Synoptic monitoring as an approach to discriminating between point and diffuse source contributions to zinc loads in mining impacted catchments

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Abstract

One of the global legacies of industrialisation is the environmental impacts of historic mineral exploitation. Recent national initiatives to manage the impacts on ground and surface waters have driven the need to develop better techniques for assessing understanding of the catchment-scale distribution and characterisation of the relative contribution of point and diffuse contaminant sources. The benefits of a detailed, multidisciplinary investigation are highlighted through a case study focused on the Rookhope Burn, a tributary of the River Wear, which falls within a significantly mine impacted area of the North Pennines Orefield, UK. Zinc (Zn) has been identified as the contaminant of concern within this catchment, which is judged by the Environment Agency to be at risk of failing to achieve good water quality status in the context of the Water Framework Directive. The results of synoptic flow monitoring and sampling for chemical determinations of major and trace elements have been used to calculate mass balances of instream and inflow chemical loads in the Rookhope Burn. Despite a dominant impact on the water quality from a mine outburst (especially Zn [1.45 to 2.42 mg/l], Fe [2.18 to 3.97 mg/l], Mn [3.69 to 6.77 mg/l], F [3.99 to 4.80 mg/l] and SO_4 [178 to 299 mg/l]), mass balance calculations combined with geological mapping have facilitated the identification of significant, previously unknown, subsurface contributions of Zn contaminated groundwater (with Zn concentrations in excess of 0.4 to 0.9 mg/l and 0.18 to 0.36 mg/l) to the Burn. The subsurface contributions exhibit spatial correspondence to mine workings with associated mineral veins and adits, or to points of suspected karst groundwater resurgence. These findings reiterate the challenges posed in decision making with

respect to remediation, in this case in the context of the management of significant subsurface contributions.

Keywords: mine water, diffuse pollution, zinc, hydrogeology, conceptual models.

1. Introduction

In many industrialised countries the majority of mining environmental problems are legacies of the past[1]. The recognition of the extensive nature of the environmental impacts, which threaten local ecosystems and human health has driven initiatives for remediation, e.g. the USGS Abandoned Mine Lands Initiative[1, 2] and the UK recognition of the impact of historic metal sites in the context of the Water Framework Directive (2000/60/EC [3]). Releases of polluting substances that cannot be easily traced back to a discrete contaminant source are referred to as diffuse pollutants. Diffuse source water pollution from current and historic mining activities can severely impact the water quality especially with regards to acidification and metal loading [4, 5 6, 7]. This has particular relevance in the context of the Water Framework Directive (2000/60/EC), which aims to achieve “good status” for all surface waters (ecological [physico-chemical, biological, specific pollutant and hydromorphological] and chemical components) and groundwaters (quantitative and chemical components) by 2015. In order to implement effective mine water management programmes the extent and distribution of diffuse sources of contaminants is required [8]. Determining the nature and extent of the diffuse contributions within a catchment can be difficult and requires a multidisciplinary approach[2]. If it was possible to identify a homogeneous catchment the impact of both point and diffuse contaminant loading would be cumulative and the signature of point source loading would be spiked, whereas that of diffuse loading would be incremental (Figure 1). In practice, catchments are not homogeneous and the contaminant loading may be subject to a combination of point and diffuse inputs, non-conservative behaviour, as well as dilution where the stream passes through contaminant-free stretches of the catchment. Consequently, more complex contaminant loading patterns result. An added variable is that of seasonality, which results from variations in groundwater residence times.

This paper addresses the difficulty of discriminating between diffuse and point source impacts of historical mining of lead-zinc mineralization on the water quality in the context of the Rookhope Burn, a southerly flowing tributary of the River Wear, North Pennine, UK. Sources of contaminated drainage have been identified through reviews of earlier work on the catchment [9-11] and through synoptic monitoring and chemical analysis. The results of the analyses have been interpreted in the context of the geological setting and used to determine the importance of individual sources of contaminated drainage and identify the existence of natural attenuation processes within the catchment.

The Northumbria River Basin District Management Plan [12] identified the Rookhope Burn as being at risk of moderate ecological status. The secondary groundwater body that underlies the catchment has been identified as being at risk from mines and minewater pressures.

Data published by [9, 10, 13], together with historic water quality data provided by the Environment Agency indicate that the key contaminant of concern within the Rookhope catchment is Zn. Zn is of particular concern in the context of its environmental impact, especially in the aquatic environment, owing to its toxicity to aquatic biota. This is acknowledged in its “specific pollutant” designation in the European Water Framework Directive (2000/60/EC). The current UK EQS (Environmental Quality Standard) for Zn ranges from 0.008 to 0.125 mg/ l, the higher value reflecting the beneficial effect of hardness (EC Dangerous Substances Directive 76/464/EEC, Table 2b). The maximum point source contribution of Zn to the Rookhope Burn (2.42 mg/l) is comparable with peak concentrations determined in other mining-affected watercourses, e.g Lapus River catchment northwestern Romania [14], South Korea [15], but do not reach the concentrations reported in run-off waters monitored in Cabezo Rajao, in Southeast Spain [16]. However, it should be noted that concern with respect to the impacts of Zn being over estimated has encouraged further research with respect to the EQS in the context of zinc’s “specific pollutant” status [17, 18], which allows due consideration of natural background and bioavailability concentrations in the determination of the EQS.

2. The Rookhope Catchment

Situated towards centre of the North Pennines Area of Outstanding Natural Beauty designation, the Rookhope catchment exemplifies the mining industrial heritage of the area. The source of the catchment lies within grouse moorlands at an elevation of approximately 600 to 540 m OD. Below this, the area is characterised by a relatively treeless landscape primarily given over to hill farming. The catchment bears the scars of abandoned quarries and mine workings, including: numerous mounds of rock and mine waste; remnants of open vein workings; remnants of former mill buildings; disused shafts, and areas of former leats (artificial water channels). Settlement is largely focused on the areas of Rookhope and Eastgate with additional isolated farmsteads. Many of the farms were also once utilised for mining, for example Wolf Cleugh and Lintzgarth (Table 2).

The catchment is underlain by mineralized Dinantian (Brigantian and Asbian) limestones, capped by Namurian sandstones and mudstones of the Yoredale Group [19] (Table 1). Strata are almost horizontal, with a slight regional dip to the east. The Stainmore and Alston formations comprise sequences of limestone, mudstone, siltstone and sandstone, with occasional developments of seat earth and coal. The limestones are typically only a few metres thick and become increasingly common towards the base of the Stainmore Formation. The Great Limestone is up to 15 m thick and the Alston Formation is dominated by thick limestones. Mineralization is hosted by faults, which are typically normal and of limited vertical throw, and by local occurrences, associated with the limestone, of horizontal mineral replacement referred to as flats. Primary minerals include galena, quartz, and siderite with traces of sphalerite, pyrite, and localised chalcopyrite. Secondary minerals include: limonite, psilomelane, cerrusite, malachite and occasionally azurite. Where flats have formed, significant quantities of fluorite, galena and calcite together with some quartz and chalcedonic silica may be present.

Superficial deposits comprise: glacial till below ~370 m OD; river terrace deposits associated with the River Wear; ribbons of alluvial deposits associated with all of the river valleys, and blanket peat, which caps the higher ground [20]. Anthropogenic deposits, including mine waste and construction materials associated with both mining and railway construction, are also evident throughout.

The Rookhope catchment comprises an area in the order of 37 km^2 and the southerly flowing stream contributes a discharge ranging from 100 to 2300 l/s to the River Wear at Eastgate (Figure 2). Rainfall and temperature vary with altitude. An annual effective rainfall of ~1000 mm has been calculated for Eastgate with monthly effective rainfall varying between 53 and 116 mm. The hydrograph for the Rookhope Burn is flashy, i.e. there are frequent, rapid, short term changes in stream flow and the stream responds rapidly to runoff events. A desk study and reconnaissance visits have contributed to the development of a conceptual model of the hydrogeology of the catchment. Four hydrogeological zones that reflect the underlying geology have been identified: [1] upland peat capping the interbedded shales and sandstones with an interbedded limestone (Upper Felltop Limestone) at the lower end of the zone; [2] interbedded shales and sandstones with an interbedded limestone (Lower Felltop Limestone); [3] Till capped bedrock, including the Great Limestone, characterised by the presence of dolines (shake holes), which is indicative of karstic void forming processes, and [4] more resistant Alston Formation bedrock characterized by a number of waterfalls, for example Turn Well (NY94882 39868). The presence of mudstones encourages surface run-off, which may recharge underlying sandstones and then re-emerge as springs and the presence of dolines facilitates fast flow to the stream, thereby further contributing to the flashiness of the hydrograph.

Although previously worked during a number of phases that are likely to date back to at least the Roman period, the majority of the lead mines were exploited during the period 1692 to 1882 [21] (Table 2 [22, 23]). More recently, driven by the need for high quality fluorspar for steel-making, fluorspar has been the principal mineral to be exploited in the catchment. Fluorspar mining continued until 1999, when the Grove Rake Mine (Figure 2, Table 2) closed. Frazer's Grove Mine comprises four underground mines: Frazer's Hush, Rake level/Firestone Incline workings, Grove Rake and Greencleugh [13]. [9, 10, 13] have contributed significantly to the understanding of Frazer's Grove Mine hydrogeology and hydrochemistry. Further descriptive detail of the mine is provided in these references. Sixteen main centres of former mining have been identified within the catchment (Figure 2, Table 2). 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 [24]. Of particular note in the context of the inputs to the Rookhope catchment are the Boltsburn and Tailrace Levels.

The Tailrace Level extends from its portal (NY91624 42779) to Frazer's Grove Mine via Rispey Shaft (NY91117 42739) and Wolfcleugh Old Pumping Shaft (NY90168 43230), a distance of approximately 2850 m. It is suspected that not all of the adits that were associated with the Tailrace Level have been recorded and that there are likely to be additional connections between some of the mining areas. This level drains abandoned mine workings with a component of surface run-off entering the level via crown holes [9]. [9, 10, 13] demonstrated that two thirds of the Frazer's Grove water-make comes from the Great Limestone aquifer with the remaining one third from the Firestone Sill and surface inflows. They 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 chemistry of the groundwater is stratified, reflecting the influence of variations in the bedrock geology (Table 1). Three waters were characterised: Type I associated with the Firestone Sill, comprising moderately mineralized Ca-HCO_3-SO_4 waters with less than 4 mg/l Zn; Type II associated with the Great Limestone, comprising highly mineralized Ca-SO_4 water with up to 40 mg/l Zn, and Type III associated with the deepest workings, comprising mineralized Ca-HCO_3-SO_4 water with up to 13 mg/l Zn and an increasing Cl content and temperature with depth. The cessation of pumping after closure of Frazer’s Grove mine (1998) resulted in the water table rising above the aquifer and discharging mine water with peak Zn concentrations as high as 35.6 mg/l via the Tailrace Level (Figure 2), the lowest surface discharge point at 364 m OD.

Boltsburn Level (Table 2) at 332 m OD is not directly connected to Frazer’s Grove Mine. It was sampled during the monitoring of rebound at Frazer’s Grove Mine [10] and was considered to have a chemistry typical of Great Limestone groundwater, but with variable Fe concentrations (1 – 10 mg/l).

3. Methodology

Synoptic flow monitoring and sampling for chemical determinations of major ions and trace elements was carried out, including both instream sampling points along the Rookhope Burn and tributary inflow sites (locations of potential contaminant discharge to the Rookhope Burn). The British Geological Survey database of mine adits informed the identification of potential point source contributions. Monitoring and sampling were carried out in May 2007, June 2007 and January 2008. The visits were scheduled to coincide with different hydrological conditions and the sampling points were chosen using topographic maps, aerial photographs and field investigation in order to cover the stream stretches upstream and downstream of visible mine water discharges, or at the confluence of major tributaries. In practice it was difficult to predict the stage of the river owing to the flashiness of the river hydrograph. It was considered that the May 2007 visit was the closest to baseline conditions, whilst the June 2007 visit coincided with the tail effect of a storm event. Immediately prior to the commencement of monitoring, there was a groundwater outburst from an abandoned mine shaft at Wolfcleugh (NY91059 42828; point 7, Figure 2), which had a marked impact on the chemistry of the Rookhope Burn.

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 with H_2SO_4 (0.16 N or 1.6 N) and bromocreosol green indicator. Samples for chemical analysis were filtered in the field using a disposable 0.45 μm cellulose-acetate cartridge filter and collected in polyethylene bottles. Chemical analyses were carried out in the laboratories of the British Geological Survey. Major and trace elements of 1% HNO_3 field-preserved, filtered samples were determined by ICP-AES (Varian Vista Axial). Fe (II) was determined by colorimetric analysis of 2–2 dipyridyl spiked samples. The major anions Cl, SO_4, NO_3 and F were determined by ion chromatography (Dionex DX-

600). Duplicate samples and blanks using cleaned field equipment were included at each sampling event for quality control.

Discharge was determined for each sampling point, during each of the sampling campaigns, using the velocity-area method [25]. A Columbia 2 Digital Stream Meter, an impeller-type flow meter, was used to measure stream velocity. In order to achieve consistency, on each occasion monitoring was carried out at pre-determined monitoring positions (marked by posts in the river bank) and at each monitoring point, where the stage allowed it, the velocity was determined at the same distances across the channel. Discharge was derived from the mean of the values calculated using the mid-section and mean-section formulae. Inevitably there are problems associated with this type of monitoring. The variability in discharge is, in part, attributed to the form of the river bed, which is occupied by significant volumes of mine and rock waste through which groundwater flow bypasses the flow monitoring. This is particularly evident in places where the watercourse bifurcates around islands of rock and at low stages, water can be seen draining from the rock islands to the channel, on one or both sides of the island.

Contaminant loadings were determined utilizing an approach comparable with that of [5]. At each instream or inflow measuring point the contaminant load was calculated from the product of the discharge and contaminant concentration. The contaminant load distribution along the study stream helped to identify sources and sinks along the Rookhope Burn, based on an assumption that the load at the end of a stream segment includes the load from the point upstream plus the contribution from all surface and subsurface inflows along the stream segment. Increases in load between instream sites, were attributed to a source associated with the monitored stream segment. If the instream contaminant load decreased between sites, a sink (chemical, biological or physical attenuation of metal load) was assumed to be responsible for the removal of contaminant load, except in locations where this was associated with a reduction in discharge. The cumulative instream load, as defined by [5], was determined at the base of the catchment by calculating the sum of the increases in loads entering the stream. This provides a minimum estimate of the total load of contaminant added to the stream. The cumulative instream attenuation was, similarly, defined as the sum of all the negative values of change in load.

4. Results

4.1 Discharge

Discharges of inflow and instream sampling points are reported in Tables 3 and 4. Figure 3, which summarises the flow monitoring in the Rookhope Burn stream, demonstrates that there is not a simple linear increase in discharge down the channel. Two stretches of rapid increase in discharge are notable, namely between sample points 9 and 11 (4890 m to 4960 m downstream of the head of the catchment, Figure 2) and between sample points 19 and 21 (7155 m to 7400 m). The only obvious contributions to these two stretches comprise, respectively, groundwater drainage from the Tailrace Level (sample point 10) and the surface water contribution from Bolts Burn (sample point 20), but the volumes derived from adding these contributions to the upstream discharge do not fully account for the increase in discharge in these stretches. Additionally, the data suggest that there have been losses in discharge between monitoring points 21 and 24 (except in June 2007, during the tail end of the storm event).

Following the first monitoring visit (May 2007) it was suspected that worked mineral veins were forming flow paths for previously unrecognised groundwater contributions to the Rookhope Burn. To explore further the nature of the contribution in the stretch between sample points 9 and 11, flow monitoring was carried out in August 2007 at closely spaced intervals across the fault/ mineral vein associated with the Tailrace Level (point 10, Figure 2, Table 5). Giving due allowance for the variability that results from the flow monitoring technique described above, the discharge measurements indicate a groundwater contribution to the stream immediately downstream of the Tailrace Level. Examination of the historic maps, geology map and aerial photographs established that this increase is associated with a point that aligns with a series of mine workings, immediately to the east of the surface expression, of the northeast to southwest-trending mineral vein with which the Tailrace Level is associated. Comparable with the discharge from the Tailrace Level, the groundwater contribution was characterised by lower temperature, pH, electrical conductivity and total dissolved solids and higher dissolved oxygen concentration on the northern side of the channel (Table 5). Examination of historic records indicated that the increase in discharge downstream of Bolts Burn, between sample points 19-21, was likely to be mine water from an adit that was driven into Red Vein from the south bank of the river, immediately downstream of Bolts Burn. Subsequent investigation in this area identified the presence of a drainage adit at NY93778 42712, with minimal discharge (0.486 l/s on 11 May, 2009), which was insufficient to account for the increased discharge between sample points 19 and 21.

4.2 Hydrogeochemistry

4.2.1 Inflows

To assist with the interpretation of the contaminant loading in the catchment consideration has been given to the geochemistry of the contributing waters, which include: minewater; seepages from the mine waste; the Rookhope Burn water quality, and contributions from other adits and surface waters (Tables 3 and 4). The minewaters were classified as Ca-HCO_3-SO_4 water, from: the mine water outburst at Wolfcleugh (sample point 7), Tailrace Level (sample point 10) and Boltsburn Level (sample point 18). These waters were found to be near neutral (pH 6 to 7), highly ionized, with elevated concentrations of: Ca (27-125 mg/l), Mg (5 to 20 mg/l), K (6 to 8 mg/l at the outburst), HCO_3 (73 to 234 mg/l), SO_4 (16 to 299 mg/l) and F (1 to 5 mg/l). Ca:Mg weight ratios in the mine waters were generally high (>6). They were characterized by Zn concentrations in the range 0.04 to 2.42 mg/l, the higher concentrations being associated with the mine water outburst (sample 7). Sample 7 was also found to be enriched with Mn (3.69 to 6.77 mg/l). When compared with the minewater types defined by [13], they appear to fall within the Type III category, but were generally more dilute. Water from other adits (sample points 26 and 29, Figure 2) comprised dilute Ca-HCO_3 and Ca-HCO_3-Cl water with neutral to slightly alkaline pH values and lower concentrations of Ca, Mg and SO_4. The Ca:Mg ratio was found to be marginally higher than that of the minewaters (~7.5). These waters were also characterised by lower concentrations of F and Zn than the mine waters. Their chemistry suggests that the discharge from these adits is largely surface water drainage through the unsaturated zone.

Seepages from the mine waste heaps at Wolf Cleugh (sample point 27) and the tributary receiving the drainage from the area of spoil heaps to the west of Rookhope Burn at Rookhope village (sample point 28) exhibited different chemistries. Sample point 28 had elevated Zn (0.67 - 0.92 mg/l), Pb (0.13 - 0.32 mg/l) and SO_4 (138 - 143 mg/l) concentrations. The seepage at sample point 27 appears to have been diluted by surface water, exhibiting lower concentrations of these determinands. F was relatively elevated in both samples (1.89 mg/l in sample point 28, and 1.70 mg/l in sample point 27). Both sample points were dry during the baseflow sampling in May 2007. Surface waters from the tributaries: Brecken Sike, Rispey Sike, Redburn and Bolts Burn (sample points: 4, 12, 15 and 20) exhibited lower ionic strength and comprised Ca-Na-Mg-Cl-SO_4 waters. The surface waters exhibited lower Ca:Mg ratios and Zn concentrations ranging from 0.01 to 0.06 mg/l.

4.2.2 Rookhope Burn

Water chemistry of the samples obtained from the synoptic monitoring of the Rookhope Burn is reported in Table 4. The analyses for the May 2007 sampling campaign are considered to be the closest to the stream base flow conditions and are plotted in Figure 4 against distance from the headwaters of Rookhope Burn to its confluence with the River Wear at Eastgate. Sample inflow chemistries are also shown. The plots for F, HCO_3, SO_4, Ca and Mn all exhibit a significant increase in concentration between sample points 6 and 9, which are attributed to the input from the Wolfcleugh mine water outburst described above. Downstream, the concentration of these determinands decreased to the proximity of sample point 11, where it levelled out (except for a slight increase in Ca and alkalinity) between sample points 11 and 13, before a general decrease again in the direction of Eastgate. A second decrease occurred downstream of sample point 13 and appears to be coincident with the outcrop of the Great Limestone in the bed of the river. Fe concentrations (mainly reduced) were higher in the headwaters of the catchment, whereas, upstream concentrations of Zn were in the order of 0.15 - 0.68 mg/l, but increased steeply in the stretch between sample points 6 and 9 respectively, reaching ~1 mg/l in sample 9 in May 2007, immediately downstream of the mine outburst at Wolfcleugh. Between sample points 9 and 11 the Zn concentration decreased substantially to 0.42 - 0.21 mg/l. Between sample points 11 and 13 there was a levelling of the concentration of Zn, before a further progressive decrease downstream to Eastgate (0.09-0.11 mg/l).

These results indicate that the major changes in the Rookhope Burn stream chemistry occurred at, or immediately downstream of, the location of the mine water outburst at Wolfcleugh. More subtle variations along the catchment point to additional contributions from: mineralized groundwater, seepages from mine waste, surface water and to the influence of changes in the bedrock geology. Along the majority of the length of the Rookhope Burn concentrations of Zn exceeded the EQS (aquatic life-standards quoted for salmonid and the more sensitive cyprinid life), calculated on the basis of the hardness of each sample, during the May 2007 sampling campaign. Exceptions were the headwaters of Rookhope Burn (sample point 1) and the point immediately downstream of Grove Rake Mine (sample point 3), which did not exceed either of the EQS Zn values. However Zn concentrations were above the EQS value for salmonid fish life in the subsequent monitoring campaigns. From sample point 6 (upstream of the mine outburst) to sample point 19 (downstream of Boltsburn Level) all of the water samples in the burn were above the threshold value for cyprinid life related to the water hardness. The remaining stretch of Rookhope Burn, to its confluence with the River Wear, had Zn concentrations above the EQS value for salmonid fish life.

4.2.3 Zinc Load

The hydraulic data, which indicate gaining and losing reaches in the stream, have been combined with chemical measurements to derive Zn loads in Rookhope Burn in order to assess the impact of these reaches on the stream water quality. Figure 5 illustrates the spatial variation in Zn concentrations and the Zn load along the Rookhope Burn and Table 6 summarises the gains and losses in Zn load at the 11 stream segments defined by sample locations in the stream. The Zn load profiles differ from the concentration profiles in that they display two distinct peaks in load. The greatest increase occurs between sample positions 9 - 11 (upstream and downstream of the Tailrace Level resepectively, ~4890 m and 4960 m downstream of the head of the catchment), in May 2007 and January 2008. In June 2007 the Zn load contribution in the stretch between sample points 6 and 9, located upstream and downstream of the Wolfcleugh mine water outbreak was the largest in the Rookhope Burn. The second loading peak entered Rookhope Burn in the stretch between sample positions 16-19 and 19-21, respectively, in May - June 2007 and January 2008.

For the river stretches characterised by an increase in the metal load, mass balance calculations have been made between the net changes in instream load and the inflow loads measured along the same stretches in order to further elucidate the relative influence of inflows on the stream. The inflow source contributing to stretch 6-9 is the Wolfcleugh mine water outburst (sample point 7) with a Zn load of 85 mg/s in May 2007 (Zn 2.42 mg/l), 294 mg/s in June 2007 (Zn 2.34 mg/l) and 10 mg/s in Jan 2008 (Zn 1.45 mg/l). Water from this inflow point source contributes to 66 to 82 % of the total Zn load in May and June 2007, but only the 3.5 % in January 2008. For this stream segment, the difference between the net change in instream load and the inflow load of Wolfcleugh mine water outburst leaves a negative balance of -60 mg/s in May and June 2007 and -20 mg/s in January 2008. This denotes that the measured inflow load entering stretch 6 - 9 is greater than the net change in load measured for the stream segment, indicating a possible removal of Zn through physical or chemical processes. Field evidence of ochre precipitation in the immediate vicinity suggests that Zn mass is lost by chemical precipitation/ adsorption. Commonly observed Fe oxy-hydroxide and SO_4 mineral precipitation downstream of the river's confluence with SO_4 Fe(II) rich- mine drainage is generally associated with a decrease in dissolved concentrations of trace metals, including Zn, due to adsorption on the Fe mineral precipitates [26, 27].

In contrast, along stretches 9 - 11 and 16 - 19 the gains in Zn load in the stream cannot be attributed only to the sampled inflows. The only inflow in stretch 9 - 11 was Tailrace level (sample point 10) with a Zn load of: 10 mg/s in May 2007 (Zn 0.29 mg/l); 4 mg/s in June 2007 (Zn 0.07 mg/l), and 0.8 mg/s in January 2008 (Zn 0.04 mg/l). The balance indicates an unsampled Zn inflow of: +50 mg/s in May

2007; -0.7 mg/s in June, and +302 mg/s in January 2008. Similarly, Boltsburn level (sample point 18) alone cannot account for the increased load in stretch 16 - 19 where a balance of unsampled Zn inflows of: +30 mg/s in May 2007; +65 mg/s in June 2007 and + 8 mg/s in January 2008 have been determined. The results suggest a significant inflow of subsurface Zn-rich water to the stream that contributes to the Zn loading in these areas.

The greatest apparent net Zn load losses occur along the stretches 13 - 16 and 21 - 23 (except in June 2007). Cumulative Zn loads at Eastgate (Table 7), at the downstream end of the study catchment, ranged from 130 mg/s to 360 mg/s through the 3 sampling events, with instream cumulative attenuation along the study stream ranging between 80 and 140 mg/s. The sampled visible inflow loads accounted for 75 to 85 % of the cumulative instream Zn load in May and June 2007, but only 6 % in January 2008.

5. Discussion

The most significant impact on the water quality of the Rookhope Burn that has been identified during the course of this study is the point source contribution of mine water from the outburst at Wolfcleugh. The National Grid Reference (NY391059 542828) of the location of the outburst indicates that it is situated on Rispey Vein. The elevation of the shaft was estimated to be ~375 m OD, which places it marginally above the Tailrace Level ~365 m OD at river level. This suggests that there was a collapse of the underground workings, resulting in a blockage somewhere downstream of Rispey Vein causing an increase in pore water pressures and consequential outburst of minewater. Remedial measures, which entailed capping the shaft and feeding the discharge into an outlet channel, were carried out at some point between the June 2007 and January 2008 monitoring visits. Coincidental with this, the discharge from the outburst of mine water at Wolfcleugh appears to have reduced (35 l/s in May 2007; 126 l/s in June 2007 and 6.8 l/s in January 2008). During the monitoring period the chemistry also appears to have ameliorated (Table 3), with reductions in the concentration of SO_4, F, Fe, Mn and Zn. The synoptic monitoring commenced in the order of five months after the outburst occurred. During the period prior to the outburst it is likely that the stratification of the water chemistry in Grove Rake Mine described by [13] and [9, 10] and attributed to the geological influences on the geochemistry was disrupted as a consequence of the build up of pore water pressure, squeezing water into previously unconnected areas of the mine workings. Upon the release of this pressure, the stratification would have been further disturbed, facilitating the release of more acidic mine water with the acidity being attributed to its contact with pyritic shales, as seen in Grove Rake Mine. It is possible that the apparent improvement in the water quality represents the re-establishment of stratification in the mine water. Further monitoring is required to determine more conclusively whether this is the case. The discharge data indicate that the engineering works have confined the flow from the outburst, which appears to have resulted in an increased contribution to the Rookhope Burn via the bed of the stream.

Known point sources, suspected to contribute Zn loading to the stream via drainage adits include the discharge from the Tailrace and Boltsburn levels. Comparison of the analyses determined during this study (0.29 mg/l and 0.06 mg/l respectively during the baseflow conditions in May 2007) with those reported by [10] indicate that the chemistry of the water was similar. The Tailrace Level is known to receive a surface water contribution [10]. Nevertheless, the significant reduction in Zn and SO_4 concentrations after the May 2007 sampling suggest improvements in the quality of the groundwater contribution (Table 3), with reductions in electrical conductivity, alkalinity, F and Mn also being evident. Furthermore, the postulated blockage associated with the outburst is thought to have affected the discharge from the Tailrace Level (34 l/s in May 2007; 61 l/s in June 2007 and 19 l/s in January 2008). The improvement in the groundwater chemistry and reduction in discharge appear to be responses to the reduction in head brought about by the release of minewater via the mine outburst and subsequent remedial engineering. The chemistry of the discharge from the Boltsburn Level also showed an improvement during the monitoring period; however the improvement was more variable than, and not as progressive as, that of the discharge from the Tailrace Level, suggesting that the variation represents seasonality of the water quality.

Further to the known point source contributions, this work has identified two previously unidentified sources of contaminated groundwater, which are suspected to emanate from the bed of the river and contribute 15 to 25 % of the cumulative Zn load in the Rookhope Burn during the May and June 2007 sampling. These subsurface contributions, however, become dominant in January 2008 when approximately 95% of the Zn load entered the stream through these zones. Analysis of the discharge data and Zn loading indicate the presence of one such zone between sampling positions 9 and 11, where a contribution in the vicinity of the Tailrace Level is suspected.

A second point occurs between sampling positions 16 and 19. The focus for this input has not been established. Mineral veins cross the stream downstream of the Boltsburn

Level, but closely spaced analysis of the physico-chemical conditions carried out in May 2009 failed to locate the ingress. As the calculation of the Zn load uses the discharge data, any error in the measurement, or calculation of discharge would impact on the calculation of the Zn load. The potential for some loss of flow to the bed of the river, where it comprises a significant thickness of boulders cannot be entirely precluded. Whilst the accuracy of the discharge cannot be verified, a relative increase in discharge was observed on each occasion. Furthermore, subtle increases in the pH, alkalinity, Ca and Mg between sample points 16 and 19 suggest another source of groundwater. Additionally, the concentration profiles for F and SO_4 during base flow sampling (Figure 4) indicate dilution as a consequence of this input. The geological setting of these points suggests that the increased discharge is attributable to the karst hydrogeology in this area. A number of shake holes (dolines) have been identified to the south of the river (centred on NGR NY93338 42874 and NY93489 42828) in the stretch between sampling locations 16 and 19. The dolines are situated in an area where there is a thin cover of glacial till, close to the feather edge of the sandstones and mudstones, which cap the Great Limestone. Thus it is likely that recharge via the dolines occurs and indicates the presence of a mature karst system that resurges to the Rookhope Burn via the easterly dipping Great Limestone. The lower concentrations of SO_4 in this water indicate less contact with the mineralization and this is reflected in the lower Zn concentration, when compared with the concentration from the Tailrace Level and from farther upstream.

Whether the contributions in the stretches between sampling locations 9 - 11 and 16 - 19 should be classified as point or diffuse sources has been the subject of considerable discussion. Using the approach presented in the introduction these are clearly point source contributions, however at a closer scale the detail of the point of the emissions has not been fully resolved, particularly in the zone between sampling locations 17 and 19, where it is suspected that the contribution occurs over a zone in the river bed, which might be considered a diffuse input.

Analysis of the Zn loading has also established the existence of Zn sinks. The greatest apparent net Zn load losses occurred along the stretches 13 - 16 and 21 - 23 (except in June 2007). The reduction in the Zn load between points 13 and 16, downstream of the Tailrace Level, was associated with a significant decrease in the Zn concentration in the river (Figure 5), which is likely to be a consequence of attenuation by chemical precipitation of Zn. The reduction in flow suggests that significant dilution is unlikely. The decrease in load determined between points 21 and 23 also coincides with a measured decrease in discharge (in May 2007 and January 2008). It is difficult to tell whether this reflects flow loss below the bed of the river, or unmeasured flow in the stream sediments. It is also possible that there are karstic losses from the bed of the river to the Great Limestone.

Seepage water (sample positions 27 and 28) emanating from waste heaps, characterised by elevated SO_4, Pb, Zn and F, is considered to be representative of diffuse contaminant sources in the catchment.

F has been shown to be a good indicator of mining impacted groundwater in other catchments [28] and the evidence from this work suggests it to be a good indicator in the Rookhope catchment. From Table 4 it can be seen that elevated F concentrations are associated with both point (mine water) and diffuse (mine waste-derived) inputs. The concentration of F (0.20 to 4.48 mg/l) in the Rookhope Burn increases steadily down the catchment, suggesting diffuse contributions, in the mining impacted area, with local, spiked point source contributions that are locally masked by the minewater contribution from the outburst at Wolfcleugh. The increased loading in a downstream direction indicates the F to be more dispersed and conservative than Zn (Figure 6). SO_4 shows a similar, dispersed contribution, which is comparable with that observed by [5]. Locally there is a reduction in the F load associated with a reduction in the discharge determined for sample point 23. This may be indicative of karstic losses of stream water to the bed of the river, as hypothesised above.

The measured concentrations indicate that F might also be a contaminant of concern. Whilst the WHO guideline for drinking water quality is 1.50 mg/l [29] , [30] suggested that F concentrations in the river environment be limited to 0.5 mg/l, based on the toxic effects on invertebrates and fish in soft waters with low ionic content. Toxicity was concluded to be related to water hardness however, and with increased hardness safe levels of F could be increased to 1.0 to 1.5 mg/l [30]. The guideline values are lower than the concentrations determined in the vicinity of the Tailrace Level and during baseflow conditions throughout much of the Rookhope Burn downstream of Grove Rake. Further research is required to understand the ecological impacts.

6. Conclusions

Zn has been identified as the key contaminant of (ecological) concern in the Rookhope catchment, where it generally exceeds the EQS values for salmonid and cyprinid life. Synoptic sampling and contaminant load calculations have demonstrated that Zn primarily reaches the stream via point sources of mine water. Zn sinks gave also been identified. This may be particularly important in the context of any future changes in the catchment either as a consequence of climate change, or anthropogenic influences. In considering remedial target measures to achieve “good status” further work is required to determine the actual ecological impacts of the levels of contamination that have been identified. F has been shown to be a good indicator of the contribution of dispersed contamination to the Rookhope Burn. The measured concentrations indicate that F might also be a contaminant of concern with values > 1.5 mg/l during baseflow conditions throughout much of the Rookhope Burn downstream of Grove Rake.

High resolution water monitoring, in conjunction with a good conceptual model, can be used to discriminate between point and diffuse sources and subsequently assess the implications of their distribution. In this case study, building on the work of earlier authors [9, 10, 13], this has facilitated the characterisation of the five most significant source contributions of Zn to the Rookhope Burn: the known contributions via drainage adits (Tailrace Level and Boltsburn Level); previously unknown sources of mine water entering via the bed of the stream; suspected karst groundwater resurgence to the bed of the stream, and the mine water ingress via a recent mine water outburst. The remedial measures for the outburst incorporated a permanent drainage discharge to the Rookhope Burn, which will also comprise a long term point source contribution of Zn to the stream. Nonetheless, the results of the synoptic sampling and the work of [10] indicate that the quality of the Burn is likely to ameliorate with time.

The triggering of the outburst raises the question of the stability of the underground workings and the risk of designing remediation schemes for a single point, which could be made obsolete in the event of a comparable outburst elsewhere in the catchment. Furthermore, the mine water contribution to the bed of the river highlights the difficulty in designing remedial schemes for mine water contamination, demonstrating the need for more detailed understanding of the hydrology associated with abandoned workings.

The results from this research highlight the need for an iterative approach to such studies, as the interpretation of the results of the synoptic sampling and analysis has, in part, relied upon an untested, conceptual understanding of the hydrogeology of the catchment. For example, the explanation for the increase in the Zn loading between sampling points 16 and 19 could be underpinned with dye tracing, via the dolines located at NGR NY93338 42874 and NY93489 42829, in order to confirm the existence of karst flow paths in the stretch between sample points 16 and 19.

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FIGURE CAPTIONS

Figure 1. Hypothetical plots of cumulative Zn load from point and diffuse contaminant sources.

Figure 2. Location plan of Rookhope catchment showing the sampling points.

Figure 3. Discharge along the Rookhope Burn with indicated sampling point numbers.

Figure 4. Instream and inflow total dissolved element concentrations versus distance from Rookhope Burn headwaters to the River Wear (May 2007 sampling).

Figure 5. Instream and inflow concentrations and load of Zn versus distance in Rookhope Burn.

Figure 6. Load profiles of F and SO_4 in Rookhope Burn.

TABLE CAPTIONS

Table 1: Stratigraphical context.

Table 2: Centres of mining within the Rookhope Catchment.

Table 3: Sampling point location, major ion and trace element concentrations, field measurements and discharges of inflows in Rookhope catchment.

Table 4: Sampling point location, major ion and trace element concentrations, field measurements and discharges of Rookhope Burn.

Table 5: Discharge and field measurements determined south, mid and north channel in the vicinity of the Tailrace Level (NY 91631 42732) on 11 August, 2007.

Table 6: Summary of changes in Zn load at the 11 stream segments defined by sample locations in Rookhope Burn.

Table 7: Cumulative instream Zn loading, instream attenuation and cumulative measured inflow contributions to the total Zn load in Rookhope Burn.

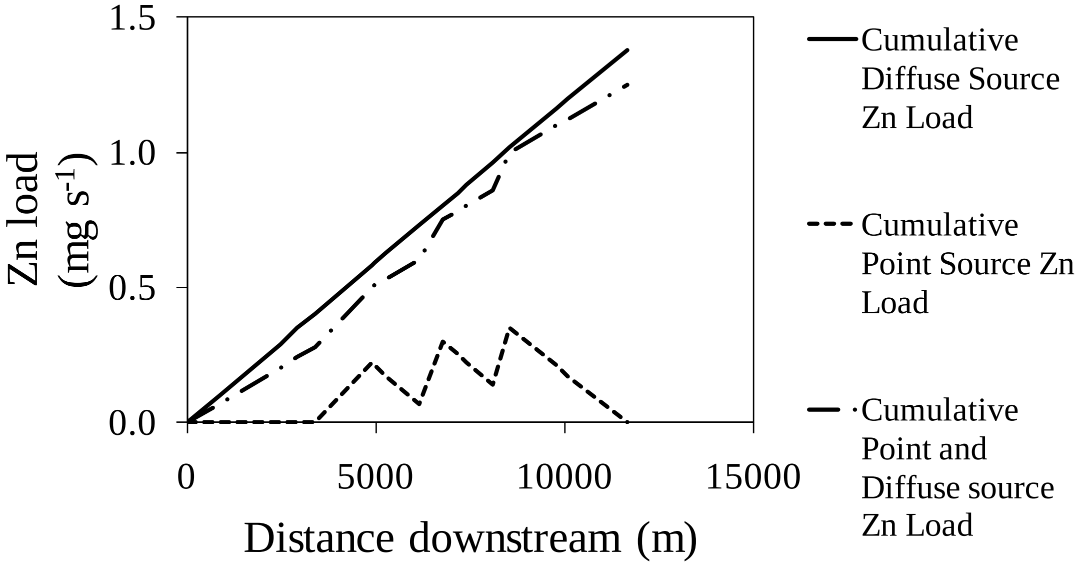

Zn load (mg s-1)
1.5
1.0
0.5
0.0
0
5000
10000
15000
Distance downstream (m)
Cumulative Diffuse Source Zn Load
Cumulative Point Source Zn Load
Cumulative Point and Diffuse source Zn Load

Figure 1

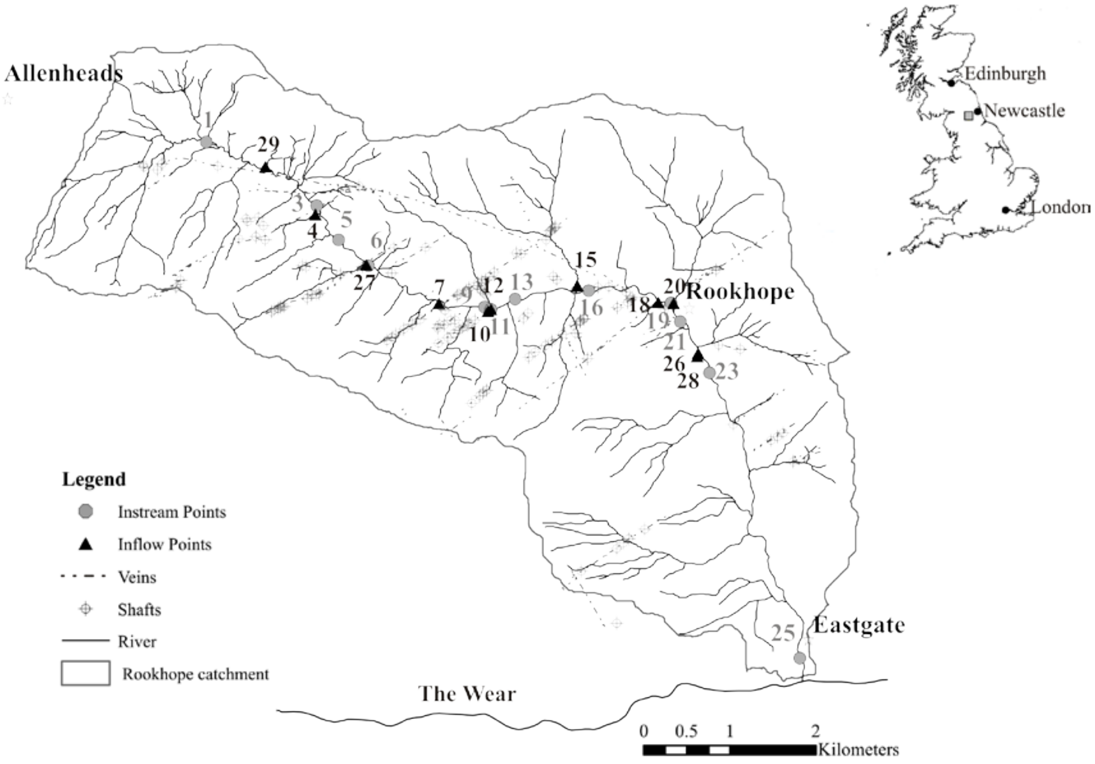

Allenheads
1
29
3
4
5
6
27
7
9
12
13
10
11
15
16
18
20
Rookhope
19
21
26
28
23
25
Eastgate
The Wear
Legend
Instream Points
Inflow Points
Veins
Shafts
River
Rookhope catchment
0
0.5
1
2
Kilometers
Edinburgh
Newcastle
London

Figure 2

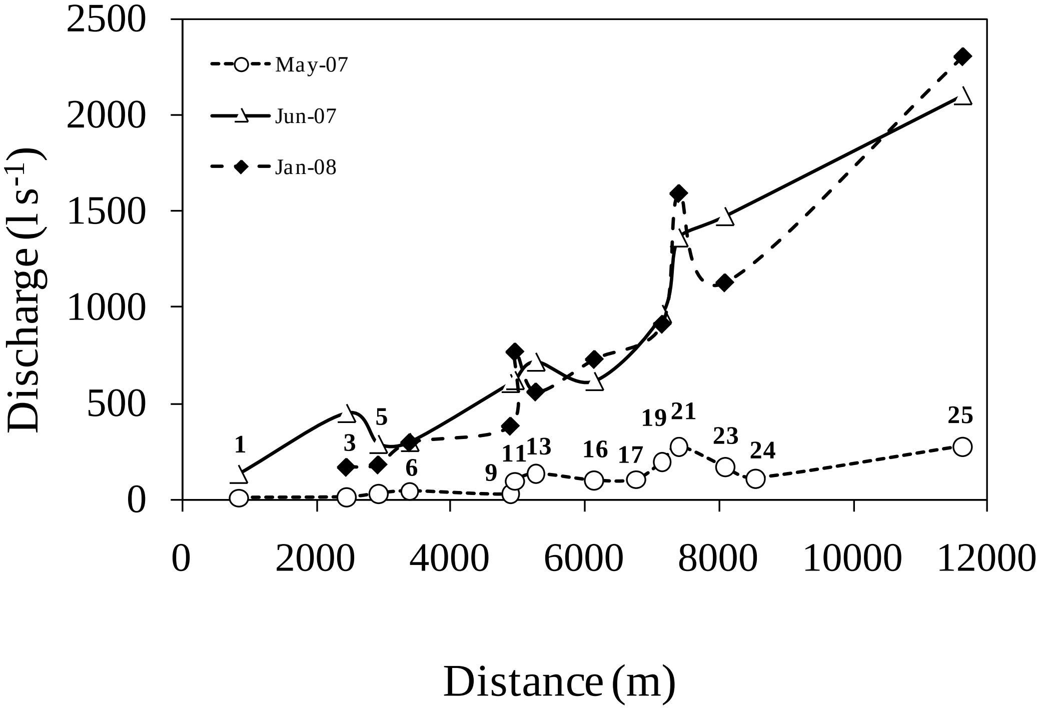
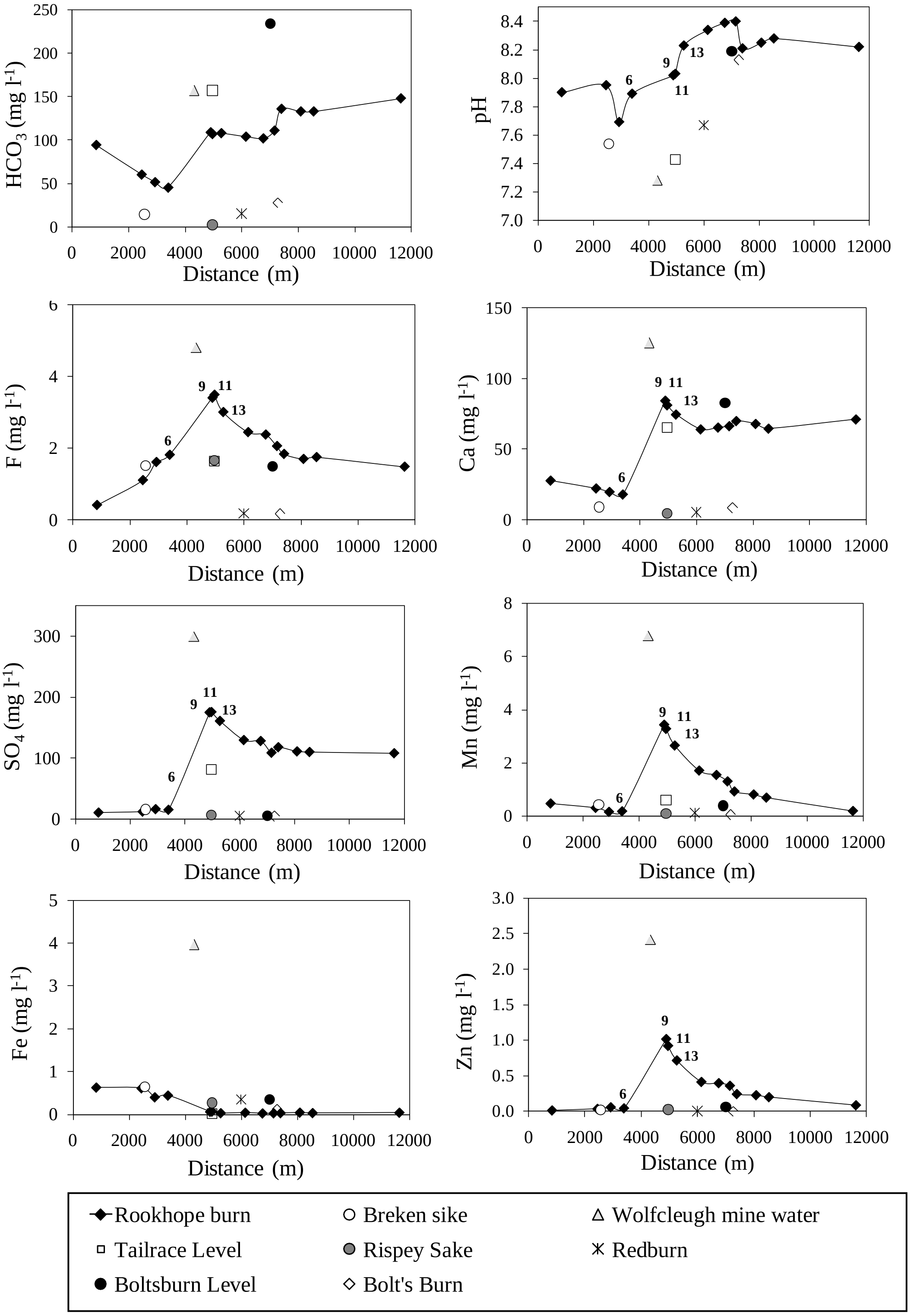

May-07
Jun-07
Jan-08
Discharge (l s-1)
Distance (m)
0
500
1000
1500
2000
2500
0
2000
4000
6000
8000
10000
12000
1
3
5
6
9
11
13
16
17
19
21
23
24
25

Figure 3



HCO$_3$ (mg l^{-1})
0
50
100
150
200
250
pH
7.0
7.2
7.4
7.6
7.8
8.0
8.2
8.4
F (mg l^{-1})
0
2
4
6
Ca (mg l^{-1})
0
50
100
150
SO$_4$ (mg l^{-1})
0
100
200
300
Mn (mg l^{-1})
0
2
4
6
8
Fe (mg l^{-1})
0
1
2
3
4
5
Zn (mg l^{-1})
0.0
0.5
1.0
1.5
2.0
2.5
3.0
0
2000
4000
6000
8000
10000
12000
Distance (m)
6
9
11
13
Rookhope burn
Breken sike
Wolfcleugh mine water
Tailrace Level
Rispey Sake
Redburn
Boltsburn Level
Bolt's Burn

Figure 4

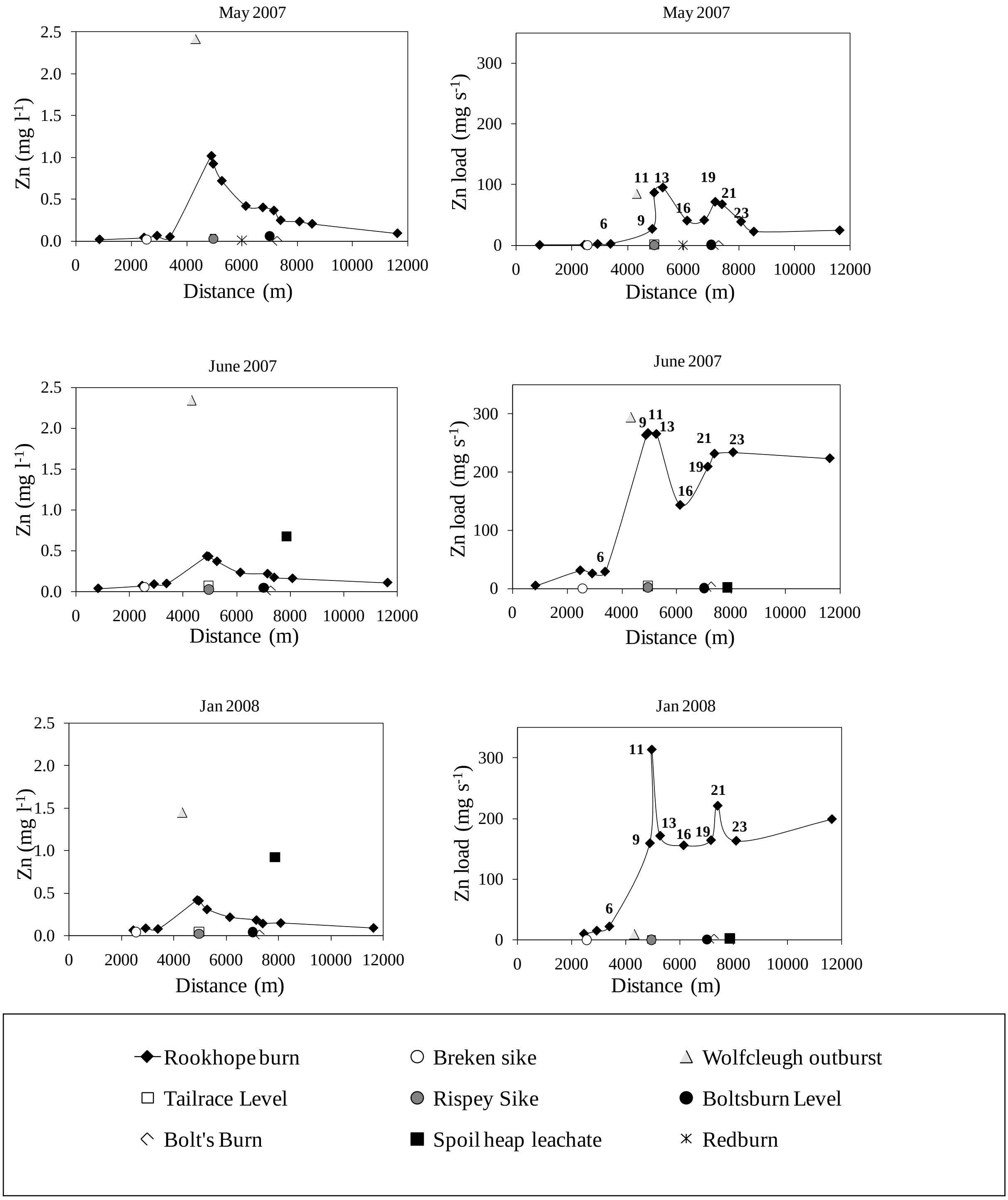

May 2007
Zn (mg l-1)
Distance (m)
May 2007
Zn load (mg s-1)
Distance (m)
6
9
11
13
16
19
21
23
June 2007
Zn (mg l-1)
Distance (m)
June 2007
Zn load (mg s-1)
Distance (m)
6
9
11
13
16
19
21
23
Jan 2008
Zn (mg l-1)
Distance (m)
Jan 2008
Zn load (mg s-1)
Distance (m)
6
9
11
13
16
19
21
23
0.0
0.5
1.0
1.5
2.0
2.5
0
100
200
300
0
2000
4000
6000
8000
10000
12000
Rookhope burn
Breken sike
Wolfcleugh outburst
Tailrace Level
Rispey Sike
Boltsburn Level
Bolt's Burn
Spoil heap leachate
Redburn

Figure 5

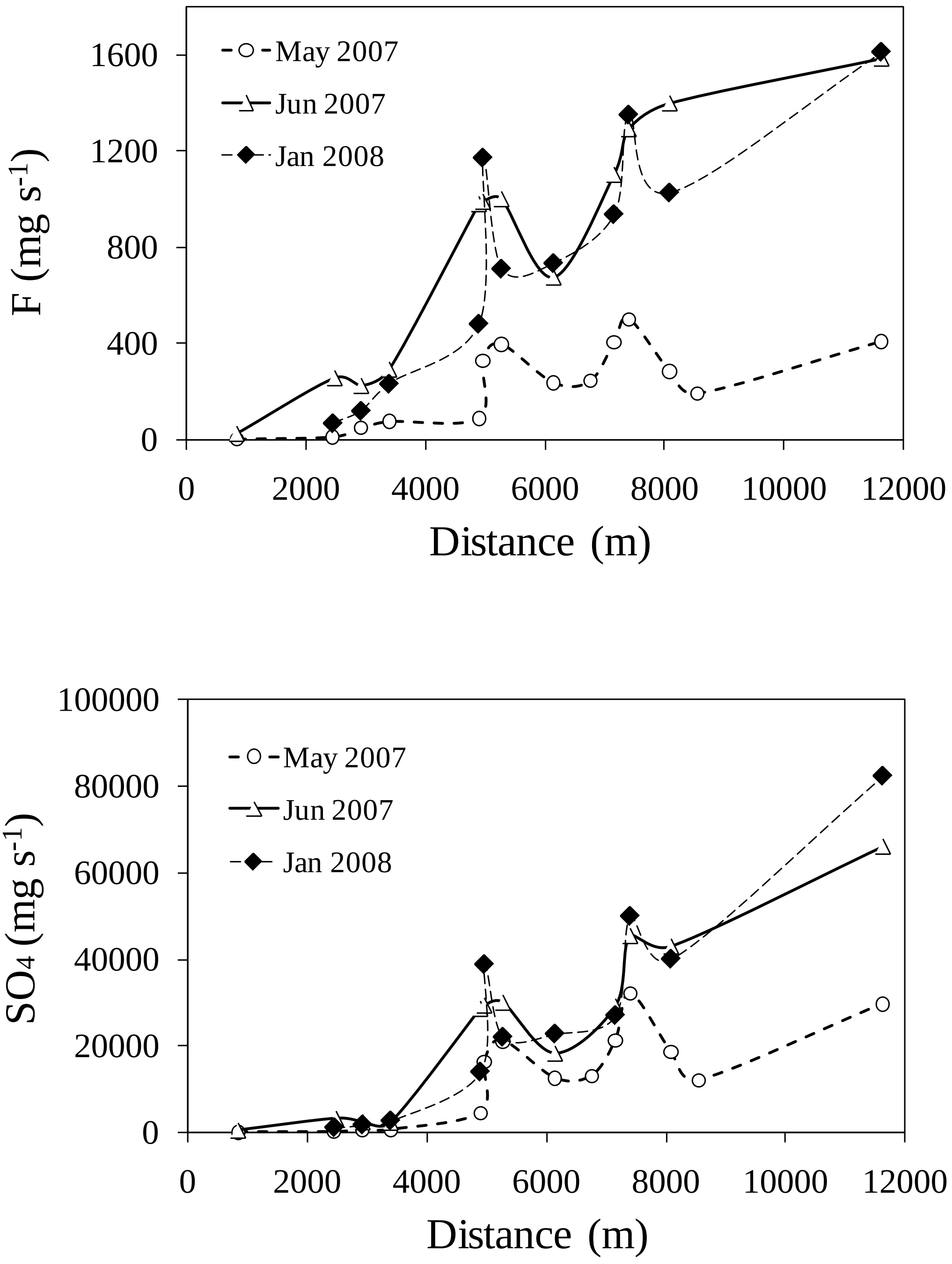
May 2007
Jun 2007
Jan 2008
F (mg s-1)
1600
1200
800
400
0
0
2000
4000
6000
8000
10000
12000
Distance (m)
May 2007
Jun 2007
Jan 2008
SO4 (mg s-1)
100000
80000
60000
40000
20000
0
0
2000
4000
6000
8000
10000
12000
Distance (m)

Figure 6

Table 1

Group	Formation	Member
Yoredale	Stainmore	Grindstone Sill
		Upper Felltop Limestone
		Sandstone
		Lower Felltop Limestone
		High Grit Sill
		Low Grit Sill
		Crag Limestone
		Firestone Sill
		Little Limestone
		Great Limestone
	Alston	Four Fathom Limestone
		Three Yard Limestone
		Five Yard Limestone
		Scar Limestone
		Tynebottom Limestone
		Jew Limestone

Table 2

Mine area/ name	**National Grid Reference**	**Date of operation, where known**	**Description/ References.**
Frazer's Hushes	388222 544469	Early	Hushes (water flushed workings) for iron-rich flats associated with the Lower Felltop Limestone.
Frazer's Hush and Greencleugh Mines/ Greencleugh Vein and Red Vein	388833 544438	Recent	Worked for fluorspar. Connected underground with Groverake Mine (Young in Scrutton, 1995). Greencleugh Vein joins Red Vein at 389978 544174, which crosses Boltsburn Vein at 393592 542820 and continues in a southeasterly trend.
Frazer's Grove Mine	389559 544153	Particularly active between 1880 and 1900, closing in 1903 and 1999.	Early working of iron ore flats associated with the Lower Felltop Limestone. Subsequent working for galena and fluorspar. (Carruthers and Strahan, 1923). Reopened and comprised four separate mines: Frazer's Hush, Rake Level/ Firestone Incline workings, Incline workings, Grove Rake and Greencleugh (Johnson and Younger, 2002; Younger 1999). Originally referred to as a Grove Rake Mine. Levels flooded.
Breckon Sike Level	389112 543608		Associated with West Groverake (Dunham, 1990). Open cast workings quarried for iron in the Upper and Lower Felltop limestones.
Wolf Cleugh New Vein	390849 542945		Greenwell's Level worked for lead, Hawk Sike for iron.
Wolf Cleugh Old Vein (Thorny Slitt Level)	390139 543272	Late 1700s, 1818-1846, 1901-1912	Worked for lead, primarily from the Little Limestone and White Hazle. Subsequently worked for fluorspar.
Rispey Vein, Shaft and Mill	391090 542800	1889 Smelt mill constructed	Exploited for lead and iron carbonate, the ore coming from both the Little and Great limestones (Dunham, 1990; Fairbairn, 1996). Weardale Lead Company built Rispey Mill (Dunham, 2002).
Scarsike Veins (Tailrace Water Level).	391631 542732		East and West Scarsike Veins were worked for lead. The Tailrace Water Level was driven from a level of 364 m OD in Scarsike Vein, then turns north west and continues as a crosscut via Rispey Engine and Wolfcleugh shafts to Groverake Whimsey Shaft (a total distance of 2.8 km). Dunham (1990) reported that it was understood to be partially blocked between Wolfcleugh and Groverake mines.
Straitlegs (Straightleggs) Vein and Level	392060 542880		Level driven south from the burn to the vein (not shown on the current 1: 50 000 scale geology sheet) (Dunham, 1990; Fairbairn, 1996).
Redburn Mine	392328 543621		North-eastern end of Rispey Vein. Barren ironstone trials adjacent (Fairbairn, 1996).
Lintzgarth Arch	392448 542979	Built in 1737	Remnant of the former Lintzgarth Mill, which was and incorporated a silver refining furnace (Fairbairn, 1996).
Fulwood Mine	392568 542537		Worked for the ironstone flats associated with the Great Limestone (Fairbairn, 1996).
Boltsburn Mine	393679 542802	Boltsburn West Level driven in the early 1800s.	Worked primarily for fluorspar, but early workings for lead. Vein crosses the Rookhope Burn.
Brandon Walls Vein	394652 541118	Dates at least to 1662 (Fairbairn, 1996)	Mined for lead ore and ironstone. Ironstone was worked in the Great Limestone on both sides of the valley at Brandon Walls Iron Mine (394777 541231) and Hanging Walls Mine.
Stotfield Burn Mine	394302 542377	1863 to 1887, 1914, 1950s.	Worked for lead and then fluorspar (Weardale Lead Company).
Captain's Cleugh Mine	395295 541063	Early iron. Lead 1850 to 1858.	The shaft (395295 541063) was worked for iron ore in the Great Limestone. Subsequent lead production noted by Dunham (1990) and Fairbairn (1996).

Table 3

Site	Description	Easting	Northing	Date	Sample Code	T	pH	Eh	Cond	Alk (HCO_3)	Ca	Mg	Na	K	Cl	SO_4	NO_3	F	Tot S	Si	Ba	Sr	Mn	Tot Fe	Fe(II)	Al	Zn	Pb	Average Discharge
						°C		mV	uS/cm	mg/l																			l/s
29	Adit u/s Grove Rake mine	389050	544411	27/6/07	WD229	8.5	6.59	260	127	94	21.5	6.91	8.10	1.77	52.4	9.15	0.03	0.22	3.50	3.54	0.033	0.072	3.10	6.04	6.00	0.013	0.051	<0.0	4.51
4	Brecken Sike	389631	543858	02/5/07	WD104	14.3	7.54	390	94	15	8.98	2.67	3.28	0.82	4.63	16.3	0.12	1.52	5.43	0.74	0.006	0.03	0.448	0.646	0.690	0.071	0.018	<0.01	0.60
				27/6/07	WD204	11.0	5.98	368	46	3	4.31	1.42	2.75	<0.5	3.05	8.08	<0.02	0.59	3.10	0.65	0.007	0.01	0.106	1.02	0.754	0.264	0.055	0.026	3.79
				28/1/08	WD304	4.5	5.35	551	51	59	3.44	1.19	2.61	0.65	3.47	7.47	0.28	0.44	3.09	1.13	0.008	0.01	0.075	0.497	0.458	0.145	0.039	0.010	5.45
27	Leachate waste heap on river bank	390216	543275	27/6/07	WD227	10.9	5.68	414	nd	10	4.53	1.16	2.78	0.584	3.31	4.63	0.231	1.70	1.92	0.875	0.006	0.008	0.030	0.728	0.522	0.450	0.094	0.127	nd
7	Wolfcleugh mine water outbreak	391059	542828	02/5/07	WD107	9.5	7.28	293	785	157	125	20.7	8.23	8.01	11.0	299	0.17	4.80	90.7	3.17	0.012	0.34	6.77	3.97	3.930	0.411	2.42	<0.01	35.00
				27/6/07	WD207	9.6	6.43	293	614	108	98.9	18.3	8.16	6.72	11.0	256	0.64	4.36	73.2	3.02	0.011	0.28	5.21	2.83	2.541	0.463	2.34	<0.01	125.75
				28/1/08	WD307	8.9	6.38	321	527	151	79.4	13.8	7.65	5.69	13.3	178	0.69	3.99	54.8	2.67	0.011	0.25	3.69	2.18	2.100	0.291	1.45	0.010	6.67
10	Tailrace Level	391631	542732	02/5/07	WD110	8.5	7.43	434	434	157	65.4	10.2	8.04	3.28	11.6	81.4	0.85	1.63	24.1	2.53	0.008	0.25	0.607	0.016	<0.1	0.021	0.291	<0.01	33.80
				27/6/07	WD210	8.7	6.77	376	241	82	37.1	6.06	7.10	1.80	8.72	22.5	1.64	1.29	7.20	2.07	0.008	0.15	0.166	0.153	0.150	0.083	0.067	0.069	61.32
				28/1/08	WD310	7.7	6.29	521	218	73	26.9	4.62	6.15	1.50	8.98	16.2	2.19	1.04	5.81	2.06	0.007	0.11	0.163	0.103	0.093	0.057	0.042	0.046	18.65
12	Rispey Sike	391668	542756	02/5/07	WD112	14.0	6.56	445	63	<5	4.41	1.21	3.79	1.07	5.92	6.74	0.25	1.66	2.63	1.36	0.006	0.01	0.099	0.274	0.268	0.230	0.026	<0.01	0.50
				27/6/07	WD212	10.9	5.51	437	nd	10	2.02	0.844	3.10	<0.5	3.27	4.29	0.11	0.38	1.80	0.80	0.007	0.01	0.217	0.848	0.671	0.321	0.023	0.042	78.32
				28/1/08	WD312	5.7	4.69	540	44	<5	1.91	0.898	3.40	0.70	5.17	4.85	0.38	0.27	2.02	1.35	0.007	0.01	0.211	0.507	0.500	0.237	0.021	0.025	8.09
15	Redburn	392669	543032	02/5/07	WD115	15.6	7.67	337	85	15	5.26	2.22	6.12	0.82	11.2	5.49	0.04	0.18	2.34	1.81	0.005	0.019	0.141	0.353	0.243	0.018	0.006	<0.01	7.50
18	Boltsburn Level	393607	542837	02/5/07	WD118	8.9	8.19	348	529	234	82.8	12.7	10.1	4.57	13.3	76.4	0.38	1.49	22.5	3.37	0.014	0.36	0.398	0.058	<0.1	<0.01	0.060	<0.01	8.70
				27/6/07	WD218	9.8	7.34	382	337	113	47.0	7.74	8.73	2.73	9.97	36.9	0.94	1.40	11.0	2.67	0.011	0.22	0.151	0.325	0.170	0.020	0.047	<0.01	13.73
				28/1/08	WD318	7.0	6.92	423	374	122	48.0	7.41	9.33	2.60	17.8	37.0	1.87	1.34	11.4	2.73	0.011	0.22	0.173	0.244	0.170	<0.25	0.041	0.01	14.20
20	Bolts Burn	393785	542828	02/5/07	WD120	11.5	8.13	406	91	28	8.55	2.23	5.13	0.69	7.91	5.00	0.05	0.18	2.06	1.88	0.007	0.03	0.062	0.123	0.121	0.016	<0.0	<0.01	0.86
				27/6/07	WD220	10.4	6.97	305	nd	5	3.15	1.20	4.34	<0.5	6.39	4.56	0.21	0.12	1.88	1.26	0.009	0.01	0.112	0.372	0.289	0.133	0.013	<0.01	221.99
				28/1/08	WD320	4.9	6.42	394	48	5	2.78	1.13	4.33	0.54	6.91	5.59	0.79	0.09	2.13	1.69	0.010	0.01	0.087	0.179	0.210	0.085	0.013	0.010	137.13
28	Discharge from waste heaps- Rookhope village	394067	542244	27/6/07	WD228	12.0	7.69	233	410	64	65.0	10.7	3.40	1.10	4.04	138	0.11	1.89	40.3	0.80	0.020	0.10	0.603	0.498	0.455	0.111	0.675	0.325	2.46
				28/1/08	WD328	2.9	7.27	282	448	122	64.0	10.0	3.31	1.38	5.51	138	0.14	1.88	43.3	1.12	0.016	0.09	0.422	0.299	0.370	0.055	0.922	0.132	2.58
26	Adit dischage d/s point 28	394058	542209	27/6/07	WD226	9.2	7.65	299	162	57	25.7	3.34	3.67	1.12	4.38	16.7	1.67	0.09	3.91	1.11	0.015	0.105	0.021	0.285	0.215	0.106	<0.0	<0.01	12.37
				28/1/08	WD326	6.7	7.38	460	158	127	20.9	2.79	3.67	1.28	7.87	9.50	3.13	0.08	3.35	1.41	0.012	0.092	0.016	0.086	0.060	0.040	<0.0	0.010	14.66

nd= not detected

Table 4

Site	Description	Easting	Northing	Date	Sample Code	T	pH	Eh	Cond	Alk (HCO_3)	Ca	Mg	Na	K	Cl	SO_4	NO_3	F	Total S	Si	Ba	Sr	Mn	Tot Fe	Fe(II)	Al	Zn	Pb	Average Discharge
						°C		mV	uS/cm	mg/l																			l/s
1	Rookhope Burn - headwaters	388362	544696	02/5/07	WD101	15	7.90	294	194	94	27.7	4.90	6.53	2.80	14.29	10.66	0.06	0.41	3.83	2.40	0.053	0.106	0.469	0.629	0.613	0.050	0.015	<0.01	7
				27/6/07	WD201	11	6.37	348	48	9	5.32	1.38	3.93	0.57	5.36	4.78	0.03	0.20	2.09	0.832	0.019	0.017	0.199	1.67	1.37	0.246	0.035	<0.01	134
3	Rookhope Burn - d/s Grove Rake adit	389645	543961	02/5/07	WD103	18	7.95	413	179	60	22.2	4.37	6.56	2.35	12.77	12.29	0.02	1.10	4.72	0.666	0.023	0.078	0.305	0.613	0.542	0.040	0.037	<0.01	11
				27/6/07	WD203	13	7.03	299	64	8	6.38	1.65	4.07	0.81	5.06	7.47	0.11	0.57	2.88	0.836	0.014	0.020	0.184	0.992	0.742	0.268	0.068	0.024	450
				28/1/08	WD 303	5	6.21	503	76	34	5.88	1.55	4.42	0.90	7.20	6.97	0.37	0.41	2.96	1.14	0.012	0.021	0.151	0.426	0.426	0.142	0.060	0.01	166
5	Rookhope Burn (intermediate location)	389900	543562	02/5/07	WD105	20	7.69	441	177	52	19.7	4.35	7.45	2.21	13.03	16.25	0.06	1.61	6.05	0.491	0.018	0.067	0.153	0.403	0.332	0.073	0.059	<0.01	30
				27/6/07	WD205	13	6.81	328	61	12	6.89	1.79	4.14	0.82	5.21	8.89	0.08	0.78	3.28	0.840	0.013	0.019	0.158	0.916	0.681	0.272	0.087	0.023	289
				28/1/08	WD305	6	6.41	505	88	44	7.26	1.87	4.87	1.02	8.51	9.97	0.51	0.67	3.77	1.27	0.013	0.022	0.141	0.488	0.488	0.155	0.083	0.01	179
6	Rookhope Burn at footbridge Wolf Cleugh	390241	543261	02/5/07	WD106	19	7.89	381	166	45	17.9	3.85	6.68	1.87	12.43	15.20	<0.0	1.81	5.36	0.442	0.016	0.056	0.174	0.443	0.373	0.071	0.044	<0.01	42
				27/6/07	WD206	13	6.92	295	67	9	6.83	1.76	4.38	0.79	5.08	8.23	0.07	0.98	3.20	0.847	0.013	0.018	0.156	0.904	0.686	0.284	0.095	0.026	299
				28/1/08	WD306	6	6.44	498	83	88	6.42	1.68	4.42	0.92	8.13	9.24	0.53	0.79	3.37	1.20	0.011	0.020	0.123	0.453	0.453	0.164	0.074	0.011	294
9	Rookhope Burn- upstream Tailrace level	391591	542785	02/5/07	WD109	17	8.02	294	551	109	84.4	14.8	7.94	5.78	11.04	174.45	0.13	3.40	57.1	2.05	0.015	0.240	3.44	0.066	0.118	0.038	1.02	<0.01	26
				27/6/07	WD209	11	7.23	276	127	32	22.0	4.74	5.06	1.79	5.89	47.40	0.30	1.62	14.3	1.20	0.013	0.064	0.877	0.869	0.690	0.269	0.435	0.026	606
				28/1/08	WD309	7	6.63	450	225	83	25.7	5.19	5.73	2.35	7.05	36.85	0.61	1.27	16.3	1.68	0.011	0.081	0.975	0.578	0.544	0.163	0.419	0.01	26
11	Rookhope Burn- d/s Tailrace level	391668	542756	02/5/07	WD111	17	8.03	385	547	107	81.1	14.4	7.62	5.55	11.27	174.90	0.14	3.48	55.7	2.00	0.015	0.236	3.28	0.070	0.085	0.041	0.922	<0.01	94
				27/6/07	WD211	11	7.29	270	177	28	22.5	4.79	4.95	1.79	5.89	47.48	0.23	1.60	14.4	1.22	0.013	0.063	0.855	0.855	0.506	0.263	0.430	0.026	621
				28/1/08	WD311	7	6.64	432	220	93	25.5	5.16	5.69	2.32	9.57	50.65	1.01	1.53	16.3	1.66	0.011	0.080	0.951	0.531	0.530	0.157	0.410	0.01	767
13	Rookhope Burn	391946	542876	02/5/07	WD113	17	8.23	427	521	108	74.5	13.7	7.93	5.18	11.17	160.40	0.20	3.00	51.5	2.05	0.015	0.230	2.66	0.034	<0.050	0.039	0.718	<0.01	132
				27/6/07	WD213	11	7.37	287	149	25	20.9	4.42	5.05	1.68	6.00	42.06	0.21	1.40	12.8	1.20	0.012	0.060	0.741	0.810	0.712	0.246	0.370	0.028	716
				28/1/08	WD313	5	6.87	316	191	54	20.6	4.15	5.31	1.87	9.42	39.48	0.86	1.27	12.5	1.50	0.011	0.064	0.699	0.441	0.440	0.149	0.307	0.01	558
16	Rookhope Burn	392799	542973	02/5/07	WD116	16	8.34	440	455	104	64.0	11.2	7.25	3.91	11.39	129.19	0.15	2.44	38.3	1.96	0.016	0.203	1.71	0.045	<0.050	0.032	0.416	<0.01	97
				27/6/07	WD216	11	7.46	292	140	18	16.0	3.52	5.29	1.30	6.90	29.86	0.19	1.10	9.32	1.21	0.011	0.051	0.481	0.716	0.575	0.205	0.232	0.020	616
				28/1/08	WD316	7	7.12	458	168	93	17.8	3.71	5.97	1.69	10.12	31.31	0.87	1.01	10.4	1.63	0.010	0.061	0.521	0.364	0.360	0.114	0.214	0.01	728
19	Rookhope Burn d/s Boltsburn Level	393756	542833	02/5/07	WD119	11	8.40	402	447	111	66.3	11.7	8.15	4.18	10.01	108.44	0.13	2.05	37.8	2.12	0.015	0.225	1.30	0.032	<0.050	0.018	0.362	<0.01	197
				27/6/07	WD219	11	7.60	313	150	24	18.0	3.72	5.44	1.41	6.81	30.33	0.28	1.14	9.38	1.27	0.011	0.058	0.395	0.715	0.574	0.192	0.217	0.018	965
				28/1/08	WD319	5	7.22	405	173	59	17.7	3.46	5.70	1.60	10.38	29.71	0.91	1.03	9.40	1.53	0.010	0.060	0.402	0.340	0.340	0.109	0.180	0.01	911
21	Rookhope Burn d/s Bolts Burn	393862	542610	02/5/07	WD121	11	8.21	351	476	136	69.9	12.6	9.52	4.18	10.93	117.45	0.31	1.83	36.1	2.39	0.015	0.278	0.924	0.035	<0.050	0.012	0.245	<0.01	274
				27/6/07	WD221	11	7.59	316	163	29	19.3	4.13	5.50	1.37	6.85	33.43	0.47	0.95	10.1	1.34	0.011	0.076	0.322	0.612	0.526	0.168	0.170	0.020	1361
				28/1/08	WD321	5	7.21	352	179	29	18.5	3.86	5.58	1.31	9.54	31.40	1.10	0.85	9.97	1.58	0.010	0.075	0.304	0.298	0.300	0.098	0.139	0.01	1591
23	Rookhope Burn d/s spoil heaps	394203	542016	02/5/07	WD123	9	8.25	358	453	133	67.9	11.9	9.36	3.84	10.98	110.63	0.17	1.69	33.9	2.19	0.015	0.262	0.810	0.047	<0.050	0.010	0.229	<0.01	168
				27/6/07	WD223	10	7.66	324	82	29	18.0	3.81	5.70	1.23	6.89	29.26	0.43	0.95	9.08	1.29	0.011	0.069	0.283	0.666	0.511	0.167	0.159	0.020	1472
				28/1/08	WD323	7	7.24	550	194	141	21.6	4.38	6.01	1.67	9.83	35.56	1.11	0.91	11.5	1.73	0.011	0.087	0.307	0.268	0.270	0.082	0.145	0.01	1127
25	Rookhope Burn at Eastgate	395248	538715	02/5/07	WD125	9	8.22	354	480	148	71.1	11.8	10.6	3.75	15.14	107.62	1.44	1.48	32.8	1.33	0.016	0.308	0.186	0.046	<0.050	<0.01	0.088	<0.01	276
				27/6/07	WD225	10	7.99	288	191	42	25.3	4.23	6.04	1.36	8.10	31.49	1.50	0.75	9.62	1.31	0.012	0.106	0.136	0.559	0.484	0.125	0.106	0.018	2099
				28/1/08	WD325	5	7.39	376	221	49	24.9	4.14	6.18	1.43	11.49	35.75	2.55	0.70	10.9	1.52	0.011	0.110	0.142	0.216	0.200	0.063	0.086	0.01	2304

Table 5

Sample Location	**Rookhope Burn Point 9**	**+10 m**	**+20 m**	**+30 m**	**+42 m**	**+52 m**	**+62 m**	**Tailrace Level Point 10**	**+2 m d/s Tailrace Level**	**+10 m**	**Rookhope Burn Point 11**
Discharge (l/sec)	47.6	159.4	82.8	128.1	118.6	102.8	116.8	7.8	198.8	107.9	76.8
pH	7.47 7.50 7.51	7.47 7.50 7.51	7.6 7.59 7.59	7.52 7.58 7.59	7.64 7.62 7.61	7.67 7.63 7.65 7.66* 7.65 7.63	7.66 7.65 7.63 7.65* 7.65 7.64	6.59	7.64 7.64 7.25	7.66 7.66 7.66 7.54* 7.53 7.52	7.60 7.61 7.60
Temperature (ºC)	13.0 12.9 13.0	13.9 13.9 13.9	13.9 13.8 13.9	13.6 13.6 13.8	13.6 13.4 13.6	13.4 13.4 13.4 13.5* 13.5 13.5	13.4 13.3 13.4 13.4* 13.4 13.4	8.8	13.3 13.3 10.2	13.3 13.2 13.3 13.3* 12.9 12.9	13.2 13.1 13.0
Conductivity (µS/cm)	102 437 438	441 440 442	439 442 442	0 438 443	12 430 440	440 nd 440 440* 440 395	440 440 440 440* 436 440	383	437 438 398	405 437 437 436 430 431	431 434 433
Total Dissolved Solids	51 218 219	220 220 221	220 221 221	0 219 221	5 215 220	220 0 220 220* 220 198	220 220 220 220* 218 220	191	219 219 199	203 218 219 218* 214 215	215 317 217
Dissolved Oxygen (ppm)	9.4 9.29 9.30	9.40 9.29 9.30	8.80 9.39 9.31	9.83 9.40 9.21	8.18 9.31 8.99	9.06 9.35 9.18 9.22* 9.33 9.15	9.41 9.12 9.28 9.14* 9.49 9.39	8.50	9.48 9.65 10.18	9.11 9.59 9.20 8.00* 9.55 9.66	9.29 9.20 9.40

*Stream bifurcates

Table 6

Stream stretch	**Net change in zinc load May 2007 (mg/s)**	**Net change in zinc load June 2007 (mg/s)**	**Net change in zinc load Jan 2008 (mg/s)**
1-3	0.3	26	n/a
3-5	1.4	-6	5
5-6	0.1	3	7
6-9	25	235	137
9-11	60	3	155
11-13	8	-2	-142
13-16	-54	-122	-16
16-19	30	66	8
19-21	-4	22	57
21-23	-29	2	-58
23-25	-14	-10	36

Table 7

	May 07	**June 07**	**Jan 08**
Min cumulative Zn loading (mg/s)	128	358	278
Min cumulative Zn attenuation (mg/s)	-104	-140	-79
Min cumulative inflow Zn loading (mg/s)	95	306	16
Min cumulative inflow Zn loading (% cumul. load.)	75	85	5.6
Wolfcleugh mine water outbreak (% cumul. load.)	66	82	3.5