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Combining ground stability investigation with exploratory drilling for mine water geothermal energy development; lessons from exploration and monitoring

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Abstract: Mine water geothermal energy's potential for decarbonization of heating and cooling in the UK has led to increased national interest and development of new projects. In this study, mine water geothermal exploration has been coupled with ground investigation techniques to assess ground stability alongside seasonal mine water hydrogeology and geochemistry. Drilling operations in late 2020 at Dollar Colliery, Clackmannanshire, Scotland, encountered mined coal seams with varying conditions (void, intact, waste, etc.), reflecting different techniques used throughout a protracted mining history. We found that time and resources spent grouting casing through worked mine seams (ensuring hydraulic separation) can be saved by accessing deeper seams where those above are unworked. Continued assessment of existing water discharges and completion of boreholes with slotted liners into mined coal seams and fractured roof strata allowed chemical and water level changes to be monitored across a 1 year period. Mine water heads and mine discharge flow rates vary seasonally and are elevated between late autumn and early spring. The mine water has a low dissolved solute content. Dissolved sulfate-^{34}S isotope data suggest increased pyrite oxidation during lower water levels. These findings can inform future building decisions, whereby housing developments on site could use the mine water for heating.

Supplementary material: Borehole data and completion diagrams are available at https://doi.org/10.6084/m9.figshare.22188801

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Ahead of a potential new-build housing development on the outskirts of Dollar, Clackmannanshire, Scotland, project stakeholders were required to conduct a ground stability investigation (GSI) drilling programme as the study area is a 'Development High Risk Area' (The Coal Authority 2022). Such activities explore the state and depth of the coal seams and workings associated with the abandoned Dollar Colliery beneath the development site. The developer wishes the new-build project to approach operational carbon neutrality and thus instigated exploration of the potential for mine water contained in these partially flooded coal workings to provide low-carbon heating to the houses, via the use of heat pumps.

A previous, confidential TownRock Energy pre-feasibility study, dated March 2018, had identified that mine water geothermal energy extraction could be feasible for heating 25–35 new-build houses in this location, owing to the presence of overlapping, flooded coal seams (TownRock Energy 2018). Since then, the 25–35 houses have been included in a larger application for up to 200 houses, which extends south beyond the area underlain by coal mines (Clackmannanshire Council 2022) where the total heat demand is uncertain. Mine water geothermal investigation (MWGI) often involves significant upfront capital expenditure, but inclusion as part of necessary GSI work may present a means to reduce capital expenditure whilst screening sites for potential. Thus, because GSI was necessary for the planned housing development to proceed, it was postulated that the investigation could be adapted to include geothermal appraisal. This research programme was funded by the Energy Technology Partnership (ETP) and the Engineering and Physical Sciences Research Council (EPSRC) with the aim of exploring the subsurface and assessing the depth, stability and condition of the coal seams and workings below the site (GSI), simultaneously assessing the mine water characteristics and their geothermal potential.

Mine water geothermal energy

Mine water geothermal energy is a low-carbon heating and/or cooling resource which uses abandoned and flooded mine workings coupled with ground source heat pump technology (Jessop *et al.* 1995; Banks *et al.* 2004; Ramos *et al.* 2015; Younger 2016). This resource has been implemented since the 1980s (Jensen 1983; Wieber and Pohl 2008; Michel

2009; Korb 2012), but has seen an increase in interest and uptake over recent years (Walls *et al.* 2021). In the UK, projects are being established at locations where there are existing thermal resources brought to the surface, such as pumping and treatment sites (The Coal Authority 2018, 2020; Banks *et al.* 2019). Similarly, projects that access abandoned roadways or workings at depth to form 'open loop with reinjection' mine water heat pump systems are being researched and deployed (Monaghan *et al.* 2021; Banks *et al.* 2022). The need for low-carbon heat is becoming increasingly important during the climate crisis and will be a crucial challenge to overcome if the UK is to reach net-zero by 2050. Plans to terminate installation of gas boilers in new build houses in the UK by 2025, and in Scotland by 2024 (Scottish Government 2019), mean that heat pumps and district heating networks are imperative to achieve this goal. Mine water can provide a source of low-grade heat (and even 'coolth') for large-scale heating networks (Verhoeven *et al.* 2014). Challenges associated with the uptake of mine water geothermal systems, determined by a global assessment of case studies (Walls *et al.* 2021), indicate that there are key decisions and practices during the planning, construction and operational stages that can optimize system longevity. In some cases, poor management of mine water chemistry has been a contributing factor to system or component failure, including corrosion and iron oxyhydroxide scaling (Korb 2012; Steven 2021). A sound understanding of mine water chemistry prior to system installation is therefore beneficial, as it can inform engineering solutions to mitigate operational risks and help avoid premature decommissioning (Walls *et al.* 2021).

Mine water geothermal systems have mine water brought to the surface via pumping from shafts or boreholes (Banks *et al.* 2019), or by gravity drainage through engineered structures (e.g. adits or shafts). In these locations mine water can have its thermal energy transferred to a heat demand via appropriately sized heat exchangers and heat pumps (Athresh *et al.* 2016; Farr *et al.* 2016). Understanding the available thermal resource, and therefore the scale of heating or cooling capacity, requires a sound understanding of the resource volume, potential flow rates from abstraction wells (James Hutton Institute 2016) or from gravity drainages (Farr *et al.* 2016; Walls *et al.* 2022) and subsurface flow pathways. Good practice during resource assessment includes sinking pilot MWGI boreholes into mine voids to assess openness and condition and to construct monitoring wells during hydrogeological analysis from pumping tests (Palumbo-Roe *et al.* 2021; Walls *et al.* 2021).

Ground stability investigation

Ground stability investigation (GSI) describes localized invasive data collection via trial pits or boreholes, sunk to provide details of subsurface conditions prior to construction on a development site (Healy and Head 1984; BS 5930:2015 +A1:2020). For this study area, GSI was initiated as the site is considered to be a 'Development High Risk Area' (The Coal Authority 2022) owing to shallow workings. Standard GSI operations provide details of the groundwater heads and flows, rock or sediment thicknesses, the nature and depth of faults and voids, and the risk of gas migration (The Coal Authority *et al.* 2019). Importantly for this study, they also provide insight into stability, thickness of overburden and need for grouting of mine voids (or other ground stabilization actions) prior to development. Investigating the condition of coal seams, in areas where they are predicted to be close to the surface, requires GSI of bedrock often to a depth of around 30 m. The pattern of collapsed overlying strata depends on the mining method and dimensions of coal extraction: longwall mining may involve complete collapse of roof structure, whereas methods such as pillar and stall may result in localized, uneven or asymmetric subsidence and settlement (Younger and Adams 1999; Andrews *et al.* 2020). Because construction of buildings typically increases surface loads, it also increases the likelihood of collapse and subsidence issues. GSI data interpretation identifies areas of land that are unsuitable for construction without remediation by consolidation or stabilization methods. Changes in fluid pressures resulting from abstraction and reinjection of mine water for thermal exploitation may also result in additional risks of ground movement (Todd *et al.* 2019).

Synergy between GSI and MWGI

Common estimates use a '1 in 10' rule-of-thumb to estimate the height of strata that may collapse following removal of material when mining (Healy and Head 1984; Bell 1986). Assuming a maximum subsurface void height of 3 m (for major underground roadways), workings within 30 m (3 m × 10) of the surface are identified as a risk (Abbate 2016). Realistically, the affected height will often be less, as there are relatively few coal seams in the UK greater than 1.5 m thick. Younger and Adams (1999) described a different approach whereby the affected height above longwall seams is more closely related to the width, depth and thickness of the worked panel.

Shallow flooded coal mines are both a subsidence risk and a potential thermal resource for new developments, but a depth boundary where subsidence risk from mine voids becomes significant is not absolute. The methods of MWGI and GSI have broad overlaps as both require drilling through bedrock in search of fractures, voids or coal seams. As mentioned above, MWGI often involves significant upfront capital expenditure, but inclusion in necessary GSI work may present a means to reduce capital expenditure whilst screening sites for geothermal potential.

Some crossover differences between methods remain, crucially the ideal diameter of the boreholes. The default diameter of GSI boreholes in this study was 5 inches (127 mm), restricting any installed polyethylene liners to 50 mm internal diameter (ID), leaving space for an adequate annulus for hydraulic sealing. MWGI pilot boreholes can prove presence or absence of a hydraulically productive horizon with boreholes of this diameter, but their application is limited to water sampling and water level monitoring. Wider diameter boreholes would be required for installation of electrical submersible pumps (minimum 100 mm ID), capable of undertaking test pumping to prove suitability of workings for mine water geothermal application. Falling head tests would be feasible in narrower diameter boreholes, but would provide less accurate transmissivity data for the responsive horizon. Similarly, the restricted borehole diameter may accommodate only slimline geophysical probes or CCTV surveys, limiting the additional borehole characterization.

Geological setting

The study area on the outskirts of Dollar, Clackmannanshire, lies above coal seams from the Scottish Lower Coal Measures (LCMS) formation of Westphalian age (Fig. 1). The coal seams of this study are part of a syntectonic synclinal structure with dip (in the study area) of up to *c.* 13° to the north (Armstrong *et al.* 1974*a*). The sequence of major coal seams found at the site is described in Table 1. During deposition in the Carboniferous Period, development of the sedimentary basin was controlled by normal movement on the east–west-trending Ochil fault immediately to the north of the syncline (Rippon *et al.* 1996). Superficial deposits are 2.5–10 m thick, present as horizons of glacial till and glacio-fluvial sands and gravels. In some portions of the study area, the sands and gravels are absent (Armstrong *et al.* 1974*b*).

Mining history

Within the area of the coal-bearing syncline, some workings have detailed accounts of coal extraction (Coalsnaughton and Wallsend Seams mined in the 1940s and 1950s; National Coal Board 1954, 1955), some merely record the outline of old workings without internal detail (Alloa Splint and old portions of Coalsnaughton; Bald 1838) and some workings are entirely unrecorded on mine plans (Alloa Rough). Workings of these seams date back many centuries, with the earliest record of mining in Clackmannanshire from the Church Legate Aeneas Silvus, who later became Pope Pius II, during the reign of James I. On a visit to the area at the beginning of the 15th century he reported seeing ‘poor people begging in rags at Church doors given pieces of black stone, with which they went away happy’ (Dollar Museum 2014).

Initially, working was via a number of vertical shafts on and around the site, many of which were connected to a horizontal drainage adit (the Day Level) running subparallel to the Kelly Burn, shown in plan view in Figure 2 and cross-sectional view in Figure 3. The Day Level was driven into the hillside for mine water drainage, to allow dry working conditions for miners (Younger and Adams 1999). Many of these early mines are to the west of the site and have little detail recorded except for the outer extent and locations of at least eight shafts, with more elsewhere in the coal-bearing syncline (National Coal Board 1955). To facilitate additional mining, developments first saw completion of a water wheel engine to drain the mines via a deeper pit and allow access to workings as deep as 28 m below ground level. Later, the Day Level was extended to reach a new steam engine in a pit at Kelly Bank whereby water was raised from a working level of 36 m depth (Dollar Museum 2014). These developments were prior to a legal dispute in 1840, which saw the cessation of mining in Dollar until reopening in 1943 (Dollar Museum 2014).

Much of the total area of worked coal in the syncline was from the Dollar Colliery at West Pitgober (56.1632°N,

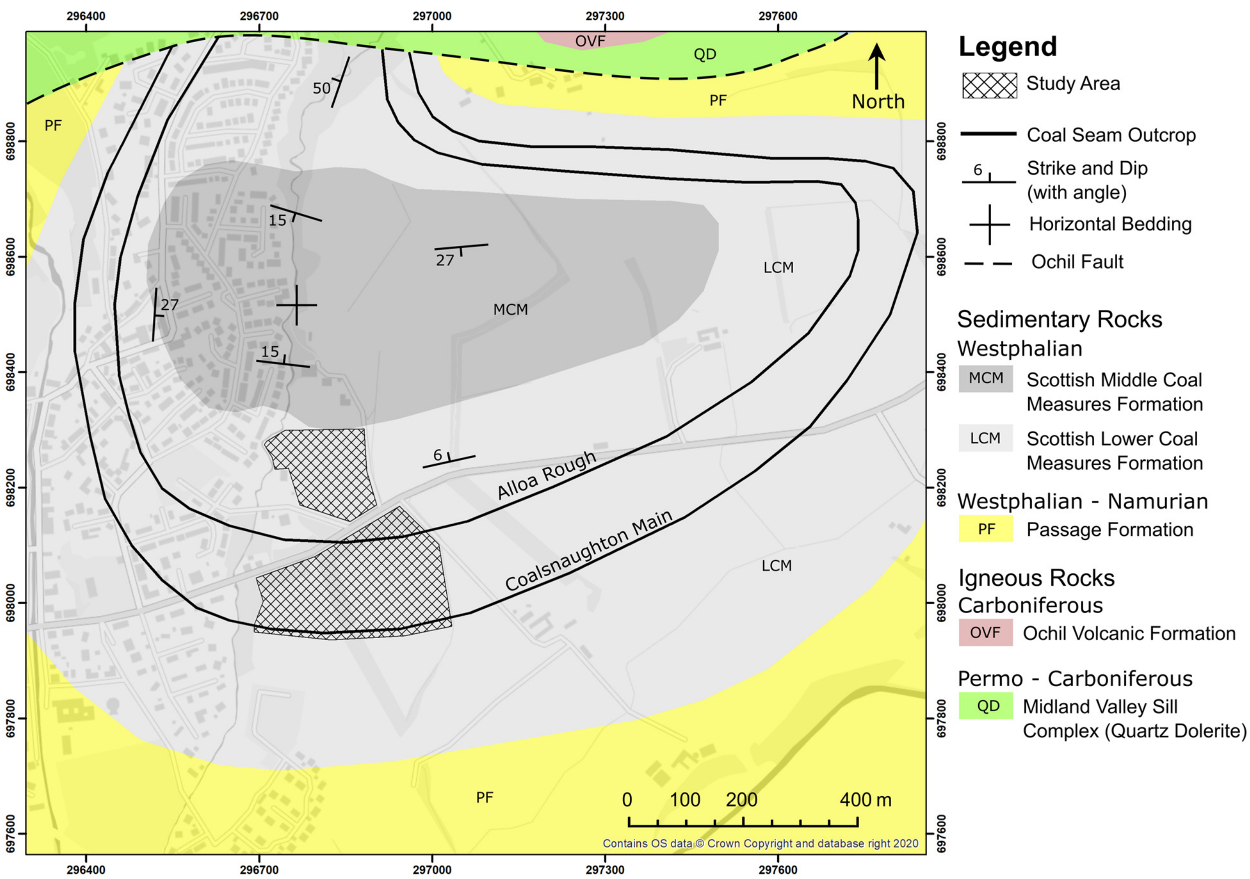

Fig. 1. Simplified geological map of the eastern extent of Dollar, Clackmannanshire. Sources: British Geological Survey; Armstrong *et al.* (1974*a*); OS data © Crown copyright and database rights 2022.

Table 1. *Details of coal seams present beneath the site*

Scottish Lower Coal Measures' seam	Status	Working method	Elevation from BH04 (m OD)
Coal Mosie or McNeish Coal Seam	Unworked	n.a.	53.7
Alloa Rough or Cherry	Worked across the site, extent unrecorded	Pillar and stall	44
Alloa Splint	Extensively worked, older areas recorded in poor detail	Mostly pillar and stall. Small portion of longwall from Dollar drifts 1–3	40.5
Wallsend	A short distance above (and mostly grouped with) the Coalsnaughton Main	Panels of longwall working, probably grouped with Coalsnaughton elsewhere	Grouped with Coalsnaughton
Coalsnaughton Main	Extensively worked, details accurately recorded in most areas	Panels of longwall workings. Areas of old workings are probably pillar and stall	12.2

n.a., not applicable. Depths as read from BH04, converted to metres above Ordnance Datum (m OD is effectively equal to metres above sea-level).

3.6587°W), which produced via three drift mines (Dollar 1, 2 and 3). These were mine roadways that were driven northwards towards the Ochil Hills following the Coalsnaughton Main Coal Seam at *c.* 13° from horizontal from 1943 as a response to the increase in coal demand during World War II (Dollar Museum 2014). Most of the coal extraction by Dollar Colliery was from the Coalsnaughton Main Seam but active workings in the Wallsend and Alloa Rough Seams were also accessed from the same drift mines. Three years after the operations from these drifts stopped in 1953, Dollar Colliery opened a new, separate, coal prospect between 1956 and 1960, with the driving of two new drifts (Dollar 4 and 5) south-southwestwards into stratigraphically lower and hydraulically separate seams. These southern drift mines remained active until 1973 (Dollar Museum 2014).

Hydrogeological setting

The Kelly Burn is the principal watercourse adjacent to the study area, defining its western boundary. It flows from the north as one of many streams that drain water from the Ochil Hills into the River Devon, south of the study area. The Kelly

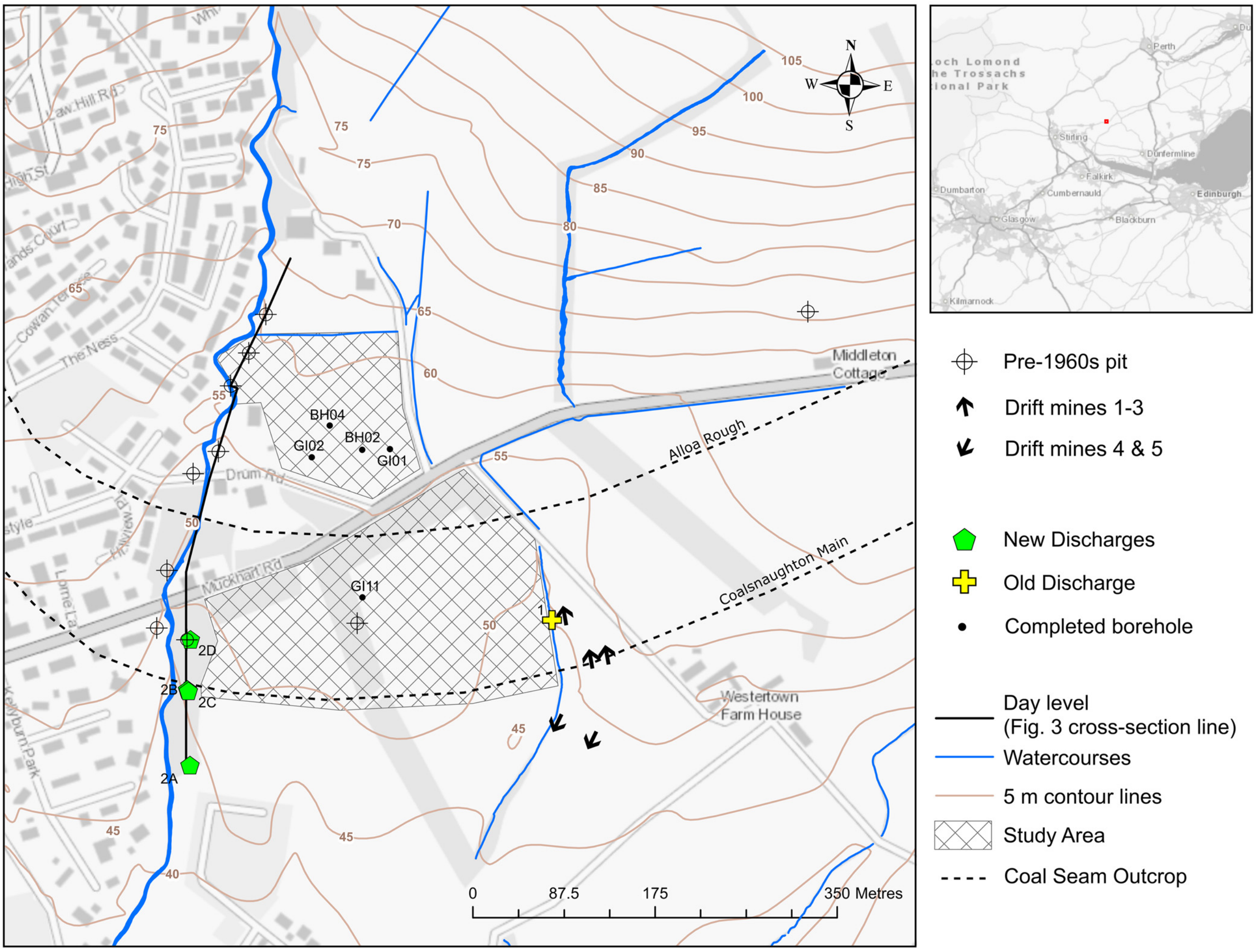

Fig. 2. Topographic and hydrological map of the study area and surroundings with notable locations pertaining to the coal seams shown. Numbers correlate with discharge sample names. Arrows indicate orientation of drift mines from Dollar Colliery. Pit names can be seen in Figure 4. Source: OS data © Crown copyright and database rights 2022.

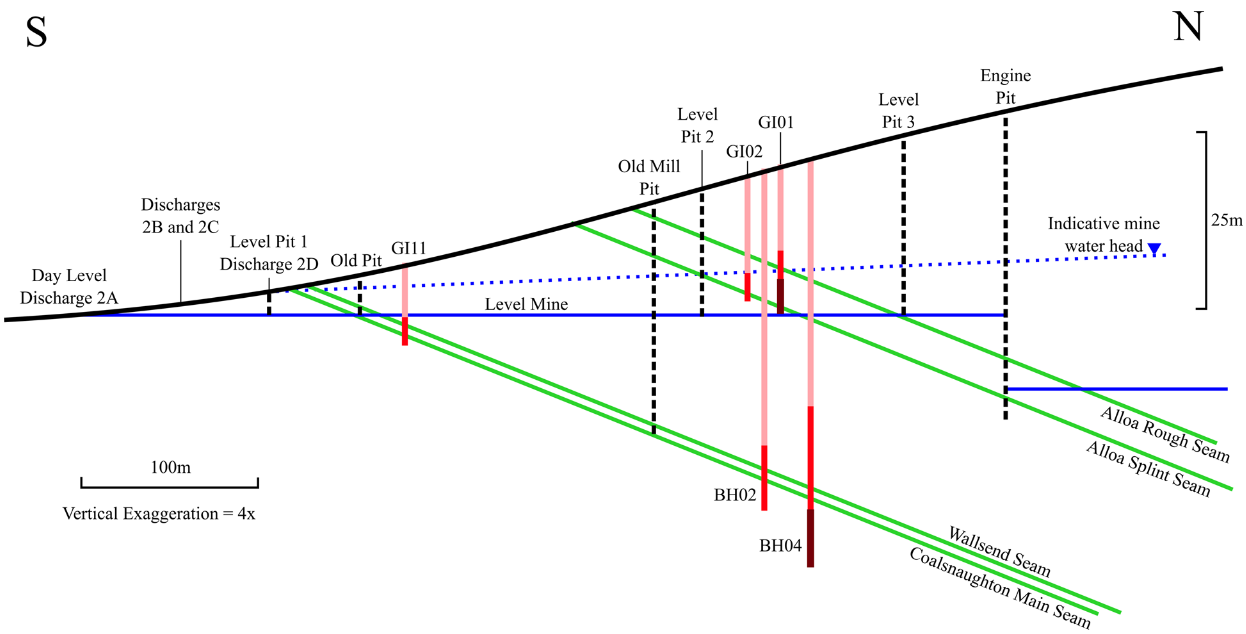

Fig. 3. Schematic cross-section through the coal seams with pit locations, along the line of the Day Level (shown in Fig. 2) in the western part of the study area. The five completed boreholes have been projected onto the cross-section from their locations 100–150 m along-strike, to the east. Pink reflects plain screen liner and red reflects slotted screen liner. Vertical brown sections at the base of GI01 and BH04 depict where each borehole was backfilled before completion with liner.

Burn was the recipient watercourse for the water discharged from the Day Level during mining operations. A small, perennial, unnamed burn defines the eastern extent of the study area, similarly flowing southwards into the River Devon. It was the recipient of Discharge 1, described below.

Despite the Dollar Colliery expanding southwards into a deeper coal prospect via Dollar Drifts 4 and 5, the northern workings (accessed via Dollar 1–3 and the Day Level) in the local syncline remain hydrogeologically separate. This is demonstrated by mine water discharges at the southern margin (lowest elevation) of the northern workings, and the absence of worked coal seams spanning the separating anticline. Although the early Day Level was designed to be the lowest elevation access point to the surface for mine water drainage, there remain other locations across the site that connect the workings to the surface and present potential flow pathways for discharging mine water.

Interpretation of mine abandonment plans, and other historical data available in the Dollar Museum, suggested that the Day Level has the potential to drain water from all existing mine workings beneath the site and is the potential overflow point with the lowest elevation. However, upon investigation, no open mine entry at the site of the Day Level was found, despite its position being identified. On multiple site visits, and after a small pit was dug prior to drilling, no significant mine water flow was identified from the Day Level. Any water that pooled there was indicative of fresh meteoric water (i.e. not mine water). We therefore hypothesize that the Day Level flow ceased following mine closure, probably as a result of a subsurface blockage, most probably caused by, for example, obstruction of flow paths by collapsed strata or waste debris, or accumulations of iron (oxy)hydroxide ‘ochre’ or swollen clays from mudstone.

An existing ochreous discharge (Discharge 1) was identified in November 2020 on the eastern side of the site (56.163739°N, 3.659694°W), located close to the Dollar No. 2 drift mine (National Coal Board 1955), and the National Coal Board’s Dollar Mine No. 1 bore (most probably an exploratory borehole dating from 1953; Figure 4 depicts it encountering intact Coalsnaughton Main coal at 22.6 ft (6.9 m) below surface level). The flow from Discharge 1 was reported to be related to a collapse of land near the backfilled Drift 1, 2 and 3 entrances, most probably between 1960 and 1973 (and when Dollar No. 4 and 5 drifts were operating). Tim MacInness recalled that:

> When the shafts [drifts] 1, 2 and 3 were closed at the Dollar mine, the shaft entrance was filled in. When the shafts 4 and 5 were opened a car park was made, where the entrance to the old mine shafts 1, 2 and 3 had been. Unfortunately, insufficient filling material had been put over the old entrance. One day, when the men had finished their shift, and went to collect their cars, they found that the ground covering the car park had collapsed, taking several cars into the abyss (Dollar Museum 2014).

According to Harry Chalmers, former miner, interviewed in 2006 by Val Toon:

> A field collapsed, right, a big hole, just caved in … they drive lorry loads of rubble and tip it in into the hole to fill it in.… It’s still there and the overflow from the mine is down in the field (Dollar Museum 2014).

Methods

Desk study

The study area was derived from an existing project between TownRock Energy and Harviestoun Home Farm (Figs 1 and 2), where there are existing plans to develop housing. Scrutiny of available mine abandonment plans and local

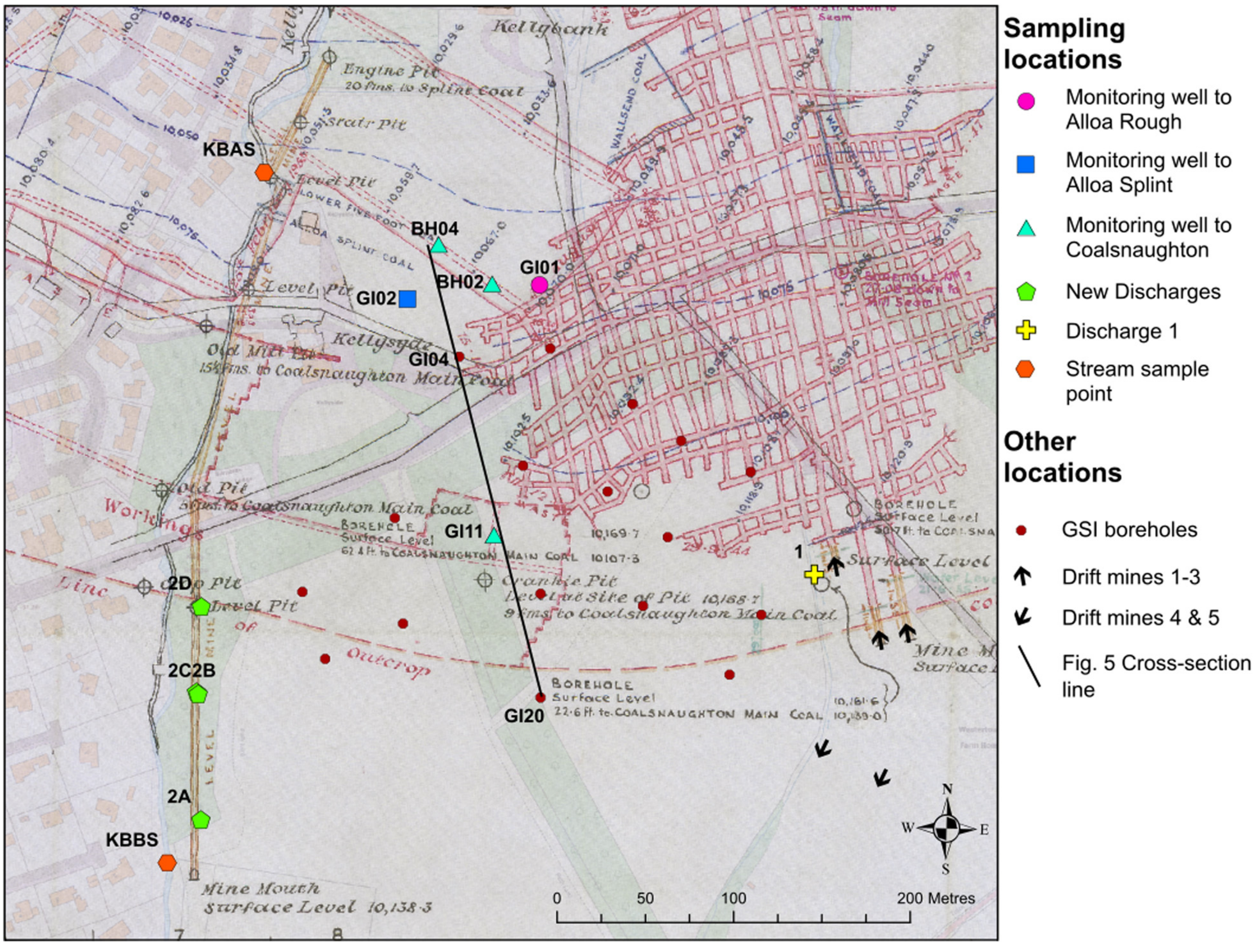

Fig. 4. Borehole and sampling locations overlain on the mine abandonment plan for the Coalsnaughton Main Seam, where red outlines show the extent and details of workings. Numbers correlate with discharge sample names. KBAS, Kelly Burn above site; KBBS, Kelly Burn below site. Arrows indicate orientation of drift mines from Dollar Colliery. Sources: National Coal Board (1955); mine plan as base map: Copyright Coal Authority. All rights reserved 2022.

museum archives informed understanding of operation dates and extent of the mine workings. Georeferencing of mine plans on geographical information system (GIS) software allowed identification of drilling locations to satisfy surface restrictions and subsurface drilling targets. The project team obtained a permit 'to enter or disturb Coal Authority mining interests' to access coal seams with up to 24 boreholes using air-mist flush drilling.

Ground investigation

Compressed air and water mist were used to flush drill cuttings to the surface, whilst providing lubrication and temperature regulation at the interface between the drill bit and the bedrock. This method was selected in preference to water flush drilling as there were not easily accessible, reliable water supplies on site. Because none of the boreholes were to be cored, interpretation of subsurface conditions relied on drilling penetration rates, water strikes and cuttings returned to the surface with the air-mist flush.

All drilling was completed using a 23 ton (20.9 tonne) top driven rotary drill rig suited to open hole or coring applications, primarily for mineral exploration, water well drilling, geothermal and civil engineering applications. Drilling used a selection of three drill bits, depending on purpose:

- 6 inch (152 mm) tricone rock roller, used to progress through superficial deposits to create a large enough diameter hole for 6 inch temporary steel casing to be emplaced, and for the 5 5/8 inch tricone bit to be subsequently deployed in bedrock;
- 5 5/8 inch (140 mm) tricone rock roller, used for drilling in bedrock in boreholes to be completed with 75 mm diameter polyethylene liners;
- 5 inch (127 mm) downhole hammer, used for fast progression through bedrock in all ground investigation boreholes; 5 inch ID steel casing was used in the respective superficial deposits. As these were smaller diameter boreholes, only 50 mm ID polyethylene liners could be installed to complete the borehole as a monitoring piezometer, if required.

Stratigraphic logging of cuttings was performed to describe the depths and state of the coal seams beneath the site as accurately as the drilling method permitted. Beyond a hydraulically responsive coal seam, the water that was returned to surface along with the rock chips was used to aid borehole logging. For example, clear and colourless returning water indicated quartz-rich horizons (sandstone), brown or pale grey cloudy water indicated mudstones or siltstones and black or dark grey water with oily films indicated coal seams or very organic-rich units (shale). Alongside water and rock interpretation, the following were recorded: the penetration rate of the drill bit; any episodes of fast drilling or ‘drops’; odour (e.g. of hydrogen sulfide gas). A gas monitor was used by the drilling contractor to monitor at the borehole head for mine gases including methane, carbon dioxide, hydrogen sulfide and total oxygen concentration. The geologist’s observations were subsequently integrated with the drillers’ factual daily logs to produce integrated borehole logs showing construction and geology.

Monitoring well completion

Five boreholes were completed as monitoring wells (Fig. 4). Detailed completion diagrams can be found in the Supplementary material.

- BH02 [NS 96847 98188] and BH04 [NS 96815 98211] were completed with slotted screens into the areas of longwall panels in Coalsnaughton Main and Wallsend Seams. The boreholes are presumed to access compacted longwall mining waste (goaf).
- GI02 [NS 96798 98181] was completed with a slotted screen in the stall of presumed pillar and stall workings of the Alloa Splint Seam.
- GI11 [NS 96845 98047] was completed with a slotted screen into a void in the ‘old workings’ of the Coalsnaughton Main and Wallsend Seams; this is understood to be a stall of pillar and stall workings.
- GI01 [NS 96873 98189] was drilled though the Alloa Rough to the Alloa Splint. The lowermost portion of the hole was backfilled, sealed and the well was completed with a slotted screen in the stall of presumed pillar and stall workings of the Alloa Rough Seam.

Because a sustainable mine water geothermal system depends upon long and/or diffuse flow pathways between loci of abstraction and reinjection (Walls *et al.* 2021), it is poor practice to create potentially ‘short-circuiting’ flow pathways between seams; thus efforts were made onsite to seal potential hydraulic short-circuit connections between horizons. Hydraulic connections between superficial and bedrock aquifers were also avoided, as connection of these hydraulically separate aquifer units could lead to pollution of superficial aquifers with contaminated mine drainage. Similarly, introduction of oxidizing, lower temperature superficial groundwater to coal mine aquifers can contribute to oxidation and precipitation of iron as iron (oxy)hydroxides and a lowering of the mine water temperature. Boreholes intersecting multiple responsive coal seams were sealed using a combination of packers, shale traps, bentonite and cement-based grout. This is a time- and material-consuming exercise, suggesting that the simplest future strategy for mine water wells might be to target only one coal seam with each borehole; thus if targeting a deeper seam, it is beneficial to find a location where the upper seam(s) is unworked.

The borehole liners comprised 3 m lengths of polyethylene (75 mm ID in BH02, BH04 and GI02; 50 mm ID in GI01 and GI11); slotted screens of the same material with 5 mm slots were selected to span the responsive horizon of each borehole. For voids in worked coal seams, a 3 m slotted length was adequate, whereas evidence for fracture networks above the mined horizons in BH02 and BH04 meant that 6 and 9 m of slotted screens, respectively, were selected. Over each of the slotted screen lengths, a ‘geosock’ was secured, providing a membrane that limits the size of particles that can flow into the borehole liner, whilst allowing inflow of water. In GI01, there was some degree of borehole wall collapse between withdrawal of the drill bit and the installation of the casing string. This prevented the installation of the liner to the full depth of the borehole.

Borehole monitoring of mine water

The mine water head in each completed monitoring well was logged at 10–15 min intervals across a 15 month period using Schlumberger ‘CTD-Diver ®’ submersible sensors with electrical conductivity, water level (collected as pressure data) and temperature sensors. A Schlumberger ‘Baro-Diver ®’ barometer was deployed in the surface headworks of GI01 to record atmospheric pressure and temperature, and to allow groundwater pressures to be barometrically compensated and converted to groundwater head. The water levels were calibrated using manual Solinst ® TLC meter ‘dip-meter’ measurements each month. The dip-meter was also used to generate vertical profiles of the water column in each borehole by taking monthly readings of electrical conductivity and temperature at intervals of 2–5 m between the mine water head and the base of the borehole. The results are given in the Supplementary material.

Discharge estimation

Standard flow rate techniques could not be employed as this study did not have access to a flowmeter or material to construct weirs, and the diffuse nature of the discharges did not suit collection with a bucket and stopwatch. As an alternative, indicative flow rates from mine water discharges were estimated using measurements of each channel’s dimensions. The flow rate Q ($cm^3\ s^{-1}$) is estimated from equation (1),

$$Q = \text{depth} \times \text{width} \times V \times 0.5 \tag{1}$$

where depth and width are in centimetres and V is velocity ($cm\ s^{-1}$). The correction factor of 0.5 is applied to account for the irregular flow cross-section and slower flow at the channel edges. The width of the flow channel at the surface (cm) and the depth of the flow channel (cm) were measured with a ruler. The flow speed of the channel ($cm\ s^{-1}$) was measured by dropping a buoyant item into the flow and measuring distance covered in 1 s. Flow rates in $cm^3\ s^{-1}$ were then multiplied by 0.001, to obtain a value in $l\ s^{-1}$.

Water sampling

Water samples were collected from the drilling return fluid as flooded mine voids were encountered during the drilling period (18 November 2020 to 4 December 2020; samples 03-01 to 03-10). Following drilling, monthly sampling was conducted between 16 January 2021 and 17 December 2021 (samples 03-11 to 03-133) at the following locations (Fig. 4):

- the five monitoring wells (BH02, BH04, GI01, GI02 and GI11);

- five locations of surface mine water discharge, designated Discharges 1 and 2A to 2D;
- two samples of streamflow from the Kelly Burn, from above and below the study area.

During monthly sampling, boreholes were sampled using a Waterra inertial pump, consisting of a high-density polyethylene (HDPE) 25 mm outer diameter pipe with a VS5 stainless steel internal foot valve, inserted to the depth of the monitored mine water horizon. The borehole was purged for at least 5 min prior to collection of the water sample at an estimated flow rate of 15 l min^{-1} (Waterra 2022), indicating that *c.* 75 l of water was purged before sampling.

Field determinations of pH, temperature, oxidation–reduction potential (ORP) and electrical conductivity (EC) were made using a handheld Myron P Ultrameter. This meter automatically corrects values of pH and EC to a standard temperature of 25°C. ORP values were measured in millivolts (mV) and read from a platinum sensor and a silver chloride (Ag/AgCl)-saturated KCl reference electrode. ORP readings are 199 mV lower than true Eh (the standardized measure for oxidation–reduction potential derived from a standard hydrogen electrode; S. Robinson pers. comm., 2022) but are presented here without adjustment. In the field, total alkalinity was determined as mg l^{-1} equivalent of $CaCO_3$ with a Hach Model 16900 digital titrator, using 1.6N sulfuric acid and bromcresol green–methyl red pH indicator. Recorded values in mg l^{-1} $CaCO_3$ were then converted to meq l^{-1} (by dividing by 50.04 mg meq^{-1}). The alkalinity is assumed to be predominantly in the form of HCO_3^- at circumneutral pH values. Where required, equipment was calibrated before each day's fieldwork and all water samples were refrigerated as soon as possible after collection.

As regards samples of surface discharges and streams, samples were taken directly from as close to the discharges' source as safely possible, and from the centre of the Kelly Burn.

Separate aliquots were taken for different analyses, as detailed below. Filtration, to remove any particulate matter, was carried out using a hand-held, syringe mounted filter capsule.

(1) An aliquot for major anion analysis was filtered at 0.45 µm into clean 15 ml polypropylene screw-cap vials.
(2) An aliquot for dissolved elemental content was filtered at 0.45 µm into clean 15 ml polypropylene screw-cap vials and preserved using one drop of concentrated HNO_3 (68%, trace metal grade, Fisher Chemicals).
(3) An unfiltered aliquot for total (dissolved and undissolved) elements was collected using clean 15 ml polypropylene screw-cap vials and preserved using one drop of concentrated HNO_3 (68%, trace metal grade, Fisher Chemicals).
(4) An aliquot for $\delta^{18}O$ and $\delta^{2}H$ analysis was taken using clean 15 ml polypropylene screw-cap vials, sealed with Parafilm to prevent sample evaporation.
(5) A 1 l unfiltered aliquot of sample water was collected in a plastic flask for sulfate-$\delta^{34}S$ analysis. Sulfate was subsequently precipitated as barium sulfate, using the method of Carmody *et al.* (1998): namely, the sample was acidified to pH 3–4 by dropwise addition of concentrated HCl and then dosed with excess 5% $BaCl_2$ solution. A rapid cloudy reaction indicated the presence of sulfate via the precipitation of $BaSO_4$ crystals.

Rock chip collection

Upon delivery of rock chips to the surface via the drilling flush, organic-rich (shales and dark brown or black mudstones) and coal horizons were selected for sulfur-bearing mineral collection. The rock chips were washed using deionized water and sulfide-bearing minerals were extracted using a scalpel or mineral drill. Only one sample of coal (CM1), from the Coalsnaughton Main Seam, hosted enough collectable pyrite for analysis.

Chemical and isotopic analysis

Chemical analysis

Ion chromatography (IC) was used for determination of five anions (F^-, Cl^-, SO_4^{2-}, Br^-, NO_3^-) in the laboratories of the Department of Civil and Environmental Engineering (CEE), University of Strathclyde. An 850 Professional IC by Metrohm ion chromatograph was used. The separation utilized a Metrosep A Supp 5 anion analytical with Guard column (Metrosep A Supp 5 Guard/4.0) at 24°C with eluent comprising 1mM $NaHCO_3$ and 3.2mM Na_2CO_3 prepared in ultrapure deionized water. The flow rate was 0.7 ml min^{-1}. Calibration standards were 0.1, 0.5, 1, 5 and 10 mg l^{-1} prepared in ultrapure water. The IC method was developed according to BS EN ISO 10304-1:2009 and Metrohm customer support recommendations.

Twelve dissolved and total elements (B, Ba, Ca, Fe, K, Mg, Mn, Na, S, Si, Sr, Zn) were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) using an iCAP 6200 Duo View ICP Spectrometer, Thermo Fisher Scientific model equipped with an autosampler (Teledyne CETAC Technologies, ASX-520) and Thermo i-TEVA Version 2.4.0.81, 2010. The operating conditions are presented in the supporting material of Walls *et al.* (2022)

For determination of total aqua regia-digestible elemental content of the water samples, they were acid digested using a Microwave Accelerated Reaction System (MARS-6, CEM). Thoroughly mixed, unfiltered sample (10 ml) was transferred into MARS Xpress Plus 110 ml perfluoroalkoxy alkane (PFA) microwave digestion vessels. Samples were digested with reversed aqua regia mixture of hydrochloric and nitric acids (1:4, HCl 37%, and HNO_3 68%, trace metal grade, Fisher Chemicals), following the microwave operating parameters: operating power 800–1200–1800 W; ramp for 20 min up to 170°C; hold time 20 min at 170°C. Sample digests were brought up to 50 ml with ultrapure water using volumetric flasks, then filtered through 0.45 µm for ICP-OES analyses.

Multi-element three-point calibration standards were prepared from 1000 mg l^{-1} element stock standard solutions (Fisher Scientific) using 18.2 MΩ cm^{-1} ultrapure water (Triple Red water purification system). 68% trace metal analysis grade nitric acid (Fisher Chemicals) was added to reach a 5% final acid concentration in the standard solutions for dissolved content analyses, similarly, reversed aqua regia was added to reach 20% in the standard solutions for total aqua regia-digestible elemental content analyses. Yttrium (5 mg l^{-1}) was used as internal standard (IS) solution (Fisher Chemicals), to account for any matrix effects owing to differences between samples and standards. The IS was added through automated online addition with an internal standard mixing kit. A brief method validation study found the following linear ranges: 0.01–1 mg l^{-1} for barium and strontium, 0.5–50 mg l^{-1} for calcium, magnesium, potassium, sodium, iron and sulfur and 0.1–10 mg l^{-1} for boron, manganese, silica and zinc. Analyses proceeded when calibration curves generated correlation coefficients (R^2) >0.9980. Instrument equilibration and system's suitability were checked according to Civil and Environmental Engineering (CEE) labs Standard Operating Procedure for ICP-OES and Quality Control and Assurance procedure. CEE methods of analyses were mainly based on PD CEN/TS 17197:2018. Elemental method quantification limits were based on instrument-predicted method quantification limit values (Walls *et al.* 2022, supplementary material), obtained from the calibration parameters for each element.

Isotopes

For $\delta^{18}O$ analysis, each sample was over-gassed with a 1% CO_2-in-He mixture for 5 min and left to equilibrate for a further 24 h. A sample volume of 2 ml was then analysed using standard techniques on a Thermo Scientific Delta V mass spectrometer set at 25°C. Final $\delta^{18}O$ values were produced using the method established by Nelson (2000). For δ^2H analysis, sample and standard waters were injected directly into a chromium furnace at 800°C (Donnelly *et al.* 2001), with the evolved H_2 gas analysed on-line via a VG Optima mass spectrometer. Final values for $\delta^{18}O$ and δ^2H are reported as per mille (‰) variations v. Standard Mean Ocean Water (V-SMOW) in standard delta notation. In-run repeat analyses of water standards (international standards V-SMOW and Greenland Ice Sheet Precipitation (GISP), and internal standard Lt Std) gave a reproducibility better than ±0.3‰ for $\delta^{18}O$ and ±3‰ for δ^2H. For sulfate-$\delta^{34}S$ isotope analysis, the barium sulfate precipitate was recovered from the sampling vessel, washed repeatedly in deionized water and dried. SO_2 gas was liberated from each sample by combustion at 1120°C with excess Cu_2O and silica, using the technique of Coleman and Moore (1978), before measurement on a VG Isotech SIRA II mass spectrometer. The single pyrite (CM1) analysis was similarly run, following the technique of Robinson and Kusakabe (1975). Results are reported as per mille variations from the Vienna Canyon Diablo Troilite (V-CDT) standard in standard delta notation. Reproducibility of the technique based on repeat analyses of the NBS-127 sulfate standard was better than ±0.3‰, and was ±0.2‰ for internal chalcopyrite standard CP1, run in conjunction.

Quality assurance

Because sulfate (SO_4^{2-}) was run via IC, and sulfur elemental analysis was run via ICP-OES, correlation between the two for sulfate (meq l^{-1}) is possible (on the assumption that all sulfur is present as sulfate). These showed a strong correlation, but the ICP-derived sulfate values were selected for use in ion balance errors (IBEs) and presentation. The IBEs were determined for a total of 127 water samples based on anion analysis of F^-, Cl^-, Br^- and NO_3^-, plus field-determined alkalinity and ICP-derived sulfate (SO_4^{2-}), and ICP-OES analysis of dissolved concentrations of Ca, Fe, K, Mg, Mn and Na. Of these, 73 returned IBEs within ±5%, 36 within ±10%, 15 within ±15%, and there were three outliers beyond ±15%.

'Field blanks' were collected in parallel to discharge samples; ultrapure deionized water was carried into the field and analysed subject to the same collection and processing methods as the discharge samples (e.g. filtration, acidification, digestion). This was done to monitor for any contamination of samples during collection. Laboratory blanks were created from ultrapure deionized water and duplicates of some mine water samples were collected (Supplementary material); these were subject to the same laboratory processes as other samples to check for contamination and reproducibility. The blanks and duplicates returned acceptable values, and it was concluded that there was minimal interference from field sampling or laboratory equipment.

Results and discussion

Borehole locations

The GSI boreholes were positioned by mining engineers, irrespective of areas with anticipated voids or intact coal. Their distribution was even across the site, as far south as the Coalsnaughton Seam's projected subcrop. Figure 4 shows the GSI borehole locations on the mine abandonment plan for the Coalsnaughton Seam. Four borehole locations were initially chosen by the authors as locations for MWGI boreholes, constrained by the footprint of the projected housing development. Therefore, if they were successful, they could have been upgraded to full-scale production or injection boreholes. They were sited to have the greatest chance of connecting to open workings in the deepest seam, the Coalsnaughton. For example, BH02 was sited directly above the SE–NW longwall access roadway in the Coalsnaughton Seam, which may have remained open. BH04 was also projected to intersect the longwall access roadway in the Coalsnaughton, but it also penetrated the worked area of the Wallsend Seam above it. BH02 and BH04 were both above the highlighted area for 'old workings' in the Splint and Rough Seams, and therefore it was unclear whether they would intersect intact coal pillars, voids or collapsed workings.

Drilling

Of the 24 boreholes outlined, 18 were drilled during November and December 2020. Five of these were completed as monitoring wells into coal seams that had good evidence for responsive mine water horizons (GI01, GI02, GI11, BH02 and BH04), 13 were drilled as standard GSI boreholes and subsequently backfilled, and the remaining six were not drilled. Of these six, MWGI boreholes BH01 and BH03 were not required as their intended purpose of monitoring flooded coal seams was fulfilled by GI01, GI02, GI11, BH02 and BH04. The remaining GSI boreholes (GI05, GI06, GI07 and GI18) were not drilled, following events outlined in the 'Changes in flow regime' section below. The GSI boreholes were drilled as far as the first coal seam, which varied depending on location, whereas BH02 and BH04 were deepened to penetrate all coal seams.

The results and interpretations of the GSI study have been produced by professional mining engineers and their comments on building limitations or ground remediation works have been included in a non-public domain document and thus will not be discussed here. There are areas denoted as stable, thus the housing development can progress with mine water geothermal heating as a potential option worthy of further consideration. A series of SSE–NNW-trending boreholes (GI20, GI14, GI11, GI04, BH02, GI02 and BH04) generate a cross-sectional representation of the coal seams (Fig. 5) along the line of section shown in Figure 4. It reflects measured depths at which rockhead and coal seams were encountered, with interpretation added to show the state of workings. Detailed geological units of sandstone, mudstone and minor coals between principal coal seams are not shown.

Upon reaching the depth at which the coal seams were present, drilling apparatus responded differently to varying conditions. The findings are detailed below.

Intact coal

Where intact coal seams were encountered, drilling penetration rate showed no change. The air-mist flush returned rock chips (up to 5 mm) to the surface (the same size as had been returned from other lithologies). They remained dry, and a clear change from pale grey or brown (sandstone) chips to black vitreous (coal) chips was observed. Once the coal seam had been passed, the rock chips reverted to pale grey, reflecting a change in lithology. The intact coal seams are indicative of unworked regions or pillars in the pillar and stall workings.

Void

When entering a void, the drill bit lost all resistance from the bedrock and 'dropped' the height of the void space in the workings. This response most probably reflects entering a 'stall' of pillar and stall workings that had not been backfilled with waste material; however, voids can migrate upwards if roof strata fall to the base of the stall. The voids also produced mine water, flushed back to surface. In one case (GI02) the flush of air and mine water was lost altogether.

Mining waste

Mining waste can be used to describe the material left behind in mine voids following mineral extraction. This can be adjacent horizons of sandstones or organic-rich mudstones and shales that are deliberately packed into voids, or fallen debris from roof strata or supporting coal pillars. Mining waste may contain fragments of wood or metal. When encountering mining waste in a coal seam, the penetration rate of the drill bit was faster than the standard penetration rate. The air-mist drilling, which had previously been returning dry or damp rock chips, began moving large volumes of water to the surface. Within the water there were clasts of rock, much larger than those made by drilling intact rock. The clasts of mudstone and shale, and sometimes coal, were as large as 100 mm. They often showed oxidized iron staining on their surfaces, indicating exposure to oxidizing conditions.

Goaf

The term 'goaf' can be used simply to refer to mining waste within void spaces. However, in this paper, it is used in a more specific sense, for the structure that results from the collapse of a mine working, either by pillar collapse, pillar robbing or longwall working with deliberate controlled collapse. Goaf can thus comprise a layer of compressed roof collapse strata, but sometimes (in the case of total extraction) a distinct horizon of collapse material can be difficult to identify. This may be the case, for example, where roof sandstone collapses 'cleanly' onto pavement sandstone, as found at the Glasgow Geothermal Energy Research Field Site (GGERFS) (BGS 2020). When drilling, no change in penetration rate necessarily occurs, and therefore the goaf must be identified by other means; for example, the colour of the backwash of water, the presence of wood or oxidized rock fragments in the rock chip samples, or by downhole camera observations. Interpretation of goaf at the base of BH04 was based on field observations including return fluids with a surface film of black oil and an organic matter smell, a tightly constrained prediction for depth from BH02 and evidence for open fractures above the seam location, including slight increases in drilling rate for up to 100 mm at a time and detection of H_2S gas at surface. The secondary permeability of the fracture network in the collapsed roof strata probably forms part of the productive response zones, and hence borehole screens were designed to include these regions.

Changes in flow regime

Discharge 1 was first visited on 19 November 2020, when it was found to have clear and colourless flowing water at *c.*

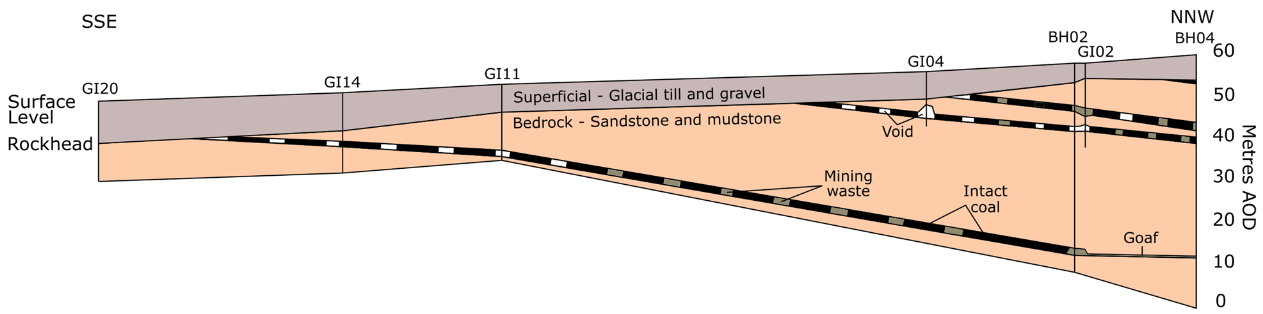

Fig. 5. Cross-sectional interpretation of borehole logs between the southernmost (GI20) and northernmost (BH04) boreholes along line of section shown in Figure 4. No vertical exaggeration. AOD; above Ordnance Datum.

7 l s^{-1} at 9.7°C. It flowed out of an old pipe, nestled in the bank of the small stream. The cascading nature of the discharge meant that dissolved iron had been oxidized at surface and deposited orange ochre on the bank of the stream. A distinct smell of H_2S was present. A sample from the discharge was collected for chemical analysis and is discussed below.

During the latter stages of the drilling period in December 2020, Discharge 1 ceased to flow (Fig. 6). At the same time, the Day Level outflow commenced flowing into the Kelly Burn on the western extent of the site. Other discharges were identified at other locations further upstream along the course of the Day Level (e.g. possibly other historical shafts). The flooding and discharges can be seen in Figure 7. Following these observations on site, accounts of the activities and results were communicated to the Coal Authority adhering to the project completion guidelines. Similarly, the discharges were sampled and analysed for reporting to The Scottish Environmental Protection Agency (SEPA); these water chemistry results have been included in the Supplementary material.

The timing of the change is believed to be associated with drilling GI11, the first borehole to penetrate the old portion of the Coalsnaughton Main Seam. It seems that the act of drilling removed or cleared some form of underground flow obstruction, permitting the mine to recommence discharging to its original (lowest elevation) outflow point, the Day Level. The details of the subsurface barrier that was preventing flow at the Day Level remain unclear, and the permanence of the new flow regime is not known.

The recommenced outflow in the vicinity of the Day Level can be separated into four individual discharges, with their locations shown in Figure 2.

- At Discharge 2A, clear colourless water pools and flows into the Kelly Burn from the exit of the Day Level. It does not show any ochre precipitation along the channel bed but does have small numbers of iron flocs amongst the organic matter, which can be seen when the channel base is disturbed. It flows at *c.* 3–6 l s^{-1} depending on recent rainfall and seasonal changes.
- At 75 m further north from the Day Level there are two discharges (2B and 2C) that combine to flow into the Kelly Burn, distinguished as two separate discharges in March 2021. They were differentiated by several factors: the source locations of the flows are *c.* 5 m apart, the electrical conductivity is around 140 μS cm^{-1} different and the channel beds of the discharges have significantly different ochre precipitation (Fig. 8).
- There is a low flow (<1 l s^{-1}) from an old pond at the highest point of the woodland (Discharge 2D), just south of the road, which discharges through an artificial drain into the Kelly Burn.

The flow rates of all discharges were measured between November 2020 and March 2022 and are plotted in Figure 9 with supporting data in the Supplementary material; the figure captures the seasonal nature of the total discharging flow rate following a peak during at the end of 2020. Immediately following the change to the flow regime and the commencement of Discharges 2A–2D they had a combined total flow rate of 27.6 l s^{-1}, much greater than the 7 l s^{-1} from Discharge 1. As mine water head lowered, Discharge 2D decreased to a negligible flow with rates far below 1 l s^{-1}, hence its omission after January 2021. The total flow rate from Discharges 2A–2D decreased through the first half of the year and dropped below the original Discharge 1 flow rate in early June 2021. Following a minimum across July, August and September of 5.6–5.8 l s^{-1}, the combined flow rate from Discharges 2A–2D rose and exceeded 7 l s^{-1} in November 2021 in response to seasonal recharge and reached 8.9–9.1 l s^{-1} between the end of November 2021 and March 2022. It is therefore suggested that the ‘draining down’ of the mine system from the elevation of Discharge 1 to that of the Discharges 2A–2D resulted in a temporary increase in the

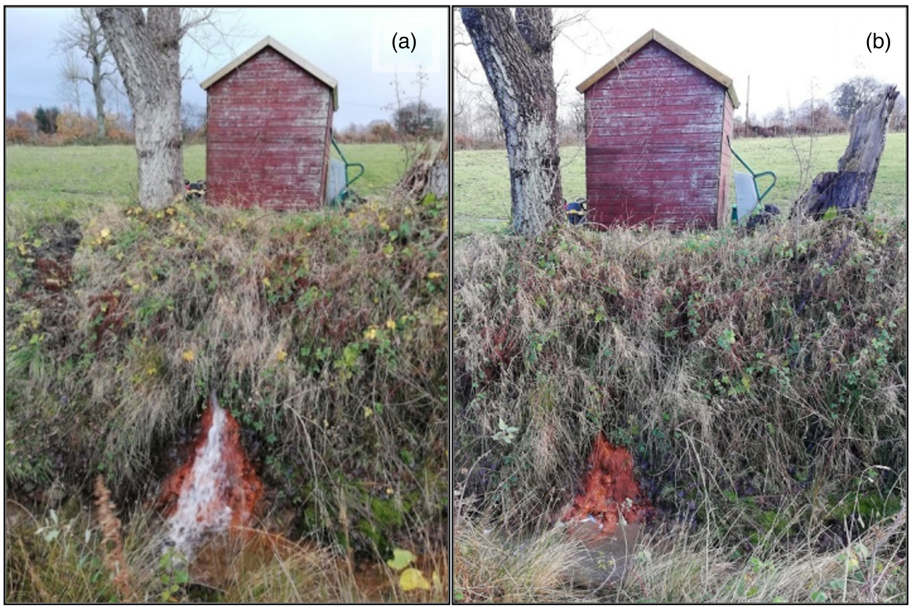

Fig. 6. (**a**) Discharge 1 before (13 November 2020) and (**b**) after (5 December 2020) it ceased to flow.

Fig. 7. (**a**) Day Level site prior to drilling period, digging to access fresh water (13 November 2020); (**b**) Day Level location following flooding and flow of mine water (Discharge 2A, 5 December 2020); (**c**) the area north of Discharge 2A upon first flooding, which since lowered to marshy ground and Discharges 2B and 2C (5 December 2020).

rate of mine water discharge. Following this, the total (2A–2D) discharge flow rate restabilized to a range between $5.6\ \mathrm{l\,s^{-1}}$ in summer months and $9.1\ \mathrm{l\,s^{-1}}$ in winter; that is similar to the original flow rate of Discharge 1 ($7.2\ \mathrm{l\,s^{-1}}$).

Fig. 8. Meeting of two discharges from 5 m apart. Discharge 2C (from the left) has a channel base with mostly organic matter, whereas Discharge 2B (from top of image) coats the channel base in orange ochre; 30 cm ruler for scale.

Borehole monitoring

Following drilling in November and December 2020, a declining mine water head was observed in the monitoring wells and corresponded to the maximum in total discharge flow rates discussed above; this is most probably a result of the draining down of the mine system from mine water head elevations controlled by Discharge 1 to the elevation of the original Day Level (Discharge 2A) (Fig. 10). We discuss data from GI01 as it was one of the earliest boreholes to have mine water head data collected and shows the best correlation between the manual dips and the electronically logged data. Following the change in flow regime described above, all boreholes exhibited a sharp mine water head decrease between 26 November 2020 and 16 January 2021; in GI01 this was from 50.96 m OD to 47.36 m OD. Mine water head continued to fall throughout the spring and summer months to a minimum of 46.93 m OD on 24 September 2021. Throughout autumn and winter, mine water head increased with aquifer recharge to a maximum of 48.58 m OD at the end of February 2022 in response to major rainfall events and decreased evapotranspiration.

The rate and magnitude of water level fall during initial de-watering (Fig. 10) is greatest in GI01, where between midday on 10 December 2020 and midday on 15 January 2021 it fell

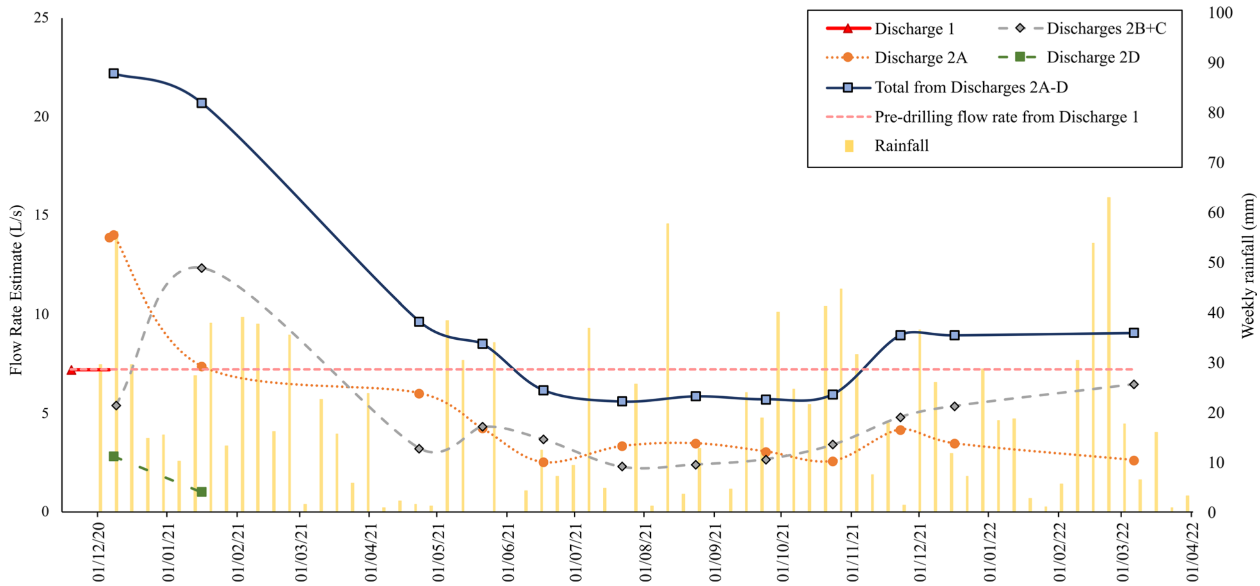

Fig. 9. Total and component mine water discharge flow rates plotted against projected extrapolated flow rate from the ceased discharge (Discharge 1), and weekly rainfall data for Tillicoultry. Sources: © SEPA, 2023. This SEPA Data is licensed under the Open Government Licence 3.0. Whilst all reasonable effort has been made to ensure that these data are accurate for their intended purpose, no warranty is given by SEPA in this regard.

1.35 m from 48.73 m to 47.38 m OD, compared with 1.34 m in GI02, 1.03 m in GI11, 1.12 m in BH02 and 1.13 m in BH04. The approximately parallel hydraulic response of each seam reflects an overall hydraulic connectivity. Because the elevation of the boreholes was extracted from a digital elevation model (DEM), the absolute accuracy of the water level data cited above is poor (1 m accuracy), but the resolution (incremental change) of the loggers is excellent (1 mm). Thus, the head in GI02 appears to be *c.* 1 m lower than that for the other boreholes, but this could merely reflect uncertainty in absolute elevations, or could equally reflect a lower mine water head owing to proximity to the Kelly Burn discharges.

Mine water temperatures vary far less seasonally than air temperatures or on-site surface water temperatures (Fig. 11), although individual temperature trends vary for each of the mine water monitoring points. GI01 shows an overall inverse trend to the average air data, whereby the lowest temperatures are observed at 8.86°C in July and the highest are 10.03°C in January, perhaps reflecting low thermal diffusivity and

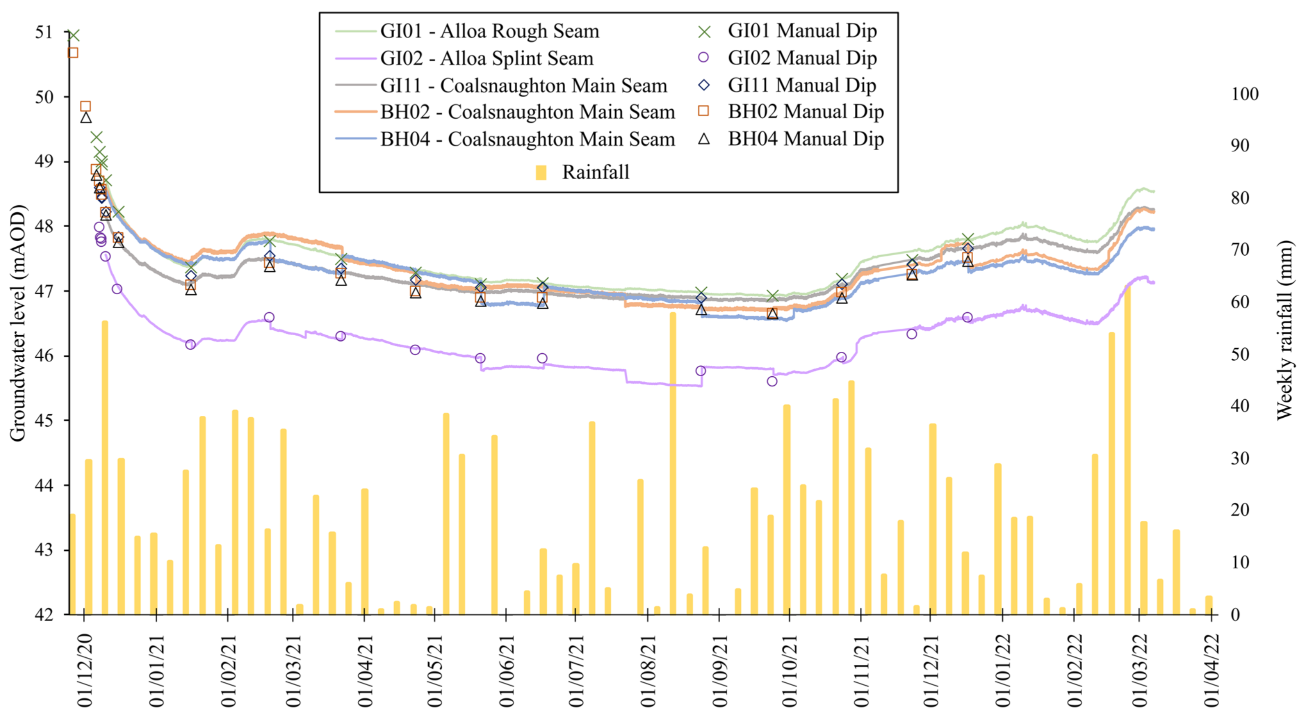

Fig. 10. Manual dip and diver data for mine water levels, plotted against weekly rainfall data for Tillicoultry. It should be noted that monthly sampling displaces the probes. Best efforts were made to ensure they were inserted at the same level as they were removed from, but discrepancies were due to adhesion between the probe string and the borehole liner. It should be noted that absolute elevation values are accurate to only *c.* 1 m OD as each wellhead elevation is derived from a digital elevation model. Sources: public sector information licensed under the Open Government Licence v3.0; Scottish Environment Protection Agency (2022).

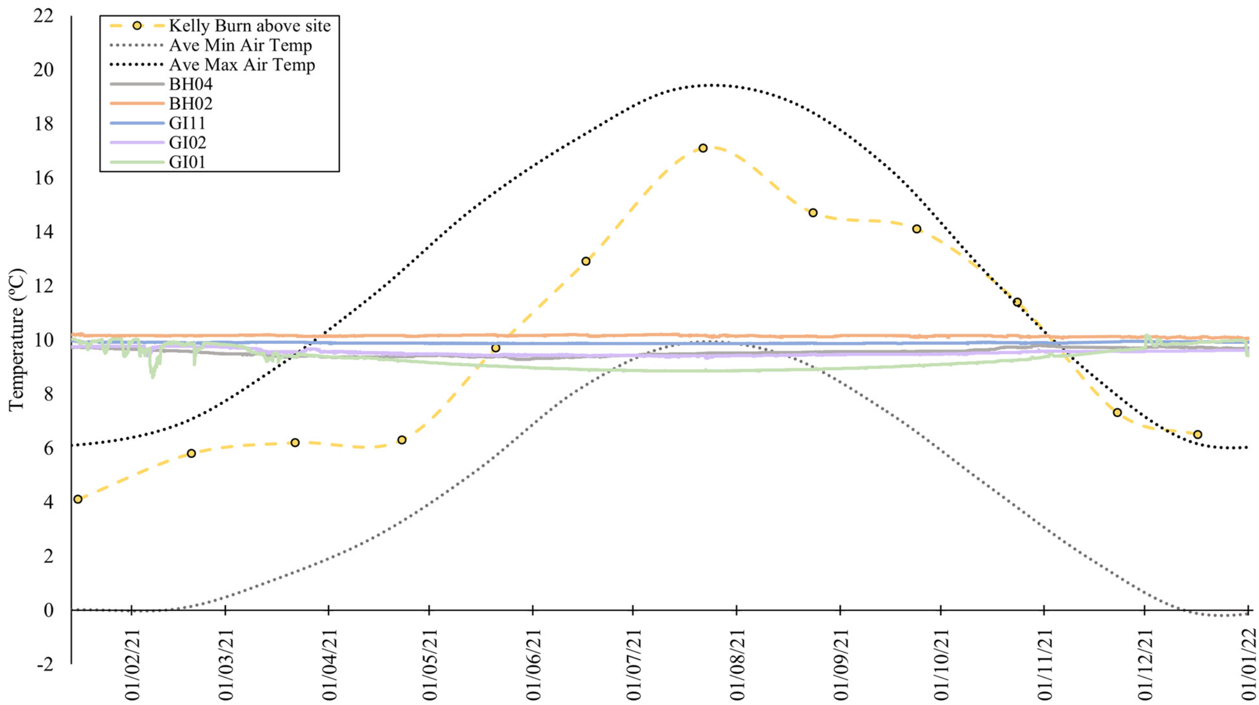

Fig. 11. Seasonal temperature data for mine water in 2021, plotted against monthly measured Kelly Burn stream temperature data and average maximum and minimum air temperature between 1991 and 2020. Mine water probes are at depths (below ground level) of 10 m in GI01, 16 m in GI02, 15 m in GI11, 16 m in BH04 and 42 m in BH02, which equate to depths below water level of *c.* 1–2 m in GI01, 6 m in GI02, 9–10 m in GI11, 6 m in BH04 and 31 m in BH02. Sources: public sector information licensed under the Open Government Licence v3.0; Met Office (2022); Hollis and Perry (2004).

delayed seasonal thermal extremes relative to those observed at the surface. Similar temperature fluctuations are observed in each of the vertical water profiles between surface and 15–20 m below ground level (BGL) (Supplementary material); however, the months that show the most extreme values are not consistent across each borehole. In the winter months, GI01 exhibits sudden increases or decreases of temperature by up to 1°C. These are probably associated with rapid percolation of infiltrating rainfall, as GI01 accesses the shallowest worked coal seam at a depth of 10 m BGL and has a mine water head less than 2 m above the mined coal seam. BH02 and BH04 are the deepest boreholes, each reaching 50 m BGL; thus BH02 exhibited the highest annual mean temperature of 10.15°C, with little variance. It should be noted that BH04's diver was set at only a shallow depth of 16 m BGL. GI11 showed the most constant temperatures with only 0.12°C of difference between the maximum and minimum. This is assumed to be a result of its southerly location in the deepest coal seam, suggesting that it has the greatest separation from infiltrating rainfall and runoff from the Ochil Hills on the northern edge of the coal-bearing syncline.

Water chemistry

All water chemistry results are presented in the Supplementary material. The Piper diagrams (Fig. 12) show that all sampled mine and stream waters are Ca-HCO_3^- type, with minor variations between boreholes and respective coal seams. The spread across the Ca-HCO_3^- region reflects an overall shallow, fresh groundwater signature. However, the tendency for some of the samples to move towards the boundary with Ca-SO_4^{2-} suggests the influence of sulfide oxidation. The low dissolved solute content, with an EC range across all boreholes and discharges of 367–626 µS cm^{-1}, most probably reflects a short residence time in the mined aquifer. The different boreholes and discharge samples create a continuous spread on the Piper diagram, indicating that samples are chemically related or evolved. The absence of clearly differentiated hydrochemical 'facies' in the mined system suggests overall hydraulic connectivity.

Monitoring of total and dissolved iron provides a means to understand the risk of iron (oxy)hydroxide (ochre) scaling on mine water geothermal infrastructure pipework or heat exchangers. Overall, lower iron concentrations are preferred, but crucially, good practice seeks to maintain iron in its dissolved, ferrous state by isolating host mine water from oxidizing environments prior to heat offtake (Bailey *et al.* 2013). Iron concentrations are presented in Table 2 and show that samples from GI02 have both the lowest median total iron concentration (0.73 mg l^{-1}) and the lowest concentration of iron that is not dissolved (0.58 mg l^{-1}); that is, total minus dissolved iron. GI11 has the greatest percentage of total iron in a dissolved state (47.9%), which overall as a proportion of total iron is still fairly low. This may suggest that there is some degree of *in situ* oxidation (or rapid oxidation during sampling), which may pose a risk of ochre scaling. There appears to be no clear correlation between iron concentration and host coal seams. The range of median values for total and dissolved iron between multiple boreholes of the Coalsnaughton Main Seam (Table 2) is greater than the range between the different seams. Similarly, manganese has a narrow range across the boreholes, around 0.2–0.5 mg l^{-1}, providing no means to differentiate dissolved or total metal signatures from each coal seam.

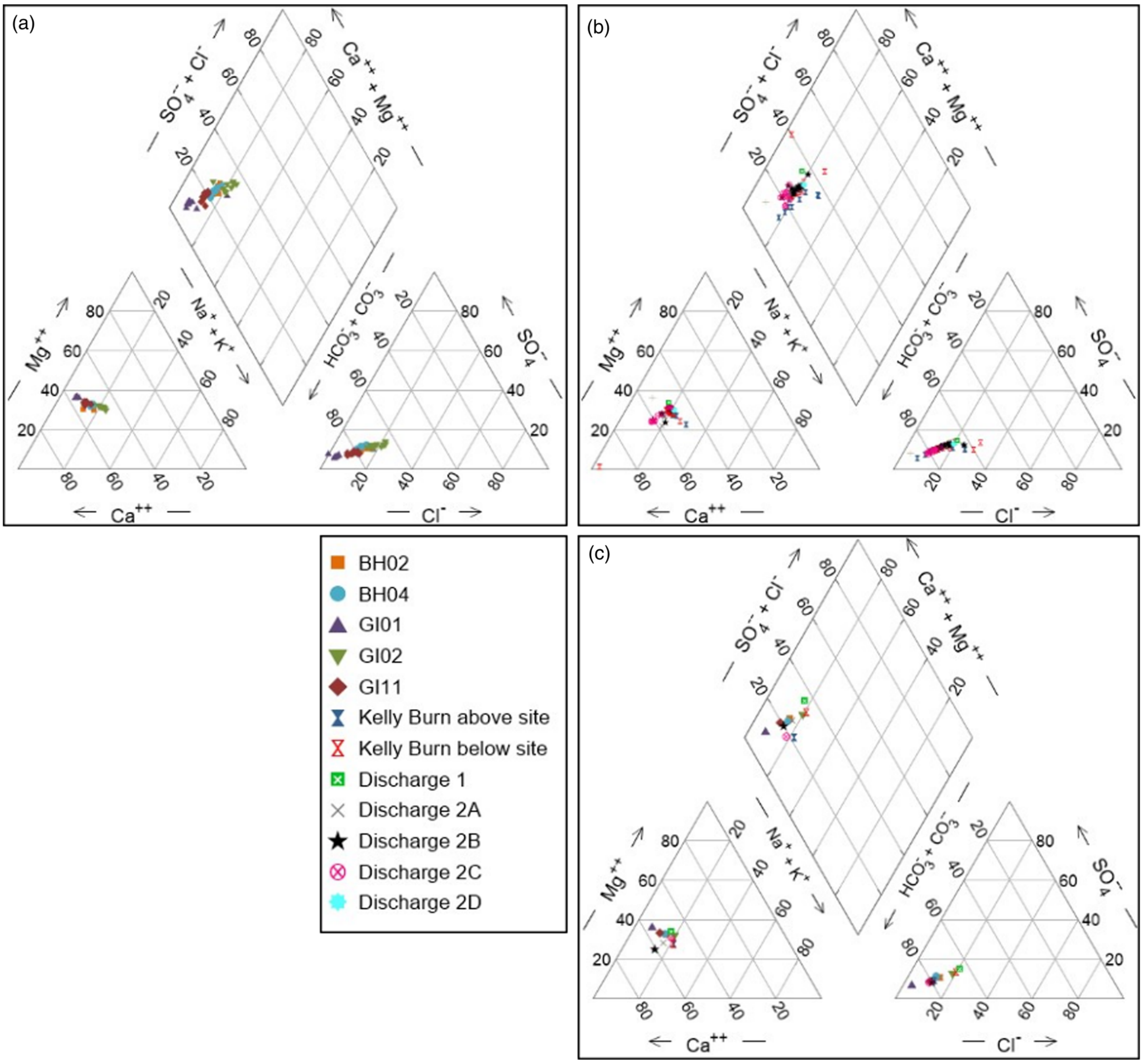

Fig. 12. Water chemistry data from sample locations presented using Piper diagrams: (**a**) borehole and (**b**) discharge water chemistry data from the entire year; (**c**) data from all points for October 2021 (including the Discharge 1 from November 2020 for comparison).

Notably, the iron (total and dissolved) concentration in the new monitored discharges (2A–2C) is lower than it was from Discharge 1 in November 2020 (Table 2) and an order of magnitude lower than the water samples from boreholes.

Elevated sulfate and iron probably reflect iron sulfide (pyrite) oxidation and dissolution, but circumneutral pH values and alkalinity-dominated water types support the common consensus that Scottish mine waters are buffered by dissolution of carbonate minerals in adjacent strata or by alkalinity in the ambient groundwater (O Dochartaigh *et al.* 2011; Farr *et al.* 2016).

Isotopic composition

Quarterly isotopic data for water sampling locations indicate a seasonal fluctuation of dissolved sulfate $\delta^{34}S$ (‰) values (Fig. 13). The broad trend from the boreholes and discharges is towards isotopically lighter values in the spring and summer, with heavier values in autumn and winter. GI11 shows the greatest variability of $\delta^{34}S$ with values typically isotopically heavier than those for other boreholes or discharges, reaching +22.2‰ in winter 2021. The CM1 sample of sulfide from coal pyrite from the Coalsnaughton Main Seam yielded a $\delta^{34}S$ value of +1.7‰. Other studies have shown sulfide from Scottish Carboniferous coal seams to have a wide range of values from −26.3 and +18.4‰, with an overall mean (cleat and banded pyrite) of +2.7‰ (Bullock *et al.* 2018). All data points in this study are isotopically heavier than both CM1 and the arithmetic mean of Bullock *et al.* (2018), but the majority fall within the dominant range of values from Scottish pyrite (Bullock *et al.* 2018). Therefore, it is likely that the sulfate in the mine water is predominantly derived from pyrite oxidation, a derivation that results in negligible fractionation from the parent pyrite. Nonetheless, there appears to be a minor component of isotopically heavy sulfur in the system, especially so in relation to GI11. Such heavy sulfate has been increasingly found in mine water systems e.g. (Burnside *et al.* 2016; Banks *et al.* 2020; Walls *et al.* 2022). Potential sources of this sulfate include evaporite dissolution, ancient brines, carbonate-associated sulfur (CAS), or reduction and fractionation of sulfate by sulfate-reducing bacteria in a closed system (Banks

Table 2. *Median and inter quartile range (IQR) values for total (tot) and dissolved (dis) iron and manganese from sampling points across the field site*

Sample location	*n*	Statistic	Fe (dis) (mg l^{-1})	Fe (tot) (mg l^{-1})	Fe (tot – dis) (mg l^{-1})	% Fe (dis) (mg l^{-1})	Mn (dis) (mg l^{-1})	Mn (tot) (mg l^{-1})
BH02 (Coalsnaughton)	11	Median	0.092	2.2	2.11	4.2	0.236	0.583
		IQR	0.145	1.69			0.377	0.198
BH04 (Coalsnaughton)	11	Median	1.53	4.27	2.74	35.8	0.338	0.369
		IQR	0.275	5.88			0.033	0.058
GI11 (Coalsnaughton)	12	Median	0.709	1.48	0.771	47.9	0.438	0.415
		IQR	0.38	1.06			0.109	0.114
GI01 (Alloa Rough)	11	Median	0.064	1.33	1.27	4.8	0.39	0.392
		IQR	0.065	1.41			0.069	0.082
GI02 (Alloa Splint)	11	Median	0.152	0.729	0.577	20.9	0.312	0.353
		IQR	0.075	0.278			0.031	0.079
Kelly Burn above site	12	Median	0.059	0.236	0.177	25.0	0.008	0.018
		IQR	0.053	0.36			0.01	0.011
Kelly Burn below site	12	Median	0.045	0.156	0.112	28.5	0.062	0.066
		IQR	0.027	0.179			0.049	0.044
Discharge 1	1	Value	1.23	0.916	−0.314	134	0.336	0.314
		IQR	N/A	N/A			N/A	N/A
Discharge 2A	13	Median	0.014	0.098	0.085	13.8	0.006	0.011
		IQR	0.01	0.226			0.002	0.012
Discharge 2B	11	Median	0.099	0.189	0.09	52.4	0.35	0.345
		IQR	0.016	0.036			0.013	0.036
Discharge 2C	10	Median	0.096	0.173	0.077	55.5	0.375	0.377
		IQR	0.055	0.14			0.095	0.126

n, number of samples. Discharge 1 was sampled only once.

et al. 2020; Monaghan *et al.* 2022; Walls *et al.* 2022). However, the former two (evaporites and brines) seem unlikely in a shallow, fresh mine water system with no Permian overburden or indication of evaporites in the local stratigraphy. Similarly, limestone in the local stratigraphy is limited, and therefore CAS seems quantitatively inadequate given the relatively modest alkalinities in the mine water. Thus, further work is needed to explore this heavy end-member, but this should not detract from an isotopic signature in the Dollar mine water system that reflects dominant derivation from pyrite oxidation. Seasonal fluctuation may reflect higher rates of pyrite oxidation during low groundwater levels of spring and summer, when more sulfide-bearing minerals become exposed to oxidizing conditions. With greater pyrite oxidation, more sulfate with a low mean value (see the Bullock *et al.* 2018 mean of *c.* +2.7‰) would be added to the system and lower the overall signature towards the mean.

Oxygen and hydrogen isotopic values from all borehole and discharge samples plot closely to the Global and (Glasgow's) Local Meteoric Water Line (GMWL, Craig 1961; LMWL, Walls *et al.* 2022), and the mean of all of the samples falls essentially within error of the population on the meteoric water lines (mean ± 1σ as follows: $\delta^{18}O = -7.8 \pm 0.3‰$; $\delta^{2}H = -52 \pm 3‰$). This indicates that the mine waters' H_2O component is derived from modern meteoric water and has not undergone significant isotope exchange with minerals or modification by evaporative processes.

Reflections

The findings of this work have been condensed into practical lessons that may apply to other exploratory programmes.

(1) One of the principal challenges at the planning and investigation stages of mine water geothermal projects is sourcing capital funding for exploration. Hybridizing GSI boreholes in areas where there are suspected shallow mine workings offers the opportunity for monitoring wells to be completed into the mine water geothermal reservoir. As our study shows, this allows for the measurement of water level and temperature, and hydrochemical monitoring. The overall budget is greater than that of GSI work alone, but less than separate campaigns of GSI and geothermal investigation. Indicative costs of combined GSI and MWGI have been included for a situation that completes three GSI boreholes as monitoring wells but is controlled by the scale of the additional MWGI work (Table 3). A depth cut-off for when this technique becomes unattractive will probably depend on individual project economics.

(2) Prior to operations beginning on site, data must be collected on existing mining-related features in order to plan investigation works and to evaluate whether investigation works have the potential to alter the hydrogeology of the investigated system.

(3) The extracted coal seam is not always the primary aquifer target, and for collapsed longwall mining there exists a fracture network above the depth of remnant material. Although the range of flow rates obtainable from longwall goaf is unclear, the screened horizon of the borehole should extend across the worked seams and height of any overlying hydraulically active fracture zone. This can be identified by using core logging or proxies from open hole drilling (minor drops or faster penetration rates; H_2S odour from fracture pockets).

(4) In locations of overlapping worked coal seams, care must be taken to avoid creating new hydraulic and thermal short-circuits between them via borehole

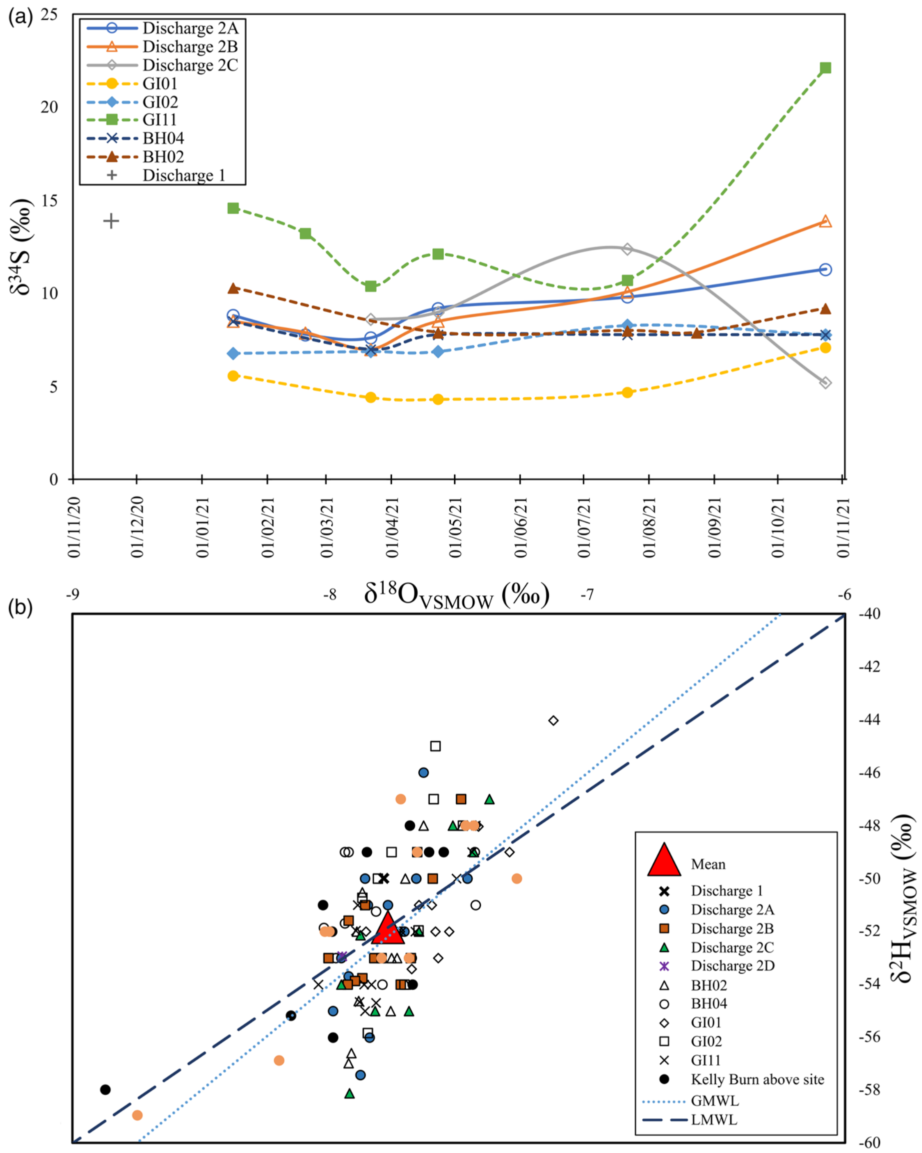

Fig. 13. (**a**) Dissolved sulfate $\delta^{34}S$ data for sampling points plotted across the sampling year (2021). (**b**) $\delta^{18}O$ and $\delta^{2}H$ stable isotope data plotted against Global and Local (Glasgow) Meteoric Water Lines (GMWL; LMWL). Sources: Craig (1961); Walls *et al.* (2022).

annulus pathways. To avoid time- and resource-consuming operations to isolate seams within boreholes, it is advised to drill to deeper target seams in places where shallower seams are unworked.

(5) Ensure water levels and throughflow rates are monitored to allow the scale of the thermal resource to be estimated. Water level and flow rate of shallow collieries can be expected to change with the seasons, reflecting periods with more intense rainfall and lower evapotranspiration. This could be reflected in higher flow rates and thus greater heat availability at specific times of the year.

Table 3. *Generic indicative costs for coupled ground stability (GSI) and mine water geothermal investigation (MWGI) for about 20 GSI boreholes, where three of these are completed as monitoring wells*

Item	Costs (£)
Mobilization	3200
GI borehole drilling and sealing	15300
Completion of three monitoring wells with 50 mm screen and liner	2600

(6) Chemical analyses allow an improved understanding of source and history of mine waters, whereby certain parameters can influence the potential for scaling (and thus engineering design) of a mine water geothermal system. Full analysis of major and minor cations, together with iron and manganese, and field analysis of temperature, pH and a redox indicator, is regarded as a minimum initial chemical suite for MWG allowing an assessment of scaling and/or corrosion potential.

Limitations

Following on from the reflections and recommendations made by the authors, we feel it is necessary to summarize some of the limitations of this technique, which may render such an approach challenging or unattractive.

(1) The depths of any boreholes are probably limited by budget constraints of the project funder. Although it may be reasonable to extend boreholes an extra few tens of metres beyond the initial target depths, the maximum depth will probably be governed by

funding and time allocation. Similarly, if mine workings are at a greater depth than GSI boreholes are mandated to reach, extending only one or two may be feasible, rather than expecting to complete multiple boreholes (e.g. five in this study).

(2) The additional time and financial resources required to upgrade GSI boreholes to monitoring wells, with liners and standpipes as a minimum, is often cost effective. However, it is accepted that there is a significant time commitment required to subsequently monitor and sample the boreholes on a monthly basis. A private investor may view work of this nature as beneficial only if they are serious about considering mine water as a thermal resource.

(3) Comprehensive mine water test pumping programmes cannot be performed on boreholes with GSI diameters (50 mm ID completion) owing to sizing, but falling head tests for indicative transmissivity values and aquifer response remain feasible.

(4) A 5 inch (127 mm) diameter GSI borehole may be too narrow for some enhanced borehole characterization or may at least require slimline probes (e.g. downhole geophysical logging or CCTV).

Conclusion

Ground investigation boreholes were drilled into the strata and workings of Dollar Colliery, Clackmannanshire, Scotland. Five were completed as mine water geothermal monitoring wells to inform a mine water conceptual model and to collect geochemistry and temperature data. The coal-bearing syncline provides a relatively small, isolated worked basin with mine workings dating back many hundreds of years, but the majority of coal extraction was in the decade following 1943. The associated ground stability report is confidential, but the use of shallow mines for mine water geothermal energy application remains plausible, provided ground stability recommendations are adhered to. The encountered coal mine conditions included voids, intact coal, mining waste and goaf, which were interpreted on the basis of wellhead observations during drilling. The Coal Authority and SEPA were informed that a change in the mine water flow regime was noted, whereby the previously established discharge ceased and water began discharging from the original Day Level. Boreholes were completed into each of the worked coal seams beneath the site, with impermeable seals installed in annuli to ensure these did not create new hydraulic connections between mined horizons. Monthly sampling of boreholes and discharges provided insight into the mine water regime within these coal workings. The mine water regime appears unstratified and hydraulically connected across the different seams and areas of working. Mine water has a low dissolved solute content and shows only minor temperature fluctuations, relative to local air and stream temperatures. Following conceptual modelling, chemistry and temperature analysis, the progression of this site towards a housing development utilizing mine water geothermal should be subject to further detailed investigation including pumping and re-injection tests. A suitable mine water geothermal configuration must consider the inherent ground stability risk, with utmost consideration for adequate monitoring and mitigation.

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