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Sustainability of thermal energy production at the flooded mine workings of the former Caphouse Colliery, Yorkshire, United Kingdom

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Abstract

Abandoned, flooded, coal mine workings are an artefact of fossil fuel exploitation that can be repurposed as a renewable energy resource. The warm subsurface waters that fill former workings can be developed to provide efficient and low-carbon heat generation using ground source heat pumps. In order to determine the long-term suitability of flooded mine workings as a sustainable thermal resource we have to understand the hydrological components of the system and how they interact in response to exploitation-related disturbance. We investigate pump induced mixing dynamics at the former Caphouse Colliery, which has been pumped since 1996 for regional water level management but only recently started to be explored as a thermal resource. Initial findings from the first 6 months of study show virtually no variation in physiochemical, major ion or stable isotope values. However, placed in context with archived values from 2004 to the present, we see a general pattern of mine water quality recovery punctuated by a doubling of Cl⁻ values (150mg/l to >300mg/l) which may suggest recent ingress of deeper-sourced saline waters. This is supported by O and H isotopic values, which are indicative of ancient, perhaps Late Pleistocene, confined waters. Sulphur isotope values (19.7-23.8‰) are abnormally high as compared to typical values for Carboniferous Coal Measures (5-10‰). There is no simple explanation, so further data collection and investigation is required, though we note that these values are similar to Lower Carboniferous seawater values. The relative stability of recent parameters suggests that Caphouse waters represent a dependable thermal resource. However, much about the hydrogeology of the Caphouse system is still uncertain, so further work is required to check the persistence of recent trends.

Key Words: Coal, Low-carbon, Energy, Heat-generation, Hydrology, Ground source heat pump

1.1 Introduction

Former coal mine workings represent an opportunity to develop a scalable low-cost and low-carbon heating resource. True thermal potential in the UK is currently uncertain but initial extractable heat estimates of 12MW for the Midland Valley of Scotland (Gillespie et al. 2013) and 55MW for the 17 largest Coal Authority pumping operations across the UK (Parker, 2011) suggest a potentially significant resource. Without active pumping, the subsurface voids that are a legacy of the coal mining process naturally flood to form large bodies of water that, unlike surface waters, maintain a relatively constant temperature through the year. This stability in temperature makes mine waters particularly attractive for ground source heat pump applications that maximise system efficiency.

1.1.1 History of the Caphouse Colliery

The former Caphouse Colliery, now the site of the National Coal Mining Museum of England (NCMME), is located in Overton, near Wakefield, Yorkshire, UK at 53.6416°N 1.6251°W at an elevation of some +147 m asl (Hope Shaft top). The Caphouse complex comprises several shafts and drifts (Brown & Goodchild, 1979) working seams throughout Westphalian Pennine Middle and Lower Coal Measures. These strata consist of cyclical fluvio-deltaic sequences of interbedded sandstone, siltstone, mudstone, coal and associated seatearth (INWATCO, 2005a). Marine influences were less frequent within the upper part of the Lower Coal Measures and the lower part of the Middle Coal Measures (Waters, 2009), leading to prolonged periods of peat accumulation and the eventual formation of thick, good quality bituminous coals (Waters and Davies, 2006). Sulphur content from elsewhere in the Yorkshire Coalfield averages $2 \pm 1\%$ and correlates strongly with iron, indicating that pyrite dominates sulphur content in the coal (Spears and Tewalt, 2009).

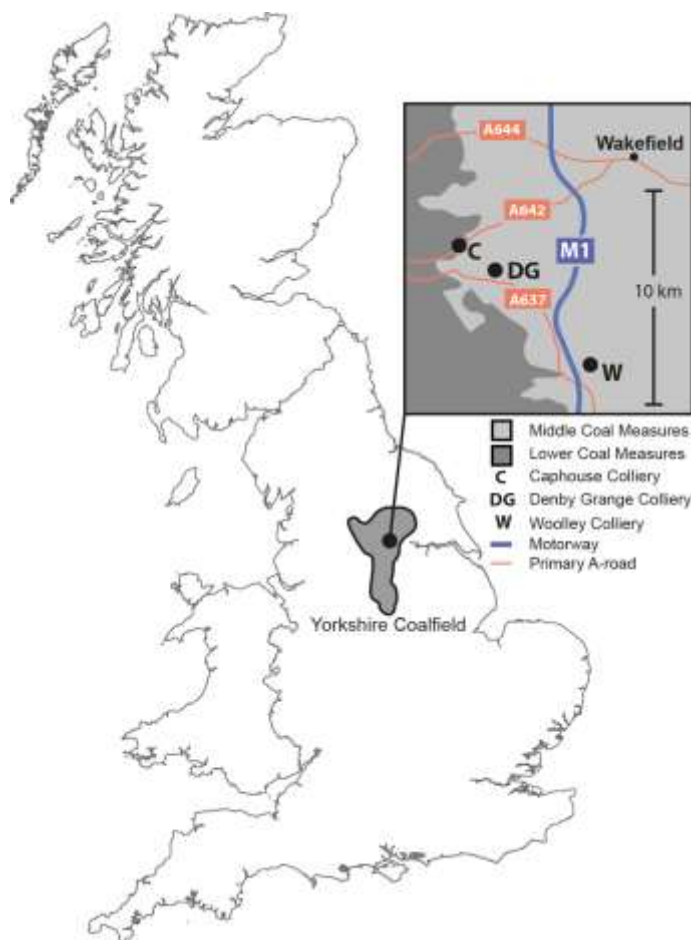


Figure 1: Location of the former Caphouse, Denby Grange and Woolley Collieries in the Yorkshire Coalfield. Inset map completed using BGS bedrock geology (1:625,000) and Ordnance Survey data.

The Caphouse shaft is believed to have been sunk in around 1790 and reached 134 m depth, working as deep as the New Hards seam, although mining in the area was known to have taken place prior to that. The shaft is now incorporated as an exhibit in the museum (Faull 2011). The Hope Shaft, some 500 m further to the south-west, was sunk in 1827, reaching 197 m deep (-50 m asl) and worked as deep as the Beeston (Whinmoor) seam. A third shaft, the Inman shaft, to 89 m depth, is now sealed and the headworks building used as a multimedia exhibit. Two fan drifts were later driven to provide ventilation to the Caphouse and Hope workings, respectively (Kruse, 2007).

The Colliery complex closed in 1985. The museum was opened as the Yorkshire Mining Museum in 1988 and became the national museum in 1995. The museum provides underground access to a worked mine level for visitors and it is, of course, imperative that this museum level is not allowed to flood. The Coal Authority (the national body responsible for managing water levels in abandoned mines) also has interests in ensuring that uncontrolled break-outs of ferruginous mine water do not occur via the numerous other abandoned mine openings in the region. In order to satisfy these museum-specific and regional interests, the Hope Shaft is thus pumped on a daily basis, by a submersible pump at c. 170 m depth (-23 m asl) to maintain mine water levels at a present depth of around 148-153 m bgl (-1 to -6 m asl). The quantity of water that must be pumped from the Hope Shaft to achieve this varies seasonally and with rainfall quantities but is typically of the order of 3000 m³/d (76 L/s) for 12-16 hr/day, with pump operation typically from 10-11 pm onwards, to take advantage of cheaper night-time electricity. The Hope and Caphouse workings are hydraulically interconnected underground and the entire Caphouse complex is interconnected with a much larger regional set of underground coal workings, including those of Denby Grange Colliery (53.6340°N 1.5942°W) and Woolley Colliery (53.5961°N 1.5338°W) (INWATCO 2005a,b). Woolley Colliery is also pumped by the Coal Authority to keep regional mine water levels under control and thus, Hope Shaft and Woolley represent two discharge points on an interconnected, partially flooded mine water system.

1.1.2 Evolution of mine water chemistry post-abandonment of workings

Coalfield abandonment leads to profound changes in the subsurface geochemical environment, as ventilated, drained voids are flooded by rising mine waters. This change in geochemical conditions often has dramatic consequences for mine water chemistry (Younger 1998). Most British Carboniferous coal-bearing strata are associated with modest quantities of pyrite, which oxidise in the unsaturated zone given good supplies of atmospheric oxygen and water to release acid, sulphate and dissolved iron (Banks et al., 1997a, b):



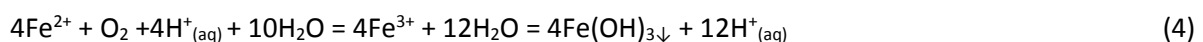
These highly soluble products are flushed into solution by rising water within the mine network following mine abandonment. In sedimentary rock sequence such as the British Carboniferous Coal Measures, much of the acid generated by this reaction will often be neutralised by reactions with carbonate minerals, such as calcite, to release alkalinity and base cations.



The Carboniferous Coal Measures also contain iron-bearing carbonates, such as siderite and ankerite, which neutralise acid, but release even more dissolved iron in the process:



On contact with oxygen, the ferrous iron (Fe²⁺) oxidises to ferric iron (Fe³⁺) and hydrolyses to produce an insoluble ochre precipitate.



The temperature of the water pumped from Hope Shaft is typically c. 14-15°C but it does vary somewhat and temperatures as low as 12°C have previously been recorded. The water at both Woolley and Hope is highly ferruginous and is treated by the Coal Authority in passive treatment systems, comprising aeration cascades, settlement ponds and polishing wetland reed-beds to encourage the reaction in Equation (4) prior to final discharge into local water courses (Banks & Banks, 2001; PIRAMID, 2003; Banks, 2007; Faraldo Sanchez, 2007). The presence of ochre particles in un-filtered water samples at Caphouse suggests that waters are at least partially oxygenated in the subsurface, so iron oxidation, hydrolysis and flocculation have already commenced prior to pumping.

1.1.3 Mine water heat flow and current capacity of heat generation at Caphouse

A heat pump of nominal 10 kW capacity was installed at Caphouse Colliery in April 2015. The heat pump can be coupled to either one of two heat exchangers, accessing the thermal energy of the mine water (and the performance of these systems will be described in future publications):

- A closed loop heat exchange unit submerged in the first aeration pond of the treatment system. This heat exchanger is connected to the heat pump evaporator by a secondary circuit filled with a propylene glycol-based heat transfer fluid. This source can be used throughout the day.
- A shell-and-tube heat exchanger through which a fraction of the pumped mine water flow from Hope Shaft is directed (i.e. an 'open loop' system, using the terminology of Banks, 2012). This source can only be used when the Hope Shaft is being actively pumped (i.e. night-time and early morning)

Heat flow in flooded mine workings is dominated by advection. Mine water bodies in flooded mines often develop density-related stratification due to the slow mixing of dilute infiltrating meteoric waters and deep-sourced saline waters under gradual flooding conditions (Nuttall and Younger 2004). Pumping encourages turbulent water mixing, which can destroy or lessen stratification. This may benefit heat-pump operations as thermal buoyancy effects can deliver deep-sourced warmer waters to pumps. However, there are also potential operational pitfalls as deep-sourced waters are comparatively saline and reducing (and, thus, potentially Fe- and Mn- rich), posing issues for equipment corrosion and scale accumulation as base metals, mobile in more saline waters, can rapidly precipitate with increased mixing of deep-sourced waters with fresher shallow waters (Younger et al. 2015). Previous studies have investigated pump-related pollution migration issues using natural tracer patterns (e.g. Elliot and Younger 2013; Wood et al. 1999). In this study we utilise measurements of temperature, conductivity, pH, major ions and stable isotopes of O, H and S to investigate the effects of pumping on mixing processes in the Hope Shaft. With this information, we hope to understand the long-term suitability of the mine water body at Caphouse for sustainable heat generation.

2.1 Methodology

2.1.1 Field sampling and onsite analysis

Pumped waters were sampled on a c. monthly basis from access taps at the main discharge point into the mine water treatment system. Meteoric control samples for O and H isotopic analysis were taken from the Holme Brook stream, Chesterfield, at 53.2389°N 1.4441°W. Physiochemical water

parameters were measured in the field during sampling: pH, temperature, and specific electrical conductance ('conductivity') were measured with a handheld Myron P Ultrameter and dissolved oxygen (DO) was measured using a Hach SensION + DO6. Alkalinity was determined as CaCO₃ with a Hach Model 16900 digital titrator, using nitric acid and bromcresol green - methyl red pH indicator. Recorded values were then multiplied by a factor of 1.2 to find the HCO₃⁻ concentration; because at pH values close to 7, bicarbonate is the utterly dominant component of alkalinity. Where required, equipment was calibrated before each day's fieldwork and all water samples were refrigerated as soon as possible after collection.

2.1.2 Major ion analysis

Major ion samples were taken in duplicate using polypropylene screw-cap vials and filtered at 0.2µm to remove particulate matter. Anion and cation concentrations were determined simultaneously using ion chromatography on Dionex equipment in the labs of the School of Engineering at the University of Glasgow. For anions a 10µl sample was passed through a Dionex IonPac AG14A guard column and AS14A-5u analytical column before analysis on an ICS-900, with the aid of displacement chemical regeneration suppression (ACRS 500). A mix of 8mM sodium carbonate/1mM bicarbonate eluent and 72mN H₂SO₄ regenerant was pumped through the system at 0.5ml/min. For cations a 10µl sample was passed through a Dionex IonPac CG12A guard column and CS12A analytical column, set to 30°C, before analysis on an ICS-1100. A 20mM methanesulfonic acid eluent was pumped through the system at 0.25ml/min and a CERS 500 was used as an electrolytic suppressor. For both anion and cation analyses a conductivity cell was used for peak detection complete with a 3 level calibration. The standard for anion measurement was an in-house developed solution and the cation standard was a Dionex Six Cation-II solution. Chromeleon 7 software was used for final data analysis and quantification.

2.1.3 Stable isotope analysis

Stable isotope analyses were undertaken at the SUERC laboratories, East Kilbride. Field samples of water for δ¹⁸O and δ²H were taken in triplicate using clean 10ml glass vials with screw caps. To ensure a tight seal and prevent any evaporation of samples caps were sealed with Parafilm.

For δ¹⁸O analysis, each sample was over-gassed with a 1% CO₂-in-He mixture for 5mins and left to equilibrate for a further 24 h. A sample volume of 2ml was then analysed using standard techniques on a Thermo Scientific Delta V mass spectrometer set at 25 °C. Final δ¹⁸O values were produced using the method established by Nelson (2000).

For δ²H analysis, sample and standard waters were injected directly into a chromium furnace at 800 °C (Donnelly et al. 2001), with the evolved H₂ gas analysed on-line via a VG Optima mass spectrometer. Final values for δ¹⁸O and δ²H are reported as per mil (‰) variations from the V-SMOW standard in standard delta notation. In-run repeat analyses of water standards (international standards V-SMOW and GISP, and internal standard Lt Std) gave a reproducibility better than ±0.3‰ for δ¹⁸O, ±3‰ for δ²H.

Sulphate isotope sampling involved direct precipitation of sulphate as BaSO₄ from fresh water samples in the field using the method of Carmody et al. (1998). Waters in 1L plastic bottles were acidified to pH 3-4 using 10% HCl and then dosed with excess 5% BaCl₂ solution. A rapid cloudy

reaction indicated the presence of sulphate via the precipitation of BaSO₄ crystals. The precipitate was recovered from the vessel and cleaned repeatedly in de-ionised water and dried prior to isotopic analyses.

For $\delta^{34}\text{S}$ analysis, SO₂ gas is liberated by combustion at 1,065 °C with excess Cu₂O and silica, using the technique of Coleman and Moore (1978), before measurement on a VG Isotech SIRA II mass spectrometer. Results are reported as per mil (‰) 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 standard was better than $\pm 0.3\text{‰}$.

3.1 Results

Field physiochemistry and major/minor ions are presented in Table 1 and associated isotopic results are presented in Table 2. Timing of sampling was mainly restricted to the morning when pump operation and NCMME opening hours typically overlap. Both physiochemical and major/minor ion parameters are largely consistent, bar Sample D, which unlike the others was taken in the afternoon, in this case within 30 minutes of pump cycle initiation. Overall the sample waters represent Na-SO₄- (HCO₃-Cl) water type and are net alkaline according to the terminology of Hedin et al. (1994) and PIRAMID (2003). Values for $\delta^{18}\text{O}$, $\delta^3\text{H}$ and $\delta^{34}\text{S}$ showed virtually no variation out with standard errors across all samples.

Sample	Date - Time	Pump duration (hh.mm)	SEC, $\mu\text{S}/\text{cm}$ (25°C)	Field, T (°C)	Field, pH	Field, DO (%)	Field, HCO ₃	Ca	Mg	Na	K	Cl	SO ₄	Br
A	21/05/2015 09.00	11.00	2774	15	6.91	nd	526	95	62	479	49	314	575	nd
B	30/06/2015 08.55	10.55	2800	15.5	6.82	27.5	528	91	60	484	52	327	564	nd
C	18/08/2015 11.00	12.00	2927	15.3	6.86	30.4	564	91	60	516	52	332	582	3.73
D	09/09/2015 17.00	00.30	2266	14.5	6.67	40.8	360	88	58	340	40	165	582	1.48
E	09/10/15 07.00	08.00	2995	15.3	6.88	nd	518	90	59	523	50	285	523	2.58

Table 1. Physiochemistry and major/minor ion concentrations. All values in mg/l, except pH units. 'nd' - not-determined. Pump duration was determined from site operational data with pumping typically initiating at 10 or 11pm.

Sample	Date	$\delta^{18}\text{O}$ (VSMOW)	$\delta^2\text{H}$ (VSMOW)	$\delta^{34}\text{S}$ (SO ₄) (VCDT)
PAP	04/03/15	-8.2	-52	23.8
A	21/05/15	-7.8	-52	nd
B	30/06/15	-8.5	-54	23.2
C	18/08/15	-7.8	-51	21.4
D	09/09/15	-8.1	-53	19.7
E	09/10/15	-8	-52	23.2
HB1	06/07/15	-6.3	-45	nd
HB2	08/10/15	-6.7	-42	nd

Table 2. O, H, S isotope systematics of H₂O and SO₄. All δ -values ‰ against Vienna Standard Mean Ocean Water (VSMOW) or Canyon Diablo Troilite (CDT) standards. Average values of triplicate analyses which reproduce well within error of reproducibility. HB indicates local meteoric water samples from the Holme Brook, Chesterfield. Sample PAP (Pre Analytical Program) was collected prior to the start of the project sampling schedule in order to gain baseline values and optimise future sampling protocol.

The comparatively low values for temperature, conductivity, chloride, sodium and alkalinity for Sample D may suggest that shallow, fresh ground waters are sampled during the initial phases of pumping before deeper-sourced, comparatively saline waters are introduced to the pump interface. Upconing of saline water in response to pumping from an overlying layer of fresher water is an established phenomenon. Chandler and McWhorter (1975) demonstrated that water extraction from a depth >30% into isotropic aquifers could result in the incipient entrainment in saline water from below. Given the total shaft depth (197mbgl), stationary pump depth (170m bgl), and variation of the water level (148-153mbgl) at the Hope Shaft; the water column decreases in depth from 49 to 44m and the pump penetrates 39 to 45% of the water column as pumping progresses. If there are any layers of comparatively saline water at the base of the mine voids then the current pump set-up theoretically allows for upconing and supply of dense, saline waters to the pump interface at any point of the pump cycle.

By way of support, dissolved oxygen measurements, which vary from 27.5 to 40.8%, may indicate increased supply of deep-sourced anoxic waters to the pump as the largest value (D) was taken soonest after pump initiation. Bromide was added to our Cation-Anion analysis from Sample C in order to provide an additional check on potential sources of salinity (Elliot et al. 2001). As Cl and Br behave conservatively in most groundwaters, Cl/Br ratios can be used provide an indication of the original water source (Davis et al. 1998). The ratios calculated from samples C to E range from 89 – 110, suggesting either atmospheric precipitation (generally Cl/Br = 50–150) or a shallow ground water (generally Cl/Br = 100–200) source for these ions. In a way of comparison, water affected by the dissolution of evaporites has a typical Cl/Br ratio value in the range of 1000–10,000.

4.1 Discussion

There has been no significant variation in analytical values after 6 months of study, bar one sample (D) known to be taken at a unique point near the initiation of pumping. Though changes in chemistry may become apparent over the next 6 months of the project, the current system dynamics at Caphouse appear to be relatively stable when sampled at similar point in the pump cycle. The chemical analysis results have been combined with historic data from previous analyses (INWATCO 2005a; Faraldo-Sanchez 2007) and continual monitoring data from the UK Coal Authority (2009 to present) for the purpose of identifying trends in Hope Shaft raw mine water composition with time.

4.1.1 Analysis of archive data

Coal Authority data have the most extensive range of parameters and are the only additional data set that includes a full suite of major ion analyses. Constant values of 1 mg/L for ammoniacal nitrogen and the discernible H₂S odour at the aeration cascades on-site demonstrate that Hope Shaft mine water is mildly reducing. Figure 2 shows iron content as a function of time. Since 2009 there has been a slow improvement in water quality with a decrease in iron from 25 to 15 mg/L with time. This is entirely consistent with the observations by Younger (1997, 2000) and Gzyl & Banks (2007) that mine water chemistry often improves with time due to flushing of vestigial acidity (secondary weathering products from pyrite oxidation) from the workings. The manganese concentrations have remained relatively stable at 0.6 to 1 mg/L. Total iron concentration is typically slightly higher than the dissolved / ferrous iron concentration. This supports the observation that a small proportion of the iron leaving the shaft has already started to oxidise and form ochre (Fe(OH)₃) flocs - and is unsurprising as it is known that a proportion of the Hope water make is derived from leakages into

the oxic environment of the fan drifts and the unflushed Caphouse workings. Total water chemistry has evolved from a Na-SO₄ water in late 2009 to a more Na-SO₄-(HCO₃-Cl) water type in recent times (Figure 3).

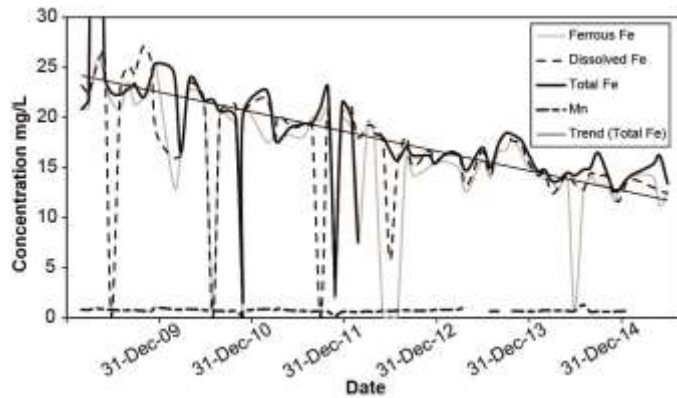


Figure 2: Variation in manganese and total, dissolved, and ferrous iron in pumped raw Hope mine water 2009 to 2015 (data courtesy of Coal Authority). Dissolved iron and manganese samples were passed through a 0.45 µm filter to exclude all particulate matter and analysed using ICP-OES method. Total and ferrous iron samples were preserved with HCl and analysed using automated discrete colorimetric method. Both methods by ESG Ltd (UKAS accreditation ISO/IEC 17025:2005).

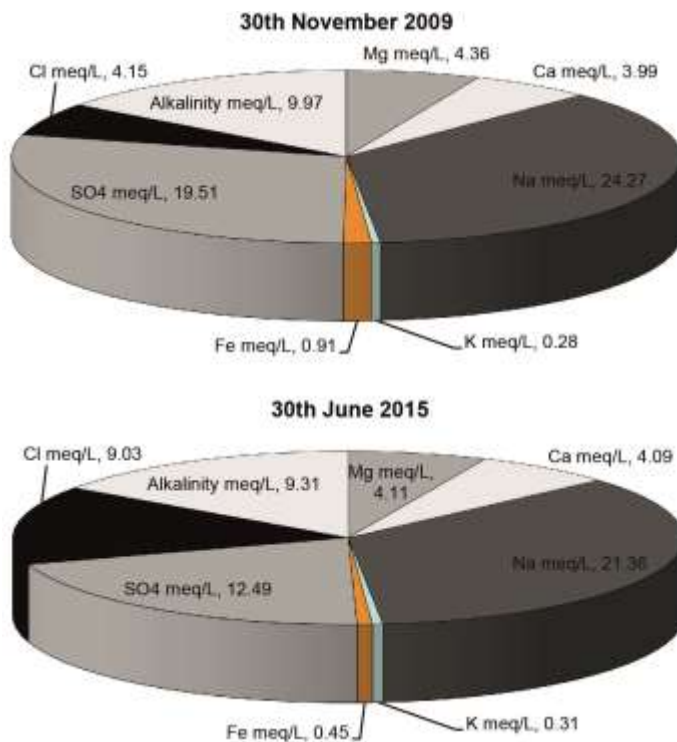


Figure 3: Pie diagrams comparing major ion (meq/L) composition of Hop Shaft mine water in November 2009 and June 2015 (data courtesy of Coal Authority).

4.1.2 Comparison of present data to archive data

As our initial data set covers May to October 2015, only legacy data from May to October in previous years were chosen for direct comparison in order to avoid any effects of seasonal variation. A Durov plot of present data and information from the Coal Authority is presented in Figure 4, which shows that cation values have remained relatively constant since 2009. Anion values are a different story: sulphate has decreased in value over time and there has been a relatively recent increase in chloride. To investigate these possible trends further, data from Figure 4 along with additional information was plotted to show SO_4 and Cl evolution since 2004. Figure 5 demonstrates a marked decrease in SO_4 levels from c. 1200 to 800 mg/l from 2004 to 2007, and a steady decrease from 2007 to modern day values of c. 600 mg/l.

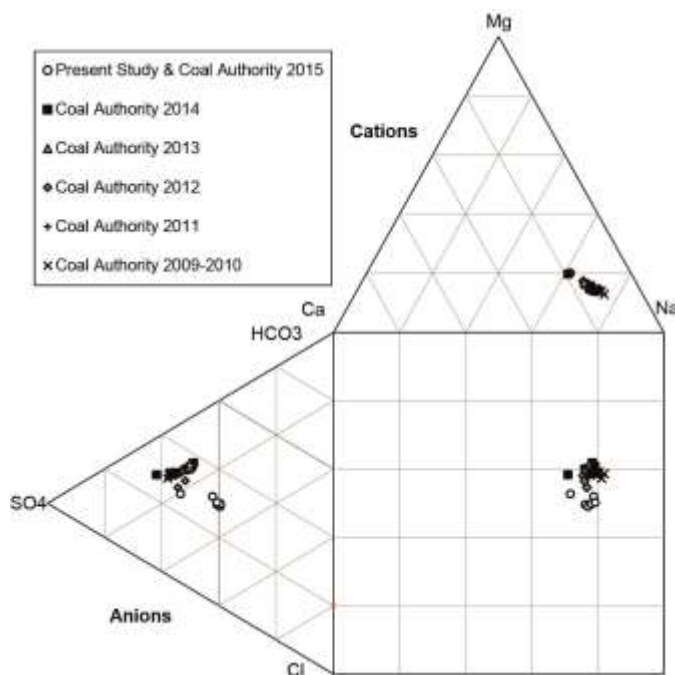


Figure 4. Durov plot for present study and Coal Authority data for May-October from 2009-2015.

Prior to 2015, chloride values typically exhibit concentrations of 120-150 mg/L. This is significantly above the background (10-40 mg/L) that would be expected in shallow Coal Measures aquifers of the area (Banks, 1997), representing evapoconcentrated chloride concentrations in rainfall influenced by marine salts and industrial contamination. This suggests that the Caphouse mine water is tapping a proportion of deep seated saline water - and during 2015, the proportion of this water appears to have increased, with the chloride concentrations rising above 300 mg/L. Calculation of molar Na/Cl ratio of c. 4-6 from the Coal Authority data suggests that the majority of the sodium is derived from sources other than a deep-seated Na-Cl formation water - for example, hydrolysis of feldspar minerals (Banks, 1997, observed a common Na- HCO_3 water chemistry in hydrochemically mature Coal Measures groundwaters).

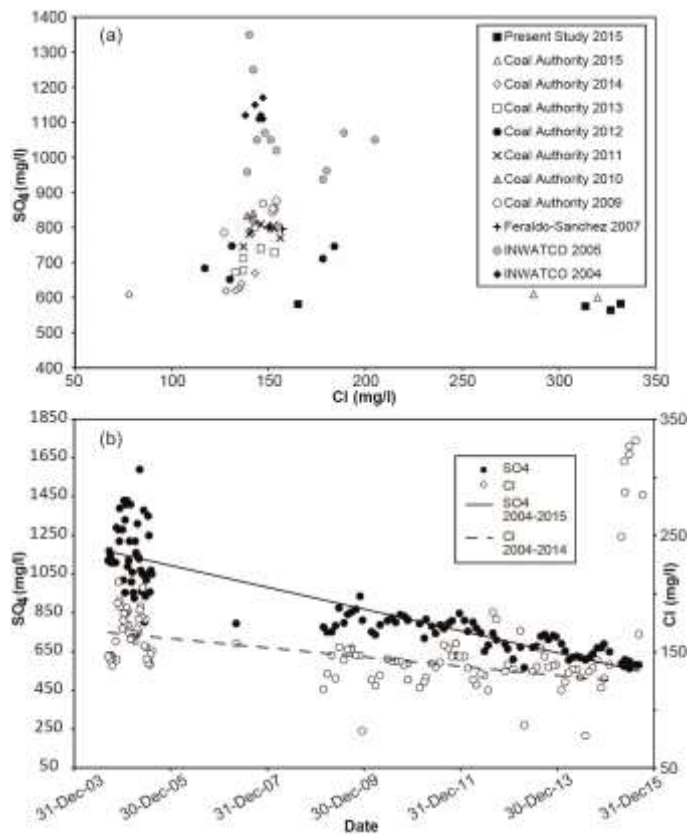


Figure 5. SO_4^{2-} and Cl^- systematics for Hope Shaft waters. (a) Cross-plot of dissolved SO_4^{2-} vs. Cl^- for present study and all available legacy data for May-October from 2004-2015. (b) Complete time series showing evolution of SO_4^{2-} and Cl^- concentrations from 2004 to present. Data sources same as (a).

4.1.3 Stable isotope values

Hope Shaft mine water $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values fall close to, or on the global meteoric water line, and show a notable similarity across several months sampling, whilst pumping was on-going; with $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of $-7.9 \pm 0.4\text{‰}$ and $-52 \pm 2\text{‰}$, being close to the analytical techniques' reproducibility. These values are distinct from Holme Brook values, whose $\delta^{18}\text{O}$ and $\delta^2\text{H}$ (Figure 6) averages of -6.5‰ and -44‰ are typical for meteoric stream waters across northern England (Younger et al. 2015). The mine water values are also slightly lighter, isotopically, than long term values (30 year average) from the regional meteoric monitoring station at Wallingford, Oxfordshire (IAEA/WMO 2015). The measured $\delta^{18}\text{O}$ and $\delta^2\text{H}$ resemble old meteoric waters, perhaps Late Pleistocene, and are similar to those found in major English aquifers (e.g. the Lincolnshire Limestone; Darling et al. 1997). There is no evidence for extensive isotopic exchange with the host lithologies which would drive both $\delta^{18}\text{O}$ and $\delta^2\text{H}$ to higher values (Sheppard 1996).

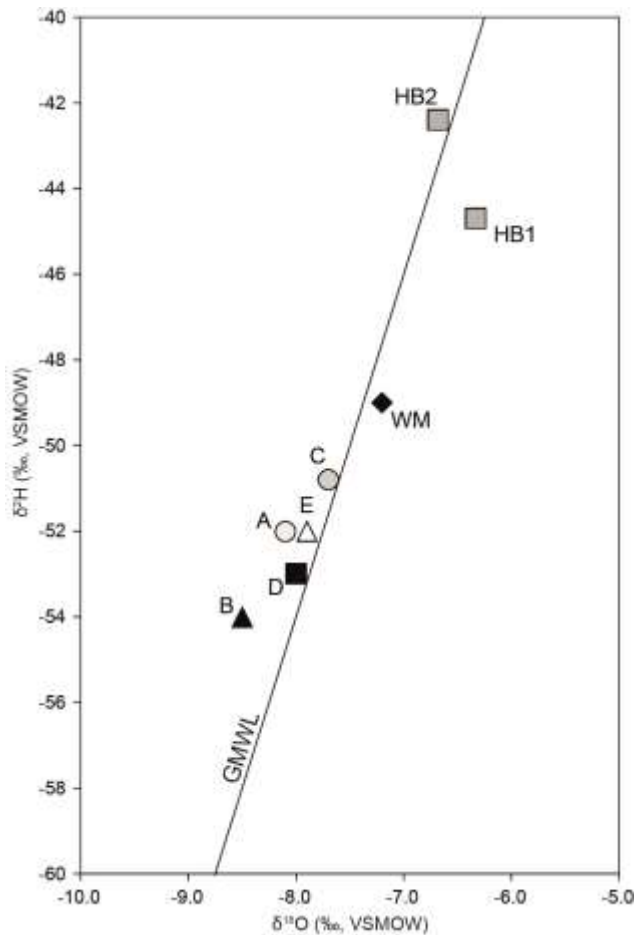


Figure 6. Plot of $\delta^{18}\text{O}$ versus $\delta^2\text{H}$ for Hope Shaft mine waters (samples A to E), as compared to local Holme Brook (HB1 and HB2) and long term meteoric values recorded at Wallingford (WM). The solid trend line represents the Global Mean Meteoric Water Line (GMWL).

Given that major ion concentrations are far higher than typical meteoric waters, and strongly suggest input from deep-sourced waters, the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values may seem somewhat paradoxical; however, this curious trend has proved to be the norm rather than the exception for contemporary studies across northern England (Younger et al. 2015). The observation need not be overly troubling, it merely suggests that the water molecules are derived from meteoric recharge, while a component of the 'salinity' may be derived from an ionically significant, but hydraulically minor, input of deeper saline water. Data reported from flooded mines and geothermal exploration in that region show a similar decoupling for far greater salinities (up to 122,000 mg/l Cl and 55,000 mg/l Na) and far greater fluid depths (600 mbgl for abandoned mines and 1600 mbgl for exploration boreholes). Younger et al. (2015) believe high concentrations of solutes to be a result of recharge during Cenozoic uplift episodes and suggest three possible mechanisms to explain this hydrogeological paradox; evaporite dissolution; high-temperature rock-water interaction with radiothermal granites; and 'freeze out' from overlying permafrost formed during cold periods. High-temperature rock interaction at Caphouse can be ruled out, as there are no known granite intrusions local to West Yorkshire. There are also no known local evaporitic deposits, and given Cl/Br ratios it is unlikely that any evaporite interaction is a major contributor. Freeze out is therefore the most likely cause of delineation between water isotopes and ion concentrations, but further work is required to investigate other possible sources for the waters of the Caphouse system. Whatever the reason, the decoupling of the solid content and the host water is notable, and becoming seen more widely in

deeper groundwater studies (Younger et al. 2015). Notwithstanding this observation, the major result remains that, during extensive pumping over several months, there was no detectable change in the O and H isotopic composition of the Hope Shaft mine water.

Carboniferous coals have typical $\delta^{34}\text{S}$ isotopic value of 0-10‰ and are largely the result of $\delta^{34}\text{S}$ fractionation during pyrite oxidation (Matthies et al. 2012; Elliot and Younger 2014). The $\delta^{34}\text{S}$ for sulphate in Hope Shaft waters, 19.7-23.8‰, is therefore surprisingly high. There are four plausible mechanisms to explain these high values: evaporite dissolution; marine signatures in deep-sourced Na-Cl waters; bacterial concentration; and repeated generation and flushing of pyrite oxidation products during water table fluctuation. Cl/Br ratios preclude evaporite- ground water interactions and O and H isotopic values exclude any major influence from deep marine sourced waters. Concentration of $\delta^{34}\text{S}$ through repeated cycles of pyrite oxidation is unlikely as the high values for Caphouse have yet to be observed in locations where this process is identified as the main source of $\delta^{34}\text{S}$ generation. Bacterial sulphate reduction in a closed system (with respect to sulphate, i.e. sulphate becoming more depleted) can lead to an increase in $\delta^{34}\text{S}$ of the residual sulphate, through continuous production of sulphide enriched in ^{32}S , through bacteriogenic isotope fractionation (Schwarcz and Burnie, 1976; Ohmoto and Goldhaber, 1997). This would lead to an increase in $\delta^{34}\text{S}$ of mine water sulphate above the typical bulk $\delta^{34}\text{S}$ in local coal-bearing groundwaters of around 4-12‰ (our data from Markham colliery averages 4.3‰; Matthies et al. 2012). If continued sampling showed sulphate concentrations decreasing accompanied by an increase in sulphate $\delta^{34}\text{S}$, then this would lend credence to the “closed-system” model, but our preliminary data do not support this model at present. There is no simple explanation for the $\delta^{34}\text{S}$ values at Caphouse, though it should be noted that sulphate $\delta^{34}\text{S}$ values of around 23.7‰ are known to be at the high end of Lower Carboniferous seawater sulphate values (Claypool et al. 1980; Boyce et al. 2003).

5.1 Conclusion

Preliminary investigation into mixing dynamics of the pumped Hope Shaft at the former Caphouse Colliery reveal little variation in physiochemical, major ion and isotopic concentrations between May and October 2015. When combined with archive data from 2004-2015 an overall picture of gradual mine water quality recovery following mine abandonment and groundwater rebound emerges. The gradual trend of decline in chloride concentration has recently been perturbed by a general doubling of chloride values in 2015. This may suggest a recent, or at least a consistent, stratification perturbation and breakthrough of deeper-sourced saline waters.

A single sample (D) has markedly lower physiochemical and major ion values. Unlike the rest of the samples so far, which are from several hours into the daily pump activity cycle, this particular sample was taken 30 minutes after pump initiation. It may be that this sample represents the pumping of shallow, relatively dilute waters prior to breakdown of stratification and the introduction of deeper, more saline waters at some point in the daily pump cycle. Regular samples throughout a single pumping cycle would help establish the validity of this hypothesis.

There is virtually no variation in isotopic data. $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values suggests the presence of ancient confined meteoric sourced waters that have had little isotopic exchange with mineral phases. These values may further signify the recent breakthrough of deeper-sourced and increasingly saline water into the Hope Shaft. $\delta^{34}\text{S}$ values are anomalously high as compared to typical values for Carboniferous Coal Measures. There is no clear explanation to offer for this, though it should be

noted that the value is at the high end of Lower Carboniferous seawater sulphate values. Further data collection, and investigation, is required in order to further clarify potential $\delta^{34}\text{S}$ sources.

Attempts to use the water at Caphouse for heat generation have only been in place since April 2015. Our initial observations suggest that water parameters are relatively stable at present and that it is unlikely that the Hope shaft will be compromised as a dependable thermal resource in the foreseeable future. However, much about the hydrogeology of the Caphouse system is still uncertain, so further work is required to check the persistence of recent trends within the pumped mine waters and to determine stratification structure of the water body incumbent within the former mine workings.

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