SHORT-TERM FLUCTUATIONS IN HEAVY METAL CONCENTRATIONS DURING FLOOD EVENTS THROUGH ABANDONED METAL MINES, WITH IMPLICATIONS FOR AQUATIC ECOLOGY AND MINE WATER TREATMENT

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ABSTRACT

The variability in heavy metal concentrations and physico-chemical parameters during rain-fed river floods that pass through abandoned metal mines is poorly understood due to the difficulties of sampling these events. Such information is essential for the characterisation of contaminant dynamics and for investigations of contaminant/ecosystem relations and the effectiveness of remediation. This study investigates the role of flood flows in contaminant mobilisation and temporary increases in toxicity at an abandoned metal mine in central Wales, UK. Flood events substantially increase the potential toxicity of river water. The principal contaminants are dissolved Pb, mobilized by increased acidity resulting from the dissolution and flushing of efflourescent salts accumulated on the surface of mine spoil. The implications of flood runoff and contaminant mobilisation for aquatic ecology and mine water treatment are discussed.

1. INTRODUCTION

Short-term fluctuations in heavy metal concentrations during rain-fed floods in rivers that run through abandoned metal mines are poorly understood due to the inaccessibility of many mine sites and the difficulty of sampling short-lived and localised storm events. As such, many remediation investigations and assessments of contaminant/ecosystem relations may not incorporate measurements of river water chemistry during high flows. If variations in heavy metal and other chemical parameters are substantial during high flows, then predictions of long-term water quality trends, ecological impacts, pollution risks and the effectiveness of remediation are likely to be seriously misunderstood (Lambing *et al*., 1999). Therefore, there is a need to monitor flood events in detail in order to quantify accurately contaminant dynamics and to allow resource managers to prioritise areas for remediation. This paper investigates variations in water quality during rain-fed flood events that pass through an abandoned metal mine in central Wales, UK. It identifies the key role of flood events in the mobilisation and transport of heavy metal contaminants in mining-affected river catchments, and the implications of such events for aquatic ecology and remediation effectiveness.

2. STUDY AREA AND METHODS

Dylife Pb/Zn mine lies at the centre of an elevated plateau between Machynlleth and Llanidloes known as the central Wales mining district (Figure 1). The mine was abandoned in 1930 and currently comprises numerous spoil heaps, shafts and adits. The mine is drained by the Afon Twymyn, a tributary of the Afon Dyfi which flows into the Irish Sea near Machynlleth. The Afon Twymyn catchment ($35km^2$) lies on Upper Silurian argillaceous sediments, mainly comprised of shales, siltstones and mudstones (British Geological Survey, 2007). The area was glaciated during the Pleistocene. Soils of the region are predominantly stagnopodzols and stagnohumic gleys (Rudeforth *et al*., 1984).

A permanent monitoring station was installed just downstream of Dylife mine in October 2007 to investigate water chemistry and river discharge during rain-fed floods. A water stage-activated ISCO 6712 automatic sampler was programmed to collect water samples at user-defined intervals throughout high flows. After collection, water samples were acidified to pH 2 to prevent adsorption or precipitation of metals in storage. Samples were then analysed for dissolved heavy metals (Pb, Zn) using a Jarrell Ash ICP-AES. A YSI 600 multi-parameter Sonde was used to record electrical conductivity and pH of the flow at 15 minute intervals. River stage was also measured at 15 minute intervals using a Druck 175 mb pressure transducer. Stream discharge was estimated from a stage-discharge relation developed by area-velocity flow gauging at the monitoring site.

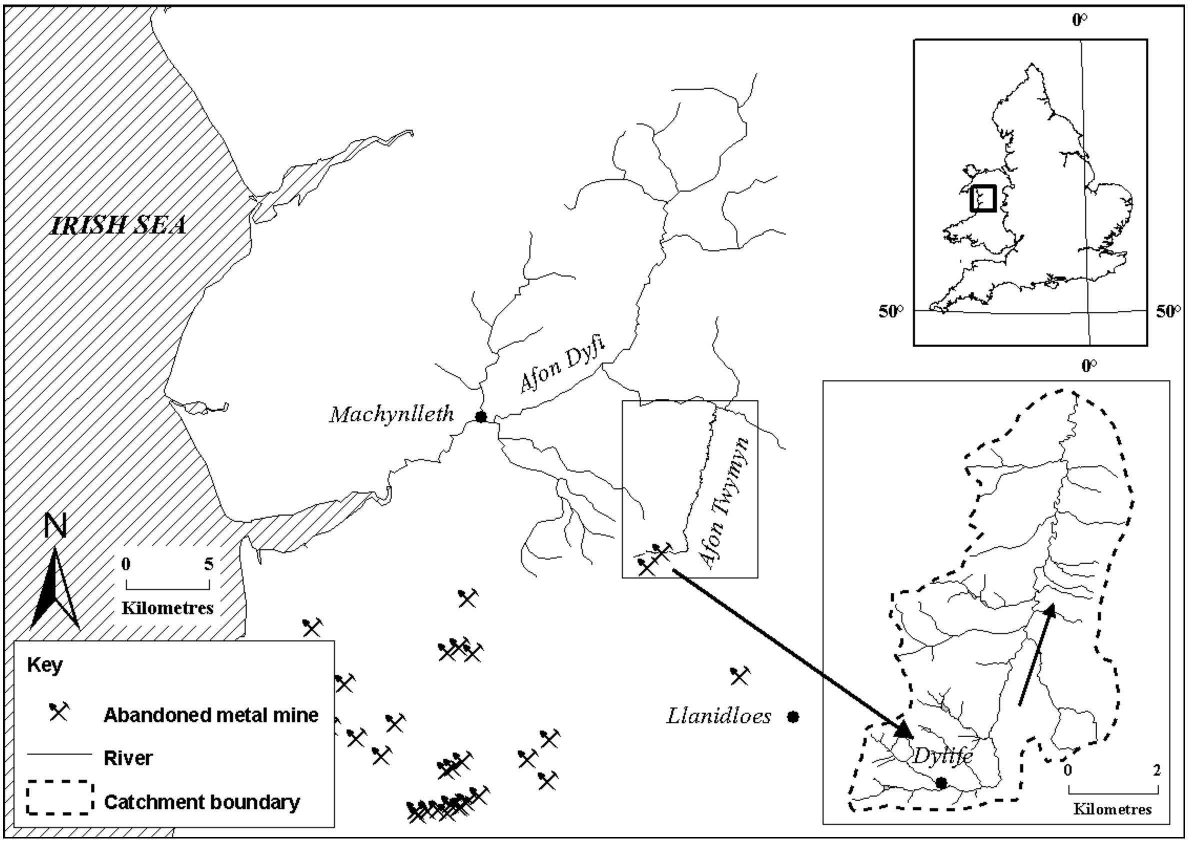

Figure 1. Map of central Wales mining district showing location of study catchment and Dylife mine

3. RESULTS AND DISCUSSION

Baseline Water Quality Patterns

Figure 2 illustrates dissolved Pb and Zn concentrations in the Afon Twymyn, measured at multiple sampling locations along the river during steady discharges that prevailed on three occasions in 2007/08. There exists a clear pattern of 'clean' upstream control sites and heavily contaminated mine sites. At the mine, both Pb and Zn fail to meet EU Environmental Quality Standards (EQSs) for surface waters. In the case of Zn, maximum concentrations are eight times greater than the EQS for this reach (Figure 2b). Mean baseline metal concentrations at the monitoring station during this sampling period were 269 µg/l Pb and 1 044 µg/l Zn. Both metals attenuate relatively quickly downstream of the mine due to both dilution by uncontaminated tributary water and precipitation/adsorption reactions. Pb, in particular, sorbs strongly to many mineral surfaces, including Fe, Mn and Al oxides. However, Zn remains elevated above the EQS for at least 15 km downstream of Dylife mine due to its greater mobility in river systems.

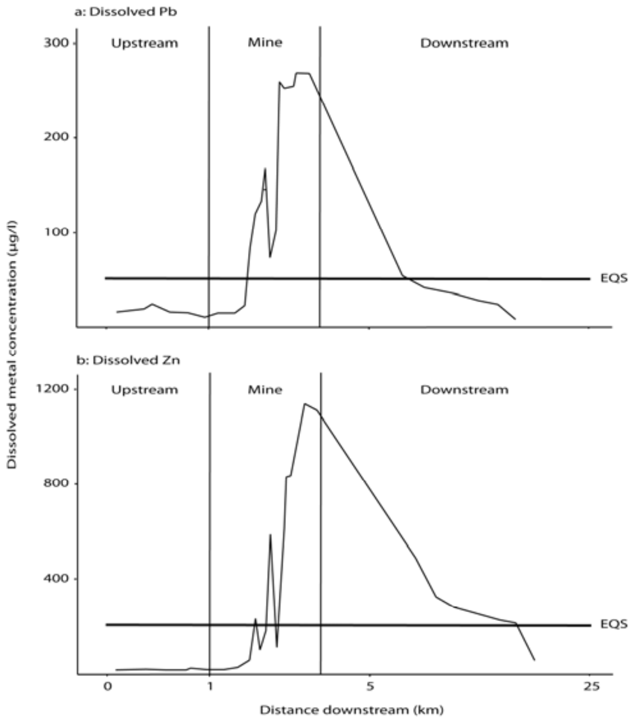

Figure 2. Dissolved a) lead and b) zinc concentrations as a function of distance (logarithmic scale) along the Afon Twymyn. Data represent mean values from three sampling occasions (March, June, October) in 2007/08.

Flood Event Water Quality Patterns

Figure 3 illustrates rainfall, stream discharge and water quality data for two flood events, one in July (Event 1) and the other in September 2008 (Event 2). Significantly, both events were preceded for 2 weeks by predominantly dry weather. Pre-event stream discharge at the mine was 0.103 m^3/s and 0.074 m^3/s in Event 1 and Event 2, respectively. Peak storm discharge was 0.435 m^3/s and 0.465 m^3/s, respectively.

Both events are characterised by highly-elevated dissolved heavy metal concentrations on the rising limb of the hydrograph, prior to peak storm discharge, the so-called ‘first flush’ effect. Peak Pb concentrations of 5 000 µg/l (Figure 3a) and 1 300 µg/l (Figure 3b) are far in excess of the mean concentration (269 µg/l Pb) observed in routine baseline sampling, when Zn was, quantitatively, the main contaminant (Figure 2). This would suggest that Pb, which is far more toxic than Zn to aquatic organisms, is highly mobile during flood events. Marked clockwise hysteresis in the relation between metal concentration and flow, with maximum concentrations reached before peak discharge, suggests that a surface source of metals is the primary origin for the spike of the contamination. The peak Zn concentration of 1 791 µg/l in Event 1 is greater than the mean baseline concentration (1 044 µg/l Zn). However, peak Zn concentration in Event 2 (692 µg/l) falls well below the baseline mean. Lower Pb and Zn values in Event 2 are likely to reflect the progressive exhaustion of readily oxidised metals through the summer and autumn, an effect which has been observed elsewhere (Canovas *et al*., 2008).

After the initial peaks in concentration, the levels of both metals attenuate quickly, reaching mean concentrations well below baseline levels for the remainder of the event. Attenuation is principally due to rain-water dilution and the fact that available contaminant has been scavenged in the first flush. The occurrence of peak Fe concentrations after peak discharge (Figure 4) indicates that adsorption onto, or precipitation with, Fe solids may have been a principal toxic metal attenuation mechanism on the falling limb of the hydrograph. The rising limb of both runoff events coincides with drops in stream pH, indicating inputs of acidity. Decreases in pH were not substantial – 0.2 units in Event 1 and 0.3 units in Event 2. However, the maintenance of a steady pH throughout an event is still indicative of inputs of acid since, without mine drainage, dilution with storm runoff would be expected to increase pH (Keith *et al*., 2001).

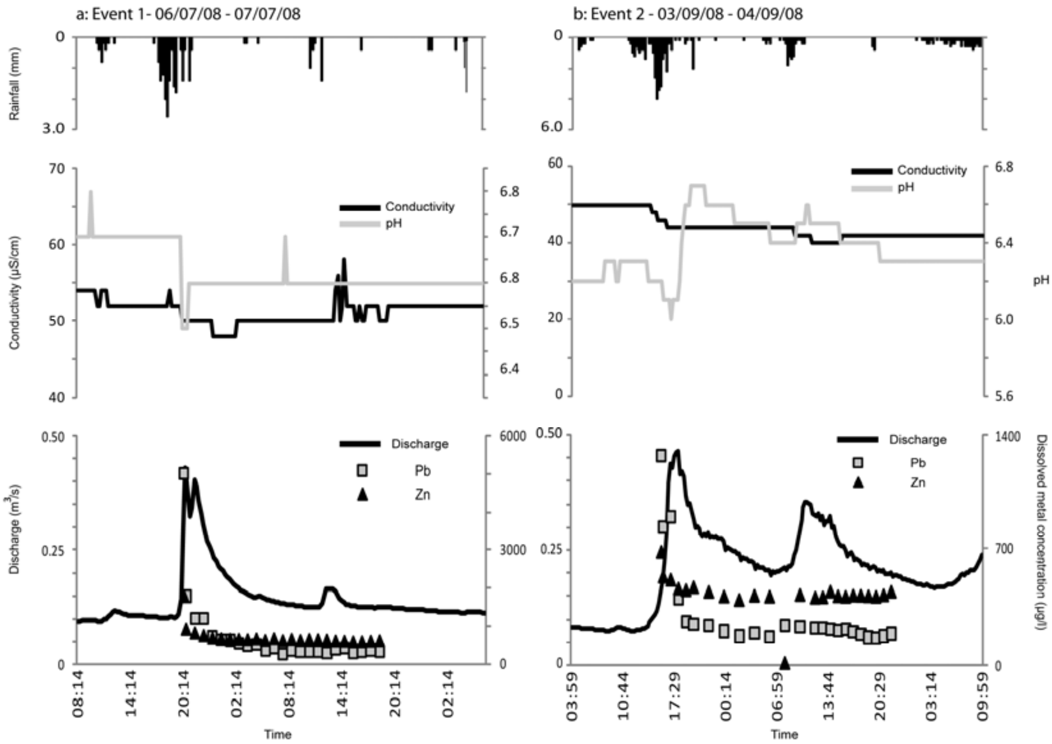

Figure 3. Rainfall, water quality and discharge data for two flood events at Dylife mine in 2008 a) Event 1 (06/07/08) and b) Event 2 (03/09/08)

Increased acidity and heavy metal concentrations during flood events can arise from oxidation of sulphides in rising groundwater emanating from mine portals. It can also have provenance in dissolution of oxidised sulphides accumulated in mine spoil and/or the river bed or its margins. The principal source of metals and acidity during flood events in this study was most likely dissolution of efflourescent salts on the surface of mine spoil. Observations during storm flow identified only one mine opening (a collapsed stope) to discharge into the river. Sampling of mine water emanating from this portal revealed relatively low heavy metal concentrations and circum-neutral pH (Byrne, 2009). Two springs draining the mine spoil, however, revealed highly elevated heavy metal concentrations, significantly greater than baseline values. This suggests that point source contributions from mine workings are of low importance during flood events and that diffuse sources from mine spoil are of greater significance. A further source of metals during these events may have been derived through ion-exchange processes in the bed sediment of the river. Byrne *et al*. (under review) found that the bed sediments of the Afon Twymyn are grossly contaminated with heavy metals. Furthermore, the majority of metals exist in the most mobile, easily exchangeable and carbonate-bound geochemical phases. During flood events, oxidising conditions and/or a drop in stream pH, as was observed in this study, could lead to the release of metals from sediment to the water column. The lack of major fluctuations in metal concentrations after the initial peak concentration suggests that surface materials (mine spoil and river bed/margins) are the only immediate contamination source.

The immediacy of the metal flush suggests that dry antecedent soil moisture conditions were very important prior to both events. The preceding two weeks of dry weather will have increased metal oxidation and availability on the surface of the mine spoil while increasing the soil moisture deficit. The increased soil moisture deficit will have minimised both interflow and deeper seated flows that might otherwise be expected to cause, in wetter months, both lateral sub-surface flows from contaminated soil or spoil and groundwater efflux from the abandoned stope.

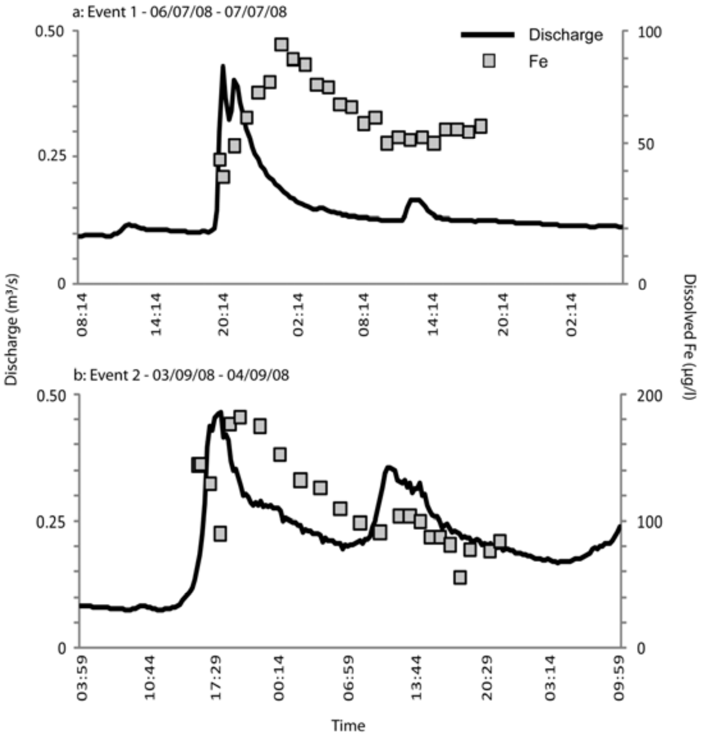

Figure 4. Dissolved iron concentrations during a) Event 1 (06/07/08) and b) Event 2 (03/09/08)

Implications for Aquatic Ecology

This study has demonstrated that flow events increase the potential toxicity of river water in the Afon Twymyn, if only for short periods. Similar occurrences have been recorded elsewhere (Lambing *et al*., 1999; Gammons *et al*., 2005). The principal contaminants in this study were dissolved lead, zinc and increased acidity, derived from the dissolution of efflourescent salts on mine spoil and/or ion-exchange involving river bed material containing displaced tailings. These conditions undoubtedly cause harm to the aquatic community and degrade biological quality. Indeed, poor Shannon-Weiner diversity scores and changes in macroinvertebrate community composition are reported for the Afon Twymyn at Dylife mine (Byrne, 2009). Negative impacts at other abandoned metal mines have included changes in behaviour (e.g. growth cycles, reproduction, competitiveness and predation) and community composition (Gerhardt *et al*., 2005; Armitage *et al*., 2007). Decreases in pH on the rising limb of the flood hydrographs are indicative of acid flushes, however, the level of change is moderated by dilution with increased discharge. The pH as measured in the full flow of the stream is not itself likely to be injurious to benthic organisms, which dwell in the microcosm of near-bed flow where temporary reduction in pH may well be deleterious.

A variety of studies have measured the impact of mine water contaminants on benthic macroinvertebrate and fish populations under long-term steady-flow conditions. However, predicted increases in the frequency and magnitude of floods across Europe due to climate change have the potential to introduce greater amounts of mine waste into river systems and further degrade biological quality. Therefore, understanding the potential toxicological impacts of high river flows will be important in the achievement of the aims of the EU Water Framework Directive (2000/60/EC) for mining-affected river catchments (Wolz *et al*., 2009).

Implications for Mine Water Treatment

The heavy metal and chemical variations observed in flood flows during this study have important implications for mine site remediation. A number of chemical and hydrological processes occurring during high flows have the potential to reduce effectiveness of any remediation. During high flows, additional sources of contaminant in river catchments will become active, sources which might not be connected to a treatment system. Long-term predictions of the contaminant removal capacity of treatment systems may be inappropriate, affecting the lifespan of the system. Instantaneous metal loads during runoff events might exceed system design limits, affecting efficiency. Predictions of potential improvements to the water quality of rivers draining abandoned mines might be over-estimated. Finally, the diffuse nature of many mine waters (Pirrie *et al*., 2003; Mayes *et al*., 2008; Mighanetara *et al*., 2009) makes it difficult to collect and route contaminated runoff to treatment areas. Many abandoned mines have substantial diffuse sources, including mine spoil and mobile metal fractions in the river bed, which might bypass treatment systems during high flows.

4. CONCLUSIONS

It has been shown in this study that rain-fed floods substantially increase the potential toxicity of river water in the Afon Twymyn. Measured metal concentrations were significantly greater than Environmental Quality Standards (EQSs). In addition, serious exceedances of EQSs are likely to have occurred for some distance downstream of Dylife mine. Peak metal concentrations on the rising limb of the hydrograph suggest a surface source of metals and acidity as the primary source of contamination. This source was most likely to be efflourescent salts on the surface of the mine spoil, and highly mobile and bioavailable metals adsorbed to the sediment of the river bed/margins. Antecedent soil moisture conditions were an important control on the availability of metals. This assessment of contaminant mobilisation and potential toxicity during high river flows has highlighted the importance of including high-resolution temporal sampling of river water chemistry under all flow conditions when investigating contaminant/ecosystem relations and developing remediation strategies.

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