Mapping Hydrological Pathways at Nantymwyn Lead Mine

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Abstract

Nantymwyn Lead Mine is one of over 1,300 known abandoned metal mines in Wales. It is ranked 11th in the top 50 highest priority metal mines requiring remediation. There is no legal obligation for the operators or owners of mines abandoned in the UK before 2000 to stop or reduce contamination from them, and there is evidence that Nantymwyn has been contaminating the River Tywi with lead and zinc for over a hundred years, and likely centuries prior to that. In this thesis, water samples were collected from across the site over 13 months, and calculated the flow of water in the streams, to show seasonal variations in flow, and metal fluxes. Additionally, a synoptic sampling technique was used to gauge water flow and concentrations along the stream at a single point in time, showing otherwise undetected inputs and losses of water and metals to the stream. Combined these methods will help guide future remediation of the site, by allowing efforts to be targeted where they will have the most effect. A water quality comparison was made to two other abandoned metal mines in Wales, Parys Mountain and Frongoch, showing that all three mines continued to contaminate unabated until extensive measures were applied to reduce environmental contamination at Frongoch.

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List of Abbreviations

All abbreviations used in the thesis are shown in full on their first use. Chemical symbols are used outside of the introduction.

Key abbreviations:

AMD	Acid Mine Drainage
EA(W)	Environment Agency (Wales)
EQS	Environmental Quality Standard
ICPMS	Inductively Coupled Plasma Mass Spectrometry
MPAES	Microwave Plasma Atomic Emission Spectroscopy
NRA	National River Authority
NRW	Natural Resources Wales
µg/l $\mu g\ L^{-1}$	Micrograms per litre
WFD	Water Framework Directive

Notes for the reader

All altitudes, unless otherwise noted, are given as metres above ordnance datum.

All depths, unless otherwise noted, are given as metres below ground level.

All photographs, unless otherwise stated, were taken by the author, or with his equipment.

1 Introduction

1.1 Background

This thesis focuses on the identification and quantification of sources of metal-contaminated streamwater downstream of an abandoned lead/zinc mine in central Wales.

In countries with expansive laws on mine operations, before a mine can open it must have feasible and funded closure plans, often supported by a government held bond to return the site to its pre-mining state if the company goes bankrupt (Thomashausen et al., 2018). Mines operating before these laws came into operation, however, often will not have a closure plan in place, with some mines left contaminating water courses decades after closure or abandonment (McCullough, 2016). While the contamination starts with the mine workings and the mine waste, it is moved by water, and this contaminated water is usually the largest risk to the environment from a mine after closure (McCullough and Lund, 2011). Water is both a valuable commodity and an essential resource for life, with drinking water especially high in demand (Todd et al., 2024b). Globally great efforts are put into minimising water losses in distribution networks, such as reducing leaks, maximising storage capacity via reservoirs, and avoiding controllable damage, such as contamination (Lackner et al., 2020). Insensitively operated mines will contaminate watercourses as soon as they begin operation, and ore processing activities are often very water-intensive, requiring careful planning for the use of water and its storage or treatment before release (Thomashausen et al., 2018; Todd et al., 2024b). Downstream deleterious impacts of these mining activities and legacy sources of contamination can restrict use of watercourses for drinking water, and affect the entire length of rivers. Actively treating this contaminated water, while technically possible, is expensive, often requiring power, chemicals, maintenance, disposal of waste sludges, and a commitment to continue treating the waters in perpetuity (Johnson and Hallberg, 2005). Passive treatment systems typically require large areas of land which are not always available near mine discharges. A key factor in reducing the environmental impact of these contaminants in the water catchment is determining their main source. Once determined, this enables the feasibility of a remediation to be determined with the aim of improving water quality and reducing the size and cost of any treatment system (Johnson and Hallberg, 2005; McCullough, 2016).

Present-day mining operations average globally a rock-to-metal ratio of 1:859, meaning for a single tonne of refined metal, 859 tonnes of waste are produced (Nassar et al., 2021). At each stage of mining operation, a small fraction of the metal is lost with the waste, for example, only 78% of zinc is recovered from ore at a refinery (Nassar et al., 2021). A continuously increasing demand for mined metals has seen current metal mining increase its contamination of water, from all stages of mining operation (Giljum et al. 2025). Historical recovery rates, with less effective methods of mining and ore recovery, transport, and refining, were lower, and as a result, historical mine wastes have a higher proportion of metals remaining in them than recently created mine wastes, and are hence sometimes re-exploited for this.

Greatly elevated concentrations of elements of concern in water and sediments as a result of mining activities and wastes have been recorded globally (Hudson-Edwards et al., 2011, Luckeneder et al. 2021, Zhou et al. 2020), not only in Europe (Davis Jr et al., 2000, Mullinger, 2004) but across the world, in Asia (Bhuyan and Bakar, 2017, Giri and Singh, 2019), Africa (Edet and Offiong, 2003, Nduka and Orisakwe, 2011), South America (Lattuada et al., 2009, Smolders et al., 2003), North America (Gunter, 2017, Nordstrom 2009), and Oceania (Rufaut et al., 2020, Wright et al., 2017). Mine hydrology is a relatively new subject, and often hydrological principles do not work on abandoned mines because of the complex underground network of shafts, winzes, stopes and adits (Younger et al., 2002a).

After the large-scale closure of metal and coal mines from the 1900s onwards, abandoned mines have become a major source of metal contamination to rivers globally (Macklin et al., 2023; Whelan et al., 2022). Over 4000 km^2 of land in Britain is contaminated with Pb from historical mining and smelting activities (Thornton, 1996). Locating, classifying, and quantifying sources of potentially toxic elements from abandoned metal mines is challenging due to the historical legacy of poorly-mapped mine workings, variations in streamflow and rainfall, and the remote location of mines.

Identification and quantification of contamination sources is an essential first step to the successful remediation of contaminated mine sites and watercourses (Kimball et al., 2002). Wales, for example, has over 1,300 known abandoned metal mines, many abandoned before any legal requirements to map the subterranean workings, let alone plan for any future contaminated water outflows causing negative effects on biota downstream (Environment Agency Wales, 2002). Metal contamination from abandoned mines can have a deleterious impact on flora and fauna and can bioaccumulate through the food chain (Gall et al., 2015; Sartorius et al., 2022; Tchounwou et al., 2012). Metal contamination of downstream floodplains during high flow events can result in those floodplains become sources of metal contamination in their own right (Lewin and Macklin, 1987; Smith et al., 2009; Szabó et al., 2020). Decades of erosion and degradation of surface and subsurface workings have increased the difficulty of managing these sites, which adversely affect over 700 km of river length in western Wales, and cause over 15% of watercourse chemical quality failures in western Wales (Coal Authority, 2020; Natural Resources Wales, 2022). With no clear responsibility for their contamination, and little budget for their remediation, any improvement to water quality reduced as a result of metal mines is achieved through targeted action to bring average water metal concentrations down to below a legal maximum threshold, or as low as can be afforded (Edwards et al., 2016).

In the United Kingdom, owners of mines abandoned before 2000 bear no responsibility for the environmental impacts of the mine after closure despite contamination from metal mining affecting over 2,500 km of watercourses across the country; all major metal mines in Wales were closed before this date (Environment Agency, 2008; Environment Agency Wales, 2002; The Mines Regulations, 2014). Metal contamination of rivers has been noted as one of the major concerns for water quality in the UK in the 21st century, with abandoned and active mines, urban storm runoff, industrial runoff and waste, and leaking landfills being the main sources involved (Whelan et al., 2022); all of which need some level of remediation or reduction to improve water quality. Natural Resources Wales (NRW) and its predecessor organisations (Environment Agency Wales 1996-2013, National Rivers Authority 1989-1996, Welsh Water Authority 1984-1989, Welsh National Water Development Authority 1973-1984, and the relevant River Authority (for

Nantymwyn South West Wales) 1965-1974) have carried out reactive and investigative water quality monitoring, and where possible flow measurements, of waters at and downstream of mines.

Contamination of freshwater can deleteriously affect the flora and fauna that rely on it. Complaints about mining's impact upon waterbodies, and subsequent damage to flora and fauna, are well-documented for hundreds of years, with public pressure being brought upon the government with "*Pollution Of The Rivers Of The Kingdom; The Enormous Magnitude Of The Evil, And The Urgent Necessity In The Interest Of The Public Health & The Fisheries For Its Suppression By Immediate Legislative Enactment*" (Fisheries Preservation Society, 1868), which resulted in a series of government reports on the state of British rivers (Rivers Pollution Commission, 1875, 1874, 1868). The Fisheries Preservation Society's report also noted evidence of fish being killed in 1861 by effluent from metal mines into the Ystwyth and Rheidol (1868). Both were studied over 60 years later alongside the Towy, with little improvement (Carpenter, 1926, 1925, 1924).

Nantymwyn, the focus of this thesis, was one of the largest lead mines in Wales in the 19th century, and was abandoned in 1932, 22 years before the first legislation relevant to it came into force (Hughes, 1992). It is one of over 1,300 abandoned metal mines in Wales, (Figure 1-1) and deleteriously impacts upon water quality in the River Towy for 65km (Coal Authority, 2016; Environment Agency Wales, 2002; Environment Agency Wales and Atkins Limited, 2011; Mayes et al., 2009; Williams, 2010). The methods applied to Nantymwyn in this project should allow any future remediation to be of maximum benefit per unit expenditure, as the sources and causes of contamination can be located, prioritised, and understood.

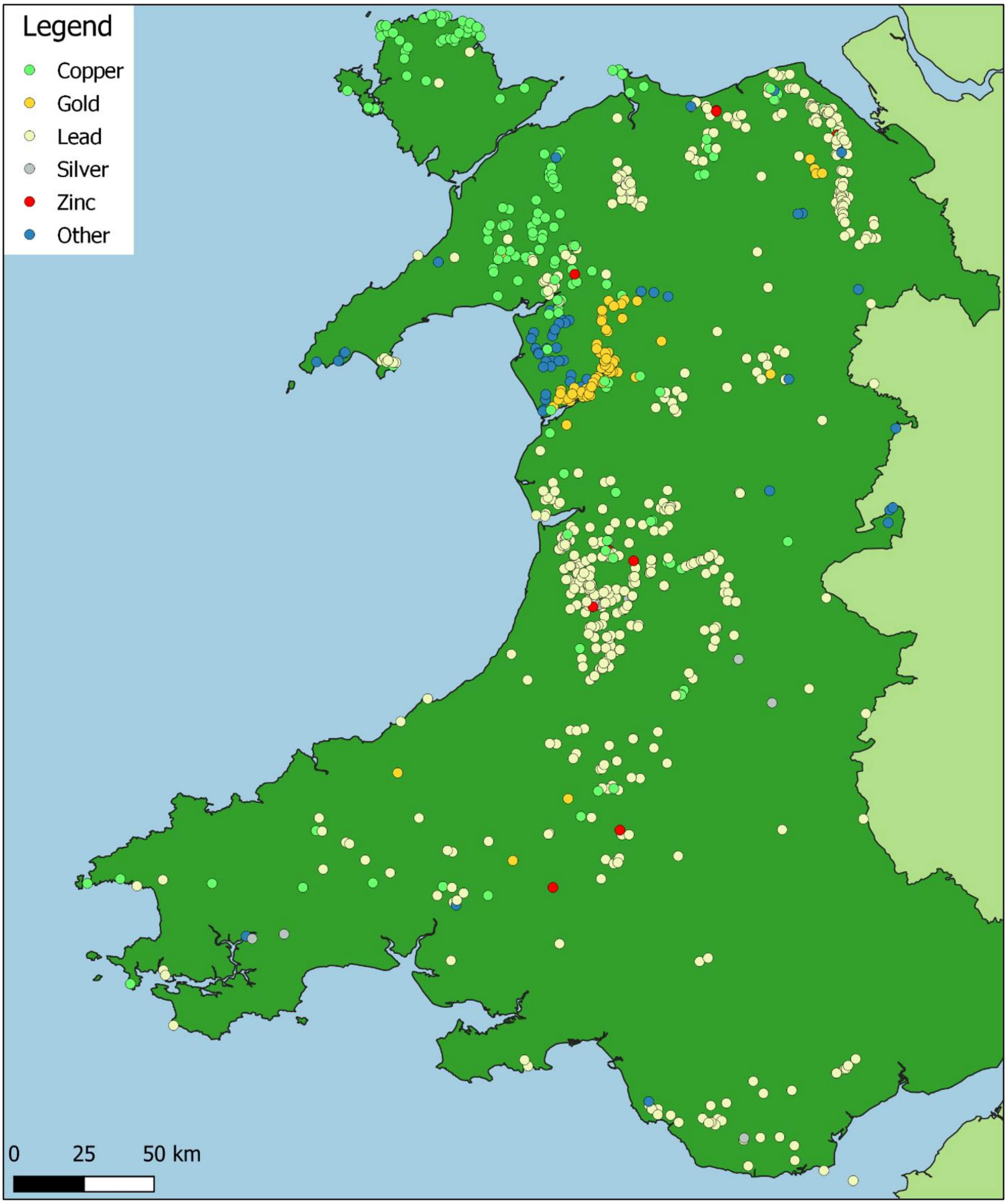

Figure 1-1 - Abandoned Metal Mines in Wales. For clarity, 638 mines without a principal ore recorded in the database are not shown. (Natural Resources Wales, 2020; Ordnance Survey, 2020)

1.2 Aims

As will be discussed in chapters 2 and 3, while the problems from metal mine contamination to watercourses are understood, and a variety of methods are available to remediate them, the pathways of metal contamination at Nantymwyn are not well understood. This lack of understanding has been one of the causes of its lack of remediation, and as use the aims of this thesis are:

1. To determine the magnitude, recent history, and temporal and downstream dynamics of streamwater metal contamination at an abandoned metal mine using historical and current data on contaminant concentrations and streamflow
2. Use/test a bromide tracer and synoptic water sampling approach to identify and quantify sources of streamwater metal contamination within and downstream of abandoned metal mines

1.2.1 Specific objectives

1. To assess variations in metal concentrations and loads with discharge and season along the Nant y Bai and Nant y Mwyn streams affected by the abandoned Nantymwyn mine, using new data collected at monthly intervals.
2. To the above new data with all available historical data to assess whether the scale of streamwater contamination is showing any sign of improvement.
3. Use a bromide tracer and synoptic sampling approach to collect and analyse a detailed field dataset of metal concentrations, loads and streamflow along the Nant y Bai stream to identify and quantify sources of metal contamination.
4. In the light of the results of 3, to discuss possible strategies for remediation at the mine, and their prospects for success.

2 Literature Review

2.1 Impacts of metal contaminated waters

Globally mines and mining activities such as smelting have severe impacts upon thousands of kilometres of watercourses, both during operation and after closure or abandonment (Bird, 2016). Mining can adversely affect nearby watercourses at all stages of the mine's life, from initial development, through operation and closure (Carter, 2000; McCullough, 2016). The many elements of concern from mines and mining activities can be harmful to river fauna and farm animals in adjacent fields, and have been linked to developmental issues in children (Feigenbaum and Muller, 2016; Royal Commission on Environmental Pollution, 1983; Sartorius et al., 2022a; Thomas et al., 1985). The foci elements of concern of this thesis are zinc (Zn), cadmium (Cd), lead (Pb), and to a lesser extent, copper (Cu), as those are most likely to be found in high concentrations in Wales (Environment Agency Wales, 2002). While Zn is an essential element at trace levels for cellular processes, at higher concentrations it can cause functional impairments, especially to children, and at high concentrations is toxic to plant and animal life (FAO, 1996; Tchounwou et al., 2012). There is no such beneficial level for Pb, however, and humans, especially children, are at risk of health damage from Pb contamination (Plumlee and Morman, 2011; Vorvolakos et al., 2016), from sources including leaded petrol (Resongles et al., 2021) as well as mines (Venkateswarlu et al., 2016), potentially leading to problems with brain and bone development and the nervous system (Ethier et al., 2012; Obeng-Gyasi, 2020; Tchounwou et al., 2012; Thomas et al., 1977). Lead can be ingested from dust or soil, or via water, and the realisation of this risk lead to the end of lead additives in petrol, which resulted in a lead dust settling from petrol powered vehicles (Royal Commission on Environmental Pollution, 1983). Ingestion of lead in childhood has also been linked to increased likelihood of being involved in crime in adulthood in the USA, both from water supplied via lead piping, and from leaded petrol (Feigenbaum and Muller, 2016; Reyes, 2007). For humans a daily intake of 140 µg Cd and above can cause skeletal damage, kidney damage and failure, and it is not believed to be beneficial at any level (FAO, 1996; Tchounwou et al., 2012).

All three metals can enter the food chain and cause harm as they bioaccumulate, with adverse impacts, for example, shown from birds drinking water with a Pb concentration of 100 μg L^{-1} (Bautista et al., 2014; Baykov et al., 1996; Chen et al., 2022; Gall et al., 2015; Goodchild et al., 2021; Sartorius et al., 2022a). Waterfowl can ingest lead from fishing weights, and a change in regulations on fishing weight use has seen a statistically significant increase in mute swan populations (Thomas et al., 1985; Wood et al., 2019). Male zebra finches have shown a statistically significant changes in development when exposed to lead while growing, including altered sexual traits (Goodchild et al., 2021). Farm animals can ingest lead while grazing, with different animals grazing at different levels, and therefore picking up more or less soil, and hence lead (Griffith, 1919; Johnson et al., 1978). Research has been carried out at Nantymwyn into the concentrations of metals from the mine in flora and fauna in the area, particularly at a farm downstream of mine on the Nant y Bai (Sartorius, 2019a). Preliminary results show concentrations of lead elevated above safe standards in horsehair (over 300 times the admissible norm of 0.5 mg kg^{-1}) , vegetation, invertebrates, soil, chicken egg yolks, and chicken blood, elevated concentrations of zinc in vegetation, invertebrates, and soil, elevated concentrations of cadmium in some soil, invertebrates, and horse hair, and elevated concentrations of copper in soil (Sartorius 2018, 2019a, 2019b, 2019c). Lead concentrations within the eggs varied seasonally, but at their highest, in May 2019, an adult human could only consume two eggs from the farm downstream of Nantymwyn before reaching the European Food Safety Authority nephrotoxicity threshold, compared to 166 commercially available eggs (Sartorius et al., 2022b).

An essential element at trace amounts, Cu deficiencies in infants leads to limited bone growth, and an adult human body contains on average 80 mg (FAO, 1996). At higher intakes it can cause skeletal problems and anaemia, as well as damage to the liver and other organs, with a safe maximum exposure of 12 mg/day for adult males, and 10 mg/day for adult females (FAO, 1996). there are three main routes for the elements into humans: ingesting, inhaling, and absorption through skin (Xu et al., 2024). Direct contact with contaminated water, including eating food that has been contaminated by said water, is the most common way to be exposed to these elements (Rahman and Singh, 2019). A study into the relative risk posed by various potentially hazards chemicals to the aquatic environment ranked Cu the 1st highest risk, Zn 3rd, Pb 11th and Cd 17th, out of a total of 71 (Johnson et al., 2017). This study considered their ecotoxicity effort concentration and medium concentration in UK river water to give a numerical value to this risk, with attempts to avoid subjectivity in the scoring system (Johnson et al., 2017).

2.2 Sources, pathways and sinks

Metal contamination from mines has occurred globally, with all continents outside of Antarctica being directly affected by active or abandoned metal mines (Macklin et al., 2023). Metal contamination from mining-affected rivers can eventually reach estuarine and coastal environments, with contaminated waters, sediments, and biota being noted from sources including active and abandoned mines in the Asia (Pan and Wang, 2012; Reza et al., 2010), Europe (Abril et al., 2021; Hudson-Edwards et al., 1999, 2008), Africa (Ahmed and Osei, 2016; Steyn et al., 2019), North America (Cravotta et al., 2014; Gusek et al., 1998), and South America (Smolders et al., 2003; UNEP, 2001). Global extraction of metal ores has increased from 2.7 gigatonnes in 1970 to 9.4 gigatonnes in 2022, as demands for metals have increased with advances in technology (Giljum et al. 2025).

Mining wastes in the form of solutes and sediments can enter watercourses when eroded through by the watercourse, from surface runoff contaminated by the mining wastes, and from contact with contaminated groundwaters (Lewin et al., 1977). For sediment transport, two main processes were identified in four metal-mine affected Welsh catchments; firstly the direct erosion of friable mine wastes, and secondly, bank erosion and vertical accretion of floodplain deposits (Foulds et al., 2014). Sediment transport is controlled by various factors including slope and velocity, and a particular cause of contamination from sediments is when a river's flow exceeds the bank full capacity and spills onto the floodplains (Bradley, 1984; Foulds et al., 2014; Gozzard et al., 2011; Lewin and Macklin, 1987). Sources of Pb and Cd at the geographically similar Wemyss mine in mid-Wales have been shown to contaminate the nearby environment though several methods, including mass movement, aerial deposition, and fluvial transport (Lewin et al., 1977). The stability of minerals dispersed by river erosion depends on the biogeochemical make up of the river water, of particular importance is pH (Hudson-Edwards et al., 1996; Onnis et al., 2024). Metal speciation is also influenced by temperature, biochemical adaptations in organisms, and lipid solubility (Tchounwou et al., 2012).

2.3 Overarching UK legislation

Contamination of water is controlled in the UK by various legislative acts, the key two relevant to abandoned metal mines are the Water Resources Act and the Water Framework Directive.

2.3.1 Water Resources Act 1991

In England and Wales, the Water Resources Act 1991 (WRA 91) outlines the principal offence that a person contravenes the act if he or she: “causes or knowingly permits any poisonous, noxious or polluting matter or any solid waste matter to enter any controlled waters.” Until 31st December 1999, Section 89(3) of the same act contained a defence that: “A person shall not be guilty under Section 85 by reason only of his permitting water from an abandoned mine to enter into controlled waters”. However, while the defence was for “permitting” a discharge, not “causing”, the complexities of abandoned mines’ ownerships and subterranean connections meant that only one successful prosecution for pollution from an abandoned mine was undertaken under this legislation, for a mine opened in 1951 and closed in 1977 (Environment Agency, 2008). This defence is no longer valid for mines abandoned or closed on or after 1st January 2000.

2.3.2 Water Framework Directive

The EU Water Framework Directive (WFD) has been the impetus for much of the investigations into contamination of river waters by abandoned metal mines in the last 20 years. The legislation was copied wholesale into UK law post-Brexit. The WFD has several overarching aims which related to abandoned metal mines, including:

- Aim to achieve good ecological and chemical status by 2015.
- No deterioration in water quality
- Progressively reduce pollution from priority substances.

The WFD was implemented in Britain via 12 River Basin Districts, eight of which identified abandoned mines as a significant pressure on water quality. Each of the approximately

5,000 WFD water bodies is assessed on a six-year cycle, with those water bodies deteriorating or not achieving good status undergoing measures to stabilise and improve water quality. The lowest score for a water body is the one it is given, regardless of other scores, so for instance the River Tywi in the second WFD cycle failed to meet the WFD standard for Zn due to the inputs of the Nant y Mwyn from the input until the tidal limits of the River Tywi, and therefore the whole river was classified as poor. The UK is currently on its third WFD cycle, and changes in sampling locations on the River Tywi, and a dispensation for WFD failures from metal mine causes due to the lack of a feasible treatment plan mean that the River Tywi is now only classified as affected for 25 km (Natural Resources Wales, 2016a). WFD priority substances include Pb, and Cd is a priority hazardous substance. Of the 1552 WFD waterbodies in Wales Not Achieving Good Status in the most recent cycle, 187 are failing due to non-coal mines, and another 9 failing due to coal mines, and 2 from quarries (Natural Resources Wales, 2022).The reporting spreadsheet only states the highest impacting cause of failure, more water bodies will be impacted by abandoned metal mines, but have other pressures causing failure ahead of them.

2.4 Welsh metal mines

Wales has a long history of mining, most recently for coal, with the last deep coal mine at Tower Colliery closing in 2008, and single drift mine continuing to this day at Aberpergwm, Neath (EnergyBuild, 2021; Smith et al., 2011). In the Victorian era, however, much of the wealth in Wales was derived from metal mining with Swansea becoming known as “Copperopolis” (Hughes, 2001). With most of the metal mines in Wales being abandoned before the second World War there are few first-hand records of their operation, extent, or even quantities of ore mined. Their histories form part of the local area’s story, and there are small organisations dedicated to researching both the mines’ histories, and their underground workings, where possible (Bick, 1983, 1978, 1977, 1976a, 1976b; Foster-Smith, 1981; Hall, 2014; Jones, 1922; Lewis, 1967; North, 1962; Timberlake, 2003; Warren, 1994). There is evidence of mining for metals in Wales during the Roman occupation of Britain, including gold in Dolaucothi (Jones et al., 1960), and 2,000 years prior to that for copper, at Great Orme (Lewis, 1996). There are 1,470 metal mines recorded in the NRW database, though some of these are repeats – Nantymwyn appears nine times (Natural Resources Wales, 2020). As can be seen in Table 2-1, Pb mines like Nantymwyn represent the largest proportion of metal mines in Wales, though it should be noted that, as Pb and Zn are often available from the same lode, that a mine principally producing Pb will often also produce Zn, and vice versa. There is also a very large proportion of mines without a recorded main ore or output metal.

Table 2-1 - Welsh non-coal mines by ore type from the NRW abandoned metal mine database (Natural Resources Wales, 2020)

Main ore/output	Number of mines
Arsenic	1
Barium	12
Copper	159
Gold	74
Lead	527
Limestone/calcite	3
Manganese	40
Silver	7
Zinc	9
Not recorded	637

The environmental problems caused by the largely unmanaged abandonment of so many mines has been known for decades, and indeed some of the mines were known for their environmental problems during operation (Campbell James et al., 1932; Carpenter, 1926, 1925, 1924; Fisheries Preservation Society, 1868; Newton, 1944). While scientific research into the methods and problems arising from contamination from these mines continued (Abdullah and Royle, 1972; Bird, 1987; Coulthard and Macklin, 2003; Davies, 1987; Hudson-Edwards et al., 2008; Johnson et al., 1978; Lewin et al., 1977; Lewin and Macklin, 1987; Macklin et al., 2023; Mighall et al., 2002; Mullinger, 2004; Smith et al., 2010; Thomas et al., 1977; Wolfenden and Lewin, 1978), a lack of government regulation meant that minimal action was taken, until the first cycle of water quality sampling and analysis for the Water Framework Directive was undertaken in 2000 (Council Directive

2000/60/EC, n.d.). This does not mean that the regulator was unaware, with routine monitoring for chemical water quality ongoing (Department of the Environment, 1978, 1975; Mullinger, 2004; National Rivers Authority, 1994; South West Wales River Authority, 1974), but the WFD requires countries to actively improve the quality of their watercourses, and in Wales the understanding that unmanaged metal mines were causing multiple failures of the WFD standards lead to the creation of a ranking of the highest impacting metal mines, and a high-level strategy for their monitoring and management in 2002 (Environment Agency Wales, 2002). This led to the remediation of Frongoch Pb/Zn mine in phases over several years from 2011-2018 (Edwards et al., 2021, 2016), funding of various research projects, including this one, and has been updated in 2008 and 2020 (Coal Authority, 2020a; Environment Agency, 2008).

The impacts of abandoned metal mines globally, as well as those in Wales, will likely be increased by changes in rainfall due to anthropogenic climate change, such as increased frequency and intensity of extreme flow and rainfall events (Arnell and Gosling, 2013; Douville et al., 2021; Foulds et al., 2014; IPCC, 2023). Extreme low flows in major rivers receiving inputs from abandoned metal mines may mean that a higher proportion of the major river's flow is mine impacted, increasing metal loads. These prolonged low flows followed by more extreme rainfalls will increase the first flush intensity of contaminants (Petach et al., 2021). Across the UK metal concentrations have been descending from their recorded peak in the 1980s (Whelan et al., 2022). This reduction, however, has had little to do with abandoned metal mines, and has been caused largely by improvements in wastewater treatment systems, the end of leaded petrol use in cars (Whelan et al., 2022).

2.5 Approaches and methods for investigating and measuring metal contamination and streamflow

2.5.1 Measuring streamflow

There are a number of methods for estimating or measuring the flow of water within a watercourse; selecting a method is guided by the size and location of the watercourse, and the data needs of an investigation.

2.5.1.1 Volumetric or bucket and stopwatch

The simplest method, used for spot measurement of the smallest watercourses that have a single contained outflow, such as a culvert with a drop at the outfall, or a natural waterfall, is the volumetric method (using a container and a stopwatch). To use this method, one simply collects a volume of water and measures the time taken to do so (Figure 2-1). This method is limited in the size of flow that can be measured using it by the practicalities of holding a vessel to catch the water, and using too small a vessel that fills very quickly increases the error in the result (Wolkersdorfer, 2008). The flow is calculated using the equation below:

$$Q = \frac{V}{t}$$

Where:

Q (L s^{-1})	Flow
V (L)	Volume of container
t (s)	Time to fill vessel

The bucket and stopwatch method should be repeated three times at the site to reduce error (Wolkersdorfer, 2008).

Figure 2-1 - An ideal site for the bucket and stopwatch method of flow measurement at Nantymwyn, as the flow is concentrated into a culvert with a large enough fall to accommodate a bucket. Sampling site reference number 88224

2.5.1.2 Dilution flow gauging

Where the previous methods are inappropriate due to excessive water turbulence, as in many hilly headwaters, or locations with coarse bedloads, tracer injection can be used. Tracer injection flow gauging techniques require thorough mixing of the tracer within the watercourse, lending the method further to small upland streams with rapid turbulent flows.

Using salts as a tracer medium for flow gauging has existed for over 100 years (Allen and Taylor, 1923), but until relatively recently the equipment required to conduct it meant that it was only used where there was no other alternative (Church and Kellerhals, 1970). Early studies involved chemical analysis of samples; later studies involved the variant ‘relative method’, in which conductivity is used to assess NaCl changes. This ‘relative method’ was developed and refined at the experimental catchments of Llyn Brianne, 10 km north of Nantymwyn, by Littlewood (1986). The advantages of digital conductivity meters, with the ability to record data and upload this to a computer for flow calculation, has made it a practical and affordable technique (Moore, 2004; Williams, 2016). Aside from the ease of acquiring it, at the low concentrations used, NaCl has minimal environmental issues to take into consideration, and generally does not require a permit (Wood and Dykes, 2002).

The method works by measuring the increase, peak, and then decrease in conductivity in the water, caused by the salt solution passing the conductivity meter (Church and Kellerhals, 1970). A known quantity of brine, or salt solution, is introduced into the water, above a suitable mixing length. The more turbulent the flow, the less mixing length is needed, and care should also be taken to avoid pools within the mixing length where the electrolyte solution will be held (Church and Kellerhals, 1970). Fully mixed into the watercourse, the solution passes the conductivity logger, which simultaneously records the conductivity increase, and the time elapsed from injection. The 'relative method' requires a bankside calibration at each gauged point, using a small volume of the same solution used in the streamflow injection. This means that there is not a need to have precisely weighed out portions of salt, nor any chemical analysis, only measurements of conductivity, and volumes of injected and saved salty solution (Church and Kellerhals, 1970; Littlewood, 1986). The formula used is:

$$Q = \frac{V \times Z}{T \times Y}$$

Where:

Q (L s^{-1})	Flow
V (L)	Volume in bucket 1 minus volume removed
Z (mL)	Volume in bucket 2
T (s)	Duration of response
Y (mL)	Volume of solution
ΔC (µS cm^{-1})	Mean conductivity rise
U (µS mL^{-1})	Bankside calibration unit response

(After Littlewood, 1986; Moore, 2004; Williams, 2016)

The bankside calibration and volumes required for the formula are recorded on site, and at a later date can be combined with the logged data from the conductivity meter. This method can be automated and activated at intervals or remotely, but this is uncommon (Kite, 1993). At some sites the NaCl tracer may be inappropriate due to acidity or elevated conductivity, and alternative conservative tracer may be used, such as KCl, and dyes such as fluorescein or rhodamine can also be used with a suitable fluorometer (Church and Kellerhals, 1970). It is also possible to use radioisotopes in a similar manner to NaCl, which can have the advantage of being able to detect sediment transfer, however, the complexity of acquiring, using, and measuring these has made their use rare (Gregory and Walling, 1973; Ward and Wurzel, 1968).

2.5.1.3 Constant rate tracer injection

The single gulp injection method has the advantage of speed and low complexity of equipment, however, the older method using a large tank of tracer injected at a constant rate over several days continues to have a place in flow gauging, when combined with synoptic sampling (Byrne et al., 2021b; Onnis et al., 2023b). As the tracer is injected over a period of days it becomes fully mixed in the stream and therefore captures flow in irregular channel sections and the hyporheic zone. Secondly, as the streamflow is calculated using the tracer concentration in the stream, sampling can be carried out rapidly at each sample site, maximising the number of samples that can be taken and increasing the spatial resolution of sampling (Byrne et al., 2021b; Onnis et al., 2023b). This combination of methods has been developed by the US Geological Survey and used extensively in the USA to understand mine impacted watercourses and inform mine site remediation (Kimball et al., 2002; Runkel et al., 2023, 2016; Walton-Day et al., 2007). It has been used less frequently in the UK but but has been utilised at legacy mining sites in need of better understanding of sources and sinks of contaminants, as it can be used at many points downstream simultaneously (Byrne et al., 2021b; Onnis et al., 2018; Todd et al., 2024a).

Tracers used for constant rate tracer injection and synoptic sampling include NaBr and LiCl, with the selection of the tracer based on the attributes of the site, especially pH, and background concentrations of each tracer, as the flow gauging is reliant on the tracer being conservative within the watercourse (Kimball et al., 2004). Streamflow estimation at each site relates the injected tracer to the observed dilution in the sampled point (Kimball et al., 2004), using the below formula:

$$Q = \frac{Q_{INJ}\,C_{INJ}}{(C_P - C_B)}$$

Where:

Q (L s^{-1})	Flow
Q_{INJ} (mL min^{-1})	Injection rate
C_{INJ} (μg L^{-1})	Concentration of the injected tracer
C_P (μg L^{-1})	Tracer plateau concentration at the synoptic sampling site
C_B (μg L^{-1})	Background tracer concentration in stream water above the injection point

(After Kilpatrick & Cobb, 1985; Kimball, 1997; Runkel et al., 2013)

2.5.1.4 Velocity-area

For larger watercourses where the volumetric method is not feasible and the waterflow is sufficiently deep and not too turbulent, the velocity-area method can be used (Gregory and Walling, 1973). The width of the watercourse is measured, and then divided into equal spaced segments across the channel. At each of the segments the depth to the riverbed, and the velocity of the water, are recorded (Figure 2-2). In deeper watercourses the velocity should be taken at two points in the water column, at 20 % and 80 % of the watercourse depth, and the mean taken. In shallower water a single velocity measurement at 60 % of the depth is sufficient (Gregory and Walling, 1973). The discharge for each segment is then calculated, and the segments summed to create the total channel discharge (Herschy, 1993). There is a balance to be had between many segments and more data, and fewer segments taking less time to complete, and reducing possible errors. To calculate the discharge of a segment, the follow equation is used:

$$Segment\ discharge = \left(\frac{V_1+V_2}{2}\right)\left(\frac{d_1+d_2}{2}\right) b$$

Where:

V_1 (m s^{-1})	velocity in segment one
V_2 (m s^{-1})	velocity in segment two
d_1 (m)	depth of segment one
d_2 (m)	depth of segment two
b (m)	width of segment

(after Gregory and Walling, 1973)

Figure 2-2 - left, V-notch weir with a constant depth logger at Nantymwyn (sampling site reference number 88204); right, an impeller type flowmeter, with graduated depth marked on the vertical support for the flow meter, and distance across the channel measured from the horizontal tape measure

To measure the velocity of the waterflow, a flow or current meter can be used. There are a variety of styles, from the simplest impeller type shown in Figure 2-2, through to electromagnetic flow meters, and doppler velocity meters (Wolkersdorfer, 2008). Electromagnetic flow meters are particularly suitable for shallow watercourses, with a minimum depth of 5 cm, compared to 15 cm for impeller flow meters. Current meters can either be handheld by an operator wading into a watercourse, or suspended on a cable across the watercourse where wading would be dangerous (Gregory and Walling, 1973).

2.5.2 Measuring metal concentrations

There are a number of methods for analysing water samples for metal concentrations, most are laboratory based, and the particular method to select will depend on the sample's expected concentrations, elements of interests (and how the method will respond to those elements) and available resources. In most cases samples have to be taken in the field for subsequent laboratory analysis. Methods relevant for the analysis of metal concentrations in water are detailed below.

2.5.2.1 Inductively coupled plasma spectroscopies

In inductively coupled plasma (ICP) spectroscopies analytes are ionized by a hot plasma, typically made from Ar, which are then measured with a spectrometer (Johnstone and Rose, 1996). Inductively coupled plasma mass spectrometry (ICP-MS) is a more recent elemental analysis technique, measuring elements themselves (Wait, 1993). This is similar to inductively coupled plasma optical emission spectroscopy (ICP-OES), but the OES has a higher limit of detection (LOD) as it measures the light emitted by the elements as they pass through the plasma (Olesik, 1991). ICP-MS can identify all but seven elements (Ar, F, H, He, N, Ne, and O), from 0.1 ppt to several thousand ppm (Thomas, 2008).ICP-MSs can give misleading results with certain elements, due to spectral overlaps of ions (McCurdy and Woods, 2004). However, the majority of ICP-MSs built in the last 20 years have also had a collision/reaction cell (CRC), which resolves issues caused by unwanted spectral overlaps, where unwanted ions appear at the same mass as the analyte ions (Tanner et al., 2002). The CRC will either cause the potentially overlapping ions to collide with others, leaving the analyte ions to enter the MS (collision mode), or be filled with a reactive gas which will resolve the overlapping ions (reaction mode) (McCurdy and Woods, 2004). In reaction mode the reactive gas must be selected with consideration to the overlapping ions that need to be prevented (McCurdy and Woods, 2004). A heavily used ICP-MS will be coupled to an autosampler and a computer and will be set to analyse several hundred samples in a run, automatically cleansing and rinsing the instrument between samples, and periodically resampling laboratory standards to assess any drift in metal concentrations (Thomas, 2008). This cleansing and rinsing step is particularly important in an ICP-MS as some elements can exhibit a memory effect, where the elevated concentrations of a previous sample affect those of the proceeding ones (Zhang et al., 2014). An autosampler, computer, ICP-MS with CRC, and associated equipment (vacuum pump, argon supply, air extraction fan, cooler) is shown in Figure 2-3.

Figure 2-3 – an Agilent Technologies ICP-MS 7900 in use for this project at Liverpool John Moores University. The ICP-MS itself is to the rear with the silver corrugated extractor hose attached, then being pointed at by the author is the autosampler and prepared samples, and then the computer and Agilent Technologies software to control the system.

2.5.2.2 Microwave plasma spectroscopies

Microwave plasma atomic emission spectroscopy (MP-AES) and microwave plasma optical emission spectrometry (MP-OES), like an ICP, passes the sample through a plasma to convert it into ions, however, it has the advantage of not requiring any expense or risk of flammable gasses to create this plasma, using nitrogen scavenged from air (Balaram, 2020). Arriving commercially in 2011, the use of a microwave plasma for elemental analysis was first considered in the 1960s, and has been used for environmental purposes, including water quality (Balaram, 2020; Hammer, 2008; Kamala et al., 2014; Mavrodineanu and Hughes, 1963). As well as advantages in safety and cost of consumable gas, the MP based instruments are less expensive to purchase than the equivalent ICP instrument, and more accurate and less time-consuming to use than an AAS instrument (Niedzielski et al., 2015). Despite these, however, the ICP-based instruments have now been a feature of commercial and government laboratories for several decades, with the NRW National Laboratory Service for instance using them since 1984, and the change in method and slight increase in limits of detection appear so far to be outweighing the cost advantages of the MP-based instruments (Brown, 1986). The reduced need for ancillaries is noticeable when comparing an MP-AES (Figure 2-4) to an ICP-MS (Figure 2-3).

Figure 2-4 - an Agilent Technologies MP-AES 4200 at Swansea University

2.5.3 Loading

After analysis of the samples for metal concentrations, loadings can be calculated as below:

$$L = Q \times C_m$$

Where:

L (mg s^{-1})	Load
Q (L s^{-1})	Stream discharge
C_m (mg L^{-1})	Concentration of the element

This formula can also be used to calculate loads using other flow gauging methods, where metal concentrations are measured concurrently to flow gauging (Byrne et al., 2021b).

2.5.4 Water quality sampling

2.5.4.1 Grab sampling

A grab sample is a single volume of water taken from the stream or river being sampled, either directly into a storage bottle for subsequent analysis (as can be seen in Figure 2-1), or into a sample bucket for subsequent division into storage bottles (Pawliszyn et al., 2012). Depending on the planned laboratory analysis, some preparation of the sample can be completed while in the field, for instance filtration, or acidification (Pawliszyn et al., 2012). The sampling bottle’s physical properties should be considered, for example, samples taken for the analysis of dissolved organic matter should be taken in chemically inert borosilicate glass (Halewood et al., 2022). To avoid any possible contamination, the sample bottle should be rinsed with the water to be sampled three times (Environment Agency, 2010, 1998). For filtered samples, the sample bottle should be rinsed with filtered sample water. After collecting the sample and securing and labelling the bottle, it should be stored out of sunlight and if possible at 4 °C.

2.5.4.2 Automatic sampling

Automatic sampling uses a computer-controlled pump to collect grab samples of water from the sampled river (Figure 2-5). These can be started via elapsed time, for instance, every hour, or from an external input, for instance an increase in river stage, or rainfall. Samples can be taken discretely, where each sample bottle represents a single point in time, or in composite, where a sample bottle has two or more samples taken into it (Pawliszyn et al., 2012). The automatic sampler will rinse it’s internal tubing between each sample with river water, and consideration should be given to the external temperature, and the need to retrieve the samples in a timely manner. When the samples are retrieved, they should be treated in the same manner as the grab samples, and bottled for subsequent analysis as required.

Figure 2-5 - An ISCO 3700 automatic watersampler in use on the Nant y Bai

2.6 Remediation methods for metal-contaminated rivers, including biochar

Both active and legacy mines can contaminate nearby watercourses, and metals can bioaccumulate in flora and fauna near the contaminated water and enter the food chain (Beane et al., 2016; Sartorius et al., 2022; 2022). In order to reduce these impacts mining areas can be treated or remediated, and there are three general areas of remediation:

1. Diversion of water away from mine and mining wastes
2. Active treatment of mine contaminated waters
3. Passive treatment of mine contaminated waters

It is not uncommon to combine aspects of both active and passive mine water treatment systems to create a semi-passive mine water treatment system, nor to use a treatment system on the remaining contaminated outflows from a site that has had diversion or capping carried out (Bates et al., 2006; Kleinmann et al., 2022; Whitehead and Prior, 2005).

2.6.1 Diversion of water away from the mine or mining wastes

Although only possible at some sites, this is the most straightforward solution to metal contamination of rivers from mining, and can often be the first stage in a solution that includes active or passive treatment. On the basis that treating contaminate waters has a cost per volume of water treated, reducing the volume of water that requires treatment will reduce the cost of building and maintaining an active or passive treatment system. Examples of this in the UK include at Frongoch, where a watercourse that was entering the open workings was diverted away from them, substantially reducing the volume of contaminated waters leaving the mine adit (Edwards et al., 2021). The newly diverted stream’s channel was then lined (Figure 2-6), to minimise contamination of the waters from mine wastes, and this comparatively clean water, with filtered Zn, Pb and Cd all reducing in concentration by >80 %, was then used to dilute the waters exiting the mine workings at the adit (Edwards et al., 2016). It has also been used at Cwm Rheidol mine in Wales (Jones, 1986), and at Wire Gill and California mines in England (Environment Agency et al., 2023). Diversion of watercourses has also been used successfully in the USA, with reductions in metal concentrations of between 64 % - 86 % (Kotalik et al., 2023; Mebane et al., 2015) and Canada, with significant increases in species abundance noted (Gunn et al., 2010).

A reduction in the volume of contaminated water can also be achieved by encapsulating mine wastes, preventing rainwater and surface runoff from penetrating the wastes and becoming contaminated with metals (Kuyucak, 1999). As with watercourse diversions, this is only possible when site conditions allow, such as hillslope and topography, wastes consistency and metal concentrations within it, and the local groundwater conditions (Kuyucak, 1999). Much of the mine wastes at the abandoned Frongoch lead mine in Wales have been reprofiled and then capped with a geotechnical clay membrane, similar to that used to line landfill sites (Figure 2-6). This capping material has then been covered with 30cm of topsoil, which was seeded with metal tolerant grasses (Edwards et al., 2016). Unfortunately, the monitoring regime at Frongoch is insufficiently frequent to isolate capping's impact on improving water quality at the site, but in combination with other remediation efforts there has been a reduction of >87 % for filtered Zn, Pb, and Cd (Edwards et al., 2021). Capping or encapsulating of mine wastes has been carried out in Africa (Ahmed and Osei, 2016; Mwandira et al., 2019), Oceania (Munksgaard and Lottermoser, 2013; Yang and Cattle, 2017), North America (Cervi et al., 2022; Chapman and Campbell, 2024), and Europe (Callery and Courtney, 2015; Kutuniva et al., 2019).

Figure 2-6 – Top, a lined and diverted stream at Frongoch lead zinc mine, mid Wales. Note mine wastes on either side of the stream. Bottom, capping the reprofiled mine wastes, with a geotechnical clay line (the white sheeting on the right) being covered with topsoil.

2.6.2 Active treatment of the mine contaminated waters

Active treatment systems for mine contaminated waters are characterised by the need for continuous external inputs, such as energy, chemicals, or labour (RoyChowdhury et al., 2015). The selection of the chemical to be used is dependent on the site water's metals and their typical concentrations, pH, acidity, and flow rate, and consideration should also be given to the availability of chemicals in the local vicinity, and site access and availability of power and maintenance (Trumm, 2010). Chemical additions are intended to raise the pH of the waters, and therefore cause the dissolved metals to form insoluble hydroxides and precipitate or co-precipitate in treatment ponds (Skousen et al., 2019). Common chemical additives include: hydrated lime ($Ca(OH)_2$), soda ash (Na_2CO_3), ammonia (NH_3), caustic soda ($NaOH$), and limestone ($CaCO_3$), all of which have a neutralisation efficiency of >90 % (Trumm, 2010). After the chemicals have been introduced to the water, the treated water flows into a settling pond so that the metals in the water can precipitate, which is sometimes encouraged with the addition of a flocculant (Trumm, 2010).

An alternative to chemical dosing is the use of electrolysis, where two electrodes have a current passed between them, with the contaminated water flowing past. The construction of the electrodes is tailored to the site's specific waters, as with chemical dosing, and there remains a need for a settling pond and possible flocculant use to capture the insoluble metal sediments that result (Morgan et al., 2017). A trial using magnesium electrodes at Cwm Rheidol (Figure 2-7) abandoned metal mine in Wales demonstrated a removal rate of 99.5 % (Rose et al., 2019). The advantages of electrolysis

Figure 2-7 - the portable Power & Water electrolysis plant at Cwm Rheidol, with generator behind. Picture courtesy of Power & Water over chemical dosing are the much reduced area needed for a treatment system, and not needing to handle potentially hazardous chemicals, but they do have an increased power usage. Active treatment systems have been used in the UK (Rose et al., 2019; Wyatt et al., 2013b), Oceania (Trumm, 2010), North America (Bates et al., 2006), South America (da Silveira et al., 2009), and Asia (Akcil and Koldas, 2006).

2.6.3 Passive treatment of the mine contaminated waters

If suitable land is available, and the site's characteristics suit it, passive treatment of mine water can deliver a high removal rate of metals with much reduced ongoing costs compared to active treatment (Trumm, 2010). There are several key types of passive treatments to remove metals from mine impacted water, which can be broadly categorised into three types of system: inorganic media passive systems (IMPs), wetland type passive systems and subsurface flow bacterial sulphate reduction systems (Skousen, 2016; Younger, 2000; Younger et al., 2002). The selection of the specific passive mine water treatment system or combination of passive mine water treatment systems will depend on the flows and concentration of metals in the mine effluent, as well as the availability of suitable land for the system, and how much hydraulic head is available (Skousen, 2016). Passive treatment systems have been used in Africa (Van Hille et al., 1999), North America (Gusek and Thomas R. Wildeman, 2002), Europe (Bailey et al., 2016; Bannister et al., 2018; Opitz et al., 2022), Asia (Sheoran, 2006) and Oceania (Trumm, 2010).

2.6.3.1 Inorganic media passive systems (IMPs)

IMPs are designed based on dissolution and/or precipitation; they raise pH, neutralise acidity and add alkalinity to mine impacted water (Younger et al., 2003). There are two principal types of IMP, the first being carbonate dissolution IMPS, such as limestone drains, where the limestone dissolves, having the effect of increasing pH and alkalinity leading to oxidation, hydrolysis and precipitation, removing up to 50 % of the Zn (Ben Ali et al., 2019; Nuttall and Younger P. L., 2000).

The second type of IMP is a system using inorganic material, such as plastic or blast furnace slag, which provides surfaces to capture precipitates e.g. Surface-Catalysed Oxidation Of Ferrous Iron reactors (SCOOFI) (Batty and Younger, 2004; Younger, 2000).

A SCOOFI reactor is a porous media with a high surface area which causes iron to precipitate on the surface of the media which in turn increases the rate at which the iron is immobilised. Due to the continuous nature of this process, iron immobilisation will occur until the SCOOFI media is blocked, with a consistent removal rate of 50 % until the media is exhausted (Younger, 2000).

2.6.3.2 Wetland type passive systems

There are three key variants of wetland passive treatment systems; aerobic wetlands, compost wetlands, and Reducing and Alkalinity Producing Systems (RAPS) (Younger et al., 2002b). These systems are somewhat climate dependent, with a reduction in efficiency of over 50 % seen when ambient temperatures drop 20 °C (Ben Ali et al., 2019).

Aerobic wetlands are ponds that are under 30 cm deep with or without wetland plants which slow down influent water and allow oxidation, hydrolysis, and particle settling (Skousen et al., 2019). To further reduce flow rates flow diverting baffles are often used to improve efficacy (Skousen et al., 2019). Aerobic wetlands are often used as a polishing treatment in conjunction with other treatments such as sulphate reducing bioreactors (Wang et al., 2024). Aerobic wetlands have been seen to reduce additional mining metal(oids) such as Pb, Cu, Zn and Cd but this has been primarily attributed to adsorption or complexation in wetland substrates or adsorption or co-precipitation with metal oxides including Fe, Al and Mn, with removal rates of >92 % (Opitz et al., 2022).

Compost wetlands or anaerobic wetlands are more commonly used in net acidic waters where the head is limiting (Younger et al., 2003). They have an anoxic substrate of compost creating an anaerobic environment where sulphate reducing bacteria thrives reducing sulphate to sulfide. That sulfide can then react with the free metal ions in the water to form insoluble metal sulphides (e.g. FeS and ZnS) that remain within the wetland, showing removal rates of over 95 % (Batty and Younger, 2004).

Reducing alkalinity producing systems (sometimes referred to as vertical flow ponds) are similar to compost wetlands but in addition they include a limestone gravel bed to maximise alkalinity generation, act as a source of sulphate reducing bacteria and remove metals through precipitation (Batty and Younger, 2004). RAPS are more efficient than compost wetlands and as a result require less land area to be effective, however, they need more hydraulic head to function as the design necessitates the water to flow downwards through the system rather than just requiring a surface flow as per a compost wetland (Batty and Younger, 2004; Younger et al., 2003). A RAPS was installed in south Wales to reduce metal concentrations from the abandoned Pelenna coal mine (Figure 2-8) and has been successfully treating the mine's outflow since 1992 with Fe removal rates of 82 % - 95 % (Wiseman et al., 2002). A vertical flow pond system can be seen at Force Crag Mine in Cumbria, a Zn and Pb mine that was abandoned in 1991, which adversely affects 60 km of river. Since 2014 the mine effluent has been captured by two parallel Vertical Flow Pond compost bioreactors, followed by a small wetland, removing

Figure 2-8 - one of the three passive minewater treatment systems at the abandoned Pelenna coal mine in South Wales. Minewater enters the system on the right and passes through it under gravity alone. Picture from (Wiseman et al. 2002).

95 % - 99 % of the Zn (Bailey et al., 2016). It is estimated, however, that the substrate will require replacing after 10 years of use, and the disposal alone of this is almost the same as the capital expenditure for building the system (Bailey et al., 2016). A similar but larger system has been in use in West Fork Pb mine in Missouri, treating 76 L s^{-1} of water and reducing the Zn concentration by 75 %, with a design life of 12 years (Gusek and Clarke-Whistler, 2005).

2.6.3.3 Subsurface flow bacterial sulphate reduction systems (SFBs)

There are two types of SFBs, in situ permeable reactive barriers, and SFBs constructed to treat mine water discharges. These are distinguished by their location, but function without scientific difference (Younger et al., 2003). These systems employ an area of semi-permeable reactive media which is placed in the flow path of mine impacted water; this creates biogeochemical processes (e.g., precipitation, sorption, oxidation/reduction, fixation, degradation) which remove the contaminant, with rates of up to 99 % seen for Cd, Cu, Zn and Al (Batty and Younger, 2004; Ben Ali et al., 2019). There are issues with these systems, the most notable of which is that there is the potential for the water to flow around rather than through the barrier, and that the barrier must be replenished or replaced due to exhaustion or clogging (Younger et al., 2003). A variation on the SFB is to include a coarse inert matrix, such as wood shavings, to the reactive media. This has the effect of increasing the dissolution rates of the reactive media before it is rendered ineffective (Ben Ali et al., 2019).

2.6.4 Biochar as an agent for treating mine contaminated waters

Biochar is a porous, carbonaceous material (Figure 2-9) produced by biomass pyrolysis at temperatures ranging from 350–1000 °C under limited oxygen conditions (European Biochar Foundation, 2016). In addition to the removal of contaminants from aqueous media studies have also highlighted several other benefits of biochar including carbon sequestration and enhancing soil fertility (Inyang et al., 2016; Kätterer et al., 2019). Its appeal is heightened as a result of its relatively low cost, simple production process and the ability to use a vast number of locally sourced feedstocks including sustainable and waste materials (Ahmad et al., 2014; European Biochar Foundation (EBC), 2016; Wang et al., 2018; Xiao et al., 2018; Zhang et al., 2015).

Biochar has six key immobilization mechanisms for inorganic contaminants in aqueous media namely: cation exchange, complexation, electrostatic attraction, cation π bonding, reduction and subsequent sorption, and precipitation (Cairns et al., 2022a). Several mechanisms can be relevant in any given biochar and these mechanisms can remove contaminants at different rates. Initial fast stage adsorption can be attributed to mechanisms such as electrostatic attraction and ion exchange whereas rate limiting steps have been seen to mainly involve chemical processes such as inner sphere complexation and co-precipitation (Ifthikar et al., 2017). The fast removal performance of biochar has been highlighted as a necessity for a successful adsorbent (Zhou et al., 2018); if the required contact time between sorbent and sorbate to remediate a contaminated water is too long then the use of that sorbent becomes impractical. This is particularly true in systems with a continuous flow where contact time between biochar and contaminant is limited.

Figure 2-9 - biochar in a porous container, allowing water to pass through the biochar for treatment, but retaining the biochar (and metals it removes) within the container. The container opening is approximately 2cm x 6cm, and 10cm tall.

Wood ash, a waste product of biomass power plants, has been used as an amendment to biochar to improve immobilisation of metals (Cairns et al., 2022b, 2020). Due to its neutralizing potential and metal removal qualities, wood ash has been suggested a feasible alternative to materials such as limestone or peat for use in mine water treatment systems (Genty et al., 2012). The increased rates of immobilisation are as a result of the wood ash mineral fraction and pH buffering capacity, with removal rates of 97 % for Zn and 86 % for Pb seen (Cairns et al., 2021). The alkali and alkaline earth metals added are central to ion exchange as well as increasing the pH of its environment inducing changes in metal speciation favourable to the immobilisation of Zn and Pb (Cerrato et al., 2016; Fidel et al., 2017).P and Si added to the biochar by the wood ash are also key in the formation of phosphates and silicates important in forming co-precipitates.

2.6.5 Treating the treatment – waste product from mine-contaminated water treatment systems

Both active and passive treatment systems require periodic maintenance, which will include the removal of the metal contaminated wastes and sludges (Macías et al., 2017). The Wheal Jane active mine water treatment system creates a sludge which is stored behind a tailings dam (Coulton et al., 2003), and this storage area will eventually be filled. Smaller treatment systems such as the Pelenna passive mine water treatment in Wales, have to have their treatment media periodically excavated, and disposed of as hazardous waste, at substantial cost (Bannister et al., 2018; Wiseman et al., 2002). Active treatment systems in Canada create in excess of 6.7 million cubic metres of sludge which requires either treatment or disposal of, again at cost (Zinck et al., 1997). There is research ongoing to further treat this waste, removing metals that could be sold on for profit, and at the same time allowing the remaining wastes to be treated as non-hazardous waste, but currently the disposal of mine water treatment systems’ wastes remains an issue (Lottermoser, 2011).

3 Area of Study

3.1 Geographical Setting

Nantymwyn lead mine (52°5'12" N; 3°46'20" W) is located north of the village of Rhandirmwyn (population 150), near Llandovery, and just over 50 km north of Swansea on the eastern side of the south-flowing River Tywi (Anglicised as Towy) (Figure 3-1). There are two flow gauging stations on the River Tywi near to Nantymwyn, Ystradffin to the north, upstream of the mine, and Dolau Hirion, downstream to the south (National River

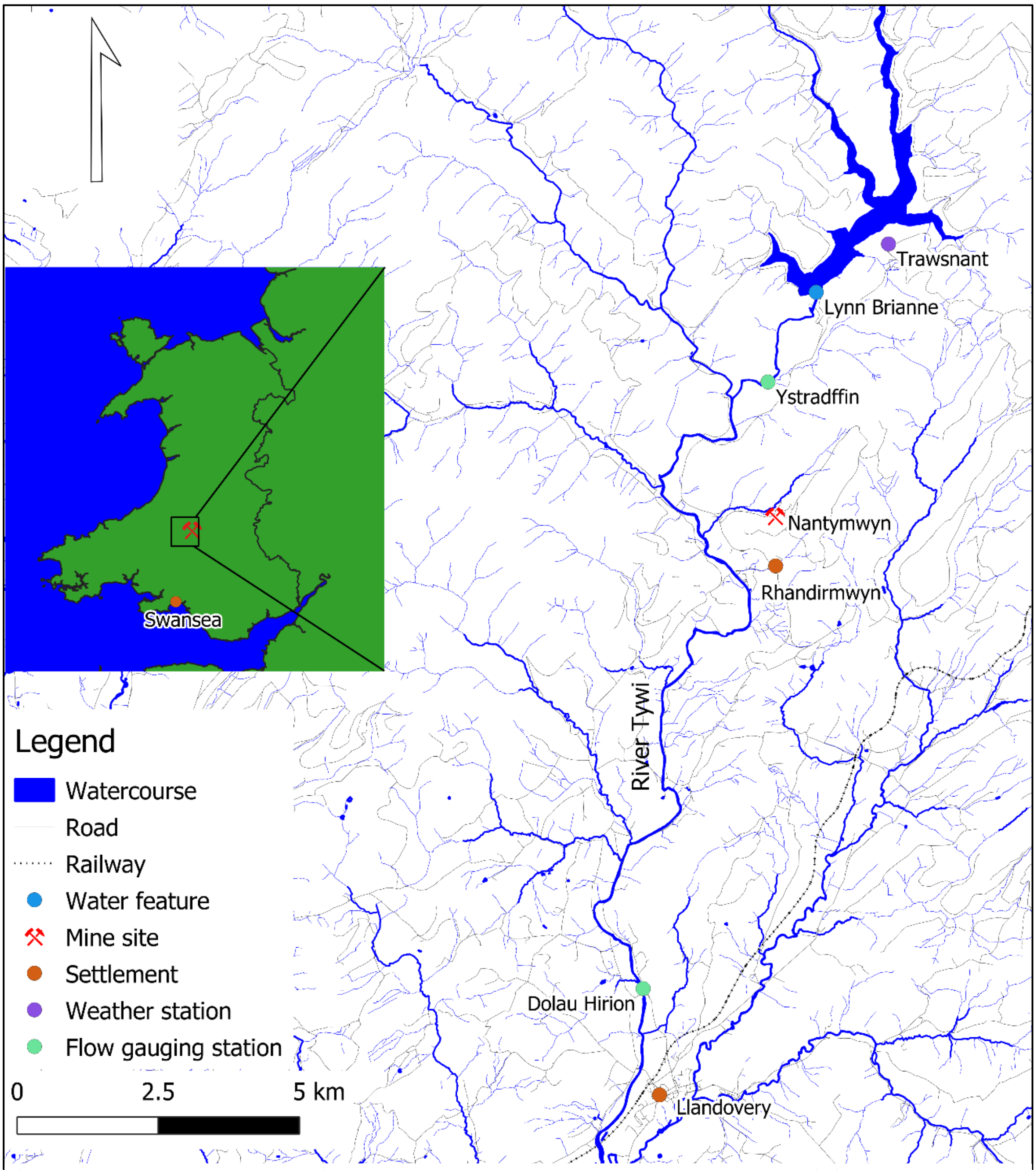

Figure 3-1 – Nantymwyn located with water features and local settlements. Nantymwyn is in the centre, with the River Tywi flowing North to South, Rhandirmwyn to the South, and Llandovery to the far South

Flow Archive, 2023a, 2023b). The mine is located 5 km downstream of the Llyn Brianne Reservoir, a river regulation reservoir constructed in 1972 in the upper reaches of the Tywi catchment, and the flows gauged at Ystradffin are heavily affected by releases from the reservoir (National River Flow Archive, 2023a). Even following the dam's construction has the ability to overtop its banks substantially, with flooding in October 1987 washed away a railway bridge in Llandeilo, with the loss of four lives (Frost and Jones, 1987; Lewin et al., 1981; Railway Inspectorate, 1990). The mean flow at Ystradffin is 4.26 m^3s^{-1}, between 1983-2023, at Dolau Hirion it is 10.215 m^3s^{-1}, for the time period of 1968-2023 (National River Flow Archive, 2023b, 2023a). The highest recorded flow at Ystradffin was 67.17 m^3s^{-1}, and at Dolau Hirion it was 374.379 m^3s^{-1}, both recorded in October 1987. This thesis focuses on two sub-catchments of the Tywi, the Nant y Bai, and the Nant y Mwyn, affected by the abandoned Nantymwyn metal mine (Figures 3-1, 3-2, and 3-4).

There are no weather stations at Nantymwyn or Rhandirmwyn, but an automatic weather station was operated at Trawsnant from 1985-1990, as part of the Llyn Brianne Acid Waters Project (Walsh and Boakes, 1991a). Two flow gauging stations on the River Tywi also record daily rainfall (Table 3-1) (National River Flow Archive, 2023b, 2023a; National Rivers Authority Welsh Region, 1992). Measurements taken for the Llyn Brianne Acid Waters Project showed that there is a positive relationship between altitude and rainfall at Trawsnant, with an average increase of 0.00119 mm mm^{-1} rain m^{-1} altitude difference[a] (Walsh and Boakes, 1991b). During orographic enhancement storms this increase was as high as 0.00318 mm mm^{-1} m^{-1} (Walsh and Boakes, 1991b). Ystradffin is situated in a steeply sided valley, and its lower mean annual rainfall compared to Dolau Hirion, despite its higher altitude, may be as a result of hill shade (Table 3-1). The highest point of the Nant y Bai stream is at an altitude of 458 m, and joins the River Tywi at an altitude of 117 m (Figure 3-2, top). The Nant y Mwyn stream descends from 365 m to 112 m (Figure 3-2, bottom). The catchment area for the Nant y Bai is 3.239 km^2; for the Nant y Mwyn, 1.156 km^2 (Figure 3-3). The highest point in the Nant y Bai catchment is 487 m, and for the Nant y Mwyn, 452 m (Figure 3-3). The upland station at Trawsnant is the best indicator of rainfall for the Nant y Bair and Nant y Mwyn catchments. Trawsnant has a mean annual

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[a] Rate of increase is expressed as millimetres increase in rainfall per unit millimetre, per metre increase in altitude (Walsh and Boakes, 1991b)

railfall of 2,032 mm, with mean monthly falls ranging from 107 mm in May, to 264 mm in December (Table 3-2). The frequency of heavy rainfall is also of note for flushing effects on the contaminated catchments, with the days with > 25 mm of rain (16.3) compared to Swansea (4.3) and southeast England (1) (Walsh and Boakes, 1991b)

Table 3-1 – Annual rainfall data at stations in the Tywi catchment (National River Flow Archive, 2023a, 2023b; Walsh and Boakes, 1991b)

Raingauge location	Mean annual rainfall (mm)	Altitude (m)	Period
Trawsnant	2,032	372	1985-1990
Ystradffin	1,711	117	1961-2017
Dolau Hirion	1,825	80	1961-2017

Table 3-2 - Mean monthly rainfall, and daily rainfall frequency at Trawsnant 1985-1991 (Walsh and Boakes, 1991b)

Month	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec
Mean rainfall (mm)	232	151	197	123	107	125	132	189	114	225	193	264

Rainfall regime	Rain days	Days >10 mm	Days > 25 mm
	236	78.3	16.3

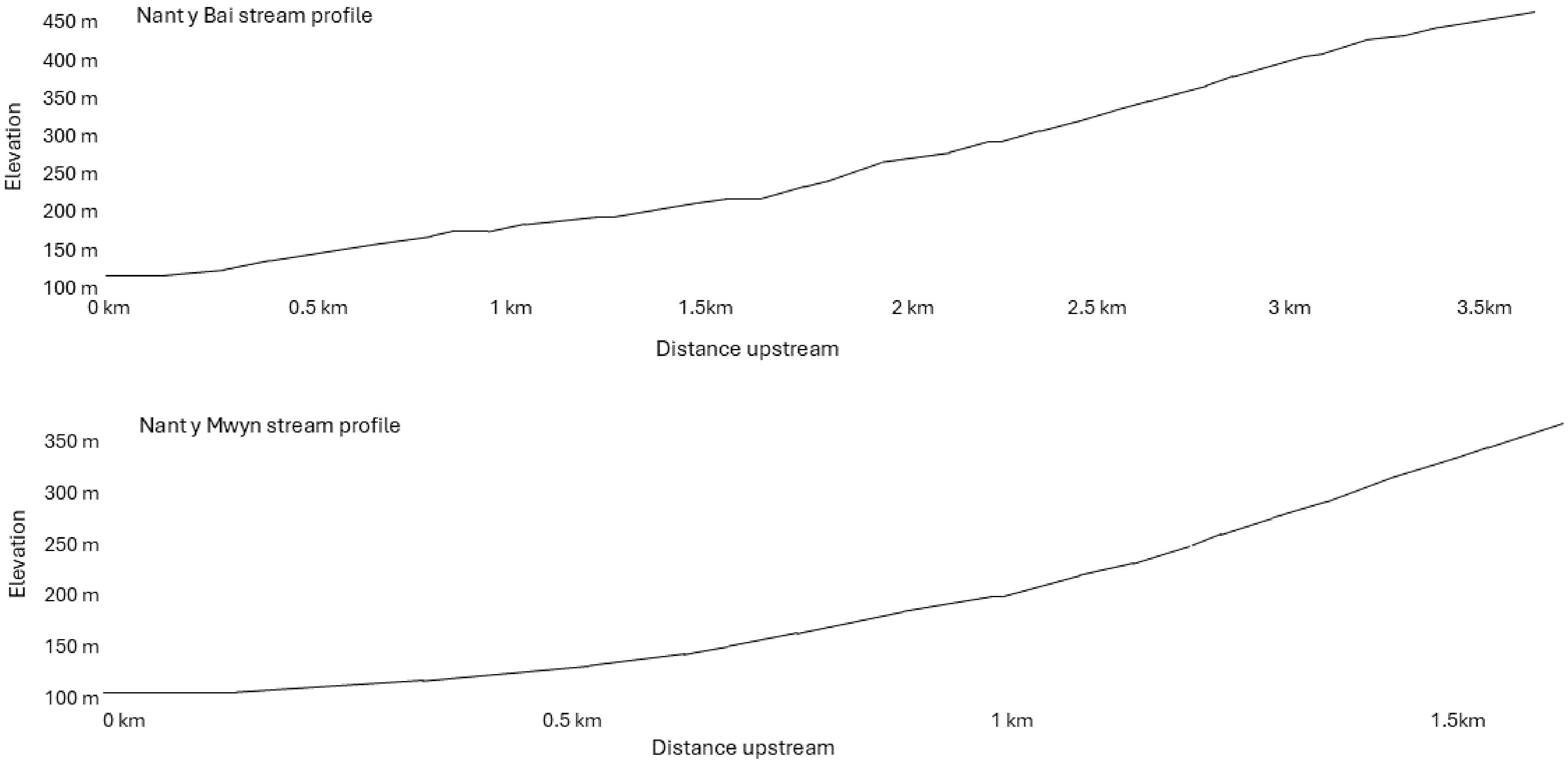


Figure 3-2 - Stream profiles of the Nant y Bai (top) and Nant y Mwyn (bottom), based on (Ordnance Survey, 2018)

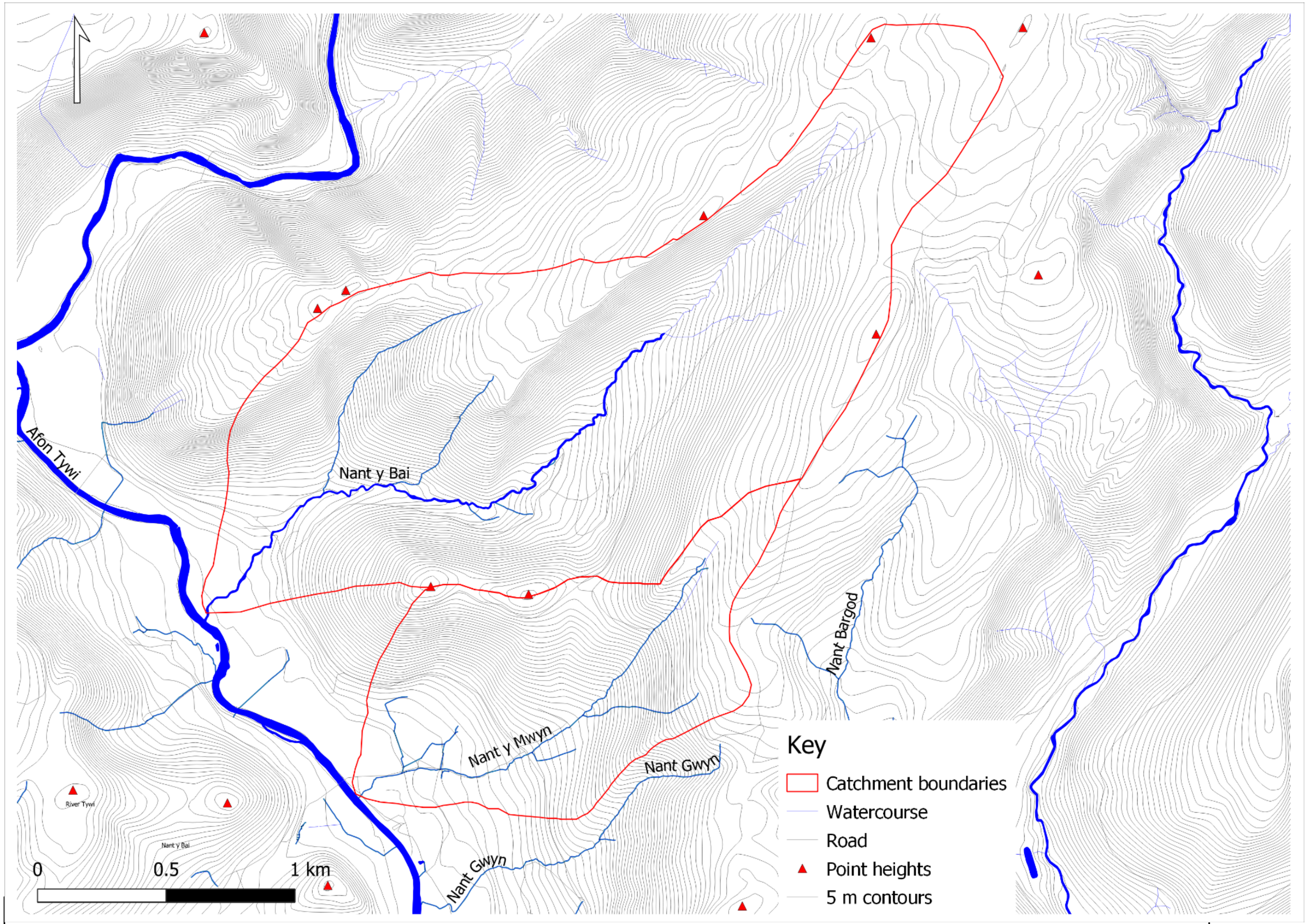


Figure 3-3 - Catchment boundaries of the two studied catchments, with 5 m contours and spot heights (Ordnance Survey, 2018)

3.2 Geological and Mining Context

Nantymwyn mine is located on Bala (Upper Ordovician) shales and grits, with mineral veins carrying lead ore in the form of galena (PbS) and zinc ore in the form of sphalerite ($(Zn,Fe)S$) (Al-Atia and Barnes, 1975; Todd et al., 2024b). The two main mineral lodes, of Silurian and Ordovician age, cross the site in a north-easterly direction, with noted pockets of secondary mineralisation in the form of Cerussite ($PbCO_3$) and arsenic bearing Pyromorphite ($Pb_5(PO_4)_3Cl$) (Bevins, 1994; Bevins and Mason, 2010). These veins, along the Abergwesyn Fault, have only undergone heavy exploitation at Nantymwyn mine, as elsewhere in the county they are steeply dipping, with short sections of mineralisation, and less than a metre wide, making them uneconomical to work (Davies et al., 2006). Despite this, the mineral lode was also worked further 7 km north east; at Abergwesyn (which later traded as East Nantymwyn, to capitalise on the main mine's name), and at Trawsnant which were managed together in the 1860s (Foster-Smith, 1981). Another mine following the same lode and trading off Nantymwyn's successful name was North Nantymwyn, which was worked from 1800-1810, and again from 1860-1864 (Foster-Smith, 1981). West Nantymwyn was yet another attempt to trade off the name and catch the same vein, this time on the west bank of the Tywi, between 1850-1852, but with little success, raising just one ton of ore (Warren, 1994). A second "West Nantymwyn", further south-west than the first, also known as Penrhiw-Rhaiadr, was worked between 1856-1857 and encountered old mine workings, but raised no ore (Foster-Smith, 1981). Where visible on the surface, this mineralisation has been considered for listing as an SSSI for geological interest since 2010, but this has not materialised (Bevins and Mason, 2010).

The surface remnants of mining activities, in the form of spoil and tailings, vary in metal concentration and grain size depending on which periods of operation they were formed under, XRF measurements showed means of 1.53 wt. % Pb and 0.18 wt. % Zn at the upper mine wastes aera, (Figure 3-4), and 3.59 wt. % Pb and 0.33 wt. % Zn at the lower mine wastes area Figure 3-6 (De-Quincey, 2020). These mine wastes cover approximately 45 acres of the mine site, and impact two streams the Nant y Bai to the north, and the smaller Nant y Mwyn to the south. The Nant y Bai flows through mine waste heaps covering around 18 ha, and the smaller Nant y Mwyn, which receives input directly from the Deep Boat Level (Figure 3-6). Both streams are circumneutral, with 75% of pH values being between 6.6 and 7.2 (n = 471). Although the site offers ecosystem services in the form of timber sales and recreational activities, the detrimental impacts on streams and habitats are a serious concern (Boldy et al., 2021). There are currently plans to use the upper mine wastes as an off-road mountain bike park (Geraint John Planning, 2024), and erosion of the mine wastes by mountain bikes is visible (Figure 3-4). As well as this diffuse contamination source, there are point sources, the largest being the Deep Boat Level on the Nant y Mwyn, an adit which drains the mine workings 228 m above it, the Upper Boat Level, which drains into the banks of the Nant y Bai (Figure 3-5), and the Pannau Adit into the Nant y Mwyn, though all three are now collapsed. In the lower photo in Figure 3-5 there are two ducks in the water of the flooded shaft. The owner stated later in the year

Figure 3-4 - the upper mine wastes at Nantymwyn, with NRW 4x4 for scale. Erosion to the mine wastes can be seen, from both surface water flow, and dirt bikers.

that they had died shortly afterwards, and later studies of fowl in the area showed their propensity to accumulate Zn (Sartorius, 2019b). The National Rivers Authority's ranked Wales's top 20 worst polluting metal mines, and judged Nantymwyn the worst affected site for biological aesthetic impact, from the blue-green algae at the Deep Boat Level (Gething, 1999). These metals-tolerant algae were thought to be especially evident as a result of high Zn concentrations preventing macroinvertebrates from surviving in the water and grazing the algae (Gething, 1999). Both the Nant y Mwyn and the Nant y Bai showed a decrease in species richness and biological quality downstream of the mine

Figure 3-5 - The collapsed Upper Boat Level, top left, and crown of the blocked Deep Boat Level, top right (P. Edwards). The flow over the crown is from the flooded shaft in the lower photo.

workings, with the Nant y Mwyn most affected, though the upstream sites showed lower quality than predicted by RIVPACS III+ (River InVertebrate Prediction And Classification Scheme) modelling. The River Tywi did not show signs of biological impact to macroinvertebrates after the mine site, though the blue-green algae from the Nant y Mwyn continued into the River Tywi (Gething, 1999). This blue-green algae was not evident at any site visits for this PhD.

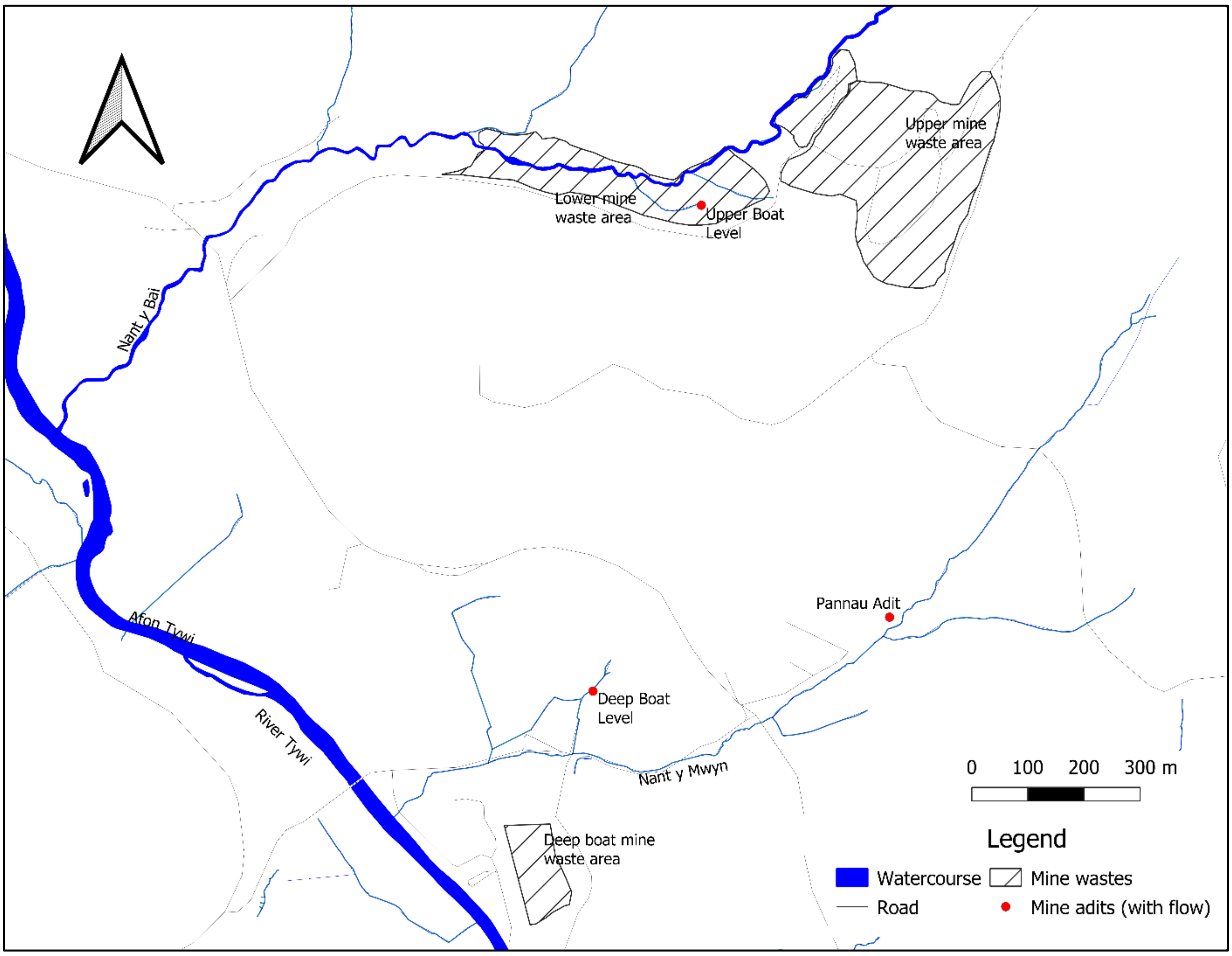


Figure 3-6 - Nantymwyn mine wastes, watercourses, and location of main mine adits

Both streams flow into the River Tywi, a 120 km long river, and an important salmon and brown trout spawning area (National Rivers Authority Welsh Region, 1994; Natural Resources Wales, 2017). Completed in 1972, the Llyn Brianne River Regulation Reservoir was built 5 km upstream from Nantymwyn to regulate the flow of the River Tywi (Figure 3-1), increasing the magnitude of low flows and to ensure a reliable water supply at the abstraction point, 55 km downstream at Nantgaredig. Carmarthen is supplied with water, after treatment, near to the abstraction point at Capel Dewi, whilst most of this supply is piped 26 km to Felindre. After treatment at Felindre treatment works drinking water is piped to Swansea, Neath, Bridgend, and the Vale of Glamorgan, and in times of drought additionally to the Neath, Afan and Tawe valleys (Welsh Water, 2019). A second abstraction point on the Tywi at Manorafon is also used during droughts to supply the upper Swansea Valley (Welsh Water, 2021). Following dam construction, the increased low flow will also have likely improved Tywi water quality by increasing dilution of metal inputs from the Nant y Bai and Nant y Mwyn. Many of the streams flowing into Llyn Brianne have been monitored, first to investigate the causes of acidification, and then for their recovery from acidification since 1981 (Edwards et al., 1990; Ormerod and Durance, 2009), allowing a comparison between these sites and the two streams at Nantymwyn.

The construction of Llyn Brianne dam used approximately 250,000 tonnes of spoil removed from the mine site (Hughes, 1992). The remaining wastes at Nantymwyn, apart from some lichens and bryophytes, remains bare. The spoil and tailings from the underground workings, principally contaminated with Pb and Zn, which are spread over the site have oxidised, increasing the rainwater dissolution of metals before the water enters the Nant y Bai (Cidu et al., 2011). The steeper hillsides away from the mine have been used for coniferous plantation since the 1960s (Figure 3-7), but most of the catchments are under rough pasture (Todd et al., 2024b).

During operations, the mine was primarily drained via the boat levels, which were flooded to allow the transport of boats loaded with ore (Fellows, 2009; Hall, 2011), one of which, the Deep Boat Level, still drains the mine into the Nant y Mwyn (Figure 3-5). Mine workings continued below the level of the Deep Boat Level vertically for another 70 m, with six levels worked for ore. During operation water was pumped from these lower levels up to the Deep Boat Level to drain from the mine via gravity (Hughes, 1992). These deepest workings were abandoned after 1900, and the water table had rebounded to the Deep Boat Level by the time the rest of the mine was abandoned in 1932 (Hughes, 1992).

The mine has complex subterranean workings, most of which are unmapped; even the mapping undertaken before closure by the well qualified mine manager Joe Nile is unlikely to have included blocked or previously abandoned workings (Fellows, 2009, 1993). Mapping performed by Joseph Argyle was destroyed by the owners, The Sulphide Corporation Ltd., on the basis of them being falsified (Hughes, 1992). The few surviving maps of the underground workings give some understanding of the connections that may still exist between the adits that remain visible on the surface. Despite Captain Nile following orders to seal the mine entrances, access has been attained through the years by various interested parties, in particular mine explorers and cavers. The 1970s was busiest in this and saw access from the South Wales Caving Club, Welsh Mines Society and individuals including David Bick and George Hall, both of whom documented the histories of various metal mines across Wales. Between them various sketch maps of the mine workings 40+ years after its closure exist (Davies, 1971; Fellows, 2009, 1993; Hall, 2011). These are, however, more useful for mine explorers, but in some cases could

Figure 3-7 - Nantymwyn looking north-west. The conifer plantation is being harvested for the first time, allowing a view across the site. Nearest the camera is the Grade II listed engine house and chimney, then the 1920s concrete ore bunker and dressing floor. The tracks graded for the forestry operations are clearly visible against the grey mine wastes. The Nant y Bai stream is in the valley, its location and flow indicated by the blue arrow.

raise awareness of a subterranean hydrological connection that is not possible to ascertain from the surface.

Along with other metal mines, Nantymwyn was highlighted in the press in early 2024 for its role in contaminating eggs in a nearby farm (Hughes, 2024; Sartorius et al., 2022a). This led to the Welsh Affairs Committee hosting a special session to investigate the scale of metal mine pollution in Wales (Welsh Affairs Committee, 2024).

3.3 History of the Nantymwyn mine

Nantymwyn (also Nant y Mwyn, Nant y Mo(w)en, Cerrigmwyn, Carreg y Mowyn, Rhandirmwyn, and Pen Cerrig y Mwyn), was the largest base metal producer in South Wales, and was worked sporadically from Roman times until final abandonment in 1932 (Fellows, 2009; Hall, 2011; Hughes, 1992). Key events in the history of the mine (Fellows, 2009; Hall, 2014, 2011; Hughes, 1992) are summarised in Table 3-3.

Table 3-3 - key events in Nantymwyn's history

Year (AD)	Activity at Nantymwyn
70-160	Roman hush working: water was stored in a dam, fed by a constructed leat, and "hushed" over the hillside to remove lighter soils and reveal heavier metals. This was often combined with fire on the surface before releasing the water, the resulting thermal shock cracking stones and exposing the metals.
1530	"Peter the German" surveys British mines, noting a medieval lead mine in use in Rhandirmwyn.
1530	The Black Book of St Davids notes an active lead mine near Llandovery
1641	Lease signed for mining, though no evidence any was happening at this time
1747	Crown Agent for Cardiganshire notes the mine as actively raising lead ore
1775	910 tons of concentrates sold
1780	John Rolley becomes manager, and the Upper Boat Level is completed, potentially supervised by Robert Shore, an advocate for this style of mine operation
1785	Deep Boat Level is started, completed 13 years later

Year (AD)	Activity at Nantymwyn
1792	Mine's terrestrial workings, and Rhandirmwyn, are painted by Warwick Smith. Around 400 people are employed in the mine, raising 1200 tons of lead concentrates
1805	John Rolley dies, being replaced by Joel R.B. Williams. Production drops to 300-500 tons p/a
1814	113 people are employed by the mine, as the price of lead drops considerably
1823	Joel Williams is dismissed, and the mine is managed by its owner, Earl Cawdor
1825	Ellis, Pugh & Co. take over management of the mine
1830	Work is suspended due to the continued low lead prices
1832	Williams, Pugh & Co. surrender their lease
1836	The Williams Brothers, Michael and William, take on the lease on the mine
1850	Lowest point of the mine, 33 fathoms (~66 metres) below the Deep Boat Level is reached
1861	The Tywi is named in Parliament as being "polluted" by metal mines (Fisheries Preservation Society, 1868)
1865	Railway line reaches Llandovery, reducing the costs of getting the ore to the smelters in Llanelli, which smelted Nantymwyn lead until 1910 (Evans, 1935)
1867	Funds raised to open "new" mine
1874	385 tons of lead, and 1,651 oz of silver, worth £6,673, is raised from the mine (Hunt, 1875)
1875	Mine liquidated and assets sold (The North Wales Chronicle and Advertiser for the Principality, 1875)
1890s	Joseph Argall, mine manager, constructs the Angred Shaft, with a steam engine at the top for pumping water out of the mine
1900	Williams Brothers leave the mine, selling their steam engine. They estimated that they had 23 miles of levels underground
1915	Production restarts, with Joseph Argall both managing the mine and owning the lease, employing 33 people
1926	The Sulphide Corporation Ltd. of Australia acquires half of Joseph Argall's company
1929	New Shaft, sinking 118 metres, is dug in just 3 months

Year (AD)	Activity at Nantymwyn
1929	Joseph Argall dies on the 30th November, being replaced by Captain Joe Nile
1930	Full scale mining begins, only to discover Argall's plans are inaccurate, and his measurements of metal concentrations in the ores optimistic
1931	Nile works on clearing out shafts and levels of mud and rockfalls, with a few tons of ore raised
1932	All work halted on the 30th November, after poor metal values found in the Deep Boat Level. With money having run out, The Nantymwyn Mine Ltd. goes into receivership (Haynes and Archibald, 1933)
1934	Mine plant equipment sold and exported South Africa
1937	The Nantymwyn Mine Ltd. is liquidated
1942	Thomas Eastwood conducts a survey into the feasibility of reopening the mine for the Second World War effort
1966	Earl of Cawdor sells the land the mine is situated on to the Economic Forestry Group
1969	Llyn Brianne Dam project acquires approx. 250,000 tonnes of rock, tailings, and spoil for use in the dam
1971	Seven tonnes of galena is picked by hand (Brown, 1986)

Initially mining operations were conducted on the surface using 'hushing', then work moved underground, resulting in a complex subsurface system of workings (Hall, 2011). Hushing is an ancient mining technique, where water is stored to be later released over ground with surface or very shallow subsurface metal ores, washing away lighter soil and leaving behind heavier ores (Timberlake, 2002). This was sometimes supplemented with fire-setting, where the ground would be heated by fire before the hushing, with the rapid change in temperature aiding the release of the ore (Timberlake, 2002). Evidence of the leats created in order to hush were visible at Nantymwyn as recently as 1973, but have subsequently been hidden, and potentially destroyed, by tree plantations (Brabham and Umar, 2011). Analysis of the peat filling some of the leats suggests that they went out of use between 520 and 620 AD (Timberlake, 2003).

Surviving records show that it was the third most productive non-ferrous metal mine in South Wales between 1824-1900, raising over 81,000 tonnes of galena (Hall, 2014). Despite approaching closure, even in the 1890s the mine supplied 2% of the UK's total Pb demand (Hall, 2011; Her Majesty's Inspectors of Mines, 1896). A reduction in the commercial value of Pb and poor decisions by the mine's management resulted in the mine closing in the 1900s, before briefly reopening in the 1920s (Hall, 2011). The mine was considered for reopening in 1942 to provide Pb for the war effort, but it the plan was abandoned as too much work was required to re-open the mine (Hughes, 1992).

The mine's Boat Levels are unusual (Roberts, 1981), with a depth of water established deliberately in order to give flotation to small boats, which were used to take ore out of the mine, and when the steam engine was in operation, bring coal into the mine to be raised up to it (Hughes, 1992). This practice is noted, though not pictured, in a painting by Warwick Smith in 1792, which also shows constructed wharves on the Tywi banks, and a watermill, which is conceivably the Nant-bai Mill (Smith, 1792a, 1792b). Nant-bai is a Welsh name; Nant means stream, and bai could mean blame, as in blaming the stream for flooding, or lead contamination, or it could be read as fault, as in geological fault (Blaenau Tywi History Group, 2014).

In 2021, as part of a survey of the archaeological features of the site, the mine area of surface workings was recorded with a Light Detection and Ranging (LiDAR) sensor attached to a drone. The principle of LiDAR is sending out a laser beam, and measuring the time taken for the reflected beam to return to the received. Two heights can be measured with a LiDAR sensor, the ground surface itself, creating a Digital Terrain Model (DTM), or the height of features on the ground, such as trees and other flora, creating a Digital Elevation Model (DEM).The LiDAR data collected in 2021 was for both DTM and DEM, at a 25 cm resolution, and has been rendered in Figure 3-8, with blending to show the OS map features through the model. On the DTM some historic mine features are visible, with potential hushing features to the south, and evidence of previous reservoirs to the north. The DEM shows how many of these features are covered by the trees and vegetation, and are not visible on the ground. The European Environment Agency's CORINE land cover map, based on satellite data and produced at a resolution of 100 m, states that the mine is covered by mixed forestry (European Environment Agency, 2020).

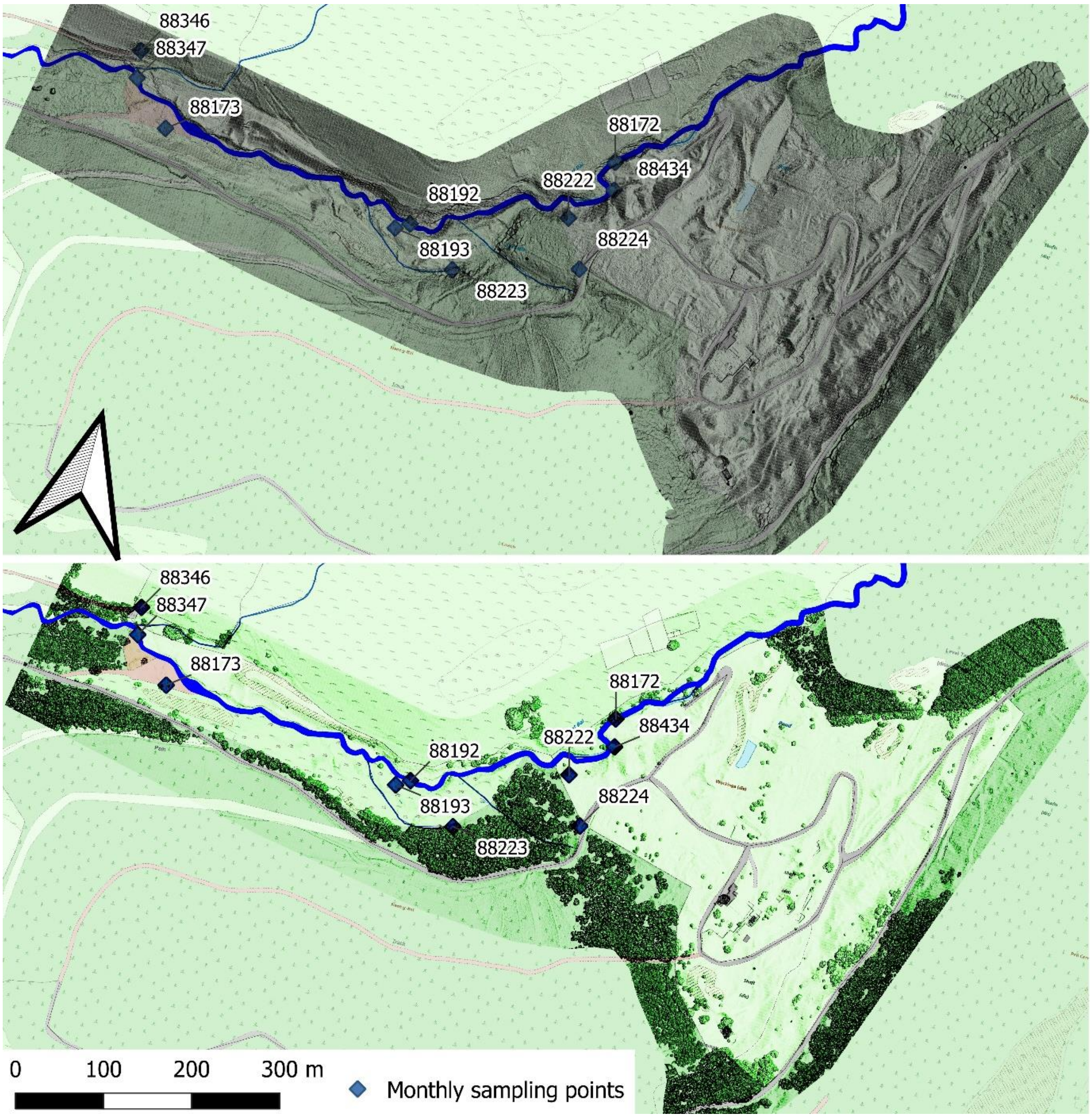


Figure 3-8 - Digital Terrain Model, top, Digital Elevation Model, bottom

3.4 Previous metal contamination studies at Nantymwyn

Concerns about the impact of contamination from abandoned metal mines were raised before the mine closed. Similar mines in both ore, scale, and period of operation located on the rivers Rheidol and Teifi were reported to increase fish mortality rates during high flow events in the 1920s (Carpenter, 1926, 1924). Contamination from metal mines more generally was raised in Parliament at least 70 years prior to that (Fisheries Preservation Society, 1868). Complaints about the impact of Nantymwyn mine on visual water quality and fish mortality were first recorded in the 19th century (Towy Board of Conservators, 1871). Independent researchers have investigated the Tywi's trace metal contamination, for which Nantymwyn is the only source (Wolfenden and Lewin, 1978). As part of a larger project, Wolfenden and Lewin sampled 12 sites on the Tywi; one above the mine, one at the outflow of the Nant y Mwyn, and ten below, discovering elevated concentrations of Cu, Zn and Pb for the 12km sampled (1978). NRW's predecessors contracted investigations into the contamination and to consider possible remediation schemes in 1974, 1986, 1997, and 2010, with studies to improve understanding of the site ongoing throughout (Brabham and Umar, 2011; Brown, 1986; Owen, 1988; South West Wales River Authority, 1974; SRK (UK) Ltd, 1997). The site's complexity and funding difficulties, however, meant none of these proposed remediation schemes were implemented.

Table 3-4 - Top 15 highest impacting metal mines in Wales (Environment Agency Wales, 2002; Mullinger, 2004).

Rank	**Mine**
1	Parys
2	Frongoch
3	Cwm Ystwyth
4	Ty'n-y-Fron
5	Dylife
6	Cwm Rheidol
7	Esgairmwyn
8	Frongoch
9	Cwm Symlog
10	Gwynfyndd
11	Nantymwyn
12	Esgairmwyn
13	Nantycreiau
14	Penycefn
15	Ystumtuen Plateau

After the publication by the Environment Agency of *A Metal Mine Strategy for* Wales in 2002, collating the top 50 metal mines by their perceived environmental impact, based on the data available at the time (Table 3-4) (Environment Agency Wales, 2002). Nantymwyn was subsequently ranked the 11th highest impacting metal mine in Wales (Mullinger, 2004). Contamination from the mine causes the River Tywi to fail Water Framework Directive (WFD) standards for Zn for approximately 25 km below the confluences with the Nant y Bai and Nant y Mwyn, with the elevated concentrations of Zn from the mine detectable in the entire 70 km of river below the mine confluences (Natural Resources Wales, 2022; Williams, 2012). In 2020 the Coal Authority took over management of non-coal mine remediation and management in Wales, and reported on mines considered to be highest impacting to the environment, ranking Nantymwyn 2nd (Coal Authority, 2020a). As part of the Coal Authority’s management, Dyfed Archaeological Trust conducted a site visit with the author of this thesis to identify historic features (Bell, 2021). This report highlighted 11 areas of the mine as being of archaeological potential, with seven areas of national importance in mining heritage, and the care and conservation needs of the site were highlighted for protection against any invasive remediation techniques (Bell, 2021). The Coal Authority itself undertook a site visit in 2018 to highlight any hazards to people accessing the site, such as collapsed shafts or unmarked voids (Coal Authority, 2019a). Water quality and related research conducted specifically into Nantymwyn is shown in Table 3-5 below:

Table 3-5 - Previous investigations of metal contamination and possible remediation strategies at Nantymwyn Mine, and mean Zn and Pb concentrations recorded in the Nant y Bai at or near to its confluence with the River Tywi

Year	Title	Type	Zn (µg L^{-1})	Pb (µg L^{-1})
1986	The Effects of Abandoned Metal Mines at Rhandirmwyn on the Quality of the Upper River Tywi (Brown, 1986)	Government report	620	330
1988	Further Studies Concerning The Effects Of Abandoned Metal Mines At Rhandirmwyn On The Quality Of The Upper River Tywi (Owen, 1988)	Government report	770	360
1992	Nant y Mwyn Mine, Llandovery, Dyfed (Hughes, 1992)	Journal article	No data collected	No data collected
1997	Nant y Mwyn Site Report (SRK (UK) Ltd, 1997)	Consultant report	950*	330*
2004	An investigation into the impact of Nantymwyn metal mine on water quality (Lowe, 2004)	Master's thesis	510	290
2009	The mobility of lead from a disused mine along the River Towy (Chinnery, 2009)	Master's thesis	620	380
2010	Enivronmental Impact and Regeneration of Rhandirmwyn Mine (Umar, 2010)	Master's thesis	330*	91*
2011	Nant y Mwyn Metal Mine Scoping Report (Environment Agency Wales and Atkins Limited, 2011)	Government report	No data collected	No data collected
2011	Developing a conceptual model for Nantymwyn (Rhandirmwyn) Lead Mine, Carmarthenshire, Wales, as a means to assess its environmental impact legacy. (Brabham and Umar, 2011)	Journal article	No data collected	No data collected

Year	**Title**	**Type**	**Zn (μg L^{-1})**	**Pb (μg L^{-1})**
2011	Assessing the hydrological and hydrogeological impacts of Nantymwyn Lead Mine contaminated mine site (Thompson, 2011)	Master's thesis	7,000	50
2012	A&R_SW_12_03 WFD Investigation: Abandoned Mines Project Afon Tywi (Williams, 2012)	Government report	490	230
2014	Land Availability Survey for Metal Mine Treatment Systems (CH2M Hill, 2014)	Consultant report	No data collected	No data collected
2019	Nant y Mwyn - Surface Water Inflow and Blow Out Prevention Report (Coal Authority, 2019b)	Government report	No data collected	No data collected
2020	Catchment Report – Tywi (Coal Authority, 2020b)	Government report	No data collected	No data collected
2020	The development of a surrogate soil to assist the revegetation and stabilisation of metal-mine tailings (De-Quincey, 2020)	PhD thesis	No data collected	No data collected
2021	Nant y Mwyn: Initial Mine Water Treatment Review (MEM, 2021)	Consultant report	No data collected	No data collected
2021	Source Apportionment of Trace Metals at the Abandoned Nantymwyn Lead- Zinc Mine , Wales (Todd et al., 2021)	Journal article	Covered in this thesis	
2022	Human health implications from consuming eggs produced near a derelict metalliferous mine: a cast study (Sartorius et al., 2022a)	Journal article	780	3,300
2022	Using Tracer Injection and Synoptic Sampling, and Salt Dilution Flow to Gauge Metal Fluxes in a Temperate Watershed in the UK (Todd et al., 2022)	Journal article	Covered in this thesis	

Year	Title	Type	Zn ($\mu g L^{-1}$)	Pb ($\mu g L^{-1}$)
2022	Treatment of mine water for the fast removal of zinc and lead by wood ash amended biochar (Cairns et al., 2022a)	Journal article	Covered in this thesis	
2024	Identification and quantification of diffuse groundwater pollution in a mineralised watershed (Todd et al., 2024a)	Journal article	Covered in this thesis	
2024	Long-term changes in water quality downstream of three abandoned metal mines (Todd et al., 2024b)	Journal article	Covered in this thesis	

*Different sampling point used.

The pre-2000 government reports are unfortunately low-quality scans of the originals which are no longer available, and this renders much of their photographs and figures illegible, with most of the 1980s reports' conclusions and data missing. What is now NRW has gone through several reorganizations, separations, and integrations, since the first of these reports was published, and their physical offices have moved, sometimes at quite short notice, with these changes. The part of NRW responsible for water quality at Nantymwyn's location has its predecessor organisations in: Environment Agency Wales 1996-2013, National Rivers Authority 1989-1996, Welsh Water Authority 1984-1989, Welsh National Water Development Authority 1973-1984, and the South West Wales River Authority 1965-1974.

The 1986 and subsequent 1988 reports for the Welsh Water Authority, a predecessor of NRW, give information on investigative monitoring undertaken as a result of complaints about poor fishing in the River Tywi immediately downstream of the Nant y Mwyn stream confluence. The position of Welsh Water before undertaking sampling along both streams was that any contamination would be in a very small geographic area and was not affecting the River Tywi (Brown, 1986). Having discovered that this was not the case, further investigations were undertaken, and these studies confirmed that the mine workings were responsible for 12 km of the River Tywi failing European Community regulations for Zn concentrations (0.03 mg L^{-1}), which it was subject to as a designated salmonid fishery (Owen, 1988). Despite the mine having closed over fifty years earlier, Owen was able to speak to a retired miner who gave some information about mine shaft and adit locations. Unfortunately, the earlier report is truncated in the NRW archive, yet this is the most complete copy available. The later report is almost complete except for the graphs. The data from both was digitised onto the NRW water quality archive. The Welsh Water Authority was privatised in 1989, and its regulatory functions passed to the National Rivers Authority. It is unclear if any of Owen's recommendations for treatment studies were completed (Bakker, 2005; Owen, 1988).

Simon Hughes's article is largely concerned with the history of the mine, however, his maps locating adits and shafts, as well as underground workings, are particularly useful for navigating the site and understanding the subterranean nature, and why certain areas of the site may have higher or lower concentrations in the mine wastes due to their previous uses (Hughes, 1992).

The 1997 SRK Consulting report gives the results of a single round of water quality sampling over the site, which was used to consider different high-level options for dealing with the wastes, and treatment of the contaminated waters (SRK (UK) Ltd, 1997). Although fewer points were sampled, the sites used corresponded to some of those used in the Welsh Water study conducted in 1986 and 1988. Unfortunately, the appendices are no longer available, but the general design of the remediation was described in the text, and consisted of reprofiling and capping the mine wastes, and lining the streams. It was proposed to treat the Deep Boat Level with a semi-passive system, the specifics of which were not described, with a total estimated cost of just under £4 million (SRK (UK) Ltd, 1997). SRK also recommend regular monitoring of both flow and water quality in order to guide remediation at the site. A lack of funding meant that none of these suggestions were adopted (Edwards, 2021a).

The first decade of the 21st century saw three Masters theses examining Nantymwyn, first in 2004 by Matthew Lowe at the University of Wales, Aberystwyth. This research was supported by EAW, having identified a data gap during the writing of *Metal Mines Strategy for Wales* (Environment Agency Wales, 2002; Lowe, 2004). Water samples and concurrent flow estimates were taken at six sites on the Nant y Bai, and four on the Nant y Mwyn, as well as two sites on the River Tywi, upstream and downstream of the mine's inflows, on eight occasions between January-March, May-June, and December 2003, and in January 2004 (Lowe, 2004). At most sites, flow was measured using a current meter, which in the irregular cross-section of these uplands streams is unlikely to be accurate (Littlewood, 1986). The thesis concluded that there was a strong positive correlation between flow and Pb concentrations, and that the mine has little to no impact on the main river, but does highlight the limitations of the low number of samples taken, and the irregular sampling frequency used.

Ella Chinnery (2009) examined the mobility of Pb from Nantymwyn, sampling and analysing sediments as well as water, undertaken from Cardiff University (Chinnery, 2009). A single run of sampling was taken, at 19 points across the mine and in the River Tywi, both upstream and downstream of the Nant y Bai and Nant y Mwyn confluence inputs. Analysis of these samples revealed that the River Tywi had elevated concentrations of Fe upstream of the mine, but not immediately downstream of the Llyn Brianne reservoir, suggesting that the tributary Doethie flows through an outcrop of Pyrite or similar (Chinnery, 2009). High concentrations of Zn and Pb were found in the mine wastes, and in presumed older sediments in the River Tywi. The Nant y Bai stream was found to have mobile Zn entering the River Tywi, where the larger flows diluted it substantially, but the main mine outflow at the Deep Boat Level was found to have very low concentrations of Zn, and overall the mine was considered to be of low environmental impact (Chinnery, 2009).This is in contrast to the research conducted at Nantymwyn before and since, which consider the Deep Boat Level to be the largest single point source of Zn for the entire River Tywi.

Another Master's thesis from Cardiff University followed in 2010 by Bappah Umar (Umar, 2010), which was summarised a year later in a journal article (Brabham and Umar, 2011). As well as detailing the history of the mine, and digitising surviving underground plans, a 3D conceptual model of the mine workings in relation to the ore bodies was created (Brabham and Umar, 2011). Evidence of secondary mineralisation on the mine wastes was found, where weathering of PbS has led to a variety of minerals on the surface not found in un-weathered wastes (Umar, 2010).The need for further investigation of the causes of metal contamination within the streams was in particular highlighted.

These three Masters theses, and the 1980s Welsh Water reports, were summarised in the 2011 Atkins report to identify potential remediation options at Nantymwyn. The report also consulted with stakeholders and conducted a walkover of the site (Environment Agency Wales and Atkins Limited, 2011). Options were given for remediation, but these were extremely basic, lacking possible locations, estimated costs, or specific methods. The report also recommends further monitoring, especially of the hydrology of the Nant y Bai (Environment Agency Wales and Atkins Limited, 2011).

Stuart Thompson's 2011 Master's thesis from Cardiff University built on Lowe's work (Lowe, 2004), taking water quality samples from 31 points across the site, on six dates between July and August (Thompson, 2011). Where possible, concurrent flow gauging was undertaken at the same time, using either bucket and stopwatch, or a flow meter, though the limitations of using a flow meter in these upland streams was highlighted (Thompson, 2011). Dye tracing was used to identify if smaller mine entries were hydraulically connected to the Nant y Bai, but this was unsuccessful in either proving or disproving any connections (Thompson, 2011). A minor reduction in concentrations of all analysed metals at all sites was found compared to Lowe's thesis (Thompson, 2011), but this could be explained by the seasonal flow variations and flushing events that may have occurred, as this reduction has not been shown since (Todd et al., 2024b).

Following the River Tywi's failure of Water Framework Directive chemical standards for Zn and Cu in the 2010 cycle of WFD reporting, an investigation was undertaken by EAW to understand the cause of these failings (Williams, 2012). The water quality sampling programme undertaken during Thompson's thesis (Thompson, 2011) was continued for a further six occasions to ensure enough data for modelling how the mine may be affecting the River Tywi (Williams, 2012). The SIMulation of CATchments Environment Agency river water chemical quality model (SIMCAT) was used to model contaminant inputs from Nantymwyn. Combined with flow and water quality sampling undertaken on the River Tywi as part of routine WFD monitoring, this showed that Nantymwyn increased the concentrations of total Zn, and dissolved Cd and Pb in the River Tywi (Williams, 2012). The elevated concentrations of total Zn continue for the entire length of the River Tywi, to it tidal limits 65 km downstream (Williams, 2012). Dissolved Pb concentrations did not breach the WFD EQS, and dissolved Cd concentrations reduce to below the WFD EQS 10 km downstream of the mine site (Williams, 2012). SIMCAT modelling was also used on the Nant y Bai, however, the model does a poor job in predicting stream flows and metal concentrations, as is it designed for major river catchments. The report recommended adjustments to the WFD monitoring points on the River Tywi used for WFD classification, which results in the River Tywi now only failing WFD EQS for total Zn for 25 km downstream of Nantymwyn (Coal Authority, 2020b).

The newly formed NRW contracted CH2M Hill in 2013 to consider the land availability for vertical flow ponds to treat contaminated mine discharges at six mines, including Nantymwyn (CH2M Hill, 2014). Three sites were considered and scored for their suitability against a criteria of access, topography, energy use, and environmental constraints, with one discarded, and the remaining two ranked into first and second preference. This possible vertical flow pond would have treated the discharge from the Deep Boat Level at Nantymwyn (CH2M Hill, 2014).

Following the list of priority metal mines from 2004, NRW has conducted a series of remediation measures at Frongoch Pb/Zn mine, substantially reducing the concentration of metals in the waters leaving the site(Edwards et al., 2021, 2016; Natural Resources Wales, 2016a). Research at other mines in the top 10 highest priority mines has continued, with experimental treatment systems at Cwm Rheidol, Frongoch, and Abbey Consols, and detailed consultant reports into those further down the top 10 (Edwards, 2021b). With Nantymwyn 11th, but based on a list compiled before an understanding of the River Tywi's metal load and the causes of it, detailed investigation at a lower cost was required, and hence this PhD was funded by the EU RDF, with support from NRW, to start in late 2018. This has resulted in several publications to date, which are built upon in this thesis (Todd et al., 2024b, 2024a, 2022, 2021)

Having been awarded an NRW contract to investigate the non-coal mine-caused failures of WFD, the Coal Authority reported on possible risks of the minewater being restricted, and blowing out of a blocked adit or shaft at metal mines across Wales (Coal Authority, 2019b). Building on Brabham and Umar's conceptual model with the Coal Authority's mine plan archive, the theoretical routes for surface water entering and exiting the mine workings at Nantymwyn were discussed, and recommendations were made for future flow and water quality monitoring to prepare for future remediation (Coal Authority, 2019b). The Coal Authority also issued an updated analysis of the WFD data and some SIMCAT modelling in 2020 (Coal Authority, 2020b). On the basis of the available data, this report estimated a total cost of £18.7 million to remediate Nantymwyn to a point at which the River Tywi would no longer fail WFD Zn standards, including treatment of water and capping of wastes (Coal Authority, 2020b).

Also in 2020, a Swansea University PhD thesis by De-Quincey was completed at Nantymwyn (De-Quincey, 2020), building on their previous work at Frongoch mine creating and testing surrogate soils (De-Quincey, 2017), to be used as a permeable low-cost capping alternative for mine wastes, and allowing revegetation of the wastes with metals tolerant grass species. This revegetation would stabilise the wastes, reduce erosion, and visually soften the waste piles, and has been used commercially at Frongoch after the completion of the capping, in areas which were not sealed with a geotechnical clay membrane (De-Quincey, 2020; Edwards et al., 2021).

Following the recommendations of the Coal Authority's 2020 report into future remediation, NRW contracted Mine Environmental Management to investigate what sort of treatment system would be best suited to the site. Two samples of water were taken from the Deep Boat Level in 2021 for analysis by Mine Environmental Management, to allow guidance for future treatment options for the water (MEM, 2021). The suggested method was to sparge the water for two hours, and then add NaOH as a base to increase the pH to 10, leaving water which passes or is close to passing the WFD chemical EQSs (MEM, 2021). The practicalities of NaOH dosing, a two hour holding time, and discharging water with pH of 10 were not considered.

Bioaccumulation of metals in animals from abandoned metal mines in Wales were studied in two papers by Sartorius as part of her PhD, one on Pb mines and bioaccumulation of Pb in freshwater macroinvertebrates (Sartorius et al., 2022b), and one specifically investigating Nantymwyn, and the accumulation of metals in eggs from chickens raised near the mine (Sartorius et al., 2022a). Two years later this research made headlines when a journalist from the Financial Times published a series of articles stating both the human health implications of this for metal contaminated foods, and more generally the lack of investment in researching or treating the legacy of metal mining in Wales (Hughes, 2024). A key finding is that eggs sold for consumption from Rhandirmwyn have concentrations of Pb so high that the quantity one would need to consume to reach the threshold for nephrotoxicity can be as low as two in a day for adults, with no safe level of consumption for children under 10 (Sartorius et al., 2022a). Sartorius also analysed blood from local sheep, horses, chickens, cats and dogs, and horsehair, but these were not made public (Sartorius, 2019a, 2019b, 2018).

4 Materials and Methods

4.1 Introduction

In order to quantify the metal concentrations and fluxes within the watercourses at Nantymwyn, samples of water, and estimates of flow, were taken across the site. Samples were collected at 17 points on the two watercourses that traverse the site, once a month for 13 months (January 2019-February 2020). Where feasible, water flow estimates were taken, using a method suitable for the site's location and flow, as detailed in section 2.5.1. Additionally, a single day of sampling after several days of continuous tracer injection was conducted on the Nant y Bai.

4.2 Research design

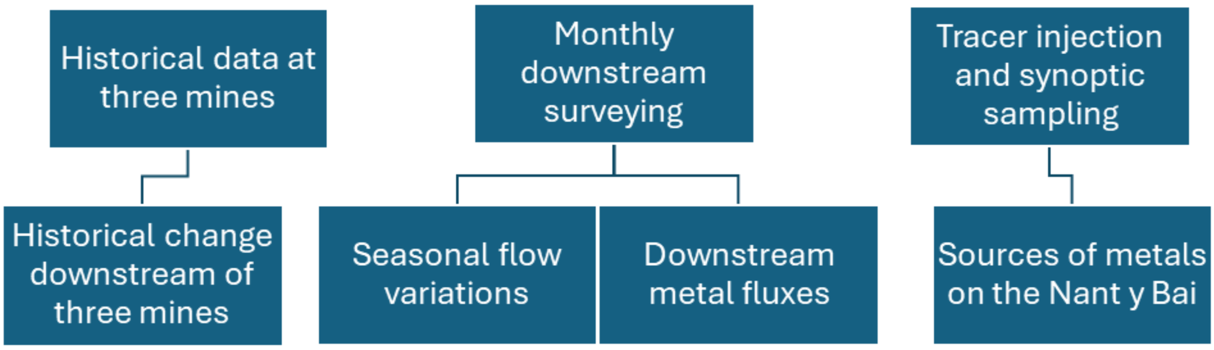


Figure 4-1 - Research design graphic

Ahead of beginning fieldwork and data collection and analysis, the research design was considered, and this is shown in a graphic below. The three data sources are shown, and how they feed into the results.

4.3 Sampling site selection

4.3.1 Monthly sampling sites

A site walkover was carried out in November 2018, accompanied by water quality experts from NRW (Paul Edwards and Thomas Williams), and the Swansea University PhD supervisory team (Dr Iain Robertson and Prof. Rory Walsh). Known mine features, water features identified from current and historic Ordnance Survey mapping, historic area photography, and areas of interest highlighted by previous research were visited, their location recorded on a GPS device, and photographs taken. After deliberation and further desk based research, water quality samples were taken at 28 points, and 17 of these were taken forward for monthly sampling and flow gauging for the following 24 months (though this was truncated by the Covid-19 pandemic after 12 months). The 17 regular monitoring points are detailed in Table 4-1., and shown in Figure 4-2

Table 4-1 - Monthly sampling points, heading upstream. U/S = Upstream, RHB = Right Hand Bank, LHB = Left Hand Bank, STR = Stream, LBI = Left Bank Inflow, RBI = Right Bank Inflow.

NRW ID	NRW sampling point name	Source	Easting	Northing	Stream
31689	Nant y Bai at entry into river	STR	277268	244225	Bai
88219	Nant y Bai at road bridge:	STR	277524	244553	Bai
88347	Nant y Bai u/s Pen y Darren	STR	277986	244727	Bai
88173	Upwelling to Nant y Bai u/s 88347	RBI	278032	244680	Bai
190103	Bai spoil heap flows RHB u/s Pen y Darren	RBI	278606	244770	Bai
88193	Nant y Bai upwellings on LHB	LBI	278313	244638	Bai
88223	Nant y Bai adit: upper boat level	LBI*	278388	244609	Bai
88224	Nant y Bai culvert:	LBI*	278527	244647	Bai
88222	Nant y Bai above adit:	STR	278500	244700	Bai
88434	Trib 1 of Nant y Bai spoil run off	LBI	278542	244744	Bai

NRW ID	NRW sampling point name	Source	Easting	Northing	Stream
88221	Nant y Bai u/s mine	STR	278698	244930	Bai
88201	Nant y Mwyn at Tywi confluence	STR	277859	243529	Mwyn
88203	Church terrace tributary:	RBI	278178	243701	Mwyn
88204	Church terrace old shaft discharge: lower boat adit portal	RBI	278235	243798	Mwyn
88439	Nant y Mwyn u/s church house terrace	STR	278173	243631	Mwyn
88183	Pannau adit	RBI	278733	243872	Mwyn
88191	Nant y Mwyn u/s conf trib	STR	278732	243856	Mwyn

*The Upper Boat Level and Nant y Bai culvert, while both located on the left side of the Nant y Bai, do not flow directly into the stream as their flows are lost to a boggy area immediately after their sampling point locations.

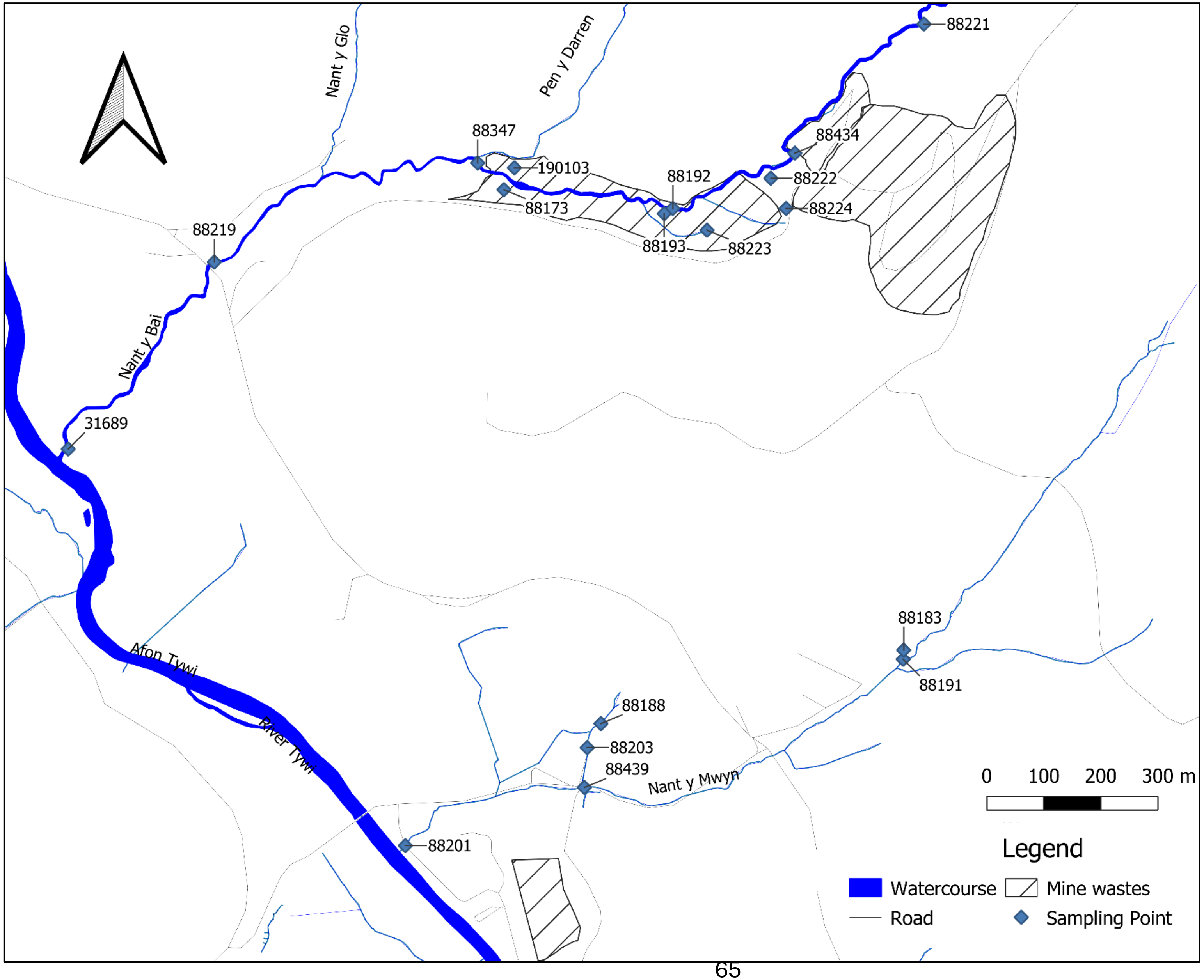


Figure 4-2 - monthly sampling locations at Nantymwyn

4.3.2 Synoptic sampling sites

Informed by the six months of monthly grab sampling and flow gauging undertaken as part of earlier research undertaken for this PhD, and with an additional site walkover with Prof. Patrick Byrne of Liverpool John Moores University, 35 sites were selected along the Nant y Bai stream (Table 4-2). On the day of sampling (16/07/2019) N-20 was dry and unable to be sampled, so the final sampling point was N-19 (Figure 4-3). As a result, detailed spatial information on metal sources was calculated and quantified for 1,825 m of the Nant y Bai, covering the stream from above the mine workings to within 200 m of its confluence with the River Tywi.

Table 4-2 - Synoptic sampling sites information. N = Nant y Bai, STR = Stream, LBI = Left Bank Inflow, RBI = Right Bank Inflow, INJ = Injection point

Site ID	Notes	Distance below injection (m)	Source	Easting	Northing	Elevation (m)
N-INJ	Injection point	0	STR	278726	244955	232
N-0	Same location as 88221*	44	STR	278698	244930	224
N-1		91	STR	278659	244908	217
N-2	Start of mine wastes	137	STR	278631	244873	218
N-3		215	STR	278590	244814	213
L-1	Inflow draining boggy patch	220	LBI	278591	244807	210
N-4		228	STR	278577	244810	210
N-5	Incised wastes LHB	298	STR	278539	244758	204
L-2	Same location as 88434	305	LBI	278552	244753	205

Site ID	Notes	Distance below injection (m)	Source	Easting	Northing	Elevation (m)
N-6	Same location as 88222	315	STR	278543	244741	204
N-7A	End of mine wastes	386	STR	278483	244711	197
N-7B	U/s second mine wastes	517	STR	278369	244669	191
N-8	In second mine wastes area	623	STR	278286	244668	182
N-9		697	STR	278225	244684	182
L-3	Draining wastes on LHB, including potentially the upper boat level and culvert	700	LBI	278227	244674	
L-4		705	LBI	278223	244676	178
L-5		712	LBI	278209	244675	171
N-10	Start of RHB mine wastes	721	STR	278200	244682	171
N-11		842	STR	278086	244689	161
L-6	Draining LHB wastes	847	LBI	278076	244686	162
N-12		859	STR	278069	244690	162
R-1		887	RBI	278043	244699	
N-13	Same location as 88347	948	STR	277995	244730	156
R-2	Pen y Darren	960	RBI	277987	244738	160
N-14		983	STR	277963	244731	154

Site ID	Notes	Distance below injection (m)	Source	Easting	Northing	Elevation (m)
L-7		1051	LBI	277899	244727	
N-15		1258	STR	277736	244711	137
R-3	Nant y Glo	1268	RBI	277726	244723	141
N-16		1280	STR	277717	244699	136
R-4		1352	RBI	277652	244670	135
N-17	Same location as 88219	1536	STR	277524	244553	128
N-18		1665	STR	277457	244465	120
L-8		1760	LBI	277419	244388	120
N-19	U/s incised floodplain	1825	STR	277384	244333	116
N-20	Same location as 31689	1965	STR	277267	244268	113

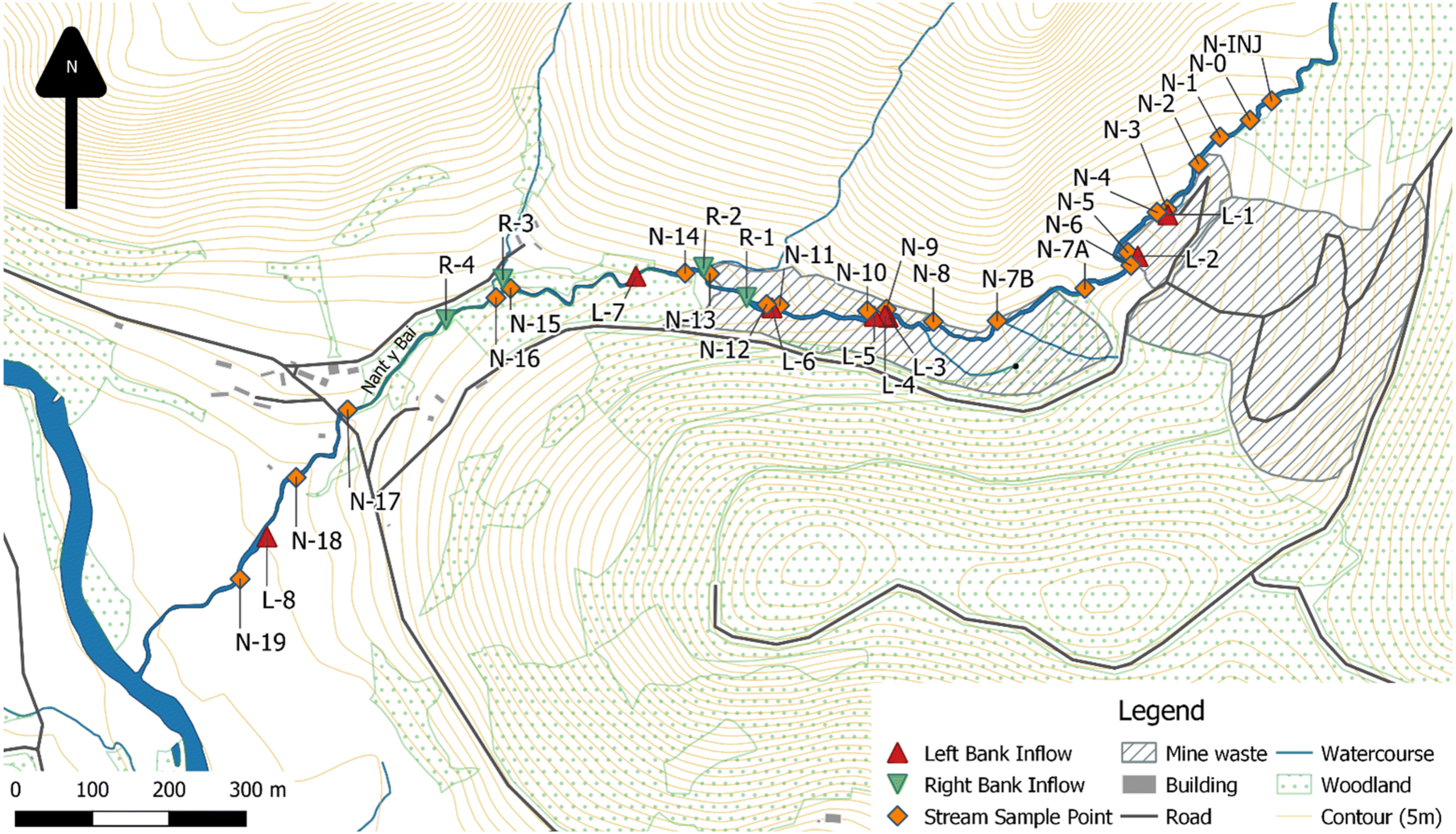


Figure 4-3 - Nantymwyn mine and landscape features, with sampling points for in-stream (N-) and inflow (L-/R-) locations

4.4 Selection of elements for analysis

The analysis of water quality samples is covered in chapter 4, of particular interest are:

- Pb – a toxic metal, mined at the site (Hall, 2014; Sartorius et al., 2022b; Todd et al., 2021)
- Zn – a toxic metal, which is often found alongside Pb ores (Sartorius et al., 2022a)
- Cd – a toxic metal and natural impurity of Zn (Davies and Lewin, 1974; Jones et al., 2013)

In common with similar studies, rather than all of the element analysed for, the results were inspected and these were the elements taken forward for further analysis (Byrne et al., 2021b, 2012; Onnis et al., 2023b, 2023a, 2018). The complete dataset is available in the appendix, section 8-2.

4.5 Water quality sampling

4.5.1 Monthly water quality sampling

Samples were taken at the 17 points across the site (detailed in Figure 4-2 and Table 4-1) monitored on a monthly basis. Samples were collected in a downstream to upstream direction (for the Nant y Mwyn starting at point 88201 and finishing at point 88191, and on the Nant y Bai starting at point 31689, and finishing at point 88221 (Figure 4-2)), to avoid contaminating downstream samples with disturbed sediments. At each sampling point, a calibrated YSI ProQuatro multi-parameter water quality sonde (YSI Inc., 2011) was placed in the watercourse, in the flow of the water, and given time to stabilise before the readings for pH, temperature, dissolved oxygen, and conductivity were measured following NRW/EA guidelines (Environment Agency, 2014). The same water quality sonde was also used as a data logger to record changes in conductivity during salt dilution flow gauging, with it also placed in the main flow of the watercourse following NRW/EA guidelines (Environment Agency, 2014). The multi-parameter water quality sonde was calibrated before each day's sampling run with a three-point pH calibration (at 4, 7, and 10), and a single point conductivity calibration (1,413 $\mu S\ cm^{-1}$), using pre-prepared YSI solutions, and the sonde's inbuilt calibration mode (Environment Agency, 2014; YSI Inc., 2011).

While the readings on the water quality sonde were stabilising (approximately 5 minutes), the bottles for water quality sampling were prepared. Samples were collected for laboratory analysis, for the elements in Table 4-3, both total and dissolved. Before travelling to the site a form for each sampling point with the planned samples to be taken, and field determinands to be recorded, was printed, as well as self-adhesive stickers to apply to the bottles before taking the sample. Every site had a bottle for total metal analysis and a second bottle for dissolved metal analysis, which required two 125 mL polyethylene bottles, one filled directly from the stream, and one first filtered through a single use Pall Lab Acrocap 0.45 µm filter using a single use Terumo 50 mL syringe. Both bottles were rinsed first with their respective sample three times, and the filter was primed with 10 ml of sample water which was disposed of, in accordance with national water quality sampling guidance (Environment Agency, 2010, 1998). The bottles were labelled following NRW protocols and kept out of sunlight before they were refrigerated in the laboratory at 4 °C, prior to analysis within the following five working days.

4.5.2 Tracer injection and synoptic sampling

In order to collect accurate streamflow and metal loading data, the measured watercourse must have a steady flow state for the duration of the tracer injection and synoptic sampling experiment. Therefore, a summer low flow period was chosen to maximise the chance of constant low flows in the stream. Following U.S. Geological Survey standard practice, (Byrne et al., 2013; Kilpatrick and Cobb, 1985; Kimball, 1997) constant-rate tracer injection and synoptic sampling was conducted on the Nant y Bai in July 2019. There are two main advantages of the technique over more traditional methods of streamflow gauging [e.g. velocity-area, gulp injection] (Byrne et al., 2021b; Onnis et al., 2023b). First, as the tracer is injected over a period of days it becomes fully mixed in the stream and therefore captures flow in irregular channel sections and the hyporheic zone. Secondly, as the streamflow is calculated using the tracer concentration in the stream, sampling can be carried out rapidly at each sample site, maximising the number of samples that can be taken and increasing the spatial resolution of sampling.

A tracer injection tank was erected at the top of the studied section of the Nant y Bai and filled with approximately 850 L of stream water, to which 35 kg of NaBr was added and thoroughly dissolved (Figure 4-4). Sodium bromide was selected as the tracer as it is known to behave conservatively in circumneutral waters (Dzombak and Morel, 1990) and has been previously used successfully for this purpose in the UK (Byrne et al., 2021). This solution was injected into the stream at a constant rate of 70 mL min^{-1} for five days using a computer-controlled pump, and terminated at the completion of the synoptic sampling. The injection site selected was above the mine workings as shown by historical aerial photographs and mapping

Samples of the solution in the injection tank were taken over the course of the injection period, confirming that the concentration remained within ±1.8% of its starting concentration during the experiment (mean 65,153mg L^{-1}, standard deviation 654). A Seametrics TempHion Multi-Parameter Water Quality Sensor with an Ag/AgCl solid-state electrode Br probe (Instrumentation Northwest Inc, 2012) was used to monitor Br levels in the stream at the end of the studied reach and synoptic sampling began when the tracer concentration had reached a plateau concentration, indicating the Br concentration in the stream was at a steady state. Synoptic samples were taken at 34 sites in the Nant y Bai catchment: at 22 stream sites and 12 inflow sites. These sites were selected during an earlier field visit in June 2019, where preliminary data from six months of spot sampling data showed an increase of metal concentrations in the stream; before and after spoil heaps; and where water was visibly entering the watercourse for example as small tributaries and river bank seeps. For the visible inflows, a sample was taken from the inflow and in the main stream above and below the inflow, the latter a distance downstream that allowed for complete mixing between the two flows.

Figure 4-4 - Tracer injection tank, with pump and pump controller shielded in the tent. The injection pipe can be seen running towards the Nant y Bai stream

Synoptic samples were collected in a downstream to upstream direction, to avoid contaminating downstream samples with disturbed sediments and from higher Br concentrations upstream (Kimball et al., 2004). At each synoptic sample point a water sample was taken in a 1 L PET bottle, following the Environment Agency standard protocol of rinsing the sample bottle with sample site water three times, (Environment Agency, 2010) and then taken to a field laboratory for preparation for analysis as soon as practicable in the same hour. At the field laboratory, the sample's pH and temperature were recorded, taken using a calibrated water quality meter (Hanna Instruments HI-98194 multiparameter) (Hanna Instruments Inc, n.d.), and three 25 mL vials filled from the larger bottle, again rinsing each vial three times with sample water. One vial was filled with the sample as collected and fixed with HNO_3 (for total metal concentrations analysis), one filled with the sample after being filtered through a 0.45 μm membrane and fixed with HNO_3 (for filtered metal concentrations analysis), and one sample was filtered through a 0.45 µm membrane (for bromide analysis) (Batley and Gardner, 1977). The HNO_3 used was Fisher Scientific Ultrapure (67-69%) for trace metal analysis. Sample vials were then sealed and stored in a fridge at 4 °C after returning from site in the evening.

4.6 Water quality analysis

4.6.1 Monthly water quality sampling

The samples were analysed at the NRW Analytical Services' Laboratory, Swansea, in an Thermo X-Series 2 Collision Cell ICPMS-CRC (Inductively Coupled Plasma Mass Spectrometry - Collision / Reaction Cell). The samples were fixed by adding 1 mL of Nitric Acid SG 1.41 (Primar Grade) per 100 mL of sample. The samples were then heated in a microwave oven to a gentle simmer to break-down complexed metals and keep them in solution (Johns, 2024; Natural Resources Wales, 2018). The samples are then fed into the instrument by a Cetac AS510 autosampler, before being nebulised and dispersed into an argon gas stream. This stream was then injected into the cone of a high temperature plasma, which dissociates, atomises, and ionises it, before it is extracted to a lower pressure region. The ions are directed to the collision/reaction cell and 93% He / 7% H2 gas. This was then passed through the quadruple mass filter, then through the ion detection system, which collects data for transmission to the computer controlling the system (Natural Resources Wales, 2018). After each sample, the instrument is rinsed for 60 seconds using a dilute acid (1% HNO_3), to reduce or remove any memory effects from the previous sample. The sample's concentrations for the elements shown in Table 4-3 were then uploaded to the NRW Water Quality Archive (datamap.gov.wales/layers/geonode:nrw_water_quality_archive_stations)..

Table 4-3 - NRW Analysis suites and limits of detection (Natural Resources Wales, 2018)

Element	**Limit of Detection (µg L^{-1})**
Aluminium	10
Cadmium	0.1
Chromium	0.5
Copper	1

Element	**Limit of Detection (μg L^{-1})**
Lead	2
Nickel	1
Zinc	5

Before the first sample was introduced to the instrument, it is set to undergo a tune, where the PlasmaLab software self-calibrates against wear or degradation of the sensors, and confirms the chemical make up of the carrier gases (Natural Resources Wales, 2018; Thermo Scientific, 2008). Individual element standards are held in the laboratory and made up annually or when required through use, from Aldrich brand analytical grade stock solution to 1,000 mg L^{-1} (Natural Resources Wales, 2018). Where the samples were expected to exceed the concentration of the standard, the sample was diluted down to bring it within the range covered by the standards.

4.6.2 Tracer injection and synoptic sampling

Total and filtered concentrations of elements (primarily for Pb, Zn, Cd, and Br, but also for 17 other elements illustrated in Table 4-4) were determined with an Agilent Technologies ICP MS 7900 with an SPS-4 autosampler. Additionally, Br concentrations were determined by Agilent Technologies IC, as Br can have a memory effect on ICP-MS (Zhang et al., 2014). The Agilent Technologies ICP MS 7900 and autosampler operate on the same principles as described in section 4.6.1, with minor differences in the software and precise design of the instrument as they are made by competing manufacturers. The instrument was calibrated with Aldrich brand multi-element standards, made up to 10, 100, 500, 1,000 and 5,000 mg L^{-1}, as well as an ultra-high purity water, and this calibration run was repeated after every ten samples were analysed, principally to check for evidence of the memory effect from Br (Zhang et al., 2014). The ICP-MS software was informed of the mid-sampling standards and continued to calibrate itself as analysis went on. The samples were analysed in order of expected increasing Br concentrations, and the instrument was set to rinse for 60 seconds using a dilute acid (1% HNO_3), and then 60 seconds with ultra high purity water, again to minimise any problems with Br memory effects.

Table 4-4 – Tracer injection and synoptic sampling analysis suite and limits of detection (where available, calculated on the ICP-MS software after calibration)

Element	**Limit of Detection (µg L^{-1})**
Silver	0.8
Aluminium	10
Arsenic	2
Beryllium	0.039
Bromine	-
Calcium	2089
Cadmium	0.4
Cobalt	1.3
Chromium	12
Copper	12
Iron	26
Potassium	-
Magnesium	-
Manganese	4
Sodium	-
Nickel	18
Lead	0.063
Antimony	3
Thallium	0.01
Vanadium	11
Zinc	14

4.7 Flow gauging

4.7.1 Monthly water quality sampling

There are a number of flow gauging methods available (Chapter 2.5.1). Of these:

- Volumetric or bucket and stopwatch – there are two sites where the bucket and stopwatch method of flow measurement was suitable, with the water concentrated by a pipe or waterfall with a drop large enough to fit a bucket under, sites 88183 and 88224, with 88224 shown in Figure 2-1.
- Velocity-area – there are no sites suitable for this method at Nantymwyn. Flow meters are best utilised in the velocity area method detailed in section 2.5.1.4, and as there are no suitable sites at Nantymwyn for that method, flow meters have not been used at Nantymwyn. There are no sites at Nantymwyn that are large enough to justify the use of an Acoustic Doppler Current Profiler boat, so this method has not been used.
- Dilution gauging – The single injection or ‘gulp’ method detailed in section 2.5.1.2 is ideal for Nantymwyn, and table salt (NaCl) was used as a tracer at 14 sampling points across the site during this project (Todd et al., 2022).
- Constant rate tracer injection as detailed in section 2.5.1.3 – this was used at the site and is covered in the next section.
- Weirs, flumes, and rated sections – these were not within the scope of this project, but the Coal Authority has installed three v-notch weirs at the site, two sized for their respective location based on the measurements taken during this project (Figure 2-2).

One site was not suitable for any method of flow gauging, the upper boat level shown in Figure 3-4, due to the extremely low velocity and flow of the water, and soft, permeable, ochreous discharge. With some difficulty a v-notch weir was installed by the Coal Authority in 2021, however, it was not possible to calibrate it, and data are not recorded

At 14 monthly monitoring points, the flow was gauged using salt dilution, following accepted protocols (Hudson et al., 2018; Littlewood, 1995; Williams, 2016). Monitoring points were visited for salt dilution flow gauging in a downstream to upstream direction, to avoid contaminating downstream conductivity readings with disturbed sediments or NaCl contamination. At each watercourse to be flow gauged, 11 L of water were taken; 1 L in bucket one, and 10 L in bucket two. The conductivity of the streamwater was recorded with a calibrated multi-parameter meter, which corrected for temperature automatically (YSI Inc., 2011), and based on this conductivity, the size and visible flow of the stream, a pre-measured quantity of NaCl (from 1 g – 250 g) was added to bucket one, and thoroughly dissolved. Knowing how much salt to use became easier the more salt dilution flow gauging was carried out, but the larger the stream, higher the flow, and higher the background conductivity of the stream water, the more salt was required in order to record a response like that in Figure 4-5. Using a clean syringe, 10 mL of this solution was taken via syringe and injected in 2 mL increments into bucket two. After each 2 mL injection and thorough mixing, the conductivity of bucket two was recorded, until all 10 mL had been injected. The YSI meter was then set to log every two seconds and placed downstream, approximately 25 times the width of the stream, or 25 meters, whichever was further, within the limitations of the particular site – for example access, additional inputs or confluences, and areas of standing or backing water. With the conductivity recordings stabilised, the bucket one was injected in a single ‘gulp’. Once

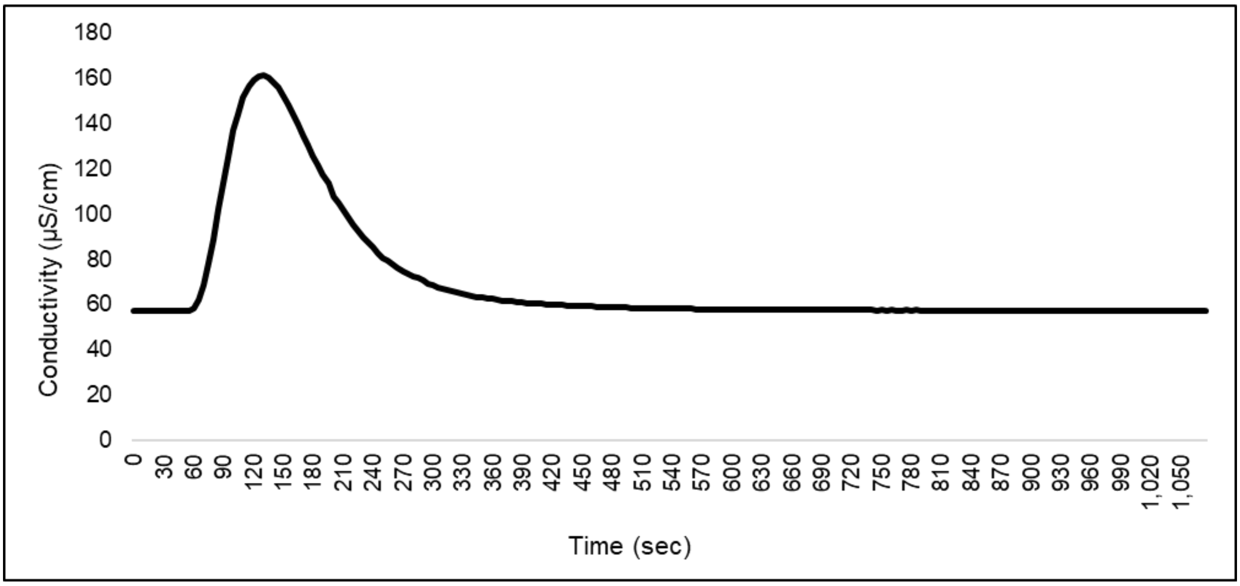


Figure 4-5 - Example of conductivity response in stream water after salt injection, logged at 2-second intervals. This data was collected at site number 88221 in May 2019.

the meter's reading returned to the pre-injection state, logging was stopped, and all the equipment rinsed with three times in stream water ready for the next site. This 'relative method' removes the need for exactly measured salt quantities, as calibration is performed at the bankside before each reach is gauged (Littlewood, 1995; Williams, 2016).

After sampling in the field, the data were retrieved from the meter, and processed in a spreadsheet. The bankside calibration and any fieldnotes were added, and the Excel spreadsheet outputted a graph like in Figure 4-5, and the estimated flow in Ls^{-1} (Williams, 2016). As with the water quality data, these were sent to NRW to be recorded on their Water Quality Archive (datamap.gov.wales/layers/geonode:nrw_water_quality_archive_stations).

4.7.2 Tracer injection and synoptic sampling

As the tracer flows downstream and the volume of water in the watercourse increases, the concentration of the tracer decreases, and this is directly related to flow (Kilpatrick and Cobb, 1985). Using the formula shown in chapter 2.5.1.4, it was possible to estimate flow based on the Br concentration measured at each sampling point (Figure 4-6) (Todd et al., 2024a). In some previous studies there has been an error introduced in the streamflow calculation as a result of variations in the injection rate (Onnis, 2019). In an effort to avoid this error, a computer controlled peristaltic pump was used, based on a

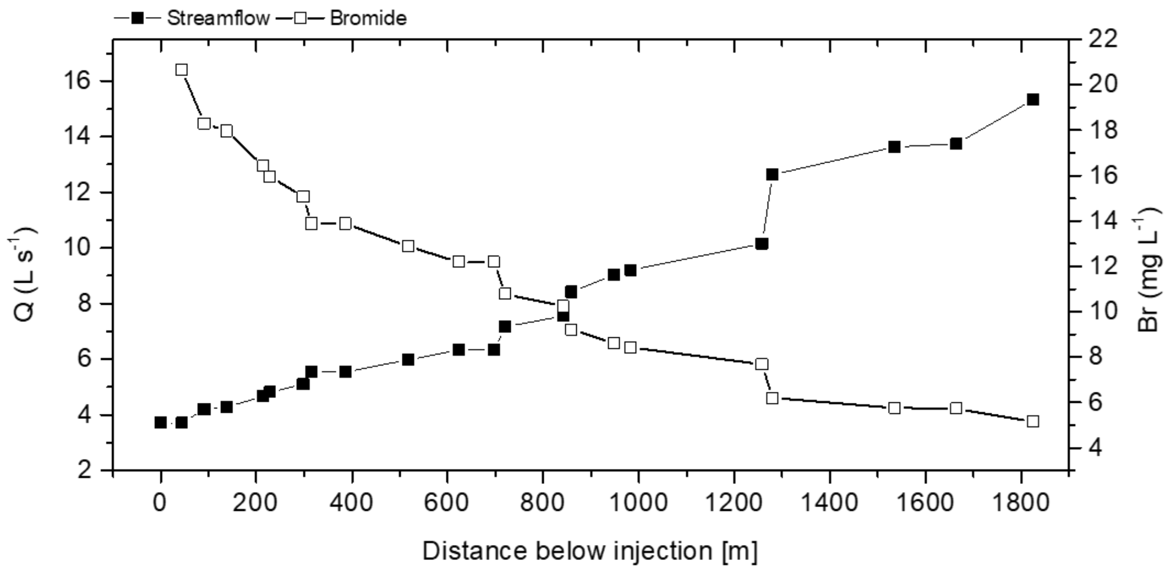


Figure 4-6 - Br concentration and streamflow calculated from the Br concentration, Nant y Bai

USGS design, which automatically compensated for battery capacity (Figure 4-7). As each revolution of a peristaltic pump's motor is equivalent to the same volume of tracer each time the pump is run, the speed of the pump (which is a product of the battery voltage) does not matter, and so the pump delivered the same volume of tracer consistently throughout the injection period. The volume injected in a minute was measured twice daily throughout the period to confirm this.

As each sampling point also had metal concentrations analysed for, and therefore loads L (mg s^{-1}) of Pb, Zn, and Cd were calculated as the product of the streamflow estimate and the metal concentration at the synoptic site, as below:

$$L = Q \times C_m$$

Where

Q (L s^{-1})	Stream discharge
C_m (mg L^{-1})	Concentration of the element

Guided by the monthly monitoring, the studied stream was divided into 21 segments, demarcated by the 22 stream synoptic sampling sites (Todd et al., 2024a). With metal loads calculated for each synoptic site, the cumulative instream load can be calculated, which is the sum of all the increases in metal loads between each stream segment. Comparing the cumulative instream load to the metal load calculated for the individual or grouped stream segments, highlights locations in the stream where metal attenuation (through chemical reactions) or metal addition (through sources) are occurring (Byrne et al., 2021). Furthermore, the percent contribution of each source can be calculated as:

$$\%Contribution = \frac{100\Delta load}{(L2 - L1)}$$

Where *L1* and *L2* are the cumulative instream load at the upstream and downstream points of a selected stream segment, and Δ*load* is the change in metal load within the segment (Byrne et al., 2021). Stream segment contributions can be combined to show the cumulative impacts of similar areas of contamination, for instance where the watercourse flows through surface mine waste.

Figure 4-7 - computer controlled peristaltic pump, with controller, pump, (battery out of sight), and flexible piping to the tracer tank, and to the Nant y Bai

4.8 Historical data analysis

Changes (or lack of changes) through time in metal concentrations downstream of the three mining sites were assessed using all available data from NRW archives between 1978 and 2021. Changes in analytical methods, and sampling equipment used, may mean that absolute values are not directly comparable (Environment Agency, 2010; Walsh et al., 2000). Data transcription from laboratory to database was done manually, and this has led to some apparent outliers, for example, a decimal place copied to the wrong location putting a result a hundred or thousand times that of the long term average. These clear errors (unrealistically high or low values) were removed from the datasets, as it would not be possible to be certain how much error had been introduced during the manual transcription. However, the potential limitations of this approach were noted. From the resultant datasets used, the Nant y Bai at Nantymwyn had 244 samples, taken between 1978 and 2021, the Dyffryn Adda Adit at Parys Mountain had 216 samples (2004-2020), and the Frongoch Stream at Frongoch had 201 samples (2004-2021). The three mines cannot represent the nuances of changes in contamination since abandonment for all of the known mines in Wales or further afield, but the variation between the three sites gives an example of a circumneutral mine, an acidic mine, and a remediated mine. At Nantymwyn, a single sampling point on the Nant y Bai downstream of the main mine site and its waste was chosen, which had the longest time period of water quality data collected. At Frongoch a similar sampling point was selected on the Frongoch Stream, both being the final sampling point before the affected stream joins a major river. As contamination from Parys Mountain is mainly directly from subterranean mine water, the more representative adit sampling point was used. Each sampling point is influenced by different contamination flows, and the mine water discharge at Parys Mountain should be noted as different to the other two sampling points.

Collection and analytical procedures remained broadly unchanged over the period of record. At each monitoring point two 125ml samples were taken, one sample was filtered through 0.45 μm filter, and stored at 4 °C prior to laboratory analysis. Since 1998 a specific EA/NRW sampling protocol, detailing methods for minimising cross-contamination of samples was followed (Environment Agency, 2010, 1998). Measurements of pH and conductivity were taken in the field using a handheld meter since 2008, and prior to this were measured in the laboratory. Temperature has always been taken in the field using a handheld meter where possible (Environment Agency, 2014). From 1979 to 2017, chemical analysis of the water sample was conducted by the National Laboratory Service in Llanelli and Exeter; initially using a Varian Techtron Atomic Absorption Spectrometer, then from 1984 using an Allied Instrumentation Plasma 200 (Brown, 1986). This was replaced by a Perkin Elmer Inductively Coupled Plasma Mass Spectrometer (ICPMS), though the date was not recorded, and then from October 2008 analyses by the EA and NRW were determined using a Thermo Fisher X Series 2 ICPMS-Collision/Reaction Cell (CRC) (Natural Resources Wales, 2018). Before 2011, flow measurements were taken by current meter, though they were usually not concurrent with water sampling, especially before 2003. Flow measurements from 2012-2020 employed salt dilution gauging (Todd et al., 2022; Williams, 2016). However, as these flow measurements were inconsistently recorded, the focus of the paper has been on concentrations rather than fluxes. Caution was taken when comparing data because of these changes in analytical method and procedure and also changes in sampling location over the period of record. In most cases changes were minor and caused by access and land ownership issues, but the major changes in adit flows at Parys Mountain after the removal of the dam in 2003 meant that only data since 2004 could be used. Data analysis comprised a) construction, description and interpretation of temporal series of annual box-and-whisker diagrams for each available year of record, and b) calculation and statistical comparison of mean metal concentrations for aggregated data for different parts of the data series. For the data comparison in b) the data for the sites were separated into segments of time. For Nantymwyn, early data for 1978-87 were compared with 2019-2020. For Parys Mountain, data for 2004-06 were compared with 2010-14, and 2015-20. For Frongoch, pre-remediation data for 2005-2011 were compared with post-remediation data for September 2018-2021. Statistical analysis utilised the Student's T test or Mann Whitney U test as appropriate.

Data from the three sites were compared to WFD Environmental Quality Standard (EQS). The WFD standards for the metals of interest at these sites are only given for total or dissolved metals (defined in the WFD as bioavailable), as shown in Table 2, and hence the only data shown is for the respective standard. The UK Technical Advisory Group for

WFD investigations provides a tool (Metal Bioavailability Assessment Tool, M-BAT), to calculate Predicted No Effect Concentrations (PNEC) for each metal (WFD-UKTAG, 2014). Calculations of a site-specific PNEC, however, requires data for dissolved organic carbon (DOC), which is not routinely collected for UK metal mines. The M-BAT is sensitive to variations in DOC, and therefore the non-site-specific standards have been used.

4.9 Mapping

All the maps in this thesis were created using QGIS 3.16 “Hanover”, a free, open-source Geographic Information System (GIS), running on Windows 11 64 bit (QGIS Development Team, 2022). Some background mapping was downloaded from the Edina Digimap system, including Ordnance Survey (OS) 1:1000, 1:10,000, 1:25,000, and 1:50,000, as both vector and raster layers, as well as a UK overview raster, digital terrain model, and the UK detailed river network (Ordnance Survey, 2020, 2018, 2013). Field site locations were recorded using Garmin eTrex 10 handheld Global Positioning System (GPS), which were uploaded to QGIS. Additional mapping outside of OS was created for this project from scratch using QGIS.

4.10 Data, graphs and figures

All numerical data for this project was initially analysed using Microsoft’s Office 365 spreadsheet software Excel (Microsoft Corporation, 2024). The majority of the graphs in this project were created using OriginPro 2020b graphing and statistical software (OriginLab Corporation, 2020).

4.11 Statistical analyses

All statistical tests were carried out following guidance and methods detailed in *Simple Statistical Tests for Geography* by McCarroll (McCarroll, 2016). These were calculated using OriginPro 2020b when software was required, as Excel has historically caused statistical errors due to the way it operates (McCarroll, 2016; Mélard, 2014; Pottel, 2001). The tests used were:

4.11.1 Mann-Whitney *U*-test

The Mann-Whitney *U*-test is a non-parametric test that shows whether the values in one sample are significantly higher or lower than another sample (McCarroll, 2016). The data are ranked in size order, and then given a number, starting with the lowest value and increasing by one for each subsequent datapoint. These ranks are then summed for the original groups, and the rank sums can either be manually compared to a significance table, or the significance will be output by the software (McCarroll, 2016).

4.11.2 Students' *t*-test

The Students' *t*-test is a parametric test which is similar to the Mann-Whitney *U*-test, but it requires a larger number of samples, and for the data to be near normally distributed (McCarroll, 2016). As a result, the Mann-Whitney *U*-test is more useful for geographic data, but the Students' *t*-test is preferred if the data are acceptable. The mean and standard deviations of the two samples are calculated, and then input into the formula below:

$$t = (Mean\ of\ A - Mean\ of\ B) \div \sqrt{a\frac{(StdevA)^2}{N\ of\ A} + \frac{(StdevB)^2}{N\ of\ B}}$$

After (McCarroll, 2016).

4.12 Modelling

It was planned to model the data collected using either SIMCAT or OTIS.

4.12.1 SIMCAT

SIMCAT (SIMulation of CATchments) is proprietary EA software based on Fortran with a visual user interface, developed for planning discharge improvement to point source sewage discharges in the 1990s (Warn, 2014). It is a one-dimensional, steady state model, calculating solute fate and transport within a river, and has been used to model metal mine contaminants within a river previously (Warn, 2014; Williams, 2010).

4.12.2 OTIS

OTIS (One-dimensional Transport with Inflow and Storage) was developed by the U.S. Geological Survey (USGS) in the late 1980s for modelling conservative solutes, especially tracers (Runkel, 2000). It does not have a visual user interface, but as it is available free to download from the USGS, it has been used in many synoptic sampling and tracer injection experiments (Byrne et al., 2021a; Garneau et al., 2015; Runkel, 2000, 1998; Walton-Day et al., 2007).

5 Results and Discussion – Monthly Sampling

5.1 Introduction

This chapter presents, analyses and discusses the implications o the result so the monthly survey along the Nant y Bai and Nant y Mwyn. Subsections of the chapter focuses on:

a) variations metal concentrations and loads with discharge and season,

b) downstream changes in metal concentrations and loads, and

c) evidence regarding historical change in metal concentrations by comparing current data with the available data from the past.

The historical subsection (c) also focuses on change at two other mines (Parys Mountain and Frongoch) as well as Nantymwyn

5.2 Variations in metal concentrations and loads with discharge and season

Of particular interest from this abandoned lead mine at Nantymwyn are Pb and Zn, but Cu and Cd follow similar patterns as for Pb and Zn of lower concentrations during higher flows, and higher concentrations during lower flows. The exception to this is Al, which has peak concentrations at peak flows, and lowest concentrations and minima flows. The data will be shown graphically on first the Nant y Bai, and then the Nant y Mwyn, from the confluence with the Tywi upstream to the furthest sampling point, including inflow sampling points in sequence. This was also the order in which the streams were sampled, to avoid any contamination from sampling affecting results or flow gauging. Analysis of metal concentration was by ICP-MS, as detailed in 4.6.1, and flow gauging by either bucket and stop watch (two sites, 88224 the Nant y Bai Culvert, and 88183 the Pannau Adit), or salt dilution flow gauging (all other sites aside from 88223 Upper Boat Level, which was not possible to flow gauge with any method), both as detailed in 4.7.1. The full dataset is available in the appendix.

5.2.1 Nant y Bai

5.2.1.1 Nant y Bai close to the Tywi confluence

Sampling point 31689 is at the lowest point of the studied stretch of the Nant y Bai, on the flood plain of the River Twyi. Flow measurements are at both extremes, highs as this this the lowest point of the stream, and lows because water is lost to the ground during dry periods. Total and filtered concentrations of the analysed metals are closely correlated, except for Pb and Al, where total concentrations are higher than filtered concentrations at particularly low flows (Figure 5-1, Figure 5-2, Figure 5-3).

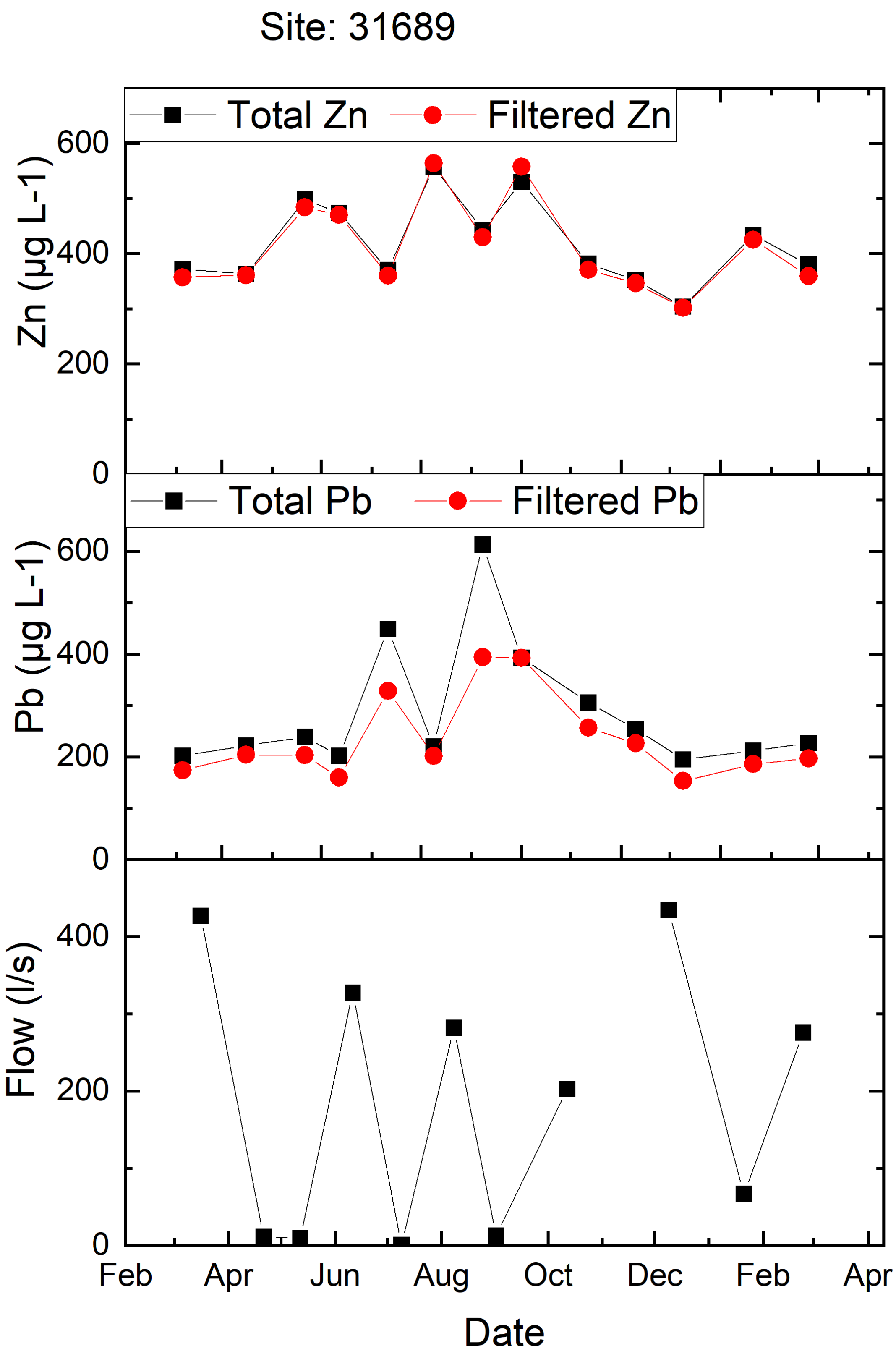


Figure 5-1 - Zn and Pb concentrations for 31689, as well as flow gauging measurements

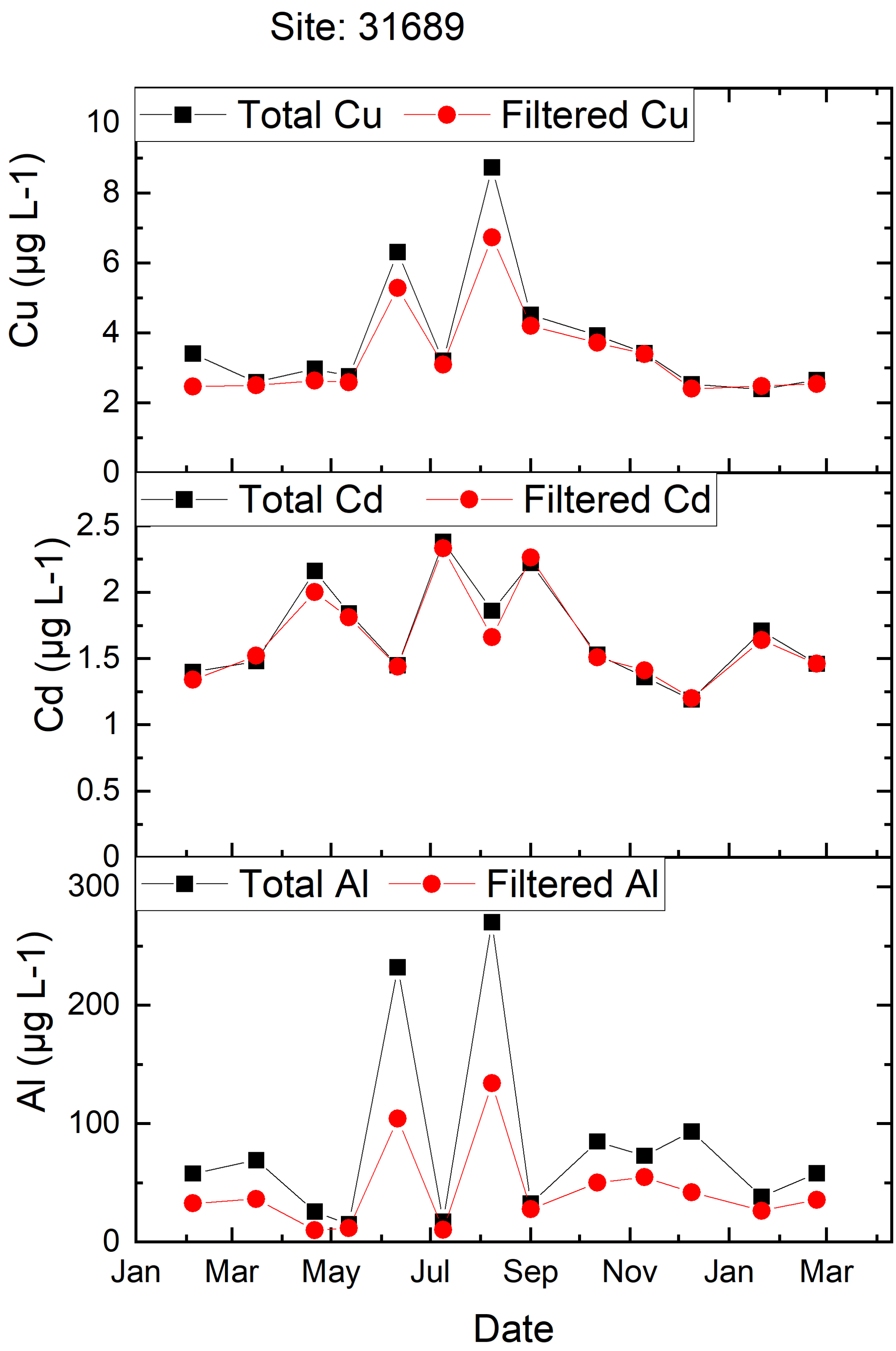


Figure 5-2 - Cu, Cd and Al concentrations for 31689

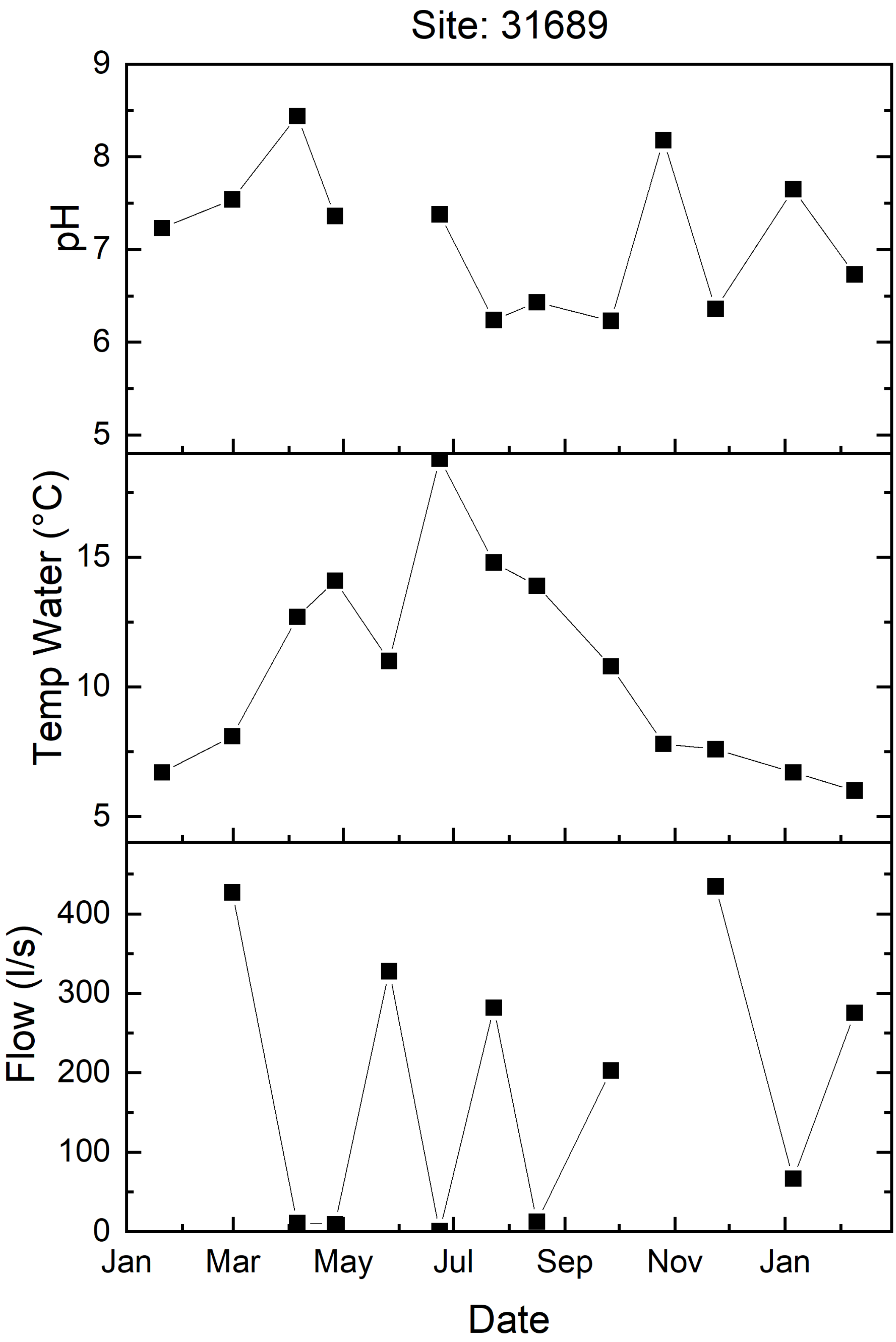


Figure 5-3 - pH and temperature readings for 31689, as well as flow gauging measurements

5.2.1.2 Nant y Bai at Road Bridge

Sampling point 88219 is the only access to the steam between 31689 and 88347, and there are no known mine workings between those two points. Two freshwater sources, the Pen y Darren and the Nant y Glo, join the Nant y Bai between 88347 and 88219, and these are not known to be mine impacted.

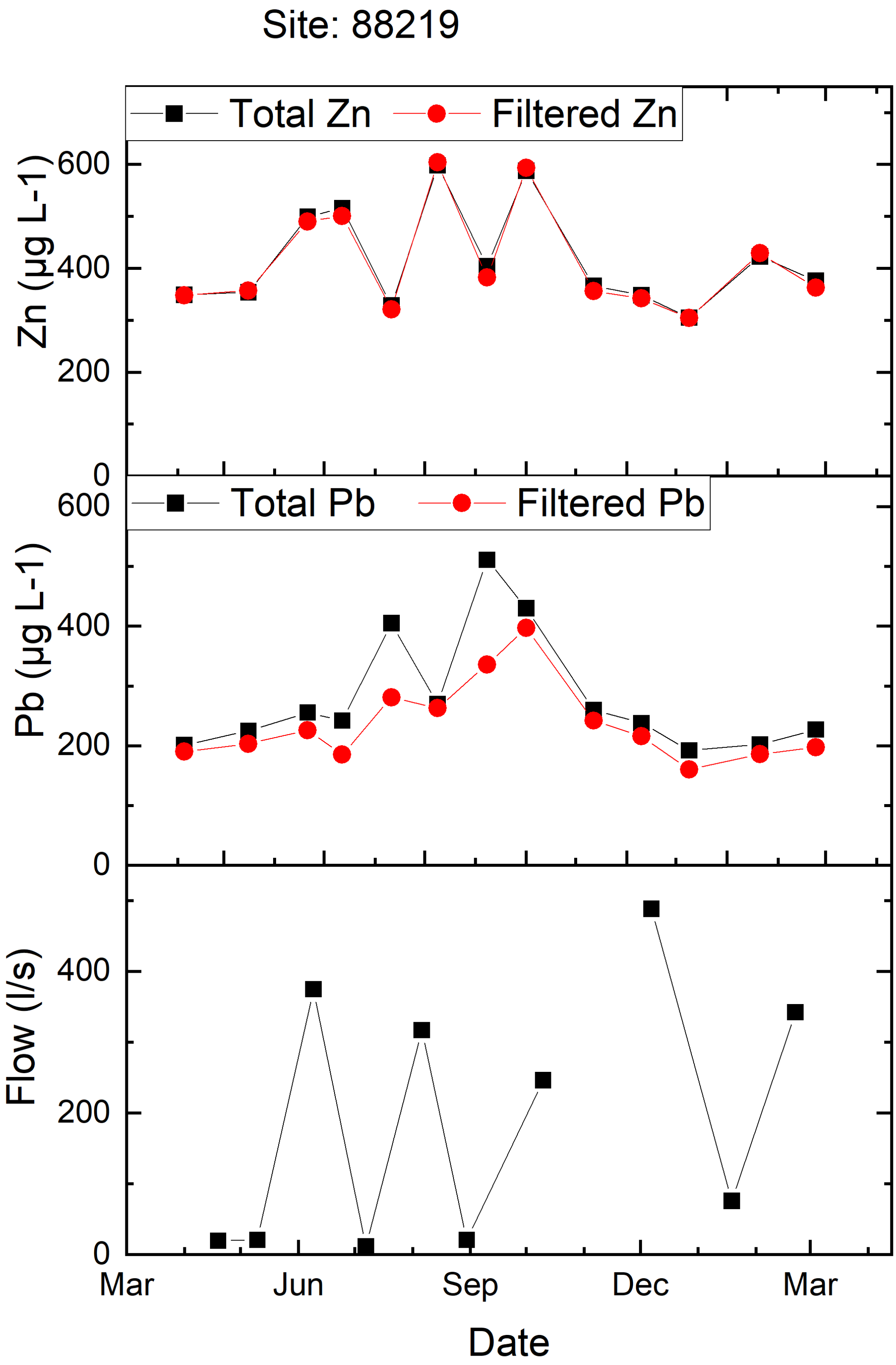


Figure 5-4 - Zn and Pb concentrations for 88219, as well as flow gauging measurements

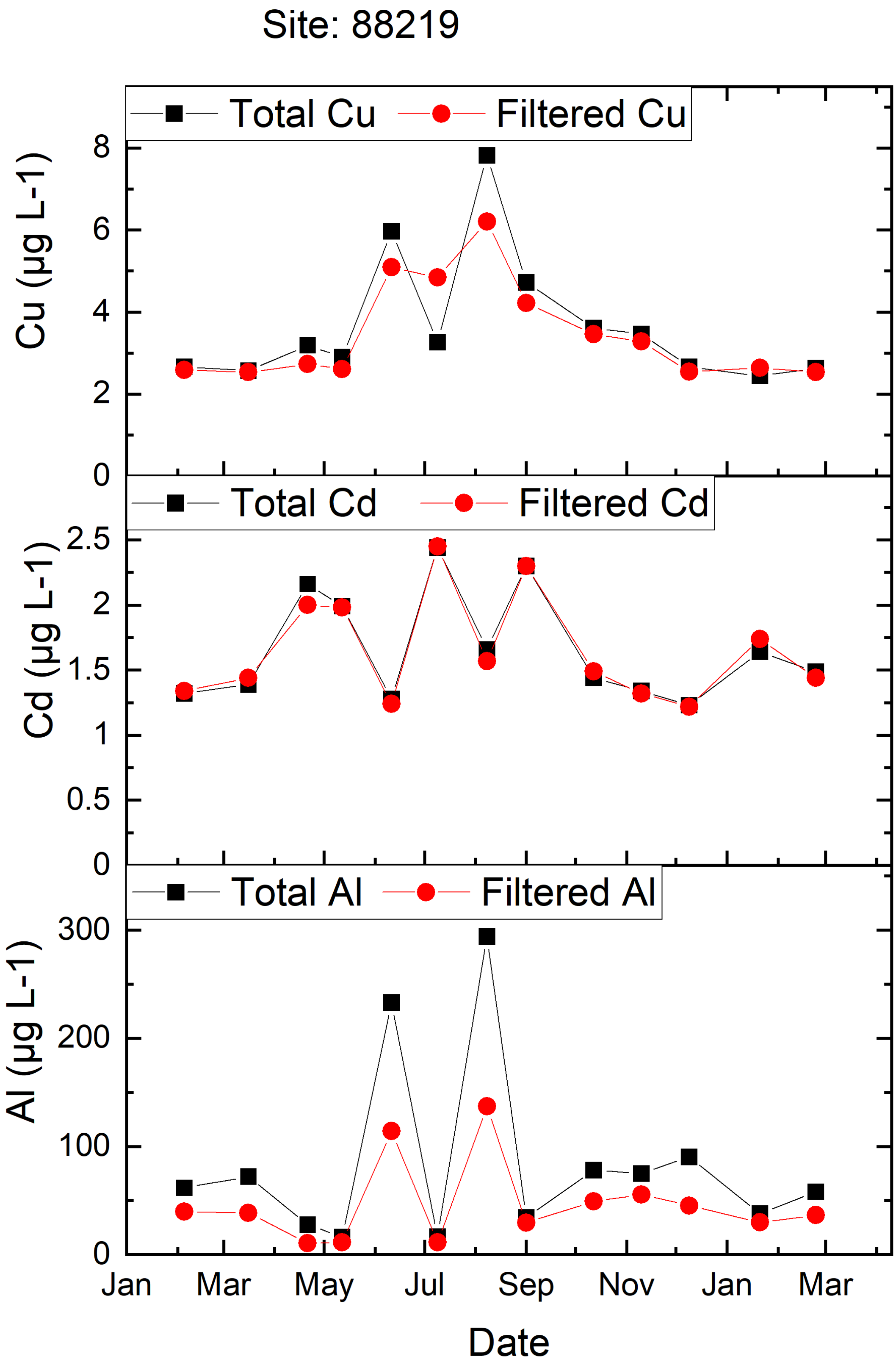


Figure 5-5 - Cu, Cd and Al concentrations for 88219

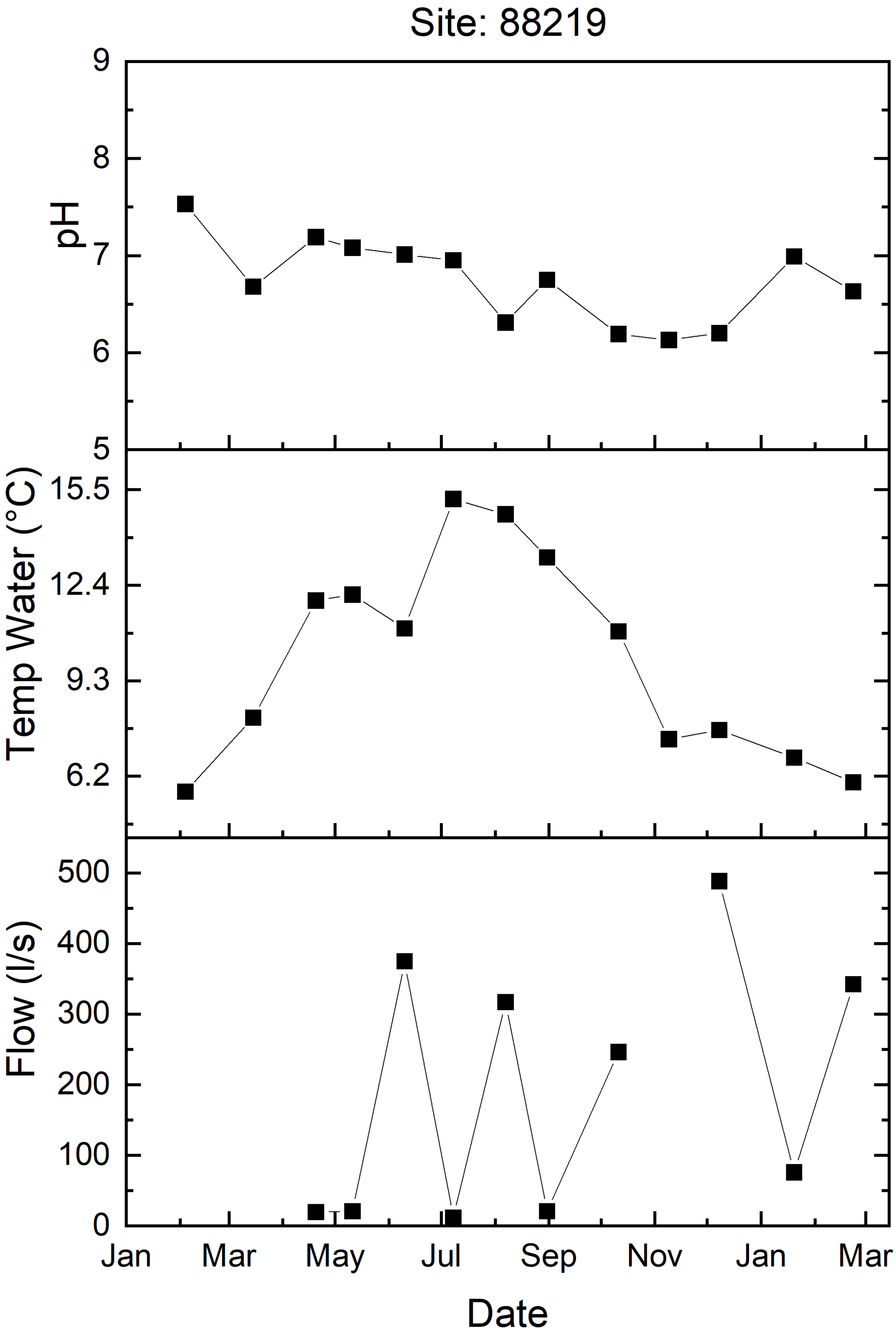


Figure 5-6 - pH and temperature readings for 88219, as well as flow gauging measurements

5.2.1.3 Nant y Bai upstream of the Pen y Darren

Sampling point 88347 is at the end of the lower mine wastes section, immediately upstream of the Pen y Darren stream.

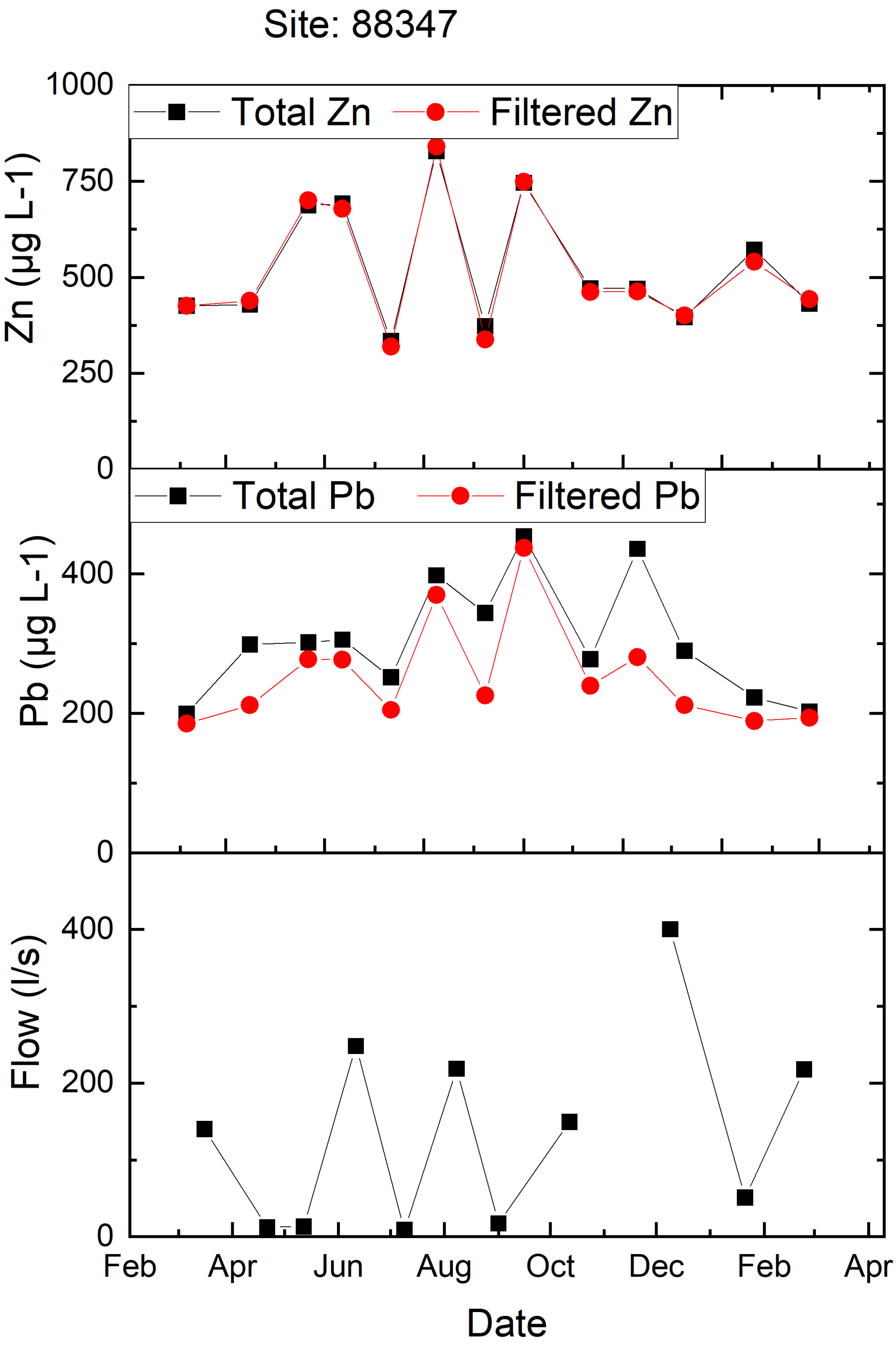


Figure 5-7 - Zn and Pb concentrations for 88437, as well as flow gauging measurements

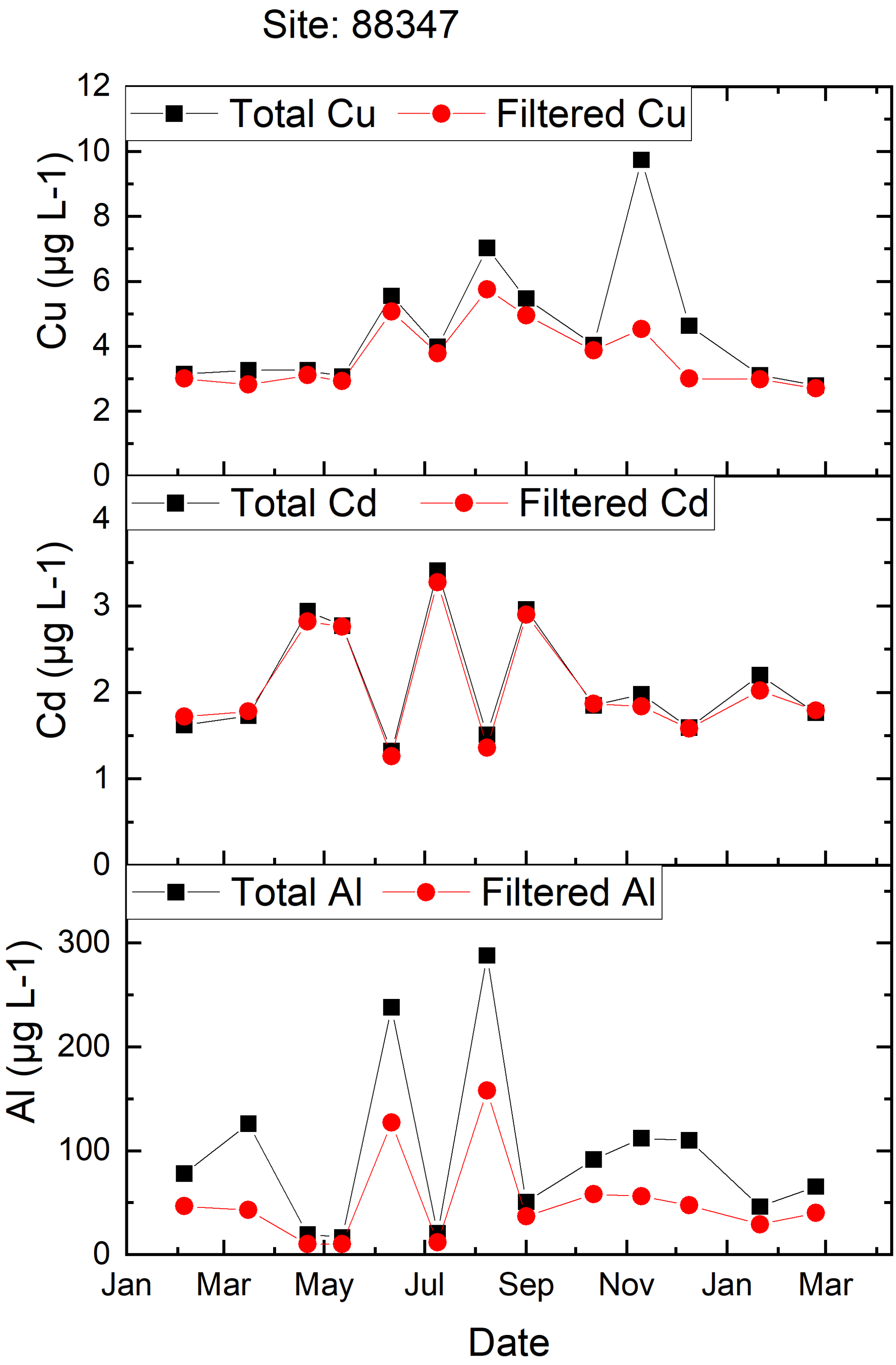


Figure 5-8 - Cu, Cd and Al concentrations for 88437

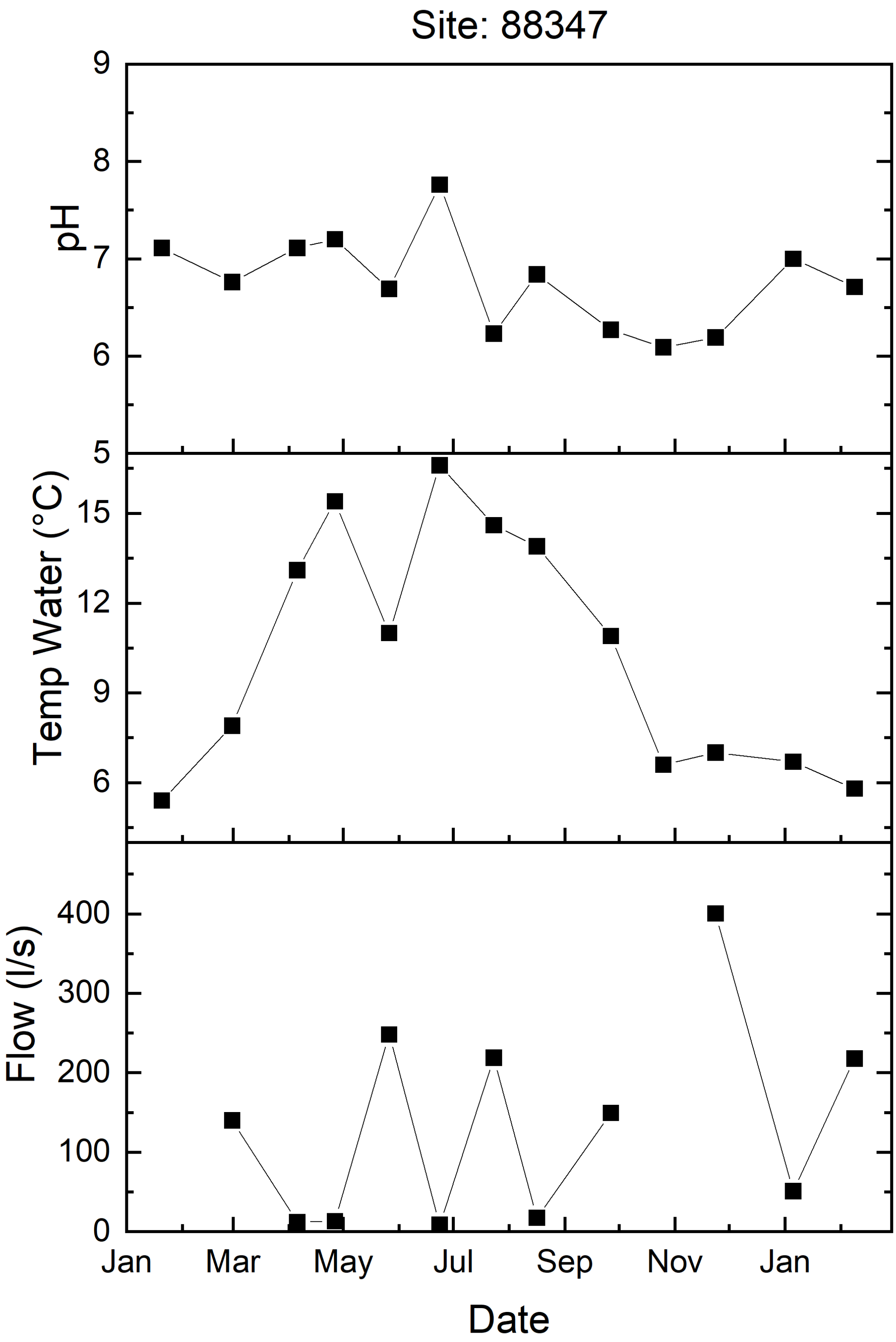


Figure 5-9 - pH and temperature readings for 88437, as well as flow gauging measurements

5.2.1.4 Upwelling to the Nant y Bai, left hand bank

Sampling point 88173 is an inflow to the Nant y Bai on the left hand bank, where historical imagery and mapping shows an ores processing building once stood.

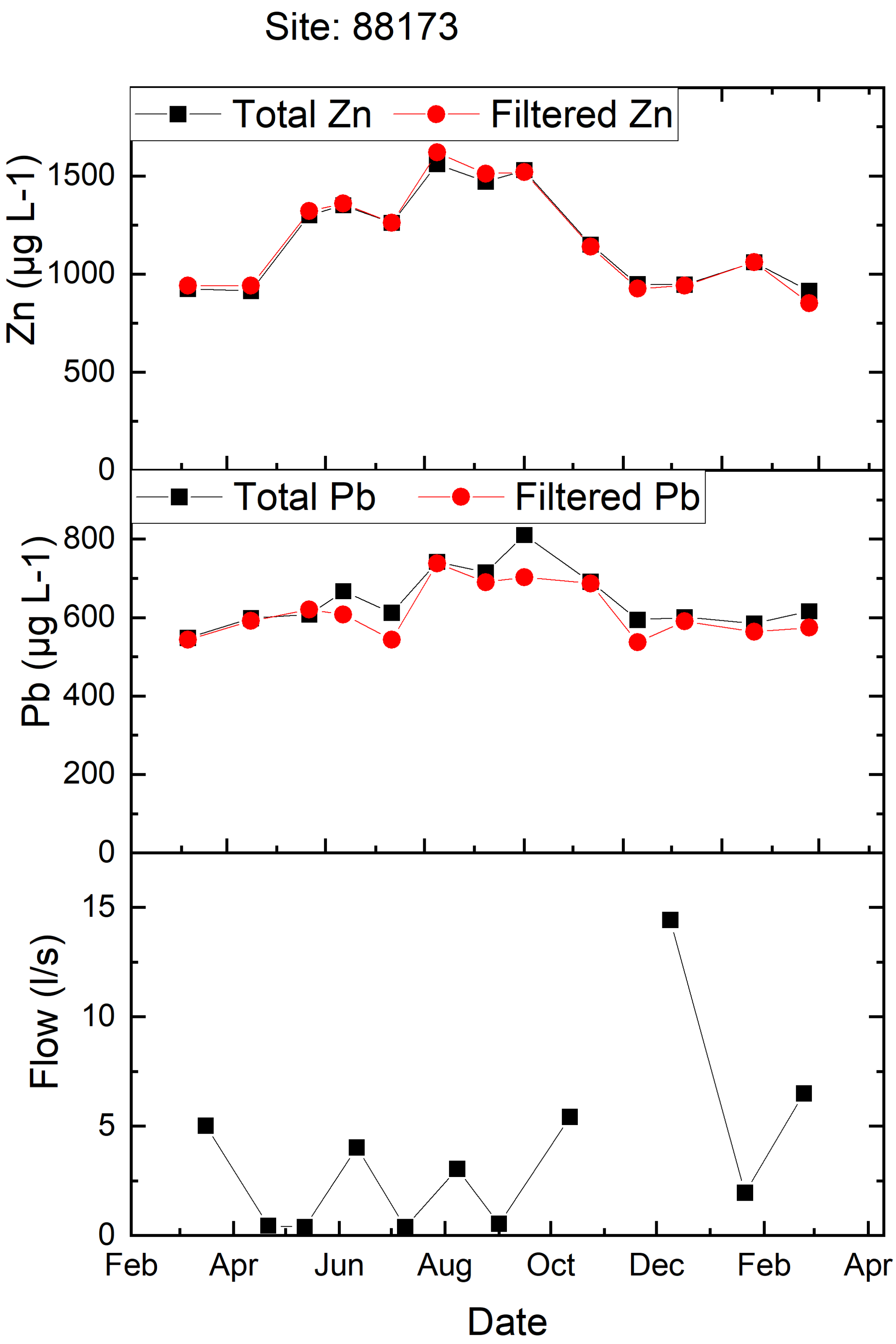


Figure 5-10 - Zn and Pb concentrations for 88173, as well as flow gauging measurements

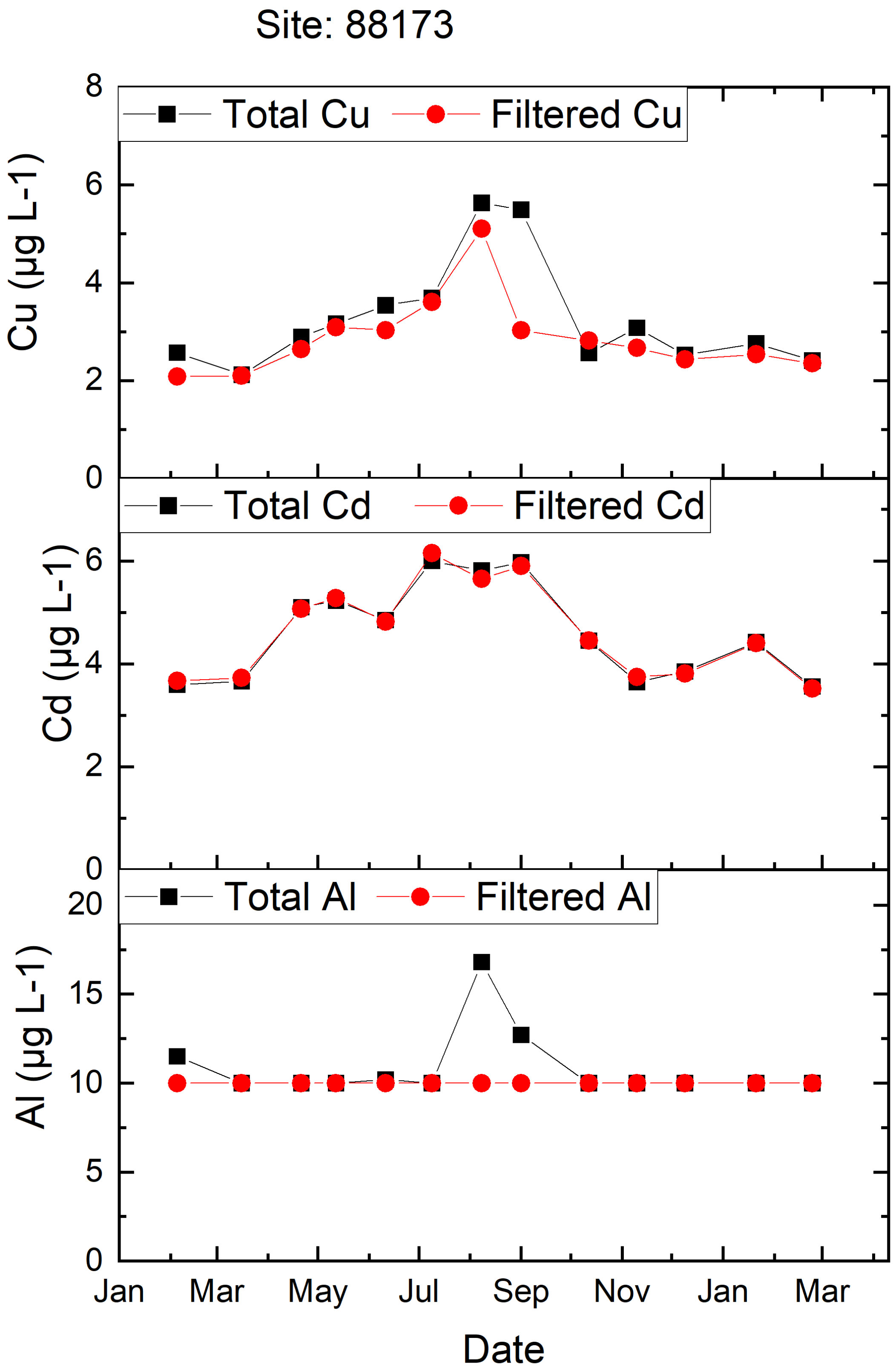


Figure 5-11 - Cu, Cd and Al concentrations for 88173

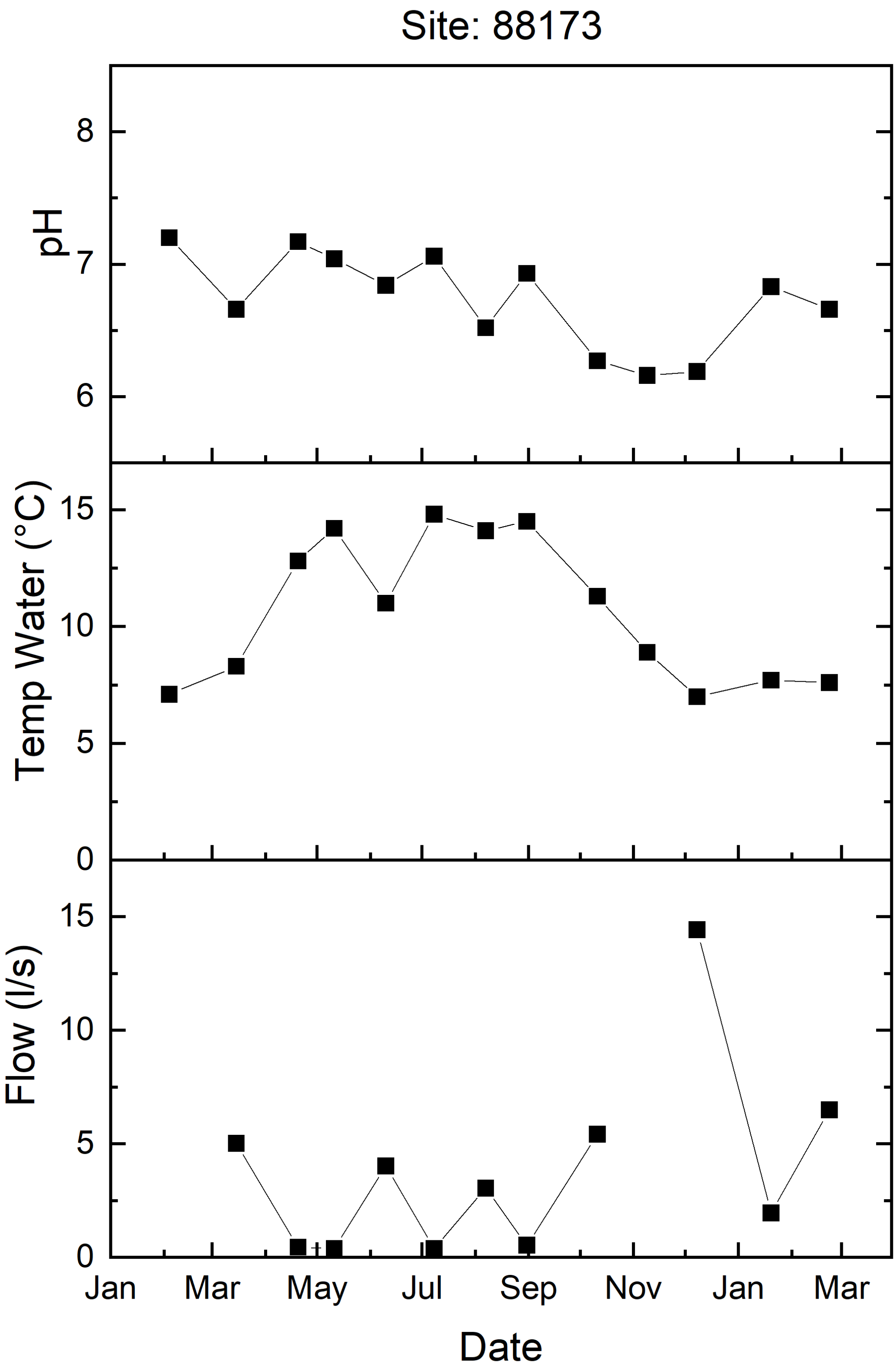


Figure 5-12 - pH and temperature readings for 88173, as well as flow gauging measurements

5.2.1.5 Flows from the spoil heap, right hand bank

Sampling point 190103 collects water flowing out of the mine wastes heaped on the right hand bank. This site is not suitable for flow gauging, and at high flows in the Nant y Bai it was not accessible.

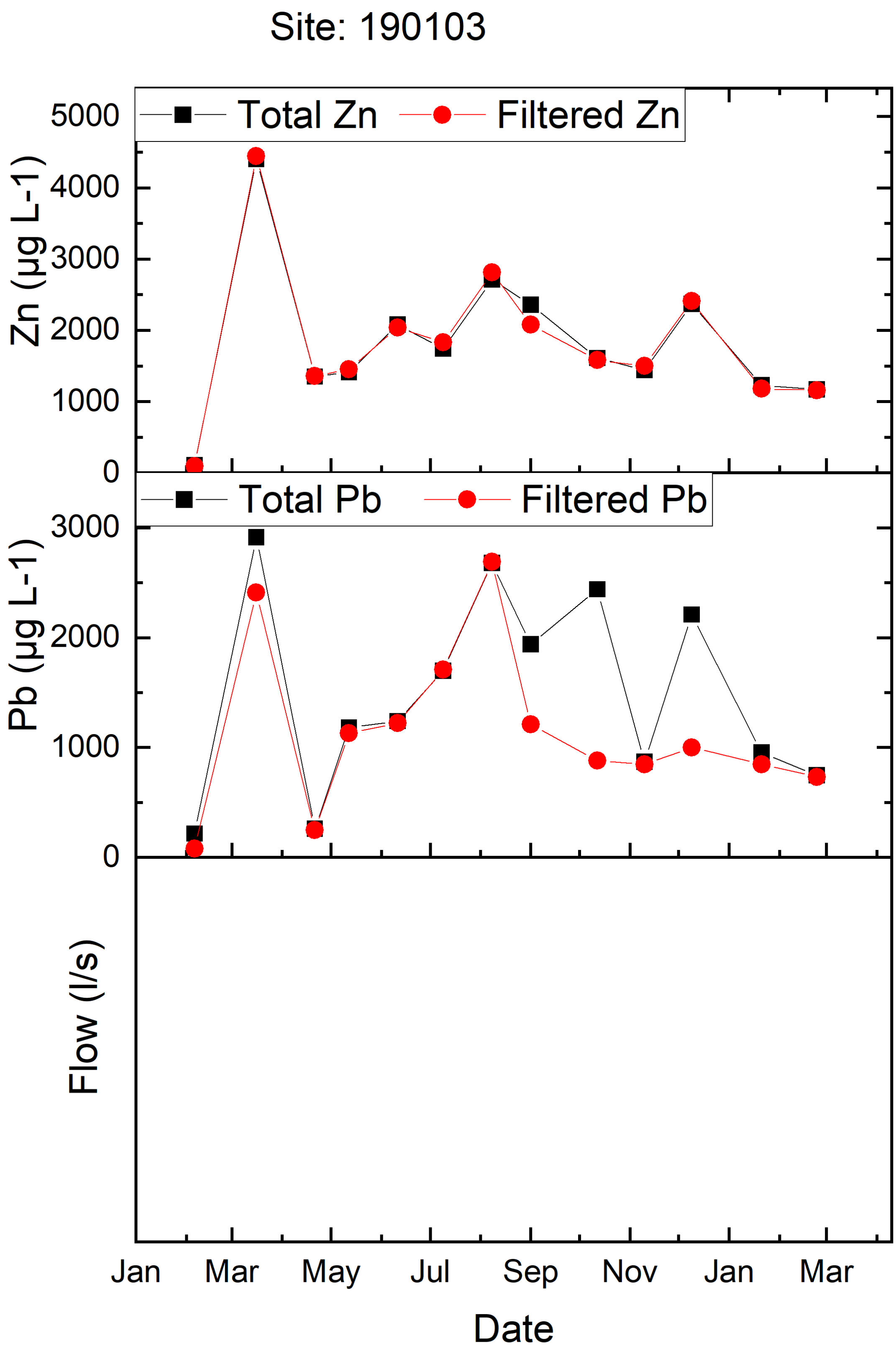


Figure 5-13 - Zn and Pb concentrations for 190103

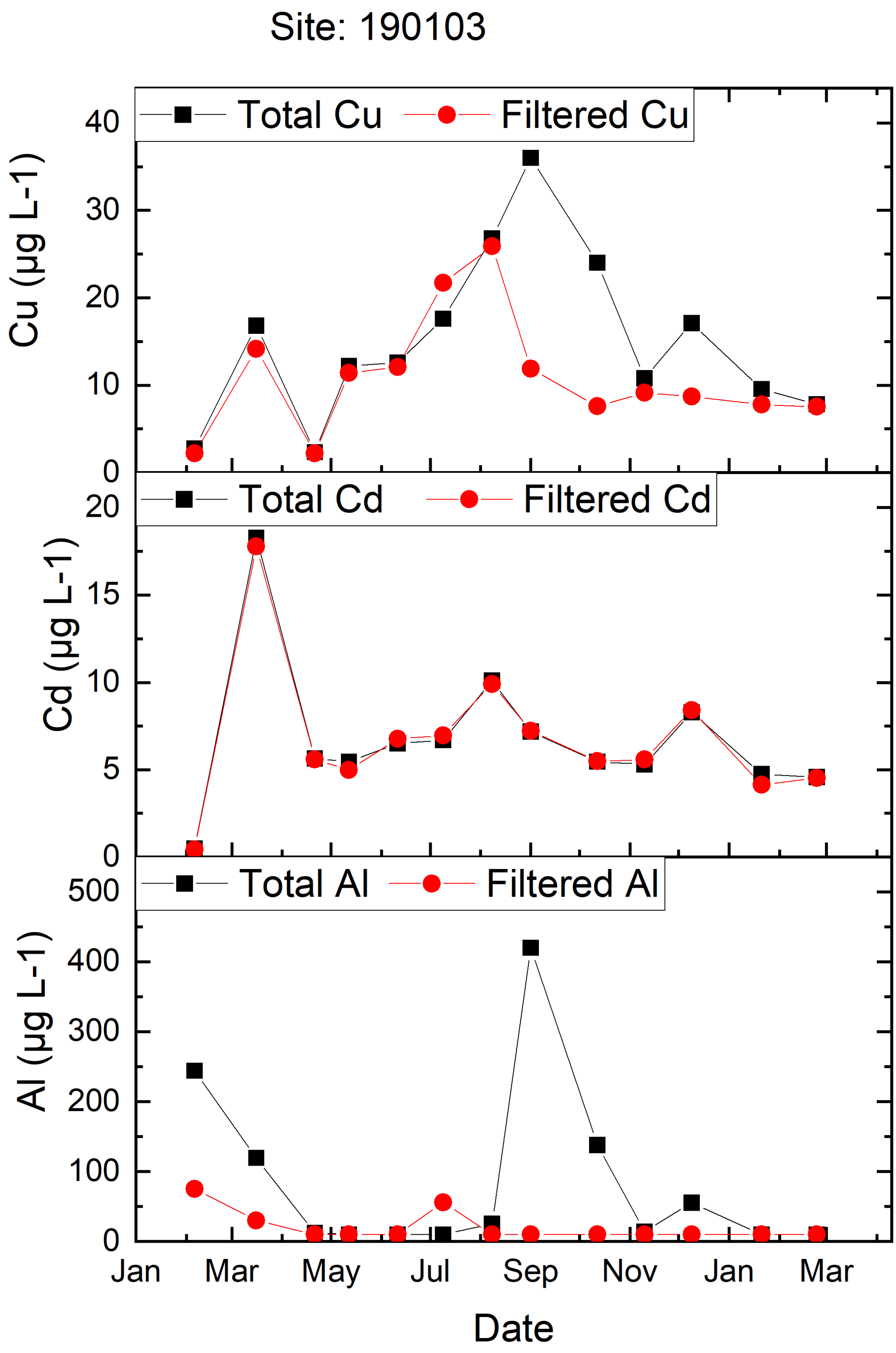


Figure 5-14 - Cu, Cd and Al concentrations for 190103

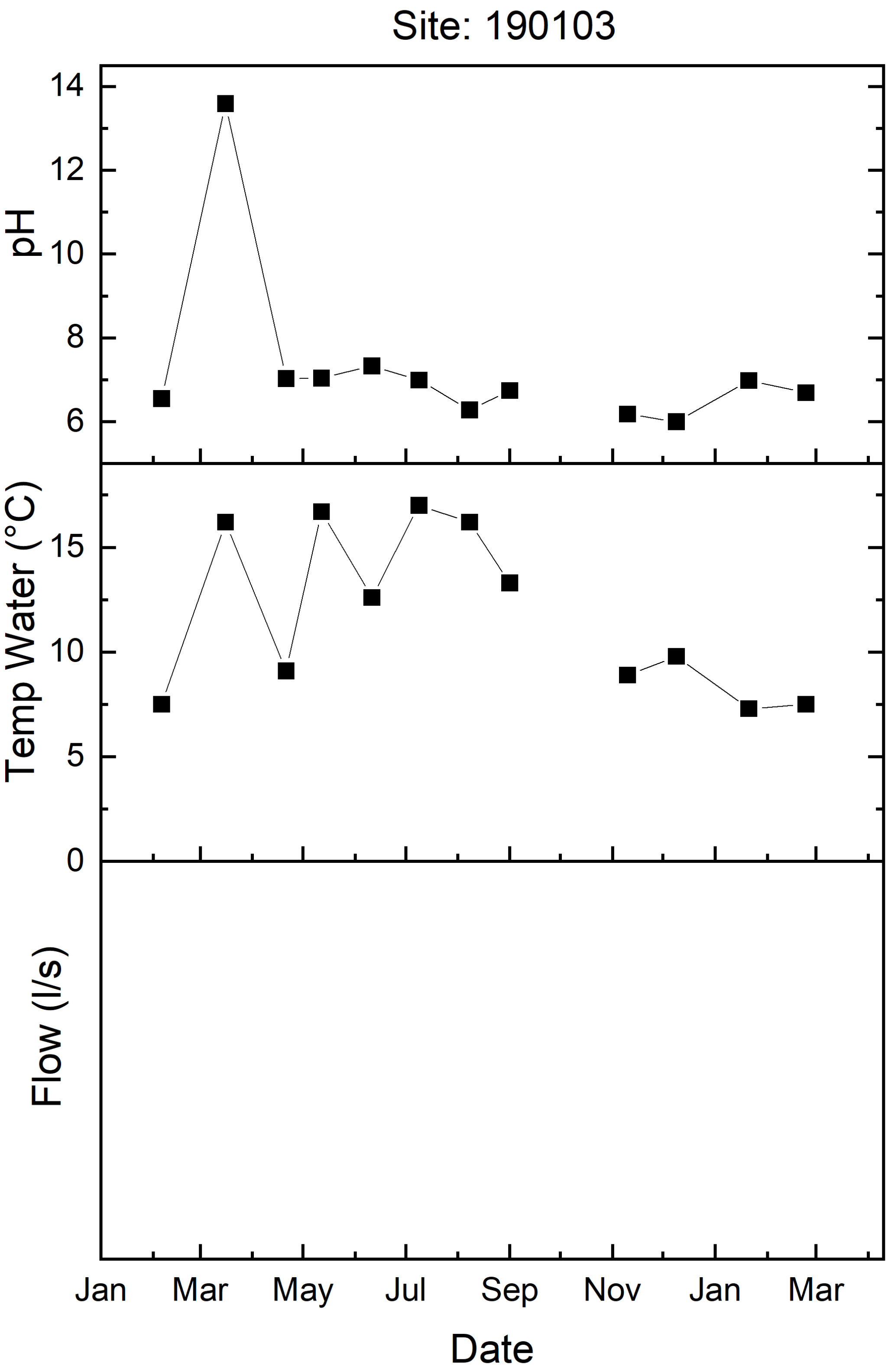


Figure 5-15 - pH and temperature readings for 190103

5.2.1.6 Upwelling to the Nant y Bai, left hand bank

Sampling point 88193 is an inflow to the Nant y Bai on the left hand bank, collecting water flowing out an upwelling in a boggy area, downstream of the Upper Boat Level and Nant y Bai Culvert. This site was very challenging to flow gauge and this was only success on three occasions.

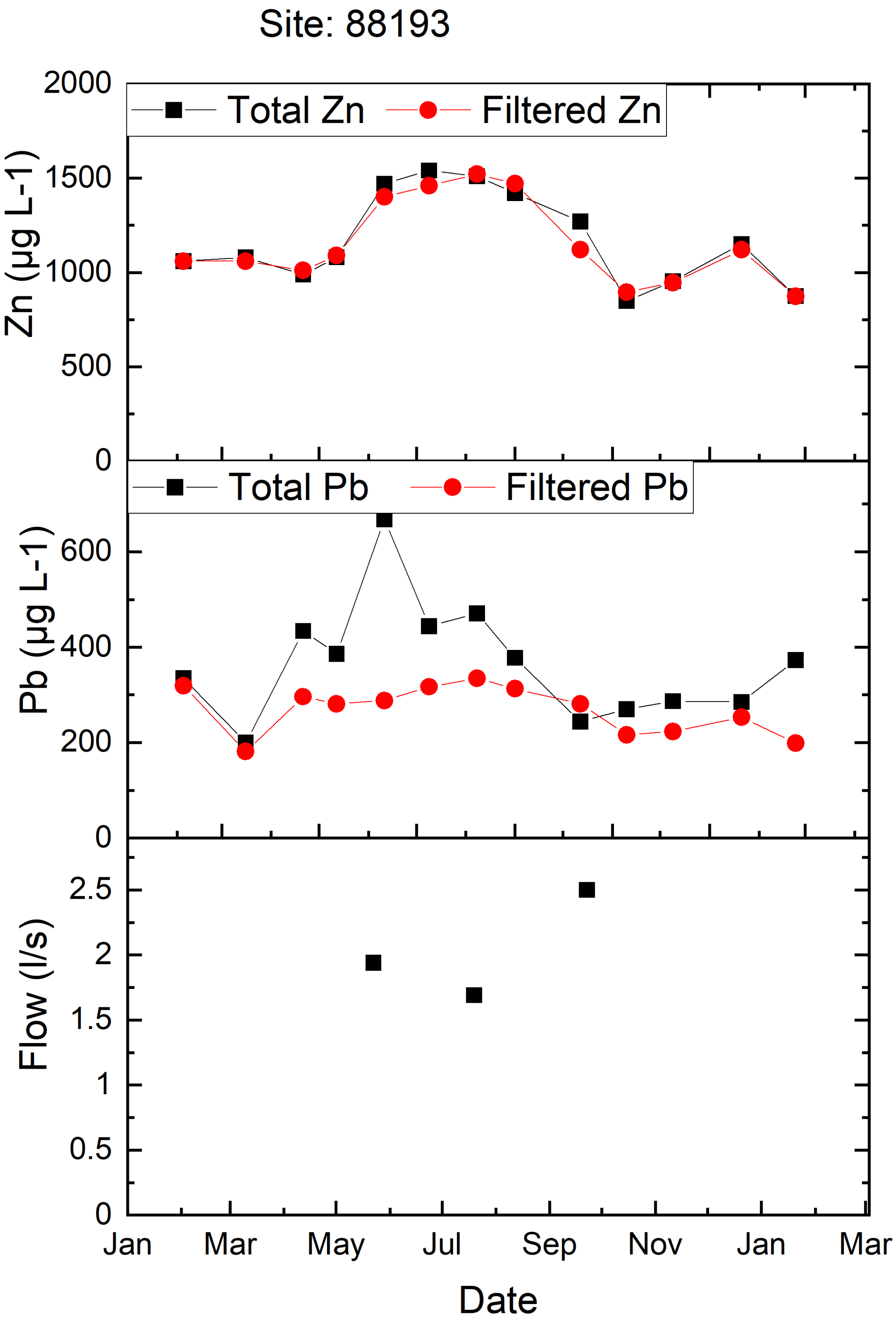


Figure 5-16 - Zn and Pb concentrations for 88193, as well as flow gauging measurements

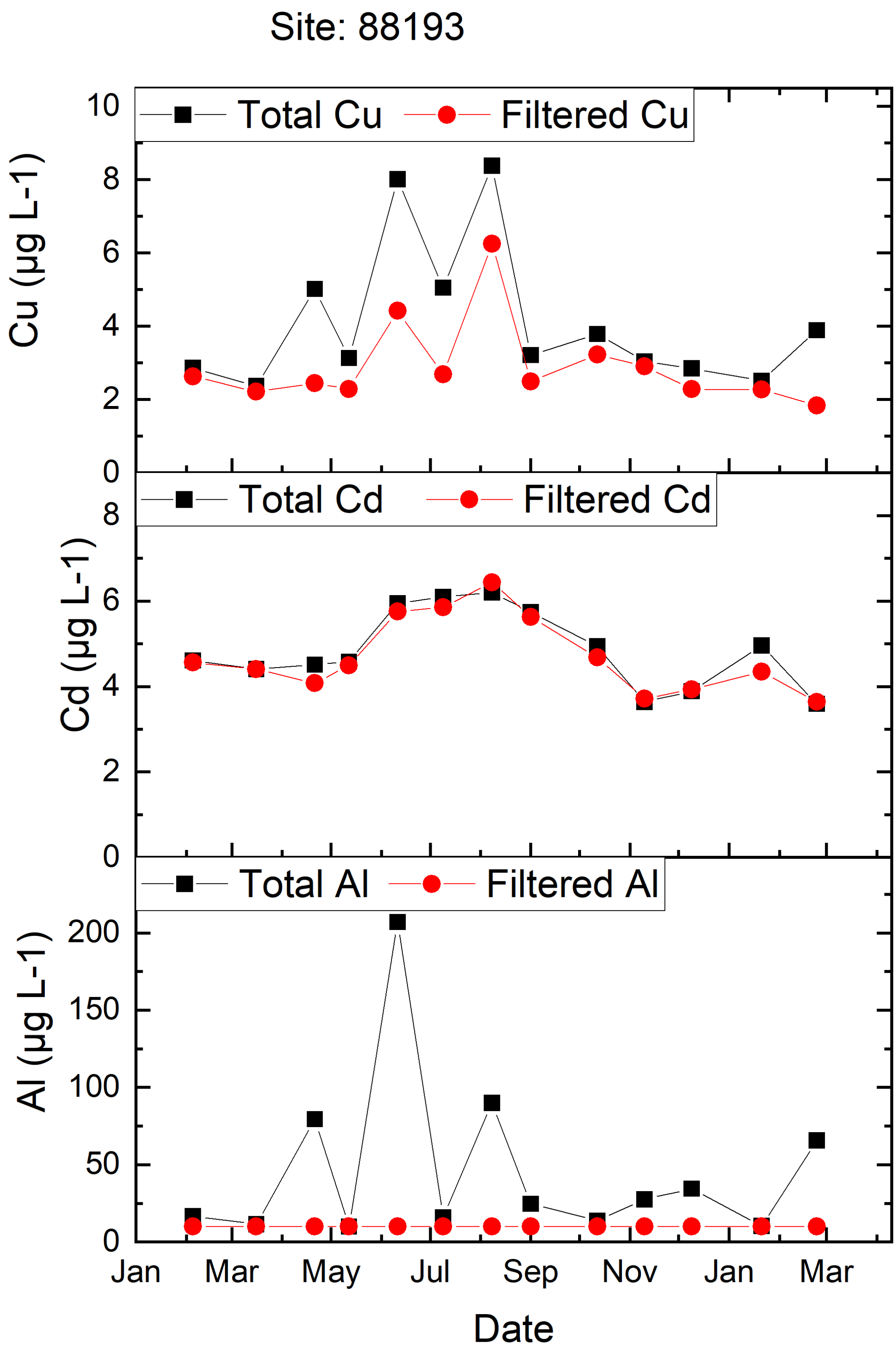


Figure 5-17 - Cu, Cd and Al concentrations for 88193

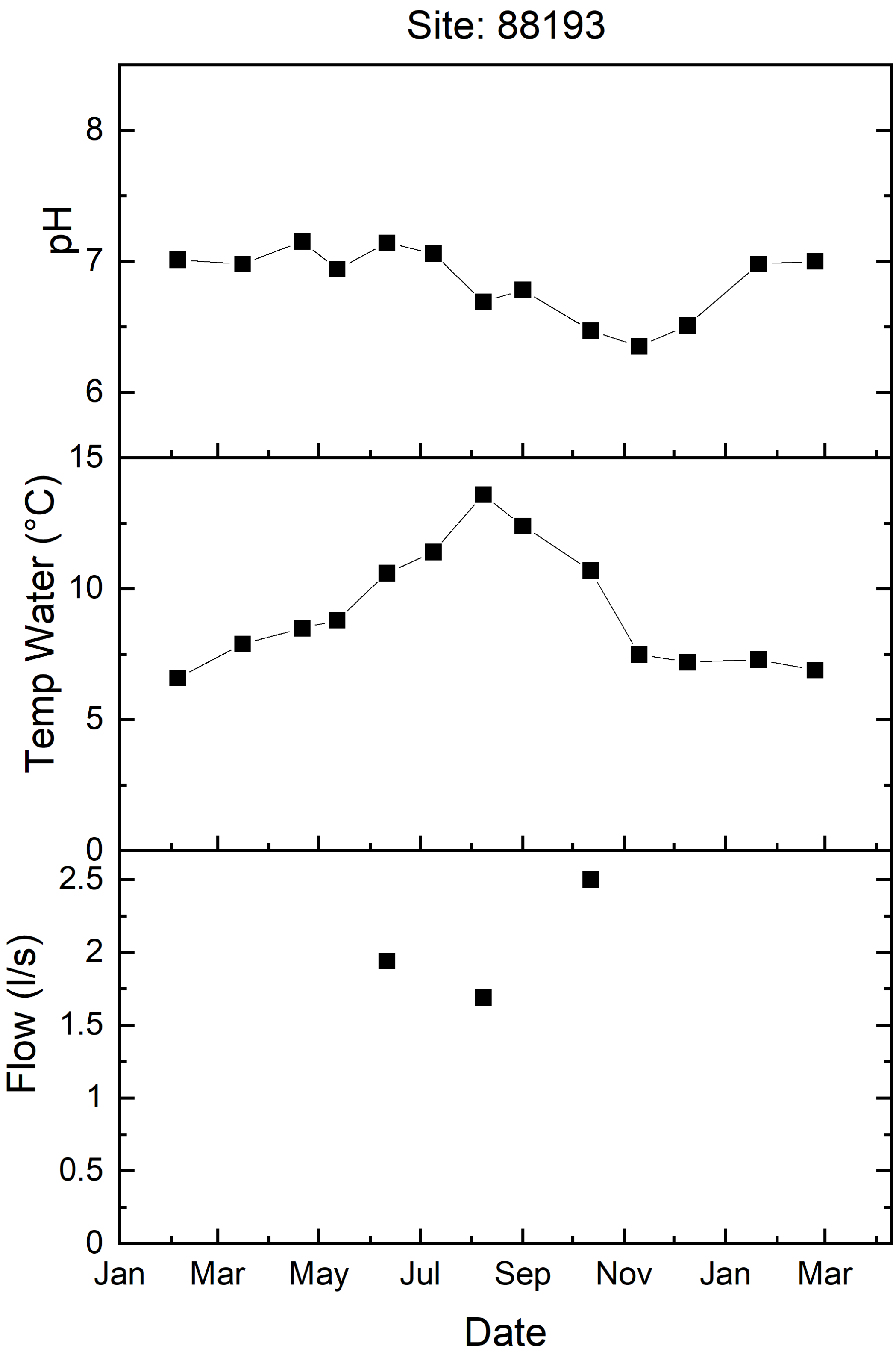


Figure 5-18 - pH and temperature readings for 88193, as well as flow gauging measurements

5.2.1.7 Upper Boat Level

Sampling point 88223 collects water from the Upper Boat Level, a semi-collapsed mine adit with a low flow output of ochreous water. It is not possible to flow gauge the Upper Boat Level due to the low flows, too low to be detected by a current meter, and the quantity of ochre, which blocks the sensor on a conductivity meter for salt dilution flow gauging.

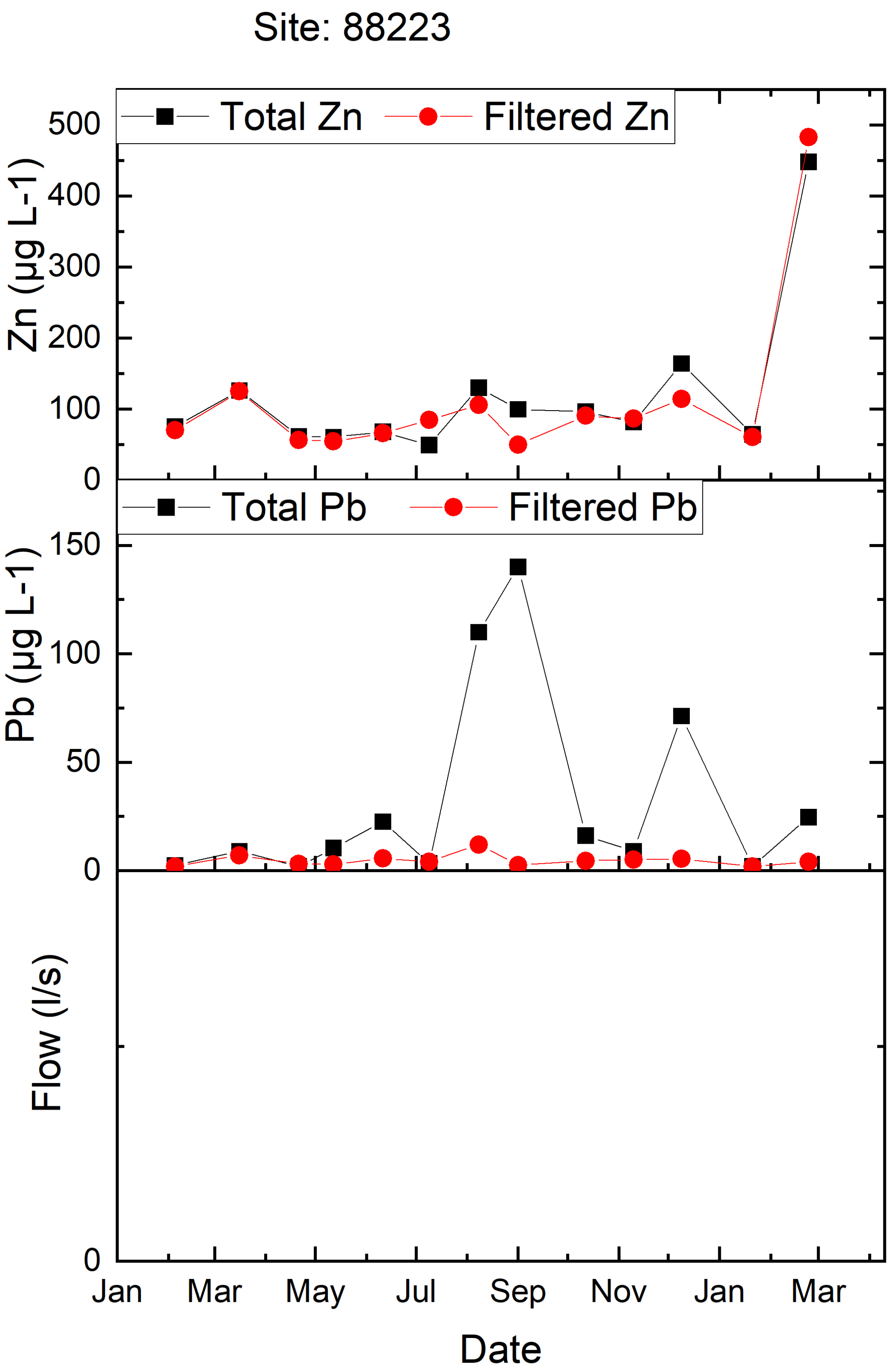


Figure 5-19 - Zn and Pb concentrations for 88223

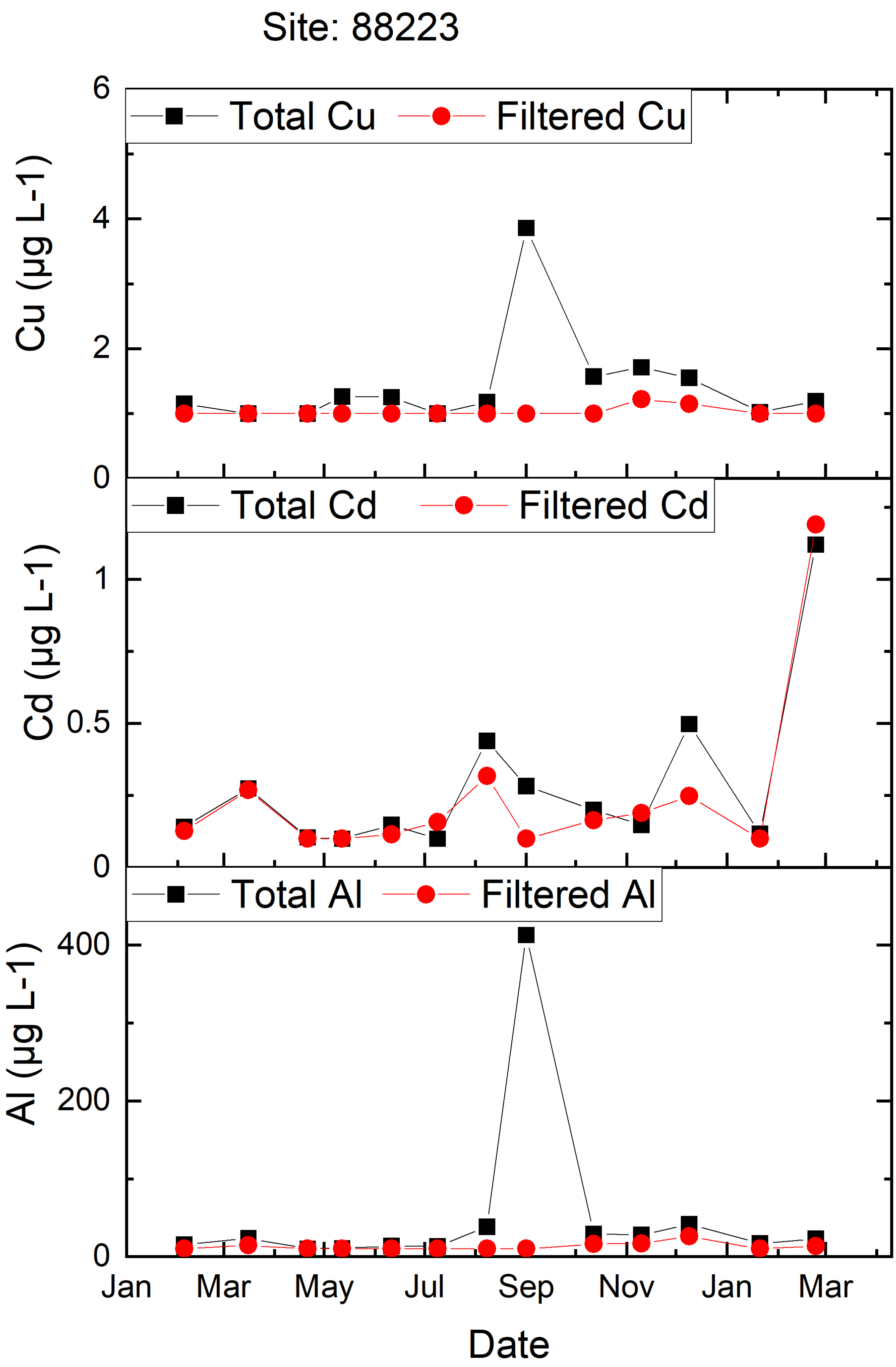


Figure 5-20 - Cu, Cd and Al concentrations for 88223

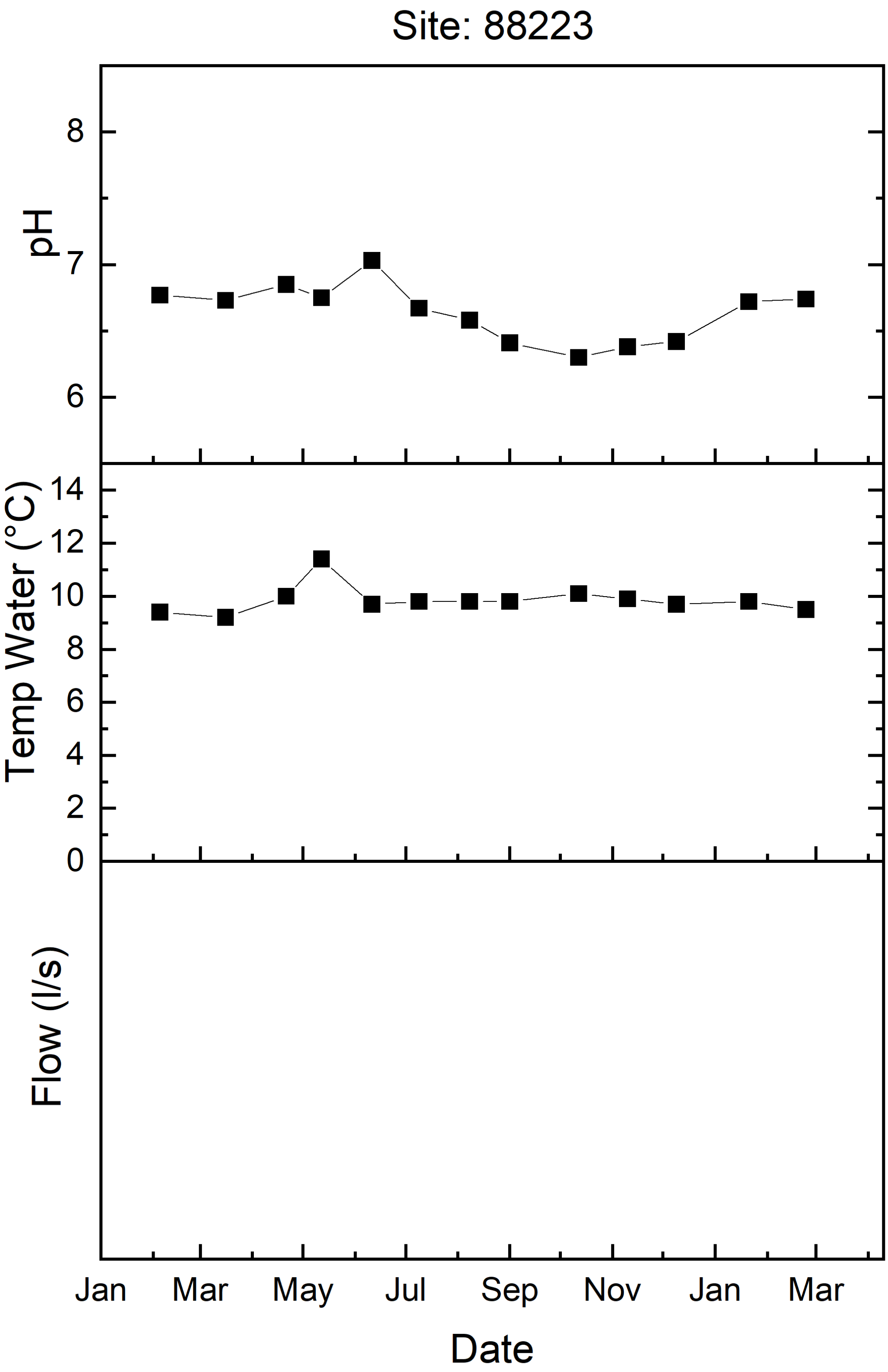


Figure 5-21 - pH and temperature readings for 88223

5.2.1.8 Nant y Bai above adit

Sampling point 88222 is in between the two main areas of mine wastes which the Nant y Bai flows through, upstream of the Upper Boat Level.

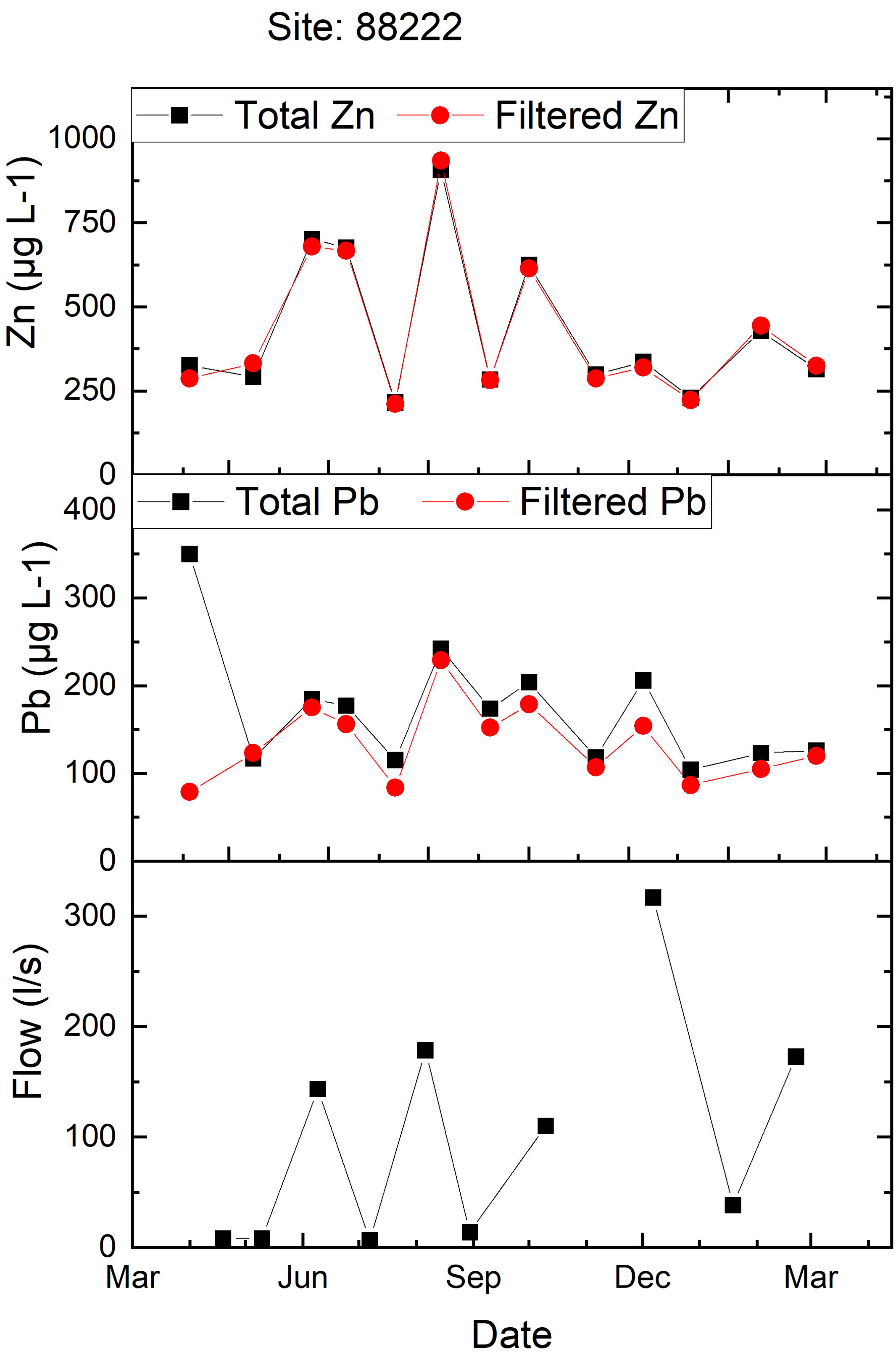


Figure 5-22 - Zn and Pb concentrations for 88222, as well as flow gauging measurements

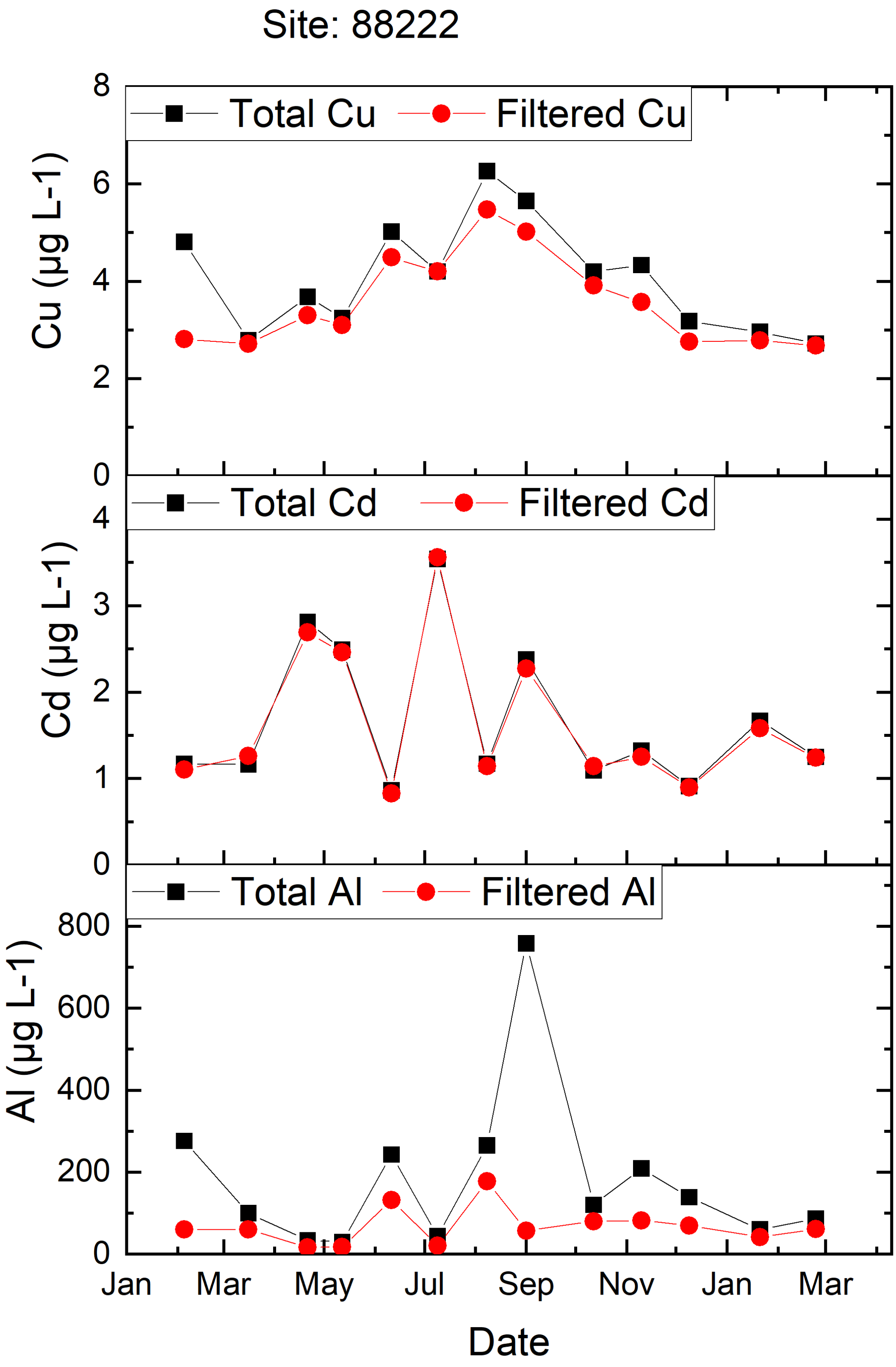


Figure 5-23 - Cu, Cd and Al concentrations for 88222

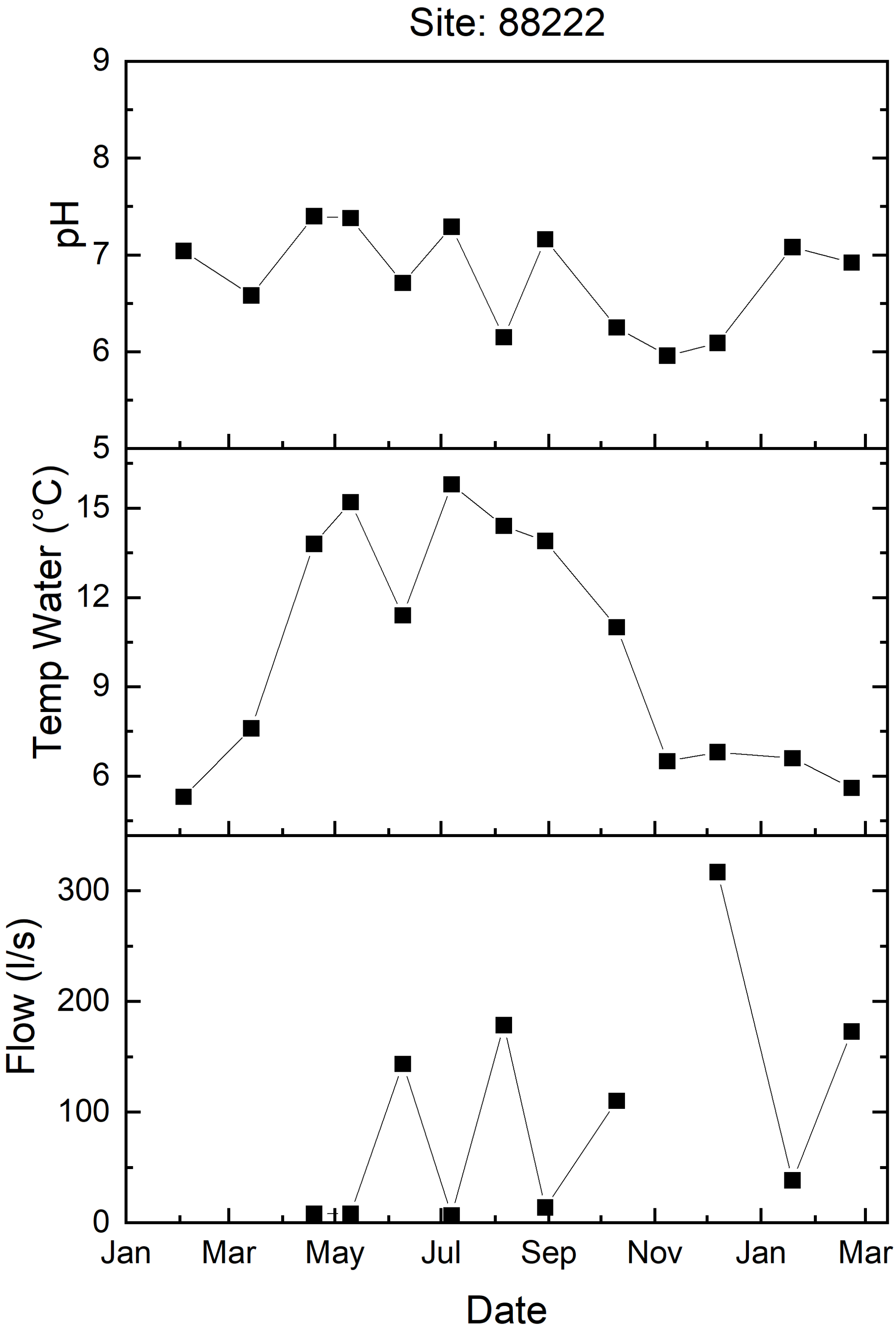


Figure 5-24 - pH and temperature readings for 88222, as well as flow gauging measurements

5.2.1.9 Nant y Bai Culvert

Sampling point 88224 conveys overland flow from mine wastes underneath a forestry track and into a boggy area, also home to the Upper Boat Level and sampling point 88193.

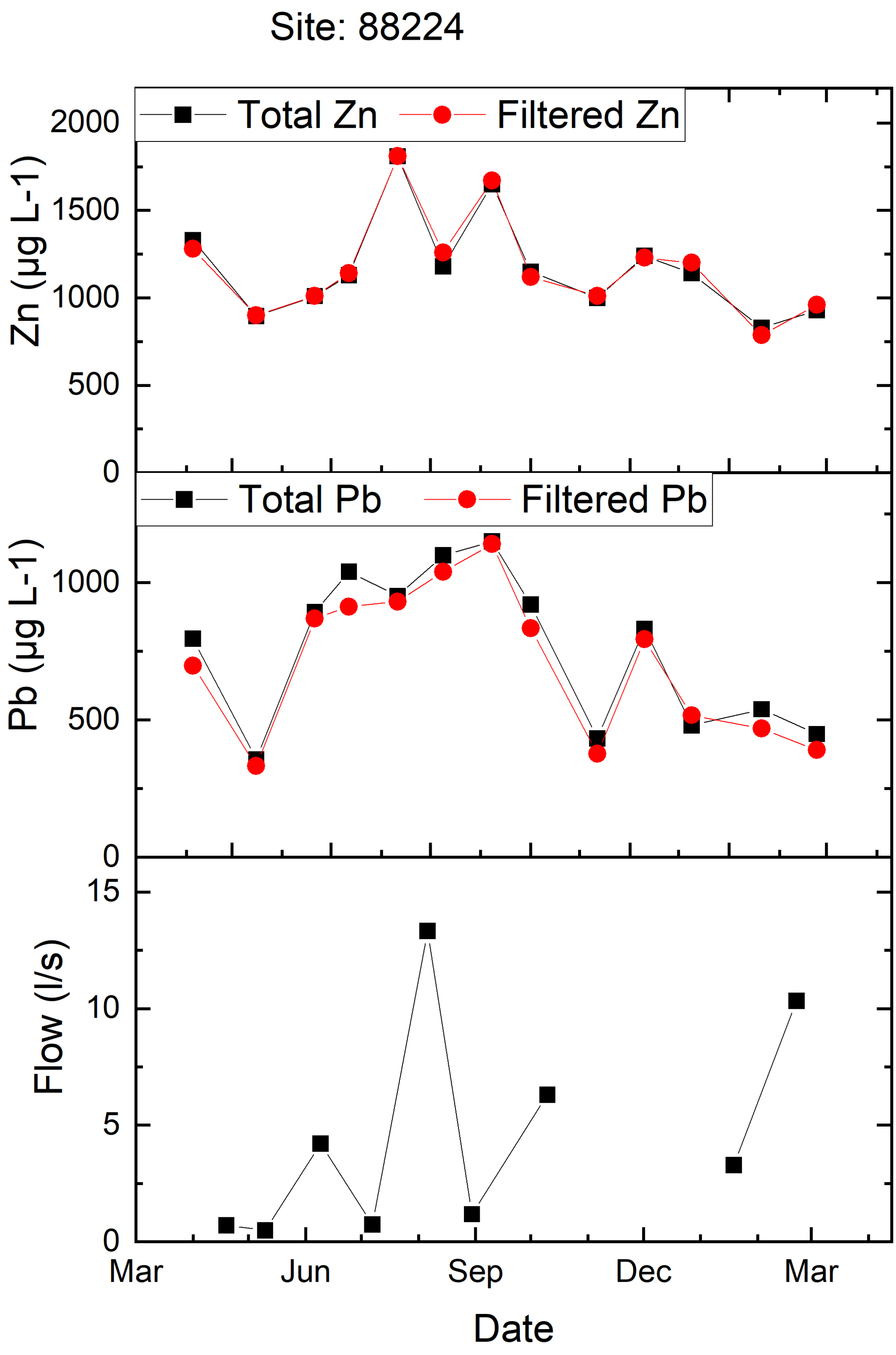


Figure 5-25 - Zn and Pb concentrations for 88224, as well as flow gauging measurements

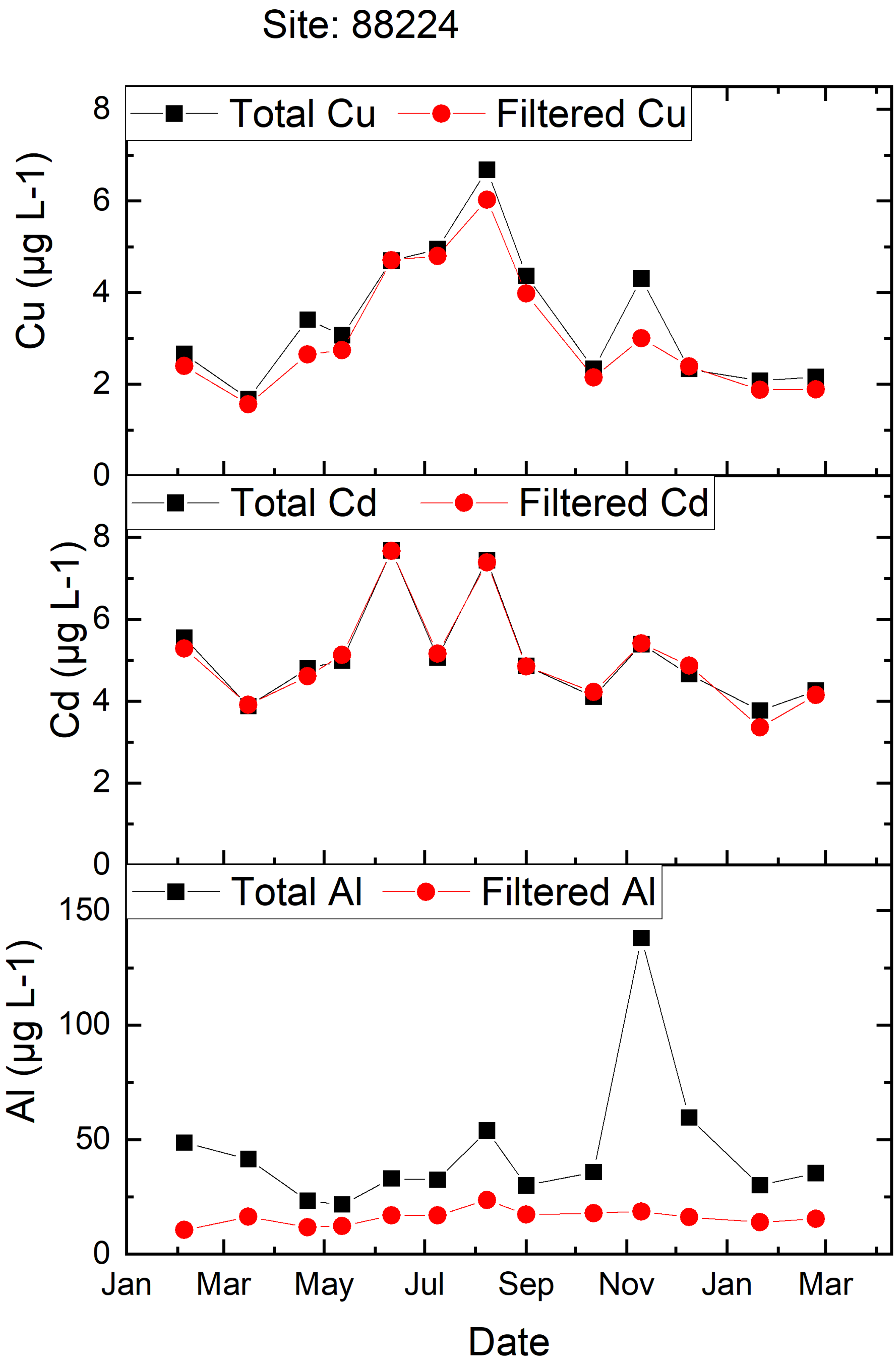


Figure 5-26 - Cu, Cd and Al concentrations for 88224

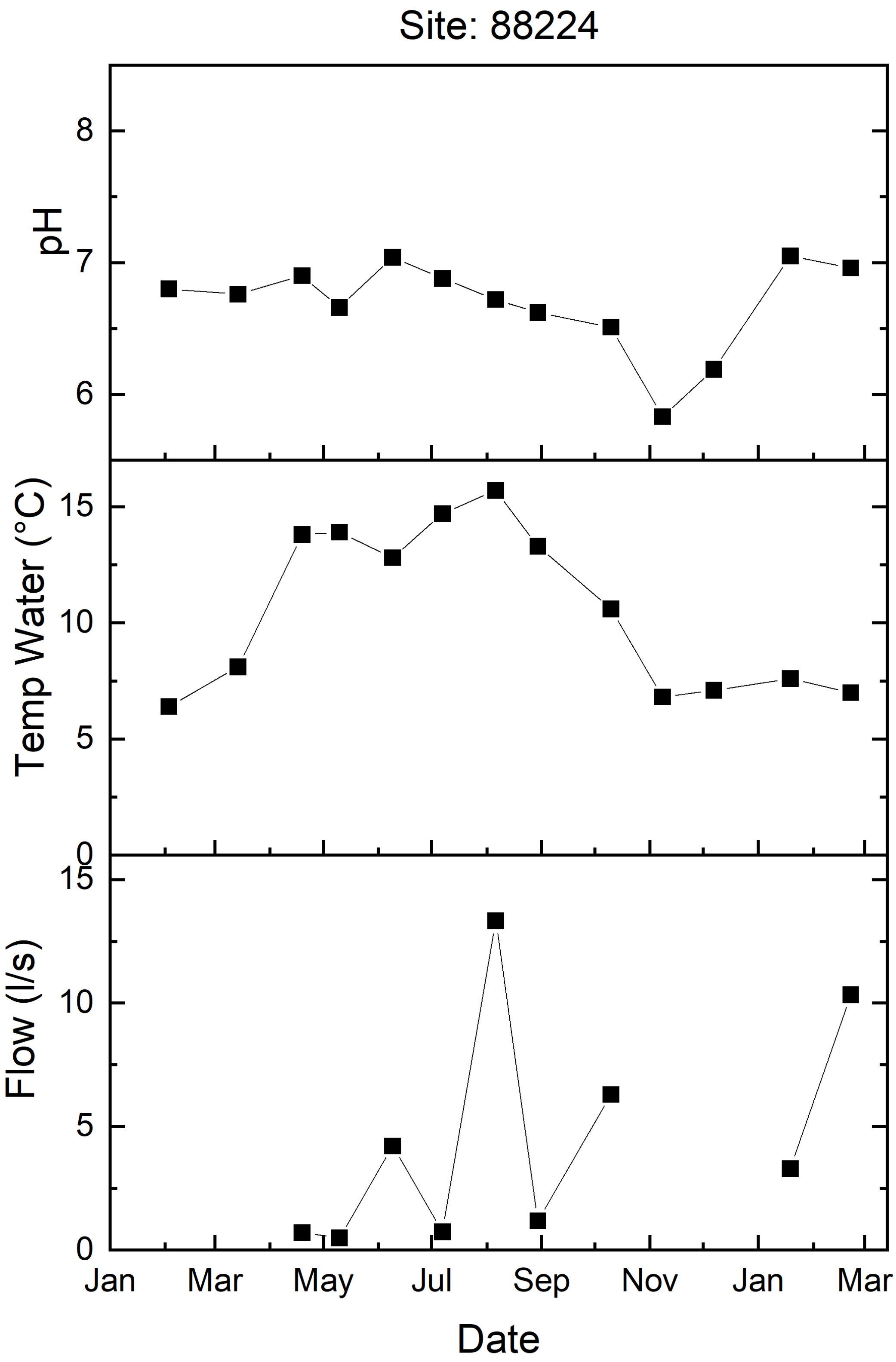


Figure 5-27 - pH and temperature readings for 88224, as well as flow gauging measurements

5.2.1.10 Nant y Bai spoil run off

Sampling point 88434 collects water flowing out of mine wastes on the left hand bank of the Nant y Bai. Flow gauging here is hindered by the low flows and shallow depth of the watercourse, but occasionally variations in the channel allowed the bucket and stopwatch method to be utilised.

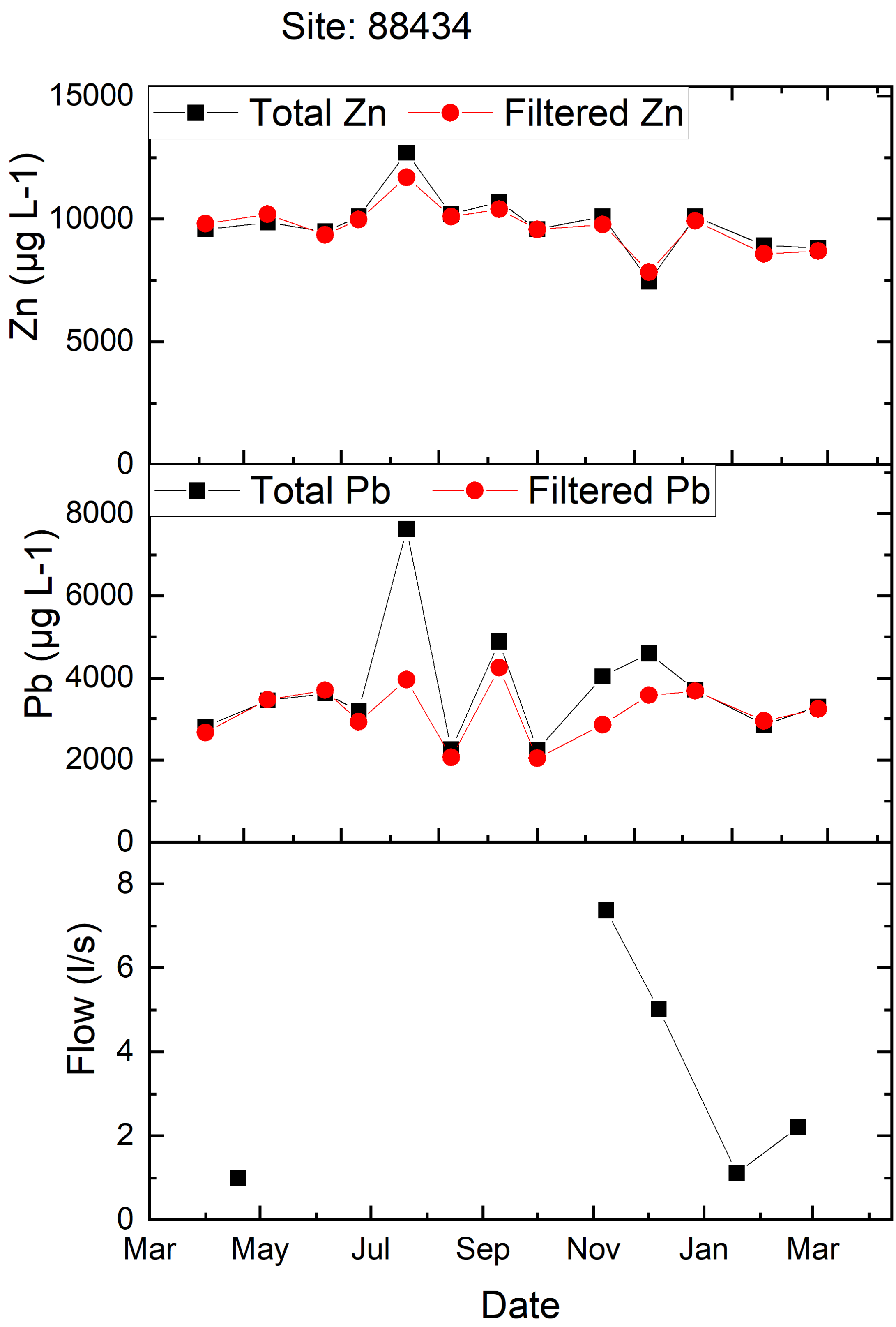


Figure 5-28 - Zn and Pb concentrations for 88434, as well as flow gauging measurements

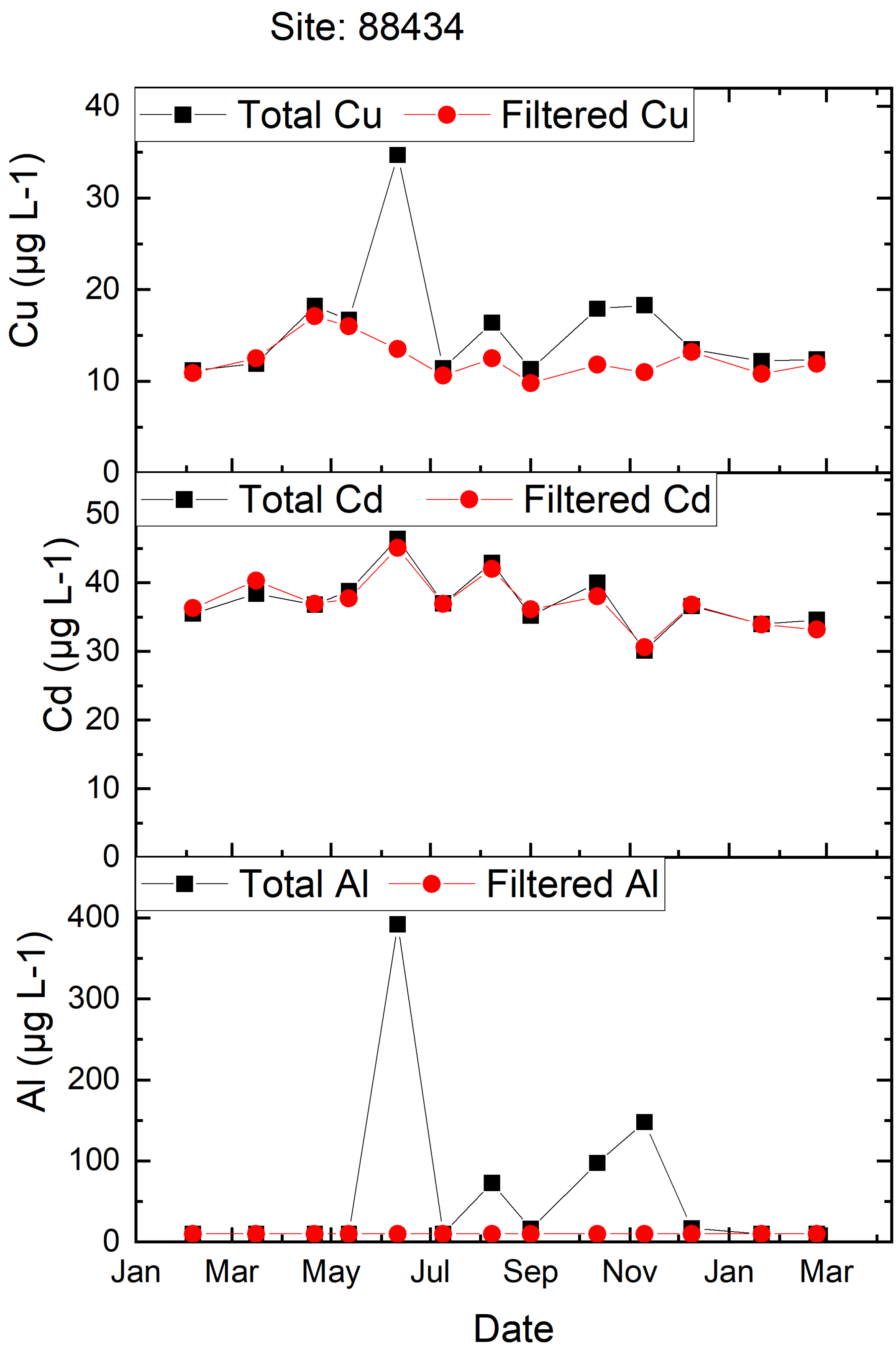


Figure 5-29 - Cu, Cd and Al concentrations for 88434

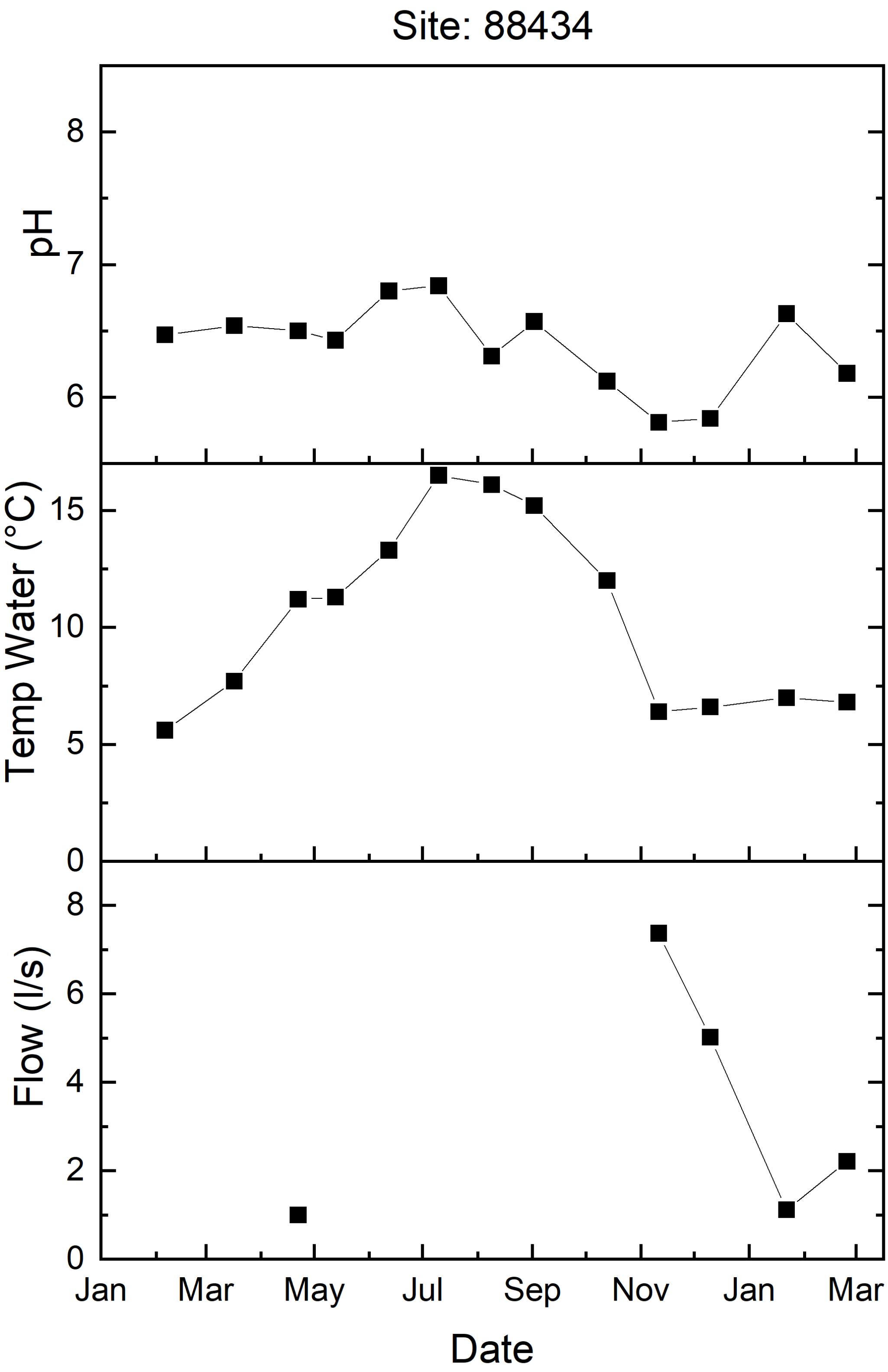


Figure 5-30 - pH and temperature readings for 88434, as well as flow gauging measurements

5.2.1.11 Nant y Bai upstream of the mine workings

Sampling point 88221 is upstream of the mine wastes, approximately 100 m above the end of visible mine wastes.

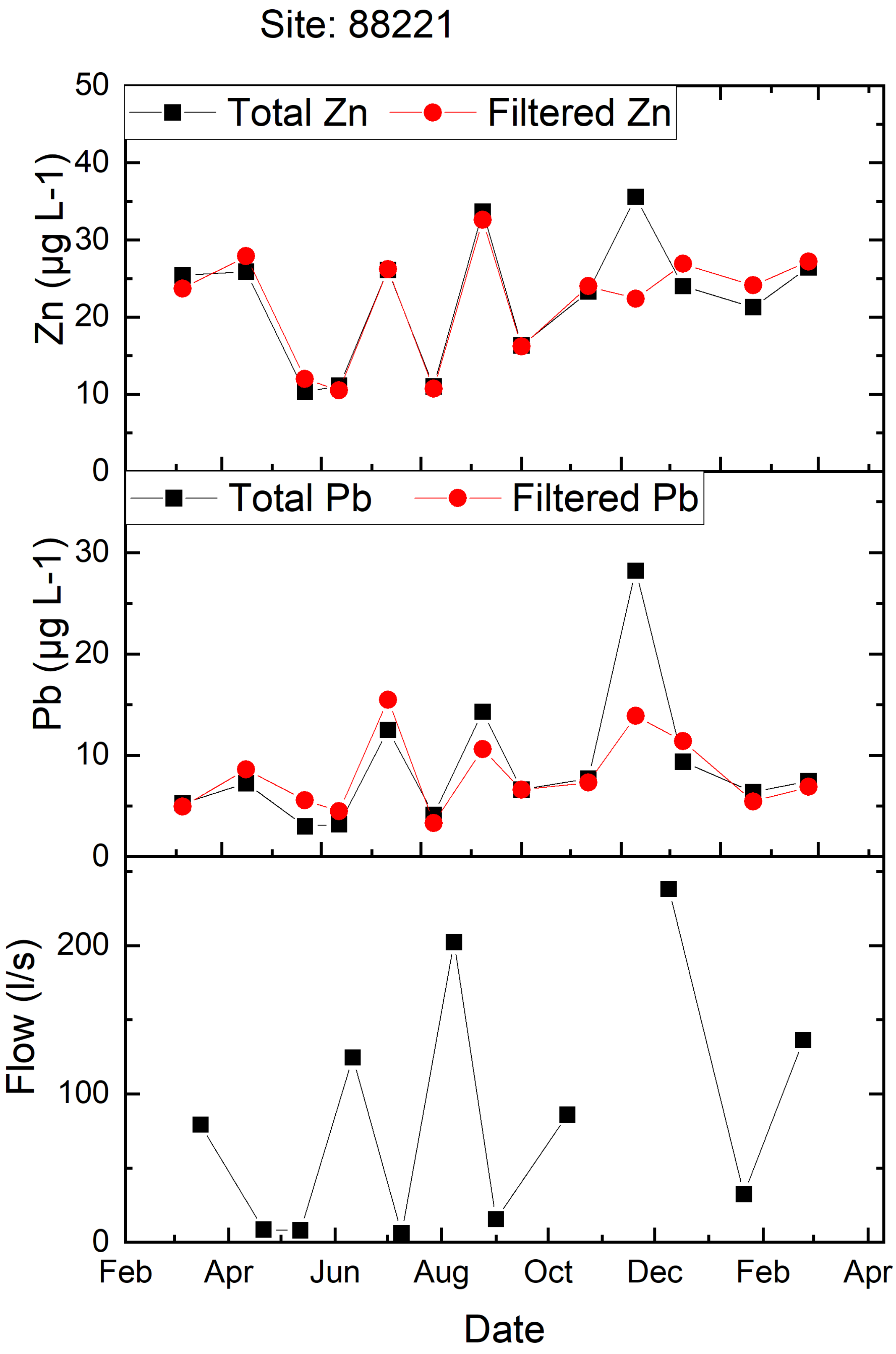


Figure 5-31 - Zn and Pb concentrations for 88221, as well as flow gauging measurements

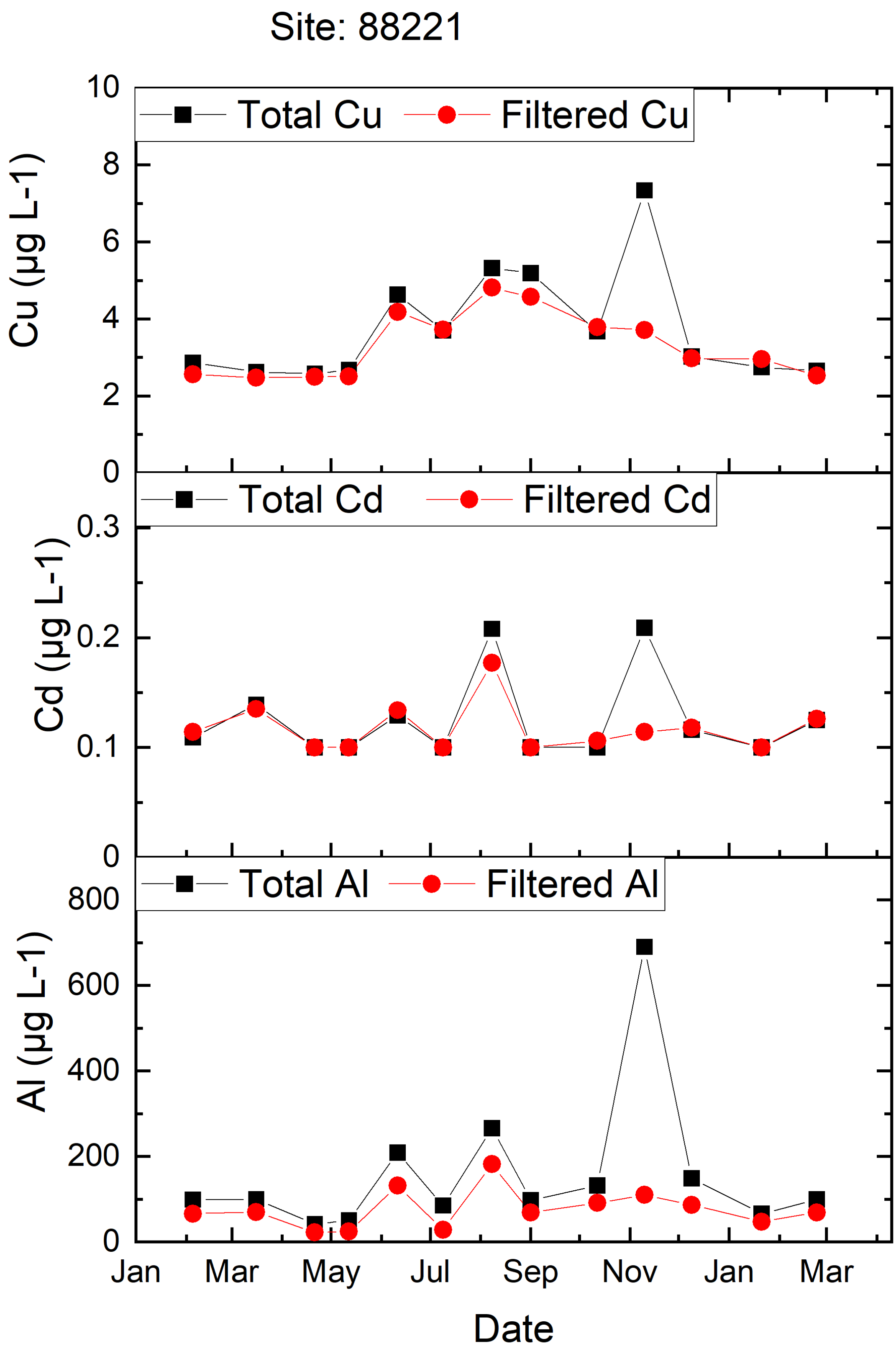


Figure 5-32 - Cu, Cd and Al concentrations for 88221

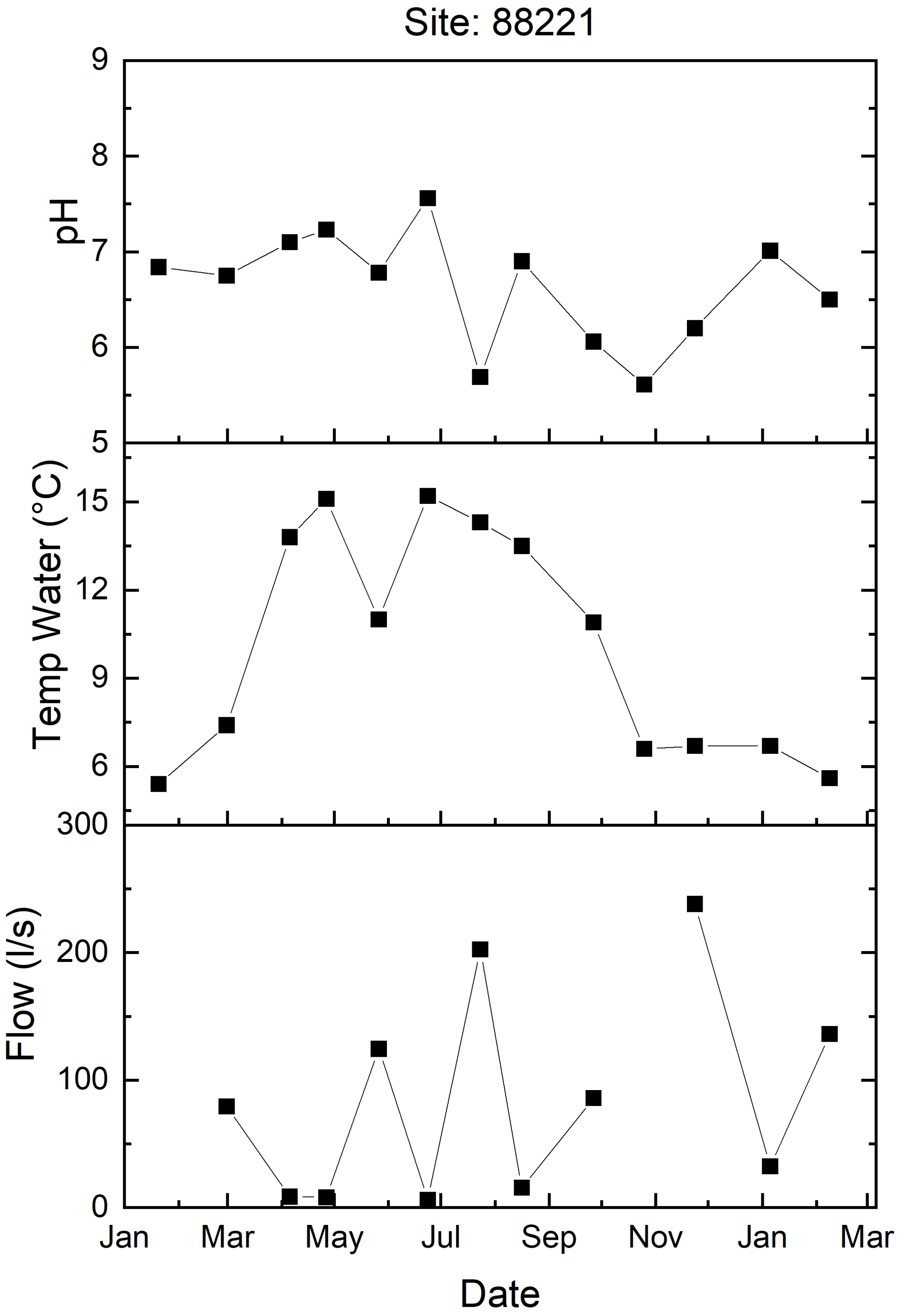


Figure 5-33 - pH and temperature readings for 88221, as well as flow gauging measurements

5.2.2 Nant y Mwyn

5.2.2.1 Nant y Mwyn close to the Tywi confluence

Sampling point 88201 is at the lowest point of the studied stretch of the Nant y Mwyn, on the flood plain of the River Twyi.

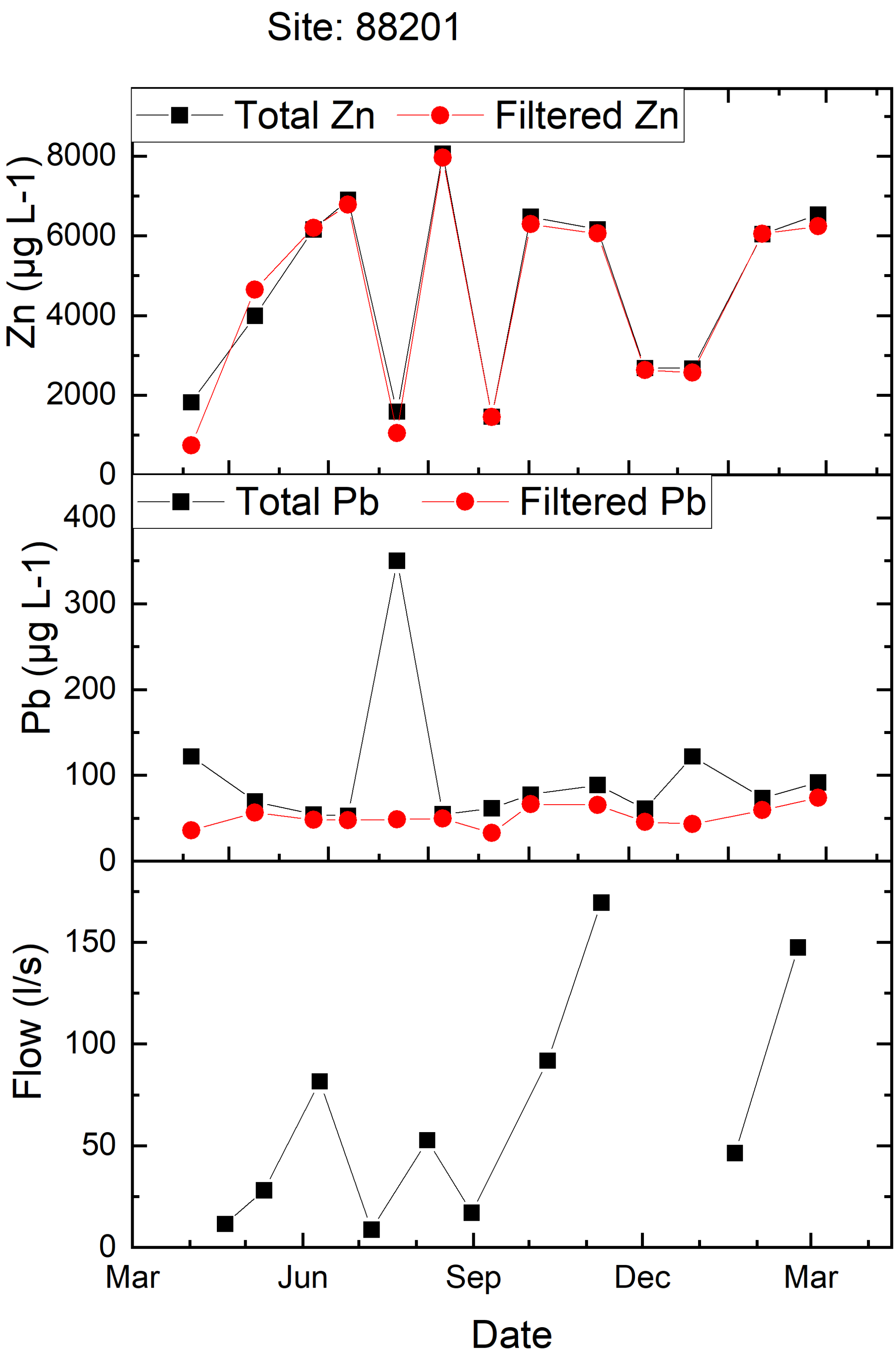


Figure 5-34 - Zn and Pb concentrations for 88201, as well as flow gauging measurements

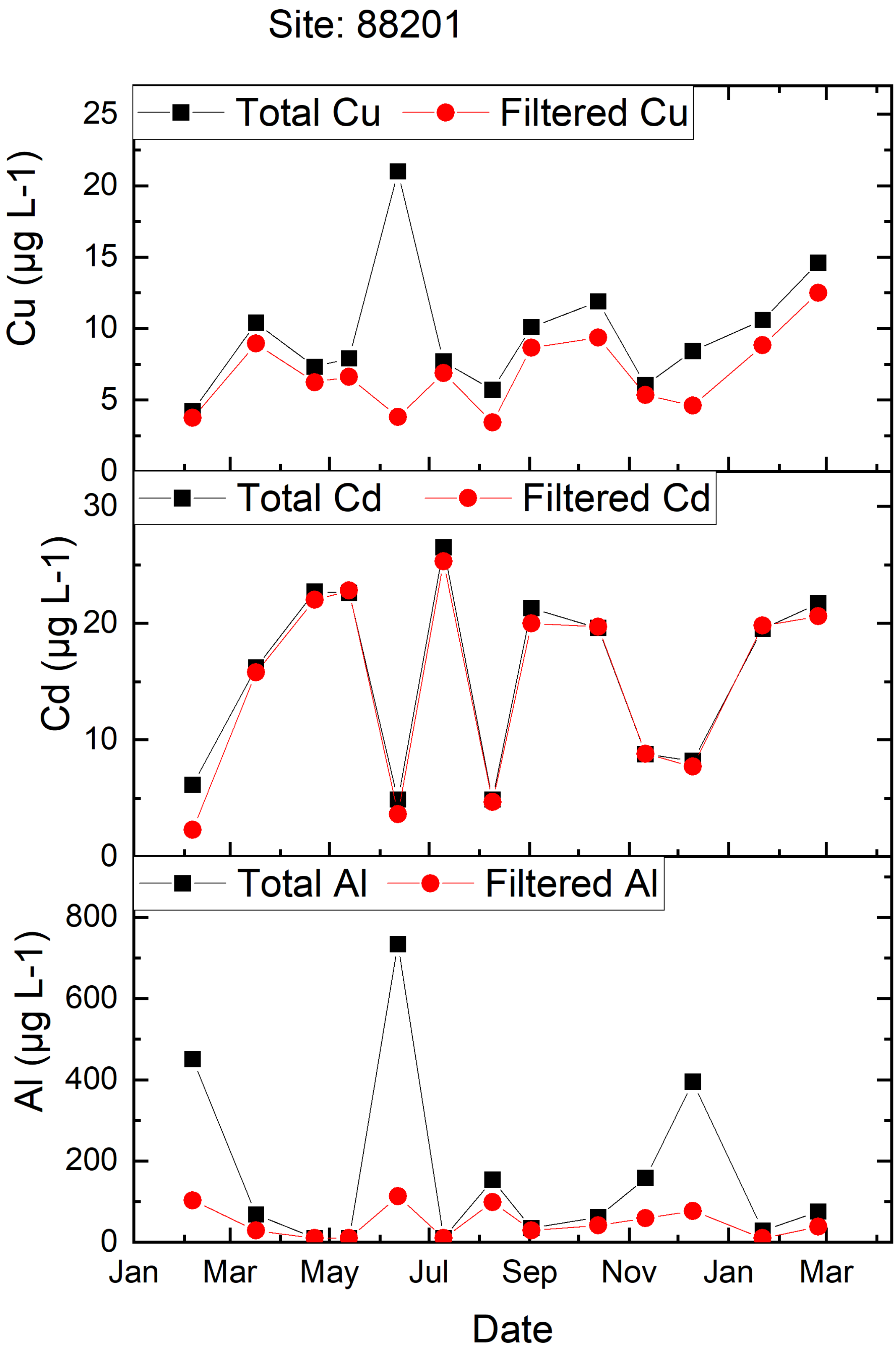


Figure 5-35 - Cu, Cd and Al concentrations for 88201

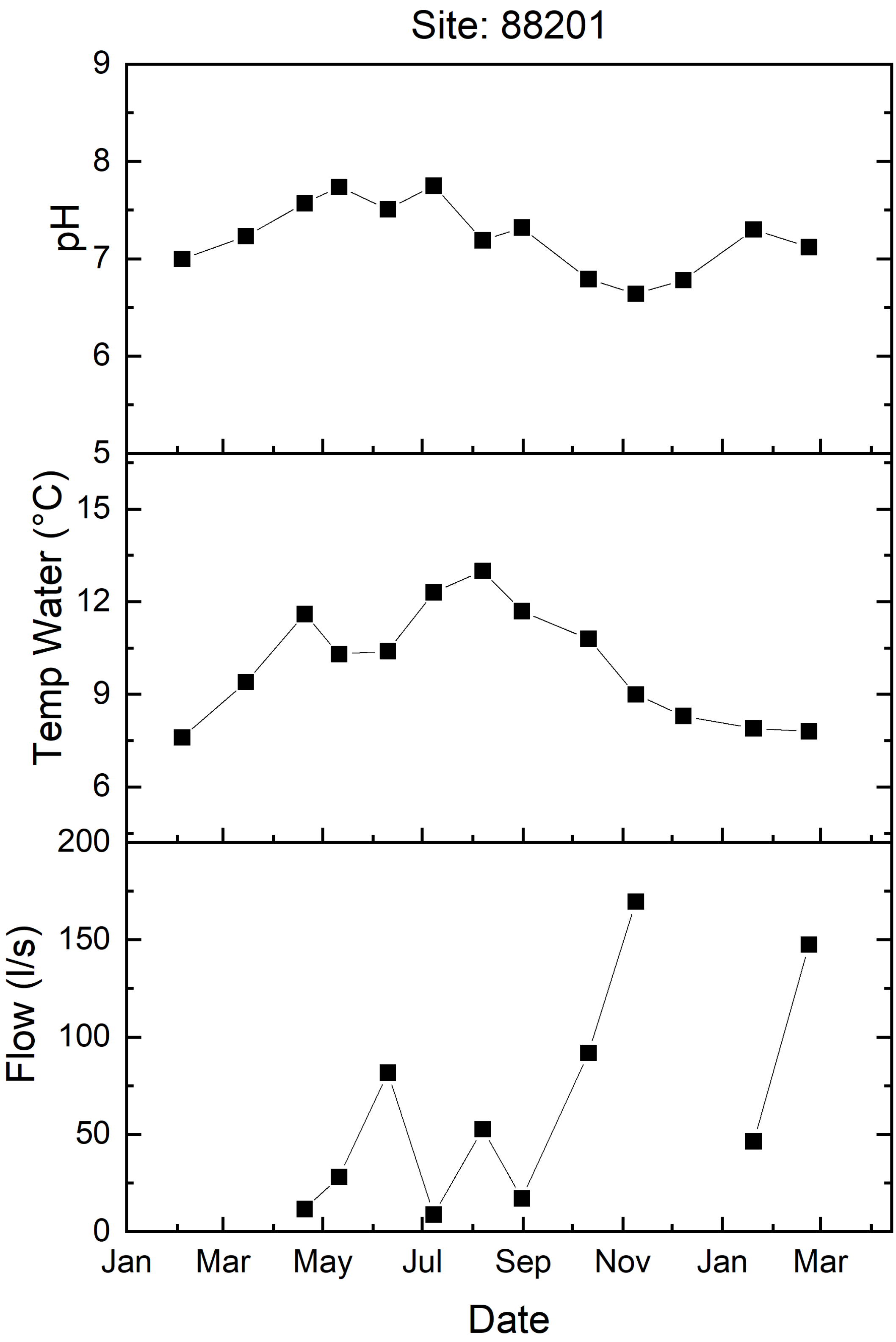


Figure 5-36 - pH and temperature readings for 88201, as well as flow gauging measurements

5.2.2.2 Church Terrace Tributary

Sampling point 88203 is an inflow to the Nant y Mwyn on the right hand bank, which receives inflows from the Deep Boat Level and two field drains.

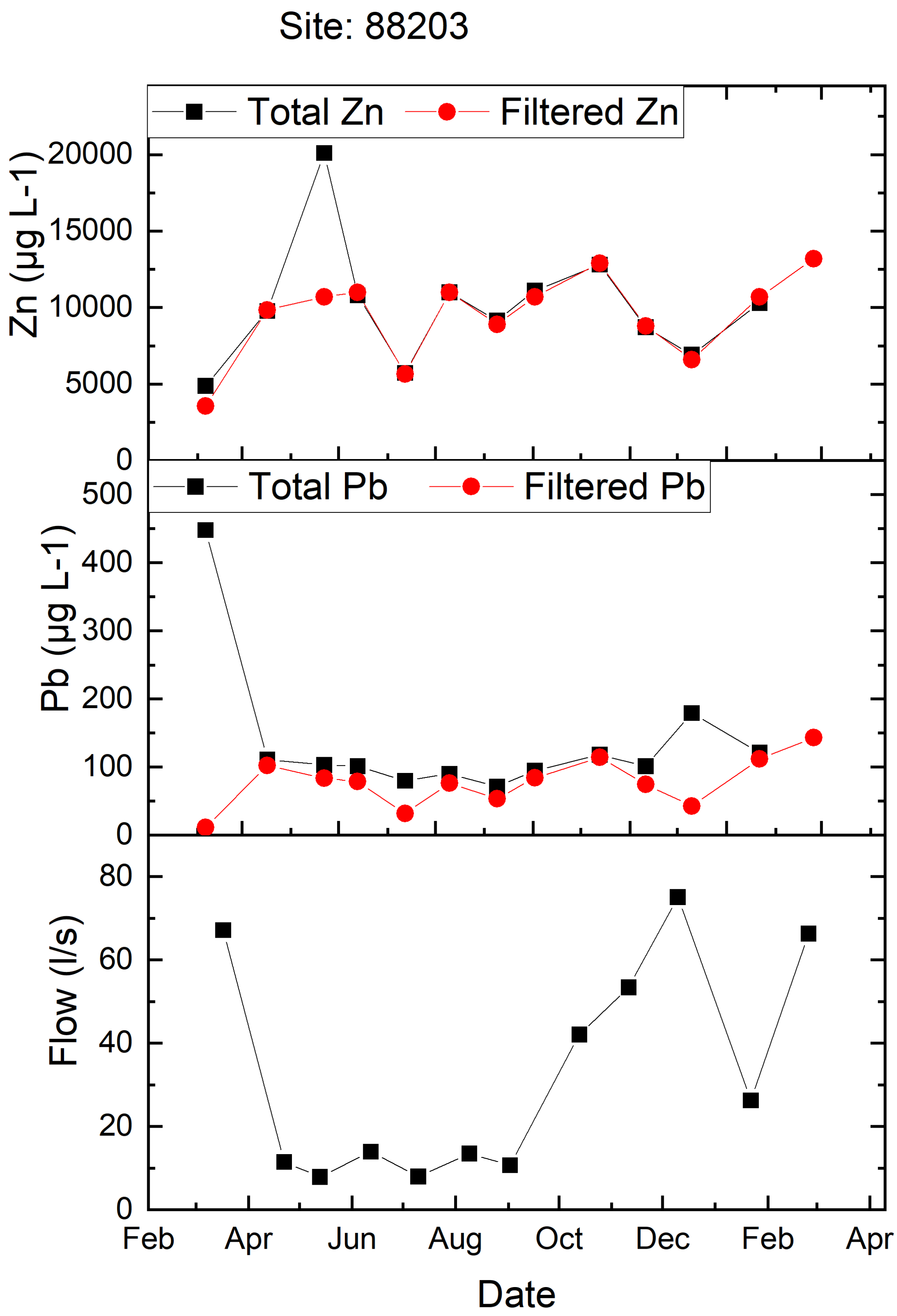


Figure 5-37 - Zn and Pb concentrations for 88203, as well as flow gauging measurements

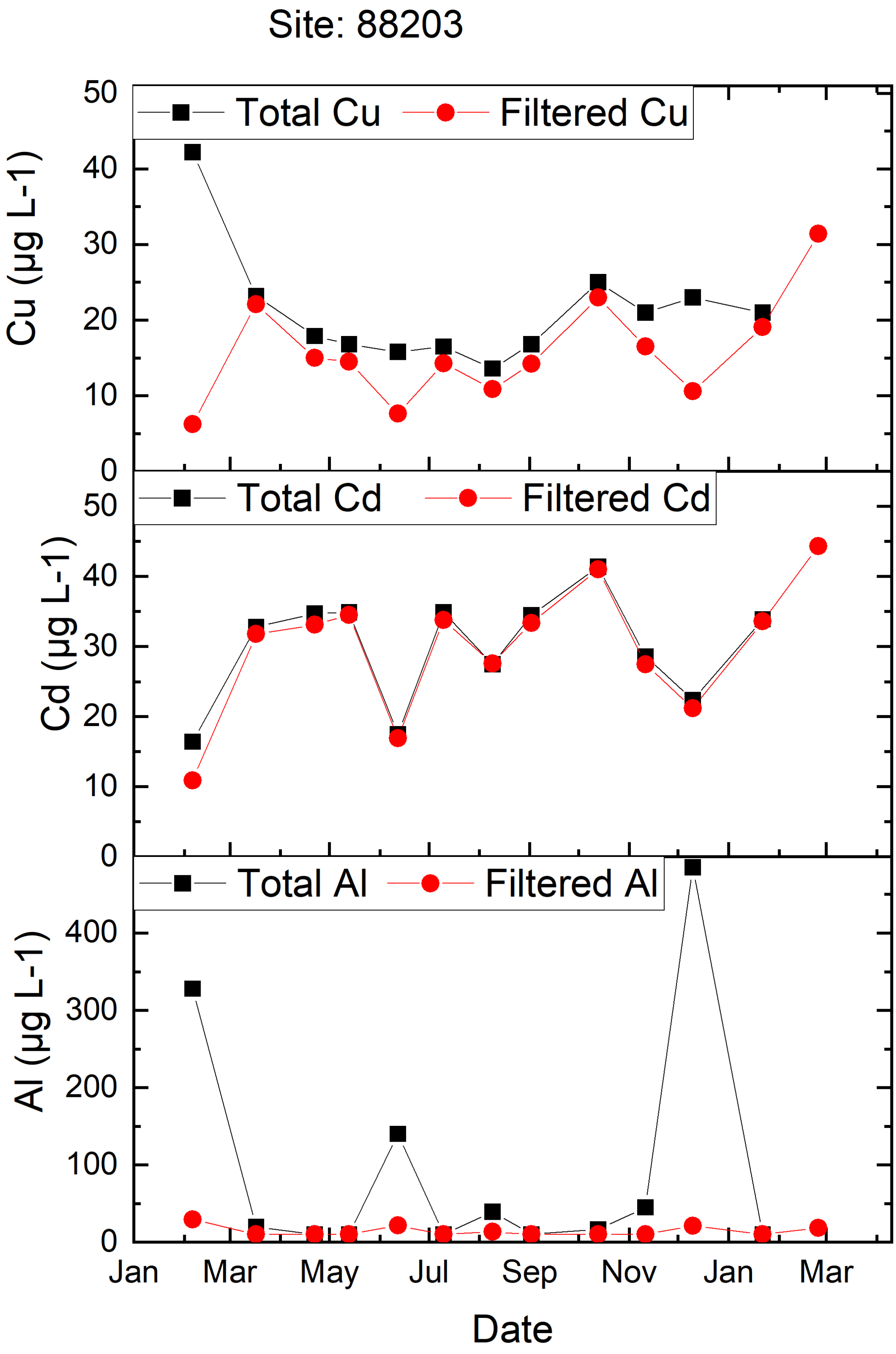


Figure 5-38 - Cu, Cd and Al concentrations for 88203

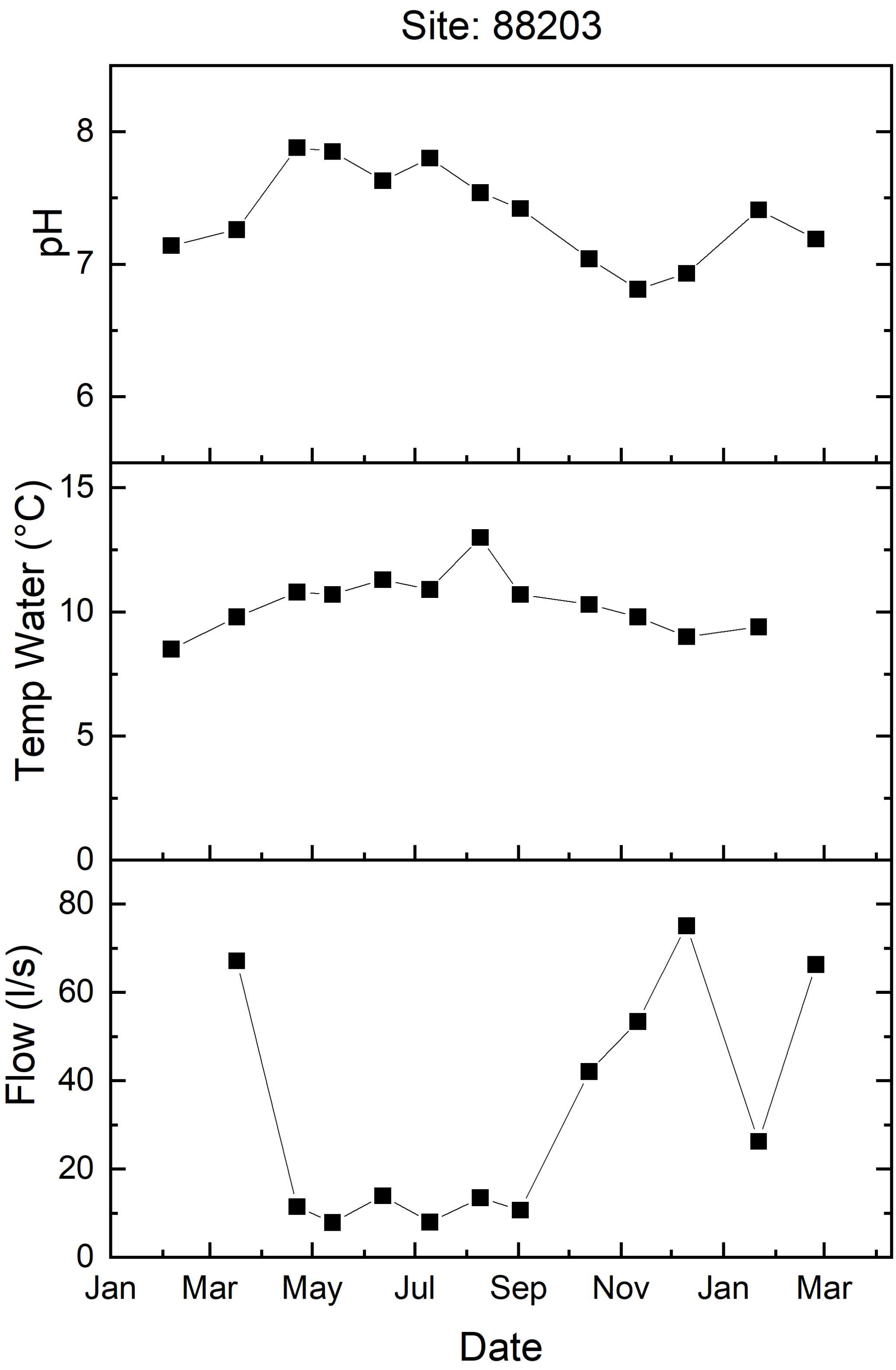


Figure 5-39 - pH and temperature readings for 88203, as well as flow gauging measurements

5.2.2.3 Deep Boat Level

Sampling point 88204 collects water flowing out of the Deep Boat Level, the lowest adit of Nantymwyn, which is blocked at its original entrance, and flows out of a upwelling approximately 25 metres away. The mine water nature of this sampling point is shown in the temperature readings, which are consistent year round without seasonal variation (Figure 5-42).

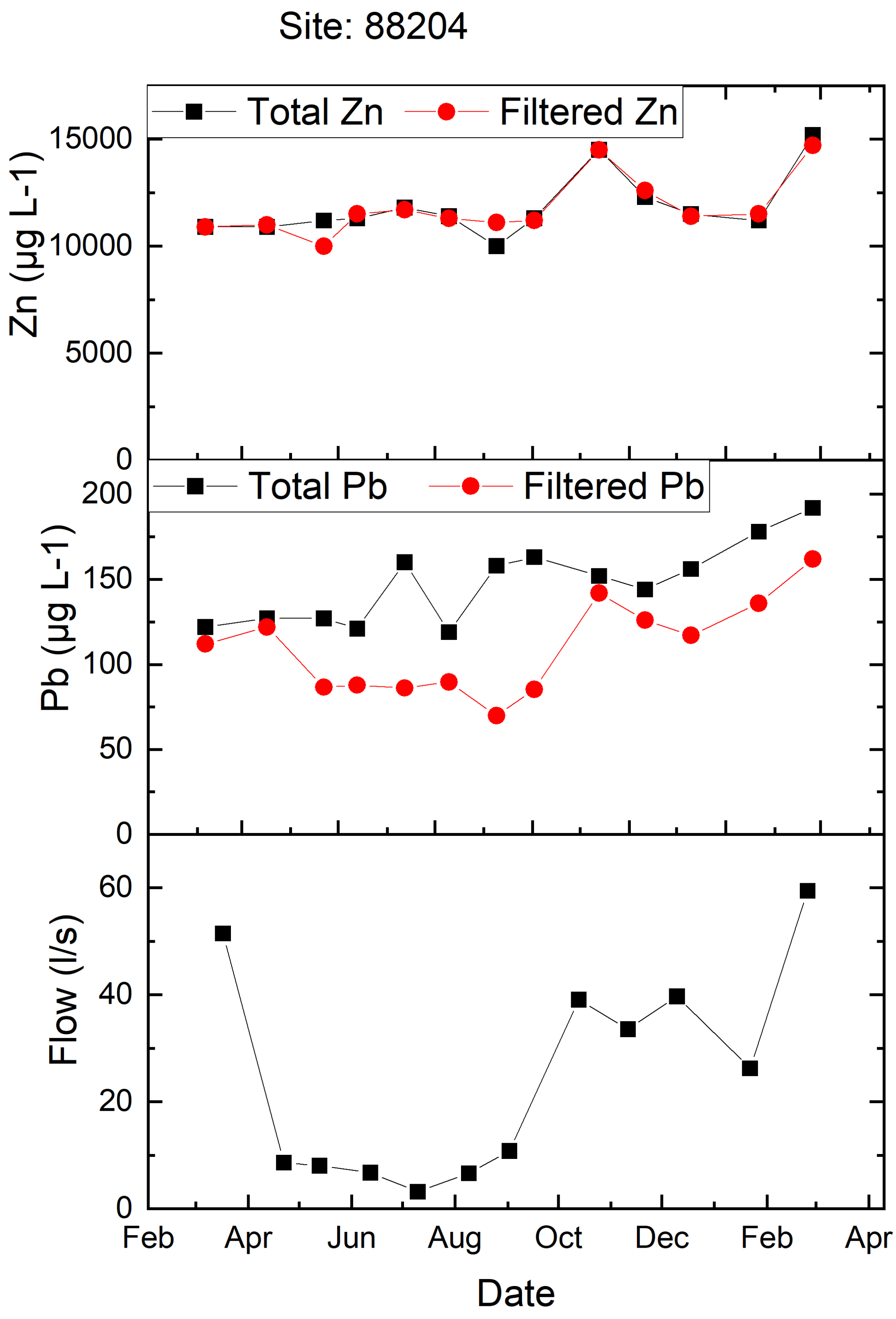


Figure 5-40 - Zn and Pb concentrations for 88204, as well as flow gauging measurements

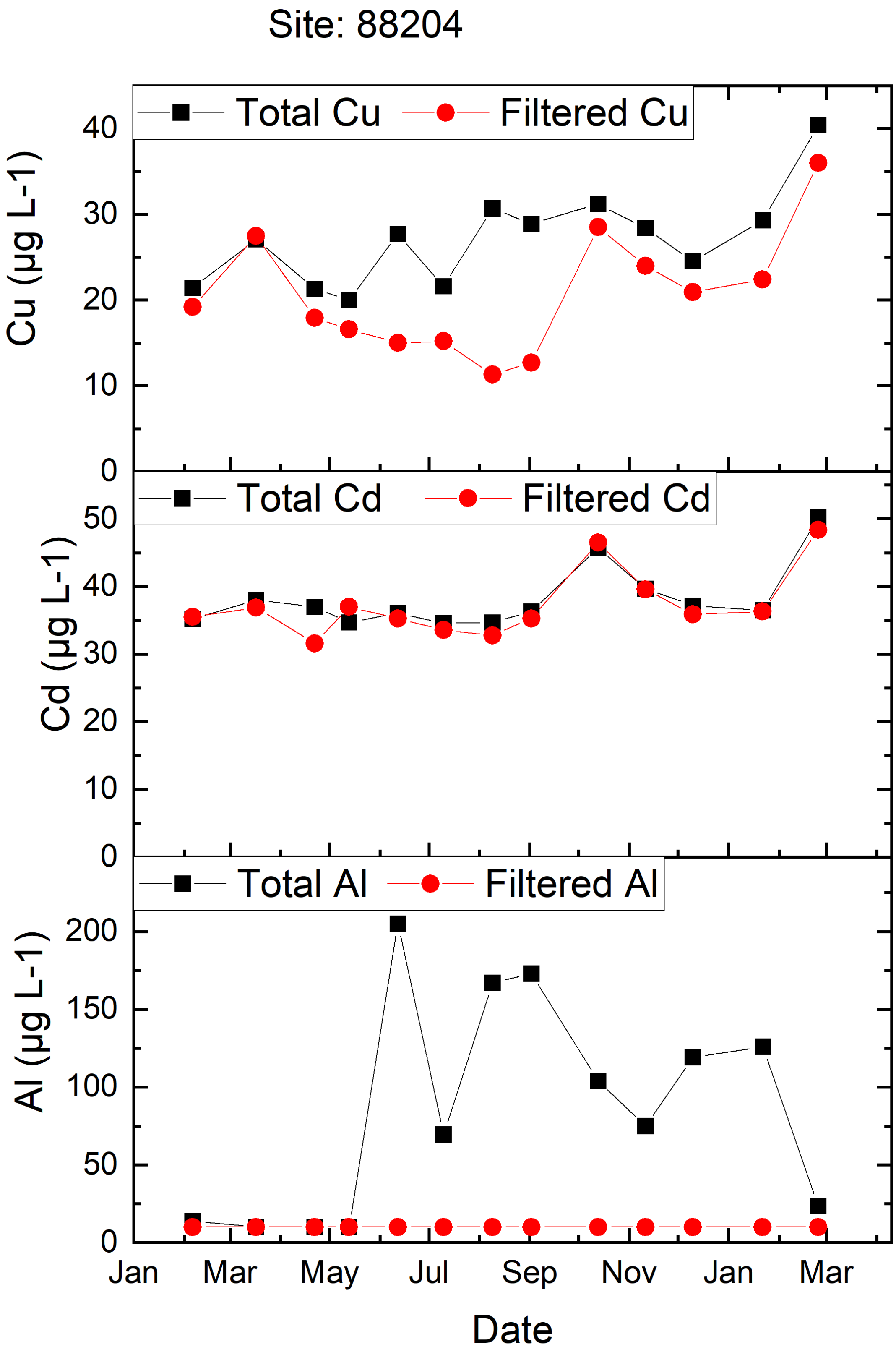


Figure 5-41 - Cu, Cd, and Al concentrations for 88204

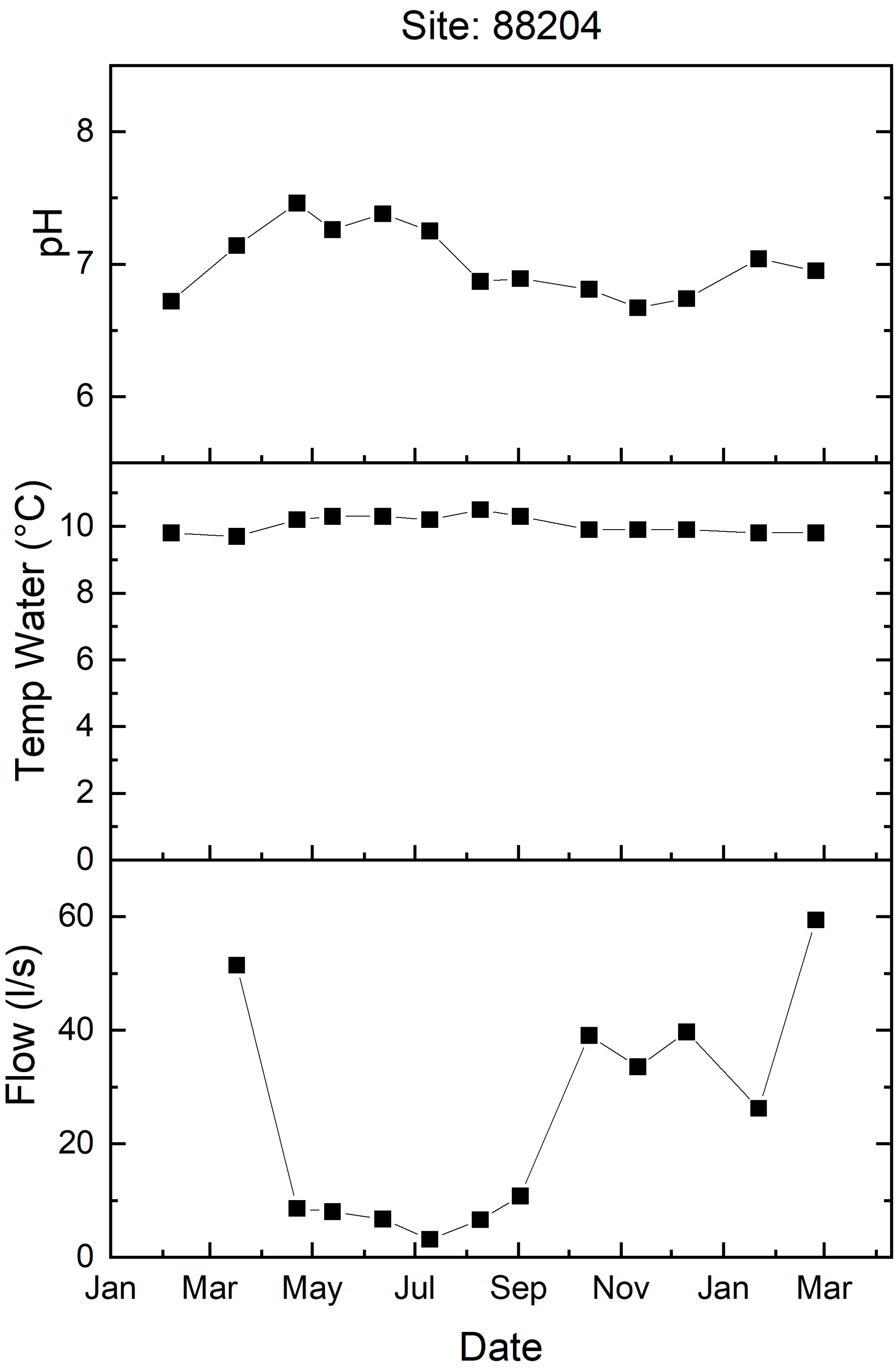


Figure 5-42 - pH and temperature readings for 88204, as well as flow gauging measurements

5.2.2.4 Nant y Mwyn upstream of Church Terrace Tributary

Sampling point 88439 is the Nant y Mwyn upstream of the Church Terrace Tributary.

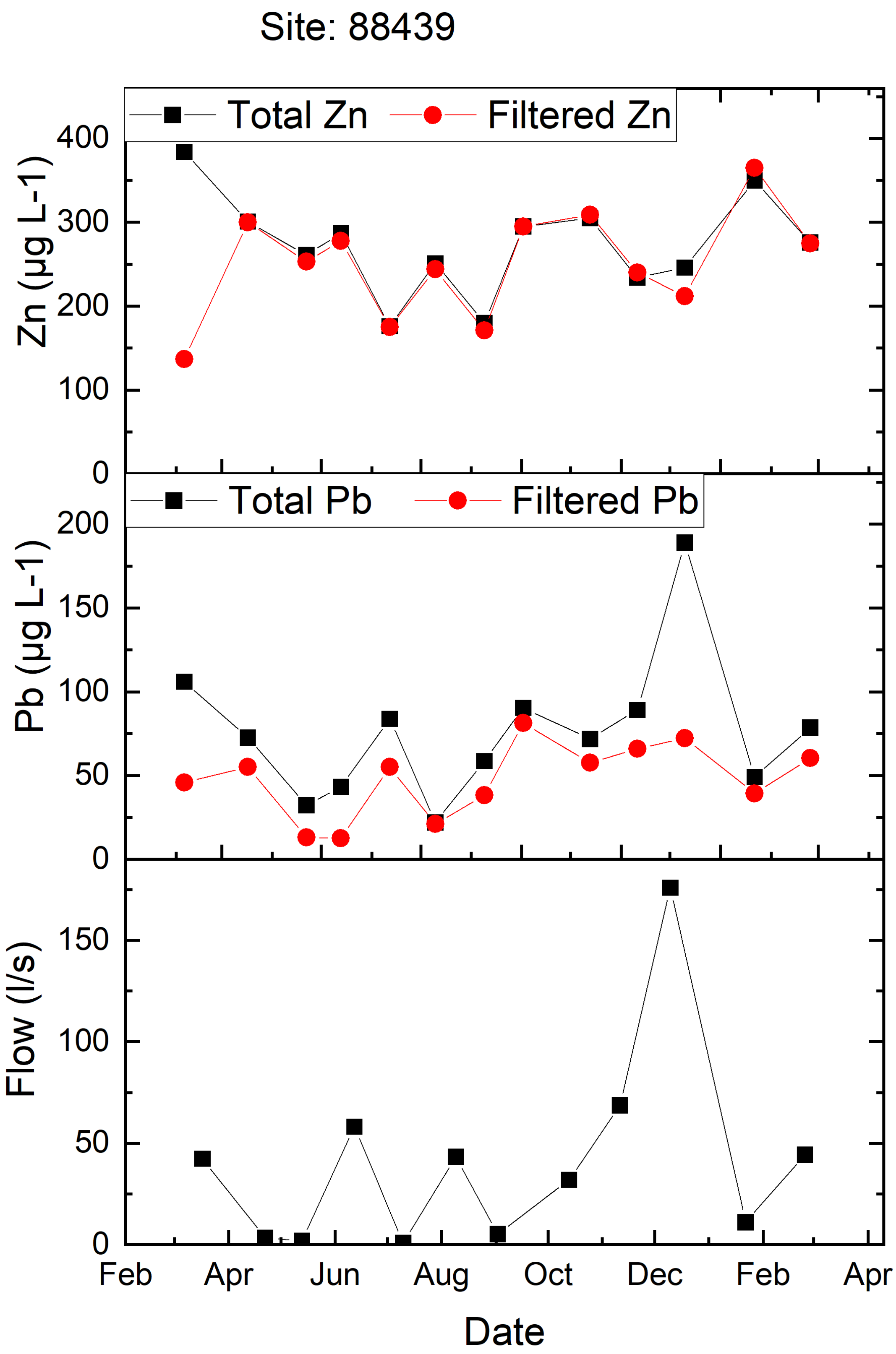


Figure 5-43 - Zn and Pb concentrations for 88439, as well as flow gauging measurements

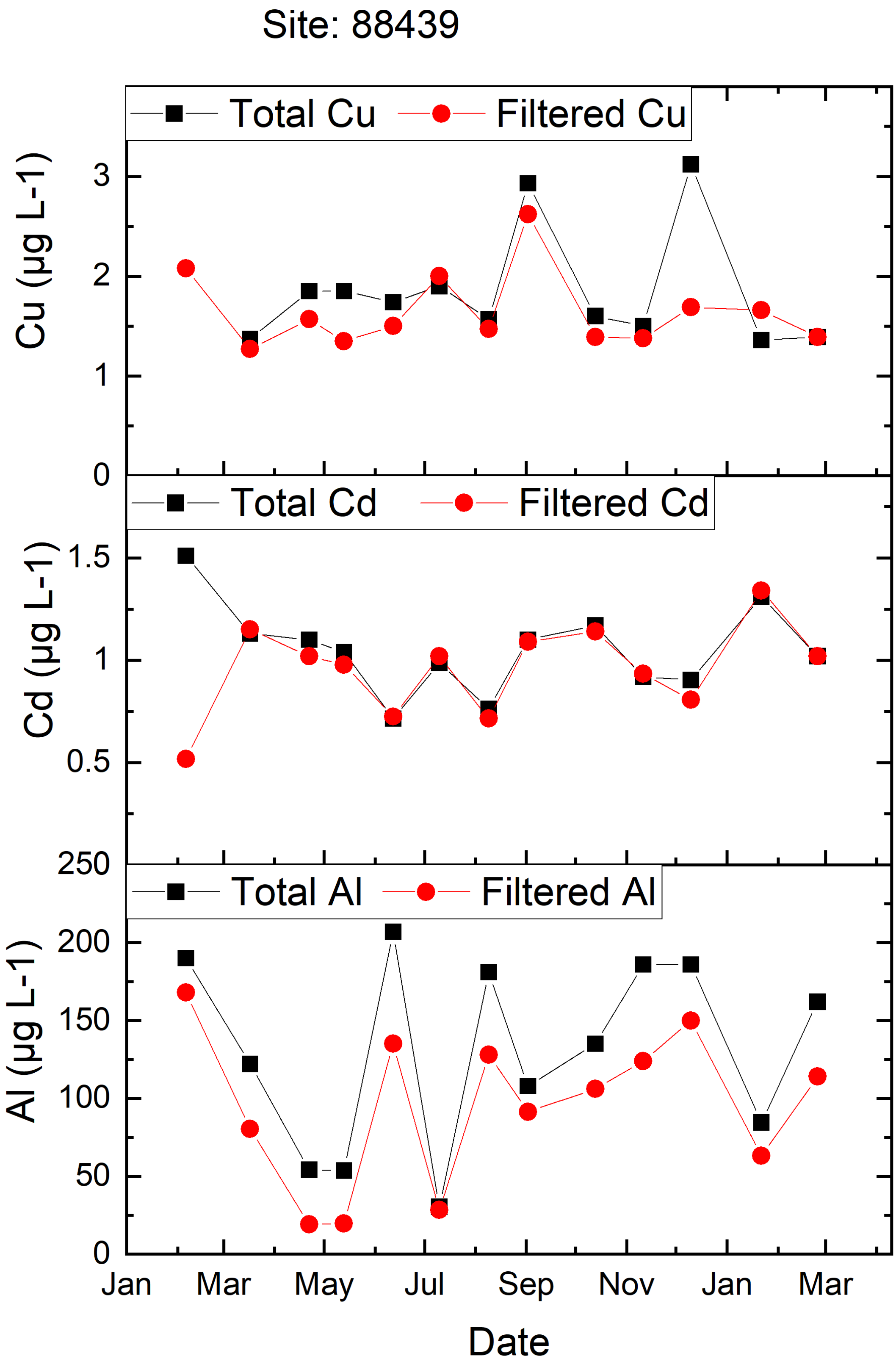


Figure 5-44 - Cu, Cd and AL concentrations for 88439

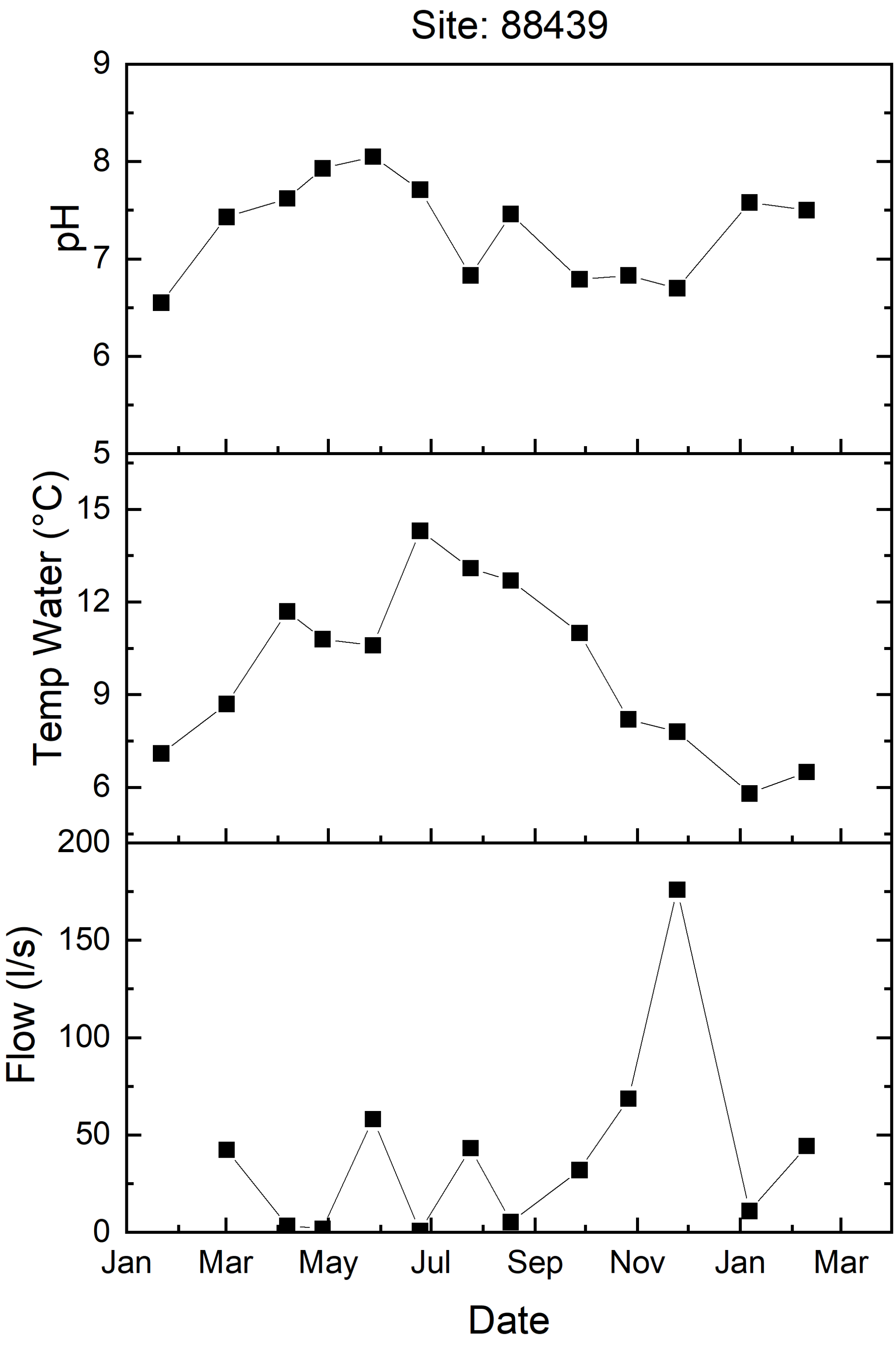


Figure 5-45 - pH and temperature readings for 88439, as well as flow gauging measurements

5.2.2.5 Pannau Adit

Sampling point 88183 collects water flowing out of the collapsed Pannau Adit. The mine water nature of this sampling point is shown in the temperature readings, which are consistent year round without seasonal variation (Figure 5-48).

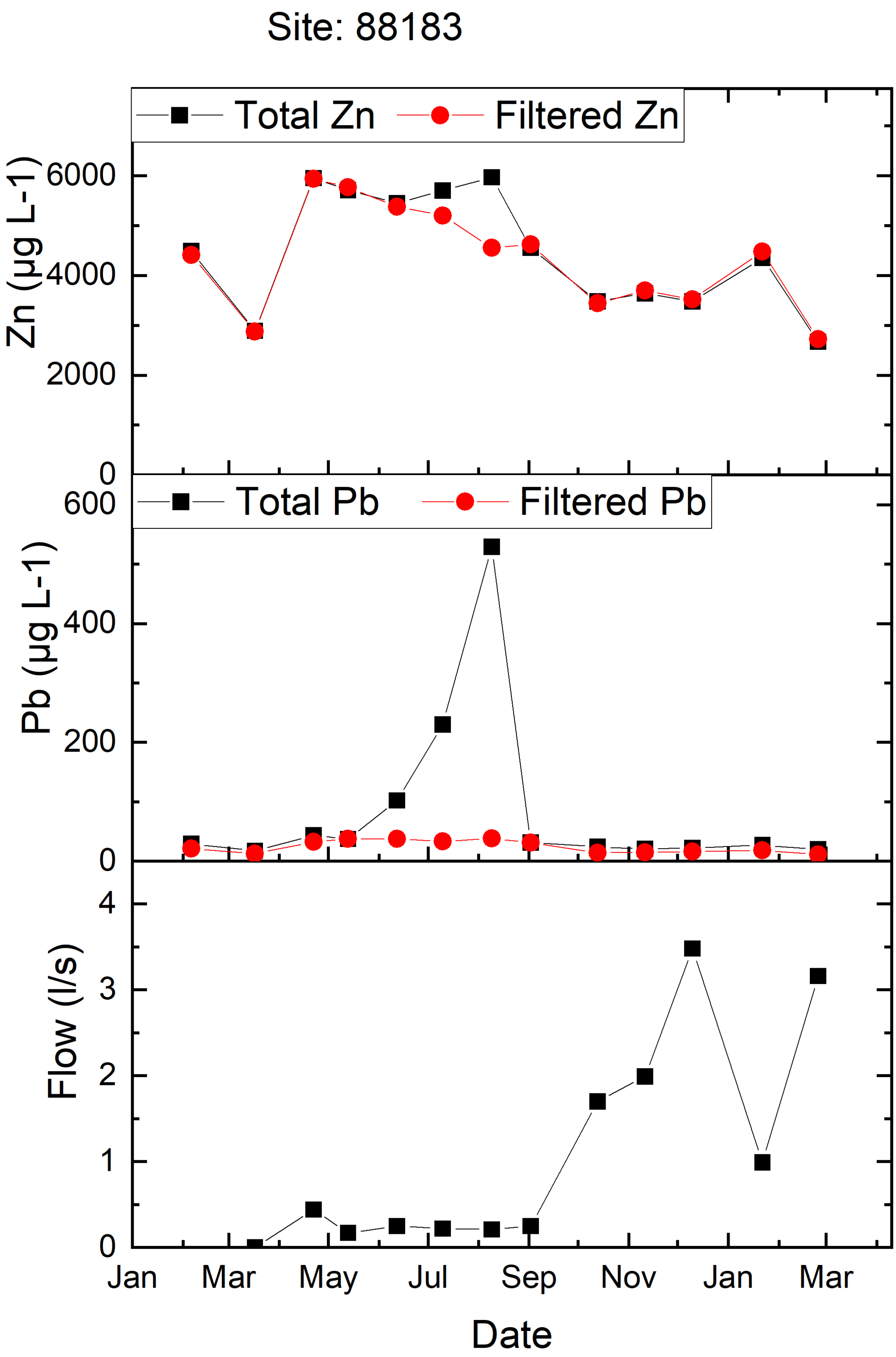


Figure 5-46 - Zn and Pb concentrations for 88183, as well as flow gauging measurements

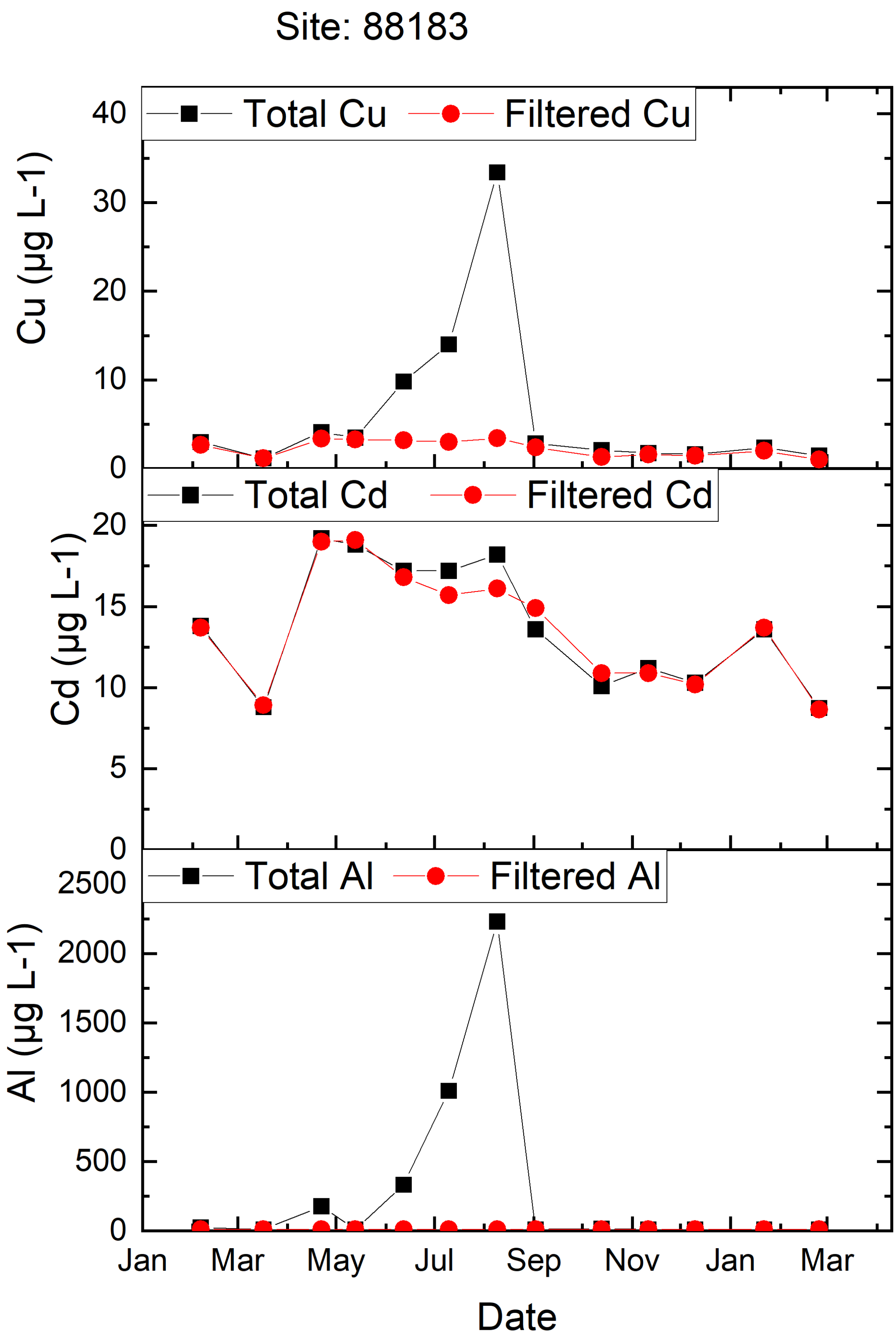


Figure 5-47 - Cu, Cd and AL concentrations for 88183

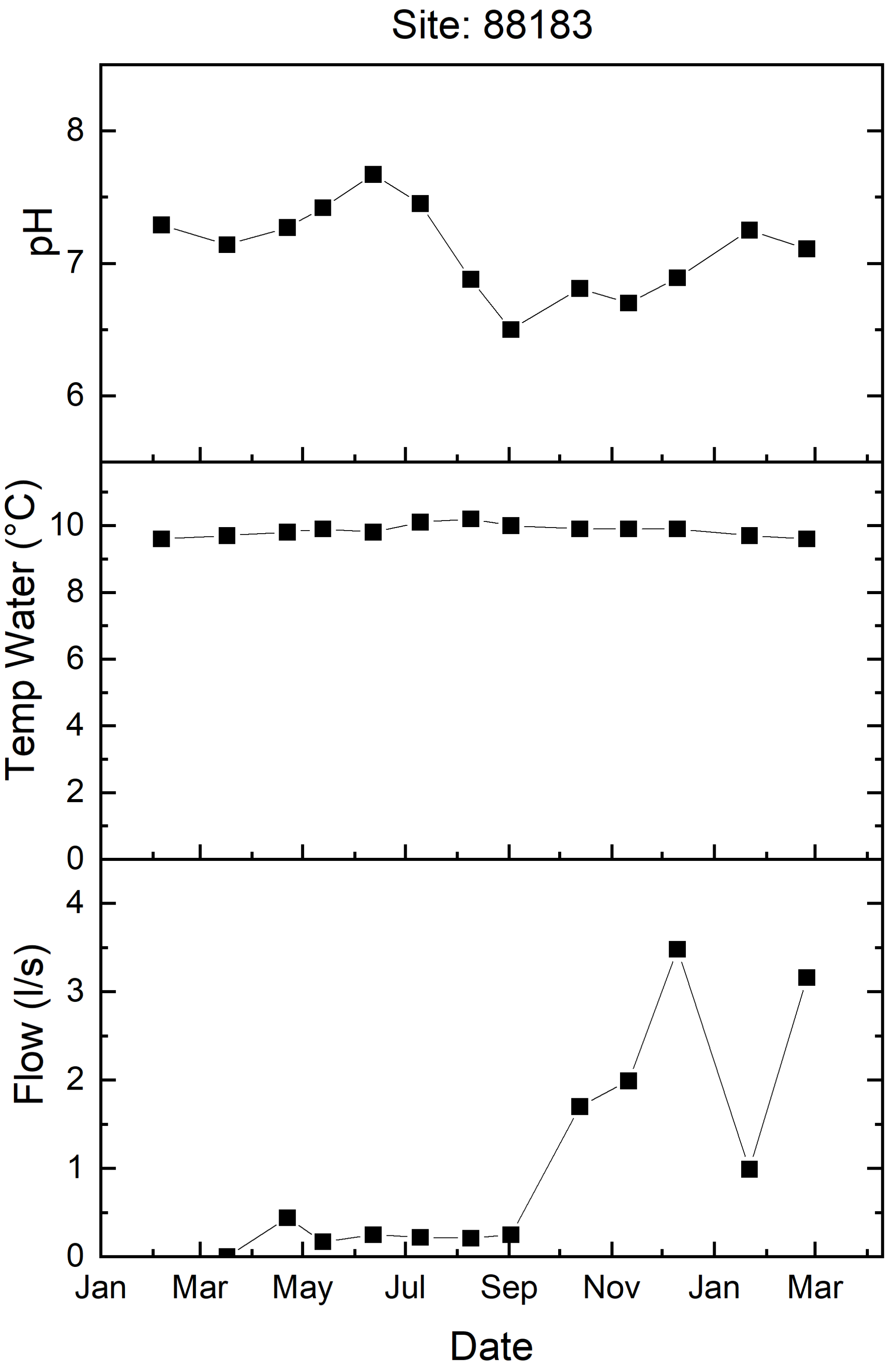


Figure 5-48 - pH and temperature readings for 88183, as well as flow gauging measurements

5.2.2.6 Nant y Mwyn upstream of Pannau Adit

Sampling point 88191 is the Nant y Mwyn upstream of the Pannau Adit, and there are no visible mine wastes above this sampling point.

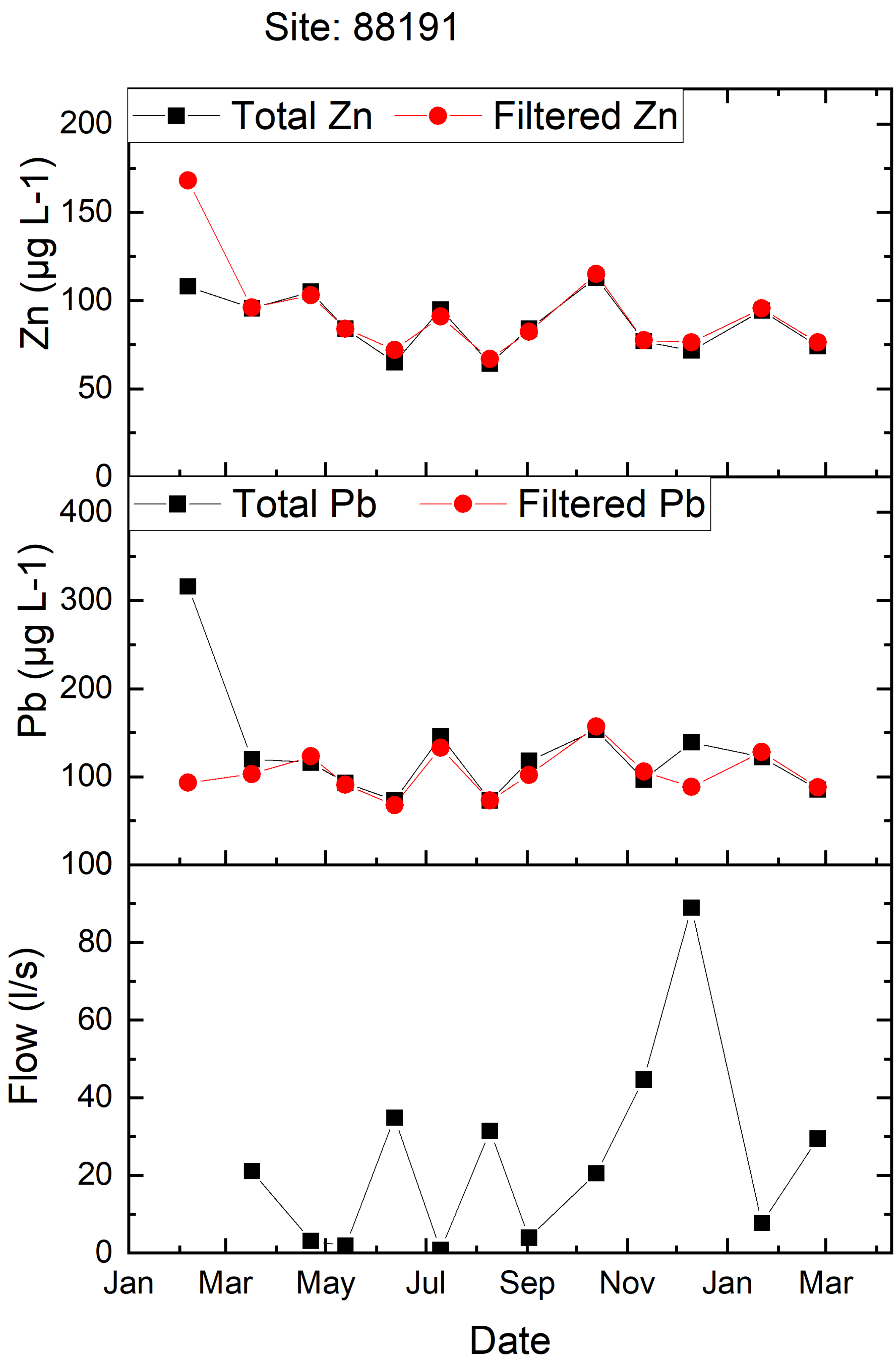


Figure 5-49 - Zn and Pb concentrations for 88191, as well as flow gauging measurements

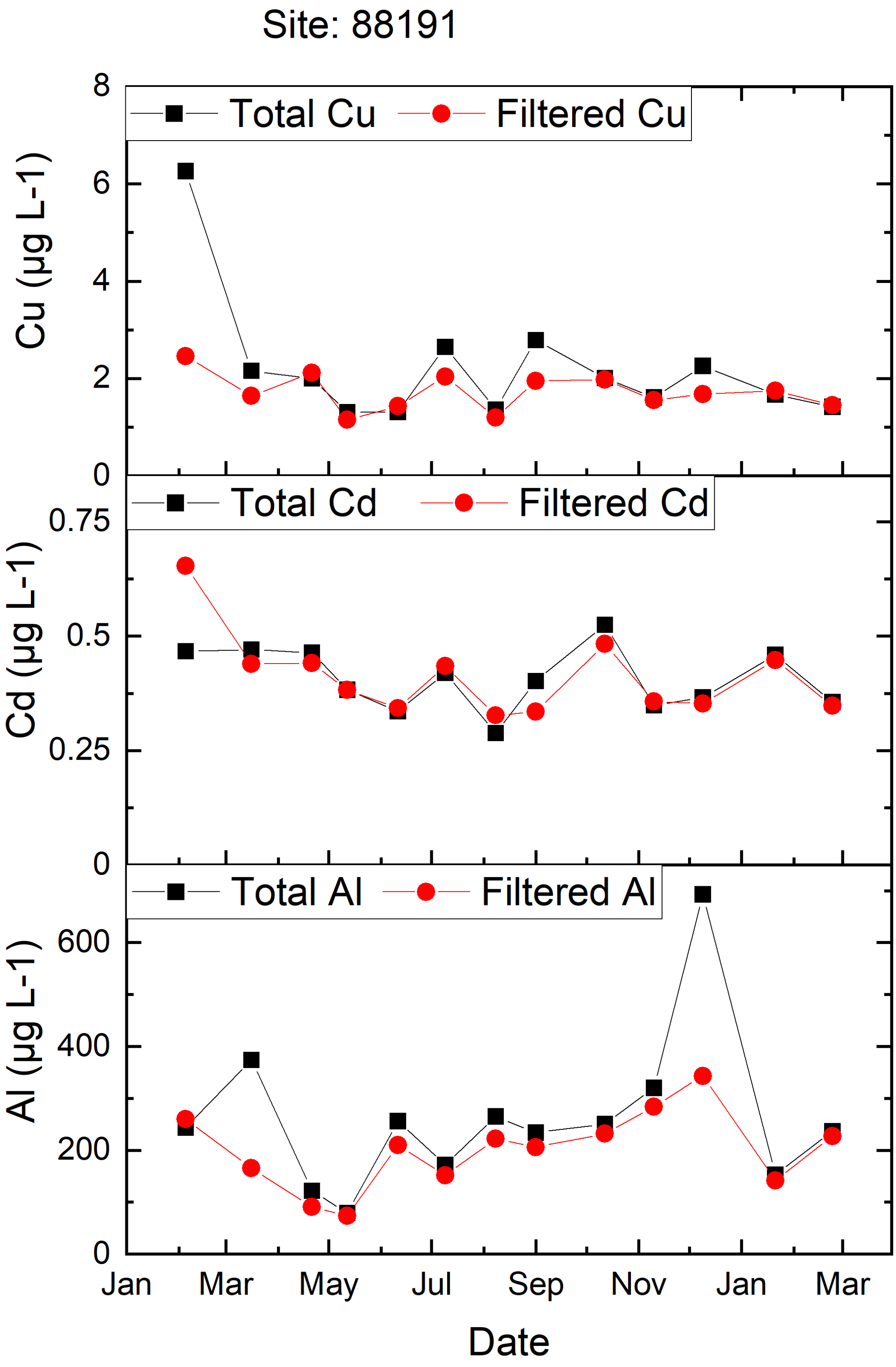


Figure 5-50 - Cu, Cd and AL concentrations for 88191

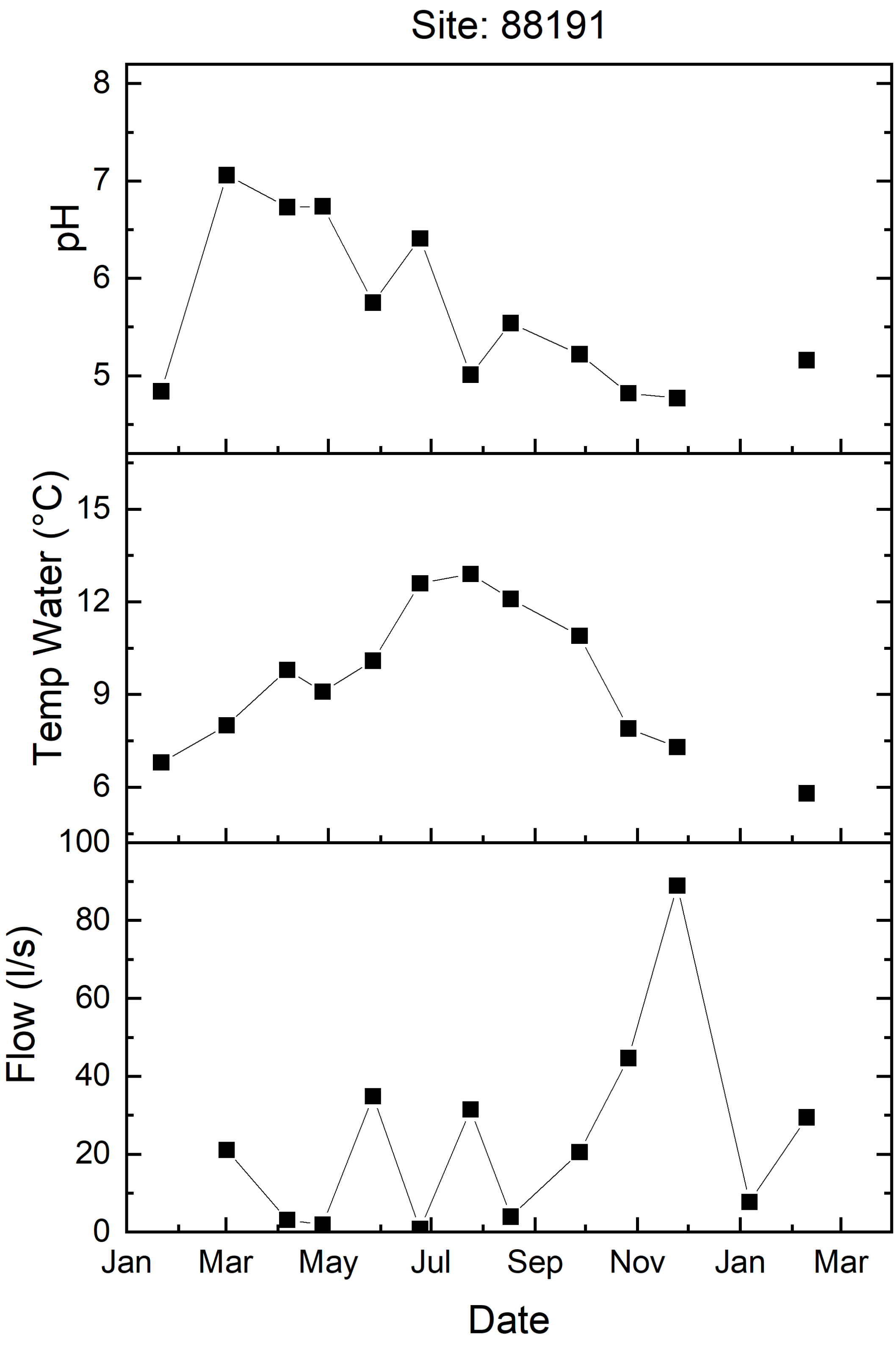


Figure 5-51 - pH and temperature readings for 88191, as well as flow gauging measurements

5.2.3 Rainfall and flows on the River Tywi

The River Tywi has flows recorded by NRW at gauging stations upstream and downstream of Nantymwyn mine (Figure 3-1). The upstream gauging station is heavily influenced by the river regulation reservoir at Llyn Brianne, which maintains flow during low rainfall periods for downstream abstraction for drinking water (Figure 5-53). After several tributary rivers have joined the River Tywi, the moderating impact of the dam and reservoir is less visible (Figure 5-54).

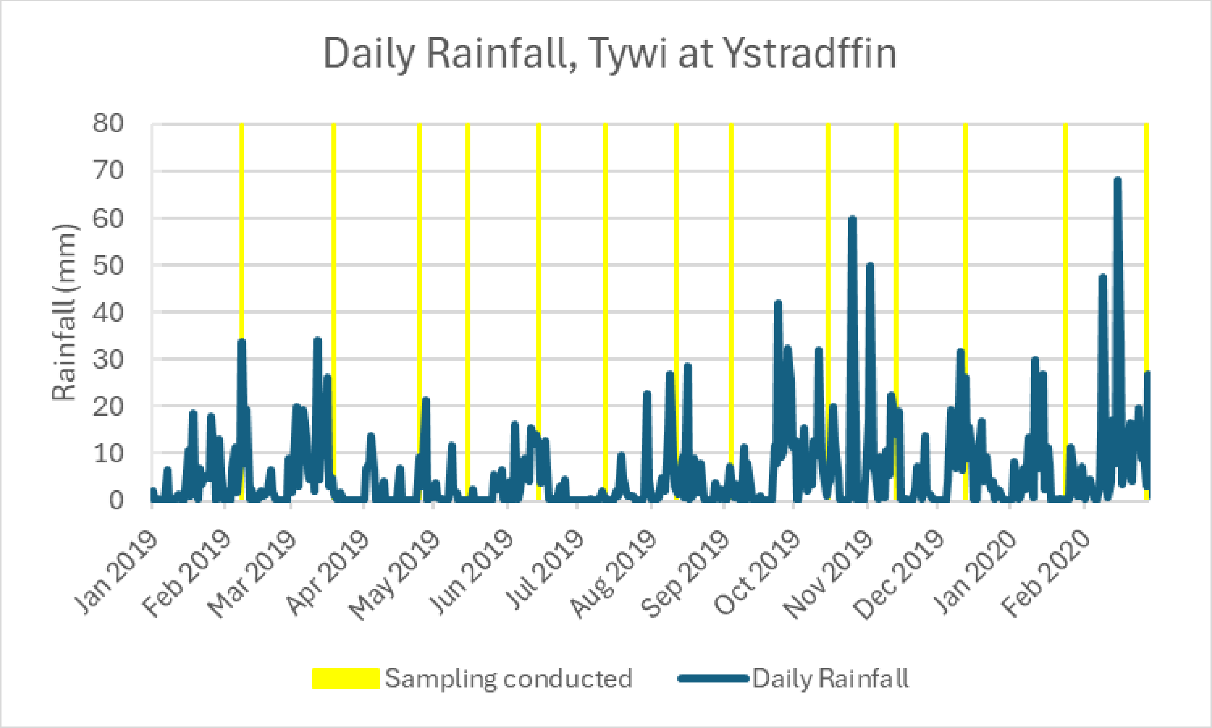


Figure 5-52 – daily rainfall recorded at the flow gauging station on the River Tywi at Ysradffin

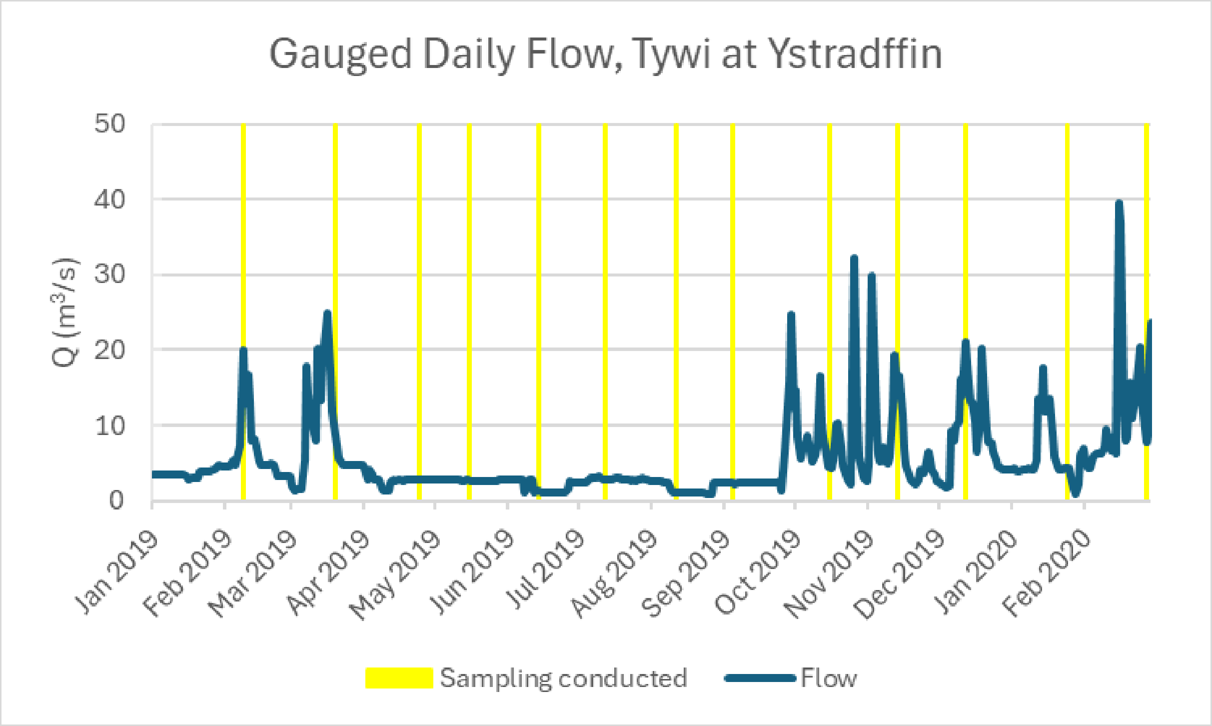


Figure 5-53 - gauged daily flow and sampling dates, Tywi at Ystradffin

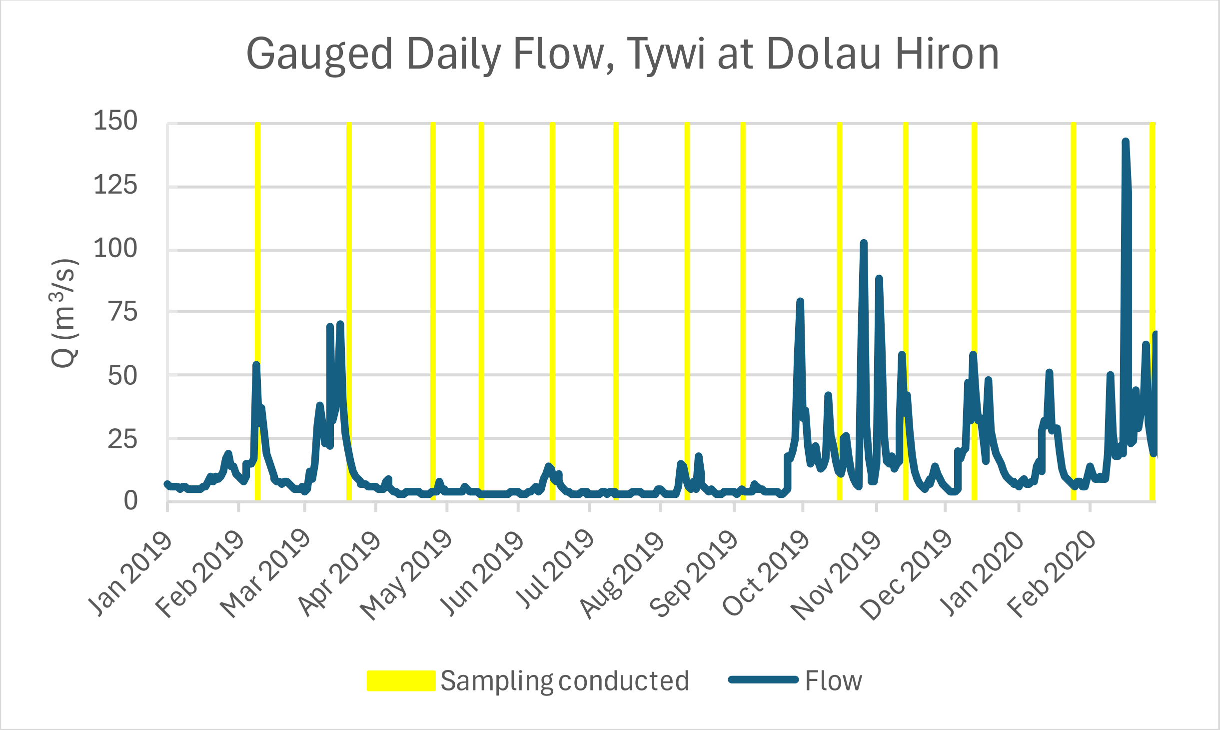


Figure 5-54 -gauged daily flow and sampling dates, Tywi at Dolau Hiron

5.3 Comparison between Nantymwyn and other Welsh abandoned metal mines

To understand if Nantymwyn is typical for an abandoned Welsh metal mine, all the historical data for it was retrieved from NRW's Water Quality Archive, and compared with that available for two other abandoned metal mines, Parys Mountain Cu mine, and Frongoch Pb-Zn mine (Figure 5-55). Historical information and the geographic setting has been given earlier in the thesis, but the mine is shown in detail in Figure 5-2a, and an overview of Parys Mountain and Frongoch are given below (Todd et al., 2024b). The complete dataset for Nantymwyn's water quality pre-2019, and Parys Mountain and Frongoch, is available from the NRW Water Quality Archive, a publicly accessible record (Natural Resources Wales, 2021), and is appended to this thesis in sections 8.6-8.8.

5.3.1 Parys Mountain

Parys Mountain mine (53°23'8'' N; 4°21'2'' W) is located 3 km south of Amlwch, Anglesey (Figure 5-2b). Its complex geology is mainly Silurian shales, with east-west trending structures carrying the mineral lodes (Bevins and Mason, 2010). These lodes contain the Cu ore as chalcopyrite ($CuFeS_2$) accompanied by quartz (SiO_2), with minor deposits of galena (PbS) and sphalerite ((Zn,Fe)S) mixed with the chalcopyrite (Bevins and Mason, 2010). As pumping technology advanced and the upper subsurface deposits were depleted the workings descended, eventually to a depth of 330 m below the main shaft entrance (Jenkins et al., 2021). Parys Mountain was mined both on the surface and below ground for Cu from the Bronze Age through to the Roman era, falling into disuse before reopening in the 1570s (Jenkins et al., 2021; Vernon, 1996). In the 18th century, a new use for Cu was found, sheathing ship hulls to reduce maritime fouling, and increase the ship's speed and longevity. Parys Mountain's deposits and location near a seaport resulted in it being the largest supplier of Cu in the World by the end of the century (Bevins and Mason, 2010; Jenkins et al., 2021). Subsurface working stopped in the 1880s, but processing of mine water to remove Cu by precipitation continued, initially under a formal arrangement, and from 1921 informally by one man until his retirement in the 1940s (Vernon, 1996). Since then, exploratory drilling and surveying has been carried out approximately every decade to assess the feasibility of reopening the mine, with limited trials of subsurface mining in 1973 (Foster-Smith, 1977) and 1988-1990, but large-scale mining has not restarted (Vernon, 1996). Licensing to mine has been held, however, since 1988, and the holder has plans to mine the subterranean workings (Bartlett et al., 2022).

Mine waste and remnants of surface working and processing cover the 200-hectare site, some of which is protected as biological and geological Sites of Special Scientific Interest (SSSIs) for the unique and rare ores and the acid-resistant lichens. Unusually for a UK metal mine the waters are highly acidic, with pH values ranging from 2.2 – 2.8 (Marsay, 2018), and this acidic water was noted for corroding mining machinery such as boilers in the 19th century (Vernon, 1996). Due to its acidic and highly metal-laden waters entering the two affected watercourses, Parys Mountain is the largest provider of Zn and Cu to the Irish Sea (Environment Agency, 2008), and was ranked the highest priority metal mine for remediation in Wales (Mullinger, 2004). As well as the effects of these metal--rich low pH waters on water quality, flora and fauna, water retained underground by a 19th century dam was deemed a flood risk to nearby housing. This dam was therefore emptied and breached in 2003, removing the flood risk (Younger and Potter, 2012). Prior to the dam's removal, mine water flowed into two streams, the Afon Goch Dulas ('Red River South') and the Afon Goch Amlwch ('Red River North'). The Afon Goch Gogledd now receives all the mine waters from Parys Mountain via the Dyffryn Adda Adit (Younger and Potter, 2012), and data from this adit discharge are used in this study, with the details on its catchment shown in Table 5.1. Trials of active treatment systems at Parys Mountain have been ongoing since 2007, including use of a high-density sludge hydroxide system (Younger and Potter, 2012), as well as laboratory trials of passive biochar-based water treatment systems using Parys Mountain water (Cairns et al., 2022b).

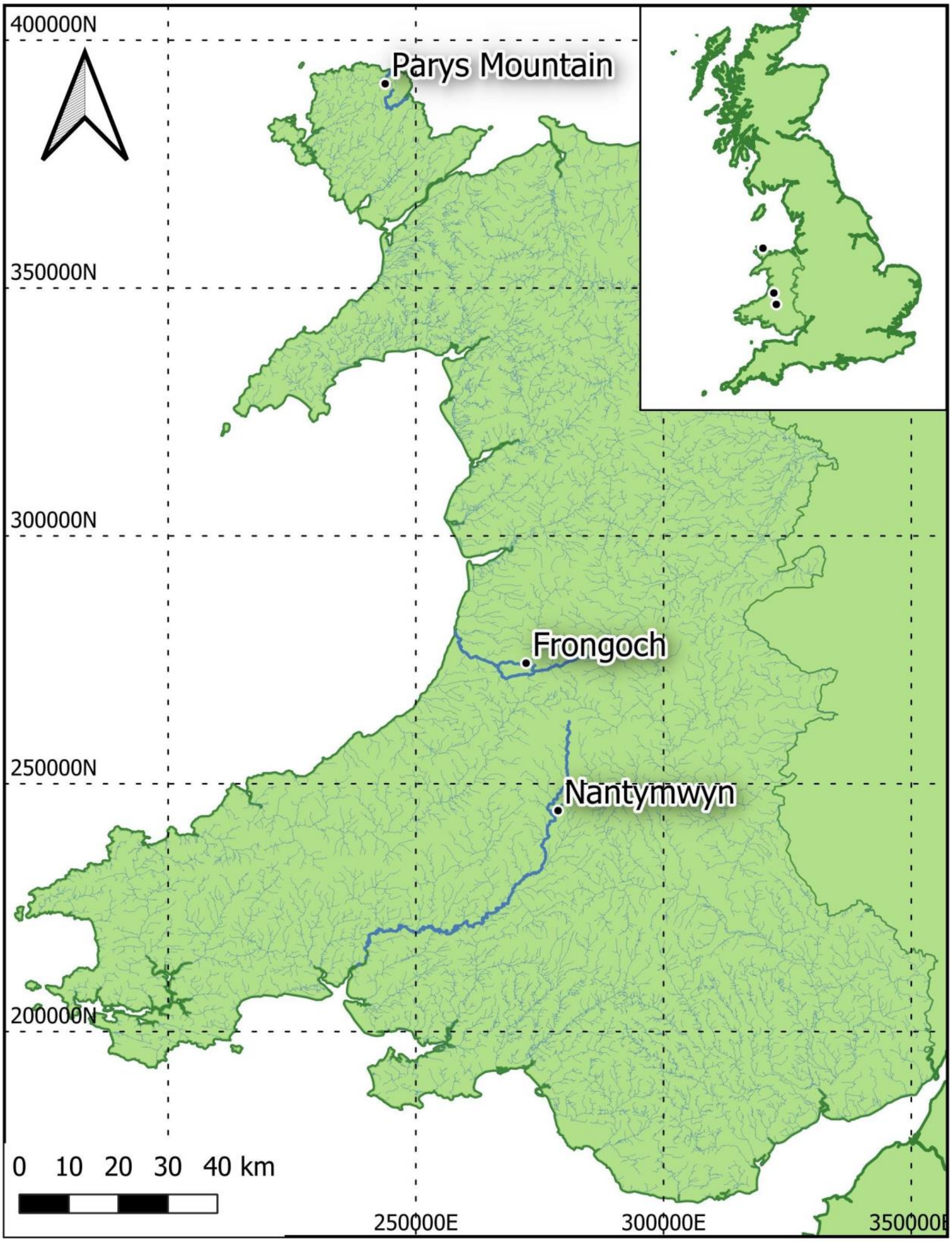


Figure 5-55 - Locations of the three abandoned metal mines, with the receiving watercourses highlighted

Table 5-1 - Catchment characteristics (National River Flow Archive, 2021; Ordnance Survey, 2020)

Mine	Sampling Location	Average annual precipitation 1961-2017 (mm)	Catchment size (from sampling location) (km^2)	Sampling location elevation (m a.s.l.)	NRW Sampling Location Number
Nantymwyn	Nant y Bai	2032	3.2	120	31689
Parys Mountain	Dyffryn Adda Adit	1109	2.0	60	26278
Frongoch	Frongoch Stream	2116	1.0	240	35690

5.3.2 Frongoch

Frongoch mine (52°21'7'' N; 3°52'35'' W) is located 15 km south-east of Aberystwyth (Figure 5-2c). Geologically based on Silurian shales, Frongoch mine is one of seven mines to work the Frongoch Fault, consisting of two lodes of galena (PbS) and one of sphalerite ((Zn,Fe)S) (Bevins and Mason, 2010). The surface workings and waste dumps cover 11 hectares, and underground it is connected hydrologically to Wemyss mine, sharing a common adit for drainage. Combined with Wemyss mine, it was the largest producer of Pb and Zn in central Wales in the 19th century (Bick, 1996). Unlike Nantymwyn and Parys Mountain, Frongoch was not worked until 1759, joining Wemyss mine as a joint complex in the mid-19th century (Lewis, 1967). Until 1879, Pb was the main export of the mine, with Zn ore being dumped in waste tips, but after this date Zn was the main export. This, continued until the closure of the mine in 1903, and Zn was again the main export when the tips were reworked for a decade until 1930 (Bick, 1996). Intermittent and informal exploration of Frongoch continued post-second World War, most recently with a borehole sunk in 1971, and areas of waste have been removed for use in construction (Bevins and Mason, 2010). The site has seen multiple studies in recent decades, including whole site analysis for reuse or remediation (Richards Moorehead & Laing Ltd, 1990), trials of experimental passive and active remediation measures (Abril et al., 2021; De-Quincey, 2020), and constant rate tracer injection and synoptic sampling for metal source location and analysis (Byrne et al., 2020).

After abandonment of the mine, streamwater from the upper Frongoch catchment and subsurface waters from Frongoch mine drained via the Frongoch Adit, out of the Frongoch catchment to the neighbouring Nant Cwmnewydion. Surface runoff flowed over spoil heaps before entering the Frongoch Stream, increasing the concentrations of metals, especially Zn, in the waters. The two impacted streams then flow into the River Ystwyth, contributing to it failing WFD standards for Pb, Zn, and Cd (Edwards et al., 2021). Frongoch mine contributes to 32 km of WFD failure for dissolved Zn in the River Ystwyth and the River Magwr (Natural Resources Wales, 2022), leading to its 2nd place ranking in the highest priority metal mine list for remediation in Wales (Mullinger, 2004).

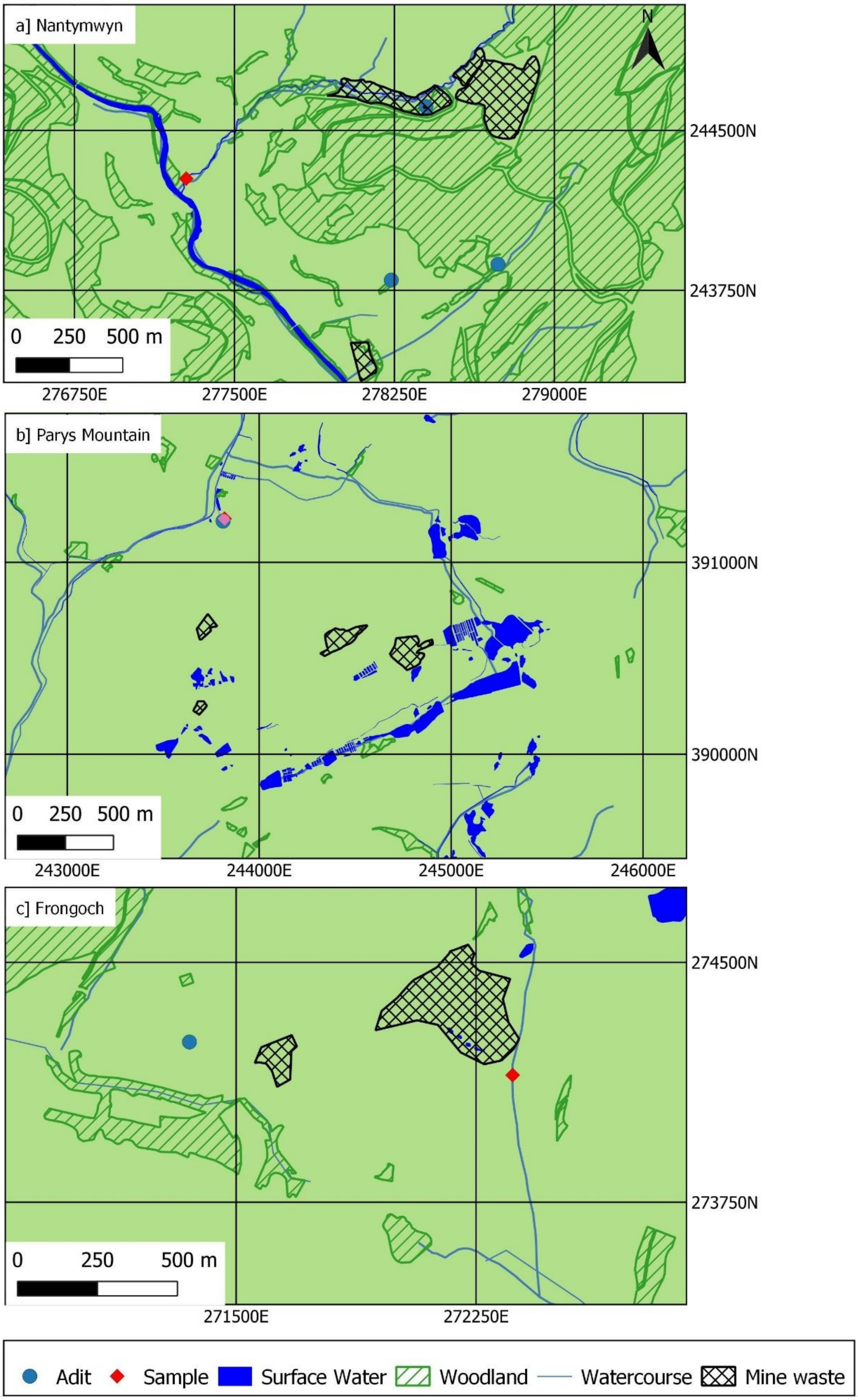


Figure 5-56 - Details of site locations, a] Nantymwyn, b] Parys Mountain, c] Frongoch. Blue circles denote mine water adits, red diamonds the sampling location. Crossed black denotes areas of mine wastes, and hatched green denotes forested areas.(Ordnance Survey, 2020; Todd et al., 2024)

Phased remediation work starting in 2011 included first diverting flow of clean water from the upper Frongoch to its original course down the Frongoch Stream, thereby preventing it from entering the underground mine workings (and becoming contaminated) and reducing flow to the Cwm Newyddion via the Frongoch Adit (Edwards et al., 2016). In the second phase, a perimeter channel was constructed to intercept clean surface water, diverting it to a flood attenuation pond to reduce peak flow from the site before it joins the Frongoch Stream. In the third phase in the first six months of 2015 mine waste was consolidated and reprofiled to encourage run-off into a series of lined ponds, which join the flood attenuation pond. Also a total of 23,000 m3 of this mine waste was capped to minimise infiltration. Finally, in May to July 2018 a further 7,600 m3 of mine waste was capped, and the remaining uncapped mine waste treated with a variety of experimental treatments to minimise run-off (Edwards et al., 2021). Catchment details for the Frongoch Stream are shown in Table 5 1, the water of which has a mean pH of 7.0 (n = 145).

5.4 History of contamination investigation at these sites

Concerns about the impact of contamination from metal mines were raised before these mines closed, with evidence of fish mortality due to metal mine contamination in the River Ystwyth noted in 1861 (Fisheries Preservation Society, 1868). Contamination from the metal mines on the rivers Rheidol and Teifi were reported to increase fish mortality rates during high flow events in the 1920s, with repeated experiments conducted in both the laboratory and in the field to confirm that both minnow and trout were susceptible to fatal consequences from Pb and Zn contamination in as little at 8 hours (Carpenter, 1926, 1925, 1924). Flood-deposited metals were noted for damaging farmland by causing harm to horses and cattle (Griffith, 1919). Harm to farmland continues today, with elevated concentrations of Pb, and Zn recorded in soils, flora, and farm products such as eggs and lamb (Alloway and Davies, 1971; Sartorius, 2018; Sartorius et al., 2022a; Smith et al., 2009). The issue of contamination from metal mines more generally was raised in Parliament at least 70 years prior to these mines' closures (Fisheries Preservation Society, 1868). After closure, the impact of metal mines on rivers were noted by regional water boards and authorities (South West Wales River Authority, 1974, 1970; South West Wales River Board, 1960) in national river surveys, including 1958, 1970, 1972, and 1975 (Department of the Environment, 1978, 1975, 1971).

The regulators for mines and mine contamination have changed repeatedly over the century since these mines closed, as have their priorities, scientific abilities, and legal frameworks. The Zn contamination to the River Ystwyth by Frongoch mine alone was recorded as 57 mg L^{-1} in 1939 (Jones, 1940), however, the cost of water quality analysis means that regular monitoring was not feasible at this time. More recently NRW and its predecessor organisations have collected and collated a large dataset encompassing all their water quality sampling points (including those associated with metal mines) that is now publicly available in digitized form on request. Without the understanding of baseline conditions provided by regular sampling, remediation and treatment of contaminated waters are either unfeasible, require several years' delay to collect baseline data, or will be inappropriate for the site, wasting resources, or affecting treatment quality. Recent monitoring regimes have succeeded in collecting baseline data, but the historical data are patchy in nature with substantial gaps.

After closure a major change to the mines was the cessation of pumping, causing the lowest levels of the mine to fill with water, while the exposed ores in the upper levels oxidise. When the water that has entered the mine reaches the lowest exit, usually an adit, it will flow out. The water will have an increase in metal concentrations, either from contact with oxides entering the mine, or by contact time in the lower levels of the mine workings. Initially after closure there can be a reduction in metal concentrations in the water leaving the mine. Minor improvements in chemical water quality on the River Ystwyth were noted between 1875 and 1922, as mines went out of operation (Newton, 1944). However, it was still contaminated by the metal mines to the point that mine-affected waters from nearby catchments were diverted into it to avoid contaminating other rivers (Newton, 1944). The River Ystwyth has several other mine complexes draining into it in addition to Frongoch, including Cwmystwyth, the 3rd highest priority metal mine for remediation in Wales (Mullinger, 2004). Complaints about pollution from the mines on the River Ystwyth are recorded from 1815, with Frongoch named in reports from 1875 (Griffith, 1919; Newton, 1944; Rivers Pollution Commission, 1875). Data on the water quality from these mines in the first decades after closure are lacking. For Frongoch, many data were lost during the Second World War (Newton, 1944), and the monitoring of all three mines was hindered by the difficulty of conducting fieldwork in remote locations and chemical analysis costs. Nantymwyn Pb mine has the most recently abandoned underground workings and has the longest dataset, although it has substantial gaps.

Shortly after the underground mining operations ceased at Parys Mountain, but while surface processing continued, it was noted that some Cu was "allowed to escape to sea" (Dewey et al., 1925). Parys Mountain has had interventions by the environmental regulator, but unlike Frongoch, this was to reduce the risk of flooding, rather than to improve water quality (Younger and Potter, 2012). The intervention, draining down the flooded workings and then removing the dam that kept the mine flooded, moved the main output of the mine and so changed which stream received the majority of the contaminated water, but not the eventual destination, the Irish Sea (Younger and Potter, 2012).

5.4.1 Long-term mean concentration for waters downstream of the three mines

Data from the three sites were compared to WFD Environmental Quality Standard (EQS). The WFD standards for the metals of interest at these sites are only given for total or dissolved metals (defined in the WFD as bioavailable), as shown in Table 5-2, and hence the only data shown is for the respective standard. The UK Technical Advisory Group for WFD investigations provides a tool (Metal Bioavailability Assessment Tool, M-BAT), to calculate Predicted No Effect Concentrations (PNEC) for each metal (WFD-UKTAG, 2014). Calculations of a site-specific PNEC, however, requires data for dissolved organic carbon (DOC), which is not routinely collected for UK metal mines. The M-BAT is sensitive to variations in DOC, and therefore the non-site-specific standards have been used.

The WFD EQS for Zn, Cd, Pb and Cu for the relevant river or catchment, and the average concentration of those metals in the water at each river site, are presented in Table 5-2. As can be seen in Table 5-2, Frongoch and Nantymwyn river waters are dominated by Zn and Pb, while Parys Mountain waters are dominated by Cu and Zn. The available metal concentration data (for total Pb and Cd, and filtered (mostly dissolved) Zn and Cu) are presented as a) annualised box-and-whisker plots (Figures 5.3-5.5), and b) means of aggregated data for different parts of the long-term record (Tables 5.4-5.6), for each mine site separately. The complete dataset is available in the Appendix, section 8.6 for Nantymwyn, 8.7 for Frongoch, and 8.8 for Parys Mountain.

Table 5-2 – Water Framework Directive (WFD) Environmental Quality Standards (EQS) for studied metal parameters (Water Framework Directive, 2015), and average metal concentration for the three mine sites using all available data 1978-2021.

Element ($\mu g\ L^{-1}$) /Determinand	WFD EQS	Nantymwyn	Parys Mountain	Frongoch pre-remediation (2004-2009)	Frongoch post-remediation (2018-2021)
Zn (dissolved, bioavailable)	12.9-15.0*	550	66,000	13,000	2,500
Cd (total)	≤ 0.08	2.9	160	27	5.5
Pb (total, bioavailable)	1.2	300	26	1,200	130
Cu (dissolved, bioavailable)	1	3.4	42,000	15	3.1
Conductivity, $\mu S\ cm^{-1}$	-	56	3600	140	97
pH	-	6.8	2.5	6.7	7.4
Temperature, °C	-	11	11	11	12
n	-	240	220	31	44

**The WFD standards for Zn vary depending on the background concentrations of the river catchment, with Nantymwyn's catchment standard 12.9 $\mu g\ L^{-1}$, Parys Mountain's 13.9 $\mu g\ L^{-1}$, and Frongoch's 15.0 $\mu g\ L^{-1}$ (Water Framework Directive, 2015).*

The data available for total Pb and Cd, and filtered Zn and Cu, are presented for each site as annualised box plots (Nantymwyn (Figure 5-57), Parys Mountain (Figure 5-58), Frongoch (Figure 5-59)). For clarity, only the metals with a WFD standard are shown in the graphs. All the monitored streams have exceeded WFD standards for all four metals for the majority of the sampling period, with only remediated Frongoch achieving sporadic passes for filtered Cu.

5.4.2 Nantymwyn

The historical record for Nant y Bai is presented in Figure 5-57 and Table 5-3. Nantymwyn has the longest dataset, spanning 42 years from 1978, but there are substantial gaps, including 22 years from 1987, and the earliest sampling was conducted annually, meaning seasonal variations are missed. It has the longest gap between sampling periods, from 1987-2019 (Figure 5-57).

Table 5-3 shows reductions in mean filtered Zn (-38%), total Cd (-47%), and total Pb (-

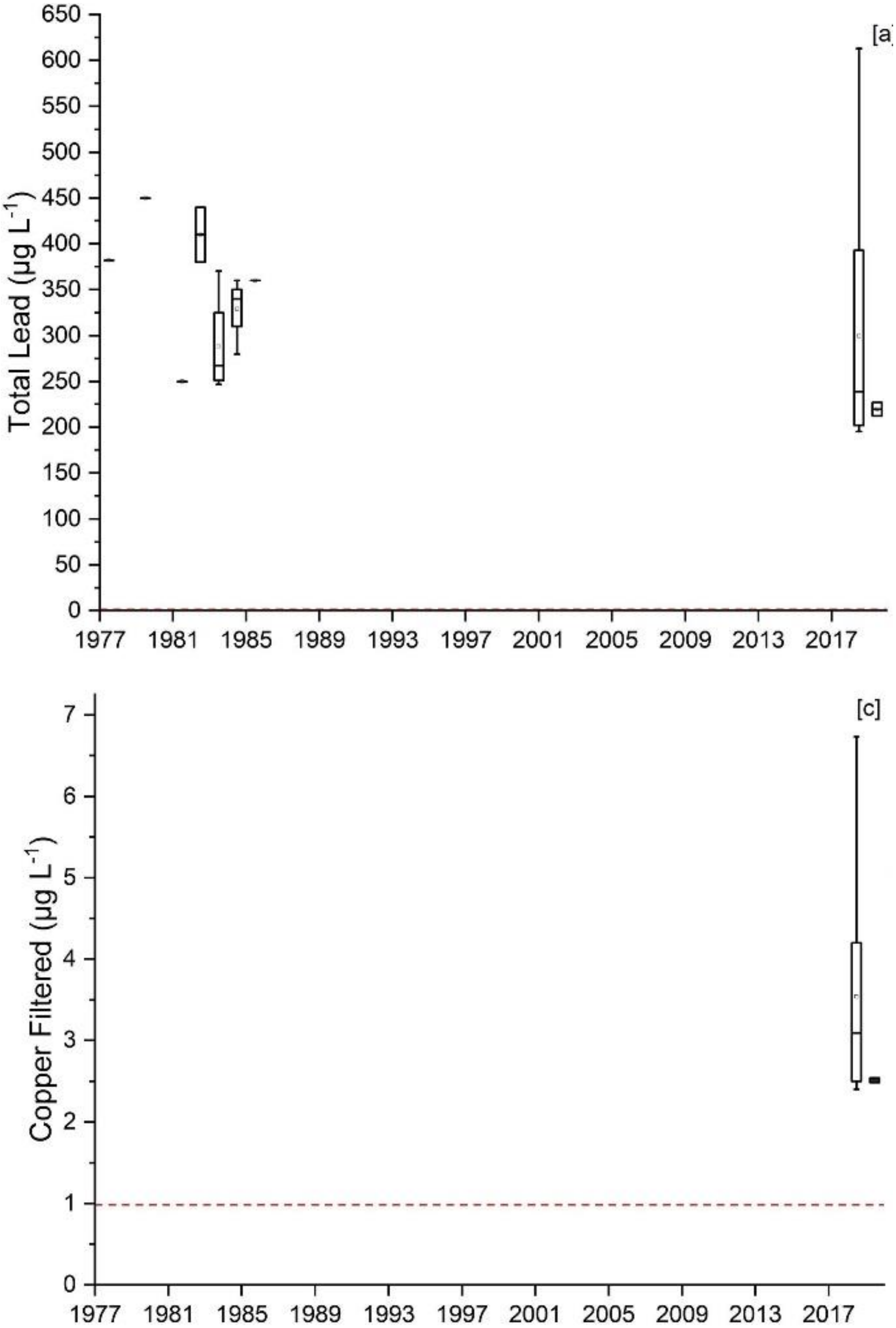
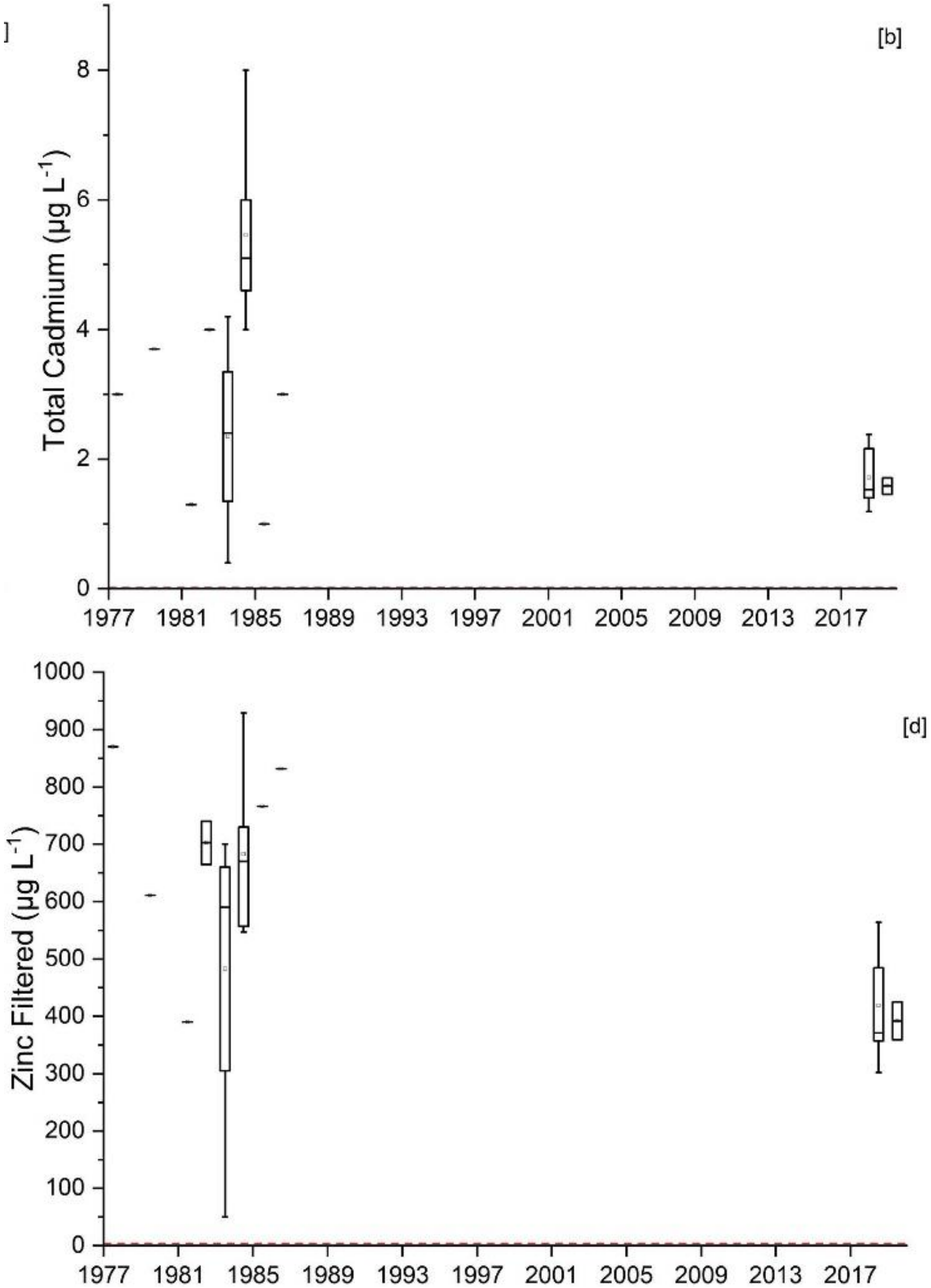


Figure 5-57 – Box and whisker plot of the temporal variation in metal concentrations, Nant y Bai, Nantymwyn 1978-2021; a) Total Pb, b) Total Cd, c) Filtered Cu, d) Filtered Zn. Boxes depict the inter-quartile range (IQR) with a horizontal line showing the median concentrations, and the mean concentrations shown by a square. The whiskers show 1.5 IQR, with outliers noted by large dots. Dashed red line denote relevant WFD EQS (Table 2).



14%), with the Zn and Cd differences being statistically significant ($p<0.05$). The sampling in the year 1985 (n=5) only ran from March – September (Brown, 1986), but comparing these data with the same period in 2019 (n=5) (the most recent sampling period covering these months) using a Mann Whitney U test showed no significant difference ($p>0.05$) in metal concentrations between the two periods. During both sampling periods the majority of the metals in the water were dissolved. In 2019, 98% of the total Zn was determined in the filtered sample at Nantymwyn which was similar to the value of 95% recorded in 1985. In 2019, 81% total Pb was found in the filtered sample which was similar to the value of 85% obtained in 1985. Similarly, 97% of the total Cd was found in the filtered sample in 2019 compared to 95% in 1985 (Brown, 1986). Cu was not monitored at Nantymwyn in 1985.

Table 5-3 - Comparison of mean metal concentrations for the Nant-y-Bai stream (Nantymwyn Mine) in 1978-87 and 2019-20 using all available data for the two periods. Statistical significances of differences were assessed using the Students' t-test.

Nantymwyn	**1978-87**			**2019-2020**			**Difference**	**Stat. Sig.**
Metal (µg L^{-1})	Mean	Standard Deviation	n	Mean	Standard Deviation	n		
Filtered Zn	660	196	16	410	83	13	-247 (-38%)	$p<0.05$
Total Cd	4	2	17	2	0	13	-2 (-50%)	$p<0.05$
Total Pb	330	299	17	290	125	13	-47 (-14%)	NS
Filtered Cu			0	3	1	13	N/A	

5.4.3 Parys Mountain

At Parys Mountain data are only available from after the draining of the underground dam in 2003, with a four-year gap in sampling from 2006-2009 (Figure 5-58). As there is regular sampling from 2010 onwards, for comparison purposes the data were split into three periods to assess possible changes in metal concentrations (Table 5-4). Although progressive and statistically significant reductions in mean total Cd (from 174 µg L^{-1} to 115 µg L^{-1}) and mean total Pb (from 33 µg L^{-1} to 23 µg L^{-1}) were recorded between 2004-06 and 2015-20, there was virtually no change in the mean filtered Zn and Cu. In addition, comparison of the same ten months filtered Zn data from 2004 and 2019 with a Mann Whitney U test showed no significant difference between the two periods ($p>0.01$). As with Nantymwyn, on average the majority of the metal in the water was dissolved. In

2019, 100% of the total Zn, total Cu and total Cd was found in the filtered samples, compared to a value of 99% determined in 2004. Similarly, 99% of the total Pb was found in the filtered sample in 2019 compared to 100% in 2004. A single sample taken at Parys Mountain in December 1990 (Walton and Johnson, 1992) at the same location as the data shown in Figure 5-58 gave Zn, Pb, and Cu concentrations taken within the range of the 15 samples taken in December between 2003-2020.

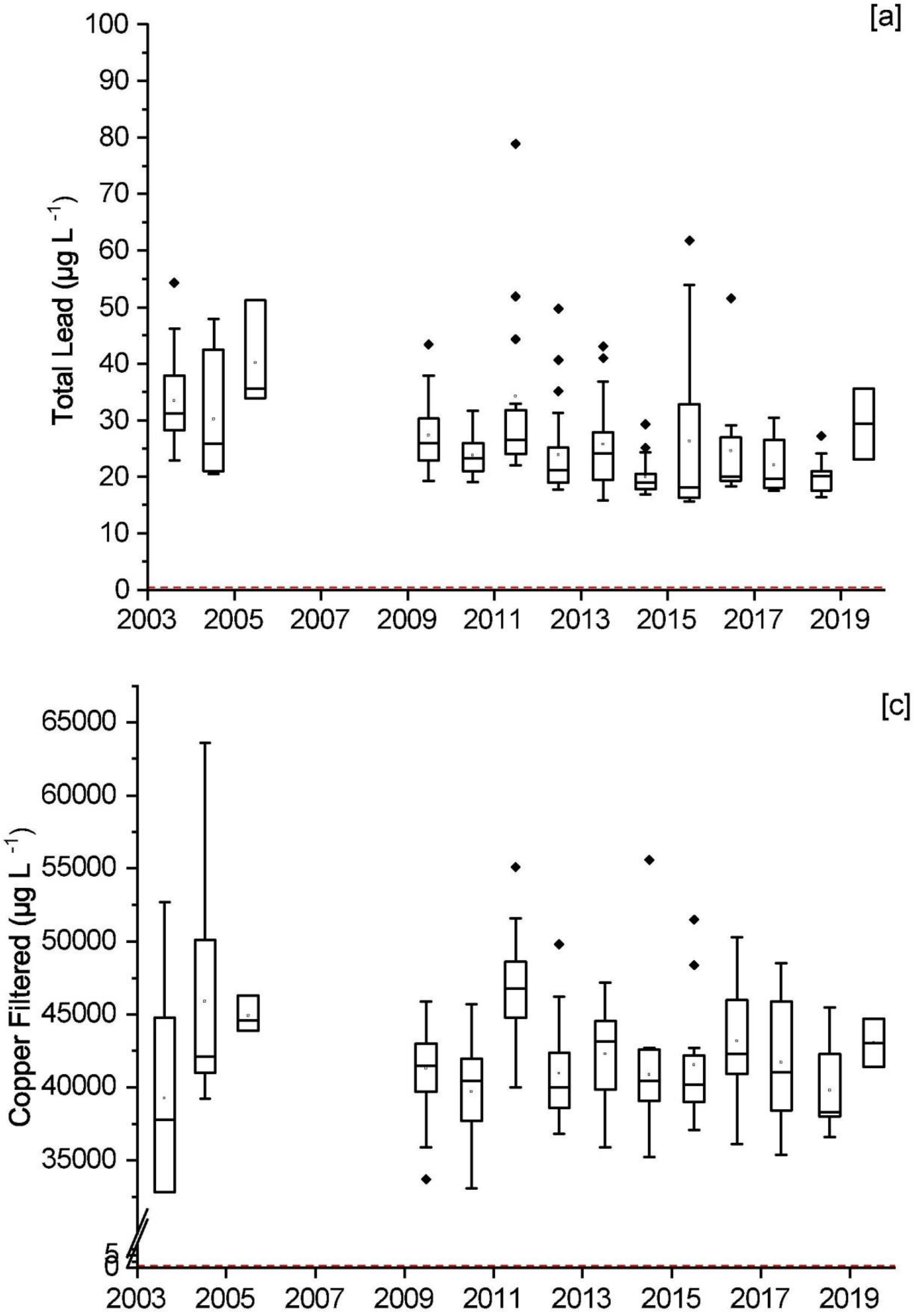


Figure 5-58 - Box and whisker plot of the temporal changes in metal concentrations, Dyffryn Adda Adit, Parys Mountain 2003-2020. a) Total Pb, b) Total Cd, c) Filtered Cu, d) Filtered Zn. Boxes depict the inter-quartile range (IQR) with a horizontal line showing the median concentrations, and the mean concentrations shown by a square. The whiskers show 1.5 IQR, with outliers noted by large dots. Dashed red line denote relevent WFD EQS (Table 2).

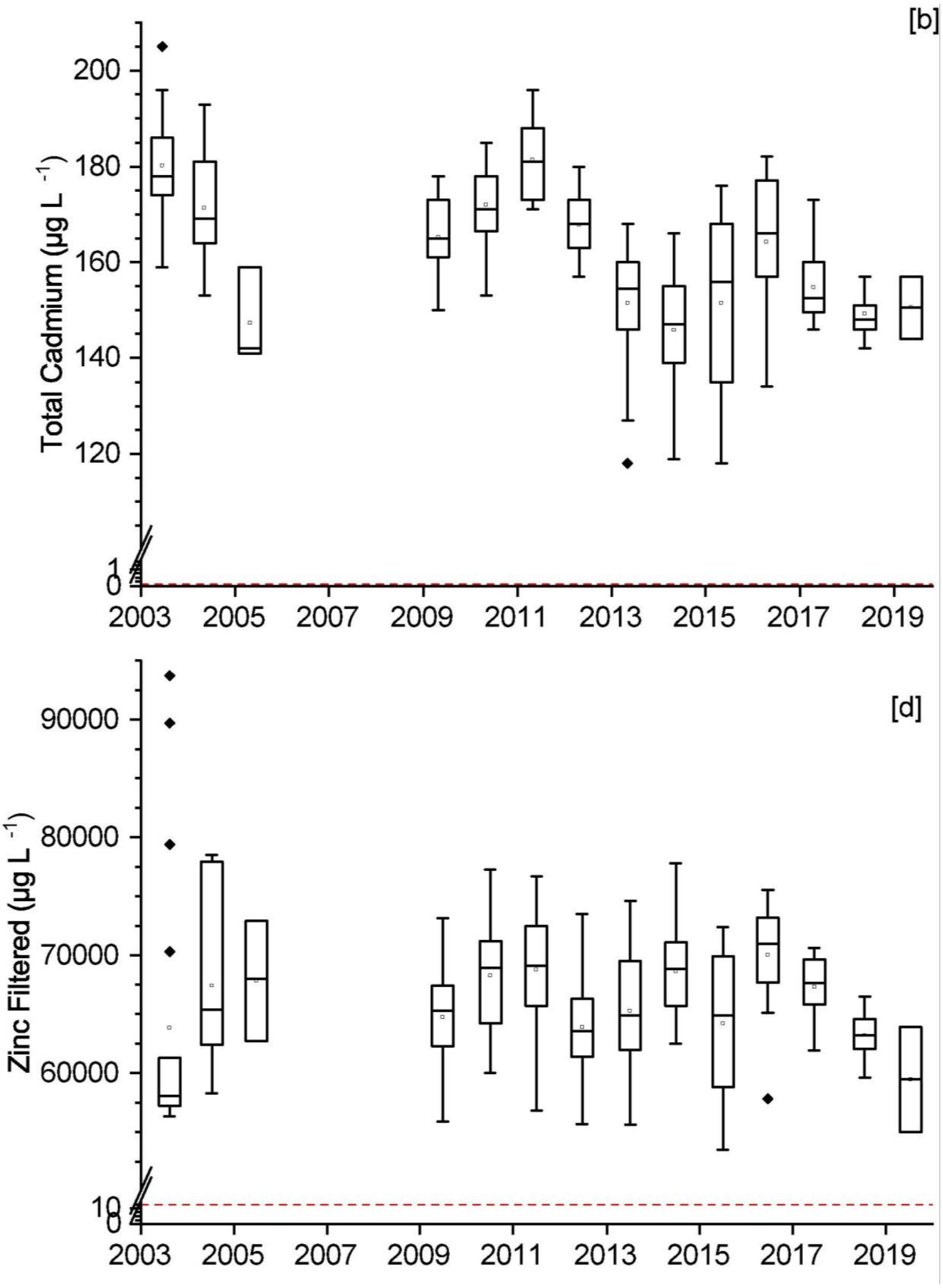

[b]
Total Cadmium (µg L -1)
200
180
160
140
120
1
0
2003
2005
2007
2009
2011
2013
2015
2017
2019
[d]
Zinc Filtered (µg L -1)
90000
80000
70000
60000
10
0
2003
2005
2007
2009
2011
2013
2015
2017
2019

Table 5-4 - Comparison of mean metal concentrations for the Dyffryn Adda Adit (Parys Mountain Mine) in 2004-06, 2010-14 and 2015-20 using all available data for the three periods. Statistical significances of differences between periods were assessed using the Students' t-test.

Parys Mountain	**a 2004-2006**			**b 2010-2014**			**c 2015-2020**		
Metal (µg L^{-1})	Mean	Standard Deviation	n	Mean	Standard Deviation	n	Mean	Standard Deviation	n
Filtered Zn	65,000	10,006	31	66,002	4,900	115	67,000	5,061	68
Total Cd	170	15	31	167	13	115	150	14	68
Total Pb	33	9	31	27	11	115	23	9	68
Filtered Cu	42,000	7,757	31	41,794	5,500	115	41,000	4,008	68

	Difference b-a	**Stat. Sig.**	**Difference c-a**	**Stat. Sig.**	**Difference c-b**	**Stat. Sig.**
Filtered Zn	+508 (+1%)	NS	+1,019 (+2%)	NS	+511 (+1%)	NS
Total Cd	-7 (-4%)	$p<0.05$	-22 (-14%)	$p<0.05$	-15 (-10%)	$p<0.05$
Total Pb	-6 (-22%)	$p<0.01$	-10 (-43%)	$p<0.01$	-4 (-17%)	$p<0.01$
Filtered Cu	-374 (-1%)	NS	-796 (-2%)	NS	-422 (-1%)	NS

5.4.4 Frongoch

Frongoch is the only site to have undergone remediation, in a series of interventions between 2011-2018. The first stage of remediation, diverting flow from the upper Frongoch to the original course and preventing it from entering the underground mine workings and becoming contaminated, reduced the flow from the Frongoch Adit by 80% (Edwards et al., 2021; Natural Resources Wales, 2016a). While the resultant adit water flowing into the Nant Cwmnewydion had higher concentrations of metals after this, the substantially reduced flow resulted in reduced metal loadings by up to 63% (Edwards et al., 2016). Additionally, the diverted flow was kept away from the mine waste as much as practicable and was able to dilute the incoming contaminated waters for a further improvement in resultant concentration of metals of concern. Waters from the sample site on the Frongoch stream shows a substantial decrease in metal concentrations after the first stage of remediation, especially for Pb, which continued to a lesser degree after each of the subsequent stages of remediation. This is likely due to the clean waters of the diverted Upper Frongoch Stream diluting contaminated surface waters from the site (Figure 5-59). Although the watercourses affected by Frongoch continue to fail WFD standards, the reduced metal concentrations have led to biological data showing a modest improvement in species richness and number between 2009 and 2019 in the Frongoch Stream (Edwards et al., 2021). Since the large-scale remediation was completed there have been a series of trials at Frongoch to treat the remaining high concentration waters, in particular using electrolysis (Abril et al., 2021). As an active

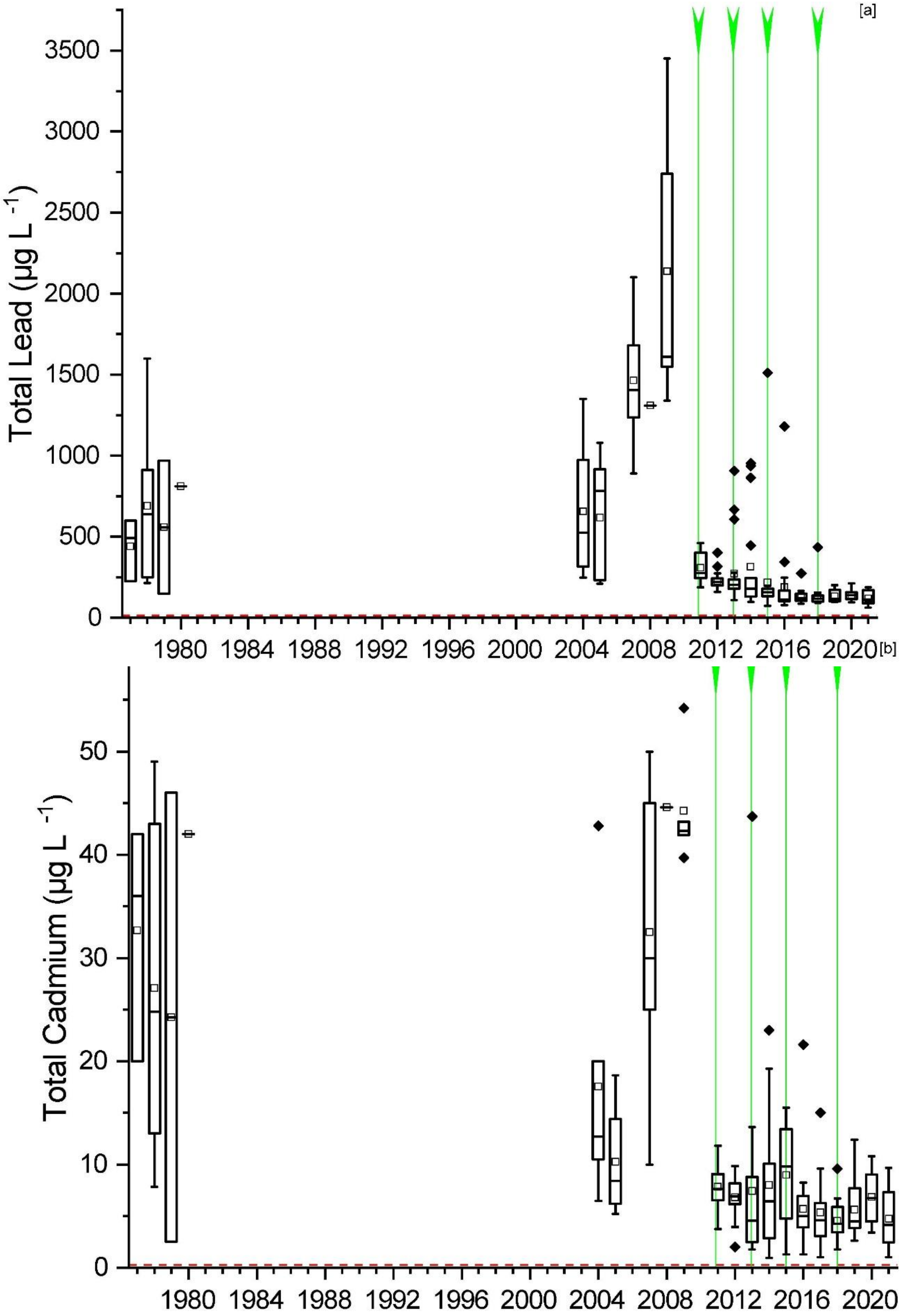
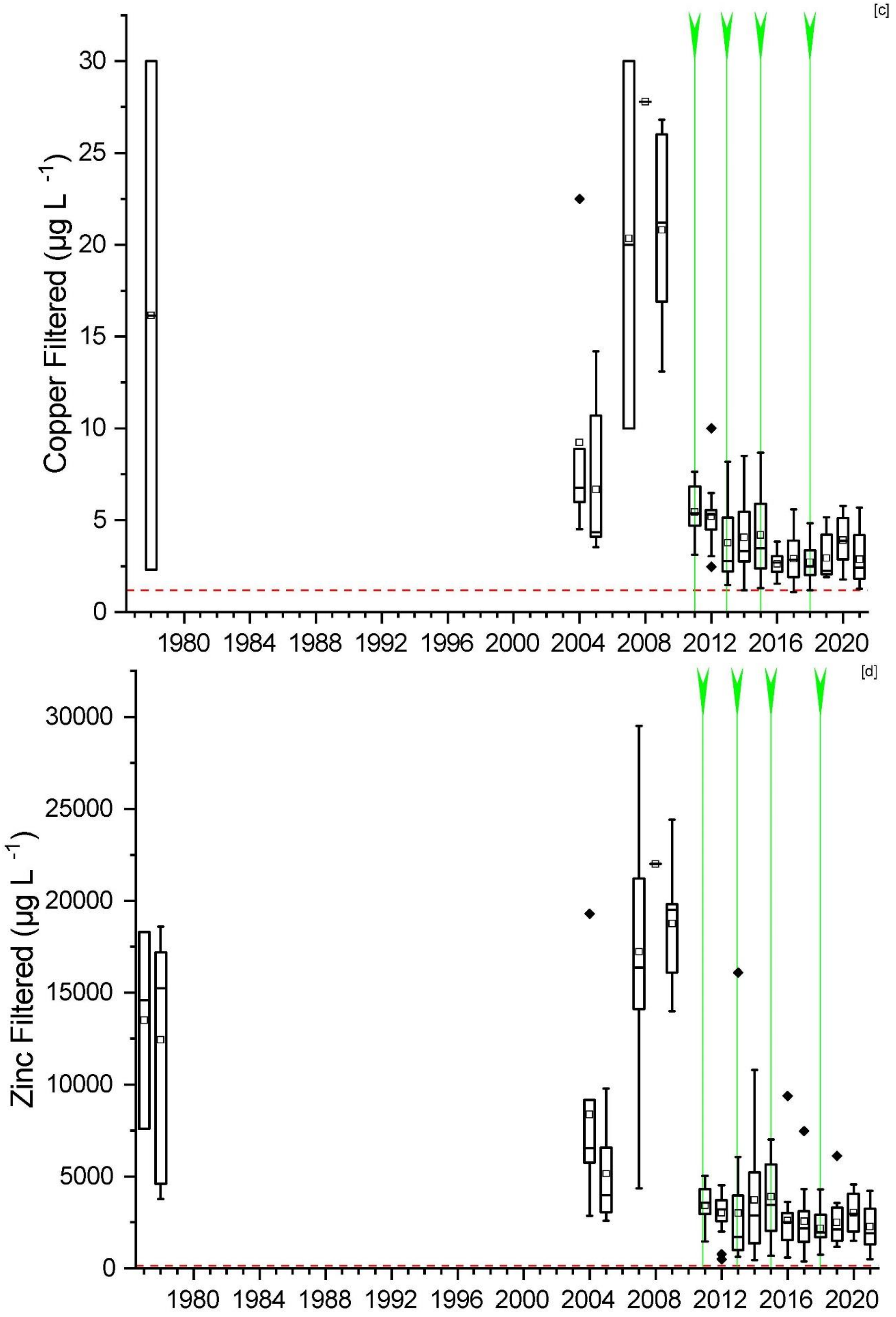


Figure 5-59 - Box and whisker plot of the temporal variation in metal concentrations, Frongoch Stream, Frongoch Lead Mine 2004-2021. a) Total Pb, b) Total Cd, c) Filtered Cu, d) Filtered Zn. Boxes depict the inter-quartile range (IQR) with a horizontal line showing the median concentrations, and the mean concentrations shown by a square.The whiskers show 1.5 IQR, withoutliers noted by large dots. Dashed red line denote relevant WFD EQS (Table 2). Green vertical lines denote interventions by NRW; stream diversion in 2011, pond and stream lining in 2013, reprofiling and capping of mine waste in 2015, and additional capping and treatment in 2018.

treatment system this has ongoing costs for power and disposal of waste products, but has the potential to bring Frongoch's waters much closer to WFD standards. A similar system has been trialled using water from Parys Mountain (Morgan et al., 2017).



To assess potential improvements, the Frongoch data (Table 5-5) was split into a pre-remediation period (2004-2010) and post-remediation period (2018-2021). It was found that there was a clear improvement in water quality with the concentration of Zn dropping from 13,810 µg L^{-1} to 2,510 µg L^{-1}, and the concentration of Pb, dropping from an average of 1,220 µg L^{-1} to 127 µg L^{-1}. The improvement in relation to successive phases of remediation is shown in the box-and-whisker annual data of Figure 5-59. The largest falls occurred following the first phase of remediation, in which the flow of the Upper Frongoch was diverted to its pre-mining course along the lower part of Frongoch, but lesser falls in metal concentrations occurred following the other remediation phases. The phases of remediation are indicated with the data in Figure 5-59. The falls in metal parameters were statistically significant (Table 5-5). As with both Parys Mountain and Nantymwyn the majority of the metal in the water is dissolved. Thus in the pre-remediation period 100% of the total Zn was also in the filtered sample and in the post-remediation period this figure was 96%.

Table 5-5 – Comparison of mean metal concentrations for the Frongoch Stream (downstream of Frongoch Mine) in 2004-11 (pre-remediation) and 2018-21 (post-remediation) using all available data for the two periods. Statistical significances of differences were assessed using the Students' t-test.

Frongoch	**2004-2011**			**2018-2021**			**Difference**	**Stat. Sig.**
Metal (µg L^{-1})	Mean	Standard Deviation	n	Mean	Standard Deviation	n		
Filtered Zn	13,000	7,639	37	2,500	1,294	34	-10,670 (-81%)	p<0.01
Total Cd	27	16	37	6	3	34	-21 (-78%)	p<0.01
Total Pb	1,200	729	37	130	37	34	-1,093 (-90%)	p<0.01
Filtered Cu	15	9	37	3	1	34	-12 (-80%)	p<0.01

5.4.5 The passage of time

Metal concentrations from the three sites have varied over the period of available data (16-42 years). The clearest changes were found at Frongoch that showed a decrease in the concentration of at least 78% of the four studied metals (Pb, Zn, Cd and Cu) after substantial remediation at the site (Table 5-5, Figure 5-59). The other unremediated sites still show variations over time, though this is not a clear indication of decreased or increased contamination from the sites. The Nant y Bai (at Nantymwyn) for instance shows a statistically significant ($p<0.05$) decrease in filtered Zn between 1978-87 and 2019-20. Although sampling in 2019-20 covered a full year from February-February (13 months), the earlier sampling is biased towards winter conditions, with 11 of the 17 sampling dates being between October-February, meaning direct comparison of the metal concentrations between the two sampling efforts may be biased by seasonal flow variations. When comparing consecutive sampling from March-September 1985 with the same months in 2019, there is no statistically significant difference between the two years' filtered Zn ($p>0.05$), and total Pb ($p>0.05$) data. There is a statistically significant ($p<0.01$) inverse relationship between flow and filtered Zn concentrations in the Nant y Bai, with low flows typically having higher concentrations of filtered Zn. The winter bias in the earlier sampling is not therefore responsible for the apparent decrease in concentrations. The smaller decrease in total Pb (14%) is also not statistically significant.

Parys Mountain also shows a statistically significant decrease in total Cd ($p<0.05$) and Pb ($p<0.01$) concentrations, but as these values are already low the actual decreases are small (10 µg L^{-1} total Pb shows as a large 43% reduction). More surprising is the sustained increase in filtered Zn concentrations, with an increase of 1,000 µg L^{-1} over 16 years shown (Figure 4). Although this 2% increase is not statistically significant ($p>0.05$ comparing the period 2004-2006 to 2015-2020,), and could be as a result of the removal of an underground dam in 2003 allowing previously submerged ores to oxides and then contaminate water entering the mine workings, it shows that the contamination from these mines is not static. Regular monitoring of abandoned mines is not only essential for creating a baseline database for remediation purposes, but also for understanding changes to the mine. Cwm Rheidol, an abandoned Pb and Zn mine with acid mine discharge on the River Rheidol, had inflow reduced through stream diversion in 2007, like Frongoch (Natural Resources Wales, 2016b). Subterranean movements within the mine workings, as wooden supports rotted and failed, and a build-up of deposited ochre on the floor and sides of the mine passages, eventually led to the adit becoming blocked, first in 1969, then again in 1992 (Edwards and Potter, 2007), and 2016. Monitoring of the site after repairs were completed in 1992 meant that a similar situation in 1994 was discovered early and resolved at a lower cost both financially and environmentally than if it had been discovered from visible contamination at a later date.

5.4.6 Implications for future contamination management and remediation

Remediated sites can still have elevated concentrations of metal in the water, especially during and after heavy rainfall (Nordstrom, 2009; Pool et al., n.d.). The Nant y Fendrod in Swansea was affected by 240 years of metal smelting, resulting in elevated concentrations of Pb, Zn, Cu, Ni and Cd in the stream (Blake et al., 2003). From the 1960s a sharp decline in the UK metal industry led to the site being remediated, with waste material being reprofiled and covered (Walsh et al., 2000). Despite this remediation, concentrations of Pb and Cu in particular increase sharply with increases in flow during storm events (Blake et al., 2007). This suggests both that the riverbed sediments remain contaminated long after the contaminating activity has ceased, and that the metals in the riverbed are being replenished by precipitation from seepage at low flows (Blake et al., 2003). Point sources of metals that are being treated must be monitored to confirm the remediation is working as designed, and cessation of monitoring has lead to contamination events that would have been avoided otherwise (Wyatt et al., 2013a).

Over longer timescales (1978-2020) than this study, it has been reported that UK water quality in general has improved, with metal concentrations one of five areas of water quality issues (out of eleven in total) considered to have improved between the start of the Industrial Revolution and today (Whelan et al., 2022). Works as a result of the EU waste water treatment and nitrates directives, and the WFD, have shown a measured improvement in eight of these areas including metal concentrations since their peak between 1980-2020 (Whelan et al., 2022). This reduction in metal concentrations, however, has not been influenced by metal mines, but by increase in number, and improvements to, sewage treatment plants, the decline in heavy industry, and the end of leaded petrol in cars. Although the datasets and time periods available are limited, Nantymwyn and Parys Mountain show that metal concentrations, albeit in some cases showing some recovery, still remain substantially elevated nearly a century after the mines were abandoned. It has been reported that the highest concentrations of metals occur during the first flows from an abandoned mine once pumping has ceased (Byrne et al., 2012). Evidence from Wheal Jane in Cornwall, England, shows that after initial abandonment, or when water first starts draining from the mine after the cessation of pumping, this can be followed by a decline in metal concentrations, but it should be noted that this decline does not bring them to a level where they do not need treatment or management (Wyatt et al., 2013b).

A modelling study of a metal mining impacted River Swale in England predicted elevated concentrations of metals in sediments and water 100 years after mining ceased, with the prediction confirmed with sediment sampling (Coulthard and Macklin, 2003). This validated model was then used to predict contamination concentrations over the subsequent 100 years to 2100, showing very little change since 2000 (Coulthard and Macklin, 2003). Combined with the data shown for the three mines studied for this project, this shows that across the UK in different catchments there has not been any substantial recovery in watercourses downstream of un-remediated metal mines. It follows that metal-mine-impacted catchments will need individual action plans, starting at data collection, and building up to a remediation design that, like that at Frongoch, includes measures for surface water, subterranean water flows, and management of surface hazards, such as fine mine waste, mine entrances, and shallow workings.

Upstream from Nantymwyn, the Llyn Brianne experimental catchments have been regularly monitored since 1981, and these non-mine impacted circumneutral upland streams have been shown climate change, such as warmer, wetter winters, and warmer instream water year round (1.4-1.7°C increase between 1981-2005) to have negative impacts on the abundance of organisms (Durance and Ormerod, 2007). High flow events caused by heavy rainfall are increasing in Wales in both frequency and intensity due to climate change, increasing the quantity of contaminated water from abandoned mines entering rivers (Douville et al., 2021; Hanlon et al., 2021). The abandoned Annapolis Pb Mine in Missouri, USA, was remediated in 2007 to reduce the elevated concentrations of Pb, Cu, As, Ni and Zn in streamwater and sediments in the Sutton Branch Creek (Gunter, 2017). As in the remediation of Frongoch in the current study, mine wastes at Sutton Branch were consolidated and stabilized on-site, capped, and then seeded with a site-specific seed mix. A settling pond was built for the direct mine drainage, and all surface water flows were diverted away from contaminated areas (Gunter, 2017). Despite these measures Pb concentrations in the creek's sediments remain elevated, and the settling pond's sediments have required periodical removal since the scheme was completed. During high flow events, concentrations of metals in the water have been elevated, and in historic floods in April 2017 the settling pond's filters were washed into the Creek (Gunter, 2017). Future climate change will not only affect how a site contaminates during extreme flow and rainfall events, but also affect the design and size of any remediation techniques used.

6 Results and discussion – synoptic sampling

6.1 Introduction

This chapter presents, analyses, and discusses the implications of the single synoptic sampling and tracer injection experiment carried out on the Nant y Bai stream in July 2019.

6.2 Site selection

6.2.1 Streamflow, pH, and Metal Concentrations

Calculated streamflows for each of the 21 stream sites, and the corresponding Br tracer concentration values are shown in Figure 6-1. Streamflow increased with distance downstream from the tracer injection point from 3.71 L s^{-1} at N-0 to 15.35 L s^{-1} at N-19, the end of the studied reach. The largest inflow on the day of sampling was the Nant y Glo (R-3), responsible for 16% of the total streamflow increase. This was also the only inflow responsible for more than a 10% increase in streamflow. Stream segments with sampled inflows accounted for 63% of the total streamflow measured in the stream, indicating that at least 37% of the streamflow on the day of sampling came from subsurface (or possibly unidentified diffuse surface) water inputs.

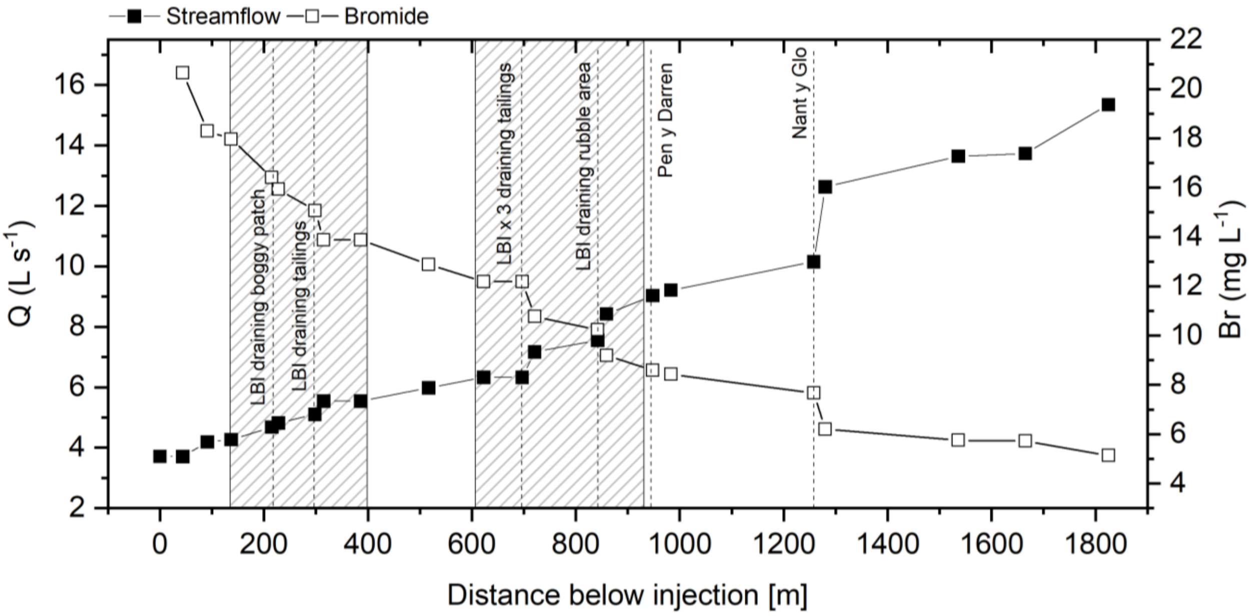


Figure 6-1 - Downstream changes in Br concentration and streamflow (Q) along the Nant y Bai. Major inflows are marked with dashed lines, and areas of mine waste with hashed boxes.

Stream pH values varied between 6.45 to 6.91, with the inflow pH values slightly lower, between 6.25 to 6.78; both are shown in Figure 6-2. Overall pH values fell (became more acidic) until a partial recovery shortly before the confluence with the Tywi. The River Tywi has historically suffered from acidification, from both coniferous plantations and from industrial pollution (Edwards et al., 1990; National Rivers Authority Welsh Region, 1992; Ormerod and Durance, 2009). The latter has reduced substantially in the last thirty years, (Lloyd et al., 1996; Reis et al., 2012; Whelan et al., 2022) and the while the wider mine site is used for conifer plantation, with approximately 40% of the Nant y Bai catchment used for this purpose, due to the mine waste near the Nant y Bai there are only a few coniferous trees growing in the immediate vicinity of the stream.

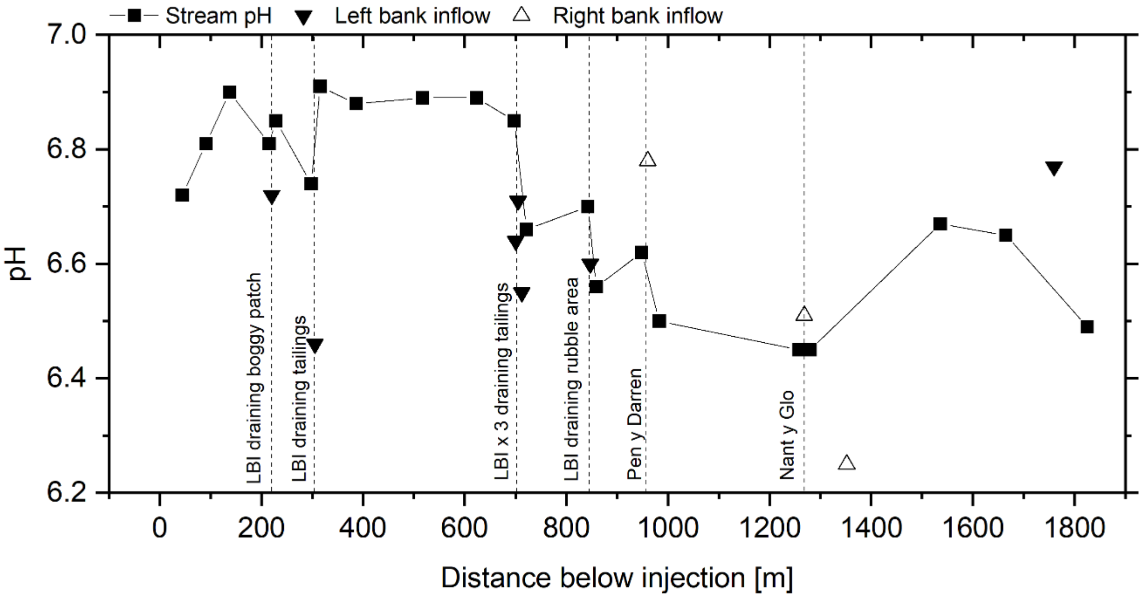


Figure 6-2 - Downstream changes in pH at stream and inflow sites. Major inflows are marked with dashed lines.

Figure 6-3 shows downstream changes in total and filtered/dissolved concentrations of Pb, Zn, and Cd along the Nant y Bai during the synoptic sampling and tracer injection experiment. Also shown are the positions of sampled tributary and other inputs and downstream changes in streamflow.

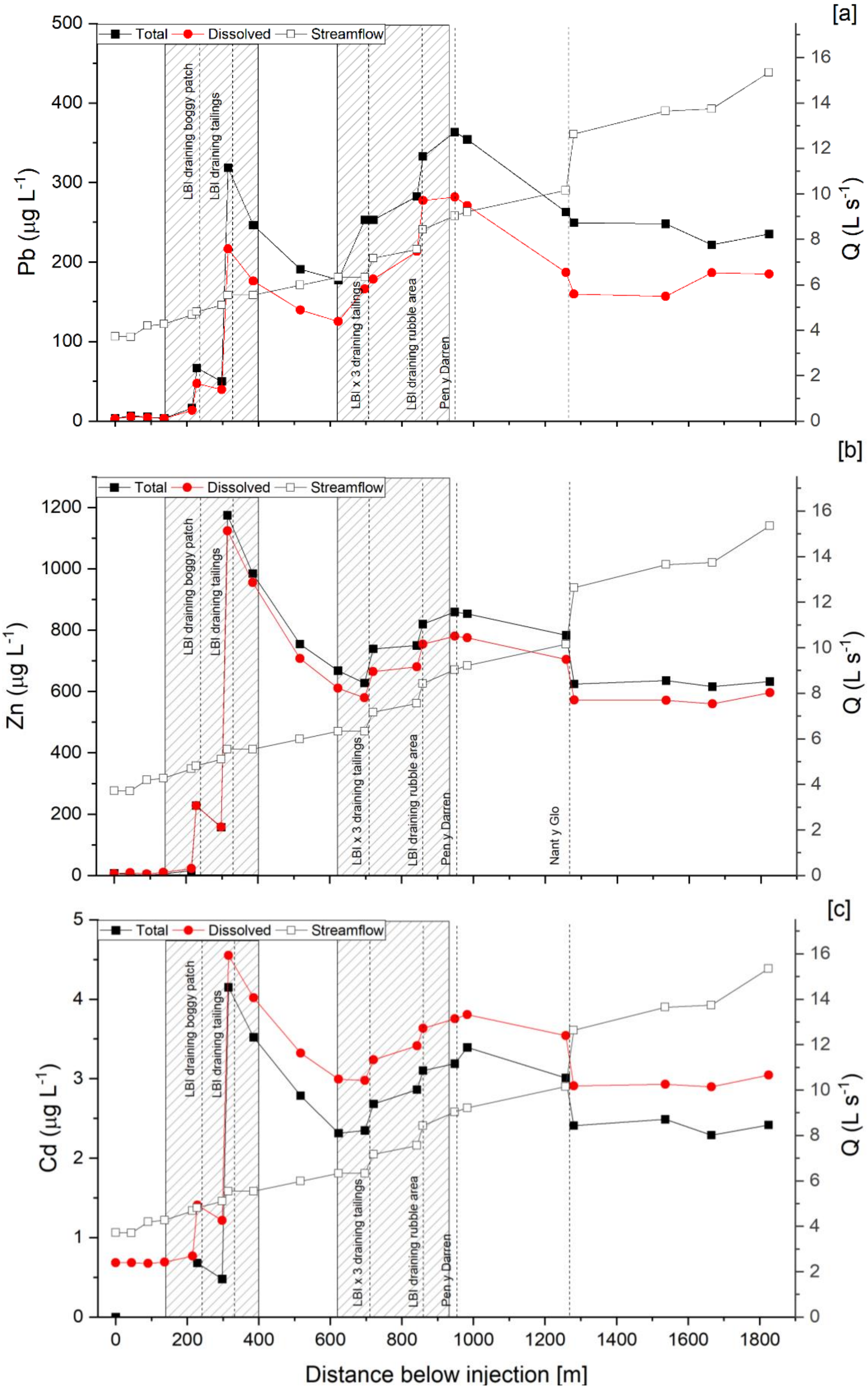


Figure 6-3 - Downstream changes in total and filtered Pb stream concentrations (a), total and filtered Zn concentrations (b), and total and filtered Cd concentrations (c), with flow (Q) superimposed.

The WFD and drinking water standards for Pb, Zn and Cd are shown in Table 5-2. Above the mine at sites N-1 to N-5, the Nan y Bai is uncontaminated by mining or mining wastes and concentrations of all three metals are low and, and for Zn, below the WFD EQS. Thus, and N-1, total and dissolved Pb concentrations were 6.84 µg L^{-1} and 5.60 µg L^{-1} respectively, total and dissolved Zn concentrations were 4.06 µg L^{-1} and 8.74 µg L^{-1} respectively, and total and dissolved Cd concentrations were below the limit of detection (0.4 µg L^{-1}) and 0.68 µg L^{-1} respectively. Concentrations of metals increased at N-5, over the upstream area of mine waste, and substantially after the left bank inflow at L-2, coincident with the Zn and Cd peak concentrations (Figure 6-3, 6-5 and 6-6). This sharp increase in the concentration of all three metals at N-6 occurs after L-2, a small (>5 cm wide) inflow draining the upper mine wastes area, demonstrating high concentrations, with filtered Zn at 10,274 µg L^{-1}, filtered Pb at 1924 µg L^{-1}, and filtered Cd at 37.4 µg L^{-1}. The main stream after this input has a filtered Pb concentration of 217 µg L^{-1}, a filtered Zn concentration of 1,124 µg L^{-1}, and a filtered Cd concentration of 4.6 µg L^{-1}. The concentration of all three metals decrease after N-6 from N-7 to N-10 until the downstream area of mine waste where Pb concentrations increase. Two non-mine-impacted tributaries, R-2 and R-3, enter the Nant y Bai between the end of the downstream area of mine waste and the sampling point at N-17, and these have a diluting effect on all three metals. The mean filtered concentration of Pb over the studied reach was 272 µg L^{-1} (range 2.6-1,924 µg L^{-1}), the mean filtered concentration of Zn was 1,058 µg L^{-1} (range 5.4-10,274 µg L^{-1}) and the mean filtered concentration of Cd was 4.5 µg L^{-1} (range 0.7-37.4 µg L^{-1}). Pb and Zn exceeded the respective EQS for 88% of the studied reach, and Cd exceeded the EQS for the entire length of the studied reach. The filtered and total concentrations were similar for all three metals of concern, indicating that metal transport was primarily in the filtered (potentially dissolved) fraction, as would be expected at such low flows. The complete dataset is available in the appendix, section 8-4.

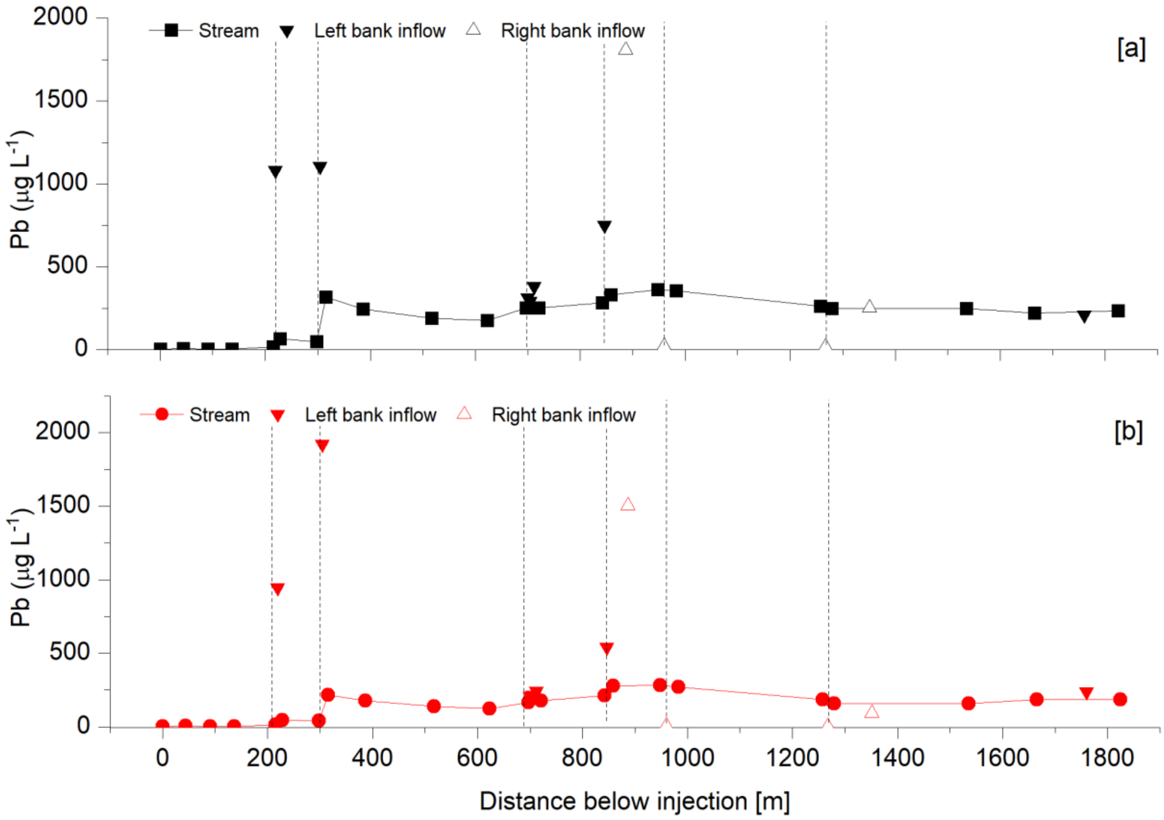


Figure 6-4 - Concentrations of Pb in the Nant y Bai stream and in inflows for total [a] and filtered [b]. Vertical lines mark major inflows as labelled in Figure 6-1.

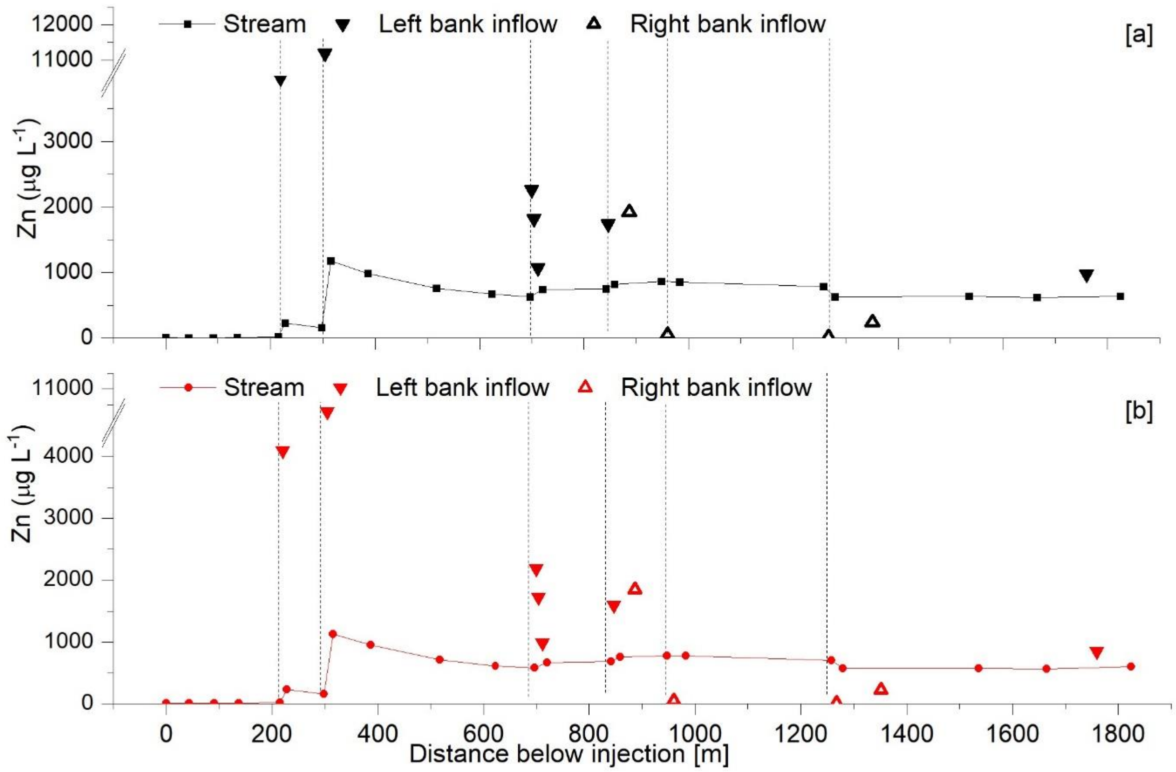


Figure 6-6 - Concentrations of Zn in the Nant y Bai stream and in inflows for total [a] and filtered [b]. Vertical lines mark major inflows as labelled in Figure 6-1.

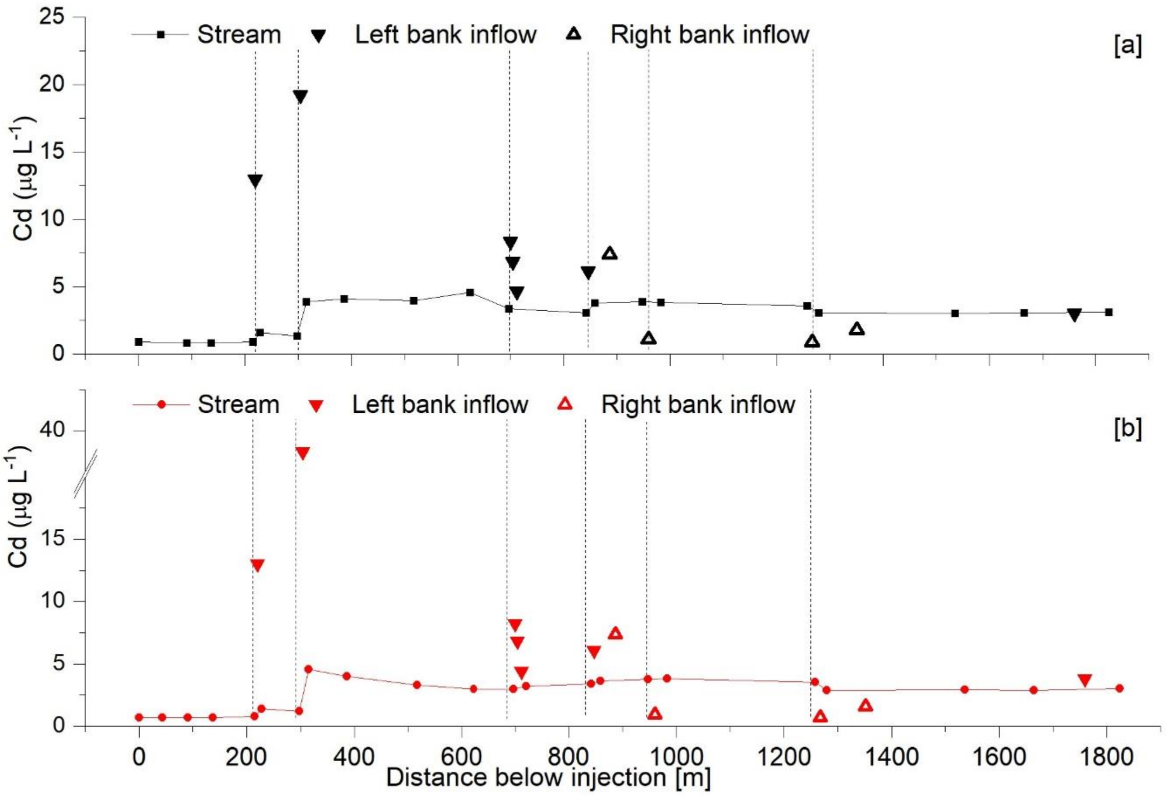


Figure 6-5 - Concentrations of Cd in the Nant y Bai stream and in inflows for total [a] and filtered [b]. Vertical lines mark major inflows as labelled in Figure 6-1.

6.2.2 Metal loadings and patterns

The loading of metals for each stream segment, and the cumulative stream load at that point, are shown in Figure 6-7. The single largest load increase over any measured stretch of stream for all three metals was at N-6, downstream of an ephemeral stream in the upper tailings. This contributed 45% of filtered Zn, 25% of filtered Pb, and 35% of filtered Cd to the stream. Other large sources (>10%) include: a) N-12, within which an inflow at L-6 contributes 18% of the filtered Pb, 10% filtered Zn, and 9% filtered Cd, and b) N-19 which contributes 12% of both filtered Zn and Cd, and 7% of filtered Pb, though that section does not have any visible inflows.

Lesser but still important sources (>5%) of filtered Zn include the area above N-12 which contributes 10%, with an inflow from the lower mine waste area at L-6. The final measured stretch flows through farmland which may have been used by the mine, as historical paintings show ore loading activities nearby (Smith, 1792). This segment, N-19, provides 8% of the filtered Zn. N-9, the first stretch in the lower mine waste area provides 6% of the filtered Zn.

Between the two areas of mine waste, from N-7A to N-9, the Pb load declined 12% for total and 11% for filtered, indicating both physical and chemical attenuation processes causing this decrease. The closeness of the percentage load reduction suggests the loss is almost entirely from the filtered fraction, unsurprisingly as the flows were very low and there would have been minimal to no suspended sediments. The difference between the instream metal load and the cumulative instream metal load at the last synoptic sample site (N-19) can be used to quantify the attenuation that occurred along the study reach. Over the whole studied reach 28% of the total Pb load added to the reach is attenuated, 24% of the total Zn, and 13% of the total Cd.

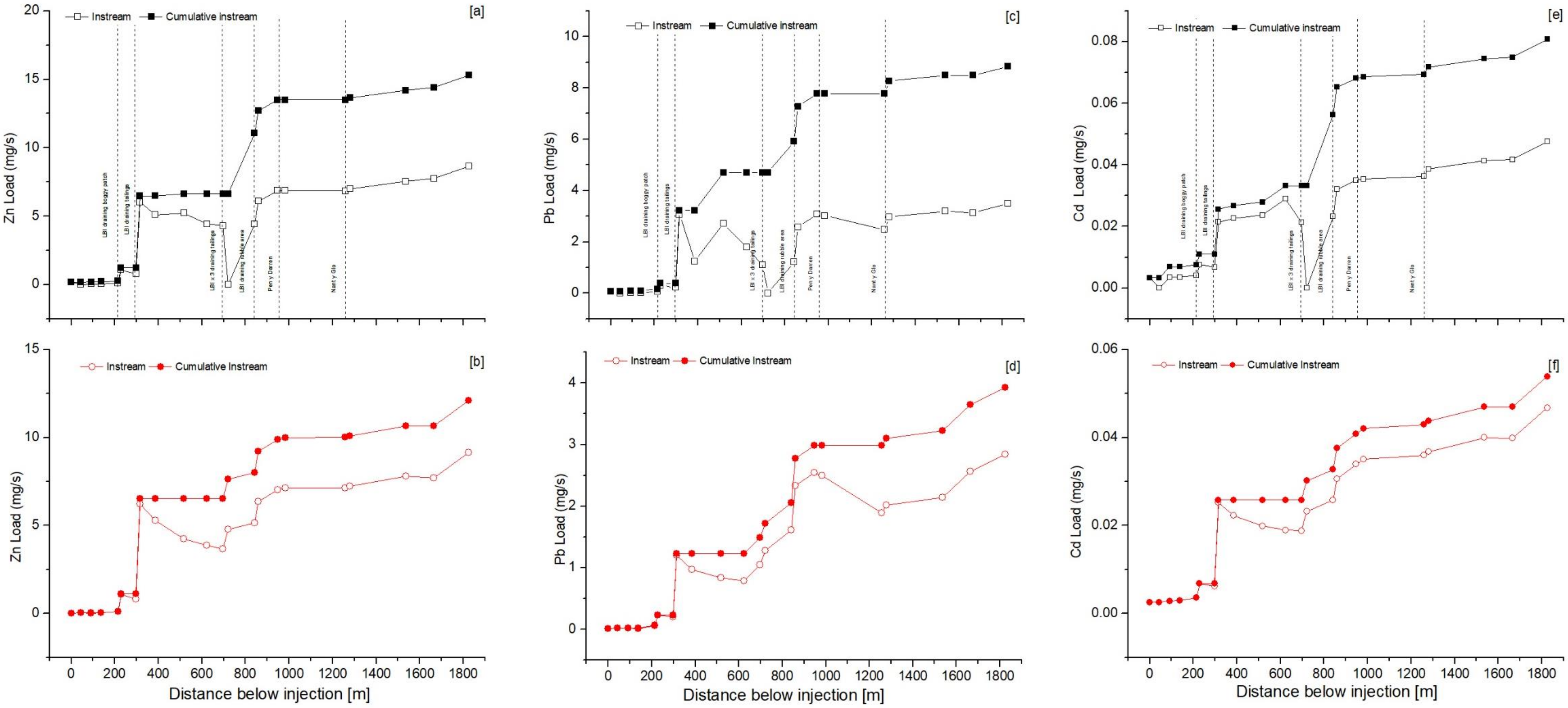


Figure 6-7 - Loading and cumulative loading for total [a] and filtered [b] Zn, total [c] and filtered [d] Pb, and total [e] and filtered [f] Cd. Vertical lines mark major inflows as labelled in Figure 6-1.

6.2.3 Major source areas of metal contamination

Identification and classification of source areas is key to successful and cost-effective mine contamination remediation (Kimball et al., 2002). Several diffuse sources of mine contamination were identified along the studied reach, characterised in two groups: visible surface run-off from mine waste, and diffuse groundwater inflows. The surface run-off from diffuse sources is of particular interest as the tracer injection experiment was conducted under steady state conditions, meaning that these sources were not directly linked to rainfall run-off as is common (Byrne et al., 2013). Studies at other sites have shown that even after remediation these surface run-off diffuse sources can cause EQS failure during and after storm events (Walsh et al., 2000). Older methods for ore processing, often relied on water, either for direct power, or as part of the processing action, but leave minimal traces of the physical infrastructure many decades after they ceased to operate (Mills et al., 2014).

The stream segments identified as metal sources to the stream were classified into four groups, dependent upon their location and the nature of the source area: Mining Inflow (MI), Non-Mining Inflow (NMI), Mining Diffuse (MD), and Non-Mining Diffuse (NMD) (Figure 6-8). Segments with a sampled inflow were put into the inflow groups, and this was subdivided into mining, when the segment was in an area with mine waste, or where historical aerial photos showed mine waste had been revegetated, or non-mine where there was no mine waste in the segment. Stream segments with no sampled inflow were allocated to the diffuse group, and again subdivided into mining and non-mining groups. The largest source of Zn, Pb, and Cd was MD, contributing 55% of the filtered Zn load, 42% of the filtered Pb load, and 49% of the filtered Cd load. By their nature, diffuse groundwater sources can only be identified in areas between sampling points, and it is likely that over a segment there will be areas of attenuation as well as increase (Palumbo-Roe et al., 2012). This means that any figure for metal load increases is a net increase over the stream segment, and if the source is to be considered for direct remediation, the segment will need to be analysed further. MI was responsible for 40% of the filtered Pb load, but just 22% of the filtered Cd and 14% of the Zn.

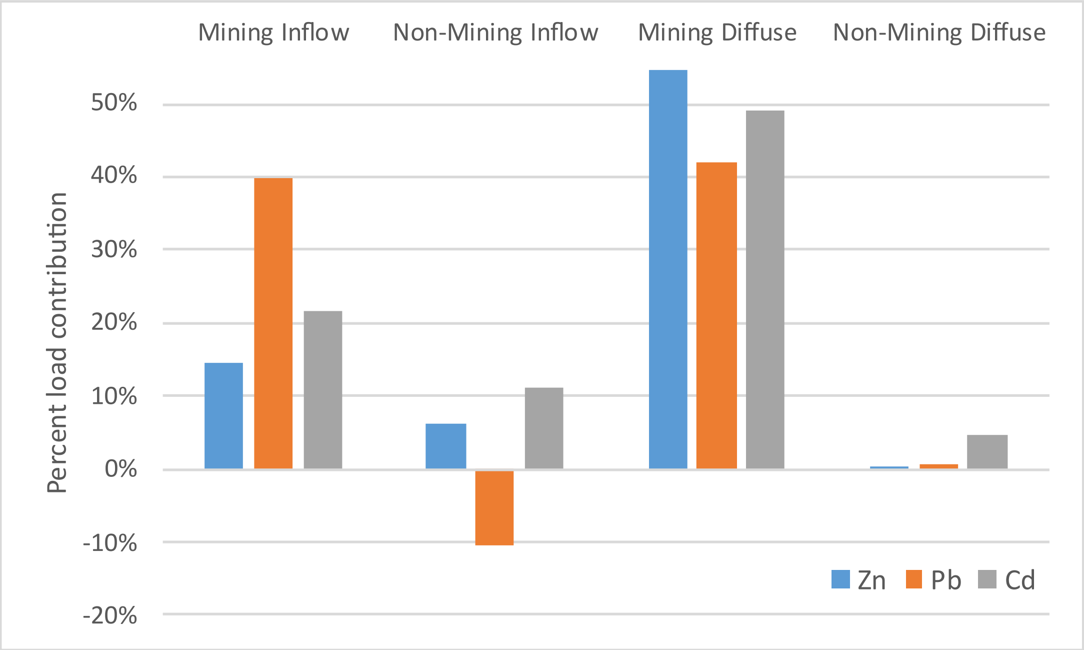


Figure 6-8 - percent contribution and grouping of source areas (Mining Inflow (MI), Non-Mine Inflow (NMI), Mining Diffuse (MD), and Non-Mining Diffuse (NMD)), to overall metal loads, filtered Zn, Pb, and Cd.

6.2.4 Informing remediation

The results from this synoptic sampling and tracer injection experiment locate and quantify sources of metal contamination during baseflow stream conditions, and while any future remediation should consider all likely flow conditions at a site, preliminary predictions can be made for improvements to water quality after remediation. To demonstrate improvements at the end of the studied reach that could be possible now that the sources at low baseflow conditions have been identified, the data from the experiment were applied to the Department for Environment, Food and Rural Affairs (DEFRA, UK) Source Apportionment Spreadsheet (DEFRA, 2018). This tool is designed to automatically calculate the importance of point and diffuse contamination sources in non-coal mining impacted catchments after inputting flow and concentration data for sampling points in a stream (DEFRA, 2018). It can then also estimate improvements in water quality at these points to model theoretical remediation strategies (DEFRA, 2018). It was planned to use OTIS (section 4.12.2) to model possible remediation strategies, however, OTIS requires a constant flow, and unfortunately after multiple failed attempts a review of the data from the Br sonde revealed the flow had varied overnight, and thus the OTIS model could not be calibrated.

The largest group source of contamination, Mining Diffuse (MD), is largely (78%) in the upper reach of the stream between 90-500 m below the tracer injection point. The mine waste here could be consolidated, reprofiled, and capped, in a similar manner to the work conducted at the Frongoch Lead Mine (Edwards et al., 2021, 2016). Although not the only method used, this remediation strategy reduced the total Zn concentrations in the Frongoch stream by 20% (Edwards et al., 2016). Using the DEFRA Source Apportionment Spreadsheet, this reduction of 20% in total Zn was input for the upper reach of the stream, and used to predict downstream concentrations in the Nant y Bai. However, with these proposed changes, the predicted decrease in total Zn concentration in the Nant y Bai was only 3% which would be of limited use to improve water quality.

The synoptic sampling and tracer injection experiment combined with the data from the Source Apportionment DEFRA spreadsheet also allows for the remediation of point sources to be modelled. The passive mine water treatment system at Force Crag Pb and Zn mine in England removes on average 97% of the Zn from the circumneutral minewaters (Jarvis et al., 2015). To model a similar removal rate of a theoretical system at Nantymwyn, a 97% reduction in total Zn from inputs L-1 and L-2 was modelled by the Source Apportionment DEFRA spreadsheet, which predicted a reduction in Zn concentrations at point N-10 of 73%. With additional work to gauge the cost and difficulty of treating or consolidating sources, this dataset can be used to predict the water quality improvements these will offer, and therefore give a balanced view of the best combination of remediation in terms of cost, difficulty, and metal reduction. While any remediation of the site, whether by passive or active treatment systems, or by reducing diffuse sources from the mine waste and subsurface inflows, would require data from higher baseflow conditions in summer and winter using the bromide tracer and synoptic sampling technique, (Onnis et al., 2023b) as well as monitoring of storm events, this demonstrates the ability of a synoptic sampling and tracer injection experiment to guide remediation of a site.

7 Conclusions and future work

7.1 Conclusions

This thesis's stated aims were to:

1. To determine the magnitude, recent history, and temporal and downstream dynamics of streamwater metal contamination at an abandoned metal mine using historical and current data on contaminant concentrations and streamflow
2. Use/test a bromide tracer and synoptic water sampling approach to identify and quantify sources of streamwater metal contamination within and downstream of abandoned metal mines

This thesis shows that the Nant y Bai and Nant y Mwyn downstream of Nantymwyn lead mine remain highly contaminated with Pb, Zn, and to a lesser extent Cd, 90 years after it was last in operation. Worked through such varied periods and thus methods, the waste materials left on the surface are a variety of grades and metal concentrations. Substantial, decaying, and poorly mapped underground workings drain through a single adit with Zn loading high enough to cause the River Tywi to fail WFD standards for at least 25 km downstream of the mine, and elevated concentrations of Zn detectable along the entire length of the River Tywi. Additionally, historical data for three mines, including Nantymwyn, showed minimal to no reduction in metal concentrations over the available period of sampling data, emphasising the need across Wales to monitor and manage the threat to freshwater that abandoned mines present.

7.1.1 Conclusions from monthly water quality sampling and comparison to other Welsh metal mines' historical data

1. Analysis of archived water quality records immediately downstream of three metal mines, Nantymwyn, Frongoch, and Parys Mountain, in Wales abandoned 90-115 years ago shows clearly that in each case Zn, Pb, Cd, and Cu concentrations remain greatly in excess of WFD Water Quality Standards 90-115 years after mines have been abandoned.

2. Downstream of the unremediated Nantymwyn mine, evidence regarding recovery over the 1978-2021 period is mixed. Large reductions in mean concentrations of dissolved (filtered) Zn (by 38 % from 661 to 414 µg L^{-1}), total Cd (by 50 % from 4 to 2 µg L^{-1}) and total

Pb (14 % reduction from 354 to 287 µg L^{-1}) were recorded for the Nant y Bai between 1978-87 and 2019-20, with the Zn and Cd changes being statistically significant. On the other hand, a more objective comparison of summer (March-October) data for the years 1985 and 2019 yielded no significant change.

3. At the unremediated Parys Mountain mine, evidence of change at the principal outlet (Dyffryn Adda Adit) is also mixed. Comparison of means for 2004-06 and 2015-20 yielded statistically significant reductions for Total Pb (by 43 % from 33 to 23 µg L^{-1}) and Total Cd (by 14 % from 174 to 152 µg L^{-1}), but virtually no change in dissolved Zn (up 2 % from 65,494 to 66,518 µg L^{-1}) and dissolved Cu (down 2% from 42,168 to 41,372 µg L^{-1}).

4. At Frongoch mine, because of data gaps, assessment of change prior to remediation was not possible. The series of remediation measures, however, led to major and statistically significant reductions in mean concentrations of the downstream Frongoch stream for all metal parameters between the pre-remediation 2004-11 and post-remediation 2019-21 periods. Mean dissolved Zn fell by 81 % from 13,180 to 2,510 µg L^{-1}, Total Pb by 90 % from 1,220 to 127 µg L^{-1}, Total Cd by 78 % from 27 to 6 µg L^{-1} and dissolved Cu by 80 % from 15 to 3 µg L^{-1}. Although most of these reductions were achieved by the diversion of the Upper Frongoch, significant reductions were also achieved by the perimeter channel, landscaping, capping and seeding measures.

5. The transferability of remediation measures used at Frongoch to other mines is limited and will vary greatly between mines. Diversion of clean upper catchment streamwater is rarely an option and is inapplicable to both the Nantymwyn and Parys Mountain case studies. The use of perimeter and lined channels, attenuation ponds and relandscaping, capping and seeding of metal spoil, however, are more transferable, especially to mines with large expanses of unvegetated spoil as is the case at Nantymwyn, but not Parys Mountain.

6. The Frongoch results show that, although metal contamination can be substantially reduced by remediation, it is unrealistic to expect that local streams can meet WFD Water Quality Standards without very costly on-site stream water treatment systems. This is partly because of the difficulties in designing remediation measures to tackle

subsurface drainage and metal sources. What is realistic, however, is that remediation as at Frongoch can lead to river reaches farther downstream meeting such standards.

7. The main limitations of the historical analysis used in this study are the patchiness of the record and the paucity of storm event samples in the datasets. The data series may be understating the magnitude of metal contamination problems and the findings of this study may apply only to metal concentrations within the low to moderate range of flow conditions. With climate change science predicting increases in magnitude-frequency of both large rainstorms (and high runoff and streamflow events) and droughts (and very low flows) (Arnell and Gosling, 2013; IPCC, 2023), this will be important to take into account in future projections of metal contamination and in the design of remediation strategies.

7.1.2 Conclusions from the identification and quantification of metal sources investigation

In July 2019 a tracer injection and synoptic sampling experiment was carried out on a 2 km section of the Nant y Bai, a stream impacted by the abandoned Nantymwyn Lead Mine, to investigate sources of mine contamination at a high spatial resolution. Diffuse and point subsurface and surface inflows of both Pb and Zn were identified and quantified over the two main areas of mine waste, as well as inputs in vegetated areas, at a much higher spatial resolution than is provided by conventional spot sampling. The experiment was conducted during very low flows for the catchment, with minimal rainfall, and demonstrated that groundwater diffuse sources of metals from an abandoned mine continue to affect watercourses despite the limited surface run-off during low baseflow conditions. The use of tracer injection and synoptic sampling allows for streamflow and water chemistry to be established along a watercourse at a single point in time.

The data from the tracer injection and synoptic sampling can be used both to quantify sources of contamination, and to model possible remediation scenarios. This powerful method can be utilised similarly at other sites where contaminant flows are poorly understood, or where sources cannot be located by visual identification or traditional spot sampling. The high spatial resolution data from the approach of tracer injection and synoptic sampling is key to informing remediation plans.

7.2 Future Work

7.2.1 Generally

Much of the developed world has a legacy of abandoned mines contaminating watercourses and soils, and this allows metals to enter the food chains of both water and land-based fauna. This problem is known about but there has been limited efforts to reduce it; often the contamination is not visible, the mines are far from main centres of population, and funding priorities take money elsewhere. For water-based contamination, synoptic sampling and tracer injection allows remediation to be targeted as accurately as possible, maximising the potential reductions in metal fluxes for a given funding quantity. Due to the practicalities of operating the tracer injection for a prolonged high-flow event, the monthly sampling with concurrent flow gauging helps both designing the synoptic sampling regime and in adding to the understand of contaminated water fluxes across a site at higher flows. While individual sites may still fail EQSs, taking a whole river catchment-based approach could see substantial water quality improvements downstream of mine congregations. There remain 40 mines on the Welsh abandoned metal mine top 50 which have not had the level of investigation Nantymwyn has, and many of these would benefit from a water quality research project combining the high spatial resolution sampling of the synoptic sampling and tracer injection with the regular concurrent flow and water quality sampling.

Data on these Welsh mines or mining areas has been collected since at least 1919 (Griffith, 1919), with annual reports generally noting contamination from the 1960s onwards. The early data of Carpenter (1924, 1926) on metal mine contamination were lost due to bombing in the Second World War (Newton, 1944). Post-war data were collected by the river boards and authorities, and yet the earliest available data available from the NRW archive are from 1978. Anecdotally, these data were available on paper in the late 1970s, but to date it has not been possible to locate them. However, a future worthy project would be locating non-digitised archives of these data to extend the temporal range of environmental contamination values.

Nantywmyn was compared to two other sites that are different to each other in the amount of rainfall recorded, mine and waste layout, stream flows, and hillslope. Parys

Mountain is particularly unusual for a UK metal mine with acid mine discharge, although acid mine discharge is common from abandoned coal mines (Skousen et al., 2019). There are over 1,300 known abandoned metal mines in Wales, with 692 on the NRW database marked as “small” or “tiny” – these sites are three of only 102 marked “large” (Natural Resources Wales, 2020). Anthropogenic climate change will affect extreme low and high flows, changing how elements of concern will enter the watercourses, and their concentrations (Byrne et al. 2020). These changes are already evident in the UK and the USA, with long dry spells leading to substantial increases in concentrations during a rainfall event (Nordstrom, 2009).

NRW has a programme of regular sampling for high-priority metal mines, working through them based on their impact and ease of remediation, and an early stage of this programme is to collect data from a 12-month period from several sampling points across the studied site. From these preliminary data, sampling points for ongoing monitoring and in some cases constant flow monitoring are selected. It would be prudent to consider historical data availability when selecting these sites, to maximise the time series available for analysis. There is a general need for baseline data before any remediation programme can be designed and implemented, and the tools to collect this data have been used throughout this thesis.

7.2.2 At Nantymwyn

Previous work at Nantymwyn has highlighted the need for a sustained fieldwork campaign to record seasonal flow and metal concentration variations (with reports recommending this in 1986, 1988, 1997, 2004, 2009, 2010, 2011 (twice), 2012, 2014 and 2020), and this thesis was funded partially in order to address this. Covid meant that the planned full two years’ of sampling were not completed, and only a single use tracer injection and synoptic sampling but this thesis represents the most thorough analysis of water quality variation across the site to date. Continuous flow gauging at three points at Nantymwyn have been installed, their size and locations guided by the flow gauging undertaken during this project.

Treatment, remediation, or both, have been suggested for Nantymwyn at various levels of detail in 1974, 1986, 1997, 2004, 2011, 2013, and 2021, with progress limited partially by funding, but also by a lack of data to guide the sizing of any treatment plant, or understanding of what capping or similar could achieve. Recent national press stories on the contamination from Nantywmyn being discovered in local eggs, the perceived lack of progress since the 2002 EAW ranking of the top 50 highest impacting Welsh metal mines, and public awareness leading to government committees questioning academics and NRW leaders, may all combine to push metal mine remediation higher up the national agenda for funding. Additionally, pressures from the WFD cycle 3 will increase the need for a reduction in the Zn concentrations in the River Tywi.

As such, a passive or flow-based active/passive combination treatment system of the waters from the Deep Boat Level, situated in the unregistered land immediately adjacent to it towards the River Tywi, should be considered. With much of the mine used for forestry plantation, there is a ready source of wood ash if wood ash amended biochar was selected as a suitable passive treatment medium. The Deep Boat Level has been shown to be the largest single point source of Zn for the entire River Tywi, and as well as the flow and water quality data collect during this research, there has now been two years of continuous flow gauging, allowing accurate sizing of the treatment system. Subsequently, protection or encapsulation of the mine wastes at the main site should be considered, as they continue to be eroded by the Nant y Bai. This will be less straightforward, the wastes are varied in their metal concentrations, steepness, and particle size. One possibility would be to rework the wastes, as on the surface they contain concentrations of Zn and Pb higher than some modern mines' ores do, and reprofile the subsequent lower concentration wastes to reduce runoff and erosion. This reprofiled waste could then be hydroseeded with a surrogate soil, which will bind the material together and minimize airborne metal contaminated dusts, which have been found in other abandoned metal mines in Wales and have been considered one of the possible sources for the egg contamination. Lining the Nant y Bai with an impermeable membrane will reduce the interaction between streamwater and the contaminated bed material, but this may have unintended consequences where there are inputs from the bed of uncontaminated waters, and further investigation into the metal chemistry of the stream's subsurface bed should be considered first. Targeting the key sources identified by the synoptic sampling and tracer injection, such as L-2, will achieve the largest improvements in chemical water quality on the Nant y Bai. These improvements could be predicted over a year by comparing loadings calculated during the monthly sampling and flow gauging and removing point sources, where monitored.

7.2.3 For Global Mining-Affected Rivers

In order to achieve the best outcomes for a river system and mined environment during and after post-mining remediation, there must be a good understanding of the river system, flow of contaminants, and relationship between the river and the mine or groundwater. At recently operated sites, or those closed carefully and with a mind to minimising future risks to the environment, this will likely already be in place, but in mines abandoned prior to clear environmental legislation, or in a rush due to political upheaval or operator bankruptcy, this will not be the case. In these latter cases, techniques such as tracer injection and synoptic sampling, guided by spot sampling with concurrent flow gauging, will be a critical tool to form understanding of the river, the mine’s impacts to the river, and how best to manage the inputs of metals to the watercourse. A synoptic sampling and tracer injection carried out at Leadhills Mine, Wanlockhead in Scotland (Byrne et al. 2021b) is now forming the conceptual basis for a programme of capping of mine wastes, and lining of mining impacted watercourses, across the site. This approach has been recommended for using the Philippines, a country with both historic mining, and potentially a substantial increase in mining in the coming decade (Domingo et al., 2024).

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8 Appendices

8.1 Monthly sampling points location data

NRW ID	Sampling point name	Easting	Northing	Stream
31689	Nant y Bai at entry into river	277268	244225	Bai
88219	Nant y Bai at road bridge:	277524	244553	Bai
88347	Nant y Bai u/s Pen y Darren	277986	244727	Bai
88173	Upwelling to Nant y Bai u/s 88347	278032	244680	Bai
190103	Bai spoil heap flows RHB u/s Pen y Darren	278606	244770	Bai
88193	Nant y Bai upwellings on LHB	278313	244638	Bai
88223	Nant y Bai adit: upper boat level	278388	244609	Bai
88222	Nant y Bai above adit:	278500	244700	Bai
88224	Nant y Bai culvert:	278527	244647	Bai
88434	Trib 1 of Nant y Bai spoil run off	278542	244744	Bai
88221	Nant y Bai u/s mine	278708	244935	Bai
88201	Nant y Mwyn at Tywi confluence	277859	243529	Mwyn
88203	Church terrace tributary:	278178	243701	Mwyn
88204	Church terrace old shaft discharge: lower boat adit portal	278235	243798	Mwyn
88439	Nant y Mwyn u/s church house terrace	278173	243631	Mwyn
88183	Pannau adit	278733	243872	Mwyn
88191	Nant y Mwyn u/s conf trib	278732	243856	Mwyn

8.2 Monthly sampling water chemical quality and flow gauging data

Date/Sampling point number	Aluminium-Al [µg/l]	Al-Filtered [µg/l]	Cadmium – Cd [µg/l]	Cd Filtered [µg/l]	Copper – Cu [µg/l]	Cu Filtered [µg/l]	Lead - as Pb [µg/l]	Pb Filtered [µg/l]	Zinc - as Zn [µg/l]	Zn-Filtered [µg/l]	Cond @ 25C [µS/cm]	Temp Water [°C]	pH in-situ	Flow [l/s]
07/02/2019														
31689	58	33	1.4	1.3	3.4	2.5	200	170	370	360	52	6.7	7.2	
88173	12	10	3.6	3.7	2.6	2.1	550	540	920	940	87	87	7.2	
88193	17	10	4.6	4.6	2.9	2.6	340	320	1100	1100	52	6.6	7	
88219	62	40	1.3	1.3	2.7	2.6	200	190	350	350	52	5.7	7.5	
88221	99	66	0.11	0.11	2.9	2.6	5.3	4.9	25	24	45	5.4	6.8	
88222	280	60	1.2	1.1	4.8	2.8	350	79	330	290	47	5.3	7	
88223	15	10	0.14	0.13	1.2	1	2.4	2	76	70	190	9.4	6.8	
88224	49	11	5.6	5.3	2.7	2.4	800	700	1300	1300	91	6.4	6.8	
88347	78	47	1.6	1.7	3.1	3	200	190	430	430	53	5.4	7.1	
88434	10	10	36	36	11	11	2800	2700	9600	9800	100	5.6	6.5	
08/02/2019														
88183	25	10	14	14	3	2.7	29	21	4500	4400	200	9.6	7.3	
88191	2400	260	0.47	0.65	6.3	2.5	320	93	110	170	59	6.8	4.8	
88201	4500	100	6.2	2.3	42	3.7	1200	36	1800	750	85	7.6	7	
88203	3300	30	16	11	42	6.3	450	11	4900	3600	140	8.5	7.1	
88204	14	10	35	36	21	19	120	110	11000	11000	230	9.8	6.7	
88439	4200	170	1.5	0.52	14	2.1	1100	46	380	140	14	7.1	6.6	
190103	240	75	0.49	0.43	2.8	2.2	220	81	110	96	88	7.5	6.6	
18/03/2019														
31689	69	36	1.5	1.5	2.6	2.5	220	200	360	360	50	8.1	7.5	430
88173	10	10	3.7	3.7	2.1	2.1	600	590	910	940	78	8.3	6.7	5
88193	11	10	4.4	4.4	2.4	2.2	200	180	1100	1100	89	7.9	7	
88219	72	39	1.4	1.4	2.6	2.5	230	200	350	360	50	8.1	6.7	

Date/Sampling point number	Aluminium-Al [µg/l]	Al-Filtered [µg/l]	Cadmium – Cd [µg/l]	Cd Filtered [µg/l]	Copper – Cu [µg/l]	Cu Filtered [µg/l]	Lead - as Pb [µg/l]	Pb Filtered [µg/l]	Zinc - as Zn [µg/l]	Zn-Filtered [µg/l]	Cond @ 25C [µS/cm]	Temp Water [°C]	pH in-situ	Flow [l/s]
88221	100	70	0.14	0.14	2.6	2.5	7.2	8.6	26	28	43	7.4	6.8	79
88222	100	60	1.2	1.3	2.8	2.7	120	120	290	330	45	7.6	6.6	
88223	23	15	0.27	0.27	1	1	9	7.1	130	130	160	9.2	6.7	
88224	42	16	3.9	3.9	1.7	1.6	360	330	900	900	89	8.1	6.8	
88347	130	43	1.7	1.8	3.3	2.8	300	210	430	440	52	7.9	6.8	140
88434	10	10	38	40	12	13	3500	3500	9900	10000	99	7.7	6.5	
190103	120	30	18	18	17	14	2900	2400	4400	4400	160	16	14	
19/03/2019														
88183	10	10	8.8	8.9	1.2	1.2	17	13	2900	2900	150	9.7	7.1	
88191	370	170	0.47	0.44	2.2	1.6	120	100	96	96	77	8	7.1	21
88201	68	28	16	16	10	8.9	70	57	4000	4700	140	9.4	7.2	
88203	20	10	33	32	23	22	110	100	9800	9800	210	9.8	7.3	67
88204	10	10	38	37	27	28	130	120	11000	11000	220	9.7	7.1	51
88439	120	81	1.1	1.2	1.4	1.3	73	55	300	300	76	8.7	7.4	42
23/04/2019														
31689	26	10	2.2	2	3	2.6	240	200	500	480	64	13	8.4	11
88173	10	10	5.1	5.1	2.9	2.6	610	620	1300	1300	100	13	7.2	0.45
88193	79	10	4.5	4.1	5	2.4	430	300	990	1000	110	8.5	7.2	
88219	28	10	2.2	2	3.2	2.7	260	230	500	490	64	12	7.2	20
88221	42	22	0.1	0.1	2.6	2.5	3	5.6	10	12	56	14	7.1	8.5
88222	33	16	2.8	2.7	3.7	3.3	190	180	700	680	60	14	7.4	8
88223	10	10	0.1	0.1	1	1	2	3.1	62	57	26	10	6.9	
88224	23	12	4.8	4.6	3.4	2.7	890	870	1000	1000	71	14	6.9	0.7
88347	19	10	2.9	2.8	3.3	3.1	300	280	690	700	70	13	7.1	12
88434	10	10	37	37	18	17	3600	3700	9500	9400	120	11	6.5	1
190103	12	10	5.6	5.6	2.3	2.2	260	250	1400	1400	110	9.1	7	

Date/Sampling point number	Aluminium-Al [µg/l]	Al-Filtered [µg/l]	Cadmium – Cd [µg/l]	Cd Filtered [µg/l]	Copper – Cu [µg/l]	Cu Filtered [µg/l]	Lead - as Pb [µg/l]	Pb Filtered [µg/l]	Zinc - as Zn [µg/l]	Zn-Filtered [µg/l]	Cond @ 25C [µS/cm]	Temp Water [°C]	pH in-situ	Flow [l/s]
24/04/2019														
88183	180	10	19	19	4.1	3.4	43	32	6000	5900	260	9.8	7.3	0.44
88191	120	91	0.46	0.44	2	2.1	120	120	110	100	62	9.8	6.7	3.1
88201	10	10	23	22	7.3	6.2	54	48	6200	6200	210	12	7.6	12
88203	10	10	35	33	18	15	100	84	20000	11000	260	11	7.9	11
88204	10	10	37	32	21	18	130	87	21000	10000	270	10	7.5	8.6
88439	54	19	1.1	1	1.9	1.6	32	13	260	250	99	12	7.6	3.4
14/05/2019														
31689	15	12	1.8	1.8	2.8	2.6	200	160	470	470	64	14	7.4	9.5
88173	10	10	5.2	5.3	3.2	3.1	670	610	1400	1400	110	14	7	0.38
88193	10	10	4.6	4.5	3.1	2.3	390	280	1100	1100	110	8.8	6.9	
88219	16	11	2	2	2.9	2.6	240	190	520	500	64	12	7.1	21
88221	50	24	0.1	0.1	2.7	2.5	3.2	4.5	11	11	57	15	7.2	8
88222	30	17	2.5	2.5	3.2	3.1	180	160	680	670	61	15	7.4	8.2
88223	11	10	0.1	0.1	1.3	1	10	3	61	55	230	11	6.8	
88224	22	12	5	5.1	3.1	2.7	1000	910	1100	1100	75	14	6.7	0.49
88347	17	10	2.8	2.8	3.1	2.9	310	280	690	680	70	15	7.2	13
88434	10	10	39	38	17	16	3200	2900	10000	10000	120	11	6.4	
190103	10	10	5.5	5	12	11	1200	1100	1400	1500	58	17	7	
15/05/2019														
88183	10	10	19	19	3.5	3.3	37	37	5700	5800	290	9.9	7.4	0.17
88191	79	73	0.38	0.38	1.3	1.2	93	91	84	84	63	9.1	6.7	1.9
88201	10	10	23	23	7.9	6.6	53	48	6900	6800	220	10	7.7	28
88203	10	10	35	35	17	15	100	79	11000	11000	280	11	7.9	7.9
88204	10	10	35	37	20	17	120	88	11000	12000	280	10	7.3	8
88439	54	20	1	0.98	1.9	1.4	43	13	290	280	94	11	7.9	1.9

Date/Sampling point number	Aluminium-Al [µg/l]	Al-Filtered [µg/l]	Cadmium – Cd [µg/l]	Cd Filtered [µg/l]	Copper – Cu [µg/l]	Cu Filtered [µg/l]	Lead - as Pb [µg/l]	Pb Filtered [µg/l]	Zinc - as Zn [µg/l]	Zn-Filtered [µg/l]	Cond @ 25C [µS/cm]	Temp Water [°C]	pH in-situ	Flow [l/s]
13/06/2019														
31689	230	100	1.5	1.4	6.3	5.3	450	330	370	360		11		330
88173	10	10	4.9	4.8	3.5	3	610	540	1300	1300	89	11	6.8	4
88193	210	10	6	5.8	8	4.4	670	290	1500	1400	99	11	7.1	1.9
88219	230	110	1.3	1.2	6	5.1	410	280	330	320	41	11	7	370
88221	210	130	0.13	0.13	4.6	4.2	13	16	26	26	37	11	6.8	120
88222	240	130	0.86	0.83	5	4.5	120	84	220	210	38	11	6.7	140
88223	14	10	0.15	0.12	1.3	1	23	5.6	68	66	240	9.7	7	
88224	33	17	7.7	7.7	4.7	4.7	950	930	1800	1800	86	13	7	4.2
88347	240	130	1.3	1.3	5.6	5.1	250	210	330	320	40	11	6.7	250
88434	390	10	46	45	35	14	7600	4000	13000	12000	110	13	6.8	
190103	10	10	6.5	6.8	13	12	1200	1200	2100	2000	63	13	7.3	
14/06/2019														
88183	330	10	17	17	9.8	3.2	100	37	5500	5400	300	9.8	7.7	0.25
88191	260	210	0.34	0.34	1.3	1.4	73	68	65	72	66	10	5.8	35
88201	730	110	4.9	3.6	21	3.8	350	49	1600	1100	95	10	7.5	82
88203	140	22	18	17	16	7.6	80	32	5700	5700	200	11	7.6	14
88204	210	10	36	35	28	15	160	86	12000	12000	290	10	7.4	6.8
88439	210	140	0.72	0.73	1.7	1.5	84	55	180	180	74	11	8.1	58
11/07/2019														
31689	17	10	2.4	2.3	3.2	3.1	220	200	560	560	72	19	7.4	0.66
88173	10	10	6	6.2	3.7	3.6	740	740	1600	1600	110	15	7.1	0.38
88193	16	10	6.1	5.9	5.1	2.7	440	320	1500	1500	120	11	7.1	
88219	17	11	2.4	2.5	3.3	4.8	270	260	600	600	72	15	7	12
88221	85	29	0.1	0.1	3.7	3.7	4.1	3.3	11	11	63	15	7.6	6.1
88222	44	20	3.5	3.6	4.2	4.2	240	230	910	940	67	16	7.3	6.7

Date/Sampling point number	Aluminium-Al [µg/l]	Al-Filtered [µg/l]	Cadmium – Cd [µg/l]	Cd Filtered [µg/l]	Copper – Cu [µg/l]	Cu Filtered [µg/l]	Lead - as Pb [µg/l]	Pb Filtered [µg/l]	Zinc - as Zn [µg/l]	Zn-Filtered [µg/l]	Cond @ 25C [µS/cm]	Temp Water [°C]	pH in-situ	Flow [l/s]
88223	13	10	0.1	0.16	1	1	3.3	4.2	50	85	260	9.8	6.7	
88224	33	17	5.1	5.2	5	4.8	1100	1000	1200	1300	69	15	6.9	0.74
88347	21	12	3.4	3.3	4	3.8	400	370	830	840	77	17	7.8	8.8
88434	10	10	37	37	11	11	2300	2100	10000	10000	120	17	6.8	
190103	10	56	6.7	7	18	22	1700	1700	1700	1800	63	17	7	
12/07/2019														
88183	1000	10	17	16	14	3	230	33	5700	5200	280	10	7.5	0.22
88191	170	150	0.42	0.44	2.7	2	150	130	95	91	61	13	6.4	0.77
88201	10	10	27	25	7.7	6.9	55	50	8100	8000	230	12	7.8	8.7
88203	10	10	35	34	17	14	90	77	11000	11000	260	11	7.8	8
88204	70	10	35	34	22	15	120	90	11000	11000	270	10	7.3	3.2
88439	30	28	0.99	1	1.9	2	22	21	250	240	100	14	7.7	0.82
10/08/2019														
31689	270	130	1.9	1.7	8.7	6.7	610	390	440	430	46	15	6.2	280
88173	17	10	5.8	5.7	5.6	5.1	720	690	1500	1500	99	14	6.5	3.1
88193	90	10	6.2	6.4	8.4	6.3	470	340	1500	1500	100	14	6.7	1.7
88219	290	140	1.7	1.6	7.8	6.2	510	340	400	380	45	15	6.3	320
88221	270	180	0.21	0.18	5.3	4.8	14	11	34	33	39	14	5.7	200
88222	270	180	1.2	1.1	6.3	5.5	170	150	280	280	40	14	6.2	180
88223	38	10	0.44	0.32	1.2	1	110	12	130	110	250	9.8	6.6	
88224	54	24	7.4	7.4	6.7	6	1200	1100	1700	1700	79	16	6.7	13
88347	290	160	1.5	1.4	7	5.8	340	230	370	340	44	15	6.2	220
88434	73	10	43	42	16	13	4900	4300	11000	10000	100	16	6.3	
190103	25	10	10	9.9	27	26	2700	2700	2700	2800	81	16	6.3	
11/08/2019														
88183	2200	10	18	16	33	3.4	530	38	6000	4600	300	10	6.9	0.21

Date/Sampling point number	Aluminium-Al [µg/l]	Al-Filtered [µg/l]	Cadmium – Cd [µg/l]	Cd Filtered [µg/l]	Copper – Cu [µg/l]	Cu Filtered [µg/l]	Lead - as Pb [µg/l]	Pb Filtered [µg/l]	Zinc - as Zn [µg/l]	Zn-Filtered [µg/l]	Cond @ 25C [µS/cm]	Temp Water [°C]	pH in-situ	Flow [l/s]
88191	270	220	0.29	0.33	1.4	1.2	73	73	64	67	71	13	5	31
88201	150	99	4.9	4.7	5.7	3.4	62	33	1500	1500	110	13	7.2	53
88203	39	13	28	28	14	11	71	54	9100	8900	260	13	7.5	13
88204	170	10	35	33	31	11	160	70	10000	11000	290	11	6.9	6.6
88439	180	130	0.76	0.72	1.6	1.5	59	38	180	170	77	13	6.8	43
03/09/2019														
31689	33	28	2.2	2.3	4.5	4.2	390	390	1500	560	64	14	6.4	13
88173	13	10	6	5.9	5.5	3	810	700	1500	1500	68	15	6.9	0.54
88193	25	10	5.7	5.6	3.2	2.5	380	310	1400	1500	110	12	6.8	
88219	34	30	2.3	2.3	4.7	4.2	430	400	590	590	66	13	6.8	21
88221	98	69	0.1	0.1	5.2	4.6	6.6	6.6	16	16	56	14	6.9	16
88222	760	57	2.4	2.3	5.7	5	200	180	630	610	59	14	7.2	14
88223	410	10	0.28	0.1	3.9	1	140	2.6	100	50	240	9.8	6.4	
88224	30	17	4.9	4.9	4.4	4	920	830	1200	1100	71	13	6.6	1.2
88347	51	37	3	2.9	5.5	5	450	440	750	750	69	14	6.8	17
88434	16	10	35	36	11	9.8	2300	2000	9600	9600	120	15	6.6	
190103	420	10	7.2	7.2	36	12	1900	1200	2400	2100	100	13	6.7	
04/09/2019														
88183	10	10	14	15	2.8	2.4	31	31	4600	4600	260	10	6.5	0.25
88191	230	210	0.4	0.34	2.8	2	120	100	84	82	62	12	5.5	3.9
88201	35	29	21	20	10	8.7	78	66	6500	6300	180	12	7.3	17
88203	10	10	35	33	17	14	95	84	11000	11000	250	11	7.4	11
88204	170	10	36	35	29	13	160	85	11000	11000	260	10	6.9	11
88439	110	91	1.1	1.1	2.9	2.6	90	81	300	300	84	13	7.5	5.2
190103	32	10	0.1	0.1	1	1	6.4	2	16	11				
14/10/2019														

Date/Sampling point number	Aluminium-Al [µg/l]	Al-Filtered [µg/l]	Cadmium – Cd [µg/l]	Cd Filtered [µg/l]	Copper – Cu [µg/l]	Cu Filtered [µg/l]	Lead - as Pb [µg/l]	Pb Filtered [µg/l]	Zinc - as Zn [µg/l]	Zn-Filtered [µg/l]	Cond @ 25C [µS/cm]	Temp Water [°C]	pH in-situ	Flow [l/s]
31689	85	50	1.5	1.5	3.9	3.7	310	260	380	370	50	11	6.2	200
88173	10	10	4.5	4.5	2.6	2.8	690	690	1200	1100	84	11	6.3	5.4
88193	14	10	4.9	4.7	3.8	3.2	240	280	1300	1100	88	11	6.5	2.5
88219	78	49	1.4	1.5	3.6	3.5	260	240	370	360	50	11	6.2	250
88221	130	91	0.1	0.11	3.7	3.8	7.7	7.3	23	24	42	11	6.1	86
88222	120	80	1.1	1.1	4.2	3.9	120	110	300	290	44	11	6.3	110
88223	29	16	0.2	0.16	1.6	1	16	4.5	96	91	130	10	6.3	
88224	36	18	4.1	4.2	2.3	2.2	430	380	1000	1000	83	11	6.5	6.3
88347	92	58	1.9	1.9	4	3.9	280	240	470	460	51	11	6.3	150
88434	98	10	40	38	18	12	4000	2900	10000	9800	90	12	6.1	
190103	140	10	5.5	5.5	24	7.6	2400	880	1600	1600				
15/10/2019														
88183	15	10	10	11	2.1	1.3	24	14	3500	3400	170	9.9	6.8	1.7
88191	250	230	0.53	0.48	2	2	150	160	110	120	75	11	5.2	21
88201	62	41	20	20	12	9.4	89	66	6200	6100	160	11	6.8	92
88203	17	10	41	41	25	23	120	110	13000	13000	240	10	7	42
88204	100	10	46	47	31	29	150	140	15000	15000	260	9.9	6.8	39
88439	140	110	1.2	1.1	1.6	1.4	72	58	310	310	82	11	6.8	32
12/11/2019														
31689	73	55	1.4	1.4	3.4	3.4	250	230	350	350	47	7.8	8.2	280
88173	10	10	3.7	3.8	3.1	2.7	590	540	950	930	75	8.9	6.2	
88193	28	10	3.6	3.7	3	2.9	270	220	850	900	80	7.5	6.4	
88219	75	56	1.3	1.3	3.5	3.3	240	220	350	340	47	7.4	6.1	
88221	690	110	0.21	0.11	7.3	3.7	28	14	36	22	37	6.6	5.6	
88222	210	82	1.3	1.3	4.3	3.6	210	150	340	320	41	6.5	6	
88223	28	17	0.15	0.19	1.7	1.2	8.9	5.1	82	86	140	9.9	6.4	

Date/Sampling point number	Aluminium-Al [µg/l]	Al-Filtered [µg/l]	Cadmium – Cd [µg/l]	Cd Filtered [µg/l]	Copper – Cu [µg/l]	Cu Filtered [µg/l]	Lead - as Pb [µg/l]	Pb Filtered [µg/l]	Zinc - as Zn [µg/l]	Zn-Filtered [µg/l]	Cond @ 25C [µS/cm]	Temp Water [°C]	pH in-situ	Flow [l/s]
88224	140	19	5.4	5.4	4.3	3	830	790	1200	1200	69	6.8	5.8	
88347	110	56	2	1.8	9.7	4.5	440	280	470	460	49	6.6	6.1	
88434	150	10	30	31	18	11	4600	3600	7500	7800	78	6.4	5.8	7.4
190103	14	10	5.3	5.6	11	9.2	870	850	1400	1500	56	8.9	6.2	
13/11/2019														
88183	10	10	11	11	1.7	1.6	21	15	3600	3700	180	9.9	6.7	2
88191	320	280	0.35	0.36	1.6	1.6	97	110	77	78	70	7.9	4.8	45
88201	160	59	8.8	8.8	6.1	5.3	61	46	2700	2600	110	9	6.6	170
88203	45	10	29	28	21	17	100	74	8700	8800	200	9.8	6.8	53
88204	75	10	40	40	28	24	140	130	12000	13000	250	9.9	6.7	34
88439	190	120	0.92	0.93	1.5	1.4	89	66	230	240	73	8.2	6.8	69
11/12/2019														
31689	93	42	1.2	1.2	2.5	2.4	200	150	300	300	50	7.6	6.4	430
88173	10	10	3.9	3.8	2.5	2.4	600	590	950	940	50	7	6.2	14
88193	35	10	3.9	3.9	2.9	2.3	290	220	950	950	80	7.2	6.5	
88219	90	45	1.2	1.2	2.7	2.6	190	160	310	300	49	7.7	6.2	490
88221	150	87	0.12	0.12	3	3	9.4	11	24	27	42	6.7	6.2	240
88222	140	70	0.91	0.9	3.2	2.8	100	87	230	220	44	6.8	6.1	320
88223	42	26	0.5	0.25	1.6	1.2	71	5.5	160	110	130	9.7	6.4	
88224	60	16	4.7	4.9	2.3	2.4	480	520	1100	1200	82	7.1	6.2	
88347	110	47	1.6	1.6	4.6	3	290	210	400	400	50	7	6.2	400
88434	17	10	37	37	14	13	3700	3700	10000	9900	94	6.6	5.8	5
190103	55	10	8.3	8.4	17	8.7	2200	1000	2400	2400	62	9.8	6	
12/12/2019														
88183	10	10	10	10	1.6	1.5	22	16	3500	3500	160	9.9	6.9	3.5
88191	690	340	0.37	0.35	2.3	1.7	140	88	72	76	61	7.3	4.8	89

Date/Sampling point number	Aluminium-Al [µg/l]	Al-Filtered [µg/l]	Cadmium – Cd [µg/l]	Cd Filtered [µg/l]	Copper – Cu [µg/l]	Cu Filtered [µg/l]	Lead - as Pb [µg/l]	Pb Filtered [µg/l]	Zinc - as Zn [µg/l]	Zn-Filtered [µg/l]	Cond @ 25C [µS/cm]	Temp Water [°C]	pH in-situ	Flow [l/s]
88201	400	77	8.2	7.7	8.4	4.6	120	43	2700	2600	110	8.3	6.8	180
88203	490	21	22	21	23	11	180	43	6900	6600	170	9	6.9	75
88204	120	10	37	36	25	21	160	120	12000	11000	230	9.9	6.7	40
88439	480	150	0.9	0.81	3.1	1.7	190	72	250	210	68	7.8	6.7	180
23/01/2020														
31689	38	26	1.7	1.6	2.4	2.5	210	190	430	430	56	6.7	7.7	67
88173	10	10	4.4	4.4	2.8	2.5	590	560	1100	1100	83	7.7	6.8	2
88193	10	10	5	4.4	2.5	2.3	290	250	1200	1100	93	7.3	7	
88219	38	30	1.6	1.7	2.4	2.6	200	190	420	430	54	6.8	7	76
88221	66	47	0.1	0.1	2.7	3	6.4	5.5	21	24	48	6.7	7	32
88222	60	42	1.7	1.6	3	2.8	120	110	430	440	50	6.6	7.1	38
88223	17	10	0.12	0.1	1	1	2.1	2	64	61	220	9.8	6.7	
88224	30	14	3.8	3.4	2.1	1.9	540	470	830	790	75	7.6	7.1	3.3
88347	46	29	2.2	2	3.1	3	220	190	570	540	58	6.7	7	51
88434	10	10	34	34	12	11	2900	3000	8900	8600	99	7	6.6	1.1
190103	10	10	4.7	4.1	9.6	7.8	950	850	1200	1200	93	7.3	7	
24/01/2020														
88183	10	10	14	14	2.4	2	27	18	4400	4500	190	9.7	7.3	0.99
88191	150	140	0.46	0.45	1.7	1.8	120	130	94	96				7.7
88201	29	10	20	20	11	8.8	74	59	6000	6100	160	7.9	7.3	46
88203	10	10	34	34	21	19	120	110	10000	11000	220	9.4	7.4	26
88204	130	10	37	36	29	22	180	140	11000	12000	230	9.8	7	26
88439	85	63	1.3	1.3	1.4	1.7	49	39	350	370	82	5.8	7.6	11
26/02/2020														
31689	58	36	1.5	1.5	2.7	2.5	230	200	380	360	52	6	6.7	280
88173	10	10	3.6	3.5	2.4	2.4	620	570	910	850	72	7.6	6.7	6.5

Date/Sampling point number	Aluminium-Al [µg/l]	Al-Filtered [µg/l]	Cadmium – Cd [µg/l]	Cd Filtered [µg/l]	Copper – Cu [µg/l]	Cu Filtered [µg/l]	Lead - as Pb [µg/l]	Pb Filtered [µg/l]	Zinc - as Zn [µg/l]	Zn-Filtered [µg/l]	Cond @ 25C [µS/cm]	Temp Water [°C]	pH in-situ	Flow [l/s]
88193	66	10	3.6	3.6	3.9	1.8	370	200	880	870	92	6.9	7	
88219	58	37	1.5	1.4	2.6	2.5	230	200	380	360	52	6	6.6	340
88221	100	69	0.13	0.13	2.7	2.5	7.4	6.9	26	27	45	5.6	6.5	140
88222	86	61	1.3	1.2	2.7	2.7	130	120	320	330	47	5.6	6.9	170
88223	23	13	1.1	1.2	1.2	1	25	4.1	450	480	210	9.5	6.7	
88224	35	15	4.3	4.2	2.2	1.9	450	390	930	960	78	7	7	10
88347	65	40	1.8	1.8	2.8	2.7	200	190	430	440	54	5.8	6.7	220
88434	10	10	35	33	12	12	3300	3200	8800	8700	96	6.8	6.2	2.2
190103	10	10	4.6	4.5	7.8	7.5	750	730	1200	1200	48	7.5	6.7	
27/02/2020														
88183	10	10	8.7	8.7	1.5	1	20	11	2700	2700	150	9.6	7.1	3.2
88191	240	230	0.36	0.35	1.4	1.5	85	88	74	76	62	5.8	5.2	29
88201	75	38	22	21	15	13	92	74	6500	6200	160	7.8	7.1	150
88203		18		44		31		140		13000	260		7.2	66
88204	24	10	50	48	40	36	190	160	15000	15000	280	9.8	7	59
88439	160	110	1	1	1.4	1.4	79	60	280	280	69	6.5	7.5	44

8.3 Synoptic sampling points location data

Site ID	Distance below injection (m)	Source	Easting	Northing	Elevation (m)
NYB-INJ	0	STR	278726	244955	232
NYB-0	44	STR	278698	244930	224
NYB-1	91	STR	278659	244908	217
NYB-2	137	STR	278631	244873	218
NYB-3	215	STR	278590	244814	213
LBI-1	220	LBI	278591	244807	210
NYB-4	228	STR	278577	244810	210
NYB-5	298	STR	278539	244758	204
LBI-2	305	LBI	278552	244753	205
NYB-6	315	STR	278543	244741	204
NYB-7A	386	STR	278483	244711	197
NYB-7B	517	STR	278369	244669	191
NYB-8	623	STR	278286	244668	182
NYB-9	697	STR	278225	244684	182
LBI-3	700	LBI	278227	244674	
LBI-4	705	LBI	278223	244676	178
LBI-5	712	LBI	278209	244675	171
NYB-10	721	STR	278200	244682	171
NYB-11	842	STR	278086	244689	161
LBI-6	847	LBI	278076	244686	162
NYB-12	859	STR	278069	244690	162
RBI-1	887	RBI	278043	244699	
NYB-13	948	STR	277995	244730	156
RBI-2	960	RBI	277987	244738	160
NYB-14	983	STR	277963	244731	154
LBI-7	1051	LBI	277899	244727	
NYB-15	1258	STR	277736	244711	137
RBI-3	1268	RBI	277726	244723	141
NYB-16	1280	STR	277717	244699	136
RBI-4	1352	RBI	277652	244670	135
NYB-17	1536	STR	277524	244553	128
NYB-18	1665	STR	277457	244465	120
LBI-8	1760	LBI	277419	244388	120
NYB-19	1825	STR	277384	244333	116
NYB-20	1965	STR	277267	244268	113

8.4 Synoptic sampling water chemical quality – total concentrations

The elements that were analysed for but not included in this table were below the limit of detection for all samples.

ID		23 Na	24 Mg	39 K	43 Ca	44 Ca	55 Mn	56 Fe	63 Cu	66 Zn	111 Cd	208 Pb
	Sample	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}
NYB-0000	STR	4400	2600	110	250	500	6.0	250	72	7.2		3.2
NYB-0044	STR	9400	2600	120	260	500	7.1	270	4.4	4.1		6.8
NYB-0091	STR	9400	2600	120	260	500	7.3	240	4.4	0.98		5.1
NYB-0137	STR	9300	2600	160	280	510	17	280	4.2	5.0		3.5
NYB-0215	STR	9000	2500	130	290	490	6.3	230	4.9	17		16
NYB-0220	LBI	5200	2200	370	370	670	5.2	43	9.2	4000	13	1200
NYB-0228	STR	8900	2600	170	280	530	5.0	210	4.5	230	0.68	67
NYB-0298	STR	8800	2600	160	280	530	3.3	170	4.3	160	0.48	50
NYB-0305	LBI	4800	2600	550	530	960	11	14	10	11000	40	2300
NYB-0315	STR	8500	2600	200	330	560	3.4	160	5.4	1200	4.2	320
NYB-0386	STR	8300	2600	200	310	560	2.4	140	5.2	980	3.5	250
NYB-0517	STR	8100	2500	200	290	530	2.2	100	5.3	750	2.8	190
NYB-0623	STR	8100	2500	190	300	530	1.7	90	4.8	670	2.3	180
NYB-0697	STR	8000	2500	190	290	530	2.9	140	98	630	2.4	250
NYB-0700	LBI	7000	4400	950	860	1500	3.9	110	4.8	2300	8.3	340
NYB-0705	LBI	6400	4200	630	830	1400	5.5	32	4.1	1800	6.6	320
NYB-0712	LBI	6400	4200	580	780	1400	8.3	100	16	1100	4.1	410
NYB-0721	STR	8000	2800	320	370	690	3.6	73	4.7	740	2.7	250
NYB-0842	STR	8000	2900	320	420	720	1.9	62	4.5	750	2.9	280
NYB-0847	LBI	6900	3700	430	700	1200	3.8	120	9.0	1700	6.1	820
NYB-0859	STR	7800	2800	320	410	740	4.6	84	4.8	820	3.1	330
NYB-0887	RBI	4400	1500		290	530	3.8	45	21	1900	7.3	1900
NYB-0948	STR	7800	2900	310	420	740	2.2	47	4.7	860	3.2	360
NYB-0960	RBI	4400	760	19	59	140	8.0	98	3.1	44	0.14	19

ID		23 Na	24 Mg	39 K	43 Ca	44 Ca	55 Mn	56 Fe	63 Cu	66 Zn	111 Cd	208 Pb
NYB-0983	STR	7700	2900	310	420	750	1.9	45	4.6	850	3.4	350
NYB-1258	STR	7500	2700	300	380	670	4.9	31	5.2	780	3.0	260
NYB-1268	RBI	5000	1500	400	210	430	0.89	6.5	1.9	6.6		17
NYB-1280	STR	7000	2500	320	360	630	1.7	39	4.0	620	2.4	250
NYB-1352	RBI	5600	1400	390	500	890	67	1000	3.5	230	0.96	260
NYB-1536	STR	7100	2500	340	350	630	1.2	27	4.2	640	2.5	250
NYB-1665	STR	7000	2400	340	350	620	1.2	24	4.1	620	2.3	220
NYB-1760	LBI	5800	1600	24	430	790	290	160	11	980	3.4	460
NYB-1825	STR	6700	2300	370	350	620	4.4	47	4.6	630	2.4	240
CULVERT	STR	5300	2200	200	290	520	62	350	4.6	800	3.2	580
UBL	STR	7100	9500	1900	2200	3900	480	2000	1.5	44		19

8.5 Synoptic sampling water chemical quality – filtered concentrations

The elements that were analysed for but not included in this table were below the limit of detection for all samples.

ID		23 Na	24 Mg	39 K	43 Ca	44 Ca	55 Mn	56 Fe	63 Cu	66 Zn	111 Cd	208 Pb
	Sample	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}
NYB-0000	STR	4800	2700	170	4200	4100	6.2	170	2.6	5.7	0.69	2.6
NYB-0044	STR	12000	2600	230	4000	4000	6.1	160	2.7	8.7	0.68	5.6
NYB-0091	STR	11000	2600	200	3900	4100	7.8	170	2.4	5.4	0.68	4.3
NYB-0137	STR	11000	2600	230	4300	4100	19	210	2.4	9.8	0.69	3.2
NYB-0215	STR	11000	2600	200	4200	4000	7.1	170	3.3	22	0.77	13
NYB-0220	LBI	5400	2100	420	5000	5100	5.6	13	6.5	4100	13	950
NYB-0228	STR	10000	2500	230	4000	4000	5.0	150	2.4	230	1.4	47
NYB-0298	STR	9800	2500	230	4000	3900	3.7	130	2.2	160	1.2	40
NYB-0305	LBI	4800	2500	570	7700	7500	12	2.0	5.4	10000	37	1900
NYB-0315	STR	9200	2500	250	4100	4200	3.3	110	3.5	1100	4.6	220
NYB-0386	STR	9100	2400	260	4200	4200	2.7	100	3.1	960	4.0	180

ID		**23 Na**	**24 Mg**	**39 K**	**43 Ca**	**44 Ca**	**55 Mn**	**56 Fe**	**63 Cu**	**66 Zn**	**111 Cd**	**208 Pb**
NYB-0517	STR	8900	2400	260	4300	4100	2.8	85	3.3	710	3.3	140
NYB-0623	STR	8500	2400	240	4100	3900	2.3	74	2.8	610	3.0	130
NYB-0697	STR	8500	2400	240	4200	4000	2.3	65	2.9	580	3.0	170
NYB-0700	LBI	7400	4500	970			2.6	2.2	1.6	2200	8.2	210
NYB-0705	LBI	6500	4300	660			6.0	3.5	1.7	1700	6.8	220
NYB-0712	LBI	6400	4100	580		14000	6.1	3.8	1.5	990	4.4	240
NYB-0721	STR	8400	2600	360	5300	5100	4.3	56	2.6	660	3.2	180
NYB-0842	STR	8300	2700	360	5400	5300	2.6	48	2.5	680	3.4	210
NYB-0847	LBI	6800	3500	430	11000	9900	2.5	2.6	2.4	1600	6.1	550
NYB-0859	STR	8200	2700	360	5600	5500	2.2	41	2.4	750	3.6	280
NYB-0887	RBI	4200	1500	40	3600	3600	4.1	3.4	14	1900	7.4	1500
NYB-0948	STR	7900	2700	340	5600	5400	2.9	39	2.5	780	3.8	280
NYB-0960	RBI	4300	740	72	1100	1100	8.1	67	1.2	46	0.91	8.3
NYB-0983	STR	7800	2600	360	5600	5400	2.6	37	2.6	780	3.8	270
NYB-1258	STR	7600	2500	340	4800	4800	5.6	25	3.2	700	3.5	190
NYB-1268	RBI	4800	1400	400	3000	2900	1.4	5.5		11	0.72	3.2
NYB-1280	STR	6900	2300	350	4400	4500	2.1	21	2.0	570	2.9	160
NYB-1352	RBI	5500	1300	390	6700	6500	66	340	1.0	220	1.6	91
NYB-1536	STR	6900	2200	360	4600	4400	1.7	15	2.0	570	2.9	160
NYB-1665	STR	7000	2200	360	4400	4400	1.6	15	1.9	560	2.9	190
NYB-1760	LBI	5800	1600	67	5700	5500	260	36	6.3	850	3.8	240
NYB-1825	STR	6900	2200	400	4600	4500	4.7	11	2.4	600	3.1	190
CULVERT	STR	5100	2000	230	3600	3700	64	240	2.2	720	3.7	410
UBL	STR	7200	11000	2300			480	430		41	0.74	

8.6 Historical data – Nantymwyn

Date (Sampling)	Cadmium – Cd [µg/l]	Cd Filtered [µg/l]	Conductivity [µS/cm	Copper - Cu [µg/l]	Cu Filtered [µg/l]	Lead - as Pb [µg/l]	Pb Filtered [µg/l]	pH	Temp [°C]	Zinc - as Zn [µg/l]	Zn-Filtered [µg/l]
08/02/1978	13			33		2382	1910			28620	27770
09/01/1980	3.7		52	6.6		450		6.1		611	
21/01/1982	1.3			0.4		250		5.9		390	
04/10/1983	19	18.8		5	5	34	34	6.9		5600	5400
20/10/1983		21	183		15		425	13.8			6865
03/11/1983	29	29		20	20	460	380	13.7		7650	7240
22/11/1983	28	27		5	5	47	37			9700	9700
11/01/1984	9.2	8.6		15	5	386	25			2810	2710
26/01/1984	14.4	13.4		8	8	418	365	13		3450	3400
09/02/1984	2.3	2.3		5	5	255		6		620	620
28/02/1984	0.8	0.8		12	11	319	272	13.5		6200	5750
06/03/1984	17			6		38				5000	
12/04/1984	36.3	23.9		3		70	39	7.9		9022	6097
03/05/1984	26.7			4		60				6547	
20/08/1984	31			1		13		7.5		6400	
19/12/1984		1	118		6		72	6.8			2865
21/02/1985		42	170		2		36	6.9			9500
01/03/1985	42	40		13	8	361	205			8400	8282
07/03/1985		35	183		5		46	7.2			
15/03/1985	4	4		2	4	280	240			606	547
21/03/1985		54.7	214		7		17	7.5			9500
18/04/1985		30	136		5		38	6.9			5000
02/05/1985		35.4	177		2		29	7.3			
10/05/1985	50	50		20	12	372	322			9128	9129
17/05/1985		44.1	232		7		26	7.5			

Date (Sampling)	Cadmium – Cd [μg/l]	Cd Filtered [μg/l]	Conductivity [μS/cm	Copper - Cu [μg/l]	Cu Filtered [μg/l]	Lead - as Pb [μg/l]	Pb Filtered [μg/l]	pH	Temp [°C]	Zinc - as Zn [μg/l]	Zn-Filtered [μg/l]
30/05/1985		34	233		7		23	7.6			0
31/05/1985	53.1	53		11	11	405	353			8857	8563
20/06/1985	58.4	55.7		15	13	404	321			10670	10670
27/06/1985		35.6	146		9		5	6.8			4900
11/07/1985		3	76		19		36	7.1			413
15/07/1985	56.4	54.8		14	11	424	419			8030	8030
26/07/1985		38.7	181		9		40	7.4			7100
09/08/1985		23.9	129		6		60	6.9			4600
05/09/1985		253	113		11		40	6.8			1000
09/09/1985	41.1	40.6		14	14	371	322			6541	6487
19/09/1985		38.5	172		8		68	7			
03/10/1985		7.7	129		6		2	6.9			2886
31/10/1985		19.4	213		6		50	7.3			
14/11/1985		13.4	152		7		46	6.9			8000
28/11/1985		15.3	164		8		47	6.9			6300
09/01/1986		11	134		6		26	6.7			
23/01/1986		7	101		7		85	6.6			
20/02/1986		15.7	213		5		60	7			60
01/05/1986		15	156		6		28	7.1			4800
15/05/1986	9	9	121	6	6	25	25	6.7		4000	4000
26/06/1986	19	18	202	5	5	46	42	7.6		7850	7850
10/07/1986	22	22	279	9	8	60	56	7.6		10500	10400
24/07/1986	22	20	260	8	8			7.7		2	2
19/08/1986	21	18	244	9	9	53	33	7.4			6946
05/09/1986	18.8	2	172	9	9			6.9		810	8370
17/09/1986	27.1	26.3	227	9	9			7.4		11100	11100
14/10/1986	25	24	274	13	8			7.3		11000	11000

Date (Sampling)	Cadmium – Cd [µg/l]	Cd Filtered [µg/l]	Conductivity [µS/cm	Copper - Cu [µg/l]	Cu Filtered [µg/l]	Lead - as Pb [µg/l]	Pb Filtered [µg/l]	pH	Temp [°C]	Zinc - as Zn [µg/l]	Zn-Filtered [µg/l]
29/10/1986	7	73	128	5	4			6.9		2814	2814
11/11/1986	14.3	14	122	2	2			6.8		6280	6280
03/12/1986	20.3	19.3		13	10	430	341	12.9		6582	6825
09/12/1986	12		118	6				6.9		3965	
06/01/1987	12		123	7				7.1		4447	
23/01/1987		14	189		6			7.5			5143
28/01/1987	24	19				212	47	13.1		7612	6453
19/02/1987		22	164		9			7.3			8120
31/03/1987		22	137		17			7.1			7550
28/04/1987		29	207		11			7.7			2
14/02/2003	20.26	20.32	208.7	27.9	9.89	531	287.7	14.1	9.2	6345	6387
27/02/2003	28.2	25.88	250.4	11.24	9.97	383	345.7	13.7	16	7543	7051
13/03/2003	19.15	18.89	209.5	11.29	9.76	307	268.2	13.9	14.6	5508	5496
22/05/2003	15.93	16.15	198.9	10.12	9.15	348.8	324.8	14.1	20.6	6667	6374
06/06/2003	22.88	22.33	220.3	15.29	13.46	531	457.6	14.15	20	8991	8464
19/11/2003	9.03	9.31	202	7.19	6.96	261.8	240.2	14.57	18	3582	3503
03/12/2003	14.96	14.77	210	11.38	6.69	284	248	14.67	14	5388	5498
13/01/2004	14.87	14.61	186.9	12.74	9.13	371.9	283.9	13.7	14	5009	4902
09/12/2010	22.97	23.32	271.9	8.68	7.83	230	215.2	14.81	6.5	7406	7441
10/12/2010	27.35	26.46	284	35.33	11.75	624	312.3	15.44	9.87	8555	8322
11/01/2011	13.09	12.93	190	11.97	7.72	316	216.7	13.94	12.54	4003	3988
19/01/2011	25.06	25.8	246	18	16.11	290.4	250.1	13.2	11	7511	7714
24/02/2011	18.98	19.06	226.3	11.79	10.29	301.8	265.9	14.16	17.2	6034	5818
19/04/2011	24.88	24.44	298	9.52	8.27	280	251	15.14	22.46	6912	7207
19/07/2011		13.85	214		10.02		237.8		26.36		4116
28/07/2011	28.59	27.74	302	12.28	10.29	367.4	293.5	14.97	28.59	8658	8667
05/08/2011	29.81	30.08	311	14.02	12.77	532.8	471.2	15.3	27.19	8919	9052

Date (Sampling)	Cadmium – Cd [µg/l]	Cd Filtered [µg/l]	Conductivity [µS/cm	Copper - Cu [µg/l]	Cu Filtered [µg/l]	Lead - as Pb [µg/l]	Pb Filtered [µg/l]	pH	Temp [°C]	Zinc - as Zn [µg/l]	Zn-Filtered [µg/l]
10/08/2011		29.59	312		11.36		408	10.79	24.4		9350
18/08/2011	26.17	26.68	298.2	12.3	11.05	383.6	328.7	14.43	24.66	8263	7360
30/08/2011	24.54	25.2	297	13.56	10.4	351.5	294.1	13.17	24.36	7464	7372
06/10/2011	20.09	20	232	13.36	11.39	405.1	281.8	13.52	21.68	6106	6198
19/10/2011	21.01	19.96	247	16.88	11.55	379.6	249.1	14.81	18.62	6525	6094
01/11/2011	8.98	8.72	170.5	8.86	6.98	258.6	188.3	13.81	21.6	2535	2667
15/11/2011	19.95	19.8		9.41	8.39	264.3	204.6	5.82	8.8	6143	5679
18/11/2011	21.29	21.67	240.1	10.76	9.45	326.6	247.7	13.84	21.9	6864	6586
04/01/2012	13.03	13.14	191	10.25	6.86	260.1	205	13.69	15.8	4111	3950
13/01/2012	22.68	22.97	302.6	12.79	11.14	276.5	243.4	13.94	14.2	6855	6715
28/02/2012	19.66	20.17	224.7	11.22	8.91	268.5	197.5	14.49	18.2	6038	5821

8.7 Historical data – Frongoch

Date (Sampling)	Lead - as Pb [µg/l]	Pb Filtered [µg/l]	Cd Filtered [µg/l]	Cadmium - Cd [µg/l]	pH	Zn-Filtered [µg/l]	Zinc - as Zn [µg/l]	Cu [µg/l]	Cu Filtered [µg/l]	Conductivity [µS/cm]	Temp [°C]
21/06/1977	224			20	6.8	7600	7990	9		110	
01/09/1977	493	340	10	42		18300	21800	6			
19/10/1977	600	500		36	6.8	14600	16900	18			
10/01/1978	913	630		43	6.1	18600	21950	30		135	
21/03/1978	638.8	541.7	28.9	29.7	6.9	14349.5	15508.1	4.1			
21/03/1978	249.9	187.5	7.2	7.8	7.8	3760.2	4451.2	15.2	2.3		
15/05/1978	401.9			19.9			6484	9.7			
18/07/1978	812	720			6.5	16100	18400	30			
25/09/1978	214	190	13	13	7.1	4600	5220	11		110	
28/11/1978	1600	860	40	49	6	17200	20100	35	30		
06/02/1979	970			46	6.6		15750	22		127	
23/07/1979	148			2.5	6.3		1551	11.2			
06/11/1980	810			42	6.3		20000	10			
12/07/2004	726	632	6.29	6.44	7.22	2850	2880	5.66	4.52		15.08
04/08/2004	975	864	20.3	20	7.57	9160	9810	11.7	7.31		14.61
15/09/2004	322	178	10.3	10.5	7.12	5760	5830	7.15	6	117.3	13.56
10/11/2004	1350	1100	42.1	42.8	6.58	19300	20400	28.4	22.5	155	10.06
29/11/2004	248	182	12.7	12.7	7.03	6120	6080	7.17	6.22	116	7.98
07/12/2004	317	216	12	12.7	6.89	6960	7340	10.5	8.89	118	9.81
31/01/2005	210	164	11.4	11.4	6.69	6440	6430	6.31	5.57	119	7.19
14/02/2005	299	208	6	6.18	6.91	3050	3120	5.06	4.34	111	7.12
07/04/2005	784	688	14.3	14.4	7.01	6560	6690	12.7	10.7	114.2	8.1
20/04/2005	231	183	5.17	5.2	6.97	2600	2640	5.99	4.28	111	9.7
19/05/2005	801	1190	11.9	18.6	6.99	9790	6290	9.66	14.2	105	13.93
13/06/2005	1080	444	8.23	8.38	7.21	3550	3780	6.49	3.54	110	15.54

Date (Sampling)	Lead - as Pb [µg/l]	Pb Filtered [µg/l]	Cd Filtered [µg/l]	Cadmium - Cd [µg/l]	pH	Zn-Filtered [µg/l]	Zinc - as Zn [µg/l]	Cu [µg/l]	Cu Filtered [µg/l]	Conductivity [µS/cm]	Temp [°C]
19/07/2005	916	817	7.53	7.67	7.23	3990	4090	4.35	4.1	105	16.26
30/01/2007	1270	1230	50	50	6.2	29500	27100	40	30	190	
27/02/2007	890	920	20	10	6.4	10800	9470	70	10	109	
27/03/2007	1200	1120	40	40	6.6	21000	21700	30	20	167	
24/04/2007	1420	1270	10	10	6.7	4350	4270	10	10	120	
22/05/2007	1390	1370	30	30	6.8	15200	13800	20	20	156	
26/06/2007	2100	2040	30	30	6.7	15800	14200	20	10	169	
24/07/2007	1710	1250	50	50	6.2	23200	24100	40	30	164	
21/08/2007	1650	1580	40	30	6.4	20200	20100	30	30	164	
25/09/2007	2060	1680	40	40	6.6	15300	15600	40	30	170	
18/10/2007	1270	1180	30	30	6.5	16900	17100	20	10	159	
13/11/2007	1100	1040	25	20	6.3	13000	13000	20	16	143	
11/12/2007	1500	1220	46.4	50	6.4	21400	25500	30	28	176	
09/12/2008	1310	1140	44.1	44.6	5.97	22000	23100	35.7	27.8		6.77
16/02/2009	1340	1240	41.6	41.9	6.01	19800	20100	30.3	26		9.16
12/03/2009	3450	864	40	42.3	6.55	14000	15500	47.8	13.1		8.63
19/08/2009	1610	1320	53.1	54.2	7	24400	24800	34.1	26.8	187	17.27
27/10/2009	2740	1190	38.3	39.7	6.96	16100	16800	49.6	16.9	164	13.84
07/12/2009	1550	1150	42.1	43.2	6.73	19500	19400	33.4	21.2	105	7.68
22/03/2011	411	260	7.28	7.39	7.36	2960	3060	8.46	7.35	98	11.54
14/04/2011	250	212	4.24	4.14	7.44	1600	1550	3.37	3.18	93	10.45
20/04/2011	290	222	3.89	3.72	7.55	1470	1400	3.37	3.27	94	17.19
08/06/2011	275	203	5.41	5.41	7.43	1940	1980	3.89	3.13	99	
15/07/2011	401	350	11.5	11.8	7.1	4970	4790	7.32	7	54	
22/08/2011	424	318	11.7	11.6	6.94	4620	4830	7.32	7.63	110	
09/09/2011	383	180	8.56	8.36	6.44	3770	3540	6.56	6.84	94	
22/09/2011	255	179	8.9	9.07	6.24	4320	4090	5.37	5.37	104	

Date (Sampling)	Lead - as Pb [µg/l]	Pb Filtered [µg/l]	Cd Filtered [µg/l]	Cadmium - Cd [µg/l]	pH	Zn-Filtered [µg/l]	Zinc - as Zn [µg/l]	Cu [µg/l]	Cu Filtered [µg/l]	Conductivity [µS/cm]	Temp [°C]
13/10/2011	189	140	6.49	6.52		3060	3120	5.52	4.71		
03/11/2011	243	185	9.88	10.1	6.6	5030	4670	7.34	6.45	104.2	
24/11/2011	215	166	8.04	8.4	6.98	3900	4060	6.24	5.83	101.5	
09/12/2011	204	151	7.66	7.4	6.77	3580	3520	6.1	5.12	108.1	4.9
14/12/2011	460	205	7.5	7.59	6.55	3390	3560	7.67	4.89	106.9	4.1
11/01/2012	274	204	7.22	7.33	6.79	3270	3330	5.34	4.81	102.3	
20/01/2012	250	212	8.85	8.98	6.5	4130	4100	6.14	5.48	104	6
06/02/2012	186	157	7.56	7.44	6.09	3490	3410	6.17	5.85	105.6	3.1
29/02/2012	208	170	7.98	8.16	6.41	3790	3930	6.14	5.56	102.3	9.1
12/03/2012	203	148	6.53	6.43	6.55	3070	3040	6.25	5.2	100.4	11.3
20/03/2012	200	149	6.07	6.13	6.61	2810	2800	5.23	5.07	99.9	9.5
27/03/2012	225	181	4.89	4.93	6.31	2100	2040	5.38	4.79	78.7	14.8
04/04/2012	174	100	1.89	2	7.26	772	808	3.84	2.46	94.5	7.4
27/04/2012	180	135	4.65	4.68	6.61	2010	1950	4.32	3.53	90.4	9.4
03/05/2012	203	167	6.63	6.78	6.89	3010	2860	5.06	4.5	96.6	9.4
11/05/2012	239	194	8.46	8.38	6.88	3650	3730	5.89	5.34	97.9	10.6
23/05/2012	221	189	6.85	6.88	7.34	3160	3120	5.66	5.31	100.2	18.4
14/06/2012	316	221	9.56	9.85	6.98	4490	4400	7.71	6.4	80.5	13.8
05/07/2012	210	165	7.31	7.38	7.2	3330	3290	5.9	5.45	90.2	15.6
27/07/2012	230	187	8.15	8.07	7.55	4230	4070	6.99	6.47	96.8	16.9
10/08/2012	247	204	6.48	6.42	7.32	2710	2800	6.01	5.47	93.2	19.2
05/09/2012	170	141	4.49	4.49	6.94	2030	2080	4.18	3.94	90.9	16.4
13/09/2012	242	193	7.6	7.53	6.82	3540	3770	6.48	10	97.8	12.8
26/09/2012	228	138	3.83	3.93	7.35	500	1690	3.82	3.03	84.7	10.5
10/10/2012	223	180	8.19	8.48	7.04	3710	4100	5.97	5.38	96.6	10.8
26/10/2012	221	181	9.42	9.24	7.15	4530	4660	7.03	6.48	92.3	9.7
27/11/2012	401	185	5.93	6.2	6.72	2580	2450	7.07	4.24	67.2	7

Date (Sampling)	Lead - as Pb [µg/l]	Pb Filtered [µg/l]	Cd Filtered [µg/l]	Cadmium - Cd [µg/l]	pH	Zn-Filtered [µg/l]	Zinc - as Zn [µg/l]	Cu [µg/l]	Cu Filtered [µg/l]	Conductivity [µS/cm]	Temp [°C]
12/12/2012	159	129	6.42	6.62	6.5	2980	3150	5.07	4.81	92.8	4
12/02/2013	233	186	5.86	5.96	7.09	2610	2690	5.02	4.36	94.9	4
27/02/2013	214	177	6.01	6.29	6.92	2830	2920	4.98	4.17	90.4	4.3
12/03/2013	180	138	3.03	3.14	7.21	1500	1490	3.34	2.8	87.6	2.5
27/03/2013	121	98.5	2.2	2.25	7.2	979	962	2.33	2.21	86.5	4
10/04/2013	906	117	1.66	2.17	7.27	777	950	9.76	1.95	87.8	7.3
24/04/2013	145	102	1.73	1.75	7.24	677	696	1.91	1.48	85.8	10
16/05/2013	109	52.8	1.72	1.88	7.51	622	658	1.98	1.55	81.4	9.3
29/05/2013	200	152	5.5	5.62	7.32	1890	1910	3.27	2.75	87	12.4
12/06/2013	182	152	3.57	3.52	7.15	1670	1670	3.53	3.31	91.6	15.1
26/06/2013	176	131	2.39	2.46	7.57	987	1050	2.54	2.35	86.4	15.5
01/07/2013	187	120	2.49	2.53	7.42	987	1080	2.78	2.32	85.9	16
25/07/2013	206	157	2.51	2.59	6.96	1070	1030	2.67	2.19	93.3	19.5
06/08/2013	235	173	5.6	5.55	6.84	1740	1700	2.91	2.52	64.9	16.3
27/08/2013	279	226	9.34	9.34	6.68	3980	4050	6.03	5.98	99.9	15.6
17/09/2013	666	348	41.5	43.7	6.63	16100	17100	50	8.15	156.5	10.6
17/10/2013	135	89.2	3.2	3.35	7.48	1530	1500	2.46	2.15	91.4	11.6
28/10/2013	607	232	11.2	11.5	7.3	4180	4560	7.48	3.81	99.7	10.8
13/11/2013	236	208	13.4	13.6	7	5910	5530	7.91	7.38	105.1	7.9
29/11/2013	216	192	13	12.5	7.1	6060	6140	8.53	8.19	106.2	7.4
10/12/2013	183	148	8.48	8.18	7.3	3960	4080	6.64	5.9	99.6	7.1
13/01/2014	178	159	10.2	10	7.23	5220	5370	5.42	5.46	102.3	5.4
28/01/2014	952	215	8.25	8.85	6.8	3640	3840	9.72	3.33	95.6	5.6
11/02/2014	445	211	9.11	10.1	6.75	4620	4130	6.5	3.67	97.2	4.2
27/02/2014	207	167	8.44	8.74	7.11	4060	4070	5.78	5.16	102	6.8
11/03/2014	157	124	6.29	6.43	7.13	2890	3100	4.97	4.52	99.9	7.8
31/03/2014	118	84.9	3.02	2.92	7.14	1350	1390	3.37	2.76	93.3	11.5

Date (Sampling)	Lead - as Pb [µg/l]	Pb Filtered [µg/l]	Cd Filtered [µg/l]	Cadmium - Cd [µg/l]	pH	Zn-Filtered [µg/l]	Zinc - as Zn [µg/l]	Cu [µg/l]	Cu Filtered [µg/l]	Conductivity [µS/cm]	Temp [°C]
07/04/2014	935	478	24.5	23	7.1	10800	10500	11.4	6.57	120.1	10.6
23/04/2014	130	97.4	3.41	3.53	7.39	1680	1720	3.45	3.23	92.6	11.7
12/05/2014	243	177	6.18	6.3	7.09	2740	2760	3.81	3.21	96.9	10.8
28/05/2014	115	84.8	2.11	2.21	7.29	1030	1010	1.96	1.88	89.2	14.4
09/06/2014	864	550	18.8	19.3	7.18	7170	7240	11.9	8.52	106.9	15.7
10/07/2014	170	102	1.68	1.68	7.41	779	784	1.9	1.83	92.2	19.2
29/07/2014	234	139	2.97	2.85	7.48	1260	1290	3.77	3.25	97.2	18.6
30/09/2014	109	60.8	0.981	0.936	7.48	452	469	1.35	1.2	98.8	14.3
14/10/2014	96.8	2	2.49	2.39	7.4	1420	1260	2.33	1.68	100.1	10.3
27/11/2014	177	148	12.6	12.6	6.93	6120	6270	7.77	7.28	115.4	7.1
10/12/2014	207	153	13.4	13.7	6.91	7810	7680	6.75	5.64	121.7	5.6
16/01/2015	192	145	11.3	11.3	6.68	5430	5540	6.01	5.17	107.7	4.9
27/01/2015	166	129	13	13.2	6.78	6530	6320	7.36	6.72	112	5.7
10/02/2015	164	142	12.3	12.1	6.98	6020	6050	7.57	6.86	110.6	4.5
26/02/2015	1510	222	12.7	13.2	6.78	5650	5660	12.8	3.73	98.9	6.8
20/03/2015	158	137	14.9	14.6	7.04	7010	7020	8.82	8.69	112.7	6.6
31/03/2015	190	137	13.4	14.1	7.45	5390	5500	7.06	5.93	102.3	7.4
13/04/2015	179	156	15	15.5	7.2	5660	5570	5.97	5.73	108.2	8.2
30/04/2015	171	141	14	14.1	7.31	4680	4770	6.15	5.79		10.1
13/05/2015	107	82.2	9.96	9.8	7.16	3110	3110	3.68	3.41	96	13.1
28/05/2015	145	114	15.6	15.2		5480	5720	6.3	5.9		
11/06/2015	184	158	13.1	13.4	6.86	6060	6270	6.81	6.3	112.8	13.7
29/06/2015	172	141	5.93	6.02	6.95	3450	3320	3.21	2.76	101.9	16.5
15/07/2015	150	104	4.53	4.72	7.2	2230	2160	2.58	2.27	97.8	17.6
24/08/2015	134	77.5	2.34	2.24	7	1000	1110	2.44	1.75	89.3	15.5
09/09/2015	96.9	72.9	2.08	2.08	6.95	1150	1240	2.3	2.08	92.8	14.1
15/10/2015	71.5	60.7	1.2	1.3	7.26	681	686	1.4	1.3	88.3	9.5

Date (Sampling)	Lead - as Pb [µg/l]	Pb Filtered [µg/l]	Cd Filtered [µg/l]	Cadmium - Cd [µg/l]	pH	Zn-Filtered [µg/l]	Zinc - as Zn [µg/l]	Cu [µg/l]	Cu Filtered [µg/l]	Conductivity [µS/cm]	Temp [°C]
30/10/2015	129	81.4	4.28	4.79	7.09	2010	2020	2.12	1.86	94.2	11.2
13/11/2015	198	102	4.47	4.77	6.9	2040	2120	3.38	2.37	98.6	8.8
26/11/2015	130	87.7	3.72	3.84	6.87	1980	2030	3	2.38	95.6	8.1
03/12/2015	155	116	5.75	5.87	6.85	3000	2830	3.95	3.48	99.9	9.3
16/12/2015	149	104	6.02	6.28	6.66	3190	3110	3.82	3.46	94	9.4
06/01/2016	108	91.9	6.8	7.03	7.32	3280	3220	3.66	3.45	97.4	6.8
26/01/2016	1180	273	21.2	21.6	6.68	9380	11500	11.7	3.55	128.2	7.4
25/02/2016	86.3	69.2	4.64	4.6	6.92	2600	2540	3.06	2.82	98.6	5.3
11/03/2016	93.8	73	4.96	4.79	6.81	2480	2550	2.81	2.76	98	6.3
21/03/2016	112	88.3	5.92	6	7.09	3500	3300	3.38	3.02	100.6	7.9
11/04/2016	78.4	61	3.72	3.9	7.19	1670	1620	2.15	2.05	89.3	8
27/04/2016	113	93.1	4.27	4.3	7.29	1960	2020	2.77	2.42	95.7	9.2
11/05/2016	110	81.7	2.21	2.32	7.12	1140	1120	1.86	1.62	95.6	14.9
26/05/2016	99.8	70.9	1.61	1.6	7.46	765	744	1.89	1.69	90.8	13.4
08/06/2016	104	74.1	1.27	1.29	7.3	594	592	1.57	1.54	93.1	19.4
20/06/2016	248	134	4.42	4.68	7.09	1430	1450	4.02	2.65	83.8	15
11/07/2016	238	150	7.75	7.39	6.76	3280	3290	3.31	2.6	96.2	14.4
27/07/2016	205	150	6.55	6.8		2710	2690	3.7	3.38		
10/08/2016	112	84.7	5.17	5.21	7.05	2670	2630	3.01	2.84	94.2	14.2
30/08/2016	110	83.6	4.88	5.16	7.05	2520	2460	2.91	2.83	94.2	15.8
16/09/2016	102	87.1	3.69	3.94	7.12	2020	1960	2.57	2.31	95.5	15.4
28/09/2016	85.7	61.2	2.24	2.34	7.41	1080	1170	1.78	1.6	88.4	13.5
10/10/2016	131	105	5.54	5.3	7.35	2760	2790	3.27	3.06	96.4	10.5
15/11/2016	343	124	6.74	7.21	7.25	2390	2700	4.14	2.59	91.8	10.3
01/12/2016	128	100	7.82	8.23	7.11	3620	3640	4.2	3.85	99.6	5.1
04/01/2017	96.6	73.7	4.7	4.73	6.64	2210	2270	2.64	2.32	94.2	5.8
18/01/2017	124	94.2	7.2	7.4	6.93	3600	3530	3.92	3.7	99.2	6.5

Date (Sampling)	Lead - as Pb [µg/l]	Pb Filtered [µg/l]	Cd Filtered [µg/l]	Cadmium - Cd [µg/l]	pH	Zn- Filtered [µg/l]	Zinc - as Zn [µg/l]	Cu [µg/l]	Cu Filtered [µg/l]	Conductivity [µS/cm]	Temp [°C]
30/03/2017	274	190	14.7	15	6.96	7460	7340	7	5.6	106.4	10.2
25/04/2017	110	83.5	4.26	4.18	7.16	2100	2200	2.23	1.89	93.1	10.4
18/05/2017	142	115	2.46	2.54	7.25	1060	1080	1.96	1.92	88.2	14.2
14/06/2017	166	47.2	0.89	1.01	7.21	372	416	1.87	1.1	82.7	15.1
13/07/2017	112	88.5	1.65	1.6	7.22	702	706	1.51	1.42	86	17.7
22/08/2017	102	70.7	3.56	3.57	7.28	1810	1820	2.48	4.09	86.7	16.1
28/09/2017	136	105	8.86	9.62	7.52	4320	4600	5.57	4.12	98.5	13.6
18/10/2017	87.5	63.8	4.85	5.07	7.2	2260	2420	2.98	3.03	97.4	11.1
15/11/2017	153	71.3	4.31	4.47		2160	2320	3.49	2.69		
15/12/2017	106	80.2	4.98	4.97	6.73	2610	2590	3.03	3	101.5	4.3
18/01/2018	122	58	4.88	5.22	7.45	2600	2830	3.16	2.54	96.5	5
22/02/2018	121	94.4	6.8	6.69	7.43	3760	3670	4.04	3.76	98.4	4.8
15/03/2018	91.8	67.5	3.73	3.42	7.22	1720	1660	2.16	1.9	89.8	8.4
02/04/2018	434	109	4.01	4.67	6.84	1990	2180	8.91	3.36	97	7.2
11/04/2018	109	82.4	6.2	5.87		2920	2990	4.49	3.6		
19/04/2018	143	110	6.63	6.4	6.97	3390	3130	3.36	3.28	154.2	14.7
08/05/2018	117	75.6	3.64	3.6	7.28	1750	1910	2.51	2.34	94.7	13.9
12/06/2018	99.4	72	2.03	2.08	7.6	886	928	2.27	2.14	95.5	20.1
09/07/2018	137	63.9	1.79	1.97	7.61	779	779	3.35	2.6	95.1	25
22/08/2018	115	96.7	3.62	3.56	7.52	1690	1700	2.09	1.87	109.1	18.5
19/09/2018	99.5	58.3	1.72	1.77	7.69	760	789	1.48	1.2	107	14.4
22/10/2018	152	132	9.44	9.59	7.64	4300	4240	4.79	4.83	104.6	10.9
12/11/2018	98.4	73	3.57	3.8	7.45	1920	1880	2.14	2.02	92.2	8.9
11/12/2018	103	81.7	4.61	4.7	6.9	1980	2060	2.72	2.41	91.8	8.1
22/01/2019	117	65.2	4.51	4.48	7.11	2200	2350	2.44	1.92	93.2	4.4
12/02/2019	103	77.3	3.67	3.85	6.56	1690	1720	2.26	2.09	89.5	6.5
02/04/2019	201	173	12.6	12.4	7.16	6120	6420	4.77	4.32	108.6	9.6

Date (Sampling)	Lead - as Pb [µg/l]	Pb Filtered [µg/l]	Cd Filtered [µg/l]	Cadmium - Cd [µg/l]	pH	Zn-Filtered [µg/l]	Zinc - as Zn [µg/l]	Cu [µg/l]	Cu Filtered [µg/l]	Conductivity [µS/cm]	Temp [°C]
30/04/2019	99.8	75.8	2.64	2.6	7.19	1300	1270	2.31	1.96	88.9	14
19/06/2019	102	68.9	2.68	2.72	7.34	1180	1230	2.21	2.06	82.8	14.9
16/07/2019	142	131	5.16	5.59	7	2650	2660	3.32	2.98	101.8	21.8
22/08/2019	96.9	78.1	3.67	4.14	6.97	1500	1510	2.48	2.25	90.2	14.9
26/09/2019	172	96.3	5.11	5.42	6.91	2110	2110	4.81	3.31	89.3	14.9
23/10/2019	121	93.3	8.76	8.73	7.36	3540	3690	5.33	5.16	93	9.9
18/11/2019	107	92.3	7.67	7.68	7.23	3300	3360	4.47	4.21	85.5	6.7
12/12/2019	177	83.6	3.83	3.98	7.16	1880	1950	3.37	2.2	82.3	6.2
20/01/2020	101	75.3	5.06	5.25	7.37	2340	2340	3.24	2.8	86.2	5.3

8.8 Historical data – Parys Mountain

Date (Sampling)	Lead - as Pb [µg/l]	Pb Filtered [µg/l]	Cadmium – Cd [µg/l]	Cd Filtered [µg/l]	pH	Zinc - as Zn [µg/l]	Zn- Filtered [µg/l]	Copper – Cu [µg/l]	Cu Filtered [µg/l]	Conductivity [µS/cm]	Temp [°C]
02/03/2004	41.2	40.3	159	162	2.71	56700	57100	44400			9.98
08/03/2004	32.5	31.3	169	166	2.67	57600	57200	41800	40700		10.3
15/03/2004	31.2	31.1	168	170	3	58400	58100	39900	39900		10.16
22/03/2004	39.1	36.5	175	175	3.08	57800	57400	38500	38400		10.56
29/03/2004	30.5	29.8	176	177	3.04	57500	58100	36600	37800		10.28
05/04/2004	30	29.1	178	176	3.05	58500	58400	35400	36500		10
19/04/2004	33.7	34.1	177	176	2.98	56200	56700	31600	31500		10.6
04/05/2004	30.8	31.8	178	183	3.07	55900	57200	30600	31400		10.63
17/05/2004	25.8	25.6	186	188	2.66	57600	57900	33200	32900		11.4
01/06/2004	26.1	25.6	188	187	2.81	57300	57000	32800	32800		11.1
14/06/2004	28.3	27.2	185	186	2.73	68100	70300	36100	37300		12.7
12/07/2004	22.9	23.6	195	200	2.9	82300	79400	31000	29800		10.9
09/08/2004	23.8	23.1	196	193	2.8	92900	93700	32200	32500		10.9
06/09/2004	32.7	20.3	205	200	2.71	93200	89700	47900	46200		12.33
05/10/2004	54.3	50.7	182	183	2.6	62900	61300	53600	52100		11.63
29/11/2004	46.2	45.6	173	174	2.59	56400	56300	52600	52700		10.04
13/12/2004	37.9	37.7	174	172	2.61	59900	59500	50500	50100		9.84
26/01/2005	42.5	44.5	164	171	2.63	63700	65400	48900	50100		10.24
15/02/2005	35.6	36.1	160	161	2.67	63200	62400	44600	43900		10.06
22/03/2005	21	21.4	171	169	2.59	654000	64400	42200	41300		10.71
14/04/2005	25.8	25	165	164	2.69	63500	62900	41400	41000		10.69
12/05/2005	24.6	23.7	169	168	2.71	63000	62400	48600	48200		11.55
22/06/2005	26.3	25.5	193	190	2.71	65500	65500	42400	42100		12.43
11/07/2005	20.5	20.7	179	178	2.59	65300	65700	39000	39500		12.45
09/09/2005	21.1	20.4	181	182	2.54	79300	78000	40000	39200		11.58

Date (Sampling)	Lead - as Pb [µg/l]	Pb Filtered [µg/l]	Cadmium – Cd [µg/l]	Cd Filtered [µg/l]	pH	Zinc - as Zn [µg/l]	Zn-Filtered [µg/l]	Copper – Cu [µg/l]	Cu Filtered [µg/l]	Conductivity [µS/cm]	Temp [°C]
05/10/2005	20.5	20.3	181	181	2.58	72200	77900	38400	41400		12.17
27/10/2005	46.9	46.2	168	170	2.54	78000	78500	62800	63600		11.2
06/12/2005	47.9	47.2	153	154	2.55	59100	58300	55500	54700		10.69
13/01/2006	35.6	35.5	159	170	2.63	67500	72900	42700	44600		10.57
16/03/2006	33.9	34.2	142	142	2.58	63600	62700	47100	46300		10.31
28/03/2006	51.2	50.1	141	148	2.56	68200	68000	44300	43900		10.53
13/01/2010	43.4	34.1	166	164	2.41	57300	59200	44000	44400	4014	8.66
20/01/2010	32.1	30.6	167	157	1.99	66100	66800	48100	45200	3824	8.51
25/01/2010	36.7	32.1	161	166	2.24	62400	62300	43200	44300	3887	8.21
29/01/2010	37.9	36	151	146	3.97	56500	55900	42600	41400	3785	5.51
03/02/2010	30.1	31.2	154	149	2.33	61100	57100	43200	41700	3943	10.22
10/02/2010	28.9	26.8	166	162	2.5	61900	60800	42200	41400	3921	10
16/02/2010	28.7	26.5	159	159	2.44	64300	61600	44600	41600	3841	9.86
26/02/2010	28.9	23.2	164	154	2.61	61800	62700	39600	40200	3649	9.53
04/03/2010	23.3	22.3	163	157	2.68	65500	63000	40300	39700	3661	10.53
10/03/2010	24.5	20.5	159	159	2.48	61300	64100	37200	38100	3730	10.1
15/03/2010	19.3	17.5	161	160	2.48	58700	65300	40800	39200	3652	10.72
22/03/2010	20	20	154	163	2.47	56800	65800	33300	35900	3591	11.04
29/03/2010	22.8	21.4	161	151	2.39	60700	62300	37200	38000	3640	10.52
12/07/2010	21.3	20	163	168		72100	68700	37000	33700		
09/08/2010	23.9	22.9	176	178	2.1	62900	68800	40500	42800	4046	11.63
11/08/2010	20.5	21.1	178	184	2.5	71000	73100	45700	44100	3990	
26/08/2010	21	20.8	175	174	2.65	73500	69200	40500	44200	4714	14.27
03/09/2010	22	20.2	173	174	2.65	73200	67000	44100	39600	3830	
09/09/2010	29.8	25.2	174	176	2.6	70500	68700	43100	40600	3897	12.82
24/09/2010	30.3	30.2	171	179	2.45	74700	65300	48100	41900	4160	11.1
19/10/2010	24	24.9	173	180	2.65	70400	68600	45800	41200	4217	11

Date (Sampling)	Lead - as Pb [µg/l]	Pb Filtered [µg/l]	Cadmium – Cd [µg/l]	Cd Filtered [µg/l]	pH	Zinc - as Zn [µg/l]	Zn- Filtered [µg/l]	Copper – Cu [µg/l]	Cu Filtered [µg/l]	Conductivity [µS/cm]	Temp [°C]
04/11/2010	26	24.2	167	171	2.41	66000	63800	44000	42400	4070	11.9
10/11/2010	31.5	29.7	174	169	2.47	68900	65600	47100	45900	4290.2	10.9
26/11/2010	33.3	27.7	174	180	2.41	69100	67200	44700	42800	426	9.8
30/11/2010	25.9	52.9	164	176	2.39	68800	67400	46300	43000	4177	9.4
08/12/2010	23.9	24.2	150	165	2.56	68800	62600	45100	41300	4041	9.1
21/01/2011	25.9	27.5	171	167	2.41	58100	61500	39200	42300	4058	9.8
01/02/2011	25	24.2	174	174	2.49	67900	67200	42400	42700	4131	10.1
09/02/2011	27.4	27.3	163	156	2.45	63800	60000	42000	40500	4158	10.7
28/02/2011	25.9	26.5	171	159	2.42	65600	62900	42400	40600	4162	10.7
15/03/2011	22.2	23.2	167	166	2.5	65600	64400	42100	41500	3435	10.6
28/03/2011	24.6	23.2	166	167	2.38	66900	64000	40500	40100	3893	11.42
20/06/2011	23	21.3	177	172	2.86	68300	69900	35500	34800	3803	12
04/07/2011	23.6	21.3	171	166	2.57	70700	69200	34800	36600	3781	12.1
03/08/2011	22.5	21.2	167	180	2.63	69500	68600	33400	35500	3707	11.2
15/08/2011	21.2	21.2	172	171	2.3	68200	71600	33600	34800	3730	11.77
06/09/2011	30.4	28.1	153	150	2.19	63700	62700	33100	33100	3687	11.17
13/09/2011	20.7	24.5	164	164	2.56	66600	67900	36900	39200	3828	11.46
30/09/2011	19.8	18.9	184	182	2.42	69800	73100	41600	42900	4058	11.64
07/10/2011	19.8	20.3	181	180	2.46	76100	70600	42600	39600	4137	11.15
13/10/2011	19.1	19.6	179	184	2.25	81700	73900	43600	40900	4114	11.18
27/10/2011	26.9	27.8	170	161	2.22	67100	68200	41000	38800	4104	11.1
08/11/2011	20.8	20.7	183	178	2.28	70000	71700	42600	41700	4109	11.2
15/11/2011	21.3	21.3	185	179	2.84	72900	77300	40500	42600	4134	10.9
29/11/2011	23.5	19.9	166	172	2.52	65800	70800	37500	40400	3832	10.99
15/12/2011	31.7	26.5	176	178	2.21	72100	69800	47000	45700	4116	10.89
17/01/2012	29.4	26.8	194	192	2.21	73400	76700	49600	51600	4402	10.76
10/02/2012	31.8	31.2	171	168	2.13	68200	64600	43800	44800	4143	10.69

Date (Sampling)	Lead - as Pb [µg/l]	Pb Filtered [µg/l]	Cadmium – Cd [µg/l]	Cd Filtered [µg/l]	pH	Zinc - as Zn [µg/l]	Zn- Filtered [µg/l]	Copper – Cu [µg/l]	Cu Filtered [µg/l]	Conductivity [µS/cm]	Temp [°C]
24/02/2012	28.6	27.9	171	181	2.16	64500	66800	45700	47100	4101	10.94
13/03/2012	25.7	28.4	181	181	2.37	69100	69100	46400	46800	4156	10.87
20/04/2012	24	20.7	183	180	2.18	71800	66300	45400	42100	4069	10.98
27/04/2012	26.5	23.9	180	50	2.21	70600	69500	45300	500	3730	10.9
24/05/2012	24	21.6	173	177	2.5	66900	69200	41000	42900	3940	11.8
13/06/2012	22.6	20.3	178	174	2.27	71100	68600	41500	40000	3840	11.3
19/06/2012	23.3	22.8	174	181	2.1	65600	70300	43700	44700	4119	11.9
12/07/2012	22	21.3	184	183	2.34	70100	67600	47000	45200	4189	11.8
17/07/2012	24.1	24.4	186	179	2.36	68500	72500	44300	47500	4218	12.2
06/08/2012	23.6	25.9	187	192	2.44	70800	74000	48800	51000	4264	12.4
14/08/2012	26.9	24.6	192	187	1.98	75500	71400	50600	46200	430	12.44
04/09/2012	25.4	25.1	190	192	1.94	74800	75500	49500	49600	4129	11.8
13/09/2012	25	24	190	184	2.45	77100	74800	48600	47100	4205	11.3
02/10/2012	101	45.4	196	203	2.2	68000	74700	49100	55100	4539	11.5
17/10/2012	44.3	63.9	173	167	2.22	65000	65700	51200	48600	4417	11.4
31/10/2012	27	29	172	171	2.24	60000	65100	46700	47100	4099	11
13/11/2012	33	29.4	172	171	6.19	63000	60400	47700	46400	259	10.6
05/12/2012	78.9	73.8	188	184	2.17	60800	64000	50500	51200	4258	10.8
18/12/2012	51.9	56.1	173	166	2.24	60700	56800	45300	45000	4180	10.8
09/01/2013	49.7	46.9	173	173	1.96	54900	59800	48100	49800	4081	10.67
16/01/2013	40.6	40.3	168	162	2.22	60500	55700	46600	44400	3922	10.5
06/02/2013	35.1	30.9	163	161	2.28	60000	59100	49100	46200	3905	10.5
20/02/2013	31.4	28.1	165	163	2.3	60800	57900	46900	44800	3835	10.7
06/03/2013	22.5	23.2	171	171	2.33	60900	63200	44700	44700	3811	10.7
20/03/2013	20.8	20.6	163	170	2.48	57700	63300	36800	39600	3652	10.6
11/04/2013	20.7	20.5	157	162	2.38	58200	60400	37900	40000	3726	10.7
17/04/2013	21.8	24.9	163	158	2.52	60400	63900	39000	38700	1837	10.4

Date (Sampling)	Lead - as Pb [µg/l]	Pb Filtered [µg/l]	Cadmium – Cd [µg/l]	Cd Filtered [µg/l]	pH	Zinc - as Zn [µg/l]	Zn- Filtered [µg/l]	Copper – Cu [µg/l]	Cu Filtered [µg/l]	Conductivity [µS/cm]	Temp [°C]
01/05/2013	17.7	18.7	169	168	4.26	63900	61400	42300	38600	3673	11.1
15/05/2013	20.4	20.4	162	167	2.43	67000	63400	39800	39900	3648	11.6
05/06/2013	18.8	17.8	161	172	2.39	61100	63600	39200	37700	3715	11
17/06/2013	17.8	17.3	170	168	2.46	66400	66300	39600	40100	502	11.4
26/06/2013	20.6	18.2	165	169	2.45	66100	65800	35400	38200	3631	12
19/07/2013	18.7	18.6	174	173	2.44	67200	66900	35900	36800	3439	12.3
24/07/2013	18.8		168		2.42	64100		36100		3535	12
16/08/2013	25.1	19.9	173	167	2.43	63200	63600	38400	38500	3824	12
21/08/2013	21.1	21	157	178	2.42	66100	69000	40700	40800	3901	11.6
04/09/2013	18.9	16.6	178	174	2.42	63100	69800	39400	39200	3890	11.7
17/09/2013	17.8	18.2	180	180	2.46	63900	67700	38200	40900	3973	11.2
02/10/2013	19.7	19.8	174	177	2.39	73900	73500	41400	41400	3975	11.3
16/10/2013	25.6	26	172	169	2.49	69100	63600	41700	38000	3984	11
29/10/2013	28.3	72.6	162	164	2.39	67000	58100	42400	39000	4062	11.1
13/11/2013	21.4	22.4	165	176	2.43	63100	66000	43900	44800	4061	11
04/12/2013	21.7	23.1	175	162	2.16	67700	67400	42900	42400	3956	10.6
11/12/2013	21.3	21.3	170	182	2.38	65600	63900	42600	41700	3871	10.8
17/12/2013	28.2	28.3	168		2.36	64800	63900	40000	38000	3904	10.7
22/01/2014	43	42.5	118	155	2.34	62500	59600	45800	44000	3995	10.7
29/01/2014	41	40.9	155	151	2.29	68300	74600	44400	44000	3825	10.6
21/02/2014	36.8	35	157	154	2.34	64900	63000	45400	44800	3874	10.6
24/02/2014	41	39.4	146	153	2.36	60100	61300	41900	47200	3853	10.6
12/03/2014	27.4	27.2	142	147	2.13	55700	57000	44300	43900	3742	10.8
17/03/2014	26.4	26.4	146	150	2.28	57300	58000	44400	45300	3812	10.7
30/04/2014	21.9	20.6	150	148	2.39	63500	62200	40000	37900	3558	12
14/05/2014	17	17.8	146	146	2.5	61300	62700	33900	37100	3445	12.1
21/05/2014	18.3	18.2	147	145	2.52	64500	64600	34300	35900	3517	11.8

Date (Sampling)	Lead - as Pb [µg/l]	Pb Filtered [µg/l]	Cadmium – Cd [µg/l]	Cd Filtered [µg/l]	pH	Zinc - as Zn [µg/l]	Zn- Filtered [µg/l]	Copper – Cu [µg/l]	Cu Filtered [µg/l]	Conductivity [µS/cm]	Temp [°C]
28/05/2014	22.8	21.8	147	145	2.47	63100	61700	39900	39400	3664	11.7
11/06/2014	23.6	22.6	135	131	2.41	57500	55600	36800	35900	3721	12.1
25/06/2014					2.43					3749	12.5
16/07/2014					2.4					1948	14.2
30/07/2014	18.3	17.2	148	164	2.39	67300	71400	38900	41600	3666	11.5
14/08/2014	15.8	17.7	160	159	2.51	69000	72100	42200	44200	3630	13.6
27/08/2014	22.7	20.6	127	153	2.54	52200	68300	30300	41700	3705	12.9
11/09/2014	17.5	17.4	160	162	2.46	70400	69600	39200	40300	3647	11.1
16/09/2014	17.3	16.8	157	157	2.49	68300	69400	39800	38300	3682	11.5
13/10/2014	22	23.1	163	162	2.45	69200	69700	45000	44300	4094	11.2
20/10/2014	24.6	23.7	160	162	6.11	71600	71300	44800	45300	323	12.1
04/11/2014	30.7	27.7	155	146	2.4	68900	63000	46500	43100	4152	11.1
05/11/2014	25.6	24.5	165	157	2.29	69600	63900	46900	43200	2478	11.2
12/11/2014	26.4	26.8	164	160	2.35	67800	67100	46500	45200	4070	11.2
13/11/2014	27.6	25.2	167	157	2.45	75400	67700	45600	46600	4028	11.2
26/11/2014	20.5	19.7	154	161	2.36	64600	65200	43500	42600	3912	10.5
11/12/2014	20.7	20.7	166	161	2.35	70300	68200	42500	42700	2116	10
15/01/2015	29.3	28.7	155	155	2.29	65800	63200	43500	39100	4268	9.3
26/01/2015	24.3	23.3	149	152	2.36	61100	65300	42500	42600	3995	9.8
09/02/2015	18.5	19.6	153	155	2.33	62600	62500	39000	40300	3876	10.7
24/02/2015	19.3	19.8	157	154	2.44	65900	67000	40600	40900	3878	9.2
12/03/2015	18.2	18.7	151	163	2.5	65300	66500	41000	40000	3538	10.4
26/03/2015	20	18.3	157	152	2.47	67800	65900	42200	39600	3732	10.5
17/04/2015	20	18.8	153	150	2.4	65100	71100	40200	40600	3808	11
01/05/2015	17.8	17.8	156	156	2.46	68300	71100	39400	42700	3762	10.8
15/05/2015	20.5	20	119	127	2.36	66000	62800	43000	39700	3775	11.1
29/05/2015	19.9	19.8	132	138	2.37	65400	65700	41300	41100	3785	11.3

Date (Sampling)	Lead - as Pb [µg/l]	Pb Filtered [µg/l]	Cadmium – Cd [µg/l]	Cd Filtered [µg/l]	pH	Zinc - as Zn [µg/l]	Zn- Filtered [µg/l]	Copper – Cu [µg/l]	Cu Filtered [µg/l]	Conductivity [µS/cm]	Temp [°C]
18/06/2015	18.2	18	142	135	2.45	66400	68200	39400	42600	3848	11.3
23/06/2015	17.6	17.3	145	134	2.46	72200	71000	42800	41600	3804	12.8
13/07/2015	18.3	17.2	139	137	2.51	74000	69700	41000	38400	3773	12.3
06/08/2015	17.8	18.3	141	137	2.49	72300	69500	37700	36700	3663	13.4
03/09/2015	16.9	17.2	137	141	2.65	69300	70300	34600	36100	3570	11.4
08/10/2015	16.9	16.6	139	136	2.63	70800	73500	34400	35200	2959	12.3
10/11/2015	25.1	27.1	134	143	2.47	72900	74300	40400	42700	3264	12.6
14/12/2015	54	52.7	176	175	2.28	79200	77800	57000	55600	4662	11.1
20/01/2016	61.8	64	122	135	2.27	59800	58800	51900	51500	3908	10.1
11/02/2016	35.3	36.5	121	122	2.38	60300	56900	46800	48400	3990	10.5
04/03/2016	32.8	34.1	118	119	2.42	53400	53500	42400	42700	3915	10.2
12/04/2016	21.5	22.2	135	135	2.61	57100	56500	44100	42200	3707	10.7
18/05/2016		14.7		148	2.52		65200		39100	3503	11.3
26/05/2016	15.6	15.9	150	146	2.59	61500	62300	36300	37100	3478	11.6
13/06/2016	16	16.3	152	145	2.57	63600	62800	39200	38800	3567	11.3
06/07/2016	15.9	15.6	156	152	2.53	71400	69900	43100	41500	3521	12.2
18/08/2016	17.1	15.8	171	160	2.51	73300	68900	44300	40800	3552	11.5
06/09/2016	16.3	16.8	162	159	2.52	63200	64900	38600	39000	3771	12.8
27/10/2016	17.1	16.6	165	166	2.44	71200	70900	40200	39800	3767	11.2
16/11/2016	18.1	17.7	173	168	2.57	72900	72400	38600	39000	3787	10.9
09/12/2016	20.4	19.8	168	150	2.54	74200	71800	43200	40200	3833	11.1
05/01/2017	20	19.6	168	160	2.58	79400	75500	45600	43200	3713	9.9
06/03/2017	25.1	25	145	147	2.39	62800	65100	38800	40000	4009	10.7
12/04/2017	22	22.1	166	165	2.46	69000	67700	42800	42200	3839	10.9
02/05/2017	19.6	18.8	164	159	2.51	71900	71000	42900	42300	3605	12.1
08/06/2017	51.5	45.5	134	133	2.51	59300	57800	36500	36100	3916	11.9
11/07/2017	19.8	19.2	177	171	2.48	76100	73200	46800	46000	3987	11.2

Date (Sampling)	Lead - as Pb [µg/l]	Pb Filtered [µg/l]	Cadmium – Cd [µg/l]	Cd Filtered [µg/l]	pH	Zinc - as Zn [µg/l]	Zn- Filtered [µg/l]	Copper – Cu [µg/l]	Cu Filtered [µg/l]	Conductivity [µS/cm]	Temp [°C]
04/08/2017	18.3	17.5	164	162	2.44	71500	70500	43700	43100	3951	11.7
11/09/2017	19.3	18.1	157	158	2.56	72100	71400	42700	41700	3782	12
06/10/2017	18.7	18.7	169	164	2.54	72400	70300	43300	40900	3908	11.2
17/11/2017	29.1	22.7	180	178	2.38	77700	74900	51300	49200	4101	11.1
15/12/2017	27	27.2	182	186	2.31	71400	73200	49200	50300	4261	9.9
03/01/2018	26.9	26.2	162	163	2.41	67900	66400	49600	46300	4122	10.3
06/02/2018	24.2	22.3	173	162	2.35	68000	66100	49000	48500	3747	10.6
09/03/2018	17.9	18.6	153	148	2.52	64600	70100	40400	39500	3671	10.4
26/04/2018	20.2	19.5	150	148	2.59	64000	66700	39600	41700	1911	11.3
16/05/2018	19	18.8	149	149	2.61	78900	63900	39600	39700	3599	11.1
11/06/2018	18.1	17.3	150	150	2.57	69500	70000	40500	40400	3654	11.8
09/07/2018	18.2	18.2	153	156	2.52	66400	68600	38000	37300	3543	11.2
14/08/2018	17.6	17.2	148	152	2.57	69800	69300	38400	35400	3600	11.6
17/09/2018	17.7	17.8	152	149	2.67	73300	70600	36800	35900	3642	11.6
19/10/2018	28.2	27.5	163	159	2.55	66400	68800	45100	47600	4060	11.7
16/11/2018	30.4	30.5	158	150	2.4	64500	61900	43900	42600	4068	11.6
05/12/2018	26.1	26.7	146	153	2.41	61300	65500	41200	45500	4153	10.8
05/02/2019	17.1	16.5	156	154	2.56	62200	64700	35400	36600	1909	10.1
25/02/2019	20.3	21.2	147	140	2.51	65000	59600	44100	40600	2005	11
22/03/2019	27.2	28.1	151	148	2.58	61400	62000	43500	45500	2186	10.9
30/04/2019	16.7	16.5	149	152	2.51	62700	63200	36000	36600	3596	11.4
23/05/2019	17.6	18.1	146	148	2.49	60800	61200	36400	36900	3793	11.4
17/06/2019	20.1	20.3	148	152	2.49	61900	64800	38800	38300	3763	11.5
17/07/2019	18.3	18	146	146	2.49	61300	61500	39200	38100	3693	11.6
14/08/2019	19.6	19.4	146	141	2.55	62800	66500	36900	38000	3822	11.4
04/09/2019	16.4	16.1	155	152	2.56	66100	64300	38900	38200	3558	11.8
17/10/2019	21.9	21.9	147	148	2.44	61200	62800	39000	39500	3936	11.3

Date (Sampling)	Lead - as Pb [µg/l]	Pb Filtered [µg/l]	Cadmium – Cd [µg/l]	Cd Filtered [µg/l]	pH	Zinc - as Zn [µg/l]	Zn-Filtered [µg/l]	Copper – Cu [µg/l]	Cu Filtered [µg/l]	Conductivity [µS/cm]	Temp [°C]
29/10/2019	24.1	24.7	142	152	2.39	63800	64500	42300	43200	3975	10.4
27/11/2019	21	21.1	157	152	2.36	63600	62100	42600	42300	4072	11.2
05/12/2019	20.8	21.5	150	152	2.23	60700	64600	40900	43800	4063	10.8
31/01/2020	23.1	22.9	157	148	2.47	69700	63900	46900	44700	3986	11
18/02/2020	35.6	34.2	144	148	2.35	57700	55000	42500	41400	3977	10.7