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Journal of Hydrology 634 (2024) 131011

Contents lists available at ScienceDirect

Journal of Hydrology

journal homepage: www.elsevier.com/locate/jhydrol

Research papers

Long-term changes in water quality downstream of three abandoned metal mines

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ARTICLE INFO

Keywords:
Lead mine
Abandoned metal mine
Metal pollution
Water quality
Remediation

ABSTRACT

Abandoned metal mines pollute rivers with both acidic and circumneutral metal-rich waters, sometimes from well-mapped mines, but often from long-abandoned adits with limited historical records. Changes in water quality over the monitored timescales were calculated for three mines across Wales (Nantymwyn, Parys Mountain and Frongoch), each abandoned since the early 20th century. Using all available spot sampling data provided by the environmental regulator, it was found that there was a sustained input of metals to the receiving watercourses with no or limited reduction in the concentrations from the mines without remediation, despite the passage of time and impacts of weathering. At Nantymwyn, comparison with five months' sampling in 2019 showed no significant change ($p > 0.05$) in metal concentrations compared to the same months in 1985. Parys Mountain showed an increase in filtered zinc concentrations of 2 % between 2004 and 2020. At Frongoch, however, a substantial reduction in its environmental impact was observed after remediation, including a 90 % reduction in total lead concentrations. Realisation that the pollution from these sites does not reduce over the decades since abandonment should galvanize the resolve to understand the highest priority sites, and where possible remediate them.

1. Introduction

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). Amongst the many elements of concern, zinc (Zn), cadmium (Cd), lead (Pb) and copper (Cu), the foci of this paper, 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; Thomas et al., 1985). While Zn is an essential element at trace levels for cellular processes, at higher levels it can cause functional impairments, especially to children, and at high concentrations is toxic to plant and animal life (WHO, 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 pollution (Plumlee and Morman, 2011), including problems with brain and bone development and the nervous system (Tchounwou et al., 2012; Thomas et al., 1977). Both 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} (Chen et al., 2022; Gall et al., 2015; Goodchild et al., 2021). For humans a daily intake of 140 μg Cd per day and above can cause skeletal damage, kidney damage and failure, and it is not believed to be beneficial at any level (WHO, 1996; Tchounwou et al., 2012). While Cu is an essential element

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https://doi.org/10.1016/j.jhydrol.2024.131011
Received 23 June 2023; Received in revised form 15 February 2024; Accepted 16 February 2024
Available online 7 March 2024

at trace amounts, at higher levels it can cause skeletal problems and anaemia, as well as damage to the liver and other organs (WHO, 1996).

Water is both a valuable commodity and an essential resource for life, with drinking water especially in demand. Globally, huge efforts are put into minimising wastage, such as leaks, maximising stores, via reservoirs, and avoiding controllable damage, such as pollution. Insensitively operated mines will pollute 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). 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, Zheng et al. 2020), including sites 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), Oceania (Rufaut et al., 2020, Wright et al., 2017), and Europe (Davis et al., 2000, Mullinger, 2004).

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). In the UK, metal pollution of rivers has been noted as one of the major concerns for water quality 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 South West Wales River Authority 1965–1974) have carried out reactive and investigative water quality monitoring, and where possible flow measurements, of waters at and downstream of mines. Despite limited assessment of the scale of metal contamination at sites for particular periods, there have been few attempts to explore possible changes in pollution levels over longer timescales since mine abandonment, mainly because of the temporal patchiness of stream metal data. This study tackles this research gap by collating and using all the available data for sites downstream of three contrasting abandoned metal mine sites in Wales (Figs. 1 and 2): Nantymwyn in Carmarthenshire, Parys Mountain

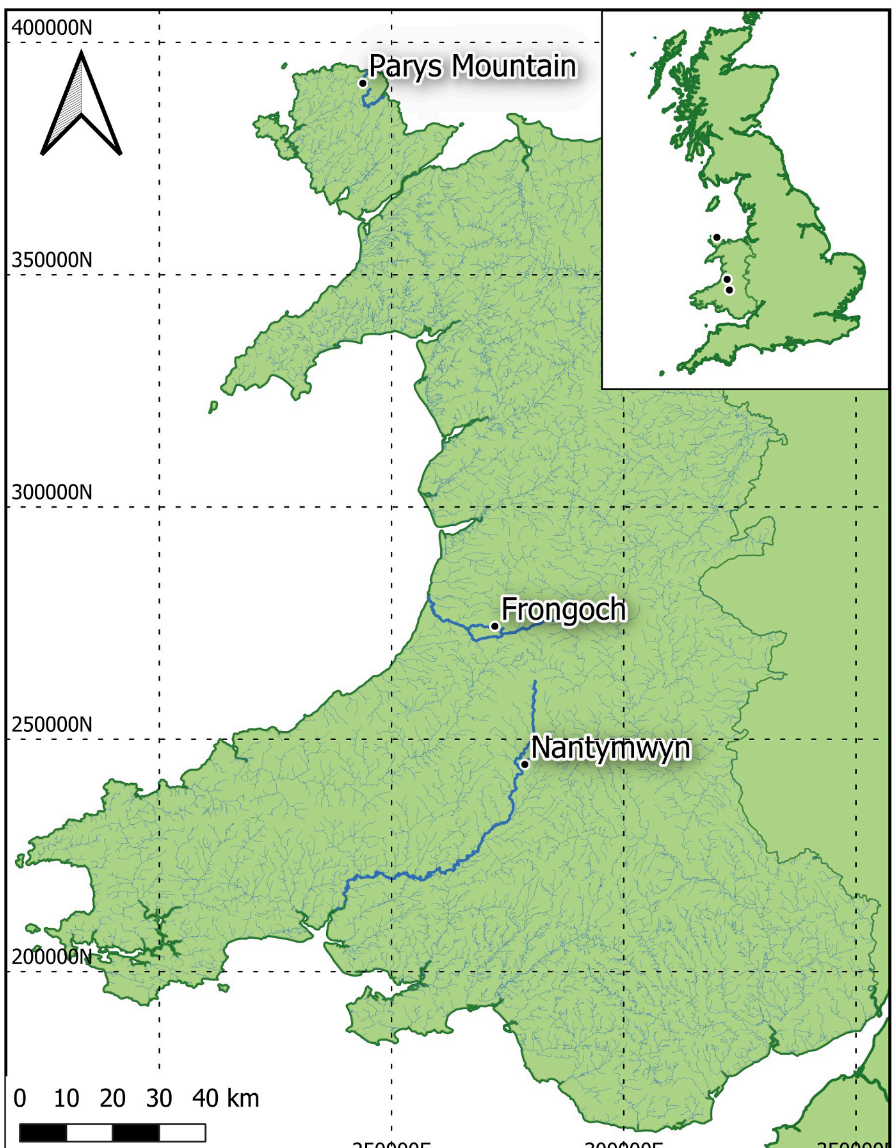

Fig. 1. Locations of the three abandoned metal mines, with the receiving watercourses highlighted, Wales, UK.

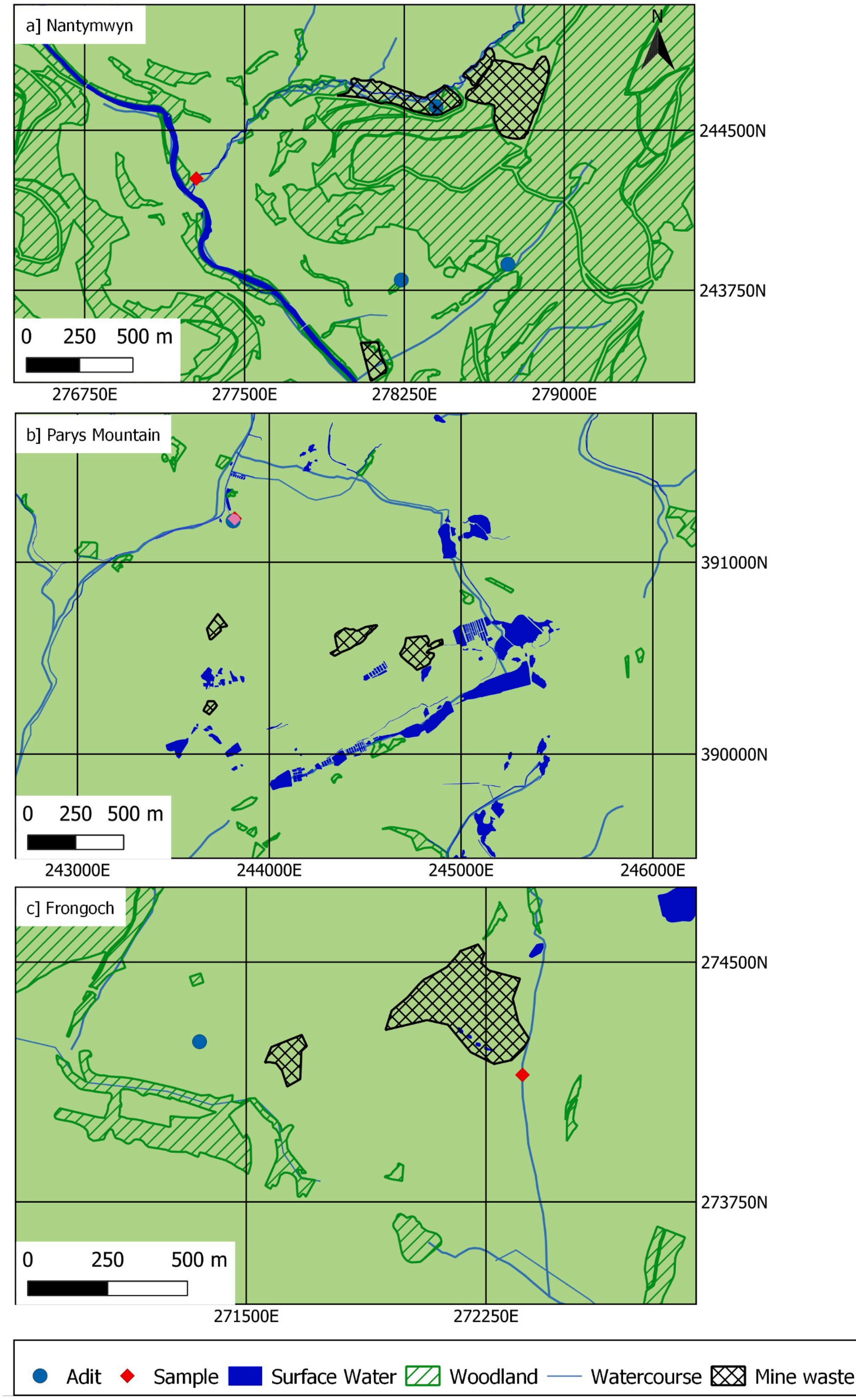

Fig. 2. Details of site locations, a] Nantymwyn, b] Parys Mountain, c] Frongoch. Blue circles denote mine water adits, red diamonds the sampling location. Crossed black denotes areas of mine wastes, and hatched green denotes forested areas. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

in Anglesey, and Frongoch in Ceredigion. These three sites vary in their size, elevation, period of operation, ore type, and date of closure or abandonment. The aim of the study is to use long-term data to assess the scale of recovery of streams immediately downstream of mines without remediation (Nantymwyn and Parys Mountain), compared with a mine that has undergone remediation measures (Frongoch).

2. Study areas

2.1. Nantymwyn

Nantymwyn (52°5′12′′ N; 3°46′20′′ W) is located 10 km north of Llandovery, Carmarthenshire, on the eastern side of the River Tywi

(Fig. 2a). It is located on Bala (Upper Ordovician) shales and grits, with mineral veins carrying galena (PbS) and sphalerite ((Zn,Fe)S) (Al-Atia and Barnes, 1975). The two main worked mineral lodes cross the site in a north-easterly direction, with noted pockets of cerussite ($PbCO_3$) and arsenic-bearing pyromorphite ($Pb_5(PO_4)_3Cl$) (Bevins, 1994). The mine operated irregularly from pre-Roman times, becoming one of the largest Pb mines in Wales in the 19th century (Hughes, 1992). Initially mining operations were conducted on the surface, then work moved underground, resulting in a complex subsurface system of workings (Hall, 2011). Existing records show that between 1824 and 1900 it was the third most productive non-ferrous metal mine in South Wales, raising over 81,000 tonnes of galena (Hall, 2014). A reduction in the commercial value of Pb and poor decisions by the mine's management resulted in the mine closing in 1900, before briefly reopening in 1915, and again in 1926, before final closure in 1932 (Hall, 2011).

The mine was drained by two main adits in the form of boat levels, horizontal shafts kept flooded to allow the transport of boats loaded with ore (Fellows, 2009; Hall, 2011). One of these, the Deep Boat Level, still drains the mine into the Nant y Mwyn (Nant is Welsh for stream). Mine workings continued below the level of the Deep Boat Level vertically for another 70 m, with six levels worked for ore, and during operation water was pumped up to the Deep Boat Level to drain 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 was considered for reopening in 1942 to provide Pb for the manufacturing needs of the Second World War (1939–1945), but the plan was abandoned as the work was prohibitively expensive (Hughes, 1992). Two streams are affected by the mine workings. To the north the Nant y Bai (the focus of this study) which flows through spoil heaps covering around 18 ha, and to the south the smaller Nant y Mwyn, which receives input directly from the Deep Boat Level. Both streams are circumneutral, with 75 % of pH values being between 6.6 and 7.2 ($n = 471$) (Natural Resources Wales, 2020). Although the site offers ecosystem services in the form of timber sales and recreational activities, the detrimental impacts on streams and habitats remain a serious concern (Boldy et al., 2021). Both streams flow into the River Tywi, which provides drinking water to Carmarthen, Neath, Bridgend, the Vale of Glamorgan, and Swansea via an abstraction point at Nantgaredig, and in times of drought it also supplies the Neath, Afan, and Tawe Valley (Welsh Water, 2019). The 120 km long river is 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, increasing the magnitude of low flows to ensure a greater reliable water supply at the abstraction point, 55 km downstream at Nantgaredig. These higher minimal low flows will also have improved the water quality of the River Tywi by increased dilution of metal inputs from the Nant y Bai and Nant y Mwyn. Dam construction used approximately 250,000 tonnes of spoil removed from the mine site (Hughes, 1992). Many of the streams flowing into Llyn Brianne have been monitored since 1981, first to investigate the causes of acidification, and then for their recovery from acidification (Edwards et al., 1990; Ormerod and Durance, 2009), allowing a comparison between these sites and the two streams at Nantymwyn. The remaining spoil at Nantymwyn apart from some lichens and bryophytes remains bare, with principal contamination from Pb and Zn. The spoil and tailings from the underground workings 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, but most of the catchments are under rough pasture.

Complaints about the impact of the mine on visual water quality and fish mortality were first recorded in the 19th century (Towy Board of Conservators, 1871). NRW's predecessor organisations contracted investigations into river pollution and possible remediation schemes in 1974, 1986, 1997, and 2010, with studies to improve understanding of the site ongoing throughout the period (Brabham and Umar, 2011), but the site's complexity and funding difficulties prevented implementation. Nantymwyn mine has been ranked the 11th of the top 50 highest priority metal mines for remediation in Wales (Mullinger, 2004). It causes the River Tywi to fail Water Framework Directive (WFD) standards for Zn for approximately 25 km (NRW, 2022; Williams, 2012). In 2020, NRW engaged the Coal Authority to review the "Reasons for Not Achieving Good WFD Status" and options for remediation (Coal Authority, 2020). Data from the Nant y Bai at the final sampling point before its confluence with the River Tywi were used for this study, with the details on its catchment shown in Table 1.

2.2. Parys Mountain

Parys Mountain mine (53°23′8′′ N; 4°21′2′′ W) is located 3 km south of Amlwch, Anglesey (Fig. 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 1880 s, 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 to 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 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

Table 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	1742	3.1	120	31,689
Parys Mountain	Dyffryn Adda Adit	1109	2.0	60	26,278
Frongoch	Frongoch Stream	2116	1.0	240	35,690

systems using Parys Mountain water (Cairns et al., 2022).

2.3. Frongoch

Frongoch mine (52°21′7′' N; 3°52′35′' W) is located 15 km south-east of Aberystwyth (Fig. 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 ha, 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 (deEdwards 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).

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 m^3 of this mine waste was capped to minimise infiltration. Finally, in May to July 2018 a further 7600 m^3 of mine waste was capped, and the remaining uncapped mine waste treated with a variety of experimental treatments to minimise run-off (deEdwards et al., 2021). Data for the Frongoch Stream were used for this study, which has a mean pH of 7.0 (n = 145) and its catchment details are shown in Table 1.

2.4. Pollution investigation history at the three sites

Concerns about the impact of pollution from metal mines were raised before these mines closed, with evidence of fish mortality due to metal mine pollution in the River Ystwyth noted in 1861 (Fisheries Preservation Society, 1868). Metal mines on the rivers Rheidol and Teifi were reported to increase fish mortality rates during high flow events in the 1920s (Carpenter, 1926, 1924), with flood-deposited metals damaging farmland causing harm to horses and cattle (Griffith, 1919). Harm to farmland continues today, with elevated levels of elements of concern recorded in soils, flora, and farm products such as eggs and lamb (Sartorius et al., 2022). The issue of pollution from metal mines more generally was raised in Parliament at least 70 years prior to mine closure (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 pollution have changed repeatedly over the century since these mines closed, as have their priorities, scientific abilities, and legal frameworks. The Zn pollution 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 polluted 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 polluted by the metal mines to the point that mine-affected waters from nearby catchments were diverted into it to avoid polluting 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, changed which stream received the majority of the polluted water, but not the eventual destination, the Irish Sea (Younger and Potter, 2012).

3. Data and methods

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 to a minor extent (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. 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). At Nantymwyn, a single sampling point on the Nant y Bai downstream of the main mine site and its waste was chosen. At Frongoch a similar sampling point was selected on the Frongoch Stream. As pollution 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 pollution flows, and the mine water discharge at Parys Mountain should be noted as different to the other two sampling points. There is balance of long-term data availability against sampling point similarity, and broad trends over the sampling periods should be evident.

Collection and analytical procedures remained broadly unchanged over the period of record. At each monitoring point two 125 ml 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, 1998, 2010). 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 to 2021 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. Results

4.1. WFD standards and long-term mean concentration for waters downstream of the three mines

The WFD EQS for Zn, Cd, Pb and Cu for the relevant river or catchment, and the average concentration of those metals at each site, are presented in Table 2. As can be seen in Table 2, Frongoch and Nantymwyn are dominated by Zn and Pb, while Parys Mountain is 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 (Figs. 3-5), and b) means of aggregated data for different parts of the long-term record (Tables 3-5), for each mine site separately.

The data available for total Pb and Cd, and filtered Zn and Cu, are presented for each site as annualised box plots, Fig. 2 for Nantymwyn, Fig. 3 for Parys Mountain, and Fig. 4 for Frongoch. 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.

4.2. Nantymwyn

The historical record for Nant y Bai is present in Fig. 3 and Table 2. 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 to 2019 (Fig. 3).

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

Table 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*	551	66,092	13,180	2,510
Cd (total)	$\leq$ 0.08	2.9	163.3	26.9	5.5
Pb (total, bioavailable)	1.2	303	26	1,220	127
Cu (dissolved, bioavailable)	1	3.4	41,713	15.4	3.1
Conductivity, $\mu S\ cm^{-1}$	–	55.6	3602	139.4	96.7
pH	–	6.77	2.51	6.72	7.35
Temperature, °C	–	10.7	11.1	11.2	11.6
n	–	244	216	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).

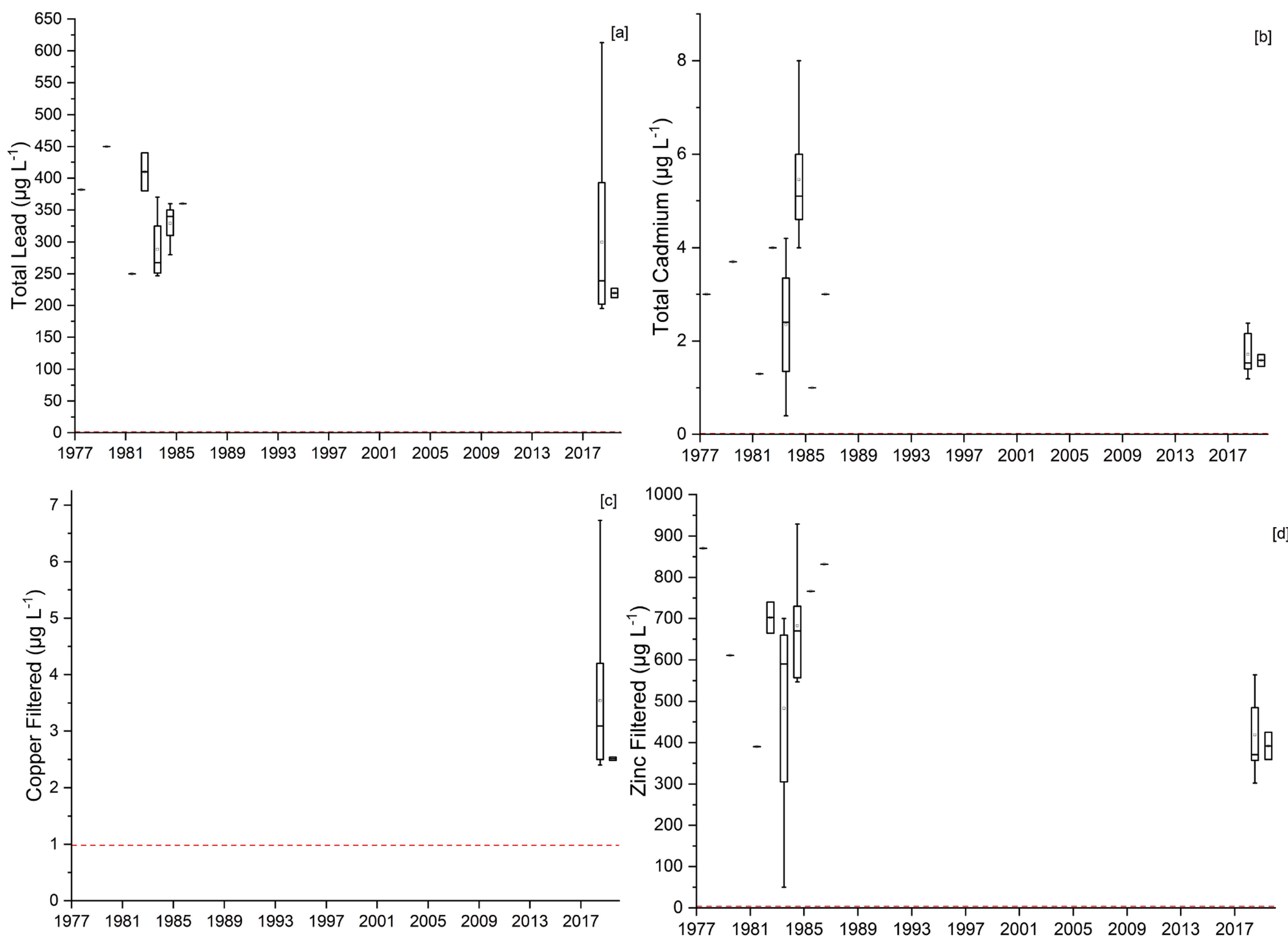

Fig. 3. Box and whisker plot of the temporal variation in metal concentrations, Nant y Bai, Nantymwyn 1978–2021; a) Total Pb, b) Total Cd, c) Filtered Cu, d) Filtered Zn. Boxes depict the inter-quartile range (IQR) with a horizontal line showing the median concentrations, and the mean concentrations 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). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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.

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 to 2009 (Fig. 4). 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 4). Although progressive and statistically significant reductions in mean total Cd (from 174

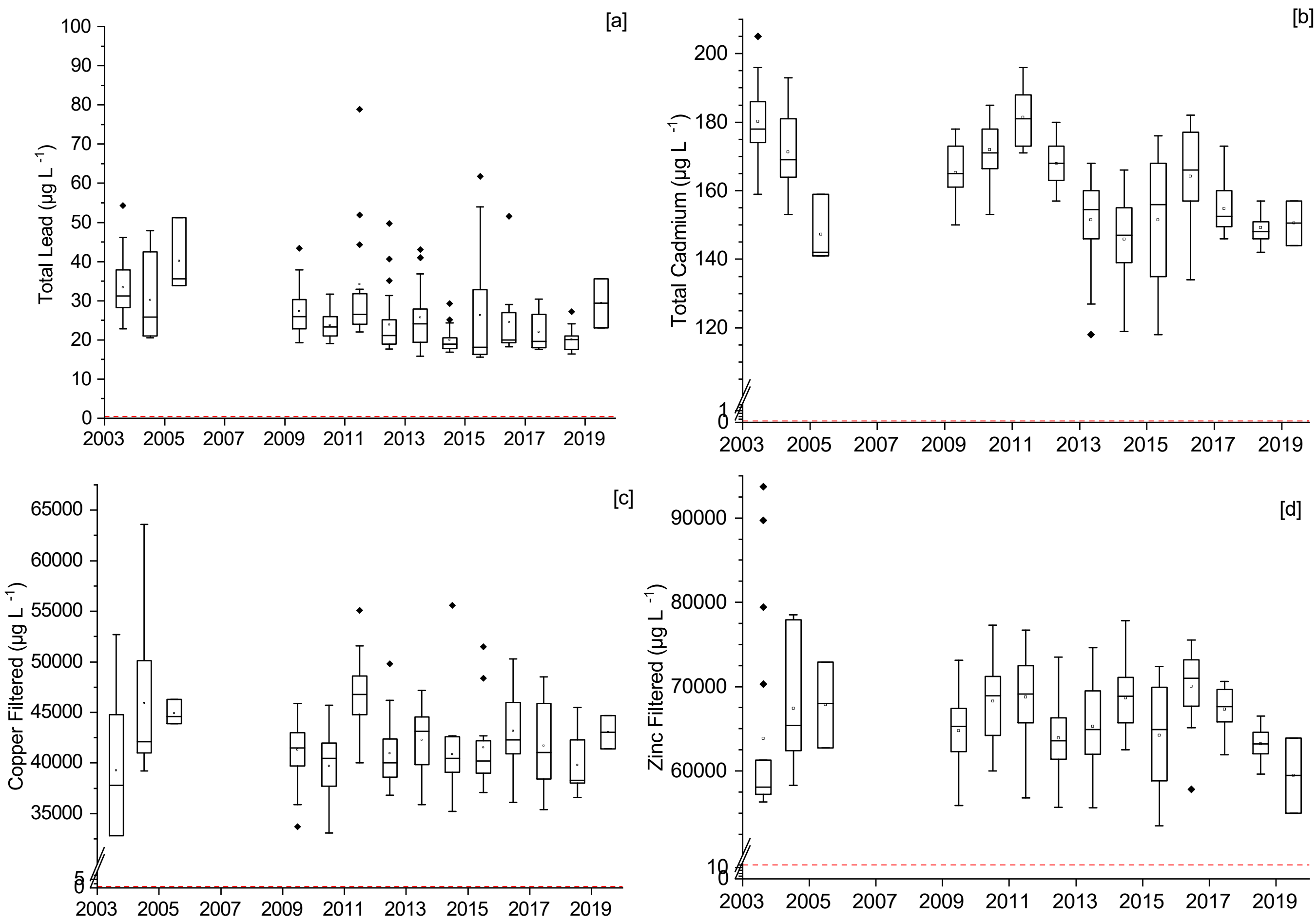

Fig. 4. Box and whisker plot of the temporal changes in metal concentrations, Dyffryn Adda Adit, Parys Mountain 2003–2020. a) Total Pb, b) Total Cd, c) Filtered Cu, d) Filtered Zn. Boxes depict the inter-quartile range (IQR) with a horizontal line showing the median concentrations, and the mean concentrations 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). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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 Fig. 4 gave Zn, Pb, and Cu concentrations taken within the range of the 15 samples taken in December between 2003 and 2020.

4.4. Frongoch

Frongoch is the only site to have undergone remediation, in a series of interventions between 2011 and 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 %. 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 polluted waters for a further improvement in resultant concentration of metals of concern. 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 due to the clean waters of the diverted Upper Frongoch Stream diluting polluted surface waters from the site (Fig. 5). Despite the fact that 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 (deEdwards 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 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) 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 Fig. 5. The largest falls occurred following the first

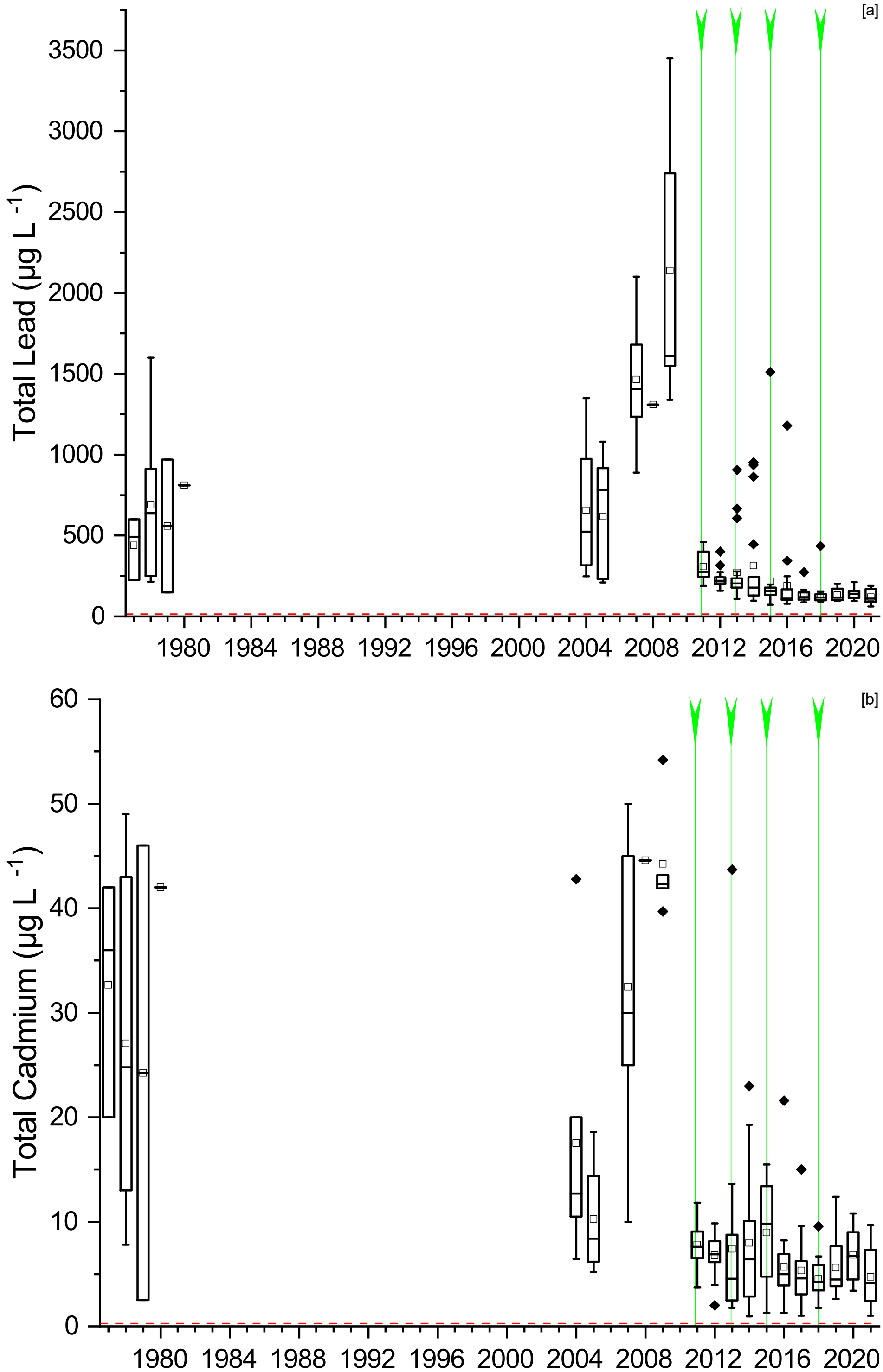

Fig. 5. Box and whisker plot of the temporal variation in metal concentrations, Frongoch Stream, Frongoch Lead Mine 2004–2021. a) Total Pb, b) Total Cd, c) Filtered Cu, d) Filtered Zn. Boxes depict the inter-quartile range (IQR) with a horizontal line showing the median concentrations, and the mean concentrations 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. (For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)

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 Fig. 5. The falls in metal parameters were statistically significant (Table 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 %.

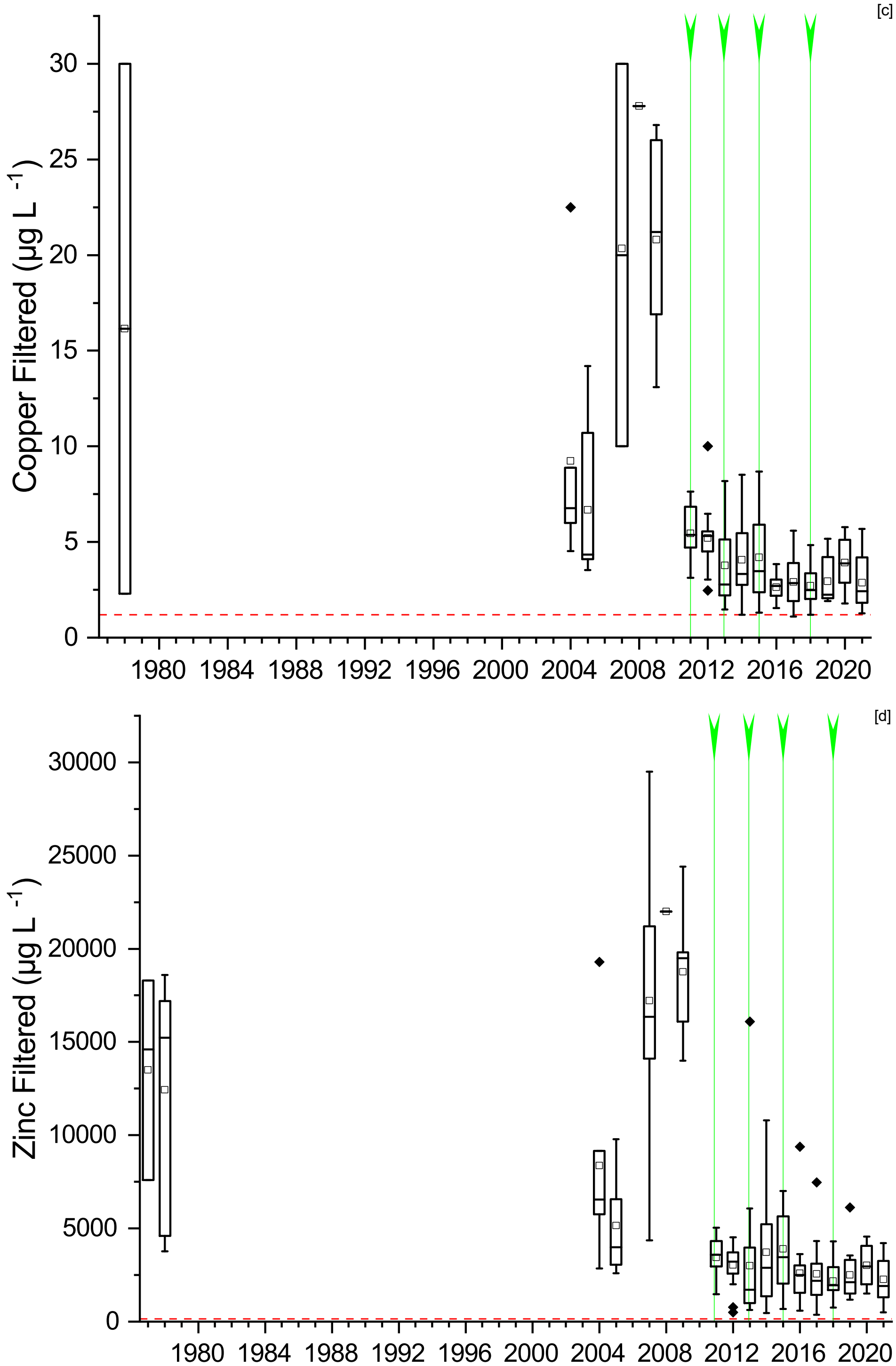

Fig. 5. (*continued*).

Table 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 Student's *t*-test.

Nantymwyn	1978–87			2019–2020			Difference	Stat. Sig.
Metal (µg L^{-1})	Mean	Standard Deviation	n	Mean	Standard Deviation	n		
Filtered Zn	661	196	16	414	83	13	−247 (−38 %)	$p < 0.05$
Total Cd	4	2	17	2	0	13	−2 (−50 %)	$p < 0.05$
Total Pb	334	299	17	287	125	13	−47 (−14 %)	NS
Filtered Cu			0	3	1	13	N/A	

Table 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 Student's *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	65,494	10,006	31	66,002	4,862	115	66,513	5,061	68
Total Cd	174	15	31	167	13	115	152	14	68
Total Pb	33	9	31	27	11	115	23	9	68
Filtered Cu	42,168	7,757	31	41,794	5,514	115	41,372	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

Table 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 Student's *t*-test.

Frongoch	2004–2011			2018–2021			Difference	Stat. Sig.
Metal (μg L^{-1})	Mean	Standard Deviation	n	Mean	Standard Deviation	n		
Filtered Zn	13,180	7,639	37	2,510	1,294	34	−10,670 (−81 %)	$p < 0.01$
Total Cd	27	16	37	6	3	34	−21 (−78 %)	$p < 0.01$
Total Pb	1,220	729	37	127	37	34	−1,093 (−90 %)	$p < 0.01$
Filtered Cu	15	9	37	3	1	34	−12 (−80 %)	$p < 0.01$

5. Discussion

5.1. 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, Fig. 5). The other unremediated sites still show variations over time, though this is not a clear indication of decreased or increased pollution 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. However, while 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. 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 ($p > 0.05$).

Parys Mountain also shows a statistically significant decrease in total Cd ($p < 0.05$) and Pb ($p < 0.01$) concentrations between 2004–2020, 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 1000 μg L^{-1} over 16 years shown (Fig. 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 oxidise and then pollute water entering the mine workings, it shows that the pollution 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, 2016). Subterranean movements within the mine workings, as wooden supports rotted and failed, and polluted water 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 pollution at a later date.

5.2. Remediation must be targeted

Remediated sites can still have elevated levels of metal in the water, especially during and after heavy rainfall (Nordstrom, 2009; Pool et al., 2013.). The Nant y Fendrod in Swansea was affected by 240 years of metal smelting, resulting in elevated levels 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, levels 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 polluted long after the polluting 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 from such monitoring at the abandoned Wheal Jane tin mine in Cornwall, a long-term decay of the concentrations of both Zn and Fe has been observed between 1991 and 2011 (Wyatt et al., 2013), which may be similar to that experienced at Frongoch and Nantymwyn in the initial decades after closure.

5.3. Implications for future pollution management and remediation

Over longer timescales than the 1978–2021 record used in 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 and 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., 2013).

A modelling study of a metal mining impacted watercourse 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 pollution levels 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, and changes to extreme flows and pollutant transport due to climate change (Byrne et al., 2020), this shows that there has been and will not be 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 showing the harmful effects of climate change 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 polluted water from abandoned mines entering rivers (Douville et al., 2021; Hanlon et al., 2021). Additionally, an increase in the occurrence of droughts would increase the severity of subsequent rainfall flushing oxidised pollutants into watercourses, as well as increasing the proportion of a river's flow coming from a polluted groundwater source (Hanlon et al., 2021; Nordstrom, 2009). The abandoned Annapolis Pb Mine in Missouri, USA, was remediated in 2007 to reduce the elevated levels 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, levels 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 pollutes during extreme flow and rainfall events, but also affect the design and size of any remediation techniques used.

5.4. Limitations and future research needs

Data on these mines or mining areas has been collected scientifically since at least 1919 (Griffith, 1919), with annual reports generally noting pollution from the 1960s onwards. The invaluable early data of Carpenter (1924, 1926) on metal mine pollution 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 in this report are from 1978. Anecdotally, these data were available on paper in the late 1970s, but to date we have not been able to locate them. However, a future worthy project would be locating non-digitised archives of these data to extend the temporal range of environmental pollution values.

The three sites 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" – the sites used for this study are three of only 102 marked "large" (Natural Resources Wales, 2020). The three mines cannot represent the nuances of changes in pollution 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. Anthropogenic climate change will affect extreme low and high flows, changing how elements of concern will enter the watercourses, and their levels (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.

6. Conclusions

1. Analysis of archived water quality records immediately downstream of three metal mines in Wales abandoned 90–115 years ago shows clearly that in each case metal 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), total Cd (by 50 % from 4 to 2 μg/L) and total Pb (14 % reduction from 354 to 287 μg/L) 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) and Total Cd (by 14 % from 174 to 152 μg/L), but virtually no change in dissolved Zn (up 2 % from 65,494 to 66,518 μg/L) and dissolved Cu (down 2 % from 42,168 to 41,372 μg/L).
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, Total Pb by 90 % from 1,220 to 127 μg/L, Total Cd by 78 % from 27 to 6 μg/L and dissolved Cu by 80 % from 15 to 3 μg/L. 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 pollution 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 pollution problems and the findings of this study may apply only to metal concentrations withing 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 pollution and in the design of remediation strategies.

Research data.

The data used in this article are available from the NRW Data Archive, via https://naturalresources.wales/evidence-and-data/accessing-our-data/request-environmental-data/?lang=en.

CRediT authorship contribution statement

Aaron M.L. Todd: Investigation, Visualization, Formal analysis, Writing – original draft, Writing – review & editing. **Iain Robertson:** Writing – review & editing, Supervision, Investigation, Funding acquisition. **Rory P.D. Walsh:** Writing – review & editing, Methodology, Investigation, Conceptualization. **Patrick Byrne:** Writing – review & editing, Software, Methodology, Investigation. **Paul Edwards:** Writing – review & editing, Investigation. **Thomas Williams:** Writing – review & editing, Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

This work was supported by the EU Knowledge Economy Skills Scholarships (KESS 2), funding Aaron's PhD, allowing this research to be undertaken. KESS 2 is a pan-Wales higher level skills initiative led by Bangor University on behalf of the HE sector in Wales. It is part funded by the Welsh Government's European Social Fund (ESF) convergence programme for West Wales and the Valleys.

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