Geochemical and isotopic characterisation of groundwater from the Magnesian Limestone aquifer, South of the Butterknowle Fault

ECAR Programme

Commercial Report CR/25/070

BRITISH GEOLOGICAL SURVEY
ECAR PROGRAMME
COMMERCIAL REPORT CR/25/070

Keywords

sulphate contamination, water isotopes, sulphur isotope, coal mine water, groundwater.

Bibliographical reference

PALUMBO-ROE, B, LAMB, A, BOWES, MJ 2025. Geochemical and isotopic characterisation of groundwater from the Magnesian Limestone aquifer, South of the Butterknowle Fault. *British Geological Survey Commercial Report*, CR/25/070. 96 pp.

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Keyworth, Nottingham British Geological Survey 2025

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Acknowledgements

The authors would like to thank Diane Steele and John P Collins along with other members of the Environment Agency (EA) team in Newcastle for assistance with coordination and site access for field activities. We would also like to thank local landowners for allowing us access to monitoring sites.

We acknowledge the BGS Inorganic Geochemistry Laboratories for the chemical analyses and the Stable Isotope Facility at Keyworth for undertaking the isotope analyses.

Thanks also extended to British Geological Survey staff: David Macdonald for advice on the sampling strategy and Pauline Smedley for a thorough review of this report.

This report was funded under the ‘36520 - Supply of Geological Products and Services Framework’ between BGS-UKRI and EA England.

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Summary

This report details the results of a geochemical and isotope study of selected EA monitoring boreholes and public water abstraction boreholes from the Magnesian Limestone aquifer and underlying Coal Measures, focussing on the area around Bishop Middleham and Sedgefield, south of the Butterknowle Fault, Co Durham. The groundwater sampling was carried out during January and February 2024 from 39 sites by Environment Agency staff. The dataset expands a previous isotope study with sampling undertaken in July 2018, to improve the understanding of the source of elevated dissolved sulphate in the Magnesian Limestone aquifer in the study area. The application of stable isotopes ($\delta^{34}S_{SO4}$, $\delta^{18}O_{SO4}$, $\delta^{18}O_{H2O}$, and $\delta^{2}H_{H2O}$) integrated with hydrochemical data has supported aspects of the current conceptual hydrogeological model, but limitations in some of the data interpretation persist due to uncertainties regarding the representativeness of certain samples in reflecting aquifer conditions and water chemistry.

1 Introduction

This report was commissioned by the Environment Agency and presents the chemical and isotopic data of groundwater samples obtained in January/February 2024 from boreholes in the Magnesian Limestone and Coal Measures aquifers, focussing on the area around Bishop Middleham and Sedgefield, south of the Butterknowle Fault, Co Durham (Figure 1). This dataset expands the previous isotope study presented in Palumbo-Roe et al. (2023) reporting on many of the same boreholes sampled in July 2018. The data are used to improve the understanding of the source of elevated dissolved sulphate in the Magnesian Limestone aquifer in the study area.

1.1 SUMMARY OF THE REPORT STRUCTURE

After describing the background of the groundwater quality pressures, and approach in Chapter 2, the analytical result tables are reported in Chapter 3. In Chapter 4 we provide more background on the selected boreholes and current understanding of the origin of the dissolved sulphate in groundwater. The distribution of historical and current (2024) dissolved sulphate concentrations, together with chloride and conductivity, in groundwaters across various borehole groups, is illustrated in Chapter 5 and a description of the water types and main physicochemical parameters in Chapter 6. The isotope data obtained in this study are compared with the previous study from 2017/18 and data from the additional boreholes sampled in 2024 also described in Chapter 7. We discuss the sources of sulphate by integrating the isotopic evidence and hydrochemical data in Chapter 8. A summary of the main findings and conclusions is given in Chapter 9.

More data are presented in the form of tables or diagrams in the appendices. Appendix 1 reports the Piper plots of the 39 boreholes using WIMS data. Appendix 2 shows the time series of sulphate and chloride for each borehole. Appendix 3 provides the scatterplots of sulphate versus major and some minor and trace elements for some selected boreholes: Dalton Piercy boreholes, Stillington boreholes, the borehole group near Hartlepool, and selected boreholes with increasing trends of sulphate and chloride: Amerston Hall, Coal Lane, Hopper House, Red Barns, Waterloo Plantation and Stony Hall L. Finally, the time series illustrating the chemical changes associated with high-pH groundwater records at Elstob Hill are shown in Appendix 4.

2 Background and methodology

Groundwater quality of the Magnesian Limestone aquifer has been studied extensively over many decades. The study by WSP (2023) provides a comprehensive review of past investigations and illustrates the current situation with respect to groundwater quality and the updated conceptual hydrogeological model. A summary is given in the sections below. This study focuses on the application of stable isotopes integrated with hydrochemical data to inform and improve aspects of the current conceptual hydrogeological model.

2.1 GEOLOGICAL AND HYDROGEOLOGICAL SETTING

The Permian Magnesian Limestone forms a north-south trending escarpment extending from the north–east of England near Sunderland to Nottingham in the East Midlands (Bearcock & Smedley, 2009), dipping towards the east. The Magnesian Limestone comprises a series of marine limestones, dolomites, marls and evaporites reflecting transgressions, regressions and evaporation of a shallow tropical sea (Powell et al., 1992; Smith 1995). The nomenclature referring to the Magnesian Limestone sequence was revised in 1986 by Smith et al. (1986) to aid in naming consistency with other regions and the current and traditional nomenclature of the Permian stratigraphy are compared in Table 1 and both used in Figure 1.The Middle and Upper Magnesian Limestone units are separated locally in the County Durham region by marls and siltstones (formerly Middle Permian Marls; Allen et al., 1997), which forms a leaky aquitard between the Middle and Upper Magnesian Limestone divisions. In the County Durham region, the Middle Magnesian Limestone is more porous than the Upper and Lower, but permeability is variable due to dispersed fracturing. Some vertical hydraulic conductivity is present and the three units are generally treated as one aquifer (Allen et al., 1997). The Magnesian Limestone aquifer units are underlain by Carboniferous strata and overlain by superficial deposits of varying thickness. The superficial deposits primarily comprise glacial and associated glaciolacustrine and glaciofluvial sediments of Late Devensian age, overlain by younger Flandrian deposits (Price et al., 2007). They are thin or absent towards the north-west of the Co. Durham region, thickening to 85 m and forming an increasingly confining layer towards the south-east of the region.

The Magnesian Limestone aquifer forms an important source of potable water in the region as well as supporting industrial, commercial and recreational uses (Palumbo-Roe et al., 2019). Transmissivity values in Co. Durham have an interquartile range of 139 – 564 m^2/day (Allen et al., 1997) with localised variations. Higher transmissivity values are generally found in fault zones. The Middle Magnesian Limestone has greater porosity than the upper and lower divisions along with greater hydraulic conductivity than the more competent lower division (Upper and Middle Magnesian Limestone hydraulic conductivities of greater than 12 m/day can be found). Where sulphate cements are present in the Middle Magnesian Limestone, lower transmissivities can be found (Northumbrian River Authority, 1969; Allen et al., 1997). The recharge area is located at the western edge of the outcrop towards Bishop Auckland and groundwater flow is predominantly towards the east and south-east towards the sea. In areas of thinner drift cover, surface water-groundwater interaction is likely with gains and losses in various settings (Palumbo-Roe et al., 2019).

Table 1 - Subset of the Upper Permian succession with "traditional" and current nomenclature (Bearcock & Smedley, 2009; Smith et al., 1986; Allen et al., 1997).

Former geological formation	**Current lexicon formations & subdivisions**	**BGS Lexicon Description**
Upper Permian Marls	Roxby Formation	Primarily mudstone and siltstone, sulphates (gypsum, anhydrite) towards base (0 – 130m thick)
Upper Magnesian Limestone	Seaham Formation	Predominantly thin-bedded limestone – some dolostone (1 – 32m thick)
	Roker Formation	Oolitic dolostone, bed of fine-grained dolomite - some breccias (up to 80 m offshore)
Middle Permian Marls	Hartlepool Anhydrite	Anhydrite rock (up to 150m thick)
	Edlington Formation	Mudstone, subordinate siltstone and sandstone (0 – 65m thick)
Lower Evaporite Group	Fordon Evaporite Formation	Varied sequence of evaporites (anhydrite, halite) with some gypsum and dolostones (up to 396m, thin residue at outcrop)
Middle Magnesian Limestone	Ford Formation	Dolomite (shelf-edge reef, lagoonal beds, off-reef beds) (1 – 150m thick)
Lower Magnesian Limestone	Raisby Formation	Fine-grained dolostones, fine-grained limestone (20 – 40m thick; up to 73m in East Durham)

2.2 GROUNDWATER QUALITY PRESSURES

Groundwater from the Magnesian Limestone aquifer is predominantly of calcium-magnesium bicarbonate (Ca-Mg-HCO_3) type, as mineral reactions involving calcite and dolomite dominate the groundwater chemistry.

The main pressures known to cause high sulphate quality issues in the aquifer to the south of Butterknowle Fault, as summarised by the WSP conceptual model (2023), include:

- Mine water intrusion and potential migration of rebounding high sulphate mine waters from abandoned coal mines further to the west.

- Dissolution and leakage from the overlying evaporite-rich marls, e.g. the Edlington and Roxby Formations as part of the English Zechstein evaporite deposits, enhanced by groundwater abstraction.
- Saline intrusion near the coast around Hartlepool. A detailed investigation into saline intrusion occurring within the Skerne Magnesian Limestone groundwater body within the vicinity of Hartlepool was also carried out in 2018 (JBA, 2018).

2.3 APPROACH

This study follows the previous isotope study presented in Palumbo-Roe et al. (2023), reporting on many of the same boreholes sampled in July 2018 and expanding the number of boreholes sampled, in order to increase confidence in the assessment using a larger dataset and to assess temporal variability. New to the approach used in Palumbo-Roe et al. (2023) is that we also analysed the $\delta^{18}O_{SO4}$ of the dissolved sulphate, as well as the $\delta^{34}S_{SO4}$; the dual isotope analysis ($\delta^{34}S_{SO4}$, $\delta^{18}O_{SO4}$) can help to distinguish the dissolved sulphate sources. It was deemed important, especially given some overlaps of the isotopic signatures of the potential end-members from the previous assessment, to complement the dual isotope analysis ($\delta^{34}S_{SO4}$, $\delta^{18}O_{SO4}$) of groundwater sulphate with other stable isotope tracers ($\delta^{18}O_{H2O}$, and $\delta^{2}H_{H2O}$) and hydrochemical parameters.

Considering the main water quality issues and pressures, the EA aided by BGS designed a sampling campaign to provide further insights into the current conceptual groundwater model using stable isotopes. The approach consisted of selecting the boreholes according to initial groups; these groups were based on the current conceptual hydrogeological model and previous analysis of borehole logs and geology undertaken by the EA and analysis of the EA water quality database (WIMS) by BGS, and representing:

a) Coal Measures boreholes;

b) Magnesian Limestone observation boreholes historically impacted by coal mine water rebound;

c) Magnesian Limestone observation and public water supply (PWS) abstraction boreholes outside the historical mine water plume; and,

d) Magnesian Limestone observation and PWS abstraction boreholes near Hartlepool.

The lists are reported in Data availability

This work uses Environment Agency water quality data from the Water Quality Archive (Beta), which is available under the Open Government Licence v3.0.

Table 2 and Table 3. The boreholes were sampled by the EA on 22–26 January 2024 and on 7 February 2024, and analysed for major, minor and trace elements and for the stable isotopes $\delta^{34}S_{SO4}$, $\delta^{18}O_{SO4}$, $\delta^{18}O_{H2O}$, and $\delta^{2}H_{H2O}$ in the BGS laboratories. Data availability

This work uses Environment Agency water quality data from the Water Quality Archive (Beta), which is available under the Open Government Licence v3.0.

Table 2 lists the boreholes sampled, as well as including the list from 2018 (17–24 July 2018) and where additional borehole depth profiling of physicochemical parameters was undertaken. Six boreholes were also sampled on 29th June 2017: Foumarts Lane, and 12th July 2017: Ketton Hall (NRA 26), Low Copelaw 1 (NRA D), Stillington OBH2, Stillington OBH4, Stony Hall C, Stony Hall L.

Compared to 2018 and 2017, in 2024 greater borehole depths could be reached for the water sampling (see section 2.4). This will be accounted for in the data comparison and interpretation.

Fifteen new boreholes were added to the 2018 list, while 4 boreholes were removed from the list. The boreholes added were: Aycliffe, Bishop Middleham, Butterwick, Camerons Brewery Stockton Street, Chilton East House, Dalton Piercy No 7, Elstob Hill, Home Farm, Hope House, Red Barns, Rushyford NE, Stillington No.2, Stillington OBH1, Stillington OBH3, Swan Carr. The boreholes not included, and the reasons for the exclusion, were as follows:

- Amerston Hall No 2, as it was showing similar sulphate concentration and isotope values to Amerston Hall No 1 in 2018;
- Coal Lane No2, also with similar composition to Coal Lane No1 in 2018;
- Ketton Hall borehole was classified as centre-plume after the work of White Young Green in 2008. The sulphate concentration time series, from the WIMS database, showed high variability, also confirmed by the 2017 (SO_4 67 mg/L) and 2018 (10 mg/L) data. The sulphur isotope values in both sampling dates were quite high (+37.9 and +47.1‰), and interpreted as evidence of microbial reduction of sulphate and enrichment of the residual sulphate in the heavier sulphur isotope ^{34}S (Palumbo-Roe et al., 2021). Hence the microbial reduction of the sulphate overprints the original sulphur signature and new sampling would have not been able to bring any new insights into sources;
- Newton Ketton borehole was classified as borehole at the edge of the mine water plume impacted area (White Young Green, 2006). It has been unlisted as it shows similar sulphate variability to Ketton Hall and similar high sulphur isotope values.

Following the water sampling and chemical analysis, a hydrochemical characterisation was carried out identifying the sulphate concentration distribution by each group and using isotopes and trace elements to constrain, where possible, the source of sulphates (and validate the initial grouping), but also identifying confounding factors that can attenuate sulphate by dilution (mixing with less SO_4-concentrated water) or biogeochemical reduction processes of sulphate to insoluble sulphides.

A parallel study, carried out by BGS for the EA and reported in Bowes et al. (2024), highlighted the chemical variations in borehole water from within stagnant casing sections and how some historical data from the Water Quality Archive (open WIMS data) might reflect the “altered” composition due to water stagnation and possibly insufficient purging, in certain boreholes, rather than the true aquifer composition. These changes, which were apparent from a change towards high pHs, can be particularly relevant in the present study, if chemical processes involve dissolved sulphur species (via redox process causing reduction of sulphate to sulphide and resulting in lower sulphate concentrations). For this reason, the findings were considered in the present study during the data interpretation. The boreholes for which the depth hydrochemical profiles are available and part of this study are: Elstob Hill, Great Isle, Hart Reservoir, Heley House, NCB22 (Home Farm), Newton Ketton, Stillington OBH2, OBH3, OBH4 and Swan Carr.

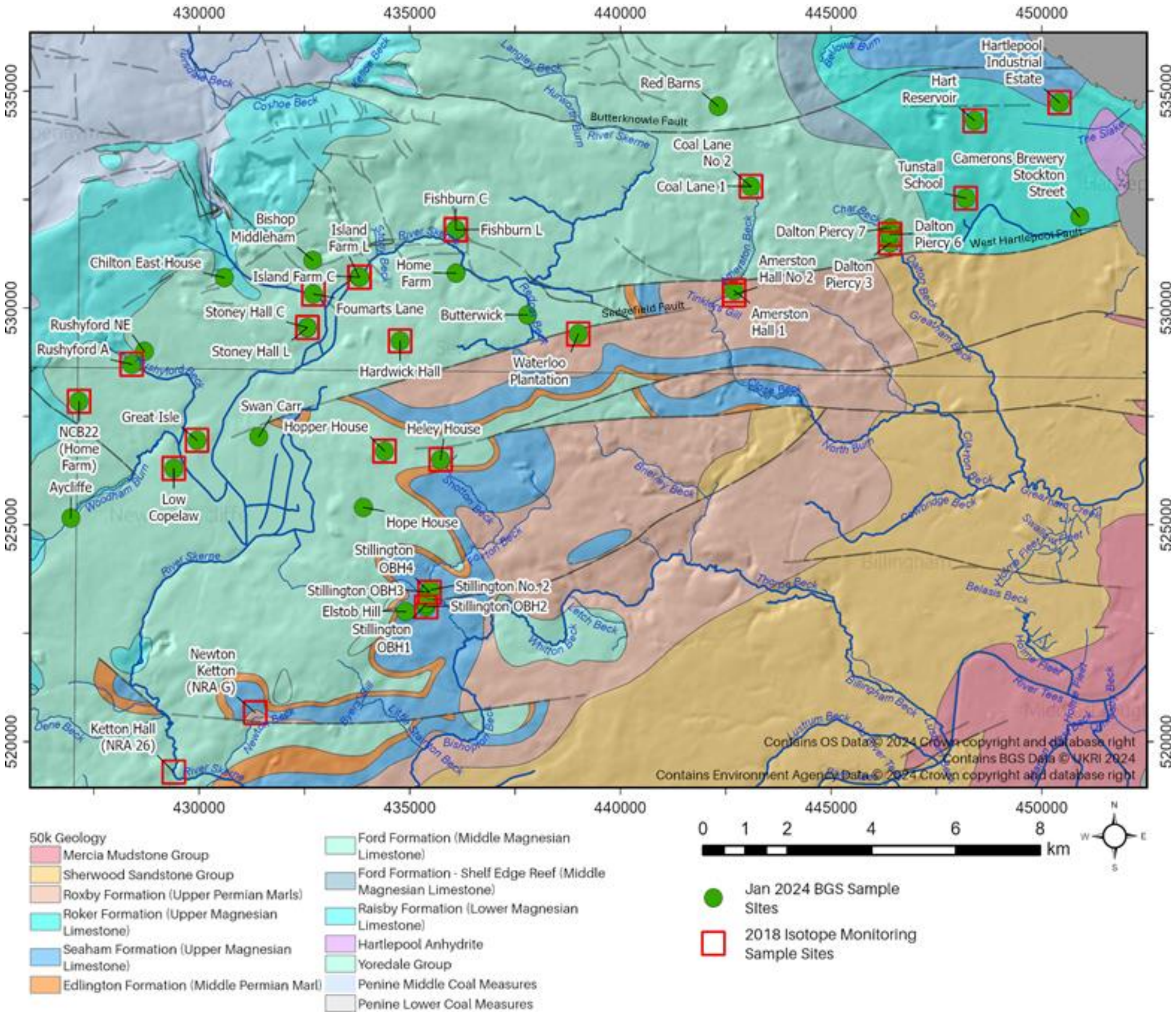


Figure 1 Study area.

2.3.1 Data availability

This work uses Environment Agency water quality data from the Water Quality Archive (Beta), which is available under the Open Government Licence v3.0.

Table 2 Borehole list (WIMS CODE: Water Quality Data Archive sampling point code) in 2018 and 2024 with information where additional borehole depth profiling was undertaken.

WIMS CODE	Site Name	Easting	Northing	Sampled in 2018	Sampled in 2024	Borehole Profiling
454F1130	AMERSTON HALL NO 1	442760	530310	Y	Y	N
454F1129	AMERSTON HALL NO 2	442740	530290	Y	N	N
453F0243	AYCLIFFE	426970	525100	N	Y	N
453F0232	BISHOP MIDDLEHAM	432730	531150	N	Y	N
453F0242	BUTTERWICK	437830	529850	N	Y	N
455F0170	CAMERONS BREWERY STOCKTON STREET	450950	532100	N	Y	N
453F0231	CHILTON EAST HOUSE	430570	530670	N	Y	N
454F1107	COAL LANE NO 1	443140	532790	Y	Y	N
454F1108	COAL LANE NO 2	443120	532840	Y	N	N
454F1103	DALTON PIERCY NO 3	446430	531640	Y	Y	N
454F1146	DALTON PIERCY NO 6	446430	531760	Y	Y	N
454F1147	DALTON PIERCY NO 7	446410	531850	N	Y	N
454F1115	ELSTOB HILL	434927	523011	N	Y	Y
453H0002	FISHBURN C	436089	531811	Y	Y	N
453C0003	FISHBURN L	436097	531799	Y	Y	N
453F0285	FOUMARTS LANE	432650	530320	Y	Y	N
453F0274	GREAT ISLE (NRA 6)	429950	526950	Y	Y	Y
453F0291	HARDWICK HALL	434770	529240	Y	Y	N
455F0160	HART RESERVOIR	448410	534310	Y	Y	Y
455F0181	HARTLEPOOL IND ESTATE REPLACEMENT	450424	534735	Y	Y	N
454F1111	HELEY HOUSE	435740	526500	Y	Y	Y
453F0292	HOME FARM	436100	530800	N	Y	N
454F1112	HOPE HOUSE	433940	525380	N	Y	N
454F1110	HOPPER HOUSE	434400	526720	Y	Y	N
453H0001	ISLAND FARM C	433855	530681	Y	Y	N
453C0001	ISLAND FARM L	433855	530681	Y	Y	N
453F0253	KETTON HALL (NRA 26)	429450	519300	Y	N	N
453F0238	LOW COPELAW 1 (NRA D)	429420	526320	Y	Y	N
453F0236	NCB22 (HOME FARM)	427140	527850	Y	Y	Y
453F0283	NEWTON KETTON (NRA G)	431330	520670	Y	N	N
455F0163	RED BARNS	442320	534650	N	Y	N
453F0233	RUSHYFORD 'A'	428400	528670	Y	Y	N
453F0234	RUSHYFORD NE	428750	528960	N	Y	N
454F1154	STILLINGTON NO.2	435530	523510	N	Y	N
454F1161	STILLINGTON OBH1	435390	523160	N	Y	N
454F1162	STILLINGTON OBH2	435400	523130	Y	Y	Y
454F1163	STILLINGTON OBH3	435480	523450	N	Y	Y
454F1164	STILLINGTON OBH4	435500	523450	Y	Y	Y
453F0295	STONY HALL C	432570	529550	Y	Y	N
453F0296	STONY HALL L	432570	529550	Y	Y	N
453F0239	SWAN CARR	431416	527033	N	Y	Y
455F0161	TUNSTALL SCHOOL	448180	532560	Y	Y	N
454F1105	WATERLOO PLANTATION	439100	529370	Y	Y	N

Table 3 Borehole groups and additional observations (EA source). Abbreviations: PWS: Public Water Supply; OB: Observation Borehole; MOB: Mine water impacted Observation Borehole; SOB: Saline Observation Borehole; SPB: Saline 3rd Party Borehole; ML: Magnesian Limestone; Und ML: Undifferentiated Magnesian Limestone; UML, MLM, LML: Upper, Middle and Lower Magnesian Limestone)

Site Name	Screened geology	Assigned group	Comments
AMERSTON HALL NO 1	UML	PWS	Anhydrite/gypsum noted in log
AMERSTON HALL NO 2	UML	PWS	Anhydrite/gypsum noted in log
AYCLIFFE	LML	MOB	Confined
BISHOP MIDDLEHAM	ML & Coal	MOB	
BUTTERWICK	LML	MOB	Unconfined
CAMERONS BREWERY STOCKTON ST	Und. ML	SPB	
CHILTON EAST HOUSE		MOB	Confined
COAL LANE NO 1	Und. ML	PWS	Anhydrite/gypsum noted in log
COAL LANE NO 2	Und. ML	PWS	Anhydrite/gypsum noted in log
DALTON PIERCY NO 3	Und. ML	PWS	Anhydrite/gypsum noted in log
DALTON PIERCY NO 6	Und. ML	PWS	Anhydrite/gypsum noted in log
DALTON PIERCY NO 7	Und. ML	PWS	
ELSTOB HILL	UML	OB	Confined/High pH in borehole casing/dominated by abstraction
FISHBURN C	Coal Measures	Coal Seam	
FISHBURN L	Und. ML	MOB	
FOUMARTS LANE		MOB	Confined
GREAT ISLE (NRA 6)	MML & LML	MOB	High pH confirmed by log/ confined
HARDWICK HALL	Und. ML	ML	Unconfined
HART RESERVOIR	Und. ML	SOB	High pH in borehole casing/ possibly influenced by abstraction (based on daily fluctuations)/unconfined
HARTLEPOOL IND ESTATE REPLACEMENT	UML	SOB	Possibly influenced by abstraction (based on daily fluctuations)/confined
HELEY HOUSE	MML & LML	MOB	High pH confirmed by log/ confined
HOME FARM	Und. ML	MOB	
HOPE HOUSE	MML & LML	PWS	
HOPPER HOUSE	MML & LML	PWS	Anhydrite/gypsum noted in log
ISLAND FARM C	Coal Measures	Coal Seam	Confined
ISLAND FARM L	MML & LML	MOB	Confined
KETTON HALL (NRA 26)		MOB	
LOW COPELAW 1 (NRA D)	MML	MOB	Confined
NCB22 (HOME FARM)	MML	MOB	Unconfined/borehole in coal measures backfilled with grout just below the base of the MML/High pH
NEWTON KETTON (NRA G)		MOB	High pH in borehole casing/ confined
RED BARNS	MML & LML	OB	
RUSHYFORD 'A'		MOB	Confined
RUSHYFORD NE		MOB	Unconfined
STILLINGTON NO.2	Und. ML	PWS	Anhydrite/gypsum noted in log
STILLINGTON OBH1		OB	Confined/Influenced by abstraction/Anhydrite/gypsum noted in log/ High pH confirmed by log
STILLINGTON OBH2	MML	OB	Confined/Influenced by abstraction/Anhydrite/gypsum noted in log/ High pH confirmed by log
STILLINGTON OBH3	Drift	OB	Confined/Influenced by abstraction/Ironstone and marl noted in log/ High pH confirmed by log
STILLINGTON OBH4		OB	Confined/Influenced by abstraction/Ironstone and marl noted in log/ High pH in borehole casing
STONY HALL C	Coal Measures	Coal Seam	Confined
STONY HALL L	Und. ML	MOB	Confined
SWAN CARR	MML	MOB	Confined/High pH in borehole casing
TUNSTALL SCHOOL	Und. ML	SOB	Dominated by abstraction/unconfined
WATERLOO PLANTATION		PWS	Anhydrite/gypsum noted in log

2.4 GROUNDWATER SAMPLING

Groundwater sampling was undertaken at a combination of EA observation boreholes and third party owned abstractions.

Samples obtained at third party abstractions were collected from sample taps on headworks or in pump houses. In all cases the tap was opened and the water ran for a couple of minutes before filling the sample bottle(s); ensuring fresh samples were collected.

Geotech geosub pumps were used to obtain samples from EA and Mining Remediation Authority ((MRA) Fishburn) groundwater monitoring observation boreholes. Borehole specific pump depths were calculated before sampling. Pumps were lowered to two thirds of the way down the water column in the screened or open holed section of each borehole to obtain a representative aquifer sample. The standard maximum depth of the geosub pump is 60 metres; extension tubing allowed sampling to deeper depths. The pump extension was not available during previous sampling rounds in 2018, therefore, as a result there may be a difference in the analysis.

Pumping continued until stabilisation of field determinands (pH, temperature, dissolved oxygen (DO), oxidation-reduction potential (ORP) and specific electrical conductance (SEC at 25 °C)) were observed using a YSI EX01 multiparameter sonde. The sonde was installed in a sealed flow through cell to prevent contact with air. Sample bottles were filled from tubing on the outflow point of the flow through cell. Field determinands were recorded at the same time as filling sample bottles. Alkalinity determination (colorimetric) via Hach Digital Titrator was undertaken whilst on site or at the end of each sampling day. The titration process was repeated until two identical alkalinity results were obtained at each site to ensure data accuracy. A minimum of six sample bottles were filled at each site; an additional bottle was filled at a small number of sites for strontium isotope analysis (Table 4). Filtering was undertaken in the field whilst filling a number of the bottles using filters and syringes.

Table 4 List of the different samples collected including bottle type and sampling procedure.

Sample Type	**Bottle**	**Sampling procedure**
F/A Cations	30ml LDPE – Pre-dosed with conc. HNO3	Do not rinse! Fill with 0.45um filtered water to just above shoulder of bottle
F/UA Anions	60ml LDPE	Fill with 0.45um filtered water– no headspace
F/UA NPOC	30ml HDPE	Fill with 0.45um filtered water– no headspace
F/UA SO4 S/O	250ml HDPE/LDPE	Fill with 0.45um filtered water– no headspace
UF/UA D/δ^{18}O	15ml HDPE	Submerge in beaker of unfiltered sample water and cap underwater - no headspace
UF/UA Bulk	500/250ml LDPE	Fill with un-filtered water - no headspace
F/UA δSr	60ml HDPE	Fill with 0.45um filtered water– no headspace
Key: *A = Acidified UA = Un-acidified F = Filtered UF = Unfiltered*		

2.5 ANALYTICAL METHODS

Chemical analysis was undertaken of 39 water samples collected by EA staff. Following receipt by the Laboratory, 0.5% v/v HCl was added to all filtered/acidified (F/A) samples (submitted as 1% v/v HNO_3) to create the F/A splits for ICP-MS. The field data supplied by the EA have been included in the report.

Determination of Cl^-, SO_4^{2-}, NO_3^-, NO_2^-, Br^-, F^-, HPO_4^{2-} was by ion chromatography and major and trace elements (Ca, Mg, Na, K, Si, P, S, Ba, Sr, Mn, Fe, Li, Be, B, Al, Ti, V, Cr, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Y, Zr, Nb, Mo, Cd, Sn, Sb, Cs, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Tl, Pb, Bi, Th, U) were determined by inductively-coupled plasma mass spectrometry (ICP-MS), with independent QC checks providing 96 +/- 3% accuracy (in-house QC solution) and 98 +/- 4% accuracy (NIST SRM 1643e). The Non Purgeable Organic Carbon (NPOC) content was determined using a Shimadzu TOC-V CPH analyser with an associated ASI-V auto-sampler. All analyses were carried out at the in-house BGS laboratory in Keyworth, UK and are included in the UKAS Accreditation Schedule for this laboratory. Only a selection of the analytical suite is reported in this report (Table 5).

The isotope analyses were carried out in the Stable Isotope Facility, BGS, Keyworth. The samples were 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 mil), 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.

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 $BaSO_4$. Sulphur isotope analysis of barium sulphate ($\delta^{34}S$) was by Continuous Flow Isotope Ratio Mass Spectrometry (CFIRMS). The instrumentation comprises a Thermo Fisher EA IsoLink coupled to a Thermo Finnigan Delta V isotope ratio mass spectrometer via a ConFlo IV interface. Sulphur isotope ratios ($\delta^{34}S$) are reported in per mil (‰) relative to VCDT. $\delta^{34}S$ ratios were normalised using a 3-point calibration using the barium sulphate international reference materials IAEA-SO-5 (+0.5‰), IAEA-SO-6 (-34.05‰) and NBS-127 (+21.1‰). The precision (1σ) for within-run standards was <0.5 ‰. Oxygen isotope ($\delta^{18}O$) analysis of samples was carried out using an Elementar vario PYRO cube elemental analyser (EA) coupled to an isoprime precisION isotope ratio mass spectrometer (IRMS) with an onboard centrION continuous flow interface system. The EA inlet converts solid samples into gas via high-temperature pyrolysis (1450 °C). The pyrolised gas mixture is passed through an adsorption column to trap and purify the CO, which is passed online to the IRMS for determination of $\delta^{18}O$. Oxygen isotope data are reported in delta (δ) notation in per mil (‰) relative to the international reference scale VSMOW. Oxygen isotope ratios were blank and linearity corrected, then normalised to VSMOW using a three-point calibration comprising the barium sulphate international reference materials IAEA-SO-6 (−11.35 ‰), NBS127 (+8.59 ‰), and IAEA-SO-5 (+12.13 ‰). The precision (1σ) for within-run standards was <0.5 ‰.

3 Analytical results

The field physicochemical parameters of temperature, pH, conductivity and dissolved oxygen (DO), the major elements and a selection of minor and trace elements analysed in the water samples collected in January-February 2024 are presented in Table 5. The water $\delta^{18}O$ and δ^2H and $\delta^{34}S$ and $\delta^{18}O$ of the dissolved sulphate are reported in Table 6.

Table 5 Hydrochemical analysis

Coal Measures boreholes

Sample	DATE	T°C	pH	Cond µS/cm	DO (mg/l)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	HCO_3 (mg/l)	SO_4 (mg/l)	Cl (mg/l)
FISHBURN C	24/1/24	11.4	7.25	749	3.50	31.7	11.8	139	7.25	482	177	41.1
ISLAND FARM C	25/1/24	9.3	7.72	2988	1.46	182	91.2	406	21.9	725	973	215
STONY HALL C	25/1/24	10.7	7.38	2457	0.19	169	78.7	304	12.1	636	836	97.4

Sample	DATE	NO_3 (mg/l)	Br (mg/l)	F (mg/l)	SiO_2 (mg/l)	Li (µg/l)	B (µg/l)	Ba (µg/l)	Sr (µg/l)	Mn (µg/l)	Fe (µg/l)	Rb (µg/l)	U (µg/l)
FISHBURN C	24/1/24	0.883	0.187	0.356	4.24	204	281	126	411	237	443	8.97	0.660
ISLAND FARM C	25/1/24	9.94	1.03	0.3	14.3	379	432	9.45	2517	273	14090	35.9	3.10
STONY HALL C	25/1/24	2	0.432	0.3	10.8	242	1219	19.1	4484	198	3343	21.7	0.134

Magnesian Limestone boreholes – Historical mine water plume area

Sample	DATE	T °C	pH	Cond µS/cm	DO (mg/l)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	HCO_3 (mg/l)	SO_4 (mg/l)	Cl (mg/l)
AYCLIFFE	26/1/24	10.6	6.97	1269	4.12	143	77.4	34.8	4.67	452	222	51.6
BISHOP MIDDLEHAM	24/1/24	10.7	7.24	941	0.41	100	45.9	35.5	2.30	368	126	52.9
BUTTERWICK	23/1/24	10.6	7.09	1133	0.36	114	49.7	68.3	3.19	502	142	54.1
CHILTON EAST	23/1/24	10.1	7.14	962	2.84	116	40.5	26.2	3.07	395	68.0	53.6
FISHBURN L	24/1/24	11	7.16	1055	2.46	104	54.3	48.3	2.02	434	150	46.2
FOUMARTS LANE	24/1/24	10	7.32	874	0.18	91.7	43.5	33.8	1.56	339	108	54.6
GREAT ISLE	25/1/24	9.8	7.08	1242	0.70	131	73.2	42.3	3.77	402	237	62.9
HELEY HOUSE	23/1/24	8.8	8.15	388	3.47	28.7	24.0	19.7	3.65	187	0.126	19.9
HOME FARM	23/1/24	9.8	7.01	1086	1.10	138	46.4	33.6	3.67	467	129	50.8
ISLAND FARM L	25/1/24	9.7	7.16	986	0.34	110	46.2	32.9	2.99	480	73.2	65.0
LOW COPELAW	26/1/24	9.9	7.41	994	0.17	100	46.1	44.0	5.61	327	158	64.6
NCB22 (HOME FARM)	25/1/24	9.6	8.10	806	8.92	89.7	35.6	30.8	5.39	325	69.1	41.6
RUSHYFORD A	24/1/24	9.7	7.22	1378	3.72	105	56.1	99.4	4.70	372	148	167
RUSHYFORD NE	22/1/24	9.9	7.22	863	2.03	91.1	44.5	26.7	1.57	357	61.8	55.1
STONY HALL L	25/1/24	10.4	7.13	2141	0.16	181	97.2	190	4.21	510	656	102
SWAN CARR	25/1/24	10.4	7.24	923	1.64	92.1	48.7	31.9	3.12	316	112	47.1

Sample	DATE	NO_3 (mg/l)	Br (mg/l	F (mg/l)	SiO_2 (mg/l	Li (µg/l	B (µg/l	Ba (µg/l	Sr (µg/l	Mn (µg/l	Fe (µg/l	Rb (µg/l	U (µg/l
AYCLIFFE	26/1/24	24.4	0.099	0.612	7.89	42	85	35.3	315	1.4	16.4	2.76	2.76
BISHOP MIDDLEHAM	24/1/24	5.72	0.166	1.68	6.42	12	27	48.7	674	23.7	26.4	1.20	2.99
BUTTERWICK	23/1/24	1.69	0.172	0.430	10.5	35	62	89.1	175	342	141	1.61	2.90
CHILTON EAST HOUSE	23/1/24	55.5	0.075	0.443	8.21	8	53	113	122	2.4	3.5	1.11	1.53
FISHBURN L	24/1/24	32.5	0.147	0.419	6.44	30	27	65.2	104	1.2	6.4	1.21	1.46
FOUMARTS LANE	24/1/24	0.24	0.157	1.39	7.89	10	74	74.1	240	171	755	0.81	1.08
GREAT ISLE	25/1/24	21.5	0.121	0.473	9.11	35	76	24.9	197	31.8	116	1.39	1.35
HELEY HOUSE	23/1/24	0.02	0.077	1.03	1.91	16	27	71.6	500	127	842	2.13	0.03
HOME FARM	23/1/24	24.0	0.129	0.408	5.13	21	27	101	130	4.8	4.4	2.06	3.16
ISLAND FARM L	25/1/24	22.6	0.096	0.836	6.42	8	27	52.2	131	31.5	2.9	1.30	1.28
LOW COPELAW	26/1/24	0.69	0.086	0.334	7.44	24	105	58.5	214	803	191	2.75	1.73
NCB22 (HOME FARM)	25/1/24	13.6	0.216	0.332	11.5	9	66	60.2	180	16.8	12.2	0.92	1.39
RUSHYFORD A	24/1/24	20.7	0.139	1.53	7.02	42	61	48.1	118	3.3	57.1	1.64	1.42
RUSHYFORD NE	22/1/24	17.4	0.106	1.58	7.42	7	27	80.4	115	3.0	11.8	1.05	1.20
STONY HALL L	25/1/24	2	0.449	0.679	15.3	129	260	14.3	142	204	572	4.04	0.61
SWAN CARR	25/1/24	16.3	0.094	1.21	7.89	23	27	52.7	146	2.5	20.4	1.78	1.51

Table 5 (cont) Hydrochemical analysis

Magnesian Limestone boreholes – Public Water Supply Dalton Piercy boreholes

Sample	DATE	T °C	pH	Cond µS/cm	DO (mg/l)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	HCO_3 (mg/l)	SO_4 (mg/l)	Cl (mg/l)
DALTON	23/1/24	7.8	7.35	1511	5.84	182	77.1	50.5	4.47	329	465	85.3
DALTON	23/1/24	10.1	7.32	1443	5.45	153	70.3	65.6	2.81	324	358	117
DALTON	23/1/24	10	7.50	1104	8.47	91.9	48.7	66.6	2.89	322	130	123

Sample	DATE	NO_3 (mg/l)	Br (mg/l)	F (mg/l)	SiO_2 (mg/l)	Li (µg/l)	B (µg/l)	Ba (µg/l)	Sr (µg/l)	Mn (µg/l)	Fe (µg/l)	Rb (µg/l)	U (µg/l)
DALTON PIERCY 3	23/01/24	2.99	0.345	1.15	10.2	84	58	20.1	2404	0.8	3.1	2.13	2.39
DALTON PIERCY 6	23/01/24	3.33	0.448	1.46	9.46	83	27	33.8	2055	0.3	3.7	2.19	1.89
DALTON PIERCY 7	23/01/24	5.76	0.397	1.40	7.64	33	27	60.4	868	0.2	1.2	1.66	1.13

Magnesian Limestone boreholes – Public Water Supply and Observation boreholes Stillington group

Sample	DATE	T °C	pH	Cond µS/cm	DO (mg/l)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	HCO_3 (mg/l)	SO_4 (mg/l)	Cl (mg/l)
STILLINGTON NO. 2	23/01/24	10.7	7.37	1029	4.25	123	41.2	42.0	2.32	374	160	64.8
STILLINGTON OBH1	22/01/24	10.9	7.26	711	0.32	73.4	39.9	23.5	2.37	367	48.7	20.4
STILLINGTON OBH2	22/01/24	11	8.52	358	0.23	19.6	19.2	21.7	1.85	111	14.6	43.3
STILLINGTON OBH3	22/01/24	10.7	7.76	737	0.21	70.9	41.9	25.8	2.06	356	96.7	24.5
STILLINGTON OBH4	22/01/24	10.9	9.03	346	0.24	6.1	24.2	27.9	2.04	141	0.965	38.8

Sample	DATE	NO_3 (mg/l)	Br (mg/l)	F (mg/l)	SiO_2 (mg/l)	Li (µg/l)	B (µg/l)	Ba (µg/l)	Sr (µg/l)	Mn (µg/l)	Fe (µg/l)	Rb (µg/l)	U (µg/l)
STILLINGTON NO.2	23/1/24	1.24	0.268	0.844	12.0	73	60	39.0	2007	85.8	14.0	1.95	1.13
STILLINGTON OBH1	22/1/24	5.28	0.061	0.695	8.02	19	27	56.0	363	8.3	1.6	2.07	1.26
STILLINGTON OBH2	22/1/24	0.60	0.104	0.488	2.13	21	27	18.4	144	85.6	190	1.89	0.005
STILLINGTON OBH3	22/1/24	0.95	0.094	0.767	9.63	31	61	37.2	952	108	4530	0.95	0.461
STILLINGTON OBH4	22/1/24	0.02	0.153	0.431	0.845	32	27	3.98	36.2	26.9	33.3	1.37	0.014

Magnesian Limestone boreholes – Public Water Supply and Observation boreholes outside historical mine water plume

Sample	DATE	T °C	pH	Cond µS/cm	DO (mg/l)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	HCO_3 (mg/l)	SO_4 (mg/l)	Cl (mg/l)
AMERSTON HALL 1	23/1/24	9.6	7.34	961	4.56	95.6	49.9	42.3	2.87	434	106	53.7
COAL LANE 1	23/1/24	9.8	7.62	753	6.37	62.7	35.6	46.5	2.63	313	84.1	39.2
ELSTOB HILL	26/1/24	11.1	7.57	636	0.20	61.3	40.8	17.7	2.29	338	35.0	17.2
HARDWICK HALL	23/1/24	10.4	7.16	918	3.49	105	48.9	25.5	1.73	453	80.9	36.2
HOPE HOUSE	23/1/24	10.2	7.52	709	4.46	75.3	38.8	22.9	2.53	347	62.5	23.2
HOPPER HOUSE	23/1/24	9.9	7.42	892	4.70	91.8	46.3	31.7	3.42	355	117	41.7
RED BARNS	23/1/24	10.5	7.37	876	5.36	85.4	49.1	32.4	2.32	379	100	37.5
WATERLOO PLANTATION	23/1/24	10.4	7.36	985	6.03	115	46.6	31.9	2.42	413	134	40.8

Sample	DATE	NO_3 (mg/l)	Br (mg/l)	F (mg/l)	SiO_2 (mg/l)	Li (µg/l)	B (µg/l)	Ba (µg/l)	Sr (µg/l)	Mn (µg/l)	Fe (µg/l)	Rb (µg/l)	U (µg/l)
AMERSTON HALL 1	23/1/24	11.8	0.134	1.14	8.17	14	27	51.0	359	1.1	7.3	1.63	1.67
COAL LANE 1	23/1/24	3.99	0.165	1.27	6.93	19	27	95.8	516	0.3	1.3	1.36	1.07
ELSTOB HILL	26/1/24	0.705	0.060	0.889	17.1	33	27	120	420	125	22.3	1.94	1.20
HARDWICK HALL	23/1/24	13.0	0.077	1.08	8.13	9	27	148	265	3.9	20.7	0.71	1.99
HOPE HOUSE	23/1/24	2.17	0.069	1.42	7.89	13	27	95.6	177	39.6	2.4	1.42	1.26
HOPPER HOUSE	23/1/24	11.9	0.107	1.17	8.36	17	27	41.2	158	7.2	11.8	1.44	1.58
RED BARNS	23/1/24	24.5	0.167	0.718	6.85	10	27	74.2	205	0.6	2.5	1.22	1.32
WATERLOO PLANTATION	23/1/24	8.71	0.128	0.799	9.33	23	27	33.5	705	0.3	5.2	1.57	1.59

Table 5 (cont) Hydrochemical analysis

Magnesian Limestone boreholes near Hartlepool

Sample	DATE	T °C	pH	Cond µS/cm	DO (mg/l)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	HCO_3 (mg/l)	SO_4 (mg/l)	Cl (mg/l)
CAMERONS BREWERY STOCKTON STREET	24/1/24	11.4	7.41	1722	4.74	151	64.7	122	3.54	308	291	251
HART RESERVOIR	07/2/24	11.1	8.85	1026	0	27.9	44.3	111	3.83	210	22.4	215
HARTLEPOOL INDUSTRIAL ESTATE	07/2/24	11.2	7.18	2624	0.03	161	76.0	263	4.92	159	142	594
TUNSTALL SCHOOL	07/2/24	10.9	7.44	1118	0.62	110	46.9	56.3	2.36	327	152	105

Sample	DATE	NO_3 (mg/l)	Br (mg/l)	F (mg/l)	SiO_2 (mg/l)	Li (µg/l)	B (µg/l)	Ba (µg/l)	Sr (µg/l)	Mn (µg/l)	Fe (µg/l)	Rb (µg/l)	U (µg/l)
CAMERONS BREWERY STOCKTON STR.	24/1/24	4.30	0.802	1.76	13.4	111	55	16.4	2487	101	5.7	3.81	1.37
HART RESERVOIR	07/2/24	0.2	0.656	0.737	3.38	18	27	37.5	175	42.0	341	2.15	0.034
HARTLEPOOL INDUSTR. EST.	07/2/24	2	1.694	1.11	12.1	44	27	45.2	1148	108	419	4.51	1.84
TUNSTALL SCHOOL	07/2/24	3.34	0.280	1.36	10.6	44	27	24.3	1473	5.4	29.6	1.88	1.08

Table 6 Sulphate concentration, $\delta^{34}S$ and $\delta^{18}O$ of dissolved sulphate and water $\delta^{18}O$ and $\delta^{2}H$ data

Coal Measures boreholes

SAMPLE	DATE	SO_4 mg/l	$\delta^{34}S_{SO4}$ ‰ VCDT	$\delta^{18}O_{SO4}$ ‰ VSMOW	$\delta^{18}O_{H2O}$ ‰ VSMOW2	$\delta^{2}H_{H2O}$ ‰ VSMOW2
FISHBURN C	24/1/2024	177	+18.8	+10.1	-7.13	-47.9
ISLAND FARM C	25/1/2024	973	+23.2	+13.6	-8.40	-57.8
STONY HALL C	25/1/2024	836	+13.6	+11.5	-8.51	-58.2

Magnesian Limestone boreholes – Historical mine water plume area

SAMPLE	DATE	SO_4 mg/l	$\delta^{34}S_{SO4}$ ‰ VCDT	$\delta^{18}O_{SO4}$ ‰ VSMOW	$\delta^{18}O_{H2O}$ ‰ VSMOW2	$\delta^{2}H_{H2O}$ ‰ VSMOW2
AYCLIFFE	26/1/24	222	+4.5	+5.7	-7.88	-56.0
BISHOP MIDDLEHAM	24/1/24	126	+0.1	+3.5	-8.22	-55.8
BUTTERWICK	23/1/24	142	+8.4	+6.1	-8.01	-54.4
CHILTON EAST HOUSE	23/1/24	68.0	+5.2	+3.6	-7.88	-53.4
FISHBURN L	24/1/24	150	+3.1	-2.4	-8.24	-57.8
FOUMARTS LANE	24/1/24	108	-0.9	+4.3	-8.21	-55.6
GREAT ISLE (NRA 6)	25/1/24	237	+4.3	-1.8	-8.10	-57.2
HELEY HOUSE	23/1/24	0.126	nd	nd	-8.08	-54.5
HOME FARM	23/1/24	129	+4.4	+3.3	-7.81	-52.8
ISLAND FARM L	25/1/24	73.2	+5.7	+5.1	-7.44	-51.6
LOW COPELAW 1 (NRA D)	26/1/24	158	+4.6	+4.6	-7.67	-54.8
NCB22 (HOME FARM)	25/1/24	69.1	+6.2	+9.7	-8.43	-57.1
RUSHYFORD A	24/1/24	148	+6.2	-0.1	-7.99	-53.9
RUSHYFORD NE	22/1/24	61.8	+4.5	+0.9	-8.21	-55.7
STONY HALL L	25/1/24	656	+6.6	+7.3	-8.27	-56.9
SWAN CARR	25/1/24	112	+3.4	+2.4	-8.05	-56.5

Table 6 (cont) Sulphate concentration, $\delta^{34}S$ and $\delta^{18}O$ of dissolved sulphate and water $\delta^{18}O$ and $\delta^{2}H$ data

Magnesian Limestone boreholes – Public Water Supply Dalton Piercy boreholes

SAMPLE	DATE	SO_4 mg/l	$\delta^{34}S_{SO4}$ ‰ VCDT	$\delta^{18}O_{SO4}$ ‰ VSMOW	$\delta\ ^{18}O_{H2O}$ ‰ VSMOW2	$\delta^{2}H_{H2O}$ ‰ VSMOW2
DALTON PIERCY NO 3	18/7/18	456	+10.2	nd	-7.96	-52.7
DALTON PIERCY NO 3	23/1/24	465	+10.5	+9.5	-8.07	-53.3
DALTON PIERCY NO 6	18/7/18	459	+10.2	nd	-7.95	-53.3
DALTON PIERCY NO 6	23/1/24	358	+10.0	+9.8	-7.93	-52.8
DALTON PIERCY NO 7	23/1/24	130	+12.1	+7.2	-7.91	-52.0

Magnesian Limestone boreholes – Public Water Supply and Observation boreholes Stillington group

SAMPLE	DATE	SO_4 mg/l	$\delta^{34}S_{SO4}$ ‰ VCDT	$\delta^{18}O_{SO4}$ ‰ VSMOW	$\delta\ ^{18}O_{H2O}$ ‰ VSMOW2	$\delta^{2}H_{H2O}$ ‰ VSMOW2
STILLINGTON NO.2	23/1/24	160	+8.7	+9.7	-7.91	-53.9
STILLINGTON OBH1	22/1/24	48.7	+4.4	+7.7	-8.14	-56.4
STILLINGTON OBH2	22/1/24	14.6	+16.7	+8.8	-8.18	-54.9
STILLINGTON OBH3	22/1/24	96.7	+8.6	+9.2	-8.14	-55.3
STILLINGTON OBH4	22/1/24	0.965	nd	nd	-8.13	-54.4

Magnesian Limestone boreholes – Public Water Supply and Observation boreholes outside historical mine water plume

SAMPLE	DATE	SO_4 mg/l	$\delta^{34}S_{SO4}$ ‰ VCDT	$\delta^{18}O_{SO4}$ ‰ VSMOW	$\delta\ ^{18}O_{H2O}$ ‰ VSMOW2	$\delta^{2}H_{H2O}$ ‰ VSMOW2
AMERSTON HALL 1	23/1/24	106	+3.3	+2.2	-8.24	-55.2
COAL LANE 1	23/1/24	84.1	+8.2	+2.7	-7.91	-52.3
ELSTOB HILL	26/1/24	35.0	-0.9	+10.6	-7.99	-56.5
HARDWICK HALL	23/1/24	80.9	+2.0	+3.4	-8.16	-54.8
HOPE HOUSE	23/1/24	62.5	+3.9	+2.5	-8.10	-53.7
HOPPER HOUSE	23/1/24	117	+4.3	+1.1	-8.19	-56.6
RED BARNS	23/1/24	100	+3.4	+3.0	-8.13	-54.5
WATERLOO PLANTATION	23/1/24	134	+6.5	+4.5	-7.97	-54.2

Magnesian Limestone boreholes near Hartlepool

Sample	DATE	SO_4 mg/l	$\delta^{34}S_{SO4}$ ‰ VCDT	$\delta^{18}O_{SO4}$ ‰ VSMOW	$\delta\ ^{18}O_{H2O}$ ‰ VSMOW2	$\delta^{2}H_{H2O}$ ‰ VSMOW2
CAMERONS BREWERY STOCKTON STREET	24/1/24	291	+9.9	+9.5	-7.47	-52.8
HART RESERVOIR	07/2/24	22.4	+16.5	+11.8	-7.62	-50.8
HARTLEPOOL INDUSTRIAL ESTATE	07/2/24	142	+12.1	+8.4	-7.47	-50.6
TUNSTALL SCHOOL	07/2/24	152	+14.0	+9.6	-7.83	-52.8

4 Borehole background

4.1 THE COAL MEASURES BOREHOLES

The Coal Measures boreholes sampled in this study belong to the South of Butterknowle Fault mine water block. It is considered that mine water levels in the South of Butterknowle mine water block are recovered and controlled by gravity-fed discharges and discharges to the Permian. Based on direction of dip and mining connections, most of the mine water is likely flowing from west to south-east or south. The South of Butterknowle Fault mine water block is made of 5 subdivisions (Low Butterknowle, Butterknowle-Evenwood, Woodhouses-Shildon, Eldon-Chilton, Fishburn-Mainsforth-Thrislington) and, as part of this investigation water samples were obtained from 3 coal seam boreholes in the Fishburn-Mainsforth-Thrislington sub-block; the sub-block represents working in the east, concealed by the Permian aquifer and with restricted connectivity to the north due to the Butterknowle Fault.

They are Stony Hall C (colliery Mainsforth, seam Bottom Busty (Q2), depth 128 mbgl), Island Farm C (colliery Mainsforth, seam Bottom Busty (Q2), depth 111.65 mbgl) and Fishburn C (colliery Fishburn, seam Harvey (N), depth 183 mbgl). These monitored locations in the mine water block are considered well connected, with relatively flat hydraulic gradients (approximately 0.002) across the area (Hydrogeological Conceptual Model for South of Butterknowle Fault Mine Water Block technical note).

Mine water data from the Eldon-Chilton sub-block, representing workings in the centre of the main block, are not available to this study. The block was described in WYG (2006) as blocks 1-4 and responsible for the contamination of the Permian Magnesian Limestone following a south-eastern gradient.

4.2 THE MAGNESIAN LIMESTONE BOREHOLES WITHIN THE HISTORICAL COAL MINE WATER PLUME

Significantly elevated levels of sulphate were observed in the Permian groundwaters when mine waters recovered to levels higher than the connections between the mine workings and the Permian aquifer, since cessation of mine dewatering (in 1976 the last pumps in the main Durham coal field were turned off). The core of the contamination plume, as described by White Young Green (WYG, 2006), was in the areas to the north east of Newton Aycliffe, around the boreholes Rushyford, Great Isle, Low Copelaw, Aycliffe, while the periphery of the plume was around Chilton East House, Foumarts Lane, Bradbury, Mordon, Hope House, Howe Hills, Lea Hall; the existence of a diffuse plume was described around Home Farm and Lizards Farm boreholes.

After a first flush between 1975 and 1990 of mine water with high sulphate, as well as iron, calcium, sodium and chloride, the high concentrations in the Magnesian Limestone aquifer mostly appear to have declined to a plateau.

There are areas within the Fishburn and Chilton mine water blocks where there are upward vertical gradients from the Coal Measures to the Magnesian Limestone. Paired borehole analysis for the two group boreholes Stony Hall and Island Farm has shown a change in groundwater type and an increase in sulphate because of Coal Measures heads rising above the Magnesian Limestone groundwater level at the beginning of 1998 (WSP, 2023).

4.3 THE MAGNESIAN LIMESTONE BOREHOLES OUTSIDE THE HISTORICAL MINE WATER PLUME

The areas with high sulphate concentrations are not limited to the historical mine water plume area with localised areas around the abstraction and monitoring boreholes at Dalton Piercy, at Stillington and some boreholes in Hartlepool. Some of these boreholes have gypsum described in their logs (Table 3).

4.3.1 Dalton Piercy boreholes

The Dalton Piercy borehole group includes six public water supply (PWS) abstraction boreholes, inland of Hartlepool and constructed into the Magnesian Limestone Ford and Raisby Formations. Only Dalton Piercy BH3, BH 4, BH 5, BH 6 and BH 7 are operational. BH 2 is no longer in use and has been backfilled (WSP, 2023). The Magnesian Limestone groundwater is here enriched in sulphate with concentrations exceeding the drinking water standard (DWS) of 250 mg/L. The shallower screened BH3, BH4 and BH5 have higher sulphate concentrations than BH6 and BH7, the latter being with the widest and deepest screens/open hole sections. BH7 is the lowest in SO_4.

Elevated concentrations of chloride were reported in the period 1970 to 1990s, with a decrease from 2000 onwards. The WSP report indicates that the Dalton Piercy boreholes show signs of seawater intrusion in historical data prior to 2000. In the Hartlepool area, this seawater intrusion affected several shoreline sites and extended several kilometres inland, leading to elevated concentrations of chloride (Cl) and sulphate (SO_4). Since the 2000s, nearly all samples have shown lower chloride concentrations (< 200 mg/L), suggesting that the aquifer began to recover during this period.

The primary control on sulphate levels in recent years is thought to be the dissolution of gypsum/anhydrite, with concentrations varying based on the segment of the aquifer being sampled. This is influenced by factors such as borehole depth, screen depth, the fissure network, local geology, and pumping rates, including the duration of pumping and shutdown periods. Notably, reductions in abstraction or shutdown periods at BH6 and BH7 are followed by lower sulphate concentrations at the start of pumping, but these levels tend to rise again with continued operation. Both boreholes generally show lower sulphate concentrations when abstraction rates are reduced. This suggests that the elevated sulphate levels, likely caused by gypsum/anhydrite dissolution, are drawn into the boreholes by pumping, rather than originating from up the hydraulic gradient or from areas adjacent to the boreholes. WSP (2023) identified two evaporite sequences as potential sources of sulphate at Dalton Piercy: the Billingham Anhydrite and the Hartlepool Anhydrite. The authors noted that, to the south, the West Hartlepool Fault displaces the younger Triassic Sherwood Sandstone Formation and the Roxby Formation (with the Billingham Anhydrite at its base) into contact with the Magnesian Limestone. They suggest this could be a closer source of elevated sulphate for the Dalton Piercy boreholes, compared to the Hartlepool Anhydrite near the coast.

The previous isotope study (Palumbo-Roe et al. 2023) included one sample taken from each of Dalton Piercy BH3 and BH6 in 2018. The other boreholes at Dalton Piercy (including BH7 which is the “low sulphate” borehole) were not sampled. The study solely based on the isotope data concluded that given the similarity of the $\delta^{34}S$ values to the Permian evaporites and the presence of anhydrite or gypsum noted in the logs, a gypsum dissolution source was plausible. In this study we followed the recommendation of WSP to undertake the sulphur isotope analysis of groundwater from BH7 and resampled BH3 and BH6.

4.3.2 Stillington Group boreholes

There are currently two active PWS boreholes at Stillington and four observation boreholes. The PWS boreholes are Stillington No2, a shallow borehole (73.6 m deep, abstracting from the Seaham Formation) and Stillington No3, a deep borehole (122.0 m deep, abstracting from the Ford Formation). Stillington OBH1 (Seaham Formation), OBH2 (Ford Formation), OBH3 (Seaham Formation), and OBH4 (Seaham and Ford Formations) are the four observation boreholes. Gypsum/ anhydrite is a feature of the Edlington Formation which lies between the Seaham Formation and the Ford Formation.

The abstraction boreholes show a baseline of relatively low concentrations and periods of consistently higher concentrations (WSP, 2023). This distribution has been interpreted as due to the presence of two distinct groundwaters, a low sulphate baseline and a higher sulphate water that is drawn in under pumping conditions. A recent sustained increase in sulphate concentrations was noted at Stillington No2 which has been more consistently abstracted since 2018.

Previous assessments summarised by WSP (2023) generally interpreted the source of high sulphate due to gypsum/ anhydrite dissolution as a result of pumping inducing flow from the Edlington Formation or from formation water at depth. Under normal conditions, heads in the (lower) Ford Formation are higher than those in the (upper) Seaham Formation, but this can be reversed under conditions of heavy pumping from the lower aquifer. New data evaluation by WSP tentatively suggests that: i) there is a source of high sulphate (and high iron) to the south of Stillington (and south of the monitoring boreholes), predominantly in the Ford Formation (as found at OBH2), but also in the Seaham Formation (at OBH1); ii) sulphate is pulled into the abstraction by pumping; iii) sulphate concentrations have declined over time, suggesting that the source is finite and is undergoing dilution; iv) under unpumped conditions, the sulphate source does not migrate towards the abstractions and concentrations fall to a relatively low baseline, similar to the overall Magnesian Limestone baseline. The overall conclusion of the WSP (2024) report is that the data explanation above is consistent with the source of sulphate being a body or plume of mine water lying south of Stillington, but it remains possible that the source is localised gypsum / anhydrite dissolution at a location to the south.

In 2017 and 2018 Stillington OBH2 and OBH4 were both sampled and analysed for sulphur isotopes. However, sulphate concentrations in the samples were low compared to their historical highs and the sulphur isotope analysis suggested bacterial sulphate reduction had lowered the dissolved sulphate concentration. The bacterial reduction and fractionation of sulphur isotopes can obscure the original source signature and hampered the analysis of the likely source. In this study we analysed groundwater from Stillington No 2, and the four observation boreholes OBH1 to 4. Hydrochemical logging of Stillington OBH2, OBH3 and OBH4 was also carried out in a parallel study (Bowes et al., 2024).

4.3.3 Boreholes near Hartlepool

Boreholes in the Hartlepool area have enhanced concentrations of both sulphate and chloride (ESI, 2009; WSP, 2023). A recent investigation was undertaken by JBA, 2018 on the source of salinity around the abstraction boreholes at Camerons Brewery. The study concluded that uncertainties still remain and there are a number of potential sources of salinity: i) recent saline intrusion from the coast driven by current abstraction; ii) historical saline intrusion from the coast dating from times of higher abstraction in both the Magnesian Limestone and the Coal Measures; iii) mine water rebound; and natural anhydrite dissolution.

In this study we sampled one of the two abstraction boreholes at Camerons Brewery, Camerons Brewery Stockton Street, and we also repeated the sampling of Tunstall School, Hart Reservoir and Hartlepool Industrial Estate Replacement borehole (drilled in 2010 as replacement of the original borehole drilled on behalf of Northumbrian Water Authority (NWA) in 1976).

The 2018 samples showed a wide range of sulphate sulphur isotope values, and additional sampling was recommended to continue the investigation.

5 Distribution of sulphate, chloride and conductivity

Figure 2 illustrates the distribution (median, interquartile range and outliers) of historical and current (2024) dissolved sulphate concentrations in groundwaters across the various borehole groups. There is a wide range of sulphate concentrations and high levels are not confined to the Coal Measures boreholes or the mine water plume-impacted area; high concentrations are measured in the Dalton Piercy, Stillington, and Hartlepool borehole group, as noted in previous investigations (ESI, 2009; WSP, 2023).

Figure 3 highlights the historical trends in sulphate concentrations by showing the sulphate distribution in each borehole across time ranges (1970-2000, 2000-2005, 2005-2015, 2015-2018, 2018-2022, and this study samples: 2024).

Among the mine water plume-impacted boreholes: Aycliffe (NRA 2), Great Isle (NRA 6), NCB 22 (Home Farm), Low Copelaw No 1, Rushyford A and Stony Hall L had the largest SO_4 concentrations with the historical median value well exceeding the water drinking standard (WDS) for SO_4 of 250 mg/L. The survey in January 2024 indicates that only Stony Hall L maintains its high concentrations above 250 mg/l.

Outside the mine water plume area, boreholes Dalton Piercy No 3, No 4, No 5, No 6, No 7, Stillington No 2, Stillington OBH1 and OBH2, OBH4, Camerons (Stockton Street), Hart Reservoir, and Tunstall School had historically high SO_4 concentrations above 250 mg/l. The survey of January 2024, complemented with the most recent WIMS data from 2018 to 2022 where the 2024 survey was not carried out, indicates that Dalton Piercy No 3, No 4, No 5, No 6 and Camerons (Stockton Street) maintain high concentrations above 250 mg/l.

Figure 4 and Figure 5 show the chloride distributions. The survey in January 2024 and the latest WIMS data (2018-2022) indicate that the following boreholes have relatively high chloride concentrations above the DWS Cl threshold of 250 mg/l or the WFD failure Cl threshold of 188 mg/L: Island Farm C (215 mg/L), Rushyford A (167 mg/L), Dalton Piercy 4 (166 mg/L), Stillington No 3 (190 mg/L), Camerons Stockton Street (251 mg/L), Hart Reservoir (215 mg/L), Hartlepool Industrial Estate Replacement (594 mg/L).

Figure 6 and Figure 7 illustrate the conductivity distributions to complement the sulphate and chloride data.

The time series plots for sulphate and chloride for each borehole are shown in Appendix 2, updated with the latest data from this study. Although a trend analysis was outside the scope of this study, the data indicate rising sulphate concentrations for Stony Hall C, Stony Hall L, Island Farm C (among the high sulphate boreholes), and Amerston Hall No1, and No2, Coal Lane No 1 and No 2, Hope House, Hopper House, Red Barns, Waterloo Plantation, and possibly Bishop Middleham (among the relatively low sulphate boreholes). Appendix 3, section 13.4 reports scatterplots of sulphate versus major and minor/trace elements for Amerston Hall No1, Coal Lane No 1 and No 2, Hopper House, Red Barns, Waterloo Plantation, and Stony Hall L.

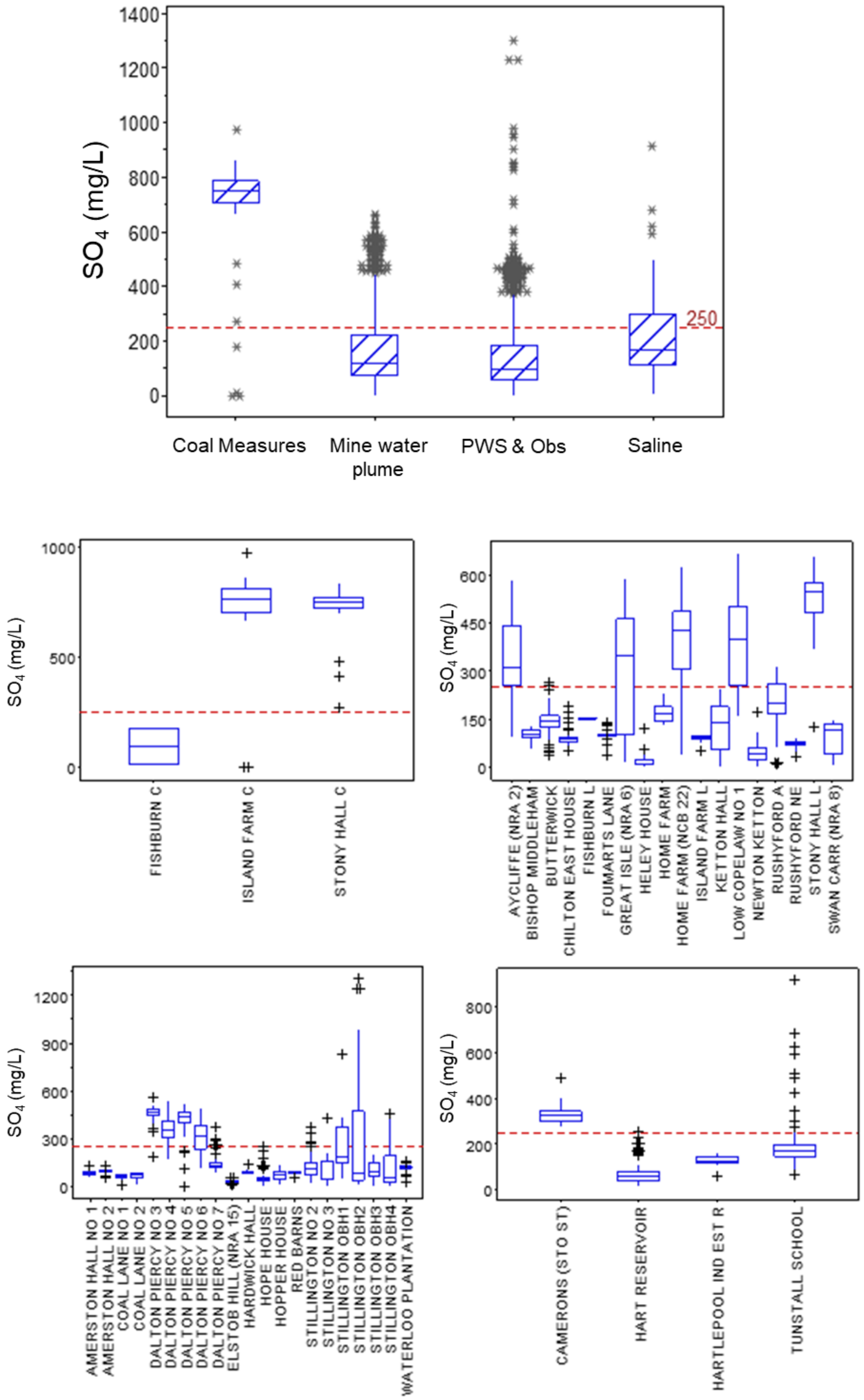


Figure 2 Box and Whisker plots illustrating the distribution of groundwater dissolved sulphate of 4 groups of boreholes for all time periods: “Coal Measures”, “Magnesian Limestone”, “Mine water plume”, “PWS & Obs”, and “Saline” boreholes near Hartlepool (top graph), followed by each of these groups (left to right); red line indicates the Drinking Water Standard (DWS) for sulphate of 250 mg/L. Contains Environment Agency data.

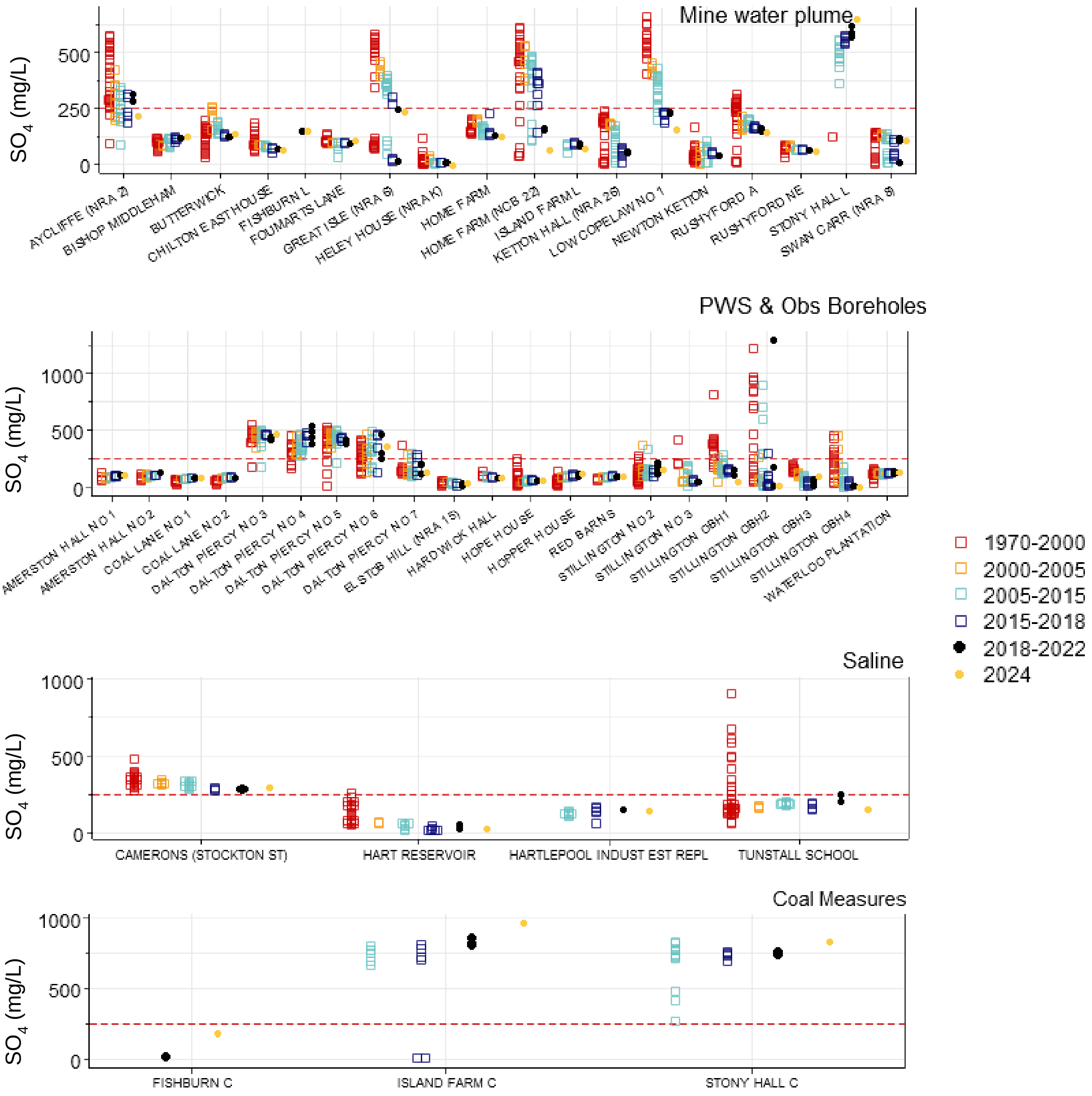


Figure 3 Plots of individual values showing the dissolved sulphate distribution in each borehole by time ranges (1970-2000, 2000-2005, 2005-2015, 2015-2018, 2018-2022, and 2024). Red line at 250 mg/L is the DWS for sulphate. Contains Environment Agency data.

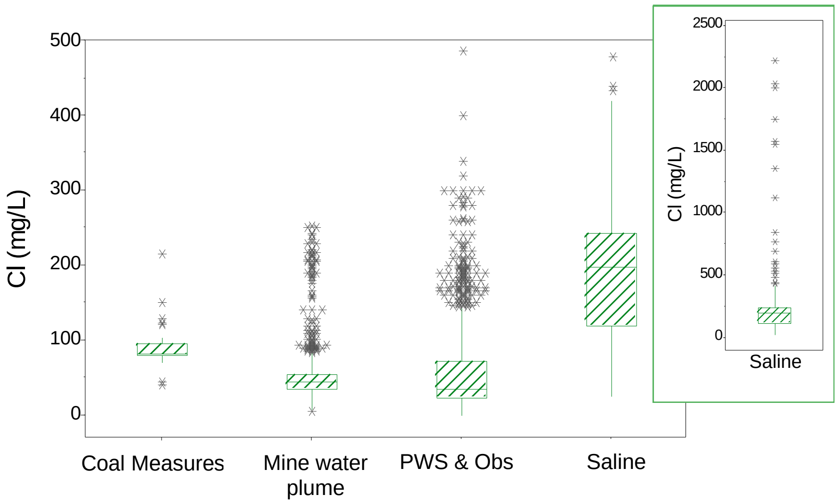


Figure 4 Left: Box and Whisker plot illustrating the distribution of groundwater chloride (groups of boreholes as previous Figure 2); Y scale truncated to 500mg/L. Right: full scale showing the many outliers for Tunstall School - max Cl values 2220 mg/l. Contains Environment Agency data.

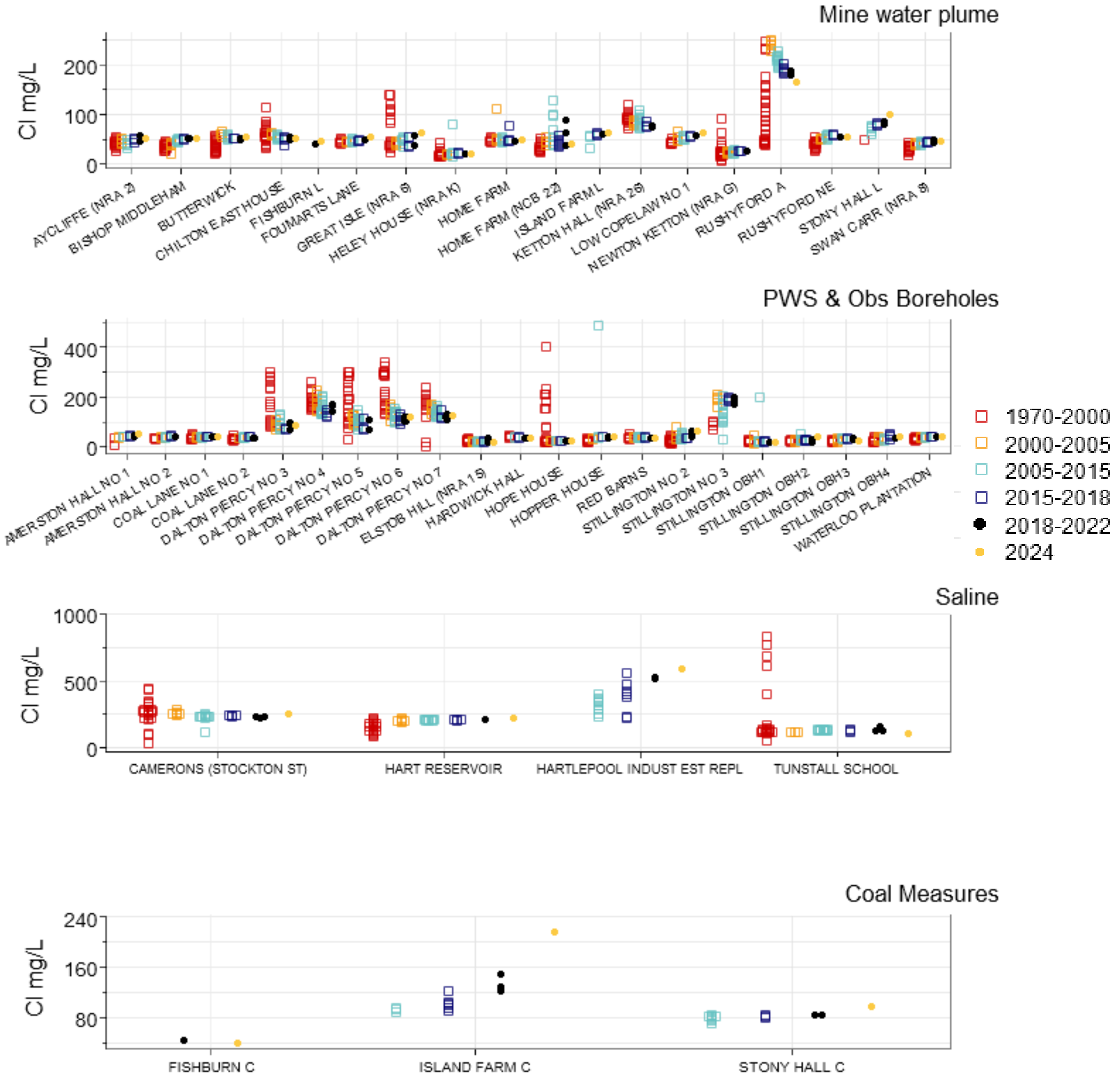


Figure 5 Individual values plots - Chloride (Tunstall Scholl Cl values pre-2000 > 1000 mg/l). Contains Environment Agency data.

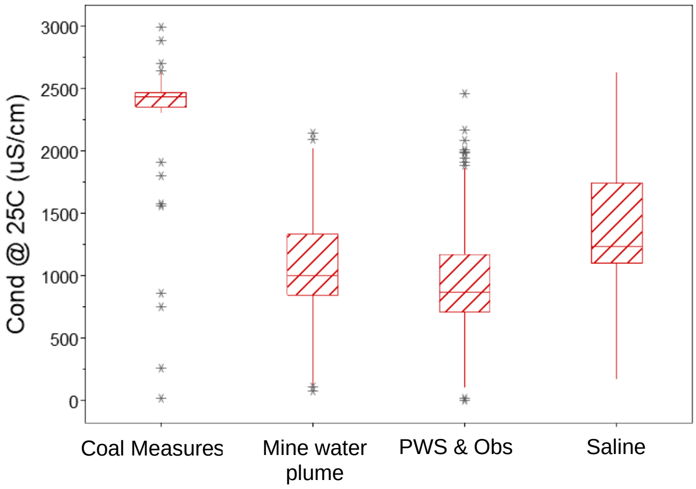


Figure 6 Box and Whisker plot of distribution of conductivity (groups as per Figure 2). Contains Environment Agency data.

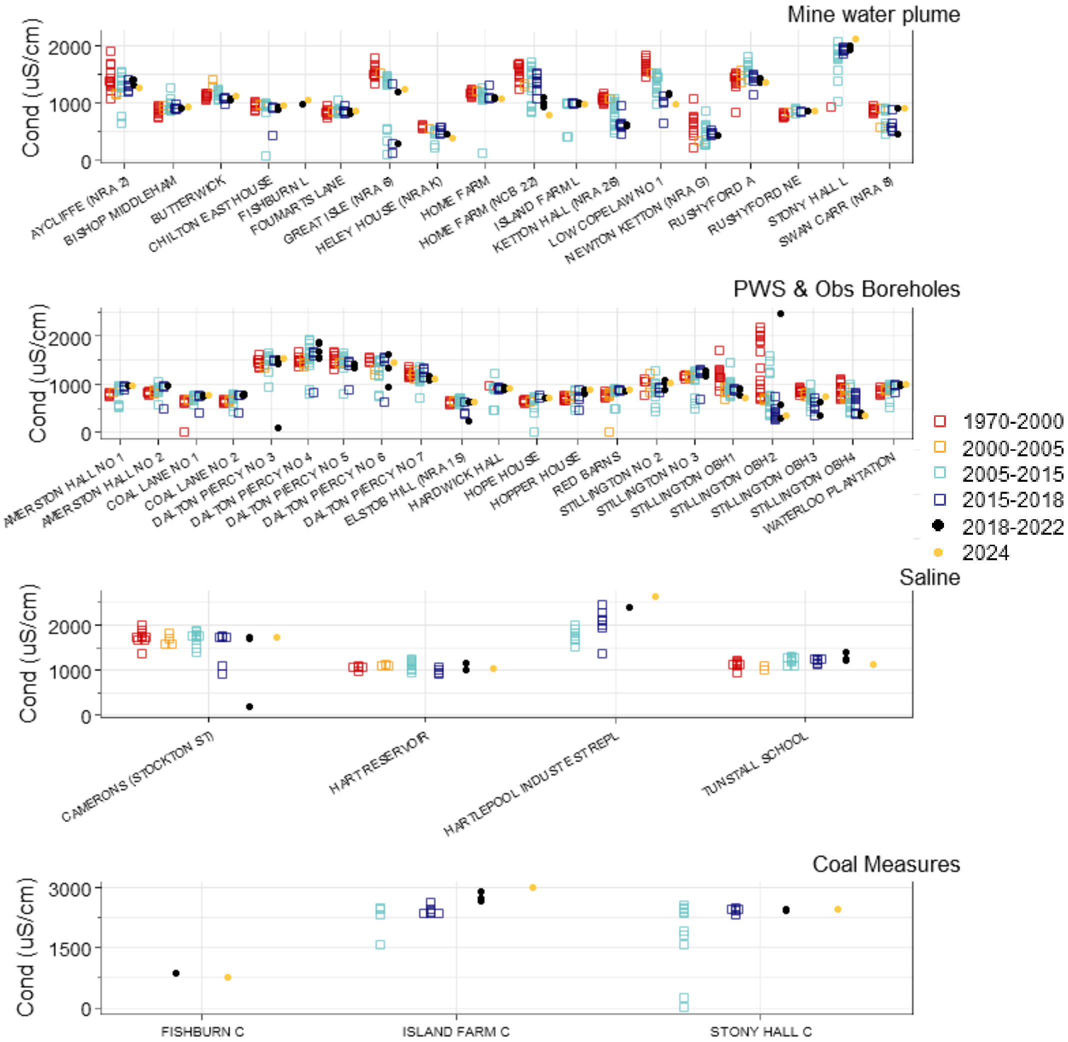


Figure 7 Individual Values plots – Conductivity. Contains Environment Agency data.

6 Water types and physicochemical characteristics

The Piper plots showing the historical data archived in WIMS (data until 2022) for each borehole are presented in Appendix 1 and the water types in Table 7. The Piper plots in Appendix 1 also distinguish the samples with pH > 8 with a different colour symbol. This is noted in relation to the parallel study, carried out by the BGS team, conducting a depth geochemical profiling of high pH boreholes in the Magnesian Limestone aquifer (Bowes et al, 2024). The hydrochemical logging highlighted a significant vertical stratification of the physicochemical parameters in each borehole and how CO_2 degassing and water stagnation in the borehole can significantly alter the physicochemical parameters including pH as well as water chemistry. High pH zones >pH 8.5 were often accompanied by low conductivity and negative redox potential. Review of the WIMS chemical analyses from historical groundwater monitoring, identified a compositional change in major-ions proportions within high pH samples, including Ca and alkalinity decreases. Some of the compositional “anomalies” of those high pH records included sulphate, one of the main contaminants in the aquifer, showing sulphate concentrations decreasing wherever pH measurements were high. Therefore, the interpretation of water chemistry and data dispersion from the main water type—observed in some Piper plots in Appendix 1—should be approached with caution when relatively higher pH values than the baseline (median: 7.34; 25th – 75th percentile: 7.17 – 7.6; n = 4516) are noted. Two obvious cases are Heley House and Stillington OBH4 boreholes which have very low sulphate concentrations, respectively, 0.13 mg/l and 0.97 mg/l (Table 5) in the January 2024 sampling.

Table 7 Borehole water types from piper plots in Appendix 1, using WIMS data

PTCODE	BOREHOLE NAME	GROUP	WATER TYPE	Comments
453H0002	FISHBURN C	Coal Measures	$Na-HCO_3$	
453H0001	ISLAND FARM C	Coal Measures	$Na-SO_4$	
453F0295	STONY HALL C	Coal Measures	$Na-SO_4$	
453F0243	AYCLIFFE (NRA 2)	Mine water plume	$Ca-Mg-HCO_3-SO_4$	
453F0232	BISHOP MIDDLEHAM	Mine water plume	$Ca-Mg-HCO_3$	
453F0242	BUTTERWICK	Mine water plume	$Ca-Mg-HCO_3$	
453F0231	CHILTON EAST HOUSE	Mine water plume	$Ca-Mg-HCO_3$	
453C0003	FISHBURN L	Mine water plume	$Ca-Mg-HCO_3$	
453F0285	FOUMARTS LANE	Mine water plume	$Ca-Mg-HCO_3$	
453F0274	GREAT ISLE (NRA 6)	Mine water plume	$Ca-Mg-HCO_3$	High pH samples with different composition
454F1111	HELEY HOUSE (NRA K)	Mine water plume	$Ca-Mg-HCO_3$	With a minor group Na-dominant
453F0292	HOME FARM	Mine water plume	$Ca-Mg-HCO_3$	
453F0236	NCB 22 (HOME FARM)	Mine water plume	$Ca-Mg-SO_4-HCO_3$	
453C0001	ISLAND FARM L	Mine water plume	$Ca-Mg-HCO_3$	
453F0253	KETTON HALL (NRA 26)	Mine water plume	No dominant type	High pH water with Na-Mg-Cl composition

PTCODE	BOREHOLE NAME	GROUP	WATER TYPE	Comments
453F0238	LOW COPELAW NO 1	Mine water plume	Ca-Mg-SO_4-HCO_3	
453F0283	NEWTON KETTON (NRA G)	Mine water plume	Mg-HCO_3	High pH water with Na composition
453F0233	RUSHYFORD A	Mine water plume	No dominant type	
453F0234	RUSHYFORD NE	Mine water plume	Ca-Mg-HCO_3	
453F0296	STONY HALL L	Mine water plume	SO_4 with no dominant cations	
453F0239	SWAN CARR (NRA 8)	Mine water plume	Ca-Mg-HCO_3	High pH water with Mg composition
454F1130	AMERSTON HALL NO 1	PWS & Obs Boreholes	Ca-Mg-HCO_3	
454F1129	AMERSTON HALL NO 2	PWS & Obs Boreholes	Ca-Mg-HCO_3	
454F1107	COAL LANE NO 1	PWS & Obs Boreholes	Ca-Mg-Na-HCO_3	
454F1108	COAL LANE NO 2	PWS & Obs Boreholes	Ca-Mg-Na-HCO_3	
454F1103	DALTON PIERCY NO 3	PWS & Obs Boreholes	Ca-Mg-Na-SO_4	With some mixing
454F1101	DALTON PIERCY NO 4	PWS & Obs Boreholes	Ca-Mg-Na-SO_4	With some mixing
454F1102	DALTON PIERCY NO 5	PWS & Obs Boreholes	Ca-Mg-Na-SO_4	With some mixing
454F1146	DALTON PIERCY NO 6	PWS & Obs Boreholes	Ca-Mg-Na-SO_4	With some mixing
454F1147	DALTON PIERCY NO 7	PWS & Obs Boreholes	No dominant type	
454F1115	ELSTOB HILL (NRA 15)	PWS & Obs Boreholes	Ca-Mg-HCO_3	With high pH samples of different composition
453F0291	HARDWICK HALL	PWS & Obs Boreholes	Ca-Mg-HCO_3	
454F1112	HOPE HOUSE	PWS & Obs Boreholes	Ca-Mg-HCO_3	With some mixing
454F1110	HOPPER HOUSE	PWS & Obs Boreholes	Ca-Mg-HCO_3	With some trend HCO_3-SO_4
455F0163	RED BARNS	PWS & Obs Boreholes	Ca-Mg-HCO_3	
454F1154	STILLINGTON NO 2	PWS & Obs Boreholes	Ca-Mg-HCO_3-SO_4	Mixing trend Ca-Mg and SO_4-HCO_3
454F1159	STILLINGTON NO 3	PWS & Obs Boreholes	HCO_3-(Cl) with no dominant cations	
454F1161	STILLINGTON OBH1	PWS & Obs Boreholes	Ca-Mg-HCO_3-SO_4	Mixing trend Ca-Mg and SO_4-HCO_3
454F1162	STILLINGTON OBH2	PWS & Obs Boreholes	Ca-Mg-HCO_3-SO_4	Mixing trend Ca-Mg and SO_4-HCO_3, high pH samples with different composition
454F1163	STILLINGTON OBH3	PWS & Obs Boreholes	Ca-Mg-HCO_3-SO_4	Mixing trend Ca-Mg and SO_4-HCO_3
454F1164	STILLINGTON OBH4	PWS & Obs Boreholes	Ca-Mg-HCO_3-SO_4	Mixing trend Ca-Mg and SO_4-HCO_3 , high pH samples with different composition
454F1105	WATERLOO PLANTATION	PWS & Obs Boreholes	Ca-Mg-HCO_3	
455F0170	CAMERONS (STOCKTON ST)	Saline	No dominant type	

PTCODE	BOREHOLE NAME	GROUP	WATER TYPE	Comments
455F0160	HART RESERVOIR	Saline	Cl with no dominant cations	With a trend to Na-Cl water with high pH
455F0181	HARTLEPOOL INDUST EST REPL	Saline	Cl with no dominant cations	
455F0161	TUNSTALL SCHOOL	Saline	Ca-(Mg,Na)-HCO_3-(SO_4,Cl)	With some Na-Cl water samples

The Piper diagram in Figure 8 plots the new data from 2024. The graph shows the boreholes arranged by symbols and colours, broadly distinguishing the boreholes in the Coal Measures, the Magnesian Limestone boreholes historically impacted by the mine water plume, the Magnesian Limestone observation wells and public water supply boreholes, and the Magnesian Limestone saline boreholes near the coast at Hartlepool.

The majority of the Magnesian Limestone groundwater samples are of Ca-Mg-HCO_3 type with some waters relatively more enriched in Na and SO_4 and others in Na and Cl. The Coal Measures boreholes are Na-enriched, Na-SO_4 or Na-HCO_3 type.

The pH is neutral for most boreholes (Table 5), except for Hart Reservoir (pH 8.85), Heley House (pH 8.15), NCB22 (Home Farm) (pH 8.10), Stillington OBH2 (pH 8.52), Stillington OBH4 (pH 9.03).

Among the Coal Measures boreholes Island Farm C and Stony Hall C are distinctively Na-SO_4 type waters, with similar proportions of major ions and relatively high conductivity of 2990 and 2460 µS/cm, respectively. Instead, the other Coal Measures borehole Fishburn C, with lower conductivity of 750 µS/cm, is a Na-HCO_3 water. All the Coal Measures waters, with a neutral pH (range of 7.2 – 7.7), are saturated or supersaturated with respect to calcite and dolomite, and undersaturated with respect to gypsum and halite. Dissolved oxygen (DO) concentrations are respectively 0.2 mg/l in Stony Hall C, 1.5 mg/l in Island Farm C and 3.5 mg/l in Fishburn C. The presence of nitrate in Island Farm C (NO_3 10 mg/l) contrasts with the expected moderately reducing conditions suggested by the high dissolved iron concentration at neutral pH and relatively low DO. Filtered iron concentrations are high for Island Farm C (~15 mg/l) and Stony Hall C (~5 mg/l), while they are much lower in Fishburn C (0.5 mg/l).

The Magnesian Limestone boreholes Stony Hall L and Rushyford A differ in composition from the main Ca-Mg-HCO_3 type; Stony Hall L is of Na-SO_4 type like Stony Hall C, associated with similar high conductivity of 2150 µS/cm; Rushyford A is of Cl-HCO_3-SO_4 type with a conductivity of 1380 µS/cm.

A variable chemical composition is observed within the Stillington group of boreholes, with Stillington No 2, OBH1 and OBH3 of Ca-HCO_3 type, while OBH2 and OBH4 of Mg-HCO_3 type, associated with a low sulphate content (<15 mg/L). This is accompanied by lower conductivity of ~350 µS/cm and high pH >8.5 in OBH2 and OBH4, compared to the other boreholes in the group (conductivity in the range of 700–1000 µS/cm and pH 7.2–7.8). Based on the evidence from the parallel study on the same boreholes (Bowes et al., 2024), we interpret the water compositions in Stillington OBH2 and OBH4 as affected by stagnant water conditions probably in the cased sections of the borehole, altering the water chemistry. The stagnation might have influenced in particular the lowering of the sulphate content (OBH4 SO_4 < 1 mg/L and OBH2 SO_4 15 mg/L), possibly by sulphate reduction. Similar water type is shown by Heley House. Here sulphate is 0.13 mg/L, pH 8.15, conductivity 390 µS/cm.

Within the Magnesian Limestone saline group, all the 4 boreholes analysed show different proportions of major elements and conductivity values: Hartlepool Industrial Estate borehole conductivity is the highest of the group with 2620 µS/cm, followed by Camerons Brewery (1720 µS/cm), Tunstall School (1120 µS/cm) and Hart Reservoir (1030 µS/cm). Hartlepool Industrial Estate borehole and Hart Reservoir are both Na-Cl waters, although it is noted that Hart Reservoir composition might be affected by stagnation, suggested by the elevated pH of 8.9 in contrast to the other pH neutral boreholes in the group (pH 7.2–7.4); Tunstall School does not have the enrichment in chloride like the other boreholes in the group, with a tendency towards the Ca-HCO_3 waters; Camerons Brewery Stockton Street borehole has no dominant cations or anions.

The Dalton Piercy borehole group has also variable composition, with Dalton Piercy No 7 enriched in HCO_3 (Ca-HCO_3 water) and with lower conductivity of 1100 µS/cm compared to No 3 and No 6, both Ca-SO_4 waters and higher conductivity of ~1500 µS/cm. Eltsob Hill with a conductivity of 640 µS/cm is a Mg-HCO_3 water.

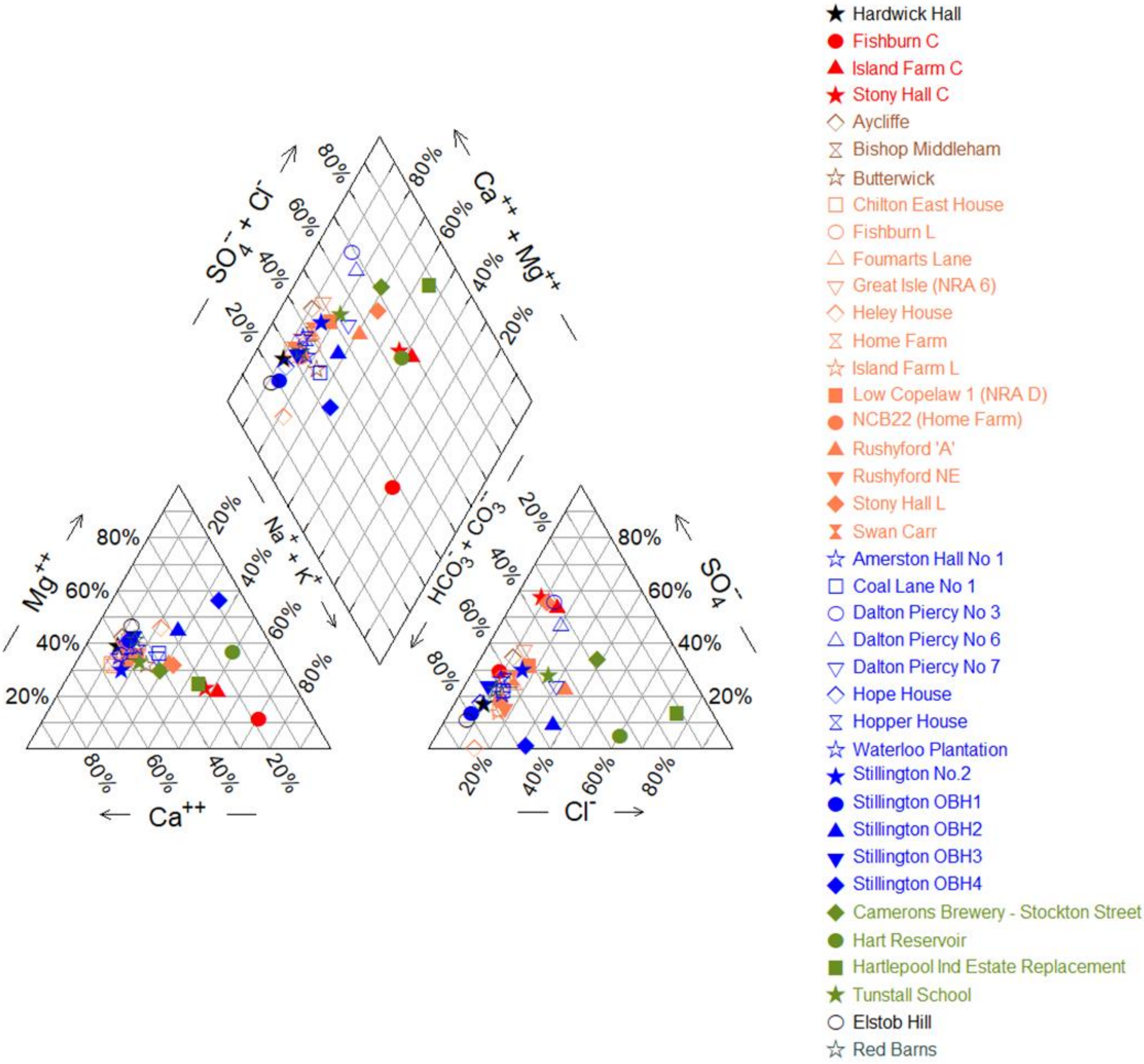


Figure 8 Piper plot for the 2024 water chemistry data.

7 Isotope data comparison of 2024 and 2018 sampling dates

Figure 9 shows where significant differences were measured in sulphate-sulphur isotope, sulphate concentrations, and water stable isotopes for sites that were sampled in both July 2018 and January-February 2024. It is worth noting that while Fishburn C shows differences between dates in both sulphate concentrations and water isotopes, differences in sulphur isotopes could not be assessed, as they were not measured in 2018 due to sulphate concentrations being below 1 mg/L.

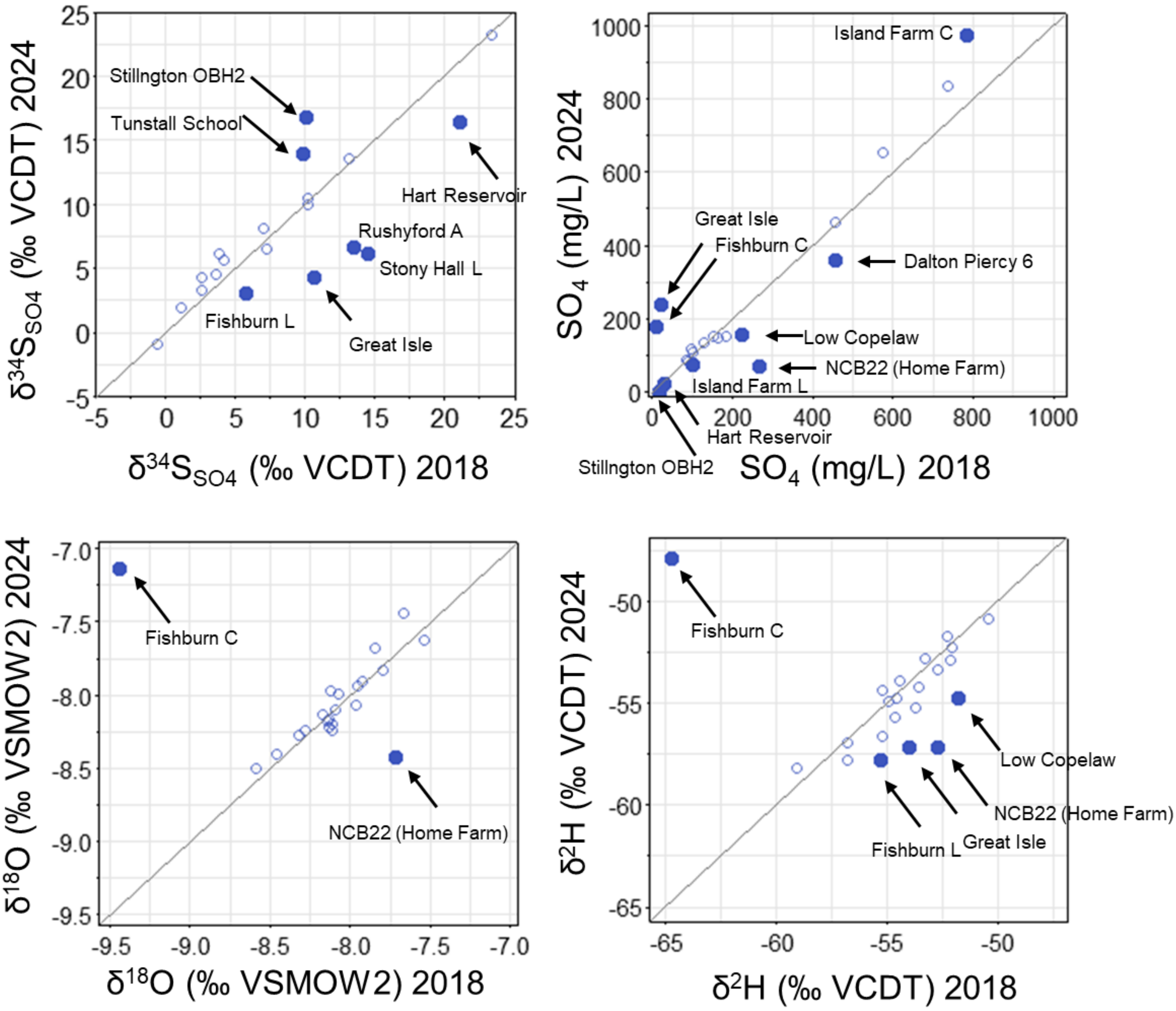


Figure 9 Comparison of sulphate-sulphur isotopes, of sulphate and of water stable isotopes for sites that were sampled in both July 2018 and January-February 2024 (sites with large difference between the sampling dates are shown by full circle symbols).

7.1 WATER OXYGEN AND HYDROGEN ISOTOPES

Figure 10 and Figure 11 illustrate the water stable isotope $\delta^{18}O$ and $\delta^{2}H$ relationship in the groundwater samples from July 2018 and January/February 2024.

The $\delta^{18}O$ and $\delta^{2}H$ values in the 28 groundwater samples collected during the summer of 2018 and previously reported in Palumbo-Roe et al. (2023) indicated the meteoric origin of all groundwaters including also the Coal Measures groundwater, as samples plotted close to the Global Meteoric Water Line (GMWL) in the $\delta^{18}O$ - $\delta^{2}H$ plots; a similar recharge for the water in many of the Magnesian Limestone boreholes was also inferred, so that the net difference in the $\delta^{18}O$ and $\delta^{2}H$ values was minimal and around $\delta^{18}O$ -8.1‰ and $\delta^{2}H$ -54‰ (values consistent with previous analysis in Bearcock and Smedley (2009)). Groundwater from the Coal Measures boreholes, Fishburn C, Stony Hall C and Island Farm C, with lower $\delta^{18}O$ - $\delta^{2}H$ values than the Magnesian Limestone observation boreholes, highlighted different groundwater system(s). The samples from the “saline” boreholes Hartlepool Ind Estate replacement, Tunstall School and Hart Reservoir instead plotted on the GMWL to the right of the Magnesian Limestone borehole group, with relative enrichment in ^{18}O and ^{2}H suggesting a component of modern seawater, as previously suggested by Bearcock and Smedley (2009). On the basis of the stable isotope signature it was also possible to infer an upward vertical hydraulic gradient from the Coal Measures to the Magnesian Limestone in Stony Hall L, and Fishburn L, which were the paired boreholes respectively to Stony Hall C, and Fishburn C. Evidence of similar mixing between the Coal Measures borehole Island Farm C and the Magnesian Limestone borehole Island Farm L was instead missing. Other boreholes, Coal Lane 1 & 2, Low Copelaw 1, Dalton Piercy 3 & 6, Newton Ketton (NRAG) and NCB22 (Home Farm) departed from the main Magnesian Limestone group. Repeated sampling was recommended to confirm the patterns.

Comparison of the newly acquired and larger dataset of 39 samples with the previous one highlights the following:

7.1.1 Coal Measures boreholes water isotope results

- The meteoric water isotope signature of the mine waters is confirmed with the new data, as the Coal Measures boreholes are aligned on the GMWL, with no evidence of waters that have undergone significant contribution of formation waters.
- The strong connectivity between Stony Hall C, the Coal Measures borehole, and Stony Hall L, the paired Magnesian Limestone borehole, inferred from the 2018 water isotopes, is confirmed.
- Also confirmed are the slightly more negative $\delta^{18}O$ and $\delta^{2}H$ values of the Coal Measures boreholes compared to the Magnesian Limestone boreholes, except for Fishburn C.

  The $\delta^{18}O$ and $\delta^{2}H$ values of Stony Hall C and Island Farm C Coal Measures boreholes are aligned on the GMWL slightly to the left of the main Magnesian Limestone aquifer group, and did not vary greatly with the time of sampling ($\delta^{2}H$ from –59.1‰ to −56.8‰ and $\delta^{18}O$ values from −8.6‰ to −8.4‰), despite different depths of sampling (60 m in 2018, and deeper, in the screen section in 2024 (Stony Hall C ~130 mbgl; Island Farm C ~100 mbgl)). These findings suggest a lack of in-casing borehole stratification and give some confidence that the 2018 analysis was representative of the aquifer conditions. They might also corroborate a flow conceptual model of a Permian aquifer source of recharge to these coal seams, rather than recharge through shallow workings, which could cause larger variability in the isotopic signature.

  Fishburn C, with a $\delta^{18}O$ value of -7.13‰ and $\delta^{2}H$ of -47.9‰, is greatly enriched in ^{18}O and ^{2}H, plots on the opposite side of the $\delta^{18}O$ - $\delta^{2}H$ graph compared to the 2018 sample ($\delta^{18}O$ -9.43‰ and $\delta^{2}H$ -64.7‰). The different values of the two sampling times might be an artefact of different sampling depths (60 m depth for the 2018 sample,132 m from the screened section for the sample collected in 2024), either due to in-borehole or in-aquifer stratification. The highly depleted composition of the 2018 groundwater sample from Fishburn C is hard to explain.

7.1.2 Magnesian Limestone boreholes water isotope results

- The isotopic signature of groundwater from Hardwick Hall borehole is consistent with the previous analysis, representing the baseline conditions in the Magnesian Limestone aquifer, with $\delta^{18}O$ -8.2‰ and $\delta^{2}H$ -54.8‰.
- Negligible or minor temporal variation (value difference between 2018 and 2024 within the analytical precision) is shown in many Magnesian Limestone observation boreholes where repeated sampling was carried out.
- A temporal difference is evident for the observation boreholes Great Isle, Low Copelaw, NCB22 (Home Farm) and the abstraction borehole Waterloo Plantation, noted also in the sulphur isotope data. Further evidence for Great Isle and Low Copelaw boreholes is available and integrated as described below, otherwise more data are needed to explain those variations.
- The signature of Coal Lane and Dalton Piercy borehole group has not changed, above the GMWL and is slightly enriched in ^{18}O and ^{2}H compared to the baseline.
- A greater tendency of the January 2024 samples to lie slightly below the GMWL in the $\delta^{18}O$ - $\delta^{2}H$ graph (Figure 12) is evident, suggesting some isotopic fractionation by evaporation. The boreholes with a probable “evaporative” signature are Fishburn L, Aycliffe, Low Copelaw, Camerons Brewery, Island Farm L, and also Great Isle, Swan Carr and Elstob Hill. The last three boreholes were part of a parallel study by BGS (Bowes et al., 2024) finding that the groundwater was highly stratified prior to the borehole purging/sampling and the sample could have represented a mixture of fresh groundwater from the aquifer and casing water, hence likely impacted by evaporation.
- Stillington group of observation boreholes clusters together and with a signature similar to the Hardwick Hall borehole (baseline) (Figure 12).
- The “saline” boreholes near the coast at Hartlepool, especially Hart Reservoir and Hartlepool Ind Estate replacement and to a lesser extent Tunstall School, have a relative enrichment in ^{18}O and ^{2}H compared to the main Magnesian Limestone group. These data are compatible with a signature of seawater mixing suggested by Bearcock and Smedley (2009). The water sample from the borehole Camerons Brewery Stockton Street added in 2024 lies off the GMWL.

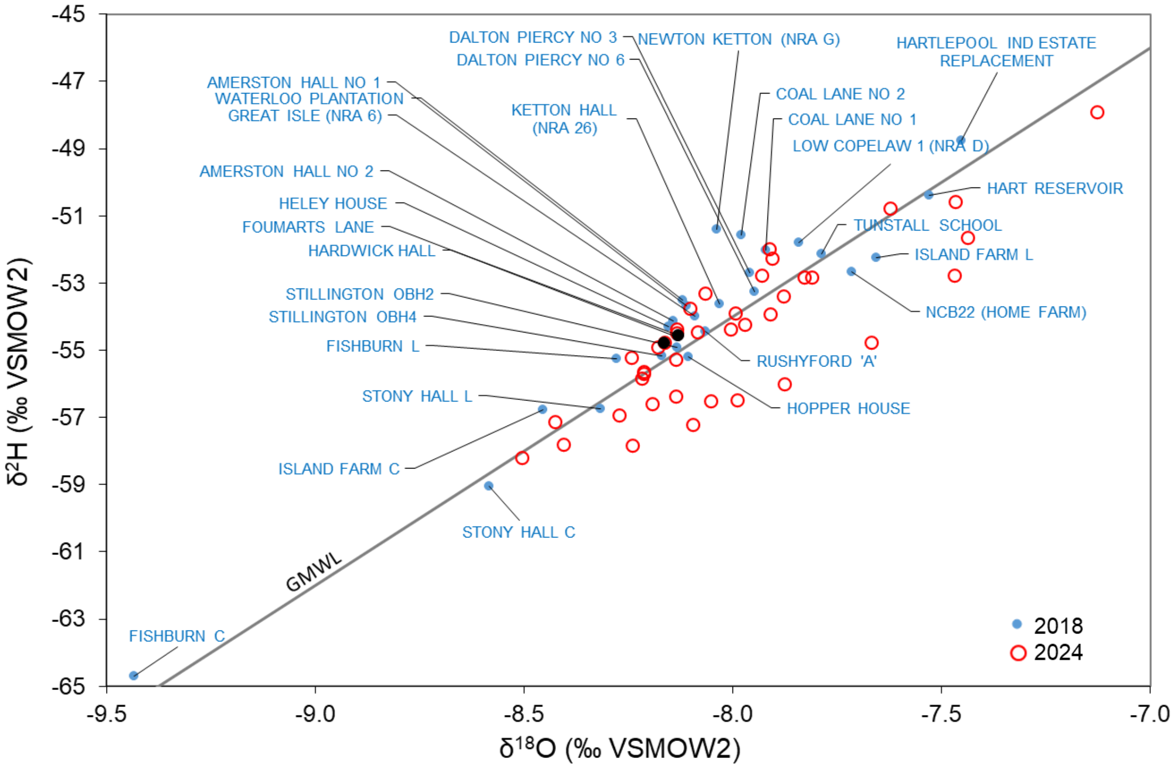


Figure 10 δ¹⁸O and δ²H in groundwater in the Magnesian Limestone aquifer and Coal seam boreholes sampled in July 2018 (blue circles) and January/February 2024 (red circle), with 2018 data labelled. GMWL: global meteoric water line.

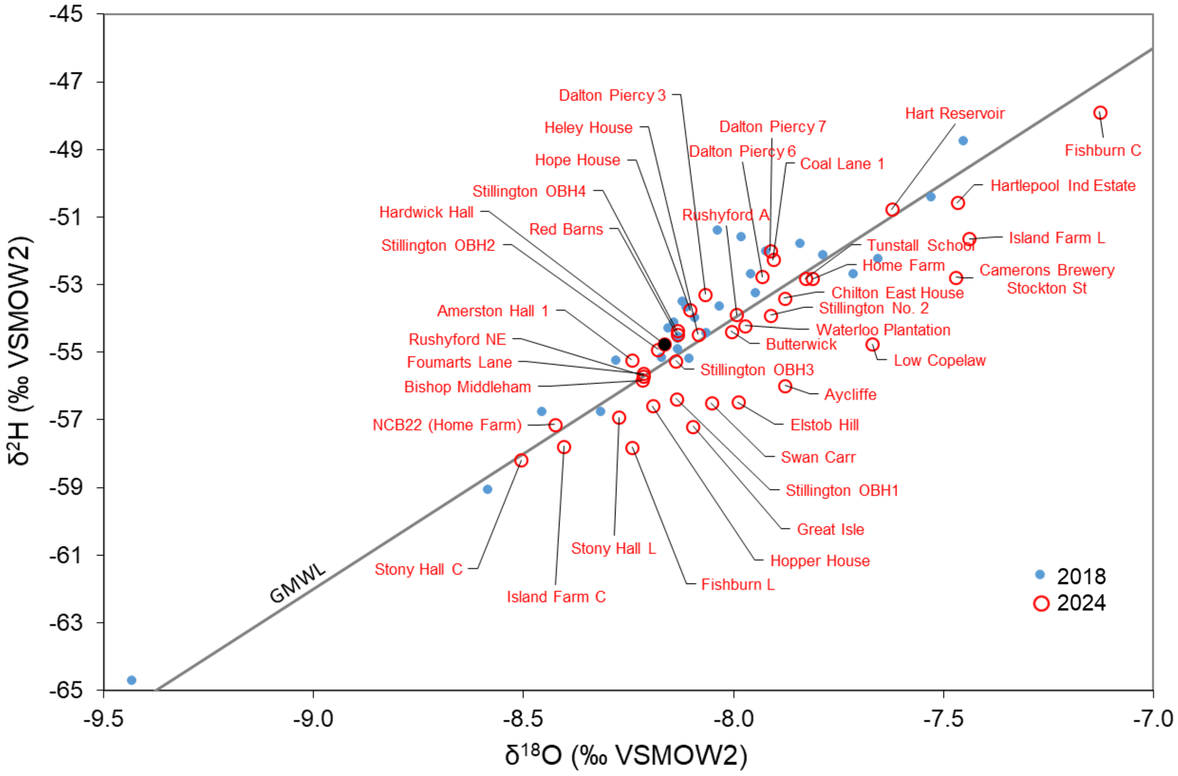


Figure 11 δ¹⁸O and δ²H in groundwater in the Magnesian Limestone aquifer and Coal seam boreholes sampled in July 2018 (blue circles) and January/February 2024 (red circle), with 2024 data labelled. GMWL: global meteoric water line.

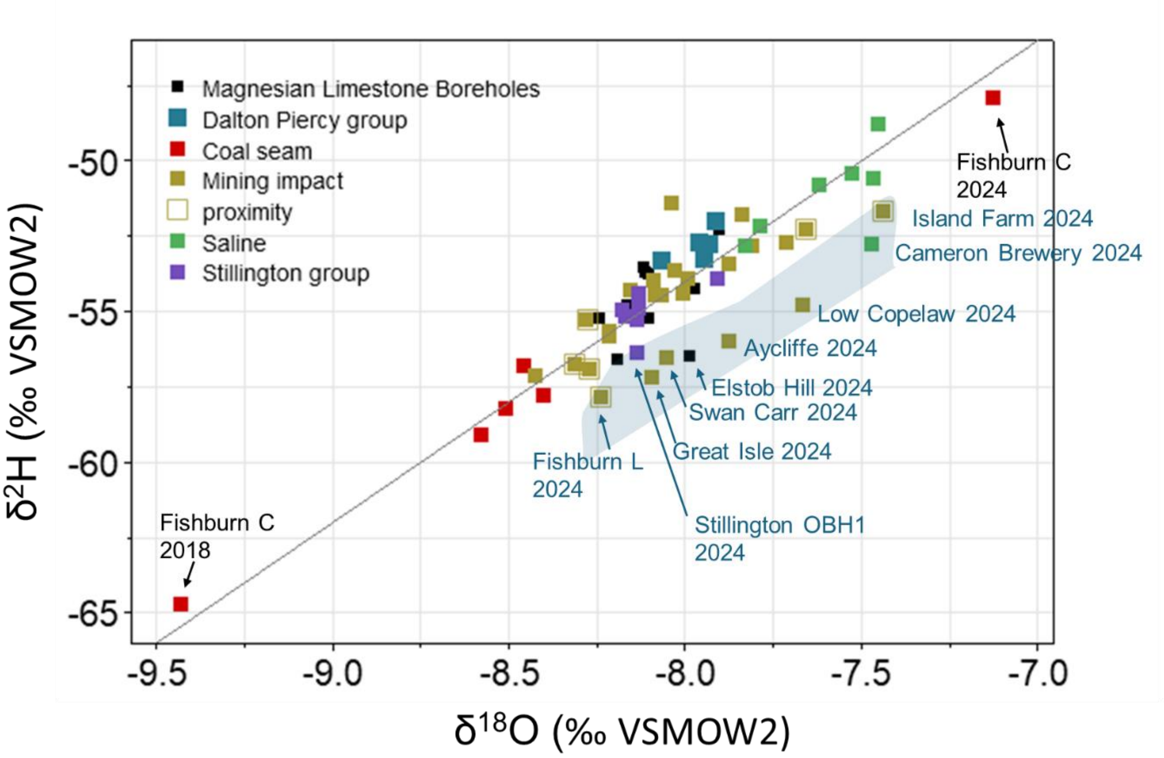


Figure 12 $\delta^{18}O$ and $\delta^{2}H$ in groundwater in the Magnesian Limestone aquifer and Coal seam boreholes - all data; symbols by borehole groups (the Magnesian Limestone boreholes paired to the coal seams ones are labelled as “proximity”); grey line: global meteoric water line (GMWL); shaded area highlights samples departing from the GMWL.

7.2 SULPHUR AND OXYGEN ISOTOPES OF DISSOLVED SULPHATE

Figure 13 shows the distribution of sulphate (SO_4) and sulphur ($\delta^{34}S$) and oxygen ($\delta^{18}O$) isotope ratios in the dissolved sulphate (SO_4) in boreholes from the present study and comparison with samples taken in 2017 and 2018. Table 8 also reports the mean and standard deviation (SD) of sulphate $\delta^{34}S$ in resampled boreholes. $\delta^{34}S$ values are reported in per mil (‰) relative to VCDT (see method section 2.5).

Table 8 Sulphate $\delta^{34}S$ in resampled boreholes

Site	N	$\delta^{34}S$ (‰ VCDT) 2024	$\delta^{34}S$ (‰ VCDT) 2018	$\delta^{34}S$ (‰ VCDT) 2017	$\delta^{34}S$ (‰ VCDT) Mean	SD
Amerston Hall 1	2	+3.3	+2.5		+2.9	0.6
Coal Lane 1	2	+8.2	+6.9		+7.6	0.9
Dalton Piercy 3	2	+10.5	+10.2		+10.3	0.2
Dalton Piercy 6	2	+10.0	+10.2		+10.1	0.1
Fishburn C	2	+18.8	nd		-	-
Fishburn L	2	+3.1	+5.7		+4.4	1.9
Foumarts Lane	3	-0.9	-0.7	-0.4	-0.7	0.3
Great Isle	2	+4.3	+10.7		+7.5	4.5
Heley House	0	nd	nd			
Hardwick Hall	2	+2.0	+1.0		+1.5	0.7
Hart Reservoir	2	+16.5	+21.1		+18.8	3.3
Hartlepool Industrial Estate Replacement	2	+27.0	+12.1		+19.5	10.5
Hopper House	2	+4.3	+2.6		+3.5	1.3
Island Farm C	2	+23.2	+23.4		+23.3	0.1
Island Farm L	2	+5.7	+4.2		+4.9	1.1
Ketton Hall	2		+47.1	+37.9	+42.5	6.5
Low Copelaw	3	+4.6	+3.5	+17.8	+8.6	8.0
NCB22 (Home Farm)	2	+6.2	+3.8		+5.0	1.7
Rushyford A	2	+6.2	+14.5		+10.4	5.8
Stillington OBH2	2	+16.7	nd	+27.0	+21.9	7.3
Stillington OBH4	2	nd	+24.7	7.5	+16.1	12.2
Stony Hall C	3	+13.6	+13.1	+13.0	+13.2	0.3
Stony Hall L	3	+6.6	+13.5	+13.0	+11.1	3.8
Tunstall School	2	+14.0	+9.8		+11.9	2.9
Waterloo Plantation	2	+6.5	+7.2		+6.9	0.5

nd: isotope analysis not carried out in water samples with sulphate concentration less than 1 mg/L

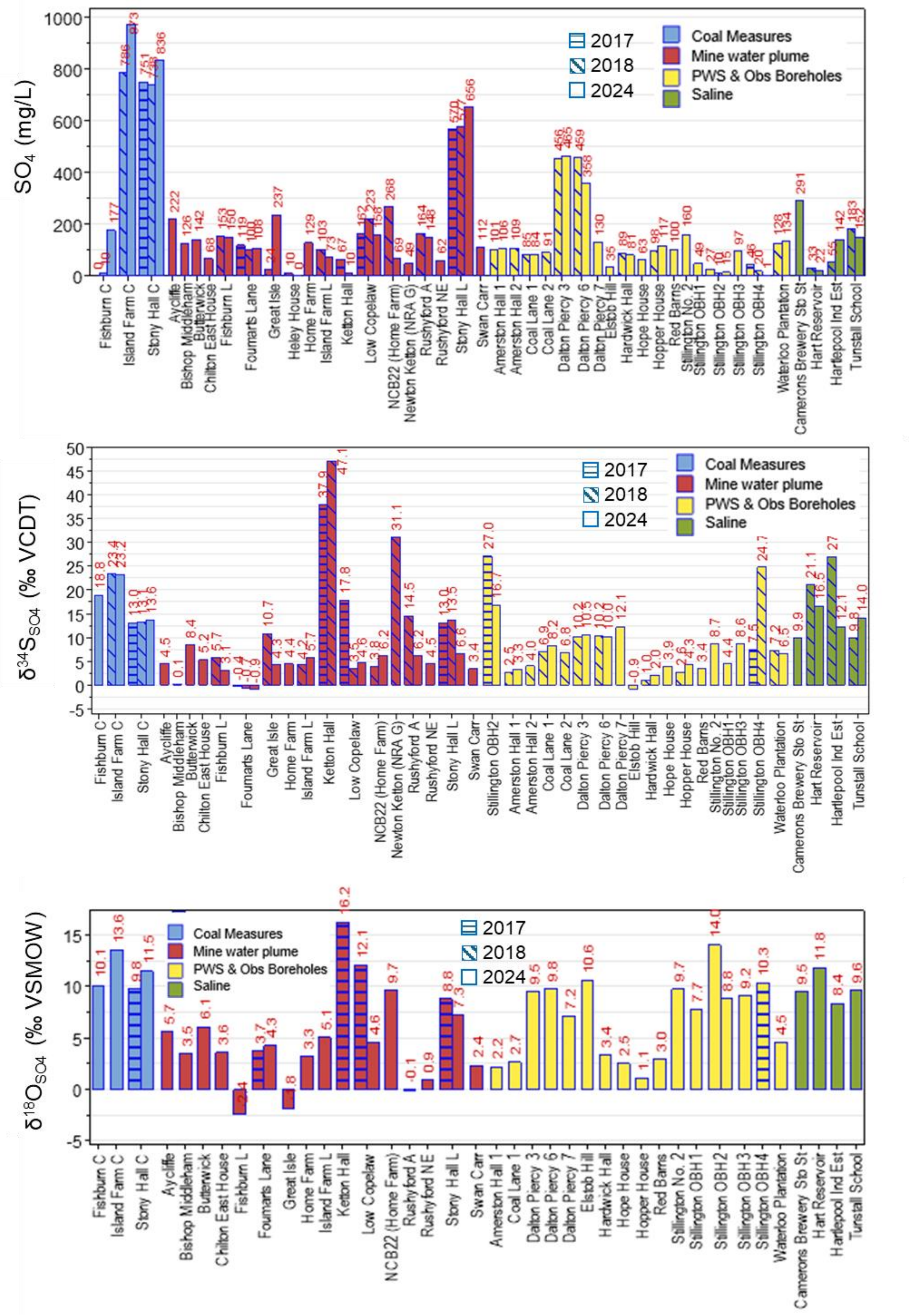


Figure 13 Distribution of sulphate (SO_4) and sulphur ($\delta^{34}S$) and oxygen ($\delta^{18}O$) isotope ratios of the dissolved sulphate (SO_4) in boreholes from 2024, 2018 and 2017.

7.2.1.1 COAL MEASURES BOREHOLES

The sulphate isotope composition of Stony Hall C remained very stable across the three sampling dates, with an average sulphate $\delta^{34}S$ value of +13.2‰ (SD 0.3) and $\delta^{18}O$ value of +10.6‰ (SD 0.8) (Table 8). Similarly, the Island Farm C borehole showed no change in $\delta^{34}S$ between 2018 and 2024 with an average of +23.3‰ (SD 0.1); $\delta^{18}O$ was measured in 2024 at +13.6‰. Also, the water isotope values remained stable over time. Both boreholes have similar high sulphate concentrations at around 700 –1000 mg/l.

In Fishburn C, a $\delta^{34}S$ value of +18.8‰ and $\delta^{18}O$ of +10.1‰ and a sulphate concentration of 177 mg/l was measured in 2024, with a similar enrichment shown by the other mine waters in the mine water block. The very low-sulphate water sampled in 2018 precluded $\delta^{34}S$ measurement, so temporal difference in sulphur isotopes could not be assessed. This discrepancy may again be due to the 2018 groundwater sample having been taken from within the casing and possibly affected by microbial sulphate reduction. .

7.2.1.2 MAGNESIAN LIMESTONE BOREHOLES PAIRED TO THE COAL SEAM BOREHOLES

Island Farm L with SO_4 73 mg/l and $\delta^{34}S$ +5.7‰ and Fishburn L with SO_4 150 mg/l and $\delta^{34}S$ +3.1‰ in 2024 sampling broadly confirmed the 2018 pattern of groundwater with lower $\delta^{34}S$ and much lower sulphate content, compared to the respective coal seam boreholes (Table 8). The value of $\delta^{18}O_{SO4}$ analysed in the 2024 samples (but not in 2018) is +5.1‰ and –2.36‰, respectively for Island Farm L and Fishburn L, with lower values compared to the coal seam boreholes (range +9.8‰ to +13.6‰). A slight difference also exists in the water isotopes between the 2018 and 2024 samples, with the 2024 samples lying further from the GMWL. The isotopic differences observed between the Coal Measures/Magnesian Limestone boreholes correspond to a chemical compositional difference too, with Island Farm L and Fishburn L being Ca-Mg-HCO_3 waters and the Coal Measures boreholes Island Farm C and Fishburn C Na-SO_4 and Na-HCO_3, respectively. It can be concluded that the chemical and isotope data of Island Farm L/C and Fishburn L/C boreholes all converge to indicate no direct connectivity through the boreholes between the Magnesian Limestone and Coal Measures aquifers.

Stony Hall L showed no or very small changes in the high sulphate concentration (570–577 mg/l) and sulphate sulphur isotope values of +13‰ and +13.5‰ between the previous summer samples of July 2017 and July 2018, respectively; a strong similarity in those values to Stony Hall C suggested a large contribution of mine water in the Magnesian Limestone borehole. The 2024 sampling in January indicates a slight increase in sulphate (656 mg/l) compared to the previous samplings, but a very different sulphur isotope value of +6.6‰, which is closer to Island Farm L and Fishburn L’ s isotopic ratios. The water isotopes remain instead broadly unchanged in time and similar to the coal seam borehole (Figure 9). It is possible that the variation reflects a seasonality effect, with a larger contribution of sulphate with a depleted sulphur isotope signature which is typical of sulphide oxidation.

7.2.1.3 MAGNESIAN LIMESTONE BOREHOLES WITHIN THE MINE WATER PLUME

The boreholes within the historical mine water plume resampled in 2024 are Foumarts Lane, Great Isle, Heley House, Low Copelaw, NCB22 (Home Farm), Rushyford A, and the 3 boreholes paired with the Coal Measures boreholes Island Farm L, Fishburn L and Stony Hall L, discussed in 7.2.1.2. The analytical results are in Table 5 and Table 6.

Comparison of data from the different sampling dates (Table 8) indicates variable $\delta^{34}S$ in all boreholes, except for more constant values in Foumarts Lane with a $\delta^{34}S$ mean of -0.67‰ (SD 0.3). As in 2018, we were not able to analyse the isotope composition of the sulphate in the Heley House borehole groundwater due to insufficient sulphate (see 7.2.1.6). In Great Isle and Low Copelaw the change in $\delta^{34}S$ correlates (negatively) with the sulphate content, with higher $\delta^{34}S$ values associated with lower SO_4. This is attributable to isotope fractionation during bacterial sulphate reduction, as was previously shown in 2017-2018 data for Ketton Hall (Palumbo-Roe et al, 2023).

The newly sampled boreholes Aycliffe, Bishop Middleham, Butterwick, Chilton East House, Home Farm, Rushyford NE, and Swan Carr show a range of $\delta^{34}S$ values from +0.1‰ to +8.4‰ and $\delta^{18}O$ from +0.9‰ to +6.1‰ (all analytical results in Table 5 and Table 6).

7.2.1.4 MAGNESIAN LIMESTONE BOREHOLES OUTSIDE HISTORICAL MINE WATER PLUME

Outside the historical mine water plume the boreholes resampled in 2024 are Amerston Hall 1, Coal Lane 1, Dalton Piercy 3, Dalton Piercy 6, Hardwick Hall, Hopper House, Stillington OBH2 and OBH4, and Waterloo Plantation. Also, we resampled the boreholes near Hartlepool: Hart Reservoir, Hartlepool Industrial Estate Replacement, and Tunstall School, and further described in 7.2.1.5.

Both sulphate and sulphur isotope concentrations are reproducible in Hardwick Hall borehole, representing the Magnesian Limestone baseline, with a SO_4 of 81 mg/l, and a $\delta^{34}S$ value of +2.0‰ (previously SO_4 89 mg/l, and $\delta^{34}S$ 1.0‰) Similarly, the abstraction boreholes Amerston Hall 1, Coal Lane 1, Dalton Piercy 3, Dalton Piercy 6, Hopper House, and Waterloo Plantation show constant $\delta^{34}S$ values with SD <1.

The $\delta^{34}S$ variability of Stillington OBH4 was already noted, with values changing from +7.5‰ to +24.7‰ from 2017 to 2018, corresponding to a SO_4 concentration decrease from 46 mg/L to 20 mg/L. In 2024 a further decrease in SO_4 (<10 mg/L) has prevented the isotope analysis. Similarly, Stillington OBH2 shows high $\delta^{34}S$ variability, as follows: $\delta^{34}S$ +27‰ and SO_4 27 mg/L in 2017, undetermined and SO_4 <10 mg/L in 2018, $\delta^{34}S$ +16.8‰ and $\delta^{18}O$ +8.8‰ and SO_4 14.55 mg/L in 2024. As per Great Isle and Low Copelaw data, this pattern has been interpreted as a sign of reduction of sulphate and the enrichment in the heavier sulphur isotope ^{34}S of the residual sulphate in solution.

The newly sampled boreholes Dalton Piercy No 7, Elstob Hill, Hope House, Red Barns, Stillington No 2, Stillington OBH1 and Stillington OBH3 show a range of $\delta^{34}S$ from -0.9‰ to +8.7‰ and $\delta^{18}O$ from +2.5‰ to +10.6‰ (all analytical results in Table 5 and Table 6). Stillington No 2 and Stillington OBH3 with concentrations of 160 mg/L and 97 mg/L, respectively, have very similar $\delta^{34}S$ of +8.7‰, +8.6‰ and also $\delta^{18}O$ of +9.7‰ and +9.2‰.

7.2.1.5 MAGNESIAN LIMESTONE BOREHOLES NEAR HARTLEPOOL

Among the saline Magnesian Limestone boreholes near Hartlepool, all repeated analyses of Hart Reservoir, Hartlepool Industrial Estate Replacement, Tunstall School show $\delta^{34}S$ variability of the replicates with SD equal to or greater than 3‰, with the greatest difference observed in Hartlepool Industrial Estate. The same pattern is found of high variability and high $\delta^{34}S$ corresponding to relatively low SO_4 concentrations, observed in other boreholes ($\delta^{34}S$ from +27‰ to 12‰ and SO_4 from 55 to 142 mg/L). This pattern has been interpreted as a sign of reduction of sulphates and the resulting decrease in concentration associated with the enrichment in the heavier sulphur isotope ^{34}S of the residual sulphate in solution. The potential impact of different sampling depths between 2018 and 2024 is unknown.

Camerons Brewery Stockton Street borehole has been sampled in 2024 and SO_4 is 291 mg/L, $\delta^{34}S$ value +9.9‰, $\delta^{18}O$ +9.5‰ (all analytical results in Table 5 and Table 6).

7.2.1.6 MISSING SULPHUR ISOTOPE DATA: BOREHOLE HELEY HOUSE

Isotope analysis of the dissolved sulphate in Heley House borehole was not achievable due to the very low SO_4 concentration of 0.13 mg/L. The sample also had low conductivity of 388 µS/cm and a pH of 8.15. The borehole was one of the boreholes selected for carrying out a geochemical depth profiling which showed clear stratification of the borehole water. It is likely that the sample does not represent the true aquifer conditions.

8 Sources of the dissolved sulphate

8.1 ISOTOPE EVIDENCE

All data available from 2017 to 2024 are considered and plotted as follows: the oxygen isotope composition of dissolved sulphate ($\delta^{18}O_{SO4}$) relative to the oxygen isotope composition of water ($\delta^{18}O_{H2O}$) in Figure 14, the $\delta^{34}S_{SO4}$ versus $\delta^{18}O_{SO4}$ in Figure 15 and Figure 16, and the $\delta^{34}S_{SO4}$ versus the concentrations of dissolved SO_4 in Figure 17. The graphs complement each other to infer the sulphur sources contributing to the dissolved sulphate, but also to recognise isotopic fractionation which might change the source isotope signature.

The diagram $\delta^{18}O_{SO4}$ versus $\delta^{18}O_{H2O}$ (Figure 14) shows that there is a much wider variation in the $\delta^{18}O$ of the sulphate (from -2.4 to +13.6‰) in contrast to the homogeneous $\delta^{18}O$ of the water in the groundwater samples (from -8.5 to -7.1‰). During oxidation of sulphide minerals, a percentage of the oxygen comes from available oxygen gas (O_2) in the system and the rest is derived from available water. The $\delta^{18}O$ value of the resulting sulphate will reflect the dominant source of oxygen. Van Stempvoort & Krouse (1994) defined the area for sulphate formed via biotic or abiotic sulphide oxidation, which is labelled as Area B in Figure 14. In the figure there is a small number of samples with relatively low $\delta^{18}O_{SO4}$ falling in this area. The majority of the data lie above these samples, with ^{18}O-enriched SO_4 compared to the oxygen isotopic ratio of the water. Interpretation of the relatively ^{18}O-enriched SO_4 is uncertain, as many mechanisms can play a role; the main controls on ^{18}O-enriched SO_4 are: atmospheric oxygen oxidation ($\delta^{18}O$ for air +23.5‰) of SO_3^{-2}, dissolution of evaporite sulphate, microbial sulphate reduction which enriches residual $SO_4(aq)$ in ^{18}O. The enrichment in ^{18}O can also result from oxidation of intermediate sulfoxyanions during the formation of aqueous SO_4 under O_2-limited conditions (Seal, 2003, Seal and Cravotta, 2006); from dissolution of ferrous- and ferric-sulphate minerals, e.g. melanterite, with high $\delta^{18}O_{SO4}$ acquired by isotope exchange between dissolved sulphate (and/or short-lived intermediate sulphur species) and very low pH (<0) (Taylor and Wheeler, 1994).

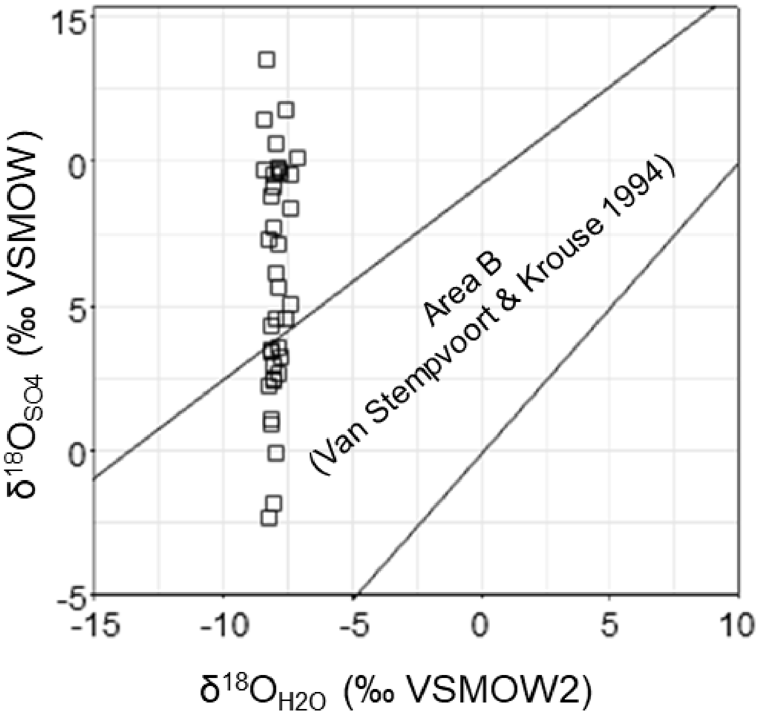


Figure 14 $\delta^{18}O_{SO4}$ as a function of $\delta^{18}O_{H2O}$, with the area defined by Van Stempvoort and Krouse (1994) for sulphate derived from sulphide oxidation.

Figure 15 shows the distribution of δ^{34}S and δ^{18}O for the dissolved sulphate. The samples falling in the zone B of Figure 14 are plotted with red symbols. For reference, the isotopic composition of gypsum/anhydrite from Permian evaporites is δ^{34}S = +10.0 to +11.1‰, and δ^{18}O = +10.8 to +13.6‰, whilst that in Triassic mudstones and sandstones had δ^{34}S = +11.2 to +20.8‰, and δ^{18}O = +12.6 to +15.1‰ (Bottrell et al., 2006; Heaton, 2004). The δ^{34}S and δ^{18}O values of the dissolved sulphate in seawater are 21.2‰ and 9.5‰, respectively. Our sample sulphate displays a wide range of δ^{18}O values (-2.4‰ to +16.2‰) and a very wide range of δ^{34}S values (-0.9‰ to +47.1‰).

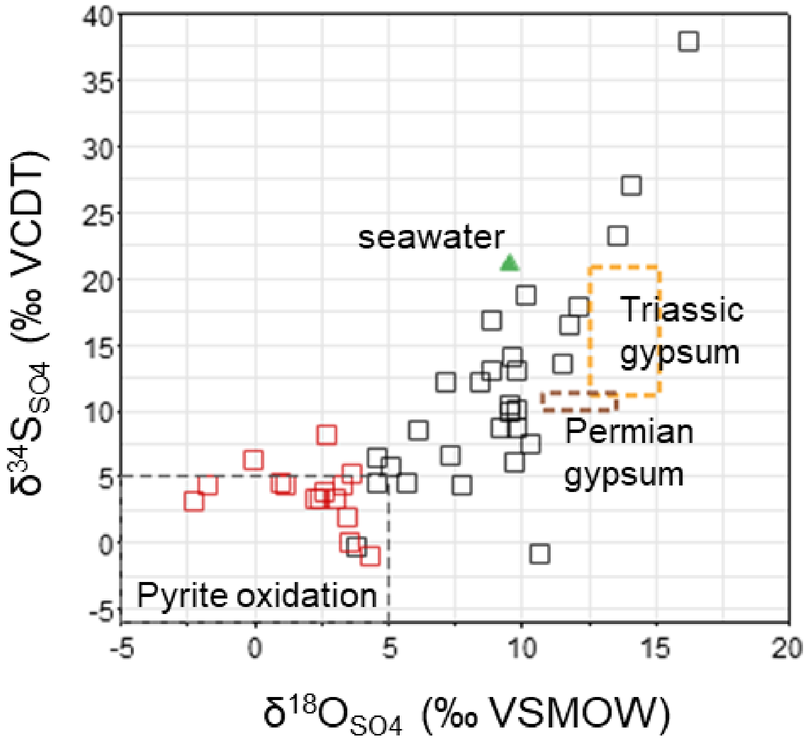


Figure 15 δ^{34}S$_{SO4}$ as a function of δ^{18}O$_{SO4}$; samples in zone B from Figure 14 are plotted with red symbols; potential end-members of sulphate sources are indicated.

Three main pieces of evidence can be drawn from the sample distribution:

i) The graph indicates that the samples with ^{18}O depleted sulphate (red symbols), identified in the zone B of Figure 14, also have relatively low δ^{34}S$_{SO4}$ (mostly <5‰). This corroborates the previous evidence from the δ^{18}O$_{SO4}$ versus δ^{18}O$_{H2O}$ relationship to suggest that for these groundwaters (listed in Table 9) the source of sulphate is not a marine, as it would result in significantly higher δ^{34}S and δ^{18}O sulphate signatures; sulphate from sulphide mineral oxidation is more likely.

ii) There is a broad trend of increasing δ^{18}O$_{SO4}$ with δ^{34}S$_{SO4}$ towards the evaporites/seawater compositions, but overall there is great data dispersion and the lack of a linear relation δ^{34}S - δ^{18}O, which would be expected from a system with the mixing of two sources of sulphate and/or a single fractionation process (Krouse and Mayer, 2000).

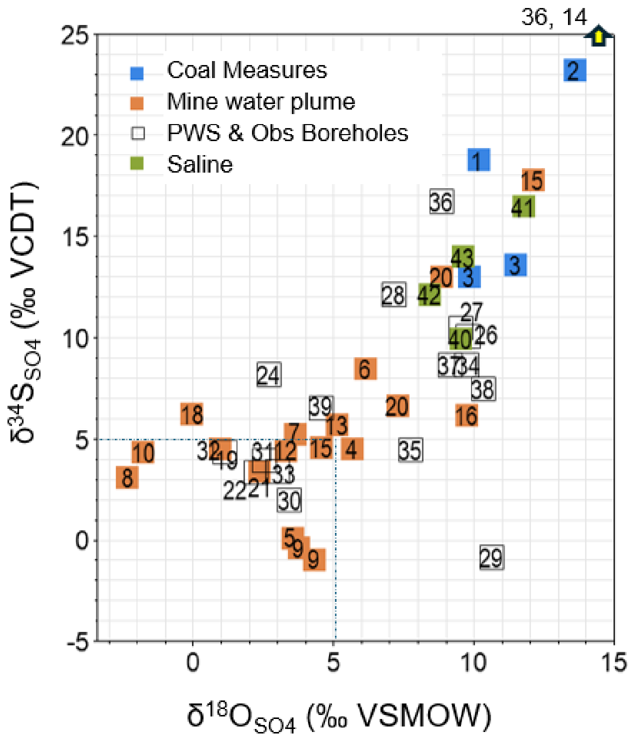
iii) A few samples are far more enriched in ^{18}O$_{SO4}$ and ^{34}S$_{SO4}$ than expected from a gypsum or seawater source. This is further considered using the relationship between δ^{34}S$_{SO4}$ and SO$_4$. In fact, enrichment in ^{18}O and ^{34}S of the dissolved sulphate accompanied by the lowering of SO$_4$ concentrations, can be a sign that the water has undergone bacterial SO$_4$ reduction (as discussed above in section 7.2).

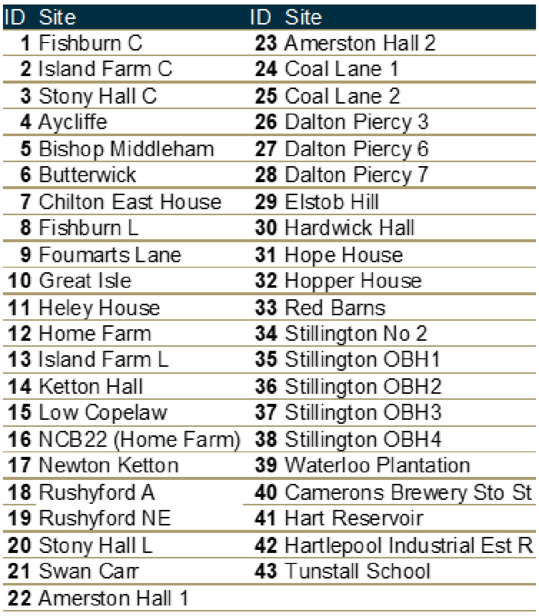
By grouping the samples by borehole group (Figure 16), the enrichment in both ^{34}S and ^{18}O of the Coal Measures and the saline boreholes is evident, but overall there is much diversity, and some of the PWS and observation boreholes also have relatively high δ^{34}S$_{SO4}$ and δ^{18}O$_{SO4}$ values.

Table 9 List of groundwater samples from 2024 where the $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ indicate sulphide mineral oxidation as the likely dissolved sulphate source.

ID	Site	Type	Sulphate δ34S (‰) V-CDT	Sulphate δ18O (‰) V-SMOW	SO_4^{2-}
5	Bishop Middleham	Mine water Impacted	0.1	3.5	126
7	Chilton East House	Mine water Impacted	5.2	3.6	68
8	Fishburn L	Mine water Impacted	3.1	-2.4	150
9	Foumarts Lane	Mine water Impacted	-0.9	4.3	108
10	Great Isle (NRA 6)	Mine water Impacted	4.3	-1.8	237
12	Home Farm	Mine water Impacted	4.4	3.3	129
18	Rushyford A*	Mine water Impacted	6.2*	-0.1	148
19	Rushyford NE	Mine water Impacted	4.5	0.9	62
21	Swan Carr	Mine water Impacted	3.4	2.4	112
33	Red Barns	In between saline and mine water	3.4	3.0	100
30	Hardwick Hall	Mag Limestone background	2.0	3.4	81
23	Amerston Hall 1	Public Water Supply	3.3	2.2	106
24	Coal Lane 1*	Public Water Supply	8.2*	2.7	84
31	Hope House	Public Water Supply	3.9	2.5	63
32	Hopper House	Public Water Supply	4.3	1.1	117

*less confidence in the assessment based on the relatively higher S isotope ratios





ID	Site	ID	Site
1	Fishburn C	**23**	Amerston Hall 2
2	Island Farm C	**24**	Coal Lane 1
3	Stony Hall C	**25**	Coal Lane 2
4	Aycliffe	**26**	Dalton Piercy 3
5	Bishop Middleham	**27**	Dalton Piercy 6
6	Butterwick	**28**	Dalton Piercy 7
7	Chilton East House	**29**	Elstob Hill
8	Fishburn L	**30**	Hardwick Hall
9	Foumarts Lane	**31**	Hope House
10	Great Isle	**32**	Hopper House
11	Heley House	**33**	Red Barns
12	Home Farm	**34**	Stillington No 2
13	Island Farm L	**35**	Stillington OBH1
14	Ketton Hall	**36**	Stillington OBH2
15	Low Copelaw	**37**	Stillington OBH3
16	NCB22 (Home Farm)	**38**	Stillington OBH4
17	Newton Ketton	**39**	Waterloo Plantation
18	Rushyford A	**40**	Camerons Brewery Sto St
19	Rushyford NE	**41**	Hart Reservoir
20	Stony Hall L	**42**	Hartlepool Industrial Est R
21	Swan Carr	**43**	Tunstall School
22	Amerston Hall 1		

Figure 16 Same as Figure 15 with Borehole label No and legend ID, area limited by dotted line as in Figure 15 to delineate the isotopic composition of sulphate from pyrite oxidation.

Figure 17 shows $\delta^{34}S_{SO4}$ versus dissolved SO_4 and indicates that the samples with red symbols in Figure 14, and listed in Table 9, have sulphate mostly between 50 and 100 mg/L. Compared to the dual isotope $\delta^{34}S_{SO4}$ - $\delta^{18}O_{SO4}$, the $\delta^{34}S_{SO4}$ - SO_4 graph plots more data, as it includes the 2018 samples that were not analysed for $\delta^{18}O_{SO4}$ (Figure 18). It is reasonable to assume that the 2018 water samples with black symbols but close to the red ones, are groundwaters with sulphate derived by sulphide oxidation.

By plotting the samples by borehole groups (Figure 19), it is evident that there is not a clear separation between the borehole groups with overlapping and dispersion of each group, as observed in the previous graphs.

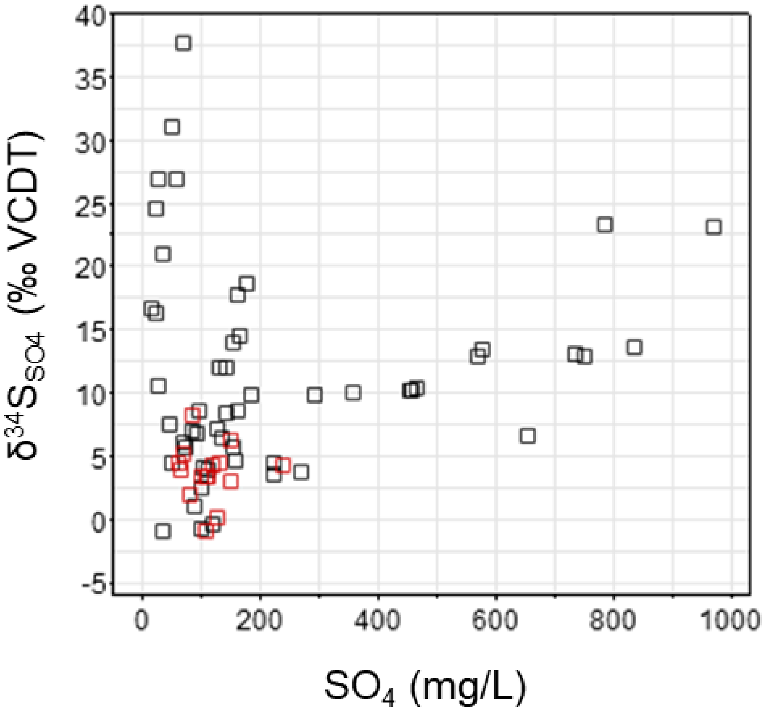


Figure 17 $\delta^{34}S_{SO4}$ versus the concentrations of dissolved SO_4.

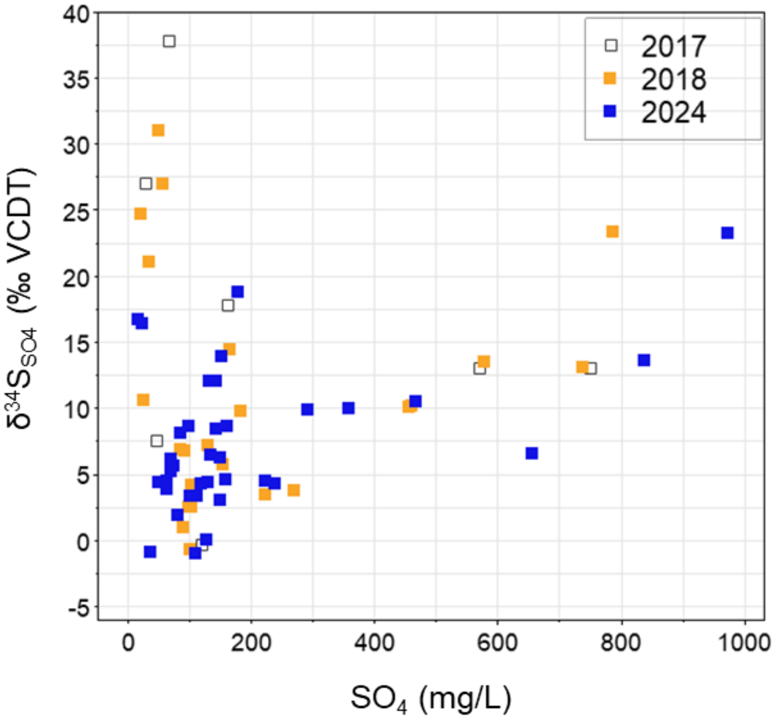
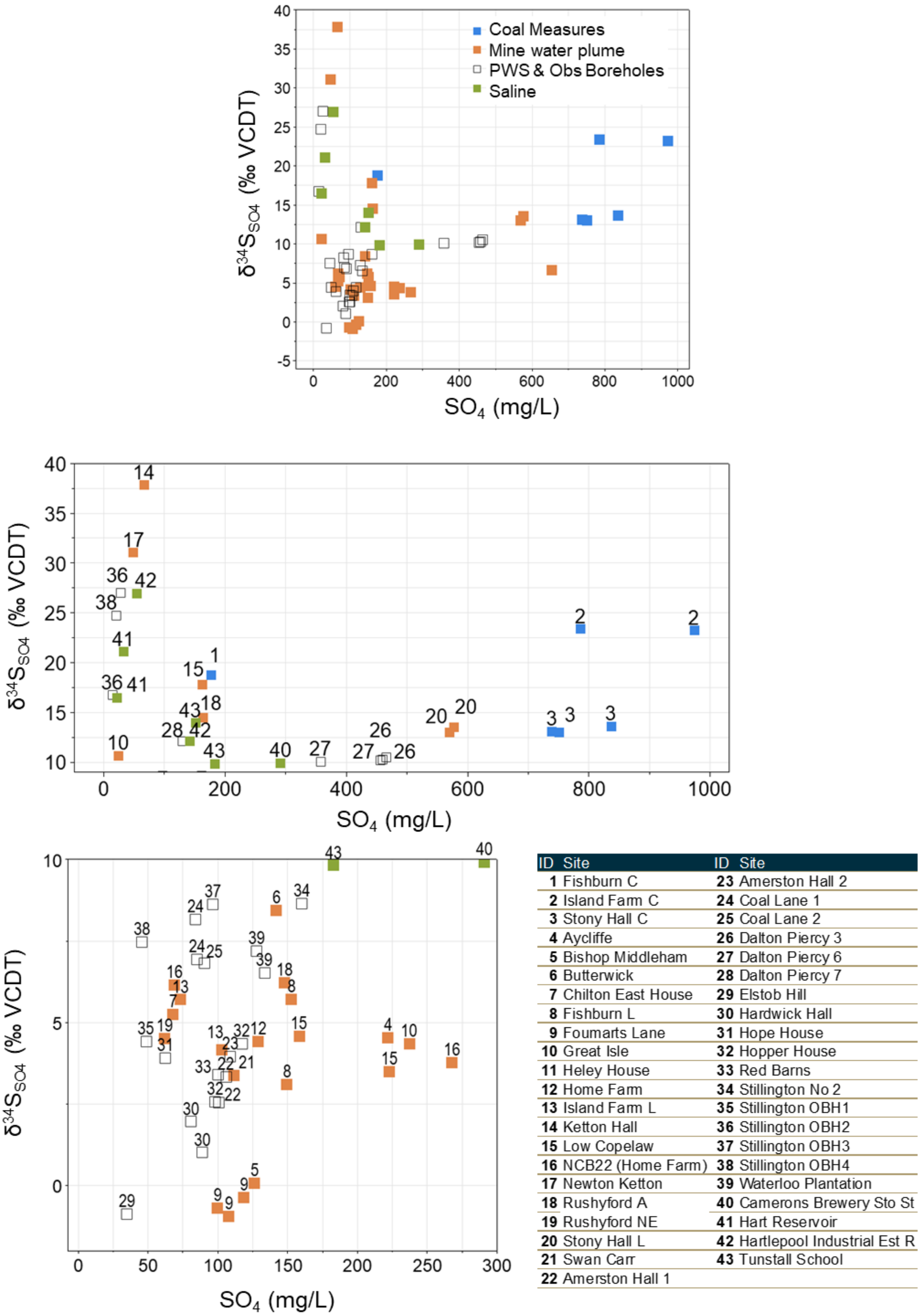


Figure 18 Samples grouped by sampling date in the $\delta^{34}S_{SO4}$ versus dissolved SO_4 plot.



ID	Site	ID	Site
1	Fishburn C	**23**	Amerston Hall 2
2	Island Farm C	**24**	Coal Lane 1
3	Stony Hall C	**25**	Coal Lane 2
4	Aycliffe	**26**	Dalton Piercy 3
5	Bishop Middleham	**27**	Dalton Piercy 6
6	Butterwick	**28**	Dalton Piercy 7
7	Chilton East House	**29**	Elstob Hill
8	Fishburn L	**30**	Hardwick Hall
9	Foumarts Lane	**31**	Hope House
10	Great Isle	**32**	Hopper House
11	Heley House	**33**	Red Barns
12	Home Farm	**34**	Stillington No 2
13	Island Farm L	**35**	Stillington OBH1
14	Ketton Hall	**36**	Stillington OBH2
15	Low Copelaw	**37**	Stillington OBH3
16	NCB22 (Home Farm)	**38**	Stillington OBH4
17	Newton Ketton	**39**	Waterloo Plantation
18	Rushyford A	**40**	Camerons Brewery Sto St
19	Rushyford NE	**41**	Hart Reservoir
20	Stony Hall L	**42**	Hartlepool Industrial Est R
21	Swan Carr	**43**	Tunstall School
22	Amerston Hall 1		

Figure 19 (Top) Samples symbolised by borehole groups in the $\delta^{34}S_{SO4}$ versus dissolved SO_4 plot. (middle and bottom) subzones of top graph with sample labelled (ID in table).

Interpretation of the sample distribution in the $\delta^{34}S_{SO4}$ versus the dissolved SO_4 diagram (Figure 19) reveals the following groups:

- The presence of groundwater with $\delta^{34}S_{SO4}$ values < +5 ‰ and SO_4 from ~80 to ~150 mg/L from abstraction and observation boreholes and from some boreholes historically impacted by the mine water plume.

These groundwaters with relatively low sulphate concentrations contain isotopically lower sulphate (both sulphur and oxygen), which is typical of sulphate derived from the oxidation of sulphide minerals, and therefore discounting other origins of the dissolved sulphate, like evaporite mineral dissolution or a more ^{34}S-enriched source, such as the deep mine water sampled at Stony Hall C or Island Farm C.

This can be further tested by calculating the S-isotope composition and sulphate concentration of a hypothetical groundwater from the study area, derived from a sulphate-rich mine water (e.g. Stony Hall C with SO_4 740 mg/L, $\delta^{34}S_{SO4}$ +13‰) diluted by recharge (represented by a very dilute water with 5 mg/l SO_4 and a $\delta^{34}S$ value of +0‰). A 1% mine water contribution would result in a groundwater with 12 mg/l SO_4 and a $\delta^{34}S$ value of +7.8‰; while a 13% contribution would give 100 mg/l SO_4 and a $\delta^{34}S$ value of +12.4‰.

Similarly, the dilution of a groundwater enriched in SO_4 (500 mg/l) sourced from Permian evaporites ($\delta^{34}S$ +10.2‰), using the same diluting recharge end-member (5 mg/l SO_4 and a $\delta^{34}S$ value of +0‰), would yield groundwater with 10 mg/l SO_4 and a $\delta^{34}S$ value of +5‰ when the high-sulphate groundwater fraction is 1%, and with 100 mg/L SO_4 and a $\delta^{34}S$ value of +9.6‰ when the high-sulphate source fraction is 20%.

In both cases, whether it is sulphate-rich mine water or Permian evaporites mixing with freshwater, the diluted groundwaters would have $\delta^{34}S_{SO4}$ values that are too high compared to the actual measurements.

These calculations support the conclusion at this stage of the investigation that, despite the presence of evaporites in the geological sequence, gypsum is not a major contributor to the relatively high sulphate baseline concentrations measured in boreholes such as Hardwick Hall, Amerston Hall 1, Hope House, and Hopper House. This also applies to many boreholes historically impacted by the mine water pollution plume, such as Rushyford A (SO_4 148 mg/L, $\delta^{34}S_{SO4}$ +6.2‰, $\delta^{18}O_{SO4}$ -0.1‰), Bishop Middleham (SO_4 126 mg/L, $\delta^{34}S_{SO4}$ +0.1‰, $\delta^{18}O_{SO4}$ +3.5‰), Fishburn L (SO_4 150 mg/L, $\delta^{34}S_{SO4}$ +3.1‰, $\delta^{18}O_{SO4}$ -2.4‰), Home Farm (SO_4 129 mg/L, $\delta^{34}S_{SO4}$ +4.4‰, $\delta^{18}O_{SO4}$ +3.3‰), Foumarts Lane (SO_4 108 mg/L, $\delta^{34}S_{SO4}$ -0.9‰, $\delta^{18}O_{SO4}$ +4.3‰).

The geological occurrence of the sulphide minerals (e.g. glacial till, coal mine waste, ^{34}S-depleted-mine water plume) and the hydrogeological pathways of water-rock interactions are yet to be fully determined, but they likely vary across different boreholes. For example, a consistently low $\delta^{34}S_{SO4}$ value, the lowest in the dataset, was observed in water samples from the Foumarts Lane borehole (mean/SD: -0.7±0.3‰). This contrasts with the general higher variability and higher $\delta^{34}S_{SO4}$ of other mine water impacted boreholes. The pH-neutral ferruginous waters contain very high concentrations of arsenic (commonly associated with pyrite) in the suspended particulate fraction, suggesting the weathering of As-bearing pyrite and mobilisation of the secondary weathering products.

- The presence of groundwater with $\delta^{34}S_{SO4}$ <5‰ and SO_4 from ~160 mg/L to ~300 mg/L from Aycliffe, Great Isle, Low Copelaw, NCB22 (Home Farm) boreholes.

These ^{34}S-depleted high-sulphate waters represent some of the boreholes most affected by the mine water plume. Some of the $\delta^{34}S_{SO4}$ measurements are relatively low, between 3.5‰ and 4.5‰, and for boreholes with repeated sampling, temporal variability has been observed along with much higher $\delta^{34}S_{SO4}$. This is the case at Great Isle, Low Copelaw and NCB22 (Home Farm); here the $\delta^{34}S$ correlates (negatively) with the sulphate content, with higher $\delta^{34}S$ (and $\delta^{18}O_{SO4}$) associated to lower SO_4. This is attributable to isotope fractionation during bacterial sulphate reduction, as shown in 2017-2018 data for Ketton Hall (not included in this round of sampling). If we consider the low $\delta^{34}S$ records in these boreholes, they are typical of sulphate derived from the oxidation of sulphide minerals, while simple mixing calculations between ^{34}S-enriched mine waters like Stony Hall C and a ^{34}S-depleted diluted recharge indicates that a contribution of mine water like Stony Hall C is not evident in a borehole such as Great Isle (NRA 6) with 240 mg/L SO_4 and $\delta^{34}S_{SO4}$ +4.3‰, $\delta^{18}O_{SO4}$ -1.8‰).

- The presence of groundwater with $\delta^{34}S_{SO4} \geq +10$‰ and a range of sulphate concentrations.

Within these ^{34}S-enriched sulphate groundwater samples we notice ^{34}S-enriched high-sulphate waters from the Coal Measures boreholes: Island Farm C and Stony Hall C, and Stony Hall L, together with the public water supply Dalton Piercy 3 and 6 and the saline Camerons Brewery Stockton Street boreholes. Stillington No 2 and Stillington OBH3 sampled in 2024 have lower SO_4 concentrations, respectively 160 and 97 mg/L, but with very similar $\delta^{34}S$ values of +8.7‰, +8.6‰ and also $\delta^{18}O$ of +9.7‰ and +9.2‰, and very close to Dalton Piercy No 3 and No 6 boreholes.

Given the similar ^{34}S-enriched sulphate of these high sulphate groundwaters, we will attempt to further characterise the waters on the basis of selected hydrochemical parameters in Section 8.2.

- Groundwater from the Magnesian Limestone boreholes near Hartlepool (saline) with $\delta^{34}S_{SO4}$ >10‰ and a wide range from low to medium (< 300 mg/L) SO_4 concentrations.

Among the saline Magnesian Limestone boreholes near Hartlepool, all repeated analyses of Hart Reservoir, Hartlepool Industrial Estate Replacement, Tunstall School show $\delta^{34}S$ variability of the replicates with SD equal or greater than 3‰, with the greatest difference observed in Hartlepool Industrial Estate Replacement. This site shows the same pattern of high variability and of high $\delta^{34}S$ corresponding to relatively low SO_4 concentrations, observed in other boreholes (e.g. Stillington OBH2 and OBH4). This pattern has been interpreted as a sign of reduction of sulphate and the resulting decrease in concentration associated with the enrichment in the heavier sulphur isotope ^{34}S of the residual sulphate in solution. In this case, there is less certainty in using sulphur isotopes to determine the origin of the dissolved sulphate. If instead sulphate behaves conservatively, concentrations around 150 mg/L and $\delta^{34}S_{SO4}$ +12‰, $\delta^{18}O_{SO4}$ +8‰ could be due to the contribution of more than one source of ^{34}S-enriched sulphate, including seawater. Camerons Brewery Stockton Street, sampled in 2024, with SO_4 of 291 mg/L, has a $\delta^{34}S_{SO4}$ value of +9.9‰, $\delta^{18}O_{SO4}$ +9.5‰, that can be interpreted as dissolution of local evaporites, too low for a large contribution of sea water.

- The presence of waters with $\delta^{34}S_{SO4}$ >> +10‰ and very low SO_4 concentrations from Ketton Hall, Newton Ketton, Hartlepool Ind Est, Stillington OBH2 and OBH4 and Hart Reservoir boreholes.

These are boreholes where redox processes clearly overprint the sulphate source signature. The dissolved oxygen measurements in 2024 are <0.3 mg/L, indicating prevailing anoxic conditions at the time of sampling (Figure 20). The repeated sampling shows also high variability in the sulphur isotope ratio (Table 8); this suggests variable redox conditions, perhaps related to variation between standing water in the borehole cased sections and more representative samples taken in 2024 from the open sections of aquifer, and should be investigated further. The borehole stratification of the physicochemical conditions was observed in the last 4 boreholes listed above, as part of the parallel study on high pH boreholes (Bowes et al, 2024).

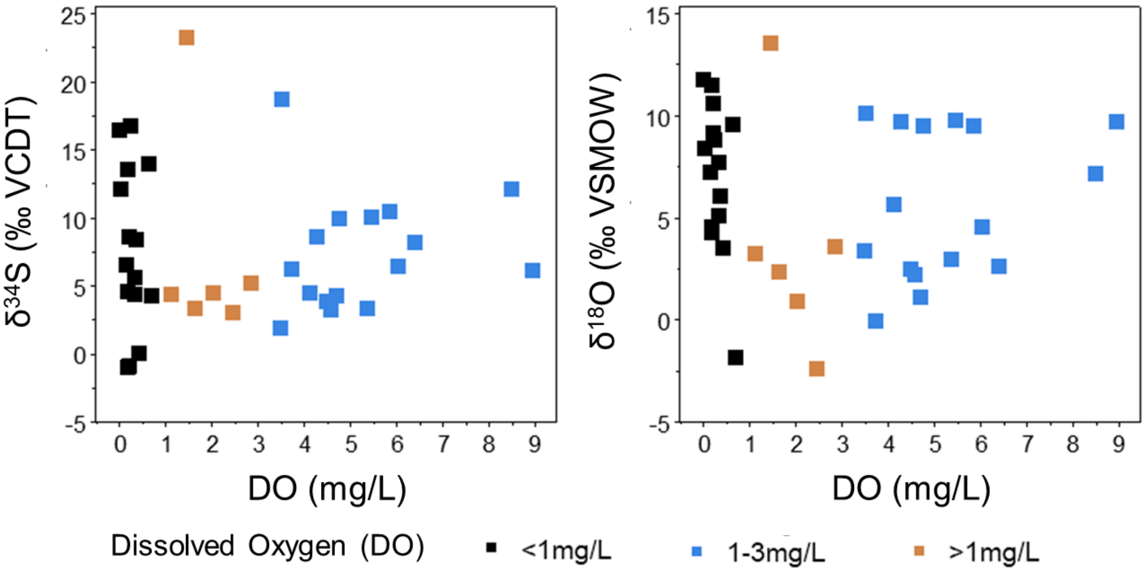


Figure 20 $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ versus dissolved oxygen in 2024 groundwater samples

8.2 HYDROCHEMICAL DATA INTEGRATION

In this section, scatter diagrams are produced to illustrate variations of selected major ions and trace elements relative to sulphate and chloride. To facilitate the comparison, not all boreholes are included in the plots, but we selected the boreholes highest in sulphate and with probable different sources of sulphate: three Magnesian Limestone boreholes with the highest salinities (both Cl and SO_4): Stillington No 2, Dalton Piercy No 3 and Camerons Brewery waters, and two Coal Measures boreholes Stony Hall C and Island Farm C. An obvious choice for Dalton Piercy's dissolved sulphate is the dissolution of local evaporites, while the ^{34}S enriched sulphate of the mine water from the Coal Measures boreholes could be an indication of more complex cycles of S oxidation and/or water-rock interactions. Previous studies have inferred that the borehole at Camerons Brewery Stockton Street was historically impacted by seawater intrusion (JBA, 2018).

Using WIMS historical data, the relationship between sulphate and chloride and sodium and chloride is shown in Figure 21 and related to a pure water-seawater mixing line (seawater SO_4/Cl molar ratio: 0.052; Na/Cl molar ratio: 0.858). Figure 22 shows the scatterplots magnesium, sodium, potassium and bicarbonate vs sulphate.

As shown in Figure 21, all waters have a sulphate enrichment compared to seawater composition indicating an additional source of sulphate. The Coal Measures waters have the highest sulphate enrichment (median value of the ratio is ~3), while Camerons Brewery borehole waters, perhaps not surprisingly, are broadly the least enriched (median value of the ratio is 0.48).

In the Na vs Cl plot, the Stillington No 2, Dalton Piercy No 3 and Camerons Brewery waters aligned along the line representing a hypothetical dilution of seawater by a non-mineralised water (Na/Cl molar ratio median values 1.412, 0.957, 0.805, respectively), suggesting a single source of salinity, similar to seawater, for these elements. The Coal Measures waters show instead a great enrichment in Na with respect to the marine composition (Na/Cl molar ratio median value > 4) (Figure 29). The largest concentrations in both sodium and chloride are shown by the Camerons Brewery waters, although with some data point dispersion. The Coal Measures boreholes are greatly enriched also in potassium and bicarbonate (Figure 22).

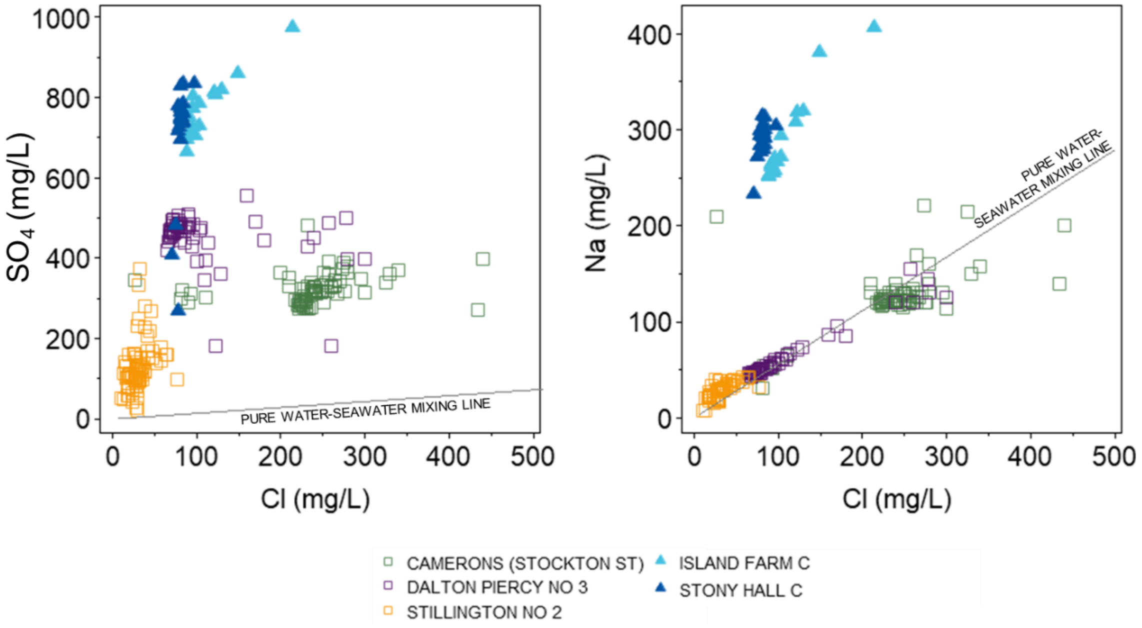


Figure 21 SO$_4$-Cl and Na-Cl plots along the pure water-seawater mixing line. Contains Environment Agency data.

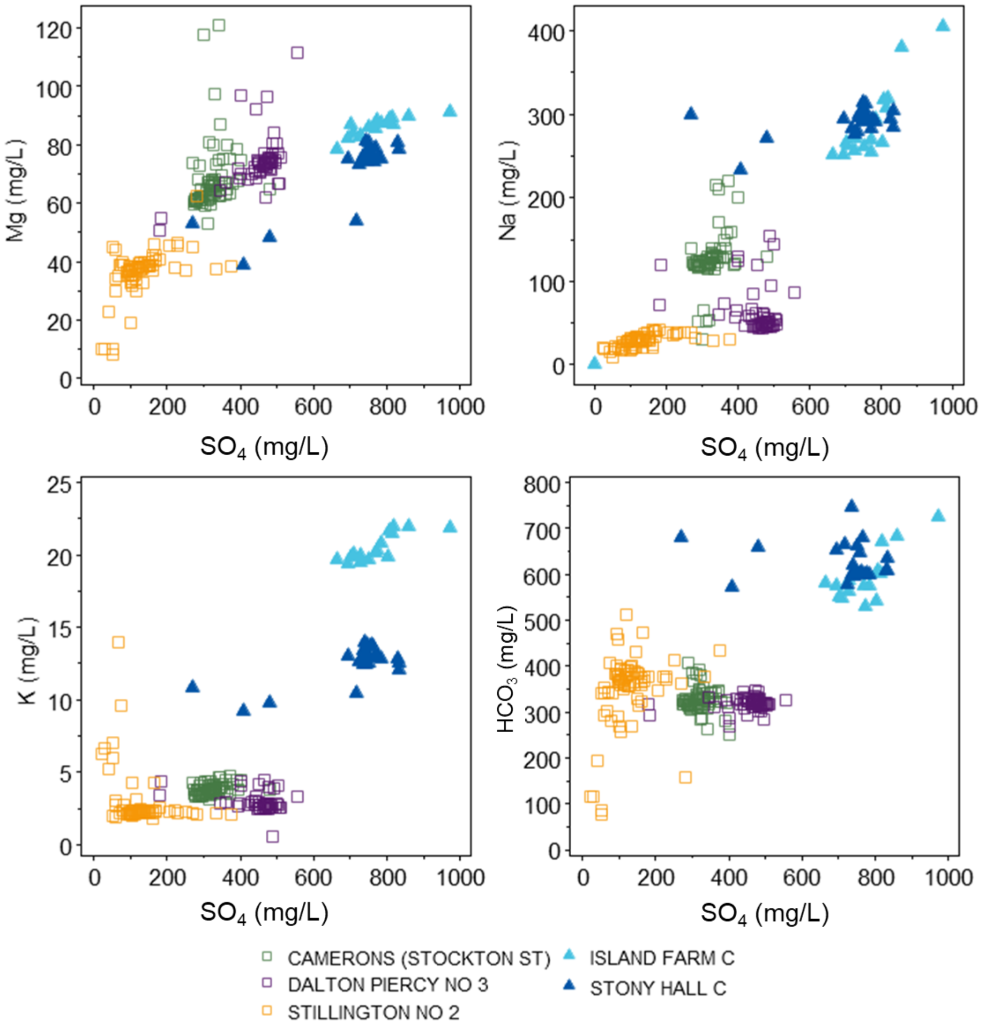


Figure 22 Mg-SO$_4$, Na-SO$_4$, K-SO$_4$, HCO$_3$-SO$_4$ plots. Contains Environment Agency data.

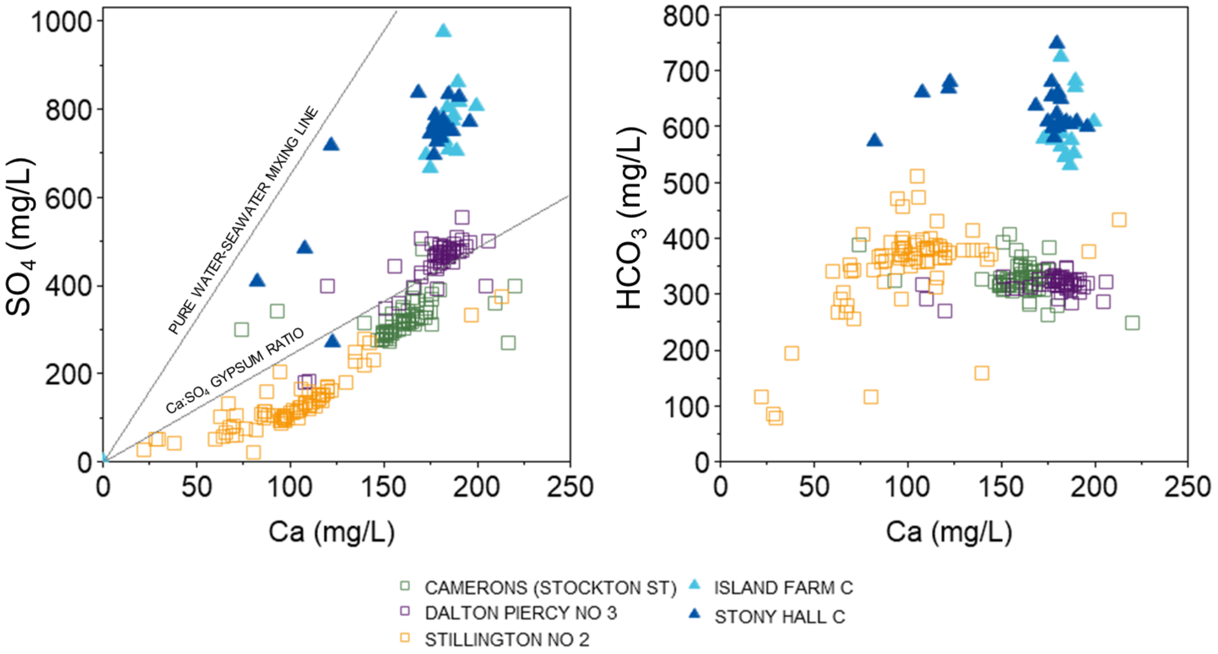


Figure 23 right: SO_4-Ca plot with the pure water – seawater dilution line and the gypsum dissolution line; left: HCO_3-Ca plot. Contains Environment Agency data.

In Figure 23 (left), the sulphate versus calcium graph shows that the Dalton Piercy No 3 waters have Ca and SO_4 following a 1:1 stoichiometric relationship, which indicates that the sulphate plausibly comes from the dissolution of gypsum, while Camerons Brewery waters remain just below the line. The “excess” in Ca relative to the gypsum dissolution line, shown by Stillington No 2 instead, is likely related to a higher calcium carbonate (and/or dolomite) component, as shown in the bicarbonate versus calcium graph (Figure 23, right). The Coal Measures waters have a SO_4/Ca ratio much higher than gypsum and with greater alkalinity (HCO_3), presumably due to the enhanced carbonate dissolution associated to the neutralisation of H_2SO_4 from coal pyrite oxidation in the coal mine aquifer.

Strontium (Sr) is an indicator of groundwater residence time in carbonate aquifers. It is also highly enriched in brines with levels controlled by strontium-containing barite or barite saturation. The element is present in both calcite and gypsum. Sr is enriched in all these groundwaters, with the greatest enrichment in Stony Hall C, while the other Coal Measures borehole Island Farm C shows similar concentrations to Dalton Piercy No 3, Stillington No 2, and Camerons Brewery; Figure 24 explores the relationships between Sr and Ca, HCO_3 and SO_4. A correlation is noted between Sr and SO_4 within each of the Magnesian Limestone boreholes, but not those of the Coal Measures and a correlation is noted between Sr and Ca within each of the boreholes. Strontium correlation with HCO_3 in each borehole is not strong. A possible interpretation of the above data is that in the Magnesian Limestone boreholes Dalton Piercy No 3, Stillington No 2, and Camerons Brewery the strontium contribution is mainly from evaporite minerals, which accounts for the linear correlation between Sr and Ca, SO_4 rather than HCO_3. The lack of a correlation between sulphate and strontium in the Coal Measures borehole waters suggests other/additional sources of strontium.

Fluoride (F) concentrations are the lowest in the Coal Measures borehole waters due to the relative abundance of dissolved Ca.

The apparent enrichment in lithium (Li), boron (B), bromide (Br) (Figure 25, Figure 26, Figure 27), together with high Sr, Na and K of Stony Hall C and Island Farm C could suggest a contribution from deep-seated, brackish to saline groundwaters typical of the deep coal-bearing strata in their unmined state, given a similar enrichment described by Edmunds (1975). Differences between the relative enrichment of these tracers in the two Coal Measures boreholes requires further interpretation.

There is a broad trend of increasing Li with the groundwater K and Na (Figure 26), as Li concentrations are likely to be proportional to the extent of water interaction and residence time.

Bromide to chloride ratio is extensively used in understanding sources of salinity. Different original sources of salt would result in distinct ranges of Br/Cl ratios. Seawater has a constant Br/Cl mass ratio of 0.00347. The Br/Cl ratio is higher in brines of the NE England Coalfield (Br/Cl mass ratio > 0.005, Edmunds, 1975). The Br/Cl ratio in groundwater impacted by dissolution of halite is much lower than the seawater ratio. The Br/Cl vs SO_4 graph in Figure 27 shows that the Coal Measures samples plot towards the typical mass ratio of 0.005 reported for Coal Measures brines, although the same applies to some samples from Dalton Piercy No 3. For the Coal Measures boreholes, the only data available for bromide are from this study, some historical data are also available for the other boreholes. Comparing the boreholes based on the 2024 data only (Figure 28), the differences are more pronounced between the higher ratios in Stony Hall C and Island Farm C and the lower ratios in Dalton Piercy No 3, Camerons Brewery, and Stillington No 2. Camerons Brewery borehole has the Br/Cl ratio closest to seawater.

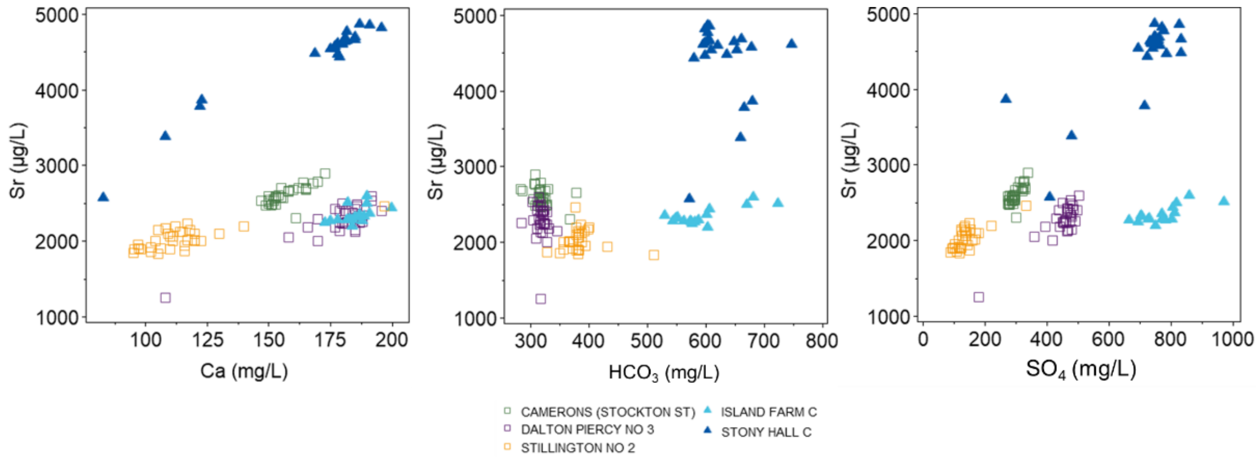


Figure 24 Relationships between Sr and Ca, HCO_3, SO_4. Contains Environment Agency data.

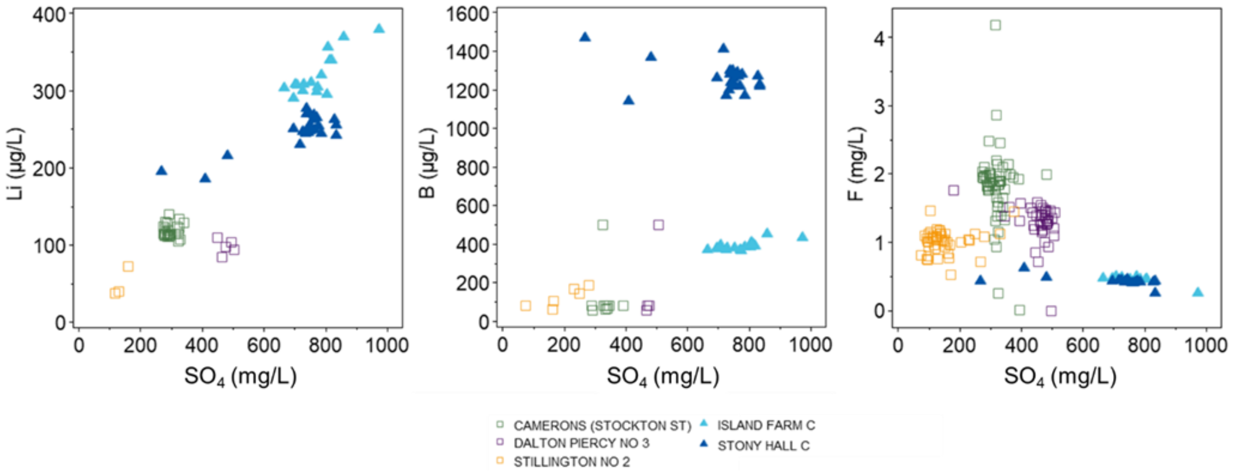


Figure 25 Li-SO_4, B-SO_4, and F-SO_4 plots. Contains Environment Agency data.

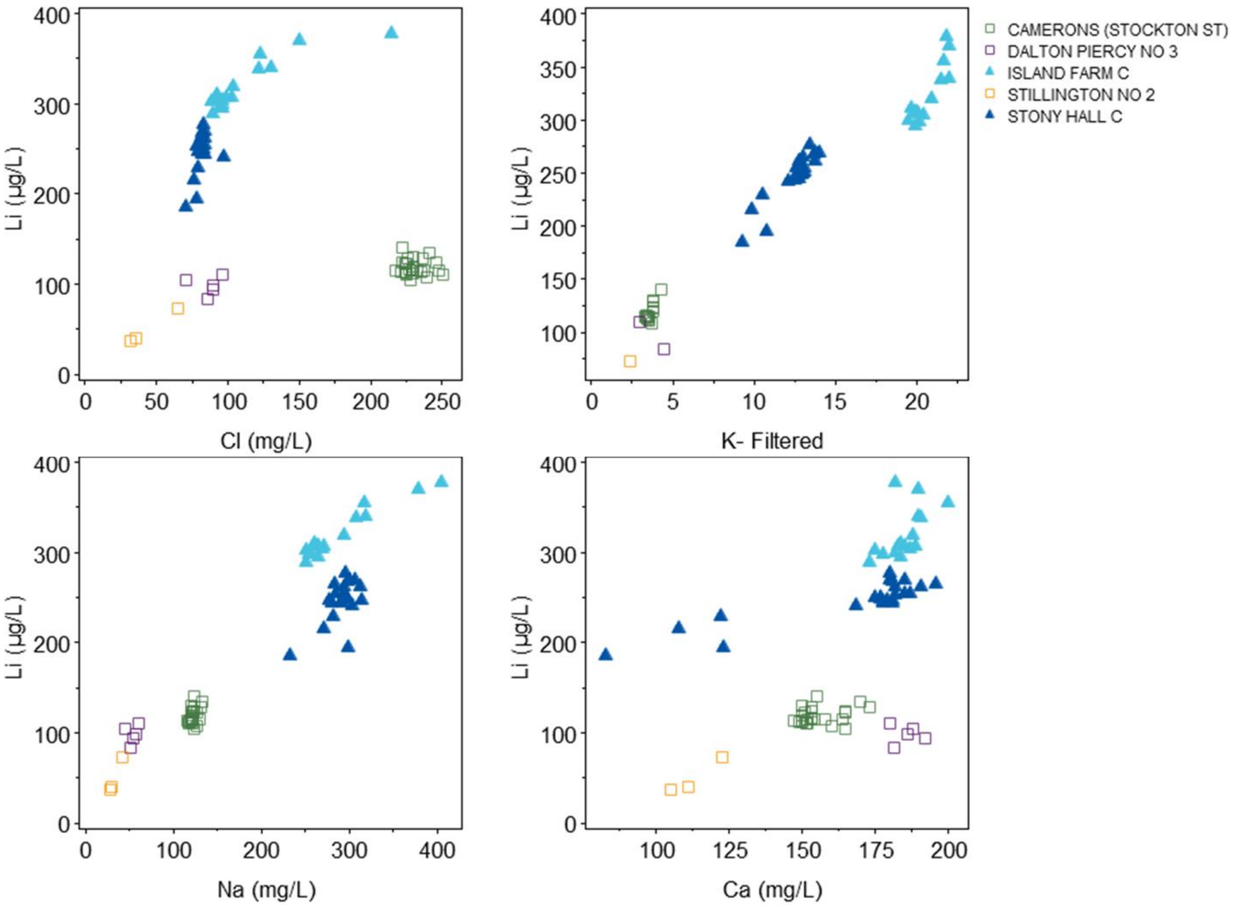


Figure 26 Li-Cl, Li-K, Li-Na, and Li-Ca plots. Contains Environment Agency data.

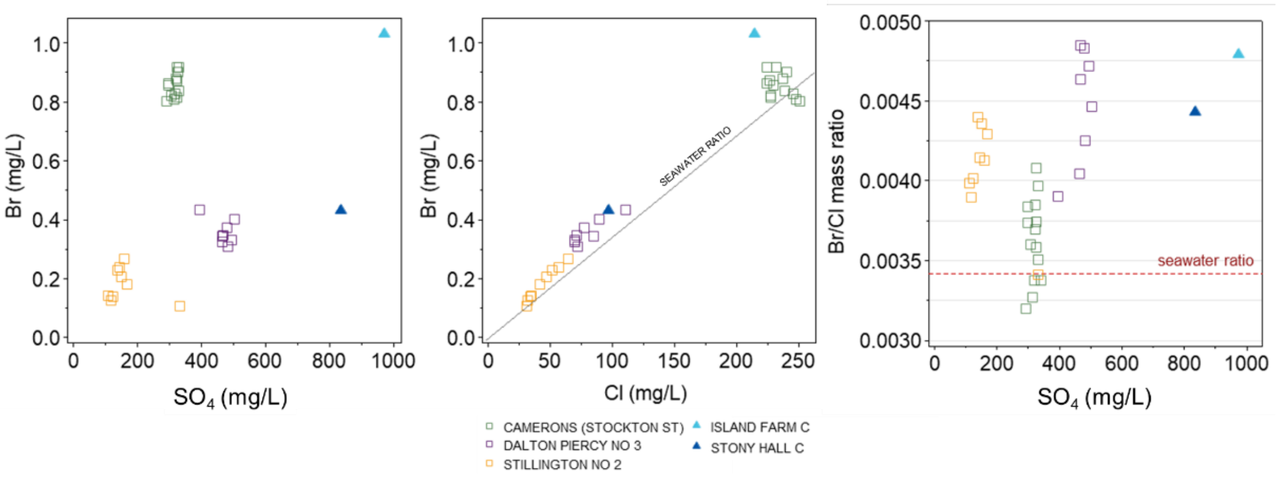


Figure 27 Br-SO_4, Br-Cl, and Br/Cl-SO_4 plots. Contains Environment Agency data.

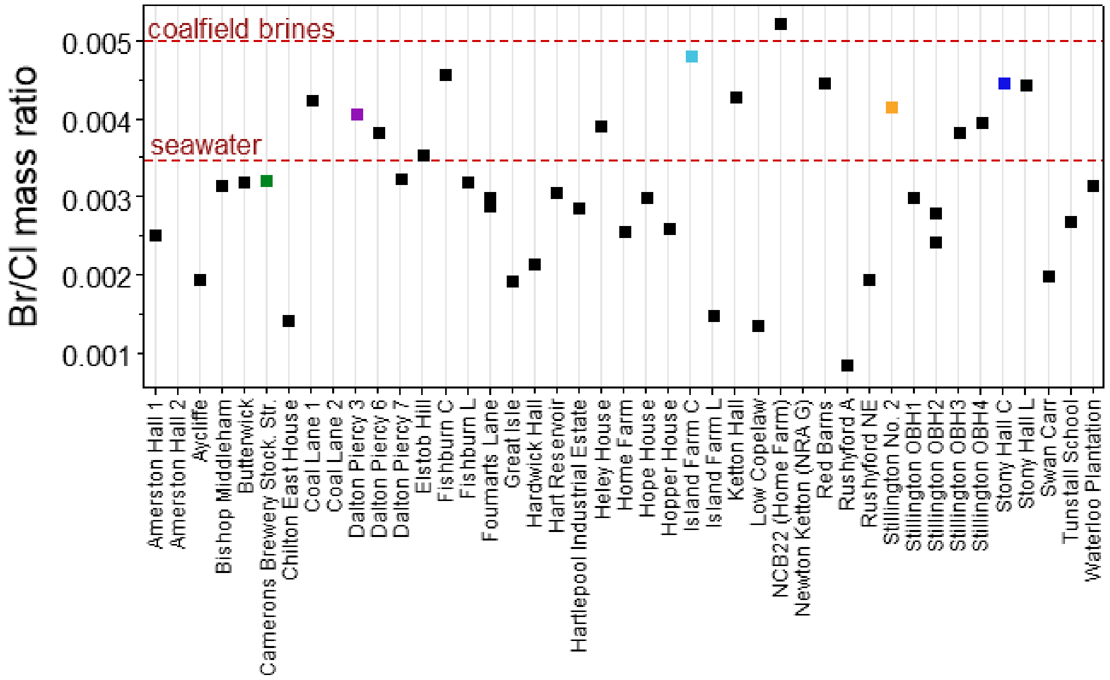


Figure 28 Groundwater Br/Cl mass ratio in all boreholes sampled in 2024.

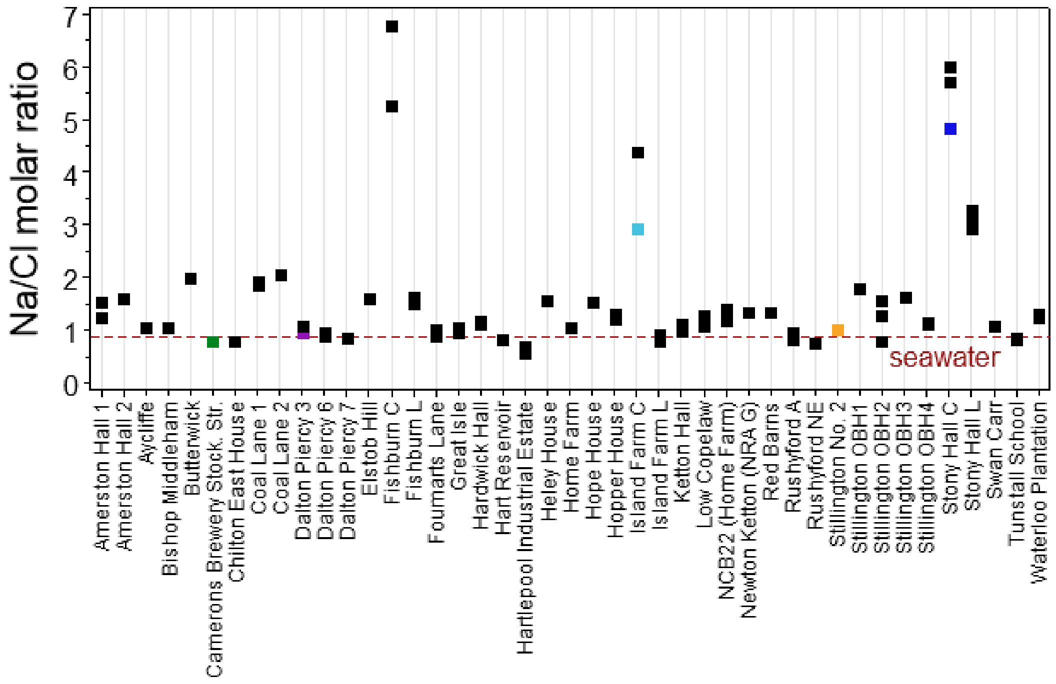


Figure 29 Groundwater Na/Cl molar ratio in all boreholes sampled in 2017, 2018 and 2024.

9 Summary of the main findings and concluding remarks

The study area exhibits a wide range of dissolved sulphate concentrations and S-isotope compositions in groundwater from the Magnesian Limestone aquifer. Sulphate distribution varies from west to east, near the coast, and in dispersed hot spots. Previous investigations identified several sources of sulphate in the Skerne Magnesian Limestone aquifer, including a coal mine water plume, contributions from dissolution of gypsum and anhydrite from Permian evaporites, and seawater intrusion near Hartlepool, likely induced by water abstraction. Over the past two to three decades, anthropogenic pressures contributing to sulphate contamination in the aquifer have decreased, primarily due to the full rebound of mine workings and reduced water abstraction. Consequently, overall sulphate concentrations have decreased in the areas of the aquifer(s) monitored, though some areas still exceed the drinking water standard of 250 mg/L. Given the historical presence of multiple sulphate sources in the groundwater, and their transient nature, understanding the present-day system is challenging.

This study complements earlier investigations with new hydrochemical and isotopic data (including sulphur and oxygen isotopes of sulphate and water stable isotopes) to evaluate the relative contributions of sulphate sources and understand the geochemical processes in the aquifer. In a previous BGS study, which was the first to analyse sulphur isotopes in the coal mine water from the area, little difference was found between the sulphur isotope composition of the mine water sulphate and that of the Permian evaporites, or of the seawater. Recent research indicates that ^{34}S-enriched sulphate with values closer to a marine sulphate signature is indeed widespread in coal mine water across the UK and other European coal mining regions (Banks and Boyce, 2023). By carrying out this study, it was possible to further evaluate the potential and limitation of the application of sulphur isotopes as environmental tracers in the study settings. The data were complemented by water isotope data and hydrochemical data. The main findings of the geochemical and isotopic characterisation of the 39 boreholes investigated, with a focus on sulphate, are reported below; however, much more information is contained in each section of the report.

Coal Measures groundwaters

The 2024 sampling confirmed that the mine waters have a dominant component of meteoric water rather than formation water, consistent with findings in many other coalfields. An isotope signature slightly depleted in ^{18}O and ^{2}H compared to the main Magnesian Limestone aquifer group was observed at Stony Hall C and Island Farm C Coal Measures boreholes. Based on the data (although limited) from two sampling dates, some observations can be made: if the water isotope data remain consistent, it may indicate recharge from a reservoir with well-mixed waters. This would support a flow conceptual model suggesting a Permian aquifer source of recharge to the mine workings, rather than recharge through shallow workings, which would likely result in greater variability in the isotopic signature.

Both Stony Hall C and Island Farm C mine waters have ^{34}S-enriched sulphate, consistent with previous observations from EU and UK flooded coal mine systems, confirming that the origin of dissolved sulphate in coal mine waters cannot be fully explained by pyrite oxidation. Similar to the water δ^{18}O and δ^{2}H, the sulphur isotope ratios are remarkably constant, with average sulphate δ^{34}S +13.2‰ (SD 0.3) at Stony Hall C and +23.3‰ (SD 0.1) at Island Farm C. The latter is significantly higher than the δ^{34}S of Permian gypsum, which is +10.9‰ and slightly higher than the δ^{34}S of seawater (+21.2‰). They are of Na-SO_4 water type and have SO_4/Cl and Na/Cl molar ratios much greater than modern seawater. These ratios indicate that there are sources of sulphate and sodium other than sea water. The apparent enrichment in lithium, boron, bromide, together with high strontium, sodium and potassium of Stony Hall C and Island Farm C could suggest a contribution of carboniferous brines to the mine waters to account for some of the salinity. Processes of desorption of alkali metals from minerals might have affected the water composition. The Br/Cl mass ratio of 0.005, greater than the constant seawater ratio of 0.0034, is also an indication of brine contribution. However, compositional differences between the two mine waters warrant further investigation for a more thorough interpretation.

Although samples collected from both Stony Hall C and Island Farm C boreholes were deeper in 2024 compared to 2018, the difference is not apparent in the water composition.

By contrast, the large variability in $\delta^{18}O$ and $\delta^{2}H$ at Fishburn C between 2018 and 2024 could be due to sampling at different depths in a stratified groundwater system. Similar variability was observed in the chemical composition with SO_4 <10mg/L in 2018 and 177 mg/L in 2024. Given the latest increase in sulphate content at Fishburn C, it was possible to analyse the sulphate $\delta^{34}S$ in this sampling round and it was found to be +18.8‰ with a corresponding $\delta^{18}O$ value of +10.1‰. Should this $\delta^{34}S$ value be confirmed in future sampling, it would further support the presence of ^{34}S-enriched mine waters in the mine water block.

Magnesian Limestone groundwaters historically impacted by the mine water plume

The strong connectivity between Stony Hall C Coal Measures borehole and the paired Stony Hall L Magnesian Limestone borehole, inferred from the 2018 water isotopes, has been confirmed. This results in elevated sulphate concentrations in the Magnesian Limestone borehole (650 mg/L in January 2024).

On the evidence of the sulphur and oxygen isotopes of dissolved sulphate, it appears that, aside from that specific occurrence mentioned above, the other monitored boreholes in the Magnesian Limestone aquifer, historically impacted by mine water rebound, derive their dissolved sulphate from the oxidation of sulphide minerals rather than from a ^{34}S-enriched source like the deep mine water sampled at Stony Hall C or Island Farm C. An evaporite mineral dissolution source, as only source of sulphate, is also unlikely. The sulphate concentrations in these boreholes range from <1 mg/L to 240 mg/L, hence below the drinking water standard (DWS) of 250 mg/L. The sampling in 2024 has highlighed that all the resampled boreholes but one have variable $\delta^{34}S$ between the sampling dates, also associated to variable sulphate concentrations. The impact of the different sampling depth between 2018 and 2024 on the variability is unclear. In many cases there is evidence of the impact of reducing conditions, in the borehole water sampled, on some of the lower sulphate concentrations and higher S isotope ratios values.

Magnesian Limestone groundwaters outside the historical mine water plume

The sulphur and oxygen isotope compositions of the dissolved sulphate, indicate that, despite the presence of evaporites in the geological sequence, gypsum is not a major contributor to the sulphate baseline concentrations measured in boreholes such as e.g. Hardwick Hall, Amerston Hall 1, Hope House, and Hopper House. These groundwaters with low sulphate concentrations contain isotopically depleted sulphate (both sulphur and oxygen), which is more typical of sulphate derived from the oxidation of sulphide minerals.

The Dalton Piercy group of boreholes

The previous isotope study (Palumbo-Roe et al. 2021) included one sample each taken from Dalton Piercy BH3 and BH6 in 2018. The other boreholes at Dalton Piercy (including BH7 which is the “low sulphate” borehole) were not sampled. On the evidence of the isotope data, it was concluded that given the similarity of the $\delta^{34}S$ values to the Permian evaporites and the presence of anhydrite or gypsum noted in the logs, a gypsum dissolution source was plausible. In this study we followed the recommendation of WSP (2023) to undertake the sulphur isotope analysis of groundwater from BH7.

The isotopic signature of sulphur in the dissolved sulphate of boreholes Dalton Piercy No 3 and Dalton Piercy No 6 in 2024 was consistent with the 2018 samples, with $\delta^{34}S$ values of +10.5‰ and +10‰ respectively. The $\delta^{18}O_{SO4}$ in these boreholes is +9.5‰ and +9.8‰. Dalton Piercy No 6 differed from the other two in a slightly higher $\delta^{34}S$ of +12.1‰ and a lower sulphate concentration of 130 mg/l. The $\delta^{18}O_{SO4}$ in this borehole is +7.2‰.

In the case of overlapping $\delta^{34}S$ ranges of possible sulphate sources in groundwater, like here with both the Permian evaporites and the deep mine waters with a similar ^{34}S-enriched sulphate, it requires using additional information to identify sulphate sources. The Ca/SO_4 molar ratios show that the Dalton Piercy No 3 waters have Ca and SO_4 following a 1:1 stoichiometric relationship, which indicates that the sulphate plausibly comes from the dissolution of gypsum. These data agree with the isotope data showing $\delta^{34}S$ values coincident with the Permian evaporite values and the presence of anhydrite or gypsum noted in the logs.

The Stillington group of boreholes

In this study we analysed groundwater from Stillington No 2, and the four observation boreholes. In 2017 and 2018, Stillington OBH2 and OBH4 were both sampled and analysed. Hydrochemical logging of Stillington OBH2, OBH3 and OBH4 was also carried out.

The repeated analysis of OBH2 and OBH4 confirmed that isotopic fractionation during bacterial reduction of sulphate overprints the isotopic composition of the source. Borehole stratification was observed during the hydrochemical logging of the physicochemical parameters and it is likely that localised conditions favourable to reducing the sulphate have been created. The other newly sampled boreholes are relatively low in sulphate and have very similar δ^{34}S values of +8.7‰, +8.6‰ and δ^{18}O of +9.7‰ and +9.2‰, and very close values to Dalton Piercy No 3 and No 6 boreholes. The other borehole OBH1 has much lower sulphate concentrations (49 mg/L) and a δ^{34}S values of +4.4‰ and δ^{18}O of +7.7‰.

The saline boreholes near Hartlepool

The saline boreholes all have very variable isotopic composition and sulphate concentration (as shown in Figure 13). The temporal variability combined with the potential impact of different sampling depths between 2018 and 2024, makes the interpretation of these results uncertain in terms of addressing the source of sulphate. Additionally, some of the isotopic composition might have been modified by microbial reduction. In general, assuming the lack of sulphate microbial reduction, SO_4 concentrations around 150 mg/L, $\delta^{34}S_{SO4}$ +12‰ and $\delta^{18}O_{SO4}$ +8‰, observed at Hartlepool Industrial Estate Replacement, could be due to the contribution of more than one source of ^{34}S-enriched sulphate including seawater.

Camerons Brewery Stockton Street, sampled for the first time in 2024, with SO_4 of 291 mg/L, with $\delta^{34}S_{SO4}$ +9.9‰ and $\delta^{18}O_{SO4}$ +9.5‰, might derive its sulphate from dissolution of local evaporites, as the sulphur isotope value is too low for a large contribution of seawater. However, the Br/Cl mass ratio, and Na/Cl molar ratio values in 2024, suggest a seawater contribution for those elements.

Redox processes in the aquifer

The current conceptual model of the Skerne Magnesian Limestone aquifer, developed by WSP (2023), indicates that the unconfined part of the aquifer (broadly corresponding to our study area) is dominated by oxidising conditions, which transition to more reducing conditions in the confined part of the water body, located to the east of Newton Aycliffe and Sedgefield.

The sulphur isotopes of sulphate, in combination with very low dissolved oxygen in some of the boreholes sampled in 2024, suggest the occurrence of sulphate-reducing conditions. As a result of the chemical reaction, sulphate concentrations are lowered. In a parallel study (Bowes et al. 2024), some of these boreholes were subject to geochemical depth profiling which showed important water stratification in the borehole. An extreme case was the Heley House borehole with a very low SO_4 concentration of 0.13 mg/L within the cased section, which prevented the analysis of the sulphur isotopes.

Therefore, it is thought that these redox conditions are niches of limited extent or effect of water stratification in the cased borehole sections, and not inferred as representative aquifer conditions., Iit would be important to investigate the earlier and newly-collected data more thoroughly to assess their representativeness of the aquifer.

The overprinting of SO_4 reduction on the measured sulphate concentrations and the effects of artefacts should be studied prior to evaluating the contribution of the various sources to the aquifer sulphate concentrations.

Rising trends in sulphate concentrations

Analysis of time series was outside the scope of the report. However, it is clear that sulphate concentrations have been increasing, at least over the last 5 years up to 2024 in groundwater from Stony Hall C, Stony Hall L, Island Farm C (among the high sulphate boreholes), and Amerston Hall No 1, and No 2, Coal Lane No 1 and No 2, Hope House, Hopper House, Red Barns, Waterloo Plantation, and possibly Bishop Middleham (among the relatively low sulphate boreholes).

10 Recommendations

Recommendations for further assessment are outlined below.

Coal Measures groundwaters

A limited water isotope dataset of the Coal Measures (CM) aquifer(s) was obtained consisting of three boreholes sampled twice, with preliminary observations on recharge mechanisms. Consideration should be given to designing a programme of chemistry and water-isotope monitoring of these sites and selected adjacent Magnesian Limestone (ML) boreholes to address the source(s) of recharge and connectivity. The use of additional environmental tracers of groundwater residence time might be beneficial, potentially including δ^{13}C-DIC, ^{87}Sr/^{86}Sr, and CFCs/SF_6 along with a comprehensive suite of trace elements (e.g. Co, Ni, Pb, Rb, Sr, Li, Cs) and previously measured analytes.

The Stillington group of boreholes

More targeted hydrochemical investigation is needed to be able to review WSP (2023) assumptions regarding the source of the sulphate in the Stillington group boreholes. This should be based on future collection of samples representative of the open-hole aquifer conditions.

The saline boreholes near Hartlepool

Given the spatial and temporal variability within the area of Hartlepool, a more detailed analysis of existing data and further sampling is recommended to investigate the source of salinity. Future sampling should be representative of the aquifer conditions and not be taken from cased sections.

Redox processes in the aquifer

Sulphur isotopes point to microbial reduction of sulphate in groundwater from some boreholes. It is thought that these strongly reducing conditions are redox niches of limited extent or are an effect of in-borehole water stratification. Investigating the existing chemical data from the cased borehole sections, including available data for redox-sensitive parameters (DO, Eh, NO_3, NH_4, As, U, Se, Fe, Mn, Mo), would help to clarify the impact of in-borehole artefacts and the representativeness of previously collected data. It would also help to guide future sampling strategies.

A more thorough investigation of the redox conditions in the groundwater from the openhole/screened sections of the aquifer is also warranted, at least using existing water chemistry data, although obtaining a comprehensive dataset might involve new sampling.

Rising (and falling) trends in sulphate concentrations

It is is recommended that where sulphate trends in groundwater occur, they be assessed further. This should involve aggregating the data with other available quality indicators and where possible, with groundwater levels and pumping histories, to explore the underlying causes of the variations, including the sometimes notable spikes in concentrations.

Appendix 1 Piper plots

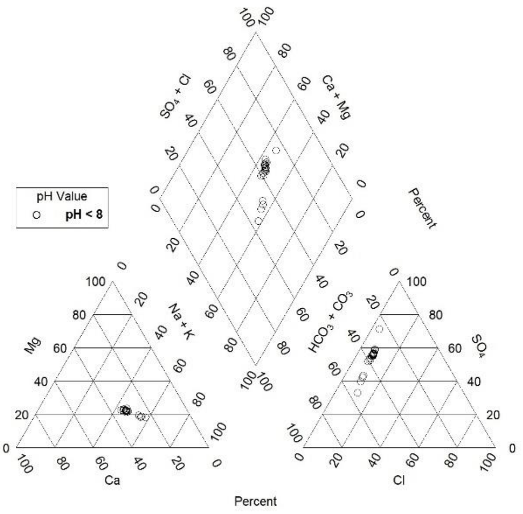
This Appendix reports the Piper plots for the following boreholes using the WIMS database up to 2022. Contains Environment Agency water quality data from the Water Quality Archive (Beta) Open WIMS data. This archive is provided as open data under the Open Government Licence with no requirement for registration.

PTCODE	BOREHOLE NAME	GROUP	WATER TYPE	Comments
453H0002	FISHBURN C	Coal Measures	Na-HCO_3	
453H0001	ISLAND FARM C	Coal Measures	Na-SO_4	
453F0295	STONY HALL C	Coal Measures	Na-SO_4	
453F0243	AYCLIFFE (NRA 2)	Mine water plume	Ca-Mg-HCO_3-SO_4	
453F0232	BISHOP MIDDLEHAM	Mine water plume	Ca-Mg-HCO_3	
453F0242	BUTTERWICK	Mine water plume	Ca-Mg-HCO_3	
453F0231	CHILTON EAST HOUSE	Mine water plume	Ca-Mg-HCO_3	
453C0003	FISHBURN L	Mine water plume	Ca-Mg-HCO_3	
453F0285	FOUMARTS LANE	Mine water plume	Ca-Mg-HCO_3	
453F0274	GREAT ISLE (NRA 6)	Mine water plume	Ca-Mg-HCO_3	High pH samples with different composition
454F1111	HELEY HOUSE (NRA K)	Mine water plume	Ca-Mg-HCO_3	With a minor group Na-dominant
453F0292	HOME FARM	Mine water plume	Ca-Mg-HCO_3	
453F0236	NCB 22 (HOME FARM)	Mine water plume	Ca-Mg-SO_4-HCO_3	
453C0001	ISLAND FARM L	Mine water plume	Ca-Mg-HCO_3	
453F0253	KETTON HALL (NRA 26)	Mine water plume	No dominant type	High pH water with Na-Mg-Cl composition
453F0238	LOW COPELAW NO 1	Mine water plume	Ca-Mg-SO_4-HCO_3	
453F0283	NEWTON KETTON (NRA G)	Mine water plume	Mg-HCO_3	High pH water with Na composition
453F0233	RUSHYFORD A	Mine water plume	No dominant type	
453F0234	RUSHYFORD NE	Mine water plume	Ca-Mg-HCO_3	
453F0296	STONY HALL L	Mine water plume	SO_4 with no dominant cations	
453F0239	SWAN CARR (NRA 8)	Mine water plume	Ca-Mg-HCO_3	High pH water with Mg composition
454F1130	AMERSTON HALL NO 1	PWS & Obs Boreholes	Ca-Mg-HCO_3	
454F1129	AMERSTON HALL NO 2	PWS & Obs Boreholes	Ca-Mg-HCO_3	
454F1107	COAL LANE NO 1	PWS & Obs Boreholes	Ca-Mg-Na-HCO_3	
454F1108	COAL LANE NO 2	PWS & Obs Boreholes	Ca-Mg-Na-HCO_3	

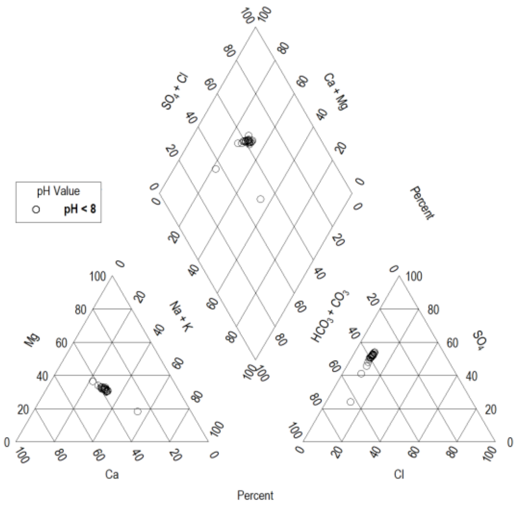
PTCODE	BOREHOLE NAME	GROUP	WATER TYPE	Comments
454F1103	DALTON PIERCY NO 3	PWS & Obs Boreholes	Ca-Mg-Na-SO_4	With some mixing
454F1101	DALTON PIERCY NO 4	PWS & Obs Boreholes	Ca-Mg-Na-SO_4	With some mixing
454F1102	DALTON PIERCY NO 5	PWS & Obs Boreholes	Ca-Mg-Na-SO_4	With some mixing
454F1146	DALTON PIERCY NO 6	PWS & Obs Boreholes	Ca-Mg-Na-SO_4	With some mixing
454F1147	DALTON PIERCY NO 7	PWS & Obs Boreholes	No dominant type	
454F1115	ELSTOB HILL (NRA 15)	PWS & Obs Boreholes	Ca-Mg-HCO_3	With high pH samples of different composition
453F0291	HARDWICK HALL	PWS & Obs Boreholes	Ca-Mg-HCO_3	
454F1112	HOPE HOUSE	PWS & Obs Boreholes	Ca-Mg-HCO_3	With some mixing
454F1110	HOPPER HOUSE	PWS & Obs Boreholes	Ca-Mg-HCO_3	With some trend HCO_3-SO_4
455F0163	RED BARNS	PWS & Obs Boreholes	Ca-Mg-HCO_3	
454F1154	STILLINGTON NO 2	PWS & Obs Boreholes	Ca-Mg-HCO_3-SO_4	Mixing trend Ca-Mg and SO_4-HCO_3
454F1159	STILLINGTON NO 3	PWS & Obs Boreholes	HCO_3-(Cl) with no dominant cations	
454F1161	STILLINGTON OBH1	PWS & Obs Boreholes	Ca-Mg-HCO_3-SO_4	Mixing trend Ca-Mg and SO_4-HCO_3
454F1162	STILLINGTON OBH2	PWS & Obs Boreholes	Ca-Mg-HCO_3-SO_4	Mixing trend Ca-Mg and SO_4-HCO_3, high pH samples with different composition
454F1163	STILLINGTON OBH3	PWS & Obs Boreholes	Ca-Mg-HCO_3-SO_4	Mixing trend Ca-Mg and SO_4-HCO_3
454F1164	STILLINGTON OBH4	PWS & Obs Boreholes	Ca-Mg-HCO_3-SO_4	Mixing trend Ca-Mg and SO_4-HCO_3 , high pH samples with different composition
454F1105	WATERLOO PLANTATION	PWS & Obs Boreholes	Ca-Mg-HCO_3	
455F0170	CAMERONS (STOCKTON ST)	Saline	No dominant type	
455F0160	HART RESERVOIR	Saline	Cl with no dominant cations	With a trend to Na-Cl water with high pH
455F0181	HARTLEPOOL INDUST EST REPL	Saline	Cl with no dominant cations	
455F0161	TUNSTALL SCHOOL	Saline	Ca-(Mg,Na)-HCO_3-(SO_4,Cl)	With some Na-Cl water samples

COAL MEASURES BOREHOLES AND PAIRED MAGNESIAN LIMESTONE BOREHOLES

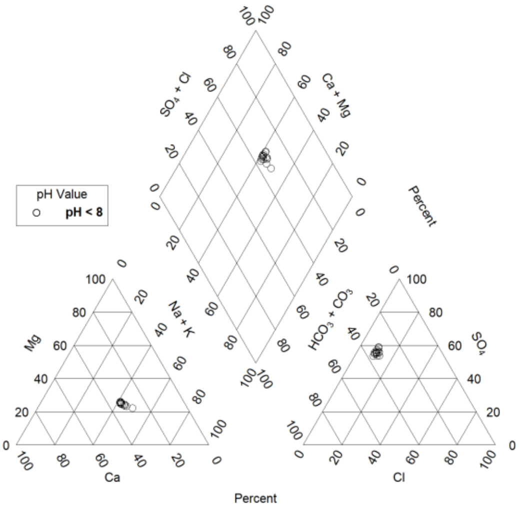
Stoney Hall C



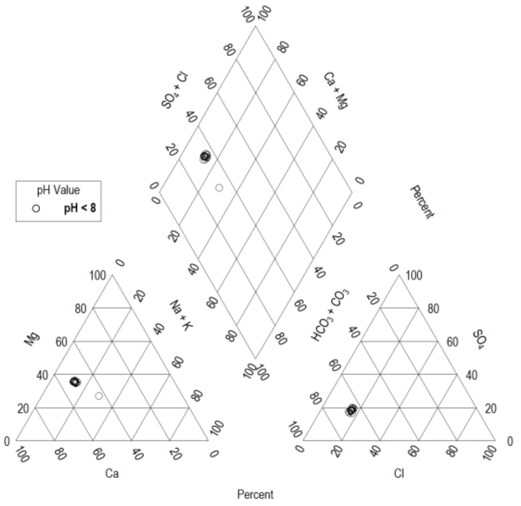
453F0296 - BOREHOLE 25-3-344 STONY HALL L



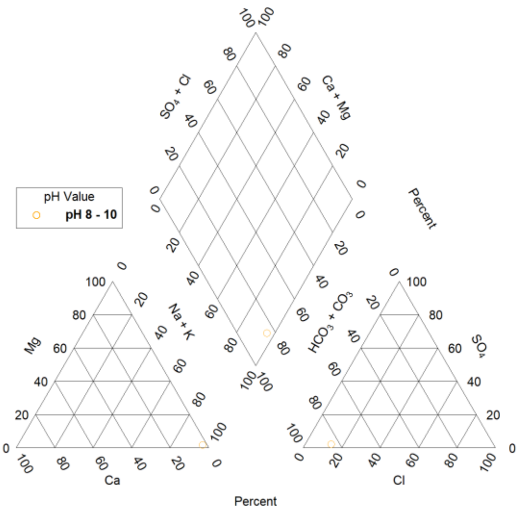
Island Farm C



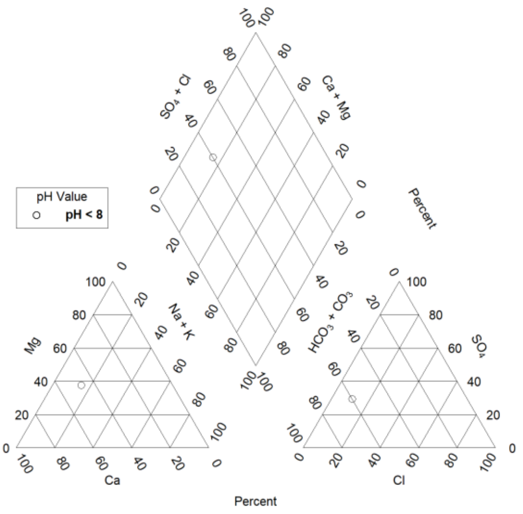
453C0001 - ISLAND FARM L BISHOP MIDDLEHAM BOREHOLE 25-3-353



Fishburn C

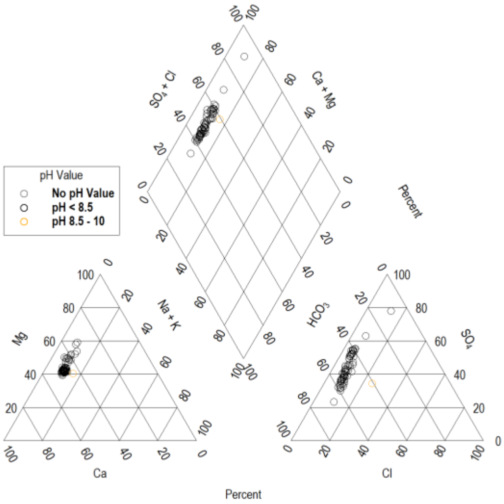


Fishburn L

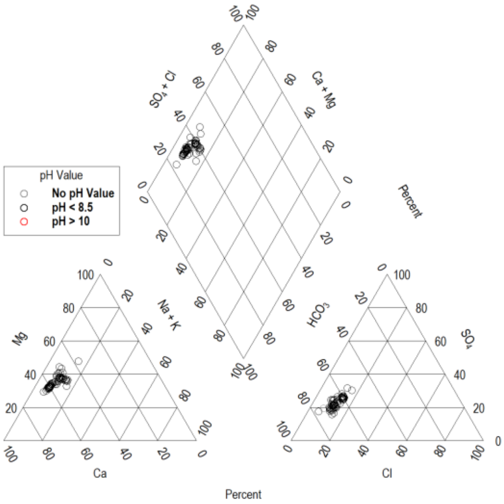


HISTORICAL MINE WATER PLUME BOREHOLES

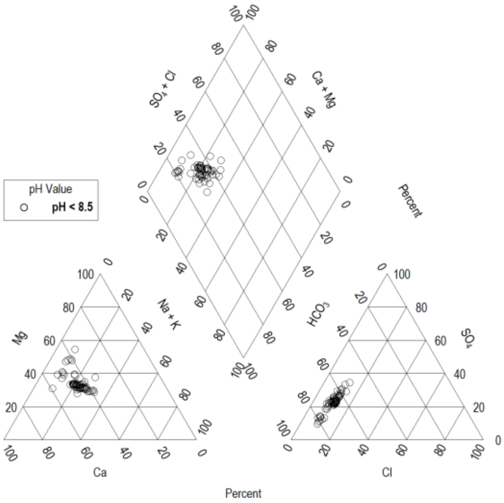
453F0243 - BOREHOLE 25-3-41 AYCLIFFE (NRA 2)



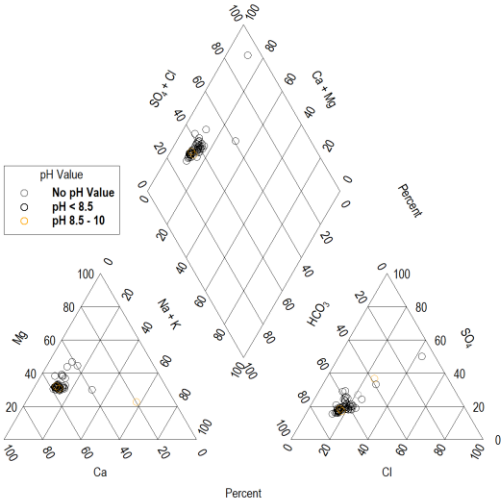
453F0232 - BOREHOLE 25-3-6 BISHOP MIDDLEHAM OBH



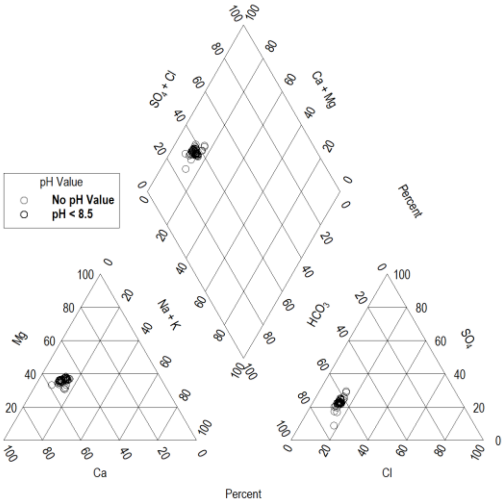
453F0242 - BOREHOLE 25-3-38 BUTTERWICK



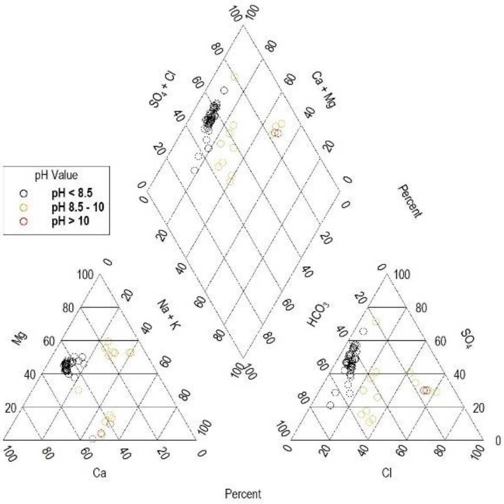
453F0231 - BOREHOLE 25-3-3 CHILTON EAST HOUSE



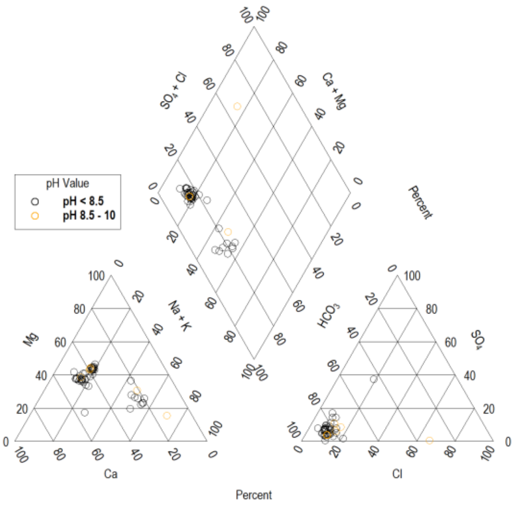
453F0285 - BOREHOLE 25-3-330 FOUMARTS LANE



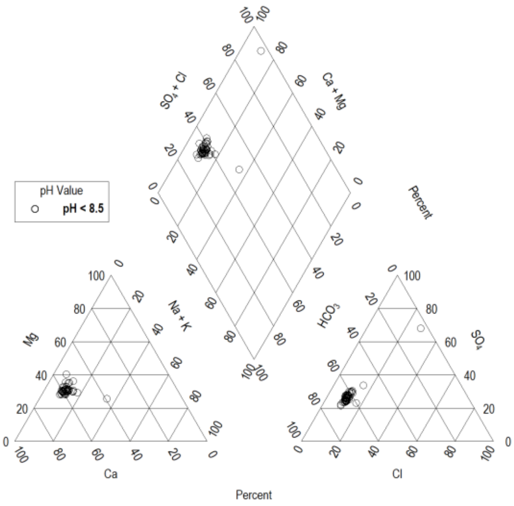
453F0274 - BOREHOLE 25-3-29 GREAT ISLE (NRA 6)



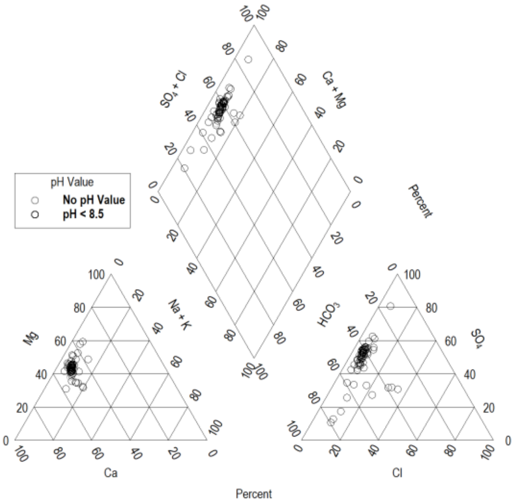
454F1111 - BOREHOLE 25-4-27 HELEY HOUSE (NRA K)



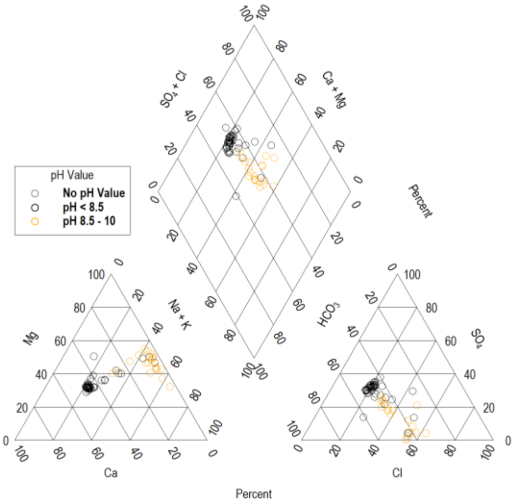
453F0292 - BOREHOLE 25-3-337 HOME FARM



453F0236 - BOREHOLE 25-3-25 HOME FARM (NCB 22)



453F0253 - BOREHOLE 25-3-76 KETTON HALL (NRA 26)



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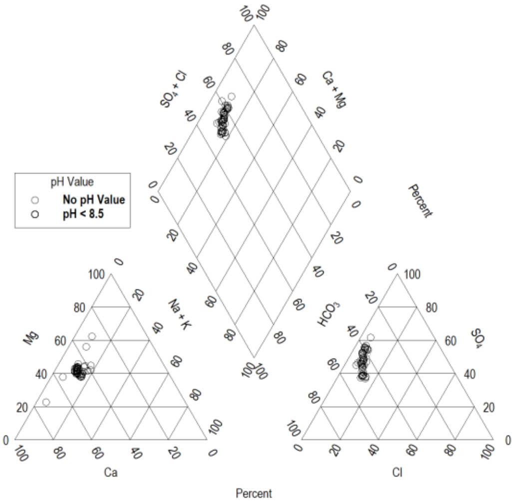
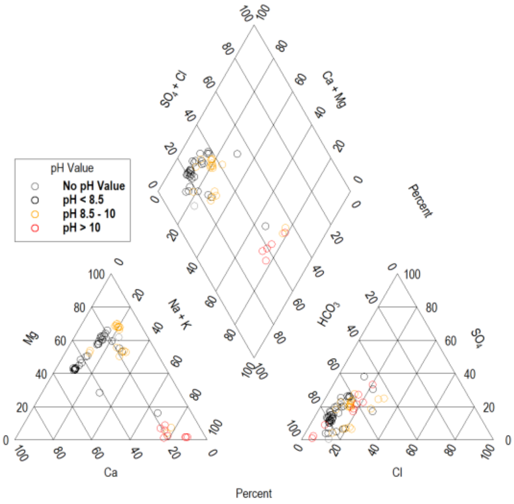


453F0283 - BOREHOLE 25-3-78 NEWTON KETTON (NRA G)



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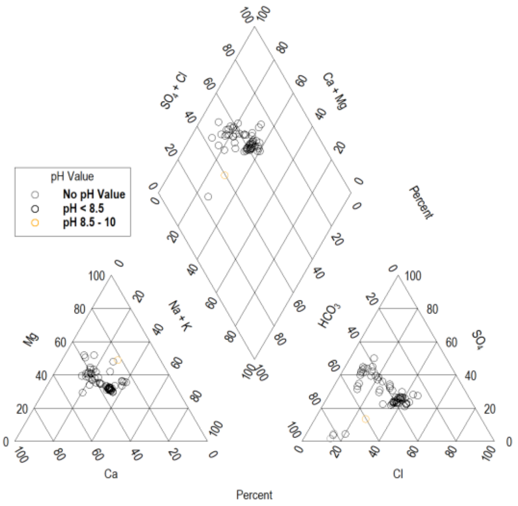
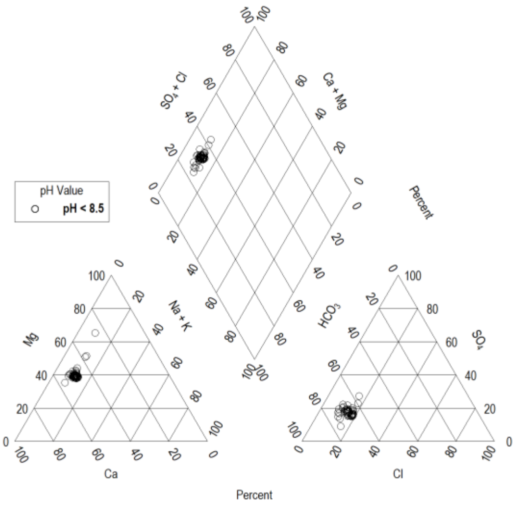
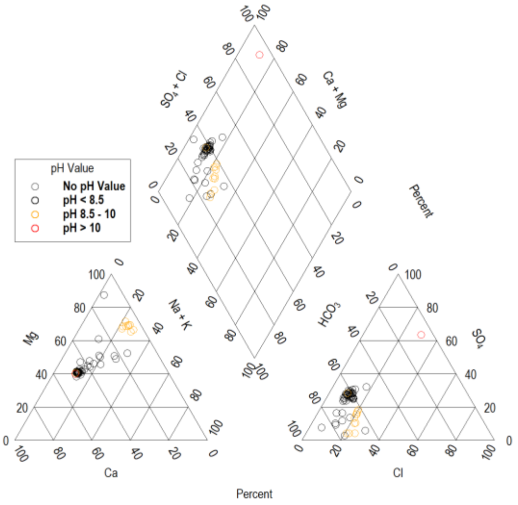


453F0234 - BOREHOLE 25-3-22 RUSHYFORD NE

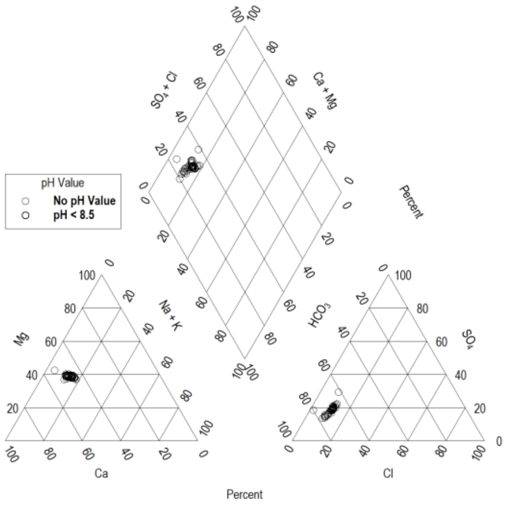


453F0239 - BOREHOLE 25-3-30 SWAN CARR (NRA 8)

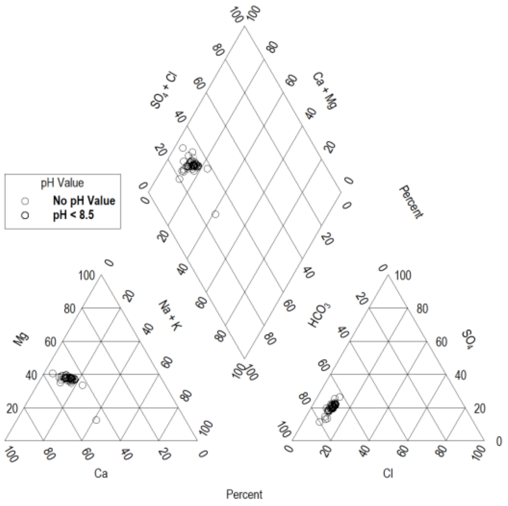


OBSERVATION BOREHOLES AND PUBLIC WATER SUPPLY BOREHOLES

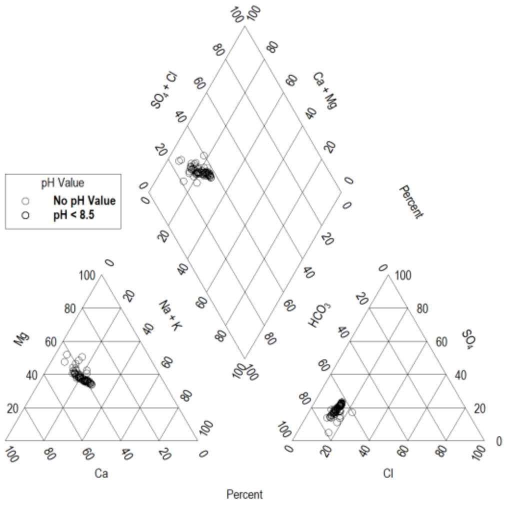
454F1130 - AMERSTON HALL NO 1, BOREHOLE 25-4-8C



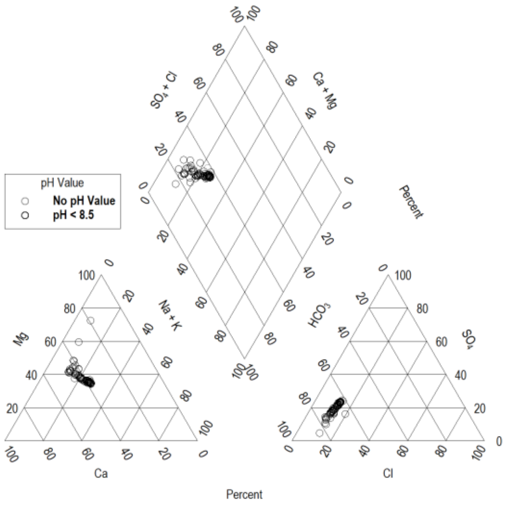
454F1129 - BOREHOLE 25-4-8B AMERSTON HALL NO 2



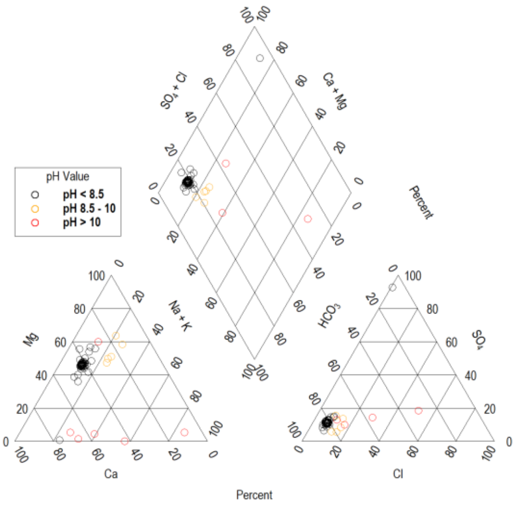
454F1107 - BOREHOLE 25-4-1A COAL LANE NO 1



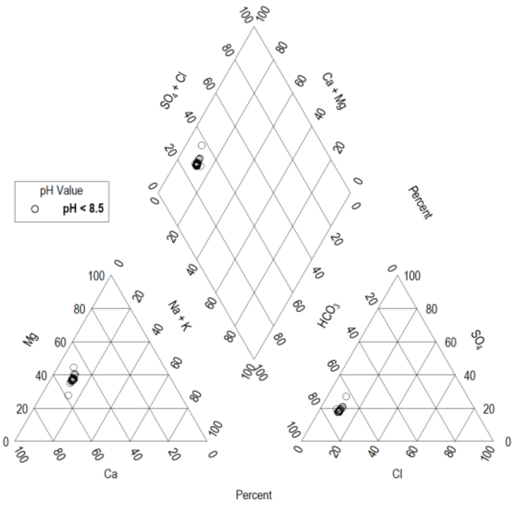
454F1108 - BOREHOLE 25-4-1B COAL LANE NO 2



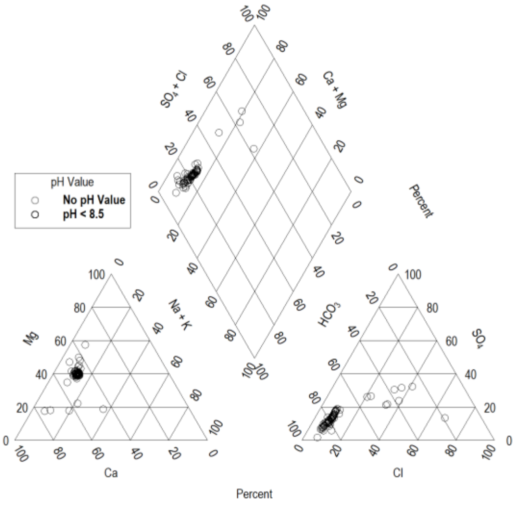
454F1115 - BOREHOLE 25-4-35 ELSTOB HILL (NRA 15)



453F0291 - BOREHOLE 25-3-336 HARDWICK HALL



454F1112 - BOREHOLE 25-4-28 HOPE HOUSE



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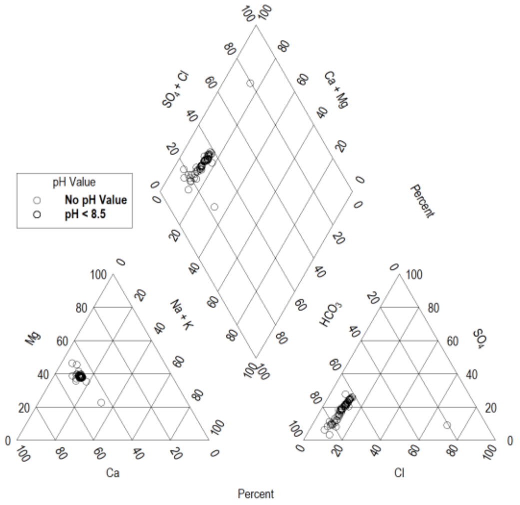
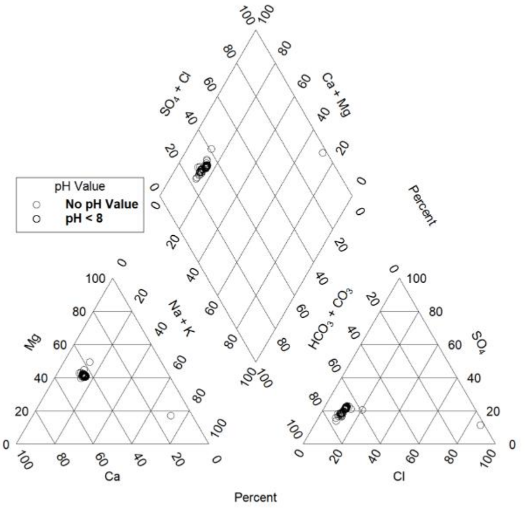
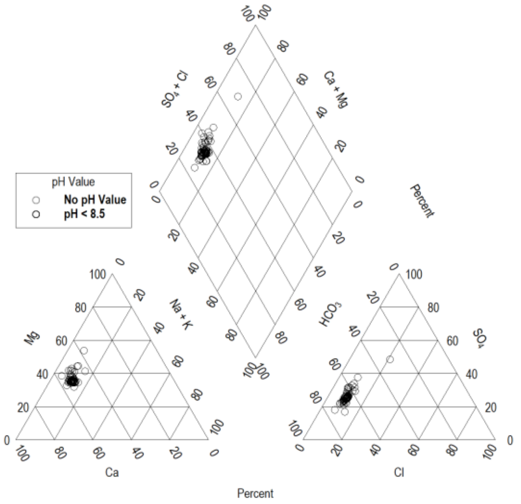


455F0163 - BOREHOLE 25-5-179 RED BARNS

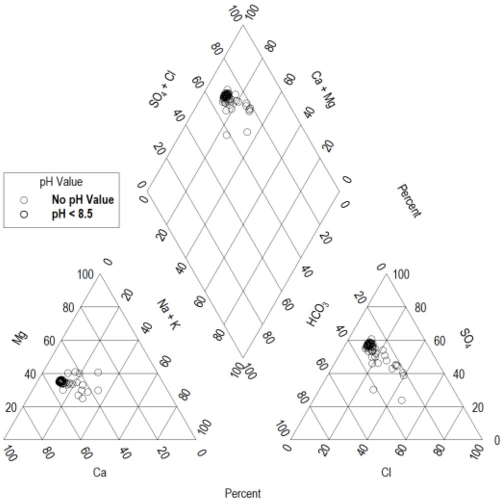


454F1105 - BOREHOLE 25-4-9 WATERLOO PLANTATION

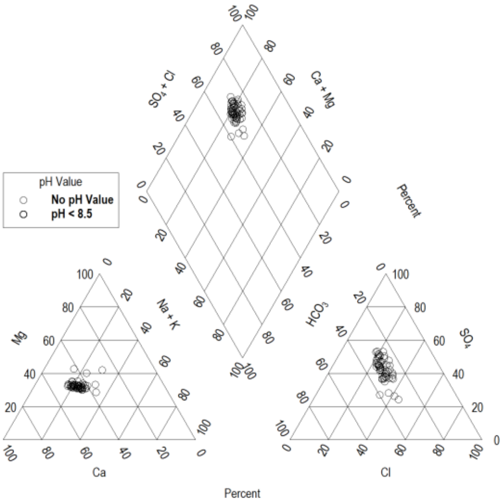


Dalton Piercy Group

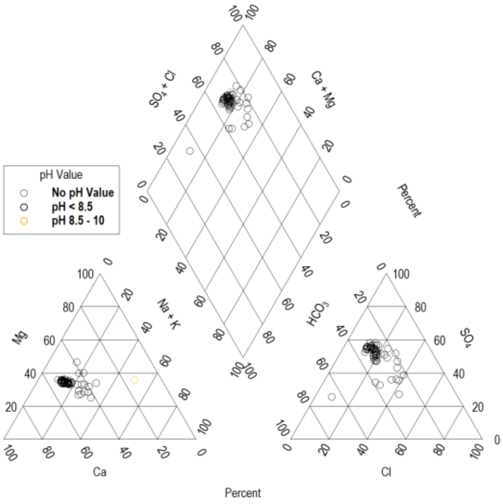
454F1103 - BOREHOLE 25-4-6 DALTON PIERCY NO 3



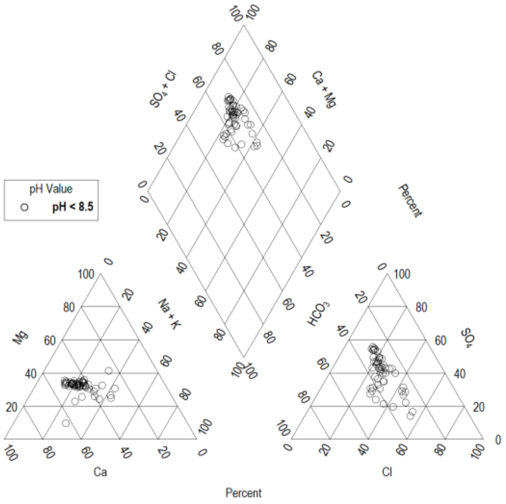
454F1101 - BOREHOLE 25-4-4 DALTON PIERCY NO 4



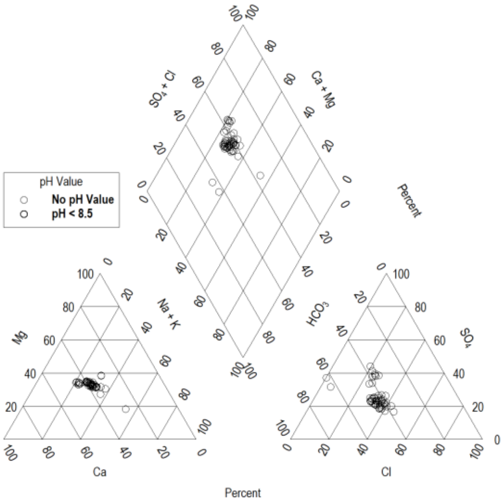
454F1102 - BOREHOLE 25-4-5 DALTON PIERCY NO 5



454F1146 - BOREHOLE 25-4-180 DALTON PIERCY NO 6

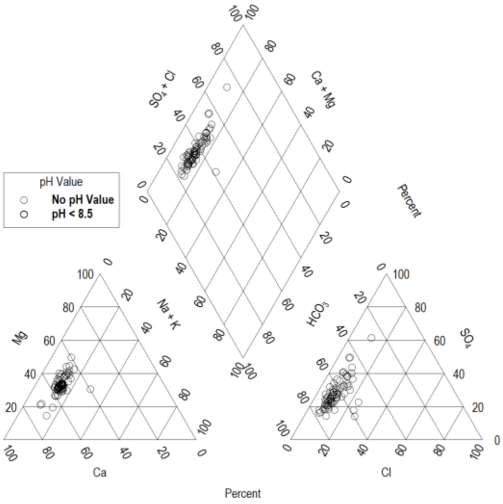


454F1147 - BOREHOLE 25-4-181 DALTON PIERCY NO 7

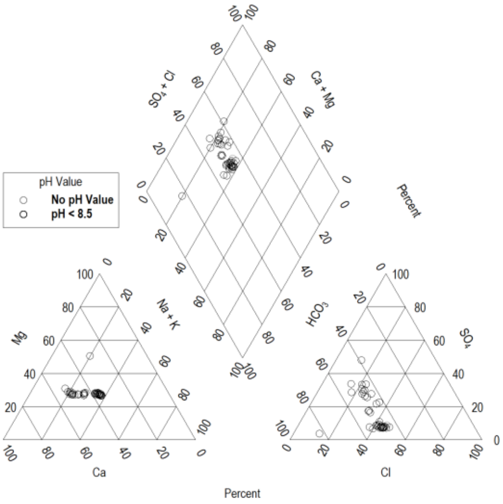


Stillington Group

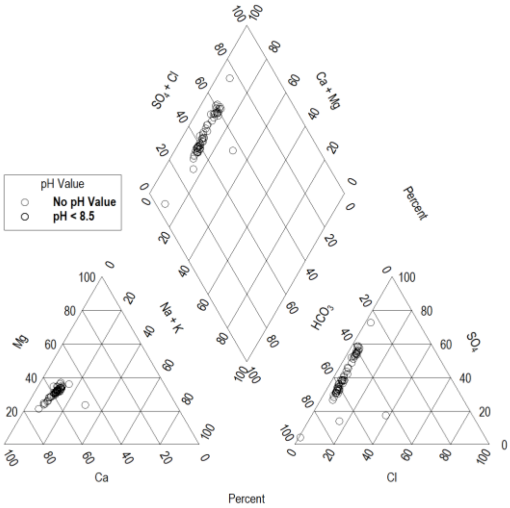
454F1154 - BOREHOLE 25-4-34B STILLINGTON NO 2



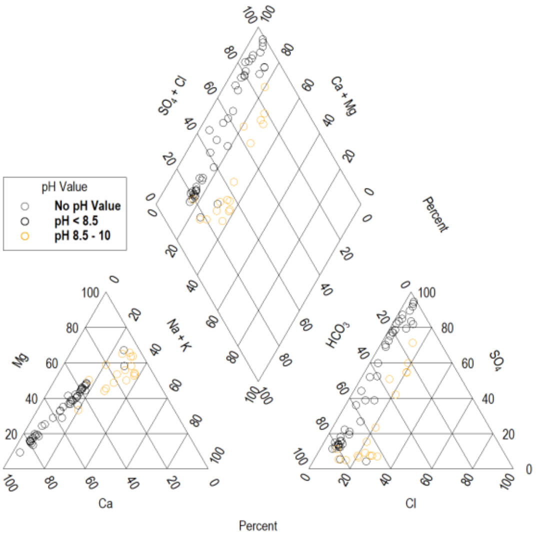
454F1159 - BOREHOLE 25-4-34C STILLINGTON NO 3



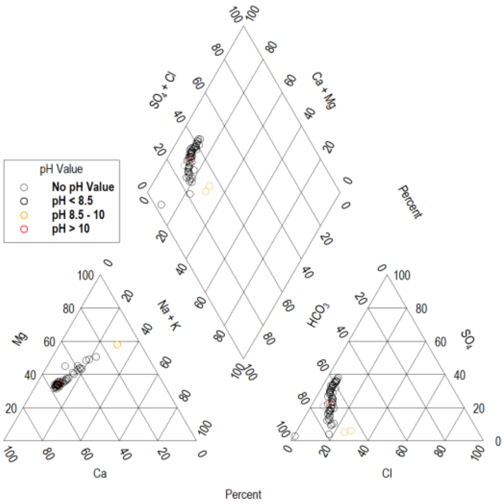
454F1161 - BOREHOLE 25-4-342 STILLINGTON OBH1



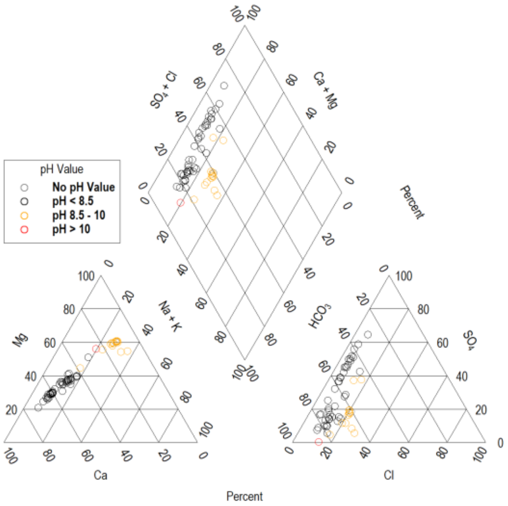
454F1162 - BOREHOLE 25-4-343 STILLINGTON OBH2



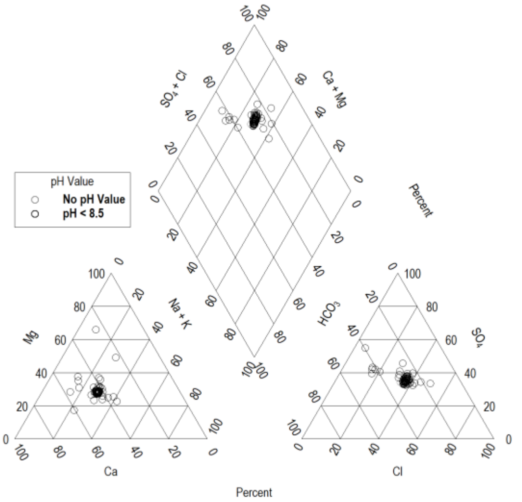
454F1163 - BOREHOLE 25-4-344 STILLINGTON OBH3

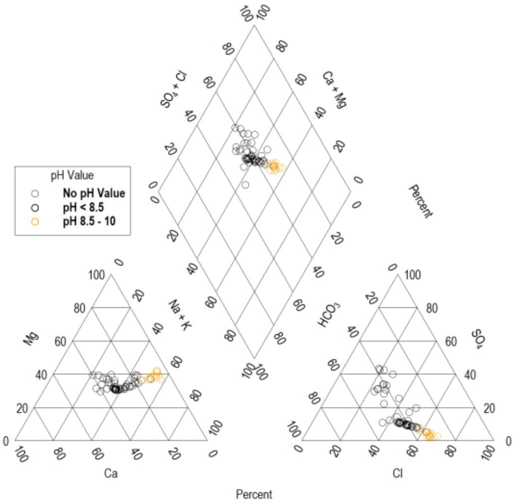


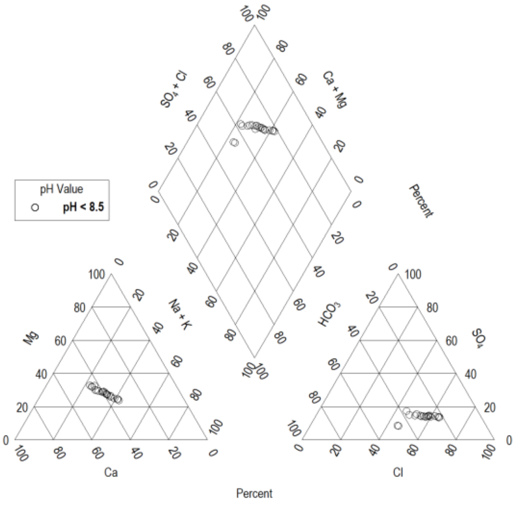
454F1164 - BOREHOLE 25-4-345 STILLINGTON OBH4

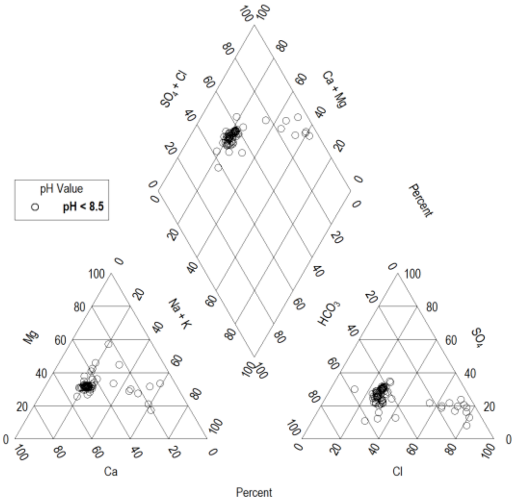


SALINE BOREHOLES


455F0170 - BOREHOLE 25-5-50A CAMERONS (STOCKTON ST)


455F0160 - BOREHOLE 25-5-111 HART RESERVOIR


455F0181 - BOREHOLE 25-5-112B, HARTLEPOOL INDUSTRIAL ESTATE REPLACEMENT BOR


455F0161 - BOREHOLE 25-5-113 TUNSTALL SCHOOL

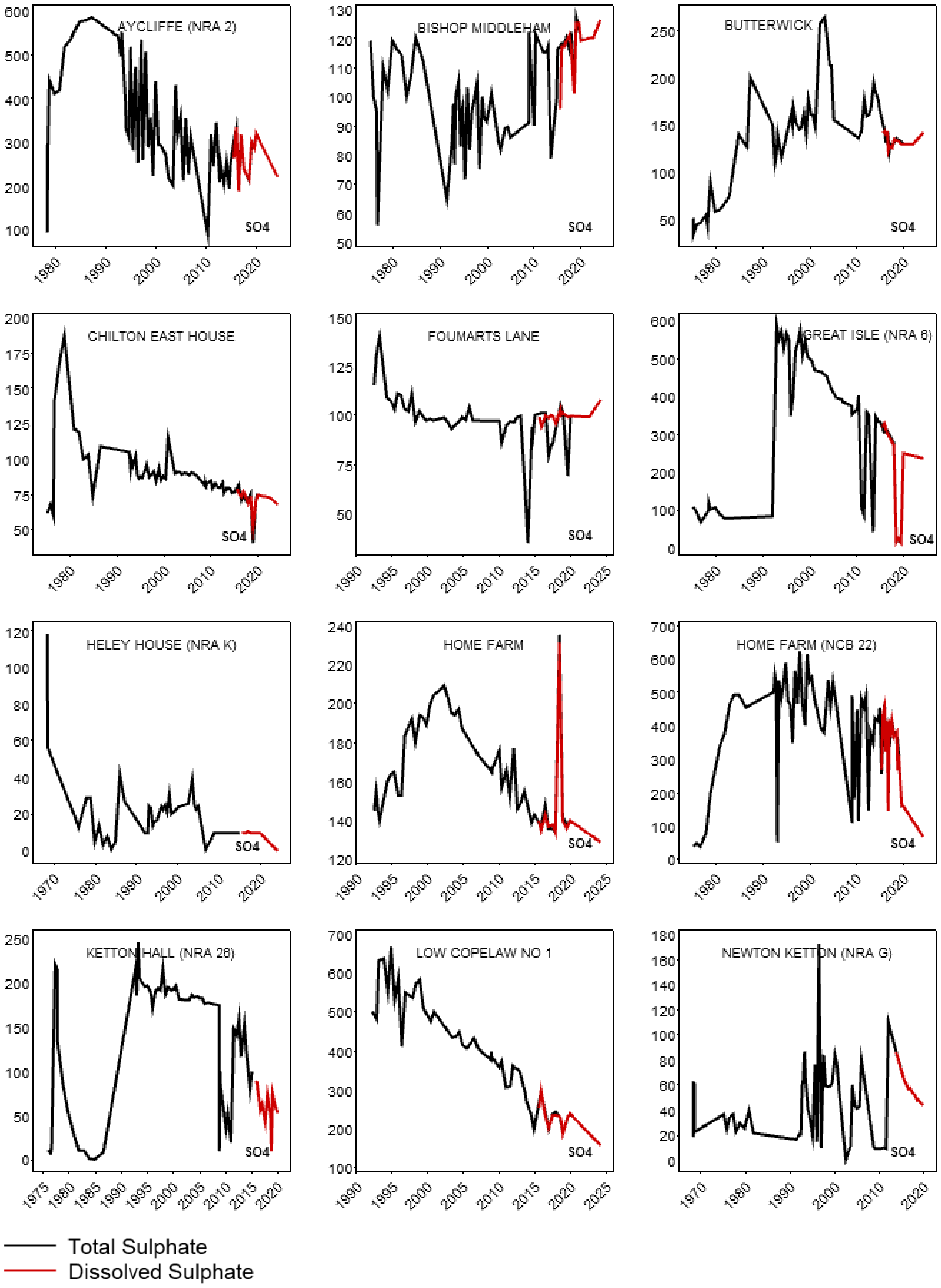
Appendix 2 Time series

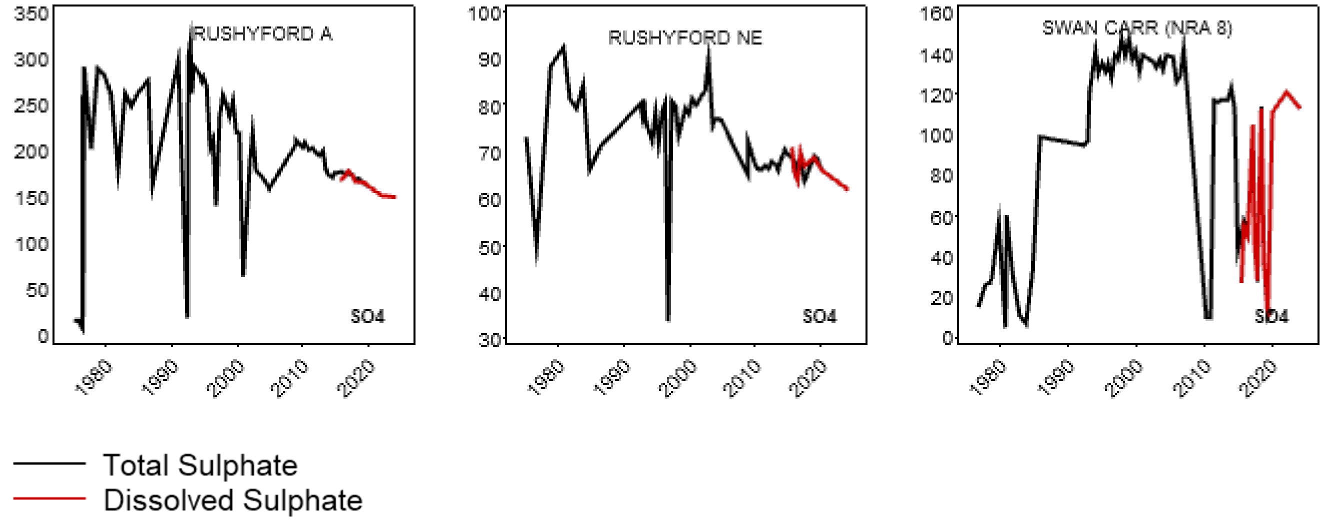
The time series plots for sulphate and chloride for each borehole are shown below, updated with the latest data from this study. Contains Environment Agency water quality data from the Water Quality Archive (Beta) Open WIMS data. This archive is provided as open data under the Open Government Licence with no requirement for registration

A description of the trends is not, however, provided as detailed analyses of the temporal behaviour was undertaken in WSP (2023) and JBA (2018).

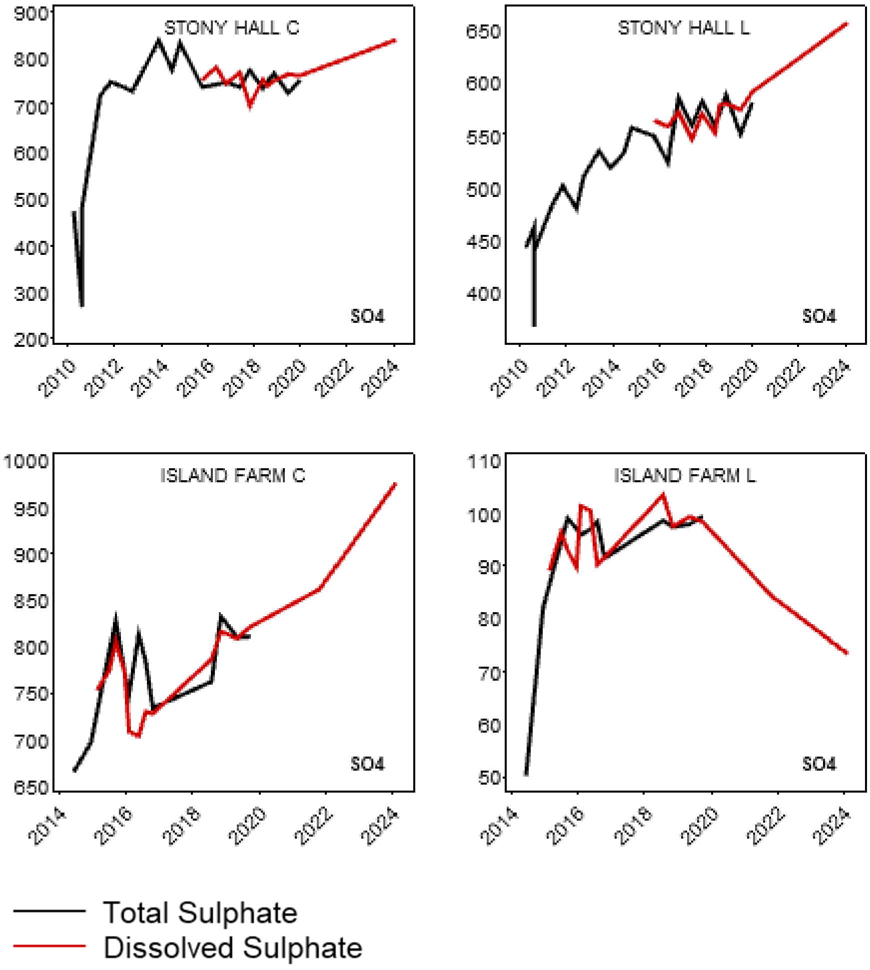
It is noted what is reported in JBA (2018), in the context of the saline boreholes near Hartlepool, regarding the need of cleaning up some of the WIMS data in order to interpret the trends with greater confidence. Adding to this, in light of the recent findings of important water quality stratification in some boreholes (Bowes et al. 2024), it is possible that some of the variations in water quality reflect localised changes rather than the aquifer “status”.

SULPHATE TIME SERIES IN MAGNESIAN LIMESTONE BOREHOLES WITH HISTORICAL MINE WATER PLUME IMPACT

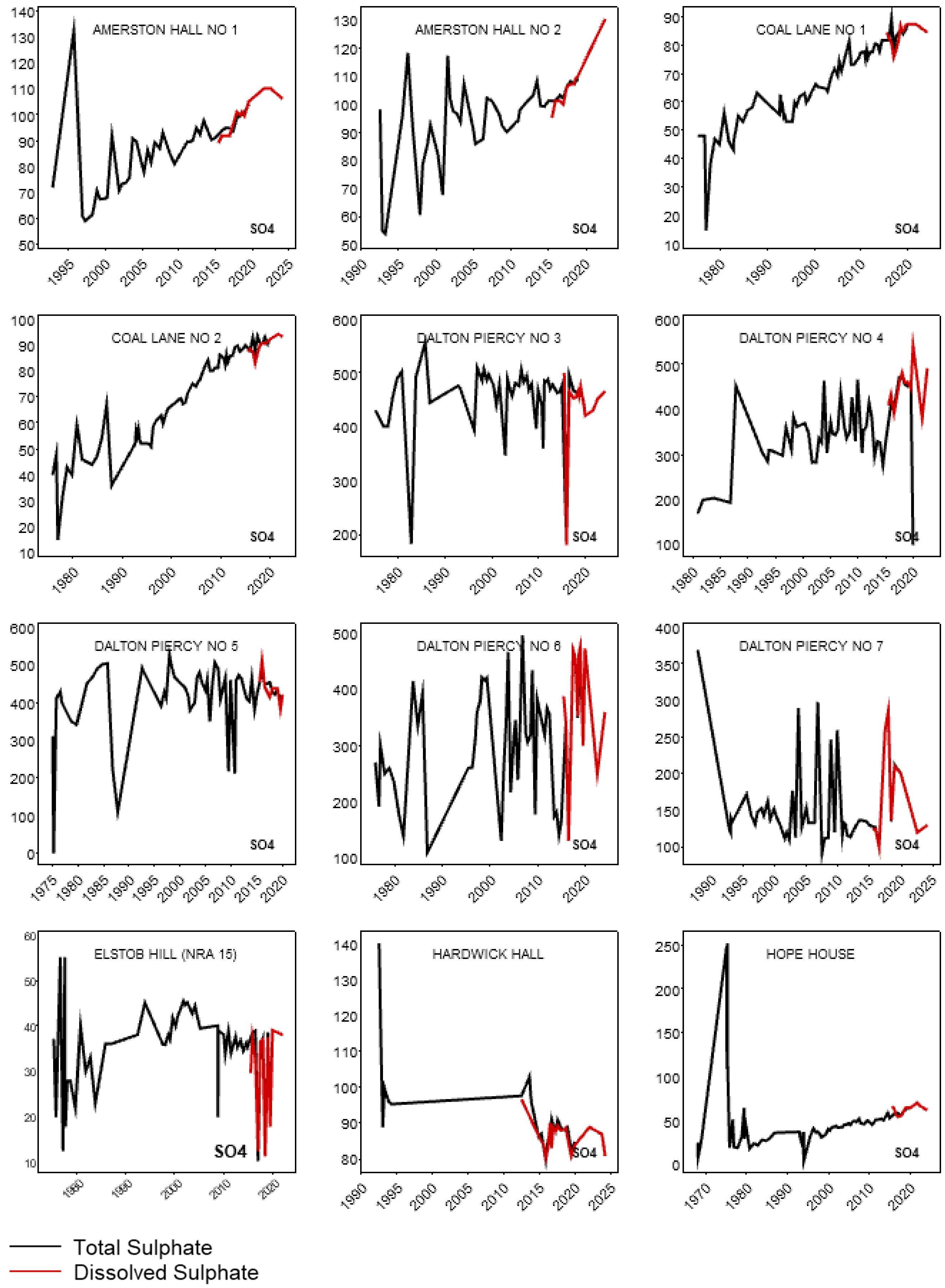


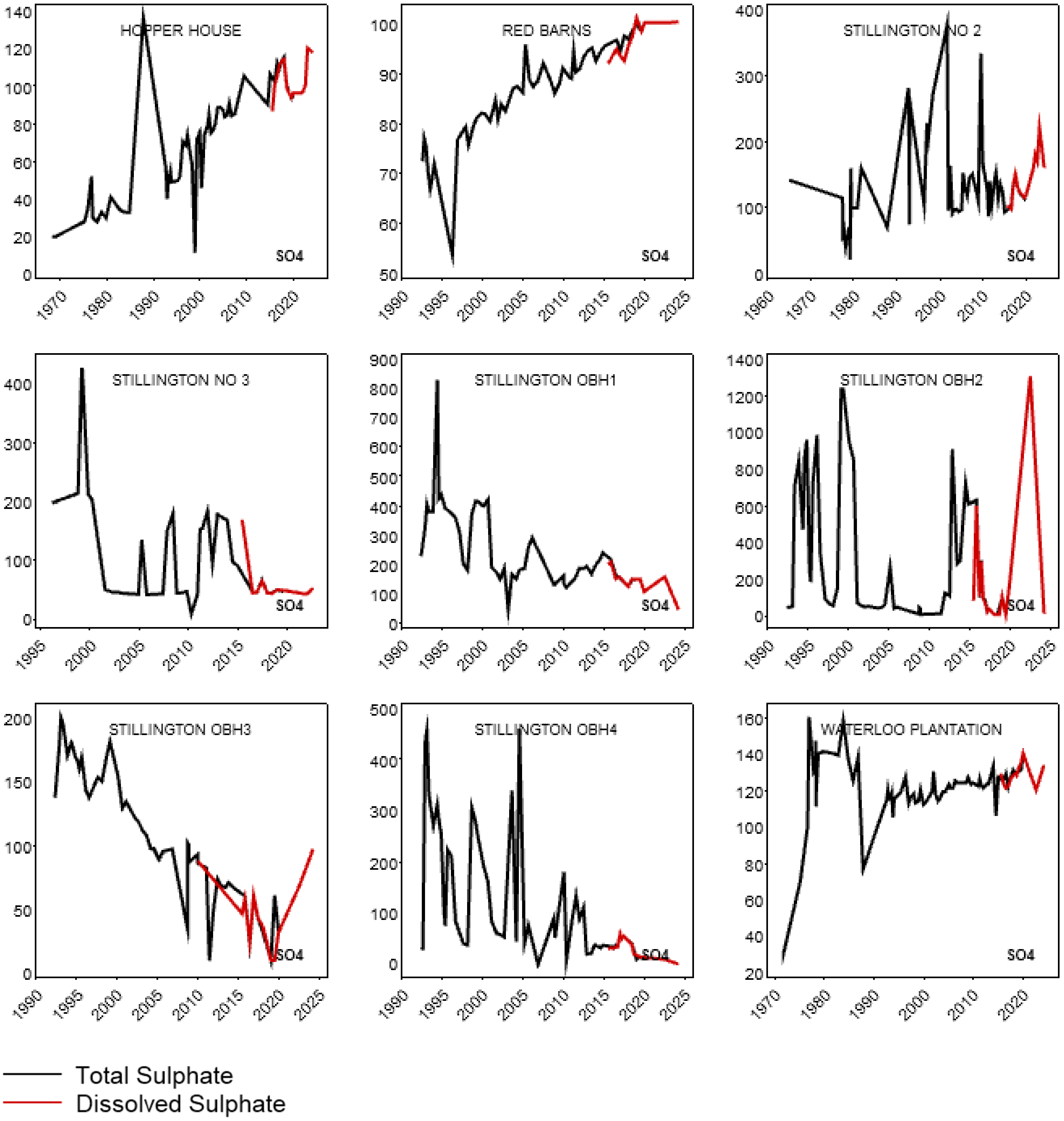


SULPHATE TIME SERIES IN COAL MEASURES BOREHOLES AND PAIRED MAGNESIAN LIMESTONE BOREHOLES

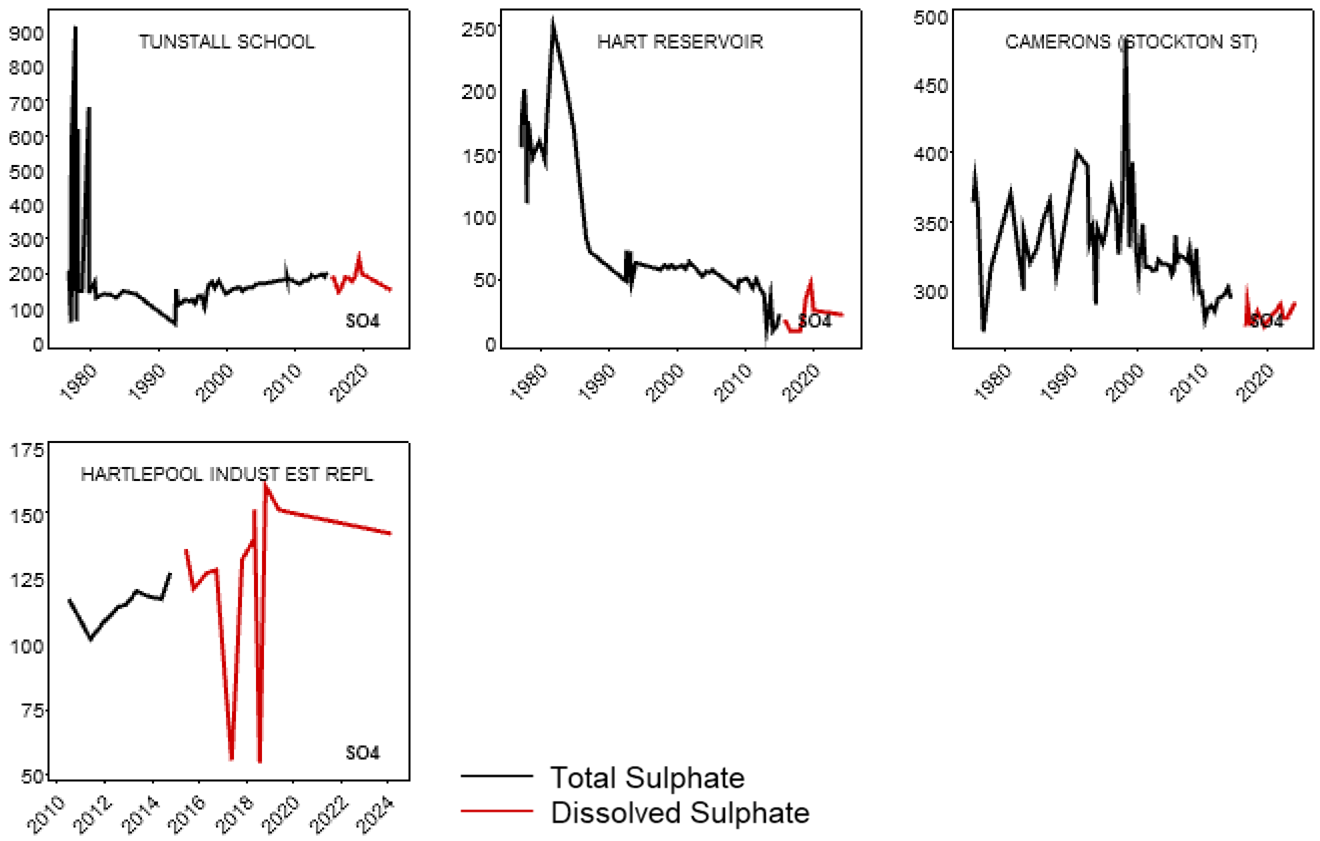


SULPHATE TIME SERIES IN MAGNESIAN LIMESTONE OBSERVATION AND PUBLIC WATER SUPPLY BOREHOLES

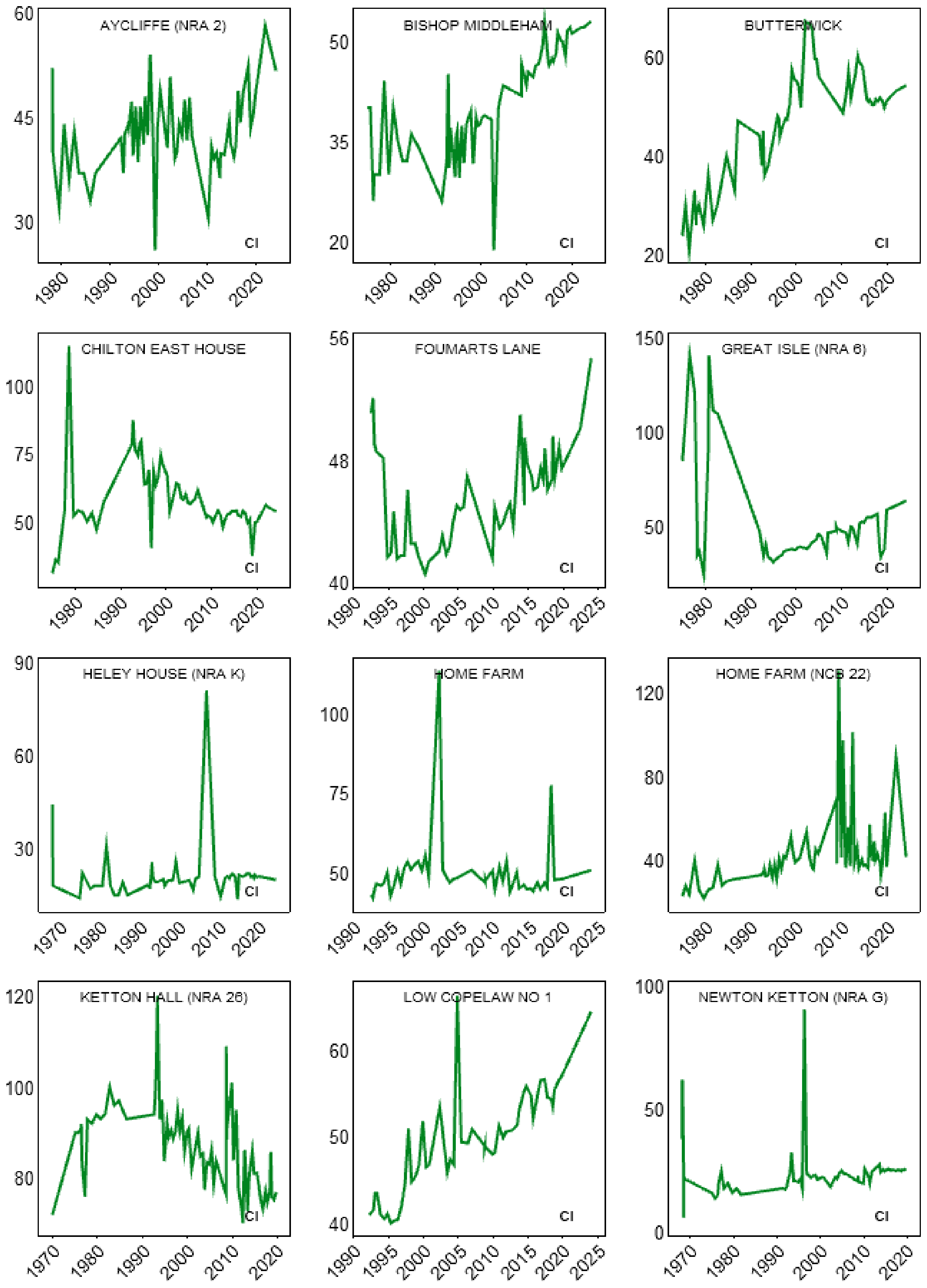


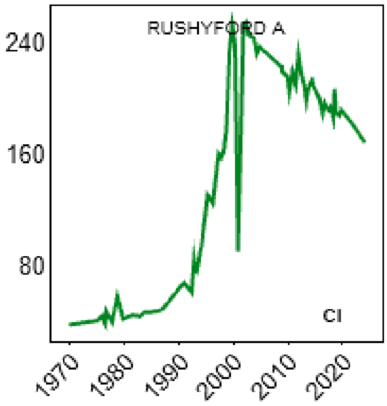

HOPPER HOUSE
SO4
0
20
40
60
80
100
120
140
1970
1980
1990
2000
2010
2020
RED BARNS
SO4
50
60
70
80
90
100
1990
1995
2000
2005
2010
2015
2020
2025
STILLINGTON NO 2
SO4
0
100
200
300
400
1960
1970
1980
1990
2000
2010
2020
STILLINGTON NO 3
SO4
0
100
200
300
400
1995
2000
2005
2010
2015
2020
STILLINGTON OBH1
SO4
0
100
200
300
400
500
600
700
800
900
1990
1995
2000
2005
2010
2015
2020
2025
STILLINGTON OBH2
SO4
0
200
400
600
800
1000
1200
1400
1990
1995
2000
2005
2010
2015
2020
2025
STILLINGTON OBH3
SO4
0
50
100
150
200
1990
1995
2000
2005
2010
2015
2020
2025
STILLINGTON OBH4
SO4
0
100
200
300
400
500
1990
1995
2000
2005
2010
2015
2020
2025
WATERLOO PLANTATION
SO4
20
40
60
80
100
120
140
160
1970
1980
1990
2000
2010
2020
Total Sulphate
Dissolved Sulphate

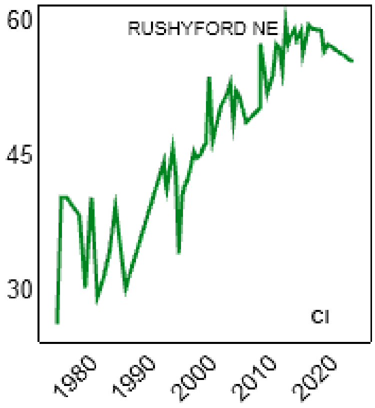
SULPHATE TIME SERIES IN MAGNESIAN LIMESTONE BOREHOLES NEAR HARTLEPOOL (SALINE)

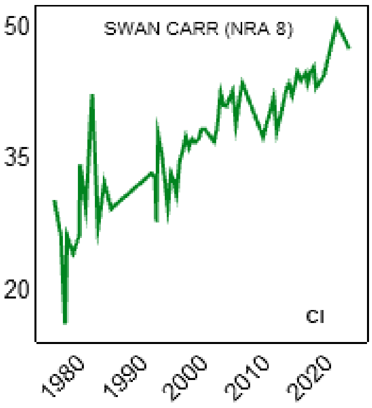


CHLORIDE TIME SERIES IN MAGNESIAN LIMESTONE BOREHOLES WITH HISTORICAL MINE WATER PLUME IMPACT

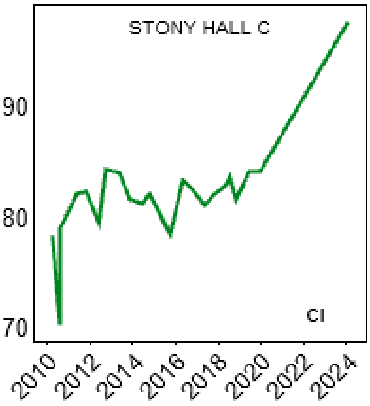


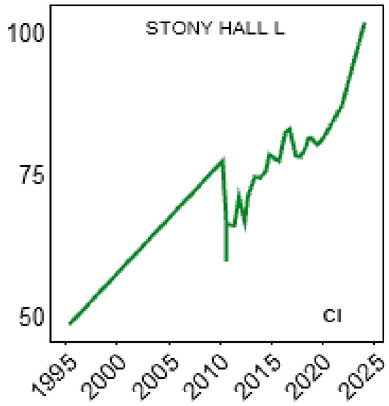


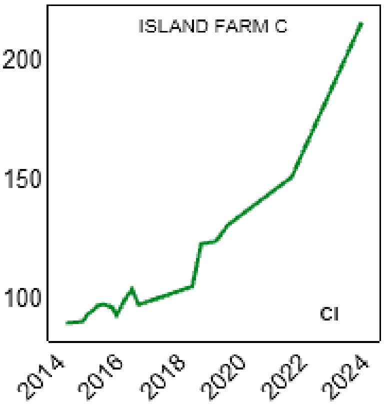


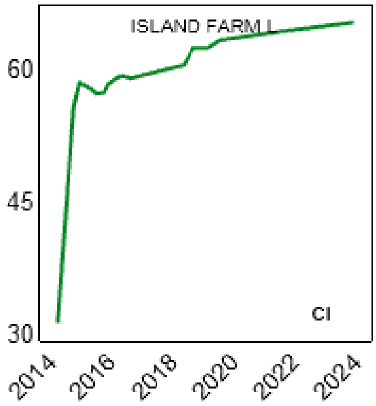


CHLORIDE TIME SERIES IN COAL MEASURES BOREHOLES AND PAIRED MAGNESIAN LIMESTONE BOREHOLES

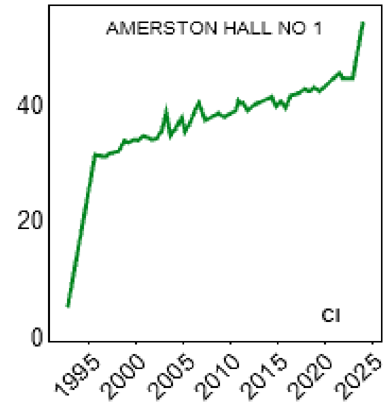


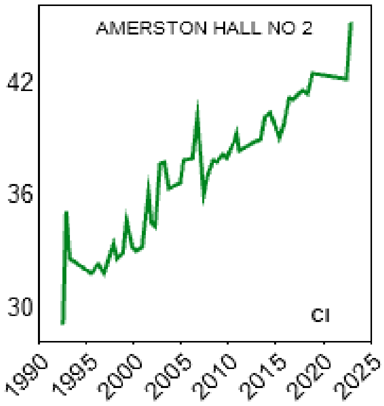


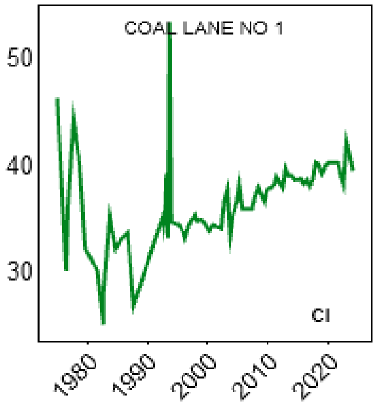


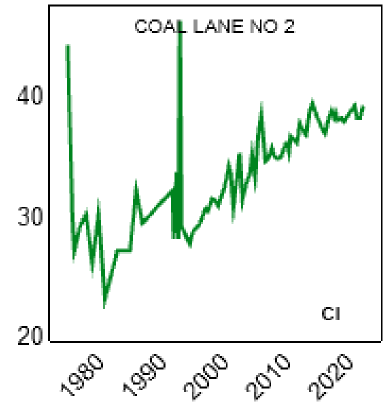


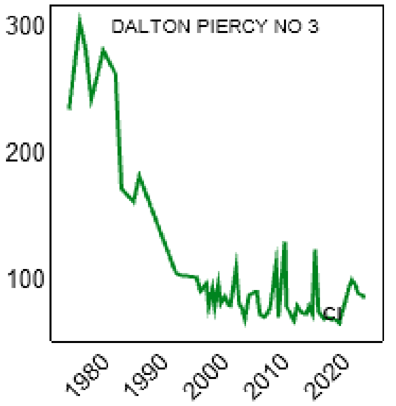
CHLORIDE TIME SERIES IN MAGNESIAN LIMESTONE OBSERVATION AND PUBLIC WATER SUPPLY BOREHOLES

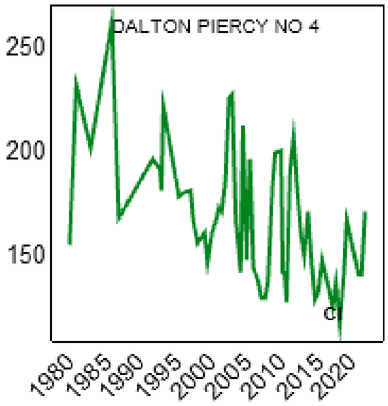


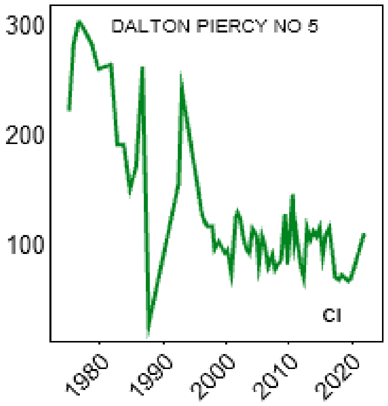


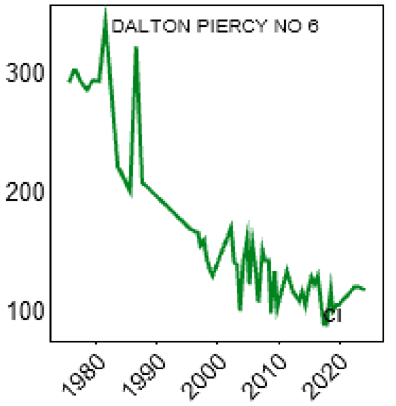


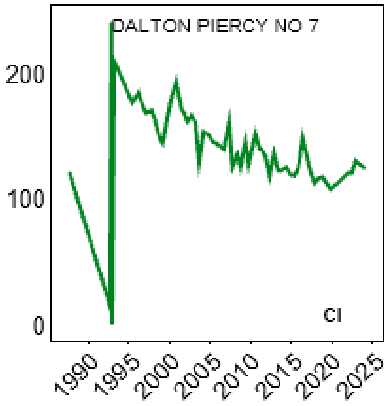


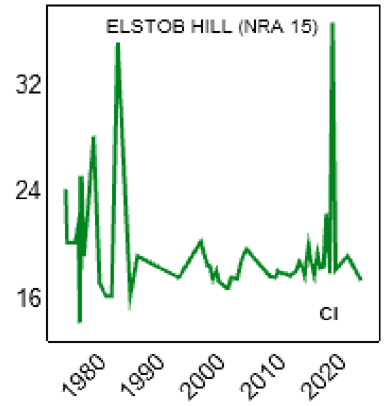


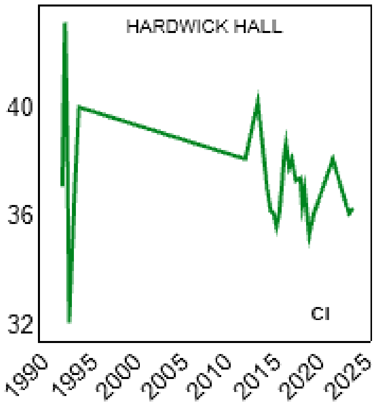


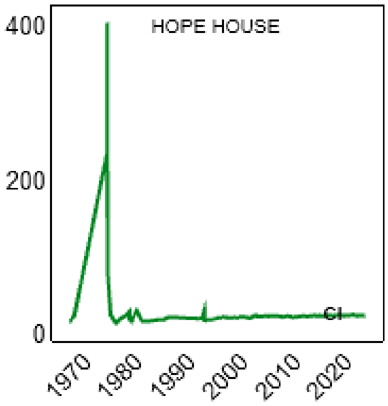


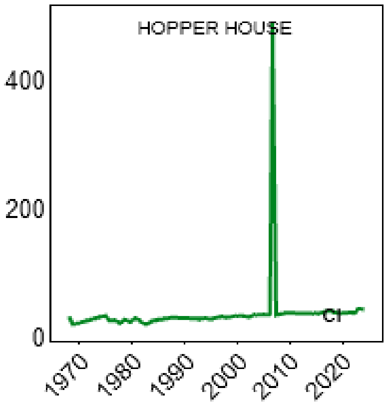


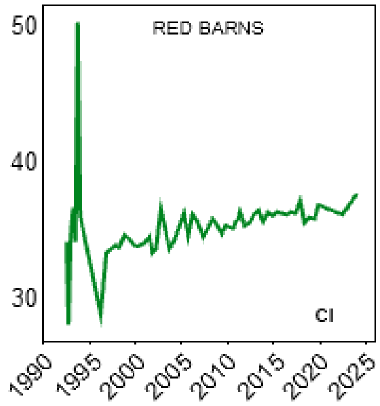


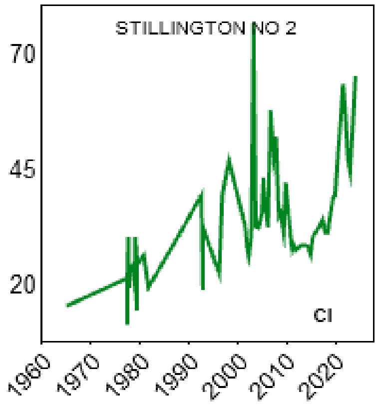


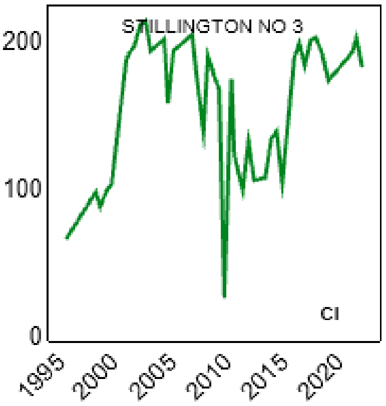


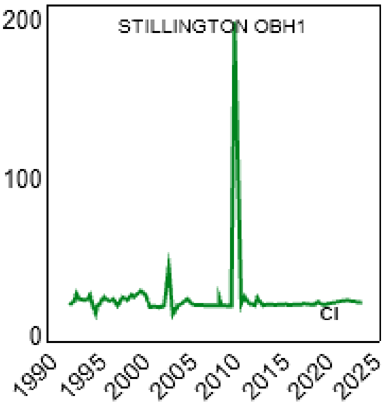


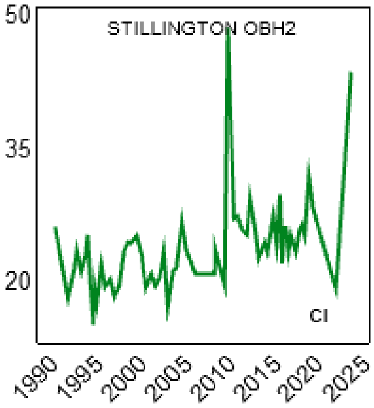

HOPPER HOUSE
400
200
0
Cl
1970
1980
1990
2000
2010
2020

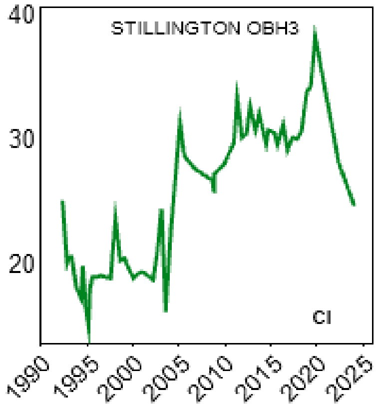

RED BARNS
50
40
30
Cl
1990
1995
2000
2005
2010
2015
2020
2025

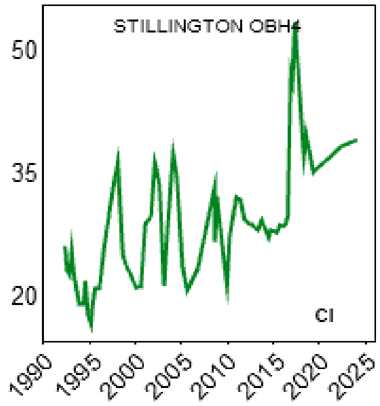

STILLINGTON NO 2
70
45
20
Cl
1960
1970
1980
1990
2000
2010
2020

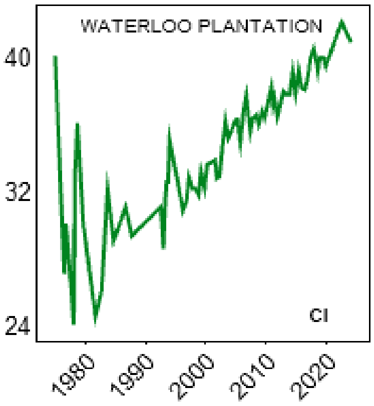

STILLINGTON NO 3
200
100
0
Cl
1995
2000
2005
2010
2015
2020


STILLINGTON OBH1
200
100
0
Cl
1990
1995
2000
2005
2010
2015
2020
2025

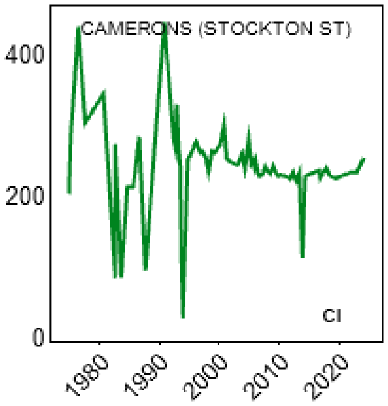

STILLINGTON OBH2
50
35
20
Cl
1990
1995
2000
2005
2010
2015
2020
2025

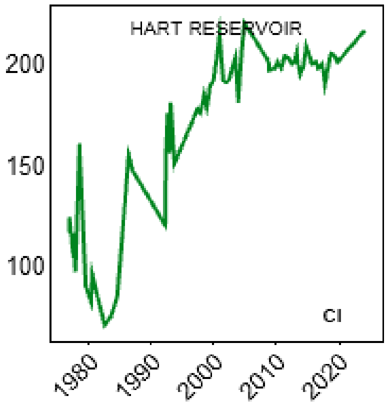

STILLINGTON OBH3
40
30
20
Cl
1990
1995
2000
2005
2010
2015
2020
2025

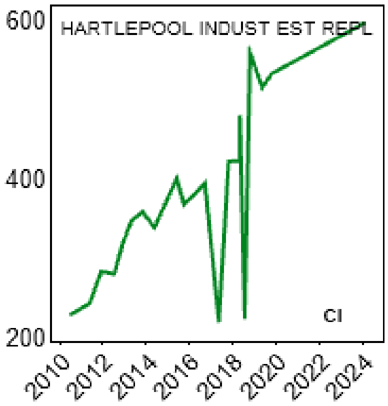

STILLINGTON OBH4
50
35
20
Cl
1990
1995
2000
2005
2010
2015
2020
2025

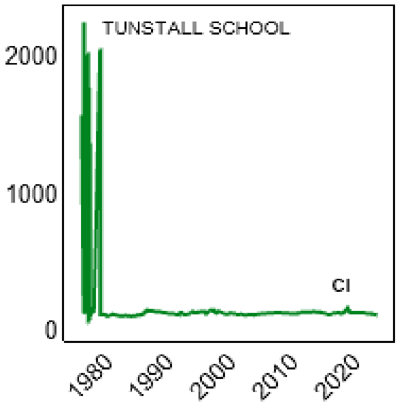

WATERLOO PLANTATION
40
32
24
Cl
1980
1990
2000
2010
2020

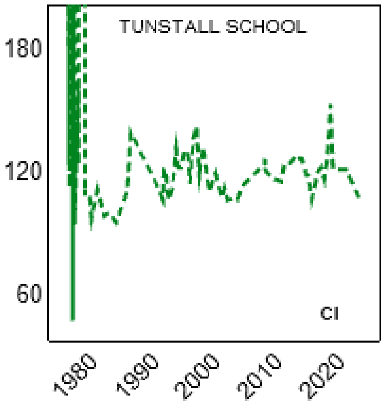
CHLORIDE TIME SERIES IN MAGNESIAN LIMESTONE BOREHOLES NEAR HARTLEPOOL (SALINE)



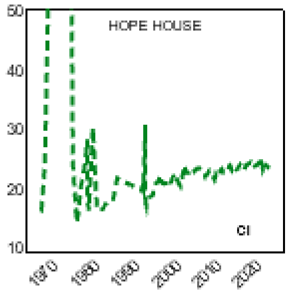


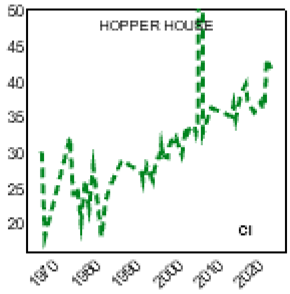


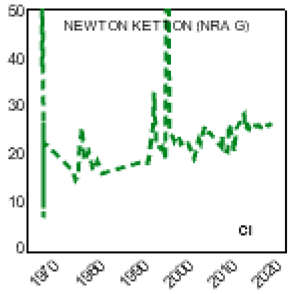


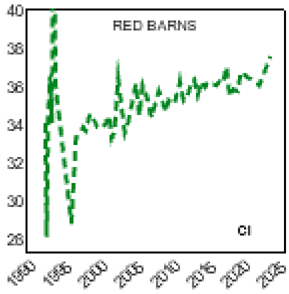


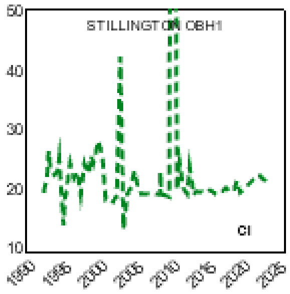
Details:







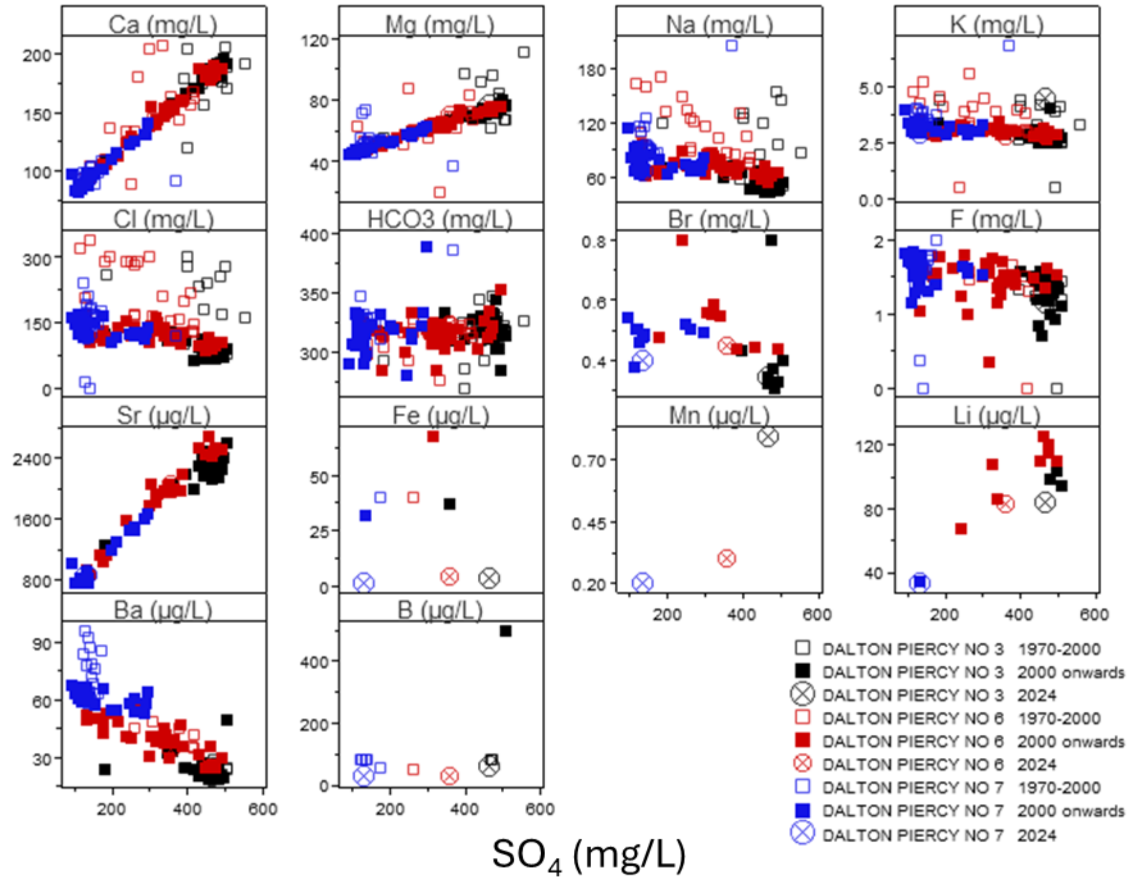




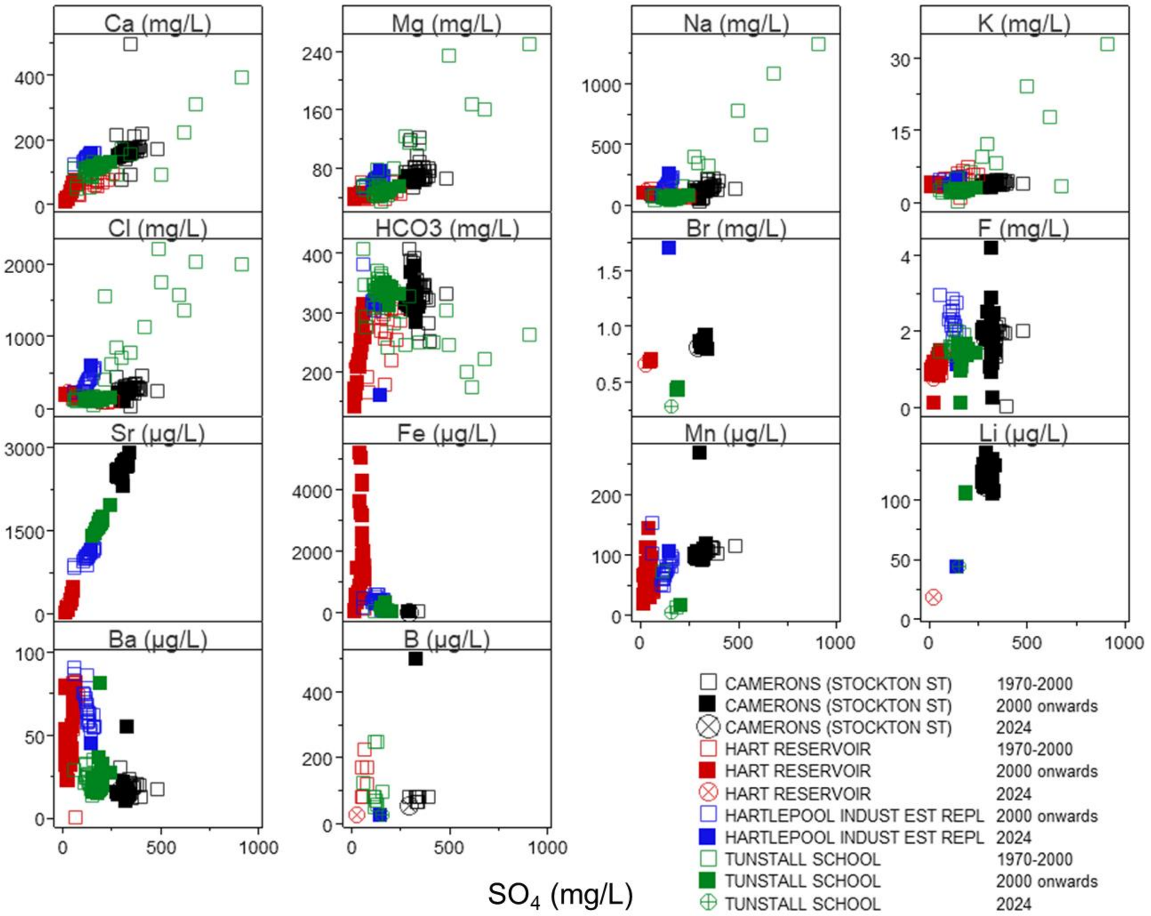
Appendix 3 Scatterplots of sulphate versus major and minor/trace elements for selected boreholes using WIMS+2024 data

Contains Environment Agency data.

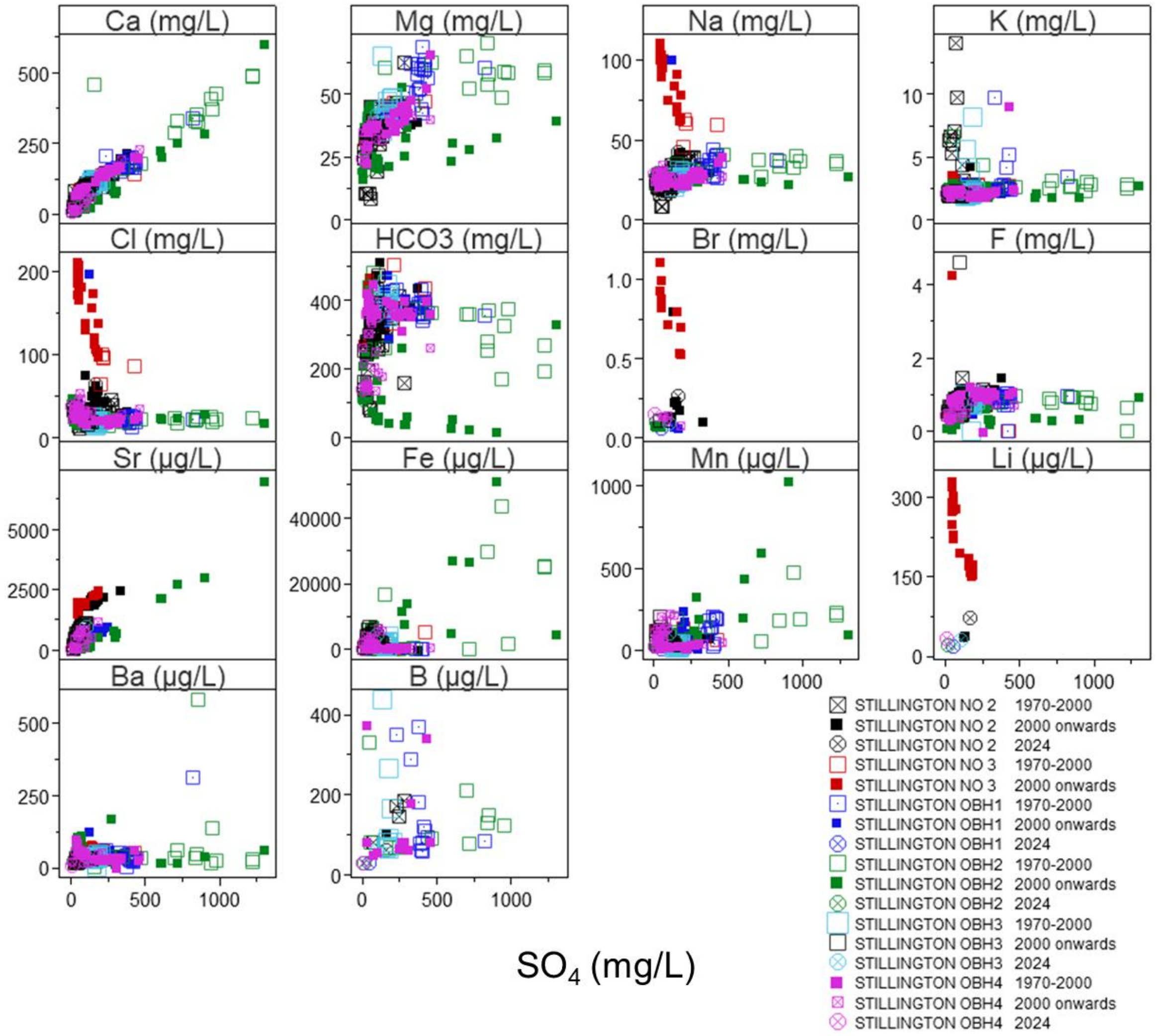
DALTON PIERCY BOREHOLE GROUP

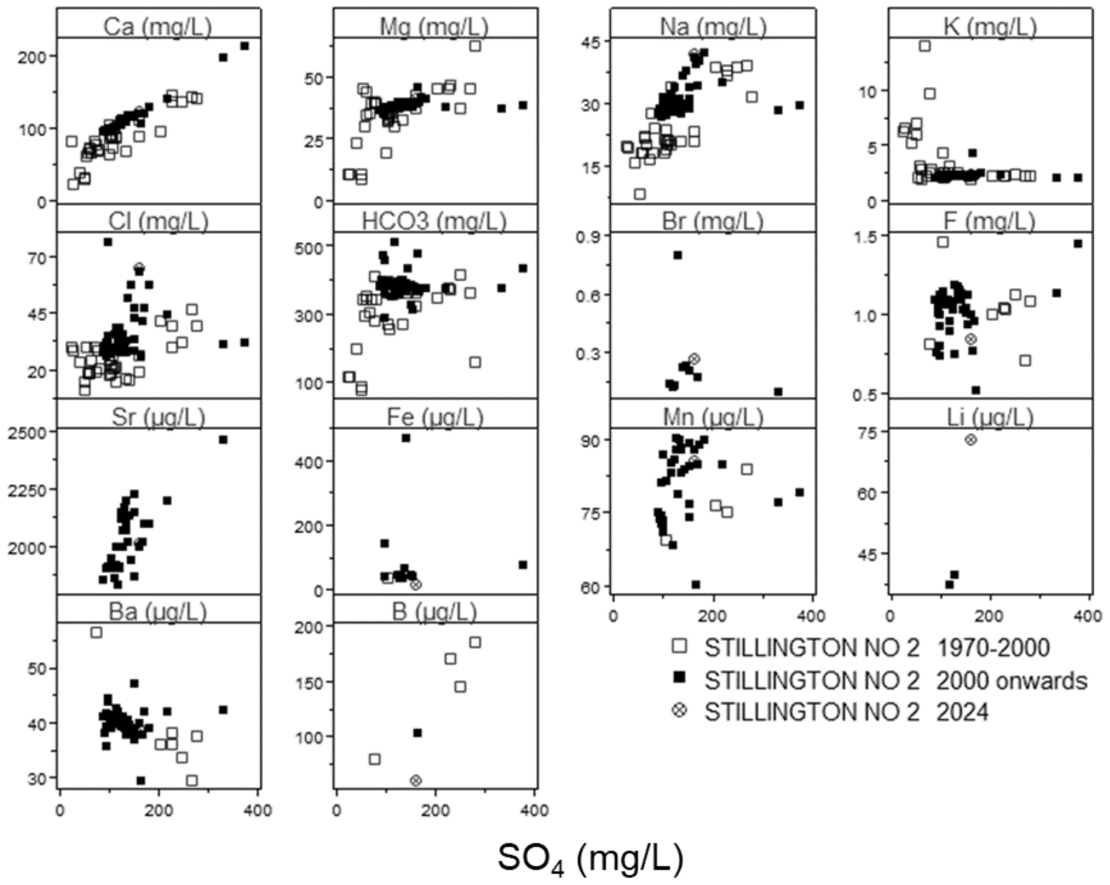


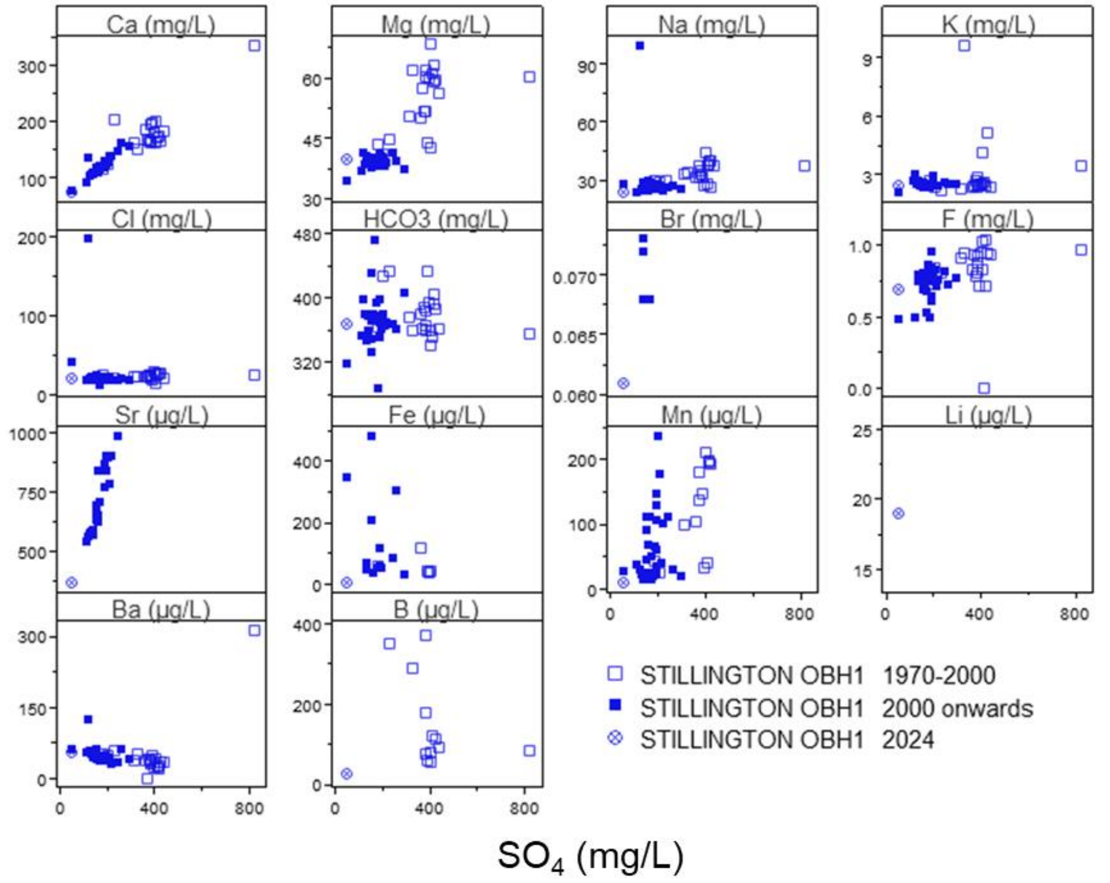
CAMERONS, HART RESERVOIR, HARTLEPOOL, TUNSTALL SCHOOL

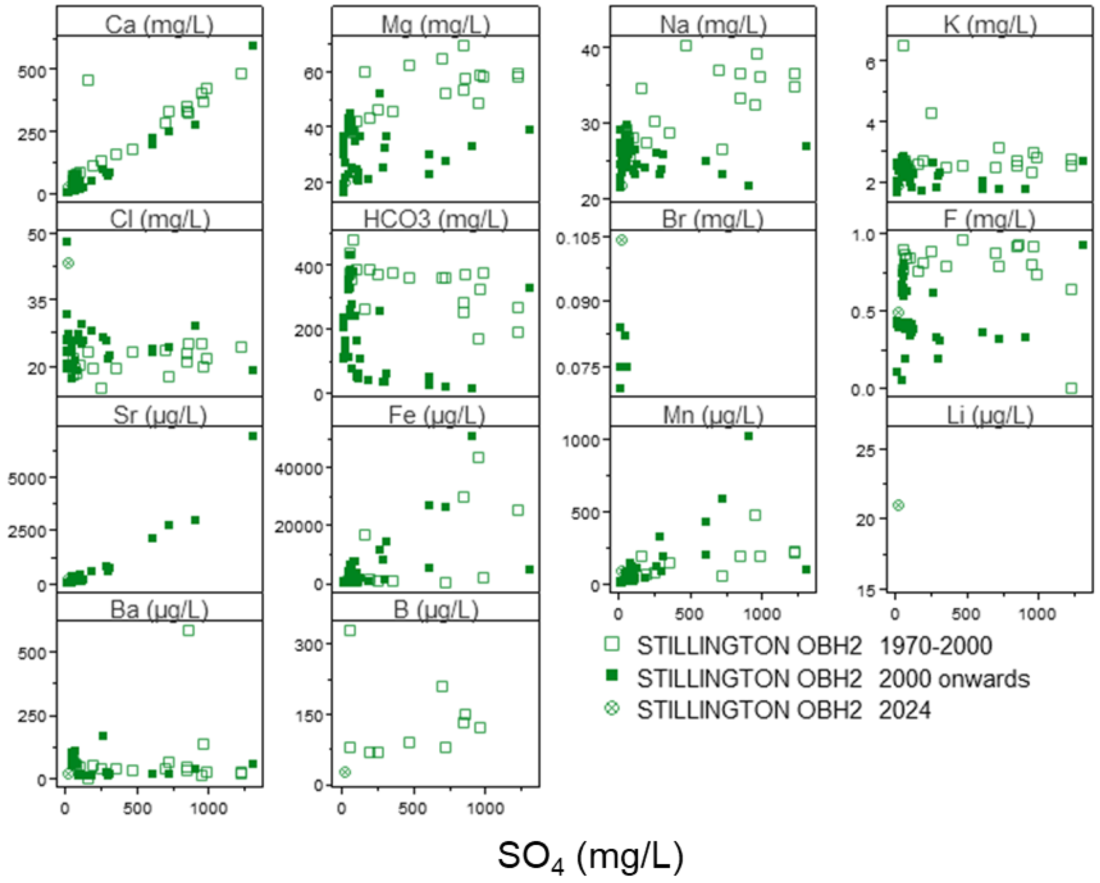


STILLINGTON BOREHOLE GROUP




Ca (mg/L)
Mg (mg/L)
Na (mg/L)
K (mg/L)
Cl (mg/L)
HCO3 (mg/L)
Br (mg/L)
F (mg/L)
Sr (µg/L)
Fe (µg/L)
Mn (µg/L)
Li (µg/L)
Ba (µg/L)
B (µg/L)
0
200
400
STILLINGTON NO 2 1970-2000
STILLINGTON NO 2 2000 onwards
STILLINGTON NO 2 2024
SO4 (mg/L)


Ca (mg/L)
Mg (mg/L)
Na (mg/L)
K (mg/L)
Cl (mg/L)
HCO3 (mg/L)
Br (mg/L)
F (mg/L)
Sr (µg/L)
Fe (µg/L)
Mn (µg/L)
Li (µg/L)
Ba (µg/L)
B (µg/L)
0
400
800
STILLINGTON OBH1 1970-2000
STILLINGTON OBH1 2000 onwards
STILLINGTON OBH1 2024
SO4 (mg/L)


Ca (mg/L)
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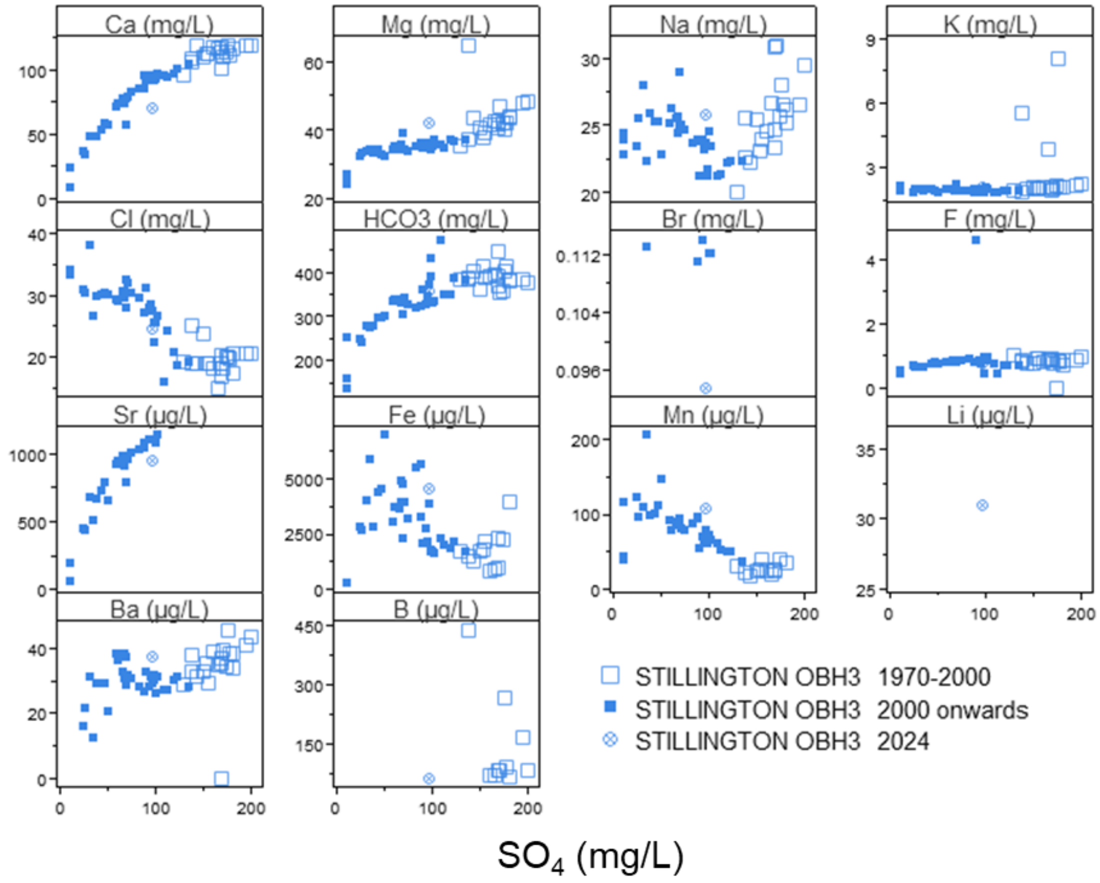
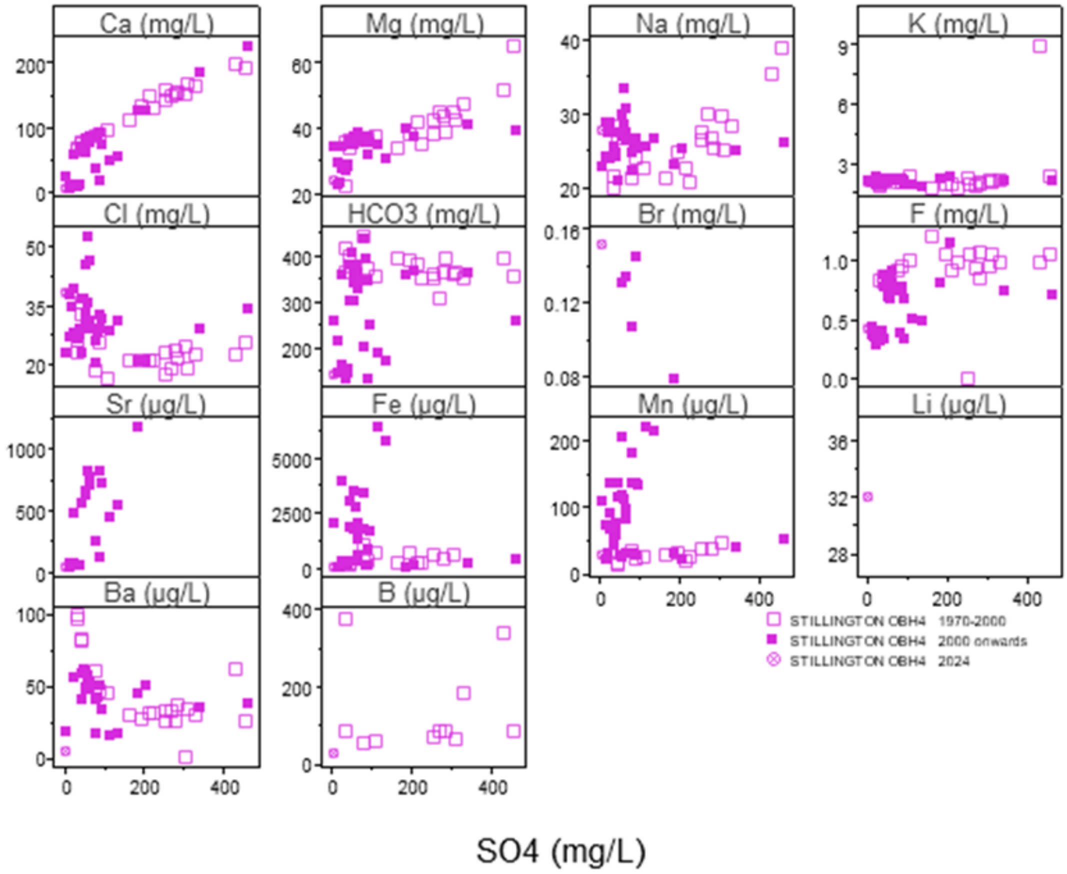
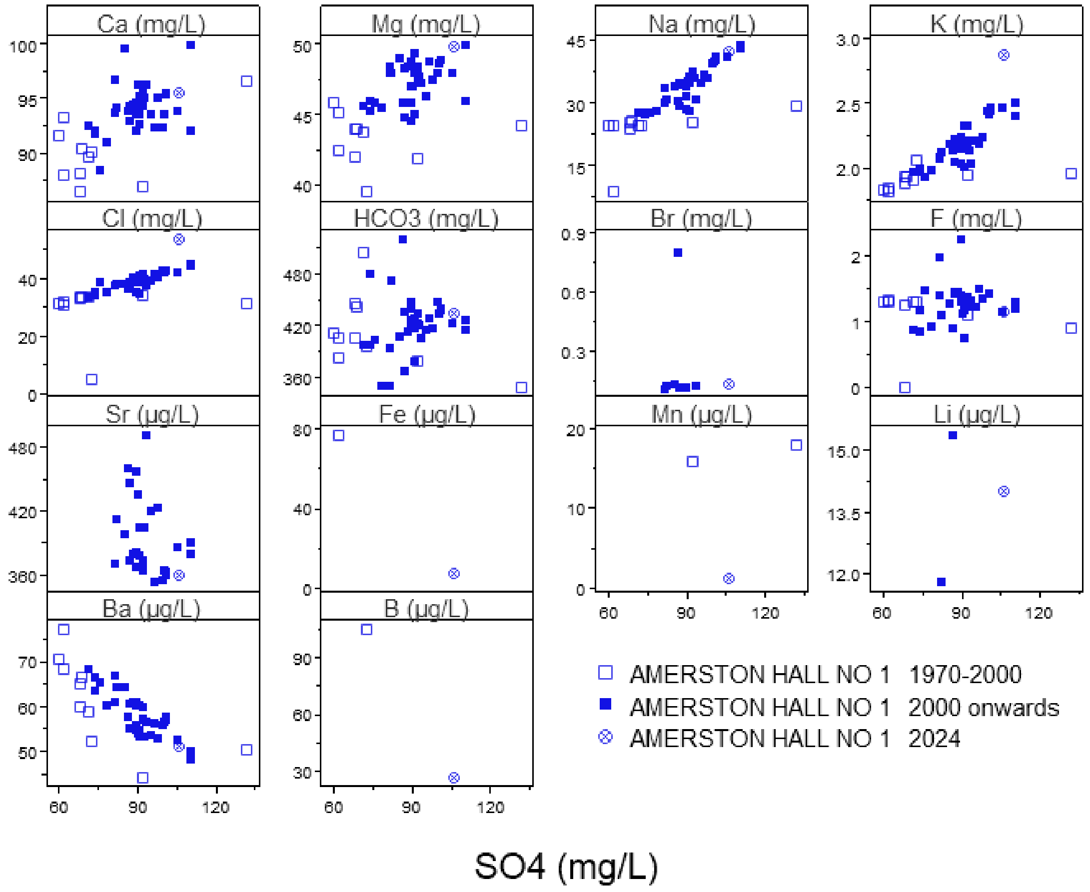
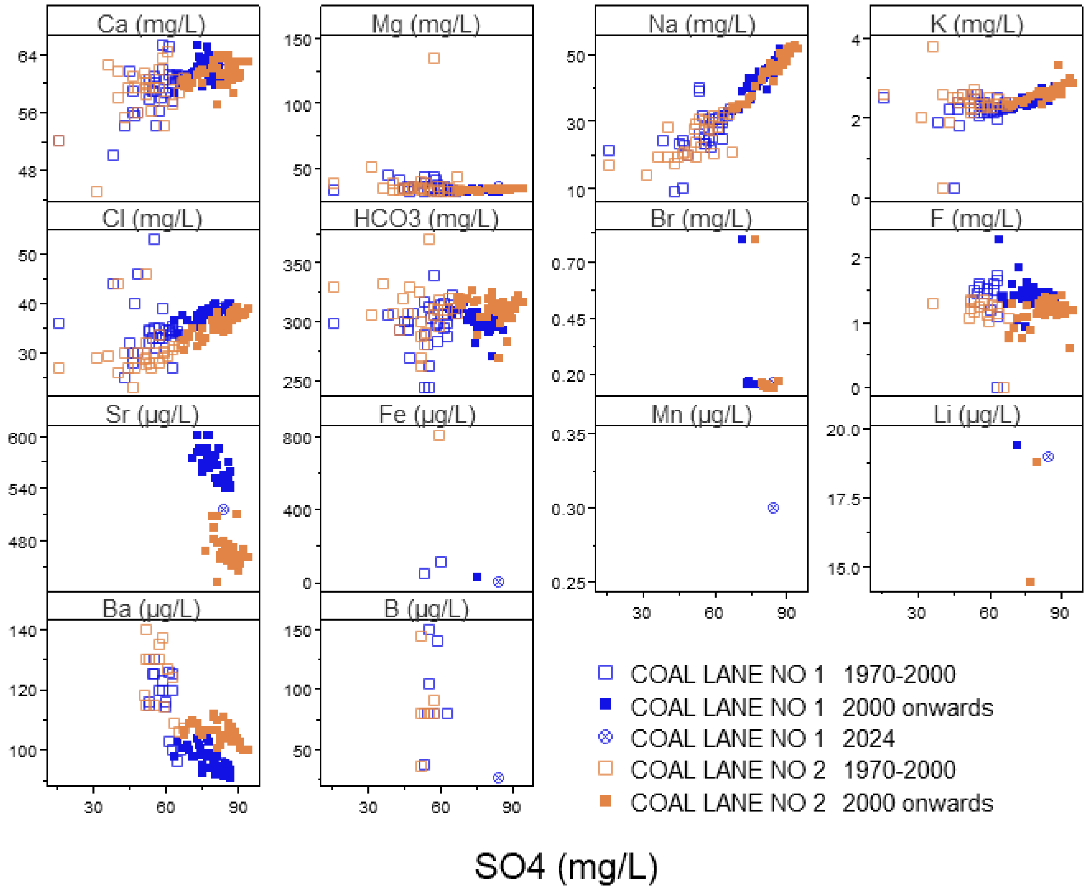
250
500
Mg (mg/L)
20
40
60
Na (mg/L)
20
30
40
K (mg/L)
2
4
6
Cl (mg/L)
20
35
50
HCO3 (mg/L)
0
200
400
Br (mg/L)
0.075
0.090
0.105
F (mg/L)
0.0
0.5
1.0
Sr (µg/L)
0
2500
5000
Fe (µg/L)
0
20000
40000
Mn (µg/L)
0
500
1000
Li (µg/L)
15
20
25
Ba (µg/L)
0
250
500
B (µg/L)
0
150
300
0
500
1000
□ STILLINGTON OBH2 1970-2000
■ STILLINGTON OBH2 2000 onwards
⊗ STILLINGTON OBH2 2024
SO_4 (mg/L)

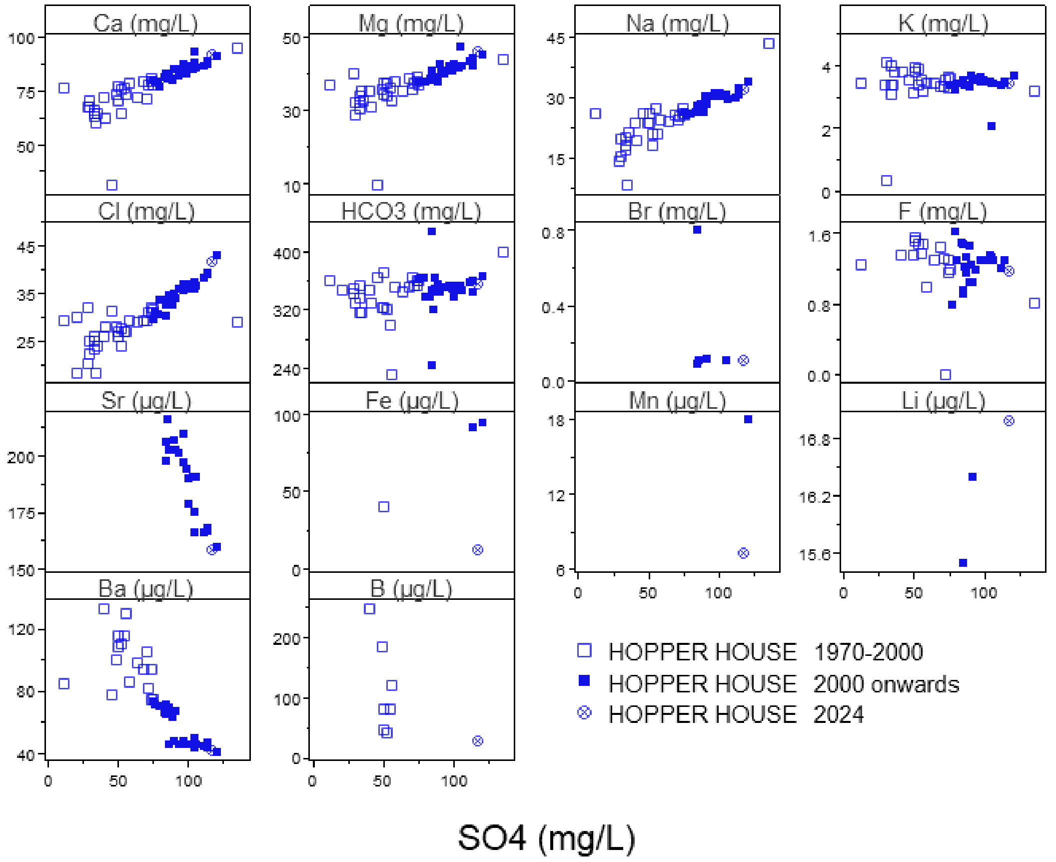

Ca (mg/L)
0
50
100
Mg (mg/L)
20
40
60
Na (mg/L)
20
25
30
K (mg/L)
3
6
9
Cl (mg/L)
20
30
40
HCO3 (mg/L)
200
300
400
Br (mg/L)
0.096
0.104
0.112
F (mg/L)
0
2
4
Sr (µg/L)
0
500
1000
Fe (µg/L)
0
2500
5000
Mn (µg/L)
0
100
200
Li (µg/L)
25
30
35
Ba (µg/L)
0
20
40
B (µg/L)
150
300
450
0
100
200
□ STILLINGTON OBH3 1970-2000
■ STILLINGTON OBH3 2000 onwards
⊗ STILLINGTON OBH3 2024
SO_4 (mg/L)


Ca (mg/L)
0
100
200
Mg (mg/L)
20
40
60
Na (mg/L)
20
30
40
K (mg/L)
3
6
9
Cl (mg/L)
20
35
50
HCO3 (mg/L)
200
300
400
Br (mg/L)
0.08
0.12
0.16
F (mg/L)
0.0
0.5
1.0
Sr (µg/L)
0
500
1000
Fe (µg/L)
0
2500
5000
Mn (µg/L)
0
100
200
Li (µg/L)
28
32
36
Ba (µg/L)
0
50
100
B (µg/L)
0
200
400
0
200
400
STILLINGTON OBH4 1970-2000
STILLINGTON OBH4 2000 onwards
STILLINGTON OBH4 2024
SO4 (mg/L)

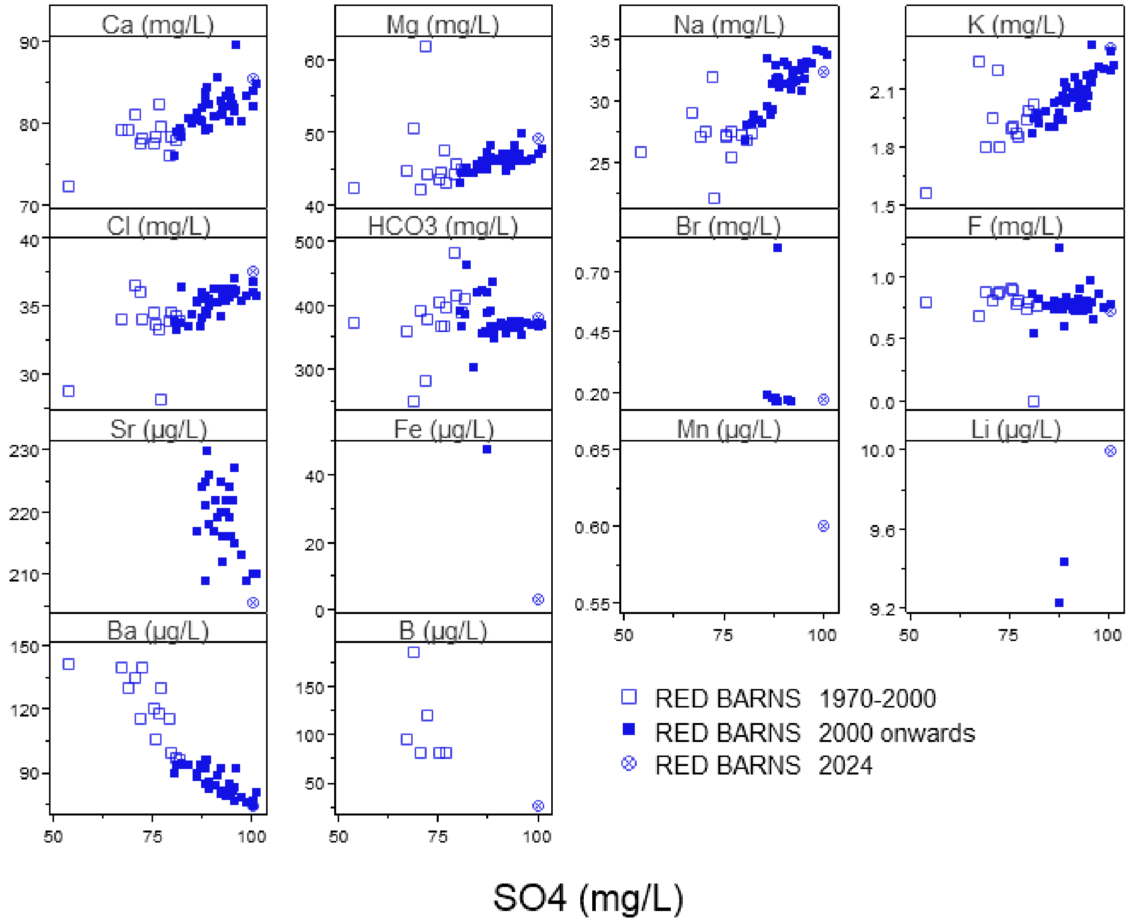
BOREHOLES WITH INCREASING TREND: AMERSTON HALL NO1, COAL LANE NO 1 AND NO 2, HOPPER HOUSE, RED BARNS, WATERLOO PLANTATION, AND STONY HALL L



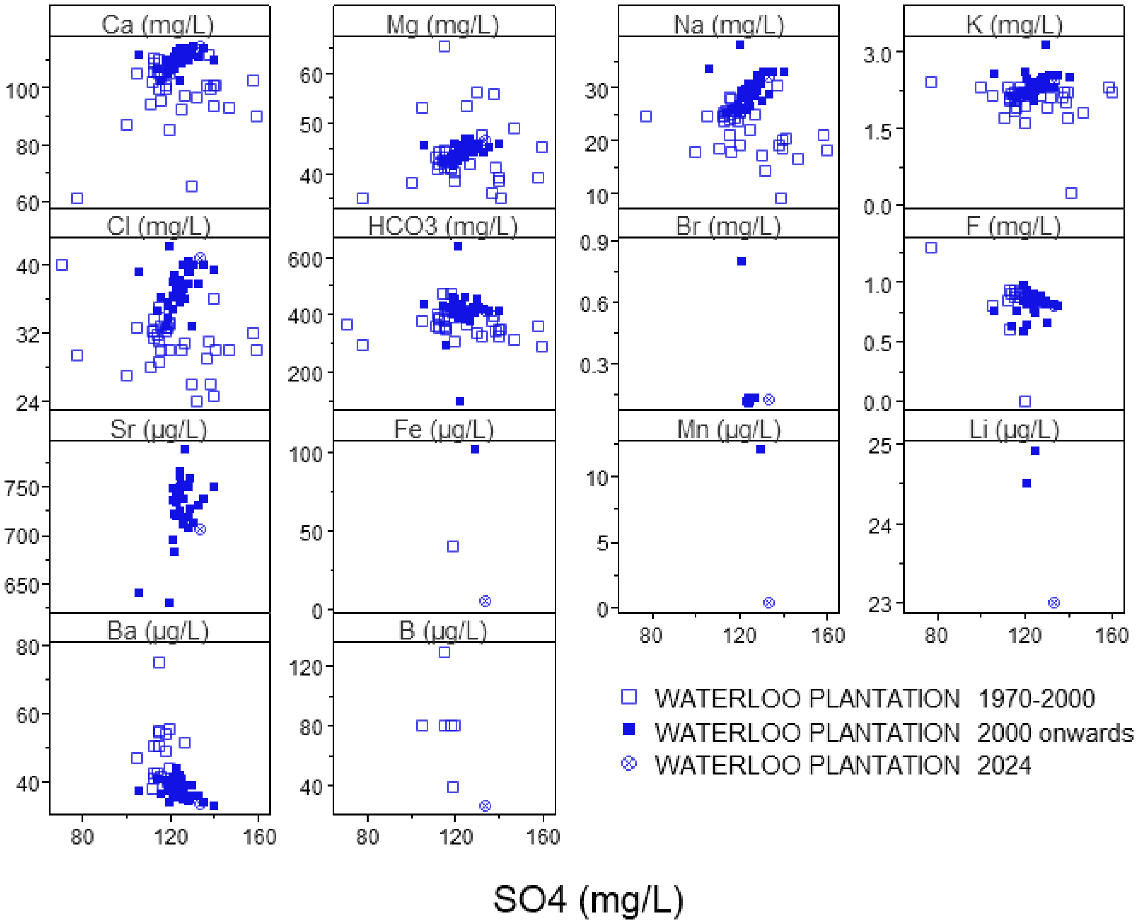




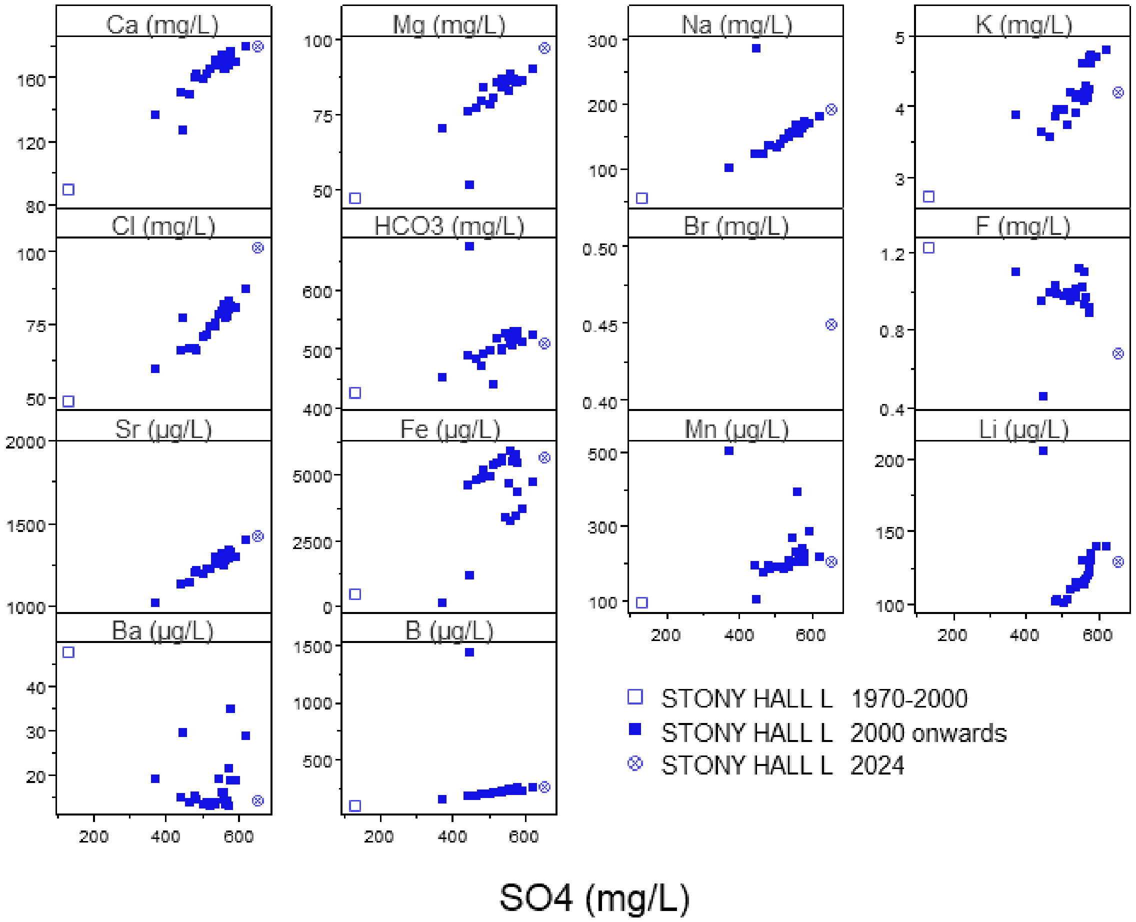
Value Cl 486 mg/L from 2006 omitted and K 14 mg/L from 1992 for Hopper house



Value Cl 50 mg/L from 1996 omitted for Red Barns

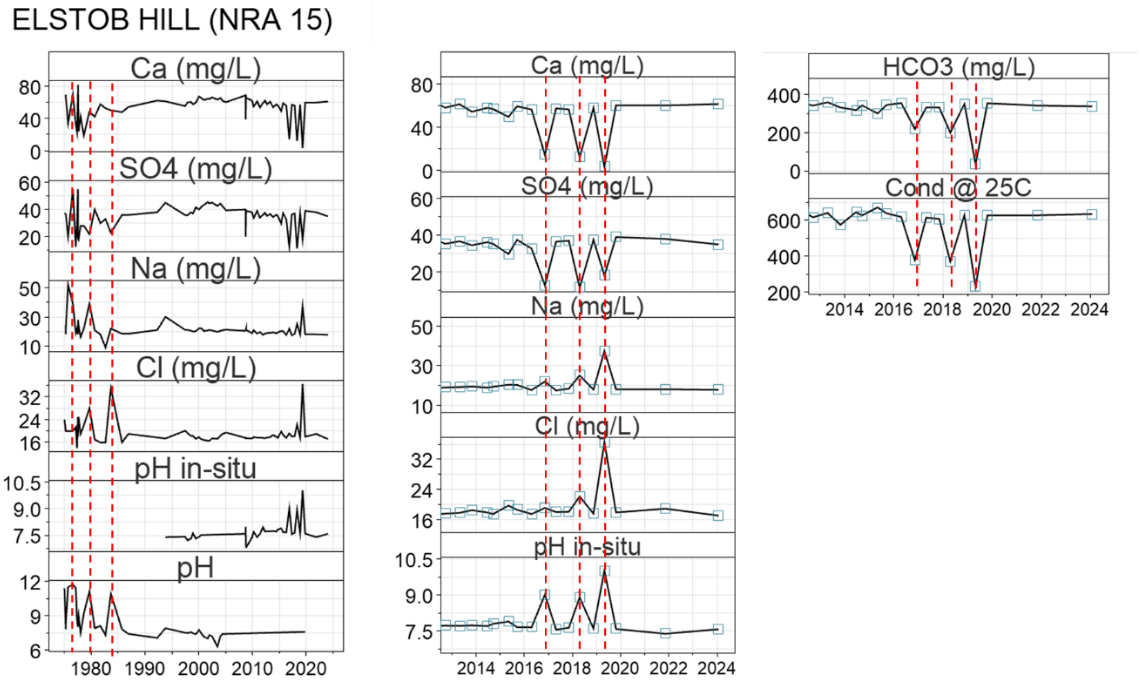


Omitted records for 1971 and 1975 for Waterloo plantation


Ca (mg/L)
80
120
160
Mg (mg/L)
50
75
100
Na (mg/L)
100
200
300
K (mg/L)
3
4
5
Cl (mg/L)
50
75
100
HCO3 (mg/L)
400
500
600
Br (mg/L)
0.40
0.45
0.50
F (mg/L)
0.4
0.8
1.2
Sr (µg/L)
1000
1500
2000
Fe (µg/L)
0
2500
5000
Mn (µg/L)
100
300
500
Li (µg/L)
100
150
200
Ba (µg/L)
20
30
40
B (µg/L)
500
1000
1500
200
400
600
□ STONY HALL L 1970-2000
■ STONY HALL L 2000 onwards
⊗ STONY HALL L 2024
SO4 (mg/L)

Appendix 4 Elstob Hill

Time series illustrating the chemical changes associated to high pH borehole records (left), with more details and additional HCO_3 and conductivity for the monitoring period 2012-2024 (middle/right). Contains Environment Agency data.



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