Source Apportionment of Trace Metals Over a Range of Stream Flows Using a Multi-method Tracer Approach

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Abstract

Pollution from abandoned mines is a major cause of environmental legislation failure. Remediation of mining-impacted river catchments must be underpinned by detailed and catchment-scale data that includes loading assessments over a range of streamflow. In this study, a constant injection tracer coupled with synoptic sampling allowed quantification of main Zn sources along a polluted UK river. Downstream of the mine workings, Zn load changes were measured under a range of flows. Our data highlight the variability of Zn dispersion in response to different streamflows. We emphasise the necessity of using a multi-tracer approach for assessing spatial and temporal metal distribution.

Keywords: multi tracer approach, metal mine waste, contaminated catchment, trace metals, hydrological variations

Introduction

Identifying and quantifying sources of mine waste in river catchments is confounded by the extensive nature of historical mining operations that have generally resulted in multiple potential sources of mine pollution across a catchment that can vary in importance as a function of hydro-meteorological conditions (Cánovas et al. 2010). The tracer injection and synoptic sampling approach, developed by the U.S. Geological Survey (Kimball et al. 2002), provided a framework to develop spatially detailed assessments of pollutant concentrations and loads to enable effective remediation. However, changes in loads and sources can occur especially during rainfall-runoff events and this is particularly problematic in temperate climates like the UK (Jarvis and Mayes 2012, Byrne et al. 2013). Here, we propose a development of this approach that provides a means to supplement spatial variation with temporal variability by integrating the tracer results with slug load estimations. The specific aim of this work was to develop a low cost and effective methodology for capturing metal load variation and to provide better advice for long-lasting remediation strategies.

Study Area and Methods

Wemyss and Graig Goch mines (central Wales, UK) were exploited for Zn and Pb sulfide ores until the beginning of the 20th century. Numerous potential point and diffuse sources of contamination are present in this catchment that cause downstream water quality to be classified as 'poor' by the European Union Water Framework Directive standards, due to their elevated Pb, Zn and Cu concentrations. These mines are drained by Nant Cwmnewyddion (fig.1) which flows eastwards into the Afton Ystwyth. Drainage from Frongoch mine emerges into the Nant Cwmnewyddion via the Frongoch Adit (F.A. in fig.1) and represents a major point source of metal contamination. Potential diffuse sources are present as waste heaps at various locations along the Nant Cwmnewyddion.

Assessment of spatial load variations

Metal loadings were established at 24 sites along a 2 km reach of the upper catchment using the tracer injection and synoptic sampling approach (Runkel et al. 2013). The major advantages of this approach over traditional methods (e.g. the velocity-area approach) for streamflow and metal loading estimation are improved accuracy and spatial coverage, and the potential to use the synoptic data for pre-mining water quality modelling and remediation modelling (Byrne et al. 2017). In July 2016 a solution of sodium bromide, with bromide (Br) concentration of 69 g/l, was injected into Nant Cwmnewyddion above the mine workings at an average rate of 195 ml/min for 31 hrs. No rain occurred during the tracer injection time. Synoptic sampling was undertaken when Br plateau concentrations were reached and proceeded from downstream to upstream. Samples were collected at stream sites and all visible inflows. Distances along the river are hereafter indicated as metric distances from the tracer injection site. Streamflow was calculated at each synoptic site by dividing the product of injection parameters (injectate discharge and Br concentration) by the sample site Br concentration (Kimball et al. 2002). Zn metal loads were calculated as the product of streamflow and Zn concentration. Source apportionment of Zn mass was conducted by comparing total Zn loads to cumulative Zn loads. Results of this experiment are referred as "flow 2" results throughout the text.

Zn load and streamflow variations

Three sites, upstream Wemyss Mine (W.M., 56 m), downstream Frongoch adit (F.A., 880 m) and Graig Goch Mine (G.G., 1645 m) were monitored during different weather conditions. Water samples were collected and in situ parameters (pH, EC and T) measured. At the most downstream site streamflow was measured through slug injection of sodium chloride, a rapid technique for discharge estimation described by Moore (2005). The monitoring samplings occurred twice and the two observed flows are hereafter called "flow 1" and "flow 3". Flow 1 sampling followed a few days of warm and dry weather; on the other hand flow 3 monitoring was undertaken under a storm event. The product of Zn concentration and streamflow data of flow 1 and flow 3 generate Zn load values for comparison between these two events and, furthermore, with flow 2 data.

Samples for Zn analysis were passed through 0.45 μm filters, acidified (2% nitric acid) and measured by Inductively Coupled Plasma Mass Spectroscopy. Samples for Br analysis were passed through 0.2 μm filters and measured by Ion Chromatography.

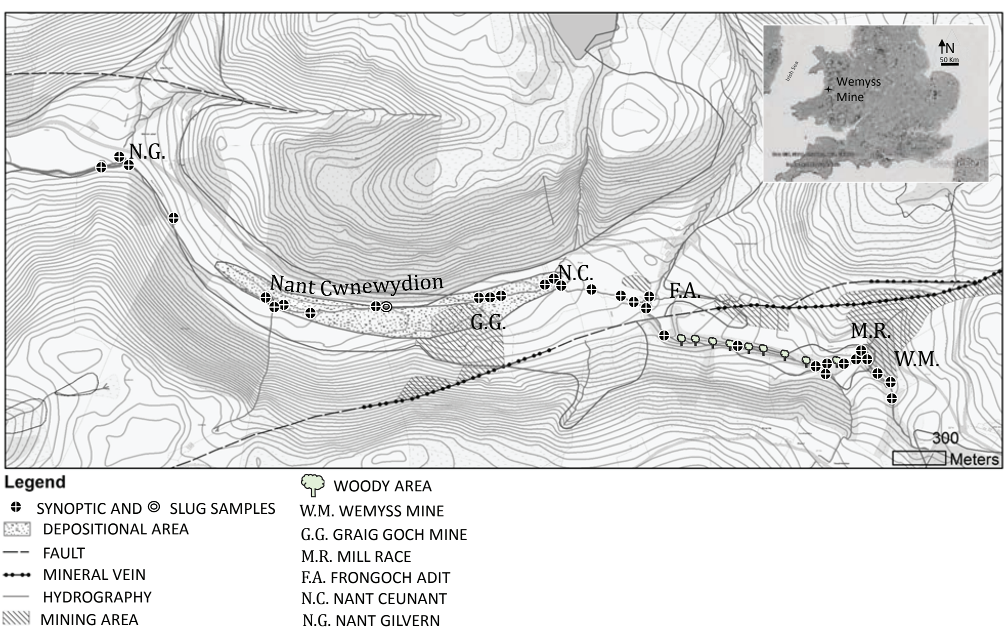

Figure 1 *Map of the study site showing geographical location, synoptic sampling sites along Nant Cwmnewyddion and main features (refer to the legend for the keys). Map created using EDINA Digimap Ordnance Survey Service (2018).*

Results and discussion

Stream water chemistry

Nant Cwmnewyddion has a pH of 6 ± 0.3, it is less acid in the headwaters and more acid at the downstream site. No important pH variations were observed during the different stream flows. Zn concentrations at Graig Goch Mine (G.G., 1645 m) are reported in table 1 for the three streamflow estimates. All of the reported Zn concentration values exceed the environmental quality Zn thresholds of 8 – 50 µg/l indicated by the UKTAG (2012).

Assessment of Zn spatial load variations

In this section data from flow 2 are discussed in order to quantify Zn sources at Nant Cwmnewyddion study reach. Along the river, flow 2 streamflow estimates (fig.2) show the influence of three main inflows Frongoch Adit (F.A.), Nant Ceunant (N.C.) and Nant Gilvern (N.G.). A gradual streamflow increase is also notable in the reach from 1314 m to 1961 m which is not directly related to any observed inflows. In figure 3.a, Zn concentration shows an articulate pattern with steep increases after Mill Race (M.R.) and Frongoch Adit (F.A.). Metal loading data indicate substantial variation along the study reach river with the major source of Zn identified as a point source input from the Frongoch Adit (F.A.). Frongoch Adit, with 3.91 mg/l Zn concentration, contributes 57% to the total Zn load and is responsible for an increase in Zn concentration (from 1.06 to 2.89 mg/l) and load (from 42 to 250 mg/s) between site 847 m and site 880 m. Furthermore, figure 3.a indicates a rise in

Table 1. *Downstream Graig Goch Mine (1645 m) data: discharge (Q), dissolved Zn concentration (mg/l) and load (mg/s).*

Streamflow	Technique	Site	Date	Weather	Q	Zn	Zn
		(m)			(l/s)	(mg/l)	(mg/s)
Flow 1	Slug	1645	09/06/2016	Dry	32	3.43	110
Flow 2	Tracer	1645	01/08/2016	Dry	146	1.95	285
Flow 3	Slug	1645	16/06/2016	Stormy	645	2.30	1484

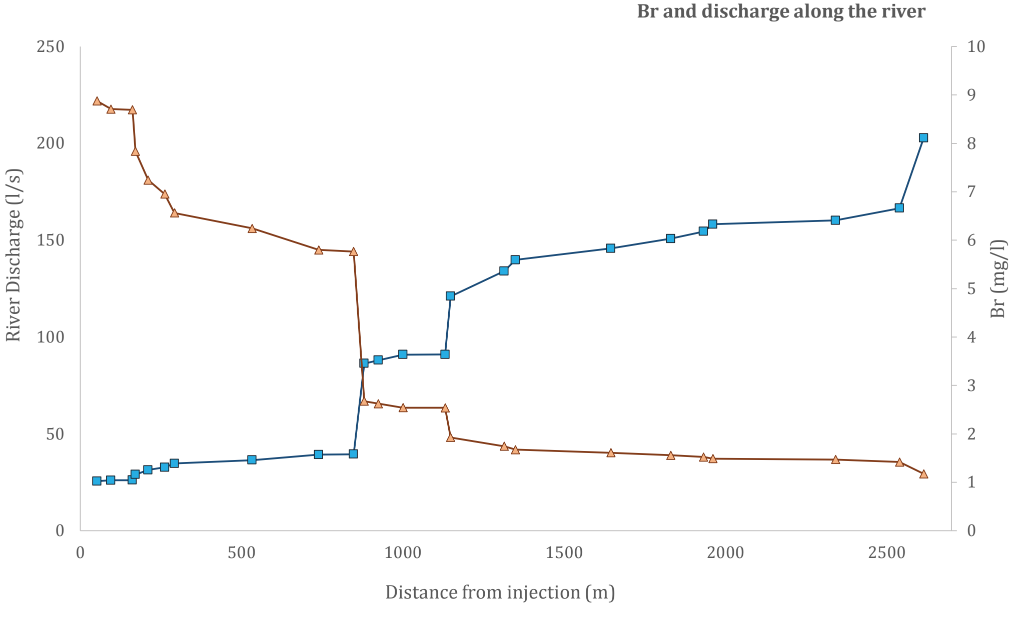

Figure 2 *Br river concentration (triangles) during long tracer injection and river discharge (squares) changes along Nant Cwmnewyddion.*

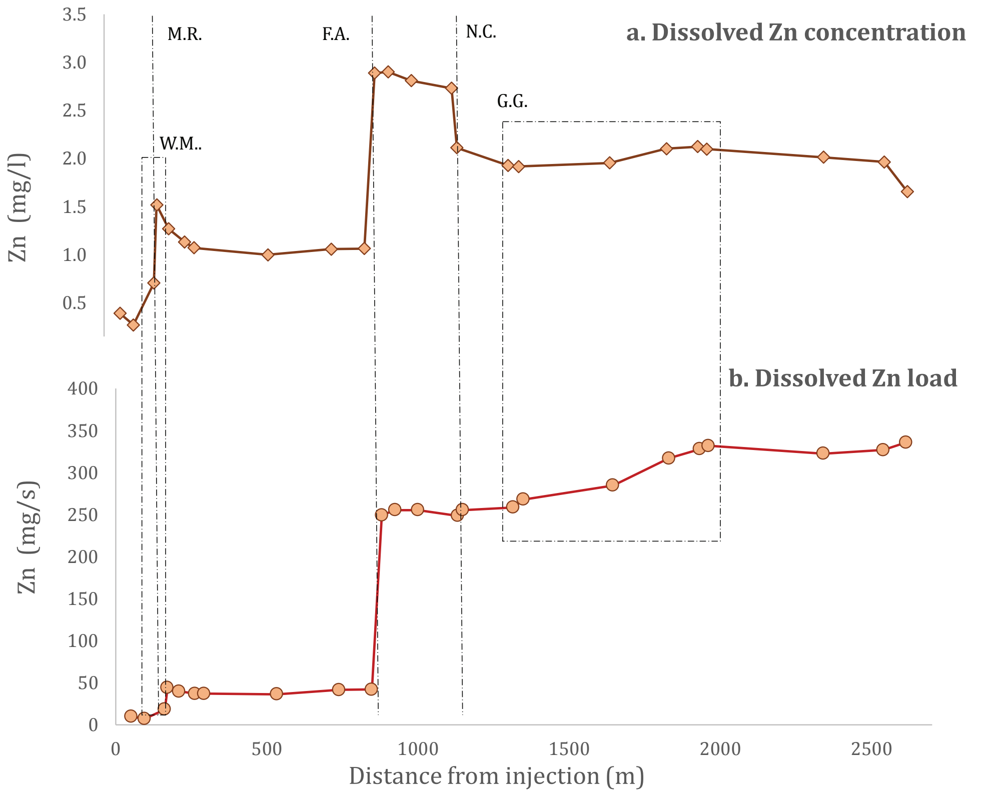

Figure 3 *Dissolved Zn concentration (a.) and load (b.) along Nant Cwmnewyddion. Inflow positions are indicated by capital letters (M.R. Mill Race, F.A. Frongoch Adit, N.C. Nant Ceunant,) and mine areas by W.M. (Wemyss Mine) and G.G. (Graig Goch Mine).*

Zn concentration from 0.70 to 1.52 mg/l from 162 m to 171 m, downstream of Mill Race (M.R.). However, it should be noted that this river runs alongside unconsolidated mine waste (Wemyss Mine) which is dominated by lateral seepages draining into the main river; the previous segment of river (95 to 162 m) contributes c. the 3% to the total Zn load (fig.4); the river reach from 95 m to 171 m is likely subject to a diffusive Zn source. In this segment, a total of 37 mg/s of Zn was gained, equivalent to 10% of the cumulative Zn load. A third area of metal sources can be identified from 1314 m to 1961 m, with Zn concentration rise from 1.93 mg/l to 2.10 mg/l and load increases from 259 to 332 mg/s. In this segment, Graig Goch mine waste dominated the left bank and a series of small pipes were seen to contribute a small discharge into Nant Cwmnewyddion water. Their Zn concentration increased constantly from down- to upstream (0.57 to 4.46 mg/l). Generally, Graig Goch Mine contributes 20% to the total cumulative load (fig.4). Summarising, three main sources are identified as contributing to the cumulative total load, Frongoch adit with 57%, Graig Goch Mine with 20% and Wemyss mine with 10% (fig.4).

Zn load and streamflow variations

At 1645 m site (downstream G.G.) streamflow estimates (tab.1) show a temporal variability of streamflow values with flow 1 (32 l/s) lower than flow 3 (645 l/s) and flow 2 falling between them (146 l/s). Zn load values (tab.1) indicate a clear proportional increase of load related to streamflow values: 110 mg/s at flow 1, 285 mg/s at flow 2 and 1484 mg/s at flow 3. These results suggest Zn dispersion responds to streamflow variations. Although flow 3 diffuse sources accounted for 30 % of the total Zn load, our data suggest that dif-

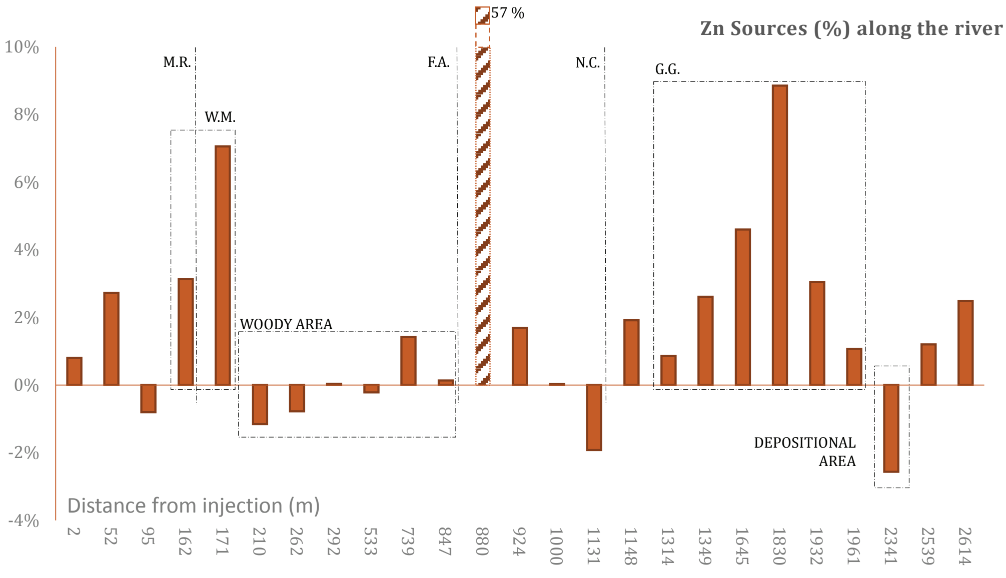

Figure 4. *Dissolved Zn sources and attenuation processes along the river reach. The dashed rectangular, representing the F.A. contribution, has been cut and value reported on top (57%). Inflow positions are indicated by capital letters (M.R. Mill Race, F.A. Frongoch Adit, N.C. Nant Ceunant,) and mine areas by W.M. (Wemyss Mine) and G.G. (Graig Goch Mine).*

fuse sources may increase in importance during higher flow conditions and rainfall-runoff events. Between 880 m and 1645 m (downstream F.A. and G.G.) differences in Zn concentration are captured in the different sampling time. The lowest, -0.39 mg/l measured during the higher flow, flow 3, indicates that the water from overland flows is carrying Zn mass with it and the dilution effect is less obvious compared to lower flow conditions, flow 1, when a variation of -1.24 mg/l was estimated. During flow 2 an average situation was observed with a variation of -0.94 mg/l of Zn in the same river segment.

Possible processes leading to an increase of diffusive pollution during high streamflow conditions, as flow 3, are mainly dissolution and washing of efflorescent salts (Cánovas et al. 2010). At the mine heaps and river channel, alternating wet - dry soil conditions may have promoted the oxidation of Zn-bearing minerals and oversaturated pore and interstitial water or pools allowed the precipitation of secondary minerals and efflorescence salts (Hudson-Edwards et al. 1999, Lynch et al. 2016). During our lower flow sampling, flow 1, efflorescent salts were noticed at different heights on the riverbank. In addition, Palumbo-Roe et al. (2013) recorded the presence of sphalerite (ZnS) at Wemyss and Graig Goch mine waste heaps. Furthermore, no difference between dissolved and total Zn have been measured, therefore Zn is most likely to come from the dissolution processes rather than colloidal suspension processes. In conclusion, dissolution of oxidised sphalerite and Zn-bearing fluorescence may be the cause of the diffuse contamination, the dispersion of which can be accentuated during high flow conditions or storm events by the rapid movement of the water in the channel and overland flow (Byrne et al. 2013).

Conclusion

The purpose of this study was to identify spatial and temporal variations in Zn load in a mining impacted river. Using a tracer injection and synoptic sampling approach sources at different river stages were identified: Frongoch Adit (57% of Zn); Wemyss Mine (10% of Zn) and Graig Goch Mine (20% of Zn). The latter two sources were diffuse in nature and possibly a result of hidden seepages and oxidation-dissolution of Zn-bearing minerals. Slug injections, conducted downstream of the mine workings at different times and river stages, captured the proportional response of Zn load to streamflow values. These data, in association with observed concentration changes, indicate that diffuse sources are likely to be more impacting during high flow conditions. This theory needs to be supported by a streamflow and Zn load database. More streamflow measurements have been undertaken along Nant Cwmnewyddion and a further tracer injection has been planned for summer 2018 at the same river reach.

In conclusion, these results highlight the benefit of using a tracer injection for source apportionment in impacted river catchments and the necessity to integrate it with over-time load monitoring to understand variability over different hydrological conditions.

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