



# Hydrochemistry and stable isotopes as tools for understanding the sustainability of minewater geothermal energy production from a 'standing column' heat pump system: Markham Colliery, Bolsover, Derbyshire, UK

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## ABSTRACT

The abandoned workings of the former Markham Colliery are still in the process of flooding. They are being exploited, via a 'standing column' heat pump arrangement in Markham No. 3 shaft, to produce thermal energy. From 2012, water was pumped from 235 m below ground level in the shaft at c. 15 °C and 2–3 l/s, through shell and tube heat exchangers coupled to a 20 kW heat pump, to supply space heating to commercial offices. The thermally spent (cool) water was returned to the same shaft at c. 250 m bgl at around 12 °C. The mine water contained iron, c. 6000 mg/l chloride, and was highly reducing. Avoiding contact with oxygen was effective in preventing problems with ochre scaling. In January 2015, taking advantage of rising water levels, the pump was repositioned at 170 m bgl, and the reinjection diffuser at 153 m bgl. Since then, both iron concentration and salinity have fallen significantly, suggesting stratification in the shaft. Stable isotope data from sampling in 2015 generally show little variation. Sulphate  $\delta^{34}\text{S}$  exhibits values typical for British Coal Measures (c. +5‰), whilst  $\delta^{18}\text{O}/\delta^2\text{H}$  indicate influence of fresh meteoric waters. Chloride and sodium concentrations have gradually increased since May 2015, possibly indicating a renewed influence of deeper, more saline, waters and reflecting the gradual rise of mine water in the shaft. Further monitoring of mine water chemistry and isotopic composition is required to better assess the sustainability of the Markham heat pump scheme and advise on optimal management of this mine water resource.

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## 1. Introduction

### 1.1. Heat from mine workings

It is well-recognised that abandoned, flooded mine workings represent (i) a store of potential thermal energy in the form of water and saturated rocks at temperatures often several °C above annual average air temperature, and (ii) a network of shafts, tunnels and workings forming a transmissive heat exchange network through which water can circulate and exchange heat with the geological environment (Banks et al., 2003, 2004; Hall et al., 2011; Watzlaf and Ackman, 2006; Raymond and Therrien, 2008; Pree and Younger, 2014; Ramos et al., 2015; Bracke and Bussmann, 2015).

Some of the world's largest (several MW scale) mine water geothermal schemes simply pump large quantities of water from the mine and

pass it through heat exchangers or heat pumps, prior to discharging the water to a surface recipient, as at Barredo colliery, Mieres, Spain (Loredo et al., 2011; Ordóñez et al., 2012; Jardón et al., 2013) or reinjecting it to another point in the mine system, as at Heerlen, Netherlands (Bazargan et al., 2008; Minewater Project, 2008; Ferket et al., 2011; Verhoeven et al., 2014). It is also possible, where deep shafts exist, to abstract water from one depth in the shaft, pass the water through a heat exchanger or heat pump, and return the thermally spent water to the same shaft at a different depth. Because there is an obvious risk of the thermally spent water returning to the production pump before it has reacquired its initial temperature (via heat exchange with the shaft walls), such a 'standing column' arrangement (Deng et al., 2005; Orío et al., 2005; O'Neill et al., 2006; Banks, 2012) is only suitable:

- (i) if the heating/cooling demand is relatively modest compared with the available recirculation length in the shaft (such that heat can be regained from the surface area of the shaft walls), or
- (ii) if there is sufficient pre-existing mine water flow along or through the shaft which is able to provide an additional source

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of thermal replenishment, or is able to remove the returned water before it reaches the abstraction point.

A 'standing column' heat pump arrangement has been installed in Shaft No. 3 of the abandoned Markham Colliery, Derbyshire, UK. It operates successfully and provides heat to a modest complex of offices at the surface.

### 1.2. History and configuration of Markham Colliery

Markham Colliery was a major colliery just north of Bolsover, Derbyshire, UK, comprising four main shafts - Shafts 1 and 4 on a northern site and Shafts 2 and 3 on a nearby southern site (53.2424°N 1.3285°W) (Fig. 1). It started operations in 1904 and worked a variety of seams in the Pennine Lower and Middle Coal Measures of the Langsettian and Duckmantian substages of the Westphalian (Pennsylvanian) Coal Measures Supergroup of the English East Midlands (Sheppard, 2005; BGS, 2012). These strata typically consist of cyclical fluvio-deltaic sequences of interbedded sandstone, siltstone, mudstone, coal and associated seatearth (INWATCO, 2005). Infrequent marine influences in the upper part of the Lower Coal Measures and the lower part of the Middle Coal Measures (Waters, 2009) resulted in 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 East Pennine Coalfields averages  $2 \pm 1\%$  and correlates strongly with iron, indicating that pyrite dominates sulphur content in the coal (Spears and Tewart, 2009).

Markham No. 3 Shaft was reportedly c. 490 m deep and 4.6 m in diameter (15 ft. brick-lined - Healeyhero, 2015). Shafts 1 and 4 of

Markham Colliery were the deepest shafts at Markham, reaching the Blackshale coal seam at c. 630 m deep (British Geological Survey borehole record SK47SE57). Markham is part of a major interconnected complex of collieries in the area, the most immediate of which are the former Ireland (53.2626°N 1.3456°W), Arkwright (53.2296°N 1.3633°W), Bolsover (53.2350°N 1.3116°W) and Duckmanton (53.2447°N 1.3521°W) Collieries (Fig. 1). These collieries worked a number of seams including (in descending order) the High Hazles, Top Hard, Waterloo, Ell, Deep Soft, Deep Hard, Piper, Low Main and Blackshale seams. During the 1980s and 1990s, the collieries of the region were progressively abandoned and Markham Colliery was closed in 1993. On closure, the water make from Markham Colliery totalled 15.2 l/s and that from the adjacent Bolsover Colliery was 18.9 l/s plus 3.8 l/s from Duckmanton Colliery. Markham's Shafts 1, 2 and 4 were backfilled on abandonment, while Shaft No 3 was left largely open, in order to vent mine gas accumulation, with a hydraulically open plug set in the shaft at the level of the Ell seam (−357 m asl).

Markham No. 3 Shaft and the land surrounding it was subsequently acquired by Alkane Energy in 1998. Initially, coal bed methane was extracted, but as water levels continued to rise rapidly following abandonment of the coalfield, the methane-rich horizons were submerged and methane extraction became uneconomic by 2006. By May 2011, the water level in Shaft No. 3 (shaft top = +71.8 m asl) was 239.5 m bgl (−167.7 m asl) (Fig. 2).

### 1.3. Mine water heat pump system at Markham

In spring 2012, Alkane Energy installed a 'standing column' heat pump arrangement in the Markham No. 3 Shaft (Fig. 3), with a pump

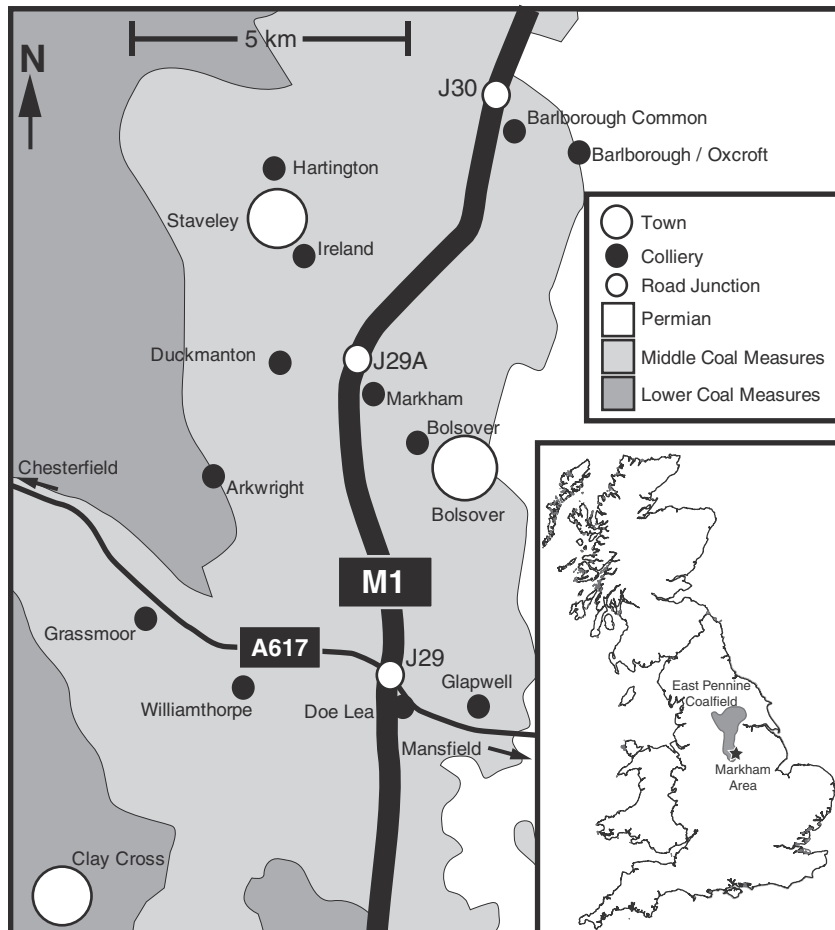


Fig. 1. Location of the former Markham and surrounding collieries based on BGS bedrock geology data (1:625,000).

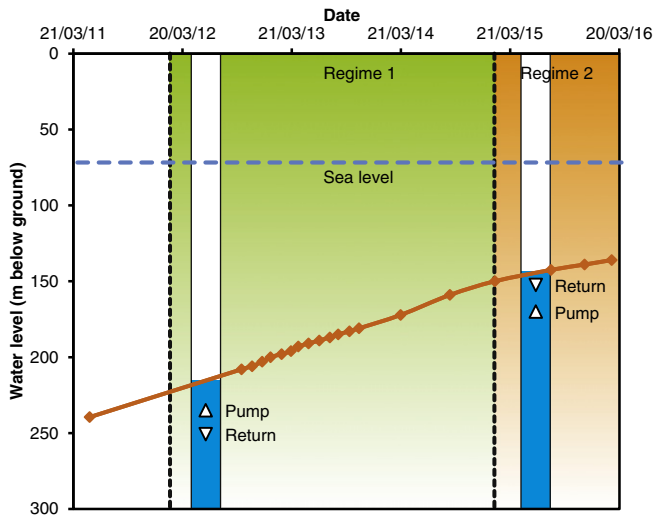


Fig. 2. Schematic of the Markham No. 3 Shaft 'standing column' heat extraction arrangement, with rise in water level plotted.

at 235 m bgl (Athresh et al., 2015). Water was passed through a sealed shell-and-tube heat exchanger arrangement, thermally coupled to a Danfoss DHP-R 20 kW heat pump (Danfoss, 2009), and the chilled water was returned to the shaft via a diffuser at 250 m bgl (this is referred to as standing column Regime 1). On 28th January 2015, mine water levels had risen sufficiently to allow the entire standing column arrangement to be raised in the shaft, with the pump now being positioned at 170 m bgl, below the reinjection diffuser at 153 m bgl (referred to as Regime 2) (Fig. 2).

No net pumping takes place at Markham and mine water levels continue to rise. The water still contains dissolved methane and is highly reducing, such that blowers are occasionally needed to disperse methane from the shaft headspace.

The objective of the study reported in this paper is to investigate whether monitoring of mine water chemistry and isotopic composition can provide information that is useful for managing or assessing the sustainability of a mine water heat pump scheme.

## 2. Methodology

### 2.1. Existing data

As part of Alkane Energy's ongoing monitoring activities, suites of chemical samples had been collected from the pumped water supply and submitted to the commercial laboratory of Environmental Scientific Group (ESG) at Bretby, Staffordshire, UK (UKAS accreditation ISO/IEC 17025:2005). These results were made available for comparison with the samples analysed in this study and provide useful insight into variations in water chemistry as shaft water levels have continued to rise and as the pump location has changed. For these data, electrical conductivity (EC), pH and alkalinity were determined in the laboratory using standard electrodes and titration against sulphuric acid. Chloride and ammoniacal nitrogen were determined by automated discrete colorimetric methods. Total sulphur was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) and then converted to sulphate. Ca, Mg, Na, K, Sr, Ba and Fe (total = unfiltered, dissolved = filtered sample) were also determined by ICP-OES. Mn and several other metals, not reported in this paper, were determined by inductively coupled plasma mass spectrometry (ICP-MS). Total and ferrous iron was also determined on hydrochloric acid-preserved aliquots using discrete colorimetric methods. Methane was determined by headspace gas chromatography–mass spectrometry (GC–MS).



Fig. 3. Upper- the headworks of Markham No. 3 Shaft, showing methane venting and the (angled) pumping and return mains of the 'standing column' heat pump system. Lower- shell and tube heat exchangers in the heat pump plant room. Photos by D. Banks.

### 2.2. Field sampling and onsite analysis

Since May 2015, pumped waters were sampled on an approximately monthly basis from a sampling tap on the rising main at the Markham No. 3 shaft top. Samples for laboratory analysis of major ions were taken in duplicate using polypropylene screw-cap vials and filtered at 0.2 µm to remove any particulate matter. Duplicate samples for metals were filtered and preserved using HNO<sub>3</sub> in clean 10 ml glass screw-

cap vials. Samples for  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  isotopic analysis were taken in triplicate using clean 10 ml glass screw-cap vials and sealed with Parafilm to prevent any sample evaporation. Meteoric control samples for  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  isotopic analysis were taken from the Holme Brook stream, Chesterfield, at 53.2389°N 1.4441°W. Sulphate- $\delta^{34}\text{S}$  isotope sampling involved direct precipitation of sulphate as  $\text{BaSO}_4$  from fresh water samples in the field using the method of Carmody et al. (1998). Waters in 1 l plastic bottles were acidified to pH 3–4 using 10% HCl and then dosed with excess 5%  $\text{BaCl}_2$  solution. A rapid cloudy reaction indicated the presence of sulphate via the precipitation of  $\text{BaSO}_4$  crystals.

Field determinations were made of pH, temperature, and EC using a handheld Myron P Ultrameter and dissolved oxygen (DO) was measured using a Hach SensION + DO6. Alkalinity was determined as  $\text{CaCO}_3$  with a Hach Model 16,900 digital titrator, using nitric acid and bromocresol green - methyl red pH indicator. Recorded values in  $\text{mg l}^{-1}$   $\text{CaCO}_3$  equivalent were then converted to meq/l (by dividing by 50.04  $\text{mg meq}^{-1}$ ) or to  $\text{mg l}^{-1}$   $\text{HCO}_3^-$  equivalent (by multiplying by 1.22). The alkalinity is assumed to be predominantly in the form of  $\text{HCO}_3^-$  at pH values close to 7. Where required, equipment was calibrated before each day's fieldwork and all water samples were refrigerated as soon as possible after collection.

### 2.3. Major ion analysis

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 10  $\mu\text{l}$  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 8 mM sodium carbonate/1 mM bicarbonate eluent and 72 mM  $\text{H}_2\text{SO}_4$  regenerant was pumped through the system at 0.5 ml/min. For cations a 10  $\mu\text{l}$  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 20 mM methanesulfonic acid eluent was pumped through the system at 0.25 ml/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.

### 2.4. Stable isotope analysis

Stable isotope analyses were undertaken at the SUERC laboratories, East Kilbride. For  $\delta^{18}\text{O}$  analysis, each sample was over-gassed with a 1%  $\text{CO}_2$ -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  $\delta^{18}\text{O}$  values were produced using the method established by Nelson (2000).

For  $\delta^2\text{H}$  analysis, sample and standard waters were injected directly into a chromium furnace at 800 °C (Donnelly et al. 2001), with the evolved  $\text{H}_2$  gas analysed on-line via a VG Optima mass spectrometer. Final values for  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  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  $\pm 0.3\%$  for  $\delta^{18}\text{O}$ ,  $\pm 3\%$  for  $\delta^2\text{H}$ .

For sulphate- $\delta^{34}\text{S}$  isotope analysis, the barium sulphate precipitate was recovered from the sampling vessel, washed repeatedly in de-ionised water and dried.  $\text{SO}_2$  gas was liberated from each sample by combustion at 1065 °C with excess  $\text{Cu}_2\text{O}$  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 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 standard was better than  $\pm 0.3\%$ .

## 3. Results

### 3.1. Hydrochemical data

Field determinations and concentrations of major/minor ions are presented in Table 1. The water samples obtained from Markham fall into three broad categories (Fig. 4):

- Type A. Samples obtained during the investigative phase in 2011, prior to the installation of the heat pump system, from 250 and 340 m depth.
- Type B. Samples obtained from 2012 up to 28th January 2015, during the trialling and operation of the 'standing column' arrangement at 235–250 m depth (Regime 1 - Fig. 3).
- Type C. Samples obtained following 28th January 2015, during the trialling and operation of the 'standing column' arrangement at 153–170 m depth (Regime 2 - Fig. 3).

A clear difference is found between samples from

- Types A & B, which typically represent very saline, ammonium-, methane- and iron-rich water.
- Type C, which represents much less saline, methane- and iron-poor water.

The Type A samples (especially the initial sample from 250 m depth, with 14  $\text{mg/l}$   $\text{SO}_4^{2-}$  and 19  $\text{mg/l}$  Ba) contain lower concentrations of sulphate and elevated concentrations of barium, compared with the other samples. This is a very strong indicator of sulphate reduction at depth in the mine, as the absence of sulphate allows barium to accumulate without its solubility being inhibited by barite ( $\text{BaSO}_4$ ) saturation. The Type A samples are also highly saline sodium-chloride waters with up to 11 g/l chloride (over 60% seawater salinity).

The Type B samples contain sodium at around 4 g/l and chloride at around 6 g/l at an approximately 1:1 M ratio. This represents deep saline formation water commonly found at depth in Coal Measures strata (Banks, 1997) and is also associated with elevated ammoniacal nitrogen, at typically 4–5 mg/l in Type B samples. Sulphate is present at 500–1700 mg/l and the meq sulphate/chloride ratio varies from 0.06 to 0.22 (by comparison standard sea water has a ratio of 0.10 - Lenntech, 2015) (Fig. 5). Otherwise, Type B waters are characterised by 8–10 meq/l alkalinity, typically around 20 mg/l iron, 2.3–4.5 mg/l manganese, 76–110 mg/l potassium and around 5 mg/l strontium. Analyses of ferrous iron, compared with total iron, strongly suggest that the iron in the groundwater is maintained in dissolved, ferrous, form due to the reducing nature of the water.

The Markham No. 3 Shaft water is reducing and contains dissolved methane at concentrations of up to 9 mg/l in Type B samples. Type C samples have not been found to contain detectable methane, however, they contain nitrate and rather low concentrations of iron and manganese (Fig. 5), which suggests more oxidising water of a shallower nature. The ferrous and dissolved iron results for the Type C samples are in the range 0.07 to 0.16 mg/l, as compared with total iron of 0.3 to 0.7 mg/l, which may suggest that some of the dissolved iron has commenced oxidation to colloidal ferric iron oxyhydroxides.

The Type C samples are far less solute-rich than Type A or B, and seem to represent shallower, fresher water. Initially (February 2015), they contained sodium at 215 mg/l and chloride at 380 mg/l, at an approximately 0.87:1 M ratio. Ammoniacal nitrogen, was <0.1 mg/l with sulphate at 404 mg/l. Otherwise, the initial Type C water was characterised by 5 meq/l alkalinity, 0.3 mg/l iron, 0.03 mg/l manganese, 17 mg/l potassium, and around 0.62 mg/l strontium. Since May 2015, some of these parameters have crept back up a little, as deeper saline water appears to have been drawn into the 'standing column'

**Table 1**

Chemical properties of waters sampled from Markham No. 3 Shaft. UoG = University of Glasgow, ESG = Environmental Scientific Group, T = temperature, EC = electrical conductivity, 'nd' = not-determined, \* denotes field determination of pH, EC or alkalinity (other determinations at ESG lab). All non-stated values in mg/l, except pH units. The upper-shaded area represents Type A samples obtained from depth in the shaft prior to the commencement of the heat pump 'standing column'. The central unshaded area represents Type B samples obtained from 235 m depth during the initial standing column configuration. The lower-shaded area represents Type C samples obtained from 170 m depth during the most recent standing column configuration.

Sample (m bgl)	Date	Lab	pH	Alkalinity (meq/L)	T (°C)	EC (µS/cm)	Mg	Na	Ca	K	Fe	Mn	Ba	Sr	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>-</sup> N	CH <sub>4</sub>
250	31/08/11	ESG	7.0	8.21	nd	24200	160	3830	528	78	10.8	1.13	19.2	8.27	6940	14	nd	4.7	2.32
340	31/08/11	ESG	6.6	7.07	nd	40900	641	8550	879	106	80.7	2.632	0.35	14.1	11700	716	nd	14.3	nd
235	15/10/12	ESG	7.1	8.61	nd	24700	216	3720	431	109	21.8	2.277	0.15	5.35	6590	1684	nd	5.0	6.64
	15/10/12	ESG	7.2	8.69	nd	24100	218	3690	435	110	21.5	3.408	0.15	5.44	6590	1723	nd	5.0	9.04
	10/01/13	ESG	7.3	7.89	nd	20500	176	3920	382	77	3.91	3.742	0.15	4.76	5820	1711	nd	3.8	0.54
	10/01/13	ESG	7.3	8.09	nd	19700	175	3920	376	76	3.93	3.69	0.15	4.73	5860	1699	nd	3.8	0.93
	28/08/13	ESG	7.9	10.01	nd	22000	191	4040	362	85	20.8	4.45	0.15	4.74	6190	511	nd	4.4	4.32
	28/08/13	ESG	7.9	9.29	nd	22600	190	4170	359	85	21.3	4.48	0.15	4.73	6140	509	nd	4.4	3.01
170	16/02/15	ESG	7.5	4.96	nd	1900	31	215	110	17	0.31	0.025	0.08	0.62	380	404	nd	0.07	<0.02
	21/05/15	UoG	7.55*	5.30*	13.5	2627*	47	361	133	57	nd	nd	nd	nd	663	403	5.0	nd	nd
	30/06/15	UoG	7.15*	5.38*	15.2	2720*	47	397	134	47	nd	nd	nd	nd	732	409	3.9	nd	nd
	10/09/15	UoG	7.26*	5.44*	13.8	3268*	52	477	139	56	nd	nd	nd	nd	900	386	3.1	nd	nd
	17/09/15	ESG	7.2	6.25	nd	3160	43	434	130	26	0.72	0.027	0.12	1.04	829	135	nd	<0.01	<0.02
	08/10/15	UoG	7.18*	5.30*	14.2	3440*	53	512	131	50	nd	nd	nd	nd	1005	134	3.4	nd	nd
	18/11/15	UoG	7.34*	5.69*	nd	3024*	58	406	166	63	nd	nd	nd	nd	821	130	4.5	nd	nd
	17/12/15	UoG	7.24*	5.75*	13.8	3022*	57	393	161	65	nd	nd	nd	nd	818	131	4.8	nd	nd

recirculation cell (and as mine waters continue to rise), although sulphate and ammoniacal nitrogen have decreased to 135 and <0.01 mg/l respectively.

In the Type C waters the SO<sub>4</sub><sup>2-</sup>/Cl<sup>-</sup> meq ratio increases abruptly to a value of 0.8 (Fig. 5). This reflects the likelihood that a major source of sulphate in the Type C waters is now sulphide oxidation products (see Stable Isotope data, below), rather than deep-seated salinity. As 2015 progresses and the salinity increases, the SO<sub>4</sub><sup>2-</sup>/Cl<sup>-</sup> meq ratio falls again back down to values of <0.2 (as observed in Type A and B waters and consistent with a sea water ratio of c. 0.1) as the deep salinity reasserts itself.

Unfortunately, we have no temperature data from Type A or B waters, and so cannot produce a temperature to depth trend for the Markham No. 3 Shaft. The average temperature of Type C water samples, after being pumped from 170 m bgl to the surface, is 14.1 ± 0.7 °C. This is within expected temperature values of 14.2 to 15.7 °C given a geothermal gradient of 28 °C/km for the upper 1 km of sedimentary crust in the UK (Busby et al., 2011) and a long term average surface atmospheric temperature of 10.16 ± 0.73 °C, recorded at the Keyworth weather monitoring station in Nottinghamshire (Darling and Talbot, 2003).

### 3.2. Stable isotope data

This study is the first to perform isotopic analysis on Markham mine waters, so captured information is restricted to Type C waters. Values obtained from May to December 2015 for δ<sup>18</sup>O, δ<sup>2</sup>H and δ<sup>34</sup>S show virtually no variation out with standard errors across all samples (Table 2).

Markham No. 3 Shaft mine water δ<sup>18</sup>O and δ<sup>2</sup>H values show remarkable consistency and fall close to, or on the global meteoric water line (Fig. 6). Values of -8.2 ± 0.3‰ and -54 ± 1‰ for δ<sup>18</sup>O and δ<sup>2</sup>H are close to the analytical techniques' reproducibility and are similar to the weighted mean average meteoric water O and H isotopes for the nearby Keyworth area (Darling and Talbot, 2003). Average values of -6.5‰ and -44‰ for δ<sup>18</sup>O and δ<sup>2</sup>H for the Holme Brook meteoric control samples are typical for stream waters across northern England (Younger et al., 2015).

In terms of comparison to other groundwater bodies, averages from 61 analyses of deep borehole freshwater samples from the Triassic Lincolnshire Limestone aquifer (-8.0 ± 0.27 and -53.7 ± 2.26, Darling et al., 1997), 50 km to the east, are remarkably similar to Markham isotopic values and suggest a similar meteoric origin and subsurface mixing history. There is no evidence for extensive isotopic exchange with the host lithologies which would drive both δ<sup>18</sup>O and δ<sup>2</sup>H to higher values (Sheppard, 1986). The values of both water bodies are in line with contour map values of 'recent' groundwaters within unconfined aquifers believed to have been recharged within the Holocene (Darling et al., 2003).

There have also been isotopic studies completed for brine waters (with TDS values 60,540 to 197,000 ppm) in undersea Middle Coal Measures mine workings in northern England (Younger et al., 2015). These data fall generally in the same region as the Markham data. Salinity varies significantly between the mine water sites, but does not appear to exert a systematic control on the δ<sup>18</sup>O and δ<sup>2</sup>H values, which appear to behave rather conservatively, retaining near original surface water characteristics, running close to the global meteoric water line.

Carboniferous coal sulphate-δ<sup>34</sup>S values typically range 0–10‰ and are largely the result of δ<sup>34</sup>S fractionation during pyrite oxidation (Matthies et al., 2012; Elliot and Younger, 2014). The average Markham sulphate-δ<sup>34</sup>S value of 4.3‰ is within the typical range of 4–12‰ observed in local groundwaters from coal-bearing formations (Matthies et al., 2012).

## 4. Discussion

It is very common for the water column in deep shafts of non-pumped coal mine systems to be strongly stratified (Nuttall and Younger, 2004), often with solute-rich saline mine water at depth in the shaft with more 'dilute' recent recharge water floating on top at shallower depth. Pumping has the potential to disturb this stratified system (Elliot and Younger, 2007, 2014). The samples of Type A water from Markham No. 3 Shaft, taken from 250 to 340 m depth show that, at that depth there was a highly saline (>60% seawater), highly reducing (sulphate-reducing and methanogenic) hydrochemical regime.

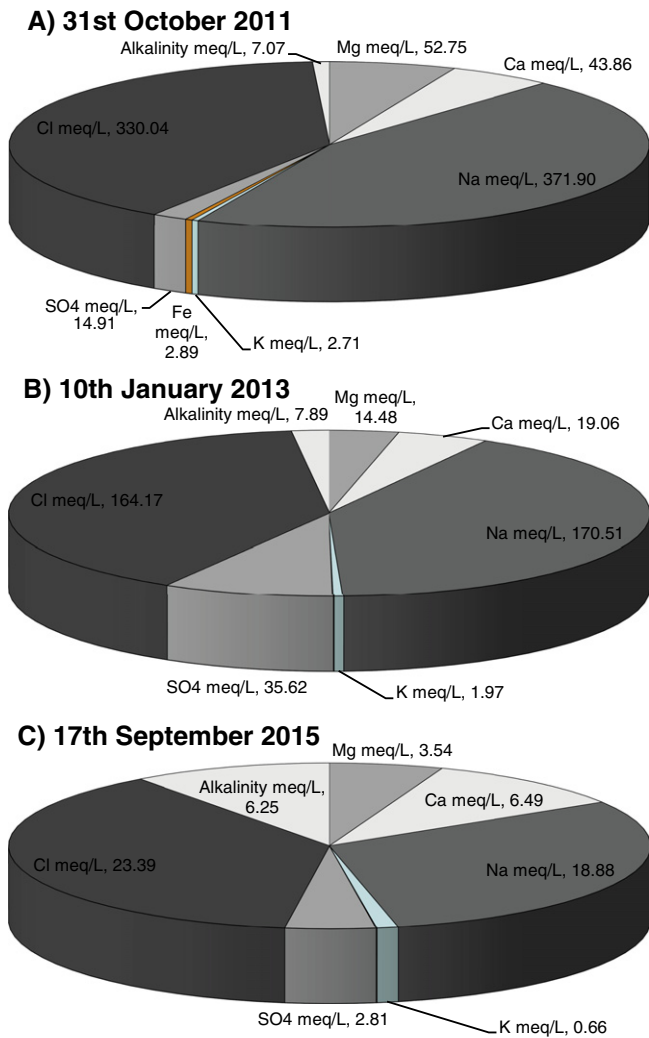


Fig. 4. Pie diagrams comparing the major ion (meq/L) composition of the Markham No. 3 Shaft mine water in October 2011 (Type A), January 2013 (Type B) and September 2015 (Type C).

When the heat pump ‘standing column’ scheme started operating, with pumping from 235 m depth, the water was somewhat less saline (c. 30% seawater) with no obvious evidence of sulphate reduction (elevated  $\text{SO}_4^{2-}$ , modest Ba and no odour of  $\text{H}_2\text{S}$  has been noted from Type B and C samples). High methane concentrations have been recorded in Type B samples, but this may have been migrating up from greater depth. The Type B waters contained high concentrations of Fe and Mn of several 10s of  $\text{mg l}^{-1}$  (Fig. 5) and also contained ammoniacal nitrogen. This suggests that the Type B waters fall within an Fe–Mn reducing, N-reducing redox regime. Thus, during the period 2012–2014 we can hypothesise that the heat pump ‘standing column’ may have been located in a transitional zone between deep, highly reducing brines below and, putatively, shallower, less saline, less reducing waters above.

When, in January 2015, the standing column pump was raised to 170 m, the ammoniacal nitrogen and dissolved iron and manganese concentrations fell sharply and the salinity reduced still further to only a few hundred  $\text{mg l}^{-1}$  chloride, suggesting that the ‘standing column’ now fell within a shallower, less saline, less reducing body of water (Type C) ‘floating’ on a deeper, denser saline water body (Type A). As the year of 2015 has progressed, the water has gradually become somewhat more saline. This could be due to the continued pumping drawing up water from depth (although this would seem unlikely if the ‘standing column’ is a closed cell, and with a pumped circulation of c. 2 l/s). It seems more likely that the continued post-closure recovery and rise of

minewater levels in the Markham-Bolsover complex has lifted the hydrostratigraphical interface slowly up the shaft, such that the pump ‘sees’ progressive increases in the proportion of deep saline water (at least until the rise in water level allows the pump to be raised once again).

The implications of this hypothesis are threefold:

- Corrosion. The presence of chloride salinity and highly reducing conditions can promote corrosion of pipes and heat exchangers. Using marine grade materials can mitigate this risk, although even stainless steel can be susceptible to corrosion under reducing conditions, where protective surface oxide layers cannot form. Thus, a knowledge of the dynamics of saline and redox interfaces will allow prognoses to be made of the risk of corrosion in pumping-heat exchange systems.

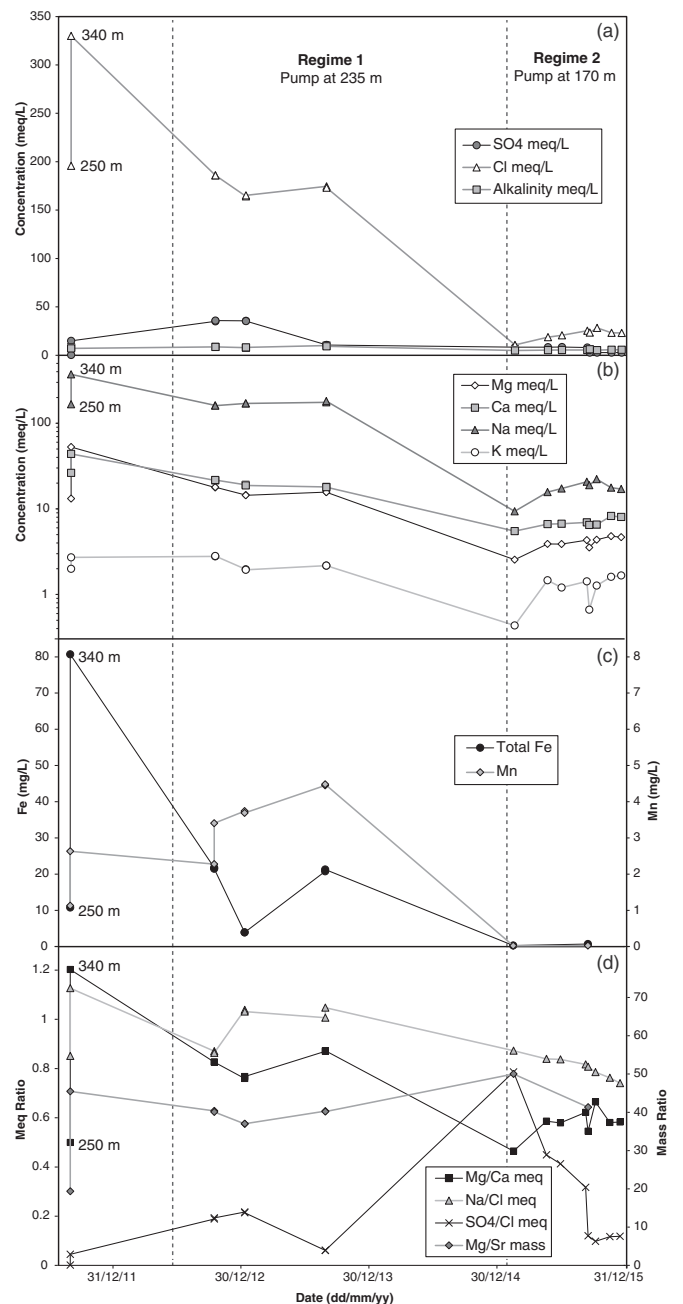


Fig. 5. Variations in Markham No. 3 Shaft water with time. (a) Major cation composition. (b) Major anion composition. (c) Total iron and manganese. (d) Key hydrochemical ratios.

**Table 2**

O, H, S isotope systematics of H<sub>2</sub>O and SO<sub>4</sub><sup>2-</sup>. All  $\delta$ -values ‰ against Vienna Standard Mean Ocean Water (VSMOW) or Canyon Diablo Troilite (CDT) standards, 'nm' = not-determined. Average values of triplicate analyses which reproduce well within error of reproducibility. Holme Brook, Chesterfield, represents local meteoric water samples.

Sample site	Date	$\delta^{18}\text{O}$	$\delta^2\text{H}$	$\delta^{34}\text{S} (\text{SO}_4)$
		(VSMOW)	(VSMOW)	(VCDT)
Markham No. 3 Shaft	21/05/15	-7.3	-49	3.8
	30/06/15	-8.1	-51	4.7
	10/09/15	-8.3	-54	4.8
	08/10/15	-8.2	-55	5.8
	18/11/15	-7.9	-53	6.3
	17/12/15	-8	-54	6.1
Holme Brook	06/07/15	-6.3	-45	nd
	08/10/15	-6.7	-42	nd
	25/11/15	-6.8	-44	nd
	17/12/15	-6.9	-45	nd

- (ii) Coal mine waters are notorious for containing elevated concentrations of iron, sulphate and manganese, ultimately due to oxidation of pyrite in the mined environment and secondary mineral weathering from the acid generated by that reaction. Precipitation of iron (and, to a lesser extent, manganese) oxyhydroxides can rapidly clog up pipework, heat exchangers and reinjection boreholes, if the iron is allowed to come into contact with oxygen (Banks et al., 2009). During the initial years of operation (when Type B waters were pumped), the Markham scheme was noteworthy for the fact that, despite relatively high dissolved iron concentrations, no serious issues with iron clogging were noted in the heat exchangers, presumably because the highly reducing nature of the water ensured that the iron remained in solution. It remains to be seen whether this will continue to be the case, now that the system is pumping less reducing waters (Type C), albeit with lower total iron concentrations.
- (iii) The fact that a hydrochemical stratification persists in the shaft suggests that (i) there is no natural significant convection or hydraulically forced advection of water in the shaft (and this has

implications for the overall thermal capacity of the 'standing column').

In terms of Type C water provenance, slowly increasing major ion concentrations suggests an increasing influence of a modest component of deeper saline water, whilst largely uniform  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values are completely consistent with fresh, meteoric waters. This phenomenon is not uncommon for other similar studies, e.g. at the nearby Caphouse Colliery (Burnside et al., in press) and across northern England (Younger et al., 2015), where 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 m bgl for abandoned mines and 1600 m bgl for exploration boreholes) is observed. This 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.

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. There are no local granite bodies and sulphate- $\delta^{34}\text{S}$  values preclude any major evaporite influence. Similar to the Caphouse Colliery (Burnside et al., in press), 'freeze-out' is the most likely cause of delineation between water isotopes and ion concentrations.

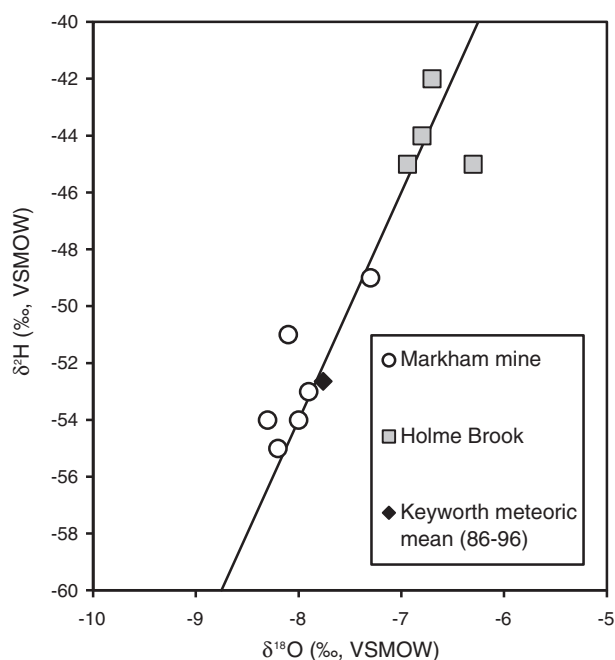
## 5. Conclusion

The abandoned workings of the former Markham Colliery are being exploited, via a 'standing column' 20 kW heat pump arrangement in Markham No. 3 Shaft, to produce thermal energy to a modest complex of offices at the surface. Though slowing, ground water rebound following closure of the colliery is still in progress. This has allowed for, and may further allow, raising of the 'standing column' arrangement in the shaft. Sampling of mine waters at three different depths since August 2011 have returned three distinct water types that represent progressively less saline waters and suggest the presence of stratification in the shaft water column.

From 2012, water was pumped from 235 m bgl in the shaft at c. 15 °C and 2–3 l/s. The thermally spent (cool) water was returned to the same shaft at c. 250 m bgl at around 12 °C, after passing through shell and tube heat exchangers. The mine water contained iron and c. 6000 mg/l chloride, but was highly reducing, so great care was taken to avoid contact with oxygen and prevent ochre scaling. Since January 2015, the pump has been re-set at a depth of 170 m bgl and extracts comparatively dilute, iron-poor waters which are returned at 153 m bgl. The salinity of these waters gradually increased as 2015 progressed. This is likely a result of continued post-closure water table recovery and rise of minewater levels in the Markham-Bolsover complex lifting the hydrostratigraphical interface slowly up the shaft, such that the pump "sees" progressive increases in the proportion of deep saline water.

There is virtually no variation in isotopic values throughout 2015.  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  compositions suggest the presence of meteoric sourced waters that have had little isotopic exchange with mineral phases. Sulphate- $\delta^{34}\text{S}$  values are typical for British Coal Measures and consistent with  $\delta^{34}\text{S}$  fractionation during pyrite oxidation.

Thermal energy has been successfully extracted from the Markham No. 3 Shaft since October 2012. Alternating pump depths, differing water chemistries and return of thermally spent waters have yet to show any detrimental effects on the geothermal resource. However, it would be wise to maintain a comprehensive water monitoring program as increasing salinity levels pose a possible threat of corrosion to the pump-heat exchange system and the extraction of less reducing waters increases the risk of ochre formation, despite the low iron concentrations. The persistent stratification in the shaft, and subsequent lack of



**Fig. 6.** Plot of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  for Markham mine waters, as compared to local Holme Brook and long term weighted mean values for meteoric water recorded at Keyworth (Darling and Talbot, 2003). The solid trend line represents the Global Mean Meteoric Water Line (GMWL).

meaningful advection, has implications for the thermal capacity of the water body should local heat demand expand in the future.

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