Source Apportionment of Trace Metals at the Abandoned Nantymwyn Lead-Zinc Mine, Wales

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Abstract

Abandoned metal mines cause longstanding stream pollution problems. The two streams at Nantymywn, Wales, the Nant y Bai and the Nant y Mwyn, cause the River Tywi to fail local standards for Zn for 35 km. In this study NaBr tracer dilution and synoptic water sampling, followed by ICP-MS laboratory analysis, were carried out in baseflow conditions along the Nant y Bai to identify and quantify sources of metals at high spatial resolution. Preliminary results enable Zn sources to be located, including one representing 34% of the stream Zn load, as well as areas of diffuse sources and attenuation.

Keywords: Metal Mine Waste, Synoptic Sampling,Tracer

Introduction

Wales has a long history of mining, more recently for coal, but historically for Pb, Zn, Cu and other base metals (Thornton 1996; Mayes and Jarvis 2012). The age of these mines and haphazard way they were closed or abandoned has left complex hydrochemical problems at many of Wales' 1,300 abandoned metal mines (Environment Agency Wales 2002; Environment Agency 2008). Recent Water Framework Directive (WFD) work has highlighted gaps in knowledge of the fluvial impacts of abandoned metal mines and Natural Resources Wales (NRW) has ranked metal mines' effects in order to remediate those that are most deleterious (Environment Agency Wales 2002; Mayes *et al*. 2009; Mayes and Jarvis 2012; Coal Authority 2016).

Nantymwyn is the largest source of metals to the Tywi, causing its failure of WFD standards for 35 km downstream of the site (Natural Resources Wales 2019). Knowing where to target remediation efforts and achieve the largest improvement in environmental quality possible for the resources available requires data on the location, size, seasonal, and inter annual variation of pollution sources (Byrne *et al*. 2021). This paper reports preliminary results of a programme to identify, quantify and apportion sources of metal pollution from the Nantymwyn mine to the Nant y Bai, a tributary of the River Tywi in central Wales, using a NaBr tracer injection and synoptic sampling approach. Developed by the US Geological Survey, this technique determines pollutant loads at a high spatial resolution that can directly assist with effective remediation (Kimball 1997; Onnis *et al*. 2018; Byrne *et al*. 2021).

Study Area

Nantymwyn mine has been worked sporadically since pre-Roman times until final abandonment in 1932. In the 1700s, Nantymwyn was one of the largest sources of Pb ore in Wales (Hughes 1992; Hall 2011). Located in the upper catchment of the River Tywi, near Llandovery, Carmarthenshire (52°5'12"N; 3°46'20"W), Nantymwyn receives mean annual rainfall of 1,711 mm (National River Flow Archive 2021), and lies on Ordovician bedrock, with a fault NE-SW (Woodcock 1987). The northern side of the steep Nant y Bai catchment terrain is mostly used for rough grazing, with the bare spoil heaps fenced off to animals, and on the southern side there is a coniferous plantation (Figure 1). The underground workings affect

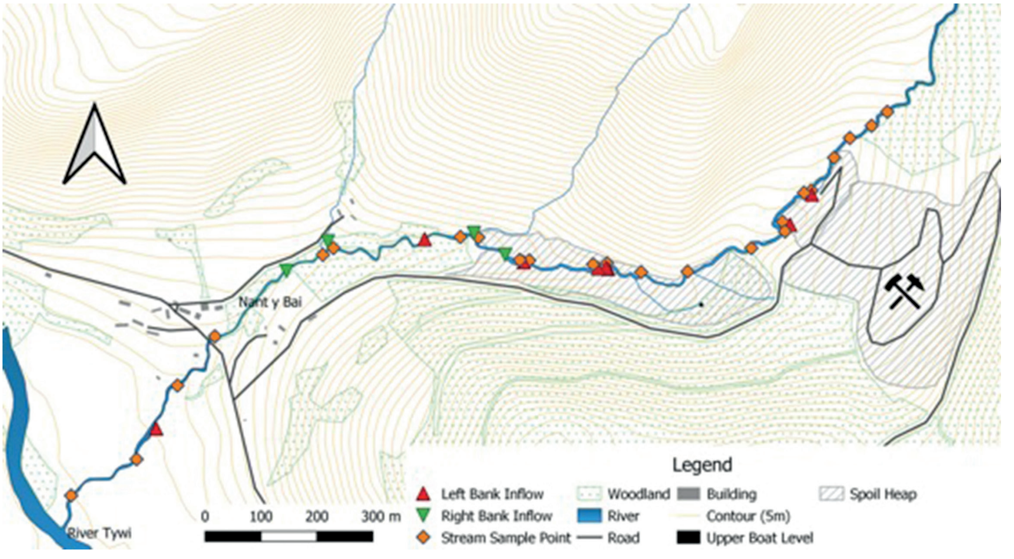

Figure 1 *Map of the study site showing synoptic sampling sites along Nant y Bai. Map created with OS data from Edina DigiMap (Ordnance Survey 2018).*

and drain to two streams, the Nant y Mwyn, and the larger Nant y Bai, with two boat levels (large adits kept flooded, allowing boats to float), and many smaller adits added as the mine expanded (Smith 1792; Roberts 1981; Fellows 2009). Varied levels of ore refinement were carried out on site as technologies progressed, leaving spoil and finings heaps of varying sized particles through which the Nant y Bai flows, as well as the Upper Boat Level's indirect outflow. The Nant y Mwyn receives the Deep Boat Level, the lowest outlet of the subterranean workings. Accumulation of trace metals from the mine in flora, and subsequent deleterious effects to fauna have been recorded (Sartorius 2020).

Methods

In July 2019 the Nant y Bai was injected with a conservative NaBr tracer at a rate of 70 mL min^{-1}, and once a plateau concentration of Br was established, synoptic sampling was carried out at 33 sample points, covering 2 km of the watercourse, following established techniques (Kimball *et al.* 2004; Runkel *et al.* 2013). Samples were collected at 22 stream sites, and the remaining samples were obtained from visible inflows (Figure 1). For the purposes of this study, point sources are those with a visible single inflow into the stream, whereas diffuse sources are those without a visible inflow.

At a temporary field laboratory each sample was split into three vials; one filtered through a 0.45 µm membrane, one filtered and fixed with HNO3, and one fixed but not filtered. Conductivity, pH and water temperature were recorded on site. Trace metals and Br analyses of the samples were carried out at Liverpool John Moores University on an Agilent Technologies ICP MS 7900 Inductively Coupled Plasma Mass Spectrometer (ICP-MS). Flow was calculated at each stream site using the Br concentration compared to the injection rate and concentration (Figure 2), and stream metal loadings were calculated as the products of metal concentrations and calculated flows (Kimball 1997; Kimball *et al.* 2002). The flow percentile during synoptic sampling was estimated at Q82 (lower than or equal to 82% of the historic flows) based on 11 data points from salt dilution flow gauging over 12 months. The nearest comparable NRW flow gauging station, on the Nant y Bustach recorded a flow percentile of Q89. After sampling was completed, two stretches of the Nant y Bai were also flow gauged via salt dilution, with the results corresponding well with the bromide tracer flow calculations.

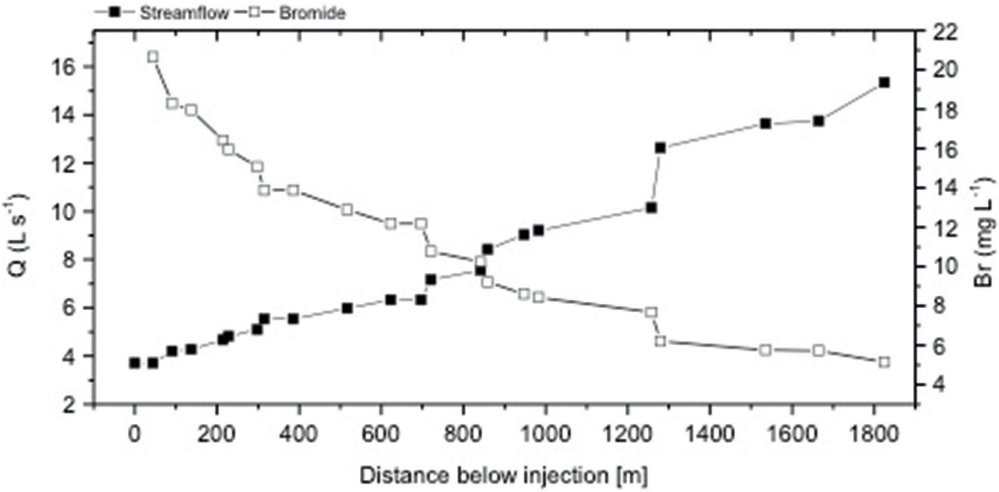

Figure 2 *Br river concentration and river discharge(Q) changes along Nant y Bai.*

Results and Discussion

The Nant y Bai exceeded the WFD long term mean standard for Zn (12.9 µg L^{-1} (dissolved) for the River Tywi) (WFD 2015) for 1600 m of the sampled stretch, peaking at 91 times the standard. Concentrations for the synoptic samplings varied from 5.3 µg L^{-1} (above the mine) to 1,124 µg L^{-1}, with a mean of 503 µg L^{-1}. The annual average environmental quality standard (AA-EQS) for Pb is 1.2 µg L^{-1} (WFD 2015); the Nant y Bai values varied from 6.5 µg L^{-1} to 1083 µg L^{-1}, with a mean of 237 µg L^{-1}. The changes in Zn concentration along the stream are shown in Figure 3

A sharp increase in Zn is shown at 315 m, just after an inflow at 305 m, draining a spoil heap (Figure 3b). This visible inflow had been previously sampled as part of a monitoring regime, but the scale of its contribution to the Zn loading was not clear. It contributes 34% of the total Zn load. Five flow measurements on the inflow at 305 m averaged 3.4 L s^{-1}; the Nant y Bai flow at the nearest point flow gauged regularly (400 m) has an average flow of 100 L s^{-1} from 10 measurements. During high rainfall, surface water flows across the upper tailings which enters the Nant y Bai both at point sources and diffuse processes. The Upper Boat Level adit flows out approximately 600 m below the injection site, with a dissolved Zn concentration of 716 µg L^{-1} on the day of synoptic sampling, but the water is lost to the boggy ground and its influence on the Nant y Bai cannot currently be calculated. Non-mine impacted water joins the Nant y Bai from the Pen y Darren and the Nant y Glo, at 960 m and 1268 m downstream from the injection site respectively and dilutes the metal concentrations in the stream. The Zn load carried by the Nant y Bai only decreases by 1% after the inflow from each stream, suggesting continued Zn input from subterranean sources.

Comparisons of successive calculated instream zinc loads along the Nant y Bai (Figure 4), indicate areas of possible attenuation notably the reduction in dissolved load between the two tailings heaps, as well as load increases that are explained by inflows, such as at 305 m and 847 m. From 1260 m onwards there is an increase in both total and dissolved load, potentially from diffuse subterranean sources. The Nant y Bai erodes through two areas of tailings, the upper (≈140-400 m) having an average Zn concentration of 1,783 mg kg^{-1}, and lower (≈620-950 m) 3,323 mg kg^{-1} (De-Quincey 2020). Dissolved Zn makes up 99% of the total Zn load at the end of the sampled stretch, consistent with regulator monitoring, and with similarly impacted streams (Byrne *et al.* 2013). The Upper Boat Level is likely adding to the Zn load as well. Over the course of the sampled stretch, 44% of the total Zn load was attenuated, compared with just 24% of the dissolved load. As the pH of the stream remains near neutral for the length sampled, the dissolved Zn remains in solution when it enters the Tywi.

Further work will be carried out on the Nant y Bai to confirm the chemical and physical

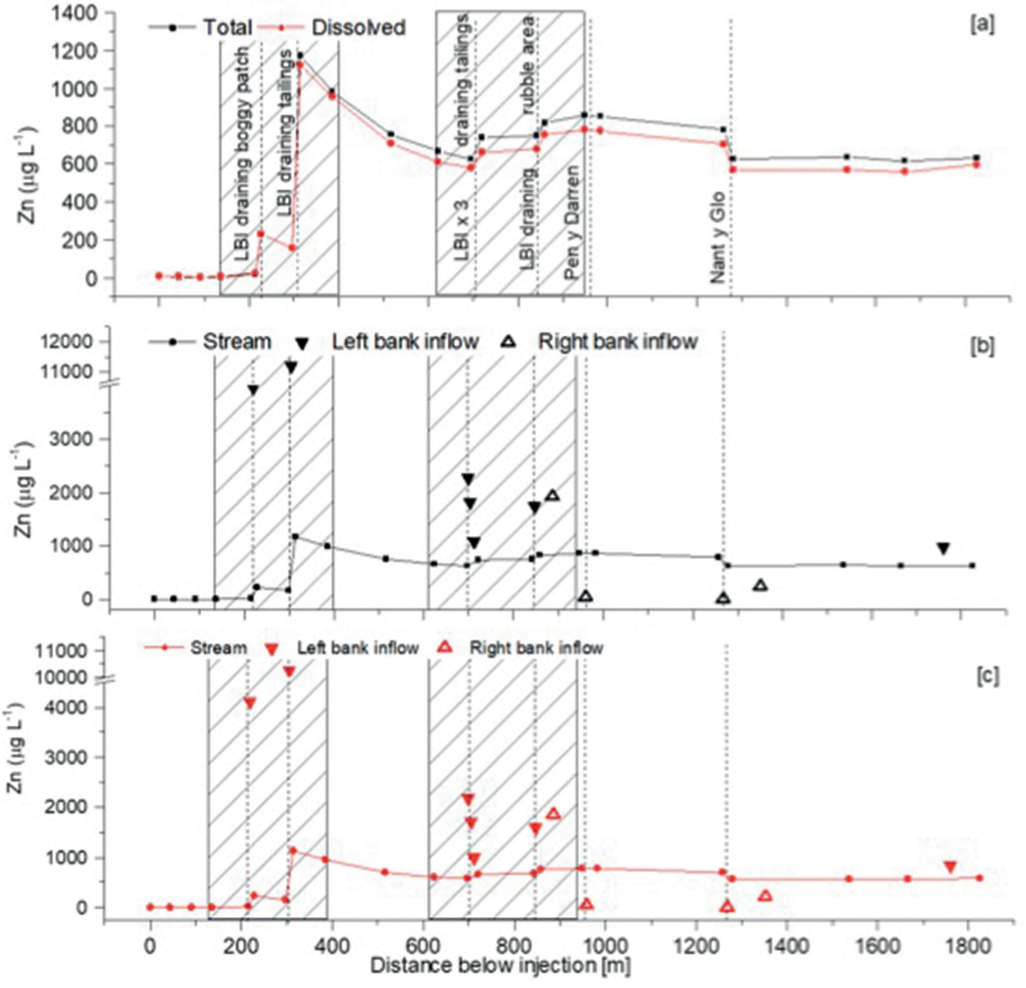

Figure 3 *Spatial profiles of stream total and dissolved Zn concentrations [a], total stream and inflow Zn concentrations [b], and dissolved stream and inflow Zn concentrations [c]. Location of major inflows indicated with vertical dashed lines. Shaded areas = upper tailings (≈140-400 m) and lower tailings (≈620-950 m). For locations of sites and inflows see Figure 1.*

processes causing the changes in Zn load, both the gradual increase downstream where there are no visible point sources, and the decrease between the two tailings areas. Each stream segment's synoptic sampling data will be assessed for cumulative inflows, revealing areas where unmeasured subterranean inflows are responsible for the increase in stream load. A series of storm surveys are planned to measure the effects of rapid flow increases on metal concentrations and detect any "flush" of pollutants after prolonged dry periods (Byrne *et al.* 2013). A second tracer injection and synoptic sampling experiment at higher flows would improve modelling of varied flow scenarios, and show flow-based changes to the diffuse and point sources identified in this report, as well as potentially identifying sources that were not flowing or underestimated on this low baseflow sampling occasion (Onnis *et al.* 2018).

Conclusion

This purpose of this study was to show variations in metal loadings along the Nant y Bai and identify sources of metals not shown by conventional spot sampling. A continuous tracer injection and synoptic sampling method identified and quantified a previously unknown source at 305 m that contributes 34% of the

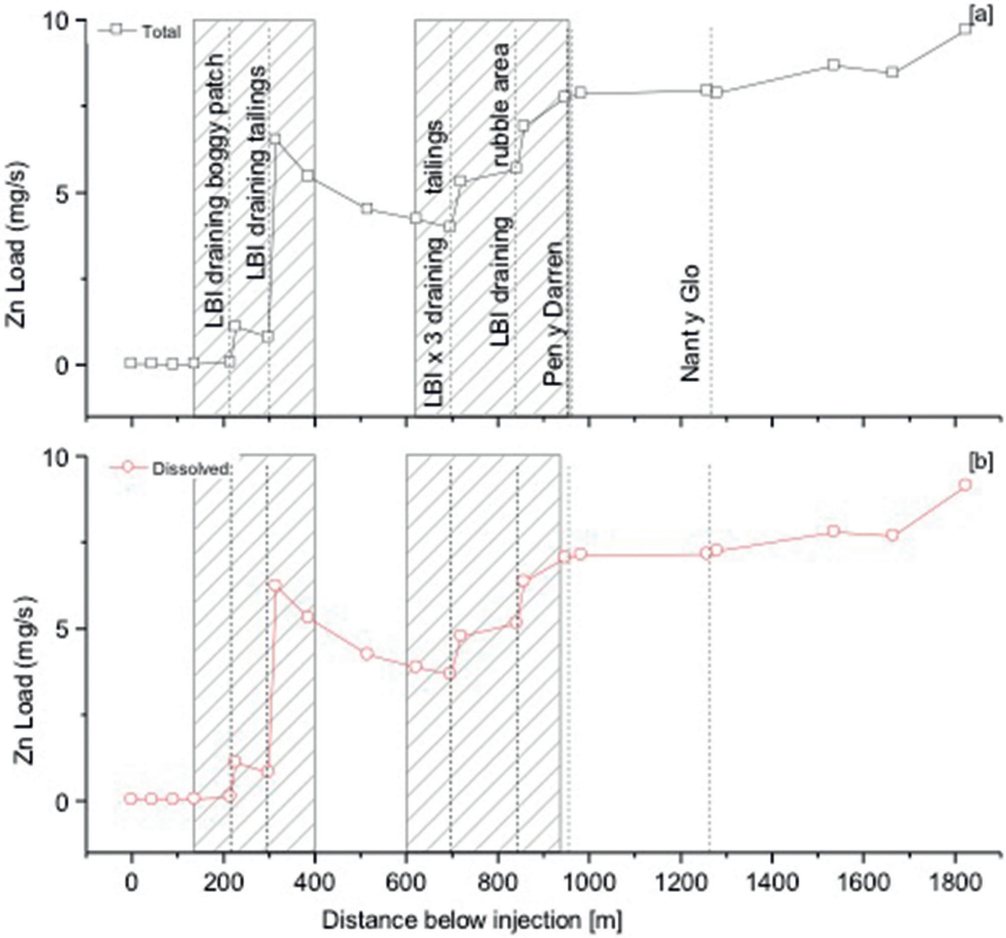

Figure 4 *Spatial profiles of total [a] and dissolved [b] instream Zn loads; total [c] Location of major inflows indicated with vertical dashed lines. Shaded areas = upper tailings (≈140-400 m) and lower tailings (≈620-950 m).*

total Zn load, despite its low flow compared to the river. Areas of diffuse inputs of pollution have been identified and further investigation into these can be planned on the basis of this information. The Nant y Bai fails WFD standards on Zn for the majority of its course.

Spot sampling with flow gauging, while a substantial improvement on just sampling, can easily miss extreme flow events, hence storm flows may not be accounted for in remediation planning. Similarly, sources with a relatively high contribution at low flows may be missed. Using tracer injection and synoptic sampling to provide high spatial resolution data brings clear advantages for regulators for both analysing mine impacts, and for assessing remediation. Further work will be carried out to investigate both sustained high flows and peak flows from storm events, as well as analyses of bed sediment along both streams. Data from the 2019 synoptic sampling will also be used to model flows and possible remediation scenarios.

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