Diffusive Gradients in Thin-Films to Assess the Processes Influencing the Flux of Trace Metals From Mine Spoil to a River System

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1.0 Abstract

The mobility of trace metals within mine wastes can be affected by different geochemical and hydrological processes. Climate change is expected to alter the severity and frequency of extreme weather conditions, which in turn will affect the hydrological conditions at mine sites and within the river systems that flow through them. Wetting and drying cycles alter the exposure and submergence times of river sediment, causing shifts in the redox conditions and potential mobility of trace metals. This project utilized river water sampling, diffusive gradients in thin films (DGT), and a laboratory-based mesocosm experiment to quantify seasonal variability in metal concentrations as well as identify the geochemical processes that control metal speciation at Wemyss mine, in central Wales. Zinc and Pb were the main contaminants identified within both river and sediment pore water, constantly exceeding environment quality standards. Higher metal concentrations were observed during the summer, when dry conditions were more common, allowing for an increase in oxidation of sulphides and the deposition of fine sediment. Initial wetting following lengthy dry periods led to metal release, most likely from mineral salts that may have formed. High flows and increased submergence facilitates a shift towards anoxic conditions, whereby Fe/Mn oxides and, more commonly at this site, sulphates become reduced. Dilution, sulphide formation and the removal of fine sediment as a result of higher flow rates leads to a decrease in metal concentrations within river water. A conceptual model is proposed to outline the various hydrological and geochemical processes that influence sediment metal pore water concentrations and release. A better understanding of these processes and the conditions that influence them is essential for future management of abandoned mine wastes.

2.0 Declaration

I declare that no portion of the work referred to in this thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.

3.0 Acknowledgements

I would first like to thank Dr Patrick Byrne for his invaluable help and advice provided throughout this project. I would also like to thank Dr Kostas Kariakoulakis, Dr Jonathan Dick and Dr Sarah Lynch for their additional advice and support.

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4.0 Introduction

4.1 - Legacy of Metal Mining

Throughout history, metal use has been key to many societies and their development (Asare and Afriyie, 2021), a trend which is still evident in the modern era. Metals and their compounds form the basis for most modern technology, such as computers, machinery and medical equipment (UNEP, 2013). The exploitation of metals by humans dates back as far as the 6th millennium BC (Radivojević *et al.* 2010; Camizuli *et al*., 2018). Evidence of early metal use exists as archaeological finds, such as tools and slag material (Radivojević *et al.* 2010). The landscape of previously exploited areas also provides evidence of the history of metal mining. Sections of land are left abandoned after mining, with features such as spoil heaps, adits, shafts, and open casts left behind (Concas *et* al., 2006; Mighanetara *et al*., 2009; Byrne *et al*., 2013; Beane *et al*., 2016; Asare and Afriyie, 2021).

With increasing use of various metals, more sources have been exploited over time, leading to the presence of metal mines around the globe. The legacy of historic metal mining can be seen in many ways, particularly in the form of contamination of the surrounding environment. Many trace metals are present in the ground around abandoned mine sites in particulate form and do not degrade over time, meaning they persist long after the site has been abandoned (Concas *et al.*, 2006; Alloway, 2013; Stefanowicz *et al.*, 2014). Previously unexposed minerals (particularly sulphides) become subject to oxidation during and after mining activities, which in turn can result in the release of soluble contaminants into water systems (Batty and Younger, 2004; Mayes *et al*., 2009). Evidence of historic mining in the now forested areas of the Morvan and Cévennes in France had been identified by Camizuli *et al*. (2018). Soils and sediments here are still high in concentrations of Cu, Zn, Cd and Pb, despite the areas now being classed as nature parks and in ‘pristine’ condition.

The UK has a history of metal mining spanning back to the Bronze Age (Palumbo-Roe *et al*., 2009; Environment Agency, 2014). The industrial revolution is when UK metal mining peaked, with an increase in the demand for various materials for production (West *et al*., 1997). Over time, many of these sites have been abandoned as demand and resources depleted or moved elsewhere. According to the Environment Agency (2002), the last metal extraction recorded in Wales was at Gwynfynydd Gold Mine, which ended production in 1998. There are estimated to be around 5500 metal mines in England and Wales, though it is believed that this number is much higher (Environment Agency, 2014).

A common recipient of pollutants from mine sites is nearby river systems (Boult *et al*., 1994; Batty and Younger, 2004; Mayes *et al*., 2009). Four hundred and fifty three water bodies within seven of the eleven River Basin Districts in the UK are estimated to be at risk of pollution from abandoned mines (Environment Agency, 2008). Variations in hydrology and geochemistry influence the mobility of contaminants, often enabling them to travel tens of kilometres downstream. This is especially true for particulate-associated metals, which can be transported and provide secondary sources of pollution (Johnson *et al*., 2005).

Once released into the environment, trace metal contaminants can have a multitude of negative impacts to organisms. While classed as essential nutrients, excess quantities of Cu, Zn and Fe have been linked to heart and liver disease (Fraga and Oteiza, 2002; Liu *et al*., 2013) as well as reducing the availability of other nutrients to organisms (Alloway, 2013). Lead and Cd have also been linked to cardiovascular and respiratory issues (Nordberg, 2009; Alloway, 2013; Liu *et al*., 2013). An increasing knowledge about the negative health and ecological effects of trace metals has highlighted the importance of identifying them at various sites and developing methods for reducing their effects and transport.

Since the creation of the Mine and Quarries Act 1969, sites that have since been abandoned are in more stable and safe conditions. Unfortunately, the same legislation does not place responsibility for the safety of previously abandoned sites on their past owners. Local authorities have been responsible for the inspection of contaminated land that may be impacting health, water pollution, ecology and property since 2000 (Mayes *et* al., 2009; Environment Agency, 2014).

The Environment Agency, as part of the River Basin Management Plan, sets out various environmental quality guidelines to be met within a river system in order to achieve ‘good’ ecological status. Various factors are considered including pollutant concentrations, nutrient levels and biological assessments (DEFRA, 2014). Among these guidelines, there exist several Environmental Quality Standards (EQS) for trace metals in water. These values represent the maximum threshold of a particular trace metal allowed at a site

(Environment Agency, 2012). Such standards exist as numerous trace metals can affect plants, as well as being responsible for health issues in humans and animals (Alloway, 2013; Liu *et* al., 2013; Candeias *et* al., 2014; Huang *et al.,* 2017).

4.2 - Mobilisation and transport mechanisms of contaminants

The pH and contaminant content of mine water, and chemistry within the rock can be determined by the pyrite or carbonate present within the host rock (Palumbo-Roe *et al*., 2013). A major issue stemming from historic mining activities is that of acid mine drainage (AMD). Sulphide-bearing minerals become exposed to oxygen in the atmosphere and water, causing oxidation (Akcil and Koldas, 2006). The drainage that follows is acidic and sulphate-rich. Depending on the amount and type of oxidised sulphide material and the gangue material within host rock, metal contamination can be a major result (Boult *et al*., 1994; Akcil and Koldas, 2006; Dean *et al*., 2013). Acid mine drainage has been highlighted as a major environmental issue of mining activity as the process continues after mining has ceased (Dold, 2014). However, numerous mines do not contribute any AMD. Another form of drainage, neutral mine drainage (NMD), has been less well documented (Heikkinen *et al*., 2009; Warrender *et al*., 2011). It does however, still pose a risk to the environments around mine sites. At these sites, acidity generated from sulphide oxidation can be buffered by carbonates and silicates in the rock (Heikkinen *et al*., 2009; Warrender *et al*., 2011; Richard *et al*., 2020). On a UK scale, Wales contains a number of abandoned Pb-Zn mines, which are common contributors of NMD (Warrender *et al*., 2011).

Sources of contamination from mine sites are primarily classified in two groups, point and diffuse sources, which together encompass a number of inputs that play a role in how pollutants can be transported from a site. Point sources are easily identified features within the landscape, such as adits and shafts (Coupland and Johnson, 2004; Environment Agency, 2008). Metal concentrations can be easily measured in the water draining them (Mighanetara *et al*., 2009), meaning they can be effectively targeted by remediation measures.

Contaminants from diffuse sources are often more difficult to measure accurately, as these sources can be present over a large area and have more widespread effects than point sources (Mighanetara *et al.*, 2009; Byrne *et al.,* 2010). Examples of diffuse sources include spoil heaps, groundwater and river bank sediment (Macklin *et* al., 2006; Environment

Agency, 2008; Gozzard *et al.*, 2011; Grover *et al.*, 2016; Lynch *et al.*, 2017). Unlike point sources, diffuse pollution originates from erosion of surface material and runoff, as well as the interactions and leaching of contaminants within surface and ground waters. As a result, it is difficult to accurately determine the full scale of pollution from these contaminant sources. Commonly, water, sediment and soil samples taken are from a particular instance in time and only provide measurements for the chemistry at that moment. Gozzard *et al.*, (2011) adopted this method, obtaining river water samples on a flow dependent basis. It is important to gain an understanding of diffuse inputs under various conditions, as they are often affected by hydrology and climate.

Tailings left around mine sites are exposed to atmospheric conditions throughout the year. Common transport processes of contaminants from these deposits include leaching and surface runoff (Grover *et al.*, 2016). Fine particles can also be present and can become weathered and windborne (Kim *et al.*, 2014). Aeolian transport leads to finer particles being transported randomly and more easily affecting organisms through inhalation (Alloway, 2013; Sebei *et al.*, 2020). Many tailings around UK sites consist of high-sided mounds and varying particle sizes (Palumbo-Roe and Colman, 2010). This paves the way for various forms of weathering as well as the potential for more surface runoff and contaminant mobility. As such, it is key to ensure that the geochemistry of these sites is identified. Coupled with knowledge of how changing conditions may affect speciation and contaminant mobility, it can become easier to determine or estimate the effects of future climates and weather-related events.

In the field, various hydrological and environmental changes have an effect on the mobility and processes by which many trace metal pollutants can be transported. Natural variations in the local climate conditions can lead to periods of drought or flood and high or low rainfall (Concas *et* al., 2006; Gozzard *et al.*, 2011; Byrne *et al.*, 2013). These hydrological variations can affect atmospheric exposure and redox conditions of the waste material as well as the river sediment (Palumbo-Roe and Colman, 2010; Zhang *et al.*, 2014; Lynch *et al.*, 2017).

Flow conditions change throughout the year, increasing and decreasing following periods of rainfall or storm events, leading to periods of deposition or erosion and suspension within and around river channels (Gozzard *et* al., 2011; Byrne *et al.*, 2013). A large fraction of metal contaminants in rivers are transported in particulate form, following the same pathways as the natural sediment within the river system (Macklin *et al*., 2006). Concas *et al*. (2006) highlighted such processes upon observing a soil heap consisting of river sediments and mine spoil transported during a flood and coming to be deposited near a destroyed dam. This is a process that is likely to occur in many river systems where mine sites are present. As a result, it is important to gain an awareness of how different sediments and tailings act under the changing conditions that come from suspension and deposition over varying time frames. An increased breadth of knowledge in this area is key to future remediation and planning with regards to managing abandoned mine sites and the river systems they have the potential to effect.

Beneath the riverbed is an immersed area in which many ground and surface water interactions occur, known as the hyporheic zone (Boulton *et* al., 1999; Cardenas, 2015; Ahamad *et al*., 2020). Processes within this area vary spatially and temporally, as well as under different hydrological conditions (Boulton *et al*., 1999). Water exchange is common within the hyporheic zone, meaning oxygen and dissolved trace metals have a pathway between surface and ground waters (Cardenas, 2015; Ahamad *et al*., 2020). Therefore, it is important to acknowledge the role that the hyporheic zone has on metal exchange between river water and sediment pore waters.

4.3 - Geochemical speciation of heavy metals

Within mine deposits and the sediments of rivers draining these sites, the way in which trace metals are bound to the materials present has an effect on mobility and the potential risk to organisms (Maiz *et* al., 1997; Byrne *et al*., 2010; Palumbo-Roe and Colman, 2010; Lynch *et al*., 2014; Sebei *et al*., 2020). Metals present in soils and sediment around and near to mine sites are often bound to Fe-Mn oxides, sulphates, organic matter, carbonates and sulphides (Hudson-Edwards *et al*., 1999; Macklin *et al*., 2006; Du Laing *et al*., 2009; Byrne *et al*., 2010; Palumbo-Roe *et al*., 2013; Zhang *et* al., 2014; Lynch *et al*., 2017). The bonds present have an effect on how easily trace metals can be mobilised and released into the surrounding environment. Over time, the metal species present at a site can be altered. Secondary minerals can be formed by sulphide weathering and interactions with leachate from host rock (Hemphill *et al*., 1991; Roussel *et al*., 2000; Palumbo-Roe and Colman, 2010; Lynch *et al*., 2014). Palumbo-Roe *et al*. (2013) identified different Pb minerals around mine sites in central Wales and assessed how these minerals affect the bioavailability of Pb at each site. In this instance, anglesite ($PbSO_4$) showed low bioavailability, whereas cerussite ($PbCO_3$) showed higher bioaccessibility.

Lynch *et al*. (2014), combined mesocosm experiments, sequential extraction and diffusive gradients in thin film (DGT) to develop the conceptual model of Fe and sulphur speciation shown in Figure 1 (below). This type of model is useful as it can be utilised to help understand how geochemical processes may be influenced under various hydrological conditions. It highlights the shifts in metal speciation as well as the processes governing the release and attenuation of contaminants.

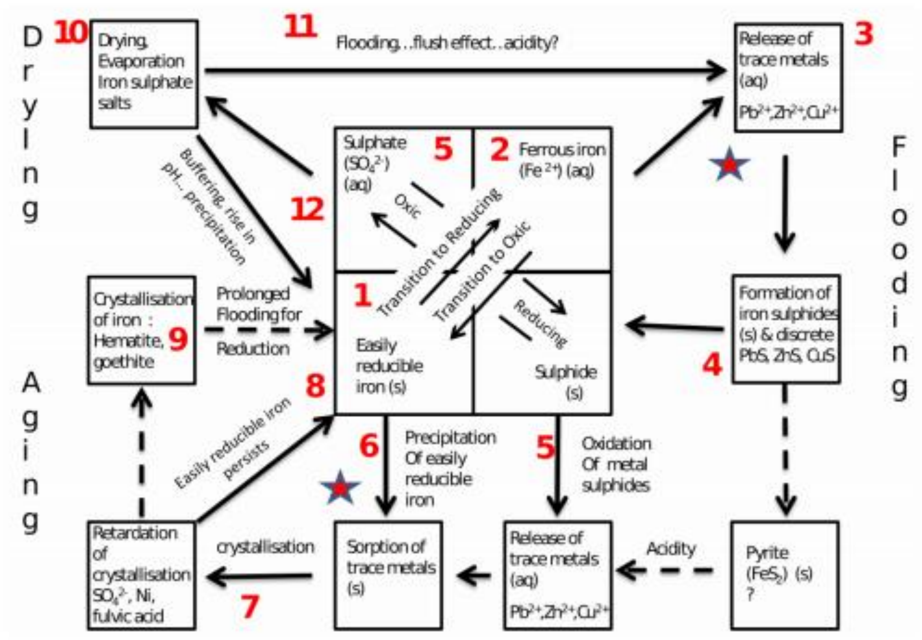


Figure 1. Conceptual model by Lynch *et al*. (2014), showing changes in iron and sulphur species, as well as the effects on the release of trace metals as a result of changing redox potential and drying over different time scales.

Surface waters are exposed to the atmosphere and typically provide an aerobic environment (Du Laing *et al*., 2009). Under these conditions, Fe and Mn can precipitate as Fe or Mn oxides, providing a suitable binding site for trace metals. Zn is commonly bound to these oxides (Du Laing *et al*., 2009; Lynch *et al*., 2017). Material high in oxides can be deposited downstream and within the river channel. As it remains submerged, oxygen within the pore waters is depleted as it is used up by organisms (Du Laing *et al*., 2009). The resulting shift toward anoxic conditions can promote reductive dissolution of the Fe/Mn oxides, enabling the release of Zn into pore water (Lynch *et al*., 2017).

Within the more anoxic conditions of submerged sediments, insoluble metal sulphides are common (Simpson *et* al., 1998; Peltier *et al*., 2005). Sulphides provide a binding site for many trace metals, meaning their precipitation can result in the reduced mobility and availability of trace metals (Du Laing *et al*., 2009).

As a result of weathering or a shift in the water table altering channel flow stage, oxygen can be introduced into previously submerged material, causing a release of contaminants that have previously been bound to sulphides within the sediment (Simpson *et al*., 1998; Peltier *et al*., 2005; Lynch *et al*., 2017). An example of such a process would be Zn released from oxidation of sphalerite (ZnS), a common sulphide mineral present at numerous mine sites (Peltier *et al*., 2005; Byrne *et al*., 2010; Lynch *et al*., 2017).

Many of these processes are covered in the conceptual model above. It is worth noting that this model has been developed through laboratory-based experimentation. Therefore, its applicability to many sites may be hindered as field conditions can be far more erratic and varying. As a result, it would be useful to build upon this model using data obtained in the field during different periods.

4.4 - Effects of changing hydrological regimes

Hydrology encompasses the variations in water level and river flow within a site and has an effect on the transport and deposition of sediments, which in turn can influence metal mobility. Topography can also play a role in the hydrological characteristics of a site (Du Laing *et al*., 2009), affecting runoff conditions, channel morphology and flow rates. The depth of bedrock has an impact on the water table, which affects groundwater levels and the submergence of sediment. This in turn will be a factor in influencing changes to redox conditions that may affect metal mobility (Lynch *et al*., 2014). As is common at many abandoned mine sites, spoil heaps are often adjacent to the river channel, leaving a steep gradient for surface runoff during rainfall events. This feature plays a role in the speed of transport of metals, as well as the time for which material is exposed to surface water (Dold, 2003).

The frequency, duration and severity of rainfall events has a large impact on contaminant mobility at a given site. The UK climate projection headline finding report (Met Office, 2021) identified the most recent decade (2009-2018) as 0.3°C warmer than the 1981-2010 average and 0.9°C warmer than the 1961-1990 average. The report also states that the previous decade has been 1% wetter than 1981-2010 and 5% wetter than 1961-1990. An important note is that extremely wet days caused by increased rainfall has increased by around 17%.

Flooding events brought on by heavy or persistent rainfall will lead to periods of submergence, which in turn may cause a shift towards anoxic conditions. As a result, there is potential for metal bound to Fe or Mn oxides to be released under the reducing conditions (Charlatchka and Cambier, 2000; Peltier *et al*., 2005). However, there may also be binding of some trace metals to sulphides under these conditions (Simpson *et* al., 1998; Peltier *et al*., 2005; Du Laing *et al*., 2009; Lynch *et al*., 2014).

Long dry periods can reduce antecedent soil moisture conditions and lead to the formation of efflorescent mineral crusts on the surface on mine tailings (Keith *et* al., 2001; Grover *et al*., 2016). These crusts are known to easily dissolve during a rainfall event, leading to the transportation of trace metals. Such a phenomenon is often referred to as a 'first flush' event. It is beneficial to gain an awareness of how metal speciation at a given site is affected by these changes, over both short and longer time frames.

Climate predictions indicate that the UK will experience more aridity in the future (Byrne *et al*., 2020), with an increase in the instances of localized heavy rainfall events depending on the area (Met Office, 2021). As a result, it is likely there will be a greater number of flood events and longer dry periods. If this is the case, sediment exposure, submergence and transport during high flow will be altered, affecting the redox conditions at numerous sites, and influencing changes in contaminant mobility. If we can enhance our knowledge of site geochemistry and the potential effects of changing redox conditions, we can better determine how some sediment will act under these conditions and if they are transported and deposited.

4.5 - Project aims and outcomes

This study aims to investigate the hydrological and geochemical factors controlling metal mobility at Wemyss mine, central Wales. This is to be achieved by the following objectives: (1) to quantify the seasonal variation in metal concentrations within river water and from contaminated sediment; (2) to determine the geochemical processes responsible for controlling metal speciation in sediments at this site; (3) develop a conceptual model outlining processes responsible for metal mobility and potential mobility under varying conditions.

5.0 Methods

5.1 - Sample Site

5.1.1 – Location and history

The site chosen to conduct this research was Wemyss mine (figure 2), a Pb-Zn mine located near to Ceredigion, Wales. This area contains 38 of the top 50 Welsh metal mines identified as having the greatest environmental impact, with Wemyss mine being included in the list (Environment Agency, 2002). The mine originally worked the Frongoch mineral lode alongside the nearby Frongoch mine (Bearcock *et* al., 2010; NRW, 2016). Both mines were worked independently until 1846, when they came under the same ownerships and were run in conjunction until their eventual closure in 1903 (NRW, 2016). Evidence of past working can clearly be seen around the site in the form of steep-sided spoil tips containing around 25 thousand tonnes of material (Merrington and Alloway, 1994) and the remains of a dressing mill (see figures 3 and 4), which immediately catch the eye. The slope created gives the potential for increased runoff into Mill Race Stream flowing through the site and the Nant Cwmnewydion on the southern edge. Due to inefficiencies in some extracting techniques, Davies (1987, cited in Palumbo-Roe *et al*., 2009) estimated that 35% of the ore raised may have been lost during dressing. This will contribute further to increased concentrations of Pb and Zn in and around the site.

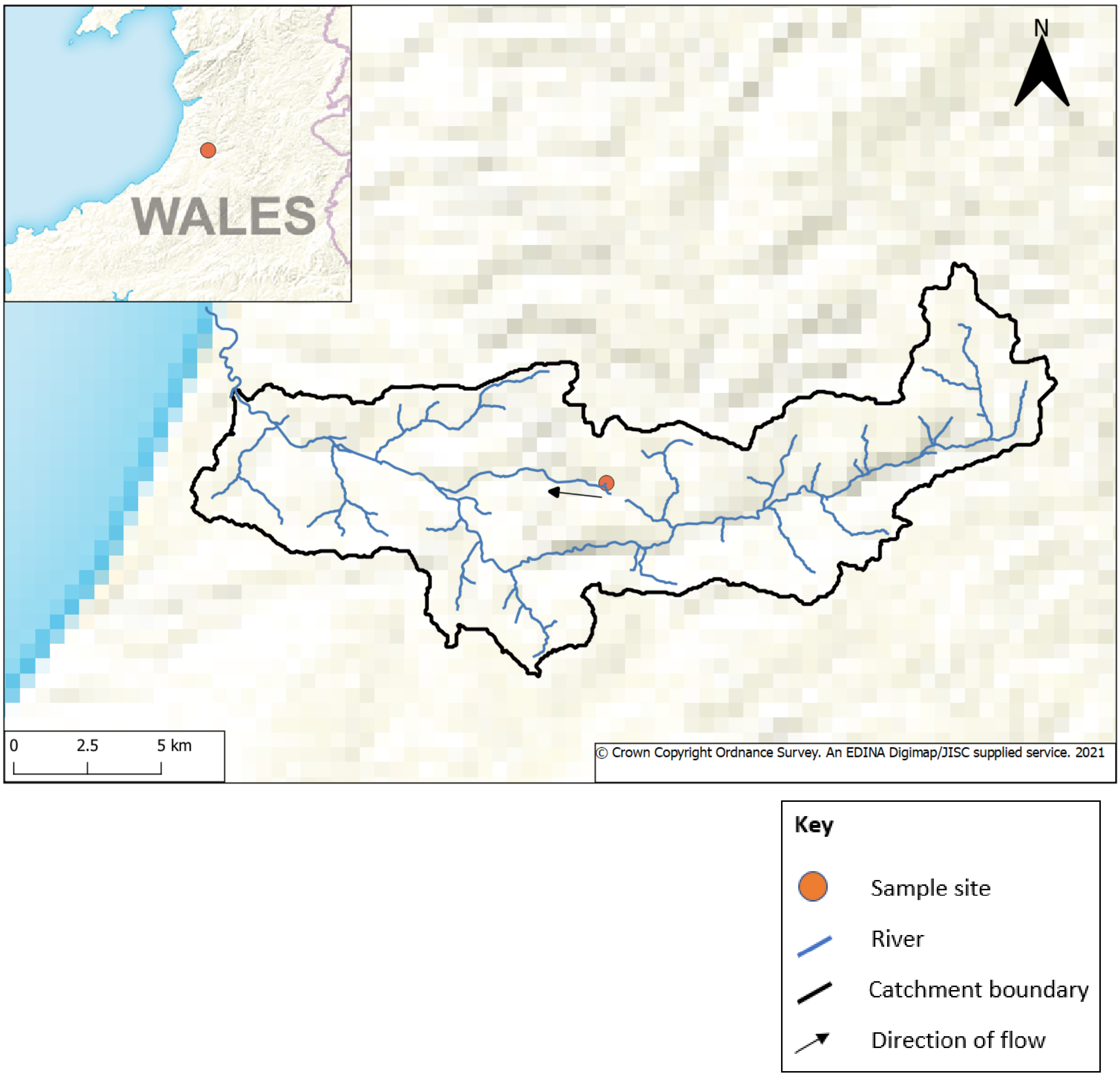


Figure 2. Map showing the position of Wemyss mine in relation to Wales and the Ystwyth catchment.

Figure 3. Main spoil heap at Wemyss mine. High sided spoil slopes down towards Mill Race Stream, flowing through the centre.

Figure 4. Remains of the dressing mill at Wemyss mine. More steep spoil is also visible here.

5.1.2 – Mineralogy

Mineralisation at Wemyss comes from the Devil's Bridge formation, which consists mostly of Silurian sandstones and mudstones (Palumbo-Roe *et al*., 2009; *Bearcock et al*., 2010; Palumbo-Roe *et al*., 2013). Like many central-Wales faults, the Frongoch fault follows an east-northeast trend (Palumbo-Roe *et al*., 2009), with the main minerals present being galena and sphalerite (Merrington and Alloway, 1994; Bearcock *et al*., 2010; Palumbo-Roe *et al*., 2013). As a result, the spoil dumped at the site contains high concentrations of Pb and Zn, which will have been leaching through the groundwater and undergoing mobilisation processes since the mine's closure (Merrington and Alloway, 1994). Sampling of surface spoil at Wemyss mine, has identified anglesite as the dominant Pb mineral (Palumbo-Roe *et al*., 2009), though it should be noted that this particular study used homogenised samples from various location within the site.

5.1.3 –Hydrology

The catchment draining Wemyss mine is that of the Nant Cwmnewydion, which leads into the Afon Magwr and finally the Afon Ystwyth. Wemyss mine has been identified as a contributor to these rivers failing to meet environmental quality standards for Zn and Pb (NRW, 2016). Gauged daily river flow data for the Ystwyth catchment can be accessed from the National River Flow Archive (NRFA). Roughly 19km downstream, at station 63001 (Pont Llolwyn), mean daily river flow is 6.113m^3/s; low flow (95% exceedance) is 0.595m^3/s; and high flow (5% exceedance) is 20.7m^3/s (NRFA, 2021a). Annual average rainfall in this region for the period 1961-1990 was 1456mm (NRFA, 2021b). Variations in flow rate, a future shift towards more aridity (Byrne *et al*., 2020) with an increase in localised rainfall events (Met Office, 2021) will play a key role in influencing changes to erosion, suspension and deposition at Wemyss mine and along the Ystwyth catchment.

Visits to the site for fieldwork allowed changes in channel conditions to be observed first-hand. The figures below (5 and 6) illustrate the variation that occurs within the channels at Mill Race Stream and the Nant Cwmnewydion. Key changes take place along the southern edge of Wemyss mine, where the Cwmnewydion flows alongside the spoil heap. Deposition dominates during the summer. Low flow means finer sediment is able to build up and remain in the channel. During the autumn, an increase in rainfall leads to higher flows, causing sediments to become suspended and transported downstream. Larger pebbles are all that remain in the channel, as they are heavier and require more energy to move.

Figure 5. Changes in river water level at the confluence of Mill Race Stream and the Nant Cwmnewydion in October 2017 (a) and July 2018 (b)

Figure 6. Changes in sediments presence at sample site 3 during October 2019 (a) and August 2019 (b)

5.2 - Fieldwork

5.2.1 – Sample times

Field visits and sample collection took place during summer (July-August) and autumn (October-November) of 2018 and 2019. These time frames have been chosen so that river water and sediment can be sampled under different hydrological conditions. Variations in stream flow make it possible to determine changes in metal mobility under different hydrological regimes, and to further investigate how these changes have occurred through additional sampling and experimentation.

5.2.2 – Sample locations

Figure 7 shows the sample points chosen for fieldwork. Each is situated at a different point along the river to provide some detail into variations in metal concentration and mobility at different stages and flow conditions. Two positions (S1 and S2) lie along Mill Race Stream as it flows through the main spoil tip where there will be interactions between stream water, sediment and the adjacent spoil. This also applies to point S3, which is situated in the Nant Cwmnewydion as it flows next to the southern edge of the spoil heap. An additional sample location (S4) is used further downstream, after Mill Race Stream and the Nant Cwmnewydion have merged. This location lies on a meander, where a small amount deposition appears to occur behind a tree growing out of the bottom of the river bank. Finally, there is a location intended to measure background (BG) metal concentrations within the river water. This location appears before the Cwmnewydion reaches Wemyss mine, where there should be no influence of mining activity affecting water chemistry. The channel bed around this area consists of mainly exposed bedrock, with several steep gradients affecting the velocity of the river water. Samples here were taken from a pooled area of the river, where flow appears to slow before moving downhill towards the mine.

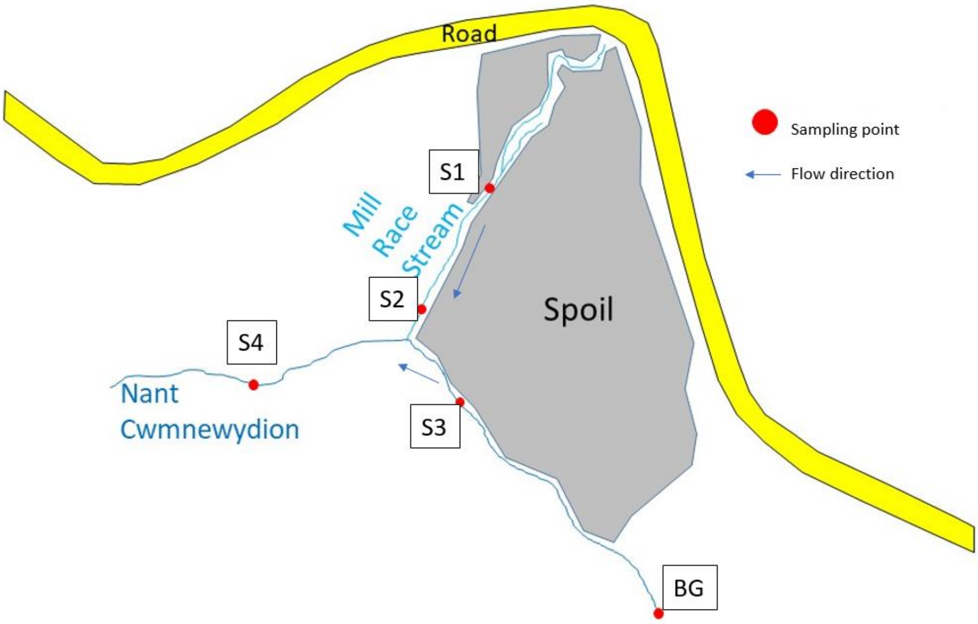


Figure 7. Map of sampling points used at the study site. Direction of flow for Mill Race Stream and Nant Cwmnewydion has also been illustrated.

5.2.3 – DGT deployment

Diffusive gradients in thin films (DGT) is utilised in this study to measure pore water metal concentrations within stream sediment. The DGT probes used for deployment are referred to as piston-style, due to their shape (see figure 8). A round plastic housing holds in a filter membrane, diffusive gel and a binding resin (Chelex 100) to accumulate metals. The filter and diffusive gel layers allow for the establishment of a concentration gradient over which analytes can diffuse and bind to the resin layer (Davison, 2016). The use of this method provides a cost-effective, *in*-situ technique for measuring metal concentrations in the field. The probes will accumulate metals within the binding layer until removed, providing a snapshot of the concentrations within the deployment medium over a given timeframe. Using DGT is beneficial for measuring bioavailable metal concentration, which poses the most risk to organisms. The devices can measure labile metal flux in water, soil and sediment, whilst leaving the conditions within the surrounding material relatively undisturbed (Bade *et al*., 2012; Menegário *et al*., 2017), an important feature as other sampling techniques require additional storage and treatment, posing a risk of contaminating samples (Omanović *et al*, 2015).

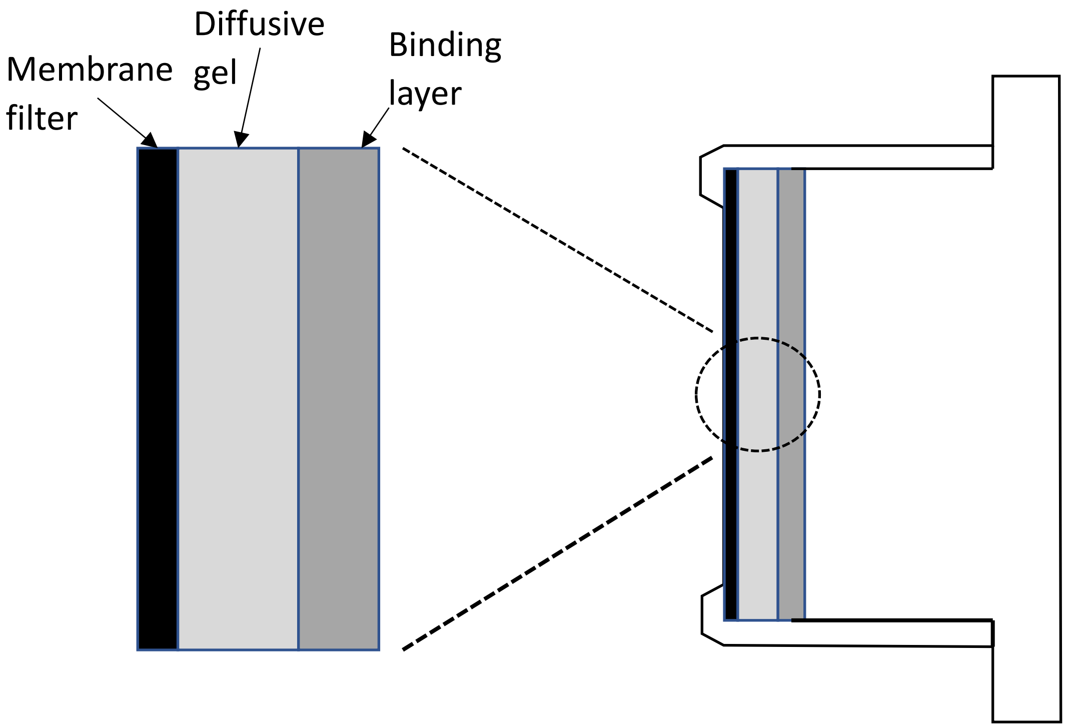


Figure 8. Internal cross section of a piston-style DGT probe

A total of 46 LSLM-NP probes were purchased from DGTresearch Ltd for use in this research. In order to deploy the small DGT devices in the field, drivepoints were constructed from acrylic sheet and holes were drilled to secure the probes using fishing wire (see figure 9). These drivepoints provide the probes with access to sediment pore waters at the sample sites, whilst also enabling them to be more easily identified upon returning to remove them. A small amount of sediment was moved, using a stainless steel trowel, in order to help insert the drivepoint and probe assembly into the sample point. Once the probe was below the sediment level, the moved material was replaced to ensure it was covered. Once deployed, time and water temperature were recorded as they are essential to later processing of the probe measurements. Once deployed, the probes remained in the sediment for one week to accumulate metals from the surrounding pore waters. This time allows for the sediment to resettle and for a diffusive gradient between the sediment pore water and the resin to be established, whilst not leaving so much time as to saturate the resin (Davison and Zhang, 1994).

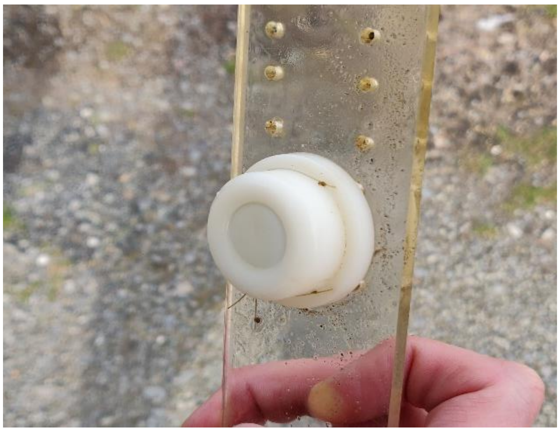


Figure 9. Recovered DGT probe still mounted to its drivepoint

Recovery of the probes was achieved by removing the drivepoints from the sediment and cutting away the fishing wire. Time and temperature were recorded again for later use. An updated version of the procedure for processing recovered DGT devices originally designed by Davison and Zhang (1994) can be obtained from their company that supplies the probes (DGTresearch Ltd), and has been used for this project. Once removed from the sediment, the probe is washed with deionised water, and the plastic cap is broken off. The filter and diffusive gel are removed, leaving the resin layer. This is placed in a 1.5ml

Eppendorf tube and eluted with 1ml of 1mol HNO_3 solution. Eluted resins are transported in a cool box back to the laboratory and stored at 4°C until they are prepared for analysis. As outlined by DGTresearch Ltd (2021), eluted samples were left immersed for at least 24 hours before analysis. Once in the laboratory, 0.5ml of this solution was diluted 20 times in a 10ml sample tube. These were then stored at 4°C for later analysis.

Once the eluent (V_e) has been analysed, the resulting concentration (c_e) is used to determine the mass (M) within the chelex binding layer. The fraction of bound metal released (f_e), also known as the elution factor, and details regarding the volume of the binding layer (V^{bl}) are also necessary. These values are typically 0.85 and 0.2 respectively (DGTResearch Ltd, 2021) This information is combined into equation 1 below.

$$M = \frac{c_e(V^{bl} + V_e)}{f_e} \qquad (1)$$

In order to further determine the concentration of an analyte measured by the DGT probe (cDGT) over the deployment time (t), it is also necessary to obtain the area of the probe window (A_p), the diffusion coefficient of the required analyte (D) and the total thickness of the diffusion layer (Δg). These values have already been determined and made available by DGTResearch Ltd (2021). Values for A_p, and Δg are typically 3.14 and 0.092 respectively, whilst D varies between each desired analyte and deployment temperature. The final result is equation 2 (below).

$$cDGT = \frac{M\Delta g}{DA_pt} \qquad (2)$$

5.2.4 – Field water sampling

Whilst DGT provides data for metals concentrations within the pore waters of stream sediments, analysis of the stream water flowing over these sediments should not be overlooked. Exchanges within the hyporheic zone play a role in affecting the chemistry of sediment pore water (Gandy *et al.*, 2007; Ahamad *et al.*, 2020). Alongside deployments of DGT probes, one stream water sample was collected at each location by immersing a 50ml sample bottle in the stream at each sample point. These samples were taken back to the laboratory and stored overnight at 4°C for processing within 24 hours. The next day, water samples were filtered using a syringe and 0.2µm, supor membrane filter.

Filtered samples were obtained from each sampling point to measure dissolved metal concentrations. Both of these sets of samples were acidified with 2% HNO_3 and stored at 4°C.

5.3 - Laboratory Work

5.3.1 Field sample analysis

All filtered water samples, as well as diluted DGT eluent were analysed using inductively coupled plasma – mass spectrometry (ICP-MS). Trace metals present within the river sediment will have likely been dissolved within the river water (Cardenas, 2015; Schroeder *et al*., 2020), although some may be present as suspended particulates. Filtering will remove any particles greater than 0.2µm, lowering the measured concentration further. Eluent from DGT resin has been diluted to provide more sample, thus lowering the concentration measured. Therefore, the precision of ICP-MS is better suited for analysis of river water and DGT samples.

Four key trace metals were chosen for analysis (Mn, Fe, Pb and Zn) as Wemyss mine is a former Pb-Zn mine, meaning the spoil is highly concentrated in these two trace metals (Merrington and Alloway, 1994; Palumbo-Roe *et al*., 2013; NRW, 2016). Given the tendency of Fe and Mn oxides to bind to trace metals (Lynch *et al*., 2014), these elements have also been included to aid in determining the mobilisation processes taking place within the sediment at this site.

5.3.2 – DGT metal uptake test

Metal uptake into DGT devices is generally assumed to be linear, following what is described as perfect sink behaviour (Davison, 2016). However, this is often not the case, especially in the field. Various factors exist to reduce the metals accumulated within the Chelex resin, including pH, saturation of the resin, resupply of metals from the deployment medium and competition with other biotic ligands and cations already present (Davison and Zhang, 1994; Mongin *et al*., 2013; Davison, 2016). As such, it was necessary to determine if the 1-week deployment time chosen for this project was acceptable, and whether any limiting factors were present. An uptake test was designed in order to ensure that the probes would not reach saturation within the deployment medium and identify any deviation from the linear, perfect sink behaviour.

Sediment taken from MRS near to deployment site 2 was placed within small buckets and taken back to the lab in order to assess the uptake of key analytes for this study by the DGT probes in use. The experimental setup is illustrated in figure 10. Seven probes were placed within the sediment and kept submerged in water collected from MRS to better replicate inputs present in the field. Lids were placed on the buckets to prevent any atmospheric interference from additional O_2. The intervals for each deployment progressed from 6 hours up to 1 week, the same time as deployment in the field. Once removed from sediment, each probe was processed in accordance with the procedure set out by DGTresearch Ltd. (2021). All eluted resins were then diluted and stored at 4°C for later analysis using ICP-MS.

Figure 10. Experimental setup employed for DGT uptake test

5.3.3 – Hydrological data

In order to gain an insight into the hydrological conditions in the study area, gauged daily river flow data was obtained from the Centre for Ecology and Hydrology (CEH) via the NRFA. The data acquired comes from a gauging station (63001) at Pont Llolwyn (grid reference SN590772), roughly 19km downstream in the Ystwyth catchment. This has been chosen as Wemyss mine lies within the catchment area highlighted in figure 10, below. Utilising the flow data from this area for the period in which fieldwork has taken place will allow conclusions to be drawn about the hydrological conditions influencing some of the results found.

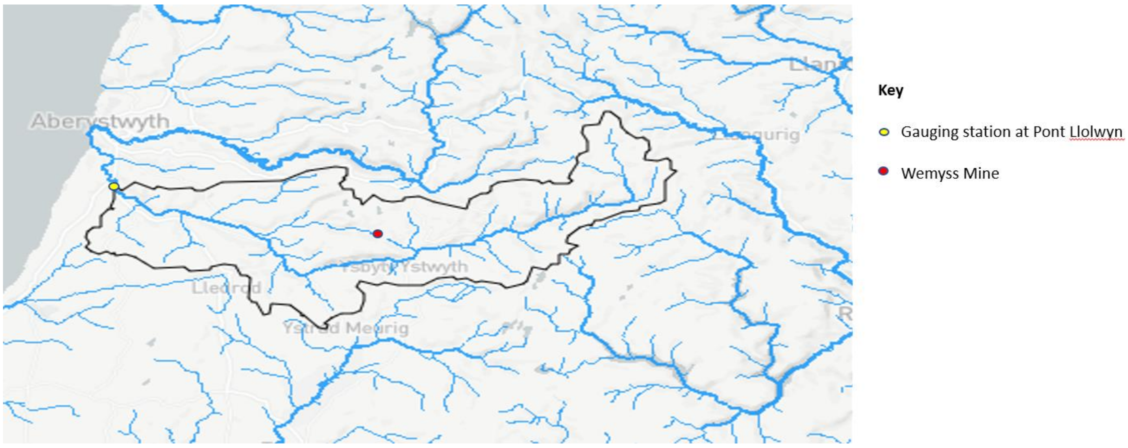


Figure 11. Map highlighting the position of Wemyss mine within the catchment area of the gauging station (63001) downstream at Pont Llolwyn (NRFA, 2021b)

5.3.4 – Mesocosm experiment

In order to gain a clearer picture of the processes governing trace metal mobility at Wemyss mine, sediment was taken from the lower end of Mill Race Stream, where it converges with the Nant Cwmnewydion and deployment site 2, in order to be used in a mesocosm experiment. The experimental setup broadly follows that of Lynch *et al.* (2017). The experiment is designed to replicate sediment inundation over different intervals. By altering the time for submersion and drying, redox conditions may begin to change, potentially altering the geochemistry within the column sediment. Analysis of the leachate water and sediment will aid in identifying the effects of these changes and metal concentrations. Performing this experiment is useful for determining the potential effects of wetting and drying cycles in the field.

The columns used for this experiment consisted of 9 uPVC drainpipes (diameter 10cm x height 40cm) with holes drilled in the side so that a tap could be inserted, allowing leachate to be easily extracted. Prior to beginning this experiment, the sediment samples were homogenised and sieved to <2mm. Using a stainless-steel trowel, sediment was inserted into the column, with larger particles being added in to help with aeration, making the conditions more similar to those in the field. All columns were left at field capacity for one week prior to beginning the experiment. When saturated, or wetted again, the water level was kept at roughly 5cm above the sediment level to simulate flooded conditions (Du Laing *et al*., 2007).

Three wetting regimes were chosen in order to simulate possible conditions in the field and are outlined in table A1 (see appendix). Each regime was run in triplicate to gain an average and identify any anomalous results. Columns 1-3 all remained saturated throughout the experimental run, providing conditions of a constant flood. Throughout the wetter months, sediment in the field will remain submerged for long periods, meaning this regime is useful for assessing the metal release towards the autumn and winter. Columns 4-6 were subjected to a cycle of 1 week wet followed by one week dry (1ww/1wd hereafter) and columns 7-9 had a cycle of 2 weeks dry followed by 1 week wet (2wd/1ww). These wetting regimes were more representative of the sporadic patterns likely to occur in the field. Wetting and drying in the natural environment are not uniform and controlled, so many variances and different patterns will occur.

During each drainage cycle, water samples were collected in 50ml falcon tubes. The volume of sample varied but averaged around 30ml per column, to ensure the leachate collected was from water already in contact with the sediment, and not the surface water that would percolate through during drainage. As columns 1-3 were all saturated, water was sampled every week, prior to topping up; the remaining columns were sampled prior to draining and once filled on each cycle.

5.3.5 – Sequential extraction procedure

After the week spent at field capacity and again at the end of the mesocosm experiment, sediment from each column was collected using a stainless steel trowel and stored in a sample bag to be used in a modified sequential extraction procedure. As the focus of this research is on the labile metal fraction, a two-step extraction procedure was adopted. The first stage is that of an acetic acid digest, to determine the concentration of metals available to organisms (Chaudhary *et al*., 2016). The methodology for this stage was adopted from Rauret *et al*. (1999). Forty millilitres of glacial acetic acid were added to 1g of sediment in a 50ml falcon tube. Allowing as little delay as possible, all tubes were mounted to an orbital shaker and shook at 30rpm for 16 hours. Once finished, the solid residue was extracted by centrifugation at 3000rpm for 20 minutes. The extractant was diluted 10 times, acidified and stored at 4°C. the remaining sediment was washed with deionised water, centrifuged again and dried overnight, with the water being discarded.

The second stage was a microwave-assisted aqua regia digest, to determine the total remaining metal concentration within the sediment. The procedure for this extraction followed ISO method 12914 (2012, cited in Santoro *et al.*,2017). One gram of sample was mixed with 8ml of aqua regia (6ml HCl and 2ml HNO_3) and placed in a microwave digester at 175°C for 20 minutes. Vessels were allowed to cool overnight before removal. Samples were then diluted to a factor of 4 and filtered. The filtrate was then diluted up to a 20 times factor and stored at 4°C for analysis.

Inductively coupled plasma – optical emission spectrometry (ICP-OES) was used to measure metal concentrations in the samples collected, as the digestions are able to extract more analytes. This was effective for Pb and Zn in acetic digest samples as wells as Pb, Mn and Zn in aqua regia samples. However, Mn and Fe were below detection range for the acetic digest and Fe was above the detection range from aqua regia. Therefore, a combination of ICP-MS and OES measurements were taken.

6. Results and Discussion

6.1 - Hydrological data summary

Using the daily gauged river flow data obtained from the CEH, figure 12 has been produced to show the hydrological conditions during the timeframe for this project. Also present are points indicating when DGT probes were deployed and water sampling occurred (marked as D1-6). Additional lines have been inserted to mark the rates for Q95, 50 and 5 flows, as these instances provide an indication of the rainfall conditions. By identifying the conditions around deployment cycles, it is possible to infer potential influencing factors related to metal concentrations. For example, increased rainfall will typically lead to an increase in water within the river channel, even if only for a brief time. Such changes would result in sediment submergence and a potentially higher rate of flow. An increase in flow rate is likely to influence erosion and the potential for sediment suspension, altering the amount and particle size of sediment present within the river channel. As was observed throughout field visits, periods of lower flow saw more sediment in the river channel; whilst the relatively wetter, higher flow conditions in autumn often lead to suspension and transport of sediment further downstream (see figures 5 and 6).

The period from autumn to spring typically sees several sharp spikes in river flow, when Q5 (20.7m^3/s) is exceeded, followed by quick decreases down to near and below Q50 (3.378m^3/s). Conditions during this time will be shifting towards more rainfall events, which will lead to increased river flow shortly after. These increases in rainfall and river flow can result in the removal of finer sediment from the river channel and occasionally lead to erosion of the spoil at the river bank (see figure A1 in appendix). River flow rates during the summer months varied between each year of this study. In 2018, rainfall appears to be very low, which would lead to lengthier dry conditions. River flows during this time dropped below Q95 (0.595m^3/s) in some instances, whereas 2019 saw an increase in wetter conditions in the early summer (June) and towards the end of the season (late August). Unlike the autumn and winter events, summer high flows do not exceed the Q95 threshold. With a reduction in rainfall intensity and frequency, flow rate decreases and suspended sediment can be deposited on the channel bed.

Both deployments 1 and 2 took place during what was a period of exceptionally low flow (0.534 and 0.252 m^3/s respectively at Pont Llolwyn). Flow rates the following year were slightly higher, as there seemed to be more rainfall events. Deployment 4 took place shortly after a peak in flow, with an average of 1.918m^3/s.

Prolonged dry conditions have been observed to cause the water in the upper section of Mill Race Stream (including the location of deployment site 1) to cease flowing. Water is still present only a few metres downstream, likely supplied from sub-surface flows that exit from the mine spoil (see figure A2 in appendix). An alternative input such as this is likely to have been subject to different redox conditions, potentially altering the chemistry of the water.

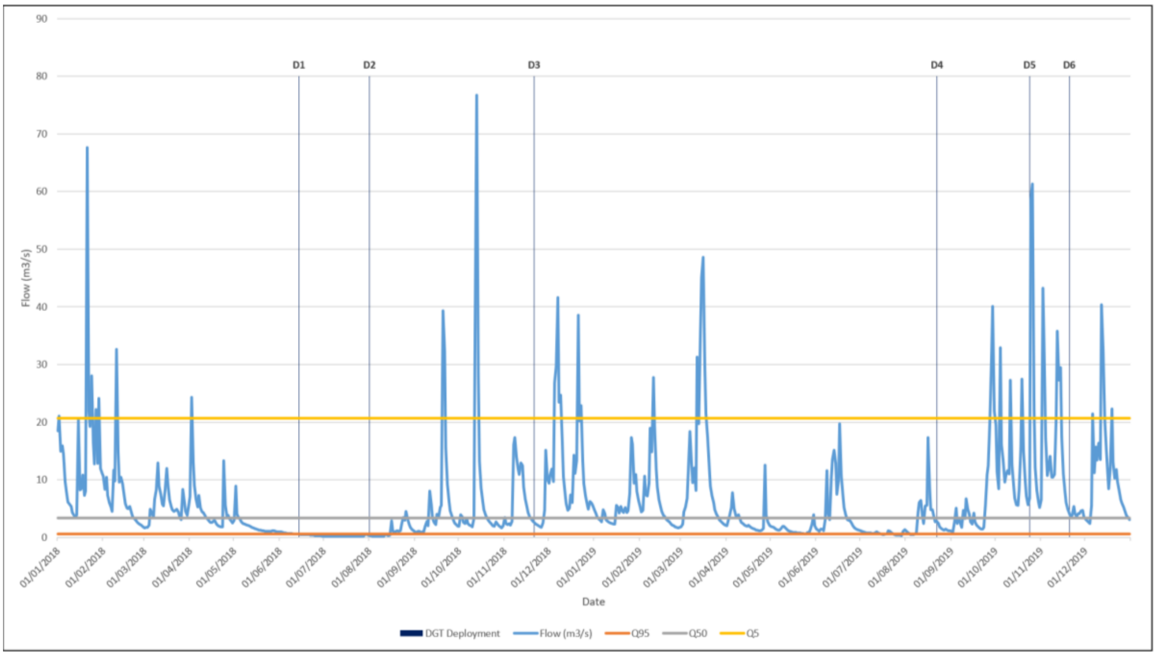


Figure 12. Gauged daily flow data for CEH site 63001 (Ystwyth at Pont Llolwyn) throughout the deployment periods (2018-2019). Including deployment markers as well as Q95, 50 and 5 thresholds.

The remaining deployments all took place during mid to late autumn. Conditions between the two years did show some variation, as with the summer months. Once again, 2018 was relatively drier, with more dispersed high flow events. The following year saw an increased occurrence in high flow during the autumn months, as well as the flow rate remaining above the Q50 threshold between both deployments. Deployment 3 took place in November 2018, shortly after a relatively small increased flow period. Average flow over this deployment period was 3.829m^3/s, just above the Q50 threshold. The fifth deployment took place during a period of greatly fluctuating flows. Over this deployment, average flow rate was (22.629m^3/s and Pont Llolwyn, which is above even the Q5 threshold. The sixth, and final deployment occurred towards late November 2019. The data shows that flow rate was on the decline at this stage, with an average flow over this deployment being 4.11m^3/s.

Higher flow rates at the study site often result in the disturbance of sediment from within the river channel. It is difficult to infer exactly what flow rate at Pont Llolwyn would result in sediment transportation at Wemyss mine, although observations in the field do provide some insight. Site 3, along the Nant Cwmnewydion at the southern edge of the spoil, is particularly susceptible to mobilisation of river sediment (see figure 6). During all autumn deployments, there was an absence of finer sediment and larger stones and pebbles remained. Sediment was also removed from site 1, albeit not to the same severity. Given that Mill Race Stream is a much smaller, shallower waterway, it is to be expected that it will have less power for the removal of sediment.

6.2 - Water sample data

Water samples have been separated into two categories (summer and autumn) and are displayed as box and whisker plots in figures 13-16, with each plot inserted onto the map of sample sites in order to illustrate the location of each sample set. The sample size for all box and whisker plots is 6 (2 water samples per site per deployment). The exception the site 1, which only contains 4 summer samples as MRS was dry above ground during one deployment.

Trace metal concentrations within waters around Wemyys mine follow a similar trend in most cases, decreasing in concentration during the autumn compared to summer. There are, however, some instances where this change is not observed. The highest concentrations measured throughout sampling are for Zn and Pb, which is expected given they are the main metals that were processed at this site. Of these two metals, Zn is present in the highest concentration (maximum concentration of 8526µg/L compared to 5864µg/L of Pb). The main metal exploited during operations was Pb, meaning Zn was often disregarded and dumped with the rest of the tailings (Bearcock *et al*., 2010). As a result, there will be more Zn present in the tailings for weathering and mobilisation.

Figure 13. Changes in Mn concentration within river water during summer and autumn at Wemyss Mine. Concentrations all in µg/L

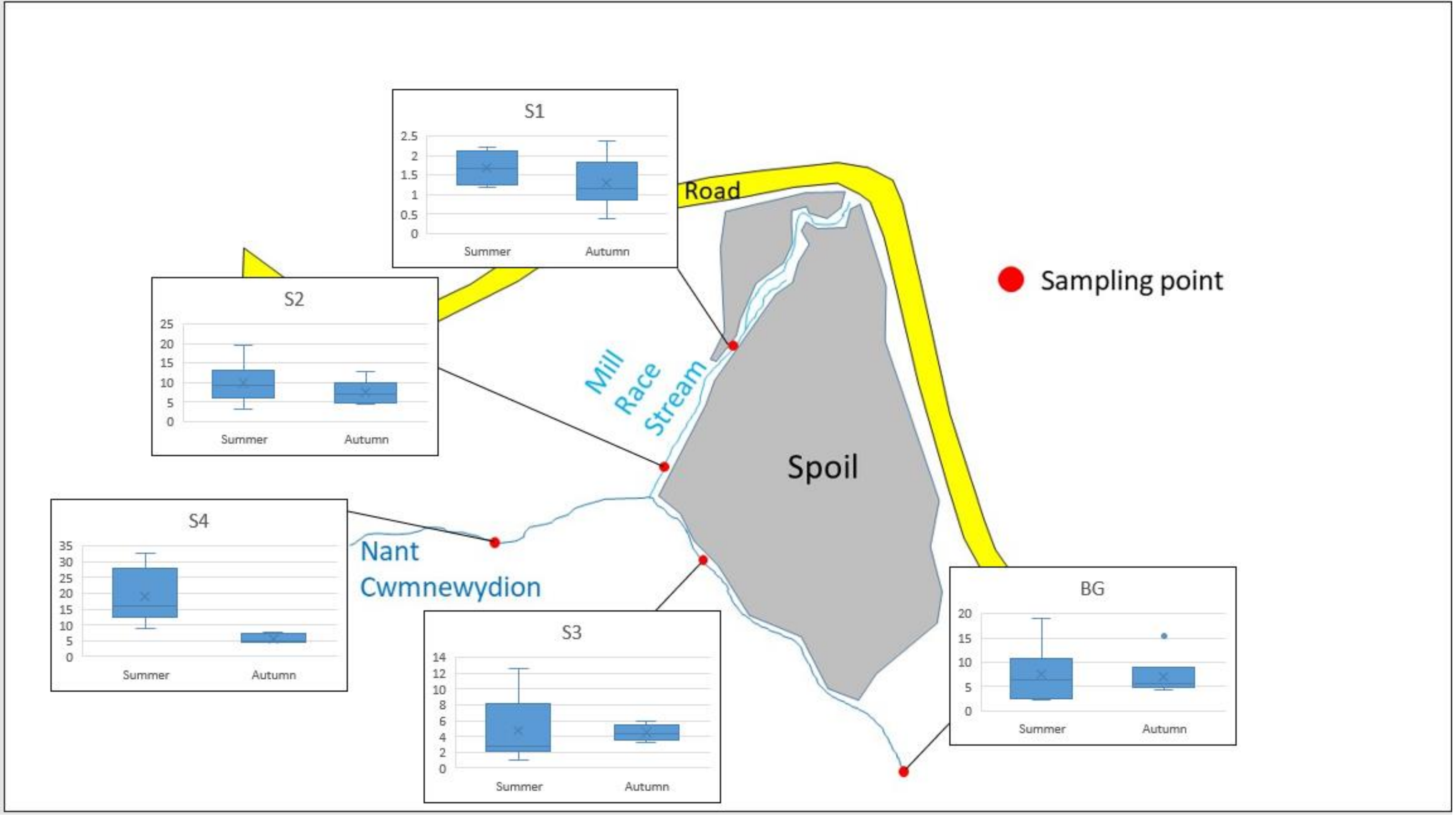


Figure 14. Changes in Fe concentration within river water during summer and autumn at Wemyss Mine. Concentrations all in µg/L

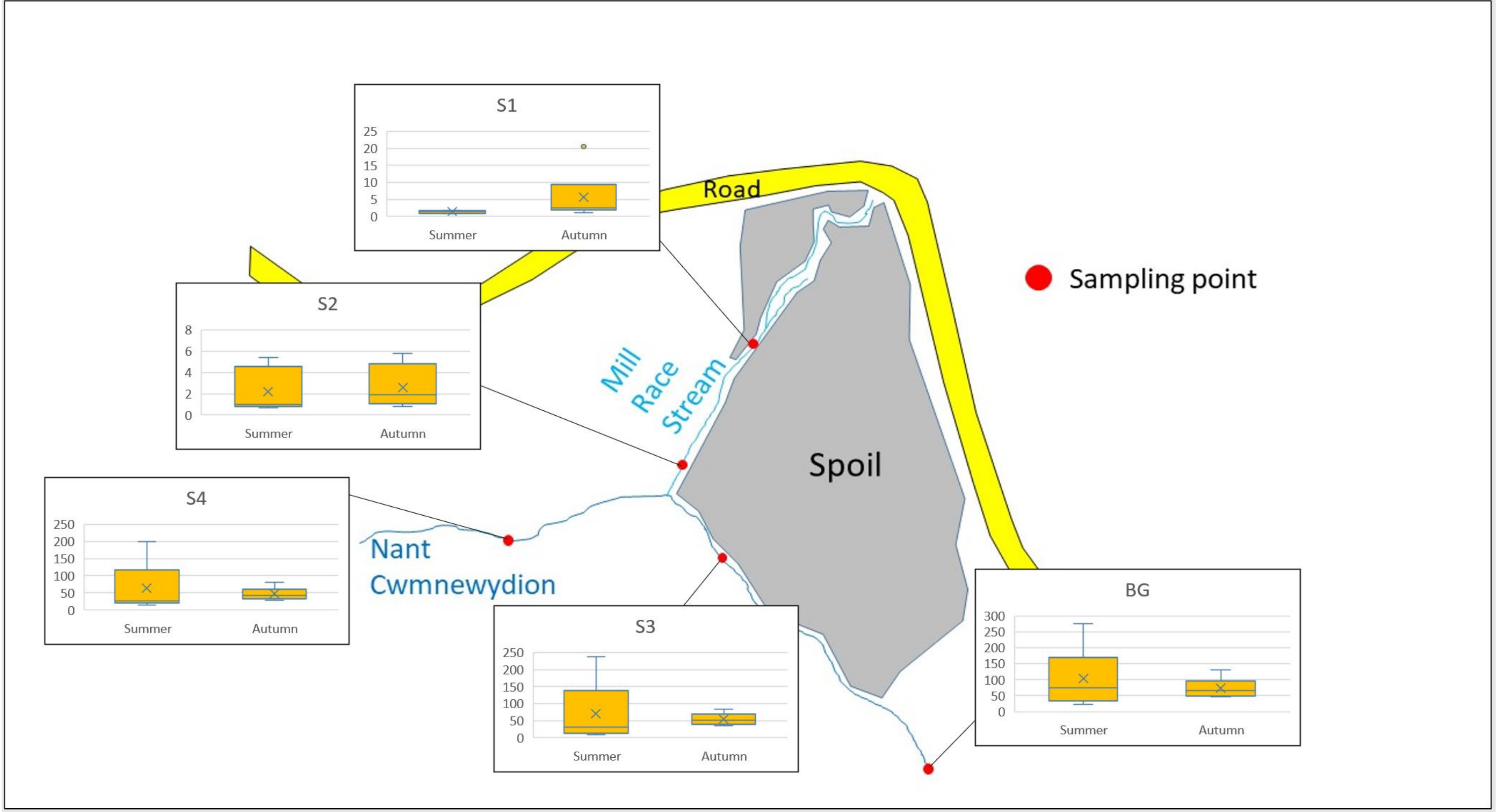


Figure 15. Changes in Zn concentration within river water during summer and autumn at Wemyss Mine. Concentrations all in µg/L

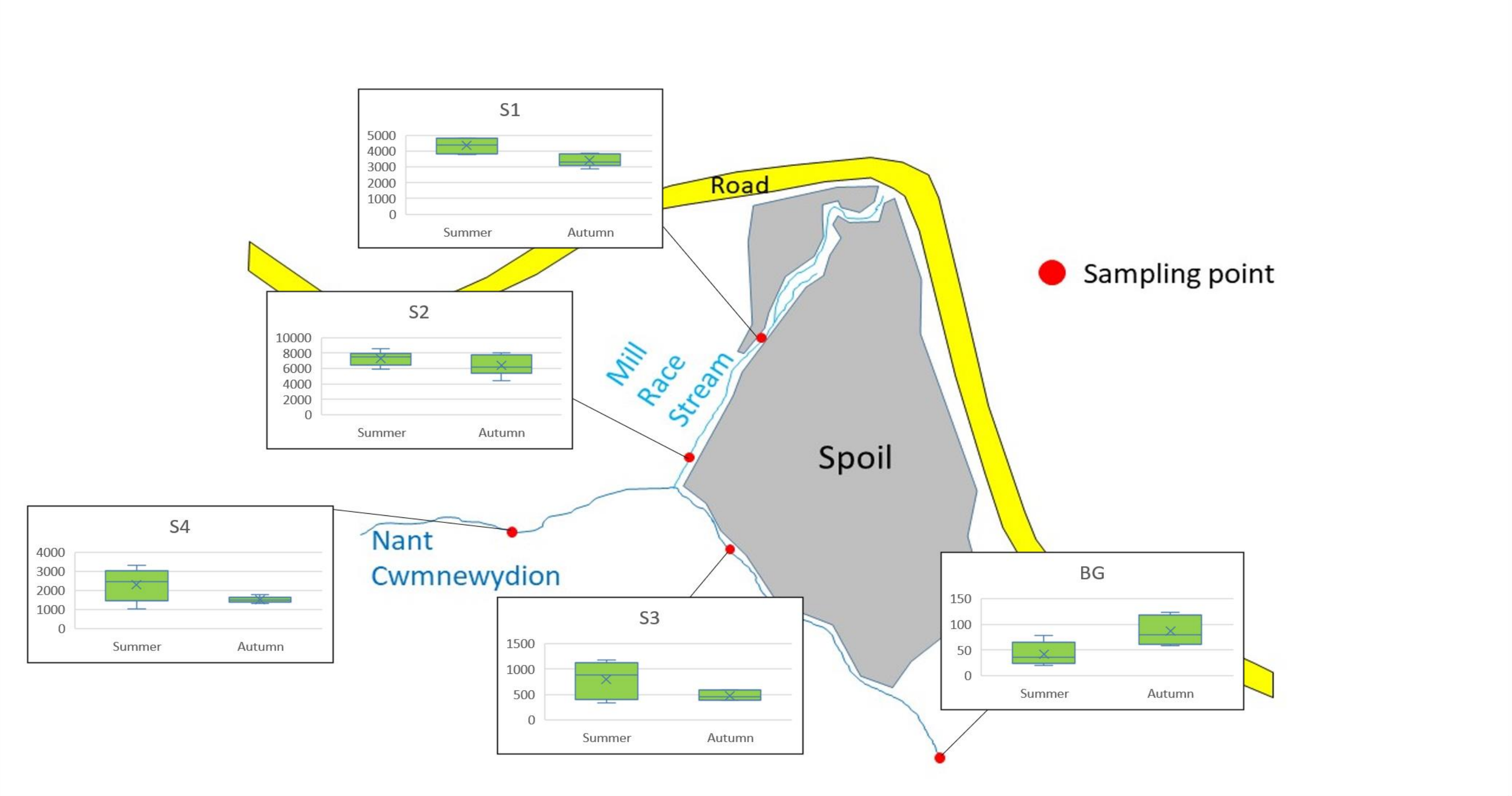
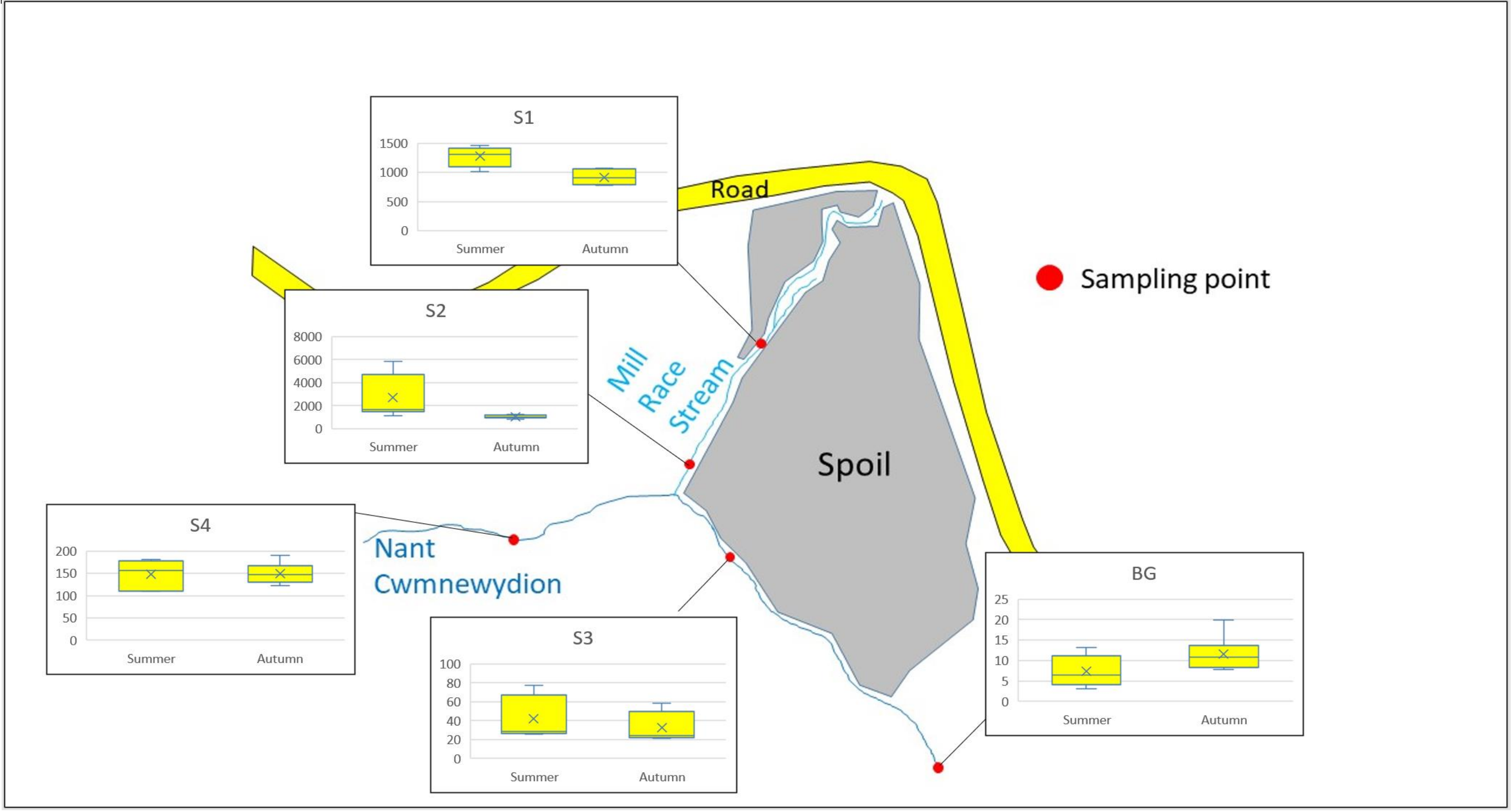


Figure 16. Changes in Pb concentration within river water during summer and autumn at Wemyss Mine. Concentrations all in µg/L



6.2.1 - Background site

The background site (BG) contains some of the lowest concentrations of contaminants measured within the river water. Manganese and iron concentrations are below 10µg/L and 300µg/L respectively in both summer and autumn. Threshold EQS values in water for Mn and Fe are 7 and 1000µg/L, respectively (Environment Agency, 2012). Concentrations of both of these metals do not decrease significantly between the two seasons. Average Mn concentration is 7.5µg/L in the summer, compared to 7.1µg/L in autumn. Iron shows a slightly greater decrease, starting at an average of 103.2µg/L in summer, decreasing to 73.5µg/L in autumn. Zinc and Pb follow different trends here that are not observed at most of the deployment sites. During the autumn, there is an increase in the concentrations nearly three-fold for both of these trace metals within the water at BG. Average Zn concentration in the summer is 42.4µg/L, increasing to 123.7µg/L in autumn. Lead concentrations increase from an average of 7.3µg/L in summer to 19.9µg/L in autumn. All Zn and Pb concentrations are far above the EQS values of 7.8µg/L and 7.2µg/L respectively.

The deployment site in question sits further upstream and remains unaffected by mine-related contamination. The sample site is within a point along the river where flow is reduced and the water sits within a pooled area. As a result, conditions at BG will not be affected by seasonal variability in river flow in the same way as other sample sites. The reduced flow conditions would allow for less sediment disturbance and oxidation during the summer, meaning reducing conditions may take over. As such, less Fe and Mn would be present within oxides and Zn and Pb would be more commonly bound to sulphides, making them more stable. The channel material around this area consists mostly of exposed bedrock material, which contains large amounts of sphalerite and galena (Merrington and Alloway, 1994; Bearcock *et al*., 2010; Palumbo-Roe *et al*., 2013). Therefore, most of the major contaminants (i.e. Zn and Pb) will be stable under reducing conditions within this material.

Higher flow and water level towards autumn will have a diluting effect, which is seen in the decreasing Mn and Fe concentrations. However, Zn and Pb concentrations rise during this time. Increased flow rate and channel topography make conditions more turbulent. The greater velocity of the water will allow for more mixing of O_2 between the water and sediment, as well as a higher potential for the erosion of the channel material. Weathering of the bedrock will expose it to oxidative conditions, allowing the Zn and Pb bound to sulphide minerals to be released, increasing their concentrations within waters at this site.

6.2.2 - Mill Race Stream

Sample sites 1 and 2 are both positioned along MRS, which flows into the NC shortly after S2. The stream here has already been in contact with mine waste to the north of the road shown in figures 13-16 and continues through the main spoil heap here. As such, concentrations of Zn and Pb are among the highest measured across all sites, yet Mn and Fe concentrations are at some of their lowest concentrations.

Three of the contaminants of interest (Mn, Zn and Pb) all follow the same pattern at both sites 1 and 2, with concentrations within the stream water decreasing in autumn. Manganese concentrations are only marginally lower in the autumn (1.3µg/L average) compared to summer (1.7µg/L average) at S1. Zinc and lead are present in the river water here in much higher concentrations. Average summer concentrations are 4354µg/L for Zn and 1273µg/L for Pb. Average autumn concentrations see reductions to 3395µg/L and 918µg/L respectively. Iron concentrations do not follow this trend. Instead, the average Fe concentration in the water during summer is 1.4µg/L and increases to 5.7µg/L in autumn.

Site 2 is responsible for the highest recorded concentrations of Zn and Pb. Average summer Zn concentrations are 7310µg/L, which decreases to 6384µg/L in autumn. Lead concentrations see a similar decrease between summer and autumn, with an average of 2704µg/L in summer dropping to 1044µg/L in autumn. Compared to S1, Mn concentrations towards S2 see an increase of near six fold. Average Mn concentration are 9.9µg/L and 7.5µg/L in summer and autumn respectively. Once again, Fe concentrations do not adhere to the same trend, with an average of 2.2µg/L in summer, increasing to 2.6µg/L in autumn.

Under the drier summer conditions, more spoil and sediment is exposed to the atmosphere, increasing oxidation. As a result, metal speciation will be altered, allowing for a change in where they are bound. At circum-neutral pH ranges, Pb has been found to have a greater sorption to Fe oxides (Wang *et* al., 2010). Given the low concentrations of Fe and Mn measured, it is likely that there is another factor responsible for the changes in the levels of dissolved Zn and Pb. Zinc has also been reported to be more mobile than Pb under oxic conditions (Merrington and Alloway, 1994), which may explain its greater concentration within MRS.

The presence of anglesite ($PbSO_4$) has been highlighted within the tailings associated with Wemyss mine (Palumbo-Roe *et al.*, 2013). It is a secondary form of PbS present at many mine sites, especially within the surface of tailings (Hemphill *et al.*, 1991; Roussel *et al.*, 2000; Palumbo-Roe *et al.*, 2013; Lynch *et al.*, 2014). Sulphide oxidation as a result of decreasing flow and rainfall, may enable the formation of sulphates here (Peltier *et al.*, 2005; Du Laing *et al.*, 2009; Zhang *et al.*, 2014). Consequently, metals would be released into the water. Under oxidising conditions, it has been noted that anglesite may act as a solubility control for Pb (Palumbo-Roe *et al.*, 2013), which may account for its lower concentration compared to Zn within the waters at Wemyss mine.

As conditions become wetter, the increased volume of water will play a role in altering the dissolved metal concentrations. As the volume of water increases, the contaminants present will become more diluted, resulting in a lower measured concentration. Although this process alone will not account for the lower concentrations measured. With increasing water level, sediment will become more submerged, and less exposed to atmospheric conditions. The resulting effect is a depletion of available oxygen, causing the conditions to become more anoxic. Initially, the oxides present (such as Fe-Mn oxides) will begin to be reduced, releasing any trace metals bound to them. With depleting oxygen, sulphides are likely to form, providing a suitable binding site for the newly available metals. The autumn deployments all took place after periods of already increased rainfall and river flow. As conditions within the sediment remain saturated, reduction is promoted, leading to the formation of sulphides (Simpson *et al.*, 1998; Peltier *et al.*, 2005; Du Laing *et al.*, 2009).

6.2.3 - Nant Cwmnewydion

Site 3 is the first sampling point showing metal concentrations within the Nant Cwmnewydion after the water begins to encounter material from Wemyss mine, providing an insight into the input that the mine waste is having on the river. Iron and Mn concentrations see a decrease at this point, whilst the main contaminants of Zn and Pb increase greatly. Summer Mn and Fe concentrations are 4.7µg/L and 71.5µg/L respectively. Autumn concentrations decrease to 4.5µg/L for Mn and 54.8µg/L for Fe. Zinc and Pb concentrations are 798.5µg/L and 41.9µg/L in the summer respectively. In the autumn, Zn concentration decreases to 475.5µg/L, whilst Pb is reduced to 32.9µg/L.

Site 4 is positioned further along the Nant Cwmnewydion, past the mine workings. This positioning provides useful data on how the convergence of the two streams has affected contaminant levels within the water. It also helps to assess the fate of the contaminated river water and any sediments that may find their way downstream. Trace metal concentrations at this site in the summer are 19µg/L Mn, 63µg/L Fe, 2306.8µg/L Zn and 148.6µg/L Pb. Autumn concentrations for Mn, Fe and Zn all decrease to 5.7µg/L, 47.5µg/L and 1513.7µg/L respectively, while Pb increase marginally to 149.7µg/L.

Once the NC begins to flow through the mine site, the sediment characteristics within the channel change. Particles consist more of previously worked spoil, which has now found its way into the channel. The spoil makes up the river bank material on the north side of S3, and some evidence of erosion is present (see figure A1), providing one pathway for the mine waste to enter the channel. Spoil material makes up all of the bank and bed material at S1 and S2, as MRS flows through the main heap. Trace metals within the spoil material, which now makes up the river sediment will be dissolved into the water, increasing the concentrations measured.

The lower overall concentrations of Zn and Pb within the NC compared to MRS can be explained by the difference in channel characteristics between the two. The river water at S3 has had less time to be in contact with the mine workings, resulting in less dissolution of contaminants. As well as this, the channel here is larger than MRS and contains more water, meaning that any contaminants present may have been diluted to a greater degree. The dilution of trace metals within the water also explains the reduction in Mn and Fe concentrations compared to BG. As made evident in concentrations at MRS, there are low levels of Mn and Fe in the water flowing through the spoil already. Coupled with some small tributaries and runoff between BG and S3, there is an increased amount of fresh water present.

It is clear that Wemyss mine has an effect on the overall Mn concentrations found to be draining the site. In the summer, the average Mn concentration at S4 is the highest of all the sites that have been sampled. Given the increased oxidation that the sediment at Wemyss mine will have undergone, there is likely to be a greater presence of oxides (including Mn) present. As the water leaves the site via the NC, any sediment that settles around the area of S4 will remain submerged, becoming subjected to reduction. As a result, Mn will be released, increasing the concentration measured.

Iron concentrations at S4 do not show a very marked change from those measured along NC, having only decreased by roughly 8µg/L after S3 in both summer and autumn. Since MRS does not provide a large input of Fe into the NC, it is clear that it has not had much effect on altering the river water concentration. The inputs of this particular trace metal have not had an effect on the larger river system. The relatively negligible change in Fe concentration also provides an indicator that it is not a major pollutant from Wemyss mine. This is not to say that Fe and Mn oxides do not have an influence on the release and adsorption of Zn trace metals. Their presence still shows that they may be present, albeit not having a large influence.

The concentrations of Zn and Pb measured at S4 are up to 3 and 5 times higher than those measured at S3. The main input of these contaminants between these two points comes from MRS, serving as an indication of the influence that MRS has on the contamination of the larger river system. It is worth noting that concentrations of Zn and Pb at S4 are up to 3 and 20 times lower than the highest recordings at S2 respectively. Given that there is sediment build up at S4 that remains somewhat submerged in all deployments, it is likely that conditions within the pore waters is more anoxic. Throughout the summer, oxides and sulphates that find their way to being deposited at this point will be depleted of their oxygen, releasing the Zn and Pb bound to them. As rainfall increases towards the autumn, reducing conditions will continue, promoting the formation of sulphides, which trace metals will bind to. As a result, the concentrations dissolved within the river water will decrease.

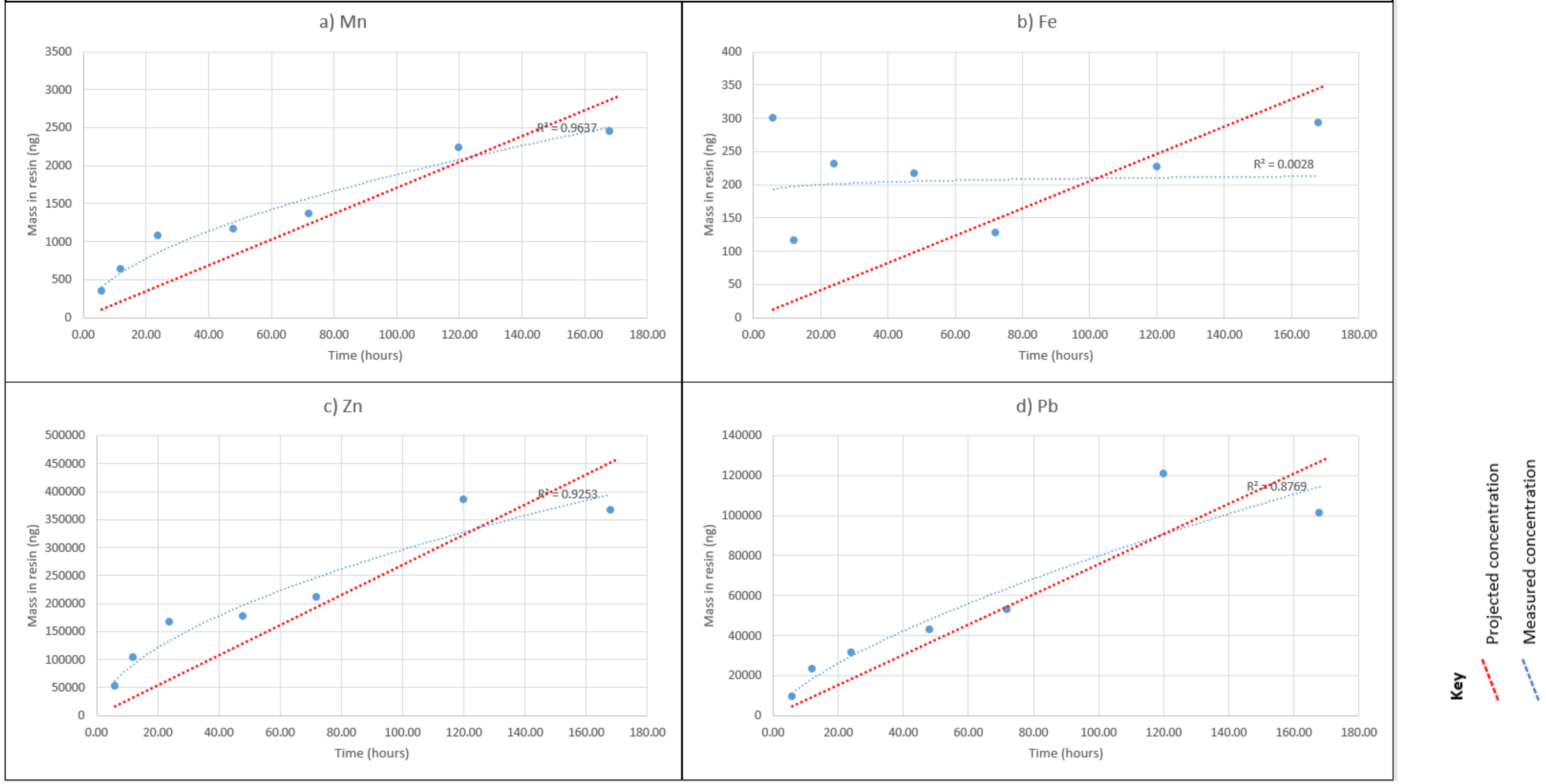
Some minor turbulence within the NC prior to S4 will promote oxidation within the water and upmost sediment, meaning that the concentrations at S4 may not be influenced by reducing conditions in the sediment alone. It is probable, with increased river flow, that more dilution is also occurring. This would lead to the lower concentrations of Zn and Pb measured when compared to S2, which provides such a large input of these metals.

6.3 - DGT metal uptake test

Metal concentrations measured using DGT assume a perfect sink, linear uptake over time to the probes (Davison, 2016). By performing a metal uptake test it is possible to assess if the deployment time used was acceptable, with no saturation of analytes or low binding of cations. Additionally, any deviation from the linear assumption of mass accumulation can be identified. Mass accumulation within the Chelex resin in DGT probes over the course of 1 week is shown in figure 17 (below), with and additional trendline (red) used to illustrate the hypothesised trendline under a perfect sink scenario. The DGT uptake curves for each analyte within sediment from Wemyss mine do not follow the exact linear trends that are assumed for calculating cDGT values. However, Mn, Zn and Pb all show strong positive correlations for metal uptake. In the case of these metals, mass uptake within the first 24 hours is relatively quick, indicating an immediate supply from the sediment and that a diffusive gradient has been quickly established. As time increases, the uptake begins to plateau, most likely as metal resupply to the area surrounding the probes is slowed. In the field, there is more resupply of trace metals available as the water is running and more material is present. Therefore, it is likely that the mass uptake is greater. As the metals within the resin did not reach a point whereby there was no more increase, it can be assumed that the 1-week deployment time was sufficient and the probes would not become saturated.

Unfortunately, Fe does not show any correlation across the experiment. This may be due to competition from other metals within the sediment, as Fe is not always present in a bioavailable form under the conditions that this spoil has been subjected to. The test sediment is under more anoxic conditions, meaning there will be more reducing conditions and the pH of the material and water is more neutral (pH5-7). Therefore, the conditions for increased Fe mobility and bioavailability are not met.

Figure 17. Mass accumulation (ng) of Mn (a), Fe (b), Zn (c) and Pb (d) within the resin layer of DGT probes over a 1-week deployment in sediment collected from Wemyss mine. An additional trend line is inserted to illustrate the perfect sink uptake assumption.



6.4 - DGT data

The data in figures 18-22 show the concentrations of labile metals present within the sediment pore waters of the river bed around Wemyss mine. Variations in the chemical speciation of minerals at Wemyss mine will play a role in the availability of metals present, and therefore how much they can be bound to the Chelex resin within the DGT devices. Therefore, seasonal variability in rainfall and river flow will influence the concentrations.

During the dry summer period in 2018, deployments 1 and 2 provided the lowest DGT measured concentrations (cDGT) for all contaminants. The effects of the lengthy dry period in which these deployments took place (see figure 12) are seen by the low concentrations of contaminants measured during this time. The sediment at this site consists of material that has likely been eroded from the exposed host rock and deposited at this location, where flow rate decreases. Given the low flow rate already in effect at this time, the sediment will have been settled and submerged for a long time. It is therefore plausible that reducing conditions could have become established (Du Laing *et al*., 2009; Wragg and Palumbo-Roe, 2011). As a result, stable sulphides will be more common and provide suitable binding sites for trace metals.

The remaining summer deployment (2019) took place following a short, increased flow event. Given the lack of data prior to this event, it can only be assumed that conditions were similar to the previous year, with low pore water concentrations still present. Following this assumption, the data for D4 provides an example of the effects of a sudden increase in river flow. Higher velocity of the water eroding the exposed host rock and disturbing the sediment at BG will aid in the oxygenation of the water around the sediment. The introduction of oxygen will facilitate the release of metals bound to sulphides.

Figure 18. DGT measured metal concentrations (µg/L) throughout deployments at the background site

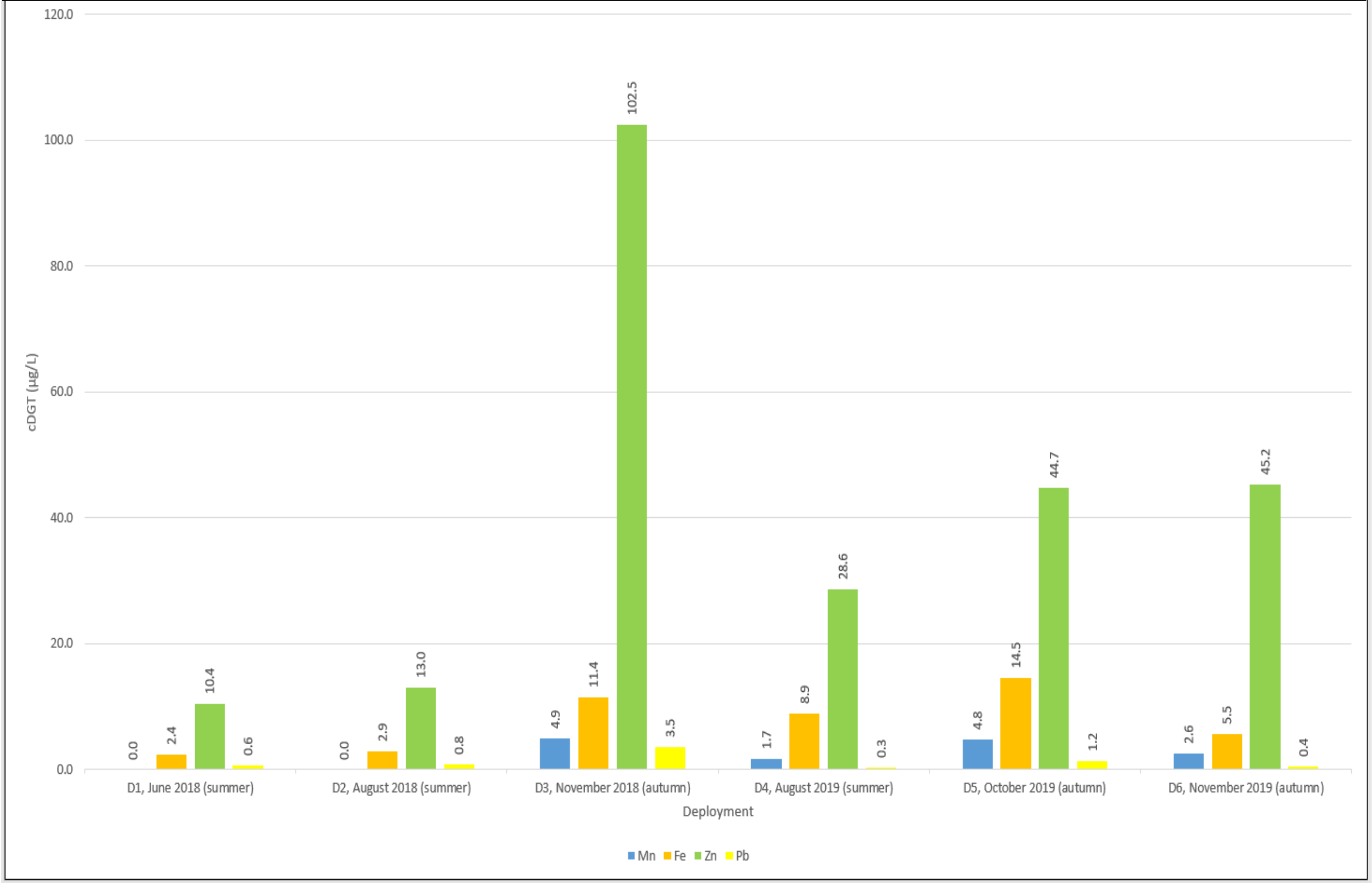


Figure 19. DGT measured metal concentrations (µg/L) throughout deployments at site 1

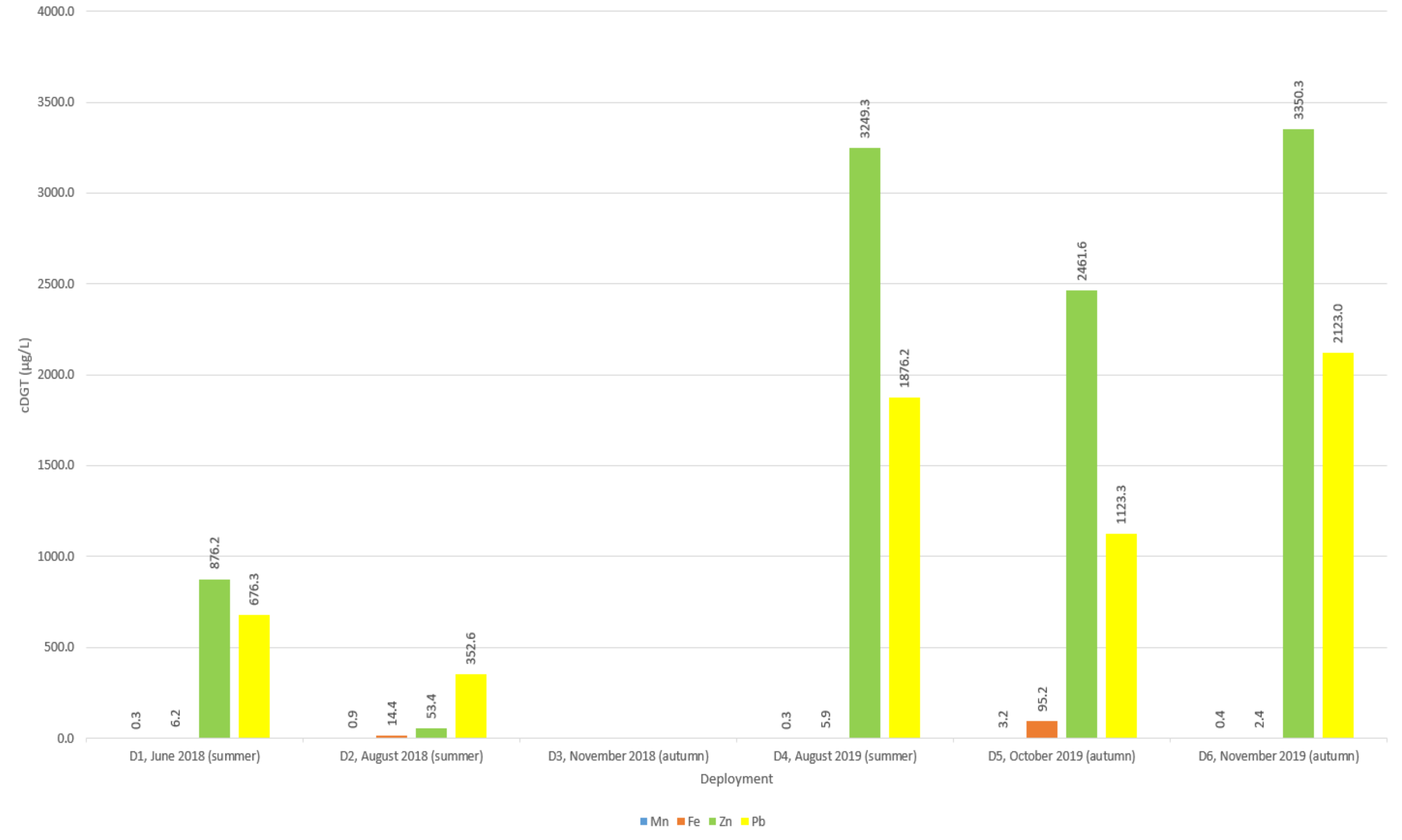


Figure 20. DGT measured metal concentrations (µg/L) throughout deployments at site 2

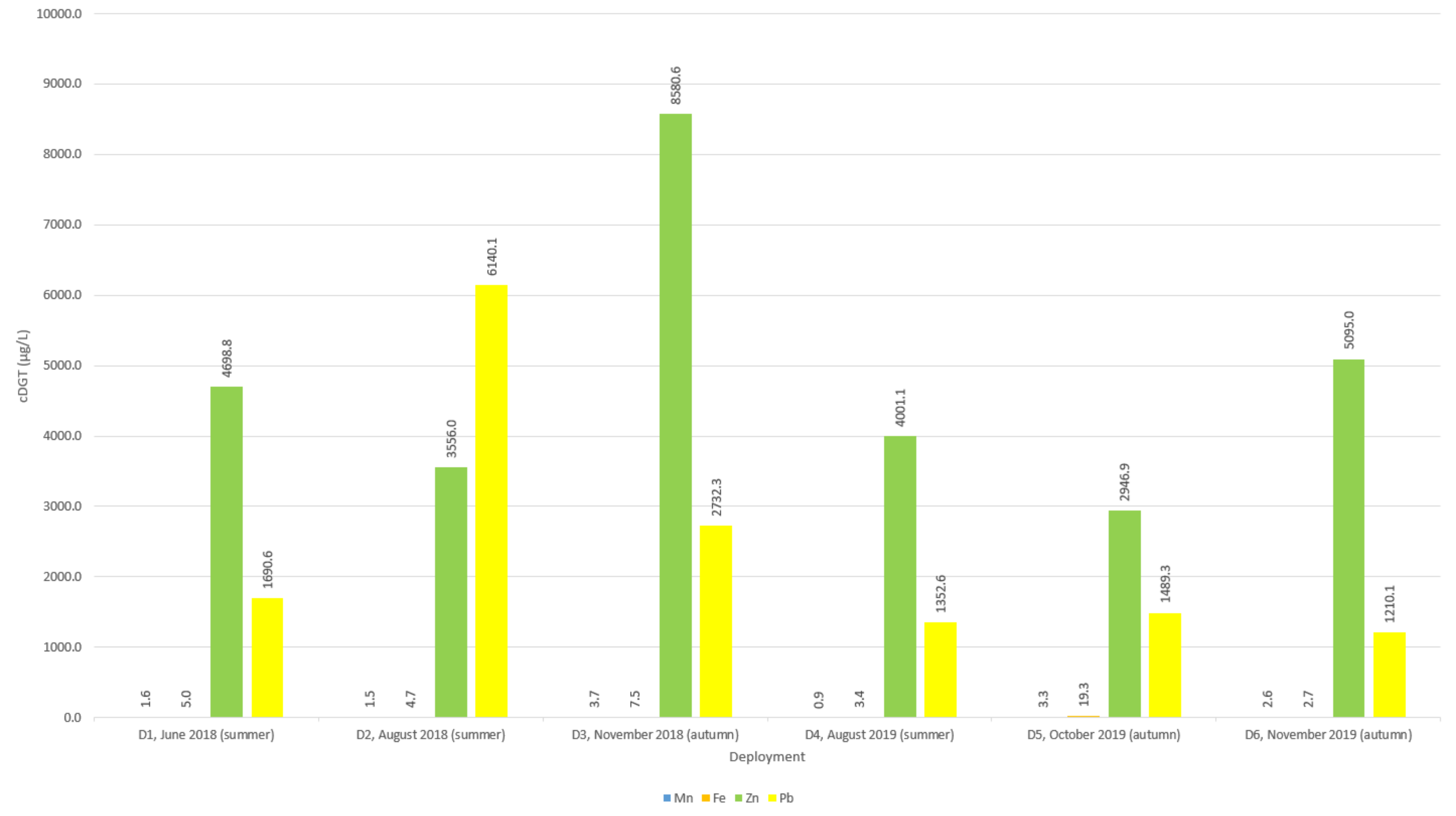
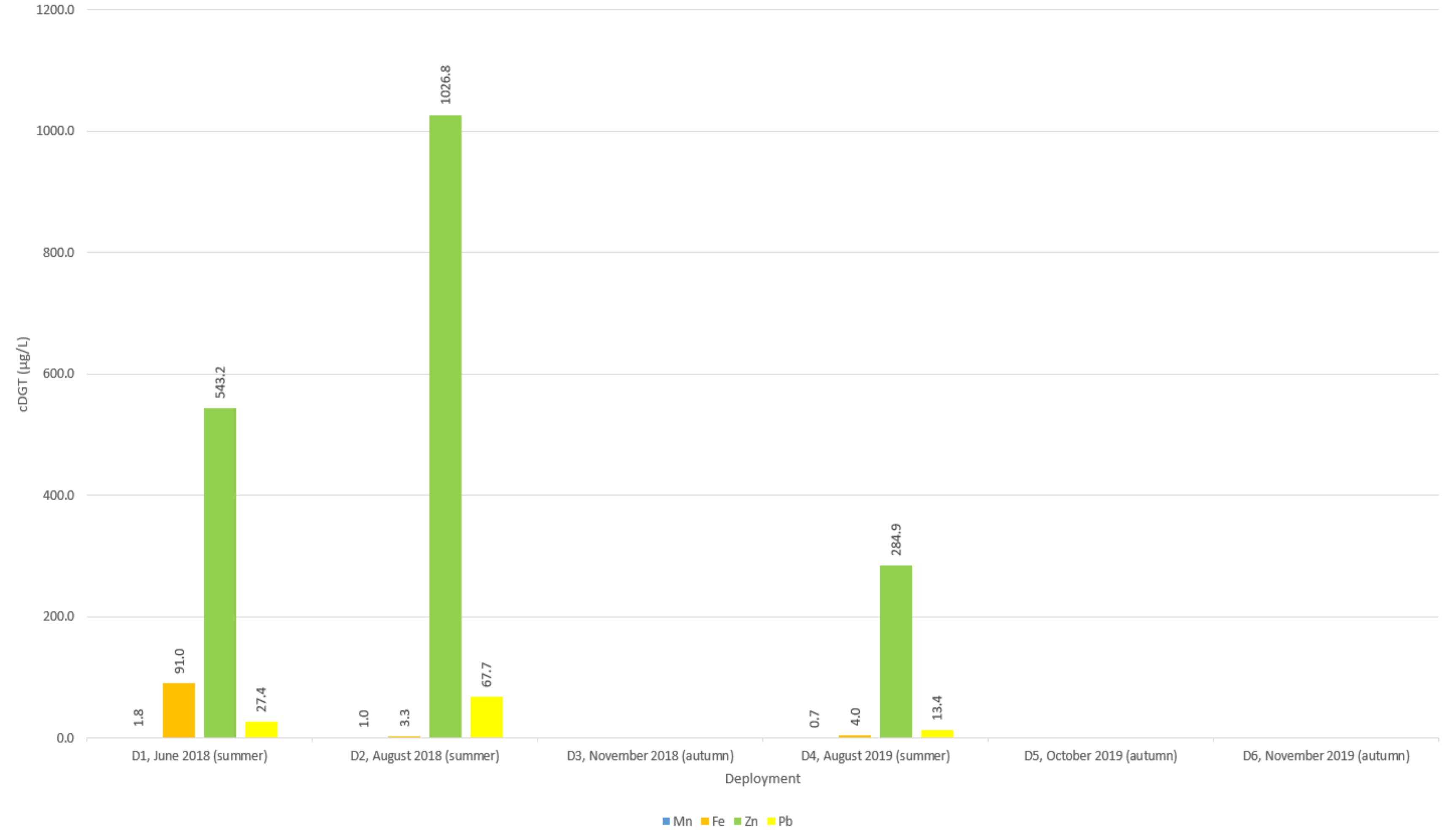


Figure 21. DGT measured metal concentrations (µg/L) throughout deployments at site 3



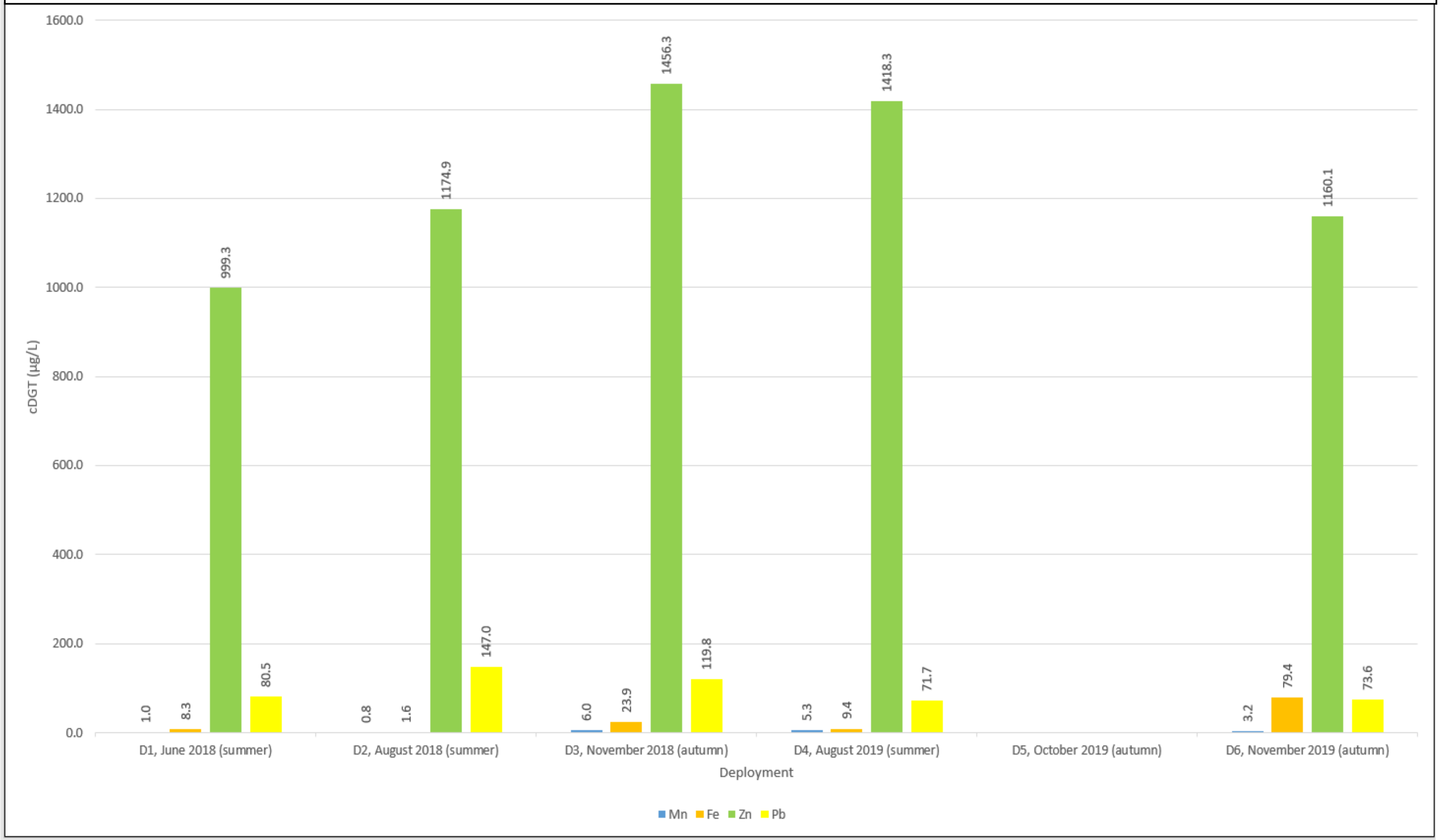


Figure 22. DGT measured metal concentrations (µg/L) throughout deployments at site 4

Moving towards autumn, as rainfall becomes more common and river flow increases, cDGT for all metals increases. This is not in accordance with the assumption that an increase in rainfall would result in more dilution of trace metals. As previously discussed, the greater turbulence and erosive capabilities of the river during this period may result in erosion of the exposed bedrock, which is known to contain PbS and ZnS (Palumbo-Roe *et al*., 2009; Bearcock *et al*., 2010). The exposure of these minerals to the more oxidative environment will lead to a release in metals bound to them. This is certainly the case for Zn, which represents the highest portion of the bioavailable metals analysed. All cDGT values for Zn exceed the EQS value of 7.8µg/L (EA, 2012). Of the metals chosen for analysis, Zn is reported as one of the more mobile metals, particularly under oxic conditions (Lynch *et al*., 2017; Xie *et al*., 2019). Therefore, increased Zn concentrations are likely under the conditions observed during this period. Manganese concentration does increase relatively sharply too. Given its affinity to form organic complexes (Das *et al*., 2011; Mongin *et al*., 2013) it is no surprise that it readily binds to the DGT devices. The increased amount of water within the channel and over the sediment may have also provided more water into the sediment pores, enabling the probes to establish a better concentration gradient.

Since DGT is designed to accumulate metals in the dissolved, bioavailable fraction, it can be assumed that the sediment pore water at BG does not contain a great amount of Pb in this form. The cDGT of Pb for this site was below 1µg/L during summer and did not exceed 4µg/L during autumn. With the exception of Mn during D1 and D2, Pb was observed to be the lowest bioavailable metal at this site. The most likely cause for this is the presence of galena within the host rock. Galena has a low bioaccessibility, meaning less would be available for binding to the Chelex resin within the DGT probes. Furthermore, the more anoxic conditions within this site will have promoted reducing conditions, meaning there is a greater occurrence of sulphides, which will be responsible for increasing the stability of Pb (Wragg and Palumbo-Roe, 2011; Palumbo-Roe *et al*., 2013; Lynch *et al*., 2018).

Downstream, at S3, we see the effect that Wemyss mine has on the labile metal concentrations within sediment of the NC. During the summer, Mn concentrations see a negligible increase (less than 2µg/L at most) between BG and S3, but Zn and Pb see large increases. At its highest, Zn increases 79-fold and Pb 87-fold. Both of these instances are during D2, when the site has undergone a lengthy dry period. The resulting low river flow led to a large amount of sediment build-up within NC at this point. As the sediment consists of mostly spoil material, the large increases in Zn and Pb concentrations are of no surprise. Since the material has already been worked and subjected to local environmental conditions for 100 years, the metals within it will not be as stable as those in the parent material (such as at BG). Low water level and atmospheric exposure of sediment will also pave the way for the oxidation of sulphides. Newly released metals will be more mobile and labile, resulting in the higher cDGT values in comparison to BG upstream.

It is vital to note the absence of some data for the autumn deployments. Due to the seasonal nature of sediment presence within the channel at this location (figure 6), there was not a suitable deployment medium for the DGT drivepoints. As a result, no deployment could be made and result were not obtained. This occurrence is not unique to S3, missing data at S1 was also due to the same lack of sediment. Further effects on the DGT data as a results of channel variations were during deployment 5 at S1 and S4. During this deployment, both drivepoints were dislodged from the sediment and washed downstream. While the device at S1 was recovered and data could be obtained, it does not accurately represent metal flux into the probe from sediment pore water for the duration of the deployment. Unfortunately, it is not possible to determine the time of removal from the sediment, meaning equations were carried out as normal, assuming recent removal and constant submergence within the stream water. The probe and drivepoint from S4 could not be recovered at all.

Sites 1 and 2 show similar trends to those found in the stream water, with generally higher cDGT values downstream at S2 compared to S1 (except for Fe, which decreases downstream). During the dry summer of 2018, bioavailable Zn decreases with time at both S1 and S2. The oxic conditions created during this time promote the binding of such metals to Fe and Mn oxides, as well as the precipitation of sulphates. As a result, they will not be as available to biota until they are dissolved.

At S1, sediment during D2 became increasingly dry, as flow ceased in the upper section of MRS. Therefore, it is likely that there was not sufficient enough water within the sediment to maintain a resupply of metals to the probe. The low cDGT values measured here are likely due to this occurrence.

The effects of dissolution after prolonged oxidating conditions is seen in D4, which took place shortly after a summer flushing event. This event yielded much higher cDGT values for Zn and Pb (3249 and 1876μg/L respectively) at S1, whereas cDGT at S2 was within the range of both summer samples from the previous year. Since S1 is capable of drying out completely, there is more likelihood for the precipitation of mineral salts within the sediment. Sudden wetting will cause these salts to dissolve and quickly enter the water (Grover *et al*., 2016; Lynch *et al*., 2018).

The higher mobility of Zn, coupled with the presence of anglesite (Palumbo-Roe *et al*., 2013) explains why more Zn is measured within the DGT probes compared to Pb. This trend is found in almost every deployment at all sites. However, at S2 during D2, Zn concentration decreased compared to D1 while Pb concentration rose. Prolonged oxidation of the channel sediment may have encouraged oxidation of Pb sulphides, allowing for the release of Pb, which in turn is dissolved within the pore waters.

During the autumn, when water present throughout MRS and the flow rate increased, S2 saw a large increase in Zn concentration for 2018, coupled with a decrease in Pb. Sparse periods of higher flow may have paved the way for some sediment deposition between them. As a result, there may have been time for reducing conditions to be established within the pore water. The increased flow prior to this deployment may have caused some disturbance and oxidation. The increased Zn mobility under these freshly oxic conditions may have enabled its dissolution into the pore water and increased bioavailability. Lead will not have been as readily mobilised, meaning the bioavailable concentration remained low. The following year, cDGT Zn increased as the wet period continued, while cDGT Pb decreased. As S2 remains wetted, oxygen may be depleted within the pore waters, allowing Pb to stabilise within sulphides. Rising water level and increased runoff may have driven the dissolution of more Zn.

Downstream, at S4, Zn dominates the bioavailable fraction of metals. Concentrations of Zn within the DGT probes here is 10 to 20 times higher than Pb. It is clear that chemical speciation within the NC sediment here favours the increasing mobility of Zn. Sediment transported this far will be oxidised and as it builds up, reduction will take over. The spoil already contains a great deal of Zn, so deposition and reduction will result in its release from oxides. The lower solubility of Pb in anglesite and its binding to sulphides will reduce its mobility here. Overall concentrations follow the same trend as the river water, higher than at S3 but lower than S2.

Site 4 is an area of accumulation for some of the transported sediment from sites 1, 2 and 3, meaning metal concentrations here will be influenced by those upstream. It is however, important to note that sediment suspension within the river water will promote oxidation. Meaning the material deposited is likely to consist of more oxides and sulphates. The reduction that follows after deposition and submergence will encourage release of contaminants bound to these minerals. Zinc is easily bound to these oxides and has a high mobility in oxic conditions, much like those at the surface of sediments here. As a result, it is likely to be more bioavailable and easily bound to the DGT probes.

In all instances of contamination for both river water and sediment pore water, the effects of sediment size should be considered. Changing hydrological conditions influence channel morphology. During the drier summer months, low flows encourage the deposition of finer sediment. Such material has a large surface area and increased cation exchange capacity (Zhang *et al*., 2014), leading to a greater availability of contaminants for dissolution. Rising water levels will submerge more of this fine sediment, increasing the quantities of contaminants dissolved in the river and pore waters.

With increasing river flow, particularly in autumn, sediment is suspended and transported downstream. The data obtained from DGT deployments shows that bioavailable Zn and Pb concentrations within this sediment are above EQS values, posing a huge risk to organisms within this system. Disturbance of this sediment will facilitate more mobilisation, releasing more contaminants into the environment. The eventual fate of all sediments is not known, but deposition like that observed at S4 will likely occur elsewhere. Submergence may result in the reductive dissolution of oxides and sulphates, releasing more metals into pore waters. As flooding and sudden increased river flows become common under future climate predictions, this cycle may continue, releasing metals here and throughout the system for years to come.

6.5 - Column experiment

Results from the mesocosm experiment show how metal concentrations within the pore waters of sediment from Wemyss mine may fluctuate under different hydrological conditions. Metal concentrations within the leachate water from each wetting regime showed different trends over time. Figures 23-25 (below) show the variations of these dissolved metals within the pore waters, with blue and red lines used to indicate wet and dry sediment respectively. Similar to concentrations in the field at S2, Zn remained the highest recorded trace metal, while the lowest was Fe.

Under saturated conditions, Mn, Zn and Pb all see reductions in leachate concentrations over the first 3 weeks, with a more pronounced decrease seen during week 2. After week 1, Zn concentration within the leachate is at its highest (26925µg/L). By the end of week 3, Zn has dropped to 14588µg/L. From this point, metal concentrations within the leachate trend upwards, although fluctuations are present. By the end of the saturated run, Mn and Zn have increased marginally from their starting values (436µg/L and 25915µg/L respectively during week 1; 445µg/L and 26478µg/L respectively after week 10). Lead, which initially had a concentration of 12523µg/L, dropped to 11657µg/L. Iron concentration at the end of the run was lower (43µg/L) compared to at the beginning (64µg/L), although this metal saw a sharp rise in concentration (increased to 285µg/L) over the same initial 3 week period compared to the other metals of interest. After this period, the concentration decreased rapidly to 54µg/L after week 4.

Figure 23. Average metal concentrations (µg/L) within leachate drained from mesocosms under a saturated regime. Mn (a), Fe (b), Zn (c) and Pb (d)

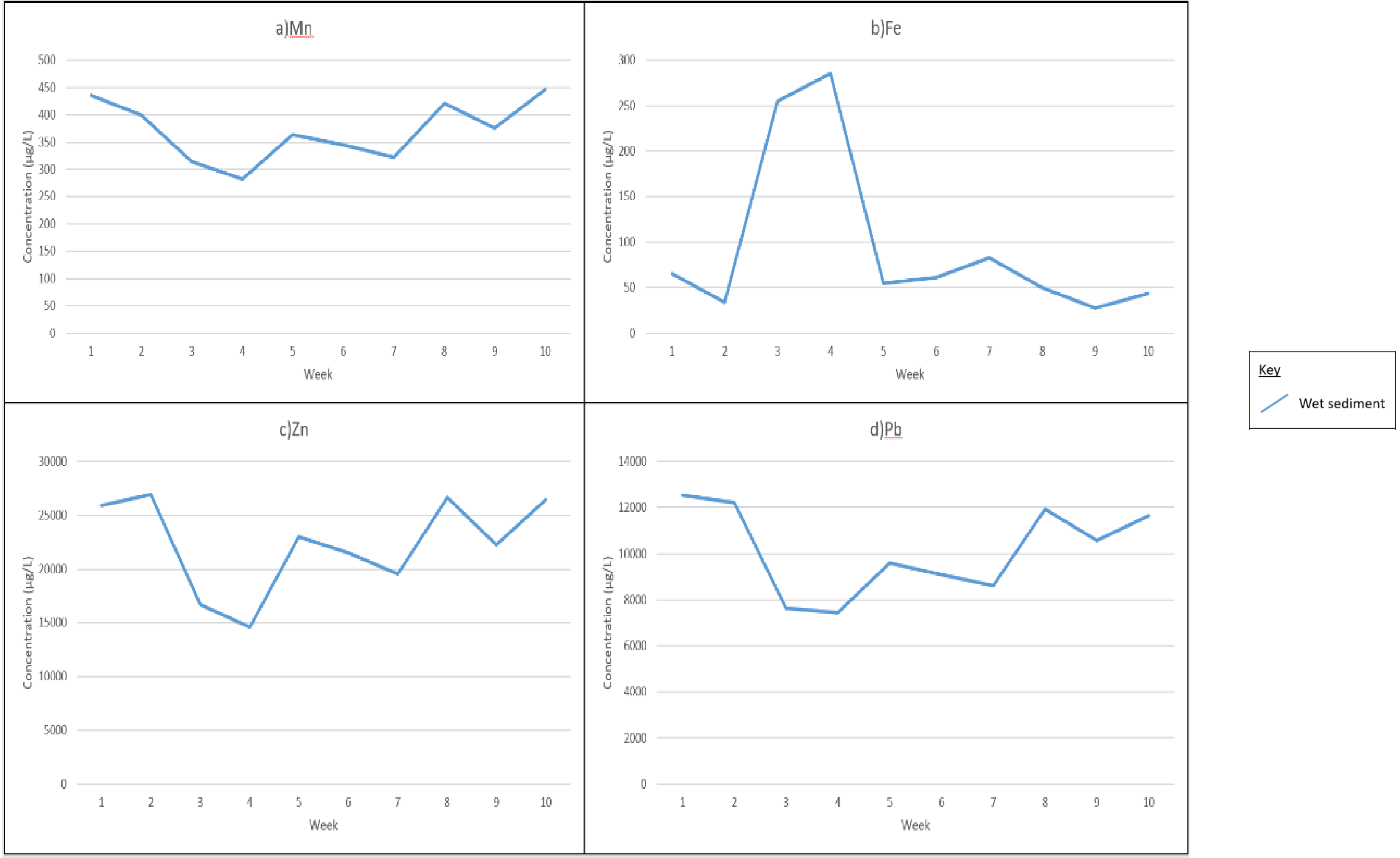


Figure 24. Average metal concentrations (µg/L) within leachate drained from mesocosms under a 1ww/1wd regime. Mn (a), Fe (b), Zn (c) and Pb (d)

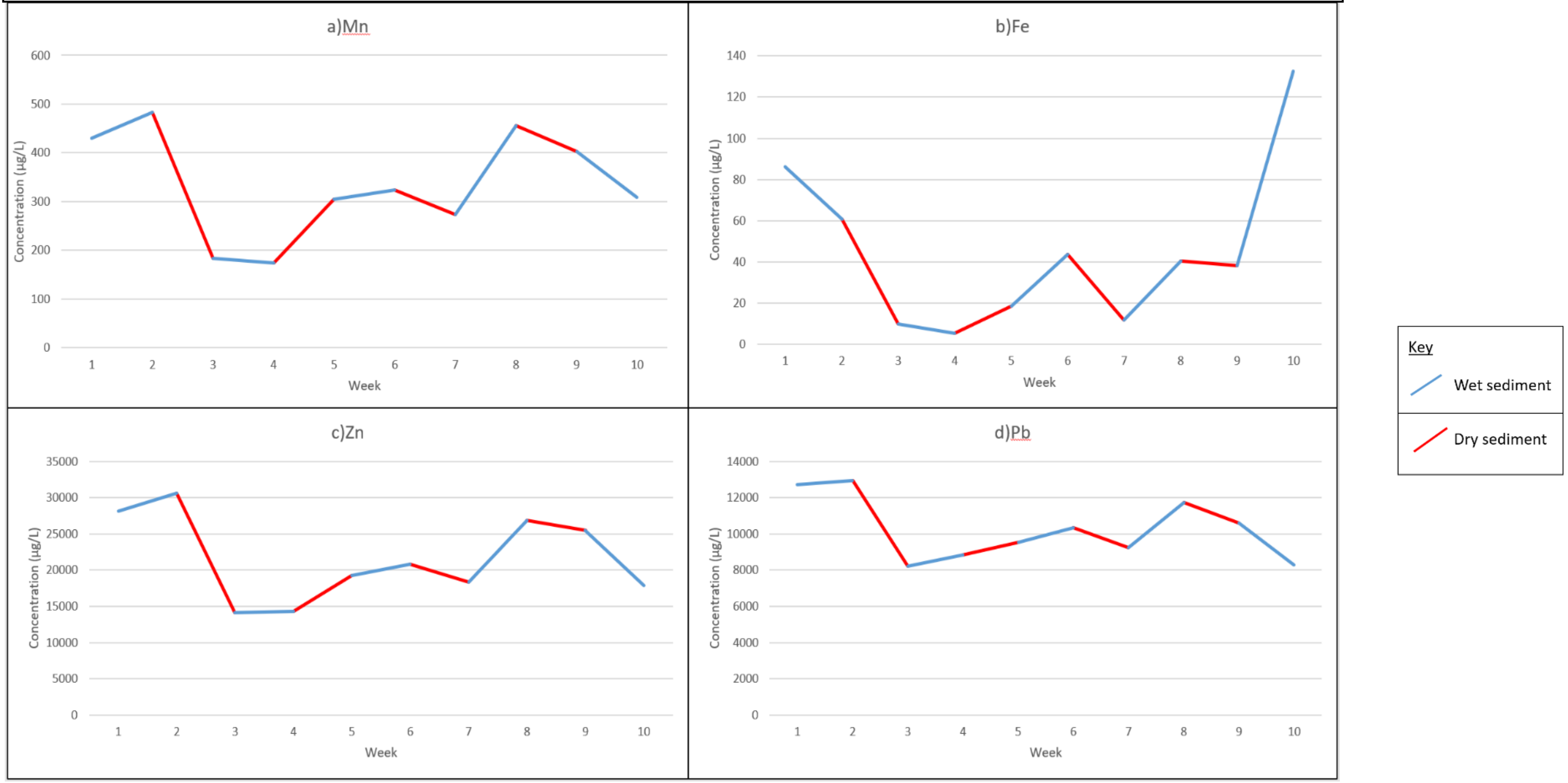
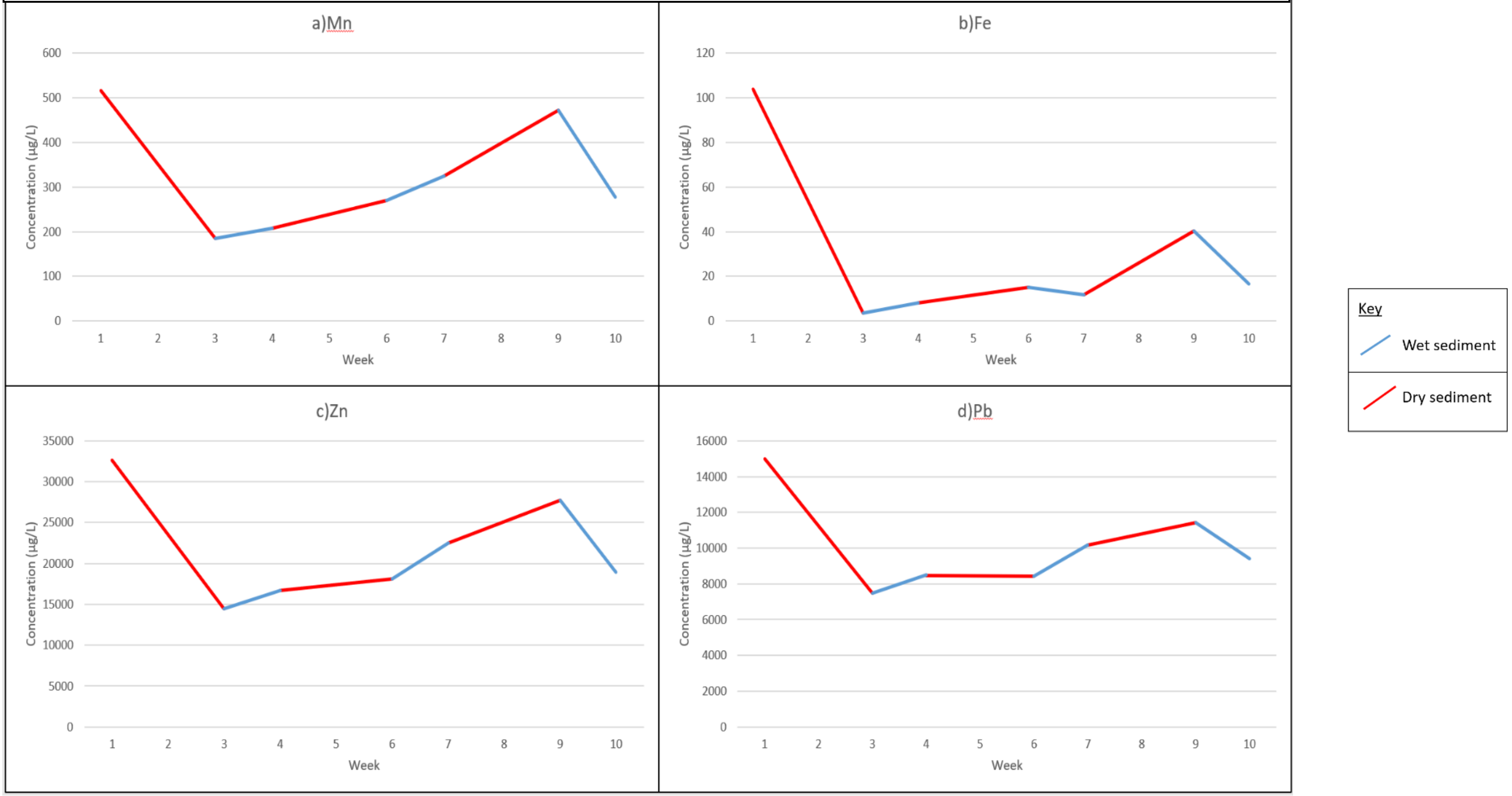


Figure 25. Average metal concentrations (µg/L) within leachate drained from mesocosms under a 2wd/1ww regime. Mn (a), Fe (b), Zn (c) and Pb (d)



Over the first 3 weeks of submergence, oxygen within the sediment will be depleted as conditions remain saturated. Reducing conditions will take over, causing mobile Zn and Pb to become bound to sulphides, leaving less dissolved within the pore waters. After this stage, metal concentrations within the leachate waters increase. As the sediment remains submerged, and more oxygen is depleted, oxides or sulphates present will also be reduced, releasing the metals that are bound to them. Reduction of Mn oxides as a control on Zn mobility under a flooded mesocosm regime has previously been suggested by Lynch *et al*. (2017). Given the low concentrations of Mn present in the leachate, there is likely to be other factors influencing the release of Zn. It is possible that Zn may become bound to sulphates which may remain under-saturated, allowing Zn to be continuously released (Lynch *et al*., 2017). Lead release is likely governed by the reduction of sulphates. Anglesite is known to be present within the material at Wemyss mine (Palumbo-Roe *et al*., 2013), meaning it will have an effect on Pb release under anoxic conditions. As oxygen is removed from the pore waters, anglesite will also be reduced, allowing for the additional release of Pb into the leachate.

The remaining regimes (1ww/1wd and 2wd/1ww) show trends between Mn, Zn and Pb, with longer dry periods also allowing Fe to follow. It appears that repeated flooding of the sediment will increase the amount of metals that can be dissolved within the pore waters. Metal concentrations within leachate water display the largest decrease following the first dry period, with subsequent wetting a drying causing more fluctuations within leachate metal concentrations. 1By the end of each repeated wetting regime, overall concentrations of each trace metal were lower than those measured at the beginning, with the exception of Fe during the 1ww/1wd run. The concentrations of metals within leachate waters was often higher after a flood. Since the sediment was submerged for longer (1week compared to 1.5 hours for sampling at the start of a flood), there had been more time allowed for the establishment of reducing conditions. Therefore, oxides will be reduced, releasing metals into the pore waters.

The shorter dry periods of the 1ww/1wd run exhibit more variations in metal concentrations. The most common occurrence was a decrease in metal concentration in the leachate water immediately following a dry period. Contact time may have played a role here, as it could take longer for some metals to dissolve, depending on their initial form. As the columns only remained dry for 1 week, it is plausible that not all of the moisture was evaporated and may have built up towards the bottom of the sediment and promoted further reduction at this level. Upon the introduction of ARW, which would be more oxygen rich, there is little evidence that much oxidation occurred when initial wetting took place. The oxidation times of many sulphides (including Zn and Pb) can take several hours (Simpson *et al*., 2000), meaning the metals found within the leachate after initial wetting had an alternative source. The lengthier dry period of the 2wd/1ww samples provided the largest increases of Mn and Zn upon initial wetting. Prolonged atmospheric exposure and a longer time allowance for moisture to evaporate will aid in the formation of oxides and mineral salts. These salts will be more soluble, meaning the metals within them will be easily dissolved upon flushing (Keith *et al*., 2001; Grover *et al*., 2016; Lynch *et al*., 2017). The formation of such salts within the upper sediment layers may have been the main source of dissolved contaminants at the beginning of floods in the 1ww/1wd run.

Leachate concentrations do not show clear trends throughout the mesocosm experiment, suggesting that some major geochemical changes may not be occurring in the sediment alone. There are likely be additional external factors in the field such as changes in hydrological conditions and the channel composition. As a result, it is likely that the sediment may not be a source for the key driving factors affecting metal concentrations. It is possible that changes within the sediment chemistry at different times of year would yield alternative results.

There are inherent issues stemming from the use of mesocosms that this experiment has highlighted. One key issue is their inability to accurately replicate field conditions. Since the columns are a confined space with a finite amount of non-flowing water present. Less dilution will occur compared to the field, and any metals flushed do not have anywhere to flow to. Conditions become exaggerated compared to those in the field, explaining how, in this case, metal concentrations were much higher than those observed at Wemyss mine. Additionally, the pH of the ARW drained from the columns is not the same as that of the river water on site. Column leachate was around pH 3.5-4, while river water at Wemyss mine was in the range of 5-7.

6.6 - Sequential extraction of column sediment

The modified 2-step sequential extraction has provided concentrations of the bioavailable and total metals within column sediment from the beginning and end of each regime (figures 26-28). The results allow for an assessment of the geochemical changes that may be occurring within the sediment as both wetting and redox conditions change.

Under a saturated regime, the labile percentage of Fe and Mn concentrations within the sediment, extracted by acetic acid digest, saw a decrease. However, this was only minor, with Fe decreasing by 0.05% and Mn by 0.04%. These figures translate to a reduction of 0.14mg/Kg and 0.17mg/Kg for Fe and Mn respectively. The residual concentrations extracted by aqua regia saw and increase in accordance with the changes in the labile percentages. Fe concentration rose by 13.1mg/Kg and Mn increased by 15.91mg/Kg. As the decrease in bioavailable metal concentration was coupled with an increase in in total concentrations, it is likely that the change was brought about by an alteration in the speciation of both Mn and Fe during the experiment. As the sediment here remained saturated, anoxic conditions would have enabled the reduction of Mn and Fe oxides, allowing for some of these metals to be dissolved and flushed out within the leachate water. As the residual concentration increased over the course of the experiment, it is likely that some of these metals became bound to other complexes within the sediment, resulting in their increased presence post-experiment. The movement of water through the column upon sampling may have also played an effect. By adding fresh ARW, the top layer of sediment was more likely to be disturbed and partially oxygenated. Furthermore, the more oxygen-rich water from the top of the sediment is allowed to travel downward as the column is drained for sampling. As such, some reactions enabling the reduction of oxides and sulphates may not have been given the most appropriate conditions and time to take place.

Figure 26. Percentage of total metal concentration extracted by acetic acid digest (for bioavailable) and aqua regia (for residual) at the beginning and end of a saturated regime. a) Fe, b)Mn, c)Pb, d)Zn

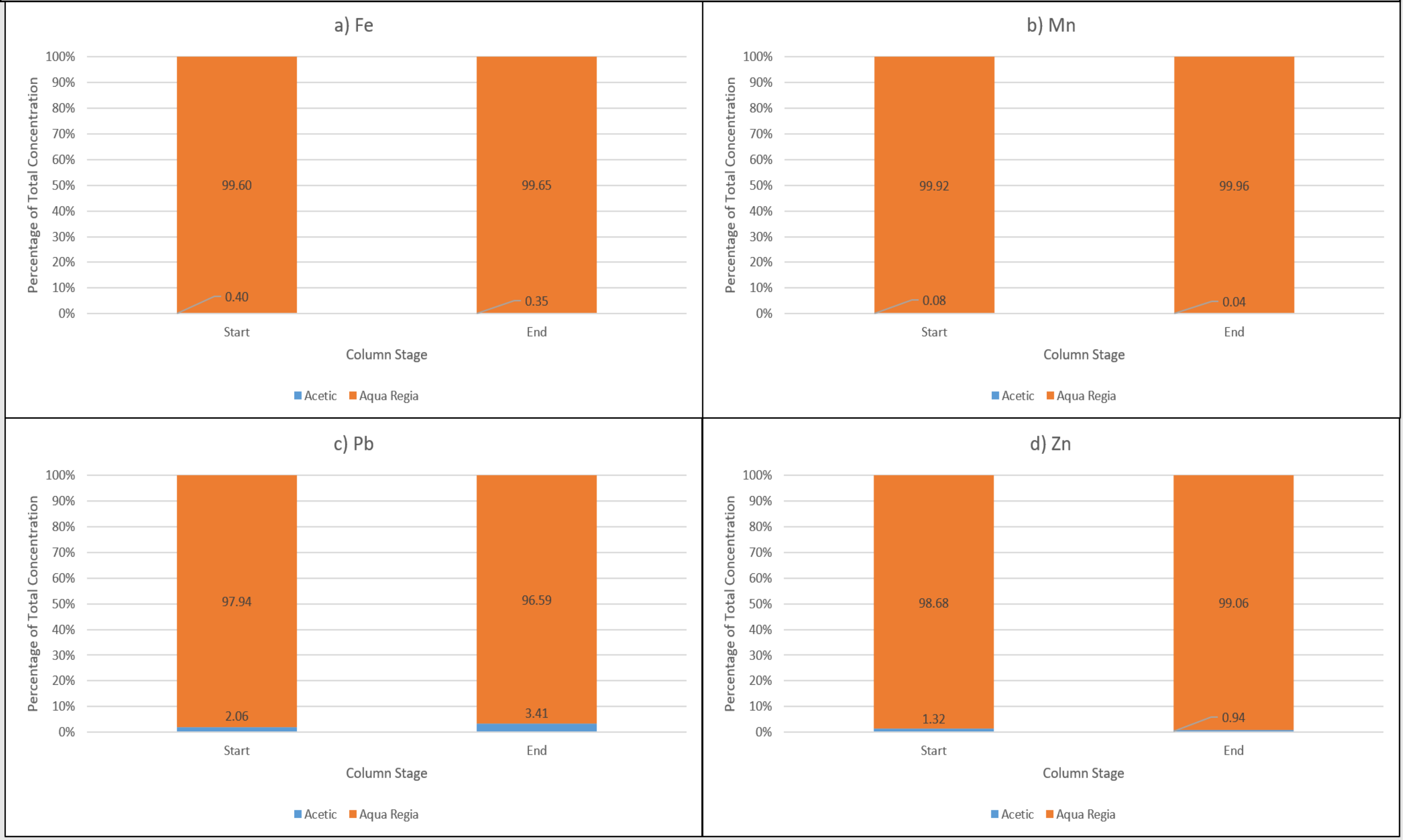


Figure 27. Percentage of total metal concentration extracted by acetic acid digest (for bioavailable) and aqua regia (for residual) at the beginning and end of a 1ww/1wd regime. a)Fe, b)Mn, c)Pb, d)Zn

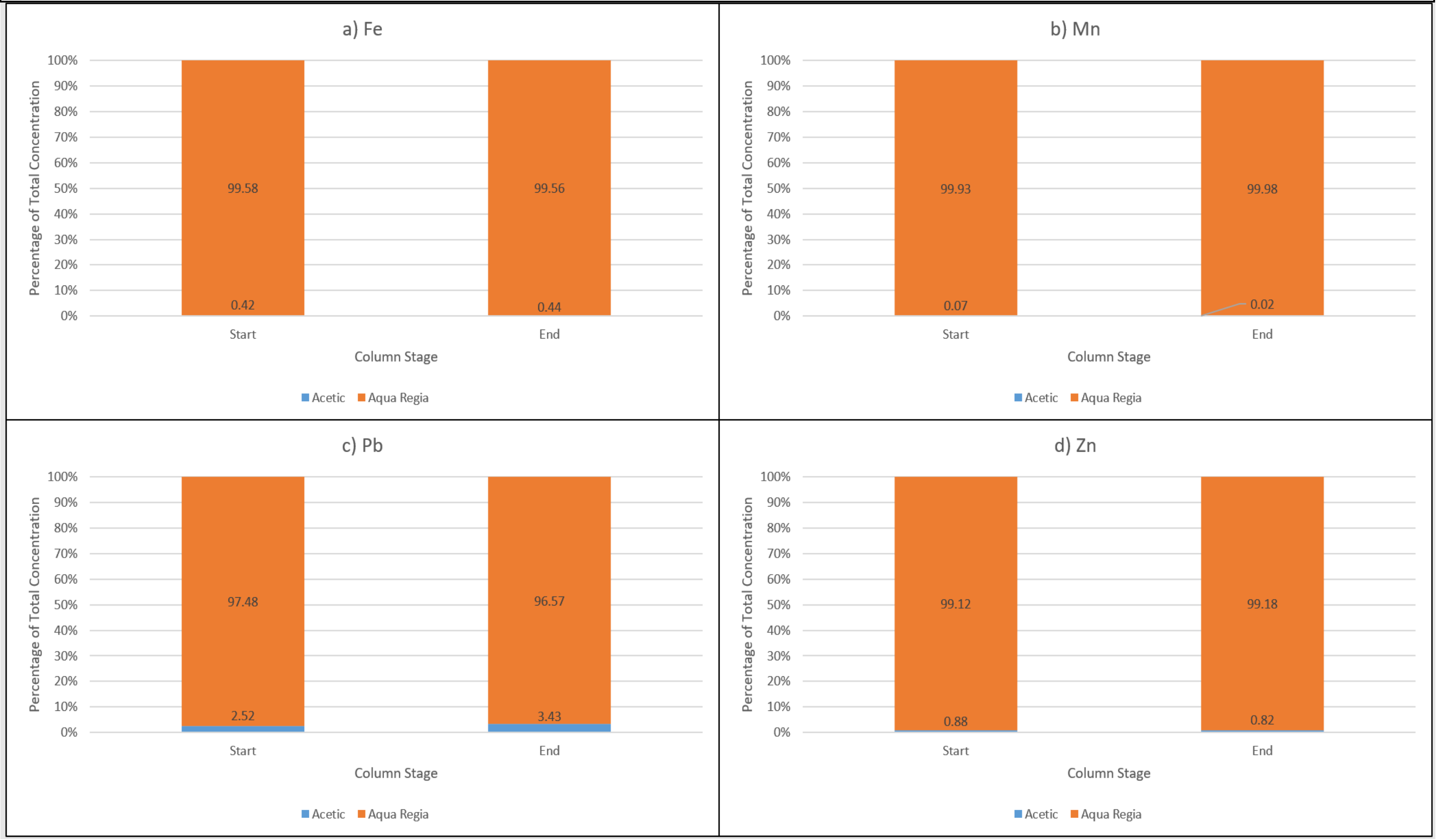
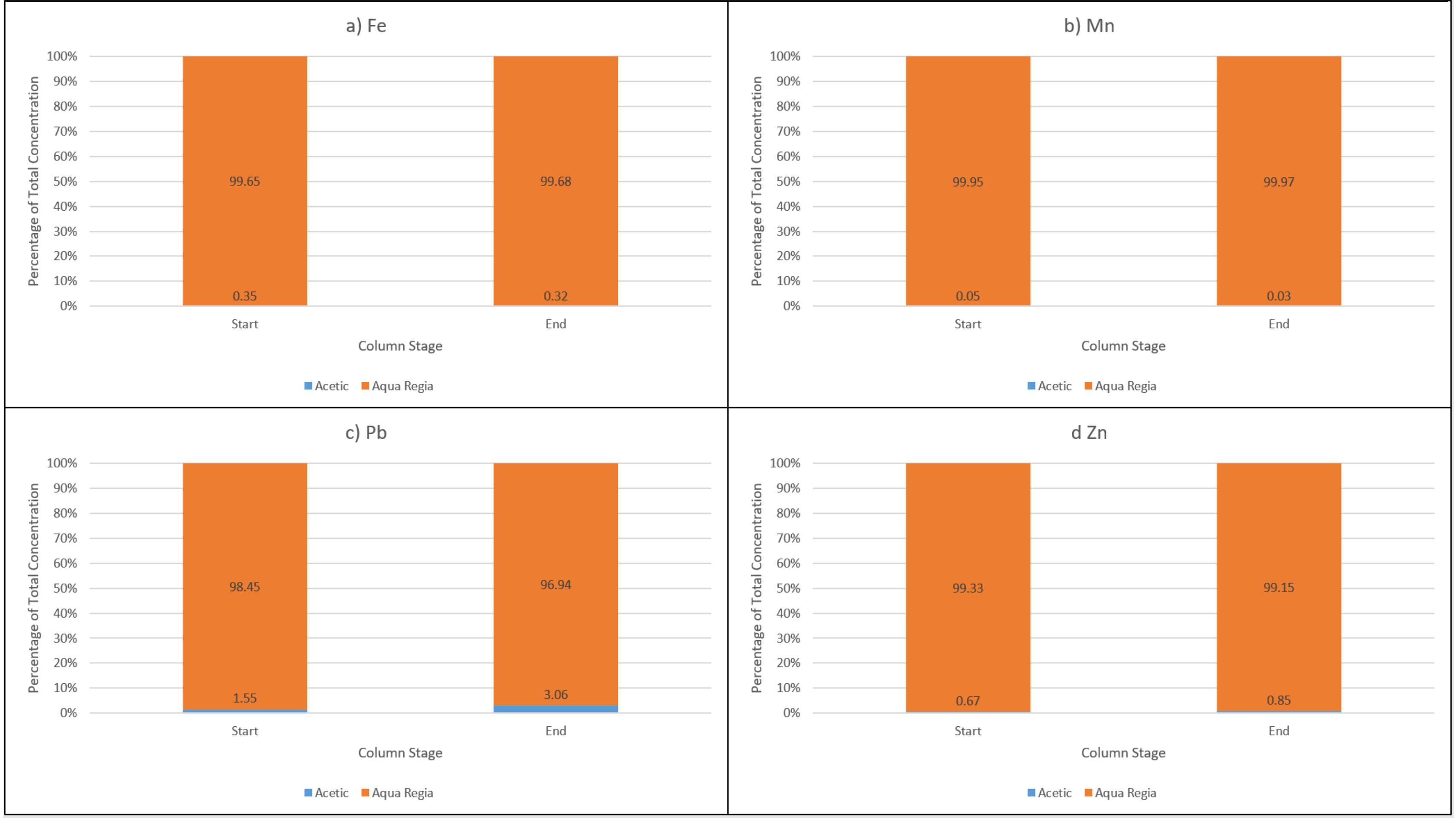


Figure 28. Percentage of total metal concentration extracted by acetic acid digest (for bioavailable) and aqua regia (for residual) at the beginning and end of a 2wd/1ww regime. a)Fe, b)Mn, c)Pb, d)Zn



Prolonged flood conditions cause an increase in the bioavailable Pb within the sediment (2.06% up to 3.41%), whilst Zn sees a minor decrease (1.32% to 0.94%). Residual concentrations changed inversely, as is expected. Total Pb concentration within the sediment saw a reduction by nearly 240mg/Kg by the end of the experiment. With the oxygen depletion that results from prolonged saturation, Pb that may be bound to sulphates will be released after reduction. Therefore, more is available in the mobile fraction towards the end of the experiment. The small increase in total Zn (70mg/Kg) may be the result of its increased binding to sulphides over time. While only a small concentration became less labile, the metals that were released upon reduction may have become bound to more stable sulphides.

Frequent wetting and drying (1ww/1wd) has very little influence on the bioavailable fractions of Fe and Mn. Iron only sees a 0.02% increase (1.59mg/Kg to 1.63mg/Kg) in the bioavailable concentration, while Mn decreases by 0.05% (0.32mg/Kg to 0.1mg/Kg). Similarly, the residual concentrations change marginally (Fe and Mn decrease by 0.45mg/Kg and 5.67mg/Kg respectively), indicating little to no alteration in the mobility of these metals under these conditions. These trace metals also saw very little changes in concentrations in the field. The minor changes from acid digests suggests that they are not present in large quantities within the sediment. Therefore, it is unlikely that frequent redox changes of Fe and Mn oxides is a major influencing factor on metal release here.

Under these same conditions, labile Pb sees a smaller increase than when saturated (a rise from 110mg/Kg at the start to 122mg/Kg at the end) whilst the decrease in Zn is slightly greater (beginning at 24.4mg/Kg and dropping to 11.6mg/Kg). Residual Pb concentration began at 4281mg/Kg and by the end of this run, had dropped to 3440mg/Kg. Zinc saw a larger decrease, starting at 2764mg/Kg and ending at 1402mg/Kg. Frequent wetting and drying introduced oxygen throughout the sediment, allowing some metals to be released due to oxidation of sulphides. Alongside this, as the top layers of sediment begin to dry, sulphate salts may begin to form (Keith *et al*., 2001; Grover *et al*., 2016). When ARW is introduced, these salts dissolve and the metals present are washed through the system. Since the sediment used for these extractions has come from the top of the columns, some of the metals previously present may have been flushed downward.

Longer dry periods (2wd/1ww) show similar results, with labile Fe decreasing 0.11mg/Kg and Mn decreasing 0.08mg/Kg. Residual concentrations show Fe decreases by 1.7mg/Kg and Mn by 23.26mg/Kg, slightly more than during the more frequent wetting regime. The fraction of bioavailable Pb rose from 83.7mg/Kg to 107.7mg/Kg and Zn saw a minor decrease of 1.85mg/Kg. The residual fraction of Pb saw a greater decrease under the longer dry periods, beginning at 5331mg/Kg and dropping to 3404mg/Kg. Total Zn did not decrease as greatly as it did under a more frequent wetting and drying cycle, beginning here at 2522mg/Kg and ending at 1768mg/Kg. Increased evaporation time from longer dry runs will enable more sulphate salts to form. The result is similar to that in the 1ww/1wd regime. More salts will be available for dissolution, allowing even more metals to be flushed through the sediment.

Conditions within the field will be similar to some aspects of the regimes chosen for the mesocosm experiment. Sites such as BG, S3 and S4 remain submerged throughout the year. Therefore, sediment beneath the channel is likely to undergo similar conditions. Flow variations and changes in the suspension and deposition of sediments will alter the redox conditions, meaning sediment will be exposed to oxygen infrequently. Future climate predictions indicate longer, drier summers with more severe storm events. Under this regime, the 2wd/1ww run is the most similar, although in reality, dry conditions in the field may persist much longer. The data representing fluctuating wet and dry cycles indicates that total metal concentration within the sediment decreases, meaning the river and channel sediment poses a risk to water quality downstream. The metals flushed have the potential to be transported downstream and it cannot be determined where they may become more stable or further diluted.

Wetter winters will increase the water level within the river, with the potential of prolonging reducing conditions. However, hydrology and geomorphology at this site indicate that higher flow rates lead to the suspension of much of the finer channel sediment, which originates from spoil material. Therefore, contaminants present can become easily oxidised and mobilised. Further transportation will occur and the eventual deposition sites are unknown.

6.7 - Conceptual Model

Both river and sediment pore water data obtained from this study has identified plausible geochemical processes that influence metal speciation and availability at Wemyss mine, as well as the effects of changing hydrological conditions. A conceptual model (figure 29) has been created to summarise the geochemical and environmental changes that occur in order to influence the mobility of Zn and Pb within this system. Similar to models proposed by Lynch *et al*. (2014 and 2017), geochemical processes that may govern metal release and attenuation are highlighted and linked to changing hydrological conditions. The model proposed by this research builds upon previous works by illustrating the additional influences caused by geomorphological changes within the river channel and the subsequent influences on geochemical processes.

The upper image (figure 29a) represents the effects of longer dry periods (typically associated with the summer months) on geochemical and geomorphological characteristics within the river channel and sediments. During this time, rainfall decreases and the flow rate within the river decreases. Lower velocity and erosional forces lead to an inability to suspend material within the water, resulting in the deposition of finer material. These finer particles, which have a high surface area and cation exchange capacity (Zhang *et al*., 2014) begin to constitute a larger portion of the riverbed material.

The main geochemical processes over the drier period are driven by the lowering water level and subsequent atmospheric exposure, which in turn increases the oxygen content within and around the sediment and spoil (Cardenas, 2015; Ahamad *et al*., 2020). Evidence from previous studies indicates that the result is an increase in sulphide oxidation, leading to a release of contaminant trace metals into the water (Peltier *et al*., 2005; Zhang *et al*., 2014). An increase in trace metals within river water over dry periods has been observed in this study. As time passes, Fe/Mn oxide and sulphate precipitation is likely to occur (Du Laing *et al*., 2009; Palumbo-Roe *et al*., 2013; Lynch *et al*., 2014), providing a sorption site for some trace metals. Based on data obtained during this project, oxidation during these drier months will lead to the greatest seasonal release of trace metals. Over time, mineral salts may precipitate onto the adjacent material, providing a source of highly soluble contaminants (Grover *et al*., 2016).

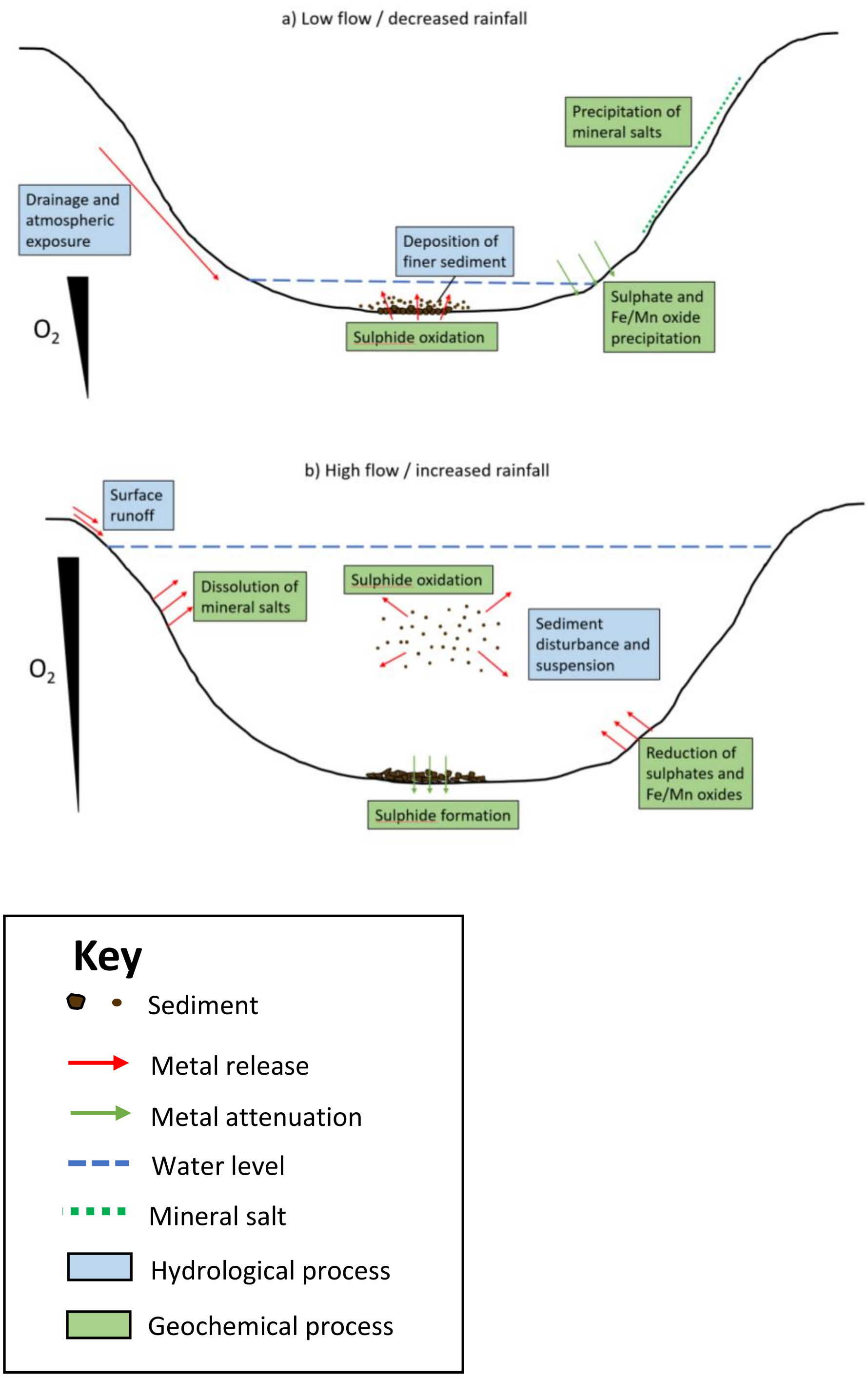


Figure 29. Conceptual model of hydrological changes influencing river channel geomorphology, as well as the potential geochemical processes affecting metal release and attenuation.

Figure 29b illustrates the potential consequences of increasing rainfall, and the resulting higher flow that follows. After a period of prolonged dry conditions, sudden rainfall will lead to an initial flushing event (Keith *et* al., 2001; Grover *et al.*, 2016). Dissolution of the built-up mineral salts will be the first process to occur, releasing higher concentrations of mobile trace metals into the water. While the dissolution of salts is a result of higher rainfall, it will occur upon the first wetting of the material. As such, water level would remain initially low, and flow rates would not increase greatly.

Towards the autumn and winter months, continued rainfall leads to increased river flow and a rising water level. More material within the channel becomes submerged, meaning oxygen is more likely to be depleted nearer to the riverbed and within the sediment pore waters. Consequently, Fe/Mn oxides and sulphates begin to be reduced, becoming a source of trace metals released into the river and pore waters (Du Laing *et al*., 2009, Zhang *et al*., 2014; Lynch *et al*., 2017). Decreasing oxygen supply is an influencing factor on the precipitation of sulphides (Simpson *et al*., 1998; Peltier *et al*., 2005). Prolonged submersion and reducing conditions will allow for the sorption of many trace metals to sulphides, which in turn decreases metal mobility and concentrations within the river and pore waters (Du Laing *et al*., 2009).

Higher variability in rainfall and river flow has an effect on the particle sizes of material that comprises the river channel. High flow will disturb the sediment on the river bed, leading to suspension and transportation. This process has been observed at Wemyss mine during this study, and is likely to be an occurrence at many other sites, given the fine particles present in many mine wastes (Palumbo-Roe and Colman, 2010). Disturbance of river sediment will expose it to more oxygen, allowing for the oxidation of sulphides. The suspended material is known to contain large concentrations of trace metals, meaning its eventual deposition downstream may allow the same redox processes to occur elsewhere. The cycling of deposition and suspension could occur numerous times leading up late autumn and winter, although evidence from this study (Figure 6) suggests that, once river flow has increased beyond a certain point, deposition of finer material is far less likely to occur until a more drastic decrease in flow rate.

The conceptual model illustrates the fluctuations that occur in many river channels, as well as the potential influences on geochemical process that occur within the sediments. Therefore, it provides an indication of key trace metal transport and mobility altering mechanisms. Knowledge of these processes and the possible knock-on effects of their occurrence under future climate predictions are vital in the implementation of future remediation and management strategies.

7. Conclusions

The legacy of metal mining practices is still evident at Wemyys mine within the landscape and the contamination of the river water flowing through the site. This study set out to investigate the hydrological and geochemical processes controlling the mobility of trace metals at Wemyss mine. In order to achieve this, three objectives were incorporated: 1) to quantify the seasonal variation in metal concentrations within river water and from contaminated sediment; 2) to determine the geochemical processes responsible for controlling metal speciation at the study site; 3) to develop a conceptual model outlining the processes governing metal mobility and potential mobility under varying conditions.

7.1 - Seasonal variability

Measurement of dissolved trace metal concentrations within river and sediment pore waters highlights the variability that take place throughout the year. River water concentrations for Mn, Zn and Pb were typically higher in summer than autumn at most sample sites. Sediment pore water metal concentrations showed a less defined seasonal variation, although this was due, in part, to the effects of hydrological changes throughout the year. Based on field observations, hydrological conditions and the effects on channel geomorphology are believed to be a key driving factor on metal concentrations. Changing flow conditions leads to variances in suspension and deposition throughout the year, which in turn affects the presence of finer sediment within the river channel. This material has the potential to provide more mobile and easily dissolved metals to the river and sediment pore waters.

7.2 - Geochemical processes

During the summer, low rainfall and decreased river flow promote atmospheric exposure and oxidation of river sediment, which is likely to facilitate the release of metals bound to sulphides. First flush wetting results in an initial release of more soluble metals that were likely precipitated as mineral salts. Metal concentrations within leachate from mesocosms under a 2wd/1ww regime also showed increases on first flushing events. Towards autumn, as conditions become wetter, dissolved metal concentrations decrease as water level increases and oxygen is depleted. The resulting conditions become more reducing, causing a potential release of metals bound to oxides and sulphates within the sediment into the river water. Leachate metal concentrations from the saturated mesocosm indicated such an increase over the timeframe employed. The decrease in most metal concentrations towards autumn is potentially caused by the sorption of trace metals to precipitated sulphides.

Low concentrations of Fe and Mn compared to Zn and Pb throughout this study indicate that the reduction of Fe/Mn oxides is not a major factor in the sorption or release of trace metals at Wemyss mine. Analysis of material from this site by other researchers has indicated the presence of sulphates, specifically anglesite, the reduction of which would facilitate metal release.

7.3 - Conceptual model

The proposed conceptual model (figure 29) illustrates the potential effects of changing hydrological conditions on geochemical processes and channel morphology. It is evident that variations in rainfall and the subsequent effects on river flow play an important role in the concentrations of trace metals within river and sediment pore waters. The model suggests that hydrological conditions influence the ability of the river to erode, suspend or deposit material, which effects the geochemical processes occurring within and around the river channel. Observations of changing sediment characteristics in the field, coupled with the metal concentrations measured under varied hydrological regimes indicate that the processes illustrated will reoccur and pose a threat for years to come.

7.4 - Key findings

By employing field water sampling, DGT deployment and a laboratory-based mesocosm experiment, this project has identified a seasonal variation in metal concentrations within river water at Wemyss mine. The geochemical processes that influence this variation have been theorized and an alternative driving factor has been identified for this study site. Hydrological variations and the subsequent effect on channel morphology appear to be vital in the release of metals into the Nant Cwmnewydion. Finer sediment within the river channel have been linked to increases in metal concentrations within the river water, most commonly during the summer, when rainfall is typically lower and river flow would be reduced. Suspension and removal of these particles occurs towards autumn, as rainfall becomes more frequent and river flow increases. The variability in local environmental conditions, as well as those downstream, will allow for the processes believed to be taking place at this site, reoccurring both here and downstream over different areas and time frames. This study has highlighted the importance of further addressing the effects of hydrological and geomorphological changes within river channels, and the effects on trace metal contamination.

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9.0 Appendix

Figure A1. Spoil adjacent to the Nant Cwmnewydion at S3. Evidence of the eroded bank is visible at the bottom of the spoil.

Figure A2. Dry channel at Mill Race Stream with evidence of an output from subsurface flow in the lower area.

	Wetting Regime					
	Saturated		**1wk wet / 1wk dry**		**2wk dry / 1wk wet**	
Week	Sample	Top-up/drain	Sample	Top-up/drain	Sample	Top-up/drain
0	🟦	🟩	🟦	🟩	🟦	🟩
1	🟦	🟩	🟦	🟩	🟦	🟥
2	🟦	🟩	🟦	🟥		
3	🟦	🟩	🟦	🟩	🟦	🟩
4	🟦	🟩	🟦	🟥	🟦	🟥
5	🟦	🟩	🟦	🟩		
6	🟦	🟩	🟦	🟥	🟦	🟩
7	🟦	🟩	🟦	🟩	🟦	🟥
8	🟦	🟩	🟦	🟥		
9	🟦	🟩	🟦	🟩	🟦	🟩
10	🟦	🟥	🟦	🟥	🟦	🟥

Key	
Take water sample	🟦
Top-up water	🟩
Drain water	🟥

Table A1. Wetting and drying schedule employed for the mesocosm experiment. Additional markers indicate when water samples were obtained.