Secondary minerals in the abandoned mines of Nenthead, Cumbria as sinks for pollutant metals

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Abstract: Direct observations made during underground hydrogeochemical surveys of abandoned lead–zinc mines has highlighted the precipitation of secondary zinc minerals within abandoned lead–zinc mine workings in the north Pennines. Chemical analysis of mine waters has shown that molar concentrations of sulphate exceed those of zinc by two or three orders of magnitude, although they are released in equimolar proportions following the weathering of sphalerite. The excess of sulphate over zinc indicates that there must be significant sinks for zinc within the mine workings. Secondary zinc mineral sinks (principally hydrozincite and smithsonite) are the most likely explanation for the deficit in molar zinc concentrations and these minerals have been identified underground. In addition to the secondary zinc minerals, secondary calcite and aragonite from the workings have also been shown to provide sinks for zinc (by coprecipitation and solid-solution incorporation of zinc in these minerals). Calculation of the molar quantities of zinc and sulphate involved showed that as little as 5% of the zinc, weathered daily from the mineral deposits within the workings, is found to leave the mine dissolved in the mine water. However, this is sufficient to adversely impact the ecology of the receiving waters of the River Nent, which currently receives five circumneutral zinc-rich mine water discharges and drainage from a disused aqueduct.

The River Nent lies in NE Cumbria on the Alston Block, the most northern block of the North Pennine Orefield as described by Dunham (1990). The area has experienced over two centuries of intensive galena (PbS) and sphalerite (ZnS) mining, as lead and zinc and mining continued in the area until the early twentieth century. During this time over 90 adits were created throughout the valley, some of these adits currently discharge mine water into the River Nent, which has its headwaters above the village of Nenthead (NY 7810 4370) and flows approximately NW for 8 km to join the South Tyne at the town of Alston (NY 7170 4560) (see Fig. 1).

The River Nent has a poor abundance and diversity of fish and invertebrates because of the aquatic concentrations of zinc. Figure 2 shows how zinc concentrations along the River Nent (measured monthly at Nenthead, Nenthall and Nent Force over a 1-year period) typically exceed the environmental quality standard (EQS) for salmonids of 0.5 mg l^{-1} for a river of this hardness,i.e. 200 mg l^{-1} as $CaCO_3$ (Fig. 2) (Mance & Yates 1984). Other ecotoxic metals are also present, for example lead and cadmium are usually found at concentrations of less than 0.1 mg l^{-1}. Water samples were also analysed for arsenic, but this was below detection (or at very low concentrations). However, zinc concentrations exceed those of the other ecotoxic metals by several orders of magnitude (the mine water discharges typically have zinc concentrations in the range 2–10 mg l^{-1}). This is due to the different solubilities of the mineral oxidation products involved. Sphalerite (ZnS) becomes oxidized to zinc sulphate, which is soluble, and galena (PbS) is oxidized to lead sulphate, which is insoluble and coats the ore mineral sealing it from further oxidation.

The River Nent receives five mine water discharges and a metal-rich drainage from a disused aqueduct at Rampgill. Figure 1 shows where these discharges enter the main river. Characterization of the mine waters over a period of 2 years has been carried out at monthly intervals by Nuttall & Younger (1999). In addition to these point sources of metal contamination, contaminated river sediments, bank deposits and tailings material means that there are diffuse inputs of metal contamination occurring along the entire length of the river.

Zinc is an essential micronutrient for mammals and birds (Förstner & Wittman 1981) and the limit for zinc in potable water supply is set at

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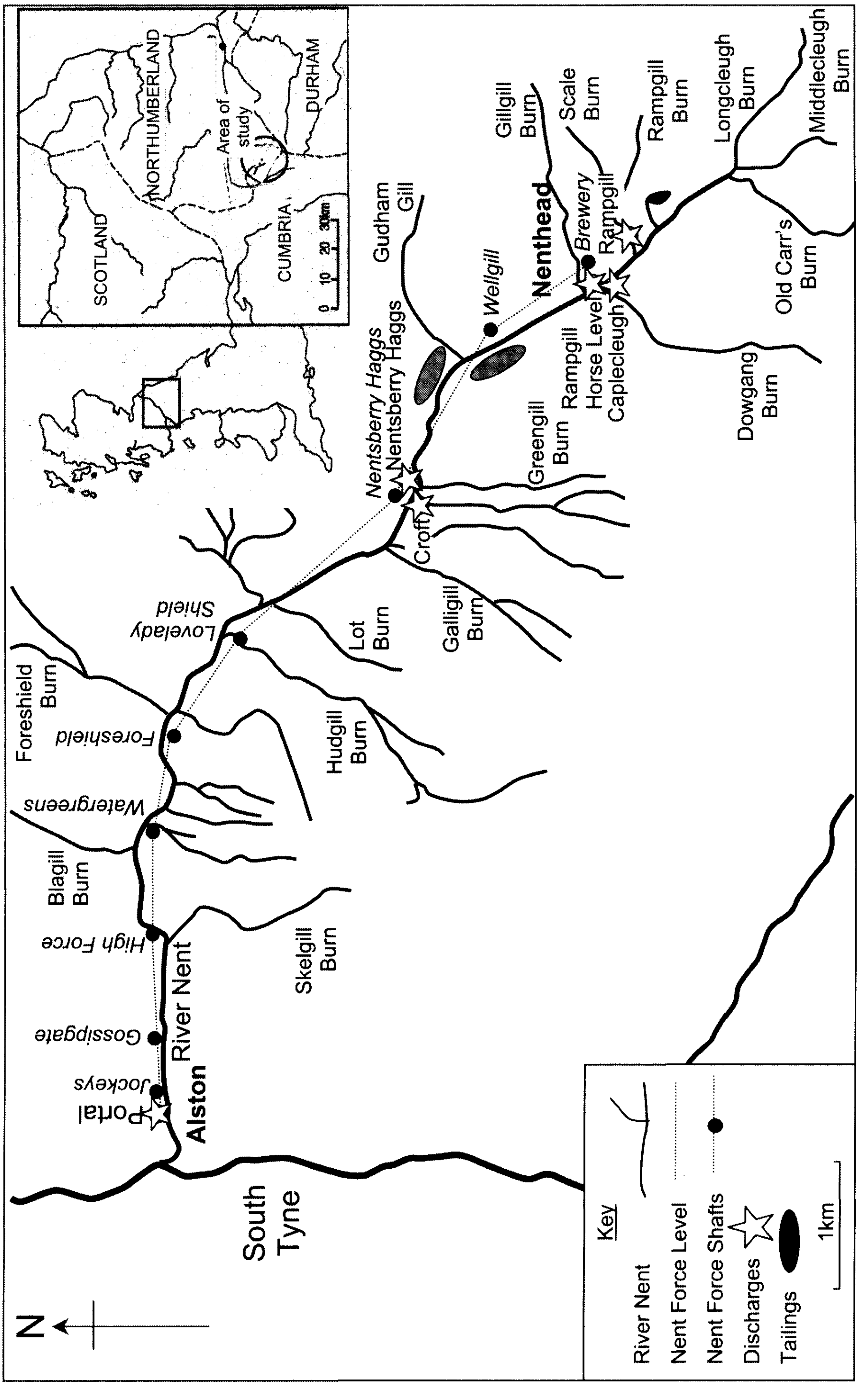

Fig. 1. Map of the Nent Valley showing the main inputs of metal contamination.

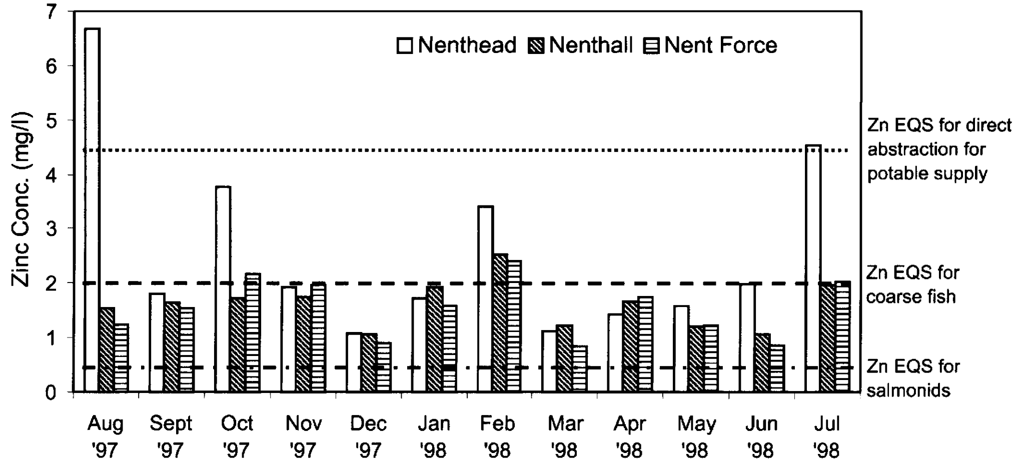

Fig. 2. Graph showing zinc concentrations at various points along the River Nent with respect to various regulatory limits.

4.5 mg l^{-1} (this is shown on Fig. 2). Above this concentration it is not harmful to humans but would affect the taste of the water. However, zinc can be very toxic to fish and invertebrates, with the free zinc ion (Zn^{2+}) being the most toxic species (Alabaster & Lloyd 1980). This species predominates in low pH waters, but geochemical modelling (carried out by the authors using WATEQ4F, Ball & Nordstrom 1991) has shown that around half of the zinc present in the Nent Valley mine waters is present in the Zn^{2+} form. In fish, zinc binds to the layer of mucus that normally coats the body surface. This causes excessive amounts of mucus to be produced and eventually the fish will suffocate (Handy & Eddy 1990). Zinc concentrations in the main river are typically 1–2 mg l^{-1} and zinc-tolerant filamentous green algae are the only thriving species. The algae become especially prolific during the summer months because there are few invertebrates present to graze upon it. It is postulated that their fungus-based digestive system cannot cope with zinc (which has fungicidal properties), therefore they are not present in the quantities and diversity expected for an unpolluted river of this type (A. Lewis, Environment Agency pers. comm.).

Geological setting

The rock types present and the structures throughout the North Pennine Orefield control the nature and spatial distribution of the mineralization (refer to Fig. 3 for a stratigraphic column). This area was so mineralogically productive due

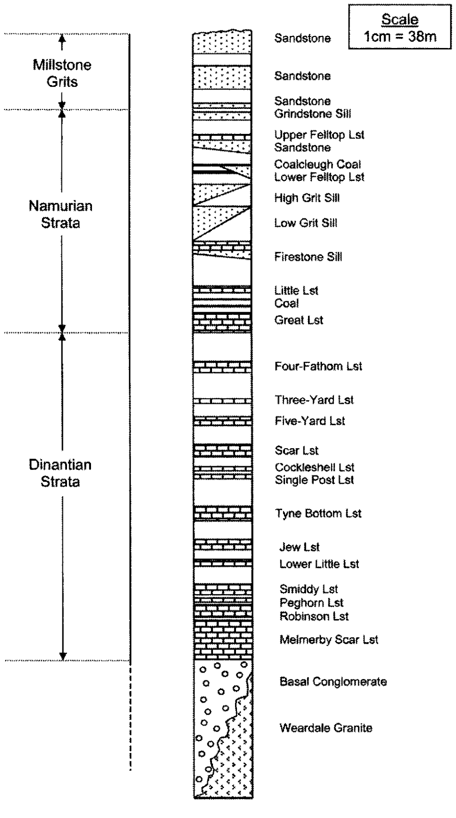

Fig. 3. Generalized vertical section showing the Carboniferous sequence within the Alston Block.

to the presence of specific rock types (notably limestone in this area), which are capable of transporting mineral bearing solutions due to their physical and chemical properties (e.g. the existence of joints and faults and the chemical reactivity of limestone are both important). The Carboniferous rocks contained within the Alston Block dip at up to 10° E and rest unconformably on basement rocks of Lower Palaeozoic folded slates (formed from Ordovician and Silurian mudstones and volcanic ash deposits) and greywackes (Dunham 1981).

Volcanism during the Lower Devonian caused the basement rocks of the Alston Block to be intruded by granitic stocks and batholiths, one of which is the Weardale Granite (Johnson 1981). These stocks were not directly responsible for orefield mineralization, as they pre-date the mineralized Carboniferous rocks and were exposed to surface weathering during the early Carboniferous. Evidence for former surface exposure of these granites comes from borehole data obtained from Rookhope during the 1960s (Dunham *et al.* 1965). Consequently, the only contributions these igneous rocks may have made towards the mineralization of the area is by forming an effective heat conductor during orefield mineralization and by releasing metals to hydrothermal fluids circulating within them.

Transgression and regression of the Lower Carboniferous Sea created coal, sandstone and limestone cyclothems. The rocks deposited during the Lower Carboniferous up to the base of the Great Limestone are termed 'the Dinantian strata' (Fig. 3). Rocks deposited from the Great Limestone through to the Millstone Grits are loosely referred to as 'the Namurian strata' (Fig. 3). Above the Namurian strata, numerous coal seams of the Coal Measures were formed during more than 30 cyclic depositional events (Johnson 1981).

The mineral deposits at Nenthead can be classified as Pennine-type, strata-bound deposits (Evans 1993). They provide important resources worldwide for the metals lead and zinc, and are also economic sources of barite and fluorite. In the Alston Block, faults became active due to crustal movements from the end of the Carboniferous creating a conduit network for mineralization. Hot fluids emanating from a deep source (in this case, a postulated mantle hotspot), circulated upwards through fissures, scavenging metals and fluorine from the pre-existing sedimentary and igneous rocks (Dunham 1981). The mineralization resulted from low-to medium-temperature (50–219°C) hydrothermal solutions emplaced around approximately 270 Ma (Dunham 1990). A series of productive veins and flats were produced throughout the orefield with the Great Limestone providing an especially mineralogically productive host.

Sampling methods

Mine waters were sampled at the discharge point every month over a two year period. For every water sample taken, field measurements were taken for temperature, pH, conductivity and alkalinity. Three samples were collected from each discharge in polythene bottles: one sample for anions, one unfiltered sample for cations and one sample filtered in the field (at 0.45 μm) for cations. Analysis for the anions fluoride, chloride, sulphate and nitrate was carried out using a Dionex DX-100 ion chromatograph. Cations, dissolved silica and hardness data were provided following analysis by the Environment Agency (EA). For the Caplecleugh and Nent Force Level discharges, flow was measured using a velocity area method, chosen as the only easy approach. All the other discharges were measured using a bucket and stopwatch. Water sampled underground was taken according to the method used for the surface samples. Underground minerals were collected in bags, some of each sample was ground for X-ray diffraction (XRD) analysis and the remainder of the sample was mounted onto slides in preparation for analysis by the scanning electron microscope (SEM).

Rampgill Mine

The underground surveys were carried out in Rampgill Mine due to relative ease of access. Water and mineral samples were collected over the course of several different visits. Rampgill Level was driven in 1736 and was widened to a horse level in 1800. The mine was active until 1886, by which time over 140 000 t of lead ore had been raised (Fairbairn 1993). The high productivity of the mine is due to the fact that it exploited 'flats' within the Great Limestone. Rampgill Horse Level (Fig. 1) drains the top northeastern part of the Nent Valley. It receives water from the Rampgill Mine complex and also from the adjacent workings of Smallcleugh Mine. The Rampgill Horse Level also contains the most upstream shafts to reach the Nent Force Level (marked on Fig. 1): Brewery Shaft (NY 4355 7833) and Engine Shaft (NY 7896 4361). Both of these shafts drain water from the Rampgill workings into the Nent Force Level below.

Groundwater percolating through the roof and dripping from an ore hopper in the vicinity of the Engine Shaft were sampled and analysed for zinc. Both of these seepages contain relatively high zinc concentrations (6.5 and 10 mg l^{-1} Zn, respectively), which perhaps indicates the presence of mineralized strata above this part of the mine. Indeed, these workings have the Rampgill Firestone Level workings directly above them (Critchley 1998). The concentration of zinc in these groundwater roof seepages shows that water is percolating through the workings and dissolving zinc.

Primary and secondary zinc minerals found in the Nent Valley

Sphalerite (ZnS) is a primary zinc mineral that can be found at Nenthead. It formed following precipitation of hydrothermal brines in veins and flats within the Carboniferous host rocks.

Some secondary zinc minerals are also found at Nenthead, and it is thought that these minerals may be partly responsible for the attenuation of zinc concentrations within mine workings. Secondary minerals have been directly observed by the authors within mine workings (e.g. in Rampgill Horse Level) and forming crusts and cements on spoil heaps and tailings dams (e.g. Brownley Hill Tailings Dam; XRD has shown that these precipitates are composed of hydrozincite). The secondary zinc minerals hemimorphite ($Zn_4[Si_2O_7](OH)_2.H_2O$), smithsonite ($ZnCO_3$) and hydrozincite ($5ZnO.2CO_2.3H_2O$) have all been found in mines in the Nenthead area (Dunham 1990). Hydrozincite and smithsonite were directly observed by the authors, their presence being confirmed following analysis by XRD. Hydrozincite is believed to form closes to mine entrances where ventilation is better, and smithsonite precipitation is usually favoured deeper within the mine workings where concentrations of carbon dioxide are greater (T. E. Bridges pers. comm.).

Other mineral sinks for zinc

Geochemical modelling using the WATEQ4F code of Ball & Nordstrom (1991) was performed on mine water data from Rampgill Horse Level. The following minerals were found to be at saturation and could theoretically precipitate from solution as secondary minerals: aragonite, calcite, dolomite, ferrihydrite, fluorite, goethite, quartz and amorphous zinc oxide (hydrozincite was not predicted because it is not included in the WATEQ4f database).

Calcite, aragonite, hydrozincite, smithsonite and goethite were identified by XRD in secondary precipitates from this mine. Most of the stalactites analysed were composed of calcite, aragonite and hydrozincite. The presence of aragonite is not surprising because it may precipitate chemically in preference to calcite from a solution that is charged with strontium, lead or zinc ions, presumably due to the metal ions causing distortions within the crystal lattice (Mondadori 1988). Mondadori (1988) also suggests Alston Moor as a good locality for aragonite. Coetzee *et al.* (1998) discovered that aragonite was forming in preference to calcite as a scale deposit during physical water treatment when zinc was present in the water. Zinc in particular, was found to decrease the rate of calcite nucleation and promote the crystallization of calcium carbonate in the aragonite form (Coetzee *et al.* 1998). XRD analysis also showed that the tailings dams (see Fig. 1) had secondary precipitates of hydrozincite. During war time, spoil reworking zinc oxide was also found in some of the older spoil heaps. This was noted as it reduced the efficiency of the reprocessing by lowering the flotability of the zinc ore (Dawson 1947).

The secondary deposits of calcareous minerals from Rampgill Mine were examined qualitatively using SEM. Zinc was found in all of these minerals (see Fig. 4 for an example). This suggests that the precipitation of all of these underground minerals (and especially aragonite) form interstitial sinks for zinc (i.e. the zinc is incorporated within the crystal lattice of the mineral). This is in addition to the inferred 'main phase sink'of hydrozincite and smithsonite within the workings. Attenuation of zinc concentrations may also occur by sorption onto mineral surfaces underground.

Zinc deficits in the Nent Valley mine waters

The concept of zinc deficits has been addressed by Younger (1999), who studied the mine water chemistry of a fluorspar (previously lead–zinc) mine, Frazer's Grove in Weardale County Durham (see also Johnson & Younger 2002), and found that molar concentrations of sulphate are in excess of zinc concentrations by two or three orders of magnitude. The excess of sulphate over zinc indicates that there must be significant sinks for zinc within the mine workings, as both components are sourced in equimolar proportions by sphalerite weathering. Weathering of other sulphide minerals such as galena (PbS), chalcopyrite ($CuFeS_2$) and pyrite (FeS_2) account for only a small amount of the total sulphate produced daily (less than 1%). The system studied by Younger (1999) showed that

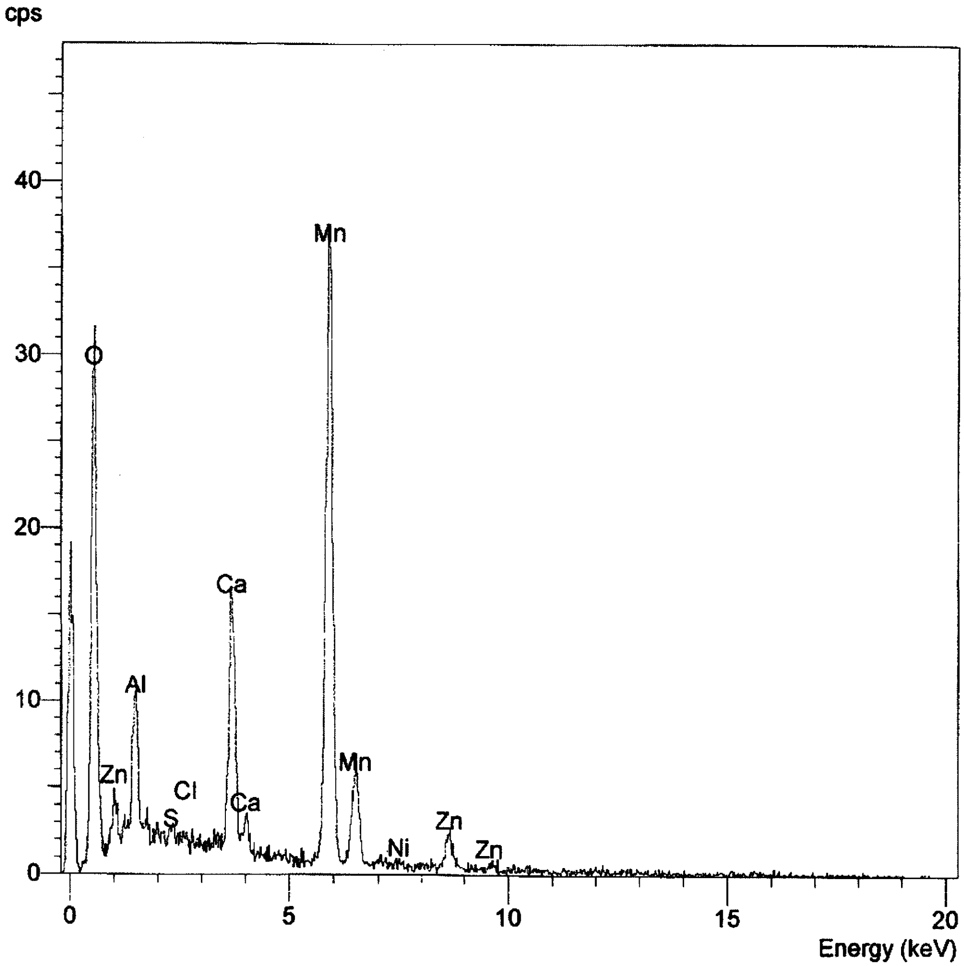

Fig. 4. Output from the qualitative SEM analysis of one of the calcareous secondary minerals found underground showing incorporated zinc.

attenuation of zinc was happening over relatively short distances within the mine. This suggests the presence of a carbonate sink for zinc that has rapid precipitation kinetics.

The main assumptions made whilst calculating zinc deficits are as follows:

- Sulphate is transported conservatively from the sites of sphalerite oxidation, evidence for this comes from geochemical modelling (using WATEQ4F, Ball & Nordstrom 1991) which shows that the feasible sinks for sulphate (gypsum and goslarite) are undersaturated and therefore not precipitating in large quantities underground.
- Significant pyrite oxidation and subsequent precipitation as ochre is not taking place (this would lead to an overestimation of the sulphate attributed to sphalerite oxidation). Evidence for this comes from the lack of ochre noticed on underground observations (it occurs in localized patches). In addition, there is no evidence for significant iron attenuation because iron concentrations found in water samples taken deep within the workings (usually less than 1 mg l^{-1}) are comparable with those found at the mine entrance.

The zinc deficit data for the Nent Valley mines are calculated using mine water flow rates and zinc and sulphate concentrations to calculate the amount of zinc and sulphate produced per day in mg l^{-1}. The number of moles of zinc and sulphate produced per day was calculated

Table 1. *Results of zinc-deficit calculations for mines in the Nent Valley (24 February 1998)*

Mine	Moles of SO_4^{2-} day^{-1}	Moles of Zn day^{-1}	Moles of SO_4^{2-} day^{-1} other sources	Moles of SO_4^{2-} as Zn deficit	Molar ratio S:Zn	Zn dissolved (kg/day^{-1})	Kg Zn leaving mine per day	% Zn lost from mine per day
Caplecleugh	2946	172	2.65	2772	17	191	11.18	5.8
Rampgill Horse Level	1404	53	21	1331	26	90	3.44	3.8
Haggs	647	21	0.8	626	31	42	1.43	3.2
Croft	351	9	1.7	340	39	23	0.59	2.6
Nent Force	4478	103	7	4368	43	290	6.71	2.3

by dividing the amount produced per day (in mg) by the gram formula weight (i.e. by 65 and 96 for zinc and sulphate, respectively, for this example data from samples taken on 24 February 1998 were used). The amount of sulphate sourced from other sulphide minerals (e.g. galena and pyrite) was also calculated using the concentrations of other metals (e.g. iron, copper and cadmium) bearing in mind that pyrite (FeS_2) is a bisulphide (i.e. it has the molar ratio 1:2). This amount of sulphate attributable to weathering of the other sulphide minerals was then subtracted from the total amount of sulphate present. The remaining value then represents the amount sulphate attributed to the zinc deficit. As zinc and sulphate are sourced in equimolar amounts, the number of moles of sulphate created must equal the number of moles of zinc produced. When the molar data are converted back into a mass for zinc (by converting the number of moles produced into kg values) the deficits of zinc become apparent. The results obtained from calculating molar ratios of S:Zn are presented in Table 1.

The results show that very little zinc (up to 6% calculated as a percentage of the total amount of zinc dissolved per day) actually leaves the mine in comparison to the amount released per day from sphalerite oxidation. The missing zinc must be forming minerals within the workings. Smithsonite has been recorded by Dunham (1990) as being present in the mines, and the mineral hydrozincite has also been directly observed by the author underground in Scraithole Mine (NY 8032 4694) in the adjacent West Allen Valley, where large quantities of this mineral can be directly observed precipitating from mine water.

Zinc deficits can also be described by Fig. 5. The poor correlation between zinc and sulphate on the x–y plots for each site shows that there is little relationship between the amount of zinc and sulphate in the discharges (i.e. the maximum R^2 value is around 0.6 and, for Rampgill, it is as low as 0.04). This is perhaps due to water mixing from different branches in the mine in addition to mineral precipitation or sorption of zinc. When all the data are combined on an x–y plot the sites lie in distinct clusters (reflecting the individual chemistry of each mine) but there is no discernible trend in the relationship between zinc and sulphate in the mine waters (Fig. 6). If zinc and sulphate were released from the workings in a 1:1 ratio (i.e. attenuation of zinc was not taking place) we would expect to find a much more significant correlation between the zinc and sulphate concentrations.

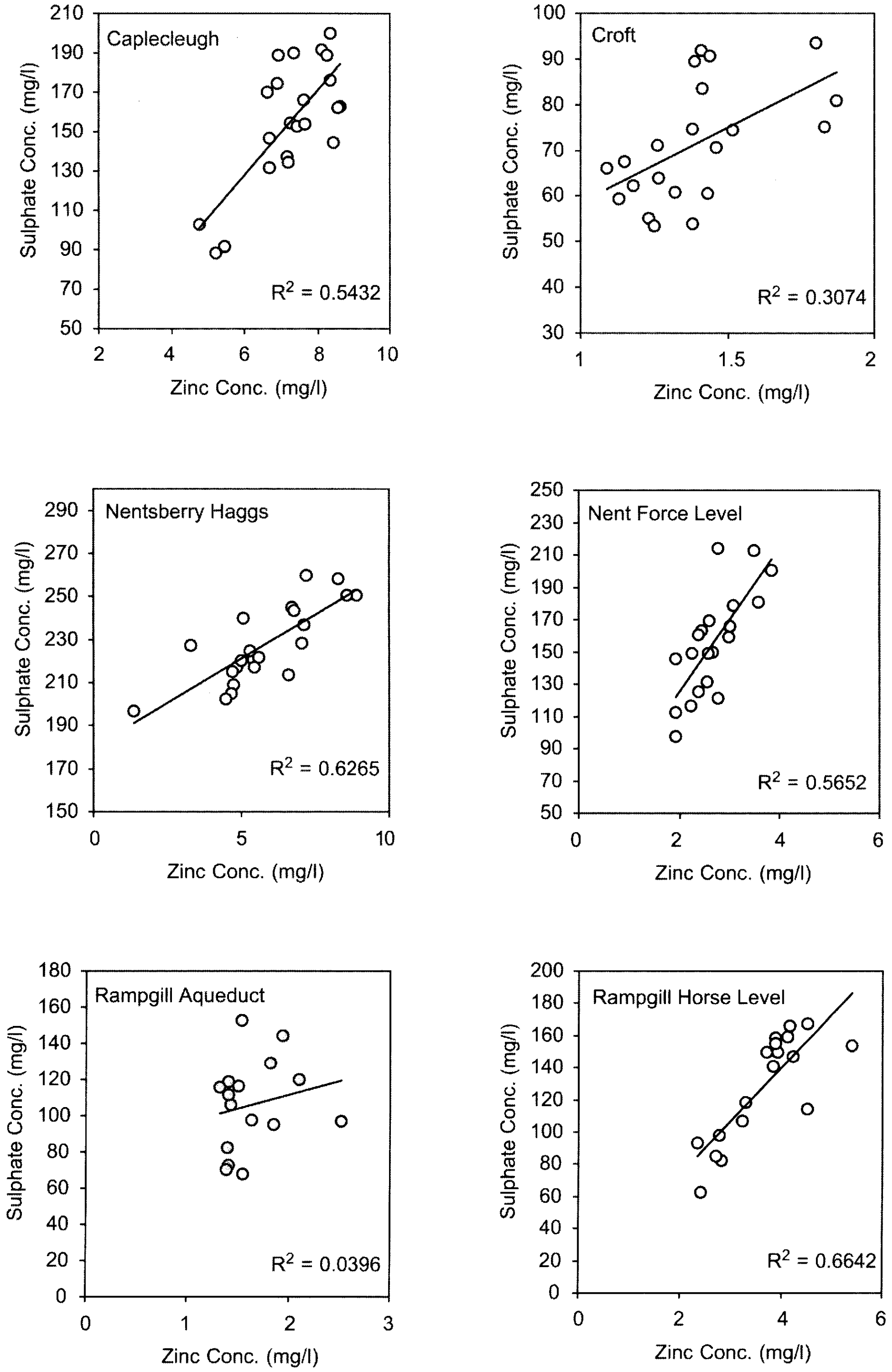

Fig. 5. *x–y* plots showing the lack of correlation between zinc and sulphate in each of the mine waters studied.

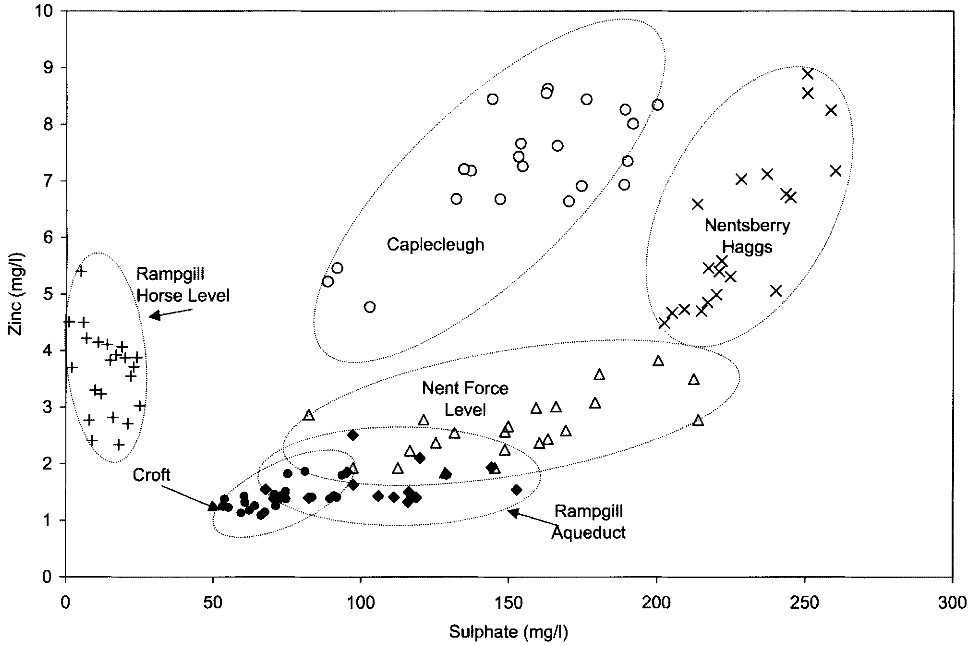

Fig. 6. Combined x–y plot for zinc and sulphate at all of the sites. Clusters are apparent but there is no discernible trend.

Table 2. *Modelled mine water zinc concentrations in the absence of mineral sinks for zinc*

Site	Average mine water Zn concentration ($mg\,l^{-1}$)	Mine water Zn concentration if no 'sinks' existed ($mg\,l^{-1}$)
Caplecleugh	7.35	126
Rampgill Horse Level	4.15	108
Haggs	5.06	159
Croft	1.15	45
Nent Force	2.59	112

Consequences for mine water chemistry in the absence of mineral sinks for zinc

When considering the data presented in Table 1, if the total amount of zinc weathered from sphalerite each day did not form secondary minerals, become incorporated into carbonate minerals or be adsorbed onto surfaces within the workings then mine water zinc concentrations would be almost two orders of magnitude greater than normal, by this theory.

Table 2, shows the likely zinc concentration of the five Nent Valley mine waters if mineral sinks were not in existence. These zinc-rich mine waters would then have a substantial impact on the Nent and are also likely to have a negative impact upon the South Tyne further downstream (Fig. 1), which is important for its fisheries and as a water resource. These calculations highlight the importance of metal sinks and show that, under the right conditions, large quantities of zinc can be removed from solution. Nuttall & Younger (2000) successfully emulated the precipitation of smithsonite in a passive treatment reactor as a means of treating mine waters to remove zinc by inducing a rise in pH (and, hence, smithsonite precipitation) within a closed limestone reactor.

Conclusions

Secondary zinc minerals and other carbonate minerals that sequester zinc interstitially precipitate within mine workings and on spoil heaps. These minerals provide effective 'sinks' for zinc because when comparing molar ratios of zinc and sulphate only around 5% of the zinc calculated to weather daily from the workings actually leaves the mine. Smithsonite precipitation has already formed a basis for a treatment system that passively removed zinc from these circum-neutral mine waters. The main phase 'sink' minerals appear to be precipitates of hydrozincite and smithsonite, with the other sinks being interstitial zinc within the carbonates calcite and aragonite and sorption of zinc within the workings. If these natural mechanisms of zinc removal were not occurring then the water quality emanating from the Nent Valley mines would contain increased concentrations of zinc and would have an even greater impact on the Nent River system.

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