British Geological Survey

Natural Environment Research Council

UK Geoenergy Observatories: Glasgow Borehole Test Pumping - Groundwater Chemistry

UK Geoenergy Observatories Programme

Open Report OR/21/030

BRITISH GEOLOGICAL SURVEY

UK GEOENERGY OBSERVATORIES PROGRAMME

OPEN REPORT OR/21/030

UK Geoenergy Observatories: Glasgow Borehole Test Pumping - Groundwater Chemistry

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Keywords

groundwater, chemistry, inorganic, organic, stable isotopes, dissolved gases.

Front cover

BGS scientists monitoring groundwater level during test pumping at GGA01 on Site 1 of the Glasgow Observatory

Bibliographical reference

PALUMBO-ROE B, SHORTER K M, FORDYCE F M, WALKER-VERKUIL K, Ó DOCHARTAIGH B E, GOODDY D C, DARLING W G 2021. UK Geoenergy Observatories: Glasgow Borehole Test Pumping - Groundwater Chemistry. *British Geological Survey Open Report*, OR/21/030. 73pp.

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Acknowledgements

Clyde Gateway are thanked for site access to enable the UK Geoenergy Observatory, Glasgow project and the environmental groundwater assessments, with permissions in place from Glasgow City Council, South Lanarkshire Council and the Scottish Environment Protection Agency. Dr Ryan Pereira, Heriot-Watt University Lyell Centre is thanked for the provision of ultrapure water for the water chemistry determination. Scottish Water Scientific Services are thanked for their assistance with the organic pollutant analysis and the UK Centre for Ecology and Hydrology, Wallingford for access to the equipment for the chemical analysis of ammonium.

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Summary

The United Kingdom Geoenergy Observatory (UKGEOS) in Glasgow comprises 12 boreholes: 11 at the Cuningar Loop, South Lanarkshire and one seismic observation borehole in Dalmarnock in east Glasgow. Boreholes are drilled into superficial deposits, unmined bedrock and mined bedrock to characterise the geological and hydrogeological setting, and to provide access for baseline monitoring and mine water abstraction/ reinjection. The aims of the Observatory include de-risking key technical barriers to low-temperature shallow mine water heat energy and heat storage from groundwater in former coal mine workings; and providing environmental characterisation and monitoring to assess any change in ambient conditions.

This report describes the groundwater sampling and analysis methods and the groundwater chemistry of the Glasgow Observatory boreholes during the test pumping carried out between 14 January 2020 and 21 February 2020. The report accompanies the UKGEOS Glasgow Test Pumping Groundwater Chemistry Data Release.

Test pumping was undertaken following borehole installation to obtain data about the physical properties of the aquifers, as well as the hydraulic connectivity between individual boreholes and target aquifer horizons (mine workings, bedrock, and superficial deposits) across the Cuningar Loop sites of the Glasgow Observatory. Two types of tests were carried out on nine boreholes at the Cuningar Loop: a step drawdown test (SDT) and a constant rate test (CRT). A third type of test was carried out on one borehole only (GGB04): a slug (falling/rising head) test, due to very low yield observed on borehole cleaning.

Groundwater chemistry samples were collected during the nine CRTs to provide an initial hydrochemical characterisation of the aquifers and, where more than one sample was obtained during the test, to measure changes in selected constituents during pumping to complement observed hydraulic responses. The samples were taken at approximately two- and four- hour intervals into the CRT, or only after approximately four hours, where only one sample was retrieved. No samples were collected from GGB04 due to the very low yield.

Fifteen groundwater samples were collected for analysis of major, minor and trace elements, hexavalent chromium (CrVI), non-purgeable organic carbon (NPOC), stable isotopes (δ^2H, $\delta^{18}O$, $\delta^{13}C$-DIC), total petroleum hydrocarbons (TPH), polycyclic aromatic hydrocarbons (PAH), volatile organic compounds (VOC), dissolved gases (carbon dioxide (CO_2), methane (CH_4), ethane (C_2H_6)), and tracers (chlorofluorocarbons (CFC) and sulphur hexafluoride (SF_6)). In addition, field measurements of water temperature, pH, specific electrical conductance (SEC), redox potential (Eh) and dissolved oxygen (DO) were made.

The water samples were taken from: two boreholes into the superficial deposits; two boreholes into the unmined bedrock; three boreholes into the Glasgow Upper mine workings; and another two into the Glasgow Main mine workings.

The mine water temperatures measured in the Glasgow Main mine workings (depth of screened boreholes 84–88 m) were higher (12.4 °C) than those (11.9–12.1 °C) in the Glasgow Upper mine workings (46–54 m). With the exception of one of the boreholes in the superficial deposits (GGA06r), the following sequence of groundwater temperature (T) increase was found: $T_{Superficial\ deposits} < T_{Bedrock} < T_{Glasgow\ Upper} < T_{Glasgow\ Main}$, consistent with increasing depth.

The sampling reveals that the groundwaters from all the aquifer units are mineralised (SEC median 1690 µS/cm, range 1570–1940 µS/cm), with near neutral pH, and comprise bicarbonate–type waters with sodium (Na) as the dominant cation, except for boreholes GGA03r in bedrock and GGA09r in superficial deposits where calcium (Ca) is the major cation. They contain sufficient alkalinity (HCO_3 median 811 mg/L, range 731–943 mg/L) (net–alkaline waters) to neutralise the mineral acidity represented by the high dissolved iron (Fe) (median 2550 µg/L, range 417–19500 µg/L) and manganese (Mn) (median 411 µg/L, range 260–3100 µg/L) content. Anoxic conditions are common to all the groundwaters, showing DO < 0.5 mg/L; nitrate (NO_3) concentrations are consistently undetectable (< 0.6 mg/L). Concentrations of ammonium (NH_4) are high, up to 23 mg/L. Sulphate (SO_4) median is 174 mg/L and range 115–371 mg/L.

Based on statistical cluster analysis, we were able to distinguish three hydrochemical facies, corresponding to a principal group represented by the mine waters and two small clusters consisting of the superficial deposits and the unmined bedrock aquifers, respectively.

Groundwaters from boreholes in the Glasgow Upper mine workings and in the Glasgow Main mine workings have uniform composition suggesting good lateral connectivity of the aquifers associated with each mine working. Greater compositional differences are present between groundwaters sampled from different boreholes within the superficial deposits, and within the bedrock aquifer, suggesting poorer connectivity in these units.

The groundwater composition in the Glasgow Upper and Glasgow Main mine workings is typical of that reported in other Carboniferous mined aquifers in Scotland, with the majority of parameter concentrations being within the ranges reported in previous baseline surveys. For example, SO_4 concentrations of between 154 mg/L and 200 mg/L are close to the 90th percentile value of the Scottish baseline dataset. Iron concentrations range between 1870 and 4940 µg/L, Mn between 334–438 µg/L, and very low concentrations of trace metals such as As, Ni, Cu, Zn and Pb are present.

Groundwaters sampled from boreholes targeting the Gourock Sand Member of the Quaternary superficial deposits, which are overlain at this location by ~8 m of made ground, were found to be highly mineralised, consistent with previous studies of Glasgow groundwaters. It is likely that solute concentrations in these waters are elevated by anthropogenic inputs from the urban and industrial environment.

There were no detections of PAH or VOC in any sample. There are only a few detections of TPH, but, where they have been detected (GGA03r and GGA05), they are at concentrations very close to the detection limits.

The stable isotope ($\delta^{18}O$ and $\delta^{2}H$) composition of all the groundwaters shows a general correspondence with the global meteoric water line (GMWL), indicating that the groundwaters represent recharge from local groundwater consistent with the current climate. Most of the groundwaters have $\delta^{13}C$ values of dissolved inorganic carbon (DIC) in a narrow range from -11.4 to -10.6 ‰ (median value of -10.9 ‰), and most fall within the upper range (i.e. heavier $\delta^{13}C$) of values reported by previous studies in both the Coal Measures Group aquifer across the Midland Valley of Scotland and the River Clyde waters. The $\delta^{13}C$ of DIC averaging -10.9 ‰ combined with the high alkalinity of the groundwaters is consistent with a closed system/confined aquifer where the DIC $\delta^{13}C$ values gradually evolve from the soil gas CO_2 $\delta^{13}C$ signature (~ -26‰) towards the rock composition ($\delta^{13}C$ ~ 0 ‰, if marine carbonate, though this remains to be tested), and may well also reflect a contribution to $\delta^{13}C$ from the dissolution of rock carbonate by sulphuric acid (H_2SO_4) produced during pyrite oxidation in former coal workings.

Groundwaters from the Glasgow Upper and the Glasgow Main show a narrow range of dissolved CH_4 and CO_2 gas concentrations (Glasgow Upper CH_4 117–145 µg/L; CO_2 134–152 mg/L; Glasgow Main CH_4 174–185 µg/L; CO_2 120–123 mg/L). These values lie within the upper range of groundwaters reported in other studies from Carboniferous sedimentary rocks in the Midland Valley of Scotland. Higher concentrations of CH_4 and CO_2 were also present in groundwater samples from borehole GGA09r in the superficial deposits (CH_4 406 µg/L, CO_2 218 mg/L) and GGB05 in the bedrock (CH_4 297 µg/L, CO_2 256 mg/L).

The effect of test pumping on groundwater composition through time was negligible (with changes close to the analytical reproducibility) suggesting minimal induced mixing of different water bodies, or that any induced mixing was distant from the abstraction borehole.

Interpretation of residence time data from CFC-11, CFC-12 and SF_6 suggests that the average mean residence time of the groundwater is more than 45 years in all the aquifer units. Cross plots of SF_6, CFC-11 and CFC-12 suggest a piston type flow model is more likely than a binary mixing model (i.e. very modern mixed with older water), although this may be an artefact of the sampling and storage process for SF_6 and not necessarily a reflection of the concentrations present in the groundwater. Assuming a piston flow model, the waters have approximate recharge dates of 1968-1974 for the Glasgow Main; 1948-57 for the Glasgow Upper; 1948-1957 for the bedrock and 1950-1973 for the superficial deposits. The youngest waters occur in the deepest boreholes installed within the Glasgow Main mine workings. This underlies the complexity of the

groundwater flowpaths; however, as groundwater heads are generally upward, younger residence times at depth are not unexpected. Groundwater residence times in the superficial deposits are variable. This might reflect the mixing of rainfall recharge at the site with upwelling water from the deeper aquifers.

1 Introduction

In 2015, the British Geological Survey (BGS) and the Natural Environment Research Council (NERC) were tasked with developing new centres for research into the subsurface environment to aid the responsible development of new low-carbon energy technologies in the United Kingdom (UK) and internationally. Glasgow is one of two UK Geoenergy Observatories (UKGEOS) (Figure 1).

The Glasgow Observatory comprises a network of boreholes across five sites into the superficial deposits, mined and unmined bedrock in the Dalmarnock area in the east of Glasgow City (Site 10 on Figure 1b) and at the Cuningar Loop on the River Clyde in Rutherglen, South Lanarkshire (Sites 1, 2, 3 and 5 on Figure 1b). These were designed to characterise the geological and hydrogeological setting as a research infrastructure to de-risk key technical barriers to low-temperature shallow mine water heat/storage in an urbanised former mine setting (Monaghan et al. 2017, 2019). The borehole network is intended also for baseline monitoring to assess the environmental status before and during the lifetime of the project. Figure 1c shows the details of the 11 boreholes located at the Cuningar Loop.

Test pumping was carried out at nine of the Cuningar Loop boreholes in January and February 2020 to characterise the hydraulic properties of the target aquifer horizons (mine workings, bedrock, and superficial deposits), and to determine the extent to which these are hydraulically connected (Shorter et al. 2021; Figure 1c). Groundwater samples were collected during constant-rate pumping tests and analysed to provide an initial hydrochemical characterisation of the aquifers and, where more than one sample was obtained during the test, to measure changes in selected constituents during pumping, to complement observed hydraulic responses. Fifteen groundwater samples were obtained and were analysed to determine the concentrations of selected chemical parameters at the BGS and associated laboratories.

This report details the groundwater sampling protocols used during the test pumping, the analysis methods, and the groundwater hydrochemistry. The report accompanies the dataset: UKGEOS Glasgow Test Pumping Groundwater Chemistry Data Release.

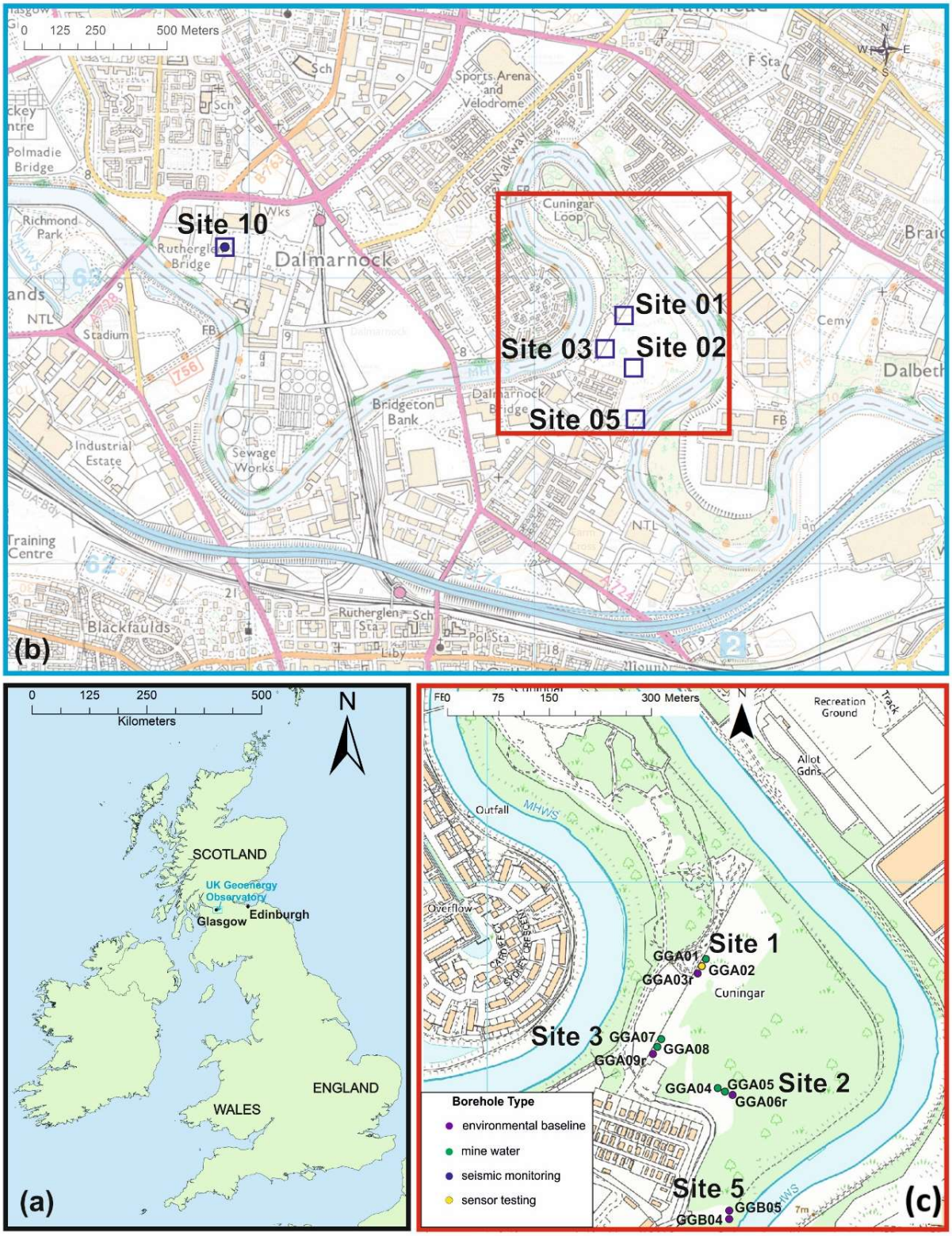


Figure 1 (a) Location of the Glasgow Observatory in the UK (b) position of Observatory sites (c) detail of Cuningar Loop mine water and environmental baseline characterisation and monitoring boreholes. Contains Ordnance Survey data © Crown Copyright and database rights 2021. Ordnance Survey Licence No. 100021290 EUL.

1.1 CITATION GUIDANCE

This report accompanies the release of the test pump groundwater hydrochemistry dataset.

Any use of the data should be cited to:
Palumbo-Roe B, Shorter K M, Fordyce F M, Walker-Verkuil K, Ó Dochartaigh B, Gooddy D, Darling W G. (2021). UKGEOS Glasgow Test Pumping Groundwater Chemistry Data Release. NERC EDS National Geoscience Data Centre. (Dataset) DOI 10.5285/53ded3f2-a4e9-4f49-8084-2c8b3b485268
this report cited as:
Palumbo-Roe B, Shorter K M, Fordyce F M, Walker-Verkuil K, Ó Dochartaigh B E, Gooddy D, Darling W G. 2021. UK Geoenergy Observatories Glasgow: Borehole Test Pumping - Groundwater Chemistry, British Geological Survey Open Report, OR/21/030

1.2 SUMMARY OF GLASGOW OBSERVATORY BOREHOLES AND TESTED BOREHOLES

1.2.1 Overview of the Glasgow Observatory

The Glasgow Observatory includes 12 boreholes (Figure 1, Table 1). Five are *mine water boreholes* that are drilled into, and screened against, individual former mine workings; five are *environmental baseline monitoring boreholes* that are drilled into, and screened against, targeted zones in bedrock above the Glasgow Upper mine working, or in superficial deposits overlying bedrock. Two boreholes were not available for hydrogeological testing: borehole GGA02 is a fully cased sensor testing borehole and GGC01 is a seismic monitoring borehole in Dalmarnock, c. 2 km WNW of the main borehole cluster at the Cuningar Loop.

Table 1 Glasgow Observatory borehole infrastructure

Site name	Borehole ID	Borehole type	Target horizon
Site 1	GGA01	Mine water	Glasgow Upper mine working
Site 1	GGA02	Sensor testing	N/A (No borehole screen)
Site 1	GGA03r	Environmental baseline	Bedrock
Site 2	GGA04	Mine water	Glasgow Upper mine working
Site 2	GGA05	Mine water	Glasgow Main mine working
Site 2	GGA06r	Environmental baseline	Superficial deposits
Site 3	GGA07	Mine water	Glasgow Upper mine working
Site 3	GGA08	Mine water	Glasgow Main mine working
Site 3	GGA09r	Environmental baseline	Superficial deposits
Site 5	GGB04	Environmental baseline	Superficial deposits
Site 5	GGB05	Environmental baseline	Bedrock
Site 10	GGC01	Seismic monitoring	N/A (No borehole screen)

Note: Boreholes GGA02 and GGC01 were not included in the test pumping as these were not installed with borehole screen (GGC01) or successfully completed with borehole screen (GGA02).

Table 2 summarises the 10 boreholes that were included in the test pumping and the dates testing was carried out. The screened target zone in each of the 10 boreholes is between 1.8 and 3.6 m long. Above the screened section the remainder of each borehole is cased off to prevent inflow to the borehole from any other zone and the borehole annulus is sealed and cemented.

Table 2 Description of test zone (screened section) and dates of test pumping carried out on the Glasgow Observatory boreholes

Borehole	Aquifer unit	Description of screened section (test zone)	Date of step drawdown test	Date of constant rate test	Date of falling/rising head test
GGA01	Glasgow Upper mine working	Overlying sandstone roof and Glasgow Upper mine working waste	14/01/2020	15/01/2020	-
GGA03r	Bedrock	Sandstone below rockhead, above Glasgow Upper mine working	17/01/2020	First test: 20/01/2020 Second test: 18/02/2020	-
GGA04	Glasgow Upper mine working	Overlying sandstone roof and Glasgow Upper mine working position coal and mudstone	27/01/2020	28/01/2020	-
GGA05	Glasgow Main mine working	Overlying sandstone roof and Glasgow Main mine working void, to mudstone floor	22/01/2020	23/01/2020	-
GGA06r	Superficial	Sand and gravel	30/01/2020	31/01/2020	-
GGA07	Glasgow Upper mine working	Overlying mudstone and Glasgow Upper mine working, coal pillar and void	06/02/2020	07/02/2020	-
GGA08	Glasgow Main mine working	Overlying sandstone/siltstone and Glasgow Main mine roadway (void and waste)	03/02/2020	04/02/2020	-
GGA09r	Superficial	Sand and gravel	10/02/2020	11/02/2020	-
GGB04	Superficial	Sand and gravel	-	-	17/02/2020 - 19/02/2020
GGB05	Bedrock	Sandstone below rockhead, above Glasgow Upper mine working	13/02/2020	14/02/2020	

Note: GGB04 was included in the test pumping but only a slug (falling/rising head) test was possible due to the very low yield and no groundwater samples were collected.

2 Methodology

2.1 SUMMARY OF TEST PUMPING

The test pumping programme was carried out after all boreholes had been drilled, installed with Boode® borehole casing (henceforth, referred to as borehole casing) and cleaned via abstraction of water either until water quality parameters stabilised or for a maximum of two hours. There was a minimum of five days between borehole flushing and the test pumping starting.

The programme was started on 14 January 2020 and completed on 21 February 2020. A sub-contractor, Drilcorp, were commissioned to carry out the test pumping. The Drilcorp team included a hydrogeologist to manage the test pumping alongside BGS hydrogeologists. Two types of tests were carried out on nine of the boreholes: a step drawdown test (SDT) and a constant rate test (CRT). Shorter et al. (2021) report the test pumping in detail, a summary is given below.

The SDT consisted of four or five steps of increasing pump rate. Each step was one hour long, except for the SDT on GGA03r, where a sustainable flow rate could not be achieved throughout the SDT, resulting in four steps being carried out of varying lengths.

During the CRT, the borehole was pumped for five hours and recovery was manually monitored for a further one hour. The samples for groundwater chemistry determination were taken at approximately two hours and four hours into the CRT, or after approximately four hours, where only one sample was retrieved. Problems were encountered during the first CRT carried out on GGA03r, resulting in a second one being conducted a month later. Ninety minutes into the first CRT on GGA03r, the pump switched off due to the excessive water level drawdown. After 30 minutes, it was possible to turn the pump back on for another 30 minutes of pumping, during which a sample was retrieved. After the sampling, the test pumping was halted due to excessive drawdown. No sampling was conducted during the second CRT carried out on GGA03r.

On one borehole only (GGB04), a third type of test was carried out: a slug (falling/rising head) test due to very low yield observed on borehole cleaning, meaning that a SDT and CRT were not considered feasible. No sample was retrieved from this borehole during this time period (see Section 2.2 for details on sampled boreholes). Table 3 summarises the type of pumping test on each borehole.

Table 3 Pumping rate and type of pump used for the test pumping of each borehole

Borehole	Pumping rates used during step drawdown test (L/s)	Pumping rate of constant rate test (L/s)	Type of pump used
GGA01	4.8/10.3/15/19.7/24.9	20	Grundfos SP 95-4 submersible pump
GGA03r	0.13/0.17/0.28/0.28	0.16 – 0.19	E-tech VS2/7 submersible pump for first CRT
GGA04	4/7.9/11.7/15.5/19.8	15	Grundfos SP 95-4 submersible pump
GGA05	5/10/14.9/19.9/25	20	Grundfos SP 95-4 submersible pump
GGA06r	0.12/0.26/0.4/0.62	0.5	Grundfos SQ 1-35 submersible pump
GGA07	5/10.1/15/20/25	20	Grundfos SP 95-4 submersible pump
GGA08	5/10.1/15.2/20.2/25.2	20	Grundfos SP 95-4 submersible pump
GGA09r	0.12/0.22/0.42/0.62	0.5	Grundfos SQ 1-35 submersible pump
GGB04	NA	NA	NA
GGB05	1/2/2.8/3.5/4.3	6.6	E-Tech VS15/8 submersible pump

2.2 BOREHOLES SAMPLED

Sampling for groundwater chemistry determination was carried out on nine of the 10 boreholes in which test pumping was conducted (Table 4). GGB04 was not sampled as a falling/rising slug test was performed on this borehole rather than a SDT and CRT due to the very low yield.

Table 4 Groundwater samples taken during the test pumping

Site	Borehole ID	Sample taken after 2 hours of pumping	Sample taken after 4 hours of pumping
1	GGA01	✓	✓
1	GGA03r	✓*	
2	GGA04	✓	✓
2	GGA05	✓	✓
2	GGA06r	✓	✓
3	GGA07	✓	✓
3	GGA08	✓	✓
3	GGA09r		✓
5	GGB04	No sampling	
5	GGB05	✓	✓

*The sample in GGA03r was taken after one hour 55 minutes due to rapidly falling water level in the borehole resulting in the pump test being cut short.

2.3 SAMPLING SET-UP

The test pumping was carried out using equipment provided by Drilcorp. A sample tap was fitted to the rising main of the pump used in the test pumping, allowing a continuous flow of groundwater to be drawn from the rising main into a flow-through cell or to be collected for sample purposes (Figure 2). One end of the Y-tubing was used to connect the flow-through cell to the sample tap, whilst a second shorter end of the Y-tubing connected the sample tap to a plastic beaker into which the temperature probe was placed. Four of the probes for field parameter measurements (pH, specific electrical conductance (SEC), redox potential (Eh) and dissolved oxygen (DO)) were placed securely into the lid of the flow-through cell, ensuring all connections were air tight.

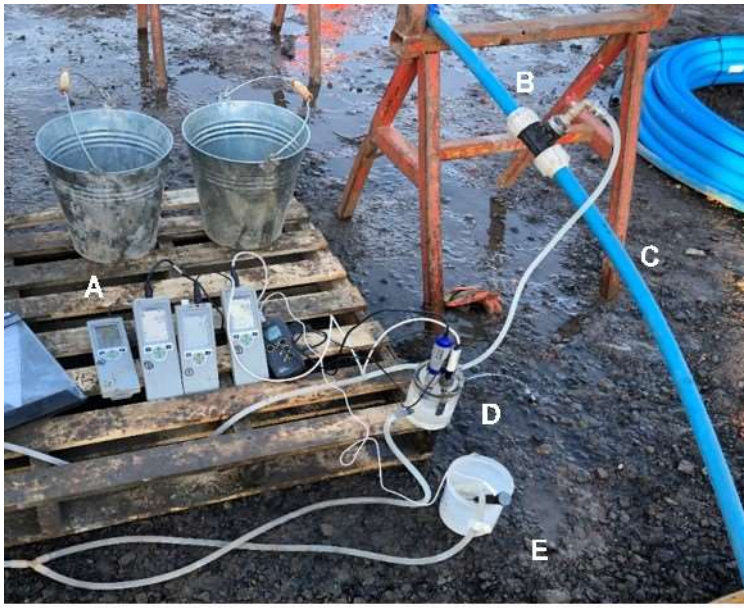


Figure 2 Borehole set up for recording field parameters and taking samples. A: Field parameter meters. B: Sampling tap. C: Rising main. D: Flow-through cell. E: Temperature probe. This example is from GGA03r, an environmental baseline borehole.

2.4 FIELD PARAMETER MEASUREMENTS AND FIELD OBSERVATIONS

At each borehole measurements of key physico-chemical parameters were obtained in the field.

Specific electrical conductance, pH, DO, Eh and temperature were measured on site, using portable meters in a flow-through cell (see set-up in Figure 2) and for the temperature probe, in a beaker. The water in the beaker with the temperature probe was constantly flowing through the beaker and over flowing out of it, meaning the water was regularly changed.

The meters were calibrated/checked according to manufacturer instructions each day as follows:

- Groundwater pH was determined using a Mettler Toledo® SevenGo pro pH meter and Jenway® gel probe calibrated with commercially available buffer solutions (pH 4, 7, 9). The sample pH was recorded to the nearest 0.01 pH unit.
- Redox potential was assessed using a Mettler Toledo® SevenGo pro ion meter and VWR® Eh probe with a 0.1 mV sensitivity, checked with commercially available Zobell's solution of known Eh. The field Eh measurements were translated to the standard hydrogen electrode (SHE) using temperature-dependent conversion tables appropriate to the VWR® probe and recorded to the nearest 1 mV.
- Specific electrical conductance was measured using a Mettler Toledo® Seven2Go Pro conductivity meter and probe, with a sensitivity of 0.1 µS/cm, calibrated with commercially available buffer solutions. The sample SEC was recorded to the nearest 1 µS/cm.
- Dissolved oxygen was determined using a Mettler Toledo® Seven2Go Pro DO meter and InSitu® DO probe. The DO probe was calibrated with commercially available saturated sodium sulphite solution (0% DO). The sample DO was recorded to the nearest 0.1 mg/L.
- Water temperature was recorded using a Hanna® waterproof thermistor thermometer to the nearest 0.1 °C.

Parameters were monitored at regular intervals throughout the constant rate test and at the time of sample collection.

Alkalinity was measured a minimum of three times on each sample, using a Hach Digital Titrator and either 0.16 N or 1.6 N sulphuric acid, and the bromocresol green indicator method. The field total alkalinity measurements were reported as field bicarbonate (HCO_3) concentrations.

Observations on the groundwater sample condition were noted during collection. Examples of these observations include descriptions of the water colour and any noticeable groundwater odour.

2.5 SAMPLE COLLECTIONS AND ANALYSES

All groundwater samples were analysed for the following constituents:

- Non-purgeable organic carbon (NPOC) and total inorganic carbon (TIC)
- The stable isotopes - deuterium (δ^2H), oxygen 18 ($\delta^{18}O$) and carbon 13 of dissolved inorganic carbon (DIC) ($\delta^{13}C_{DIC}$)
- Major and trace cations and anions
- Chromium speciation (CrVI)
- Ammonium (NH_4)
- Total petroleum hydrocarbons (TPH)
- Polycyclic aromatic hydrocarbons (PAH)
- Volatile organic compounds (VOC)
- Methane, ethane and carbon dioxide (CH_4, C_2H_6, CO_2)

In addition, the following analyses were carried out on the four-hour samples:

- Chlorofluorocarbons (CFC-12 and CFC-11)
- Sulphur hexafluoride (SF_6)

No viable samples were obtained for noble gases (helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe)).

Sample splits were collected at the boreholes, according to the methods outlined in following sections.

2.5.1 Filtered waters inorganic cation, anion, Cr(VI) and NH_4

Groundwater samples for inorganic major, minor and trace cations, anions and chromium speciation (CrVI) analysis were taken using a disposable plastic syringe and 0.45 µm cellulose disposable filter. All sample bottles were rinsed with filtered sample water three times before being filled.

Post sample collection, the sample for inorganic major, minor and trace cations was acidified using 1% (v/v) concentrated nitric acid (HNO_3) on return to the office at the end of each day of sampling. On submission to the laboratory, these samples were acidified further with 0.5% (v/v) concentrated hydrochloric acid (HCl).

2.5.2 Filtered water NPOC

A sample for dissolved organic carbon (DOC, as non-purgeable organic carbon (NPOC)) was collected using a glass syringe from the stainless-steel beaker. The sample was filtered through a 0.45 µm silver filter into a glass vial.

2.5.3 Unfiltered water for stable isotopes

Unfiltered groundwater samples for determination of stable isotopes of δ^2H, $\delta^{18}O$ and $\delta^{13}C_{DIC}$ were taken by filling the sample bottles to the top and ensuring no air was left in the bottles. All sample bottles were rinsed with sample water three times before being filled.

2.5.4 Unfiltered water samples for TPH, PAH and VOC

A clear glass bottle for TPH and amber glass bottle dosed with sodium thiosulphate for PAH were filled with unfiltered sample water directly from the sample tap fitted to the rising main of the pump (Figure 2).

An amber glass vial dosed with sodium thiosulphate for VOCs was filled with unfiltered sample water directly from the sample tap fitted to the rising main of the pump (Figure 2).

2.5.5 Unfiltered water samples for dissolved gases

An amber glass bottle for CFC and a clear glass bottle for SF_6 were filled by submerging the bottles in an overflowing container with unfiltered sample water directly from the sample tap fitted to the rising main of the pump (Figure 2). This was to ensure no air bubbles were left in the bottles

and avoid contact with the atmosphere. The samples were taped shut to ensure no contamination from outside sources.

A sample of dissolved gases (CH_4, C_2H_6, CO_2) was collected in a metal container 'gas bomb' with two screw taps on either end. The gas bomb was filled with unfiltered sample water directly from the sample tap fitted to the rising main of the pump (Figure 2). The sample was collected at a 45 degree angle ensuring no air bubbles were left in the gas bomb. The screw inlet and outlet taps were tightened to ensure no air bubbles entered while disconnecting from the sample tap.

2.6 SAMPLE TRANSPORT AND ANALYSIS

Groundwater samples for NPOC, stable isotopes, major and minor ions and Cr(VI) were analysed at the BGS laboratories in Keyworth. Ammonium was analysed at Wallingford on UKCEH equipment and the dissolved gas samples were analysed at BGS Wallingford; the TPH, PAH and VOCs were analysed by the Scottish Water laboratory in Edinburgh.

All groundwater samples were stored in a cool box upon collection and refrigerated at the end of each sampling day. Samples were transferred to the analytical laboratories within 48 hours or as soon as possible, to avoid degradation of the samples prior to analysis.

The groundwater samples were included in the same analytical runs as the UKGEOS Glasgow baseline surface water chemistry samples that were being collected at the same time (Fordyce et al. 2021). As such, the samples are subject to the same analytical methodologies and quality control (QC) procedures as the UKGEOS surface water chemistry dataset 1. The analytical methods and data quality controls are summarised in Appendix 1 and described in full in Fordyce et al. (2021).

Exceptions include parameters that were measured in the groundwater samples only. These include VOCs, CH_4, C_2H_6, CO_2, CFC-12, CFC-11, SF_6 and the analytical methods for these parameters are described in full in Appendix 1.

3 Data Presentation

3.1 DATASET

3.1.1 Chemical data

The Glasgow Observatory test pumping groundwater chemistry dataset that accompanies this report is presented in Excel® table format:

Filename: UKGEOSGlasgow_TestpumpingGWChemData.xlsx

It contains the field parameter (pH, temperature, Eh, DO, SEC, Field HCO_3) measurements at the time of sample collection and the results of inorganic and organic chemical analyses for each of the 15 groundwater samples collected during test pumping. The first sheet in the workbook holds the dataset. The second sheet contains a guide to abbreviations used in the dataset.

The dataset includes descriptive information about the samples noted during fieldwork, such as location and groundwater condition.

For the chemical data, the parameter name, element chemical symbols, analytical method, units of measurement and long-term lower limit of detection (LLD) and lower limit of quantification (LOQ) are reported in header rows at the top of the table.

Whilst the long-term LLD/LOQ are documented at the top of the Excel® sheet, run-specific LLD/LOQ are given in the body of the table at the head of each analytical batch. Data below detection are recorded as < the run-specific LLD. These varied slightly between analytical runs, and cases where samples with high mineral content had to be diluted prior to analysis. For example, the LLD for NPOC is < 0.5 mg/L. If a sample underwent 2-fold dilution prior to analysis, this is reported as < 1 mg/L in the dataset. Therefore, the < LLD values reported in the dataset reflect the conditions in each analytical run, as opposed to the long-term LLD/LOQ recorded at the top of the dataset.

In the Excel® sheet, the inorganic chemical data are reported in alphabetical order by chemical symbol in mg/L for the major and minor cations and anions, followed by trace element data in µg/L. Stable isotope data are then reported in ‰ Vienna Pee Dee Belemnite (VPDB) for δ^{13}C-DIC and ‰ Vienna Standard Mean Ocean Water (VSMOW2) for δ^{18}O and δ^{2}H. Total inorganic carbon data are reported in mg/L following the isotope data. This is followed by the dissolved gas data, starting with CFC data in pmol/L, SF_6 data in fmol/L, the modern fractions and year of recharge of both CFC and SF_6 data, CH_4 and C_2H_6 in µg/L and CO_2 in mg/L. Finally, data for organic parameters are reported in mg/L for NPOC and TPH and µg/L for PAHs and VOCs.

3.1.2 Field parameters

Field parameters were monitored throughout the constant rate test, at approximately 10–60 minute intervals. These are included as an additional time-series groundwater field parameter dataset accompanying this report and presented in Excel® table format:

Filename: UKGEOSGlasgow_TestpumpingGWFieldData_V2.xlsx

It contains the results of the field parameters (temperature, pH, DO, SEC, Eh and field bicarbonate) recorded throughout the constant rate test on each borehole. The first sheet in the workbook holds the dataset. The second sheet contains a guide to abbreviations used in the dataset.

In the Excel® sheet, the boreholes are listed in numerical order. The field parameters are reported in the order: pH, temperature, Eh corrected, DO, SEC and field-HCO_3.

These time-series field measurement data are presented in graphs in Appendix 2 for information, but are not further described in this report.

3.2 DATA ANALYSIS IN THIS REPORT

In this report, the groundwater chemistry data are described by grouping the boreholes based on the target horizon the water is drawn from, starting with the shallowest boreholes on-site and

proceeding towards the deepest boreholes (sequence: superficial deposits boreholes, bedrock boreholes, Glasgow Upper mine workings and Glasgow Main mine workings boreholes).

Cross reference to the dataset Excel® file sample ID of the labels and names used for the purpose of this report (referring either to the borehole or the target horizon) is provided in Table 5; furthermore, to represent groundwater data obtained respectively at about two and four hours from the start of the test pumping, samples are referred to as e.g. GGA01-2H or GGA01-4H.

Table 5 Sample ID list with reference to abbreviated names in this report, site, borehole and target horizon details

Sample ID	Short name	Site	Borehole ID	Target horizon
GGA01 PTD/BGS-GGA01-22	GGA01-2H	Site 1	GGA01	Glasgow Upper
GGA01 PTE/BGS-GGA01-30	GGA01-4H	Site 1	GGA01	Glasgow Upper
GGA03r-PTD/BGS-GGA03r-19	GGA03r-2H	Site 1	GGA03r	Bedrock
GGA04-PTD/BGS-GGA04-17	GGA04-2H	Site 2	GGA04	Glasgow Upper
GGA04-PTE/BGS-GGA04-18	GGA04-4H	Site 2	GGA04	Glasgow Upper
GGA05-PTD/BGS-GGA05-34	GGA05-2H	Site 2	GGA05	Glasgow Main
GGA05-PTE/BGS-GGA05-35	GGA05-4H	Site 2	GGA05	Glasgow Main
GGA06r-PTE/BGS-GGA06r-06	GGA06r-4H	Site 2	GGA06r	Superficial deposits
GGA07-PTD/BGS-GGA07-38	GGA07-2H	Site 3	GGA07	Glasgow Upper
GGA07-PTE/BGS-GGA07-39	GGA07-4H	Site 3	GGA07	Glasgow Upper
GGA08-PTD/BGS-GGA08-61	GGA08-2H	Site 3	GGA08	Glasgow Main
GGA08-PTE/BGS-GGA08-62	GGA08-4H	Site 3	GGA08	Glasgow Main
GGA09r-PTE/BGS-GGA09r-07	GGA09r-4H	Site 3	GGA09r	Superficial deposits
GGB05-PTD/BGS-GGB05-08	GGB05-2H	Site 5	GGB05	Bedrock
GGB05-PTE/BGS-GGB05-09	GGB05-4H	Site 5	GGB05	Bedrock

The groundwater hydrochemistry description is based on the samples collected after four hours of pumping. Only the four-hour samples were collected for all boreholes and so use of the 4 hour sample analysis data allows for a more consistent comparison. The samples after four hours of pumping were also preferred as they should be more representative of the wider groundwater unit. The sample from GGA03r was the only exception, as it was taken after one hour 55 minutes due to the rapidly falling water level in the borehole, which resulted in the pumping test being cut short.

Where groundwater samples were also obtained after two hours of pumping, the data are displayed in graphs along with the four-hour samples.

Chemical parameters where the majority of data are below the LLD or LOQ are not displayed. These include: silver (Ag), aluminium (Al), beryllium (Be), bismuth (Bi), cadmium (Cd), copper (Cu), gallium (Ga), hafnium (Hf), orthophosphate (HPO_4), molybdenum (Mo), niobium (Nb), nitrite (NO_2), antimony (Sb), selenium (Se), tin (Sn), tantalum (Ta), thorium (Th), titanium (Ti), tungsten (W), PAH, TPH and VOC. Lanthanum (La) is displayed as a representative of the Rare Earth Element (REE) group; most of the other REEs are close to or below the LLD/LOQ.

Rounding off to three significant figures was applied in reporting the values.

The variability of parameter concentrations between samples was determined as:

(i) the relative percent difference (RPD = absolute difference divided by average, multiplied by 100) of parameter total concentrations where the number of samples was two;

(ii) the relative standard deviation (RSD= standard deviation divided by average, multiplied by 100), where the number of samples was more than two.

The RPD and RSD were calculated using the two-hour samples and four-hour samples to determine the effect of pumping on the major ion composition through time, and using all the samples from the same borehole lithology to estimate the variability across each target horizon.

Summary statistics and graphs for this report were prepared in Excel® and Minitab® software packages.

Cluster analysis of observations was used as an exploratory data analysis method with the aim of splitting the data under consideration into a number of groups, which are similar in their characteristics or behaviour (Reimann et al. 2008). The Ward's minimum variance method was used to form groups based on their similarity as defined by specified characteristics and the Pearson distance. The geochemical dataset used for cluster analysis consisted of the following parameters: calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), HCO_3, chloride (Cl), sulphate (SO_4), bromide (Br), fluoride (F), silicon (Si), barium (Ba), strontium (Sr), manganese (Mn), iron (Fe), boron (B), vanadium (V), chromium (Cr), cobalt (Co), nickel (Ni), zinc (Zn), arsenic (As), rubidium (Rb), yttrium (Y), zirconium (Zr), uranium (U), NH_4, NPOC. Inorganic traces that were below LLD for some of the samples were not included as variables. The data were standardised to convert all variables to a common scale by subtracting the means and dividing by the standard deviation before the distance matrix was calculated, to minimise the effect of scale differences.

The Piper diagram in Figure 3 (Piper 1944) to assess water type was generated using the Geochemist’s Workbench® software package. Mineral saturation indices were determined using the PHREEQC modelling package (Parkhurst and Appelo 1999).

4 Results

4.1 PHYSICO-CHEMICAL PARAMETERS, MAJOR, MINOR AND TRACE CONSTITUENTS

The physico-chemical parameters and inorganic major, minor and trace element chemical data for the groundwater samples are summarised in the following sections, based on the target horizon and their distribution across the boreholes shown in Appendix 3. The summary statistics for the whole dataset is reported in Appendix 4.

4.1.1 Superficial deposits boreholes

Boreholes GGA06r at Site 2 and GGA09r at Site 3 targeting the superficial deposits were sampled after approximately four hours of pumping (Table 5). When reporting the groundwater parameter values, the boreholes are always listed in the order GGA06r, GGA09r, unless specified otherwise.

Groundwaters from boreholes GGA06r and GGA09r are highly mineralised with SEC values of 1610 and 1690 µS/cm at the time of sampling. The superficial deposits water temperature in borehole GGA06r is 12.1 °C, while the temperature of GGA09r is slightly cooler at 11.4 °C. They have a neutral pH (7.14, 7.01). The DO is almost depleted (0.1 mg/L) and Eh slightly reducing (215, 207 mV).

Major cations (Ca, Mg, Na, and K), major anions (SO_4, Cl, HCO_3), and non-ionic solutes (uncharged solutes such as Si) typically are present in natural waters at concentrations greater than 1 mg/L (Hem 1985). Based on their major ion composition, the superficial deposits groundwaters are HCO_3–type waters with high field-alkalinity (769, 943 mg/L as HCO_3) and Na as the dominant cation for borehole GGA06r and Ca for GGA09r (Figure 3). The elemental concentrations are as follows: Na 160, 118 mg/L and Ca 121, 165 mg/L; concentrations of Mg are 49, 50 mg/L and K 21, 22 mg/L. Sulphate and Cl are higher in GGA06r groundwaters than in GGA09r (SO_4 174, 115 mg/L and Cl 77, 55 mg/L). Silicon is 6.02 mg/L and 5.53 mg/L.

The redox sensitive species nitrate (NO_3) is < 0.6 mg/L in accordance with the DO close to 0 mg/L, while NH_4 concentrations are very high (19, 22 mg/L). In addition, both dissolved Fe and Mn are high (Fe 1410, 2380 µg/L and Mn 1940, 3100 µg/L).

Dissolved organic matter concentrations as NPOC are 4.7 mg/L and 5.2 mg/L.

The minor and trace element concentrations, respectively, in GGA06r and GGA09r groundwaters are as follows: the halogen Br is 0.49, 0.33 mg/L and F low, with 0.19, 0.14 mg/L. Trace alkali metals are low, below or close to the LLD: lithium (Li) < 8 µg/L, caesium (Cs) <0.05 and 0.05 µg/L, Rb 8.8, 11.4 µg/L. Barium has the highest concentrations in the superficial deposits compared to the mine waters and bedrock, with 93, 97 µg/L. The other trace alkaline earth metal Sr has concentrations of 574 µg/L and 1100 µg/L. Transition metals other than Fe and Mn have the following concentrations: Co 2.77, 3.25 µg/L; Cr-Total 0.20, 0.26 µg/L, Ni 5.04, 4.55 µg/L, V 0.24, 0.42 µg/L and Zn 1.8, 1.5 µg/L. The Cr speciation data are all below the LLD values of 0.05 for Cr(VI) and 0.04 for Cr(III). The metalloid B is 512, 736 µg/L, As is 1.14, 0.94 µg/L; lead (Pb) is 0.04 µg/L in both samples and thallium (Tl) <0.03 µg/L. The REE lanthanum (La) is 0.061 µg/L and 0.058 µg/L. Uranium groundwater concentrations are highest in the superficial deposits compared to the mine waters and bedrock with 2.37 µg/L and 1.16 µg/L. Zirconium is 0.097, 0.242 µg/L. Yttrium is 0.21, 0.24 µg/L.

4.1.2 Bedrock boreholes

Borehole GGA03r at Site 1 was sampled after two hours of pumping and GGB05 at Site 5 both at two and four hours of pumping (Table 5). The description of the groundwater hydrochemistry for GGA03r-2H and GGB05-4H is given below. When reporting the borehole parameter values, the boreholes are always listed in the order GGA03r, GGB05, unless specified otherwise.

Groundwaters from the bedrock boreholes GGA03r and GGB05 are highly mineralised with SEC values of 1570 µS/cm and 1930 µS/cm, respectively at the time of sampling. Temperatures are 11.7 and 11.5 °C and the pH is 7.13 and 6.93, indicating near-neutral waters. The DO is almost depleted (0.18, 0.04 mg/L) and Eh slightly reducing (240, 159 mV).

The bedrock groundwater samples are HCO_3–type with Ca as the dominant cation for borehole GGA03r and Na for GGB05 (Figure 3). Major cations and anions respectively for GGA03r and GGB05 waters are as follows: Ca 139, 126 mg/L; Mg 75, 55 mg/L; Na 98,175 mg/L; K 9, 23 mg/L; field-HCO_3 742, 731 mg/L; SO_4 220, 367 mg/L and Cl 52, 67 mg/L. Silicon is 5.87 mg/L and 6.82 mg/L.

The redox sensitive species NO_3 is < 0.6 mg/L; instead, concentrations of the anoxic species of nitrogen, NH_4, are very high, although relatively lower (3.4 mg/L) in GGA03r, than in GGB05 (16.6 mg/L). Consistently with the DO close to 0 mg/L, also both dissolved Fe and Mn are high (Fe 417, 19180 µg/L and Mn 260, 610 µg/L), with a remarkable high Fe concentration in GGB05 groundwaters.

Dissolved organic matter (as NPOC) concentration is 2.33 mg/L and 2.34 mg/L.

The minor and trace element concentrations, respectively, in GGA03r and GGB05 groundwaters are as follows: the halogen Br is 0.54, 0.53 mg/L, and F <0.1, 0.16 mg/L. Trace alkali metals are: Li 19, 36 µg/L, Cs 0.14, 0.26 µg/L and Rb 18, 58 µg/L. The trace alkaline earth metal Ba is 130, 26 µg/L and Sr 3690, 2160 µg/L. Transition metals other than Fe and Mn have the following concentrations: Co 5.46, 3.56 µg/L; Cr-Total <0.05, 0.1 µg/L, Ni 6.02, 7.61 µg/L, V 0.07, 0.05 µg/L and Zn 9.8, 7.5 µg/L. The Cr speciation data available only for GGA03r waters are below the LLD values of 0.05 for Cr(VI) and 0.04 for Cr(III). Boron is 157, 312 µg/L and As 2.5, 4.1 µg/L. Lead is 0.17, 0.05 µg/L and Tl 0.04, 0.07 µg/L. The REE lanthanum (La) is 0.018, 0.024 µg/L. Uranium concentrations are 0.65, 0.30 µg/L. Zirconium is 0.012, 0.05 µg/L and Y is 0.086, 0.117 µg/L.

4.1.3 Glasgow Upper mine working boreholes

Samples were obtained both at two and four hours during test pumping carried out on the boreholes installed in the Glasgow Upper mine working GGA01 (located at Site 1), GGA04 (located at Site 2) and GGA07 (located at Site 3). The physico-chemical parameters and major, minor and trace element composition of the samples after four hours of pumping (GGA01-4H, GGA04-4H and GGA07-4H) are reported as minimum, maximum and median values.

Groundwaters from the three Glasgow Upper boreholes are highly mineralised with SEC values of 1690–1750 µS/cm, median 1750 µS/cm at the time of sampling. The temperature is 11.9 °C in all the three samples. The pH range is 7.02–7.21, median 7.1, indicating neutral waters. The DO is almost depleted (0.06–0.16 mg/L, median 0.06 mg/L) and the Eh reducing (128–160 mV, median 131 mV).

The groundwater samples are HCO_3–type waters with Na as the dominant cation (Figure 3).

Calcium range and median values are 106–108 mg/L, 107 mg/L; Mg 53–54 mg/L, median 53 mg/L; Na 172–186 mg/L, median 178 mg/L; K 18.1–18.9 mg/L, median 18.9 mg/L; field-HCO_3 807–839 mg/L, median 819 mg/L; SO_4 166–199 mg/L, median 178 mg/L and Cl 71.2–75.9 mg/L, median 71.2 mg/L. Silicon is 4.99–5.11 mg/L, median 5.00 mg/L.

The redox sensitive species NO_3 is < 0.6 mg/L, consistently with the DO close to 0 mg/L. Ammonium concentration is high (15.5–23, median 15.9 mg/L) and both dissolved Fe and Mn are also high, (Fe 2560–4940 µg/L, median 3500 µg/L and Mn 369–438 µg/L, median 411 µg/L).

The dissolved organic matter (as NPOC) concentration is 1.81 mg/L to 3.04 mg/L, median 2.07 mg/L.

The minor and trace element concentrations are as follows: the halogen Br is 0.48–0.56 mg/L, median 0.51 mg/L, and F 0.16–0.18 mg/L, median 0.17 mg/L. Trace alkali metals are: Li 29–32 µg/L, median 31 µg/L, Cs 0.17–0.22 µg/L, median 0.22 µg/L and Rb 40.6–42.4 µg/L, median 41.3 µg/L. The trace alkaline earth metal Ba is 38.2–46.2 µg/L, median 40.2 µg/L and Sr 1990–2290 µg/L, median 2024 µg/L. Transition metals other than Fe and Mn have concentrations: Co 1.09–2.01 µg/L, median 1.44 µg/L; Cr-Total 0.1–0.21, median 0.12 µg/L, Ni 3.13–3.86 µg/L, median 3.65 µg/L, V 0.07–0.12 µg/L, median 0.09 µg/L and Zn 2.3–6.3 µg/L, median 2.4 µg/L. The Cr speciation data are all below the LLD values of 0.05 for Cr(VI) and 0.04 for Cr(III). Boron is 323–368 µg/L, median 357 µg/L; As 0.5–2.27, median 0.93 µg/L; Pb 0.03–0.05 µg/L, median 0.04 µg/L and Tl 0.05µg/L, median 0.05 µg/L. The REE La is 0.009–0.018 µg/L, median 0.014 µg/L. Uranium

concentrations are 0.382–0.531 µg/L, median 0.51 µg/L. The concentration of Zr is 0.07–0.108 µg/L, median 0.07 and Y is 0.069–0.121 µg/L, median 0.102 µg/L.

4.1.4 Glasgow Main mine working boreholes

Samples were obtained both at two and four hours during test pumping carried out on the two boreholes installed in the Glasgow Main mine working of the Glasgow Observatory, GGA05 at Site 2 and GGA08 at Site 3. The description of the samples after four hours of pumping (GGA05-4H and GGA08-4H) is given below. When reporting the borehole parameter values, the boreholes are always listed in the order GGA05 and GGA08, unless specified otherwise.

Groundwaters from boreholes GGA05 and GGA08 are highly mineralised with SEC values of 1670, 1690 µS/cm, respectively at the time of sampling. The temperature is 12.4 °C in both boreholes. The pH is 7.13, 7.21, indicating neutral waters. The DO is almost depleted (0.04, 0.11 mg/L) and Eh slightly reducing (133, 155 mV).

The groundwater samples are HCO_3–type with Na as dominant cation (Figure 3). Major cations and anions respectively for GGA05 and GGA08 groundwaters, are as follows: Ca 107 mg/L in both boreholes; Mg 54.7, 55.3 mg/L; Na 174, 174.2 mg/L; K 19.1, 19.2 mg/L; field-HCO_3 833, 826 mg/L; SO_4 154, 156 mg/L and Cl 70.9, 71.8 mg/L. Silicon is 5.01 mg/L and 5.11 mg/L.

The redox sensitive species NO_3 is < 0.6 mg/L and NH_4 concentration high (15 and 13.8 mg/L), consistently with the DO close to 0 mg/L; both dissolved Fe and Mn are high (Fe 1870, 1920 µg/L and Mn 334, 327 µg/L).

Dissolved organic matter (as NPOC) concentration is 2.65 mg/L and 2.07 mg/L.

The minor and trace element concentrations, respectively, in GGA05 and GGA08 groundwaters are as follows: the halogen Br is 0.45mg/L in both boreholes, and F 0.15, 0.16 mg/L. Trace alkali metals are: Li 30, 32 µg/L, Cs 0.15, 0.14 µg/L and Rb 40.7, 40.9 µg/L. The trace alkaline earth metal Ba is 45.6, 46.6 µg/L and Sr 1910, 1930 µg/L. Transition metals other than Fe and Mn have concentrations: Co 0.32, 0.31 µg/L; Cr-Total 0.14µg/L in both boreholes, Ni 3.18, 2.41 µg/L, V 0.13, 0.15 µg/L and Zn 4.4, 2.1 µg/L. The Cr speciation data are all below the LLD values of 0.05 for Cr(VI) and 0.04 for Cr(III). Boron is 371 µg/L in both samples and As 0.13, 0.09 µg/L. Lead is < 0.03 µg/L and Tl < 0.03 µg/L. The REE La is < 0.007 µg/L. Uranium concentrations are 0.59, 0.57 µg/L. The concentration of Zr is 0.082, 0.079 µg/L and Y is 0.088, 0.099 µg/L.

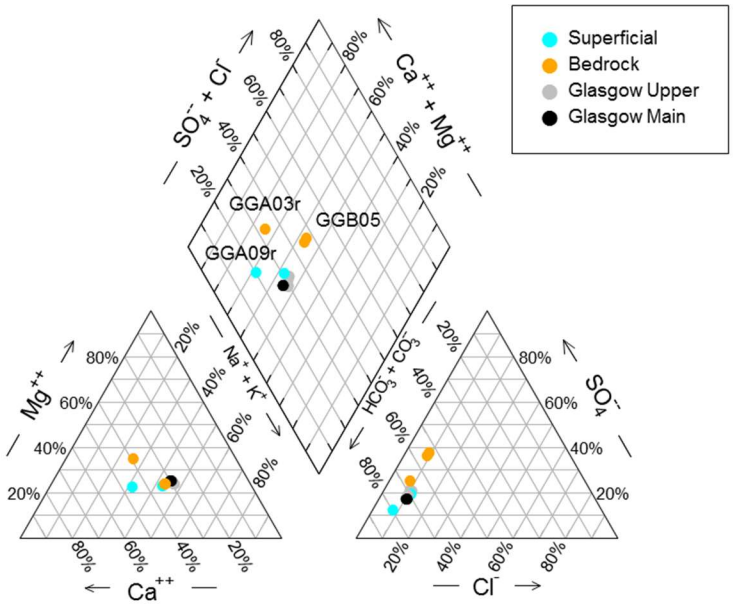


Figure 3 Piper diagram showing the compositions of groundwater from the UKGEOS Glasgow Observatory boreholes, from different target horizons.

4.2 TEMPORAL VARIATIONS: EFFECT OF PUMPING ON MAJOR ION COMPOSITION

Analysis of the relative percent difference (RPD) in water parameters calculated using the two-hour samples and four-hour samples shows the effect of pumping on the water chemical composition through time and if any change was detected.

The RPD calculated for the major cations and anions for each borehole is as follows:

- Boreholes from superficial deposits: samples were taken only at the end of the test pumping; therefore, the effect of pumping on the chemical composition cannot be assessed.
- Bedrock boreholes: the RPD between GGB05-2H and GGB05-4H for the major elements is on average 3%, ranging between 1–6%.
- Glasgow Upper mine working boreholes: the variability of major elements within each Glasgow Upper mine working borehole between the 2H- and 4H-samples is low with an average RPD of 1% in both GGA04 and GGA07, but slightly higher (4%) in GGA01.
- Glasgow Main mine working boreholes: the variability of major elements within each Glasgow Main mine working borehole between the 2H- and 4H-samples is very low with an average RPD of 0.6 and 0.3%, respectively, in GGA05 and GGA08.

The effect of pumping on water composition was therefore negligible (close to the analytical reproducibility), suggesting minimal induced mixing of different water bodies, or that any induced mixing was distant from the abstraction borehole.

4.3 SPATIAL VARIATIONS BETWEEN BOREHOLES OF THE SAME TARGET HORIZON

Compositional differences within boreholes from the same target horizon are quantified as relative standard deviations (RSD) and can be used as an indicator of the aquifer connectivity. Groundwaters from boreholes in the Glasgow Upper mine workings and in the Glasgow Main mine workings have noticeably very uniform composition (RSD on average for all the major elements 3%, 0.6%, respectively), suggesting good lateral connectivity of the aquifer hosted within each mine working. This contrasts with the greater variability between the two superficial deposits boreholes GGA06r and GGA09r, located respectively at Site 2 and at Site 3 (RSD is on average for all the major elements 21%, ranging 1–41%). Similarly, variability between the groundwaters sampled from the bedrock boreholes, GGA03r at Site 1 and GGB05 at Site 5, determined as RSD, is on average for all the major elements 21%, ranging 4–44%, with a greater variability of K and Na. This signifies poorer connectivity in these units. Initial hydrogeological data from the test pumping suggests high spatial variability in the aquifer properties of the superficial deposits and bedrock (Shorter et al. 2021); this is corroborating evidence indicating poor lateral connectivity in each of these aquifers.

4.4 SPATIAL VARIATION AMONG TARGET HORIZONS AND COMPARISON WITH SCOTTISH BASELINE GROUNDWATER CHEMISTRY

Using a multivariate statistical approach, the main patterns in the chemical composition of the 15 groundwater samples were explored using cluster analysis. One primary application of cluster analysis is to investigate how the samples relate to each other, and to thereby possibly detect similarities between the aquifers they represent. The dendrogram in Figure 4 shows the resulting three clusters of samples, suggesting three main hydrochemical facies, corresponding to a principal group represented by the mine waters and two small clusters consisting of the superficial deposits and the bedrock boreholes, respectively. Analysis of the similarity between samples in each cluster confirms the greater heterogeneity is in the superficial deposits groundwaters and bedrock aquifer units compared to the mine waters. The relatively wide variation in composition of the groundwaters in superficial deposits and bedrock likely reflect the spatial heterogeneity of these lithological units and differences in water-rock interactions.

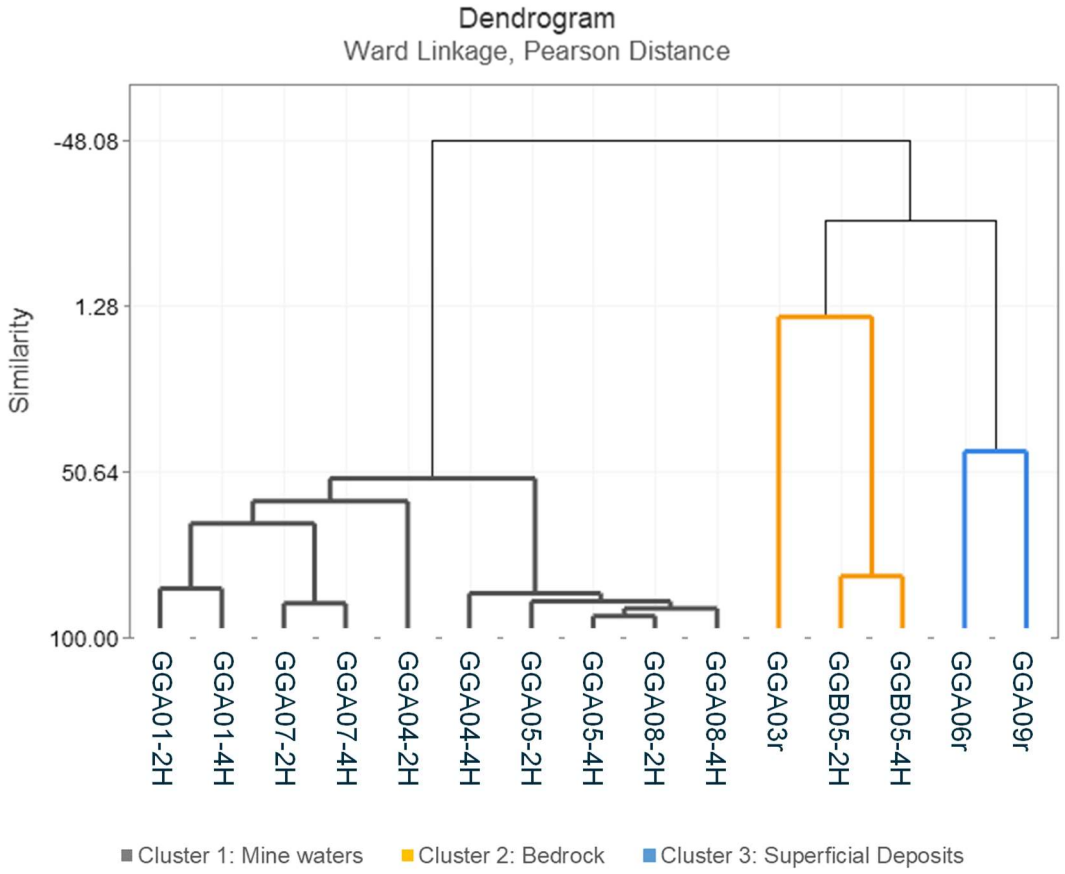


Figure 4 Dendrogram showing the cluster analysis of the 15 groundwater samples with the y axis representing similarity between observations.

4.4.1 Superficial deposits

It has long been known that groundwaters beneath cities carry a fingerprint from urban activities. Overall, the highly mineralised groundwater composition and variable quality of GGA06r and GGA09r boreholes, both targeting the Gourock Sand Member within the Quaternary superficial deposits and both with ~ 8 m of made ground above the superficial deposit units, is similar to observations in previous studies of the Glasgow Quaternary groundwater system (Ó Dochartaigh et al. 2019). Groundwater from Quaternary aquifers in Glasgow generally have higher conductivity (typically greater than 1000 µS/cm), higher pH and higher average concentrations of most major ions and many trace metals compared to baseline Quaternary groundwaters from rural areas outside Glasgow (Ó Dochartaigh et al. 2015). Widespread elevated concentrations of major ions in Glasgow are likely to be linked to contamination from urban waste material, such as cement, metals, mine spoil or chemicals from activities such as building, manufacturing, mining and industrial processes (Ó Dochartaigh et al. 2019). In particular, in the superficial deposits groundwaters in the present study, K (~ 20 mg/L) and field-HCO_3 (943 mg/L in GGA09r) are the most enriched among the major ions, compared to the 95th percentile values of 4.29 mg/L and 211 mg/L, respectively, reported in the Scottish aquifer baseline dataset (Ó Dochartaigh et al. 2015). Of particular significance are also the concentration of NH_4, up to 22 mg/L, and B, up to 736 µg/L. Elevated NH_4 and B concentrations in groundwater are commonly noted in several of the land contamination and regeneration investigation reports within the urban area of Glasgow, which have been collated by BGS as part of the Clyde Urban Super Project (CUSP) (Ó Dochartaigh et al. 2019).

Compared to the other lithologies in the present study, groundwater in the superficial deposits is distinctively enriched in some of the minor and trace elements Ba, Br, Cr-Total, La, U, V, Y, Zr, as well as NPOC, and depleted in Li and Cs (Figures in Appendix 3). It is likely that the concentrations of these parameters are enhanced by anthropogenic inputs from the urban and industrial environment, although it is outside the scope of this report to ascertain these sources. In general, among the above enriched constituents, anthropogenic B can be present in urban

aquifers due to discharge from water treatment plants, as it is a component of detergents and used as a fertiliser (Hasenmueller and Criss 2013). With respect to the relatively higher Ba concentrations of samples from both the superficial deposits boreholes and from the bedrock borehole GGA03r, it is noticeable that they are also slightly oversaturated in barite ($BaSO_4$) (See Figure 6). Barite solubility exercises a strong control on the upper limit of dissolved Ba in water (Hem 1985) and oversaturation in those samples might indicate slow reaction kinetics or mixing. All the other waters are at saturation with respect to barite. Anthropogenic contributions of Br are probably also significant in urban areas, as road runoff, and industrial discharges can release Br compounds to the water environment (Winid 2015).

Chromium, which is a known surface water and groundwater contaminant in Glasgow related to a history of chromite-ore processing (Bearcock et al. 2019; Farmer et al. 1999; Palumbo-Roe et al. 2017; Whalley et al. 1999), is above the detection limit only in the groundwater samples from the superficial deposits. Similarly, La, given its low solubility in water at neutral pH (Wood 1990), is mostly below the detection limit, except for the boreholes in the superficial deposits (La 0.06 µg/L).

Some of the elements found relatively enriched in the boreholes screened in the superficial deposits of Glasgow are not exclusively associated to urban anthropogenic sources, as they can be found also in elevated concentrations in coal mine waters. This is the case for example of Br and B which are found enriched in the Coal Measures source rocks (Edmunds et al. 1989) and in the groundwater from Carboniferous Mined aquifers in Scotland (Br up to 127 mg/L, B up to 814 µg/L) (MacDonald et al. 2017).

4.4.2 Carboniferous unmined bedrock and Glasgow mine workings

Groundwaters in Carboniferous sedimentary aquifers in Scotland, where not extensively mined, are mostly of bicarbonate type, with cations dominated by Ca or Ca-Mg and typically moderately to highly mineralised (SEC 353–1450 µS/cm, median 694 µS/cm) with a slightly alkali pH (6.7–8.0, median 7.3) (MacDonald et al. 2017). Where Carboniferous rocks have been extensively mined for coal, groundwater is also moderately to highly mineralised (SEC 311–1700 µS/cm, median 740 µS/cm) with near neutral pH (6.3–7.7, median 7.0). They are of a wide range of chemical types, with no particular type dominating. An observed increased alkalinity, and the near neutral pH of 'Carboniferous Mined' waters, is attributed to the dissolution of carbonate minerals that buffers the acidity produced by pyrite oxidation. Iron and Mn concentrations, although with a large range, are usually high, and often higher in the mine waters. No widespread corresponding increases in trace metals such as Ni, Cu, Zn and Pb are, however, seen.

Comparison between the groundwater chemistry from Coal Measures units in this study (bedrock, Glasgow Upper mine working and Glasgow Main mine working) and the Scottish baseline groundwater chemistry dataset (MacDonald et al. 2017) highlights that the majority of parameter concentrations are within the ranges reported in Scottish Carboniferous Mined aquifers. Exceptions are the concentrations of NH_4, which are consistently greatly above the baseline 90th percentile of 1.01 mg/L. Iron is between the 90th percentile value of 9360 µg/L and the 95th percentile of 35200 µg/L for GGB05 waters, while As is above the 90th percentile value of 0.8 µg/L in all the unmined bedrock boreholes and in GGA01 and GGA04 Glasgow Upper mine working boreholes. Field and lab HCO_3 are above the 90th percentile value of 581 mg/L, while B is close to the 90th percentile values of 371 µg/L. Sulphate concentrations are mostly between the 75th percentile value of 118 mg/L and the 90th percentile value of 270 mg/L, except for higher concentrations (367 mg/L) in bedrock GGB05 groundwater.

4.5 NET-ACIDITY AND NET-ALKALINITY

All the groundwaters had near–neutral pH; however, pH alone can be a misleading characteristic in mine waters. The net–acidity or net–alkalinity of a solution, not the pH, is probably the best single indicator of the severity of acid mine drainage (Rose and Cravotta 1988).

Mine water acidity can be approximated with the equation below, originally presented by Hedin et al. (1994).

$$Acidity_{Calc} = 50\left[\frac{2Fe^{2+}}{56} + \frac{3Fe^{3+}}{56} + \frac{3Al}{27} + \frac{2Mn}{55} + 1000(10^{-pH})\right] \text{ in mg/L as } CaCO_3$$

Net–alkalinity is then determined by subtracting acidity from field alkalinity.

The sampled mine waters are net–alkaline, in accordance with the majority of Scottish mine waters, predominantly associated with flooded mine workings (Younger 2001). Figure 5 plots all water samples according to the mine water classification scheme of Younger (1995), modified by Rees et al. (2002). In the diagram, the alkalinity-acidity balance is reported on the y-axis, while the x-axis refers to the balance between SO_4 and Cl. The major anions other than bicarbonate (i.e. SO_4 and Cl) are clues to the genesis of a given mine water. The processes which favour dominance of one over the other represent opposite ends of a hydrogeological spectrum ranging from undisturbed Coal Measures (high Cl from brines), to extensively mined Coal Measures, in which pyrite oxidation processes dominate leading to high SO_4 concentrations and high acidity, which are characteristic of acid mine waters. The mine water samples from the present study plot in the net-alkaline mine water field and far to the left of the pumped deep mine water field. Pumped mine water discharges often show a greater Na, K, and Cl component due to interaction with deep basin brines and extensive ion exchange. However, this is not exclusive to pumped discharges, and similar enrichment has been shown in free drainage and flooded mine workings too, e.g. in South-Wales (Rees et al. 2002). The groundwaters from the superficial deposits and bedrock fall in the same field as the mine waters (Figure 5).

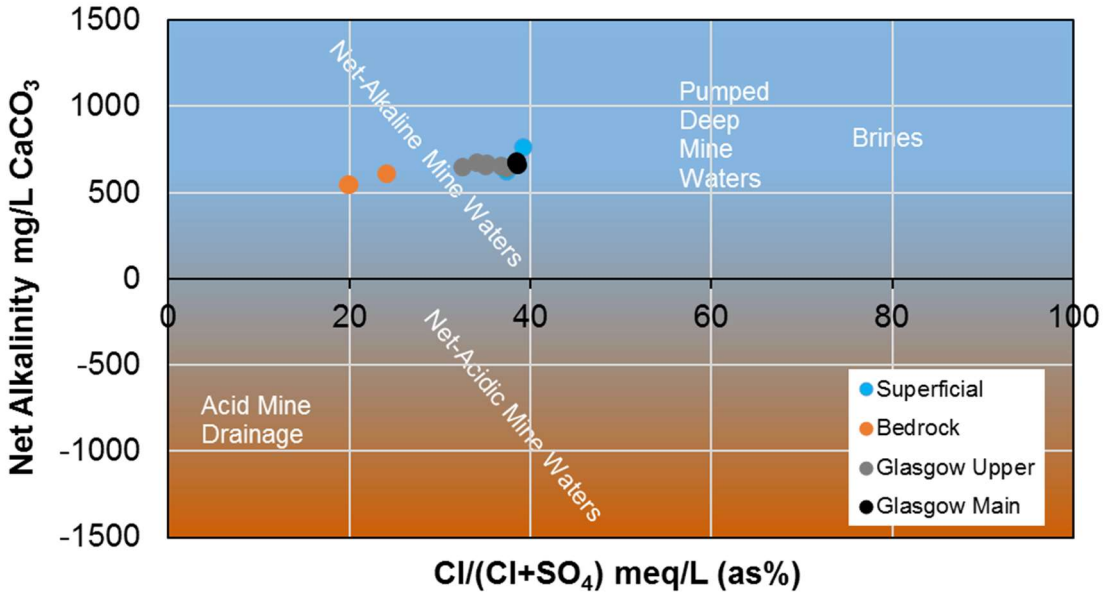


Figure 5 Groundwater samples plotted according to the mine water classification scheme of Younger (1995), modified by Rees et al. (2002).

4.6 SATURATION INDEX

Saturation indices calculated using PHREEQC (Parkhurst and Appelo 1999) and the database phreeqc.dat, indicate that all the waters are saturated with respect to calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$, siderite ($FeCO_3$), rhodochrosite ($MnCO_3$), amorphous ferric hydroxide $Fe(OH)_3$(a), gibbsite $Al(OH)_3$, and barite ($BaSO_4$), and remain undersaturated with respect to gypsum, halite and jarosite (Jarosite-K: $KFe_3(SO_4)_2(OH)_6$) (Figure 6). Estimated equilibrium carbon dioxide partial pressure (P_{CO_2}), computed from the result of water analysis using PHREEQC, is significantly higher than atmospheric values (Figure 7), suggesting the local system is not in equilibrium with air.

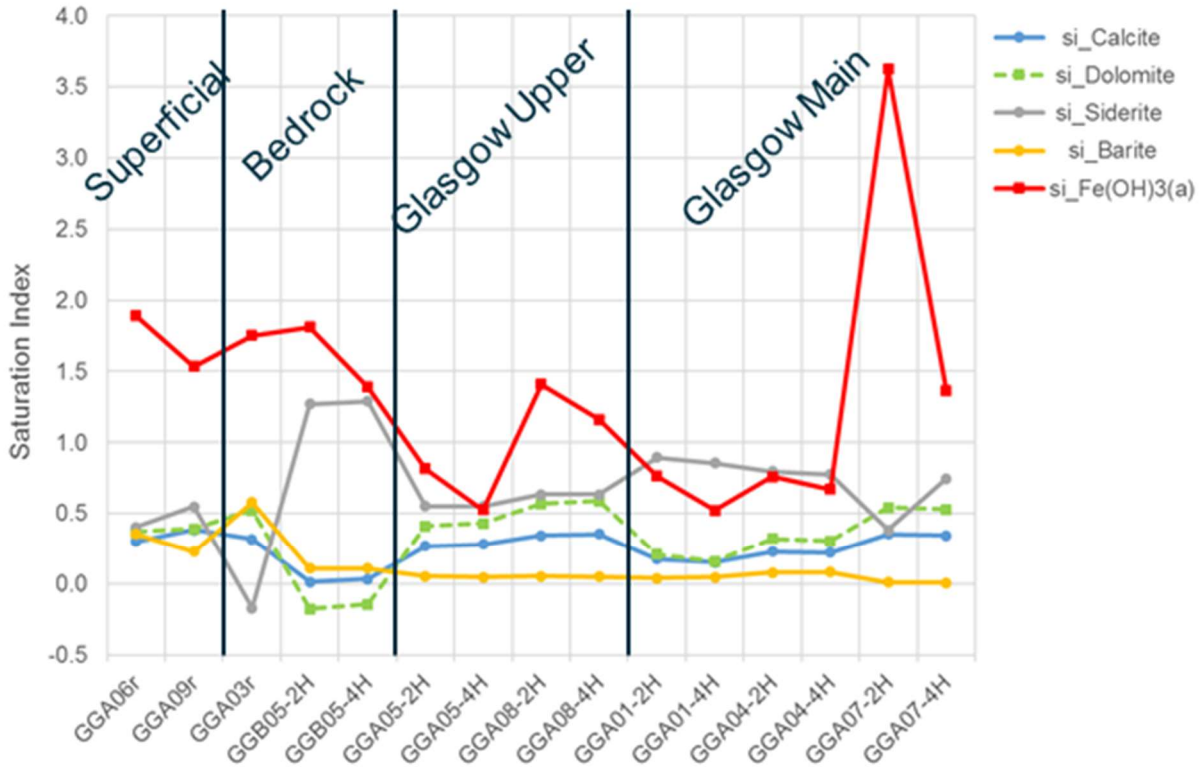


Figure 6 Groundwater saturation indices of selected minerals:calcite, dolomite, siderite, barite and amorphous ferric hydroxide $Fe(OH)_3(a)$, for each of the boreholes.

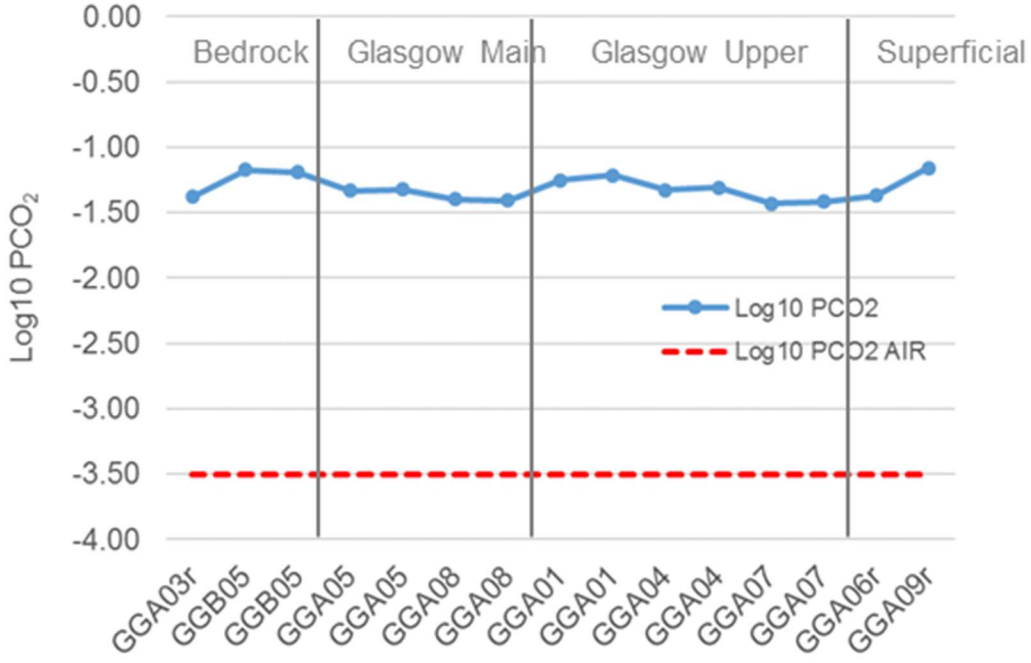


Figure 7 Groundwater carbon dioxide partial pressure across the boreholes.

4.7 PAH, TPH AND VOC

There were no detections of PAH or VOC in any sample. There are only a few detections of TPH, but where they have been detected (GGA03r and GGA05) they are at concentrations very close to the detection limits.

4.8 ISOTOPIC COMPOSITION

A plot of oxygen ($\delta^{18}O$) and deuterium ($\delta^{2}H$) isotopic values (Figure 8) shows that all the groundwaters fall broadly on the global meteoric water line (GMWL) suggesting a meteoric origin with minimal evaporation prior to recharge. The groundwater samples are homogeneous with a narrow range of $\delta^{18}O$ values from -7.51 ‰ to -7.41 ‰ (median value -7.5 ‰) and $\delta^{2}H$ from -49.0 ‰ to -47.6 ‰ (median value of -48.4‰), regardless of borehole target horizon/aquifer. The only sample slightly enriched in heavier isotopes compared to the rest of the groundwaters is GGB05-2H from the bedrock aquifer with $\delta^{18}O$ -7.41, $\delta^{2}H$ -47.9. All values lie within the range of groundwater samples reported from Carboniferous sedimentary aquifers across the Midland Valley of Scotland (Ó Dochartaigh et al. 2011) and the River Clyde surface water samples from the Glasgow Observatory (Fordyce et al. 2021 and Figure 8). They also plot slightly above the GMWL, consistent with the Glasgow Observatory surface waters, as is typical for waters more generally in the west of Scotland, which are known to be more enriched, especially in $\delta^{2}H$, due to the influence of moist isotopically-enriched Atlantic weather fronts and higher rainfall (Birkel et al. 2018; Darling et al. 2003). Figure 8 also plots the River Clyde water isotope composition (Fordyce et al. 2021), which varies from season to season and is more depleted in heavy isotopes in the colder months and enriched in the warmer months. It is noted that the groundwater $\delta^{18}O$ and $\delta^{2}H$ isotope values match the surface water isotope composition measured during the winter months of December 2019 and January 2020; they also correspond broadly to the middle values of the surface water isotope range. This pattern has been observed in many groundwater recharge study cases, where the mean $\delta^{2}H$ and $\delta^{18}O$ composition of groundwater is similar to the mean amount-weighted $\delta^{2}H$ and $\delta^{18}O$ composition of precipitation within its recharge area (Drever 1997). Acquisition of future monthly monitoring groundwater data will facilitate quantification of any temporal trends; comparison with the seasonal variations in the River Clyde can be used to infer river to aquifer connectivity and recharge patterns.

Most of the groundwaters have $\delta^{13}C_{DIC}$ values in a narrow range from -11.4 to -10.6 ‰ (median value of 10.9 ‰) (Figure 9). Exceptions are a lighter $\delta^{13}C$ value of -12.8 ‰ in groundwater from borehole GGA09r in the superficial deposits, and a heavier value of -7.1 ‰ for the GGA03r, bedrock borehole. The $\delta^{13}C$ values mostly fall in the upper range (i.e. heavier $\delta^{13}C$) of both the Coal Measures Group aquifer across the Midland Valley of Scotland ($\delta^{13}C$ -22 ‰ to -10 ‰) (Ó Dochartaigh et al. 2011), and the River Clyde waters ($\delta^{13}C$ -14.1 ‰ to -10.5 ‰) (Fordyce et al. 2021). In a closed system/confined aquifer the progressive dissolution of marine carbonate minerals ($\delta^{13}C$ = 0 ‰, Clark and Fritz 1997) by soil CO_2 ($\delta^{13}C$ ~ -26 ‰ (Darling and Gooddy 2007) would results in groundwater DIC $\delta^{13}C$ evolving towards −13 ‰ (Bottrell et al. 2019). The average groundwater $\delta^{13}C$ value of -10.9 ‰, coupled with the high alkalinity of the groundwaters is consistent with this scenario, but also reflects a further contribution to $\delta^{13}C$ from rock carbonate (cement and/or matrix) via precipitation/redissolution reactions, conceivably facilitated by sulphuric acid (H_2SO_4) produced during pyrite oxidation in former coal workings. Other relevant processes that can complicate the interpretation of groundwater $\delta^{13}C$ values include methanogenesis, sulphate reduction and methane oxidation (Sharma et al. 2013). Highly depleted $\delta^{13}C$ values, generally lower than -30 ‰ are expected where the oxidation of methane (CH_4) occurs and on the contrary, enriched $\delta^{13}C$ values, in the range of +10 ‰ to +30 ‰ are expected under active biogenic methanogenesis in highly-reducing anaerobic conditions. During bacterial sulphate reduction, production of an internal, isotopically-light organic source of CO_2 would shift towards a bicarbonate composition depleted in ^{13}C. Overall, these extreme values are not observed in the UKGEOS groundwaters. Carbon dioxide degassing can also influence the measured $\delta^{13}C$ values with a positive shift in $\delta^{13}C_{DIC}$ (Kendal and Doctor 2003). With additional chemical and isotopic information from the planned monthly groundwater monitoring, the effects of these processes can be evaluated further.

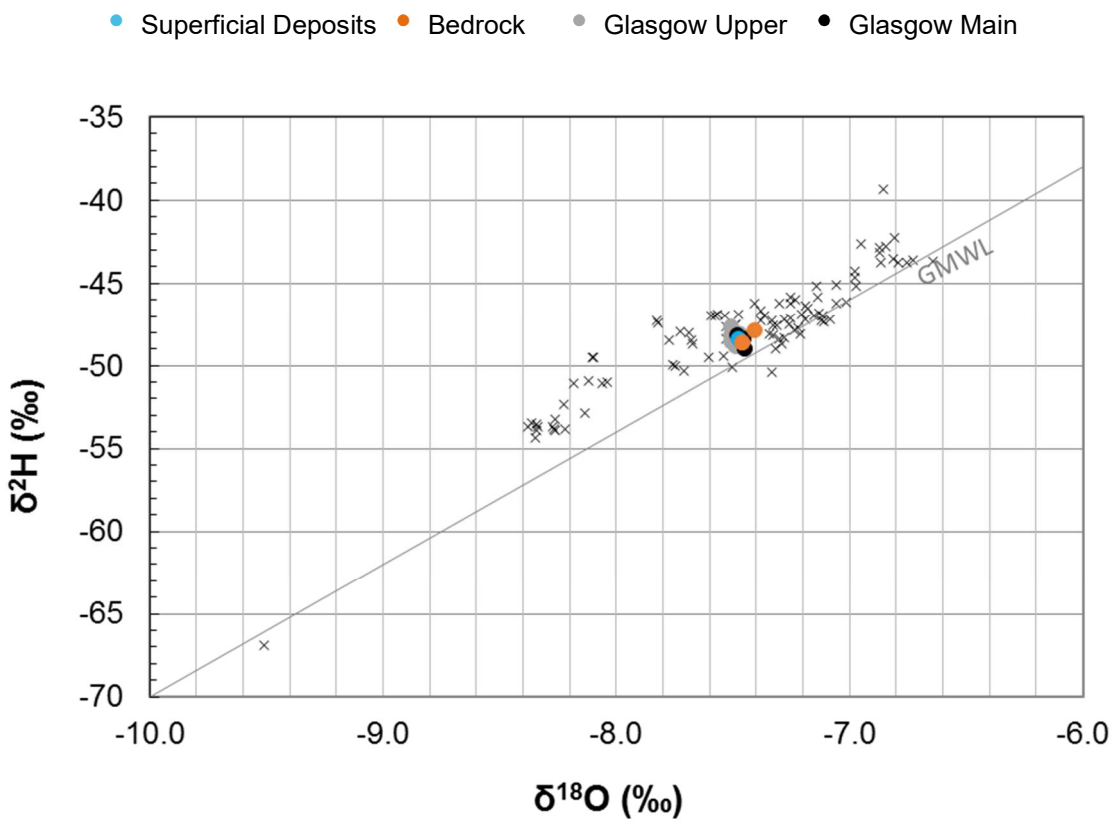


Figure 8 Plot of water δ^2H versus $\delta^{18}O$ stable isotope data with reference to the GMWL in UKGEOS test pump groundwaters, against monthly surface water (cross symbols) from the baseline UKGEOS Glasgow Surface Water Chemistry 1 dataset (Fordyce et al. 2021).

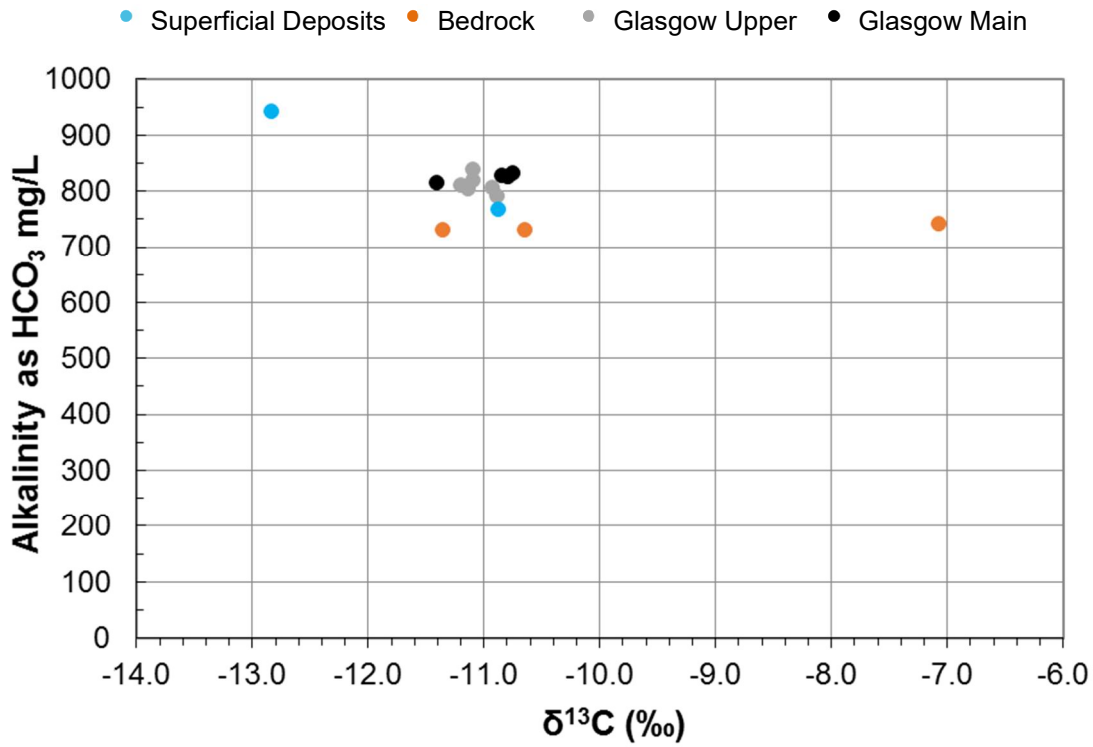


Figure 9 Plot of field-HCO_3 versus $\delta^{13}C$ stable isotope data in groundwaters from the UKGEOS Glasgow observatory sampled during pumping tests.

4.9 DISSOLVED GASES

Concentrations of carbon dioxide (CO_2) and methane (CH_4) were measured on all groundwaters sampled after four hours during the test pumping. Carbon dioxide concentrations ranged between 105 mg/L and 256 mg/L, and CH_4 between 22 µg/L and 406 µg/L (Figure 10). Ethane (C_2H_6) concentrations were below the detection limit (< 1 µg/L).

Groundwaters from the Glasgow Upper and the Glasgow Main have a narrower range of dissolved CH_4 and CO_2 gas concentrations (Glasgow Upper CH_4 117–145 µg/L; CO_2 134–152 mg/L; Glasgow Main CH_4 174–185 µg/L; CO_2 120–123 mg/L) than groundwaters from the bedrock and superficial deposits (Figure 10). All the waters' values are within the upper range of concentrations reported in groundwaters from the Carboniferous sedimentary rocks of the Midland Valley of Scotland (Ó Dochartaigh et al. 2011). Coal mine water commonly contains elevated concentrations of CO_2 and this is confirmed by the calculated P_{CO2} values (cf. Section 4.6). High CO_2 pressure likely results from CO_2-producing processes such as the neutralisation of acidity by naturally occurring carbonates and the oxidation of coal (Hem 1985). Coal can also contain a significant amount of methane. When the coal is mined (or a borehole drilled into an intact seam) the coal is fractured and the stored gas desorbs into the mine workings.

However, these relatively high concentrations are not exclusive to the mine workings groundwater, as the samples from borehole GGA09r in superficial deposits and GGB05 in bedrock have high CO_2 and CH_4 concentrations (CH_4 406 µg/L, CO_2 218 mg/L and CH_4 297 µg/L, CO_2 256 mg/L, respectively). This may be due to the presence of sporadic organic matter pockets or coal waste in the made ground. By contrast, the other boreholes GGA06r in superficial deposits and GGA03r in bedrock show the lowest dissolved gas concentrations (CH_4 22 µg/L, CO_2 124 mg/L and CH_4 37 µg/L, CO_2 105 mg/L, respectively). Overall these results are consistent with the inorganic chemistry and pumping tests showing fairly uniform results in coal workings and more variability in the bedrock and superficial deposits.

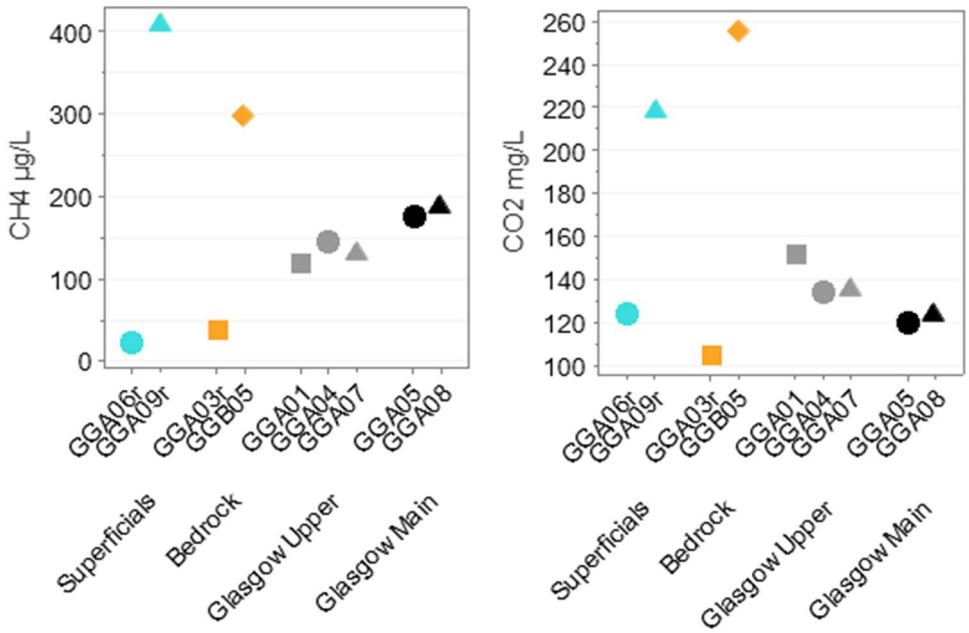


Figure 10 Distribution of dissolved CH_4 and CO_2 in groundwater samples.

4.10 CFC AND SF_6 DATA

Table 6 shows CFC and SF_6 data for the nine boreholes from the Cuningar Loop sites sampled during January and February 2020. Only the four-hour samples were analysed except for GGA03r, sampled after two hours during pumping. Concentrations are shown in pmol/L for CFC-12 and CFC-11, and in fmol/L for SF_6. The data have been corrected for excess air and then interpreted in two ways: (1) converted to a modern fraction value (0–1) by dividing the current atmospheric air saturated water equilibrium value by the measured concentration – this assumes

that there is binary mixing between modern water (within the last decade) and pre 1948 water; and (2) estimating a year of recharge by comparison with historic values from the North Atlantic Atmospheric Mixing Ratio and assuming piston flow through the aquifer (Darling et al. 2012; Chambers et al. 2019).

Table 6 Summary data for CFC-12, CFC-11 and SF6 for the UKGEOS Glasgow test pump groundwater samples

Sample ID	Aquifer unit	CFC-12	CFC-11	SF_6	CFC-12	CFC-11	SF_6	CFC-12	CFC-11	SF_6
		pmol/L		fmol/L	Modern Fraction			Year of Recharge		
GGA01 PTE	Glasgow Upper mine working	0.13	0.07	0.012	0.04	0.01	0.003	1956	1955	<1970
GGA03r-PTD	Bedrock	0.00	0.16	0.000	0.00	0.03	0.000	<1948	1957	<1970
GGA04-PTE	Glasgow Upper mine working	0.13	0.08	0.006	0.04	0.01	0.001	1957	1955	<1970
GGA05-PTE	Glasgow Main mine working	0.61	0.97	0.010	0.20	0.18	0.002	1968	1968	<1970
GGA06r-PTE	Superficial Deposits	0.00	0.03	0.012	0.00	0.01	0.003	<1948	1952	<1970
GGA07-PTE	Glasgow Upper mine working	0.00	0.01	0.000	0.00	0.00	0.000	<1948	1950	<1970
GGA08-PTE	Glasgow Main mine working	0.76	2.33	0.012	0.25	0.43	0.003	1970	1974	<1970
GGA09r-PTE	Superficial Deposits	1.00	2.06	0.005	0.33	0.38	0.001	1972	1973	<1970
GGB05-PTE	Bedrock	0.06	0.02	0.000	0.02	0.00	0.000	1952	1951	<1970

Concentrations of CFC-12 vary from 1.00 pmol/L to < LLD with a mean of 0.30 pmol/L. Concentrations of CFC-11 vary from 2.33 pmol/L to 0.01 pmol/L with a mean of 0.64 pmol/L. Concentrations for SF_6 vary from 0.012 fmol/L to < detection limit with a mean of 0.006 fmol/L. It is noticeable that boreholes installed in the Glasgow Main mine workings, GGA05 at Site 2 and GGA08 at Site 3, have groundwater with higher concentrations of CFC-12 (0.61 and 0.76 pmol/L) and CFC-11 (0.97 and 2.33 pmol/L) than in the other boreholes, which translates to younger waters (year of recharge range 1968–1974 over a whole range <1948 to 1974), or a higher fraction of modern water (0.18–0.43 over a whole range from 0 to 0.43) (Table 6). This difference is less clear for the SF_6 tracer which shows consistently negligible modern fractions or the year of recharge before 1970.

Lumped parameter models provide a simplified description of the behaviour of groundwater flow in an aquifer. With groundwater tracers, we can use these models to better understand the likely flow mechanisms occurring within an aquifer system (i.e. piston flow, exponential mixing of a range of travel times characterised by a mean value, and binary mixing of two end members); hence, determine the relative 'age' of the water, or the relative contribution of different water bodies (Darling et al. 2012).

Figure 11 shows tracer plots for SF_6 versus CFC-12. Tracer data from the UKGEOS boreholes sampled suggest that there is some conformance towards a piston flow type of model since most of the data fall close to this line. However, concentrations of SF_6 in these waters are very low, and

indeed fall below the piston flow line for a number of samples. Atmospheric concentrations of SF_6 are very low and fairly constant prior to 1970; hence, before that date it is challenging to use SF_6 as a tracer of piston flow, i.e. there is little difference in concentration between waters of 1940s origin and 1970s (at 10°C, aqueous concentrations vary by just 0.05 fmol/L). The data do suggest however, that a piston flow model is more likely than a binary mixing model of modern water (in the last few years) and older water (pre 1970s). However, it could be the case that these very low concentrations of SF_6 are an artefact of the sampling and storage process and not necessarily a reflection of the concentrations present in the groundwater.

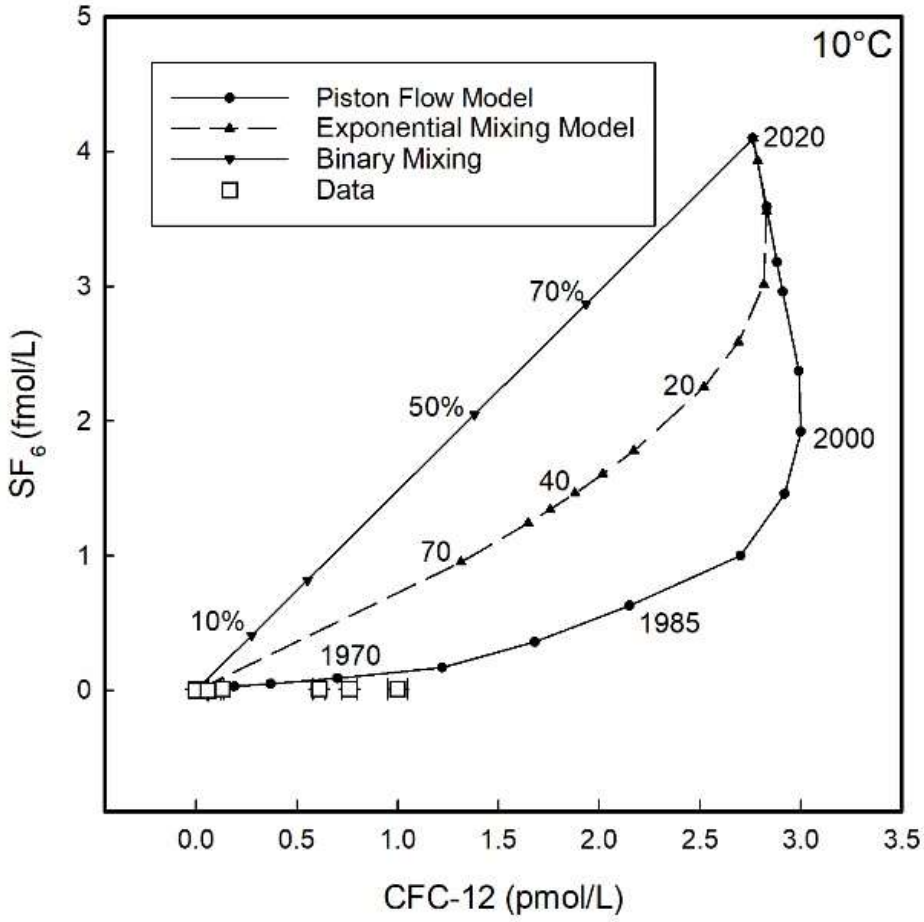


Figure 11 Tracer plots showing SF_6 versus CFC-12 in the test pump groundwater samples. The lines represent the expected relationship between the two tracers if boreholes sample a single flow path without hydrodynamic dispersion (piston flow model), an exponential distribution of travel times (exponential mixing model) with mean travel times ranging from 0 to 500 years, and a binary mixture of very old (zero tracer concentration) and modern water (binary mixing model).

The atmospheric concentrations of both CFC-12 and CFC-11 have been increasing rapidly since the late 1940s, which means the piston flow curve can be extended back further than the 1970s allowed by the use of SF_6. Figure 12 shows a tracer plot for CFC-11 versus CFC-12 in the test pump groundwater samples. Although the separation is relatively small, the majority of the data (with the exception of GGA08-PTE, which is from the Glasgow Main mine workings) fits on the piston flow line, corroborating the evidence from the SF_6 data. This tends to suggest that the dominant flow mechanism occurring in the aquifer system is piston flow, rather than the mixing of old and young waters (the modern fraction column in Table 6). Hence, based on the CFC-12 and CFC-11 data, the waters have an approximate recharge dates of 1968-74 for the Glasgow Main; 1948-57 for the Glasgow Upper; 1948-57 for the Bedrock and 1950-1973 for the superficial deposits. These data are corroborated by the very low SF_6 concentrations.

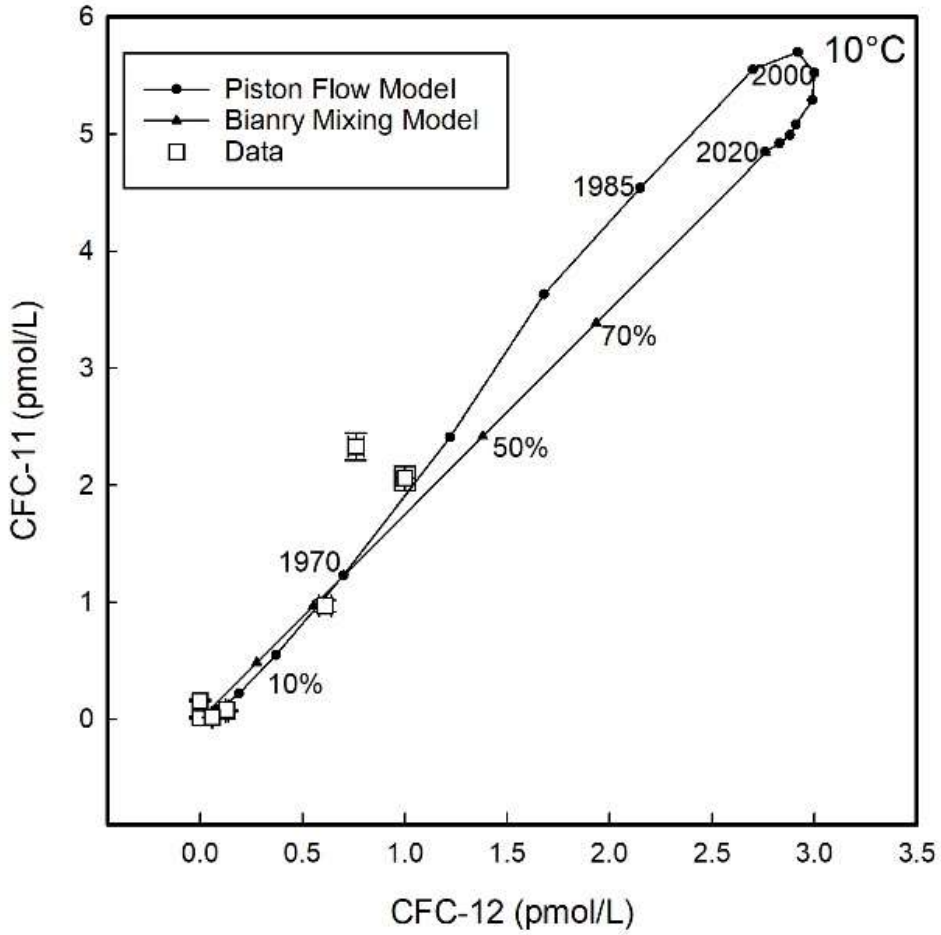


Figure 12 Tracer plots showing CFC-11 versus CFC-12 in the test pump groundwater samples. The lines represent the expected relationship between the two tracers if boreholes sample a single flow path without hydrodynamic dispersion (piston flow model), an exponential distribution of travel times (exponential mixing model) with mean travel times ranging from 0 to 500 years, and a binary mixture of very old (zero tracer concentration) and modern water (binary mixing model).

Figure 13 shows how tracer concentration varies as a function of borehole depth. The two tracers are relatively consistent in terms of how concentration varies with depth. In both cases some of the highest concentrations (indicating younger waters) occur in the deepest boreholes installed within the Glasgow Main mine workings. This underlies the complexity of the groundwater flowpaths, and also suggests that although there is evidence that the mine workings are connected (Shorter et al. 2021), flow in this undisturbed state is likely to be restricted. The groundwater levels at the site indicate general upward movement of water, as this is a discharge zone for groundwater (Shorter et al. 2021), therefore younger residence times at depth are not unexpected. Groundwater residence times in the superficial deposits are variable. This likely reflects the mixture of rainfall recharge at the site, with upwelling water from the deeper aquifers.

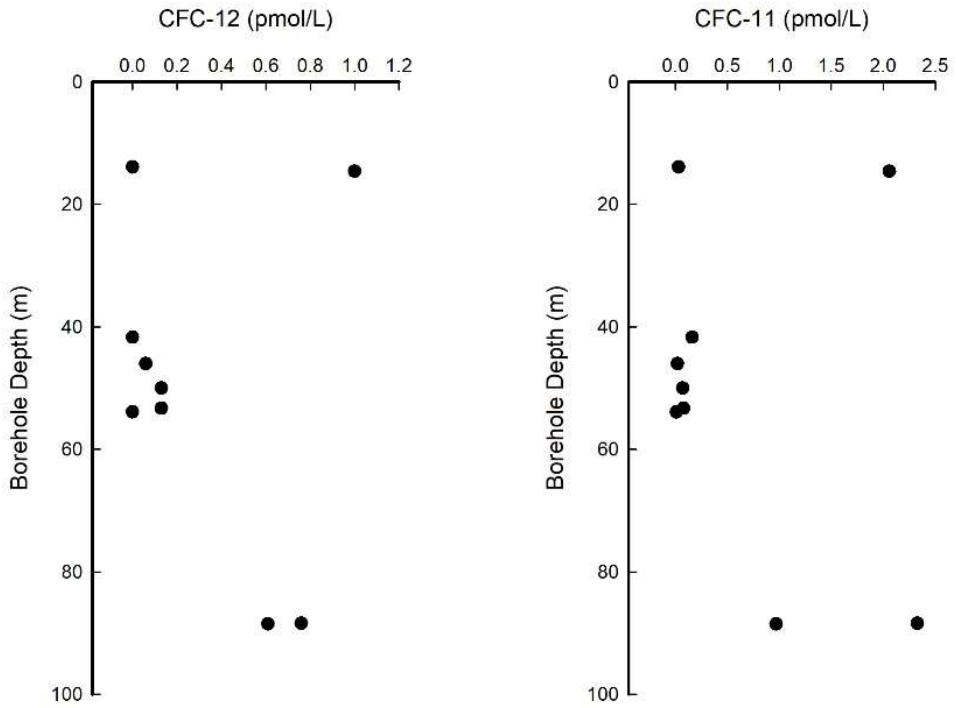


Figure 13 The relationship between borehole depth and tracer concentration for CFC-12 and CFC-11 in the test pump groundwater samples.

5 Conclusions

The chemistry of groundwater samples obtained at approximately two hours and four hours during constant rate test pumping of nine boreholes at the UK Geoenergy Observatory at Cuningar Loop is presented. The 15 groundwater samples are taken from: two boreholes screened in the superficial deposits; two boreholes screened in the bedrock; three boreholes screened in the Glasgow Upper mine working; and another two into the Glasgow Main mine workings. Despite the small numbers of samples per target horizon, limiting the ability to generalise the results, some indication of the geochemical characteristics of each aquifer and their relationships can be given.

- During the sampling carried out in January and February 2020, the mine water temperatures (measured at the surface from a flow-through cell) were consistently higher (12.4 °C) in the Glasgow Main mine workings (depth of screened boreholes 84–88 m) than those (11.9–12.1 °C) in the Glasgow Upper mine workings (46–54 m). With the exception of one of the boreholes in the superficial deposits (GGA06r), the following sequence of groundwater temperature (T) increase was observed: $T_{Superficial\ deposits} < T_{Bedrock} < T_{Glasgow\ Upper} < T_{Glasgow\ Main}$, consistent with increasing depth.

- The sampling reveals that all the groundwaters are mineralised (SEC median 1690 µS/cm, range 1570-1940 µS/cm), with near neutral pH, and comprise HCO_3–type waters with Na as the dominant cation, except for boreholes GGA03r in bedrock and GGA09r in superficial deposits where Ca is the major cation. The groundwater contains sufficient alkalinity (field-HCO_3 median 811 mg/L, range 731–943 mg/L) (net–alkaline waters) to neutralise the mineral acidity represented by the high dissolved Fe (median 2550 µg/L, range 417–19500 µg/L) and Mn (median 411 µg/L, range 260–3104 µg/L) content. Anoxic conditions are common to all the groundwaters, showing DO < 0.5 mg/L. Nitrate concentrations are undetectable (< 0.6 mg/L). Sulphate median is 174 mg/L and range 115–371 mg/L.

- Based on statistical cluster analysis it was possible to distinguish three hydrochemical facies, corresponding to a primary group represented by the mine waters and two small clusters consisting of the superficial deposits and the bedrock aquifers, respectively. Groundwaters from boreholes in the Glasgow Upper mine working and in the Glasgow Main mine working have uniform composition suggesting good lateral connectivity of the aquifer associated within each mine working. By contrast, compositional differences within boreholes from the same target horizon are greater for the superficial deposits and the bedrock boreholes, suggesting poorer connectivity in these units.

- The mine water composition is typical of Scottish Carboniferous mined aquifers reported in other studies (Ó Dochartaigh et al. 2012). For example, SO_4 concentrations are between 154 mg/L and 200 mg/L and are close to the 90th percentile value of the Scottish baseline dataset (MacDonald et al. 2017). Compared to the other aquifer units, groundwater in the superficial deposits is distinctively enriched in NH_4 and B, but also relatively higher in some of the minor and trace elements: Ba, Br, Cr-Total, La, U, V, Y, Zr, as well as NPOC. This is consistent with highly mineralised groundwater composition of variable quality that has been observed in previous studies of the Glasgow Quaternary groundwater system (Ó Dochartaigh et al. 2019). It is possible that the concentrations of several parameters are elevated by anthropogenic inputs from the urban and industrial environment.
  The elevated trace elements concentrations across the different target horizons/aquifers mean that there is no one element that can be used to fingerprint groundwater from different horizons.

- There were no detections of PAH or VOC in any sample. There are only a few detections of TPH, but, where they have been detected (GGA03r and GGA05), they are at concentrations very close to the detection limits.

- Groundwater stable isotope composition shows a general correspondence with the global meteoric water line indicating that the groundwaters represent recharge from local rainfall consistent with the current climate. In all groundwaters a narrow range of $\delta^{18}O$ values from -7.51 ‰ to -7.41 ‰ (median value -7.5 ‰) and $\delta^{2}H$ from -49.0 ‰ to -47.6 ‰ (median value of -48.4 ‰) are observed, regardless of the borehole target horizon/aquifer. The values correspond to the middle of the annual range of isotope values reported previously in the River Clyde (Fordyce et al. 2021). The River Clyde water isotope composition varies from season to season and is more depleted in heavy isotopes in the colder months and enriched in the warmer months. The groundwaters, which were collected in January and February 2020, plot close to the surface water values for these months, consistent with the main months for groundwater recharge. Further monitoring of groundwater stable isotopes will enable any seasonal variability to be identified, and therefore whether there is some river water entering the mine workings.

- The carbon isotope signature of DIC measured in the mine water and bedrock groundwater samples is clearly heavier than a characteristically low $\delta^{13}C$ value of a dominant soil CO_2 contribution to DIC ($\delta^{13}C$ ~ -26 ‰). The $\delta^{13}C$ averaging -10.9 ‰ combined with the high alkalinity of the groundwaters is consistent with a closed system/confined aquifer where the DIC $\delta^{13}C$ values gradually evolve towards the rock composition ($\delta^{13}C$ ~ 0 ‰, if marine carbonate, though this remains to be tested), and may well also reflect a contribution to $\delta^{13}C$ from the dissolution of rock carbonate by sulphuric acid (H_2SO_4) produced during pyrite oxidation in former coal workings.

- Groundwaters from the Glasgow Upper and the Glasgow Main have a narrower range of dissolved CH_4 and CO_2 gas concentrations (Glasgow Upper CH_4 117–145 µg/L; CO_2 134–152 mg/L; Glasgow Main CH_4 174–185 µg/L; CO_2 120–123 mg/L) than groundwaters from the bedrock and superficial deposits. This is consistent with major and trace element concentrations, which show fairly uniform results in coal mine working groundwaters and more variability in the bedrock and superficial deposits. These values lie in the upper range of groundwaters from Carboniferous sedimentary rocks in the Midland Valley of Scotland (Ó Dochartaigh et al. 2012).
  Coal mine waters commonly contain elevated concentrations of CO_2 and this is confirmed by the calculated P_{CO2} values, which are significantly higher than atmospheric values, also suggesting the system is locally not in equilibrium with air. Higher concentrations of CH_4 and CO_2 were also present in groundwater samples from borehole GGA09r in the superficial deposits (CH_4 406 µg/L, CO_2 218 mg/L) and GGB05 in the bedrock (CH_4 297 µg/L, CO_2 256 mg/L).

- The relative percent difference in water major chemistry between the two and four hour samples shows that the effect of pumping on groundwater composition is negligible (close to the analytical reproducibility) in all the boreholes where test pumping was conducted, suggesting minimal induced mixing of different water bodies, or that any induced mixing was distant from the abstraction borehole.

- Interpretation of residence time data from CFC-11, CFC-12 and SF_6 suggests that the average mean residence time of the groundwater is more than 45 years in all the aquifer units. The low concentrations of SF_6 suggest a piston type flow model is more likely than a binary mixing model (of very modern water mixed with older water), although this may be an artefact of the sampling and storage process and not necessarily a reflection of the concentrations present in the groundwater. Assuming a piston flow model, the waters have approximate recharge dates of 1968-74 for the Glasgow Main; 1948-57 for the Glasgow

Upper; 1948-57 for the bedrock and 1950-1973 for the superficial deposits. The youngest waters occur in the deepest boreholes installed within the Glasgow Main mine workings. This underlies the complexity of the groundwater flowpaths, however as groundwater heads are generally upward, younger residence times at depth are not unexpected. Groundwater residence times in the superficial deposits are variable. This likely reflects the mixture of rainfall recharge at the site with upwelling water from the deeper aquifers.

Appendix 1 Analytical Methods and Data Quality Control

The UKGEOS Glasgow test pump groundwater samples were submitted for chemical laboratory analysis in the same batches as surface water samples being collected by the project for baseline monthly monitoring. The analytical methods used to determine major and trace element concentrations, laboratory alkalinity, chromium speciation, dissolved organic carbon (NPOC), total petroleum hydrocarbons (TPH), polycyclic aromatic hydrocarbons (PAH) and stable isotopes are summarised here and given in full in the UKGEOS Glasgow baseline surface water chemistry report (Fordyce et al. 2021). In addition, ammonium (NH_4), volatile organic compounds (VOC), methane (CH_4), ethane (C_2H_6), carbon dioxide (CO_2), sulphur hexafluoride (SF_6) and chlorofluorocarbons (CFC) were determined in the samples according to the methods outlined here.

To ensure data quality, the groundwater samples were analysed where possible using methods accredited to ISO17025:2017 by the United Kingdom Accreditation Service (UKAS). As part of data quality control (QC), time versus concentration plots showed no systematic analytical drift either within or between batches for any of the following analytical methods.

The lower limits of detection (LLD) and/or limits of quantification (LOQ) for the analytical methods are outlined in Table 7.

Table 7 Long-term measurement and analytical limits of detection and limits of quantification

Symbol	Parameter	Units	LLD	LOQ	Analytical Method
Major & Minor Anions:					
Br	Bromide	mg/L	0.01	0.04	IC
Cl	Chloride	mg/L	0.05	0.15	IC
F	Fluoride	mg/L	0.005	0.010	IC
Lab-HCO_3	Lab bicarbonate	mg/L	5	NA	Lab-Titrator
HPO_4	Orthophosphate	mg/L	0.01	0.03	IC
NO_2	Nitrite	mg/L	0.005	0.010	IC
NO_3	Nitrate	mg/L	0.03	0.10	IC
SO_4	Sulphate	mg/L	0.05	0.20	IC
Major & Minor Cations:					
Ca	Calcium	mg/L	0.3	0.6	ICP-MS
K	Potassium	mg/L	0.04	0.07	ICP-MS
Mg	Magnesium	mg/L	0.003	0.005	ICP-MS
Na	Sodium	mg/L	0.4	0.7	ICP-MS
P-Total	Total Phosphorus	mg/L	0.005	0.020	ICP-MS
S-Total	Total Sulphur	mg/L	0.03	0.06	ICP-MS
Si	Silicon	mg/L	0.04	0.09	ICP-MS
Trace Elements:					
Ag	Silver	µg/L	0.04	0.07	ICP-MS
Al	Aluminium	µg/L	0.6	2	ICP-MS
As	Arsenic	µg/L	0.04	0.08	ICP-MS
B	Boron	µg/L	53	114	ICP-MS
Ba	Barium	µg/L	0.05	0.10	ICP-MS
Be	Beryllium	µg/L	0.08	0.20	ICP-MS
Bi	Bismuth	µg/L	0.08	0.20	ICP-MS
Cd	Cadmium	µg/L	0.005	0.010	ICP-MS
Ce	Cerium	µg/L	0.004	0.007	ICP-MS
Co	Cobalt	µg/L	0.006	0.020	ICP-MS
Cr-Total	Total Chromium	µg/L	0.04	0.07	ICP-MS
Cr(VI)	Chromium VI	µg/L	0.05	NA	HPLC
Cr(III)	Chromium III	µg/L	0.04	NA	HPLC
Cs	Caesium	µg/L	0.04	0.08	ICP-MS
Cu	Copper	µg/L	0.05	0.20	ICP-MS
Dy	Dysprosium	µg/L	0.003	0.007	ICP-MS
Er	Erbium	µg/L	0.003	0.006	ICP-MS
Eu	Europium	µg/L	0.003	0.007	ICP-MS
Fe	Iron	µg/L	0.4	0.80	ICP-MS
Ga	Gallium	µg/L	0.04	0.09	ICP-MS

Table 7 cont.

Symbol	Parameter	Units	LLD	LOQ	Analytical Method
Gd	Gadolinium	µg/L	0.005	0.020	ICP-MS
Hf	Hafnium	µg/L	0.006	0.020	ICP-MS
Ho	Holmium	µg/L	0.003	0.006	ICP-MS
La	Lanthanum	µg/L	0.003	0.006	ICP-MS
Li	Lithium	µg/L	7	15	ICP-MS
Lu	Lutetium	µg/L	0.003	0.006	ICP-MS
Mn	Manganese	µg/L	0.2	0.30	ICP-MS
Mo	Molybdenum	µg/L	0.2	0.40	ICP-MS
Nb	Niobium	µg/L	0.01	0.03	ICP-MS
Nd	Neodymium	µg/L	0.005	0.010	ICP-MS
Ni	Nickel	µg/L	0.01	0.03	ICP-MS
Pb	Lead	µg/L	0.02	0.05	ICP-MS
Pr	Praseodymium	µg/L	0.003	0.007	ICP-MS
Rb	Rubidium	µg/L	0.05	0.20	ICP-MS
Sb	Antimony	µg/L	0.04	0.07	ICP-MS
Se	Selenium	µg/L	0.07	0.20	ICP-MS
Sm	Samarium	µg/L	0.005	0.010	ICP-MS
Sn	Tin	µg/L	0.08	0.20	ICP-MS
Sr	Strontium	µg/L	0.2	0.30	ICP-MS
Ta	Tantalum	µg/L	0.006	0.020	ICP-MS
Tb	Terbium	µg/L	0.004	0.008	ICP-MS
Th	Thorium	µg/L	0.03	0.05	ICP-MS
Ti	Titanium	µg/L	0.06	0.20	ICP-MS
Tl	Thallium	µg/L	0.02	0.04	ICP-MS
Tm	Thulium	µg/L	0.003	0.007	ICP-MS
U	Uranium	µg/L	0.009	0.02	ICP-MS
V	Vanadium	µg/L	0.02	0.03	ICP-MS
W	Tungsten	µg/L	0.06	0.02	ICP-MS
Y	Yttrium	µg/L	0.006	0.020	ICP-MS
Yb	Ytterbium	µg/L	0.004	0.009	ICP-MS
Zn	Zinc	µg/L	0.2	0.40	ICP-MS
Zr	Zircon	µg/L	0.009	0.020	ICP-MS
Ammonium:					
NH_4	Ammonium	mg/L	0.01	NA	Colorimetry
Inorganic Carbon:					
TIC	Total inorganic carbon	mg/L	NA	NA	From $CaCO_3$
Dissolved Organic Carbon:					
NPOC	Non-purgeable organic carbon	mg/L	0.5	NA	Carbon Analyser
PAH:	Polycyclic aromatic hydrocarbons				
Benzo(b)fluoranthene		µg/L	0.001	0.004	HPLC-FD
Benzo(k)fluoranthene		µg/L	0.001	0.003	HPLC-FD
Benzo(a)pyrene (BaP)		µg/L	0.0005	0.0016	HPLC-FD
Benzo(ghi)perylene		µg/L	0.001	0.004	HPLC-FD
Indeno(1,2,3-cd)pyrene		µg/L	0.002	0.005	HPLC-FD
PAH-Total		µg/L	0.005	0.012	HPLC-FD

Table 7 cont.

Symbol	Parameter	Units	LLD	LOQ	Analytical Method
TPH:	Total petroleum hydrocarbons				
TPH (C8-C10)		mg/L	0.003	0.003	GC-FID
TPH (C10-C40)		mg/L	0.042	0.042	GC-FID
TPH (C8-C40)		mg/L	0.045	0.045	GC-FID
VOC:	Volatile organic compounds				
Chloromethane		µg/L	NA	1	GC-MS
Vinyl chloride		µg/L	NA	1	GC-MS
Chloroethane		µg/L	NA	1	GC-MS
Trichlorofluoromethane		µg/L	NA	1	GC-MS
1,1-Dichloroethene		µg/L	NA	1	GC-MS
Diethyl ether		µg/L	NA	1	GC-MS
Acrylonitrile		µg/L	NA	10	GC-MS
Dichloromethane		µg/L	NA	1	GC-MS
trans 1,2-Dichloroethene		µg/L	NA	1	GC-MS
Methyl tert-butyl ether		µg/L	NA	1	GC-MS
Hexane		µg/L	NA	1	GC-MS
Iso propyl ether		µg/L	NA	1	GC-MS
cis 1,2-dichloroethene		µg/L	NA	1	GC-MS
Bromochloromethane		µg/L	NA	1	GC-MS
Trichloromethane		µg/L	NA	1	GC-MS
2,2-Dichloropropane		µg/L	NA	1	GC-MS
1,2-Dichloroethane		µg/L	NA	1	GC-MS
2-Methyl-1,3-dioxolane mg/L		µg/L	NA	0.1	GC-MS
1,1,1-Trichloroethane		µg/L	NA	1	GC-MS
1,1-Dichloropropene		µg/L	NA	1	GC-MS
Cyclohexane		µg/L	NA	1	GC-MS
Tetrachloromethane		µg/L	NA	1	GC-MS
Benzene		µg/L	NA	1	GC-MS
Dibromomethane		µg/L	NA	1	GC-MS
1,2-Dichloropropane		µg/L	NA	1	GC-MS
Trichloroethene		µg/L	NA	1	GC-MS
Bromodichloromethane		µg/L	NA	1	GC-MS
trans 1,3-Dichloropropene		µg/L	NA	1	GC-MS
cis 1,3-Dichloropropene		µg/L	NA	1	GC-MS
1,1,2-Trichloroethane		µg/L	NA	1	GC-MS
Toluene		µg/L	NA	1	GC-MS
1,3-Dichloropropane		µg/L	NA	1	GC-MS
Octane		µg/L	NA	1	GC-MS
Dibromochloromethane		µg/L	NA	1	GC-MS
1,2-Dibromoethane		µg/L	NA	1	GC-MS
Tetrachloroethene		µg/L	NA	1	GC-MS
1,1,1,2-Tetrachloroethane		µg/L	NA	1	GC-MS
Chlorobenzene		µg/L	NA	1	GC-MS
Ethylbenzene		µg/L	NA	1	GC-MS

Table 7 cont.

Symbol	Parameter	Units	LLD	LOQ	Analytical Method
m,p-Xylene		µg/L	NA	2	GC-MS
Tribromomethane		µg/L	NA	1	GC-MS
Styrene		µg/L	NA	1	GC-MS
1,1,2,2-Tetrachloroethane		µg/L	NA	1	GC-MS
o-Xylene		µg/L	NA	1	GC-MS
Total xylene		µg/L	NA	3	GC-MS
1,2,3-Trichloropropane		µg/L	NA	1	GC-MS
Isopropylbenzene		µg/L	NA	1	GC-MS
Bromobenzene		µg/L	NA	1	GC-MS
n-Propylbenzene		µg/L	NA	1	GC-MS
2-Chlorotoluene		µg/L	NA	1	GC-MS
4-Chlorotoluene		µg/L	NA	1	GC-MS
1,3,5-Trimethylbenzene		µg/L	NA	1	GC-MS
tert-Butylbenzene		µg/L	NA	1	GC-MS
1,2,4-Trimethylbenzene		µg/L	NA	1	GC-MS
sec-Butylbenzene		µg/L	NA	1	GC-MS
1,3-Dichlorobenzene		µg/L	NA	1	GC-MS
1,4-Dichlorobenzene		µg/L	NA	1	GC-MS
4-Isopropyltoluene		µg/L	NA	1	GC-MS
1,2-Dichlorobenzene		µg/L	NA	1	GC-MS
n-Butylbenzene		µg/L	NA	1	GC-MS
1,2-Dibromo-3-chloropropane		µg/L	NA	1	GC-MS
N.N-Dimethylaniline		µg/L	NA	1	GC-MS
1,3,5-Trichlorobenzene		µg/L	NA	1	GC-MS
1,2,4-Trichlorobenzene		µg/L	NA	1	GC-MS
Naphthalene		µg/L	NA	1	GC-MS
Hexachlorobutadiene		µg/L	NA	1	GC-MS
1,2,3-Trichlorobenzene		µg/L	NA	1	GC-MS
Dissolved Gases:					
CH_4	Methane	µg/L	0.1	NA	Flame ionisation detector
C_2H_6	Ethane	µg/L	1	NA	Flame ionisation detector
CO_2	Carbon dioxide	mg/L	0.1	NA	Thermal conductivity detector
SF6	Sulphur hexafluoride	fmol/L	0.02	NA	GC-ECD
CFC 11	Chlorofluorocarbons	pmol/L	0.01	NA	GC-ECD
CFC 12		pmol/L	0.01	NA	GC-ECD

LLD: lower limit of detection LOQ: lower limit of quantification NA: not applicable

INORGANIC PARAMETER ANALYSIS

Major, minor and trace element cation analysis by ICP-MS

Major, minor and trace element cation analysis was carried out at the BGS Inorganic Chemistry Laboratories by inductively coupled mass spectrometry (ICP-MS). The method is fully accredited by UKAS to the requirements of BS EN ISO/IEC 17025:2017. In terms of precision, repeat measurements of standards included in the analytical runs and the analytical replicate results showed good precision of the data with RSD of ≤ 5%.

In terms of accuracy, all recoveries were 100 ± 5-6%, except for bismuth (Bi 108%), manganese (Mn 107%), nickel (Ni 107%) and total sulphur (S-Total 110%) in one of the standards and these results should be treated with caution.

Major and minor anion analysis by ion chromatography

Major and minor anion analysis was carried out at the BGS Inorganic Chemistry Laboratories by ion chromatography. The method is fully accredited by UKAS to the requirements of BS EN ISO/IEC 17025:2017. Repeat measurements of the QC standards included in the sample batches and the analytical replicate results showed good precision of the data with RSD of ≤ 5%. Similarly, the measured results for analytical QC standards demonstrated good recovery (100 ± 5%), relative to the target values, except where parameter concentrations were present in low abundance in one of the standards for chloride (Cl) and sulphate (SO_4) and these results should be treated with caution.

As a further check on the quality of the inorganic water chemistry analysis, the ionic balance of the samples was assessed. The ionic balance is based on the principle of electrical neutrality in natural water, meaning that the equivalent concentration of positively charged cations, is equal to the concentration of negatively charged anions. Therefore, the sum in milliequivalents of major cations and anions should be nearly equal, adding to approximately 0 (Hem 1985). The ionic balance was ± 5% for all the test pump groundwater samples, demonstrating the robustness of the analytical methods.

Chromium speciation analysis by high performance liquid chromatography (HPLC) – ICP-MS

The determination of trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)) was carried out using a High-Performance Liquid Chromatography (HPLC) system coupled to an ICP-MS at the BGS Inorganic Chemistry Laboratories. This analysis is not UKAS accredited, but is an established method (Hamilton et al. 2020). The percentage recoveries of each QC check standard included in the analysis were 100 ± 5% demonstrating good accuracy of the technique. Similarly, analytical replicate measurements showed good precision of the data (RSD ≤ 5%) (Table 8). All Cr speciation results were reported below the LLD; therefore, it was not possible to check the efficiency of the chromatographic separation against the total chromium (Cr-Total) determined by ICP-MS in the filtered acidified sample.

Table 8 Results for quality control standards included in the Cr(VI and III) speciation HPLC-ICP-MS analysis

Standard	Number of Measurements	Results	Cr(VI) µg/L	Cr(III) µg/L
QC1	4	Target value	5	5
		BGS mean	5.17	5.04
		% RSD	1	1
		% recovery	103	101

Laboratory total alkalinity and total inorganic carbon analysis

Total alkalinity in mg/L (expressed in terms of bicarbonate (lab HCO_3)) was determined using a UKAS accredited titrimetric method at the BGS Inorganic Chemistry Laboratories. Total inorganic carbon (TIC) in mg/L was calculated by dividing the titrimetrically measured bicarbonate by 5.0801.

The percentage recoveries for a QC check standard measured before each analytical run were 100 ± 5% demonstrating good accuracy of the method. Analytical replicate measurements showed good precision of the data also (RSD ≤ 5%) (Table 9).

As a further check on data quality, the field and laboratory alkalinity measurements were compared. These showed good agreement with RSD ≤ 10%.

Table 9 Results for quality control standards included in the laboratory total alkalinity/ bicarbonate analysis

Standard	Number of Measurements	Results	HCO_3 mg/L
QC200	6	Target	200
		BGS mean	201
		% RSD	1
		% recovery	100

Ammonium analysis

Ammonium was determined on a Seal Analytical AA3 automated colorimeter using the salicylate method at 630 nm at Wallingford on UKCEH equipment. A six-point calibration was used, with a range of 0-2 mg/L NH_4. Accuracy and precision were monitored also by participation in the Laboratory of the Government Chemist (LGC) Aquacheck inter-laboratory proficiency testing scheme for waters. Results for standards show good accuracy of the data (recovery 100 ± 5%) and precision (RSD ≤ 5%).

ORGANIC PARAMETER ANALYSIS

Non-purgeable organic carbon analysis by carbon analyser

The analysis of non-purgeable organic carbon (NPOC) was carried out on a carbon analyser at the BGS Inorganic Geochemistry Laboratories. The method is fully accredited by UKAS to the requirements of BS EN ISO/IEC 17025:2017.

Results for QC standards included in the analysis showed good accuracy (recoveries 100 ± 5%) and precision (RSD < 5%) of the data.

Total petroleum hydrocarbon analysis by GC-FID

Total petroleum hydrocarbon (TPH) concentrations were determined by gas chromatography flame ionisation detector (GC-FID) at the Scottish Water testing laboratory.

The LOQ (based on 10 times the standard deviation of laboratory blanks) rather than the LLD were reported with the data, due to a change in legislation affecting Scottish Water laboratory operating protocols. Analysis was carried out following UKAS accredited method ISO 17025. However, UKAS accreditation was withheld from TPH analysis dating from March 2019 onwards due to issues with method performance.

None-the-less, results for QC check standards and repeat measurements show good accuracy (recovery 100 ± 5%) and precision (RSD < 10%) of the data (Table 10).

Table 10 Results for quality control standards included in the GC-FID TPH analysis

TPH Compound	% Recovery	% RSD
C8-C10	103	13
C10-C40	82	13

Polycyclic aromatic hydrocarbon analysis by HPLC-FD

Polycyclic aromatic hydrocarbon (PAH) contents were analysed using high performance liquid chromatography fluorescence detection (HPLC-FD) at the Scottish Water testing laboratory. The LOQ (based on 10 times the standard deviation of laboratory blanks) rather than the LLD were

reported with the data, due to a change in legislation affecting Scottish Water laboratory operating protocols. Analysis was carried out according to UKAS accredited method ISO 17025. However, UKAS accreditation was withheld from PAH analysis of samples GGA09R_PTE, GGB05_PTD and GGB05_PTE, due to issues with method performance.

The results for QC check standards and repeat measurements show good accuracy (recovery 100 ± 10%) and precision (RSD < 10%) of the data (Table 11), given that a significant proportion of the data are close to or below the LOQ. The results for benzo(k)fluoranthene and benzo(g,h,i)perylene show poorer recoveries (< 90%) again because the majority of the data are below the detection limit and should be treated with caution.

Table 11 Results for quality control standards included in the HPLC-FD PAH analysis

PAH Compound	% Recovery	% RSD
Benzo(b)fluoranthene	92	5
Benzo(k)fluoranthene	91	4
Benzo(a)pyrene (BaP)	106	5
Benzo(g,h,i)perylene	94	5
Indeno(1,2,3-cd)pyrene	89	6
PAH-Total	92	4

Volatile organic compound analysis

Volatile organic compounds were analysed by the Scottish Water laboratory in Edinburgh. A known volume of sample is transferred to a headspace vial. This vial is then heated for a set period of time to drive the volatile solvents into the headspace. A portion of the headspace is then injected into a gas chromatograph where the solvents of interest are separated prior to mass spectrometer detection (GC-MS). The response for the sample with respect to the internal standard is compared with those from calibration standards.

This analysis is not UKAS accredited. All the parameters in the method are analysed in the same way, but only those detailed below are controlled via control charts (Table 12). The remaining parameters are assessed against set limits (+/-25% of nominal value).

Table 12 Method Performance of certain VOC parameters controlled via control charts

Compound	% Recovery	% RSD
Diethyl Ether	95	7
Trichloromethane	100	4
Benzene	100	4
Toluene	100	4
Tetrachloroethene	102	5
Styrene	101	4
1,3,5-Trichlorobenzene	104	3

STABLE ISOTOPE ANALYSIS

The test pump groundwater samples were sent to the NERC Isotope Geoscience Laboratories (NIGL) for analyses of stable isotopes of carbon ($\delta^{13}C$), oxygen $\delta^{18}O$ and deuterium $\delta^{2}H$. The $\delta^{18}O$ analytical method is not UKAS accredited, but is a well-established protocol (e.g. Ryves et al. 2020). The $\delta^{13}C$ and $\delta^{2}H$ analytical methods are UKAS accredited.

Carbon stable isotope analysis

Stable carbon isotopes were determined using an isotope ratio mass spectrometer (IRMS). Repeat measurements carried out during the sample runs on samples and standards show that

overall analytical reproducibility for these samples was typically better than 0.1‰ for $\delta^{13}C$ (1σ) (RSD ≤ 7%). Similarly, the measured results for a secondary in-house standard (CCS) demonstrated good recovery (100 ± 5 %) relative to the preferred value (Table 13).

Table 13 Results for quality control standards included in the $\delta^{13}C$ stable isotope IRMS analysis

$\delta^{13}C$ ‰ VPDB	MCS primary lab standard	CCS secondary lab standard
Number of measurements	12	10
NIGL mean	-0.7	-22.4
% RSD	7	<1
In-house preferred value		-22.3
% recovery		100

MCS: primary laboratory standard calibrated to international CRM NBS-19-IAEA
CCS: in-house secondary laboratory standard
RSD: relative standard deviation

Deuterium stable isotope analysis

Deuterium stable isotopes were determined using a continuous flow IRMS with liquid autosampler. Repeat measurements show good precision of the data (RSD ≤ 5%) (Table 14)

Table 14 Results for repeat measurements on quality control standards included in the IRMS $\delta^{2}H$ stable isotope analysis

$\delta^{2}H$ VSMOW2 (‰)	CA-LO calibration	CA-HI calibration
	IAEA CRM SMOW2/SLAP	IAEA CRM SMOW2/SLAP
Number of measurements	8	8
NIGL mean	-311.1	-48.5
% RSD	<1	<1

RSD: relative standard deviation

Oxygen stable isotope analysis

Oxygen isotope ($\delta^{18}O$) measurements were made using the CO_2 equilibration method with an IRMS plus Aquaprep device.

Repeat measurements show good precision of the data (RSD ≤ 5%) (Table 15).

Table 15 Results for repeat measurements on quality control standards included in the IRMS $\delta^{18}O$ stable isotope analysis

$\delta^{18}O$ ‰ VSMOW2	CA-LO calibration	CA-HI calibration
	IAEA CRM SMOW2/SLAP	IAEA CRM SMOW2/SLAP
Number of measurements	12	12
NIGL mean	-39.3	-7.3
% RSD	<1	<1

RSD: relative standard deviation

DISSOLVED GASES

Methane, ethane and carbon dioxide

Dissolved gas samples were analysed in batches of approximately 20 at the BGS Wallingford laboratories. A headspace technique was used. This involved the transfer of the water and gas in the sampling cylinder (of known volume, range 47–55 cm^3) to an evacuated glass bulb of known volume (range 117–123 cm^3), at a laboratory temperature maintained at 21±0.5°C.

The displacement process uses helium gas from the same source as used by the gas chromatograph (GC). Aliquots of the headspace gas are then expanded into a sampling loop (volume 0.25 cm^3) attached to the evacuated inlet system of the GC, from where they are admitted via a 6-port gas-sampling valve to a 1/8th-inch (3.175 mm) OD Porapak-Q packed stainless steel column maintained at 100°C. Eluting methane and ethane (if present) are detected by a flame ionisation detector (FID), while CO_2 is measured by a thermal conductivity detector (TCD). The dissolved-phase detection limits are ~0.1 µg/l for CH_4, ~1 µg/l for C_2H_6 and ~0.1 mg/L for CO_2. Since CH_4 concentrations can be highly variable, canned gas standards covering the deciles from 100 ppm to 10% CH_4 are used for calibration before and after each batch, with the standard chosen being within the same decile as the sample with the highest CH_4 value during the run. The FID response is very linear over six orders of magnitude, so single-point calibration is generally used. Two consecutive standard gas aliquots must agree to within ± 5% in peak area to be acceptable. Concentrations of C_2H_6 and CO_2 vary much less, and a single canned gas standard is used for each (100 ppm for C_2H_6 and 3% for CO_2), with the same ± 5% peak area protocol applying to aliquots before and after each batch. A locked spreadsheet is used to back-calculate dissolved gas concentrations (in ccSTP/l) by comparing headspace compositions with gas standards and using the appropriate Ostwald partition coefficient values for the lab temperature. Results are usually recalculated to give concentrations in mg/L or µg/L as required.

Chlorofluorocarbons and sulphur hexafluoride

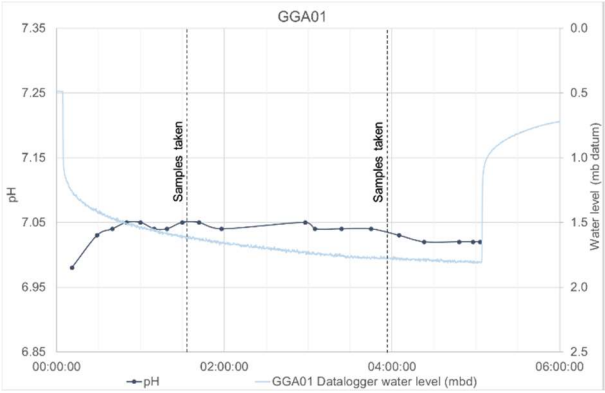
The methodology for the CFCs and SF_6 analysis is described in the paper by Gooddy, et. al. (2006). The CFCs and SF_6 were measured by gas chromatography with an electron capture detector (GC-ECD) after pre-concentration by cryogenic protocols, based on the methods of Oster et al. (1996) and Busenberg and Plummer (2000), respectively. The detection limit of CFC-11 and CFC-12 concentrations in water was 0.01 pmol/L, whereas SF_6 was 0.1 fmol/L.

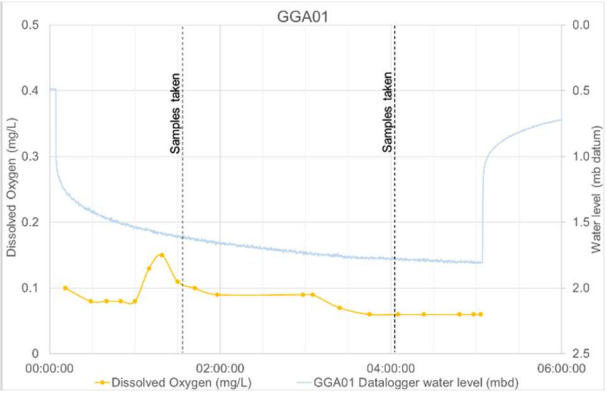
There are no commercially available reference standards for CFCs and SF_6 compounds. Calibration is against a reference gas from the Mace Head atmospheric monitoring station in Galway, Ireland, which is then used to calibrate a local atmospheric air standard. Air values are converted to aqueous concentrations via Henry's Law for a given recharge temperature (assumed to be 8 °C). Precision is based on triplicate measurements of the standard air sample. Typical RSD is <3%.

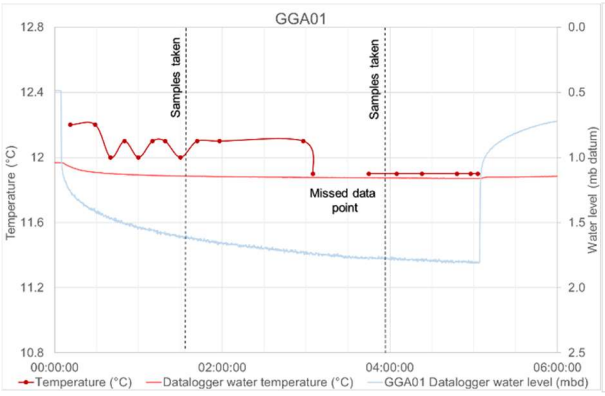
Appendix 2 Plots of Field Parameter Measurements Throughout the Constant Rate Tests

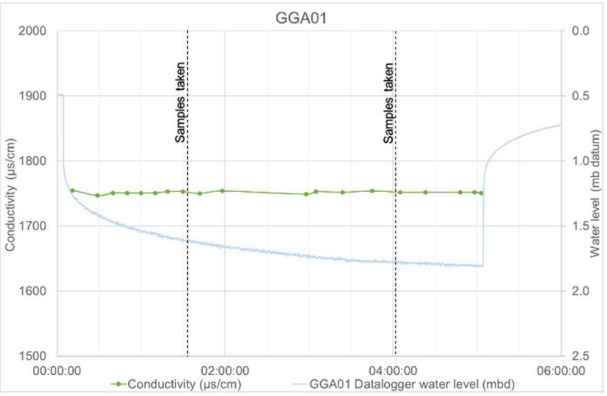
Time-series plots of individual field parameter measurements recorded throughout the constant rate tests are presented in the following set of graphs with the position of the groundwater samples highlighted to show the physico-chemical parameter evolutions before and after sampling. The graphs also show the continuous groundwater level and temperature measurements from data loggers installed the boreholes; Shorter et al. (2021) provide full details of the data loggers. The graphs are arranged by borehole and the boreholes are presented in numerical order.

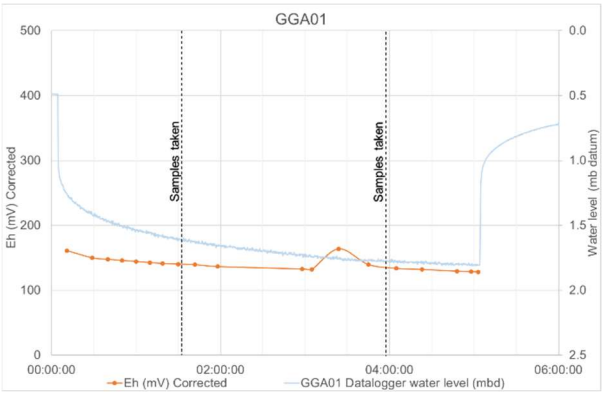
GGA01


GGA01
pH
Water level (mb datum)
Samples taken
Samples taken
7.35
7.25
7.15
7.05
6.95
6.85
0.0
0.5
1.0
1.5
2.0
2.5
00:00:00
02:00:00
04:00:00
06:00:00
pH
GGA01 Datalogger water level (mbd)

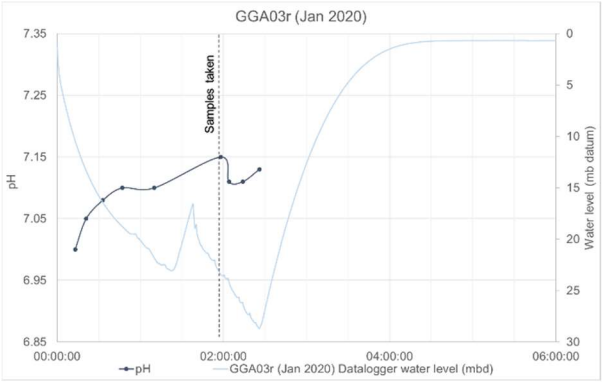

GGA01
Dissolved Oxygen (mg/L)
Water level (mb datum)
Samples taken
Samples taken
0.5
0.4
0.3
0.2
0.1
0
0.0
0.5
1.0
1.5
2.0
2.5
00:00:00
02:00:00
04:00:00
06:00:00
Dissolved Oxygen (mg/L)
GGA01 Datalogger water level (mbd)

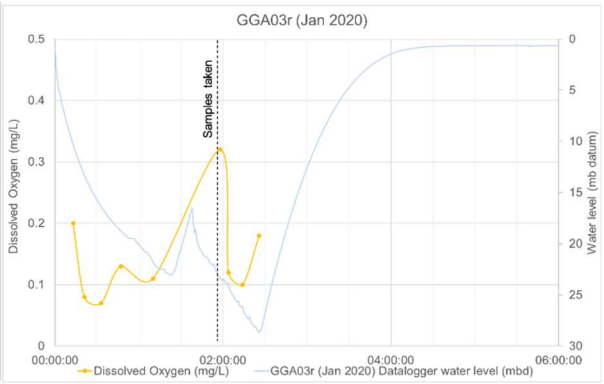

GGA01
Temperature (°C)
Water level (mb datum)
Samples taken
Samples taken
Missed data point
12.8
12.4
12
11.6
11.2
10.8
0.0
0.5
1.0
1.5
2.0
2.5
00:00:00
02:00:00
04:00:00
06:00:00
Temperature (°C)
Datalogger water temperature (°C)
GGA01 Datalogger water level (mbd)

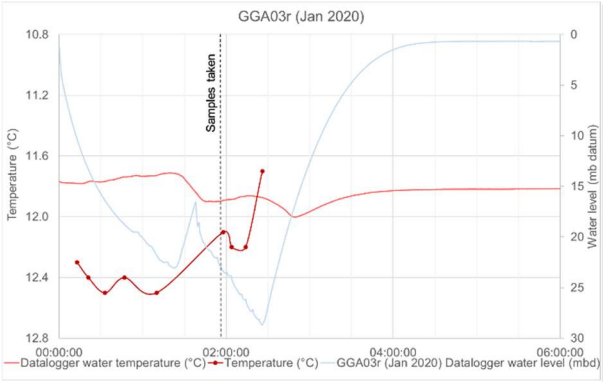

GGA01
Conductivity (µs/cm)
Water level (mb datum)
Samples taken
Samples taken
2000
1900
1800
1700
1600
1500
0.0
0.5
1.0
1.5
2.0
2.5
00:00:00
02:00:00
04:00:00
06:00:00
Conductivity (µs/cm)
GGA01 Datalogger water level (mbd)

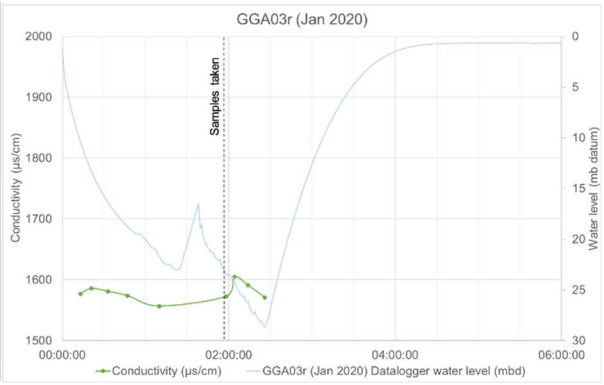

GGA01
Eh (mV) Corrected
Water level (mb datum)
Samples taken
Samples taken
500
400
300
200
100
0
0.0
0.5
1.0
1.5
2.0
2.5
00:00:00
02:00:00
04:00:00
06:00:00
Eh (mV) Corrected
GGA01 Datalogger water level (mbd)

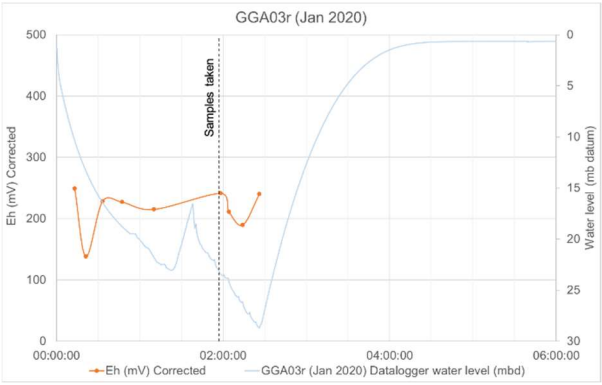
GGA03r (Jan 2020)



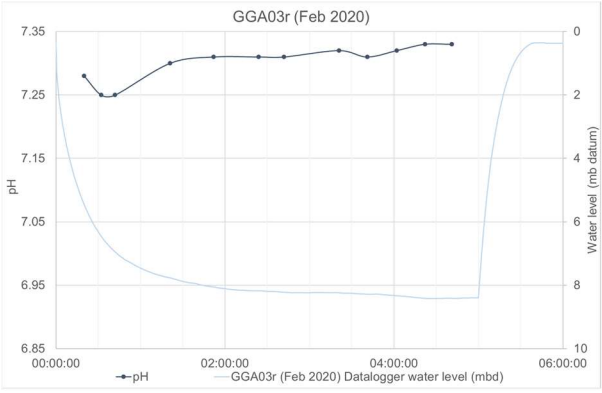


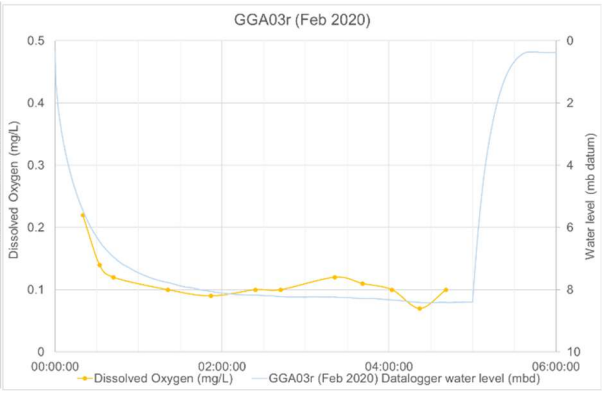


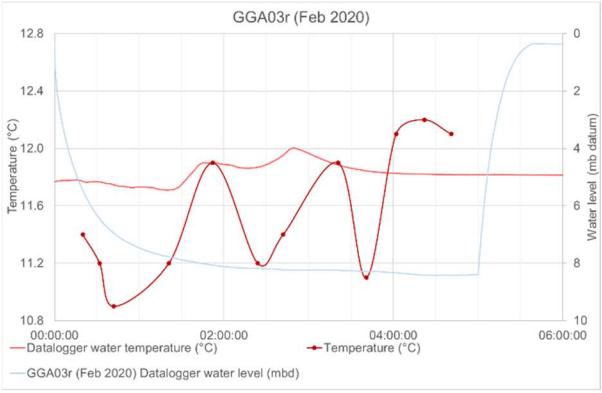


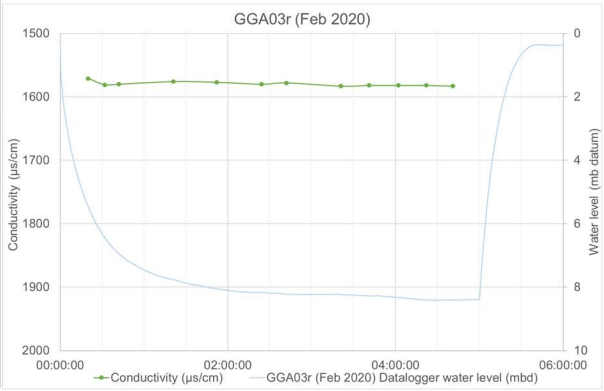


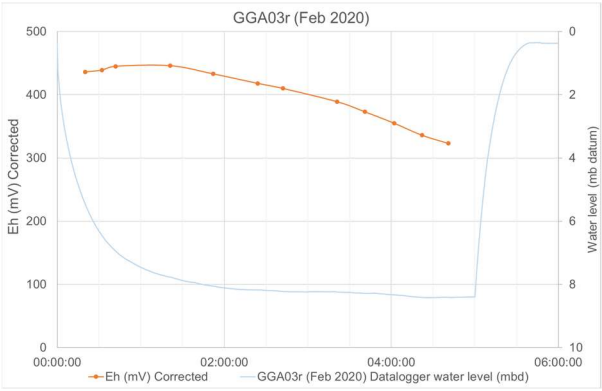
GGA03r (Feb 2020)



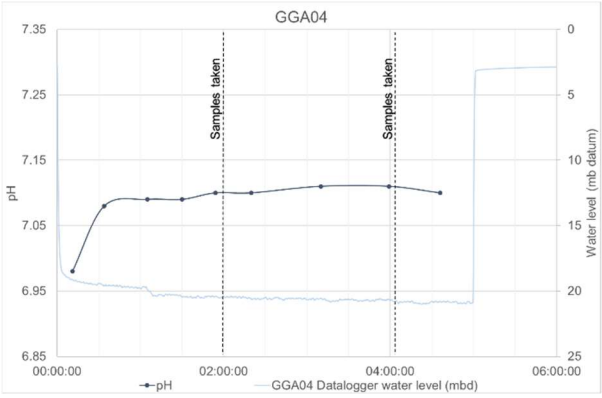


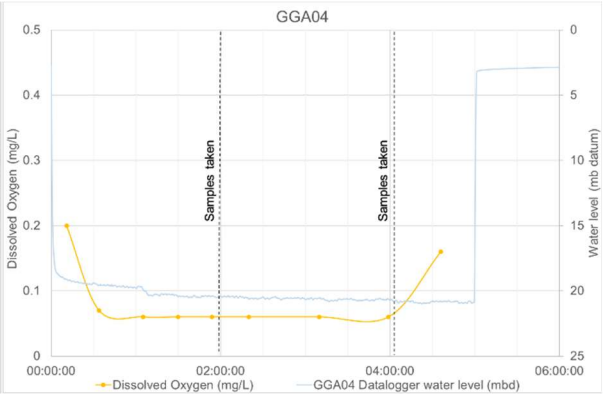


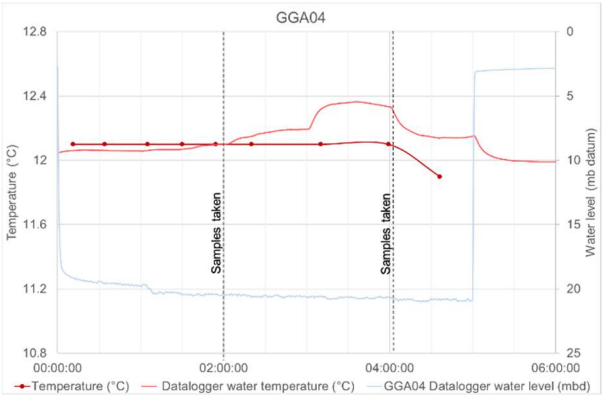


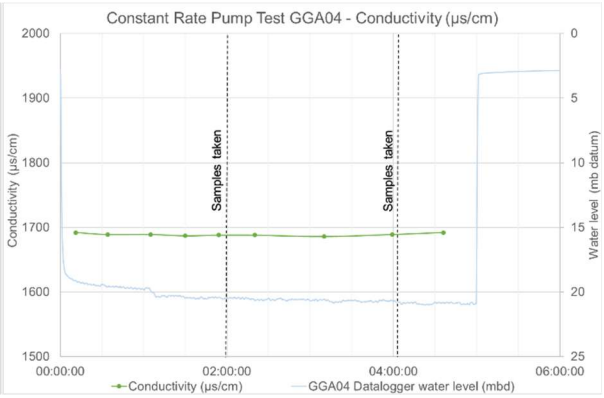


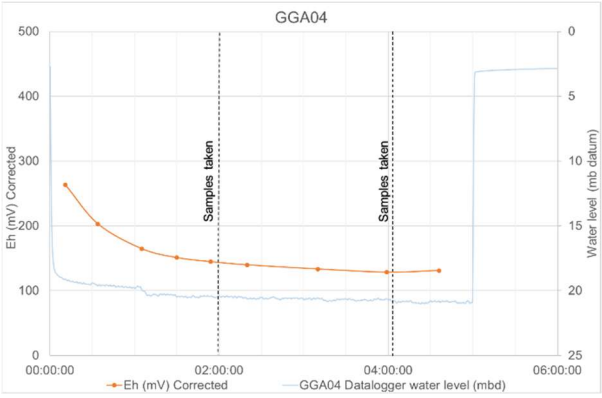
GGA04


GGA04
pH
Water level (mb datum)
Samples taken
Samples taken
7.35
7.25
7.15
7.05
6.95
6.85
0
5
10
15
20
25
00:00:00
02:00:00
04:00:00
06:00:00
pH
GGA04 Datalogger water level (mbd)

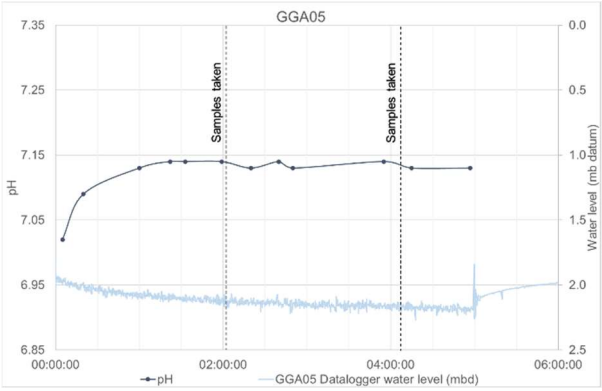

GGA04
Dissolved Oxygen (mg/L)
Water level (mb datum)
Samples taken
Samples taken
0.5
0.4
0.3
0.2
0.1
0
0
5
10
15
20
25
00:00:00
02:00:00
04:00:00
06:00:00
Dissolved Oxygen (mg/L)
GGA04 Datalogger water level (mbd)

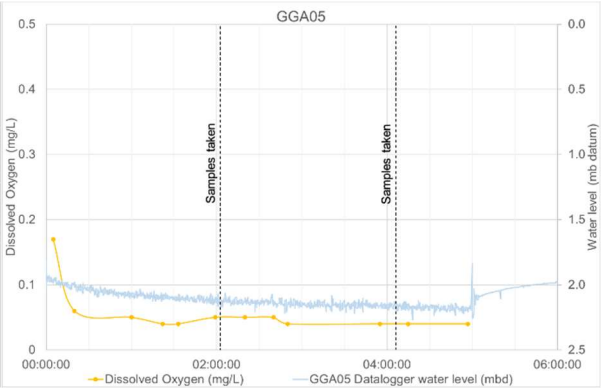

GGA04
Temperature (°C)
Water level (mb datum)
Samples taken
Samples taken
12.8
12.4
12
11.6
11.2
10.8
0
5
10
15
20
25
00:00:00
02:00:00
04:00:00
06:00:00
Temperature (°C)
Datalogger water temperature (°C)
GGA04 Datalogger water level (mbd)

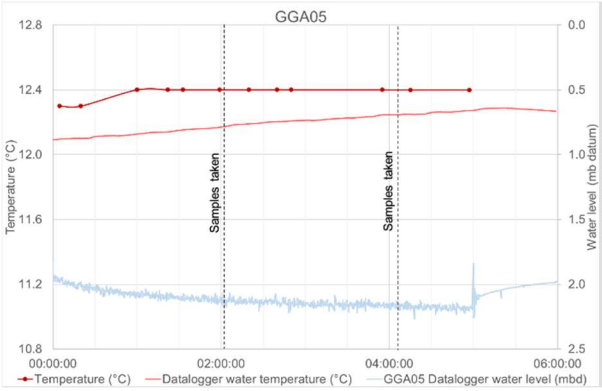

Constant Rate Pump Test GGA04 - Conductivity (µs/cm)
Conductivity (µs/cm)
Water level (mb datum)
Samples taken
Samples taken
2000
1900
1800
1700
1600
1500
0
5
10
15
20
25
00:00:00
02:00:00
04:00:00
06:00:00
Conductivity (µs/cm)
GGA04 Datalogger water level (mbd)

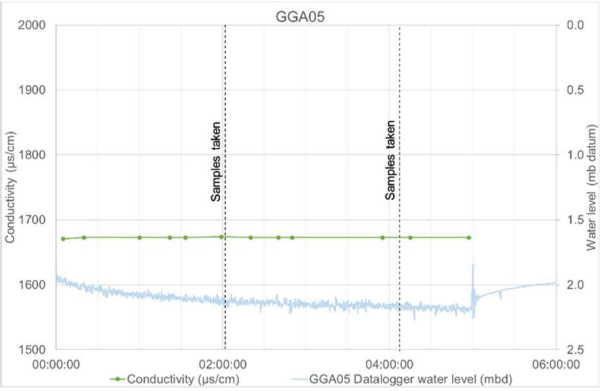

GGA04
Eh (mV) Corrected
Water level (mb datum)
Samples taken
Samples taken
500
400
300
200
100
0
0
5
10
15
20
25
00:00:00
02:00:00
04:00:00
06:00:00
Eh (mV) Corrected
GGA04 Datalogger water level (mbd)

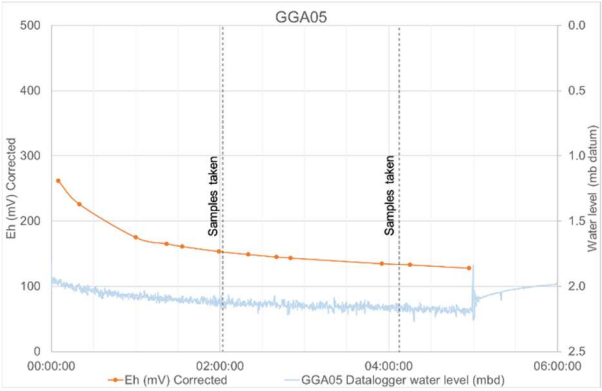
GGA05


GGA05
pH
Water level (mb datum)
Samples taken
Samples taken
pH
GGA05 Datalogger water level (mbd)

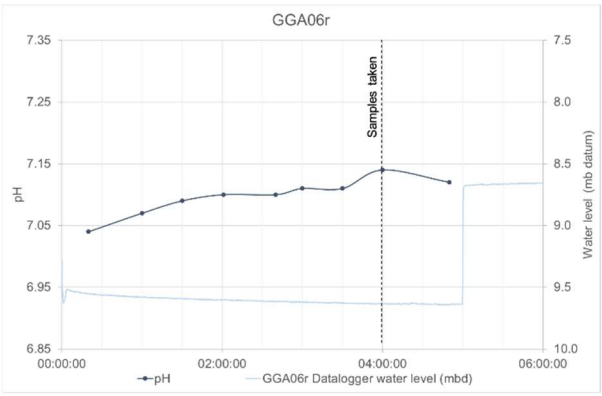

GGA05
Dissolved Oxygen (mg/L)
Water level (mb datum)
Samples taken
Samples taken
Dissolved Oxygen (mg/L)
GGA05 Datalogger water level (mbd)

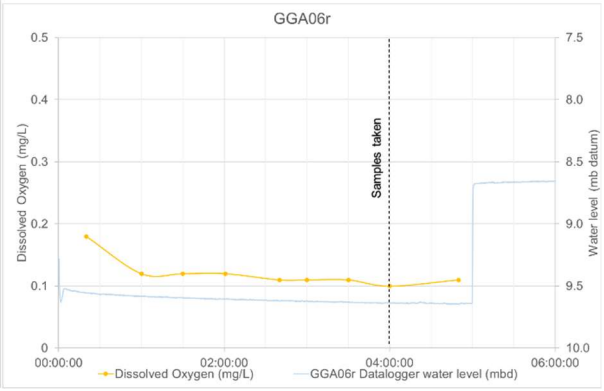

GGA05
Temperature (°C)
Water level (mb datum)
Samples taken
Samples taken
Temperature (°C)
Datalogger water temperature (°C)
GGA05 Datalogger water level (mbd)

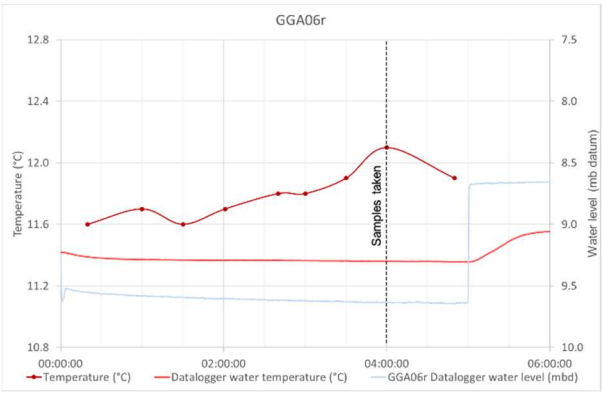

GGA05
Conductivity (µs/cm)
Water level (mb datum)
Samples taken
Samples taken
Conductivity (µs/cm)
GGA05 Datalogger water level (mbd)

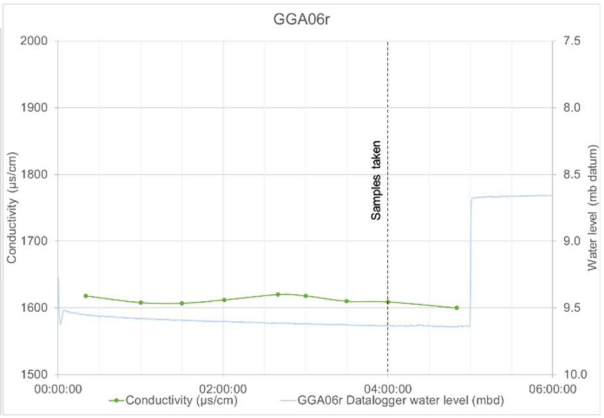

GGA05
Eh (mV) Corrected
Water level (mb datum)
Samples taken
Samples taken
Eh (mV) Corrected
GGA05 Datalogger water level (mbd)

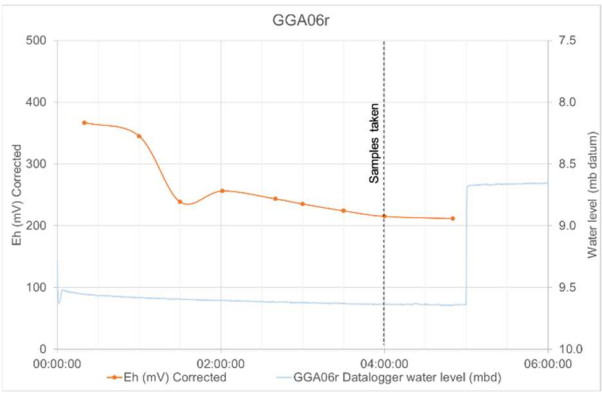
GGA06r


GGA06r
pH
Water level (mb datum)
Samples taken
pH
GGA06r Datalogger water level (mbd)

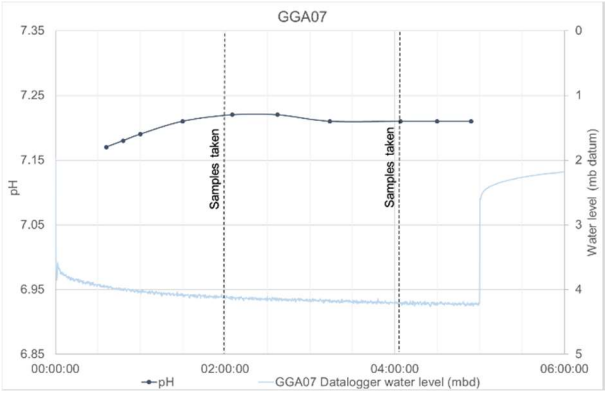

GGA06r
Dissolved Oxygen (mg/L)
Water level (mb datum)
Samples taken
Dissolved Oxygen (mg/L)
GGA06r Datalogger water level (mbd)

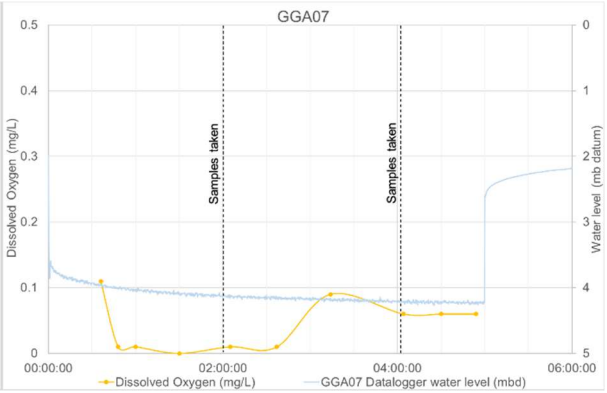

GGA06r
Temperature (°C)
Water level (mb datum)
Samples taken
Temperature (°C)
Datalogger water temperature (°C)
GGA06r Datalogger water level (mbd)

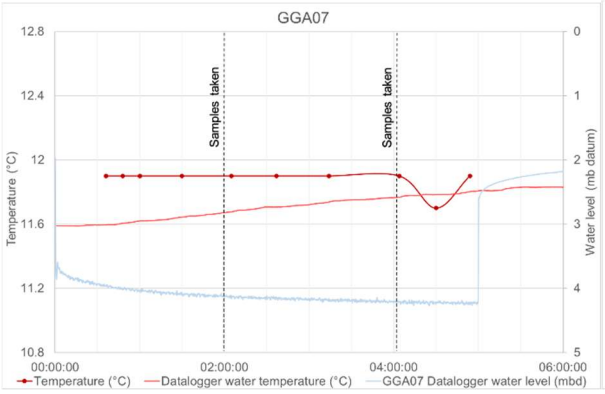

GGA06r
Conductivity (µs/cm)
Water level (mb datum)
Samples taken
Conductivity (µs/cm)
GGA06r Datalogger water level (mbd)

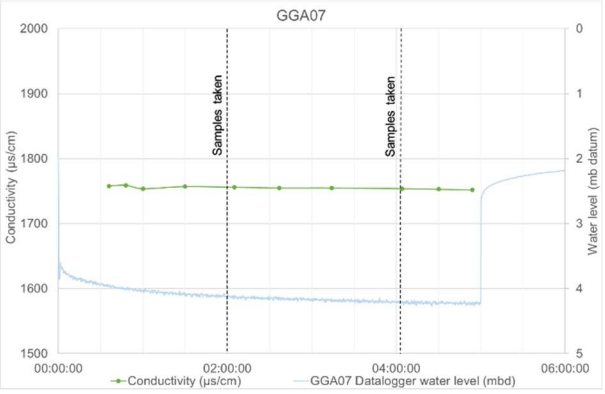

GGA06r
Eh (mV) Corrected
Water level (mb datum)
Samples taken
Eh (mV) Corrected
GGA06r Datalogger water level (mbd)

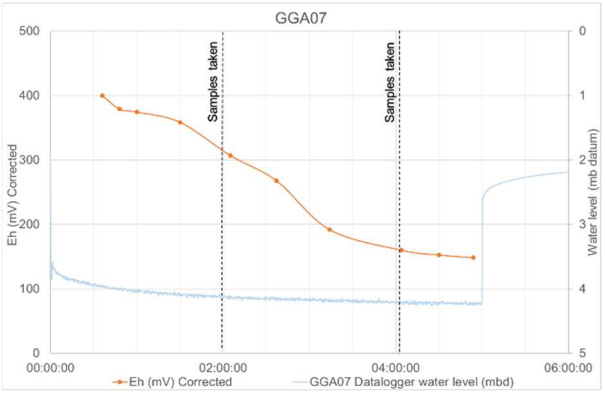
GGA07


GGA07
pH
Water level (mb datum)
Samples taken
Samples taken
7.35
7.25
7.15
7.05
6.95
6.85
0
1
2
3
4
5
00:00:00
02:00:00
04:00:00
06:00:00
pH
GGA07 Datalogger water level (mbd)

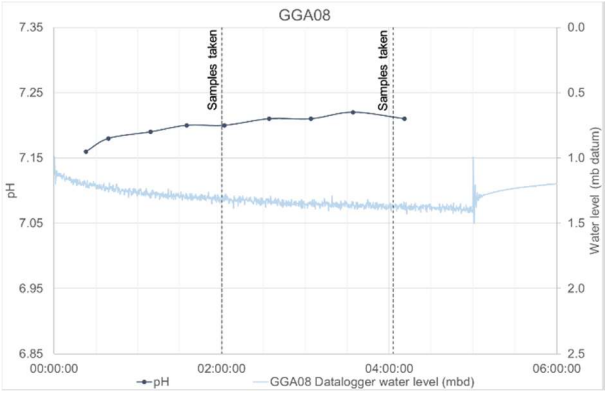

GGA07
Dissolved Oxygen (mg/L)
Water level (mb datum)
Samples taken
Samples taken
0.5
0.4
0.3
0.2
0.1
0
0
1
2
3
4
5
00:00:00
02:00:00
04:00:00
06:00:00
Dissolved Oxygen (mg/L)
GGA07 Datalogger water level (mbd)

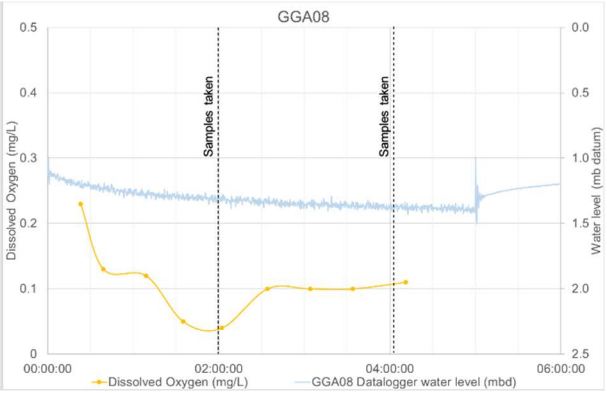

GGA07
Temperature (°C)
Water level (mb datum)
Samples taken
Samples taken
12.8
12.4
12
11.6
11.2
10.8
0
1
2
3
4
5
00:00:00
02:00:00
04:00:00
06:00:00
Temperature (°C)
Datalogger water temperature (°C)
GGA07 Datalogger water level (mbd)

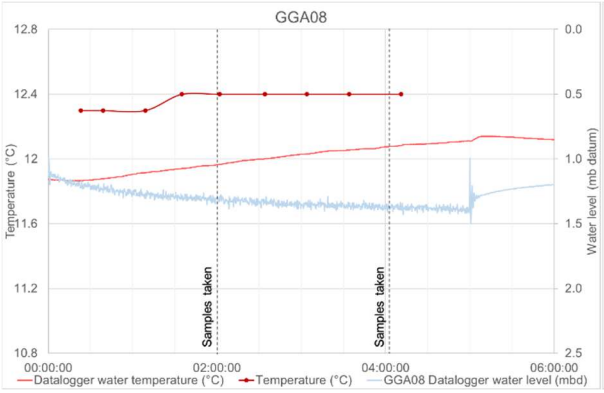

GGA07
Conductivity (µs/cm)
Water level (mb datum)
Samples taken
Samples taken
2000
1900
1800
1700
1600
1500
0
1
2
3
4
5
00:00:00
02:00:00
04:00:00
06:00:00
Conductivity (µs/cm)
GGA07 Datalogger water level (mbd)

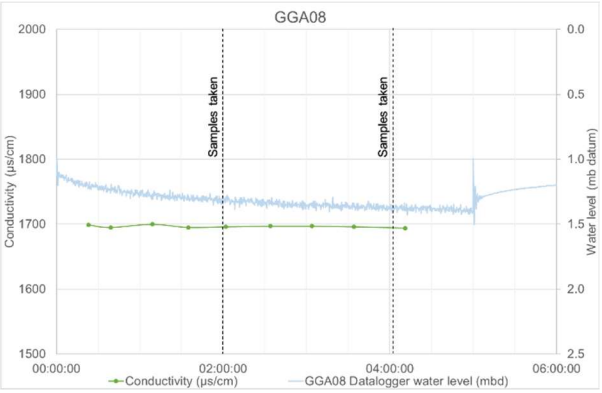

GGA07
Eh (mV) Corrected
Water level (mb datum)
Samples taken
Samples taken
500
400
300
200
100
0
0
1
2
3
4
5
00:00:00
02:00:00
04:00:00
06:00:00
Eh (mV) Corrected
GGA07 Datalogger water level (mbd)

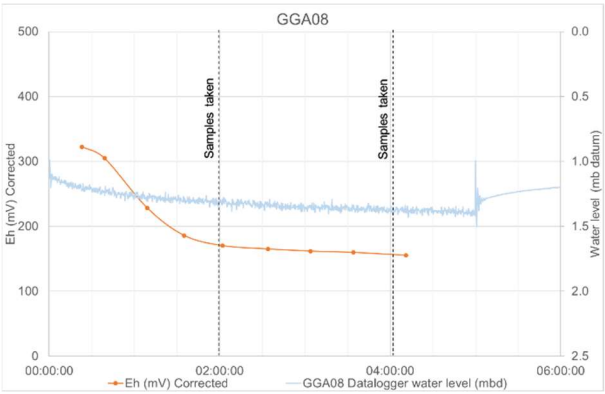
GGA08


GGA08
Samples taken
Samples taken
pH
Water level (mb datum)
pH
GGA08 Datalogger water level (mbd)

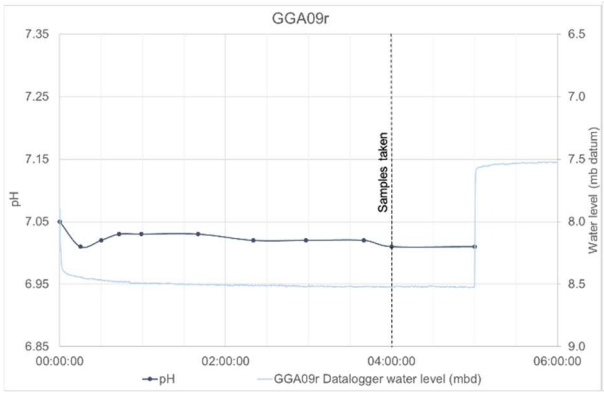

GGA08
Samples taken
Samples taken
Dissolved Oxygen (mg/L)
Water level (mb datum)
Dissolved Oxygen (mg/L)
GGA08 Datalogger water level (mbd)

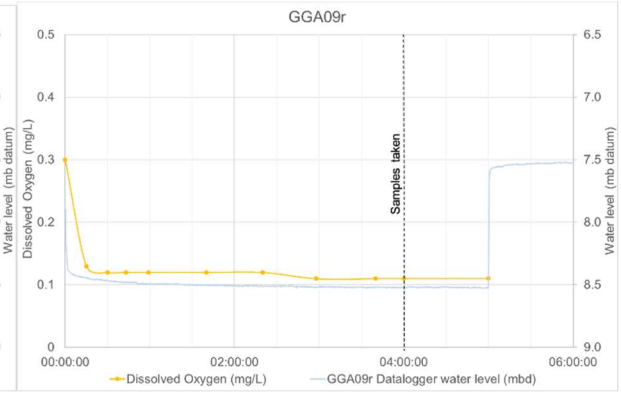

GGA08
Samples taken
Samples taken
Temperature (°C)
Water level (mb datum)
Datalogger water temperature (°C)
Temperature (°C)
GGA08 Datalogger water level (mbd)

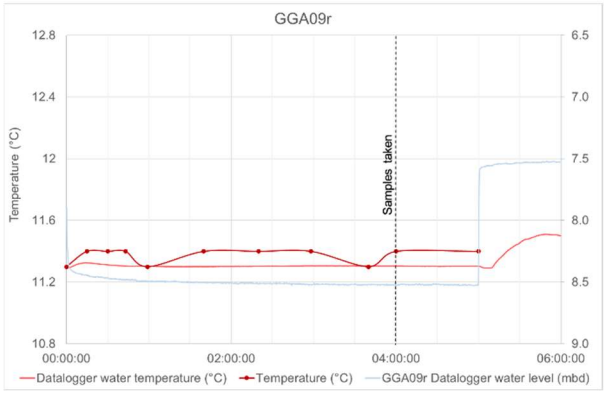

GGA08
Samples taken
Samples taken
Conductivity (µs/cm)
Water level (mb datum)
Conductivity (µs/cm)
GGA08 Datalogger water level (mbd)

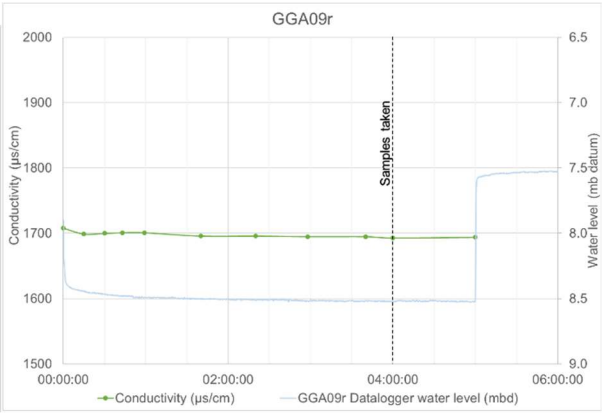

GGA08
Samples taken
Samples taken
Eh (mV) Corrected
Water level (mb datum)
Eh (mV) Corrected
GGA08 Datalogger water level (mbd)

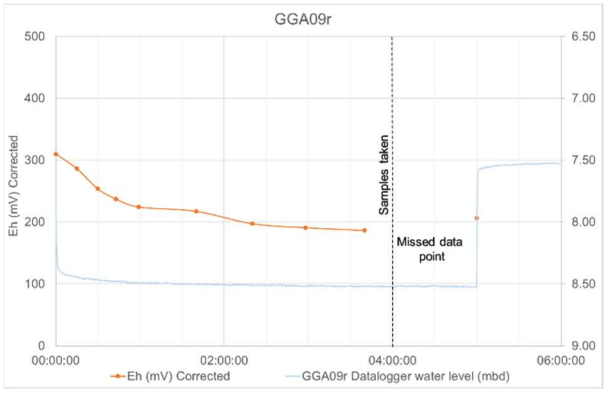
GGA09r


GGA09r
pH
Water level (mb datum)
Samples taken
7.35
7.25
7.15
7.05
6.95
6.85
6.5
7.0
7.5
8.0
8.5
9.0
00:00:00
02:00:00
04:00:00
06:00:00
pH
GGA09r Datalogger water level (mbd)

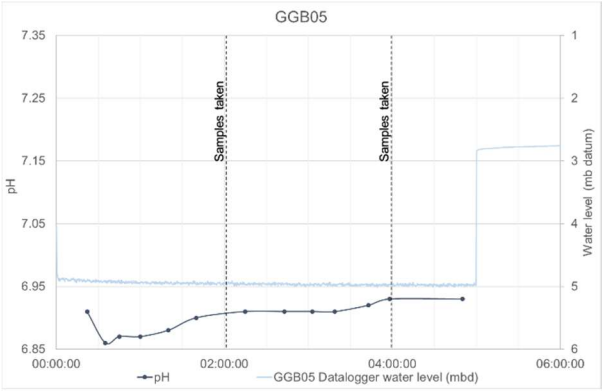

GGA09r
Dissolved Oxygen (mg/L)
Water level (mb datum)
Samples taken
0.5
0.4
0.3
0.2
0.1
0
6.5
7.0
7.5
8.0
8.5
9.0
00:00:00
02:00:00
04:00:00
06:00:00
Dissolved Oxygen (mg/L)
GGA09r Datalogger water level (mbd)

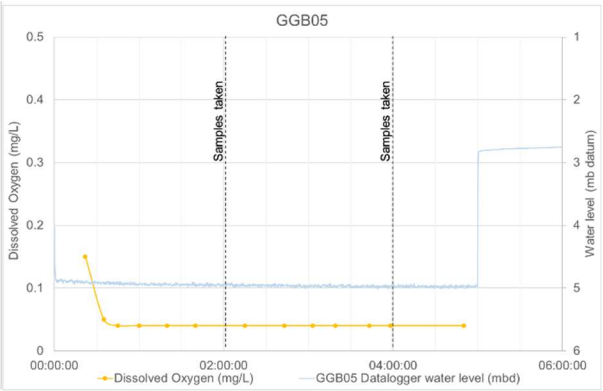

GGA09r
Temperature (°C)
Water level (mb datum)
Samples taken
12.8
12.4
12
11.6
11.2
10.8
6.5
7.0
7.5
8.0
8.5
9.0
00:00:00
02:00:00
04:00:00
06:00:00
Datalogger water temperature (°C)
Temperature (°C)
GGA09r Datalogger water level (mbd)

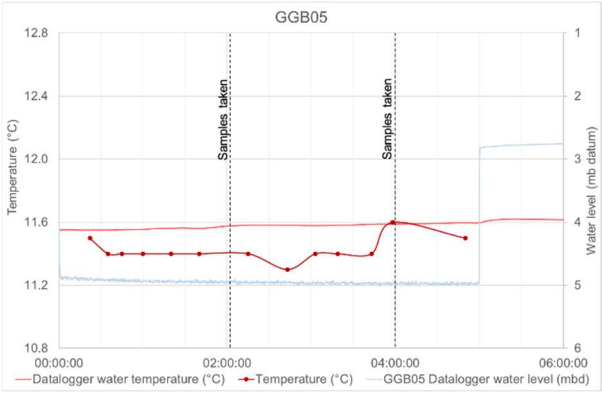

GGA09r
Conductivity (µs/cm)
Water level (mb datum)
Samples taken
2000
1900
1800
1700
1600
1500
6.5
7.0
7.5
8.0
8.5
9.0
00:00:00
02:00:00
04:00:00
06:00:00
Conductivity (µs/cm)
GGA09r Datalogger water level (mbd)

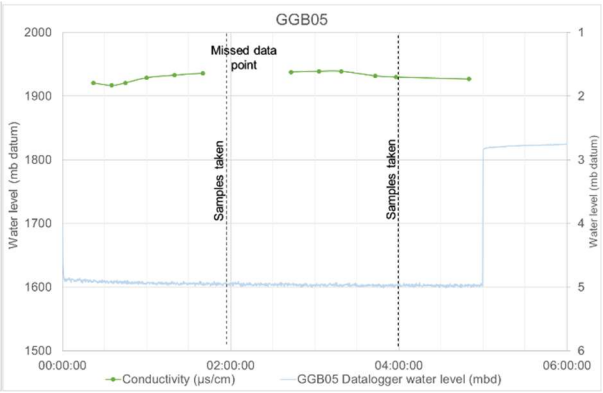

GGA09r
Eh (mV) Corrected
Samples taken
Missed data point
500
400
300
200
100
0
6.50
7.00
7.50
8.00
8.50
9.00
00:00:00
02:00:00
04:00:00
06:00:00
Eh (mV) Corrected
GGA09r Datalogger water level (mbd)

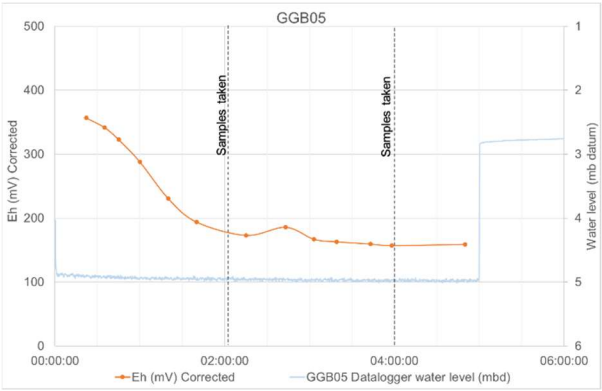
GGB05


GGB05
pH
Water level (mb datum)
Samples taken
Samples taken
7.35
7.25
7.15
7.05
6.95
6.85
1
2
3
4
5
6
00:00:00
02:00:00
04:00:00
06:00:00
pH
GGB05 Datalogger water level (mbd)


GGB05
Dissolved Oxygen (mg/L)
Water level (mb datum)
Samples taken
Samples taken
0.5
0.4
0.3
0.2
0.1
0
1
2
3
4
5
6
00:00:00
02:00:00
04:00:00
06:00:00
Dissolved Oxygen (mg/L)
GGB05 Datalogger water level (mbd)


GGB05
Temperature (°C)
Water level (mb datum)
Samples taken
Samples taken
12.8
12.4
12.0
11.6
11.2
10.8
1
2
3
4
5
6
00:00:00
02:00:00
04:00:00
06:00:00
Datalogger water temperature (°C)
Temperature (°C)
GGB05 Datalogger water level (mbd)


GGB05
Water level (mb datum)
Missed data point
Samples taken
Samples taken
2000
1900
1800
1700
1600
1500
1
2
3
4
5
6
00:00:00
02:00:00
04:00:00
06:00:00
Conductivity (µs/cm)
GGB05 Datalogger water level (mbd)


GGB05
Eh (mV) Corrected
Water level (mb datum)
Samples taken
Samples taken
500
400
300
200
100
0
1
2
3
4
5
6
00:00:00
02:00:00
04:00:00
06:00:00
Eh (mV) Corrected
GGB05 Datalogger water level (mbd)

Appendix 3 Plots of Test Pump Groundwater Field and Inorganic Chemistry Parameters

Plots of field parameter, major ion, minor and trace element concentrations in groundwaters from the UKGEOS Glasgow Observatory boreholes, sampled during test pumping in January – February 2020 are presented in Figure 14 to 26. The boreholes sampled are divided into the target horizons/ aquifers from which the water was abstracted (c.f. Table 1). The empty or full symbols represent, respectively, the sample taken at two- or four-hours during pumping.

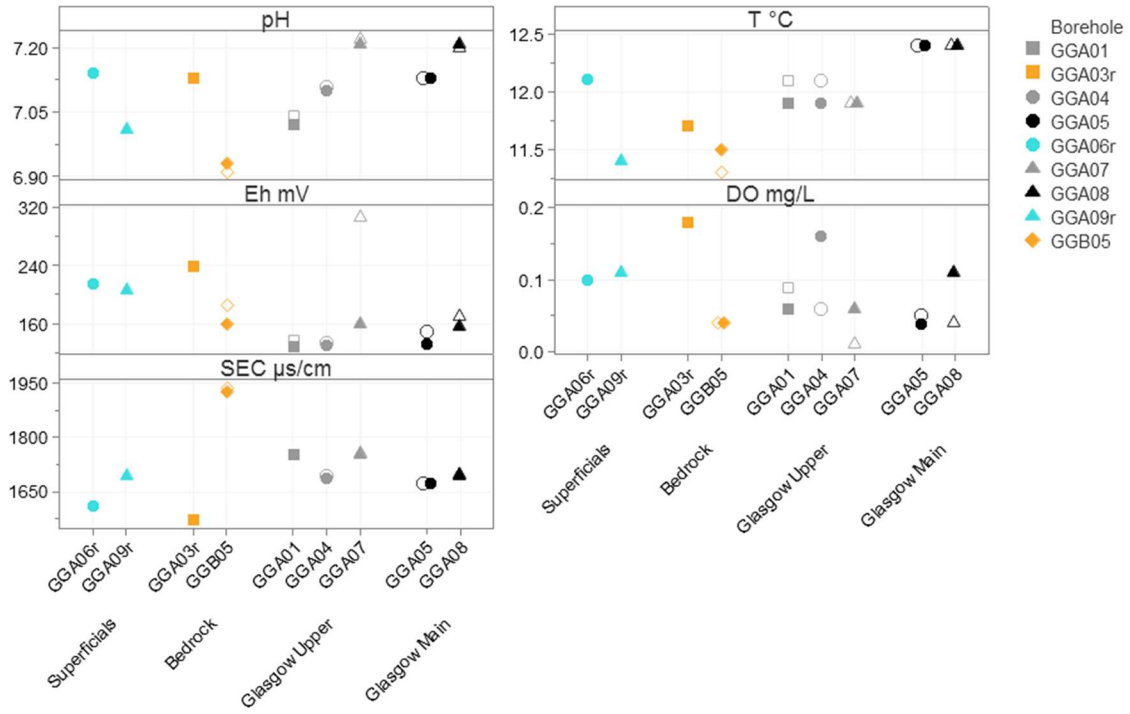


Figure 14 Individual value plots showing the distribution of pH, temperature (T), redox potential (Eh), dissolved oxygen (DO) and specific electrical conductance (SEC).

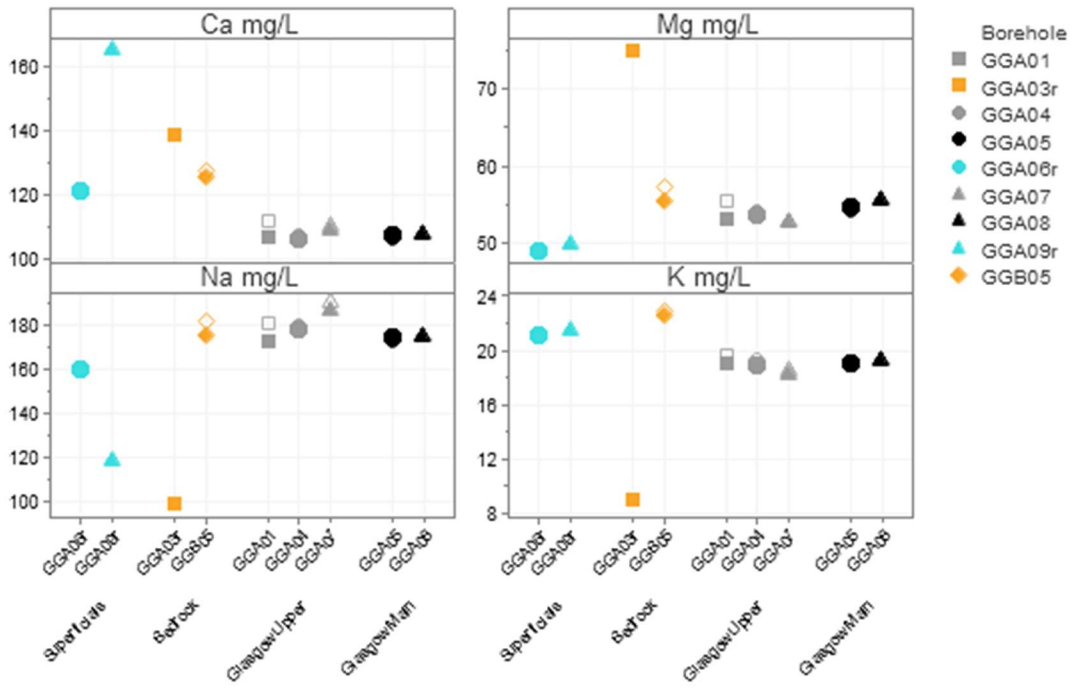


Figure 15 Individual value plots showing the distribution of major cations (calcium, magnesium, sodium and potassium).

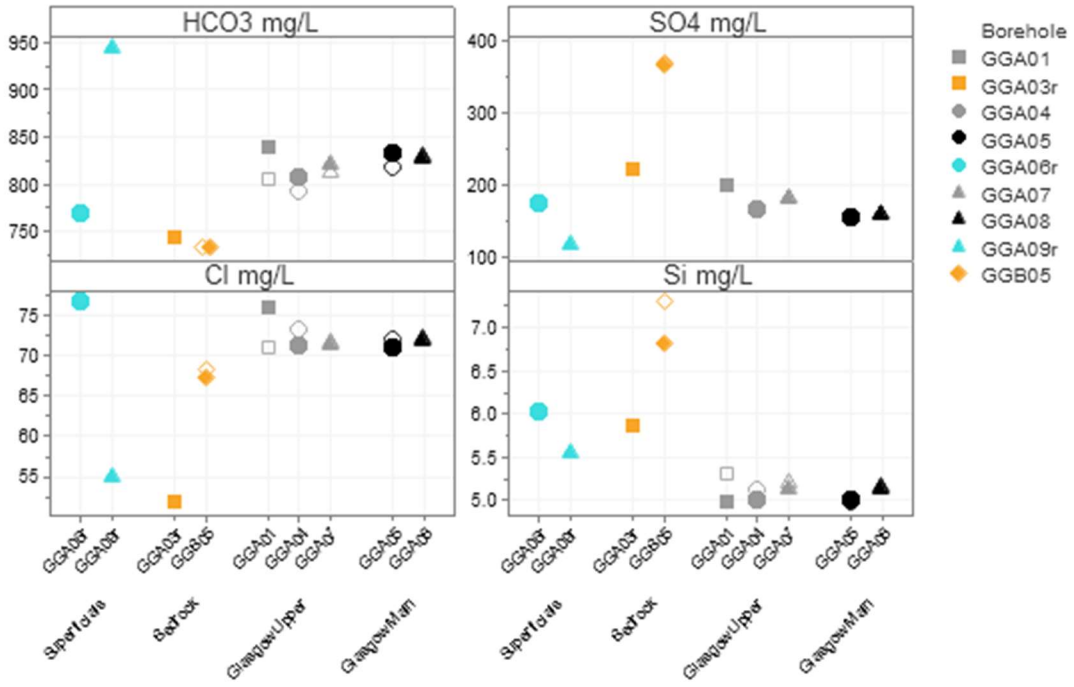


Figure 16 Individual value plots showing the distribution of major anions (field-alkalinity as HCO_3, sulphate, chloride) and silicon.

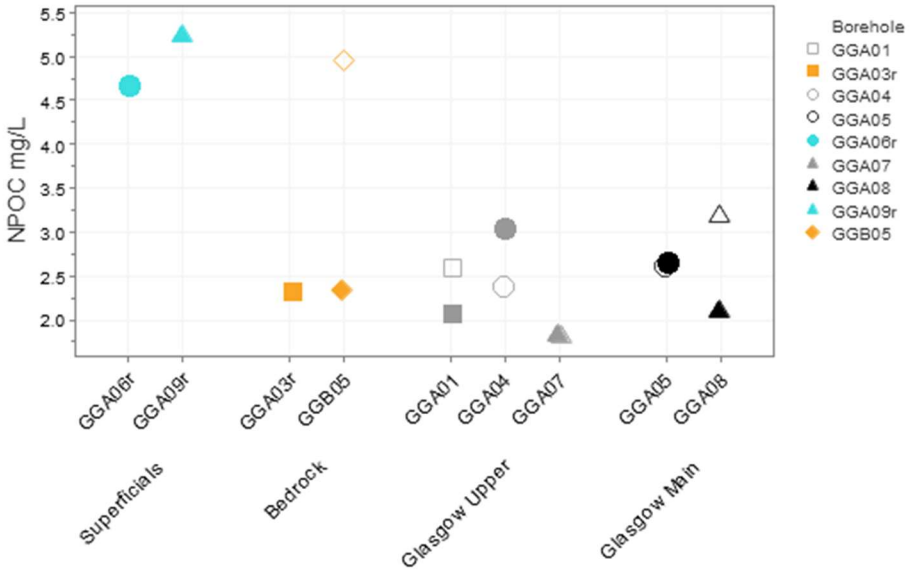


Figure 17 Individual value plots showing the distribution of non-purgeable organic carbon.

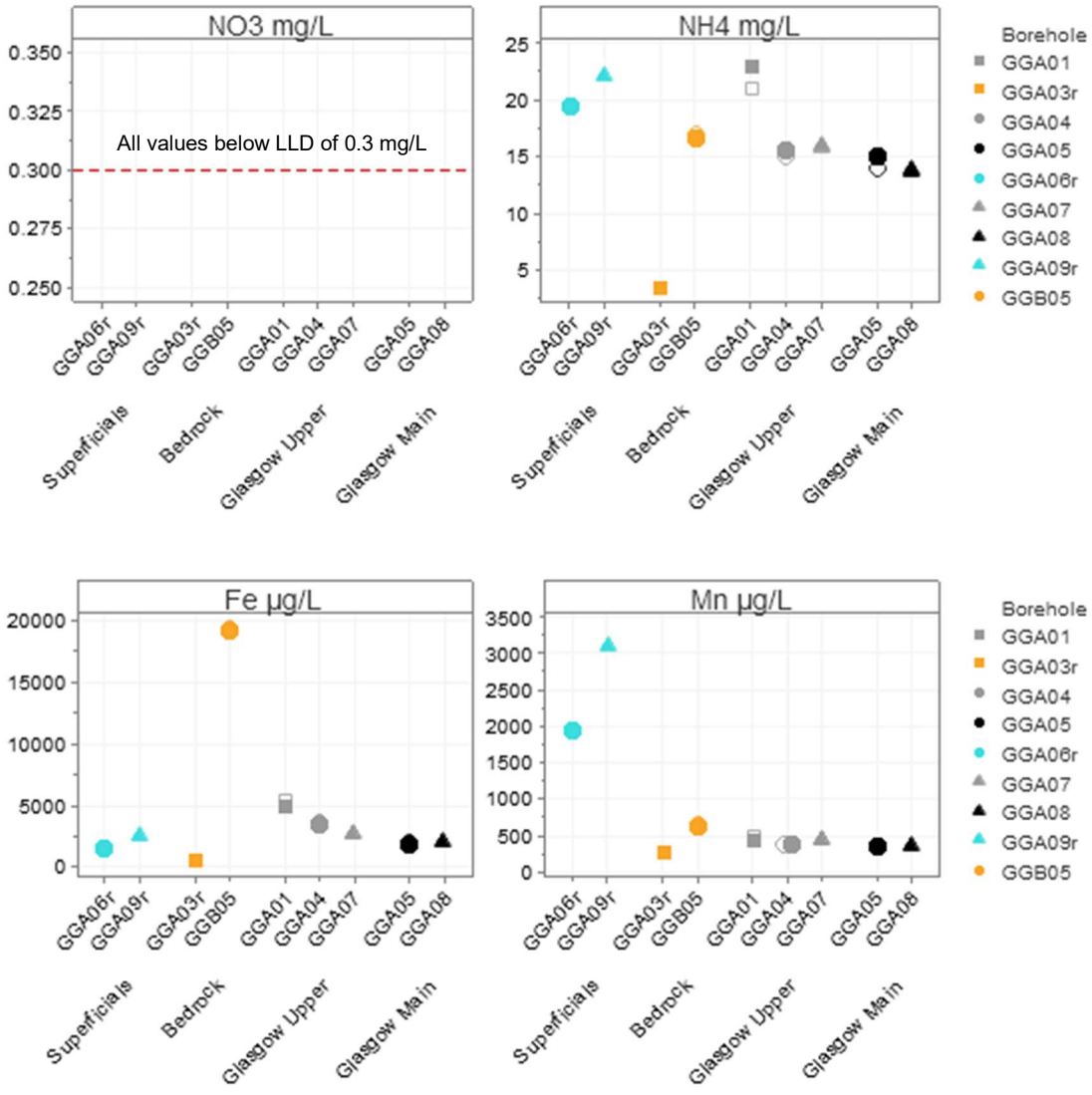


Figure 18 Individual value plots showing the distribution of nitrate, ammonia, iron and manganese.

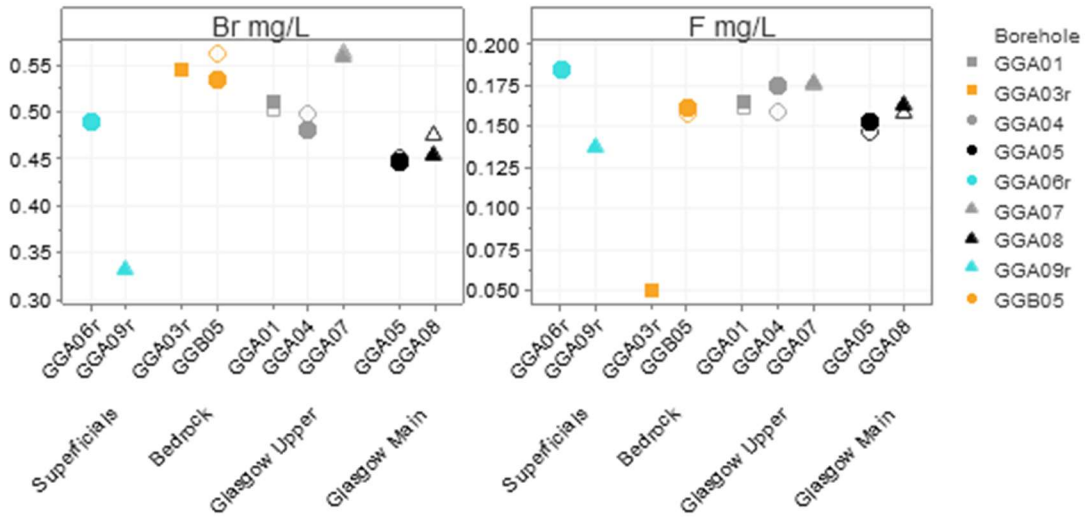


Figure 19 Individual value plots showing the distribution of bromide and fluoride.

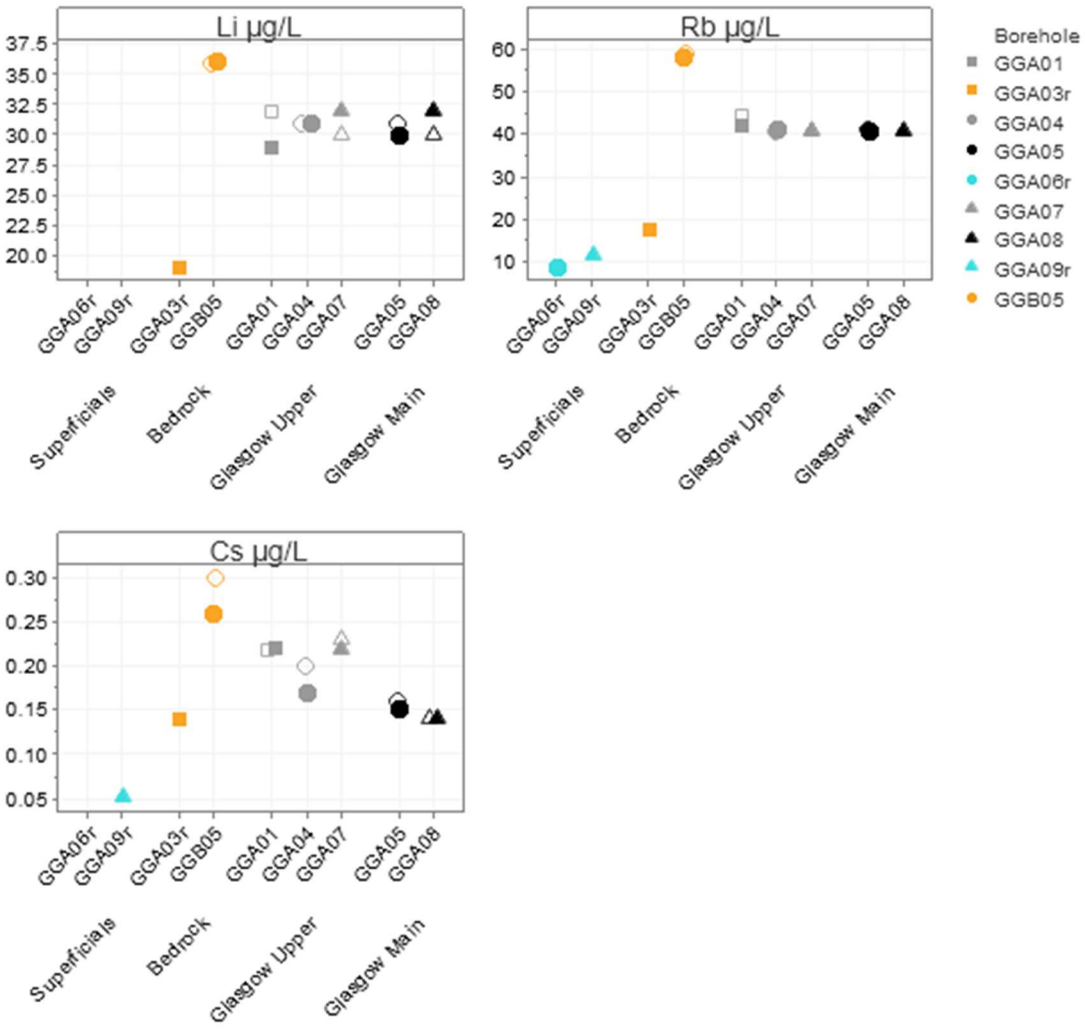


Figure 20 Individual value plots showing the distribution of lithium, rubidium and caesium. Where symbols are missing this is because concentration was below the detection limit.

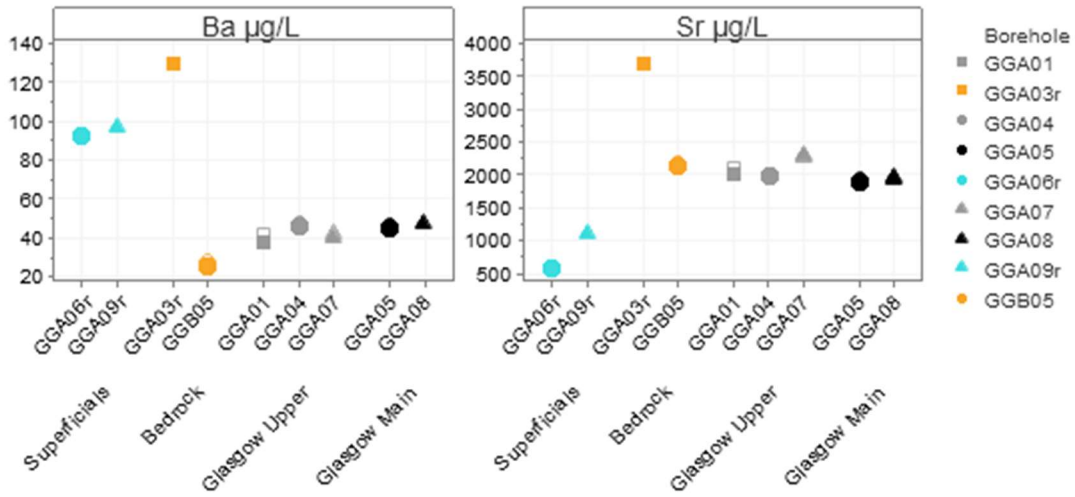


Figure 21 Individual value plots showing the distribution of barium and strontium.

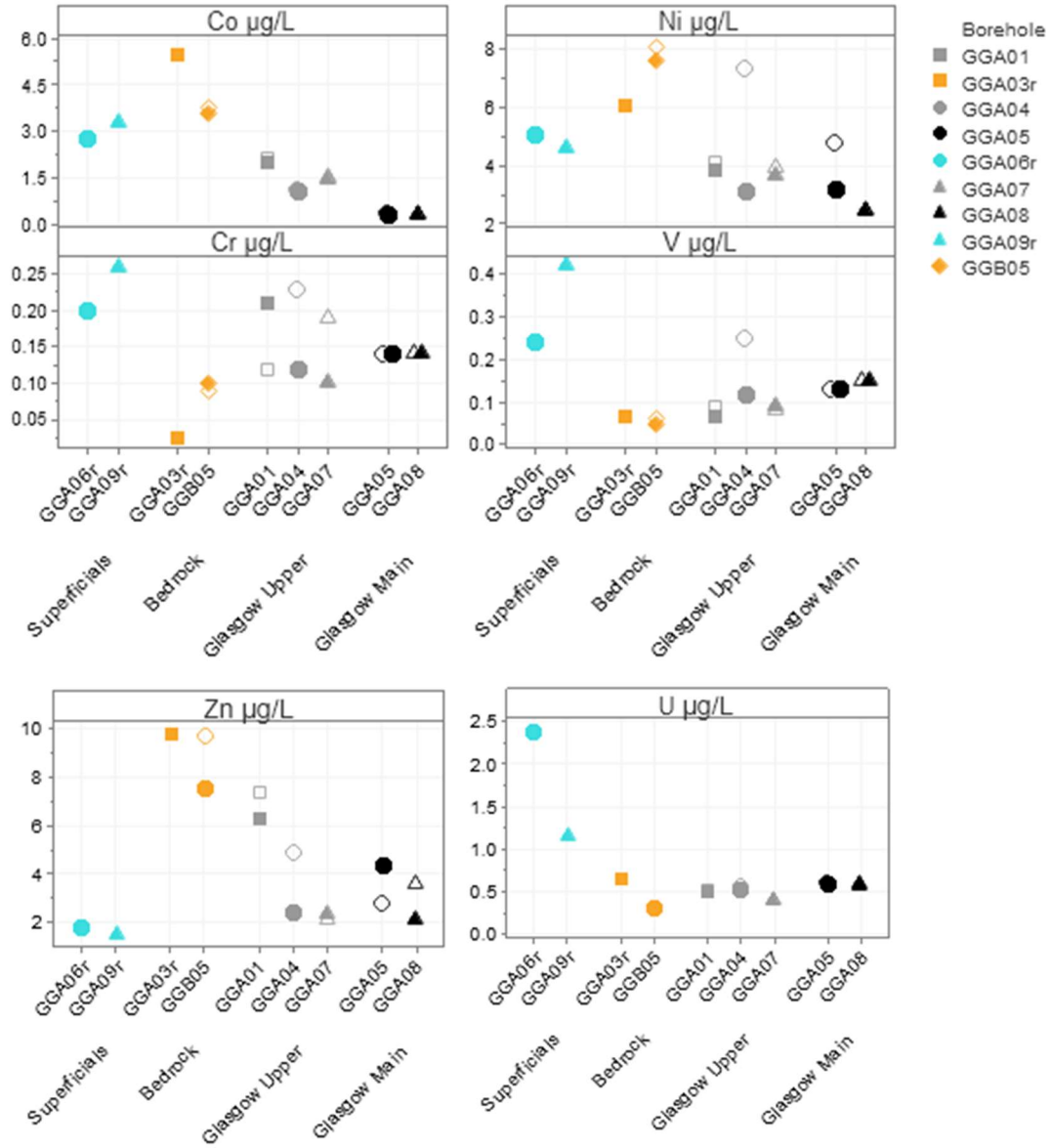


Figure 22 Individual value plots showing the distribution of cobalt, chromium, nickel, vanadium, zinc and uranium.

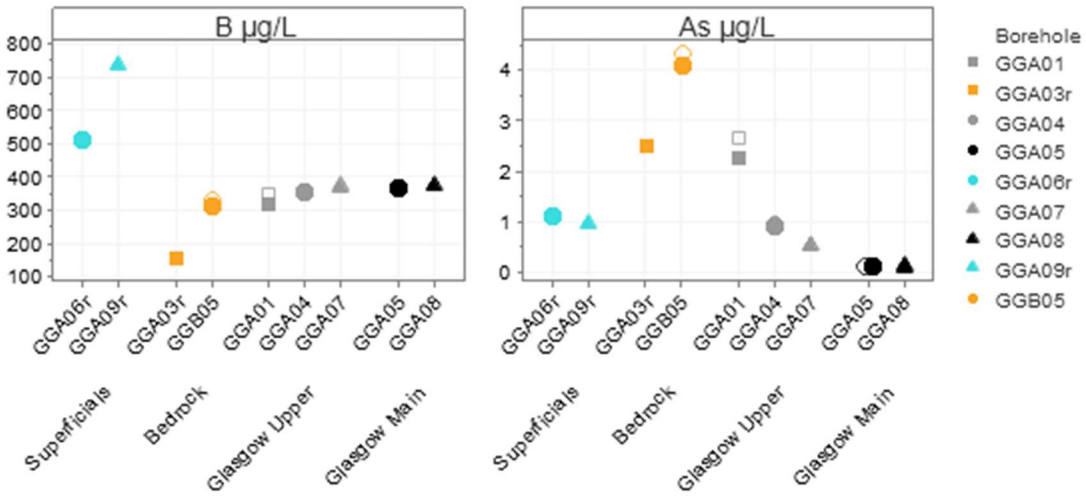


Figure 23 Individual value plots showing the distribution of boron and arsenic.

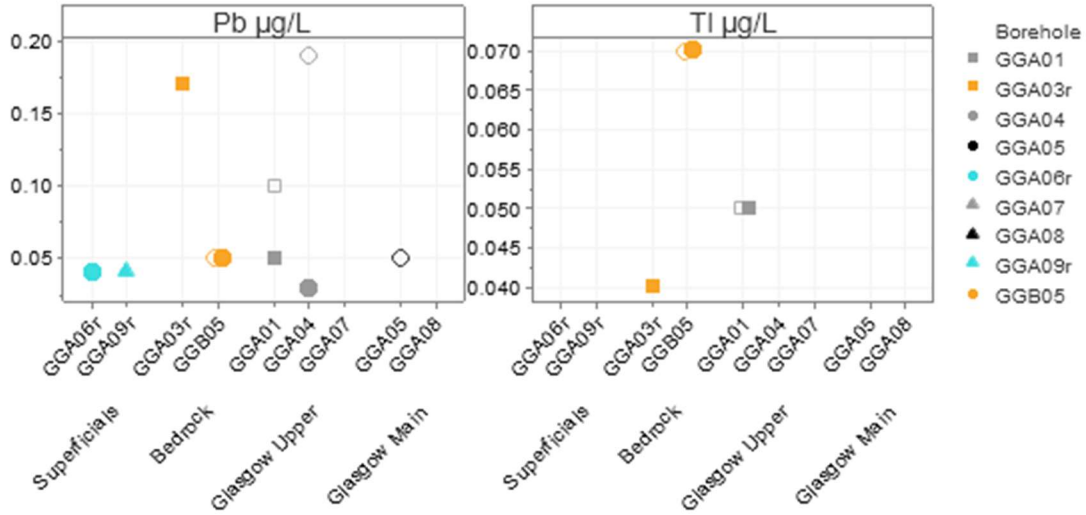


Figure 24 Individual value plots showing the distribution of lead and thallium. Where symbols are missing this is because concentration was below the detection limit.

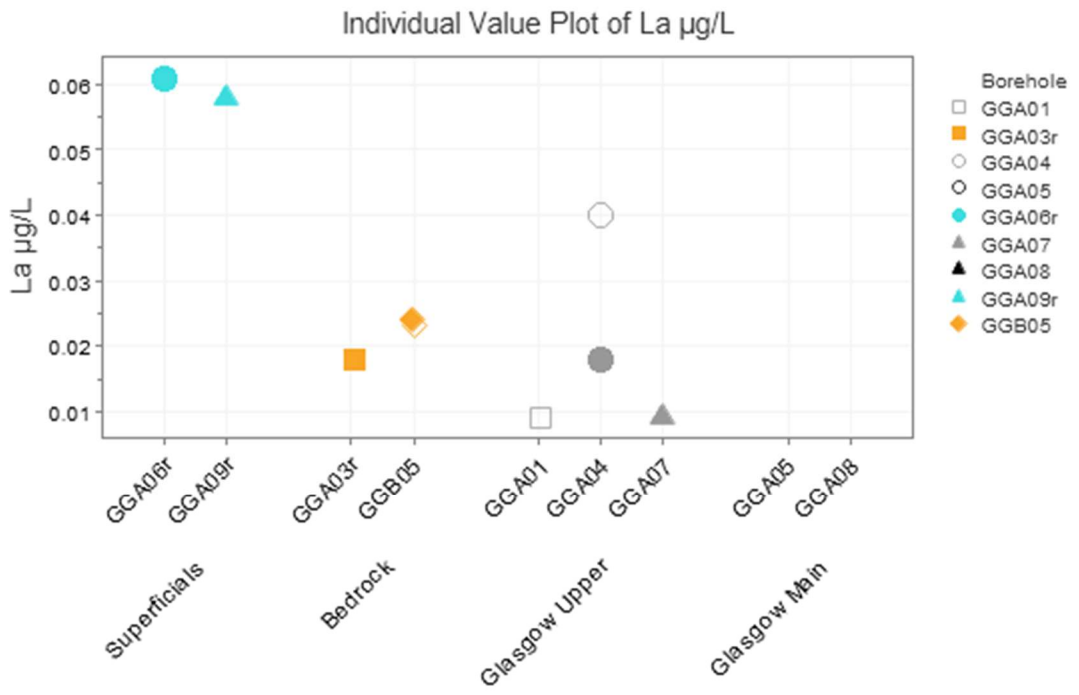


Figure 25 Individual value plots showing the distribution of lanthanum.

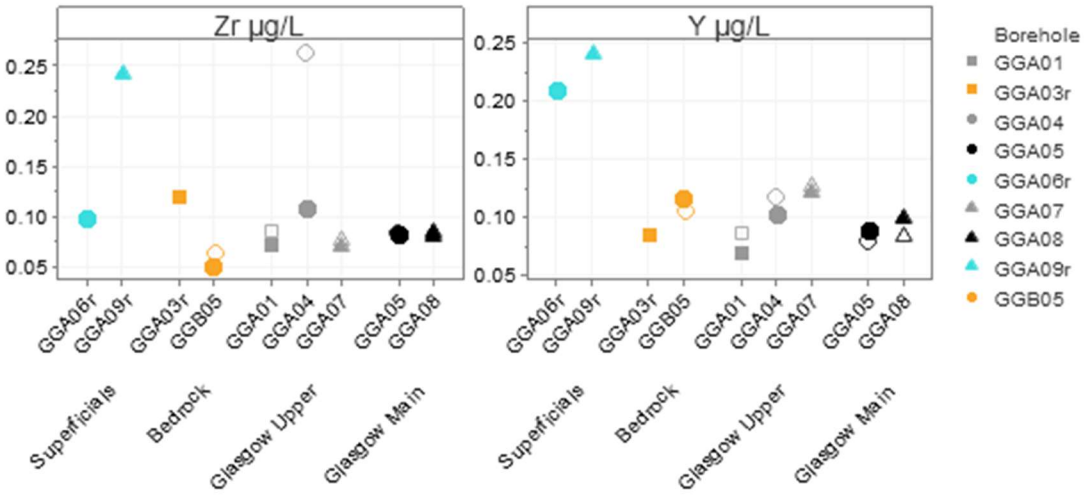


Figure 26 Individual value plots showing the distribution of zirconium and yttrium.

Appendix 4 Summary Statistics

Summary statistics of field parameter, major and minor ion, trace element and stable isotope compositions, for the test pump groundwater samples. For the purposes of calculating summary statistics, data below the LLD were set to half the LLD value.

Variable	Units	Min	Max	Mean	Median	SD	Count
pH		6.91	7.22	7.10	7.13	0.0986	15
Eh	mV	128	307	174	159	50	15
DO	mg/L	0.01	0.18	0.08	0.06	0.05	15
SEC	µs/cm	1570	1940	1730	1700	100	15
Ca	mg/L	106	165	117	108	16.7	15
Mg	mg/L	49.1	75.0	55.1	54.4	5.91	15
Na	mg/L	98.4	189	168	175	25.4	15
K	mg/L	9.03	22.9	19.1	19.2	3.14	15
Cl	mg/L	51.7	76.7	69.3	71.2	6.97	15
SO_4	mg/L	115	371	197	174	74.0	15
field HCO_3	mg/L	731	944	806	811	52.7	15
NO_3	mg/L	<0.6					15
Br	mg/L	0.329	0.563	0.494	0.499	0.061	15
F	mg/L	0.050	0.185	0.155	0.161	0.031	15
Si	mg/L	4.97	7.29	5.50	5.14	0.713	15
Ba	µg/L	26.0	130	54.2	46.2	28.9	15
Sr	µg/L	574	3690	2010	2000	652	15
Mn	µg/L	260	3100	688	411	783	15
Fe	µg/L	417	19500	4860	2550	6010	15
Li	µg/L	<8	36	27	31	10	13
B	µg/L	157	736	377	368	122	15
V	µg/L	0.05	0.42	0.14	0.12	0.10	15
Cr	µg/L	0.03	0.26	0.15	0.14	0.06	15
Co	µg/L	0.31	5.46	1.96	1.49	1.54	15
Ni	µg/L	2.41	8.10	4.68	4.13	1.83	15
Zn	µg/L	1.50	9.80	4.57	3.60	2.89	15
As	µg/L	0.09	4.34	1.42	0.94	1.43	15
Rb	µg/L	8.75	59.2	38.0	40.8	14.5	15
Y	µg/L	0.07	0.24	0.12	0.10	0.05	15
Zr	µg/L	0.05	0.26	0.11	0.08	0.06	15
Cs	µg/L	<0.05	0.3	0.18	0.17	0.07	14
La	µg/L	<0.007	0.061	0.019	0.009	0.019	9
Tl	µg/L	<0.03	0.07	0.029	0.015	0.021	5
Pb	µg/L	<0.03	0.19	0.056	0.04	0.053	10
U	µg/L	0.303	2.37	0.670	0.558	0.511	15
NH_4	mg/L	3.40	23.0	16.1	15.8	4.64	15
NPOC	mg/L	1.8	5.3	2.9	2.6	1.1	15
$\delta^{13}C$	‰	-12.8	-7.1	-10.9	-10.9	1.2	15
$\delta^{18}O$	‰	-7.51	-7.41	-7.47	-7.47	0.03	15
$\delta^{2}H$	‰	-49.0	-47.6	-48.4	-48.4	0.4	15

Glossary

BGS	British Geological Survey
$CaCO_3$	calcium carbonate (alkalinity)
CCS	isotope laboratory in-house secondary standard
CFC	chlorofluorocarbons
CH_4	methane
C_2H_6	ethane
CO_2	carbon dioxide
CRT	constant rate test
Cr(III)	trivalent chromium
Cr(VI)	hexavalent chromium
CRM	certified reference material
CUSP	Clyde Urban Super Project
$\delta^{13}C$	ratio of stable isotopes 13carbon: 12carbon
$\delta^{18}O$	ratio of stable isotopes 18oxygen: 16oxygen
$\delta^{2}H$	ratio of stable isotopes 2hydrogen: 1hydrogen
DIC	dissolved inorganic carbon
DO	dissolved oxygen
Eh	redox potential
EQS	environmental quality standard
FD	fluorescence detection
FID	flame ionisation detector
GC	gas chromatograph
GC-ECD	gas chromatography electron capture detector
GC-FID	gas chromatography flame ionisation detector
GC-MS	gas chromatography mass spectrometry
GMWL	global meteoric water line
HCl	hydrochloric acid
HCO_3	bicarbonate
HNO_3	nitric acid
HPLC	high performance liquid chromatography
IAEA	International Atomic Energy Authority
IC	ion chromatography
ICP-MS	inductively coupled plasma mass spectrometry
IRMS	isotope ratio mass spectrometry
LGC	Laboratory of the Government Chemist
LLD	lower limit of detection
LOQ	limit of quantification
MCS	isotope laboratory primary standard
NERC	Natural Environment Research Council
NIGL	NERC Isotope Geoscience Laboratory
NPOC	non-purgeable organic carbon
PAH	polycyclic aromatic hydrocarbons
QC	quality control
REE	rare earth elements
RPD	relative percent difference
RSD	relative standard deviation
SDT	step drawdown test
SEC	specific electrical conductance
SEPA	Scottish Environment Protection Agency
SHE	standard hydrogen electrode
T	temperature
TCD	thermal conductivity detector
TIC	total inorganic carbon

TPH	total petroleum hydrocarbons
UK	United Kingdom
UKAS	United Kingdom Accreditation Service
UKGEOS	United Kingdom Geoenergy Observatories project
UKRI	United Kingdom Research and Innovation
VOC	Volatile organic compounds
VPDB	Vienna Pee Dee Belemnite
VSMOW	Vienna Standard Mean Ocean Water
WFD	European Union Water Framework Directive
WNW	west-north-west

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