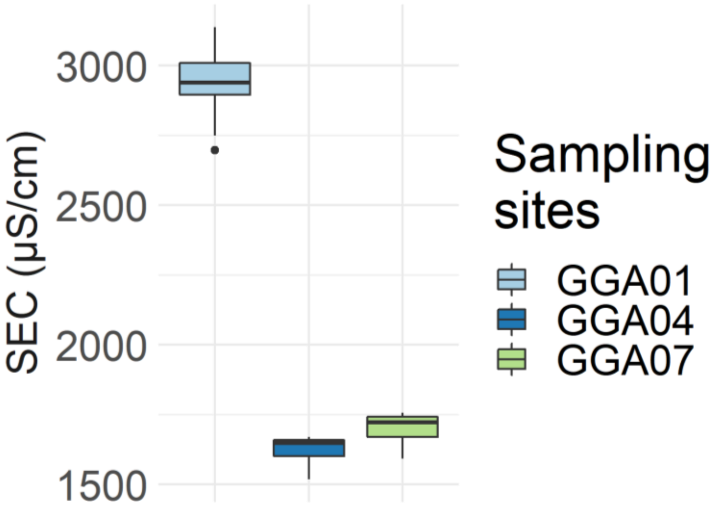
UK Geoenergy Observatories: Glasgow baseline groundwater and surface water chemistry dataset release June 2021 - January 2022

UK Geoenergy Observatories Programme

Open Report OR/23/029



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OPEN REPORT OR/23/029

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Front cover: Box and whisker plot showing SEC in groundwaters from Glasgow Upper mine workings boreholes.

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UK Geoenergy Observatories: Glasgow baseline groundwater and surface water chemistry dataset release June 2021 - January 2022

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Summary

This report follows the Glasgow baseline groundwater and surface-water chemistry dataset release report September 2020 – May 2021 (data release/ monitoring period 1) (Bearcock et al., 2022), and describes baseline water chemistry sampling and analysis results for groundwater and surface water at the United Kingdom Geoenergy Observatory (UKGEOS) in Glasgow between June 2021 and January 2022. The report accompanies the Glasgow Observatory groundwater chemistry data release and the Glasgow Observatory surface water chemistry data release for the same periods (data release/ monitoring period 2). The monitoring period is eight months long, with six rounds of surface water and groundwater sampling during this time. Sampling during non-consecutive months was a result of COVID-19 restrictions and construction activities at site.

The Glasgow Observatory comprises twelve boreholes drilled into the main hydrogeological units, known as target horizons. 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, reduced iron (Fe), non-purgeable organic carbon (NPOC) and total inorganic carbon (TIC), polycyclic aromatic hydrocarbons (PAH), total petroleum hydrocarbons (TPH), volatile organic compounds (VOC), ^{2}H and ^{18}O abundance in water ($\delta^{2}H$ and $\delta^{18}O$), ^{13}C abundance in dissolved inorganic carbon (DIC) ($\delta^{13}C_{DIC}$), ammonium (NH_4), dissolved gases (methane, ethane and carbon dioxide (CH_4, C_2H_6, CO_2)), noble gases (helium, neon, argon, krypton, and xenon (He, Ne, Ar, Kr and Xe)), chlorofluorocarbons (CFC-12 and CFC-11), sulphur hexafluoride (SF_6), and sulphide (S^{2-}).

The pH of groundwater samples (range 6.6 – 7.4) is circum-neutral, with a similar range across all target horizons. Groundwater from all four horizons is highly mineralised with median SEC values 1440 µS/cm - 1670 µS/cm. GGA01, installed in the Glasgow Upper mine working, had the most highly mineralised groundwater with a range of 2930 µS/cm – 3140 µS/cm. The range of recorded groundwater temperatures is largest in the superficial deposits (11.0°C – 16.6°C). The bedrock and mine workings groundwaters all have similar temperatures, and a narrower range of 10.1°C – 13.4 °C. In all target horizons the dissolved oxygen concentration is very low, all DO values are ≤0.81 mg/L.

In general major elements and physico-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 chemistry of most groundwater samples is unchanged from pumping tests conducted in early 2020 (Palumbo-Roe et al., 2021), and the previous period of baseline monitoring that spanned the period from September 2020 to May 2021 (Bearcock et al., 2022). Groundwaters are generally HCO_3 type, with no dominant cation. The exception is GGA01, where groundwaters changed from HCO_3 type during the pumping test to Ca-SO_4 type at the start of the previous round of monitoring

(September 2020). During this monitoring period the concentrations of Ca and SO_4 in GGA01 have continued to increase, albeit at a slowing rate, while HCO_3 concentrations, which had initially fallen, are slowly increasing. Oxidation of sulphide minerals (e.g. pyrite) could have caused the dominance of the SO_4 anion in GGA01 groundwaters.

Dissolved organic carbon (as NPOC) is present in the range 1.05 mg/L to 5.46 mg/L, except for one outlier of 23.5 mg/L at GGA01. NPOC concentrations in the superficial deposits, with a median 4.39 mg/L, are at the upper end of this range, while all other target horizons have similar, lower, median values (medians from 2.32 mg/L to 2.54 mg/L).

Groundwater samples from two boreholes have low ammonium (NH_4) concentrations throughout the monitoring period (GGB04 in the superficial deposits and bedrock borehole GGA03r have a combined median of 3.15 mg/L). The remaining groundwaters in the Glasgow Observatory have high NH_4 concentrations (combined median 23.2 mg/L).

There was a large concentration range of trace elements in the Glasgow Observatory groundwaters. In general, the lowest concentrations were found in groundwaters from the Glasgow Main mine workings. In contrast the highest trace element concentrations were found in the groundwaters from the Glasgow Upper mine workings and the superficial deposits. TPH was detected in low concentrations in all units at some point during the sampling period. VOCs were not detected in any groundwater sample.

Water stable isotopes (δ^2H and $\delta^{18}O$), inorganic carbon $\delta^{13}C$ and groundwater residence time data were consistent with findings from the pumping test results and previous monitoring period (Bearcock et al., 2022; Palumbo-Roe et al., 2021). Groundwaters are recharged by modern recharge from local rainfall.

Median concentrations of dissolved methane (CH_4) in the groundwaters range from 16.6 µg/L in the superficial deposits to 224 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). Dissolved ethane (C_2H_6) was below detection limits in all but one sample (5.2 µg/L at GGA01). Dissolved CO_2 has a median value of 141 mg/L with little variation between units.

Water chemistry cluster analysis shows that the superficial deposits, bedrock, mine working, and surface water samples cluster into statistically distinct groups. Notable exceptions are groundwaters from GGA01 which form their own separate group, and GGB05 groundwaters from the bedrock horizon which group with the mine workings.

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, non-purgeable organic carbon (NPOC) and total inorganic carbon (TIC), polycyclic aromatic hydrocarbons (PAH), total petroleum hydrocarbons (TPH), ^2H and ^{18}O abundance in water (δ^2H and $\delta^{18}O$) and carbon 13 abundance in dissolved inorganic carbon (DIC) ($\delta^{13}C_{DIC}$), .

While both the Clyde and Tollcross Burn have a near-neutral to alkaline pH (7.3 – 8.7), the pH values measured at the Tollcross Burn tend to be higher (median 8.3 from the Tollcross Burn and 7.7 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 872 µs/cm) than those measured in the River Clyde samples (median 372 µs/cm). Surface water samples are all generally Ca-HCO_3 type. The samples taken from the Tollcross Burn tend to have a greater HCO_3 proportion than the river Clyde samples.

Most detected trace elements are present in higher concentrations in the River Clyde than in the Tollcross Burn. 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 (median 4.18 µg/L) than elsewhere within the Glasgow Observatory (median 0.4 µg/L). In general, the surface water results are consistent with findings from previous work (Bearcock et al., 2022; 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 Observatory is located in the east of the 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 conducted during pumping tests 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 approximately simultaneously to gain insight on correlations or impacts between the subsurface and surface. Sampling was, however, halted during the early part 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 were released with an accompanying report by Bearcock et al. (2022).

Between June 2021 and January 2022, a further six sampling rounds were undertaken for both surface water and groundwater. The data collected from these six rounds are presented in this report, which summarises and provides a brief discussion to the accompanying dataset. The future intention is to sample every quarter.

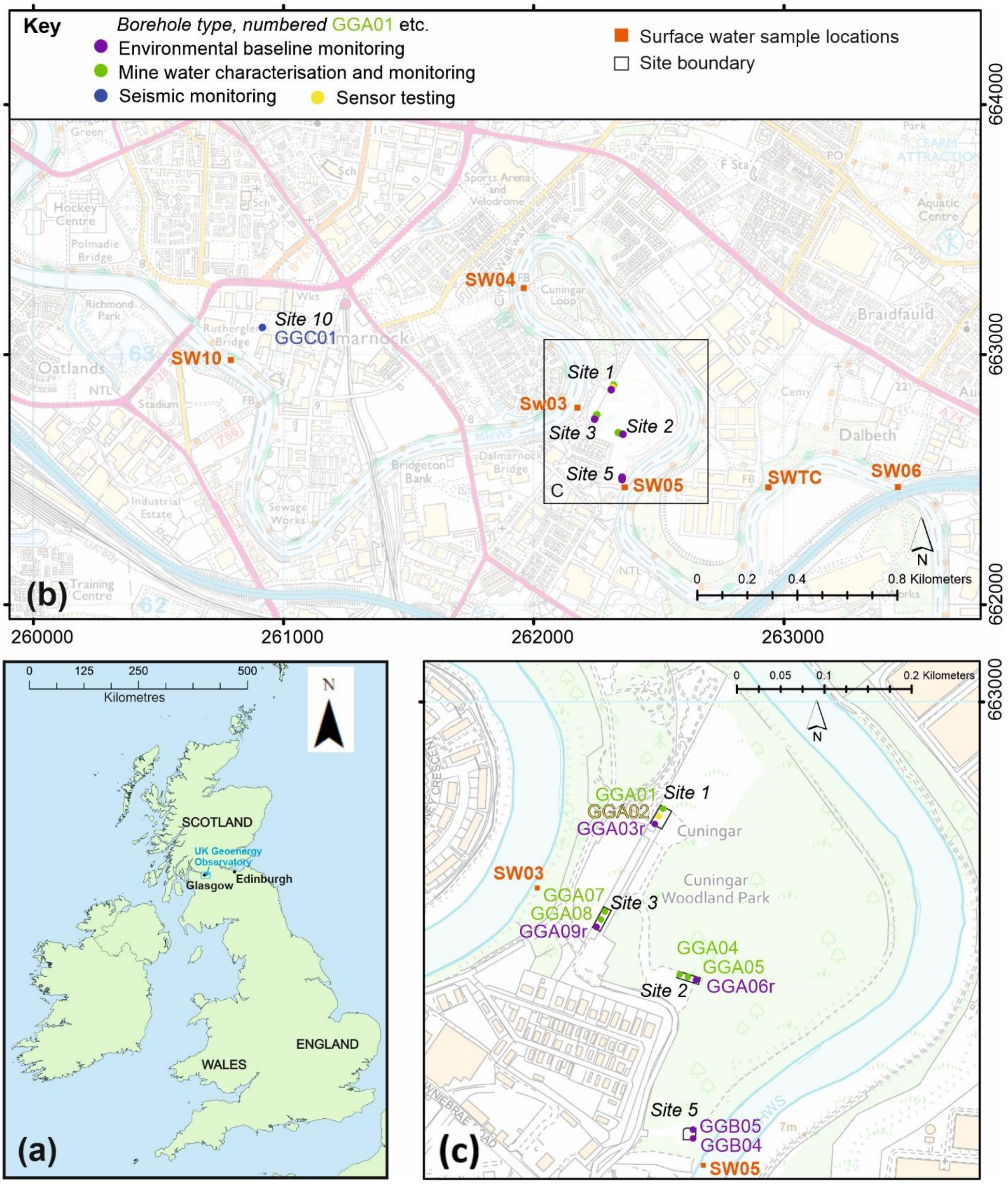

Figure 1 (a) Location of the Glasgow Observatory in the UK (b) position of Observatory sites (c) detail of Cuningar Loop mine water and environmental baseline characterisation and monitoring boreholes. *Contains OS data © Crown copyright and database rights [2023]. OS AC0000824781 EUL*

1.1 CITATION GUIDANCE

This report accompanies the release of the baseline water chemistry June 2021 – January 2022.

Any use of the data should be cited to:
Walker-Verkuil K, Mulcahy A, Bearcock J M, Palumbo-Roe B, MacAllister D J, Darling W G, Gooddy D C (2023), UKGEOS Glasgow groundwater and surface water chemistry dataset release (2021–2022). NERC EDS National Geoscience Data Centre. (Dataset) DOI: https://doi.org/10.5285/9da2a537-b8f5-4520-bed8-5c629dce0bd9
this report cited as:
Bearcock J M ,Palumbo-Roe B, Mulcahy A, Walker-Verkuil K, MacAllister D J, Darling W G, Gooddy D C , 2023, UK Geoenergy Observatories: Glasgow baseline groundwater and surface water chemistry dataset release June 2021 - January 2022. *British Geological Survey Open Report*, OR/23/029. 144pp.

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 through, individual former mine workings; five are environmental baseline monitoring boreholes that are drilled into, and screened through, 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 1b). The locations on the River Clyde were chosen to be 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 at SW10 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 SAMPLING

Samples were taken during rounds in June 2021, July 2021, August 2021, October 2021, November 2021, and January 2022. Sampling times and sites were irregular because of COVID-19 limitations and site construction restrictions. In addition, surface water site SW3 could not be sampled during rounds 22-24 because on-going construction reduced access to the site. Other than this all boreholes and surface water sites were sampled during each round.

The sampling set up, field parameter measurements and observations, sampling techniques, sample storage and transport, and analyses were consistent with those previously used for baseline monitoring at the Glasgow Observatory, and more details can be found in Bearcock et al. (2022) and Fordyce et al. (2021). A summary of analysis techniques can be found in Appendix 1.

2.2 SAMPLE COLLECTION

The groundwater was sampled for the following determinands:

- Major, minor, and trace elements
- Non-purgeable organic carbon (NPOC) and total inorganic carbon (TIC)
- Polycyclic aromatic hydrocarbons (PAH)
- Total petroleum hydrocarbons (TPH)
- Volatile organic compounds (VOC)
- ^{2}H and ^{18}O abundance in water ($\delta^{2}H$ and $\delta^{18}O$)
- ^{13}C abundance in 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) (round 26 only)
- Sulphur hexafluoride (SF_6)
- Noble gases - helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) (round 26 only)
- Sulphide (S^{2-})
- Reduced Fe (Fe^{2+})

The surface water was sampled for the following determinands:

- Major, minor, and trace elements
- Non-purgeable organic carbon (NPOC) and total inorganic carbon (TIC)
- Polycyclic aromatic hydrocarbons (PAH)
- Total petroleum hydrocarbons (TPH)
- ^{2}H and ^{18}O abundance in water ($\delta^{2}H$ and $\delta^{18}O$)
- ^{13}C abundance in dissolved inorganic carbon (DIC) ($\delta^{13}C_{DIC}$)

Reduced iron was analysed for the first time in samples collected during sampling round 21 (June 2021). For the sampling rounds reported here, sulphide, which was introduced during the previous monitoring period, was added to the regular analysis suite while Cr speciation was removed (but with continued monitoring of total chromium).

Except for Fe^{2+}, the sampling techniques are described in detail in previous UKGEOS publications (Bearcock et al., 2022; Fordyce et al., 2021; Palumbo-Roe et al., 2021), and summarised in Appendix 1.

2.2.1 Collection of unfiltered water for the analysis of Fe^{2+}

The samples for Fe^{2+-} were analysed at an external laboratory, SOCOTEC, who provided 125 mL bottles pre-dosed with concentrated HCl for the analysis of Fe^{2+}. The sample bottle was filled to the brim with unfiltered water and the cap was screwed on, taking care to avoid air bubbles. Whilst in the field the samples were stored with ice packs and refrigerated on return to the BGS laboratories in Keyworth. The samples were subsequently couriered to SOCOTEC laboratory in Burton-on-Trent. The analysis methodology is summarised in Appendix 1.

3 Data Presentation

3.1 DATASET

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

> Dataset name: UKGEOS Glasgow groundwater and surface water chemistry dataset release (2021-2022)
>
> Filenames: UKGEOSGlasgow_GroundWaterChemData2_Release.xlsx, UKGEOSGlasgow_SurfaceWaterChemData3_Release.xlsx

It contains the field parameter (pH, temperature, Eh (corrected to the standard hydrogen electrode (SHE) using temperature-dependent conversion tables appropriate to the VWR® probe), 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 June 2021 and January 2022. 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 the limit of 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 ions, followed by trace element data in µg/L. Stable isotope data are then reported in ‰ relative to Vienna Pee Dee Belemnite (VPDB) for δ^{13}C-DIC and ‰ relative to Vienna Standard Mean Ocean Water (VSMOW2) for δ^{18}O and δ^{2}H. Total inorganic carbon data are reported in mg/L, 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 Euclidean 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 to assess water type in Figure 2, Figure 3 and Figure 8 (Piper, 1944) 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.

4.1.1 Physico-chemical parameters

Table 2, below, summarises the physico-chemical parameters measured during groundwater baseline monitoring at the Glasgow Observatory between June 2021 and January 2022. Other than the temperature (discussed below), there are no clear temporal trends for any of the measured physico-chemical parameters (Appendix 3)

The pH is circum-neutral, and ranges from 6.6 to 7.4, with a similar range across all target horizons. These values are slightly lower than those recorded in the previous data release (range 6.8 to 7.8).

Groundwater temperatures are a function of the ambient land surface temperatures and the geothermal gradient. In the UK the temperature at the surface is the dominant influence up to around 15 m below ground level (bgl), and aquifers at depths greater than 15 m bgl are dominated by the background geothermal gradient, although they can be modified by groundwater flow (Bloomfield et al., 2013). The largest range of groundwater temperatures at the Glasgow Observatory is recorded in the near-surface superficial deposits (11.0°C – 16.6°C).The bedrock and mine workings groundwater temperatures are less variable and are all measured between 10.1°C and 13.4°C, which are more typical of groundwater at depth (Bloomfield et al., 2013). Appendix 3.

The dissolved-oxygen concentrations (DO) are low, with all measured values ≤0.81 mg/L, indicating almost anoxic groundwater conditions. Variations are small and there is no clear temporal trend, or relationship with depth of target horizon.

The Eh measurements ranged between 9.7 mV and 357 mV, indicating iron/sulphate reducing conditions. Without full analyses of sulphide species it is not possible to distinguish iron-reducing from sulphate-reducing conditions (Chapelle et al., 2009). The mine workings had the most reducing redox conditions (median Eh of 108 mV and 66.3 mV for the Glasgow Upper and Main workings, respectively), while the superficial deposits and bedrock horizons had slightly higher Eh values (medians of 167 mV and 176 mV, respectively). The most oxidised groundwaters were sampled at GGA03r where the Eh ranged from 220 mV to 357 mV. There were only two other measurements greater than 200 mV, both from the superficial deposits horizon, but from different boreholes. There is no clear temporal trend of Eh measurements. However, these data have a smaller range in all target horizons compared to those discussed in the first data release report (Bearcock et al., 2022).

The specific electrical conductance (SEC) values showed that all groundwaters were highly mineralised: the minimum value was 1270 µS/cm, and median values of all target horizons were >1440 µS/cm. The range of values measured at each individual borehole was small, with no evidence of seasonality. GGA01, installed in the Glasgow Upper mine workings, had the most mineralised groundwater with a range of 2930 µS/cm – 3140 µS/cm. This range is significantly higher than those found in the groundwater of other boreholes screened into the Glasgow Upper mine workings: GGA04 (1520 µS/cm – 1660 µS/cm) and GGA07 (1590 µS/cm – 1730 µS/cm).

4.1.2 Major and minor ions

4.1.2.1 WATER TYPE

To understand the water type of the groundwaters, Piper diagrams are used to summarise the major ion data. Figure 2 presents the data from the superficial deposits and bedrock boreholes, while the data from the mine workings are presented in Figure 3. Plots are interpreted based on the identification of hydrochemical facies (Drever, 1997).

All the superficial deposits and bedrock groundwaters are HCO_3 type with no dominant cation (Figure 2). There is some variation in the cation percentages, mostly a variation in percentage of Ca (a continuum of ~30% to ~50% Ca) and corresponding variation in Na+K (~30% to ~50% Na +K) and a stable percentage of Mg (~20% Mg). Groundwaters at GGA03r are distinct, however, with a higher percentage of Mg (~35%). When compared to the Piper diagram presented in the previous data release report (Bearcock et al., 2022), these groundwaters have very similar major-ion proportions. GGB04, however, has less variability with increased Ca and Mg proportions, and corresponding decreased Na+K proportion.

The mine waters form two distinct clusters on the Piper diagram (Figure 3) and have a very similar distribution to that reported in the previous data release (Bearcock et al., 2022). Most of the groundwaters from the mine workings are HCO_3 type, with no dominant cation. GGA01 is distinct as it has Ca-SO_4 type water. In the previous data release a clear difference in GGA01 water chemistry was observed when compared to the composition measured during initial pumping tests. The data reported here show that there has been no further change of the hydrochemical facies, and that changes to the water type largely occurred in the five-to-seven-month period between the initial pumping tests and the first release of groundwater data.

Table 2 Range and median of groundwater physico-chemical parameters from the Glasgow Observatory boreholes between June 2021 and January 2022. 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	6.6	7.2	7.0	18	0	6.9	7.4	7.1	12	0
Temperature (°C)	11	16.6	16.6	18	0	10.8	13.2	11.9	12	0
Eh (mV)	78.5	253	167	18	0	90.1	357	176	12	0
Dissolved oxygen (mg/L)	0.04	0.64	0.21	18	0	0.1	0.42	0.24	12	0
Specific electrical conductance (µs/cm)	1270	1670	1440	18	0	1450	1700	1560	12	0

	Glasgow Upper mine workings					**Glasgow Main mine workings**				
	Min	**Max**	**Median**	**n**	**n(c)**	**Min**	**Max**	**Median**	**n**	**n(c)**
Parameter										
pH	6.7	7.3	7.1	18	0	7	7.4	7.1	12	0
Temperature (°C)	10.1	12.8	12.2	18	0	10.8	13.4	12.4	12	0
Eh (mV)	29.3	131	108	18	0	9.7	110	66.3	12	0
Dissolved oxygen (mg/L)	0.11	0.61	0.27	18	0	0.1	0.81	0.35	12	0
Specific electrical conductance (µs/cm)	1520	3140	1670	18	0	1490	1630	1560	12	0

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

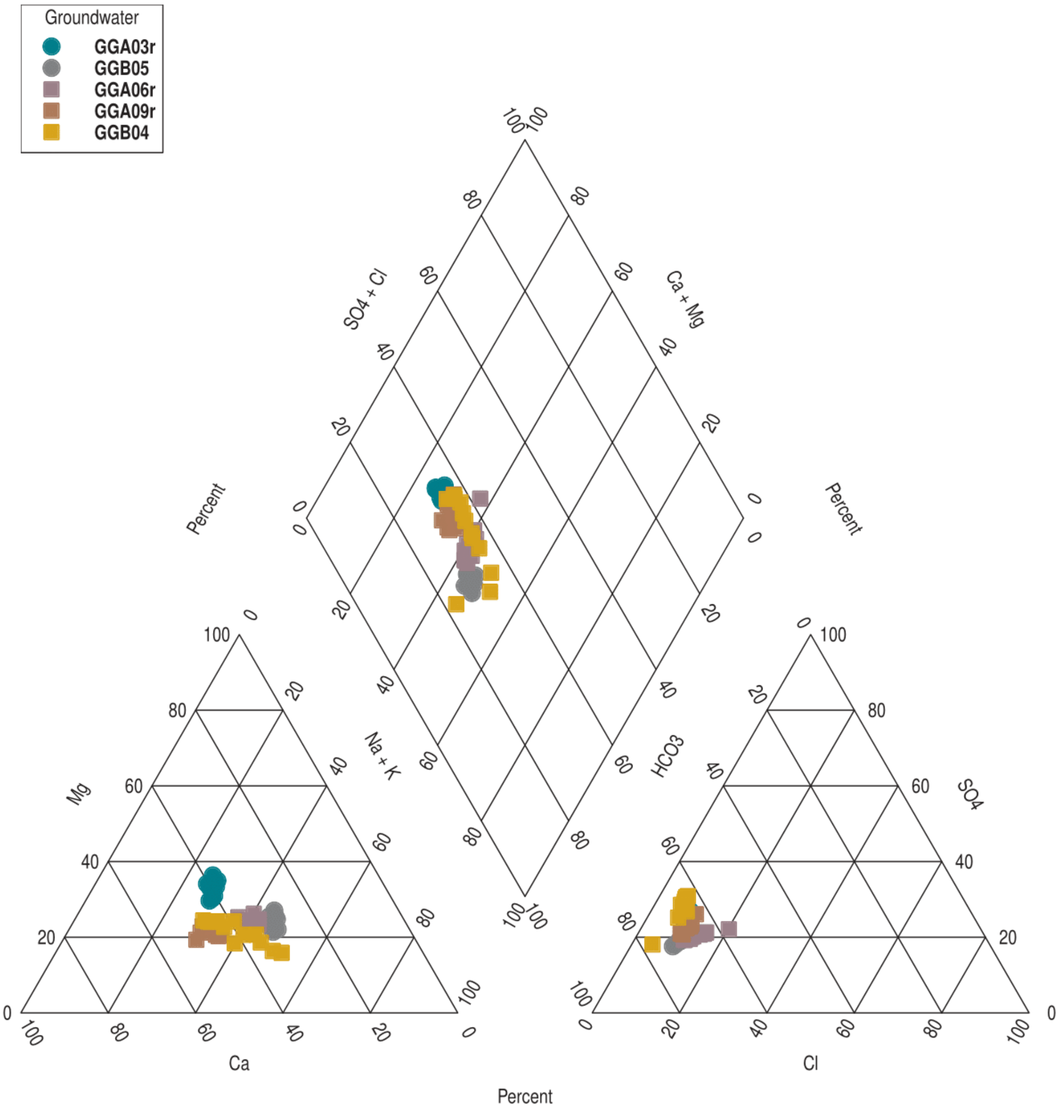

Figure 2 Piper plots for non- mine workings groundwaters. Squares represent bedrock boreholes and circles boreholes drilled into the superficial deposits.

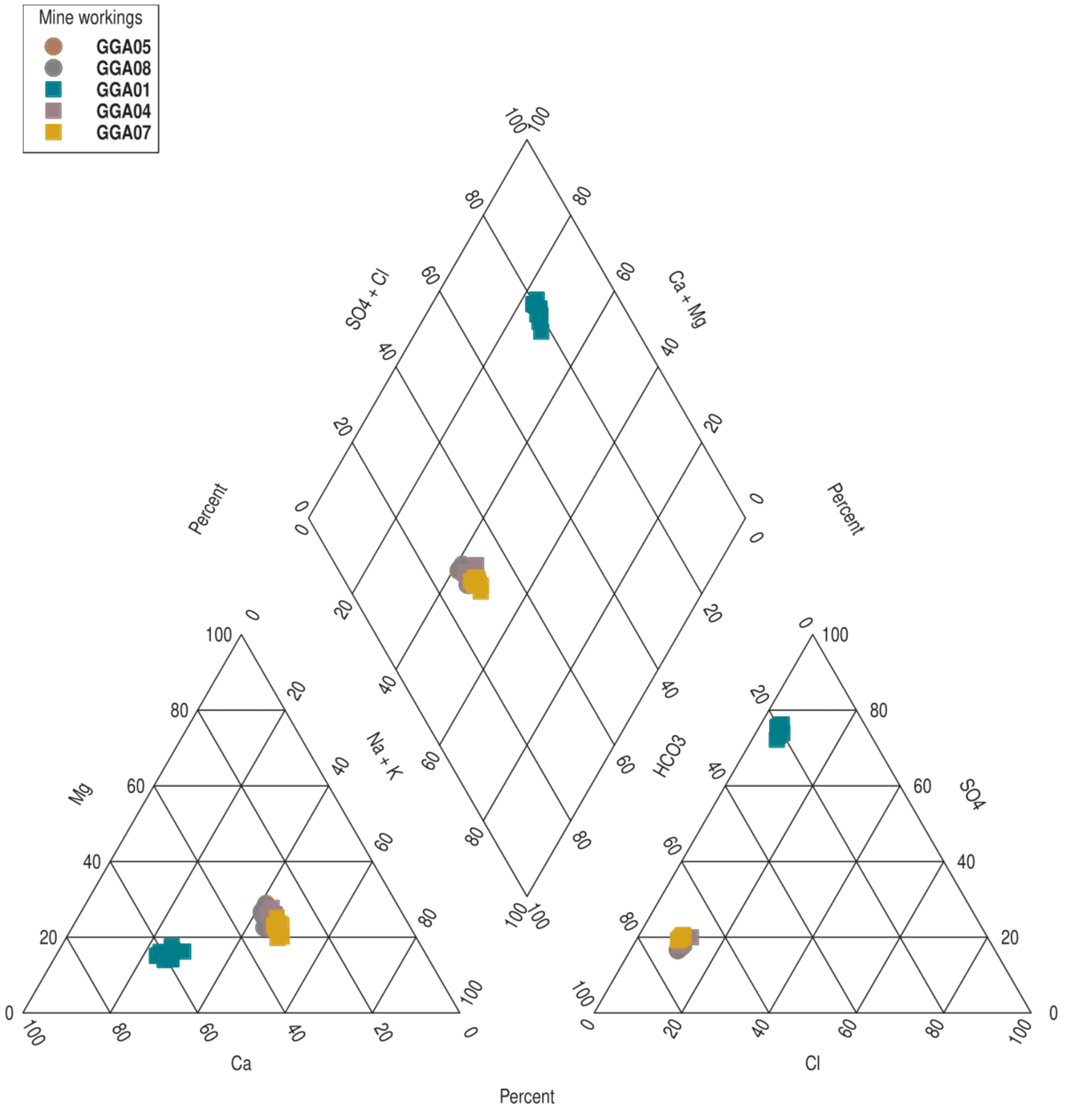

Figure 3 Piper plots for mine workings groundwaters. Squares represent boreholes drilled into Glasgow Upper mine workings and circles boreholes drilled into Glasgow Main mine workings.

4.1.2.2 MAJOR IONS

Minimum, maximum, and median values of the major ions in groundwater samples are presented in Table 3 (boreholes in bedrock and superficial deposits) and Table 4 (boreholes in mine workings). Except for groundwater from GGA01 (397 mg/L -467 mg/L), the range of Ca in the mine waters is narrow (104 mg/L - 117 mg/L). The box and whisper plot in Appendix 4 clearly show concentrations of Ca in superficial deposits and bedrock horizons are more variable between sites (105 mg/L – 164 mg/L), and tend to have higher concentrations (medians of 130 mg/L and 125 mg/L for the superficial deposits and bedrock groundwaters, respectively) than those in the mined horizons (medians of 112 mg/L and 108 mg/L for the Upper and Main mine workings, respectively). Borehole GGB05 in the bedrock horizon (median 106 mg/L) has Ca concentrations similar to those in the mine workings, while GGA03r, also in the bedrock, median (139 mg/L) has concentrations more like those in the superficial deposits. At all sites there is a trend of increasing Ca concentration over the monitoring period.

Concentrations of Mg are all within the range 40.3 mg/L to 79.9 mg/L. Concentrations within the superficial deposits tend to be at the lower end of this range (40.3 mg/L – 54.5 mg/L) compared to those measured in the other target horizons (49.9 mg/L – 79.9 mg/L).

Highest concentrations of Na are found in groundwaters at GGA01 (197 mg/l – 216 mg/L), with measured concentrations at all other sites in the range 102 mg/L – 204 mg/L. While maximum concentrations are similar for each target horizon (excluding GGA01), the lower concentrations are found in groundwaters in the superficial deposits and bedrock horizons, with minimum values of 102 mg/L and 105 mg/L, respectively.

The groundwaters in the bedrock have the largest range of K concentrations (range 9.67 mg/L 20.9 mg/L. With the exception of groundwaters from GGA01 (29.4 mg/L – 31.7 mg/L), all other measured concentrations in the Glasgow Observatory groundwaters are within this range. The K concentrations in the mine waters (excluding GGA01) are within a narrow range (17.7 mg/L – 20.3 mg/L), while each site within the unmined target horizons are distinct from each other, but as a group span a larger concentration range (see box and whisker plots in Appendix 4).

All groundwaters, except GGA01 (476 mg/L – 519 mg/L), have measured HCO_3 concentrations within the range 555 mg/L to 864 mg/L. The remaining mine waters tend to have concentrations at the upper end of this range (761 mg/L to 864 mg/L), while the unmined target horizons have a greater spread of concentrations (555 mg/L – 823 mg/L). At each individual site the ranges tend to be much smaller (e.g. GGB04 592 mg/L – 638 mg/L), with differences between sites causing large ranges in these target horizons (see box and whisker plots in Appendix 4).

The largest range of Cl concentrations is found in the groundwaters in the superficial deposits 33.8 mg/L – 113 mg/L). Groundwater concentrations measured from all other target units are within this range. The mine waters have a narrow range of Cl concentrations (59.6 mg/L to 70.5 mg/L), except for one outlier at GGA01 (91.6 mg/L).

Apart from groundwaters at GGA01 (1410 mg/L to 1510 mg/L) the SO_4 concentrations measured in groundwaters across the Glasgow Observatory range from 142 mg/L – 224 mg/L. The superficial deposits and bedrock have similar, large ranges (166 mg/L – 231 mg/L, and 168 mg/L – 224 mg/L for the groundwaters in superficial deposits and bedrock, respectively), while the mine waters (excluding GGA01) have a slightly narrower range of 142 mg/L to 191 mg/L. Sulphate concentrations measured in groundwaters at GGA01 show a relatively small, but steady, increase over the monitoring period.

The Piper plot water type classification shows that GGA01 has a distinctly different groundwater major ion chemistry compared to other sites across the Glasgow Observatory. In particular, the Ca and SO_4 concentrations are far in excess of those recorded in groundwaters from the other boreholes during this monitoring period, and are slowly, but steadily, increasing.

Where there are large ranges of major ion concentrations in target horizons, it is a result of differences between each boreholes' groundwater geochemistry within that target horizon, rather than large changes over time at each site. For example, the two boreholes in the bedrock horizon (GGA03r and GGB05) have different major ion groundwater chemistry to each other. The major ion groundwater chemistry of GGB05 is like that observed in the mine waters. Except for GGA01, the mined horizons tend to have a greater similarity between sites (across both Glasgow Main and Glasgow Upper workings) than the superficial deposits or bedrock horizons.

4.1.2.3 MINOR ELEMENTS/IONS

Minimum, maximum, and median values of the minor ions in groundwater samples are presented in Table 3 (boreholes in bedrock and superficial deposits) and Table 4 (boreholes in mine workings).

Phosphorus concentrations are generally low in the groundwaters across the Glasgow Observatory, with most values below or close to the detection limit (<0.01 mg/L). There is one outlier (0.13 mg/L) measured in groundwater at GGB04 in January 2022. Other than this, P was measured at concentrations of 0.04 mg/L or less across the Observatory.

Silicon measured in groundwaters across the Glasgow Observatory was highest at GGA01 (13.4 mg/L – 15.5 mg/L). Aside from this the largest range was observed in the superficial deposits (5.33 mg/L – 8.47 mg/L) and all other groundwater Si concentrations were measured within the range 5.11 mg/L – 6.44 mg/L.

The halogen elements (F and Br) have narrow concentration ranges across all the groundwaters in the Glasgow Observatory: Br concentrations are all within the range < 0.50 mg/L – 0.68 mg/L, while the F concentrations are within the range <0.25 mg/L – 0.32 mg/L.

Nitrate in groundwater at the Glasgow Observatory is mostly below detection limit except at GGA03r where five of the six measurements range between 0.51 mg/L and 1.56 mg/L.

Sulphide, which was analysed at three boreholes from the last data release as a pilot study, was measured at all sites during this latest phase of baseline monitoring. Concentrations were generally low across the Glasgow Observatory (<0.02 mg/L – 0.06 mg/L) except for three sites, spread across the target horizons. GGB04 in the superficial deposits had measured concentrations of <0.02 mg/L to 0.26 mg/L, GGA07 in the Glasgow Upper mine workings had measured concentrations of 0.12 mg/L to 0.35 mg/L, and GGA05 in the Glasgow Main mine workings had measured concentrations of 0.02 mg/L to 1.09 mg/L.

Table 3 Summary of the major ions and minor elements from groundwater samples retrieved from the Glasgow Observatory boreholes targeting the superficial deposits and bedrock during sampling between June 2021 and January 2022.

		Superficial deposits					**Bedrock**				
		Min	**Max**	**Median**	**n**	**n(c)**	**Min**	**Max**	**Median**	**n**	**n(c)**
Major ions (mg/L)											
Calcium	Ca	114	164	130	18	0	105	145	125	12	0
Magnesium	Mg	40.3	54.5	45.2	18	0	52.8	79.7	66	12	0
Sodium	Na	102	172	128	18	0	105	192	150	12	0
Potassium	K	10.6	20	13.5	18	0	9.7	20.9	14.8	12	0
Bicarbonate (field measured)	HCO_3	555	802	708	18	0	661	824	763	12	0
Chloride	Cl	33.8	113	63.6	18	0	50.6	70.6	61.1	12	0
Sulphate	SO_4	166	231	187	18	0	168	224	195	12	0
Total Alkalinity	HCO_3	585	822	711	18	0	720	843	782	12	0
Minor ions (mg/L)											
Phosphorus – total	P	0.01	0.13	0.02	18	0	<0.007	<0.005	<0.005	12	12
Sulphur – total	S	60.7	84.3	68.3	18	0	59.4	80.8	70.3	12	0
Silicon	Si	5.33	8.47	6.23	18	0	5.4	6.44	5.99	12	0
Bromide	Br	0.27	0.63	0.41	18	0	0.39	0.62	0.54	12	0
Fluoride	F	0.06	0.29	0.14	18	0	0.07	0.32	0.16	12	0
Nitrate	NO_3	<0.3	<0.3	<0.3	18	18	<0.3	1.56	<0.3	12	7
NPOC (mg/L)		3.58	5.46	4.39	18	0	1.05	2.96	2.32	12	0

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

Table 4 Summary of the major ions and minor elements from groundwater samples retrieved from the Glasgow Observatory boreholes targeting the mine workings during sampling between June 2021 and January 2022.

		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	104	467	112	18	0	107	115	109	12	0
Magnesium	Mg	49.9	79.2	56.9	18	0	53.5	63.1	56.6	12	0
Sodium	Na	170	216	196	18	0	165	175	170	12	0
Potassium	K	17.7	31.7	19.5	18	0	18.8	20.1	19.2	12	0
Bicarbonate (field measured)	HCO_3	476	864	787	18	0	761	803	784	12	0
Chloride	Cl	59.6	91.6	68.3	18	0	68.8	71	69.7	12	0
Sulphate	SO_4	157	1510	187	18	0	142	155	150	12	0
Total Alkalinity	HCO_3	387	850	803	18	0	801	828	809	12	0
Minor ions (mg/L)											
Phosphorus - total	P	<0.007	0.012	0.008	18	6	0.009	0.013	0.0105	12	0
Sulphur – total	S	57.3	501	68.5	18	0	52	58.3	54.6	12	0
Silicon	Si	5.22	15.5	6.15	18	0	5.11	5.52	5.22	12	0
Bromide	Br	<0.5	0.703	0.553	18	2	0.338	0.491	0.44	12	0
Fluoride	F	<0.25	0.289	0.19	18	3	0.166	0.264	0.192	12	0
Nitrate	NO_3	<0.3	<1.5	<0.3	18	18	<0.3	<0.3	<0.3	12	12
NPOC (mg/L)		2	23.5	2.4	16	0	2.13	3.37	2.54	12	0

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

4.1.3 Dissolved organic carbon

Minimum, maximum, and median values of dissolved organic carbon (as non-purgeable organic carbon - NPOC) in groundwater samples are presented in Table 3 and Table 4 with the major and minor ions. NPOC is mostly present in the Glasgow Observatory groundwaters in the range 1.05 mg/L to 5.46 mg/L, except for one outlier of 23.5 mg/L at GGA01. This was the only sample which required filtration prior to NPOC analysis on account of precipitation/flocculation within the sample. The median values in groundwaters from the bedrock, Glasgow Upper and Glasgow Main mine workings horizons are similar (2.32 mg/L, 2.43 mg/L and 2.54 mg/L respectively), while concentrations within the superficial deposits are generally at the higher end of the range (median 4.39 mg/L).

4.1.4 Trace elements

For a full list of all trace elements tested, refer to Appendix 2. Table 5 and Table 6 provide a summary of a selection of trace elements, consistent with those presented in the previous data release report (Bearcock et al., 2022). 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. In general, the lowest concentrations were found in groundwaters from the Glasgow Main mine workings, where the trace element compositions in samples from both boreholes were similar. In contrast, the highest trace element concentrations were found in the groundwaters from the Glasgow Upper mine workings and the superficial deposits. The trace element chemistry of the groundwaters from GGA01 was different to that of the other boreholes in the Glasgow Upper mine workings. The three boreholes sampled in the superficial deposits each had distinct trace element chemistries. These differences between boreholes gave the Glasgow Upper mine workings and the superficial deposits large ranges of trace element concentrations within each target horizon. A brief description is given below; data distributions are clearer on the box and whisper plots (Appendix 4).

As the Glasgow Observatory is based around mine waters Mn and Fe are discussed separately as they are common in mine waters in their reduced forms. The remaining trace elements are subsequently discussed, grouped by target horizons.

4.1.4.1 MANGANESE AND IRON

Concentrations of Mn and Fe are generally high across the Glasgow Observatory groundwaters, and while both are considered trace elements in natural waters, both are present in concentrations reported in mg/L.

Manganese is highest in the superficial deposits (1.57 mg/L – 7.25 mg/L), with the highest concentrations measured in samples from GGB04 (median: 6.72 mg/L). Mn concentrations in groundwater samples from this borehole are over 2.5 times those at GGA09r (median: 2.60 mg/L) and GGA06r (median: 2.04 mg/L). When combined with data from the previous monitoring period (September 2020 – May 2021) groundwater Mn concentrations at GGB04 are steadily increasing; Mn is c. 5mg/L at the start of the first monitoring period, and c. 7 mg/L by January 2022. The last four samples (August, October and November 2021 and January 2022) oscillate between 6.62 mg/L and 7.25 mg/L, which might indicate the concentrations are beginning to stabilise.

Groundwater samples from GGA01 have Mn concentrations of ~1 mg/L, which remained relatively constant during this monitoring period, however they were higher than the concentrations measured during the previous monitoring period (GGA01 median September 2020 to May 2021: 897 µg/L). Most of the increase in concentration occurred between April and June 2021(Bearcock et al., 2022).

All other groundwater samples from the bedrock and remaining mine workings horizons had Mn concentrations in the range 330 ug/L to 625 µg/L and remained fairly constant at each site.

There is a large range of total Fe concentrations across the Glasgow Observatory, a minimum concentration of 5 µg/L was recorded at GGA03r in the bedrock horizon and a maximum concentration of 47.8 mg/L was recorded at GGA01.

The median concentration of Fe at GGA01 (46.9 mg/L) was at least 11.3 times the median value at the other Glasgow Upper mine workings sites (GGA04 median: 4.13 mg/L; GGA07 median: 2.02 mg/L), and over 200 times the median value of the Glasgow Main mine workings sites (1.94 mg/L). During this monitoring period the GGA01 Fe groundwater concentrations increased from 42.7 mg/L to 47.8 mg/L, which continues the trend observed in the previous monitoring period where Fe concentrations were first measured at 32.5 mg/L in September 2020 (Bearcock et al., 2022).

In the superficial deposits horizon concentrations of Fe in groundwaters from GGB04 (median: 9.25 mg/L) were over 2.5 times those at GGA09r (median: 1.91 mg/L) and GGA06r (median: 921 µg/L). In the bedrock horizon, there was a notably large difference in Fe concentrations between the two boreholes. The median of 22.3 µg/L in the groundwaters at GGA03r, and the median value of groundwater samples at GGB05 is 200 times higher, at 4.48 mg/L. The concentration of Fe in groundwaters at GGB05 generally decreases over the monitoring period, continuing the trend from the previous monitoring period (Bearcock et al., 2022): the concentration in September 2020 was >5 mg/L, in January 2022 it was c. 4.4 mg/L.

As reduced Fe (Fe^{2+}) was a new analysis added into the monitoring suite in June 2021, there are no previous data to provide a comparison. It should be noted that Fe^{2+} and total Fe are analysed in two separate laboratories, with different sampling methodologies. The concentrations of Fe^{2+} commonly exceeded those of total Fe, which were likely caused by the Fe^{2+} sample being unfiltered and the bottle being pre-dosed with HCl, while the Fe total sample was filtered and acidified later. The oxidised iron should therefore not be calculated using the analyses of Fe total and Fe^{2+}.

The dominance of dissolved iron as Fe^{2+} is consistent with the redox conditions; also, given the circum-neutral pH of the groundwaters, the Fe would only be stable in solution if it was reduced. The distribution of Fe^{2+} therefore is the same as total dissolved Fe. Only the boreholes within the Glasgow Main workings had similar concentrations across both boreholes in this target horizon (medians: 2.02 mg/L and 2.01 mg/L for GGA05 and GGA08 respectively). In the superficial deposits, groundwaters at GGB04 (median: 8.42 mg/L) had Fe^{2+} concentrations four times higher than those at GGA09r (median: 2.1 mg/L) and eight times higher than those at GGA06r (median: 975 µg/L). In the bedrock groundwaters from GGB05 (median 4.55 mg/L) had Fe^{2+} concentrations over 50 times greater than those at GGA03r (median 85 µg/L). In the groundwaters from the Glasgow Upper horizon the greatest Fe^{2+} concentrations were found at GGA01 (median 47.4 mg/L), which were 11 times greater than those at GGA04 (median 4.15 mg/L) and 22 times greater than those at GGA07 (median 2.1 mg/L)

4.1.4.2 SUPERFICIAL DEPOSITS

In samples taken from GGB04 there are concentrations higher than those at GGA09r and GGA06r for Ba and Sr, and most transition metals especially Mn and Fe (discussed above) as well as Co, and Ni. Concentrations of Ba are about two times higher in GGB04 (median: 318 µg/L) than at GGA09r (median: 140 µg/L), and over four times as high as concentrations at GGA06r (median: 69.4 µg/L). Concentrations of Sr are similar at GGB04 (median: 959 µg/L) and GGA09r (median: 929 µg/L), and both are 1.5 times higher than concentrations at GGA06r (median: 570 µg/L). Concentrations of Co in groundwaters from GGB04 (median: 9.81 µg/L) are over four times those at GGA09r (median: 2.05 µg/L) and GGA06r (median: 2.36 µg/L). Concentrations of Ni in groundwaters from GGB04 (median: 35.5 µg/L) are ten times those at GGA09r (median: 3.54 µg/L) and 8.5 times GGA06r (median: 4.13 µg/L).

Monitoring from September 2020 to January 2022 (both the previous monitoring period and the period presented in this report) indicates that concentrations of Sr are slowly but steadily increasing, while concentrations of Ba, Co, and Ni seem to oscillate over time, suggesting natural variations.

4.1.4.3 BEDROCK

There are significant differences in the trace element chemistry of the two bedrock boreholes, where not only is there a large difference between the median concentrations, but there is no overlap of concentrations between sites (see Appendix 4). At GGB05 median groundwater concentrations of Rb, Li, B and As are 1.6 to 6 times higher than at GGA03r, while U, Sr, Mo, Mn, and Ba are 1.2 to 3 times higher in groundwaters at GGB03r than those at GGB05. Additionally, Sn concentrations are below the detection limit in groundwaters from GGB05, and concentrations measured in GGA03r groundwaters are around 10 times the detection limit.

4.1.4.4 GLASGOW UPPER MINE WORKINGS

Concentrations of trace elements across the groundwaters in the mine workings tended to be similar, except for GGA01. Most of the discussion in the following section is based on the differences of GGA01 groundwaters to the other groundwaters sampled from the other Upper mine workings boreholes.

The median concentration of As at GGA01 (11.9 µg/L) was at least 6.6 times the median value at the other Glasgow Upper mine workings sites (GGA04 median: 1.8 µg/L; GGA07 median: 0.2 µg/L). The concentrations of As at GGA01 were variable, but relatively constant throughout the reported monitoring period, following an increase (from 2.27 µg/L to 11.6 µg/L) between the pumping tests (January 2020) and last sample in the previous monitoring period (May 2021) (Bearcock et al., 2022). It therefore appears that the concentrations of As in the groundwaters at GGA01 have stabilised.

The median concentration of Co at GGA01 (8.7 µg/L) was at least 5.8 times the median value at the other Glasgow Upper mine workings sites (GGA04 median: 1.5 µg/L; GGA07 median: 0.3 µg/L). Like As, the Co concentrations at GGA01 increased from the pumping tests and throughout the previous monitoring period (from 2.01 µg/L to 9.09 µg/L (Bearcock et al., 2022)). In comparison the range of Co concentrations measured during the period covered in this report (7.7 µg/L to 9.06 µg/L) have stabilised.

The median concentration of Li at GGA01 (55.0 µg/L) was 1.8 times the median value at the other Glasgow Upper mine workings sites (both GGA04 and GGA07 medians: 30.5 µg/L). There was no obvious trend over the monitoring period.

The median concentration of Mo at GGA01 (7 µg/L) was at least 7.8 times the median value at the other Glasgow Upper mine workings sites (GGA04 median: 0.9 µg/L; GGA07 median: <0.2 µg/L). During the monitoring period the Mo concentrations at GGA01 remained relatively constant. However, they were slightly lower than the concentrations measured during the previous monitoring period (GGA01 median September 2020 to May 2021: 8 µg/L) (Bearcock et al., 2022). This suggests the groundwater Mo concentrations may have stabilised.

The median concentration of Ni at GGA01 (19.5 µg/L) was at least 5.9 times the median value at the other Glasgow Upper mine workings sites (GGA04 median: 3.3 µg/L; GGA07 median: 1.9 µg/L). During this monitoring period the Ni concentrations increased slightly from c. 19 µg/L to c. 20.5 µg/L. Although the concentrations measured during the current round continue the increasing trend observed during the last monitoring round, where Ni concentrations started at c.14 µg/L in September 2020 (Bearcock et al., 2022), the rate of increase appears to have slowed.

The median concentration of Rb at GGA01 (69.2 µg/L) was at least 1.7 times the median value at the other Glasgow Upper mine workings sites (GGA04 median: 39.6 µg/L; GGA07 median: 38.9 µg/L). During this monitoring period the Rb concentrations increased from 63.4 µg/L to 74.6 µg/L in November 2021, before decreasing to 65.3 µg/L in January 2022. Although the latest measurement represents a relatively large concentration drop, it is still representative of the data which tend to be quite noisy, and generally increase over the two monitoring periods.

The median concentration of Sr at GGA01 (3700 µg/L) was at least 1.5 times the median value at the other Glasgow Upper mine workings sites (GGA04 median: 1934 µg/L; GGA07 median: 2473 µg/L). During this monitoring period the Sr concentrations increased from c. 3570 µg/L to c.3900. µg/L, which continues the trend observed in the previous monitoring period where Sr concentrations were first measured at 3100 µg/L in September 2020 (Bearcock et al., 2022).

The median concentration of W at GGA01 (1 µg/L) was at least 10 times the median value at the other Glasgow Upper mine workings sites (GGA04 median: 0.1 µg/L; GGA07 median: <0.06 µg/L). The median concentration of U at GGA01 (1.5 µg/L) was at least 2.1 times the median value at the other Glasgow Upper mine workings sites (GGA04 median: 0.7 µg/L; GGA07 median: 0.3 µg/L). Both W and U had stable concentrations throughout the monitoring period, which were comparable to those observed during the previous monitoring period (Bearcock et al., 2022).

Barium is the only element to be much higher in the other Glasgow Upper mine workings groundwaters compared to those at GGA01. The median Ba concentrations are at least 1.4 times higher at GGA04 (median: 55.0 µg/L) and GGA07 (median: 50.9 µg/L) than at GGA01 (median: 35.2 µg/L).

Many of the chemical changes in GGA01 groundwater samples discussed above are small, they are however above the analytical error. The changes are close to the duplicate errors (see Appendix 1) so these trends must be treated with caution.

4.1.4.5 GLASGOW MAIN MINE WORKINGS

The trace element concentrations in the Glasgow Main workings (GGA04, and GGA07) were similar to each other, with no obvious trends in the data.

Table 5 Summary of trace elements recorded in groundwater samples sampled between June 2021 and January 2022. Data are from the superficial deposits and bedrock horizons 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**	66.5	323	140	18	0	37.1	64.4	50.9	12	0
Strontium	**Sr**	545	1090	923	18	0	1990	3900	2880	12	0
Manganese	**Mn**	1570	7250	2600	18	0	394	625	466	12	0
Total iron	**Fe**	752	9880	1910	18	0	5	4890	2230	12	0
Lithium	**Li**	<7	<7	<7	18	18	18	33	25	12	0
Boron	**B**	343	662	474	18	0	171	403	265	12	0
Aluminium	**Al**	1.6	7.1	2.7	18	0	<0.6	1.9	0.8	12	1
Titanium	**Ti**	<0.3	0.4	0.13	18	5	<0.3	0.25	<0.06	12	11
Vanadium	**V**	0.11	0.39	0.18	18	0	<0.02	0.08	0.035	12	1
Chromium	**Cr**	0.1	0.33	0.16	18	0	<0.04	0.15	0.05	12	6
Cobalt	**Co**	1.72	11.8	2.42	18	0	2.6	3.8	3.49	12	0
Nickel	**Ni**	2.83	39	4.13	18	0	4.38	5.92	5.17	12	0
Copper	**Cu**	<0.05	0.17	0.09	18	1	<0.05	0.28	0.115	12	5
Zinc	**Zn**	0.8	10.3	1.85	18	0	3	5.5	3.8	12	0
Gallium	**Ga**	<0.07	0.05	<0.04	18	17	<0.07	<0.04	<0.04	12	12
Arsenic	**As**	0.28	0.83	0.595	18	0	0.19	2.48	1.12	12	0
Selenium	**Se**	<0.07	0.1	<0.07	18	12	<0.07	<0.07	<0.07	12	12
Rubidium	**Rb**	5.63	11.2	7.28	18	0	18.7	47.3	31.4	12	0
Yttrium	**Y**	0.131	0.452	0.18	18	0	0.03	0.046	0.039	12	0
Zircon	**Zr**	0.065	0.319	0.116	18	0	0.027	0.054	0.043	12	0
Molybdenum	**Mo**	<0.2	0.9	0.55	18	2	0.4	1.3	0.75	12	0
Cadmium	**Cd**	<0.005	0.007	<0.005	18	13	<0.005	0.058	0.012	12	3
Tin	**Sn**	<0.08	3.15	<0.08	18	12	<0.08	1.23	0.505	12	6
Caesium	**Cs**	<0.04	0.08	0.05	18	6	0.17	0.24	0.21	12	0
Lanthanum	**La**	0.027	0.077	0.044	18	0	0.004	0.015	0.008	12	0
Cerium	**Ce**	0.048	0.149	0.078	18	0	0.009	0.034	0.015	12	0
Praseodymium	**Pr**	0.005	0.017	0.009	18	0	<0.003	0.004	<0.003	12	9
Neodymium	**Nd**	0.025	0.087	0.0465	18	0	<0.005	0.015	0.009	12	1
Samarium	**Sm**	<0.005	0.019	0.01	18	1	<0.005	0.005	<0.005	12	11
Gadolinium	**Gd**	0.009	0.022	0.014	18	0	<0.005	<0.005	<0.005	12	12
Dysprosium	**Dy**	0.01	0.05	0.018	18	0	<0.003	0.004	<0.003	12	9
Holmium	**Ho**	<0.003	0.024	0.005	18	2	<0.003	<0.003	<0.003	12	12
Erbium	**Er**	0.01	0.117	0.0145	18	0	<0.003	0.004	<0.003	12	11
Thulium	**Tm**	<0.003	0.03	<0.003	18	12	<0.003	<0.003	<0.003	12	12
Ytterbium	**Yb**	0.013	0.323	0.0185	18	0	<0.004	0.007	<0.004	12	9
Lutetium	**Lu**	<0.003	0.079	0.004	18	3	<0.003	<0.003	<0.003	12	12
Tungsten	**W**	<0.06	0.07	<0.06	18	15	<0.06	0.07	<0.06	12	9
Thallium	**Ti**	<0.02	0.04	0.02	18	7	<0.02	0.05	0.035	12	1
Uranium	**U**	0.517	2.25	1.18	18	0	0.428	0.716	0.549	12	0

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

Table 6 Summary of trace elements recorded in groundwater samples during sampling between June 2021 and January 2022. Data are 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**	34.5	55.9	50.9	18	0	48.6	51.6	50.9	12	0
Strontium	**Sr**	1860	3970	2470	18	0	1890	1990	1950	12	0
Manganese	**Mn**	345	1010	406	18	0	330	364	434	12	0
Total iron	**Fe**	1950	47800	4130	18	0	1350	2050	1940	12	0
Lithium	**Li**	28	60	31.5	18	0	29	32	30	12	0
Boron	**B**	350	466	401	18	0	357	419	392	12	0
Aluminium	**Al**	0.7	5.4	2.35	18	0	<0.6	2.2	0.95	12	1
Titanium	**Ti**	<0.3	0.5	0.285	18	3	<0.3	0.24	<0.06	12	10
Vanadium	**V**	<0.02	0.22	0.165	18	1	0.06	0.14	0.115	12	0
Chromium	**Cr**	0.07	0.27	0.09	18	0	0.12	0.17	0.13	12	0
Cobalt	**Co**	0.21	9.06	1.49	18	0	0.17	0.262	0.243	12	0
Nickel	**Ni**	1.8	20.6	3.28	18	0	1.74	1.91	1.82	12	0
Copper	**Cu**	<0.05	0.14	<0.05	18	12	<0.05	0.09	<0.05	12	8
Zinc	**Zn**	<0.2	3.7	1.1	18	1	<0.2	3	0.45	12	2
Gallium	**Ga**	<0.07	<0.04	<0.04	18	18	<0.07	<0.04	<0.04	12	12
Arsenic	**As**	0.15	12.8	1.81	18	0	0.08	0.13	0.105	12	0
Selenium	**Se**	<0.07	0.1	<0.07	18	15	<0.07	0.2	<0.07	12	10
Rubidium	**Rb**	36.1	74.6	41.7	18	0	36	41.9	38.7	12	0
Yttrium	**Y**	0.051	0.179	0.119	18	0	0.053	0.07	0.0685	12	0
Zircon	**Zr**	0.078	0.253	0.123	18	0	0.045	0.082	0.068	12	0
Molybdenum	**Mo**	<0.2	7.3	0.9	18	6	<0.2	<0.2	<0.2	12	12
Cadmium	**Cd**	<0.005	<0.005	<0.005	18	18	<0.005	<0.005	<0.005	12	12
Tin	**Sn**	<0.08	<0.08	<0.08	18	18	<0.08	<0.08	<0.08	12	12
Caesium	**Cs**	0.21	0.42	0.25	18	0	0.13	0.15	0.14	12	0
Lanthanum	**La**	0.009	0.103	0.0165	18	0	0.005	0.006	0.005	12	0
Cerium	**Ce**	0.019	0.161	0.031	18	0	0.009	0.016	0.011	12	0
Praseodymium	**Pr**	0.003	0.016	0.004	18	0	<0.003	<0.003	<0.003	12	12
Neodymium	**Nd**	0.013	0.066	0.0215	18	0	<0.005	0.012	0.009	12	1
Samarium	**Sm**	<0.005	0.016	0.007	18	6	<0.005	<0.005	<0.005	12	12
Gadolinium	**Gd**	<0.005	0.016	0.0095	18	2	<0.005	0.005	<0.005	12	10
Dysprosium	**Dy**	0.005	0.017	0.012	18	0	0.005	0.009	0.007	12	0
Holmium	**Ho**	<0.003	0.004	<0.003	18	13	<0.003	0.003	<0.003	12	11
Erbium	**Er**	0.003	0.011	0.009	18	0	0.006	0.009	0.008	12	0
Thulium	**Tm**	<0.003	<0.003	<0.003	18	18	<0.003	<0.003	<0.003	12	12
Ytterbium	**Yb**	0.005	0.013	0.01	18	0	0.009	0.016	0.012	12	0
Lutetium	**Lu**	<0.003	<0.003	<0.003	18	18	<0.003	0.003	<0.003	12	9
Tungsten	**W**	<0.06	1.13	0.09	18	6	<0.06	<0.06	<0.06	12	12
Thallium	**Ti**	<0.02	<0.02	<0.02	18	18	<0.02	<0.02	<0.02	12	12
Uranium	**U**	0.251	1.53	0.704	18	0	0.522	0.615	0.574	12	0

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

4.1.5 PAH, TPH and VOC

4.1.5.1 Superficial deposits

There were three polycyclic aromatic hydrocarbon (PAH) detects in the superficial deposits groundwaters, all within one sample from GGB04 during sampling round 21. Detected hydrocarbons were: Benzo(b)fluoranthene, Benzo(a)pyrene, and Benzo(ghi)perylene, and all were measured at concentrations close to the detection limit.

Table 7 summarises the total petroleum hydrocarbon (TPH) results, the majority of which were below the laboratory detection limit. Most detects were measured during round 24.

There were no VOCs detected in superficial deposits groundwaters during the monitoring period.

Table 7 Summary of TPH values min, max and mean values in superficial deposits groundwaters

	Min	Max	Median	n	n(c)
TPH (mg/L)					
TPH (C8-C10)	<0.004	0.013	<0.003	18	14
TPH (C10-C40)	<0.046	0.633	<0.042	18	14
TPH (C8-C40)	<0.05	0.645	<0.045	18	14

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

4.1.5.2 Bedrock

No PAH and no VOCs were detected in any of the bedrock groundwaters during the monitoring period.

During sampling round 21 TPH (C10-C40) and TPH (C8-C40) were detected in the groundwaters at GGA03r, while TPH (C8-C10) were detected in groundwater samples from both GGA03r and GGB05 collected during sampling rounds 23 and 24.

4.1.5.3 Glasgow Upper mine working

No PAH and no VOCs were detected in any of the Glasgow Upper mine working groundwaters during the monitoring period.

Table 8 summarises the total petroleum hydrocarbon (TPH) results, the majority of which were below the laboratory detection limit. Most detects were TPH (C8-C10) and detected in all sites during sampling round 24.

Table 8 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	0.016	<0.003	18	13
TPH (C10-C40)	<0.042	0.057	<0.042	18	17
TPH (C8-C40)	<0.045	0.073	<0.045	18	17

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

4.1.5.4 Glasgow Main mine working

No PAH and no VOCs were detected in any of the Glasgow Main mine working groundwaters during the monitoring period.

During sampling round 24 TPH (C8-C10) were detected in groundwater samples from both GGA05 and GGA08. Otherwise TPH were all below detection limits.

4.1.6 Stable isotopic composition

The δ^{2}H and δ^{18}O of all groundwater samples ranges from -51.9‰ to -48.8‰ (median -50.7‰ ±0.7‰) and from -7.55‰ to -7.18‰ (median -7.44‰, ±0.07‰), respectively, indicating a very stable groundwater isotope signature across all sites.

The very modest temporal and spatial variation across and within lithological units is shown in Table 9 and in Figure 4, where the groundwater samples cluster closely on the global meteoric water line (GMWL). A relative larger variability, although still modest, is observed in borehole GGB04 in the superficial deposits, consistent with previous monitoring (Bearcock et al., 2022).

The carbon isotopic composition δ^{13}C of dissolved inorganic carbon (DIC) in the groundwater samples ranges from -17‰ to -7.7‰ (median -11.2‰ ± 2‰). The isotopic signature of both Glasgow Upper and Glasgow Main mine workings groundwaters is very similar and constant (Table 9), plotting in Figure 5 around the median $\delta^{13}C_{DIC}$ value of -11‰ and high alkalinity (except for GGA01 samples characterised by a lower alkalinity, but similar δ^{13}C). Consistent with patterns observed in previous monitoring, GGA03r borehole in the bedrock and GGB04 borehole in the superficial deposits plot separately from the main group, to the left ($\delta^{13}C_{DIC}$ median in GGA03r -7.9‰ ±1.2‰) and to the right ($\delta^{13}C_{DIC}$ median in GGB04 -16.7‰ ±0.1‰) in Figure 5 respectively.

Table 9 $\delta^{13}C_{DIC}$, δ^{18}O and δ^{2}H min, max median, and SD values of groundwaters within each target horizon between June 2021 and January 2022.

Variable	Target horizon	Min	Max	Median	SD	n
$\delta^{13}C_{DIC}$ PDB ‰	Superficial deposits	-17.0	-10.9	-11.9	2.5	18
	Bedrock	-11.4	-7.7	-10.9	1.7	12
	Glasgow Main	-11.4	-10.6	-11.1	0.2	12
	Glasgow Upper	-11.8	-10.4	-11.2	0.3	18
δ^{18}O VSMOW2 ‰	Superficial deposits	-7.53	-7.27	-7.42	0.08	18
	Bedrock	-7.55	-7.39	-7.50	0.05	12
	Glasgow Main	-7.49	-7.18	-7.41	0.08	12
	Glasgow Upper	-7.54	-7.37	-7.45	0.05	18
δ^{2}H VSMOW2 ‰	Superficial deposits	-51.4	-48.8	-50.5	0.7	18
	Bedrock	-51.9	-49.0	-51.1	0.8	12
	Glasgow Main	-51.5	-49.8	-50.6	0.6	12
	Glasgow Upper	-51.4	-48.8	-50.8	0.7	18

n = number of samples

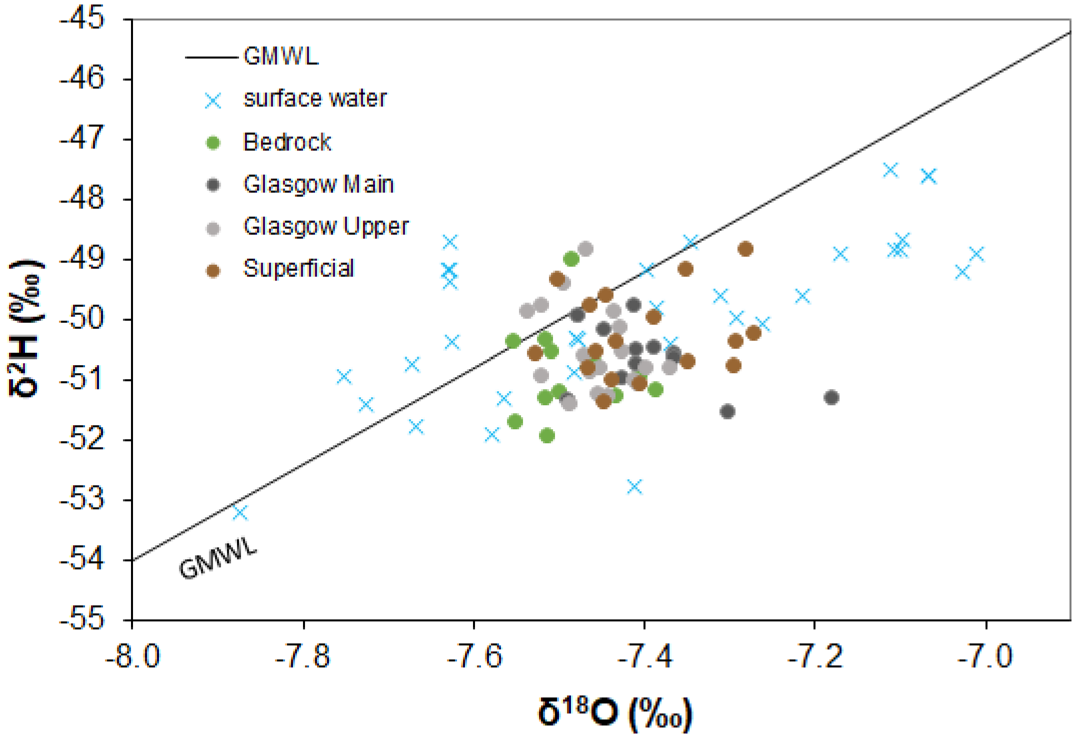

Figure 4 Plot of water δ^2H versus δ1^{8}O isotope data with reference to the global meteoric water line (GMWL) (Craig, 1961) in groundwaters grouped by lithological unit, against monthly surface water (cross symbols) for the same monitoring period.

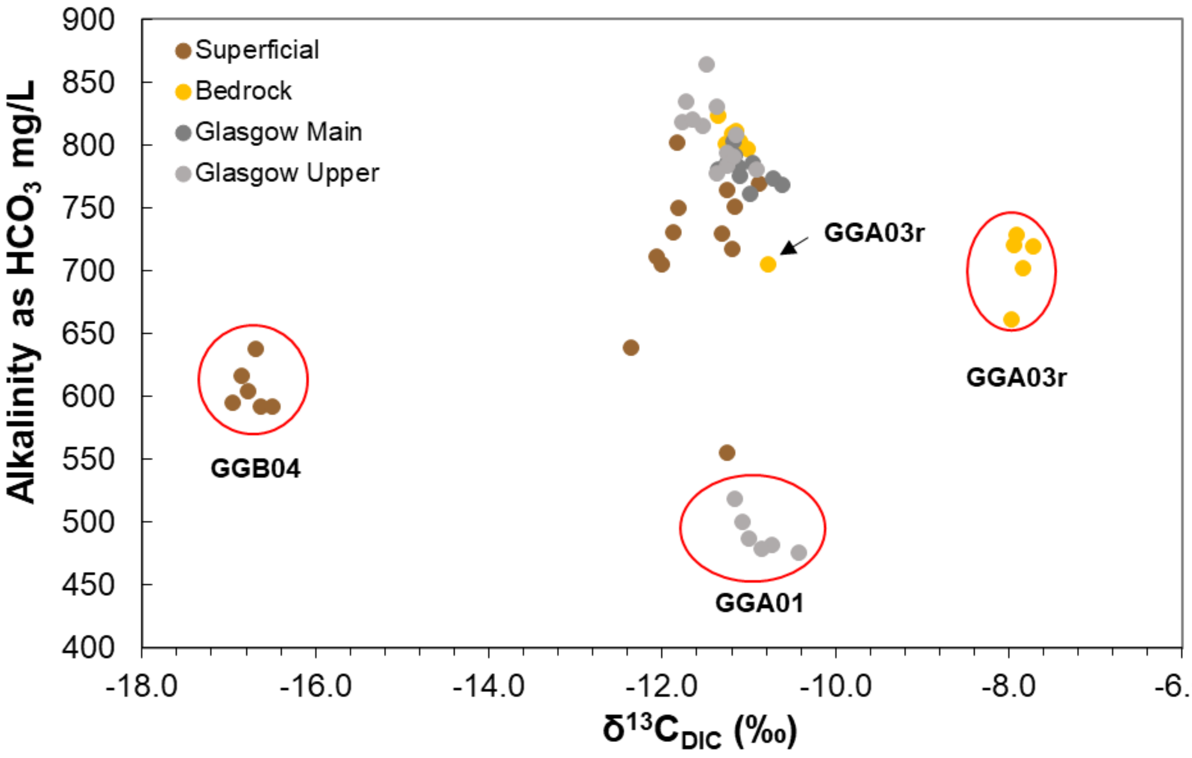

Figure 5 Plot of field-HCO_3 versus $\delta^{13}C_{DIC}$ isotope data in groundwaters from the Glasgow observatory.

4.1.7 Ammonium (NH_4)

Elevated ammonium concentrations were observed in all the Glasgow Observatory groundwaters. NH_4 concentrations above 1 mg/L are generally found in old, reducing groundwaters or as a result of pollution (Shand et al., 2007). There is a large range of NH_4 across the unmined target horizons (Table 10). This is due to two boreholes (GGB04 and GGA03r) having a much lower NH_4 groundwater concentration (combined median: 3.15 mg/L) than the remaining boreholes' groundwaters (combined median of all target horizons excluding GGB04 and GGA03r: 13.2 mg/L). With the exception of groundwaters from the superficial deposits the concentrations of NH_4 are >12 mg/L when the Eh is <150mV, and <4 mg/L when the Eh is >200 mV (Figure 6).

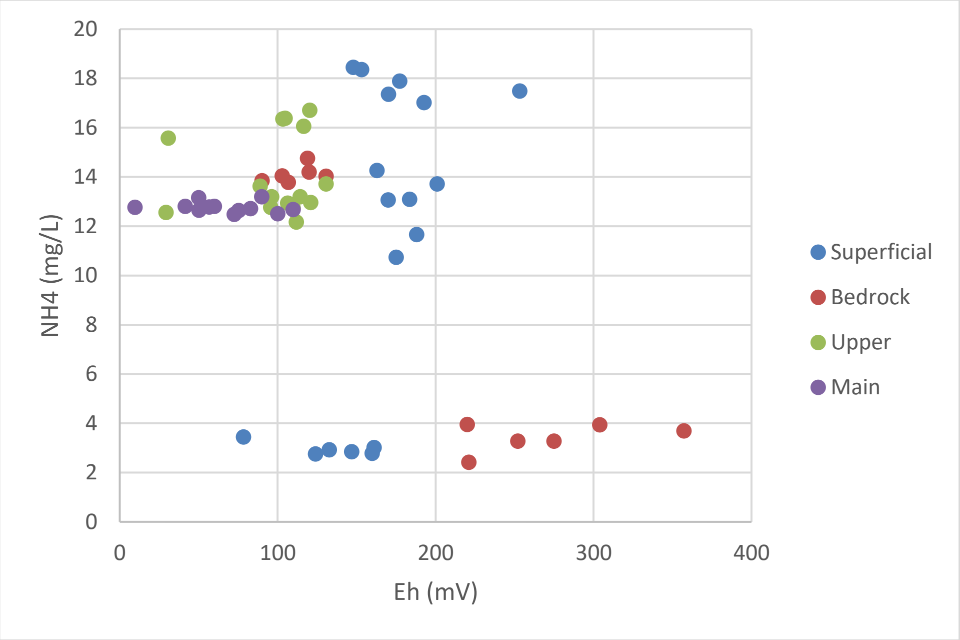

Figure 6 Relationship between NH_4 and Eh

Table 10 Summary of NH_4 data for Glasgow Observatory groundwaters.

NH_4 (mg/L)	Min	Max	Median	n	n(c)
Superficial deposits	2.76	18.5	13.1	18	0
Bedrock	2.42	14.8	8.87	12	0
Glasgow Upper mine workings	12.2	16.7	13.4	18	0
Glasgow Main mine workings	12.5	13.2	12.7	12	0

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

4.1.8 Dissolved gases

All radon analyses were below the detection limit (<10 Bq/L).

Dissolved methane (CH_4) is present generally at low concentrations with a median of 70 µg/L; however, the concentration distribution ranges widely between 0.3 µg/L and 710 µg/L. The range and median CH_4 values across the target horizons indicate that the superficial deposits have the lowest median CH_4 value of 17 µg/L, followed by the bedrock boreholes (64 µg/L), and Glasgow Main (145 µg/L), while Glasgow Upper has the highest CH_4 median value of 224 µg/L. The same pattern and similar concentrations were observed in the previous monitoring period (Bearcock et al., 2022).

The box plot of CH_4 data distribution across the different boreholes (Figure 7) shows the presence of three outliers for the Glasgow Upper borehole GGA01 (CH_4 710 µg/L), the superficial deposit borehole GGA06r (CH_4 270 µg/L), and the bedrock borehole GGA03r (CH_4 263 µg/L). From analysis of the time series, it is noticeable that those high peaks all correspond to samples taken during round 23 in August 2021 (Walker-Verkuil et al., 2023).

There is only one ethane (C_2H_6) measurement recorded above the laboratory detection limit of 1 ug/L from all the boreholes throughout the whole monitoring period. This was measured at GGA01 during round 23 in August 2021 (C_2H_6 5.2 µg/L), corresponding also to the CH_4 concentration outliers.

Dissolved carbon dioxide (CO_2) concentrations ranged between 5.5 mg/L and 219 mg/L, with a median of 141 mg/L, which was slightly higher than the median for the previous monitoring period (116 mg/L (Bearcock et al., 2022)). The median values for each target horizon are similar to each other. The lowest value (5.5 mg/L) is an outlier (the next lowest value is 80 mg/L), this value was measured in a sample from the superficial deposit borehole GGA09r sampled in July 2021 (Figure 7). This is the borehole with the largest temporal variability, as previously observed.

Table 11 Summary of Dissolved CH_4, C_2H_6 and CO_2 data in Glasgow Observatory groundwater sites.

Variable	Target horizon	Min	Max	Median	n	n(c)
Methane (CH_4) (µg/L)	Superficial deposits	0.7	270	16.6	18	0
	Bedrock	1.5	263	64.2	12	0
	Glasgow Upper	0.4	710	224	18	0
	Glasgow Main	0.3	215	145	12	0
Ethane (C_2H_6) (µg/L)	Superficial deposits	<1	<1	<1	18	18
	Bedrock	<1	<1	<1	12	12
	Glasgow Upper	<1	5.2	<1	18	17
	Glasgow Main	<1	<1	<1	12	12
Carbon Dioxide (CO_2) (mg/L)	Superficial deposits	5.5	219	155	18	0
	Bedrock	94.6	167	121	12	0
	Glasgow Upper	96.2	181	136	18	0
	Glasgow Main	110	145	132	12	0

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

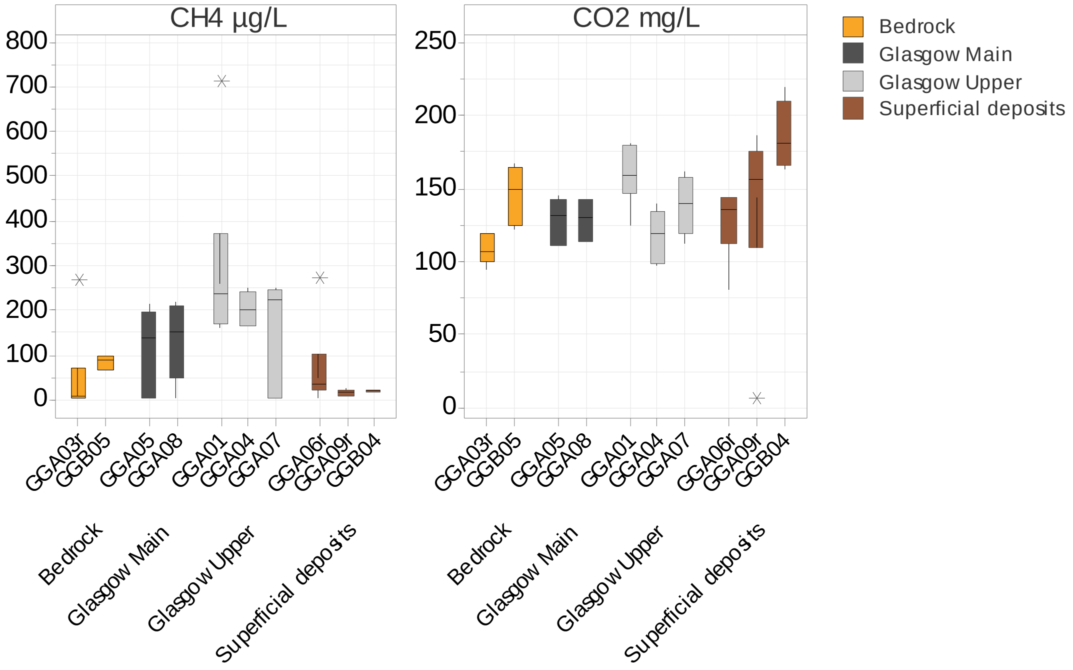

Figure 7 Distribution of dissolved methane and carbon dioxide in groundwater from boreholes grouped by target horizon

4.1.9 CFC and SF_6

Data for the sampling that took place in January 2022 for groundwater residence time indicators are shown in Table 12.

Samples GF26-11 and GF26-16 are duplicates and agree well with a mean value of 0.11±0.00 for CFC-12 and 0.24±0.09 for CFC-11. Data for SF_6 is below the detection limit which is reflected in both samples.

Concentrations vary from 0.09-0.29 (mean 0.16) pmol/L, 0.12-0.54 (mean 0.24) pmol/L and 0.0-0.02 fmol/L (mean 0.01) for CFC-12, CFC-11 and SF_6 respectively. This corresponds to modern fractions ranging from 0.03-0.11 (mean 0.06), 0.03-0.04 (mean 0.03) and 0.0-0.04 (mean 0.002) for CFC-12, CFC-11 and SF_6 respectively. Similarly, in terms of recharge year this ranges from 1955-1963 (mean 1958), 1954-1962 (mean 1959) and <1970 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 as previously observed.

Highest concentrations (youngest ages) are observed in the shallowest wells which have been constructed in the superficial deposits. There is little variation in groundwater ages between the sampling round in February 2021 although this round appears to show marginally older mean ages, for example 1958 compared with 1964 for CFC-12 and 1959 compared with 1961 for CFC-11. This suggests there have been few or no perturbations in the groundwater system over the past year.

Table 12 Groundwater residence time indicators sampling data from January 2022.

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
GF26-08	GGA05	0.16	0.28	0.01	0.06	0.06	0.00	1959	1961	<1970
GF26-09	GGA03r	0.29	0.54	0.02	0.11	0.12	0.00	1963	1954	<1970
GF26-10	GGA08	0.22	0.32	0.02	0.08	0.07	0.00	1961	1962	<1970
GF26-11	GGA04	0.11	0.32	0.01	0.04	0.07	0.00	1956	1962	<1970
GF26-12	GGA09r	0.20	0.17	0.01	0.07	0.04	0.00	1960	1958	<1970
GF26-13	GGA01	0.10	0.16	0.00	0.04	0.03	0.00	1956	1958	<1970
GF26-14	GGA06r	0.27	0.12	0.00	0.10	0.02	0.00	1963	1957	<1970
GF26-16	GGA04	0.11	0.15	0.00	0.04	0.03	0.00	1956	1958	<1970
GF26-17	GGA07	0.09	0.19	0.00	0.03	0.04	0.00	1955	1959	<1970
GF26-18	GGB05	0.09	0.16	0.00	0.03	0.03	0.00	1955	1958	<1970

4.1.10 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.

During this monitoring period samples were taken for the analysis of noble gases in round 26 (January 2022). The existence of results from two sampling rounds permits a comparison of excess air (EA) values for individual boreholes. Ideally these should be similar; where they differ significantly the higher EA value would be assumed to reflect an element of air contamination during sampling. The noble gas data taken in round 26 can therefore be compared to that taken during round 17 in February 2021 (reported in Bearcock et al. (2022)). There can be no comparison for GGA01 and GGB04, as there were no samples for these sites from round 26.

On this basis, the following results are suspect: Round 17 – GGA04, GGA05; Round 26 – GGA06r, GGA08, GGB05. In the case of GGA03r, both EA values are high, and it remains to be seen whether this is due to sampling difficulties during both rounds or some constant factor such as borehole construction. As the noble gases were only sampled once during each monitoring period more data may be required to understand better the cause of the high EA values. For the remaining apparently satisfactory samples, there appears to be a relationship with hydrogeological situation. Thus, concentrations for superficial deposits groundwaters lie within the ranges 3–6 cm^3STP/kg, while those for mine waters are in the range 5–10 cm^3STP/kg. The most reliable bedrock water (Round 17 GGB05) also lies within the mine water range. Given that both these water types come from the Middle Coal Measures, it implies that the EA differences between these and waters from the superficial deposits are porosity related.

Excluding GGA03r, GGA06r, GGA08 and GGB05 (see above), Round 26 derived recharge temperatures (NGTs) range from 9.7 to 11.2°C, averaging 10.4°C (Table 13). These can be compared with Round 17 waters (now excluding GGA03r, GGA04 and GGA05 on the basis of EA, see above) which give a range of 9.7 to 12.8°C with an average of 10.6°C (Table 13). With a typical NGT precision of ±1°C, the averages are indistinguishable from the Holocene mean annual air temperature in the general area.

With exclusions as above, Round 26 helium concentrations lying in the range $4.93–20.5 \times 10^{-8}$ cm^{3}STP/g are comparable to those from Round 1 ($8.98–23.5 \times 10^{-8}$ cm^{3}STP/g) and do not greatly exceed the atmospheric equilibrium value for water at 10°C of $\sim 4.7 \times 10^{-8}$ cm^{3}STP/g, suggesting that the sampled waters have not been in residence long enough to have acquired significant ^{4}He in the aquifer, whether directly from U-Th decay or by mixing with ‘old’ water enriched in ^{4}He.

Table 13 Noble gas sampling data from January 2022

Sample ID		**GF26-14**	**GF26-11**	**GF26-17**	**GF26-09**	**GF26-18**	**GF26-08**	**GF26-12**	**GF26-10**
Borehole		**GGA06r**	**GGA04**	**GGA07**	**GGA03r**	**GGB05**	**GGA05**	**GGA09r**	**GGA08**
Helium	cm^{3}STP/g	9.58E-08	2.05E-07	7.92E-08	4.24E-07	1.65E-07	2.05E-07	4.93E-08	2.06E-07
±		1.23E-08	1.76E-08	8.21E-09	3.62E-08	1.51E-08	1.77E-08	5.08E-09	1.77E-08
Neon	cm^{3}STP/g	3.96E-07	3.51E-07	3.32E-07	7.28E-07	3.42E-07	3.03E-07	2.59E-07	3.03E-07
±		1.16E-08	6.31E-09	6.01E-09	1.26E-08	6.17E-09	6.01E-09	4.83E-09	5.55E-09
Argon	cm^{3}STP/g	0.000394	0.000453	0.000453	0.000666	0.000454	0.000433	0.000417	0.000423
±		5.75E-06	6.60E-06	6.60E-06	9.68E-06	6.61E-06	8.61E-06	6.08E-06	6.18E-06
Krypton	cm^{3}STP/g	8.76E-08	9.82E-08	9.90E-08	1.25E-07	9.57E-08	9.64E-08	9.51E-08	8.49E-08
±		4.50E-09	5.00E-09	5.04E-09	6.37E-09	4.88E-09	4.91E-09	4.84E-09	4.36E-09
Xenon	cm^{3}STP/g	1.34E-08	1.36E-08	1.36E-08	1.68E-08	1.35E-08	1.34E-08	1.42E-08	1.36E-08
±		1.09E-09	1.10E-09	1.10E-09	1.37E-09	1.09E-09	1.09E-09	1.15E-09	1.10E-09
NG temp	ºC	21.95	11.15	10.38	8.76	11.64	10.55	9.69	13.68
±		0.20	0.22	0.11	0.05	0.23	0.12	0.19	0.10
Excess air	cm^{3}STP/kg	11.01	8.29	8.31	28.82	10.81	5.62	3.11	11.13
±		0.19	0.20	0.27	0.34	0.23	0.11	0.16	0.24

4.1.11 Saturation index

Mineral saturation indices were calculated using PHREEQC (Parkhurst and Appelo, 1999) and the thermodynamic database phreeqc.dat, and based on the corrected field-measured redox values (Eh) (Table 14). Most groundwaters are supersaturated with respect to calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$, siderite ($FeCO_3$), and 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 supersaturated 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 ($CaSO_4.2H_2O$). Groundwater in GGA01 in the Glasgow Upper mine workings is close to saturation with respect to gypsum (SI -0.1).

Carbon dioxide partial pressure (P_{CO2}), computed from the result of water analysis using PHREEQC, with median values of $10^{-1.3}$ to $10^{-1.2}$ are significantly higher than atmospheric values around $10^{-3.4}$, suggesting a local system not in equilibrium with air, as in confined aquifers.

Table 14 Mineral saturation indices (SI) and carbon dioxide equilibrium partial pressures (*P* CO2(g)) for the groundwater grouped by target horizon during the monitoring period.

MINERAL	Target horizon	Mean	Min	Median	Max
SI Calcite	Bedrock	0.3	0.0	0.2	0.6
	Glasgow Main mine working	0.3	0.1	0.2	0.5
	Glasgow Upper mine working	0.2	0.0	0.2	0.4
	Superficial deposits	0.1	-0.3	0.2	0.4
SI Dolomite	Bedrock	0.5	0.0	0.5	1.1
	Glasgow Main mine working	0.5	0.2	0.5	1.0
	Glasgow Upper mine working	0.3	-0.5	0.4	0.8
	Superficial deposits	0.0	-0.8	0.1	0.5
SI Siderite	Bedrock	-0.4	-2.8	-0.2	1.0
	Glasgow Main mine working	0.5	0.4	0.5	0.8
	Glasgow Upper mine working	0.9	0.5	0.8	1.5
	Superficial deposits	0.4	-0.1	0.4	1.0
SI Rhodochrosite	Bedrock	0.2	-0.1	0.1	0.4
	Glasgow Main mine working	0.1	-0.1	0.0	0.3
	Glasgow Upper mine working	0.1	-0.2	0.1	0.2
	Superficial deposits	0.8	0.5	0.8	1.2
SI Gibbsite	Bedrock	0.4	0.1	0.4	0.6
	Glasgow Main mine working	0.5	0.0	0.5	0.9
	Glasgow Upper mine working	0.9	0.3	0.9	1.3
	Superficial deposits	1.1	0.9	1.0	1.4
SI Fe(OH)3(a)	Bedrock	0.6	0.0	0.4	2.0
	Glasgow Main mine working	-0.6	-1.5	-0.7	0.2
	Glasgow Upper mine working	0.2	-0.8	0.2	1.3
	Superficial deposits	0.7	-0.2	0.6	2.3
SI Goethite	Bedrock	6.0	5.4	5.8	7.5
	Glasgow Main mine working	4.8	3.9	4.7	5.6
	Glasgow Upper mine working	5.6	4.6	5.6	6.7
	Superficial deposits	6.1	5.2	6.1	7.6
SI Barite	Bedrock	0.1	0.0	0.1	0.2
	Glasgow Main mine working	0.0	0.0	0.0	0.1
	Glasgow Upper mine working	0.2	0.1	0.1	0.5
	Superficial deposits	0.6	0.2	0.6	1.0
SI Gypsum	Bedrock	-1.3	-1.4	-1.3	-1.2
	Glasgow Main mine working	-1.4	-1.5	-1.4	-1.4
	Glasgow Upper mine working	-1.0	-1.4	-1.3	-0.1
	Superficial deposits	-1.2	-1.4	-1.2	-1.1

MINERAL	Target horizon	Mean	Min	Median	Max
SI Jarosite-K	Bedrock	-6.3	-8.2	-6.8	-2.7
	Glasgow Main mine working	-10.1	-12.9	-10.1	-7.9
	Glasgow Upper mine working	-6.5	-11.0	-7.4	-2.0
	Superficial deposits	-5.4	-8.3	-5.5	-1.3
SI Quartz	Bedrock	0.2	0.1	0.2	0.2
	Glasgow Main mine working	0.1	0.1	0.1	0.1
	Glasgow Upper mine working	0.3	0.1	0.2	0.6
	Superficial deposits	0.2	0.1	0.2	0.3
SI SiO2(a)	Bedrock	-1.2	-1.2	-1.2	-1.1
	Glasgow Main mine working	-1.2	-1.3	-1.2	-1.2
	Glasgow Upper mine working	-1.1	-1.2	-1.2	-0.8
	Superficial deposits	-1.1	-1.2	-1.2	-1.0
P CO2(g)	Bedrock	$10^{-1.4}$	$10^{-1.7}$	$10^{-1.3}$	$10^{-1.1}$
	Glasgow Main mine working	$10^{-1.4}$	$10^{-1.6}$	$10^{-1.3}$	$10^{-1.2}$
	Glasgow Upper mine working	$10^{-1.3}$	$10^{-1.5}$	$10^{-1.3}$	$10^{-1.2}$
	Superficial deposits	$10^{-1.2}$	$10^{-1.5}$	$10^{-1.2}$	$10^{-0.9}$

4.2 SURFACE WATER

Fordyce et al. (2021) identified that the Tollcross Burn and the River Clyde have 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 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. They therefore separated discussion of the Tollcross Burn site 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. 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.

4.2.1 Physico-chemical parameters of surface water samples

Table 15 summarises the physico-chemical parameters measured during water monitoring at the Glasgow Observatory surface-water sites between June 2021 and January 2022.

While both water bodies have a near-neutral to alkaline pH (Clyde median 7.7, Tollcross median 8.3) and show a narrow range in pH values, the pH values measured at the Tollcross Burn tend to be higher: 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 in summer months. The dissolved oxygen values follow the inverse trend, with highest values in the winter months and dissolved oxygen concentrations decreasing as water temperature increases, in line with solubility constraints. In the warmer months there was a larger spread of dissolved oxygen concentrations between sampling sites.

The Eh measurements range from 330 mV to 538 mV. 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=6) than the River Clyde (n=27) during this monitoring period.

The SEC values 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).

All physico-chemical parameters show a similar range to that reported in the previous data releases (Bearcock et al., 2022; Fordyce et al., 2021), with the exception of temperature, which reflects the different sampling months of this data release.

Table 15 Physico-chemical parameters for Glasgow Observatory surface water sites between June 2021 and January 2022.

	River Clyde					Tollcross Burn				
Field parameters	**Min**	**Max**	**Median**	**n**	**n(c)**	**Min**	**Max**	**Median**	**n**	**n(c)**
pH	7.3	8.1	7.7	27	0	7.8	8.7	8.3	6	0
Temperature (°C)	6.4	22.1	11.6	27	0	7.3	16.3	12.4	6	0
Eh (mV)	330	538	427	27	0	392	465	441	6	0
Dissolved oxygen (mg/L)	4.64	11.6	9.9	27	0	8.59	11.3	9.65	6	0
Specific electrical conductance (µs/cm)	160	546	372	27	0	824	976	872	6	0
Field bicarbonate HCO_3 (mg/L)	52.5	172	99.2	27	0	324	417	384	6	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 8) 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 generally Ca-HCO_3 type with some mixing towards no dominant type. The samples taken from the Tollcross Burn can be distinguished from the River Clyde samples on account of having the combination of some of the greatest proportions of HCO_3 and a higher proportion of Mn.

4.2.2.2 MAJOR IONS

Minimum, maximum and median values of the major ions in surface water samples are presented in Table 16. 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 different as the major ions are clearly split into two populations.

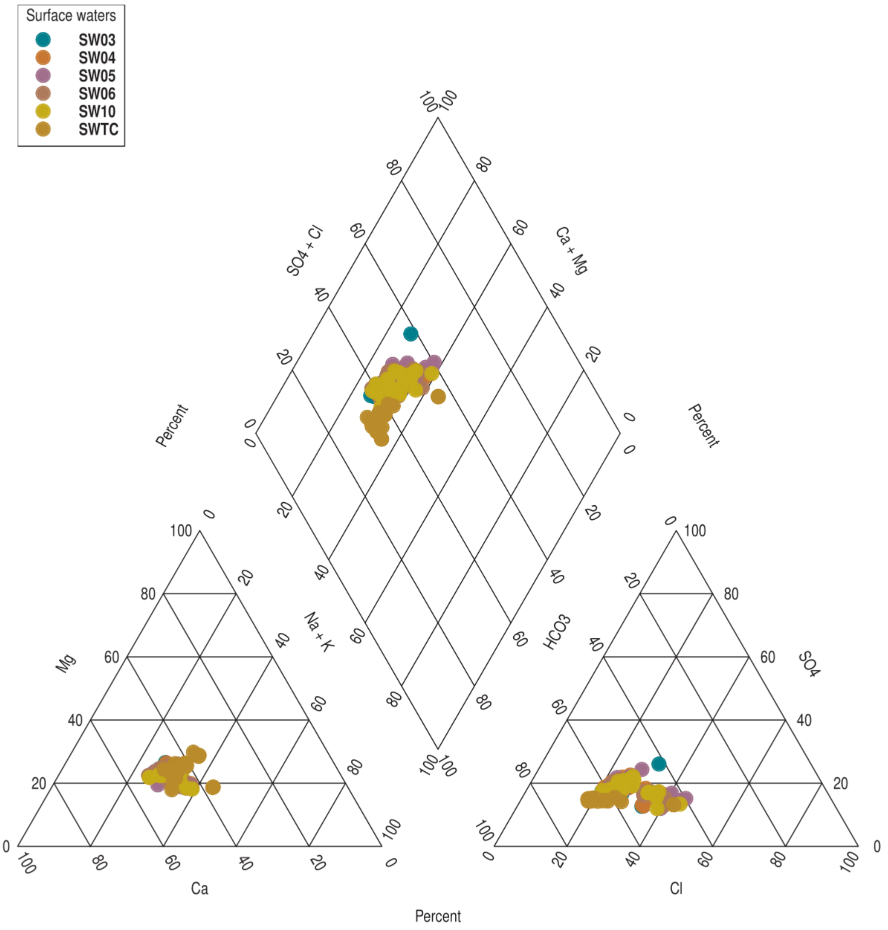

Figure 8 Piper plot for surface waters.

4.2.2.3 MINOR ELEMENTS

Minimum, maximum, and median values of the minor elements in surface water samples are presented in Table 16. The Tollcross Burn has higher concentrations of Si, Br, F than those measured in the River Clyde. However, nitrogen and phosphorus, and NPOC (the nutrient species) concentrations 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. These observations are consistent with the previous monitoring period (Bearcock et al., 2022).

Table 16 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	14.8	45.8	32.1	27	0	72.9	79.7	75.4	6	0
Magnesium	Mg	4.12	15.6	9.56	27	0	25.8	37.1	30.9	6	0
Sodium	Na	9.9	41	23.2	27	0	60.4	83.4	72.1	6	0
Potassium	K	1.8	7.08	3.56	27	0	10.3	14.3	12	6	0
Bicarbonate (field measured)	HCO_3	0	6.27	1.7	27	0	324	417	384	6	0
Chloride	Cl	13.3	47.7	30.1	27	0	58.5	70.4	62.9	6	0
Sulphate	SO_4	13.7	48.5	30.9	27	0	58.3	72.5	68.2	6	0
Total Alkalinity	HCO_3	45.7	182	106	27	0	336	428	398	6	0
Minor ions (mg/L)											
Phosphorus - total	P	0.038	0.352	0.128	27	0	0.028	0.074	0.0555	6	0
Sulphur – total	S	5.14	18.2	11.3	27	0	21.6	27.1	24.3	6	0
Silicon	Si	1.15	4.2	6.8	27	0	3.79	6.07	4.58	6	0
Bromide	Br	0.0171	0.109	0.0413	27	0	0.132	0.218	0.184	6	0
Fluoride	F	0.0397	0.0949	0.0681	27	0	0.149	0.210	0.185	6	0
Nitrite	NO_2	0.0185	1.45	0.135	27	0	<0.01	0.0475	0.0281	6	1
Nitrate	NO_3	5.06	15.5	10.4	27	0	5.66	6.87	6.09	6	0
NPOC (mg/L)		3.81	17.3	5.66	27	0	2.52	4.65	2.64	6	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 17 provides a summary of those trace elements consistent with those presented in the previous data release report (Bearcock et al., 2022). Appendix 3 shows time series plots for a selection of trace elements, and elements of interest are discussed below.

About half the trace elements in Table 17 are present in higher concentrations in the River Clyde than in the Tollcross Burn. Of the remainder Sr, Li, B, Rb and U, are higher in the Tollcross Burn; while Co, V, Ni, Cu, Zn, As, Mo, Cd, Sn, Sb, and Cs 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. An exception to this is the Cr concentration at site SW10. This is opposite a former chemical processing works, known to produce chromite ore processing residue (COPR), and hence provides an input of Cr to the River Clyde.

Table 17 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	52.9	141	90.6	27	0	53.1	68.6	60.9	6	0
Strontium	Sr	80.2	312	189	27	0	1010	1380	1170	6	0
Manganese	Mn	28.7	230	51.8	27	0	18.4	43.4	30.7	6	0
Total iron	Fe	24.9	430	290	27	0	12	22.9	17.4	6	0
Lithium	Li	<7	<7	<7	22	22	12	16	13	6	0
Boron	B	<53	<53	<53	22	22	100	150	126	6	0
Aluminium	Al	6.9	106	27.3	27	0	7.2	11.4	8.45	6	0
Titanium	Ti	<0.06	2.8	0.55	26	2	<0.06	0.08	<0.06	6	5
Vanadium	V	0.33	0.87	0.56	27	0	0.33	0.63	0.505	6	0
Chromium	Cr	0.11	7.81	0.37	27	0	0.12	0.15	0.125	6	0
Cobalt	Co	0.155	0.363	0.212	27	0	0.142	0.276	0.204	6	0
Nickel	Ni	1.26	1.88	1.54	27	0	1.16	1.59	1.22	6	0
Copper	Cu	0.85	2.07	1.11	27	0	0.89	2.24	1.24	6	0
Zinc	Zn	2.5	22.7	4.2	27	0	4.3	8	6.45	6	0
Arsenic	As	0.28	0.68	0.44	27	0	0.29	0.42	0.39	6	0
Selenium	Se	0.1	0.21	0.14	27	0	0.12	0.58	0.215	6	0
Rubidium	Rb	1.81	7.27	3.66	27	0	14.7	21.2	17.9	6	0
Yttrium	Y	0.009	0.322	0.084	27	0	0.019	0.042	0.027	6	0
Zircon	Zr	0.013	0.248	0.07	27	0	0.025	0.044	0.0365	6	0
Molybdenum	Mo	0.2	1.1	0.5	27	0	0.5	1.0	0.65	6	0
Cadmium	Cd	<0.005	0.018	0.008	27	1	<0.005	0.02	0.012	6	1
Tin	Sn	<0.08	<0.08	<0.08	22	22	<0.08	<0.08	<0.08	6	6
Antimony	Sb	0.11	0.5	0.19	27	0	0.16	0.54	0.19	6	0
Caesium	Cs	<0.04	0.14	0.06	25	8	<0.04	0.06	0.05	6	1
Lanthanum	La	<0.003	0.243	0.0515	26	1	<0.003	0.006	0.0027	6	3
Cerium	Ce	<0.004	0.441	0.073	27	2	<0.004	0.006	0.0035	6	3
Neodymium	Nd	<0.005	0.329	0.07	27	4	<0.005	0.009	0.0065	6	1
Europium	Eu	<0.003	0.017	0.004	24	8	<0.003	<0.003	<0.003	6	6
Gadolinium	Gd	0.012	0.079	0.023	27	0	<0.005	<0.005	<0.005	6	6
Dysprosium	Dy	<0.003	0.054	0.0155	24	4	<0.003	0.004	0.0022	6	3
Erbium	Er	<0.003	0.031	0.0085	24	4	<0.003	0.006	0.0027	6	3
Ytterbium	Yb	<0.004	0.026	0.009	25	5	<0.004	0.008	<0.004	6	4
Lead	Pb	0.05	1.42	0.37	27	0	0.03	0.25	0.04	6	0
Uranium	U	0.082	0.224	0.148	27	0	0.346	0.463	0.364	6	0

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

4.2.4 PAH and TPH

Many samples analysed for PAHs and TPHs were below the detection limit. Table 18 summarises the detected PAH and TPH results. The most prevalent PAH is benzo(a)pyrene, which is measurable in most samples in both rivers at similar concentrations.

Table 18 Summary of min and max concentrations of organic parameters recorded in the samples retrieved from the River Clyde and Tollcross Burn between June 2021 and January 2022.

	River Clyde					**Tollcross Burn**				
	Min	**Max**	**Median**	**n**	**n(c)**	**Min**	**Max**	**Median**	**n**	**n(c)**
PAH (ug/L)										
Benzo(b)fluoranthene	<0.0036	0.0094	<0.0036	27	19	<0.0036	0.0131	<0.0036	6	4
Benzo(k)fluoranthene	<0.003	<0.003	<0.003	27	27	<0.003	0.0037	<0.003	6	5
Benzo(a)pyrene	<0.0016	0.0069	0.002	27	9	<0.0016	0.0089	0.0024	6	1
Benzo(ghi)perylene	<0.0036	0.0039	-0.0036	27	23	<0.0036	0.0049	<0.0036	6	4
Indeno(1,2,3-cd)pyrene	<0.0049	0.0118	<0.0049	27	17	<0.0049	0.0195	<0.0049	6	4
PAH-Total	<0.0151	0.0194	<0.0151	27	24	<0.0151	0.0411	<0.0151	6	4
TPH (mg/L)										
TPH (C8-C10)	<0.004	0.012	<0.03	26	20	<0.003	0.016	<0.003	6	4
TPH (C10-C40)	<0.053	0.108	<0.042	26	19	<0.042	0.555	<0.042	6	5
TPH (C8-C40)	<0.057	0.108	<0.045	26	19	<0.045	0.555	<0.045	6	5

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

4.2.5 Stable 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 –53.2‰ to –47.5‰, median –49.6‰, and from δ^{18}O –7.87‰ to –7.01‰, median –7.40‰ (Table 19,

Figure 9). The median values for this monitoring period are similar to the previous monitoring period (Bearcock et al. 2022).

Table 19 $\delta^{13}C_{DIC}$, δ^{18}O and δ^{2}H min, max, median and SD values of surface water samples during the monitoring period.

Variable		Min	Max	Median	SD	n
$\delta^{13}C_{DIC}$ PDB ‰	Surface water	-14.1	-9.6	-11.0	1	31
δ^{18}O VSMOW2 ‰	Surface water	-7.87	-7.01	-7.40	0.25	33
δ^{2}H VSMOW2 ‰	Surface water	-53.2	-47.5	-49.6	1.4	33

n = number of samples

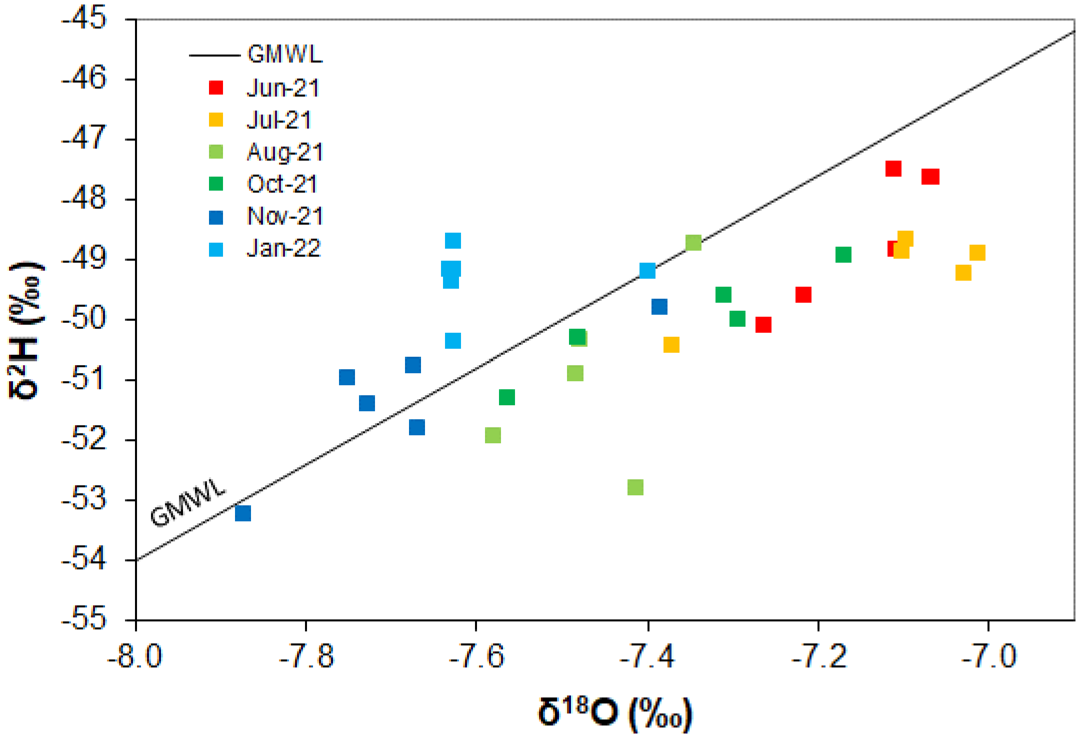

Figure 9: $\delta^{18}O$ VSMOW2 (‰) and $\delta^{2}H$ VSMOW2 (‰) in surface water samples of the River Clyde and the Tollcross Burn during the monitoring period Jun-21 to Jan-22 plotted against the GMWL.

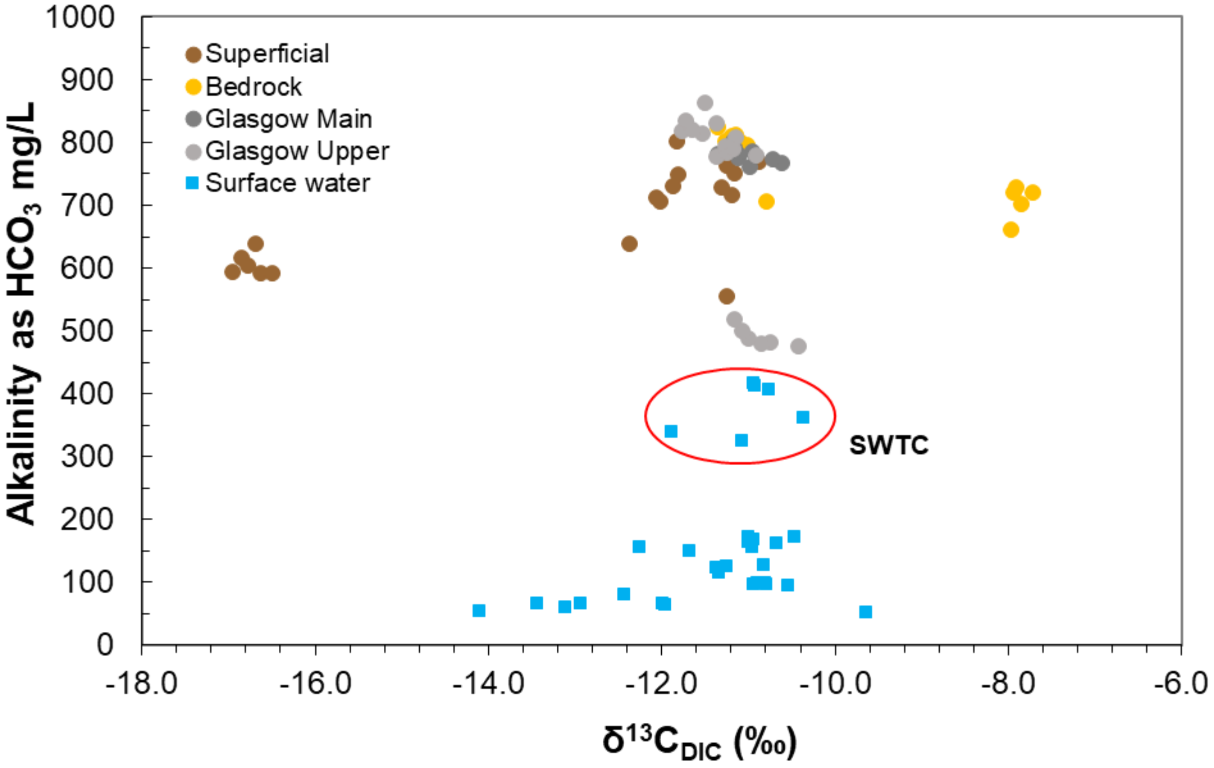

Figure 10 Plot of field-measured HCO_3 versus $\delta^{13}C_{DIC}$ isotope data in surface waters compared with the groundwater samples from the Glasgow observatory. SWTC = Tollcross Burn.

5 Discussion

5.1 CLUSTER ANALYSIS

Cluster analysis was performed using the Ward linkage method, as described in Section 3.2. The cluster analysis shows that the superficial deposits, the bedrock, and the mine workings (Figure 11) are clustered into statistically distinct groups, with some notable exceptions. The groundwaters from the bedrock borehole GGB05 are clustered with the mine workings, largely on account of a similar major ion chemistry. The groundwater from GGA01, in the Glasgow Upper mine workings is grouped separately as a result of its distinct major ion and trace element chemistry, discussed in Sections 4.1.2 and 4.1.4. The groundwaters from GGB04 in the superficial deposits are grouped with the other groundwaters from the superficial deposits but form a separate cluster within this grouping on account of their dissimilar trace element chemistry (see Section 4.1.4.2).

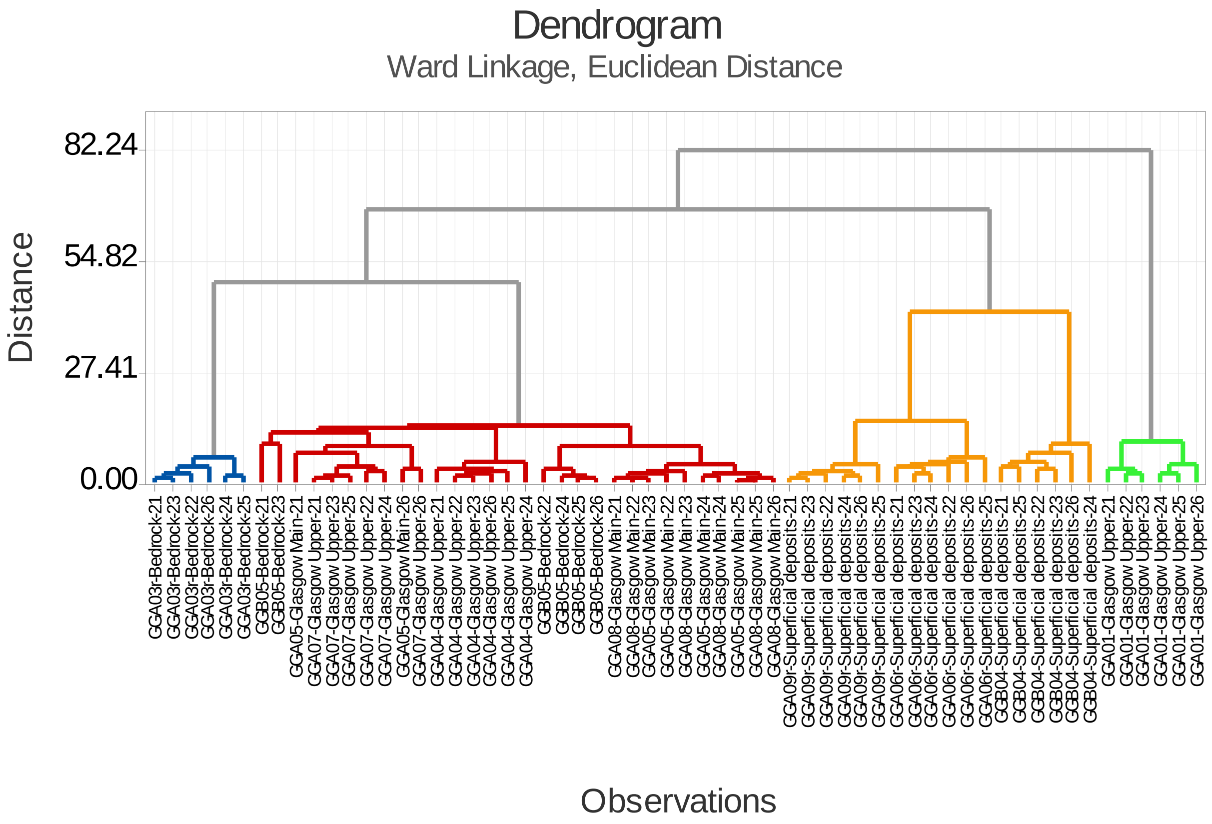

Figure 11 Cluster analysis of groundwaters using: field-HCO_3, Ca, Mg, Na, K, Cl, SO_4, NO_3, Br, NO_2, HPO_4, F, Si, Ba, Sr, Mn, Fe-Total, Li, B, Al, Ti, V, Co, Ni, Cu, Zn, As, Se, Rb, Y, Zr, Mo, Cd, Sn, Sb, Cs, La, Ce, Pb, U, NH4

5.2 RELEVANCE OF UK GEOENERGY OBSERVATORIES BASELINE WATER CHEMISTRY DATA

5.2.1 Comparison to previous data

Data from this monitoring period ("monitoring period 2" June 2021 – January 2022) were compared to data from the previous monitoring period ("monitoring period 1" September 2020 – May 2021 (Bearcock et al., 2022)), and the pumping tests (Palumbo-Roe et al., 2021). Except for GGA01 any observed changes were limited to one or two elements and the change was relatively small.

5.2.1.1 GGA01

At GGA01 there were some changes in groundwater chemistry, continuing the trends observed during the previous monitoring period (Bearcock et al., 2022). The following section discusses the changes at GGA01. Care must be taken to not place too much significance on individual data points, as the duplicate taken during round 25 was sampled at GGA01 and the results indicated that the relative standard deviation (RSD) was greater than the acceptable value of 20% for many parameters (see Appendix 1).

Ca and SO_4 concentrations at GGA01 increased significantly from January 2020 to January 2022, with the rate of increase slowing over time (Figure 12). During pumping tests in early 2020 the concentrations of Ca and SO_4 were 108 mg/L and 199 mg/L, respectively. At the start of monitoring period 1 the concentrations of Ca and SO_4 were 331 mg/L and 1160 mg/L, respectively. At the start of monitoring period 2 the concentrations of Ca and SO_4 were 397 mg/L and 1410 mg/L, respectively, and by the end of monitoring period 2 the concentrations were 467 mg/L and 1510 mg/L, respectively.

HCO_3 was measured during the early 2020 pumping tests to be c. 830 mg/L, this dropped to 450 mg/L at the start of monitoring period 1. Throughout monitoring periods 1 and 2 HCO_3 concentrations have largely remained stable, with step changes observed in the last round(s) of each monitoring period. The HCO_3 concentration was 519 mg/L at the end of monitoring period 2 (Figure 13).

Iron concentrations increased from 4.9 mg/L in the pumping tests to 32 mg/L at the start of monitoring period 1, further increasing to 41.3 mg/L by the start of monitoring period 2, and 47.8 mg/L by the end of monitoring period 2. While the rate of change is slowing, Fe concentrations in groundwaters at GGA01 are still increasing (Figure 14). Elements that are commonly associated with Fe (Mn, Ni, As, Co) or Ca (Rb, Sr) were also observed to have increased concentrations in GGA01 groundwaters from the pump tests and throughout monitoring period 1 (Bearcock et al., 2022). Figure 14 shows Fe, Ni, As and Co. While Fe has continued to increase, the associated elements' concentrations (including Mn, not shown in Figure 14) appear to have stabilised in monitoring period 2. Pearson linear correlation coefficients (r) were calculated for elements which appeared to be associated with one another. There is a statistically significant strong positive correlation ($p < 0.005$) between Fe and associated elements Mn, Co, Ni and As (r values of 0.86, 0.73, 0.88, and 0.84, respectively). Of the elements associated with Ca, Sr has continued to increase, while Rb concentrations appear to have stabilised. There is a strong positive correlation between Ca and Sr ($r = 0.89$, $p < 0.005$), and moderate positive correlation between Ca and Rb ($r = 0.63$, $p < 0.005$).

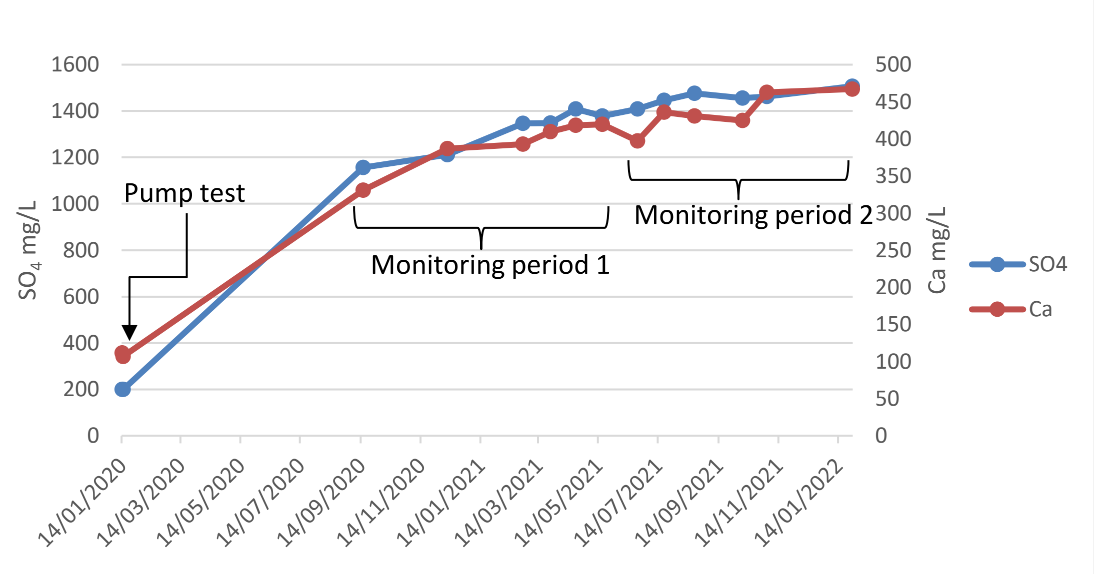

Figure 12 SO_4 and Ca concentrations in GGA01 groundwater.

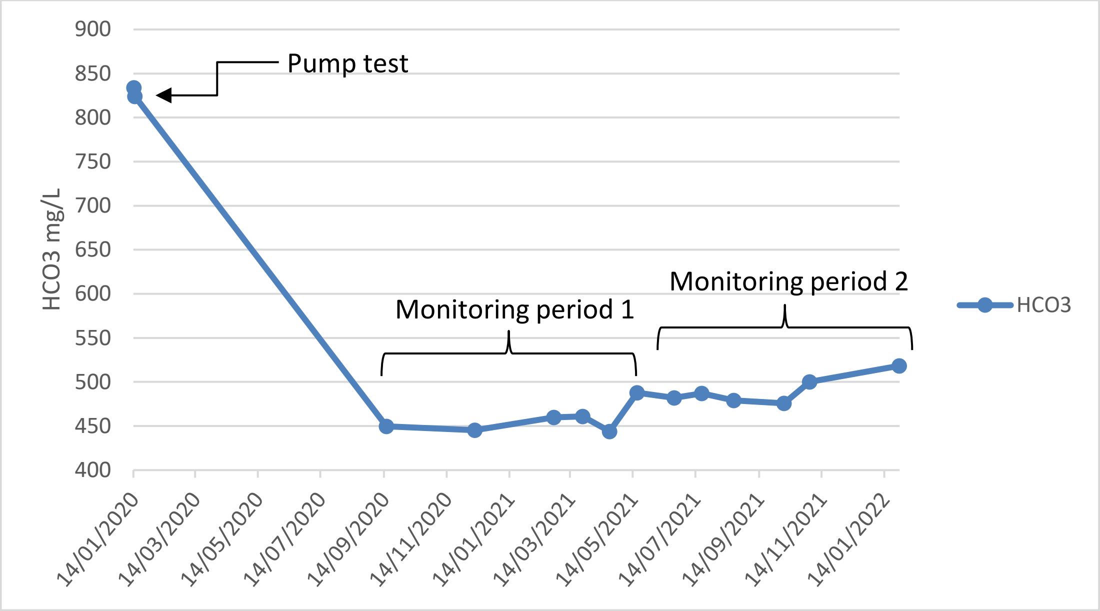

Figure 13 Field HCO_3 concentrations in GGA01 groundwater.

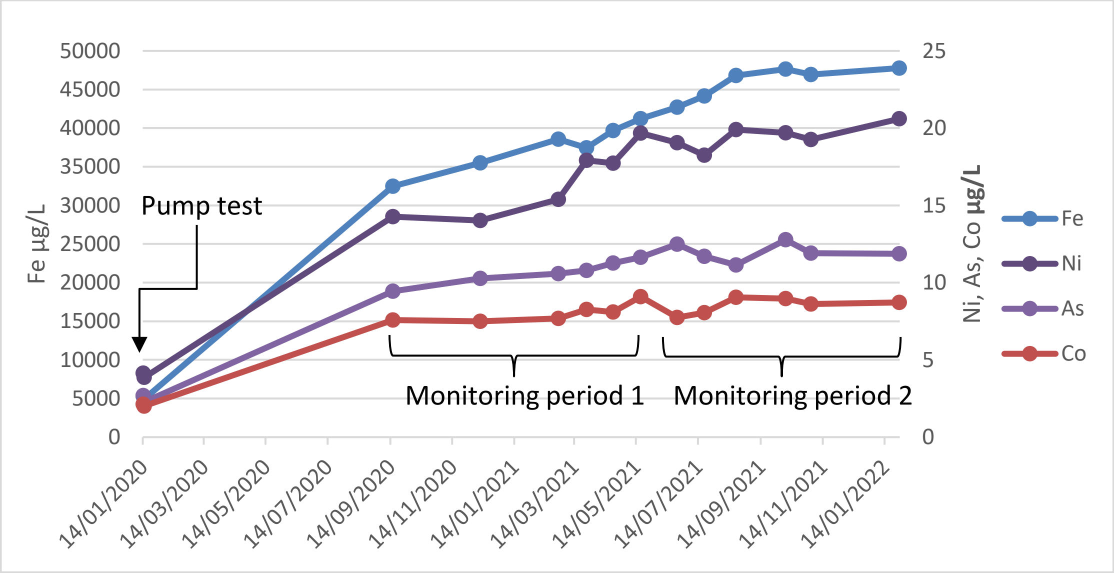

Figure 14 Fe, Ni, As and Co concentrations in GGA01 groundwater.

As discussed in the monitoring period 1 data release report (Bearcock et al., 2022) the hydrochemical processes consistent with increasing SO_4, Ca, and Fe, and decreasing HCO_3 are the oxidation of pyrite (FeS_2) with neutralisation of the protons, produced in the sulphide oxidation reaction, by carbonate dissolution, plus CO_2 degassing. There is a strong positive linear relationship between Fe and SO_4 ($r = 0.94$, $p<0.005$). However, the observed molar ratio of Fe to SO_4 is around 0.05, much smaller than the 0.5 generated by the stoichiometry of pyrite, which indicates that Fe is retained within the subsurface system and precipitated. Field observations of ochreous material at the top of the borehole casing, and positive saturation indices of $FeOH_3$ (0.14-1.29) confirms this suggestion.

Groundwater chemistry is dependent on the aquifer material characteristics and hydrogeologic conditions at the site. The screened section at GGA01 is open 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). Under the confined conditions of the aquifer within the Glasgow Upper mine workings, pyrite oxidation might normally be limited owing to the limited availability of oxygen in water (confirmed by very low DO values < 0.2 mg/L); however, the disturbance of the 1.2 m of packed mine waste during drilling or pumping may have caused conditions favourable to oxidation by allowing the entry of air. The oxygen and deuterium isotopic signature of groundwater remains fairly stable from the pumping tests, throughout monitoring period 1 and monitoring period 2 which argues against significant ingress of oxygenated freshwater to account for the enhancement of oxidation.

5.2.2 Comparison to other relevant data sets

With the exception of groundwaters from GGA01, the remaining samples were typical of groundwater (Ó Dochartaigh et al., 2017; Ó Dochartaigh et al., 2011) and surface water (Fordyce et al., 2004; Smedley et al., 2017) in and around Glasgow. This is discussed in full for monitoring period 1 by Bearcock et al. (2022).

5.2.3 Water quality standards

To assess the water quality at the Glasgow Observatory sampling 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 previous UKGEOS reports (Bearcock et al., 2022; 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 Scotland, 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 28 and on the time series plots of the chemistry data (Appendix 3).

Mean concentrations of parameters over the reported monitoring period 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, which also were generally below limits required for good river status. Data not within AA or MAC are detailed below.

- The mean NO_3 concentration in both the River Clyde (10.4 mg/L) and Tollcross Burn (6.1 mg/L) exceed the AA of 5.7 mg/L.
- The mean HPO_4 concentration in both the River Clyde (0.42 mg/L) and Tollcross Burn (0.087 mg/L) exceed the AA of 0.069 mg/L, in fact most individual measurements exceed this value in both watercourses.
- The mean Al concentration in the River Clyde (32.7 µg/L) exceeds the AA of 15 µg/L, and on 15 occurrences (SW05 from round 21, and all samples in rounds 24, 25, and 26) the Al concentration exceeds the MAC of 25 µg/L (27.3 µg/L – 106 µg/L).
- The mean total Cu concentrations in the River Clyde is 1.2 µg/L and Tollcross Burn 1.4 ug/L. When compared to the bioavailable Cu AA of 1 µg/L, given that the only a fraction of the total concentration is deemed to be bioavailable, Cu is not considered to be exceeding the quality threshold.
- The AA limit for the combined total of benzo(ghi)perylene and indeno(1,2,3-cd)pyrene is 0.002 µg/L. The detection limit for each of these compounds is greater than the AA (0.0036 µg/L and 0.0049 µg/L, respectively). Around a third of all surface water samples had detectable benzo(ghi)perylene and/or indeno(1,2,3-cd)pyrene; however, it is difficult to calculate a meaningful mean, given half the detection limit of indeno(1,2,3-cd)pyrene is greater than the AA limit.

- While the mean concentration of Mn was below the AA (123 µg/L) for both water courses, it is worthy of note that during sampling Round 23 (August 2021) all Mn concentrations in samples from the River Clyde (125 µg/L -230 µg/L) exceeded the AA.

While the results presented here span an eight month period, we can be confident that the AA exceedances are representative, as each parameter with a mean above the AA was also highlighted for AA exceedances in the previous data release report (Bearcock et al., 2022).

6 Conclusions

Baseline surface-water and groundwater chemistry monitoring was carried out in the Glasgow Observatory over eight months between June 2021 and January 2022. This represented a continuation of the surface-water (Fordyce et al., 2021) and groundwater (Bearcock et al., 2022) baseline monitoring activities at the Glasgow Observatory.

The set of 111 samples derived from this period of baseline monitoring (60 groundwater samples, 33 surface water samples, 12 blanks, and 6 field duplicates) were analysed to determine:

- Field measured physicochemical parameters,
- Major and minor ions, and trace elements,
- 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,
- ^{2}H and ^{18}O abundance in water ($\delta^{2}H$ and $\delta^{18}O$)
- ^{13}C abundance in 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,
- Noble gases - helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) for one round of groundwater samples,
- Sulphide (S^{2-}) for groundwaters only, and
- Reduced Fe (Fe^{2+}) for groundwaters only.

Analyses have shown that the groundwaters are all circumneutral (pH 6.6 – 7.4) and are highly mineralised (SEC 1269 µS/cm – 3138 µS/cm). Except for the groundwater at GGA01 in the Glasgow Upper mine workings, all the groundwaters are HCO_3 type with no dominant cation.

The groundwater at GGA01 has changed since the pump tests, from HCO_3 type to Ca-SO_4 type. Concentrations of Ca, SO_4, and Fe initially increased rapidly and have continued to increase at a slower rate, although there are some signs that concentrations may be stabilising. Several associated trace elements, Co, As, Ni, Mn, Rb, and Sr, followed the Ca, SO_4 and Fe trend, demonstrating significant positive correlation. This ongoing change in groundwater character may be induced by sulphide oxidation and neutralisation processes, caused by a possible "disturbance" of the packed waste during borehole construction and oxidation of pyrite from the screened section of borehole GGA01, during the pumping phases.

Cluster analysis indicates that groundwater samples within each target horizon are generally most similar to other groundwater samples from within the same target unit. The exceptions to this are samples from GGB05 from the bedrock groundwaters, which are more similar to the groundwater from the mine workings, and GGA01 which forms its own distinct cluster. The groundwaters within the superficial deposits are distinct from the other groundwaters on account of their major and trace element concentrations.

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.

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 ion 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). Further analysis methods not covered in these two reports (noble gases, sulphide (S^{2-}) and radon (Rn)) are described in the first combined groundwater and surface water data release report (Bearcock et al., 2022). Analysis of reduced iron (Fe^{2+}) is not covered by any of these reports, so the methodology provided by the external laboratory is provided in this section. Where 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.

Where there are sample-specific QC concerns, for example the UKAS accreditation was lost or there is another reason to treat the sample with caution, it is noted in a field in the data release spreadsheet. Affected parameters are typically TPH, PAH and occasionally VOC.

Ionic mass balance calculations for each of the samples resulted in a percentage balance of within ± 5% when calculated with lab bicarbonate concentrations. While we would usually expect the field bicarbonate data to give better ionic balances than the lab bicarbonate data, in this instance three of the field bicarbonate ionic balances showed percentages outside the acceptable range of ± 5%. This is probably indicative of errors in the subjective assessment of the colour change whilst doing the alkalinity titration in the field. Despite this, the vast majority of the field ionic mass balances are still within the acceptable range of ± 5%.

The long- term lower limits of detection (LLD) and/or limits of quantification (LOQ) for the analytical methods typical of the instruments used for analysis can be found in Bearcock et al. (2022), Fordyce et al. (2004), or (Palumbo-Roe et al., 2021).

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 7.3% in QC1, 5.7% in QC2 and 25% in QC3)
- Beryllium (RSD of 55.9% in QC1)
- Aluminium (RSD of 6.2% in QC1)
- Vanadium (RSD of 9.5% in QC3)
- Iron (RSD of 5.6% in QC3)
- Zinc (RSD of 13.4% in QC3)
- Silver (RSD of 6.6% in QC1)
- Cadmium (RSD of 11.9% in QC3)
- Lead (RSD of 5.9% in QC3)
- Uranium (RSD of 6.2% in QC3)

A good accuracy of these reference materials was demonstrated with most recoveries 100 ± 5%. The exceptions to this were:

- Beryllium (Accuracy of 88% in QC1 and 87% in QC3)
- Silicon (Accuracy of 91% in QC2)
- Sulphur (Accuracy of 109% in QC2)
- Vanadium (Accuracy of 92% in QC3)
- Zinc (Accuracy of 106% in QC1 and 107% in QC3)
- Molybdenum (Accuracy of 93% in QC3)
- Cadmium (Accuracy of 128% in QC3)
- Bismuth (Accuracy of 107% in QC1)
- Uranium (Accuracy of 94% in QC3)

Laboratory blanks were inserted throughout each analytical run. Most were below the detection limits for each element. The exceptions to this were:

Beryllium (3 of the 59 blanks analysed had detectable Be)
Boron (1 of the 48 blanks analysed had detectable B)
Magnesium (7 of the 59 blanks analysed had detectable Mg)
Silicon (24 of the 53 blanks analysed had detectable Si)
Sulphur (1 of the 53 blanks analysed had detectable S)
Vanadium (1 of the 53 blanks analysed had detectable V)
Iron (4 of the 57 blanks analysed had detectable Fe)
Nickel (1 of the 57 blanks analysed had detectable Ni)
Zinc (1 of the 51 blanks analysed had detectable Zn)
Strontium (1 of the 50 blanks analysed had detectable Sr)
Lead (1 of the 52 blanks analysed had detectable Pb)

Results for most field duplicate samples showed good robustness of the sampling method, with good variability between sample-pairs (RSD ≤ 10%) of the major (Ca, Mg, Na, K) and minor elements Si and F, acceptable variability (<20%) for the trace elements Ba, Sr, Mn, Li, B, Ti, Cr, Co, Ni, Rb, Y, Zr, Cs, U, with the exception of duplicate pair GGA01 round 25 where RSD is greater than the acceptable value of 20% for most elements.

Total Fe, Al, V, Cu, Zn, As, Mo, Cd, Sn, REEs, Tl, Pb show more variability (RSD < 20%) between some sample pairs, 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, SO_4 and NO_3 had an RSD of 8.8%, 7.4% and 6.6% 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, where Cl, SO_4, NO_3 and F had recoveries of 106%, 107%, 107% and 94% respectively.

Laboratory blanks were inserted throughout each analytical run. All were below the detection limits for each element.

Results for most field duplicate samples showed good robustness of the sampling method, with good variability between sample-pairs (RSD ≤ 10%) of Cl, SO_4, Br, F (NO_3 below LOQ) with the exception of duplicate pair GGA01 round 25, where RSD is greater than the acceptable value of 20% for SO_4.

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 100.8%) and precision (RSD 1.5%).

Results for field duplicate samples showed good robustness of the sampling method also, with variability between sample-pairs (RSD <10%), with the exception of duplicate pair GGA01 round 25, where RSD is greater than the acceptable value of 20%.

As a further check on data quality, the field and laboratory alkalinity measurements were compared. These showed good agreement with most analyses' (n=92) RSD ≤ 10%, and the remainder (n=8) 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. 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 good variability between sample-pairs (RSD ≤ 5%).

Sulphide analysis

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 ($C_6H_8O_6$). Sulphide analysis by Segmented Flow Analysis was carried out by SOCOTEC at their laboratories in Burton upon Trent. 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%.

Field duplicates had sulphide concentrations ≤ LOQ, except for duplicate pair GGA01 round 25, RSD 0% and duplicate pair GGA04 round 26 with a high RSD 28%.

Reduced iron analysis

The analysis of reduced iron (Fe^2) by discrete colorimetric analysis was carried out by SOCOTEC at their laboratories in Burton upon Trent. The method is UKAS accredited, however specific QC data were unavailable for this reporting period. The limit of detection for the method is 10 µg/L

The Fe^{2+} content of the groundwater samples is determined by treating the sample with a solution of 1,10 phenanthroline hydrate, after the sample has been buffered to a pH between 3.5 and 5.5. Any ferrous iron present reacts with the 1,10 phenanthroline to form an orange-red complex that absorbs light at 510 charge nm.

Results for field duplicate samples generally showed very low variability between sample-pairs (RSD ≤ 5%), with the exception of duplicate pair GGA03r round 23, where RSD is 79%, and GGA01 round 25, where RSD is 43%.

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 ≤ 10%), with the exception of duplicate pair GGA01 round 25, where RSD is greater than the acceptable value of 34%. 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.

Results for QC check standards and repeat measurements showed some questionable accuracy (recovery 100 ± 21%) and precision (RSD < 19%) of the data. The C8-C10 data reported had a recovery of 112.2%, and an RSD of 7.4%. The C10-C40 data reported had a recovery of 120.7%, and an RSD of 19%. RSD was statistically out of control from the period between March and June 2022, which partly accounts for the high value. However, the last sample was taken on January 27th 2022 so there is the possibility the data may be unaffected by this.

Results for field duplicate samples showed good robustness of the sampling method (RSD ≤ 10%), for sample-pairs with values greater than LOQ (GGA03r round 23 and GGB05 round 25).

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 20). The results for Indeno(1,2,3-cd)pyrene show slightly poorer accuracy (recovery 100 ± 12%) and precision (RSD is <8%).

Results for field duplicate samples showed all values below LOQ.

Table 20 Results for quality control standards included in the HPLC-FD PAH analysis

	Results reported up to September 2021		Results reported after August 2021	
PAH Compound	**% Recovery**	**% RSD**	**% Recovery**	**% RSD**
Benzo(b)fluoranthene	103.6	4.3	102.5	5.8
Benzo(k)fluoranthene	104.1	3.7	102	5.2
Benzo(a)pyrene (BaP)	98.3	4	96.2	5.8
Benzo(g,h,i)perylene	106.5	5.4	105.8	6.2
Indeno(1,2,3-cd)pyrene	111.4	7.4	109.5	7.6
PAH-Total	106.4	4.2	104.9	4.8

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 21). The remaining parameters are assessed against set limits (+/-25% of nominal value).

Results for field duplicate samples showed all values below LOQ.

Table 21 Method performance of certain VOC parameters controlled via control charts

	Results reported from January 2020 to March 2022	
Compound	**% Recovery**	**% RSD**
Diethyl Ether	103.9	7.1
Trichloromethane	99.6	4
Benzene	100.3	4
Toluene	99.3	3.6
Tetrachloroethene	98.3	4.9
Styrene	98.9	3.9
1,3,5-Trichlorobenzene	95.7	5.2

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 ≤ 6%). Similarly, the measured results for a secondary in-house standard (CCS) demonstrated good recovery (100 ± 5 %) relative to the preferred value (Table 22).

Field duplicate $\delta^{13}C$ measurements show RSD ≤ 1% for all sample pairs, except for pair GGA01 (GF25-11 and GF25-12) with RSD of 19%.

Table 22 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	15	5
NIGL mean	-0.7	-22.4
% RSD	5.2	<1
In-house preferred value		-22.3
% recovery		99.6

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 23).

Field duplicate $\delta^{2}H$ measurements show RSD ≤ 1% for all sample pairs.

Table 23 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	27	28
NIGL mean	-309.3	-49
% RSD	<1	1.6

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 24). Field duplicate $\delta^{18}O$ measurements show RSD ≤ 1% for all sample pairs.

Table 24 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	36	36
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. 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 (September 2021) are presented in Table 25. Associated with these is a maximum measurement uncertainty (the highest of the two instruments) of c. 16%. The LOD is 10 Bq/L. Radon concentrations of all the field duplicate samples were lower than the LOD.

Table 25 Typical method performance of Scottish Water's two liquid scintillator counters

Instrument	% Bias	% RSD
Radon 101B	-0.3	6.0
Radon 101C	-1.2	5.1

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). Air-saturated water (ASW) calibration samples 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.

Noble gases Ne, Ar, Kr and Xe concentrations of the field duplicate pair GGA04 round 26 showed a RSD <10%, while He had RSD 35%.

Methane, ethane, and carbon dioxide analysis

The analysis of CH_4, C_2H_6, and CO_2 was undertaken at the BGS Wallingford laboratories, using a headspace technique. Eluting methane and ethane (if present) were detected by a flame ionisation detector (FID), while CO2 was measured by a thermal conductivity detector (TCD).

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.

The CH_4 concentrations of field duplicate samples showed good robustness of the sampling method (RSD <5%), except for sample-pairs GGA03r round 23 and GGA01 round 25 with RSD >35%). The CO_2 concentrations of field duplicate samples showed good robustness of the sampling method (RSD <10%).

Chlorofluorocarbons and sulphur hexafluoride analysis

The CFC and SF6 analyses were analysed at the BGS Wallingford laboratories. 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%.

CFC-12, CFC-11, SF6 results for the field duplicate pair GGA04 round 26 showed respectively RSD 1%, 51%, and 71%. Duplicate data for the CFCs is in excellent agreement for CFC-12 although CFC-11 appears to have a larger error than would normally be expected (+/-5%). The values obtained are close to detection limits and agreement on the absolute age for CFC-11 is good (+/- 2 years). SF6 duplicates are below the quantifiable limit of detection, with a modern fraction <0.5% and an age older than 1970.

Appendix 2 Summary statistics

Summary statistics of field parameter, major and minor ion, trace element and stable isotope compositions, for the groundwater samples (Table 26) and surface water samples (Table 27) taken between June 2021 and January 2022 are presented in this appendix. For the purposes of calculating summary statistics, data below the LLD were set to half the LLD value.

Table 26 Summary statistics for all groundwater samples collected between June 2021 and January 2022

Variable	Units	Min	Max	Mean	Median	SD	n	n(c)
pH		6.64	7.36	7.04	7.04	0.16	60	0
Temperature	°C	10.1	16.6	12.3	12.2	1.15	60	0
Eh	mV	9.7	357	131	118	67.6	60	0
DO	mg/L	0.04	0.81	0.28	0.25	0.151	60	0
SEC	µs/cm	1270	3140	1690	1570	457	60	0
HCO_3 (field measured)	mg/L	476	864	723	769	104	60	0
Ca	mg/L	104	467	152	115	97.1	60	0
Mg	mg/L	40.3	79.7	56.5	54.4	10.1	60	0
Na	mg/L	102	216	161	170	33.8	60	0
K	mg/L	9.67	31.7	18	18.9	5.47	60	0
Total Alkalinity	mg/L	387	850	732	799	132	60	0
Cl	mg/L	33.8	113	64.9	68.9	13.6	60	0
SO_4	mg/L	142	1510	308	179	388	60	0
NO_3	mg/L	<0.3	1.56	0.268	<0.3	0.304	60	55
Br	mg/L	<0.5	0.703	0.481	0.48	0.111	60	2
NO_2	mg/L	<0.05	<0.25	0.0315	<0.05	0.0226	60	60
HPO_4	mg/L	<0.1	0.447	0.0772	<0.1	0.077	60	57
F	mg/L	0.0643	0.322	0.181	0.175	0.0623	60	3
Si	mg/L	5.11	15.5	6.85	6	2.71	60	0
SiO_2	mg/L	10.9	33.1	14.7	12.8	5.8	60	0
Sulphide as S	mg/L	<0.02	1.09	0.0783	0.02	0.171	60	26
Ba	µg/L	34.5	323	86.6	52.3	80.7	60	0
Sr	µg/L	545	3970	2030	1960	1030	60	0
Mn	µg/L	330	7250	1470	466	1900	60	0
Fe-Total	µg/L	5	47800	7230	2010	13300	60	0
Fe Reduced	µg/L	40	50200	7400	2100	13700	60	0
Li	µg/L	<7	60	23.7	29	16	60	18
B	µg/L	171	662	390	392	90.1	60	0
Al	µg/L	<0.6	7.1	2.07	1.8	1.35	60	2
Ti	µg/L	<0.06	0.5	0.174	0.15	0.133	60	29
V	µg/L	<0.02	0.39	0.128	0.12	0.0734	60	2
Cr	µg/L	<0.04	0.33	0.126	0.12	0.0651	60	6
Co	µg/L	0.17	11.8	3.16	2.2	3.24	60	0
Ni	µg/L	1.74	39	8.17	3.82	10.5	60	0
Cu	µg/L	<0.05	0.28	0.0722	0.06	0.0573	60	26
Zn	µg/L	<0.2	10.3	2.25	1.8	1.88	60	3
Ga	µg/L	<0.04	0.05	0.0247	<0.04	0.00694	60	59
As	µg/L	0.08	12.8	1.83	0.425	3.48	60	0
Se	µg/L	<0.07	0.2	0.0466	<0.07	0.0285	60	49
Rb	µg/L	5.63	74.6	31.2	37	19.4	60	0
Y	µg/L	0.03	0.452	0.118	0.095	0.085	60	0
Zr	µg/L	0.027	0.319	0.106	0.093	0.0607	60	0
Nb	µg/L	<0.01	0.02	0.0072	<0.01	0.00516	60	49
Mo	µg/L	<0.2	7.3	1.14	0.45	1.98	60	20
Cd	µg/L	<0.005	0.058	0.0053	<0.005	0.00831	60	46
Sn	µg/L	<0.08	3.15	0.279	<0.08	0.57	60	48
Sb	µg/L	<0.04	0.07	0.0212	<0.04	0.00691	60	58
Cs	µg/L	<0.04	0.42	0.167	0.16	0.101	60	6
La	µg/L	0.004	0.103	0.0279	0.0135	0.0274	60	0
Ce	µg/L	0.009	0.161	0.05	0.031	0.0434	60	0
Pr	µg/L	<0.003	0.017	0.0058	0.004	0.00471	60	21
Nd	µg/L	<0.005	0.087	0.0272	0.0175	0.0216	60	2

Variable	Units	Min	Max	Mean	Median	SD	n	n(c)
Sm	µg/L	<0.005	0.019	0.0062	0.0037	0.00453	60	30
Eu	µg/L	<0.003	0.005	0.0019	<0.003	0.00097	60	50
Gd	µg/L	<0.005	0.022	0.0085	0.008	0.00606	60	24
Tb	µg/L	<0.004	0.004	0.0020	<0.004	0.00025	60	59
Dy	µg/L	<0.003	0.05	0.0118	0.0095	0.00982	60	9
Ho	µg/L	<0.003	0.024	0.0036	<0.003	0.0045	60	38
Er	µg/L	<0.003	0.117	0.0161	0.009	0.0269	60	11
Tm	µg/L	<0.003	0.03	0.0037	<0.003	0.00679	60	54
Yb	µg/L	<0.004	0.323	0.0363	0.012	0.0799	60	9
Lu	µg/L	<0.003	0.079	0.0084	<0.003	0.0198	60	42
Hf	µg/L	<0.006	<0.006	0.003	<0.006	0	60	60
Ta	µg/L	<0.006	<0.006	0.003	<0.006	0	60	60
W	µg/L	<0.06	1.13	0.137	<0.06	0.291	60	42
Tl	µg/L	<0.02	0.05	0.0175	<0.02	0.0113	60	38
Pb	µg/L	<0.02	0.31	0.0242	<0.02	0.0403	60	39
Bi	µg/L	<0.08	0.04	<0.08	<0.08	0	60	60
Th	µg/L	<0.03	0.015	<0.03	<0.03	0	60	60
U	µg/L	0.251	2.25	0.853	0.635	0.531	60	0
NH_4	mg/L	2.42	18.4	11.9	13	4.7	60	0
NPOC	mg/L	1.05	23.5	3.42	2.62	2.90	58	0
$\delta^{13}C$	‰	-17	-7.72	-11.5	-11.2	2.02	60	0
$\delta^{18}O$	‰	-7.55	-7.18	-7.43	-7.44	0.0747	60	0
$\delta^{2}H$	‰	-253	9.02	-162	-202	119	4	0
CFC-12	pmol/L	0.0324	0.108	0.0625	0.0583	0.0288	9	0
CFC-11	pmol/L	0.0246	0.116	0.0538	0.0411	0.0284	9	0
SF_6	fmol/L	0	0.024	0.0089	0.012	0.00844	9	0
CH_4	µg/L	0.3	710	112	70.2	124	60	0
C_2H_6	µg/L	<1	5.2	0.578	<1	0.607	60	59
CO_2	mg/L	5.5	219	137	142	33.1	60	0
Benzo(b)fluoranthene	µg/L	<0.0018	0.0038	0.0018	<0.001	0.00025	60	59
Benzo(k)fluoranthene	µg/L	<0.003	<0.003	0.0015	<0.003	0	60	60
Benzo(a)pyrene	µg/L	<0.00016	0.0035	0.0008	<0.000	0.00034	60	59
Benzo(ghi)perylene	µg/L	<0.0036	0.0036	0.0018	<0.003	0.00023	60	59
Indeno(1,2,3-cd)pyrene	µg/L	<0.0049	<0.004	0.0024	<0.004	0	60	60
TPH (C8-C10)	mg/L	<0.003	0.016	0.0034	<0.003	0.00395	60	45
TPH (C10-C40)	mg/L	<0.042	0.633	0.036	<0.042	0.0806	60	54
TPH (C8-C40)	mg/L	<0.045	0.645	0.0379	<0.045	0.082	60	54
Iso propyl ether	µg/L	<10	<10	5	<10	0	60	60
1,2-Dibromo-3-chloropropane	µg/L	<10	<10	5	<10	0	60	60
N.N-Dimethylaniline	µg/L	<1	<10	4.93	<10	0.581	60	60
1,2,4-Trichlorobenzene	µg/L	<1	<10	4.93	<10	0.581	60	60
Naphthalene	µg/L	<1	<10	4.93	<10	0.581	60	60
1,2,3-Trichlorobenzene	µg/L	<1	<10	4.93	<10	0.581	60	60

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

Table 27 Summary statistics of surface water samples collected between June 2021 and January 2022

Variable	Units	Min	Max	Mean	Median	SD	n	n(c)
pH		7.28	8.73	7.85	7.75	0.319	33	0
Temperature	°C	6.4	22.1	12.8	11.9	5.06	33	0
Eh	mV	330	538	432	430	44.8	33	0
DO	mg/L	4.64	11.6	8.73	9.67	2.49	33	0
SEC	µs/cm	160	976	463	413	228	33	0
HCO_3 (field measured)	mg/L	52.5	417	160	126	112	33	0
Ca	mg/L	14.8	79.7	40	34.5	19.2	33	0
Mg	mg/L	4.12	37.1	14.2	11.7	9.05	33	0
Na	mg/L	9.9	83.4	32.5	27.5	20.8	33	0
K	mg/L	1.8	14.3	5.67	4.84	3.58	33	0
Total Alkalinity	mg/L	45.7	428	167	132	115	33	0
Cl	mg/L	13.3	70.4	35.1	31.1	16.1	33	0
SO_4	mg/L	13.7	72.5	38.6	36.4	16.9	33	0
NO_3	mg/L	5.06	15.5	9.66	10.2	3.65	33	0
Br	mg/L	0.0171	0.217	0.0701	0.0451	0.0582	33	0
NO_2	mg/L	<0.01	1.45	0.357	0.109	0.43	33	1
HPO_4	mg/L	<0.01	0.864	0.362	0.233	0.334	33	3
F	mg/L	0.0397	0.21	0.0908	0.0812	0.0479	33	0
Si	mg/L	1.15	6.07	3.25	3.54	1.33	33	0
SiO_2	mg/L	2.46	13	6.96	7.57	2.85	33	0
Ba	µg/L	52.9	141	83.5	82	21.2	33	0
Sr	µg/L	80.2	1380	382	230	398	33	0
Mn	µg/L	18.4	230	66.6	49	52.5	33	0
Fe-Total	µg/L	12	430	196	285	153	33	0
Li	µg/L	<7	16	5.32	<7	3.98	33	27
B	µg/L	<53	150	44.8	<53	40.1	33	27
Al	µg/L	6.9	106	28.4	17.5	26.4	33	0
Ti	µg/L	<0.06	2.8	0.633	0.39	0.774	33	8
V	µg/L	0.33	0.87	0.564	0.55	0.136	33	0
Cr	µg/L	0.11	7.81	1.01	0.36	1.77	33	0
Co	µg/L	0.142	0.363	0.232	0.212	0.0618	33	0
Ni	µg/L	1.16	1.88	1.48	1.49	0.197	33	0
Cu	µg/L	0.85	2.24	1.25	1.16	0.36	33	0
Zn	µg/L	2.5	22.7	7.42	4.5	5.57	33	0
Ga	µg/L	<0.04	0.04	0.0256	<0.04	0.00747	33	30
As	µg/L	0.28	0.68	0.426	0.42	0.0908	33	0
Se	µg/L	0.1	0.58	0.167	0.14	0.0877	33	0
Rb	µg/L	1.81	21.2	6.87	5.45	5.71	33	0
Y	µg/L	0.009	0.322	0.0918	0.057	0.0909	33	0
Zr	µg/L	0.013	0.248	0.0739	0.049	0.0651	33	0
Nb	µg/L	<0.01	0.01	0.0053	<0.01	0.00121	33	31
Mo	µg/L	0.2	1.1	0.53	0.5	0.234	33	0
Cd	µg/L	<0.005	0.02	0.00924	0.008	0.00393	33	2
Sn	µg/L	<0.08	0.04	<0.08	<0.08	0	33	33
Sb	µg/L	0.11	0.54	0.226	0.19	0.107	33	0
Cs	µg/L	<0.04	0.14	0.0603	0.05	0.0401	33	11
La	µg/L	<0.003	0.243	0.0556	0.036	0.0646	33	5
Ce	µg/L	<0.004	0.441	0.0931	0.056	0.115	33	5
Pr	µg/L	<0.003	0.071	0.0165	0.01	0.0188	33	14
Nd	µg/L	<0.005	0.329	0.0759	0.041	0.0884	33	5
Sm	µg/L	<0.005	0.066	0.0177	0.01	0.0197	33	15
Eu	µg/L	<0.003	0.017	0.00489	<0.003	0.0047	33	17
Gd	µg/L	<0.005	0.079	0.0245	0.022	0.0178	33	6
Tb	µg/L	<0.004	0.009	0.00321	<0.004	0.00213	33	24
Dy	µg/L	<0.003	0.054	0.0148	0.009	0.0154	33	10
Ho	µg/L	<0.003	0.012	0.00344	<0.003	0.00275	33	19
Er	µg/L	<0.003	0.031	0.00885	0.006	0.00825	33	10
Tm	µg/L	<0.003	0.004	0.00171	<0.003	0.0006	33	29
Yb	µg/L	<0.004	0.026	0.00845	0.005	0.00716	33	11
Lu	µg/L	<0.003	0.004	0.00167	<0.003	0.000554	33	30
Hf	µg/L	<0.006	0.008	0.00336	<0.006	0.00119	33	30

Variable	Units	Min	Max	Mean	Median	SD	n	n(c)
Ta	µg/L	<0.006	<0.006	0.003	<0.006	0	33	33
W	µg/L	<0.06	0.16	0.0355	<0.06	0.024	33	31
Tl	µg/L	<0.02	<0.02	0.01	<0.02	0	33	33
Pb	µg/L	0.03	1.42	0.388	0.36	0.37	33	0
Bi	µg/L	<0.08	<0.08	0.04	<0.08	0	33	33
Th	µg/L	<0.03	<0.03	0.015	<0.03	0	33	33
U	µg/L	0.082	0.463	0.196	0.17	0.0987	33	0
NPOC	mg/L	2.52	17.3	6.14	5.17	3.39	33	0
$\delta^{13}C$	‰	-14.1	-9.65	-11.4	-11	0.984	31	0
$\delta^{18}O$	‰	-7.87	-7.01	-7.4	-7.4	0.246	33	0
$\delta^{2}H$	‰	NA	NA	NA	NA	NA	3	0
Benzo(b)fluoranthene	µg/L	<0.0036	0.0131	0.00317	<0.0036	0.00263	33	23
Benzo(k)fluoranthene	µg/L	<0.003	0.0037	0.00157	<0.0036	0.000383	33	32
Benzo(a)pyrene	µg/L	<0.0016	0.0089	0.00284	0.0022	0.0022	33	10
Benzo(ghi)perylene	µg/L	<0.0036	0.0049	0.00219	<0.0036	0.000857	33	27
Indeno(1,2,3-cd)pyrene	µg/L	<0.0049	0.0195	0.00454	<0.0049	0.00368	33	21
TPH (C8-C10)	mg/L	<0.004	0.016	0.00313	<0.003	0.00349	32	24
TPH (C10-C40)	mg/L	<0.053	0.555	0.0546	<0.042	0.102	32	24
TPH (C8-C40)	mg/L	<0.057	0.555	0.0494	<0.045	0.0946	32	24

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

Appendix 3 Time series plots

Time series plots are presented below. The graphs include data from the outset of monitoring activities: March 2019 for surface waters, and September 2020 for groundwaters. Details for data preceding that discussed in this report can be found in Fordyce et al. (2021) or Bearcock et al. (2022).

A black line on the surface water graphs represents annual average (AA) allowable concentrations, which are also presented in Table 28 along with maximum allowable concentration (MAC) for information (SEPA, 2014b, 2020a).

The graphs present data from the start of monitoring, not including the pump testing. Therefore the period of surface water data presented is March 2019 to January 2022, while the groundwater data span September 2020 to January 2022. For the purposes of graphing, where data are below the detection limit the value is replaced with half the detection limit.

SEPA rainfall data from the Dalmarnock STW station are presented on Figures 15, 16, 20, and 21 (SEPA, 2023).

Table 28 Environmental quality standards for surface water 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

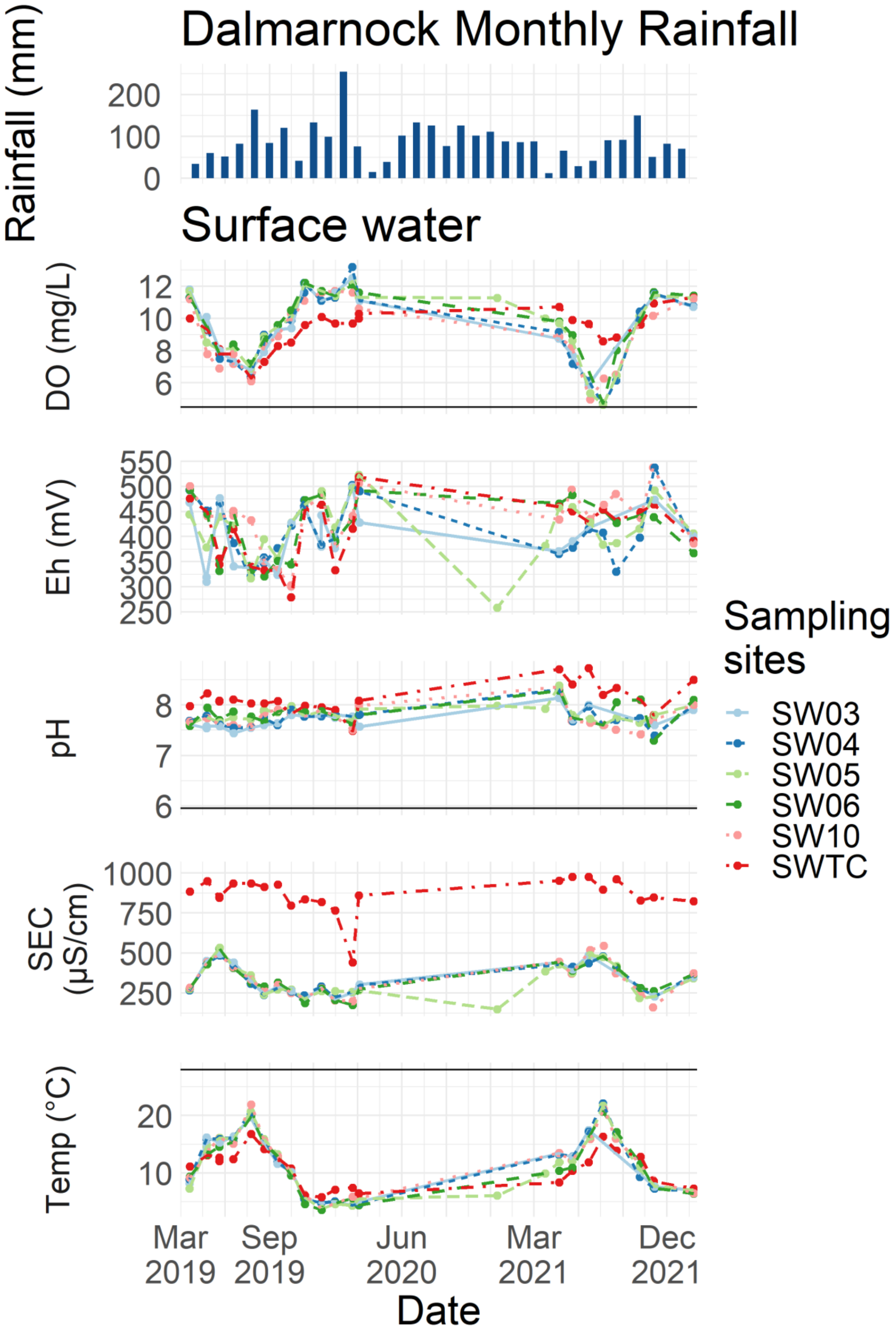

Figure 15 Time-series of field parameters measured during sampling at surface water sites. The top panel shows monthly rainfall totals at Dalmarnock. Rainfall data ©SEPA, 2023.

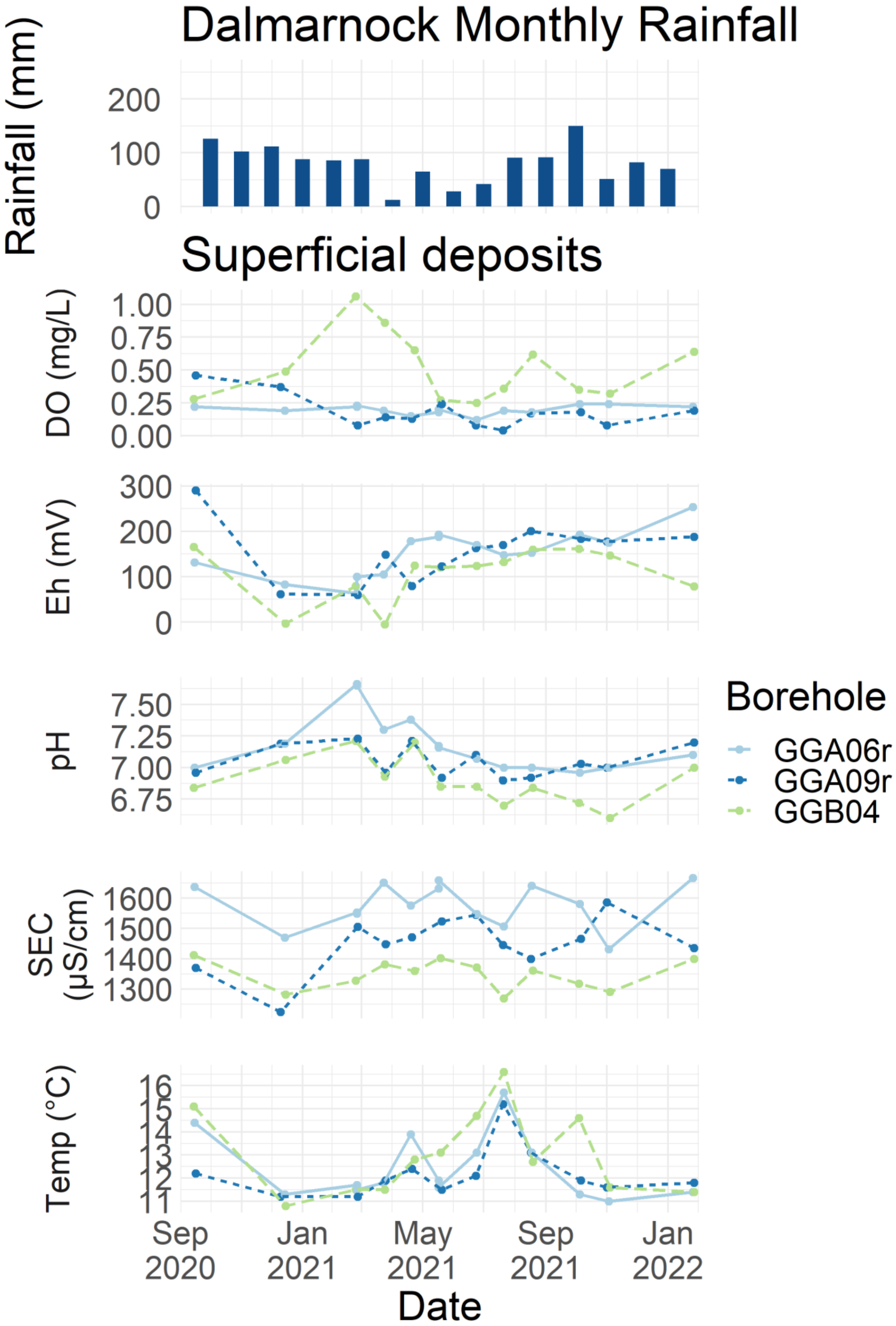

Figure 16 Time-series of field parameters measured during sampling of superficial deposit boreholes. The top panel shows monthly rainfall totals at Dalmarnock. Rainfall data ©SEPA, 2023

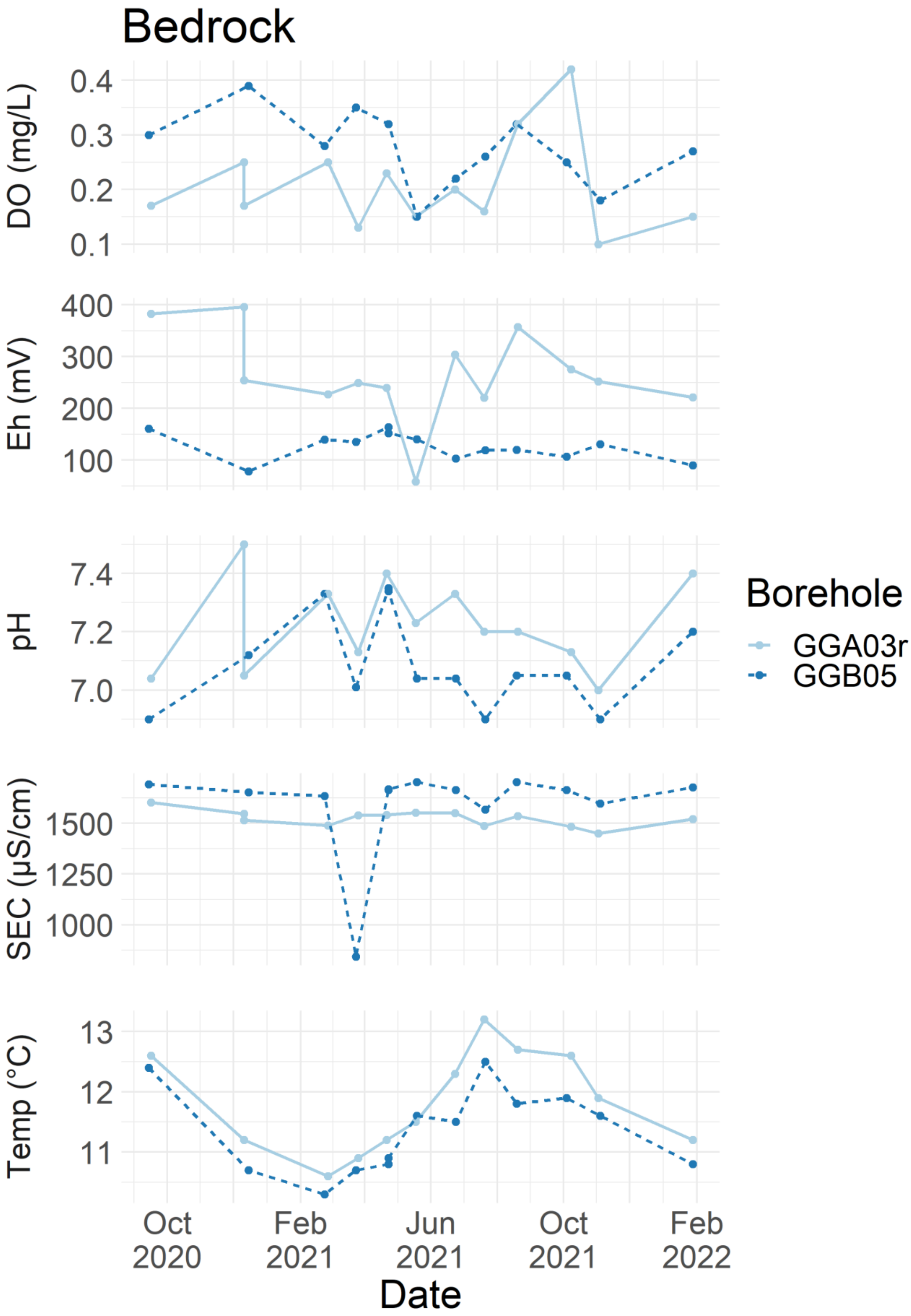

Figure 17 Time-series of field parameters measured during sampling of bedrock boreholes.

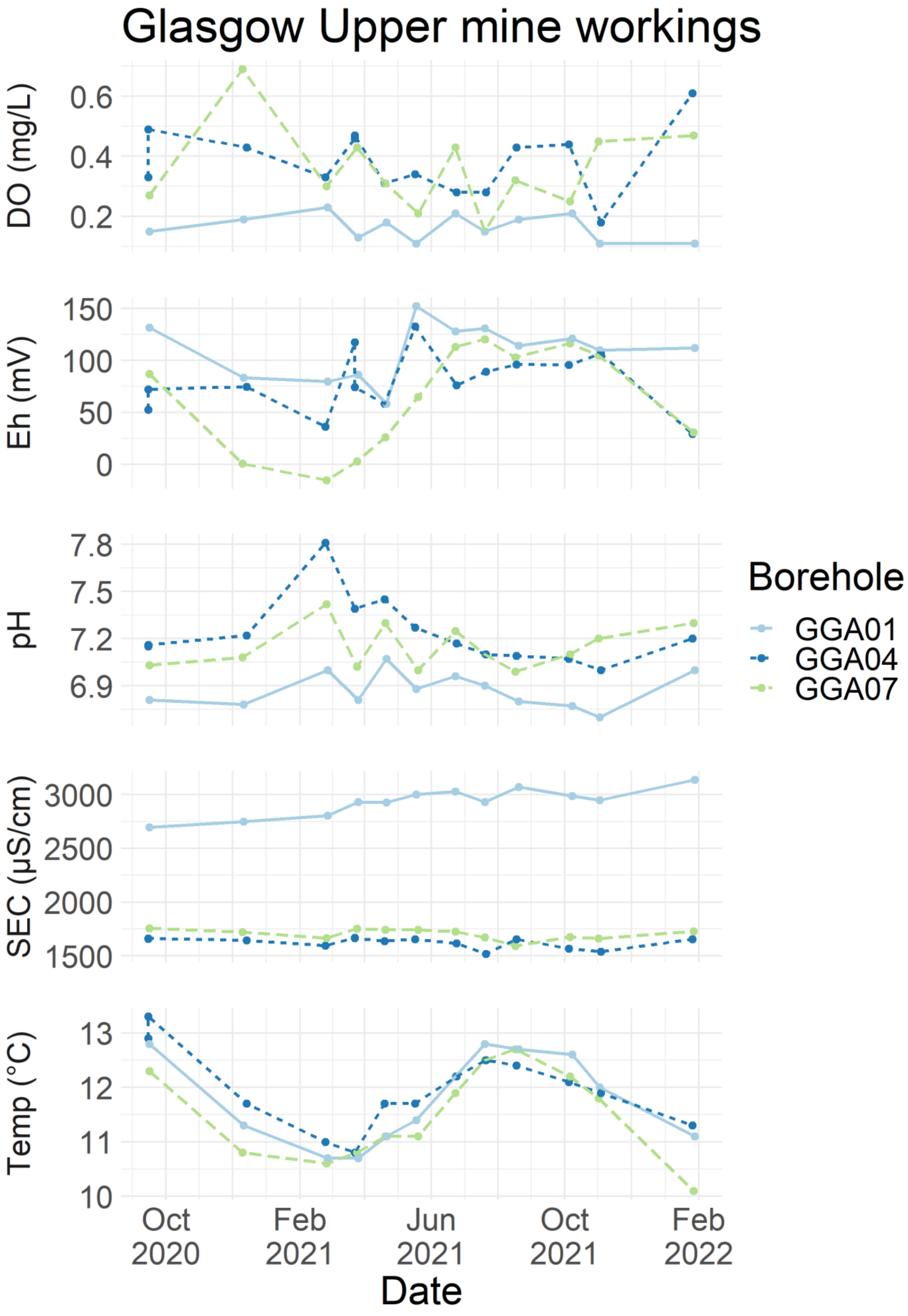

Figure 18 Time-series of field parameters measured during sampling of Glasgow Upper mine working boreholes.

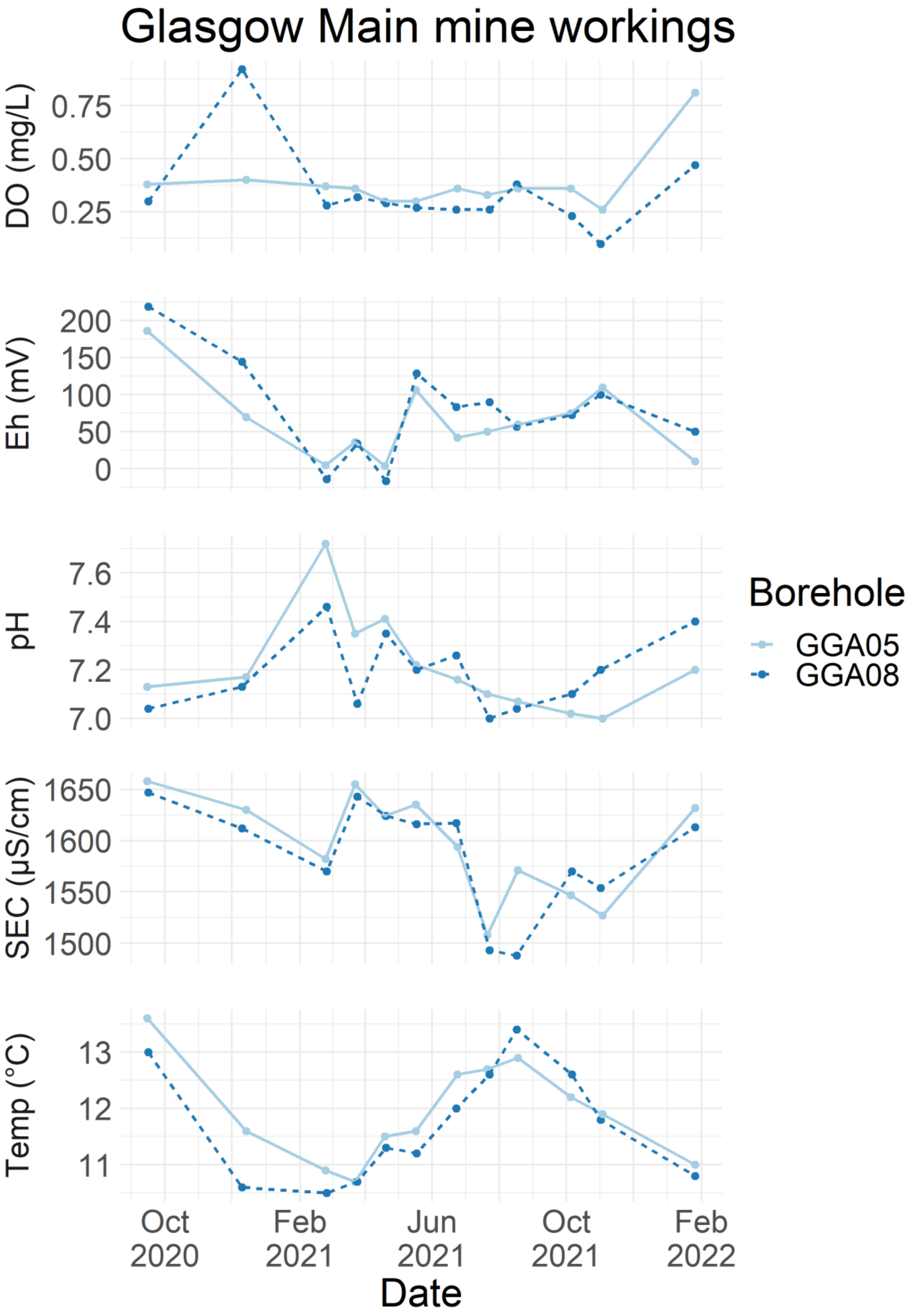

Figure 19 Time-series of field parameters measured during sampling of Glasgow Main mine working boreholes.

MAJOR IONS

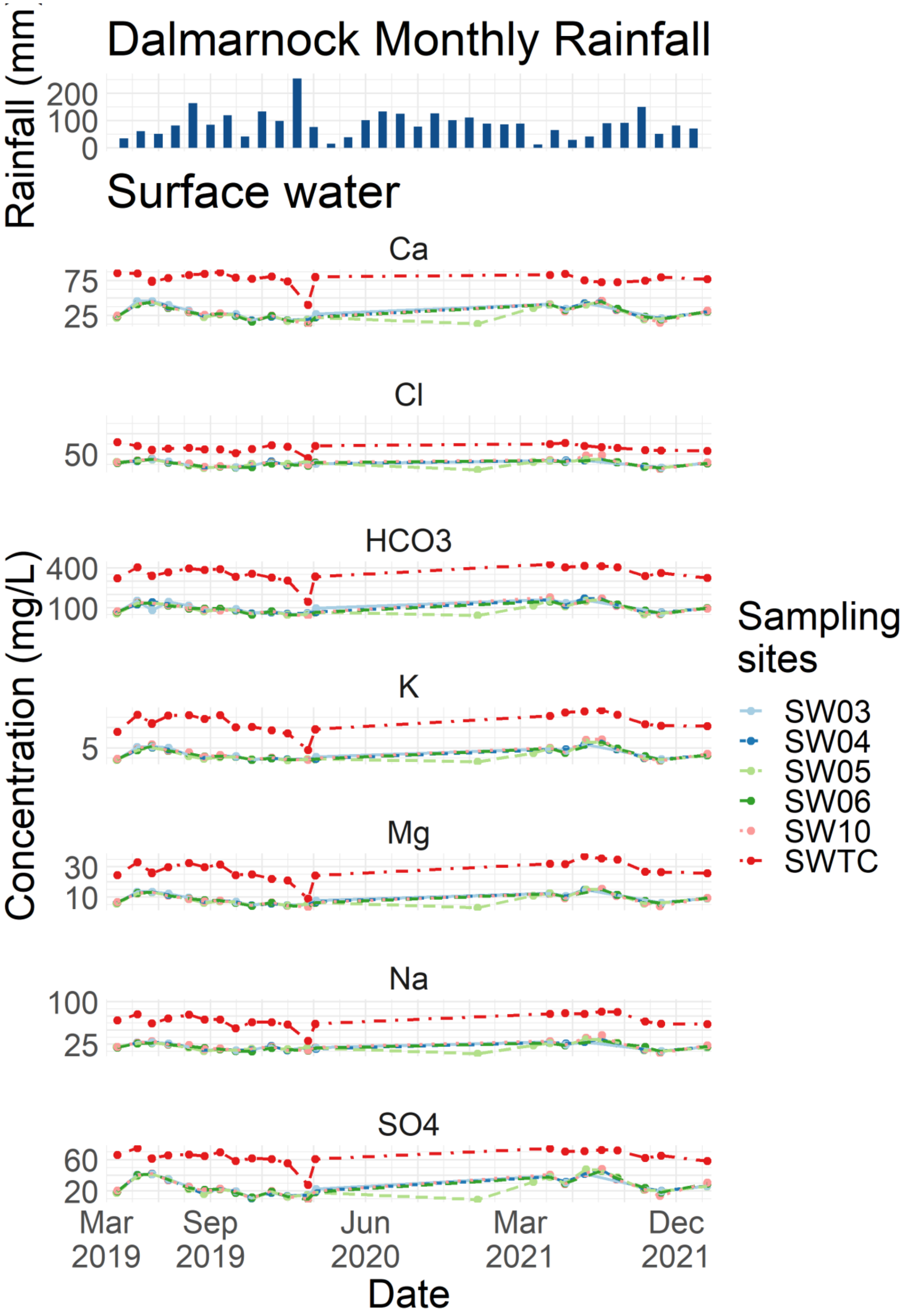

Figure 20 Time-series of major ions measured during surface water sampling. The top panel shows monthly rainfall totals at Dalmarnock. Rainfall data ©SEPA, 2023

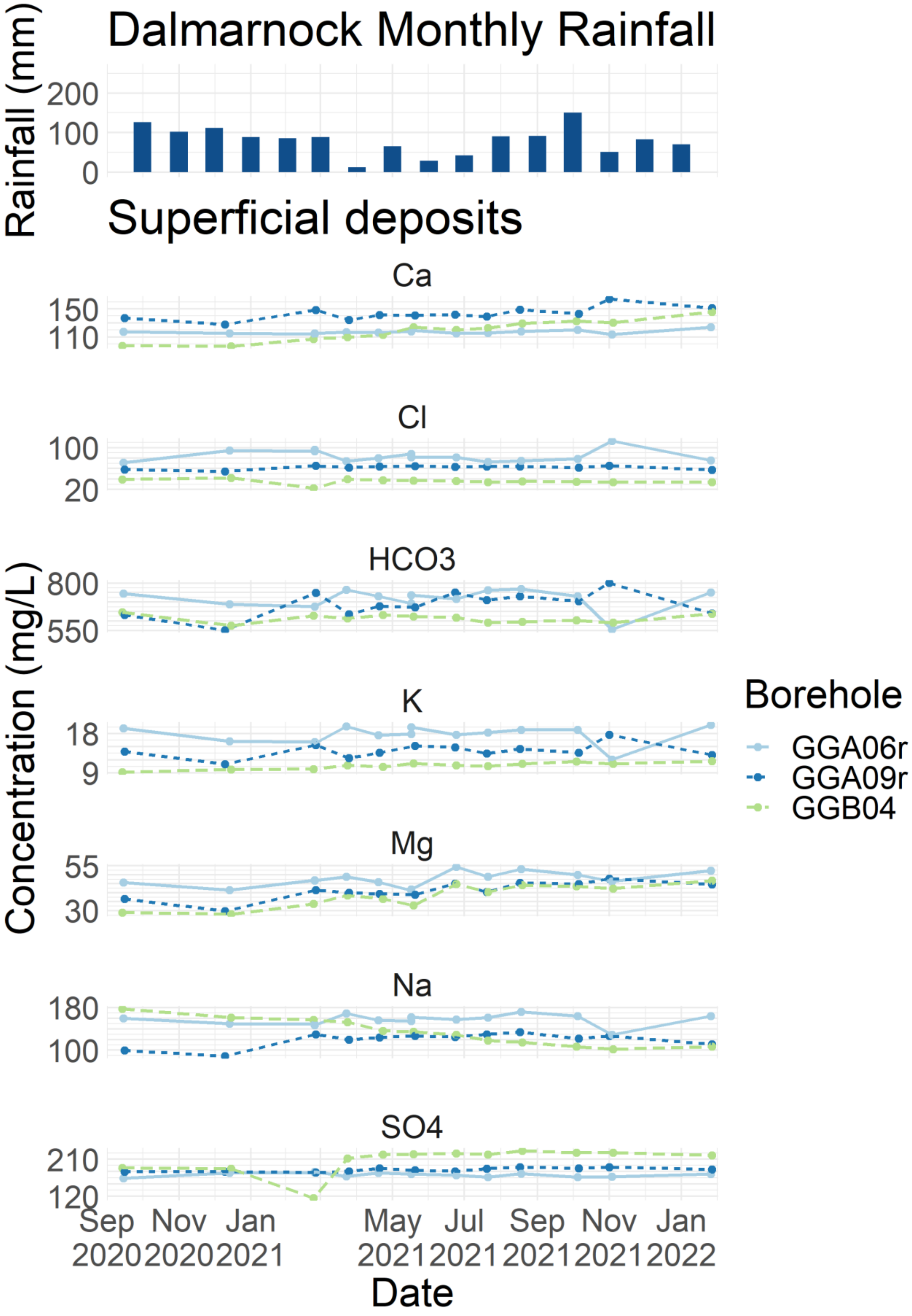

Figure 21 Time-series of major ions measured during sampling of superficial deposits boreholes. The top panel shows monthly rainfall totals at Dalmarnock. Rainfall data ©SEPA, 2023

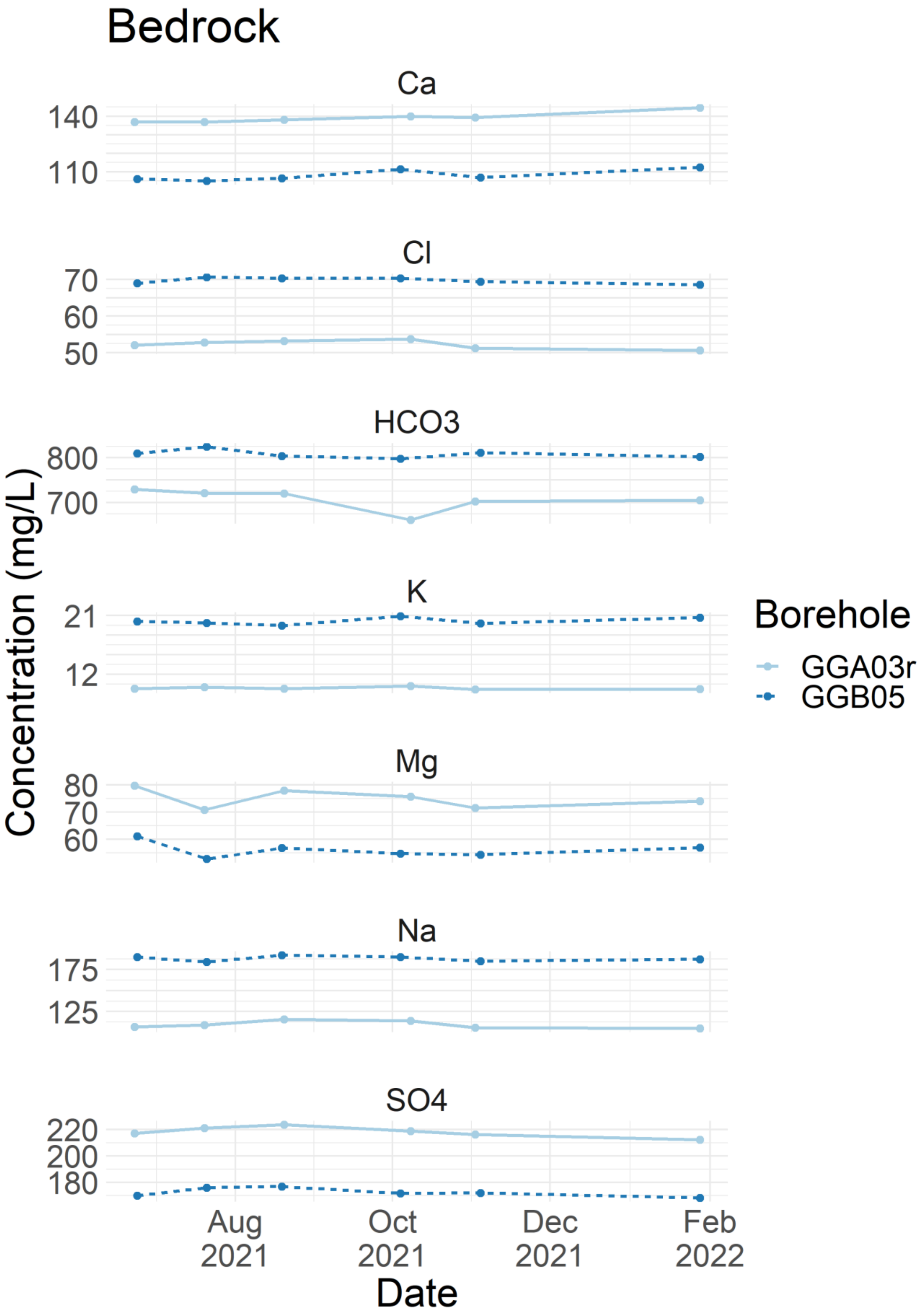

Figure 22 Time-series of major ions measured during sampling of bedrock boreholes.

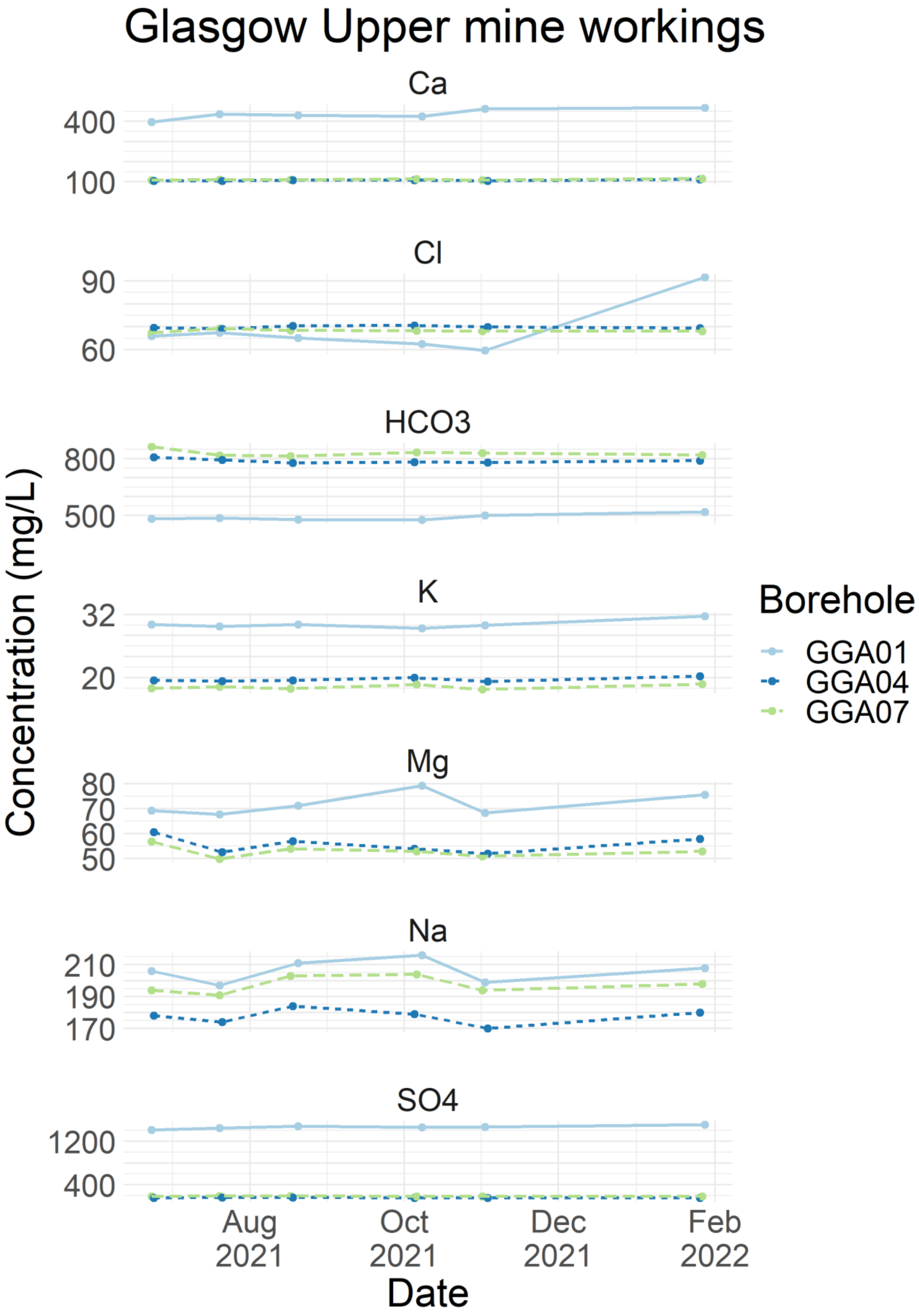

Figure 23 Time-series of major ions measured during sampling of Glasgow Upper mine working boreholes.

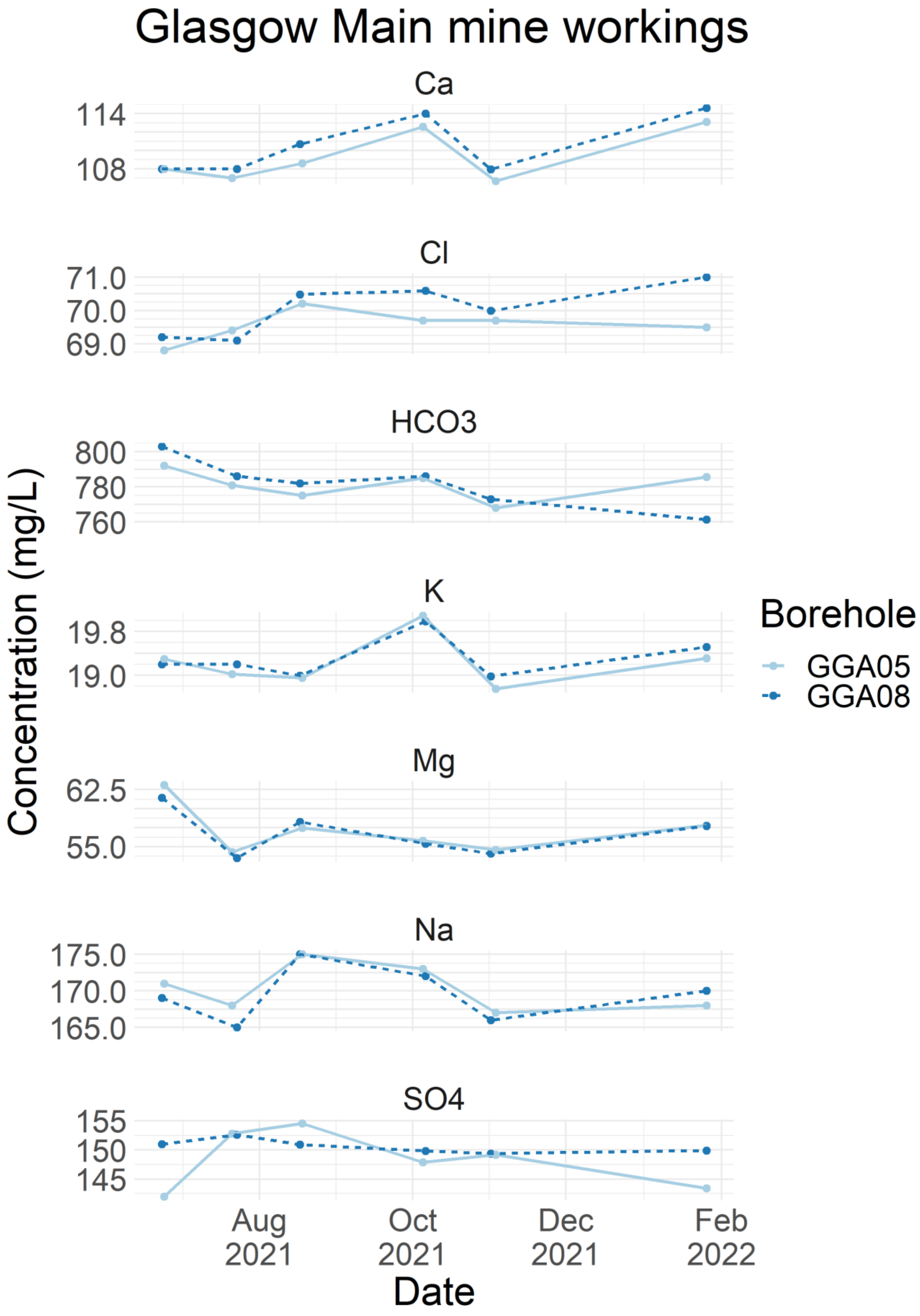

Figure 24 Time-series of major ions measured during sampling of Glasgow Main mine working boreholes.

MINOR ELEMENTS AND OTHER PARAMETERS mg/L

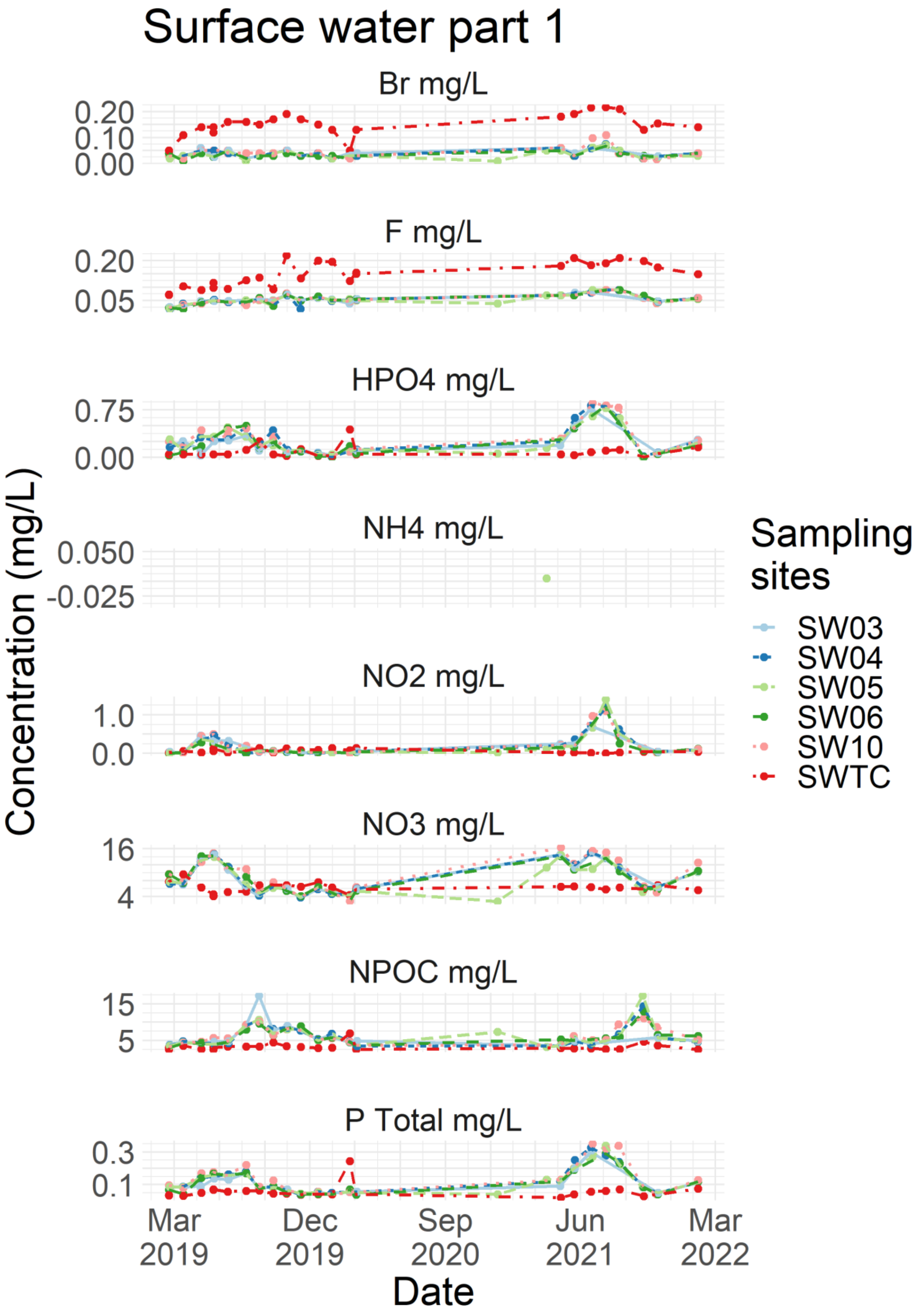

Figure 25 Time series of other parameter concentrations measured in mg/L measured during surface water sampling. EQS AA for F = 5 mg/L. Data < detection limit (DL) are set to ½ DL.

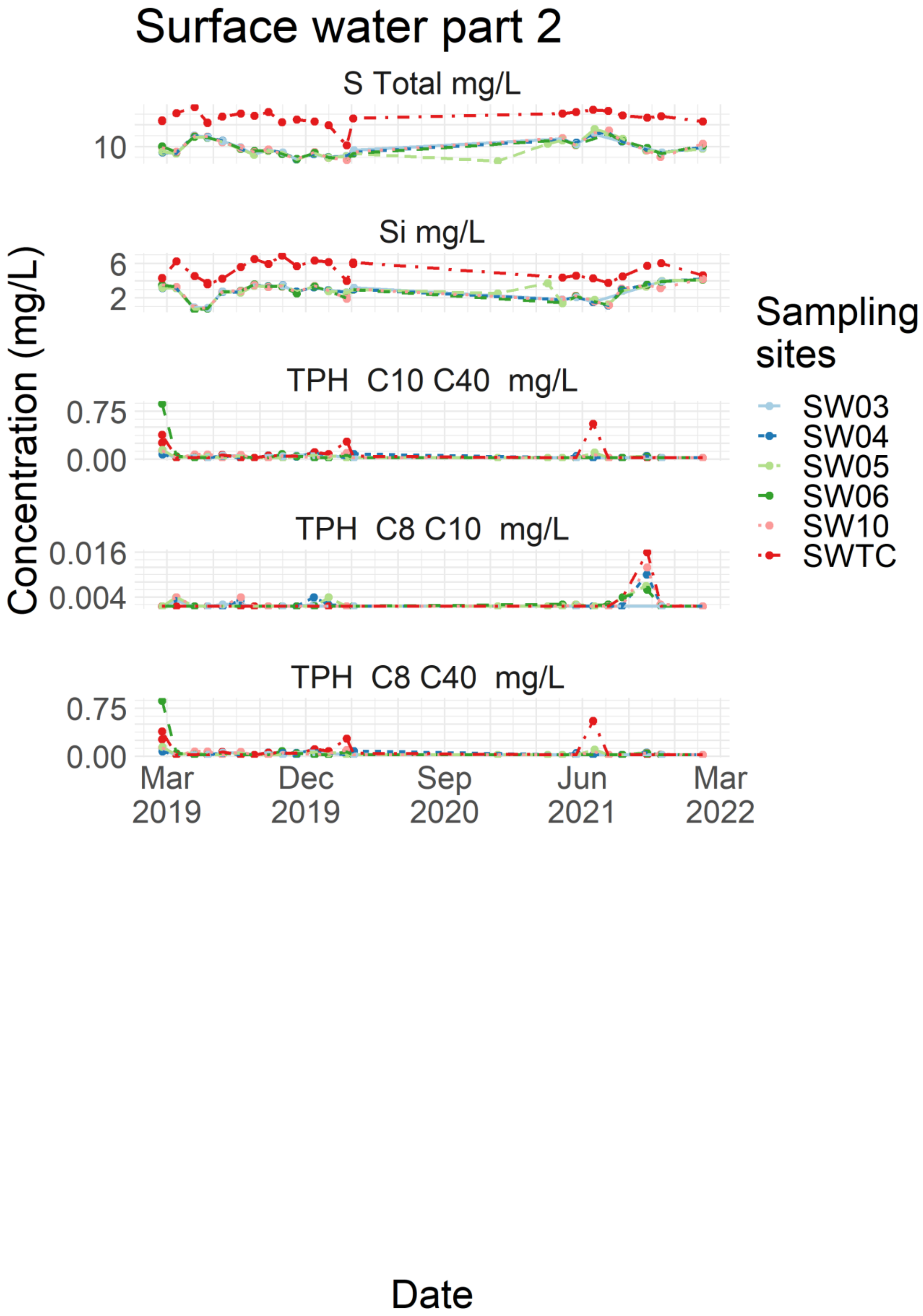

Figure 26 Time series of other parameter concentrations measured in mg/L measured during surface water sampling. Data < detection limit (DL) are set to ½ DL.

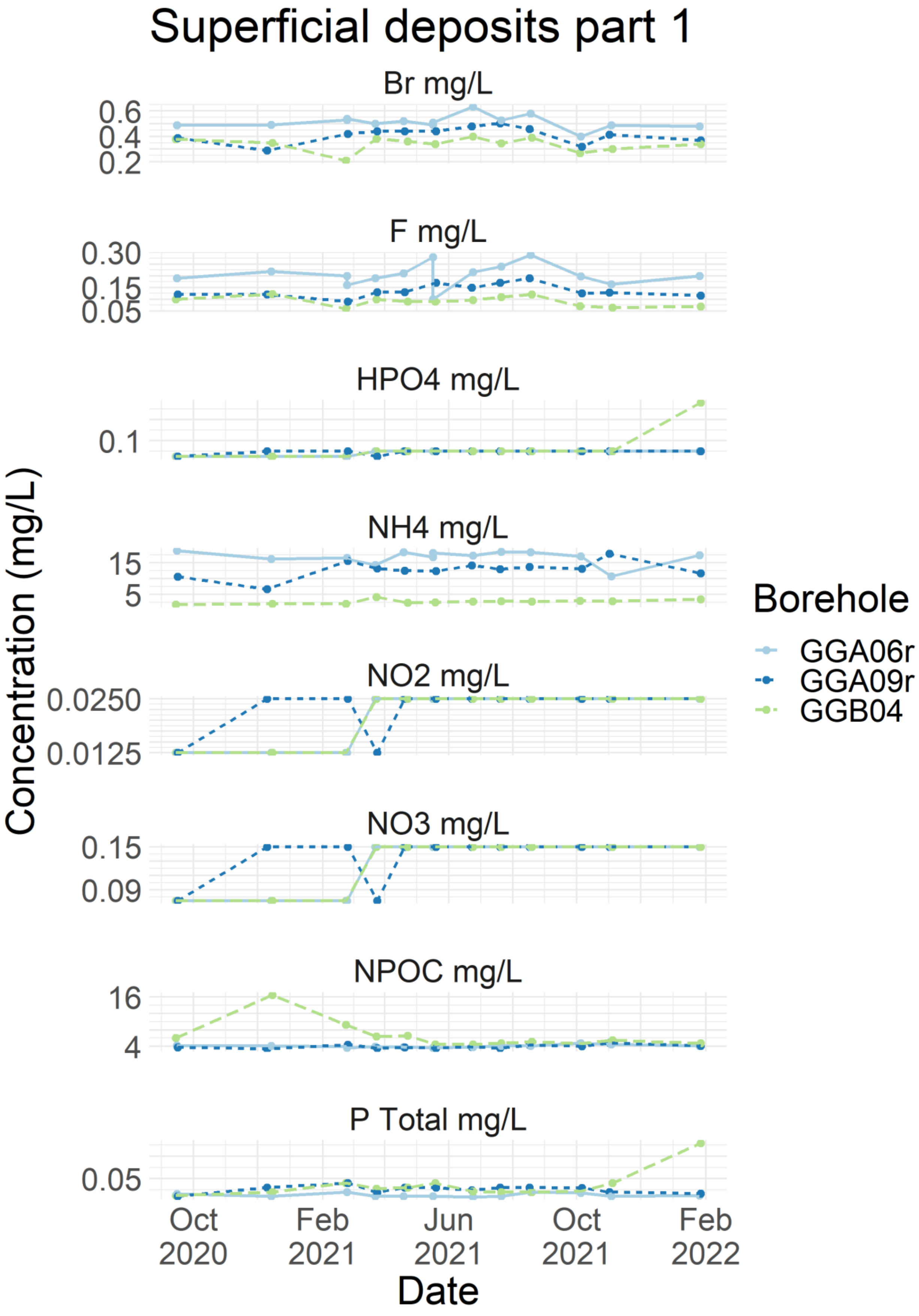

Figure 27 Time series of other parameter concentrations measured in mg/L measured during sampling of superficial deposits boreholes. Data < detection limit (DL) are set to ½ DL.

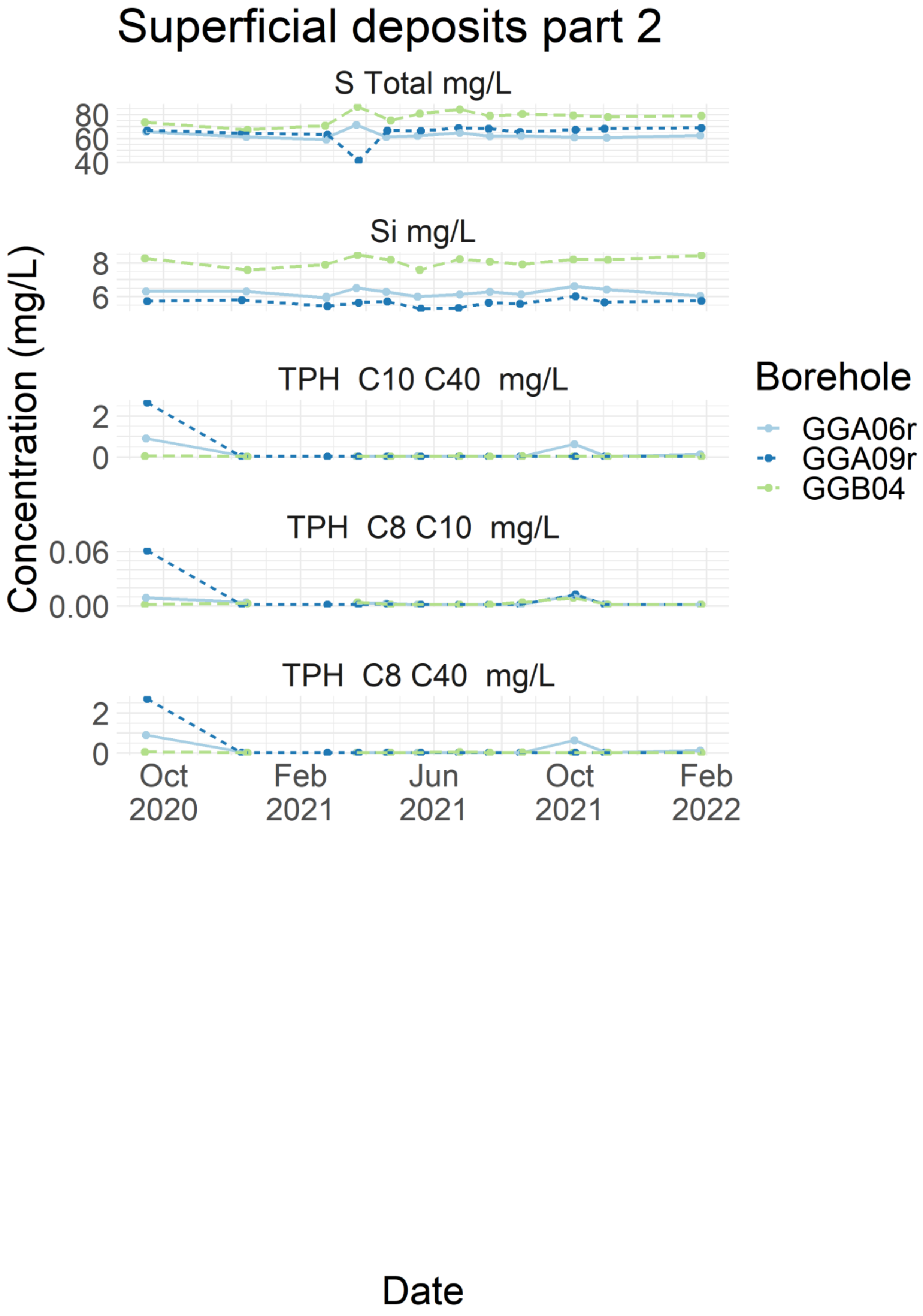

Figure 28 Time series of other parameter concentrations measured in mg/L measured during sampling of superficial deposits boreholes. Data < detection limit (DL) are set to ½ DL.

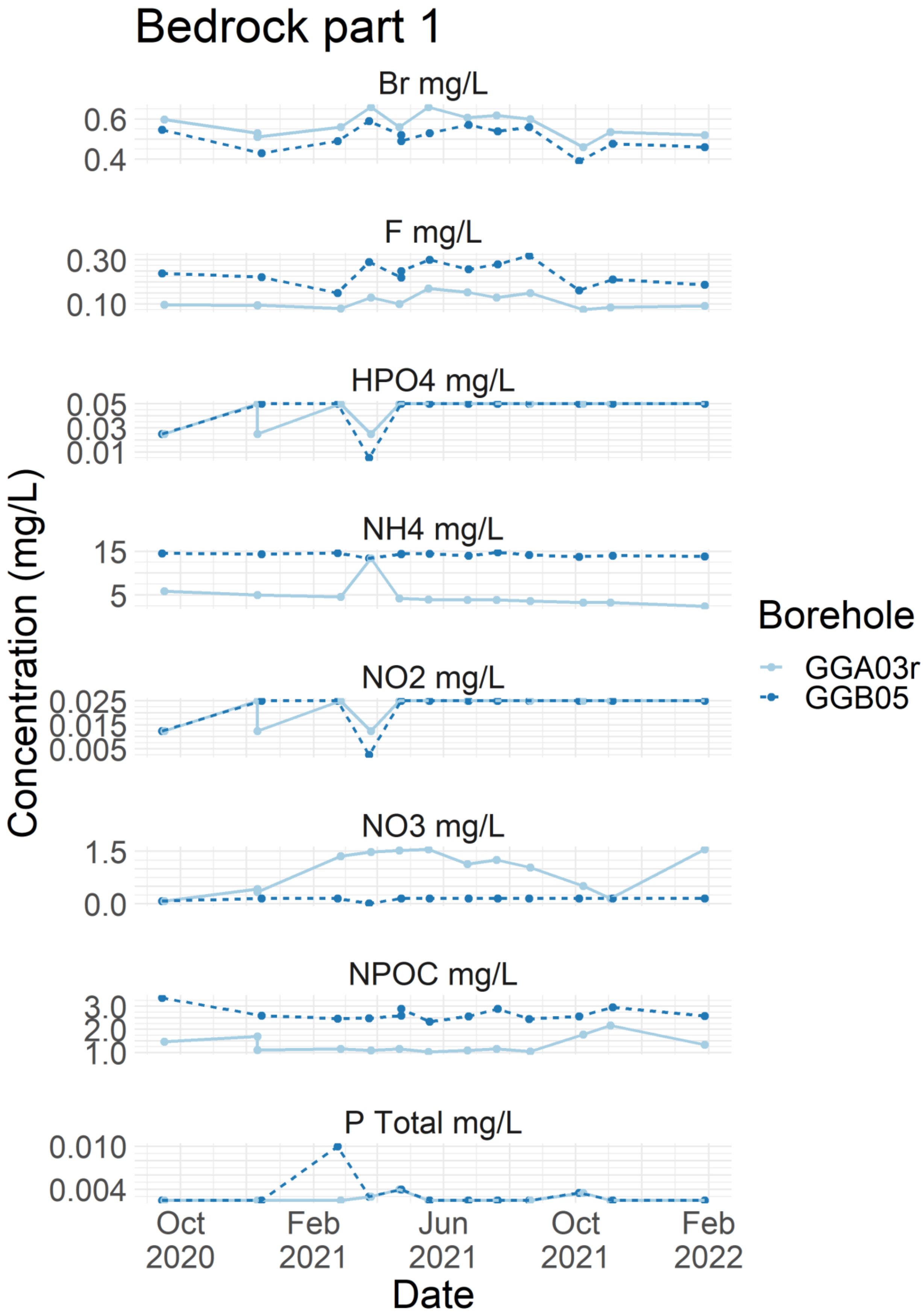

Figure 29 Time series of other parameter concentrations measured in mg/L measured during sampling of bedrock boreholes. Data < detection limit (DL) are set to ½ DL.

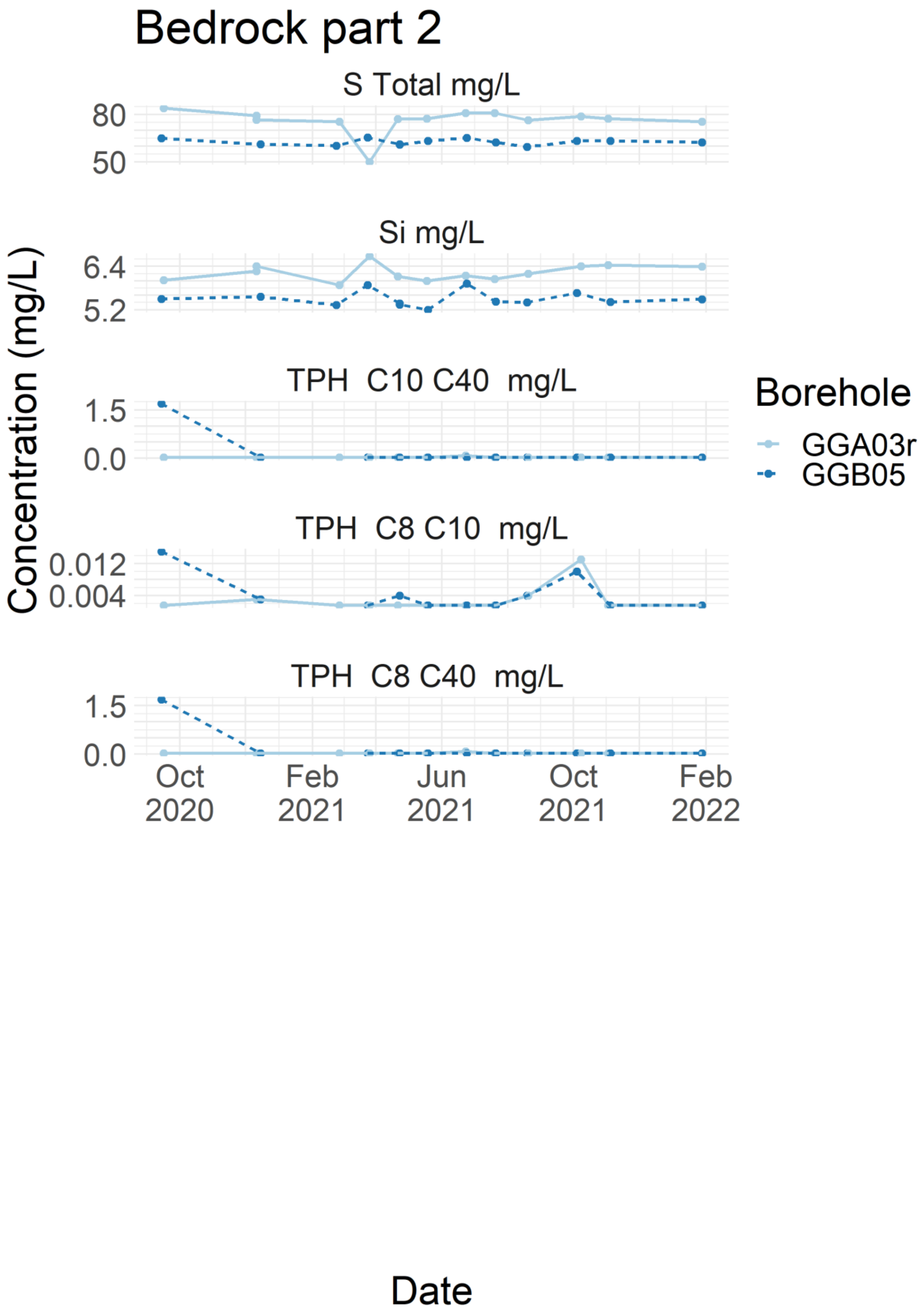

Figure 30 Time series of other parameter concentrations measured in mg/L measured during sampling of bedrock boreholes. Data < detection limit (DL) are set to ½ DL.

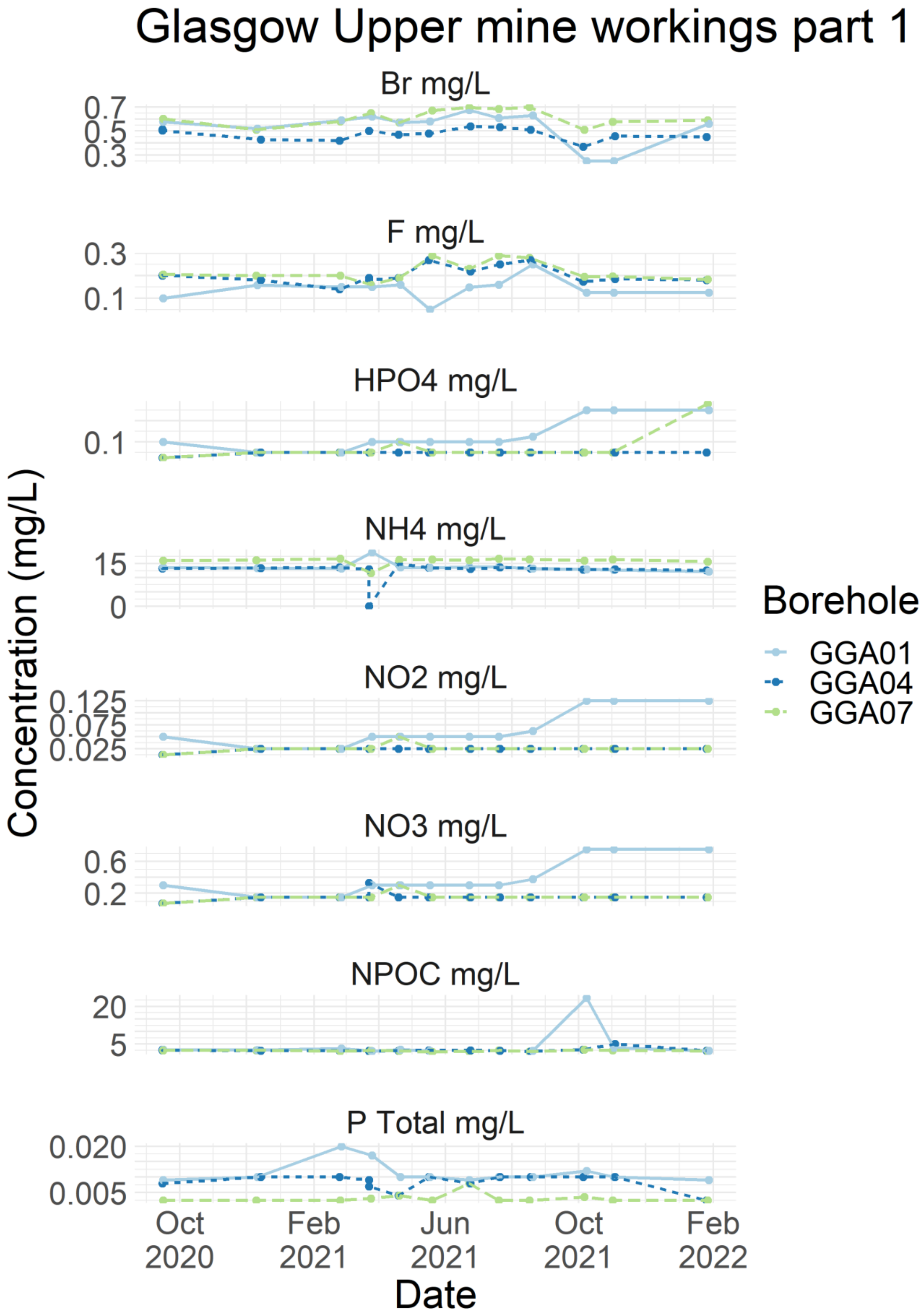

Figure 31 Time series of other parameter concentrations measured in mg/L measured during sampling of Glasgow Upper mine workings boreholes. Data < detection limit (DL) are set to ½ DL.

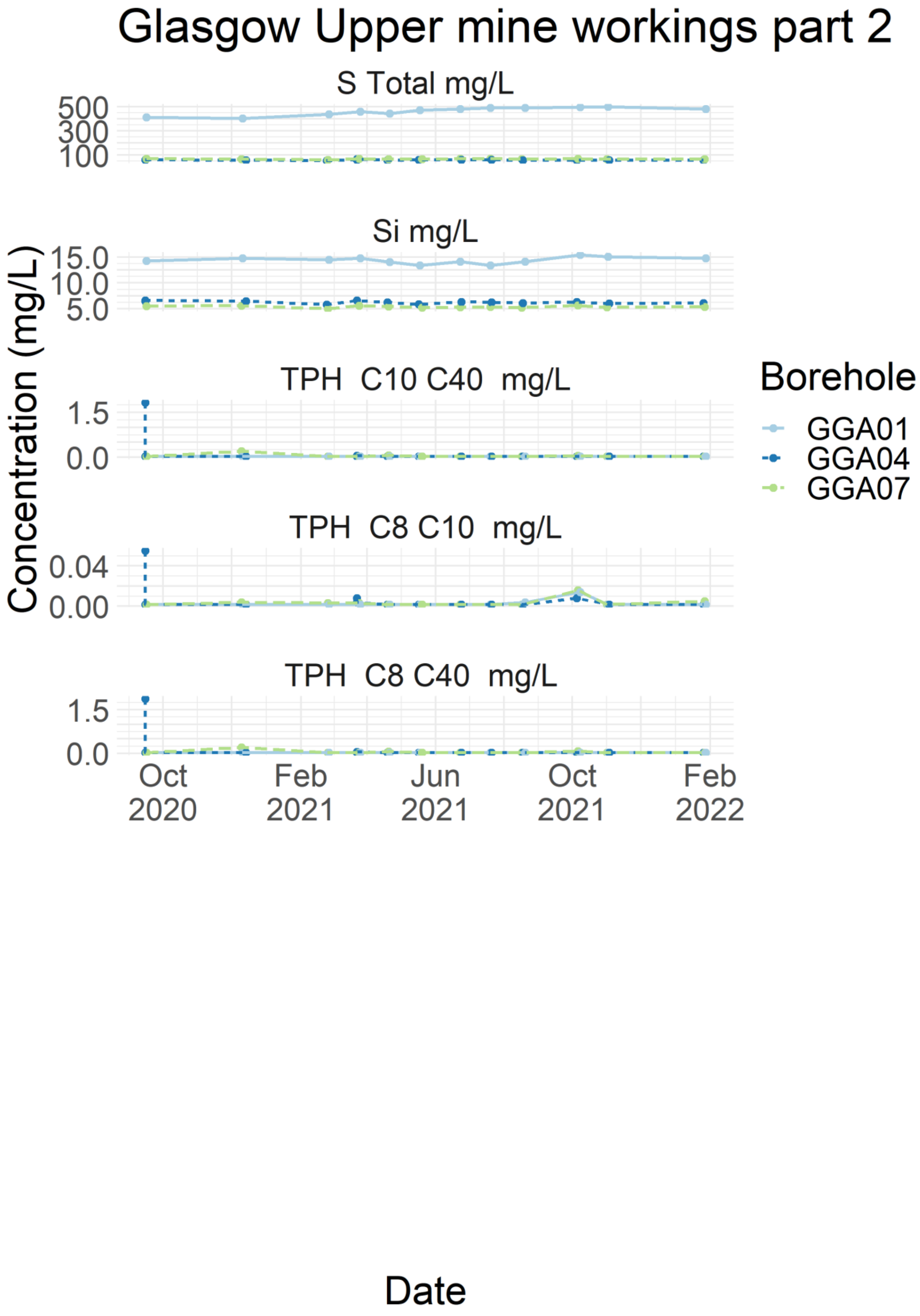

Figure 32 Time series of other parameter concentrations measured in mg/L measured during sampling of Glasgow Upper mine workings boreholes. Data < detection limit (DL) are set to ½ DL.

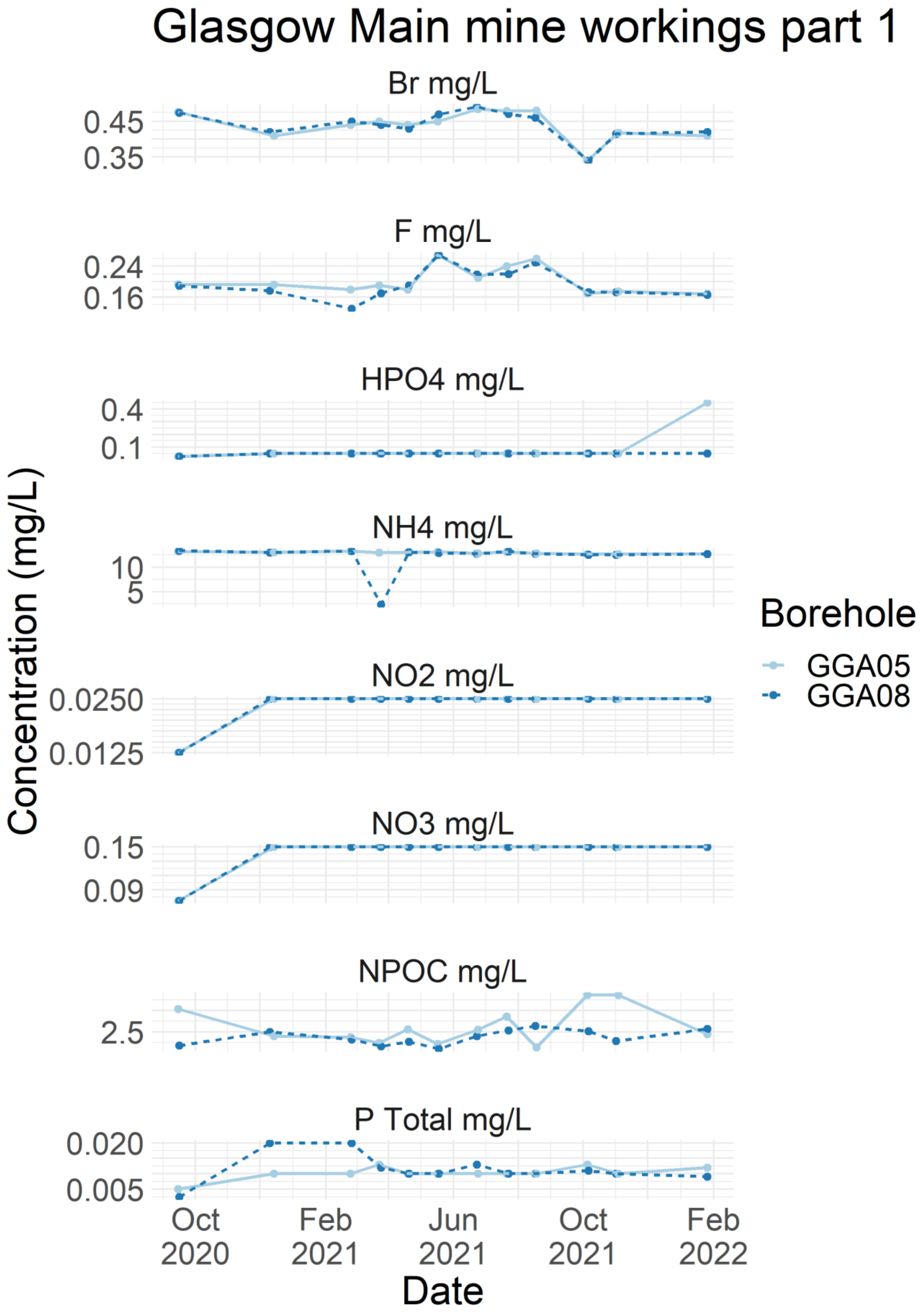

Figure 33 Time series of other parameter concentrations measured in mg/L measured during sampling of Glasgow Main mine workings boreholes. Data < detection limit (DL) are set to ½ DL.

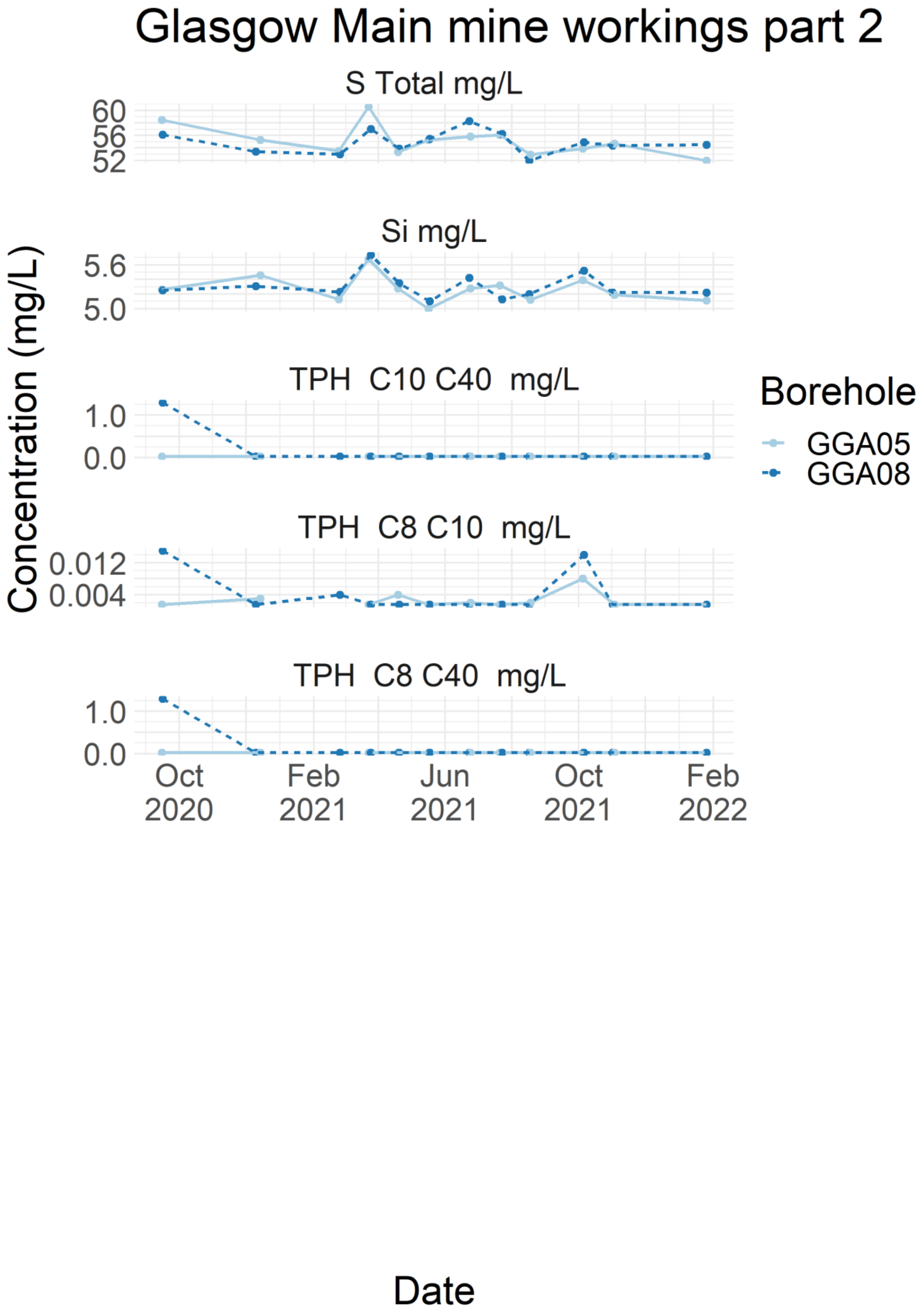

Figure 34 Time series of other parameter concentrations measured in mg/L measured during sampling of Glasgow Main mine workings boreholes. Data < detection limit (DL) are set to ½ DL.

TRACE ELEMENTS AND OTHER PARAMETERS IN µg/L

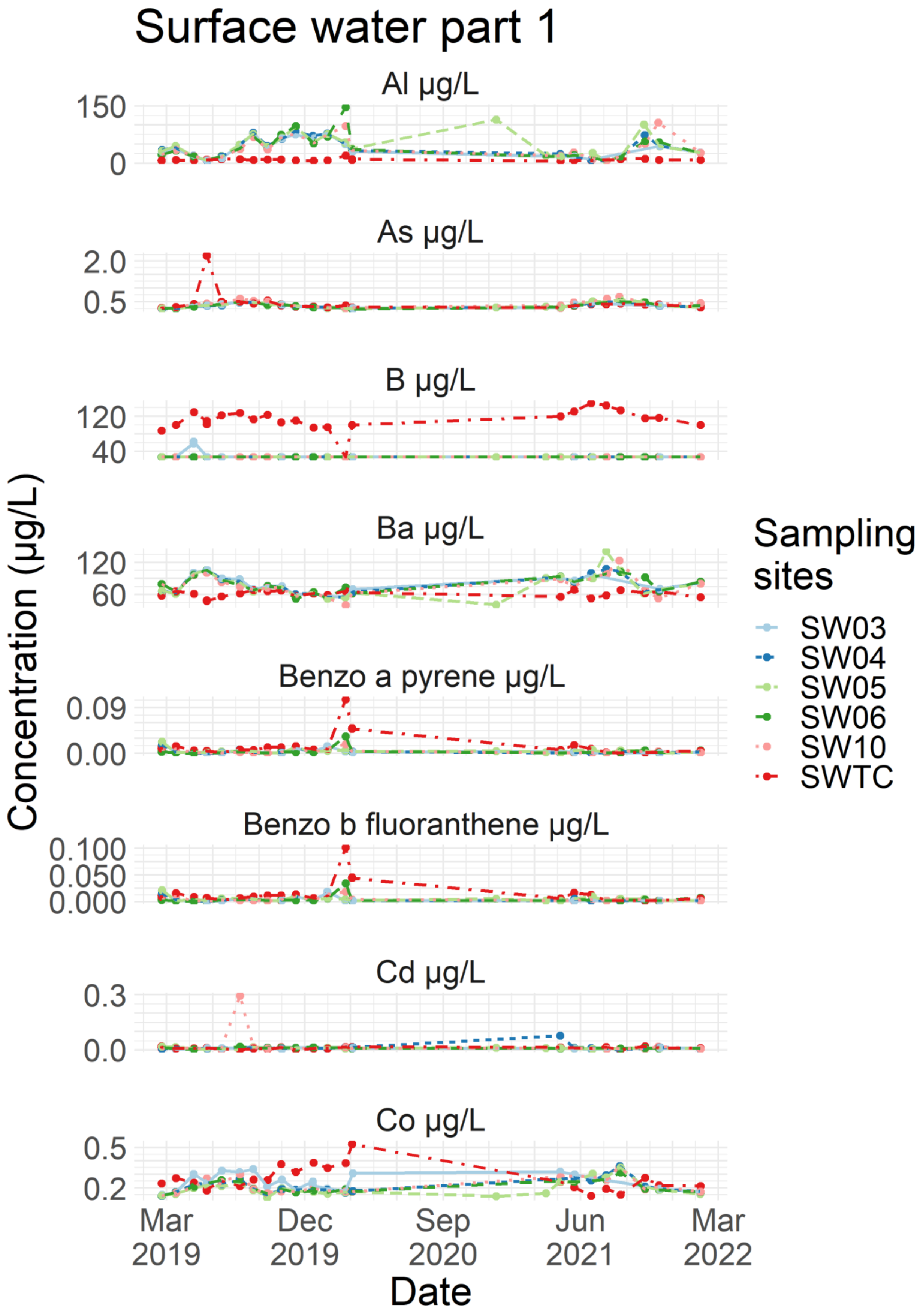

Figure 35 Time series of parameters measured in µg/L from surface water samples. EQS AA for As = 50 µg/L, B = 2000 µg/L. Data < detection limit (DL) are set to ½ DL.

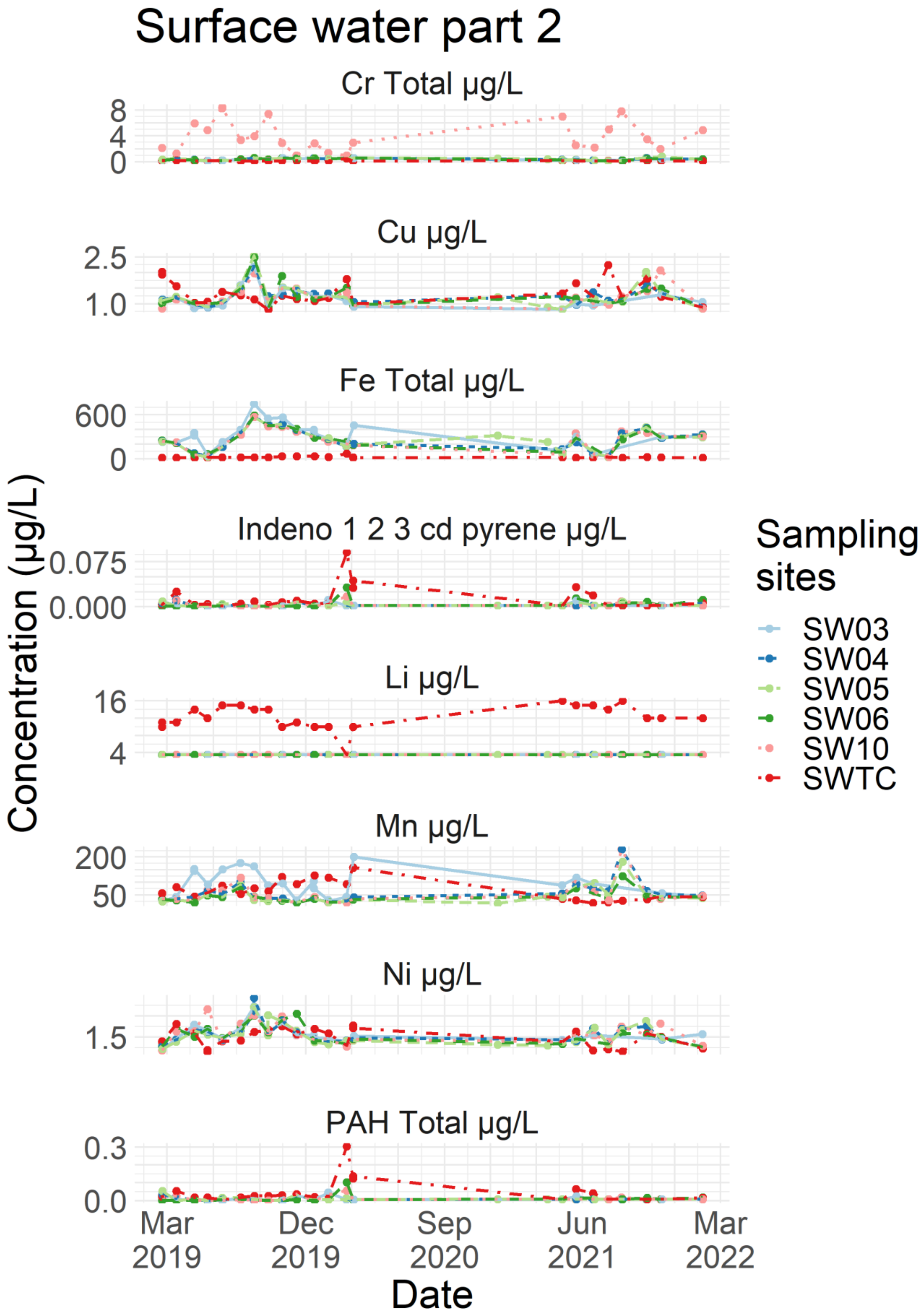

Figure 36 Time series of parameters measured in µg/L from surface water samples EQS AA for Ni = 4 µg/L. Data < detection limit (DL) are set to ½ DL.

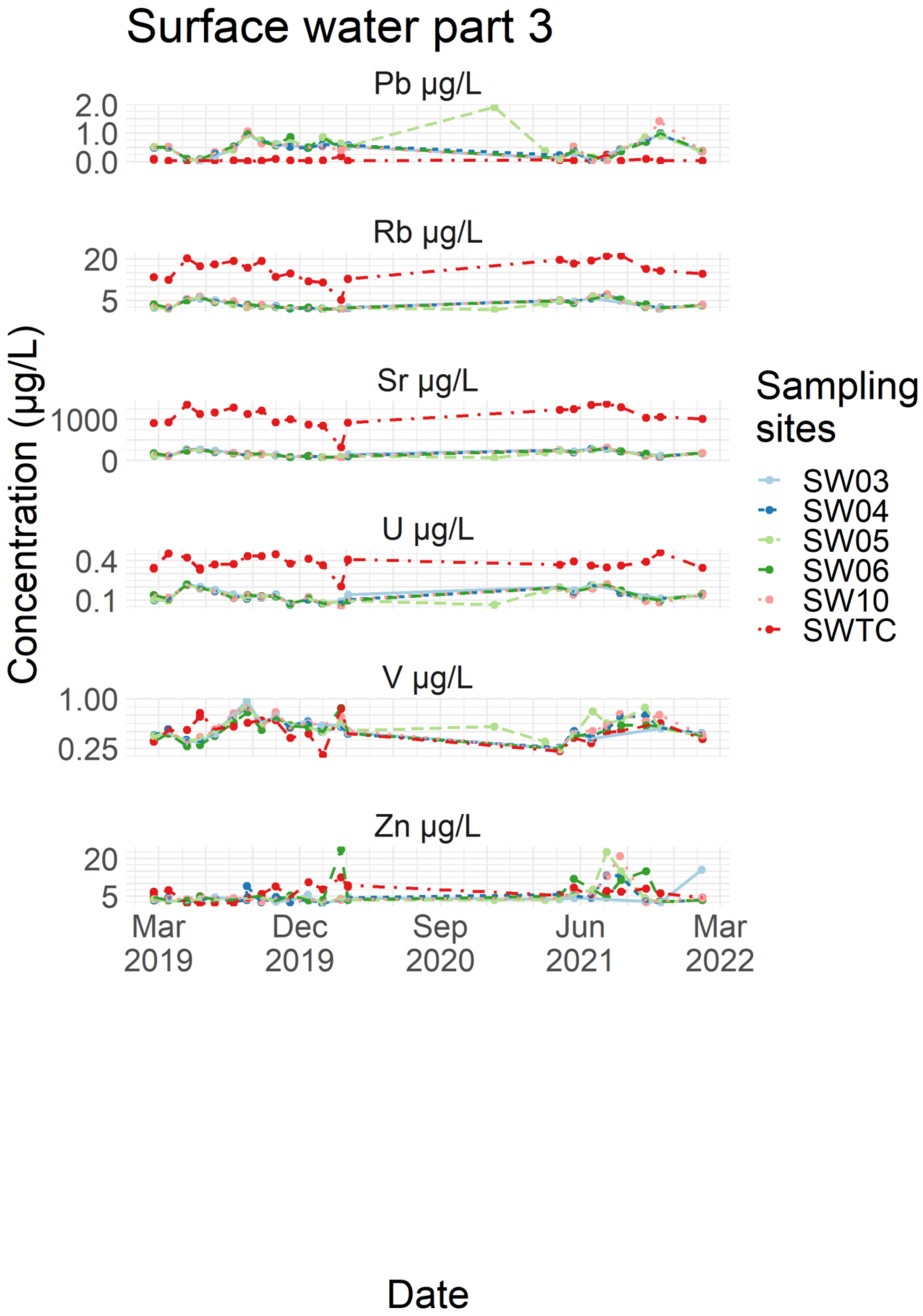

Figure 37 Time series of parameters measured in µg/L from surface water samples EQS AA for Ni = 4 µg/L. Data < detection limit (DL) are set to ½ DL.

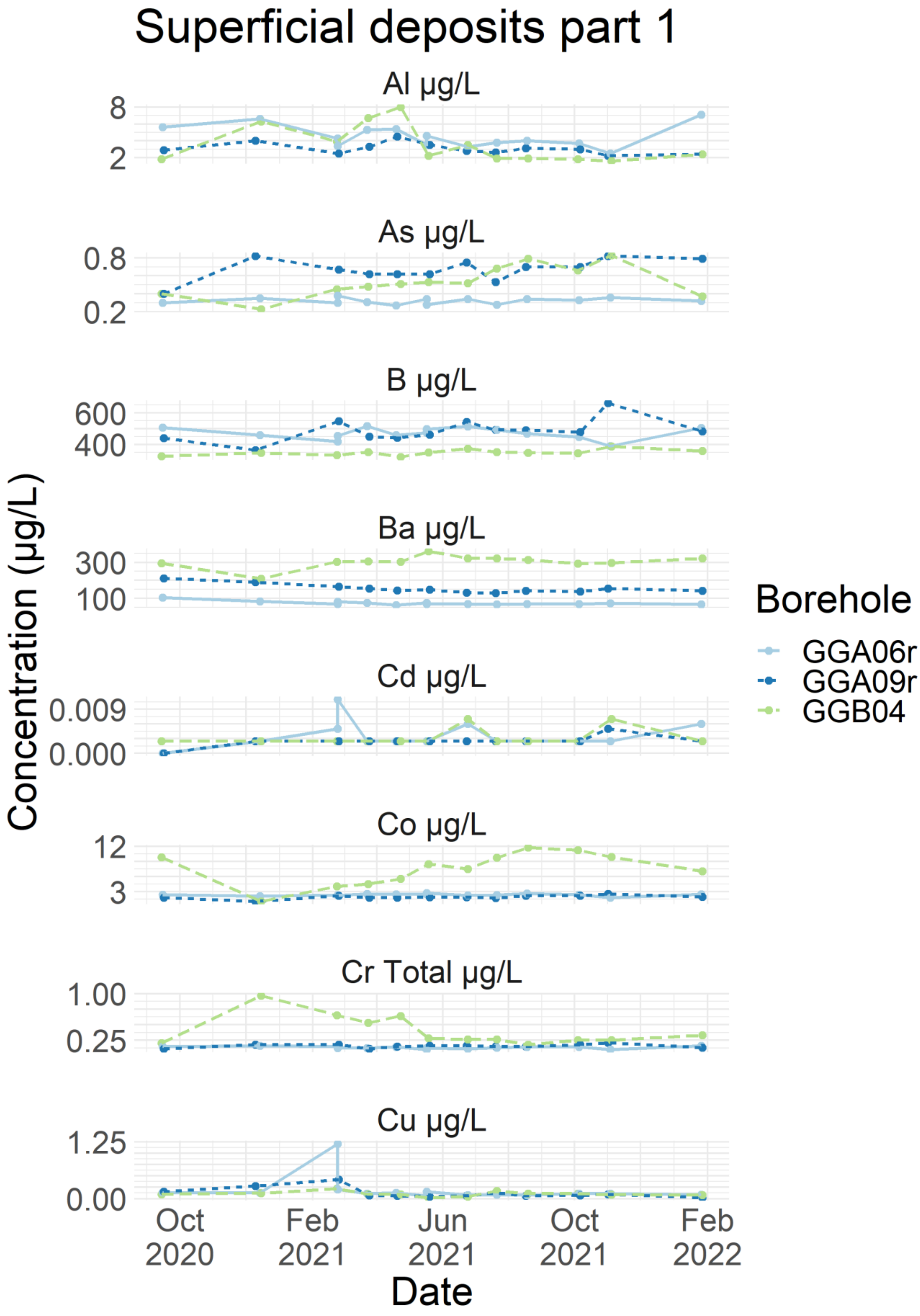

Figure 38 Time series of parameters measured in µg/L measured during sampling of superficial deposits boreholes. Data < detection limit (DL) are set to ½ DL.

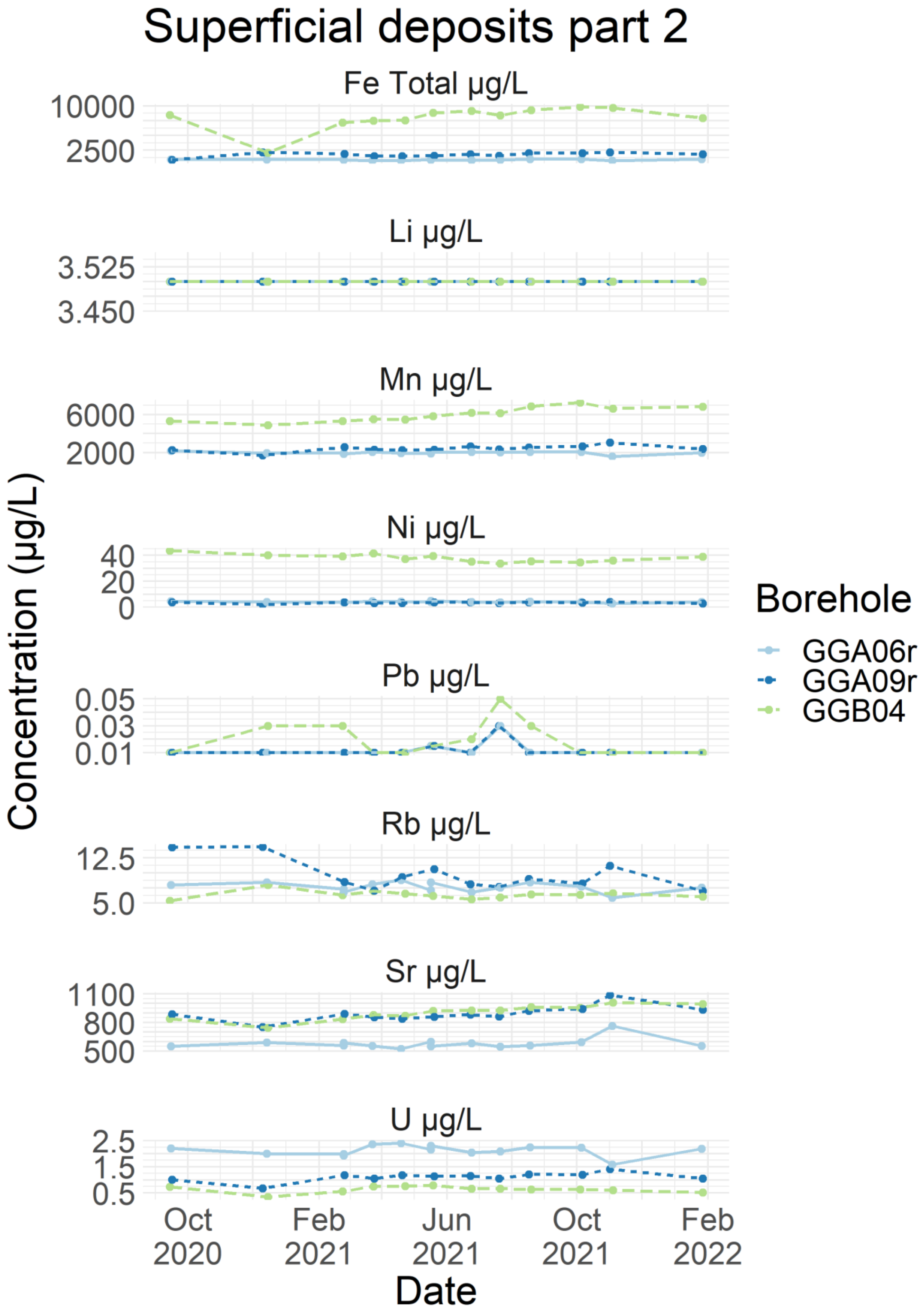

Figure 39 Time series of parameters measured in µg/L measured during sampling of superficial deposits boreholes. Data < detection limit (DL) are set to ½ DL.

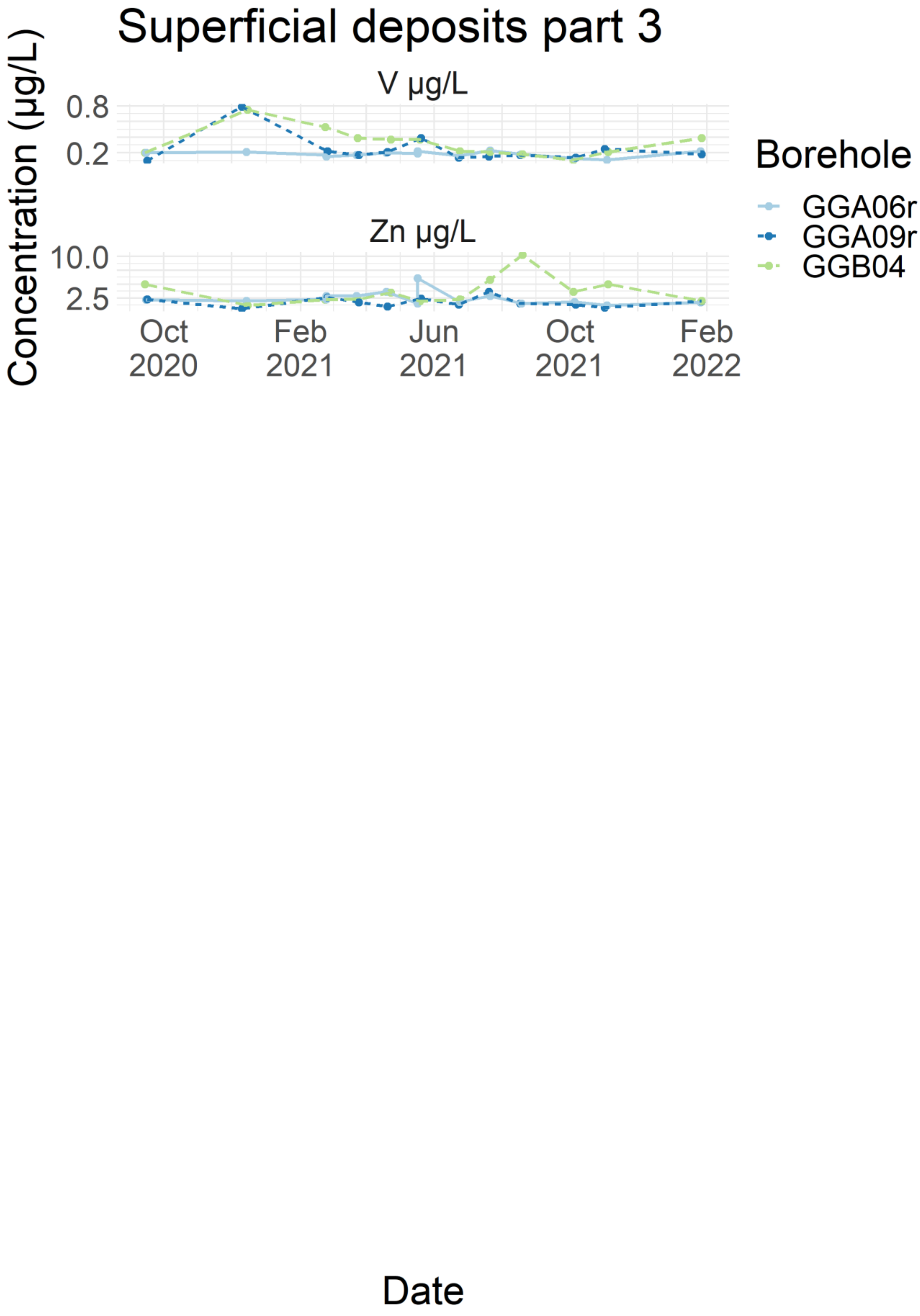

Figure 40 Time series of parameters measured in µg/L measured during sampling of superficial deposits boreholes. Data < detection limit (DL) are set to ½ DL.

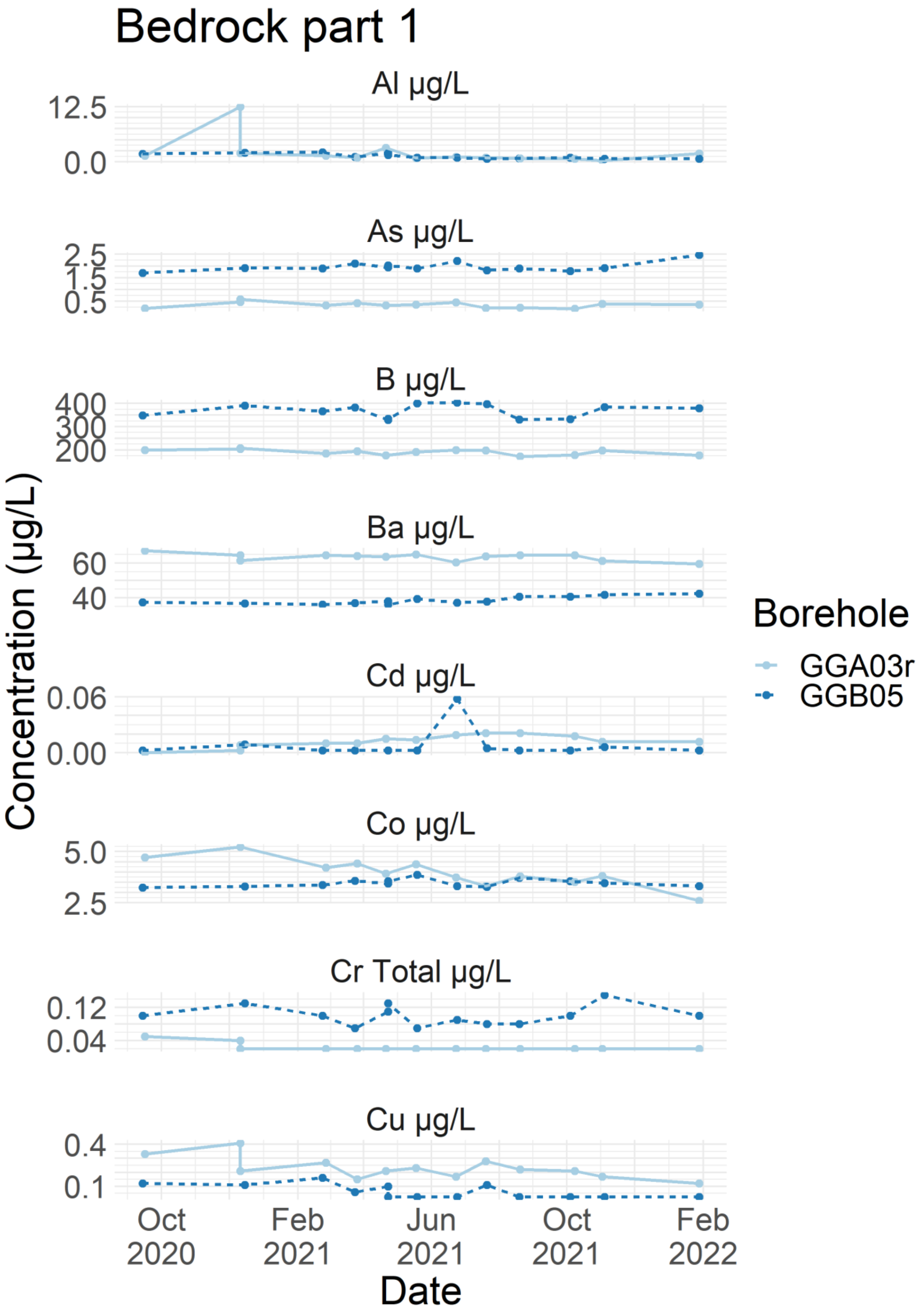

Figure 41 Time series of parameters measured in µg/L measured during sampling of bedrock boreholes. Data < detection limit (DL) are set to ½ DL.

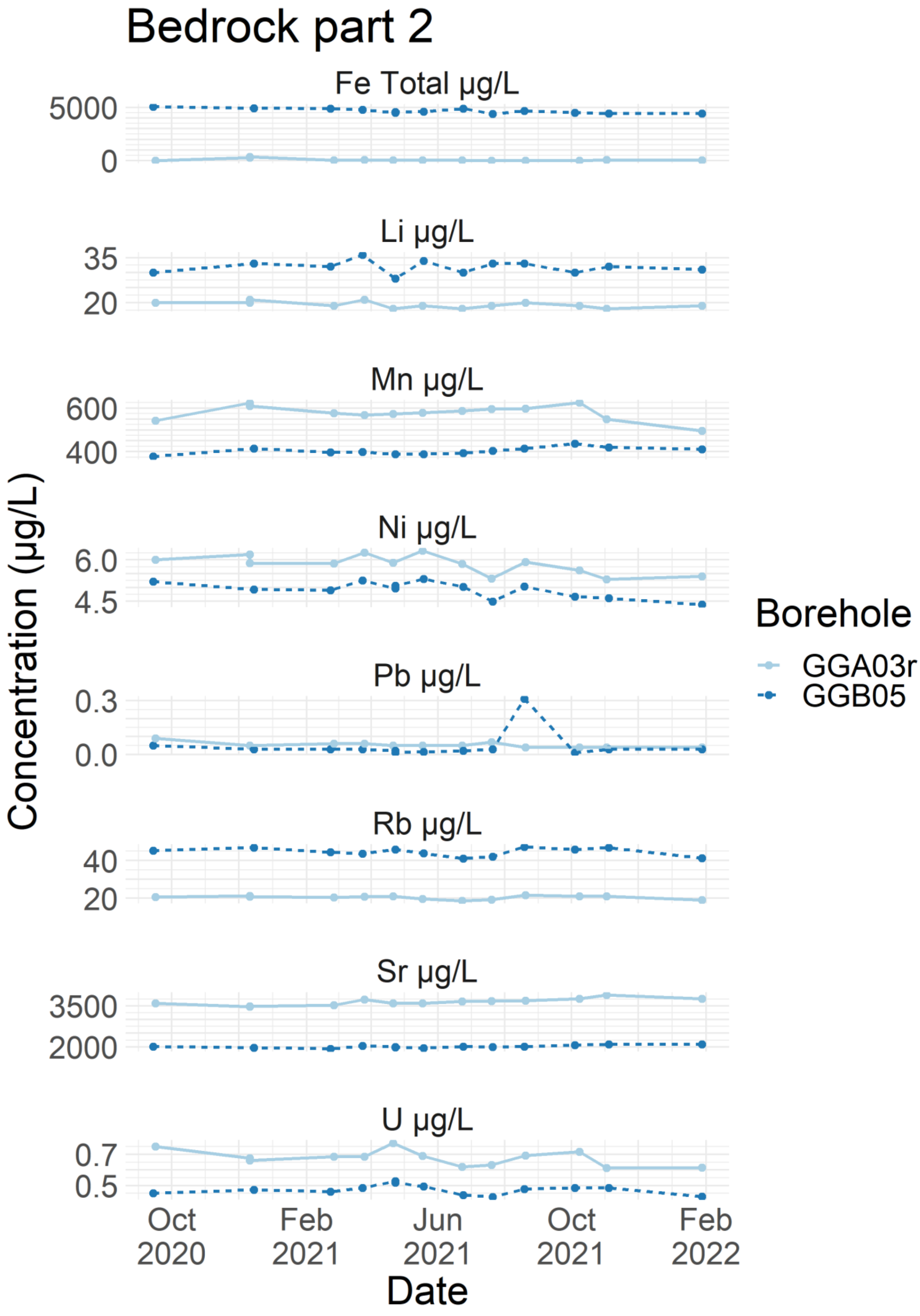

Figure 42 Time series of parameters measured in µg/L measured during sampling of bedrock boreholes. Data < detection limit (DL) are set to ½ DL.

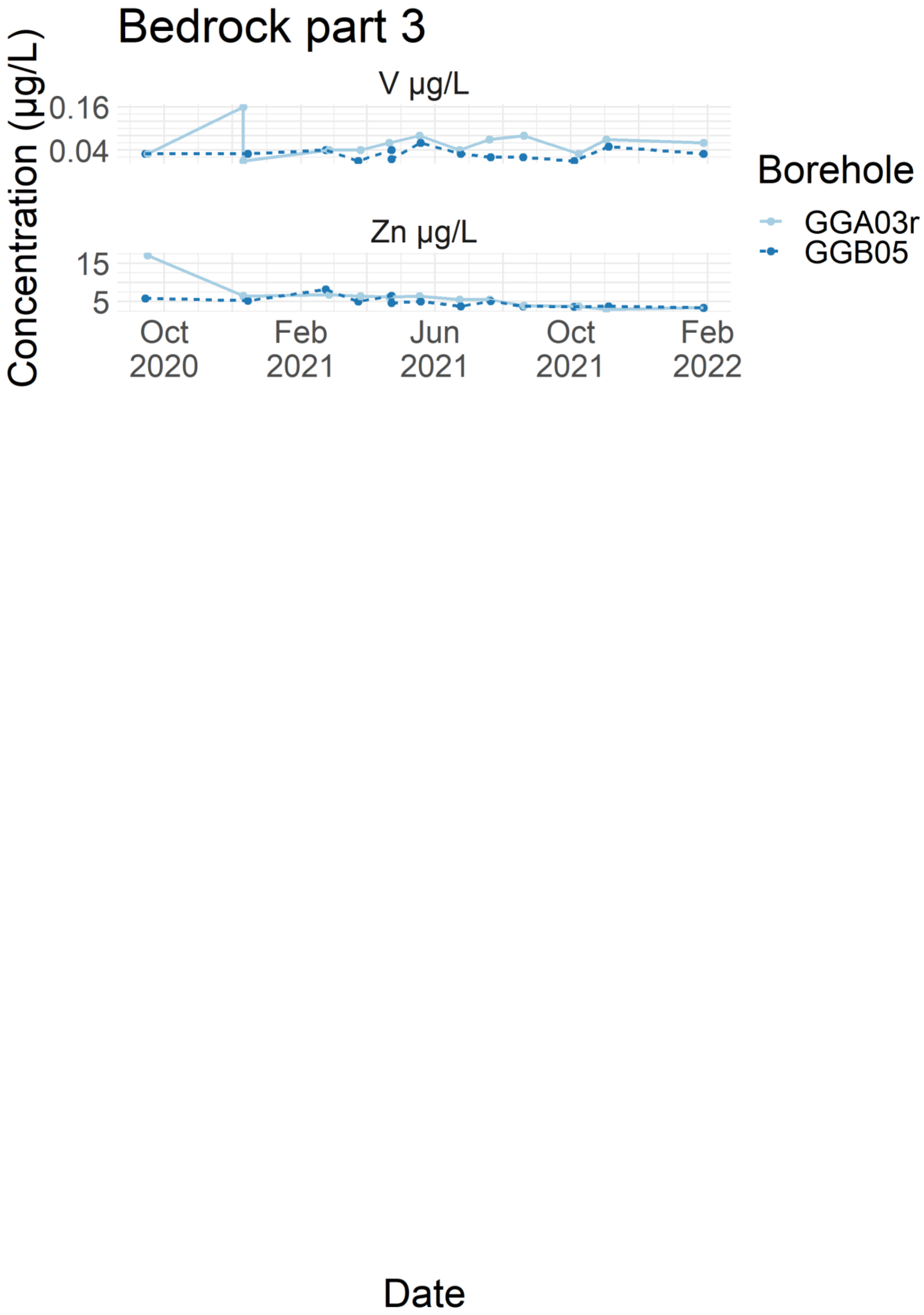

Figure 43 Time series of parameters measured in µg/L measured during sampling of bedrock boreholes. Data < detection limit (DL) are set to ½ DL.

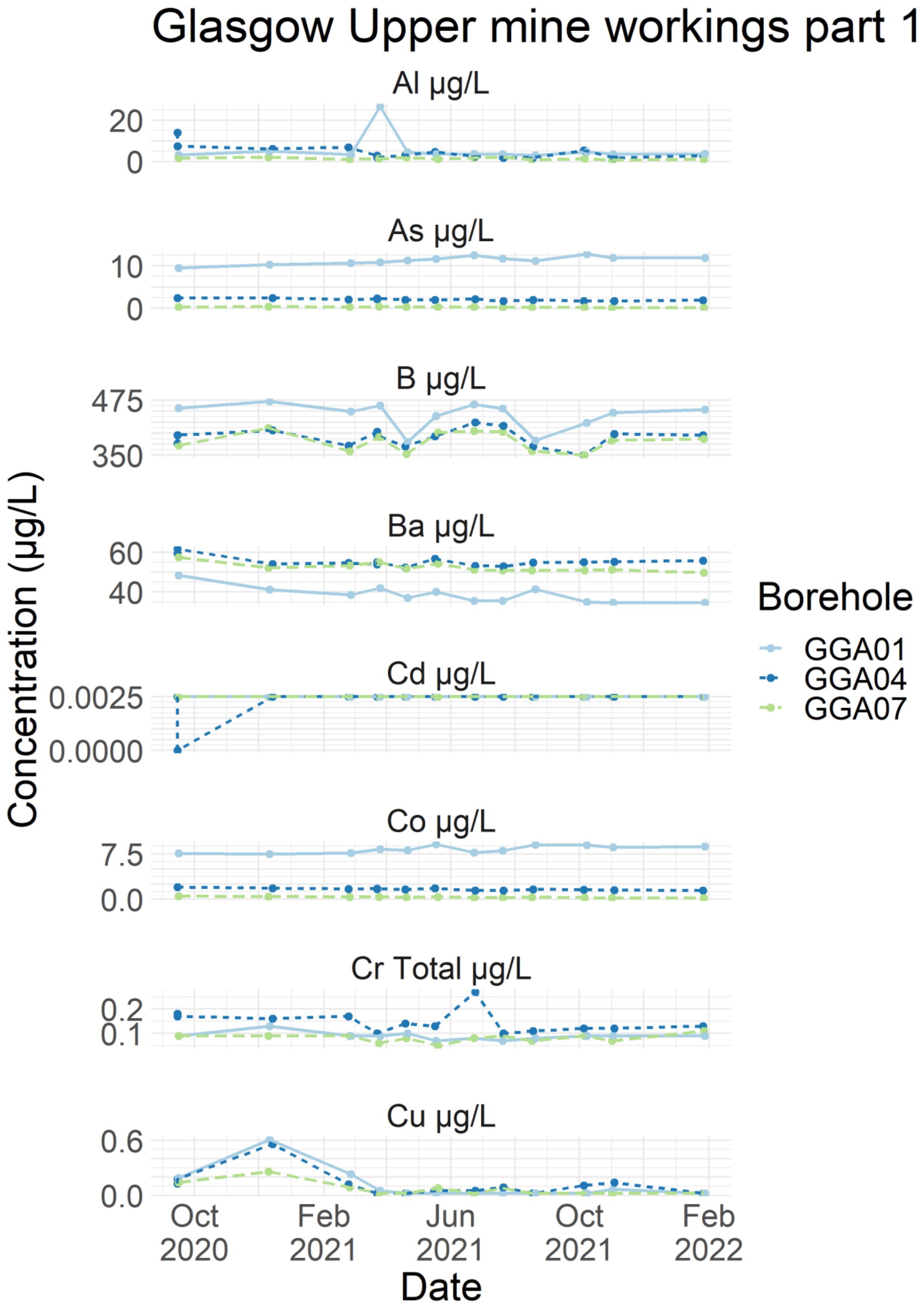

Figure 44 Time series of parameters measured in µg/L measured during sampling of Glasgow Upper mine working boreholes. Data < detection limit (DL) are set to ½ DL.

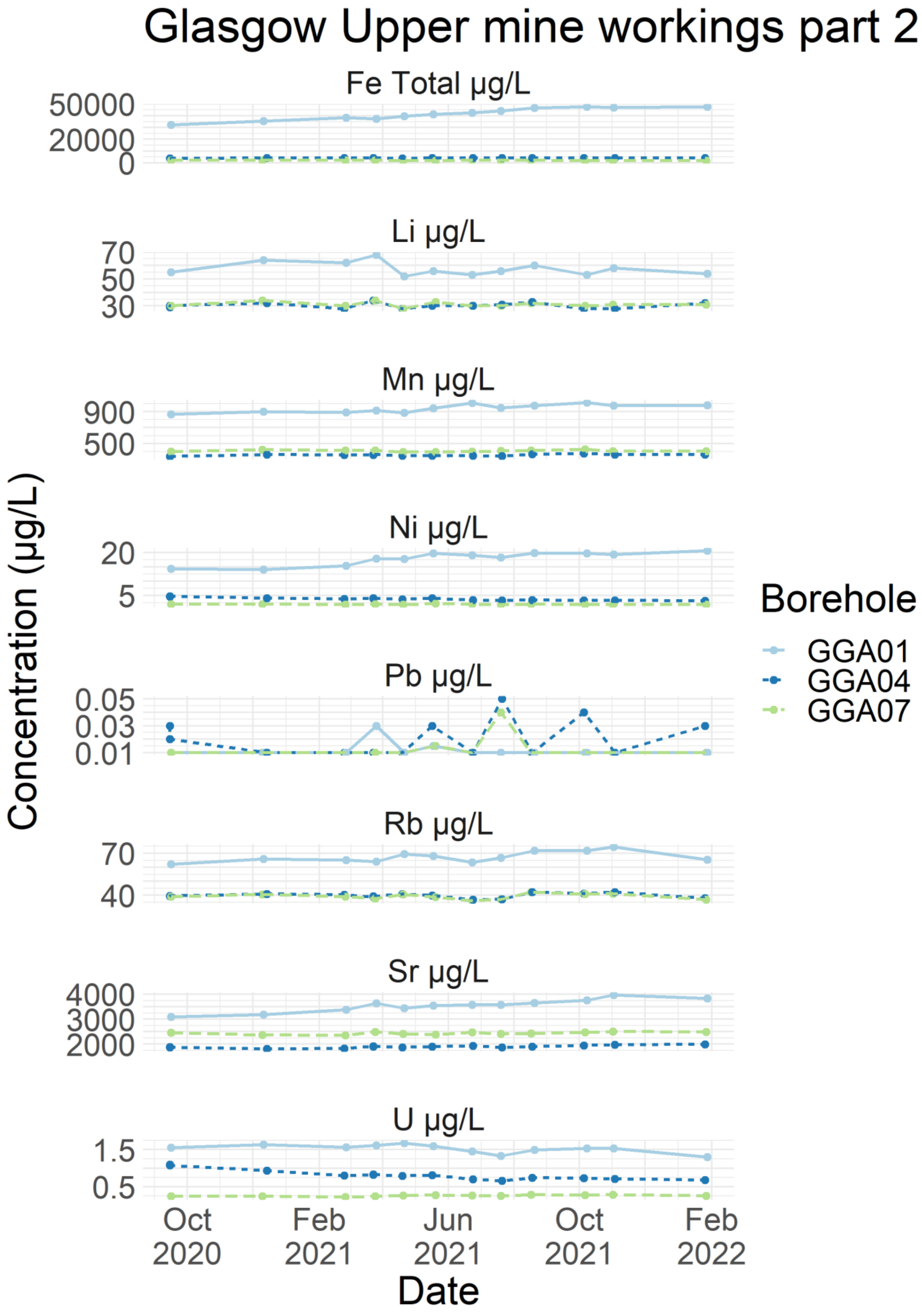

Figure 45 Time series of parameters measured in µg/L measured during sampling of Glasgow Upper mine working boreholes. Data < detection limit (DL) are set to ½ DL.

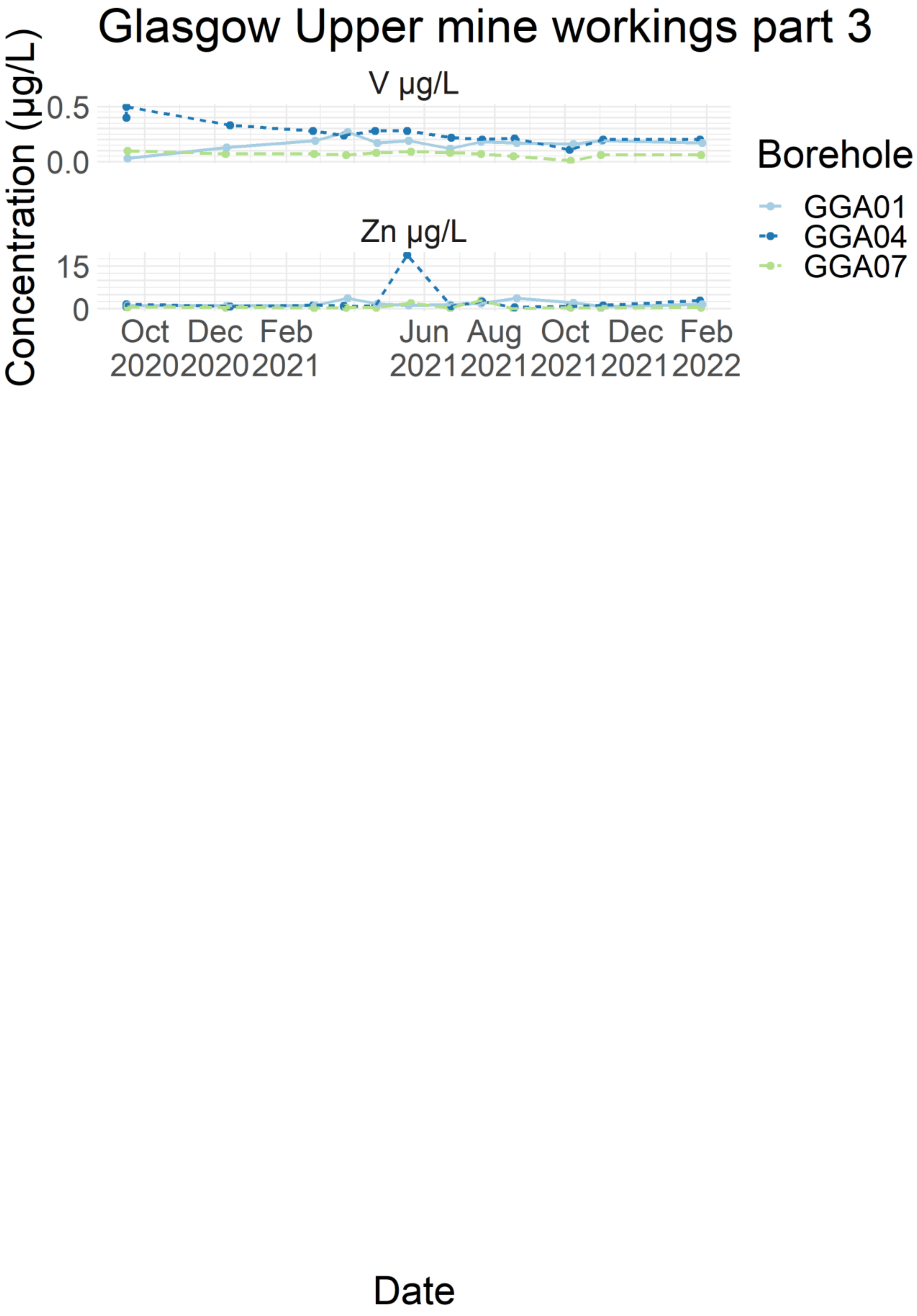

Figure 46 Time series of parameters measured in µg/L measured during sampling of Glasgow Upper mine working boreholes. Data < detection limit (DL) are set to ½ DL.

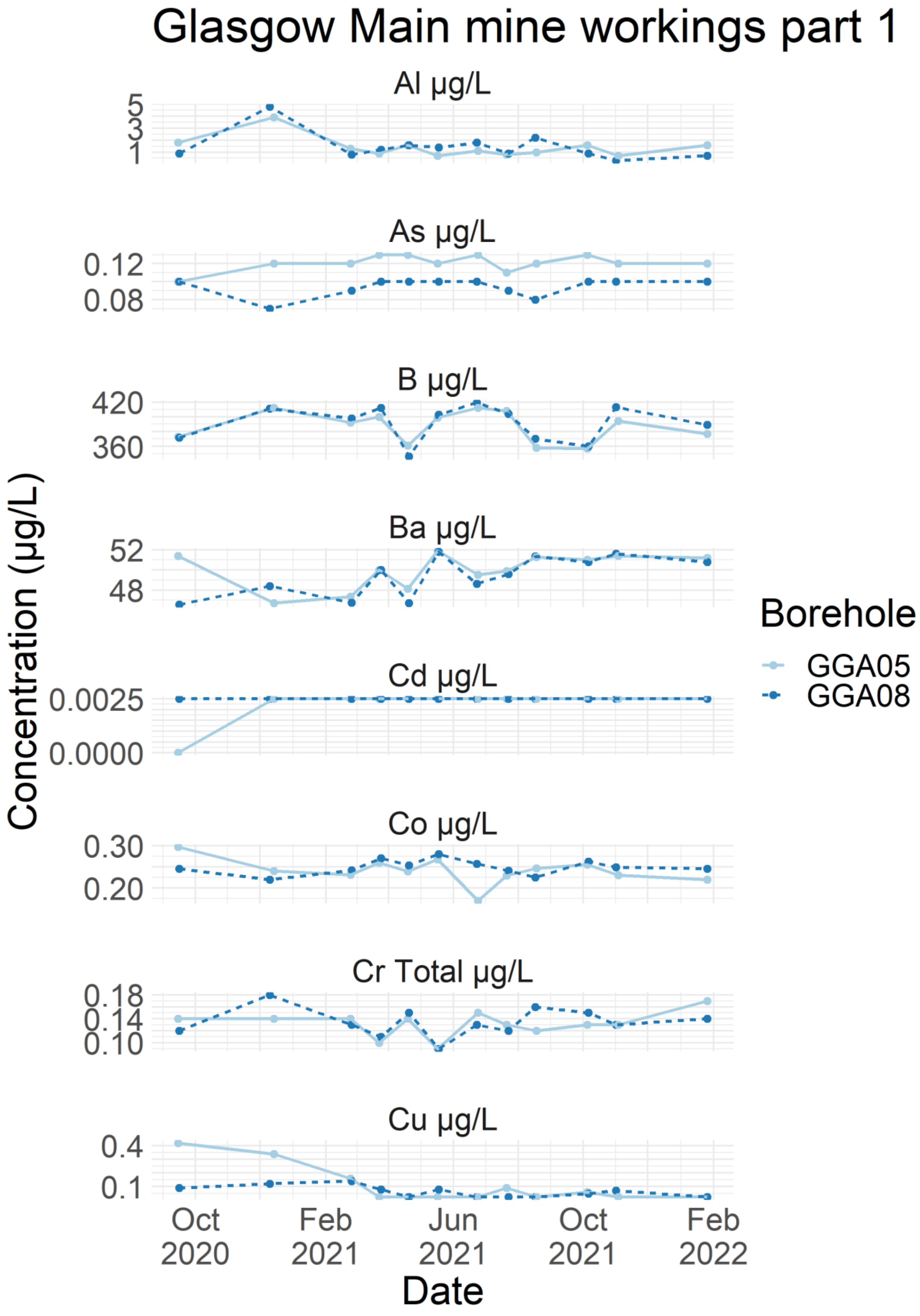

Figure 47 Time series of parameters measured in µg/L measured during sampling of Glasgow Main mine working boreholes. Data < detection limit (DL) are set to ½ DL.

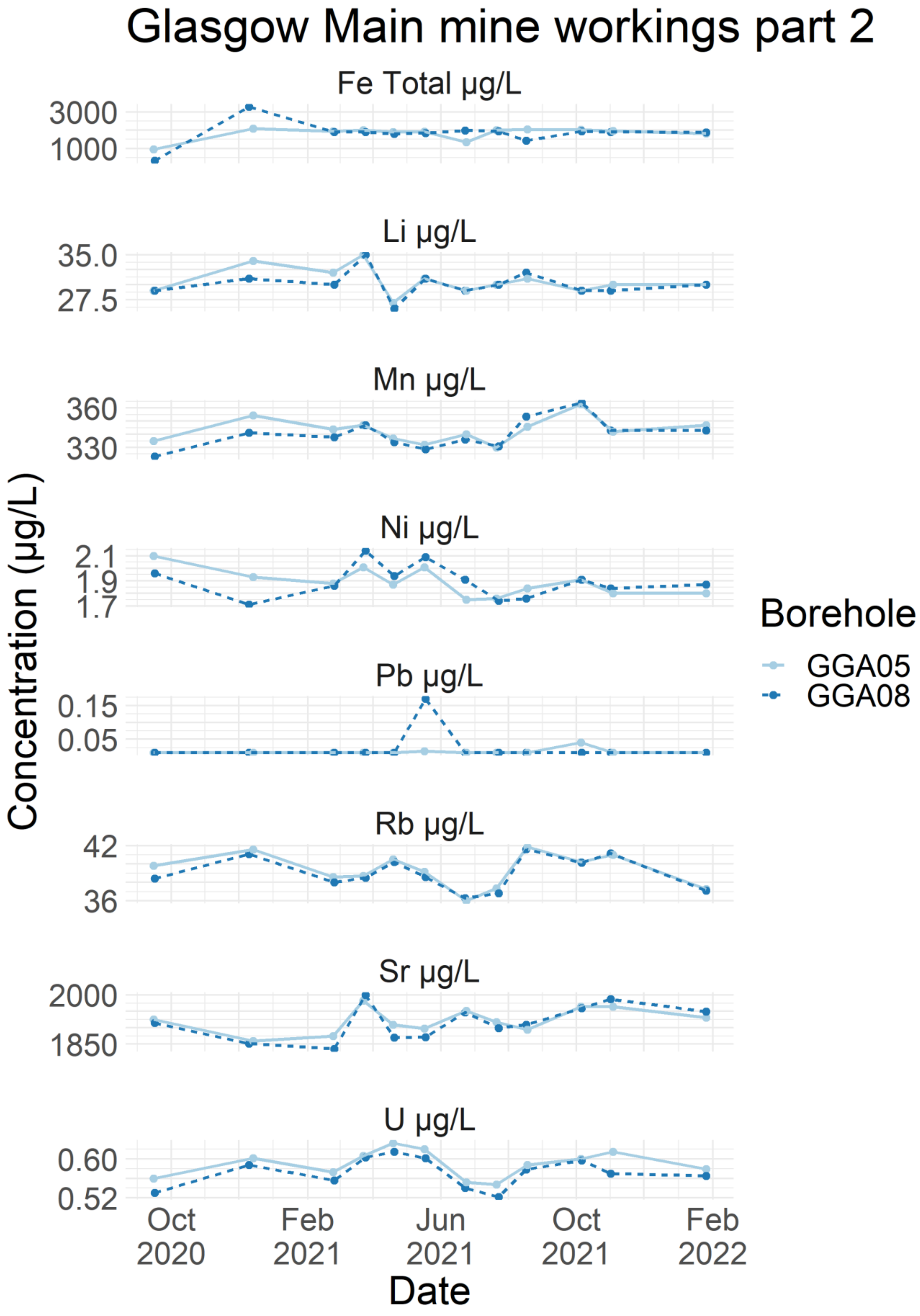

Figure 48 Time series of parameters measured in µg/L measured during sampling of Glasgow Main mine working boreholes. Data < detection limit (DL) are set to ½ DL.

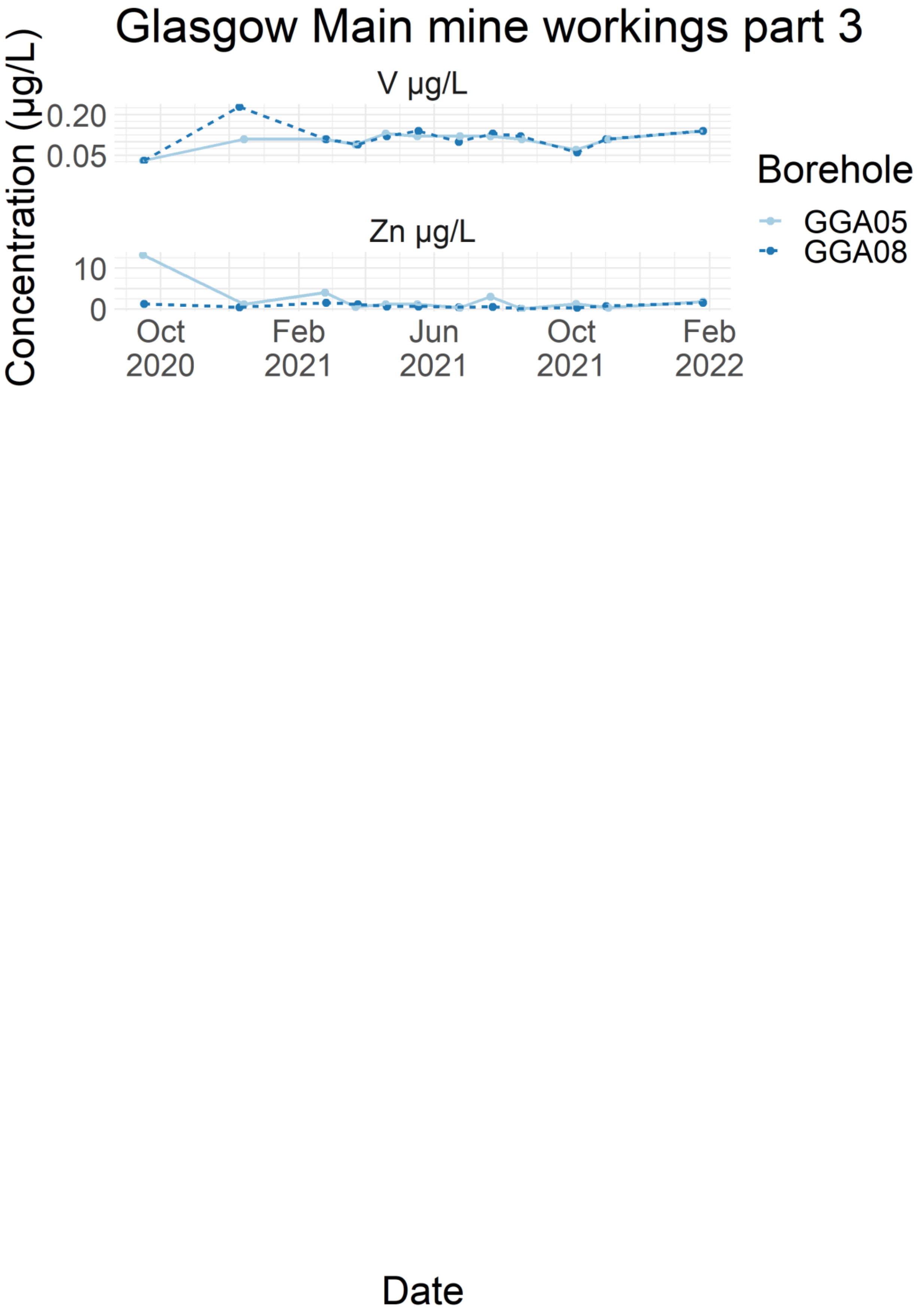

Figure 49 Time series of parameters measured in µg/L measured during sampling of Glasgow Main mine working boreholes. Data < detection limit (DL) are set to ½ DL.

Appendix 4 Box and whisker plots

Box and whisker plots are presented below. These include data from the outset of monitoring activities: March 2019 for surface waters, and September 2020 for groundwaters. Details for data preceding that discussed in this report can be found in Fordyce et al. (2021) or Bearcock et al. (2022).

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 below detection limits are set to half the value of the detection limit.

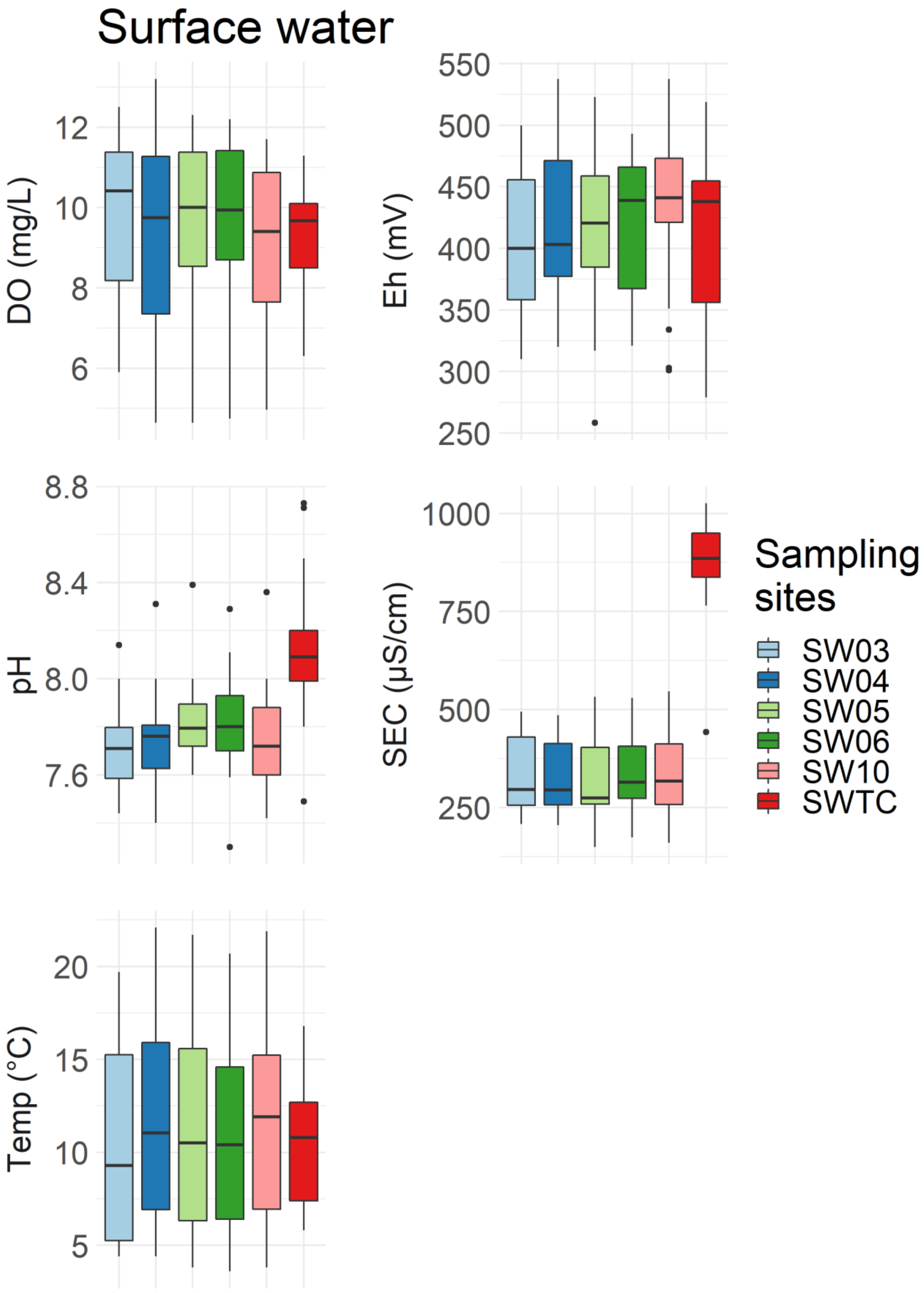

Figure 50 Boxplots showing distribution of field parameters measured during surface water sampling.

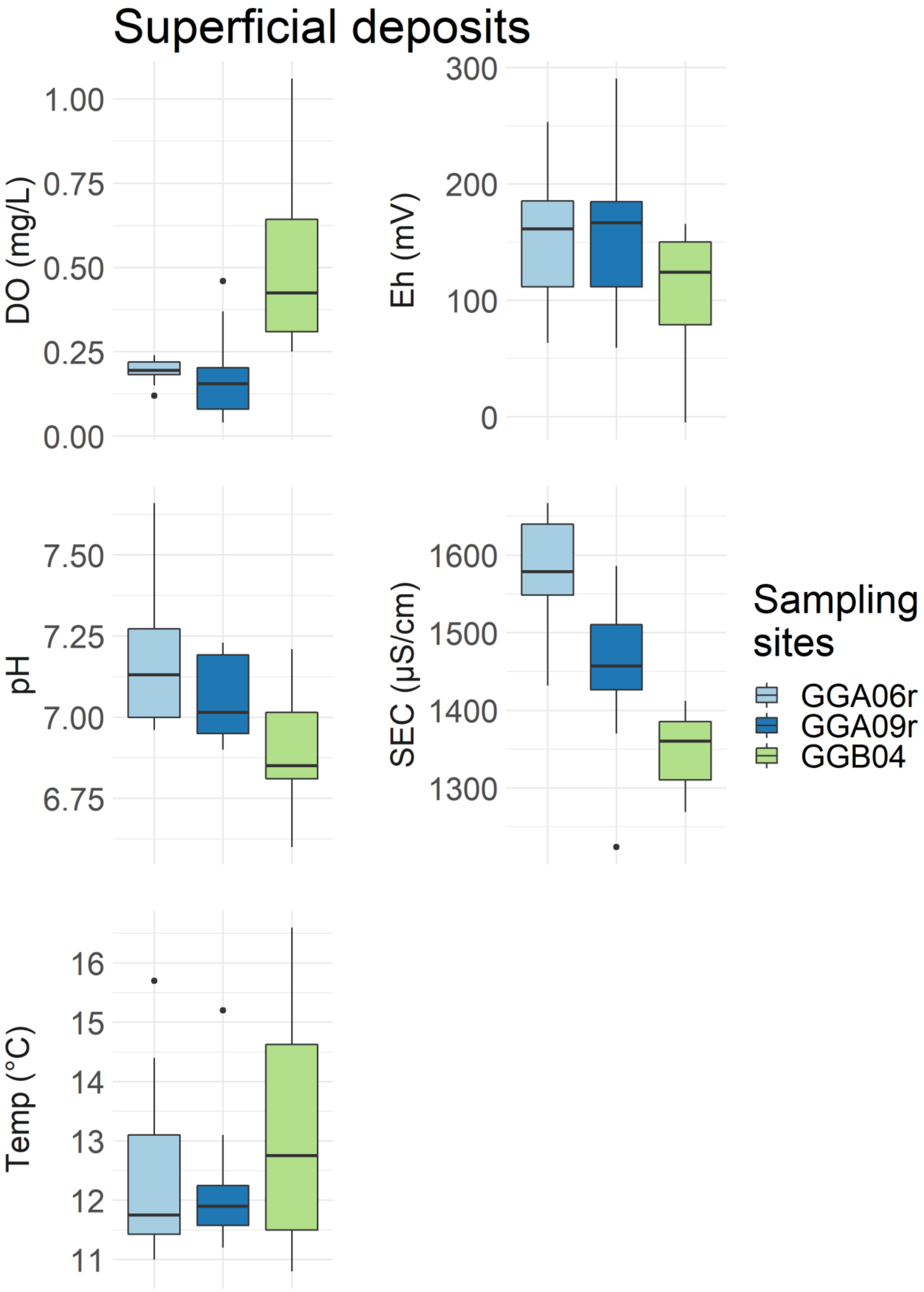

Figure 51 Boxplots showing distribution of field parameters measured during sampling of superficial deposits boreholes.

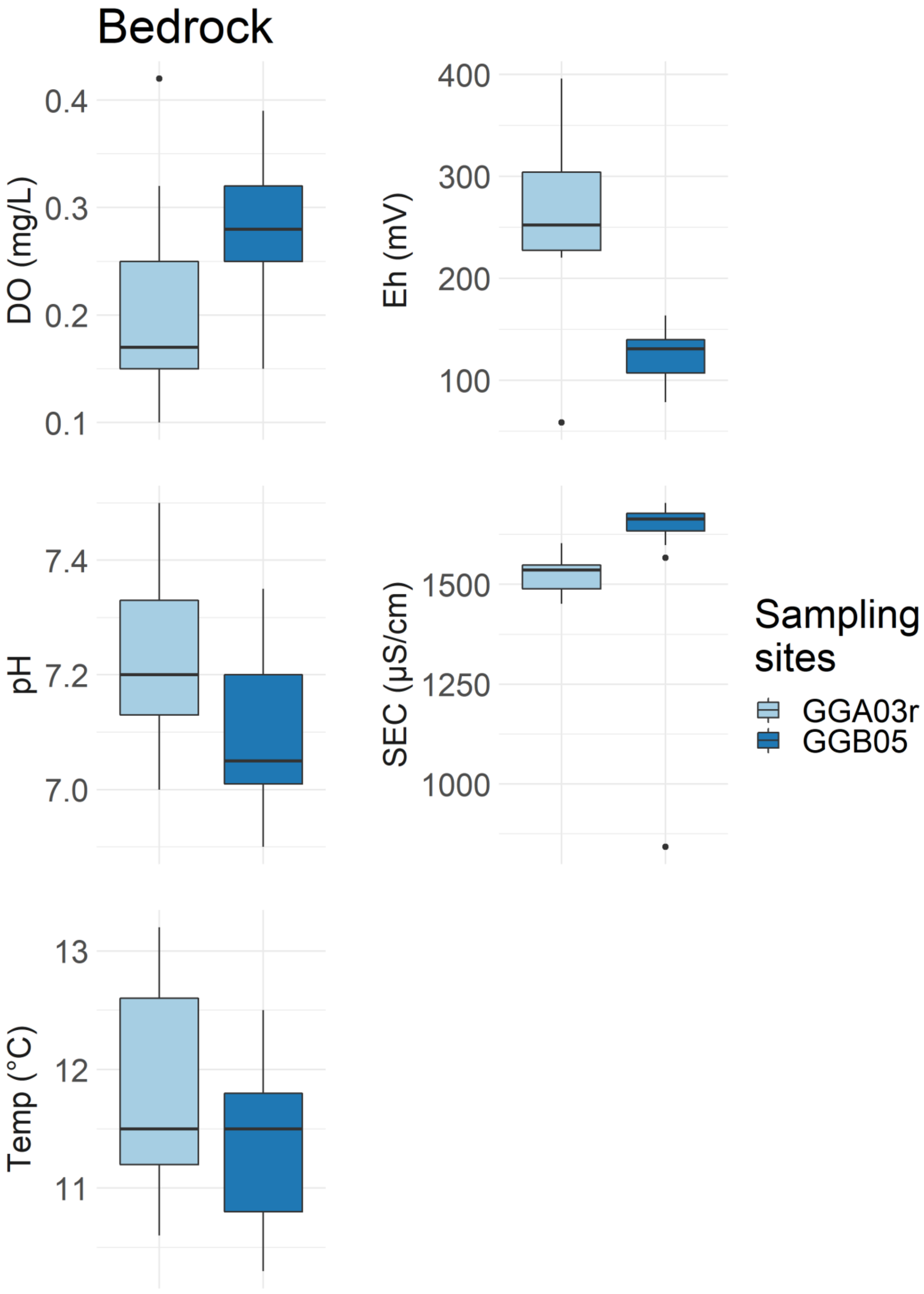

Figure 52 Boxplots showing distribution of field parameters measured during sampling of bedrock boreholes.

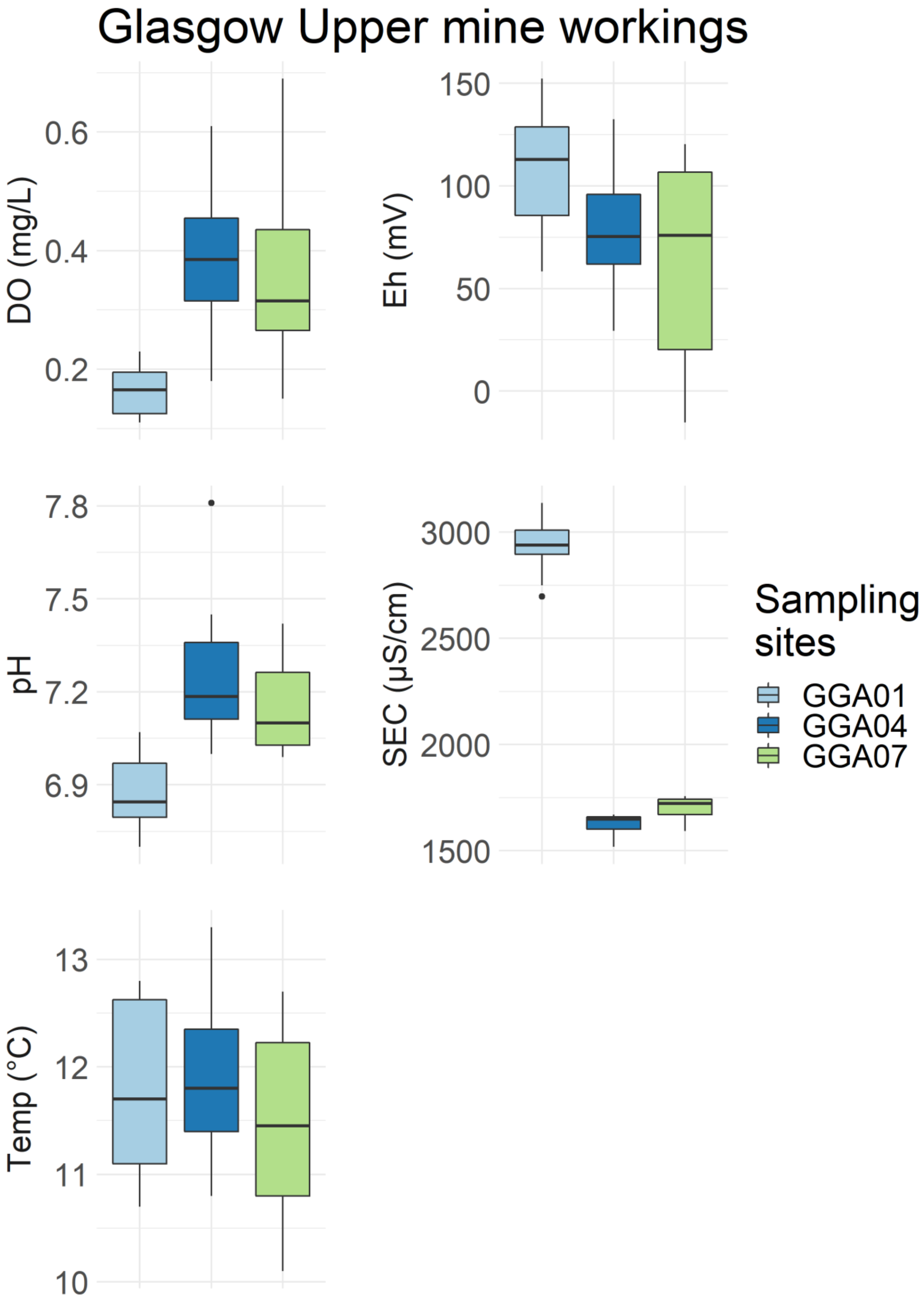

Figure 53 Boxplots showing distribution of field parameters measured during sampling of Glasgow Upper mine working boreholes.

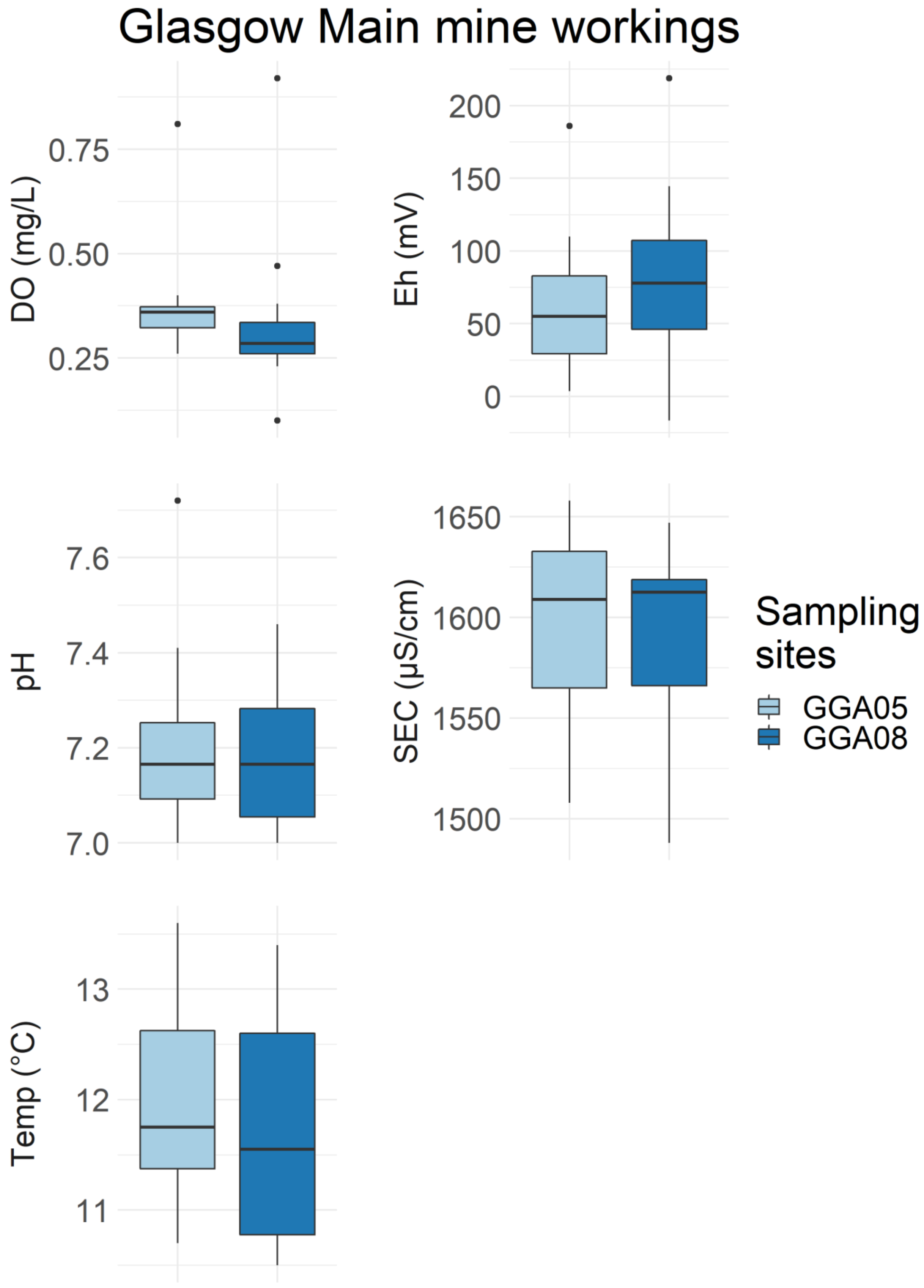

Figure 54 Boxplots showing distribution of field parameters measured during sampling of Glasgow Main mine working boreholes.

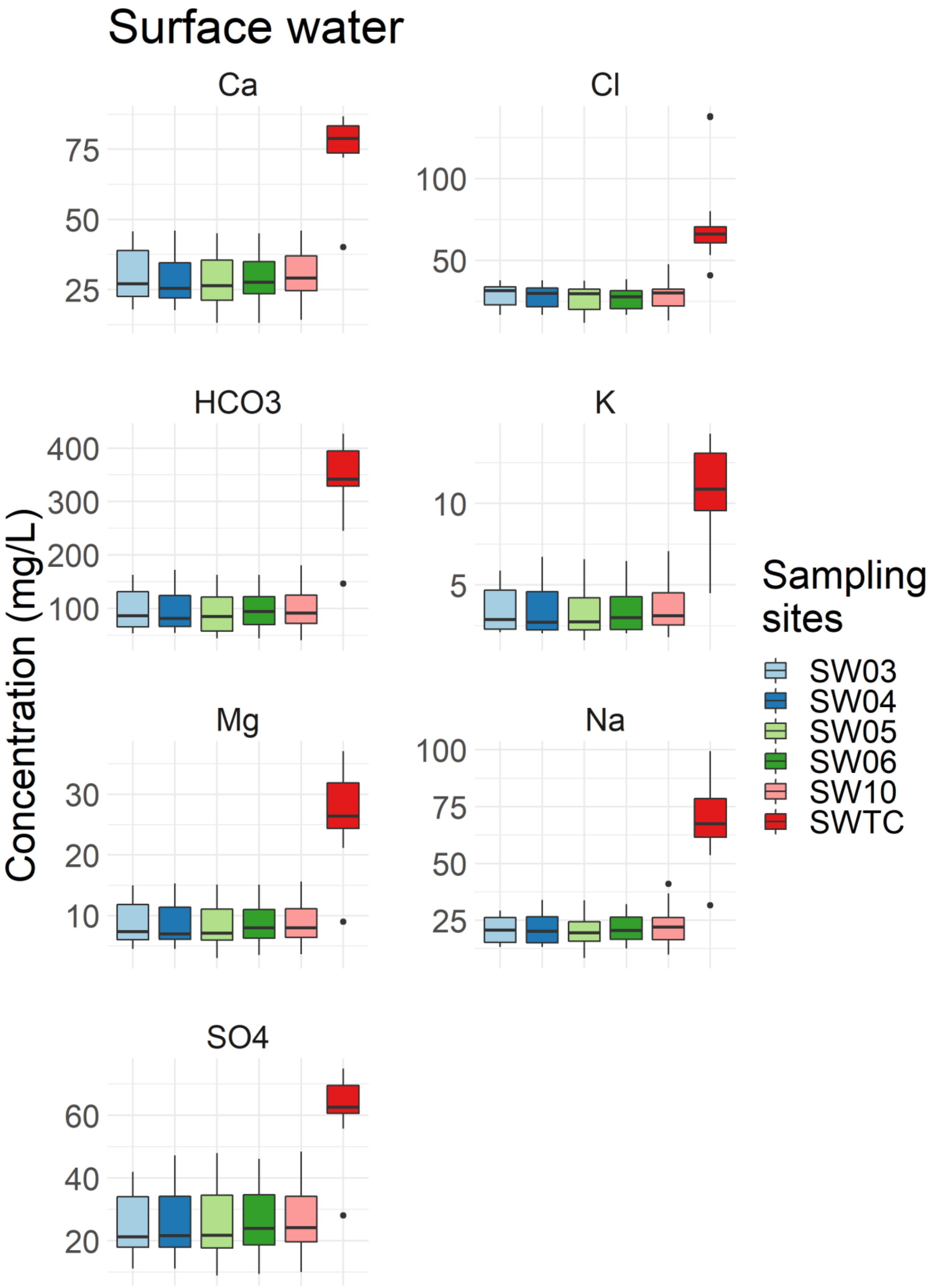

Figure 55 Boxplots showing distribution of major ions measured during surface water sampling.

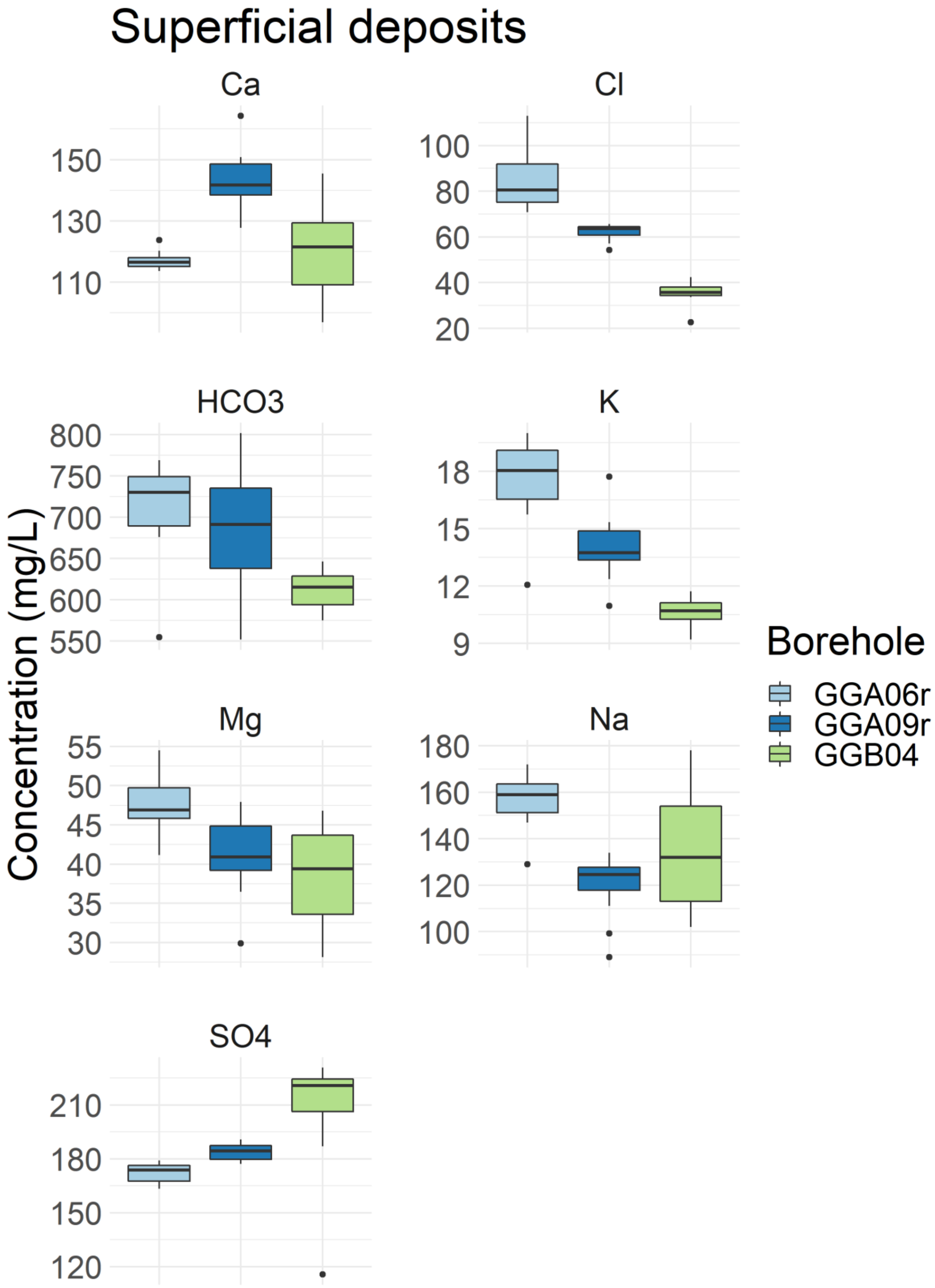

Figure 56 Boxplots showing distribution of major ions measured during sampling of superficial deposits boreholes.

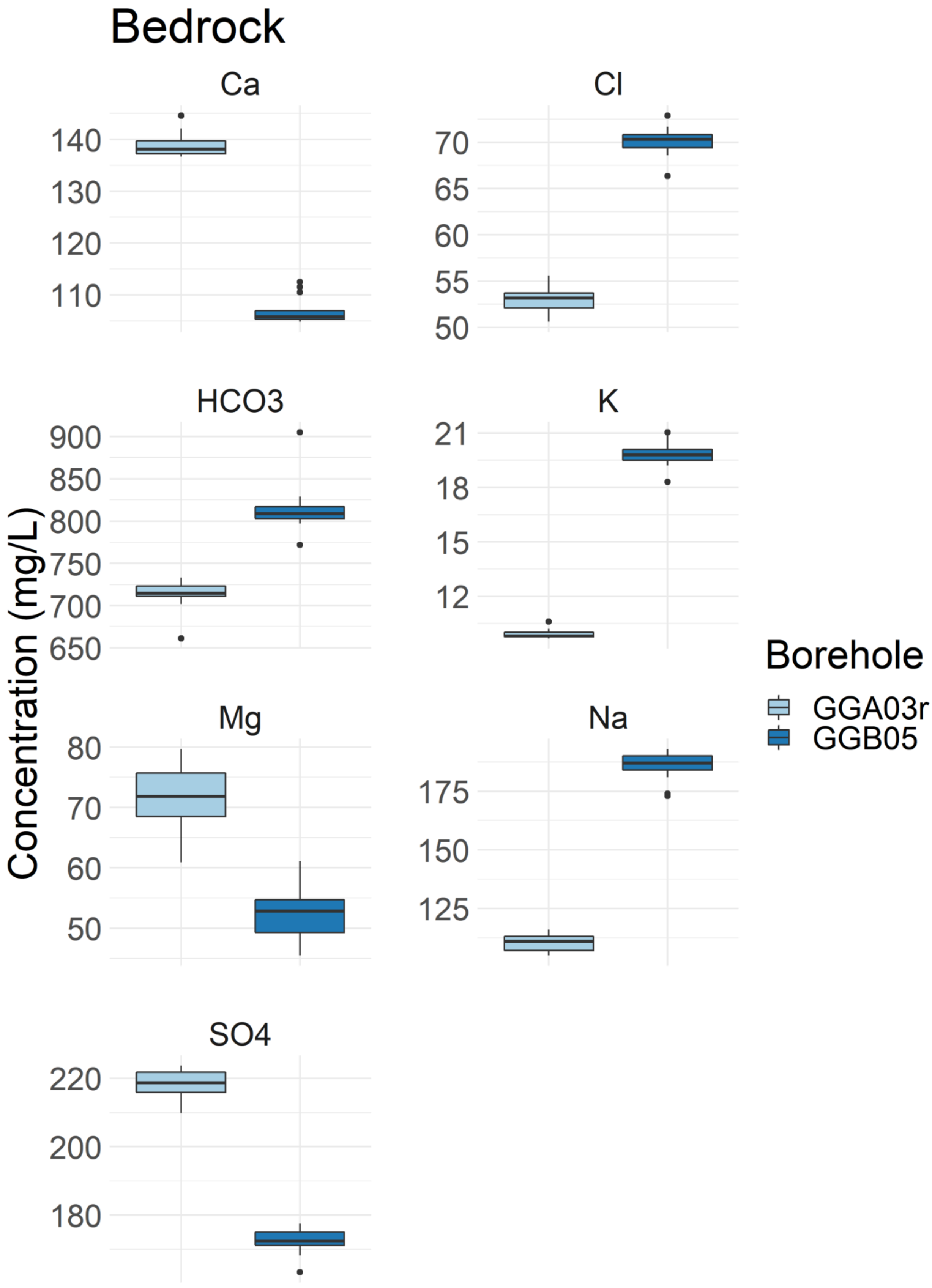

Figure 57 Boxplots showing distribution of major ions measured during sampling of bedrock boreholes.

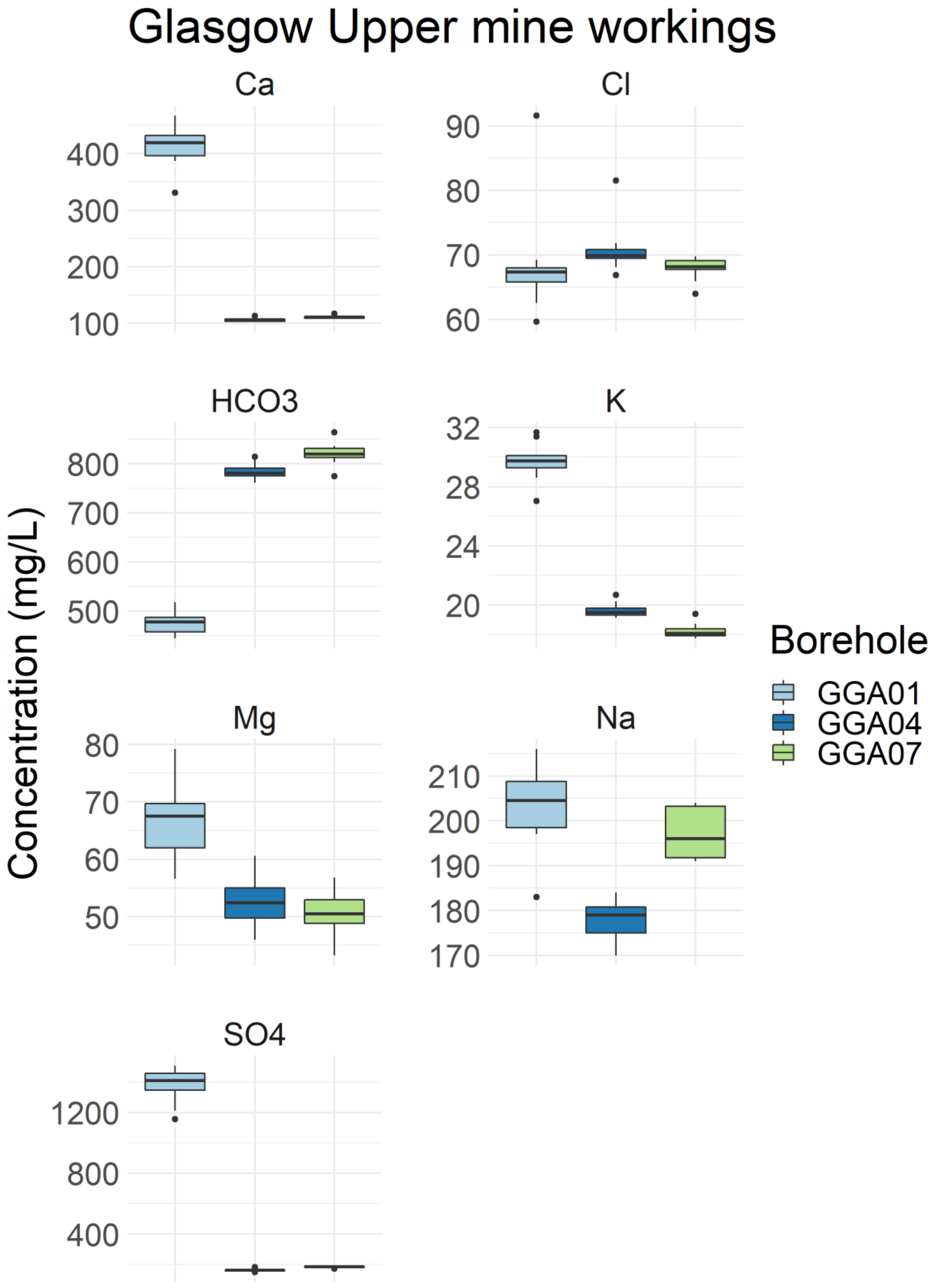

Figure 58 Boxplots showing distribution of major ions measured during sampling of Glasgow Upper mine working boreholes.

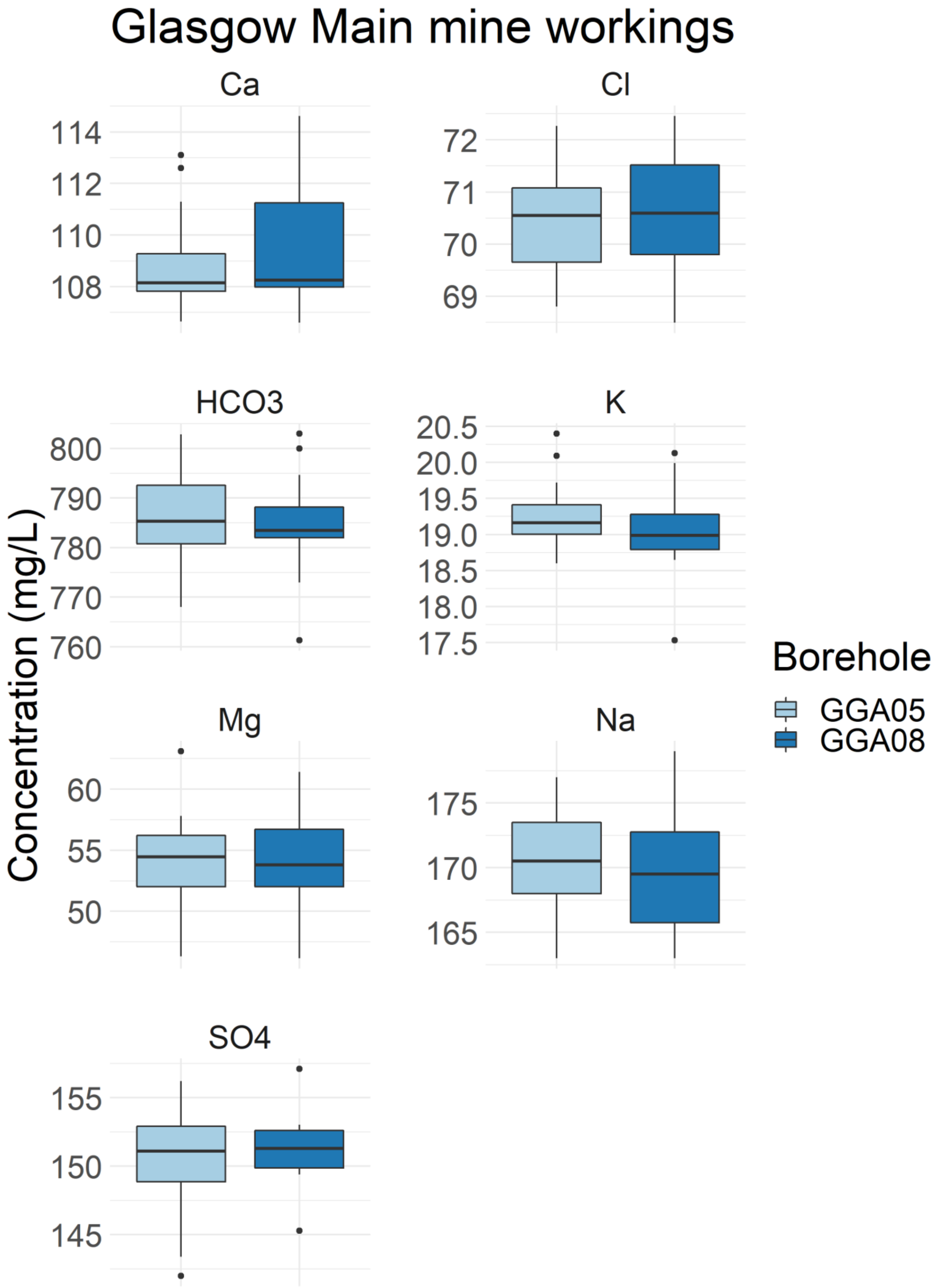

Figure 59 Boxplots showing distribution of major ions measured during sampling of Glasgow Main mine working boreholes.

MINOR ELEMENTS AND OTHER PARAMETERS mg/L

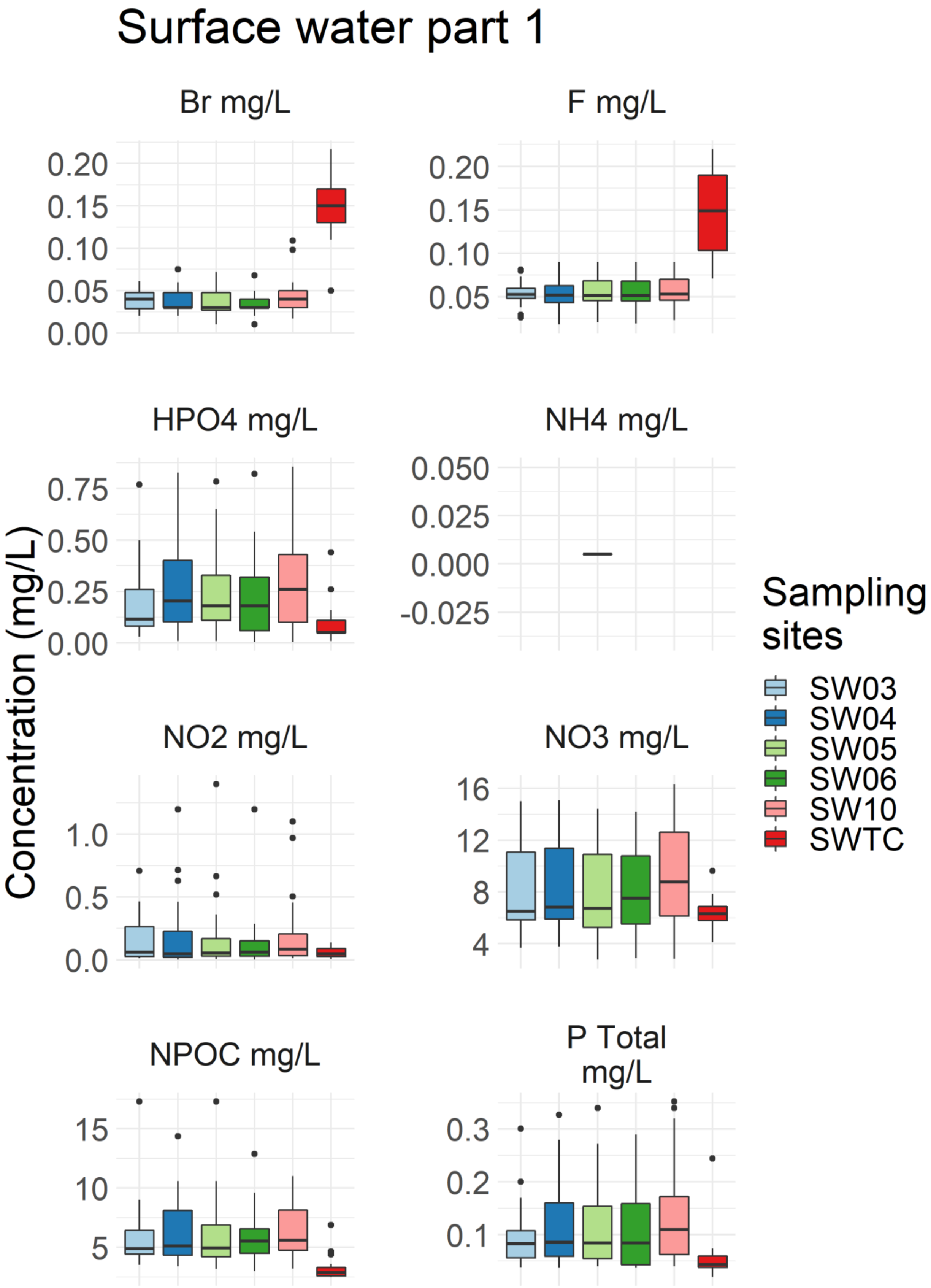

Figure 60 Boxplots showing distribution of parameters measured in mg/L measured during surface water sampling.

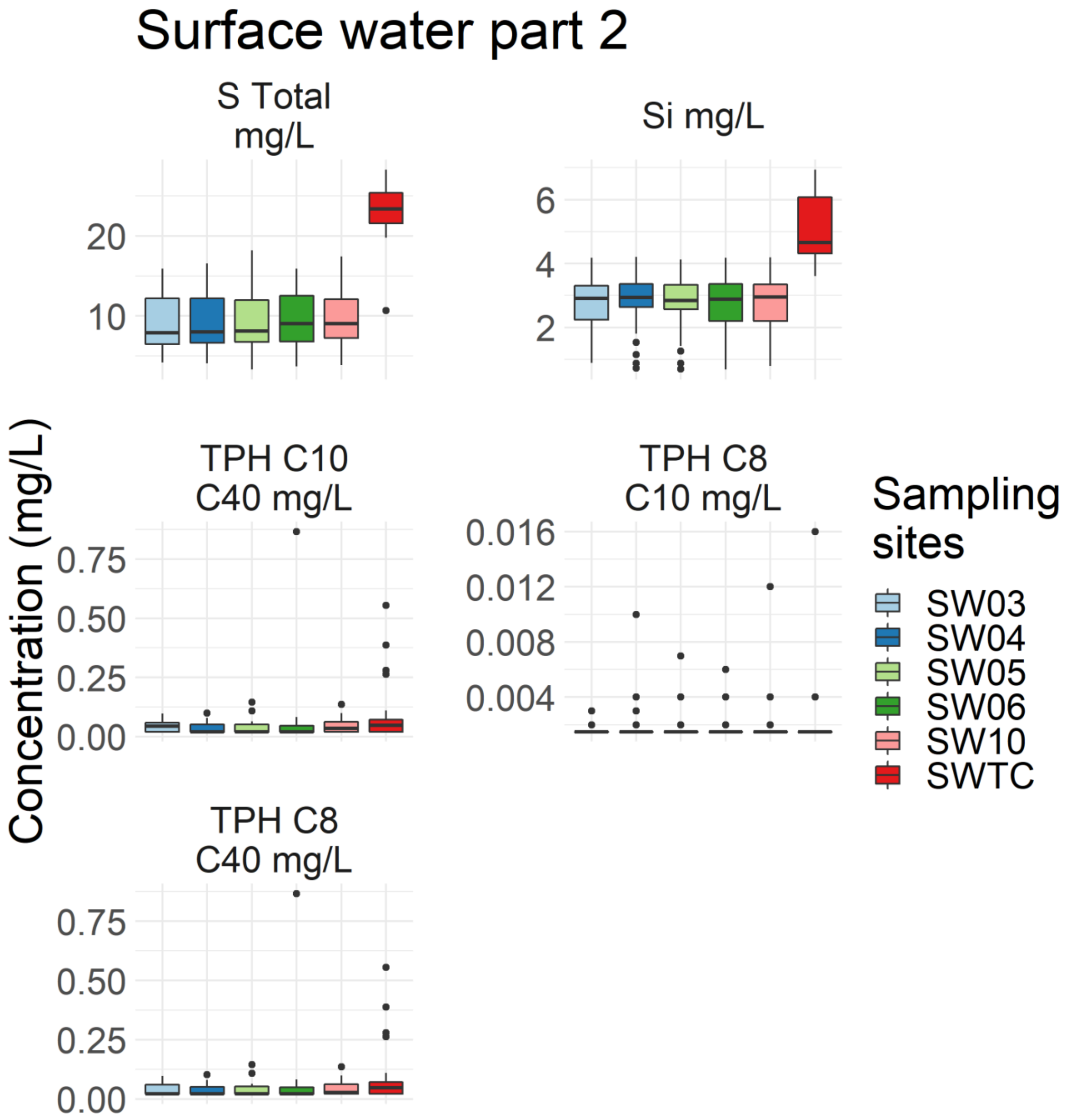

Figure 61 Boxplots showing distribution of parameters measured in mg/L measured during surface water sampling.

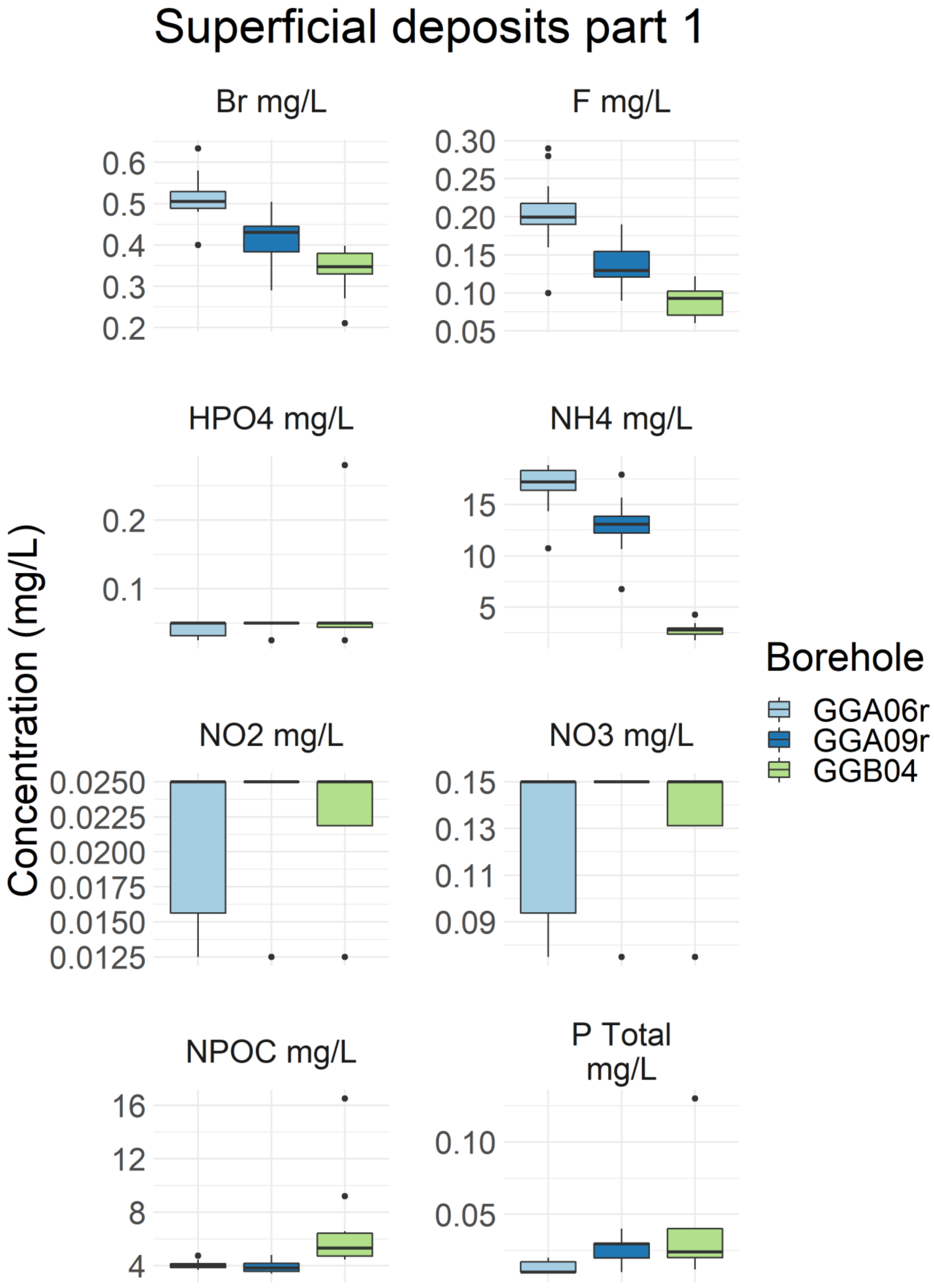

Figure 62 Boxplots showing distribution of parameters measured in mg/L measured during sampling of superficial deposits boreholes.

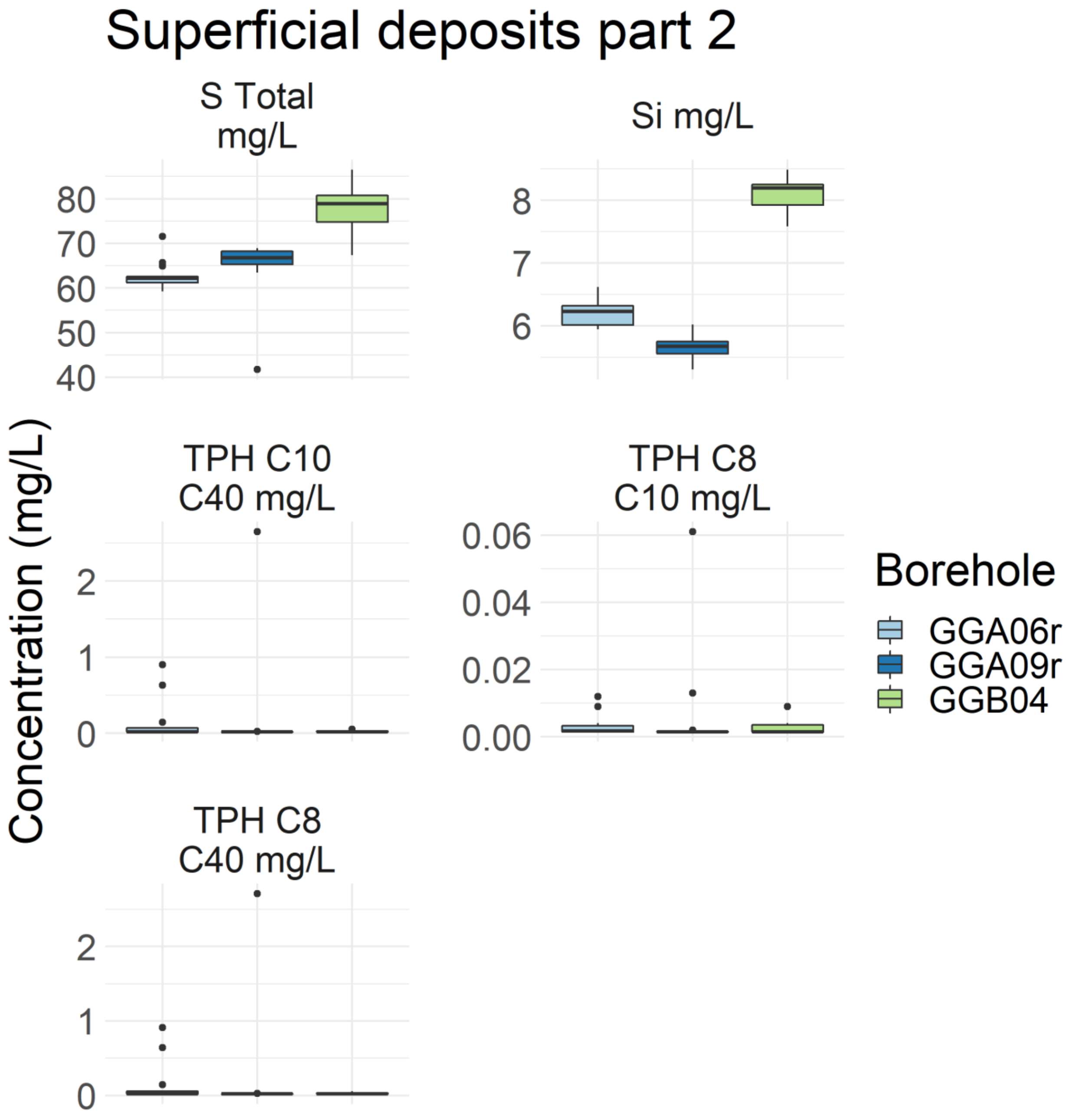

Figure 63 Boxplots showing distribution of parameters measured in mg/L measured during sampling of superficial deposits boreholes.

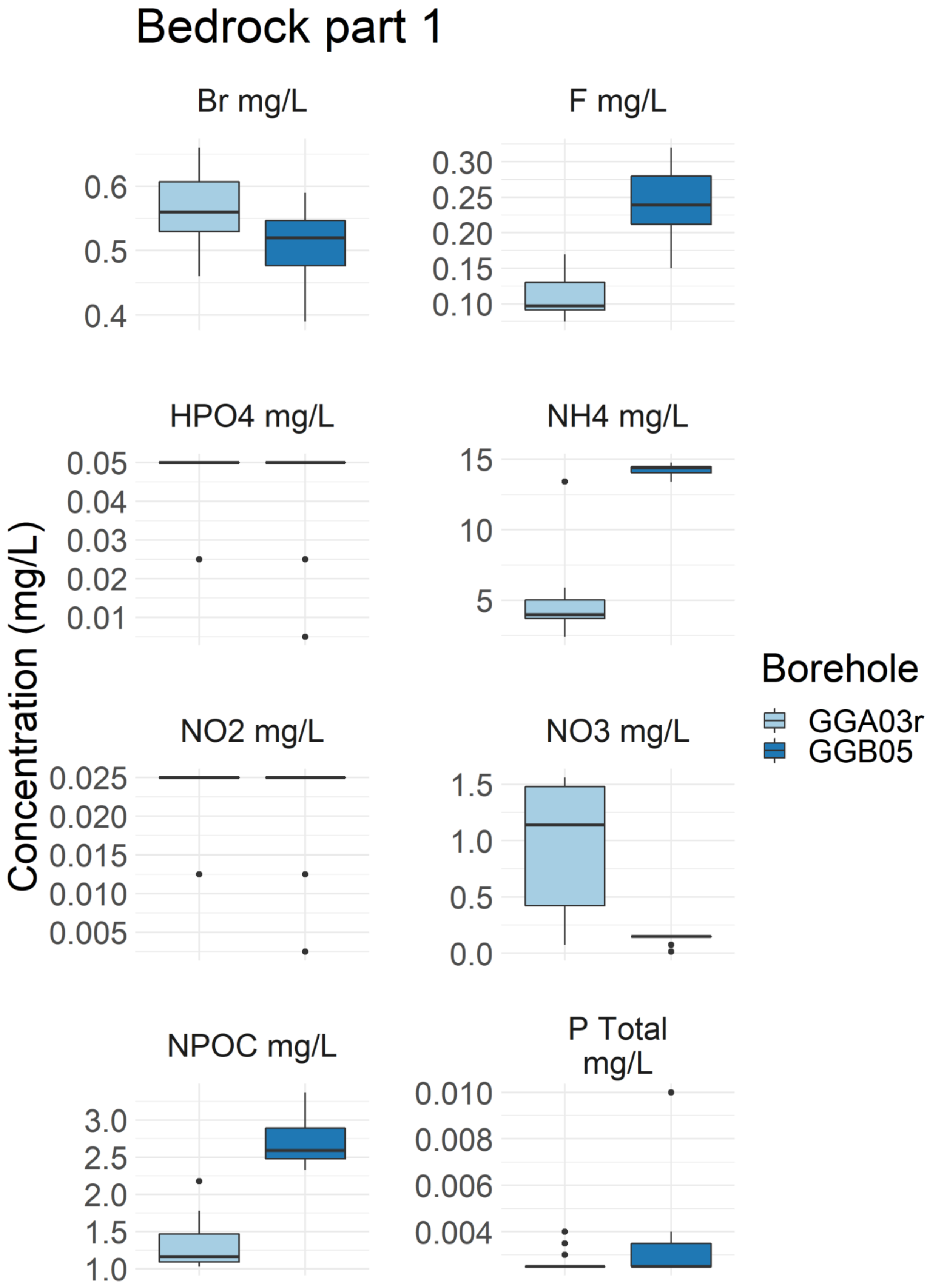

Figure 64 Boxplots showing distribution of parameters measured in mg/L measured during sampling of bedrock boreholes.

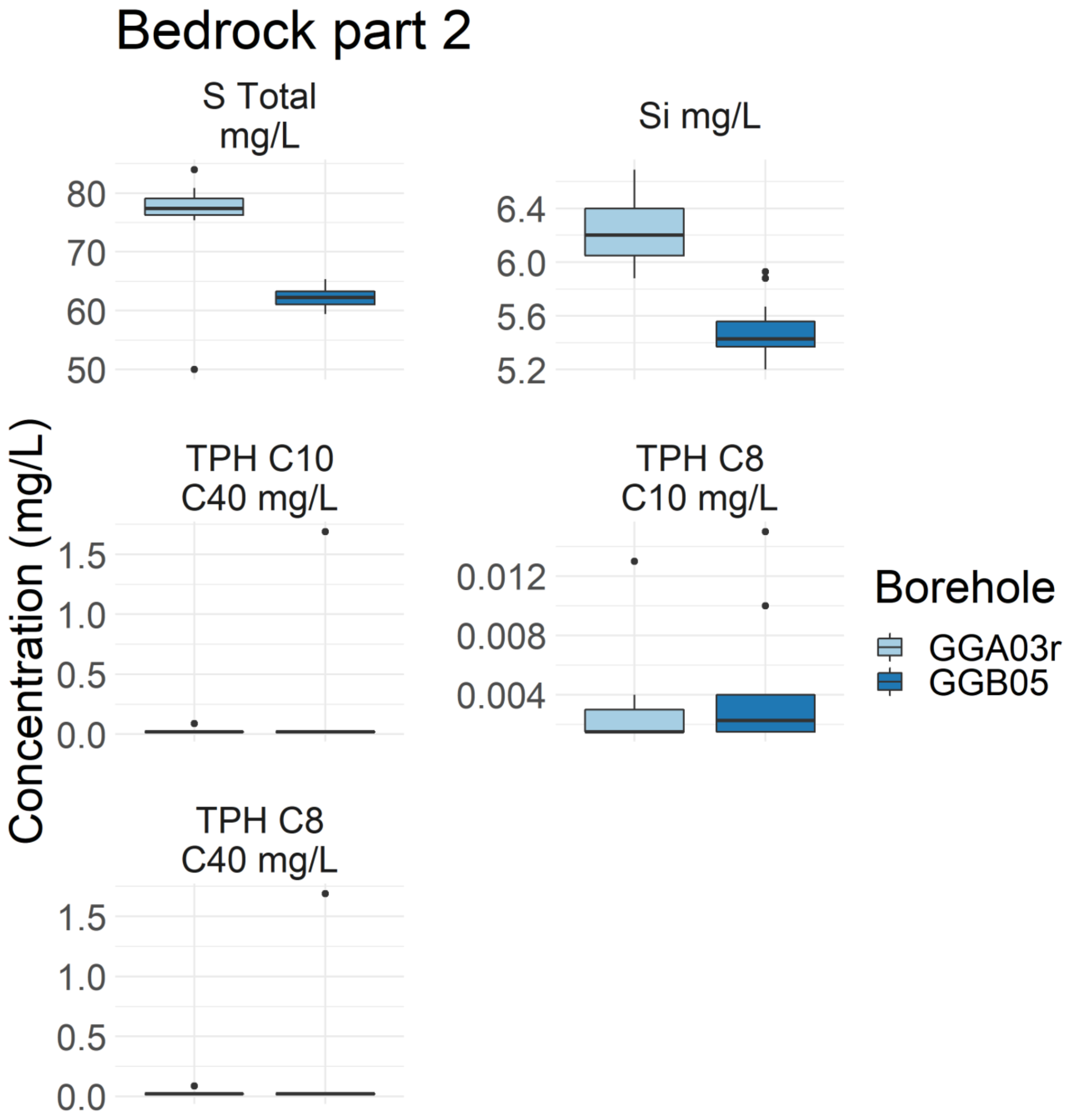

Figure 65 Boxplots showing distribution of parameters measured in mg/L measured during sampling of bedrock boreholes.

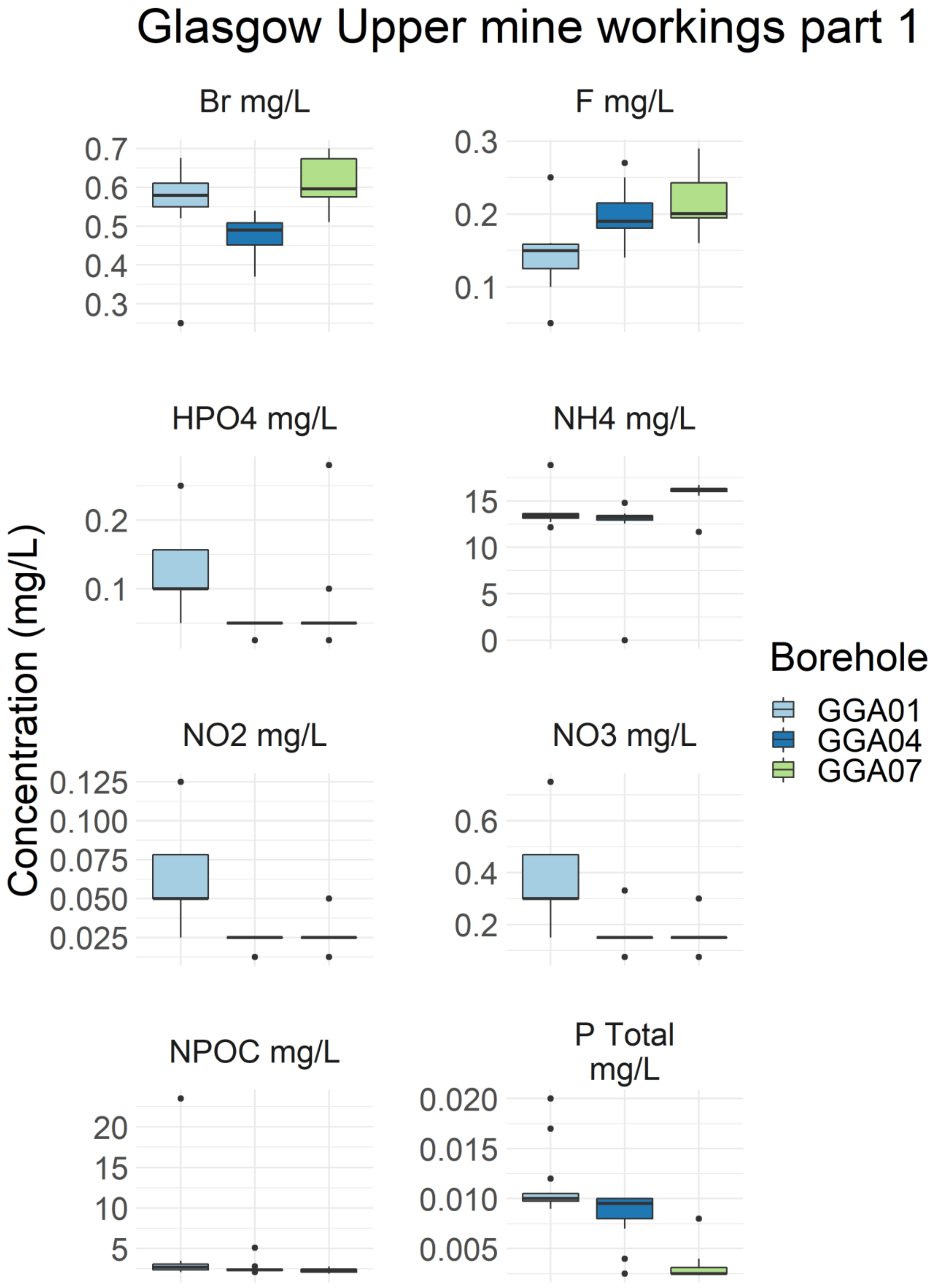

Figure 66 Boxplots showing distribution of parameters measured in mg/L measured during sampling of Glasgow Upper mine working boreholes.

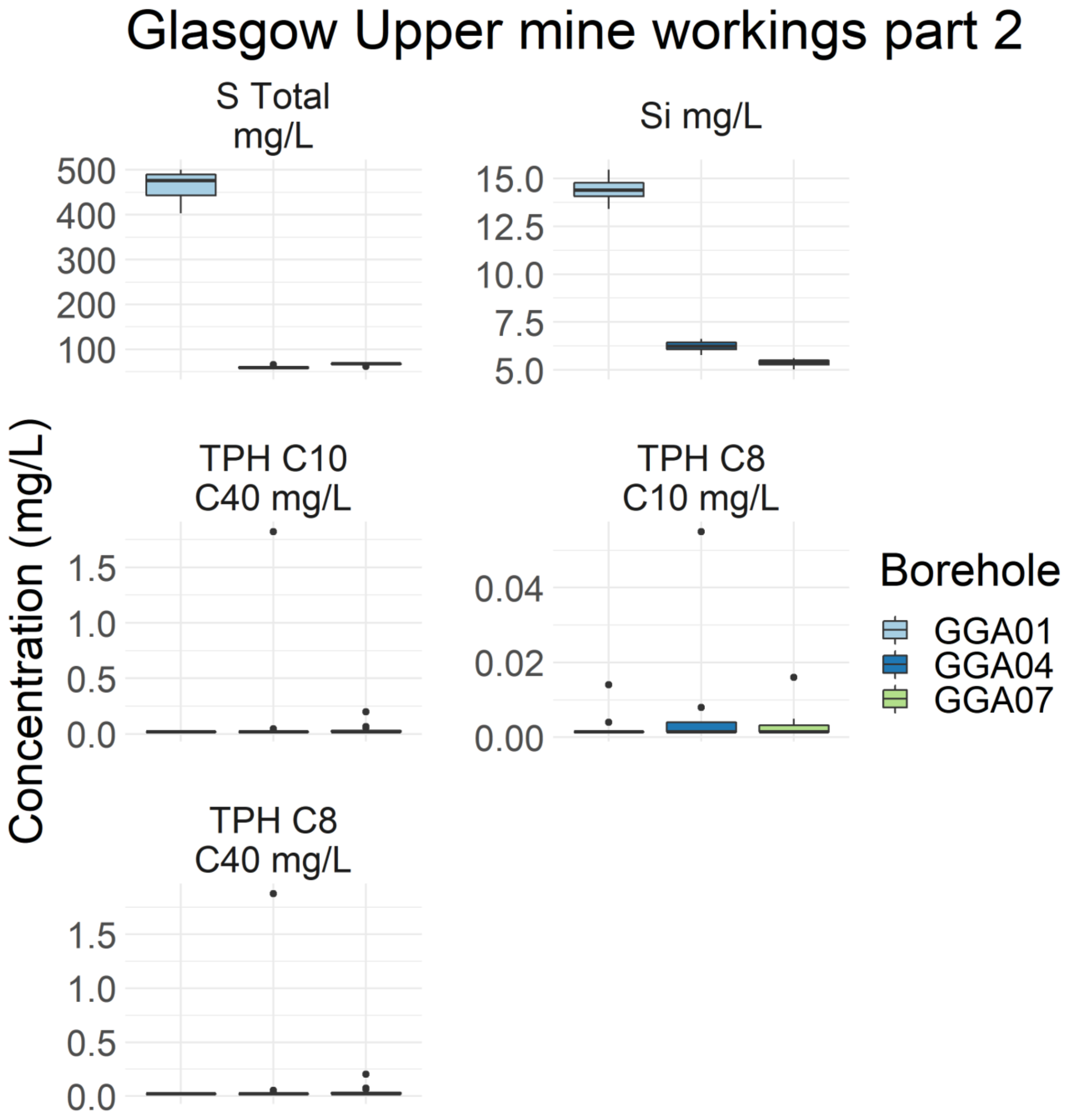

Figure 67 Boxplots showing distribution of parameters measured in mg/L measured during sampling of Glasgow Upper mine working boreholes.

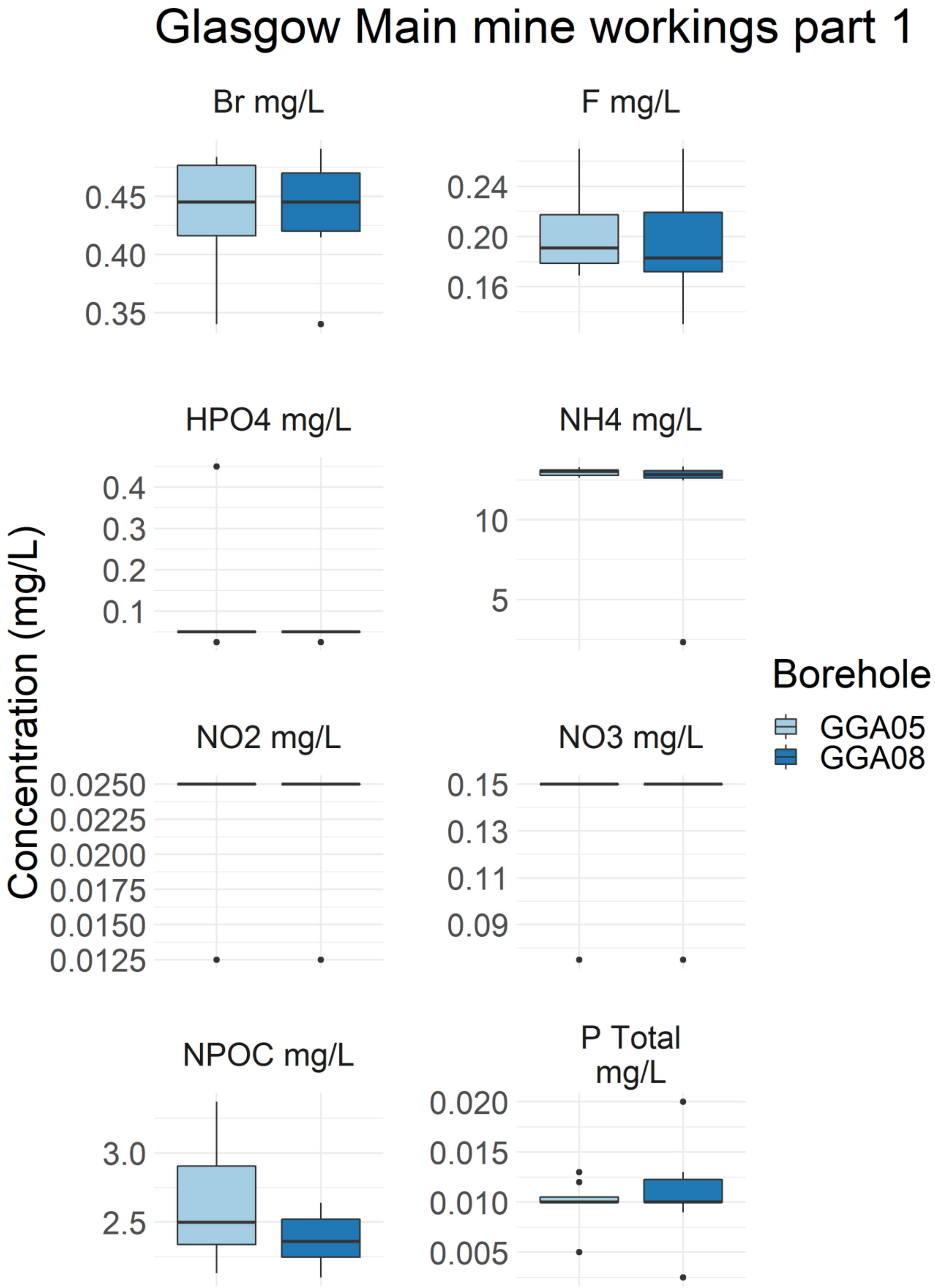

Figure 68 Boxplots showing distribution of parameters measured in mg/L measured during sampling of Glasgow Main mine working boreholes.

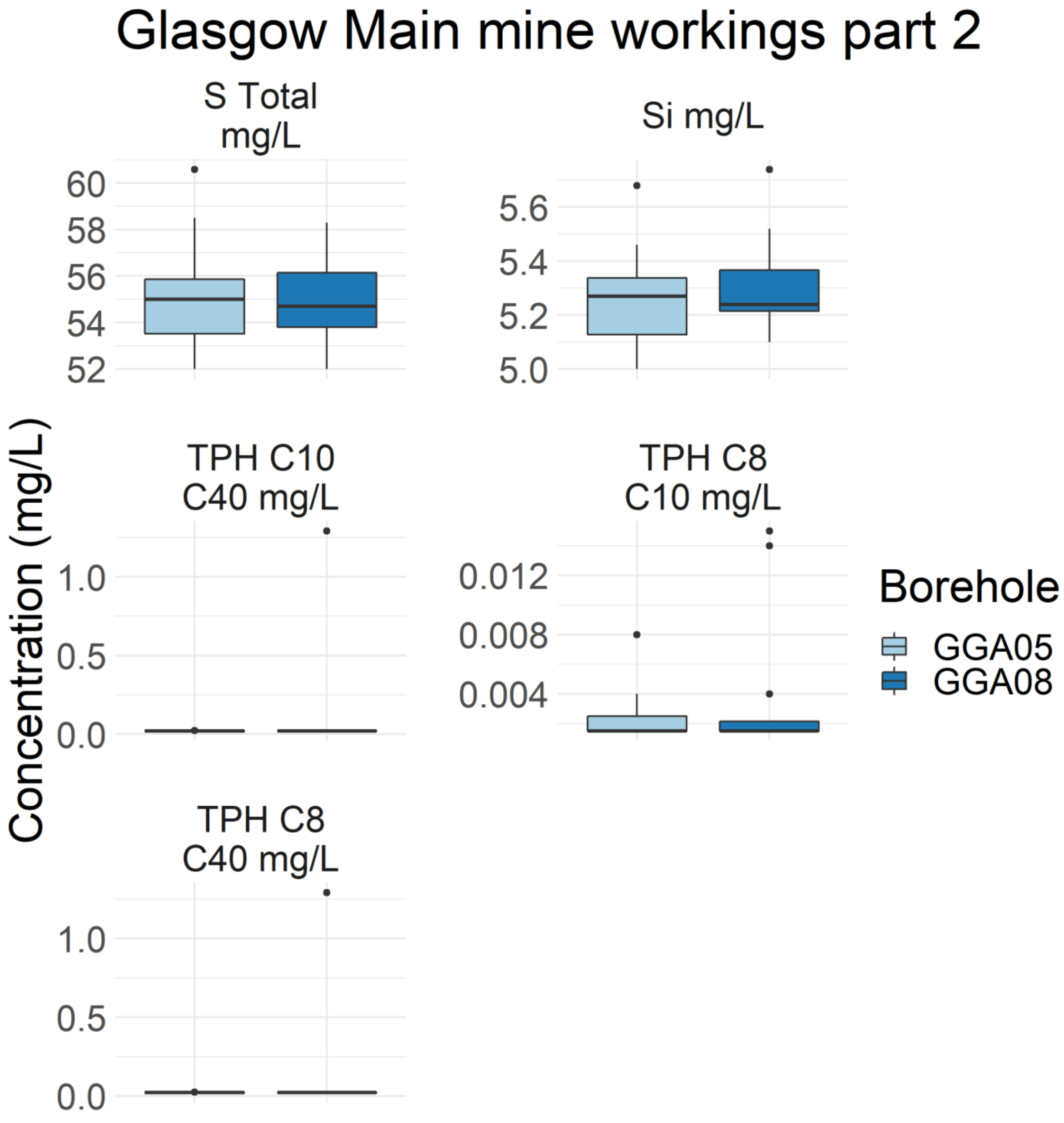

Figure 69 Boxplots showing distribution of parameters measured in mg/L measured during sampling of Glasgow Main mine working boreholes.

TRACE ELEMENTS AND OTHER PARAMETERS IN µg/L

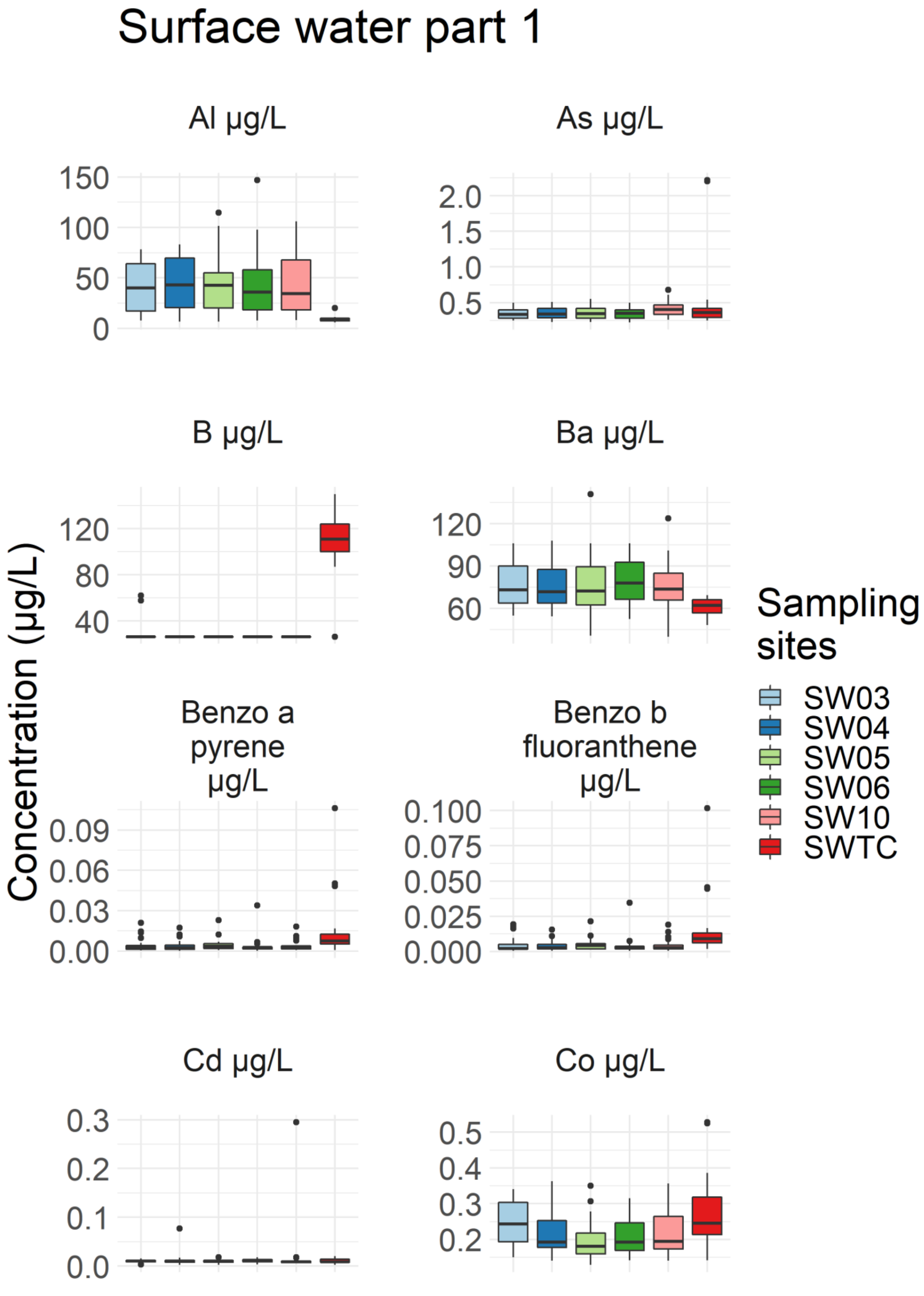

Figure 70 Boxplots showing distribution of parameters measured in µg/L measured during surface water sampling.

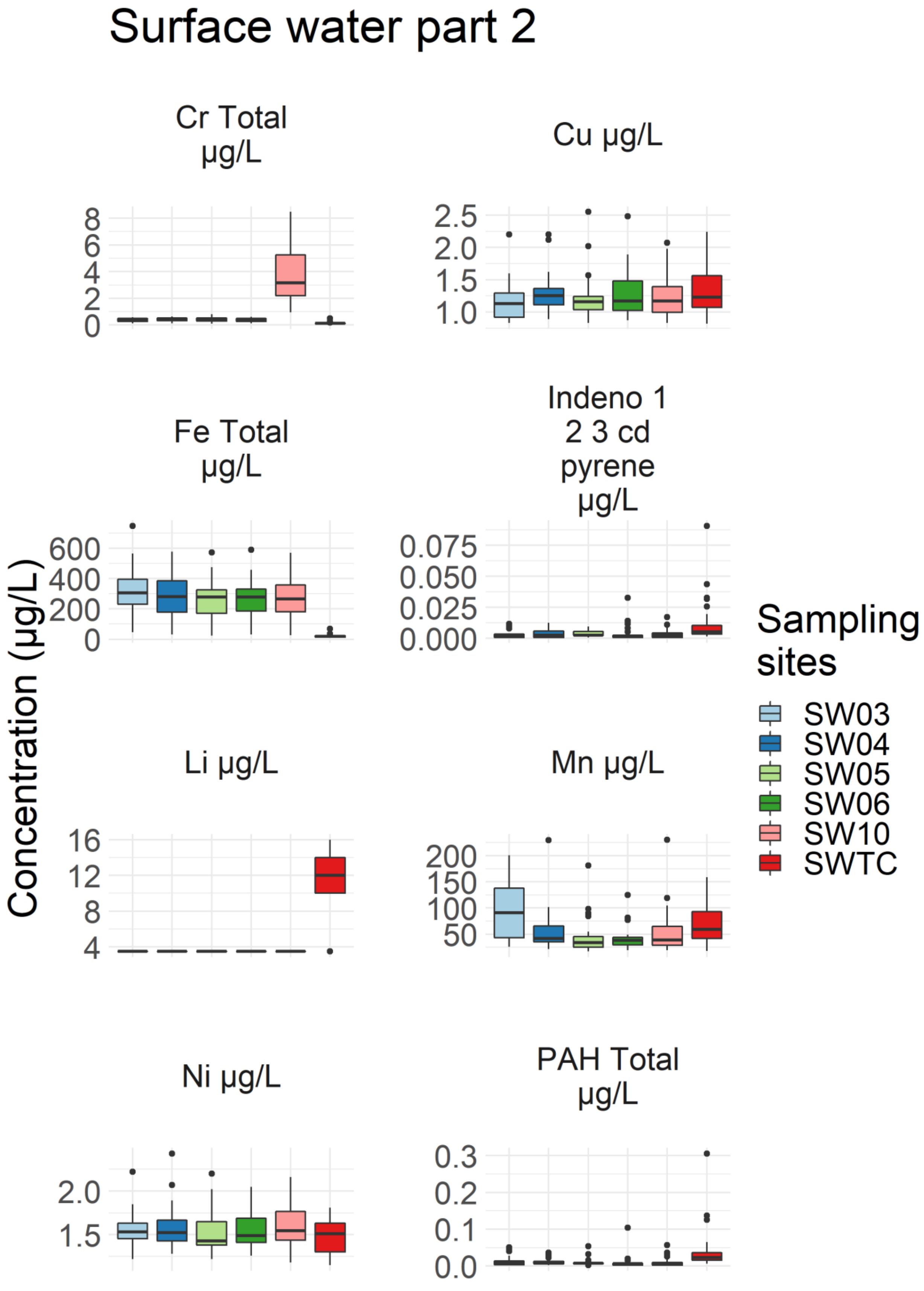

Figure 71 Boxplots showing distribution of parameters measured in µg/L measured during surface water sampling.

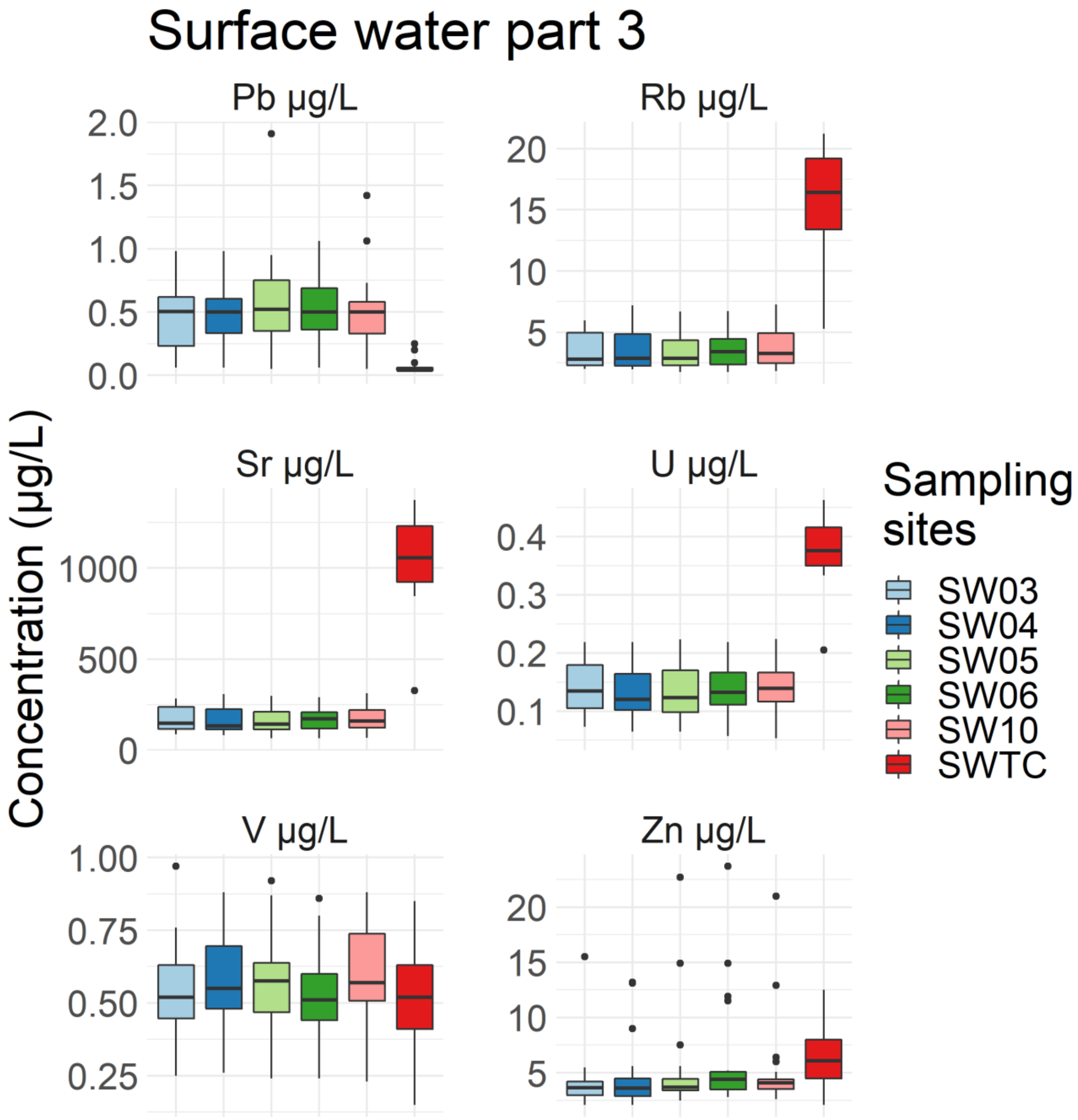

Figure 72 Boxplots showing distribution of parameters measured in µg/L measured during surface water sampling.

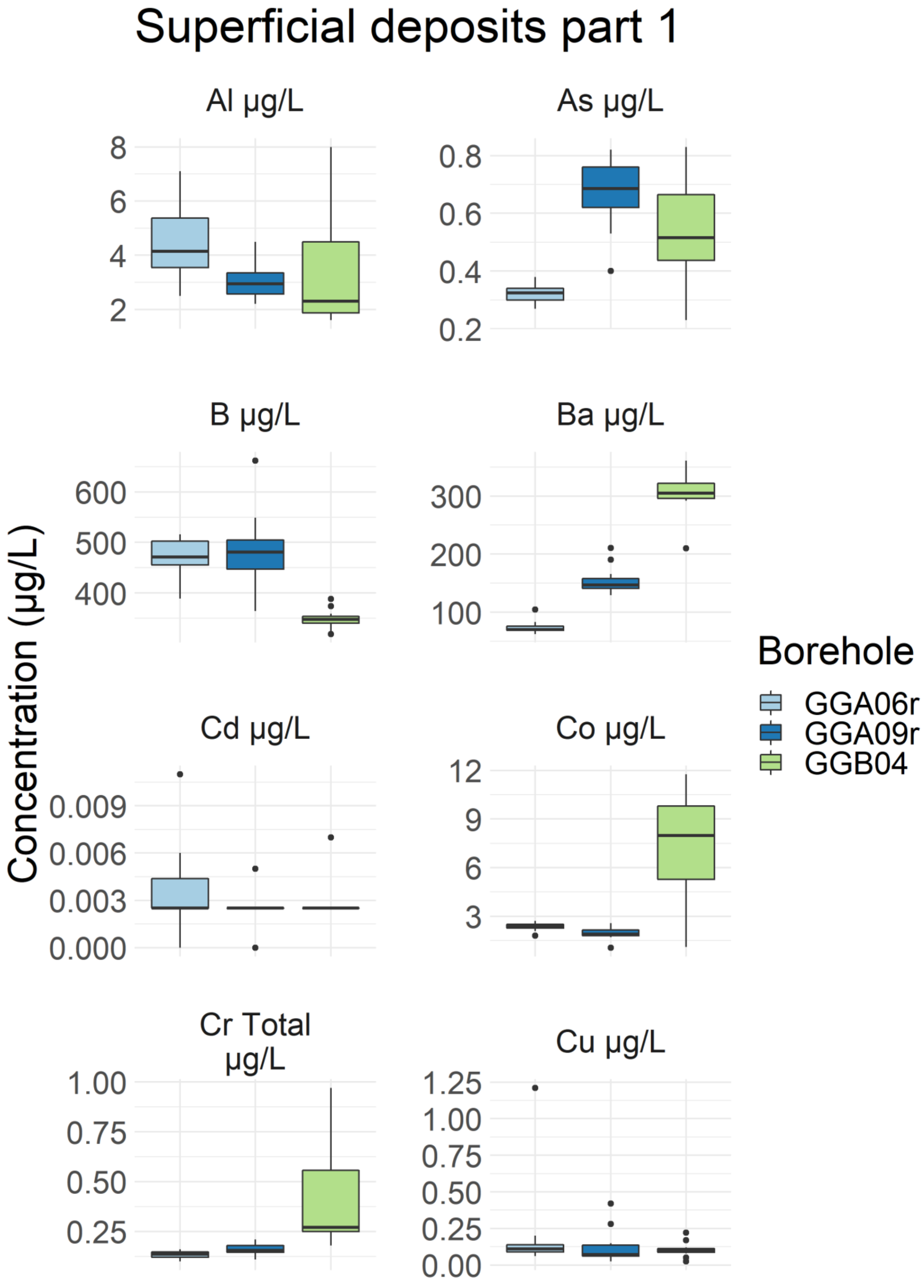

Figure 73 Boxplots showing distribution of parameters measured in µg/L measured during sampling of superficial deposits boreholes.

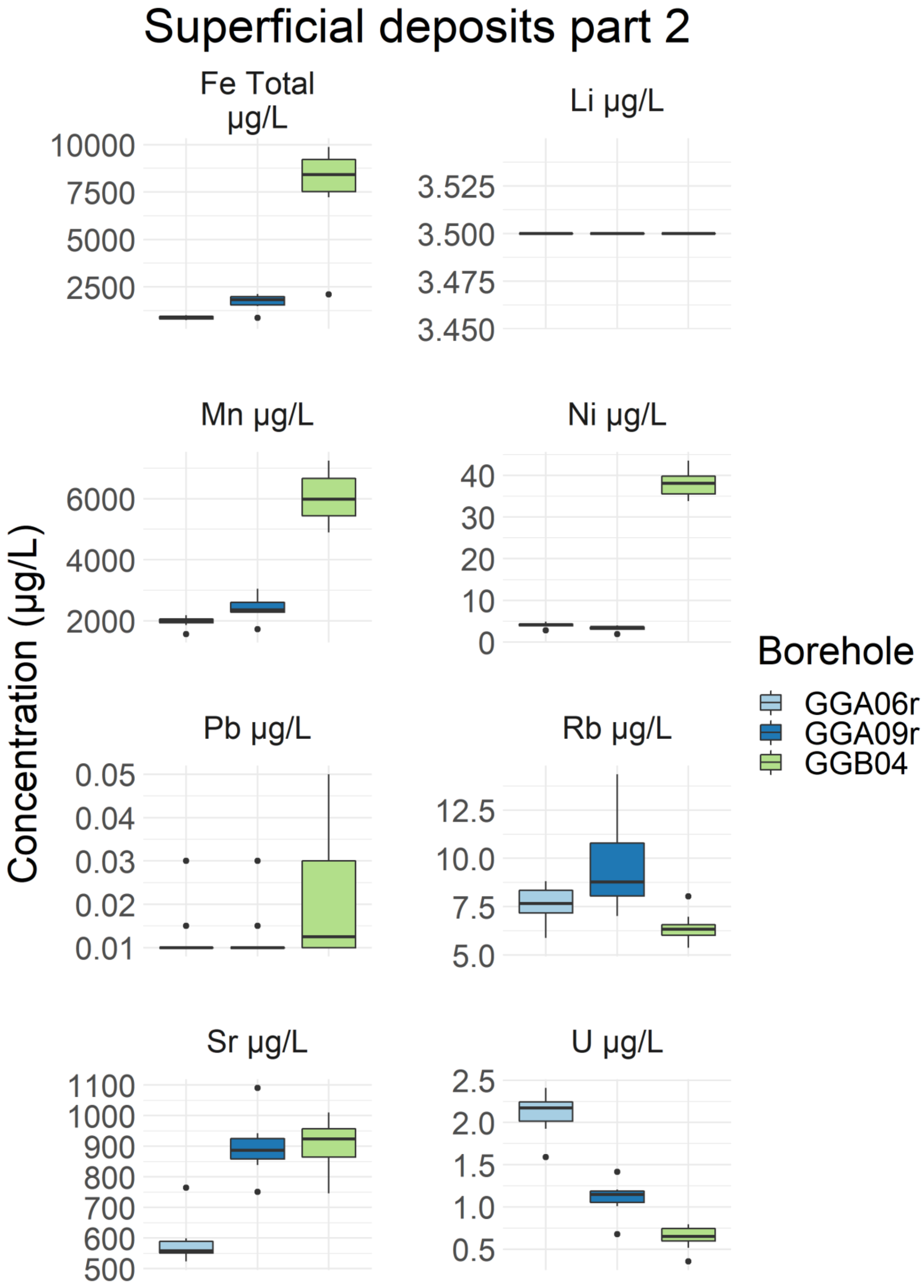

Figure 74 Boxplots showing distribution of parameters measured in µg/L measured during sampling of superficial deposits boreholes.

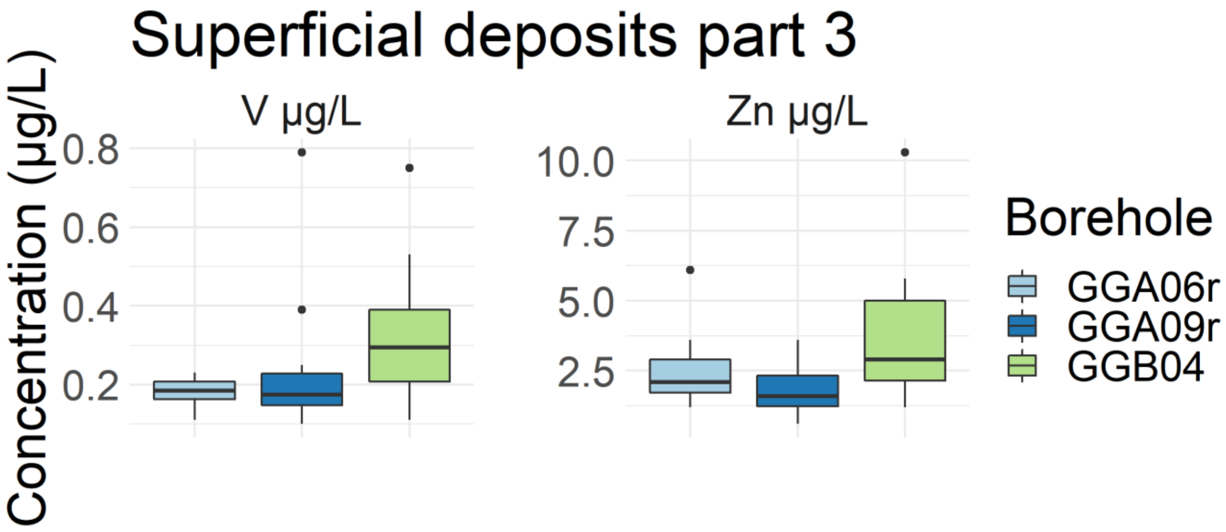

Figure 75 Boxplots showing distribution of parameters measured in µg/L measured during sampling of superficial deposits boreholes.

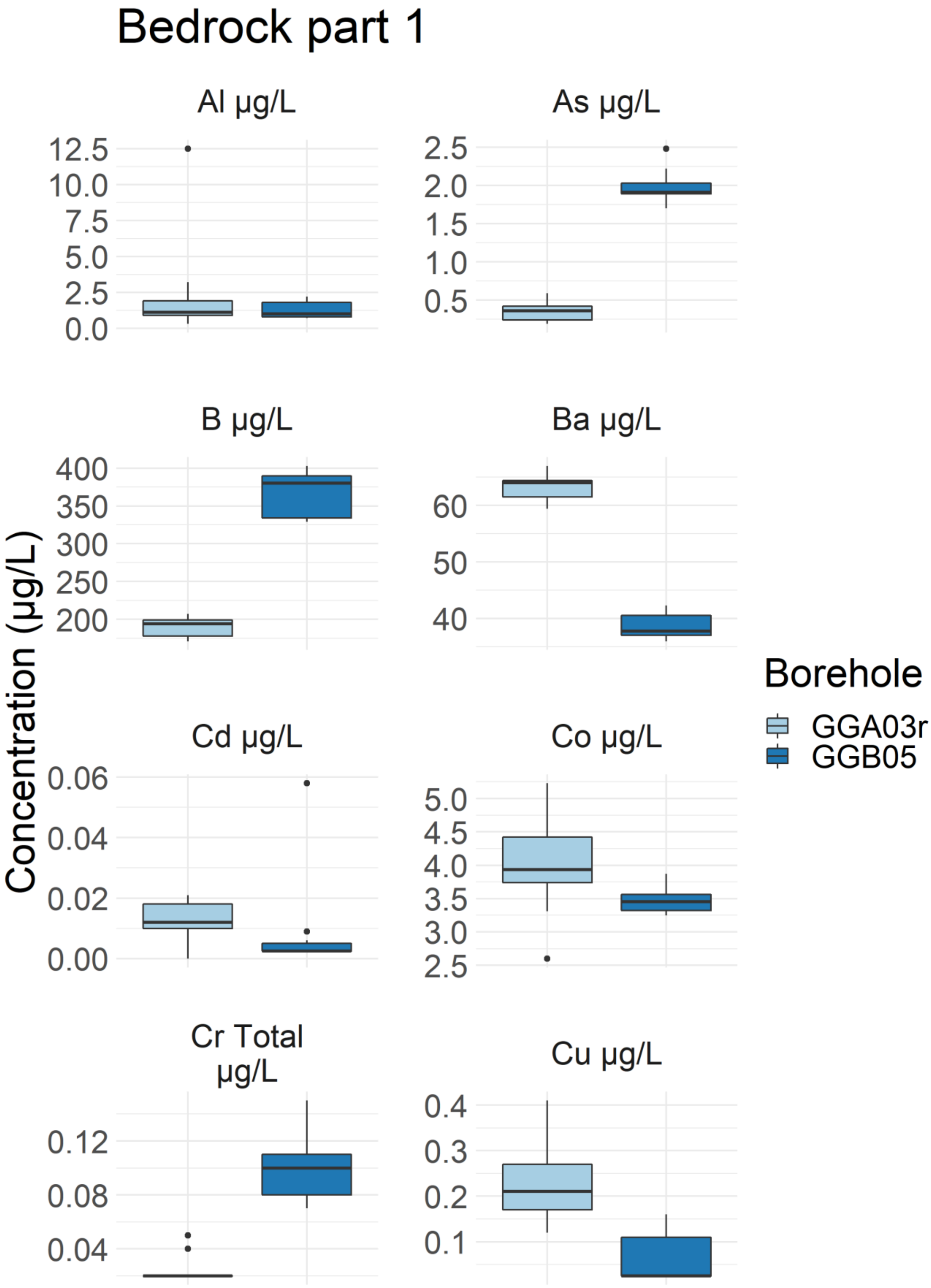

Figure 76 Boxplots showing distribution of parameters measured in µg/L measured during sampling of bedrock boreholes.

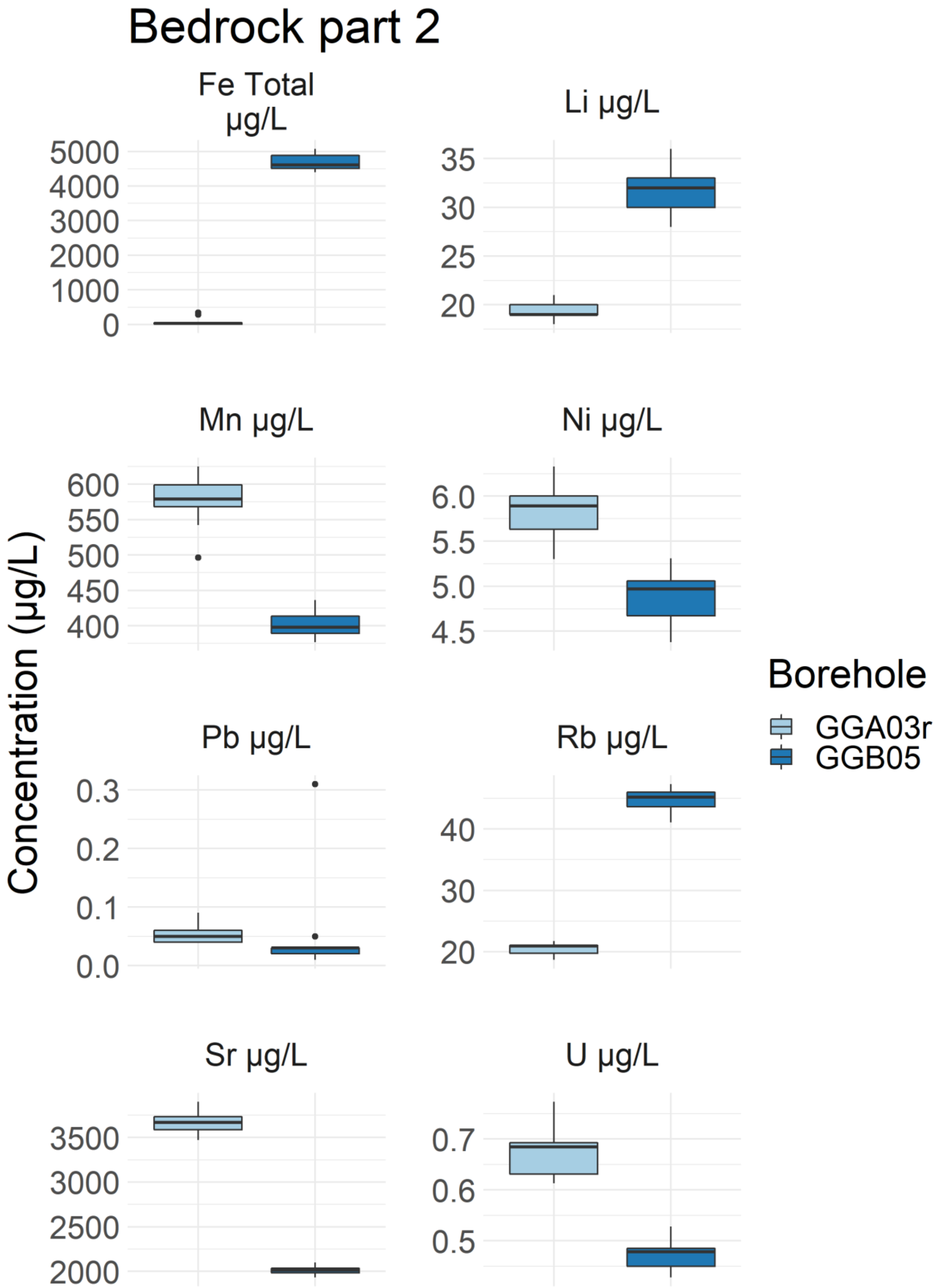

Figure 77 Boxplots showing distribution of parameters measured in µg/L measured during sampling of bedrock boreholes.

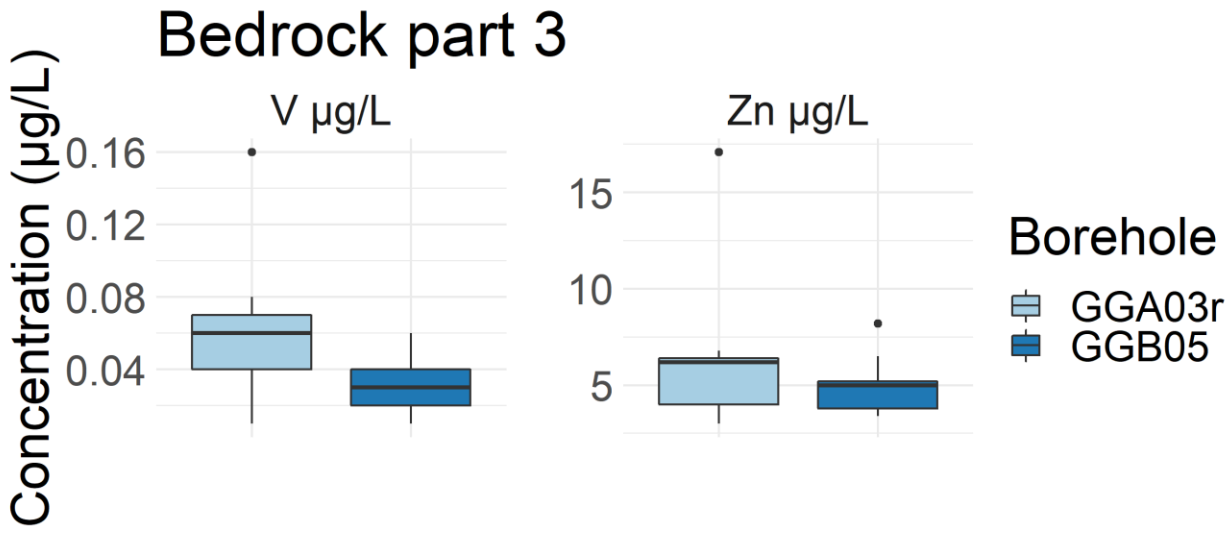

Figure 78 Boxplots showing distribution of parameters measured in µg/L measured during sampling of bedrock boreholes.

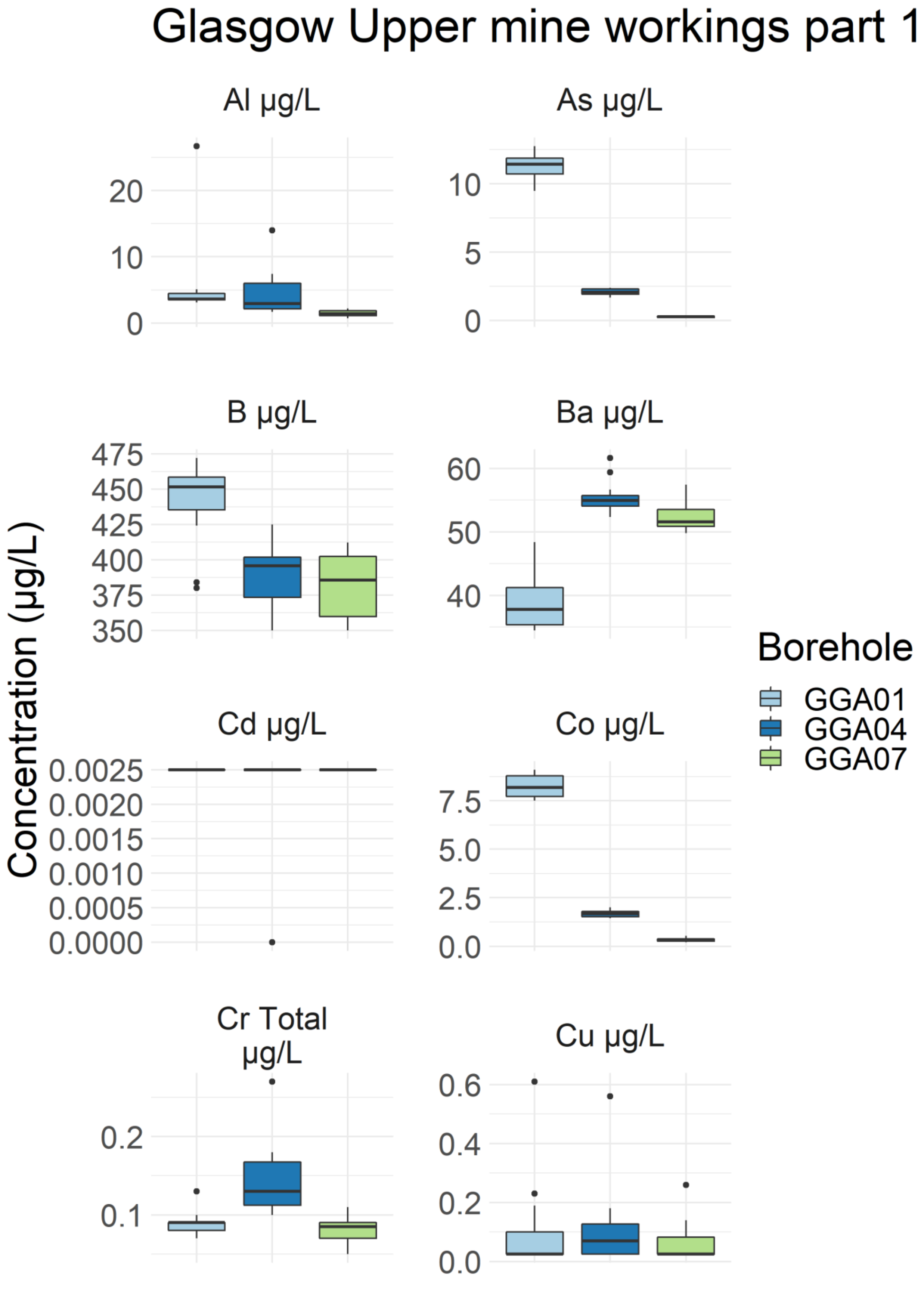

Figure 79 Boxplots showing distribution of parameters measured in µg/L measured during sampling of Glasgow Upper mine workings boreholes.

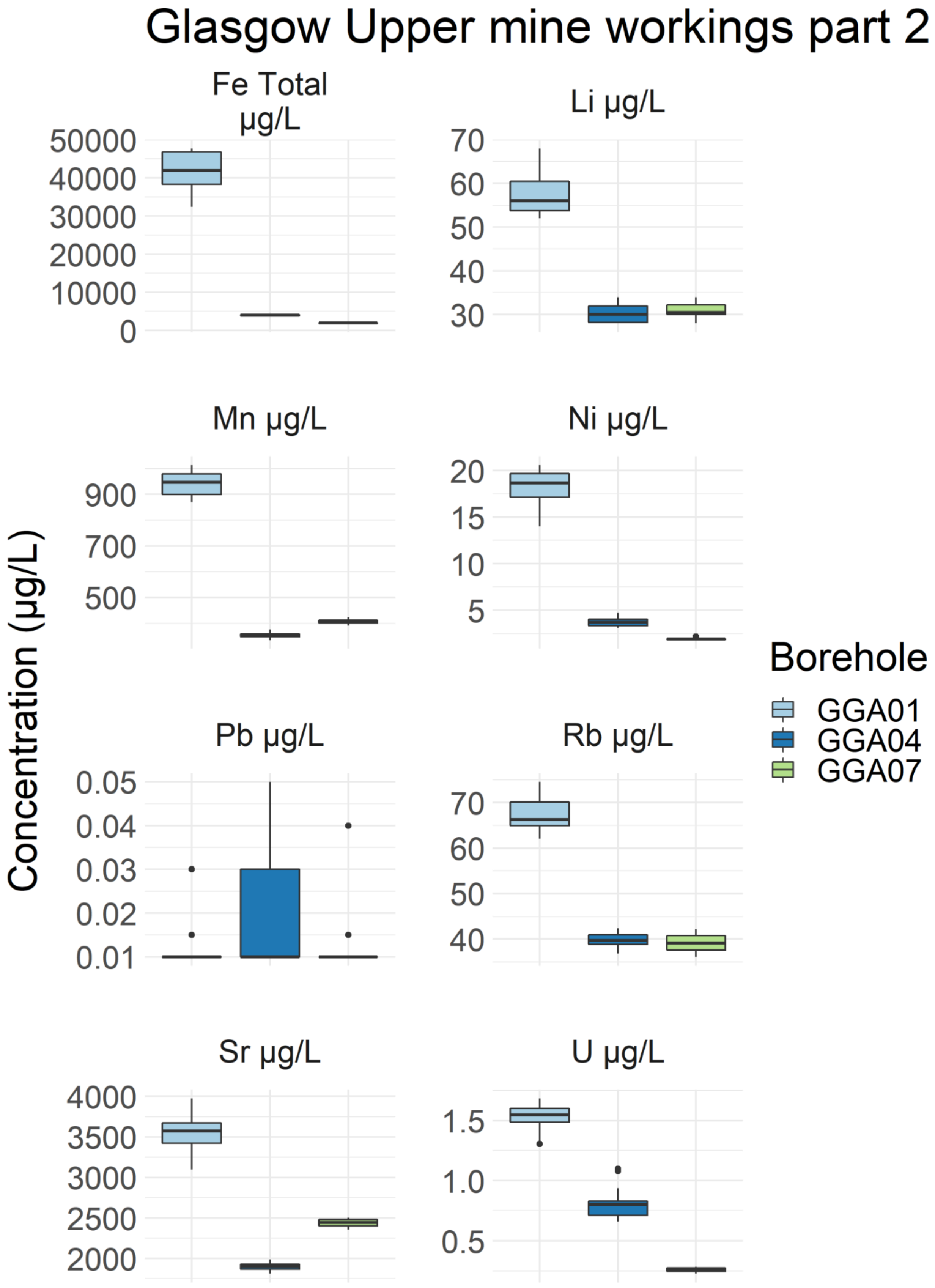

Figure 80 Boxplots showing distribution of parameters measured in µg/L measured during sampling of Glasgow Upper mine workings boreholes.

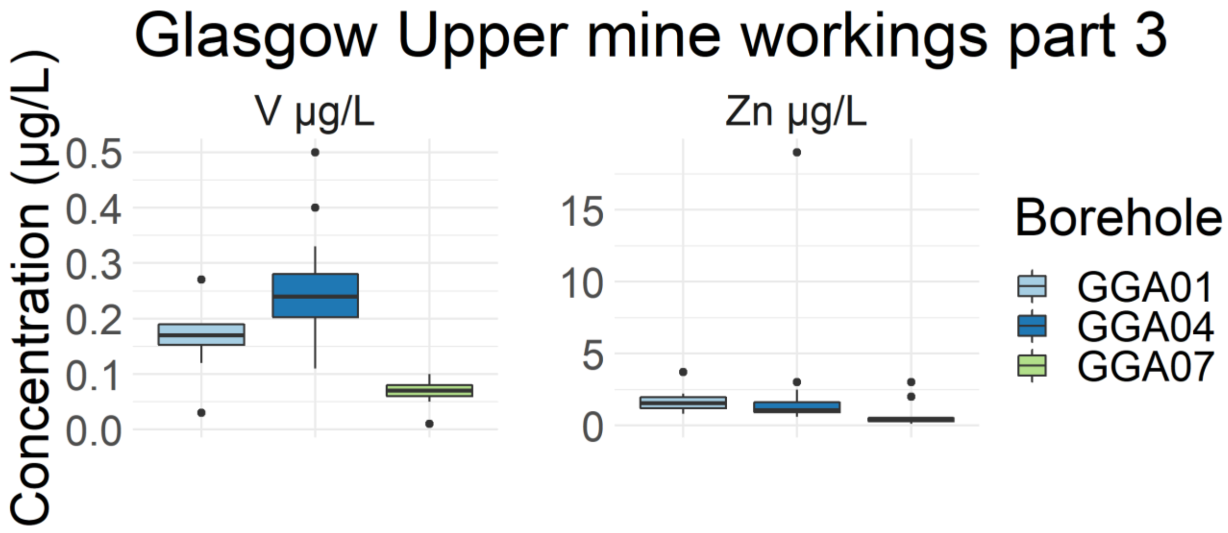

Figure 81 Boxplots showing distribution of parameters measured in µg/L measured during sampling of Glasgow Upper mine workings boreholes.

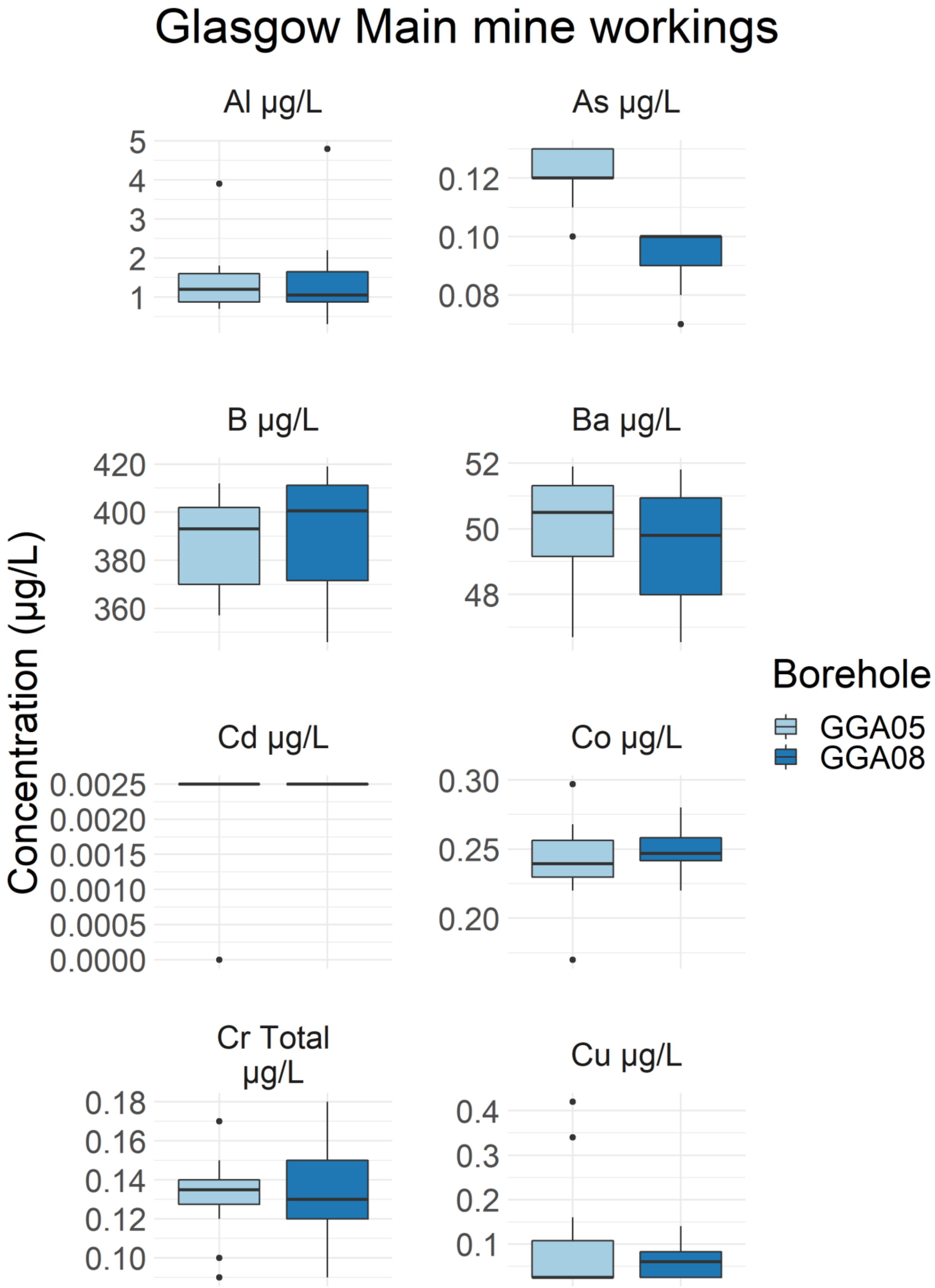

Figure 82 Boxplots showing distribution of parameters measured in µg/L measured during sampling of Glasgow Main mine workings boreholes.

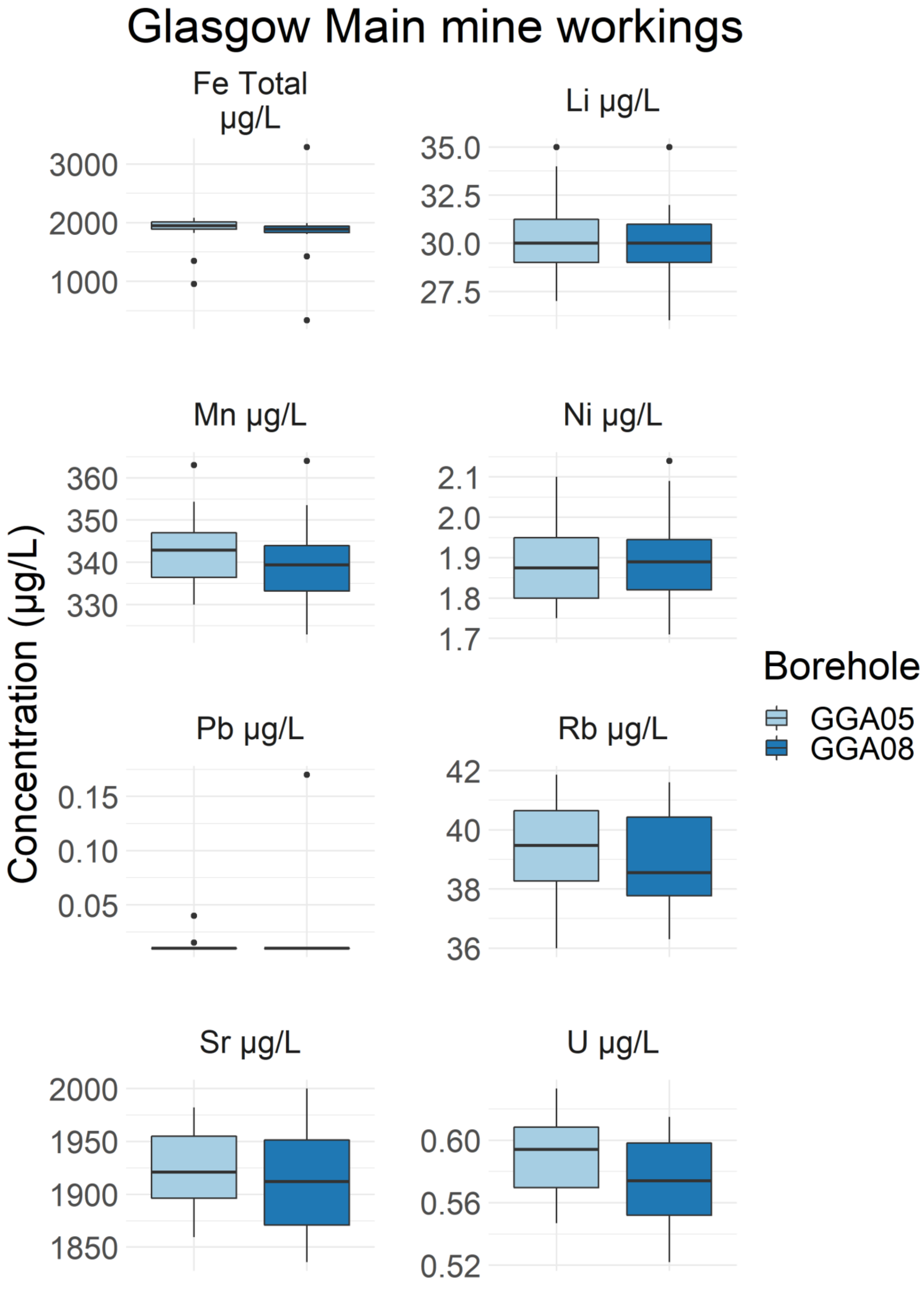

Figure 83 Boxplots showing distribution of parameters measured in µg/L measured during sampling of Glasgow Main mine workings boreholes.

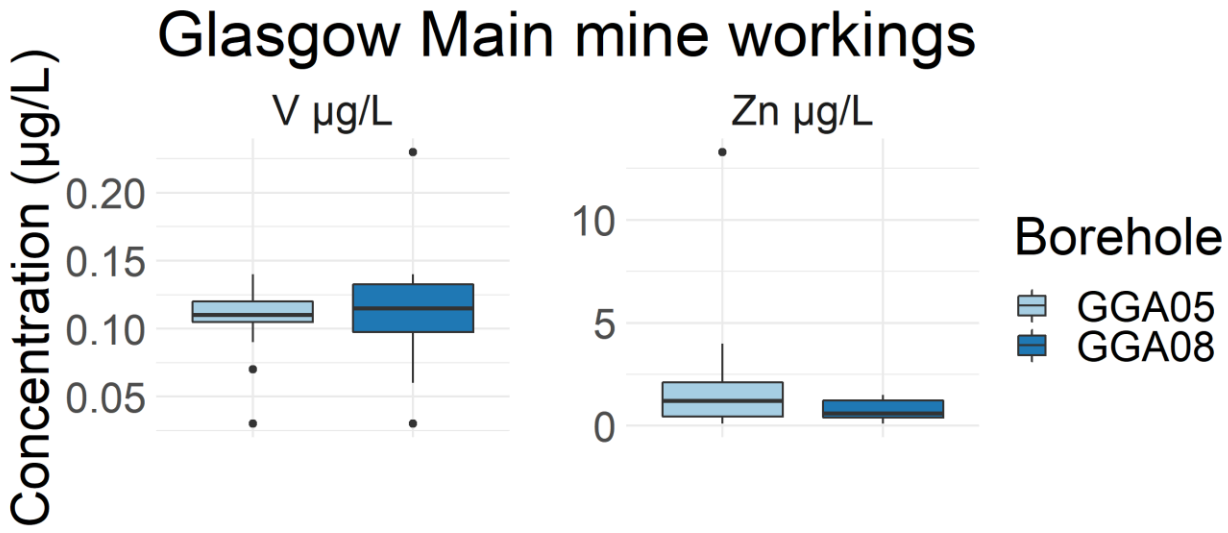

Figure 84 Boxplots showing distribution of parameters measured in µg/L measured during sampling of Glasgow Main mine workings boreholes.

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
CRM	certified reference material
$\delta^{13}C$	ratio of stable isotopes 13carbon: 12carbon in delta notation
$\delta^{18}O$	ratio of stable isotopes 18oxygen: 16oxygen in delta notation
$\delta^{2}H$	ratio of stable isotopes 2hydrogen: 1hydrogen in delta notation
DIC	dissolved inorganic carbon
DO	dissolved oxygen
Eh	redox potential
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
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
RSD	relative standard deviation
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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