Insights Into Catchment Connectivity Using Water Stable Isotopes To Address Diffuse Mine Pollution In Streams

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Abstract

We used natural water isotope tracers (δ18O, δ2H) in synoptic sampling of boreholes, mine adits and stream water to gain insights into diffuse contaminated groundwater and mine water flow pathways in the Force Crag Mine catchment, Cumbria, UK. Rapid delivery of new water (rain) into both the mine workings and shallow groundwater was seen in the isotope signature. The high degree of spatial and temporal variability of isotope concentrations in the shallow groundwater is evidence of a complex flow system, typical of upland catchments.

Keywords: Isotopes, tracers, groundwater, metal mine, diffuse pollution

Introduction

The role of diffuse groundwater pollution in mine catchments is not well studied. This is in part due to the challenges of monitoring groundwater in mine catchments, often in remote and upland sites with difficult access and the lack of easy means of detecting diffuse subsurface flow paths. Heterogeneity is a key feature of upland catchments and influences catchment water flows, but is difficult to characterise and is often simplified or overlooked. Made ground, inherent of legacy mine sites and altered hydrogeology of the mine workings add to the above complexity. Many metal mine sites are designated as protected areas, because of their natural and cultural importance; hence, undertaking intrusive investigations can present further logistic challenges.

Prediction of the impacts of diffuse groundwater pollution requires an understanding of the pathways through which water moves from a contaminant source to a receptor such as a stream. At the abandoned Force Crag Mine, NW England, monitoring infrastructure has been installed to undertake a study of these diffuse sources, and investigate the hydrological connections between the hillslopes and riparian zones to the stream. The DIFFUSE project applied a combined monitoring approach including stream-centred synoptic sampling and hillslope/riparian-centred geophysical surveys, ground investigation comprising piezometer installation and core sampling and tracer tests. The study confirmed very high zinc concentrations in the shallow groundwaters. Here we present the results of the isotopic investigation conducted to help characterising pathways contributing zinc to the stream. Since water δ18O and δ2H act conservatively as precipitation travels through the subsurface to the stream, water isotopes can be useful tracers in providing insights into hydrological processes. The results also provide initial evidence on the spatial and temporal variability of water isotopes in the upland Coledale catchment, which was previously unknown.

Study site and Methods

Force Crag Mine is situated at the head of Coledale Valley, Cumbria (54.58°N, 3.24°W). Historic mining activities exploited mineral veins hosted in the low-grade metamorphosed siltstone and mudstone bedrock of the Skiddaw Group. Lead was mined from 1839, before zinc and barite associated minerals in the late 1860's, until final abandonment in 1991 (Oswald and Pearson, 1999). The Coledale Valley delineates the upland stream catchment of the Coledale Beck, which flows approximately southwest-northeast into Newlands Beck, a tributary of Bassenthwaite. Superficial deposits of glacial till cover the valley floor, along with a complex heterogenous cover of alluvial deposits comprising clay, gravel and peat, overlain and interbedded with centuries of various grades of mine waste deposits, contributing diffuse pollution.

The site was instrumented with 16 piezometers to intercept shallow groundwater in the riparian zone, hillslope zone and mine waste in three areas A, B and C (Figure 1) to investigate possible connectivity between metal-polluted groundwater and the Beck.

The screened depths of the piezometers were chosen to span above and below the first water strike during drilling. The shallowest piezometer was screened at a depth of 0.2 to 0.6 metre below ground level (mbgl), whilst the deepest was screened at 3.5 to 5.5 mbgl, with most spanning depths of 0.4 to 1.5 mbgl. The most upslope piezometer BH1 has the deepest water level, installed in glacial till. BH2 installed within spoil is dry. Very shallow groundwater levels are encountered at BH7, BH3 and BH6 throughout the year.

We combined synoptic sampling of the surface water, groundwater and mine water inflows, in six sampling rounds, to investigate potential contaminated groundwater and mine water contributions to the Coledale Beck, and how these contributions vary at high and low flow. The sampling locations for the mine water discharges and surface waters, with the hydrochemical data, are reported in a parallel paper in these conference proceedings (Jarvis *et al.* 2023).

Rainfall and stream flow data were obtained from the Coal Authority (Force Crag, GPRS2 Rain Gauge (NC33.22); Force Crag, FC03 Coledale Beck D/S MWTS (NC33.25)- NetDL500). The rainfall amounts in the antecedent 2, 10 days (P2, P10 in mm) to each sampling event and the background streamflow (Q in L/s), a measure of the catchment moisture status, varied as follows: Apr-21 P2: 0, P10: 0, Q: 31; May-21 P2: 0, P10: 81, Q: 163; Jun-21 P2: 0, P10: 33, Q: 36; Aug-21 P2: 0, P10: 1.4, Q: 48; Nov-21- P2: 46, P10: 357, Q: 169; Feb-22 P2: 14, P10: 70, Q: 250.

Groundwater samples were obtained following a low-flow sampling method. To obtain representative samples and maintain constant head, pumping rates of <0.5 L/min were used for at least 15 minutes (to purge 3 well volumes), and until stable field

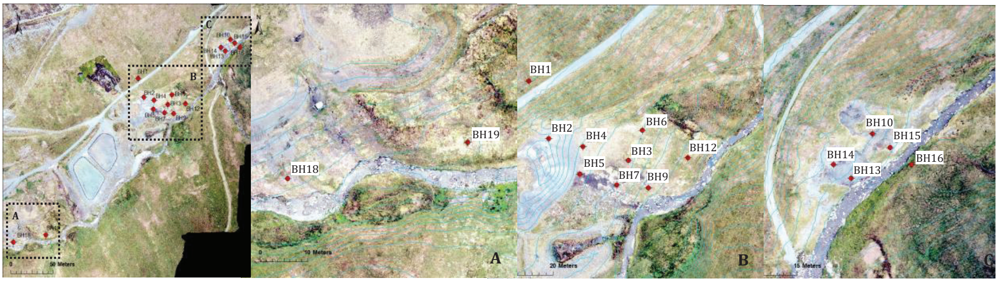

Figure 1 Location of the piezometers at Force Crag mine. ***Area A****, downstream of the confluence with the Pudding Beck, upstream of the mine buildings and treatment scheme, comprises of mainly peaty ground which remains wet underfoot even in the driest seasons.* ***Area B****, downstream of the treatment scheme around the 'Tip 3' area, is the most heterogeneous spanning the hillslope zone and riparian zone; ground cover comprises glacial till, mine waste, gravel and peat.* ***Area C****, downstream of the Birkthwaite Beck confluence around the 'Mill 2' area, is mainly covered by coarse mine waste deposits, except for BH16 situated on the southern bank on peaty ground. Aerial photo courtesy of UKCEH (2021).*

parameters were reached in the flow-through cell (pH, temp, oxidation-reduction potential, dissolved oxygen, electrical conductivity). Very low yield in some piezometers precluded pumping, instead samples were collected using 50 ml bailers (except for BH04 where a 1 L bailer was used) and the field parameters measured from a beaker containing the purged water.

The water δ^{18}O and δ^{2}H analyses were carried out in the Stable Isotope Facility, BGS, Keyworth. Isotopic ratios (^{18}O/^{16}O and ^{2}H/^{1}H) are expressed in delta units, δ^{18}O and δ^{2}H in ‰ and defined in relation to the standard Vienna Standard Mean Ocean Water 2 (VSMOW2). The analytical precision for the analyses is typically <0.05‰ for δ^{18}O and ±1.0‰ for δ^{2}H.

Results and Discussion

Water isotope composition for surface water, mine water and groundwater, plotted on a dual δ^{18}O and δ^{2}H plot, broadly falls close to the Global Meteoric Water Line (GMWL), with possible near-surface evaporative effects for some boreholes plotting below the GMWL (Figure 2).

Figure 3 shows the spatially and temporally variable δ18O values of Coledale Beck surface water, the mine water discharges and the boreholes, ordered downstream from the mine, during the synoptic sampling events. Some important points are highlighted below: i) The very small spatial δ18O variations in the Coledale Beck from upstream to downstream of Force Crag Mine in each sampling round, with standard deviation (SD) between ±0.04‰ and ±0.1‰ for δ18O, close to the analytical precision. ii) The lack of a contrasting isotopic signature between the stream and the mine water inflows. As such, the water isotope tracer approach is of limited use for identifying the relative contributions of mine water loads to the Coledale Beck in each sampling round. iii) The greater spatial variability of the shallow groundwater isotope concentrations (SD between ±0.3‰ and ±0.6‰ for δ18O) compared to the stream waters, which can be explained by the short flow paths and limited mixing, characteristic of headwater catchments. iv) From the comparison of the six synoptic sampling events, it is noticed that in Nov-21, the wettest sampling event (see P2, P10 values in Methods), the spatial variability of the isotopic composition across the catchment was the lowest (SD ± 0.22‰), which may suggest a greater connectivity of the catchment during large precipitation events, as the various components of runoff tend to converge toward the precipitation signature. This needs to be further explored with longer term monitoring including precipitation samples, but similar catchment rainfall-runoff responses are not unusual (Kendall and Caldwell, 1988).

There is considerably more temporal isotopic variation (with SD ± 0.3‰ to ±0.5‰ for δ^{18}O and SD ± 2.4‰ to 4.7‰ for δ^{2}H) than spatial variation in the Coledale Beck, as it reflects the contribution of precipitation to streamflow, with fluctuations in the isotope ratios associated with seasonal and event-based factors including provenance, temperature of the air mass and amount of precipitation. The seasonal pattern of precipitation isotope values, with tendency of higher δ^{18}O and δ^{2}H /^{18}O- and ^{2}H-enriched

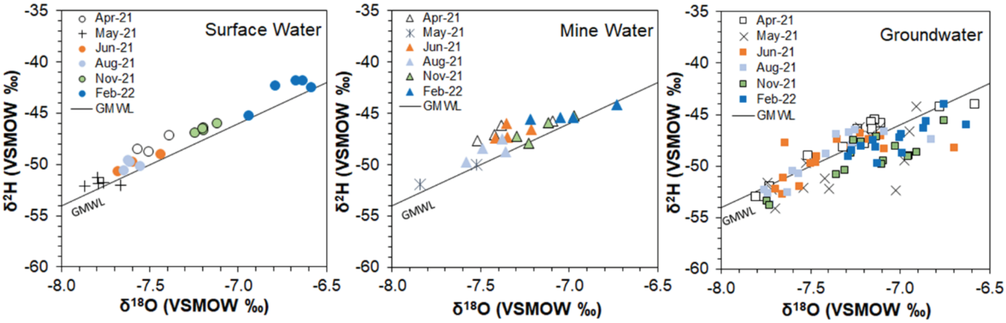

Figure 2 *δ^{2}H versus δ^{18}O values in surface water, mine water and groundwater in Force Crag mine catchment in the six sampling events from April 2021 to February 2022 against the Global Meteoric Water Line (GMWL)..*

values in summer/warmer months and lower $\delta^{18}O$ and $\delta^{2}H$ /^{18}O- and ^{2}H-depleted values in winter/colder months, is, however, not so obvious in our dataset (Figure 2). Nevertheless, day to day variability of rainfall isotope values can be large (Scheliga *et al.* 2018) and can account for the range and differences observed in our low-resolution monitoring. This is the case in the Feb-22 sampling, with the highest $\delta^{18}O$, $\delta^{2}H$ values in Coledale Beck, unexpectedly for a winter precipitation, but confirmed by the ^{18}O- and ^{2}H-enriched values ($\delta^{18}O$ -2.76‰; $\delta^{2}H$ -18.5‰) of the synchronous rain sample collected. Potentially, a similar rainfall composition accounts for the Nov-21 $\delta^{18}O$ in Coledale Beck, relatively higher compared to the April to August samples, although we do not have rain isotope analysis to support that.

The ^{18}O-enriched isotopic signal of the Nov-21 and Feb-22 heavy rainfall events (referred as "new water") was sought in the mine water and groundwater samples as evidence of rapid recharge. Figure 4 illustrates the isotope measurements across the sampling events compared with the Coledale Beck. Low isotopic variability implies an isotopically well-mixed system, where the seasonal isotopic signature of precipitation has been lost due to dispersive mixing/amalgamation of recharge water signatures. This is generally typical of aquifers where intergranular permeability predominates (Darling *et al.* 2003); a pronounced level of isotope damping is also observed in upland catchments, due to high water storage in the organic layers encouraging tracer mixing. On the contrary, larger fluctuations in the isotopic signal indicate a higher fraction of new water entering the system and can be due to preferential flow/shorter residence times/low storage. The analysis of Figure 4 indicates various isotopic responses which took place during the Nov-21 and Feb-22 wet events. Both mine water discharges from Level 1 (sample point FC30) and Level 0 (FC6) show contributions of recent precipitation in the isotopic signature of the Nov-21 samples, to suggest that the mine workings can be quickly recharged by meteoric waters draining through the overlying soils and upslope areas, consistent with Dumpleton

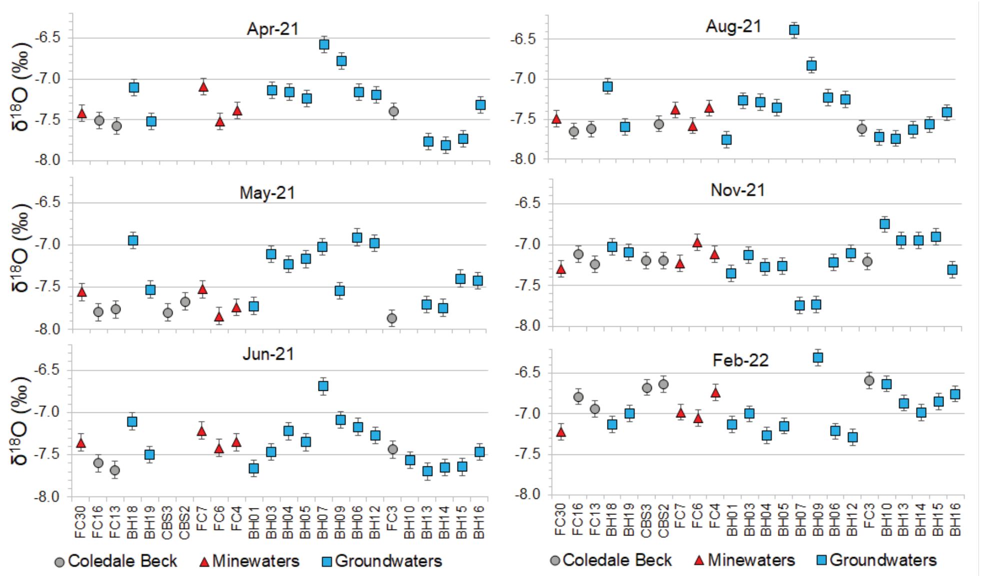

Figure 3 *δ^{18}O variation across monitoring points (from upstream to downstream the mine) by sampling event. Outside Y-axis range: May-21 BH10 δ18O -8.9‰; Feb-22 BH7 -5‰. Error bar ±0.1‰. Stream water: FC16: u/s mine; FC13: u/s Level 1 overflow A; CBS3: u/s channel C; CBS2: d/s FC8; FC3: d/s mine); mine water (FC30: Level 1; FC7: treatment plant outlet; FC6: Level 0; FC4: Level 0 + Drain B); boreholes from Figure 1.*

et al.'s (1996) hydrogeological assessment of the mine workings. However, there are differences in $\delta^{18}O$, highlighted in Figure 4, between Level 0 and Level 1 in each event. Differences are minimal in the dry sampling events in Apr-21, Jun-21 and Aug-21 and larger in May-21, Nov-21 and Feb-21, corresponding to sampling events with high amount of rainfall in the 10 days prior to sampling. Given the proximity of Level 0 and Level 1, it is likely that the isotopic signature of the rainfall contributing to both discharges (although not confirmed) is the same for any given sampling event; the observed differences may then reflect differences in the recharge (the proportion and travel time of rainfall reaching the mine workings). The water δ18O values of the mine water treatment system, sampled at the outlet (FC7), and of FC4 sampling point, which collects a mixture of culverted Level 0 discharge and crownhole overflow discharge, reflect more the largest variation with a positive δ18O peak of the Feb-22 event; this is instead dampened in Level 1 (FC30) and absent in Level 0 (FC6) samples.

At BH01 on the hillslope near Level 0, $\delta^{18}O$ values show that the monitored borehole is also very responsive to the last two rainfall events, consistent with a recharge area interpreted above.

In the riparian area downslope of Tip 3 (Figure 1, B), very responsive boreholes were identified in BH07 and BH09 (Figure 4), suggesting an active downward recharge and with large $\delta^{18}O$ variation also possibly indicating low storage. BH03, BH05, BH06 and BH12, instead, showed a much more damped response to rainfall events. The water level changes in these latter boreholes, while the isotope values remain relatively stable, suggesting the influx of water other than the new water. In the same area the invariable isotopic concentrations of BH04, a deeper low-yield (screened at 0.5 to 2.5 mbgl) piezometer, drilled at the toe of Tip 3, to intercept any potential mine water plume, are indicative of a lack of direct connection to the surface zone and consistent with a zone of low hydraulic conductivity below Tip 3.

Upstream Tip 3 area, in the riparian area in Figure 1, A, two contrasting isotope temporal variations were observed between BH18 and BH19. Given the borehole proximity, this result highlights the strong influence of local heterogeneity; in particular

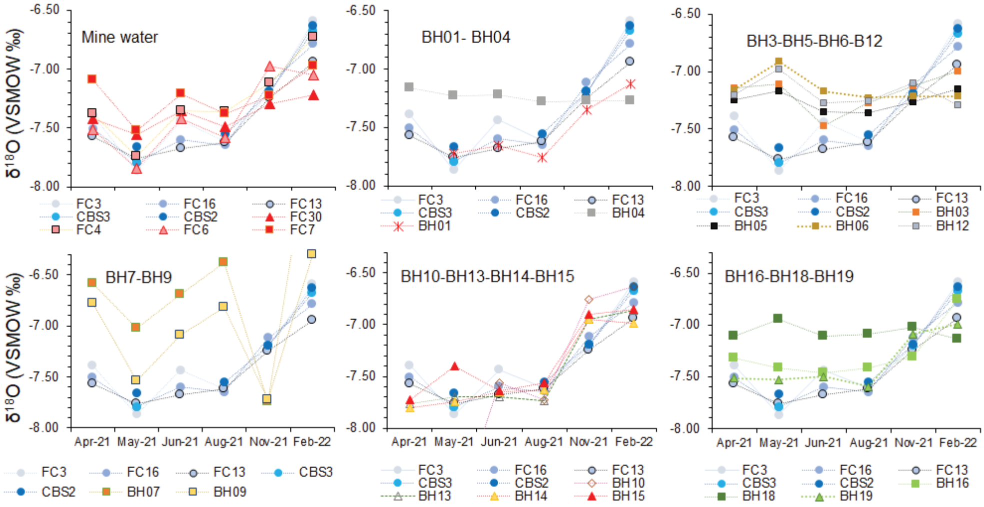

Figure 4 Temporal variation of $\delta^{18}O$ in the mine waters (FC30: Level 1; FC7: mine water treatment plant; FC6: Level 0; FC4: Level 0+Subsurface Drain B) and all boreholes compared against Coledale Beck (FC16 Coledale Beck u/s the mine; FC13 u/s Level 1 overflow A; CBS2 and CBS3 Coledale Beck receiving point source mine waters; FC3 Coledale Beck d/s the mine). δ18O outside Y-axis: BH7 -5‰ (Feb-22), BH10 -8.9‰ (May-21).

the upstream BH18 isotope signature shows no signs of new water, while BH19 changes in Nov-21 (with the highest P2), and mimics the Coledale Beck signature in the other sampling rounds.

Another group of boreholes closely mimic the Coledale Beck δ^{18}O values and patterns. This group includes the riparian BH16 (on the southern river bank opposite to the mine) and all the riparian boreholes at Mill 2 (BH10, BH13, BH14, BH15), although some differences are noted for BH16. This is interpreted as evidence of a common recharge source for these boreholes and the Beck.

High-frequency hydrometric data and low-resolution isotope measurements can complement each other to better understand the hydrologic connections and the areas that contribute to streamflow. Some clues concerning the connectivity between riparian groundwater and the Beck can be found in the hydrographs obtained for some of the boreholes. Figure 5 gives an example of high connectivity between the shallow groundwater and the stream, with the rapid response to rainfall observed in the groundwater heads of BH19, within 3 hours of rainfall events in the wet season and rapid drainage. Both peaks and recession curves of groundwater head and streamflow are coincident with each other, although heads typically rise 3-5 hours before there is a streamflow response in Coledale Beck, and rainfall events of <10mm/day can cause head responses, but do not contribute to streamflow in Coledale Beck.

Conclusions

This study, an assessment of the water isotope signature and spatial and temporal variability in groundwater, collected during synoptic sampling with surface water and mine water, in a UK abandoned mine catchment, has evidenced the high degree of variability of isotope concentrations in the shallow groundwater from various parts of the catchment and the variable relation to stream flow at the time of sampling. This highlights the complexity of various residence times, subsurface storage and mixing processes, as well as the critical dependence on catchment wetness and precipitation intensity. Based on the limited monitoring period and preliminary integration of the isotope data with hydrometric data, we infer connectivity of the groundwater to the stream, and hence a contribution of Zn-contaminated groundwater to the stream, but we expect the groundwater contribution to stream flow to be highly variable in time and space. Given concerns about climate change projections of wetter and warmer winter conditions likely to generate more extreme

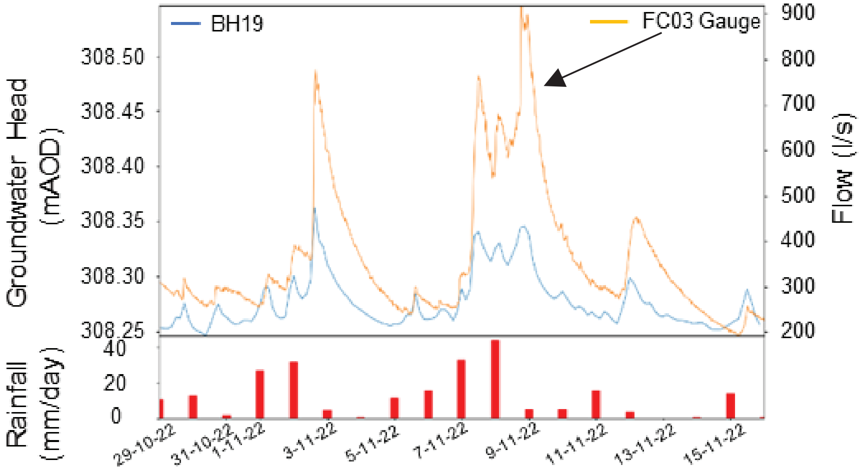

Figure 5 *Groundwater heads in metres above ordnance datum (mAOD) in borehole BH19 (blue lines) compared with rainfall (red bars) and streamflow (orange lines) between 29/10/22 to 15/11/22.*

flood events, long-term catchment scale monitoring of this type is recommended to provide baseline data to contextualise these extreme events and predict impacts.

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