Physical and Geochemical Characteristics of Contaminants in an Abandoned Metal-Impacted River Catchment under Varying Hydrological Conditions

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ABSTRACT
Aqueous and sediment-associated zinc pollution emanating from abandoned metal-mines is evident across the South Tyne River catchment in the north Pennines, UK. One of the main contributors of this pollution is known to be the River Nent (29.1 km^2), an upland tributary draining a region which was heavily mined until the 1980's. During a ~ 4 day monitoring period with variable flow conditions, concentrations of total zinc in the River Nent ranged from 0.49 – 1.73 mg/L, with the calculated total zinc flux peaking at 1175 kg/day; ~87 % of this total zinc flux is in the dissolved form. Bed sediment in the River Nent exhibits total zinc concentrations < 92,800 mg/kg. As the distance from the source increases down the South Tyne catchment the zinc and sediment concentrations decrease suggesting dilution and natural attenuation. Hysteresis patterns produced during the hydrological event indicate there are readily available sources of particulate contamination across the catchment, likely originating from the release of contaminated sediments in transient storage which were originally sourced from waste rock piles upstream. With large fluxes arising from small catchments it is imperative the dynamics between the flow-sediment-metal relationship are well understood in order to determine the most efficient remedial processes.

Key Words:Zinc, flux, hysteresis, sediment, River Tyne, River Nent

INTRODUCTION
Abandoned metal mines and poorly managed operational mine sites are known contributors of both point and diffuse source pollution across the globe.In the UK, where a large majority of coal and metal mines have been long-abandoned, it has been calculated that 50 % of the total metal flux to freshwaters of England and Wales arise from historic metal mining activity (Mayes *et al.*, 2010). The contamination of these freshwater bodies by metals such as Cadmium (Cd), Iron (Fe), Lead (Pb) and Zinc (Zn) can be detrimental to one or all of the water quality, ecology, amenity and water resource value of affected river catchments (watersheds). However, to date virtually all of the metal mine water discharges in the UK continue to flow unchecked. This is partly because of the 'orphan' nature of these sites, which fall outside the legislative framework that is invoked to address most other forms of water pollution. Nevertheless, there is an increasing drive in the UK to begin to address these problems. In so doing, a key issue is maximising the benefits to the water environment in light of the costs of installation and operation of the treatment systems. A key aspect of maximising benefits is a thorough understanding of the whole river system, and in particular the proportionate importance of point and diffuse sources, and also of particulate versus dissolved metal fractions. This paper reports on exactly these issues for a formerly heavily mined (Pb/Zn) river catchment in northern England.

Northern England has a long history of mining for both coal and metals, but the majority of these mines are now abandoned. The North Pennine Orefield was intensively worked for its lead and zinc ore; data up until 1977 indicates the output of mining the region was estimated as 4,500,000 tonnes lead and 300,000 tonnes zinc (Dunham, 1981). The South Tyne River catchment (800km^2), which ultimately feeds into the River Tyne, drains part of the North Pennine Orefield. Across the catchment visible relics of the mining era remain, such as waste rock piles, tailings, and the abandoned infrastructure used for ore processing. Previous research on the River Tyne catchment primarily focusses on either aqueous pollution (Armitage*et al.*, 2007; Nuttall, 1999; Rudall and Jarvis, 2012) or sediment contamination (Macklin *et al.*, 1997; Macklin and Dowsett, 1989),but no research has had the objective of coupling the aqueous and sediment metal behaviour to understand the best overall approach to remediation.

This paper presents data from part of an on-going investigation concerning the spatial and temporal variability of zinc fluxes across the heavily polluted South Tyne river catchment in the North Pennines, UK. The aim is to understand the dynamics of flow-sediment-metal relationships, and therefore enable a targeted remediation approach. As Zn is known to be a major contaminant in the upper tributaries (Nuttall and Younger, 2002; Gozzard, 2008), Zn is the contaminant of concern focussed on in this paper.

METHODOLOGY

Site of the study catchment

The Pennine hills are situated in northern England approximately 50 km west of the city of Newcastle Upon Tyne. Three sampling sites were strategically located across the South Tyne River catchment to capture the spatial and temporal differences at different points whilst accounting for all the major contributors, such as the River Allen (Gozzard, 2008). The most upstream site is the River Nent (~29.1 km^2); this is an upland tributary which drains one of the most heavily worked areas in the Pennines, the Nenthead mines. The Blagill sampling site is situated on the River Nent, downstream of 4 (of 5) of the main minewater discharges. Due to access restrictions and unsuitable river channel morphologies it was not possible to sample nearer the confluence of the River Nent with the River South Tyne, thus preventing the inclusion of all of the potential contamination originating from this water body. Downstream of Blagill are two other monitoring points, Featherstone (~18km downstream of Blagill) and Haydon Bridge (~40 km downstream of Blagill). Both of these are Environment Agency gauging stations. The locations of the sampling sites in relation to the catchment can be seen on Figure 1.

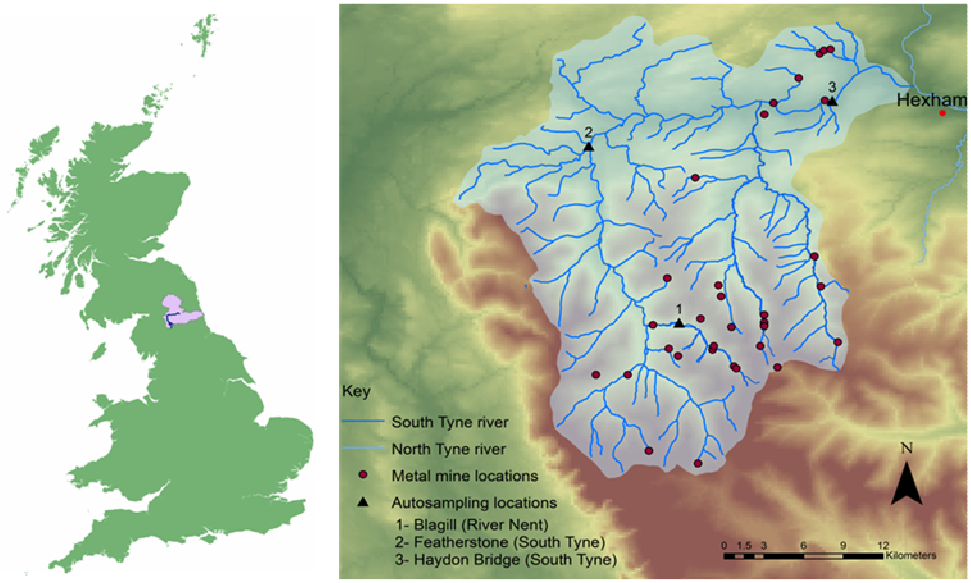


Figure 1:Location map showing the River Tyne catchment within the UK, with the South Tyne River/ River Nent marked and a larger image of the South Tyne River within its catchment and the sampling sites used in the investigation.

Sampling and analysis techniques

Flow determination

At each of the three sites the discharge was required to calculate flux. The River Nent is ungauged, and therefore 15 minute flow data was determined using a Van Essen diver and barometer in association with a stage discharge relationship curve (29 coupled data points, R^2= 0.975, p< 0.05). The flow at Featherstone and Haydon Bridge was provided by the Environment Agency at 15 minute increments.

Aqueous samples

An Aquamaticautosampler was deployed at each of the three sites to automatically take water samples from the river at pre-set intervals. The autosamplers were programmed to take ~750 ml samples approximately every two hours over four and three day periods (Blagill and Featherstone/ Haydon Bridge, respectively), depending on weather forecasts. Samples were collected in acid-washed polypropylene bottles which were completely rinsed with deionised water prior to use. The intake pipe and vessel used to collect the sample were automatically flushed with river water immediately before the actual sample intake to prevent cross contamination. The samples were regularly collected from the field, remaining in the sampling bottle for < 48 hours. Upon return to the laboratory (Newcastle University Laboratories) the samples were thoroughly mixed prior to subsamplingand aliquots were acidified with 1 % v/v HNO_3 to ensure the metals remained in solution. Samples for dissolved metals were filtered through a 0.45µm Pall Acrodisc (Supor Membrane) prior to acidification. Although there is a risk of redistribution occurring or

agglomeration of the smaller particles whilst the samples remain in the field, the relatively short time period prior to subsampling and subsequent acidification prevents any significant changes occurring.

Subsamples were taken for total cations and dissolved cations, with subsequent analysis of cation (Al, As, Ca, Cd, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Si, Zn) concentrations undertaken using Inductively Coupled Plasma- Optical Emission Spectometry (Varian Vista MPX CCD ICP-OES). Anions (SO_4^{2-}, Cl^-, HCO_3^-) are routinely analysed as part of the wider research pertaining to this investigation. However, as they are not the primary interest of the research, for logistical reasons not all anions were analysed. Blanks comprising of 1 % v/v HNO_3 (Primar Plus), standards (prepared from NIST traceable 1000 mg/L stock solution purchased from VWR/ Fisher Scientific) and certified reference material (River Water- River Thames LGC6019) were routinely analysed throughout. Any dilutions required were prepared using 1 % v/v HNO_3.

In order to gain the desired high flow event data some flexibility was required with regards to sampling time and duration, since the absolute number of samples that could be collected during any one event was limited to the number of bottles (24) in an autosampler, and a limited number of autosamplers were available for deployment. Consequentlyat both Featherstone and Haydon Bridge there is a gap in samples after the first initial peak, as seen in Figure 2. Given the importance of the Blagill site, on the River Nent, multiple autosamplers were deployed to permit uninterrupted sample collection through the event. The samples were collected in November 2010- Blagill samples were collected from 8/11/2010 @ 23:00 – 12/11/2010 @ 08:00 whereas both Featherstone and Haydon Bridge samples were collected from 9/11/2010 @ 03:00 – 9/11/2010 @ 18:00 and then 10/11/2010 @ 16:00 – 12/11/10 @ 12:00.

Sediment samples

Bed sediment was collected by hand at randomly located, accessible positions within a 10 m vicinity of the site. Disturbance of upstream bed sediment was avoided to prevent non-representative samples being collected. Up to 1.5 kg of sediment was collected from each sampling point using an inverted plastic sampling bag to capture as much of the sediment as possible. Triplicate samples were taken *in situ.* Sediment samples from the centre of the channel at Featherstone and Haydon Bridge are difficult to attain therefore samples were collected from within stream but nearer the channel edges.

Physical analysis of the bulk samples consisted of whole sample density analysis and particle size distribution. Overall density was determined following the 'Gas Jar method' outlined in British Standard 1377-2 (1990). Particle size distribution (PSD) and sample density werealso determined on the same sample. PSD followed the analytical procedure as described in British Standard 1377-2 (1990). Ten sieve apertures were used to determine the PSD of the samples (6.3mm, 5mm, 3.35mm, 2mm, 1.18mm, 600µm, 425µm, 300µm, 212µm,150µm and 63µm). The British Standard quality stainless steel sieves were cleaned with a wire brush between each sample to ensure no residue from the previous sample remained.

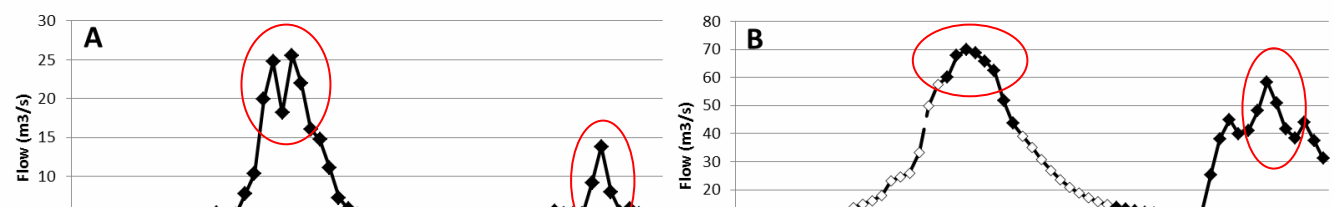
The metal content of the sediment was determined for each size fraction previously stated. Prior to digestion, each oven dried (105°c) sample was homogenized to <150 µm using a Retch Mortar grinder. Partial digestion of the sample by *aqua regia*was undertaken in compliance with British Standard 7755-3.9 (1995). Following sediment digestion, the metal concentrations were determined using ICP-OES with standards created in house using NIST traceable 1000mg/ L stock solution purchased from VWR/ Fisher Scientific. A dilution solution (HCl/ HNO_3/ 0.5 M HNO_3) was used when required and blanks of 1 % v/v HNO_3 were used throughout.

RESULTS AND DISCUSSION

Temporal and spatial variability of zinc flux across the catchment

Flow conditions

The flow conditions at each monitoring site can be seen in Figure 2. The first peak observed at Blagill corresponds with the first peak observed on the Featherstone and Haydon Bridge graphs, with a slight lag between the peak at Blagill and the peaks at Featherstone and Haydon Bridge, as expected. According to Environment Agency flow-duration data, the maximum flow during the period indicated in Figure 2 is a Q1 event at Featherstone and a Q2 event at Haydon Bridge (i.e. the flow only exceeds the flow recorded 1% and 2% of the time at Featherstone and Haydon Bridge respectively). As the site at Blagill is not subject to semi-permanent flow gauging, accurate flow-duration frequency curves are not available, but the flow conditions across the rest of the catchment suggest the data shown in Figure 2(A) represent a high flow event on the River Nent.



Zinc contamination

Concentrations of total zinc in aqueous samples across the catchment ranged from 0.10 to 1.54 mg/L. As anticipated, the average total zinc concentrations decrease as distance from the source increases. Table 1 summarises the observed zinc concentrations and fluxes during the monitored event and the calculated zinc fluxes for comparative purposes. Flux measurements are a more useful indicator of absolute pollutant release from a catchment than metal concentrations, since the former provide data on mass per unit time, which is independent of dilution effects.Nevertheless, and despite any dilution, based on the current Environment Agency (England and Wales) Environmental Quality Standards (EQS) the maximum permissible zinc annual average concentrations are exceeded at each site in each situation (Blagill and Haydon Bridge EQS 0.075 mg/L, Featherstone EQS 0.05 mg/L). It should be noted that the typical EQS compliance is usually based on annual average concentrations as opposed to the individual measurements recorded here.

Site		Zinc concentrations (mg/L)	Zinc fluxes (kg/ day)
Blagill	Minimum	0.49	119
	Maximum	1.73	1175
	Mean	0.92	326
Featherstone	Minimum	0.11	141
	Maximum	0.16	957
	Mean	0.14	397
Haydon Bridge	Minimum	0.10	226
	Maximum	0.18	1544
	Mean	0.12	679

Table 1: Observed total zinc concentrations and total zinc fluxes across the catchment during the monitoring event, November 2010

What is very clear from the summary data in Table 1 is that whilst variation in zinc concentration over the range of flow conditions is relatively small, with a maximum range of

0.49 – 1.73 mg/L at Blagill, the variation in zinc flux is very substantial; Zn flux varies by an order of magnitude at Blagill, and close to an order of magnitude at Featherstone and Haydon Bridge also. This has important implications, since large masses of zinc transported downstream during high flow events will likely result in zinc pollution issues far further downstream than would be suggested by the zinc concentration data alone.

Variation of dissolved and particulate zinc with discharge

In an effort to establish more clearly the specific sources of these very high zinc fluxes, the partitioning of zinc between particulate and dissolved phases has been investigated. It should be remembered that the 'dissolved' phase is operationally defined as all Zn passing through a 0.45μm filter. The pH, known topartially govern the dissolved/ particulate phase distribution,ranged from 7.64 to 8.12 at the upstream River Nent and remained circum-neutral at the two downstream sites. The Eh-pH diagram for oxidised waters as seen in Hem (1972) indicates that between pH ~7.5 to 8 the stable Zn phase would be $ZnCO_3$. Although the pH does vary, the dominant control on Zn contributions in this catchment is the highly variable flow, as discussed in the remainder of this paper.

Of the total zinc flux indicated in Table 1, at Blagill almost 87 % is in the dissolved form. At Featherstone the dissolved fraction is ~72 %, and at Haydon Bridge it is down to ~51 %. Figure 3 illustrates the differences between the particulate zinc flux and the dissolved zinc flux at each site during the monitored event, indicating how the different hydrological conditions affect the fluxes. The samples taken from theupstream Blagill site show a different pattern to Featherstone and Haydon Bridge, with dissolved flux rapidly increasing with small increases of flow. It is also worth noting the dissolved Zn flux at Blagill exceeds the dissolved flux at both Featherstone and Haydon Bridge. It therefore appears that zinc is mobilised in its dissolved form during rainfall events in the former mining district of the upper river catchment. As point sources of pollution in this area are rather constant in terms of discharge rate, since they arise from large 'ponds' of underground water, these increases in flux appear to arise from the large tracts of exposed waste rock in the area. With distance downstream it appears that the zinc mobilised in dissolved form becomes associated with particulates (likely via sorption), and this is reflected by more significant increases in particulate zinc flux at the downstream sites.

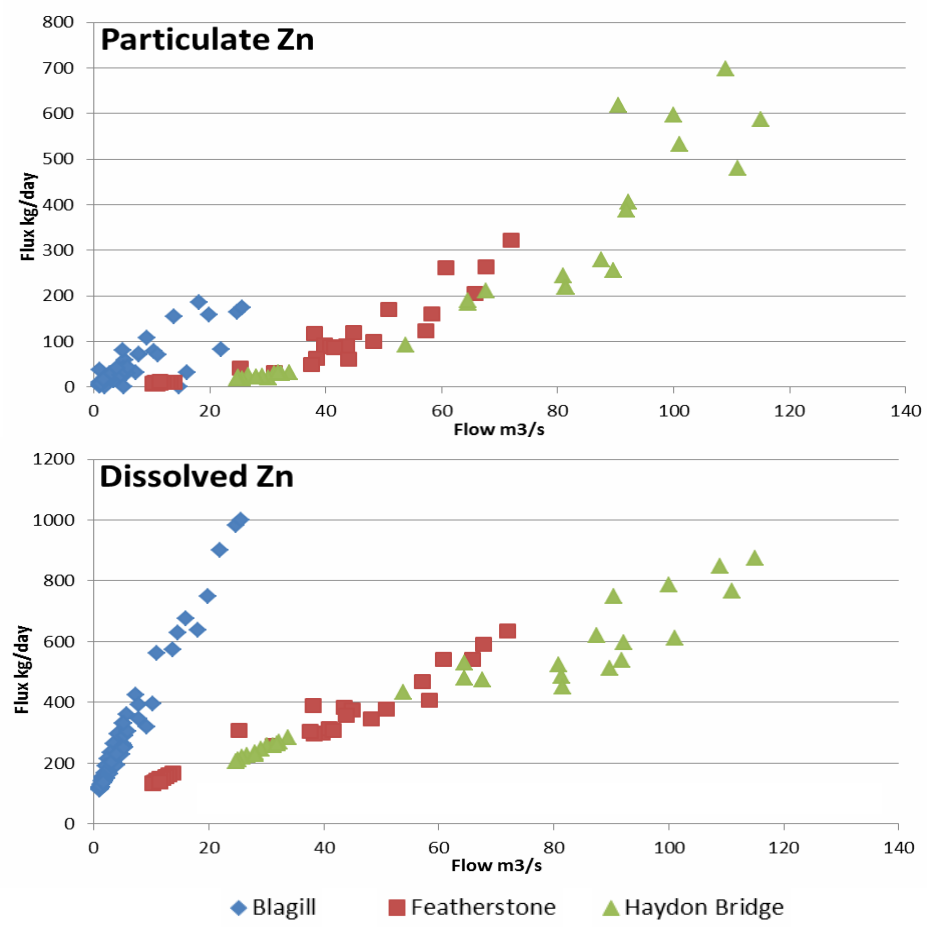


Figure 3: Differences in particulate and dissolved zinc flux with flow-rate at the 3 sites

Pollutant source insights from observable hysteresis patterns

Hysteresis loops have previously been used in hydrology and sediment transport investigations as they provide a useful insight into the complex interactions between different hydrological parameters such as rainfall intensity and catchment characteristics such as geomorphology(e.g. Johnson and East, 1982; Morehead et al., 2003; Smith and Dragovich, 2009). Hysteresis loops enable interpretations to be made regarding the transport and availability of the contaminant depending on the patterns shown by the data. A clockwise loop indicates higher concentrations on the rising limb of the hydrograph than the falling limb, with the peak of the pollutant leading the peak of the discharge (Smith and Dragovich, 2009). This is indicative of an initial delivery of fresh, readily available pollutant, for example sediment from channel banks and rapid remobilisation of sediment in transient storage areas. A gradual depletion of the contaminant of interest indicates no new sources have become available. Anticlockwise loops indicate a difference in travel time between the contaminant and the discharge peaks. Anticlockwise loops are often attributed to new sources of contamination becoming available as the flow starts to decrease, for example erosion of bed armouring during the highest flows will expose contamination which then gets transported on the receding limb of the hydrograph. Many hydrographs do not show simple hysteresis curves due to variable discharges and/or more sediment becoming available/ depleted, which creates multi-point complex patterns. If all the sampling points from each site were plotted continuously at each site any resemblance to

hysteresis would be disguised amongst the mass of data. Therefore the two peaks evident on the hydrographs in Figure 2 are evaluated separately in terms of hysteresis patterns.

Blagill

Some hysteresis patternsare visible in the Blagill data, as seen in Figure 4. The two discharge peaks (Figure 2) both result in anticlockwise loops for the dissolved zinc, showing higher concentrations on the receding limb of the hydrograph suggestingnew sources of zinc become available and are thus being transported on the falling limb of the hydrograph. The particulate data for the same location shows clockwise loopssuggesting the particulate zinc is readily available and then becomes depleted, or the flow reduces enough not to sustain particulate transport. The dashed lines returning to a point in the 'first peak' data is a result of the split in the first peak. It should be noted that higher concentrations of particulate Zn occur during the second peak, which occurred at lower flow rates.

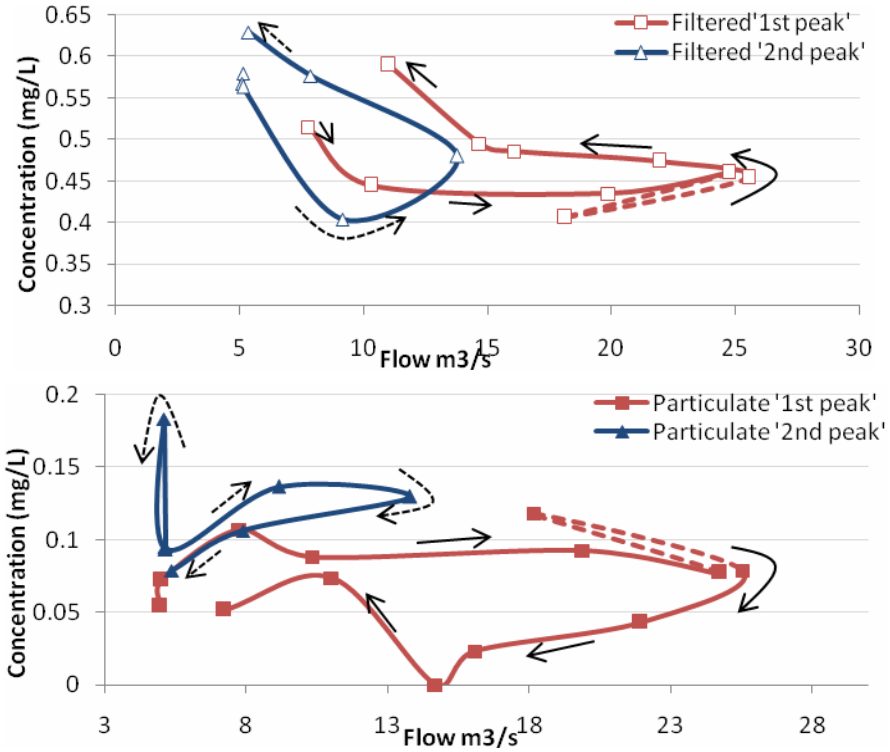


Figure 4: Dissolved and particulate zinc concentrations against flow at Blagill. Arrows indicate hysteresis direction as discussed in the text.

Featherstone

The trends notable at Featherstone (Figure 5) differ from Blagill as both the particulate and dissolved forms of zinc indicate clockwise patterns for the first peak, withhigher concentrations observed on the rising limb of the hydrograph though simultaneous peak flow/ peak concentrations occurring. However, the second peak shows anticlockwise trends in both the dissolved and particulate data. This may be a consequence of a smaller discharge peak following a larger one (Figure 2, B), with the first high flow event utilising all the readily available contaminated sediment.

Haydon Bridge

Like Featherstone, the data for Haydon Bridge (Figure 6) indicate a clockwise hysteresis loop for both the dissolved and particulate phases of zinc in the first peak discharge, indicating movement of metal contamination during the rising limb of the hydrograph as the peak discharge does not correspond with the peak flow. However, in contrast to the pattern at Featherstone, the second discharge peak also shows a clockwise pattern in both the dissolved and particulate forms, albeit showing different trajectories. The dissolved Zn indicates simple dilution effect as concentration decreases with increasing flow, where-as the particulate data shows increasing concentrations as

discharge increases with a simultaneous arrival of the peak discharge and concentration. This suggests that at Haydon Bridge particulate zinc contamination remains readily available, even following the initial high flow event.

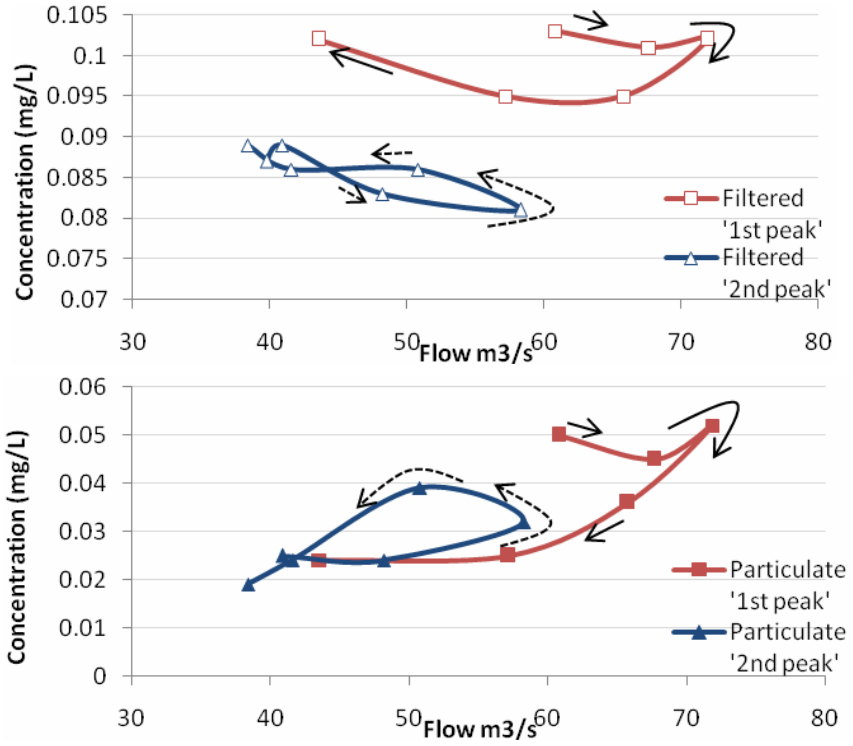


Figure 5: Dissolved and particulate zinc concentrations against flow at Featherstone. Arrows indicate hysteresis direction as discussed in the text.

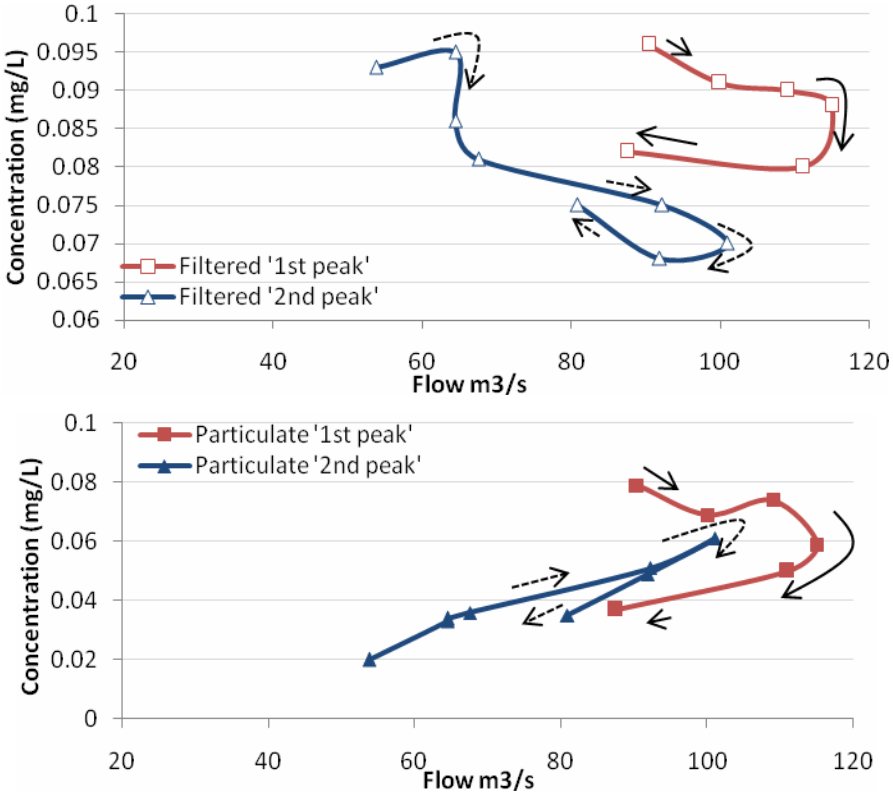


Figure 6: Dissolved and particulate zinc concentrations against flow at Haydon Bridge. Arrows indicate hysteresis direction as discussed in the text.

The clockwise direction of many of the hysteresis loops for the particulate phase zinc suggests the mobilisation of zinc-contaminated bed sediment during high flow events. Therefore as part of the investigation river bed sediments were collected from each of the sampling sites. These sediments were analysed for both physical (grain size and density) and chemical (metal content) characteristics.

River bed sediment was collected at each of the three sites on 8.3.11. Over the catchment the average whole sample density decreased from 2.97 g/cm^3 at Blagill to 2.73 g/cm^3 at Featherstone and 2.63 g/cm^3 at Haydon Bridge. Since 'natural' sediment typically has a sample density in the region of 2.65 g/cm^3 as quartz (Deer *et al.*, 1992), the results suggest the possible presence of heavy metals such as zinc and lead (also widely distributed in the rivers and riparian zones of these former Zn/Pb mining districts). Particle size distribution tests also reveal a gradual fining of sediment with distance downstream, as indicated in Figure 7.

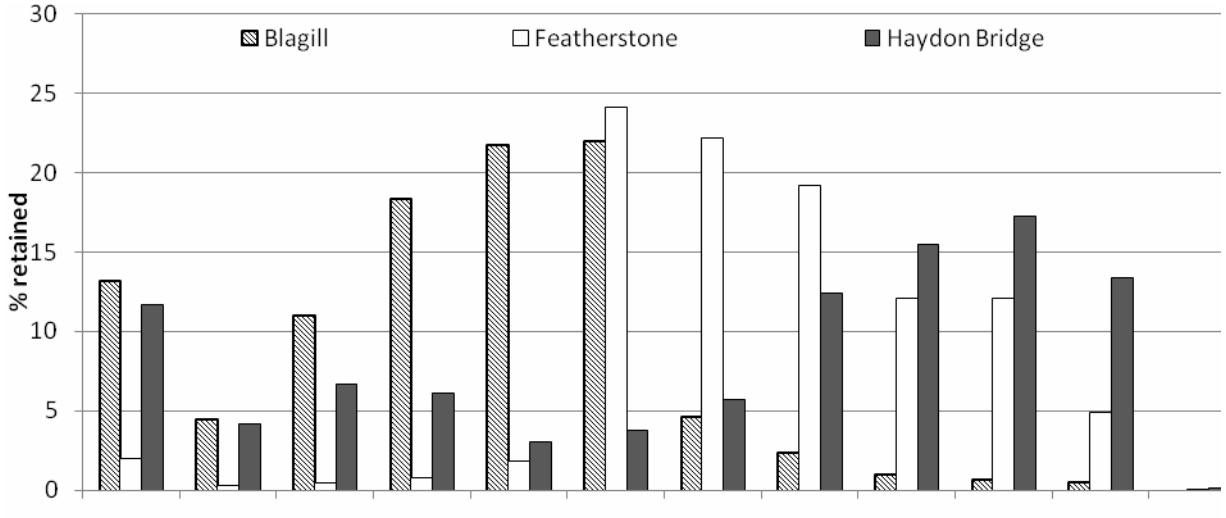


Figure 7: Particle size distribution of bed sediment collected across the catchment

Metal content was determined for each size fraction of the sediment collected, at each site, to establish the concentrations of zinc in each size fraction. The results are shown in Figure 8. Knowing the association of zinc with particular size fractions is important as it will allow greater understanding of the potential sediment dynamics within the system, and thus facilitate a more targeted approach to contaminated sediment removal or immobilisation, if deemed necessary as part of a wider ranging remediation programme within the catchment.

Figure 8 shows zinc at Blagill resides predominantly in the middle four fractions (600 – 212µm) with the maximum concentrations of 89872 mg/kg and 92795 mg/kg observed in the 425µm and 300µm fractions, respectively. However, at Featherstone the zinc concentrations are more evenly distributed across the full range of fraction sizes. The actual quantity of zinc present at Featherstone has also substantially decreased, to a maximum concentration of 3418 mg/kg in the 2 mm fraction. The concentrations at Haydon Bridge again decrease, with a maximum of 1397 mg/kg observed in the 300µm fraction. The concentration of zinc in the 600µm and 425µm fractions at Haydon Bridge are lower than the concentrations in these fractions at the other sites, which might be an artefact of sample size rather than a true indication of sediment metal concentrations in this reach of the river. The overall decrease in zinc sediment concentration downstream is considered to be most likely a result of dilution of the sediment by cleaner sediment from non-polluted sources.

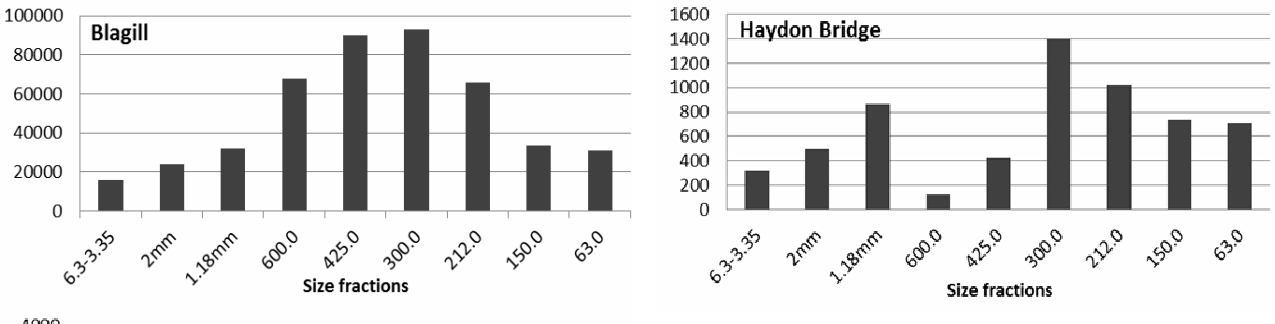


Figure 8: Zinc concentrations (mg/kg) in individual size fractions at each of the three sampled sites.

CONCLUSIONS

This ongoing study has the ultimate objective of quantifying aqueous zinc fluxes in a mining impacted catchment, with a view to identifying environmentally- and cost-effective remedial strategies for not only point sources of pollution, but also diffuse source mining pollutants associated with the waste rock piles in the vicinity of the point sources. This particular paper reports on the zinc fluxes at sampling stations on the Rivers Nent and South Tyne during a hydrological event, to evaluate how zinc concentrations vary during such events, and also investigate the possible role of contaminated sediments (likely sourced from waste rock) in contributing to the substantial metal fluxes that have been observed during such events.

The predominant source of zinc into the catchment appears to be the River Nent, which corroborates the results of previousresearch in this heavily mined catchment. Zinc fluxes in excess of 1100 kg/day were observed originating from this ~29 km^2 upland tributary, the majority of which is in the dissolved form. The high dissolved load in the River Nent is, in part, due to point sources of pollution. However, these are rather consistent in terms of their zinc flux to the river, as they effectively originate as groundwater discharges, which are less susceptible to weather events. Therefore the steep increase in dissolved zinc flux during the hydrological event discussed here (Figure 3) are due to other polluting inputs. Previous research has identified stream bed sediments as such a potential source in an adjoining catchment (Gozzard*et* al., 2011), and therefore detailed analyses of such sediments in the River Nent (and in the River South Tyne downstream of the Nent) have been undertaken. The results show veryhigh concentrations of zinc (92795 mg/kg) in the bed sediment, and this is attributed to its close proximity to the exposed, and steeply inclined, waste rock piles that lie immediately adjacent to the River Nent.

Hysteresis loops show clockwise trends for the particulate zinc at the Blagill monitoring site, which is just a few kilometres downstream from the exposed waste rock piles and point sources. Given that such clockwise patterns may be indicative of release of sediment from channel banks and rapid remobilisation of sediment in transient storage areas, it appears as though the waste rock piles may be an important pollutant source, either directly, via erosion of the finer grained particles from waste rock into the river, or via release of such sediments held in transient storage in the upper reaches of the River Nent. For dissolved zinc at Blagill hysteresis loops indicate dilution, but are anticlockwise. This is more difficult to interpret, though may be related to chemical dissolution of zinc from sediment during the hydrological event. However, further work is required to confirm this.

At both the Featherstone and Haydon Bridge monitoring sites clockwise hysteresis loops are evident during the first hydrological peak, indicating release of readily available metals. Analyses of bed sediments, which show very high zinc concentrations, strongly suggest that this is due to metal-contaminated sediment released from transient storage during the hydrological event, and originally sourced from the waste rock piles in the upper catchment. This suggestion is supported by physical analyses of the bed sediment (Figure 8), which shows a large proportion of bed sediment at these monitoring stations to be fine grained in nature, and therefore likely to be mobilised during such hydrological events.

These results demonstrate the substantial increases in metal flux associated with hydrological events occurring in this long-abandoned mining district. It appears as though the exposed waste rock piles still present in the upper catchment are a major contributory factor to the pollutant burden of the river system, particularly during such hydrological events. Therefore remedial efforts need to address these sources of pollution as well as the more easily identifiable, and measurable, point sources.

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