Investigation of sulphate sulphur isotope variations in the Skerne Magnesian Limestone Water body

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Investigation of sulphate sulphur isotope variations in the Skerne Magnesian Limestone Water body

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Foreword

This report is the published product of a commissioned study (contract: Skerne Magnesian Limestone - Isotopes; number: ENV0003281C) by the British Geological Survey (BGS) on behalf of the Environmental Agency on the sulphur isotope composition of sulphate in the Skerne Catchment in County Durham.

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Summary

This report presents the results of a sulphur isotope investigation undertaken in the Skerne catchment, located in County Durham, north of Darlington, to investigate the source of groundwater sulphate in the Magnesian Limestone Aquifer. Groundwater and surface waters in the catchment are at risk from a number of current and historic anthropogenic activities. Sulphate is the biggest risk to the public water supplies; as there is currently no cost-effective treatment available and it could render supplies unusable. The elevated sulphate could be both naturally occurring, due to the presence of gypsum or anhydrite bands in the Magnesian Limestone, or it could be due to abandoned coal mine water, or even saline intrusion pollution. Because of the large difference in the sulphate sulphur isotope composition expected between "marine sulphate", including sulphate derived from marine evaporites, and "non-marine sulphate" derived from the oxidation of sulphide in the coal seams and mine workings, sulphur isotopes were considered promising tracers to discern mine water sources from natural Permian evaporite sources of sulphate.

A survey was carried out at 28 sites where groundwater was sampled in July 2018 from boreholes in the Magnesian Limestone Aquifer and in the Coal Measures, following a pilot study comprising 7 boreholes in July 2017. A small number of surface waters, hyporheic zone waters, springs, and soil leachates, sampled during 2017-2018, were also analysed for sulphur isotopes to complement the borehole data. This has allowed the characterisation of the sulphur isotope composition of potential sources of dissolved sulphate.

Most of the Magnesian Limestone aquifer groundwaters cluster close to the Global Meteoric Water Line (GMWL) on the dual water $\delta^{18}O$ and $\delta^{2}H$ graph with no evidence of mixing with Na-rich coal mine water, the latter being more depleted in ^{18}O and ^{2}H; there is a small number of boreholes immediately in proximity of the coal seam boreholes, clearly showing signs of water mixing. With higher $\delta^{18}O$ and $\delta^{2}H$ than the main Magnesian Limestone group, and slightly offset from the GMWL, is also a small group of Magnesian Limestone boreholes. Repeated sampling would better discern the different recharge paths suggested by this single sampling event in July 2018.

Groundwaters associated with the worked and unworked coal seam boreholes in this study are of two water types: sodium sulphate ($Na–SO_4$) and sodium bicarbonate ($Na–HCO_3$) waters, variably enriched in dissolved sulphate. Two $\delta^{34}S$ measurements of the dissolved sulphate in the $Na–SO_4$ coal seam boreholes are +13.1‰ and +23.4‰. The lack of the more typical ^{34}S-depleted sulphate derived from the oxidation of pyrite is hence apparent. A similar range of high sulphate $\delta^{34}S$ values has been described in recent studies, and attributed to deep coal mine systems.

From a review of published $\delta^{34}S$ values for marine evaporites, groundwaters containing sulphate solely derived from the dissolution of Permian marine evaporites are characterised by ^{34}S-enriched sulphate ($\delta^{34}S$ values range from +8.2 to +11.1‰).

There is, therefore, less of a contrasting isotope signature between potential "evaporite" and "coal mine water" end-members. For example, one sample of coal mine water with $\delta^{34}S$ values of +13.1‰ is not too dissimilar to the average Permian evaporite sulphate with $\delta^{34}S$ value of around +10‰. This makes discrimination of the dissolved sulphate sources based on sulphur isotope less certain, especially at low sulphate concentrations.

To help the data interpretation, we have modelled the sulphate and sulphur isotope compositions of mixtures of hypothetical end-members and used the evidence from these simulations to constrain possible groundwater contributions and mixing. In particular we simulate how the HARDWICK HALL borehole, representing the Magnesian Limestone aquifer background, with a sulphate concentration of 89 mg/l, and a $\delta^{34}S$ value of +1.0‰, evolves during mixing with the following end-members: i) the coal mine waters in this study, ii) a Permian evaporite source, iii) seawater and iv) acid mine drainage.

A summary of the data interpretation based on the above modelling is as follows.

Over the mine plume area, inputs of coal mine water-derived sulphate are significant in at least one Magnesian Limestone borehole, and detectable in others, supported by the water isotope

$\delta^{18}O$ and $\delta^{2}H$ data, indicating for these samples water mixing between the coal mine water and the Magnesian Limestone aquifer.

Among the Magnesian Limestone boreholes, where gypsum or anhydrite were noted in the borehole logs, only DALTON PIERCY NO 3 and NO 6 boreholes have high sulphate concentrations and display constant $\delta^{34}S$ values of +10.2‰. Given how close this value is to the Permian evaporites' $\delta^{34}S$ values, it could be plausibly explained by a gypsum dissolution source, although a "coal mine water" contribution with a $\delta^{34}S$ signature of +13‰ cannot be totally excluded, as shown by the mixing curves. Many of the Magnesian Limestone boreholes with a sulphate concentration around 100 mg/l (range 85–130 mg/l) are characterised instead by a low $\delta^{34}S$ range (-0.7 to +7.2‰). For most of these low sulphate Magnesian Limestone boreholes, uncertainties in discriminating the source of sulphate are higher.

The contribution of sulphate from seawater is difficult to discern in the present data for the saline waters of HART RESERVOIR and HARTLEPOOL IND ESTATE REPLACEMENT boreholes, with similar $\delta^{34}S$ values of +21.1‰ and +27‰, as they fall far away from the Seawater–Magnesian Limestone mixing line.

Many samples fall far outside of these mixing envelopes, suggesting non-conservative behaviour of the sulphate. The very high $\delta^{34}S$ and low sulphate concentrations can be interpreted as a possible sign of reduction of sulphates and enrichment in the heavier ^{34}S isotope of the residual (low concentration) sulphate.

Additional samples obtained during this study include: i) A spring in the Ford Formation from AYCLIFFE QUARRY to the south east of Aycliffe Village which provides an additional background sample characterised for sulphur isotopes. The water has a SO_4 of 69 mg/l and a $\delta^{34}S$ value of +2.3‰ and well resembles the composition of HARDWICK HALL borehole. ii) A Mg–SO_4 spring, sampled in Woodham Burn and described in previous studies for its impact on the surface water quality because of its high sulphate concentrations of ~800 mg/l. It has a stable $\delta^{34}S$ value of ~ +5.5‰. iii) a surface water impacted by mine water inflow with a Mg–SO_4 composition, and a $\delta^{34}S$ value of +6.9‰.

The $\delta^{34}S$ value of +5.5‰ of the Mg-SO_4 spring at Woodham Burn points to a contribution of low $\delta^{34}S$-sulphate, as expected from the oxidation of pyrite. These data support the mechanism, hypothesised in Palumbo-Roe et al. (2020) to account for the spring composition, of dissolution of dolomite in the presence of acidic water, where the source of acidity comes from coal mine water due to the oxidation of pyrite.

There is a much narrower and lower range of $\delta^{34}S$ in surface water compared to the groundwater samples. With most $\delta^{34}S$ values less than +7‰, none of the high values measured in the boreholes were noted in the surface water, hyporheic zone or soil leachate samples, except for two samples in the hyporheic zone of Woodham Burn with $\delta^{34}S$ +36.3‰ and +13.4‰, values taken as further evidence of the sulphate reduction during the 2018 summer indicated by the hydrochemistry.

Recommendations for future work, building upon these findings, are suggested.

1 Introduction

Groundwater and surface waters within the Skerne catchment (located in County Durham, north of Darlington) are currently at risk from a number of current and historic anthropogenic activities, including water abstraction, saline intrusion and historic coal mining. These activities are resulting in a number of WFD failures and are threatening the public water supplies of Hartlepool and Wynyard (100,000 people).

A catchment-based project was commenced by the Environment Agency in 2016 to investigate the primary reason(s) for the WFD failures and how best to tackle them. A range of research-based studies were undertaken in partnership with BGS between 2018 and 2020 to better understand the geology and hydrogeology and the relationship between ground and surface water flows and chemistry, focussing on the hyporheic zone (Palumbo-Roe et al. 2019; 2020).

Whilst undertaking the hyporheic zone research studies, it was identified that sulphate was found in high concentrations across the whole of the catchment; within surface water, groundwater and soils. Sulphate is the biggest risk to the public water supplies; as there is currently no cost-effective treatment available, it could render supplies unusable. Therefore, it is important to identify the major source(s) of the dissolved sulphate.

The complex geology and hydrogeology of the catchment make the understanding of the sources of the high sulphate difficult. The Skerne catchment is underlain by the Magnesian Limestone principal aquifer, which comprises a series of marine limestones and dolomites, marls and evaporites of Permian age (Zechstein Group) (Figure 1) and overlies unconformably Carboniferous Coal Measures. The Edlington, the Roxby and the Hartlepool Anhydrite formations contain evaporite minerals such as gypsum and anhydrite. A layer of superficial drift deposit, predominantly glacial till, covers the Magnesian Limestone, with areas of thin drift where groundwater-surface water interaction occurs. Mining took place in mining blocks which underlie the Magnesian Limestone and with the mine closures and the cessation of mine dewatering, groundwater levels have risen since the late 1970s in both the mine workings and the impacted Magnesian Limestone boreholes. Groundwaters with high salinity (Na up to 4600 mg/l, Cl up to 9000 mg/l) have been found in the coastal areas, particularly around Hartlepool and are associated with saline intrusion (Bearcock and Smedley, 2009).

Therefore, the elevated sulphate could be both naturally occurring, due to the presence of gypsum or anhydrite bands in the Magnesian Limestone, or could be due to mine water, or even saline intrusion pollution.

Based on several successful studies of river and groundwater bodies applying sulphur isotope ratios ($\delta^{34}S$) as a tracer of natural or anthropogenic sources of sulphate (e.g. Gammons et al. 2013; Longinelli & Edmond, 1983; Otero et al. 2008; Trettin et al. 2007), the BGS in collaboration with the Environment Agency carried out a program of water sampling between 2017 and 2018 to characterise the sulphur isotope composition of sulphate in the Skerne Magnesian Limestone Water body, with the aim to distinguish between different sulphate sources. The purpose of this report is to present the findings of the sulphur isotope investigation undertaken in the Skerne catchment. We summarise previous literature on the $\delta^{34}S$ signature of sulphate of natural and anthropogenic origin, of relevance to the study area; we present and interpret the $\delta^{34}S_{SO4}$ and water $\delta^{18}O$ and $\delta^{2}H$ of 28 groundwaters, complemented by a small number of surface waters, hyporheic zone waters, springs, and soil leachates, sampled during 2017-2018, to help determine sources of water and dissolved sulphate in the catchment.

Table 1 Bedrock geology in the study area

AGE	GROUP	FORMATION	BGS LEXICON OF ROCK UNIT
Permian	Zechstein Group	Roxby Formation	Mudstone and siltstone, reddish brown, with subordinate sandstone. Sulphates (gypsum, anhydrite) common towards base. Previous name: Upper Permian Marl
		Seaham Formation	Predominantly thin-bedded limestone (calcite mudstone/wackestone with some interbedded coquina, packstone, grainstone, mudstone and concretionary limestone) with some dolostone. Previous name: Upper Magnesian Limestone
		Edlington Formation	Mudstone, red-brown, with subordinate siltstone and sandstone, greenish-grey sandstone more common in Nottinghamshire. Dolostone and gypsum/anhydrite locally common. Previous names: Middle Permian Marls; Permian Middle Marls
		Hartlepool Anhydrite Formation	Anhydrite rock; translucent blue-grey and grey with a faint to well-marked, coarsely marbled appearance that results from an anastomosing (penemosaic) net of pale brown dolostone.
		Ford Formation	Dolomite that comprises three distinct facies: shelf-edge reef that separates a broad belt of back-reef and lagoonal beds to the west from a belt of fore-reef talus aprons and off-reef beds to the east. Previous name: Middle Magnesian Limestone
		Raisby Formation	Cream, brown and grey, fine-grained dolostone with grey, fine-grained limestone. Previous name: Lower Magnesian Limestone

2 Sulphur isotope signature of potential sources of sulphates

A description of the sulphur isotope distribution in the sulphate of different origins and pathways is given in the following paragraphs.

2.1 PERMIAN MARINE EVAPORITE SULPHATES IN THE MAGNESIAN LIMESTONE SEQUENCE

Significant contrasts between marine gypsum deposits of different ages can be expected due to the systematic shifts of sulphate $\delta^{34}S$ and $\delta^{18}O$ in seawater over the geological timescale, as these changes are preserved in the isotope signatures of evaporite layers formed from seawater (Claypool et al. 1980).

The following studies report relevant sulphur isotope measurements:

The work of Taylor (1983) on the Mercia Mudstones and associated sulphate horizons in the English Midlands, reported much lower values of +10 to +12‰, for the Upper Permian sulphate horizons compared to the Mercia Mudstones Triassic sulphate horizons. Highly distinctive isotope signatures of evaporites from different ages were indeed used in the study of Kloppmann et al. (2014) to assess the provenance and trades of artwork, tracing medieval and renaissance alabaster works of art back to quarries.

Bottrell et al. (2006) studied the leachate solutions from Permian Marl drill chippings of the Cawood Marsh borehole, in a study of the saline groundwaters in the Selby Triassic sandstone aquifer in Yorkshire; the authors found high concentrations of sulphate in the Middle Permian Marl with a restricted range of sulphate $\delta^{34}S$ values (+8.2 to +10.2‰) and $\delta^{18}O$ (+9.3 to +11.7‰).

Similar values are documented by Heaton (2004), finding that the sulphate minerals, anhydrite and gypsum, in Permian marls and evaporites (Hartlepool Anhydrite Formation, Roxby Formation, Billingham Anhydrite Formation, Hayton Anhydrite Formation) had $\delta^{34}S$ values = +10.0 to +11.1‰, and $\delta^{18}O$ = +10.8 to +13.6‰, whilst those in Triassic mudstones and sandstones had $\delta^{34}S$ = +11.2 to +20.8‰, and $\delta^{18}O$ = +12.6 to +15.1‰.

2.2 MODERN SEAWATER

The Magnesian Limestone groundwater in the area of Hartlepool is believed to be impacted by seawater intrusion (Bearcock and Smedley, 2009); if so, the groundwater composition is expected to contain relatively high sulphate associated with high chloride and sodium concentrations.

Evidence of seawater intrusion with a modern seawater $\delta^{34}S$ and $\delta^{18}O$ value of the dissolved sulphate in seawater of + 21.24‰ and +9.5‰, respectively (Tostevin et al. 2014; Longinelli & Craig 1967), should be diagnostic in these samples; the waters are also expected to differ in their water $\delta^{18}O$ and $\delta^{2}H$ isotopic composition from the main Magnesian Limestone groundwater body.

2.3 NON-MARINE SULPHATE

Non-marine sulphate sources such as the oxidation of sulphides are typically depleted in ^{34}S with respect to marine sulphate. The sulphate in water derived simply by oxidation of pyrite will correspond to the original sulphide in sulphur isotopic composition, since this process carries little or no sulphur isotopic fractionation (Nriagu et al. 1991).

Potential non-marine sulphate sources of sulphate in the study area are described below.

2.4 COAL MINE WATER

Poor quality mine water is known to have historically entered the Magnesian Limestone from the underlying Coal Measures (EA, 2012).

UK Coal Measures pyrite can exhibit a wide range of $\delta^{34}S$, from <-20‰ up to +12‰ and rarely higher. Mean values tend to be in the range of 0 to +5‰.

Coal Measures brine samples collected between 650 and 750 m bgl in the Selby area had sulphate $\delta^{34}S$ ranges from +3.9 to +11.7‰, while $\delta^{18}O$ ranged from +2.6 to +11.9‰ (Bottrell et al 2006).

The recent studies of Banks et al. (2020) and Banks and Boyle (2023) have investigated the sulphur isotopic composition of dissolved sulphate in coal mine waters in Europe and in the East Midlands, South Yorkshire and Tyneside mining areas of England. They found that most mine waters emerging by shallow gravity drainage have dissolved sulphate $\delta^{34}S$ values of <+10‰, suggesting a derivation of sulphate from the oxidation of pyrite. Deeper mine waters, pumped from boreholes or shafts, tended to be more saline with dissolved sulphate $\delta^{34}S$ values of >+14‰ and, in two cases, >+30‰.

2.5 QUATERNARY DEPOSITS

The glacial till as a source of sulphate was hypothesised as an additional source of sulphate to explain high sulphate in some boreholes in the area of Darlington (Lamont-Black et al. 2002 and 2005). According to the authors, incorporation into the till of pyrite-rich material from the Coal Measures outcrop (which was traversed by the glacier that deposited the till) and its subsequent oxidation with secondary soluble sulphate minerals from the weathering of the pyrite, would provide the high-sulphate levels in particular hydrogeological settings in the Darlington area. This possibility is supported by the frequent inclusion of coal fragments in the till. A sulphur isotope composition of the sulphate reflecting the original sulphide, and typically depleted in ^{34}S compared to an evaporite mineral source of sulphate, would be expected.

Table 2 gives more details on the potential sources of sulphate in the Quaternary deposits around Woodham Burn, one of the areas of surface water-groundwater connectivity in the Skerne catchment, studied in Palumbo-Roe et al. (2019, 2020).

Table 2 Potential quaternary sources of sulphate in the groundwater at Woodham Burn

	Lithology	Sulphate source	References
Quaternary	Alluvium: Clay silt sand gravel	Coal and pyrite	Price et al. (2007)
	Tyne and Wear Glaciolacustrine deposits: pale grey to greyish brown laminated, micaceous clays and silts with some fine quartz and coal sand partings. Well developed in the area of the Carrs	Coal and pyrite	Samuel (1979)
	Wear Till Formation: Silty or sandy clay with gravel, cobbles and/or boulders. Range of local and exotic clasts. Firm to stiff, extremely consolidated, stony, brown/blue with lenses of clay, silty clay, sand and sand and gravel.	Gypsum, pyrite, coal; less susceptible to leaching because of the low permeability.	Price et al. (2007)
	Maiden's Hall Sand and Gravel Formation and Ebchester Sand and Gravel formations. Glaciofluvial sand and gravel	Includes Coal Measures strata therefore pyrite	Price et al. (2007)

2.6 ANTHROPOGENIC DEPOSITS

Agricultural lime, which is used to adjust the acidity of soil is produced as a by-product from a number of Magnesian Limestone quarries in County Durham, where the primary purpose of extraction has been the production of aggregates or for use in the steel and chemical industry. According to a survey over the period 2005 to 2012, agricultural lime had been produced at six quarries in County Durham: Thrislington Quarry, Crime Rigg Quarry, Coxhoe Quarry, Aycliffe Quarry, Witch Hill Quarry and Bishop Middleham Quarry (Source: County Durham Plan - Minerals

& Waste Technical Paper (April 2014) downloaded from https://durhamcc-consult.objective.co.uk/file/2911111). The potential contribution of agricultural lime from these local quarries to the dissolved sulphate "pollution" would not, however, differ in sulphur isotope signature from the Magnesian Limestone "baseline", and therefore is difficult to discriminate on the basis of the isotope approach only.

2.7 ISOTOPIC FRACTIONATION

The most important sulphur isotopic fractionation is due to the dissimilatory reduction of sulphate to sulphide, while the sulphide oxidation carries little or no sulphur isotopic fractionation. Bacterial sulphate reduction is accompanied by a characteristic large fractionation of sulphur isotopes, which produces sulphides as much as 40 to 60‰ lower in $\delta^{34}S$ than the sulphate. Where sulphate is only partially reduced, isotope fractionation then results in an increase in the $\delta^{34}S$ of the residual sulphate compared with the initial sulphate (Canfield, 2001). It is therefore important to consider and ascertain the potential role of sulphate reduction which can overprint the source signature.

3 Material

The sulphate sulphur isotope dataset focuses on groundwater samples, but also includes a small range of other water types. The full list is reported in the Appendices and a summary sample description is given below.

3.1 BOROHOLE SAMPLES

Groundwater samples from boreholes into the Magnesian Limestone and boreholes in the Coal Measures were collected in:

- July 2017: 7 boreholes sampled by the EA staff on 12/07/2017
- July 2018: 7 boreholes resampled + 21 additional boreholes sampled by EA staff on 17-18/07/2018 and 24/07/2018.

Borehole locations are shown in Figure 1 and description reported in Appendix 1 and Appendix 2.

3.2 ADDITIONAL SAMPLES

Additional samples, collected by BGS during the hyporheic zone study reported in Palumbo-Roe et al. (2019, 2020), were also analysed for sulphur isotopes to provide a first dataset to study the sulphur isotope distribution across other compartments of the Skerne catchment and complement the groundwater data. Location of the additional samples is shown in Figure 1. Background information on the sampling methodology and analytical methods can be found in the above reports.

The samples analysed for sulphate $\delta^{34}S$ are:

- a Magnesian Limestone spring at Aycliffe Quarry (in Figure 1, NZ29524 22571) sampled by BGS staff on 17/07/2018 (Figure 2).

- Surface water from the Skerne catchment (Locations: A02, WB, BRAD.B, D01, F01 in Figure 1).

- Hyporheic water from the Woodham Burn ("WB" in Figure 1, NZ29380 27080).
  Pore water was sampled and analysed from the sediment bed depth profile of the Woodham Burn in two occasions.

- High sulphate spring water ("Bubbly Spring" in Figure 1, NZ29380 27080).
  A high-sulphate spring impacting surface water at Woodham Burn (Palumbo-Roe et al. 2020) was sampled in two occasions (Figure 3).

- Rock and soil leachates.
  Soils samples from Woodham Burn and one marl rock sample from Aycliffe Quarry were leached with deionised water to extract soluble sulphate for sulphur-isotope analysis (sample location and method in Palumbo-Roe et al. 2020).
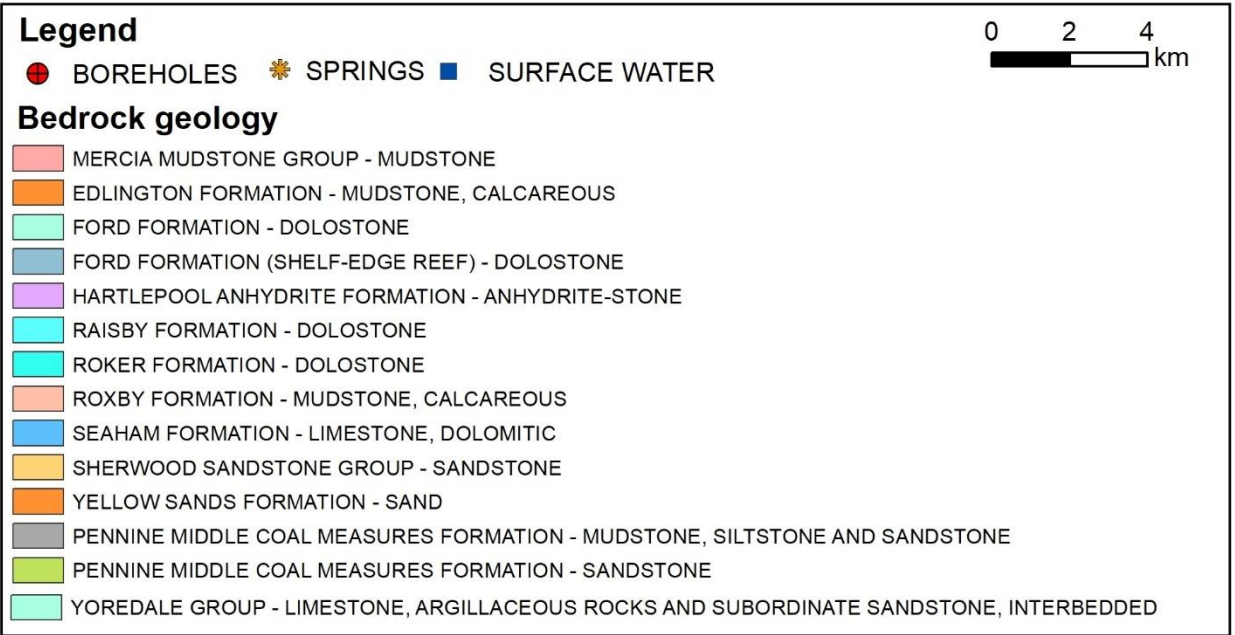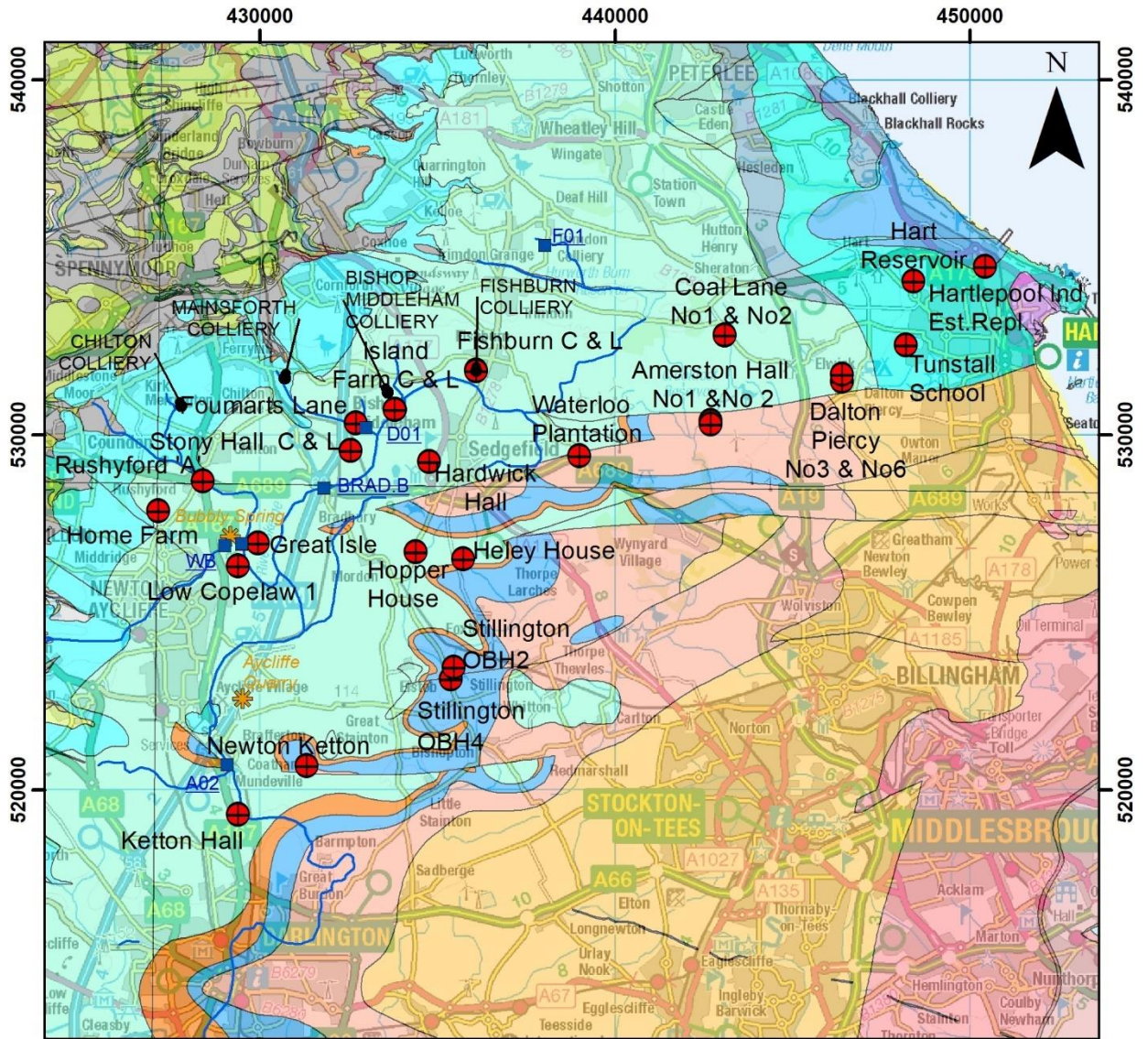
Figure 1: Bedrock geology and water sampling locations for sulphur isotope analysis. Contains Ordnance Survey data © Crown Copyright and database right 2023.

Figure 2 Springs at Aycliffe Quarry [NZ29524 22571].

Figure 3 Spring through the stream bed at Woodham Burn [NZ29172 277154] [Bubbly site].

4 Analysis

Chemical analysis was undertaken by the BGS laboratories except for the July 2018 borehole samples for which the EA provided the chemical analysis. Classification of water types was obtained using the Geochemist workbench software.

The sulphur isotope analysis of the dissolved sulphate was carried out in the Stable Isotope Facility, BGS, Keyworth. For a small number of samples, additional $^{18}O/^{16}O$ ratios of the sulphate were determined.

Sulphate was recovered from the untreated 60 ml water samples which were acidified with HCl, boiled, and 10 ml of 1N $BaCl_2$ added for precipitation of $BaSO_4$. Analyses were performed on Thermo-Finnigan elemental analysers linked to a Delta XLPLUS continuous flow isotope ratio mass spectrometer. $^{34}S/^{32}S$ ratios were determined on SO_2 formed by oxidative combustion of 300 to 600 micrograms $BaSO_4$ in tin capsules with V_2O_5 at 1000°C, with an average replication of ±0.2‰. $^{18}O/^{16}O$ ratios were determined on CO formed by reductive pyrolysis of 150 to 250 micrograms $BaSO_4$ in silver capsules at 1400°C, with an average replication of ±0.3‰. $\delta^{34}S$ and $\delta^{18}O$ values were converted to the VCDT and VSMOW scales, respectively, through within-run analyses of the following standards: NBS-127 (Accepted $\delta^{34}S$ and $\delta^{18}O$ of NBS-127 = +21.1‰ versus VCDT, and +9.3‰ versus VSMOW, respectively), SO6 (Accepted $\delta^{34}S$ and $\delta^{18}O$ of SO6 = -34.05‰ versus VCDT, and -11.35‰ versus VSMOW, respectively).

The 28 boreholes sampled by EA in July 2018 were also analysed for water $\delta^{18}O$ and δ^2H. The waters were equilibrated with CO_2 using an Isoprime Aquaprep for oxygen isotope analysis performed on an Isoprime 100 mass spectrometer. For hydrogen isotope analysis, an on-line Cr reduction method was used with a EuroPyrOH-3110 system coupled to a Micromass Isoprime mass spectrometer. Isotopic ratios ($^{18}O/^{16}O$ and $^2H/^1H$) are expressed in delta units, $\delta^{18}O$ and δ^2H (‰, parts per mille), and defined in relation to the International standard, VSMOW2 (Vienna Standard Mean Ocean Water2). Analytical precision is typically +/-0.05‰ for $\delta^{18}O$ and +/-1.0‰ for δ^2H.

5 Results

5.1 WATER OXYGEN AND HYDROGEN ISOTOPES IN GROUNDWATER

Stable water $\delta^{18}O$ and δ^2H were analysed for the 2018 boreholes (Table 4).

The relationship between $\delta^{18}O$ and δ^2H in most of the groundwater samples shows a general correspondence with the Global Meteoric Water Line (GMWL), indicating that the groundwaters represent recharged local modern rainfall (Figure 4). The Magnesian Limestone main group clusters around $\delta^{18}O$ -8.1‰ and δ^2H -54‰, values consistent with previous analysis in Bearcock and Smedley (2009) for the Magnesian Limestone aquifer.

There is, however, a clear separation of three of the mine water boreholes (FISHBURN C, STONY HALL C, ISLAND FARM C) from the main group of Magnesian Limestone boreholes. These mine water boreholes have the lowest isotopic ratios. On the other end of the global meteoric water line, with higher $\delta^{18}O$ and δ^2H values than the Magnesian Limestone group, and slightly offset from the GMWL, is the coal seam borehole NCB22 Home Farm. The water isotope values indicate different recharge systems for these coal seam boreholes.

Although for many of the Magnesian Limestone aquifer groundwaters there is no evidence of mixing with coal mine water, for FISHBURN L and STONY HALL L, the Magnesian Limestone boreholes located closest to the coal seam boreholes, and thought to be impacted by mine water, the isotopic composition is intermediate between the coal seam and the Magnesian Limestone boreholes, indicating the water mixing and connectivity between the coal mine workings and the Magnesian Limestone aquifer. Evidence of similar mixing between ISLAND FARM C and ISLAND FARM L boreholes is missing, as, ISLAND FARM L remains in Figure 4 to the right of the Magnesian Limestone borehole group, and slightly offset from the GMWL.

It is also noted that the boreholes COAL LANE 1 & 2, LOW COPELAW 1, DALTON PIECY 3 & 6, NEWTON KETTON (NRAG) and NCB22 (HOME FARM) separate from the main Magnesian Limestone borehole group. For these boreholes, repeated sampling would allow us to discern the different recharge paths suggested by this single sampling event in July 2018.

The highest $\delta^{18}O$ and δ^2H values are from the 3 saline boreholes, with e.g. HARTLEPOOL IND ESTATE REPLACEMENT borehole with values of $\delta^{18}O$ -7.45‰ and δ^2H -48.7‰, and are compatible with a signature of seawater mixing suggested by Bearcock and Smedley (2009).
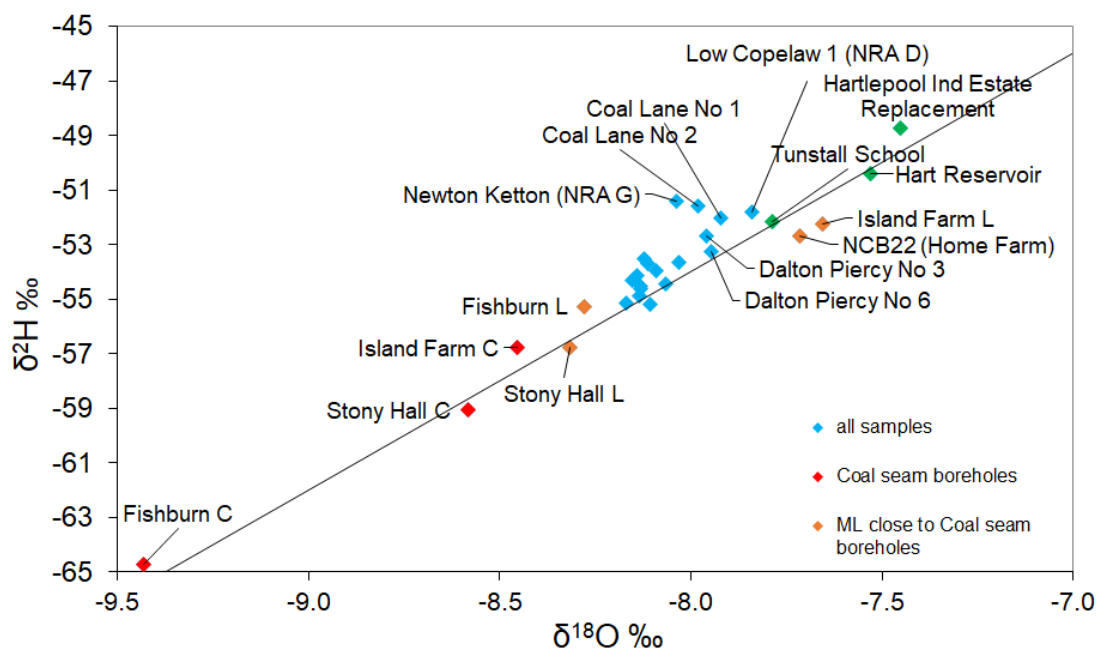
Figure 4 $\delta^{18}O$ and δ^2H in groundwater in the Magnesian Limestone aquifer and Coal seam boreholes and the global meteoric water line.

5.2 GROUNDWATER SULPHUR ISOTOPE DATA

Table 3 and Table 4 report the data and sampling date for all the groundwater samples. For the water sampled in 2017, both $\delta^{34}S$ and $\delta^{18}O$ of the dissolved sulphate are available. For the water sampled in 2018 only $\delta^{34}S$ is available, while additional water $\delta^{18}O$ and δ^2H were measured and also reported in Table 4. Figure 5 shows the large range of $\delta^{34}S$ of sulphate in the groundwaters, from -0.7 to +47.1‰. The following paragraphs examine the temporal and spatial data variability, grouping the borehole description based on initial comments provided by the EA (Appendix 2).

Table 3 Sulphate concentration and $\delta^{34}S$ and $\delta^{18}O$ of sulphate in groundwater samples from EA Boreholes (2017).

BGS CODE	SAMPLE NAME	SAMPLING DATE	SO_4^{2-} mg/l	$\delta^{34}S_{SO4}$ ‰ vs VCDT	$\delta^{18}O_{SO4}$ ‰ vs VSMOW
14067-0016	STONY HALL C	12/07/2017	751	+13.0	+9.8
14067-0017	STONY HALL L	12/07/2017	570	+13.0	+8.8
14067-0018	LOW COPELAW	12/07/2017	162	+17.8	+12.1
14067-0020	STILLINGTON OBH2	12/07/2017	27	+27.0	+14.0
14067-0019	STILLINGTON OBH4	12/07/2017	46	+7.5	+10.3
14067-0021	KETTON HALL	12/07/2017	67	+37.9	+16.2
14061-0026	FOUMARTS LANE	29/06/2017	119	-0.4	+3.7

Table 4 Sulphate concentration, $\delta^{34}S$ and $\delta^{18}O$ of sulphate and $\delta^{18}O$ and δ^2H of water in groundwater samples from EA Boreholes (2018).

BGS CODE	SAMPLE NAME	SAMPLING DATE	SO_4^{2-} mg/l	$\delta^{34}S_{SO4}$ ‰ vs VCDT	$\delta^{18}O_{H2O}$ ‰ VSMOW2	δ^2H_{H2O} ‰ VSMOW2
DAR 01	AMERSTON HALL NO 1	18/07/2018	101	+2.5	-8.11	-53.7
DAR 02	AMERSTON HALL NO 2	18/07/2018	109	+4.0	-8.14	-54.1
DAR 04	COAL LANE NO 1	18/07/2018	85	+6.9	-7.92	-52.0
DAR 05	COAL LANE NO 2	18/07/2018	90.7	+6.8	-7.98	-51.6
DAR 06	DALTON PIERCY NO 3	18/07/2018	456	+10.2	-7.96	-52.7
DAR 07	DALTON PIERCY NO 6	18/07/2018	459	+10.2	-7.95	-53.3
DAR 08	FISHBURN C	24/07/2018	10	nd	-9.43	-64.7
DAR 09	FISHBURN L	24/07/2018	153	+5.7	-8.28	-55.3
DAR 10	FOUMARTS LANE	17/07/2018	100	-0.7	-8.13	-54.6
DAR 11	GREAT ISLE (NRA 6)	18/07/2018	24.1	+10.7	-8.09	-54.0
DAR 12	HARDWICK HALL	17/07/2018	88.8	+1.0	-8.13	-54.5
DAR 13	HELEY HOUSE	17/07/2018	10	nd	-8.15	-54.3
DAR 14	HART RESERVOIR	18/07/2018	32.6	+21.1	-7.53	-50.4
DAR 15	HARTLEPOOL IND ESTATE REPLACEMENT	18/07/2018	55	+27.0	-7.45	-48.7
DAR 16	HOPPER HOUSE	18/07/2018	98.4	+2.6	-8.11	-55.2
DAR 17	ISLAND FARM C	17/07/2018	786	+23.4	-8.46	-56.8
DAR 18	ISLAND FARM L	17/07/2018	103	+4.2	-7.66	-52.2
DAR 19	KETTON HALL (NRA 26)	17/07/2018	10	+47.1	-8.03	-53.6
DAR 20	LOW COPELAW 1 (NRA D)	18/07/2018	223	+3.5	-7.84	-51.8
DAR 21	NCB22 (HOME FARM)	18/07/2018	268	+3.8	-7.71	-52.7
DAR 22	NEWTON KETTON (NRA G)	17/07/2018	48.8	+31.1	-8.04	-51.4
DAR 23	RUSHYFORD 'A'	17/07/2018	164	+14.5	-8.07	-54.4
DAR-25	STILLINGTON OBH2	17/07/2018	10	nd	-8.13	-54.9
DAR 26	STILLINGTON OBH4	17/07/2018	20.4	+24.7	-8.17	-55.2
DAR 27	STONY HALL C	18/07/2018	738	+13.1	-8.58	-59.1
DAR 28	STONY HALL L	18/07/2018	577	+13.5	-8.32	-56.8
DAR 29	TUNSTALL SCHOOL	18/07/2018	183	+9.8	-7.79	-52.1
DAR 30	WATERLOO PLANTATION	18/07/2018	128	+7.2	-8.12	-53.5
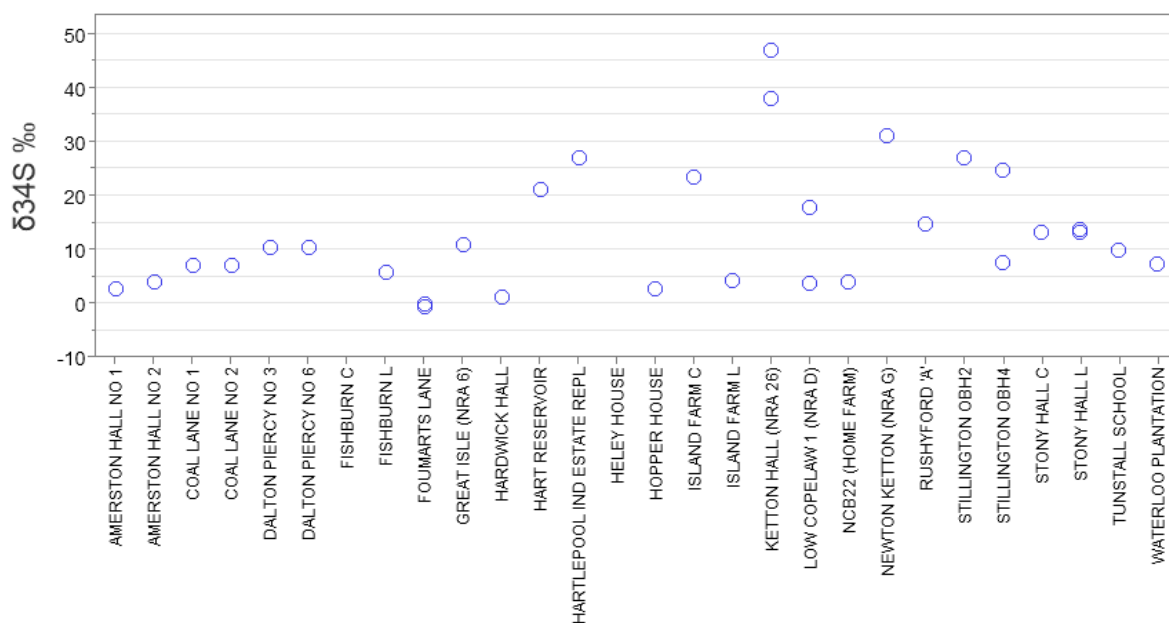
Figure 5 $\delta^{34}S$ isotope values in groundwaters sampled in 2017 and 2018.

5.3   TEMPORAL VARIABILITY

Comparison of the $\delta^{34}S$ data in the small number of boreholes sampled both in July 2017 (Table 3) and in July 2018 (Table 4) suggests a stable sulphur isotope signature for STONY HALL C and STONY HALL L boreholes with a $\delta^{34}S$ of +13‰ in 2017 and 2018. FOUMARTS LANE's $\delta^{34}S$ is also stable with a value of -0.4‰ in 2017 and -0.7‰ in 2018. The remarkably high $\delta^{34}S$ value of KETTON HALL borehole of +37.9‰ in 2017 is confirmed in 2018 (+47.1‰).

Very different $\delta^{34}S$ values are measured in LOW COPELAW between 2017 (+17.8‰) and 2018 (+3.5‰), the much higher $\delta^{34}S$ in 2017 corresponding to a lower sulphate concentration (possible sign of reduction of sulphates to sulphide and enrichment in the heavier sulphur isotope of the residual sulphate).

STILLINGTON OBH4 also has different $\delta^{34}S$ in 2017 and 2018, increasing from +7.5‰ to +24.7‰ from 2017 to 2018, while the sulphate concentration decreased from 46 to 20 mg/L. Although the sulphate content in STILLINGTON OBH2 was too low (10 mg/L) in 2018 to obtain an isotope measurement and therefore to compare the two sampling rounds, it is noticed that the measurements in 2017 with $\delta^{34}S$ +27‰ and sulphate 27 mg/L are not too dissimilar to STILLINGTON OBH4 in 2018.

These observations are integrated in the data discussion in the following paragraphs.

5.4   WORKED/UNWORKED COAL SEAM BOREHOLES

The boreholes associated with coal seams are ISLAND FARM C, STONY HALL C, and FISHBURN C (Fishburn seam).

The water isotopic composition suggests a different recharge system for these boreholes, with much lower $\delta^{18}O$ and $\delta^{2}H$ values, compared to the main Magnesian Limestone aquifer (Figure 4, section 5.1).

The groundwaters associated with these boreholes are of two types: sodium sulphate (Na-SO$_4$) and sodium bicarbonate (Na-HCO$_3$) waters (Table 5); sulphate concentrations of ~ 750 mg/l are similar for ISLAND FARM C and STONY HALL C, while sulphate is very low in FISHBURN C (SO$_4$ 10 mg/l). The trace element composition (e.g. Fe, Sr and B) is also very variable (Appendix 3, Appendix 4). Salinity and compositional variations are known in mine workings and mine waters, derived by the extent of meteoric recharge in the mine workings, as well as the abundance and variability of coal measure brines (Edmunds, 1975) or reaction products of sulphide oxidation and acid neutralisation.

The sulphur isotope composition is not similar: $\delta^{34}S$ is +13.1‰ in STONY HALL C and +23.4‰ in ISLAND FARM C (Table 5). In the deep mine Coal Authority borehole FISHBURN C, $\delta^{34}S$ was not measured, because of the low sulphate content in the sample.

Table 5 Coal seam borehole water type, sulphate and $\delta^{34}S$

BGS CODE	Sample	EA Comments	Water Type	SO_4^{2-} mg/l	$\delta^{34}S_{SO4}$ ‰ vs VCDT
DAR 27	STONY HALL C	Second plume source	$Na\text{-}SO_4$	738	+13.1
DAR 17	ISLAND FARM C	Unworked coal seam	$Na\text{-}SO_4$	786	+23.4
DAR 08	FISHBURN C	Worked coal seam	$Na\text{-}HCO_3$	10	nd

5.5 MAGNESIAN LIMESTONE BOREHOLES

5.5.1 Magnesian Limestone boreholes in close proximity to coal seam boreholes

The results for the groundwaters from boreholes in the Magnesian Limestone in the same locations as the coal seam boreholes are summarised in Table 6.

The almost identical sulphur isotopic values (~+13‰) between the 2017-2018 analyses of STONY HALL L and STONY HALL C boreholes, associated with high sulphate, indicate a constant and strong impact of the underlying coal mine workings on the Magnesian Limestone borehole.

The chemistry of the other boreholes ISLAND FARM L and FISHBURN L, instead, differs from the associated coal seam boreholes, and reflects the Magnesian Limestone $Ca\text{-}HCO_3$ composition. They both have low $\delta^{34}S$ values (+4.2 – +5.7‰). ISLAND FARM L, therefore, also differs from ISLAND FARM C for the S isotope composition, while the comparison is not possible for Fishburn L, as the $\delta^{34}S$ measurement of the respective coal seam borehole is not available.

Of note is NCB22 (HOME FARM) borehole, which was originally drilled by the National Coal Board as an exploration borehole, through the Magnesian Limestone and into the Coal Measures underneath. Some time later the borehole was partially backfilled by the EA to screen out the coal measures, as the borehole was a potential cross connection between aquifers. The borehole. since the 1990s, has been a Magnesian Limestone only borehole (EA personal communication). Groundwater from this borehole is similar in the $\delta^{34}S$ and sulphate concentration to groundwater in ISLAND FARM L and FISHBURN L boreholes.

Table 6 Water type, sulphate and $\delta^{34}S_{SO4}$ in Magnesian Limestone boreholes overlying the coal seams

BGS CODE	Sample	EA Comments	Water Type	SO_4^{2-} mg/l	$\delta^{34}S_{SO4}$ ‰ vs VCDT
14067-0017	STONY HALL L 2017	Rapidly rising sulphate	$Na\text{-}SO_4$	751	+13.0
DAR 27	STONY HALL L 2018	Rapidly rising sulphate	$Na\text{-}SO_4$	577	+13.5
DAR 17	ISLAND FARM L	Unknown high sulphate	$Ca\text{-}HCO_3$	103	+4.2
DAR 08	FISHBURN L	Potential plume	$Ca\text{-}HCO_3$	153	+5.7
DAR 21	NCB22 (HOME FARM)	Connectivity with coal seam?	$Ca\text{-}HCO_3$	268	+3.8

5.5.2 Magnesian Limestone boreholes in the mine plume area

Table 7 lists the Magnesian Limestone boreholes within the mine plume area and their sulphur isotopic composition. There is a large range of water types and of both sulphate and sulphur isotope concentrations.

RUSHYFORD 'A' borehole from the mine plume source area, has a NaCl composition, a SO_4 of 164 mg/l and a $\delta^{34}S$ value of +14.5‰, similar to the coal seam borehole STONY HALL C (+13.1‰).

LOW COPELAW borehole, in the centre of the plume, shows very different $\delta^{34}S$ values in 2017 (+17.8‰) and 2018 (+3.5‰), corresponding to a change from Mg to Ca – bicarbonate water; the lower $\delta^{34}S$ value in 2018, is very similar to the nearby NCB22 (HOME FARM) borehole value, together with similar sulphate concentrations of ~250 mg/l and same water type (Ca-HCO$_3$). The higher isotopic ratio value in 2017, corresponding to lower sulphate concentration, can be interpreted as a possible sign of reduction of sulphates and enrichment in the heavier sulphur isotope of the residual sulphate.

Within the boreholes with low-sulphate, < 50 mg/l, a similar isotopic fractionation is suggested for the very high $\delta^{34}S$ values of +31.1‰ and +47.1‰, respectively, for NEWTON KETTON (NRA G) and KETTON HALL (NRA 26). The remarkably high $\delta^{34}S$ value of KETTON HALL borehole was also evident in 2017 (+37.9‰). The isotopic fractionation due to the sulphate reduction overrides the sulphate source signature in these boreholes, unfortunately. GREAT ISLE (NRA 6) is low in SO$_4$ (24 mg/L) and total dissolved solids, with a $\delta^{34}S$ value of +10.7‰.

Table 7 Water type, sulphate and $\delta^{34}S_{SO4}$ in the Magnesian Limestone boreholes within the mine plume

BGS CODE	Sample	EA Comment	Water Type	SO$_4^{2-}$ mg/l	$\delta^{34}S_{SO4}$ ‰ vs VCDT
DAR 23	RUSHYFORD 'A'	Source area of plume	Na-Cl	164	+14.5
14067-0018	LOW COPELAW 1 (NRA D) 2017	Centre plume	Mg-HCO$_3$	162	+17.8
DAR 20	LOW COPELAW 1 (NRA D) 2018	Centre plume	Ca-HCO$_3$	223	+3.5
DAR 11	GREAT ISLE (NRA 6)	Centre plume	Mg-HCO$_3$	24	+10.7
14067-0021	KETTON HALL (NRA 26) 2017	Centre plume	Mg-HCO$_3$	67	+37.9
DAR 19	KETTON HALL (NRA 26) 2018	Centre plume	Na-Cl	10	+47.1
DAR 13	HELEY HOUSE	Mid plume	Mg-HCO$_3$	10	nd
DAR 22	NEWTON KETTON (NRA G)	Edge of plume	Mg-HCO$_3$	49	+31.1

5.5.3   High-sulphate Magnesian Limestone boreholes outside mine water plume area

Boreholes DALTON PIERCY NO 3 and DALTON PIERCY NO 6, with very similar SO$_4$ concentrations of 456 mg/l and 459 mg/l, respectively, have also identical $\delta^{34}S$ values of +10.2‰. They are Ca-SO$_4$ water types.

Table 8 Water type, sulphate and $\delta^{34}S_{SO4}$ in the Magnesian Limestone boreholes with high sulphate ~450 mg/l

BGS CODE	Sample	EA Comment	Water Type	SO$_4^{2-}$ mg/l	$\delta^{34}S_{SO4}$ ‰ vs VCDT
DAR 06	DALTON PIERCY NO 3	Anhydrite/gypsum noted in log	Ca-SO$_4$	456	+10.2
DAR 07	DALTON PIERCY NO 6	Anhydrite/gypsum noted in log	Ca-SO$_4$	459	+10.2

5.5.4   Low-sulphate Magnesian Limestone

Table 9 lists the Magnesian Limestone boreholes with a sulphate around 100 mg/l (range 85–130 mg/l). The waters in this borehole list are all Ca-HCO$_3$ water type and are characterised by a low $\delta^{34}S$ range (-0.7 to +7.2).

This list includes HARDWICK HALL borehole, representing a Magnesian Limestone background potential end-member (EA communication), with a sulphate of 89 mg/l, and a $\delta^{34}S$ of +1.0‰.

Table 9 Water type, sulphate and $\delta^{34}S_{SO4}$ in the Magnesian Limestone boreholes with sulphate ~100 mg/l

BGS CODE	Sample	EA Comment	Water Type	SO_4^{2-} mg/l	$\delta^{34}S_{SO4}$ ‰ vs VCDT
14061-0026	FOUMARTS LANE-2017	Unknown high sulphate	Ca-HCO$_3$	119	-0.4
DAR 10	FOUMARTS LANE-2018	Unknown high sulphate	Ca-HCO$_3$	100	-0.7
DAR 12	HARDWICK HALL	Mag Limestone background	Ca-HCO$_3$	89	+1.0
DAR 01	AMERSTON HALL NO 1	Anhydrite/gypsum noted in log	Ca-HCO$_3$	101	+2.5
DAR 16	HOPPER HOUSE	Anhydrite/gypsum noted in log	Ca-HCO$_3$	98	+2.6
DAR 02	AMERSTON HALL NO 2	Anhydrite/gypsum noted in log	Ca-HCO$_3$	109	+4.0
DAR 05	COAL LANE NO 2	Anhydrite/gypsum noted in log	Ca-HCO$_3$	91	+6.8
DAR 04	COAL LANE NO 1	Anhydrite/gypsum noted in log	Ca-HCO$_3$	85	+6.9
DAR 30	WATERLOO PLANTATION	Anhydrite/gypsum noted in log	Ca-HCO$_3$	128	+7.2

5.5.5 Saline boreholes near Hartlepool

HART RESERVOIR (SO$_4$ 33 mg/l) and HARTLEPOOL IND ESTATE REPLACEMENT (SO$_4$ 55 mg/l) boreholes, both saline waters (respectively Na-Cl and Ca-Cl waters), have similar $\delta^{34}S$ of +21.1‰ and +27‰.

TUNSTALL SCHOOL (SO$_4$ 183 mg/l), although grouped with the saline boreholes in Appendix 2, is a Ca-HCO$_3$ water, and also has a much lower $\delta^{34}S$ value of +9.8‰ compared to the saline boreholes. There is likely a greater contribution of a calcium bicarbonate water with low $\delta^{34}S$ in this borehole than in the others, also reflected in the chemical composition. The difference with the other boreholes is also evidenced in the $\delta^{18}O$ and δ^2H composition (Figure 4).

Table 10 Water type, sulphate and $\delta^{34}S_{SO4}$ in the Magnesian Limestone boreholes near Hartlepool

BGS CODE	Sample	EA Comment	Water Type	SO_4^{2-} mg/l	$\delta^{34}S_{SO4}$ ‰ vs VCDT
DAR 14	HART RESERVOIR	Saline	Na-Cl	32.6	+21.1
DAR 15	HARTLEPOOL IND ESTATE REPLACEMENT	Saline	Ca-Cl	55	+27.0
DAR 29	TUNSTALL SCHOOL	Saline	Ca-HCO$_3$	183	+9.8

5.6 SPRINGS

A spring in the dolomites and dolomitic limestones of the Middle Magnesian Limestone (Ford formation) from AYCLIFFE QUARRY (NZ29524 22571) to the south east of Aycliffe Village was sampled by BGS staff during a visit in July 2018, to provide an additional background sample for sulphur isotope values. The sample has a SO$_4$ of 69 mg/l and a $\delta^{34}S$ of +2.3‰.

The Mg-SO$_4$ spring sampled in Woodham Burn and described in Palumbo-Roe et al. (2020) for its chemical composition, which is very constant and enriched together with sulphate in Sr (~ 980 µg/l), Li (~ 160 µg/l), Rb (~ 7 µg/l) and U (~ 4 µg/l), B (~ 250 µg/l) compared to all the other waters in Woodham Burn, but generally low in Fe, has also a very constant $\delta^{34}S$ value of +5.6 (SO$_4$ 840 mg/l) and +5.4‰ (SO$_4$ 796 mg/l), respectively in 01/08/2018 and 05/02/2019.
For both springs, full chemical analysis is available in Palumbo-Roe et al 2020, Table 25.

5.7 SURFACE WATERS FROM THE SKERNE CATCHMENT

Sulphur isotope ratios of dissolved sulphate were measured for 11 surface water samples (Table 11), indicating a narrow range of $\delta^{34}S$ from +5 to +6.9‰, except for one location (Woodham Burn) with a lower $\delta^{34}S$ (range +3.6 to +5‰).

Table 11 Sulphate concentration and $\delta^{34}S$ of sulphate in surface water samples in separate sampling rounds (details on sampling locations are reported in Palumbo-Roe et al., 2019, 2020)

BGS CODE	Location	Sampling Date	SO_4^{2-} mg/l	$\delta^{34}S_{SO4}$ ‰ vs VCDT	$\delta^{18}O_{H2O}$ (‰)	δ^2H_{H2O} (‰)
14061-0006	D01 - Mainsforth Stell Tributary	28/06/2017	160	+6.8	-	-
14067-0001	A02 - Skerne at Coatham Mundeville	13/07/2017	106	+5.8	-	-
DAR 31	F01 - Langley Beck -Upper Skerne	19/07/2018	1914	+6.9	-7.62	-50.4
DAR 32	BRAD.B - Skerne at Bradbury	19/07/2018	135	+6.6	-7.33	-50.9
DAR 33	A02 - Skerne at Coatham Mundeville	19/07/2018	134	+5.0	-7.09	-48.1
DAR 34	WB - Woodham Burn	18/07/2018	468	+3.6	-7.84	-52.6
14412-10	Woodham Burn Concrete Slab	05/02/2019	514	+3.6	-	-
14412-13	Woodham Burn Cow Field	05/02/2019	524	+5.0	-	-
14412-17	Woodham Burn Little House	06/02/2019	492	+5.0	-	-
14412-22	Woodham Burn Bubbly Point	06/02/2019	765	+4.4	-	-
14412-28	Woodham Burn Bench	06/02/2019	324	+4.8	-	-

The surface water sample (FC01), located on Langley Beck in the upper reach of the Skerne catchment, due south of Trimdon Colliery at 438025 535332, was sampled on 19/07/2018 during very low flow conditions. The sampling point is considered to be impacted by mine water (JBA, 2017). The water sample with a SO_4 concentration of 1914 mg/l has a $\delta^{34}S$ value of +6.9‰. High concentrations of Li (947 µg/L), B (504 µg/l), Sr (1175 µg/l), Mn (747 µg/l), but low Fe (23 µg/l), are associated with the high sulphate. It is noted that similar trace element enrichments and a $\delta^{34}S$ value of +5.5‰ were measured in the high sulphate spring at Woodham (see section 5.9).

5.8 ROCK AND SOIL LEACHATES

Soil samples from Woodham Burn and one marl rock sample from Aycliffe Quarry were leached with deionised water to extract soluble sulphate. This fraction represents the portion available to be readily mobilised by runoff into the stream. The concentration of soluble sulphate and $\delta^{34}S$ of the sulphate is reported in Table 12. Full anion analysis in water-soluble extracts from Woodham Burn can be found in Palumbo-Roe et al. (2020).

In the soil samples, a range of $\delta^{34}S$ values from -13.3 to +6.1‰ is observed, with the most negative isotopic ratios at lower depth in the soil profiles. The positive values are closer to the ones observed in stream water. These very low $\delta^{34}S$ values have been previously reported for waterlogged soils (Stack and Rock, 2011).

The one rock sample of Magnesian Limestone has high soluble sulphate (1351 mg/kg rock) and a negative $\delta^{34}S$ value of -4.7‰. This negative value is difficult to explain as being associated with the dissolution of a Permian gypsum mineral phase present in the marl. Further analysis of similar specimens would help to interpret the result.

5.9 HYPORHEIC WATER FROM THE WOODHAM BURN AND HIGH SULPHATE SPRING WATER

Pore water was sampled from the sediment bed of the Woodham Burn during the study characterising the hyporheic exchange in the high-sulphate stream (Palumbo-Roe et al. 2020).

Sulphur isotope concentrations of the dissolved sulphate were analysed for a subset of samples in two occasions (August 2018 and February 2019; Table 13).

The sharp increase from $\delta^{34}S$ +6.1‰ to $\delta^{34}S$ +36.3‰ observed in the depth profile at location "Concrete slab" suggests a residual sulphate enriched in ^{34}S as a result of sulphate reduction,

and supports the interpretation based on the hydrochemistry (increased alkalinity, decrease in SO_4) in Palumbo-Roe et al. 2020.

Consistently slightly higher pore water $\delta^{34}S$ values than the surface water ones are shown through the sediment depth profile of Bench location, while a very uniform $\delta^{34}S$ profile is observed at Bubbly point consistently with the upward ground flow observed at this location.

Table 12 Sulphate concentration and $\delta^{34}S$ of sulphate in water leachates from soils around Woodham Burn and one Magnesian Limestone rock sample from Aycliffe Quarry

SAMPLE	SITE	NRG	SAMPLING DATE	Water Leachate analysis (1:10 S:L ratio)		
				SO_4^{2-} (mg/l)	SO_4^{2-} (mg/kg)	$\delta^{34}S_{SO4}$ (‰)
Aycliffe Quarry Dolomite 60 OD	Aycliffe Quarry	NZ 29524 22571	17/07/2018	135	1351	-4.7
HA3 0.00 – 0.30 m	WOODHAM BURN	NZ 29430 27038	18/07/2018	low SO_4	nd	nd
HA3 0.30 – 0.73 m	WOODHAM BURN	NZ 29430 27038	18/07/2018	low SO_4	nd	nd
HA3 0.80 – 1.05 m	WOODHAM BURN	NZ 29430 27038	18/07/2018	3.37	34	+2.3
HA3 1.05 – 2.03 m	WOODHAM BURN	NZ 29430 27038	18/07/2018	low SO_4	nd	nd
HA4 0.00 – 0.35 m	WOODHAM BURN	NZ 29164 27136	18/07/2018	low SO_4	nd	nd
HA4 0.35 – 0.75 m	WOODHAM BURN	NZ 29164 27136	18/07/2018	low SO_4	nd	nd
HA4 0.70 – 1.35 m	WOODHAM BURN	NZ 29164 27136	18/07/2018	8.36	84	+3.3
HA4 1.35 – 1.65 m	WOODHAM BURN	NZ 29164 27136	18/07/2018	12.1	121	-2.2
HA5 0.00 – 0.70 m	WOODHAM BURN	NZ 29063 26979	18/07/2018	13.4	134	+6.1
HA5 0.70 – 1.05 m	WOODHAM BURN	NZ 29063 26980	18/07/2018	29.2	292	+5.7
HA5 1.05 – 1.75 m	WOODHAM BURN	NZ 29063 26981	18/07/2018	96.2	962	-13.3
Ploughed field near bench site	WOODHAM BURN	NZ 29147 27096	18/07/2018	low SO_4	nd	nd

Table 13 Sulphate concentration and $\delta^{34}S$ of sulphate in sediment pore water (HZ) and overlying surface water (SW)

Location	Type	Position	SO_4^{2-} (mg/l)	$\delta^{34}S_{SO4}$ (‰)	SO_4^{2-} (mg/l)	$\delta^{34}S_{SO4}$ (‰)
			01/08/2018		05/02/2019	
Concrete Slab	SW	overlying surface water	585	+4.6	514	+3.6
Concrete Slab	HZ	0-10 cm sediment depth	337	+6.1	-	-
Concrete Slab	HZ	10-20 cm sediment depth	22	+36.3	-	-
Bench	SW	overlying surface water	491	+4.1	324	+4.8
Bench	HZ	0-10 cm sediment depth	239	+13.4	765	+5.7
Bench	HZ	10-20 cm sediment depth	218	+5.4	217	+6.4
Bench	HZ	20-50 cm sediment depth	194	+6.7	201	+6.6
Bench	HZ	50-90 cm sediment depth	140	+7.6	150	+7.6
Bubbly point	SW	overlying surface water	790	+5.1	765	+4.3
Bubbly point	HZ	0-10 cm sediment depth	869	+5.2	-	-
Bubbly point	HZ	50-90 cm sediment depth	848	+5.4	-	-
Bubbly point	SPRING	spring at Woodham Burn	840	+5.6	796	+5.4

6 Discussion

The isotopic signal of the dissolved sulphate in water is often used to recognize different sources of sulphur and to trace the sulphur cycle. In the case of the Skerne catchment, quantification of each sulphur source is of particular interest due to the special conditions prevailing in the watershed, influenced by sulphur from several potential origins, giving rise to localised very high sulphate concentrations in surface water and groundwater (SO_4> 500 mg/l). The most obvious potential sources of high sulphate in the Magnesian Limestone aquifer, based on the current hydrogeological understanding, include dissolution of Permian evaporites, contamination by coal mine water plume(s), and, along the coast, seawater contamination (e.g. seawater intrusion/ atmospheric deposition of marine SO_4 aerosols). Furthermore, there might be some sulphur sources that may have significant, but localised, or even diffuse effects on the sulphate concentration and its isotope signature, for example due to oxidation of sulphide minerals such as pyrite (FeS_2) in the Glacial Till formation or contributions from fertilisers and soil runoff. We have therefore undertaken a sulphate sulphur isotope survey focussed on the Magnesium Limestone aquifer complemented by the collection of potential end-members of sulphate sources.

Sulphate from gypsum in the evaporites and sulphate from oxidation of pyrite are known for contrasting sulphur isotope ratios. We assumed therefore that we would have seen this contrast in this study, expecting that the coal mine waters were reflecting the $\delta^{34}S$ signature of the sulphide oxidation. This is not however the case. From the analysis of two groundwater samples from coal seam boreholes (which were clearly identifiable in the dual water isotope graph for plotting off the rest of the Magnesian Limestone boreholes on the GMWL), we find that the high-sulphate coal seam boreholes do not show the low $\delta^{34}S$ composition typical of pyrite oxidation, illustrated for example in the studies by Gammons et al. (2010) in acid mine drainage associated with abandoned coal mines in central Montana, USA, or by Nordstrom et al. (2007) in the Animas River Watershed, San Juan County, Colorado. In fact, the boreholes STONY HALL C and ISLAND FARM C, both Na-SO_4 mine waters, with SO_4~700 mg/l and enriched in iron (Fe > 1 mg/l), show high $\delta^{34}S$ values of +13.1 and +23.4‰, similarly described by Banks and Boyce (2023) in deep mine waters, together with enrichment in Cl, K, Sr, B (see also section 2.4). The $\delta^{34}S$ value of +13.1‰ in STONY HALL C did not change between the 2017 and 2018 samples, suggesting a constant source of sulphate. The even higher $\delta^{34}S$ value of +23.4‰ measured in ISLAND FARM C borehole, was also typical of a shaft mine water from Caphouse Colliery, Yorkshire, with $\delta^{34}S$ of +19.7 to +23.8‰, described by Burnside et al. 2016. The plausible explanations for these high $\delta^{34}S$ values are detailed in the study by Banks and Boyce (2023) and comprise i) evaporitic or marine brines, ii) evaporite mineral dissolution or iii) partially-closed-system microbial sulphate reduction.

Groundwaters containing sulphate solely derived from the dissolution of Permian marine evaporites are expected with a ^{34}S-enriched sulphate ($\delta^{34}S$ values of +10.0 to +11.1‰ according to Heaton (2004) or +8.2 to +10.2‰ according to Bottrell et al. (2006)).

There is, therefore, less of a contrasting isotope signature between potential "evaporite" and "coal mine water" sources of sulphates in the Magnesian Limestone aquifer. For example, one sample of coal mine water with $\delta^{34}S$ values of +13.1‰ is not too dissimilar to the average Permian evaporite sulphate with $\delta^{34}S$ value of around +10‰ (from +8.2 to +11.1‰). This makes discrimination of the dissolved sulphate sources based on sulphur isotope less certain, especially at low sulphate concentrations.

Groundwaters in the Magnesian Limestone boreholes display a wide range in $\delta^{34}S$ for sulphate, without a general relationship between $\delta^{34}S$ and sulphate concentrations (Figure 6). Beside borehole STONY HALL L, clearly impacted by coal mine water, DALTON PIERCY NO 3 and No 6 boreholes are also high in sulphate with a $\delta^{34}S$ values of +10.2‰. Given how close this value is to the Permian evaporites' $\delta^{34}S$ values, described in section 2.1, it could be plausibly explained by a gypsum dissolution source, although a "coal mine water" contribution with a $\delta^{34}S$ signature of +13‰ cannot be totally excluded, because of the small difference between the two values. HARDWICK HALL borehole, representing a Magnesian Limestone background potential end-member was found to have a SO_4 concentration of 89 mg/l and a $\delta^{34}S$ value of +1‰.
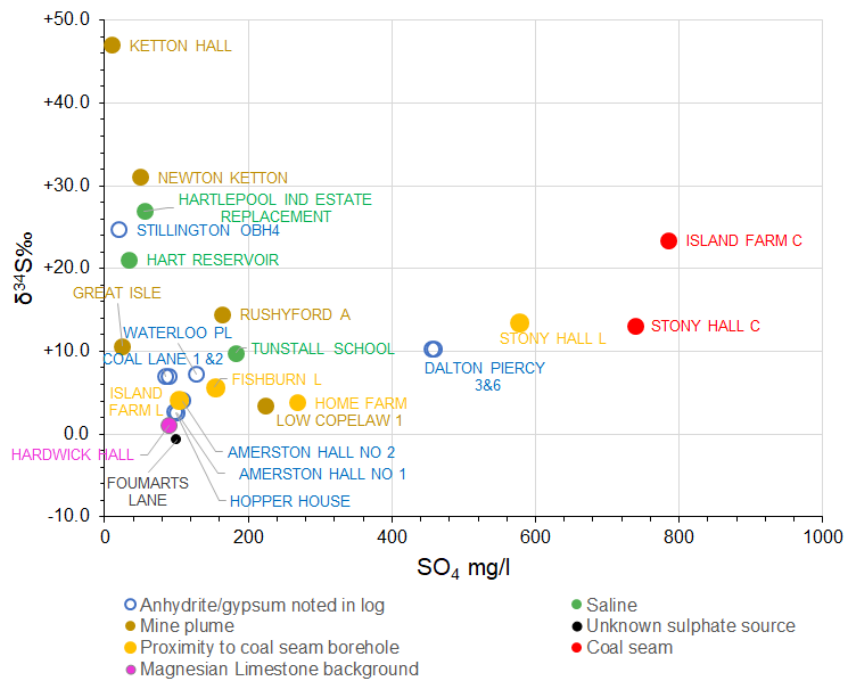
Figure 6 Plot of $\delta^{34}S$ vs. SO_4 (mg/l) in the 2018 boreholes.

6.1   END-MEMBER MIXING MODELLING

To help the data interpretation, using the data from this survey and data from the literature, we model the sulphate and sulphur isotope compositions of mixtures of hypothetical end-members. Evidence from these calculations can be used to explain some of the observations and validate initial hypothesis. Of note when plotting the results in a $\delta^{34}S$ versus SO_4 concentration plot, is that a mixture of two conservative end-members forms a curve (hyperbolas) rather than straight lines (Kendall and Caldwell, 1998).

Mixing curves in Figure 7 were modelled using a baseline Magnesian Limestone groundwater end-member with low SO_4 concentration (89 mg/l) and a low $\delta^{34}S$ value (+1‰), mixing with:

i)   high concentration SO_4 (2000 mg/l) marine sulphate end-member having $\delta^{34}S$ values corresponding to the range for <u>Permian evaporites</u> (+10.2‰)

ii)   high concentration SO_4 (2649 mg /l) and high $\delta^{34}S$ value (+21‰) corresponding to the <u>modern seawater</u> end-member

iii)   high concentration SO_4 (2000 mg /l) and low $\delta^{34}S$ value (-5‰) corresponding to an <u>Acid mine drainage (AMD)</u> end-member

iv)   <u>Magnesium-sulphate spring</u> with high concentration SO_4 (800 mg/l) and a $\delta^{34}S$ value of +5.5‰

v)   STONY HALL C <u>coal mine water</u> with high SO_4 concentration (740 mg/l) and a $\delta^{34}S$ value of +13‰

vi)   ISLAND FARM C <u>coal mine water</u> with high concentration SO_4 (790 mg/l) and a $\delta^{34}S$ value of +23.4‰

Similar calculations were carried out by using a "dilute recharge" end-member with 50 mg/l SO_4 and a $\delta^{34}S$ value of +0‰.

The following graphs show how the samples (from 2018 sampling) plot with respect to the hypothetical binary mixing lines (Figure 8 to Figure 10). STONY HALL L falls on the mixing line between the end-member "STONY HALL C coal seam water" and the end-member "baseline Magnesian Limestone", with an estimated contribution of ~85 % mine water (Figure 8). DALTON PIERCY borehole data can be interpreted as mixing of the Magnesian Limestone with either coal mine water or an evaporite source (Figure 9). The $\delta^{34}S$ value of +5.5‰ of the Mg-SO_4 spring at Woodham burn is too low for a SO_4 solely derived from evaporite dissolution, which would have resulted in a $\delta^{34}S$ closer to DALTON PIERCY boreholes of ~ +10‰; it rather points

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to a contribution of low δ³⁴S -sulphate, like the values expected from the oxidation of pyrite. These data support the mechanism, hypothesised in Palumbo-Roe et al. (2020) to account for the spring composition, of dissolution of dolomite in presence of acidic water, where the source of acidity comes from coal mine water due to the oxidation of pyrite.

At intermediate sulphate concentrations, and with low δ³⁴S values, HOME FARM and LOW COPELAW 1 align on the mixing line "sulphate spring-Magnesian Limestone", while RUSHYFORD A on the mixing line "ISLAND FARM C- Magnesian Limestone".

For most of the low sulphate Magnesian Limestone boreholes, uncertainties in discriminating the source of sulphate are higher, as Figure 9 indicates the convergence of all the mixing lines towards the Magnesian Limestone baseline value; however, WATERLOO, AMERSTON HALL, HOPPER HOUSE and ISLAND FARM L align towards the end of the Magnesian Limestone end-member of the ISLAND FARM C- Magnesian Limestone mixing line.

Many samples fall far outside of these mixing envelopes. This could indicate either non-conservative behaviour (reaction) in the subsurface, or that the end-member compositions are not correctly defined. They plot on the top left of δ³⁴S vs SO₄ graphs, i.e. with very low sulphate and very high δ³⁴S values. These boreholes are KETTON HALL, NEWTON KETTON, STILLINGTON, HARTLEPOOL, HART RESERVOIR (Figure 8). For these sites the very high δ³⁴S can be interpreted as a possible sign of reduction of sulphates and enrichment in the heavier sulphur isotope of the residual (low concentration) sulphate.

The contribution of salinity and sulphate from seawater is difficult to discern with the present sulphur isotope data for HART RESERVOIR and HARTLEPOOL IND ESTATE REPLACEMENT boreholes, as both saline waters (respectively Na-Cl and Ca-Cl waters), with similar δ³⁴S of +21.1‰ and +27‰ fall far away from the Seawater–Magnesian Limestone mixing line (Figure 10). TUNSTALL SCHOOL falls instead on the Stony Hall C-dilute recharge mixing line towards the dilute recharge end-member.
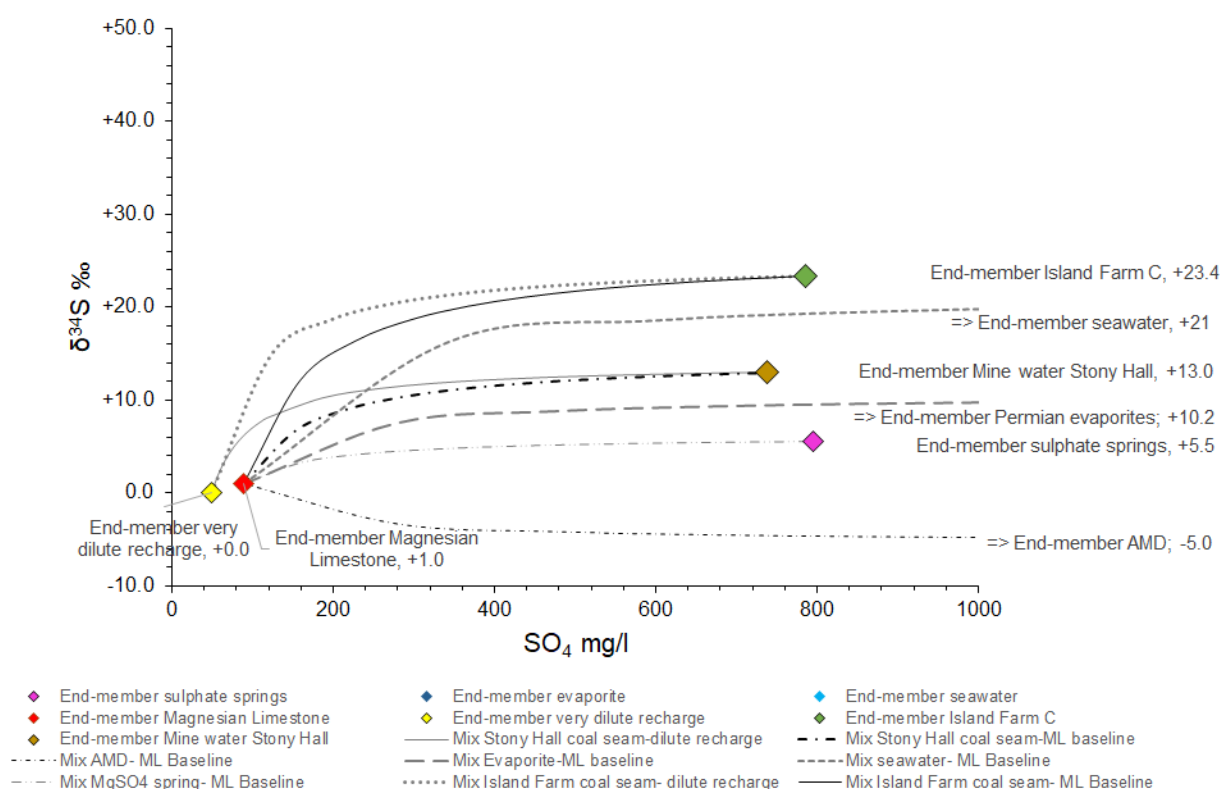
Figure 7 The sulphur isotope composition of sulphate plotted vs sulphate concentration along hypothetical binary mixing lines between the Magnesian Limestone end-member and potential high sulphate end-members. The mixing lines are also derived for a more diluted recharge end-member.
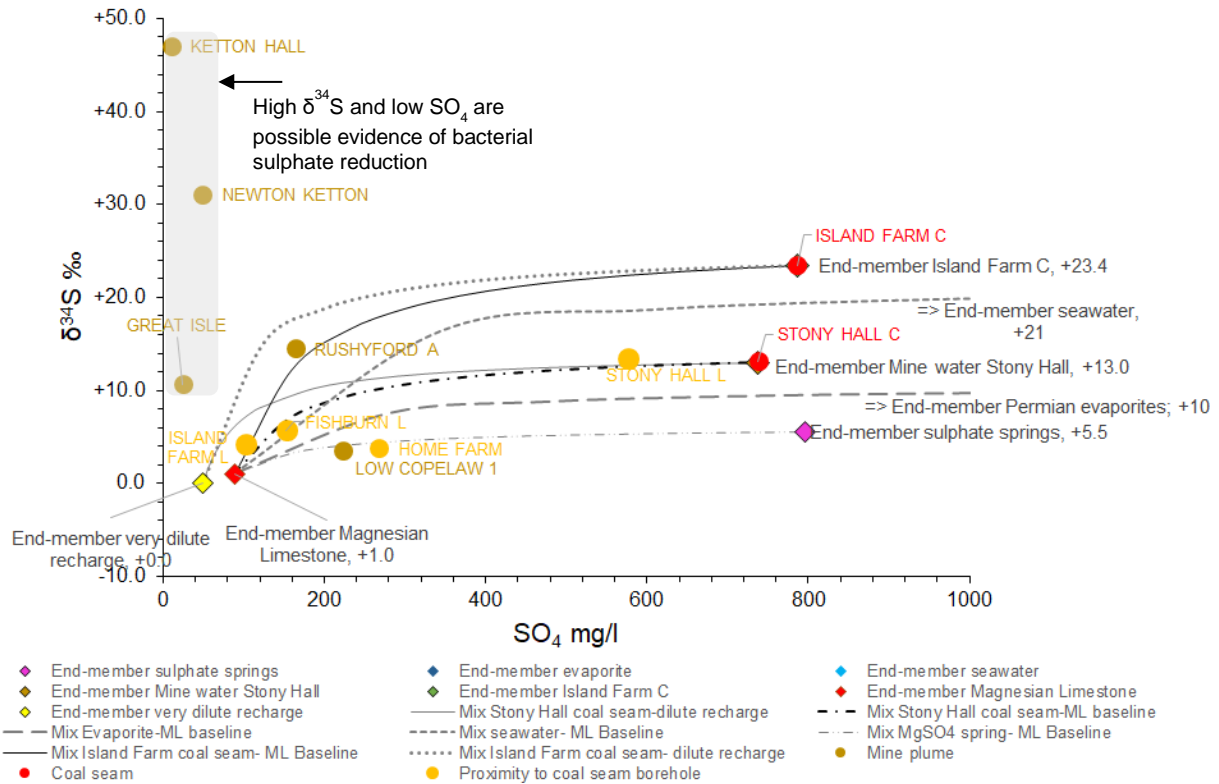
Figure 8 The sulphur isotope composition of sulphate plotted vs sulphate concentration in boreholes from the coal mine seams, and the Magnesian Limestone boreholes in the mine plume area. The curves are hypothetical binary mixing lines between potential low and high sulphate end-members in the study area.
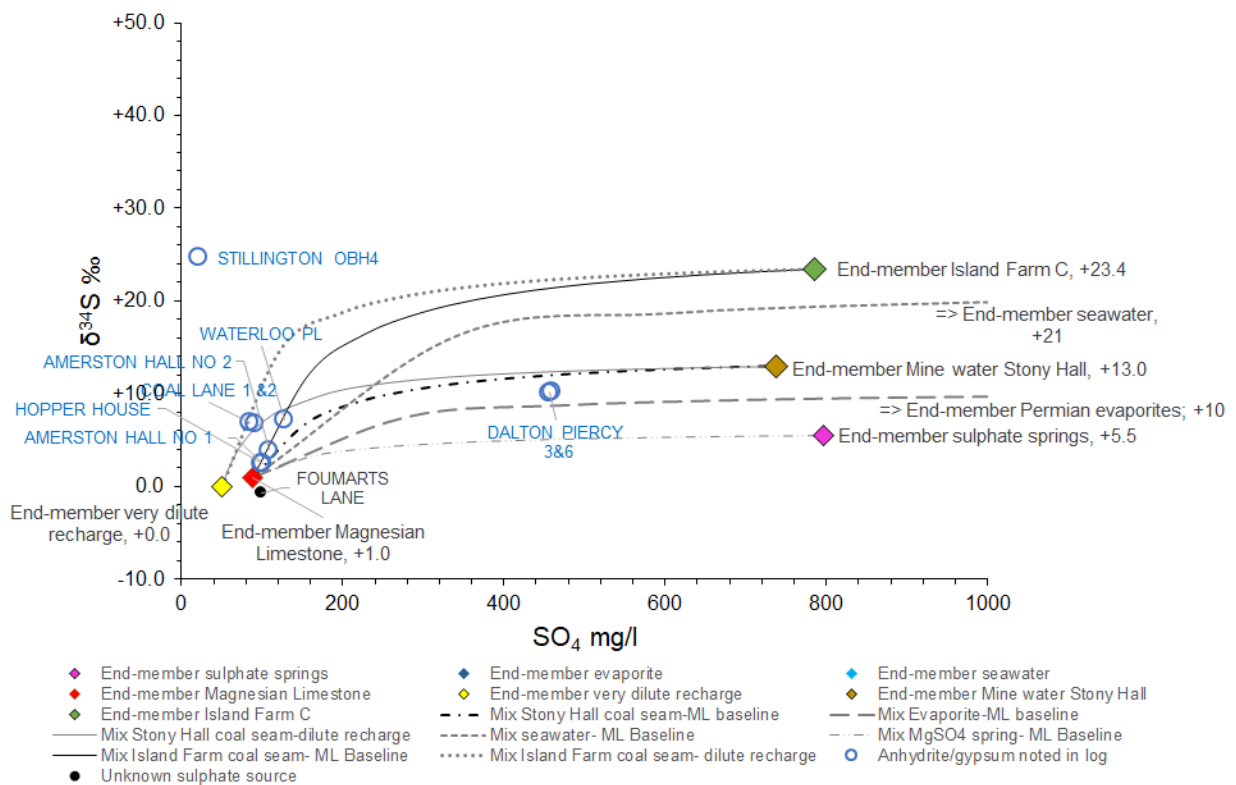
Figure 9 The sulphur isotope composition of sulphate plotted vs sulphate concentration in boreholes from the Magnesian Limestone boreholes. The curves are hypothetical binary mixing lines between potential low and high sulphate end-members in the study area.
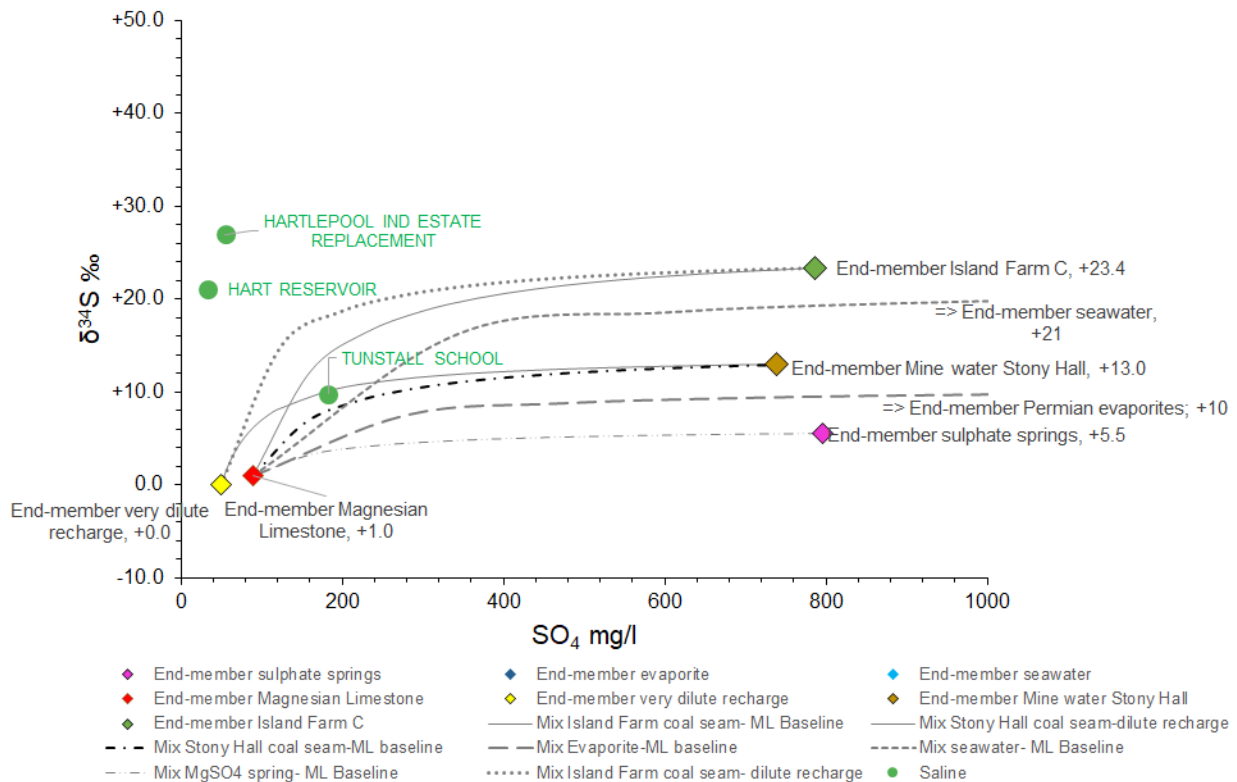
Figure 10 The sulphur isotope composition of sulphate plotted vs sulphate concentration in boreholes from the Magnesian Limestone boreholes, noted for being "saline". The curves are hypothetical binary mixing lines between potential low and high sulphate end-members in the study area.

6.2 SURFACE WATER, HYPORHEIC ZONE AND SOIL

Although a full assessment of the extent of sulphur isotope variations in surface water, hyporheic zone and soil was outside the scope of the project, the much narrower and lower range of δ^{34}S in surface water compared to the groundwater samples was shown. With most values < +7‰, none of the high values measured in the boreholes were noted in the surface water, hyporheic zone and soil leachate samples, except for two samples in the hyporheic zone of Woodham Burn with δ^{34}S values of +36.3‰ and +13.4‰, where sulphate reduction during the 2018 summer sampling was indicated by the hydrochemistry.

The surface water survey has also provided the sulphur isotope value of an additional potential end-member previously sampled by the EA in the upper reach of the Skerne catchment (FC01) and considered to be impacted by mine water. It is noted the resemblance of FC01 with the high sulphate spring at Woodham burn, in terms of trace metal composition and its δ^{34}S value of +6.9‰ is close to the δ^{34}S of +5.5‰ measured in the high sulphate spring at Woodham burn.

7 Conclusions and recommendations

7.1 CONCLUSIONS

The aim of the study was to investigate the source of groundwater sulphate in the Skerne Magnesian Limestone Aquifer using a sulphur isotope approach. The elevated sulphate could be both naturally occurring, due to the presence of gypsum or anhydrite bands in the Magnesian Limestone, or it could be due to abandoned coal mine water, or even saline intrusion pollution. Sulphate from gypsum in the evaporites and sulphate from oxidation of pyrite are known for contrasting sulphur isotope ratios. We hypothesised therefore that we would have seen this contrast in source terms in this study of the Skerne Magnesian Limestone groundwaters, expecting that coal mine waters would reflect the δ^{34}S signature of sulphide oxidation and therefore be identifiable.

The conclusions reached are summarised below and general and specific recommendations follow.

- Coal seam boreholes: We found that the high-sulphate coal seam boreholes do not show the expected low δ^{34}S composition typical of pyrite oxidation and there is less of a contrasting isotope signature between potential "evaporite" and "coal mine water" sources of sulphates in the Magnesian Limestone aquifer.
- For the low-sulphate groundwaters, the small difference in sulphate δ^{34}S of the potential sulphate source terms made the discrimination of the dissolved sulphate source based solely on sulphur isotopes less certain.
- For the high-sulphate Magnesian Limestone boreholes, the δ^{34}S measurements provided clear evidence of coal mine water-derived sulphate in at least one Magnesian Limestone borehole (STONY HALL L) and plausible evidence in other boreholes within the mine plume area.
- The additional water isotope δ^{18}O and δ^{2}H data, which complemented the sulphur isotope analyses, proved very useful to distinguish the coal seam boreholes from the Magnesian Limestone boreholes and especially the Magnesian Limestone boreholes where mixing with coal mine water occurs.
- Among the Magnesian Limestone boreholes where gypsum or anhydrite were noted in the borehole logs, only DALTON PIERCY NO 3 and NO 6 boreholes have high sulphate (~500 mg/L) concentrations and display constant δ^{34}S values of +10.2‰. Given how close this value is to the Permian evaporites' δ^{34}S values, it could be plausibly explained by a gypsum dissolution source, although a "coal mine water" contribution cannot be totally excluded.
- The contribution of salinity and sulphate from seawater within the "saline" boreholes in the Hartlepool area was difficult to discern with the present sulphur isotope data.
- Sulphate reduction can occur in the confined sections of aquifers. Where sulphate is only partially reduced, isotope fractionation results in an increase in the δ^{34}S of the residual sulphate compared with the initial sulphate. The very high δ^{34}S and low sulphate concentrations found in some boreholes could be interpreted as a possible sign of reduction of sulphates. KETTON HALL, LOW COPELAW and STILLINGTON boreholes were among the boreholes with high δ^{34}S, although significant temporal variability was noted between the sampling in 2017 and 2018 for some of them.
- We measured the sulphur isotope values of additional high-sulphate waters: i) a Mg-SO$_4$ spring, sampled in Woodham Burn and described in previous studies for its impact on the surface water quality because of its sulphate concentrations of ~800 mg/L. It has a stable δ^{34}S value of ~ +5.5‰; ii) a surface water impacted by mine water inflow with a Mg-SO$_4$ composition, and a δ^{34}S value of +6.9‰. These relatively low δ^{34}S values pointed to a contribution of low δ^{34}S-sulphate, as expected from the oxidation of pyrite.

In conclusion, the analysis of the sulphur isotope composition of sulphate in the groundwater sampled from 28 sites from boreholes in the Magnesian Limestone Aquifer and in the Coal Measures, and additional samples from surface water, pore water and soils from the Skerne has

provided a valuable new dataset to support a better conceptualisation of the cause of poor-quality groundwater within the Skerne Magnesian Limestone groundwater body. The data and interpretation provided could be made stronger and some gaps in knowledge best addressed following the recommendations below.

7.2   RECOMMENDATIONS FOR FUTURE WORK

Additional sampling:

- The coal seam borehole STONY HALL C δ^{34}S composition was stable over the 2017 and 2018 sampling, suggesting a constant source of sulphate, but it is also very different from the other coal seam borehole ISLAND FARM C. As only two coal seam boreholes could be characterised in this study, it is highly recommended to expand the δ^{34}S dataset of the coal mine waters to constrain the "mine water" source term better.
- Repeated monitoring is recommended to confirm the temporal δ^{34}S variability observed especially in some of the boreholes with a high δ^{34}S.
- A survey of the springs is recommended as it would contribute significantly to the characterisation of sources of sulphate to the Skerne river.

Data integration:

- Isotopic measurements are best used along with measurements of major and minor trace elements and hydrologic data to test hypotheses about hydrologic and geochemical mechanisms. A detailed hydrogeochemical assessment of the mine water and the Magnesian Limestone aquifer is therefore recommended. The EA Water quality data archive WIMS would provide very valuable hydrochemical data to define the temporal changes in the boreholes and help constrain the redox environment that potentially impacts the sulphur isotopes. However, new sampling and chemical analyses are recommended as relevant trace elements are often not included in the WIMS database or are below detection limits.
- The data need to be interpreted in the context of the regional hydrogeology, and more work could be done on the land management and associated sulphur source characterisation.
- The use of water δ^{18}O and δ^{2}H has proved very useful and it is advised to accompany the sulphur isotope analysis.
- A pilot study to test the usefulness of strontium isotopes (^{87}Sr/^{86}Sr) is recommended, as they have proven a valuable addition to the tracer mix in numerous studies.

Methods:

- Some critical δ^{34}S measurements are missing (e.g. FISHBURN C), due to very low sulphate concentrations of the samples collected. This could be addressed in further sampling by acquiring larger volumes of sample.
- Additional analysis of δ^{18}O of the sulphate is recommended to support data interpretation.

Appendix 1 Borehole list (2017 sampling)

BGS CODE	SAMPLE NAME	SAMPLING DATE	
14067-0016	STONY HALL C	12/07/2017	NZ3257029550
14067-0017	STONY HALL L	12/07/2017	NZ3257029550
14067-0018	LOW COPELAW	12/07/2017	NZ2940026300
14067-0020	STILLINGTON OBH2	12/07/2017	NZ3539023106
14067-0019	STILLINGTON OBH4	12/07/2017	NZ3547023445
14067-0021	KETTON HALL	12/07/2017	NZ2940019300
14061-0026	FOUMARTS LANE	29/06/2017	NZ3271330321

Appendix 2 Borehole list (2018 sampling)

WIMS SITE CODE	NAME	EA Comment	DATE	SITE NAME	NGR
454F1130	Amerston Hall No 1	Anhydrite/gypsum noted in log	18/07/2018	BOREHOLE 25-4-8C, AMERSTON HALL NO 1	NZ4270 030400
454F1129	Amerston Hall No 2	Anhydrite/gypsum noted in log	18/07/2018	BOREHOLE 25-4-8B AMERSTON HALL NO 2	NZ4270 030300
454F1107	Coal Lane No 1	Anhydrite/gypsum noted in log	18/07/2018	BOREHOLE 25-4-1A COAL LANE NO 1	NZ4310 032800
454F1108	Coal Lane No 2	Anhydrite/gypsum noted in log	18/07/2018	BOREHOLE 25-4-1B COAL LANE NO 2	NZ4310 032800
454F1103	Dalton Piercy No 3	Anhydrite/gypsum noted in log	18/07/2018	BOREHOLE 25-4-6 DALTON PIERCY NO 3	NZ4640 031500
454F1146	Dalton Piercy No 6	Anhydrite/gypsum noted in log	18/07/2018	BOREHOLE 25-4-180 DALTON PIERCY NO 6	NZ4640 031700
TBC1	Fishburn C	Worked coal seam	24/07/2018	FISHBURN C - COAL MEASURES HARVEY SEAM BOREHOLE	NZ3608 931811
TBC2	Fishburn L	Potential plume, same location as above	24/07/2018	FISHBURN L MAGNESIAN LIMESTONE BOREHOLE	NZ3609 731799
453F0285	Foumarts Lane	unknown high sulphate	17/07/2018	BOREHOLE 25-3-330 FOUMARTS LANE	NZ3271 330321
453F0274	Great Isle (NRA 6)	Centre plume	18/07/2018	BOREHOLE 25-3-29 GREAT ISLE (NRA 6)	NZ2995 026950
453F0291	Hardwick Hall	Mag Limestone background	17/07/2018	BOREHOLE 25-3-336 HARDWICK HALL	NZ3477 029240
454F1111	Heley House	Mid plume	17/07/2018	BOREHOLE 25-4-27 HELEY HOUSE (NRA K)	NZ3573 226502
455F0160	Hart Reservoir	Saline	18/07/2018	BOREHOLE 25-5-111 HART RESERVOIR	NZ4840 734317
455F0181	Hartlepool Ind Estate Replacement	Saline	18/07/2018	BOREHOLE 25-5-112B, HARTLEPOOL INDUSTRIAL ESTATE REPLACEMENT BOREHOLE	NZ5042 434735
454F1110	Hopper House	Anhydrite/gypsum noted in log	18/07/2018	BOREHOLE 25-4-24 HOPPER HOUSE	NZ3440 026700
453H0001	Island Farm C	Unworked coal seam	17/07/2018	ISLAND FARM C BISHOP MIDDLEHAM BOREHOLE 25-3-352	NZ3381 130710
453C0001	Island Farm L	unknown high sulphate	17/07/2018	ISLAND FARM L BISHOP MIDDLEHAM BOREHOLE 25-3-353	NZ3380 130710
453F0253	Ketton Hall (NRA 26)	Centre plume	17/07/2018	BOREHOLE 25-3-76 KETTON HALL (NRA 26)	NZ2940 019300
453F0238	Low Copelaw 1 (NRA D)	Centre plume	18/07/2018	BOREHOLE 25-3-27 LOW COPELAW NO 1 (NRA D)	NZ2940 026300
453F0236	NCB22 (Home Farm)	Connectivity with coal seam?	18/07/2018	BOREHOLE 25-3-25 HOME FARM (NCB 22)	NZ2715 027846
453F0283	Newton Ketton (NRA G)	edge of plume	17/07/2018	BOREHOLE 25-3-78 NEWTON KETTON (NRA G)	NZ3133 020670
453F0233	Rushyford 'A'	Source area of plume	17/07/2018	BOREHOLE 25-3-21 RUSHYFORD A	NZ2840 028700
454F1162	Stillington OBH2	Anhydrite/gypsum noted in log	17/07/2018	BOREHOLE 25-4-343 STILLINGTON OBH2	NZ3539 023106
454F1164	Stillington OBH4	Anhydrite/gypsum noted in log	17/07/2018	BOREHOLE 25-4-345 STILLINGTON OBH4	NZ3547 023445
453F0295	Stony Hall C	Second plume source	18/07/2018	BOREHOLE 25-3-343 STONY HALL C	NZ3257 029550
453F0296	Stony Hall L	Rapidly rising sulphate	18/07/2018	BOREHOLE 25-3-344 STONY HALL L	NZ3257 029550
455F0161	Tunstall School	Saline	18/07/2018	BOREHOLE 25-5-113 TUNSTALL SCHOOL	NZ4819 732529
454F1105	Waterloo Plantation	Anhydrite/gypsum noted in log	18/07/2018	BOREHOLE 25-4-9 WATERLOO PLANTATION	NZ3900 029400

Appendix 3 Chemical analysis of borehole sampling 2017

Sample	pH	Cond µS/c	DO %	Ca mg/l	Mg mg/l	Na mg/l	K mg/l	HCO_3 mg/l	SO_4^{2-} mg/l	Cl^- mg/l	NO_3^- mg/l	Ba µg/l	Sr µg/l	Fe µg/l	Mn µg/l	B µg/l	Li µg/l	Co µg/l	Ni µg/l	As µg/l
STONY HALL C	7.14	2540	2.2	185	78.6	304	12.7	661	751	78.4	2.92	21.0	4977	3222	320	1255	242	5.97	6.9	0.45
STONY HALL L	7.09	2010	1.9	178	81.0	156	4.27	539	570	77.2	4.64	12.2	1331	5192	187	224	118	0.25	0.6	0.12
LOW COPELAW	8.15	822	1.5	55	45.3	36.6	6.25	253	162	51.0	3.54	26.4	219	3466	123	101	34	0.07	0.7	0.08
STILLINGTON OBH4	7.21	775	1.5	86	38.7	34.1	2.42	380	46	48.4	3.33	51.2	807	2088	102	39	58	0.07	0.3	0.10
STILLINGTON OBH2	8.40	433	1.6	13	33.1	21.1	2.60	197	27	21.1	<0.15	4.1	55.5	485	43.7	42	26	<0.01	<0.1	0.03
KETTON HALL	9.04	652	1.3	5	43.3	54.2	2.72	186	67	76.1	<0.15	1.5	22.5	38	63.4	67	63	<0.01	<0.1	0.15
FOUMARTS	7.30	832	nd	90	41.1	29.2	1.5	365	119	51.4	1.23	67.2	227	282	140	62	9	0.19	0.6	0.16

Appendix 4   Chemical analysis of borehole sampling 2018

WIMS SITE CODE	Sample	DATE	pH/ pH_In situ	Cond µS/cm	DO %	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	Alk as HCO$_3$ (mg/l)	SO$_4^{2-}$ (mg/l)	Cl$^-$ (mg/l)	Total N (mg/)	Ba (µg/l)	Sr (µg/l)	Fe (µg/l)	Mn (µg/l)	B (µg/l)
454F1130	AMERSTON HALL NO 1	18/07/18	7.3	936	33.4	95.6	48.9	41.2	2.47	439	101	42	2.74	56.8	359	30	10	100
454F1129	AMERSTON HALL NO 2	18/07/18	7.36	931	41.3	93.8	46.6	42.1	2.45	411	109	41.6	2.44	45.5	416	30	23.8	100
454F1107	COAL LANE NO 1	18/07/18	7.67	730	53.1	60.7	33	48.2	2.66	302	85	39.4	0.79	93.8	549	30	10	100
454F1108	COAL LANE NO 2	18/07/18	7.52	752	29.6	61	34.1	50.2	2.86	311	90.7	38.4	1.05	103	459	30	10	100
454F1103	DALTON PIERCY NO 3	18/07/18	7.33	1455	50.2	182	70.5	46.9	2.74	323	456	68.2	0.64	19.7	2260	30	10	100
454F1146	DALTON PIERCY NO 6	18/07/18	7.21	1602	49.8	186	72.2	72.1	3.16	313	459	118	0.55	25.6	2700	30	10	100
TBC1	FISHBURN C	24/07/18	9.31		1.2	4.08	1.77	193	4.39	484	10	44.1	0.2	61.2	81	66.8	10.8	880
TBC2	FISHBURN L	24/07/18	7.17		34.1	109	52.5	39.6	1.8	397	153	41.4	7.52	69.3	99.2	30	10	100
453F0285	FOUMARTS LANE	17/07/18	7.35		4	92.3	41	31.9	1.93	357	100	49.5	1.44	107	259	23400	301	100
453F0274	GREAT ISLE (NRA 6)	18/07/18	9.28	324	1.2	11.9	18.5	20.2	1.37	110	24.1	33.2	0.2	12.5	20	30	10	100
453F0291	HARDWICK HALL	17/07/18	7.15		36	103	45.3	27.5	1.91	428	88.8	36.3	3.19	122	289	30	10.5	100
454F1111	HELEY HOUSE	17/07/18	8.25		1.8	37.1	24.9	20.7	3.8	271	10	20.5	0.2	72.9	398	2010	151	100
455F0160	HART RESERVOIR	18/07/18	8.57	789	1.2	29.5	41.9	105	3.86	218	32.6	202	0.2	32.8	188	684	71.4	100
455F0181	HARTLEPOOL IND ESTATE REPLACEMENT	18/07/18	7.41	1391	1.3	113	52.8	76.7	4.55	382	55	223	0.2	87.1	840	453	102	100
454F1110	HOPPER HOUSE	18/07/18	7.41	800	27.1	83.2	41	30.4	3.56	349	98.4	36.7	2.39	46.2	194	30	10	100
453H0001	ISLAND FARM C	17/07/18	6.71		12	188	87.6	294	20.9	575	786	104	0.2	13.6	2270	16500	387	385
453C0001	ISLAND FARM L	17/07/18	7.12		4.5	115	48.3	34.8	3.23	435	103	60.2	4.75	51.5	146	30	114	100
453F0253	KETTON HALL (NRA 26)	17/07/18	9.28		11.2	4.26	22.6	53.1	2.46	121	10	85.8	0.2	10	20	30	17.4	100
453F0238	LOW COPELAW 1 (NRA D)	18/07/18	7.44	1132	1.3	114	58.3	43.9	6.12	382	223	53.6	0.2	56.2	248	1310	869	122
453F0236	NCB22 (HOME FARM)	18/07/18		1212	47	141	62.8	29.9	4.77	388	268	33.5	7.23	47.9	267	30	10	100
453F0283	NEWTON KETTON (NRA G)	17/07/18	8.83		2.2	11	38.1	21.2	5.8	187	48.8	25	0.2	15.3	99.7	156	50.2	100
453F0233	RUSHYFORD 'A'	17/07/18	8.07		2.1	102	56.3	108	4.97	199	164	205	0.31	51.4	116	1230	59.8	100
454F1162	STILLINGTON OBH2	17/07/18	9.25		1.5	4.98	16	21.6	1.7	110	10	26.3	0.2	10	28	47.2	10	100
454F1164	STILLINGTON OBH4	17/07/18	7.86		0.9	60.8	34.5	28.9	2.36	360	20.4	39.5	0.2	56.4	490	3930	137	100
453F0295	STONY HALL C	18/07/18	7.21	2393	1.6	185	74.3	307	13.8	678	738	83.5	0.2	19.6	4700	3340	348	1300
453F0296	STONY HALL L	18/07/18	7.14	1938	2.1	176	85.5	172	4.73	517	577	81.1	0.2	19.1	1330	5520	205	257
455F0161	TUNSTALL SCHOOL	18/07/18	7.3	1222	9.9	111	47.6	61.3	2.71	335	183	120	1.1	25.6	1640	30	10	100
454F1105	WATERLOO PLANTATION	18/07/18	7.25	955	30.7	112	45.2	32.4	2.5	412	128	39.1	1.96	34.9	707	30	10	100

Appendix 5 Chemical analysis of springs

Sample	pH	Cond µS/cm	DO %	Ca mg/l	Mg mg/l	Na mg/l	K mg/l	HCO$_3$ mg/l	SO$_4^{2-}$ mg/l	Cl$^-$ mg/l	NO$_3^-$ mg/l	Ba µg/l	Sr µg/l	Fe µg/l	Mn µg/l	B µg/l	Li µg/l	Co µg/l	Ni µg/	As µg/l
AYCLIFFE QUARRY Spring	8.17	835		87.9	48.8	16.0	2.33	415	68.7	25.0	16.3	197	149	3.5	1	27	10	<0.05	<0.1	0.08
Bubbly point Spring Aug-18	7.14			263	158	85.2	11.9	736	840	36.8	0.8	27.7	1192	3.5	1	182	178			
Bubbly point Spring Feb-19	6.94	2345	3.6	263	150	86.8	11.9	740	796	38.4		43.9	1213	116	13.5	191	177		0.43	0.06

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