Cave and Karst Science, Vol.52, No.3, (2025) 95 – 100
Transactions of the British Cave Research Association

ISSN 1356-191X

Karst groundwater exhibits piston-like response to heavy rainfall during winter Storm Franklin in 2022 (Derbyshire, UK)

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Abstract: The hydrology of karst regions which have experienced mining is complex, and the impact of drainage from mines and mine waste can have a strong negative impact on water quality within springs and rivers. This can be diffuse and affect water quality under base flow conditions, but acute events can also occur when highly mineralised groundwater is displaced by high rainfall events. This study reports changes in the chemistry of a karstic conduit during an extreme rainfall event in 2022. The site, Goodluck Mine in Derbyshire (UK), has a long mining history and abundant mine waste underground and on the surface. Water which has equilibrated with this waste could be displaced into the Derwent–Trent river system, and affect water quality downstream. We report a strong displacement of water during a named storm in February 2022, which created a pronounced piston effect where older groundwater was displaced by infiltrating rainwater. The older water has a higher temperature and conductivity than the baseflow water, and so originated from a perched water body in the unsaturated zone. However, whereas acid mine drainage would result in this water having lower pH than the baseflow water, we find that similar events later in the year had higher than baseline pH. Consequently, we conclude that the water displaced had mineralized in contact with country rock, not with mine waste deposits. The approach used here can straightforwardly be transferred to other mined karst regions to identify local histories of piston-flow water.

Keywords: epikarst hydrology; extreme weather events; industrial legacy pollution; water quality.

***Received**: 06 June 2025; **Accepted**: 08 October 2025.*

Introduction

Karst hydrology is complex, and becomes more complex when it is impacted by historical anthropogenic activity such as quarrying or mining (Andriani and Walsh, 2009). Multiple hazards can arise from this interaction, ranging from flooding to both transient and persistent pollution impacts on groundwater and surface water which is wholly or partially derived from orphan industrial sites (Parise and Gunn, 2007). Where historical mining has left a legacy of persistent, bioavailable pollutants such as heavy metals, complex patterns of distribution and accumulation arise partitioning hazardous materials between soil, biofilm plant and animal inventories (Hansson *et al*., 2019). These inventories may be accessed and remobilized during environmental events outside normal variability, such as during flooding (Mayes *et al*., 2021), and the spatial and temporal occurrence of storm events is itself subject to influence from climate change (Shaw, 2019). Forecasting the impacts of legacy heavy-metal mining in karst areas influenced by extreme storm rainfall on aquatic ecosystems, water resources and derived fluvial sediments is therefore very challenging indeed. Nevertheless, there is a need to be able to predict and manage these impacts as part of both natural environment stewardship and human water usage monitoring.

The southern Peak District of Derbyshire, England (Figs 1a and b) has a history of lead mining dating back at least to the Roman occupation of the region (Bradwell, 2014). This is part of lead mining activity throughout the Pennine Hills of northern England, of which the Peak District is the southernmost extent. Mining continued beyond the Roman period (Kiernan and Van de Noort, 1992; Ford and Rieuwerts, 2000), with increasing production in the 18th century reaching peak production in the early 19th century (Willies, 1990). The industry had declined to a remnant by 1850, leaving a legacy of mines and waste tips across the region (Lageard *et al*., 2008), which are incompletely mapped and managed on an *ad hoc* basis depending on land ownership and their proximity to other infrastructure. The region also has well-developed karst drainage (Gunn *et al*., 2006) formed within the Tournasian–Brigantian age Peak Limestone Group, which is over 500m thick (Waters *et al*., 2007). This region is potentially subject to the problems and complexities of managing heavy metal pollution from these legacy sites into karstic groundwater outlined above. This groundwater is ultimately exported from the region via rivers and flows into the Trent, the largest catchment region in England. This water then passes through regions where river water is used for recreation, agriculture and public supply for the urban populations of the cities of Derby and Nottingham before passing into the Humber estuary and debouching into the North Sea. Analysis of baseline groundwater within these catchments shows little evidence of contamination, and good water quality (Abesser and Smedley, 2008), but it remains important to consider whether this can change during abnormal flow scenarios.

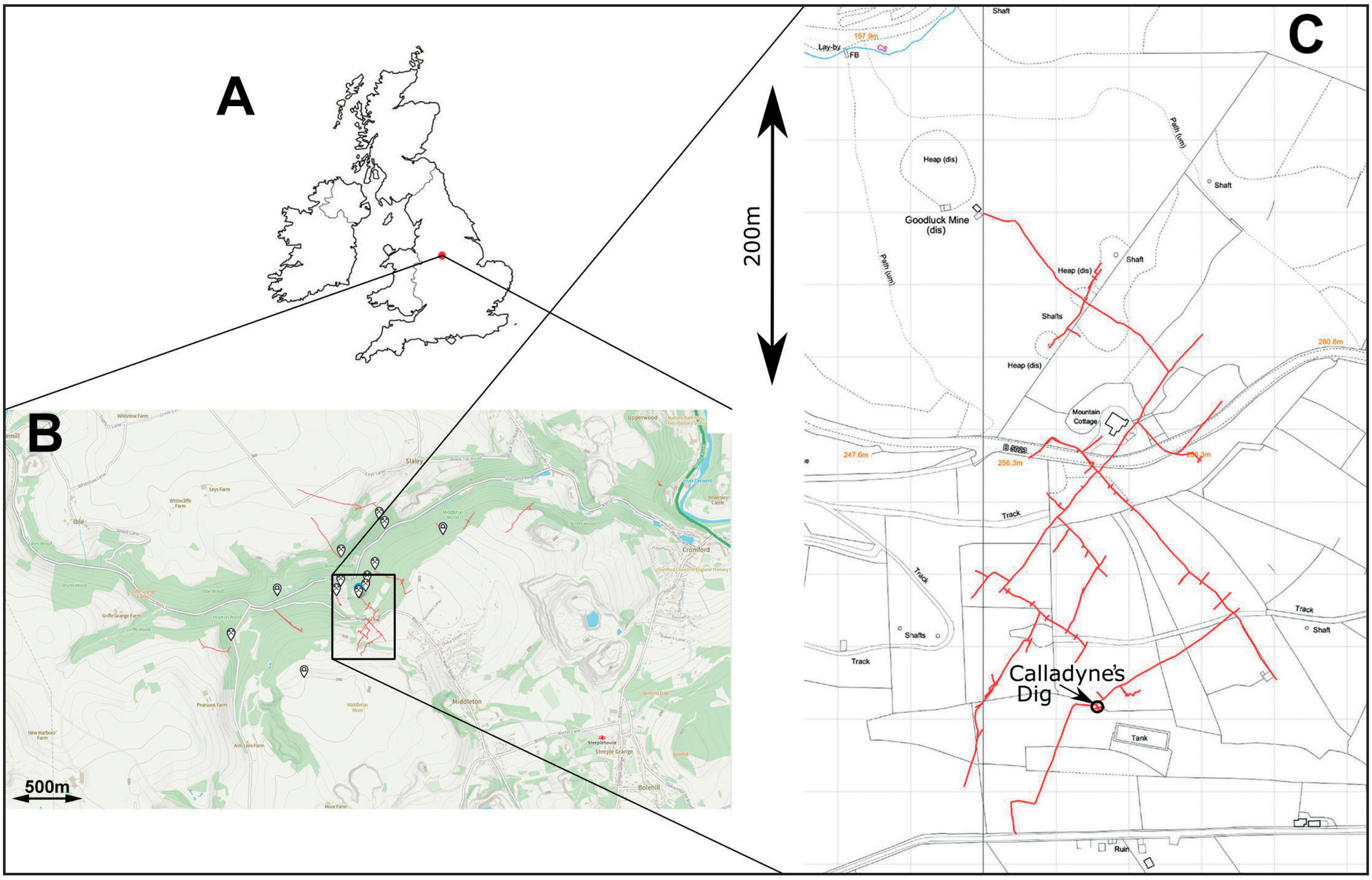

Figure 1:
A: *Location of Goodluck Mine in the UK;*
B: *Mine survey located within the Via Gellia (from Peak District Caving* [https://peakdistrictcaving.info/home/the-caves/derwent-south/good-luck-mine]*;*
C: *location of Calladyne's Dig within the Mine Survey (Flindall and Hayes, 1972).*

Via Gellia and Goodluck Mine

The Via Gellia road (Fig.1b) runs through a steep, wooded valley cut into the Monsal Dale Limestone, with the Lower Matlock Lava Member (Waters, 2003) cropping out on both valley sides at the break in slope between the steep sides and the sloping moorland to the north and south. The Bee Low Limestone Formation, an Asbian age fine- to medium-grained calcarenite, outcrops below the lava in the steep valley sides, both sides of the valley. The valley has a long history of lead mining, including the exceptionally well-preserved Goodluck Mine (British National Grid location 4526973 356505; Fig.1c). Goodluck Mine consists of several early 19th Century shafts connected by an adit, which access the Silver Eye and Goodluck veins, the latter of which contains about 5% granular galena (Ford and Rieuwerts, 2000). The mine was worked extensively through the 1830s, but was essentially exhausted by 1840 with only sporadic subsequent extraction from then until 1952, when the adit entrance was demolished before efforts to open it again starting in 1970 (D. Barrie, pers. comm). It was approved for public access as a heritage site in 2007. The modern survey (Fig.1c) is not a complete record of the mining works, which are considerably more extensive. However, the miners used previous mineworks to dump rock and gangue waste from ongoing workings, and they are consequently generally filled with loose, coarse gravel. The extent of accessible workings today largely reflects the work of the Goodluck Mine Preservation Society, who maintain and continue to clear this important piece of industrial archaeology.

At the farthest extent of the mine, at Jubilee Dig and Calladyne's Dig (the latter marked on Fig.1c) the workings intersect natural cave passageway, and a small streamway is accessible for a few metres. This streamway takes water from above and south of the mine, and at the point of intersection with the mine is at approximately 50m below land surface. At Calladyne's Dig, the stream enters as a small cascade, and is captured into an artificial (aluminium and plastic) channel, which pools the water before it exits via gravel into the Jubilee Dig to the east. This karstic streamway drains the unmined limestone of the valley side, the extensive spoil-filled shafts within its catchment, and the surface deposits of spoil left after mining. Dye-testing has not been performed at Goodluck Mine, but the water might drain into the Bonsall Brook in the Via Gellia valley or, more likely, to Meerbrook Sough, although it is possible that drainage is via the Alabaster Sough or Cromford Sough (Ford and Gunn, 2007).

The 2021 / 2022 winter storm season in the UK

The winter of 2021 / 22 saw six named storms impact on the UK, with three triggering a rare "Red Warning" for extreme winds associated with storms Arwen (26–27 November 2021), Dudley (1–17 February 2022) and Eunice (18 February 2022). Three of the storms (Dudley, Eunice and Franklin) occurred within a single week (16 to 21 February 2022) representing an unusually severe winter weather impact (Kendon, 2022). Persistent and heavy rain throughout the week, together with snow at higher levels, caused flooding in England, Wales and Northern Ireland. Three sites on the rivers Severn, Mersey and Derwent recorded their highest ever levels (Kendon, 2022). Around 400 properties were flooded (Kendon, 2022), with severe flood warnings issued for several major rivers including the River Derwent, its tributaries the Wye and the Amber, and the Trent, into which the Derwent flows (Environment Agency historical data – https://www.data.gov.uk/dataset/d4fb2591-f4dd-4e7f-9aaf-49af94437b36/historic-flood-warnings2#licence-info). Estimates from the HadUK-Grid dataset (Hollis *et al*., 2019) suggest that more than 200mm of rain fell across parts of the Pennines, with the region experiencing whole-month February 1991–2020 rainfall averages in a 9-day period (Kendon, 2022). West Yorkshire, about 40km north of the Via Gellia study site,

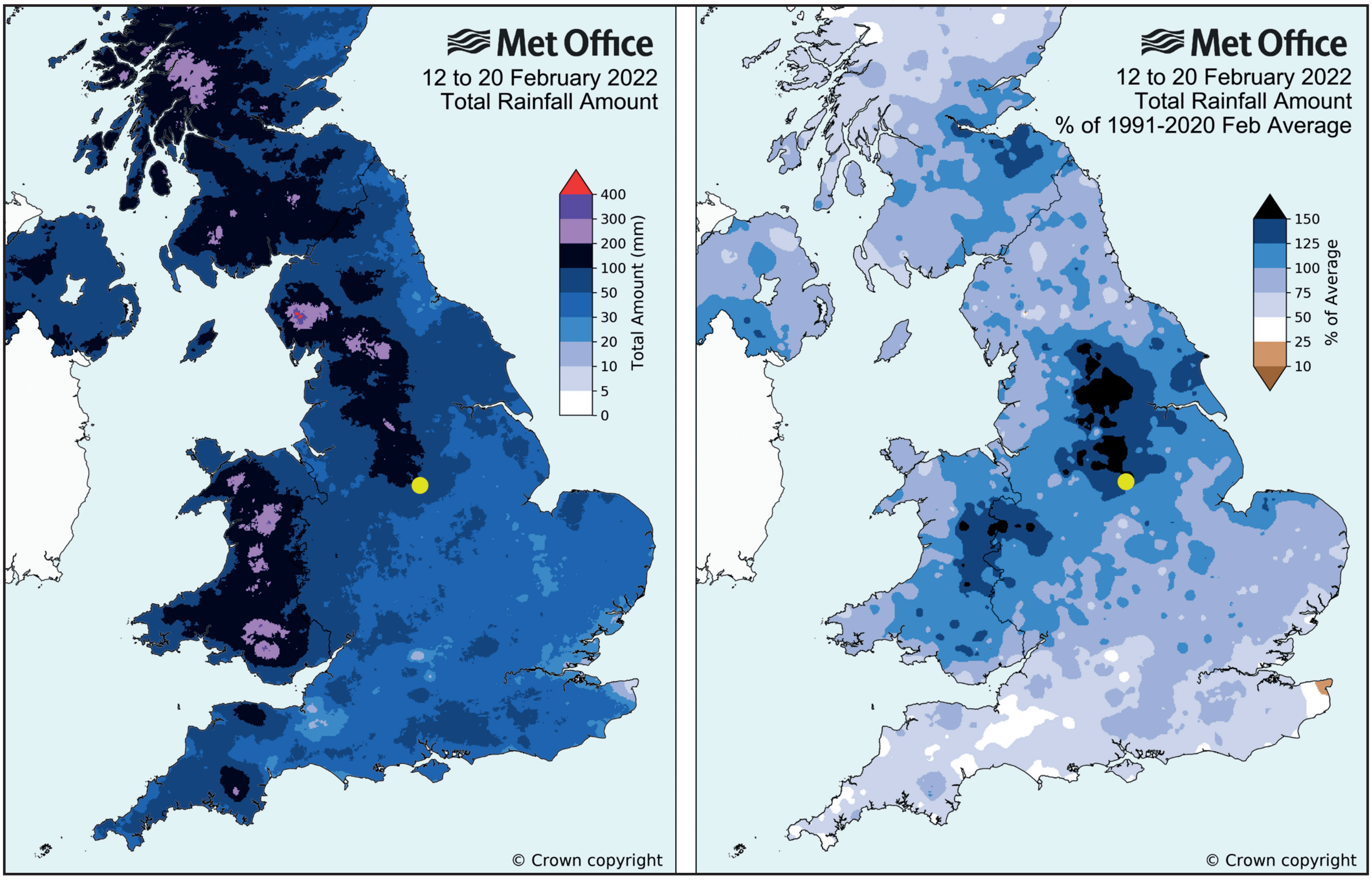

***Figure 2**:*
*(**Left**) total rainfall amount 12–20 February 2022; (**right**) percentage of average 1991–2000 total rainfall for February observed during 12–20 February 2022. The location of Goodluck Mine is indicated by the yellow circle.*
Reproduced with permission from M Kendon (Kendon, 2022). The maps are based on the HadUK-Grid dataset (Hollis et al.*, 2019).*

experienced 224% of the whole-month February 1991–2020 rainfall average (Kendon, 2022). The area around the Via Gellia study site itself experienced ~150% whole-month February 1991–2020 rainfall average during the 9-day period 12 to 20 February 2022 (Fig.2).

Methodology

A cave monitoring station was installed in the streamway at Calladyne's Dig in Goodluck Mine in December 2021. The station includes air temperature and CO_2 recording and water isotope sampling in addition to the automatic and manual sampling described here. However, here we report data only from a water temperature and conductivity logger (Onset Hobo U4-001 device) and a water temperature and pH logger (Onset Hobo MX2501). These measurements were made in a plastic water bath into which streamway water is funnelled via a v-shaped aluminium channel. Under normal flow conditions, the water bath takes less than 10 minutes to fill, giving constant water depth for the loggers while not providing significant smoothing for the logger records if recording is done at lower frequency. The conductivity was recorded every 2 hours and pH every 0.5 hours. The pH logger was calibrated using Onset 4, 7 and 10 pH buffer solutions before deployment and during manual sampling visits. Both loggers were also corrected by external calibration using data collected from a Myron Ultrameter during manual sampling visits. The Ultrameter was calibrated using 1413 mS and 4, 7 and 10 pH buffer solutions the day before the visit. External correction was done post-hoc by reconciling logger data to start and end values from the ultrameter for each phase of deployment, assuming linear drift for the periods in between. The data were then inspected visually for jumps or drifts that might arise from this correction procedure, and remaining gradient changes (e.g. day 150 to day 225) or abrupt transitions (around day 280) do not arise from this process. Data from the pH logger are not available for the entire period. It was not installed until day 150 because initial problems with calibration caused the instrument to be returned to the laboratory.

Manual sampling visits, including the external correction measurements outlined above, occurred on: 10/12/2021, 28/01/2022, 06/05/2022, 14/06/2022, 04/07/2022 and 11/11/2022.

Samples were recovered for bulk and trace element analysis by ICP-OES and dissolved inorganic carbon content evaluation. All samples were filtered at 0.22mm using an in-line PES filter and a plastic piston-syringe before being placed into sample bottles and stored at 4°C until analysed. Samples for chemistry were recovered into a 30ml bottle produced with 1ml of 5% $HNO_{3(aq)}$, which is the wash-acid used in the ICP-OES instrument and therefore represents a blank solution. Analysis was done at Northumbria University using a Perkin Elmer Optima 8000 instrument The selection of the analytical lines used in the results was based on the Perkin Elmer recommendations for the Optima 5300DV spectrometer. Calibration standards are diluted from SPEX CertiPrep 100ppm multistandard, diluted with 18.2 MW ultra-pure water.

Samples for Dissolved Inorganic Carbon (DIC) analysis were filtered into a new 12 mL exetainer that had been dosed with 20 mg of analytical grade $Sr(OH)_2.8H_2O$ powder providing excess hydroxide and strontium to trigger precipitation of the DIC as strontianite, following the approach suggested by Bastianini (2021) following Singleton *et al*., (2012). The octahydrate form of the hydroxide was selected because this is more soluble, facilitating the displacement reaction. The reaction was given at least a month to complete at 4°C, inside the sealed exetainer tube. Solid strontianite was then recovered by filtration and the mass measured using a Mettler-Toledo microbalance.

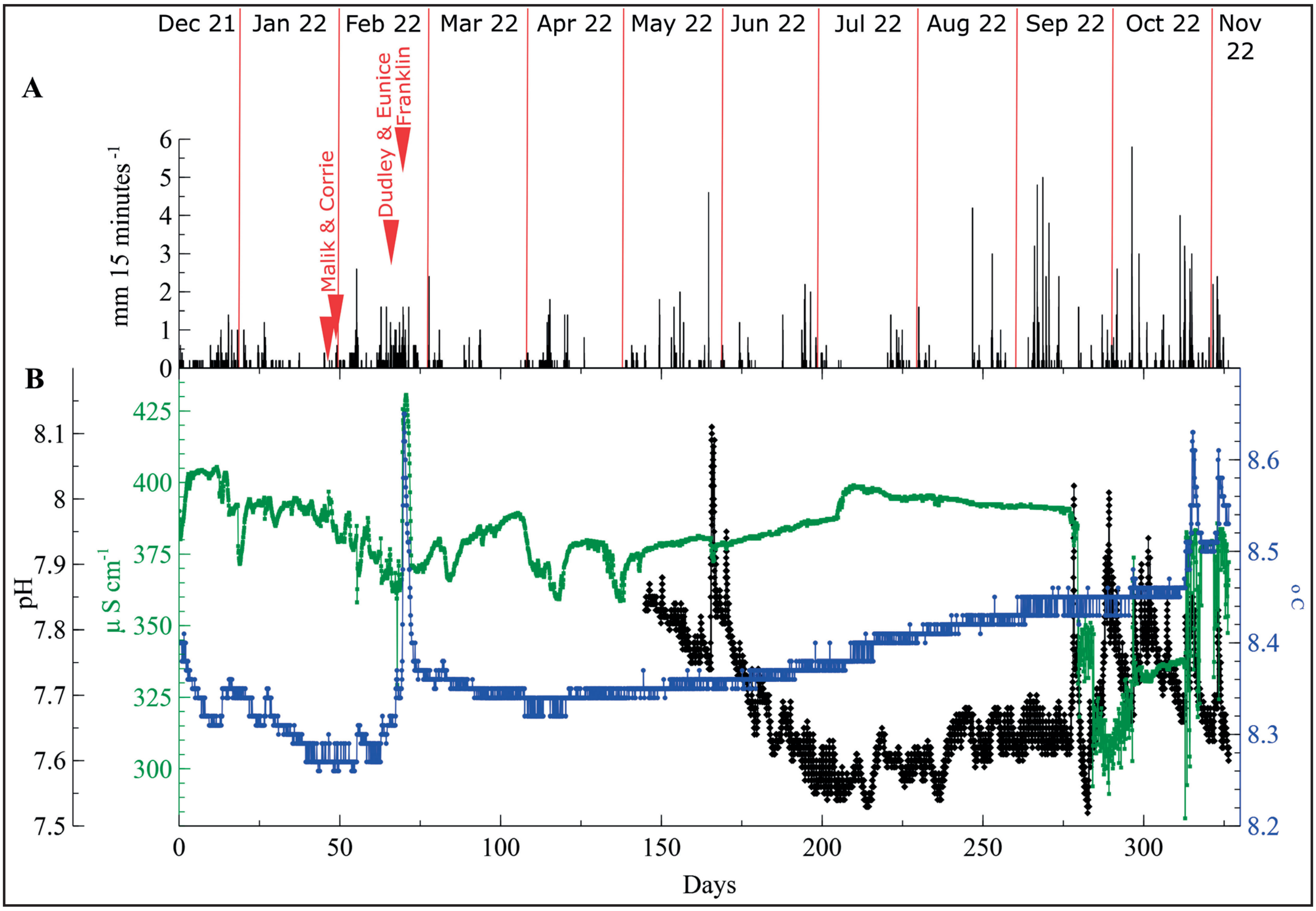

***Figure 3: (A)** rainfall at the Environment Agency weather station at Longcliffe in mm per 15 minutes.*
***(B)**: pH (black), conductivity (green) and temperature (blue) in the streamway at Calladyne's Dig.*

Results

Figure 3 shows water temperature and water conductivity in the streamway in Calladyne's Dig from December 2021 to November 2022, and pH from water in the same streamway is recorded from May 2022 to November 2022. Rainfall values shown on Figure 3 are from publicly available UK Environment Agency data for the closest meteorological station (Longcliffe – WISKI ID 104003 – at 53° 05′ 38.94″ N 001° 39′ 34.16″ W), a horizontal distance of 4.3km from the mine entrance. The major storms of the 2021–2022 winter season described in section 2.3 are marked.

Water conductivity increased very rapidly in late February, which is embedded within a period of variable conductivity lasting until late spring (early May). From early May until mid-September conductivity is high, rising and generally stable aside from a broad peak in early July, after which the conductivity falls slowly. A major transition to lower conductivity occurs in mid-September, followed by a period of amplified variability between values close to the spring–summer values (~275–400 mS cm^{-1}) and the low values first established in late September (~300–325 mS cm^{-1}).

Water temperature is generally more stable than conductivity, although the abrupt conductance peak in late February occurs simultaneously with temperature as a brief peak with amplitude ~0.4°C. From the end of March to November, the water temperature rises slowly, with two additional abrupt peaks in October and November; these again correspond to peaks in conductivity.

Unfortunately, the pH logger was not in place during the February peak recorded in other parameters, but it was in place during the later two peaks in October and November. In both cases, the peak is reflected initially in a shift of ~0.2 units to a higher pH value, followed by a fall back to base-level after less than 24 hours at the higher value. The same characteristic is found at the transition to lower conductivity in September, with an initial peak to above pH 8 followed by a drop to almost pH 7.5 during the period of falling conductivity. Other peaks in pH that occur at the end of May, end of September and in early October, are respectively associated with a small decrease in conductivity (~5 mS cm^{-1}), a strong decrease in conductivity (~30 mS cm^{-1}) and no consistent change in conductivity. These peaks are superimposed onto a longer trend in pH that is the inverse of conductivity, with falling values from the start of the record to early July, followed by a slow rise in pH to the abrupt transition in September. Additional variability in pH is quasi-cyclic with an amplitude of 0.05–0.1 units and a wavelength of around 8 days. This extremely low-amplitude variability may be environmental, or might relate to instrument variability, and these two effects are impossible to diagnose from the current dataset. We therefore do not offer an interpretation of this fine-scale variability.

Although not every peak in rainfall corresponds to an abrupt change in conductivity, and/or temperature and/or pH, the abrupt peaks in February (temperature and conductivity, pH not known), early October (pH and minimum in conductivity), late October (temperature, conductivity and pH) and November (temperature, conductivity and pH) all correspond to major rainfall events. The peak in pH (small decrease in conductivity) in late May, the abrupt transition in pH and conductivity in September and the pH peaks at the end of September and in early October also correspond generally to significant rainfall events, but other rainfall events of the same size do not cause conductivity/pH responses in the groundwater. Consequently it is challenging to infer a causative relationship.

Analysis of water samples from monitoring visits provides the summary spanning the period shown in Table 1.

***Table 1**: Chemical summary of water in the Calladyne's Dig streamway during monitoring visits.*

Date	pH	Conductivity ($mS\ cm^{-1}$)	Ca $mg\ L^{-1}$	Dissolved Inorganic Carbonate $mg\ L^{-1}$	Mg $mg\ L^{-1}$	Ba $mg\ L^{-1}$	Cr $mg\ L^{-1}$	Cu $mg\ L^{-1}$	Zn $mg\ L^{-1}$
10/12/21	7.5	0.78	66.22	137.8	1.43	0.41	0.23	0.12	0.32
28/01/22	7.6	0.39	58.25	115	1.24	0.37	0.22	0.11	0.29
06/05/22	7.0	0.376	79.68	206.75	2.23	1.52	1.29	0.71	1.70
24/06/22	7.4		82.33		3.25	3.19	2.79	1.55	3.66
04/11/22	7.3	0.3874	81.50	45.92	1.60	0.36	0.90	0.94	0.34

Discussion

Impact of Storm Franklin

The change in groundwater conditions during storms Eunice, Dudley, and Franklin (Fig.4) began on 20 February (Day 69), between storms Eunice (18 February) and Franklin (21 February). The stream water temperature peak reached maximum during the night of 20/21 February and corresponds to the extreme rain related to Storm Franklin. Streamwater conductivity peaked in the late morning of 21 February, after rainfall had stopped. The two events have the same duration despite decoupling of peak timing and the trajectory of the return to background conditions, with temperature showing a pronounced asymmetry not found in the conductivity data. It is worth noting that streamwater temperature does not actually return fully to the same value as before the event, rather stabilising at 8.35°C, ~0.05°C higher than before. Initially temperature continues to fall as it had been doing before the storm, before rising again after the start of April, presumably as longer spring days warmed the ground.

The periods of raised values in both streamwater temperature and conductivity lasted almost 72 hours. At peak, the anomaly in conductivity was 65 $mS\ cm^{-1}$. Although we lack flux data, the close correspondence with rainfall makes it highly likely that high conductivity corresponded to high discharge, making flux and conductivity positively correlated (Evans and Davies, 1998). Generally, flux and discharge are inversely related in karst systems due to the time required for water passing into the aquifer to equilibrate with the limestone (Ford and Williams, 2007), but positive correlation is known in karst settings (Le Mesnil *et al*., 2022). This water is also warm relative to background, and so must have been displaced from the soil, epikarst or aquifer where seasonal changes are significantly damped by soil insulation (at least 2m depth, (Garcia Gonzalez *et al*., 2012)). Consequently, the changes observed during the February Storm Peak reflect a piston effect, where rapid input of new water via the soil displaces water at depth that was otherwise isolated from groundwater flow (Ashton, 1966). The lag time (~8 hours and duration of the event (~72 hours) are within the typical range of piston events, although they are relatively short and long respectively (Ashjari *et al*., 2024). As both these values depend primarily upon the volume of water storage capacity available in the epikarst, with short timings reflecting low storage capacity, the combination found here of fast response and long memory are not expected. It is likely that this reflects the wider connectivity of conduits in the aquifer, but resolving exactly what has given rise to these characteristics of the hydrograph is beyond the scope of this study. The longer duration of the change in temperature relatively to conductivity (Fig.4) reflects the shift from purely displaced water to a mixture of displaced and new rainwater, which is typical of piston events in karst settings.

Understanding the cause of the conductivity change during the February storm peak would require a larger water chemistry dataset than that currently available. However, as confirmed other karst systems, conductivity will largely reflect the Ca and dissolved carbon concentrations derived by bedrock dissolution.

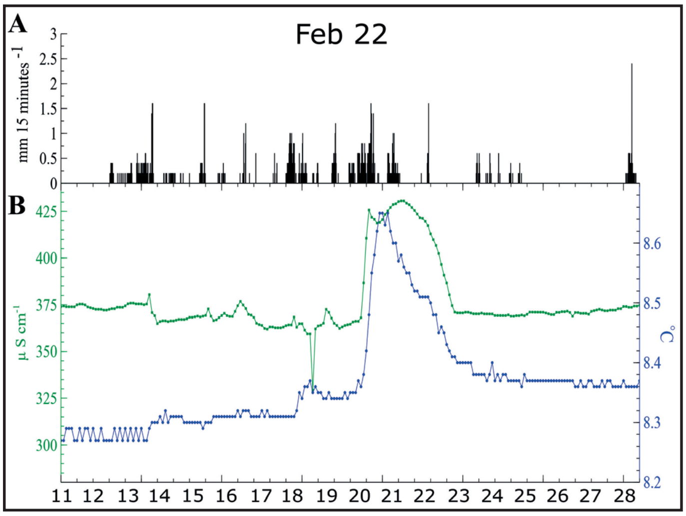

***Figure 4**: **(A)** rainfall at the Meteorological Office weather station at Longcliffe in mm per 15 minutes;*
***(B)** conductivity (green), and temperature (blue) in the streamway at Calladyne's Dig.*

For water quality, the important question is whether concentrations of potentially harmful contaminants that are likely derived from mining waste (Ba, Cr, Cu, Zn) are also raised in high conductivity water. Unfortunately, the pH logger was not in place to record this peak, but smaller simultaneous peaks in temperature and conductivity are recorded in October and November 2022, and both of these show higher pH, which is incompatible with a strong input of acid mine drainage-affected water (Wolkersdorfer, 2008). In the two peaks where temperature, conductivity and pH are all registered, the former two measurements fall back to baseflow values after about 72 hours. However, pH returns more rapidly. The asynchronous and early fall of pH compared to conductivity is consistent with the first flush of displaced water being drawn from a body that has equilibrated fully with bedrock, followed by water that has not equilibrated fully and so retains higher $CO_{2(aq)}$ and consequently lower pH. A change in the water source is also the most likely explanation for the different shapes of the temperature and conductivity curves in the February piston-flow event described above.

At least for the Goodluck Mine site, the combined temperature/conductivity/pH behaviour is a positive finding, because it is not likely that this water was more contaminated with the zinc, barium, lead and cadmium than under background conditions. The quality of the water remains high, even under strong piston-flow scenarios.

Other impacts on cave streamwater behaviour

It is likely that the prominent transition in conductivity to lower values in September (Fig.3) reflects recharge of normal winter groundwater pathways shortly (~6 days) after the first period of sustained rainfall at the end of the summer. The summer period of relatively low rainfall, and therefore water deficit, is reflected in the stable, rising, trend in conductivity (falling trend in pH) from May to July, and high but slowly falling conductivity (low but slowly rising pH) from July to August.

The maximum in conductivity (minimum in pH) during this period corresponds to the longest period without rainfall in summer 2022 (>18 days). It is likely that this maximum records the water that has dwelt in the soil and epikarst for the longest time, and has thus degassed most completely. Presuming equilibrium between soil CO_2 and geogenic carbon derived from limestone dissolution, this implies loss to atmosphere of CO_2 that is derived from Carboniferous limestone. Variance in conductivity (for example in April 2022), in pH in late May 2022, and in conductivity and pH in late September–October 2022, does not relate to significant changes in rainfall (Fig.3) and cannot fit into this framework. Such variance must reflect changes in groundwater routing not forced by rainfall. Data available do not support attribution of the cause of these effects, but they provide important evidence that not all changes in this system are a primary impact of local rainfall effects.

Conclusions

Here we report a piston-like groundwater flow event arising from extreme winter rainfall in Derbyshire, UK during February 2021. This piston-like flow into Calladyne's streamway in Goodluck Mine displaced a body of groundwater that was not affected by contamination from historical mine waste. During the flow event, it is likely that the piston-like flow first displaced water that has been in contact with ground air before mobilising deeper phreatic water, which had not equilibrated with air. Whereas no other event in the 12-month period analysed here is of the same size, other piston-like events are found that are also related generally to periods of high rainfall.

The potential for identifying and understanding synoptic groundwater movement in historically mined karst regions from this type of data is clear, and provides a framework for additional sampling and investigation. The finding that piston-like events transport water that is less affected by historical mining contamination from storage is potentially important, because it implies that drainage under normal flow is more focussed into areas where mine waste is stored than it is along pathways utilized during high-flow conditions. This change in pathway behaviour implies that extreme flow events carry reduced risk of contaminating water resources. The potential for automated conductivity and pH logging to be a key part of providing the highly-resolved spatial and temporal observations that are needed to test this hypothesis fully is clear, but only when the logging is supported by manual or auto sampling of water that can be subjected to more-advanced analysis.

Acknowledgements

This paper is one output of the "Reforesting Limestone" project, generously funded by The Woodland Trust. Sponsorship for equipment was provided by Tempcon, and we are grateful for their help and advice as well as for the components that their sponsorship allowed us to put into the project. Sebastian Breitenbach, Andrew McLeod, Sam Jones and Carol Mahoney assisted with fieldwork, as did David Barrie and the members of the Goodluck Mine Preservation Society, whose generosity in providing access to the mine – and good company – were greatly appreciated. Michael Kendon is thanked for permission to reprint figures from his excellent report on the storm events:
(https://www.metoffice.gov.uk/binaries/content/assets/metofficegovuk/pdf/weather/learn-about/uk-past-events/interesting/2022/2022_01_storms_dudley_eunice_franklin_r1.pdf).
Cal Hazell is thanked for assisting with the ICP-OES analyses. John Gunn is thanked for his advice on sourcing appropriate rainfall data. The paper has benefitted from discussion by two reviewers, Ian Fairchild and John Gunn.

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