

## Tracing sources and fate of zinc in a mining-impacted river catchment: insights from flow measurements, synoptic sampling, and zinc isotopes

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**Abstract** This paper reports on the comprehensive monitoring of the Rookhope Burn catchment in the Weardale valley, northern Pennines (UK), which has been subject to lead, zinc, and fluorspar mining for over two centuries. Zinc is the major contaminant in surface waters, exceeding the Environmental Quality Standard value for salmonid fish. Synoptic flow monitoring and water sampling have been carried out, including both inflow and instream sampling points along the Rookhope Burn, with the purpose of tracing both point and diffuse sources of Zn throughout the catchment. The Zn load profile suggests an important role for Zn-rich groundwater contributions to the stream bed and has also established the existence of Zn sinks. Evidence from hyporheic zone sampling suggests Zn reaction or surface complexation with Mn oxide surfaces forming on stream bed sediments as a potential mechanism responsible for the observed metal attenuation. Current work is focused on testing the potential of Zn isotopes to fingerprint sources and pathways of Zn in the aquatic system. Preliminary results show significant variation in the stream water Zn isotopic signature from the headwaters to the base of the catchment.

**Key Words** Zinc, abandoned mines, metal load, hyporheic zone, isotopes, northern Pennines

### Introduction

Understanding contaminant sources and contaminant pathways is fundamental to optimising the location and methods for remediation of a catchment. The mechanisms by which metal attenuation occurs and potential mobility of the sequestered contaminants are important in the prospect of successful remediation.

This report summarises the findings of an integrated investigation aimed at determining the importance of point and diffuse zinc sources in the mining-impacted Rookhope Burn catchment, in the Weardale valley, northern Pennines, UK. Zinc is the major water contaminant in the catchment.

### Materials and Methods

#### *Study area*

The Rookhope catchment comprises an area of 37 km<sup>2</sup>, and the southerly flowing stream contributes a discharge ranging from 100 to 2300 L/s to the River Wear at Eastgate (NY 952 390). The hydrograph for the Rookhope Burn is flashy, with rapid, short term changes in stream flow in response to runoff events.

Four hydrogeological domains that reflect the underlying geology have been identified: upland peat capping interbedded shales and sandstones with an interbedded limestone (Upper Felltop Limestone) at the lower end of the zone; interbedded shales and sandstones with an interbedded limestone (Lower Felltop Limestone); till capped bedrock, including the Great Limestone, characterised by the presence of dolines (also known as shake or sink holes), which is indicative of karstic void forming processes, and; more resistant limestone bedrock (Alston Formation) characterized by a number of waterfalls.

The carbonate-hosted lead, zinc, fluorite and baryte mineral deposits of the Northern Pennine Orefield have been worked over thousands of years from pre-Roman times to the end of the last century. The main period of lead production was from around 1750 to 1920 and for fluorspar from 1900 to 1999, when the Grove Rake Mine closed. Abandoned quarries, the remnants of mine workings, and piles of abandoned mine waste characterise the landscape. The driving of mine drainage adits to dewater the mines was common practice in the North Pennines and this had the effect of altering the local hydrogeological regime. Johnson and Younger (2002) carried out underground and surface sampling of waters from Frazer's Grove prior to and during groundwater rebound following cessation of pumping, and established that the groundwater chemistry is stratified, reflecting the influence of variations in the bedrock geology.

**Sampling programme and analyses**

Synoptic flow monitoring and sampling for chemical determinations of major ions and trace elements were carried out, at instream sampling points along the Rookhope Burn and tributary inflow sites (locations of potential contaminant discharges) in May 2007, June 2007, January 2008, and April 2009. Stream velocity was measured using a Columbia 2 digital stream meter and stream discharge was determined using the velocity-area method. Water pH, temperature, Eh, and conductivity were measured in the field using a water quality multiparameter meter. Alkalinity was determined by titration immediately after sample collection, using a Hach digital titrator. Samples for chemical analysis were passed through 0.45 µm filters. Major and trace elements were determined by ICP-MS in subsamples field-preserved using 1% HNO<sub>3</sub>. The major anions, Cl, SO<sub>4</sub>, NO<sub>3</sub>, and F, were determined by ion chromatography on unacidified subsamples.

The Rookhope Burn hyporheic zone (HZ) was also sampled at 6 sites. Hyporheic water samples were collected using a low-flow inertial pump from a 50 mm diameter stainless-steel piezometer inserted 30 cm into the streambed sediments at each sampling point. Surface water samples were also collected at each hyporheic sampling point. Stream bed sediments were collected at each site where hyporheic sampling was carried out, air-dried and sieved to remove the size fraction greater than 150 µm. No attempt was made to obtain a vertical profile of the HZ using multi-level samplers at this stage; nevertheless the approach used provided a preliminary insight into the hydrochemistry of the HZ.

Six surface water samples were analysed for Zn isotope analysis at the “Mass Spectrometry and Isotope Geochemistry Laboratories”, Department of Earth Science and Engineering, Imperial College London, using the method detailed in Peel et al. (2010).

**Results and discussion**

**Zinc loadings**

The Zn concentrations and Zn loads, calculated from the product of discharge and the Zn concentration, were plotted against distance downstream from the head of the catchment (Figure 1). Mass balance calculations, based on the assumption that the load of a stream segment includes the load from the point upstream plus the contribution from all surface and subsurface inflows along the stream segment, were used to identify the sources and sinks of Zn. From this analysis, it is evident that the most significant impact on the water quality of the Rookhope Burn is the contribution of mine water from the outburst at Wolfcleugh (point 7, Zn concentration range: 2400–1400 µg/L; pH 7.3–6.1), which is considered to have occurred as a response to excess pressure that built up as a consequence of a downstream collapse within the underground mine workings. With no visible inflows to account for some of the Zn loadings to the stream, it appears that there must be a significant contribution of dispersed contaminated groundwater to the bed of the Rookhope Burn. The cumulative Zn load at the base of the catchment ranged from 100 to 400 mg/s over four sampling seasons, while the cumulative Zn attenuation ranged between 80 to 140 mg/s. This suggests that Zn does not behave conservatively in the alkaline water that characterises this catchment.

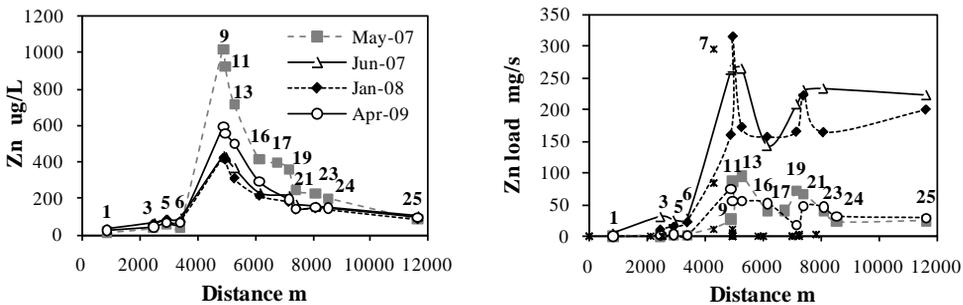


Figure 1 Zinc concentrations and loads in the Rookhope Burn. Inflows zinc loads with asterisk symbols

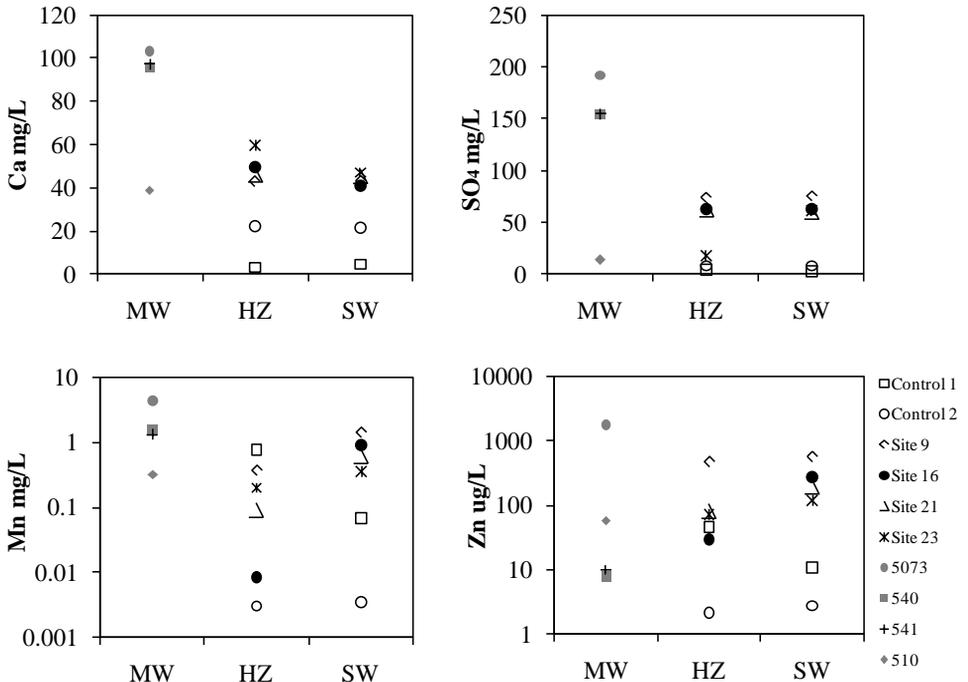
**Metal attenuation in the hyporheic zone**

Figure 2 shows that for relatively conservative elements such as SO<sub>4</sub> and Ca, differences were minimal between the surface water and the hyporheic water concentrations, while greater differences were observed between the hyporheic and mine waters. This suggests negligible physical mixing of surface and contaminated mine water in the HZ at the sampling points. However, given the absence of groundwater sampling at the study sites and the heterogeneity of the mine water compositions, it is not possible to draw definitive conclusions at this stage.

For sites 9, 16, 21, and 23, Mn and Zn do not behave conservatively, with a significant decrease in concentration in the hyporheic zone waters compared to the surface waters. Decreased concentrations of Zn and Mn in the hyporheic zone compared to surface waters have been previously described by Benner et al. (1995), who suggested that it might be due to reaction or surface complexation with metal oxides concurrently forming on stream bed sediments. Evidence of black-coated boulders in the stream bed, presumably indicating microbial Mn(II) oxidation, has been found in the Rookhope Burn downstream of the zone of subsurface contaminated groundwater inflow.

**Use of zinc isotope tracers**

Results of the analyses of six samples show significant variation in the stream water Zn isotopic signature ( $\delta^{66/64}\text{Zn}$  normalised against the Lyon reference standard) from the Rookhope Burn headwaters ( $\delta^{66/64}\text{Zn} = +0.39\text{‰}$ ) to its confluence to the River Wear ( $\delta^{66/64}\text{Zn} = +1.42\text{‰}$ ). Among the potential Zn sources, the  $\delta^{66/64}\text{Zn}$  signature of the Wolfcleugh mine water outburst, is  $+0.53\text{‰}$ , while it is  $+0.15\text{‰}$  for mine spoil seepage and  $+0.25\text{‰}$  for mine spoil samples. There is an enrichment in heavier Zn isotopes in the ochre sediment ( $\delta^{66}\text{Zn} = +0.65\text{‰}$ ) compared to the mine water (Wolfcleugh mine water) from which the ferric oxyhydroxides-rich sediment precipitates. This result provides field-based evidence to substantiate the laboratory work of Balistrieri et al. (2008), which indicated Zn isotopic fractionation during the adsorption of Zn by amorphous ferric



**Figure 2** Concentrations of dissolved Ca, SO<sub>4</sub>, Mn and Zn in surface water (SW) and related hyporheic zone (HZ) water at 6 sites along the Rookhope catchment. Mine water composition range (MW) also plotted

oxyhydroxides. The enrichment in heavier isotopes of Zn in surface water at the base of the catchment compared with the headwaters is unexpected and inconsistent with the anticipated mechanism of attenuation, adsorption onto Fe and Mn oxyhydroxides. Therefore, additional sources of heavy Zn isotopes or other mechanisms of isotopic fractionation are implied. Isotope fractionation during both physical and biogeochemical processes may significantly complicate the tracing of Zn emission sources using its isotopes. Current research is focussed on better defining processes controlling changes in the zinc isotope ratios in the different catchment compartments.

### Conclusions

Distinctive increases in Zn load in the Rookhope Burn occur as a result of major visible point sources of mining-related contamination (mine adits) and subsurface diffuse contributions of mine water through the river bed.

Catchment monitoring has also indicated the significance of natural attenuation along the Rookhope Burn. Preliminary findings of a study of the shallow hyporheic zone have indicated that Zn and Mn are co-attenuated in this zone, probably during oxide precipitation.

The catchment surface water shows a large range in Zn isotope values, warranting further investigation. The relative abundances of Zn isotopes in natural waters may be used to fingerprint sources of this metal and/or to probe important biogeochemical reactions. Yet, our ability to interpret these measurements is limited because of the paucity of published studies that explore the mechanisms of Zn isotope fractionation, and poor understanding of how these elements fractionate during weathering reactions. More work is needed to gain further insight on the fractionation behaviours of Zn isotopes and other transition element isotopes to make them valuable geochemical probes in biogeoscience.

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