Using Tracer Injection and Synoptic Sampling, and Salt Dilution Flow to Gauge Metal Fluxes in a Temperate Watershed in the UK

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Abstract

Nantymwyn Lead Mine has substantial subterranean workings, surface mine waste tips, collapsed adits and two streams which cross the workings and waste. One of >1,300 abandoned metal mines in Wales, it causes elevated levels of lead and zinc in the streams, and in flora and fauna near the mine site. Two methods of measuring pollutant fluxes were used; a constant rate injection and synoptic sampling at a constant flow, and monthly flow gauging and sampling over a year. These show surface and subsurface pollutant inputs, attenuation, and temporal changes in flow and the proportion of pollution from source areas.

Keywords: Metal Mine Waste, Synoptic Sampling, Flow Gauging, Lead Pollution

Introduction

The impacts of metal mines is felt globally on watercourses, flora and fauna, with a multitude of overlapping causes, including legislative restrictions, metal market values, age of the mine, and methods used to work it (Tost *et al.* 2020; Sartorius *et al.* 2022). Metal mines continue to deleteriously impact these areas after their closure or abandonment, with mines in the UK only legally requiring post-closure remediation by the operator after 1999 (Environment Agency 2008). Successful remediation of a mine must consider sources of pollutants and the routes they take from the source to the area they are causing harm. Additionally ongoing pressures to the mine and its remediation from land use change and an increased frequency of extreme weather events as a result of climate change must be considered (Hanlon *et al.* 2021). Locating pollutant sources, quantifying their impact, and accurately describing pollutant fluxes across the impacted waterbody are therefore crucial to successful and cost-effective remediation of abandoned mine (Byrne *et al.* 2020).

Wales alone has over 1,300 abandoned metal mines, with only the 50 rated highest impacting on watercourses being investigated to confirm their impact and possibility of treatment or remediation (Environment Agency Wales 2002). Nantymwyn is one such mine, with known impacts causing the River Tywi to fail Water Framework Directive (WFD) standards for zinc for 69km. Investigative work by the environmental regulator traditionally only records pollutant concentrations at the confluence with the main waterbody, which lacks the nuance to target remediation. In this project two methods of quantifying the pollutant fluxes at both temporal and spatial levels were used, for the former samples were taken concurrently with salt dilution flow gauging, for the later synoptic sampling and constant rate tracer injection method was used (Kimball *et al.* 2004).

Study Area

Nantymwyn Lead Mine is located in the upper catchment of the River Tywi, near Llandovery, Carmarthenshire (52°5'12"N; 3°46'20"W) and was mined sporadically from pre-Roman times until abandonment in 1932 (Hall 2011). Accurate maps of the underground workings were only kept in the final decades of the mine's operation, however falsified documents were discovered and destroyed by the final operator, leaving little clarity on their extent (Hall 2011). Two adits drain to

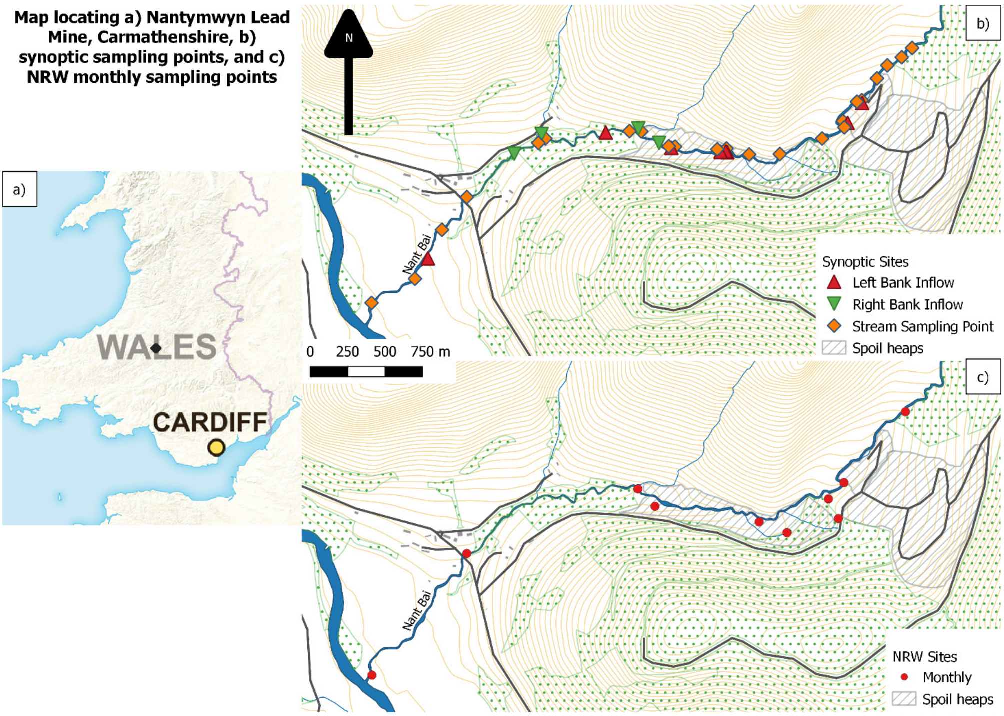

Figure 1 Location of a) Nantymwyn within Wales, b) location of synoptic sampling points along the Nant Bai, and c) location of monthly sampling points along the Nant Bai (Ordnance Survey 2020)

the surface, the Upper Boat Level joining the Nant y Bai, and the Deep Boat Level the smaller Nant y Mwyn. On the surface the Nant y Bai flows through unconsolidated spoil and tailings that cover approximately 20 hectares. Soil, blood, and plant samples taken near to the river have shown elevated levels of zinc and lead (Sartorius *et al.* 2022).

Methodology

Monthly Sampling

On one day a month for twelve months sampling was conducted at the sites shown in Figure 1c, working upstream to avoid any possible contamination and following national guidelines (Environment Agency 2010). These sites were selected to divide the stream into areas of interest, above the mine, between the two areas of mine waste, below the main mine area, above farmland, and before the confluence with the River Tywi, as well at four inputs. Continued sampling was prevented by the Covid-19 pandemic. Two 125 ml polypropylene bottles were used to collect one sample directly from the sampling point, and one filtered through a 0.45 µm membrane, for subsequent analysis by ICP-MS. Concurrent to the sampling a calibrated multi parameter probe was used to take pH, conductivity, and temperature readings. After the sample had been collected the flow of the watercourse was estimated by salt dilution flow gauging using the single injection method (Littlewood 1986; Moore 2004; Williams 2016). Comparative flow gauging was carried out in July 2019 to compare the results of each method on the same stretch of stream and at the same time; the salt dilution flow gauging gave a result within 10% of the synoptic sampling. This would be expected as the synoptic sampling includes the flow in the hyporheic zone due to the temporal length of injection (Moore 2004). To the south of the site is a second stream which was also flow gauged and sampled on a monthly basis, but is not included in this paper for clarity.

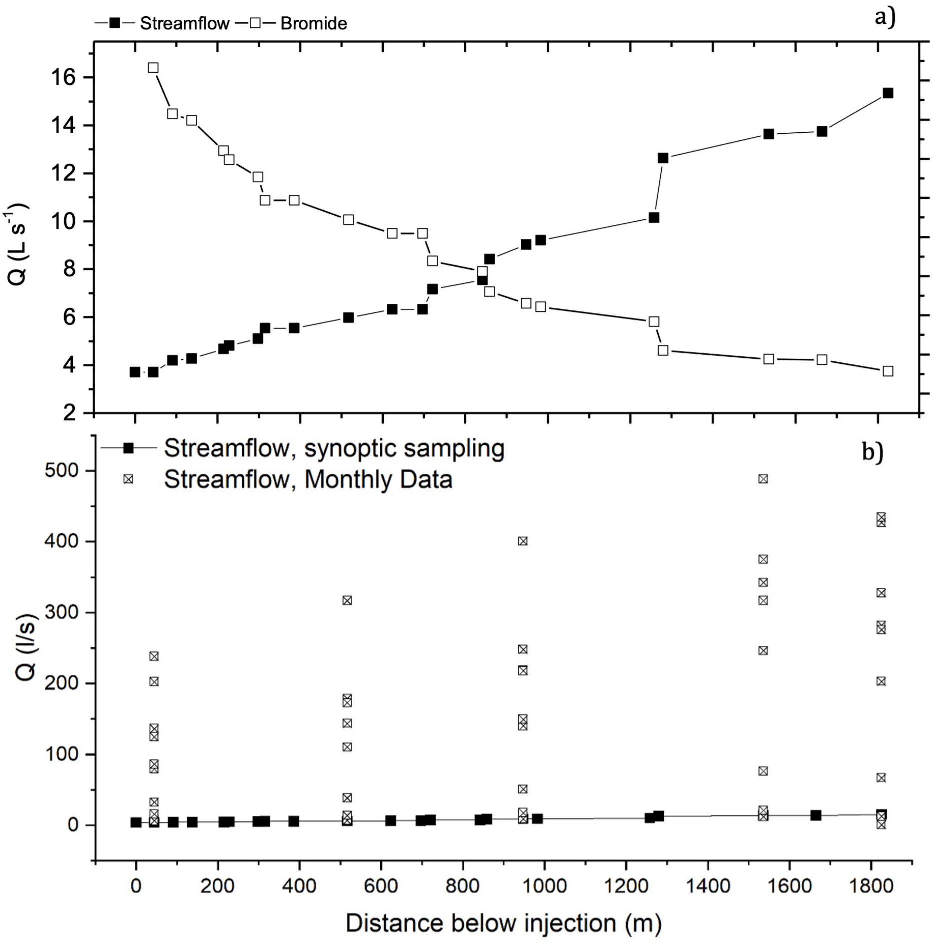

Figure 2 *a) Br river concentrations and river discharge (Q) changes along the Nant y Bai, b) river discharge (Q) for synoptic sampling and monthly sampling*

Synoptic Sampling

In July 2019 a constant rate injection apparatus was set up to deliver 70 ml min^{-1} NaBr tracer into the stream, and after three days when the Br had reached a plateau concentration at the most downstream point in the stream sampling was conducted, heading upstream to avoid any cross-contamination of sites (Kimball 1997; Todd *et al.* 2021). 33 Sites were selected, guided by the results of the monthly sampling. Where visible inputs were found, a sample was taken from the input, and upstream and downstream of it, the same as suspected inputs, and at changes to the stream, such as entering or leaving areas of mine waste. At each site a sample was taken, being split at a field laboratory into three bottles, one filtered through a 0.45 µm membrane, one fixed with HNO3, and one fixed and filtered. These were later analysed via Inductively coupled plasma mass spectrometry (ICP-MS), and the flow calculated as a product of the Br concentration at each stream site. Nearby flow gauging sites on the River Twyi are flow controlled by the Llyn Brianne reservoir, but a proxy stream suggested by NRW was Q89 on the day of sampling (Edwards 2021). These low flow conditions were selected due to the high likelihood of consistency of flows over several days, minimising changes in Br concentrations to allow for future modelling (Byrne *et al.* 2020).

Results and Discussion

The Br concentration and calculated streamflow at each point in the Nant y Bai are shown in Figure 2a, with Figure 2b showing the comparison between a single day's low flow high spatial resolution flow gauging from the synoptic sampling, to 12 months' data at a lower spatial resolution. The lowest flow months (April, May, July and September 2019) align with the flows recorded in the Q89 flow during the synoptic sampling, and while monthly sampling will miss extreme events, the highest recorded flows (March, June and December 2019) are up to 43 times greater than the lowest. Despite the increase in flow over the course of the stream (Fig 1a) on the day of synoptic sampling, the instream Zn load (Fig 3a and 3b) notably decreases from 300-700 metres downstream from the injection point, showing attenuation in the mine waste that the stream flows through. However, Fig 3c and 3d show an increase in Zn load after the mine waste from the monthly monitoring data, but the lower spatial resolution means that this method is unable to show increases or decreases between the two sampling points, due to time restraints on a day's sampling routine, and accessibility of the stream in between the points where the stream enters a steep sided gorge.

The inclusion of flow gauging is an intrinsic part of assessing an impacted river, while quicker and easier to collect, concentration data alone will miss the increased pollutant load. For instance, the highest total Zn load at the confluence with the Nant y Bai to the River Twyi is 155 mg s^{-1}, in March 2019, while the concentration is 363 μgL^{-1}. In September 2019 the concentration for total Zn was 1530 $\mu g\ L^{-1}$, but as the flow was substantially lower the total Zn load was 19.2 mg s^{-1}. At no point during either sampling regime did the stream at its confluence with the River Tywi meet the Water Framework Directive standard for Zn of 12.9 $\mu g\ L^{-1}$ (Water Framework Directive 2015).

Combined these two methods should allow areas of pollutant inputs to be found, synoptic sampling at this site revealed one input at 305 metres below injection responsible for 34% of the stream Zn load on the day of sampling (Todd *et al.* 2021). However, this single day of low flow is not representative of the stream over the year, and while one day a month is also not fully representative of the variations in flow and pollutant fluxes across the site, the salt dilution flow gauging and concurrent sampling does allow for continued monitoring of variations without the time and cost of a multiple day synoptic sampling regime over different flows. Despite the attenuation effects the synoptic sampling recorded after the input at 305m, the monthly sampling shows an increase in both total and dissolved Zn load after both areas of mine waste.

When considering remediation for a site, knowing the location of sources, their relative size in both flow and concentration, and their variation, are crucial. Both passive and active treatment systems can cost millions, and targeted treatment can allow for more sites to be treated to the same standard (Edwards *et al.* 2016). At Nantymwyn, small diversions of surface water flows and encapsulating some areas of riverbed where the sediments are mobile and polluted could deliver substantial improvements in water quality at most river flows with low capital expenditure. At low flows reducing the input at 305m will reduce Zn loads markedly, as water diversion efforts at Frongoch did in 2011 (Edwards *et al.* 2016). At higher flows the monthly sampling guides a reduction in the impact of the upper mine waste areas, by reprofiling or encapsulation of the waste.

Conclusion

Both methods used allow for a better understanding of pollutant fluxes across a site, as well as inputs into larger rivers, and their costs and advantages can be balanced against each other for assessment of a site ahead of remediation or reuse. Understanding seasonal flow and load changes allows the upper flow limits of a treatment system to be set to collect the maximum expected flow, while ensuring that the lower average flows during summer are adequately treated. However the higher spatial resolution of synoptic sampling and tracer injection prevents hidden or subterranean inputs from being missed and causing future issues. Any hydrologically complex site that will undergo remediation would benefit from the application of both

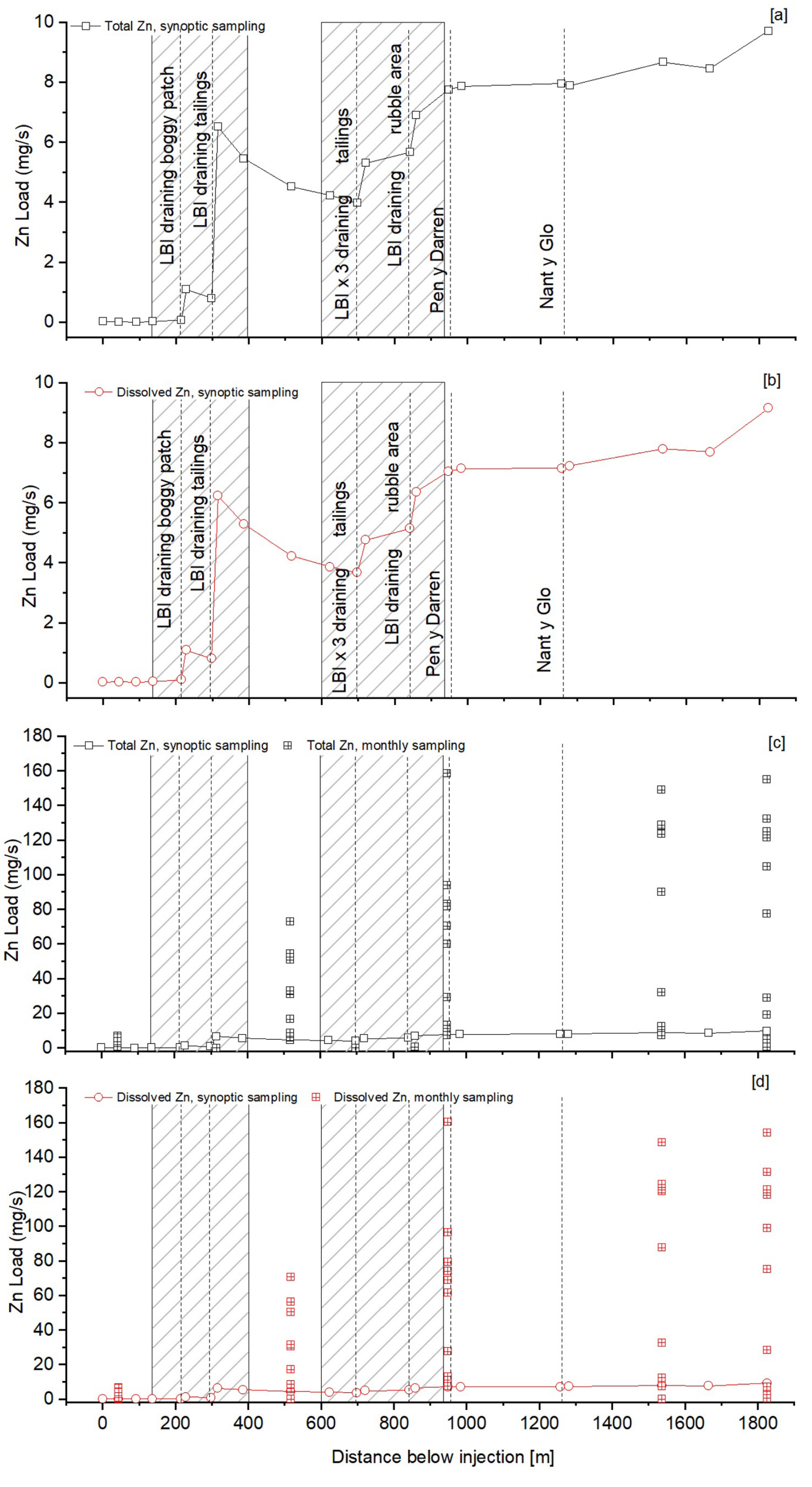

Figure 3 *a) total Zn load, synoptic sampling, b) dissolved Zn load, synoptic sampling, c) total Zn load, monthly sampling and synoptic sampling, d) dissolved Zn load, monthly sampling synoptic sampling*

methods, with the monthly monitoring guiding the location of the sites for synoptic sampling, and the data from both offering a powerful tool for planning and delivering remediation. At Nantymwyn the preliminary monthly data fed into the selection of sites for the synoptic sampling and tracer injection, which then led to the discovery of a source of 34% of that day's Zn load. This information and others from both methods is crucial to understanding and planning remediation the site These methods can be used with minimal adaptation on other sites to guide or improve understanding and remediation attempts.

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