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Article

Source apportionment of mine contamination across streamflows

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ABSTRACT

Globally, metals released by mine waste represent a challenge for protecting water quality and ecosystems. Understanding metal dispersion in catchments is critical for developing efficient remediation strategies and reducing contamination from mining activities. Efforts to address the issue have been constrained by diffuse sources and variation of source contributions across streamflows. In the UK, metal source apportionment is typically addressed using monitoring strategies with low spatial resolution, which can underestimate the contribution of diffuse sources. In this proof-of-concept study, diffuse sources were accurately apportioned in a mining-impacted catchment in Mid-Wales (UK), using a hydrogeochemical approach with combined continuous tracer injections, gulp injections, and streambed sediment geochemistry. The continuous tracer injections identified a major Zn and Pb point source, diffuse sources due to mine waste tip runoff, and potential ground-water contributions. Variations in source contributions were estimated during high and low flow conditions, with Zn having similar sources and importance across streamflows and Pb being released mainly from overground tips during high flow conditions (22% Pb under low flow and 80% Pb under high flow). The distribution of metal-bearing sediment along the stream sheds light on metal release mechanisms across streamflow conditions. This hydrogeochemical approach for source apportionment, builds on common monitoring methods, and represents a substantial advance in accounting diffuse mine contamination sources, understanding potential metal release mechanisms, and designing remediation strategies.

1. Introduction

Identifying and remediating mine contamination sources is a major global challenge facing environmental managers. The extensive nature of historical mining operations and multiple potential contamination sources confound source apportionment in impacted watersheds (Baresel et al., 2006). Traditionally, point sources of mine contamination (e.g., adits and small tributaries draining mine wastes) have been the focus of monitoring as they are generally easily located and quantified in terms of metal loading input to watersheds (Mayes et al., 2010; Environment Agency 2008). In recent years, a plethora of research has established diffuse sources of mine drainage (e.g., mine spoil runoff and groundwater efflux) as critical sources of metal loading at the watershed scale (e.g., Environment Agency,2021; Jarvis et al., 2019; Runkel et al., 2016). Diffuse contamination can be episodic, associated with rainfall events that mobilise sediment-bound and aqueous metals into stream channels (Cánovas et al., 2010; Gozzard et al., 2011), or continuous subsurface and groundwater contaminated efflux (Andarani et al., 2021; Mighanetara et al., 2009; Runkel et al., 2016).

Worldwide, governments and regulators attempt to protect water quality from metal contamination through legislation and strategic plans. China legislated the Action Plan for Water Contamination Prevention and Control (Zhou et al., 2021), and the USA established the Clean Water Act (Rotman et al., 2021). The UK Government has specifically highlighted the need to reduce contamination of the water environment from abandoned metal mines in a recent 25 Year Environment Plan (DEFRA and HM Government, 2021), with legally binding targets being listed in the new Environment Bill (UK-Parliament, 2021). Such legislation responds to the Water Frame Directive established by the European Union (Brack et al., 2017). In the UK, a rich metal mining history has produced significant quantities of toxic materials that contaminate approximately 3000 km of watercourses (Mayes et al.,

2010). Contamination from abandoned metal mines is a major cause of failure to achieve environmental objectives set out in statutory River Basin Management Plans (Environment Agency, 2021). Furthermore, extreme weather events such as drought and flooding are becoming more frequent as a consequence of climate change (Arnell et al., 2021), enhancing the need to apportion diffuse sources in mining-impacted catchments. Flooding events can increase the chances of water-and sediment-borne dispersion (Foulds et al., 2014), and drought events exacerbate the detrimental effect of contaminated groundwater input in riverine systems (Byrne et al., 2020).

The UK approach to source apportionment of mine contamination, used by environment regulators, stems from Environmental Agency reports such as the Abandoned Mines and the Water Environment (Environment Agency, 2008) and the Prioritisation of Abandoned Non-coal Mine Impacts on the Environment Project (Environment Agency, 2012a). A past report by the Environment Agency (2008) flagged the inadequacy of monitoring methods to apportion mining sources, failing to implement strategies to reach EU Water Frame Directive 2000/60/EC (WFD) targets (DEFRA, 2014). Consequently, the Environment Agency (2012a) scheme called for a national-scale screening of water quality data and 338 metal mines were identified as potential metal sources in waterbodies (Mayes et al., 2009). These results helped to focus monitoring and remediation schemes, although further investigations are needed to accurately apportion metal sources at the catchment scale. Mayes et al. (2008) concluded that metal loading-base methods, such as those described in Mayes et al. (2005, 2008) and Kimball et al. (2002), are adequate to apportion instream metal contribution from point and diffuse sources. These methods can measure metal load variation across streamflows (Mayes et al., 2005; 2008) and capture spatially detailed metal inputs from diffuse sources (Kimball et al., 2002). Although, the method proposed in Kimball et al. (2002), the continuous tracer injection, has been rarely implemented in the UK (Onnis et al., 2018; Byrne et al., 2020, Byrne et al., 2020) and the scarcity of detailed source apportionment underestimates diffuse source driving major attention and remediation strategies onto point sources.

The methods described by Mayes et al. (2005, 2008), in this manuscript referred as the "common method", have been applied extensively in the literature and by UK environmental authorities (Mighanetara et al., 2009; Gozzard et al., 2011; Jones et al., 2013; Jarvis et al., 2019). The common method involves identifying unknown sources along a main mining-impacted catchment via reconnaissance surveys, water quality, and discharge monitoring (Mayes et al., 2008). Instream waters are sampled up- and downstream point and suspected diffuse sources and on intermediate locations along the main channel. Flow measurement can be collected using V-notch, bucket, stopwatch, and velocity-area methods or interpolated with GIS-based methods (Mayes et al., 2008). Gulp injections have recently become the most ubiquitous method for gauging streamflow (Jarvis et al., 2019; Onnis et al., 2018; Edwards, 2022) because they can be used to take measurements in irregular channels with rocky sections and shallow water (Moore, 2005; Richardson et al., 2017). Flow measurement coupled with aqueous metal concentrations allows metal loads to be calculated along the channel. The UK Department for Environment, Food and Rural Affairs (DEFRA, 2022) recognised the efficiency of the common method but highlighted the need to increase sampling frequency and locations to inform water treatment schemes. The low sampling resolution cannot locate and quantify specific diffuse sources such as subsurface and groundwater inflows or mobilisation of metals from transient sources such as streambed sediments limiting potential water quality improvements to remediation of point sources only. Furthermore, due to scarce waste and sediment monitoring, instream metal loads are rarely associated with the respective sources. Therefore, metal dispersion mechanisms remain unknown.

This research evaluates the benefits of adding the continuous tracer injection (Kimball et al., 2002) and sediment analysis to the common method. During the continuous tracer injection, a salt tracer is injected into the stream upstream of the mining area at a known concentration and rate. Dilution of the tracer with distance downstream reveals water entering the stream from tributaries or diffuse subsurface sources and is used to establish streamflows at high spatial resolution (De Giudici et al., 2018; Runkel et al., 2016). Combining the streamflows with metal concentrations allows the calculation of metal load variation along the stream length; hence, sources and sinks of metal mass instream water samples are collected along the main channel and tributaries. Therefore previously unknown sources can be apportioned (Runkel et al., 2018; Byrne et al., 2017). The continuous tracer injection requires steady flow through a few days to allow the tracer to be dispersed in the stream water. This requirement limits the applications, and although it is extensively used in the USA, only a few cases of continuous tracer injection applied in the UK were conducted by the authors in Wales (Onnis et al., 2018; Byrne et al., 2020) and in Scotland (Byrne et al., 2020). Metal load variations along the stream are then associated with streambed sediment geochemistry and mineralogy to identify processes releasing metals across the different streamflow conditions.

This study aims to demonstrate the application of a "hydrogeochemical approach" capable of identifying and quantifying point and diffuse metal sources across streamflows by combining the monitoring advantages of gulp injection, continuous injection, and streambed geochemistry. Using an exemplar study site in central Wales (UK), the specific objectives are to i) identify and quantify instream Pb and Zn loading from point sources and diffuse sources under a range of streamflows combining the continuous tracer injection with the common method; ii) establish the geochemical processes driving metal dispersion from in-channel and stream bank sediment; iii) demonstrate the efficiency of the hydrogeochemical approach in apportioning diffuse metal sources by comparing estimated Zn and Pb metal sources with historical data. The work presented here supports the development of improved conceptual models of mine contamination dynamics and accurate metal source apportionment that directly inform mine site remediation decisions.

2. Materials and methods

2.1. Study site

The study site is the Nant (stream) Cwmnewydion which flows into the Nant Magwr, a tributary of the Afon Ystwyth in Mid Wales, UK (Fig. 1). This stream is impacted by historical metal mining, causing failures of environmental quality standards (EQS, DEFRA, 2014) for Pb, Zn, and Cd up to 19 km downstream in the Afon Ystwyth (Environment Agency, 2012b; Natural Resources Wales, 2016). The watershed lies within a Special Landscape Area of National Importance for its ecological and archaeological values (Dyfed Archaeological Trust, 2016) and exemplifies a common conflict between the remediation of mine sites and the protection of human heritage (Mayes et al., 2010). The area is mainly underlain by Silurian mudstones and sandstones of the Devil's Bridge Formation of Upper Llandovery (Telychian) age (438.5–433.4 Ma) (British Geological Survey, 2004). The permeability of the Silurian basement is low and limited to fracturing in the mined areas. The hills around the Nant Cwmnewydion watershed are also covered by glacial deposits (diamicts), and the valleys contain recent alluvium (clay, silt, sand, and gravel) (Fig. 1). In the upstream part of Nant Cwmnewyddion (0–1.5 km) the streambed is dominated by the rock basement with a 0.5–1 m width. Moving downstream (1.5–2.5 km), the water level occasionally disappears into the streambed composed by pebbles and coarse sand under low flow conditions. In the following 2.5–3.0 Km, the rock basement characterised the streambed. Around 3 km, the streamside alternated depositional and erosional banks, with fluvial deposits dominating the streambed towards the confluence with the Afon Ystwyth. The hydrogeology of the stream is highly influenced by the mining works. A southwest-northeast trending normal fault contains the exploited Frongoch mineral lode comprising Cu, Pb, Zn, and Ag. The
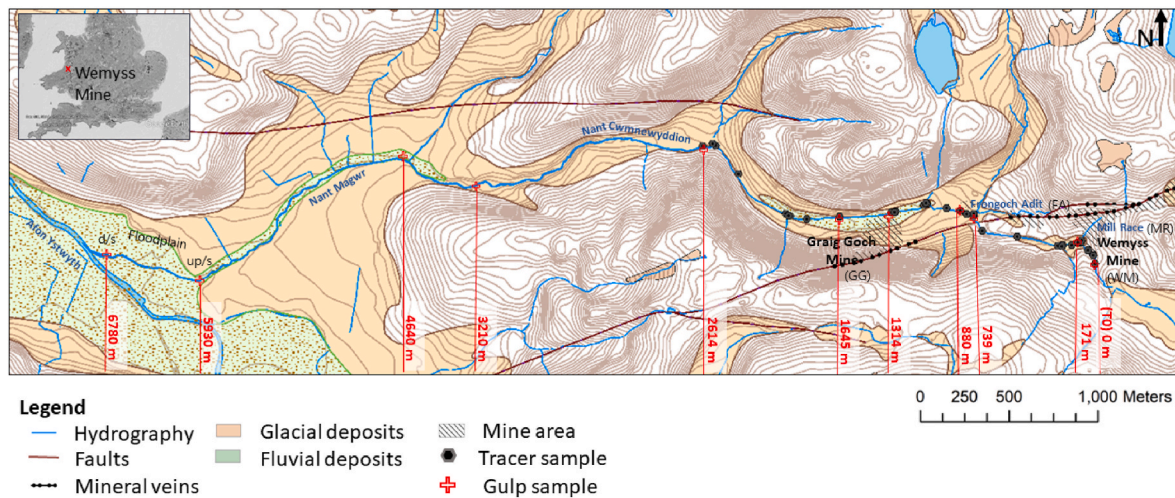
Fig. 1. Tracer injection and gulp injection sample sites along the Nant Cwmnewydion and the Nant Magwr. Red text = the distance along the stream below the injection site (T0, 0m). WM = Wemyss Mine; MR = Mill Race; FA Frongoch Adit; GG = Graig Goch Mine; floodplain upstream (up/s) and downstream (d/s) sample areas. DiGMapGB-50 [SHAPE geospatial data], Scale 1:50000, Tiles: ew178, Updated: 1 October 2013, BGS, Using: EDINA Geology Digimap Service (www.digimap. edina.ac.uk, Downloaded: 03-06-2016), modified with ArcGIS v.10.

Frongoch, Wemyss and Graig Goch mines exploited this mineral lode in the 18th and 19th centuries. The Frongoch Mine works were located in the adjacent Nant Cell catchment, although, underground works connected the listed mines. The minerals present in the ore veins are sulfides, including galena, sphalerite, and occasional pyrite, as well as gangue minerals comprising mainly quartz, feldspar, illite, and chlorite. Other reported Pb-bearing minerals are anglesite and plumbojarosite (Palumbo-Roe and Dearden, 2013).

2.2. Analysis of historical streamflow and metal concentration data

Annual hydrograph records at the downstream Afon Ystwyth gauge station 63001 (Ystwyth at Pont Llolwyn) indicate a 'flashy' stream system with high inter- and intra-annual variability with minimum and maximum daily streamflow values of 0.8 and 74.7 m^3/s, respectively, in 2016 (NRW station 63001). An analysis of historical flow records by Lynch et al. (2017) identified extended periods (weeks) with streamflow higher or lower than the annual mean (8.37 m^3/s in 2016). The observed high variability is typical of the temperate maritime UK climate, which is influenced by the North Atlantic Oscillation, storm tracks, and blocking anticyclones (Watts et al., 2015). In this study, streamflow percentiles (Q values) were derived from daily flow data spanning 1963 to 2017 (NRW station 63001). At Nant Cwmnewydion, the streamflow estimated at the floodplain upstream location, coordinate 52°22′13″N, 003°54′27″W (5930 m in Fig. 1), were defined as low flow when lower than 394 L/s (Q75 and above), high flow when more than 900 L/s (Q25 and below), and moderate flow when falling between Q25 and Q75 (USGS, 2011). Very high flows were classified as having Q values less than Q5 (streamflow above 2102 L/s). Streamflow conditions are reported hereafter as the date of the sampling campaign, followed by very high flow (vHF), high flow (HF), moderate flow (MF), or low flow (LF).

Historical metal concentration and load data were extracted from reports produced by the consultancy Atkins (2008) and the regulator Natural Resources Wales (Environment Agency, 2012b; Natural Resources Wales, 2016; Williams, 2016). Atkins (2008) monitored the Nant Cwmnewydion monthly from January to December 2007 and collated historical data provided by Environment Agency (1975–1980), Applied Geology Ltd, and Environment Agency reports. Sample sites were chosen following the main inputs and outputs of the hydrogeological system. The streamflow was gauged using various methods depending on the stream segment (electromagnetic flow meter, gauge boards, and weirs). The analysis presented in Environment Agency

(2012b) followed the diversion of a clean stream to prevent it from entering the Frongoch mine workings implemented in 2011 (Natural Resources Wales, 2016). The streamflows were collected at strategic locations following previous works. Furthermore, streamflow and water quality modelling was implemented through the Low Flow Enterprise software and the mathematical mass balance model at a catchment scale (SIMCAT). Finally, Natural Resources Wales monitored the area from 2016 by measuring the streamflow with gulp injection (Williams, 2016).

2.3. Source apportionment under steady streamflow conditions

2.3.1. Continuous tracer injection and metal concentration analysis

High spatial resolution streamflow measurements were estimated under MF with a continuous tracer injection (see Kimball et al., 2002). The tracer injection started on the Nant Cwmnewydion above Wemyss Mine to 2614 m downstream (where 0 m, or T0, is the tracer injection site; Fig. 1). A solution of 69 g/L Br, obtained by dissolving 35 kg NaBr in 370 L of stream water, was injected into the stream at a constant rate of 195 mL/min for 31 h starting at 13.00 on 29/07/2016. The experiment requires steady streamflow conditions from the injection time until the end of sampling. The steady flow was monitored by measuring the water level with a pressure transducer at 1615 m downstream from the injection. The pressure averaged 146,800 psi (relative standard deviation, RSD = 0.04%) during the sampling time 12.00 p.m.–6 p.m., and 146,700 psi (RSD = 0.12%) during the overall tracer injection time (31 h). At the same location, Br tracer arrival was recorded with a Br probe (INW TempHion Bromide probe). Bromide concentration increased from the stream background value of 0.08 mg/L, to the stable plateau concentration of 1.76 mg/L (Relative Standard Deviation = 4%). During the plateau time, synoptic water sampling of 24 stream sites and 22 visible inflows was conducted on 30/07/2016 with an average interval of about 10 min between sampling points (Fig. 2a). Sampling points were located based on their proximity to mining waste, observed mineral precipitations, downstream and upstream of identified inflows, and at regular intervals in long stream segments with no clear source evidence (Fig. 1). Inflow samples included tributaries and riparian seeps. Physicochemical parameters, including pH, electrical conductivity (EC), and temperature were recorded at all sample points. At each sample sites a water sample was collected and split into three aliquots: i) 0.45 μm filtered and acidified with 1% v/v of HNO_3 (for filtered cation analysis); ii) unfiltered and acidified with 1% v/v of HNO_3 1% (for unfiltered, total, cation analysis); and iii) 0.45 μm filtered unacidified (for anions
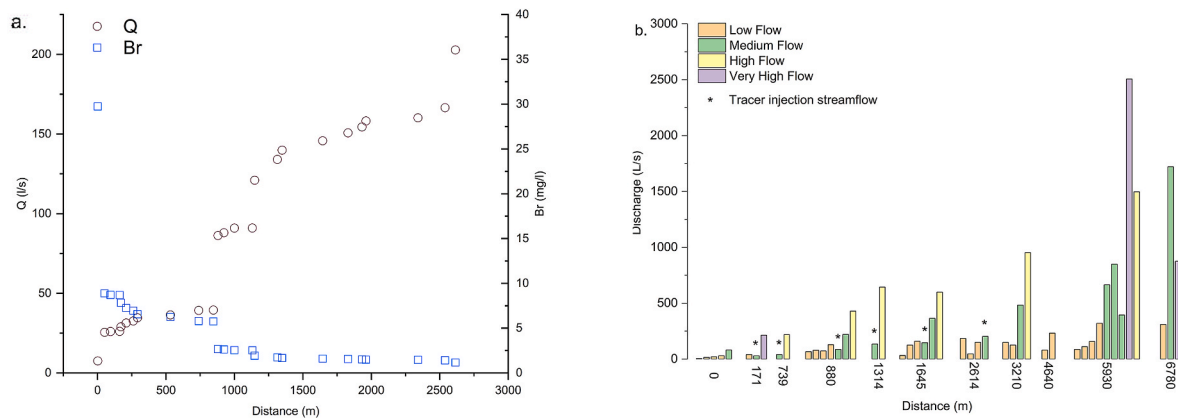
Fig. 2. (a) Bromide concentrations and streamflow estimates from the steady-state continuous tracer injection (from 0 m to 3000 m) and (b) streamflow estimates from gulp injections under variable streamflows (from 0 m to 6780 m). Streamflows estimated with the continuous tracer injection are indicated by the arrow in (b).

analysis). Ultrapure acid (67%) for trace metal analysis and 0.45 μm regenerated cellulose filters (Whatman SPARTAN) were used to process the samples. Samples were filtered, then acidified within 1 h of collection at an on-site processing laboratory. Samples were stored in Nalgene polyethylene bottles. Bromide analysis was carried out by IC (Ion Chromatography Dionex ICS-25000) and ICP-MS (Inductively Coupled Plasma-Mass Spectrometry Varian 810). Filtered and unfiltered cations (Ca, K, Mg, Na, Si, Zn, Pb, Fe, Mn, Al, Cd, Cu, Al, As, Co, Sr, Ag, Li, Tl, Mo, Ni, Au, Ce) were measured using ICP-AES (Inductively Coupled Plasma - Atomic Emission Spectrometer-Varian 810), ICP-OES (ICP-Optical Emission Spectrometer Thermo Scientific iCAP 6500 Duo) and ICP-MS (ICP- Mass Spectrometer Varian 720 for 2016 and Agilent 7900 for 2017 analysis). Water analysis included TMDA 70 (Certified Reference Waters for Trace Elements – Environment Agency, 2008), EP-H (Matrix Material Environ MAT Drinking water), repetition of standards and sample duplicates to ensure data precision and accuracy. The limit of detection (LOD) was verified with field and laboratory blanks. The data and analysis presented herein focused on Zn and Pb as these are the major contaminants of concern in this watershed (Foulds et al., 2014), and generally, in metal mining-impacted watersheds (Crane et al., 2017; Jabłońska-Czapla et al., 2016; De Giudici et al., 2014). The LOD values for Zn and Pb were 10 μg/l and 0.33 μg/l, respectively. Zinc and Pb values for certified materials were within the certified confidence values. Precision for Zn and Pb, expressed as the relative standard deviations (RSD%) and calculated as the standard deviation and average ratio, were within 0.9% and 0.02%, respectively.

2.3.2. Source apportionment data from the continuous tracer injections

Analysis of metal concentrations and streamflows focussed on identification and quantification of mine contamination sources. These were determined using the method described in Kimball et al. (2002), Runkel et al. (2013), and Byrne et al. (2017), and are described as follows. Please, refer to the original papers for further information.

1) Streamflow at each synoptic sampling site was calculated as:

$$Q = \left(\frac{q \left(C_{inj} - C_{bg} \right)}{C_p - C_{bg}} \right)$$

Where:
  Q = stream streamflow
  q = injection streamflow
  C_{inj} = injectate concentration
  C_{bg} = salt concentration in natural water (background).
  C_p = tracer concentration during plateau

2) Metal loads at each synoptic sample site were calculated as the product of metal concentration and streamflow.
3) Metal load increases between instream sites highlighted source locations and contributions, while a decrease in load between instream sites indicated loss of metal mass by chemical attenuation processes. If increases in loading occurred at adjacent stream segments, the metal loads for these segments were summed to represent the total loading contribution from source areas.
4) The increase of metal loads for each segment was summed to calculate the cumulative instream metal load, which does not consider the loss of metal loads due to attenuation processes.
5) The measured metal loads in each segment, regardless of their increase or decrease, were summed to calculate the total instream load.
6) The contributions of a stream segment or groups of stream segments were calculated as a percentage of the cumulative metal loading at the furthest downstream sampled point.
7) Effective inflow concentrations were calculated as the ratio of metal load and streamflow occurring up and downstream of an inflow. Differences between effective inflow concentrations and measured inflow concentrations indicated the input of unsampled metal-enriched water or dilution of sources.

2.4. Source apportionment under variable streamflows

Low, medium, high, and very high streamflow conditions were captured between June and October in 2016 and 2017 by salt gulp injection (Fig. 2b). Streamflows were measured for a subset of eleven sampling sites (Fig. 1) by undertaking 45 gulp injections of NaCl. Gulp injections were performed from the downstream to the upstream sites within 48 h across 13 different site visits. Streamflow variability may have occurred across the difference days and this was monitored through the daily values provided by the NRW station 63001. The site visits on the 17/06/2016, 28/07/2017, 12/09/2019 provided a complete set of data that allowed low, medium, and high flow load calculations. The NaCl was dissolved in 10–20 L of stream water and injected into the stream. Instream EC was monitored about 20 m downstream from the NaCl injection point, which corresponded to about 20 times the stream width as per guidelines (for details on the method refer to Richardson et al., 2017, and Jarvis et al., 2019). Seven of the eleven sample sites were located between 0 m and 2614 m (Fig. 1), corresponding to the location of the majority of mine sites and waste. Four other sample sites extended downstream to the confluence with the Nant Magwr (Fig. 1). Streamflow was measured three or more times at most sample sites. Exceptions to this were at sites located at 739 m, 1645 m, and 4640 m where only two measurements were taken due to logistical difficulties. A wide range of streamflows were identified with the frequency of very high flow accounted for 10%, HF 40%, medium flow

40%, and low flow 10% (Fig. 2b).

2.5. Geochemistry of in-channel and bank sediment

Within the study reach, five discrete zones were identified for sampling in-channel and stream-bank sediments based on the location of mine workings, mine wastes and sediment depositional areas. The sample zones were located upstream of the Wemyss Mine tips (at 0 m, T0), and next to the Wemyss Mine tips (at 171 m, WM) and Graig Goch Mine tips (1645 m, GG), in the depositional area at 3210 m and the floodplain at 5930 (up/s) and 6740 m (d/s) (Fig. 1). Sixty-eight sediment samples were collected along transects perpendicular to the stream channel on the 18th, 19th, 20th, and 26th of July 2016. The transects captured variations in fluvial morphology (depositional or erosional areas) and sedimentology (sediment texture and layering). The sediment was sampled with a stainless steel trowel or hand augers to a maximum depth of 40 cm to capture the sediment likely interacting with the streamwater. Roots, leaves, and pebbles were removed and about 0.5 kg of sediment was collected in a plastic bag. The samples were transported to the laboratory and left to dry at about 21 °C. Different grain sizes were separated on a vibration platform (Fritsch) using Endcotts sieves. Following Wentworth size classes, the sieving separated: very coarse sand (2–1 mm), coarse sand (1–0.5 mm), medium sand (0.5–0.25 mm), fine sand (0.25–0.125 mm), very fine sand (0.125 mm - 63 μm) and silt and clay (less than 63 μm).The elemental composition of the sediment was determined by p-XRF (Skyray Genius 9000XRF). The p-XRF analysis was carried out for each size fraction to reduce physical matrix effects and repeated six times to increase data precision. Element peak positions were determined with a standard of silver, and data accuracy was quantified with the Fresh Water Sediment CRM016 (Sigma Aldrich). The arithmetic mean of metal concentrations for each transect was calculate to obtain a representative value of the sampled area. Geochemical and mineralogical investigations were carried out on subsets of ten samples with high metal concentrations to better identify the metal-bearing minerals. Samples sieved to <2 mm were mounted in epoxy-impregnated polished mounts and analysed with a Jeol8100 Superprobe (WDS) with an Oxford Instrument INCA microanalytical system (EDS). Metal-bearing phases were detected using backscatter electron images (BSEM) and energy dispersive detection (EDS). Energy data were collected between 0 and 20 eV using a 15 kV accelerating voltage and a spot size of 1 μm.

3. Results and discussion

3.1. High spatial resolution source apportionment under steady streamflow conditions

3.1.1. Zinc and lead metal concentrations and loads

In the Nant Cwmnewydion, the synoptic sampling captured high spatial resolution Zn and Pb concentrations (Fig. 3) under moderate steady-state streamflow conditions (30/07/2016, MF, Q45, Fig. 2). Filtered and unfiltered concentrations are presented and discussed, the filtered concentrations contained the most bioavailable Zn and Pb and are less subject to sampling artifacts (such as inclusion of debris); unfiltered samples included colloidal and suspended particles dispersed in the streamwater (Runkel et al., 2013). Zinc filtered and unfiltered concentrations showed similar patterns (Fig. 3a), increasing from 0.39 mg/L (at 0 m) to 1.66 mg/L (at 2614 m). The first increase in filtered Zn (from 0.70 to 1.52 mg/L) occurred at 162–170 m, at a stream segment in the proximity of Wemyss Mine receiving Zn concentrations from Mill Race Stream (at 164 m, 5 mg/L), at a culvert (at 167 m, 3.70 mg/L), and at a left bank inflow (at 168 m, 1.14 mg/L). The highest instream concentration (2.90 mg/L) was observed downstream of the Frongoch Adit inflow (at 880 m); the Frongoch Adit concentration was 3.91 mg/L of filtered Zn. Lead concentrations initially increased at Wemyss Mine (162–171 m) from 24 to 171 μg/l for filtered Pb and 37–191 μg/l for

unfiltered Pb (Fig. 3c). In this stream segment, Mill Race Stream (164 m) had a filtered Pb concentration of 1030 μg/l and unfiltered Pb concentration of 1470 μg/l, the culvert (167 m) showed 280 μg/l filtered Pb, and the left bank inflow (168 m) 171 μg/l filtered Pb. The second increase in Pb concentrations was observed between 847 m and 880 m, where concentrations increased from 109 to 127 μg/l for filtered Pb and from 126 to 206 μg/l for unfiltered Pb, potentially due to high concentrations in the Frongoch Adit inflow at 862 m (123 μg/l filtered and 223 μg/l unfiltered Pb).

Filtered and unfiltered Zn loads displayed three principal increases along the study reach (Fig. 3b). A slight increase was observed around the Wemyss Mine tips (95–171 m) and Mill Race Stream (164 m). The largest increase (from 41 mg/s to 257 mg/s) was downstream of the Frongoch Adit (862 m) in the 847–880 m stream segment. Filtered and unfiltered Zn loads showed a moderate and constant increase in the stream segments next to Graig Goch Mine (1148–1961 m). The latter likely captured diffuse Zn sources that were not detectable on the Zn chemograph (Fig. 3a) but were indicated in the load increase (Fig. 3b). Lead loads (Fig. 3d), especially the unfiltered Pb loads, showed a sharp increase at 880 m, downstream of Frongoch Adit (862 m). The second-largest filtered and unfiltered Pb load increase was at Wemyss Mine (162–171 m). In contrast to the Zn load patterns, after Frongoch Adit input, the Pb loads decreased particularly from 880 m to 1148 m (Fig. 3d).

3.1.2. Zinc and lead sources

Overall, comparisons between the reported load increases and cumulative Zn loads at the furthest downstream point (2614 m) allowed three primary Zn source areas to be identified: the Frongoch Adit (847–880 m, 57%), the Graig Goch Mine (1148–1961 m, 21%), a segment along Wemyss Mine (95–171 m, 12%) (Fig. 4). The Pb sources were Frongoch Adit (847–880 m, 51%), and different segments near the Wemyss Mine (0–52 m and 162–171 m; 22%) (Fig. 4). A decrease in Pb load observed at Graig Goch Mine (1148–1961 m; Fig. 3d) is shown as a negative percentage in Fig. 4 indicating that Pb is likely being attenuated by co-precipitation or sorption processes.

The ephemeral inflow, Mill Race Stream, contributed to the increase in stream Pb and Zn loads observed between 161 m and 171 m. However, effective inflow concentrations (see session 2.3.2) of Zn and Pb calculated at the stream segment 162 m–171 m were 77% Zn and 46% Pb higher than the observed concentrations from Mill Race Stream. This difference indicated that unsampled and diffuse subsurface water in this stream segment may contribute to the increase in metal concentrations and loads. At 847–880 m, effective inflows concentrations resulted in 13% filtered Zn and 15% filtered Pb higher than measured Frongoch Adit concentrations, suggesting instream contribution from unsampled subsurface water at this location. In the stream segment adjacent to the Graig Goch Mine (1148–1961 m) the inflow increased by 18% (Fig. 2a), although the drainage pipes, which concentrations averaged 2.7 mg/L Zn and 11.6 μg/L Pb, had not enough flow to account for the observed streamflow increase. This increase suggested a previously unknown subsurface hydrological connection between the stream and underground mine workings at Graig Goch Mine. Whilst there was a net loss of filtered Pb load along this stream section (−1%), an increase in filtered Zn loading accounted for 20% of the total stream Zn loading along the study reach and may be explained by the efflux of Zn-enriched groundwater from the Graig Goch mine workings.

3.2. Source apportionment under variable streamflows

3.2.1. Zinc and lead metal concentrations and loads

Metal concentrations captured at different streamflow conditions (Fig. 2) are presented in Fig. 5 as box plots and raw data versus stream length. Average (or mean) Zn concentrations (Fig. 5a) increased first at 171 m (from 0.16 to 1.33 mg/L), downstream of Mill Race Stream and the Wemyss Mine tips. A second increase was recorded downstream of
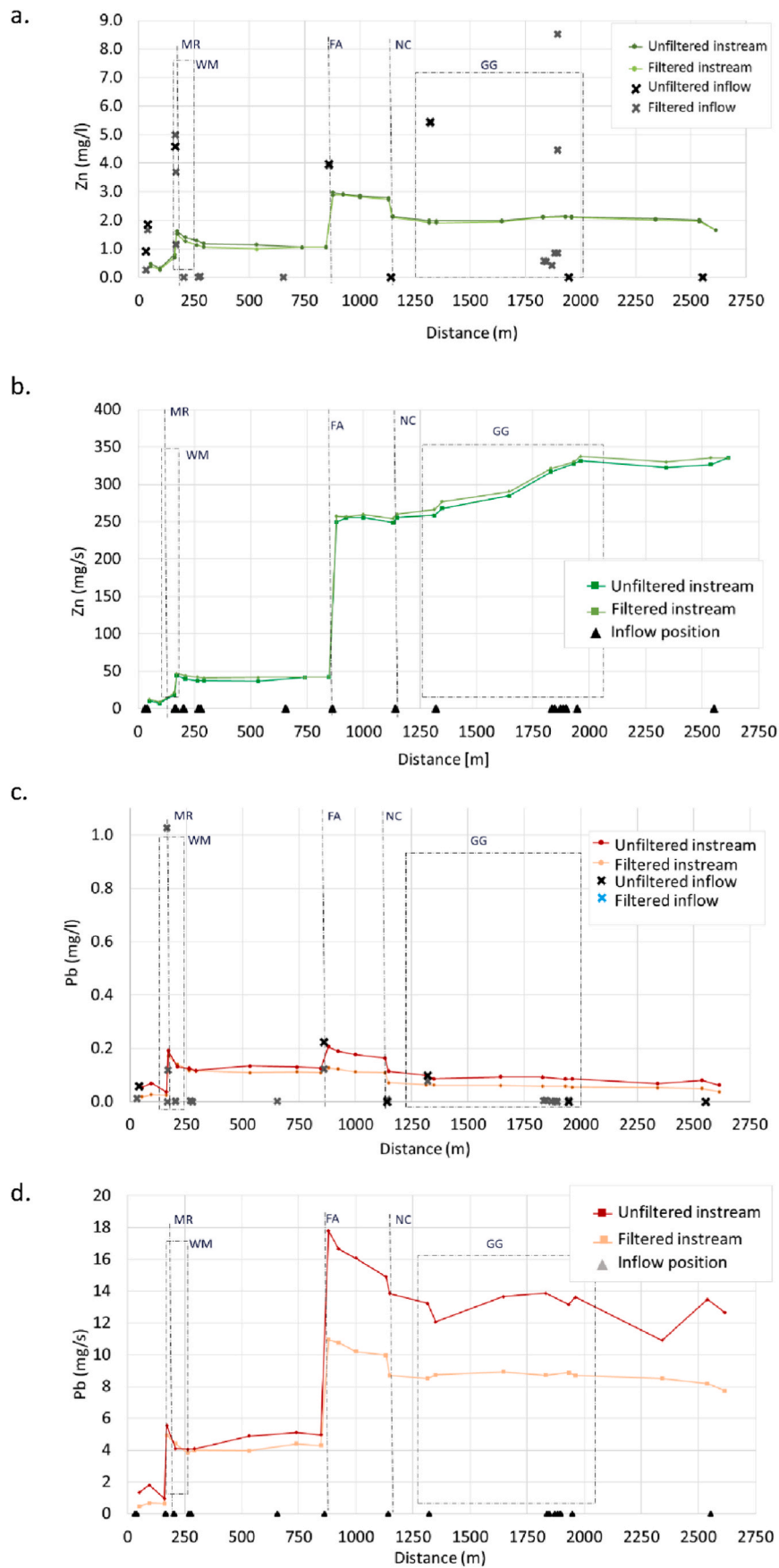
Fig. 3. Spatial profiles of Zn and Pb concentrations (a, b) and loads (c, d) derived using the continuous tracer injection at medium streamflow conditions (30/07/2016, MF). WM = Wemyss Mine; MR = Mill Race Stream; FA = Frongoch Adit; NC = Nant Ceunant; GG = Graig Goch Mine.
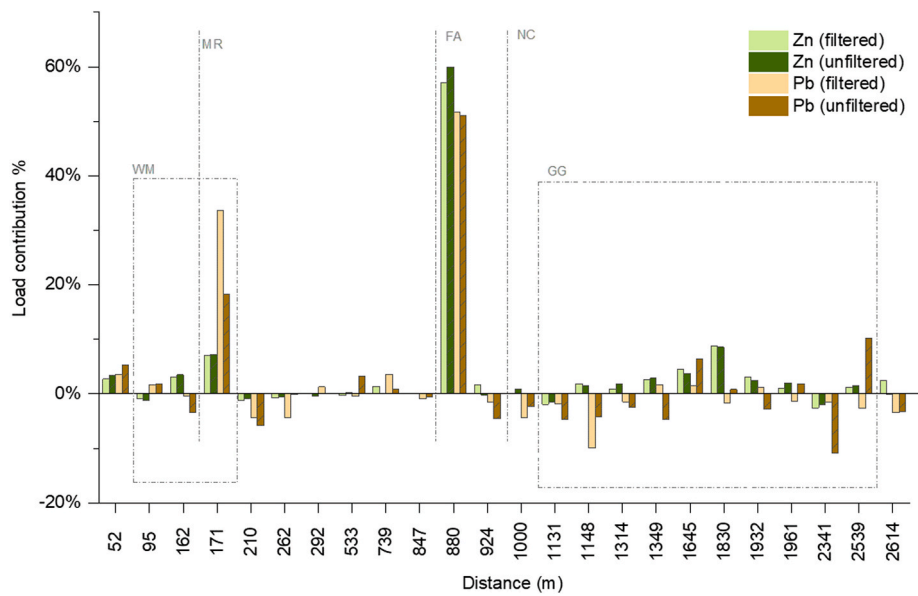
Fig. 4. Stream segment contribution and attenuation percentages of Zn and Pb derived with the continuous tracer injection. WM = Wemyss Mine; MR = Mill Race Stream; FA = Frongoch Adit; NC = Nant Ceunant; GG = Graig Goch Mine.
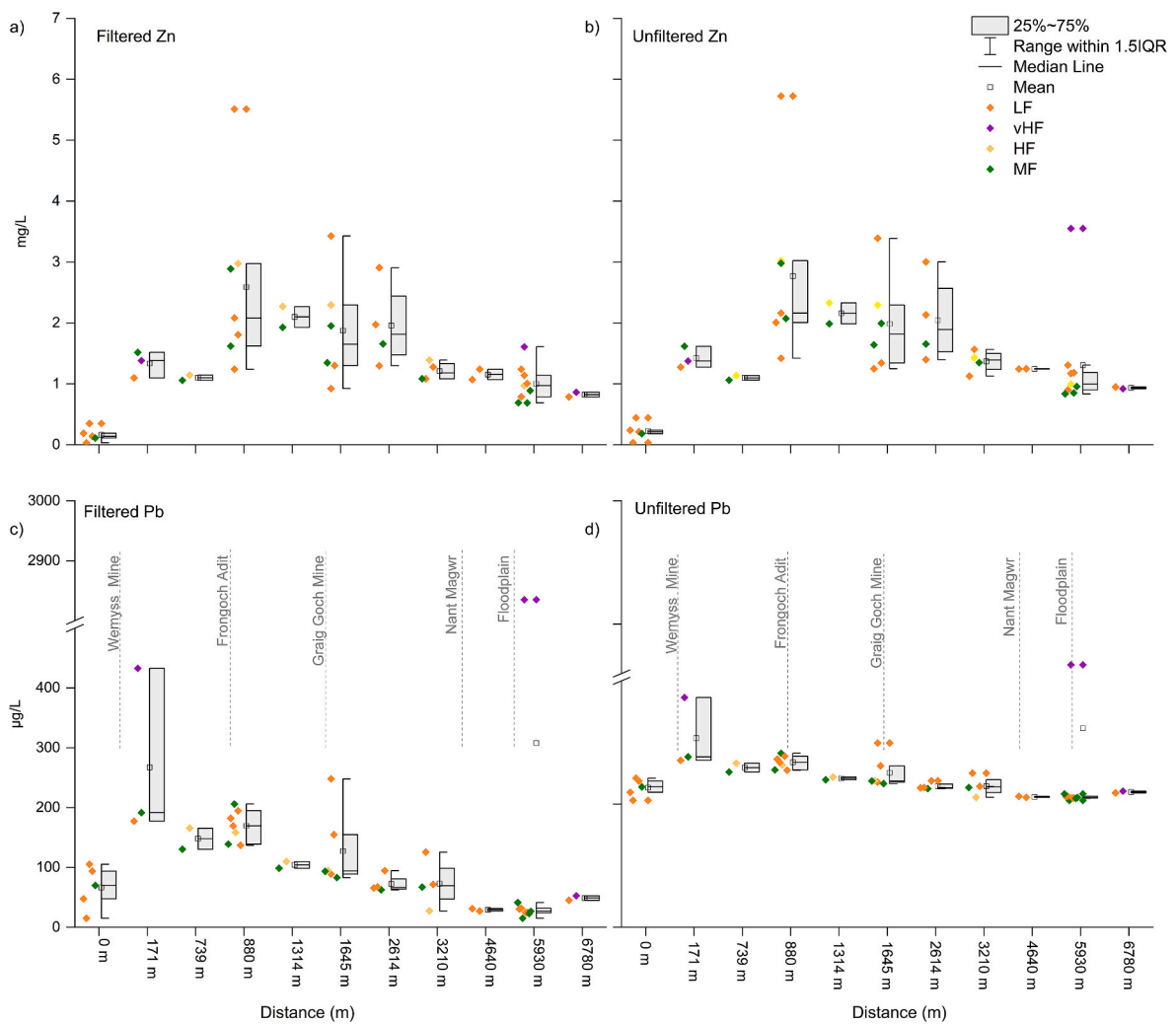

Fig. 5. Box plots and data points of Zn (a, b) and Pb (c, d) concentrations along the entire stream. These concentrations are measured under low (LF), moderate (MF), high (HF), and very high (vHF) streamflow conditions represented by different colours.

Frongoch Adit (880 m), recording the highest average concentration of 2.59 mg/L. Further downstream, Zn concentrations decreased to 0.90 mg/L at 6780 m. The first concentration increase for Pb was recorded at 171 m (Fig. 5b), with similar average values for filtered (393 µg/l, the highest averaged value) and unfiltered Pb (432 µg/l). A slight increase for unfiltered Pb was recorded downstream of Frongoch Adit, at 880 m. Around Graig Goch Mine, the average Pb concentrations decreased, showing different Min-Max concentration ranges for filtered and unfiltered Pb (Fig. 5c and 5d). Unfiltered Pb ranged from 83 µg/l to 248 µg/l, whereas filtered Pb varied from 46 µg/l to 102 µg/l. Whilst the average

Pb concentrations decreased downstream of Graig Goch Mine, unfiltered Pb concentration showed the highest max concentration (2835 µg/l) at 5930 m under very high streamflow conditions (Fig. 5d).

3.2.2. Zinc and lead sources

Metal loads estimated under all the studied streamflows are presented in Fig. 6 as cumulative and total instream loads. The sources identified with the continuous tracer injections (Fig. 4) contributed differently to Pb and Zn instream loads at low (28/07/2017, LF), moderate (12/09/2017, MF and 30/07/2016, MF), and high flow

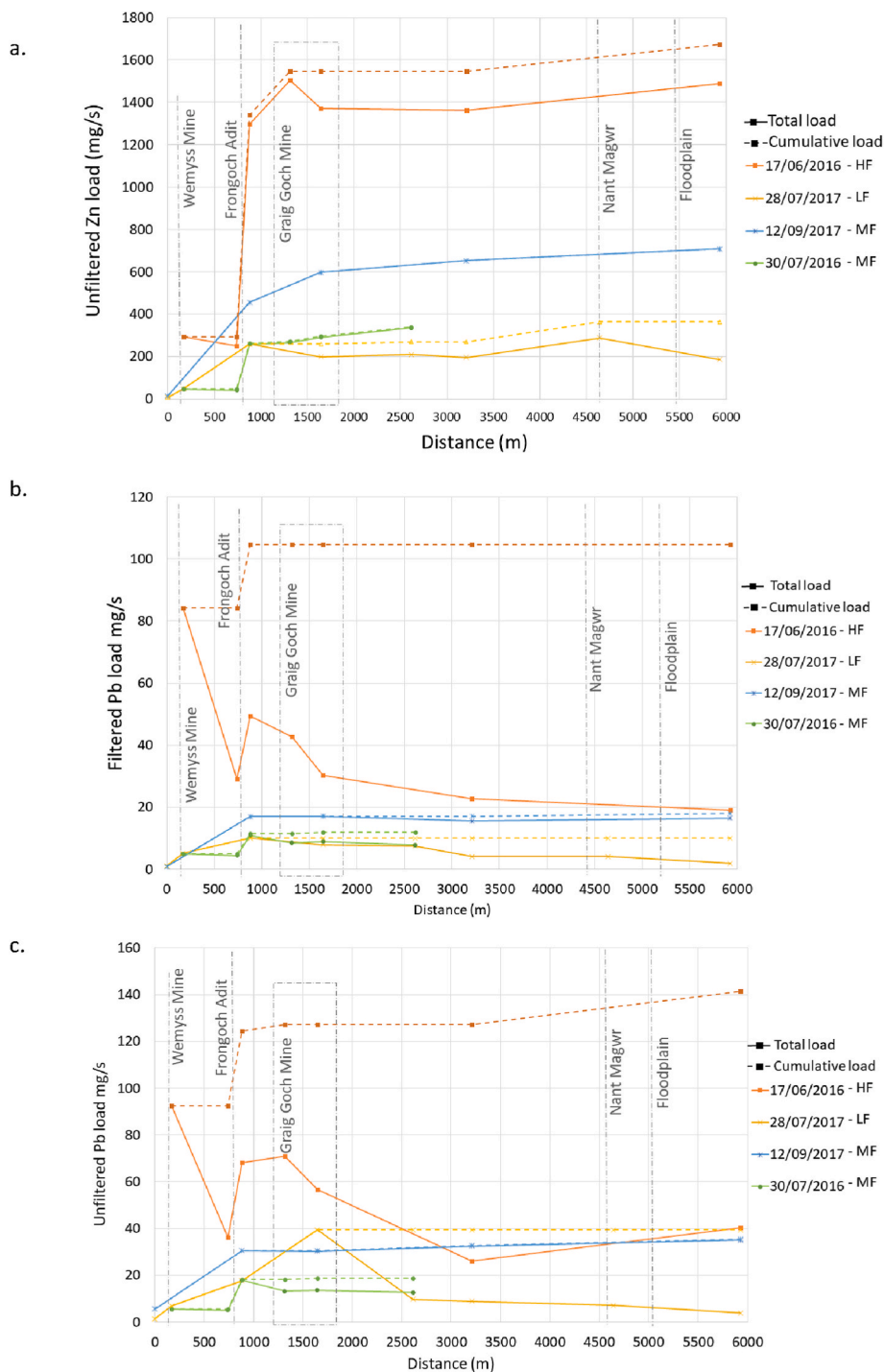**Fig. 6.** Loads of Zn (a) and Pb (b, c) along the entire stream under low (LF), moderate (MF) and high (HF) streamflow conditions represented by different colours. Loads are expressed both as total (dashed line) and cumulative (continuous line). The data extracted from the continuous tracer injection data experiments are shown. Filtered and unfiltered Zn showed the same patterns, so only the unfiltered graph is here presented.

conditions (17/06/2016, HF) (Fig. 6). As filtered and unfiltered Zn concentrations showed highly similar spatial patterns (Fig. 5a), only unfiltered Zn loads are presented and discussed in Fig. 6 a. Frongoch Adit (862 m) was the largest source of Zn under low, medium, and high streamflow conditions contributing up to 68% of the total stream Zn load under high flow conditions (Fig. 6a). This inflow also contributed 49% filtered Pb and 27% unfiltered Pb loads under low flow, and 20% filtered Pb and 25% unfiltered Pb loads under high flow conditions (Fig. 6b). Therefore, under high flow conditions, there were important sources of Zn (32% unfiltered Zn) and Pb (75% filtered Pb and 80% unfiltered Pb) in other locations along the stream. The Wemyss Mine stream segment (0–171 m) accounted for 20% unfiltered Zn, 80% filtered Pb, and 73% unfiltered Pb of the total load (Fig. 6). Other sources upstream T0 may be present to the Frongoch Mine mining works, although these metal loads are more likely to contribute to the adjacent Nant Cell watershed. At the Graig Goch Mine (1314–1645 m), the high flow monitoring (Fig. 6) showed an initial increase of Zn load followed by a decrease, with an overall contribution of 13% of the cumulative Zn load. Unfiltered Pb load increased 2% at 1314 m then decreased 11% at 1645 m. Filtered Pb overall decreased by 18% (Fig. 6b, and 5c).

3.3. Geochemical processes driving metal dispersion

As commonly occurs in mining-impacted stream systems, the Nant Cwmnewydion Zn- and Pb-enriched sediments were located mainly in the former mining area. The mine waste at Wemyss Mine displayed the highest concentrations of Zn (1.3–4.6 g/kg) and Pb (7.4–24.7 g/kg) recorded in the watershed, likely due to the presence of the ore minerals galena and sphalerite and secondary weathering minerals such as anglesite and Zn- and Pb-bearing Fe-oxides (Fig. 7a). These concentration ranges and minerals have been observed at other mine sites in Mid Wales (Byrne et al., 2010; Lynch et al., 2018). Erosion of the surface mine waste at the Wemyss Mine likely exposed the ore minerals to oxidation, resulting in the formation of new secondary minerals (Nordstrom, 2011a) and enhancing metal release into sediment pore and instream water (Palumbo-Roe and Dearden, 2013). Sphalerite is highly soluble under circum-neutral conditions, and its oxidation produces the aqueous phases Zn^{2+} and SO_4^{2-} (Palumbo-Roe et al., 2009). Galena, which has lower solubility at circum-neutral pH, generates secondary anglesite when oxidised by oxygen (Lynch et al., 2018). Zinc and Pb liberated by sulfide and sulfate minerals can be adsorbed or co-precipitated with Fe-oxides forming tertiary minerals (Hudson-Edwards et al., 1996, Hudson-Edwards, 2018) (Fig. 7). These secondary
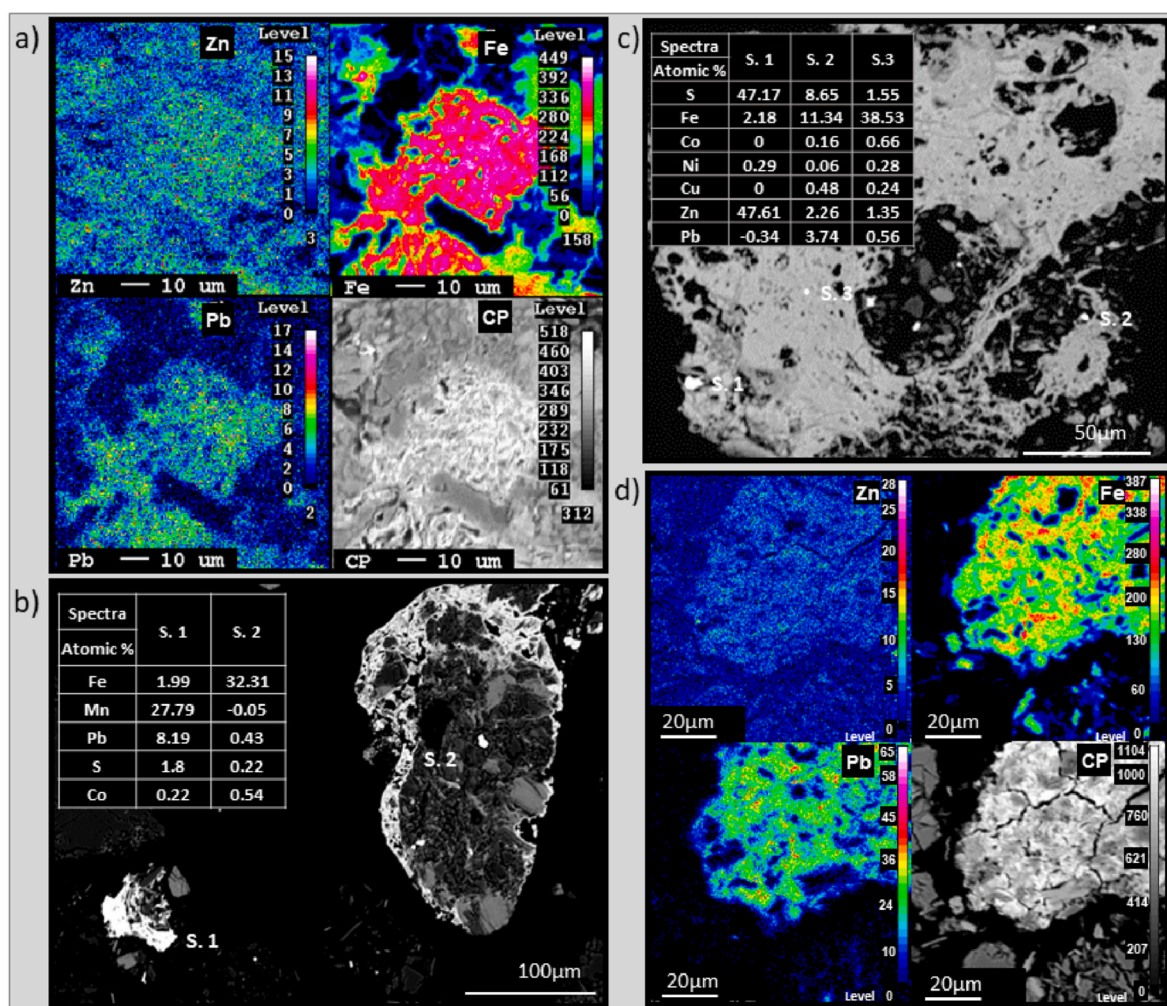

Fig. 7. Electronic microprobe images and chemical maps of selected metal-bearing soil grains. a) Sample from Wemyss Mine (WM) waste tip. Zn- and Pb-bearing Fe oxide coating on silicate mineral. b) Sample from Graig Goch Mine (GG) stream bank sediment. A mudstone grain is shown on the right, with silicate and monazite minerals covered by Zn- bearing Fe oxides (s.2). A Mn–Pb oxide occurs in the lower left, and this is associated with low concentrations of Fe, Zn, Cu and Co (s.2). c) Sample from the depositional area at 3210 m at the stream middle length. Secondary Fe-oxide cementation around silicate, rutile, and sphalerite (s.1) minerals. Lead-sulfate (s.2) and trace amount of Ni, Co, and Zn are often associated with the Fe-oxide (s.3). d) Sample from the floodplain area at 5930 m (up/s). Pb- and minor Zn-bearing Fe oxide coating on silicate minerals.

and tertiary minerals were observed in the mine tips and the streambed sediment and helped in interpreting the processes controlling the Zn and Pb load trends in the water. The observed Fe-oxides adsorbed Pb onto their surface enhancing instream Pb loads attenuation during low and moderate flows, as observed at the 95–162 m stream segment in Fig. 4. Although, under high streamflow conditions, the entrainment of Pb-bearing minerals likely contributed to the unfiltered Pb load (Byrne et al., 2013), which accounted for 7% more than the filtered Pb load (Fig. 6c). Furthermore, the Zn- and Pb-bearing minerals were potentially leached during high flow conditions as a result of mineral mobilisation, pH decrease (which decreased from an average of 7.0, RSD 7%, under low flow, to 6.6, RSD 7%, under high flow), and oxidation conditions (Jarvis et al., 2019) contributing to the filtered Zn and Pb load increase (Fig. 6).

Around the Graig Goch Mine (1131–2539 m), sediment Pb and Zn concentrations were lower than those in the Wemyss Mine wastes (4.5 g/kg and 1.0 g/kg, respectively), possibly due to the re-profiling of the stream banks or lower presence of mine waste. However, Pb- and Zn-bearing tertiary minerals such as Mn- and Fe-oxyhydroxides and phosphate minerals were detected by Jeol8100 Superprobe (WDS) analysis. The presence of Pb-bearing Mn oxyhydroxides in the stream sediments (Fig. 7b) corroborated the presence of subsurface water flows because the Pb-bearing Mn oxides likely formed when stream water entered the hyporheic zone, increasing its oxygen concentration and promoting the formation of these tertiary phases (Gandy et al., 2007). The Mn oxides likely incorporated metals other than Pb that were undetectable (Fig. 7b). Fuller and Harvey (2000) studied Pinal Creek, a stream with similar characteristics (sand and gravel channel and the presence of mining-affected groundwater) and reported a shallow hyporheic zone where Mn oxides affected metal transport by taking up metals, including Zn, Co, and Ni. Because these minerals have low solubility under the prevailing geochemical conditions (Gandy et al., 2007), aqueous Pb was unlikely to be released to the stream water across the observed streamflow conditions (Fig. 6b). The increase of unfiltered Pb concentrations (Fig. 5d) and load at 1645 m (Fig. 6c) could be due to the entrainment of Pb-bearing particles due to runoff and suspension processes exacerbated under high flow conditions. Furthermore, the low Zn concentrations in the sediment suggested that the Zn source identified in this segment (Fig. 4) was more likely due to the input of Zn enriched groundwater.

Decreases in stream metal loads under medium and, mainly, low streamflows were recorded in the Nant Cwmnewydion around 3210 m and the Nant Magwr floodplain at 5800–6740 m (Fig. 6). In the middle reach at 3210 m (Fig. 1) high Pb concentrations were recorded in the sediments (3.8–20.3 g/kg), while Zn showed concentrations similar to those at Graig Goch Mine (1.5–0.8 g/kg). Here, poorly crystalline Zn- and Pb-bearing Fe-oxide rims were found around silicates, rutile, and sphalerite (Fig. 7c). These tertiary minerals suggest metal attenuation processes such as co-precipitation, adsorption, or physical deposition of instream suspended particles. Such processes may account for the decrease in unfiltered Pb recorded at 3210 m (Fig. 6c). In the floodplain (up/s and d/s in Fig. 1), soil concentrations were lower (Pb ≤ 1.10 g/kg and Zn 0.3–2.7 g/kg). In the floodplain soils, Pb and Zn were associated with phyllosilicates and tertiary Fe- and Mn- oxyhydroxides (Fig. 7d). These metals can be stored in depositional areas for decades, potentially causing negative impacts on the ecosystem (Dennis et al., 2009). However, these minerals can also release metals under high flow conditions, as observed in Fig. 6a, and 5 c for unfiltered Zn and Pb loads.

3.4. Source apportionment comparison with historical data

The knowledge gained from the previous studies highlighted how water quality monitoring and metal source apportionment are in continuous evolution sicking accurate metal source apportionment to better focus remediation resources. Improvement in the instream water quality of Nant Cwmnewydion were achieved following surface water

diversion at Frongoch Mine in 2011 which reduced the Frongoch Adit flow by 80% of the Frongoch Adit and the overall load in kg/year decreased from 16,000 to 7500 for Zn and 990 to 390 for Pb. The recognition of Frongoch Adit as a source was evident in monitoring studies by the Environment Agency and Atkins (2008). Variations of Zn and Pb sources across streamflow conditions were identified with metal load being the lowest under low flow conditions and the highest concentrations being measured at Mill Race Stream under high flow. Williams (2016) highlighted the flow gauging method used by the previous reports to likely miss-estimate the flow due to the shallow and pebble nature of the riverbed. Further monitoring adopted gulp injections for gauging the streamflow and focused on the apportionment of the Wemyss Mine and Mill Race Stream as metal sources to the Nant Cwmnewydion. Results indicated that Mill Race Stream became enriched with metals moving downstream and contributed to 42% Zn and 64% Pb. The Wemyss Mine tips contributed through runoff, seepages, tailings entrainment by 44% Zn and 28% Pb. The percentage discard may indicate unsampled sources or an error in the streamflow estimation. Finally, the common method allowed to identify two major metal sources, Frongoch Adit and Wemyss Mine, although, Graig Goch was not recognised as a significant one.

3.5. Source apportionment of mine contamination across streamflows: a hydrogeochemical approach

The application of the hydrogeochemical approach (the continuous tracer injections, gulp injections, and sediment geochemistry analysis) facilitated the identification of metal load spatial and temporal trends and proposed reasoning on metal release mechanisms across streamflow conditions. The results gained with the hydrogeochemical approach at Nant Cwmnewyddion allowed the design of a better monitoring plan and remediation strategies which included Zn sources along Graig Goch mine. The resources designated to environmental regulators and local authorities are often limited and only a thorough understanding of the source mechanism and apportion can prioritise and secure resources for the necessary interventions. An estimate cost for the application of the hydrogeochemical approach would be only a fraction of the intervention coast, usually a couple of million pound (Jarvis et al., 2019), designated to the area. This hydrogeochemical approach contributed towards filling the gaps identified by DEFRA (2022) and should be integrated to the common method in other suitable mining-impacted streams to build on previous data and generate high-quality data required to inform mine site remediation and rehabilitation decisions.

Fig. 8 proposes the additional steps of the hydrogeochemical approach (steps 2, 3, and 4) to the UK *common approach* (step 1). The loading-based method is commonly used as a monitoring strategy in the UK (step 1) to identify and monitor sources such as surface waste tips and mine drainage across streamflow conditions (Jarvis et al., 2019; Mayes et al., 2013). The importance of streamflow gauging through gulp injections emerged from this study, in line with Williams (2016) and Jarvis et al. (2019). The monitoring of diffuse sources is conducted with low spatial sampling resolution, potentially causing an underestimation of metal loads released by diffuse sources. The limitation of this method has been highlighted in this study for the Nant Cwmnewydion, where metal-rich groundwater and subsurface inputs were not captured by previous investigations, with monitoring instead focussed on drainage from the Frongoch Adit and the surface waste tips at Wemyss Mine (Atkins, 2008).

Step two (the continuous tracer injections) of the proposed approach applies a spatially detailed sampling grid and instream metal loads (Kimball et al., 2002). Once the tracer is uniformly dispersed across the studied stream segment, the sampling can occur at any point along it, regardless of riverbed conditions. Detailed spatial metal load patterns can reveal metal inputs from subsurface and groundwater or transient sources such as streambed sediments (Byrne et al., 2017). In the case of Wemyss Mine, for example, the effective inflow concentrations of Pb and
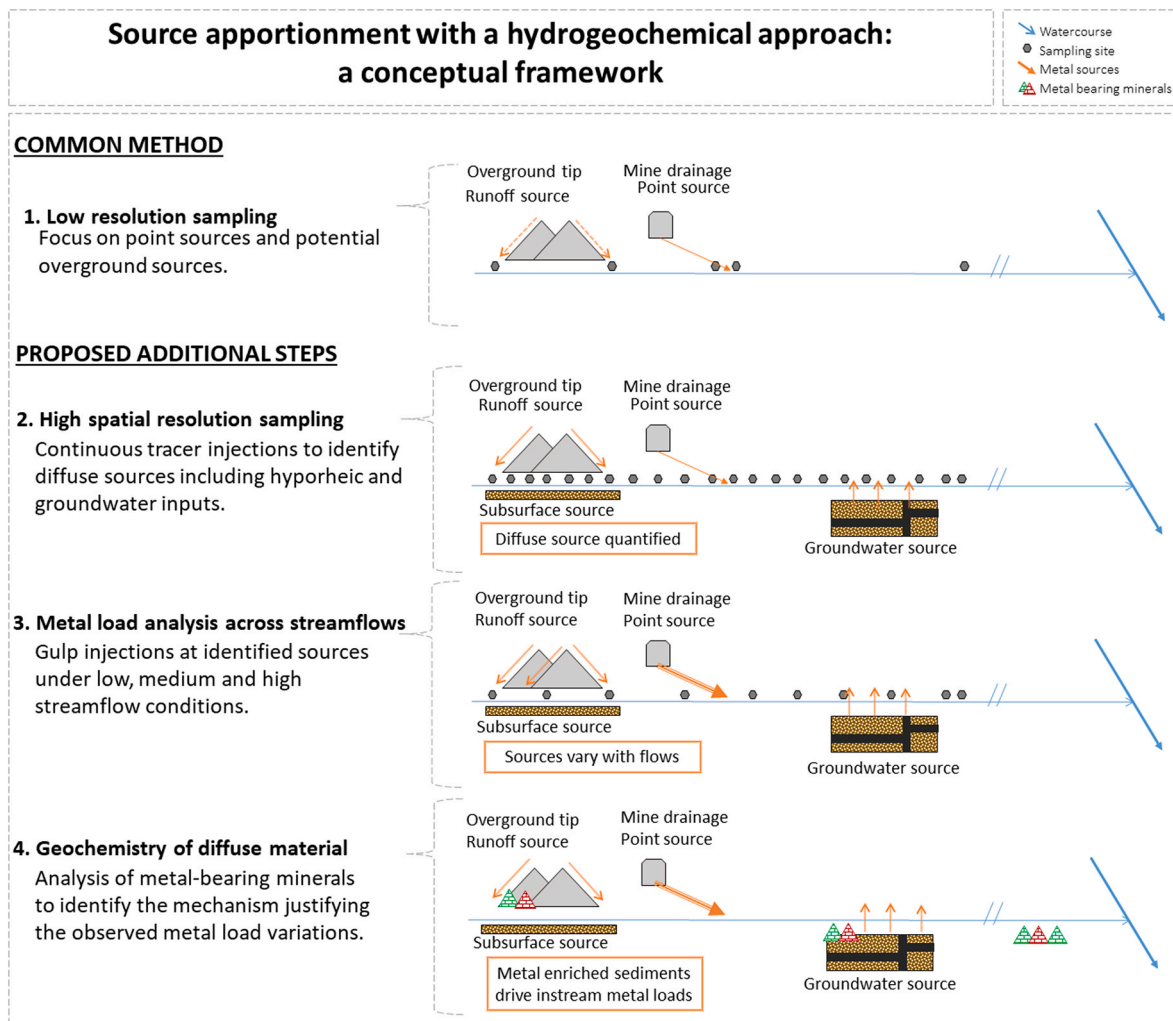
Fig. 8. The sketch illustrates the hydrogeochemical approach proposed by this research to apportion metal sources. In the first step, the common method applied in the UK identifies mining areas that require further monitoring and a potential remediation strategy. The hydrogeochemical approach apportions the sources with a high spatial resolution (step 2) across streamflow conditions (step 3) and provides potential explanations for metal load variations via sediment and waste geochemistry (step 4).

Zn were higher than those measured at the Mill Race Stream tributary, highlighting the presence of additional metal inputs from the streambed sediments. Furthermore, the groundwater Zn source identified at Graig Goch Mine highlighted the potential of the continuous tracer injection to identify diffuse subsurface sources of mine contamination.

Step three is the application of gulp injection and water quality to the various sources identified from step one and two (Fig. 8). This step is similar to the common method (step 1), however, its sample density is designed to capture metal loads from surface waste runoff, subsurface, and groundwater sources across streamflow conditions. Metals released from surface waste tips are known to increase during high flow conditions due to increased runoff (Zhu et al., 2007), infiltration of oxygenated water (Lynch et al., 2014), and enhanced particle suspension (Nordstrom, 2011b). In the Nant Cwmnewydion, the stream segment adjacent to the Wemyss Mine surface tips contributed to an increase in unfiltered Pb contribution from 22% under low streamflow conditions to 80% of the total load under high streamflow conditions (Fig. 6 c.).

The fourth and final step presents the integration of geochemical and mineralogical characterisation of waste and streambed sediments to identify the mechanisms driving instream metal releases (Fig. 8). Metal-bearing wastes and sediment release metals to stream water depending on the geochemical and hydrological conditions (e.g. pH, EC, temperature, streamflow) (Nordstrom, 2011b). Mine surface tips, often located

in the headwaters, contain primary sulfide and gangue minerals (Hudson-Edwards et al., 1996). Erosion and runoff processes can enhance the dissolution and weathering of the sulfide minerals due to oxidation and leaching processes (Palumbo-Roe et al., 2009). Secondary minerals in streambed sediment can adsorb or co-precipitate metals locally, attenuating the metal impact on the stream water (Cidu et al., 2011; De Giudici et al., 2017). Furthermore, such minerals may contribute to the instream metal load under high streamflow conditions due to entrainment, desorption, and dissolution processes (Lynch et al., 2014; De Giudici et al., 2019). The geochemical and mineralogical characterisation of the waste and streambed sediment at Nant Cwmnewydion contributed to the identification of the processes driving metal release across streamflow conditions. The surface mine tips at Wemyss Mine, enriched in Zn- and Pb-bearing minerals (such as sulfides and Fe- and Mn-hydroxides), contributed to the aqueous and suspended particle metal instream loads and were exacerbated under high flow conditions. Lead-bearing Mn oxides observed in the stream sediment along Graig Goch Mine suggested metal attenuation due to subsurface and groundwater interactions. Finally, Pb and Zn-bearing minerals in downstream depositional areas highlighted the watershed-scale impact of the upstream mining activities. Therefore, a systematic study of the sediment geochemistry and mineralogy is proposed to explain in particular diffuse metal sources along the stream, with a recommendation to not neglect

downstream stretches where waterborne metal-bearing particle deposits and aqueous metal precipitates/are absorbed in depositional areas often co-existing with farmland and grazing lands. These depositional areas have been proved in this and other studies to become diffuse metal sources under high flow conditions.

4. Conclusions

Monitoring in mining-impacted catchments often record poor water and ecological status due to the release of potentially toxic metals from point and diffuse sources. Diffuse contamination sources in particular have proved problematic to monitor and therefore to address in mine site remediation schemes. Common methods in the UK focus on point sources and variation of metal sources across stream variations. Although, data point are often at low spatial resolution which may underestimates the overall loading contribution from diffuse sources. On the other hand, continuous tracer injections were developed in the USA to apportion diffuse sources at a high spatial resolution under prolonged steady streamflow conditions. This research combined the two source apportionment methods and, in combination with soil geochemical investigation, proposed a hydrogeochemical approach. In the Nant Cwmnewydion study site, the continuous tracer injection and gulp injections accurately measured metal load at a high spatial resolution across various streamflows. The Frongoch Adit was confirmed as one of the main Zn and Pb sources. Furthermore, Wemyss Mine was a diffuse source of Pb and Zn via: i) water runoff and infiltration of surface waste; ii) shallow subsurface water, and; iii) a temporally-variable point source (Mill Race Stream). Graig Goch Mine was a source of Zn load to the stream manly via groundwater input due to historical underground mine workings connected to the streambed via alluvial deposits. Stream sediment along the catchment were enriched in metals, with primary minerals, such as sphalerite and galena, being concentrated in mining areas, and metal-bearing Fe-hydroxide and clay being dispersed up to 6 km downstream the mine, highlighting the broader catchment mining-impact. The distribution of the metal-bearing minerals across the catchment allowed to justify observed variations in instream metal load across various streamflows.

The hydrogeochemical approach was successfully applied under low, medium and high streamflow conditions. As such, this research demonstrate its potential to be applied further afield in mining-impacted watersheds characterised by well-defined seasonal hydrological patterns or poorly predictable weather conditions Applying the presented hydrogeochemical approach in other areas worldwide will originate a more robust understanding of diffuse sources in mining-impacted rivers under various climate change scenarios.

Author contributions

PO and PB designed the study. PO and PB wrote the manuscript. PO, IF, PB, KHE, and TS assisted with fieldwork. PE and TW provided previous data and method insight. All authors contributed to and reviewed the manuscript.

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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.

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