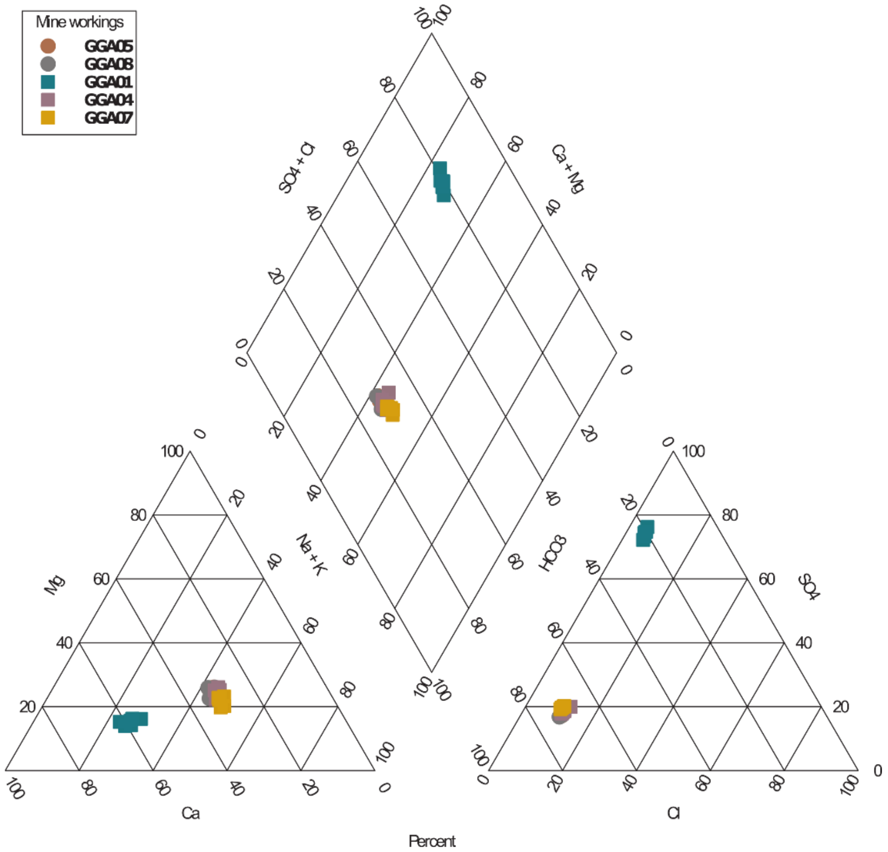
UK Geoenergy Observatories: Glasgow baseline groundwater and surface water chemistry dataset release September 2020 - May 2021

UK Geoenergy Observatories Programme

Open Report OR/22/038



BRITISH GEOLOGICAL SURVEY

UK GEOENERGY OBSERVATORIES PROGRAMME

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Front cover: Piper diagram showing water types of groundwaters in the mine workings.

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UK Geoenergy Observatories: Glasgow baseline groundwater and surface water chemistry dataset release September 2020 - May 2021

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Summary

This report describes baseline water chemistry sampling and analysis results for groundwater and surface water at the United Kingdom Geoenergy Observatory (UKGEOS) in Glasgow between September 2020 and May 2021. The report accompanies the Glasgow Observatory groundwater chemistry data release and the Glasgow Observatory surface water chemistry data release for the same periods. While the reporting period is nine months long, the global Covid-19 pandemic meant sampling was not always possible during this time. The groundwater data release contains data from six monthly sampling rounds, and the surface water data release contains data from three to five monthly sampling rounds (site dependant).

The Glasgow Observatory comprises twelve boreholes drilled into the main hydrogeological units, known as target units. These are the superficial deposits, bedrock, Glasgow Upper mine workings and Glasgow Main mine workings. The ten boreholes used for groundwater sampling are located at the Cuningar Loop in South Lanarkshire. There are two additional boreholes in the Observatory, one seismic monitoring borehole in Dalmarnock in the east end of Glasgow, and one borehole used for sensor testing. Three boreholes are drilled into the superficial deposits, two into the unmined bedrock, three into the Glasgow Upper mine workings and two into the Glasgow Main mine workings. The boreholes are designed to assist geological and hydrogeological characterisation, including baseline water chemistry monitoring, and to act as mine water abstraction and reinjection wells. The aims of the Observatory are to: 1) provide baseline environmental characterisation, 2) assess changes in ambient conditions induced by mine water abstraction/re-injection cycles and, 3) provide data and evidence to de-risk low-temperature shallow mine water heat energy and heat storage in former coal mine workings.

Groundwater sampling was conducted using either a submersible or bladder pump. Field parameters (pH, specific electrical conductance (SEC), redox potential (Eh) and dissolved oxygen (DO)) were measured in a flow-through cell. The flow-through cell was discharged to a plastic beaker containing a thermometer probe. Field parameters were measured for a period of 20 minutes and at least three readings were taken five minutes apart. After field parameters were taken, the flow cell was disconnected and samples were taken directly from the pump discharge tube. Field alkalinity was measured by titration against H_2SO_4.

Groundwater samples were analysed for: major, minor, and trace elements, chromium speciation (Cr (III) and Cr (VI)), non-purgeable organic carbon (NPOC) and total inorganic carbon (TIC), polycyclic aromatic hydrocarbons (PAH), total petroleum hydrocarbons (TPH), volatile organic compounds (VOC), stable isotopes - deuterium (δ^2H), oxygen 18 ($\delta^{18}O$) and carbon 13 of dissolved inorganic carbon (DIC) ($\delta^{13}C_{DIC}$), ammonium (NH_4), methane, ethane and carbon dioxide (CH_4, C_2H_6, CO_2), chlorofluorocarbons (CFC-12 and CFC-11), sulphur hexafluoride (SF_6), and sulphide (S^{2-}).

The pH of groundwater samples (range 6.78 – 7.81) is circum-neutral to alkaline, with a similar range across all target units. Groundwater from all four lithologies is highly mineralised with median SEC values >1470 µS/cm. GGA01, installed in the Glasgow Upper mine working, had the most highly mineralised groundwater with a range of 2697 µS/cm – 3002 µS/cm. This range is significantly higher than those found in the groundwater of other boreholes screened into the Glasgow Upper mine workings: GGA04 (1597 µS/cm – 1669 µS/cm) and GGA07 (1664 µS/cm – 1756 µS/cm). The Glasgow Main mine workings boreholes, GGA05 and GGA08, had a combined SEC range of 1570 µS/cm – 1658 µS/cm. The range of recorded groundwater temperatures is largest in the superficial deposits (10.8°C – 15.1°C), reflecting the near-surface environment. The bedrock and mine workings all have similar ranges (bedrock 10.3°C – 12.6 °C, Glasgow Upper mine workings 10.6 °C – 13.3 °C, Glasgow Main mine workings 10.5 °C – 13.6 °C). In all target units the dissolved oxygen concentration is very low, the medians range from 0.23 mg/L to 0.31 mg/L.

In general major elements and physio-chemical parameters measured in the groundwater samples have concentration ranges similar to those found in bedrock and mine workings across the Carboniferous sedimentary aquifers of the Midland Valley (Ó Dochartaigh et al., 2011). The water from most groundwater samples is unchanged from pumping tests conducted in early 2020

(Palumbo-Roe et al., 2021). Groundwaters are HCO_3 type, with no dominant cation. However, groundwater in GGA01 has evolved since the pumping test and now has Ca-SO_4 type water. Oxidation of iron sulphide minerals (e.g. pyrite) could have caused the dominance of the SO_4 anion in GGA01 groundwaters.

Dissolved organic carbon (as NPOC) has the largest range and the highest concentrations in the superficial deposits' groundwaters (3.44 mg/L – 16.49 mg/L), the highest concentrations were all found in the groundwater at GGB04 (4.51 mg/L – 16.49 mg/L). Broadly similar concentrations were recorded in the bedrock (1.03 mg/L – 3.37 mg/L) and mine workings (Glasgow Upper mine workings: 1.91mg/L – 3.16 mg/L, Glasgow Main mine workings: 2.10 mg/L – 3.04 mg/L). The Ammonium (NH_4) concentrations are high in all Glasgow Observatory groundwaters, with similar median values in all target units (12.9 mg/L – 13.5 mg/L).

There was a large concentration range of trace elements in the Glasgow Observatory groundwaters, but there was no clear distribution. The lowest concentrations, and smallest ranges of each trace element tended to be in the Glasgow Main groundwaters, while the highest median and max concentrations of each trace element were found across the superficial deposits, bedrock and Glasgow Upper groundwaters.

Some PAHs were detected in the superficial and bedrock boreholes, with TPH detected in low concentrations in all units at least once during the sampling period. VOCs were detected in the superficial deposits and Glasgow Main mine workings.

Water stable isotopes, carbon 13 of DIC and residence time data were consistent with findings from the pumping test results (Palumbo-Roe et al., 2021). Groundwaters are recharged by modern recharge from local rainfall.

Median concentrations of dissolved CH_4 in the groundwaters range from 21 µg/L in the superficial deposits to 202 µg/L in the Glasgow Upper mine workings. These values lie within the upper range of groundwaters reported in other studies from Carboniferous sedimentary rocks in the Midland Valley of Scotland (Ó Dochartaigh et al., 2011). The highest concentration was found in borehole GGA04 (991 µg/L) and the superficial deposit borehole GGA09r, the latter being consistent with previous data (Palumbo-Roe et al., 2021). Dissolved CO_2 has a median value of 116 mg/L with little variation between units.

Cluster analysis revealed that the superficial deposits, the bedrock, the mine workings and the surface water samples are each clustered into statistically distinct groups. Borehole GGB04 generally clusters separately from the other boreholes drilled into the superficial deposits. GGB04 displays clear differences in concentrations and trends during the monitoring for a number of trace elements including Co, Mn, Fe, Ni and also in concentrations of NH_4. It is possible that these differences are driven by migration of elements from the made ground at the site into the superficial deposits. Borehole GGA01, drilled into the Glasgow Upper mine workings is also distinct. This can be explained by the behaviour and concentrations of major and trace elements during the monitoring period. Trace elements As, Ba, Co, Fe, Li, Mn, Mo, Ni, Rb, Si, Sr, U and W, all have different concentrations to those observed in the other Glasgow Upper mine working boreholes. The packed waste that GGA01 is drilled into may act as a source for the elevated trace elements.

Surface water samples were taken using an angular beaker and telescopic rod. Samples were taken from the River Clyde and the Tollcross Burn. Surface water samples were analysed for: major, minor, and trace elements, chromium species (Cr (III) and Cr (VI)), non-purgeable organic carbon (NPOC) and total inorganic carbon (TIC), polycyclic aromatic hydrocarbons (PAH), total petroleum hydrocarbons (TPH), and stable isotopes - deuterium (δ^2H), oxygen 18 ($\delta^{18}O$) and carbon 13 of dissolved inorganic carbon (DIC) ($\delta^{13}C_{DIC}$).

While both the Clyde and Tollcross Burn have a near-neutral to alkaline pH and show a narrow range in pH values, the pH values measured at the Tollcross Burn tend to be higher (median 8.4 from the Tollcross Burn and 7.9 from the Clyde). The waters all follow a similar temporal trend, with the highest value each month measured at the Tollcross Burn. The SEC measurements are higher in the Tollcross Burn samples (median 953 µs/cm) than those measured in the River Clyde samples (median 385 µs/cm).

The surface water samples all have similar major ion proportions. The River Clyde samples are Ca-HCO_3 type. The samples taken from the Tollcross Burn are also Ca-HCO_3 type, but can be distinguished from River Clyde samples as they have lower Ca concentrations and higher HCO_3 concentrations.

Most trace elements are present in higher concentrations in the River Clyde than in the Tollcross Burn; exceptions to this are Sr, B, and Rb, which are higher in the Tollcross Burn, and Co, Ni, Zn, As, Y, and Sb, which have similar concentrations in both watercourses. With the exception of Cr, the trace element concentrations are similar between all sites on the River Clyde, which would be expected given these sites are all on a relatively short stretch of the same river. The Cr concentrations are much higher at the sampling site closest to a former chemical works than elsewhere within the observatory. In general, the surface water results are consistent with findings from previous work (Fordyce et al., 2021).

1 Introduction

In 2015, the British Geological Survey (BGS) and the Natural Environment Research Council (NERC) began 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. The UK Geoenergy Observatory in Glasgow is the first of these new centres and is designed with the objective of de-risking key technical barriers to low-temperature shallow mine water heat/storage in an urbanised former mine setting (Monaghan et al., 2017; Monaghan et al., 2021).

The Glasgow Observatory is located in the east of Glasgow city region (Figure 1a) and comprises a network of 12 boreholes located across five sites and six surface water sampling locations (Figure 1b). The sampling locations extend from Dalbeth to Dalmarnock, with the main borehole cluster (11 boreholes) at the Cuningar Loop on the River Clyde. The boreholes, which extend through made ground into the superficial deposits, mined and unmined bedrock were designed to characterise the geological and hydrogeological setting of the research infrastructure. Two of the boreholes are not available for hydrogeological testing. The sampling network of groundwater and surface water 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.

A baseline sampling regime was designed to ensure a greater understanding of the chemistry of the groundwater and surface water around the Observatory. Surface water sampling was carried out monthly at five sites along the River Clyde and one site at the Tollcross Burn from February 2019 to March 2020. The results from these 14 sampling rounds were released as part of "surface water dataset release 1" by Fordyce et al. (2021). Surface water data were released on their own until the new boreholes were drilled. Groundwater sampling was carried out during pumping tests carried out on 10 boreholes at the Glasgow Observatory in January and February 2020. A test pumping data release summarising the results of these samples was produced by Palumbo-Roe et al. (2021). Once the monitoring boreholes were ready to be sampled, it was intended to sample groundwaters and surface waters around the same time in order to gain insight on correlations or impacts between the subsurface and surface. Sampling was, however, halted during the start of the COVID-19 pandemic in April 2020 and restarted in September 2020. Monthly sampling was not completely re-started until February 2021 for the groundwater samples and April 2021 for most of the surface water samples. Six sampling rounds were carried out between September 2020 and May 2021, the data collected from these six rounds are presented in this report, which summarises and provides a brief discussion to the accompanying dataset. Monthly groundwater and surface water sampling from June 2021 onwards will be reported in a separate, future dataset.

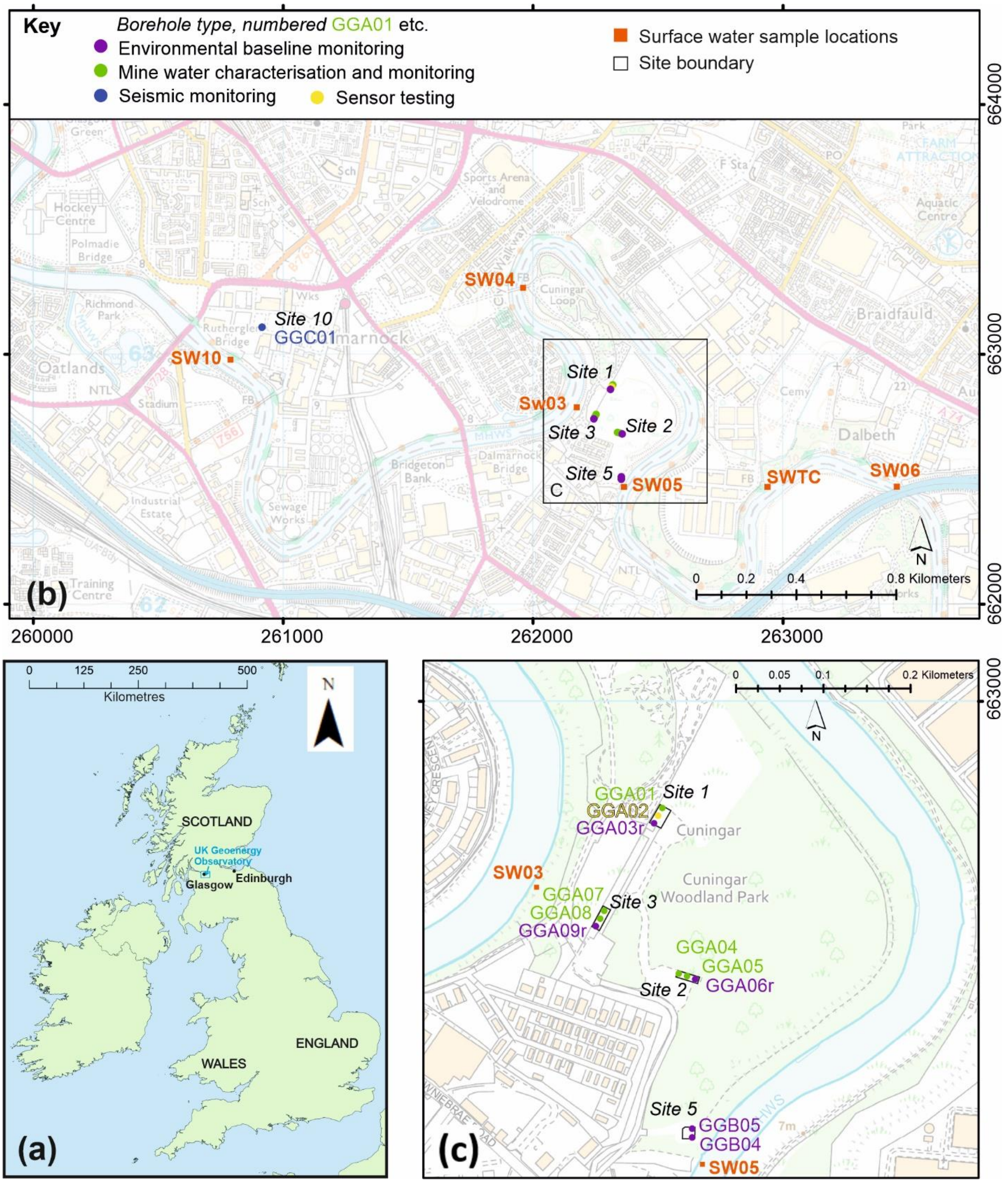

Figure 1 (a) Location of the Glasgow Observatory in the UK (b) position of Observatory sites (c) detail of Cuningar Loop mine water and environmental baseline characterisation and monitoring boreholes. Contains Ordnance Survey data © Crown Copyright and database rights 2022. Ordnance Survey Licence No. 100021290 EUL

1.1 CITATION GUIDANCE

This report accompanies the release of the baseline water chemistry September 2020 - May 2021 dataset.

Any use of the data should be cited to:

Walker-Verkuil K, Bearcock J M, Mulcahy A, Palumbo-Roe B, Macallister D J, Gooddy D C, Darling W G, 2022. UKGEOS Glasgow groundwater and surface water chemistry dataset release (2020–2021). NERC EDS National Geoscience Data Centre. (Dataset) DOI: https://doi.org/10.5285/63f9a557-77d5-4a87-9afc-bd7b099bcd7c

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1.2 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.

The main surface water body adjacent to the Glasgow Observatory at the Cuningar Loop is the River Clyde. The only other open surface water body in the vicinity is the Tollcross Burn. Six surface water sampling locations were selected, comprising five on the River Clyde and one on the Tollcross Burn (SWTC in Figure 1). The locations on the River Clyde were chosen proximal to the borehole cluster at the centre of the Observatory in the Cuningar Loop. In addition, far-field control sample locations on the River Clyde were selected approximately 1.5 km upstream of the Cuningar Loop boreholes at location SW06 and approximately 2 km downstream adjacent to the Site 10 seismic monitoring borehole (Figure 1) (Fordyce et al., 2021).

Table 1 Glasgow Observatory borehole infrastructure, adapted from Monaghan et al. (2021)

Site name	Borehole ID	Borehole type	Target horizon	Screen depth from as-built datum (m)	Screened formation	Screened lithology
Site 1	GGA01	Mine water	Glasgow Upper mine working	44.81-48.41	Scottish Middle Coal Measures	Sandstone roof and Glasgow Upper mine working waste
Site 1	GGA02	Sensor testing	N/A (No borehole screen)	N/A	N/A	N/A
Site 1	GGA03r	Environmental baseline	Bedrock	37.00-39.81	Scottish Middle Coal Measures	Sandstone bedrock
Site 2	GGA04	Mine water	Glasgow Upper mine working	47.40-51.00	Scottish Middle Coal Measures	Sandstone roof and Glasgow Upper mine working position, coal and mudstone
Site 2	GGA05	Mine water	Glasgow Main mine working	83.60-86.30	Scottish Middle Coal Measures	Sandstone roof and Glasgow Main mine working, void to mudstone floor
Site 2	GGA06r	Environmental baseline	Superficial deposits	11.79-13.76	Gourock Sand Member	Sand and gravel
Site 3	GGA07	Mine water	Glasgow Upper mine working	50.91-53.61	Scottish Middle Coal Measures	Mudstone roof and Glasgow Upper mine working, coal pillar and void
Site 3	GGA08	Mine water	Glasgow Main mine working	85.08-87.70	Scottish Middle Coal Measures	Overlying sandstone-siltstone and Glasgow Main mine roadway void
Site 3	GGA09r	Environmental baseline	Superficial deposits	11.43-13.33	Gourock Sand Member	Sand
Site 5	GGB04	Environmental baseline	Superficial deposits	10.09-11.99	Gourock Sand Member	Sand and gravel
Site 5	GGB05	Environmental baseline	Bedrock	42.39-44.19	Scottish Middle Coal Measures	Sandstone bedrock
Site 10	GGC01	Seismic monitoring	N/A (No borehole screen)	N/A	N/A	N/A

2 Methodology

2.1 SUMMARY OF BOREHOLES AND SURFACE WATER SITES SAMPLED

Table 2 summarises the samples that were taken from each sampling round during September 2020 to May 2021. Sampling rounds are irregular, owing to the COVID-19 pandemic.

Table 2 Sites sampled during each of the six sampling rounds.

	September 2020	December 2020	February 2021	March 2021	April 2021	May 2021
Site 1	X	X	X	X	X	X
Site 2	X	X	X	X	X	X
Site 3	X	X	X	X	X	X
Site 5	X	X	X	X	X	X
SW03	X				X	X
SW04	X				X	X
SW05	X	X		X	X	X
SW06	X				X	X
SW10	X				X	X
SWTC	X				X	X

2.2 SAMPLING SET-UP

After the boreholes had been drilled they were installed with Boode® borehole casing and cleaned prior to test pumping. The cleaning involved abstraction of water for two hours, or until water quality parameters stabilised. There was a minimum of five days between borehole flushing and commencement of pump tests. As part of the pump tests most boreholes were sampled for chemical analyses after 2 and 4 hours of pumping (Palumbo-Roe et al., 2021). Owing to the Covid-19 pandemic it was then five to seven months before each borehole was sampled.

The groundwater sampling of the 10 borehole locations was carried out by pumping the groundwater with either a submersible or bladder pump (Figure 2). The five mine water and two environmental monitoring bedrock boreholes were pumped using a permanently installed 42 mm SS High Performance Bladder Pump with a 42 mm drop tube lower in-take assembly extended to the screened section of the borehole. The environmental monitoring superficial boreholes were pumped using a dedicated WaSP P5 submersible pump, which was installed for each sampling round.

Mine working and environmental bedrock boreholes used the pre-installed bladder pumps with a water discharge tube and airline installed between the pump and the surface. They required a 12v battery to power a BP ProPlus (100 psi) Control Unit/Compressor to fill the bladder and control pumping to the surface. The bladder has a volume of 126 ml. The controller was set to an appropriate fill and discharge time to allow most efficient pump rate, which was usually around fill time 10s and discharge time 10s. An efficient pump rate is evidenced by a continuous discharge of water, which occurs when the fill time is exactly long enough to completely fill the bladder, and the discharge time matches the time required to discharge the full 126 ml.

On each sampling visit each superficial borehole’s dedicated WaSP submersible pump was gradually lowered, to limit the disruption to the water column, to the desired depth at the screened section. The pump comprised a plastic discharge tube and power cable running to the surface. The power cable was attached to the WaSP-F1 low flow controller, which was powered by a 12v battery. The flow rate was adjusted until it was approximately 500 ml per minute.

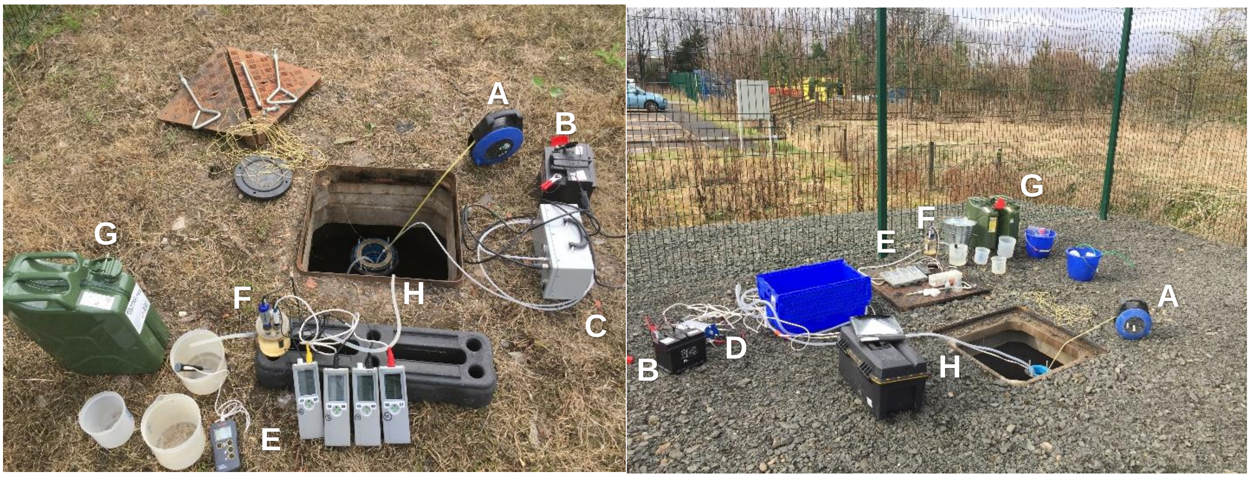

Figure 2 Example of Bladder Pump set up at GGB05 (left) and WaSP submersable set up at GGA09r (right). A: Water level dipper. B: 12v Battery. C: BP ProPlus (100 psi) Control Unit/Compressor connected to air line and battery. D: WaSP-F1 low flow controller connected to battery. E: Field parameter meters and thermometer. F: Flow-through cell. G: Jerry can for water waste dispossal. H: Water discharge tubing from borehole.

The discharge from both set ups was diverted to four of the probes for field parameter measurements (pH, specific electrical conductance (SEC), redox potential (Eh) and dissolved oxygen (DO)) that were placed securely into the flow-through cell. The flow cell discharged to a plastic beaker which had a thermometer probe placed in. Field parameters were taken over 20 minutes, with a minimum three readings taken five minutes apart. GGB05 could not achieve this requirement due to its low recharge rate. After field parameters were taken, the flow cell was disconnected and sampling was done directly from the pump discharge tube. All waste water was collected in a jerry can and discharged offsite at a suitable drain.

2.3 FIELD PARAMETER MEASUREMENTS AND FIELD OBSERVATIONS

At each sample site measurements of key physico-chemical parameters and bicarbonate were obtained in the field. The equipment and methodology were the same as that used by Palumbo-Roe et al. (2021) when sampling groundwaters, and the same as Fordyce et al. (2021) when sampling surface waters. Extensive description of the methodology is contained within those reports.

2.4 SAMPLE COLLECTION

The groundwater was sampled for the following analyses:

- Major, minor, and trace elements
- Chromium species (Cr (III) and Cr(VI))
- Non-purgeable organic carbon (NPOC) and total inorganic carbon (TIC)
- Polycyclic aromatic hydrocarbons (PAH)
- Total petroleum hydrocarbons (TPH)
- Volatile organic compounds (VOC)
- Stable isotopes - deuterium (δ^2H), oxygen 18 (δ^{18}O) and carbon 13 of dissolved inorganic carbon (DIC) ($\delta^{13}C_{DIC}$)
- Ammonium (NH_4)
- Radon (Rn)
- Methane, ethane and carbon dioxide (CH_4, C_2H_6, CO_2)
- Chlorofluorocarbons (CFC-12 and CFC-11)
- Sulphur hexafluoride (SF_6)
- Noble gases - helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) (round 17 only).
- Sulphide (S^{2-}) (for limited samples in round 15 only)

The surface water was sampled for the following analyses:

- Major, minor, and trace elements
- Chromium species (Cr (III) and Cr(VI)
- Non-purgeable organic carbon (NPOC) and total inorganic carbon (TIC)
- Polycyclic aromatic hydrocarbons (PAH)
- Total petroleum hydrocarbons (TPH)
- Stable isotopes - deuterium ($\delta^{2}H$), oxygen 18 ($\delta^{18}O$) and carbon 13 of dissolved inorganic carbon (DIC) ($\delta^{13}C_{DIC}$)

With the exception of noble gases, Rn and S^{2-} the sampling techniques are described in detail in previous UKGEOS publications (Fordyce et al., 2021; Palumbo-Roe et al., 2021). Noble gas samples had been taken during the pumping tests, but none of the samples were viable, while Rn and S^{2-} were new measurements in September 2020 (sampling round 15).

Radon was added to the groundwater sampling suite, and was sampled at every groundwater site from round 15 onwards. Three samples for the analysis of S^{2-} were taken during round 15 only. These samples were taken to inform the design of the geothermal infrastructure at the Glasgow Observatory . Each sample was taken from a different target horizon: bedrock (GGA05), Glasgow Upper mine workings (GGA07) and Glasgow Main mine workings (GGA08). Noble gases were sampled during round 17 only.

2.4.1 Collection of unfiltered water sample for radon analysis

The samples for Rn were analysed in Edinburgh by Scottish Water. Amber glass vials provided by Scottish Water and pre-dosed with sodium thiosulphate were filled directly from the pump tubing, minimising any interaction with air. The samples were stored in a cool box with ice packs and transferred to a refrigerator on return to the laboratory.

2.4.2 Collection of unfiltered water sample for sulphide analysis

The samples for S^{2-} were analysed at an external laboratory, SOCOTEC, who provided all bottles and pre-prepared buffer for sample collection. An unfiltered water sample was fixed on site using SAOB (sulphide antioxidant buffer). The buffer is a mixture of sodium hydroxide (NaOH), ethylenediaminetetraacetic acid (EDTA) and ascorbic acid ($C_6H_8O_6$). A 60 mL HDPE bottle, pre-filled with SAOB (Sulphide A), was decanted into a 120 mL HDPE bottle (Sulphide B), then the Sulphide A bottle was filled to the brim with unfiltered sample water and transferred to the Sulphide B bottle. Whilst in the field the samples are stored with ice packs, and refrigerated on return to the laboratory.

2.4.3 Collection of unfiltered water for noble gas analysis

While samples for noble gases have been taken previously at the Glasgow Observatory (Palumbo-Roe et al., 2021), viable samples were not collected, so the methodology was not previously reported. Samples were collected directly from the sample tubing, connected to copper piping of approximately 7ml capacity. Either end of the tubing was clamped gradually, in turn, while the water was flowing to ensure air was excluded.

2.5 SAMPLE TRANSPORT AND ANALYSES

All 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 S^{2-} samples were sent, with ice packs, to the BGS laboratories in Keyworth, where they were refrigerated before being couriered the same day to SOCOTEC laboratory in Burton-on-Trent for next day delivery. The turnaround time for the results was seven days, or better.

Samples for major, minor and trace element analysis (including Cr speciation), NPOC and TIC, stable isotopes, were analysed at the BGS laboratories in Keyworth. Ammonium was analysed at Wallingford on UKCEH equipment and the dissolved gas, CFC, SF6, and nobles gas samples were analysed at BGS Wallingford. The TPH, PAH, Radon and VOCs were analysed by the Scottish Water laboratory in Edinburgh.

A detailed description of sample analysis is provided in Fordyce et al. (2021) and Palumbo-Roe et al. (2021), and a summary is provided in Appendix 1, along with discussion of the quality control of the data presented in this report. Where parameters are presented for the first time in the Glasgow Observatory (Rn, S^{2-}, noble gases) the methodology is presented in Appendix 1.

3 Data Presentation

3.1 DATASET

3.1.1 Chemical data

The dataset that accompanies this report is presented in Excel® table format:

- Dataset name: UKGEOS Glasgow groundwater and surface water chemistry dataset release (2020–2021)
- Filenames: UKGEOSGlasgow_GroundWaterChemData1_Release.xlsx, UKGEOSGlasgow_SurfaceWaterChemData2_Release.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 samples collected during baseline monitoring between September 2020 and May 2021. 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 contamination present at site.

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.

3.2 DATA ANALYSIS IN THIS REPORT

In this report, a summary of the results of the baseline monitoring of the groundwater and surface water within Glasgow Observatory is presented. A short discussion of the results follows. Where appropriate the boreholes are grouped according to their target horizon (superficial deposits boreholes, bedrock boreholes, Glasgow Upper mine workings and Glasgow Main mine workings boreholes). Summary statistics and graphs for this report were prepared in Microsoft ® Excel® and R 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 (Templ 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), bicarbonate (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), ammonium (NH_4), and dissolved organic carbon (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 diagrams in Figure 3, Figure 4 and Figure 9 (Piper, 1944) to assess water type were generated using R/ RStudio® (R Core Team, 2020) and the smwrGraphs package (Lorenz and Diekoff, 2017). The Mineral saturation indices were determined using the PHREEQC modelling package (Parkhurst and Appelo, 1999). The plots in Appendix 3 and Appendix 4 were generated using R/ RStudio® (R Core Team, 2020) and the ggplot2 package.

4 Results

4.1 GROUNDWATER

In the tables and discussion below the boreholes are grouped according to their target horizons. In depth order, from shallow to deep, these are: superficial deposits, bedrock, Glasgow Upper mine workings, and Glasgow Main mine workings. Time-series graphs of the period covered in this report are presented in Appendix 3, while box and whisker plots display the data distribution in Appendix 4. In the section below the results are discussed with regards to the data distribution, and where relevant any time series changes are reported. As sampling did not occur on consecutive months, temporal variations may not be clear in the available data.

4.1.1 Physico-chemical parameters

Table 3 summarises the physico-chemical parameters measured during water monitoring sampling at the Glasgow Observatory boreholes between September 2020 and May 2021.

The pH (range 6.78 – 7.81) is circum-neutral to alkaline, with a similar range across all lithologies. At each site there are pH variations of around 0.5 pH units. However, there are no clear temporal patterns associated with these variations.

The recorded groundwater temperature shows the largest range in the superficial deposits (10.8°C –15.1°C), reflecting the near-surface environment. The bedrock and mine workings have similar ranges (bedrock 10.3°C – 12.6 °C, Glasgow Upper mine workings 10.6 °C – 13.3 °C, Glasgow Main mine workings 10.5 °C – 13.6 °C). It should be noted these measurements were from September 2020 to May 2021, no samples were taken during the hotter summer months. The coldest groundwater temperatures were measured between December and March in the superficial groundwaters, and during February and March for the bedrock and mine workings groundwaters.

There was a large range of Eh measurements (corrected to the standard hydrogen electrode (SHE) using temperature-dependent conversion tables appropriate to the VWR® probe) in all horizons, so a generalisation of these results should be treated with some caution. The median values show that the mine workings' groundwaters are the most reduced, with values of 73 mV in the Glasgow Upper mine working and 53 mV in the Glasgow Main. At GGA03r the measured Eh reduces from 400 mV in September 2020 to <100 mV in May 2021. However, duplicates taken in December 2020 gave Eh readings with 150 mV difference. At GGA07 the groundwater's Eh reduced from c. 80 mV in September 2020 to c. -15 mV in February 2021, before recovering to 65 mV in May 2021. In boreholes targeting the Glasgow Main mine workings the groundwater Eh reduces from c. 200mV in September 2020 to c. 0 mV between February and April 2021, by May 2021 the Eh was 100 mV. The continued monitoring should clarify if the temporal variations reported in groundwater Eh are seasonal trends, or variation caused by analytical tolerances.

In all horizons the dissolved oxygen (DO) concentration is very low (medians 0.23 mg/L – 0.31 mg/L). The range of DO concentrations is narrow in all target layers, with the largest range found in the near-surface superficial deposits (0.08 – 1.06mg/L). In GGB04 the groundwater DO increased from c. 0.25 mg/L to c. 1 mg/L between September 2020 and February 2021, but by May 2021 the concentration had decreased, back to c. 0.25 mg/L.

Groundwater from all four lithologies is highly mineralised with median specific electrical conductance (SEC) values >1470 µS/cm. GGA01 installed in the Glasgow Upper mine workings was the most highly mineralised groundwater with a range of 2700 µS/cm – 3000 µS/cm. This range is significantly higher than those found in the groundwater of other boreholes screened into the Glasgow Upper mine workings: GGA04 (1600 µS/cm – 1670 µS/cm) and GGA07 (1660 µS/cm – 1760 µS/cm). The screen in GGA01 exposes sandstone, mudstone, coal and about 1.2 m of packed mine waste. In comparison the screen in GGA04 exposes sandstone, mudstone and Glasgow Upper coal seam, while the screen in GGA07 exposes mudstone and Glasgow Upper coal seam present as part of a pillar and a water-filled void. It is likely that these differences and especially the presence of mine waste, influence the observed higher range in SEC in GGA01. In March 2021 there was a significant drop in SEC at GGB05 from c. 1660 µS/cm (n=3) to

842 µS/cm, which reverted to c. 1670 µS/cm (n=3) by April 2021. This lower value looks likely to be an outlier, although there is no clear reason why this should be. Continued monitoring should clarify the temporal variability.

The Glasgow Main mine workings' boreholes, GGA05 and GGA08, had a combined SEC range of 1570 µS/cm – 1660 µS/cm. The screened portions of GGA05 and GGA08 exposed sandstone, mudstone, and a water-filled void. Below the screened section and water-filled void in GGA08, the floor of this mine working contains mine waste/debris.

4.1.2 Major and minor ions

4.1.2.1 WATER TYPE

The major ions are presented in Piper diagrams to understand the water type of the groundwaters. Figure 3 presents the data from the superficial and bedrock boreholes, while the data from the mine workings are presented in Figure 4. Plots are interpreted based on the identification of hydrochemical facies (Drever, 1997).

Table 3 Range and median of groundwater physico-chemical parameters from the Glasgow Observatory boreholes between September 2020 and May 2021. Data are split according to screened target horizon.

	Superficial deposits					**Bedrock**				
	Min	**Max**	**Median**	**n**	**n(c)**	**Min**	**Max**	**Median**	**n**	**n(c)**
Parameter										
pH	6.8	7.7	7.2	20	0	6.9	7.5	7.2	14	0
Temperature (°C)	10.8	15.1	11.8	20	0	10.3	12.6	11.1	14	0
Eh (mV) corrected	-5	291	113	20	0	58	396	162	14	0
Dissolved oxygen (mg/L)	0.08	1.06	0.23	20	0	0.13	0.39	0.25	14	0
Specific electrical conductivity (µs/cm)	1220	1660	1470	20	0	843	1700	1580	14	0
	Glasgow Upper mine workings					**Glasgow Main mine workings**				
	Min	**Max**	**Median**	**n**	**n(c)**	**Min**	**Max**	**Median**	**n**	**n(c)**
Parameter										
pH	6.8	7.8	7.1	20	0	7.0	7.7	7.2	12	0
Temperature (°C)	10.6	13.3	11.4	20	0	10.5	13.6	11.2	12	0
Eh (mV) corrected	-15	152	73	20	0	-17	219	53	12	0
Dissolved oxygen (mg/L)	0.11	0.69	0.31	20	0	0.27	0.92	0.31	12	0
Specific electrical conductivity (µs/cm)	1600	3000	1730	20	0	1570	1660	1630	12	0

n = number of samples, n(c) = number of samples censored

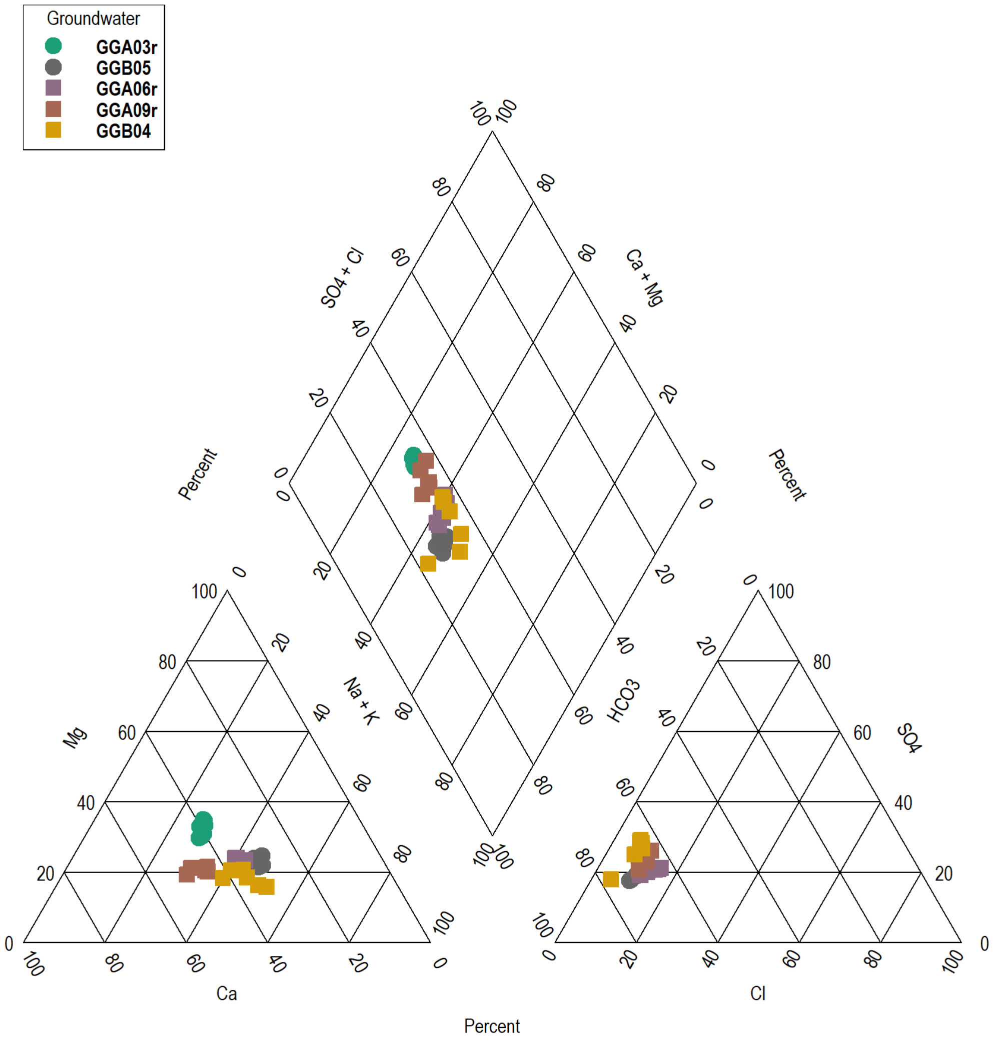

Figure 3 Groundwater piper-plots. Squares represent bedrock boreholes and circles boreholes drilled into the superficial deposits.

All the superficial and bedrock groundwaters are HCO_3 type with no dominant cation (Figure 3). While there is some variation in cation proportions, it is not possible to distinguish between groundwaters sampled from the superficial deposits and the bedrock.

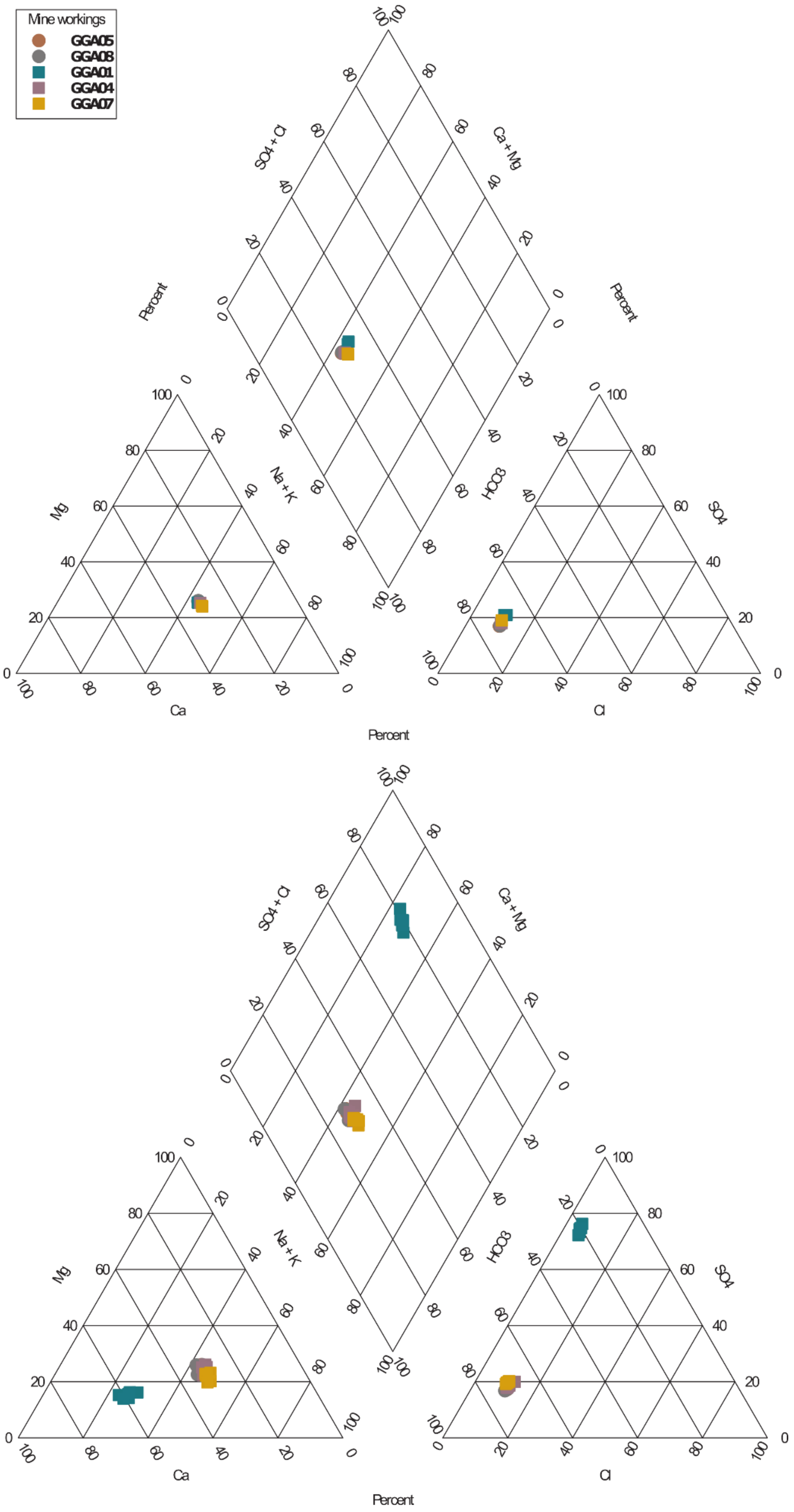

Figure 4 Mine workings piper plots. Squares represent boreholes drilled into Glasgow Upper mine workings and circles boreholes drilled into Glasgow Main mine workings. The plot on the top shows samples from the boreholes taken during the pumping test. The plot on the bottom shows samples taken from the boreholes during the baseline monitoring.

During the pumping tests, reported in full in Palumbo-Roe et al. (2021), the groundwaters sampled in all boreholes targeting mine workings were HCO_3 type with no dominant cation (Figure 4). After a gap of five to seven months the baseline monitoring commenced, and the groundwater samples taken over the following nine months form two distinct clusters on the Piper diagram (Figure 4). GGA01 plots separately from the remaining mine workings' groundwaters, with Ca-SO_4 type water. The water from all the other mine workings is unchanged from the pumping tests, they are HCO_3 type, with no dominant cation. While there is no dominant cation, there is less Ca and more Na+K than GGA01, and the Mg proportion is similar.

4.1.2.2 MAJOR IONS

Minimum, maximum and median values of the major ions in groundwater samples are presented in Table 4 and Table 5.

With the exception of GGA01 (331 mg/L – 419 mg/L), which skews the maximum value for the groundwaters in the Glasgow Upper mine workings, Ca is present at every borehole within the Glasgow Observatory within a relatively narrow range (97 mg/L – 149 mg/L). The Ca concentration increases slightly, but consistently over the course of the reported monitoring period in groundwaters at GGA01 (from 331 mg/L to 419 mg/L) and GGB04 (from 97 mg/L to 123 mg/L).

Magnesium concentrations are all within 43 mg/L – 77 mg/L, except for those within the superficial deposits (28 mg/L – 49 mg/L), which have lower concentrations.

Sodium and K are generally higher within the mine workings' groundwaters (Na range 163 mg/L – 211 mg/L, median 179 mg/L; K range 18 mg/L – 31 mg/L, median 19 mg/L) than those in the superficial deposits and bedrock boreholes (Na range 89 mg/L – 193 mg/L, median 150 mg/L; K range 9 mg/L – 21 mg/L, median 15 mg/L). The highest Na and K concentrations were measured at GGA01. Sodium at GGB04 showed a slight but consistent decrease over the monitoring period (178 mg/L – 135 mg/L).

The lowest HCO_3 concentrations were measured in groundwaters from GGA01 (444 mg/L – 488 mg/L). Concentrations in the superficial deposits' groundwaters (552 mg/L – 765 mg/L) are generally lower than in the rest of the groundwaters (711 mg/L – 905 mg/L).

The chloride groundwater concentration was generally similar across all samples, the largest range was within the superficial deposits (23 mg/L – 96 mg/L), all other measured values were within this range.

Sulphate had a large groundwater concentration range, on account of high values at GGA01. With the exception of GGA01 (which steadily increased from 1160 mg/L to 1410 mg/L), the SO_4 was generally similar across all groundwater samples, and the range of values in groundwaters sampled at boreholes within the superficial deposits (115 mg/L – 223 mg/L) encompassed all other measured values.

4.1.2.3 MINOR ELEMENTS

Minimum, maximum and median values of the minor elements in groundwater samples are presented in Table 4 and Table 5.

Phosphorus is generally present in low concentrations. The groundwaters in the superficial deposits have the largest range of total P (0.01 mg/L – 0.043 mg/L) with all other groundwater measurements within the range <0.005 mg/L – 0.017 mg/L.

Silicon measured in groundwaters was highest at GGA01 (13.4 mg/L – 14.8 mg/L), the widest range of concentrations was found in the superficial deposits (5.29 mg/L – 8.49 mg/L), with all other groundwater Si concentrations measured within the range of 5.02 mg/L – 6.69 mg/L.

The halogen elements have narrow concentration ranges across all the groundwaters: the bromide (Br) concentrations are all within the range 0.21 mg/L – 0.66 mg/L, while the fluoride (F) concentrations are within the range <0.1 mg/L – 0.3 mg/L.

The NO_3 measured in the groundwaters are mostly below detection limits. The exceptions to this are one detection in the Glasgow Upper mine workings (0.33 mg/L), and most of the analyses from bedrock borehole GGA03r (0.34 mg/L – 1.56 mg/L).

Sulphide, which was analysed at three boreholes during round 15, was measured at 0.02 mg/L (GGA05, a borehole in the bedrock, and GGA08 a borehole in Glasgow Main mine workings) and 0.92 mg/L (GGA07 a borehole in Glasgow Upper mine workings).

4.1.3 Dissolved organic carbon

Minimum, maximum and median values of dissolved organic carbon (as NPOC) in groundwater samples are presented in Table 4 and Table 5 with the major and minor ions.

The NPOC had the largest range and the highest concentrations in the superficial deposits' groundwaters (3.44 mg/L – 16.5 mg/L), the highest concentrations were all found in the groundwater at GGB04 (4.51 mg/L – 16.5 mg/L). Broadly similar concentrations were recorded in the bedrock (1.03 mg/L – 3.37 mg/L) and mine workings (Glasgow Upper 1.91mg/L – 3.16 mg/L, Glasgow Main: 2.10 mg/L – 3.04 mg/L).

Table 4 Summary of the major ions and minor elements from groundwater samples retrieved from the Glasgow Observatory boreholes targeting the superficial deposits and bedrock during samping between September 2020 and May 2021

		Superficial deposits					**Bedrock**				
		Min	**Max**	**Median**	**n**	**n(c)**	**Min**	**Max**	**Median**	**n**	**n(c)**
Major ions (mg/L)											
Calcium	Ca	96.9	149	117	20	0	104	142	124	14	0
Magnesium	Mg	28.2	48.9	39.6	20	0	45.5	76.7	57.8	14	0
Sodium	Na	89.1	178	150	20	0	105	193	144	14	0
Potassium	K	9.20	19.7	14.6	20	0	9.76	21.0	14.4	14	0
Bicarbonate (field measured)	HCO_3	552	765	675	20	0	711	905	752	14	0
Chloride	Cl	22.7	96.1	64.6	20	0	51.8	72.9	61.0	14	0
Sulphate	SO_4	116	222	179	20	0	163	222	194	14	0
Total Alkalinity	HCO_3	605	772	694	14	0	739	834	823	9	0
Minor ions (mg/L)											
Phosphorus – total	P	0.010	0.043	0.016	20	0	<0.005	0.01	<0.005	14	13
Sulphur – total	S	41.7	86.5	66.1	20	0	50.0	84.0	65.1	14	0
Silicon	Si	5.29	8.49	6.16	20	0	5.18	6.69	5.88	14	0
Bromide	Br	0.21	0.54	0.44	20	0	0.43	0.66	0.54	14	0
Fluoride	F	0.06	0.28	0.12	20	0	0.08	0.30	0.16	14	0
Nitrate	NO_3	<0.15	<0.3	<0.3	20	20	<0.03	1.56	<0.3	14	8
NPOC (mg/L)		3.44	16.5	3.94	20	0	1.03	3.37	2.01	14	0

n = number of samples, n(c) = number of samples censored

Table 5 Summary of the major ions and minor elements from groundwater samples retrieved from the Glasgow Observatory boreholes targeting the mine workings during samping between September 2020 and May 2021

		Glasgow Upper mine workings					Glasgow Main mine workings				
		Min	**Max**	**Median**	**n**	**n(c)**	**Min**	**Max**	**Median**	**n**	**n(c)**
Major ions (mg/L)											
Calcium	Ca	103	420	110	20	0	107	113	108	12	0
Magnesium	Mg	43.3	67.3	51.4	20	0	46.2	56.4	51.8	12	0
Sodium	Na	173	211	191	20	0	163	179	170	12	0
Potassium	K	17.9	31.4	19.5	20	0	17.5	20.4	19.0	12	0
Bicarbonate (field measured)	HCO_3	444	836	775	20	0	780	803	785	12	0
Chloride	Cl	63.9	81.5	68.5	20	0	68.5	72.5	71.3	12	0
Sulphate	SO_4	150	1410	181	20	0	145	157	152	12	0
Total Alkalinity	HCO_3	371	847	805	13	0	803	817	809	8	0
Minor ions (mg/L)											
Phosphorus - total	P	<0.005	0.017	0.007	20	7	<0.005	0.015	0.012	12	1
Sulphur – total	S	54.7	472	66.4	20	0	53.0	60.6	55.3	12	0
Silicon	Si	5.02	14.8	6.44	20	0	5.03	5.74	5.27	12	0
Bromide	Br	0.42	0.67	0.54	20	0	0.41	0.48	0.45	12	0
Fluoride	F	<0.1	0.29	0.19	20	1	0.134	0.272	0.190	12	0
Nitrate	NO_3	<0.15	0.33	<0.3	20	19	<0.15	<0.3	<0.3	12	12
NPOC (mg/L)		1.91	3.16	2.38	20	0	2.10	3.04	2.29	12	0

n = number of samples, n(c) = number of samples censored

4.1.4 Trace elements

For a full list of all trace elements tested, refer to Appendix 2. Table 6 and Table 7 provide a summary of those trace elements recorded in concentrations at least 1 order of magnitude above the laboratory detection limit in more than one sample for each lithology. Appendix 3 shows time series plots for a selection of trace elements, and the elements of most interest are discussed below.

Overall there was a large concentration range of trace elements in the Glasgow Observatory groundwaters, with no clear distribution. The lowest concentrations, and smallest ranges of each trace element tended to be in the Glasgow Main groundwaters, while the highest median and max concentrations of each trace element were found across the superficial deposits, bedrock and Glasgow Upper groundwaters. The superficial deposits and Glasgow Upper groundwaters tended to have the largest ranges on account of each category having one borehole that tended to be different from the rest of the boreholes in that category (GGB04 and GGA01).

4.1.4.1 SUPERFICIAL DEPOSITS

In the groundwaters from the superficial deposits the concentration ranges of trace elements are usually similar at each site; exceptions to these are Ni, Fe, Mn, and Co in the groundwaters at GGB04. Nickel is >7.5 times higher in the groundwaters at GGB04 than the remaining groundwater samples from superficial deposits. With the exception of samples taken in December 2020, Co, Mn, and Fe are at least 1.5, 1.9, and 3.4 times higher respectively in GGB04 groundwater samples than in the remaining groundwater samples from superficial deposits. At GGB04 groundwater samples had high concentrations of Ba, Co, Fe, Mn, and Sr (294 µg/L, 9.8 µg/L, 8450 µg/L, 5310 µg/L, and 839 µg/L, respectively) in September 2020, which dropped to concentrations of 210 µg/L, 1.09 µg/L, 2100 µg/L, 4900 µg/L, and 746 µg/L, respectively, in December 2020, and increased steadily throughout the rest of the monitoring period to concentrations of 361 µg/L, 8.5 µg/L, 8840 µg/L, 5820 µg/L and 921 µg/L, respectively, in May 2021. Continued monitoring should help to identify if these temporal changes are affected by seasonality or caused by sampling or analysis error.

4.1.4.2 BEDROCK

In the bedrock samples, there are some large differences in trace elements between the two boreholes. Iron is an order of magnitude greater in concentration in groundwaters from GGB05 than those sampled at GGA03r and concentrations at GGB05 decrease from 5080 µg/L to c. 4600 µg/L throughout the monitoring period. Additionally, Li, B, As, and Rb are between 1.5 and 5 times higher in GGB05 groundwaters than those at GGB03r, while Ba, Mn, Mo, and U are 1.4 to 3 times higher in groundwaters sampled at GGA03r than in those at GGB05.

4.1.4.3 MINE WORKINGS

Differences between groundwaters at GGA01 and those at the other Glasgow Upper mine workings sites are evident in the trace element chemistry. In the groundwaters at GGA01 the concentrations of Fe, Co, As, and Ni were steadily increasing over the monitoring period and were between 5 to 12 times higher than in groundwaters at the other Glasgow Upper mine workings sites. Throughout the monitoring period Fe increased in GGA01 groundwaters from c. 32500 µg/L to c. 41200 µg/L, Co increased from c. 7.5 µg/L to c. 9 µg/L, As increased from c. 9.5 µg/L to c. 11.5 µg/L, and Ni increased from c. 14 µg/L to c. 19.7 µg/L. Lithium, Mn, Rb, Sr and U have concentrations between 1.5 and almost 3 times higher in GGA01 groundwaters than in those at the other Glasgow Upper sites, with Mn, Rb and Sr showing an increasing trend. Throughout the monitoring period Mn increased in GGA01 groundwaters from 869 µg/L to 943 µg/L, Rb increased from 62 µg/L to 68 µg/L and Sr increased from c. 3100 µg/L to c. 3550 µg/L. Molybdenum and W in GGA01 were 7-9 times higher than the concentrations measured at the other Glasgow Upper mine workings boreholes. Continued monitoring should help to identify if these temporal changes of iron concentrations and the associated trace elements reflect real trends.

The concentrations of all trace elements in the Glasgow Main groundwaters were largely similar between the boreholes.

4.1.5 Chromium speciation

Chromium species are reported in Table 6 and Table 7. As total Cr concentration measured by ICP-MS is generally low in the groundwaters (usually up to two to three times the LLD of 0.07 µg/L) it is unsurprising that most Cr(III) and Cr (VI) measurements are below the detection limits of 0.04 µg/L and 0.07 µg/L respectively. Of the 66 groundwater samples (including duplicates) Cr(III) is above the detection limit in 24 samples, while Cr(VI) is measured above the detection limit in three samples. Where Cr species have been measured, Cr (III) is the dominant species.

Table 6 Summary of trace elements recorded in groundwater samples from the superficial deposits and bedrock target units one order of magnitude in concentration above the laboratory detection limit

Trace elements (µg/L)		**Superficial deposits**					**Bedrock**				
		Min	**Max**	**Median**	**n**	**n(c)**	**Min**	**Max**	**Median**	**n**	**n(c)**
Barium	**Ba**	63	361	152	20	0	36	67	50	14	0
Strontium	**Sr**	524	921	793	20	0	1930	3730	2750	14	0
Manganese	**Mn**	1720	5820	2260	20	0	377	623	478	14	0
Total iron	**Fe**	742	8840	1500	20	0	10	5080	2420	14	0
Lithium	**Li**	<7	<7	<7	20	20	18	36	25	14	0
Boron	**B**	319	549	446	20	0	177	401	268	14	0
Aluminium	**Al**	1.8	8.0	4.2	20	0	0.9	12.5	1.7	14	0
Titanium	**Ti**	0.07	0.79	0.24	20	0	<0.06	4.02	<0.06	14	12
Vanadium	**V**	0.14	0.79	0.21	20	0	<0.02	0.16	0.04	14	5
Cr-total	**Cr**	0.10	0.97	0.16	20	0	<0.04	0.13	0.06	14	5
Cobalt	**Co**	1.06	9.79	2.39	20	0	3.25	5.23	3.90	14	0
Nickel	**Ni**	2.0	43.5	4.3	20	0	4.9	6.3	5.6	14	0
Copper	**Cu**	<0.05	1.21	0.13	20	1	<0.05	0.41	0.16	14	2
Zinc	**Zn**	0.6	6.1	2.3	20	0	4.6	17.1	6.4	14	0
Gallium	**Ga**	<0.04	0.11	<0.04	20	16	<0.04	<0.09	<0.04	14	14
Arsenic	**As**	0.23	0.82	0.40	20	0	0.17	2.10	1.14	14	0
Selenium	**Se**	<0.07	0.86	<0.07	20	13	<0.07	0.08	<0.07	14	13
Rubidium	**Rb**	5.38	14.4	8.04	20	0	19.8	47.0	32.4	14	0
Yttrium	**Y**	0.02	0.48	0.17	20	0	0.031	0.060	0.038	14	0
Zircon	**Zr**	0.08	0.33	0.14	20	0	0.03	0.07	0.04	14	0
Molybdenum	**Mo**	<0.2	1.1	0.4	20	4	0.4	1.9	1.0	14	0
Cadmium	**Cd**	<0.005	0.011	<0.005	20	16	<0.005	0.015	0.008	14	7
Tin	**Sn**	<0.08	3.84	<0.09	20	11	<0.08	1.45	0.77	14	7
Caesium	**Cs**	<0.04	0.14	0.07	20	3	0.18	0.25	0.22	14	0
Lanthanum	**La**	0.005	0.073	0.055	20	0	0.004	0.017	0.009	14	0
Cerium	**Ce**	0.006	0.135	0.111	20	0	0.008	0.044	0.020	14	0
Praseodymium	**Pr**	<0.003	0.018	0.013	20	3	<0.003	0.005	<0.003	14	12
Neodymium	**Nd**	0.006	0.089	0.058	20	0	<0.005	0.022	0.010	14	2
Samarium	**Sm**	<0.005	0.020	0.012	20	2	<0.005	0.007	<0.005	14	13
Gadolinium	**Gd**	<0.005	0.023	0.018	20	1	<0.005	<0.005	<0.005	14	14
Dysprosium	**Dy**	<0.003	0.056	0.018	20	1	<0.003	0.005	0.003	14	7
Holmium	**Ho**	<0.003	0.021	0.004	20	4	<0.003	<0.003	<0.003	14	14
Erbium	**Er**	<0.003	0.12	0.013	20	1	<0.003	0.004	<0.003	14	9
Thulium	**Tm**	<0.003	0.028	<0.003	20	14	<0.003	<0.003	<0.003	14	14
Ytterbium	**Yb**	0.005	0.317	0.018	20	0	<0.004	0.007	0.004	14	9
Lutetium	**Lu**	<0.003	0.075	0.004	20	5	<0.003	<0.003	<0.003	14	14
Tungsten	**W**	<0.06	0.24	0.06	20	11	<0.06	<0.06	<0.06	14	14
Thallium	**Ti**	<0.02	0.03	<0.02	20	14	0.02	0.07	0.04	14	0
Uranium	**U**	0.36	2.41	1.16	20	0	0.45	0.77	0.59	14	0
Chromium (III)	**Cr**	<0.04	0.56	<0.05	20	11	<0.04	0.15	<0.05	14	9
Chromium (VI)	**Cr**	<0.05	0.06	<0.05	20	18	<0.05	0.06	<0.05	14	13

n = number of samples, n(c) = number of samples censored

Table 7 Summary of trace elements recorded in groundwater samples from the mine workings one order of magnitude in concentration above the laboratory detection limit

Trace elements (µg/L)		**Glasgow Upper mine workings**					**Glasgow Main mine workings**				
		Min	**Max**	**Median**	**n**	**n(c)**	**Min**	**Max**	**Median**	**n**	**n(c)**
Barium	**Ba**	37.1	61.7	53.7	20	0	46.6	51.9	48.2	12	0
Strontium	**Sr**	1810	3640	2380	20	0	1840	2000	1890	12	0
Manganese	**Mn**	335	943	396	20	0	323	354	337	12	0
Total iron	**Fe**	1900	41200	4000	20	0	335	3290	1900	12	0
Lithium	**Li**	28	68	34	20	0	26	35	31	12	0
Boron	**B**	353	472	396	20	0	346	412	399	12	0
Aluminium	**Al**	1.1	26.7	3.3	20	0	0.7	4.8	1.4	12	0
Titanium	**Ti**	0.07	0.89	0.39	20	0	<0.06	0.11	<0.06	12	10
Vanadium	**V**	<0.06	0.49	0.19	20	1	<0.06	0.23	0.09	12	2
Cr-total	**Cr**	0.05	0.18	0.10	20	0	0.09	0.18	0.14	12	0
Cobalt	**Co**	0.35	9.09	1.79	20	0	0.22	0.30	0.25	12	0
Nickel	**Ni**	1.87	19.7	4.05	20	0	1.71	2.14	1.95	12	0
Copper	**Cu**	<0.05	0.61	0.09	20	7	<0.05	0.42	0.09	12	4
Zinc	**Zn**	0.3	19.0	1.1	20	0	0.4	13.3	1.2	12	0
Gallium	**Ga**	<0.04	<0.09	<0.04	20	20	<0.04	<0.09	<0.04	12	12
Arsenic	**As**	0.28	11.6	2.25	20	0	0.05	0.13	0.10	12	0
Selenium	**Se**	<0.07	0.08	<0.07	20	19	<0.07	<0.07	<0.07	12	12
Rubidium	**Rb**	37.7	69.6	40.4	20	0	38.0	41.6	38.9	12	0
Yttrium	**Y**	0.05	0.22	0.11	20	0	0.01	0.14	0.07	12	0
Zircon	**Zr**	0.07	0.24	0.16	20	0	0.02	0.16	0.07	12	0
Molybdenum	**Mo**	<0.2	8.9	1.1	20	5	<0.2	0.6	<0.2	12	7
Cadmium	**Cd**	<0.005	0.010	<0.005	20	19	<0.005	0.010	<0.005	12	11
Tin	**Sn**	<0.08	<0.09	<0.08	20	20	<0.08	0.51	<0.08	12	10
Caesium	**Cs**	0.23	0.37	0.27	20	0	0.13	0.17	0.15	12	0
Lanthanum	**La**	0.008	0.158	0.018	20	0	<0.003	0.016	0.005	12	2
Cerium	**Ce**	0.020	0.260	0.034	20	0	<0.004	0.026	0.010	12	1
Praseodymium	**Pr**	<0.003	0.035	0.004	20	1	<0.003	<0.003	<0.003	12	12
Neodymium	**Nd**	0.012	0.146	0.020	20	0	<0.005	0.019	0.009	12	5
Samarium	**Sm**	<0.005	0.030	0.006	20	7	<0.005	0.006	<0.005	12	10
Gadolinium	**Gd**	<0.005	0.035	0.009	20	3	<0.005	0.007	<0.005	12	9
Dysprosium	**Dy**	0.005	0.027	0.010	20	0	<0.003	0.013	0.006	12	2
Holmium	**Ho**	<0.003	0.006	<0.003	20	15	<0.003	0.004	<0.003	12	11
Erbium	**Er**	0.004	0.016	0.008	20	0	<0.003	0.014	0.006	12	2
Thulium	**Tm**	<0.003	<0.003	<0.003	20	20	<0.003	<0.003	<0.003	12	12
Ytterbium	**Yb**	<0.006	0.014	0.010	20	1	<0.006	0.020	0.012	12	1
Lutetium	**Lu**	<0.003	0.003	<0.003	20	19	<0.003	0.004	<0.003	12	7
Tungsten	**W**	<0.06	1.35	0.12	20	6	<0.06	<0.06	<0.06	12	12
Thallium	**Ti**	<0.02	<0.02	<0.02	20	20	<0.02	<0.02	<0.02	12	12
Uranium	**U**	0.23	1.68	0.83	20	0	0.53	0.63	0.60	12	0
Chromium (III)	**Cr**	<0.04	0.16	<0.05	20	14	<0.04	0.20	<0.05	12	8
Chromium (VI)	**Cr**	<0.05	<0.07	<0.05	20	20	<0.05	<0.07	<0.05	12	12

n = number of samples, n(c) = number of samples censored

4.1.6 PAH, TPH and VOC

4.1.6.1 SUPERFICIAL DEPOSITS

There were two polycyclic aromatic hydrocarbon (PAH) detects in the superficial deposits groundwaters, both were benzo(a)pyrene at GGA6r (0.0021 µg/L) and GGB04 (0.0019 µg/L).

Table 8 summarises the total petroleum hydrocarbon (TPH) results, the majority of which were below the laboratory detection limit.

There were seven volatile organic compounds (VOC) detects, these were: iso propylether (40 µg/L at GGB04), N,N-dimethylaniline (3 µg/L at GGA09r), 1,2,4-trichlorobenzene (1 µg/L at GGA09r), naphthalene (1 µg/L at GGA09r), 1,2,3-trichlorobenzene (1 µg/L at GGA09r) and methyl-ethyl ketone (12 µg/L and 365 µg/L at GGB04).

Table 8 Summary of TPH values min, max and mean values in the superficial deposits

	Min	Max	Median	n	n(c)
TPH (mg/L)					
TPH (C8-C10)	<0.003	0.061	<0.003	17	10
TPH (C10-C40)	<0.042	2.65	<0.042	17	13
TPH (C8-C40)	<0.045	2.71	<0.045	18	14

n = number of samples, n(c) = number of samples censored

4.1.6.2 BEDROCK

There were three PAH detects in the bedrock groundwaters, all in one sample from GGB05: benzo(b)fluoranthene (0.0038 µg/L), benzo(a)pyrene (0.0028 µg/L) and indeno(1,2,3-cd)pyrene (0.0059 µg/L).

On one sampling round there were two TPH fractions (C10-C40 and C8-C40) measured at 1.69 mg/L at GGB05. The C8-C10 fraction was measured close to the detection limit in GGB05 on two sampling rounds and GGA03r on one occasion.

One volatile organic compound (VOC), hexane, was recorded above the laboratory detection limit (1 ug/L at GGA03r).

4.1.6.3 GLASGOW UPPER MINE WORKING

All PAH values were below the laboratory detection limits.

Table 9 summarises the TPH results, the majority were below the laboratory detection limit. There were no detects in the groundwaters at GGA01, while three samples at GGA04 and four samples at GGA07, had at least one TPH detect.

Table 9 Summary of TPH values min, max and mean values in the Glasgow Upper mine workings

	Min	Max	Median	n	n(c)
TPH (mg/L)					
TPH (C8-C10)	<0.003	0.055	<0.003	19	13
TPH (C10-C40)	<0.042	1.82	<0.042	19	15
TPH (C8-C40)	<0.045	1.88	<0.045	19	15

n = number of samples, n(c) = number of samples censored

There were no VOCs detected in the groundwaters in the Glasgow Upper mine workings.

4.1.6.4 Glasgow Main mine working

All petroleum aromatic hydrocarbons (PAH) were below the laboratory detection limit.

On one sampling round there were two TPH fractions (C10-C40 and C8-C40) measured at 1.29 mg/L in GGA08. The C8-C10 fractions was measured close to the detection limit in GGA05 on three occasions.

In one sample at GGA08 there were detects of 5 VOCs: 1,2-Dibromo-3-chloropropane (1 µg/L), N.N-Dimethylaniline (2 µg/L), 1,2,4-trichlorobenzene (1 µg/L), naphthalene (1 µg/L), and 1,2,3-Trichlorobenzene (1 µg/L).

4.1.7 Isotopic composition

The δ^{2}H and δ^{18}O of the groundwater samples fall on the global meteoric water line (GMWL) and display a very narrow range of values (from δ^{2}H –52.9‰ to –50.8‰, median –48.6‰; from δ^{18}O –7.57‰ to –7.23‰, median –7.47‰) (Figure 5). Previous groundwater samples, taken during pumping tests (January-February 2020) fall within these water isotope ranges (Palumbo-Roe et al., 2021) and both confirm the lack of connate water signature in the isotopic composition of the mine waters in the Glasgow Upper and Main mine workings boreholes and instead the dominance of recent meteoric recharge.

No target unit differs in the δ^{18}O median more than 0.1‰, within the uncertainties of the δ^{18}O measurements (Table 10, Figure 5). Although the fairly uniform isotopic signature of groundwater across the Glasgow Observatory conforms with a recharge model lacking localised and preferential flow paths, and averaging the local precipitation, the shallow boreholes GGB05 (bedrock) and GGB04 (superficial deposits), sampled in December 2019, and both at site 5, display an isotope signature more enriched in ^{18}O and ^{2}H isotopes than the majority of groundwater and possibly indicate selective recharge and fractionation processes.

Table 10 $\delta^{13}C_{DIC}$, δ^{18}O and δ^{2}H min, max and median values of groundwaters within each target unit during the monitoring period.

Variable	Target unit	Min	Max	Median	n
$\delta^{13}C_{DIC}$ PDB ‰	Superficial deposits	-17.1	-11.2	-12.0	20
	Bedrock	-11.6	-8.0	-9.8	14
	Glasgow Main	-11.6	-11.2	-11.3	12
	Glasgow Upper	-17.4	-10.5	-11.4	20
δ^{18}O VSMOW2 ‰	Superficial deposits	-7.57	-7.23	-7.45	20
	Bedrock	-7.57	-7.41	-7.48	14
	Glasgow Main	-7.50	-7.38	-7.47	12
	Glasgow Upper	-7.55	-7.34	-7.48	20
δ^{2}H VSMOW2 ‰	Superficial deposits	-52.6	-48.7	-50.4	20
	Bedrock	-52.7	-48.7	-50.9	14
	Glasgow Main	-52.9	-48.6	-50.9	12
	Glasgow Upper	-52.4	-49.2	-50.9	20

n = number of samples

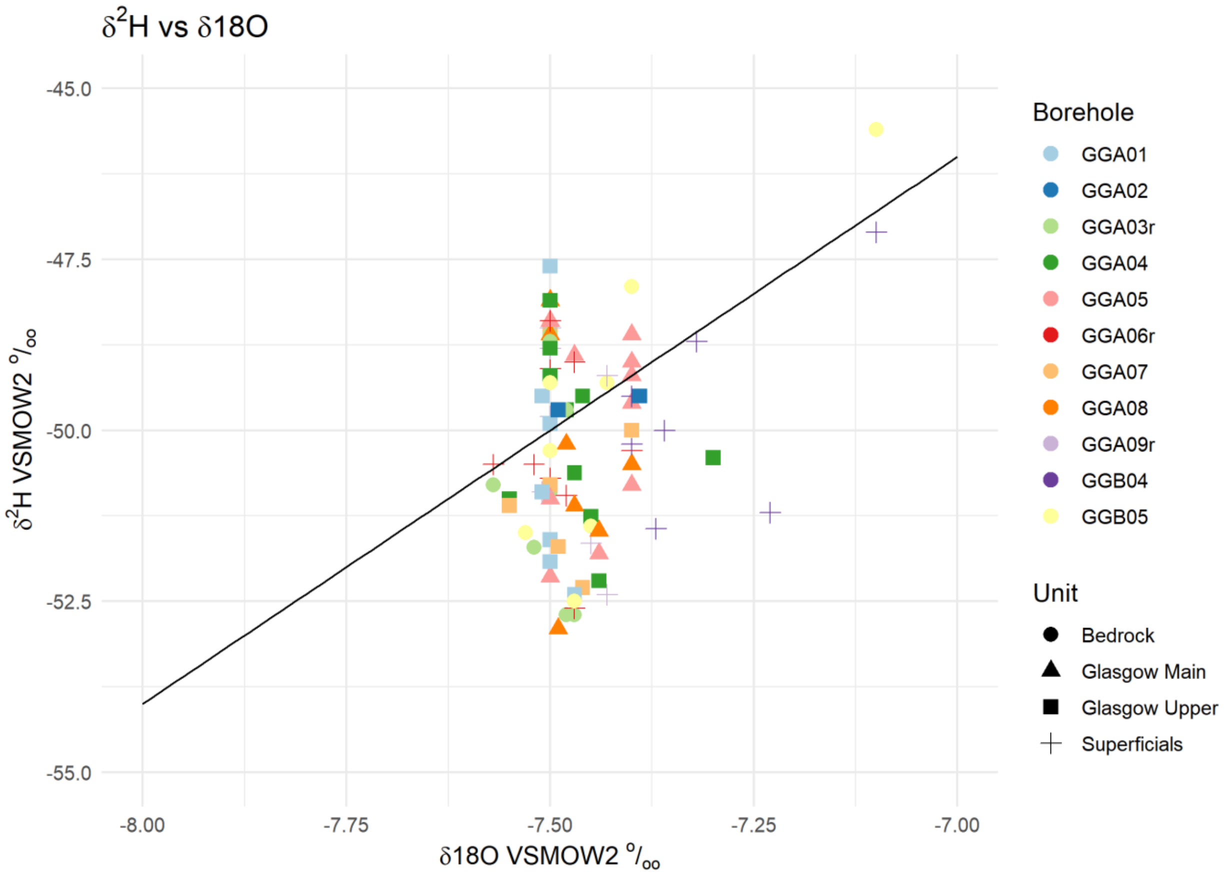

Figure 5 Plot of water δ^{2}H versus δ1^{8}O isotope data with reference to the global meteoric water line (GMWL) (Craig, 1961) in groundwaters grouped by lithological unit, against monthly surface water (cross symbols) for the same monitoring period.

The carbon isotopic composition δ^{13}C of dissolved inorganic carbon (DIC) in the groundwater samples grouped by targeted lithological units is summarised in Table 10. The δ^{13}C$_{DIC}$ values average c. –11‰ for all samples, coupled to high alkalinity, is comparable to previous measurements obtained during pumping test (Palumbo-Roe et al., 2021), (Figure 6).

The δ^{13}C$_{DIC}$ values are more tightly grouped in the Glasgow Main groundwaters (range from –11.6‰ to –11.2‰, median –11.3‰) than in the other groups (bedrock range from –11.6‰ to –8.04‰, median –9.8‰; Glasgow Upper range from –17.4‰ to –10.5‰, median –11.4‰; superficial deposits range from –17.1‰ to –11.2‰, median –12.0‰) (Table 10). The larger spread of δ^{13}C$_{DIC}$ values in the bedrock groundwaters is due to samples from GGA03r borehole, which group around a higher value of c. –8‰, and consistently with the value measured during pumping test. Instead, samples from the GGB04 borehole in the superficial deposits display a lower δ^{13}C$_{DIC}$ value of c. –17‰ and lower alkalinity than the other boreholes GGA09r and GGA06r in the superficial deposits. Most of the samples from the Glasgow Upper borehole GGA01 have δ^{13}C$_{DIC}$ values from –11.4‰ to –10.5‰, except for the sample in February 2021 with δ^{13}C$_{DIC}$ –17.4‰; all GGA01 samples are also characterised by a lower alkalinity (444 mg/L – 488 mg/L).

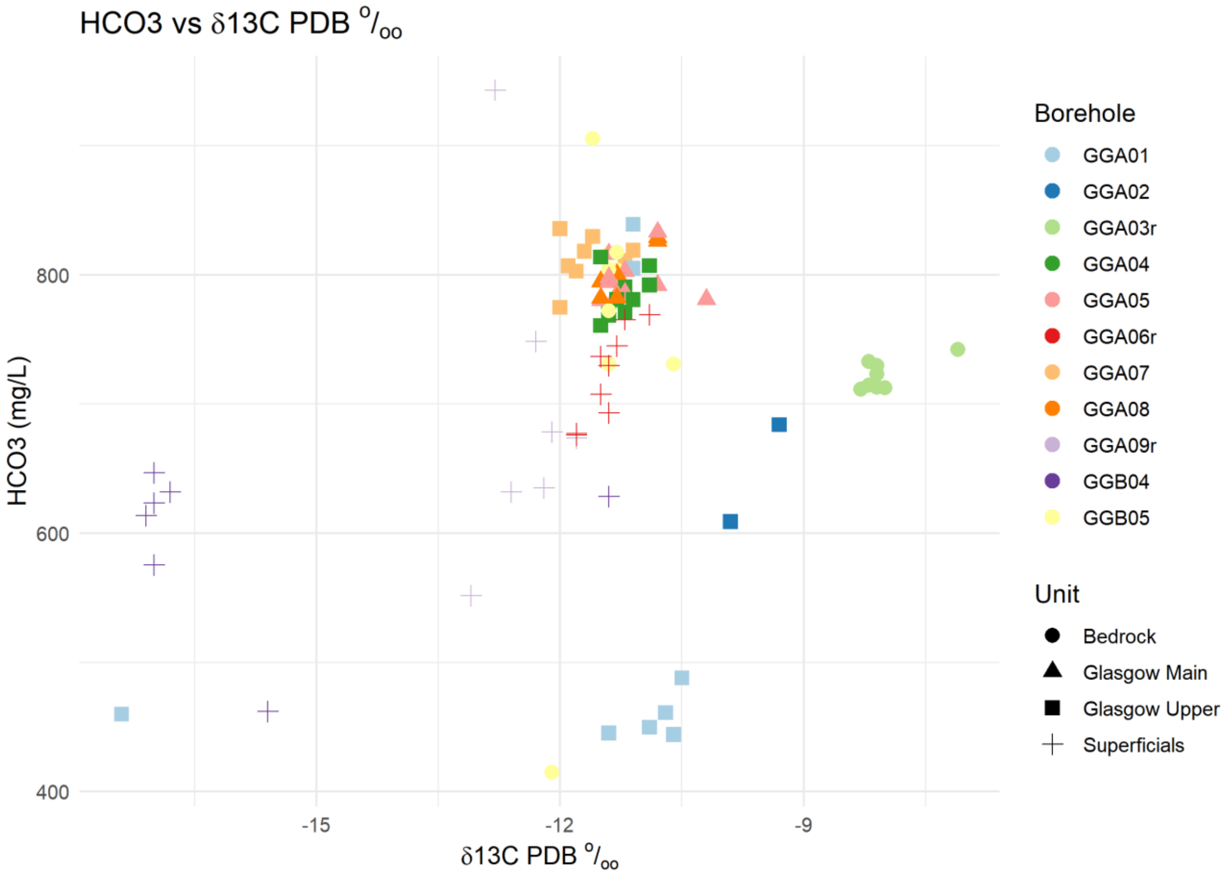

Figure 6 Plot of field-HCO_3 versus $\delta^{13}C_{DIC}$ isotope data in groundwaters from the Glasgow observatory.

4.1.8 Ammonium (NH_4)

While the groundwaters within the Glasgow Upper mine working have the largest range of ammonium (NH_4) concentrations, the median values of all the target units are similar (12.9 mg/L – 13.5 mg/L) (Table 11). The concentrations observed in all the Glasgow Observatory groundwaters are high. Concentrations above 1 mg/L are found in old, reducing groundwaters or as a result of pollution (Shand et al., 2007). Table 11 provides a summary of NH_4 data recorded in groundwater samples for each target unit.

Table 11 Summary of NH_4 data in Glasgow Observatory groundwater sites.

NH_4 (mg/L)	Min	Max	Median	n	n(c)
Superficial deposits	1.79	18.8	12.9	20	0
Bedrock	3.96	14.7	13.4	14	0
Glasgow Upper mine workings	<0.01	18.9	13.5	20	1
Glasgow Main mine workings	2.34	13.3	13.1	12	0

n = number of samples, n(c) = number of samples censored

4.1.9 Dissolved gases

All radon analyses were below the detection limit.

Dissolved methane (CH_4) concentrations are present at low concentrations with a median of 85 µg/L and range between 0.4 µg/L and 991 µg/L. Comparing the range and median CH_4 values (Table 12) across the target units indicates that the superficial deposits have the lowest median CH_4 value of 21 µg/L, followed by the bedrock boreholes (68 µg/L), and Glasgow Main (107 µg/L), while Glasgow Upper has the highest CH_4 median value of 202 µg/L. The box plot of CH_4 data distribution across the different boreholes (Figure 7) shows the presence of significantly higher outliers especially for the Glasgow Upper borehole GGA04 (CH_4 991 µg/L) and the superficial deposit borehole GGA09r. For the latter, relatively high concentrations were already observed in the pumping test (Palumbo-Roe et al., 2021). From analysis of the time series it is noticeable that those high peaks in concentrations correspond to a pattern of higher values in round 15 (September 2020), common to most boreholes (Figure 8). The high variability in space and time of these low dissolved methane concentrations observed in the monitoring boreholes are not uncommon and can be due to many factors including the sampling methodologies, vertical flows and in-well mixing highlighted by Bell et al. (2016). This variability was also shown by the field duplicate RPD% from 5.4 % to >100%.

There was a total of six ethane (C_2H_6) results recorded above the laboratory detection limit of 1 ug/L from all 10 boreholes between September 2020 and May 2021 (Table 12). Three of these results were recorded in GGA04, two in September 2020 due to a duplicate sample being taken and one in March 2021 which was close to the detection limit.

Carbon dioxide (CO_2) concentrations ranged between 85 mg/L and 187 mg/L (median 116 mg/L), with the median values for each lithology group (Table 12) not so dissimilar to the “all borehole” median. The highest value was recorded in the superficial deposit borehole GGA09r (Figure 7).

Table 12 Summary of Dissolved CH_4, C_2H_6 and CO_2 data in Glasgow Observatory groundwater sites.

Variable	Target unit	Min	Max	Median	n	n(c)
Methane (CH_4) (µg/L)	Superficial deposits	0.7	768	21	20	0
	Bedrock	1.9	267	76	14	0
	Glasgow Upper	0.4	388	107	12	0
	Glasgow Main	50	991	202	20	0
Ethane (C_2H_6) (µg/L)	Superficial deposits	<1	8	<1	18	16
	Bedrock	<1	1.5	<1	12	11
	Glasgow Upper	<1	7.2	<1	17	14
	Glasgow Main	<1	<1	<1	10	10
Carbon Dioxide (CO_2) (mg/L)	Superficial deposits	95	187	116	20	0
	Bedrock	85	171	118	14	0
	Glasgow Main	95	144	111	12	0
	Glasgow Upper	90	151	115	20	0

n = number of samples, n(c) = number of samples censored

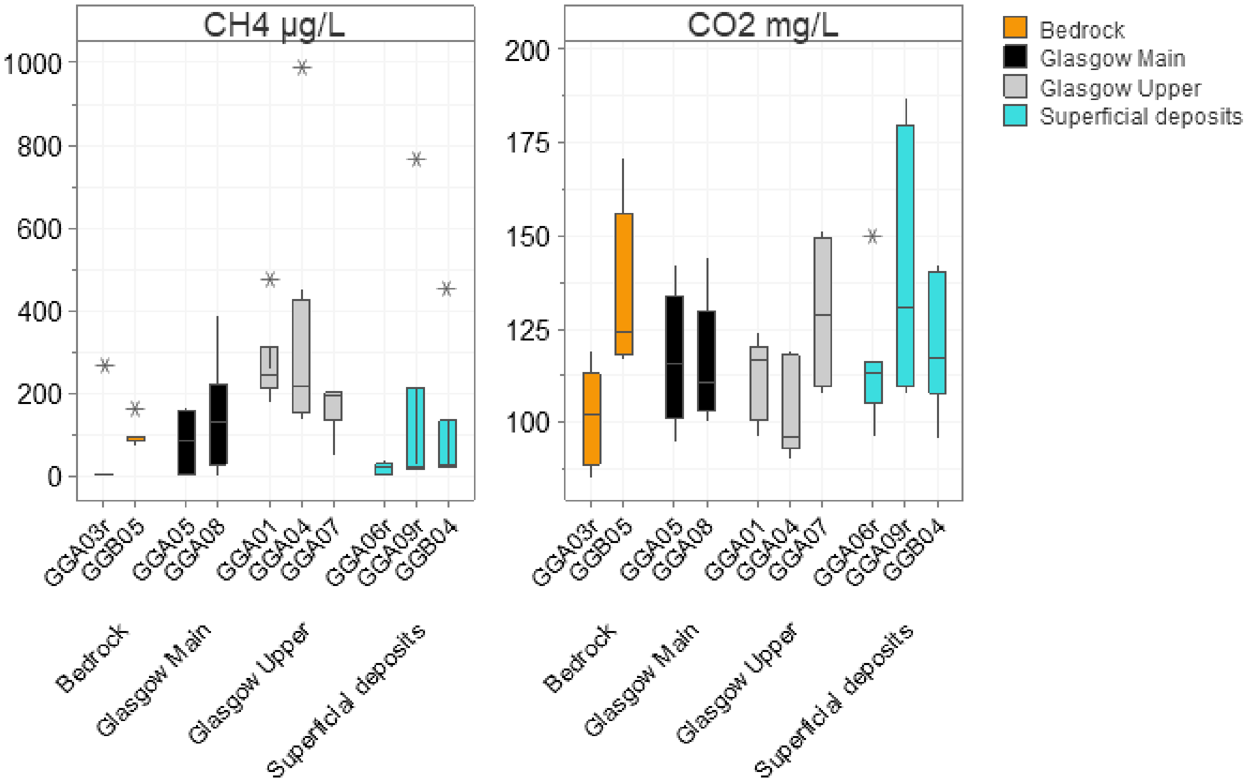

Figure 7 Distribution of methane and carbon dioxide in boreholes grouped by lithology for sampling rounds 15 to 20.

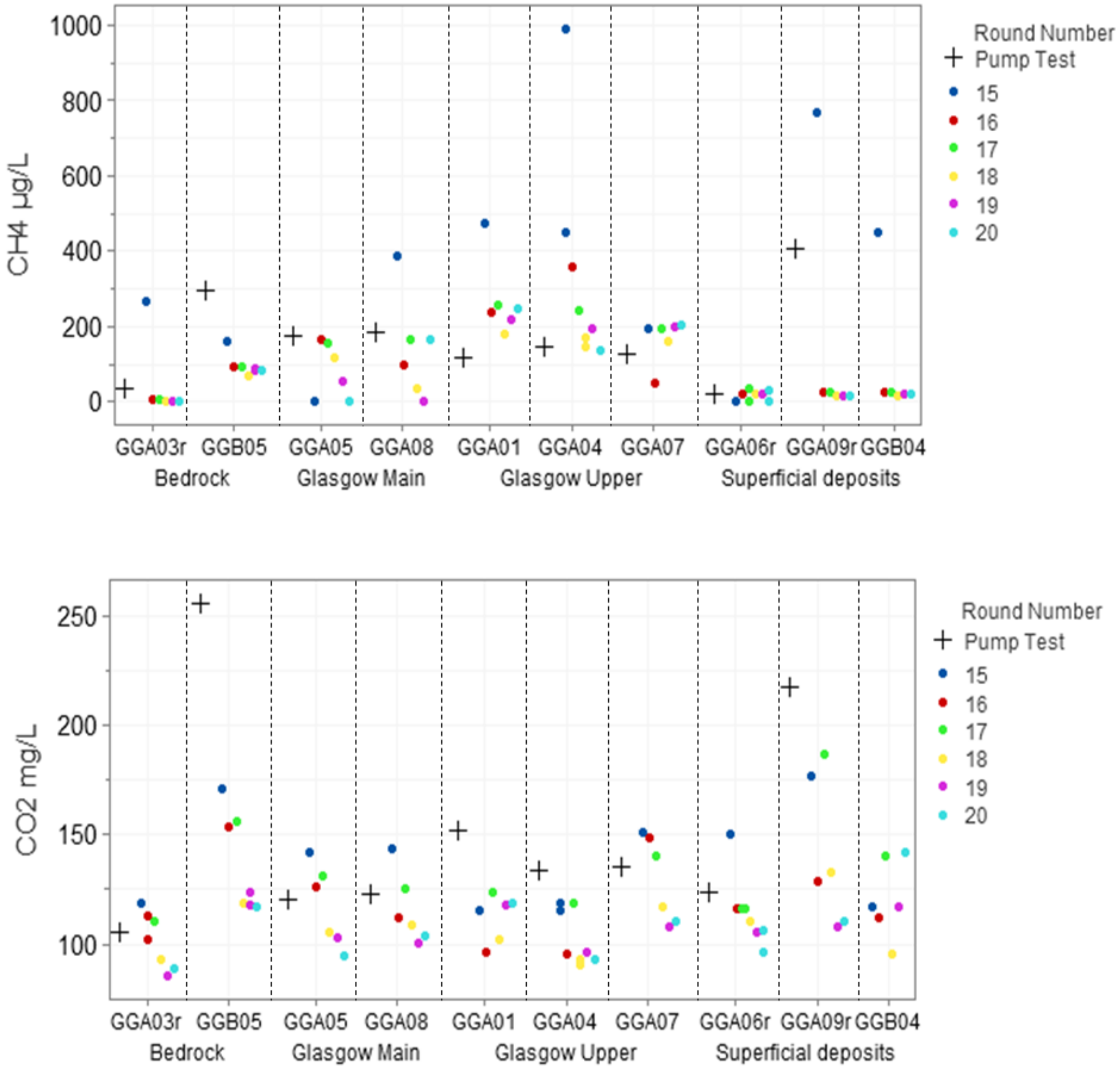

Figure 8 Times series of dissolved CH_4 and CO_2 gas concentrations in boreholes grouped by lithologies, with antecedent pumping test analysis reported for comparison.

4.1.10 CFC and SF_6 data

Data for the sampling that took place in February 2021 for groundwater residence time indicators are shown in Table 13.

Table 13 Groundwater residence time indicators sampling data from February 2021.

Sample	Borehole	CFC-12 pmol/L	CFC-11 pmol/L	SF_6 fmol/L	CFC-12 Modern Fraction	CFC-11 Modern Fraction	SF_6 Modern Fraction	CFC-12 Year of Recharge	CFC-11 Year of Recharge	SF_6 Year of Recharge
GF17-08	GGA06r	0.49	0.20	0.00	0.18	0.04	0.00	1967	1960	<1970
GF17-09	GGA04	0.22	0.26	0.00	0.08	0.05	0.00	1961	1961	<1970
GF17-10	GGA07	0.14	0.27	0.00	0.05	0.06	0.00	1957	1961	<1970
GF17-11	GGA06r	0.51	0.19	0.00	0.19	0.04	0.00	1968	1959	<1970
GF17-12	GGA03r	0.35	0.65	0.03	0.13	0.13	0.01	1964	1966	<1970
GF17-13	GGB05	0.16	0.22	0.04	0.06	0.05	0.02	1959	1960	<1970
GF17-14	GGA05	0.27	0.21	0.04	0.10	0.04	0.02	1963	1960	<1970
GF17-15	GGA09r	0.31	0.12	0.04	0.11	0.03	0.02	1964	1957	<1970
GF17-16	GGA08	0.30	0.30	0.04	0.11	0.06	0.02	1963	1962	<1970
GF17-17	GGA01	0.27	0.33	0.05	0.10	0.07	0.02	1963	1962	<1970
GF17-18	GGB04	0.70	0.47	0.06	0.25	0.10	0.03	1970	1964	1971

Samples GF17-08 and GF17-11 are duplicates and agree well with a mean value of 0.50±0.01 for CFC-12 and 0.195±0.005 for CFC-11. Data for SF_6 is below the detection limit which is reflected in both samples.

Concentrations vary from 0.14-0.70 (mean 0.34) pmol/L, 0.12-0.65 (mean 0.29) pmol/L and 0.0-0.06 fmol/L (mean 0.03) for CFC-12, CFC-11 and SF_6 respectively. This corresponds to modern fractions ranging from 0.05-0.25 (mean 0.12), 0.03-0.13 (mean 0.06) and 0.0-0.03 (mean 0.01) for CFC-12, CFC-11 and SF_6 respectively. Similarly, in terms of recharge year this varies ranges from 1957-1970 (mean 1964), 1957-1966 (mean 1961) and <1970-1971 for CFC-12, CFC-11 and SF_6 respectively. The generally good agreement between tracer ages suggests a piston flow model (i.e, minimal mixing of flow lines) as the most appropriate descriptor of the groundwater movement.

Highest concentrations (youngest ages) are observed in the shallowest wells which have been constructed in the superficial deposits. Compared with the pumping tests, maximum concentrations are slightly lower for the CFC-12 and CFC-11 data from 2021, although overall mean ages are roughly the same.

4.1.11 Noble gases

The atmospheric noble gases Ne, Ar, Kr and Xe are chemically unreactive so preserve their dissolved concentrations at the time of input to the aquifer, allowing ‘excess air’ (usually a function of recharge conditions) and recharge temperature values to be calculated. Helium (He), while also an atmospheric noble gas, is by contrast supplemented in the subsurface by U-Th series radioactive decay to provide a qualitative (and highly aquifer-specific) indication of residence time.

The derived recharge temperatures range from 7.0 to 12.8°C, averaging 10.2°C which is indistinguishable from the Holocene mean annual air temperature in the general area. Derived excess air values are mostly <10 cm^3STP/kg, typical of most groundwaters but in two cases exceed 25 cm^3STP/kg. While there might be specific hydrological reasons for such high values, they are more likely to be due to the presence of air entrained during sampling; repeat sampling should show whether the values are 'real' or simply the result of sampling difficulties. Helium concentrations ranging from 8.98 to 33.5 × 10^{-8} cm^3STP/g do not greatly exceed the atmospheric equilibrium value for water at 10°C of ~4.7 × 10^{-8} cm^3STP/g, suggesting that the sampled waters have not been in residence long enough to have acquired significant ^4He in the aquifer, whether directly from U-Th decay or by mixing with 'old' water enriched in ^4He.

Table 14 Noble gas sampling data from February 2021

Sample ID		**GF17-08**	**GF17-09**	**GF17-10**	**GF17-12**	**GF17-13**	**GF17-14**	**GF17-15**	**GF17-16**	**GF17-17**	**GF17-18**
Borehole		**GGA06r**	**GGA04**	**GGA07**	**GGA03r**	**GGB05**	**GGA05**	**GGA09r**	**GGA08**	**GGA01**	**GGB04**
Helium	cm^3STP/g	1.44E-07	3.35E-07	2.35E-07	2.89E-07	1.61E-07	2.98E-07	9.48E-08	1.91E-07	2.30E-07	8.98E-08
±		1.69E-08	3.86E-08	2.72E-08	3.35E-08	1.88E-08	3.44E-08	1.13E-08	2.23E-08	2.67E-08	1.07E-08
Neon	cm^3STP/g	2.70E-07	7.19E-07	3.60E-07	8.23E-07	3.31E-07	8.52E-07	2.74E-07	3.52E-07	3.82E-07	3.12E-07
±		4.37E-09	1.15E-08	5.80E-09	1.32E-08	5.35E-09	1.37E-08	4.44E-09	5.67E-09	6.09E-09	4.98E-09
Argon	cm^3STP/g	3.97E-04	5.95E-04	4.29E-04	6.89E-04	4.26E-04	6.55E-04	4.04E-04	4.12E-04	4.44E-04	4.18E-04
±		7.19E-06	1.07E-05	7.76E-06	1.24E-05	7.71E-06	1.18E-05	7.33E-06	7.45E-06	8.02E-06	7.55E-06
Krypton	cm^3STP/g	1.00E-07	1.22E-07	9.86E-08	1.42E-07	1.04E-07	1.34E-07	1.02E-07	9.87E-08	1.08E-07	1.05E-07
±		1.65E-09	2.04E-09	1.61E-09	2.31E-09	1.71E-09	2.19E-09	1.66E-09	1.61E-09	1.75E-09	1.70E-09
Xenon	cm^3STP/g	1.32E-08	1.44E-08	1.31E-08	1.67E-08	1.28E-08	1.56E-08	1.35E-08	1.19E-08	1.39E-08	1.41E-08
±		7.47E-10	8.18E-10	7.42E-10	9.46E-10	7.24E-10	8.85E-10	7.60E-10	6.69E-10	7.85E-10	7.97E-10
NG temp	°C	9.70	12.02	12.04	7.01	9.90	10.74	9.12	12.80	9.74	9.12
±		0.14	0.13	0.13	0.04	0.13	0.08	0.12	0.18	0.14	0.12
Excess air	cm^3STP/kg	3.55	28.01	8.70	33.21	6.92	34.74	3.75	8.27	9.58	5.73
±		0.13	0.40	0.17	0.51	0.19	0.51	0.10	0.23	0.21	0.17

4.1.12 Saturation index

Mineral saturation indices were calculated using PHREEQC (Parkhurst and Appelo, 1999) and the thermodynamic database phreeqc.dat, and based on the field measured redox values (Eh) (Table 15); most groundwaters are supersaturated with respect to calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$, siderite ($FeCO_3$), rhodochrosite ($MnCO_3$). Only bedrock boreholes are slightly undersaturated on average with respect to siderite. Groundwaters are also supersaturated with respect to gibbsite $Al(OH)_3$, barite ($BaSO_4$), quartz; on average saturated to slightly undersaturated with respect to amorphous ferric hydroxide $Fe(OH)_3(a)$, and remain undersaturated with respect to jarosite (jarosite-K: $KFe_3(SO_4)_2(OH)_6$) and gypsum ($CaSO_4.2H_2O$). It is, however, notable that groundwater in GGA01 in the Glasgow Upper mine workings is close to saturation with respect to gypsum (SI from -0.2 to -0.3).

Estimated equilibrium carbon dioxide partial pressure (P_{CO2}), computed from the result of water analysis using PHREEQC, is significantly higher than atmospheric values around $10^{-3.5}$, suggesting a local system not in equilibrium with air, as in confined aquifers. The highest partial CO_2 pressure values of $10^{-1.2}$ to $10^{-1.1}$ are greater than values in unsaturated zone dominated by soil CO_2 of $10^{-1.5}$ (Appelo and Postma, 2004), suggesting the presence of “neutralised” water, where CO_2 is produced by the buffering of the acidity released by sulphide oxidation by the carbonates of the aquifer.

Table 15 Mineral saturation indices (SI) and carbon dioxide equilibrium partial pressures (*P* CO2(g)) for the groundwater grouped by lithology and surface waters during sampling rounds 15 to 20.

MINERAL	Target Unit	Mean	Min	Max
SI Calcite	Bedrock	0.3	0.0	0.7
	Glasgow Main mine workings	0.4	0.2	0.8
	Glasgow Upper mine workings	0.3	0.0	0.9
	Superficial deposits	0.3	-0.1	0.7
	Surface water	0.1	-1.0	1.4
SI Dolomite	Bedrock	0.6	0.0	1.3
	Glasgow Main mine workings	0.7	0.3	1.6
	Glasgow Upper mine workings	0.4	-0.5	1.7
	Superficial deposits	0.3	-0.5	1.4
	Surface water	-0.1	-2.4	2.7
SI Siderite	Bedrock	-0.2	-3.0	1.1
	Glasgow Main mine workings	0.6	-0.3	1.1
	Glasgow Upper mine workings	1.0	0.4	1.5
	Superficial deposits	0.5	-0.1	1.2
	Surface water	-4.8	-7.1	-1.8
SI Rhodochrosite	Bedrock	0.2	-0.1	0.6
	Glasgow Main mine workings	0.2	0.0	0.5
	Glasgow Upper mine workings	0.1	-0.2	0.6
	Superficial deposits	0.9	0.7	1.3
	Surface water	-0.5	-1.4	0.0
SI Gibbsite	Bedrock	0.8	0.4	1.4
	Glasgow Main mine workings	0.6	0.1	1.3
	Glasgow Upper mine workings	1.1	0.4	2.2
	Superficial deposits	1.1	0.6	1.6
	Surface water	1.1	0.0	2.2
SI Fe(OH)3(a)	Bedrock	1.1	-2.2	3.1
	Glasgow Main mine workings	-0.2	-1.5	1.2
	Glasgow Upper mine workings	0.0	-2.1	1.4
	Superficial deposits	0.3	-2.0	2.4
	Surface water	2.9	1.6	3.5
SI Goethite	Bedrock	6.4	3.2	8.4
	Glasgow Main mine workings	5.2	3.9	6.7

	Glasgow Upper mine workings	5.3	3.3	6.8
	Superficial deposits	5.7	3.4	7.9
	Surface water	8.3	7.0	8.8
SI Barite	Bedrock	0.1	0.0	0.3
	Glasgow Main mine workings	0.1	0.0	0.1
	Glasgow Upper mine workings	0.2	0.1	0.5
	Superficial deposits	0.6	0.2	1.1
	Surface water	-0.1	-0.7	0.0
SI Gypsum	Bedrock	-1.3	-1.4	-1.2
	Glasgow Main mine workings	-1.4	-1.4	-1.4
	Glasgow Upper mine workings	-1.0	-1.4	-0.2
	Superficial deposits	-1.3	-1.5	-1.2
	Surface water	-2.3	-3.1	-1.7
SI Jarosite-K	Bedrock	-5.3	-15	-0.2
	Glasgow Main mine workings	-9.1	-13	-4.5
	Glasgow Upper mine workings	-7.8	-14	-1.4
	Superficial deposits	-7.4	-14	-0.3
	Surface water	-3.9	-7.4	-1.5
SI Quartz	Bedrock	0.2	0.1	0.2
	Glasgow Main mine workings	0.1	0.1	0.2
	Glasgow Upper mine workings	0.3	0.1	0.6
	Superficial deposits	0.2	0.1	0.3
	surface water	-0.2	-0.5	0.2
SI SiO2(a)	Bedrock	-1.2	-1.2	-1.1
	Glasgow Main mine workings	-1.2	-1.3	-1.2
	Glasgow Upper mine workings	-1.1	-1.2	-0.8
	Superficial deposits	-1.1	-1.2	-1.0
	Surface water	-1.5	-1.8	-1.2
P CO2(g)	Bedrock	$10^{-1.4}$	$10^{-1.8}$	$10^{-1.1}$
	Glasgow Main mine workings	$10^{-1.5}$	$10^{-2.0}$	$10^{-1.3}$
	Glasgow Upper mine workings	$10^{-1.5}$	$10^{-2.1}$	$10^{-1.2}$
	Superficial deposits	$10^{-1.4}$	$10^{-2.0}$	$10^{-1.1}$
	Surface water	$10^{-3.0}$	$10^{-3.6}$	$10^{-2.6}$

4.2 SURFACE WATER

Fordyce et al. (2021) identified that the Tollcross Burn and the River Clyde have distinctly different chemistry: the Tollcross Burn is a smaller, more mineralised urban stream compared to the River Clyde which has a large, mostly rural, catchment. They noted that the chemistry of sampling locations on the River Clyde (5 sites) demonstrated similar chemistry and temporal behaviour to each other, but were distinct from the Tollcross Burn site (SWTC). They therefore separated discussion of SWTC from the River Clyde sites. In the tables and discussion below the same approach has been taken, and surface water analyses are grouped according to the source river.

The discussion of the results in the following section is limited by the reduced sampling of surface waters caused by the global COVID-19 pandemic. Samples were only collected from the surface water sites during three of the six groundwater sampling rounds (September 2020, April and May 2021), with the exception of SW05, which was also sampled in December 2021 and March 2022. The graphs in Appendix 3 show the variation in field parameters across the sampling months. Surface water chemistry, including temporal variations, have been discussed in detail for an earlier surface water sampling period between February 2019 and March 2020, which has been published in a separate report (Fordyce et al., 2021). The results from September 2020, April and May 2021 presented here are within the ranges presented by Fordyce et al. (2021), and given the reduced number of sampling rounds, we cannot provide any additional discussion of the temporal variability of the surface water chemistry.

4.2.1 Physico-chemical parameters of surface water samples

Table 16 summarises the physico-chemical parameters measured during water monitoring at the Glasgow Observatory surface water sites between September 2020 and May 2021.

While both water bodies have a near-neutral to alkaline pH and show a narrow range in pH values, the pH values measured at the Tollcross Burn tend to be higher. The waters all follow a similar temporal trend (Appendix 3); the highest pH value each month was measured at the Tollcross Burn.

Temperature trends in both water bodies follow the seasons with the coldest temperatures recorded in the winter months, and highest temperatures recorded at the end of summer. Conversely the dissolved oxygen values follow the inverse trend, with highest values in the coldest months sampled and dissolved oxygen concentrations decreasing as water temperature increases, in line with solubility constraints.

The Eh measurements show that all surface waters are generally oxidised. There is a wider range of values in the River Clyde, compared to the Tollcross Burn; but that may, at least in part, be a result of there being fewer samples from the Tollcross Burn (n=3) than the River Clyde (n=17) during this monitoring period. The lowest Eh measurement, by quite some way, was recorded at SW05.

The SEC measurements are about twice as high in the Tollcross burn samples, as those measured in the River Clyde samples. The Tollcross Burn is a small urban stream, whose SEC has previously been shown to be particularly susceptible to rainfall events (Fordyce et al., 2021), while the River Clyde has a large, mainly rural, catchment.

Table 16 Physico-chemical parameters for Glasgow Observatory surface water sites between September 2020 and May 2021.

	River Clyde					Tollcross Burn				
Field parameters	**Min**	**Max**	**Median**	**n**	**n(c)**	**Min**	**Max**	**Median**	**n**	**n(c)**
pH	7.6	8.4	7.9	17	0	8.1	8.7	8.4	3	0
Temperature (°C)	6.1	15.9	12.9	17	0	8.4	13.2	10.4	3	0
Eh (mV) corrected	258	494	434	17	0	451	460	458	3	0
Dissolved oxygen (mg/L)	7.20	11.3	8.86	17	0	9.12	10.7	9.91	3	0
Conductivity (µs/cm)	149	446	385	17	0	907	977	953	3	0
Field bicarbonate HCO3 (mg/L)	33.4	181	118.3	17	0	383	427	406	3	0

n = number of samples, n(c) = number of samples censored

4.2.2 Major and minor ions

4.2.2.1 Water Type

The major ions are presented in a Piper diagram (Figure 9) to understand the water type. Piper diagrams are interpreted based on the identification of hydrochemical facies (Drever, 1997).

The surface waters all have similar major ion proportions, and are Ca-HCO_3 type. The samples taken from the Tollcross Burn can be distinguished from the River Clyde samples on account of having the greatest proportion of HCO_3 and a lower proportion of Ca.

4.2.2.2 Major Ions

Minimum, maximum and median values of the major ions in surface water samples are presented in Table 17. As reflected in the SEC values, the Tollcross Burn is more mineralised, the concentrations of all the major ions are more than double those measured in the River Clyde. The two rivers are therefore distinctly different as the major ion analyses are clearly split into two populations.

4.2.2.3 Minor elements

Minimum, maximum and median values of the minor elements in surface water samples are presented in Table 17. The Tollcross Burn has higher concentrations of Si, Br, F than those measured in the River Clyde, replicating the above trend. However, nitrogen and phosphorus, and NPOC (the nutrient species), are higher in the River Clyde. Sources of these parameters include fertilisers, atmospheric inputs derived from burning fossil fuels, water treatment works/ domestic sewage, farmyard slurry, landfill and soils. The River Clyde has a much larger catchment, flowing through rural areas. While there are few areas of arable farming, the majority of the catchment is improved grassland (Smedley et al., 2017), which may give rise to inputs of the nutrient species from livestock grazing.

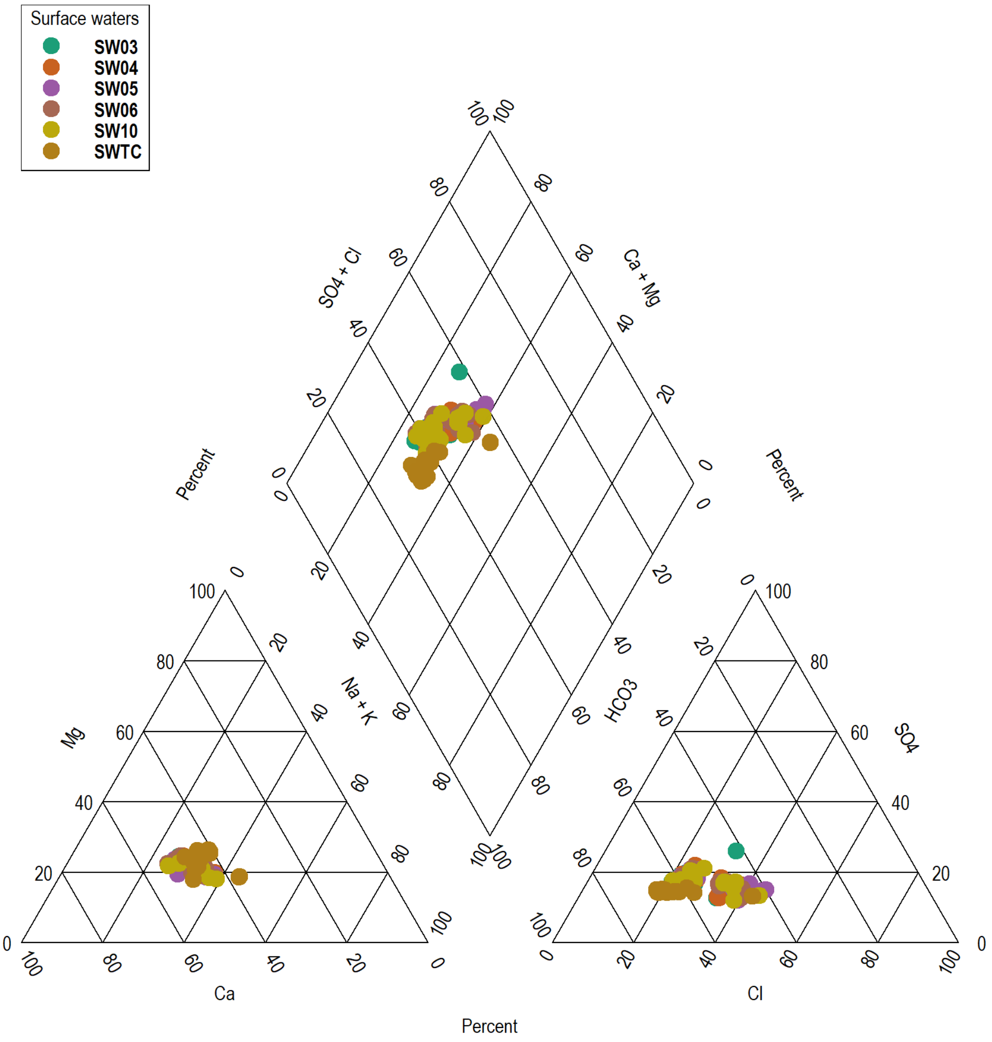

Figure 9 Surface water Piper plot.

Table 17 Summary of min, max and mean of major and minor cations and anions for surface water samples taken from the five sites along the River Clyde

		River Clyde					**Tollcross Burn**				
		Min	**Max**	**Median**	**n**	**n(c)**	**Min**	**Max**	**Median**	**n**	**n(c)**
Major ions (mg/L)											
Calcium	Ca	13.2	41.6	33.4	17	0	83.3	84.9	84.7	3	0
Magnesium	Mg	3.01	12.6	10.3	17	0	26.6	32.1	31.9	3	0
Sodium	Na	8.40	30.6	23.2	17	0	63.1	79.9	78.5	3	0
Potassium	K	1.59	5.08	3.80	17	0	12.0	13.8	12.9	3	0
Bicarbonate (field measured)	HCO_3	33.3	181	118	17	0	383	427	406	3	0
Chloride	Cl	11.8	35.8	31.5	17	0	58.1	78.0	75.2	3	0
Sulphate	SO_4	8.95	41.0	30.0	17	0	67.2	74.5	70.8	3	0
Total Alkalinity	HCO_3	107	147	128	11	0	411	412	411	2	0
Minor ions (mg/L)											
Phosphorus - total	P	0.04	0.247	0.12	17	0	0.024	0.036	0.036	3	0
Sulphur – total	S	3.31	14.0	11.0	17	0	24.6	26.0	25.4	3	0
Silicon	Si	1.42	3.75	2.18	17	0	4.40	6.21	4.60	3	0
Bromide	Br	0.014	0.057	0.036	17	0	0.181	0.186	0.182	3	0
Fluoride	F	0.038	0.079	0.070	17	0	0.185	0.212	0.205	3	0
Nitrite	NO_2	0.019	0.369	0.164	17	0	0.018	0.048	0.019	3	0
Nitrate	NO_3	2.78	16.3	11.2	17	0	6.36	6.55	6.40	3	0
NPOC (mg/L)		3.18	11.9	5.25	17	0	2.82	3.26	2.90	3	0

n = number of samples, n(c) = number of samples censored

4.2.3 Trace elements

For a full list of all analysed trace elements, refer to Appendix 2. Table 18 provides a summary of those trace elements recorded in concentrations at least 1 order of magnitude above the laboratory detection limit in more than one sample per water body. Appendix 3 shows time series plots for a selection of trace elements, and the elements of most interest are discussed below.

Most trace elements are present in higher concentrations in the River Clyde, than in the Tollcross Burn; exceptions to this are Sr, B, and Rb, which are higher in the Tollcross Burn, and Co, Ni, Zn, As, Y, and Sb, which have similar concentrations in both rivers. The trace element concentrations are similar between all sites on the River Clyde, which would be expected given these sites are all on a relatively short stretch of the same river.

4.2.4 Chromium species

In contrast to the groundwaters, where Cr species were largely undetectable, most surface water samples contain measurable concentrations of both Cr (III) and Cr (VI). In most natural environments Cr (VI) only occurs in trace amounts, and elevated concentrations are a product of industrial contamination (Farmer et al., 1999). At SW10 the concentrations of total Cr (2.57 µg/L – 6.99 µg/L) and Cr(VI) (2.22 µg/L – 6.21 µg/L) are markedly higher than in the rest of the surface water samples, with Cr(VI) clearly dominating (Cr(III) range 0.29-0.40 µg/L). In contrast in the other surface water samples, concentrations of total Cr (up to 0.57 µg/L) and Cr(VI) (up to 0.2 µg/L) are much lower with no dominant Cr species (Cr (III) measured up to 0.34 µg/L).

The SW10 sampling location is on the opposite bank of the River Clyde to the Shawfield Business Park. This is the former home of the JJ Whites chromium chemical works, where Cr(VI) pollution of soil, groundwater and surface water from COPR waste is a known issue (Farmer et al., 1999; Smedley et al., 2017). While temporal changes of Cr concentrations relating to rainfall were noted at SW10 in the first data release, owing to the COVID-19 pandemic there were too few samples taken during September 2020-May 2021 (three at each site) to form any meaningful conclusions.

Table 18 Comparison of trace element ranges in the River Clyde and Tollcross Burn

		River Clyde					Tollcross Burn				
Trace elements (µg/L)		**Min**	**Max**	**Median**	**n**	**n(c)**	**Min**	**Max**	**Median**	**n**	**n(c)**
Barium	Ba	40.6	101	86.2	17	0	55.6	69.3	68.3	3	0
Strontium	Sr	65	258	201	17	0	1140	1250	1230	3	0
Manganese	Mn	17.4	141	53.6	17	0	28.6	61	35.8	3	0
Total iron	Fe	59.8	689	285	17	0	13.3	17.7	15.2	3	0
Lithium	Li	<7	<7	<7	17	17	12	16	15	3	0
Boron	B	<53	<53	<53	17	17	120	131	122	3	0
Aluminium	Al	16.2	115	21.3	17	0	5.8	10.2	7.5	3	0
Titanium	Ti	0.06	3.13	0.36	17	0	<0.06	0.09	<0.06	3	1
Vanadium	V	0.23	0.75	0.48	17	0	0.21	0.54	0.41	3	0
Cr-total	Cr	0.24	6.99	0.38	17	0	0.12	0.14	0.13	3	0
Cobalt	Co	0.14	0.32	0.25	17	0	0.21	0.25	0.25	3	0
Nickel	Ni	1.30	1.91	1.43	17	0	1.39	1.73	1.63	3	0
Copper	Cu	0.83	1.62	1.20	17	0	1.24	1.66	1.33	3	0
Zinc	Zn	3.4	22.7	5	17	0	5.3	8.8	8.4	3	0
Arsenic	As	0.28	0.46	0.37	17	0	0.27	0.37	0.34	3	0
Selenium	Se	0.12	0.19	0.14	17	0	0.19	0.40	0.25	3	0
Rubidium	Rb	1.74	5.3	4.17	17	0	16.4	19.7	18.4	3	0
Yttrium	Y	0.02	0.29	0.07	17	0	0.027	0.039	0.029	3	0
Zircon	Zr	0.024	0.215	0.047	17	0	0.024	0.046	0.042	3	0
Molybdenum	Mo	<0.20	1.60	0.50	17	1	0.6	0.7	0.7	3	0
Cadmium	Cd	0.007	0.077	0.010	17	0	0.009	0.014	0.013	3	0
Tin	Sn	<0.08	0.22	<0.08	17	14	<0.08	<0.09	<0.08	3	3
Antimony	Sb	0.11	0.22	0.16	17	0	0.14	0.24	0.22	3	0
Caesium	Cs	<0.04	0.30	0.06	17	3	<0.04	0.05	0.05	3	1
Lanthanum	La	0.01	0.22	0.04	17	0	<0.003	0.006	0.003	3	1
Cerium	Ce	0.01	0.40	0.06	17	0	<0.004	0.011	0.006	3	1
Neodymium	Nd	0.01	0.23	0.04	17	0	<0.005	0.006	0.005	3	1
Europium	Eu	<0.003	0.017	<0.003	17	11	<0.003	<0.003	<0.003	3	3
Gadolinium	Gd	0.01	0.059	0.021	17	0	<0.005	<0.005	<0.005	3	3
Dysprosium	Dy	<0.003	0.048	0.012	17	2	<0.003	0.005	<0.003	3	2
Erbium	Er	<0.003	0.023	0.007	17	3	<0.003	0.005	<0.003	3	2
Ytterbium	Yb	<0.004	0.025	0.005	17	4	<0.004	0.005	<0.006	3	2
Lead	Pb	0.1	1.91	0.38	17	0	0.03	0.06	0.05	3	0
Uranium	U	0.065	0.2	0.166	17	0	0.37	0.407	0.395	3	0
Chromium (III)	Cr	0.09	0.40	0.23	17	0	<0.04	0.08	<0.04	3	2
Chromium (VI)	Cr	<0.05	6.21	0.14	17	3	0.07	0.11	0.10	3	0

n = number of samples, n(c) = number of samples censored

4.2.5 PAH and TPH

Many samples analysed for PAHs and TPHs were below the detection limit. Of these organic compounds only one TPH fraction (TPH C8-C10) had all analyses below the detection limit. Table 19 summarises the detected PAH and TPH results.

Polycyclic aromatic hydrocarbon concentrations tend to be higher in the Tollcross Burn, while TPH concentrations are higher in the River Clyde. The most prevalent PAH is benzo(a)pyrene, which is measurable in most samples in both rivers. There are no TPH detects in the Tollcross Burn.

Table 19 Summary of min and max concentrations of organic parameters recorded in the samples retrieved from the River Clyde and Tollcross Burn between September 2020 and May 2021

	River Clyde					**Tollcross Burn**				
	Min	**Max**	**Median**	**n**	**n(c)**	**Min**	**Max**	**Median**	**n**	**n(c)**
PAH (ug/L)										
Benzo(b)fluoranthene	<0.0036	0.0065	<0.0036	17	11	0.0058	0.0370	0.0167	3	0
Benzo(k)fluoranthene	<0.003	<0.003	<0.003	17	17	<0.003	0.015	0.006	3	1
Benzo(a)pyrene	<0.0016	0.0052	0.0023	17	5	0.0071	0.0316	0.0168	3	0
Benzo(ghi)perylene	<0.0036	0.0148	<0.0036	17	15	<0.0036	0.0170	0.0088	3	1
Indeno(1,2,3-cd)pyrene	<0.0049	0.0141	<0.0049	17	14	<0.0049	0.0620	0.0328	3	1
PAH-Total	<0.0151	0.0253	<0.0151	17	15	<0.0151	0.130	0.0646	3	1
TPH (mg/L)										
TPH (C10-C40)	<0.042	0.066	<0.045	17	11	<0.003	<0.003	<0.003	3	3
TPH (C8-C40)	<0.045	0.066	<0.049	17	11	<0.042	<0.042	<0.042	3	3

n = number of samples, n(c) = number of samples censored

4.2.6 Isotopic composition

The δ^{2}H and δ^{18}O of the surface water samples are aligned along the GMWL and range from δ^{2}H –54.8‰ to –42.6‰, median –49.0‰, and from δ^{18}O –7.98‰ to –6.70‰, median –7.43‰ (Table 20, Figure 10). Following the trend described in detail in Fordyce et al. (2021), the range of values in surface water is much larger than the range in groundwater samples for the same monitoring period; this is expected as the latter have integrated the isotopic composition of several storm and diffuse recharge events.

Values of δ^{2}H and δ^{18}O for surface waters were most negative in the December sampling event, reflecting the contribution of winter precipitation usually depleted in ^{2}H and ^{18}O isotopes relative to the summer rain. Superimposed storm- to- storm variation, due for example to the intensity or trajectory of a storm, can be as large as seasonal variation in δ^{2}H and δ^{18}O and this might account for the April surface water samples being more enriched in ^{2}H and ^{18}O than those collected in May. It is also noticeable that the surface water from Tollcross stream (SWTC) sampled on 19 May 2022 is distinct from the other May surface waters from the River Clyde.

Surface water $\delta^{13}C_{DIC}$ ranges from –20.1‰ to –10.6‰ (median –11.2‰). The spread of values is similar to that for the previous monitoring period (Fordyce et al., 2021). Surface waters sampled in September 2020 display lower $\delta^{13}C_{DIC}$ (–15.5‰ to –12.2‰) than the samples from March to May 2021 (–11.3‰ to –10.6‰). The only surface water sampled in December 2020 shows the lowest $\delta^{13}C_{DIC}$ value of –20.1‰.

Table 20 δ^{13}C$_{DIC}$, δ^{18}O and δ^{2}H min, max and median values of surface water samples during the monitoring period.

Variable	Target unit	Min	Max	Median	n
δ^{13}C$_{DIC}$ PDB ‰	Surface water	-20.1	-10.6	-11.2	20
δ^{18}O VSMOW2 ‰	Surface water	-7.98	-6.70	-7.43	20
δ^{2}H VSMOW2 ‰	Surface water	-54.8	-42.6	-49.0	20

n = number of samples

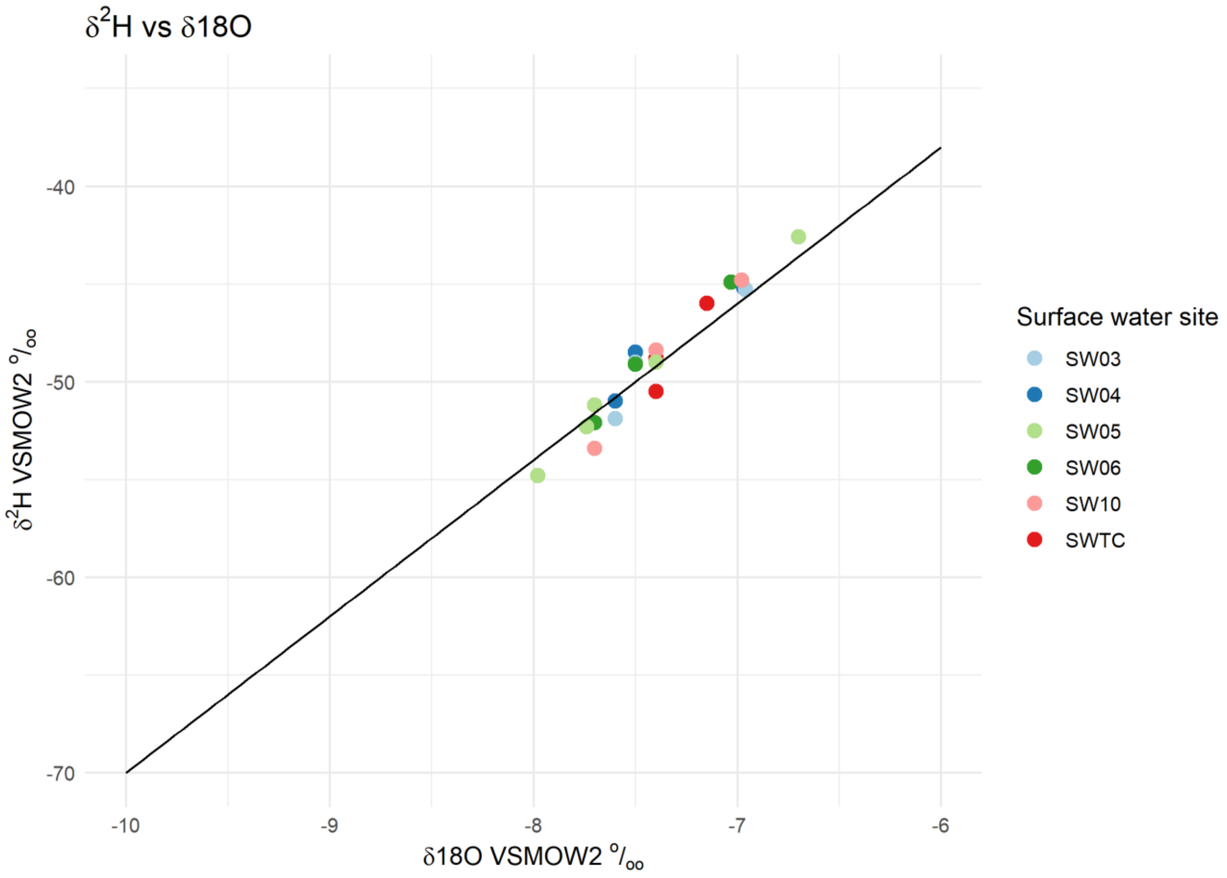

Figure 10: δ^{18}O VSMOW2 (‰) and δ^{2}H VSMOW2 (‰) plotted against the WMWL

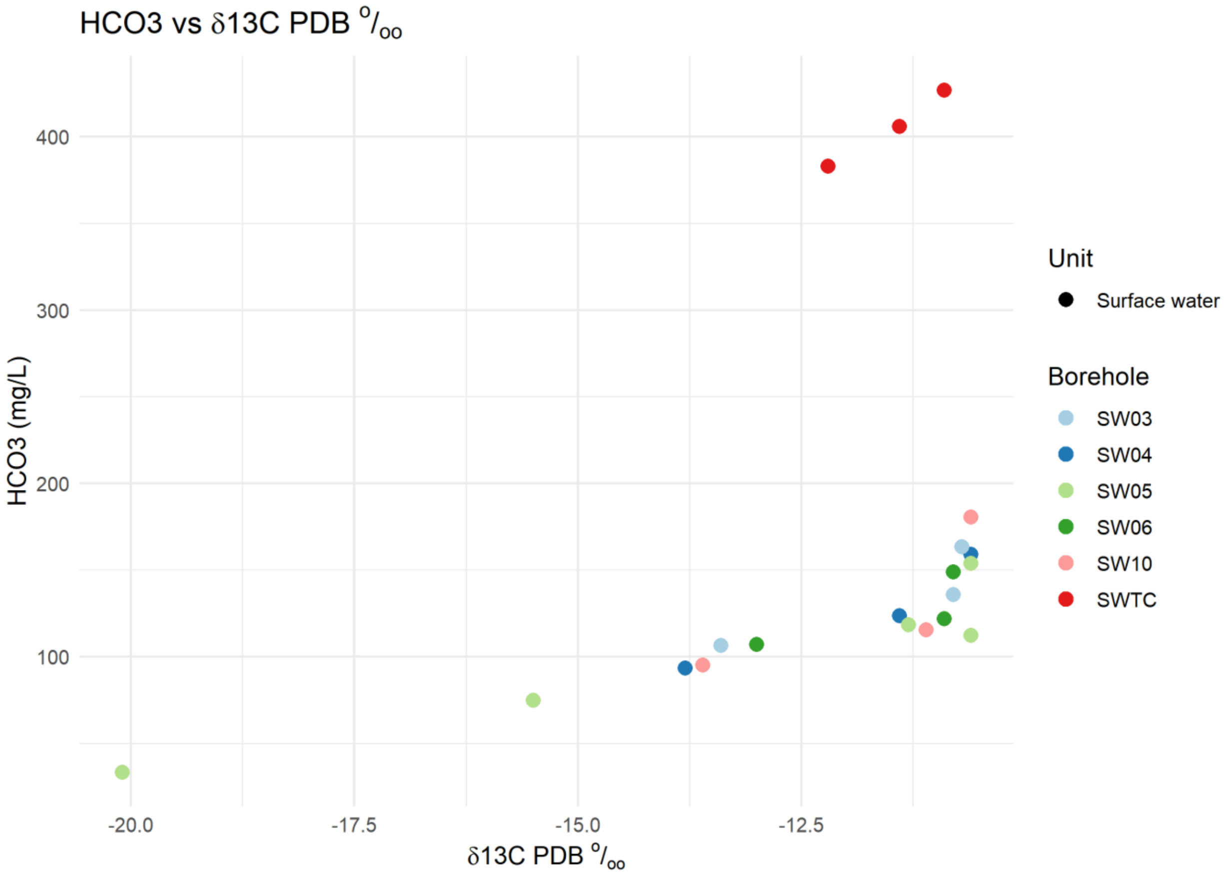

Figure 11 Plot of field-HCO_3 versus $\delta^{13}C_{DIC}$ isotope data in surface waters from the Glasgow observatory.

5 Discussion

5.1 CLUSTER ANALYSIS

Cluster analysis was performed using the Ward's minimum variance method, as described in Section 3.2. The cluster analysis shows that the superficial deposits, the bedrock, the mine workings and the surface water samples are each clustered into statistically distinct groups (Figure 12). Borehole GGB04 generally clusters separately from the other boreholes drilled into the superficial deposits. This can be explained by the trace metal chemistry as discussed in section 4.1.4.1. GGB04 displays clear differences in concentrations and trends during the monitoring period for a number of trace elements including Co, Mn, Fe, Ni and also in concentrations of NH_4. During drilling of the made ground section green to brownish green silt deposits were noted, and there was a distinctive hydrocarbon odour to the samples. GGB04 also has significant drawdown when pumped and the local hydrogeological conditions and presence of made ground may affect the groundwater chemistry.

Borehole GGA01 groundwater form also a distinct cluster from the other boreholes screened across the Glasgow Upper mine workings. This is related to the behaviour and concentrations of major and trace elements during the monitoring period (see 5.2.1).

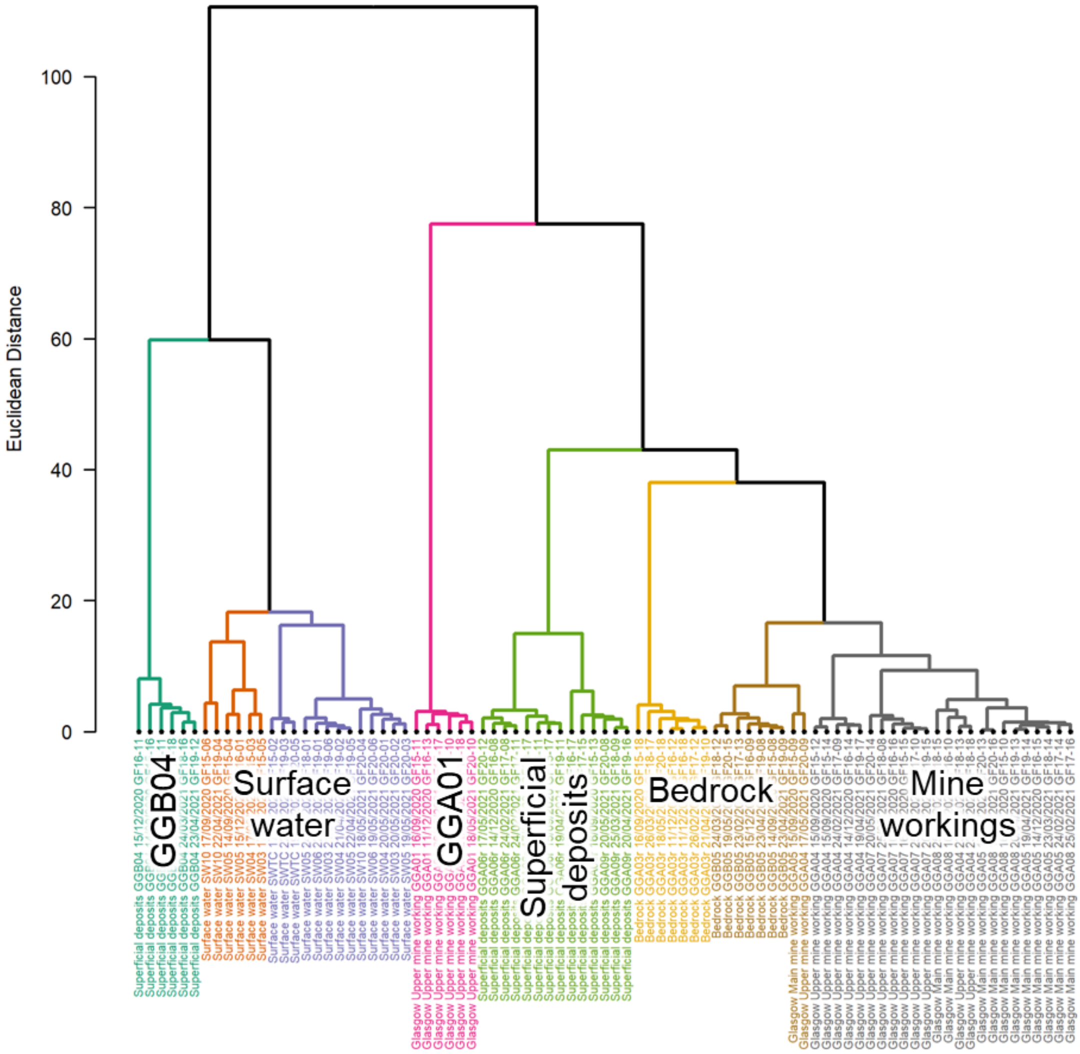

Figure 12 Dendrogram of all baseline samples.

5.2 RELEVANCE OF UK GEOENERGY OBSERVATORIES BASELINE WATER CHEMISTRY DATA

5.2.1 Comparison to pumping tests

Groundwater chemistry samples were taken during pumping tests (January-February 2020) to provide an initial characterisation of the aquifers (Palumbo-Roe et al., 2021). The most striking difference of the present dataset to these initial samples is the water chemistry of GGA01. During the pumping tests the chemistry of the groundwaters at GGA01 was largely indistinguishable from the other Glasgow Upper mine workings. However, major changes have occurred between the pumping tests in January-February 2020 and the start of the monitoring in September 2020. The pumping tests indicated that the three boreholes drilled into the Glasgow Upper mine workings have similar transmissivity and that the water level in each borehole responds to pumping in the others, suggesting the Glasgow Upper mine workings boreholes are hydraulically well connected (Palumbo-Roe et al., 2021). Groundwater samples taken from the remaining Glasgow Upper mine workings sites, have remained instead broadly constant in their hydrochemistry since the pumping tests.

At GGA01 the groundwater Ca and SO_4 concentrations had increased from 108 mg/L and 199 mg/L, respectively, at the end of the pumping tests in January 2020 to 330 mg/L and 1156 mg/L, respectively, in September 2020. The concentrations continued to increase throughout the monitoring recorded in this report (Figure 13 and Figure 14), although the rate of change appeared to be slowing. Iron concentrations increased along with Ca and SO_4 from 4.9 mg/L to 41 mg/L. Potassium concentrations also showed a step change (Figure 15) from 19 mg/L during the pumping tests to 29 mg/L in September 2020. While these elements increased, the HCO_3 decreased from 839 mg/L in the pumping tests to a range of 444 – 448 mg/L during the monitoring period (Figure 16). The pH at the end of the pumping test was 7.02, while it was lower at 6.8 in September 2020, with further oscillations between pH 6.81 and 7.07 through the monitoring period ending at pH 6.88. The trace elements Co, As, Ni, Mn, Rb, Sr increased and mimicked the Ca, SO_4 and Fe trend. It was noted that the concentrations of Fe and As measured in the pump test samples were higher in samples from GGA01 than those from the other Glasgow Upper mine workings (Fe was 1.4 to two times higher, and As was two to four times higher).

Oxidation of pyrite (FeS_2) with neutralisation of the protons, produced in the sulphide oxidation reaction, by carbonate dissolution and dissolved bicarbonate, plus CO_2 degassing, are the most plausible hydrochemical processes consistent with increasing SO_4, Ca and Fe, decreasing HCO_3 and pH. Dissolution of efflorescent pyrite oxidation salts might contribute, but it is not possible without further characterisation to determine unequivocally the relative importance. While the strong linear correlation between SO_4 and Fe (R^2=0.99) infers pyrite oxidation, the observed molar ratio Fe to SO_4 of 0.05, much smaller than the 0.5 generated by the stoichiometry of pyrite, suggests that iron is retained within the subsurface system and precipitated. This is confirmed by the positive mineral saturation index of iron oxyhydroxides ($Fe(OH)_3$(a) SI= 0.0-1.4) and field observations of ochre material abundant at the top of the borehole casing.

Groundwater chemistry is dependent on the minewater reservoir material characteristics and the hydrogeologic conditions at the site. In the case of GGA01 the screened section of GGA01 is exposed to: a sandstone ceiling with traces of pyrite; a thin seam of coal; fragments of sulphur stained coal, iron stained sandstone and mudstone, which has been interpreted as loosely packed waste within the Glasgow Upper mine working; and mudstone (interbedded claystone and siltstone) (Monaghan et al., 2020). Although under confined conditions of the aquifer hosted in the Upper Glasgow mine workings, pyrite oxidation might be limited due to the limited solubility of oxygen in water, the disturbance of the 1.2 m of packed mine waste during drilling or during pumping may have caused conditions favourable to oxidation. While these changes are observed, the oxygen and deuterium isotopic signature of groundwater remains fairly uniform and unchanged to discard any hypothesis of significant ingress of oxygenated freshwater to account for the enhancement of oxidation.

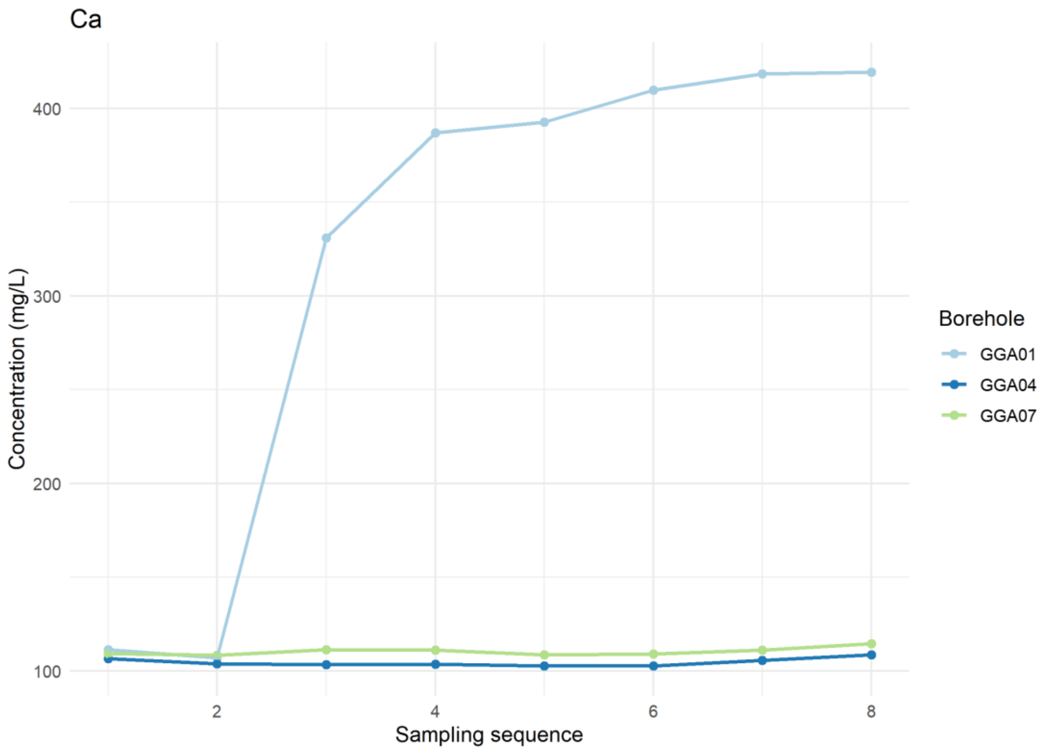

Figure 13 Ca concentrations in Upper Glasgow mine workings groundwater. Samples 1 and 2 represent the pumping test results, Samples 3-8 represent subsequent groundwater monitoring.

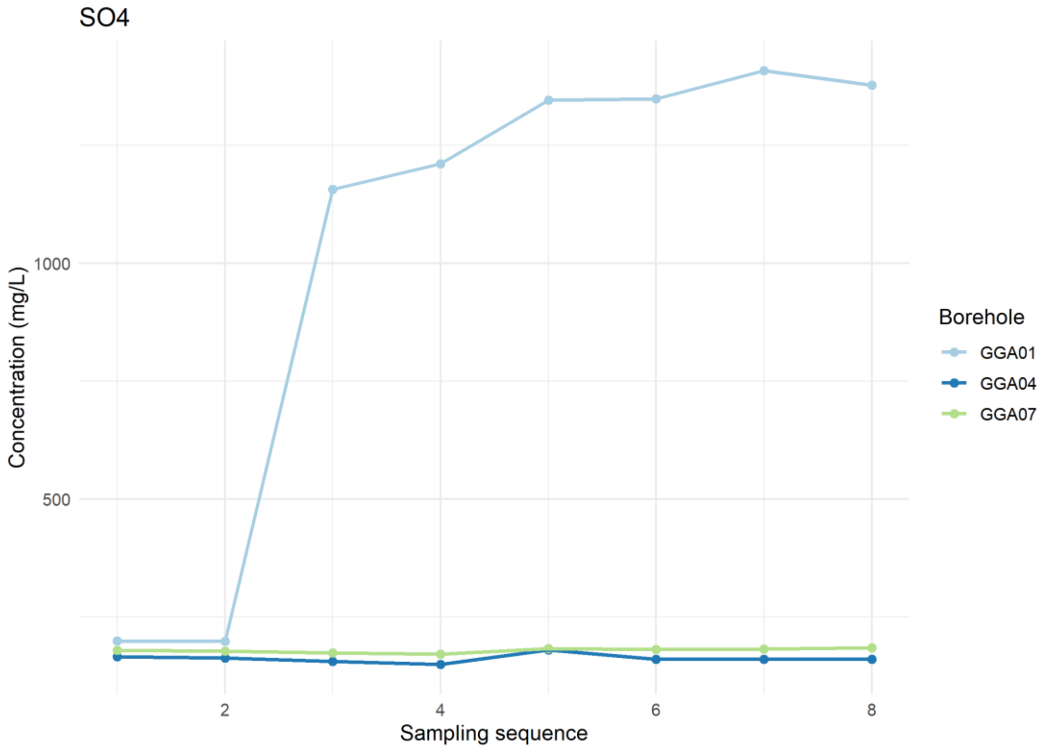

Figure 14 SO_4 concentrations in Upper Glasgow mine workings groundwater. Samples 1 and 2 represent the pumping test results, Samples 3-8 represent subsequent groundwater monitoring.

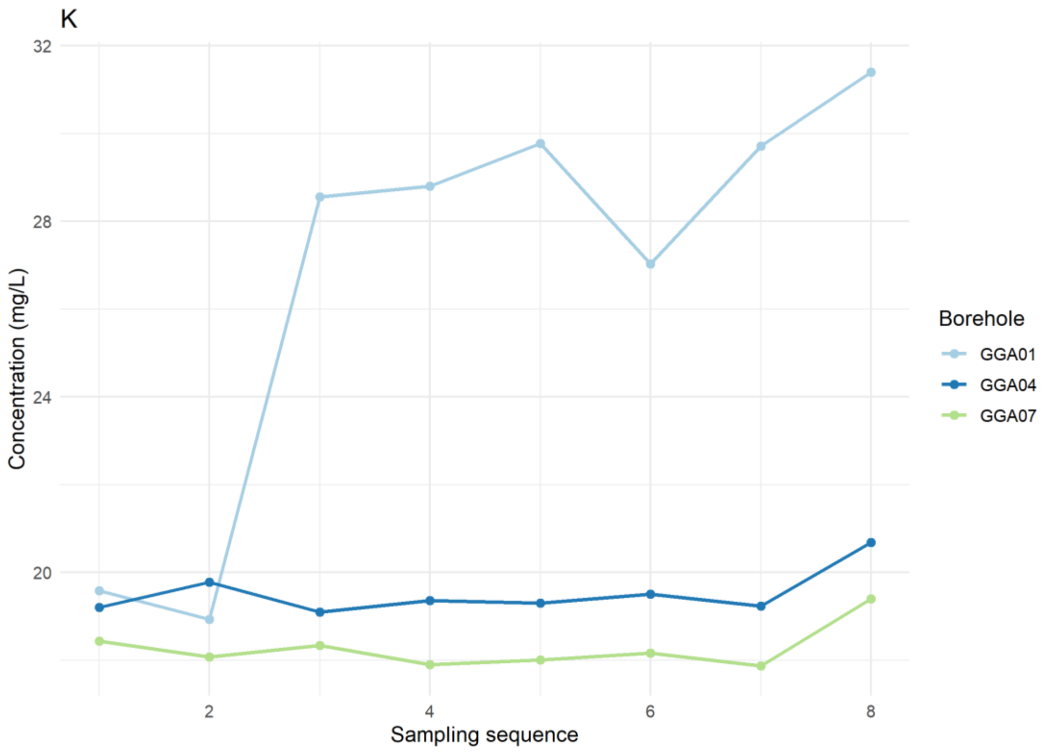

Figure 15 K concentrations in Upper Glasgow mine workings groundwater. Samples 1 and 2 represent the pumping test results, Samples 3-8 represent subsequent groundwater monitoring.

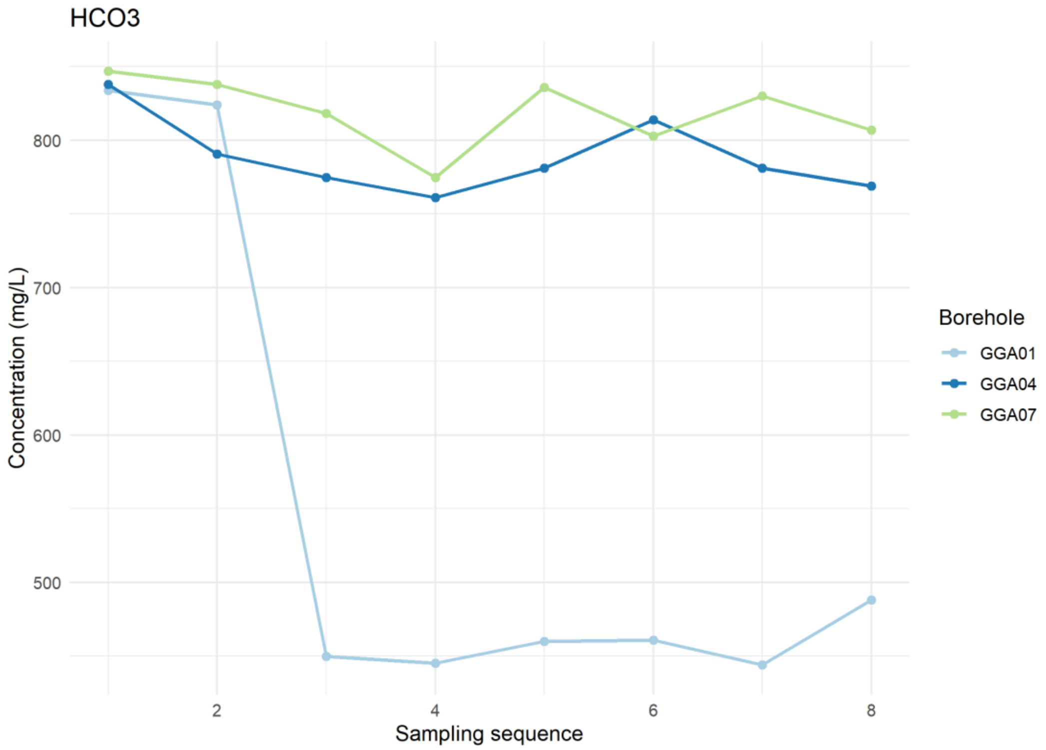

Figure 16 HCO_3 concentrations in Upper Glasgow mine workings groundwater. Samples 1 and 2 represent the pumping test results, Samples 3-8 represent subsequent groundwater monitoring.

Other than the results highlighted above, the water chemistry monitored during September 2020-May 2021 is largely similar to the pumping test results (Palumbo-Roe et al., 2021) suggesting the boreholes are well connected to their aquifers, and any post-pump test settling occurred during the hiatus between pump tests and start of baseline monitoring caused by the COVID-19 pandemic.

5.2.2 Comparison to other relevant data sets

The data obtained from superficial groundwaters monitored in this study have been compared qualitatively to those reported by Ó Dochartaigh et al. (2017), who compared natural Quaternary deposits in Glasgow with artificial deposits in Glasgow, and baseline data from Quaternary deposits in rural Scotland. Ó Dochartaigh et al. (2017) reported a major ion concentration range and Piper plot distribution in natural Glasgow Quaternary groundwaters similar to that presented in the superficial deposits in this report. They highlighted the urban groundwaters were more mineralised than the baseline groundwaters, and identified local areas of contamination which had a higher concentration of major ions. They indicated that some of the natural Glasgow Quaternary boreholes were known to intercept artificial ground made of chemical waste which probably impacted the quality of the groundwaters. There is about 7.5 – 9 m of made ground at each of the borehole sites discussed in this report. Given the area's history it is likely this contains demolition waste, which could impact the groundwaters in the superficial deposits.

Ó Dochartaigh et al. (2011) presented groundwater chemistry of the Carboniferous sedimentary aquifers of the Midland Valley. They identified high concentrations of major elements to be typical of groundwaters in Coal Measures and mine waters in the Midland Valley (Ó Dochartaigh et al., 2011). Comparison to this report (Ó Dochartaigh et al., 2011) showed that generally the major elements and physico-chemical parameters are in concentration ranges similar to those found in the bedrock and mine workings (except GGA01) boreholes in this study.

As part of the stream water geochemical atlas of the River Clyde, Smedley et al. (2017) presented data from the Clyde and its major tributaries, incorporating data from a previous study of the Clyde's urban tributaries (Fordyce et al., 2004). Summary statistics of "River" samples (The Clyde and major tributaries) and "Urban" samples (urban tributaries) were presented. The River Clyde samples of the current study were comparable to the River samples, and the Tollcross Burn samples were comparable to Urban samples, albeit neither previous study had a temporal component. In most cases data from the current study fit into the distribution of the data of the appropriate studies by Smedley et al. (2017) and Fordyce et al. (2004). The only exception to this was NO_3, which was higher in the Clyde in this study (median 11.2 mg/L, max 16.3 mg/L) than in the Clyde geochemical atlas (median 1.4 mg/L, max 11.2 mg/L) (Smedley et al., 2017). The Geochemical atlas represented a single sample snapshot in time, with the samples from the Clyde taken within a 7-day period, meaning these data have no temporal variation whereas the NO_3 data within this study varies greatly throughout the year. As the major sources of NO_3 input to rivers are controlled by rainfall and run off, the monitoring data are likely to present a larger range of NO_3 concentrations.

All surface water data from the baseline monitoring period September 2020 to May 2021 are consistent with those of the first Glasgow Observatory data release (Fordyce et al., 2021).

5.2.3 Water quality standards

To evaluate water quality, the Glasgow Observatory results were compared to water environmental quality standards (EQS). For surface waters, EQS for "good" river status were used (SEPA, 2014b, 2020a; UKTAG, 2013) consistent with Fordyce et al. (2021). There is no UK river water NO_3 standard, so commonly used European Standards were used instead (Polikane et al., 2019). It should be noted that the SEPA classify the River Clyde from North Calder to the tidal weir as a heavily modified water body with moderate, rather than good ecological status (SEPA, 2020b). However, the approach established by Fordyce et al. (2021) has been continued here: that is to compare data with the "good" EQS annual average (AA) and maximum allowable concentrations (MAC) to provide an indication of the impacts of urbanisation on the surface water chemistry. For groundwater there are currently no suitable EQS available, for example drinking water legislation is not appropriate for mine waters and overlying aquifers. The SEPA are currently working to assign groundwater assessment where there are pollution inputs (SEPA, 2014a).

However, until such EQS are available we will not compare data to inappropriate EQS. The EQS for the surface waters are shown in Table 30 and on the time series plots of the chemistry data (Appendix 3).

Mean concentrations of parameters in the River Clyde and Tollcross Burn samples were found to generally be within the AA limits required for good river status, similarly, individual values were compared to the MAC and no exceedances were found. Data not within the AA limits are detailed below:

- The mean HPO_4 concentration in the River Clyde was 0.29 mg/L compared to the AA limit of 0.069 mg/L.
- The mean NO_3 concentration in the River Clyde was 10.4 mg/L compared to the AA limit of 5.7 mg/L
- The mean NO_3 concentrations in the Tollcross Burn was 6.5 mg/L compared to the AA limit of 5.7 mg/L
- The mean Al concentration in the River Clyde was 34 µg/L compared the AA limit of 15 µg/L, in fact all values exceeded the AA limit.
- The mean Cu concentrations in the River Clyde and Tollcross Burn were 1.13 and 1.4 µg/L respectively, both exceeding the AA limit of 1 µg/L (although the limit is specifically bioavailable Cu).
- The combined mean benzo(ghi)perylene and indeno(1,2,3-cd)pyrene contents in the River Clyde and Tollcross Burn were 0.066 µg/L and 0.041 µg/L compared to the AA limit of 0.002 µg/L for these compounds combined. For both compounds the detection limit exceeded the AA value, so samples where the result was below the detection limit were set to half the detection limit for the purposes of calculating the mean. This is not an ideal method, so there is some uncertainty associated with the mean values presented here.

All these exceedances are consistent with those observed previously in the first Glasgow Observatory surface water release (Fordyce et al., 2021), and are not unexpected for surface waters within cities like Glasgow. Such environments are affected by enhanced run off, coupled with cross contamination from the sewerage network and pollution of soil, surface run off and shallow groundwater.

6 Conclusions

Baseline surface water and groundwater chemistry monitoring was carried out in and around the Glasgow Observatory over nine months between September 2020 and May 2021. This represented a continuation of the surface water monitoring described in Fordyce et al. (2021), and the first period of groundwater monitoring at the Glasgow Observatory. Previously chemical data obtained from the pump testing of the boreholes have been reported (Palumbo-Roe et al., 2021). This report accompanies the data release for the six rounds of baseline monitoring sampling which occurred during this time It provides the associated background information, along with a summary and discussion of the geochemical results.

The planned monthly collection of surface water and groundwater samples was adversely affected by the COVID-19 pandemic. There was a 5-month gap in surface water sampling at the start of the pandemic, before each site was sampled in September 2020 since the last monitoring pre-pandemic in March 2020; then there was a further 6-month gap before most surface water sites were sampled again. The groundwater test pumping was completed in January and February 2020, the COVID 19 pandemic lock down in March 2020 meant baseline monitoring of these boreholes did not commence until September 2020. There were further pauses in sampling, with groundwater sampling occurring in December 2020, and monthly sampling recommencing in February 2021.

The set of 98 samples derived from this period of baseline monitoring (60 groundwater samples, 20 surface water samples, 12 blanks, and 6 field duplicates) were analysed to determine:

- Field measured physicochemical parameters,
- Major, minor, and trace elements,
- Chromium speciation (Cr(III) and Cr(VI)),
- Non-purgeable organic carbon (NPOC) and total inorganic carbon (TIC),
- Polycyclic aromatic hydrocarbons (PAH),
- Total petroleum hydrocarbons (TPH),
- Volatile organic compounds (VOC) for groundwaters only,
- Stable isotopes: deuterium (δ^2H), oxygen 18 ($\delta^{18}O$) and carbon 13 of dissolved inorganic carbon (DIC) ($\delta^{13}C_{DIC}$),
- Ammonium (NH_4),
- Methane, ethane and carbon dioxide (CH_4, C_2H_6, CO_2) for groundwaters only,
- Chlorofluorocarbons (CFC-12 and CFC-11) for one round of groundwater samples,
- Sulphur hexafluoride (SF_6) for one round of groundwater samples, and
- Sulphide (S^{2-}) as part of a trial for a limited number of groundwater samples on one round.

Analyses of the groundwater samples have shown that the groundwaters are all circumneutral to alkaline (pH 6.8 – 7.8) and are highly mineralised (SEC 843 µS/cm – 3002 µS/cm). With the exception of the groundwater at GGA01, all the groundwaters are HCO_3 type with no dominant cation. The groundwaters within the superficial deposits are distinct from the other groundwaters on account of their major and trace element concentrations.

The groundwater at GGA01 has evolved since the pump tests, changing from HCO_3 type to Ca-SO_4 type groundwater within eight months. The concentrations of Ca, SO_4, Fe, and K have increased, while there has been a corresponding decrease in HCO_3. A number of trace elements, Co, As, Ni, Mn, Rb, and Sr, mimicked the Ca, SO_4 and Fe trend. As there were no samples taken for seven months after the pump test the initial rate of change is not clear. The chemistry of the groundwater at GGA01 does appear to be stabilising with concentrations of SO_4, Ca and Fe of c. 1400 mg/L, c. 420 mg/L and c. 41,000 µg/L, respectively, but this will be confirmed within the next data release. This shift in groundwater character may be induced by sulphide oxidation and neutralisation processes, caused by a possible “disturbance” of the packed waste and associated pyrite of the screened section of borehole GGA01, during the pumping phases.

Analyses of the surface water have shown that while the River Clyde and Tollcross Burn are both circum-neutral to alkaline and Ca-HCO_3 type, their chemistry can be distinguished. The Tollcross Burn has higher proportions of HCO_3 and the lowest Ca proportions, and is more mineralised than the River Clyde. Most trace elements are more concentrated in the River Clyde, than in the Tollcross Burn. The River Clyde samples are from multiple sites which are all generally chemically similar to each other. An exception to this is the Cr concentration at site SW10. This is opposite a former chemical processing works, known to produce COPR, and hence provide an input of Cr to the River Clyde.

With the exception of GGA01 the groundwaters and surface water samples are similar to those previously analysed from the Glasgow observatory, and wider central Scotland region. These samples are a representative baseline for the Glasgow observatory.

Appendix 1 Analytical Methods and Data Quality Control

This section provides a summary of the 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. Detailed methodologies are provided in the Glasgow Observatory 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 in the Glasgow Observatory borehole test pumping report (Palumbo-Roe et al., 2021). Analysis methods not covered in these two reports, i.e. noble gases, sulphide (S^{2-}) and radon (Rn), are described in this appendix. As these analyses are provided by external laboratories, the descriptions of the method are limited by the information provided by the laboratory.

Quality control for each analytical method is discussed below, where QC data do not meet the required quality for a given element this is noted and the analysis data for this element should be treated with caution.

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 long- term lower limits of detection (LLD) and/or limits of quantification (LOQ) for the analytical methods are outlined in Table 21. Where analyses are based on a ratio measurement (isotopes and noble gases) there are no detection limits, so these methods are not included in Table 21.

Table 21 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
S^{2-}	Sulphide	mg/L	0.02	NA	Segmented flow analysis
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

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

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

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:					
Rn	Radon	Bq/L	10	NA	Liquid scintillator counter
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	Chlorofluorocarbons	pmol/L	0.01	NA	GC-ECD

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

INORGANIC PARAMETER ANALYSIS

In the section below the analytical methods are briefly discussed. For a more detailed explanation see (Fordyce et al., 2021). The quality control of each analytical method is discussed below; where QC data do not meet the required standard for a given element this is noted and the analysis data for this element should be treated with caution.

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 for groundwater and surface water by UKAS to the requirements of BS EN ISO/IEC 17025:2017.

Repeat measurements of two certified reference materials (QC1 and QC2), and one secondary reference material (QC3) were included within the analytical runs. The results of these analytical replicates showed mostly good precision of the data, as the RSD was ≤ 5%. The exceptions to this were:

- Lithium (RSD of 9% in QC1)
- Beryllium (RSD of 48.1% in QC3)
- Boron (RSD of 5.2% in QC2)
- Magnesium (RSD of 7% in QC3)
- Aluminium (RSDs of 9.2%, 5.1%, and 6.9% in QC1, QC2 and QC3, respectively)
- Silicon (RSD of 7.1% in QC2)
- Vanadium (RSD of 8.7%in QC3)
- Chromium (RSD of 10.5% in QC3)
- Zinc (RSD of 8.5% in QC3)
- Arsenic (RSD of 5.1% and 6.4% in QC1 and QC3, respectively)
- Cadmium (RSD of 27.7% in QC3)

A good accuracy of these reference materials was demonstrated with most recoveries 100 ± 6%. The exceptions to this were:

- Beryllium (Accuracy of 170.9% in QC3)
- Boron (Accuracy of 106.4% in QC2)
- Silicon (Accuracy of 93.9% in QC2)
- Phosphorus (Accuracy of 106.1% in QC2)
- Sulphur (Accuracy of 106.6% in QC2)
- Vanadium (Accuracy of 90.2% in QC3)
- Zinc (Accuracy of117.9% in QC3)
- Molybdenum (Accuracy of 93.9%in QC3)
- Cadmium (Accuracy of 136.6% in QC3)
- Tantalum (Accuracy of 93.7% in QC1)

Laboratory blanks were inserted throughout each analytical run. All were below the detection limits for each element, except for Si, where 28 of the 56 blanks analysed had detectable Si.

Results for field duplicate samples showed good robustness of the sampling method, with acceptable variability between sample-pairs (RSD ≤ 20%) with the exception of yttrium (Y), Ho, Lu and Pb where concentrations were close to the LOQ. Therefore, these results should be treated with caution. Al, Ti, Sm, Nd, Ce, La, Cd, Sn, Cu and Zn show more variability between some sample pairs, again in some cases due to low concentrations, even though the values are above the LOQ, so these data should be treated with care.

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. Accuracy and precision were calculated from the repeated analysis of QC standards. Three standards were used for Cl, SO_4, NO_3, and F, while one was used for Br, NO_2, and HPO_4, because these elements are above the top calibration rage of the instrument in two of the standards.

Repeat analyses of these standards showed good precision for most of the data with RSD ≤ 5%. The exceptions were evident in the analyses from the standard with the lowest concentrations, where Cl and SO_4 had an RSD of 5.4% and 7.6% respectively. The measured results demonstrated good accuracy (recovery of 100± 5% relative to the target values) except where parameter concentrations were present in low abundance in one of the standards for NO_2, and F.

Laboratory blanks were inserted throughout each analytical run. All were below the detection limits for each element, except for HPO_4, where 3 of the 70 blanks analysed had detectable Si. Two of these were very close to the detection limit, while one was two orders of magnitude and likely represents an isolated contamination issue.

Results for field duplicate samples showed good robustness of the sampling method, with acceptable variability between sample-pairs (RSD ≤ 20%) with the exception of fluoride, which shows more variability between one sample pair, even though the values are above the LOQ, so these data should be treated with care.

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%).

No robust LLD exists, as a formal validation exercise has not been performed for this technique. The LLD quoted with sample data is 3 standard deviations of run blanks multiplied by sample dilution factor. All laboratory blanks run during each analytical run had no detectable Cr species.

The majority of the Cr speciation sample results were reported below the LLD. Eighteen of the 60 results had either or both Cr (III) or Cr (IV) values above the LLD. Of these 18 samples 12 were within 15% recovery of the Total Cr results. The 6 speciation results that were out with the 15% recovery should be treated with caution.

Results for field duplicate samples showed good robustness of the sampling method also, with acceptable variability between sample-pairs (RSD ≤ 20%).

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.

A laboratory QC standard was analysed a number of times throughout each analytical run. This demonstrated a good accuracy (recovery 99.6%) and precision (RSD 0.8%).

Results for field duplicate samples showed good robustness of the sampling method also, with acceptable variability between sample-pairs (RSD ≤ 20%).

As a further check on data quality, the field and laboratory alkalinity measurements were compared. These showed good agreement with most analyses' (n=80) RSD ≤ 10%, and the remainder (n=6) RSD ≤ 20%.

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%).

Results for field duplicate samples also showed good robustness of the sampling method, with acceptable variability between sample-pairs (RSD ≤ 20%).

Sulphide analysis

Sulphide analysis by Segmented Flow Analysis was carried out by SOCOTEC at their laboratories in Burton upon Trent. The pre-treated samples were introduced into a distillation reagent stream that was segmented by air. Between each sample an antioxidant buffer was introduced into the stream. After addition of the sample a mixing coil ensured the sample and reagent were fully mixed. Distillation of the sample caused volatile hydrogen sulphide (H_2S) to be released, which was collected in a sodium hydroxide (NaOH) solution. This mixture was passed into a reaction coil that allowed time for the reaction to complete with N,N-dimethyl 1-1,4-phenylenediammonium dichloride in the presence of Iron (III) Chloride to produce methylene blue. The sample was then passed to a spectrophotometric detector, where light with a 660nm wavelength passed through the sample, and the amount of light absorbed by the sample was measured, meaning the output signal from the detector was proportional to the amount of S^{2-}in the sample. The method is UKAS accredited, and SOCOTEC report the limit of detection is 0.02 mg/L and the uncertainty for the method is 8.8%.

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.

Three QC standards were analysed throughout each analytical run and these all showed good accuracy (recoveries 100 ± 5%) and precision (RSD < 5%) of the data.

Results for field duplicate samples generally showed good robustness of the sampling method, with acceptable variability between sample-pairs (RSD ≤ 20%) except for one sampling round (GF16), the results of which should be treated with caution. All laboratory blanks were below the detection limit.

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) were reported with the data. 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.

Results for QC check standards and repeat measurements showed some good accuracy (recovery 100 ± 5%) and precision (RSD < 10%) of the data, while the remainder were within reasonable limits (max recovery 100 ± 18%, max RSD 13%). The C8-C10 data reported up to December 2020 had a recovery of 103%, and an RSD of 13%, while C8-C10 data reported during 2021 had a recovery of 103% and an RSD of 9%. The C10-C40 data reported up to December 2020 had a recovery of 82%, and an RSD of 13%, while C10-C40 data during 2021 had a recovery of 88% and an RSD of 2%.

Results for field duplicate samples also showed good robustness of the sampling method, with acceptable variability between sample-pairs (RSD ≤ 20%) with the exception of some data from TPH (C8 – C10).

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) were reported with the data. Analysis was carried out according to UKAS accredited method ISO 17025.

The results for QC check standards and repeat measurements generally show good accuracy (recovery 100 ± 10%) and precision (RSD < 10%) of the data (Table 22). The results for Indeno(1,2,3-cd)pyrene show slightly poorer accuracy (recovery 100 ± 1%) and precision (RSD is <8%).

Results for field duplicate samples also showed good robustness of the sampling method, with acceptable variability between sample-pairs (RSD ≤ 20%).

Table 22 Results for quality control standards included in the HPLC-FD PAH analysis

	Results reported up to December 2020		**Results reported after December 2020**	
PAH Compound	**% Recovery**	**% RSD**	**% Recovery**	**% RSD**
Benzo(b)fluoranthene	92	5	96	4
Benzo(k)fluoranthene	91	4	96	4
Benzo(a)pyrene (BaP)	106	5	98	4
Benzo(g,h,i)perylene	94	5	93	5
Indeno(1,2,3-cd)pyrene	89	6	89	7
PAH-Total	92	4	94	4

Volatile organic compound analysis

Volatile organic compounds were analysed by the Scottish Water laboratory in Edinburgh. 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 23). The remaining parameters are assessed against set limits (+/-25% of nominal value).

Results for field duplicate samples also showed good robustness of the sampling method, with acceptable variability between sample-pairs (RSD ≤ 20%).

During sample round 17 (Feb 2021) the VOC samples were incorrectly registered for a VOC scan (screening analysis), rather than a full analysis. In this round the detected compounds were tentatively identified, and their concentrations estimated. These VOC measurements should be treated with caution.

Table 23 Method performance of certain VOC parameters controlled via control charts

	Results reported up to December 2020		Results reported after December 2020	
Compound	**% Recovery**	**% RSD**	**% Recovery**	**% RSD**
Diethyl Ether	95	7	96	7
Trichloromethane	100	4	100	4
Benzene	100	4	100	4
Toluene	100	4	100	4
Tetrachloroethene	102	5	102	5
Styrene	101	4	101	4
1,3,5-Trichlorobenzene	104	3	104	5

STABLE ISOTOPE ANALYSIS

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 24).

Table 24 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	24	15
NIGL mean	-0.7	-22.3
% 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

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 25).

Table 25 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	21	20
NIGL mean	-309.5	-49.23
% RSD	1	1

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 26).

Table 26 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	34	35
NIGL mean	-39.3	-7.3
% RSD	<1	<1

DISSOLVED GASES

Radon analysis

Radon was analysed by a UKAS accredited liquid scintillation method at the Scottish Water laboratory in Edinburgh. Radon is highly soluble in organic solvents, so it is extracted from the water by a scintillation cocktail. Other nuclides, such as ^{40}K, ^{226}Ra, or ^{228}Ra remain in the water. A sample vial, containing the sample and scintillation cocktail is placed in a dark detection enclosure, where the scintillant converts the alpha and beta ionising radiation from the radon decay into photons of light. The intensity of the light produced during this process is proportional to the initial energy of the alpha and beta particles and hence the concentration of radon in the sample. Light intensity is measured with a liquid scintillation counter.

Sottish Water are UKAS accredited for Rn analysis on two identical liquid scintillator counters, which are regularly quality checked. Typical results from quality control standards are presented in Table 27. Associated with these is a maximum measurement uncertainty (the highest of the two instruments) of 15.8%. The LLD is 0.02 mg/L.

Table 27 Typical method performance of Scottish Water's two liquid scintillator counters

Instrument	% Recovery	% RSD
Radon 101B	97.7	5.7
Radon 101C	96.8	5.5

Noble gas analysis

Noble gas samples are analysed for He, Ne, Ar, Kr and Xe in batches of approximately 10 at the BGS Wallingford laboratories, by quadrupole mass spectrometry (QMS). Samples are collected into copper tubes of c.7 ml capacity between the clamps, with the exact volumes being calculated gravimetrically during analysis. Weighed samples are attached to a vacuum line where the inlet is pumped down to better than 5×10^{-2} mb, then the water and gas is admitted to the preparation line where a getter pump removes reactive gases such as O_2, N_2, CO_2 and CH_4. Separate fractions of Kr + Xe, Ar, and Ne + He are then isolated using cryogenic techniques, and analysed in three QMS runs, i.e. one for each fraction. Following the outgassing process, the empty sample tubes are weighed again to calculate the sample mass by difference.

Air-saturated water (ASW) calibration samples are prepared by bubbling air through tap water at a known temperature, then then extracting aliquots into clamped copper tubes and treating them as samples. These are run between every batch and the results should match their preparation temperature to within ±1°C with an excess air value of 0 ± 0.5 cm^3/g. If falling outside these limits, ASW samples are repeated until they are within range.

Output data from samples are entered digitally into a program iNoble V1, prepared and shared by the International Atomic Energy Agency (IAEA). Using iterative calculation, this produces recharge temperature and excess air values for each sample, together with the measurement precision. A ± figure for each of the measurements is reported with the data. Since there can be a lot of variation in amounts of dissolved gases, a global %RSD is not an appropriate way to report precision for this method.

Methane, ethane and carbon dioxide analysis

The methodology for analysis of CH_4, C_2H_6, and CO_2 are described in full in (Palumbo-Roe et al., 2021).

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.

Chlorofluorocarbons and sulphur hexafluoride analysis

The CFC and SF6 analyses were analysed at the BGS Wallingford laboratories, see (Palumbo-Roe et al., 2021) for the methodology. 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 Summary Statistics

Summary statistics of field parameter, major and minor ion, trace element and stable isotope compositions, for the groundwater samples (Table 28) and surface water samples (Table 29) taken between September 2020 and May 2021 are presented in this appendix. For the purposes of calculating summary statistics, data below the LLD were set to half the LLD value.

Table 28 Summary statistics for all groundwater samples collected between September 2020 and May 2021

Variable	Units	Min	Max	Mean	Median	SD	n	n(c)
pH		6.78	7.81	7.18	7.17	0.22	66	0
Temperature	°C	10.3	15.1	11.6	11.4	0.98	66	0
Eh	mV	-16.6	396	111	93.4	86.8	66	0
DO	mg/L	0.08	1.06	0.32	0.29	0.18	66	0
SEC	µs/cm	843	3000	16807	1630	400	66	0
HCO_3 (field measured)	mg/L	444	905	719	763	108	66	0
Ca	mg/L	96.9	419	141	111	81.9	66	0
Mg	mg/L	28.2	76.6	49.7	49.0	10.4	66	0
Na	mg/L	89.1	211	163	170	30.2	66	0
K	mg/L	9.20	31.4	17.6	18.7	5.25	66	0
Total Alkalinity (Feb21 onwards)	mg/L	371	847	732	787	130	44	0
Cl	mg/L	22.7	96.1	66.3	69.2	13.1	66	0
SO_4	mg/L	116	1410	279	177	330	66	0
NO_3	mg/L	<0.03	1.56	0.23	<0.3	0.33	66	59
Br	mg/L	0.21	0.67	0.49	0.49	0.09	66	0
NO_2	mg/L	<0.005	<0.1	0.02	<0.05	0.01	66	66
HPO_4	mg/L	<0.01	<0.2	0.05	<0.1	0.02	66	66
F	mg/L	<0.1	0.30	0.17	0.18	0.06	66	1
Si	mg/L	5.02	14.8	6.74	5.88	2.53	66	0
SiO_2	mg/L	10.7	31.7	14.4	12.6	5.42	66	0
Ba	µg/L	36.0	361	86.9	54.7	77.1	66	0
Sr	µg/L	524	3730	1910	1900	978	66	0
Mn	µg/L	323	5820	1260	481	1490	66	0
Fe-Total	µg/L	9.90	41200	5800	2050	10300	66	0
Li	µg/L	<7	68.0	24.1	30.0	16.7	66	20
B	µg/L	177	549	381	392	81.1	66	0
Al	µg/L	0.70	26.7	3.72	2.85	3.84	66	0
Ti	µg/L	<0.06	4.02	0.26	0.13	0.51	66	22
V	µg/L	<0.02	1.45	0.20	0.15	0.22	66	8
Cr-total	µg/L	<0.04	0.97	0.15	0.12	0.15	66	5
Co	µg/L	0.22	9.79	2.85	2.15	2.54	66	0
Ni	µg/L	1.71	43.5	8.19	4.14	11.0	66	0
Cu	µg/L	<0.05	1.21	0.16	0.12	0.18	66	14
Zn	µg/L	0.30	19.0	3.25	1.95	3.61	66	0
Ga	µg/L	<0.04	0.11	0.03	<0.04	0.02	66	62
As	µg/L	0.05	11.6	1.67	0.42	2.97	66	0
Se	µg/L	<0.07	0.86	0.06	<0.07	0.11	66	59
Rb	µg/L	5.38	69.6	31.1	38.6	18.3	66	0
Y	µg/L	0.01	0.48	0.11	0.07	0.09	66	0
Zr	µg/L	0.02	0.333	0.123	0.114	0.073	66	0
Nb	µg/L	<0.01	0.02	0.01	<0.01	0.01	66	47
Mo	µg/L	<0.2	8.90	1.30	0.45	2.26	66	50
Cd	µg/L	<0.005	0.015	0.004	<0.005	0.003	66	53
Sn	µg/L	<0.08	3.84	0.369	<0.08	0.695	66	48
Sb	µg/L	<0.04	0.070	0.022	<0.04	0.008	66	63
Cs	µg/L	<0.04	0.370	0.182	0.185	0.092	66	3
La	µg/L	<0.003	0.158	0.030	0.016	0.031	66	2
Ce	µg/L	<0.004	0.257	0.051	0.032	0.050	66	1
Pr	µg/L	<0.003	0.035	0.006	0.004	0.006	66	28
Nd	µg/L	<0.005	0.146	0.030	0.018	0.029	66	7
Sm	µg/L	<0.005	0.030	0.007	0.005	0.005	66	32
Eu	µg/L	<0.003	0.005	0.002	<0.003	0.001	66	57

Variable	Units	Min	Max	Mean	Median	SD	n	n(c)
Gd	µg/L	<0.005	0.035	0.009	0.007	0.007	66	27
Tb	µg/L	<0.004	0.005	0.002	<0.004	0.001	66	62
Dy	µg/L	<0.003	0.056	0.012	0.008	0.011	66	10
Ho	µg/L	<0.003	0.021	0.004	<0.003	0.005	66	44
Er	µg/L	<0.003	0.120	0.015	0.008	0.027	66	54
Tm	µg/L	<0.003	0.028	0.004	<0.003	0.007	66	60
Yb	µg/L	<0.004	0.317	0.034	0.010	0.077	66	55
Lu	µg/L	<0.003	0.075	0.008	<0.003	0.019	66	45
Hf	µg/L	<0.006	0.008	0.003	<0.006	0.001	66	65
Ta	µg/L	<0.006	0.003	0.003	<0.006	0.000	66	66
W	µg/L	<0.06	1.35	0.158	<0.06	0.334	66	41
Tl	µg/L	<0.02	0.070	0.018	<0.02	0.014	66	46
Pb	µg/L	<0.02	0.170	0.022	<0.02	0.025	66	47
Bi	µg/L	<0.08	<0.08	<0.08	<0.08	<0.08	66	66
Th	µg/L	<0.03	<0.03	<0.03	<0.03	<0.03	66	66
U	µg/L	0.228	2.41	0.93	0.72	0.58	66	66
Cr(VI)	µg/L	<0.05	0.06	0.03	<0.05	0.01	66	63
Cr(III)	µg/L	<0.04	0.56	0.07	<0.05	0.10	66	42
NH_4	mg/L	<0.01	18.9	11.9	13.3	4.92	66	1
NPOC	mg/L	1.03	16.5	3.14	2.48	2.16	66	0
Sulphide as S	mg/L	0.02	0.92	0.32	0.02	0.52	3	0
$\delta^{13}C$	‰	-17.3	-8.04	-11.7	-11.4	2.04	66	0
$\delta^{18}O$	‰	-7.57	-7.23	-7.46	-7.47	0.06	66	0
$\delta^{2}H$	‰	-52.9	-48.6	-50.6	-50.75	1.16	56	0
CFC-12	pmol/L	0.14	0.70	0.34	0.30	0.17	11	0
CFC-11	pmol/L	0.12	0.65	0.29	0.26	0.15	11	0
SF_6	fmol/L	0.00	0.06	0.03	0.04	0.02	11	0
CH_4	µg/L	0.40	991	138.8	84.6	180	66	0
C_2H_6	µg/L	<1	8.00	0.93	<1	1.53	57	60
CO_2	mg/L	85.3	187	118	116	21.6	66	0
Benzo(b)fluoranthene	µg/L	<0.0036	0.0038	0.001	<0.0036	0.0002	65	64
Benzo(k)fluoranthene	µg/L	<0.003	<0.003	<0.00	<0.003	0.0000	65	65
Benzo(a)pyrene	µg/L	<0.0016	0.0028	0.000	<0.0016	0.0003	65	62
Benzo(ghi)perylene	µg/L	<0.0036	0.0018	0.001	<0.0036	0.0000	65	65
Indeno(1,2,3-cd)pyrene	µg/L	<0.0049	0.0059	0.002	<0.0049	0.0004	65	64
TPH (C8-C10)	mg/L	<0.003	0.061	0.005	<0.003	0.010	60	39
TPH (C10-C40)	mg/L	<0.042	2.65	0.164	<0.042	0.490	60	50
TPH (C8-C40)	mg/L	<0.045	2.71	0.167	<0.045	0.498	60	51
Iso propyl ether	µg/L	<1	40.0	5.12	<10	4.55	66	65
1,2-Dibromo-3-chloropropane	µg/L	<1	1.00	4.60	<10	1.28	66	65
N.N-Dimethylaniline	µg/L	<1	3.00	4.65	<10	1.15	66	64
1,2,4-Trichlorobenzene	µg/L	<1	1.00	4.61	<10	1.26	66	64
Naphthalene	µg/L	<1	1.00	4.61	<10	1.26	66	64
1,2,3-Trichlorobenzene	µg/L	<1	1.00	4.61	<10	1.26	66	64

n = number of samples, n(c) = number of samples censored

Table 29 Summary statistics of surface water samples collected between September 2020 and May 2021

Variable	Units	Min	Max	Mean	Median	SD	n	n(c)
pH		7.58	8.71	8.00	7.94	0.32	20	0
Temperature	°C	6.10	15.9	12.1	12.8	2.23	20	0
Eh	mV	258	494	428	454	56.09	20	0
DO	mg/L	7.20	11.3	9.12	9.02	0.95	20	0
SEC	µs/cm	149	977	449	394	227	20	0
HCO_3 (field measured)	mg/L	33.3	427	163	123	110	20	0
Ca	mg/L	13.2	84.9	40.4	34.8	20.2	20	0
Mg	mg/L	3.01	32.1	12.7	10.7	8.02	20	0
Na	mg/L	8.40	79.9	29.8	24.4	20.1	20	0
K	mg/L	1.59	13.8	5.16	4.11	3.46	20	0
Total Alkalinity (Feb21	mg/L	107	412	174	140	106	13	0
Cl	mg/L	11.8	78.0	34.0	32.2	17.8	20	0
SO_4	mg/L	8.95	74.5	35.3	31.2	17.4	20	0
NO_3	mg/L	2.78	16.3	9.78	10.7	3.93	20	0
Br	mg/L	0.01	0.19	0.06	0.04	0.05	20	0
NO_2	mg/L	0.02	0.37	0.14	0.14	0.09	20	0
HPO_4	mg/L	0.04	0.63	0.26	0.19	0.17	20	0
F	mg/L	0.04	0.21	0.09	0.07	0.05	20	0
Si	mg/L	1.42	6.21	2.88	2.41	1.23	20	0
SiO_2	mg/L	3.04	13.29	6.16	5.15	2.64	20	0
Ba	µg/L	40.6	100.7	80.5	84.2	15.1	20	0
Sr	µg/L	64.9	1250	347	209	374	20	0
Mn	µg/L	17.4	141	62.2	49.6	33.2	20	0
Fe-Total	µg/L	13.3	689	268	252	210	20	0
Li	µg/L	<7	16.0	5.13	<7	4.03	20	17
B	µg/L	<53	131	41.2	<53	35.9	20	17
Al	µg/L	5.80	115	30.5	20.5	26.2	20	0
Ti	µg/L	<0.06	3.13	0.62	0.32	0.79	20	1
V	µg/L	0.21	0.75	0.44	0.47	0.16	20	0
Cr-total	µg/L	0.12	6.99	1.05	0.31	1.94	20	0
Co	µg/L	0.14	0.32	0.24	0.25	0.05	20	0
Ni	µg/L	1.30	1.91	1.52	1.44	0.18	20	0
Cu	µg/L	0.83	1.66	1.18	1.23	0.24	20	0
Zn	µg/L	3.40	22.7	6.74	5.10	4.65	20	0
Ga	µg/L	<0.04	<0.09	0.03	<0.04	0.01	20	20
As	µg/L	0.27	0.46	0.35	0.37	0.06	20	0
Se	µg/L	0.12	0.40	0.16	0.14	0.06	20	0
Rb	µg/L	1.74	19.7	6.19	4.43	5.26	20	0
Y	µg/L	0.02	0.29	0.09	0.06	0.08	20	0
Zr	µg/L	0.02	0.22	0.06	0.04	0.05	20	0
Nb	µg/L	<0.01	0.01	0.01	<0.01	0.00	20	19
Mo	µg/L	<0.2	1.60	0.63	0.55	0.36	20	1
Cd	µg/L	0.01	0.08	0.01	0.01	0.02	20	0
Sn	µg/L	<0.08	0.22	0.06	<0.08	0.05	20	17
Sb	µg/L	0.11	0.24	0.17	0.16	0.03	20	0
Cs	µg/L	<0.04	0.30	0.09	0.06	0.09	20	4
La	µg/L	<0.003	0.22	0.06	0.03	0.06	20	1
Ce	µg/L	<0.004	0.40	0.09	0.04	0.10	20	1
Pr	µg/L	<0.003	0.06	0.02	0.01	0.02	20	7
Nd	µg/L	<0.005	0.230	0.072	0.039	0.076	20	1
Sm	µg/L	<0.005	0.065	0.017	0.009	0.019	20	8
Eu	µg/L	<0.003	0.017	0.005	<0.003	0.005	20	14
Gd	µg/L	<0.005	0.059	0.024	0.020	0.017	20	3
Tb	µg/L	<0.004	0.009	0.003	<0.004	0.002	20	14
Dy	µg/L	<0.003	0.048	0.015	0.008	0.015	20	4
Ho	µg/L	<0.003	0.008	0.003	<0.003	0.002	20	13
Er	µg/L	<0.003	0.023	0.009	0.006	0.008	20	5
Tm	µg/L	<0.003	0.004	0.00	<0.003	0.00	20	18
Yb	µg/L	<0.004	0.025	0.01	0.01	0.01	20	6
Lu	µg/L	<0.003	0.004	0.00	<0.003	0.00	20	17

Variable	Units	Min	Max	Mean	Median	SD	n	n(c)
Hf	µg/L	<0.006	<0.006	0.00	<0.006	0.00	20	20
Ta	µg/L	<0.006	<0.006	0.00	<0.006	0.00	20	20
W	µg/L	<0.06	<0.06	0.03	<0.06	0.00	20	20
Tl	µg/L	<0.02	<0.02	0.010	<0.02	0.00	20	20
Pb	µg/L	0.03	1.91	0.49	0.34	0.48	20	0
U	µg/L	0.07	0.41	0.19	0.17	0.09	20	0
Cr(VI)	µg/L	0.03	6.21	0.81	0.14	1.83	20	0
Cr(III)	µg/L	0.02	0.40	0.19	0.19	0.11	20	0
NPOC	mg/L	2.82	11.9	5.49	4.91	2.54	20	0
$\delta^{13}C$	‰	-20.1	-10.6	-12.2	-11.2	2.32	20	0
$\delta^{18}O$	‰	-7.98	-6.70	-7.39	-7.43	0.33	20	0
$\delta^{2}H$	‰	-54.8	-42.6	-48.9	-49.0	3.30	19	0
Benzo(b)fluoranthene	µg/L	<0.0036	0.037	0.005	<0.0036	0.01	20	11
Benzo(k)fluoranthene	µg/L	<0.0030	0.015	0.002	<0.003	0.00	20	18
Benzo(a)pyrene	µg/L	<0.0016	0.032	0.005	0.003	0.01	20	5
Benzo(ghi)perylene	µg/L	<0.0036	0.017	0.004	<0.004	0.00	20	16
Indeno(1,2,3-cd)pyrene	µg/L	<0.0049	0.0620	0.008	<0.0049	0.01	20	15
TPH (C8-C10)	mg/L	<0.003	0.0020	0.0016	<0.003	0.000	20	20
TPH (C10-C40)	mg/L	<0.042	0.0660	0.0316	<0.042	0.016	20	14
TPH (C8-C40)	mg/L	<0.045	0.0660	0.0328	<0.045	0.015	20	14

n = number of samples, n(c) = number of samples censored

Appendix 3 Time Series Plots

Time series plots are presented below. The plots for surface waters contain data from the previous surface water release (Fordyce et al., 2021), while the groundwater plots represent the first baseline monitoring data. A black line on the surface water graphs represents annual average (AA) allowable concentrations, which are also presented in Table 30 along with maximum allowable concentration (MAC) for information (SEPA, 2014b, 2020a).

Table 30 Environmental quality standards relevant to the Glasgow Observatory data

Parameter	Unit	AA	95%ile	MAC
pH		5.95		
Temp	°C		28	
DO	mg/L	4.5		
P total	mg/L	0.069		
SO4	mg/L	400		
F	mg/L	5 (>50 mg CaCO3/L)		15 (>50 mg CaCO3/L)
HPO4	mg/L	0.069		
NO3	mg/L	5.7		
Ag	µg/L	0.05		0.1
Al	µg/L	15 (pH >6.5)		25 (pH >6.5)
As	µg/L	50		
B	µg/L	2000		
Cd	µg/L	0.09 (class 3 > 50 mg/L CaCO$_3$) to 0.25 (class 5≥ 200 mg/L CaCO$_3$)		0.6 (class 3) to 1.5 (class 5)
Co	µg/L	3		100
Cr (III)	µg/L	4.7		
Cr (VI)	µg/L	3.4		
Cr (Total)			32	
Cu	µg/L	1 (bioavailable)		
Fe	µg/L	1000		
Mn	µg/L	123 (bioavailable)		
Ni	µg/L	4 (bioavailable)		34
Pb	µg/L	1.2 (bioavailable)		14
Sn	µg/L	25		
V	µg/L	20 (class 1 ≤200 mg/L CaCO$_3$) to 60 (class 2>200 mg/> CaCO$_3$)		
Zn	µg/L	10.9 (bioavailable)		
benzo(b)fluoranthene	µg/L	0.03 (combined total)		
benzo(k)fluoranthene	µg/L			
benzo(a)pyrene	µg/L	0.05		0.1
benzo(ghi)perylene	µg/L	0.002 (combined total)		
indeno(1,2,3-cd)pyrene	µg/L			

AA - annual average, MAC - maximum allowable concentrations

Field parameters

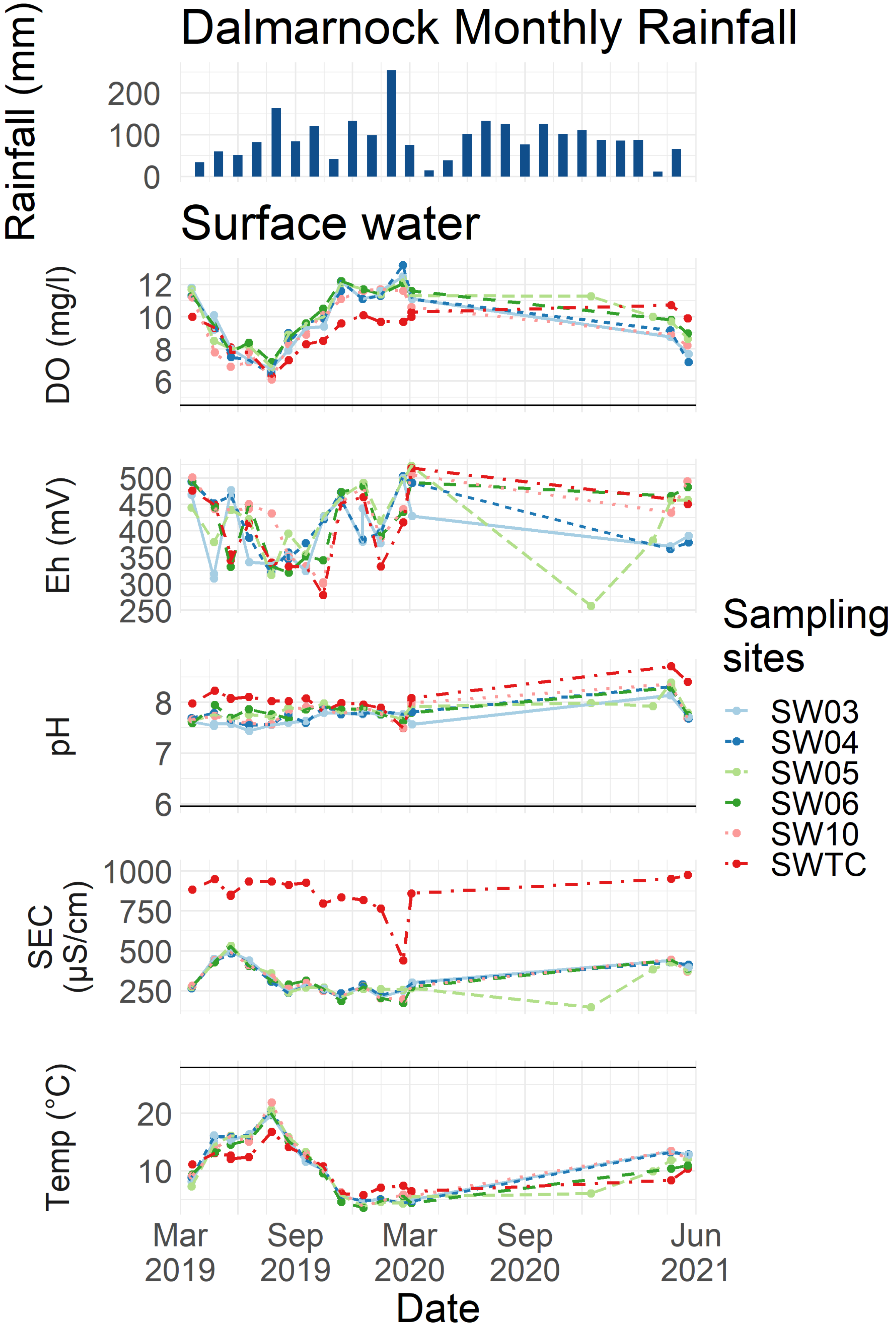

Figure 17 time-series of field parameters measured during sampling at surface water sites.

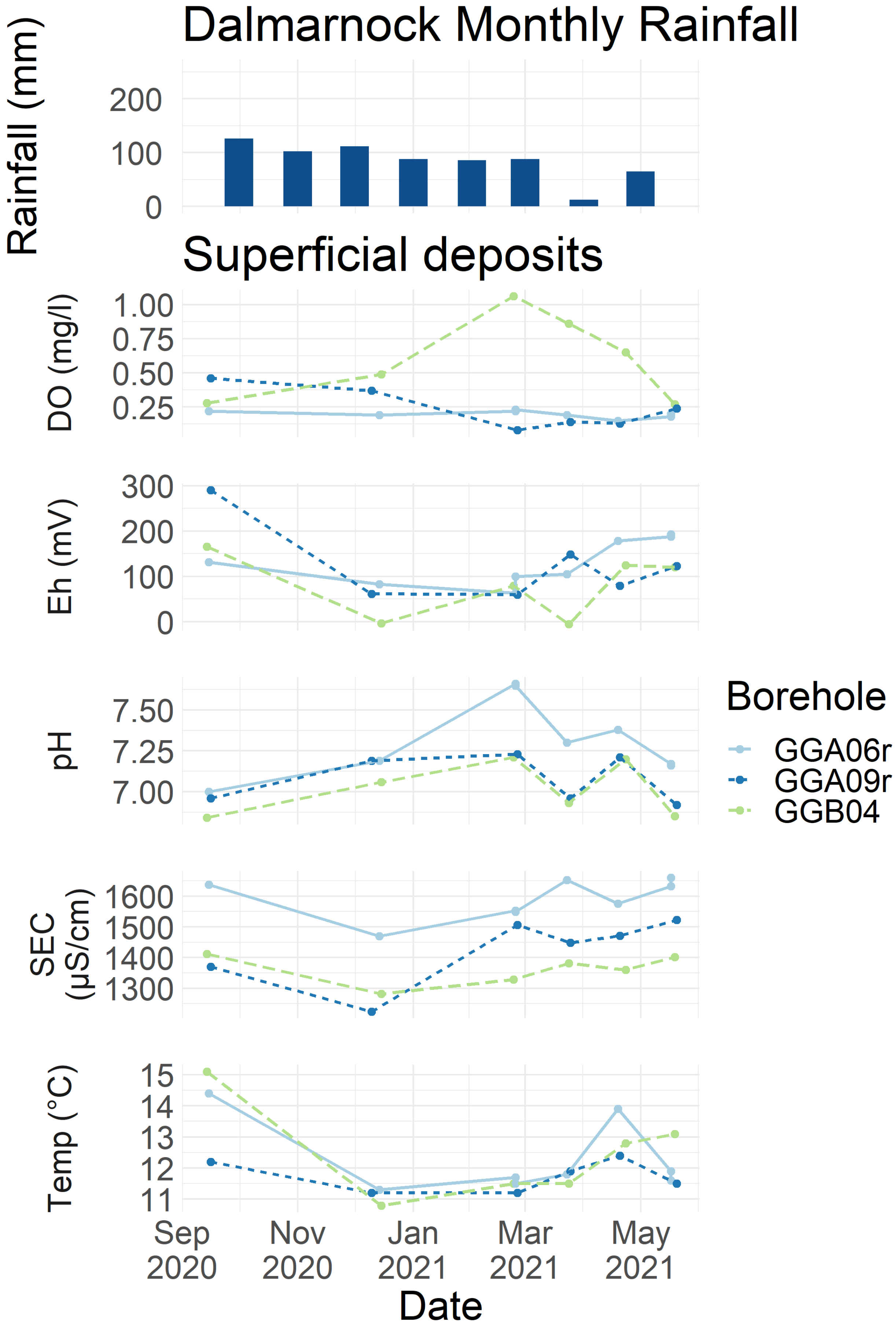

Figure 18 time-series of field parameters measured during sampling of superficial deposit boreholes.

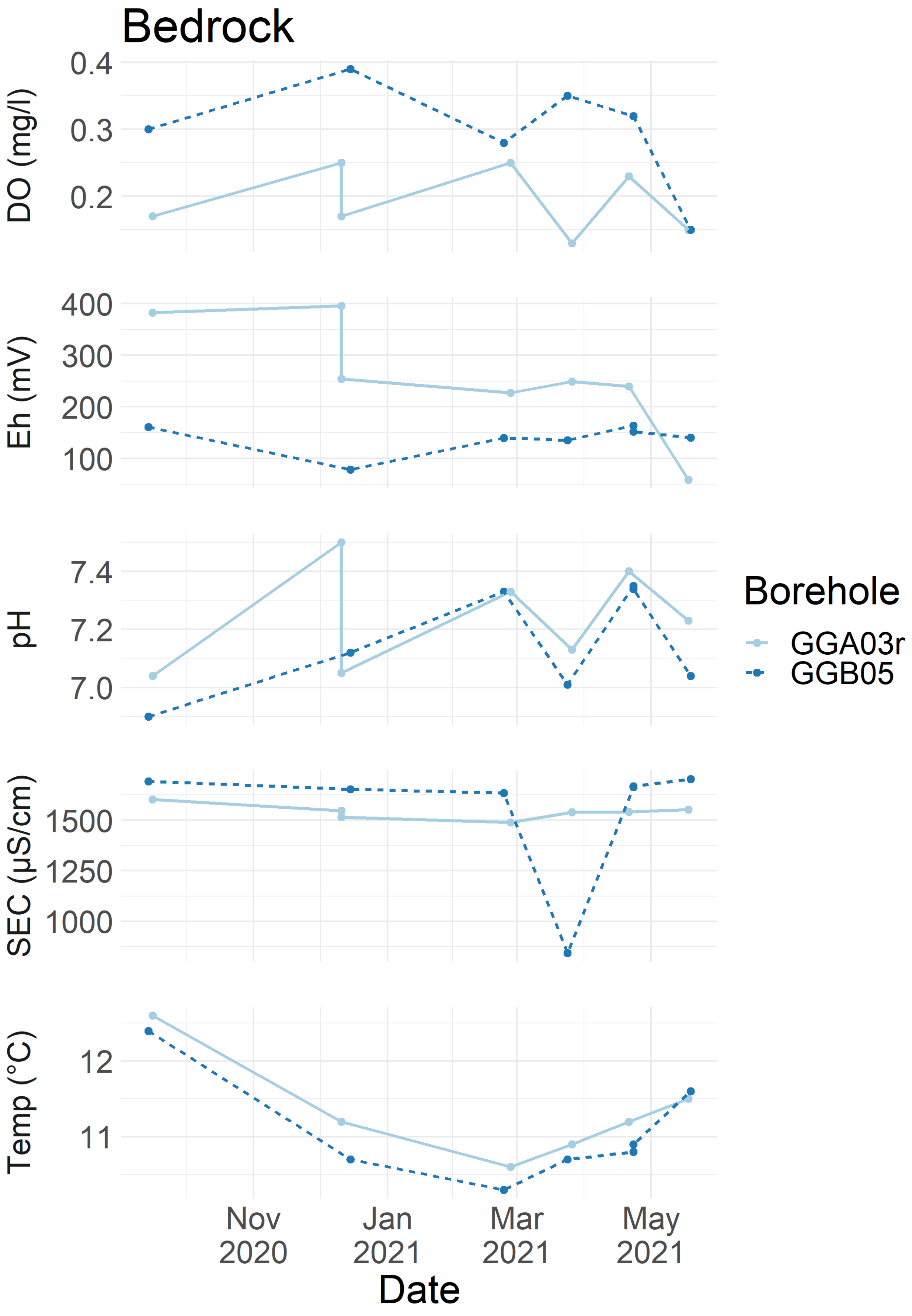

Figure 19 time-series of field parameters measured during sampling of bedrock boreholes.

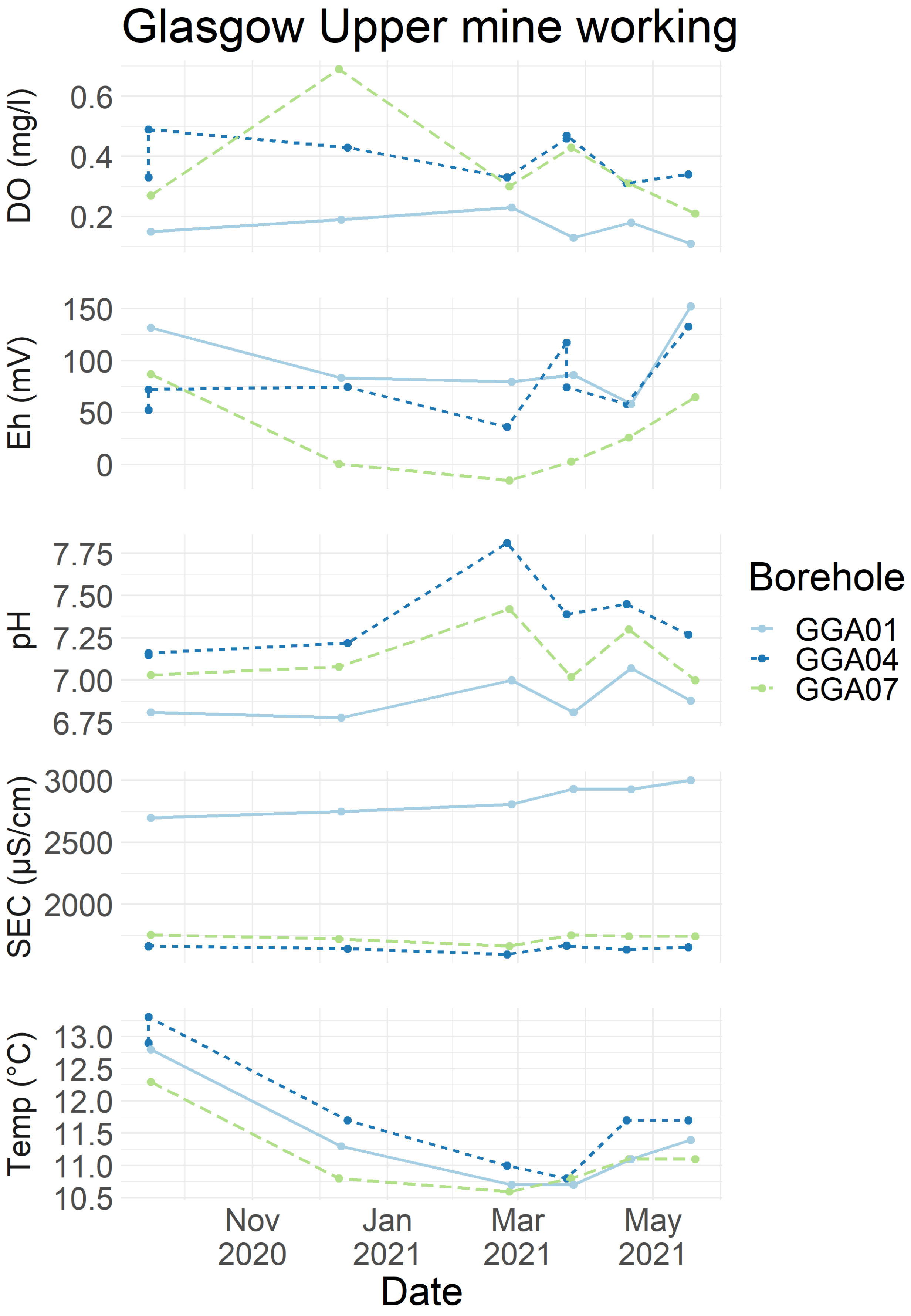

Figure 20 time-series of field parameters measured during sampling of Glasgow Upper mine working boreholes.

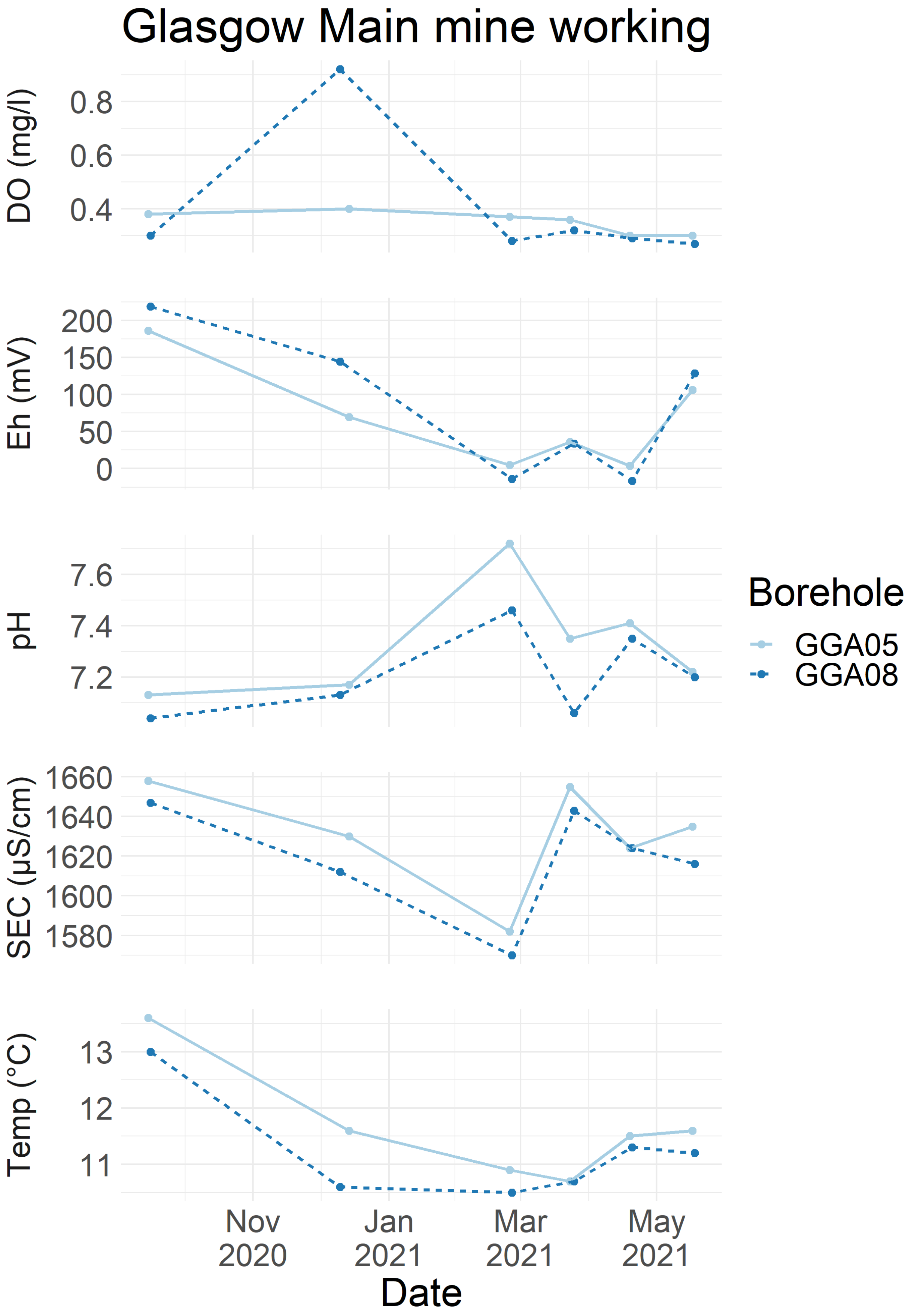

Figure 21 time-series of field parameters measured during sampling of Glasgow Main mine working boreholes.

Major ions

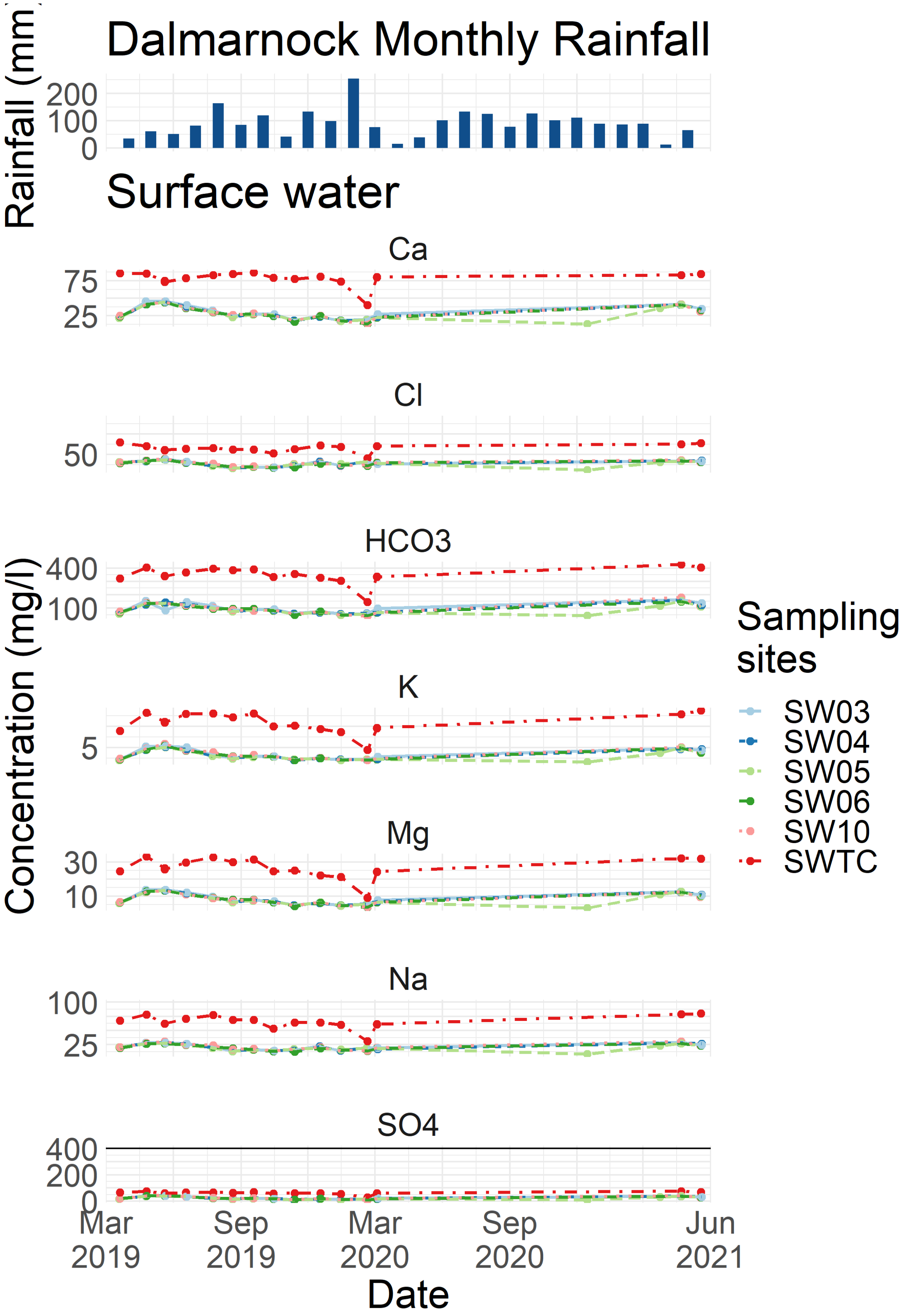

Figure 22 the top panel shows monthly rainfall totals at Dalmarnock. The remaining panels show time-series of major ion concentrations from surface water samples, there was a large gap in surface water sampling between March 2020 and March 2021 due to COVID-19 related restrictions.

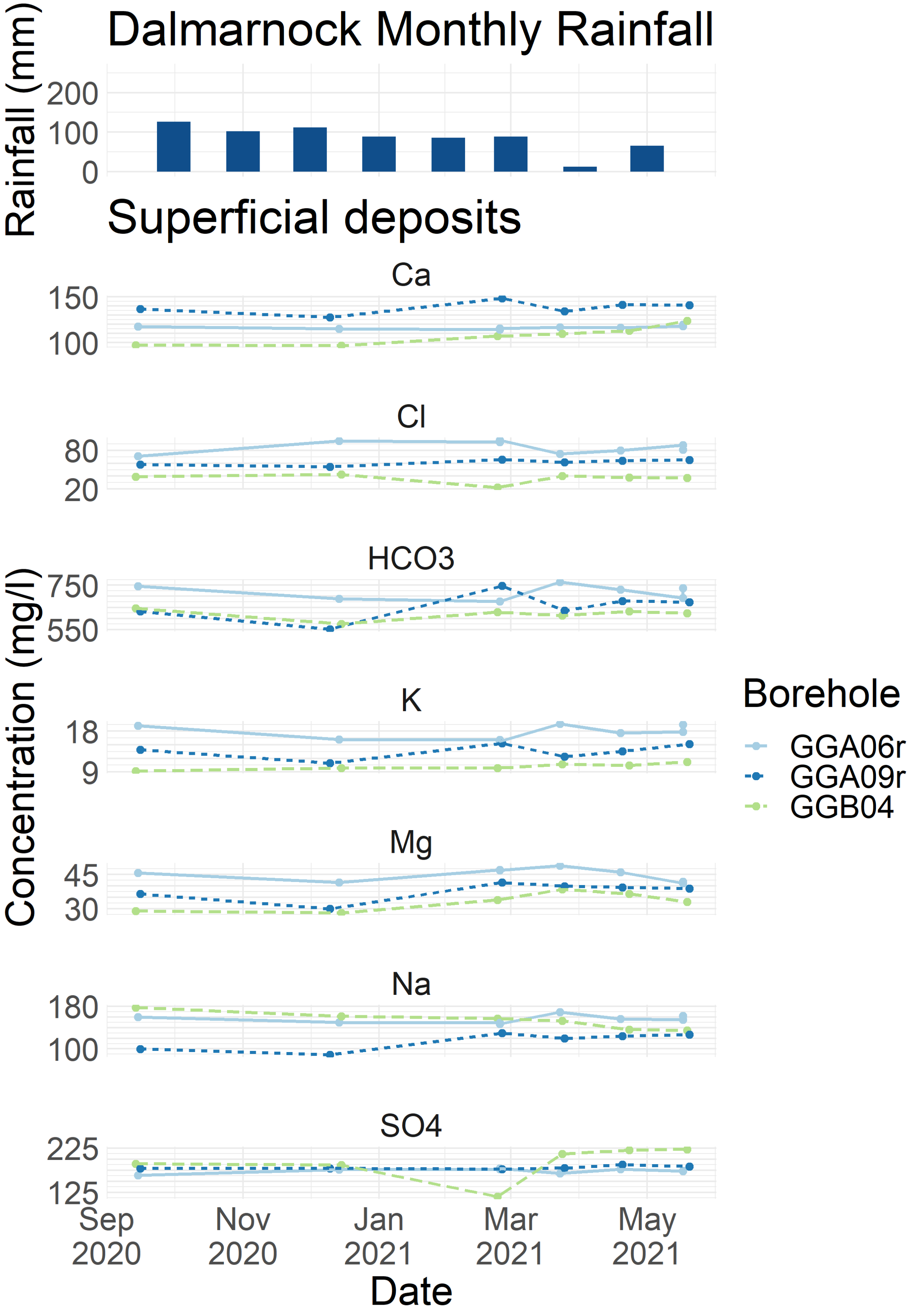

Figure 23 the top panel shows monthly rainfall totals at Dalmarnock. The remaining panels show time-series of major ion concentrations from superficial deposit boreholes.

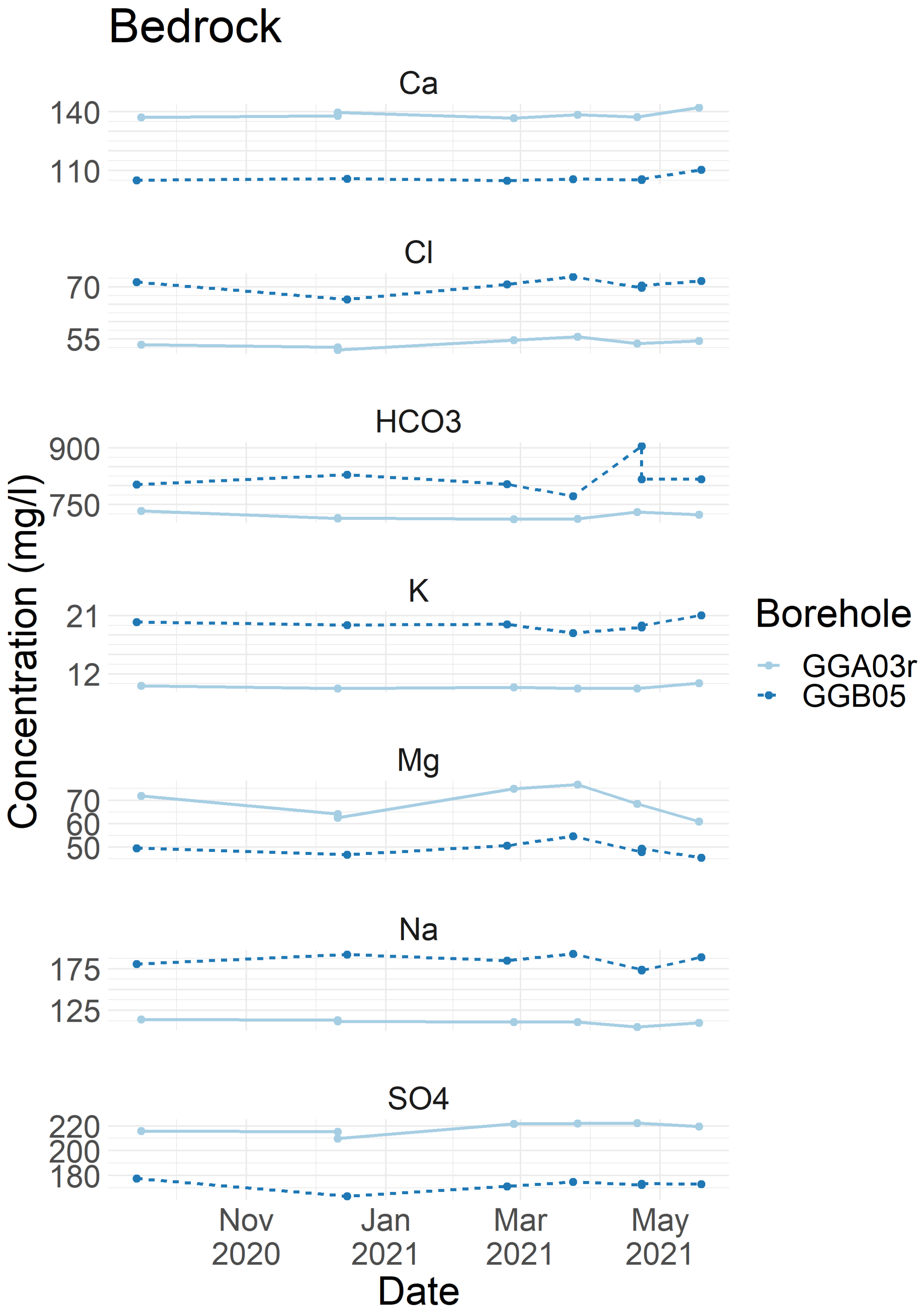

Figure 24 time-series of major ion concentrations from bedrock boreholes.

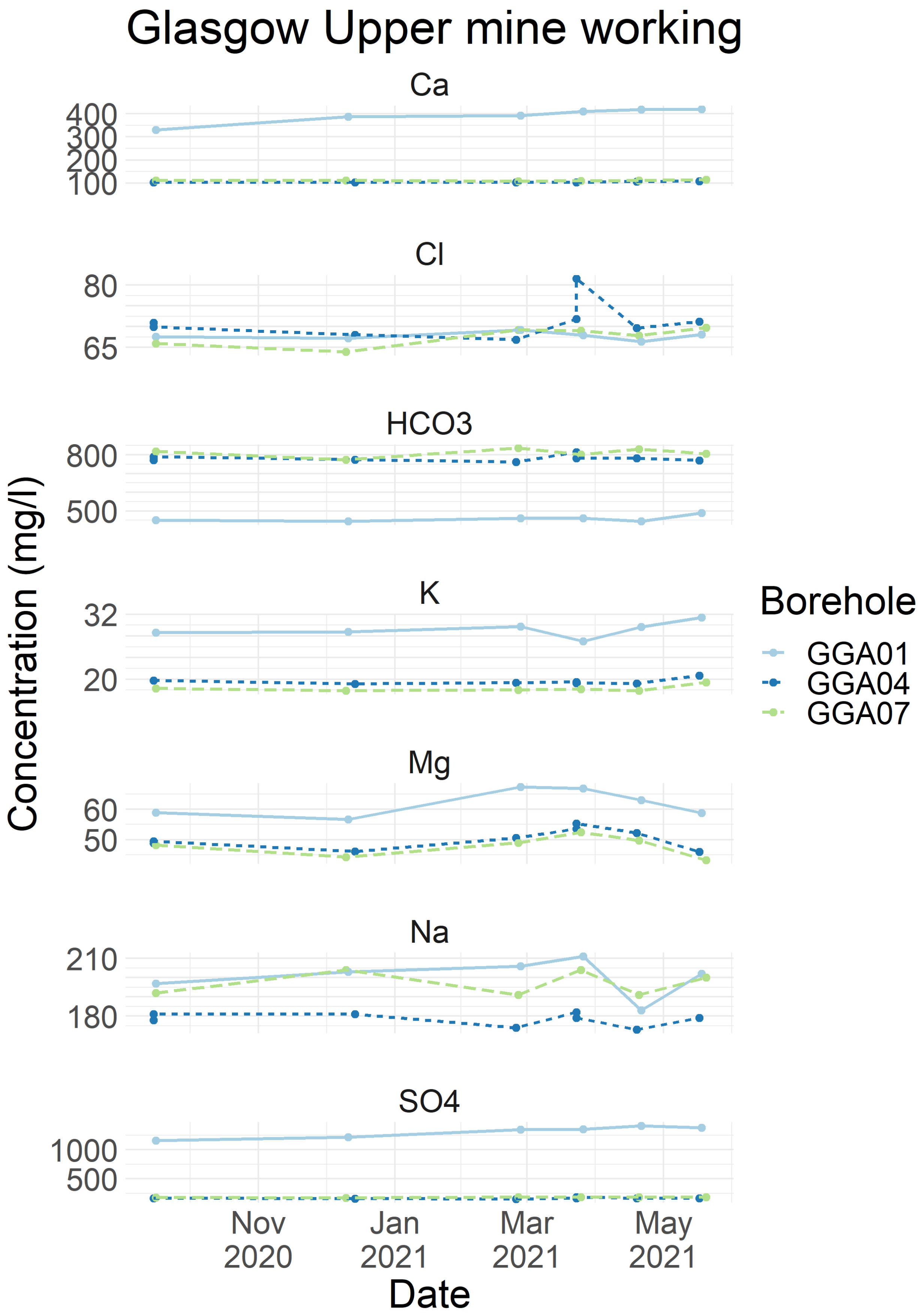

Figure 25 time-series of major ion concenatrions from Glasgow Upper mine working boreholes.

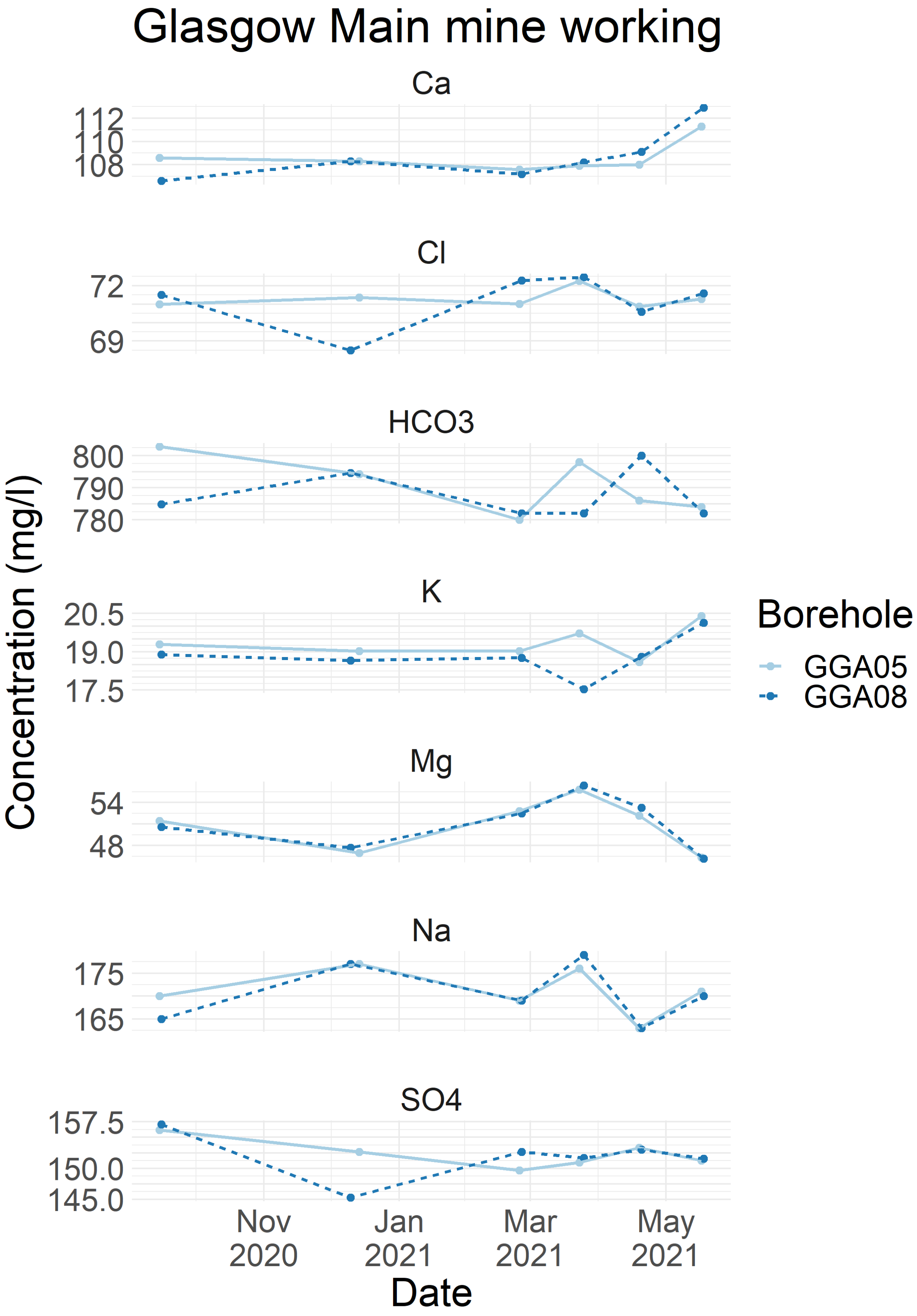

Figure 26 time-series pf major ion concentrations from Glasgow Main mine working boreholes.

Trace element in µg/L

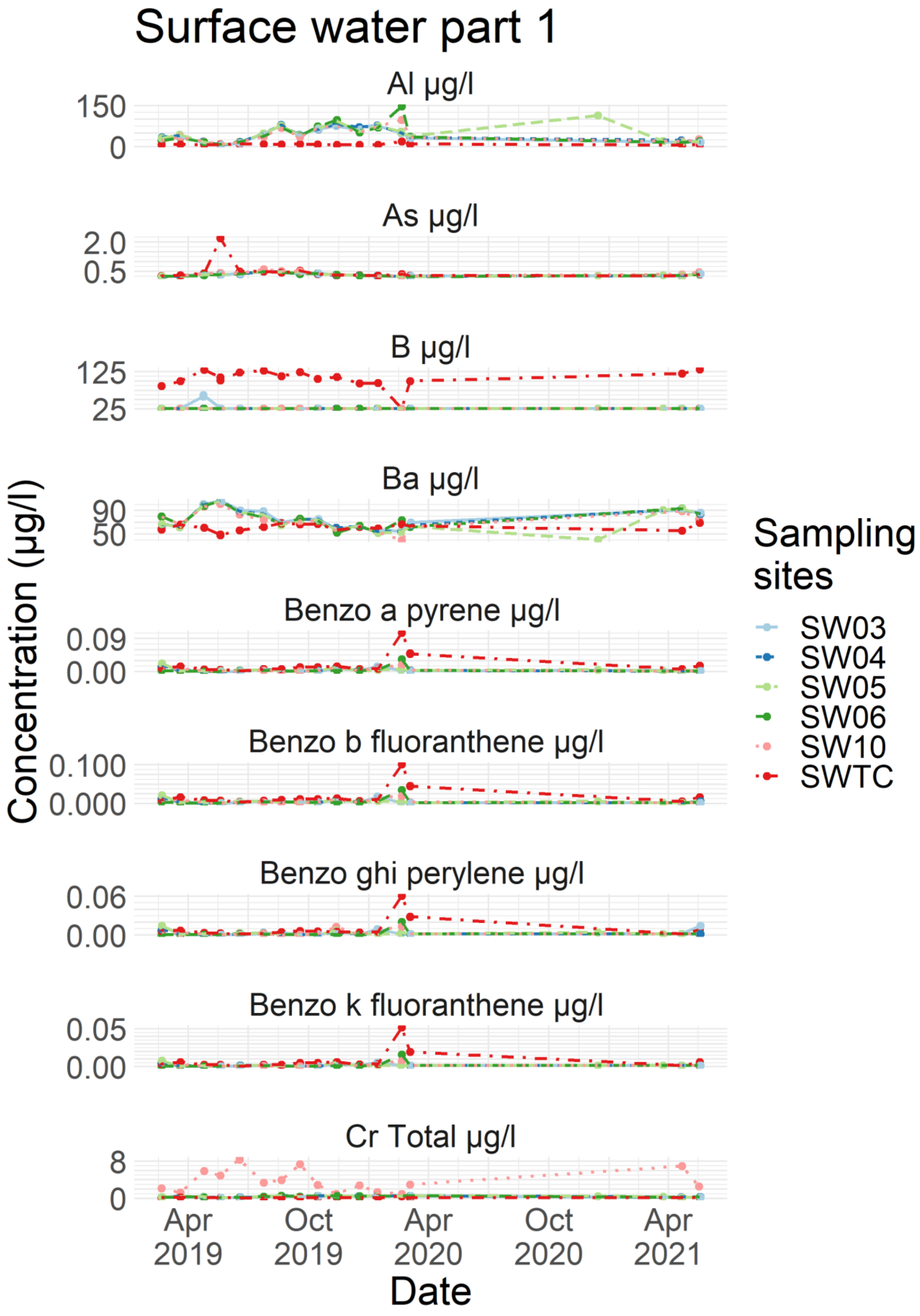

Figure 27 time series of trace element concentrations from surface water samples. EQS AA for B = 2000 µg/L, As = 50 µg/L. Data < detection limit (DL) are set to ½ DL.

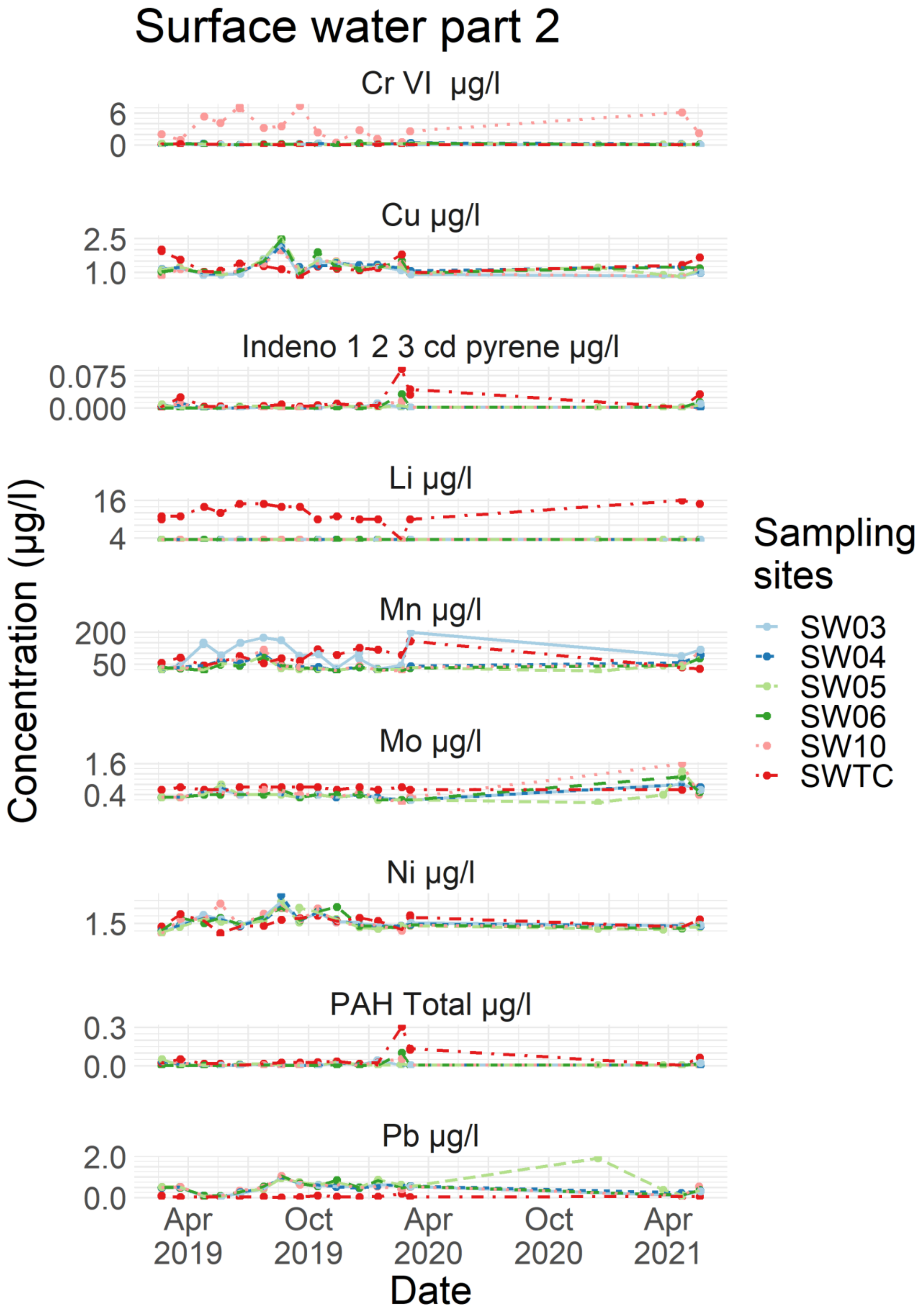

Figure 28 time series of trace element concentrations from surface water samples. EQS AA for Ni = 4 µg/L. Data < detection limit (DL) are set to ½ DL.

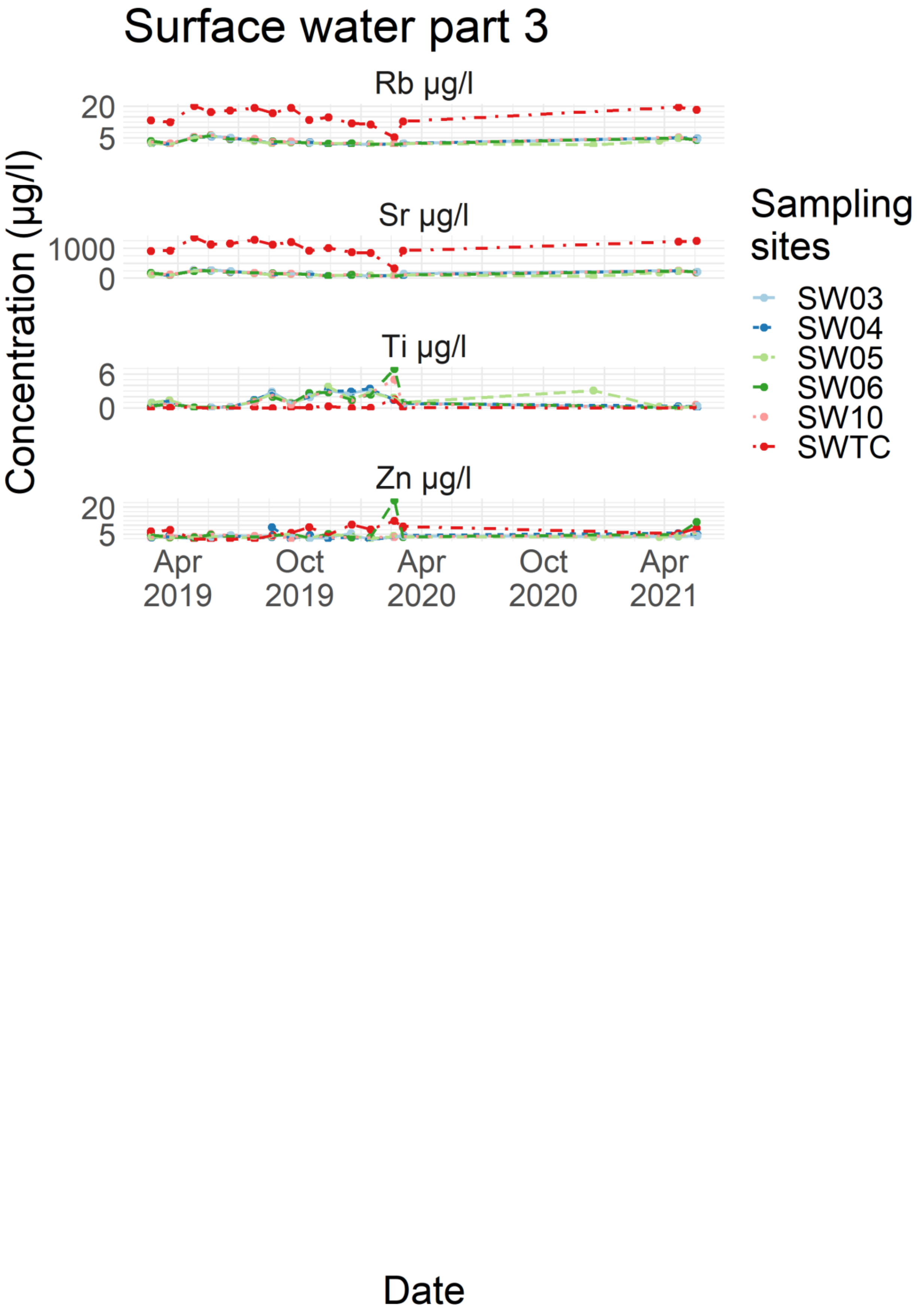

Figure 29 time series of trace element concentrations from surface water samples. Data < detection limit (DL) are set to ½ DL.

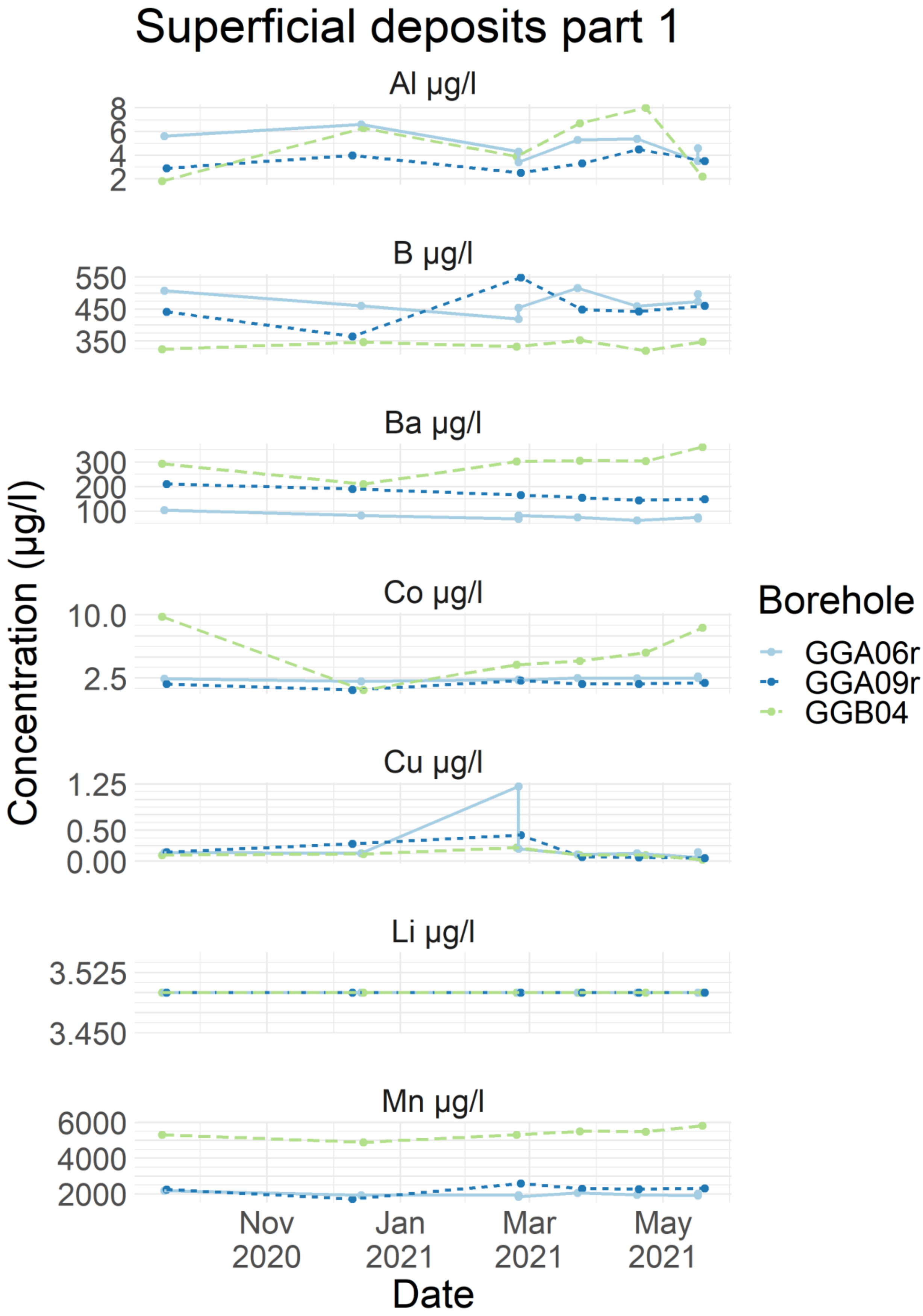

Figure 30 time series of trace element concentrations from superficial deposit boreholes. Data < detection limit (DL) are set to ½ DL.

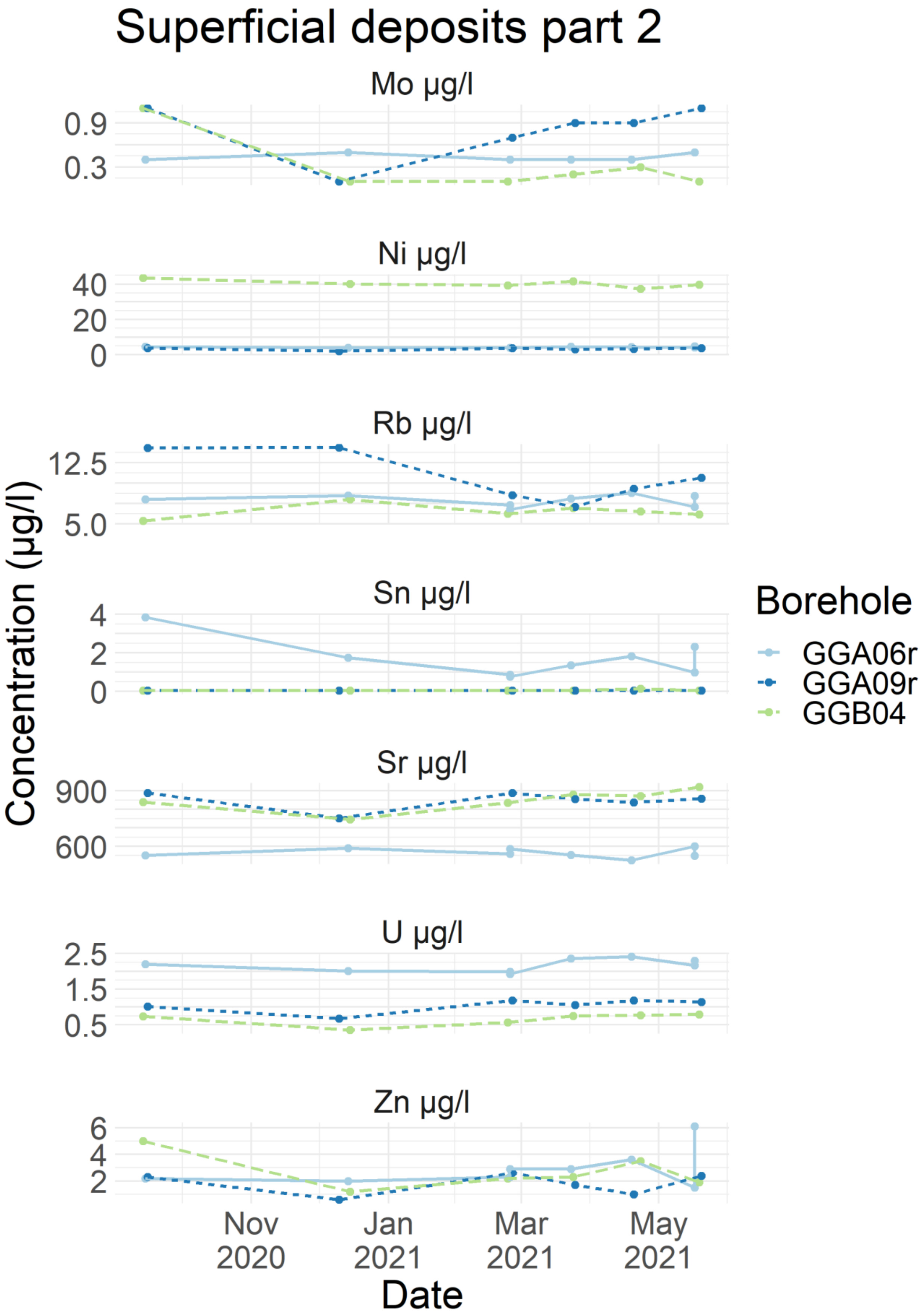

Figure 31 time series of trace element concentrations from superficial deposit boreholes. Data < detection limit (DL) are set to ½ DL.

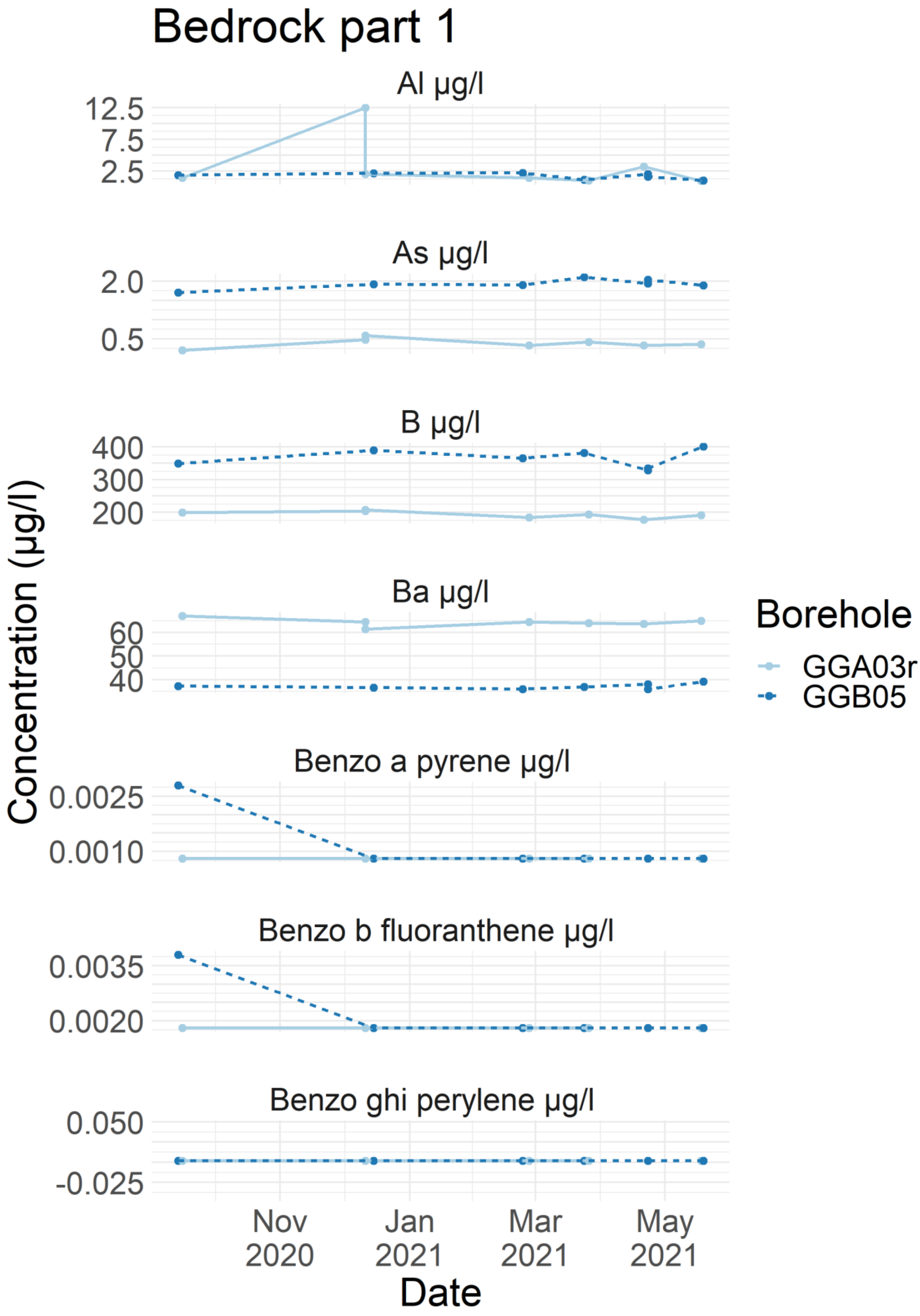

Figure 32 time-series of trace element concentrations from bedrock despoits. Data < detection limit (DL) are set to ½ DL.

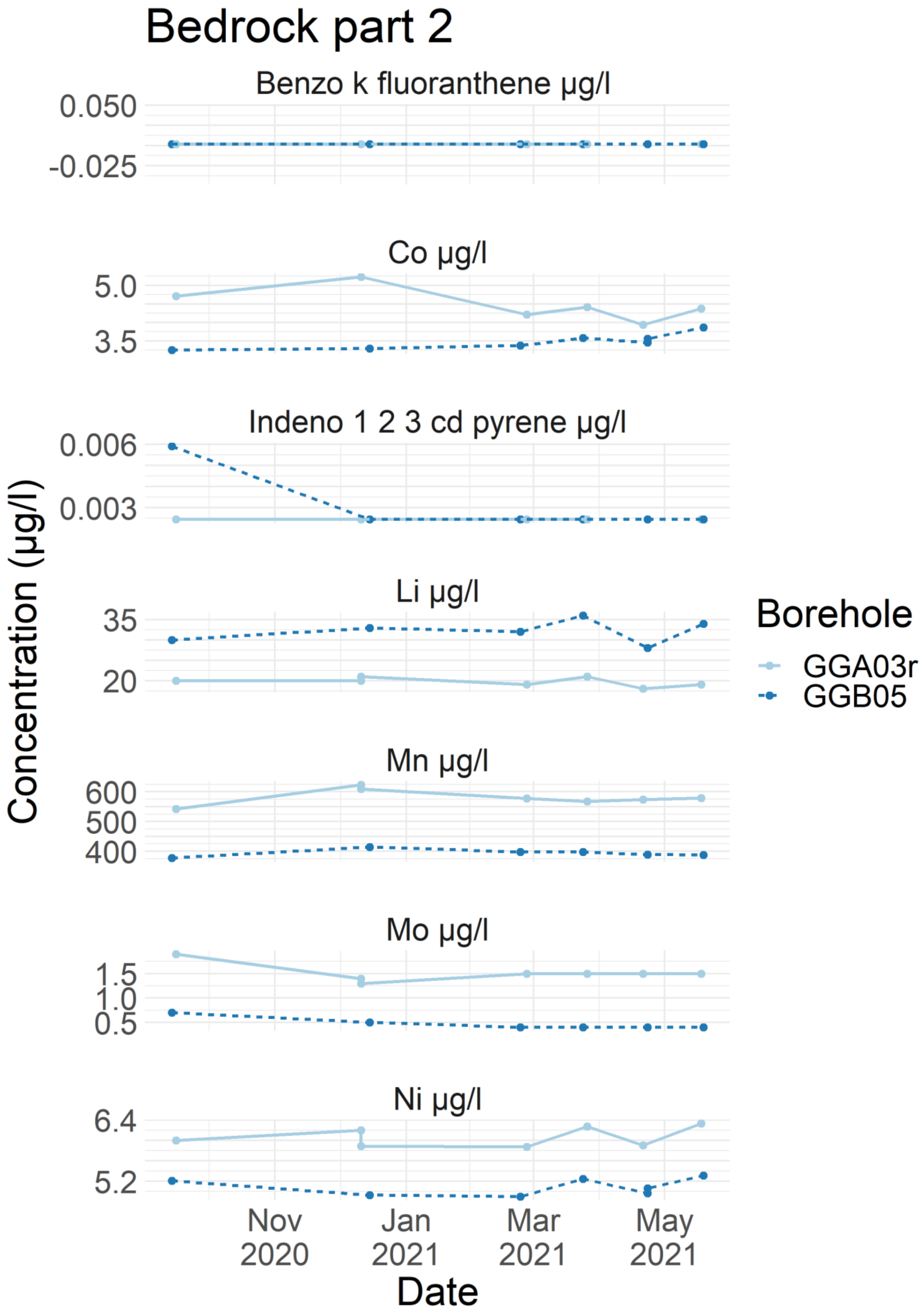

Figure 33 time-series of trace element concentrations from bedrock despoits. Data < detection limit (DL) are set to ½ DL.

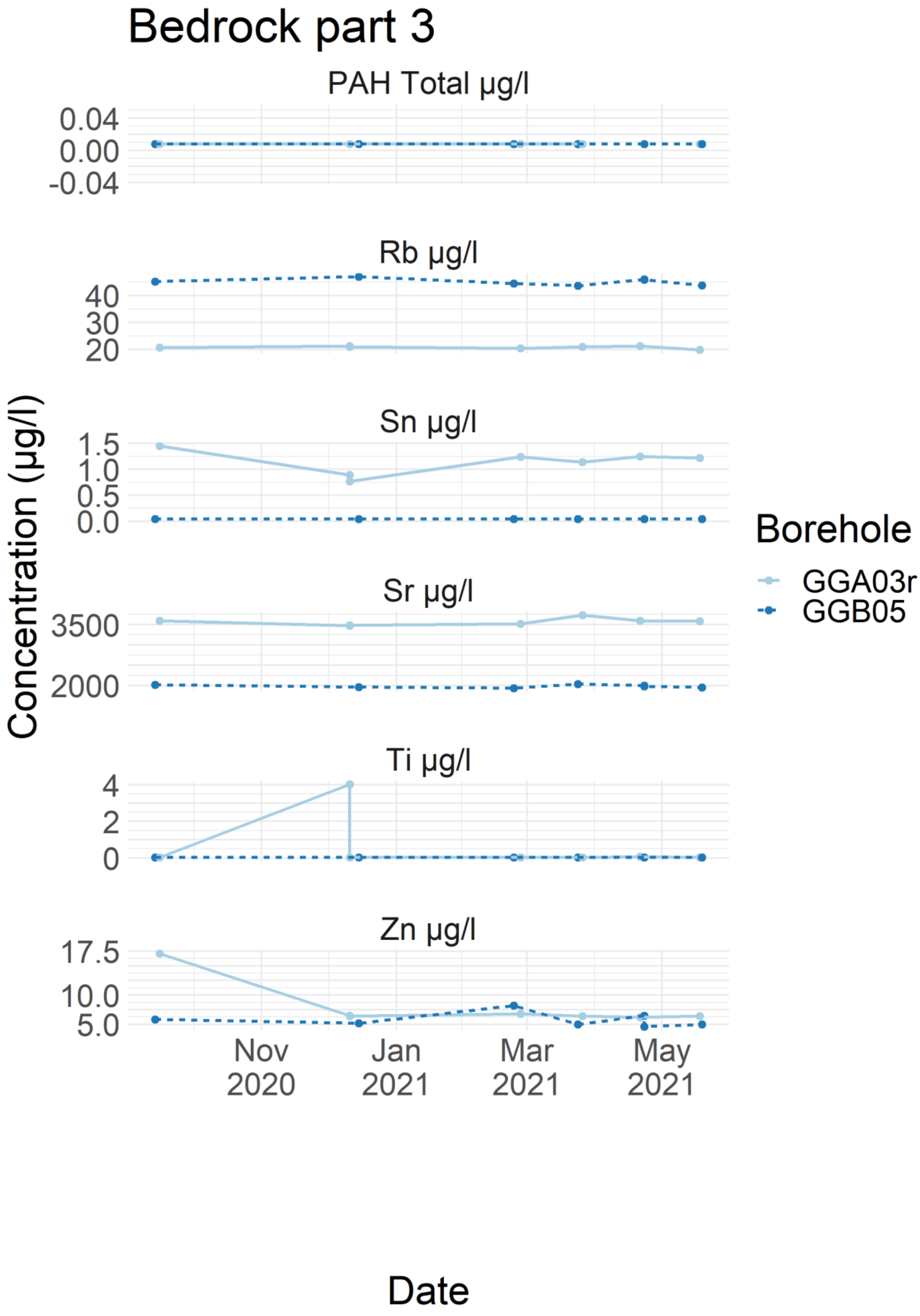

Figure 34 time-series of trace element concentrations from bedrock despoits. Data < detection limit (DL) are set to ½ DL.

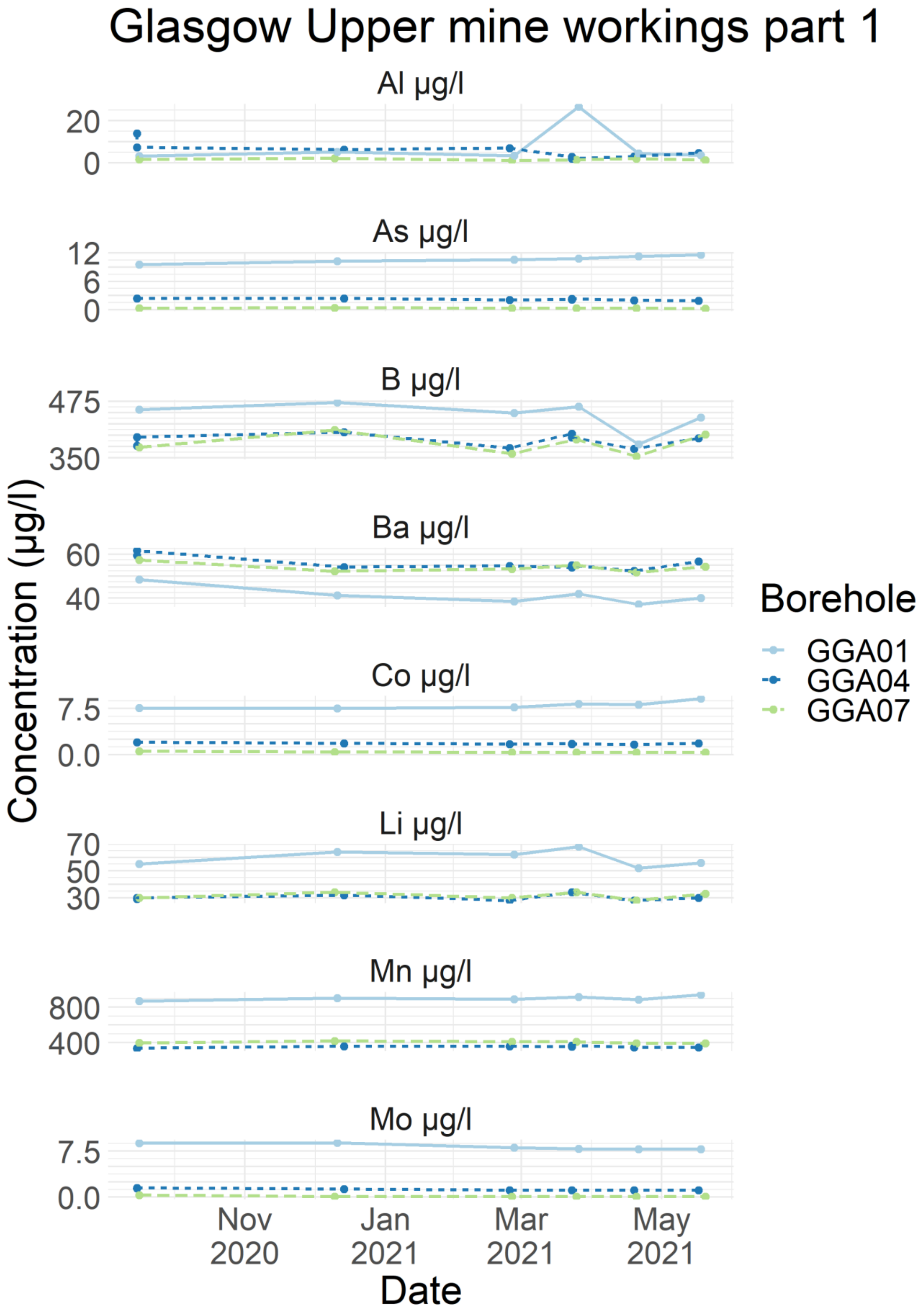

Figure 35 time-series of trace element concentrations from Glasgow Upper mine working boreholes. Data < detection limit (DL) are set to ½ DL.

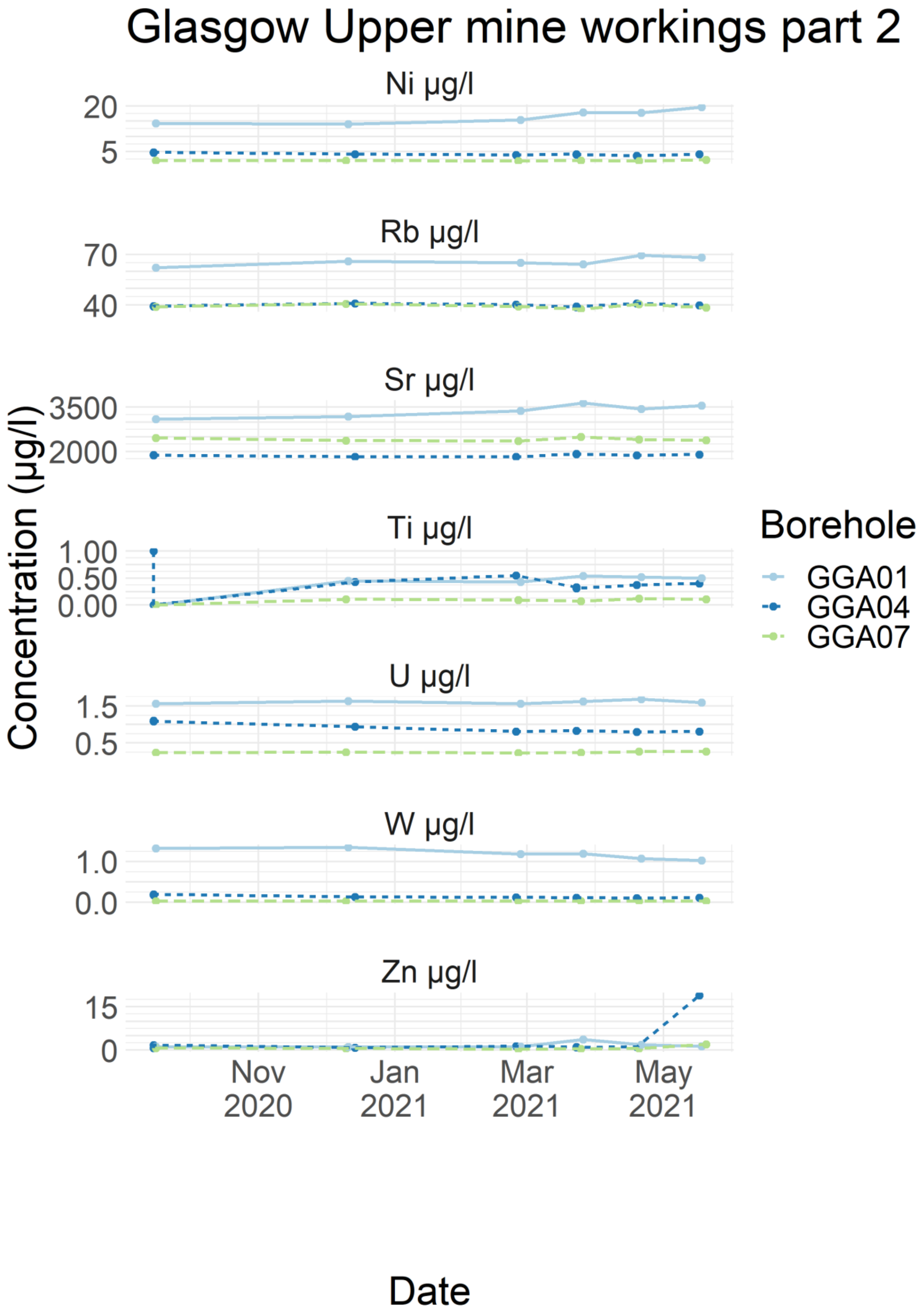

Figure 36 time-series of trace element concentrations from Glasgow Upper mine working boreholes. Data < detection limit (DL) are set to ½ DL.

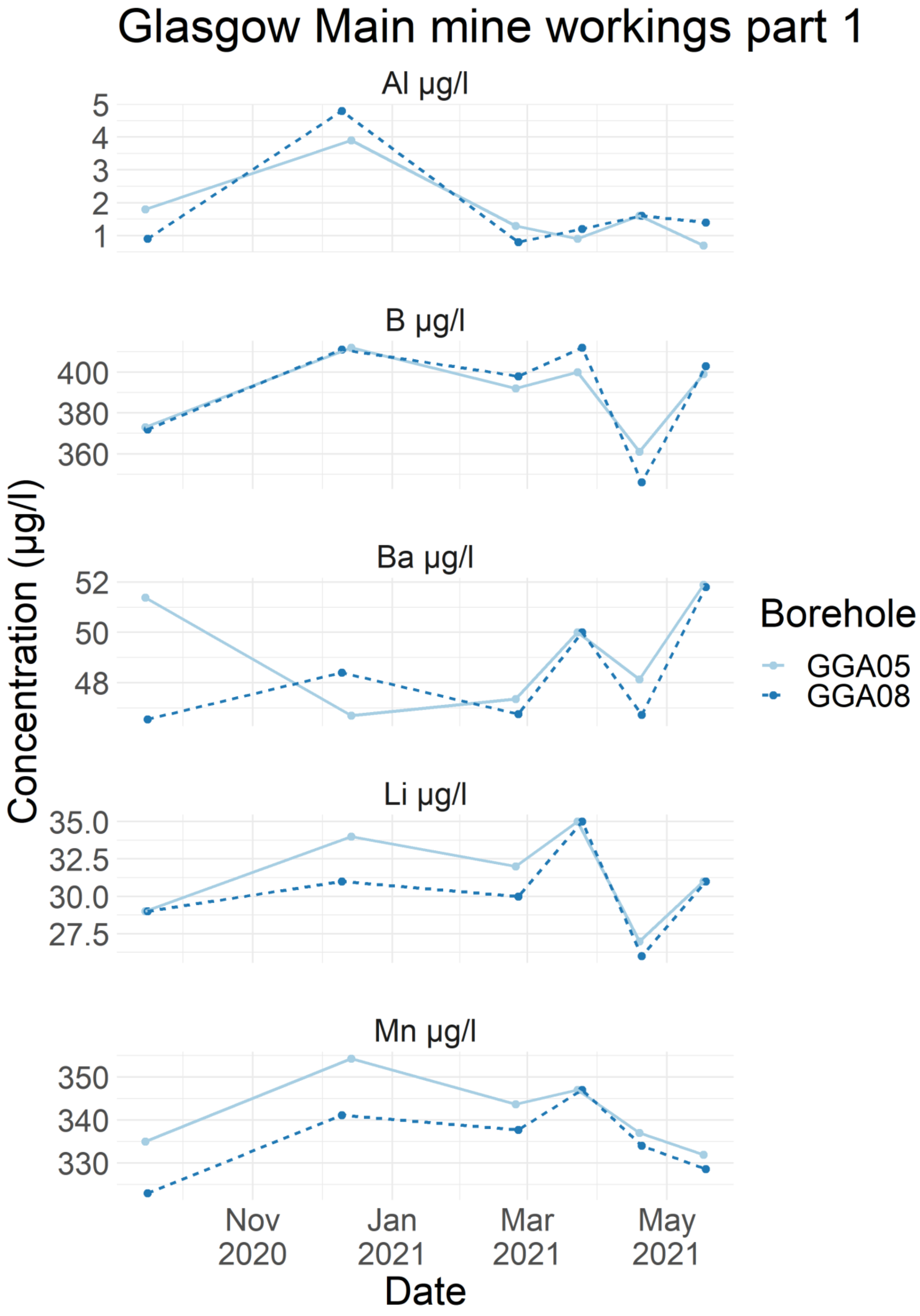

Figure 37 time-series of trace element concentrations from Glasgow Main mine working boreholes. Data < detection limit (DL) are set to ½ DL.

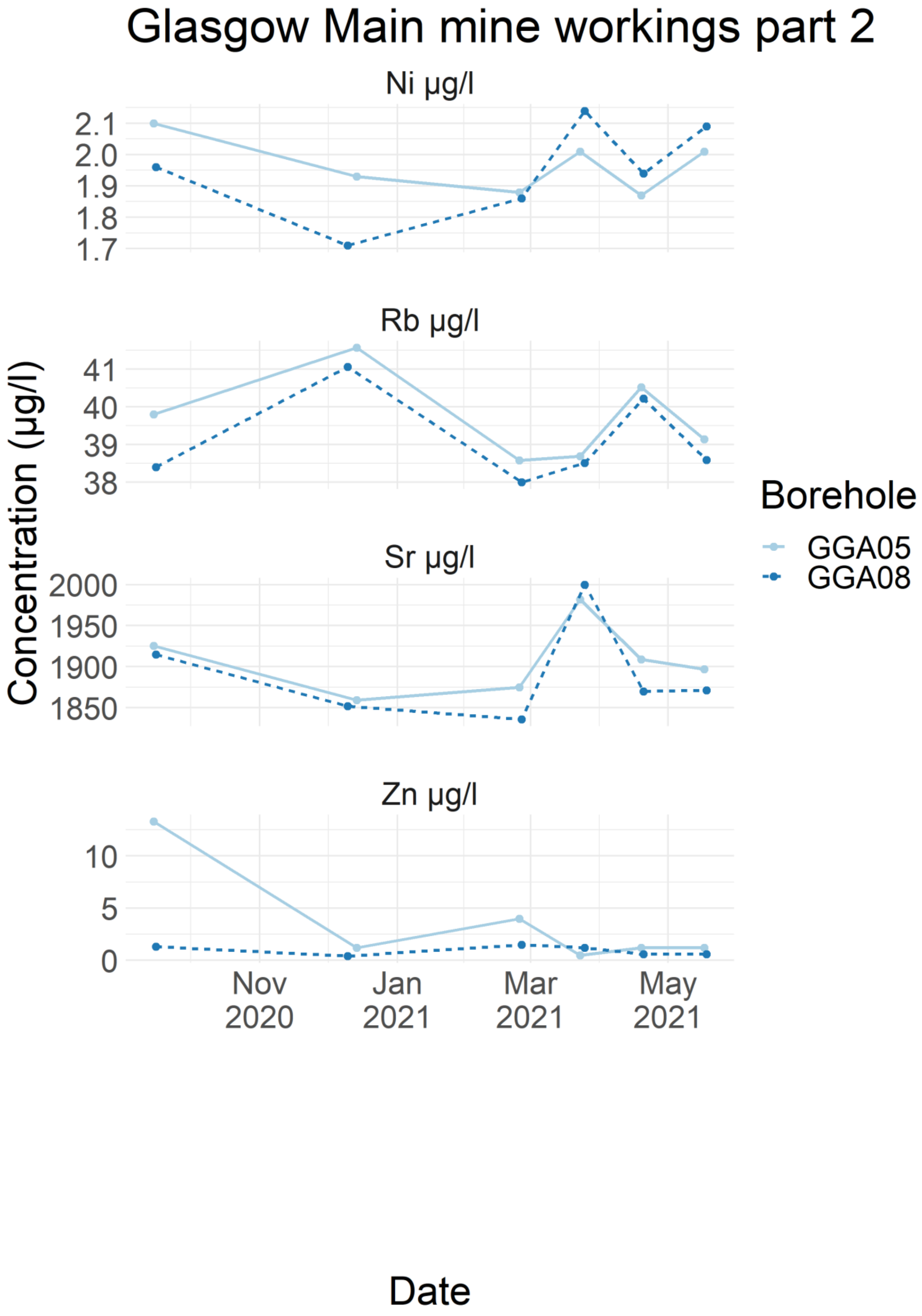

Figure 38 time-series of trace element concentrations from Glasgow Main mine working boreholes. Data < detection limit (DL) are set to ½ DL.

Other elements and TPH in mg/L

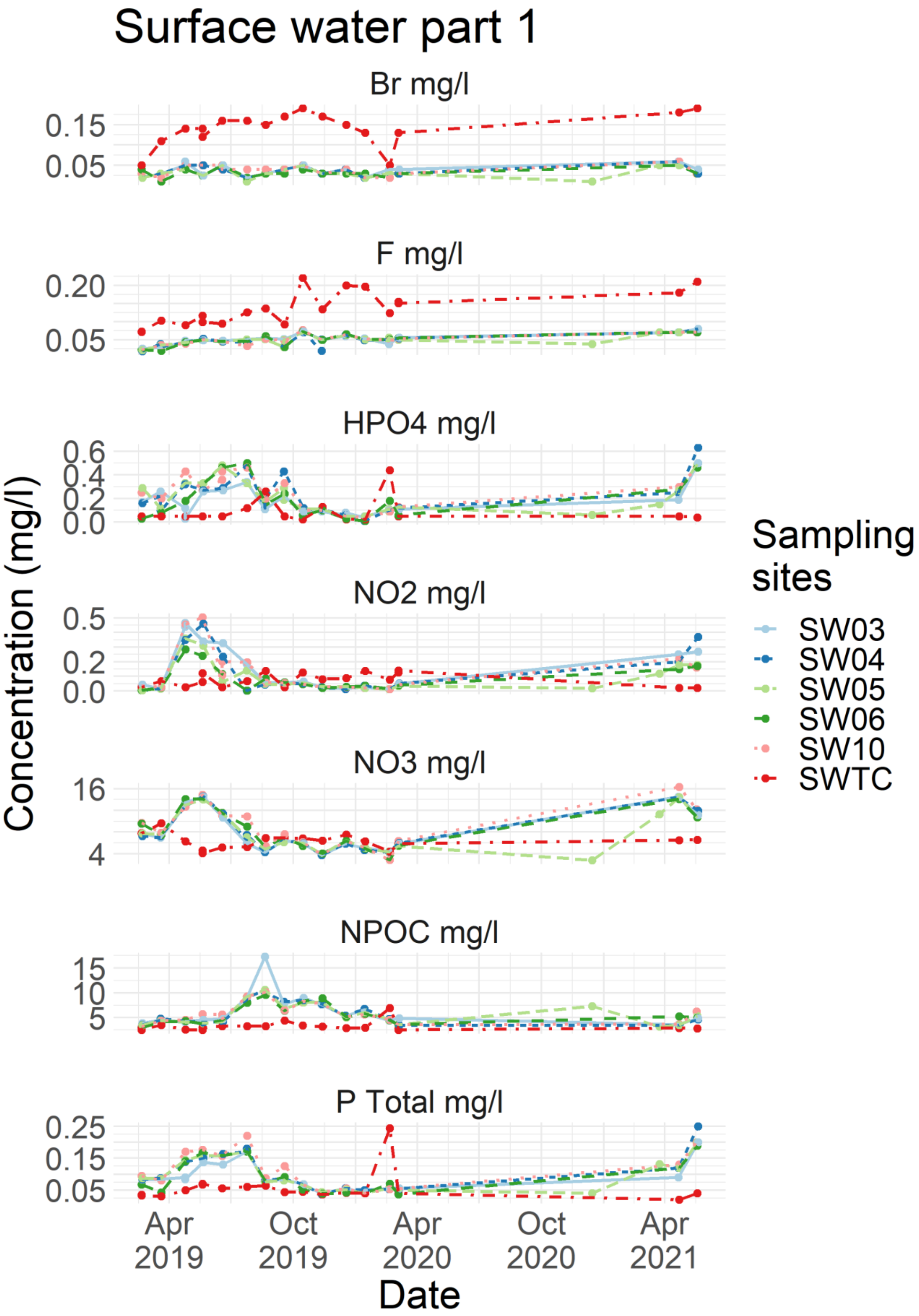

Figure 39 time series of all other parameter concentrations measured in mg/L from surface water sampling. EQS AA for F = 5 mg/L. Data < detection limit (DL) are set to ½ DL.

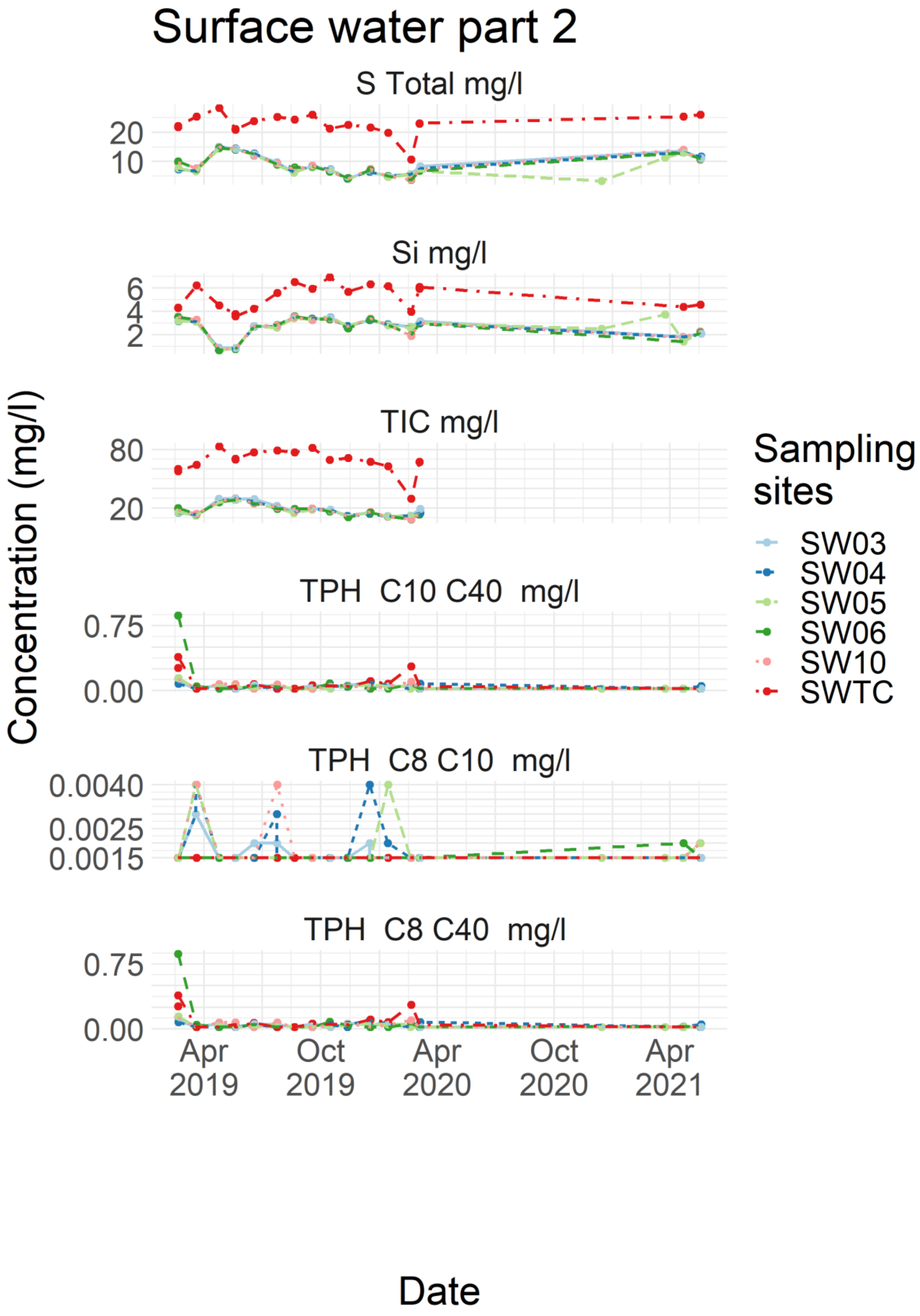

Figure 40 time series of all other parameter concentrations measured in mg/L from surface water sampling. Data < detection limit (DL) are set to ½ DL.

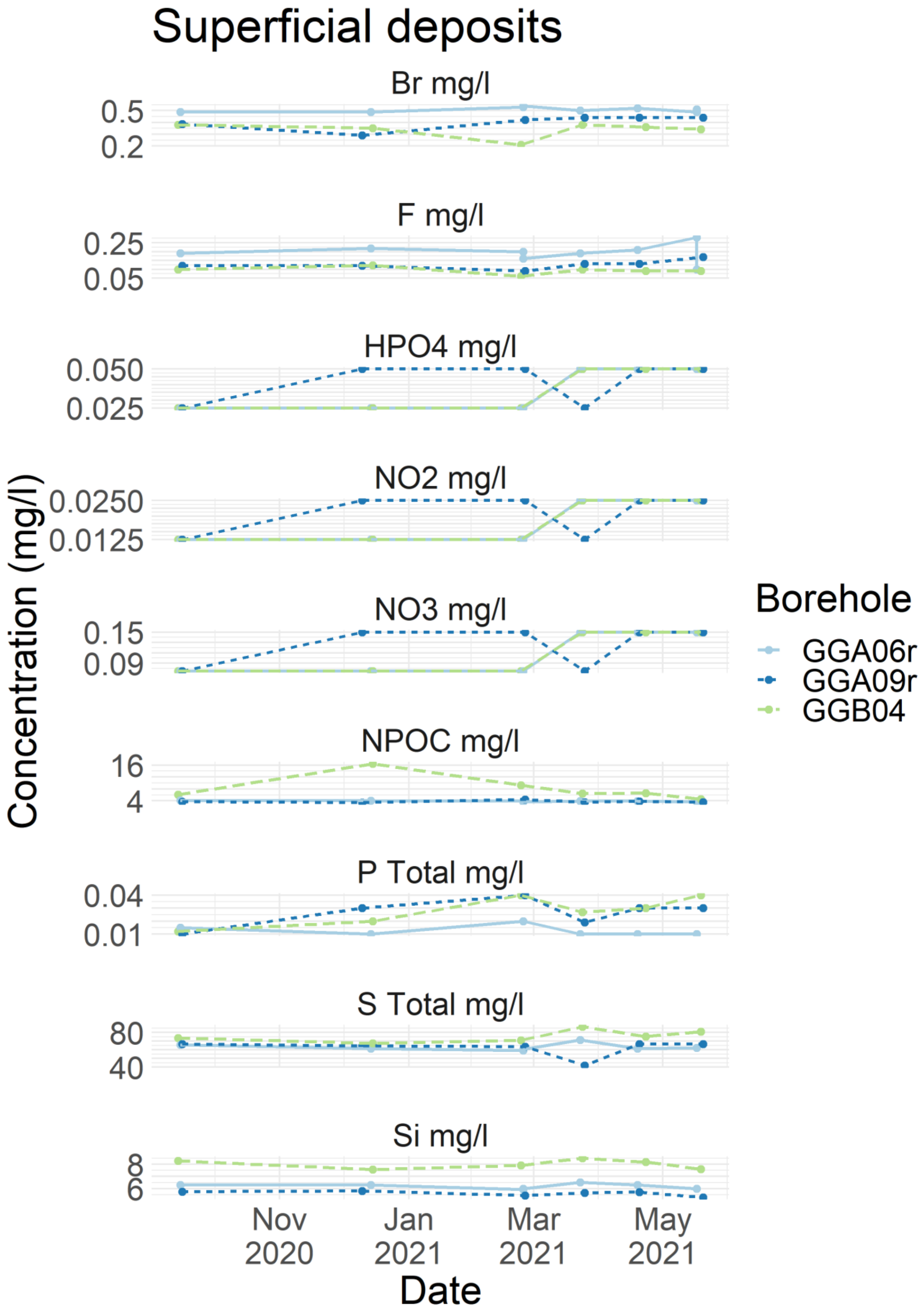

Figure 41 time series of all other parameter concentrations measured in mg/L from superficial deposit boreholes. Data < detection limit (DL) are set to ½ DL.

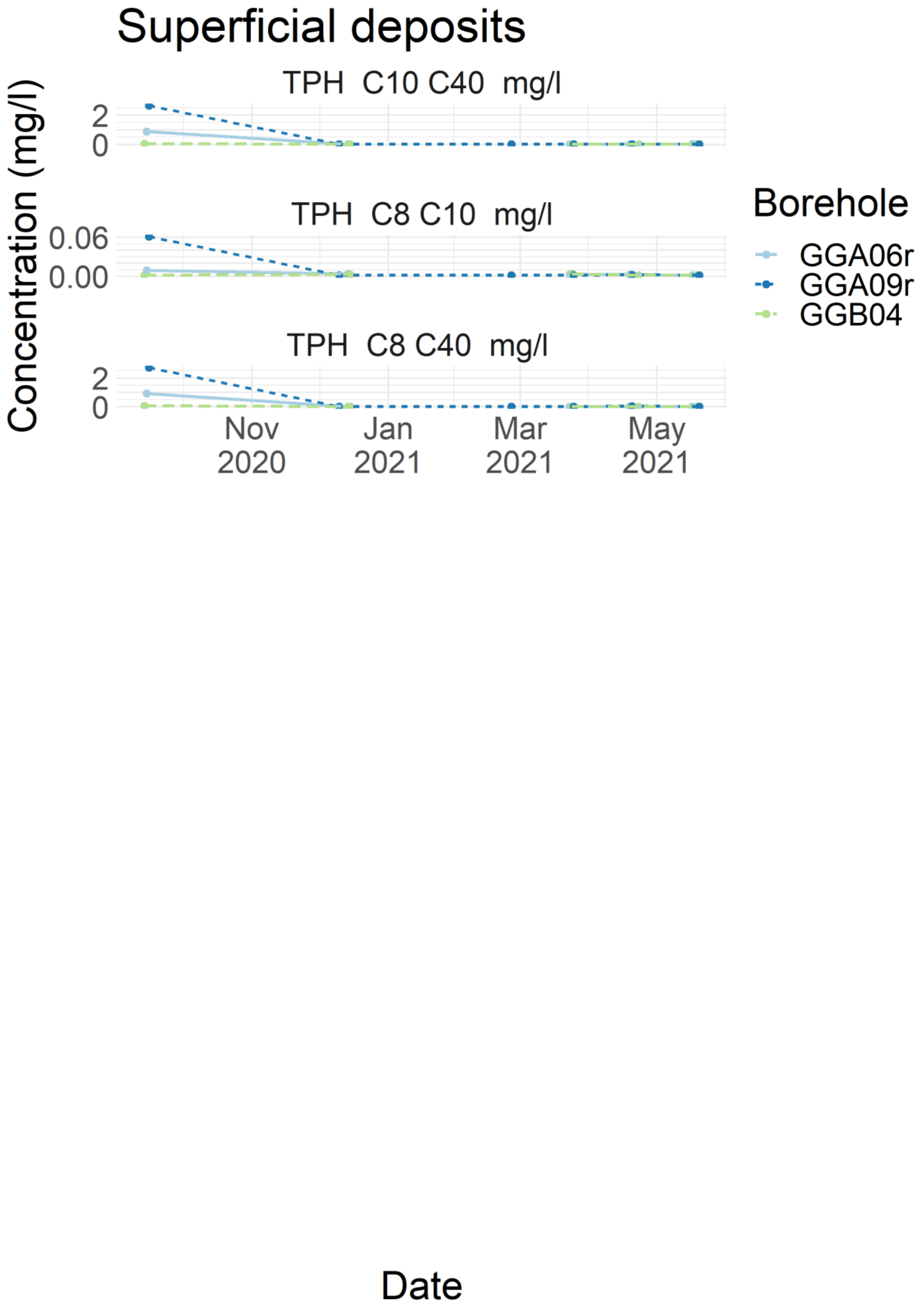

Figure 42 time series of all other parameter concentrations measured in mg/L from superficial deposit boreholes. Data < detection limit (DL) are set to ½ DL.

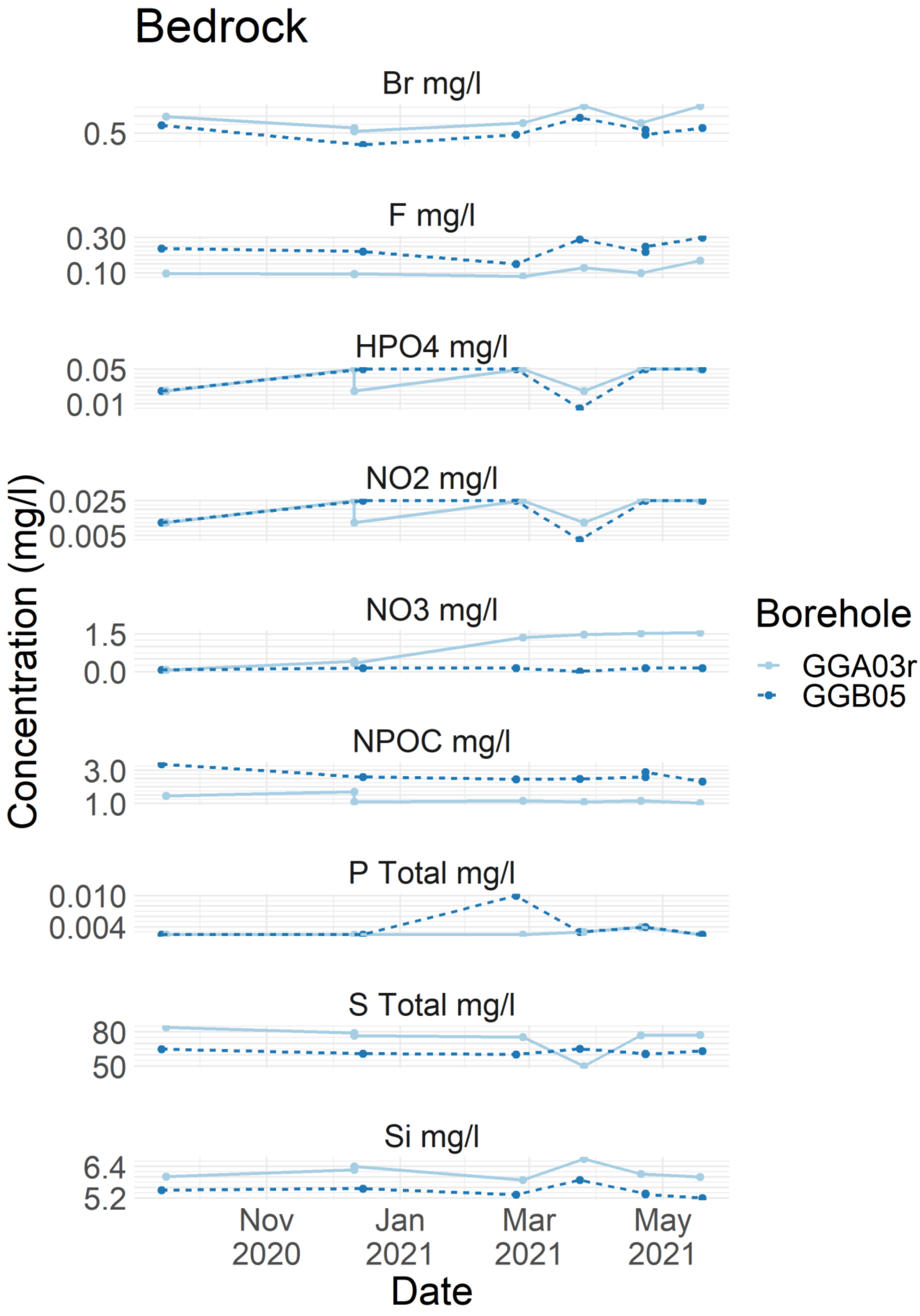

Figure 43 time-series of all other parameters concentrations measured in mg/L from bedrock boreholes. Data < detection limit (DL) are set to ½ DL.

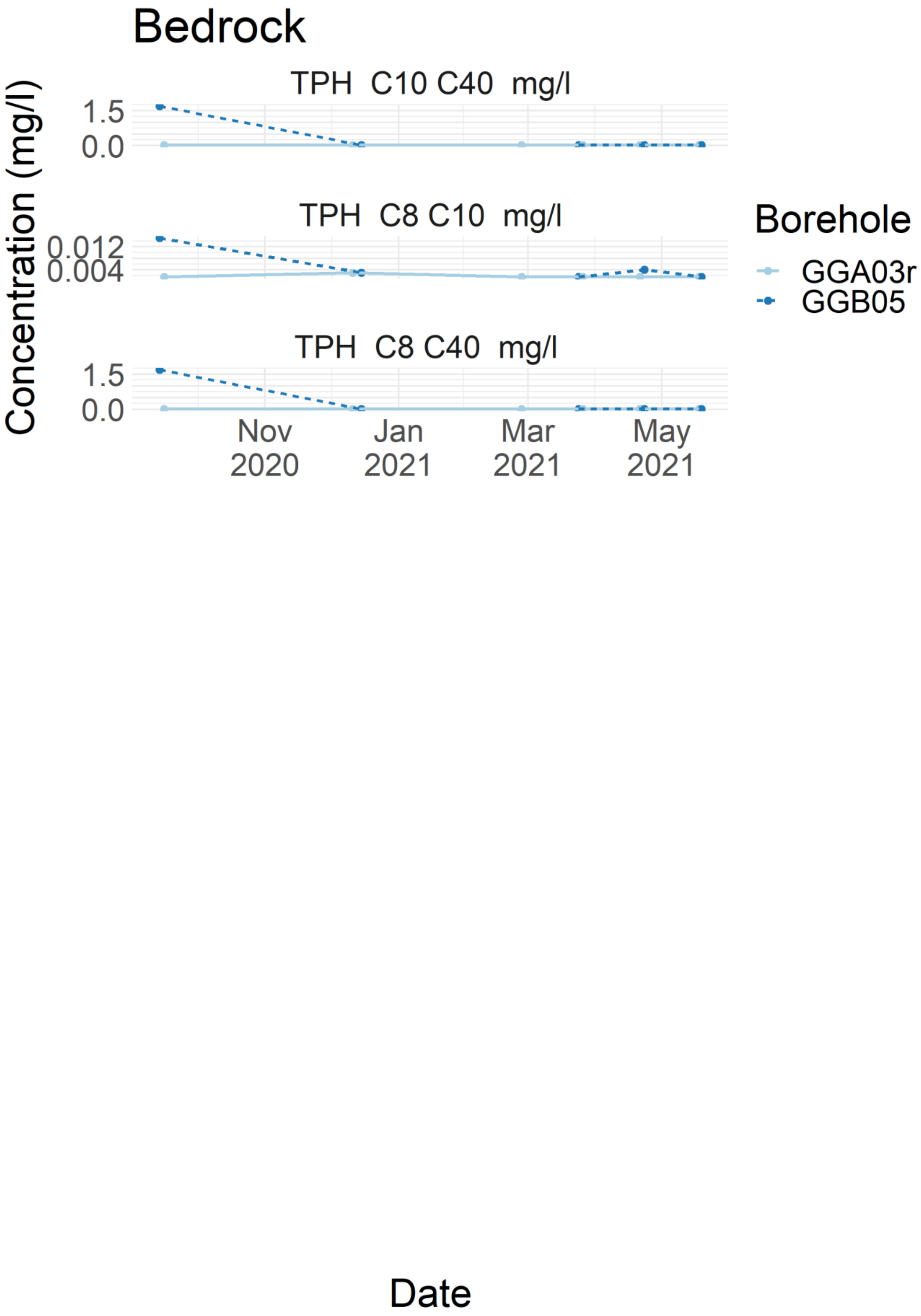

Figure 44 time-series of all other parameters concentrations measured in mg/L from bedrock boreholes. Data < detection limit (DL) are set to ½ DL.

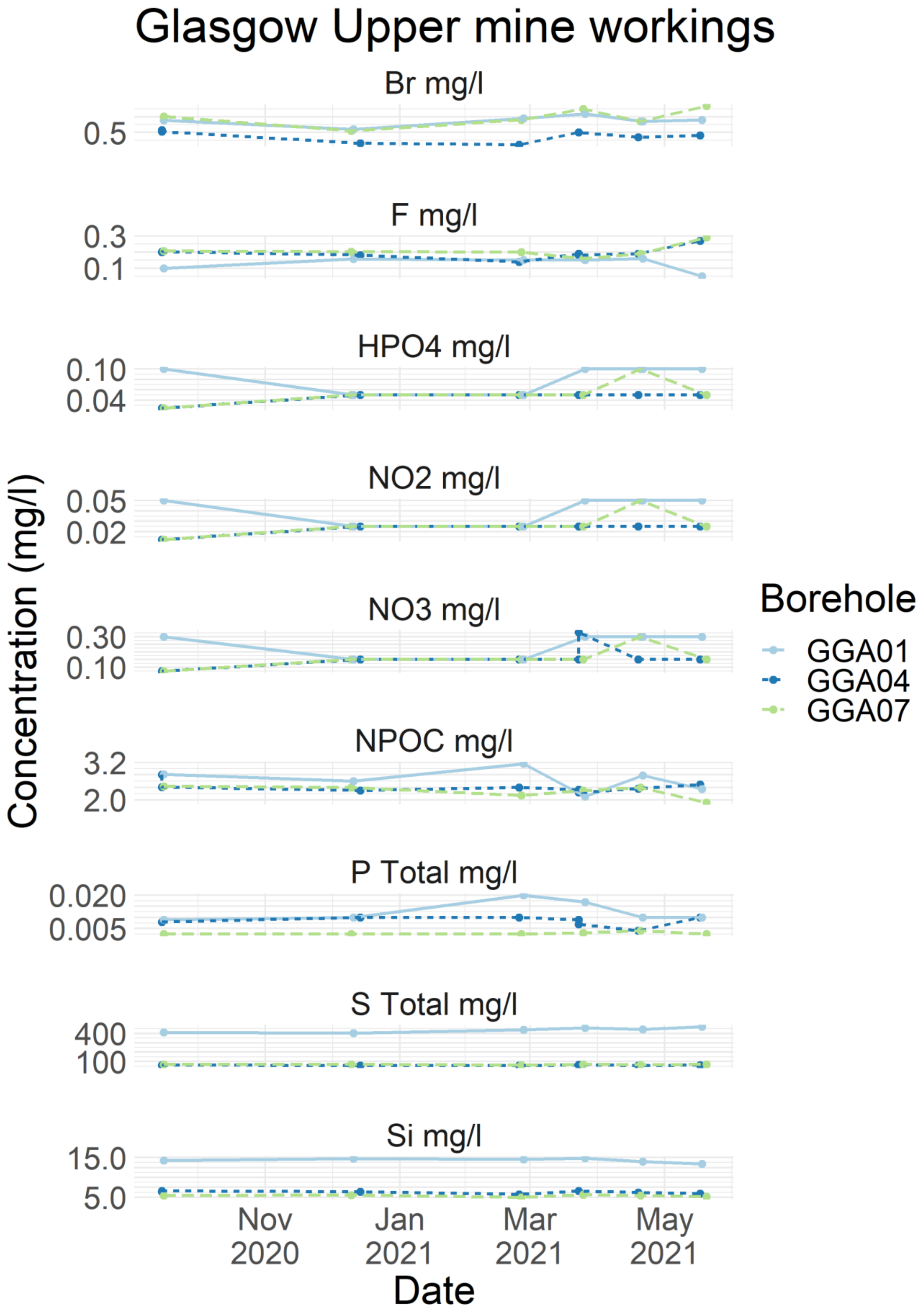

Figure 45 time-series of all other parameters concentrations measured in mg/L from Glasgow Upper mine working boreholes. Data < detection limit (DL) are set to ½ DL.

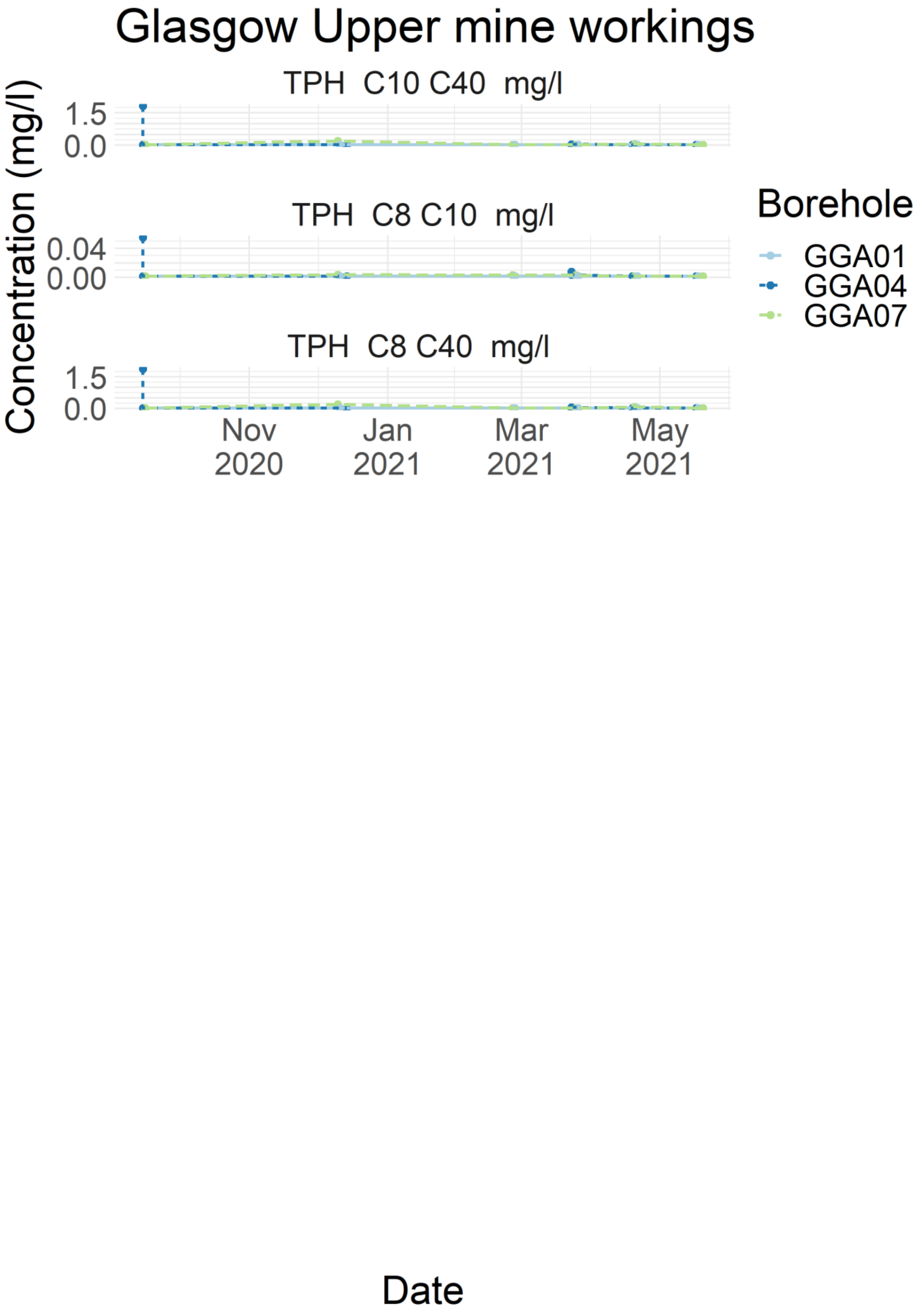

Figure 46 time-series of all other parameters concentrations measured in mg/L from Glasgow Upper mine working boreholes. Data < detection limit (DL) are set to ½ DL.

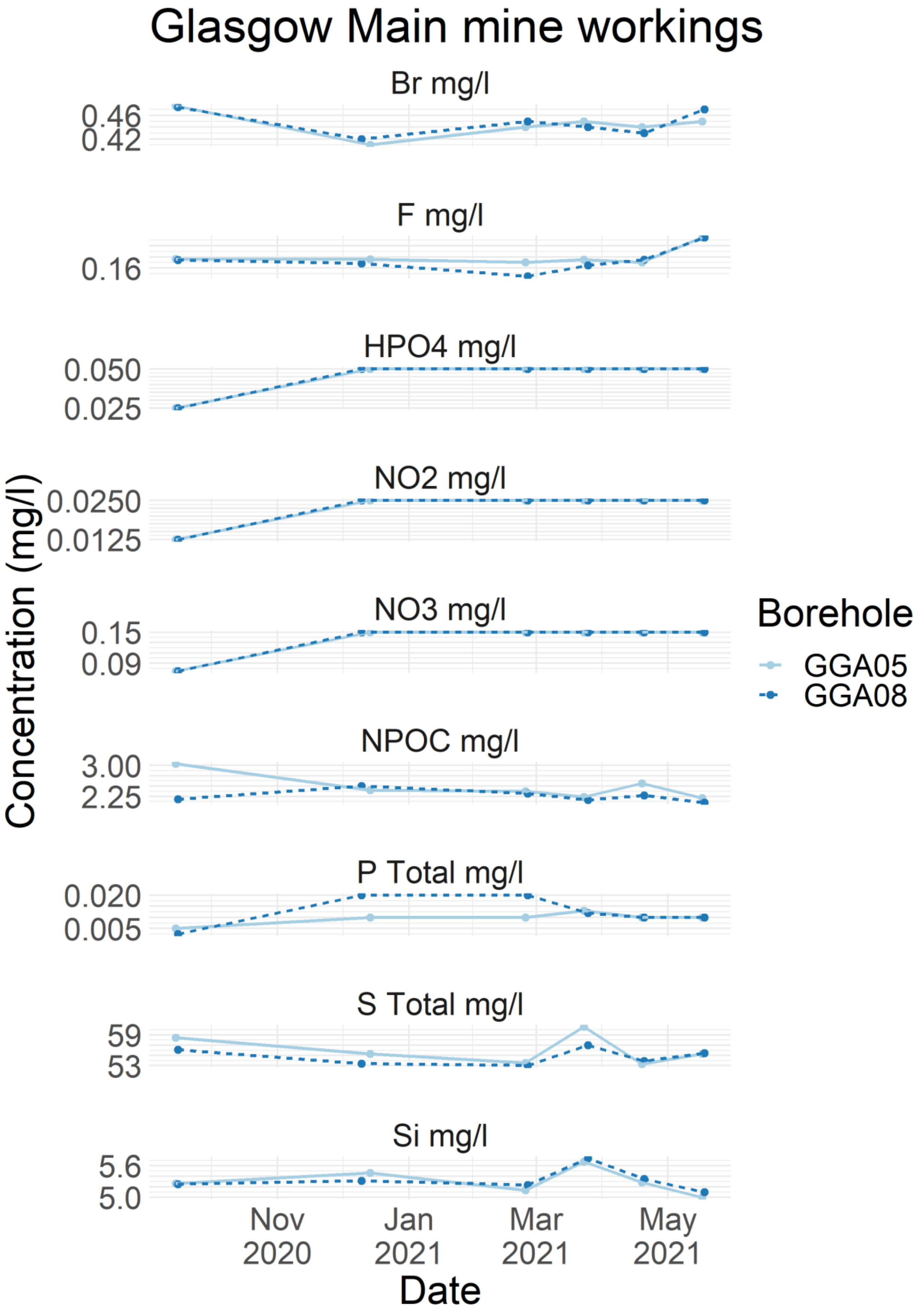

Figure 47 time-series of all other parameters concentrations measured in mg/L from Glasgow Main mine working boreholes. Data < detection limit (DL) are set to ½ DL.

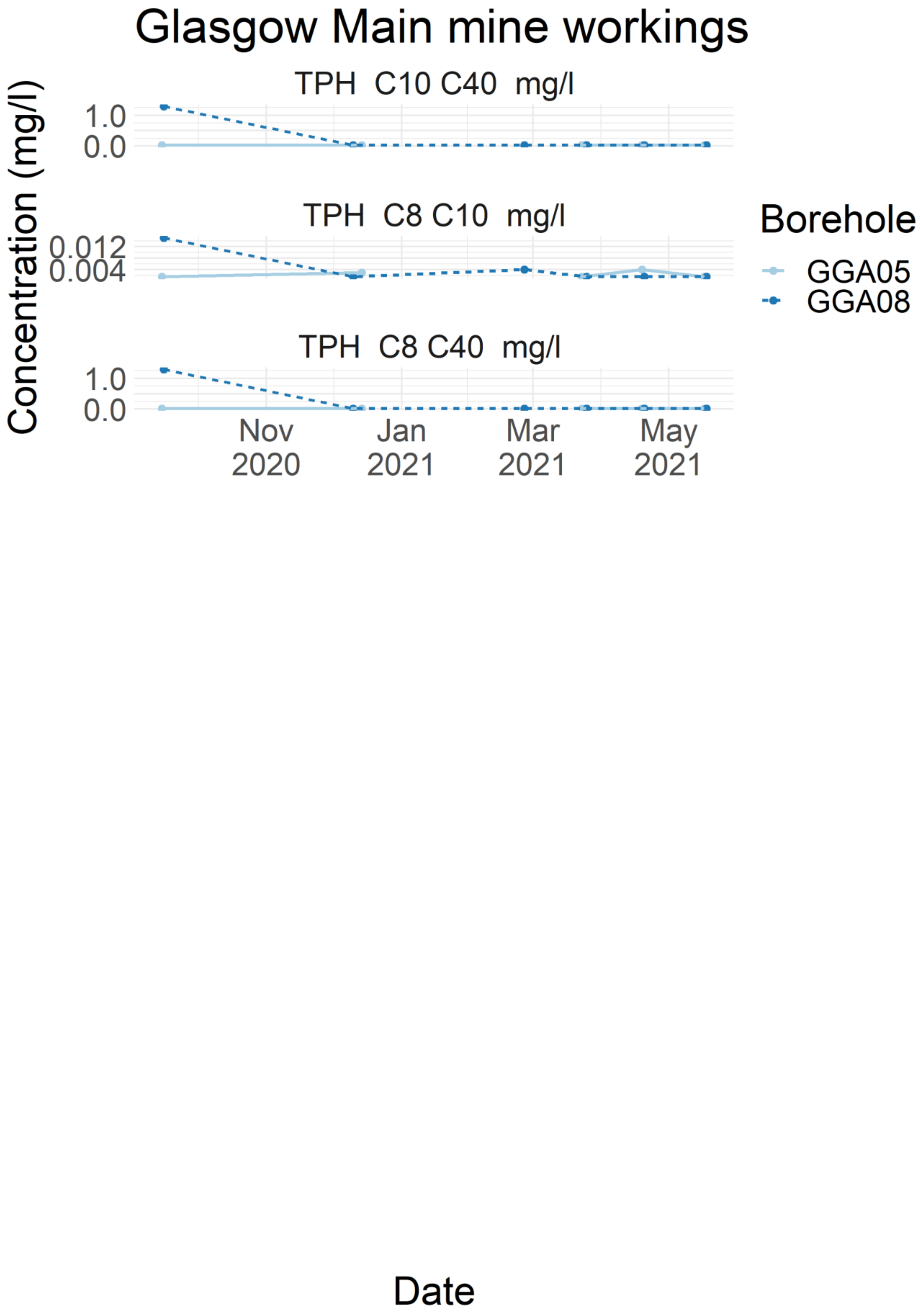

Figure 48 time-series of all other parameters concentrations measured in mg/L from Glasgow Main mine working boreholes. Data < detection limit (DL) are set to ½ DL.

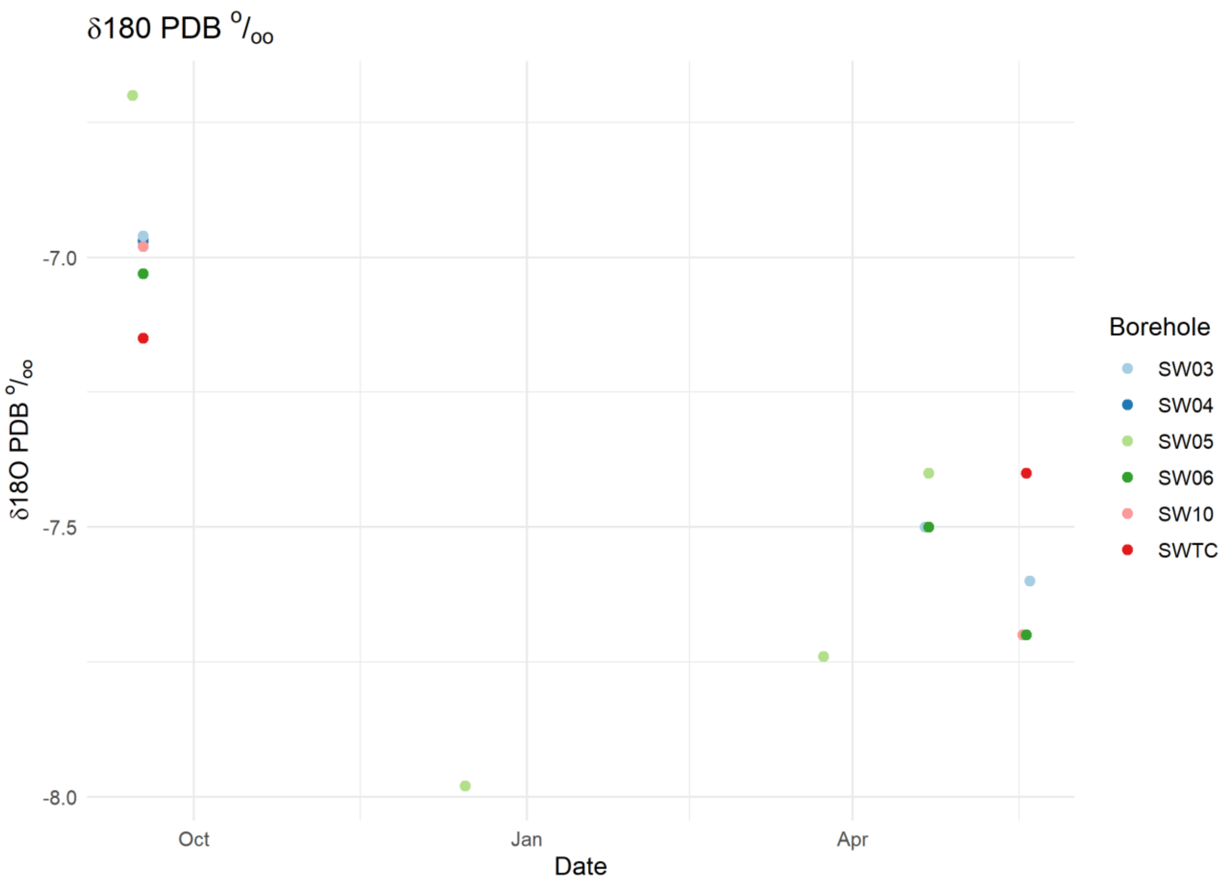

Figure 49 time-series of δ180 PDB $^{o}/_{oo}$ in surface waters.

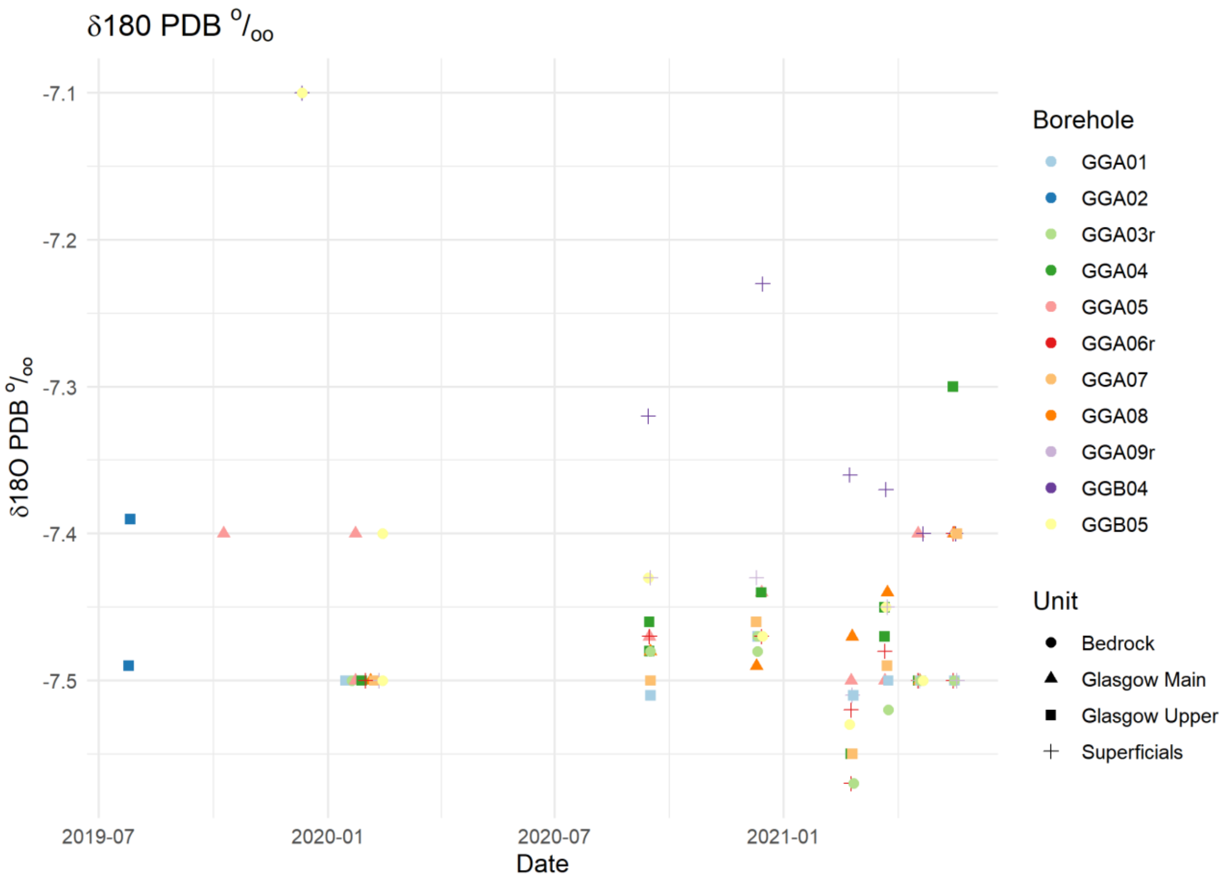

Figure 50 time-series of δ180 PDB $^{o}/_{oo}$ in groundwater.

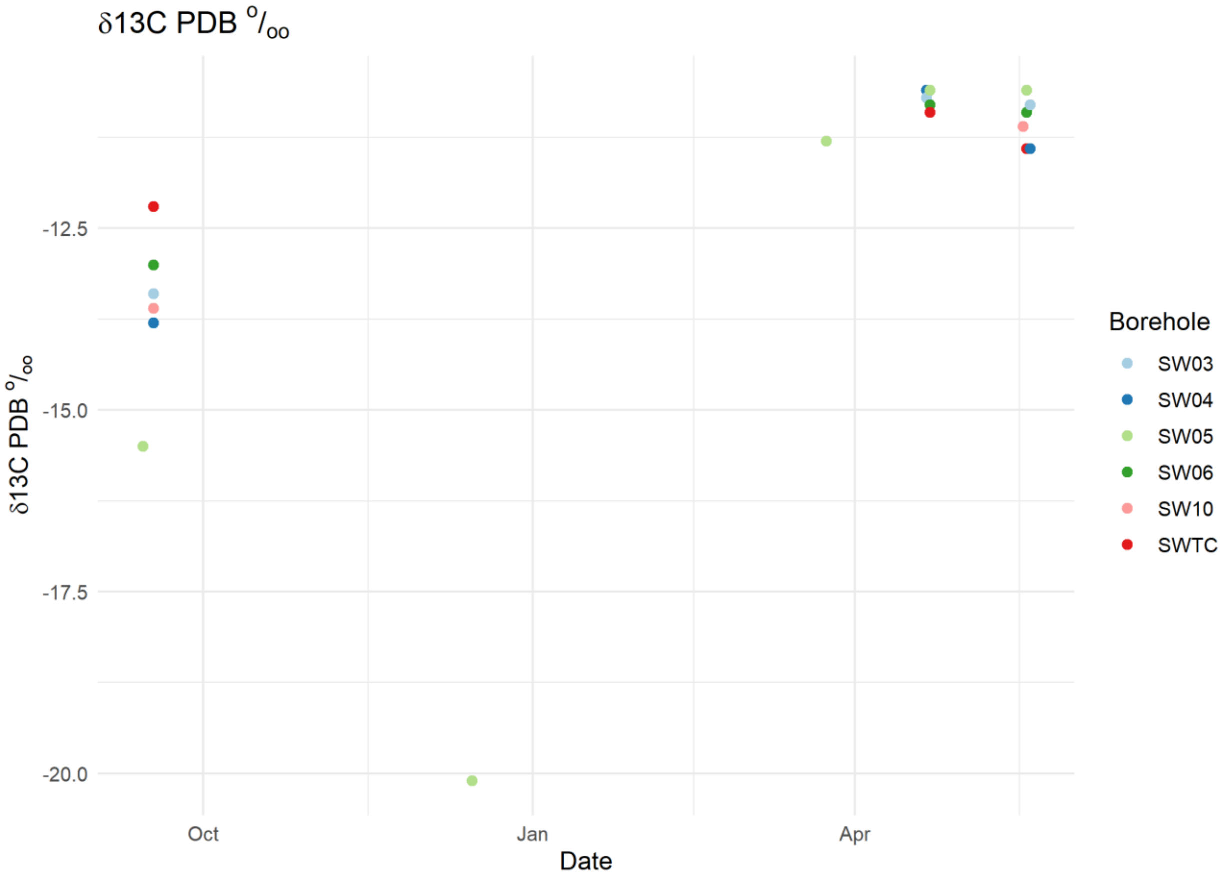

Figure 51 time-series of δ13C PDB $^{o}/_{oo}$ in surface waters.

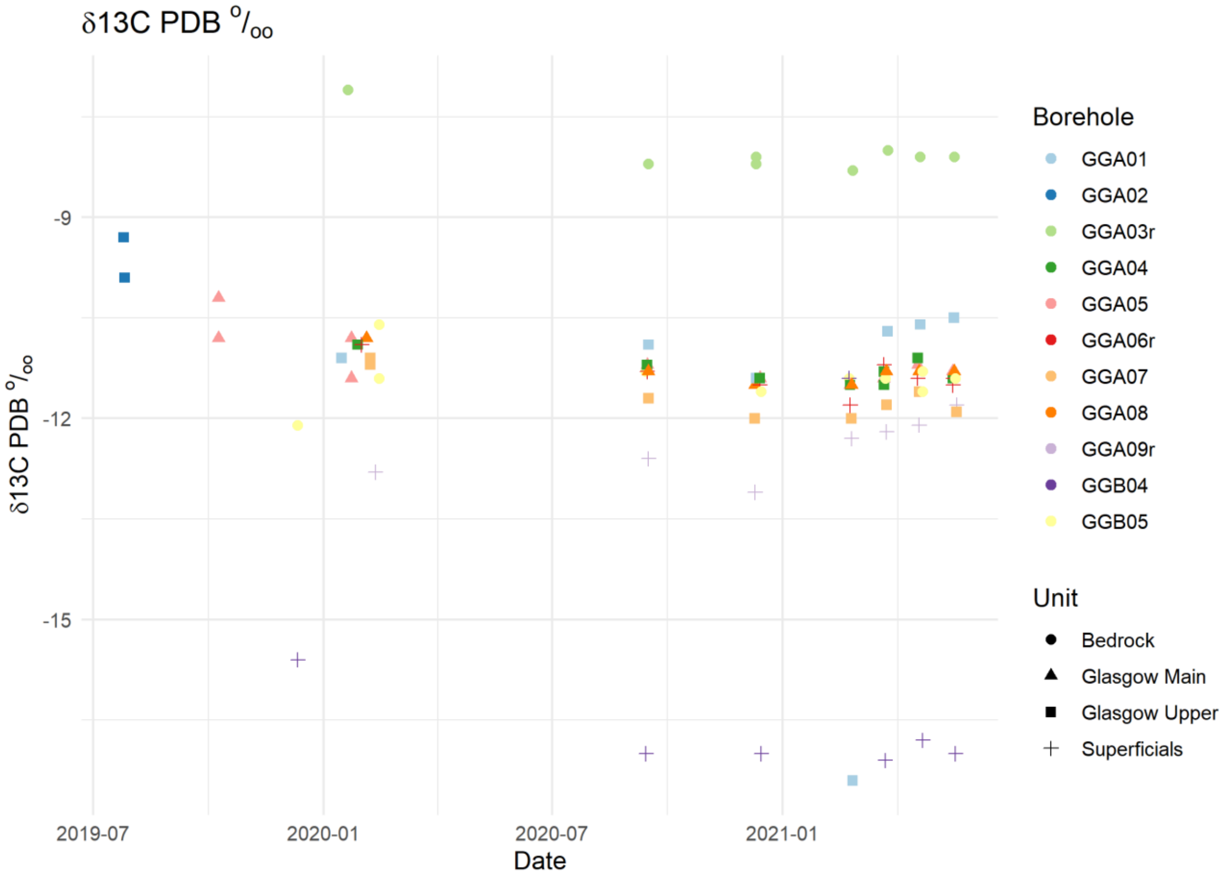

Figure 52 time-series of δ13C PDB $^{o}/_{oo}$ in groundwater.

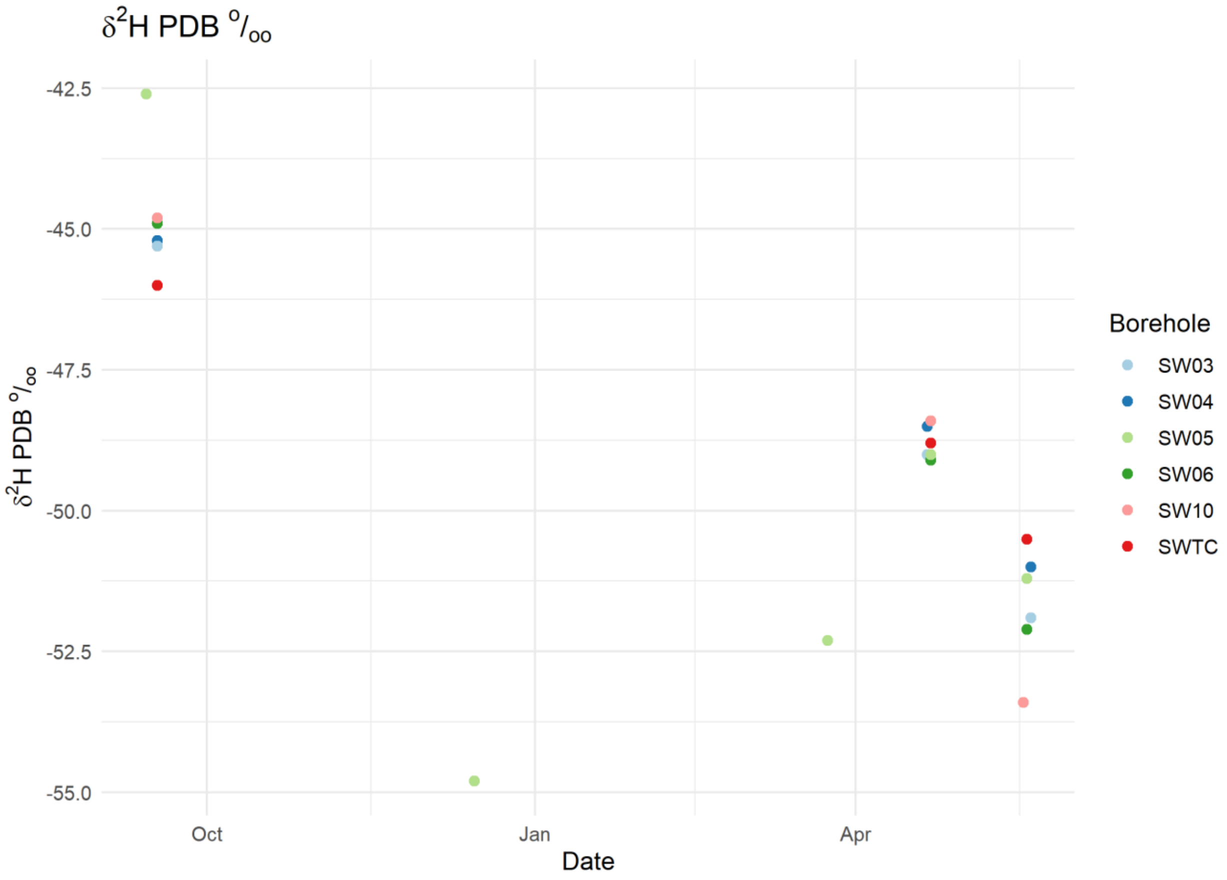

Figure 53 time-series of δ^2H PDB $^o/_{oo}$ in surface waters.

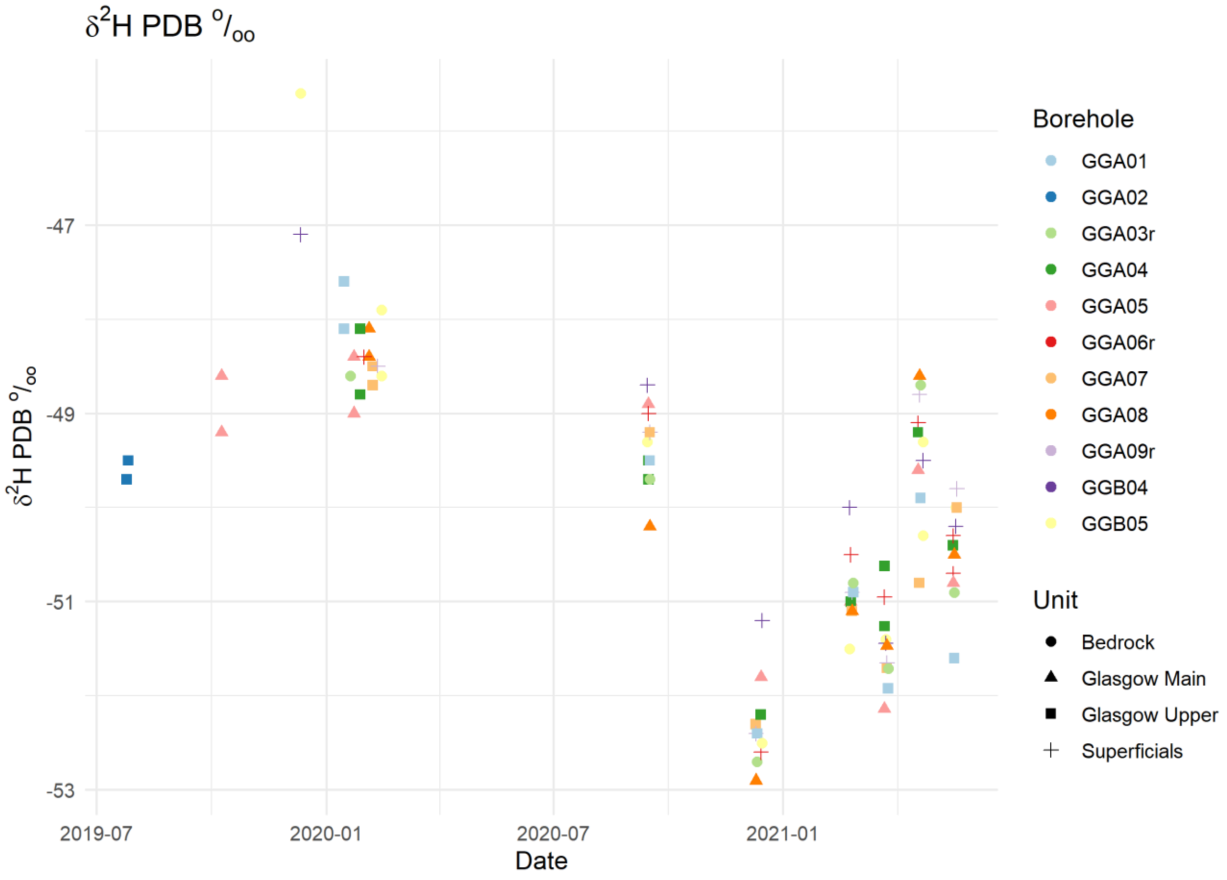

Figure 54 time-series of δ^2H PDB $^o/_{oo}$ in groundwater.

Appendix 4 Box and Whisker Plots

Field parameters

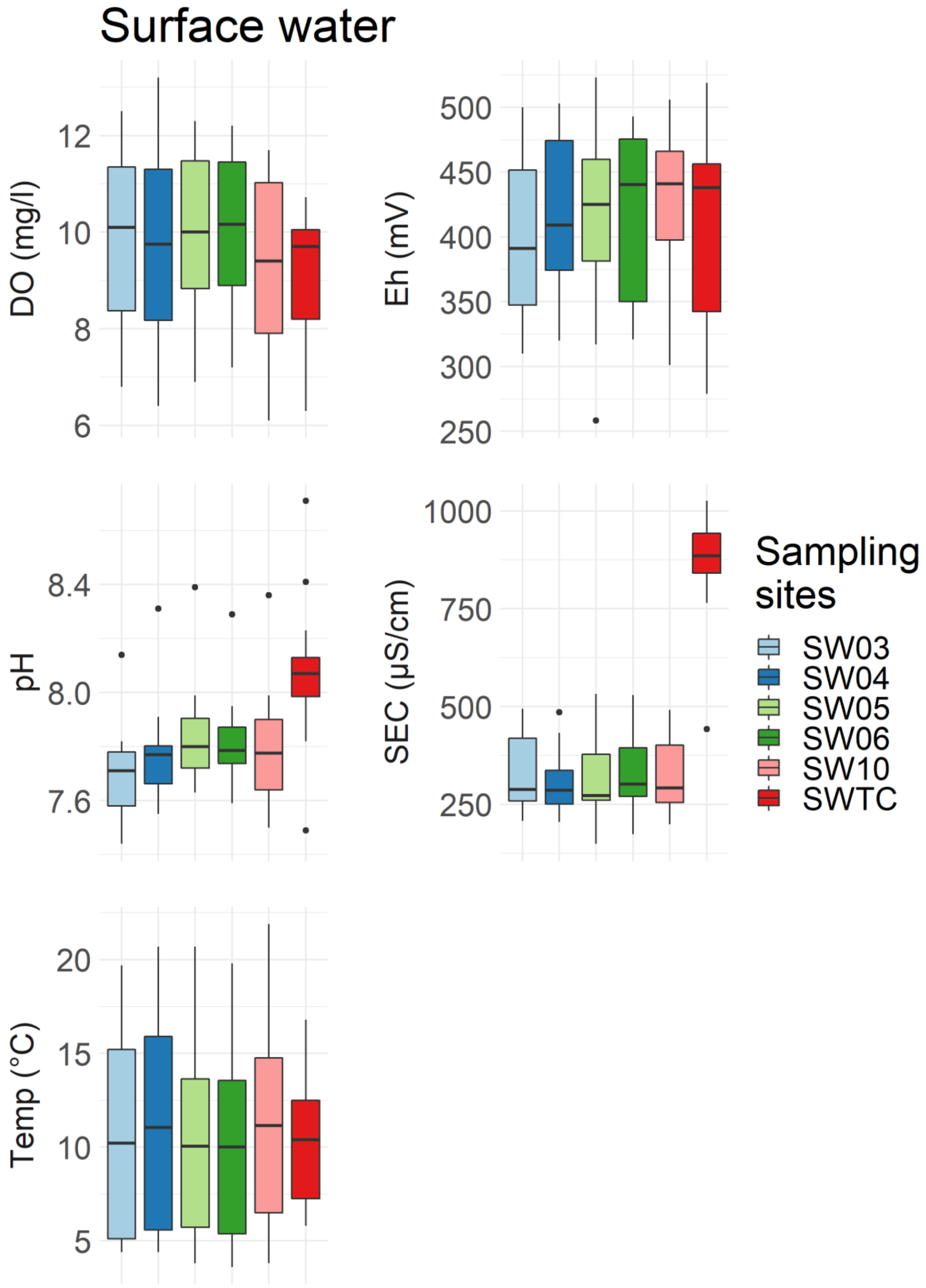

Figure 55 boxplots showing distribution of all field parameters measured during surface water sampling. The interquartile range is shown by the upper and lower bounds of each coloured box, the median is represented by the black line in the coloured box, the whiskers represent the interquartile range times 1.5 and the points represent outliers.

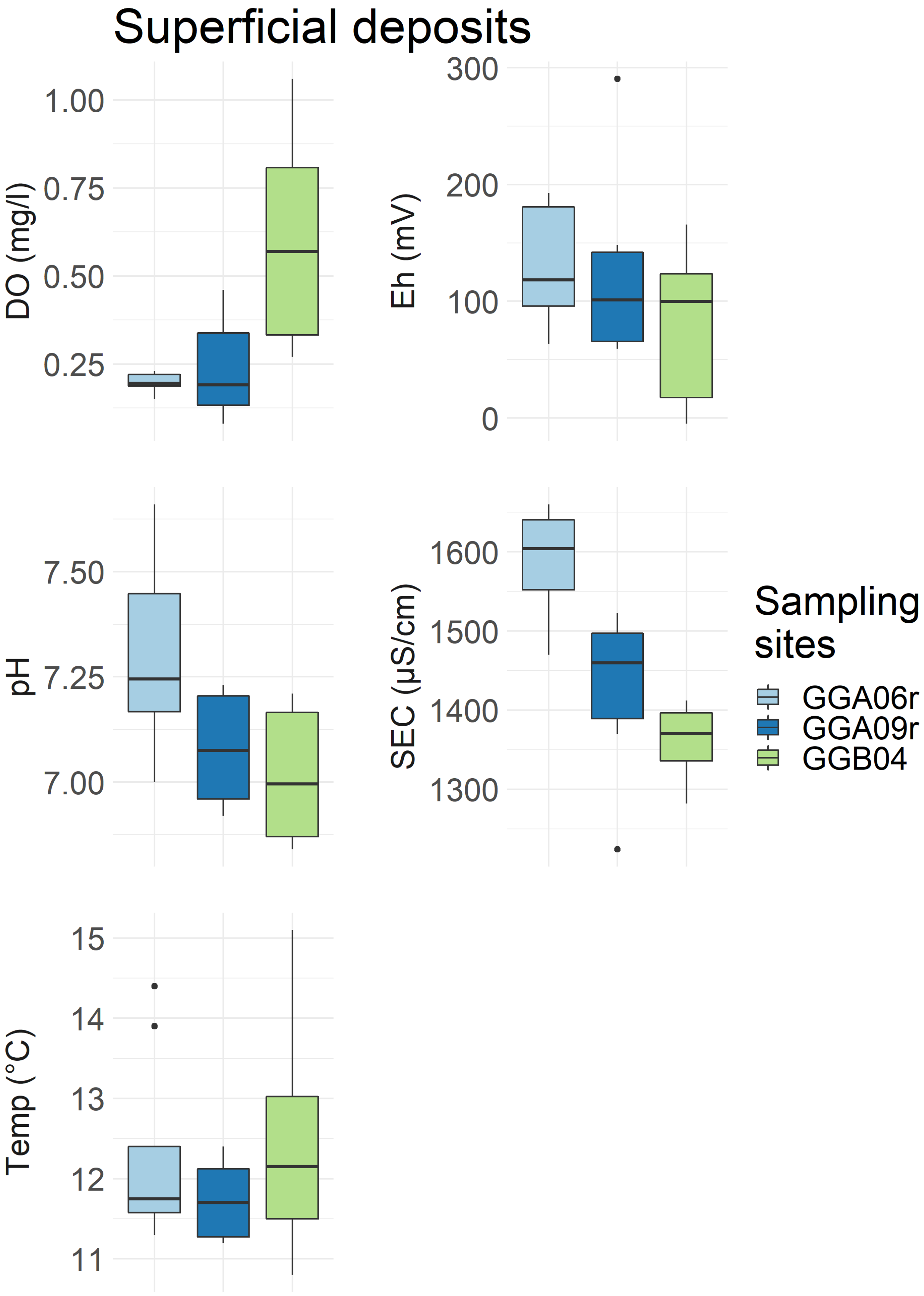

Figure 56 boxplots showing distribution of all field parameters measured during sampling of the superficial deposit boreholes. The interquartile range is shown by the upper and lower bounds of each coloured box, the median is represented by the black line in the coloured box, the whiskers represent the interquartile range times 1.5 and the points represent outliers.

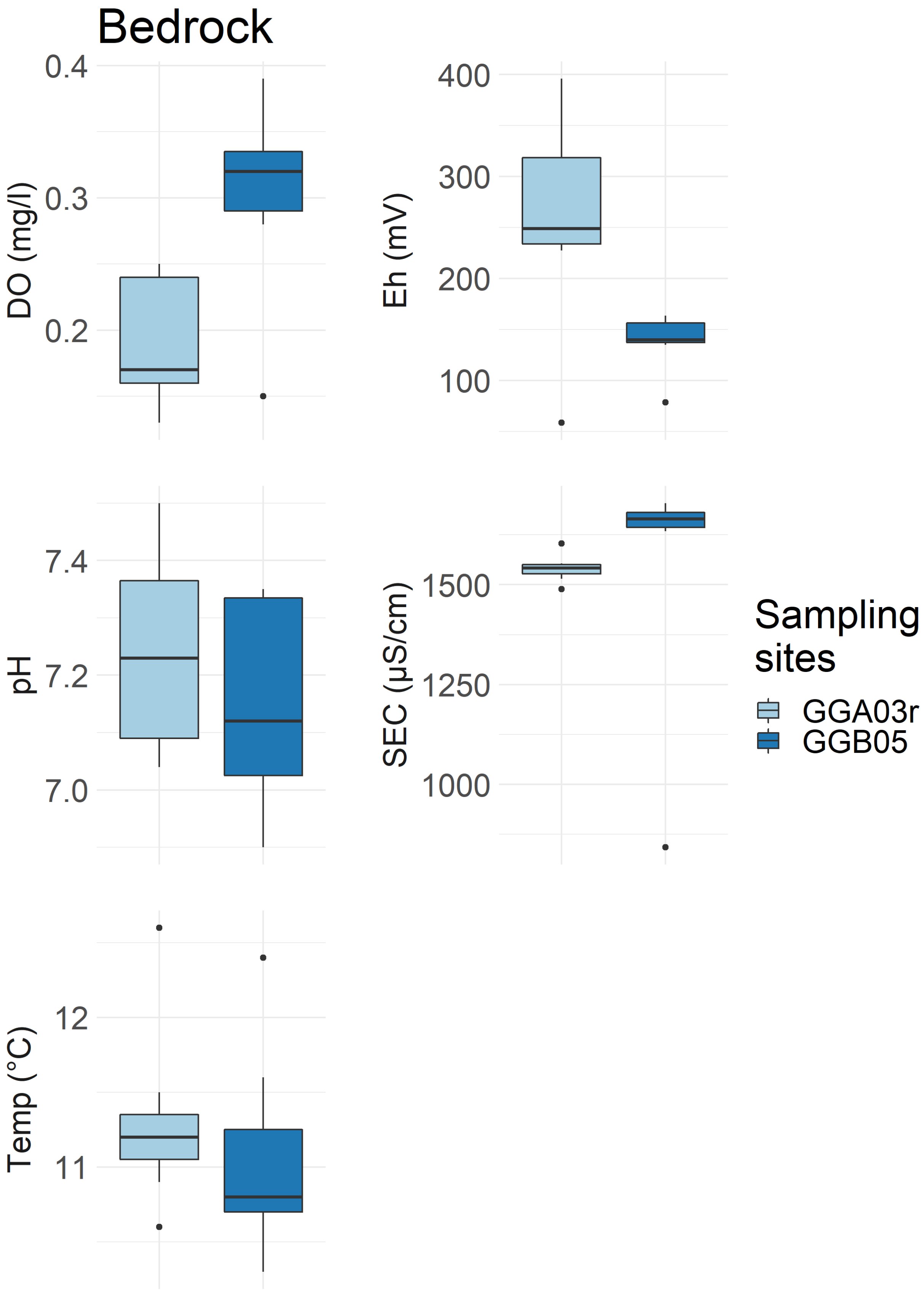

Figure 57 boxplots showing distribution of all field parameters measured during sampling of the bedrock boreholes. The interquartile range is shown by the upper and lower bounds of each coloured box, the median is represented by the black line in the coloured box, the whiskers represent the interquartile range times 1.5 and the points represent outliers.

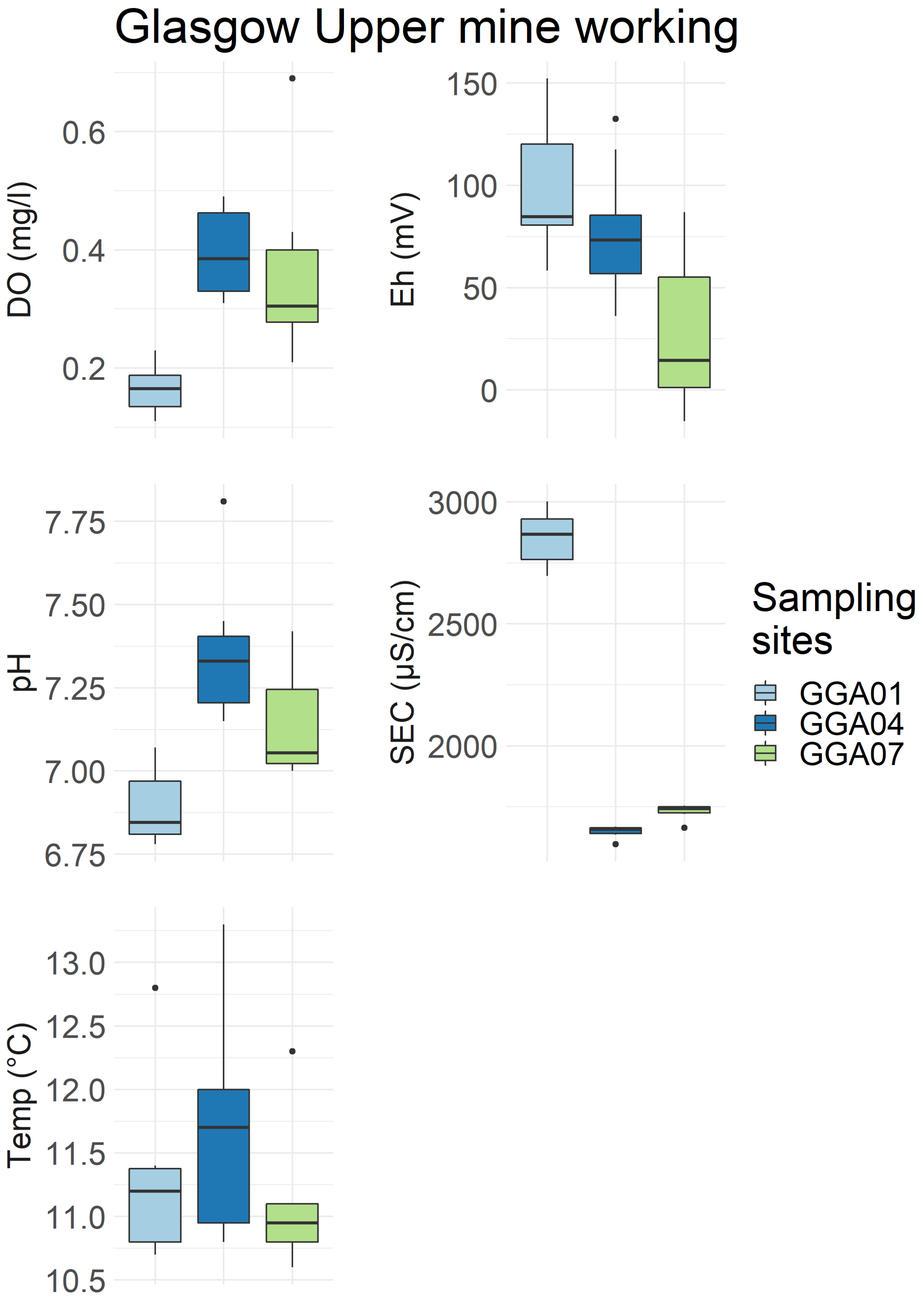

Figure 58 boxplots showing distribution of all field parameters measured during sampling of the Glasgow Upper mine working boreholes. The interquartile range is shown by the upper and lower bounds of each coloured box, the median is represented by the black line in the coloured box, the whiskers represent the interquartile range times 1.5 and the points represent outliers.

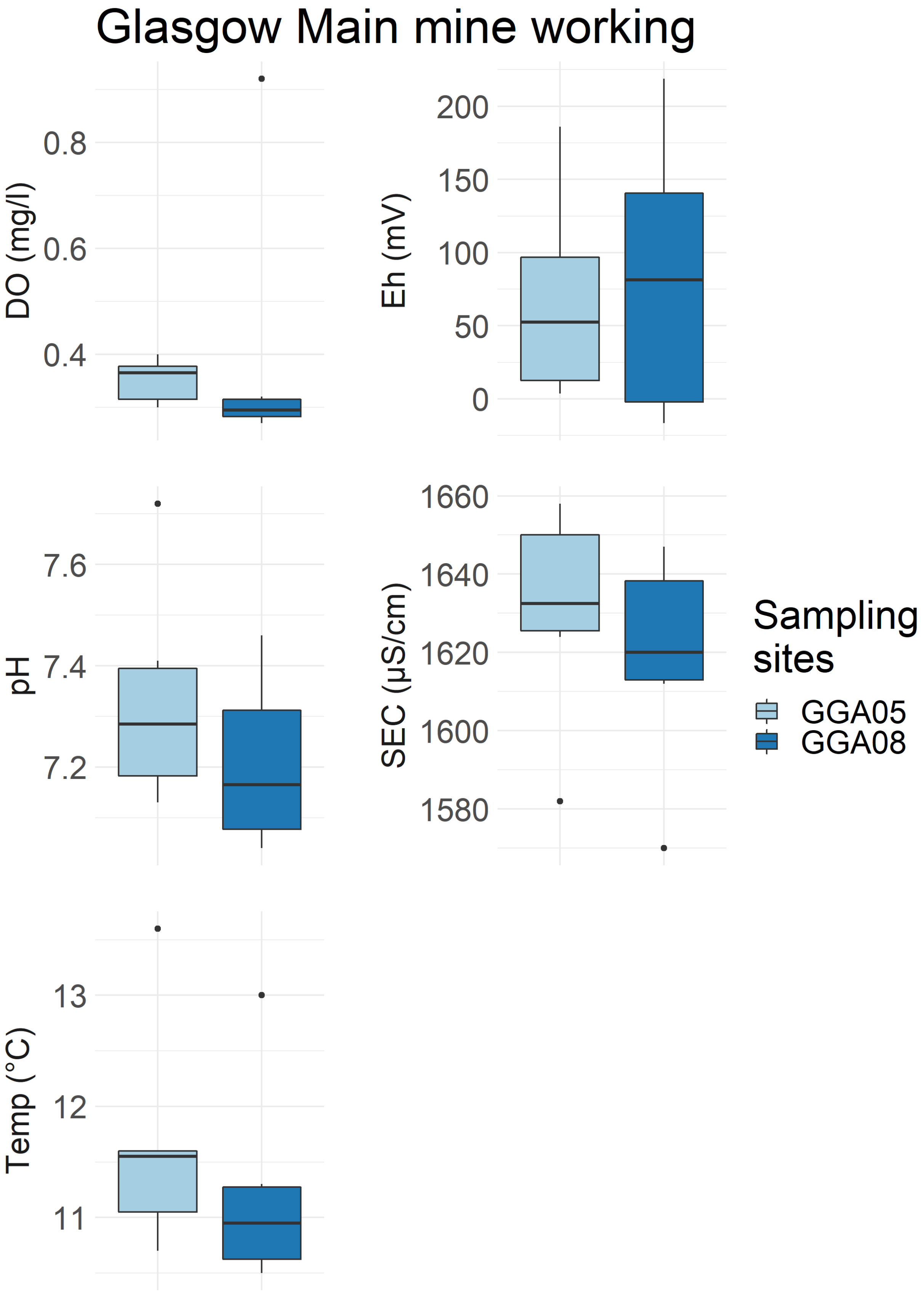

Figure 59 boxplots showing distribution of all field parameters measured during sampling of the Glasgow Main mine working boreholes. The interquartile range is shown by the upper and lower bounds of each coloured box, the median is represented by the black line in the coloured box, the whiskers represent the interquartile range times 1.5 and the points represent outliers.

Major Ions

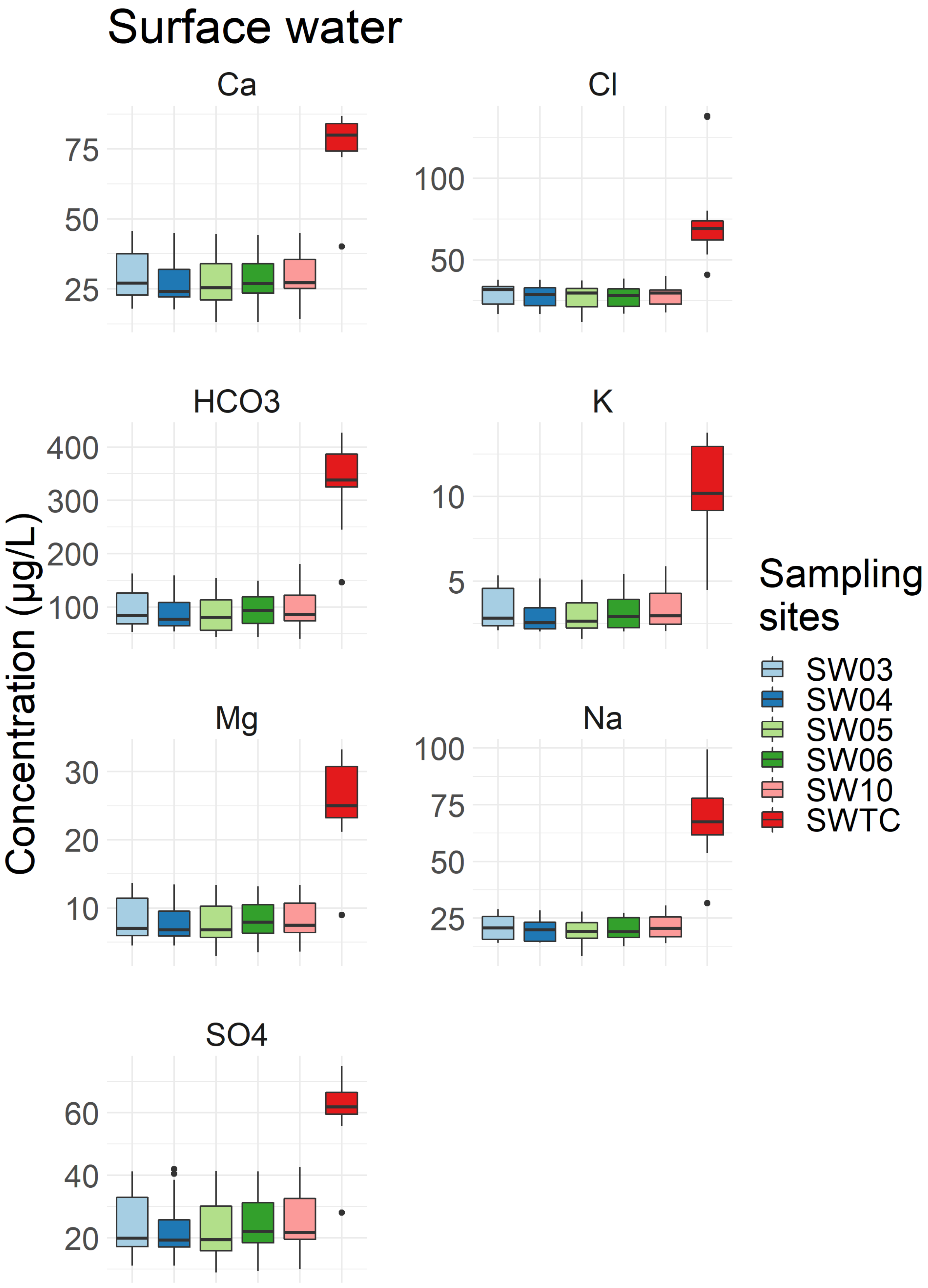

Figure 60 boxplots showing distribution of major ions concentrations from surface water sampling. The interquartile range is shown by the upper and lower bounds of each coloured box, the median is represented by the black line in the coloured box, the whiskers represent the interquartile range times 1.5 and the points represent outliers.

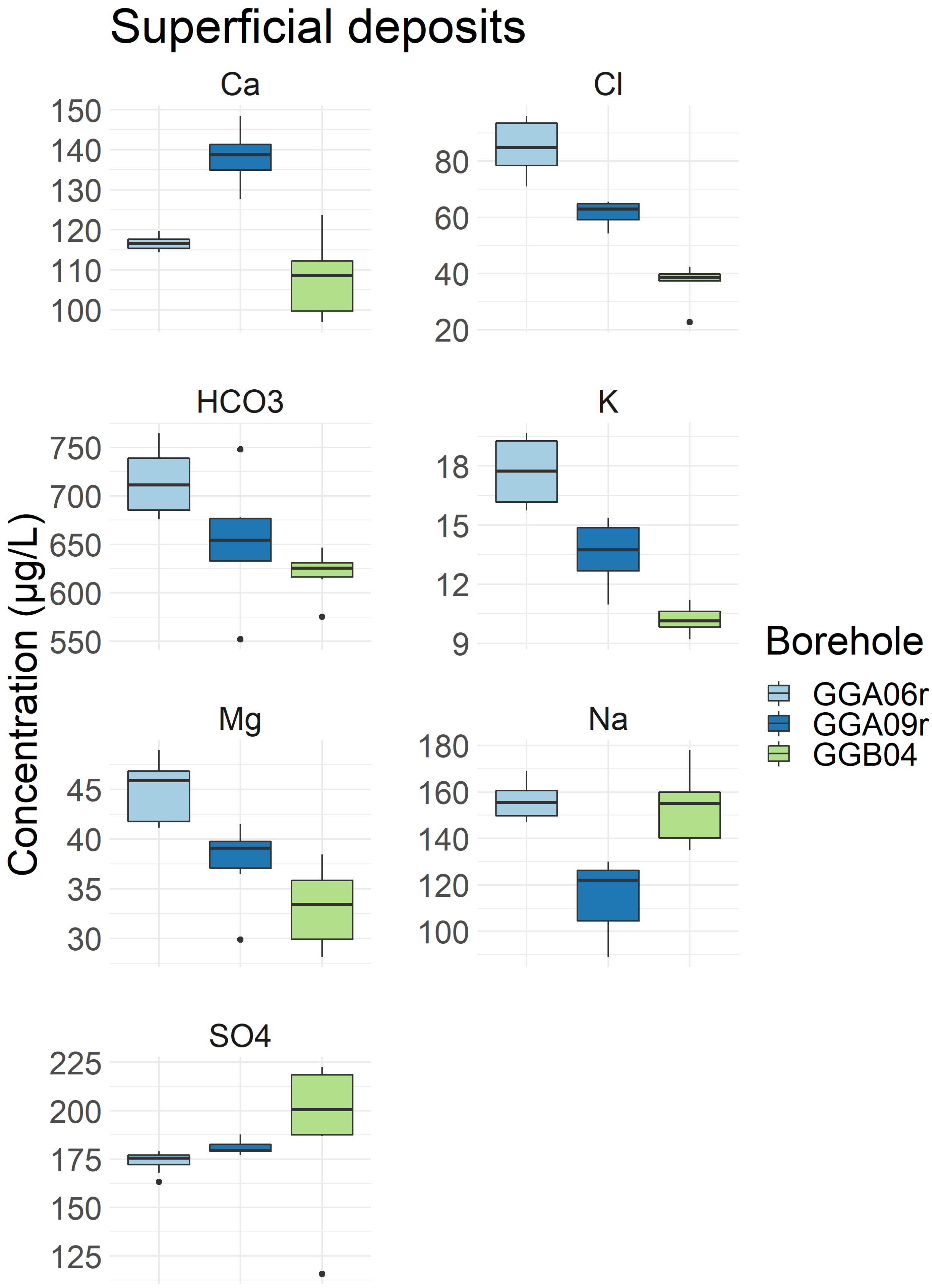

Figure 61 boxplots showing distribution of major ions concentrations from sampling of the superficial deposit boreholes. The interquartile range is shown by the upper and lower bounds of each coloured box, the median is represented by the black line in the coloured box, the whiskers represent the interquartile range times 1.5 and the points represent outliers.

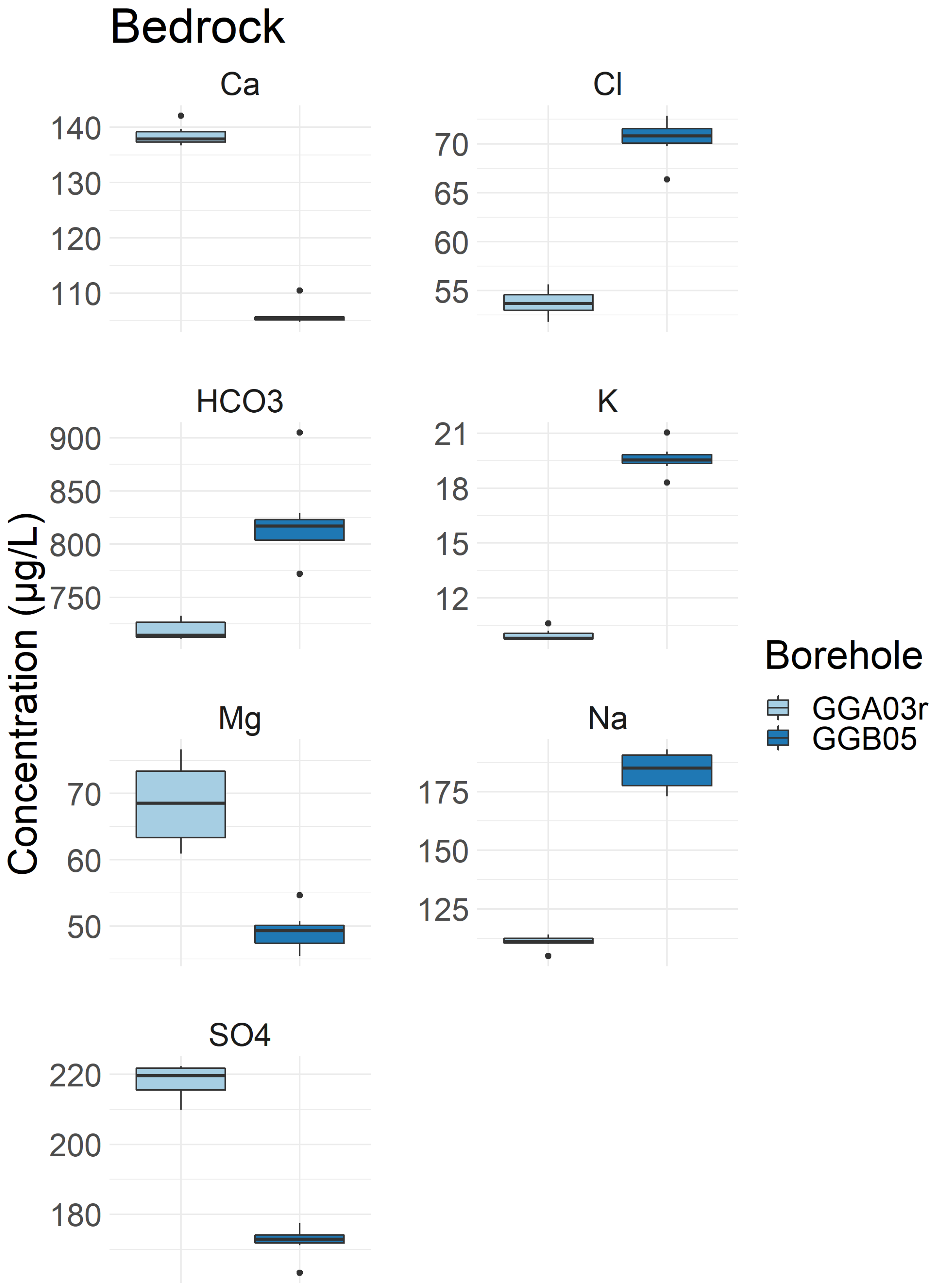

Figure 62 boxplots showing distribution of major ions concentrations from bedrock boreholes. The interquartile range is shown by the upper and lower bounds of each coloured box, the median is represented by the black line in the coloured box, the whiskers represent the interquartile range times 1.5 and the points represent outliers.

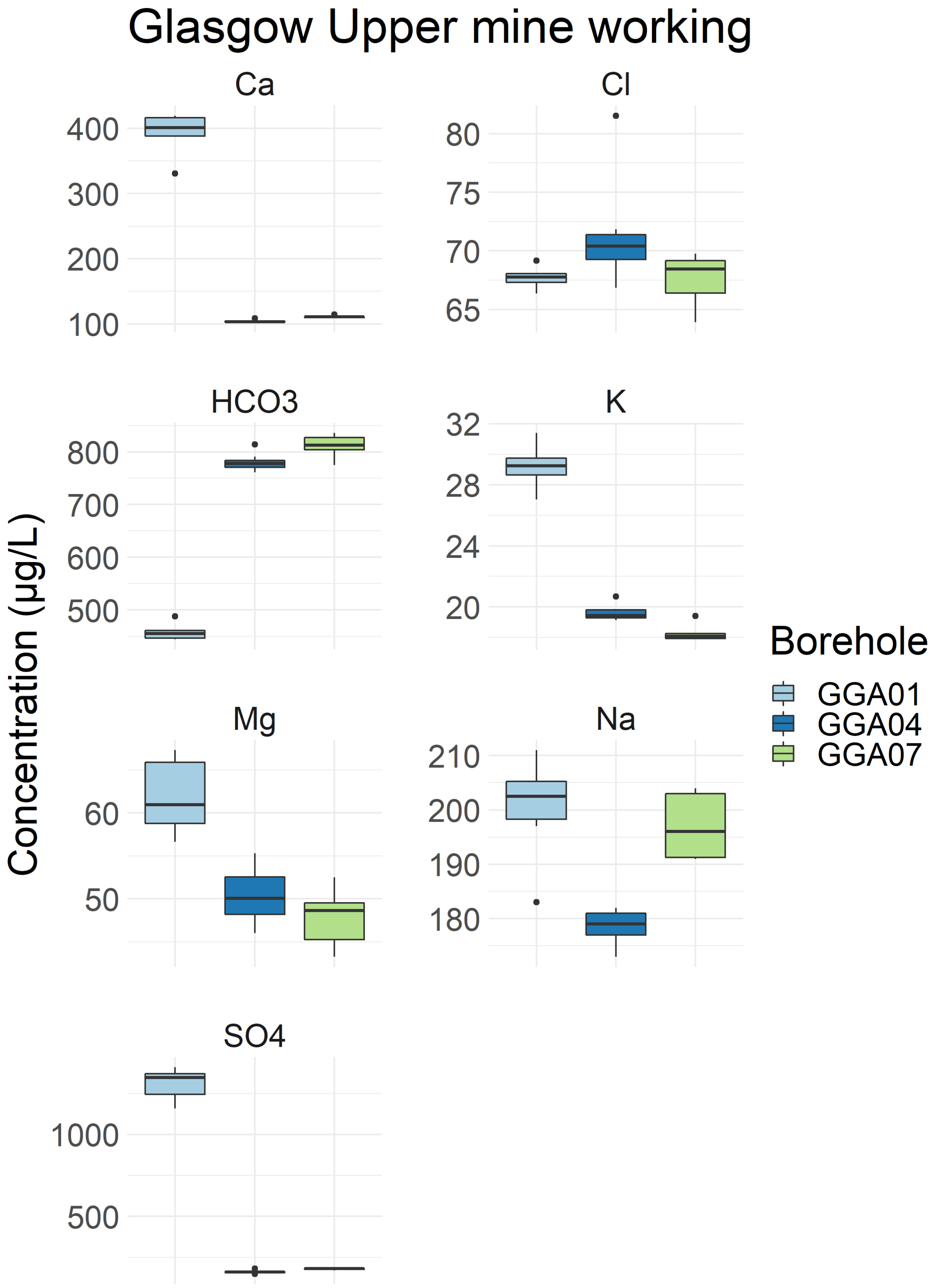

Figure 63 boxplots showing distribution of major ion concentrations from sampling of the Glasgow Upper mine working boreholes. The interquartile range is shown by the upper and lower bounds of each coloured box, the median is the black line in the coloured box, the whiskers represent the interquartile range times 1.5 and the points represent outliers.

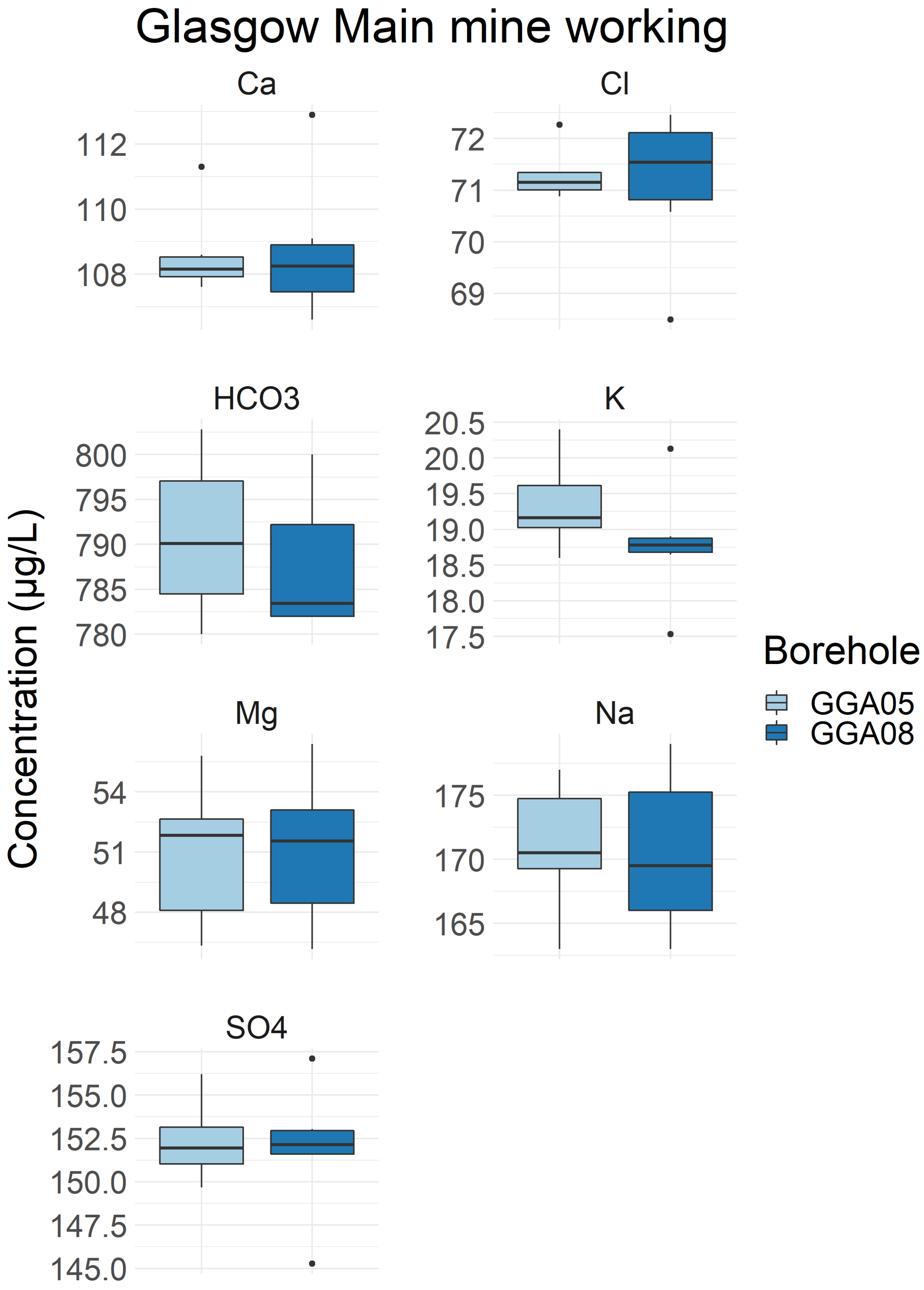

Figure 64 boxplots showing distribution of major ion concentrations from sampling of the Glasgow Main mine working boreholes. The interquartile range is shown by the upper and lower bounds of each coloured box, the median is the black line in the coloured box, the whiskers represent the interquartile range times 1.5 and the points represent outliers.

Trace elements in µg/L

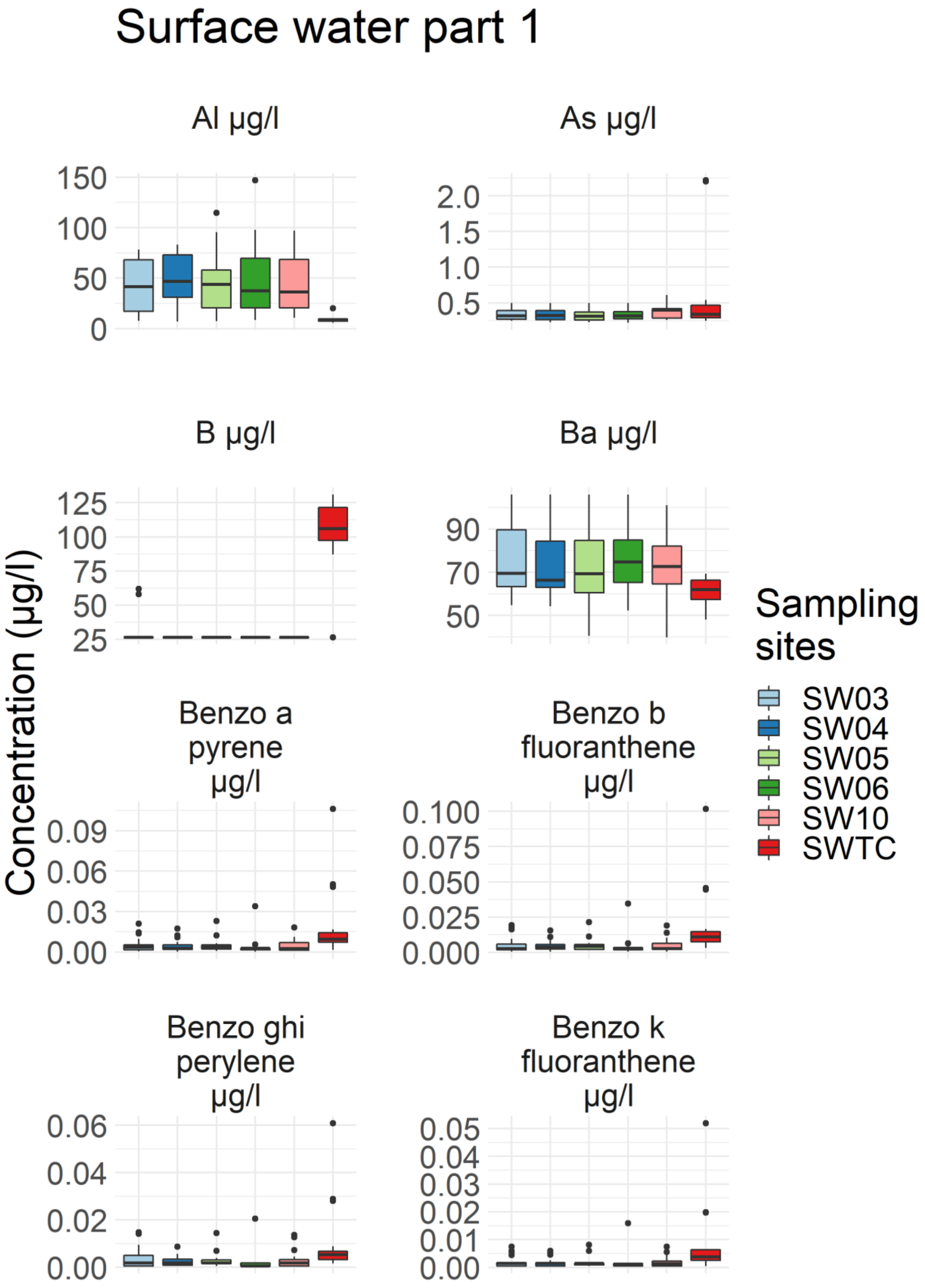

Figure 65 boxplots showing distribution of trace element concentrations from surface water sampling. The interquartile range is shown by the upper and lower bounds of each coloured box, the median is represented by the black line in the coloured box, the whiskers represent the interquartile range times 1.5 and the points represent outliers. Data < detection limit (DL) are set to ½ DL.

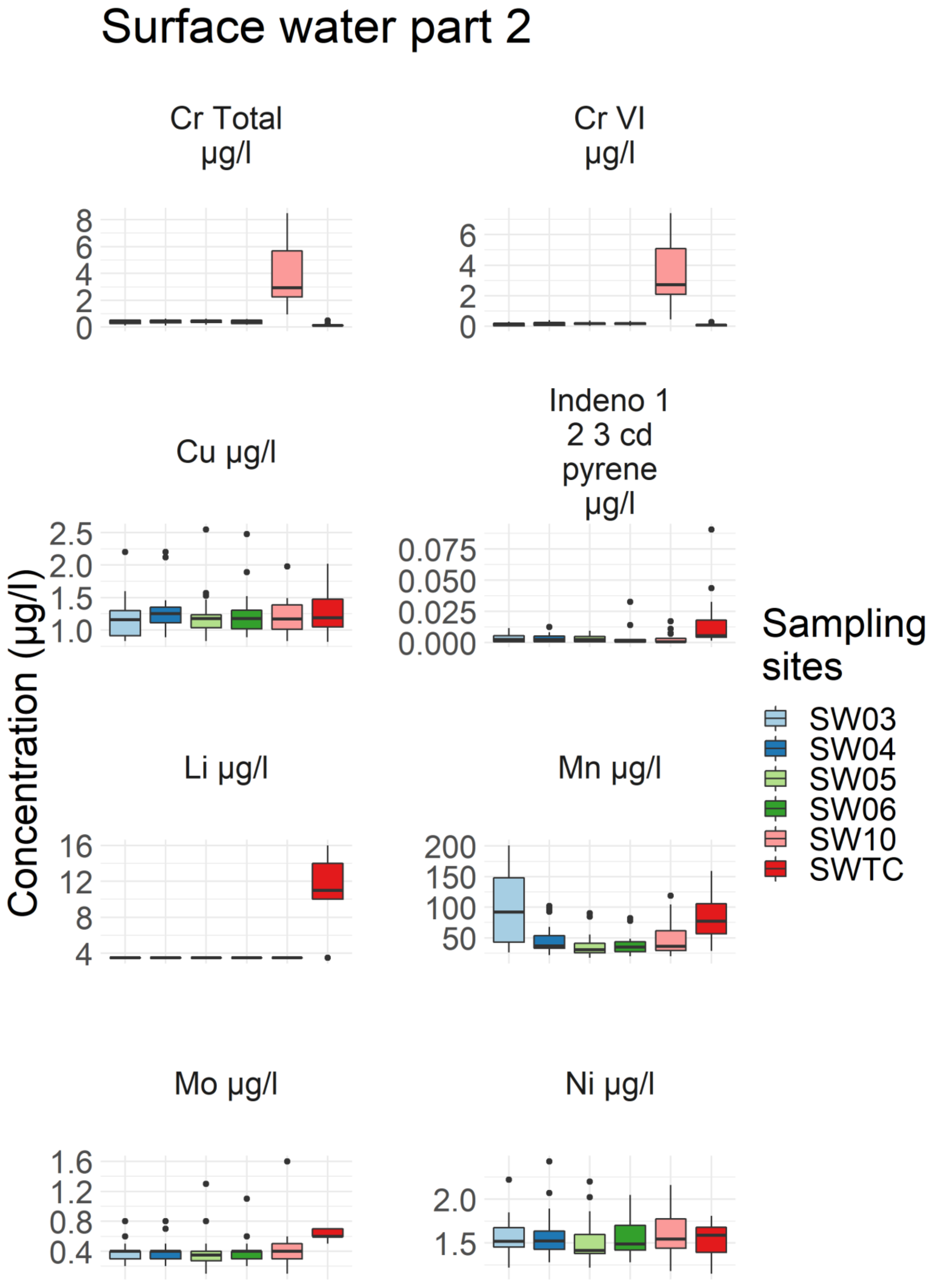

Figure 66 boxplots showing distribution of trace element concentrations from surface water sampling. The interquartile range is shown by the upper and lower bounds of each coloured box, the median is represented by the black line in the coloured box, the whiskers represent the interquartile range times 1.5 and the points represent outliers. Data < detection limit (DL) are set to ½ DL.

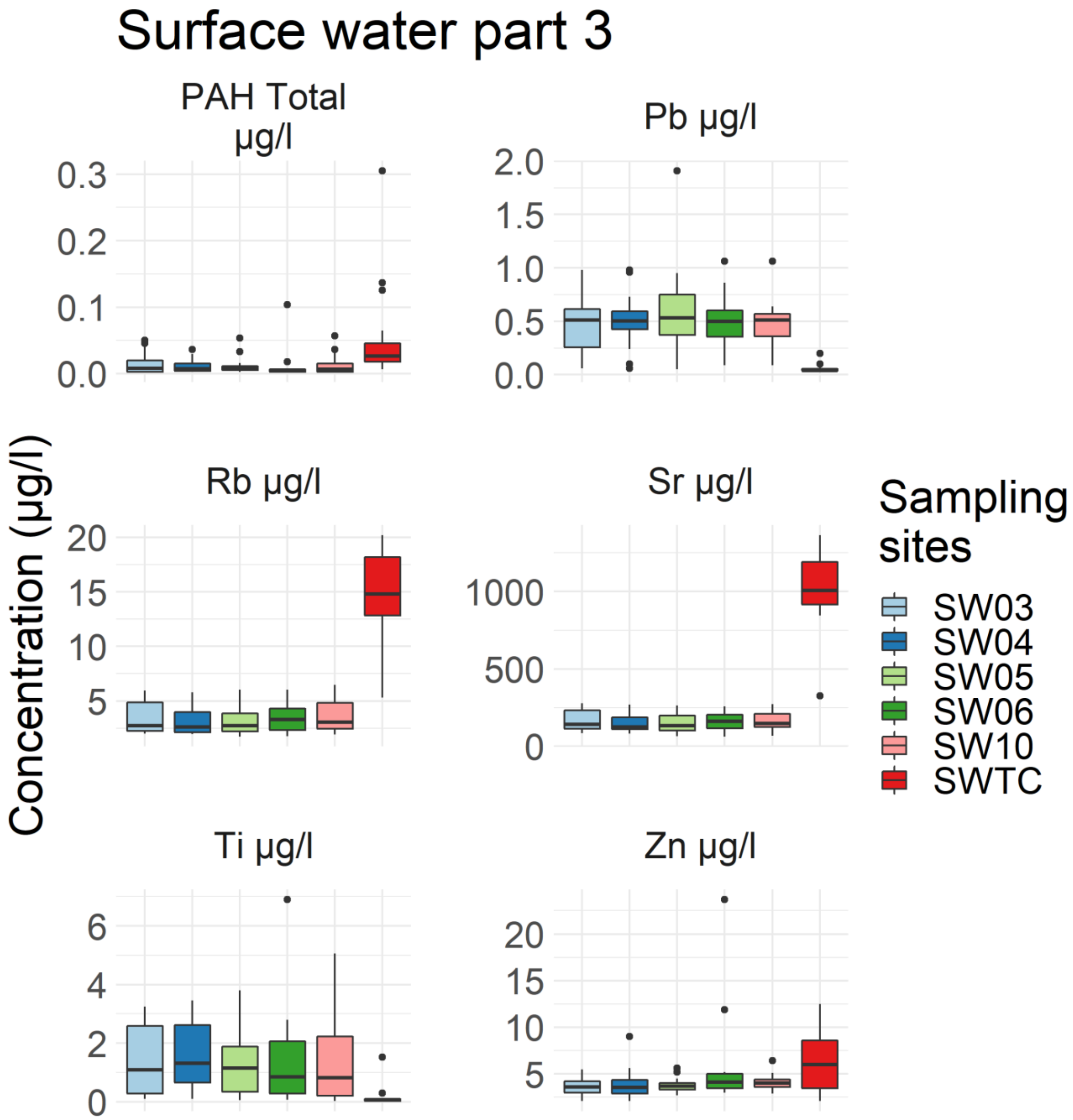

Figure 67 boxplots showing distribution of trace element concentrations from surface water sampling. The interquartile range is shown by the upper and lower bounds of each coloured box, the median is represented by the black line in the coloured box, the whiskers represent the interquartile range times 1.5 and the points represent outliers. Data < detection limit (DL) are set to ½ DL.

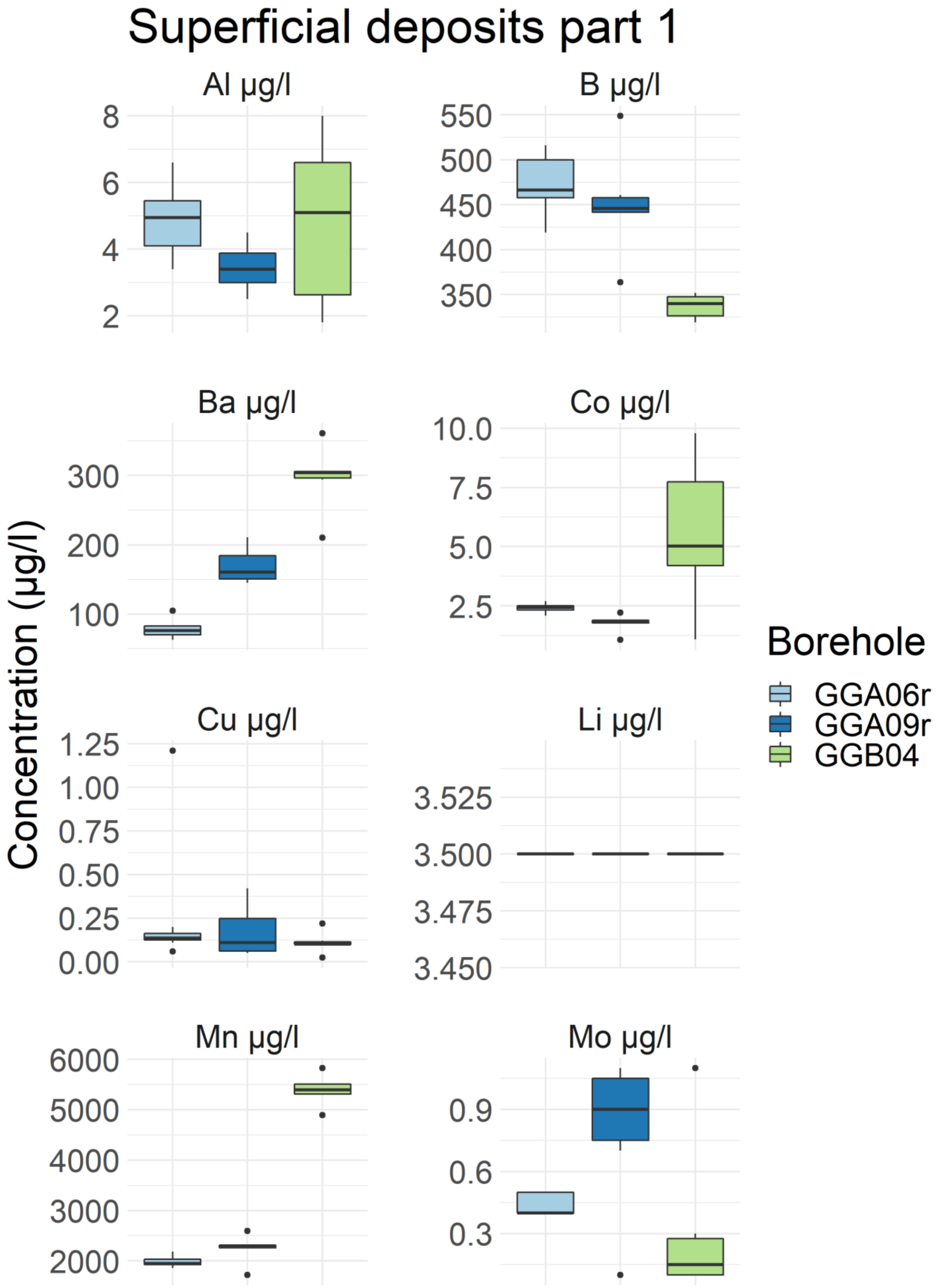

Figure 68 boxplots showing distribution of trace element concentrations from superficial deposit boreholes. The interquartile range is shown by the upper and lower bounds of each coloured box, the median is represented by the black line in the coloured box, the whiskers represent the interquartile range times 1.5 and the points represent outliers. Data < detection limit (DL) are set to ½ DL.

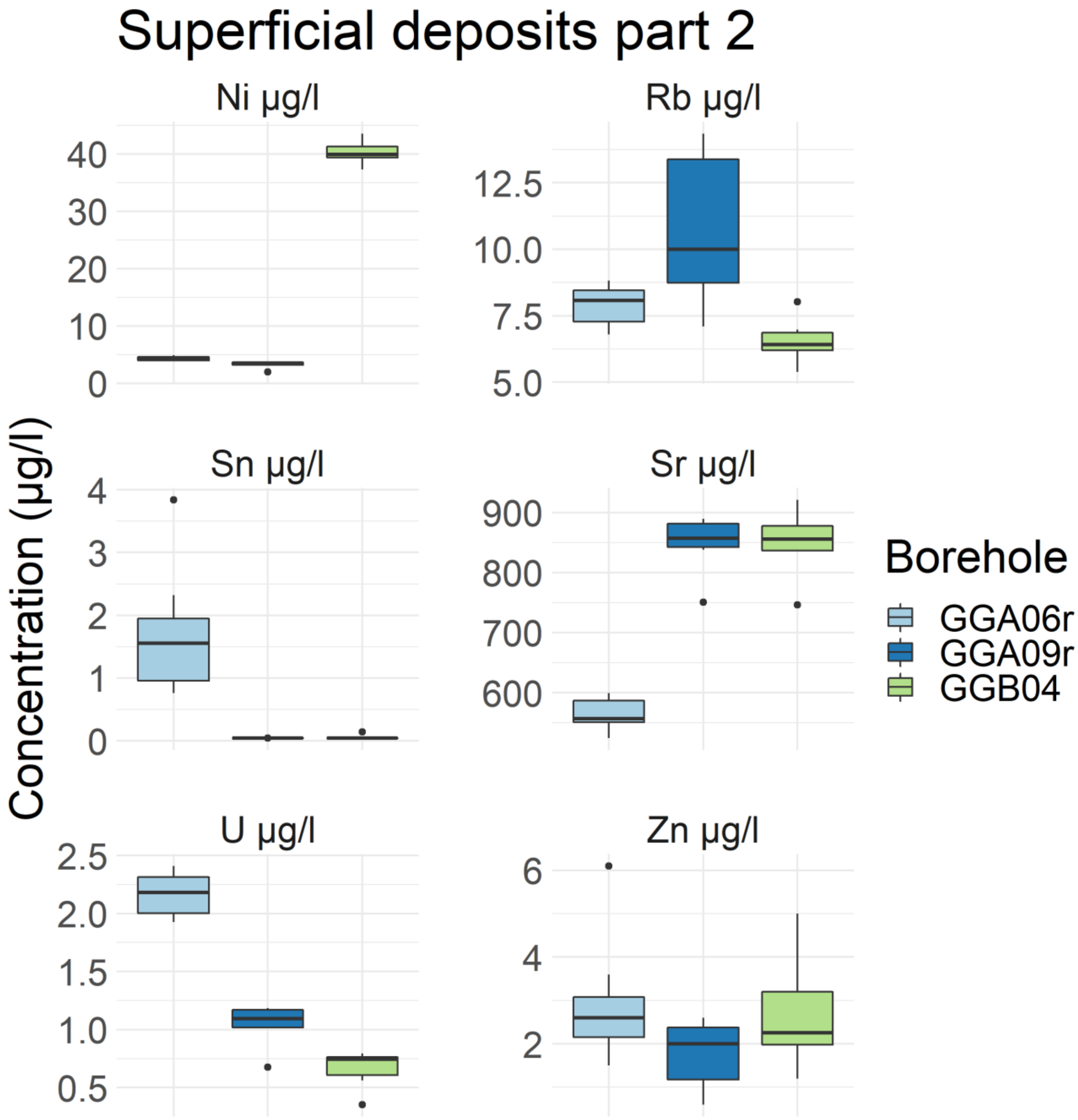

Figure 69 boxplots showing distribution of trace element concentrations from superficial deposit boreholes. The interquartile range is shown by the upper and lower bounds of each coloured box, the median is represented by the black line in the coloured box, the whiskers represent the interquartile range times 1.5 and the points represent outliers. Data < detection limit (DL) are set to ½ DL.

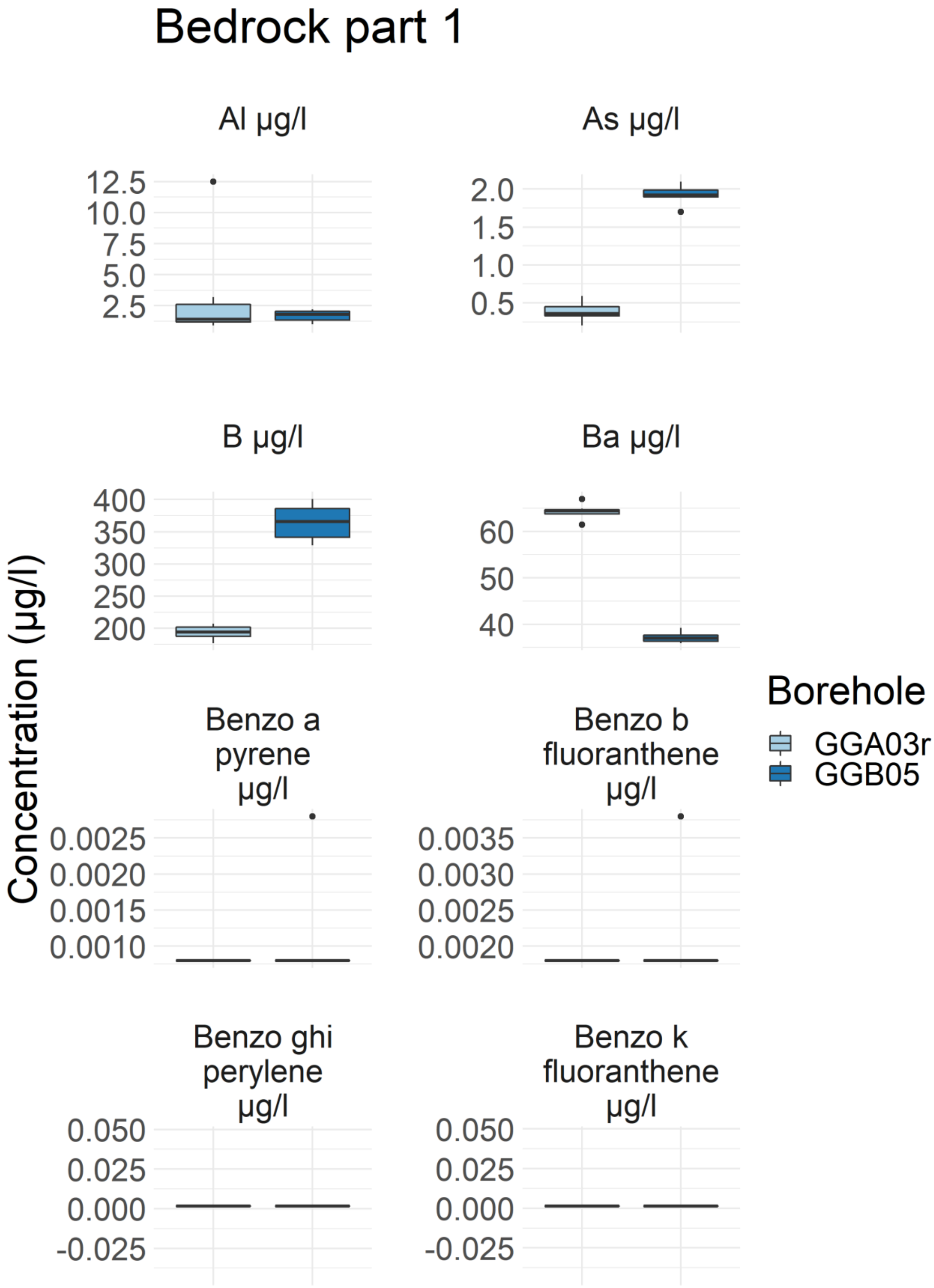

Figure 70 boxplots showing distribution of trace element concentrations from bedrock boreholes. The interquartile range is shown by the upper and lower bounds of each coloured box, the median is represented by the black line in the coloured box, the whiskers represent the interquartile range times 1.5 and the points represent outliers. Data < detection limit (DL) are set to ½ DL.

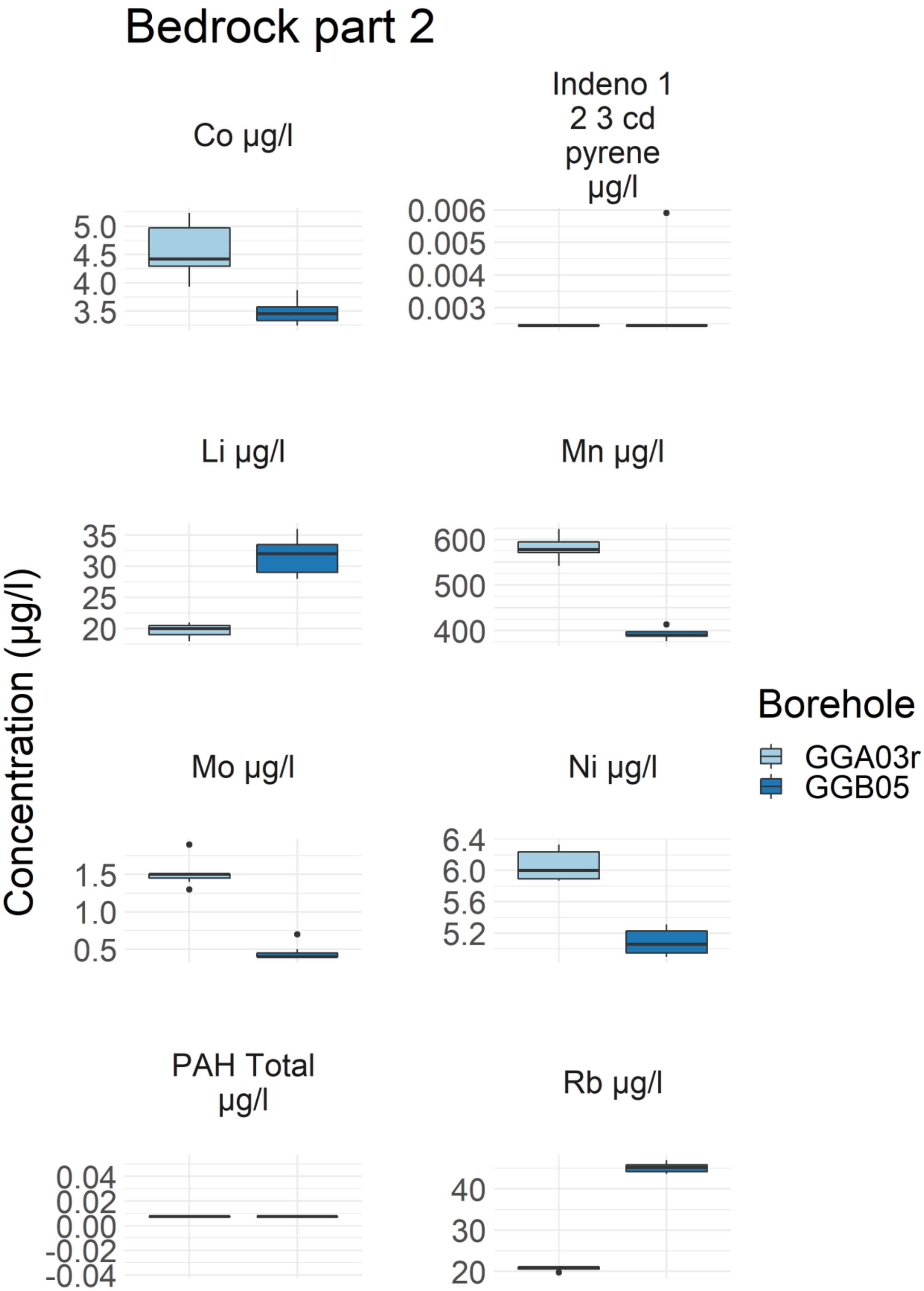

Figure 71 boxplots showing distribution of trace element concentrations from bedrock boreholes. The interquartile range is shown by the upper and lower bounds of each coloured box, the median is represented by the black line in the coloured box, the whiskers represent the interquartile range times 1.5 and the points represent outliers. Data < detection limit (DL) are set to ½ DL.

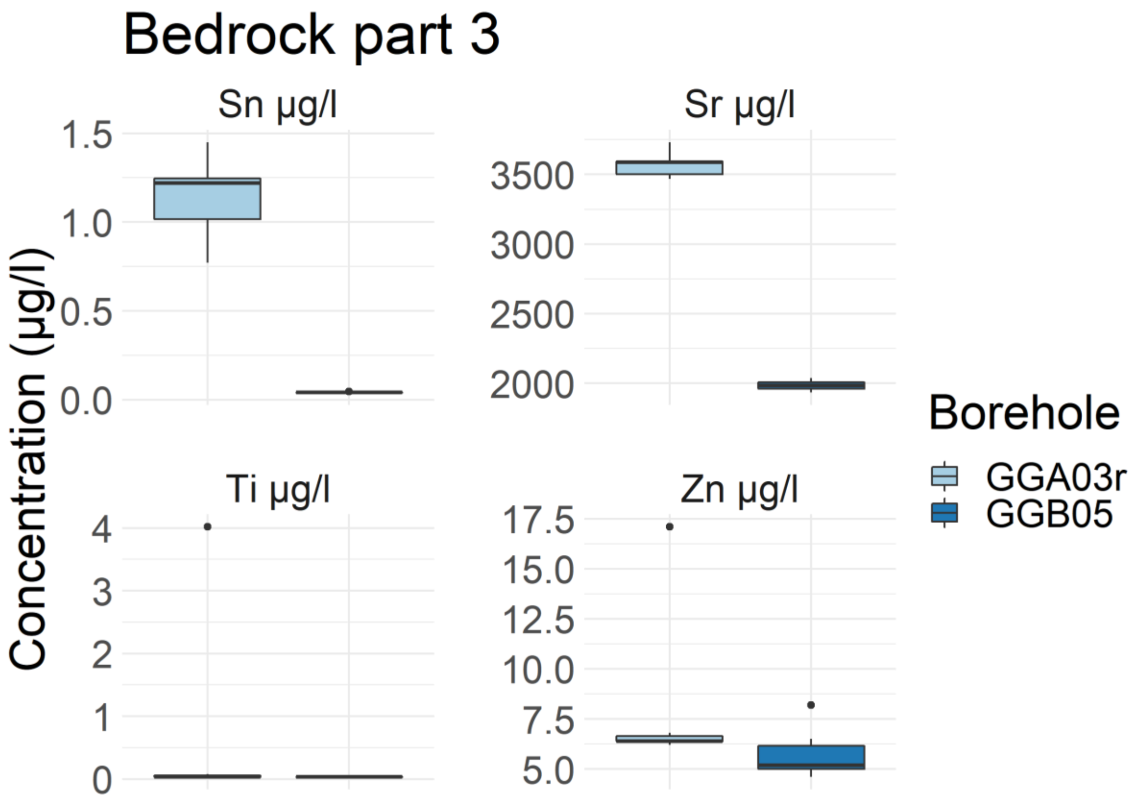

Figure 72 boxplots showing distribution of trace element concentrations from bedrock boreholes. The interquartile range is shown by the upper and lower bounds of each coloured box, the median is represented by the black line in the coloured box, the whiskers represent the interquartile range times 1.5 and the points represent outliers. Data < detection limit (DL) are set to ½ DL.

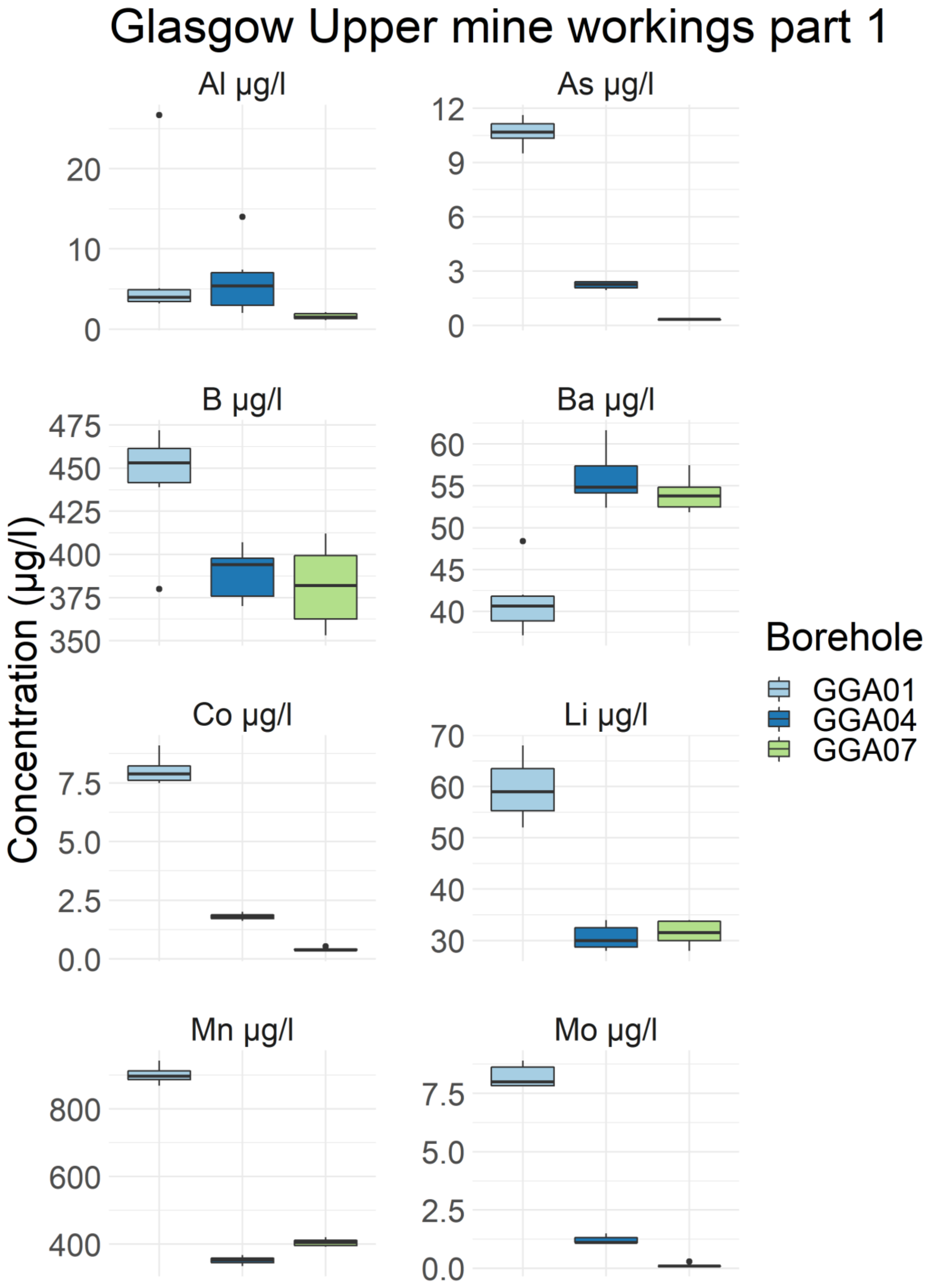

Figure 73 boxplots showing distribution of trace element concentrations from Glasgow Upper mine working boreholes. The interquartile range is shown by the upper and lower bounds of each coloured box, the median is represented by the black line in the coloured box, the whiskers represent the interquartile range times 1.5 and the points represent outliers. Data < detection limit (DL) are set to ½ DL.

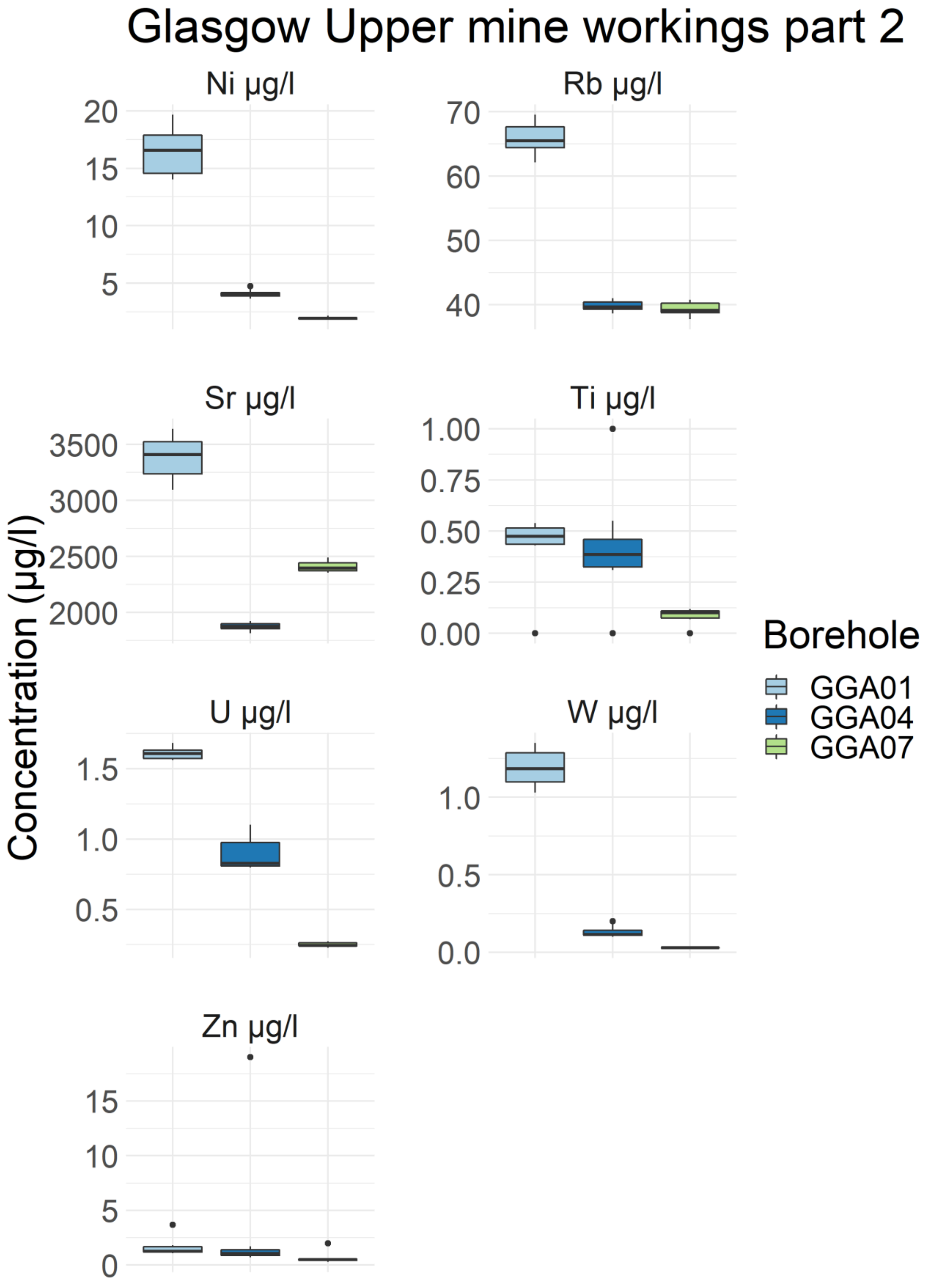

Figure 74 boxplots showing distribution of trace element concentrations from Glasgow Upper mine working boreholes. The interquartile range is shown by the upper and lower bounds of each coloured box, the median is represented by the black line in the coloured box, the whiskers represent the interquartile range times 1.5 and the points represent outliers. Data < detection limit (DL) are set to ½ DL.

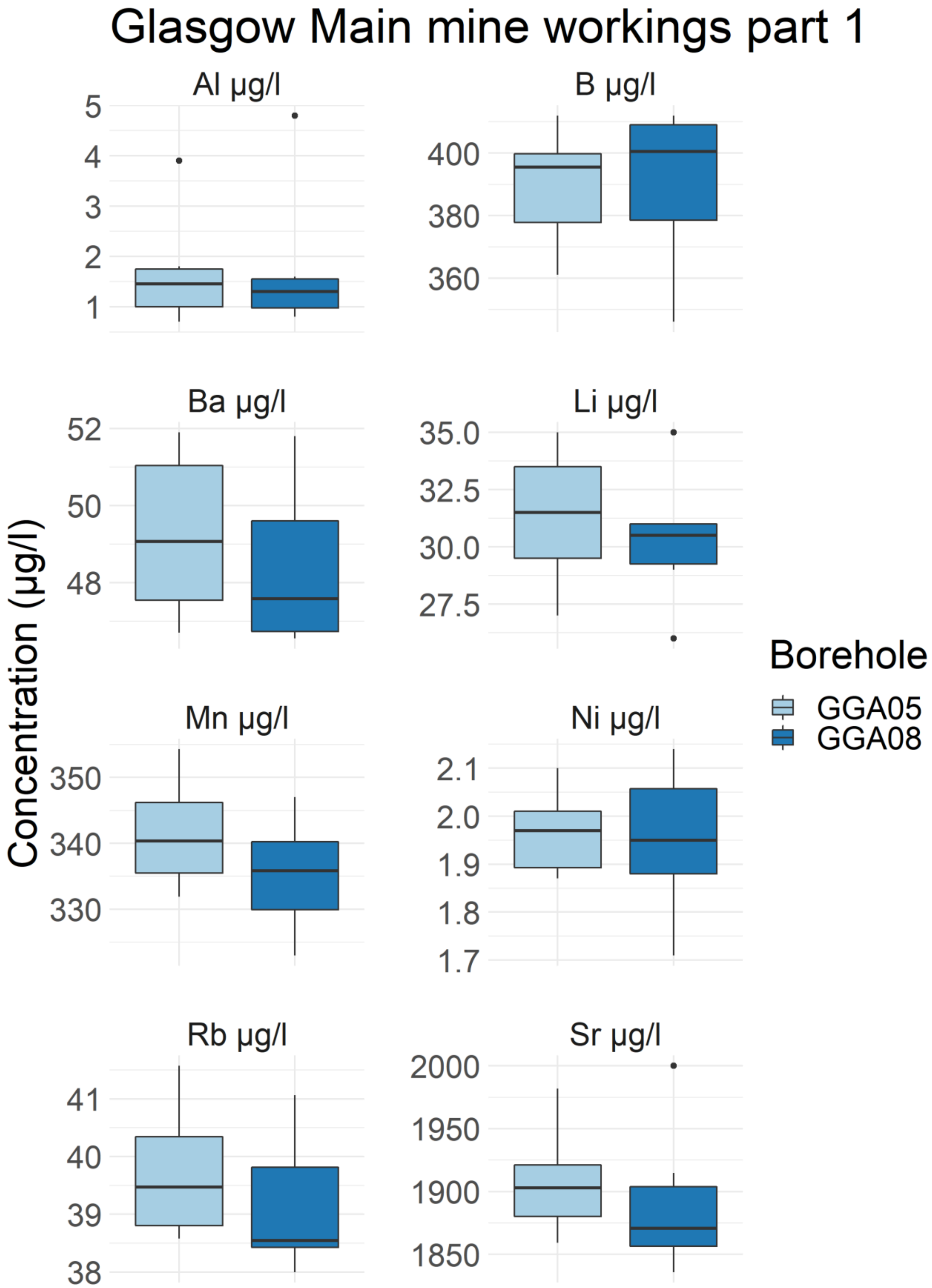

Figure 75 boxplots showing distribution of trace element concentrations from Glasgow Main mine working boreholes. The interquartile range is shown by the upper and lower bounds of each coloured box, the median is represented by the black line in the coloured box, the whiskers represent the interquartile range times 1.5 and the points represent outliers. Data < detection limit (DL) are set to ½ DL.

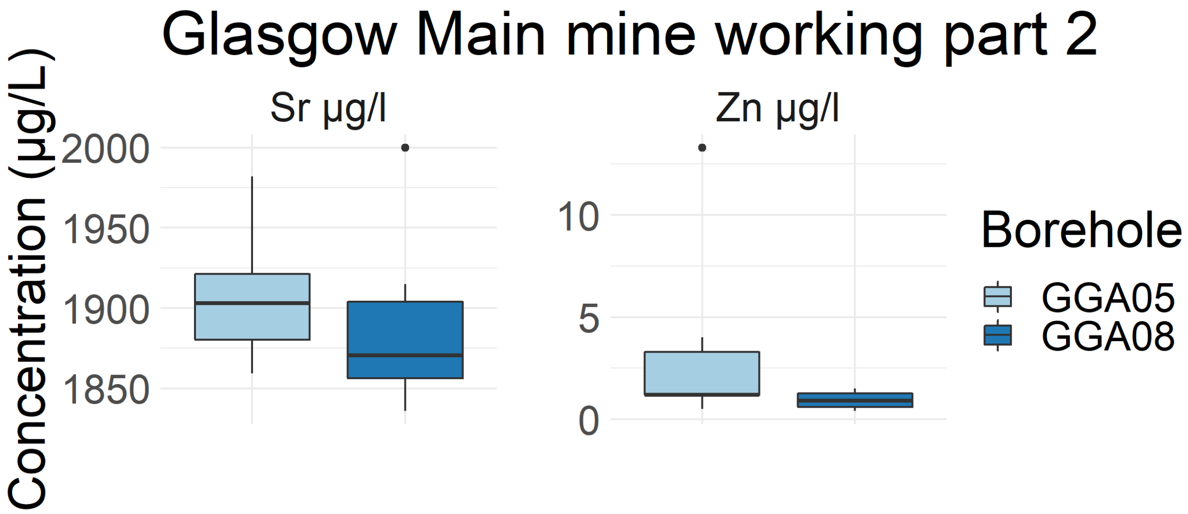

Figure 76 boxplots showing distribution of trace element concentrations from Glasgow Main mine working boreholes. The interquartile range is shown by the upper and lower bounds of each coloured box, the median is represented by the black line in the coloured box, the whiskers represent the interquartile range times 1.5 and the points represent outliers. Data < detection limit (DL) are set to ½ DL.

Other elements in mg/L

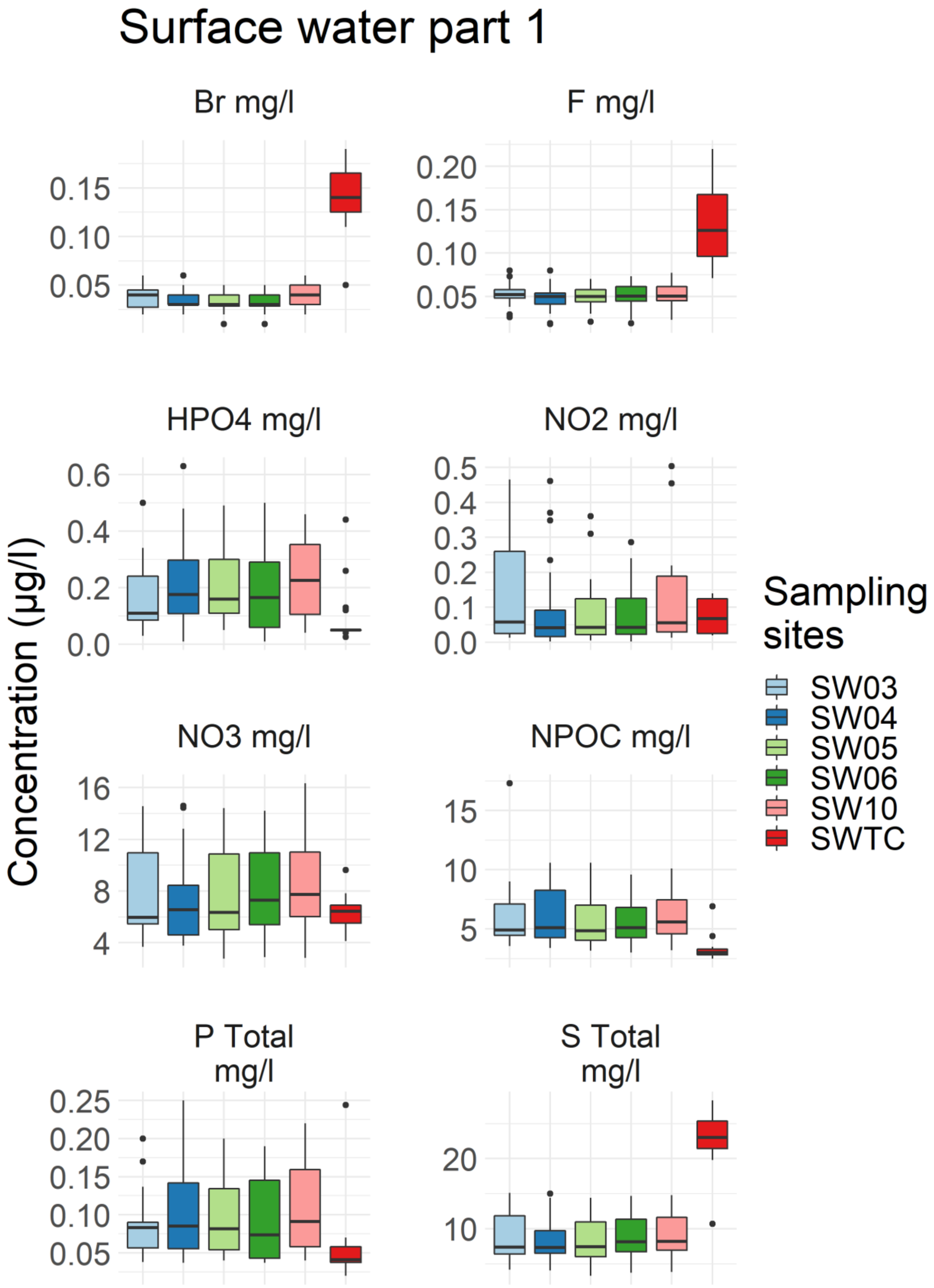

Figure 77 boxplots of all other parameter concentrations measured in mg/L from surface water sampling. The interquartile range is shown by the upper and lower bounds of each coloured box, the median is represented by the black line in the coloured box, the whiskers represent the interquartile range times 1.5 and the points represent outliers. Data < detection limit (DL) are set to ½ DL.

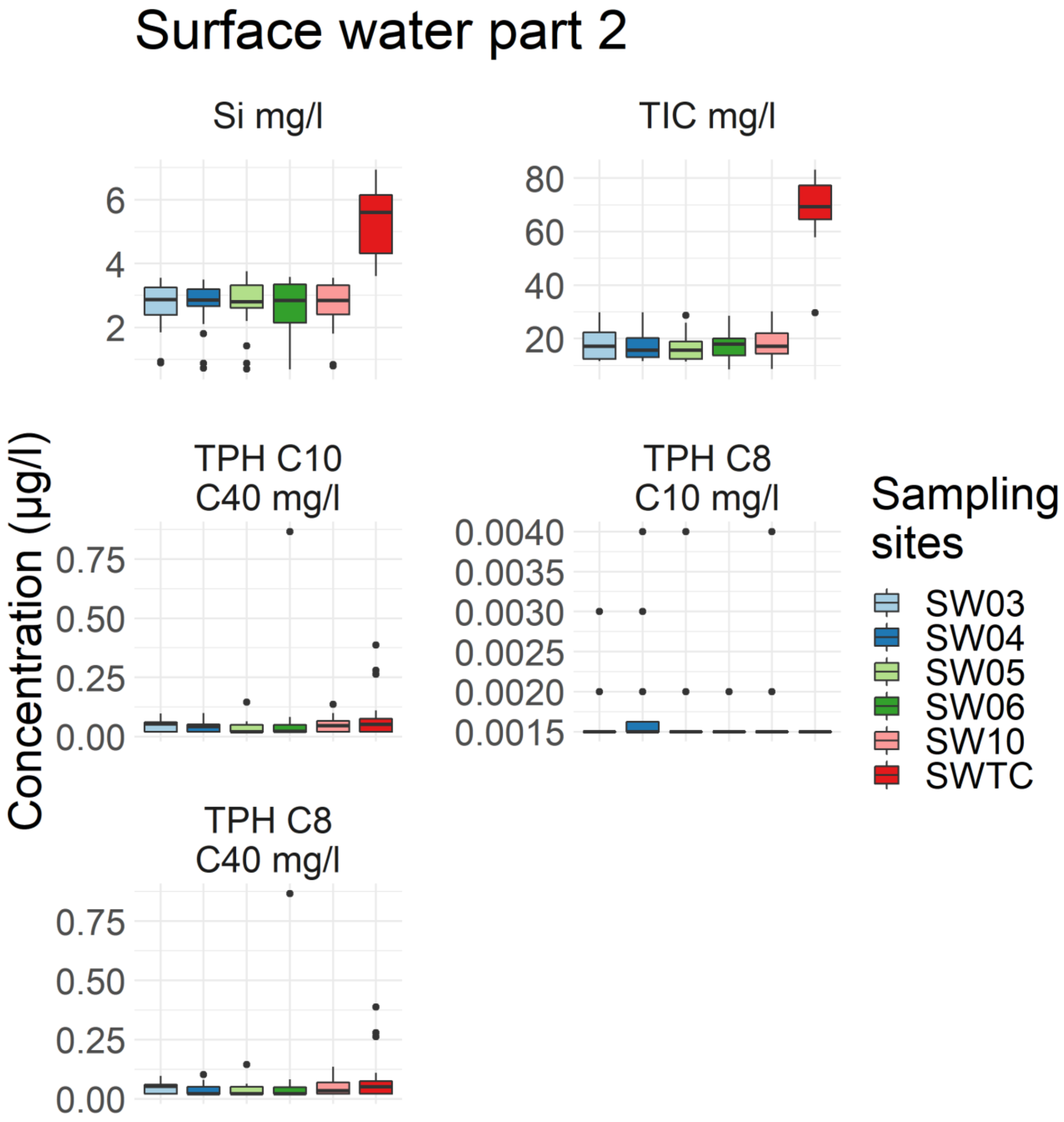

Figure 78 boxplots of all other parameter concentrations measured in mg/L from surface water sampling. The interquartile range is shown by the upper and lower bounds of each coloured box, the median is represented by the black line in the coloured box, the whiskers represent the interquartile range times 1.5 and the points represent outliers. Data < detection limit (DL) are set to ½ DL.

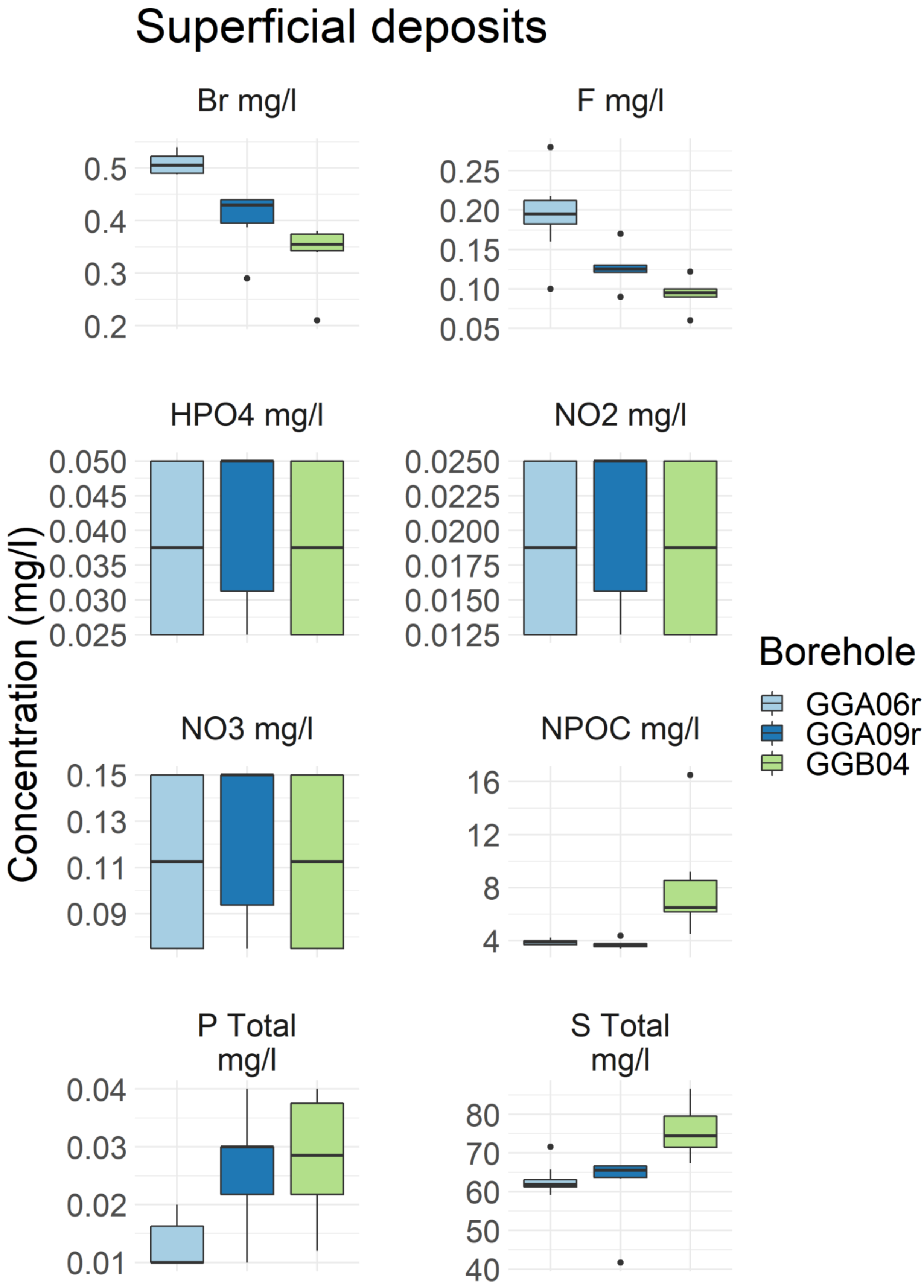

Figure 79 boxplots of all other parameter concentrations measured in mg/L from superficial deposit boreholes. The interquartile range is shown by the upper and lower bounds of each coloured box, the median is represented by the black line in the coloured box, the whiskers represent the interquartile range times 1.5 and the points represent outliers. Data < detection limit (DL) are set to ½ DL.

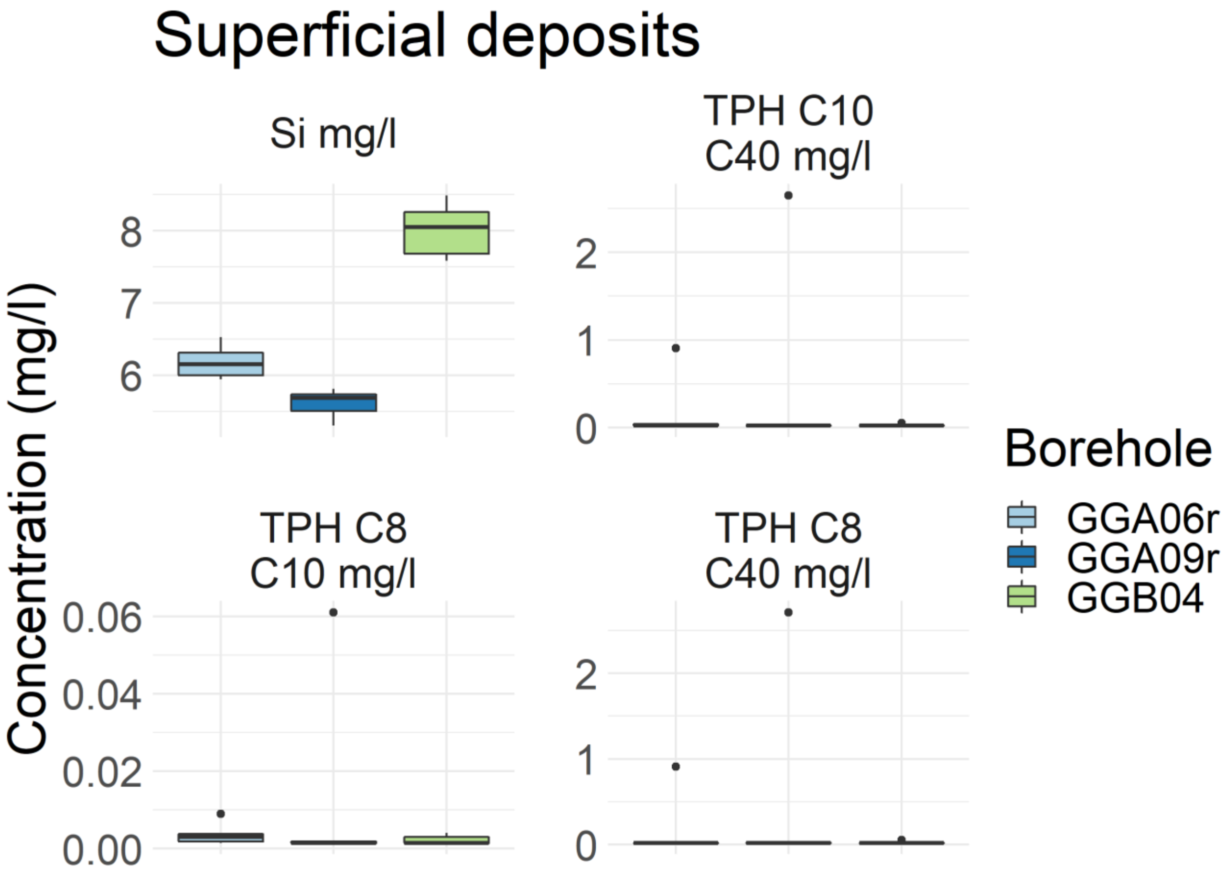

Figure 80 boxplots of all other parameter concentrations measured in mg/L from superficial deposit boreholes. The interquartile range is shown by the upper and lower bounds of each coloured box, the median is represented by the black line in the coloured box, the whiskers represent the interquartile range times 1.5 and the points represent outliers. Data < detection limit (DL) are set to ½ DL.

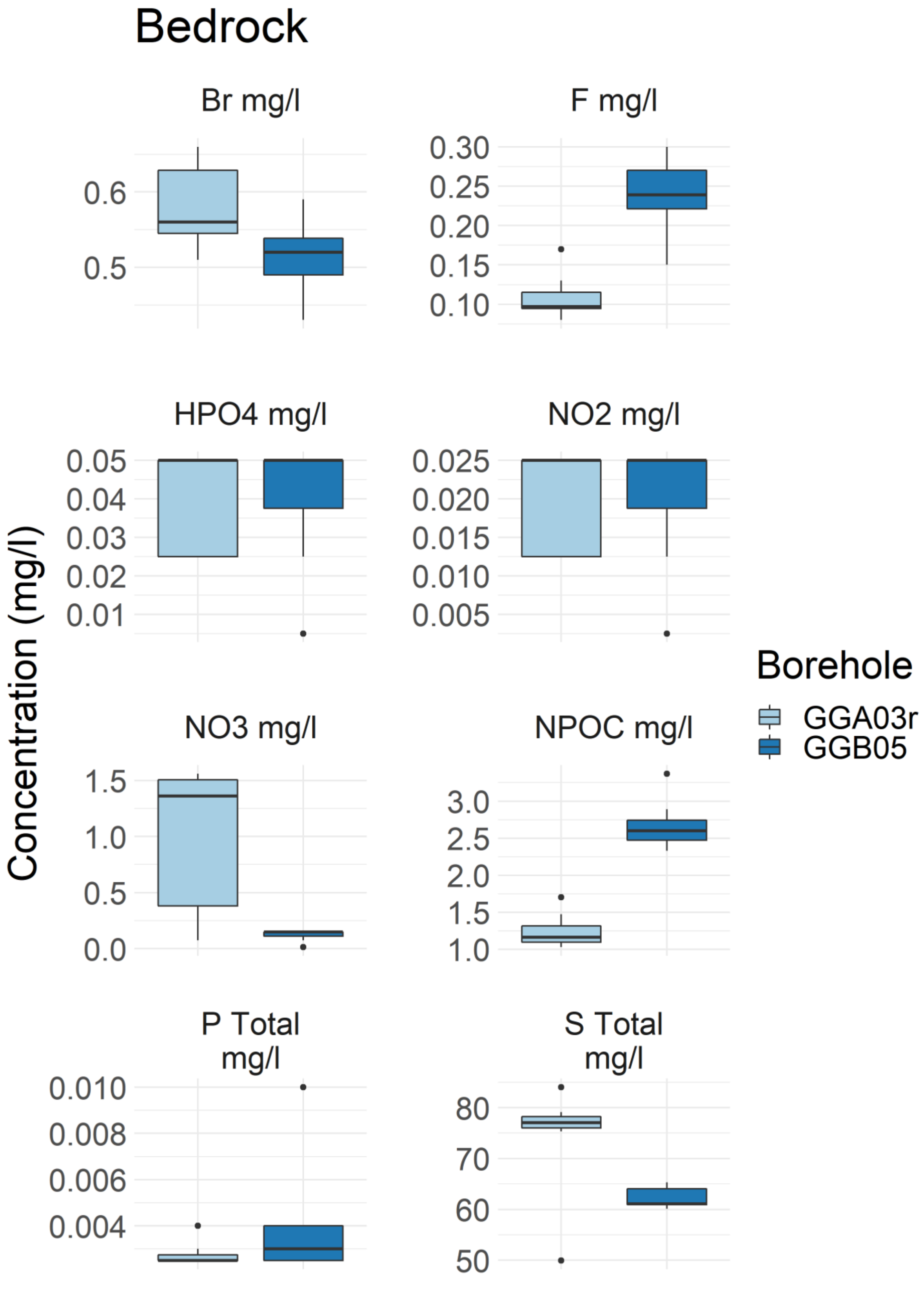

Figure 81 boxplots of all other parameter concentrations measured in mg/L from bedrock boreholes. The interquartile range is shown by the upper and lower bounds of each coloured box, the median is represented by the black line in the coloured box, the whiskers represent the interquartile range times 1.5 and the points represent outliers. Data < detection limit (DL) are set to ½ DL.

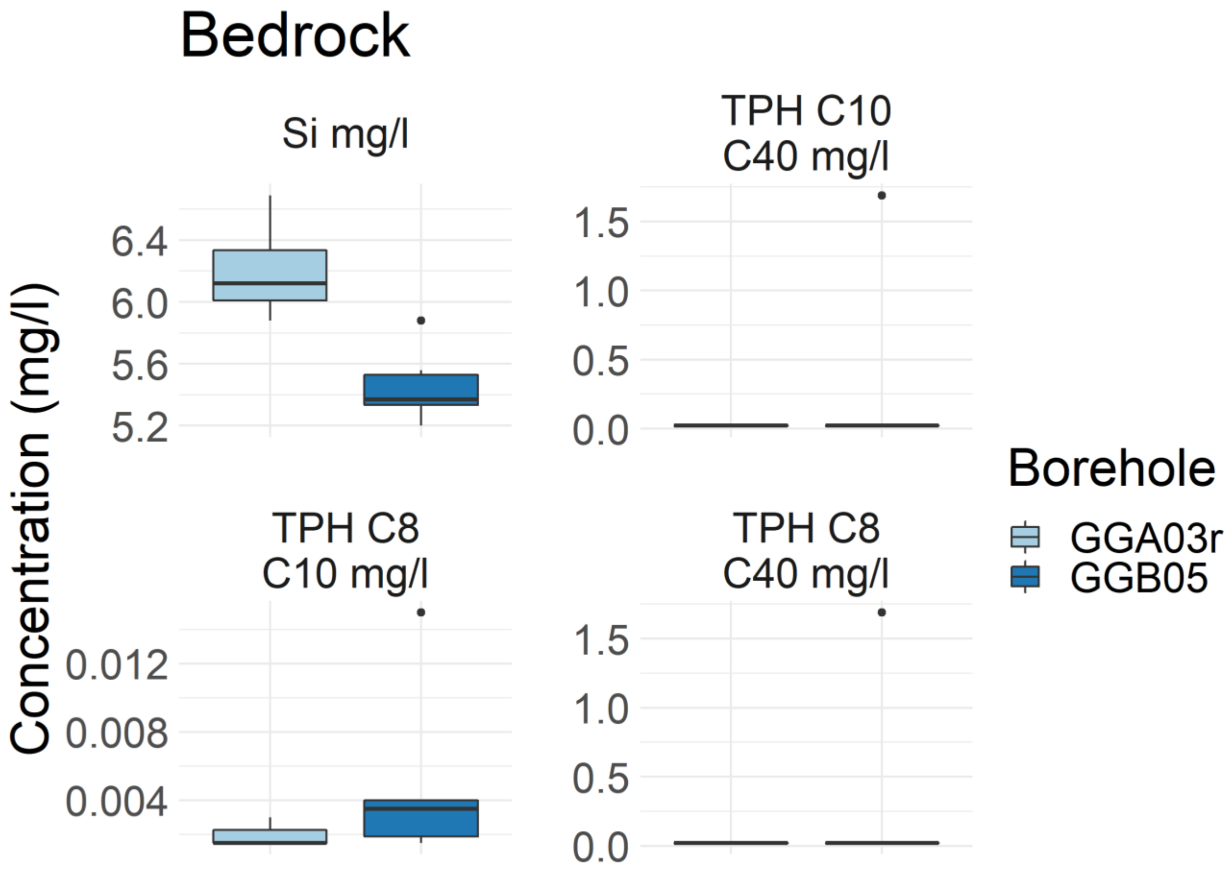

Figure 82 boxplots of all other parameter concentrations measured in mg/L from bedrock boreholes. The interquartile range is shown by the upper and lower bounds of each coloured box, the median is represented by the black line in the coloured box, the whiskers represent the interquartile range times 1.5 and the points represent outliers. Data < detection limit (DL) are set to ½ DL.

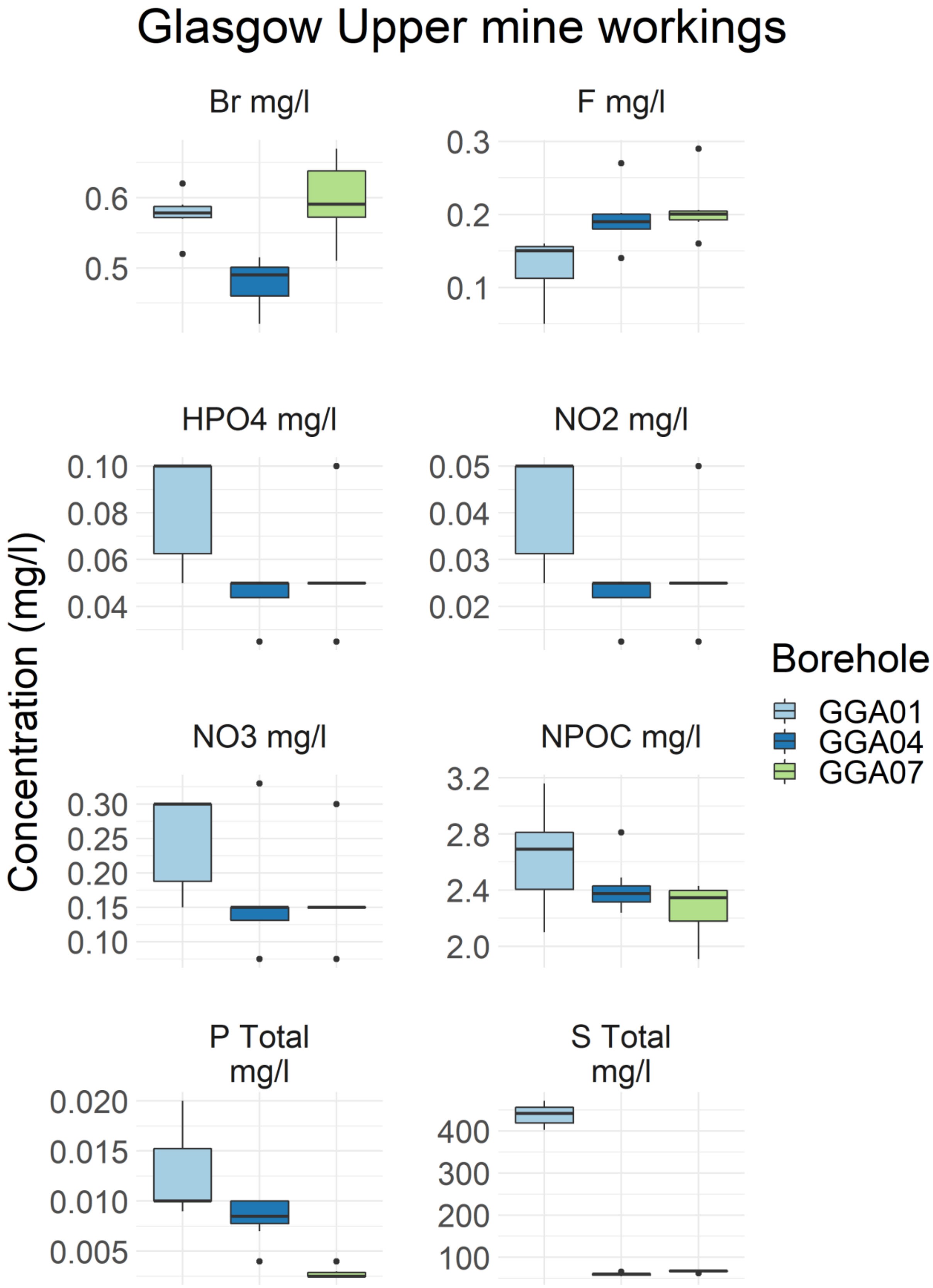

Figure 83 boxplots of all other parameter concentrations measured in mg/L from Glasgow Upper mine working boreholes. The interquartile range is shown by the upper and lower bounds of each coloured box, the median is represented by the black line in the coloured box, the whiskers represent the interquartile range times 1.5 and the points represent outliers. Data < detection limit (DL) are set to ½ DL.

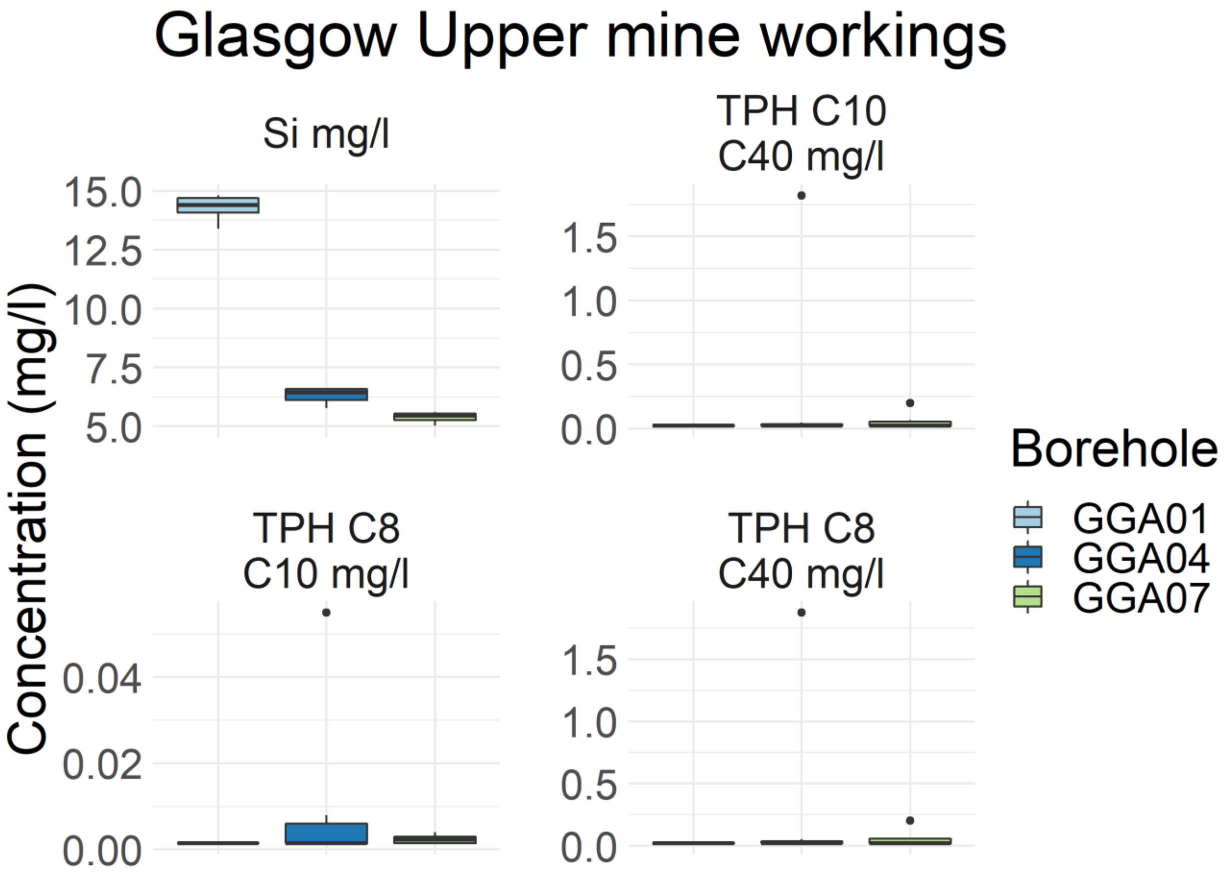

Figure 84 boxplots of all other parameter concentrations measured in mg/L from Glasgow Upper mine working boreholes. The interquartile range is shown by the upper and lower bounds of each coloured box, the median is represented by the black line in the coloured box, the whiskers represent the interquartile range times 1.5 and the points represent outliers. Data < detection limit (DL) are set to ½ DL.

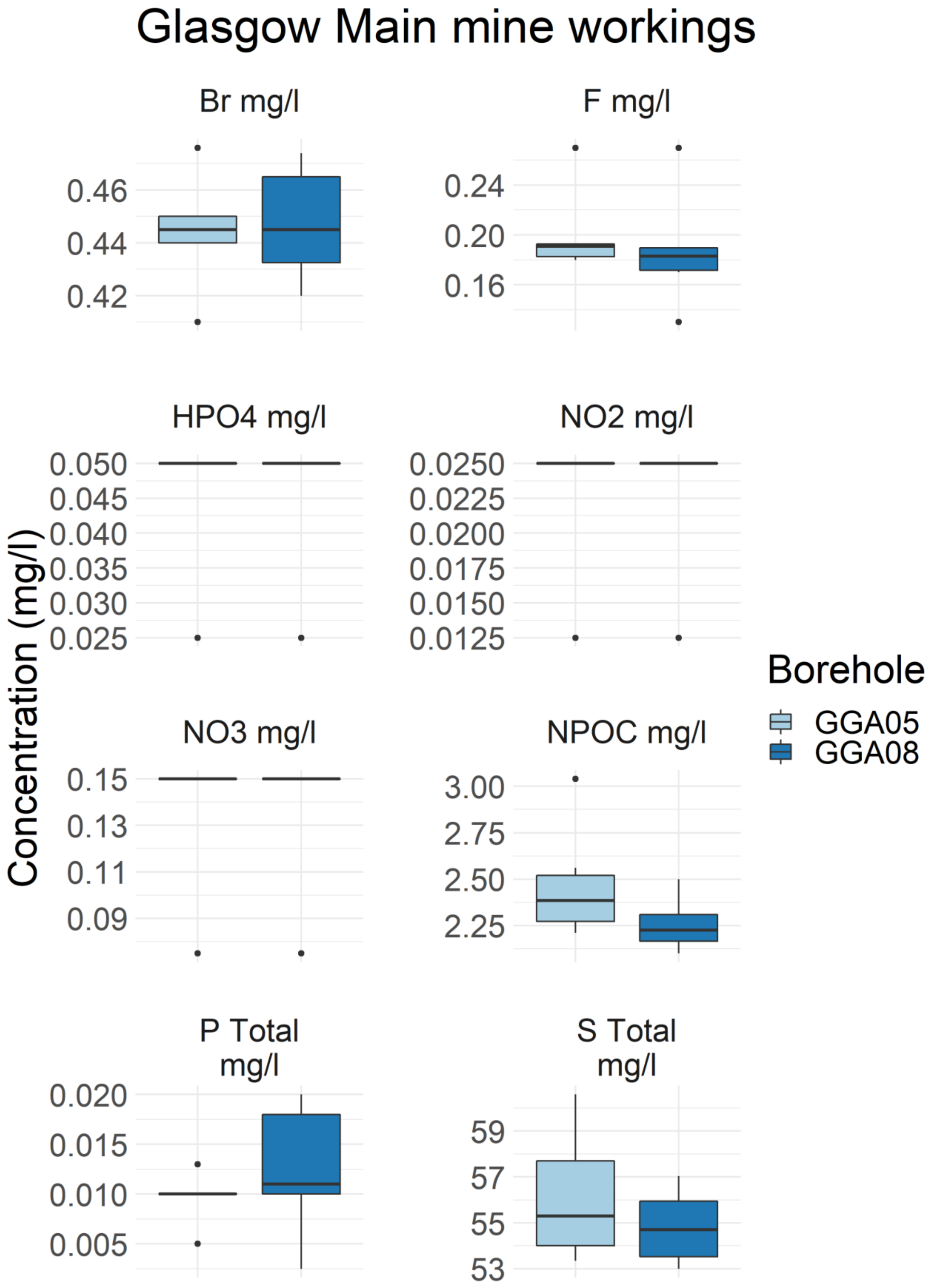

Figure 85 boxplots of all other parameter concentrations measured in mg/L from Glasgow Main mine working boreholes. The interquartile range is shown by the upper and lower bounds of each coloured box, the median is represented by the black line in the coloured box, the whiskers represent the interquartile range times 1.5 and the points represent outliers. Data < detection limit (DL) are set to ½ DL.

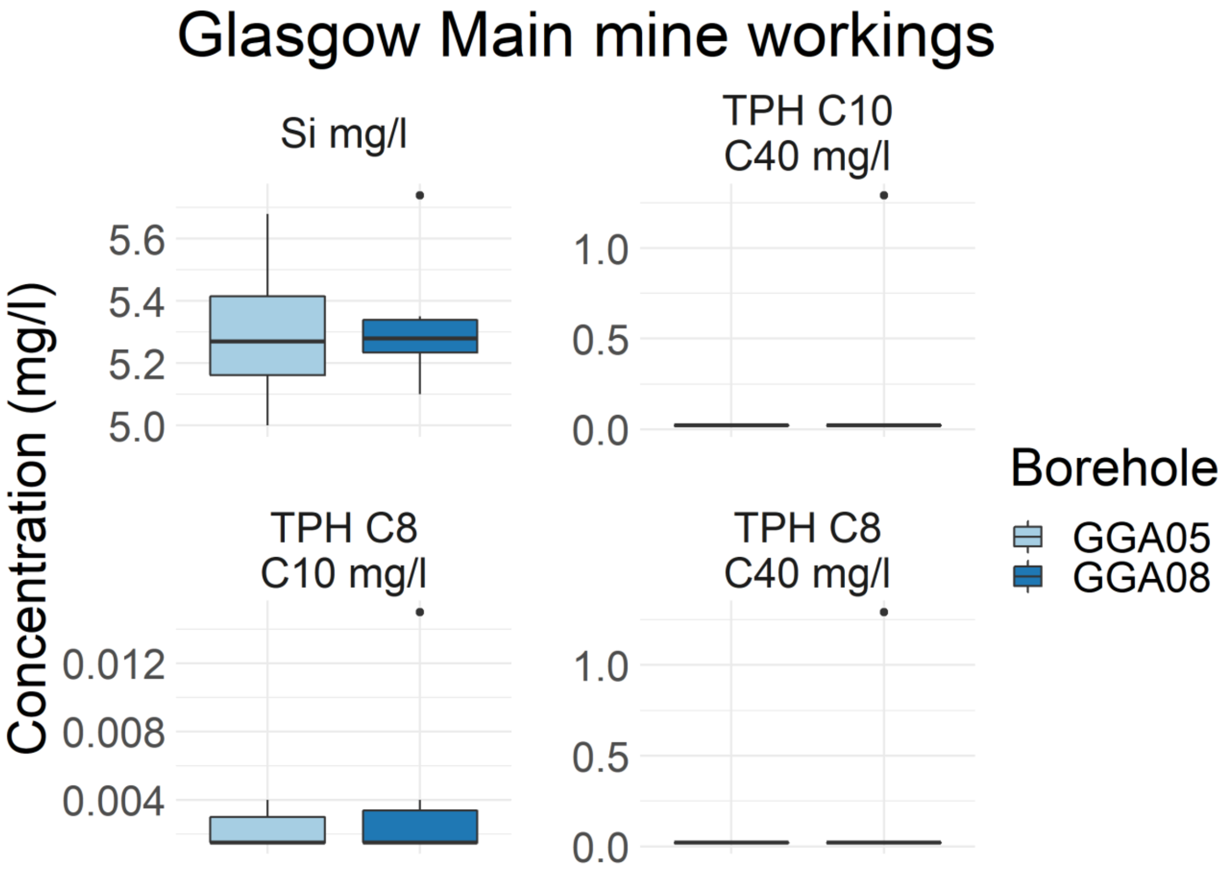

Figure 86 boxplots of all other parameter concentrations measured in mg/L from Glasgow Main mine working boreholes. The interquartile range is shown by the upper and lower bounds of each coloured box, the median is represented by the black line in the coloured box, the whiskers represent the interquartile range times 1.5 and the points represent outliers. Data < detection limit (DL) are set to ½ DL.

Glossary

ASW	Air-saturated water
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
COPR	chromite ore processing residue
Cr(III)	trivalent chromium
Cr(VI)	hexavalent chromium
CRM	certified reference material
$\delta^{13}C$	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
EDTA	ethylenediaminetetraacetic acid
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
HCO_3	bicarbonate
HDPE	high-density polyethylene
HPLC	high performance liquid chromatography
IAEA	International Atomic Energy Agency
ICP-MS	inductively coupled plasma mass spectrometry
IRMS	isotope ratio mass spectrometry
ISO	International Organization for Standardization
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
NH_4	Ammonium
NIGL	NERC Isotope Geoscience Laboratory
NPOC	non-purgeable organic carbon
PAH	polycyclic aromatic hydrocarbons
PDB	passive diffusion bag
QC	quality control
QMS	quadrupole mass spectrometry
REE	rare earth elements
RPD	relative percent difference
RSD	relative standard deviation
SAOB	sulphide antioxidant buffer
SEC	specific electrical conductance
SF_6	sulphur hexafluoride
SHE	standard hydrogen electrode
STP	standard temperature and pressure
SWTC	Tollcross Burn site

T	temperature
TIC	total inorganic carbon
TPH	total petroleum hydrocarbons
UK	United Kingdom
UKAS	United Kingdom Accreditation Service
UKCEH	United Kingdom Centre for Ecology & Hydrology
UKGEOS	United Kingdom Geoenergy Observatories
UKRI	United Kingdom Research and Innovation
VOC	Volatile organic compounds
VPDB	Vienna Pee Dee Belemnite
VSMOW2	Vienna Standard Mean Ocean Water
WNW	west-north-west

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