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UK Geoenergy Observatories Glasgow: Groundwater chemistry data collected during the borehole construction phase

UK Geoenergy Observatories Programme

Open Report OR/21/015



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UK GEOENERGY OBSERVATORIES

OPEN REPORT OR/21/015

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Two BGS scientists taking
field parameter readings
during borehole cleaning.

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UK Geoenergy Observatories Glasgow: Groundwater chemistry data collected during borehole construction

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Summary

The United Kingdom Geenergy Observatory (UKGEOS) in Glasgow comprises 11 boreholes 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 details baseline groundwater monitoring carried out during the construction phase of the Glasgow Observatory. It includes a description of the sampling methods and hydrochemical data for groundwater samples collected between December 2018 and December 2019. Eight groundwater samples and two mains water samples were analysed to determine the concentrations of selected chemical parameters at the British Geological Survey (BGS) and associated laboratories. The samples were collected to provide an initial indication of groundwater chemistry, primarily for water discharge purposes. The report accompanies the release of the construction phase groundwater hydrochemistry dataset.

Sampling locations and methodology

Groundwater samples were collected from the main Observatory borehole cluster at the Cuningar Loop, Rutherglen, South Lanarkshire from boreholes GGA02 at Site 1, GGA05 at Site 2, GGB04, GGB05 at Site 5, as well as from the seismic monitoring borehole GGC01 at Site 10 in Dalmarnock, Glasgow City. In the case of boreholes GGA02 and GGC01, they are the only groundwater chemistry samples that will be collected from these boreholes.

Water was obtained from the Glasgow Upper mine working in GGA02 and Glasgow Main mine working in GGA05 by stopping the drilling at the mine working and retrieving a sample during and after purging. Groundwater from the bedrock and the superficial deposits was drawn from borehole GGB04 and borehole GGB05, respectively.

Scope of analysis

Groundwater samples were collected for analysis of major, minor and trace elements, Cr(VI), NPOC and stable isotopes ($\delta^2\text{H}$, $\delta^{18}\text{O}$, $\delta^{13}\text{C}$). In addition, field measurements of water temperature, pH, specific electrical conductance (SEC), redox potential (Eh) and dissolved oxygen (DO) were made. Total petroleum hydrocarbons (TPH) and polycyclic aromatic hydrocarbons (PAH) were analysed in samples from GGA02 and GGA05 only.

Key Findings

Both mine waters are net-alkaline with a near-neutral pH (Glasgow Upper pH 6.92 and Glasgow Main pH 7.12); they have a high alkalinity (as field- HCO_3) (Glasgow Upper field- HCO_3 609 mg/L and Glasgow Main field- HCO_3 792 mg/L) and a high SEC of 1637 to 1723 $\mu\text{S}/\text{cm}$.

Similarly, the bedrock and the superficial deposits waters have pH values of ~7.5 and alkalinity as field- HCO_3 between 415 mg/L and 462 mg/L. The SEC is also high 1078–1183 $\mu\text{S}/\text{cm}$.

All the waters belong to the bicarbonate (HCO_3) type, with sodium (Na) as the dominant cation in the superficial deposits and bedrock groundwaters (Na- HCO_3 waters), and Na, calcium (Ca) and, to a lesser extent, magnesium (Mg) in the two mine waters (Na-Ca-(Mg)- HCO_3 water type).

Water from all four lithologies ranges in sulphate (SO_4) concentration between 165 and 302 mg/L. The chloride (Cl) range is 51–82 mg/L, with the highest value in the Glasgow Main mine

working groundwater. Iron (Fe) concentrations range between 1.8 to 2.6 mg/L in the mine water and bedrock; a much lower concentration of 0.007 mg/L is measured in the superficial deposits groundwater. Chromium(VI), a known industrial contaminant in the area, was not detected above the lower limit of detection (LLD) in any samples.

The stable isotope $\delta^2\text{H}$, $\delta^{18}\text{O}$ values plot broadly on the global meteoric water line with no evidence of evaporation prior to recharge. The O-isotope values ($\delta^{18}\text{O}$ -7.4 ‰ and -7.1 ‰) are all within the range of groundwater samples reported previously from Carboniferous sedimentary aquifers across the Midland Valley of Scotland. The mine waters have heavier $\delta^{13}\text{C}$ (-9.9 and -10.8 ‰) than the bedrock and superficial deposits (-15.6 and -12.1 ‰). All lithologies' groundwaters fall on the middle to upper range of the $\delta^{13}\text{C}$ values from -22 ‰ to -10 ‰ of groundwater samples from other studies of the Coal Measures Group across the Midland Valley of Scotland.

All samples are saturated with respect to calcite, dolomite, siderite, rhodochrosite, amorphous ferric hydroxide, gibbsite, and barite, and remain undersaturated with respect to gypsum, halite and jarosite.

Water was also obtained during the installation of the GGC01 seismic monitoring borehole. However, given the sampling method (a bailer lowered to only a few meters from the top of the borehole) and evidence of dilution during flushing and residual contamination from the tracer/additive and drilling fluid, the chemical analyses of the groundwater samples from this borehole are not to be considered representative of the unmined Coal Measures aquifer(s) intercepting the borehole. Very high concentrations of boron (B) and dissolved organic carbon (NPOC) were found, which decreased between the two sampling dates, showing an increase in groundwater flowing into the borehole after drilling and flushing. The water was alkaline, and with a SEC of 310–650 $\mu\text{S}/\text{cm}$. Sodium was the most enriched cation, with HCO_3 and Cl the most enriched anions. Chromium(VI) was not detected above the LLD in either sample. The $\delta^2\text{H}$, $\delta^{18}\text{O}$ signature of the groundwater was similar to the samples taken in the four Cuningar Loop boreholes while the $\delta^{13}\text{C}$ isotope signature was lighter.

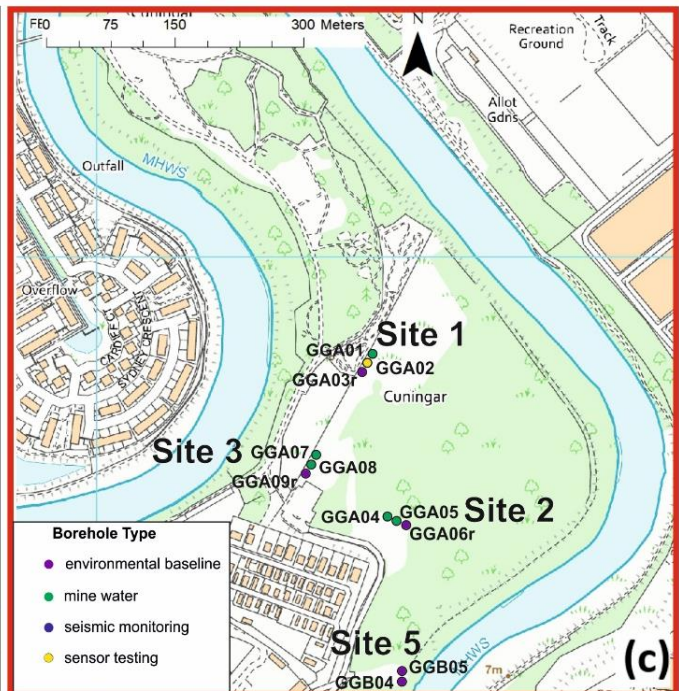
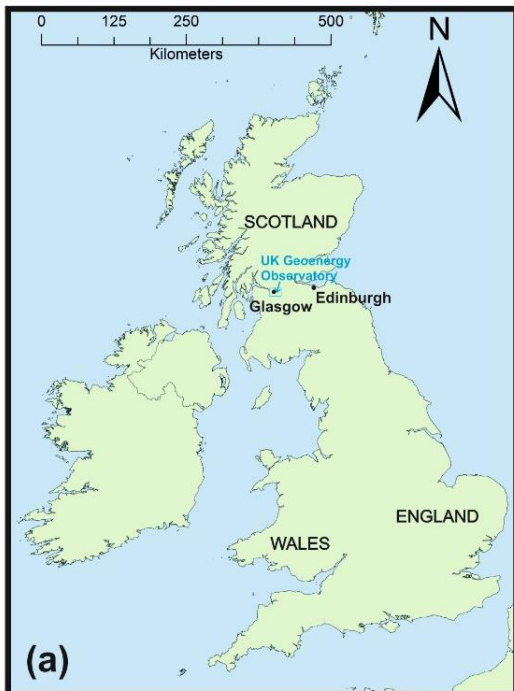
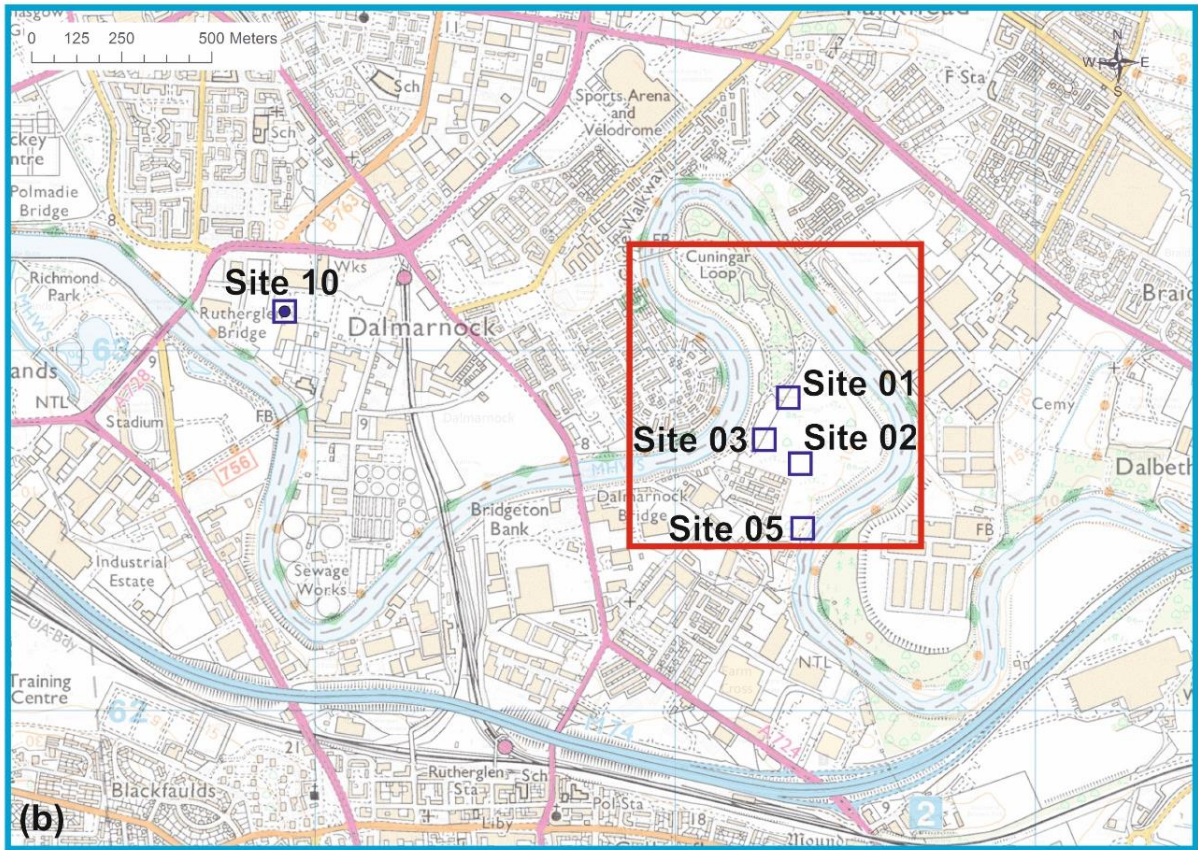
1 Introduction

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 Geenergy Observatories (UKGEOS) (Figure 1a). The aim of the Glasgow Observatory is to de-risk technical aspects of extracting/storing shallow mine water heat energy in an urbanised former coal mine setting (Monaghan et al. 2017, 2019).

The initial construction phase of the UKGEOS Glasgow project entailed installing a network of boreholes across five sites in a former coal mining area at Dalmarnock 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). Boreholes were 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. Figure 1c shows the details of the 11 boreholes located at the Cuningar Loop.

This report details groundwater sampling carried out during the construction phase of the Glasgow Observatory. It includes a description of the sampling methods and hydrochemical data for groundwater samples collected between December 2018 and December 2019. Eight groundwater samples were analysed to determine the concentrations of selected chemical parameters at the BGS and associated laboratories. The samples were obtained during the construction phase to give an initial indication of groundwater chemistry, primarily for water discharge purposes.



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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.

1.1 CITATION GUIDANCE

This report accompanies the release of the construction phase hydrochemistry dataset.

Any use of the data should be cited to:
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1.2 SUMMARY OF GLASGOW OBSERVATORY BOREHOLES

The Glasgow Observatory includes 11 boreholes at the Cuningar Loop, South Lanarkshire and one seismic observation borehole in Dalmarnock in east Glasgow (Figure 1, Table 1).

The Cuningar Loop boreholes comprise:

- Five mine water boreholes drilled into flooded, abandoned mine workings and completed with a screen and pre-formed gravel filter pack across one mine working;
- Five environmental baseline monitoring boreholes completed with a screen and gravel filter pack in bedrock above the mine workings, or in superficial deposits overlying the bedrock;
- One sensor testing borehole

The screened target zone in each borehole is between 1.8 and 3.6 m long with the remaining sections of the installation cased off to prevent groundwater inflow to the borehole from any other zone. A gravel pack is installed to 1 m above the screened section and sealed with bentonite. Full details are available in Barron et al., (2020 a,b), Elsome et al. (2020), Kearsey et al. (2019 a), Shorter et al. (2020 a,b), Monaghan et al. (2020 a,b,c), Starcher et al. (2020 a,b), Walker-Verkuil et al. (2020 a,b) and associated data packs available from ukgeos.ac.uk/data/downloads. Table 1 provides a summary of the 12 boreholes that comprise the Glasgow Observatory. Not all boreholes were sampled during the construction phase.

in Section 1.3 below details which boreholes were sampled during the construction phase and from which geological unit the sample was taken.

Table 1 Description of the Glasgow Observatory boreholes

Site	Borehole	Borehole type	Target screened unit*
Site 1	GGA01	Mine water	Glasgow Upper mine working
Site 1	GGA02	Sensor testing	Used for sensor testing, no screened unit.
Site 1	GGA03r	Environmental	Bedrock
Site 2	GGA04	Mine water	Glasgow Upper mine working
Site 2	GGA05	Mine water	Glasgow Main mine working
Site 2	GGA06r	Environmental	Superficial deposits
Site 3	GGA07	Mine water	Glasgow Upper mine working
Site 3	GGA08	Mine water	Glasgow Main mine working
Site 3	GGA09r	Environmental	Superficial deposits
Site 5	GGB04	Environmental	Superficial deposits
Site 5	GGB05	Environmental	Bedrock
Site 10	GGC01	Seismic monitoring	Five seismometers installed, no screened unit.

*The screened section in the completed boreholes extends above and below the target unit.

1.3 RATIONALE FOR GROUNDWATER SAMPLING DURING THE BOREHOLE CONSTRUCTION PHASE OF THE PROJECT

The Glasgow Observatory boreholes sampled during the construction phase were: GGA02 from Site 1, GGA05 from Site 2, GGB04, GGB05, both from Site 5 and GGC01 from Site 10. Samples were collected to gain an initial understanding of groundwater quality from the two mine workings, the overlying bedrock and superficial deposits for water discharge purposes. Therefore, not all boreholes were required to be sampled. In the case of GGC01 (fully cased after drilling) and GGA02 (completed as a sensor testing borehole) these samples represent the only groundwater that will be collected.

The data obtained provide an indication of groundwater chemistry during the construction phase of the project, in the course of either the drilling, installation, cleaning or post-cleaning of the boreholes, but before test pumping.

A summary of the groundwater samples collected, sampling procedures and parameters analysed is given in

. During installation of the GGC01 borehole, additional samples of mains water from a tap in the site office were obtained, as this was used to flush the borehole prior to sampling. The mains water analysis parameters are summarised in Table 4 (Appendix A). Groundwater sample splits, preservation techniques, lab ID and analytical techniques used are detailed in Table 5 (Appendix B).

The groundwater collection methods used during the construction phase, as detailed in Sections 2.1.1 to 2.1.3, differ from those established for long-term future groundwater monitoring at the Glasgow Observatory. Samples from GGA02, GGA05 and GGC01 were taken before the boreholes were installed with any casing or infrastructure, except for casing in the superficial deposits, meaning the borehole below the superficial casing was open. Although some purging, flushing (GGC01 only) or cleaning (the latter only for GGB04 and GGB05), of the borehole was done before the groundwater samples were collected, the samples may contain an unknown contribution of water and drilling flush, used to advance drilling. A description of the difference between borehole purging, flushing and cleaning as used in this report is provided in Table 3, Section 2.1, and further information on water and drilling flush is provided for each borehole in Sections 2.1.1, 2.1.2 and 2.1.3. As such, inferences on local hydrochemistry from these samples should be treated with caution. Once the water was collected from the boreholes (by bailers, pumps, etc.), the subsequent phases of water sampling and sample handling remained the same as for the Glasgow Observatory groundwater and surface water monitoring programmes (Fordyce et al. 2021).

Table 2 Summary of borehole construction phase groundwater samples.

Sample number	Borehole	Date sampled	Water type	Sample source	Borehole depth at time of sampling (m)*	Construction phase	Sampling method/depth	Parameter types available
BGS-GGA02-05	GGA02	25/07/2019	Groundwater from Glasgow Upper mine working	Settling tank	49	Upon drilling into the Glasgow Upper mine working, during purging.	Groundwater was purged by airlifting it from the borehole; sampled from the settling tank that the inlet pipe discharged into.	Field parameters; inorganic chemistry; stable isotopes; TPH; PAH.
BGS-GGA02-06	GGA02	26/07/2019	Groundwater from Glasgow Upper mine working	Borehole	49	Upon drilling into the Glasgow Upper mine working, after purging approx. 20 m ³ groundwater from borehole.	A Hydrasleeve™ discrete bailer was lowered to the depth of the mine working 47.8 - 48.95 m below drilling platform.	Field parameters; inorganic chemistry; stable isotopes; TPH; PAH.
BGS-GGA05-21	GGA05	09/10/2019	Groundwater from Glasgow Main mine working	Settling tank	88.5	Upon drilling into the Glasgow Main mine working, during purging.	Groundwater was purged using the drill rig from the borehole; sampled from settling tank that inlet pipe discharged into.	Field parameters; inorganic chemistry; stable isotopes; TPH; PAH.
BGS-GGA05-22	GGA05	09/10/2019	Groundwater from Glasgow Main mine working	Borehole	88.5	Upon drilling into the Glasgow Main mine working, after purging of approx. 38 m ³ water from borehole.	A Hydrasleeve™ discrete bailer was lowered to the depth of the mine working 84.66 - 85.36 m below drilling platform.	Field parameters; inorganic chemistry; stable isotopes; TPH; PAH.

Sample number	Borehole	Date sampled	Water type	Sample source	Borehole depth at time of sampling (m)*	Construction phase	Sampling method/depth	Parameter types available
GF_GW1219-GGB04	GGB04	11/12/2019	Groundwater from superficial deposits	Borehole	13.4	After drilling, installation and cleaning of borehole; before test pumping.	Sampling pump at 11 m depth below top of borehole casing; borehole pumped at 0.02 L/s for 17 mins before sampling.	Field parameters; inorganic chemistry; stable isotopes.
GF_GW1219-GGB05	GGB05	11/12/2019	Groundwater bedrock	Borehole	43	After drilling, installation and cleaning of borehole; before test pumping.	Sampling pump at 8 m depth below top of borehole casing; borehole pumped at 0.09 L/s for 24 mins before sampling.	Field parameters; inorganic chemistry; stable isotopes.
GGC010_0150	GGC01	17/12/2018	Groundwater from borehole of unmined Coal Measures	Borehole	199	Five days after the completion of drilling and 4 days after borehole flushing with mains water.	Hand bailer was used to retrieve groundwater sample from the top of the borehole.	Field parameters; inorganic chemistry; stable isotopes.
GGC010_0155	GGC01	07/01/2019	Groundwater from borehole of unmined Coal Measures	Borehole	199	25 days after the completion of drilling and 21 days after borehole flushing with mains water.	Hand bailer was used to retrieve groundwater sample from the top of the borehole.	Field parameters; inorganic chemistry; stable isotopes.

*All depths are from m below the drilling platform

TPH: total petroleum hydrocarbons. PAH: polycyclic aromatic hydrocarbons.

A full list of chemical parameters determined in each sample type, and summary of analytical laboratories and techniques, is given in Appendix B.

2 Methods

2.1 BOREHOLE SAMPLING

Sections 2.1.1 to 2.1.3 below describe the sampling methods. The boreholes have been grouped together according to the sampling method used to retrieve the groundwater samples i.e. the same method was used for sample retrieval at GGA02 and GGA05 etc.

Before retrieving groundwater samples from the boreholes, a mixture of purging, flushing or cleaning was carried out. Table 3 details these three different activities and which boreholes they were used in.

Table 3 Borehole purging, flushing and cleaning descriptions

Activity	Borehole(s) in which activity was used	Description
Borehole purging	GGA02 and GGA05	<p>Upon entering the mine working drilling ceased. Water was then abstracted from the borehole in order to purge it of water or fluids used in the drilling process.</p> <p>Purging was conducted by airlift using the drill rig.</p> <p>Borehole purging was carried out to ensure that the sample collected was as true a representation of the mine working as possible.</p>
Borehole cleaning	GGB04 and GGB05	<p>Once all drilling was completed the borehole was cleaned. This involved abstracting water from the borehole until water quality parameter readings steadied or for a maximum of 2 hours. In the case of GGB04 it was until the borehole ran dry.</p>
Borehole flushing	GGC01	<p>Once all drilling was completed the borehole was flushed with mains water to help remove all drilling fluids used.</p>

2.1.1 GGA02 and GGA05

Groundwater sampling was carried out on 25 and 26/07/19 for the GGA02 and on 9/10/19 for the GGA05. The purpose of the samples taken from GGA02 and GGA05 was to estimate mine water chemical quality for water disposal purposes. Therefore, upon entering the Glasgow Upper mine working in GGA02 and the Glasgow Main mine working in GGA05, the drilling was stopped and the boreholes cleaned by purging groundwater from each borehole using the method outlined in Table 3. Around 20 m³ was airlifted from GGA02 and around 38 m³ was purged from GGA05. During purging, a first sample was taken from the settling tank. Once purging was complete, a second sample was taken using a Hydrasleeve™ discrete bailer from the depth of each mine working. The procedures for each sample type are outlined below.

As stated in Section 1.3, water/ drilling flush was used to assist in advancing the boreholes. Where water flush only is stated, this is a mixture of mains water and re-circulated groundwater from the borehole. The use of drilling flush included the addition of a bentonite mud during drilling to the water only flush. In the case of these two boreholes:

- GGA02 was drilled with water flush only;
- GGA05 was drilled with drilling flush through the superficial deposits after which the superficial deposits were cased off before drilling advanced into bedrock, and;
- Water flush only was used in drilling the bedrock section of GGA05.

Despite only water flush being used in the bedrock sections of both boreholes, it is unknown if the bentonite mud used in the drilling flush of GGA05 during the superficial deposits drilling will have impacted the samples taken from this borehole.

2.1.1.1 SAMPLING FROM THE SETTLING TANK DURING PURGING

Physico-chemical parameter measurements were made in a plastic beaker filled with water from the settling tank just below the discharge pipe (See Section 2.2.1). Approximately half way through the purging, the sample water was collected into beakers ready for collection (See Section 2.3).

2.1.1.2 SAMPLING FROM THE MINE WORKING AFTER PURGING

A 1 L HydraSleeve™ discrete bailer, with a weight attached, was tied to a length of rope equal to the drilled depth of the mine working. The HydraSleeve™ was lowered to the depth of the mine working and was then retrieved by pulling it back out of the borehole. It has a one-way valve meaning that, once it was filled with sample water at the depth of the mine working, no further sample water could enter it. At the surface, water from the HydraSleeve™ was discharged into beakers ready for sample collection and into a plastic beaker for physico-chemical parameter determination using portable probes. For the latter, the HydraSleeve™ sampling was repeated to refresh the water in the beaker every five minutes.

2.1.2 GGB04 and GGB05

Sampling of GGB04 and GGB05 was carried out on 11/12/19 using a submersible WaSP P5 pump. The submersible pump was powered by a 12 V battery and the flow controlled by a low flow controller at surface to allow regulation of the discharge rates.

Before sampling, the water level inside the borehole was measured using a dip meter. The submersible pump was lowered into the borehole to a depth that ensured it was completely submerged. The water discharge tubing from the submersible pump was attached to the end of silicon Y-tubing, which connected the pump to a flow-through cell. Four of the physico-chemical parameter probes (pH, specific electrical conductance (SEC), redox potential (Eh) and dissolved oxygen (DO)) were securely screwed into the lid of the flow-through cell. The other outlet end of Y-tubing was placed in a beaker of sample water with the temperature probe.

Once three sets of physico-chemical parameter readings were taken, at least five minutes apart, the flow-through cell was disconnected and sampling was carried out. For GGB04 the third reading was taken less than five minutes after the second, due to dropping water level in the borehole resulting in the sample needing to be taken quickly before the borehole ran dry.

Sample water was used to rinse and fill sample collection beakers via the Y-tubing.

As stated in Section 1.3 , water/ drilling flush was used to assist in advancing the boreholes. Where water flush only is stated, this is a mixture of mains water and re-circulated groundwater from the borehole. The use of drilling flush included the addition of a bentonite mud to the water flush during drilling. In the case of these two boreholes:

- GGB04 was drilled using drilling flush;
- GGB05 was drilled using a drilling flush in superficial deposits only. The superficial deposits were then cased off to avoid contamination with the bedrock, and;
- Water flush only was used to drill the bedrock section of GGB05.

Both GGB04 and GGB05 were cleaned before this sampling took place. For GGB04 cleaning resulted in the borehole running dry when pumped. In GGB05 borehole cleaning was carried out as stated in Table 3.

2.1.3 GGC01

Two groundwater samples were taken from the top of the 199 m borehole, using a hand bailer, after completion of drilling on 12/12/18 and borehole flushing, with 12,000 litres of mains water,

on 13/12/18. The first sample was taken on 17/12/18 after the casing had been removed up to the superficial deposits and the borehole had been flushed with mains water and left to settle for four days. This sample was taken prior to the geophysical (wireline) logging undertaken on 17/12/18. The second sample was taken on 07/01/19 after the unmined Coal Measures bedrock section of the borehole had been left open and uncased for three weeks after borehole flushing. After this sample was taken the borehole was fully cased, the annulus grouted and seismometers were installed.

The samples were obtained using a disposable plastic hand bailer that was 39 mm outside diameter and 91.5 mm in length, with a volume of 1025 mL. Before sampling, the water level inside the borehole was measured using a dip meter. The hand bailer was then attached to a piece of rope and slowly lowered into the borehole until it was completely submerged. Once submerged, the hand bailer was then slowly retrieved from the borehole, ensuring that it was full of sample water.

Water from the hand bailer was discharged into beakers for sample collection and for physico-chemical parameter field measurements (See Sections 2.2 and 2.3).

Samples of mains water (used for borehole flushing) were also taken for comparison. The samples were taken in the same way, the only difference was that the beakers of sample water were filled directly from the tap.

Mains water and a polymer drilling additive were used as drilling fluids to help advance GGC01 (Kearsey et al. 2019). During drilling, an AFN-09 RADGLO UV Blue tracer was added daily to the settling tanks containing the re-circulating water used to drill the borehole. The tracer was added to allow the extent of drilling fluid ingress into core material to be assessed, for the purposes of future geomicrobiology studies on preserved core samples. More details of both the tracer and additive are in Kearsey et al. (2019) and the drilling records in the accompanying data release.

2.2 FIELD PARAMETER MEASUREMENTS AND FIELD OBSERVATIONS

At each borehole, measurements of key physico-chemical parameters were obtained in the field. Outlined below is a brief description of how field measurements and observations were carried out. For further details regarding methods in Sections 2.2 to 2.4 refer to Fordyce et al. (2021).

2.2.1 Field parameter measurements and known limitations

Specific electrical conductance, pH, DO, Eh and temperature were measured on site, using portable meters either in a beaker or a flow-through cell. When a beaker was used it was rinsed with sample water three times before the portable field parameter probes were placed into the beaker. The water in the beaker was refreshed approximately every five minutes, whilst measurements were taking place.

Parameters were monitored at least three times over an interval of five minutes (except where stated above). Post sample collection, redox measurements were translated to the standard hydrogen electrode (SHE) using temperature-dependent conversion tables appropriate to the probe.

The method by which temperature was recorded in the samples from the Glasgow Upper mine workings (GGA02) is considered to be inaccurate, as they were taken from a plastic beaker of sample water that was placed inside a metal shipping container during warm weather in July 2019. Therefore, it is likely that the recorded temperatures (17.7–23.3 °C) were affected by this environment and are not a true reflection of the temperature in the Glasgow Upper mine working at this time. Temperature measurements of groundwater without an in-line set-up are inherently difficult, however at the time of sampling no other option was available.

The use of bailed samplers and open beakers for the field measurements at GGA02, GGA05 and GGC01 exposed the samples to the atmosphere making the DO and redox potential measurements less reliable or representative of the in-situ groundwater values for these samples. As stated above for temperature, measurements of DO and redox potential without an in-line set-up are difficult, however at the time of sampling no other option was available. Therefore, the

results for temperature at GGA02 and for DO and Eh at GGA02, GGA05 and GGC01 are not presented in this report or accompanying dataset.

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. Post sample collection, the bicarbonate (HCO_3) concentration in the water was calculated using the field alkalinity values.

2.2.2 Field observations

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

2.3 SAMPLE COLLECTION AND ANALYSES

For each borehole, groundwater was retrieved and used to rinse a plastic beaker and stainless-steel beaker (for non-purgeable organic carbon (NPOC) sampling) three times before filling the beakers ready for sample collection according to the methods outlined below.

Eight sample splits were collected at the boreholes, according to the methods outlined in following sections:

- Inorganic cations
- Inorganic anions
- Hexavalent chromium (CrVI)
- Dissolved organic carbon (DOC as non-purgeable organic carbon (NPOC))/total inorganic carbon (TIC)
- Stable oxygen and deuterium isotopes ($\delta^2\text{H}$, $\delta^{18}\text{O}$)
- Stable carbon isotopes ($\delta^{13}\text{C}$) of dissolved inorganic carbon (DIC)
- Total petroleum hydrocarbons C8 – C40 (TPH) [only for GGA02 and GGA05]
- Polycyclic aromatic hydrocarbons (PAH) [only for GGA02 and GGA05]

2.3.1 Filtered waters inorganic cation, anion and Cr(VI)

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).

2.3.2 Filtered water NPOC/TIC

A sample for dissolved organic carbon (DOC, as non-purgeable organic carbon (NPOC)) and total inorganic carbon (TIC) 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.

2.3.3 Unfiltered water for stable isotopes

Unfiltered water samples for determination of stable isotopes of deuterium ($\delta^2\text{H}$), oxygen ($\delta^{18}\text{O}$) and carbon ($\delta^{13}\text{C}$) of 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.

2.3.4 Unfiltered water samples for TPH and PAH

A clear glass bottle for total petroleum hydrocarbons (TPH) and amber glass bottle for polycyclic aromatic hydrocarbons (PAH) were filled with unfiltered sample water directly from the Hydrasleeve™, plastic beakers (there was no access to a metal beaker) or settling tank.

2.4 SAMPLE TRANSPORT AND ANALYSIS

All samples were analysed at the BGS laboratories in Keyworth, except the TPH and PAH, which were analysed by the Scottish Water laboratory in Edinburgh.

All water 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 are summarised in Appendix C and described in full in Fordyce et al. (2021).

3 Data Presentation

The Glasgow Observatory groundwater chemistry dataset obtained from selected boreholes during borehole construction is presented in Excel® table format:

Filename: UKGEOSGlasgow_ConstructionPhaseGWChemData.xlsx

It contains the results of inorganic and organic chemical analyses for each of the eight groundwater and two tap water samples collected during borehole construction. 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 parts per million (mg/L) for the major and minor cations and anions, followed by trace element data in parts per billion (µg/L). Stable isotope data are then reported in ‰ Vienna Pee Dee Belemnite (VPDB) for $\delta^{13}\text{C}$ and ‰ Vienna Standard Mean Ocean Water (VSMOW2) for $\delta^{18}\text{O}$ and $\delta^2\text{H}$. Total inorganic carbon data are reported in mg/L following the isotope data. Finally, data for organic parameters are reported in mg/L for NPOC and TPH and µg/L for PAHs.

In this report, the field measurements and chemical analysis results of the groundwater samples collected from boreholes GGC01, GGA02, GGA05, GGB04 and GGB05 are presented. On the graphs, the discrete bailer groundwater samples collected for GGA02 and GGA05 are presented as these are considered more representative of the target mine workings than the settling tank samples. Both datasets are reported in UKGEOSGlasgow_ConstructionPhaseGWChemData.xlsx.

The graphs presented in this report were generated in Excel® and Geochemist's Workbench® software packages. Mineral saturation indices were determined using the PHREEQC modelling package (Parkhurst and Appelo 1999).

4 Results

Presented in Section 4.1 are the results from groundwater samples retrieved from the Cuningar Loop boreholes (GGA02, GGA05, GGB04 and GGB05). Section 4.2 details the results of groundwater samples retrieved from GGC01 at the Dalmarnock site.

4.1 BOREHOLES GGA02, GGA05, GGB04 AND GGB05

The samples from these boreholes are classified based on the stratigraphic unit the water is drawn from, and referred to as follows:

- Sample ID BGS-GGA02-06 / Borehole GGA02: Glasgow Upper mine working, 'Glasgow Upper' on graphs
- Sample ID BGS-GGA05-22 / Borehole GGA05: Glasgow Main mine working, 'Glasgow Main' on graphs
- Sample ID GF_GW1219-GGB04 / Borehole GGB04: superficial deposits, 'superficial' on graphs
- Sample ID GF_GW1219-GGB05 / Borehole GGB05: bedrock.

4.1.1 Temperature and specific electrical conductance

Groundwater temperature measurement for the Glasgow Upper mine workings (borehole GGA02) is excluded from the dataset (Section 2.2.1). The groundwater temperature from the Glasgow Main mine working was 11.9 °C. A temperature of 11.4 °C was measured in the sample from the bedrock and of 9.7 °C in the sample from the superficial deposits. Although it is noted that the Glasgow Main mine water is slightly warmer than the superficial deposits water, direct comparison is not possible as each of these samples was taken at different times of the year (i.e. superficial deposits water is the coolest but the samples were taken in December).

Both mine water samples had higher SEC than groundwater from the bedrock and superficial deposits (Figure 2), with Glasgow Upper SEC 1637 $\mu\text{S}/\text{cm}$, Glasgow Main SEC 1723 $\mu\text{S}/\text{cm}$, the bedrock SEC 1183 $\mu\text{S}/\text{cm}$ and the superficial deposits SEC 1078 $\mu\text{S}/\text{cm}$.

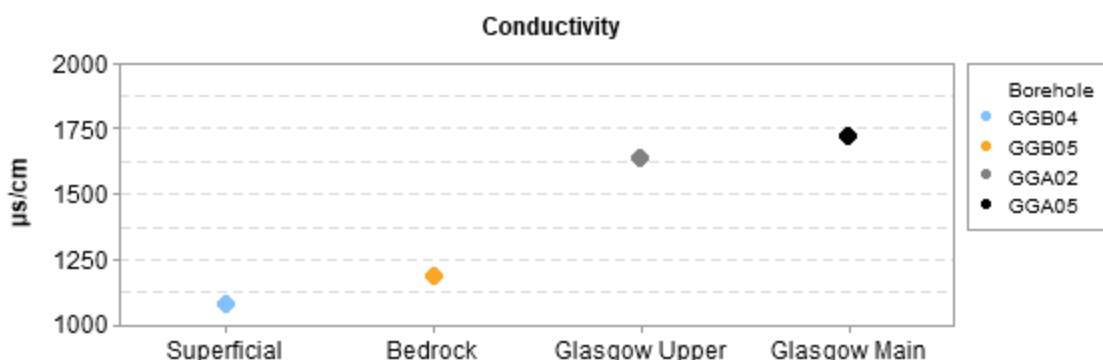


Figure 2 SEC distribution in GGA02, GGA05, GGB04 and GGB05 groundwater samples.

4.1.2 Dissolved oxygen and redox potential

Measurements of redox potential and DO are the most sensitive to sample exposure to the atmosphere during measurement. As described above (Section 2.2.1) both DO and Eh measurements of the Glasgow Upper and Glasgow Main groundwater are excluded from the dataset. The groundwater in the bedrock was almost anoxic (DO 0.3 mg/L) and with a moderately

low Eh of +150 mV. The groundwater sample from the superficial deposits had a DO of 1.1 mg/L and more reducing redox conditions (Eh -20 mV).

4.1.3 pH and alkalinity

Both the mine waters had near-neutral pH values (Glasgow Upper pH 6.92 and Glasgow Main pH 7.12) and high alkalinity (Glasgow Upper field-HCO₃ 609 mg/L and Glasgow Main field-HCO₃ 792 mg/L) (Figure 3). The bedrock and the superficial deposits pH values were higher and very similar (7.6 and 7.55, respectively), while the field alkalinity was lower than in the mine waters (bedrock field-HCO₃ 415 mg/L; superficial deposits field-HCO₃ 462 mg/L).

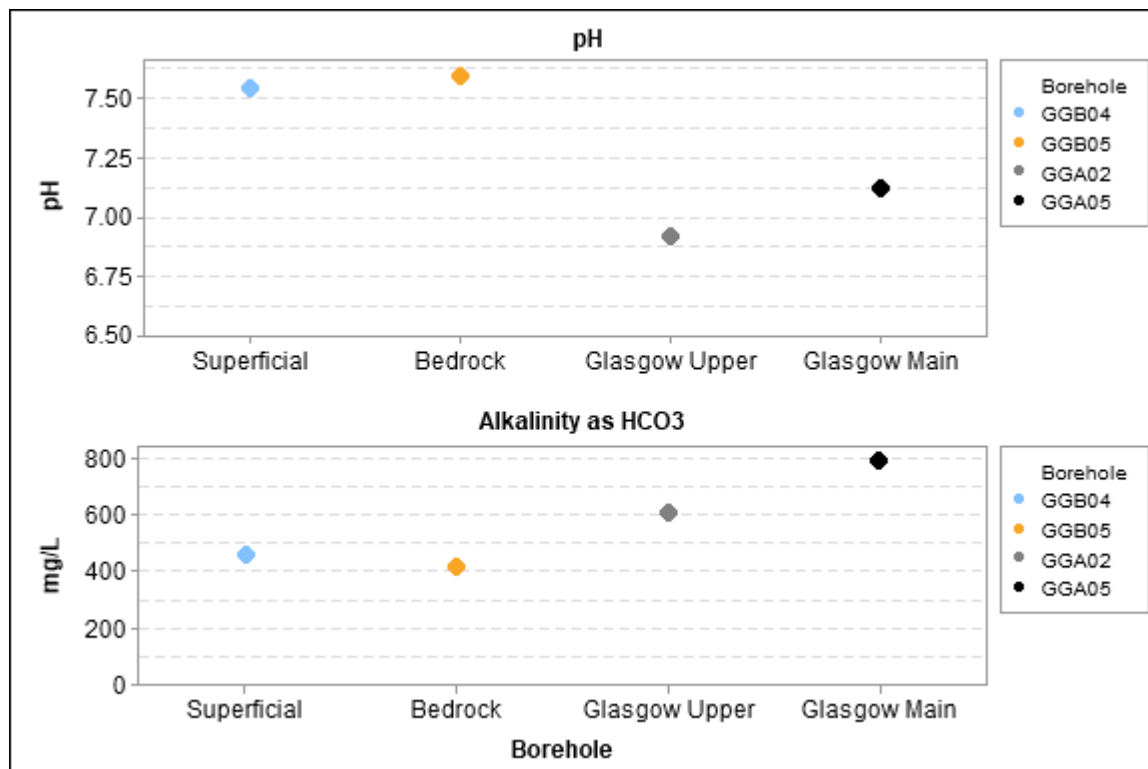


Figure 3 pH and field alkalinity distribution in GGA02, GGA05, GGB04 and GGB05 groundwater samples.

4.1.4 Non-purgeable organic carbon (NPOC)

Figure 4 shows that the amount of NPOC measured in the groundwater samples, ranged from 2 to 11.2 mg/L, with the highest values from the bedrock.

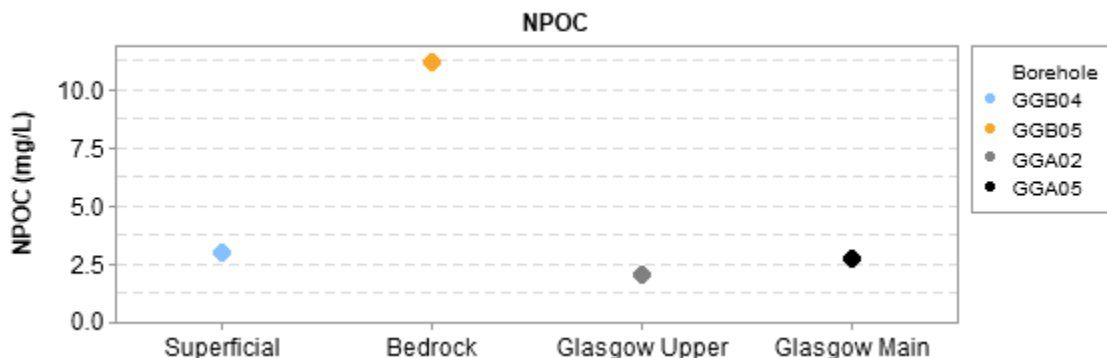


Figure 4 NPOC distribution in GGA02, GGA05, GGB04 and GGB05 groundwater samples.

4.1.5 Major ions

The major cation and anion concentrations in the four groundwater samples are illustrated in Figure 5 and Figure 6, and in the Piper Plot in Figure 7.

All the waters belong to the bicarbonate (HCO_3) type (Figure 7). Sodium (Na) is the dominant cation in the superficial deposits and bedrock groundwaters (Na– HCO_3 waters), while the two mine waters are of a sodium (Na), calcium (Ca), and to a lesser extent, magnesium (Mg) bicarbonate type (Na-Ca-(Mg)– HCO_3 waters). Sodium ranged between 138 mg/L to 193 mg/L. The highest concentrations of Na were measured in the Glasgow Main mine water and bedrock groundwater. Calcium and Mg concentrations were relatively higher in both mine waters (Glasgow Upper Ca 126 mg/L, Mg 60 mg/L; Glasgow Main Ca 107 mg/L, Mg 57 mg/L) compared to the bedrock (Ca 62 mg/L, Mg 18 mg/L), and superficial deposits (Ca 57 mg/L, Mg 30 mg/L). These trends are similar to the alkalinity distribution pattern.

Potassium concentration was distinctively higher in the groundwater sample from the superficial deposits (35 mg/L) than in the other waters (range 9.6–20 mg/L).

Sulphate (SO_4) concentrations ranged between 165 mg/L and 302 mg/L, with the highest value in the Glasgow Upper mine water (302 mg/L), and the lowest values (165 mg/L) for both the Glasgow Main mine water and bedrock. Groundwater from the superficial deposits had an intermediate value of 221 mg/L.

Chloride (Cl) concentrations ranged between 51 mg/L and 82 mg/L, with the Glasgow Main higher than the other samples. Nitrate (NO₃) concentrations were below the LLD.

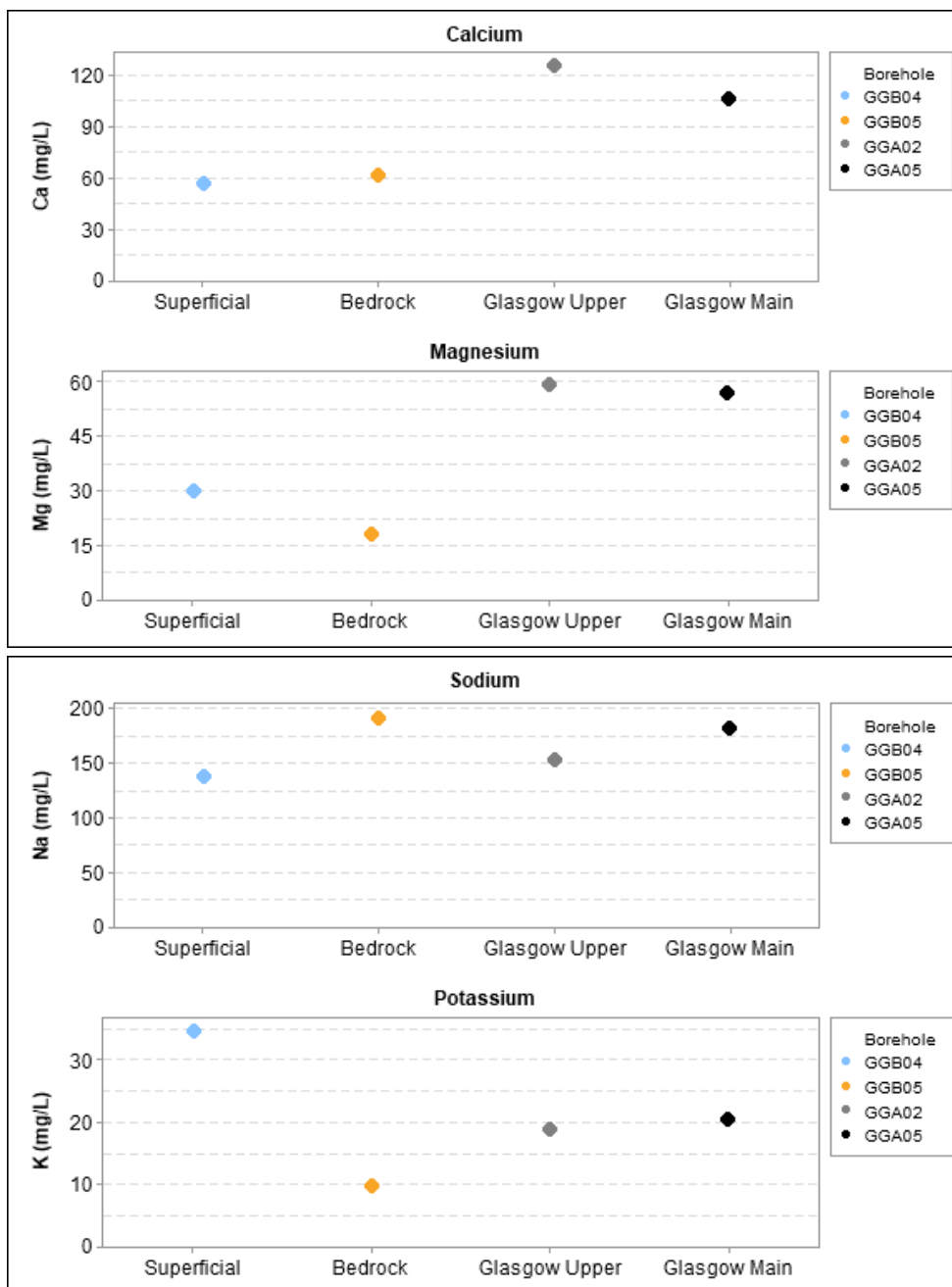


Figure 5 Calcium, Mg, Na and K distribution in GGA02, GGA05, GGB04 and GGB05 groundwater samples.

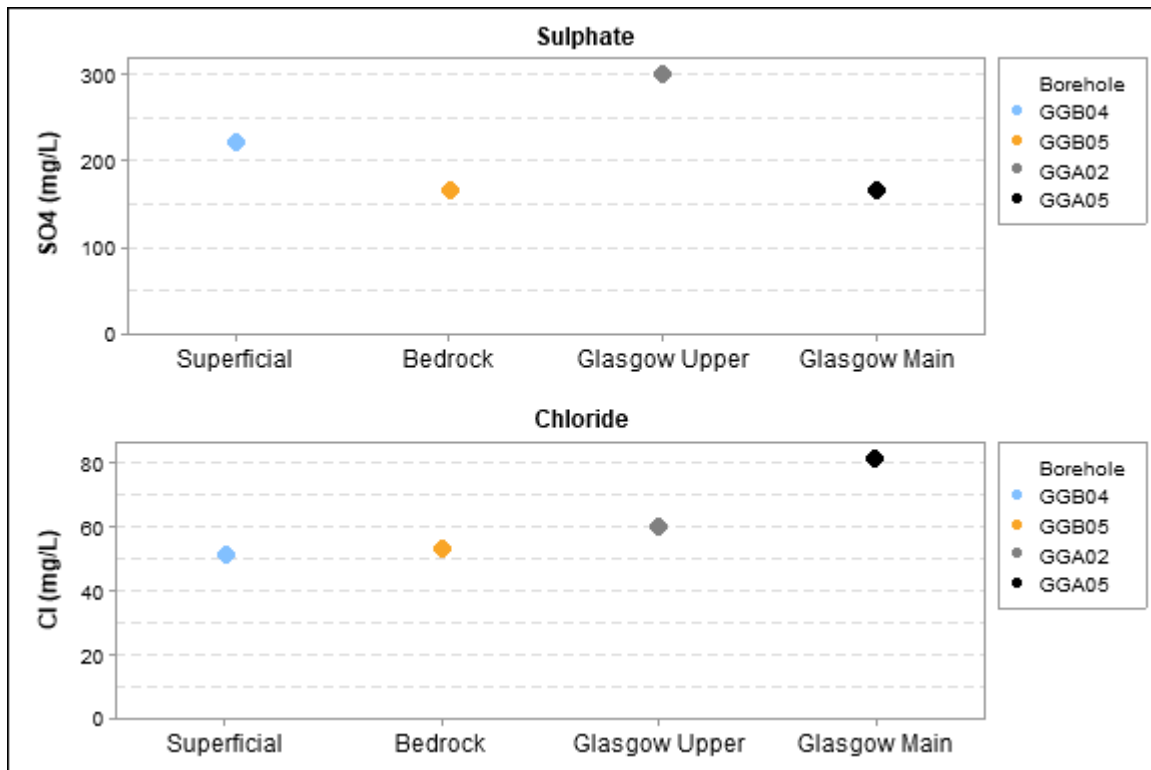


Figure 6 Sulphate and Cl distribution in GGA02, GGA05, GGB04 and GGB05 groundwater samples.

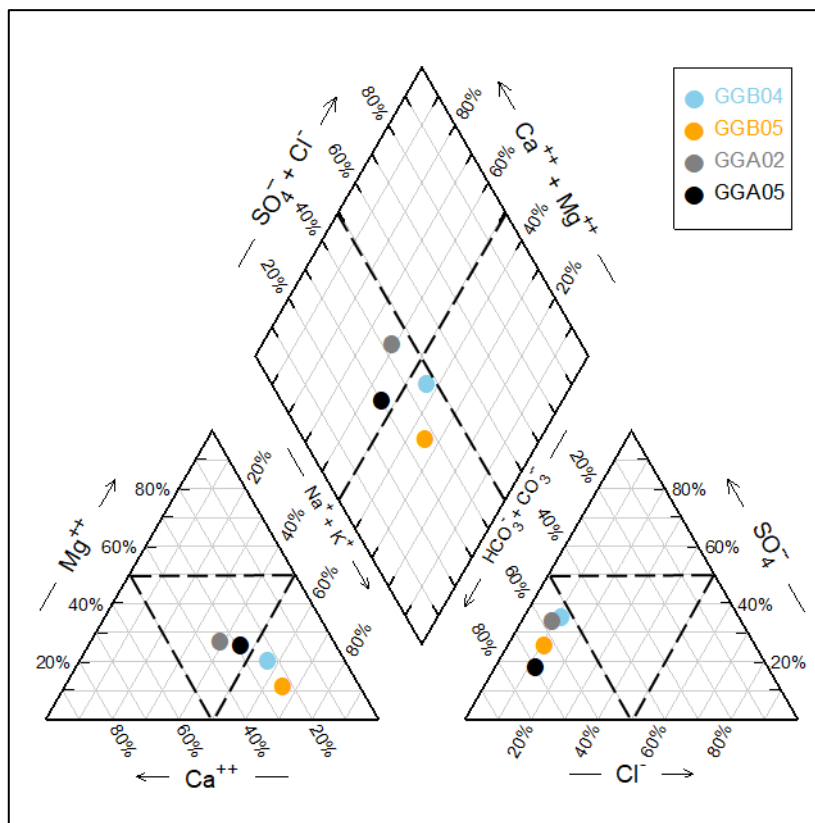


Figure 7 Trilinear Piper plot of the relative concentrations of major cations and anions in GGA02, GGA05, GGB04 and GGB05 groundwaters.

4.1.6 Iron and manganese

Iron (Fe) concentrations were high ($>1000 \mu\text{g/L}$) in the mine water samples and the groundwater from the bedrock (Glasgow Upper Fe $2619 \mu\text{g/L}$; Glasgow Main Fe $1775 \mu\text{g/L}$; bedrock Fe $2323 \mu\text{g/L}$). By contrast, Fe concentration in the groundwater sample from the superficial deposits was

very low (6.80 µg/L). A similar distribution was observed for manganese (Mn), with very low concentrations in the superficial deposits (17.7 µg/L) and higher concentrations for the other samples, although with a wider range (Glasgow Upper Mn 544 µg/L; Glasgow Main Mn 366 µg/L; bedrock Mn 2471 µg/L) (Figure 8).

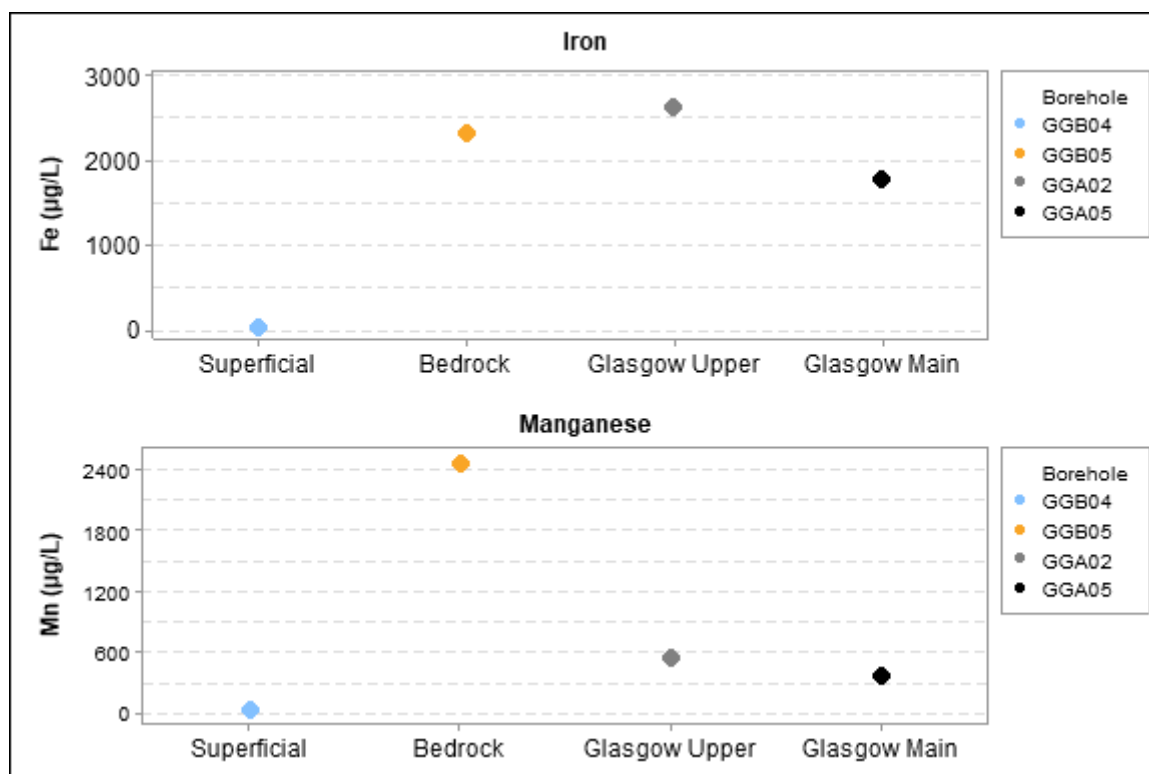


Figure 8 Iron and Mn distribution in GGA02, GGA05, GGB04 and GGB05 groundwater samples.

4.1.7 Other minor and trace elements

Figure 9 to Figure 12 show the distribution of selected minor and trace elements. Full data are reported in UKGEOSGlasgow_ConstructionPhaseGWChemData.xlsx.

Bromide (Br) concentrations ranged between 0.24 mg/L and 0.59 mg/L (Figure 9). The Br/Cl weight ratio enables small changes in bromide concentrations to be assessed in terms of salinity and is useful to reconstruct the origin of salinity and groundwater (Edmunds 1996). The Br/Cl weight ratio was similar in the Glasgow Upper mine water (Br/Cl 7.90×10^{-3}) and Glasgow Main mine water (Br/Cl 7.20×10^{-3}), and enriched compared with a sea water ratio of 3.47×10^{-3} . Br/Cl was 4.50×10^{-3} in the bedrock groundwater and 8.50×10^{-3} in the superficial deposits groundwater.

The other halogen, fluoride (F), was present in low concentrations (≤ 0.25 mg/L) (Figure 9).

Lithium (Li) concentrations ranged between 13 – 65 µg/L and rubidium (Rb) between 20–103 µg/L (Figure 10).

The alkaline earth element barium (Ba) content ranged from 51 µg/L to 129 µg/L, while strontium (Sr) ranged from 482 µg/L to 2319 µg/L, with the highest Sr values in the mine waters (Figure 11).

Boron (B) concentrations ranged between 189 µg/l and 387 µg/L, with the highest values in the mine waters. Aluminium (Al) ranged between 3–12 µg/L (Figure 122).

Other selected trace elements present in concentrations greater than 1 µg/L included cobalt (Co 0.1–20 µg/L), nickel (Ni 4–79 µg/L) and zinc (Zn 3–78 µg/L). It was noticeable that the highest concentrations of molybdenum (Mo 23 µg/L), tin (Sn 14 µg/L), and Zn were in the groundwater sample from the superficial deposits.

Hexavalent chromium (CrVI) was determined in the samples because there is a history of chromite-ore processing, and contamination of surface/ground water with Cr(VI) in the wider area

(Bearcock et al. 2019; Farmer et al. 1999; Palumbo-Roe et al. 2017; Whalley et al. 1999). The Cr(VI) concentrations in all the samples from these boreholes were below the LLD (0.05 $\mu\text{g/L}$).

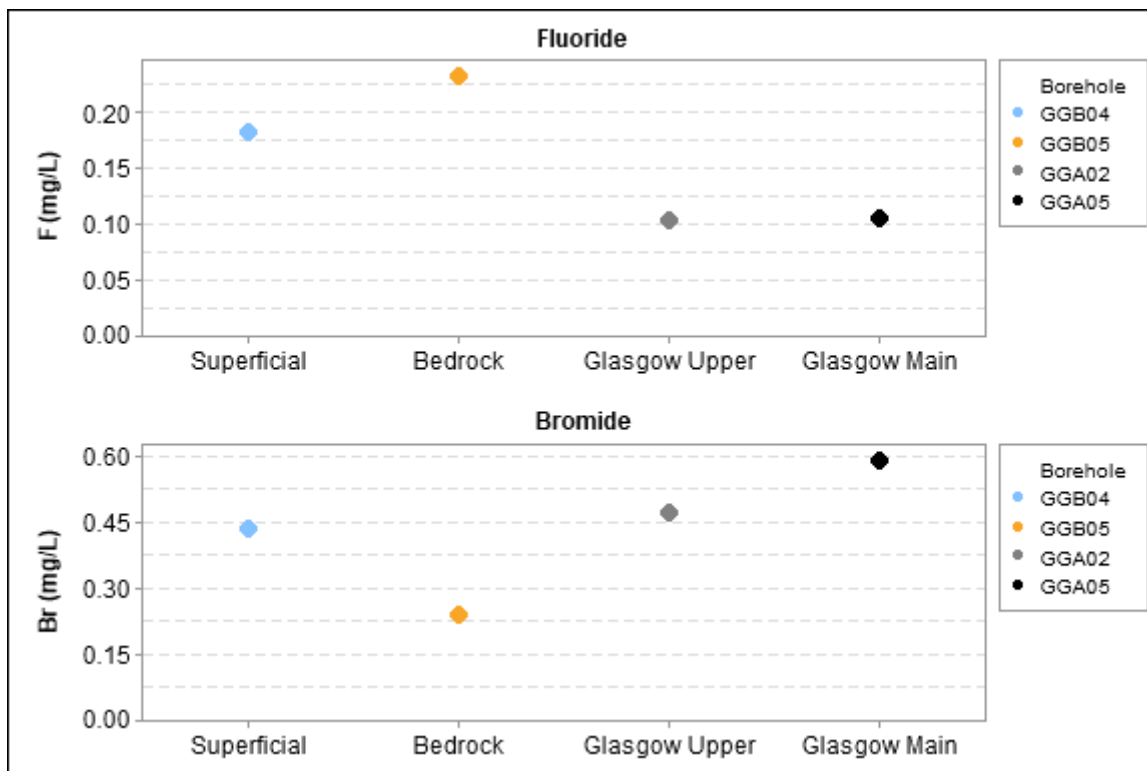


Figure 9 Fluoride and Br distribution in GGA02, GGA05, GGB04 and GGB05 groundwater samples.

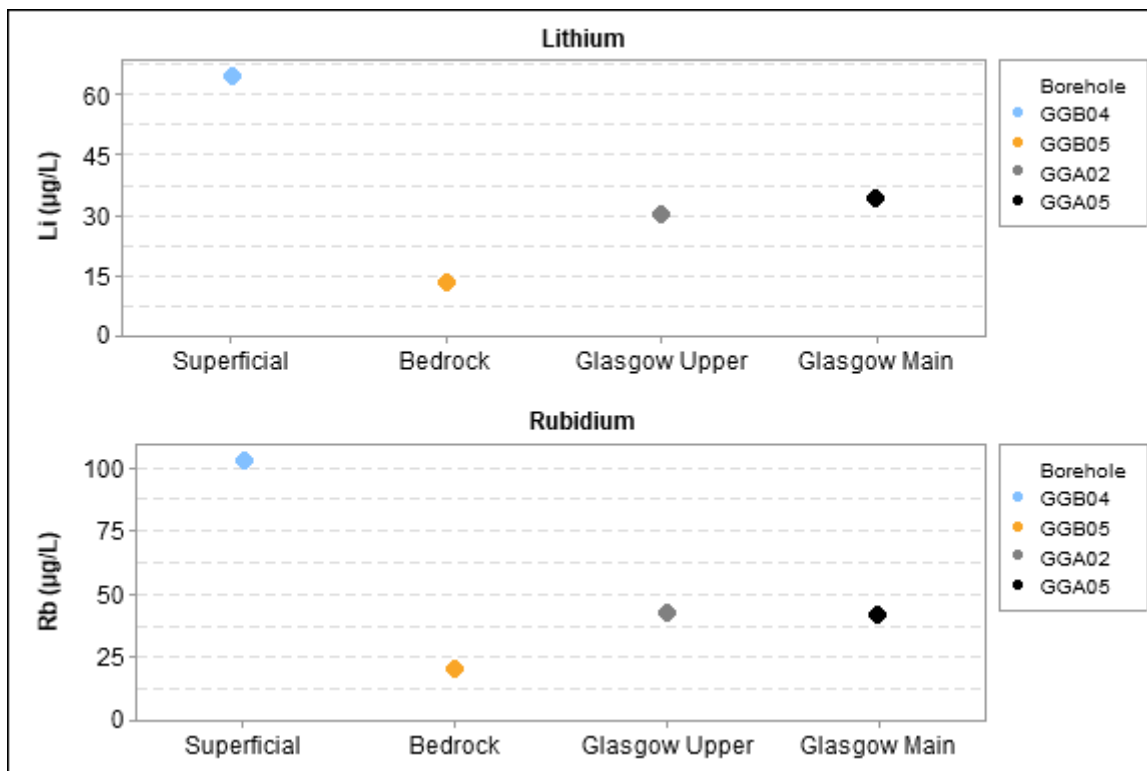


Figure 10 Lithium and Rb distribution in GGA02, GGA05, GGB04 and GGB05 groundwater samples.

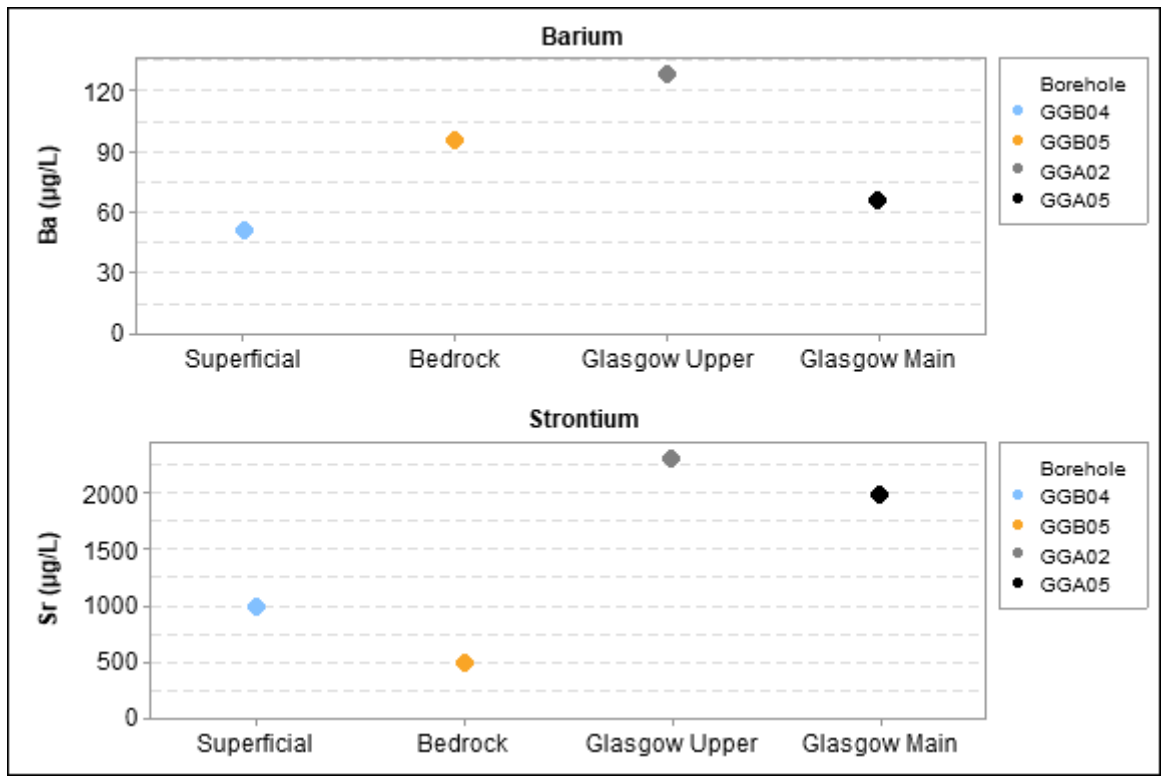


Figure 11 Barium and Sr distribution in GGA02, GGA05, GGB04 and GGB05 groundwater samples.

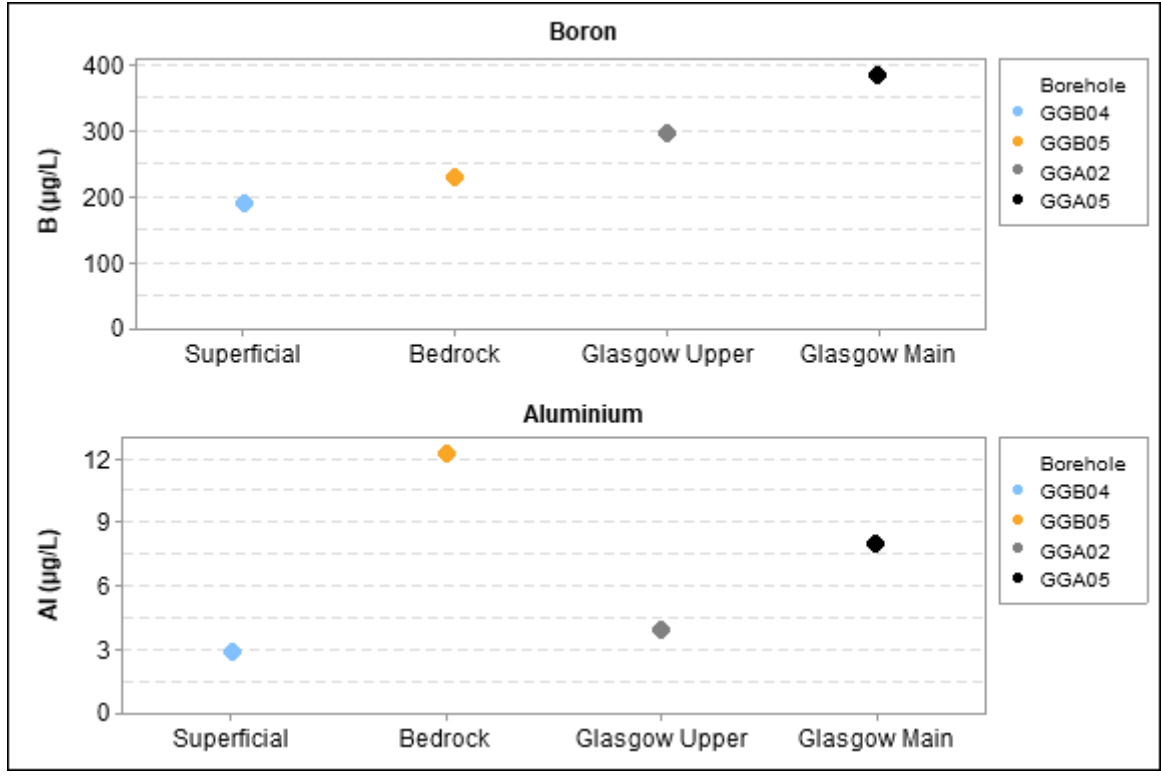


Figure 12 Boron and Al distribution in GGA02, GGA05, GGB04 and GGB05 groundwater samples.

4.1.8 PAH and TPH

Samples for PAH and TPH analysis were taken from the mine workings only. Benzo(b)fluoranthene (0.0026 µg/L) and benzo(a)pyrene (0.0009 µg/L) were the only PAH measured above the LLD from either mine working sample. TPH (C8-C40) and TPH (C10-C40) results were above the LLD for both the Glasgow Main (0.268 µg/L) and Glasgow Upper (0.36 µg/L).

4.1.9 Net-acidity and net-alkalinity

All the groundwater had near-neutral pH; however, pH alone can be a misleading characteristic in mine waters, because water that has near-neutral pH and elevated concentrations of dissolved Fe, Mn and Al can become acidic after complete oxidation of Fe/Mn and precipitation of the Fe, Mn and Al hydroxides. 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.

Both mine waters are classified as net-alkaline waters, with a net-alkalinity as CaCO₃ of 495 mg/L in Glasgow Upper mine water and 644 mg/L in Glasgow Main mine water, and in accordance with the bulk of Scottish mine waters, predominantly associated with flooded mine workings (Younger 2001).

Figure 13 plots the water samples from boreholes GGA05 (Glasgow Main) and GGA02 (Glasgow Upper) and the other boreholes GGB04 (superficial deposits) and GGB05 (bedrock) 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 SO₄ and Cl. The major anions other than bicarbonate (i.e. SO₄ 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 SO₄ concentrations and high acidity, which are characteristic of acid mine waters. The mine water samples from boreholes GGA02 and GGA05 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). Boreholes GGB04 (superficial deposits) and GGB05 (bedrock) fall in the same field as the mine waters.

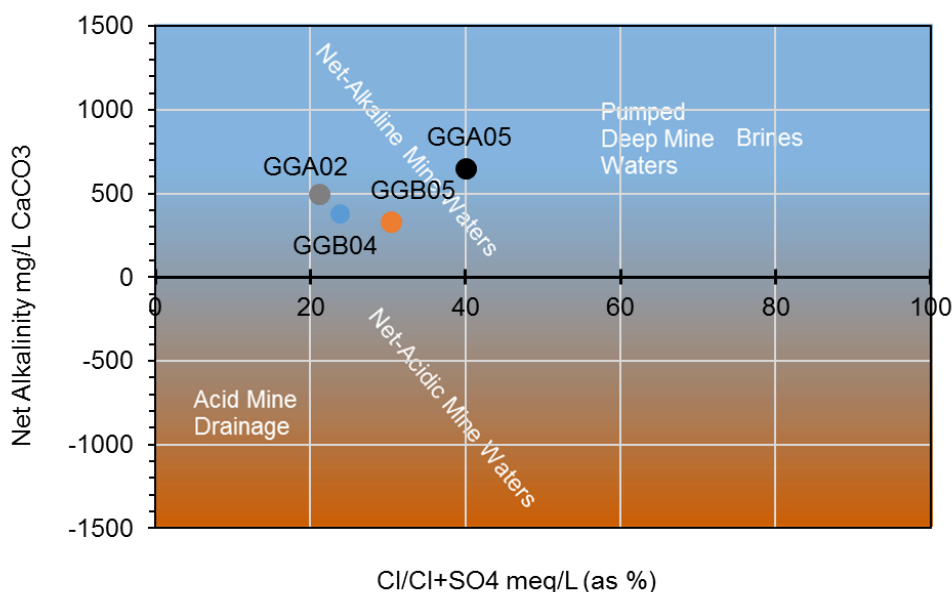


Figure 13 Groundwater samples from GGA02, GGA05, GGB04 and GGB05 boreholes plotted according to the mine water classification scheme of Rees et al. (2002).

4.1.10 Mineral saturation

Saturation indices calculated using PHREEQC (Parkhurst and Appelo 1999) and the database phreeqc.dat, indicate that all waters are saturated with respect to calcite (CaCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$), siderite (FeCO_3), rhodochrosite (MnCO_3), amorphous ferric hydroxide $\text{Fe}(\text{OH})_3(\text{a})$, gibbsite $\text{Al}(\text{OH})_3$, and barite (BaSO_4), and remain undersaturated with respect to gypsum, halite and jarosite (Jarosite-K: $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$).

4.1.11 Stable isotope data

Figure 14 shows oxygen (^{18}O) and deuterium (^2H) isotopic values expressed as δ -values against Vienna Standard Mean Ocean Water (VSMOW) standard. All the groundwater samples plot broadly on the global meteoric water line, which suggests a meteoric origin with minimal evaporation prior to recharge. The two mine water values are almost identical, with $\delta^{18}\text{O}$ -7.39 ‰ and -7.37 ‰ and $\delta^2\text{H}$ -49.5 ‰ and -49.2 ‰, respectively, for Glasgow Upper and Glasgow Main mine waters. The $\delta^{18}\text{O}$ values of the groundwater samples from the superficial deposits and from the bedrock were only slightly heavier ($\delta^{18}\text{O}$ -7.12 to -7.14 ‰). These values lie within the range of groundwater samples from Carboniferous sedimentary aquifers across the Midland Valley (Ó Dochartaigh et al. 2011).

The $\delta^{13}\text{C}$ of dissolved inorganic carbon species in groundwater depends on the $\delta^{13}\text{C}$ signature of the carbon source and the fractionation among the carbonate species in the solution (Appelo and Postma 2005). The C isotopic signature of the DIC is plotted against field alkalinity in Figure 15. This diagram is often used to show the theoretical evolution of the groundwater recharge process in carbonate systems towards older waters higher in alkalinity and increasing $\delta^{13}\text{C}$ (Bottrell et al. 2019). The results of this first sampling show that the mine waters have similar values of $\delta^{13}\text{C}$ -9.9 ‰ (Glasgow Upper) and -10.8 ‰ (Glasgow Main). With the highest $\delta^{13}\text{C}$, they are also characterised by high alkalinity (Figure 15). The superficial deposits groundwater shows a lighter $\delta^{13}\text{C}$ of -15.6 ‰. The sample of the bedrock groundwater has an intermediate $\delta^{13}\text{C}$ value of -12.1 ‰. These waters fall on the upper range of the $\delta^{13}\text{C}$ values from -22 ‰ to -10 ‰ of the groundwater samples from the Coal Measures Group across the Midland Valley of Scotland (Ó Dochartaigh et al. 2011).

4.2 BOREHOLE GGC01

Borehole flushing with 12,000 litres of mains water was undertaken on 13/12/18 after the completion of drilling, with the first water sample taken four days later. Given the sampling method, which used a bailer lowered to only a few meters from the top of the borehole, recent cleaning/flushing with mains water and potential contamination remaining from the tracer/additive and drilling fluid, the chemical analyses of the groundwater samples from this borehole are not to be considered fully representative of the unmined Coal Measures aquifer(s) properties intercepting the borehole, with little scope to evaluate them in relation to geology or hydrology.

Both groundwater samples taken on 17/12/18 (sample ID GGC010_0150) and on 07/01/19 (sample ID GGC010_0155) were alkaline (pH 9.11 and 9.13). They are freshwater, with a difference in SEC from 308 to 651 $\mu\text{S}/\text{cm}$ from the first to the second sampling event. For reference, the mains water SEC used for flushing was low in both sampling events (62 $\mu\text{S}/\text{cm}$, 58 $\mu\text{S}/\text{cm}$).

Sodium was the most enriched cation, with 57 mg/L and 133 mg/L, respectively, in GGC010_0150 and GGC010_0155. Alkalinity (as field- HCO_3) was 157 mg/L and 361 mg/L, and the next highest anion concentration was Cl with 10.4 mg/L and 28.5 mg/L; SO_4 was 6.4 mg/L and 4.9 mg/L respectively. These SO_4 concentrations were lower than the value of 7 mg/L reported in mains water used to flush the borehole.

A general pattern of concentration increase was observed between the December 2018 and January 2019 sampling for Na, Ca, Mg, K, alkalinity, Cl, Br and F. Elements that represent an exception to this trend were SO_4 , NO_3 , NO_2 , silicon (Si) and many trace elements, but in particular B. The concentration of B was very high, 16658 $\mu\text{g}/\text{L}$, in December 2018 and halved to 8716 $\mu\text{g}/\text{L}$ in January 2019. The December groundwater sample also had a very high concentration of NPOC

(1947 mg/L), which similarly to B, decreased in the January sample to 1020 mg/L. Given the relatively low concentration of these parameters in the mains water supply used to flush the borehole, it is likely these elements are associated with the drilling fluid and tracer used, and their decreasing concentration suggests a greater proportion of groundwater flowing into the borehole captured in the second sampling. No analyses of the drilling fluid or tracer have been carried out.

In terms of trace element chemistry, it should be noted that Cr(VI) concentrations were below the LLD (0.05 µg/L) in groundwater samples from GGC01. This Glasgow Observatory borehole is closest to the Shawfield redevelopment site, which is located on the south bank of the River Clyde approx. 0.3 km south-west of GGC01 at Site 10. This is the site of the former J J Whites chromite ore processing plant where contamination of soil, surface water and groundwater with Cr(VI) from Cr-waste is a known issue and is the subject of ongoing extensive remediation (Bewley and Sojka 2013; Farmer et al. 1999).

The stable isotope $\delta^2\text{H}$, $\delta^{18}\text{O}$ analysis suggests the January groundwater sample is closer in composition to the mine water samples collected from boreholes GGA02, GGA05, while the earlier December sample is similar in composition to the mains water used for borehole flushing (Section 2.1.3) (Figure 14). The December sample has a distinctively lighter $\delta^{13}\text{C}$ of -22.7 ‰ compared to the January sample ($\delta^{13}\text{C}\text{-DIC}$ -15.4 ‰) and to both mains water samples ($\delta^{13}\text{C}\text{-DIC}$ -13.3 ‰ and -14.9 ‰) (Figure 15).

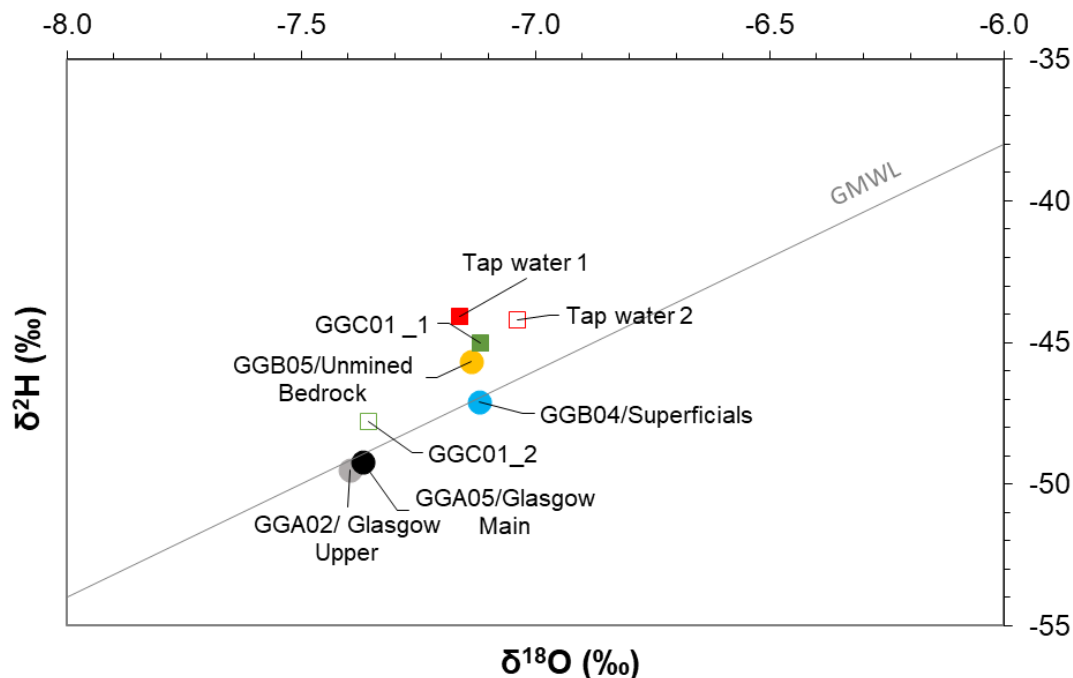


Figure 14 Water isotopic composition ($\delta^2\text{H}$ versus $\delta^{18}\text{O}$) plotted against the “global meteoric waterline” (GMWL) of samples GGA02, GGA05, GGB04 and GGB05 and GGC01_1 (Sample ID GGC010_0150 sampled on 17/12/18) and GGC01_2 (Sample ID GGC010_0155 sampled on 07/01/19). The composition of mains water (Tap water 1 and 2) used during flushing of borehole GGC01 is also plotted for comparison).

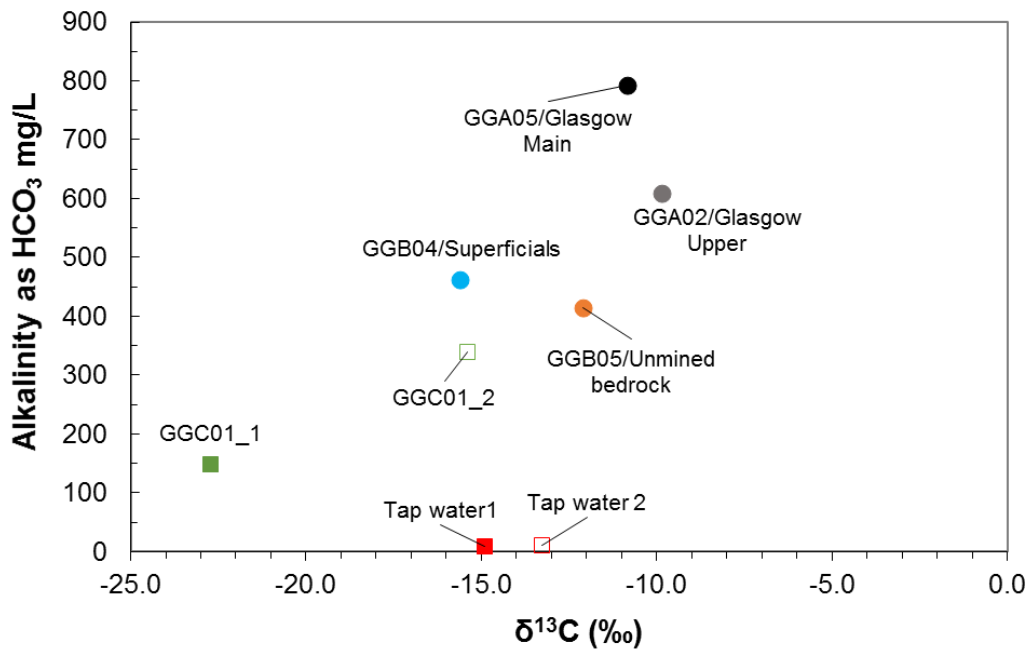


Figure 15 Field alkalinity versus $\delta^{13}\text{C}$ of dissolved inorganic carbon in samples GGA02, GGA05, GGB04 and GGB05 and GGC01_1 (Sample ID GGC010_0150 sampled on 17/12/18) and GGC01_2 (Sample ID GGC010_0155 sampled on 07/01/19). The composition of mains water (Tap water 1 and 2) used during flushing of borehole GGC01 is also plotted for comparison).

5 Conclusions

Eight groundwater samples and two mains water samples used for borehole flushing were taken between December 2018 and December 2019, during the construction phase of the Glasgow Observatory from: boreholes GGA02 from Site 1, GGA05 from Site 2, GGB04, GGB05 from Site 5, and GGC01 from Site 10.

Methods of sample collection and results of analyses are presented in this report. The data provide an indication of groundwater chemistry during the construction phase, in the course of either the drilling, installation, cleaning or post cleaning of the boreholes, but before test pumping. In the case of boreholes GGA02 and GGC01, they are the only groundwater chemistry data that will be collected from these boreholes.

Water was obtained from the Glasgow Upper mine working in GGA02 and Glasgow Main mine working in GGA05 by stopping the drilling at the mine working and retrieving a sample during and after purging. Groundwater from the bedrock and the superficial deposits was drawn from borehole GGB04 and borehole GGB05, respectively.

Groundwater samples were collected for analysis of major, minor and trace elements, Cr(VI), NPOC and stable isotopes ($\delta^2\text{H}$, $\delta^{18}\text{O}$, $\delta^{13}\text{C}$). In addition, field measurements of water temperature, pH, SEC, Eh and DO were made. TPH and PAH were analysed in samples from GGA02 and GGA05 only.

Both mine waters are net-alkaline with a near-neutral pH (Glasgow Upper pH 6.92 and Glasgow Main pH 7.12); they have a high alkalinity (as field- HCO_3) (Glasgow Upper field- HCO_3 609 mg/L and Glasgow Main field- HCO_3 792 mg/L) and a high SEC of 1637 to 1723 $\mu\text{S}/\text{cm}$.

Similarly, the bedrock and the superficial deposits waters have pH values of ~ 7.5 and alkalinity as field- HCO_3 between 415 mg/L and 462 mg/L. The SEC is also high 1078–1183 $\mu\text{S}/\text{cm}$.

All the waters belong to the bicarbonate type, with Na as the dominant cation in the superficial deposits and bedrock groundwaters (Na- HCO_3 waters), while the two mine waters are Na-Ca-(Mg)- HCO_3 type water.

Water from all four lithologies ranges in SO_4 concentration between 165 and 302 mg/L. The Cl range is 51–82 mg/L, with the highest value in the Glasgow Main mine working groundwater. Iron concentrations range between 1.8 to 2.6 mg/L in the mine water and bedrock; a much lower concentration of 0.007 mg/L is measured in the superficial deposits groundwater. Chromium(VI), a known industrial contaminant in the area, was not detected above the LLD in any samples.

The stable isotope $\delta^2\text{H}$, $\delta^{18}\text{O}$ values plot broadly on the global meteoric water line with no evidence of evaporation prior to recharge. The O-isotope values ($\delta^{18}\text{O}$ -7.4 ‰ and -7.1 ‰) are all within the range of groundwater samples reported previously from Carboniferous sedimentary aquifers across the Midland Valley of Scotland. The mine waters have heavier $\delta^{13}\text{C}$ (-9.9 and -10.8 ‰) than the bedrock and superficial deposits (-15.6 and -12.1 ‰). All lithologies' groundwaters fall on the middle to upper range of the $\delta^{13}\text{C}$ values from -22 ‰ to -10 ‰ of groundwater samples from other studies of the Coal Measures Group across the Midland Valley of Scotland.

All samples are saturated with respect to calcite, dolomite, siderite, rhodochrosite, amorphous ferric hydroxide, gibbsite, and barite, and remain undersaturated with respect to gypsum, halite and jarosite.

Water was also obtained during the installation of the GGC01 borehole. However, given the sampling method (a bailer lowered to only a few meters from the top of the borehole) and evidence of dilution during flushing and residual contamination from the tracer/additive and drilling fluid, the chemical analyses of the groundwater samples from this borehole are not to be considered representative of the unmined Coal Measures aquifer(s) intercepting the borehole. Very high concentrations of B and NPOC were found, which decreased between the two sampling dates, showing an increase in groundwater flowing into the borehole after drilling and flushing. The water was alkaline, and with a SEC of 310–650 $\mu\text{S}/\text{cm}$. Sodium was the most enriched cation, with HCO_3 and Cl the most enriched anions. Chromium(VI) was not detected above the LLD in either

sample. The $\delta^2\text{H}$, $\delta^{18}\text{O}$ signature of the groundwater was similar to the samples taken in the four Cuningar Loop boreholes while the $\delta^{13}\text{C}$ isotope signature was lighter.

Appendix A Summary of mains tap water samples

Table 4 Mains water samples collected from a tap in the site office upon drilling completion of GGC01, Dalmarnock

Sample number	Borehole	Date sampled	Water type	Sample source	Borehole depth (m)	Construction phase	Sampling method	Parameter types available
GGC010_0154	GGC01	17/12/2018	Mains water	Mains tap	NA	After completion of drilling.	Directly from mains tap	Field parameters; inorganic chemistry; stable isotopes.
GGC010_0159	GGC01	07/01/2019	Mains water	Mains tap	NA	After completion of drilling.	Directly from mains tap	Field parameters; inorganic chemistry; stable isotopes.

Appendix B Summary of groundwater sample splits

Table 5 Groundwater sample splits collected during borehole construction phase sampling

Water quality parameters	Sample splits	Analytical method	Lab
Non Purgeable Organic Carbon	Ag-filtered unacidified foil capped 14 mL glass vial (NPOC)	Carbon analyser	BGS
Oxygen and deuterium isotopes $\delta^{18}\text{O}/\delta^2\text{H}$	30 mL HDPE unfiltered unacidified Nalgene bottle (δ O-H)	Isotope ratio mass spectrometry (IR-MS)	BGS
Carbon isotopes ($\delta^{13}\text{C}$) of DIC	125 mL HDPE unfiltered unacidified Nalgene (δ C)	IR-MS	BGS
Major and trace element cations: Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Hf, Ho, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, P, Pb, Pr, Rb, S (total), Sb, Se, Si, Sm, Sn, Sr, Ta, Tb, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, Zr	Filtered acidified 30 mL HDPE Nalgene bottle (FA)	Inductively coupled plasma mass spectrometry (ICP-MS)	BGS
Major and trace element anions Br, Cl, F, HPO_4 , NO_2 , NO_3 SO_4 , HCO_3 lab	Filtered unacidified 60 mL HDPE Nalgene bottle (FUA)	Ion chromatography (IC) and ICP-MS	BGS
Cr(VI) speciation	Filtered unacidified 30 mL HDPE Nalgene bottle, for HPLC-ICP-MS (Cr(VI))	High performance liquid chromatography (HPLC)-ICP-MS	BGS
<u>Total Petroleum Hydrocarbons</u> TPH (C10-C40) TPH (C8-C10) TPH (C8-C40)	Unfiltered unacidified 1 L clear glass bottle provided by Scottish Water (TPH). Bottles are dosed with sodium thiosulphate.	Gas chromatography flame ionisation detector (GC-FID)	Scottish Water
<u>Polycyclic Aromatic Hydrocarbons</u> Benzo (a) pyrene Benzo (b) fluoranthene Benzo (ghi) perylene Benzo (k) fluoranthene Indeno (1,2,3-cd) pyrene PAH - total	Unfiltered unacidified 250 mL brown glass bottle provided by Scottish Water (PAH). Bottles are dosed with sodium thiosulphate.	HPLC fluorescence detection (HPLC-FD)	Scottish Water

Appendix C Analytical methods

The UKGEOS Glasgow borehole construction phase 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. Full details of the analytical methods used to evaluate the groundwater samples are given in the UKGEOS Glasgow baseline surface water chemistry report (Fordyce et al. 2021).

This section documents the analytical quality control (QC) information relevant to the borehole construction phase groundwater chemistry dataset.

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 QC, time versus concentration plots showed no systematic analytical drift either within or between batches for any of the following analytical methods.

5.1 INORGANIC ANALYSIS

5.1.1 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. Repeat measurements of standards included in the analytical runs and the analytical replicate results showed good precision of the data with relative standard deviation (RSD) of $\leq 5\%$, except where values were close to the lower limit of detection (LLD) or present in low concentration. This affected the following analytes, which should be treated with caution: boron (B), beryllium (Be) and lithium (Li). The RSD results for some of the lighter elements including aluminium (Al), silicon (Si) and titanium (Ti) were marginally higher (RSD 6-8%), probably as a result of tuning the ICP-MS to optimise heavier elements. This is normal and a necessary compromise.

In terms of accuracy, all recoveries were $100 \pm 5-6\%$, except where element concentrations were close to the LLD or present in low abundance for silver (Ag), arsenic (As), Be, bismuth (Bi), cerium (Ce), dysprosium (Dy), erbium (Er), europium (Eu), gallium (Ga), holmium (Ho), lanthanum (La), Li, lutetium (Lu) neodymium (Nd), terbium (Tb), thorium (Th) and ytterbium (Yb); or conversely in very high concentration (Si, recovery 107%), and these results should be treated with caution.

5.1.2 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 $\leq 5\%$. Similarly, the measured results for analytical QC standards demonstrated good recovery ($100 \pm 5\%$), relative to the target values.

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 1992). The ionic balance was $\pm 5\%$ for all the borehole construction phase water samples, demonstrating the robustness of the analytical methods.

5.1.3 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 $100 \pm 5\%$ demonstrating good accuracy of the technique. Similarly, analytical replicate measurements showed good precision of the data ($RSD \leq 5\%$) (Table 6).

The efficiency of the chromatographic separation was assessed through calculating the recovery of the sum of the measured Cr species against the total chromium (Cr-Total) measured in the FA sample. Chromium speciation results above the LLD were reported in two samples only. In these samples, recoveries were $100 \pm 15\%$ except where either the Cr-Total or Cr species were below the detection limit.

Table 6 Results for quality control standards included in the Cr(VI and III) speciation HPLC-ICP-MS analysis.

Standard	Number of Measurements	Results	Cr(VI) $\mu\text{g/L}$	Cr(III) $\mu\text{g/L}$
QC1	15	Target value	5	5
		BGS mean	5.09	5.02
		% RSD	4	3
		% recovery	102	100

5.1.4 Laboratory total alkalinity and total inorganic carbon analysis

Total alkalinity (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) was calculated by dividing the titrimetrically measured bicarbonate by a factor of 5.0801.

The percentage recoveries for a QC check standard measured before each analytical run were $100 \pm 5\%$ demonstrating good accuracy of the method. Analytical replicate measurements showed good precision of the data also ($RSD \leq 5\%$) (Table 7).

As a further check on data quality, the field and laboratory alkalinity measurements were compared. These showed broad agreement with $RSD \leq 20\%$.

Table 7 Results for quality control standards included in the laboratory total alkalinity/ bicarbonate analysis.

Standard	Number of Measurements	Results	HCO_3 mg/L
QC200	20	Target	200
		BGS mean	200
		% RSD	1
		% recovery	100

5.2 ORGANIC PARAMETER ANALYSIS

5.2.1 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 $100 \pm 5\%$) and precision ($RSD < 5\%$) of the data.

5.2.2 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.

Between February and December 2019, LLD were reported with the data (based on three times the standard deviation of laboratory blanks), but from January 2020 onwards, the more precautionary LOQ (based on 10 times the standard deviation of laboratory blanks) were stated, 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 $100 \pm 5\%$) and precision ($RSD < 10\%$) of the data (Table 8).

Table 8 Results for quality control standards included in the GC-FID TPH analysis.

TPH Compound	% Recovery	% RSD
C8-C10	100	8
C10-C40	95	10

5.2.3 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. Between February and December 2019, LLD were reported with the data (based on three times the standard deviation of laboratory blanks), but from January 2020 onwards, the more precautionary LOQ (based on 10 times the standard deviation of laboratory blanks) were stated, 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 BGS-GGA05-21 and BGS-GGA05-22, due to issues with method performance.

The results for QC check standards and repeat measurements show good accuracy (recovery $100 \pm 10\%$) and precision ($RSD < 10\%$) of the data (Table 9), given that a significant proportion of the data are close to or below the detection limit/limit of quantification. 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 9 Results for quality control standards included in the HPLC-FD PAH analysis.

PAH Compound	% Recovery	% RSD
Benzo(b)fluoranthene	99	5
Benzo(k)fluoranthene	89	5
Benzo(a)pyrene (BaP)	93	6
Benzo(g,h,i)perylene	85	5
Indeno(1,2,3-cd)pyrene	90	6
PAH-Total	91	5

5.3 STABLE ISOTOPE ANALYSIS

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

5.3.1 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 $\delta^{13}\text{C}$ (1σ) (RSD \leq 5%). Similarly, the measured results for a secondary in-house standard (CCS) demonstrated good recovery ($100 \pm 5\%$) relative to the preferred value (Table 10).

Table 10 Results for quality control standards included in the $\delta^{13}\text{C}$ stable isotope IRMS analysis.

$\delta^{13}\text{C}$ ‰ VPDB	MCS primary lab standard	KCM standard calcite	CCS secondary lab standard
Number of measurements	40	24	21
NIGL mean	-0.7	2.0	-22.4
% RSD	5	3	<1
In-house preferred value			-22.3
% recovery			100

MCS: primary laboratory standard calibrated to international CRM NBS-19-IAEA

KCM: in-house carbonate reference material, Keyworth Carrera marble (KCM), which is calibrated against NBS-19-IAEA CRM

CCS: in-house secondary laboratory standard

RSD: relative standard deviation

5.3.2 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 \leq 5%) (Table 11).

Table 11 Results for repeat measurements on QC standards included in the IRMS $\delta^2\text{H}$ stable isotope analysis.

$\delta^2\text{H}$ VSMOW2 (‰)	CA-LO calibration		CA-HI calibration	
	IAEA SMOW2/SLAP	CRM	IAEA SMOW2/SLAP	CRM
Number of measurements	30		38	
NIGL mean	-311.1		-48.5	
% RSD	<1		2	

RSD: relative standard deviation

5.3.3 Oxygen stable isotope analysis

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

Repeat measurements show good precision of the data ($\text{RSD} \leq 5\%$) (Table 12).

Table 12 Results for repeat measurements on QC standards included in the IRMS $\delta^{18}\text{O}$ stable isotope analysis.

$\delta^{18}\text{O}$ ‰ VSMOW2		CA-LO calibration		CA-HI calibration	
		IAEA SMOW2/SLAP	CRM	IAEA SMOW2/SLAP	CRM
Number of measurements		46		58	
NIGL mean		-39.3		-7.3	
% RSD		<1		<1	

RSD: relative standard deviation

Glossary

BGS	British Geological Survey
CaCO ₃	calcium carbonate (alkalinity)
CCS	isotope laboratory in-house secondary standard
CO ₂	carbon dioxide
Cr(VI)	hexavalent chromium
CRM	certified reference material
δ ¹³ C	ratio of stable isotopes ¹³ carbon: ¹² carbon
δ ¹⁸ O	ratio of stable isotopes ¹⁸ oxygen: ¹⁶ oxygen
δ ² H	ratio of stable isotopes ² hydrogen: ¹ hydrogen
Eh	redox potential
FA	filtered acidified water sample
FD	fluorescence detection
FUA	filtered unacidified water sample
GC-FID	Gas chromatography flame ionisation detector
GMWL	global meteoric water line
HCl	hydrochloric acid
HDPE	high density polyethylene
HNO ₃	nitric acid
HPLC	high performance liquid chromatography
H ₂ S	hydrogen sulphide
IAEA	International Atomic Energy Authority
IC	ion chromatography
ICP-MS	inductively coupled plasma mass spectrometry
IRMS	isotope ratio mass spectrometry
KCM	Keyworth Carrera marble in-house calcite standard
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
ORS	octopole reaction system
PAH	polycyclic aromatic hydrocarbons
QC	quality control
RSD	relative standard deviation
SEC	specific electrical conductance
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
VPDB	Vienna Pee Dee Belemnite
VSMOW	Vienna Standard Mean Ocean Water

References

British Geological Survey holds most of the references listed below, and copies may be obtained via the library service subject to copyright legislation (contact libuser@bgs.ac.uk for details). The library catalogue is available at: <https://envirolib.apps.nerc.ac.uk/olibcgi>.

- APPELO C AND POSTMA D. 2005. *Geochemistry, Groundwater and Pollution*. 2nd edition, Balkema, Rotterdam.
- BARRON, H.F., STARCHER, V., WALKER-VERKUIL, K., SHORTER, K.M. AND MONAGHAN, A.A. 2020a. Mine water characterisation and monitoring borehole GGA08, UK Geoenery Observatory, Glasgow. *British Geological Survey Open Report*, OR/20/028, 35pp, <http://nora.nerc.ac.uk/id/eprint/528081/>
- BARRON, H.F., STARCHER, V., MONAGHAN, A.A., SHORTER, K.M. AND WALKER-VERKUIL, K. 2020b. Mine water characterisation and monitoring borehole GGA05, UK Geoenery Observatory, Glasgow. *British Geological Survey Open Report*, OR/20/025, 35pp. <http://nora.nerc.ac.uk/id/eprint/528052/>
- BEARCOCK J M, SMEDLEY P L, FORDYCE F M, EVERETT P A AND ANDER E L. 2019. Controls on surface water quality in the River Clyde catchment, Scotland, UK, with particular reference to chromium and lead. The Geosciences in Europe's Urban Sustainability: Lessons from Glasgow and Beyond (CUSP). *Earth and Environmental Science: Transactions of the Royal Society of Edinburgh*, 108 (2-3), 249–267. <http://nora.nerc.ac.uk/id/eprint/521854/>
- BEWLEY R J F AND SOJKA G. 2013. In situ deliverability trials using calcium polysulphide to treat chromium contamination at Shawfield, Glasgow. *Technology Demonstration Project Bulletin*, 30. London: Contaminated Land: Applications in Real Environments (CL:AIRE).
- BOTTRELL S, HIPKINS E V, LANE J M, ZEGOS R A, BANKS D AND FRENGSTAD B S. 2019. Carbon-13 in groundwater from English and Norwegian crystalline rock aquifers: a tool for deducing the origin of alkalinity? *Sustainable Water Resource Management*, Vol. 5, 267–287.
- EDMUNDS, W M. 1996. Bromine geochemistry of British groundwaters. *Mineralogical Magazine*, 60(399), 275-284.
- ELSONE, J., WALKER-VERKUIL, K., STARCHER, V., BARRON, H.F., SHORTER, K.M. AND MONAGHAN, A.A. 2020. Environmental baseline characterisation and monitoring borehole GGB04, UK Geoenery Observatory, Glasgow., *British Geological Survey Open Report*, OR/20/030, 22pp, <http://nora.nerc.ac.uk/id/eprint/528083/>
- FARMER J G, GRAHAM M C, THOMAS R P, LICONA-MANZUR C, PATERSON E, CAMPBELL C D, GEELHOED J S, LUMSDON D G, MEEUSSEN J C L, ROE M J, CONNER A, FALICK A E AND BEWLEY R J F. 1999. Assessment and modelling of the environmental chemistry and potential for remediative treatment of chromium-contaminated land. *Environmental Geochemistry and Health*, Vol. 21, 331-337.
- FORDYCE, F M, SHORTER K M, WALKER-VERKUIL K, BARLOW T, SLOANE H J, ARROWSMITH C, HAMILTON E M, EVERETT P A AND BEARCOCK J M. 2021. UK Geoenery Observatories, Glasgow Environmental Baseline Surface Water Chemistry Dataset 1. *British Geological Survey Open Report*, OR/20/061, Edinburgh.
- HAMILTON E M, LARK R M, YOUNG S D, BAILEY E H, SAKALA G M, MASEKA K AND WATTS M J. 2020. Reconnaissance sampling and determination of hexavalent chromium in potentially-contaminated agricultural soils in Copperbelt Province, Zambia. *Chemosphere* Vol. 247, 125984.
- HEDIN, R S., NAIRN, R W. AND KLEINMANN, R L P. 1994. Passive Treatment of Coal Mine Drainage. *US Bureau of Mines Information Circular 9389*. US Department of the Interior, Bureau of Mines, Pittsburgh, PA.
- HEM J. 1992. *Study and Interpretation of the Chemical Characteristics of Natural Water*. (Reston: US Geological Survey).
- KEARSEY, T., GILLESPIE, M.; ENTWISLE, D., DAMASCHKE, M., WYLDE, S., FELLGETT, M.; KINGDON, A., BURKIN, J., STARCHER, V., SHORTER, K., BARRON, H., ELSONE, J., BARNETT, M., AND MONAGHAN, A. 2019A. UK Geoenery Observatories Glasgow: GGC01 cored, seismic monitoring borehole – intermediate data release. *British Geological Survey Open Report*, OR/19/049 36pp, <http://nora.nerc.ac.uk/id/eprint/525009/>
- MONAGHAN, A.A., O'DOCHARTAIGH, B., FORDYCE, F., LOVELESS, S., ENTWISLE, D., QUINN, M., SMITH, K., ELLEN, R., ARKLEY, S., KEARSEY, T., CAMPBELL, S.D.G., FELLGETT, M. AND MOSCA, I. 2017. UKGEOS: Glasgow Geothermal Energy Research Field Site (GGERFS): initial summary of the geological platform. Nottingham, UK, British Geological Survey Open Report, OR/17/006, 205pp, <http://nora.nerc.ac.uk/id/eprint/518636/>
- MONAGHAN, A.A., STARCHER, V., O DOCHARTAIGH, B., SHORTER, K. AND BURKIN, J. 2019. UK Geoenery Observatories: Glasgow Geothermal Energy Research Field Site: Science Infrastructure Version 2. British Geological Survey Open Report, OR/19/032, 49pp, <http://nora.nerc.ac.uk/id/eprint/522814/>

- MONAGHAN, A., STARCHER, V. AND BARRON, H. 2020A. UK Geoenery Observatories Glasgow : express data release, mine water and environmental baseline monitoring boreholes at Cuningar Loop (updated June 2020). Nottingham, UK, *British Geological Survey Open Report*, OR/20/002, 17pp, <http://nora.nerc.ac.uk/id/eprint/526889/>
- MONAGHAN, A.A., BARRON, H.F., STARCHER, V., SHORTER, K.M. AND WALKER-VERKUIL, K. 2020b. Mine water characterisation and monitoring borehole GGA01, UK Geoenery Observatory, Glasgow. *British Geological Survey Open Report*, OR/20/021, 28pp. <http://nora.nerc.ac.uk/id/eprint/528075/>
- MONAGHAN, A.A., STARCHER, V., BARRON, H.F. SHORTER, K.M. AND WALKER-VERKUIL, K. 2020c. Borehole GGA02, UK Geoenery Observatory, Glasgow. *British Geological Survey Open Report*, OR/20/022, 31pp, <http://nora.nerc.ac.uk/id/eprint/528076/>
- Ó DOCHARTAIGH B É, SMEDLEY P L, MACDONALD A M, DARLING WG AND HOMONCIK S. 2011. Baseline Scotland: groundwater chemistry of the Carboniferous sedimentary aquifers of the Midland Valley. *British Geological Survey Open Report*, OR/11/021. 105pp.
- PALUMBO-ROE B, BANKS V J, BONSOR H C, HAMILTON E M AND WATTS M J. 2017. Limitations on the role of the hyporheic zone in chromium natural attenuation in a contaminated urban stream. *Applied Geochemistry*, Vol. 83, 108-120.
- PARKHURST, D L. AND APPELO, C A J., 1999. User's guide to PHREEQC (Version 2)—A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: *U.S. Geological Survey Water-Resources Investigations Report* 99-4259, 310 p.
- ROSE, A W AND CRAVOTTA III, CA. 1998. Geochemistry of coal mine drainage. *Coal mine drainage prediction and pollution prevention in Pennsylvania*, 1, 1-22.
- REES, S.B., BOWELL, R J. AND WISEMAN, I. 2002. Influence of mine hydrogeology on mine water discharge chemistry. *Geological Society, London, Special Publications*, 198(1), 379-390.
- RYVES D B, LENG M J, BARKER P A, SNELLING A M, SLOANE H J, ARROWSMITH C, TYLER J J, SCOTT D R, RADBOURNE A D AND ANDERSON N J. 2020. Understanding the transfer of contemporary temperature signals into lake sediments via paired oxygen isotope ratios in carbonates and diatom silica: problems and potential. *Chemical Geology*, 552, 119705.
- SHORTER, K.M., STARCHER, V., BARRON, H.F., WALKER-VERKUIL, K. AND MONAGHAN, A.A. 2020a. Environmental baseline characterisation and monitoring borehole GGA03r, UK Geoenery Observatory, Glasgow. *British Geological Survey Open Report*, OR/20/023, 23pp, <http://nora.nerc.ac.uk/id/eprint/528077/>
- SHORTER, K.M., STARCHER, V., BARRON, H.F., WALKER-VERKUIL, K. AND MONAGHAN, A.A. 2020b. Environmental baseline characterisation and monitoring borehole GGA06r, UK Geoenery Observatory, Glasgow., *British Geological Survey Open Report*, OR/20/026, 23pp, <http://nora.nerc.ac.uk/id/eprint/528079/>
- STARCHER, V., BARRON, H.F., MONAGHAN, A.A., SHORTER, K.M. AND WALKER-VERKUIL, K. 2020a. Mine water characterisation and monitoring borehole GGA04, UK Geoenery Observatory, Glasgow. *British Geological Survey Open Report*, OR/20/024, 28pp, <http://nora.nerc.ac.uk/id/eprint/528078/>
- STARCHER, V., WALKER-VERKUIL, K., SHORTER, K.M., MONAGHAN, A.A. AND BARRON, H.F. 2020b. Mine water characterisation and monitoring borehole GGA07, UK Geoenery Observatory, Glasgow. *British Geological Survey Open Report*, OR/20/027, 29pp. <http://nora.nerc.ac.uk/id/eprint/528080/>
- WALKER-VERKUIL, K., STARCHER, V., BARRON, H.F., SHORTER, K.M. AND MONAGHAN, A.A. 2020a. Environmental baseline characterisation and monitoring borehole GGA09r, UK Geoenery Observatory, Glasgow. *British Geological Survey Open Report*, OR/20/029, 22pp, <http://nora.nerc.ac.uk/id/eprint/528082/>
- WALKER-VERKUIL, K., STARCHER, V., BARRON, H.F., SHORTER, K.M., ELSOME, J. AND MONAGHAN, A.A. 2020b. Environmental baseline characterisation and monitoring borehole GGB05, UK Geoenery Observatory, Glasgow. *British Geological Survey Open Report*, OR/20/031, 23pp, <http://nora.nerc.ac.uk/id/eprint/528084/>
- WHALLEY, C, HURSTHOUSE, A, ROWLATT, S, IQBAL-ZAHID, P, VAUGHAN, H AND DURANT, R. 1999. Chromium speciation in natural waters draining contaminated land, Glasgow, UK. *Water Air and Soil Pollution*, Vol. 112, 389-405.
- YOUNGER, P L. 2001. Mine water pollution in Scotland: nature, extent and preventative strategies. *Science of the Total Environment*, 265(1-3), 309-326.
- YOUNGER, P L. 1995. Hydrogeochemistry of mine water flowing from abandoned coal workings in County Durham. *Quarterly Journal of Engineering Geology*, 28, S101-S113.