY

3.1 Introduction

Previous research into water quality of the River Barlwyd catchment by Natural Resources Wales (NRW) and reports commissioned by the Llechwedd quarry, indicate that water quality is negatively impacted by slate quarrying (Buss et al., 2013; NRW 2012-unpublished data). In terms of metals, Al and Cu are the most risk-ranked toxic metals (Donnachie et al., 2014) amongst those already identified as being a problem in the River Barlwyd (Pryce and Janes 2009; Buss et al., 2013). Chemical pollution has been linked to poor ecological status in the portions of the River Barlwyd (Buss et al., 2013). There is, however, much less research undertaken previously into the effect of slate quarrying on water quality, both in the Barlwyd specifically, but also within the literature more broadly, with few studies such as Peiffer et al., (1997) citing high Al loads on catchments associated with slate quarrying. This chapter establishes a baseline for the chemical and hydrological conditions within the study area. We examine Al and Cu concentrations and additional geochemical parameters, which are related to chemical state of these metals or may directly affect bioavailability and consequently bioaccumulation of the metals found. The aim was to assess the chemical quality of the stream water across a range of hydrological conditions and to evaluate the present risks of pollution from slate quarrying to the localised and downstream environments. This is of relevance to climate change to examine the effect of temporal changes on pollution levels.

3.1.1 Aim

To establish if there is a relationship between water chemistry and slate quarrying across different stream flows.

3.1.2 Specific Objectives

Specific objectives for this research were to:

1. Determine concentrations of Cu and Al and key geochemical parameters in river water at 20 sites in the Bowydd and Barlwyd across a range of discharge conditions reflecting temporality.
2. To quantify the magnitude of water quality degradation in relation to established guideline values to link to slate quarry pollution conditions.
3. To analyse the relationship between water quality parameters and river discharge.

3.2 Materials and methods

3.2.1 Longer-term sampling of river water

To establish a baseline for metal pollution in the River Barlwyd river, an analysis of Al and Cu concentrations in river water was conducted. Al and Cu concentrations were also determined for the River Bowydd for the purpose of control. Firstly, river water samples were collected on a fortnightly basis from 14 sample sites in the River Barlwyd catchment, and 6 on the River Bowydd catchment closest to the quarry as a control river which is predicted to be less affected by quarrying (Figure 3.1).

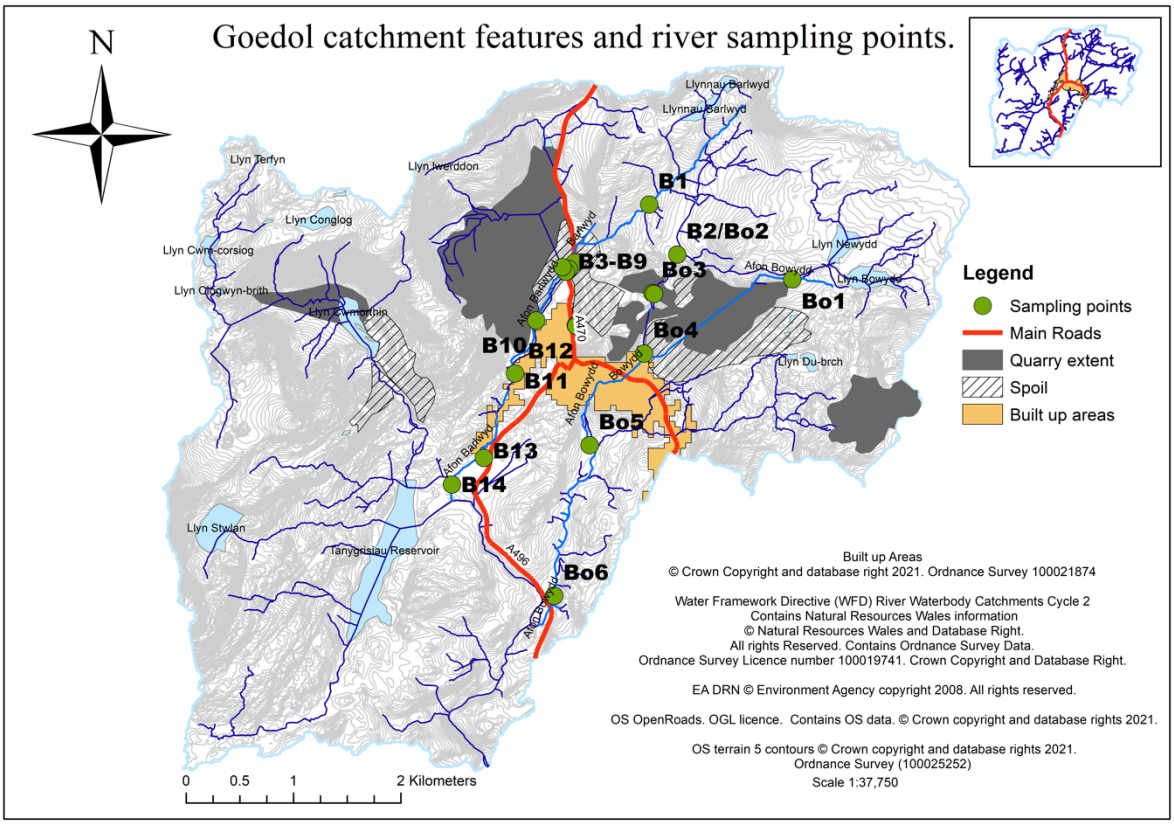


Figure 3.1 – Map of study sites and main features in the EWFD Goedol catchment.

Sampling was conducted between 25/09/2014 and 01/12/2015. Any gaps in sampling reflect times when sampling was not possible due to weather warnings or illness. In the field, and to aid the interpretation of metal concentrations (Prieto, 1998), waters at each sample site were analysed for Electrical Conductivity (EC (proportional to the quantity of dissolved ions present in solution) (using a HANNA HI-8733 probe)), temperature (using HANNA HI-92810 probe) and pH (an expression of the negative log of H^+ ion activity) (using HANNA HI-991003 probe). The pH electrode was calibrated using pH 4 and pH 7 buffers and the EC electrode was calibrated with a standard 1413 µS solution. Whilst some studies have determined these parameters upon return of water samples to the laboratory, it can be argued that more meaningful and potentially accurate measurements are made in the field at the time of sampling. Samples for turbidity analysis were collected in 10 ml bottles, refrigerated, and agitated, and subsequently analysed for turbidity by a HANNA HI-93703 machine.

Samples for metal analysis were gathered in Nalgene 125 ml bottles washed with sample water. An

aliquot was then filtered, using a plastic syringe that had been pre-washed in sample water, through a 0.45 µm cellulose nitrate filter membrane. Samples were stored in an acid-washed 30 ml Nalgene bottles. The reason behind storing in plastic Nalgene bottles is due to their general chemical inertness (Cook and Miles, 1980). Filtration is an established method for the first step of sample preparation (Laxen and Chandler, 1982). Batley and Gardner (1977) have observed that unfiltered sampling can mean that solute and suspended interact, which may affect the chemical form in which the metals are found (Bird 2003). Pearce (1991, 1992) and Fuge et al. (1991) have shown that the most important aspect is the speed at which samples can be analysed after sampling, hence the reason why samples were filtered in the field. Previous researchers show that when samples were analysed, the resultant correlations (r) between concentrations in treated and untreated samples were 0.99, 0.99 and 1.00 for Cu, Pb and Zn, respectively (Pearce, 1992). Filtering in the field was deemed unnecessary by such scientists as Fuge and Perkins (1991) and Néel et al. (2003) where sample analysis could be carried out rapidly after collection. The delay between collection and subsequent analysis, required the filtration of samples in the field in this present study.

Problems related to the choice of filter membrane size have previously been noted, which relates to the isolation of the dissolved load (Batley, 1989). Stumm and Morgan (1996) highlight the numerous advantages of using 0.45 µm filters. One of the reasons is that particles filtered by 0.45 µm filters do not settle in natural waters within days and are transported with solutes. Additionally, most bacteria and other organisms are not filtered out, meaning that bacteria can mediate chemical changes within the samples.

The advantage of using cellulose filters was shown by Danielsson (1982) and there is a better sediment load tolerance by cellulose than with other types of membrane. Conversely Marvin et al. (1970) report that filter membranes can contain appreciable metal concentrations and could contaminate the sample.

Finally, 250 µl of 10% nitric acid were added to preserve the sample (Bird et al., 2003). Samples were stored at 4°C prior to analysis (Bird et al., 2003). Acidification is necessary to preserve metal

concentrations and avoid loss of solutes due to precipitation or adsorption onto container walls or micro-particulates (Bird et al., 2003).

A sub-collection of samples collected between 10/03/2015 and 21/11/2015 were frozen following collection for subsequent total organic carbon (TOC) analysis.

3.2.2 ICP-MS analysis of water samples

ICP-MS was first used in 1983. Briefly, samples are nebulized into a fine aerosol by argon gas, and the fine droplets are separated by means of a spray chamber. The fine aerosol is transmitted into the plasma torch via a sample injector. The plasma is formed by the interaction of an intense magnetic field (produced by radiofrequency [RF] passing through a Cu coil) on a tangential flow of gas (normally argon) at about 15 l/min flowing through a concentric quartz tube (torch). This has the effect of ionizing the gas, which, when seeded with a source of electrons from a high-voltage spark, forms a very-high-temperature plasma discharge (~10,000 K) at the open end of the tube. Plasma is a partially ionised gas (Hall, 1992a): most ICP systems use an Ar plasma formed from Ar gas which is pumped at around 0.81 s^{-1}. Argon is usually chosen because it is a) inert and will not react with chemical samples easily (b) possesses a high 1st ionisation energy, which enables efficient ionisation of almost all elements, and (c) has the property of low thermal conductivity, which is significant because its heat is retained within the plasma (Jarvis and Jarvis, 1992a).

The stream of ions generated are then focused through a series of ion lenses into a mass analyser, which slows down the ion beam, and based upon element allows ions of each element to pass into the mass spectrometer in a set order. The mass spectrometer measures elemental concentration as raw ion counts, this can be scaled against the internal Ru calibration standards and processed to give elemental concentration in solution.

ICP-MS is distinguished from other methods such as flame atomic absorption of atomic emission spectroscopy by use of a plasma flame instead of a gas burning flame (Jarvis and Jarvis, 1992b). ICP-

MS is suitable for analysis of water as there is no need for preconcentration (Beauchemin et al., 1987, Garbarino and Taylor, 1987; Jarvis, 1997). Use of ICP-MS has become popular particularly in geochemical studies (Fuge and Perkins, 1991; Taylor, 1996; Bird et al., 2003) owing to superior sensitivity, simpler spectra, and the ability to give isotopic information to up to 70 elements simultaneously quickly with low volumes of liquid (Hall, 1992b; Pearce, 1992; Gabler,1997, 2002). ICP-MS has greater sensitivity and lower instrumental detection limits than any other quick multi-element method of analysis (Grey, 1989; Bird, 2003).

All analytical data are based on measurements and are as such inevitably prone to errors (Thompson, 1992). Indeed, it has been argued by Thompson and Ramsey (1995) that the quality of a result can be no better than that of the sample analysed. The need to establish the validity of geochemical data is particularly apparent where datasets are compared to environmental quality guidelines to evaluate the magnitude, and potential human and environmental health implications, of metal concentrations. Quantifying errors, some of which may be unavoidable, through internal quality control therefore occupies a key role in analytical measurement because it is imperative that data is 'fit for purpose' (Thompson and Ramsey, 1995).

3.2.2.1 Sample analysis using ICP

3.2.2.1.1 Potential for spectral interferences

Interferences could occur with the formation of molecular and doubly charged ion species whose mass-charge ratio (m/z) is the same as isotopes of interest (Tan and Horlick, 1986; Bird et al., 2003). These species are formed due to the presence of compounds derived from: a) the plasma gas (e.g., Ar^+, ArN^+), b) acids used in sample preparation (e.g., $ArCl^+$), and c) concomitant matrix elements (e.g., $^{54}Fe^+$ on $^{63}Cu^+$, $^{65}Cu^+$, $^{64}Zn^+$ and $^{66}Zn^+$) (Hall, 1992a; Bird et al., 2003). However, almost every element has an isotope that is free from spectral overlap (Hall, 1992a; Bird et al., 2003).

3.2.2.1.2 Monitoring analytical quality

Following the recommendation of Ramsey et al. (1987) and Ramsey (1997), data quality was monitored through the implication of an analytical quality control (AQC) programme during analytical procedures (Bird et al., 2003). The programme monitored trueness and precision of both the analytical procedure and instrumentation (ICP – MS), as well as monitoring potential levels of sample contamination (Bird et al., 2003).

3.2.2.1.3 Quality control during sample preparation

The equipment and reagents used during sample preparation and analysis can potentially contaminate the sample to some degree. Losses of metals can occur through sorption onto equipment to which samples are exposed, whilst samples may be enriched in metals that are incorporated into plastics during their manufacture (Scott and Ure, 1972; Bird et al., 2003). To prevent contamination during sample storage, preparation, and analysis; all glassware and storage containers were soaked in 10 % HNO_3 for at least 24 hours prior to use to remove metals from inner surfaces (Massee and Maessen, 1981; Bird et al., 2003). Hamilton (1980) states that even the highest level of quality control cannot prevent sample contamination, however, it can be assessed through the random introduction of sample blanks into the preparation and analytical stages. Sample blanks allow the background concentration to be measured and calculated and are used to adjust measured concentrations.

3.2.2.1.4 Monitoring analytical trueness

The accuracy of a single result is based on the proximity of the measured concentration to the true value and will be influenced by both random and systematic errors (Analytical Methods Committee, 1995; Bird et al., 2003). Analytical trueness for the determination of metal levels in water samples was monitored using certified (NIST1643e), which were included in each batch of analyses. The difference between measured and quoted values will give an indication of the accuracy of the data.

For these analyses, 10 ml of each sample was poured into polypropylene tubes and analysed by ICP-MS (Agilent 7700x) for Al^{27}, and Cu^{63}. Samples were spiked with a ruthenium standard (at 197 ng/ml final flow concentration). Calibration was achieved through the analysis of solutions of known concentrations: 5, 10, 20, 50,100, and 200 ng/ml. The Limit of Detection (LoD), and Limit of Quantitation (LoQ) are terms used to describe the smallest concentration of the any late being measured that can be detected (Armbruster and Pry, 2008). The limit of quantification is the lowest concentration at which the analyte can not only be reliably detected but at which some predefined goals for bias and imprecision are met and the limit of detection is the lowest quantity of a substance that can be distinguished from the absence of that substance (a *blank value*) with a stated confidence level (generally 99%) (Armbruster and Pry, 2008). Additionally, accuracy and precision were determined by the analysis of the NIST 1643e reference material and calculated as per Equations 1, 2, and 3. Accuracy and precision were found to be within acceptable limits (see Table 3.1). Some samples were low in concentration and as this approaches the limit of detection the random noise has a greater effect on the precision, and thus NIST 1643e was used to determine accuracy (see Table 3.1 under precision, equation 3).

Eq 1.

Precision

For duplicates:

$$Relative\ Percent\ difference\ \% = \left(\frac{(sample\ result - duplicate\ result)}{\left(\frac{(sample\ result + duplicate)}{2}\right)} \right) \times\ 100$$

Eq 2.

$$\%\ Precision = (SD \div mean) \times 100$$

Eq 3.

$$Accuracy = \%\ of\ certified\ NIST$$

Eq 4.

Scaled difference = (value 1 – value 2/√2)/mean of values

Table 3.1 – ICP quality control data

	Run 1 Al	*Run 1 Cu*	*Run 2 Al*	*Run 2 Cu*	*Run 3 Al*	*Run 3 Cu*
% Precision	5.59	5.41	1.80	1.58	3.70	26.16
% Accuracy	10.29	4.30	2.34	-0.91	-1.29	-5.44
RPD 1	0	0.9	8.9	4.2	-2.13	-2.13
RPD 2	27.5	4.7			-0.35	0
Scaled difference	-1.23E-05	0	0	0	0	0

3.2.3 Rainfall data

Rainfall data was collected daily from a logger at SH67938 by NRW.

3.2.4 TOC analysis

The Shimadzu TOC combustion catalytic oxidation method works by heating samples to 1,200°C in an oxygen-rich environment inside TC combustion tubes filled with a platinum catalyst. This generates CO_2 which is detected using and infrared gas analyser (NDIR). The detection limit is highly sensitive with a limit of 4 µg/L. The carbon dioxide is cooled and the dehumidified and detected by the NDIR. The concentration of TC (total carbon) is calcula0ted through comparison with a calibration curve formula. As organic carbons easily bind with metals in the river, a sub-sample of water samples were collected between 10/03/2015 and 21/11/2015 and were frozen following collection for subsequent total organic carbon (TOC) analysis. Samples were defrosted and then shaken prior to analysis. Total organic carbon (TOC) was determined in river water samples via combustion catalytic oxidation (Analytik Jena Multi NC2100S). The carbon present converts to CO_2 and is passed through scrubber tubes to remove interferences such as chlorine gas, and water vapour. The resultant CO_2 generated is measured with a non-dispersive infrared (NDIR) detector. A regression calibration curve formula then allows the TOC to be calculated (Shimadzu, 2016).

Accuracy was determined by using solutions of a known concentration every 7th sample and found to be within acceptable ranges. TOC was calculated using a regression curve formula, regressions were found to be within acceptable ranges for each calibration curve, r^2 = 99-100%.

3.2.5 River flow data

Flow data was collected to examine the effect of different flow regimes on metal concentration. At each sample point, channel cross-sections were surveyed at the start of the sampling programme. On subsequent sampling visits flow depth and flow velocity were measured and utilized alongside known cross-sectional morphology to determine discharge (equation 3.1). Channel morphology was monitored by taking 4 annual measurements and calculating the average over the year. Subsurface flow is negligible due to there being minimal groundwater flow in the Harlech dome. Flow velocity was measured using the float method with 5-10 oranges used as a float and timed over a specified distance. For portion of the river which were not straight, we used a flow meter. We focused on the velocity-area method instead of using a tracer given that the channel was accessible with relatively even cross-sections and that flow area and velocity could be reliably and consistently measured. As the Barlwyd is mostly comprised of bedrock channel, there is a reduced potential for hyporheic flow. Also, the bedrock/coarse grained nature of the channel will also reduce/minimize the changes of morphology and thus minimizes the risk hyporheic flow– not completely remove it but reduce the risk. Therefore, it is assumed that the subsurface/hyporheic flow is negligible. Although elsewhere is the Barlwyd there may be stream bed conditions in which this is a possibility. Hyporheic flow has been associated with resulting in sorption/desorption process associated with changing chemical conditions (e.g., redox conditions) and the interaction with the material. This could be important for Al/Cu water chemistry.

$$Discharge\ (Q) = Av$$

Where:

A = cross-sectional area of flow

v = flow velocity.

For site B8 (an outflow pipe), the calculation for discharge in a partially full pipe by Bengston (2014), was used, which utilises hydraulic radius and variable Manning's roughness to calculate flow.

$$Q = (1.49/n)A(Rh2/3)S1/2$$

The channel at B11 contains two portions and each was measured weekly according to depth at the tunnel.

3.2.6 Data analysis

Data was analysed using the package Data graph and Excel. Tests for normality were conducted with a Q-Q plot and Shapiro Wilks test. Statistical tests were carried out using RStudio. DataGraph for Mac was used for graphing data.

3.3 Results

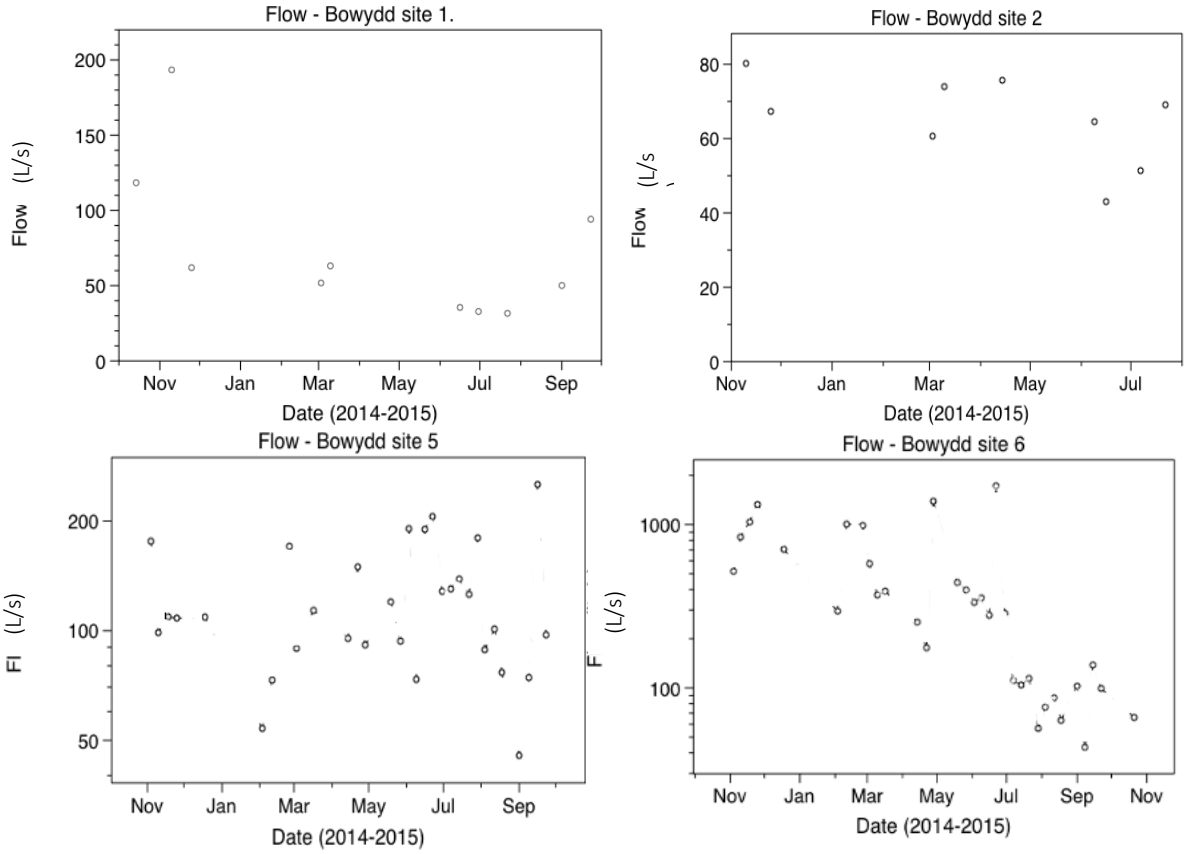
3.3.1 River Flow

River flow in the rivers Bowydd and Barlwyd logically increase with distance downstream (Figure 3.2). Flow in the River Bowydd is generally lower than that in the Barlwyd, indicative of the smaller catchment area and lower slope gradient and source height.

In terms of the flows measured, generally there is a higher flow downstream (up to 3664 L/s) and a greater range in the main body of the Barlwyd (20-3664 L/s) than the Bowydd (range (30-1009 L/s). The flow from the road discharge – B8 is high (1277-3550 L/s). Flow downstream can be high in the Barlwyd and Bowydd (3664 L/s, 1009 L/s respectively). Flows upstream are higher than Pant-yr-afon (up to max 578 L/s – B1: max 391 L/s-B6) on the Barlwyd due to slope gradient. The adits can be lower (B12 range 1-454 L/s). The range of flows is large overall (1-3664 L/s (Barlwyd)) showing the weather regime in the catchment, and regularity of landscape rain. The flow regime for the Barlwyd shows a seasonal trend (Figure 3.3) with higher flows in winter months which are associated with

winter storms and seasonality. However, it should be noted, there were health and safety concerns in measuring some higher winter flows, where some high winter flows data points are omitted.

Since mean stage depth is related to flow, our flow data was compared to mean stage depth for two gauging stations on the Barlwyd (Figure 3.4). In terms of mean stage depth there seems to be a seasonal pattern in relation to flow. Mean stage depth correlates with flows that were measured (Figure 3.4), this validates our data.



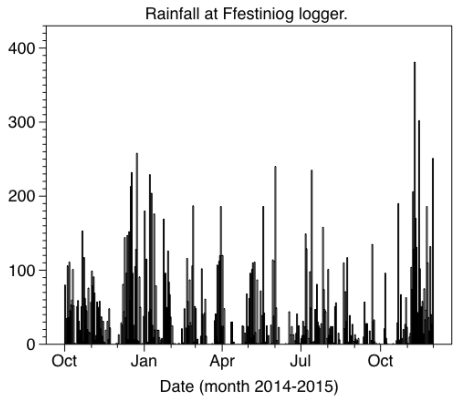


Figure 3.2 – Flow measured for the river Bowydd

Site Bo3 was closed later in the year and has few points – site Bo4 was unaccessible for flow measurements. 2014 was the fourth wettest year in the UK rainfall series from 1910 (1301 mm) (Met office). 2015 was the seventh wettest year in the UK rainfall series from 1910, with 1272 mm (Met office). Rainfall data supplied by Natural Resources Wales © Natural Resources Wales and database right. All rights reserved.

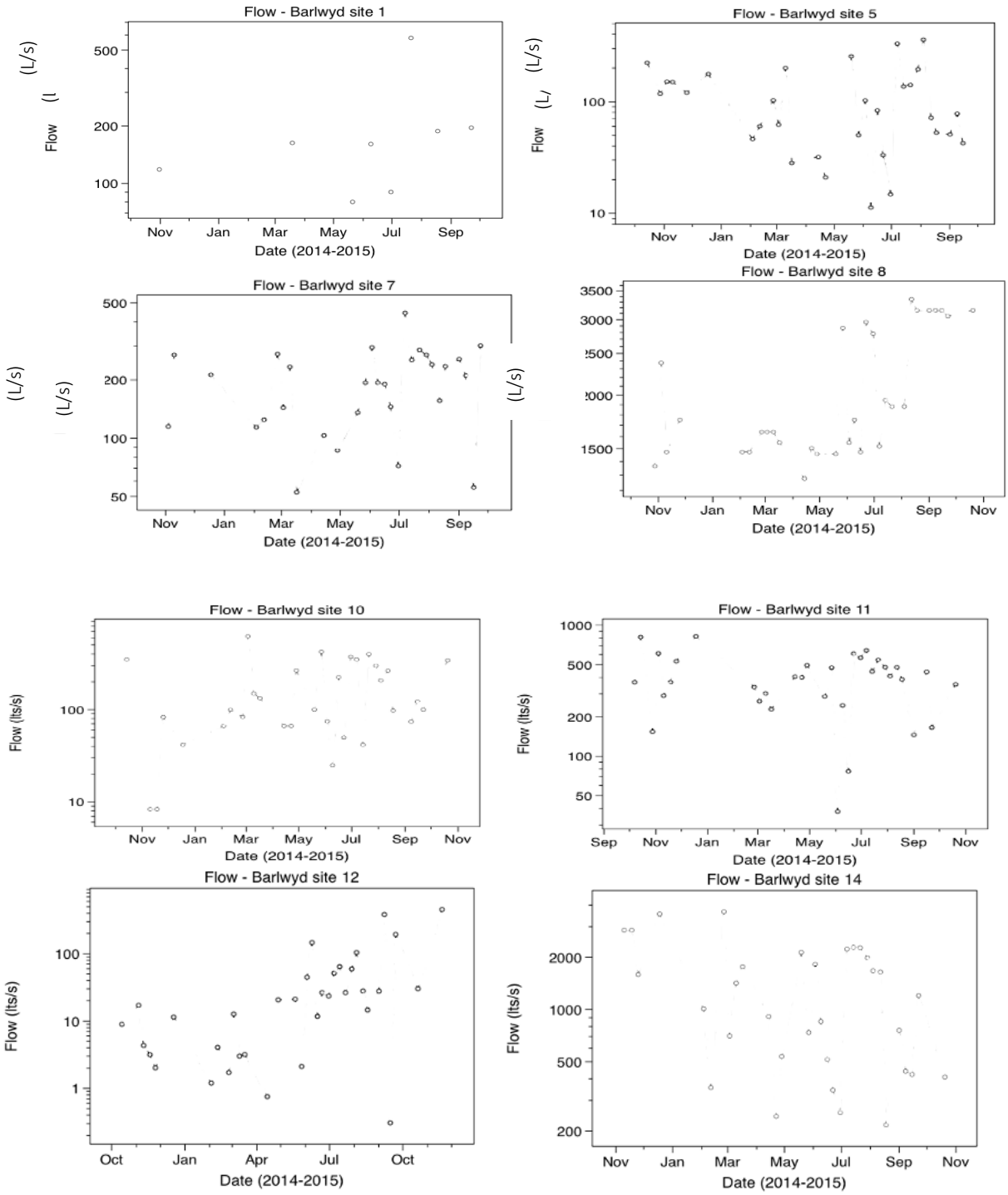
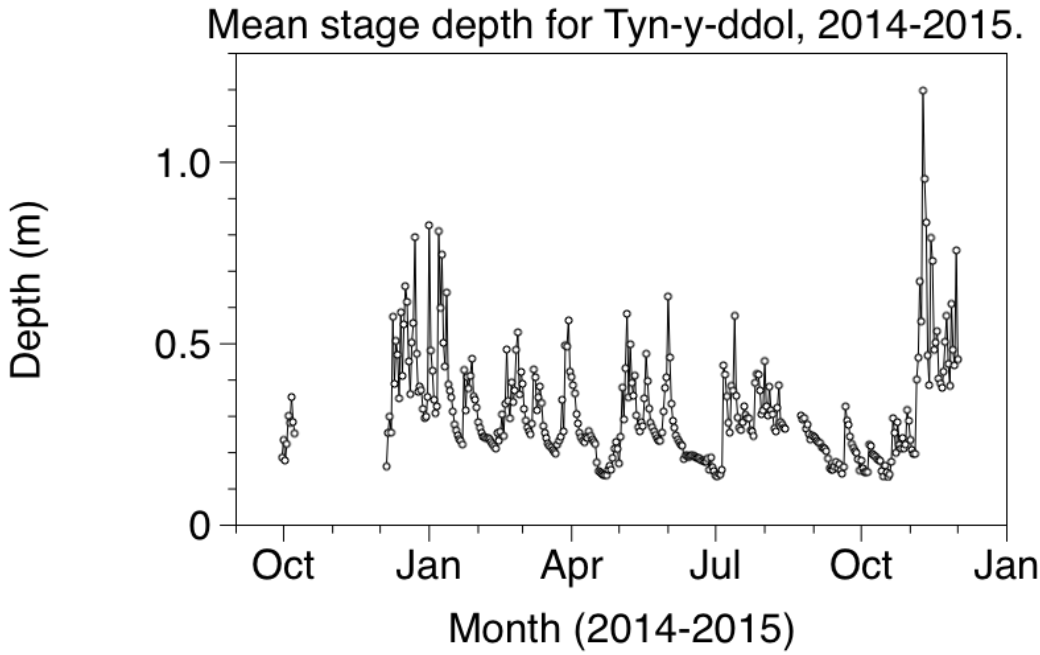


Figure 3.3 – Flow patterns for the Barlwyd

Site B1, B5, B7 B8, B10, B11, B12 and B14 are shown. Not all sites were measured owing to access problems.



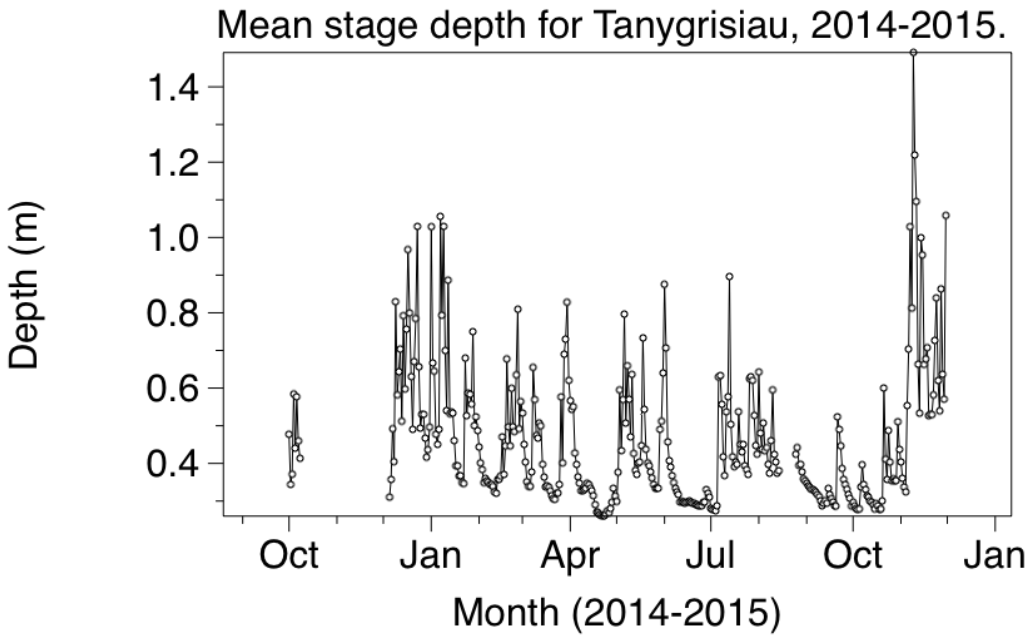


Figure 3.4 – Stage depth in relation to time at Ty'n y ddol and Tan-y-grisiau

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3.3.2 – pH

River water in the Rivers Bowydd (range: 3.75-7.65) and Barlwyd (3.4-7.62) is generally acidic (Figure 3.5) and is at times outside the recommended guidelines set by the EWFD of >=6 to <=9 for high to good status (EWFD, 2005) from source to downstream in the Bowydd (starting from Bo1), it is evident that pH transitions from acidic to neutral. Closer to the source the river can at times be extremely acidic, although at times is suitable for aquatic life (range: 3.75-7.65). Further downstream at site Bo4, which runs through slate tips, the pH is generally acidic (range: 3.98-6.92; average: 5.77) thus at times this may affect aquatic life. Downstream, beyond the quarry the water at Bo5 becomes less acidic with an average pH which is acceptable to aquatic life (range: 5.01-6.9; average: 6.04). Bo6 is largely like Bo5 with a range of (range: 5.42-6.93; average: 6.29) which falls within good-high status for the EWFD. Typically, pH increases temporally when there is more precipitation/greater flow as rainfall has a neutral pH and raises the pH of the waterbody. During dry periods in the summer the water becomes more acidic; during storms the water becomes more neutral.

On the Barlwyd the pH is also acidic and generally ranges between 3.4 and 7.62. The pH of the Barlwyd is generally lowest at B12 (Figures 3.6, 3.7) with higher pH generally found at B14. The pH in the uplands and above the point where there is a noticeable change in pollution (B1-B3) is acidic-neutral (range: 4.97-7.62; average: 6.09-6.49) and samples are generally of good-high status for the EWFD. The pH in the main body of the stream in Pant-yr-afon can at times be below water quality criteria for aquatic life (range: 3.95-6.97), but in the trunk of the stream, the pH is generally higher than in the adits. At the first adit – B4, where the quarry discharges polluted water, the pH can at times be outside the range of pH suitable for aquatic life (range: 3.95-6.82 with an average of 5.72). At this juncture in the river the water becomes primarily/more acidic. The hydro input B6 is again acidic and is derived from the uplands and has no exposure to quarry pollution, range: 4.49-6.28; average: 5.45) demonstrating the effect of peat on water upstream. The discharge from the A487 – B8 is again acidic (range: 4.21 - 5.57; average: 4.82); this perhaps illustrates geochemical processes

which occur with weathering in the slate tips. The discharge from the quarry in the west – the Oakley quarry (B10) is slightly less acidic (range: 4.78-6.56; average: 5.91).

Beyond Pant-yr-afon, downstream the aquatic pH becomes more neutral at mixing point B11 with pH ranging between 5.2 and 6.53 and an average of 6.04. The next adit from quarry sources – B12, showed consistently acidic pH (range: 3.68-4.45; average: 4.01). This will likely affect the bioavailability of metals and could explains the poverty of aquatic life here. Acidic pH at B12 lowers pH at the mixing point B13 (range: 3.4-6.3, average: 5.36). The range at B14 becomes more neutral yet can still be exceptionally low (range: 3.6-6.9; average: 5.65) the pH generally shows a higher average trend with higher rainfall/flow increasing the pH.

Typically, pH increases when there is more precipitation/greater flow, physical dilution is representative of what occurs and creates a more neutral pH and raises the pH of the waterbody. During dry periods in the summer the water becomes more acidic.

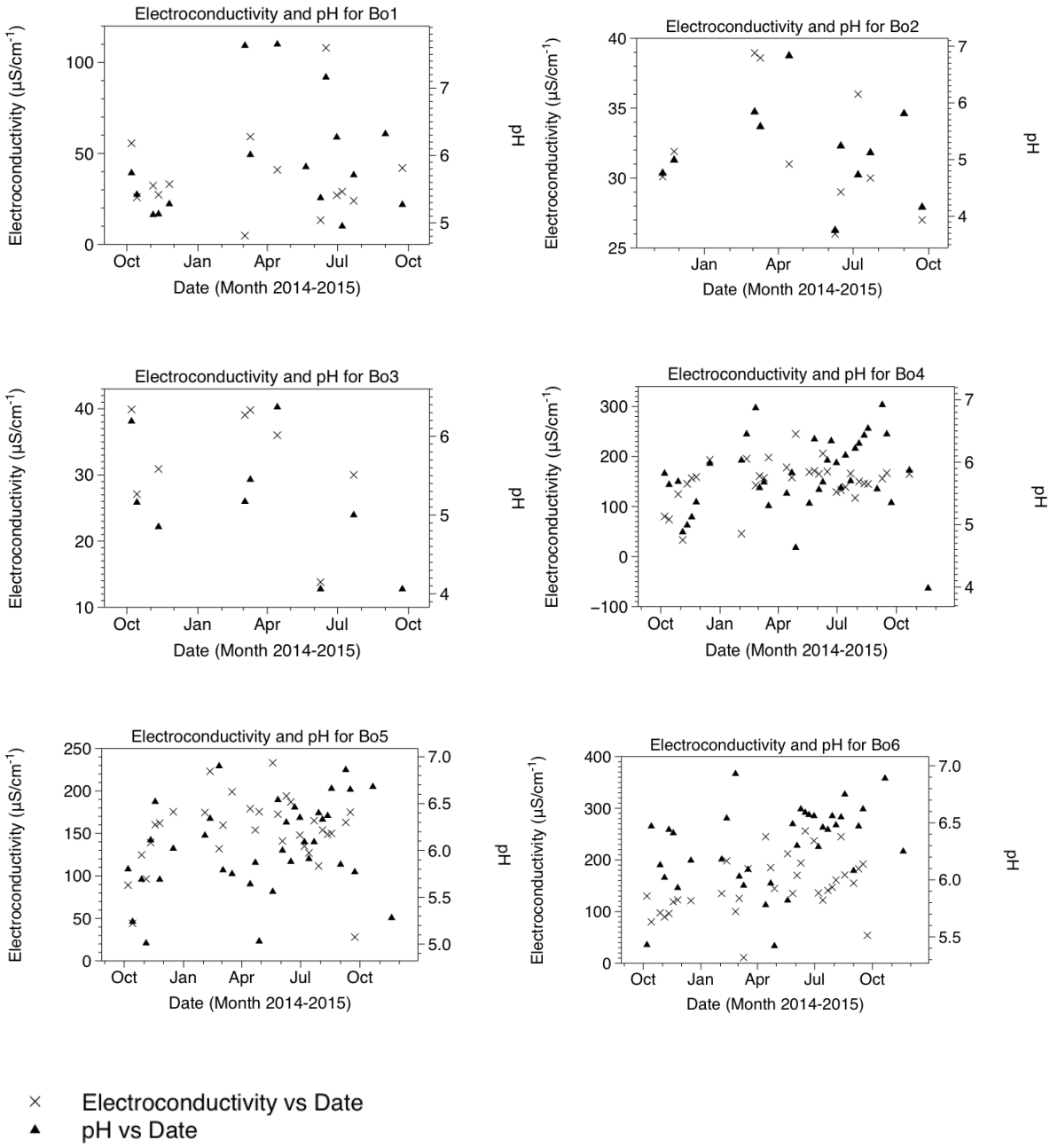


Figure 3.5 – Electroconductivity and pH in the river Bowydd (spatial and temporal representation)

The right hand axis represents electroconductivity and the left hand axis represents pH.

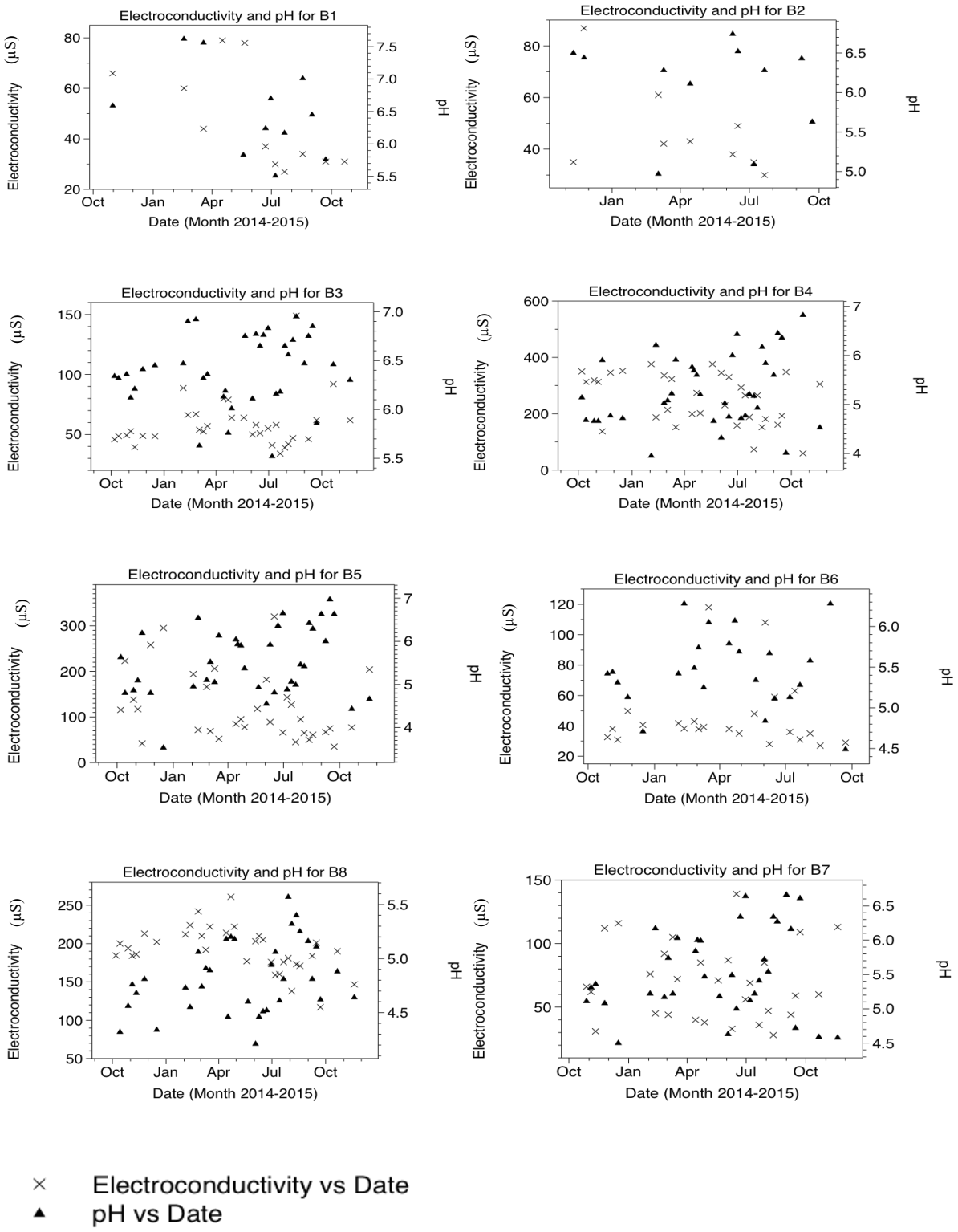


Figure 3.6 – Electroconductivity and pH in the River Barlwyd

Samples taken from 14 different sites on a reach of approximately 3 km, which is the ecologically poor region for the river.

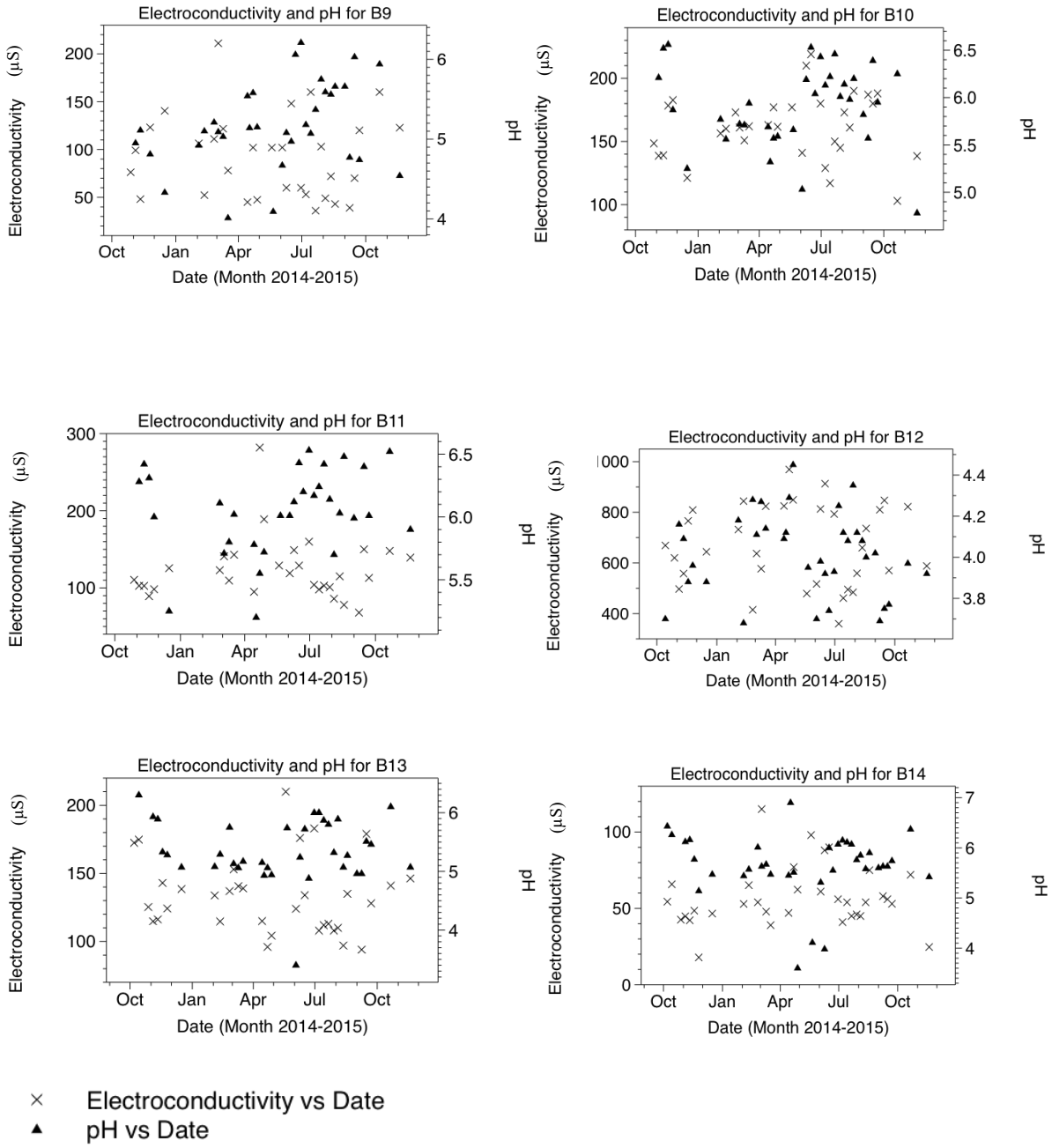


Figure 3.7 – Electroconductivity and pH in the River Barlwyd

Samples taken from 14 different sites on a reach of approximately 3 km, which is the ecologically poor region for the river.

3.3.3 Electroconductivity

Water in the River Bowydd is found to be within normal ranges for electroconductivity as defined by WHO (1992), which is between 10-1000 μS, although the range for aquatic life is defined as being at <500 μS, and can on occasions at key points, be considerably lower to that found in the Barlwyd (Figures 3.5, 3.6 and 3.7). The general range is indicative of lower water ion content, and thereby perhaps lower metal content rates from sources within the catchment. In the Bowydd, the average EC upstream of the quarry is 40 μS with a range of 13.8-39.9 μS.

Electroconductivity is mostly low but with the spatial impact of the slate tips and flowing through the quarry the electroconductivity increases at Bo4-Bo6, showing the influence of weathering of the slate tips as water flows through the quarry. Having flowed through the slate tips at Bo4, EC in water increases (range: 33.2-458 μS; average: 162 μS). Site Bo5 shows a large range (range: 28-233 μS; average: 150 μS) which reflects the flow regime change and upstream effects of the quarry. The overall impact downstream persists to a certain extent with ion content remaining similar but with less high extremes and a lower range, showing that ion content can persist (range: 54-256 μS; average: 153 μS cm). During summer months when there are dry periods the EC increases as the ions become more concentrated. Increased flows and rainfall generally tend to decrease the ion concentration due to dilution.

Electroconductivity is mostly at acceptable levels for the river Barlwyd, in terms of pollution indices (WHO, 1992), with a range between 27-969 μS (Figures 3.6, 3.7), but showing higher concentrations at some adits which are spatially located in close vicinity to the quarrying activity- B4, B8, and B12. Natural background levels are found at sites B1-B3 which are upstream of the quarry ranging between 27-149 μS, although B3 does show higher EC at times.

Spatially EC seems to increase at adits close to the quarry. Higher electroconductivity is found at B4 (range; 59-376 µS; average; 251.9 µS). This reflects the higher concentrations of metals found in this adit with up to 12 times the amount of Al and 50 times the amount of Cu as with compared with recommended EWFD guidelines found here. At B6, the hydro input, there is a low EC (range: 27-118 µS; average: 45 µS), this then has an impact downstream, thereby lowering the electroconductivity at B7 (range: 45-118 µS; average: 69 µS). Another adit which may carry surface runoff from the quarry; B8 demonstrates a slightly elevated EC (range: 117-261 µS; average: 191 µS). This is reflective of the amount of metals in this adit, where concentrations are on average 12 times recommended limits of Al and on average 100 times elevated in Cu. Interestingly the second quarry adit (B10) does not exhibit high ion concentrations with a range between 103-219 µS with an average of 161.31 µS, which is supported by a low concentration of metals (under geochemical atlas limit for Al also (range: 0.135-0.36152 mg/L; average: 0.0420 mg/L) and around 10 µg/ml (range: 3.3-19.1 µg/L; average: 6.0 µg/L for Cu), which illustrates that this source of pollution has potentially been cleaned up after EWFD legislation imposed upon it and is no longer a significant risk to the river in terms of Al, although Cu does pose some concern. The concentrations of metals at B12 were high in comparison to other sites – up to 203 times the geochemical atlas guide of Al and up to 338 times the EWFD guide for Cu, and electroconductivity demonstrated this with a higher concentration of ions in the river (range: 360-969 µS; average: 670 µS) and was generally above ion concentrations for aquatic life.

In terms of metal loading at high flow (as representative of measured flows during the sampling period), B5 shows evidence of major influx of metals to the Barlwyd, possibly owing to the adit from the quarry at B4, which is potentially exacerbated by the pumping of water from the quarry. With an influx from the hydro at B6 the hydro dilutes this concentration considerably and then increases with inputs from B10 and B8 at B11, before decreasing to a higher level than at low flow further downstream.

During low flow (as representative of measured flows during the sampling period), the trunk of the stream seems to be more affected, Al and Cu concentrations are low at B7 (Al 0.24 kg, Cu 0.015 kg) at B11 because there is no input from the hydro at times with higher concentrations of Al and Cu appearing at B11(Al, 8.63 kg, Cu 0.40 kg) which is downstream of all Pant-yr-Afon inputs than at low flow. However, there is comparatively a lower level of metals in the river compared with high flow, where there is approximately three times the amount of Cu in the river at low flow.

3.3.4 Total organic carbon (TOC)

Total Organic Carbon (TOC) concentration both in the Barlwyd and the Bowydd can at times be quite high in comparison with other upland catchments (Worrall et al., 2004; Cooper and Watts, 2002; Environmental Information Data Centre, 2015) (Figures 3.8-3.10), with a range of 0.1-13.3 mg/L, but is within expected ranges for the rivers following a pattern of high upstream TOC in the Bowydd, as the source is close to peatlands. Upstream concentrations of TOC are higher in the Bowydd and become diluted on receiving more inputs of water downstream. Concentrations of TOC for both rivers are comparable (Bowydd range: 0.1-13 mg/L and Barlwyd: 0.1-13.3 mg/L). On average, it is shown that the mean concentration of TOC is higher at B4, B5 and B6, which could bind to metals and cause lower concentrations of Al and Cu in the stream trunk at B7 (NRW, 2007). In this region, owing to small distances between site, TOC concentrations ostensibly accumulate along the river, one adit adding to another along the stream. Overall, concentrations are higher upstream (B4, B6), due to contributions from peaty upland runoff. It could be argued that the TOC simply becomes more dilute as additional tributaries contribute to the river downstream. Temporally, concentrations in the summer are found to be generally higher, perhaps owing to a smaller volume of water to which concentrates the concentration of TOC, this could also be due to a larger volume of storms being measured during the summer period.

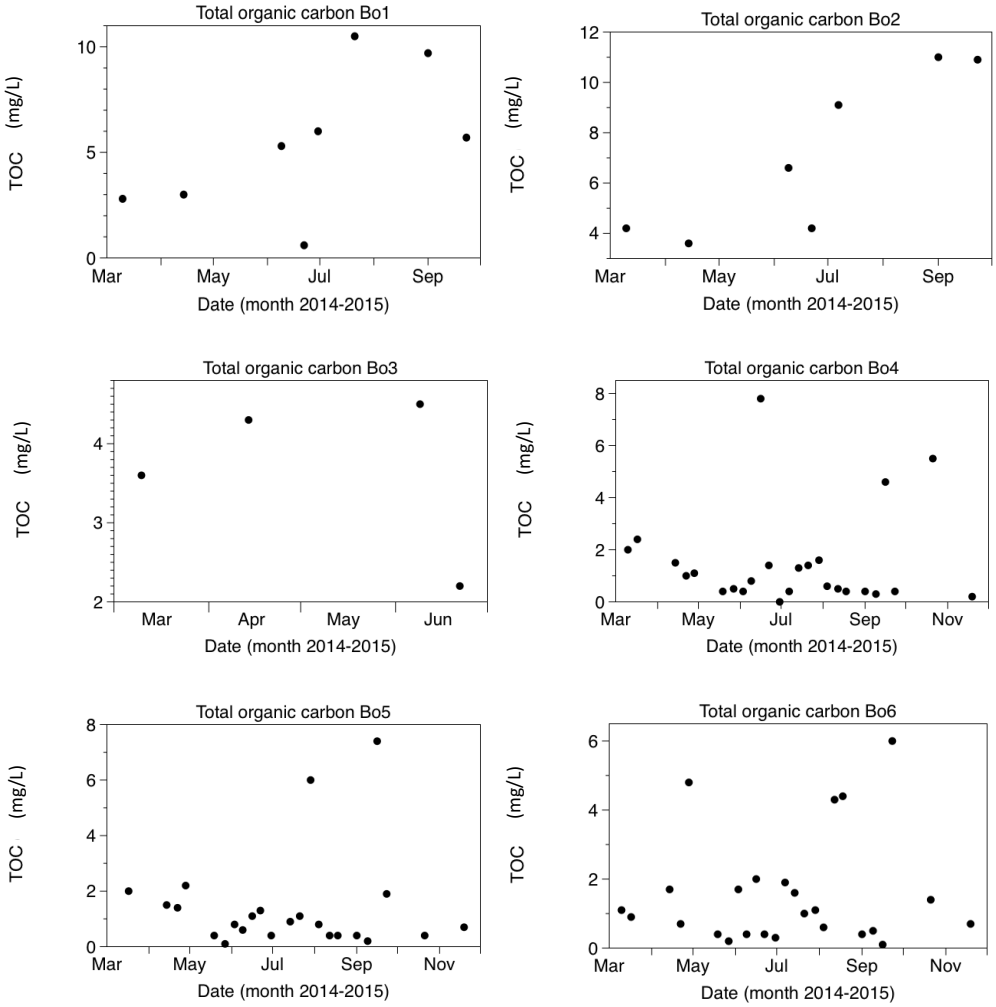


Figure 3.8 – TOC in the Bowydd sites 1-6 over the year of 2014 – 2015

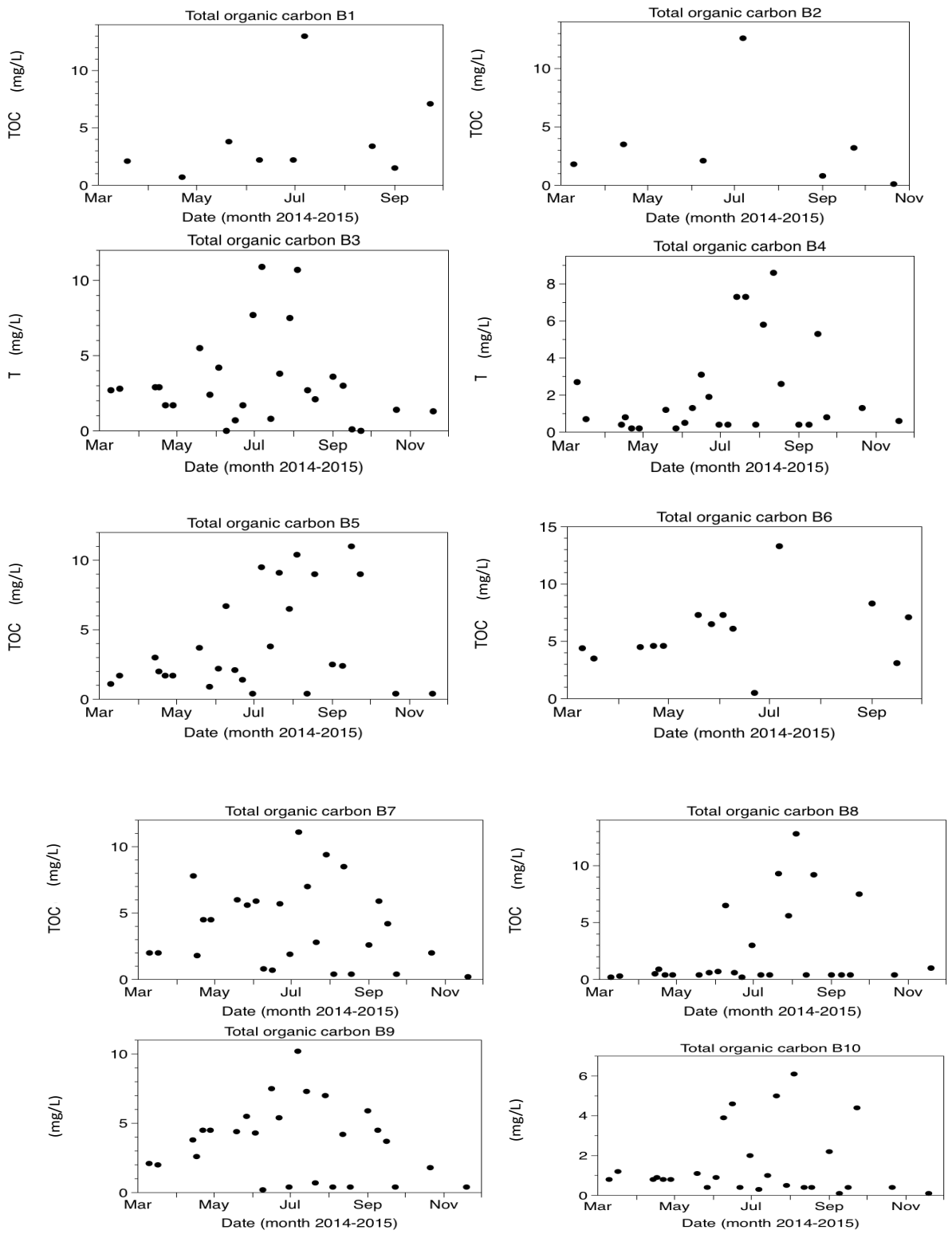


Figure 3.9 – Concentrations of TOC in the river water samples for the river Barlwyd, site 1-14 respectively

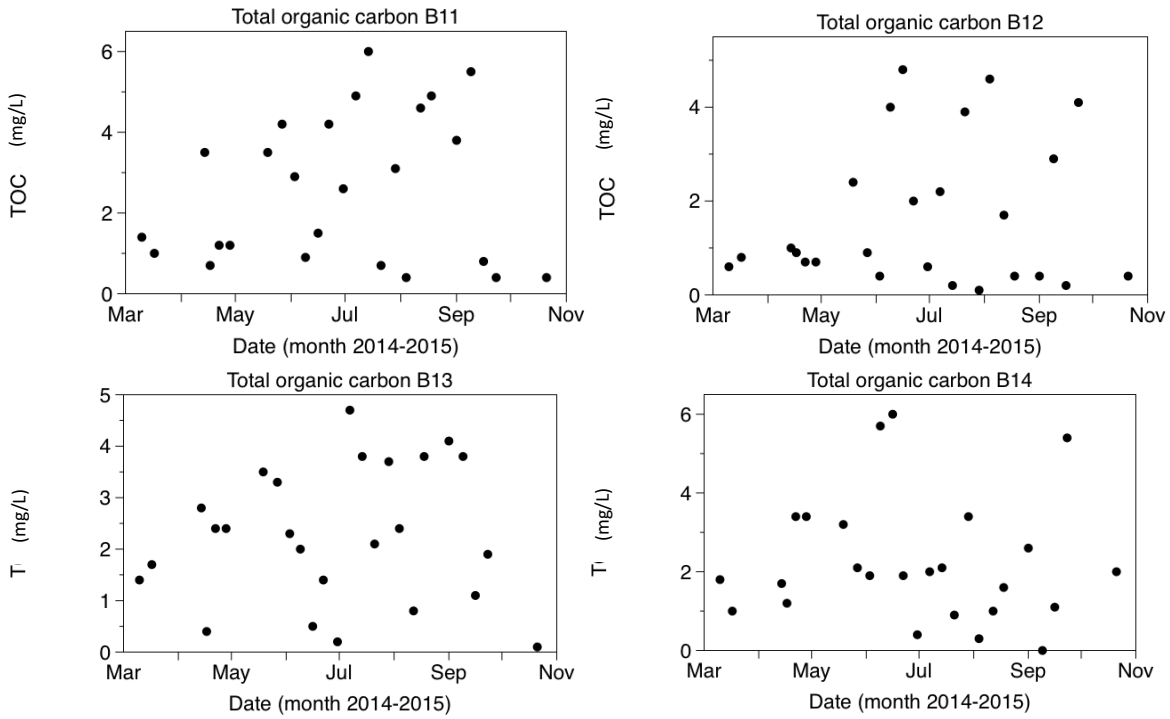
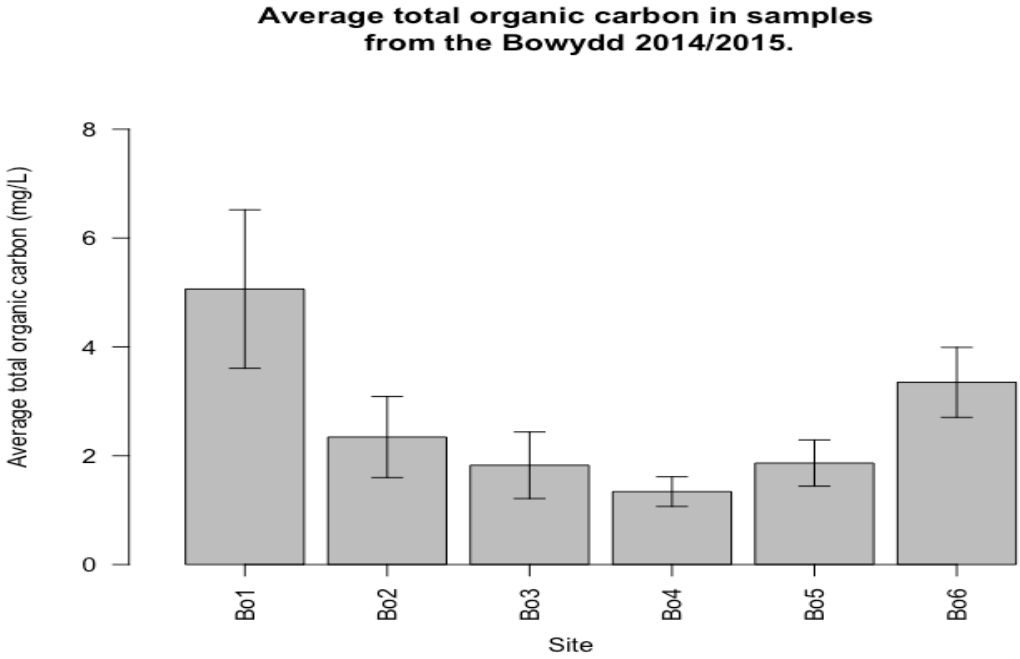


Figure 3.10 – Concentrations of TOC in the river water samples for the river Barlwyd, site 1-14 respectively

(a)



(b)

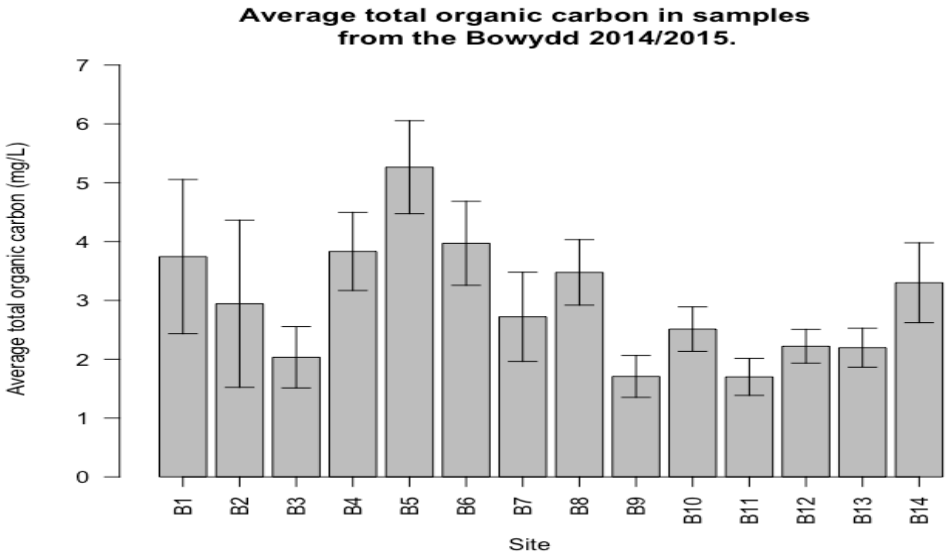


Figure 3.11 – Average dissolved organic carbon in the (a) Bowydd and (b) Barlwyd 2014/2015

3.3.5 Turbidity

Turbidity in the Barlwyd and Bowydd rivers does not correlate with what would be expected with regards to the degree of pollution found in the catchment and past results (Figure 3.12-3.14). Levels exceeding 50 NTU are unacceptable (Evans, 2011) and most results are found to be lower than this. However, these limits are set with regards to Nitrogen pollution and perhaps new limits need to be set with regards to slate quarrying. At times turbidity at site Bo2 for instance can be extremely high, circa 100 NTU, however, based upon field observations, this appeared to be related to TOC as opposed to slate waste-derived turbidity pollution, and by scientific measurement (13.3 mg/L).

There was no visual evidence of slate "cloudy-like" turbidity in the water during the sampling period, which was previously evidenced, although storms occurred where this was witnessed anecdotally during the sampling period. Typically, levels of turbidity for all sites range between 0-10 NTU with most readings being between 0 and 1 NTU.

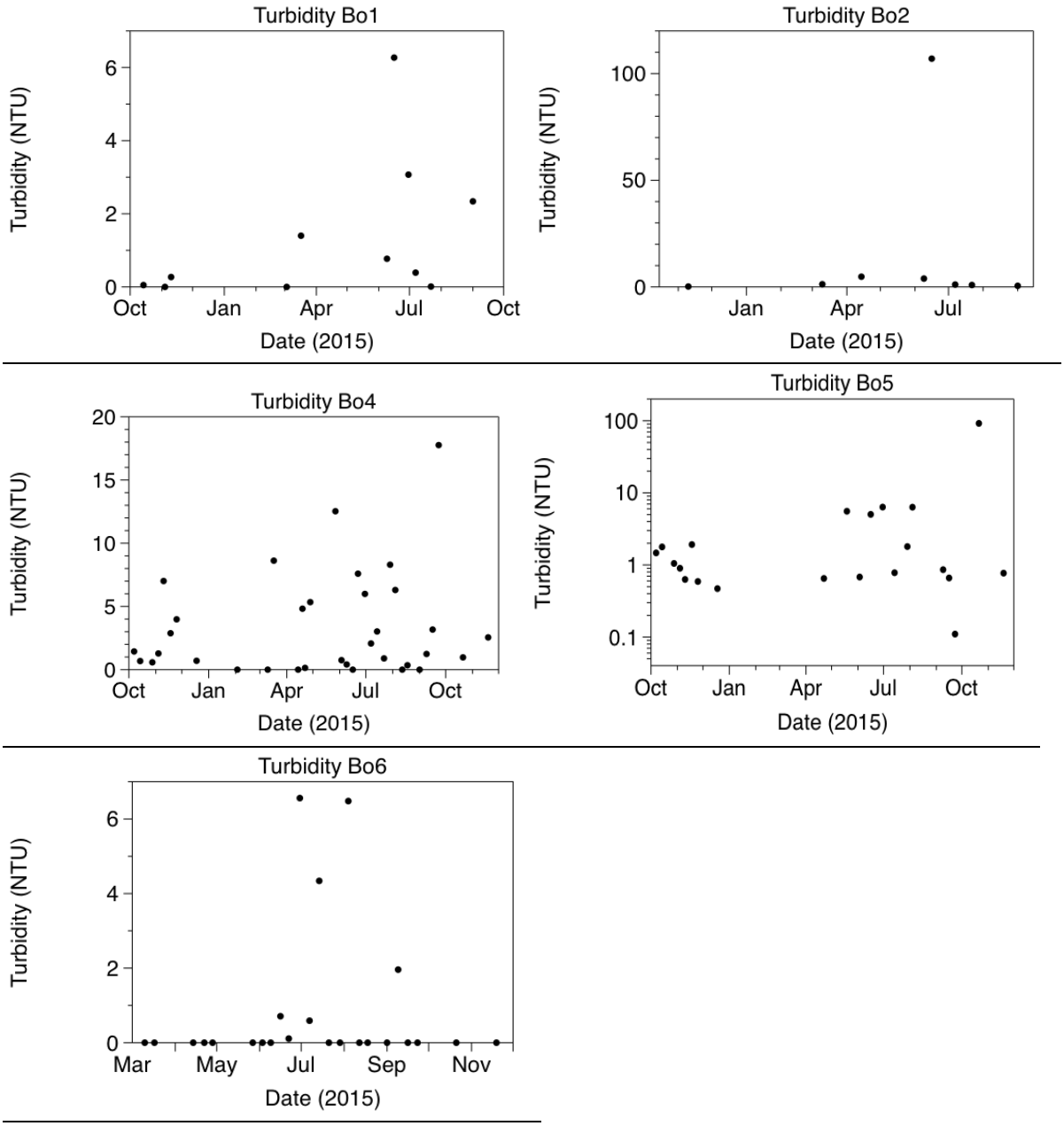


Figure 3.12 – Turbidity in the Bowydd

Few measurements were taken at Bo3 as the hydro overflow flow regime changed and thus are not included.

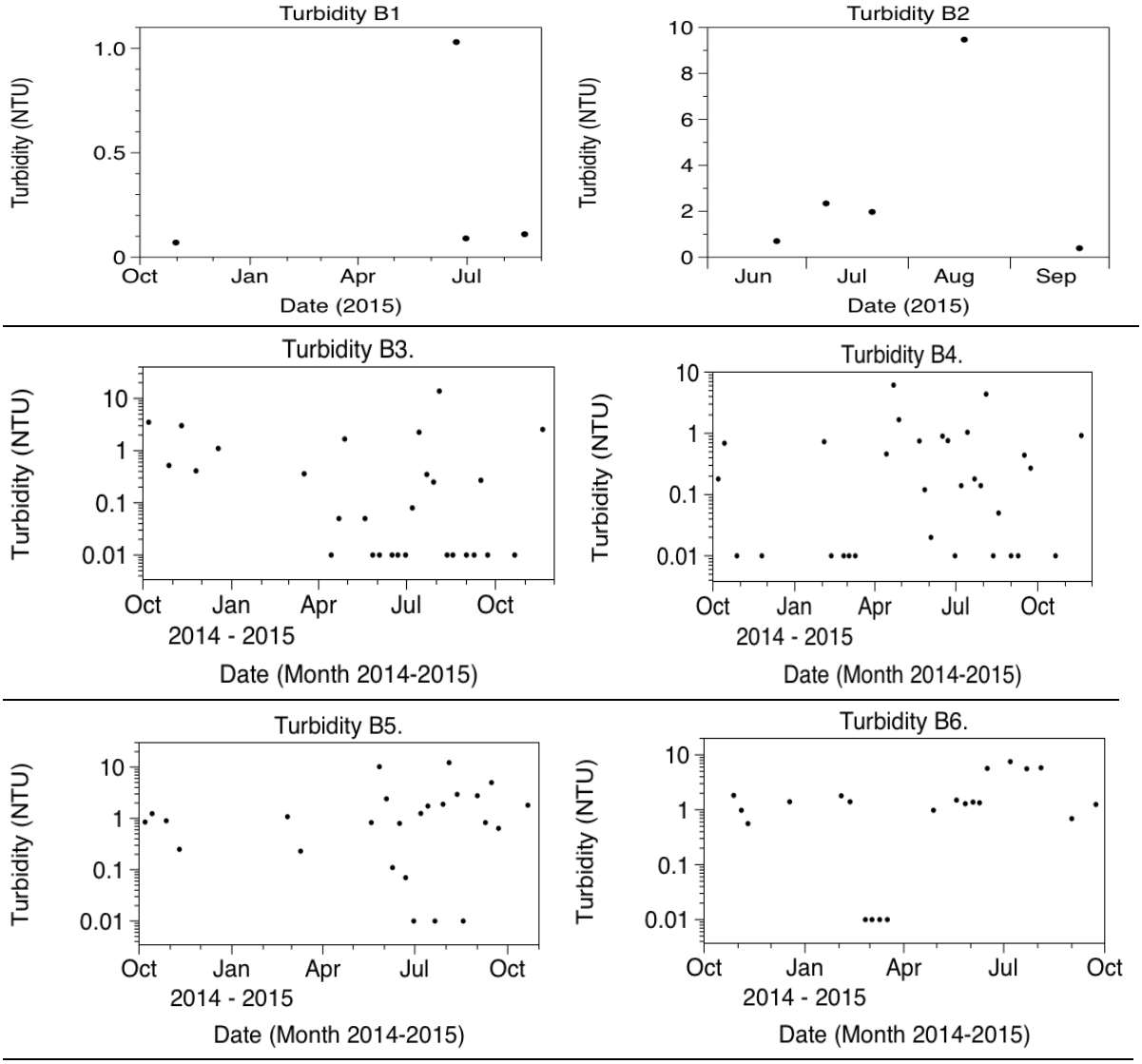


Figure 3.13 – Turbidity in the Barlwyd sites 1- 6

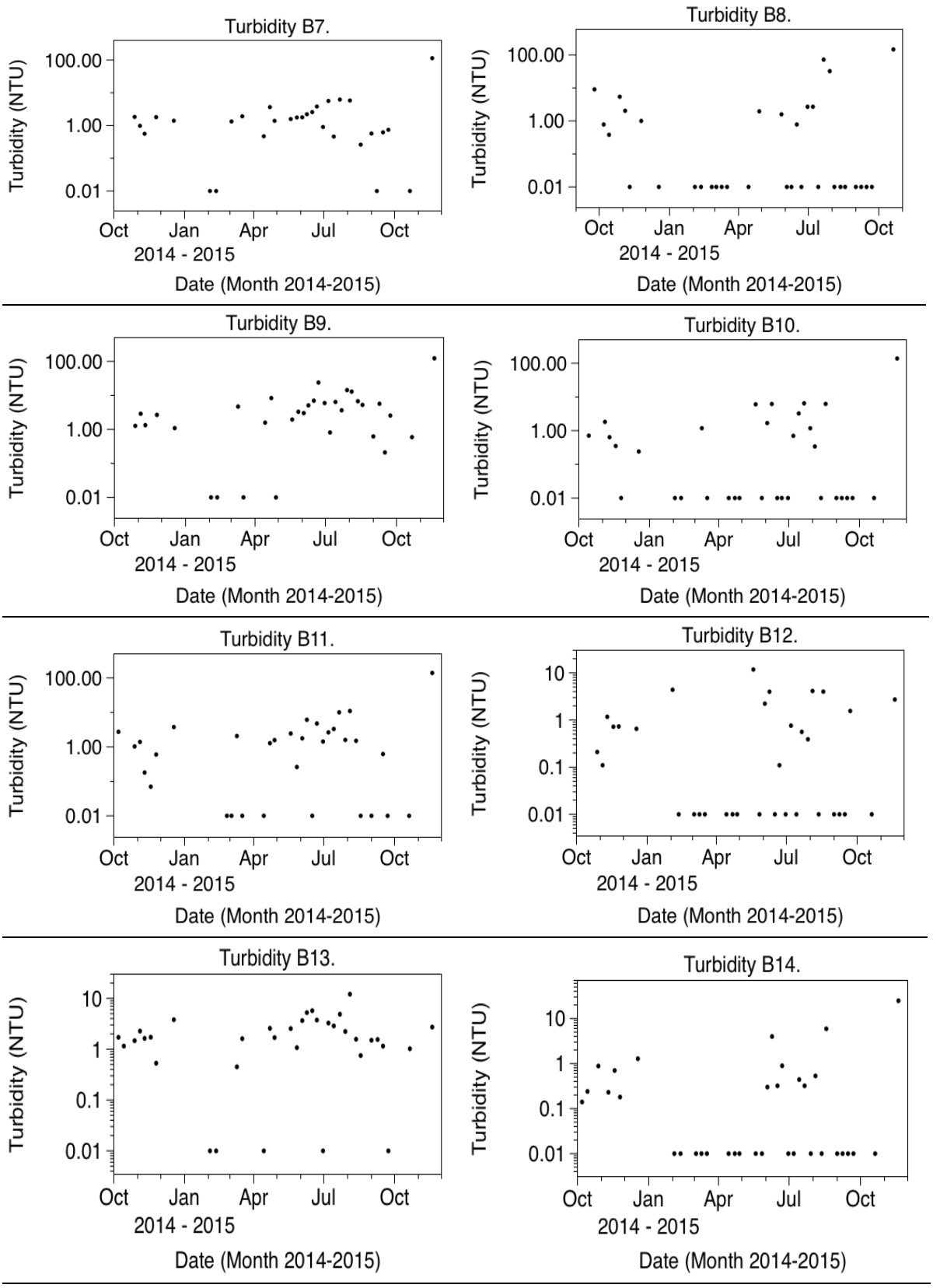


Figure 3.14 – Turbidity in the Barlwyd sites 6-14

3.3.6 Metal concentrations

3.3.6.1 Al concentrations

The geochemical atlas guideline for Al is 75.5 µg/L and the suggested EQS is 10 µg/L (Buss et al., 2013, NRW, 2007). Al in the Bowydd is shown here to be naturally enriched with upstream site Bo1; 2 times on average enriched, this is true of sites Bo2 and Bo3 where Al is 1-2 enriched (Al range = 0.02-2.44 mg/L, average 0.482,0.302, 0.105 mg/L respectively) (see Figure 3.15). Bo4 despite going through slate tips does not show elevated concentrations (range: 0.0015-0.7912 mg/L). Of note is Bo5 where the river becomes on average 8 times more enriched in Al (range: 0.0044-0.8698 mg/L; average: 0.0842 mg/L), this becomes less elevated by dilution downstream, but does have some concentration peaks (range: 0.003-2.975 mg/L; average: 0.1590 mg/L) and retains an average that is higher than Bo4. With regards to the Bowydd, the river is generally more enriched according to pollution guidelines in Al than Cu with sites reaching as much as 10 times on average as much Al, with the higher end of the spectrum being toxic to aquatic life. However, there are different levels of natural abundance of both Cu and Al in nature.

With regards to the Barlwyd (Figures 3.16a, 3.16b), at B1 the levels of both Al and Cu are predictably found to be below the geochemical atlas limit level/EWFD of Al with about half of points being slightly above limits demonstrating a slight enrichment (See Figure 3.17) (range: 0.020-0.178 mg/L; average: 0.079 mg/L), At B2 the river is mostly below limits (range: 0.022-0.142 mg/L; average: 0.066 mg/L; again, as are points at B3 (range: 0.0112-0.4207 mg/L; average: 0.086 mg/L).

A marked increase occurs at B4, the quarry input (Figures 3.16a, 3.16b, 3.17), with on average 12 times the amount of Al (range: 0.0136-2.8003 mg/L; average: 1.16 mg/L). Further downstream the river remains affected at the mixing point which demonstrated the effect on the main water body. Mixing points in Pant-yr afon generally show a decrease in metal concentration e.g., B5 the river levels of Al and Cu (range: 0.0149-12.6554 mg/L; average: 0.0816 mg/L). The Al concentrations at

B6 are low being derived from upland sources, with some higher points but generally low (Enrichment factor=1.55; range: 0.1070-1.4692 mg/L; average: 0.1176 mg/L). The road discharge B8, which may pick up dust from the road and quarry shows an elevation of both Al and on average the concentration of Al is on average 12 times elevated (range: 0.0974-2.8240 mg/L; average: 1.5548 mg/L). The Oakley quarry water – B10 is good quality with regards to Al at under 1 time elevated for Al (range: 0.135-0.36152 mg/L; average: 0.0420 mg/L). Concentrations of Al the downstream mixing site of Pant-yr-afon and Oakley remain slightly higher at 7 and 11 times the suggested limits respectively (range: 0.0163-7.825 mg/L; average: 0.3624 mg/L). B12 is markedly increased in concentrations of both Al and shows consistently high levels of Al being 203 on average times elevated (range: 2.9054-21.656 mg/L; average: 15.34 mg/L). Given the relative contribution of metals at B12, downstream there is no considerable impact at B13, although elevated the level seems to be considerably lower than at B12 and appears to be adsorbed by the body of water although it remains above averages (range: 0.0193-0.9636 mg/L; average: 0.192 mg/L; enrichment factor = 2.54). Downstream at B14, the river returns to good chemical status (range: 0.0072-0.5548; average: 0.05371 mg/L) with enrichment on average 1 time the acceptable level. By this point the metal concentration is diluted by the body of water, and the metals can possibly be found in bound forms/hydroxide precipitates having been mixed by the body of water. Moreover, pH may have risen owing to increased tributary/rainfall contributions and precipitation of the metal out of the water.

3.3.6.2 Cu concentrations

The EWFD limit for Cu is 1µg/L (EWFD, 2015). In the Bowydd, there can be elevated levels of Cu lower down in the stream at Bo2, where Cu can is on average 58 times more enriched (Figures 3.15, 3.17). At Bo4, there remains little extra input of Cu with a level of about 6 times the EWFD. However, generally, upon moving downstream the level returns to a lower level of around 7 times or 7 µg/L on average. Interestingly there seems to be a high background level of Cu in this river, which may not derive from slate quarrying. This can evidently affect aquatic life in the Bowydd. Overall, the

results show that the river is relatively unaffected by slate quarrying in terms of Cu concentrations, or by going through the slate tips, showing that the Bowydd as a control is largely unaffected by slate quarrying, owing to spatial influence and inputs. The higher input in background sites illustrates the influence of geology, naturally enriching the river in Cu.

In the Barlwyd, upstream before Pant-yr-afon at sites B1-4, (See Figures 3.16, 3.16b, 3.17) concentrations of Cu are generally enriched as with compared with the EWFD limit of 1 µg/L (range: 10-22.2 µg/L). At B4 there is a marked increase in Cu with on average 50 times the amount of Cu (range: 0.1-103.9 µg/L; average: 50.8 µg/L). Downstream the average is 28.5 times the limit (range: 0.1-0.0297 µg/L; average: 28.5 µg/L) driven primarily by winter flows. The hydro input is low in concentrations of Cu at 7.6 times (range: 0.1-0.097.8 µg/L; average: 7.6 µg/L). The road runoff at B8 on average 100 times elevated in Cu, which is exceptionally high in Cu's instance (range: 9.88-151.33 µg/L; average: 100 µg/L). High and low ranges were found in the winter months and appears not to be dependent on flow but perhaps on activity in the quarry. B10 is on average to 10 times elevated for Cu (range: 3.3-19.1 µg/L; average: 6.0 µg/L). Downstream of Pant-yr-afon at the final adit - B12 Cu levels are considerably higher being on average 338 times elevated for this site at a concentration in the range of (103.5-434 µg/L; average: 338.7 µg/L).

The relative contribution of B12 has no considerable impact downstream at B13, the level seems to be considerably lower and appears to be adsorbed by the body of water although it remains above guidelines most of the time (range (Cu) 0.8- 45 µg/L, average 13 µg/L, EF = 13). Downstream at B14, the river returns to normal levels with Cu (range: 0.1-5.9 µg/L; average: 1.7 mg/L) and is on average 1.7 times the acceptable level. By this point the metal concentration is diluted by the body of water, and the metals can possibly be found in oxidised forms having been mixed by the body of water. Moreover, pH may have risen owing to increased rainfall contributions and precipitation of Cu.

Temporally there do appear to be dates which peak in terms of metal concentration, but these do not correlate generally with maximum flows, so it must be largely dependent on location of activity at the

quarry. The pattern is largely spatially dependent upon which sampling dates offer the highest concentration at each site, although there do seem to be common sampling dates between some sites. Generally, there appears to be no seasonal pattern, although at B12 higher flows seem to drive higher concentrations of metals of around 20 mg/L of Al, and lower flows, June for example shows lower concentrations of metals around 10 mg/L. This may indicate a flushing effect which is dependent on the storm profile.

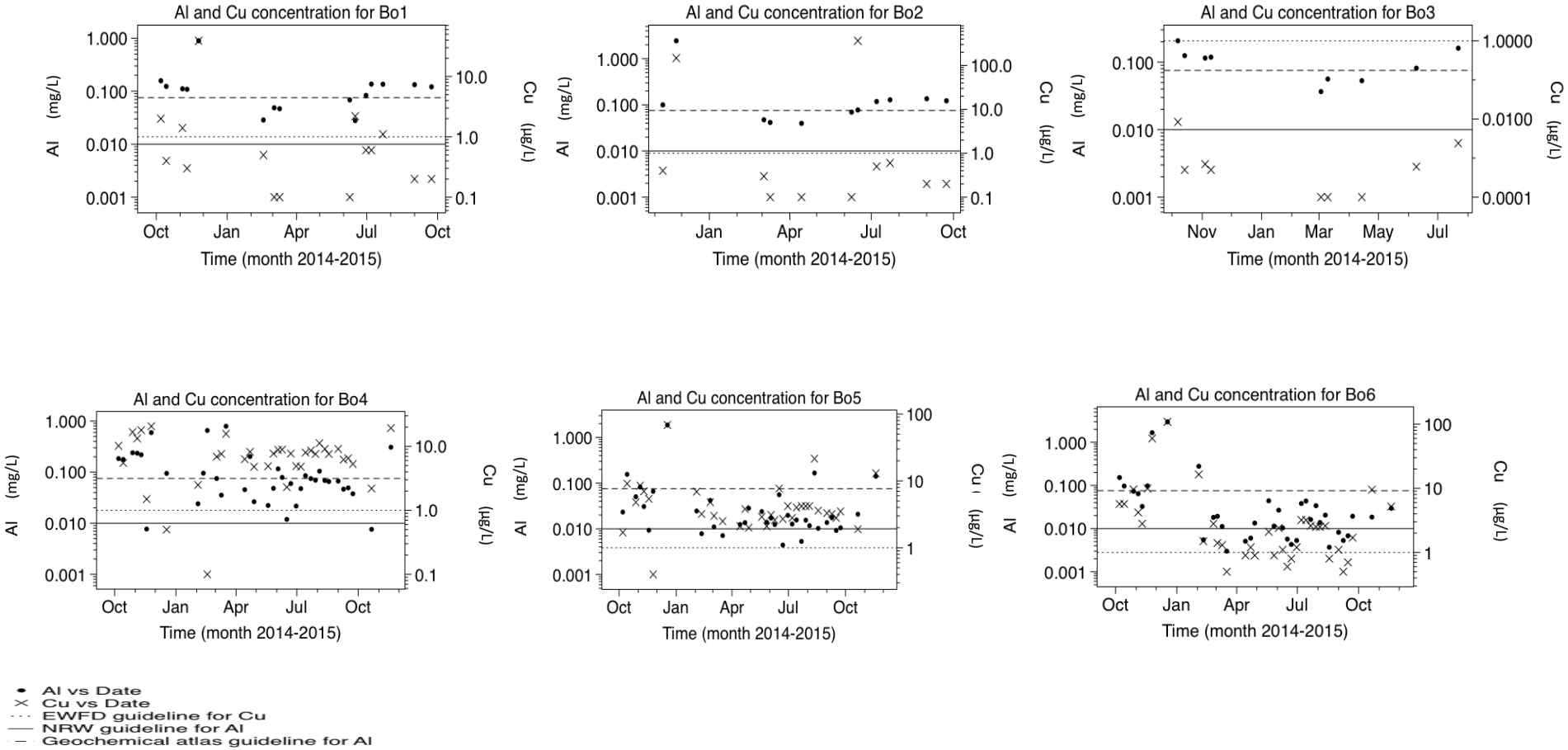


Figure 3.15 – ICP-MS analysis of Al and Cu levels in the control river – the River Bowydd

Limits used were recommended by NRW for Al and based on the geochemical atlas guidelines for the geographical area, for Cu the limit is based on the EWFD guidelines for the calcium carbonate content for the area. The left-hand axis shows Al. The right-hand axis shows Cu

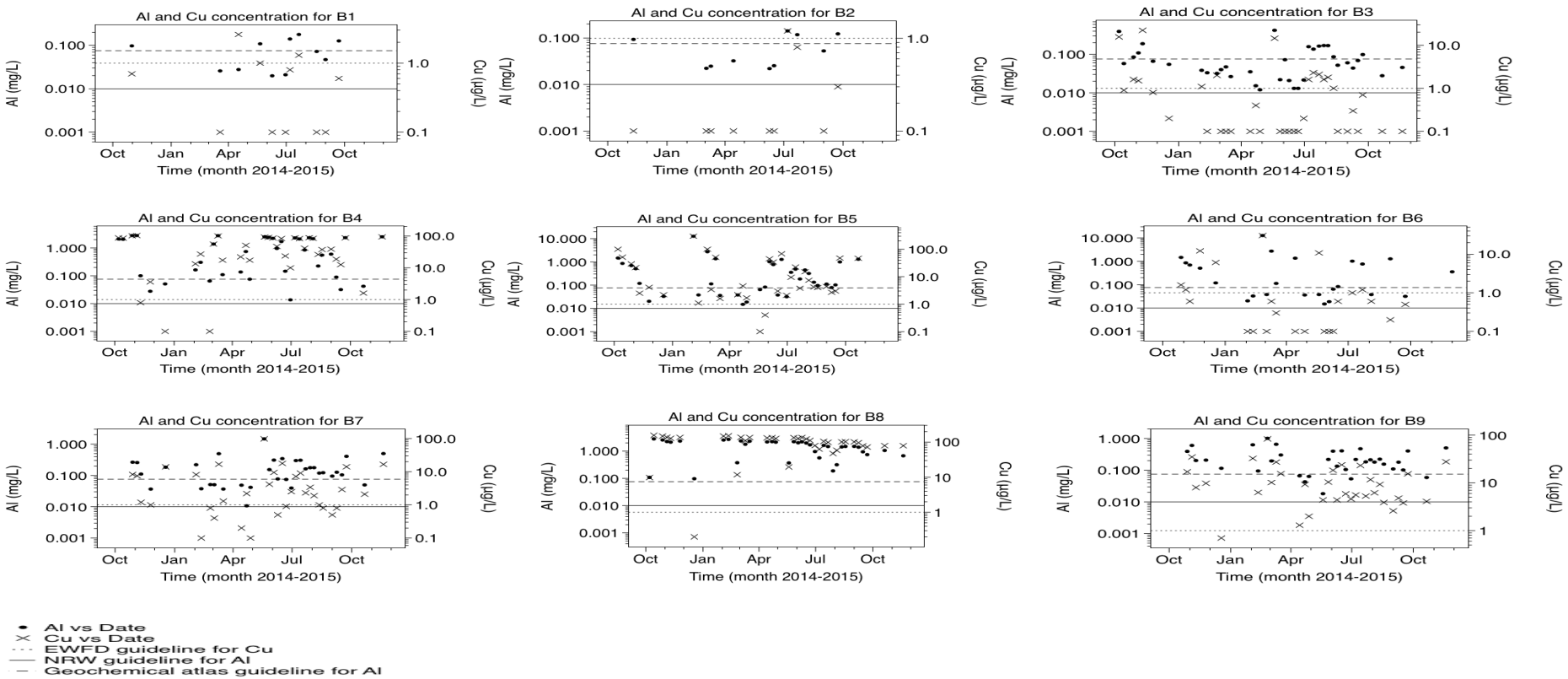


Figure 3.16a ICP-MS analysis of Al and Cu on 14 Sites on the Barlwyd respectively.

Limits used were recommended by NRW for Al and based on the geochemical atlas guide for the geographical area, for Cu the limit is based on the EWFD guidelines for the calcium carbonate content for the area. The left-hand axis shows Al. The right-hand axis shows C

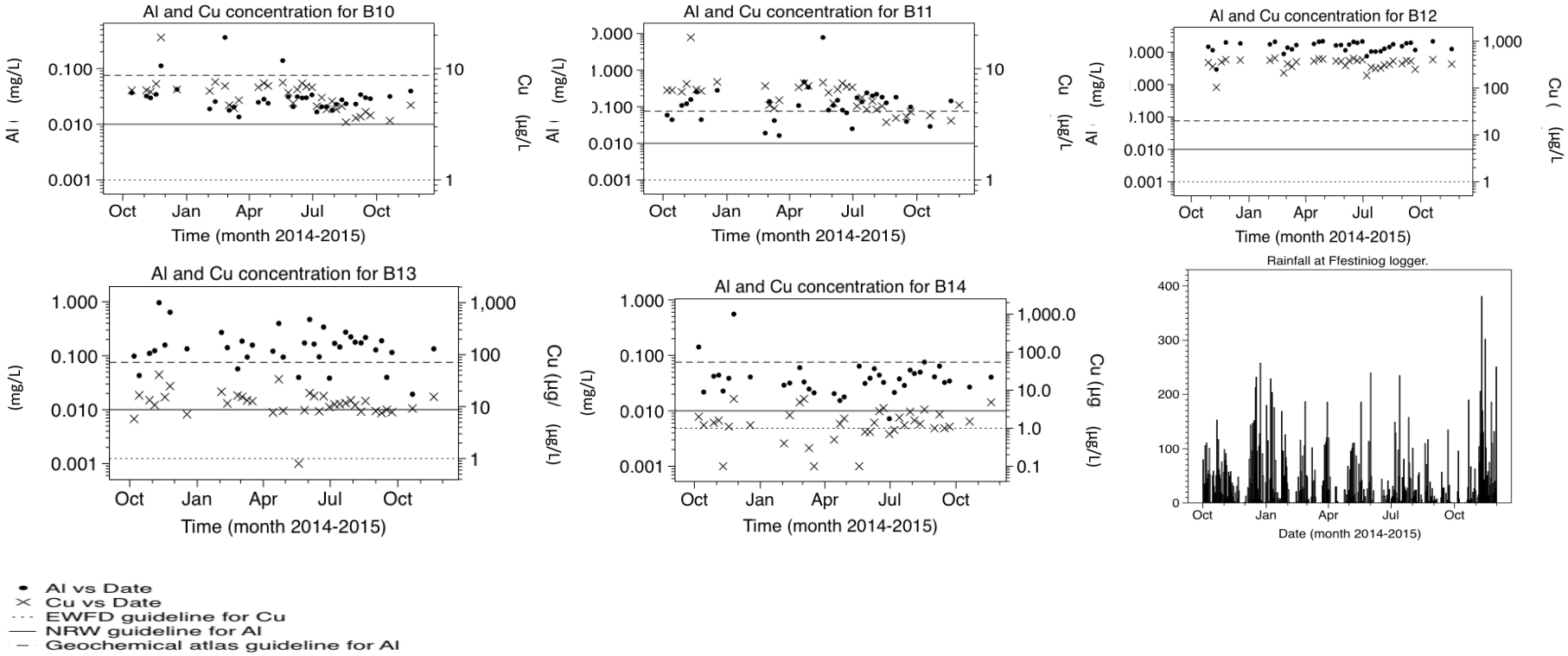


Figure 3.16b. ICP-MS analysis of Al and Cu on 14 Sites on the Barlwyd respectively

Limits used were recommended by NRW for Al and based on the geochemical atlas guidelines for the geographical area, for Cu the limit is based on the EWFD guidelines for the calcium carbonate content for the area. The left-hand axis shows Al. The right-hand axis shows Cu.

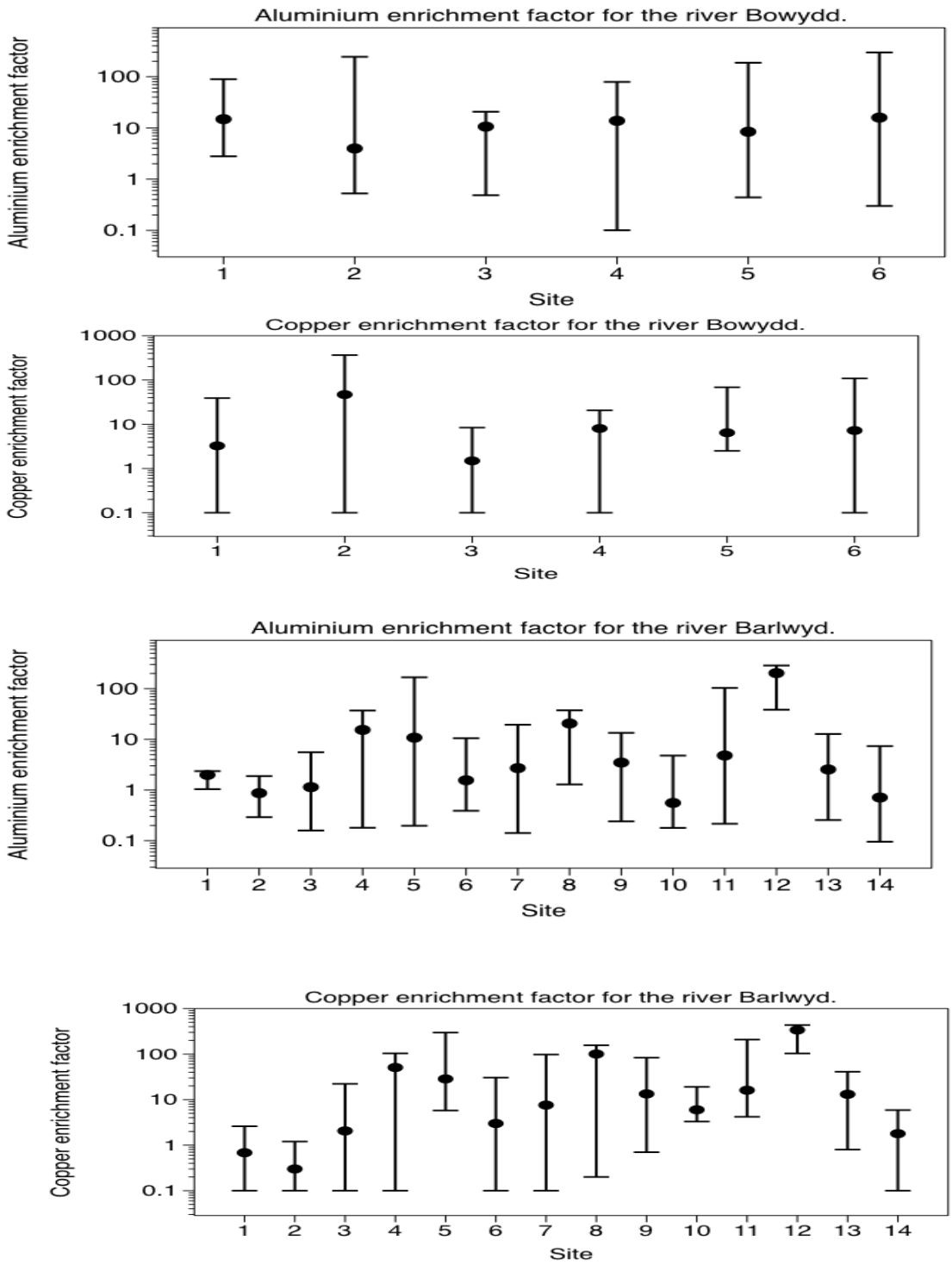


Figure 3.17 – Minimum, mean, and maximum enrichment factors for the river Barlwyd and river Bowydd

These were based on the geochemical atlas guideline for Al and the EWFD guidelines for Cu.

3.3.7 Correlations

Spearman's rank correlations were carried out to examine any positive or negative relationships between variables measured in the rivers Barlwyd or the Bowydd.

The relationship between variables Al, Cu, pH, Turbidity Flow and TOC were investigated using Spearman's rank correlation coefficient for the Bowydd (See Table 3.2). Preliminary analyses were performed to ensure no violation of the assumptions of normality, linearity, and homoscedasticity. Correlations were interpreted according to Cohen (1988, pp. 79–81). Correlations revealed a large negative correlation between TOC and Cu, $r = -0.564$, $N = 91$, $p < 0.01$. All other effects are insignificant, small, or medium.

The relationship between variables Al, Cu, pH, Turbidity Flow and TOC were investigated using Spearman's rank correlation coefficient for the Barlwyd (See Table 3.3). Preliminary analyses were performed to ensure no violation of the assumptions of normality, linearity, and homoscedasticity. Correlations were interpreted according to Cohen (1988, pp. 79–81). Correlations revealed a large positive correlation between Al and Cu, $r = 0.804$, $N = 432$, $p < 0.01$. A large negative correlation was found between Al and pH, $r = -0.675$, $N = 425$, $p < 0.01$. Cu and pH also show a large negative correlation, $r = -0.614$, $N = 426$, $p < 0.01$. All other effects are insignificant, small, or medium.

Table 3.2 – Spearman's rank-order correlations between Al, Cu, pH, turbidity, flow, and TOC in the Bowydd.

		Al	Cu	pH	Turbidity	Flow	TOC
Al	Correlation Coefficient	1.000	.309**	-.476**	.390**	-.407**	0.053
	Sig. (2-tailed)		0.000	0.000	0.000	0.000	0.618
	N	145	144	139	92	85	91
Cu	Correlation Coefficient	.309**	1.000	-0.030	0.199	.294**	-.564**
	Sig. (2-tailed)	0.000		0.727	0.057	0.006	0.000
	N	144	144	138	92	85	91
pH	Correlation Coefficient	-.476**	-0.030	1.000	-0.147	0.142	-0.080
	Sig. (2-tailed)	0.000	0.727		0.166	0.203	0.456
	N	139	138	139	91	82	89
Turbidity	Correlation Coefficient	.390**	0.199	-0.147	1.000	-0.088	-0.109
	Sig. (2-tailed)	0.000	0.057	0.166		0.525	0.337
	N	92	92	91	92	54	79
Flow	Correlation Coefficient	-.407**	.294**	0.142	-0.088	1.000	-.471**
	Sig. (2-tailed)	0.000	0.006	0.203	0.525		0.000
	N	85	85	82	54	87	53
TOC	Correlation Coefficient	0.053	-.564**	-0.080	-0.109	-.471**	1.000
	Sig. (2-tailed)	0.618	0.000	0.456	0.337	0.000	
	N	91	91	89	79	53	91

**. Correlation is significant at the 0.01 level (2-tailed).

Table 3.3 – Spearman's rank-order correlations between Al, Cu, pH, turbidity, flow, and TOC in the Barlwyd.

		Al	*Cu*	*pH*	*Turbidity*	*Flow*	*TOC*
Al	Correlation Coefficient	1.000	.804**	-.675**	.188**	-.284**	0.047
	Sig. (2-tailed)		0.000	0.000	0.001	0.000	0.443
	N	432	432	425	293	238	265
Cu	Correlation Coefficient	.804**	1.000	-.614**	.122*	-.152*	0.044
	Sig. (2-tailed)	0.000		0.000	0.037	0.019	0.481
	N	432	433	426	293	239	265
pH	Correlation Coefficient	-.675**	-.614**	1.000	-.147*	.143*	-0.072
	Sig. (2-tailed)	0.000	0.000		0.012	0.028	0.241
	N	425	426	426	293	238	265
Turbidity	Correlation Coefficient	.188**	.122*	-.147*	1.000	-0.044	-0.052
	Sig. (2-tailed)	0.001	0.037	0.012		0.576	0.424
	N	293	293	293	293	167	242
Flow	Correlation Coefficient	-.284**	-.152*	.143*	-0.044	1.000	0.124
	Sig. (2-tailed)	0.000	0.019	0.028	0.576		0.148
	N	238	239	238	167	242	137
TOC	Correlation Coefficient	0.047	0.044	-0.072	-0.052	0.124	1.000
	Sig. (2-tailed)	0.443	0.481	0.241	0.424	0.148	
	N	265	265	265	242	137	272

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

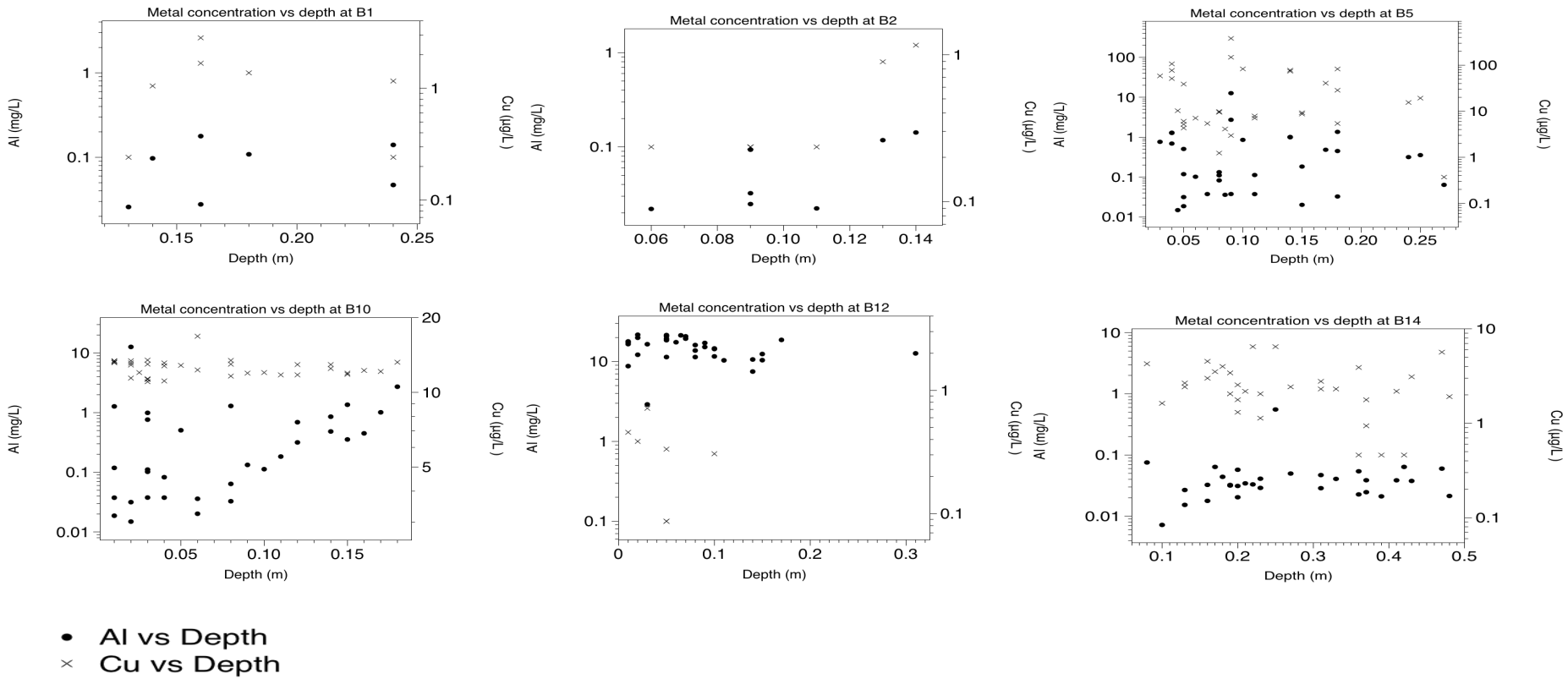


Figure 3.18 – The relationship between concentration of metals and flow depth at different sites on the Barlwyd

3.3.8 Metal flux/Load

Flux/Load was calculated according to the method of Kimball et al. (2007), the dissolved load (defined here as that passing through a 0.45 μm filter) can be defined as follows:

$M_a = C_a Q_a (0.0864)$.

where M_a is the metal flux/Load at a given location in kg/day, C_a the metal concentration measured in mg/L, Q_c the discharge at the time of sampling in m^3/s and 0.0864 is a conversion factor to obtain values in kg/day (Bird et al., 2010; Kimball et al., 2007).

Flux/Load and flow are generally quite closely related (see Figures 3.21-3.25). This is particularly true of sites B10 and B12. The effect of loading metals onto the catchment is from the B4 input can be up to 50kg/day of Al which is relatively high for the catchment. B10 an old quarry site affected shows a much lower level of loading with only 3 kg/day of Al 1 kg/day of Cu being input. At Site B12 the relationship is again close with flux very much related to flow and up to 500 kg/day of Al and 10kg/day of Cu being input into the river. At B14 the effect can be considerable with up to 100 kg/day of Al being loaded to the main body of the stream. This appears to lessen over the year, which may be the effect of quarry activity being diminished. Cu on the other hand has a much lesser loading on the river being at its highest – 1 kg/day with a similar pattern of lessening as the year goes by. Generally, the higher the flow the greater the loading, suggesting a flush of metals into the catchment at high flow as sediment is washed down. This also demonstrates the effect of the year going by there were lower activity levels.

In terms of its overall effect, we can see a high load of Al and Cu at B4 (Figures 3.19 and 3.20) being seen to extend to sites B5 and B7 downstream, followed by a reduction in load, likely associated with physical dilution at site B11 and a further decrease at B14 at high flow. At low flow, there is a lower load of Al and Cu at B4 and B7 but a higher overall effect at B11 and a comparatively similar effect downstream at B14, perhaps demonstrating the effect of B12 at lower flows. Flux and flow mirror

each other quite directly at site B5 and B12 demonstrating sensitivity of metal load to flow. However, at site B14 where there is a greater flow they are not as closely related owing to more diffuse flow input and greater flow in general with flow coming from areas without metal input, this indicates the direct influence of flow on polluted sites.

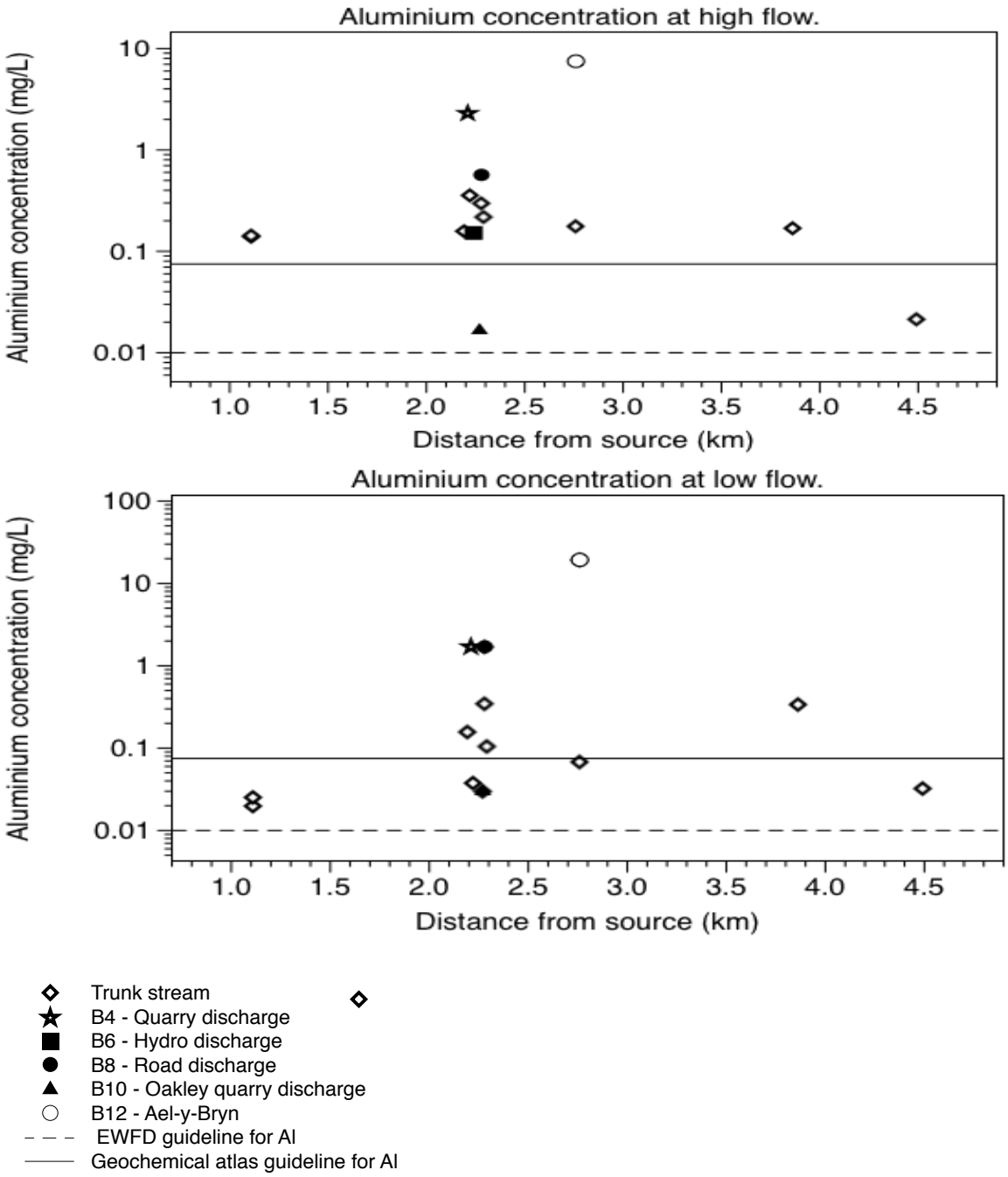


Figure 3.19 – Al concentration at high and low flow at adits and at points in the trunk stream

Geochemical atlas guides and EWFD guidelines are shown.

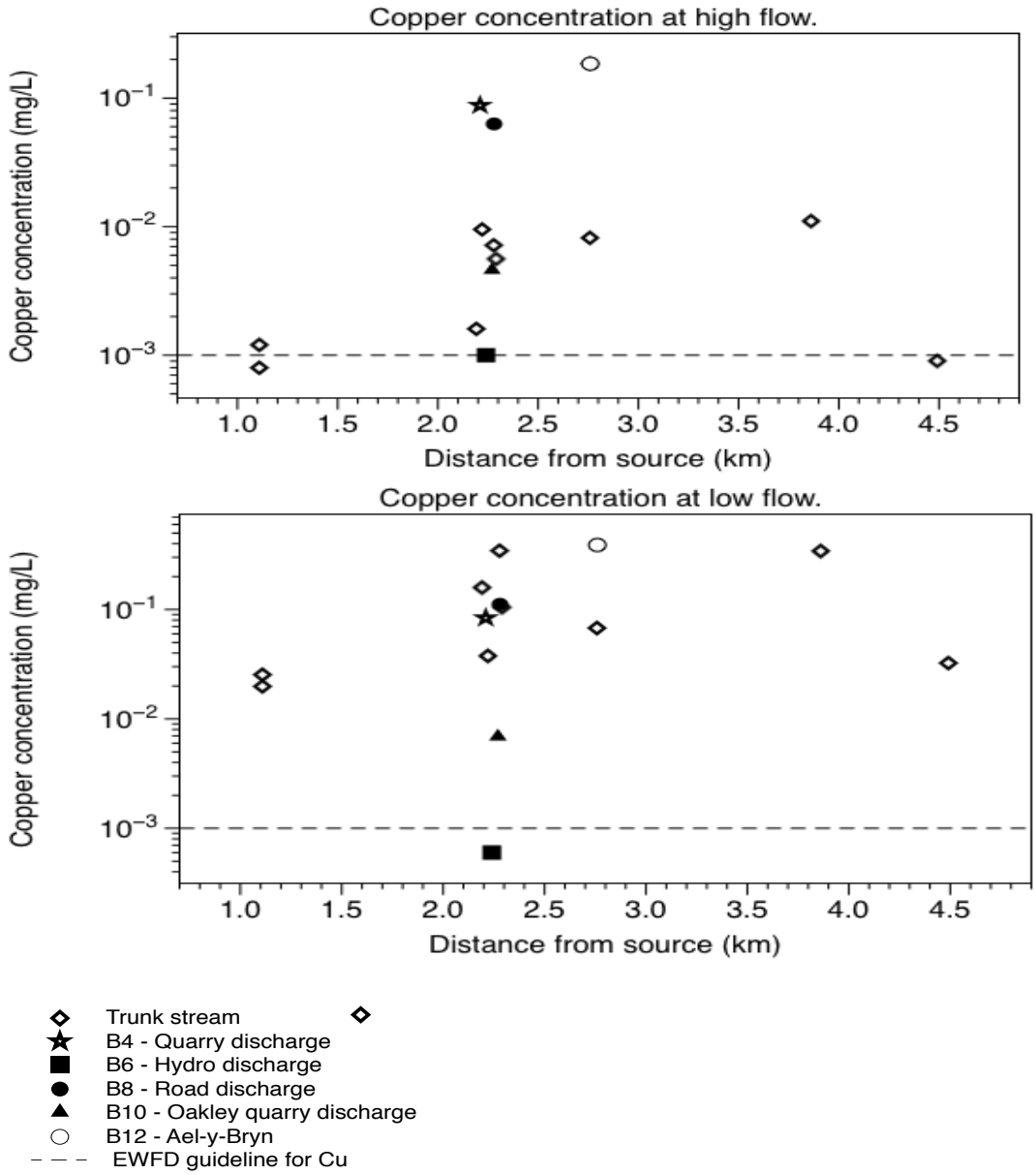


Figure 3.20 – Cu concentration at different addits and trunk stream points at low flow and high flow

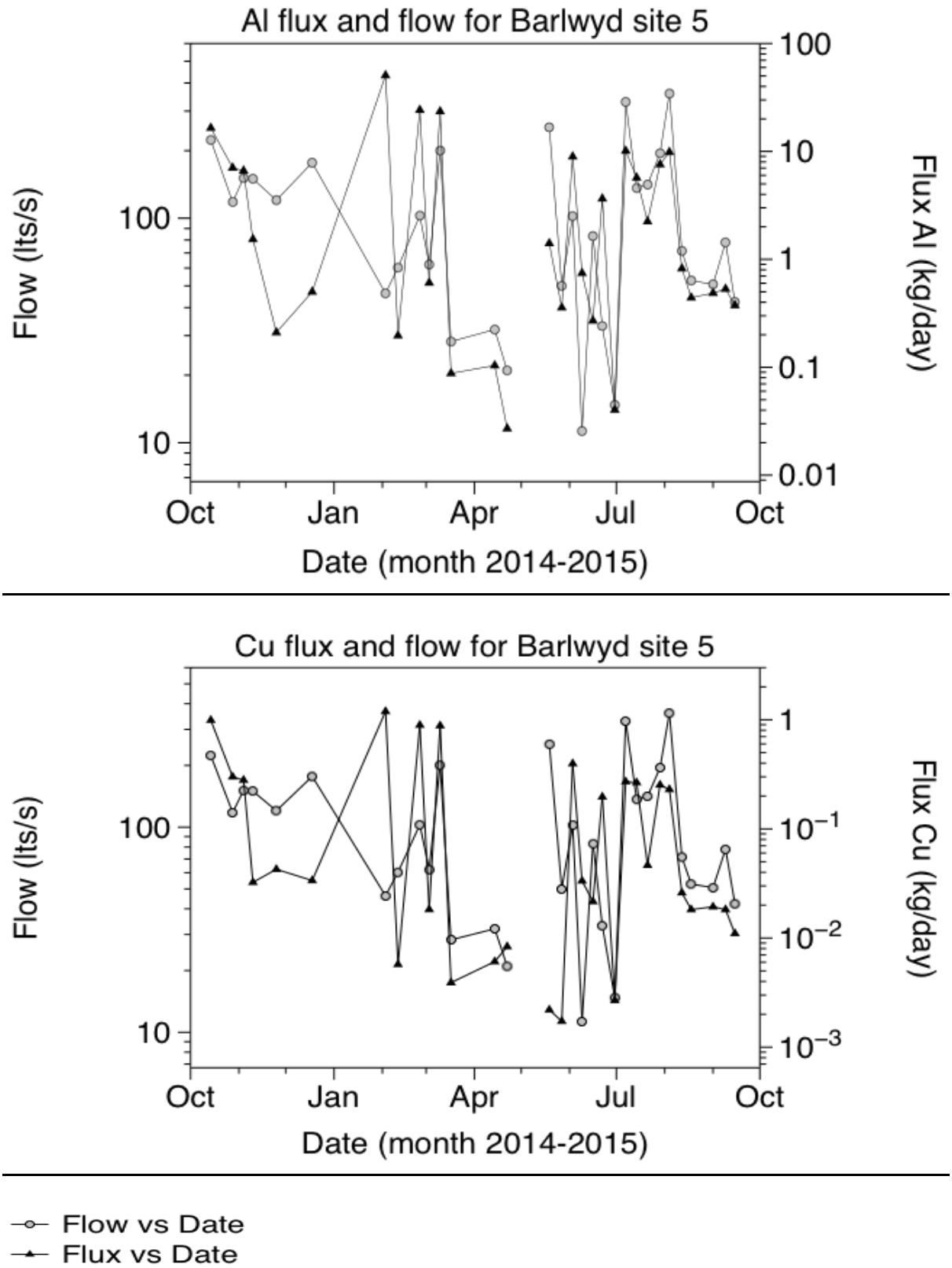


Figure 3.21 – The relationship between Al and Cu flux and flow for the Barlwyd site 5

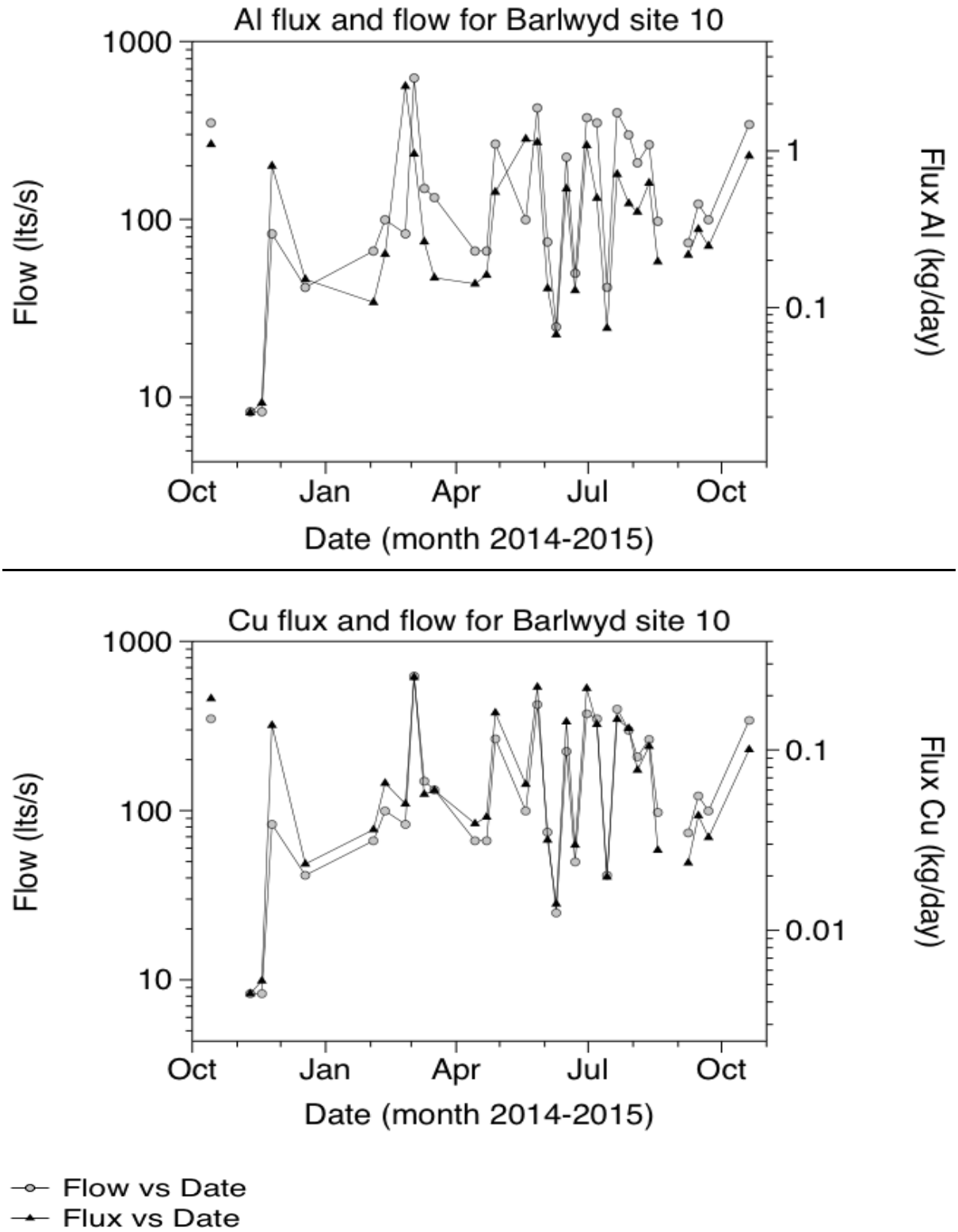


Figure 3.22 – The relationship between Al and Cu flux and flow for the Barlwyd site 10

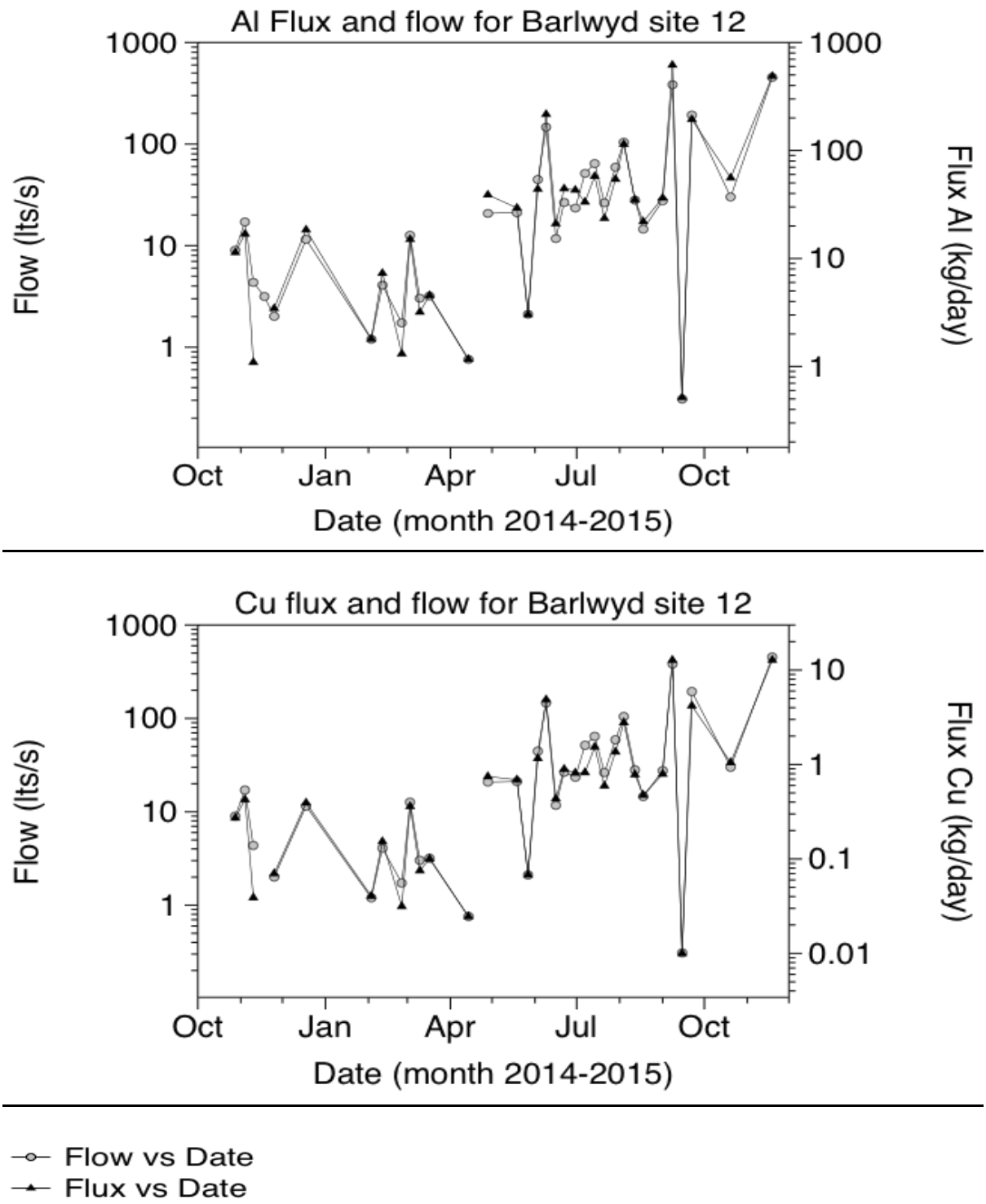


Figure 3.23 – The relationship between Al and Cu flux and flow for the Barlwyd site 12

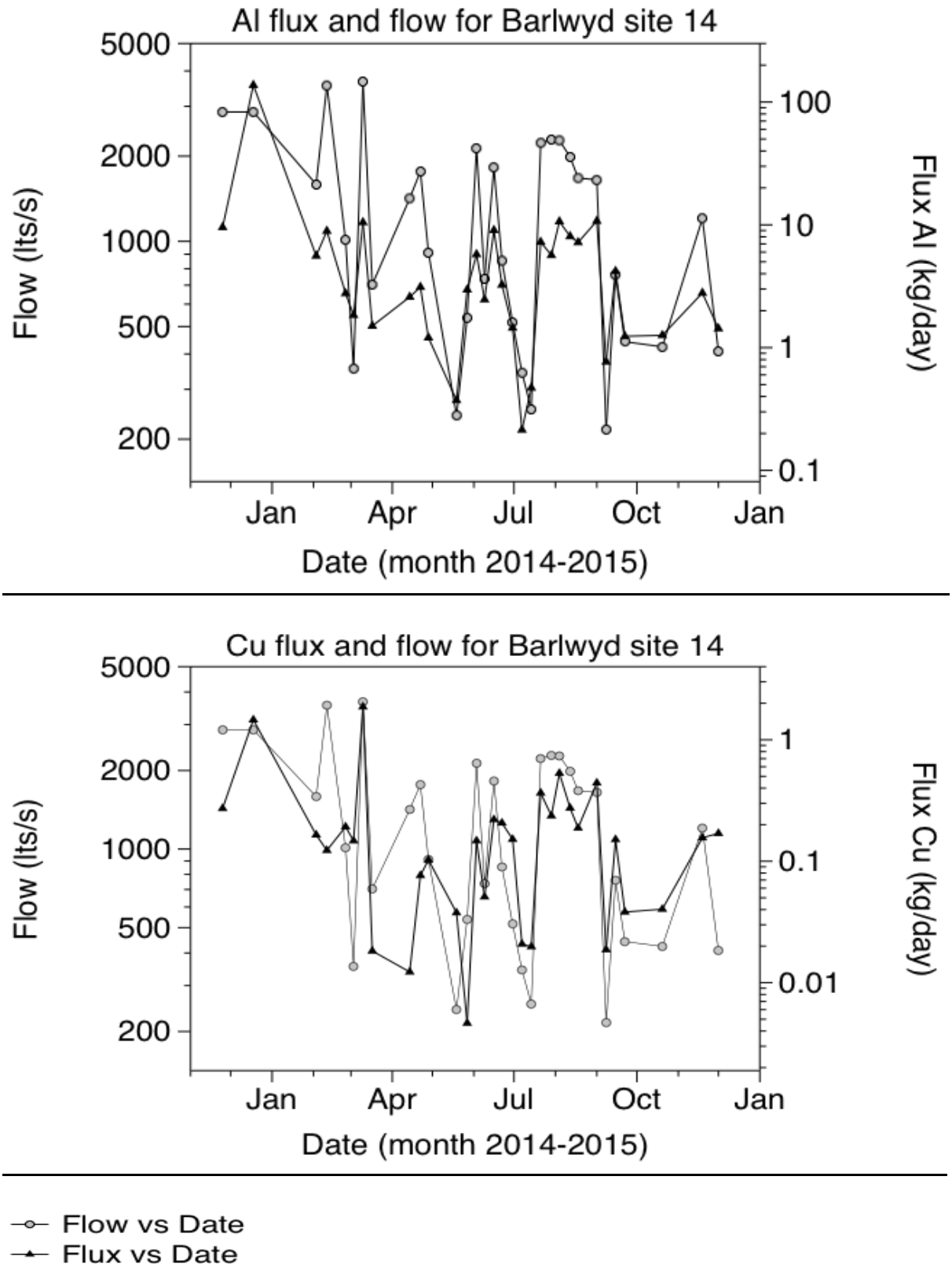


Figure 3.24 – The relationship between Al and Cu flux and flow for the Barlwyd site 14

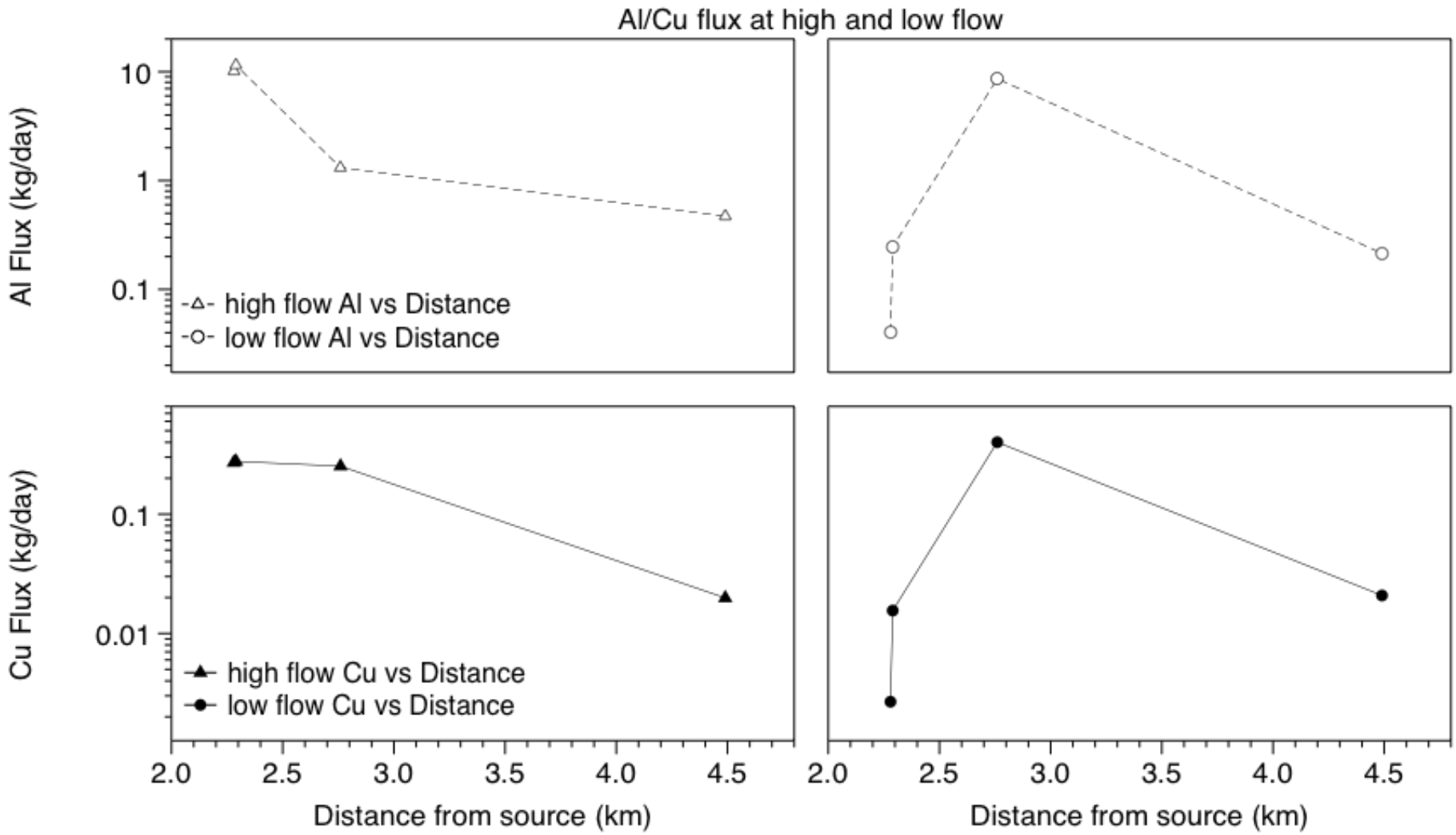


Figure 3.25 – Metal loading versus distance downstream at mixing points in the trunk of the stream

3.4 Discussion

3.4.1 Linking pollution hotspots to slate quarrying spatially for the first time.

This study was important given the lack of evidence in the literature linking Al/Cu pollution in rivers to slate quarrying. This is highly important in view of the ecosystem services that are affected by this problem internationally. Al is considered a contaminant to fish gills when the pH decreases below a certain point (Wright and Wellbourn, 2002). Cu is an EWFD concern primarily because it disrupts olfactory cues at concentrations close to or below EQS (e.g., Jones et al., 2013; Sandahl et al. 2007). The aquatic life in the river is impacted upon quite severely where the river is described as fishless in some portions. This research will facilitate global efforts to remediate rivers affected by slate quarrying.

The approach used to study this problem was to examine two rivers in 20 different locations and take samples for a yearlong study. We then processed the results looking at Al/Cu by ICP-MS. These locations were upstream and downstream of locations which have previously been demonstrated as polluted (Buss et al., 2013).

Concentrations of Al can reach up to 20 mg/L at B12 (a side adit) which far exceeds the geochemical atlas limit of 75.5 µg/L. The high loads placed on the river body from B4, B8, B12, influence water quality and consequently ecology and are indicative of a pollution hotspot. These are both diffuse and point sources of pollution, meaning that the pollution is derived not only from point source discharges but also by diffuse drainage through physical waste left on the landscape. This has been shown previously in numerous studies of metal mining-affected catchments (e.g., Pattrick and Polya, 1993; Ixer and Budd, 1998, Jarvis et al., 2008) but has been studied in much less detail in relation to slate-quarrying, with previous work focusing more on point source inputs.

The study's major finding was that slate quarrying and aquatic pollution can be linked to quarrying both by discharge from the quarry, influence by impervious surfaces and by slate tips. This can be up

to 338 times of Al can be up to 297 the amount of Cu concentrations. The high loads placed on the river body from B4, B8, B12, influence water quality and consequently ecology. These are both diffuse and point sources of pollution, meaning that the pollution is derived not only from discharges but by the physical waste left on the landscape and continuing activity in the area, urban landscape, and industrial land use. This data is of relevance to the industry globally and could be applied to policy globally in monitoring, remediation, and management efforts.

3.4.3 Streamflow impact on geochemical parameters across spatial and temporal gradients.

3.4.3.1 pH – an acidic river with pH extremes.

Generally, this is an acidic river with exceptionally low pH's at key points that are also rich in Al/Cu, which is significant for the aquatic life as these metals are more bioavailable at these points. Good chemical status for pH for rivers according to the EWFD is between 6 and 9. The majority of readings spatially were below 7 demonstrating that this is generally an acidic river, becoming more so at key pollution points upon travelling downstream and regaining a pH circa 7 at our last sampling point, B14 where there is more flow. Upstream of the site B4, the pH is between circa 5 and 7 and the pH becomes more acidic on moving downstream between sites B4-B13. Donald and Gee (1992) support the theory that water in the uplands is demonstrably acidic possibly leaching through peaty soils upstream (Saarinen et al., 2013). In Pant-yr-afon where there is a point quarry water discharge and diffuse road discharge, the water generally becomes more acidic, tending towards a pH between 4 and 6. In terms of the quarry discharge at B4, readings can at times be as low as 3.7. In Ael-y Bryn – B12, water was consistently of a pH circa 4, for the duration of the year, putting the river into poor status for the EWFD. These two locations, affected by quarrying may be indicative that the oxidisation of slate by water runoff may acidify the pH and thereby cause dissolution of metals (Herrmann et al., 1992). In terms of pH this portion of the Barlwyd is not suitable to support aquatic life and fails a chemical indicator of the EWFD. Other studies by Pryce and Janes (2009) and Buss et al., (2013), reinforce these results further. A good body of evidence supports the argument that acidic

conditions are dangerous for aquatic life. Nichols and Bulow (1973) are a classic example, whence it was shown that acidic discharges from quarries were responsible for the death of fish in the Obey river in Tennessee (Evans, 2011). Cooper and Wagner (1973) also examined the effect of acidic discharges because of quarrying and found that this was a major cause of fish deaths in Pennsylvania, USA (Evans, 2011). Extremely low pH of circa 4.5 could be responsible for the total fish losses in 90% of the sampling locations. They also found that only 10 out of 116 species found were resilient enough to withstand pH's of 4.6-5.5. The low pH's found at quarrying pollution hotspots could be seen to parallel this study and hence the poverty of aquatic life found. To support aquatic life, Cooper and Wagner (1973) claim that pH needs to be more than 5.5. Thus, one primary effect, or component affecting fish life could easily be attributed to low pH. Further downstream in the Barlwyd, at B14, the higher pH is much more appropriate to support fish life, although the levels can sometimes again drop to circa 4, which correlates with previous biodiversity abundance and species richness data.

3.4.3.2 pH and Cu/Al relationships

Low pH values in streams of the study area generally coincide with high concentrations of dissolved trace metals because acidic conditions contribute to trace-metal mobilization and transport (Moran and Wentz, 1974; Kimball et al., 1994; Broshears et al., 1996). Dissolved Al concentrations are shown to be extremely dependent on pH, and the hydrologic system (Stumm and Morgan, 1996; Nordstrom and Ball, 1986; Schemel et al., 2000). In the presence of Fe and Al precipitates, Cu concentrations can decrease with increasing pH values (Smith, 1994). Cationic Al 3+ is demonstrated to be regulated by hydrogen ions, ionic strength, organic matter and temperature (Evans., 2011). This is because there is and increased competition for binding sites between metals and hydrogen ions, dissolving carbonate metal ions, which releases free metal ions into the water column (Foster and Charlesworth, 1998). Therefore, levels of Al and Cu, and low pH combined do not support aquatic life. Apodaca et al. (2000) show that mining is responsible for a high concentration of Cu in the basin of Blue

River, Summit County, Colorado. In contrast, high pH values are associated with areas where rocks have substantial acid-neutralizing capacity and commonly coincide with low concentrations of some trace metals, such as Al and Fe. Other trace metals such as Cu may adsorb to the precipitated solids (Church et al., 1994; Schemel et al., 2000). The geology in a watershed plays a crucial role in determining the pH of streams. Low pH values in streams occur where sulphide minerals are present overall, or where minerals such as calcite, with significant acid-neutralizing capacity, are absent (Plumlee et al., 1993; U.S. Environmental Protection Agency, 1994). Thomas (2010) shows in an MSc project on the Barlwyd, that there is a high level of sulphate ions in the Barlwyd, which indicates this may be the case. At B4/B5 the consented discharge is mainly responsible for the pollution. Processes responsible could be rock weathering at B12 as there are no obvious sources. There is point road runoff also at B8 where concentrations are higher. These processes could apply to other rivers internationally.

3.4.3.3 Electroconductivity indicative of quarrying pollution.

Hotspots for pollution where Al and Cu are found in high abundance coincide with higher electroconductivity, which is indication for high levels of metals. This is evident in B4 and B8 and particularly B12 which is borderline safe limits (WHO, 1992). Conductivity is affected by temperature. However, the electroconductivity is within the normal background range for river, with some higher levels for B8, and B12, where higher levels are found. This may be because of the low pH at these locations could cause the salts to dissociate from metal ions and be found in an ionic form as opposed to being bound to metals and DOC.

3.4.3.4 Turbidity

Suspended matter content, or turbidity, plays an important role in defining the primary production and overall quality of aquatic habitat, acting as a pollutant (Bash et al., 2001; Birtwell et al., 2008; Tananaev and Debolskiy, 2014). Sediment particles also play an important role in transporting other pollutants such as Al and Cu metals in this mining systems (Literathy et al., 1994; Lacour et al., 2009; Tananaev and Debolskiy, 2014). Raised turbidity will elevate water temperature, lower dissolved oxygen, stop light from reaching aquatic plants which lower's their ability to photosynthesize and damage fish gills and eggs (Cordone and Kelley, 1961; UNESCO, 1996). Furthermore, in many countries, turbidity itself is a controlled water quality parameter, as defining organoleptic properties of drinking water and water treatment effectiveness (Lewis, 1996; Marquis, 2005). It was discovered by DeNicola and Stapleton (2002) that dissolved heavy metals in the water column had a greater impact on invertebrate communities than substrata coated with metal precipitate (Byrne et al., 2009). Thus, in the case of the river Barlwyd and Bowydd, the rivers could be more affected by the dissolved rather than the suspended load. Pryce and Janes (2009) claim that discharges from quarries such as Llechwedd and Ffestiniog contain much raw material, such as slate dust, which can pose a problem in terms of turbidity. Although there were no instances during the year of sampling of observations of high levels of turbidity, there were anecdotal reports of this type of water made during that year. This was attributed to the onset of flash storms. Generally, a dry period followed by a storm seems to cause a first flush effect on the river, and increases in turbidity (Evans, 2011). It is thought that turbidity levels of 50 NTU are the highest level that can support aquatic life (Evans, 2011) and although there are instances of 100 NTU in this dataset, this is due to organic matter during periods of heavy flow, which was evidenced by eye/flow data. The levels of turbidity are mostly low, possibly owing to a reduced level of activity in the quarry over the year. The last sampling date shows a higher level of turbidity which was during a winter storm. Chapter 4 goes on to examine storm influence on hysteresis and geochemistry.

3.4.3.5 The positive effect of TOC – influence of TOC and Al/Cu binding.

Within the context of pre-existing research into Al and Cu in rivers, TOC data sets are rare. TOC concentrations on these rivers are not particularly high, ranging between 0.1 mg/L and 13 mg/L. Dominant landscape types can be affected by sources and controls of headwater streams (Tiwari et al., 2014). Of note is that B6 is a higher average point spatially, which may result in TOC binding to metals and having a positive effect by ensuring that it is not in its bioavailable form, as metals coincidentally decrease before B7, this may be the case, but it could be simply owing to dilution given the degree of standard error. Cu and Al both tend to form strong complexes with organic ligands, as evidenced by the biotic ligand model in Cu's case (Di Torro et al., 2001; Santorre et al., 2001; Niyogi and Wood, 2004) and by previous work on Al (EA., 2012). This can decrease its biological availability (Wright and Welbourn, 2002). In terms of Al toxicity, Kroglund et al. (2002) shows that TOC can affect Al mobilisation and speciation. Increases in organic matter could lead to reductions in Al-related toxicity but can also result in increased concentrations of cationic Al as total Al is increased and pH is reduced. TOC fractionation is a concern in Fe and Al rich systems (Smith et al., 2015), and it was noted that Fe levels were comparatively high in concentration in some sites. The TOC data is significant for developing an Al biotic ligand model in the future.

Temporally, since higher extremes of TOC occur in summer, it could be that the drying of soils creates a wash-off effect in the summer as the soil will be looser and less clayish, resulting in a first flush effect in soil, also meaning that there could be a runoff effect in the soil with regards to TOC output into the river, although the impact would generally be associated with summer storms. However, as flow is predicted to be less in summer with more frequent drought due to climate change perhaps the amount of TOC washed into the river in summer flows will be less overall.

In terms of future management, a novel approach could be to use DOC to lessen the impact of metals on the river by flushing the river with DOC, although this would have to be done with caution so as

not to alter the environment too much. However, it would be an economically and environmentally friendly option for remediation.

3.4.3.6 Magnitude of impact of streamflow chemistry on water quality

There is a spatial link to the quarry with regards to influx of Al/Cu and high flow. Quarry sediment is certainly evidenced to be washed out suddenly into the river when quarrying activity is high (Evans, 2011) and can be linked to a decrease in biodiversity and poor ecological status in the river. Al/Cu can at times be greatly enriched; up to 200-300 times that of suggested limits. This certainly influences the water course, especially when combined with low pH. The flux and flow show that the load can be related to the flow, and that they correlate with each other at pollution hotspots. As water flow increases the absolute Al and Cu flux rises in each site respectively reflecting ingress of surface waters into the workings and flushing of metals as noted by other researchers in metal mining (Nordstrom, 2009). The relative contribution of point sources to the catchment outlet lessens as the flow becomes larger and the importance of diffuse flow from the catchment becomes more important as can be seen in B14. This is illustrated at high flow in metal loading diagrams (Figure 3.25). These graphs are useful in targeting key sources of instream metal flux.

3.5 Conclusions to apply to industry practice, regulation, and government policy.

This research has demonstrated several novel findings. Data shows a link between quarrying activity and pollution spatially implying global significance for remediation efforts and management in the future. There is evidence for the influence of both point and diffuse pollution from slate quarrying. It is also demonstrated that there is a positive effect of DOC on Al/Cu binding. This leads to ask could DOC improve river pollution. A novel dataset linking Al and DOC has been created which could be applied in an Al biotic ligand model to develop a more founded EQS. Temporal patterns are significant in terms of climate change, with low flows associated with more concentrated waters and higher flows associated with a larger flux. There is a relationship between flux in stream waters with

flow spatially, this is significant in terms of climate change and management considerations. pH is exceptionally low at locations where metals are in high concentrations. A unique pollution hotspot was identified at site B12 with the possibility for future study as a biological anomaly perhaps for the study of extremophiles. The river is identified as failing on chemical EWFD objectives. Causes of pollution could indicate pollution both from the slate tips and from the quarry waste which are important considerations for future management. The diffuse source of pollution is important in flow management considerations around slate quarrying areas. In this river that there are locations where the weathering process is critical, meaning that both management and land-use have not been used appropriately in these areas of the catchment. This research aptly leads to the question following in Chapter 6 which concerns pollution under storm conditions and thus leads the focus to the future and climate change.

3.5.1 Significance of findings to the management of slate quarrying for the environment in the future.

The novel findings have significance to the slate quarrying industry globally. The evidence that quarrying negatively impacts the waterbody creates a challenge for future management. It creates a justification for funding into future work addressing the problem and implications for policy and better management of waste in slate quarries. Given that this resource is both (a) in demand and (b) limited, a better use for the slate tip waste could be a solution to both (a) pollution and (b) resource limitation.

Furthermore, water around quarries needs to be managed carefully and any contaminated water may be a source for remediation efforts or metals could be reclaimed from the waters and put to practical use. Diffuse waters are a problem and given the scale of the impact of the slate waste a solution for water management around the tips needs to be developed. All affected water sources need to be targeted before they arrive at a waterbody without removing materials such as DOC which are needed in for balancing the ecology of the river.

3.5.2 Study limitations and future research directions.

3.5.2.1 Study limitations.

Practically the work was limited by practical considerations such as budget, weather, time, and availability of support. In the future sampling could be automated to improve efficiency. Furthermore, a tracer could be used to measure flow. Equipment failure could at times be an obstacle to success.

3.5.2.2 Future directions.

Additional future work could examine ions as CO_3^{+} (carbonate) and SO_4^{2-} (sulphate) and look at the effect of sediment and storm conditions on this type of pollution. Eh could also be measured to determine the form in which Al/Cu can be found. Some of these issues will be addressed in future chapters.

Interesting work could examine the interaction chemical reactions of rainwater and slate to establish how the process of pollution may occur in the slate tips. This could lead to novel solutions for remediation efforts.

These findings lead on to the future work in Chapter 4 – where the effect of storm hydrology is examined, Chapter 5 where the effect of sediment is examined, and Chapter 6 where study of remediation options is investigated.

CHAPTER 4 – THE EFFECT OF STORM HYDROLOGY ON THE GEOCHEMICAL DYNAMICS OF THE BARLWYD CATCHMENT IN RELATION TO AL AND CU

4.1 Introduction

Several researchers have previously described a post-rainfall flushing phenomenon which occurs in catchments which are affected by mining (Nordstrom, 2009; Lee et al., 2002; Lee et al., 2004; Bach et al., 2010; Bertrand-Krajewski et al., 1998). Indeed, research conducted by Evans (2011) on the Barlwyd describes the anti-clockwise pattern of hysteresis which occurs in the river with turbidity and clockwise hysteresis with metal concentrations in response to changes in discharge. This demonstrates that storm events have the potential to negatively impact aquatic ecology due to the enhanced delivery of metals, acidity and creation of elevated turbidity.

The aim of this research is to examine the effect of storm hydrology on Al and Cu concentrations and geochemistry in the River Barlwyd. This builds upon the establishment of longer-term temporal trends in geochemistry and discharge, evaluated in Chapter 3. This is particularly important with regards to future pollution events globally which are linked to climate change, where in the future it is predicted that there will be a greater frequency of winter storms for the UK, and an increase in storms generally (IPCC, 2014). Climate change is expected to affect mineral processing operations (UNEP-FI and SIWI 2005; Brown et al., 2006; Lemmen et al., 2008) The effect of winter storm events has already been documented by researchers who have reported death of cattle on flood plains owing to metals being flushed downstream from abandoned metal mines (Foulds et al, 2014). Researchers have noted seasonal variation of zinc from mines in river systems (Gozzard et al., 2011), as well as flood related risks where release of acid rock drainage and other contaminants to the environment is a concern or remobilisation of pollutants (Pearce et al., 2011; Dennis et al., 2003; Cizweski et al., 2016). Since these mine processes are highly water dependent, increased water scarcity could influence production rates, dust suppression efforts, mine drainage, and the covering of tailings (Kyhn and Elberling, 2001; Bjelkevik, 2005; IPCC, 2007; Pearce et al., 2011).

The River Barlwyd has been shown to receive acidity from quarrying-related sources (Chapter 3), reflecting the oxidation or iron pyrite and the flushing by rainwater as it filters through waste heaps (Hermann, 1989). In the case of the Barlwyd the river receives acidic water from the uplands which is influenced by peat which compounds problems. These acidic conditions can worsen pollution by increasing the competition for binding between metals and hydrogen ions and dissolve carbonate ions by releasing free ions into the water column (Foster and Charlesworth, 1998; Evans, 2011). Further impacting on water quality, Pryce and Janes (2009) evidence that the quarry creates a lot of raw material which is primarily composed of slate dust, which can cause high turbidity. This can contain high concentrations of Al and Cu at key inputs (Chapter 3) and can also contain high levels of sulphates (Thomas, 2010). This emphasises the need for research on the effects of storms on concentration of Al/Cu in the river, the geochemistry, and thereby predicted biotoxicity and bioavailability. In free ion form, which is controlled largely by pH and redox, metal ions are more toxic (Foster and Charlesworth, 1998). The pattern of metal release during a storm in relation to flow can give clues as to the processes and sources which are responsible for the presence of higher levels of metals during a storm (Evans, 2011). Studying storm events can reveal the relationship between concentration of metal and discharge. This is particularly important with respect to the EWFD and efforts to clean water in the area, by projects such as the "Dref Werdd". There is a dearth of evidence in the literature which examines the effect of storms on slate mining pollution, which emphasises the need for research.

4.2 Aim and objectives

The aim is to study the storm-driven high discharge geochemical response of the river Barlwyd in terms of pollution.

The objectives are:

(1) Establish sources/process of mobilisation of pollutants by analysing storm hydrographs.

(2) Investigate metal speciation during storm events.

4.3 Materials and methods

4.3.1 Site selection

To observe the impact of rainfall on the catchment the effect of intense rainfall was measured in detail. One storm was sampled on the 29/06/2016. Three sites, B5, B12 and B14 were selected for sampling and B1 data from Chapter 3 was used as a control as sampling methods would be too difficult in terms of addressing health and safety in this site. Sites B5 and B12 were chosen as they are major potential pollution contributors, with site B14 situated on the trunk stream downstream of these two sites (see Figure 4.1).

4.3.2 Field sampling

Initial water samples were taken prior to the storm commencing when setting up the stations. Water samples were taken during storm rainfall conditions every 20 minutes at B5 and B14 and, owing to difficulties faced with sampling (light cover/volunteer numbers/health and safety), every 30 minutes - 1hr at B12. Sampling was conducted as described in Chapter 3. Measurements of turbidity, pH, and EC were taken, as described in Chapter 3. Eh was also determined. This study used a HANNA electrode, calibrated with Zobell solution, to make measurements of Eh, Eh is another term for redox, and can affect solute metal mobility in the aqueous environment and bioavailability and toxicity to organisms (Millero, 2001). However, as argued by Runnells and Lindberg (1990) and Pehkonen (1995), there are problems in attaining reliable field-measurements of Eh with commonly used Pt

electrodes. Macalady et al. (1990) suggest that factors such as electrode poisoning, O_2 adsorption by the electrode, system disequilibria and the presence of colloidal material could all be reasons for a lack of an ideal response of Pt electrodes in natural waters. However, Nordstrom et al. (1979) have argued that Pt electrodes may give reliable measurements in Fe-rich acid mine waters.

Flow depth and velocity were measured as described in methods Chapter 3. Samples were analysed for Al and Cu concentration by ICP- MS (Section 6.1.1.3). ICP quality control data is shown in Table 4.1 below.

Table 4.1 – ICP quality control data.

	Al	Cu
% Precision	4.1227	3.441
% Accuracy	0.867	5.148
RPD	-5.818	-0.365
RPD 2		
Scaled difference	44.675	1.848

4.3.3 TOC

TOC was measured previously in Chapter 3. Accuracy was determined by using solutions of a known concentration every 7th sample and found to be within acceptable ranges. TOC was calculated using a regression curve formula; regressions were found to be within acceptable ranges for each calibration curve, r^2 = 99-100%.

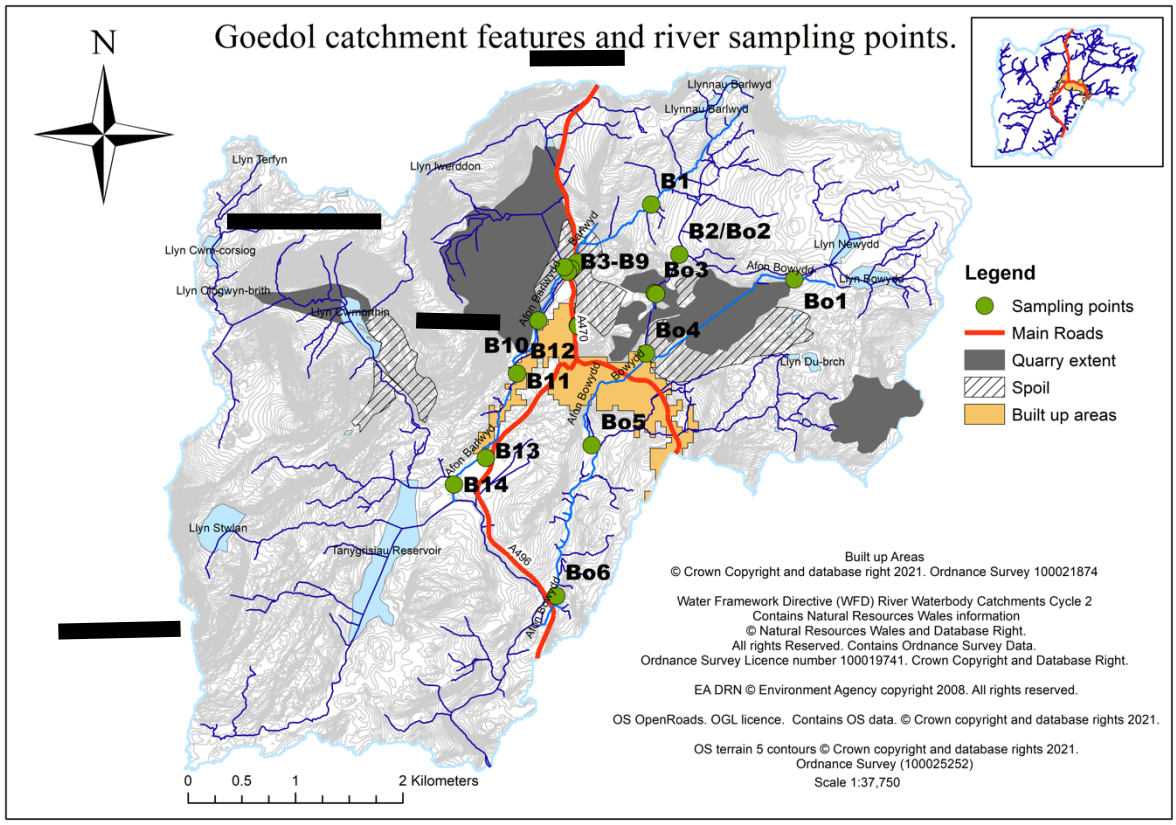


Figure 4.1 – Map of the catchment showing study sites

In this instance sites B1, B5, B12 and B14 were used as key sites from the river Barlwyd which are underlined in black.

4.4 Results

4.4.1 Flow and Rainfall

One storm was analysed on the 29/08/2016. Generally, rainfall data steadily rises through the morning and peaks at between 9.00 am and 10.00 am with a maximum of 0.74 mm falling at that time and steadily decreases to about 0.4 mm during the storm. Despite these recordings there were dry periods towards mid storm, which is when we decided to cease measurements. The storm was quite heavy in rainfall at the beginning of the storm and would be representative of storm conditions.

When the first sample was collected at 09:00 am the flow was 355.70 /s (see Figure 4.2) at site B5. Flow increases intermittently and then peaks at 12.00 pm with a peak of 5935.12 L/s. The trend then follows the rainfall pattern of decline to 887.11 L/s at 15.00 pm. Anecdotally the rain had stopped at this point, which may show that the weather station was affected by local variations due to rainfall. Flow varies according to rainfall and delivery variations in catchment. The measurement interval was more frequent at this catchment than rainfall measurements at times. The rainfall and flow show a clockwise hysteresis, where the rainfall pattern directly follows the flow variation. There is a lag time of 3 hours, where the flow steadily catches up with the rainfall profile.

With regards to flow at B12 when the first sample was taken at 7.12 am at which point the flow was at its lowest at 117.58 L/s, it peaks at 12.25 pm to 1090.81 L/s (see Figure 4.3). The flow begins to decline at 1.12 pm to 1068.18 L/s but not considerably, this is owing to the catchment still being saturated and delay in reaching the receiving stream. The pattern is reflective of rainfall, however owing to measurement difficulties at this site, we were unable to gain any later readings. The lag time here is 2.5 hours, which is relatively short. Perhaps this is owing to the slate porosity and nature of the site being largely altered anthropogenically meaning a flashier catchment.

The flow is of greater volume at site B14 as it is situated downstream (see figure 4.4). The first measurement taken at 6.41 am 3448.78 L/s peaks at 11.40 am at 20010.86 L/s and declines to a lower value of 9595.94 L/s when the rainfall had ceased. Again, the rainfall data pattern largely follows this trend but was subject to local variations so is not wholly reflective of what was occurring at this site as it is lower in elevation. The lag time here is longer at 3.5 hours, probably owing to being downstream and travel time for the tributaries is further to reach receiving river.

4.4.2 Geochemical and metal results by site

4.4.2.1 Control site

Background samples taken in Chapter 3 for site B1 are used for a control and show that during high flow (give discharge range) metal levels are around the limits for the EWFD for Cu (1 µg/L for Cu) and the geochemical atlas limit for Al (75.5 µg/L) for both Al and Cu (Al= 0.178 mg/L, Cu = 1.3 µg/L for Cu). The average pH is 6.17 and the TOC is 3.4 mg/L. The EC is low at 27 µS.

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4.4.2.2 pH

The pH measuring equipment for site B5 failed, but despite this initial measurement show that this is lower than guidelines for fish life with two measurements on the rising limb of 4.88 and 4.64 (Figure 4.2). Evidence in Chapter 3 at this site indicates that the pH decreases with increased storm flow. At site B12 pH is lowest at 7.12 am at the beginning of the storm (3.98) and has a peak 12.12 pm (5.28) (Figure 4.3). It can be observed that the pH seems to increase with on the rising limb of flow and this is possibly due to the pH of rainwater increasing the pH as the storm progresses. On the falling limb at 1.12 pm the pH decreases again to 4.84, this flow coincides with lower levels of metal which affects bioavailability of Cu and Al (see Figure 4.3). The pH affects bioavailability by determining the form of Al/Cu found; the pH at this site is generally low as found in Chapter 3.

4.4.2.3 Turbidity

The turbidity at site B5 is high at the on the rising limb of rainfall suggesting an initial flush of materials which may contain metals (Figure 4.2). The first sample was taken at 9.00 am (31.9 NTU) and 9.51(15.8 NTU), which is after the storm had commenced. This turbidity remains characteristically high with a turbidity of 9.69 NTU at 10.23 am, 7.29 NTU at 11 am and 5.02 NTU at 11.27 am. The flow data shows that the peak of turbidity occurs at the beginning of the storm before the peak in discharge. This suggests that at peak flow discharge dilutes the material (peak flow = 12.25 pm; turbidity = 2.91 NTU), and that material is flushed out in a 'first flush' (Nordstrom, 2009). The average is 5.67 NTU between the maximum and minimum (1.9-31.9 NTU). The lowest turbidity is at 2.30 pm at the end of the storm (1.9 NTU) when water was diluted. Turbidity levels remain within EWFD guidelines.

Turbidity increases with the rising limb of rainfall at B12 (see Figure 4.3). The first sample has relatively high turbidity at 5.54 NTU. But when the second sample is collected at 11.42 am in peak storm flow conditions the turbidity peaks at 119 NTU, which is exceptional. This is indicative of fine material present with turbidity increasing by 20 times and cannot be explained by concentrations of TOC alone. It varies considerably during the storm but is slow to decrease on the falling limb with high levels at 1.12 pm at the end of measuring (87 NTU), before returning to pre-storm levels at a turbidity of 7.42 NTU at the end of the storm at 1.43 pm. This data is indicative of pollution sources upstream.

Generally, the turbidity increases at this station as the storm progresses but not dramatically at site B14 (see Figure 4.4). At 6.41 am the turbidity is 1.1 NTU. This then ranges between 0.93 NTU and 4.5 NTU with an average of 2.08 NTU. The maximum of 4.05 NTU occurs at 10.40 am, on the rising limb when the storm is beginning. This shows that the storm shows a clockwise hysteresis with regards to turbidity. The minimum turbidity of 0.93 NTU occurs at 12.40 pm during the descending limb, and then returns to normal at the beginning of the storm. This suggests that the storm is

transporting material at the beginning, and then diluting material to a large degree as the storm progresses. It is illustrative of a 'flushing phenomenon', although this should be considered in view of results at other sites too, which show a pattern of decreasing turbidity as time passes. Polluted sites (B5) show "clockwise" hysteresis, i.e., higher concentrations during the rising limb of the hydrograph compared with those measured during the falling limb.

4.4.2.4 Al and Cu concentrations

Figure 4.2 shows that the Al and Cu concentrations show a negatively correlated pattern with rainfall and flow. Al and Cu decrease in concentration on the rising limb with an initial with rainfall at lower flows at site B5. The first samples at the beginning of the storm at 9.00 am were at their peak (Al:0.319 mg/L and Cu 20.2 μg/L). The Al (0.319 mg/L) concentrations and Cu (20.2 μg/L) concentration were at their highest when the turbidity is at its highest. The Al (0.121 mg/L) and Cu concentration (1.9559 μg/L) were at their lowest at 10.40 am when the flow was increasing. Site B12 also shows a high concentration at the beginning of the storm. Figure 4.3 shows that Al/Cu concentrations decrease during the storm period at site B12. When the first samples were collected at 7.12 am background concentrations of Al and Cu were high 8.563 mg/L and 216.64 μg/L which exceed recommended limits 114 times for Al and 216 times for Cu in terms of enrichment. Al concentration was at its lowest at peak flow -12.25 pm (2.362 mg/L) again suggesting a dilution of Al as the storm progresses. Cu is at its lowest at 1.12 pm on the descending limb of rainfall with a concentration of 93 μg/L which still far exceeds the limit set by the EWFD. The range for Al is 2.362-8.563 mg/L with an average of 3.741 mg/L and the range for Cu is 93.4-216.6 μg/L with an average of 121.7 μg/L. Perhaps the load would more accurately reflect metal content related to flow. This shows that the flow thus affects the concentrations of Al/Cu and turbidity during a storm, and that metals were transported in the initial portion of a storm and then diluted as the flow increases, showing evidence of the flush phenomenon observed by other researchers. The high turbidity also suggests sediment transfer initially from the quarry. It is clear therefore that turbidity and Al/Cu

concentration are linked. Downstream at B14, a different story emerges. Al concentrations gradually increase with the ascending limb of flow at site B14 (see Figure 4.4), but not to a degree which approaches the geochemical atlas guideline of 75.5 μg/L for the area, but it does exceed the suggested EQS of 10 μg/L. This conflicts with data upstream which show a decrease in Al and Cu levels. Cu remains at a steady level throughout the storm and continues to exceed the EWFD limit of 1 μg/L. The maximum of Al (0.0544 mg/L) occurs at 2.00 pm at the end of the storm whilst the maximum of Cu 2.728 μg/L occurs at 11.00 am approximately coinciding with peak flow. As the flow peaks the concentration of Al/Cu decreases reflecting the dilution by flow. Al concentration varies more than Cu (Al range: 0.0265- 0.0544 mg/L, average; 0.0416 mg/L), (Cu range: 1.7523-2.72 μg/L, average: 2.176 μg/L). The level of Cu is still twice the recommended limit by the EWFD, but in view of speciation bioavailability and toxicity the Eh-pH diagrams which will be discussed later perhaps this is not so important. The level of Al is above at B14 EQS set by NRW but below geochemical atlas guides and considerably lower than adits near the quarry. In terms of concentration this exceeds guidelines. The peak of Al does not coincide with flow. This means that peak levels of flow occur after the peak of Al/Cu which is notable for clockwise hysteresis (see Figure 4.5, Figure 4.6).

4.4.2.5 Electroconductivity

Initially the electroconductivity is higher (126 μS) at site B5 (see Figure 4.2), and as the flow peaks electroconductivity is at its lowest (24-26 μS) at several different times mid-storm. As discussed later in the Chapter, electroconductivity correlates with Al/Cu concentrations. Ions present in the water are diluted by rainfall, hence the lower electroconductivity.

Electroconductivity is at its peak during sampling at the beginning of the storm at site B12 (see Figure 4.3). (1062 μS) and exceeds water safety recommendations in terms of risk to ecology (Shropshire Wildlife Trust, 2019). On the rising limb of flow, the electroconductivity decreases considerably. EC continues to decrease until the end of the storm going down to 221μS cm^{-1} at the end of the storm

which correlates with Al/Cu levels decreasing also. It is thus shown that rainfall influences concentrations of metals at B12 also. Therefore, conductivity was closely related to flow with large flow peaks correlating to significant diminishment in conductivity.

At site B14 the electroconductivity at the beginning of the storm is considerably higher 183 µS, than at the end of the storm (21 µS) (see Figure 4.4). The general pattern is that electroconductivity decreases on the rising limb (average is 62.571µS) range; 21-183 µS). The exception is at 12.20 pm where the electroconductivity is at 140 µS. Electroconductivity can generally be related to flow, with higher flows illustrating a lower electroconductivity. This is because ions are diluted by the overall volume of water. The electroconductivity here is well within acceptable levels as far as monitoring is concerned.

4.4.2.6 ORP

ORP increases with increased rainfall showing increased oxidation at location B5 (see Figure 4.2). ORP is low when metal levels are high (151 mV, 164 mV) increases with increased rainfall and then begins to fall with decreased rainfall. The maximum of 254 mV occurs at 12.25 pm when there is peak flow. ORP is lowest when metals are high in concentration meaning that metals are in their most bioavailable form in a higher proportion.

At site B12 before the storm the ORP is relatively high with a maximum of 293 mV at 7.12 am (see Figure 4.3). The ORP reaches its minimum of 120 mV at 1.42 pm the range is between 120-293 mV. The ORP also reaches a near maximum point at 12.12 pm and stays relatively high for this site throughout the storm. The average for this site is 244 mV. The ORP at this site is comparatively high compared to the ORP at other sites. As the storm progresses the ORP becomes a higher risk to the waterbody as it becomes oxidising, but this may be balanced by an increase in pH.

The ORP at site B14 ranges from 216-294 mV and this is generally low in terms of river health indices (see Figure 4.4). The ORP is higher at the beginning of the storm (294 mV) as compared with the end (231 mV).

4.4.2.7 TOC

TOC increases as the storm progresses, perhaps meaning some Al/Cu is found in a carbon bound forms, as the free Al binds to TOC. TOC peaks at 11.27 am (11.76 mg/L) when flow peaks and is lowest at 9.00 am suggesting it coincides with flow at site B5 (see Figure 4.2). It is lowest at the beginning of the storm, 3.723 mg/L suggesting that TOC is carried by storm flow and coincides with the lag time. TOC may serve to decrease bioavailability of metals during storms.

There is no distinct pattern as with regards to TOC, and the level generally remains quite low apart from one exception of 7.133 mg/Lts 12.42 pm at site B12 (see Figure 4.3). The levels of TOC in this portion of the stream are comparatively low in relation to some rivers (Worrall et al.; Department of Environment, 2014). The average is 3.10 mg/L, and the range is 1.392 mg/L at 1.42 pm and 7.133 mg/L at the end of the storm.

TOC shows a variable pattern during the storm, but generally increases as the storm flow increases at site B14 (see Figure 4.4). The average is 3.245 mg/L with a minimum 1.097 mg/L (6.41am) and a maximum of 7.626 mg/L (1.40 pm). This may be positive for the river at this point as storms may make any bioavailable forms of metals inert by binding to them and making the less bioavailable.

4.4.2.8 Eh-pH

Eh-pH diagrams were not produced for site B5 as the ORP probe failed. Most species of Al were found to be of the Al^{3+} species by Eh/Ph diagrams at site B12 (see Figure 4.3), as Al^{3+} is more bioavailable, this could explain partially why fish are not found in this portion of the river. Two

samples were found to be of the $AlOH^{2+}$ species and one was found to be of the $Al(OH)_2^+$ species. Species prevalent in the peak storm time were the hydroxide species/oxidising acidic species, whilst those found at the rising limb and descending limb storm tended to be Al^{3+} oxidising alkaline species and ionised. This indicates that an input of rainwater has a positive effect on this portion of the stream with regards to bioavailability of metal ions.

$Al(OH)_4^-$ is the predominant species at site B14 (Figure 4.4) as the pH is much higher. In this form, the Al is not toxic, creating better conditions for aquatic life. In accordance with pH data discussed in Chapter 3, this ORP data shows that, then the more neutral the pH the more oxidising alkaline the species, i.e., the more likely Al is likely to be in hydroxide form (Hem and Roberson., 1967)

At site B12 Cu was shown to be primarily of a Cu^{2+} species which again is the most toxic and bioavailable form, and Cu and borderline Cu_2O were shown to be other species (see Figure 4.3), ORP is the determining factor in determining the species in this case. The higher ORP seems to transform the species into the Cu^{2+} boundaries, with the lower ORP in the middle of the storm transforming species into more inert specimens (Hatches).

Cu_2O is the predominant Cu species at site B14, with some samples being in the Cu^{2+} range (see Figure 4.4). The ORP varies in the storm and does not follow a general pattern with storm so the type of species according to discharge doesn't follow, it is possibly related to the geochemistry as the pH is higher here. The predominance of the Cu_2O species is positive for the ecology of the river. Generally, the inertness of the species of Al and Cu demonstrate why the river can support aquatic life downstream. This is because of increased discharge and input from tributaries at this point in the river.

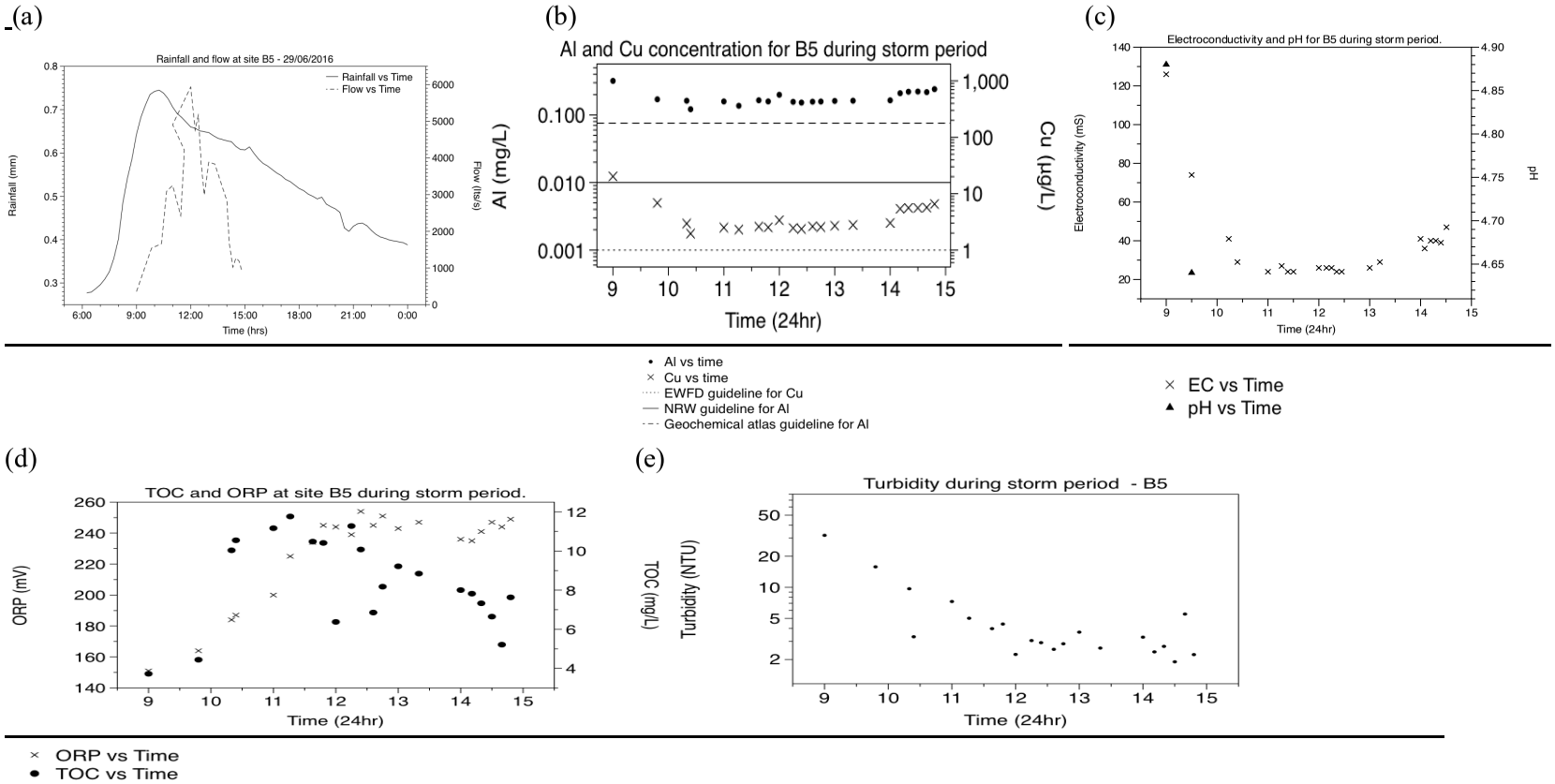

Figure 4.2 – Geochemistry and storm hydrology of the Barlwyd (site B5)

(a) Al and Cu concentrations (b) TOC and ORP, and (c) Electroconductivity and pH (d) Turbidity and (e) flow and rainfall for Site B5 during storm periods. Al and Cu concentrations are compared to geochemical atlas limits and suggested EQS for Al, and to EWFD limits for Cu. Contains Natural Resources Wales information © Natural Resources Wales and database right. All rights reserved.

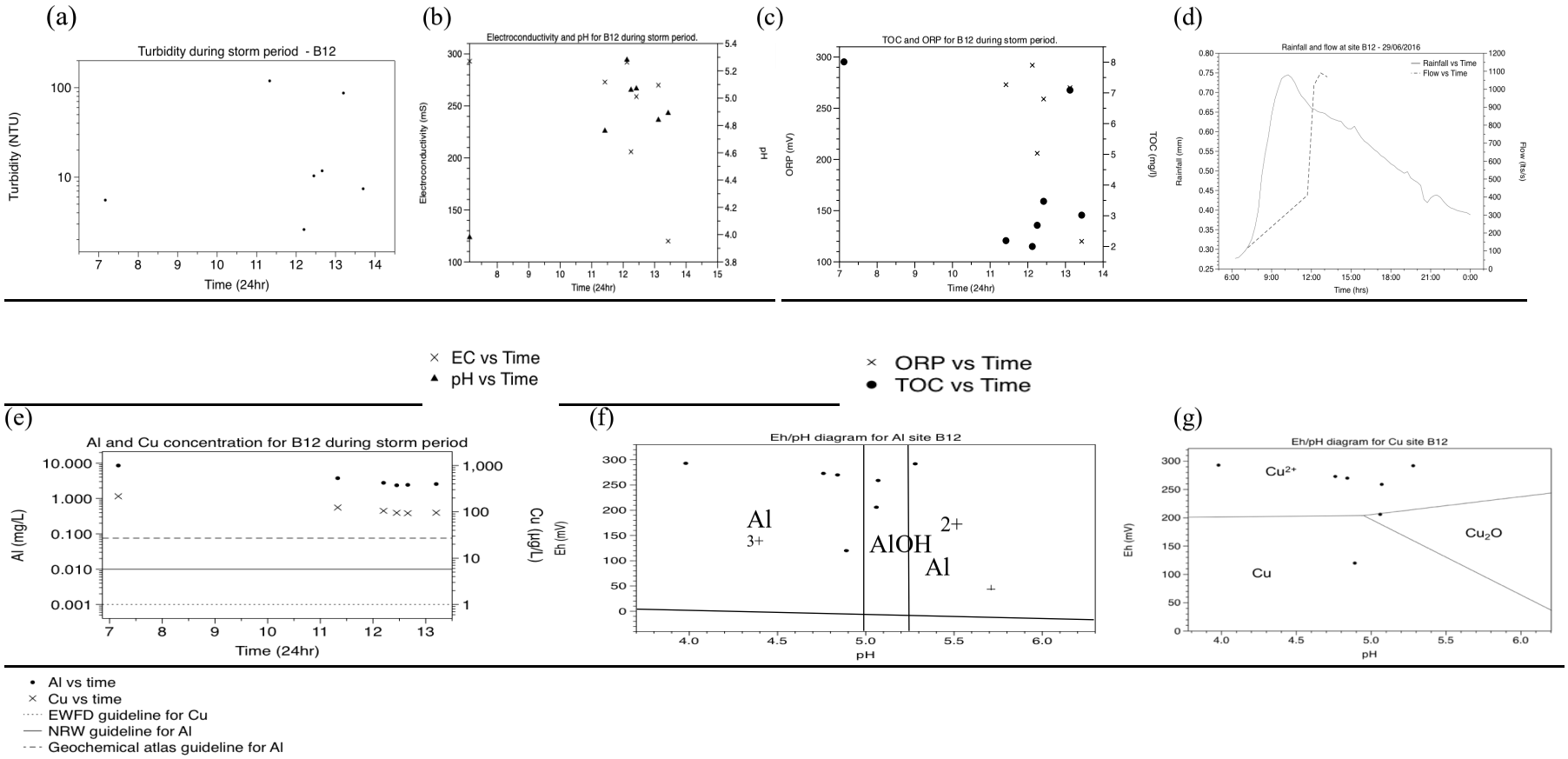

Figure 4.3 – Geochemistry and storm hydrology of the Barlwyd (site B12)

(a) Turbidity (b) Electroconductivity and pH and (c) TOC and ORP (d)Flow and rainfall (e) Al and Cu concentrations (f) Eh- pH diagram for Al at 25℃ (after HATCHES) and (g) Eh-pH diagram for Cu at 25℃ (after HATCHES) for Site B12 during storm periods.. * Al and Cu concentrations are compared to geochemical atlas limits and suggested EQS for Al ,and to EWFD limits for Cu. Contains Natural Resources Wales information © Natural Resources Wales and database right. All rights reserved.*

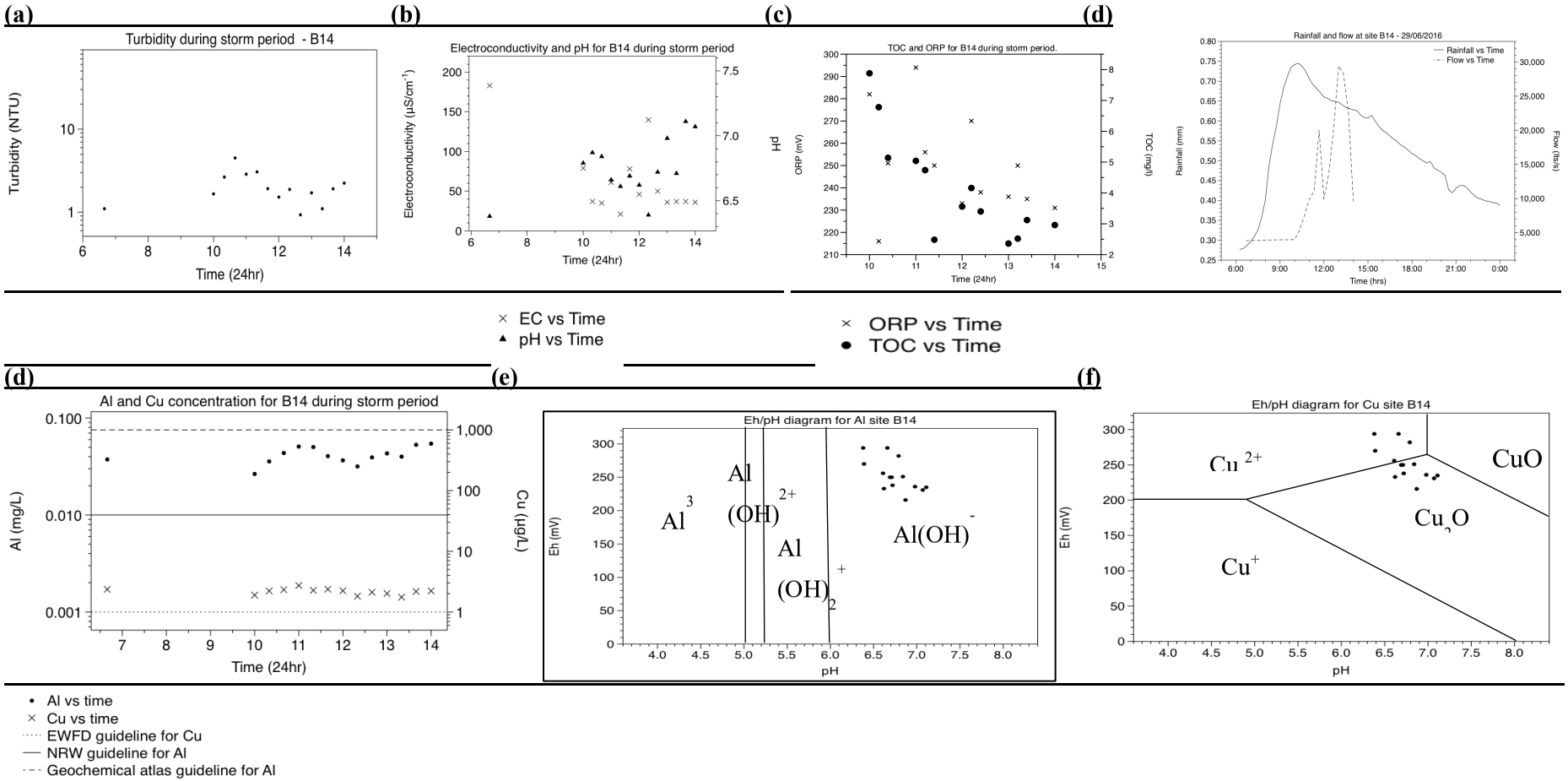

Figure 4.4 – Geochemistry and storm hydrology of the Barlwyd (site B14)

(a) Turbidity (b) Electroconductivity and pH and (c) TOC and ORP (d) Al and Cu concentrations (e) Flow and rainfall (f) Eh- pH diagram for Al at 25°C (after HATCHES) and (g) Eh-pH diagram for Cu at 25°C (after HATCHES) for Site B14 during storm periods. * Al and Cu concentrations are compared to geochemical atlas limits and suggested EQS for Al, and to EWFD limits for Cu. Contains Natural Resources Wales information © Natural Resources Wales and database right. All rights reserved.*

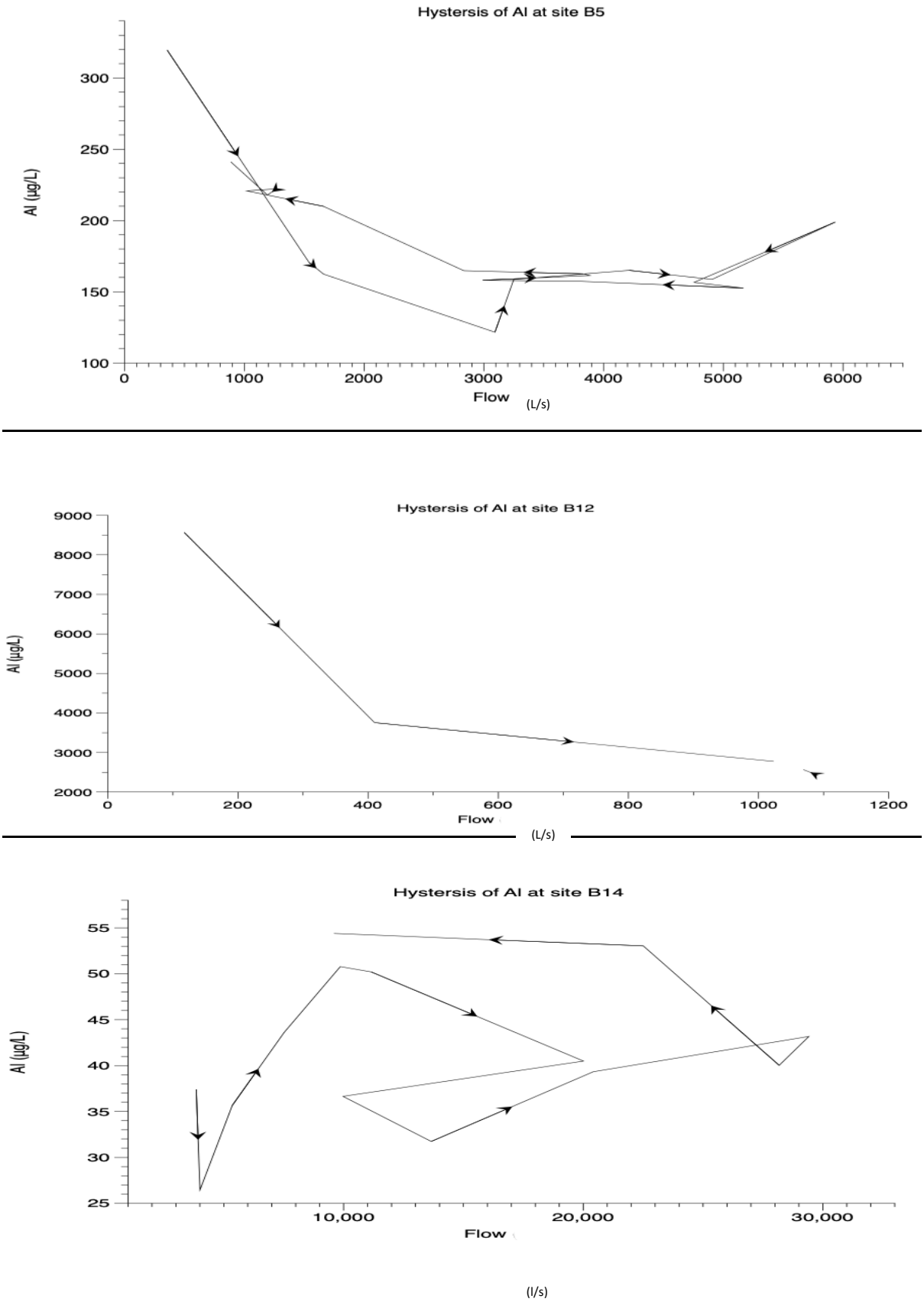

Figure 4.5 – Hysteresis loops for Cu at B5, B12 and B14

Arrows show the direction of hysteresis loops.

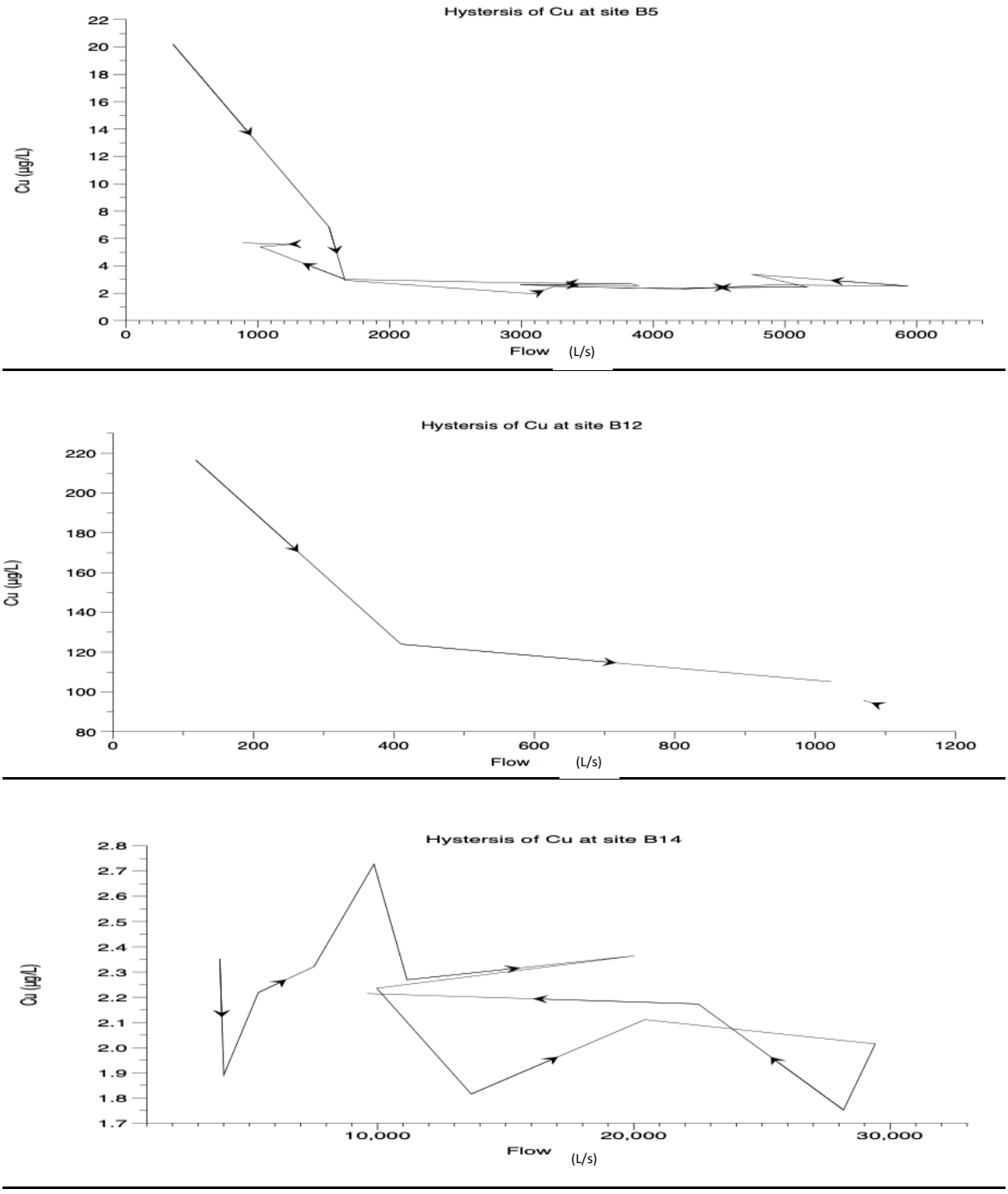

Figure 4.6 – Hysteresis loops for Cu at B5, B12 and B14

Arrows show the direction of hysteresis loops.

4.4.2.9 Correlations

At site B5 Al and Cu show a very strong positive correlation (0.93, Spearman's rho>0.8) (see Table 4.2, Figure 4.7). Furthermore Al/Cu are strongly positively correlated with Flow (Al = 0.62, Cu =-0.69, Spearman's rho <-0.60). ORP and turbidity are strongly negatively correlated (0.70 Spearman's rho <-0.6). All other factors are not significantly correlated.

At site B12 very strongly positively correlated factors are Al and Cu (0.998, Spearman's rho= >0.8) and Al/Cu (Al = (see Table 4.3, Figure 4.8). Flow is very strongly positively correlated with pH (0.86 Speaman's rho = >0.8). Al/Cu are very strongly positively correlated with EC (0.89, Spearman's rho = >0.8. ORP is strongly positively correlated with Al/Cu (Al = 0.61, Cu =0.64, Spearman's rho = >0.6). pH is very strongly negatively correlated with Al/Cu, and flow (Al= -0.94, Cu= -0.94, Flow = -0.86, Spearman's rho = <-0.80). Flow and Al/Cu are very strongly negatively correlated (Al = - 0.89, Cu=-0.90 Spearman's rho = <-0.80). EC and flow are strongly negatively correlated (-0.76, Spearman's rho <-0.60) pH and EC are strongly negatively correlated (-0.73, Spearman's rho < -0.73). All other factors are not significantly correlated.

Site B14 shows fewer positive correlations overall. ORP and pH show a strong negative correlation (-0.64, Spearman's rho = <0.60). All other factors are not significantly correlated.

Table 4.2 – Spearman's rank values at site B5.

*** denotes a very strong correlation * denotes a strong correlation*

	ORP	Al	Cu	Flow	Turbidity
ORP	1.00	-0.021	-0.08	0.27	-0.70*
Al	-0.02	1.00	0.93**	-0.62*	-0.16
Cu	-0.08	0.93*	1.00	-0.69*	-0.06*
Flow	0.27	-0.62*	-0.69*	1.00	-0.11
Turbidity	-0.70*	-0.16	-0.06	-0.11	1.00

Table 4.3 – Spearman's rank values at site B12.

***denotes a very strong correlation * denotes a strong correlation*

	ORP	Al	Cu	Flow	Turbidity	pH	EC
ORP	1.00	0.61*	0.64*	-0.49	-0.39	-0.37	0.49
Al	0.61*	1.00	0.998**	-0.89**	-0.27	-0.94**	0.89**
Cu	0.64	0.998**	1.000	-0.90**	-0.27	-0.92**	0.89**
Flow	-0.49	-0.89**	-0.90**	1.00	-0.10	0.86**	-0.76*
Turbidity	-0.39	-0.27	-0.27	-0.10**	1.0	0.02	-0.53
pH	-0.37	-0.94**	-0.93**	0.86**	0.01	1.00	-0.73*
EC	0.49	0.89**	0.89**	-0.76*	-0.53	-0.73*	1.00

Table 4.4 – Spearman's rank values at site B14.

*** denotes a very strong relationship * denotes a strong correlation*

	ORP	Al	Cu	Flow	Turbidity	pH	EC
ORP	1.00	-0.16	0.21	-0.28	-0.01	-0.64	0.49
Al	-0.16	1.00	0.35	0.28	0.50	0.39	-0.60
Cu	0.21	0.35	1.00	-0.42	0.50	-0.27	0.01
Flow	-0.27	0.27	-0.42	1.00	-0.24	0.20	-0.25
Turbidity	-0.01	0.50	0.50	-0.24	1.00	0.19	-0.51
pH	-0.64	0.39	-0.27	0.20	0.19	1.00	-0.52
EC	0.49	-0.60	0.01	-0.25	-0.51	-0.52	1.00

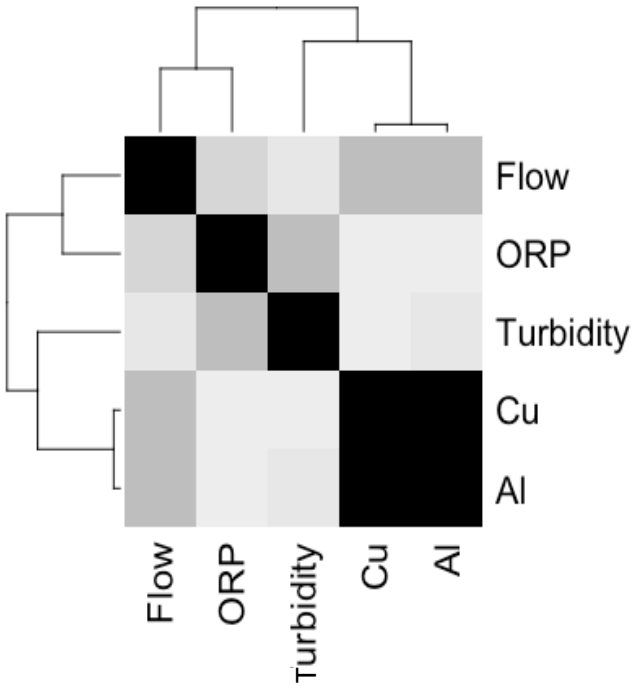

Figure 4.7 – Correlation matrix for site B5

Black represents a positive correlation shading through grey to white for a negative correlation

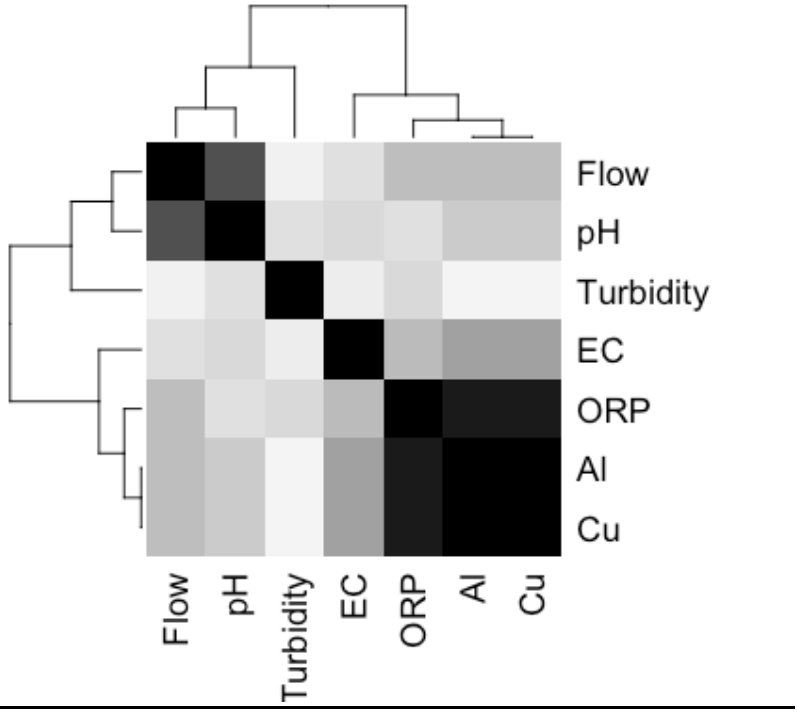

Figure 4.8 – Correlation matrix for site B12

Black represents a positive correlation shading through grey to white for a negative correlation.

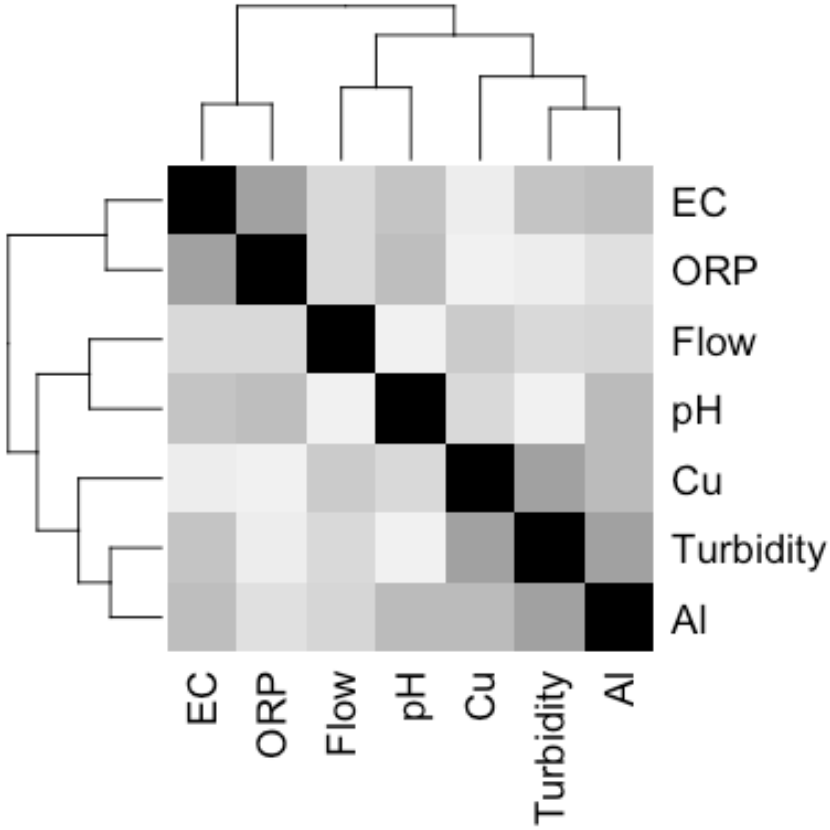

Figure 4.9 – Correlation matrix for site B14

Black represents a positive correlation shading through grey to white for a negative correlation.

4.5 Discussion

In this research we discover that storm flow could be influential in its impact on quarrying pollution in the Barlwyd catchment. This is an important discovery owing to the potential future implications of climate change. In this regard, management considerations should address flow as part of their strategy for remediation. This is a novel discovery with respect to slate quarrying specifically where the dynamics of pollution linked to storm flow are addressed. Identification of rainfall as an important variable in slate quarrying pollution will aid in remediation efforts and management strategies and will emphasise the importance to rivers of mitigating climate change internationally.

4.5.1 Analysis shows "first flush" of Al/Cu

A multi sample site geochemical analysis of water samples during a storm period was utilised as our approach. We used ICP-MS to analyse the chemistry of metals. Importantly it was demonstrated that there was a "first flush" (Younger and Blachare, 2004) of metals into the river, and that an overall dilution was witnessed, however load was increased in the catchment.

4.5.2 Spatial variations

Levels of Al/Cu during storm periods in the Barlwyd can substantially exceed EWFD and geochemical atlas guidelines. Specifically, samples taken at B5 and B12 exceed levels which are safe for aquatic life, encouraging sustainability. Samples taken downstream at B14 are within acceptable limits for aquatic life downstream for Al and around or two times the limit for Cu. At site B5, which is the mixing point for the quarry output from Llechwedd, there is an excessive amount of Al and Cu, from an Al concentration range of 0.121-0.319 mg/L, and a Cu range of 121-319 µg/L which in both cases exceeds EWFD and NRW EQS guidelines, as the storm progresses the concentrations decrease which coincides with the results of Buss et al., (2013), which shows that dilution by rainwater of the adit decreases the concentration of metals in the B12 space. At B12 the concentrations exceed the

limits to a much greater degree (range Al:2.36-8.75 mg/L; Cu 20-216 µg/L), which are again seen to decrease as the storm progresses. At B14 the concentrations are not so acute with regards to aquatic life (Al 0.0374- 0.0508 mg/L, Cu 1.75-2.35 µg/L). the trend with regards to storm is to decrease with increased flow.

4.5.3 Hysteresis patterns – clockwise at polluted sites.

The metal concentrations on the rising limb of discharge are far higher than those on the falling limb at polluted sites showing clockwise hysteresis, whilst downstream this pattern is less apparent, and the hysteresis is anti-clockwise. This is common to the most frequently recognised pattern of hysteresis: clockwise (Peart and Walling, 1988; Evans, 2011). This points to a reduction in the supply of pollutants to the river catchment before levels of discharge peak (Arnborg et al., 1967). In this case the concentration of Al/Cu tends to be higher in early periods during the storm when supply of pollutant material and fine material is higher. The significance of this is that most of the polluting material is transferred to the river whilst the discharge is increasing. A decrease in supply of pollutant material can be because of a small amount of slate sediment material by the monitoring station, particularly in the cause of B5. A pattern of clockwise hysteresis is more common at the beginning of a storm. In a study by Doty and Carter (1965) it is demonstrated that clockwise hysteresis shows that material decrease over time because of hydrological processes such as surface runoff and leaching (Evans, 2011). Novotny (1980) suggests that a fall in the levels of rainfall during the recession of the storm mean that less the pollutant material is transported in the channel of the river (Evans 2011). Observations such as these suggest that it is hydrological and physical processes on the earth surface which are responsible for the higher concentrations. Steegen et al. (2002) conversely suggest that the relationship is not indicative of exhaustion of sources of pollutants but is linked to supplies from steep inclines in the upper reaches of the catchment which are at the root cause of the clockwise hysteresis (Evans, 2011). Other authors cite higher rainfall at the beginning of the storm, which means a lessening of erosion power in the rain and inflow into the main channel after the discharge peak (Wood, 1977; Baca, 2002; Evans, 2011). Rodríguez-Blanco (2009) argues that the analysis of

hysteresis loops is a dependable way of recognising supplies of sediment (Evans, 2011). Direct information is thus needed about the different sediment sources and erosion processes in the river basin. To gain a clearer picture, thorough information of the processes and characteristics which are linked to transport of pollutants in water supplies are needed to remediate against water quality problems in the most economical and sustainable way as possible. It is these processes which govern and determine the supply of pollutants for the main channel (Salomons, 1995; Zonta et al., 2005; Evans, 2011). These components include variations in sediment supply, metals, organic matter and radionucleotides over time and space (Smith et al., 2003; Evans, 2011).

The storm hydrology is largely impacted by land use in the catchment. The slate material which is in the catchment does not store water in the same way as soil, which creates a short lag time and a flashy catchment. Together with weathering of slate by the catchment and high metal levels, storms impact the catchment quite considerably. The catchment is full of impervious surfaces. Storm hydrology is concerned with flowrate and hydrological pathways (Gregory and Walling, 1973; Martin and White, 1982; Seip et al., 1989; Christophersen et al., 1990, Giuisti and Neal, 1993). There is also no groundwater in the Harlech dome and thus there is no underground reservoir to recharge. The high rainfall in this instance may cause further problems in erosion and recycling of sediments. Alteration in flow regime can change the structure of stream channels (Arnold et al, 1967; Hammer, 1972; Douglas, 1974, Booth, 1990; Alberti., 2008), and make them stable (Dunne and Leopold, 1978; Konrad, 2000; Alberti, 2008). The result is a shift in habitat condition and overall stream health (Arnold et al 1967; Ralph et al., 1994; Alberti, 2008). Climate change and the increase of predicted storms means the implications of this are quite significant globally. It could be that future policy supports researching remediation methods and applying them to catchments in the future. These are discussed in Chapter 6.

As slate is hard and relatively impervious surface, and roads are found adjacent to pollution and B8 in Chapter 3 shows a high level of metals from the road runoff. Furthermore, the domination of the land use by the quarry has meant that the natural plant life that would normally be found in the land has

gone and Takase and Sato (1994) studied the process of retention in catchments of different land uses. They found that initial soil moisture deficit has a great effect on the rainfall retention of storm runoff. Furthermore, the lack of trees or foliage for percolation also impact the catchment. There is also a reduction in soil and plant cover in the catchment owing to the slate tips. As plants use large amounts of water in transpiration, they are responsible for flood control by reducing the amount of water that otherwise would flow downstream (Alberti, 2008). The slate tips, roads and urban environment reverse all these functions by reducing the amount of riparian vegetation. Hydrological processes interweave with biological and geomorphic processes in complex ways by formulating and sustaining aquatic habitats for a multitude of species. These processes are created by interactions between soil, vegetation dynamics, and nutrient cycling. Urbanisation affects the unique set of conditions which aquatic species have adapted to changes nutrient fluxes as well as contributing pollution. Urbanisation affects these interactions by changing both land cover and nutrient fluxes, and particularly by replacing wetlands that provide essential habitat for both fish and wildlife (Alberti, 2008). The effect that the impervious surface has on the amount, quality, and timing of flow depends on several factors: climate, morphology, geology, vegetation, and land use (Dunne and Leopold, 1978; Ziemer and Lisle, 1998; Booth and Jackson, 1997; Alberti, 2008). As a result of impervious surfaces, streams become "flashier" as their flow changes more quickly and more often (Konrad, 2000; Konrad and Booth, 2002; Booth et al., 2004). Riparian areas also act as critical transition zones between upland and aquatic environments, maintaining streambed stability. Hydrological functions are crucial for aquatic ecosystems including salmon, creating shelter for wildlife, and providing nutrients for macroinvertebrates. Urban and industrial modification of the landscape structure and processes changes proportions of impervious surfaces so that up to 55% of rainwater may drain off, as water is delivered to streams rapidly, frequently, and in large volumes (Alberti, 2008).

This catchment possesses "flashiness" that results from a combination of more areas more efficiently transport the runoff from those impervious surfaces (Dunne and Leopold, 1978; Alberti, 2008). In this catchment there may be a post-development hydrograph which shows peak flows during high-flow events increasing considerably in size. This will contribute to levels of metals flushing through the

system. A good predictor for pollution is the total impervious area in the catchment, however this can depend on the permeability of the drainage basin land cover (Booth et al., 2004), and the amount of impervious area that drains directly to streams through pipes rather than through pervious land (Walsh et al., 2005). Three parameters create flashiness: shorter lag to peak, shorter peak flow duration, and more frequent high flows (Konrad, 2000; Konrad and Booth, 2002, 2005; Booth et al., 2004). Frequent high flows contribute to river ecology (Roy et al., 2005; Walsh et al., 2005). They can also cause erosion and fragment riverbanks (MacRae and Rowney, 1992). Flashiness can also increase the frequency of small overland floods. Small rainstorms are not likely to cause large hydraulic stress in streams, even if their catchments are impervious. If these events become regular, they can potentially impact biotic conditions, although the size of these events relative to the stream is unknown (Walsh et al. 2005; Alberti, 2008).

To compound the flashy nature of the catchment, where the metals are at their highest concentration, the pH levels are also at their lowest at B12, and this is also turbid which compounds the problem of metal toxicity and metal bioavailability as the pH is low the form of metal is bioavailable. There is a decrease in metals at peak flow depending on location in the river and proximity to quarry and type of hysteresis. Overall loads of metals are higher with a larger flow ingress. Increasing concentrations of TOC as the storm progresses may have a positive impact, and correlates with the reduction in metal concentration, augmenting the proportion of TOC-metal complexes. In this way TOC could have a positive impact on metal concentrations. Generally, the storm's flashy hydrology exacerbates the flush of material through the catchment, causing intense exposure to high concentrations of metals, exceeding the EWFD chemical guidelines and thereby affecting the ecological status of the river.

4.5.4 pH is acidic below guidelines.

The EWFD guidelines state the pH in the water of rivers such as the Barlwyd needs to be between 5 and 9 for a good status. At source, B1, the river is in good status (average pH chapter 3 6.17). The pH at B5 was low (4.64-4.88) placing the river into poor status at this point. The pH at site B12 is

generally much lower and falls into the moderate/poor status (range: 3.98-5.28). Further downstream at B14 the pH is much improved, with a pH of between 6.38 and 7.11 and falls into the good status for this snapshot of time.

In terms of site B5 and B12, which are discharges from/in the vicinity of the quarry, the pH increases with increased rainfall, which means indicating amelioration in conditions with raised levels of rainfall. This phenomenon has been observed by Nordstrom (2009), and according to the author the unbinding of soluble minerals because of high discharge is the cause of this increase. However, most of the time the pH around these sites is not good enough to sustain aquatic life. These results are like other results obtained regarding the effects of acidic discharges on fish and aquatic organisms. The pH alters in response to rainfall as the pH of rainfall is higher than the river water and is a process of physical dilution increasing upon receiving rainfall. This means the river water quality is ameliorated. Nicholas and Bulow (1973) show that acidic discharges are responsible for fish death in the Obey river, Tennessee (Evans, 2011). Another study by Cooper and Wagner (1973) illustrate that the pH of river water needs to be above 5.5 to sustain aquatic life. The pH's found at sites B5 and B12 are well below this. As stated by Evans (2011) it is thus clear again that the low pH around these sites partially contribute to the lack of aquatic life in the Barlwyd. However, a pH as high as 6 can be responsible for fish death (Barry et al., 2000). As shown by Evans (2011) higher pH and more neutral pH's lower downstream from Tan-y-grisiau and lower down on the Goedol and Dwryd give rise to environments which are much more suitable for sustaining aquatic life.

4.5.5 Turbidity – peaks initially showing "first flush".

Previous studies show that the quarry contains a lot of raw material mostly in the form of a significant amount of small material, and as a result, this has caused problems which are related to high turbidity levels. This study shows that turbidity is not a significant problem in the river Barlwyd. Turbidity is considered a problem when it reaches 50 NTU (Evans, 2011). The turbidity decreases from 31.9 NTU at site B5 to 2.23 NTU during the storms., because the slate fine material is collected in an initial flush

of material from the quarries (Williams, 1989; Evans, 2011). The movement of heavy vehicles on site crushes slates creating dust and the cutting process creates dust which is washed into the river. Thus, in this instance, the effect of storms is to ameliorate the turbidity, perhaps due to raw material being diluted. At site B12 however there is a different result with the turbidity increasing from 5.87 NTU as time passes to a final turbidity of 87 NTU. This may indicate a source of pollution higher up from the adit which may be responsible for the high levels of metals. Further downstream at B14 the material again decreases in concentration from 7.42 NTU at the beginning of the storm to a minimum of 1.1 NTU during the storm. This shows a trend of turbidity in the mainstream decreasing with increased water volume, diluting water from discharges at B12 and B4. The results at B12 of higher turbidity is not adequate to sustain aquatic life. Downstream at Tanygrisiau, and in the Dwryd and Goedol the turbidity is much lower and able to sustain aquatic life. Levels upstream seem to exceed levels downstream also. As tributaries join the stream there is a weakening in the turbidity at B14. The occurrence of higher turbidity at sites which are in receipt of quarry discharges coincide with studies by Ismail and Rahaman (1994); Bakar et al. (2007) and Gilchrist et al. (2009) who have all observed this phenomenon.

4.5.6 Limitations

This study was limited by physical proximity to the study site. This study did not capture the whole storm. Timing was not perfect owing to logistical constraints and the quality and spread of the data could have been improved with more manpower and resources. Model could be improved with more manpower and resources.

4.5.7 Future directions

Follow up studies could address how to manage flows during storms, and how to remediate during the storms. One potential study could be to analyse water flow through the quarry, perhaps using rhodamine.

4.5.8 Overall conclusions and impact of study.

Implications for policy for the future could include using policy to manage permissible concentrations of metals in rivers, this research could also put in place funding for the future to mitigate and research potential solutions against the effects of climate change on quarry discharges. Furthermore, potential solutions may involve solutions such as planting trees and altering land use to change how 'flashy' the catchment is. It may be possible to derive a formula for how 'flashy a material is and use GIS to calculate an optimum land use formula to avoid flashy catchments in future developments so that pollution is minimised.

Implications for ecosystems are that a first flush of metal can cause fish death in the catchment. However, over the course of a storm, conditions are ameliorated. Perhaps flow management in these rivers is a key solution to preventing excess toxicity as rivers can be more toxic in summer months where water is more concentrated in metals. This again has implications for climate change, where flow management will be key to prevent ecosystem damage. However, prevention is better than cure, and this study emphasises the need for humanity to change its approach to resources, and work globally and collectively towards climate change mitigation, and furthermore to work with world leaders, businesses, to deliver the evidence that science is presenting regarding climate change.

4.6 Conclusions

During storm conditions this river fails to meet EWFD guidelines for pH and metal concentrations. The river Barlwyd fails to meet good chemical status guidelines. There was a clockwise hysteresis between metal concentrations and discharge. Processes responsible include rates of huge rainfall in the light of an increase of rain, leaching of metals from the slate waste and substance seepage. Hydrological process during a period of high discharge is responsible for the high concentrations of heavy metals. Furthermore, the lack of foliage and soil cover and high level of impervious surfaces cause a flashy discharge and a 'flush' of materials. It is likely that acidic peatland is responsible for the acidic conditions in this case, causing dissolution of minerals in the slate.

One contribution this study makes is that storms may be responsible dissolution of slate waste at site B12, with no source of fine material explained. This may have a greater impact on the stream. Overall, however sites in close spatial proximity to the quarry seem to ameliorate under storm conditions geochemically. This study realises the importance of storms in the context of this river with an emphasis on spatial significance. It also realises further the negative impact that slate mining has on the catchment. A wider study could be repeated with technical ameliorations, and a larger amount of people. Furthermore, the study was conducted when the quarry was not in full operation, so may not be representative of the full extent of damage. However, it is sufficient to say that the quarry is still having an impact on the river Barlwyd and affecting aquatic life.

This result has significance for future policy, in the management of rivers adjacent to slate mines. Managing water flow, waste and even vehicle movement around slate quarries need to be managed and monitored. The cutting process may be refined to create less dust or involve less water in the procedure. Remediation efforts need to be trialled to ameliorate water conditions. This will ameliorate the surrounding ecosystem for ecosystem services. Furthermore, the significance for climate change could be problematic, with the impact worsening the problem observe and having an ultimately greater impact on ecosystems. This leads to better sustainable management of both quarries and

resources. As weathering slate tips are also found to be responsible for pollution, perhaps there is a way of utilising slate waste as a material. Management of waste needs to be considered in line with weather reporting.

CHAPTER 5 – SEDIMENT – WATER EXCHANGE: USING NATURAL PARAMETERS TO MODEL SORPTION/DESORPTION OF Cu/Al FROM SLATE SEDIMENT IN THE LABORATORY

5.1 Introduction

The contamination of aquatic systems by metals, particularly in sediments, has become one of the most challenging pollution issues owing to the toxicity, abundance, persistence, and subsequent bioaccumulation of these materials (Fu et al., 2014a). Metals can be absorbed by suspended solids, and then bioaccumulated/magnified along food chains (Yang and Zhang, 2011; Gumgum et al., 1994, Fu et al., 2014a). Sediments can act as sinks and may also act as sources of heavy metals (Håkanson, 1980; Suresh et al., 2012; Fu et al., 2014a). Recent research efforts have focused on heavy metal pollution in sediments of aquatic ecosystems, with a view to effectively managing these ecosystems (Fu et al., 2014a; Vukosav et al., 2014; Xiao et al., 2014; Zhang and Shao, 2013). Thus, the distribution of trace metals in sediment close to mining exploitation can give us the evidence of anthropogenic influence on aquatic systems and aid in assessing the potential risks associated with mining waste discharge. River sediment is comprised of bedload, washload, suspended load and dissolved load (Hickin, 1995). The focus of this research is the suspended load. The suspended load moves at the same velocity as the flow, and is comprised of small particles e.g., clay and fine silt which is held in suspension owing to the electrostatic attraction surface charge of particles and water, and this keeps the particles in flow. Factors which could influence the suspended sediment load could include, climate, vegetation, anthropogenic influences, rock solubility, erodibility, relief, and slope (Hickin, 1995).

As demonstrated in Chapter 3 the metals Al and Cu are found in high concentrations in the river Barlwyd. As a fine sediment is created by the cutting process in the quarry, and river water is used in this process, sediment is of concern as with regards to water pollution.

Suspended sediment is a known risk factor for water courses (Brils et al., 2008), in addition to substances that may be associated with it (Brils et al., 2008). The EWFD has set limits for healthy

concentrations of suspended sediment in a water course of 25 mg/L (EWFD, 2003). In catchments affected by metal mining up to 90 per cent of the metals are associated with sediment rather than in aqueous forms (Gibbs, 1977; EA., 2008). Assessment of suspended sediment concentrations is often not sufficiently considered in freshwater rivers (White, 2008; Tueros et al., 2009; Chon et al., 2012). Sediment quality must be considered on a catchment management level, for persistence, bioaccumulation, adsorption, and toxicity (Brils et al., 2008).

Physicochemical reactions such as accumulation and sorption cause sedimentation of metals to organic materials or suspended solids. Metals are desorbed from sediments when the mineralogy of the water increases, when there is a decrease in redox potential, or when there is a decrease in pH (Foster and Charlesworth, 1998). Suspension initiates the release of entrapped soluble materials and oxidation of solid compounds in sediments (Foster and Charlesworth, 1998).

In aquatic sediments, the bioavailability of metals to benthic organisms depends not only on a metal's chemical form (Besser et al., 2003; Riba et al., 2004; Simpson, 2005; Zhang et al., 2014), but also sediment geochemical properties (Nobi et al., 2010; Rainbow, 2007; Zhang et al., 2014) and varies according to the exposure pathways of the organisms (Simpson et al., 2012; Zhang et al., 2014).

To estimate the relative effect of sediment on this catchment a sorption/desorption experiment was designed using river water from four sites, varying flow, concentration of sediment, and temperature. The aim was to develop sediment guidelines with regards to the EWFD, with a focus on sediments derived from slate mining.

5.1.1 Aims and objectives

5.1.1.1 Aim

To quantify the sorption/desorption of the metals Al and Cu from sediment into the dissolved water fraction by estimating the relative contribution of sediment to the Al/Cu load in the river.

5.1.1.2 Objectives

- To examine sediment particle size and reactive surface area, to identify typology.
- To analyse the chemical composition of the sediment, to identify Al and Cu source.
- To analyse the sorption/desorption pattern of quarry sediment, whether it is adsorbed or desorbed by the water phase. Parameters influencing this which will be examined will include residence time, temperature, sediment concentration, site, and geochemical parameters.
- Develop geochemical theories which explain sorption/desorption behaviour of sediment/water.

5.2 Materials and methods

Briefly Sediment samples were collected from 4 different locations in a sediment settling tank where water from the river comes following the cutting process. Sediment samples were oven dried at 40 ^{0}C. Samples were analysed for element concentrations by TxRF and particle size by laser ablation. River water was collected from 4 sites (B1, B5, B12, B14), and a subset was filtered and analysed later for Al/Cu by ICP-MS. Samples from one settling tank compartment closest to the outpipe was then weighed out at 4 different concentrations, the lowest weighable concentration, the EWFD sediment guideline, the river's maximum detected amount of sediment and an excess. The samples were agitated on a shaker at 45 rpm with river water from the 4 selected sites for different flow times (high

flow, medium flow, slow flow and 24 hr flow as defined by previous measurements) and at temperatures of 4ºC and 10ºC. Water samples were taken off the shaker and filtered twice with 10mm and 0.45µm filters and analysed by ICP-MS for concentrations of Al and Cu.

5.3 Results

5.3.1 Grain size analysis

Eight samples were taken on two separate dates from the settling tank. The samples in the first set are larger in size being a fine-coarse silt, indicating that perhaps the water weathers some of the sample with time (see Table 5.1). Overall, the samples have a mode (ϕ) of 5.16-7.542 and a mean in mm of 0.005- 0.034 (SD = +/- 0.71-1.62) (see Figure 5.1). The skewness was -0.052-0.736 and there was a kurtosis of 0.575-2.718. The specific reactive surface area ranges from 0.706 -1.87 units. The composition of the sample ranged from: clay 4.7-22.3%, 67.4-88.9%, sand 0-34.5%, gravel 0% (see Figure 5.2 and Table 5.1). The graphical parameters showed that the sediment used is a very fine silt-coarse silt; moderately-poorly sorted; fine-skewed-near symmetrical and is mesokurtic/platykurtic (Folk and Ward, 1957). There is generally no pattern in relation to location in the settling tank and particle size. However, the last 4 samples were collected later (8/10/14) and show a higher content of clay particles and a lower mean (mm) and higher ϕ.

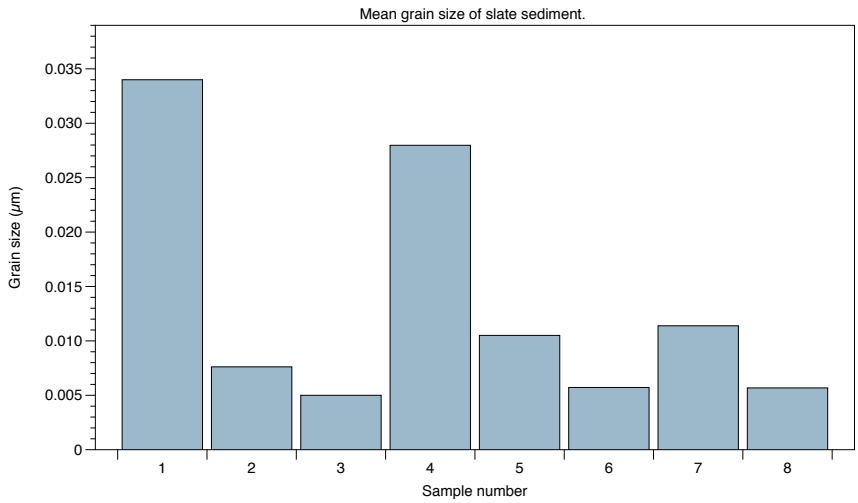

Figure 5.1 – Mean grain size in sediment samples

Samples 1-8, moving anti-clockwise around the settling tank, samples 1-4 and samples 5-8 were taken on different dates

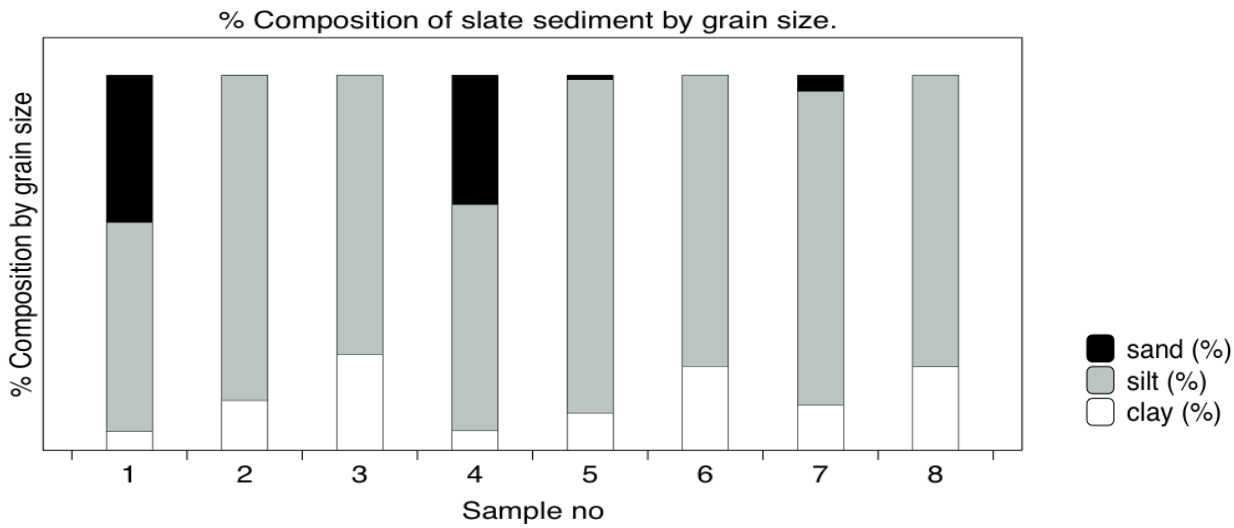

Figure 5.2 – Composition of slate sediment used in experiment according to particle size

Samples 1-4 were taken on from settling tank on 07/07/14, 1, 3, 8 and 16 respectively. Samples 5-8 were taken on 8/10/14 from the settling tanks 1, 3, 8 and 16 respectively. Sample 8 was used as it was closest to the river water supply, so most representative of what was in the water supply.

Table 5.1 – Grain size characteristics for different sorting tanks, organised chronologically

Sorting tank	Sample no	Mode	Mean	Sorting	Skewness	Kurtosis	S.D.	Graphic parameters	Specific reactive area	Clay (%)	Silt (%)	Sand (%)	Gravel (%)
1	1	4.869	0.034	1.987	-0.225	2.792	1.627	coarse silt, very poorly sorted, near symmetrical, mesokurtic	15.69	5.2	60.3	35	0
3	2	7.037	0.008	0.841	-0.095	2.719	0.851	very fine silt, moderately sorted near symmetrical, mesokurtic	6.451	13.3	86.7	0	0
8	3	7.790	0.005	0.705	-0.114	2.565	0.718	very fine silt, moderately sorted, near symmetrical, mesokurtic.	4.832	39.5	60.5	0	0
16	4	5.160	0.028	1.600	0.292	2.375	2.017	medium silt, poorly sorted fine-skewed, platykurtic	15.04	4.7	67.4	28	0
1	5	6.573	0.011	1.109	-0.267	2.822	1.133	fine silt, poorly sorted, near symmetrical, mesokurtic	7.99	9.9	88.9	1.2	0
3	6	7.450	0.006	0.711	-0.099	2.586	0.722	very fine silt, moderately sorted, near symmetrical, mesokurtic	5.078	22.4	77.6	0	0
8	7	6.456	0.012	1.307	-0.337	2.583	1.349	fine silt, poorly sorted, coarse-skewed, mesokurtic	7.923	12.1	83.6	4.3	0
16	8	7.461	0.006	0.697	-0.052	2.511	0.711	very fine silt, moderately sorted, near symmetrical, mesokurtic	5.06	22.3	77.7	0.0	0

The sediment used in the sorption/desorption experiment had a mean (ϕ) of 7.461 and a mean in mm of 0.006 (SD = +/- 0.711). The skewness was -0.050 and there was a kurtosis of 2.511.The specific reactive surface area for this experiment was 5.06. The composition of the sample we used was 22.3% clay and 77.7% silt. The graphical parameter showed that the sediment was a very fine silt, was moderately sorted, near symmetrical and mesokurtic (see Figure 5.2). All additional samples are described in Table 5.1.

5.3.2 TxRF analysis

Al and Cu are of importance due to their toxicity and abundance in the water column of this river. Metals which were found to be high in the sediment which is released into the settling chamber and discharged into the river were Al (average = 197400 mg/kg, 38.3%) and Fe (average: 186200 mg/kg, 36.1%) (see Figure 5.3 and Table 5.2). Fe is of particular interest in Cu rich systems owing to its binding capacity with DOM, thereby lessening the binding ability of Cu and enhancing Cu's toxicity. In the presence of precipitating Fe and Al oxides, DOM fractionates (McKnight et al., 1992, 2002). The other metal of focus Cu was much lower in concentration with an average of 186 mg/kg (0.1%). Other metals of interest to Al's chemistry are S (Sulphur) (2.7%), Ca (Calcium) (1.9%) and K (Potassium) (13.3%), which were also present in elevated levels in comparison to those <1%. Sulphur can form $Al_2(SO_4)_3$ and Al can also be the cation of Ca and K. The alums, double salts of formula $MAl(SO4)_2 \cdot 12H_2O$ (where *M* is a singly charged cation such as K+), K forms the salt; Al potassium sulphate, also known as potassium alum or potash alum.

Table 5.2 – Elemental composition per metal analysed

(N.B. some metals have not been measured thus this is not a total composition)

Element	***% of total minerals analysed***
Al	38.3
P	0.2
S	2.7
K	13.3
Ca	1.9
Ti	3.6
V	0.1
Cr	0.1
Mn	2.6
Fe	36.1
Ni	0.1
Cu	0.1
Zn	0.2
Ga	0.0
As	0.0
Br	0.0
Rb	0.3
Sr	0.1
Y	0.1
Ba	0.2
Pb	0.1

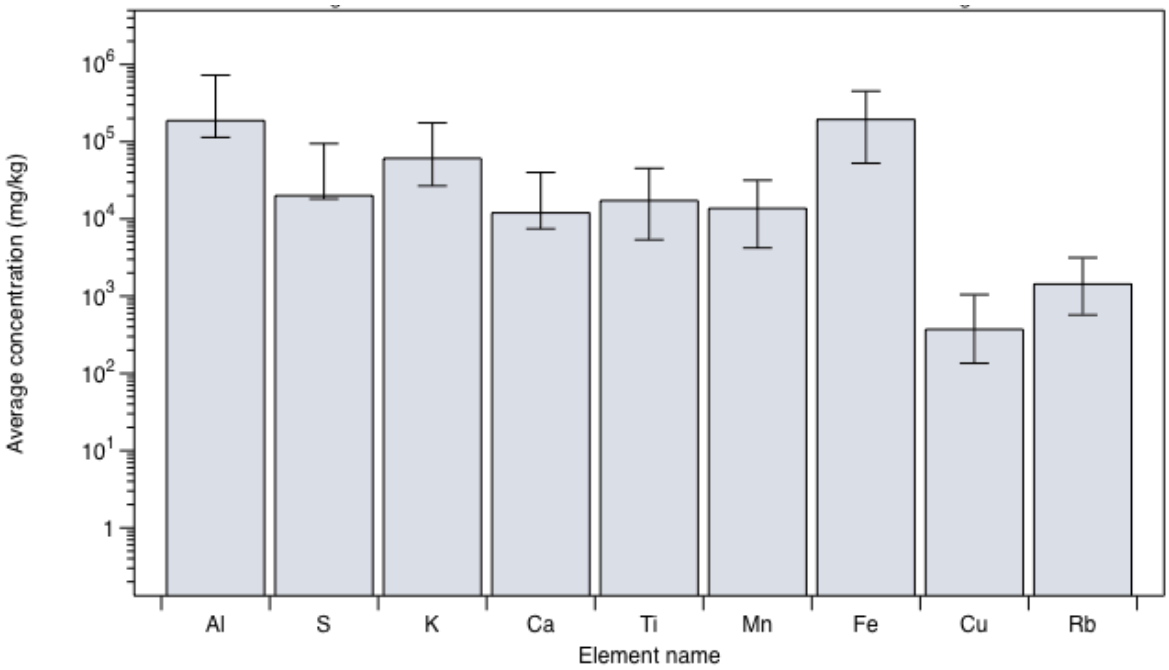

Figure 5.3 – Elemental analysis of sediment with TxRF

This shows elemental composition of sediment derived from the quarry which was used for the sorption/desorption experiment. Highlighted bars are those which are of prime interest (an average of 8 samples was taken) with respective minimum and maximum for each metal.

5.3.3 Sorption/Desorption of metals analysis using graphic interpretation

Percentage increase or decrease of Al/Cu was calculated owing to there being two dates upon which collected river water and hence different starting concentrations. The percentage change was calculated as follows.

$$Increase\ or\ decrease$$
$$= concentration\ measured\ after\ experiment - Sc(starting\ concentration)$$
$$\%\ Increase\ or\ decrease = \left(\frac{Increase\ or\ decrease}{sc}\right) * 100$$

5.3.3.1 Influence of site

Site geochemistry and uniqueness has a pronounced effect on the trend for Al/Cu sorption/desorption (see Tables, 5.3, 5.4). Site governs whether the Al/Cu is sorbed or desorbed. At site B1, the site nearest the source (see Tables 5.3, 5.4, Figures 5.4, 5.5), there is a trend for desorption under all conditions of pH at 4 ℃ (Al -233(0.324 mg/L), Cu- 87% (-0.123 mg/L). For Cu there is a trend for absorption at 4°C 521% (-0.324 mg/L) - 706% (0.1105 mg/L). At 10°C the trend is mostly for sorption for Al and Cu (at Al -28 - -77%, Cu 1270% (0.0013 mg/L) - 6371% (0.0064 mg/L).

Moving downstream to site B5, the pH is lower and shows a pattern of desorption (see Tables 5.3, Table 5.4, Figures 5.6 and 5.7) (4°C- Al; -98 -93%, (-0.1309 - 0.123 mg/L) % Cu; -73 -58%; (-0.0032 - 0.004 mg/L) 10°C Al -92 to -16% (-0.0032- -0.0032 mg/L, Cu 73-9%, (0.0032 - 0.004 mg/L). The pH is again low with a pH of 5. Downstream from B5, at the adit B12, due to the low pH (see Tables 5.3, 5.4 and Figures 5.8, 5.9) there is absorption at 4°C (4°C Al 151-159% (11.331-11.975 mg/L) Cu (0.1532-0.2081 mg/L). At B5 however there is a different trend at for B12 at 10°C mostly showing desorption Al -10 -2% (-1.5132 - 0.0074 mg/L, Cu -19- -6% - (-0.0638 - 0.0226 mg/L).

At B14 (See Tables 5.3, 5.4, Figures 5.10, 5.11) there is again a difference in the general trend for Al and Cu sorption at different temperatures (see Tables 5.3, 5.4 and Figure 5.7). B14 shows a variable pattern according to metal and temperature. At 4°C for Al there is a pattern of absorption/desorption into the water column (-618-73% - 73% (-0.1324 - 0.0158mg/L). For site B14 at 10°C there is a trend for desorption and absorption of Al at all flows (-24%-109% (-0.201-0.0449 mg/L). At site B14 for Cu the trend is for absorption, Cu the trend is a pattern of absorption at 4°C into the water column (100-270% (0.009-0.0024 mg/L). At 10°C for Cu pattern is for absorption (106-408% (0.0011-0.0041 mg/L).

5.3.3.2 Influence of SSC

In terms of patterns of the effect of change in concentration of SSC (see Table 5.4 Figure 5.4-5.11), there is very little evidence to suggest that higher concentrations of sediment lead to higher metal transfer. Under each set of conditions, the effect is usually a constant pattern or a random one which is not logical. The most consistent effect is shown at B12 where all effects seen are constant at both temperatures. There are rarely occasions where there is a logical pattern e.g., increasing SSC leads to decreasing desorption for site B5 for the metal Al at low flow at 10°C / increasing SSC leads to increasing sorption for site B14 for the metal Cu at high flow at 10°C. However, these results exist in isolation and are not sufficient to draw conclusions from given the bulk of evidence presented.

5.3.3.3 Influence of flow

Again, flow does not seem to have an influence on the amount of metal absorbed (Table 5.4, Figure 5.4-5.11). The effect of increasing flow as with SSC seems to have a random or constant effect on metal absorption with results most consistent at sites B12 and B14. On some occasions, increasing flow time increases desorption e.g., B5 for Cu at 10°C for 24 hr flow shows a higher degree of sorption as with compared with the desorption shown with other flow conditions. However, given the body of evidence, this again is not sufficient to draw conclusions with, and is an isolated effect. Statistically the flow time is also not significant.

5.3.3.4 Influence of temperature

On most occasions with regards to Al (see Table 5.4 Figures 5.4-5.11), increased temperature serves to increase or decrease absorption. At site B1 and B5 increased temperature increases absorption. However, at site B12 and B14 increased temperature decreases absorption. This effect is largely site dependent and may depend on other geochemical parameters. Generally, the metal Cu shows at three

out of four sites that increasing temperature increases absorption (see Table 5.4, Figures 5.4-5.11), with the exception being at B12, which generally demonstrates a different absorption/desorption pattern.

5.3.3.5 Geochemical parameters

5.3.3.5.1 DOC

DOC could have an effect at site B5 where it is relatively high (9.5 mg/L) (see Table 5.3) where the pH could alter the form in which it is found and can mean that some species of Al or Cu may possibly bind to it, thereby explaining the pattern of desorption. The concentration of DOC decreases as the volume of water increases upon moving downstream, possibly as it becomes more dilute, and relative to peaty inputs from uplands. It may also be altered in form on moving downstream.

5.3.3.5.2 Electroconductivity

EC is relatively low at B1 (30 – 30.6 $\mu S/cm^{-1}$) (see Table 5.3) and increases at B5 (52.5 -143 $\mu S/cm^{-1}$) and B12 although this water for the 4°C was collected during a storm so is relatively low in terms of EC (B12 – EC – 360 $\mu S/cm^{-1}$) which is low for this site. Again, the 10°C water is also low for this site (602 $\mu S/cm^{-1}$). Site B14 has a low EC (41-104.4 $\mu S/cm^{-1}$).

5.3.3.5.3 pH

As in previous chapters, pH was found to be acidic (range; 4.02-6.45) (see Table 5.3). Site B1 was the most neutral with a pH of 5.51/6.45 on respective dates. Site B5 was slightly more acidic with a pH of 4.88/5. The most acidic adit was B12 with a pH of 4.25/4.02. The most downstream site, B14 had a more neutral pH of 6.15/5.6.

Table 5.3 – Geochemical parameters of river water used in the sorption-desorption experiment

Date	*Experimental Temp (°C)*	*Site*	*pH*	*Turbidity (NTU)*	*DOC (mg/L)*	*EC ($\mu S/cm^{-1}$)*
07/07/2015	4	B1	5.51	0	13	30
07/07/2015	4	B5	4.88	1.25	9.5	143
07/07/2015	4	B12	4.25	0.76	2.2	360
07/07/2015	4	B14	6.15	0	2	41
01/09/2015	10	B1	6.45	0	1.5	30.6
01/09/2015	10	B5	5	2.77	2.5	52.5
01/09/2015	10	B12	4.02	0	0.4	602
01/09/2015	10	B14	5.6	0	2.6	104.4

Table 5.4 – Absorption/desorption summary of findings

Site	*Metal*	*°C*	*Trend*	*Range Min %*	*Range Max %*	*Range min (mg/L)*	*Range max (mg/L)*	*Effect of change in SSC*	*Effect of increasing flow*	*Effect of increased temp*
B1	Al	4	Desorption	-233%	-87%	-0.3274	-0.123	Constant	Constant	Increases absorption
B1	Al	10	Absorption	-28%	77%	0.0136	0.0049	Random	Random	
B1	Cu	4	Absorption	-521%	706%	-0.324	0.1105	Random	Longer time Less sorption	Increases absorption
B1	Cu	10	Absorption	1270%	6371%	0.0013	0.0064	Random	Random	
B5	Al	4	Desorption	-98%	-93%	-0.1309	-0.123	Constant	Constant	Increases absorption
B5	Al	10	Desorption	-92%	-16%	-0.0032	-0.0003	At low flow increases with increased SSC	Constant	
B5	Cu	4	Desorption	-73%	-58%	-0.007	-0.0056	Constant	Constant	Increases absorption
B5	Cu	10	Desorption	-73%	9%	-0.0032	0.004	Constant	Increased sorption at 24hr flow.	
B12	Al	4	Absorption	151%	159%	11.331	11.975	Constant	Constant	Decreases absorption
B12	Al	10	Desorption	-10%	2%	-1.532	0.2679	Constant	Constant	
B12	Cu	4	Absorption	82%	112%	0.1532	0.208	Constant	Constant	Decreases absorption
B12	Cu	10	Desorption	-19%	-6%	-0.0638	-0.0226	Constant	Constant	
B14	Al	4	Absorption/desorption	-618%	73%	-0.1324	0.0158	Random	Random	Decreases absorption
B14	Al	10	Absorption/desorption	-24%	109%	-0.0102	0.0449	Random	Random	
B14	Cu	4	Absorption	100%	270%	0.0009	0.0024	Yes at high flow	Random	Increases absorption
B14	Cu	10	Absorption	106%	408%	0.0011	0.0041	Random	Random	

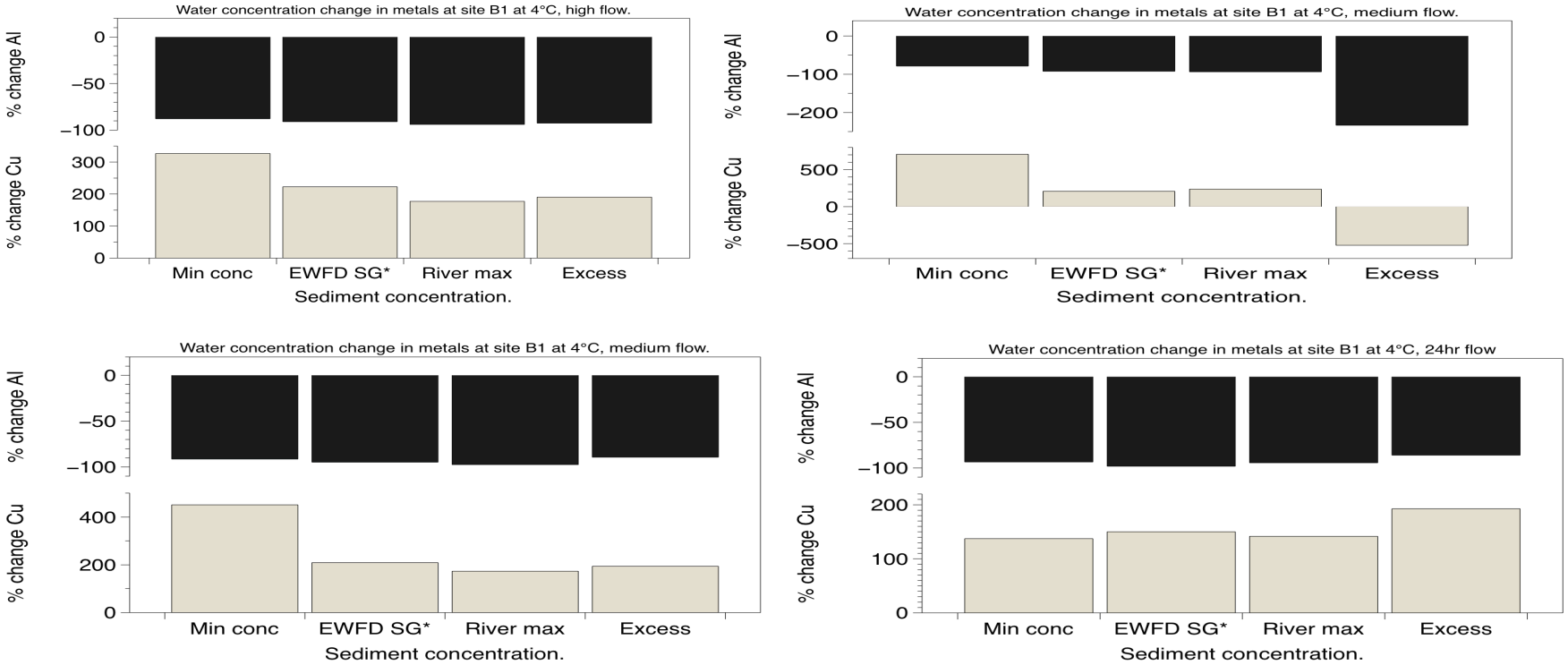

Figure 5.4 – Concentration change in Al and Cu in mg/L at site B1 at 4 °C.

4 Different concentrations of sediment were used, a minimum concentration, the European Water Framework directive sediment guideline, the maximum found in the river and an excess. Times were modelled according high (11 hours), medium (18 hours) low (21 hours) and an excess flow based on 24hr.*

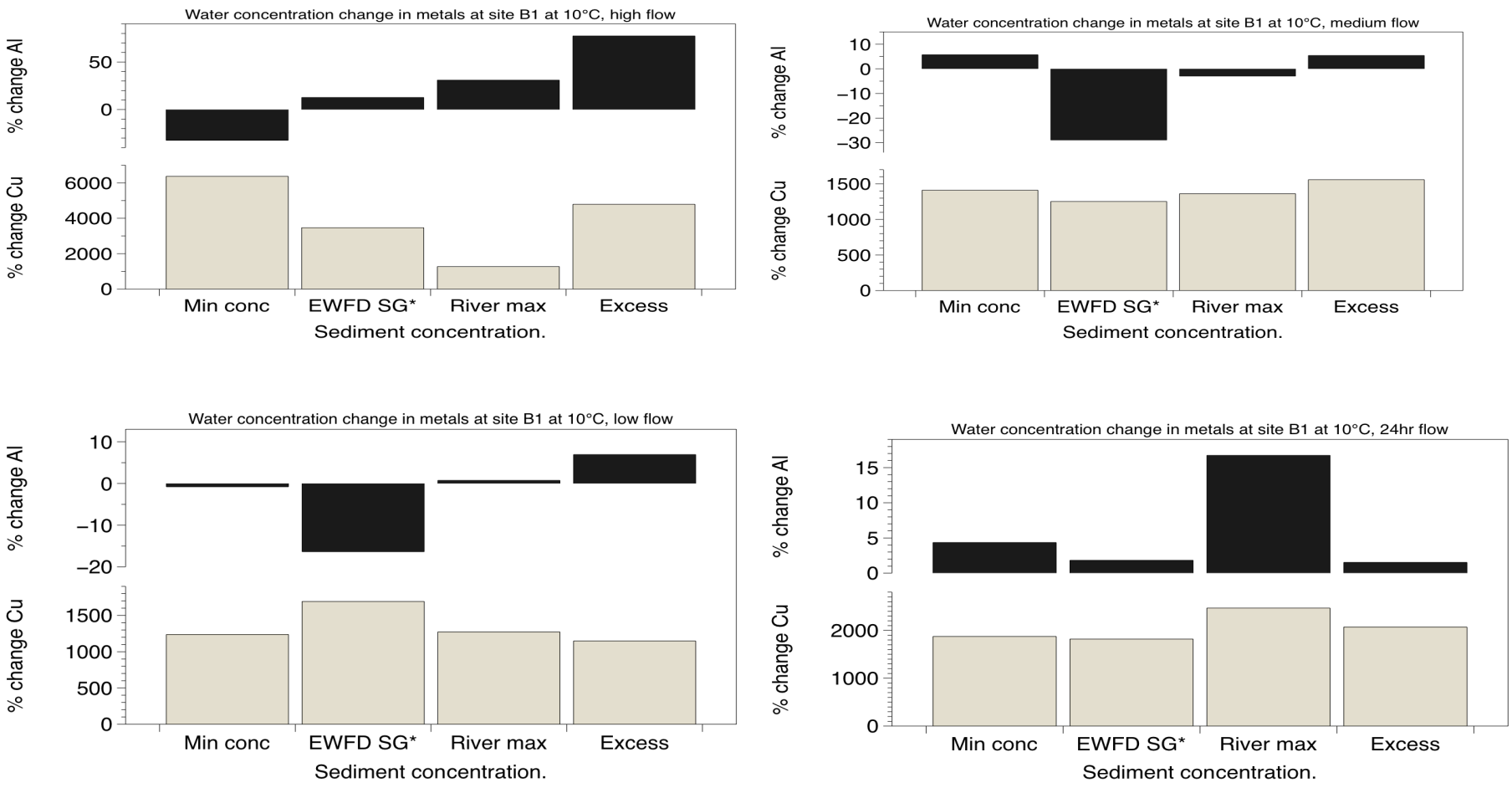

Figure 5.5 – Concentration change in Al and Cu in mg/L at site B1 at 10°C.

4 Different concentrations of sediment were used, a minimum concentration, the European Water Framework directive sediment guideline, the maximum found in the river and an Excess. Times were modelled according high (11 hours), medium (18 hours) low (21 hours) and an excess flow based on 24hr.*

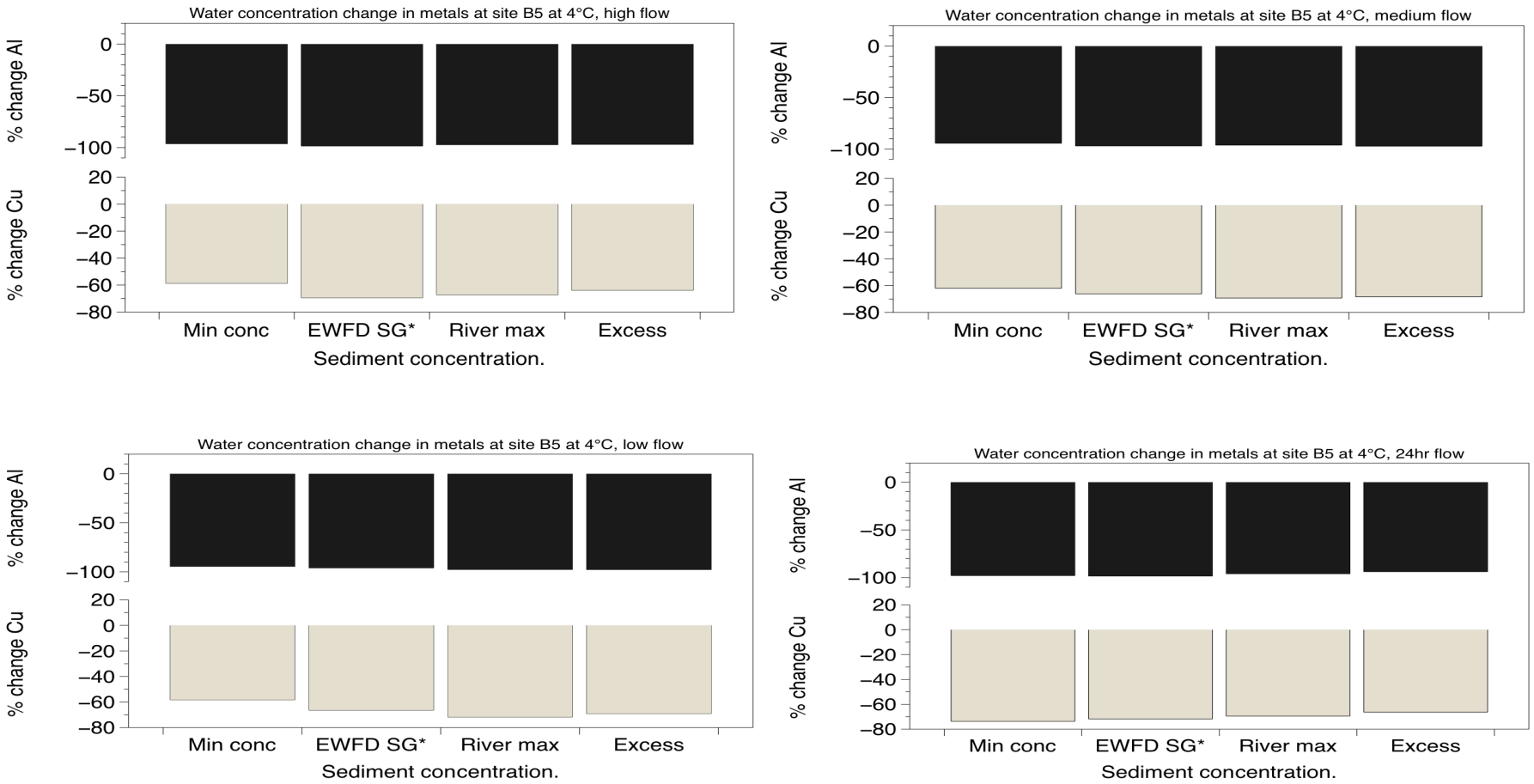

Figure 5.6 – Concentration change in Al and Cu in mg/L at site B5 at 4°C.

4 Different concentrations of sediment were used, a minimum concentration, the European Water Framework directive sediment guideline, the maximum found in the river and an Excess. Times were modelled according high (11 hours), medium (18 hours) low (21 hours) and an excess flow based on 24hr.*

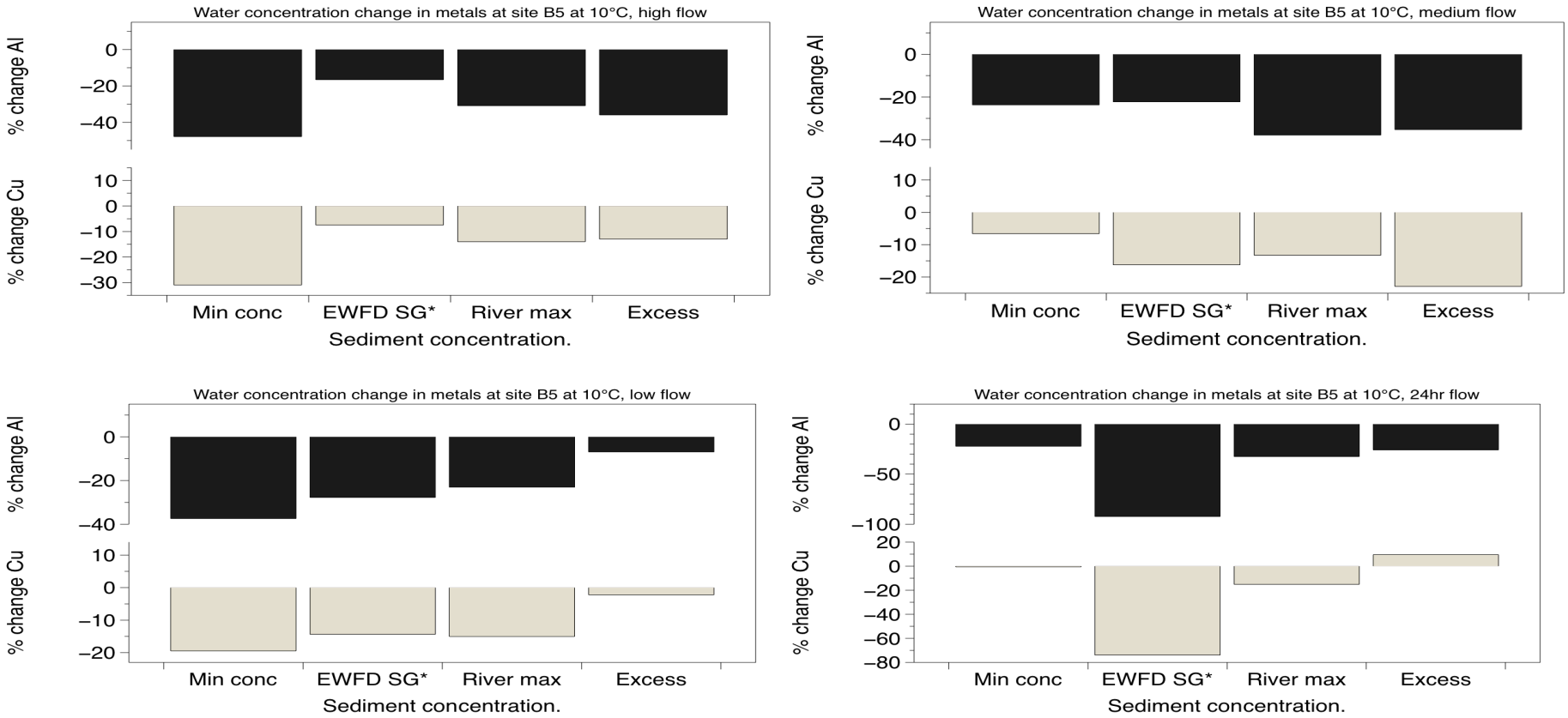

Figure 5.7 – Concentration change in Al and Cu in mg/L at site B5 at 10℃.

4 Different concentrations of sediment were used, a minimum concentration, the European Water Framework directive sediment guideline, the maximum found in the river and an Excess Times were modelled according high (11 hours), medium (18 hours) low (21 hours) and an excess flow based on 24hr.*

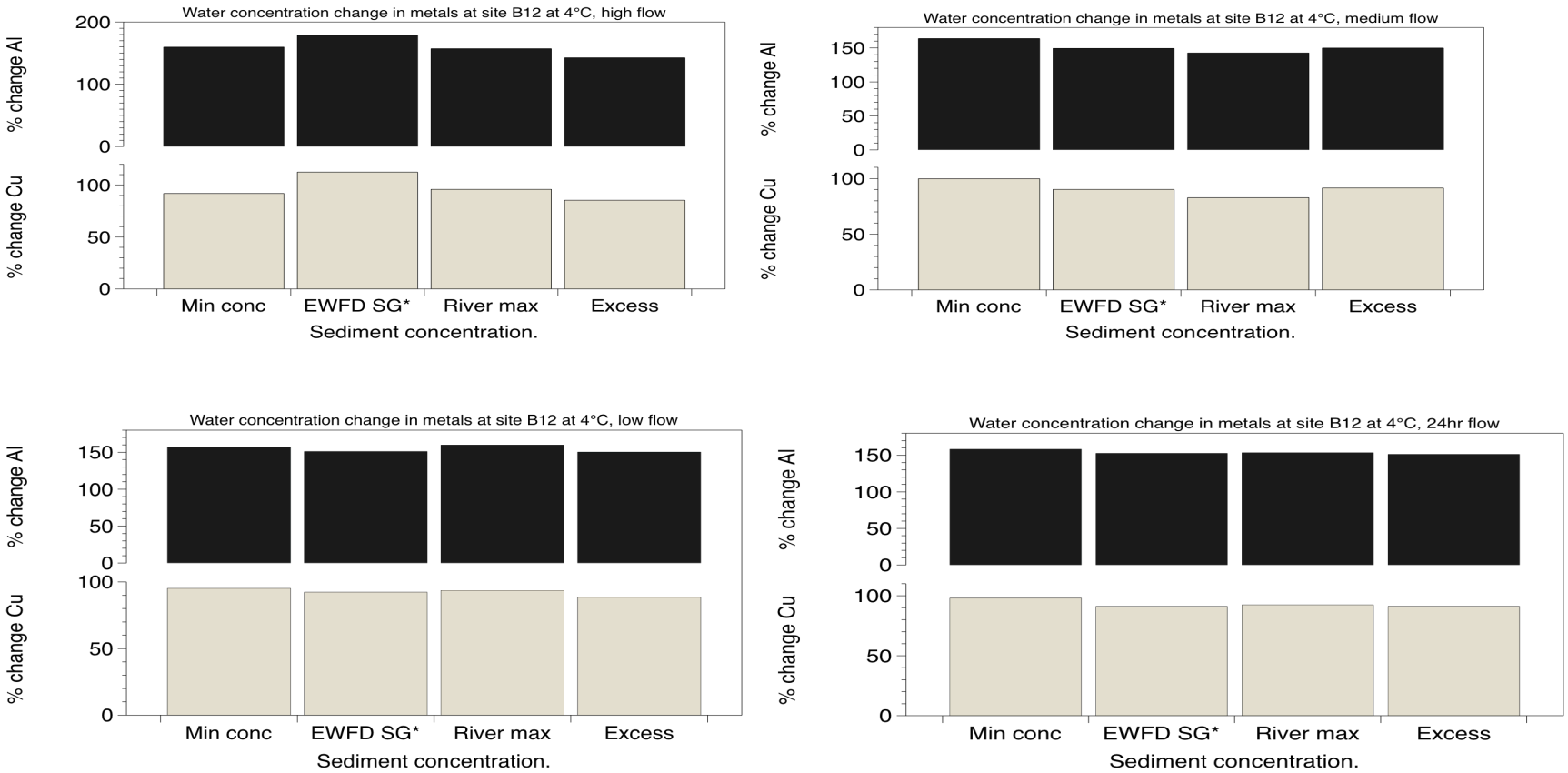

Figure 5.8 – Concentration change in Al and Cu in mg/L at site B12 at 4°C.

4 Different concentrations of sediment were used, a minimum concentration, the European Water Framework directive sediment guideline, the maximum found in the river and an Excess. Times were modelled according high (11 hours), medium (18 hours) low (21 hours) and an excess flow based on 24hr.*

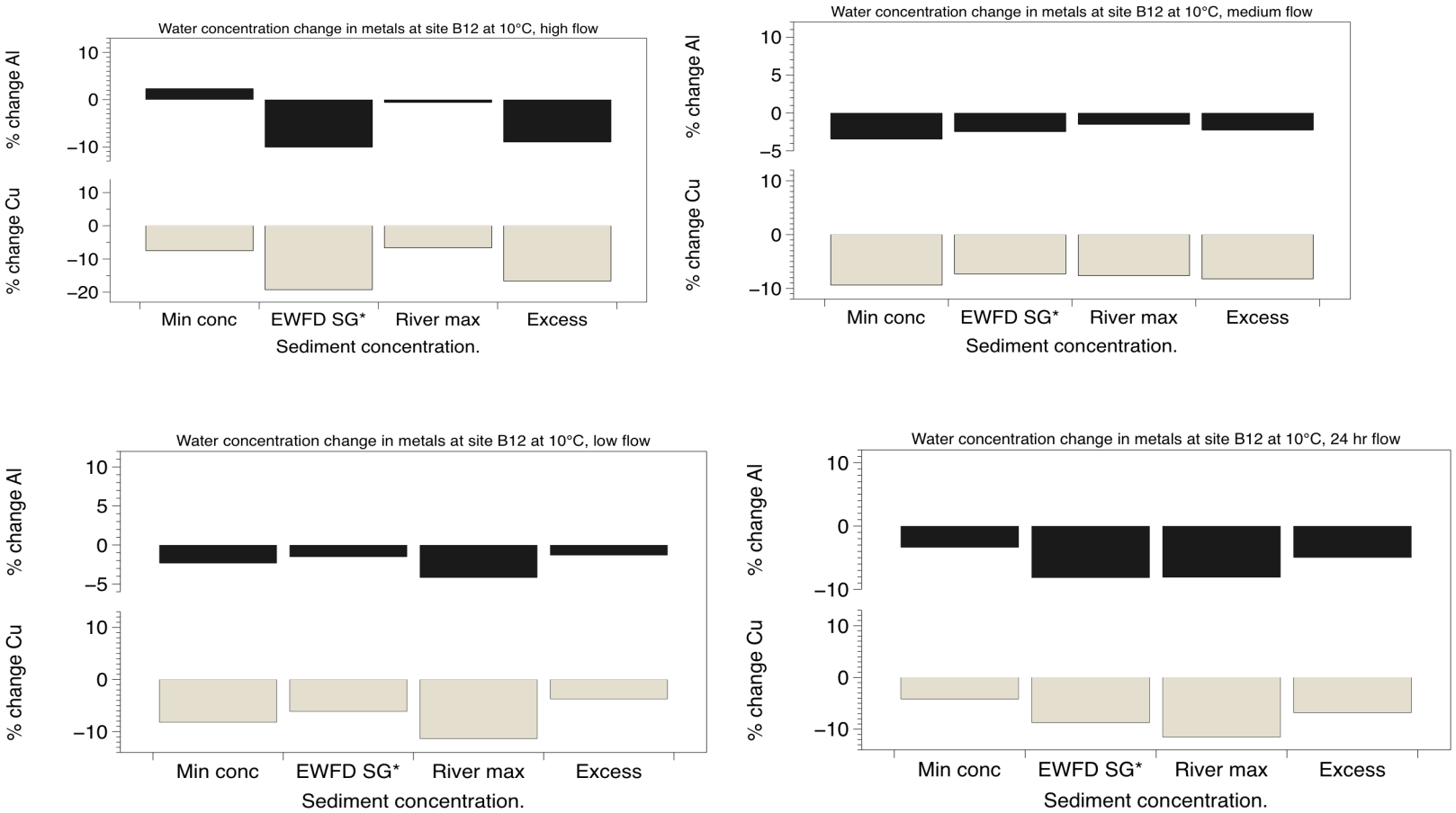

Figure 5.9 – Concentration change in Al and Cu in mg/L at site B12 at 10℃.

4 Different concentrations of sediment were used, a minimum concentration, the European Water Framework directive sediment guideline, the maximum found in the river and an Excess. Times were modelled according high (11 hours), medium (18 hours) low (21 hours) and an excess flow based on 24hr.*

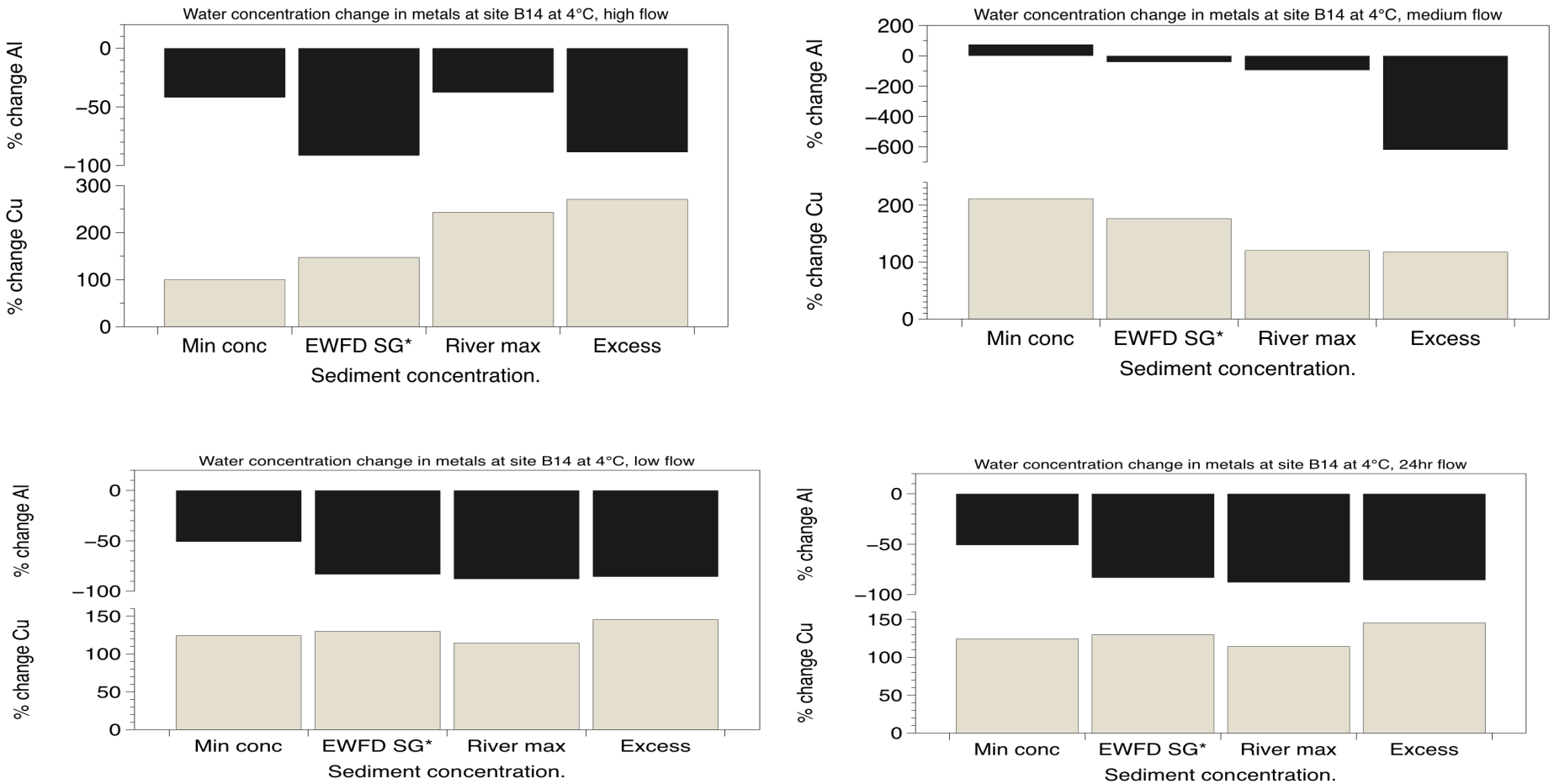

Figure 5.10 – Concentration change in Al and Cu in mg/L at site B14 at 4°C.

4 Different concentrations of sediment were used, a minimum concentration, the European Water Framework directive sediment guideline, the maximum found in the river and an Excess Times were modelled according high (11 hours), medium (18 hours) low (21 hours) and an excess flow based on 24hr.*

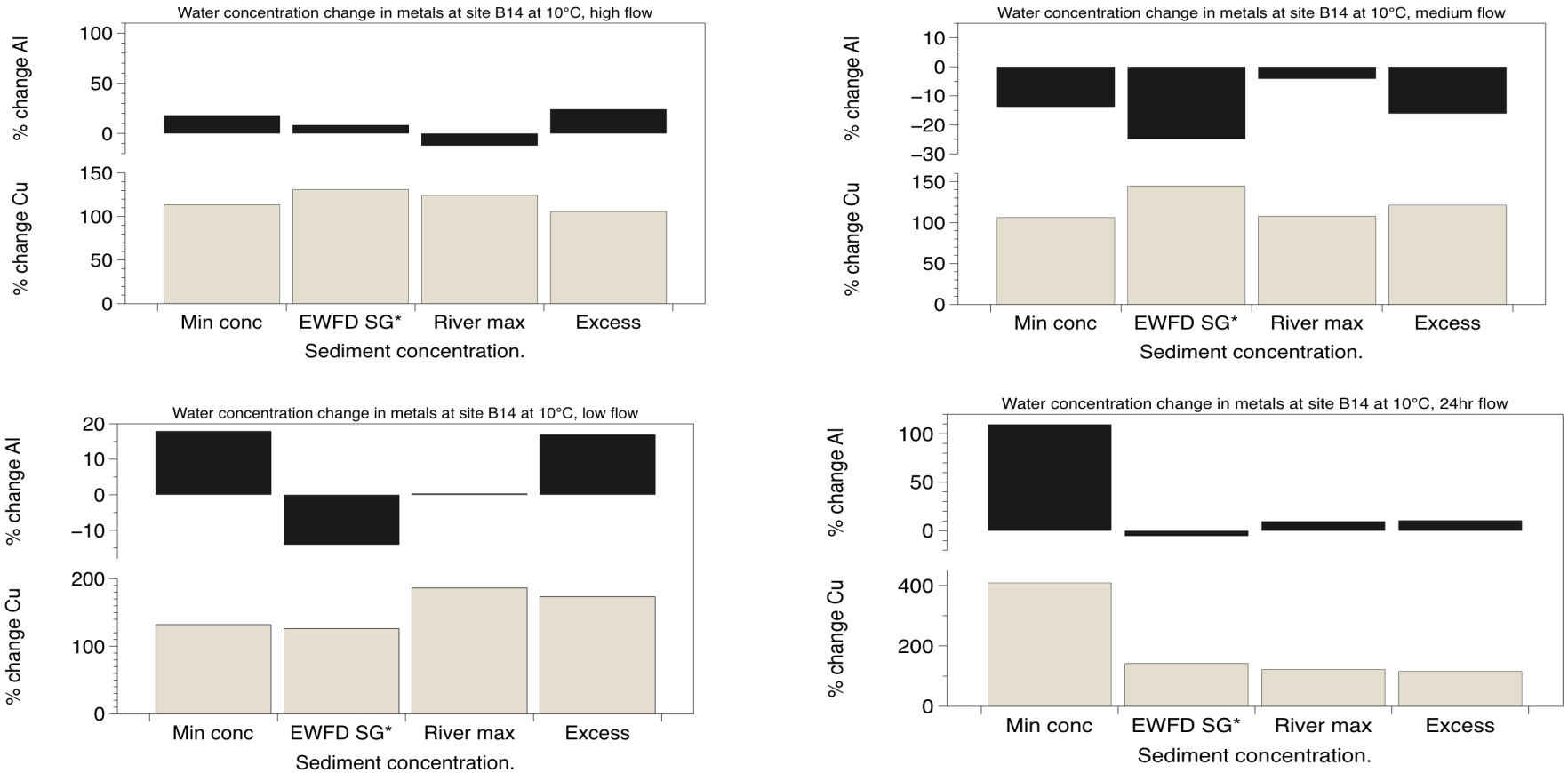

Figure 5.11 – Concentration change in Al and Cu in mg/L at site B14 at 10℃.

4 Different concentrations of sediment were used, a minimum concentration, the European Water Framework directive sediment guideline, the maximum found in the river and an Excess. Times were modelled according high (11 hours), medium (18 hours) low (21 hours) and an excess flow based on 24hr.*

5.3.4 Results of ANOVA

A three way between-groups analysis of variance was conducted to explore the impact of site, sediment concentration and time (analogous to flow rate) on change in Al. The interaction between time and site (F (9,67) = 0.003, p =1.00), site and sediment concentration (F (9,67) = 0.124, p = 1.00) and sediment concentration and time were not significant (F (9,67) = 0.0.003 p = 1.00). The three-way interaction between site, sediment concentration and time was also not significant (F (27,67) = 0.003, p = 1.00). There was a statistically significant effect for site F (3,67) = 9.152 p = 0.000) and the effect size was medium (partial eta squared = 0.288) (Cohen, 1988). Post-hoc comparisons using the Tukey HSD test indicated that the mean score for site B1 (M = -0.65, SD = 0.719) was significantly different from site B12 (M =-5.192, SD = 0.719). It also indicated that the site B5 (M =-0.179, SD = 0.719) differed significantly from site B12 (M = 5.192, SD = 0.719). Site B12 (M = - 5.192, SD = 0.719) also differed significantly from site B14 (M = -0.009, SD = 0.719). The main effect for sediment concentration did not reach statistical significance (F (3,67) = 0.003, p =0.99). The main effect for time did not reach statistical significance (F (3,67) = 0.003, p = 1.00).

A three way between-groups analysis of variance was conducted to explore the impact of site, sediment concentration and time on change in Cu. The interaction between time and site (F (9,67) = 1.00, p = 0.003), site and sediment concentration (F (9,67) 0.006, p = 1.00), and sediment concentration and time were not significant (F (9,67) = 0.005, p = 1.000). The three-way interaction between site, sediment concentration and time was also not significant (F (27,67) = 0.006, p = 0.471). There was a statistically significant main effect for site (F (3,67) = 5.143, p=0.002) and the effect size was medium (partial eta squared = 0.193) (Cohen, 1988). Post-hoc comparisons using the Tukey HSD test indicated that the mean score for Site B1(M = 0.017, SD = 0.012) was significantly different from group B12 (M = 0.18, SD = 0.012). It also indicated that the groups site B5 (M = -0.017, SD = 0.007) differed significantly from site B12 (M = 0.018, SD = 0.012). Site B14 (M = 0.018, SD = 0.012) also differed from site B12 (M = 0.018, SD = 0.012). The main effect for sediment concentration did not

reach statistical significance ($F(3,67) = 0.10$, $p = 0.999$). The main effect for time did not reach statistical significance ($F(3,67) = 0.001$, $p = 1.00$).

5.4 Discussion

Sediments can have a major impact on rivers acting as a source of pollution. Chapter 5 shows substantial pollution in the river Barlwyd as have others (Bray, 1996; Buss et al., 2013; Pryce and Janes 2009). The aims of this study were to establish the properties of sediment and the degree to which it acts as a pollutant. The type of sediment was confirmed as a clay smectite of the dioctahedral type. There is evidence to show that the sediment is enriched in Al and Cu and thus could act as a source of pollutants in the river Barlwyd. The picture emerging is a complex one, owing to the clay's chemical and physical properties, and is dependent on several geochemical parameters and sediment composition.

5.4.1 Slate composition – chemical and particle size

Firstly, the slate sediment is a clay/silt type composition in terms of particle size. Due to its fine particle characteristics, it is likely that it is dissolved into the river. It also has a high reactive surface where it is dissolved into the water fraction. Fine particles, especially clay minerals, organic matter and Fe hydroxides, can adsorb large quantities of metals through cation exchange processes (Förstner et al, 1979; Salomons and Förstner, 1984). It has also been suggested that clays accumulate high concentrations of metals through mechanical processes alone, without the aid of chemical reactions (Jenne, 1976). This means that metal concentrations are usually greatest in the clay size fraction, while the lowest concentrations are usually observed in the quartz-dominated silt and fine sand fractions (Horowitz, 1991). This also means there is a greater surface area for reaction.

In terms of composition, the components of slate sediment are comprised of 38.3% of Al in slate sediment, which likely accounts for the high levels of Al. The amount of Cu in the sediment is lower,

although the relatively high levels of Cu may possibly be accounted for perhaps by water chemistry i.e., pH, its solubility in water and the sensitivity of biological organisms to Cu. As the level of Cu in the water is less than that of Al this is appropriately reflected in water chemistry results. This provides some evidence as what is occurring in the river and a link between geology and the pollution can be established. This correlates with slate being described as having high levels of gibbsite which is rich in Al.

Previous studies have shown the composition of some slates, having been described as a smectite type. Extensional basins in Wales, the northern Lake District and the Isle of Man are described as having a larger variety of species in clay mineral assemblages (Merriman, 2002). Na-bearing clays may have been created from low-temperature interflow of hydrothermal fluids and seawater in the extensional basins (Merriman, 2002). Such fluids appear to have been missing in the convergent basins through dearth of volcanic activity in the early stages of basin growth. Regional diversity in clay mineral assemblages indicate that where mud rocks have evolved in the higher heat-flow extensional basins they generate a distinctively diverse assemblage that classically includes both the K-rich and Na-rich characteristics of the 2:1 dioctahedral reaction series, and sporadic pyrophyllite (Merriman., 2002). On a more localized measure, Na clays are especially frequent in the aureoles of sub-volcanic intrusions in Wales (Merriman and Roberts, 1985; Jiang and Peacor, 1993; Merriman, 2002). Although Na clay minerals are common in more local hydrothermal aureoles, their wider distribution can also be associated with the major volcanic centres in Wales. Around the Snowdon volcanic centre in north Wales, intermediate Na/K mica and paragonite are important components of clay assemblages in the Cambrian slates, to the north and west, and in assemblages in the Ordovician slates to the south and east of the centre such as that found in Blaenau Ffestiniog (Merriman and Roberts, 1985; Merriman, 2002). This is consistent with findings that mica, gibbsite and montromillite are those clays which have been found in slate previously and have high Al content.

Researchers have also shown that sodic fluids were channelled into long-lived fracture zones, on a regional scale. Inside the Menai Straits fault zone in north Wales, it has been demonstrated by two

TEM (transmission electron microscopy) studies that retrogression of clay assemblages is because of fluids with elevated Na/K ratios (Jiang et al., 1990; Dong et al., 2002).

Fe has been found in high concentration both in the river previously (Buss et al., 2013) and in the TxRF analysis is also significant. Dissolved metals co-precipitate with the Fe and manganese oxides, and therefore become concentrated on the surface of fluvial sediments (Horowitz, 1991). Organic molecules transported within the fluvial sediment load also act as a focus for the accumulation of metals (e.g., Swanson et al., 1966; Gibbs, 1973). Metals are bound to organic molecules by a variety of processes, including adsorption, chemical bonding and physical trapping. This could help explain the results which are at times conflicting to expectations.

5.4.2 Site dependency – a pH dependent mechanism

The concentration of metals in, and pH of, mine drainage waters is dependent on factors such as

- The supply of oxygen and carbon (as fixed or bicarbonate).
- the grain size and composition of the pyrite or metal sulphides.
- the presence of Fe- and sulphur-oxidising bacteria.
- temperature
- any neutralisation of the acid solutions by reaction with carbonate minerals (Rose and Cravotta, 1998)

Mine water may be directly discharged as seen here. High metal concentrations in mine drainage results from the oxidation of metal-bearing sulphide minerals, most commonly pyrite [FeS_2], which host metallic and metalloid elements such as arsenic, cadmium, Cu, lead and zinc (Younger et al., 2002).

The more distinct properties a certain clay possesses, the more complex the overall behaviour will be (Preocanin, 2016). The most significant finding was that variation of Al/Cu sorption/desorption was dependent on site. As each site has different geochemical parameters, these could be responsible for

the varying sorption/desorption patterns. Site B12 was of relevance, as all sites were statistically significantly different to B12. Site B12 has a very low pH which sometimes changes the form in which the metal is found, with Al oxides converting to ionised Al, and are thus more bioavailable and bio toxic. Interestingly, site B1 also shows a high degree of Cu is exactly balanced by adsorbed cations. Some of the cations in 2:1 clays are held in the interlayer spaces and can diffuse only very slowly into the outer solution. Perhaps this is where the Al layers are held so tightly (Wild, 1993). Both processes result in faster Cu release rate with lower pH. However, low pH can reduce the negative charge of organic matter clay particles, which may explain the complexity of the results.

The water at B5 has a pH of 4.88/5 and contains a relatively high concentration of metals, having mixed with water and sediment from the quarry at B4 and shows a desorpative pattern under all conditions. There may be a two-stage consecutive mechanism acting here, in which dissolved metals adsorb initially onto the exterior surface of the sediment and, in time, may migrate back into the clay matrix. The water is potentially saturated with metals already as the water is taken from here and has already mixed with sediment in the cutting process. High pH promotes adsorption of metals into water e.g., site B1 at 10 ºC, where the pH is 6.45. Low temperature weakens the strength of metal association and impacts metal retention by sediments, thereby explaining absorption at 4 ºC. H^+ occupies more adsorption sites at low pH, thereby precipitating soluble and carbonate bound metals at higher pH levels.

Al and Cu reveal a different type of behaviour. This is because of ionic charge and the chemistry of the clay. Cu absorbs in this water much more readily. Al is found at higher concentrations in the sediment and may be held more tightly on the gibbsite plane. Furthermore, there is a possibility that DOC may play a role where is higher in concentration in the 4 ºC water. Adsorption is strongly influenced by pH; the amount of adsorption of metals by particulates can increase by 100 % as pH increases by 1-2 critical units (Benjamin and Leckie., 1982). An increase in pH, or changes in oxidation-reduction potential or metal concentrations can lead to the direct precipitation of dissolved metals out of solution (Salomons and Förstner, 1984).

The mechanism of adsorption/desorption can be explained by a clay type pH dependent mechanism. As the clay found is postulated to be of a smectite type based on chemical composition, particle size and previous findings (Merriman, 2002), it is more adsorbent of metals than other types of clay, particularly at low pH where metals become more tightly adsorbed.

When there is a change in pH, or redox potential in water the solubility of the sediment will change. Protons dissociate from the surfaces and edges of clay minerals and from acidic groups in humus (aluminosilicates and hydrous (hydrated) oxides of Fe and Al) dependent upon pH. Dissociation can lead to a pH dependent negative charge, which increases as the pH is raised (Wild, 1993). Hydrous oxides of Fe and Al can be positively charged at low pH by absorption of protons, and thus may adsorb to the negative charge in the clay type (Wild, 1993). This may explain the results found at B12 at 10 ºC, where Al is absorbed by changes in Cu^{2+} clay.

The smectites in clay are the same to those that are found in soil. Smectites are a 2:1 clay mineral and hold non-exchangeable cations which have a relatively high charge density so that silicate sheets are held tightly. In the presence of sufficient water many cations are distributed in a diffuse layer. Al has a high affinity for cation adsorption. Metals conversely such as Cu form similar complexes at surfaces that contain hydroxyl groups, particularly those of hydrated Fe manganese and Al oxides (Nordstrom, 2009). Complex Cu ions do not undergo cation exchange hence less desorption at low pH. Cu is only displaced by extraction with acid or with strong complexing agents. Interlayer cations and charged 2:1 clay surfaces interact strongly with polar solvents; when it is in an aqueous medium, clay expands, and the phenomenon is known as crystalline swelling (Harward and Brindley, 1966). The degree of swelling is regulated by an equilibrium between relatively strong swelling forces and electrostatic forces of attraction between the negatively charged phyllosilicate layer and the positively charged interlayer cation (Chatterjee, 2004). As site B12 is low pH positive charges could be developed on the surfaces of hydrated oxides of Fe and Al. This increases the negative charge on the surface of clay which in turn repels metal ions and thus adsorption into the aqueous phase (Wild, 1993).

A plausible explanation as to why the results are so complex are that charging behaviour of clay platelets is based on the different surfaces exposed to the solution. The basal planes of clay have a permanent charge irrespective of pH (Preocanin., 2016). Edge surfaces conversely exhibit amphoteric behaviour and pH dependent charge that is characteristic of oxide minerals. The background solution affects the basal planes and edges in different ways. When measured electrokinetically clay is negative over the full pH range. Different planes such as on kaolinite can have different charging properties (a gibbsite and a silica plane). Montmorillonite possesses relatively high cation exchange properties. The slate sediment we have identified behaves in a complex manner. The electrolyte concentration and pH affect the behaviour. There is also an electrical interfacial layer (EIL) of charged particles in aqueous solution on the two planes. The formation of the so-called electrical interfacial layer (EIL) of charged particles in aqueous solutions is one central aspect (Preocanin, 2016).

The formation of the EIL on a single crystal plane is defined by the overall surface charge density (immobile, Stern layer) and the diffuse layer properties (electrolyte composition and concentration). The former arises from the specific adsorption of potential/charge-determining ions and/or the permanent charge due to isomorphic substitution. Electrolyte ions may have twofold effects. First, they may form ion pairs with the charged surface and thus screen the charge within the immobile layer. The higher the affinity of a given ion to a specific surface is, the more effective the screening will be. Sufficiently high affinity may lead to overcharging (i.e., charge inversion) which could explain the sorption/desorption pattern. Second, electrolyte ions will neutralize the net charge of the immobile layer in the diffuse part of the EIL. The higher the charge of an ion is, the more effective the screening will be. Increasing the electrolyte concentration will enhance screening. The ion-exchange properties are obviously also dependent on the salt concentration. The behaviour of a Na-clay in high concentrations of calcium or some other cation different from sodium transforms the clay either partially or completely into another form, like what happens at low pH (Preocanin et al., 2016). If there are high concentrations of Ca then the clay will fully transform into another form completely or partially. At low pH protons play a part in ion exchange, basal planes are prone to reactions in

gibbsite at pH 3-10. The physical and chemical properties of water have been showed to change near basal surfaces where the ionisation of water becomes more pronounced. It has been proposed that Al could dissolve from the gibbsite and partially reabsorb (Lutzenkirchen et al., 2010; Adekola et al., 2011; Lutzenkirchen et al., 2010; Preocanin et al., 2016). Preocanin et al. (2016) present a good body of evidence which suggests that clay is anisotropic (see Figure 5.12). Overall exposed surface area will be greater when the sediment is fine and there will be a greater surface area to react, and there will be less weathering required to release metals.

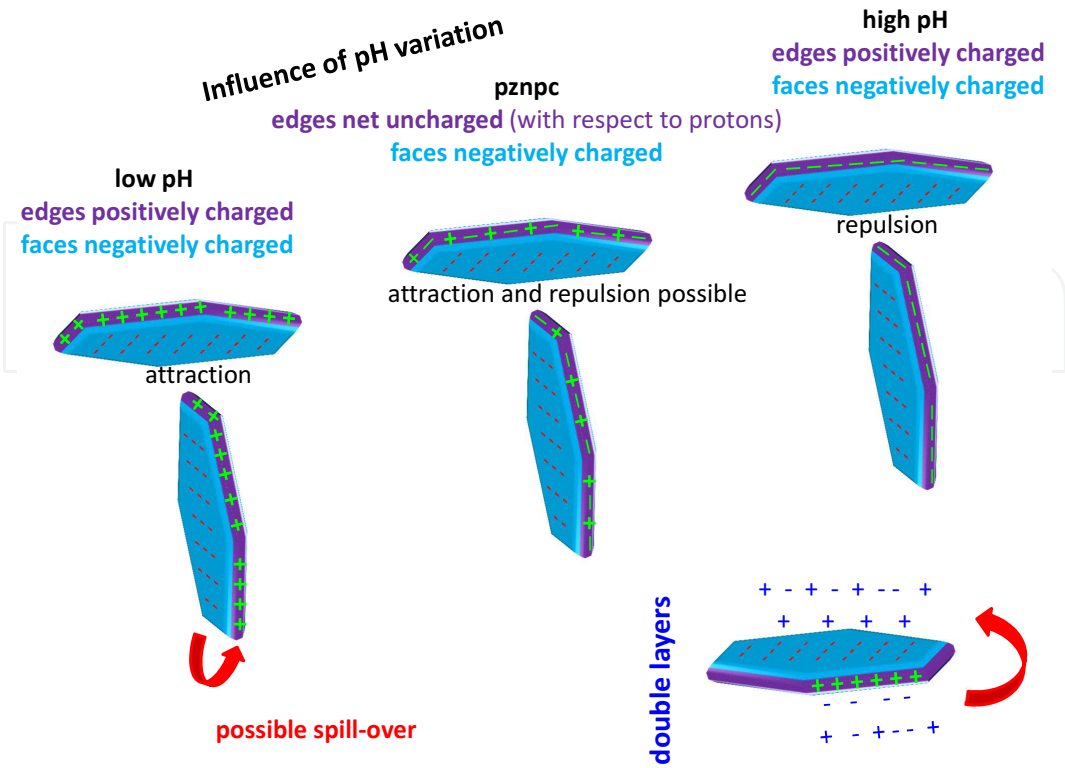

Figure 5.12 – Clay ionic structure and the electrical interfacial layer (bottom) (Preocanin et al., 2016)

Scenarios of low Ph, Point of zero net proton charge (pznpc) middle and high pH.

Preocanin et al. (2016) state that both the gibbsite and the silica basal plane exhibit pH-dependent behaviour, suggesting proton uptake and/or release from the surface functional groups on the two planes. Whereas some clays (such as kaolinite) do not exhibit strong interlayer cation exchange,

others (such as montmorillonite or illite) possess relatively high cation exchange capacities. Exposing the latter to strongly concentrated electrolyte solutions will cause an exchange of the interlayer ions (i.e., exposure of a sodium clay to a sufficiently concentrated calcium solution will transform the clay to the calcium form at equilibrium) and was shown to have repercussions on modelling metal ion adsorption. The effect of the master variables pH and ionic strength on clay particles makes the adsorption/desorption highly complex (Preocanin et al., 2016). Each site must thus be treated as unique because of its composition and exposure of sediment to the aqueous phase.

5.4.3 Relative contribution of additional factors – SSC, temperature, flow and geochemical parameters

The results conflict with prediction in our hypothesis in showing a higher complexity than our initial hypothesis. It would be expected that increasing the sediment concentration would increase Al/Cu sorption/desorption in the water column. Sediment concentration seems to have no bearing on the degree of pollution. Temperature does seem to have an effect in some sites, whereby a higher temperature enhances the sorption of Al/Cu from the sediment. Li et al. (2013) found comparable results with heavy metals, finding that metal absorption in water is greater at higher temperatures. When temperature is increased, chemical reactions are accelerated and DO and dissolutions of hydroxides and carbonates are augmented, thereby heightening the release rate of water soluble and exchangeable fraction of the sediment (Li et al., 2013). This may be relevant in the context of climate change, and the influence of increasing temperatures on aquatic pollution derived from metals such as Al/Cu derived from anthropogenic influences.

In terms of flow rate there is little evidence to indicate that increasing the residence time increased the number of metals absorbed/desorbed. The limiting factors may thus be geochemical parameters. This conflicts with Li et al. (2013) who show that an increase in flow rate increases heavy metal absorption to the aquatic phase when looking at heavy metal absorption from sewerage. As the experiment was run in a closed envFement, perhaps it is not an ideal model of flow, as DO would not be increased by

increasing residence time artificially. Geochemical parameters such as redox, and DOC may also be of importance. Overall, it is the balance of metals, pH, cations anions and DOC which are influencing the concentration of metals and absorption into water of the quarry pollution. Furthermore, temporal variations at the time of water sampling may have an influence on differences between the two temperature datasets.

5.4.4 Study limitations and future directions

Limitations of this study include that it was not possible were to statistically assess the effect of temperature as there were only being two ranges assessed limited owing to practical limitations and this offered too few degrees of freedom. The different sets of water were used owing to practical time limitations and capacity of conducting the experiment, the different geochemical properties may have influenced the results under differing temperature conditions.

Additional caveats are that flow may not be representative as shorter times should ideally have agitated more to represent the degree of turbulence. Had we added this factor, this may have been too many factors to represent. To enhance statistical robustness of each variable could also have used a larger number of levels of each factor and then used a mixed model to statistically assess our findings more effectively. Furthermore, longer times may be needed to assess whether the desorption then becomes sorption at a later stage of experimentation. The experiment was also conducted in an anoxic envFement and thus may not be representative of the increased DO encountered in the natural envFement. It may perhaps be better to model the flow using a peristaltic pump and sediment in a column-based experiment, as DO could change the release of metals at different rates. The ORP of the water could also be monitored before and after the experiment. The oxidation-reduction potential of sediment also influences the amount of adsorption that can occur. In reducing conditions, when sediment has high water content, metals form insoluble sulphides (Coulthard et. al., 2005). In contrast, in oxidising conditions when water content is low, metals become more mobile. Therefore, a change from reducing to oxidising conditions within sediment can cause the release of metals into solution

(Förstner, 1987). As previously outlined the influence of calcium could also be important, and sodium, as with regards effect on clay in solution. Thus, these too could also be measured in the water. An interesting and simple caveat might include adding sediment to the river/distilled water and looking at the pH change.

Another avenue for future research would be to examine the catchment further downstream for sediment remobilisation from the floodplain. Further research also needs to confirm exactly what the EQS for Al is to be clearer of what limit should be set in the water column. Furthermore, given the importance of silicates with regards to Al, perhaps this should also be investigated as a function of absorption.

Additional factors which could have been assessed which are known to affect metal release include DO, salinity, redox potential, bioturbidation and physical disturbance. Additionally, AVS (Acid Volatile Sulphides) are thought to affect metal release from sediment, and these could have been measured. To further complement the data an analysis of the suspended sediment and its metal content in the river could be conducted.

The goal of setting sediment guidelines for the EWFD is yet to be established. The results would require more experimental work to characterise the clay further and repetition of the experiment. Furthermore, it is not possible to derive guidelines for the EWFD for sediment concentrations from this data, as it is variable and has no specific pattern. However, pH in combination with sediment concentration could provide a basis for remediation in this river, as levels of Al/Cu can be high at this low pH which could indicate a need for liming or other methods of remediation.

5.5 Conclusions

Based on this data, it is proposed that the relative contribution of sediment toxicity is pH dependent/type dependent. We propose that the sorption/desorption pattern is due to the clay type present in the rock and water chemistry. Sediment found is like a Na^+/K^+ dioctahedral clay rich sediment. The magnitude and mechanism of sediment sorption/desorption is pH mediated/geochemical. This study characterises slate sediment derived from quarrying and its relative Al/Cu toxicity to the water column for the first time. The degree of Al/Cu pollution made to the water column has been assessed. This pollution can be toxic in terms of Cu, exceeding the EWFD and Al when coupled with pH and temperature. Because the sediment is a clay type, the sorption/desorption behaviour is more complex than anticipated, and further work would be needed to establish fields of attraction in this sediment. It is clear from these results however that the suspended load can be toxic according to geochemical conditions, releasing metals into the aqueous phase.

CHAPTER 6 – REMEDIATION OF SLATE QUARRYING POLLUTION BY BIOCHAR AND ZEROVALENT IRON

6.1 Introduction

According to the WHO, the scarcity of water has created challenges for up to 40% of the world's population (WHO, Fu et al., 2014). Therefore, protecting water against degradation through wastewater treatment is of critical importance (Fu et al., 2014). Having earlier established a link between slate quarrying and high levels of Al and Cu in river water in the Barlwyd catchment, it is vital that the effluents from slate extraction and processing are treated to reduce metal levels. Several methods have been used to clean industrial water including chemical precipitation (Roman Ross et al., 2006; Meunier et al., 2006; Matlock et al., 2002), electrochemical treatment (Meunier et al., 2006), electro dialysis (Meunier et al., 2006), evaporative recovery (Bouhamed et al., 2012), solvent extraction (Li et al., 2012), ultra-filtration (Zondervan and Roffel, 2007), ion exchange (Oehmen, 2006; Azarudeen et al., 2013), oxidation/reduction (Ramos et al., 2009; Ding et al., 2015, Sun et al., 2014a), reverse osmosis (Akin et al., 2011), filtration (Leupin et al., 2005), adsorption, (Zou et al., 2015; Sun et al., 2012; Sun et al., 2016a; Sun et al., 2015., Sun et al., 2016b, Sun et al., 2013., Sun et al., 2014b) and membrane technologies (Zondervan and Roffel, 2007; Gao et al., 2014; Zou et al., 2016). Unfortunately, most of these methods suffer from various drawbacks particularly in terms of economics (Zou et al., 2016).

Zerovalent iron and biochar are environmentally friendly and cost-effective ways of solving the problem (Chatterjee et al., 2010; Wang et al., 2019; Guan et al., 2015; Zhou et al., 2014). Adsorption is regarded as a simple and effective method of reducing metal levels in water using these methods. Biochar has a proven evidence base for cleaning metals from effluents, due to its charged surface and absorptive properties towards metals (Chen et al., 2018). Micropores in biochar are accountable for high absorptive capacity and surface area (Oni et al., 2019). Different types of biochar have different absorption capacities. Biochar has been found in soils around the world because of vegetation fires

and historic soil management practices. Intensive study of biochar rich dark earths in the Amazon, has led to a wider appreciation of biochars unique properties as a soil enhancer (Zhou et al., 2014). FeO is also shown to be efficient at removal of Cu (Chen et al., 2008; Li et al., 2017; Zou et al., 2016), but there is no evidence previous studies in the literature with regards to the use of biochar/FeO in removing Al from water. It has been postulated that a method of extracting the metal from the effluent could be formulated and the product subsequently used for utilitarian purposes.

6.1.1 Aims and objectives

6.1.1.1 Aim

To evaluate two methods of remediation, biochar and zerovalent iron on removal of Al/Cu from samples of slate quarrying affected river water.

6.1.1.2 Objectives

1. To quantify water quality removal of Al and Cu when treated with FeO or biochar.
2. To analyse the effect of site, treatment, and residence time on efficiency.

6.2 Materials and methods

6.2.1 Biochar and wood ash production and FeO properties

Biochar was made by pyrolyzing (450°C for 48 h) the mechanically chipped trunks and large branches of *Fraxinus excelsior* L., *Fagus sylvatica* L. and *Quercus robur* L. (BioRegional HomeGrown®; BioRegional Charcoal Company Ltd, Wallington, Surrey, UK). Complete incineration of 10 t of this wood-based biochar at 870°C, yielded 571 kg of wood ash (Reed et al., 2017). Biochar was milled to a homogenous powder, and the materials were sieved to <5 mm before

use (Reed et al., 2017). The physical and chemical properties of the biochar are found in Reed et al., 2017 and are detailed in Table 6.1. Total elemental analysis was performed with a S2 Picofox TXRF Spectrometer (Bruker Corp., Billerica, MA). Specific surface area was determined by the BET (Brunauer-Emmett-Teller) N2 adsorption method using a TriStar 3020 analyzer (Micromeritics Inc., Norcross, GA). Cation exchange capacity (CEC) was determined according to the method of Sumner and Miller (1996). Details of FeO chemical properties are detailed in table 6.2 and 6.3.

Table 6.1 – Physical and chemical properties of the biochar used in the study, data supplied with material (Reed et al., 2017)

Property	*Result*
Specific surface area (m^2 g^{1})	39±4.3
Moisture content (g kg^{1})	3.95 ± 0.07
Dry bulk density (g cm^{3})	0.46 ± 0.012 a
pH	10.42 ± 0.02
Cation exchange capacity ($mmol_c$ kg^{1})	129±5
Electrical conductivity (mS cm^{1})	4.8±0.1
DOC (mg C kg^{1})	1646±33a
EON (mg N kg^{1}	21.8±1.0
Total C (%)	84.3±0.5a
Total N (%)	0.58 ± 0.02 a
C:N ratio	146±4a
Extractable NO_3 (mg N kg^{1})	0.74 ± 0.43
Extractable NH^b_4 (mg N kg^{1})	14.1 ± 14.1
Extractable free amino acids (mg N kg^{1})	0.25 ± 0.02
Extractable P (mg kg^{1})	1129±100a
Total P (g kg^{1})	1.1±0.1
Total K (g kg^{1})	4.2±0.2
Total Ca (g kg^{1})	13.1±0.4
Total Mn (mg kg^{1})	293±12
Total Zn (mg kg^{1})	80±2
Total Cu (mg kg^{1})	12±1
Total As (mg kg^{1})	<0.5
Total Pb (mg kg^{1})	48.0 ± 2.8
Total S (g kg^{1})	0.69 ± 0.02
Total Cl (g kg^{1})	0.35± 0.03

Values above represent the mean of three replicates ± standard error. Letters indicates statistically significant differences between the two amendments ($P < 0.05$). DOC, dissolved organic carbon, EON, extractable organic nitrogen. Total Cd levels were below detection limits (<5 mg kg^{1}).

Table 6.2 – Chemical composition of FeO

Element	*% Composition*
Iron (Fe)	~ 95%
Carbon (C)	~ 1.8%
Oxygen (O)	< 1%
Silicon (Si)	~ 1%
Phosphorus (P)	< 0.1%
Sulfur (S)	~ 1%

Data above was supplied with FeO material. Certifiable 95+% Pure, ~325 Mesh particle, 2.3gm/cm^3 (Hepure technologies Inc. 2018), FeO purchased in 2015

Table 6.3 – Trace Metal Analysis: mass spec semi quantitative results of FeO utilised in experiment

Element	***Result (wt%)***	***Element***	***Result (wt%)***
Boron	< 0.0002	*Cobalt*	0.0029
Magnesium	0.0042	*Nickel*	0.0207
Al	0.0249	*Cu*	0.0575
Titanium	0.0278	*Zinc*	0.0031
Vanadium	0.0075	*Zirconium*	0.0004
Chromium	0.0623	*Molybdenum*	0.0129
Manganese	0.3552		

6.2.2 Sample preparation

Removal of metals has been attempted with biochar and soil previously (Rao, 2017; Zheng et al., 2020) and was shown to be effective. Another method is remediation with FeO, which has also proved successful (Liang et al., 2019; Fu et al., 2014) in this study we looked at comparing the two for efficacy. Water was collected from 3 different sites in the river: B5, B12, B14. The pH, EC, and

temperatures were measured in each case and a small sample was filtered and acidified as described in the methods section of Chapter 3.

6.2.3 Biochar and wood ash production

A peristaltic pump (ISMATEC IP High Precision multichannel pump) was used to pump water through 3.17 mm diameter tubes at a rate of 4ml/min^{-1} (See Figure 6.1). This is a slower flow rate than most papers have utilised, but the column size was smaller, and the rate is more effective with the column size. The pH was measured at 30 minute intervals. 50 ml centrifuge tubes with the bottoms sawn off were used as columns. A quantity of 10 g of FeO/Biochar and 10 g of sand were added to 6 tubes and 3 replicates of each treatment were trialled for each site. Water was collected in a prewashed bottle at 30 minute intervals for 6.5 hours. The pH was also measured at half an hour interval using a calibrated pH meter (HANNA HI-991003). Each sample of water was filtered through bottles with no 1 10 mm Whatman paper and was subsequently aliquot filtered through 0.45 μm cellulose nitrate filter membranes and stored in an acid-washed 30 ml Nalgene bottle. Finally, 3 drops of 10% nitric acid were added to preserve the sample. Samples were refrigerated at 4°C prior to analysis.

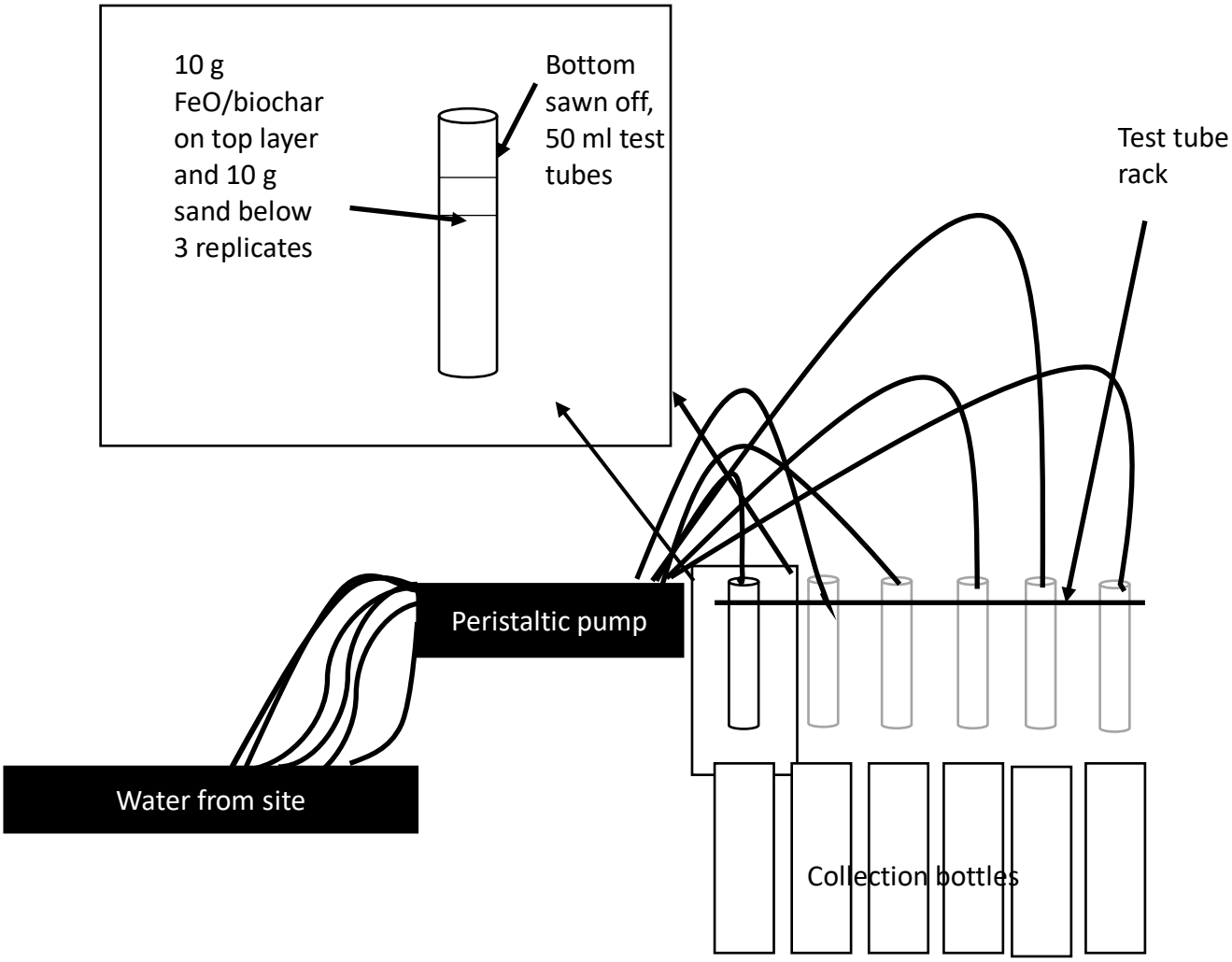

Figure 6.1 – Diagrammatic representation of laboratory model of remediation.

6.2.4 Removal of metals from sorbents – Aqua regia digest

To establish how much Al/Cu was removed an aqua regia digest was conducted. A total of 0.5 g of biochar/FeO was placed in a boiling tube and 2 ml of Aqua Regia was added and inserted in a hot block at 100 ^{o}C for 1 hour. Samples were allowed to cool and 18 ml of deionised water was added. Samples were vortexed, filtered with 0.45 µm nitrate cellulose filters and then placed into acid washed Nalgene 30 ml bottles.

Environmental studies have utilized environmental pollution studies in several cases (Gäbler, 1997; Gruiz et al., 1998; Jain and Ali, 2000), often these use hydrofluoric acid (HF) or HF-strong acid mixes. Although total digests provide a more effective dissolution of silicate minerals (Totland et al., 1992) and enable greater metal recovery (Harrison and Laxen, 1977), its debated that the potential benefits are offset by the prolonged analytical time, inherent safety concerns (de Groot et al., 1982; Marr and Cresser, 1983) and the potentially limited usefulness of data relating to total concentrations (Chao and Sanzolone, 1992). Competing ions were not measured owing to a lack of resources.

Since most pollutants are not bound to the silicate fraction (Ure, 1996), the use of partial leaches with strong mineral acids such as HNO_3, HCl, H_2SO_4 and $HClO_4$ is commonplace in studies of metal content in soils and sediments. Several thorough reviews of sediment and soil decomposition techniques have been written by Sulcek and Povondra (1989); Jarvis (1992) and Kennedy et al. (1997). Sulphuric acid can create insoluble sulphates during digestion (Agemian and Chau, 1976) and is therefore infrequently used in environmental studies. Aqua regia (a 3:1 mixture of HNO_3 and HCl) has been described a pseudo-total technique Scancar et al. (2002) describe aqua regia (a 3:1 mixture of HNO_3 and HCl) as a pseudo-total technique and has been widely established, particularly in Europe (Ure, 1996). Walsh et al. (1997) described that aqua regia is a very efficient extractant, due to the complexation power of the chloride ion, and the catalytic effect of Cl_2 and NOCl. A study by Cook et al. (1997) has shown that recoveries of Cu and Zn using aqua regia represented 99 and 100 percent, respectively, of HF derived totals. However, considering the Cl^- content, aqua regia does have certain limitations with respect to subsequent analysis by ICP-MS, due to spectral interferences (Walsh et al., 1997), which is the reason AAS was chosen.

6.2.5 AAS

A Varian 240 atomic mass spectrometer (AAS) was used to measure the concentration of metals in the aqua regia digests. AAS machines are amongst the machines most used to measure the

concentrations of metallic elements in water samples (Kunkel and Manahan, 1973; Karadede and Ünlü, 2000; Jung, 2001). According to Shirkhanloo et al. (2011), AAS is an economical and easy way to quantify metals as with compared to ICP-MS. The machine was used to measure Al and Cu. The process works by aspirating up a small sample through a plastic tube into a flame which is hot enough to break molecules up to form atoms. These atoms are enough to absorb light from the cathode lamp, and the residual light is sent to the detector via a wavelength selector. The elemental concentrations are thus measured by absorption (Figure 6.2). The radioactivity is reflected at the corrected at the correct wavelength through the flame and the density of the nuclear emiis consequently measured (Figure 6.2). It requires standards with known analyte content to establish the relation between the measured absorbance and the analyte concentration and relies therefore on the Beer-Lambert Law.

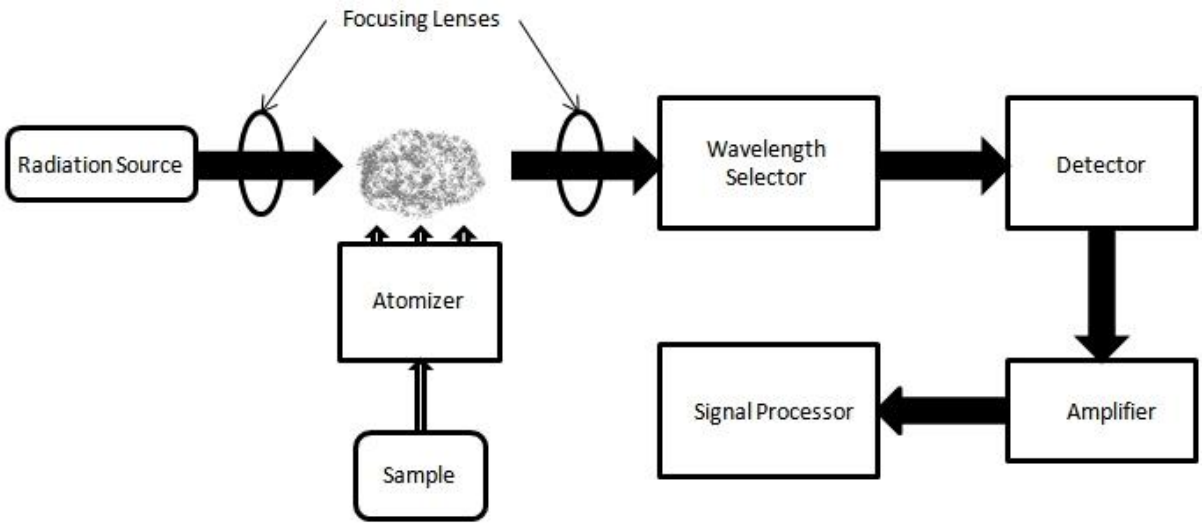

Figure 6.2 – Atomic absorption spectrometry (AAS).

6.2.6 Statistical methods

To assist in the evaluation of the geochemical data, a range of statistical tests were carried out, most notably one sample T tests, Wilcoxon's rank and three-way ANOVA. The major distinction in statistical analysis is whether the data is parametric or non-parametric. Unless the dataset is transformed non-parametric tests must be performed. If a dataset in skewed, parametric statistical

tests should not be used, unless the data set is transformed first to create a normally distributed dataset (Swan and Sandilands, 1995). However, a range of non-parametric tests exist for use on non-parametric datasets. In these studies, we used both parametric tests and non-parametric tests as revealed by a KS test. The effect of treatment with biochar and FeO was examined as compared with time 0. The data was both parametric and non-parametric for different sites. The statistical test used were the one sample T -tests for parametric data and Wilcoxon's test using SPSS. The statistical significance of these tests was assessed at the 95% (α = 0.05) confidence limits; and the corresponding levels of significance are displayed along with the statistical results. Three-way ANOVA was used to look at the effect of treatment, time, and site as this is considered a robust statistical test, and there are multiple factors. ANOVA was used to look at differences in metal removal between groups of treatment time and site.

6.3 Results

6.3.1 Efficiency of Biochar and FeO removal

6.3.1.1 Removal of Al by biochar and FeO

Removal of Al by biochar at site B5 is initially more efficient (see Figure 6.3). There is a large variation in the biochar dataset. At time 0.5 hr at site B5 there is 36.07% (S.D. 27.74%) removal. This removal of Al by biochar ranges between 12% (S.D. 21.22%) – 41% (S.D. 5.52%). This removal of Al by biochar remains consistently low, showing no decline in efficiency. The starting pH at this site is 6.14. Addition of biochar does not affect the pH considerably. At site B12 the starting pH is low at 3.95 and the addition of biochar increases the pH to between 4.98-6.28. At site B12 initial removal of Al with biochar is 84% (S.D. 9.2%). Removal ranges between 16% (S.D. 3.93%) -84% (S.D. 9.2%). The pH also declines with time from circa 6 to circa 4.9. This suggests biochar may work at optimum pH's. Removal of Al at site B14 by biochar is initially 39.10% (S.D. 0.47) but increases to 54% (S.D.

5.05%) at time 1 hr and remains between circa 50-60% throughout the experiment. The pH is higher than at site B12 with an initial pH of 5.38 and the pH increases to 6.27-7.46 and ranges between 3.35-7.46 and has a more variable pH than site B5 or B12.

Removal of Al by FeO is more efficient than with biochar generally (See Figure 6.3) and the variation is much lower. Removal of Al by FeO at site B5 ranges between 44% (S.D. 7.94)- 83% (S.D. 0.95%). Efficiency is high between 0.5-2 hr and then gradually declines from 61% (S.D. 11.8%) to 44% (S.D. 0.9%) by the end of the experiment. FeO's efficiency at site B12 is good ranging between 97% (S.D. 2.5%) at time 0.5 and 93% (S.D. 4.99%, time 2 hr). Efficiency is good with 94% (S.D. 3.79%) removal at time 6.5 hr. Site B14 removal of Al with FeO is also high initially with a range between 26% (S.D. 3.4) - 92% (S.D. 2.0). Initially at time 0.5 hr the removal is 84% (S.D. 5.11%) and increases to 92% (S.D. 1.99%) at time 3 hr). Removal of Al then declines in efficiency at time 6.5 hr to 26 (S.D. 34.17%). pH at site B14 is 5.38 and varies between 3.35- 7.46.

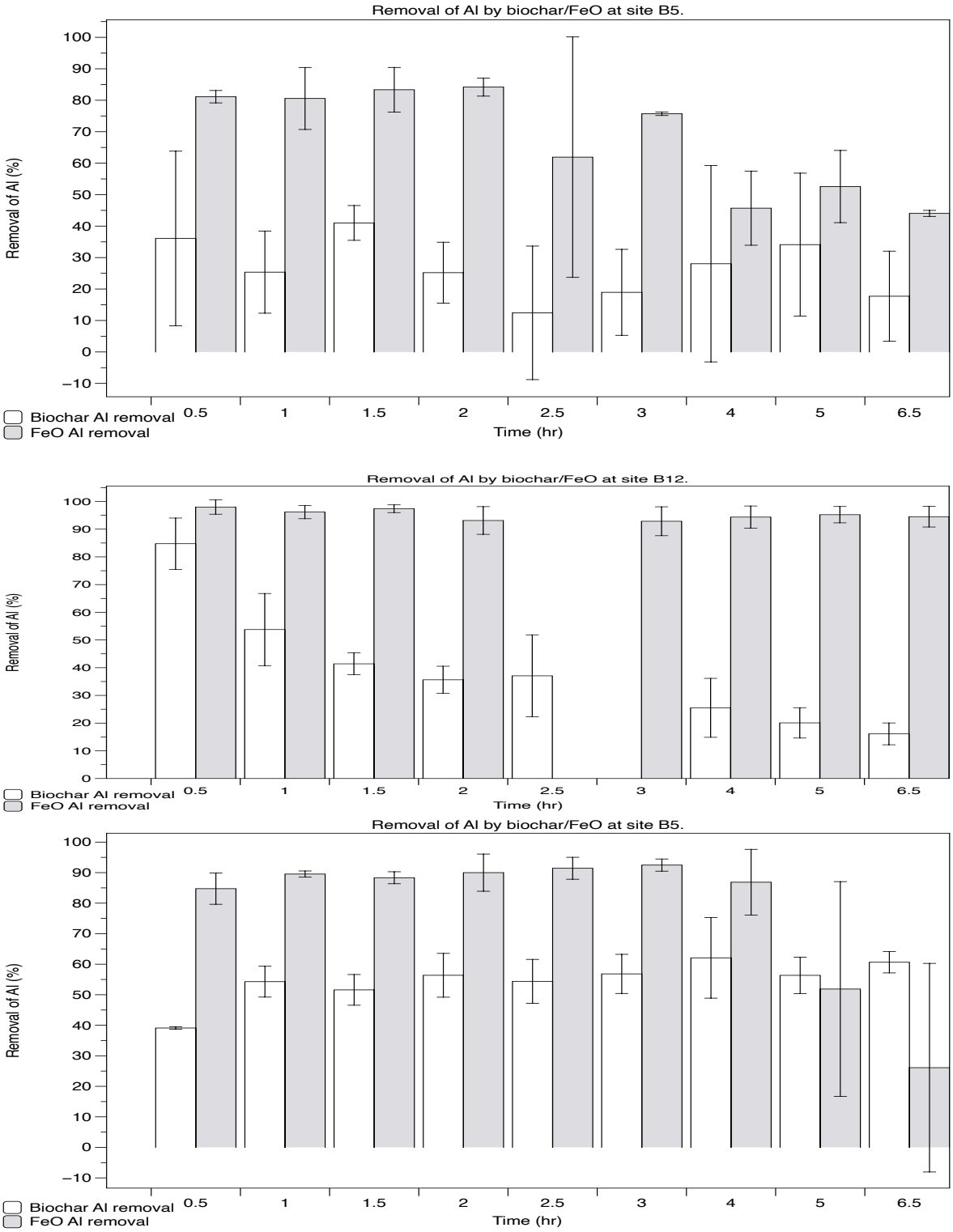

Figure 6.3 % Removal of Al from river water using biochar/FeO at site B5, B12 and B5 as compared with starting concentrations respectively for each period.

6.3.1.2 Removal of Cu by biochar and FeO.

Removal of Cu by biochar contrasts sharply with the removal of Al, suggesting biochar can absorb Cu with a different chemical behaviour to Al possibly as Cu has different charges to Al and that al is amphoteric (See Figure 6.4). At site B5 initial removal rates are 56% (S.D. 17.87%) increasing to 86.9% (S.D. 10.6%) at time 2.5 hr. Efficiency throughout remains consistently high, only decreasing in efficiency at time 6.5 hr to 56.9% (S.D. 7.4%). At site B12 removal of Cu with biochar is lower with an initial removal of 44%. Biochar gradually decreases in efficiency to 19% (S.D. 2.56). Removal of Cu with biochar at site B14 ranges between 70% (S.D. 6.59) -76% (S.D. 2.70) with a consistently high removal. However, the initial concentrations at site B14 (0.06 mg/L) were lower than at sites B5 (0.218 mg/L) and B12 (8.531 mg/L). This suggests that biochar is more efficient at removal of Cu at higher initial pH's and lower concentrations of Cu, as the biochar may become saturated.

FeO is relatively efficient at removal of Cu from this river at all sites, enough to have a positive impact on chemical measures of the EWFD (see Figure 6.4). Removal of Cu at site B5 with FeO ranges between 63 (S.D. 8%) – 91% (S.D. 7%) and is variable with time, however efficiency does not decrease, and unusually increases from 69 % (S.D. 10.00%) to 84% at time 6.5 hr (S.D. 3.26). Removal of Cu with biochar at site B12 shows exceptionally high removal starting at 97% (S.D.0.32%) and ending at 86% (S.D.10.36%) at time 6.5h. This is an incredibly positive outcome for removal of Cu. FeO is relatively efficient at site B14, initially removing 55% (S.D. 4.78%) increasing in efficiency to 88% (S.D. 4.13%) (time 4hr) and ending at high efficiency at time 6.5 hr (86% S.D. 9.6%).

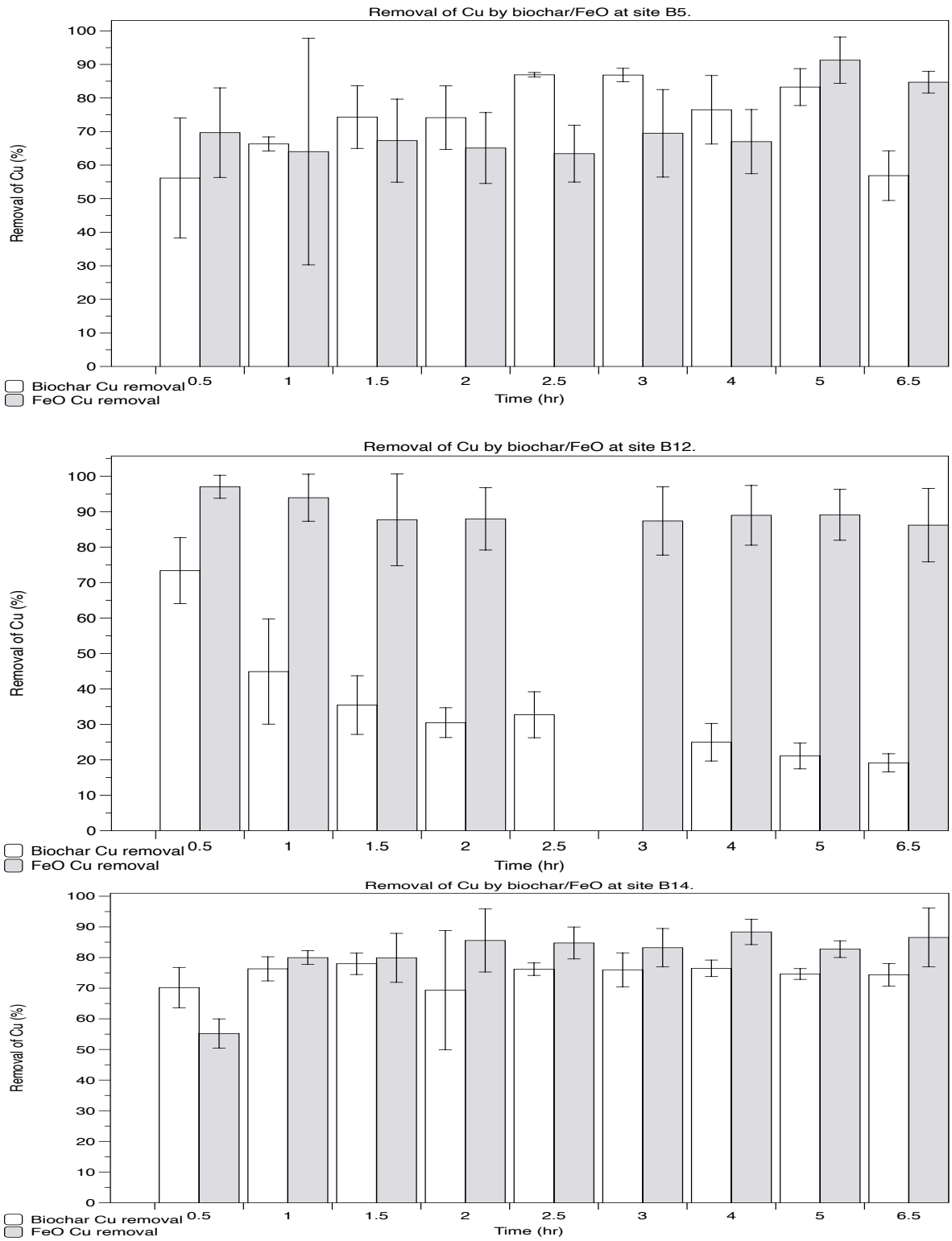

Figure 6.4 % Removal of Cu from river water using biochar/FeO at site B5, B12 and B5 respectively.

Table 6.4 – Aqua regia digest of biochar and FeO following adsorption

Site/treatment	*Al (mg/kg)*	*Cu (mg/kg)*
B5 FeO	*0.014383*	*0.000421*
B12 FeO	*0.018395*	*0.006813*
B14 FeO	*0.012183*	*0.00441*
B5 biochar	*0.003810*	*0.049*
B12 biochar	*0.010050*	*0.000045*
B14 biochar	*0.007327*	*0.000037*

6.3.1.3 pH after addition of remediation material.

The pH declines in the midway through the experiment with water from sites B5 and B14 (see Figures 6.4-6.6). At site B12 the pH decreases throughout the experiment. The pH change is a site dependent mechanism for both sites.

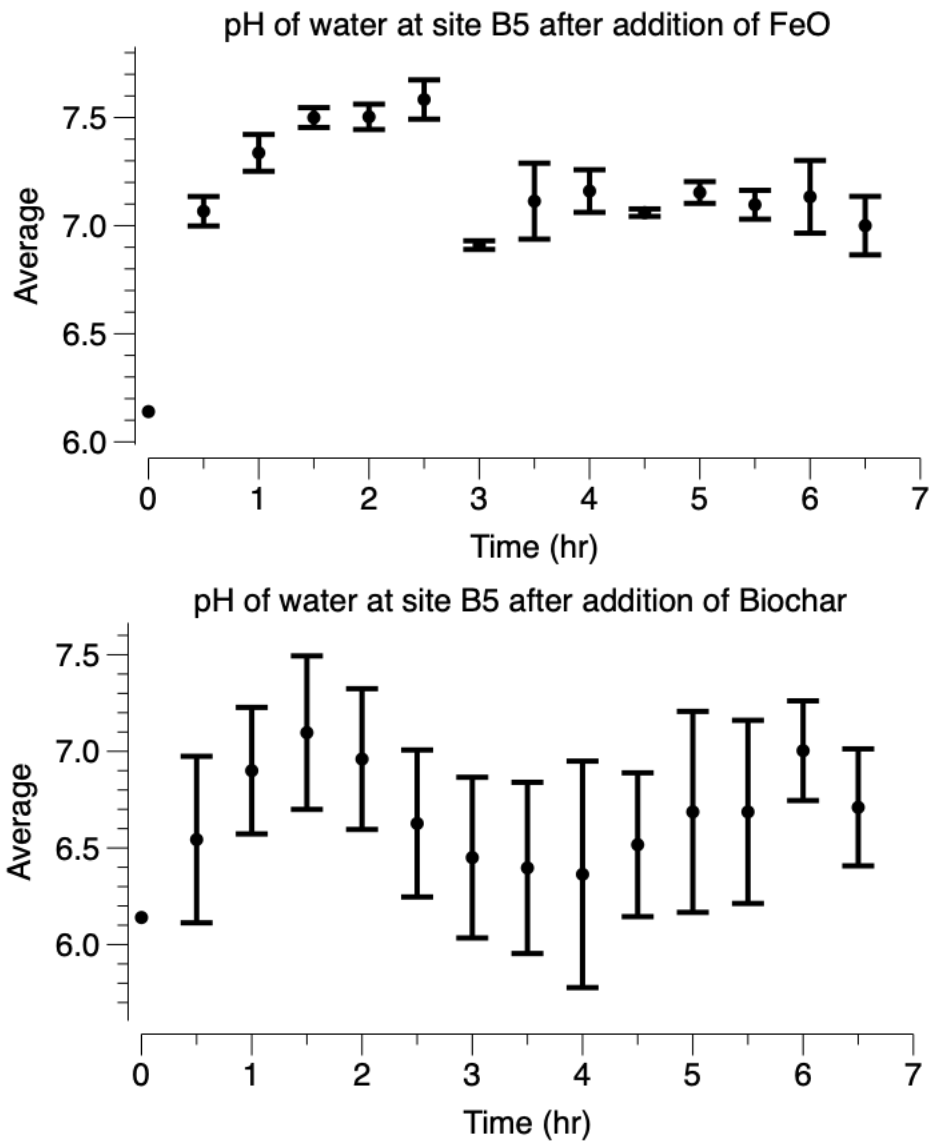

Figure 6.5 – pH of water from site B5 after addition of FeO/Biochar with standard deviations shown.

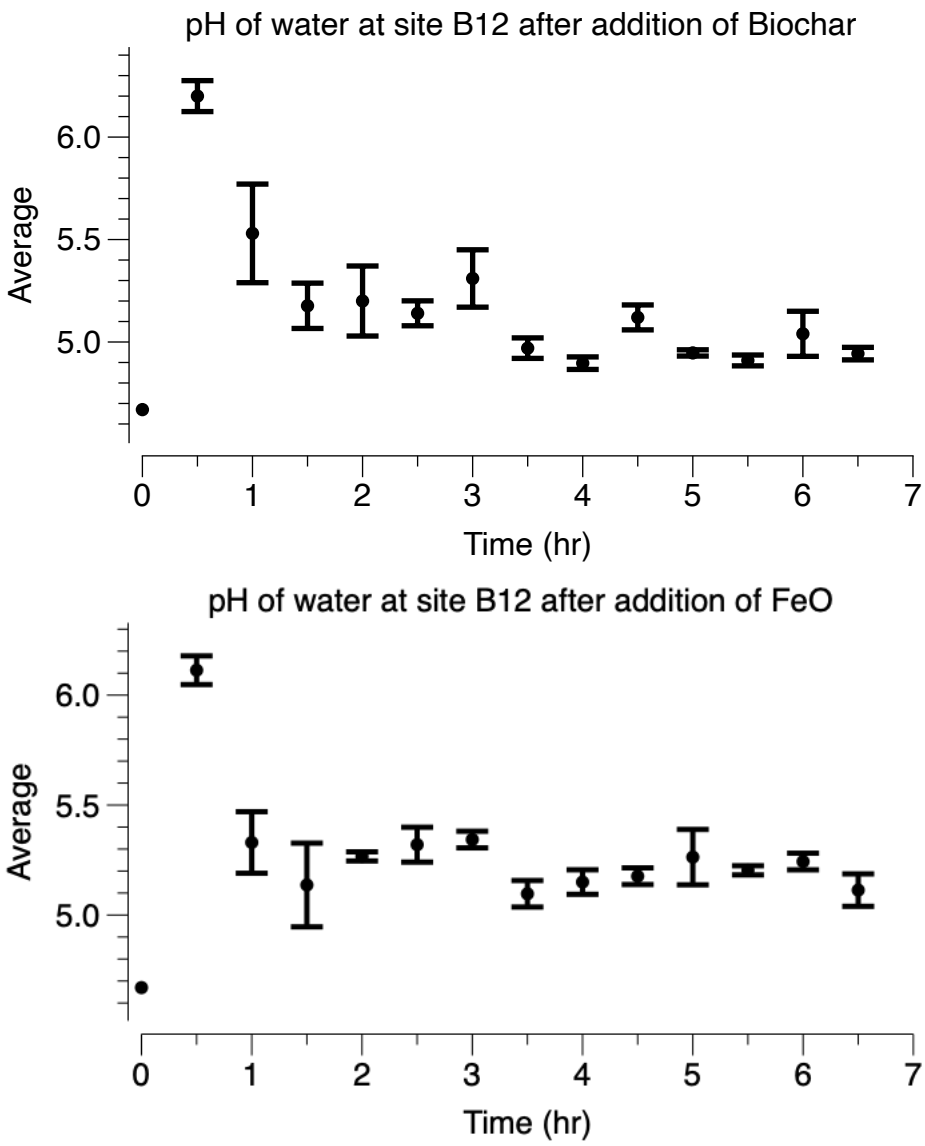

Figure 6.6 – pH of water from site B12 after addition of FeO and Biochar with standard deviations shown.

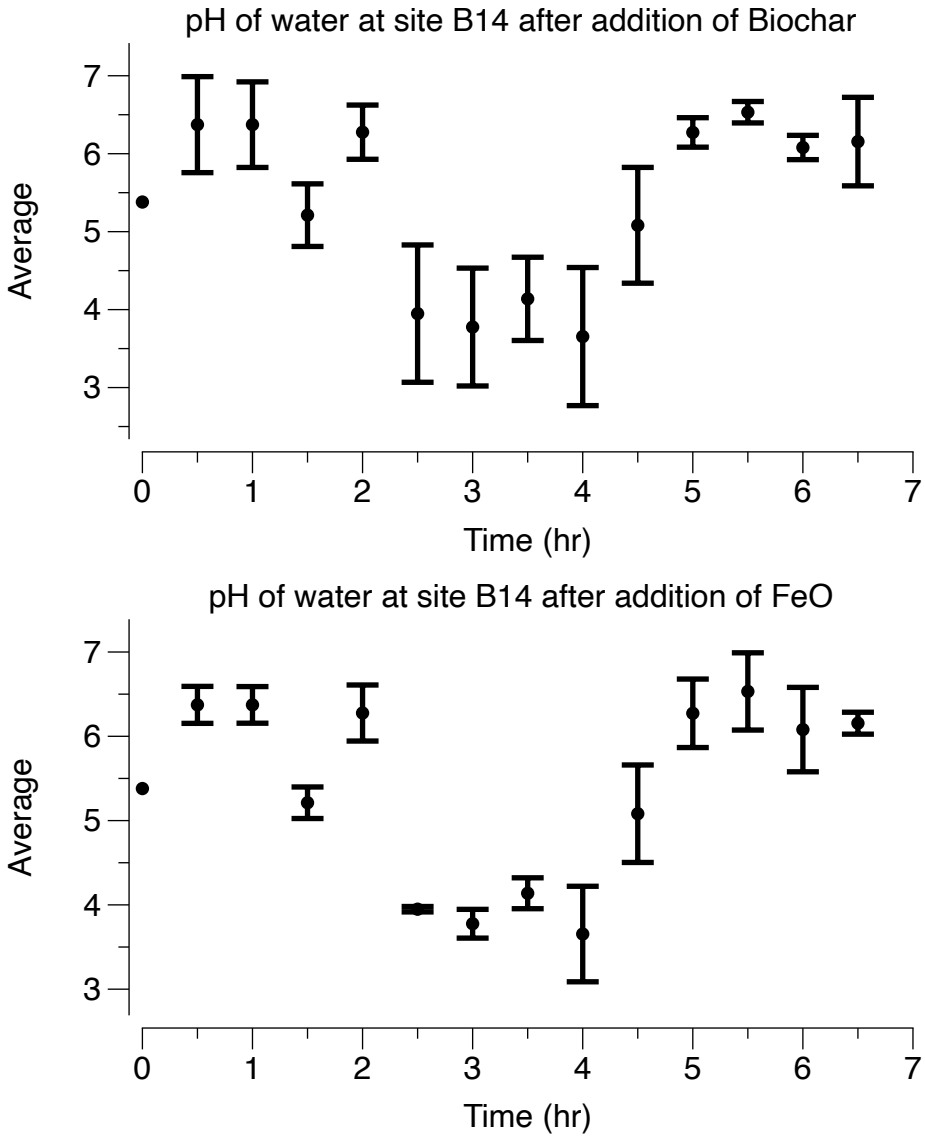

Figure 6.7 – pH of water from site B14 after addition of FeO/Biochar

6.3.2 Statistical analysis

6.3.2.1 T-test and Wilcoxon signed rank test

Data was found to be a mixture of parametric and non-parametric for each site with regards to looking at effect of biochar and FeO as with compared with time 0. A mixture of Wilcoxon's and one sample T tests were used to look at the effect of biochar and FeO on each site. Each site was tested against starting concentrations to see the effect of treatment.

The KS (Kolmogorov Smirnov) test revealed normal data at site B5 for Biochar with regards to Al. A one sample T-test was conducted to explore the effect of Biochar on Al concentrations at site B5. There was found to be a significant difference ($P= 0.000 < 0.05$). Sites B12 and B14 when treated with FeO had non-parametric datasets ($P = 0.039<0.05$, $P = 0< 0.05$ resp). Wilcoxon's signed rank test was conducted for these data sets and data was found to be significant.

The KS for treatment with FeO on site B12 showed that the data was normal. A one sample t-test was conducted to look at the difference before and after treatment. There was found to be a significant difference.

The KS tests for treatment with FeO and Al found the data to be non-parametric for sites B5 and B14 ($P= 0.000<0.05$). A Wilcoxon's signed rank test was conducted to explore the effect of Biochar on concentrations of Al at time 0 and after treatment. The median of differences between site B5 and B14 after treatment of FeO was significant ($p=0.000>0.05$). Therefore we can conclude that the two sets of data are significantly different in both cases.

The Cu data for site B12 treated with Biochar is normal ($P = 0.24>0.05$). A one sample t test was conducted to examine the difference before and after treatment. The t-test showed a significant difference. The data for all sites B12 and B14 were found to be non-parametric with regards to Cu and

Biochar (KS= 0.024, 0.001, 0, =<0.05 respectively). A Wilcoxon's signed rank test was conducted to explore the effect of Biochar on levels of Cu at time 0 and after treatment. The median of differences between sites after treatment of biochar was significant (p=0.000>0.05). Therefore, we can conclude that the two sets of data are significantly different in both cases.

Tests of normality for B5 and B14 treated with FeO revealed normal data with regards to concentrations of Cu. One sample T tests were conducted and revealed a significant difference before and after treatment.

The KS test for Cu removal with FeO at site B12 showed that the data was normal (p= 0.017>0.05). A Wilcoxon's signed rank test was conducted to explore the effect of treatment on levels of Cu. The median of differences between sites after treatment of FeO was significant (p=0.000<0.05). Therefore we can conclude that the two sets of data are significantly different in both cases.

6.3.2.2 ANOVA

A three way between-groups analysis of variance was conducted to explore the impact of treatment time and site on change in Al. The interaction between time and site (F (16,162) =3.078, p = 0.000) and between site and treatment (F (2.108) = 14.551 p = 0.000) were significant. The interaction between time and treatment was not significant (F (8,108) = 2.538, p = 0.014). The three-way interaction between time, treatment and site was significant (F (16,162) = 6.667, p = 0.000). There was a statistically significant main effect for site (F=(2,162) =50.970, p=0.000), time F=(8,162) =7.965, p=0.000) and treatment (F=(1,162) =348.301, p=0.000). The effects size for site, time and treatment were large ((partial eta squared = 0.486, 0.420, 0.763) (Cohen, 1988)).

A three way between-groups analysis of variance was conducted to explore the impact of treatment, time and site and time on change in Cu. The interaction between time and site (F (2,162) = 7.503, p = 0.000), site and treatment concentration (F (8,162) = 115.373, p = 0.000) time and treatment (F

(16,162) = 7.919, p = 0.000) were significant. The three-way interaction between time, treatment and site was significant (F (16,162) =5.253, p = 0.000). There was a statistically significant main effect for site (F (2,162) = 18.831, p=0.000), time (F (8,162) =4.710 p=0.000) and treatment F (1,162) =142.144, p=0.000) The effect size was large for time, treatment and site (partial eta squared = 0.259, 0.260,0.570 respectively, was large (Cohen, 1988).

6.4 Discussion

Concentrations Al and Cu in river water have been shown to occur at concentrations above EWFD guidelines for Cu and EQS levels for Al (Chapter 3). The water being treated would however not be river water but quarrying affected water. We have used river water for ease of access, with the limitations being that there will be some mixing and dilution of metals owing to addition of river water. Furthermore, there less subsurface flow in the mine water, and a different geochemistry. However, mine water diverted from the river water it is likely to be representative. It is shown that remediation with biochar and FeO are plausible options for remediation. The use of FeO in the case of Al and Cu and Biochar on Cu, have a significantly different effect on the. In the case of Al and FeO this is a novel discovery, which is previously unreported in the literature.

FeO and biochar are found to have a significant effect on the levels of Al and Cu in river water, and thus may have an impact on mine waters treated also. FeO is shown to be more overall effective than biochar with Al, and biochar is more efficient with Cu. Time and site are also shown to be significant factors governing the efficacy, probably owing to saturation of sites in the case of time and owing to geochemistry such as difference in pH and Al/Cu concentrations in site.

The FeO absorption mechanism is affected by pH (Zou et al., 2016). When the pH is low, iron corrosion increases and produces plentiful hydrogen, which is conducive to the hydrogenation reaction whereby hydrogen is added to the complex, thereby reducing Al/Cu (Zou et al., 2016; Dror et al., 2012; Li et al., 2012). A plausible explanation is that more oxygen-containing groups (e.g., oxide

or oxyhydroxide) become deprotonated and the surface becomes negatively charged as pH increases, which is favourable for adsorbing more heavy metal ions via electrostatic interactions. It assumes that the adsorption properties of nFeO are influenced strongly by solution pH. Several mechanisms have been proposed for how FeO works including absorption, reduction, oxidation and at high pH, electrostatic interactions. Absorption is the most widely accepted mechanism. In terms of Al/Cu several mechanisms could be involved. Adsorption is the most accepted reaction mechanism for the removal of heavy metal ions, due to the abundant oxygen containing functional group on the surface of adsorbents (Zou et al., 2016; Han et al., 2016) show that a mixture of acid washed FeO and zerovalent Al as reactivate medium in permeable reactive barriers. The mechanism is described as having four interaction processes, reduction, adsorption hydroxide precipitates and electron transfer (see Figure 6.7). The process is complex and could include may kinds of coexistent heavy metal ions. In this case the water from the river contains a wide range of metals, and thus the process could be complicated. The main solvent water plays a considerable role in adsorption. DFT (density functional calculations) show that water could be transformed into H^+ and OH^-, with a positive activation barrier as beneficial to the adsorption process of heavy metals (Zou et al., 2016).

Reduction could also be a mechanism with FeO acting as an electron donor to many heavy metal ions. Furthermore Fe^{2+} could also be responsible for reduction. With nFeO and Pb^{2+} about 47% was Pb^0 was formed by reduction reaction (Liu et al., 2013; Zou et al., 2016).

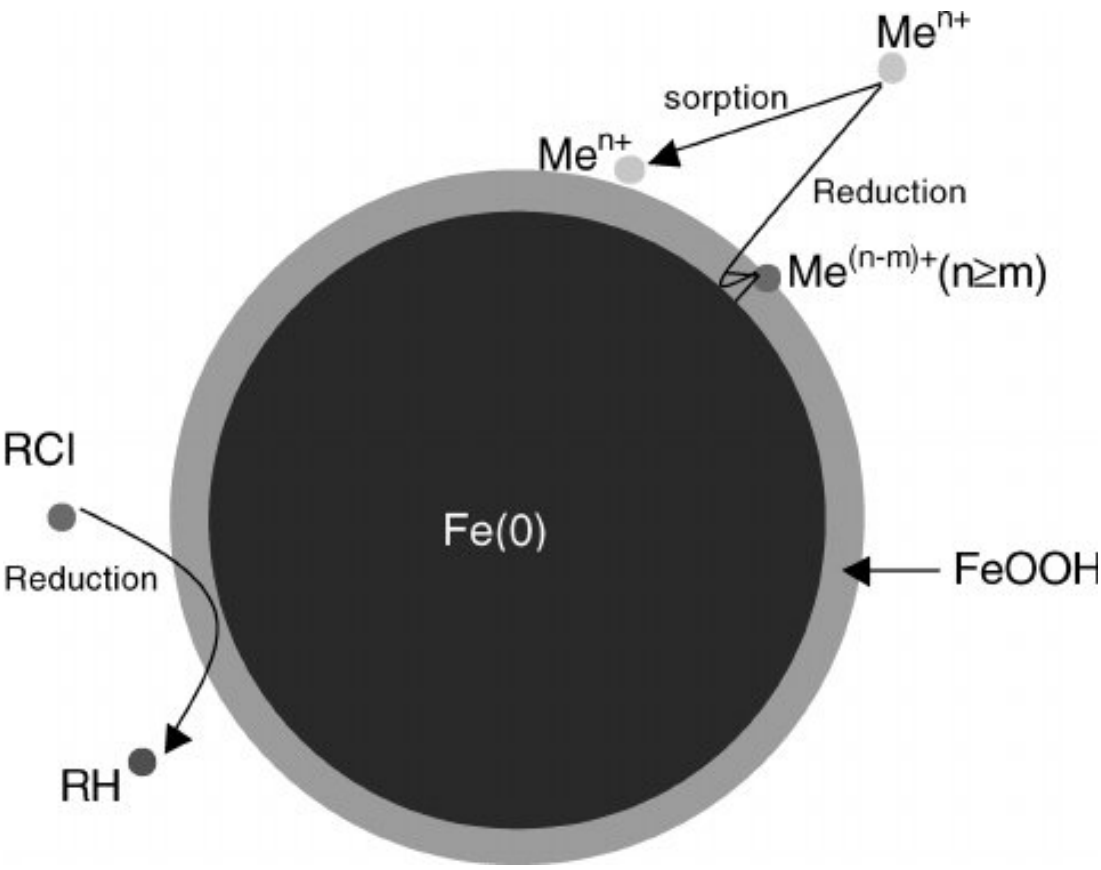

Figure 6.8 – The core-shell model of zero-valent iron nanoparticles.

The core consists of mainly Zero-valent iron and provides the reducing power for reactions with environmental contaminants. The shell is largely iron oxides/hydroxides formed from the oxidation of zero-valent iron. The shell provides sites for chemical complex formation (e.g., chemisorption) (Daniel W. Elliott.- Zou et al., 2016).

The Fe^{2+} formed, could trigger a rapid contaminant oxidation with the formation of hydroxyl radicals (eq 1, 2 and 3) (Zou et al., 2016). Oxidation could result in the formation of Al oxides and hydroxides (see eq 4 and 5) in the presence of DO. The same could occur for Cu (eq 6 and 7).

$Fe^0 + O_2 + 2H^+ \rightarrow H_2O_2 + Fe^{2+}$ (Equation 1)

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\cdot}OH + OH^-$ (Equation 2)

$2Fe^{3+} + Fe^0 \rightarrow 3Fe^{2+}$ (Equation 3)

$2Al^{3+} + 3FeO \rightarrow Al_2O_3 + Fe^{2+}$ (Equation 4)

$3OH^- + Al^{3+} \rightarrow Al(OH)_3$ (Equation 5)

$Cu^{2+} + 2OH^- \rightarrow CuOH_2$ (Equation 6)

$Cu^{2+} + FeO \rightarrow CuO + Fe^{2+}$ (Equation 7)

nFeO is effective for the removal of arsenic from water. One proposed mechanism is that there are two stages of transformation upon adsorption on the nFeO surface (Yan et al., 2012, Fu et al., 2016). Stage one is the breaking of As-O bonds on the surface, and the second stage involves reduction and diffusion of arsenic across the thin oxide layer enclosing the nanoparticles (see Figure 6.9). Perhaps mechanisms such as this could be involved with Al^{3+}.

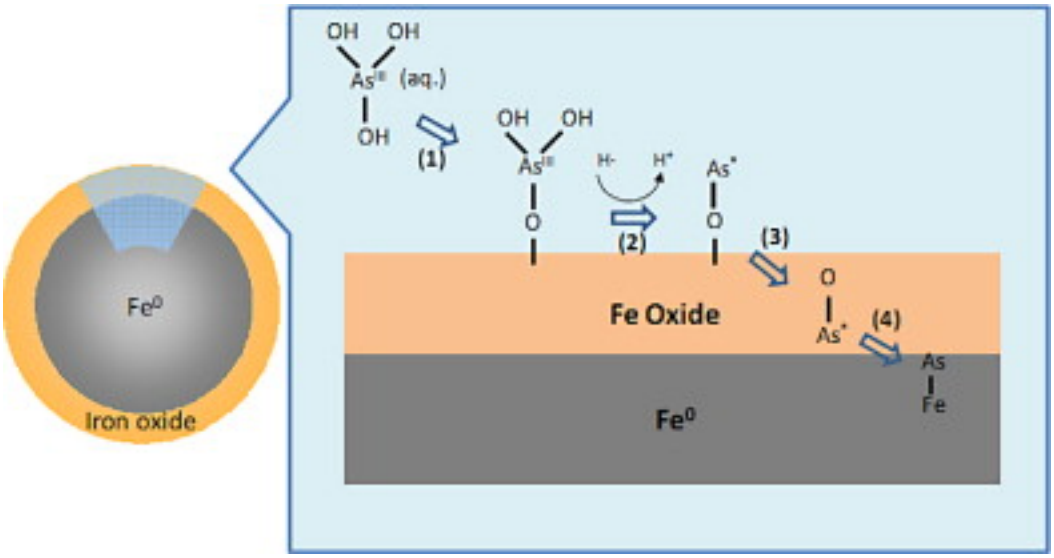

Figure 6.9 – Proposed mechanism of As (III) – nFeO reactions (Yan et al., 2012).

Coinciding with the increase of Fe^{2+} and OH^- concentration the precipitation of $Fe(OH)_2$ and $Fe(OH)_3$ occurs. There could also be oxidation to Al hydroxides. The mechanism could be dependent on the pH, site also has a significant effect due to different geochemistry and pH's at different sites also differ. B12 is acidic and the pH stays roughly the same. At B14 the addition of FeO causes the pH to drop to low levels (3.52-3.81) and then increase again (6.29-7.74). Biochar and FeO could be combined to maximise the withdrawal of Al and Cu from the water. This has been attempted before

using chitosan to attach FeO to biochar (Zou et al., 2016). The results suggested that both the chitosan and the FeO particles on the biochar surfaces played important role in the enhanced removal of cationic heavy metals. The resulted iron modified biochar showed excellent ability to remove various contaminants, including heavy metals. In addition, the modified biochars are ferromagnetic and could be easily collected by a magnet (Zou et al., 2016).

The mechanism for the removal of metals with biochar is pH related. Biochar is negatively charged due to the presence of more -OH functional groups, and its behaviour is linked with pH (Kolodoynska et al., 2012). Solution pH strongly influences the surface charge of biochar when added to water. Low pH influences biochar in the case of removal of Al. When the surface net charge is zero the charge is known as zero charge (pH_{PZC}). Biochar is negatively charged when solution pH is > pH_{PZC}, and binds to metal cations such as Cd^{2+}, Pb^{2+}, and $Cu^{2+,}$ and the biochar is negatively charged. Biochar is positively charged when solution pH is < pH_{PZC}, binds metal anions such as $HAsO_4^{2-}$ and $HCrO_4^{-}$. Thus, the level of biochar binding is at its greatest with Cu at the right pH. Biochar characteristics affects metal sorption also such as surface functional groups, surface area and porosity, negative charge, mineral content and cation exchange capacity (Tan et al., 2015). There are several different mechanisms which have been proposed to govern heavy-metal sorption by biochar, these include cation exchange; precipitation; complexation; chemical reduction; and electrostatic interaction (Tan et al., 2015). A caveat in this however is that heavy metals which are bound to the biochar surface tend to be desorbed depending on the type of chemical interaction. Metals are desorbed readily by binding through cation exchange, electrostatic interaction or physical adsorption are easily desorbed, whilst heavy metals that form a surface precipitation or undergo complexation are less readily desorbed.

pH is a crucial parameter in the sorption process optimization. The pH governs the surface charge of the adsorbent and the degree of ionization and speciation of the metal ions in solution. Metal ions start to hydrolyse at higher pH's and precipitation happens. As pH increases, the competition of M(II) ions and protons for binding sites lessens and more binding sites are released, this augments the adsorption

effectiveness. It was discovered by Kolodynska et al. (2012) that the maximum adsorption efficiency was achieved at a pH of about 5.0 for Cu(II) (6.34 mg/g). This is roughly the pH range which was observed for B5 and B14 following addition of Biochar, which explains why there was more efficient removal of Cu at this pH.

It was found by Kolodynska et al. (2012) by studying biochar in the presence of competing ions that the selectivity of the applied adsorbents towards Cu(II) and Pb(II) ions was seriously affected by the presence of Zn(II) and Cd(II) competing ions as the adsorption capacity increases with the decrease of their concentration in the solutions. This may have affected our results too, as the river water is affected by a mixture of different metal ions. Furthermore, kinetic data has shown that the mechanism of metal ions sorption by the BC samples is complex and probably a combination of external mass transfer, intraparticle diffusion through the macropores and micropores of BC and sorption processes (Kolodynska et al., 2012). In a river system biochar would reduce waters acidity and therefore have a double positive effect, reducing liming needs and removing metals. This is particularly apparent at site B12 when biochar is effective at absorbing Cu the negative charge on the COO^-. Using biochar is also positive as it is a natural resource and could be safely disposed. Biochar in this was as well as its uses in soil could become a bioeconomy, as it is a bioresource.

In previous studies reported in the literature, five mechanisms have been proposed to govern metal sorption by biochar from aqueous solutions, namely, complexation, cation exchange, precipitation, electrostatic interactions, and chemical reduction (Beesley et al., 2015). However, the role that each mechanism plays for each metal varies considerably depending on the target metals and adsorbents. In Biochar, complexation and cation exchange have been found to be the two main adsorption mechanisms in systems containing multiple heavy metals, with cation exchange being the most significant particularly in this case as there are multiple metals removed. It is demonstrated in the data presented biochar is effective at removal of Cu. The pore structure of biomass/biochar is significant when investigating the adsorption mechanism of each material. Fei et al. (2017) described the molecular-level adsorption of Pb(II) and Cu(II) to peat biomass mainly through carboxyl groups (–

COOH), this may apply as a mechanism in this case with Cu. There is evidence that both electrostatic interactions and complexation with biochar surfaces are responsible for Cr adsorption and reduction. Complexation and cation exchange probably are the two main adsorption mechanisms in multiple-heavy-metal systems, which is relevant in this case and may act on other metals found in the mixture. In summary, heavy metals are adsorbed on the surface of biomass/biochar via exchange mainly with Ca, K, and Mg but also with protons from carboxyl and hydroxyl groups. In addition, if these latter functional groups are present at high amounts on the bioadsorbent surface, they can also complex heavy metals from the aqueous solutions (see Figure 6.10). Finally, it is important to note that the amount of either mineral or carboxyl groups can differ depending on the composition of the original biomass and, in the case of biochar, as a function of the pyrolysis conditions employed (Beesley et al., 2015) (Figure 6.11).

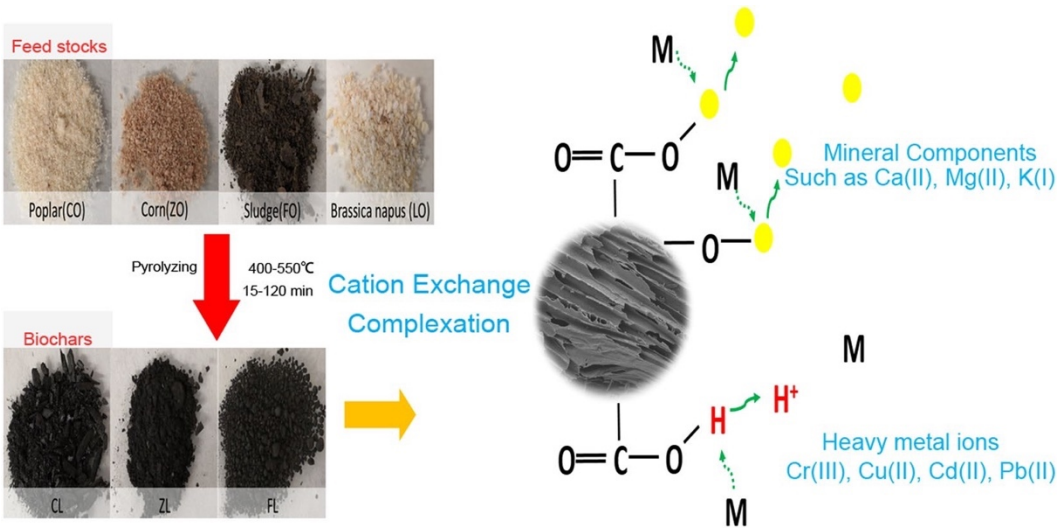

Figure 6.10 – Mechanisms of metal (M) sorption to biochar via cation exchange and complexation after pyrolysis (Zhao et al., 2019)

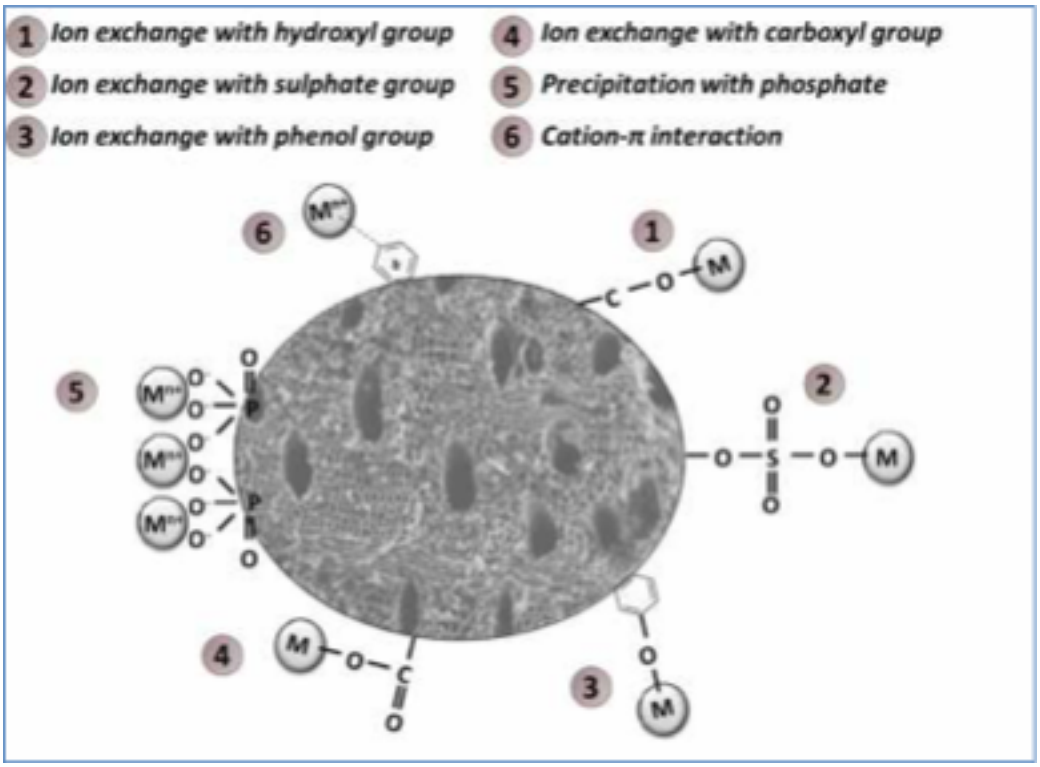

Figure 6.11 Proposed mechanisms of chemisorption in biochar (Beesley et al., 2015)

Apart from a pure ion exchange between biochar surface and metal, a non-stoichiometric release of protons and other cations from the surface of biochars has been found (Uchimiya et al. 2010a, Harvey et al. 2011); more metals are adsorbed than protons or cations are released, and sorption can occur at pH below the point of zero net charge (Sanchez-Polo and Rivera-Utrilla 2002). This explains why biochar do not fit a double exponential model. The immobilisation of metals by biochar cannot, in these instances, be purely attributed to ion exchange alone. It may be the case that electrostatic interaction between the positively charged metal cations and π-electrons associated with either C=O ligands or C=C of a shared electron 'cloud' on aromatic structures of biochar is responsible and metal sorption is an endothermic physical process (Kannan and Rengasamy 2005; Liu and Zhang, 2009; Harvey et al., 2011; Beesley et al., 2015). Carbon from a benzene ring could donate an electron to the structure which is then 'delocalized' resulting in an 'electron cloud' or a π-cloud above and below the planar surface of that benzene ring (Beesley et al., 2015). Metal cations are positively charged at this pH due to 'missing' electron(s) from their d-orbitals so when a positively charged cation approaches the benzene ring, the electron cloud becomes polarized and there is a weak electrostatic interaction

between the negatively charged planar surface of the benzene ring and the positively charged metal cation (See Figure 6.10, Figure 6.11). Zarić shows that bond energies of cation-π interactions are in the range 1 to 30 kcal mol^{-1}(Zarić 2003, Beesley et al., 2015), while the bond energies of transition metal-carbon bonds are usually an order of magnitude higher (>100 kcal mol^{-1}) (Simoes and Beauchamp, 1990; Beesley et al., 2015).

It is widely reported that addition of biochar to soils has resulted in pH increases (Yamato et al., 2006; Chan et al., 2007; Uchimiya et al., 2010b; Van Zwieten et al., 2010; Bell and Worrall, 2011). It is observed that pH is raised in all cases with this study (B5 starting pH 5.38, range with biochar 6.02-7.41, B12 starting pH, 3.95, range with biochar 4.93-6.28, B14 starting pH = 6.14 range with biochar 3.35-7.46). Studies have reported that soil pore water pH increases after biochar application to circumneutral and acidic contaminated substrates (Beesley et al., 2010; Beesley et al. 2011; Beesley and Dickinson, 2011; Karami et al., 2011; Zheng et al., 2012; Beesley et al., 2013), explaining changes in metal and As mobility in pore water. Various other studies report a soil liming effect of biochar, often resulting from alkaline biochar (Namgay et al., 2010; Fellet et al., 2011; Sizmur et al., 2011). Sizmur et al (2011) noted an especially beneficial increase in soil pH of more than 4 units when a nettle-derived biochar was added to a mine soil (pH 2.7). Jones et al. (2012) report a liming effect of adding woody biochar (450℃) to a rotational maize/grass planted agricultural soil (pH increased from 6.86 to 7.18 after 2 years, but back to 6.6 after 3 years). The pH of biochar recovered from the soil (aged) decreased by 2 units over the 3-year experimental duration, showing that biochars liming effect may be transient, thus the effects on metals and metalloids may also be transient (Sizmur et al., 2011).

6.5 Conclusions

FeO is a significantly effective treatments for removal of Al and Cu in river water. Biochar is significantly effective in the removal of Cu. Both may also remove other metals present in the river. FeO is more efficient at removal of Al and Cu overall. Further work is needed to establish the mechanism and derive a model involving kinetic models. Additional metals could be evaluated to see the scope for FeO for cleaning the wastewater. Future avenues could involve testing on a larger scale more like river conditions, to enable the test to be transferred into real-life scenarios and be used as a remediation option. Additional work is required to understand the exact mechanism in the case of Al/Cu with biochar and FeO.

CHAPTER 7 – FINAL DISCUSSION

7.1 Introduction

The aim of this thesis was to evaluate the effect of slate quarrying on the Barlwyd catchment and investigate the potential remediation strategies which could be used to address slate quarrying pollution in general. Specific aims were to examine the geochemistry, hydrology, sediment-aquatic phase exchange, and study the effect of biochar and zerovalent iron as a remediation strategy. Slate quarrying is of global economic importance and thus solutions could revolutionise the river environment for aquatic life. In the context of climate change this could become more relevant as increased frequency of storms becomes more prevalent, as pollution could potentially become a greater problem (Foulds et al., 2014). Thus, the magnitude of this problem could potentially become worse, leading to larger scale problems downstream as sediments are remobilised. Slate quarrying was chosen as a subject in this thesis as it is an under researched area yet has a global presence as far as mining is concerned, and thereby consequent environmental impacts, specifically in this context the aquatic environment. Al/Cu are the most toxic and present metals amongst the toxic sludge created in the mining process (Donnachie et al., 2014; Buss et al., 2013).

7.2 Geochemistry of the catchment

Cu and Al have been shown previously to be present at extremely high levels (Buss et al., 2013; Bray et al., 1996,1997). This appeared typical on a temporal and spatial scale at site B4/B5 and B12- Ael-y Bryn justifying the need for further research in this field. In this study high levels of Al and Cu are identified at B4, B5, B8 and B12. Furthermore, there is a low pH at each of these sites and its specifically linked to high levels of Al and Cu. TOC is measured for the first time in this river. Together, these findings illustrate an interesting geochemical picture for the river and are signatures of pollution hotspots. The assessment of the Barlwyd in this case puts it in the poor chemical status in terms of EU legislation, which invariably would lead to a poor aquatic status as demonstrated

previously by additional assessments by others. Interestingly, TOC is high for a river of this size, and the pH is low, which accounts for the low biodiversity found in this river. The TOC dataset is significant, and the data produced could be used to create a model and be input to the biotic ligand model. The pH and levels of metals exceed EWFD guidelines and place the river into poor chemical status. This likely impacts on the ecology, placing that into poor status too. Spatially the pollution is in the vicinity of slate pollution delivered by a consented discharge, diffuse pollution from the A487, and pollution which has filtered through a slate tip. This demonstrates that both historical pollution from the slate tips and more recent pollution generated from slate cutting can be held accountable for the mining pollution. Weathering of the slate tip may account for some of the pollution found in the vicinity of the quarry. Temporally the summer periods concentrate metals more with less dilution, and thus could be more toxic to the river, this is due to a lower dilution of metals. However, in Chapter 4 we show that storms bring a flush of metals, this may not have been caught in any one time slot during our sampling regime. pH is also of concern as the pH in Pant-yr-afon and B12 was below 6 and is thus not suitable for aquatic life. This combined with metal concentrations means that metals are bioavailable and in their most toxic form. In view of this, reaching the EWFD objectives are not likely unless remediation work is conducted, particularly in view of the evidence that the slate tips are contributing to the pollution. Despite the cessation of slate quarrying in the area, the river may continue to be affected. Given the amount of waste and evidence with metal mining, this may be considerable, research into closed mines may be necessary. However, despite this, the problem is highly localised and there are hotspots of pollution in the river.

7.3 Storm hydrology and the implications of climate change

The hydrology of the Barlwyd catchment has been affected by land cover and human alteration (see Figure 7.1). The lack of foliage due to the slate tips being uninhabitable by much plant life due to poor soil quality, means that the lag time after rain is shortened in duration and makes it a flashy catchment. Furthermore, slate and the surrounding urban environment are impervious surfaces such as the slate tips in comparison to soil grasslands and this makes the catchment even more flashy.

Turbidity accompanies this rainfall in a clockwise hysteresis, bringing slate silt down into the river and contributing to coincidentally high levels of metals. As a result, this leads to poor ecological status. The hysteresis is clockwise with regards to metal concentration, and this is likely owing to an exhaustion of material at B5. The hysteresis at B12 could be attributed to other processes as there is no known supply aside from the slate tips. This could be because of erosion by heavy rainfall here and dissolution of slate mineral by acidic water from the uplands. Hydrological processes are therefore responsible for the introduction of pollutants into the catchment. Positive effects of storm water are limited, but DOC washout may have a positive effect by binding with the Al/Cu and not being so bioavailable. In terms of speciation of metals, the combination of low pH and ORP mean the metals are in their most bioavailable form making this toxic to the river water, as determined by Eh/pH diagrams. Future work could observe or model speciation using software. The negative correlation with pH demonstrates the damaging effect that pH has with regards to metals, when pH is low metals are in high concentration. This is detrimental to the ecology of the river in a localised manner.

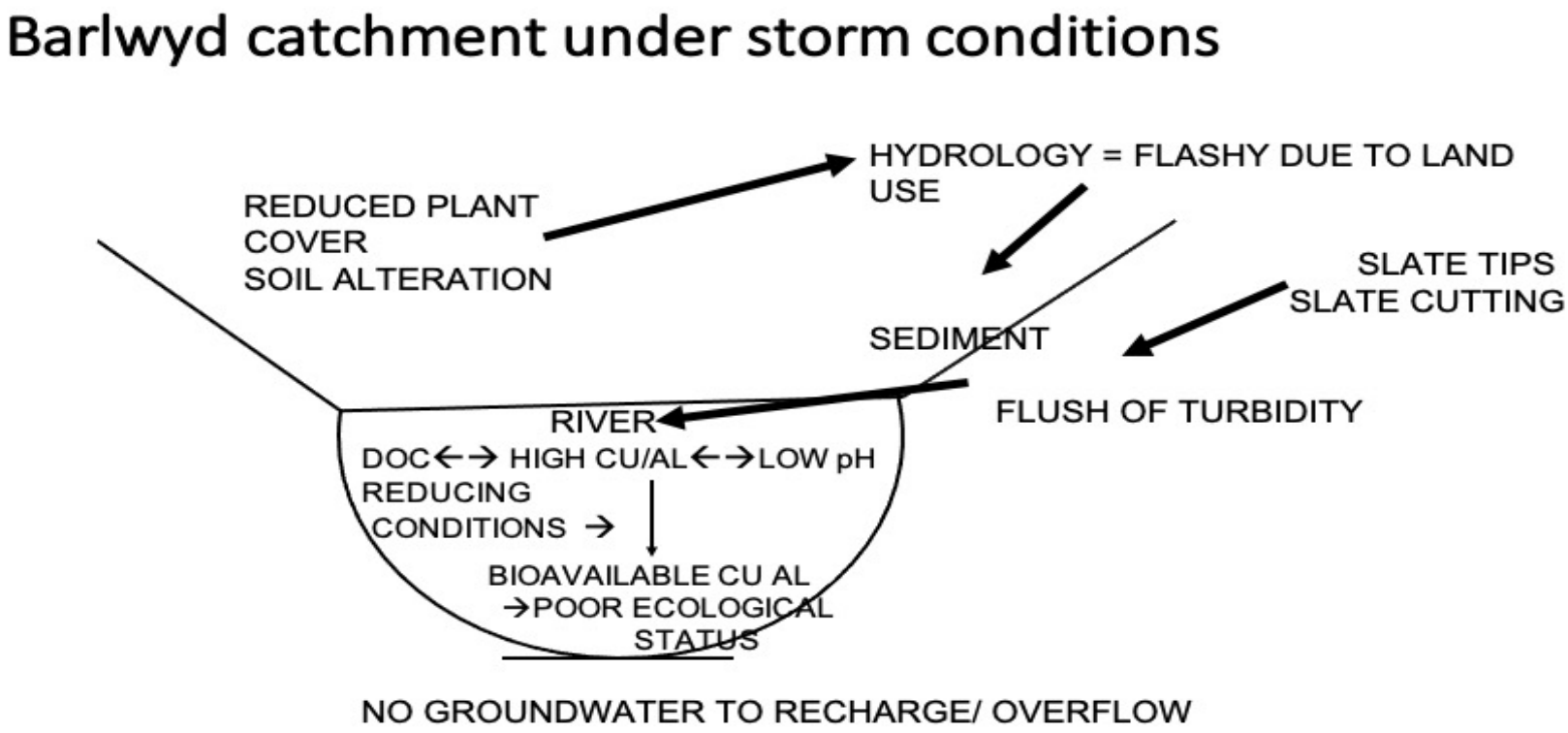

Figure 7.1 – Model of the river and factors affecting the chemistry and ecology of the catchment

7.4 The effect of sediment on water chemistry

In Chapter 5 the exchange of sediment was examined and a type of dioctahedral Na rich smectite clay was identified. It was revealed that pH greatly affected the amount of exchange which takes place between the sediment and the clay. As the pH from the uplands is acidic, liming could alter this dynamic. As the exchange is not pronounced enough to account for all the pollution found at B12, perhaps there is another mechanism of weathering with the slate tips which needs further investigation. Thus, in the quarrying process the method of storage of slate material is of importance to the surrounding environment. That sediment does not have a large effect on the water quality may be reflective of the difference in water quality at B5 and B12. B12 shows a higher amount of pollution and may reflect that pollution from the slate tips has a higher impact at this portion of the river, where slate cutting is not the reason for this pollution. This indicates that the problem is historic and because of the sediment. The experiment failed to estimate the sediment guidelines perhaps owing to experimental design. The minimal impact of sediment on the water may mean that sediment is not as impactful as previously thought. This could indicate that it is weathering of the slate tips which cause the main source of pollution. This is reflected also by the amount of pollution found in Chapter 3 at site B12, and the amount of turbidity found at B12 during a storm.

The low pH at the stream seems to impact the river more severely whereby the pH at B5 brings about a greater degree of pollution by sediment. This means that where the low pH found at B5 will have an impact on the degree of pollution at the site. DOC also may influence the results, whereby DOC may bind to the dissolved contaminant (see Figure 7.2). A model such as that designed by Eggleton and Thomas, reproduced in Figure 7.2, may be how the sediment behaves in water, although it is finer and may dissolve more readily. As shown in Figure 7.2, it may associate other clay particles which may clump together by electrostatic charges overlying waters releasing metals in solution (Eggleton and Thomas, 2004). Mobilisation of heavy metals from sediments to the water column can occur via changes in pH. This can happen either by dissolving unstable metal compounds, precipitating heavy metals by the preferential absorption onto suspended particle surface, or through the creation of

insoluble metal sulphides (Mwashote, 2003; Souza et al., 1986; Mohan, 1997; Kim et al., 1998). Kinetic processes that govern metal release during changes in redox potential need to be investigated further (Eggleton and Thomas, 2004).

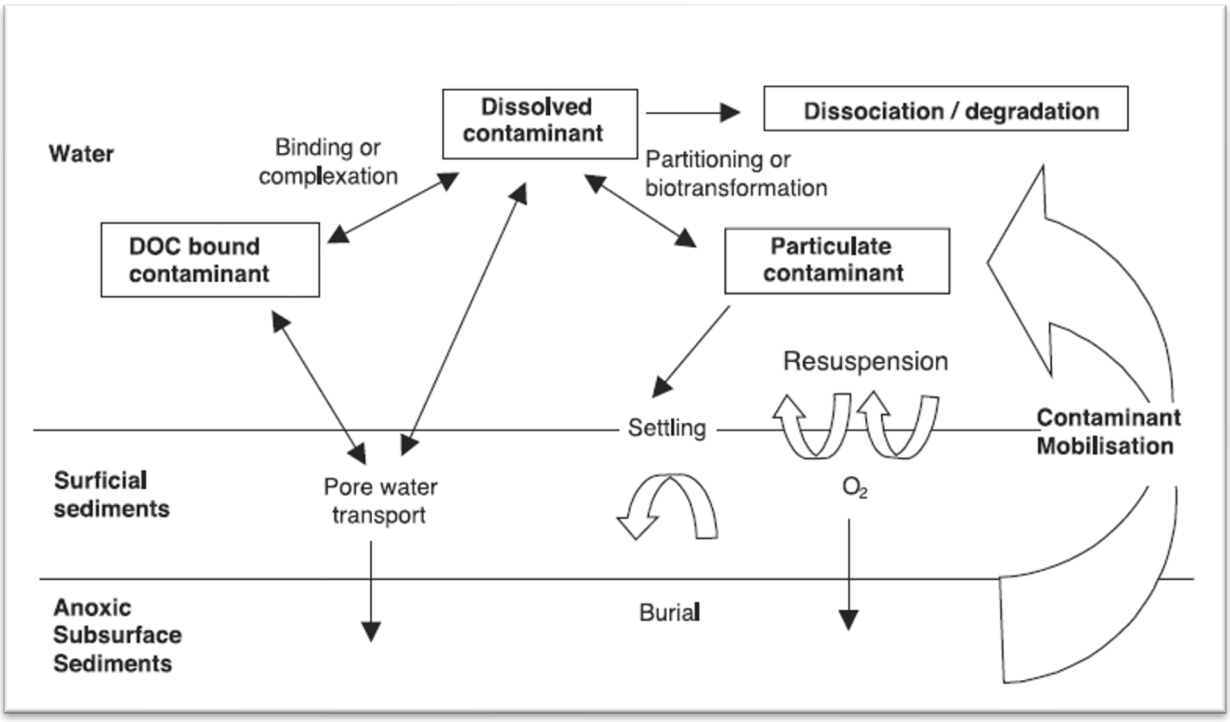

Figure 7.2 – A model of sediment cycling (Eggleton and Thomas, 2004)

7.5 Remediation with biochar and FeO

Adsorption is the most historically effective and utilised technology globally to clean wastewater (Maksoud et al., 2020). In Chapter 6 the effects of biochar and FeO on Al/Cu concentrations were examined. Biochar was found to be efficient with regards to Cu but not Al whilst FeO was efficient at removal of both Cu and Al. This reflects the different mechanisms of removal by biochar and FeO and are influenced by both starting concentration and pH as documented in the literature. Mechanisms of removal are shown to be influenced by pH in literature studies. pH is ideal for the removal of metals at site B5 and B14 but is not as effective at site B12. Thus, pH for removal by FeO and biochar is ideal at acidic pH's but not lower pH's such as those found at B12. The river water at B5 is most

like that found in the wastewater and is thus reflective of what could occur in the river. This is promising news for the cleansing of the wastewater. The mechanism and kinetics of these approaches are dependent on several factors such as surface morphology, magnetic behaviour of the adsorbent and the experimental conditions like pH, adsorbent concentration, irradiation time, temperature, and the initial dosage of pollutant.

FeO has numerous advantages such as its non-toxic nature, abundance, low-cost, ease to synthesize, and bioavailability. FeO has significant advantages over other adsorbents, such as their low-cost and ease of separation of suspending adsorbents to be used again to reduce cost, as well as the ease to synthesize. Furthermore, FeO and biochar have an advantage over other adsorbents in that they occur naturally in high abundance, associating next to no cost, can always be renewed, and are low energy. Usage of bio-sorbents promotes the remediation of water pollution and concepts like recycling, reuse, and the circular economy. Despite this FeO and biochar face many obstacles that require further research and development such as experimentation on a larger scale and on wastewater systems.

Future work could include combining biochar and FeO to maximise metal removal. One team has explored this already but not within this context or with Al. FeO and biochar were linked using chitosan beads. It could also be possible to alter the dose of Al to produce a Langmuir and Freundlich absorption curve. Nano Zerovalent iron which has been modified for stabilisation could also be utilised (Shu et al., 2010). Pristine nFeO tends to aggregate quickly due to the weak Van der Waals forces, high energy, and intrinsic magnetic interactions (Zhang, 2003). There is evidence that FeO particles can be supported by porous materials such as clays, resins, and carbon materials, to enhance their dispersion and stability (Shu et al., 2010; Sunkara et al., 2010).

The reaction mechanisms of FeO with contaminants varies with the contaminants, including oxidation reduction, adsorption, surface precipitation, surface complexation and co-precipitation. Additional studies should be performed to unravel the reaction mechanism between FeO and contaminants.

More detailed studies need to be performed, which include type of contaminants, FeO contaminant interactions, size of FeO initial pH batch or column interactions, temperature, hardness, DO and the presence of natural organic compounds. An additional caveat is how DO can be utilised more effectively in FeO systems.

A novel approach could be to use biochar created with remains of the *Rhododendron ponticum* in the hillside which are alien species. This could then be used to create a novel biochar, and trialled firstly in the laboratory and then, if successful, in the field. This could create a virtuous circle, whereby volunteers from the Dref Werdd environmental charity collect the rhododendron and then it is used to create biochar.

An extensive study looking at types of biochar could be conducted, with different types of wood and other sources of ligncellulose including crop residues could be examined and different pyrolysis temperatures, to attempt to maximise the efficiency of biochar and yield the best efficiency with this water. Pyrolysis temperature may affect the efficiency of the biochar. It is shown increase in pyrolysis temperature of biochars increases their aromaticity whilst the abundance of oxygenated functional groups diminishes (Harvey et al., 2011; McBeath et al., 2011). So, increasing pyrolysis temperature increases the proportion of cations sorbed due to 'weak' electrostatic bonding (i.e., cation-π interactions) and decreases the proportion due to stronger chemisorption (i.e., by cation exchange). Therefore, lower temperature pyrolysis should result in effective short term metal immobilisation due to the formation of inner and outer sphere complexes with oxygenated (acid) functional groups, but with time these may diminish in the soil environment (within the first 90 days after application; Zimmerman et al., 2011). Thereafter there may be a release of metals back into solution. Higher pyrolysis temperatures result in a negative surface charge that should remain stable for longer, but metals will be weakly (physically) adsorbed to biochar surfaces and immobilisation easily reversed.

Large scale studies utilising biochar and zerovalent iron in the field have not yet been conducted. There is a need to examine the practical utility of FeO on a commercial scale. As the effluents contain

several other pollutants, it is recommended that researchers work on actual effluents which have more practical significance.

Additional studies could include combining FeO with other technologies could be conducted, as FeO is practically difficult to treat wastewater or groundwater. The use of permeable reactive barriers in combination with FeO could be conducted. As the performance deteriorates in situ, more studies with combinations of technologies could be utilised with more economically viable materials such as biochar. Further research could examine the interaction between FeO and water.

7.6 Future questions for research

Further questions for research which arise from Chapters 3 and 4 are the exact mechanism required to weather the slates. Additional questions into what remediation strategies could be utilised could be studied. Microbial mechanisms could be analysed for removing metals by studying which extremophiles are found in the river. Bioremediation via bacteria, fungi and protozoa have been shown to show high resistance of heavy metals in wastewater (Munner, 2005). Research shows that these potential microbial consortia are effective for remediation of heavy metals contaminated water and wastewater. This makes microbial species significant for remediation. Sharma et al. (2000) showed that *Klebsiella pneumoniae* has potential to bioaccumulate heavy metals at high concentrations (15 mM), thus making this a potential solution for remediation. Furthermore, the survival of *Euplotes mutabilis* (a ciliate protozoa) in industrial wastewater containing high concentrations of heavy metals (Cd, Pb, Cu and Cr) have been evaluated in the past (Rehman et al., 2008). In their report, Rehman et al. (2008) observed that the ciliate, *E. mutabilis* showed tolerance against Cd (22 g/ml), Cr(60 g/ml), Pb (75 g/ml) and Cu (22 g/ml). In addition, it was observed that after 96 h inoculation of the *E. mutabilis* in the medium containing 10 g/ml) of metal ions, the live protozoan could remove 97% of Pb and 98% of Cr from the medium. The acid digestion of ciliate revealed 89% of Pb and 93% of Cr ions being accumulated in the organism. In general, the metal uptake ability of *E. mutabilis,* was evidenced by its survival and growth in water containing 10 g/ml

of metal ions. By using the heat-killed organism, no metal uptake was observed (Rehman et al., 2008). Advantages of this could include that it is low cost and biological and making it easy to dispose of. It is not entirely clear how this could be applied to our study site and would require further large-scale trials. Perhaps these protozoa could be grown in nets, which may filter the water.

Fungi such as *Fusarium oxysporum* have also been studied previously (Sanyal et al., 2005). Sanyal et al. (2005) demonstrated that in the presence of the *F. oxysporum*, metal carbonates are formed by the reaction of the heavy metal ions with carbon dioxide created by the fungus during metabolism. This is a completely biological method for production of crystals of metal carbonates. This is advantageous as the reaction leads to detoxification of the aqueous solution and could have great potential for bioremediation of heavy metals. Furthermore, the metals absorbed were not toxic to the fungus which grew readily after absorbance (Sanyal et al., 2005). In terms of our study sit, this reaction could be utilised to cleanse the water in a water cleansing system.

Speciation studies could be utilised with regards to FeO, and biochar and Al/Cu. Reaction kinetics could be analysed using Langmuir or Freundlich isotherms by conducting batch and column experiments. The limitation of this experiment is that the efficiency of the adsorbent is measured but not the efficiency of removal over time. This is promising for the future and questions which need to be answered are how Aqua mine Al and Cu for utilitarian purposes. Additional mechanisms of remediation would be interesting to research such as electrocoagulation, perhaps using solar or wind power to power the experiment. A combined approach of FeO/Biochar with maximisation of cleansing efficiency could be used in filters in our study site, specifically at locations where the slate is being cut. However, this approach with FeO may be costly, but biochar may be generated from materials such as invasive species like the Rhododendron or lignocellulosic feedstock).

Future research questions in hydrology could assess plant cover by the river and soil percolation. Furthermore, watershed models could be used to assess the catchment such as INCA (Whitehead et al., 2009). Models could look at predicted lag times with impervious surfaces and without impervious

surfaces to predict outcomes. Climate predictions could also be used to predict future levels of pollution using a model. PHREEQC could also be used to look at the redox conditions and geochemistry (Parkhurst et al., 1999).

As the exchange is not pronounced enough to account for all the pollution found at B12, perhaps there is another mechanism of weathering with the slate tips which needs further investigation. This is again of global importance. Perhaps electron microscopy or filming of the interaction between water and slate on a microscale may reveal more of the dynamic process. That sediment does not have a large effect on the water quality may be reflective of the difference in water quality at B5 and B12. B12 shows a higher amount of pollution and may reflect that pollution from the slate tips has a higher impact at this portion of the river, where slate cutting is not the reason for this pollution. This indicates that the problem is historic and because of the sediment. Perhaps electron microscopy or filming of the interaction on a microscale between water and slate on a microscale may reveal more of the dynamic process, this may lead to solutions in how to contain the pollution from the slate tips.

7.7 Recommendations for the remediation of the river

There are several methods which can be used to treat the water which is resultant from the quarry. Remediation has been researched in extensively, including the use of phytoremediation, adjustment of flows to the catchment, chemical treatment and biological treatment, liming, and wetland recovery of water. Several authors have reviewed acid mine drainage remediation methods extensively (Johnson and Hallberg., 2005; Fu et al., 2014; Khin et al., 2012; Akpor and Muchie., 2010). The most common method is to use a chemical-neutralising agent (Coulton et al., 2003). Utilisation of lime, slaked lime, calcium carbonate, sodium hydroxide or magnesium oxide and hydroxide are the standard methods (Johnson and Hallberg, 2005). When using these agents, the cost and efficiency need to be balanced, for example in comparison to lime, sodium hydroxide is up to 1.5 times more efficient, but is about 9 times the cost. Furthermore, the disadvantage is the disposal of the sludge generated. Parsons (1977) shows that in Cedar Creek, U.S.A. that aquatic life can be ameliorated by stopping the water flow

from quarries which are rich in metals. A small-scale trial could be done with the quarry wastewater to look at the effect. Another mechanism is to adjust the flow of water from quarries (Cairns et al., 1971; Diefffenbach, 1974). Other methods could be to use biological or chemical agents to treat the water, such as FeO, zeolites or biochar (Chapter 6).

Biological agents have also been used recently, where there has been a lot of interest given to establishing artificial wetlands as a method of lessening the impact of quarries on water quality. Webb et al. (1998) show that wetlands are remediated by sulphate reducing bacteria (SRB). The bacteria create hydrogen sulphide which dissociate the metals from the toxic solution in the river, and this is deposited. However, longer term studies need to be conducted with regards to wetlands (Shearon and Shearon, 2006). Kumar Rai et al. (2019) investigated the action of three wetland plants *Pistia stratiotes* (water lettuce) *Spirodela polyrhiza* (a duckweed), and *Eichhornia crassipes* (water hyacinth) for synchronized multi-metallic removal of six hazardous/non-essential metals (Fe, Cu, Cd, Cr, Zn, Ni) and As (a metalloid) from a Ramsar site of a biodiversity hotspot. The authors showed a high removal (>79%) of different metals in a 15-day experiment in microcosms. The authors identified these wetland plants as a passive eco-friendly remediation option of hazardous heavy metals from wastewater. At our study site water may be re-diverted into wetlands and then diverted back into the river. The geographical area for this however is unclear. Another option in bioremediation is the use of non-living algae biomass (bioresins) for the stripping of metals from solution has also been studied (Brown, 1996). Brown studied four bioresin materials which included materials derived from two different species of microalgae. The results showed that bioresins are derived from one biomass type in binding Cu, Ni and Pb ions in water (Brown, 1996). Bioremediation is a relatively low-cost, low-technology method and is thus economical, furthermore since it is a natural process, it is environmentally safe. These again would be advantageous at our study site as they are passive.

Metal-organic frameworks (MOFs) have also been suggested as excellent platforms for the removal of harmful species from water (Mon et al., 2018). MOFs are a class of crystalline inorganic–organic hybrid porous materials. High-processability, low- cost and long-lifetime of an adsorbent are three

key features for MOF's (Mon et al., 2018). Advances have been made in the field, but the number of MOFs utilised in water remediation is still scarce and mainly limited to some MIL, ZIF and UiO derivatives. Water stable MOF's need to be developed (Mon et al., 2018). Researchers working in the field of MOFs should widen the spectrum of organic ligands used to construct MOFs (Mon et al., 2018). Further research in this field and exactly how they can be applied to water systems, and our study site is required.

Reverse osmosis is a potential option for remediation. Membranes act as a molecular filter to remove nearly all dissolved minerals in reverse osmosis. Water passes through a membrane while the dissolved and particulate matter is left behind. The process is very effective for removal of ionic species from solution. The resulting concentrated by-product solutions make eventual recovery of metals more feasible. This is an expensive method and is sensitive. This has been applied in large scale also. In a study by Pawlak et al. (2005), who carried out a pilot study over a 30-day period on experimenting the efficacy of a reverse osmosis membrane module, showed that the total arsenic concentration in a feed water averaged 60 ppb during the test period and was reduced over time.

One method used is to prevent the weathering of material. This works principally by preventing oxygen and water from reaching the material. This includes the use of sediment or organic material or clay (Johnson and Hallberg, 2005). This could be effective to prevent the degradation of the slate tips. Further research would be required on a small scale to see whether this would be effective and robust enough on a large scale.

The recent and exciting advance in technology involved the use of electricity to remove metals from wastewater, known as electrocoagulation (Jack et al., 2014). This involves passing wastewater through an electrolytic cell containing steel plates. The iron ions are released at a rate directly proportional to the electrical current. The iron ions then cause metals to coagulate. The coagulant can be settled out or removed with filtration. This has been shown to effective with Cu from distillery water. A trial was run which was shown to remove 95% of Cu from wastewater (Jack et al., 2014).

This is being trialled by NRW, and to create a virtuous circle the electricity could be generated with water from by hydro, or alternatively by solar power to ensure a sustainable and lasting solution.

7.8 Conclusions

Slate quarrying is found to have an impact on water quality. A year of sampling revealed spatial and temporal variations in metals and geochemistry. A flushing effect of materials was found to be created by storm hydrology which in the view of climate change is significant. The modification of the land is also likely to influence hydrology. Sediment was found to influence the catchment but not proportional to sediment exposure, perhaps revealing that slate tip weathering may have a more significant effect. This was found to be affected by pH. Biochar was found to have a significant effect on removal of Cu, but not Al, perhaps owing to how biochar is charged. Zerovalent iron was found to be efficient at the removal of Al and Cu, owing to its absorptive properties and the pH mediated mechanism. This is promising for future removal of these and other metals from the wastewater, providing a remediation strategy. The low pH found in this river therefore seems to be a crucial factor in the degree of pollution. The Al/Cu concentrations could be typical of those found in slate mines globally and thus could be a significant finding. Therefore, a range of other remediation strategies could also be investigated with this wastewater in the future.

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