UK Geoenergy Observatories: Glasgow groundwater and surface water chemistry dataset release September 2022 - January 2024

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Glasgow Observatory site technician operating the mine water abstraction and reinjection system.

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B Palumbo-Roe, J M Bearcock, K Walker-Verkuil, J Brickell, A Mulcahy, K E Parker

Contributors

P Smedley, T Barlow, D King

Editors

M J Spence

Keyworth, Nottingham British Geological Survey 2025

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British Geological Survey offices

Nicker Hill, Keyworth,
Nottingham NG12 5GG
Tel 0115 936 3100

BGS Central Enquiries Desk
Tel 0115 936 3143
email enquiries@bgs.ac.uk

BGS Sales
Tel 0115 936 3241
email sales@bgs.ac.uk

The Lyell Centre, Research Avenue South,
Edinburgh EH14 4AP
Tel 0131 667 1000
email scotsales@bgs.ac.uk

Natural History Museum, Cromwell Road,
London SW7 5BD
Tel 020 7589 4090
Tel 020 7942 5344/45
email bgslondonstaff@bgs.ac.uk

Cardiff University, Main Building, Park Place,
Cardiff CF10 3AT
Tel 029 2167 4280

Geological Survey of Northern Ireland, 7th Floor,
Adelaide House, 39-49 Adelaide Street, Belfast, BT2 8FD
Tel 0289 038 8462
www2.bgs.ac.uk/gsni/

Natural Environment Research Council, Polaris House,
North Star Avenue, Swindon SN2 1EU
Tel 01793 411500   Fax 01793 411501
www.nerc.ac.uk

UK Research and Innovation, Polaris House,
Swindon SN2 1FL
Tel   01793 444000
www.ukri.org

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Summary

This report describes the hydrochemical monitoring of groundwater and surface water at the UK Geoenergy Observatory in Glasgow (UKGEOS Glasgow) from September 2022 to January 2024. This period coincides with the start of the operational phase for the Observatory, which is designed for research and innovation in mine water geothermal energy and thermal energy storage. Six sampling rounds were completed, with samples collected from 10 boreholes and 6 surface water monitoring points. It is preceded by the previous Glasgow Observatory monitoring report: *Glasgow baseline groundwater and surface water chemistry dataset release June 2021-January 2022 report (Bearcock et al. 2023).*

The groundwater sampling, methods and quality of the water analyses are discussed. The results from the groundwater monitoring include field measurements of redox potential (ORP), pH, dissolved oxygen, electrical conductivity, alkalinity and water temperature, as well as chemical analyses of major, minor, and trace elements, reduced iron, dissolved sulphide, non-purgeable organic carbon (NPOC), polycyclic aromatic hydrocarbons (PAH), total petroleum hydrocarbons (TPH), volatile organic compounds (VOC), oxygen and deuterium isotopes (δ^2H and $\delta^{18}O$), carbon isotopes in dissolved inorganic carbon (DIC) ($\delta^{13}C_{DIC}$), ammonium (NH_4), dissolved gases radon, methane, ethane and carbon dioxide (Rn, CH_4, C_2H_6, CO_2). The results from the surface water monitoring include the same parameters except for NH_4, VOC, reduced iron, sulphide and dissolved gases.

The new monitoring data indicates that the character of the groundwaters has generally remained unchanged since January 2022, except for the Glasgow Upper mine working borehole GGA01. Following prolonged pumping at the start of the operational phase, the water at GGA01 transitioned from a sulphate (SO_4) type to a bicarbonate (HCO_3) type. This change brought the water chemistry in line with that of other boreholes screened into the Upper Glasgow mine workings. Some variations in the composition of other mine waters were observed, although they were less pronounced than the step change observed in GGA01. Some of these changes can be directly linked to mixing induced by abstraction and injection activities within the mine workings during specific periods of the operational phase. Other changes are observed in the bedrock boreholes, exemplified by peaks in arsenic (As) above the max baseline values measured in GGA03r and GGB05, but with concentrations remaining low (< 5 µg/L). These anomalies will be further examined to determine their causes and assess, through further monitoring, if they are isolated occurrence or indicative of a long-term trend.

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 was the first of these new centres to be built 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 groundwater and surface water monitoring is intended also 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.

As part of the baseline sampling program, 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, simultaneous baseline monitoring of groundwaters and surface waters was planned. The start of sampling was, however, halted during the early part of the COVID-19 pandemic in April 2020 and restarted in September 2020. 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). A further six sampling rounds were undertaken between June 2021 and January 2022 and the associated chemical data released with an accompanying report by Bearcock et al. (2023).

Hereafter, the Glasgow Observatory has entered the operational stage and quarterly monitoring of surface water and groundwater has been undertaken. Six sampling rounds were carried out between September 2022 and January 2024.

This report accompanies the water chemical data release from these six rounds of groundwater and surface water monitoring, with start date 20/09/2022 and end date 12/01/2024, and provides a description of the sampling set-up and of the hydrochemistry results, with summary statistics of the analytes for the monitoring period. The report appendices provide details of the analytical methods, the quality control process of the dataset and present the time series for both surface water and groundwater monitoring points from the outset of the monitoring activities.

1.1 CITATION GUIDANCE

This report accompanies the release of the water chemistry September 2022 – January 2024.

Any use of the data should be cited to:

Walker-Verkuil, K., Palumbo-Roe, B., Bearcock, J., Brickell, J., Mulcahy, A., Parker, K. (2025). UKGEOS Glasgow groundwater and surface water chemistry dataset release (2022-2024). NERC EDS National Geoscience Data Centre. (Dataset). https://doi.org/10.5285/fbe7a056-edd7-4e40-8d00-be0b8d2b511b

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1.2 OVERVIEW OF THE GLASGOW OBSERVATORY

The Glasgow Observatory includes 12 boreholes (Figure 1, Table 1). Five are mine water boreholes that are drilled into, and screened 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).

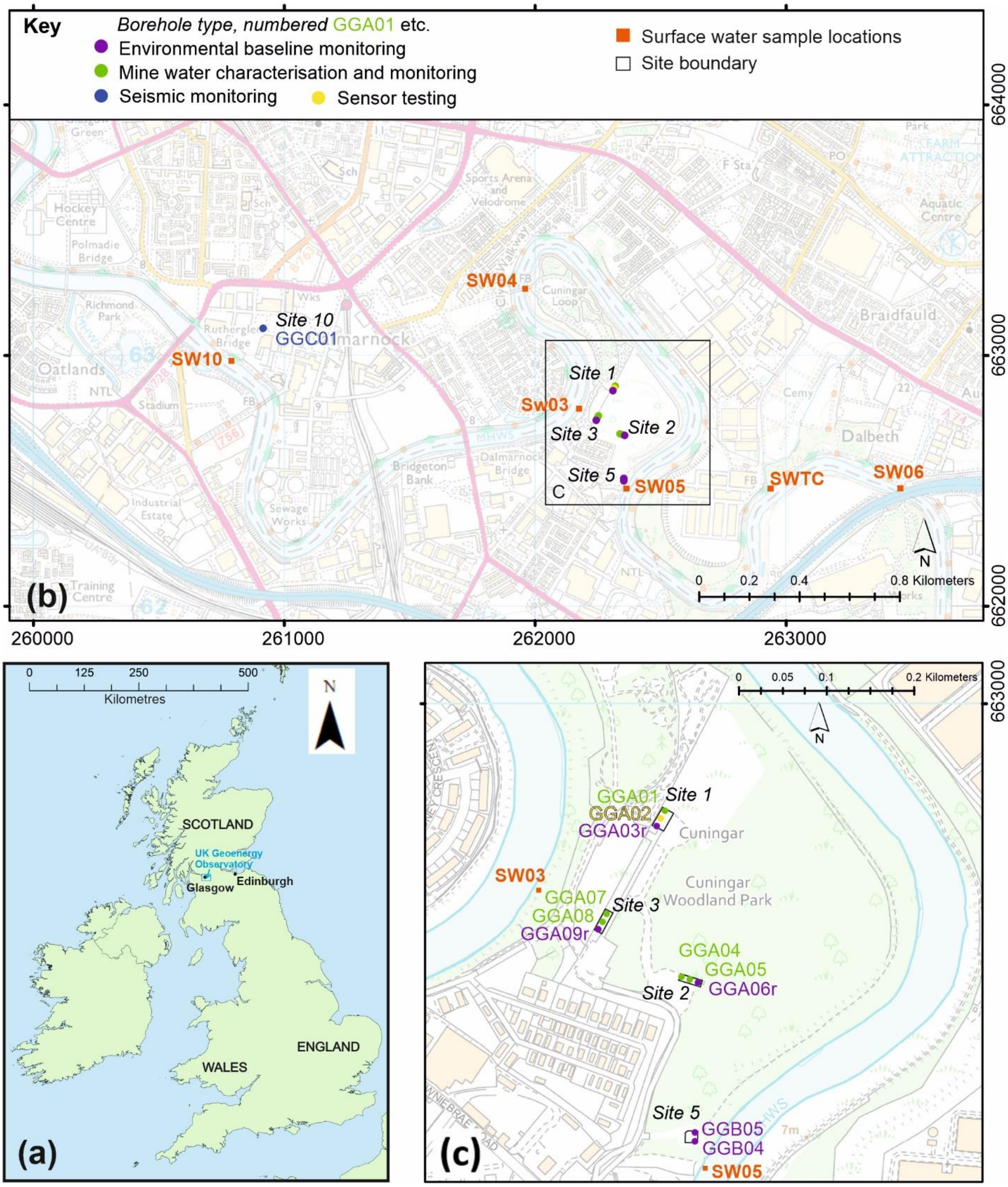


Figure 1 (a) Location of the Glasgow Observatory in the UK (b) position of Observatory sites (c) detail of Cuningar Loop mine water and environmental baseline characterisation and monitoring boreholes. Contains OS data © Crown copyright and database rights [2025] OS AC0000824781.

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 MONITORING

Samples were taken during six monitoring rounds (from round 27 to round 32), during the operational phase of the UKGEOS Glasgow Observatory, between 20/09/2022 and 12/01/2024, as detailed in Table 2, and in-between on site-testing, as summarised in Figure 2.

Table 2 Sampling round dates and boreholes and surface water sites sampled during each round

Borehole / Surface Water ID	Round 27	Round 28	Round 29	Round 30	Round 31	Round 32
	Sep-22	Jan-23	Jun-23	Oct-23	Dec-23	Jan-24
Start Date:	20/09/22	23/01/23	31/05/23	16/10/23	04/12/23	08/01/24
End Date:	23/09/22	26/01/23	06/06/23	20/10/23	08/12/23	12/01/24
Boreholes:						
GGA01	No sample	✓	✓	✓	✓	✓
GGA03r	✓	✓	✓	✓	✓	✓
GGA04	✓+Duplicate	✓+Duplicate	✓	✓	✓	✓
GGA05	No sample	No sample	✓	✓	✓	✓
GGA06r	✓	✓	✓	✓	✓	✓
GGA07	No sample	No sample	✓	✓	✓+Duplicate	✓
GGA08	No sample	No sample	✓	✓	✓	✓+Duplicate
GGA09r	✓	✓	✓+Duplicate	✓	✓	✓
GGB04	✓	✓	✓	✓	✓	✓
GGB05	✓	✓	✓	✓+Duplicate	✓	✓
Surface Water sites:						
SW03	✓	✓	✓	✓	✓	✓
SW04	✓	✓	✓	✓	✓	✓
SW05	✓	✓	No sample	✓	✓	✓
SW06	✓	✓	✓	✓	✓	✓
SW10	✓	✓	✓	✓	✓	✓
SWTC	✓	✓	✓	✓	✓	✓

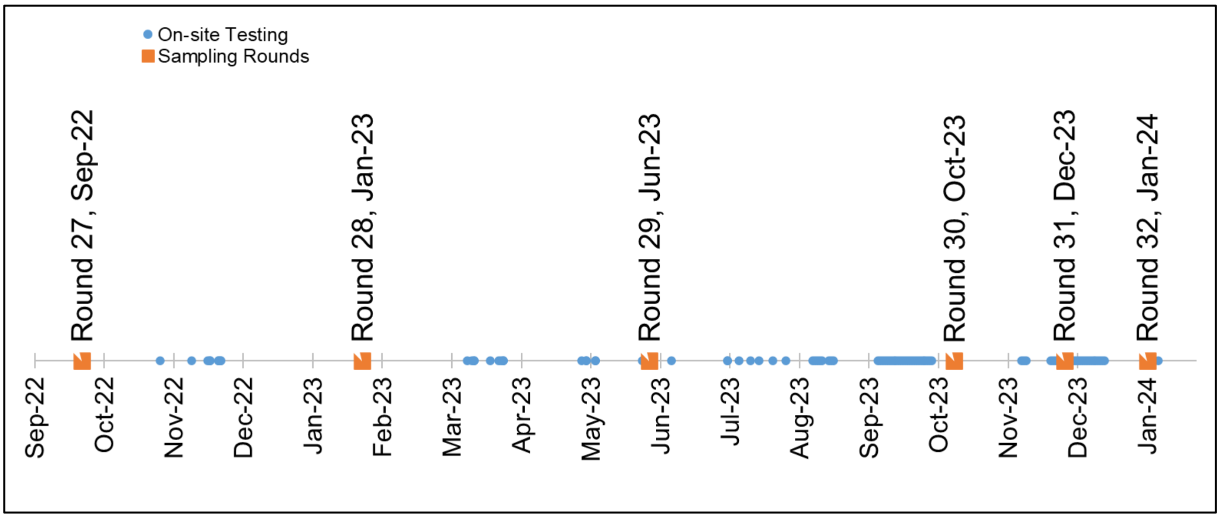


Figure 2 Timeline of sampling rounds and on-site testing at the UKGEOS Glasgow Observatory during the period September 2022 – January 2024.

2.2 SAMPLE COLLECTION, ANALYSES AND QUALITY CONTROL

2.2.1 Sampling set-up

Prior to this monitoring period, the five mine water (GGA01, GGA04, GGA05, GGA07 and GGA08) and two environmental monitoring boreholes (GGA03r and GGB05, in the bedrock) were pumped using a permanently installed 42 mm SS High Performance Bladder Pump, with a 42 mm drop tube in-take assembly extended to the screen section of the borehole casing. The environmental monitoring boreholes GGA06r, GGA09r, GGB04 in the superficial deposits were pumped using a dedicated WaSP P5 submersible pump, which was deployed for each sampling round.

With the completion of the geothermal infrastructure and installation of wellheads on four of the boreholes (2 for abstraction and 2 for injection), the following changes were made to the groundwater sampling procedure (Table 3):

- The two abstraction boreholes (GGA05 and GGA07) each have a SP 46-6 Grundfos submersible groundwater pump installed to a depth of 25 m below wellhead. These boreholes were sampled by setting the selected borehole pump to extract the mine water at a rate of 12 L/s and a minimum of 3 borehole volumes were purged before samples were collected. Sample water was extracted from the abstraction line through a sample tap at a flowrate of approximately 500 ml per minute.
- The two injection boreholes (GGA01 and GGA08) have no borehole pump installed and so groundwater samples were instead collected by manual inertial lift pumping using a 12 mm ID foot valve connected to 12 mm ID x 16 mm OD polyethylene tubing. A dedicated foot valve and tube was used for each well. The sample collection depth was 23 m below the wellhead and a volume of 10 L was pumped prior to sampling. The four probes for field parameter measurement (pH, specific electrical conductance (SEC), redox potential (Eh), dissolved oxygen (DO) and an associated temperature probe) were placed securely in a 1 L plastic beaker. Field parameters were recorded over a 20 minute period, with a minimum of three readings taken five minutes apart from the static 1L water sample.
- During round GF31, GGA05 was also sampled by inertial lift pumping as the GGA05 borehole pump was in use at the time.

The sampling method for the other boreholes was the same as that used for their sampling prior to September 2022. Mine working (GGA04) and environmental bedrock (GGA03r and GGB05) boreholes were sampled using pre-installed bladder pumps with a water discharge tube and airline installed between the pump and the surface. These require a 12v battery to power a BP ProPlus (100 psi) Control Unit/Compressor to fill the bladder and control pumping to the surface. The bladder has a volume of 126 ml. The controller is set to an appropriate fill and discharge time to provide the most efficient pump rate, which is usually achieved at a fill time of 10s and discharge time of 10s. An efficient pump rate is evidenced by a continuous discharge of water, which occurs when the fill time is exactly long enough to completely fill the bladder, and the discharge time matches the time required to discharge the full 126 ml. Superficial deposits (GGA06r, GGA09r, and GGB04) boreholes were sampled via dedicated WaSP submersible pump, which is lowered gradually (to limit the disruption to the water column) to the desired depth at the casing screen section. The pump comprises a plastic discharge tube and power cable running to the surface. The power cable was attached to the WaSP-F1 low flow controller, which is powered by a 12v battery. The flow rate was adjusted until it was approximately 500 ml per minute, or the lowest flow rate which could be achieved with continuous flow.

Groundwater pumped using the Grundfos submersible pumps or bladder pumps was passed through a flow cell for field parameter measurements (pH, specific electrical conductance (SEC), redox potential (Eh) and dissolved oxygen (DO)). The flow cell discharged into a plastic beaker which had a thermometer probe placed in. Field parameters were taken over 20 minutes, with a minimum three readings taken five minutes apart. GGB05 could not always be pumped for 20 minutes due to its low recharge rate and variable rest water level. Following field parameter measurement the flow cell was disconnected and sampling was done directly from the pump discharge tube.

All wastewater was collected in a jerry can and discharged offsite at a suitable drain.

Surface water sampling was carried out using an extendable telescoop from the banks of the River Clyde and Tollcross Burn. At each sampling location the plastic telescoop and a plastic beaker were rinsed in sample water. Sample waters were then collected in the plastic telescoop and transferred to the plastic beaker for the field parameter measurements. The probes from the portable meters were placed carefully in the beaker in a customised holder to ensure that they did not touch the sides or bottom of the beaker, or each other. The meters were left to stabilise before the readings were recorded for each location on a standardised field sheet.

At each sampling location, many splits of each water sample were collected for various chemical analyses (Table 4, Table 5). A detailed description of the analytical methods can be found in Bearcock et al. (2022), Fordyce et al. (2004), and Palumbo-Roe et al. (2021). Analysis of noble gases (helium, neon, argon, krypton, and xenon (He, Ne, Ar, Kr and Xe)), chlorofluorocarbons (CFC-12 and CFC-11), sulphur hexafluoride (SF_6), carried out during previous monitoring, was discontinued.

Table 3 Groundwater sampling set-up since the start of the operational phase.

Borehole	groundwater sampling set-up
GGA01	Footvalve
GGA03r	Bladder
GGA04	Bladder
GGA05	Sample tap
GGA06r	Wasp
GGA07	Sample tap
GGA08	Footvalve
GGA09r	Wasp
GGB04	Wasp
GGB05	Bladder

Table 4 Summary of the water sample splits collected at each location including a list of the parameters determined for each split. The mode of preservation, analytical method and lab location is indicated also.

Water Quality Parameters	Sample Splits	Analytical Method	Lab
Field Measurements:			
Temperature (°C)	No sample - measured in field	Portable meter	-
pH	No sample - measured in field	Portable meter	-
Redox potential (Eh)	No sample - measured in field	Portable meter	-
Specific electrical conductance	No sample - measured in field	Portable meter	-
Dissolved oxygen (DO)	No sample - measured in field	Portable meter	-
Alkalinity (as HCO_3)	No sample - measured in field	Titration	-
Laboratory Measurements:			
Non Purgeable Organic Carbon	Ag-filtered unacidified foil capped 14 mL glass vial (NPOC)	Carbon analyser	BGS
Oxygen and deuterium isotopes $\delta^{18}O/\delta^2H$	30 mL unfiltered unacidified HDPE Nalgene® bottle (δO-H)	Isotope ratio mass spectrometry (IRMS)	BGS
Carbon isotopes $\delta^{13}C$	125 mL unfiltered unacidified HDPE Nalgene® (δC)	IRMS	BGS
Major, minor and trace element cations: Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Hf, Ho, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, P-Total, Pb, Pr, Rb, S-Total, Sb, Se, Si, Sm, Sn, Sr, Ta, Tb, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, Zr	0.45µ Filtered acidified 30 mL HDPE Nalgene® bottle (FA)	Inductively coupled plasma mass spectrometry (ICP-MS)	BGS
Major and minor anions Br, Cl, F, HPO_4, NO_2, NO_3 SO_4, HCO_3 (lab)	0.45µ Filtered unacidified 60 mL HDPE Nalgene® bottle (FUA)	Ion chromatography (IC) and ICP-MS	BGS
Total Petroleum Hydrocarbons TPH (C10-C40) TPH (C8-C10) TPH (C8-C40)	Unfiltered unacidified 1 L clear glass bottle dosed with sodium thiosulphate.	Gas chromatography flame ionisation detector (GC-FID)	Scottish Water
Polycyclic Aromatic Hydrocarbons Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(ghi)perylene, Benzo(k)fluoranthene, Indeno(1,2,3-cd)pyrene, PAH - Total	Unfiltered unacidified 250 mL brown glass bottle dosed with sodium thiosulphate.	HPLC fluorescence detection (HPLC-FD)	Scottish Water
Ammonium (NH_4)		Colorimetric analysis	UKCEH
Radon (Rn)	Amber glass vials pre-dosed with sodium thiosulphate	liquid scintillation	Scottish Water
Methane, ethane and carbon dioxide (CH_4, C_2H_6, CO_2)	Unfiltered unacidified sample in metal container	Gas chromatography	BGS
Sulphide (S^{2-})	Unfiltered 120 mL HDPE bottle, prefilled with SAOB (sulphide antioxidant buffer).	Segmented Flow Analysis	SOCOTEC
Reduced Iron (Fe^{2+})	Unfiltered water in 125 mL bottles pre-dosed with concentrated HCl	Colorimetric analysis	SOCOTEC

Table 5 List of determinands analysed in UKGEOS Glasgow groundwater and surface water samples from September 2022 to January 2024

Determinands	Groundwater	Surface water
Inorganic Chemistry Data	✓	✓
NPOC and TIC	✓	✓
PAH	✓	✓
TPH	✓	✓
VOC	✓	n/a
δ^2H and δ^{18}O	✓	✓
$\delta^{13}C_{DIC}$	✓	✓
NH_4	✓	n/a
Rn	✓	n/a
Dissolved gases CH_4, C_2H_6, CO_2	✓	n/a
S^{2-}	✓	n/a
Fe^{2+}	✓ except for round 30	n/a
CFC-12, CFC-11, SF_6	No	n/a
He, Ne, Ar, Kr, Xe	No	n/a

Note: n/a indicates these parameters are not analysed for surface waters

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 (2022-2024)
> Filenames: UKGEOSGlasgow_GroundWaterChemData3_Release.xlsx, UKGEOSGlasgow_SurfaceWaterChemData4_Release.xlsx

It contains the following analysis data, for the period September 2022 to January 2024:

- field parameters: pH, temperature, Eh (referenced to the standard hydrogen electrode (SHE) using temperature-dependent conversion tables appropriate to the VWR® probe), dissolved oxygen (DO), specific electrical conductivity (SEC) and alkalinity (Field HCO_3)
- inorganic and organic chemical analyses.

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 any 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. 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 inorganic chemical data groups (i.e. major cations, major anions, etc.) are reported in alphabetical order by chemical symbol. The reporting units are mg/L for major and minor ions, and µg/L for trace elements. 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; 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 in µg/L for PAHs and VOCs.

3.2 DATA ANALYSIS IN THIS REPORT

In this report, a summary of the results of the monitoring period September 2022 – January 2024 of the groundwater and surface water within Glasgow Observatory is presented. A short discussion of the results follows.

The boreholes are grouped according to their target horizon (superficial deposits boreholes, bedrock boreholes, Glasgow Upper mine workings and Glasgow Main mine workings boreholes). Minimum, maximum, and median concentrations, total number of samples (n), and number of samples censored n(c) (i.e. non detect, as measurement below detection limit) are reported for each parameter in tables. Where the dataset has greater than 80% of non-detect (n(c)), the data range (minimum and maximum values) is only quoted.

The Mineral saturation indices were determined using the PHREEQC modelling package (Parkhurst and Appelo, 1999) and the phreeqc.dat database.

4 Results

4.1 GROUNDWATER HYDROCHEMICAL CHARACTERISTICS

This section presents the hydrochemical characteristics of the groundwaters at the Glasgow Observatory sampled between September 2022 and January 2024. In the tables 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.

4.1.1 Physico-chemical parameters

Table 6 summarises physico-chemical parameters measured during groundwater monitoring at the Glasgow Observatory between September 2022 and January 2024.

pH is circum-neutral in all groundwaters and ranges from 6.7 to 7.4, with a slightly lower median and wider range of pH values in the superficial deposits than the other target horizons.

Groundwater temperature has a median value of around 11.5 °C in all target horizons, with a range of several degree differences during the monitoring period, possibly influenced by ambient air temperature at the time of the measurement.

Eh values range between 33 mV and 425 mV: median values for each target horizon are similar, between 110 and 180 mV.

Dissolved oxygen (DO) concentrations are generally low and stable, with average values of <0.5 mg/L indicating anoxic conditions. The Glasgow Main workings groundwater shows a slightly wider range of concentrations, between 0 mg/L and 3 mg/L.

The specific electrical conductance (SEC) ranges from 1300 to 1750 µS/cm, indicating that all groundwaters are moderately mineralised. The lowest values and widest range were measured in the superficial deposits, while the mine workings have a relatively constant and higher conductivity.

Table 6 Range and median of groundwater physico-chemical parameters from the Glasgow Observatory boreholes between September 2022 and January 2024. Data are split according to screened target horizon.

	Superficial Deposits					Bedrock				
Parameter	**Min**	**Max**	**Median**	**n**	**n(c)**	**Min**	**Max**	**Median**	**n**	**n(c)**
pH	6.67	7.18	6.87	18	0	6.95	7.13	7.02	12	0
Temperature (°C)	7.6	15.6	11.9	18	0	8.8	12.6	11.5	12	0
Eh (mV)	76	277	166	18	0	54	296	115	12	0
Dissolved oxygen (mg/L)	0.08	0.96	0.28	18	0	0.20	0.59	0.28	12	0
Specific electrical conductance (µs/cm)	1309	1754	1591	18	0	1473	1679	1580	12	0

	Glasgow Upper mine workings					Glasgow Main mine workings				
Parameter	**Min**	**Max**	**Median**	**n**	**n(c)**	**Min**	**Max**	**Median**	**n**	**n(c)**
pH	6.96	7.36	7.05	15	0	6.99	7.20	7.10	8	0
Temperature (°C)	8.4	14.1	11.6	15	0	9.1	14.3	11.6	8	0
Eh (mV)	33	425	111	15	0	73	182	152	8	0
Dissolved oxygen (mg/L)	0.20	1.40	0.41	15	0	0.03	2.99	0.91	8	0
Specific electrical conductance (µs/cm)	1626	1739	1647	15	0	1588	1687	1617	8	0

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

4.1.2 Water Type

Figure 3 and Figure 4 present Piper (Piper, 1944) diagrams showing the hydrochemical facies of groundwater grouped respectively by target unit and by individual borehole. Piper diagrams are interpreted based on the identification of hydrochemical facies (Drever, 1997).

All groundwaters are HCO_3 type with no dominant cation. Major ion ratios in the Glasgow Upper (GGA01, GGA04, GGA07) and Main (GGA05 and GGA08) mine workings are relatively constant and similar (Figure 3). Ratios are more variable for the bedrock (GGA03r, GGB05) and superficial deposits (GGA06r, GGA09r, GGB04), with GGB05 groundwater having a higher percentage of Na + K and lower Ca + Mg. Within the superficial deposit boreholes GGA06r has a lower percentage of Ca and higher Na than the other two boreholes, and GGB04 has higher percentage of SO_4 and lower HCO_3.

When compared to the Piper diagrams presented in the previous data release reports (Bearcock et al., 2022; 2023), the groundwaters have very similar major ion proportions, except for GGA01. Figure 5 shows how the GGA01 groundwater samples changed from Ca-SO_4 type, in the “baseline” monitoring period (pre-September 2022), to a Na-HCO3 water type in the current operational phase (September 2022 – January 2024).

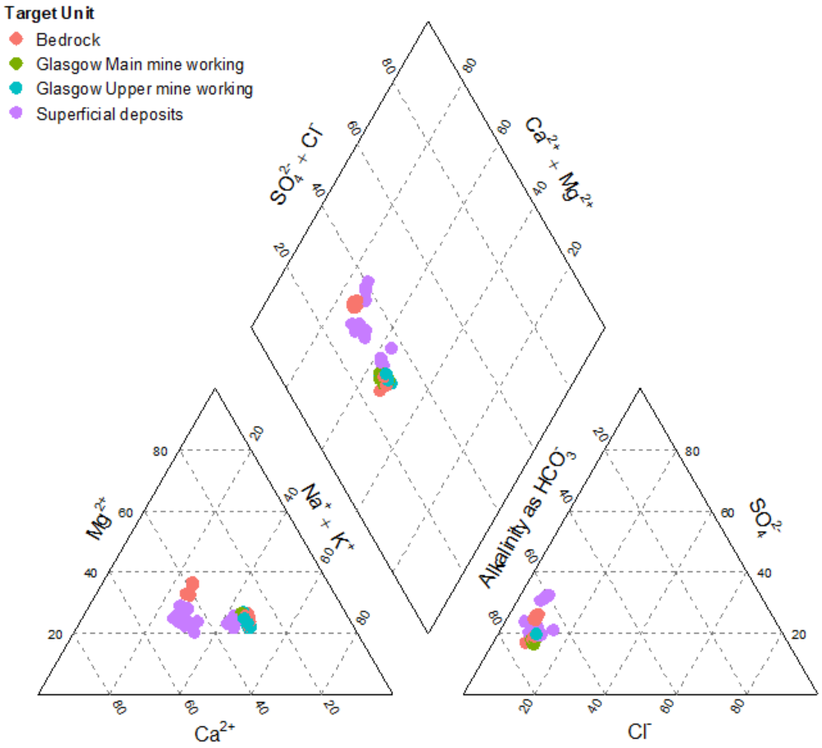


Figure 3 Piper plot representing the groundwater types of each target unit during the monitoring period.

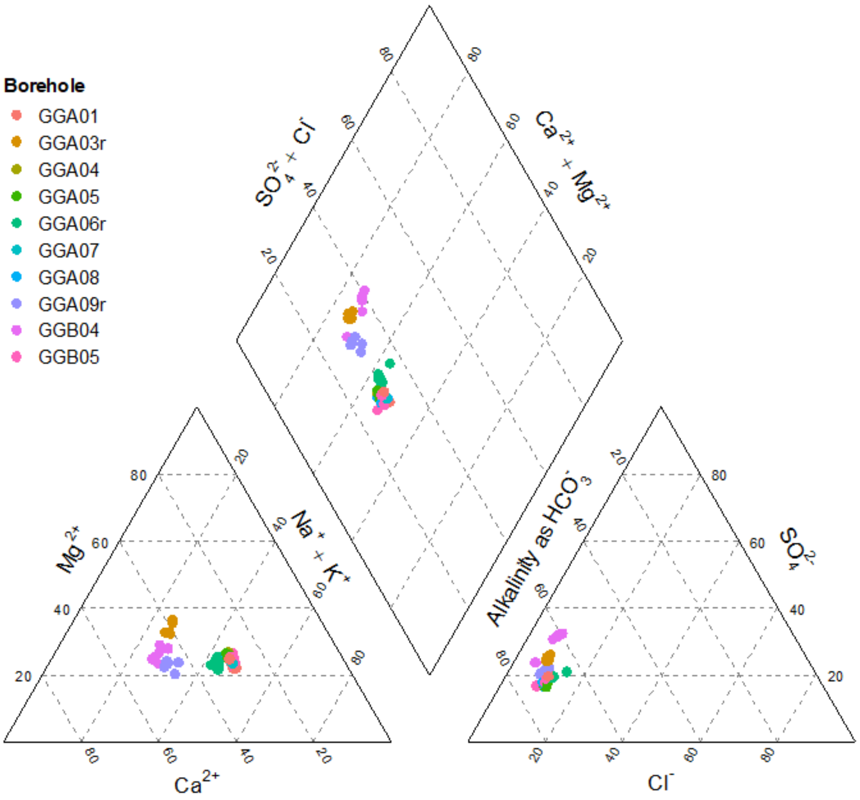


Figure 4 Piper plot representing the groundwater types in each borehole during the monitoring period.

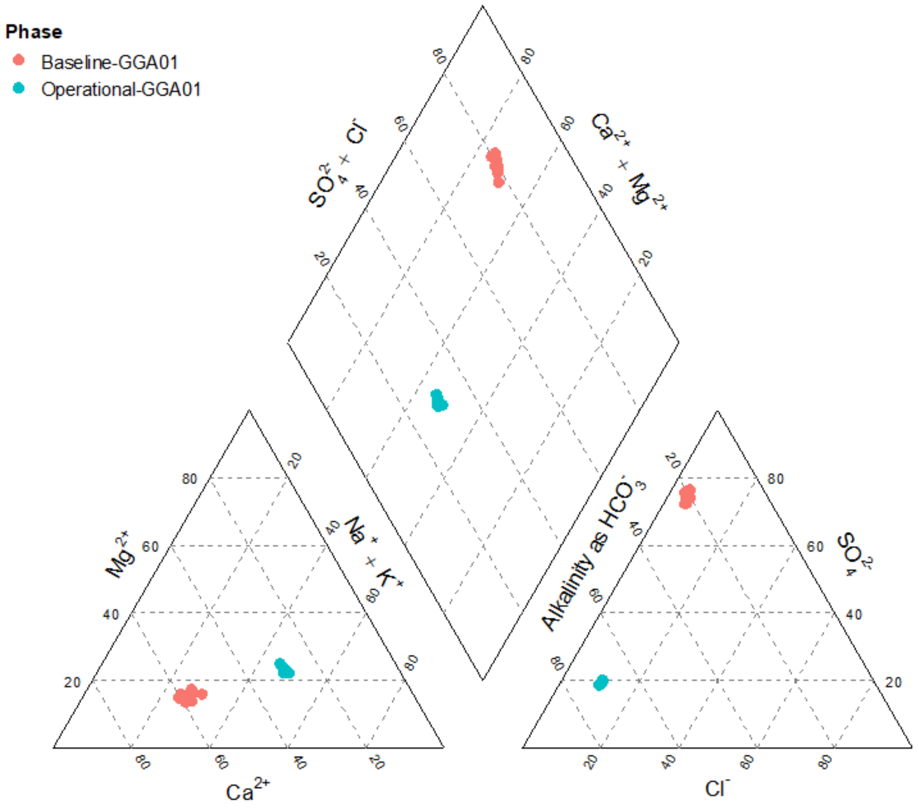


Figure 5 Piper plot showing GGA01 groundwater samples in the “baseline” monitoring period (pre-September 2022) and the current operational phase (September 2022 – January 2024).

4.1.3 Major ions, minor elements, nutrient species (N and P) and dissolved organic carbon

Table 7 and Table 8

present minimum, maximum, and median values of the major ions, minor ions and the Non Purgeable Organic Carbon (NPOC) in groundwater samples, respectively, from boreholes in bedrock and superficial deposits, and boreholes in the mine workings.

The mine waters from both the Glasgow Upper and Main mine workings are, on average, enriched in Na, K, HCO_3 and Cl compared to the bedrock and superficial deposits aquifers and show very low variability within each mine working. Calcium, silicon and SO_4 are, on average, lower in the mine waters. The concentration of magnesium varies more widely in the bedrock boreholes and has a higher median value than in the other target horizons.

Elevated NH_4 concentrations were observed in all the Glasgow Observatory groundwaters, with median values between 9 and 17 mg/L. Ammonium concentrations above 1 mg/L are generally found in old, reducing groundwaters or as a result of pollution (Shand et al., 2007). Concentrations fall within a narrower range in the mined target horizons.

Nitrate in groundwater at the Glasgow Observatory is mostly below detection limit, but was occasionally reported up to a maximum concentration of 1.69 mg/L, in accordance with the anoxic groundwater conditions.

Total phosphorus concentrations are generally low in groundwaters across the Glasgow Observatory. The superficial deposits have the largest concentrations (0.006 – 0.13 mg/L), while values in the mine waters and bedrock are below or close to the detection limit (<0.005 mg/L).

NPOC in the Glasgow Observatory groundwaters is mostly present in the range 1.15 mg/L to 5.76 mg/L, except for one outlier of 32.4 mg/L in the superficial deposits. The median values in groundwaters from the bedrock, Glasgow Upper and Glasgow Main mine workings are similar, while concentrations within the superficial deposits are generally at the higher end of the range.

Bromide is present at low concentration and within a similar range (0.3 mg/L – 0.8 mg/L) in all the groundwaters analysed. Fluoride concentrations are very low, between 0.06 mg/L – 0.3 mg/L, and on average are higher in the mine waters than in the bedrock and superficial deposits.

4.1.4 Sulphide

As per previous rounds, sulphide concentrations were mostly lower or close to the detection limit of 0.02 mg/L, with the exception of GGB04 in the superficial deposits in round 28 with 1.08 mg/L, and GGA05 in the Glasgow Main mine workings with 0.21 mg/L in round 31.

4.1.5 Trace elements

Minimum, maximum, and median concentrations of trace elements in groundwater samples are presented in Table 9 (boreholes in bedrock and superficial deposits) and Table 10 (boreholes in mine workings).

Large differences between the superficial deposits and the other target horizons are observed in the median concentrations of Ba and Sr; the highest Ba median of 109 µg/L and lowest Sr median of 953 µg/L are measured in the superficial deposits, compared to a Ba median range 37 – 47 µg/L and Sr median range 1924 – 2847 µg/L in the other borehole types.

Concentrations of Fe are generally high across all the Glasgow Observatory groundwaters (median values range from 1941 to 3178 µg/L). The dominance of dissolved iron as reduced iron (Fe^{2+}) is consistent with the redox conditions and the circum-neutral pH of the groundwaters. Manganese concentrations have similar range and median values in the bedrock and mine waters (median range 355 – 412 µg/L) but are higher in the superficial deposits.

Boron concentrations are higher in the superficial deposits (median: 510 µg/L) compared to the bedrock (median: 258 µg/L), the Glasgow Upper mine workings (median: 396 µg/L) and the Glasgow Main mine workings (median: 397 µg/L). The superficial deposits also differ from the other aquifers in that they have lower concentrations of Li, Rb, Cs and higher concentrations of Al, Ti, V, Cr, Co, Ni, Se, Zr, Sb, Tl, U (refer to Table 9 for individual values).

The median arsenic concentration is 2.14 µg/L in the bedrock groundwaters (range 0.18 – 4.39 µg/L) and lower (median <1 µg/L) in the mine waters and superficial deposits.

Table 7 Summary of the major ions, minor elements and dissolved organic carbon from groundwater samples retrieved from the Glasgow Observatory boreholes targeting the superficial deposits and bedrock during sampling between September 2022 and January 2024

		Superficial Deposits					Bedrock				
		Min	Max	Median	n	n(c)	Min	Max	Median	n	n(c)
Major ions (mg/L)											
Ca	Calcium	111	181	141	18	0	100	148	118	12	0
Mg	Magnesium	42.5	54.2	49.0	18	0	48.5	77.0	63.8	12	0
Na	Sodium	78.9	168	120	18	0	94.9	187	141	12	0
K	Potassium	11.4	21.1	16.9	18	0	8.36	19.7	14.1	12	0
HCO_3	Total Alkalinity	549	868	766	18	0	718	827	784	12	0
Cl	Chloride	36.1	94.0	60.6	18	0	49.3	72.3	56.0	12	0
SO_4	Sulphate	160	237	190	18	0	143	218	184	12	0
HCO_3	Bicarbonate (from field alkalinity)	528	864	744	18	0	685	812	774	12	0
Minor ions (mg/L)											
P	Phosphorus - total	0.006	0.133	0.023	18	0	<0.005	0.011		12	8
S	Sulphur – total	59.1	84.4	69.0	18	0	57.7	79.0	68.4	12	0
Si	Silicon	5.33	9.03	6.15	18	0	5.19	7.27	6.03	12	0
Br	Bromide	0.31	0.67	0.40	18	0	0.36	0.77	0.48	12	0
F	Fluoride	0.06	0.22	0.12	18	0	<0.005	0.26	0.12	12	1
NO_3	Nitrate	<0.30	0.67		18	17	<0.30	0.99		12	10
NO_2	Nitrite	<0.05			18	18	<0.05			12	12
NH_4	Ammonia	3.24	22.95	17.35	18	0	2.58	15.6	8.89	12	0
NPOC	Non-purgeable organic carbon	1.58	32.41	4.49	18	0	1.15	5.51	2.48	13	0

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

Table 8 Summary of the major, minor elements and dissolved organic carbon from groundwater samples retrieved from the Glasgow Observatory boreholes targeting the mine workings during sampling between September 2022 and January 2024.

		Glasgow Upper mine workings					Glasgow Main mine workings				
		Min	Max	Median	n	n(c)	Min	Max	Median	n	n(c)
Major ions (mg/L)											
Ca	Calcium	101	109	106	15	0	103	107	105	8	0
Mg	Magnesium	48.3	57.9	53.5	15	0	52.9	56.4	54.5	8	0
Na	Sodium	172	197	180	15	0	168	195	174	8	0
K	Potassium	17.4	19.1	18.3	15	0	17.3	19.1	18.4	8	0
HCO_3	Total Alkalinity	804	834	823	15	0	805	830	820	8	0
Cl	Chloride	68.5	72.2	70.7	15	0	70.2	76.3	73.5	8	0
SO_4	Sulphate	145	181	164	15	0	141	180	148	8	0
HCO_3	Bicarbonate (from field alkalinity)	760	817	793	15	0	769	827	795	8	0
Minor ions (mg/L)											
P	Phosphorus - total	<0.005	0.013		15	8	<0.005	0.018	0.009	8	3
S	Sulphur – total	54.3	65.5	59.7	15	0	50.8	64.1	53.8	8	0
Si	Silicon	4.92	6.94	5.29	15	0	4.89	5.28	4.98	8	0
Br	Bromide	0.35	0.74	0.48	15	0	0.39	0.72	0.54	8	0
F	Fluoride	0.15	0.24	0.18	15	0	0.13	0.20	0.16	8	0
NO_3	Nitrate	<0.30	1.69		15	14	<0.30			8	8
NO2	Nitrite	<0.05	0.064		15	14	<0.05			8	8
NH_4	Ammonia	13.00	17.08	15.12	15	0	12.85	15.95	14.39	8	0
NPOC	Non-purgeable organic carbon	1.87	5.35	2.16	15	0	1.80	3.42	2.45	8	0

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

Table 9 Summary of trace elements recorded in groundwater samples sampled between September 2022 and January 2024. 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)**
Ag	**Silver**	<0.04	0.19		18	17	<0.04			12	12
Al	**Aluminium**	1.40	6.80	3.70	18	0	1.20	3.30	2.10	12	0
As	**Arsenic**	0.26	1.13	0.59	18	0	0.18	4.39	2.14	12	0
B	**Boron**	326	751	511	18	0	150	394	258	12	0
Ba	**Barium**	47.7	217	109	18	0	44.4	57.0	47.2	12	0
Be	**Beryllium**	<0.08			18	18	<0.08			12	12
Bi	**Bismuth**	<0.08			18	18	<0.08			12	12
Cd	**Cadmium**	<0.005	0.011	0.0025	18	10	<0.005	0.055	0.0025	12	8
Ce	**Cerium**	0.014	0.126	0.089	18	0	0.010	0.056	0.028	12	0
Co	**Cobalt**	2.03	8.88	2.51	18	0	2.19	5.12	2.93	12	0
Cr	**Chromium**	0.11	0.34	0.18	18	0	<0.04	0.13	0.08	12	4
Cs	**Caesium**	<0.04	0.08	0.05	18	7	0.12	0.24	0.20	12	0
Cu	**Copper**	0.06	0.66	0.12	18	0	<0.05	0.14	0.03	12	7
Dy	**Dysprosium**	0.008	0.046	0.017	18	0	<0.003	0.006	0.004	12	4
Er	**Erbium**	0.006	0.109	0.013	18	0	<0.003	0.005	0.002	12	6
Eu	**Europium**	<0.003	0.005	0.002	18	10	<0.003			12	12
Fe	**Total iron**	185	7938	2084	18	0	3.0	4423	2439	12	0
Ga	**Gallium**	<0.04	0.08		18	15	<0.04			12	12
Gd	**Gadolinium**	0.006	0.021	0.016	18	0	<0.005	0.006	0.003	12	9
Hf	**Hafnium**	<0.006			18	18	<0.006			12	12
Ho	**Holmium**	<0.003	0.021	0.004	18	1	<0.003			12	12
La	**Lanthanum**	0.008	0.069	0.047	18	0	0.006	0.025	0.014	12	0
Li	**Lithium**	<7			18	18	16.0	33.0	24.5	12	0
Lu	**Lutetium**	<0.003	0.070	0.004	18	3	<0.003			12	12
Mn	**Manganese**	1798	8917	2874	18	0	281	448	412	12	0
Mo	**Molybdenum**	<0.20	2.00	0.40	18	4	<0.20	1.00	0.50	12	1
Nb	**Niobium**	<0.02	0.02		18	15	<0.02			12	12
Nd	**Neodymium**	<0.005	0.078	0.052	18	1	<0.005	0.027	0.013	12	1
Ni	**Nickel**	3.37	37.06	4.01	18	0	3.41	5.30	4.18	12	0
Pb	**Lead**	<0.02	0.10	0.02	18	7	<0.02	0.10	0.02	12	4
Pr	**Praseodymiu**	<0.003	0.016	0.010	18	1	<0.003	0.007	0.002	12	6
Rb	**Rubidium**	6.23	10.40	7.82	18	0	16.25	48.65	30.13	12	0
Sb	**Antimony**	<0.04	0.07	0.02	18	13	<0.04			12	12
Se	**Selenium**	<0.04	0.27	0.07	18	7	<0.04			12	12
Sm	**Samarium**	<0.005	0.015	0.010	18	3	<0.005	0.006		12	10
Sn	**Tin**	<0.08	18.93	0.06	18	9	<0.08	0.27	0.06	12	6
Sr	**Strontium**	549	1102	953	18	0	1903	3849	2847	12	0
Ta	**Tantalum**	<0.006			18	18	<0.006			12	12
Tb	**Terbium**	<0.004	0.004		18	17	<0.004			12	12
Th	**Thorium**	<0.04			18	18	<0.04			12	12
Ti	**Titanium**	<0.06	0.28	0.17	18	3	<0.06			12	12
Tl	**Thallium**	<0.02	0.06	0.03	18	8	<0.02	0.08	0.02	12	5
Tm	**Thulium**	<0.003	0.026	0.002	18	12	<0.003			12	12
U	**Uranium**	0.38	2.37	1.43	18	0	0.38	0.49	0.45	12	0
V	**Vanadium**	0.11	0.52	0.19	18	0	<0.02	0.08	0.04	12	2
W	**Tungsten**	<0.06			18	18	<0.06			12	12
Y	**Yttrium**	0.07	0.38	0.18	18	0	0.04	0.08	0.05	12	0
Yb	**Ytterbium**	0.010	0.268	0.017	18	0	<0.004	0.005	0.002	12	8
Zn	**Zinc**	1.60	29.60	4.25	18	0	1.10	19.10	2.35	12	0
Zr	**Zircon**	0.06	0.34	0.12	18	0	0.03	0.10	0.05	12	0

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

Table 10 Summary of trace elements recorded in groundwater samples during sampling between September 2022 and January 2024. 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)**
Ag	**Silver**	<0.04			15	15	<0.04			8	8
Al	**Aluminium**	0.90	3.40	2.10	15	0	1.00	2.80	2.10	8	0
As	**Arsenic**	0.08	1.87	0.75	15	0	0.14	0.71	0.19	8	0
B	**Boron**	315	433	396	15	0	383	424	397	8	0
Ba	**Barium**	32.7	55.9	37.8	15	0	37.2	51.1	47.6	8	0
Be	**Beryllium**	<0.08			15	15	<0.08			8	8
Bi	**Bismuth**	<0.08			15	15	<0.08			8	8
Cd	**Cadmium**	<0.005	0.017	0.0025	15	9	<0.005	0.017	0.0025	8	6
Ce	**Cerium**	<0.004	0.031	0.016	15	4	<0.004	0.011	0.006	8	2
Co	**Cobalt**	0.23	1.54	1.29	15	0	0.26	1.45	0.31	8	0
Cr	**Chromium**	0.07	0.12	0.10	15	0	0.05	0.16	0.14	8	0
Cs	**Caesium**	0.17	0.26	0.23	15	0	0.14	0.22	0.16	8	0
Cu	**Copper**	<0.05	1.45	0.21	15	6	<0.05	1.19	0.12	8	3
Dy	**Dysprosium**	<0.003	0.011	0.005	15	2	<0.003	0.007	0.005	8	1
Er	**Erbium**	<0.003	0.008	0.006	15	2	<0.003	0.007	0.005	8	1
Eu	**Europium**	<0.003			15	15	<0.003			8	8
Fe	**Total iron**	23	4428	3178	15	0	1743	3296	1941	8	0
Ga	**Gallium**	<0.04	0.02	0.02	15	15	<0.04			8	8
Gd	**Gadolinium**	<0.005	0.009	0.006	15	7	<0.005	0.006		8	7
Hf	**Hafnium**	<0.006			15	15	<0.006			8	8
Ho	**Holmium**	<0.004			15	15	<0.004			8	8
La	**Lanthanum**	<0.004	0.015	0.008	15	4	<0.004	0.005	0.003	8	4
Li	**Lithium**	29.0	34.0	32.0	15	0	29.0	34.0	32.5	8	0
Lu	**Lutetium**	<0.004	0.003		15	14	<0.004	0.003		8	7
Mn	**Manganese**	231	442	365	15	0	341	441	355	8	0
Mo	**Molybdenum**	<0.2	8.60	0.20	15	5	<0.2	0.50		8	7
Nb	**Niobium**	<0.01			15	15	<0.01			8	8
Nd	**Neodymium**	<0.005	0.023	0.014	15	3	<0.005	0.010	0.005	8	4
Ni	**Nickel**	2.65	3.93	2.96	15	0	1.88	4.40	2.17	8	0
Pb	**Lead**	<0.02	1.36	0.01	15	9	<0.02	0.38	0.02	8	4
Pr	**Praseodymiu**	<0.003	0.004	0.002	15	11	<0.003			8	8
Rb	**Rubidium**	36.28	44.90	40.49	15	0	35.94	42.50	39.41	8	0
Sb	**Antimony**	<0.04			15	15	<0.04	0.12		8	7
Se	**Selenium**	<0.04			15	15	<0.04			8	8
Sm	**Samarium**	<0.006	0.005		15	14	<0.006			8	8
Sn	**Tin**	<0.08	0.11		15	14	<0.08			8	8
Sr	**Strontium**	1822	2323	2144	15	0	1836	2233	1924	8	0
Ta	**Tantalum**	<0.006			15	15	<0.006			8	8
Tb	**Terbium**	<0.004	0.002	0.002	15	15	<0.004			8	8
Th	**Thorium**	<0.04			15	15	<0.04			8	8
Ti	**Titanium**	<0.06	0.33	0.08	15	8	<0.06	0.07	0.03	8	5
Ti	**Thallium**	<0.02	0.04		15	14	<0.02			8	8
Tm	**Thulium**	<0.003			15	15	<0.003			8	8
U	**Uranium**	0.34	0.68	0.42	15	0	0.36	0.63	0.56	8	0
V	**Vanadium**	<0.02	0.24	0.08	15	1	<0.02	0.13	0.08	8	1
W	**Tungsten**	<0.06	0.10	0.03	15	9	<0.06			8	8
Y	**Yttrium**	0.01	0.11	0.07	15	0	0.02	0.07	0.06	8	0
Yb	**Ytterbium**	<0.004	0.011	0.008	15	1	<0.004	0.012	0.009	8	0
Zn	**Zinc**	0.90	27.90	8.40	15	0	0.80	42.20	6.55	8	0
Zr	**Zircon**	0.01	0.20	0.06	15	0	<0.009	0.11	0.04	8	1

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

4.1.6 PAH, TPH and VOC

In the superficial deposits' groundwaters all polycyclic aromatic hydrocarbon (PAH) were below the detection limit of 0.0151 µg/L. The majority of total petroleum hydrocarbons (TPH) were also below the laboratory detection limits i.e. (TPH (C8-C10) <0.003 mg/L, TPH (C10-C40) <0.042 mg/L, TPH (C8-C40) <0.045 mg/L). Most detections were measured during round 27 or 28 with a maximum value of TPH (C8-C10): 0.01 mg/L and TPH (C10-C40), TPH (C8-C40): 0.326 mg/L. There were no VOCs detected.

In the bedrock groundwaters total PAH and VOCs were not detected in any sample during the monitoring period; a value of 0.0049 ug/L for Benzo(b)fluoranthene was measured. During sampling round 28, TPH (C8-C10), TPH (C10-C40) and TPH (C8-C40) were detected in GGA03r, with values respectively of 0.042 mg/L, 0.149 mg/L, 0.192 mg/L and TPH (C8-C10) in GGB05 with a value of 0.016 mg/L. From sampling rounds 29 to 32 only C8-C40 TPH was measured and values were always below the detection limit of 0.04 mg/L.

In the Glasgow Upper mine working groundwaters no total PAH and no VOCs were detected during the monitoring period. Benzo(a)pyrene was detected once with a value of 0.0025 ug/L. During sampling round 27 only, TPH (C10-C40) and TPH (C8-C40) were detected in GGA04 at a concentration of 0.404 mg/L, while C8-C10 TPH was detected in GGA04 and GGA01 in round 28 at 0.003 and 0.009 mg/L. From sampling rounds 29 to 32 only TPH (C8-C40) were measured and concentrations were always below the detection limit of 0.04 mg/L.

In the Glasgow Main mine working groundwaters, no total PAH and no VOCs were detected during the monitoring period. TPH (C8-C40) was detected in groundwater from GGA08 at a concentration of 0.108 mg/L during sampling round 29. Otherwise TPH were all below detection limits.

4.1.7 Stable isotopic composition

The graphs in Figure 6 and Figure 7 show the latest (September 2022 – January 2024) data vs data previously reported in the "baseline" monitoring reports (pre-September 2022).

The groundwater $\delta^{2}H$ and $\delta^{18}O$ isotopic composition is fairly uniform across all the target units during the monitoring period, with the $\delta^{2}H$ and $\delta^{18}O$ ranging from -51.7‰ to -48.2‰ and from -7.61‰ to -7.28‰, respectively (Table 11). The groundwater samples cluster closely on the global meteoric water line (GMWL) in the dual $\delta^{2}H$ - $\delta^{18}O$ isotope plot, consistent with aquifer recharge from modern precipitation and with previous monitoring (Figure 6).

The median $\delta^{13}C$ of dissolved inorganic carbon (DIC) is similar across the groundwater groups, but with a larger variability in the superficial deposits and bedrock groundwaters compared to the mine waters (Table 11). The isotopic signature of both Glasgow Upper and Glasgow Main mine working groundwaters is similar, plotting on Figure 7 around the median $\delta^{13}C_{DIC}$ value of -11‰ and high alkalinity. In contrast, groundwaters from GGA03r in the bedrock and GGB04 in the superficial deposits plot separately from the main group in Figure 7: GGA03r has a higher $\delta^{13}C_{DIC}$ median of -7.5‰ ±0.3‰, while GGB04 has a lower $\delta^{13}C_{DIC}$ median of -16.6‰ ±0.9‰. These differences, which are similar to patterns observed in previous monitoring, likely reflect differences in the origin of the DIC pool. A higher proportion of isotopically light inorganic carbon from soil-derived CO_2 or degradation of organic matter could account for the lower $\delta^{13}C_{DIC}$ value for the shallow GGB04 borehole, while the subsequent reaction of soil- derived CO_2 with $\delta^{13}C_{-}$ enriched bedrock carbonates could explain the higher $\delta^{13}C_{DIC}$ values in GGA03.

Table 11 $\delta^{13}C_{DIC}$, $\delta^{18}O$ and $\delta^{2}H$ min, max median, and SD values of groundwaters within each target horizon between September 2022 and January 2024.

Variable	Target horizon	Min	Max	Median	SD	n
$\delta^{13}C_{DIC}$ PDB ‰	Superficial deposits	-18.6	-10.8	-12.8	2.4	17
	Bedrock	-16.9	-7.3	-11.1	2.8	13
	Glasgow Upper	-12.4	-10.9	-11.4	0.4	15
	Glasgow Main	-11.5	-10.9	-11.2	0.3	8
$\delta^{18}O$ VSMOW2 ‰	Superficial deposits	-7.60	-7.28	-7.42	0.08	17
	Bedrock	-7.61	-7.41	-7.49	0.07	13
	Glasgow Upper	-7.56	-7.39	-7.45	0.05	15
	Glasgow Main	-7.49	-7.41	-7.44	0.03	8
$\delta^{2}H$ VSMOW2 ‰	Superficial deposits	-51.6	-48.2	-50.2	0.8	17
	Bedrock	-51.6	-48.8	-50.6	0.7	13
	Glasgow Upper	-51.7	-48.6	-50.8	0.7	15
	Glasgow Main	-51.1	-49.5	-50.5	0.5	8

n = number of samples

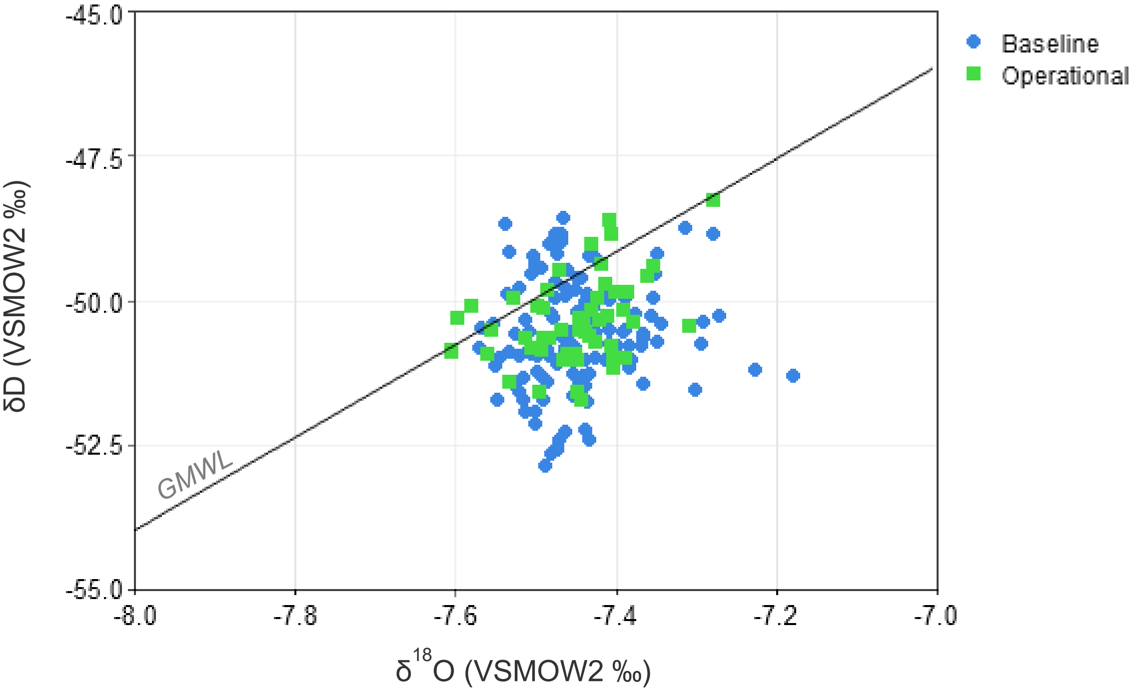


Figure 6 Plot of water $\delta^{2}H$ versus $\delta^{18}O$ isotope data with reference to the global meteoric water line (GMWL) (Craig, 1961) in groundwater samples between September 2022 and January 2024 (operational phase), compared against the pre-September 2022 monitoring period.

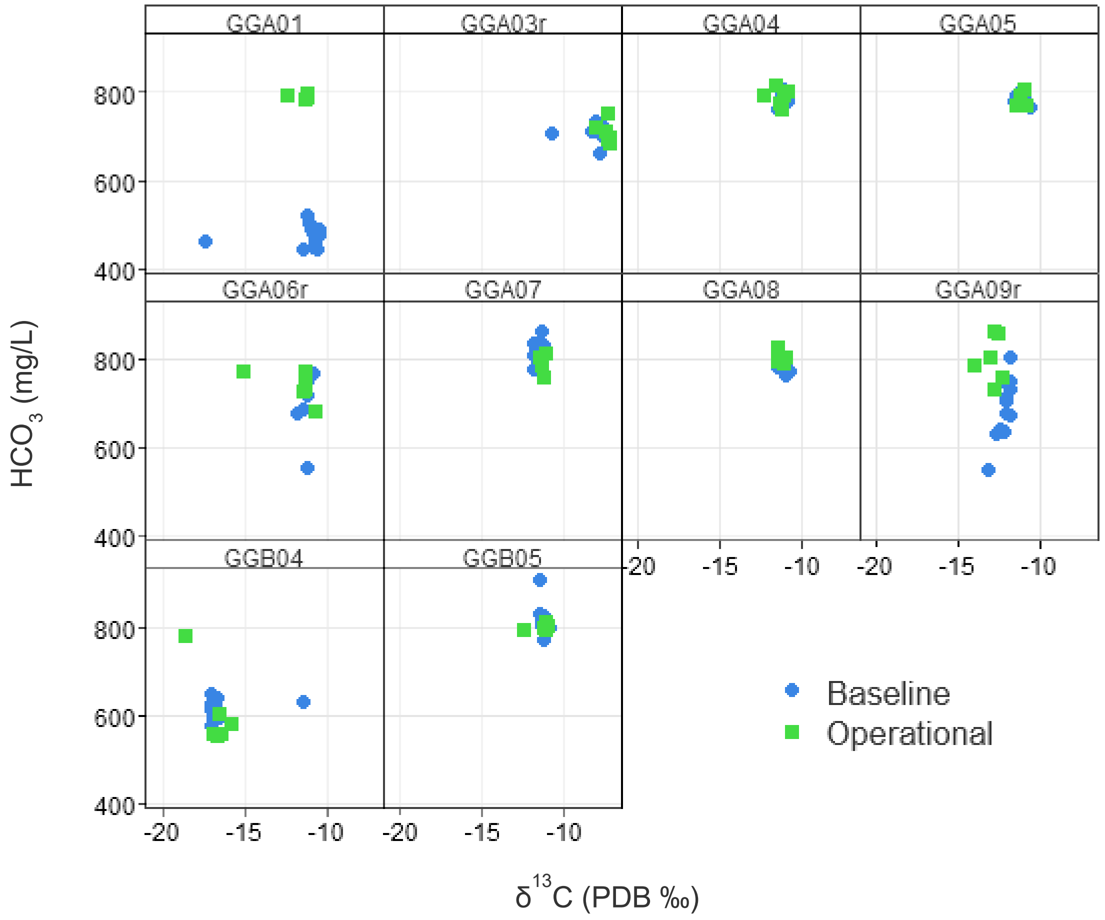


Figure 7 Plot of HCO_3 versus $\delta^{13}C_{DIC}$ isotope data for each borehole between September 2022 and January 2024 (operational phase), compared against the pre-September 2022 monitoring period. Superficial deposits: GGA06r, GGA09r, GGB04; Bedrocks: GGA03r, GGB05; Glasgow Upper mine workings: GGA01, GGA04, GGA07; Glasgow Manin mine workings: GGA05, GGA08.

4.1.8 Dissolved gases

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

Figure 8 shows the latest (September 2022 – January 2024) data vs data previously reported in the “baseline” monitoring reports (pre-September 2022).

Dissolved methane (CH_4) concentrations ranged from 0.6 µg/L to 421 µg/L. The superficial deposits and the bedrock boreholes had lower median concentrations (21 µg/L and 68 µg/L, respectively) compared to the Glasgow Main (median: 174 µg/L), and Glasgow Upper boreholes (median: 173 µg/L).

No ethane was detected.

Dissolved carbon dioxide (CO_2) concentrations ranged from 109 mg/L to 229 mg/L, with a higher median concentration of 179 mg/L in the superficial deposits compared to the other units (median range: 136–142 mg/L) (Table 12, Figure 8).

Similar variation in CH_4 and CO_2 concentrations was observed in the previous monitoring period.

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

Variable	Target horizon	Min	Max	Median	SD	n	n(c)
Methane (CH_4) (µg/L)	Superficial deposits	0.8	161	18	47	17	0
	Bedrock	0.6	97	16	42	13	0
	Glasgow Upper	0.7	425	174	114	15	0
	Glasgow Main	0.6	223	173	75	8	0
Ethane (C_2H_6) (µg/L)	Superficial deposits	<1				17	17
	Bedrock	<1				13	13
	Glasgow Upper	<1				15	15
	Glasgow Main	<1				8	8
Carbon Dioxide (CO_2) (mg/L)	Superficial deposits	118	229	179	38	17	0
	Bedrock	113	219	142	29	13	0
	Glasgow Upper	109	158	141	15	15	0
	Glasgow Main	121	148	136	8	8	0

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

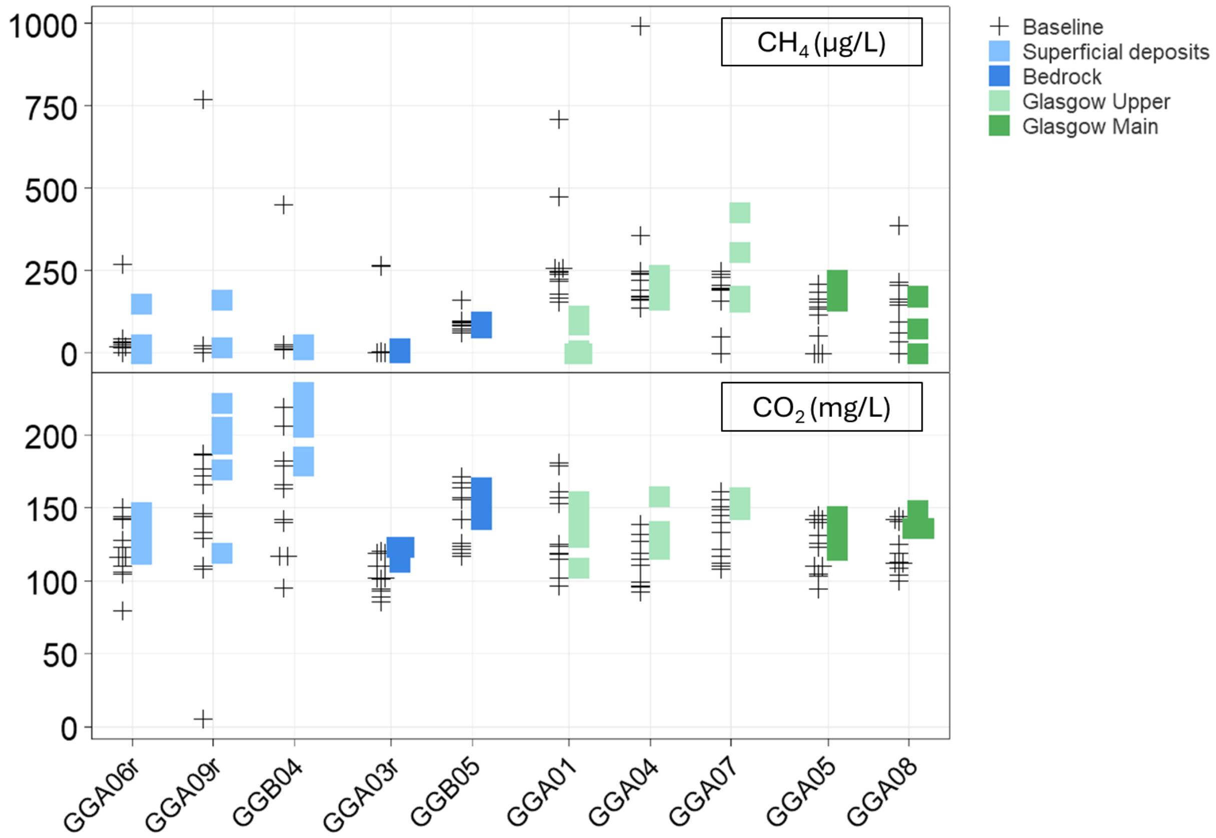


Figure 8 Distribution of dissolved CH_4 and CO_2 in each borehole between September 2022 and January 2024 (operational phase), compared against the pre-September 2022 monitoring period.

4.1.9 Saturation index

Mineral saturation indices were calculated using PHREEQC (Parkhurst and Appelo, 1999) and the thermodynamic database phreeqc.dat (Table 13). Most groundwaters are in equilibrium with respect to carbonate minerals (calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$, siderite ($FeCO_3$), and rhodochrosite ($MnCO_3$)), barite ($BaSO_4$) and quartz (SiO_2).

Waters are supersaturated with respect to gibbsite $Al(OH)_3$, and amorphous ferric hydroxide $Fe(OH)_3$(a), but are undersaturated with respect to jarosite (jarosite-K: $KFe_3(SO_4)_2(OH)_6$), gypsum ($CaSO_4.2H_2O$) and halite (NaCl).

Median carbon dioxide partial pressure (P_{CO2}) values calculated from the ground water analysis using PHREEQC ranged from $10^{-1.8}$ to $10^{-1.3}$ atm. These are significantly higher than atmospheric values around $10^{-3.4}$ atm.

Table 13 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 phase	Target horizon	Mean	Min	Median	Max
SI Calcite	Bedrock	0.2	-0.1	0.2	0.8
	Glasgow Main mine working	0.3	-0.2	0.3	0.7
	Glasgow Upper mine working	0.4	-0.1	0.3	1.4
	Superficial deposits	0.3	-0.1	0.2	1.3
SI Dolomite	Bedrock	0.2	-0.5	0.1	1.4
	Glasgow Main mine working	0.5	-0.6	0.6	1.1
	Glasgow Upper mine working	0.7	-0.5	0.5	2.7
	Superficial deposits	0.4	-0.4	0.3	2.7
SI Siderite	Bedrock	0.4	-1.5	0.5	1.6
	Glasgow Main mine working	0.4	-0.1	0.4	0.9
	Glasgow Upper mine working	-0.4	-4.1	-0.1	1.5
	Superficial deposits	0.1	-1.6	0.3	1.5
SI Rhodochrosite	Bedrock	0.1	-0.6	0.0	0.9
	Glasgow Main mine working	0.0	-0.7	0.0	0.7
	Glasgow Upper mine working	0.0	-0.5	-0.1	0.9
	Superficial deposits	0.0	-1.2	0.0	0.8
SI Gibbsite	Bedrock	1.3	0.6	1.1	2.4
	Glasgow Main mine working	1.4	0.4	1.3	2.2
	Glasgow Upper mine working	0.9	0.3	0.9	2.0
	Superficial deposits	0.9	0.3	0.9	2.0
SI Fe(OH)3(a)	Bedrock	0.6	-0.5	0.1	2.7
	Glasgow Main mine working	1.4	0.0	1.5	2.9
	Glasgow Upper mine working	0.5	-2.6	0.6	3.0
	Superficial deposits	1.0	-0.6	0.7	3.2

Mineral phase	Target horizon	Mean	Min	Median	Max
SI Goethite	Bedrock	6.0	4.9	5.5	8.1
	Glasgow Main mine working	6.8	5.3	7.0	8.2
	Glasgow Upper mine working	5.8	2.8	6.0	8.5
	Superficial deposits	6.4	4.7	6.1	8.7
SI Barite	Bedrock	0.2	-0.3	0.2	1.0
	Glasgow Main mine working	-0.1	-0.4	-0.1	0.2
	Glasgow Upper mine working	0.1	-0.4	0.0	0.5
	Superficial deposits	0.1	-0.4	0.1	0.6
SI Gypsum	Bedrock	-1.5	-2.7	-1.3	-0.1
	Glasgow Main mine working	-2.3	-2.8	-2.4	-1.3
	Glasgow Upper mine working	-1.7	-2.8	-1.8	-0.2
	Superficial deposits	-1.5	-2.7	-1.4	-0.2
SI Jarosite-K	Bedrock	-7.0	-11.3	-7.2	0.2
	Glasgow Main mine working	-6.9	-12.2	-6.5	-4.2
	Glasgow Upper mine working	-8.5	-15.9	-8.5	-1.8
	Superficial deposits	-6.0	-11.0	-6.7	1.4
SI Quartz	Bedrock	0.2	-0.5	0.2	0.6
	Glasgow Main mine working	0.0	-0.2	0.0	0.2
	Glasgow Upper mine working	0.1	-0.5	0.1	0.5
	Superficial deposits	0.1	-0.2	0.1	0.5
SI SiO2(a)	Bedrock	-1.2	-1.9	-1.2	-0.8
	Glasgow Main mine working	-1.3	-1.5	-1.3	-1.1
	Glasgow Upper mine working	-1.3	-1.8	-1.2	-0.8
	Superficial deposits	-1.2	-1.5	-1.2	-0.9
P CO2(g)	Bedrock	$10^{-1.4}$	$10^{-2.3}$	$10^{-1.3}$	$10^{-0.9}$
	Glasgow Main mine working	$10^{-1.8}$	$10^{-2.3}$	$10^{-1.8}$	$10^{-1.2}$
	Glasgow Upper mine working	$10^{-1.7}$	$10^{-2.7}$	$10^{-1.4}$	$10^{-1.0}$
	Superficial deposits	$10^{-1.5}$	$10^{-2.5}$	$10^{-1.4}$	$10^{-1.1}$

4.2 SURFACE WATER HYDROCHEMICAL CHARACTERISTICS

This section presents the hydrochemistry of surface waters at the 5 sampling locations on the River Clyde and at the additional monitoring site on the Tollcross Burn, sampled between September 2022 and January 2024. Samples from the River Clyde sites are reported as a separate group to those from the Tollcross Burn, given the different hydrochemistry observed in pre- September 2022 monitoring rounds.

4.2.1 Physico-chemical parameters of surface water samples

Table 14 summarises physico-chemical parameters for Glasgow Observatory surface-water samples collected between September 2022 and January 2024.

The surface water samples have a near-neutral to alkaline pH (Clyde median pH 7.8, Tollcross median pH 8.2) and show a narrow range of pH values, but the pH values measured at the Tollcross Burn tend to be higher (>8).

Temperature trends for both water bodies follow the seasons with the coldest temperatures recorded in the winter months and highest temperatures in summer months (Appendix 2). Dissolved oxygen concentrations show the opposite trend, with higher values in the winter months and lower values at higher water temperatures, in line with solubility constraints.

Eh ranges from 255 mV to 518 mV. There is a wider range of values in the River Clyde compared to the Tollcross Burn but this may, at least in part, be a result of there being fewer samples from the Tollcross Burn (n=6) than the River Clyde (n=29) during this monitoring period.

SEC values are much higher in the Tollcross Burn samples (median 1019 µS/cm) than those measured in the River Clyde samples (median 322 µS/cm). 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).

Table 14 Physico-chemical parameters for Glasgow Observatory surface water sites between September 2022 and January 2024.

	River Clyde					Tollcross Burn				
Field parameters	**Min**	**Max**	**Median**	**n**	**n(c)**	**Min**	**Max**	**Median**	**n**	**n(c)**
pH	6.82	8.24	7.81	29	0	8	8.25	8.18	6	0
Temperature (°C)	2.4	21.2	7.2	29	0	5.7	13.2	8.65	6	0
Eh (mV)	255	518	381	29	0	354	417	388	6	0
Dissolved oxygen (mg/L)	4.2	12.7	10.9	29	0	9.3	11.7	10.6	6	0
Specific electrical conductance (µS/cm)	275	578	322	29	0	1000	1633	1019	6	0

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

4.2.2 Water Type

The major ions are presented in a Piper diagram in Figure 9.

The surface waters all have similar major ion proportions and are generally Ca-HCO_3 type with some dispersion towards no dominant cations type. Samples from the Tollcross Burn (SWTC) can be distinguished from River Clyde samples on account of them having a higher proportion of HCO_3 and Mg. Enrichment in Na and Cl is evident in a few samples from sampling round 31 (SW04, SW06, SWTC; Figure 10).

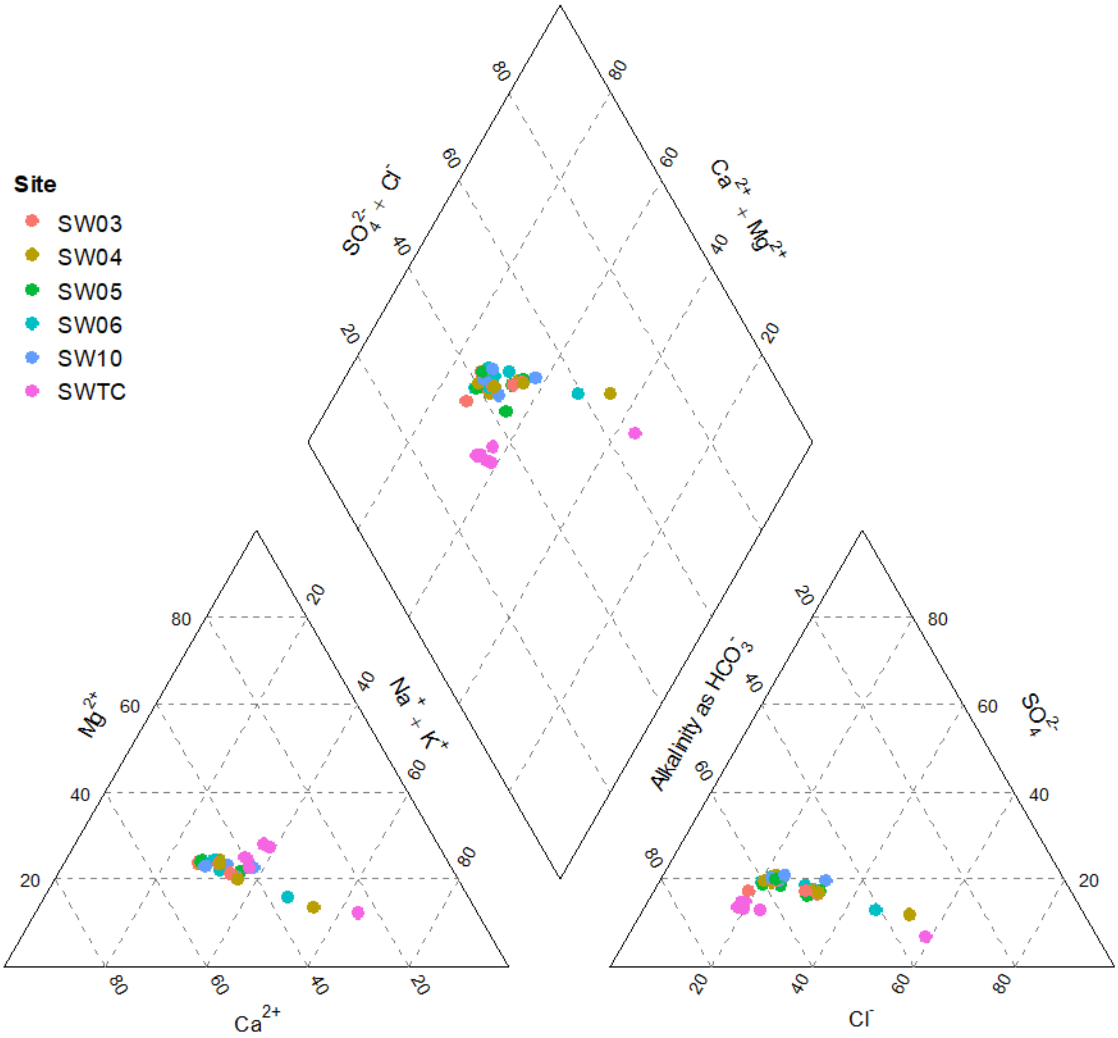


Figure 9 Piper plot for surface waters grouped by monitoring location.

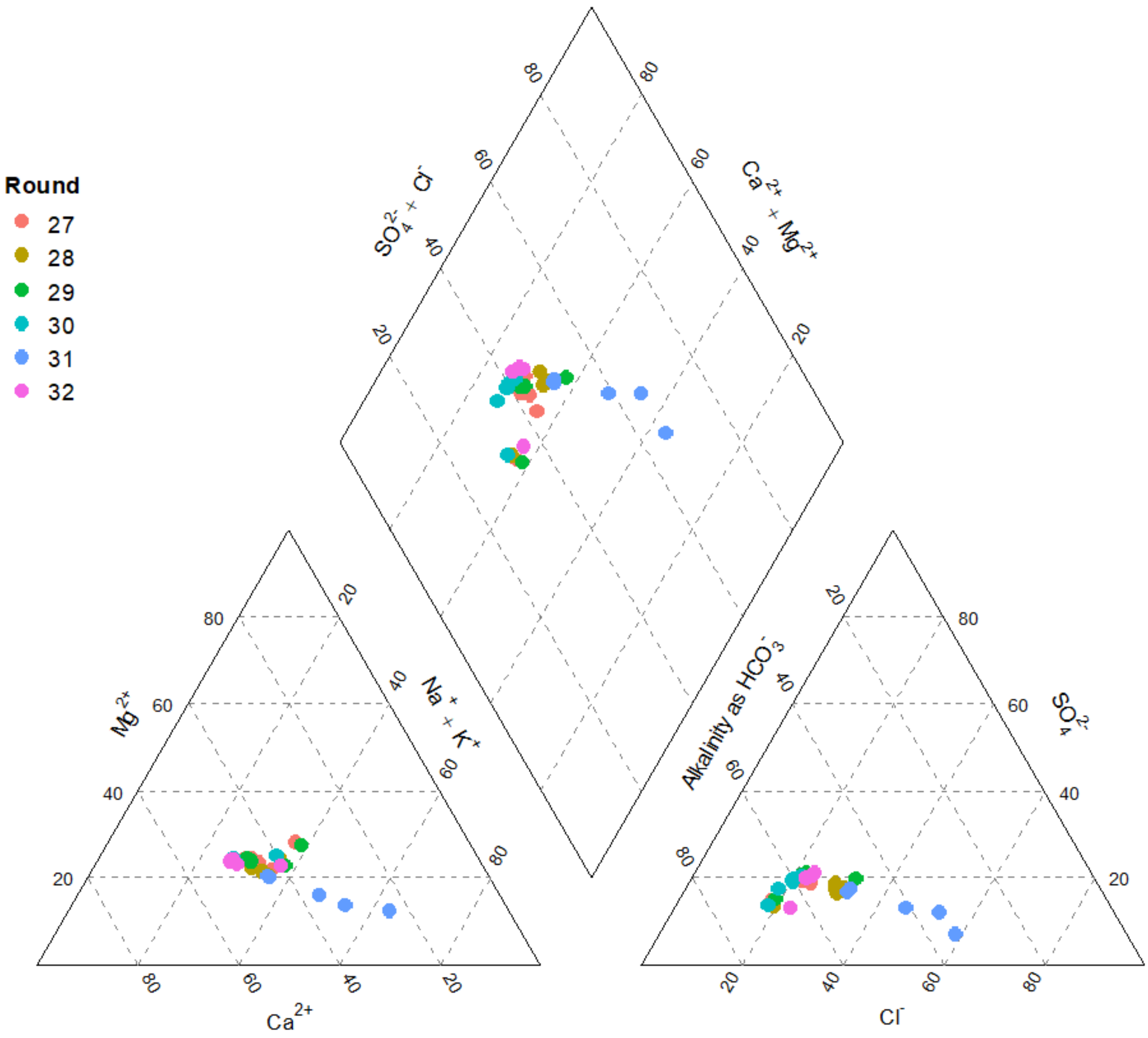


Figure 10 Piper plot for surface waters grouped by sampling round.

4.2.3 Major and minor ions and dissolved organic carbon

Minimum, maximum and median concentrations for major ions, minor ions and dissolved organic carbon in surface water samples are presented in Table 15.

Previously reported differences in water quality between the Tollcross Burn and the River Clyde continue to be observed: major element concentrations are higher in the Tollcross Burn samples compared to the River Clyde. A spike in Na and Cl concentrations in the Tollcross Burn in Dec-23 resulted in a sharp increase in SEC.

As previously observed, the Tollcross Burn has higher concentrations of Si, Br, F than the River Clyde. However, nitrogen, phosphorus, and NPOC (nutrient species) concentrations are higher in the River Clyde.

Table 15 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 between September 2022 and January 2024

		River Clyde					Tollcross Burn				
		Min	**Max**	**Median**	**n**	**n(c)**	**Min**	**Max**	**Median**	**n**	**n(c)**
Major ions (mg/L)											
Ca	Calcium	23.1	44.1	30.9	29	0	72.5	85.5	79.1	6	0
Mg	Magnesium	6.62	15.4	8.66	29	0	22.5	36.6	31.9	6	0
Na	Sodium	15.4	62.6	20.3	29	0	76.9	215	82.6	6	0
K	Potassium	2.28	6.59	3.21	29	0	10.06	14.52	13.04	6	0
HCO_3	Bicarbonate (field measured)	44	156	96	29	0	155	430	318	6	0
Cl	Chloride	18.7	94.7	26.6	29	0	66.5	310	73.0	6	0
SO_4	Sulphate	19.1	48.4	26.5	29	0	50.1	76.9	66.8	6	0
HCO_3	Total Alkalinity	81.1	172	108	29	0	309	459	439	6	0
Minor ions (mg/L)											
P	Phosphorus - total	0.049	0.412	0.087	29	0	0.013	0.032	0.018	6	0
S	Sulphur – total	7.06	17.6	10.0	29	0	20.1	28.2	25.2	6	0
Si	Silicon	0.24	4.18	3.81	29	0	4.21	6.27	5.64	6	0
Br	Bromide	0.025	0.163	0.037	29	0	0.148	0.253	0.187	6	0
F	Fluoride	0.045	0.077	0.059	29	0	0.122	0.210	0.176	6	0
NO_2	Nitrite	0.06	0.60	0.08	29	0	<0.025	0.04	0.03	6	3
NO_3	Nitrate	6.35	15.4	8.81	29	0	5.39	7.15	6.09	6	0
NPOC	Non-purgeable organic carbon	3.65	7.05	4.57	29	0	2.34	3.01	2.55	6	0

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

4.2.4 Trace elements

Minimum, maximum, and median values of the trace elements in surface water samples are presented in Table 16.

As in previous sampling periods, trace element concentrations in the River Clyde are typically similar to, or higher than, those in the Tollcross Burn, with the exception of Sr, Li, B, Rb and U.

Concentrations are also similar in samples from the River Clyde, with the exception of Cr, which was higher 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. During the monitoring period Cr concentrations at SW10 ranged between 6.2 to 12.4 µg/L, with values > 10 µg/L not recorded during the baseline monitoring.

Table 16 Comparison of trace element concentrations in the River Clyde and Tollcross Burn surface water samples between September 2022 and January 2024

		River Clyde					Tollcross Burn				
Trace elements (µg/L)		**Min**	**Max**	**Median**	**n**	**n(c)**	**Min**	**Max**	**Median**	**n**	**n(c)**
Ag	**Silver**	<0.04			29	29	<0.04			6	6
Al	**Aluminium**	23.2	85.2	32.8	29	0	4.6	12.1	5.95	6	0
As	**Arsenic**	0.24	0.6	0.37	29	0	0.25	0.36	0.29	6	0
B	**Boron**	<53			29	29	94	159	139	6	0
Ba	**Barium**	65.8	117	77.8	29	0	52.9	67.7	62.0	6	0
Be	**Beryllium**	<0.08			29	29	<0.08			6	6
Bi	**Bismuth**	<0.08			29	29	<0.08			6	6
Cd	**Cadmium**	<0.005	0.015	0.009	29	1	0.006	0.024	0.02	6	0
Ce	**Cerium**	0.005	0.349	0.098	29	0	<0.004	0.008	0.005	6	2
Co	**Cobalt**	0.17	0.367	0.205	29	0	0.239	1.097	0.521	6	0
Cr	**Chromium**	0.13	12.36	0.41	29	0	0.09	0.13	0.105	6	0
Cs	**Caesium**	<0.04	0.13	0.02	29	18	0.05	0.08	0.06	6	0
Cu	**Copper**	0.71	1.36	1.02	29	0	1.05	2.28	1.48	6	0
Dy	**Dysprosium**	<0.003	0.033	0.017	29	3	<0.003	0.004	0.0035	6	2
Er	**Erbium**	<0.003	0.015	0.011	29	4	<0.003	0.005		6	4
Eu	**Europium**	<0.003	0.013	0.005	29	6	<0.003			6	6
Fe	**Total iron**	28.6	862	285	29	0	12.8	22.8	18.8	6	0
Ga	**Gallium**	<0.04			29	29	<0.04			6	6
Gd	**Gadolinium**	0.011	0.058	0.028	29	0	<0.005	0.005		6	5
Hf	**Hafnium**	<0.006	<0.006		29	29	<0.006			6	6
Ho	**Holmium**	<0.003	0.007	0.004	29	10	<0.003			6	6
La	**Lanthanum**	0.005	0.253	0.073	29	0	<0.003	0.005	0.0027	6	3
Li	**Lithium**	<7			29	29	12	19	15	6	0
Lu	**Lutetium**	<0.003			29	29	<0.003			6	6
Mn	**Manganese**	33	246	51.3	29	0	17.3	50.1	38.8	6	0
Mo	**Molybdenum**	<0.2	1.1	0.3	29	5	<0.2	0.6	0.6	6	1
Nb	**Niobium**	<0.01			29	29	<0.01			6	6
Nd	**Neodymium**	<0.005	0.24	0.1	29	1	<0.005	0.016	0.006	6	2
Ni	**Nickel**	1.23	1.76	1.38	29	0	1.14	1.96	1.58	6	0
Pb	**Lead**	0.05	2.27	0.53	29	0	<0.02	0.12	0.03	6	1
Pr	**Praseodymium**	<0.003	0.057	0.018	29	4	<0.003			6	6
Rb	**Rubidium**	2.39	6.69	3.15	29	0	14.67	23.26	20.97	6	0
Sb	**Antimony**	0.1	0.36	0.14	29	0	0.18	0.5	0.24	6	0
Se	**Selenium**	0.11	0.18	0.14	29	0	0.14	0.51	0.34	6	0
Sm	**Samarium**	<0.005	0.051	0.02	29	4	<0.005			6	6
Sn	**Tin**	<0.08	0.19		29	26	<0.08			6	6
Sr	**Strontium**	125	304	168	29	0	983	1438	1265	6	0
Ta	**Tantalum**	<0.006			29	29	<0.006			6	6
Tb	**Terbium**	<0.004	0.007	0.002	29	22	<0.004			6	6
Th	**Thorium**	<0.03			29	29	<0.03			6	6
Ti	**Titanium**	<0.12	2.3	0.67	29	1	<0.06			6	6
Tl	**Thallium**	<0.02			29	29	<0.02			6	6
Tm	**Thulium**	<0.003			29	28	<0.003			6	6
U	**Uranium**	0.109	0.218	0.151	29	0	0.316	0.444	0.412	6	0
V	**Vanadium**	0.35	0.79	0.49	29	0	0.25	0.52	0.42	6	0
W	**Tungsten**	<0.06			29	29	<0.06			6	6
Y	**Yttrium**	0.014	0.186	0.1	29	0	0.02	0.036	0.0265	6	0
Yb	**Ytterbium**	<0.004	0.014	0.01	29	5	<0.004	0.006	0.003	6	3
Zn	**Zinc**	2.6	45.7	4.2	29	0	1.9	8.5	7.2	6	0
Zr	**Zircon**	0.015	0.183	0.074	29	0	0.016	0.035	0.023	6	0

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

4.2.5 PAH and TPH

Many samples analysed for PAHs and TPHs were below the detection limit. Table 17 summarises the detected PAH and TPH results. The most prevalent PAH is benzo(a)pyrene, which is measurable in most samples, as in previous rounds.

Table 17 Comparison of PAH and TPH concentrations in the River Clyde and Tollcross Burn surface water samples between September 2022 and January 2024

	River Clyde					**Tollcross Burn**				
Variable	**Min**	**Max**	**Median**	**n**	**n(c)**	**Min**	**Max**	**Median**	**n**	**n(c)**
PAH (ug/L)										
Benzo(a)pyrene µg/L	<0.0016	0.0846	0.0023	28	6	0.0016	0.0058	0.0040	6	0
Benzo(b)fluoranthene µg/L	<0.0036	0.0904	0.0018	28	16	<0.0036	0.0063	0.0031	6	3
Benzo(ghi)perylene µg/L	<0.0036	0.0555		28	25	<0.0036	0.0043		6	5
Benzo(k)fluoranthene µg/L	<0.003	0.0383		28	26	<0.003	0.0015		6	6
Indeno(1,2,3-cd)pyrene µg/L	<0.0049	0.0289	0.0025	28	20	<0.0049	0.0146	0.0025	6	4
PAH-Total µg/L	<0.0151	0.2131		28	25	<0.0151	0.025		6	5
TPH (mg/L)										
TPH (C10-C40) mg/L	<0.053	0.161	0.065	6	1	<0.042	0.104		2	1
TPH (C8-C10) mg/L	0.003	0.012	0.009	6	0	<0.003	<0.003		2	2
TPH (C8-C40) mg/L	<0.046	0.172		25	20	<0.045	0.104		6	5

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

4.2.6 Stable isotopic composition

The graphs in Figure 11 and Figure 12 show the latest (September 2022 – January 2024) data vs data previously reported in the “baseline” monitoring reports (pre-September 2022).

The δ^2H and δ^{18}O of the surface water samples are aligned along the GMWL and range from δ^2H –54.5‰ to –43.5‰ and from δ^{18}O –-8.25‰ to –-7.44‰ (Figure 11, Table 18), with a range similar to the previous monitoring period (Bearcock et al. 2023).

The $\delta^{13}C_{DIC}$ ranges from -13.6‰ to -9.7‰, as per previous monitoring rounds (Figure 12, Table 18).

Table 18 $\delta^{13}C_{DIC}$, δ^{18}O and δ^2H min, max, median values for surface water samples collected between September 2022 and January 2024.

	River Clyde					**Tollcross Burn**				
	Min	Max	Median	n	n(c)	Min	Max	Median	n	n(c)
$\delta^{13}C_{DIC}$ PDB ‰	-13.6	-9.7	-11.3	29	0	-12.7	-10.6	-11.3	6	0
δ^{18}O VSMOW2 ‰	-8.25	-6.88	-7.31	29	0	-7.96	-7.25	-7.44	6	0
δ^2H VSMOW2 ‰	-54.5	-43.5	-48.6	29	0	-52.6	-47.4	-50.1	6	0

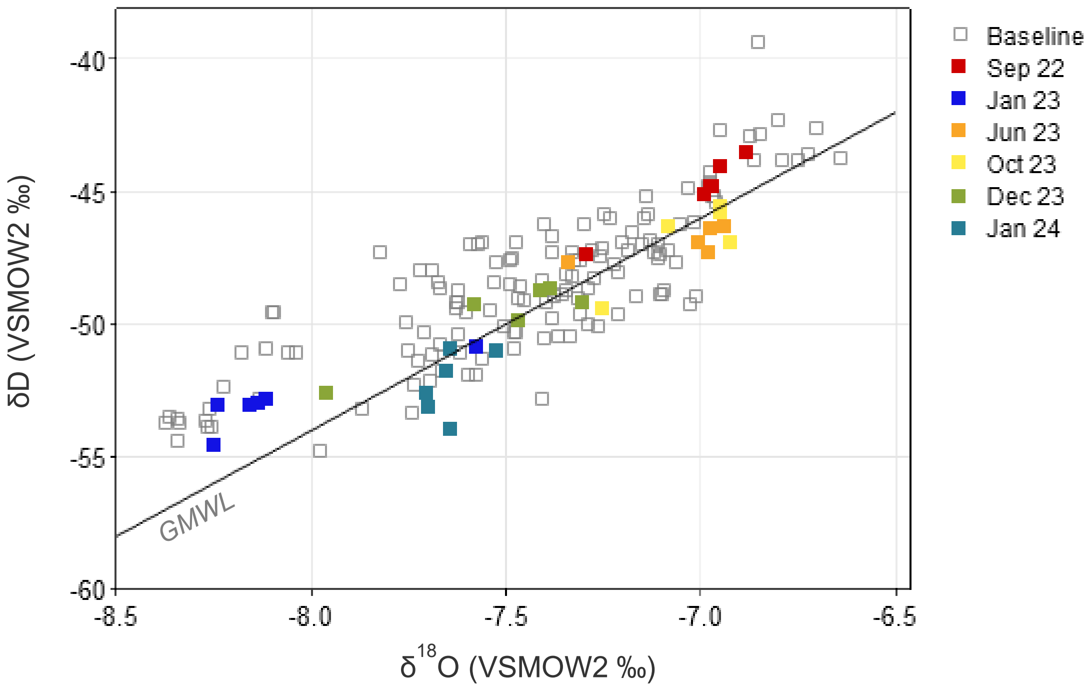


Figure 11: δ18O VSMOW2 (‰) and δ2H VSMOW2 (‰) for surface water samples collected from the River Clyde and Tollcross Burn between September 2022 and January 2024, plotted alongside previous (pre-September 2022) monitoring data (GMWL: global meteoric water line).

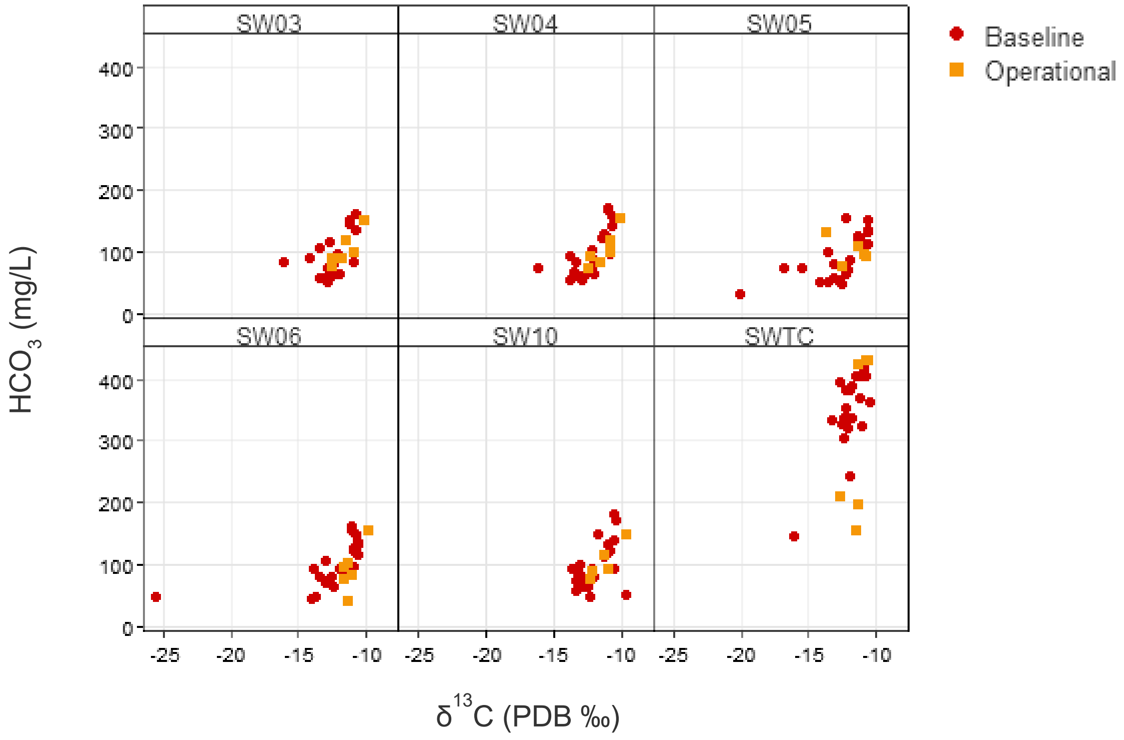


Figure 12 Plot of field-measured HCO_3 versus $\delta^{13}C_{DIC}$ for surface water samples collected from the River Clyde and the Tollcross Burn between September 2022 and January 2024. The new data is plotted alongside previous (pre- September 2022) monitoring data. SWTC = Surface Water Tollcross Burn.

4.3 COMPARISON WITH PRE-SEPTEMBER 2022 MONITORING DATA

Groundwater and surface water monitoring has continued during the operational phase of the UKGEOS Glasgow Observatory, which started in September 2022. The graphs in Appendix 2 show variation in monitored parameters since the start of monitoring: March 2019 for surface waters, and September 2020 for groundwaters.

The character of the groundwaters generally remained unchanged, except for the Glasgow Upper mine working borehole GGA01.

4.3.1 Glasgow Upper mine working borehole GGA01

The groundwater chemistry in borehole GGA01 has undergone a number of changes from when it was first sampled in 2020. After borehole construction and the first pumping tests in January/February 2020 (Palumbo-Roe et al., 2021; Shorter et al., 2021), electrical conductivity and iron concentration increased and the water type changed from HCO_3 type to Ca-SO_4 type (Bearcock et al., 2022). This may have been due to the disturbance of loosely packed waste during borehole construction leading to pyrite oxidation within the Glasgow Upper mine working, as observed by Monaghan et al., 2020. The groundwater composition at GGA01 has now returned to a HCO_3 water type and is similar to the other boreholes in the Glasgow Upper mine workings after prolonged pumping at the start of the operational phase (Figure 3 and Figure 4). The time series data shown in Appendix 2 illustrate a step change at the start of the operational phase, with a large decrease in SEC from a baseline median value of 2900 µS/cm to 1700 µS/cm, associated with a large decrease in SO_4 (from baseline median 1400 mg/L to 170 mg/L), Fe (from 42 mg/L to 0.9 mg/L) and Mn (from 1 mg/L to 370 µg/L), and in all the major elements except for HCO_3, which instead increases with Cl remaining constant. pH has increased from the pre-September 2022 median value of 6.8, and shows an increasing trend since the start of the operational phase from 6.99 to 7.25 at the end of round 32. Accompanying these changes, a significant decrease is observed in As (from a pre-September 2022 median of 12 µg/L to < 1 µg/L) and also in concentrations of B, Co, Li, Ni, Rb, Sr, U (Appendix 2).

4.3.2 Other boreholes

Compositional changes or trends in chemistry from sampling round 15 (representing the start of the baseline groundwater monitoring data) to round 32 (last round of operational phase monitoring period reported here) are illustrated in the control charts for selected elements (SO_4, total Fe and As) in Appendix 3.

Although smaller in magnitude than the large and sudden change in GGA01 composition, some variations in the other mine waters are directly linked to water mixing during abstraction and injection events within the mine workings at specific times during the operational phase.

An increase in the concentration of As in boreholes GGA07, GGA08 and GGA05, in the mine workings, is observed from September 2022 to January 2024; however, concentrations remain low (As <1 µg/L). This is likely linked to the parallel increase in iron concentrations in these boreholes. Arsenic concentrations in borehole GGA04 (Glasgow Upper mine workings) show a decreasing trend since the start of monitoring (from 2 µg/L to 1 µg/L) and this has continued during the operational phase. Arsenic concentrations in boreholes GGA03r and GGB05 (bedrock), exceed the maximum values observed prior to September 2022, though concentrations remain below 5 µg/L.

Arsenic is included in the list of hazardous substances to groundwater and is a Water Framework Directive (WFD) UK specific pollutant, with an Environmental Quality Standard of 50 µg/L in freshwater (SEPA, 2020a, 2014a). Arsenic is of particular relevance to coal mine water geothermal schemes given its presence at trace levels in iron sulphide minerals or secondary products of sulphide oxidation. These may be present in the coal seam bedrock matrix and/or in mine working waste and voids.

In borehole GGB04 (superficial deposits) Ca, Mg and K continue to increase while Na decreases and anion concentrations remain constant. Manganese concentrations continue to increase with a peak of 9 mg/L, while Fe remains constant or lower. For the other boreholes GGA06r and

GGB04 in the superficial deposits the observed variations are mostly within the baseline minimum and maximum values.

Concentrations changes are being monitored in relation to operational changes, pumping regimes, and sampling methods to identify any relationships that might be present.

4.4 SURFACE WATER QUALITY

To assess the water quality at the Glasgow Observatory the water chemistry 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., 2023; Bearcock et al., 2022; Fordyce et al., 2021). There is no UK river water NO_3 standard, so commonly referenced 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.

From September 2022 to January 2024 monitored parameters for the River Clyde and Tollcross Burn samples were generally within the AA limits 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 total P concentration in the River Clyde (0.12 mg/L) exceeded the AA of 0.069 mg/L.
- The mean NO_3 concentration in both the River Clyde (9.6 mg/L) and Tollcross Burn (6.1 mg/L) exceed the AA of 5.7 mg/L.
- The mean HPO_4 concentration in the River Clyde (0.16 mg/L) and exceeded the AA of 0.069 mg/L, in fact most individual measurements exceed this value.
- The mean Al concentration in the River Clyde (34.8µg/L) exceeds the AA of 15 µg/L. the MAC of 25 µg/L is exceeded in 26 of the 29 samples.
- The mean total Cu concentrations in the River Clyde is 1.1 µg/L and Tollcross Burn 1.5 µg/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.

The AA exceedances correspond to the ones highlighted in the previous data release report (Bearcock et al., 2023).

5 Conclusions

Surface water and groundwater chemistry monitoring was carried out in the Glasgow Observatory over six rounds of sampling between September 2022 and January 2024, during which the Observatory entered into full operation.

Changes in water chemistry during Observatory operation are shown in the time series and control charts provided in the Appendices. The character of the groundwaters generally remained unchanged except for the Glasgow Upper mine working borehole GGA01. Following prolonged pumping at the start of the operational phase, the water chemistry has now returned back to bicarbonate type from sulphate type and is similar to the other boreholes in the Glasgow Upper mine workings. Other smaller changes are noted for the other boreholes screened in the Glasgow Upper and Main mine workings. The variations can be explained by water mixing during abstraction and injection events within the mine workings during the operational phase, and they will be more obvious for parameters with large concentration differences between end-member waters which mix.

Arsenic is of particular relevance to coal mine water geothermal schemes given its presence at trace levels in iron sulphide minerals, or secondary products of sulphide oxidation that may be present in the coal seam bedrock matrix and/or in mine working waste and voids. Arsenic concentrations in boreholes GGA03r and GGB05, which are screened in the sandstone bedrock above Glasgow Upper mine workings, have increased, although concentrations remain low (<5 µg/L).

Concentration changes are being monitored in relation to operational changes, pumping regimes, and sampling methods to identify any relationships that might be present.

Appendix 1 Data Quality Control

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).

Where analyses are provided by external laboratories, the descriptions of the method are limited by the information provided by the laboratory.

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.

Long-term lower limits of detection (LLD) and/or limits of quantification (LOQ) for the analytical methods used can be found in Bearcock et al. (2022), Fordyce et al. (2004).

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.

FIELD DATA QUALITY CONTROL AND FIELD DUPLICATES

As a quality control (QC) measure of the field method, one field duplicate sample set was collected in every sampling round, from a location chosen at random. The field duplicate sample set was collected in exactly the same way as the primary sample set from that location. As a further QC check, two field blank water samples were included in each monthly batch of samples. These samples were made back in the office using Type 1 ultrapure (UP) water and were a check on any contamination from the sampling method or equipment (Johnson 2005). A detailed description of the field data quality control method is provided in Fordyce et al. (2021). The results for field duplicate analyses are reported in Table 19 and described in the following sections with the other QC associated to the relevant analysis.

Table 19 Results for water field duplicate analyses

Round Number		**27**	**27**			**28**	**28**		
Sample ID		**GF27-08**	**GF27-10**	**Mean**	**RSD (%)**	**GF28-09**	**GF28-10**	**Mean**	**RSD (%)**
Field duplicate		**Dup B**	**Dup A**			**Dup A**	**Dup B**		
Borehole		**GGA04**	**GGA04**			**GGA04**	**GGA04**		
Date		**21/09/22**	**21/09/22**			**24/01/23**	**24/01/23**		
Analyte	**Units**								
Field parameters									
pH		6.98	7.00	6.99	0.2	7.03	7.05	7.04	0.2
Temperature	°C	13.6	14.1	13.9	2.6	11.3	11.3	11.3	0.0
Eh	mV	70	33	52	50.8	111	94	102	12.0
DO	mg/L	0.4	0.4	0.4	7.3	0.3	0.3	0.3	9.4
SEC	µS/cm	1629	1646	1638	0.7	1626	1634	1630	0.3
Field-HCO_3	mg/L	776	794	785	1.6	795	816	805	1.9
Major & Minor Anions									
Lab-HCO_3	mg/L	802	804	803	0.2	814	809	812	0.5
Cl	mg/L	70.2	70.4	70.3	0.2	69.2	69.4	69.3	0.2
SO_4	mg/L	154	154	154	0.0	150	150	150	0.3
NO_3	mg/L	<0.3	<0.3			<0.3	<0.3		
Br	mg/L	0.40	0.45	0.43	8.1	0.35	0.37	0.36	3.9
NO_2	mg/L	<0.05	<0.05			<0.05	<0.05		
HPO_4	mg/L	<0.1	<0.1			<0.1	<0.1		
F	mg/L	0.185	0.183	0.184	0.6	0.214	0.210	0.212	1.4
Major & Minor Cations									
Ca	mg/L	100	101	101	0.8	103	106	105	1.6
Mg	mg/L	57.4	57.9	57.7	0.6	49.0	49.5	49.3	0.7
Na	mg/L	169	172	171	1.2	178	180	179	0.8
K	mg/L	18.5	18.7	18.6	0.6	18.8	19.5	19.1	2.6
P-Total	mg/L	0.01	0.01	0.01	12.9	<0.005	<0.005		
S-Total	mg/L	59.3	59.4	59.3	0.2	55.2	55.8	55.5	0.7
Sulphide as S	mg/L	<0.02	<0.02			<0.02	<0.02		
Si	mg/L	6.59	6.94	6.77	3.7	5.97	6.32	6.15	4.0
SiO_2	mg/L	14.1	14.8	14.5	3.7	12.8	13.5	13.1	4.0
NH_4	mg/L	14.1	14.3	14.2	1.0	13.7	13.6	13.7	0.5
Trace Elements									
Ba	µg/L	55	56	56	0.8	53	53	53	0.1
Sr	µg/L	1877	1880	1878	0.1	1822	1826	1824	0.1
Mn	µg/L	360	365	363	0.9	326	332	329	1.2
Fe-Total	µg/L	3910	3873	3891	0.7	3951	3964	3958	0.2
Reduced Fe	µg/L	4260	4400	4330	2.3	4150	4160	4155	0.2
Li	µg/L	29	29	29	0.0	31	31	31	0.0
Be	µg/L	<0.08	<0.08			<0.08	<0.08		
B	µg/L	388	410	399	3.9	315	338	327	5.0
Al	µg/L	3.80	3.20	3.50	12.1	3.20	3.10	3.15	2.2
Ti	µg/L	<0.3	<0.3			0.33	0.28	0.31	11.6
V	µg/L	0.15	0.14	0.15	4.9	0.17	0.18	0.18	4.0
Cr-Total	µg/L	0.12	0.11	0.12	6.1	0.11	0.11	0.11	0.0
Co	µg/L	1.38	1.34	1.36	2.3	1.33	1.33	1.33	0.2
Ni	µg/L	2.59	2.74	2.67	4.0	2.93	2.89	2.91	1.0
Cu	µg/L	<0.05	<0.05			<0.05	<0.05		
Zn	µg/L	15.30	8.40	11.85	41.2	2.30	2.10	2.20	6.4
Ga	µg/L	<0.04	<0.04			<0.04	<0.04		
As	µg/L	1.52	1.56	1.54	1.8	1.52	1.51	1.52	0.5
Se	µg/L	<0.04	<0.04			<0.07	<0.07		
Rb	µg/L	41.19	41.39	41.29	0.3	41.81	43.66	42.74	3.1
Y	µg/L	0.07	0.06	0.06	11.6	0.07	0.07	0.07	3.0
Zr	µg/L	0.21	0.13	0.17	35.6	0.12	0.11	0.12	10.4
Nb	µg/L	<0.01	<0.01			<0.01	<0.01		
Mo	µg/L	0.80	0.80	0.80	0.0	<0.2	<0.2		
Ag	µg/L	<0.04	<0.04			<0.04	<0.04		
Cd	µg/L	0.01	<0.005	0.01		<0.005	<0.005		
Sn	µg/L	<0.08	<0.08			<0.08	<0.08		
Sb	µg/L	<0.04	<0.04			<0.04	<0.04		

Round Number		**27**	**27**			**28**	**28**		
Sample ID		**GF27-08**	**GF27-10**	**Mean**	**RSD (%)**	**GF28-09**	**GF28-10**	**Mean**	**RSD (%)**
Field duplicate		**Dup B**	**Dup A**			**Dup A**	**Dup B**		
Borehole		**GGA04**	**GGA04**			**GGA04**	**GGA04**		
Date		**21/09/22**	**21/09/22**			**24/01/23**	**24/01/23**		
Analyte	**Units**								
Cs	µg/L	0.25	0.25	0.25	0.0	0.20	0.21	0.21	3.4
La	µg/L	0.01	0.01	0.01	41.6	0.01	0.01	0.01	12.9
Ce	µg/L	0.02	0.01	0.02	21.4	0.03	0.03	0.03	0.0
Pr	µg/L	<0.003	<0.003			0.00	0.00	0.00	0.0
Nd	µg/L	0.01	0.01	0.01	18.4	0.02	0.01	0.02	17.7
Sm	µg/L	<0.005	<0.005			<0.005	<0.005		
Eu	µg/L	<0.003	<0.003			<0.003	<0.003		
Gd	µg/L	<0.005	<0.005			0.01	0.01	0.01	0.0
Tb	µg/L	<0.004	<0.004			<0.004	<0.004		
Dy	µg/L	0.01	0.01	0.01	0.0	0.01	0.01	0.01	12.9
Ho	µg/L	<0.003	<0.003			<0.003	<0.003		
Er	µg/L	0.01	0.00	0.00	15.7	0.01	0.01	0.01	12.9
Tm	µg/L	<0.003	<0.003			<0.003	<0.003		
Yb	µg/L	0.01	0.01	0.01	8.3	0.01	0.01	0.01	8.3
Lu	µg/L	<0.003	<0.003			<0.003	<0.003		
Hf	µg/L	<0.006	<0.006			<0.006	<0.006		
Ta	µg/L	<0.006	<0.006			<0.006	<0.006		
W	µg/L	0.07	0.07	0.07	0.0	0.08	0.08	0.08	0.0
Tl	µg/L	<0.02	<0.02			<0.02	<0.02		
Pb	µg/L	<0.02	<0.02			<0.02	<0.02		
Bi	µg/L	<0.08	<0.08			<0.08	<0.08		
Th	µg/L	<0.03	<0.03			<0.03	<0.03		
U	µg/L	0.61	0.59	0.60	2.2	0.64	0.64	0.64	0.1
Stable Isotopes									
δ^{13}C (PDB)	‰	-11.1	-11.1	-11.1	0.1	-12.4	-12.9	-12.6	2.9
δ^{18}O (VSMOW2)	‰	-7.50	-7.41	-7.5	0.8	-7.53	-7.63	-7.58	0.9
δD (VSMOW2)	‰	-48.7	-48.6	-48.7	0.2	-50.0	-49.7	-49.8	0.2
Dissolved gases									
CH_4	µg/L	174	161	168	5.5	238	173	206	22.4
C_2H_6	µg/L	<1.0	<1.0			<1.0	<1.0		
CO_2	mg/L	129	123	126	3.4	158	118	138	20.5
Organic parameters									
NPOC	mg/L	2.85	3.99	3.42	23.7	2.16	2.16	2.16	0.0
Benzo(b)fluoranthene	µg/L	<0.0036	<0.0036			<0.0036	<0.0036		
Benzo(k)fluoranthene	µg/L	<0.0030	<0.0030			<0.0030	<0.0030		
Benzo(a)pyrene	µg/L	<0.0016	0.00			<0.0016	<0.0016		
Benzo(ghi)perylene	µg/L	<0.0036	<0.0036			<0.0036	<0.0036		
Indeno(1,2,3-cd)pyrene	µg/L	<0.0049	<0.0049			<0.0049	<0.0049		
PAH-Total	µg/L	<0.0151	<0.0151			<0.0151	<0.0151		
TPH (C8-C10)	mg/L	<0.003	<0.003			0.003	0.003	0.003	0.0
TPH (C10-C40)	mg/L	<0.042	0.40			<0.042	<0.042		
TPH (C8-C40)	mg/L	<0.045	0.40			<0.045	<0.045		

Round Number		**29**	**29**			**30**	**30**		
Sample ID		**GF29-12**	**GF29-15**	**Mean**	**RSD (%)**	**GF30-08**	**GF30-17**	**Mean**	**RSD (%)**
Field duplicate		**Dup A**	**Dup B**			**Dup A**	**Dup B**		
Borehole		**GGA09r**	**GGA09r**			**GGB05**	**GGB05**		
Date		**31/05/23**	**31/05/23**			**19/10/23**	**19/10/23**		
Analyte	**Units**								
Field parameters									
pH		6.86	6.86	6.86	0.0	6.96	7.04	7.00	0.8
Temperature	°C	13.1	13.8	13.5	3.7	11.6	11.5	11.6	0.6
Eh	mV	163	159	161	1.5	58	80	69	21.8
DO	mg/L	0.1	0.1	0.1	38.6	0.3	0.2	0.3	16.3
SEC	µS/cm	1754	1793	1774	1.6	1642	1645	1644	0.1
Field-HCO_3	mg/L	858	858	858	0.0	812	812	812	0.0
Major & Minor Anions									
Lab-HCO_3	mg/L	868	922	895	4.3	815	822	818	0.6
Cl	mg/L	61.7	60.4	61.1	1.5	70.5	72.5	71.5	2.0
SO_4	mg/L	196	196	196	0.1	159	163	161	1.7
NO_3	mg/L	<0.3	<0.3			<0.3	<0.3		
Br	mg/L	0.42	0.44	0.43	2.4	0.41	0.45	0.43	6.8
NO_2	mg/L	<0.05	<0.05			<0.05	<0.05		
HPO_4	mg/L	<0.1	<0.1			<0.1	<0.1		
F	mg/L	0.108	0.115	0.112	4.5	0.194	0.197	0.195	1.1
Major & Minor Cations									
Ca	mg/L	181	192	187	4.3	104	105	105	1.2
Mg	mg/L	54.2	58.6	56.4	5.6	54.6	54.6	54.6	0.0
Na	mg/L	126	121	124	2.9	185	187	186	0.8
K	mg/L	18.0	19.5	18.8	5.7	19.2	19.4	19.3	0.7
P-Total	mg/L	0.03	0.03	0.03	2.8	0.01	0.01	0.01	0.0
S-Total	mg/L	69.8	68.7	69.2	1.1	60.4	60.9	60.7	0.7
Sulphide as S	mg/L	n/a	n/a			0.02	<0.02	0.02	
Si	mg/L	5.71	5.71	5.71	0.0	5.23	5.16	5.20	1.0
SiO_2	mg/L	12.2	12.2	12.2	0.0	11.2	11.0	11.1	1.0
NH_4	mg/L	19.2	23.5	21.3	14.3	15.3	15.4	15.4	0.7
Trace Elements									
Ba	µg/L	111	120	116	5.5	49	47	48	2.3
Sr	µg/L	1066	1144	1105	5.0	2002	2032	2017	1.0
Mn	µg/L	3292	3544	3418	5.2	441	425	433	2.6
Fe-Total	µg/L	2214	2661	2437	13.0	3938	3966	3952	0.5
Reduced Fe	µg/L	2260	2430	2345	5.1	n/a	n/a		
Li	µg/L	<7	<7			33	34	34	2.1
Be	µg/L	<0.08	<0.08			<0.08	<0.08		
B	µg/L	751	796	774	4.1	388	411	400	4.1
Al	µg/L	2.40	2.20	2.30	6.1	1.50	1.30	1.40	10.1
Ti	µg/L	0.17	0.16	0.17	4.3	<0.06	<0.06		
V	µg/L	0.28	0.35	0.32	15.7	0.05	0.05	0.05	0.0
Cr-Total	µg/L	0.19	0.24	0.22	16.4	0.13	0.09	0.11	25.7
Co	µg/L	2.71	2.87	2.79	4.2	2.91	3.31	3.11	9.0
Ni	µg/L	4.22	4.31	4.27	1.5	3.53	3.69	3.61	3.1
Cu	µg/L	0.19	0.09	0.14	50.5	0.14	0.09	0.12	30.7
Zn	µg/L	3.10	1.10	2.10	67.3	4.70	3.00	3.85	31.2
Ga	µg/L	<0.04	<0.04			<0.04	<0.04		
As	µg/L	0.84	0.95	0.90	8.7	2.34	2.27	2.31	2.1
Se	µg/L	0.08	0.10	0.09	15.7	<0.07	<0.07		
Rb	µg/L	10.40	11.05	10.73	4.3	45.95	44.27	45.11	2.6
Y	µg/L	0.20	0.20	0.20	0.7	0.05	0.05	0.05	2.7
Zr	µg/L	0.23	0.26	0.25	8.3	0.05	0.03	0.04	27.6
Nb	µg/L	<0.01	0.01	0.01		<0.01	<0.01		
Mo	µg/L	0.90	0.70	0.80	17.7	0.40	0.30	0.35	20.2
Ag	µg/L	<0.04	<0.04			<0.04	<0.04		
Cd	µg/L	0.007	0.006	0.007	10.9	0.01	<0.005	0.01	
Sn	µg/L	<0.08	<0.08			<0.08	<0.08		
Sb	µg/L	<0.04	<0.04			<0.04	<0.04		
Cs	µg/L	0.08	0.07	0.08	9.4	0.24	0.24	0.24	0.0
La	µg/L	0.07	0.06	0.06	7.7	0.02	0.02	0.02	0.0

Round Number		**29**	**29**			**30**	**30**		
Sample ID		**GF29-12**	**GF29-15**	**Mean**	**RSD (%)**	**GF30-08**	**GF30-17**	**Mean**	**RSD (%)**
Field duplicate		**Dup A**	**Dup B**			**Dup A**	**Dup B**		
Borehole		**GGA09r**	**GGA09r**			**GGB05**	**GGB05**		
Date		**31/05/23**	**31/05/23**			**19/10/23**	**19/10/23**		
Analyte	**Units**								
Ce	µg/L	0.11	0.11	0.11	2.5	0.05	0.05	0.05	4.5
Pr	µg/L	0.02	0.01	0.01	15.7	0.01	0.01	0.01	0.0
Nd	µg/L	0.08	0.08	0.08	2.8	0.01	0.02	0.02	25.0
Sm	µg/L	0.01	0.02	0.01	15.7	<0.005	<0.005		
Eu	µg/L	<0.003	<0.003			<0.003	<0.003		
Gd	µg/L	0.02	0.02	0.02	15.7	<0.005	<0.005		
Tb	µg/L	<0.004	<0.004			<0.004	<0.004		
Dy	µg/L	0.02	0.02	0.02	6.7	0.01	0.01	0.01	0.0
Ho	µg/L	0.004	0.004	0.004	0.0	<0.003	<0.003		
Er	µg/L	0.014	0.014	0.014	0.0	0.005	0.005	0.005	0.0
Tm	µg/L	<0.003	<0.003			<0.003	<0.003		
Yb	µg/L	0.02	0.02	0.02	0.0	0.01	<0.004	0.01	
Lu	µg/L	<0.003	<0.003			<0.003	<0.003		
Hf	µg/L	<0.006	<0.006			<0.006	<0.006		
Ta	µg/L	<0.006	<0.006			<0.006	<0.006		
W	µg/L	<0.06	<0.06			<0.06	<0.06		
Tl	µg/L	0.03	0.03	0.03	0.0	<0.02	0.02	0.02	
Pb	µg/L	<0.02	<0.02			0.03	<0.02	0.03	
Bi	µg/L	<0.08	<0.08			<0.08	<0.08		
Th	µg/L	<0.03	<0.03			<0.03	<0.03		
U	µg/L	1.58	1.66	1.62	3.4	0.46	0.47	0.47	0.8
Stable Isotopes									
δ^{13}C (PDB)	‰	-12.6	-12.7	-12.6	0.5	-11.2	-11.4	-11.3	0.9
δ^{18}O (VSMOW2)	‰	-7.45	-7.45	-7.45	0.0	-7.41	-7.41	-7.41	0.1
δD (VSMOW2)	‰	-50.3	-50.0	-50.2	0.4	-50.3	-50.4	-50.4	0.2
Dissolved gases									
CH_4	µg/L	161	16.6	88.8	115.0	97	94	95.5	2.2
C_2H_6	µg/L	<1.0	<1.0			<1.0	<1.0		
CO_2	mg/L	222	232	227	3.1	164	163	163	0.4
Organic parameters									
NPOC	mg/L	5.30	5.85	5.57	7.0	2.30	2.10	2.20	6.4
Benzo(b)fluoranthene	µg/L	<0.0036	<0.0036			<0.0036	<0.0036		
Benzo(k)fluoranthene	µg/L	<0.0030	<0.0030			<0.0030	<0.0030		
Benzo(a)pyrene	µg/L	<0.0016	<0.0016			<0.0016	<0.0016		
Benzo(ghi)perylene	µg/L	<0.0036	<0.0036			<0.0036	<0.0036		
Indeno(1,2,3-cd)pyrene	µg/L	<0.0049	<0.0049			<0.0049	<0.0049		
PAH-Total	µg/L	<0.0151	<0.0151			<0.0151	<0.0151		
TPH (C8-C10)	mg/L								
TPH (C10-C40)	mg/L								
TPH (C8-C40)	mg/L	<0.045	<0.045			<0.040	<0.040		

Round Number		**31**	**31**			**32**	**32**		
Sample ID		**GF31-10**	**GF31-17**	**Mean**	**RSD (%)**	**GF32-09**	**GF32-13**	**Mean**	**RSD (%)**
Field duplicate		**Dup B**	**Dup A**			**Dup A**	**Dup B**		
Borehole		**GGA07**	**GGA07**			**GGA08**	**GGA08**		
Date		**07/12/23**	**07/12/23**			**10/01/24**	**10/01/24**		
Analyte	**Units**								
Field parameters									
pH		7.04	7.03	7.04	0.1	7.20	7.20	7.20	0.0
Temperature	°C	11.4	11.6	11.5	1.2	10.1	9.6	9.9	3.6
Eh	mV	138	139	138	0.6	182	169	175	4.9
DO	mg/L	0.1	0.2	0.1	80.8	1.2	1.2	1.2	3.5
SEC	µS/cm	1657	1651	1654	0.3	1621	1615	1618	0.3
Field-HCO_3	mg/L	760	760	760	0.0	796	796	796	0.0
Major & Minor Anions									
Lab-HCO_3	mg/L	833	825	829	0.6	819	789	804	2.6
Cl	mg/L	70.6	70.7	70.6	0.1	73.9	72.3	73.1	3
SO_4	mg/L	165	164	164	0.5	165	163	164	1
NO_3	mg/L	<0.3	<0.3			<0.3	<0.3		
Br	mg/L	0.45	0.47	0.46	3.6	0.718	0.720	0.72	0.2
NO_2	mg/L	<0.05	<0.05			<0.5	<0.5		
HPO_4	mg/L	<0.1	<0.1			<0.05	<0.05		
F	mg/L	0.185	0.182	0.183	1.1	0.127	0.213	0.17	36
Major & Minor Cations									
Ca	mg/L	107	107	107	0.2	104	105	105	0.6
Mg	mg/L	52.6	51.4	52.0	1.7	55.7	54.7	55.2	1.3
Na	mg/L	188	188	188	0.0	174	175	175	0.4
K	mg/L	18.6	18.6	18.6	0.3	17.6	17.8	17.7	1.0
P-Total	mg/L	0.01	0.01	0.01	10.9	<0.005	<0.005		
S-Total	mg/L	60.8	59.7	60.3	1.2	57.3	57.8	57.5	0.7
Sulphide as S	mg/L	<0.02	<0.02			0.02	<0.02	0.02	
Si	mg/L	5.19	5.09	5.14	1.4	4.97	4.99	4.98	0.3
SiO_2	mg/L	11.1	10.9	11.0	1.4	10.6	10.7	10.7	0.3
NH_4	mg/L	15.2	15.5	15.3	1.2	14.7	15.2	15.0	2.6
Trace Elements									
Ba	µg/L	35	36	35	1.5	44	43	44	0.7
Sr	µg/L	2206	2245	2225	1.3	2041	2033	2037	0.3
Mn	µg/L	439	442	441	0.5	396	394	395	0.3
Fe-Total	µg/L	3277	3178	3227	2.2	2886	2721	2803	4.2
Reduced Fe	µg/L	3430	3460	3445	0.6	3000	2880	2940	2.9
Li	µg/L	34	34	34	0.0	29	29	29	0.0
Be	µg/L	<0.08	<0.08			<0.08	<0.08		
B	µg/L	387	383	385	0.7	383	407	395	4.3
Al	µg/L	2.00	2.00	2.00	0.0	2.80	2.00	2.40	23.6
Ti	µg/L	<0.06	<0.06			<0.06	<0.06		
V	µg/L	<0.02	0.02	0.02		0.06	0.04	0.05	28.3
Cr-Total	µg/L	0.05	0.07	0.06	23.6	0.16	0.10	0.13	32.6
Co	µg/L	1.02	1.01	1.02	0.5	1.16	0.88	1.02	19.5
Ni	µg/L	2.82	2.96	2.89	3.4	4.40	2.53	3.47	38.2
Cu	µg/L	0.32	1.23	0.78	83.0	0.08	<0.05	0.08	
Zn	µg/L	14.00	22.70	18.35	33.5	2.40	2.80	2.60	10.9
Ga	µg/L	<0.04	<0.04			<0.04	<0.04		
As	µg/L	0.80	0.75	0.78	4.6	0.71	0.23	0.47	72.2
Se	µg/L	<0.07	<0.07			<0.07	<0.07		
Rb	µg/L	39.92	40.49	40.21	1.0	36.18	36.33	36.26	0.3
Y	µg/L	0.10	0.09	0.09	4.6	0.03	0.03	0.03	0.0
Zr	µg/L	0.03	0.03	0.03	16.8	0.02	0.03	0.03	21.0
Nb	µg/L	<0.01	<0.01			<0.01	<0.01		
Mo	µg/L	0.20	0.20	0.20	0.0	0.50	<0.2	0.50	
Ag	µg/L	<0.04	<0.04			<0.04	<0.04		
Cd	µg/L	<0.005	0.02	0.02		<0.005	<0.005		
Sn	µg/L	<0.08	<0.08			<0.08	<0.08		
Sb	µg/L	<0.04	<0.04			0.12	<0.04	0.12	
Cs	µg/L	0.22	0.23	0.23	3.1	0.17	0.19	0.18	7.9

Round Number		**31**	**31**			**32**	**32**		
Sample ID		**GF31-10**	**GF31-17**	**Mean**	**RSD (%)**	**GF32-09**	**GF32-13**	**Mean**	**RSD (%)**
Field duplicate		**Dup B**	**Dup A**			**Dup A**	**Dup B**		
Borehole		**GGA07**	**GGA07**			**GGA08**	**GGA08**		
Date		**07/12/23**	**07/12/23**			**10/01/24**	**10/01/24**		
Analyte	**Units**								
La	µg/L	0.01	0.01	0.01	25.7	<0.003	<0.003		
Ce	µg/L	0.02	0.02	0.02	15.7	0.00	<0.004	0.00	
Pr	µg/L	0.00	<0.003	0.00		<0.003	<0.003		
Nd	µg/L	0.02	0.02	0.02	25.4	<0.005	<0.005		
Sm	µg/L	<0.005	<0.005			<0.005	<0.005		
Eu	µg/L	<0.003	<0.003			<0.003	<0.003		
Gd	µg/L	0.01	0.01	0.01	10.9	<0.005	<0.005		
Tb	µg/L	<0.004	<0.004			<0.004	<0.004		
Dy	µg/L	0.01	0.01	0.01	0.0	0.00	0.00	0.00	0.0
Ho	µg/L	<0.003	<0.003			<0.003	<0.003		
Er	µg/L	0.01	0.01	0.01	9.4	0.00	<0.003	0.00	
Tm	µg/L	<0.003	<0.003			<0.003	<0.003		
Yb	µg/L	0.01	0.01	0.01	14.1	0.01	0.01	0.01	12.9
Lu	µg/L	<0.003	<0.003			<0.003	<0.003		
Hf	µg/L	<0.006	<0.006			<0.006	<0.006		
Ta	µg/L	<0.006	<0.006			<0.006	<0.006		
W	µg/L	<0.06	<0.06			<0.06	<0.06		
Tl	µg/L	<0.02	<0.02			<0.02	<0.02		
Pb	µg/L	0.08	0.12	0.10	28.3	<0.02	<0.02		
Bi	µg/L	<0.08	<0.08			<0.08	<0.08		
Th	µg/L	<0.03	<0.03			<0.03	<0.03		
U	µg/L	0.43	0.42	0.43	1.5	0.43	0.42	0.43	0.7
Stable Isotopes									
$\delta^{13}C$ (PDB)	‰	-11.4	-11.4	-11.4	0.1	-11.5	-11.7	-11.6	0.0
$\delta^{18}O$ (VSMOW2)	‰	-7.42	-7.44	-7.43	0.2	-7.41	-7.46	-7.43	0.5
δD (VSMOW2)	‰	-50.6	-51.7	-51.2	1.5	-51.2	-50.6	-50.9	0.0
Dissolved gases									
CH_4	µg/L	154	157	156	1.4	0.60	473	237	141
C_2H_6	µg/L	<1	<1			<1	<1		
CO_2	mg/L	152	157	155	2.3	136	156	146	9.7
Organic parameters									
NPOC	mg/L	1.65	1.90	1.78	10.0	3.02	2.86	2.94	3.8
Benzo(b)fluoranthene	µg/L	<0.0036	<0.0036			<0.0036	<0.0036		
Benzo(k)fluoranthene	µg/L	<0.0030	<0.0030			<0.0030	<0.0030		
Benzo(a)pyrene	µg/L	<0.0016	<0.0016			<0.0016	<0.0016		
Benzo(ghi)perylene	µg/L	<0.0036	<0.0036			<0.0036	<0.0036		
Indeno(1,2,3-cd)pyrene	µg/L	<0.0049	<0.0049			<0.0049	<0.0049		
PAH-Total	µg/L	<0.0151	<0.0151			<0.0151	<0.0151		
TPH (C8-C10)	mg/L								
TPH (C10-C40)	mg/L								
TPH (C8-C40)	mg/L	<0.040	<0.040			<0.040	<0.040		

INORGANIC PARAMETER ANALYSIS

In this section 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 6.8% in QC1)
- Beryllium (RSD of 6.8% in SLRS6)
- Boron (RSD of 5.5% in QC2)
- Magnesium (RSD of 5.8% in SLRS6)
- Aluminium (RSD of 5.8% in QC1)
- Silicon (RSD of 5.8% in QC2)
- Vanadium (RSD of 5.2% in SLRS6)
- Chromium (RSD of 7.6% in SLRS6)
- Manganese (RSD of 6.1% in SLRS6)
- Cobalt (RSD of 5.7% in SLRS6)
- Zinc (RSD of 14.3% in SLRS6)
- Cadmium (RSD of 26.6% 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 SLRS6)
- Silicon (Accuracy of 94% in QC2)
- Sulphur (Accuracy of 109% in QC2)
- Vanadium (Accuracy of 94% in SLRS6)
- Iron (Accuracy of 92% in SLRS6)
- Copper (Accuracy of 105% in SLRS6)
- Zinc (Accuracy of 122% in SLRS6)
- Niobium (Accuracy of 94% in QC1)
- Molybdenum (Accuracy of 89% in SLRS6)
- Cadmium (Accuracy of 128% in QC3)
- Barium (Accuracy of 93% in QC1 and of 94% in SLRS6)
- Ytterbium (Accuracy of 94% in QC1)
- Thorium (Accuracy of 94% in QC1)

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

- Lithium (13 of the 50 blanks analysed had detectable Li)
- Beryllium (4 of the 50 blanks analysed had detectable Be)
- Sodium (4 of the 50 blanks analysed had detectable Na)
- Magnesium (2 of the 50 blanks analysed had detectable Mg)
- Silicon (21 of the 50 blanks analysed had detectable Si)
- Phosphorous (7 of the 50 blanks analysed had detectable P)

- Titanium (5 of the 50 blanks analysed had detectable Ti)
- Vanadium (1 of the 50 blanks analysed had detectable V)
- Manganese (2 of the 50 blanks analysed had detectable Mn)
- Cobalt (5 of the 50 blanks analysed had detectable Co)
- Copper (1 of the 50 blanks analysed had detectable Cu)
- Gallium (4 of the 50 blanks analysed had detectable Ga)
- Arsenic (1 of the 50 blanks analysed had detectable As)
- Rubidium (1 of the 50 blanks analysed had detectable Rb)
- Yttrium (4 of the 50 blanks analysed had detectable Y)
- Cadmium (1 of the 50 blanks analysed had detectable Cd)
- Lanthanum (2 of the 50 blanks analysed had detectable La)

Field blank water samples were included in the analytical runs; most were below the detection limits for each element, with the following exceptions:

- Calcium, 1 of the 12 blanks had Ca slightly above the detection limit with 0.13 mg/l
- Magnesium, 6 of the 12 blanks had Mg above the detection limit but not greater than 0.018 mg/l.
- Potassium, 1 of the 12 blanks had K slightly above the detection limit with 0.05 mg/l
- Chloride, 3 of the 12 blanks had detectable Cl, but not greater than 0.18 mg/l
- Barium, 4 of the 12 blanks had detectable Ba but not greater than 0.35 µg/l
- Strontium, 6 of the 12 blanks had detectable Sr but not greater than 1.3 µg/l
- Manganese, 5 of 12 blanks had detectable Mn but not greater than 1 µg/l
- Iron, 4 of the 12 blanks had detectable Fe but not greater than 0.9 µg/l
- Aluminium, all the blanks had detectable Al but not greater than 2.2 µg/l
- Vanadium, 2 of the 12 blanks had detectable V but not greater than 0.03 µg/l
- Nickel, 10 of the 12 blanks had detectable Ni but not greater than 0.12 µg/l
- Copper, 4 of the 12 blanks had detectable Cu but not greater than 0.4 µg/l
- Zinc, 6 of the 12 blanks had detectable Zn but not greater than 2.3 µg/l
- Cadmium, 1 of the 12 blanks had detectable Cd (0.007 µg/l)
- Lead, 2 of the 12 blanks had detectable Pb but not greater than 0.04 µg/l

Results for most field duplicate samples (Table 19) showed good precision of the measurement process, including both field sampling and laboratory analysis, with small variability between sample-pairs (RSD ≤ 10%) of the major (Ca, Mg, Na, K) and minor elements Si, and of the trace elements Ba, Sr, Mn, Li, B, Cs, Rb, U.

Acceptable variability (<20%) is shown by P-Total, Fe-Total, Ti, Se, Y, Cd, and most REE where detectable.

The elements Al, V, Cr-Total, Ni, Cu, Zn, As, Zr, Mo, La, Ce, Nd, and Pb showed more variability (RSD 10 to >20%) between some sample pairs.

Major and minor anion analysis by ion chromatography (IC)

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 range of the instrument in two of the standards. Repeat analyses of these standards showed good precision for most of the data with RSD ≤ 5%, except for NO_3 slightly above (RSD of 5.1%).

The measured results demonstrated good accuracy (recovery of 100± 5% relative to the target values) except for F with recovery of 93% in QC/100.

Most field blanks were below the detection limits for each element. The exception to this is for Cl in 2 blanks, with values 0.09 and 0.17 mg/l.

Results for most field duplicate samples (Table 19) showed good precision of the measurement process, including both field sampling and laboratory analysis; there is small variability between sample-pairs (RSD ≤ 10%) of Cl, SO_4, Br, F (NO_3 below LOQ), with the exception of duplicate pair GGA08 round 32, where RSD is greater than 10% for the element F (using LIMS code 30698, see following paragraph).

Repeated analysis of anions by IC for round 32

The processed IC results under LIMS codes 30525 (sampling round 32) showed concentrations of anions, especially the principal anions Cl and SO_4, which are appreciably lower than values for the corresponding samples from five previous monitoring rounds. These reductions are not matched by corresponding lower concentrations of the principal cations, Na and Ca. The cation analysis results by ICP-MS are entirely consistent with the previous sampling rounds. There was therefore apparent inconsistency in the results, which required further investigation. A reanalysis of the anions by IC was carried out under LIMS code 30698, as a check on the lower concentrations and an independent review of the analytical data undertaken. The outcome of the reanalysis and independent review is presented in the following paragraphs.

The results from the second run of analyses are more in line with the anion data from the previous rounds, but the delay took the analysis outside the recommended holding times and scope of UKAS accreditation. The detailed laboratory QC data show that both IC sample runs were completed in full accordance with the documented analytical operating procedure AG 2.3.19, with the expected complement of calibration, QC, drift standards and blanks. Results for QC analyses from both runs were within tolerance for the method. There are therefore no grounds for rejecting either set of data on the basis of analytical procedures.

The repeat analysis reported higher concentrations of Cl, Br and SO_4 and less variation between repeat samples (RSD% between 0.2 and 1.5 for LIMS 30698 vs 11.9 and 17.1 for LIMS 30525; see Table 20 below). Note that the minor anion F is present at low concentration and has a noisy response through all the monitoring rounds. HPO_4 results are close to or below detection limits in all samples.

Table 20 Comparison of analysis data for re-runs of archived groundwater field duplicate samples from sampling round 32. Note lower RSD% and higher reported anion concentrations in repeat analysis (LIMS code 30698).

ID	LIMS	Ca	Mg	Na	K	Cl	SO_4	Br	F
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Original analysis of duplicates									
GF32-09	30525-0009	104	55.7	174	17.6	59.0	131	0.421	0.134
GF32-13	30525-0013	105	54.7	175	17.8	49.5	111	0.330	0.128
RSD%		0.6	1.3	0.4	1.0	12.4	11.9	17.1	3.1
Repeat analysis of duplicates									
GF32-09	30698-0016					73.9	165	0.718	0.127
GF32-13	30698-0013					72.3	163	0.720	0.213
RSD%						1.5	1.0	0.2	35.7

A separate check on data quality is provided by considering the charge-balance errors. Errors are here calculated with the addition of NH_4. This has been analysed by an external lab and the data were not available to the BGS lab for inclusion in the lab charge-balance calculations. The NH_4 concentrations in the UKGEOS groundwater samples are exceptionally high and provide a non-trivial contribution to the overall balance. Including the NH_4 in the charge-balance calculations of the groundwater samples (30525-0008 to -0018) yields an average charge-balance error of 2.27 ± 1.59% (1σ). In the absence of any other contributing factors, this would suggest that there is a slight deficit of anions relative to cations. Given that the cation results are consistent with the previous monitoring runs, that could suggest that the reported anions are lower than they should be. Comparison with the charge-balance calculations using the data for the groundwater samples from 30698 adds weight to this interpretation. The higher concentrations of the anion data for

30698 yield an average charge balance (again including NH_4) of -0.83 ± 0.67% (1σ), i.e. the absolute balances are improved and have a smaller standard deviation than with the 30525 data.

The 30698 results could not be accredited because of the risk of sample degradation and changes to concentrations during extended storage. The greatest risk in these samples concerns the N species which are known to be prone to oxidation, such that early analysis is required. NH_4 and NO_2 will potentially oxidise to NO_3. This effect was apparent, where results for NO_3 and NO_2 in the groundwater samples from 30525 were all below detection, but significant NO_3 was detected in some samples in 30698. The NO_3 and NO_2 data for 30698 are therefore probably unreliable and the 30525 results for these should be preferred.

Cl and SO_4 (and Br, F) are usually considered to be stable and less susceptible to changes in concentration during sample storage. This allows greater confidence in the later analysis for these determinands.

Given the evidence of the charge balances and replicate data coupled with the history of previous rounds, and the recommendation of the independent review, it was chosen to take the 30698 anion data for all samples in the round (32), with the exception of the data for NO_3 and NO_2 where the 30525 results should be used. As the data for NO_2 and NO_3 in the groundwater samples are below detection limits in any case, they are not represented by actual concentrations.

The reason for the discrepancy between the 30525 and 30698 anion data is unclear. It can be speculated that a drop in sensitivity may have taken place during 30525 IC analysis, but which could not be detected by the regular QC bracketing.

Laboratory total alkalinity 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.

A laboratory QC standard was analysed a number of times throughout each analytical run. This demonstrated a good accuracy (recovery 101%) and precision (RSD 1.6%).

Results for field duplicate samples generally showed very low variability between sample-pairs (RSD ≤ 10%) (Table 19).

As a further check on data quality, the field and laboratory alkalinity measurements were compared. These showed good agreement with most samples (n=92) with comparable analyses (RSD ≤ 10%), two with analyses RSD ≤ 20%. For three surface water samples the RSD is between 47 and 59%; the disparity between field- and lab-HCO_3 reflects inaccuracy of the field-HCO_3 measurement, as the ionic balance using the lab-HCO_3 data is better than that of the field-HCO_3 data. Therefore, the field-HCO_3 for these samples should be treated with caution.

All but one blanks were below detection limit.

Total inorganic carbon (TIC) in mg/L was calculated by dividing the lab-HCO_3 (mg/L) by 5.0801.

Table 21 Surface water sample list with high relative standard deviation (RSD) between field- and lab-HCO3

Sample ID	BGS LIMS ID
GF31-01	30506-0001
GF31-02	30506-0002
GF32-05	30525-0005

Charge balance data

Ionic mass balance calculations for each of the samples resulted in a percentage balance of within ± 5% when calculated with lab bicarbonate concentrations. The majority of the ionic mass balances calculated with the field bicarbonate are also within the acceptable range of ± 5%. While we would usually expect the field bicarbonate data to give better ionic balances than the lab data, in this instance five 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.

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 (Table 19) also showed good precision of the measurement process, including both field sampling and laboratory analysis, with low variability between sample-pairs (RSD < 3%), except for GGA09r round 29 with RSD 14%.

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.

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 unfiltered 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. It should be noted that Fe2+ and total Fe are analysed in two separate laboratories, with different sampling methodologies.

The concentrations of Fe^{2+} commonly exceeded those of Fe Total, 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+}.

Results for field duplicate samples generally showed very low variability between sample-pairs (RSD ≤ 5%) (Table 19).

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 (Table 19) generally showed good precision of the measurement process, including both field sampling and laboratory analysis, with acceptable variability between sample-pairs (RSD ≤ 10%), with the exception of duplicate pair GGA04 round 27, where RSD is 24%. 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 field duplicate samples showed values ≤ LOQ.

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.

Results for field duplicate samples showed all values below LOQ.

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

Results for field duplicate samples showed all values below LOQ.

Table 22 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 23).

Field duplicate $\delta^{13}C$ measurements show RSD ≤ 1% for all sample pairs, except for pair GGA04 (round 28) with RSD of 2.9%.

Table 23 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 24).

Field duplicate $\delta^{2}H$ measurements show RSD < 0.5% for all sample pairs, but GGA07, round 31 with 1.5%.

Table 24 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 25). Field duplicate $\delta^{18}O$ measurements show RSD ≤ 1% for all sample pairs.

Table 25 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. The LOD is 10 Bq/L. Radon concentrations of all the field duplicate samples were lower than the LOD.

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 the headspace gas chromatography (GC) 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).

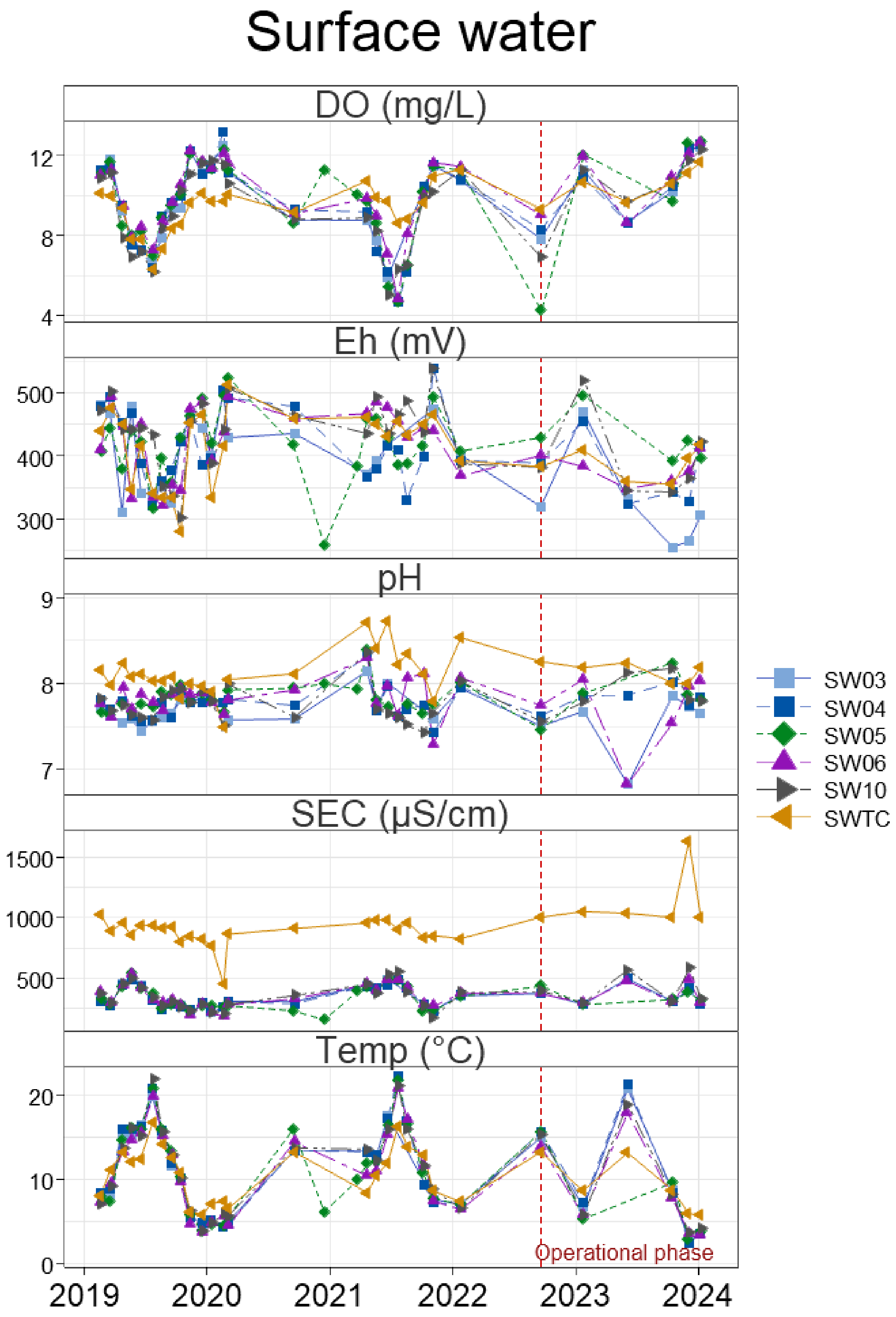
Since CH_4 concentrations can be highly variable, canned gas standards covering the deciles from 100 ppm to 10% CH_4 are used for calibration before and after each batch, with the standard chosen being within the same decile as the sample with the highest CH_4 value during the run. The FID response is 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 very high variability (RSD >100%), in sample-pairs GGA04 round 28, GGA09r round 29 and GGA08 round 32, while RSD<10% in the other rounds. The CO_2 concentrations of field duplicate samples showed good precision of the measurement process, including both field sampling and laboratory (RSD <10%), except for GGA04 round 28 with RSD 20.5%. C_2H_6 was always below detection.

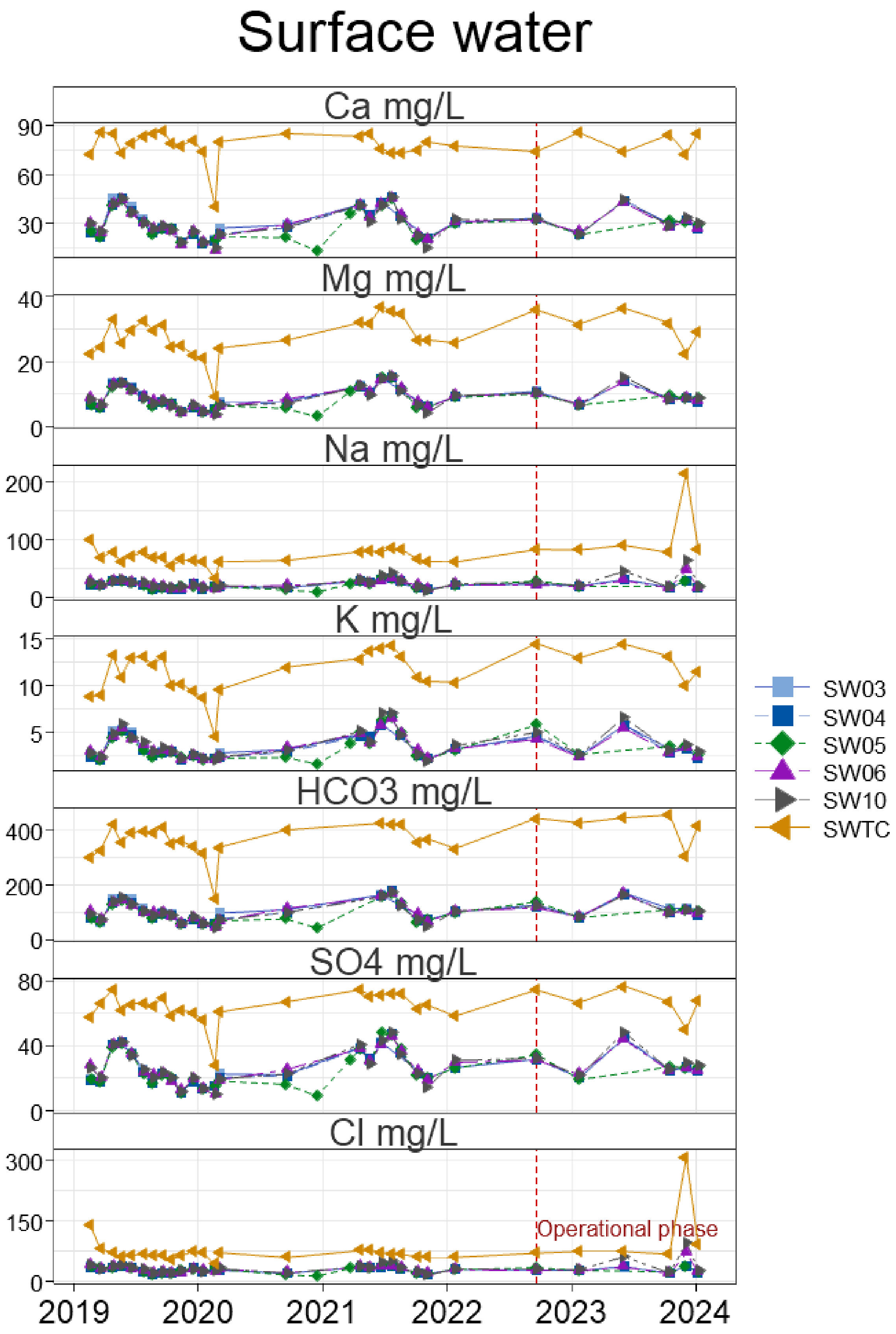
Appendix 2 Time series plots

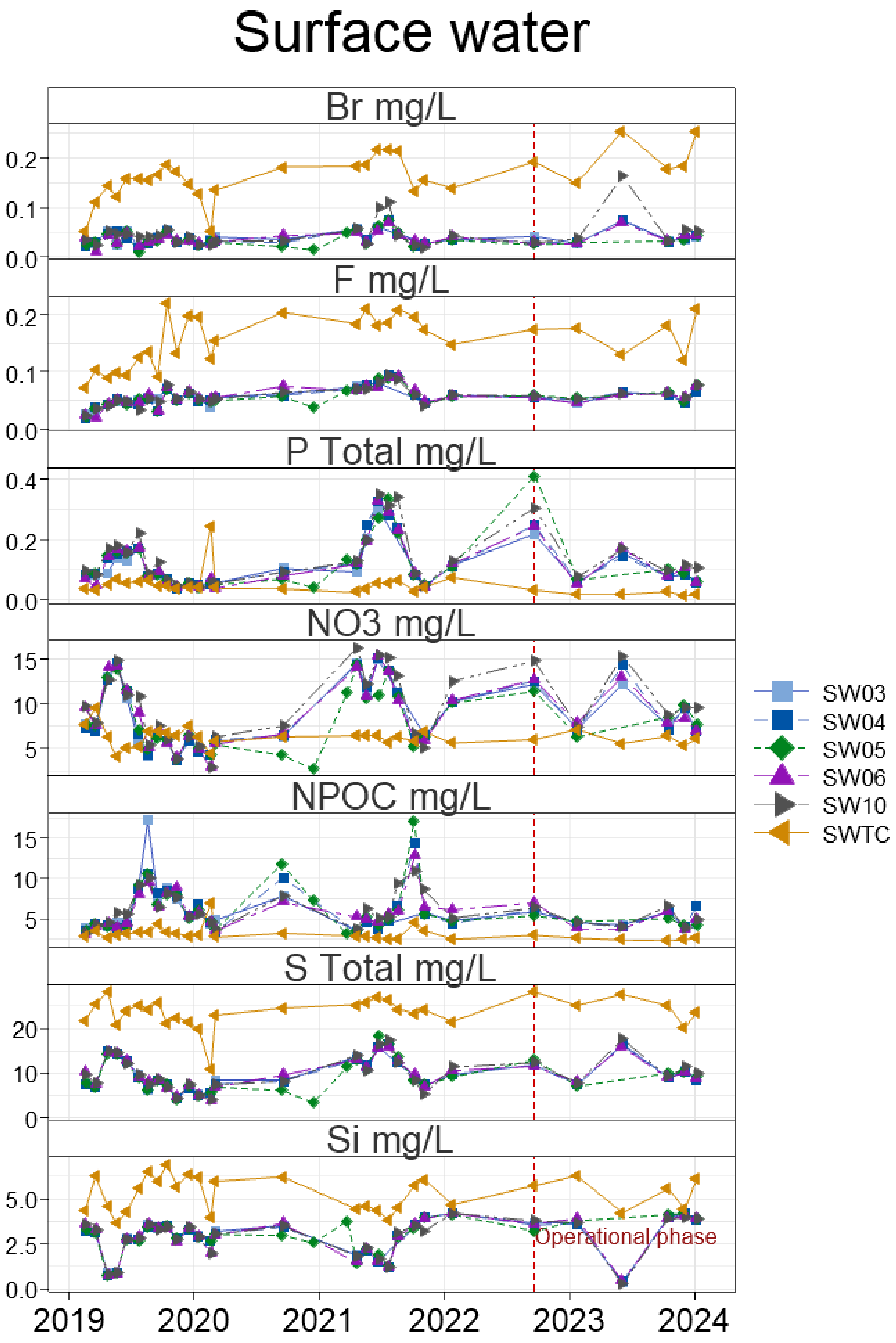
Time series plots are presented below. The graphs include data from the outset of monitoring activities: March 2019 for surface waters, and September 2020 for groundwaters. Details for data preceding that discussed in this report can be found in Fordyce et al. (2021) or Bearcock et al. (2022, 2023). Where data are below the detection limit, the value is replaced with half the detection limit.

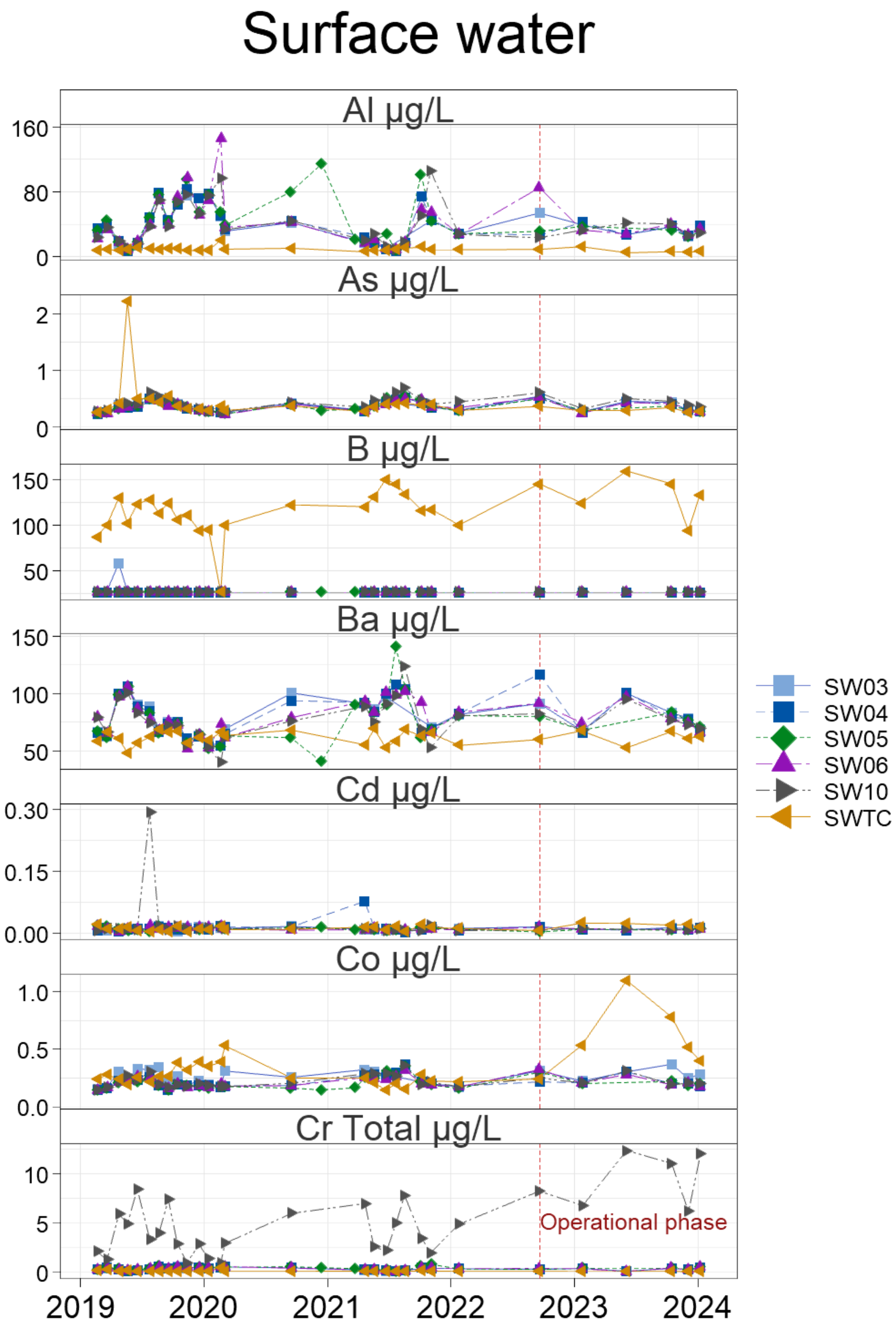
SURFACE WATER FIELD PARAMETERS

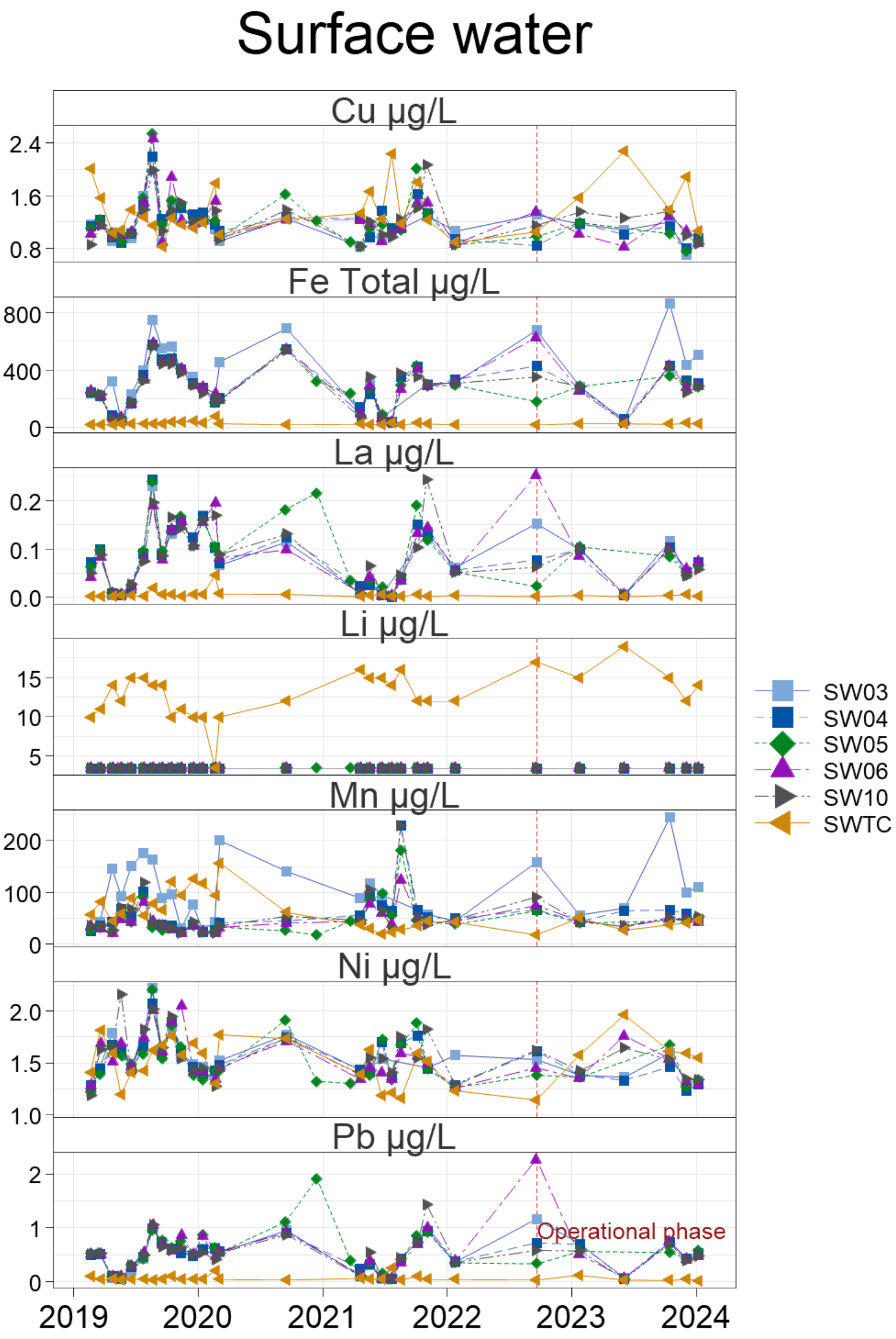


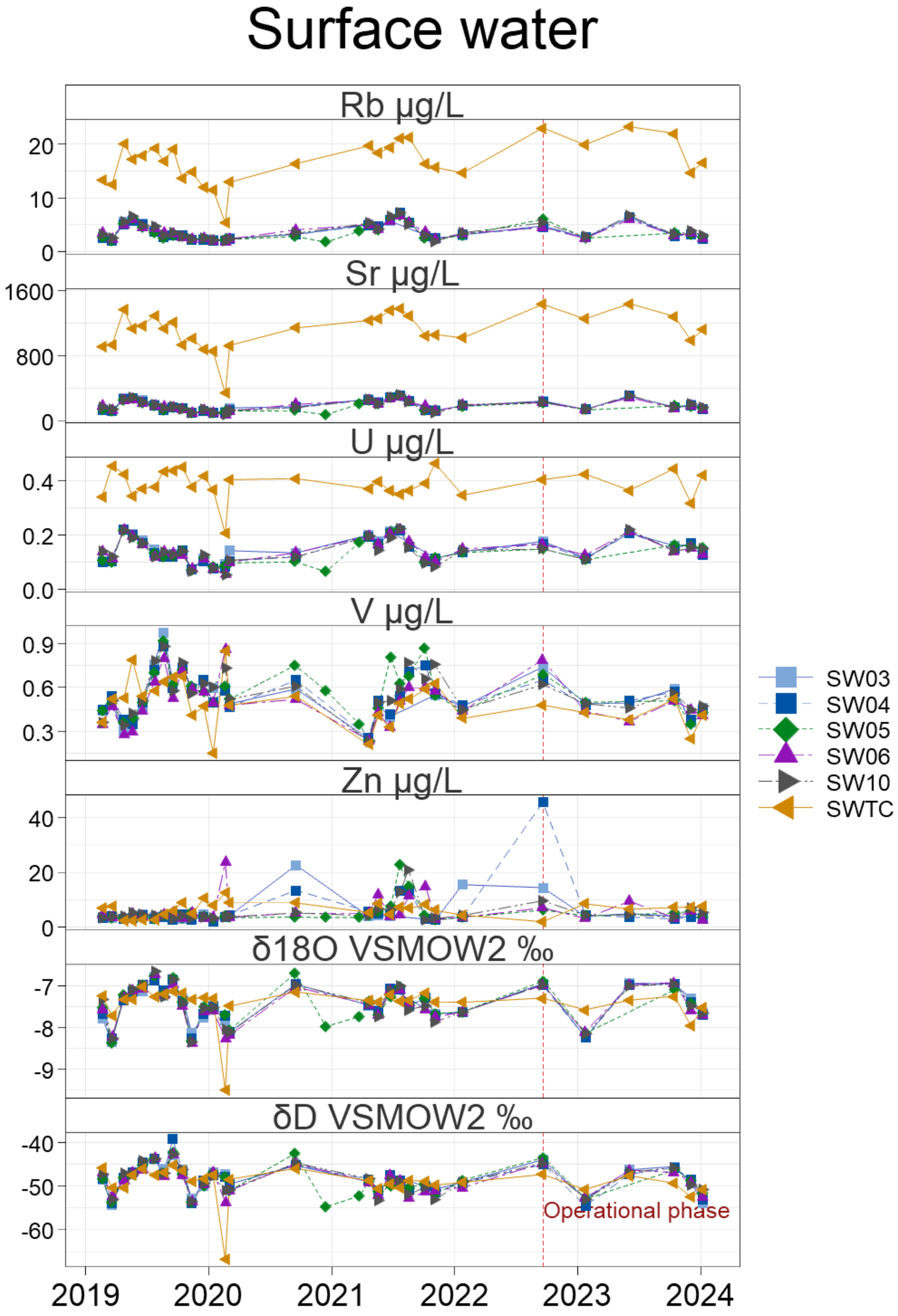
SURFACE WATER MAJOR IONS

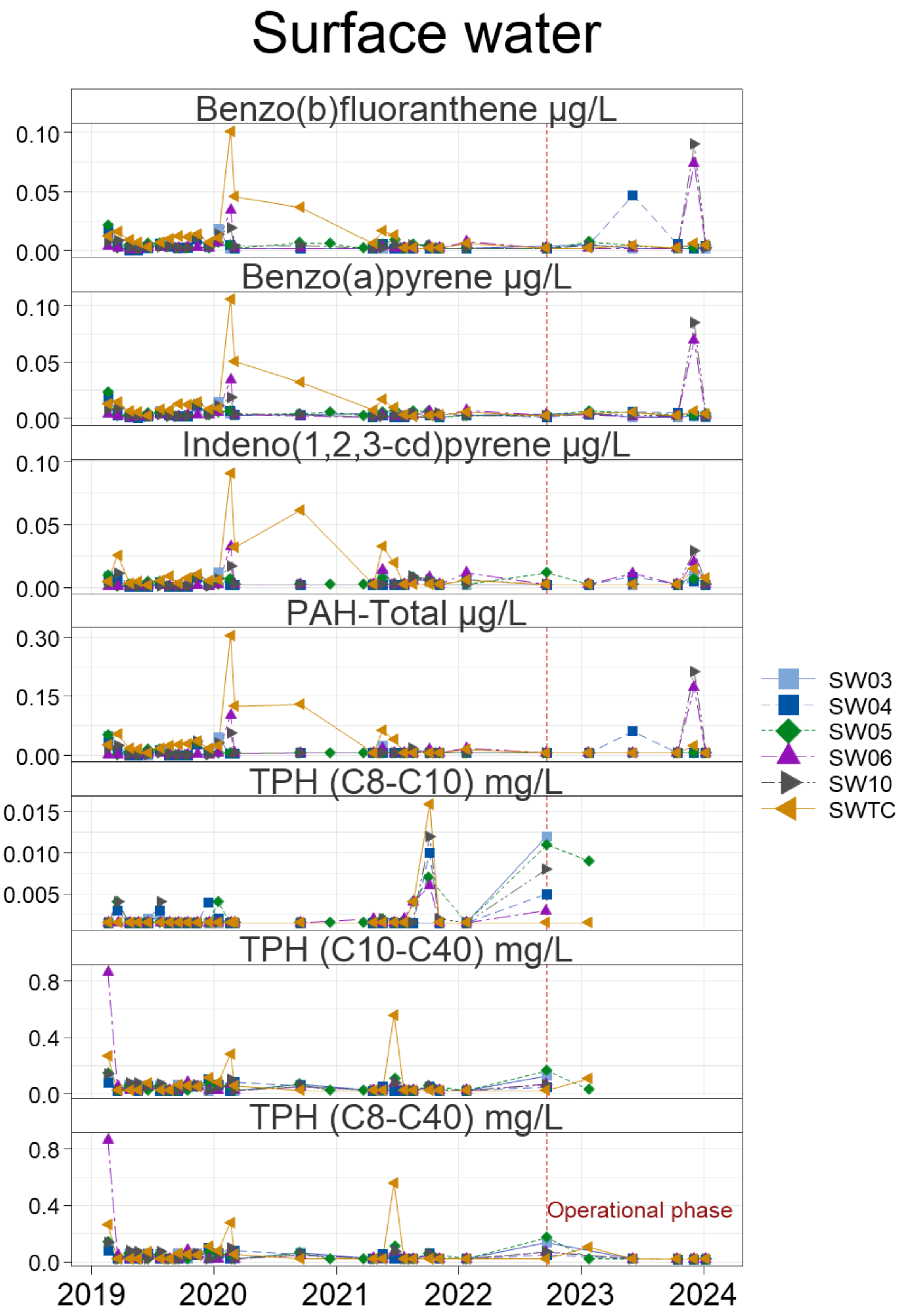


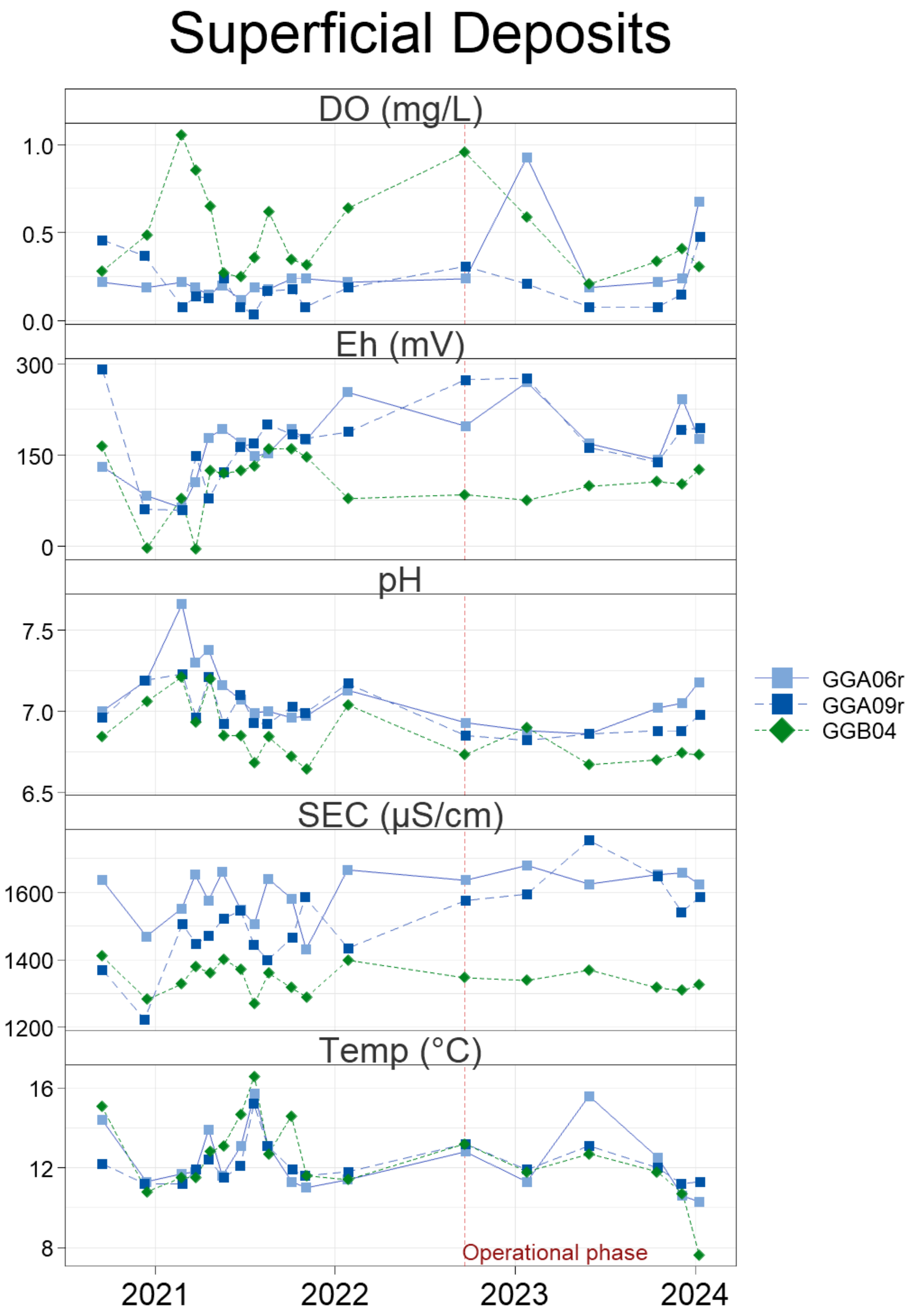

Surface water
Br mg/L
0.2
0.1
0.0
F mg/L
0.2
0.1
0.0
P Total mg/L
0.4
0.2
0.0
NO3 mg/L
15
10
5
NPOC mg/L
15
10
5
S Total mg/L
20
10
0
Si mg/L
5.0
2.5
0.0
Operational phase
2019
2020
2021
2022
2023
2024
SW03
SW04
SW05
SW06
SW10
SWTC


Surface water
Al µg/L
160
80
0
As µg/L
2
1
0
B µg/L
150
100
50
Ba µg/L
150
100
50
Cd µg/L
0.30
0.15
0.00
Co µg/L
1.0
0.5
0.0
Cr Total µg/L
10
5
0
Operational phase
2019
2020
2021
2022
2023
2024
SW03
SW04
SW05
SW06
SW10
SWTC

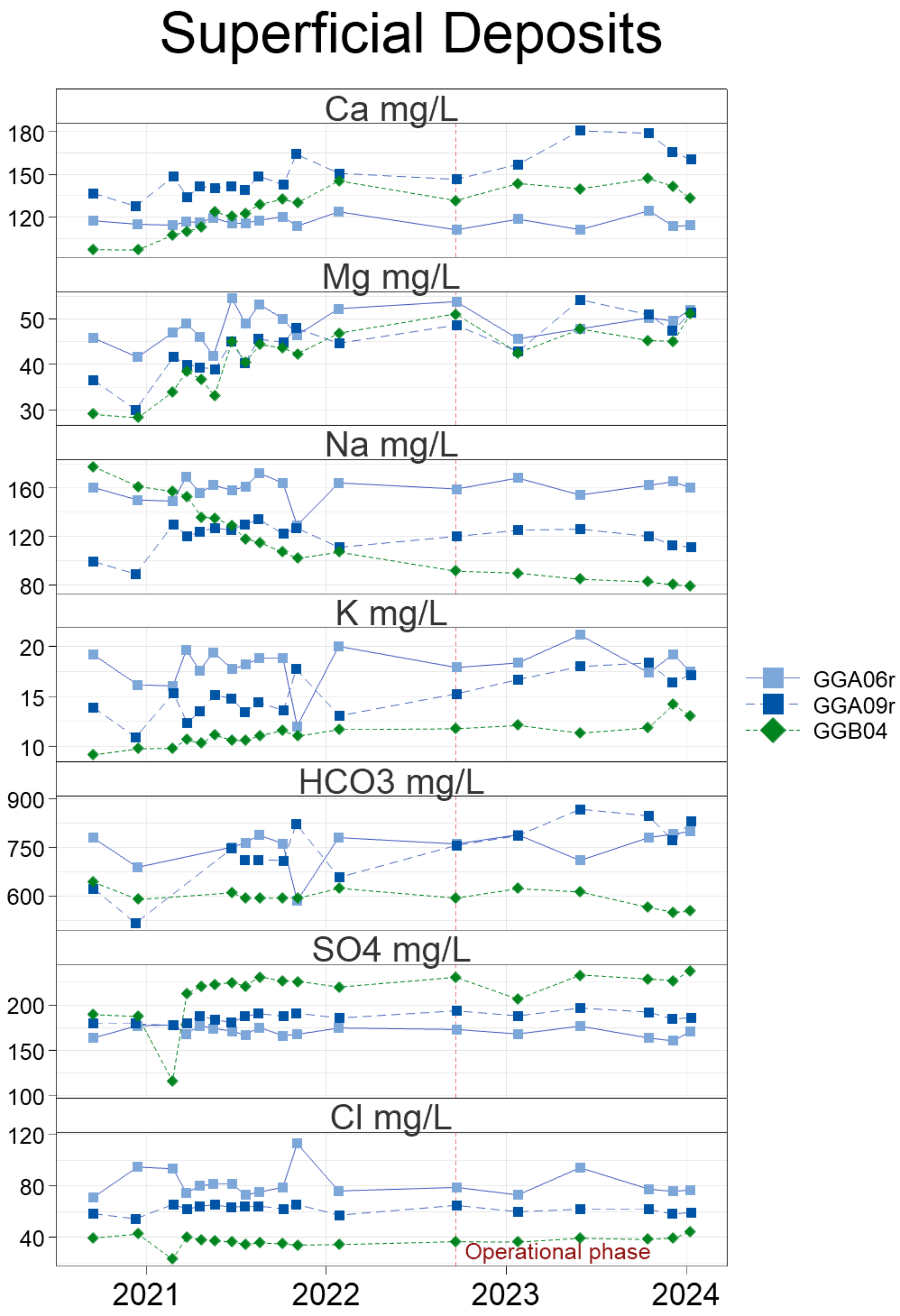

Surface water
Cu µg/L
2.4
1.6
0.8
Fe Total µg/L
800
400
0
La µg/L
0.2
0.1
0.0
Li µg/L
15
10
5
Mn µg/L
200
100
0
Ni µg/L
2.0
1.5
1.0
Pb µg/L
2
1
0
Operational phase
2019
2020
2021
2022
2023
2024
SW03
SW04
SW05
SW06
SW10
SWTC


Surface water
Rb µg/L
20
10
0
Sr µg/L
1600
800
0
U µg/L
0.4
0.2
0.0
V µg/L
0.9
0.6
0.3
Zn µg/L
40
20
0
δ18O VSMOW2 ‰
-7
-8
-9
δD VSMOW2 ‰
-40
-50
-60
Operational phase
2019
2020
2021
2022
2023
2024
SW03
SW04
SW05
SW06
SW10
SWTC

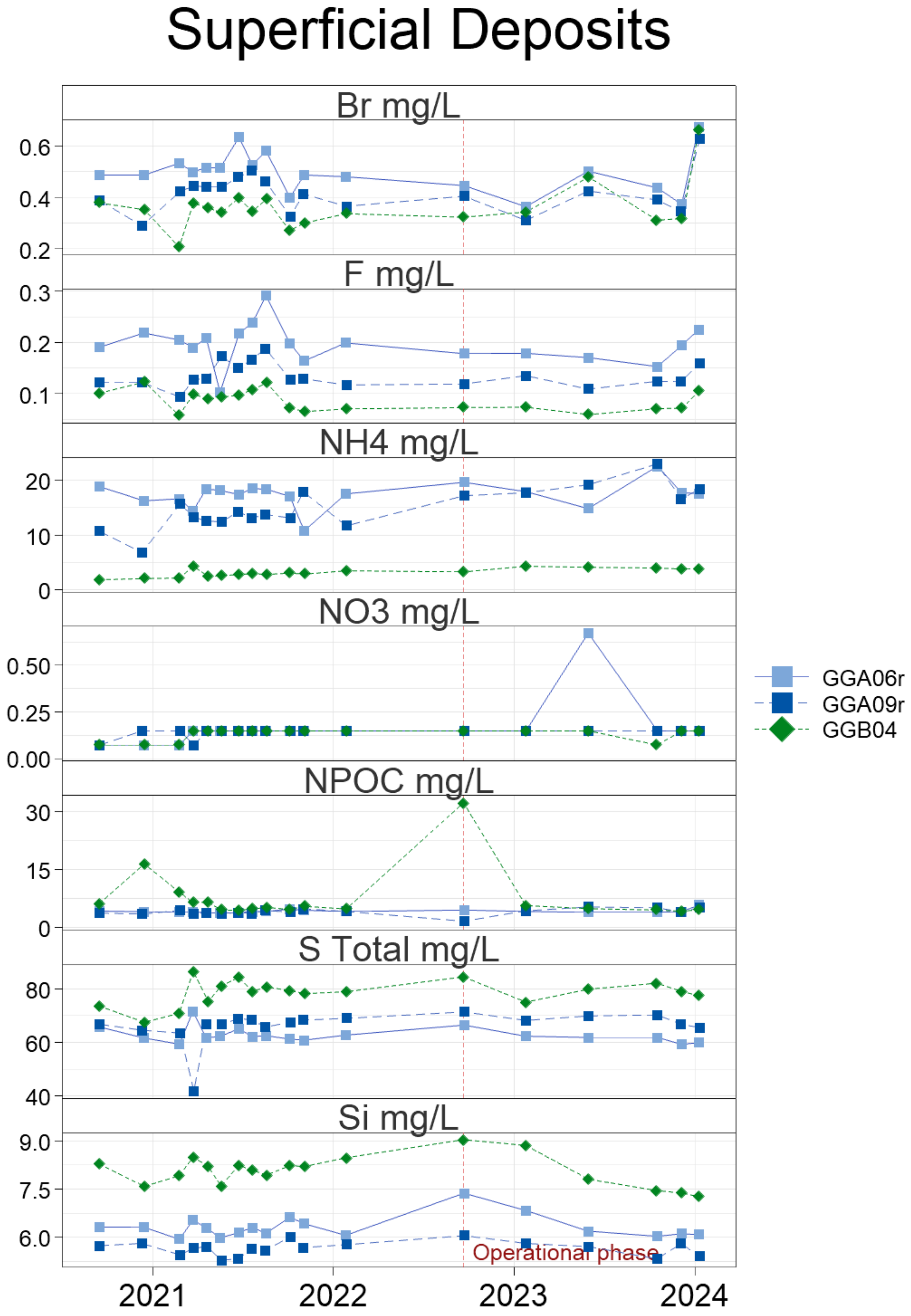

Surface water
Benzo(b)fluoranthene µg/L
Benzo(a)pyrene µg/L
Indeno(1,2,3-cd)pyrene µg/L
PAH-Total µg/L
TPH (C8-C10) mg/L
TPH (C10-C40) mg/L
TPH (C8-C40) mg/L
0.10
0.05
0.00
0.30
0.15
0.015
0.010
0.005
0.8
0.4
0.0
2019
2020
2021
2022
2023
2024
Operational phase
SW03
SW04
SW05
SW06
SW10
SWTC

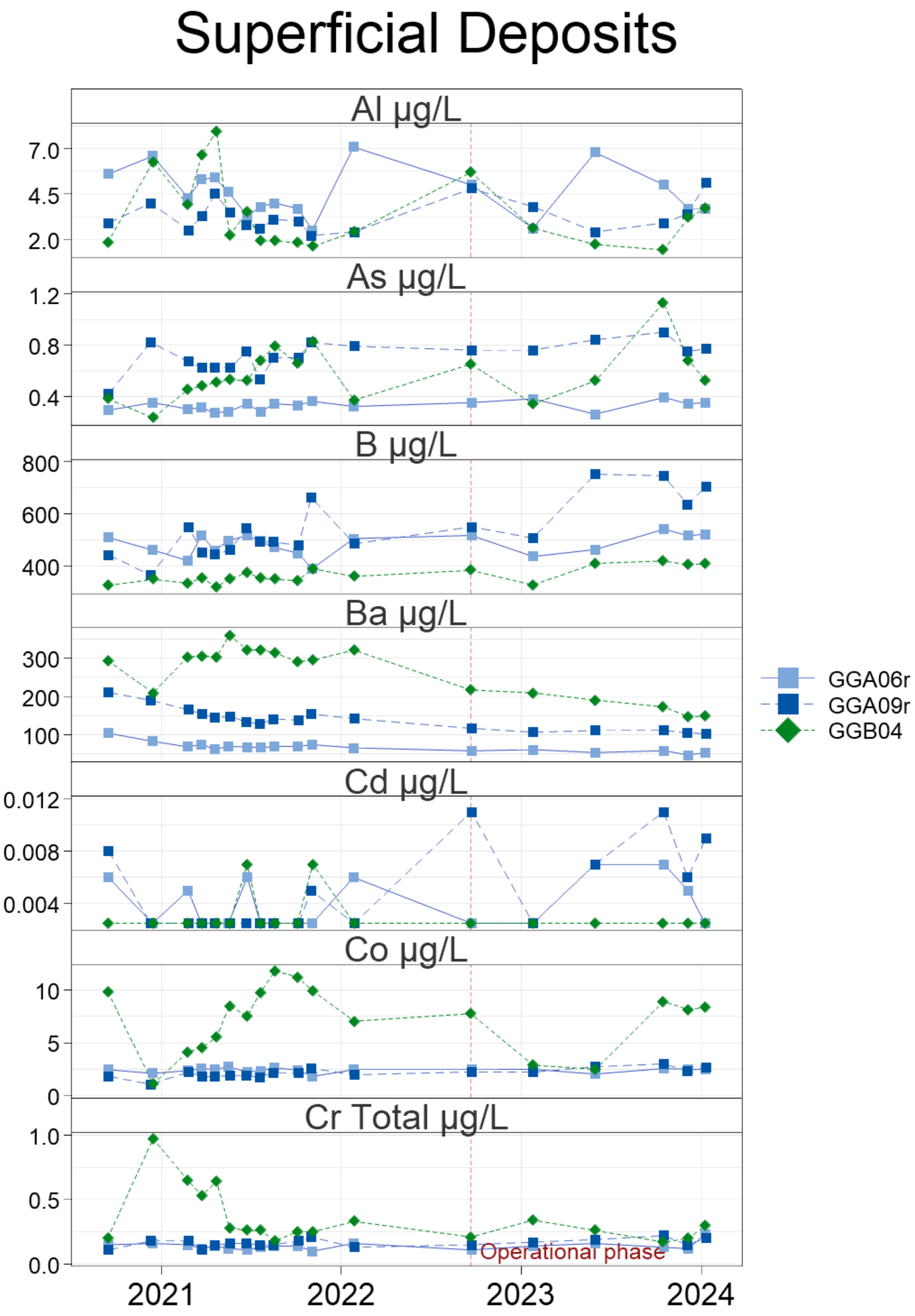

Superficial Deposits
DO (mg/L)
1.0
0.5
0.0
Eh (mV)
300
150
0
pH
7.5
7.0
6.5
SEC (µS/cm)
1600
1400
1200
Temp (°C)
16
12
8
Operational phase
2021
2022
2023
2024
GGA06r
GGA09r
GGB04

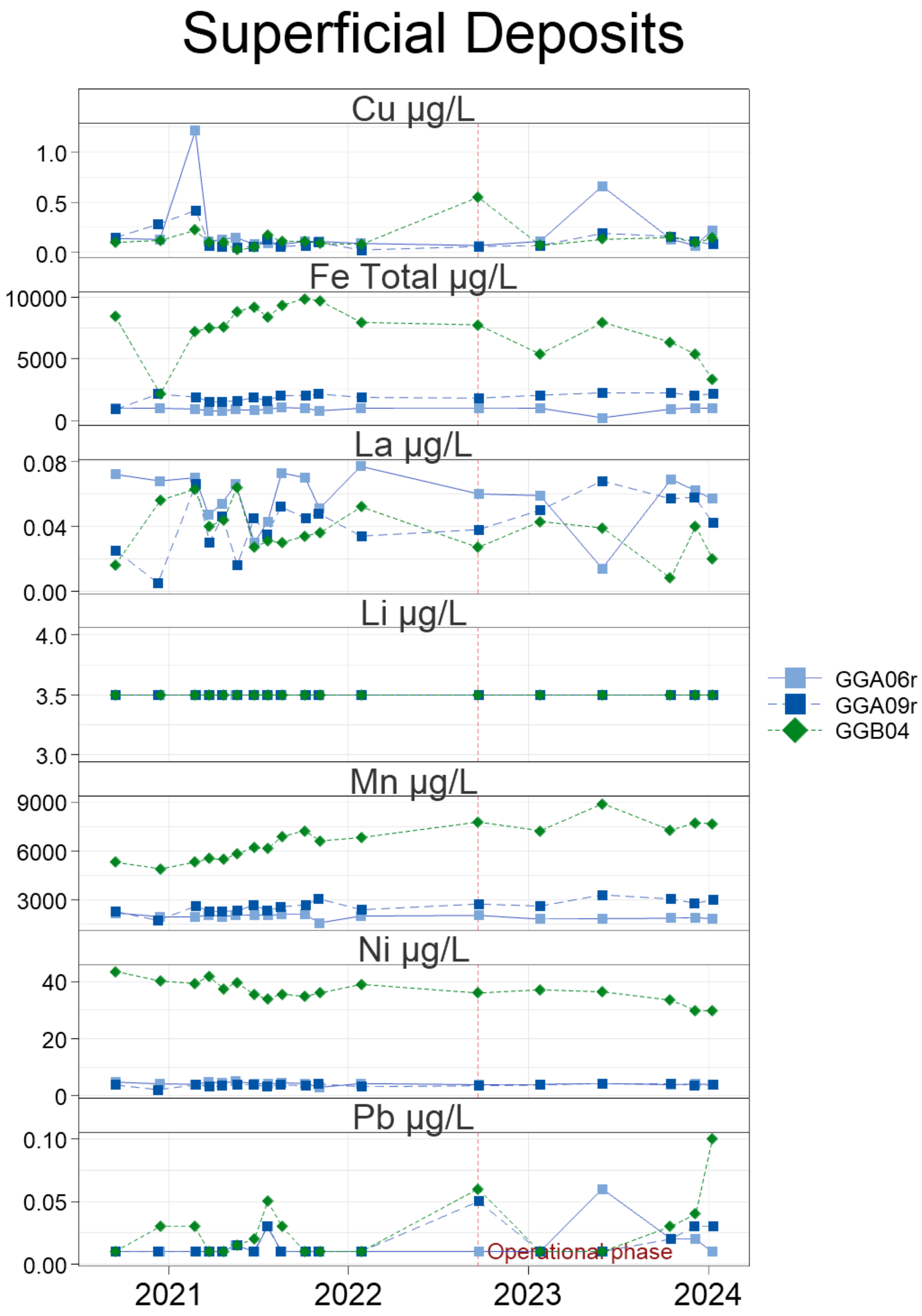
SUPERFICIAL DEPOSITS MAJOR ELEMENTS

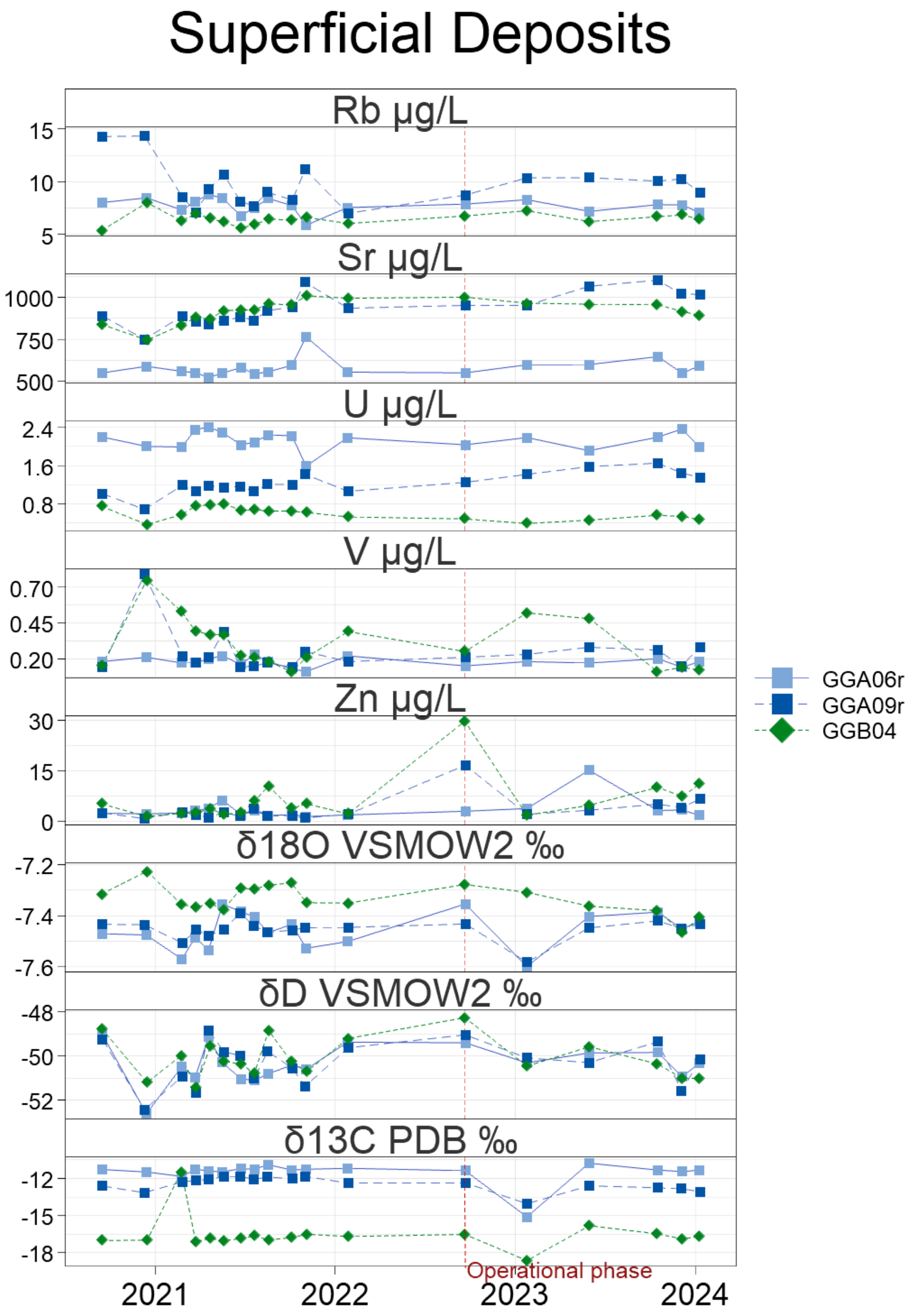


SUPERFICIAL DEPOSITS MINOR ELEMENTS, TOTAL SULPHUR AND DISSOLVED ORGANIC CARBON

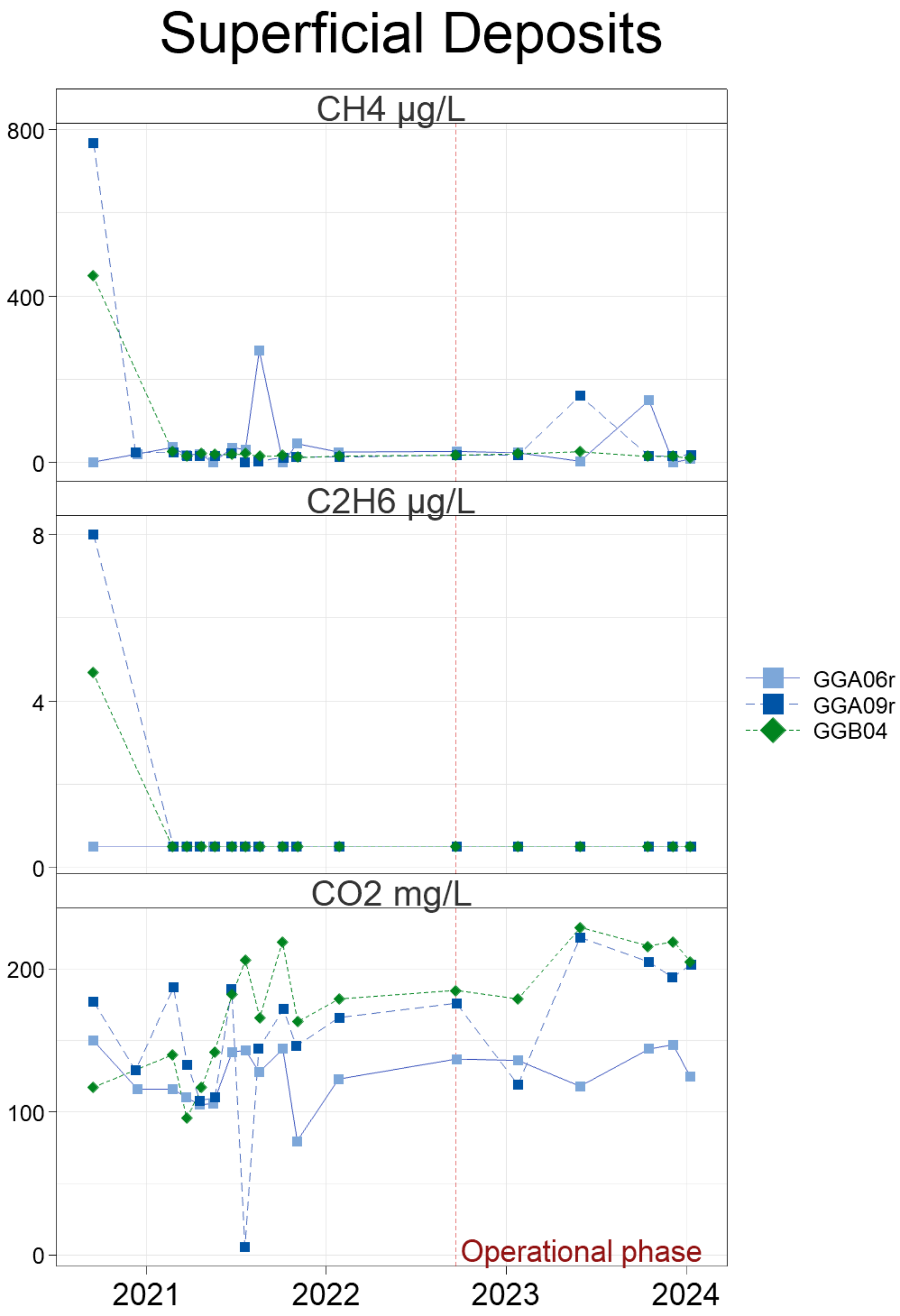


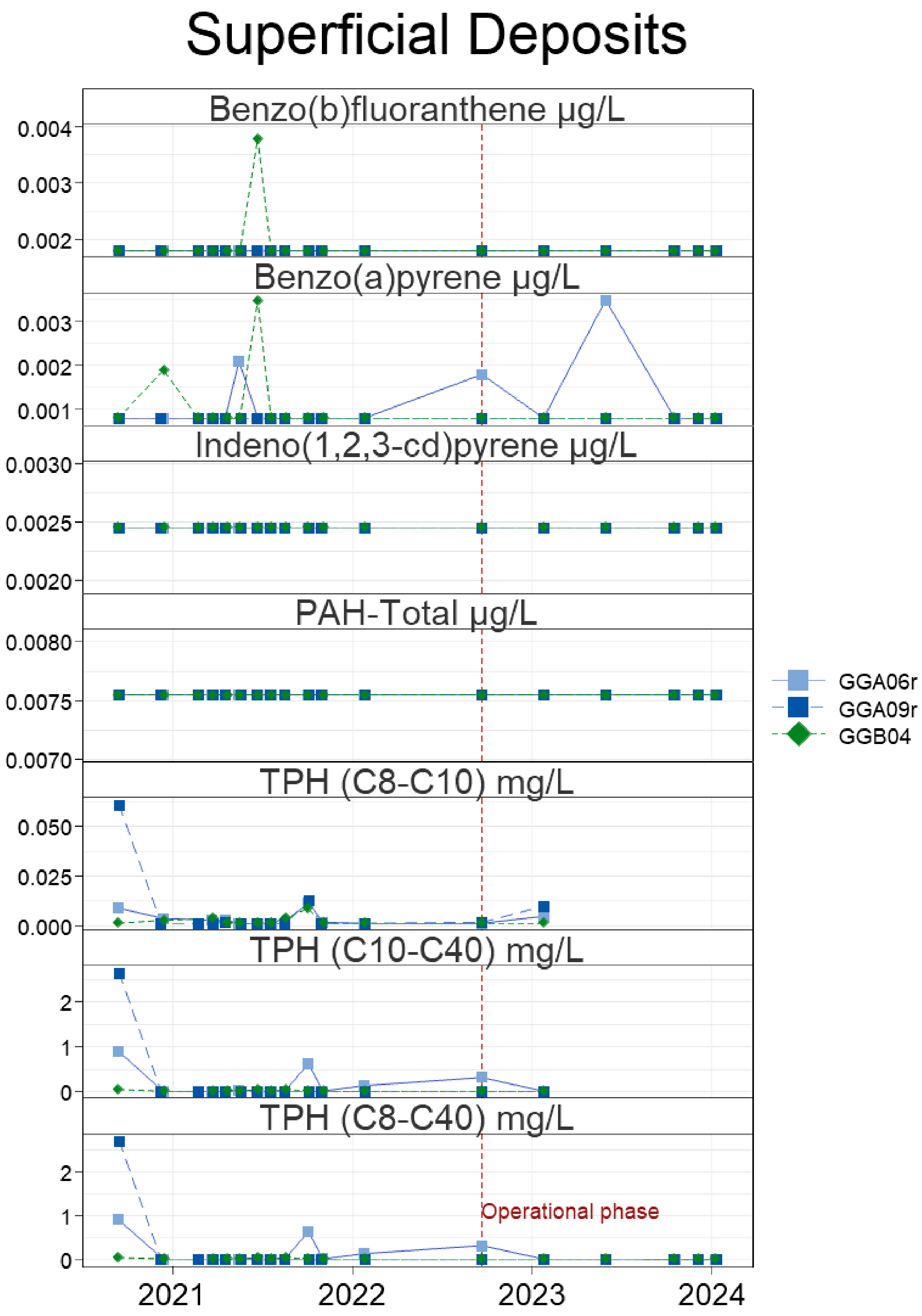

Superficial Deposits
Al µg/L
7.0
4.5
2.0
As µg/L
1.2
0.8
0.4
B µg/L
800
600
400
Ba µg/L
300
200
100
Cd µg/L
0.012
0.008
0.004
Co µg/L
10
5
0
Cr Total µg/L
1.0
0.5
0.0
Operational phase
2021
2022
2023
2024
GGA06r
GGA09r
GGB04


Superficial Deposits
Cu µg/L
1.0
0.5
0.0
Fe Total µg/L
10000
5000
0
La µg/L
0.08
0.04
0.00
Li µg/L
4.0
3.5
3.0
Mn µg/L
9000
6000
3000
Ni µg/L
40
20
0
Pb µg/L
0.10
0.05
0.00
Operational phase
2021
2022
2023
2024
GGA06r
GGA09r
GGB04

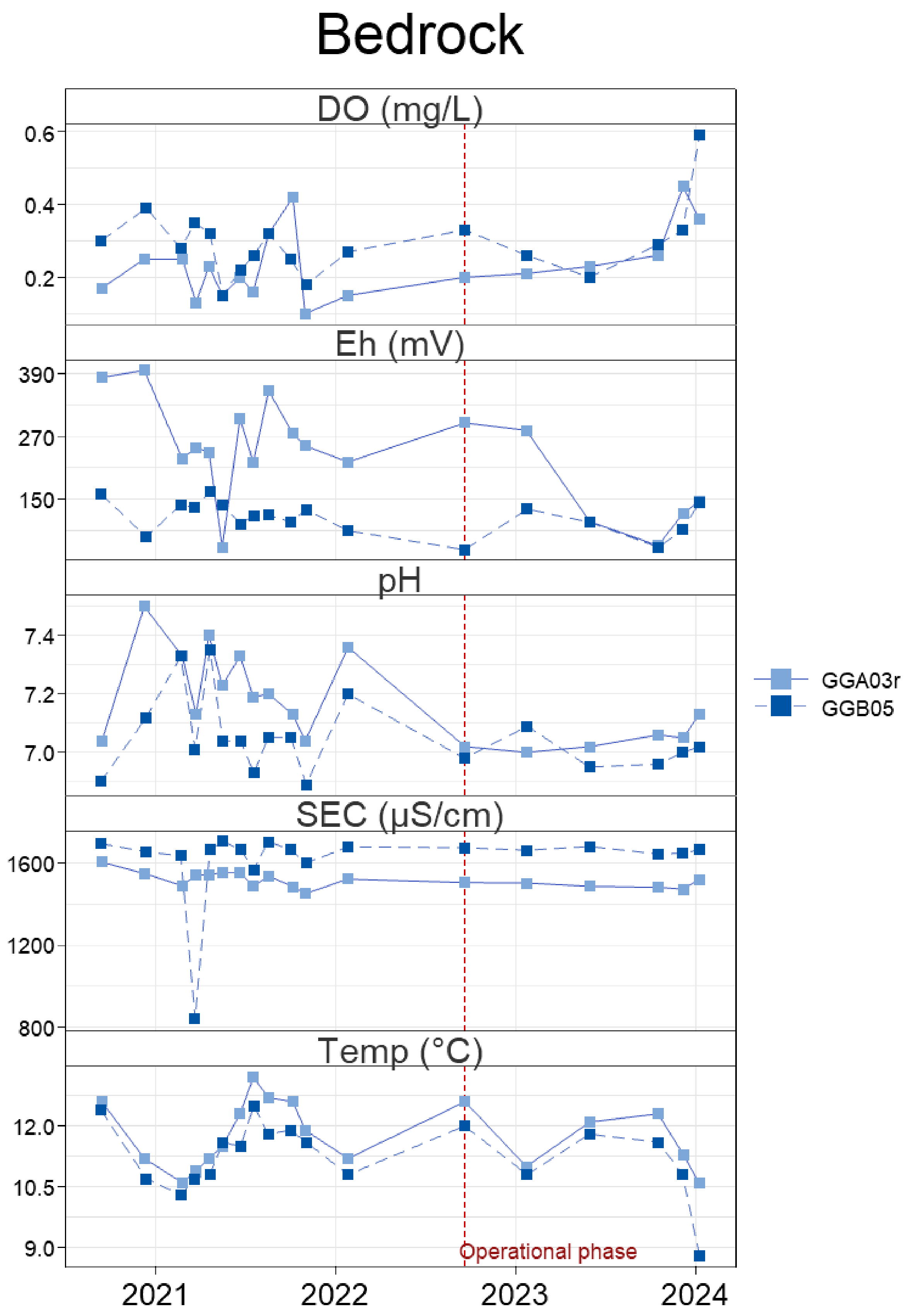

Superficial Deposits
Rb µg/L
15
10
5
Sr µg/L
1000
750
500
U µg/L
2.4
1.6
0.8
V µg/L
0.70
0.45
0.20
Zn µg/L
30
15
0
δ18O VSMOW2 ‰
-7.2
-7.4
-7.6
δD VSMOW2 ‰
-48
-50
-52
δ13C PDB ‰
-12
-15
-18
Operational phase
2021
2022
2023
2024
GGA06r
GGA09r
GGB04

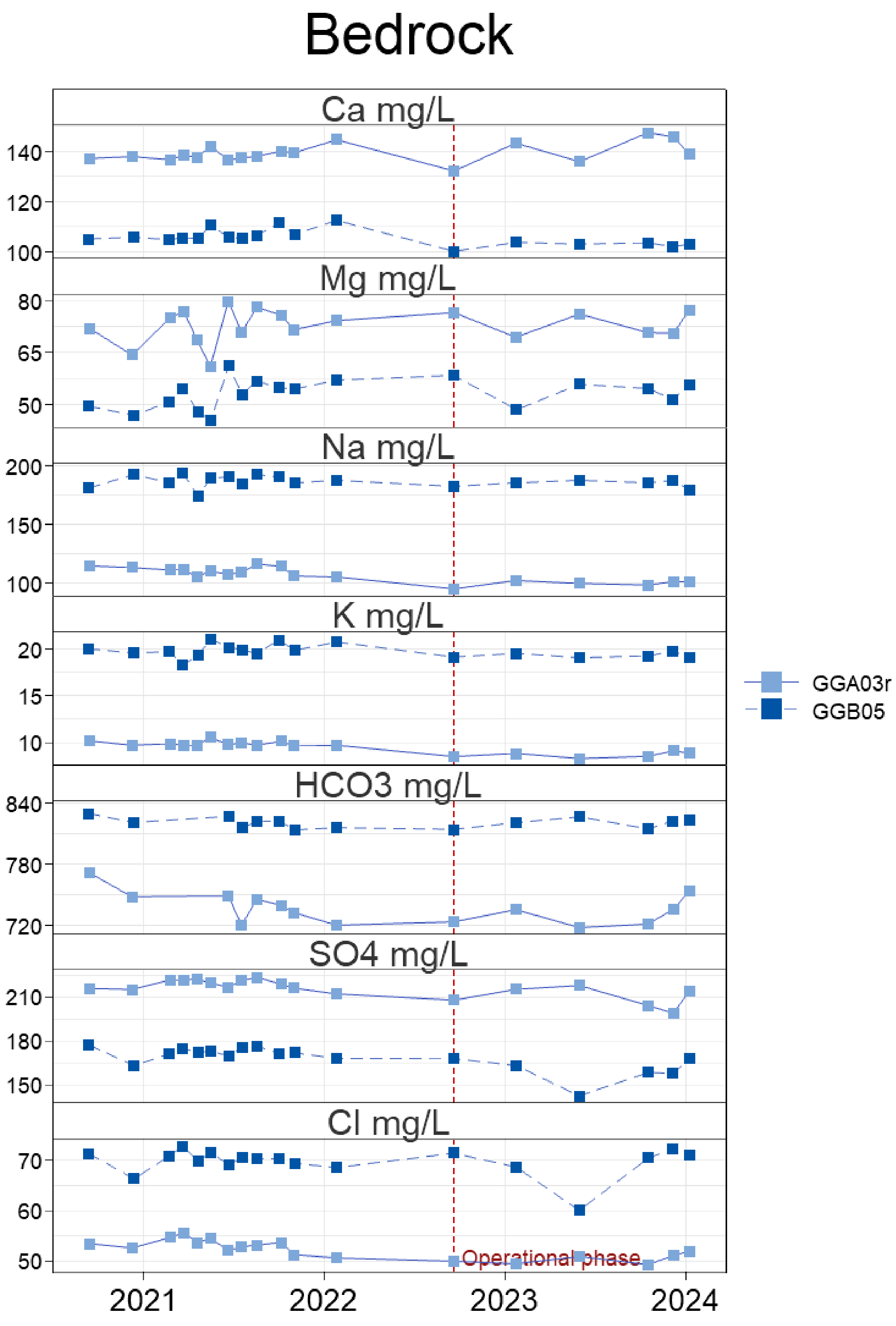
SUPERFICIAL DEPOSITS DISSOLVED GASES CO_2 AND CH_4

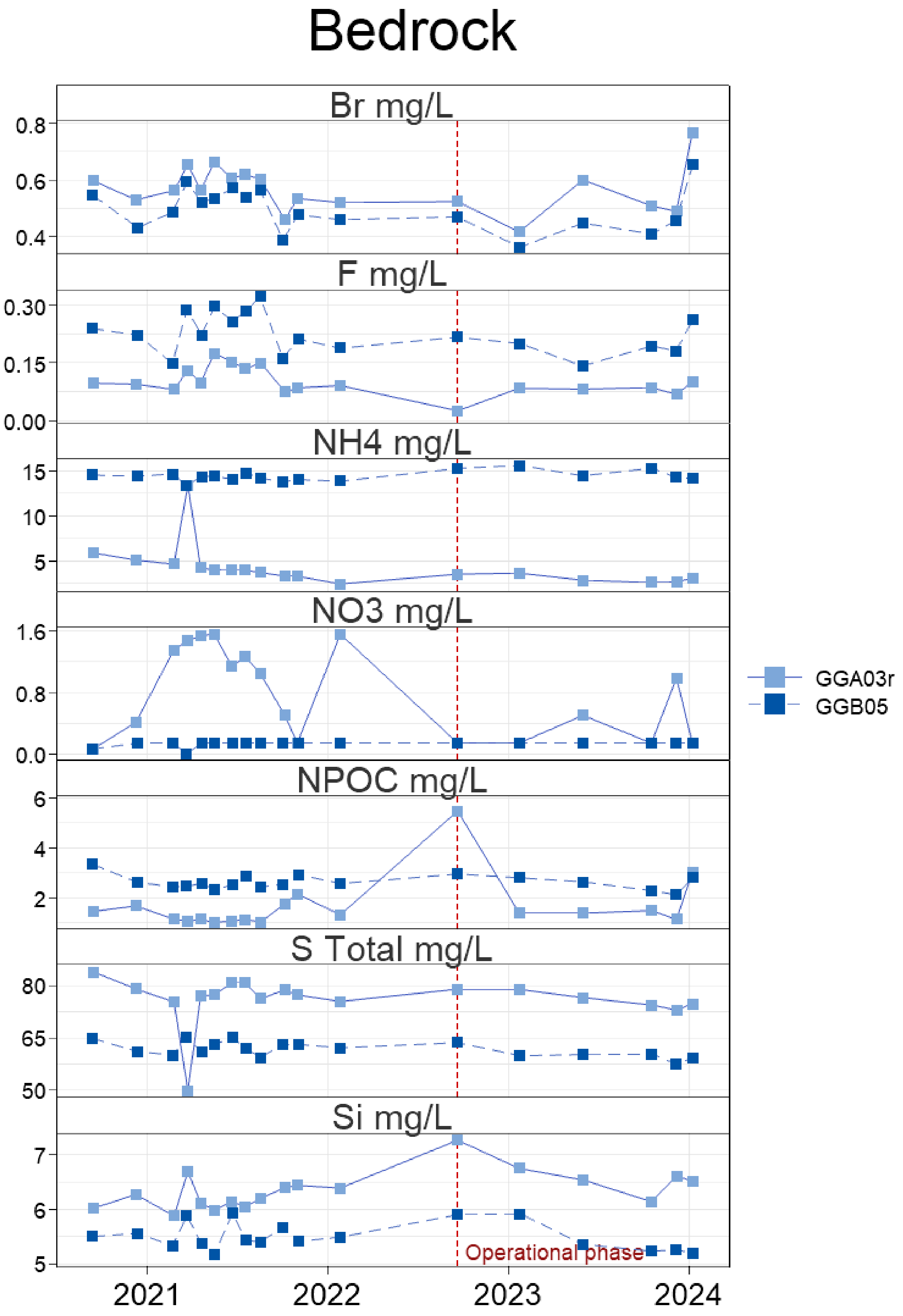



Superficial Deposits
Benzo(b)fluoranthene µg/L
0.004
0.003
0.002
Benzo(a)pyrene µg/L
0.003
0.002
0.001
Indeno(1,2,3-cd)pyrene µg/L
0.0030
0.0025
0.0020
PAH-Total µg/L
0.0080
0.0075
0.0070
TPH (C8-C10) mg/L
0.050
0.025
0.000
TPH (C10-C40) mg/L
2
1
0
TPH (C8-C40) mg/L
2
1
0
Operational phase
2021
2022
2023
2024
GGA06r
GGA09r
GGB04

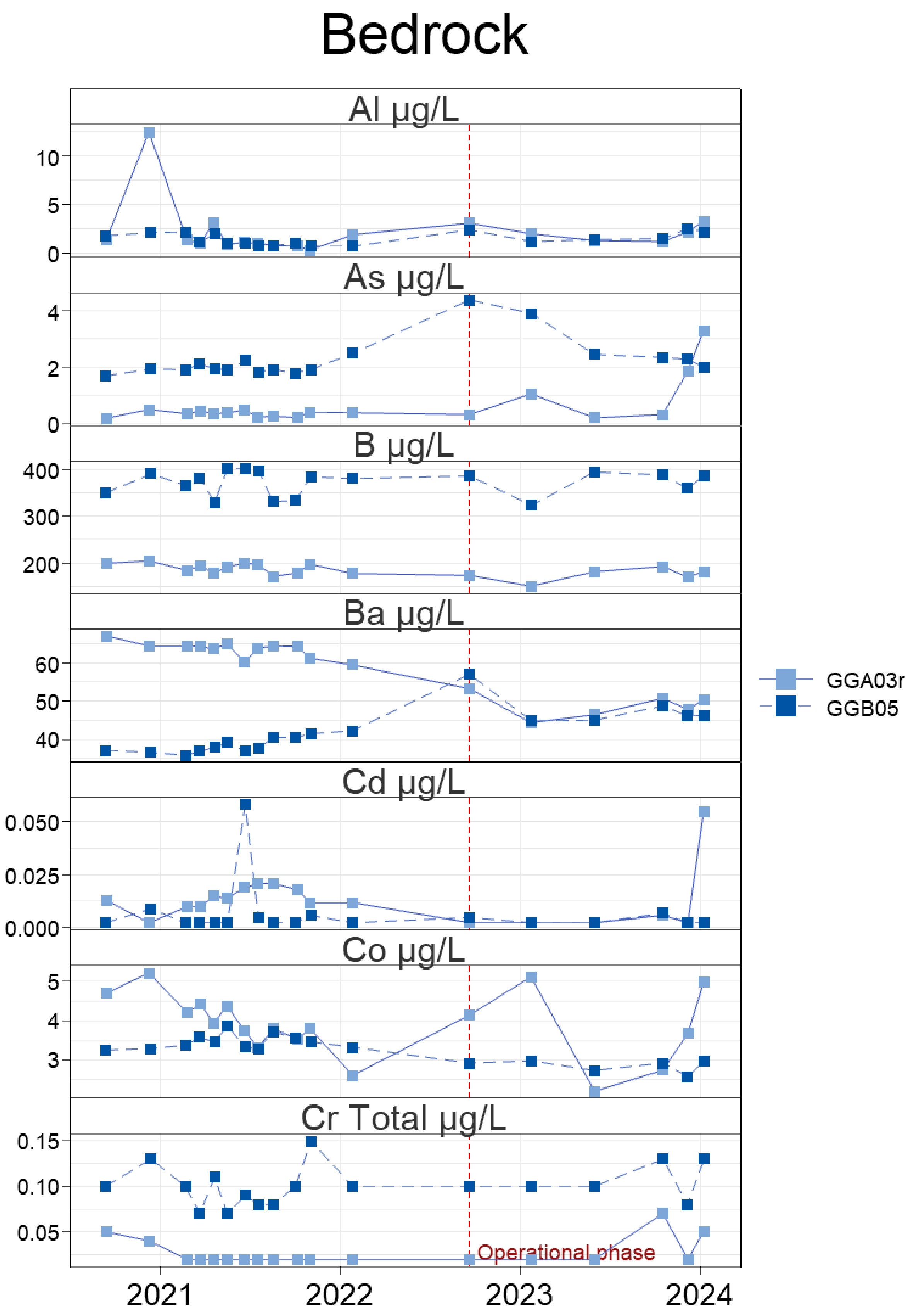
BEDROCK FIELD PARAMETERS



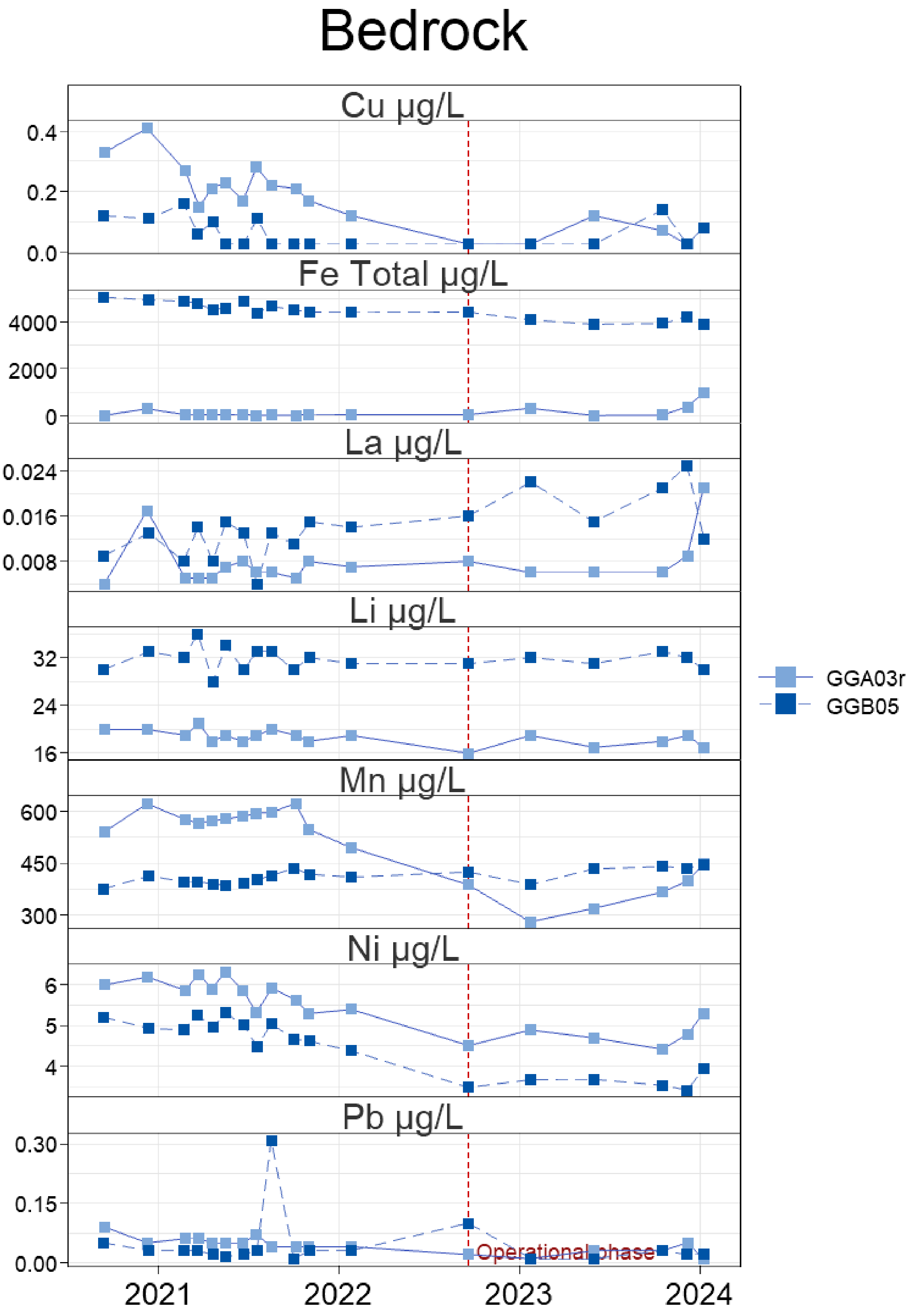

Bedrock
Ca mg/L
140
120
100
Mg mg/L
80
65
50
Na mg/L
200
150
100
K mg/L
20
15
10
HCO3 mg/L
840
780
720
SO4 mg/L
210
180
150
Cl mg/L
70
60
50
Operational phase
2021
2022
2023
2024
GGA03r
GGB05

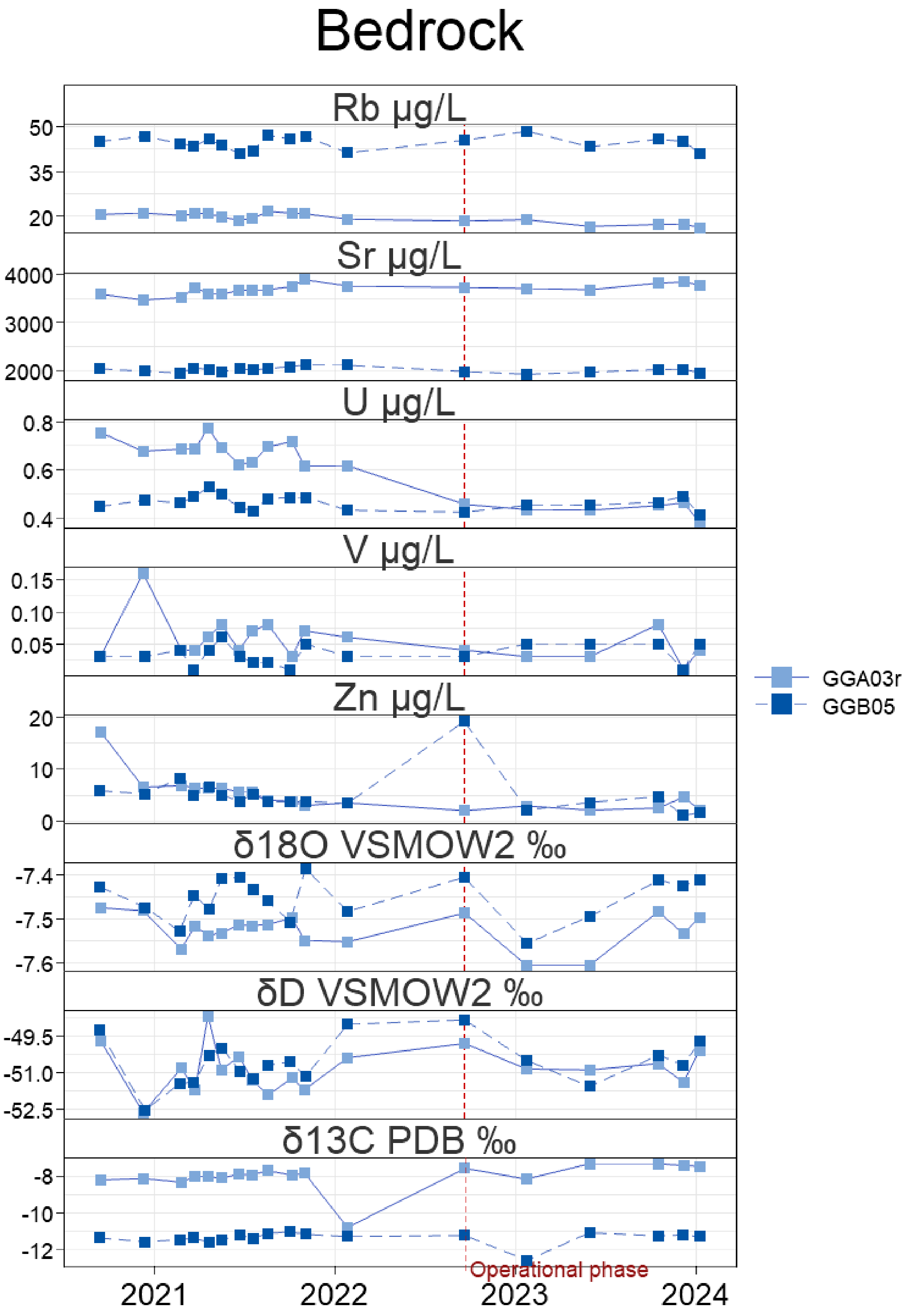

Bedrock
Br mg/L
0.8
0.6
0.4
F mg/L
0.30
0.15
0.00
NH4 mg/L
15
10
5
NO3 mg/L
1.6
0.8
0.0
NPOC mg/L
6
4
2
S Total mg/L
80
65
50
Si mg/L
7
6
5
Operational phase
2021
2022
2023
2024
GGA03r
GGB05

BEDROCK TRACE ELEMENTS PART 1

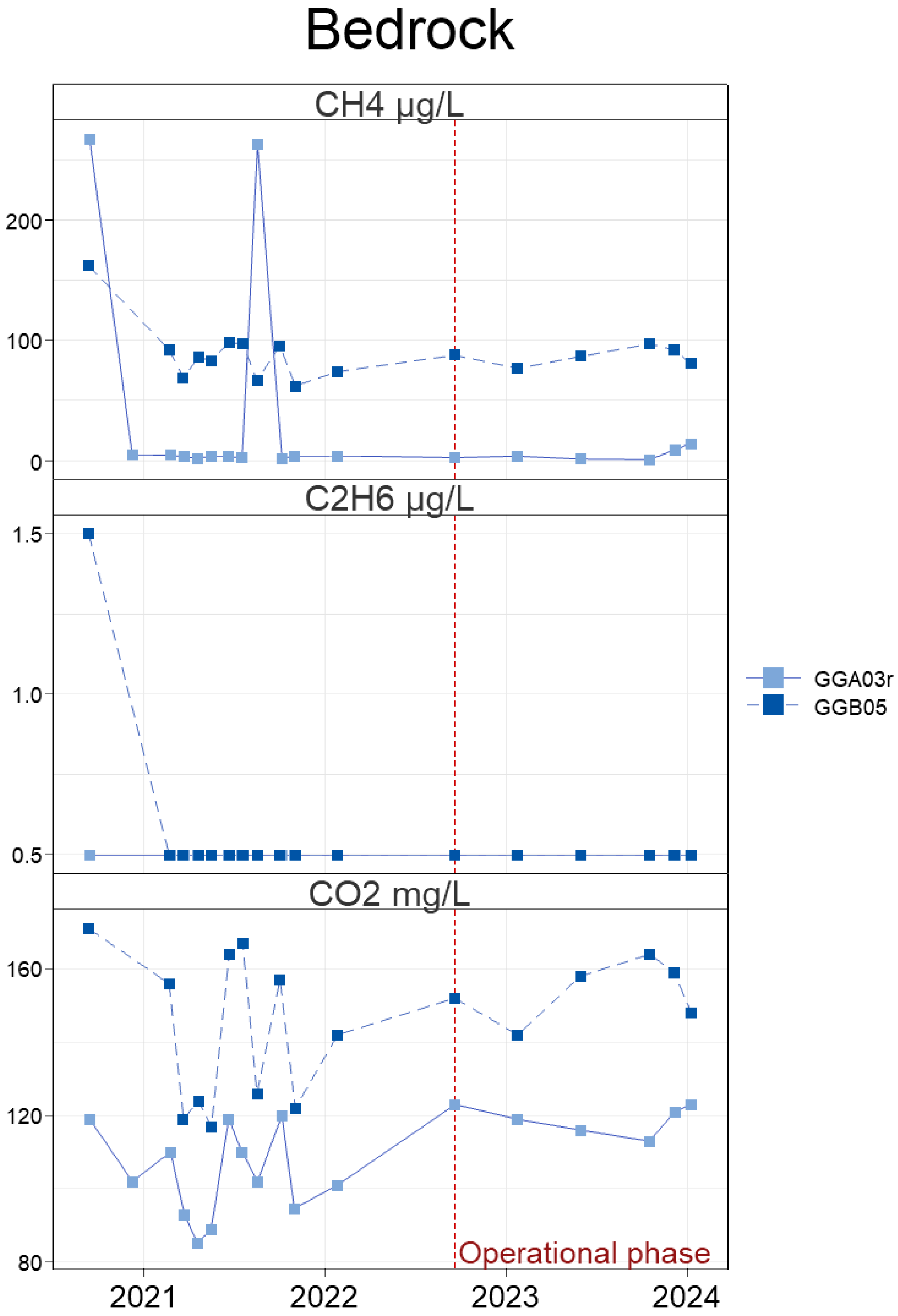


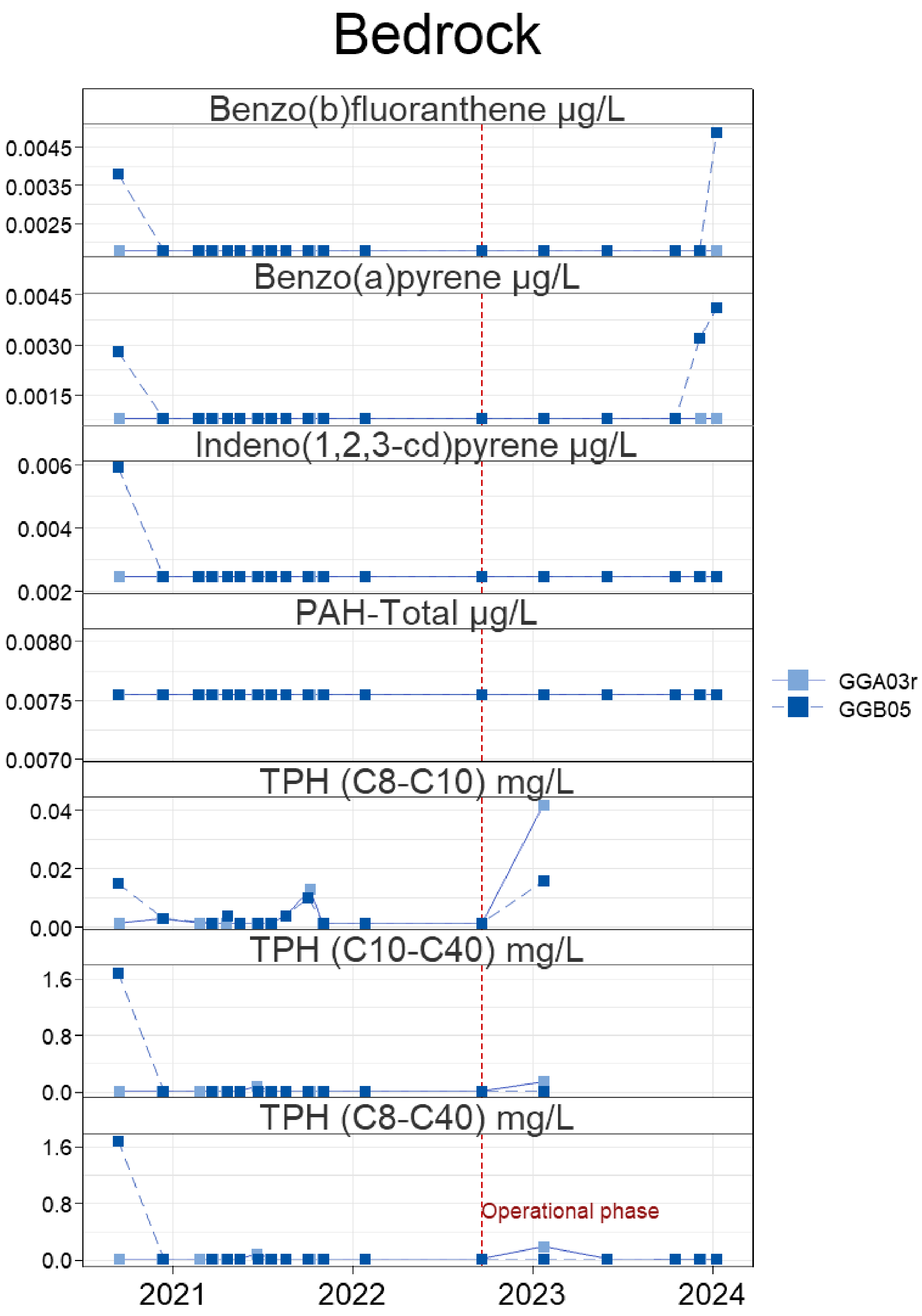
BEDROCK TRACE ELEMENTS PART 2

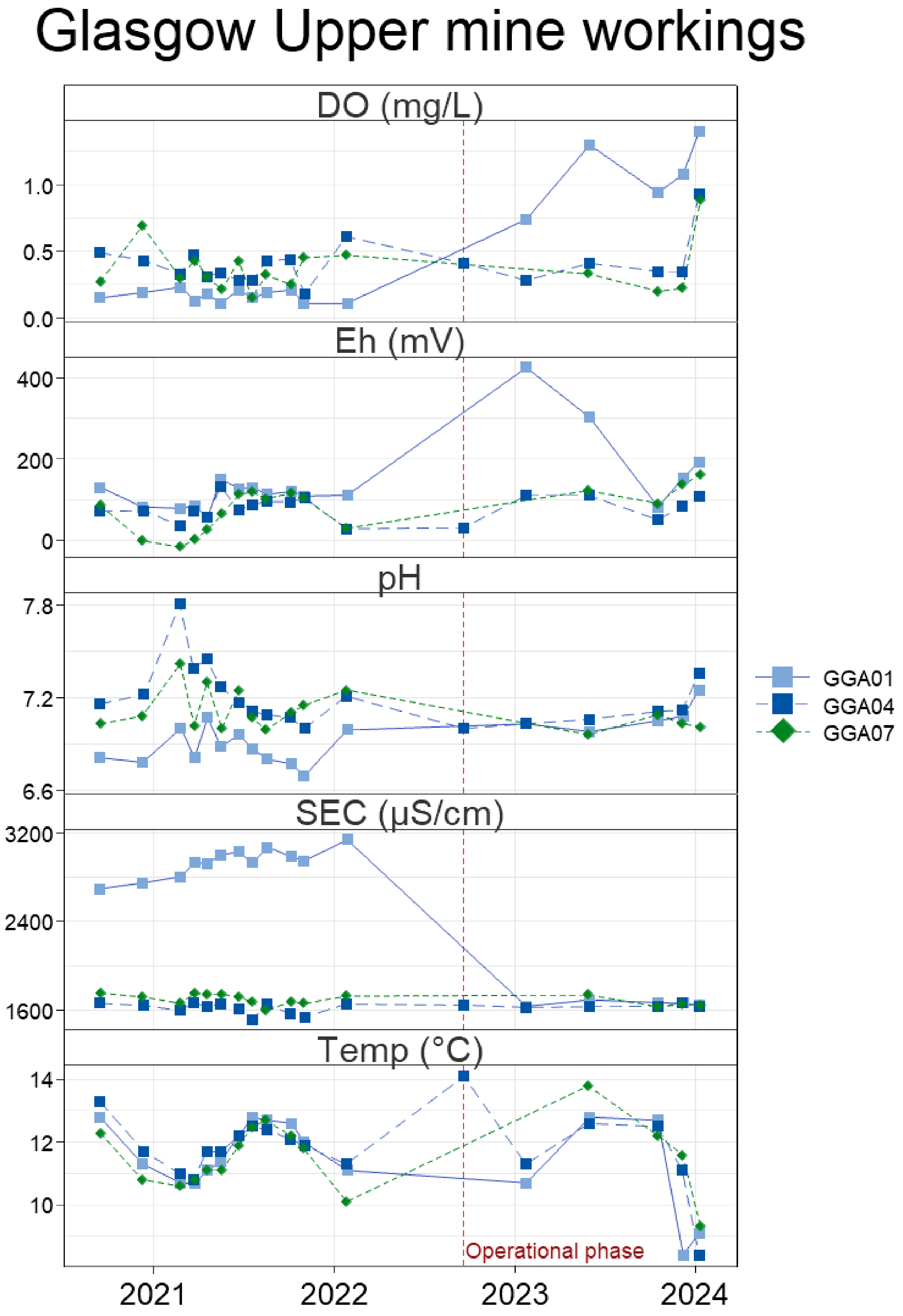


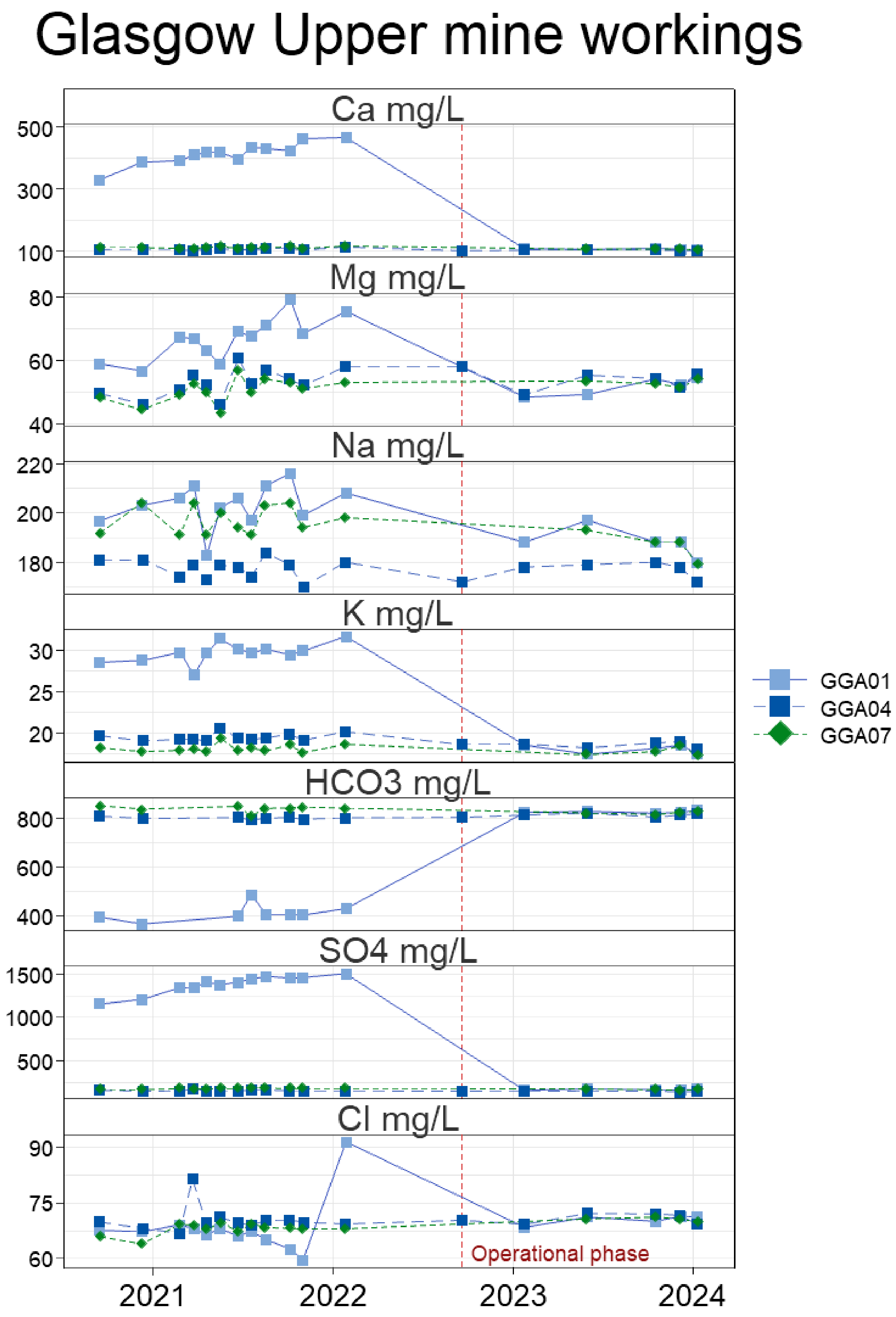

Bedrock
Rb µg/L
50
35
20
Sr µg/L
4000
3000
2000
U µg/L
0.8
0.6
0.4
V µg/L
0.15
0.10
0.05
Zn µg/L
20
10
0
δ18O VSMOW2 ‰
-7.4
-7.5
-7.6
δD VSMOW2 ‰
-49.5
-51.0
-52.5
δ13C PDB ‰
-8
-10
-12
Operational phase
2021
2022
2023
2024
GGA03r
GGB05

BEDROCK DISSOLVED GASES CO_2 AND CH_4

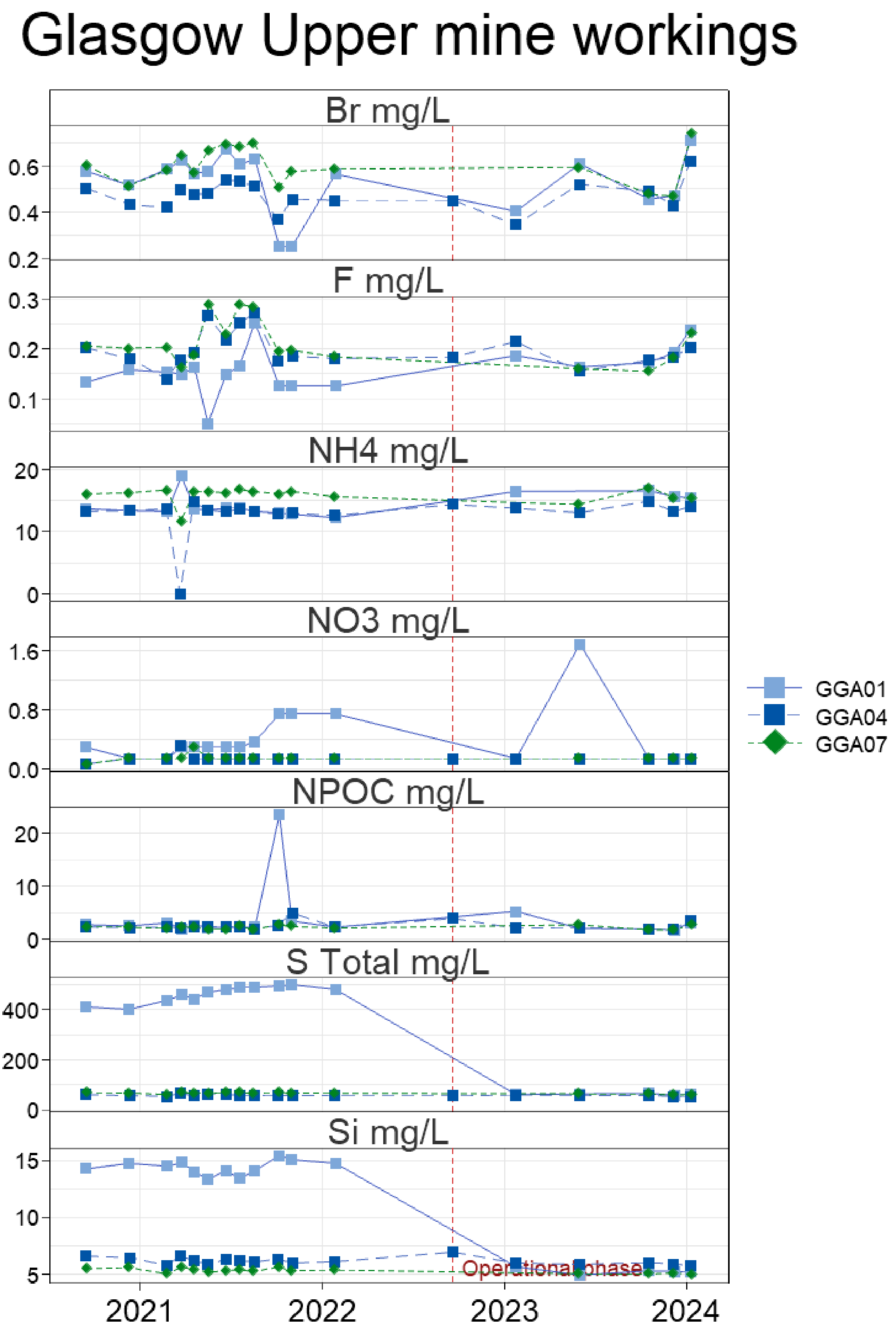


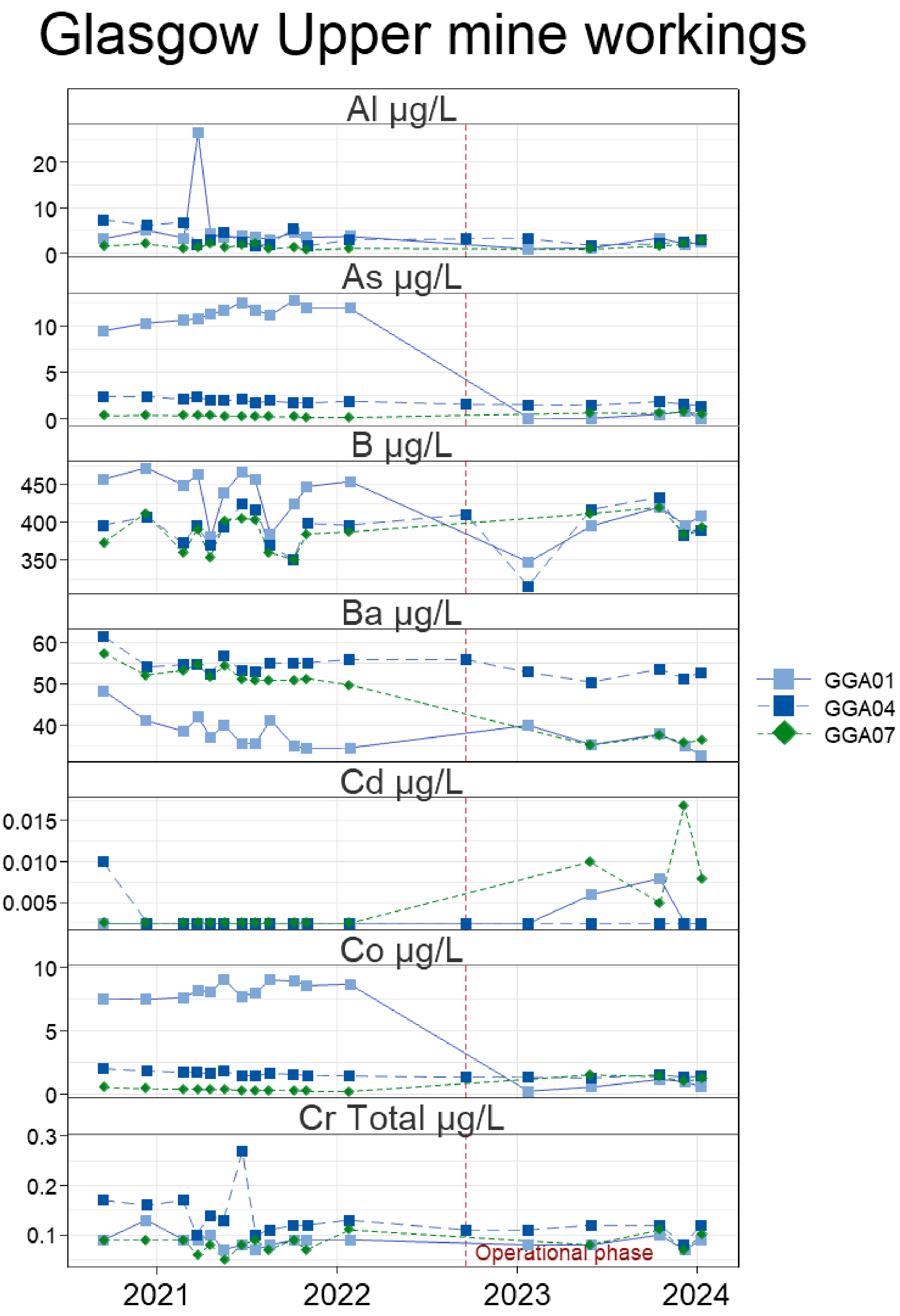

Bedrock
Benzo(b)fluoranthene µg/L
0.0045
0.0035
0.0025
Benzo(a)pyrene µg/L
0.0045
0.0030
0.0015
Indeno(1,2,3-cd)pyrene µg/L
0.006
0.004
0.002
PAH-Total µg/L
0.0080
0.0075
0.0070
TPH (C8-C10) mg/L
0.04
0.02
0.00
TPH (C10-C40) mg/L
1.6
0.8
0.0
TPH (C8-C40) mg/L
1.6
0.8
0.0
Operational phase
2021
2022
2023
2024
GGA03r
GGB05

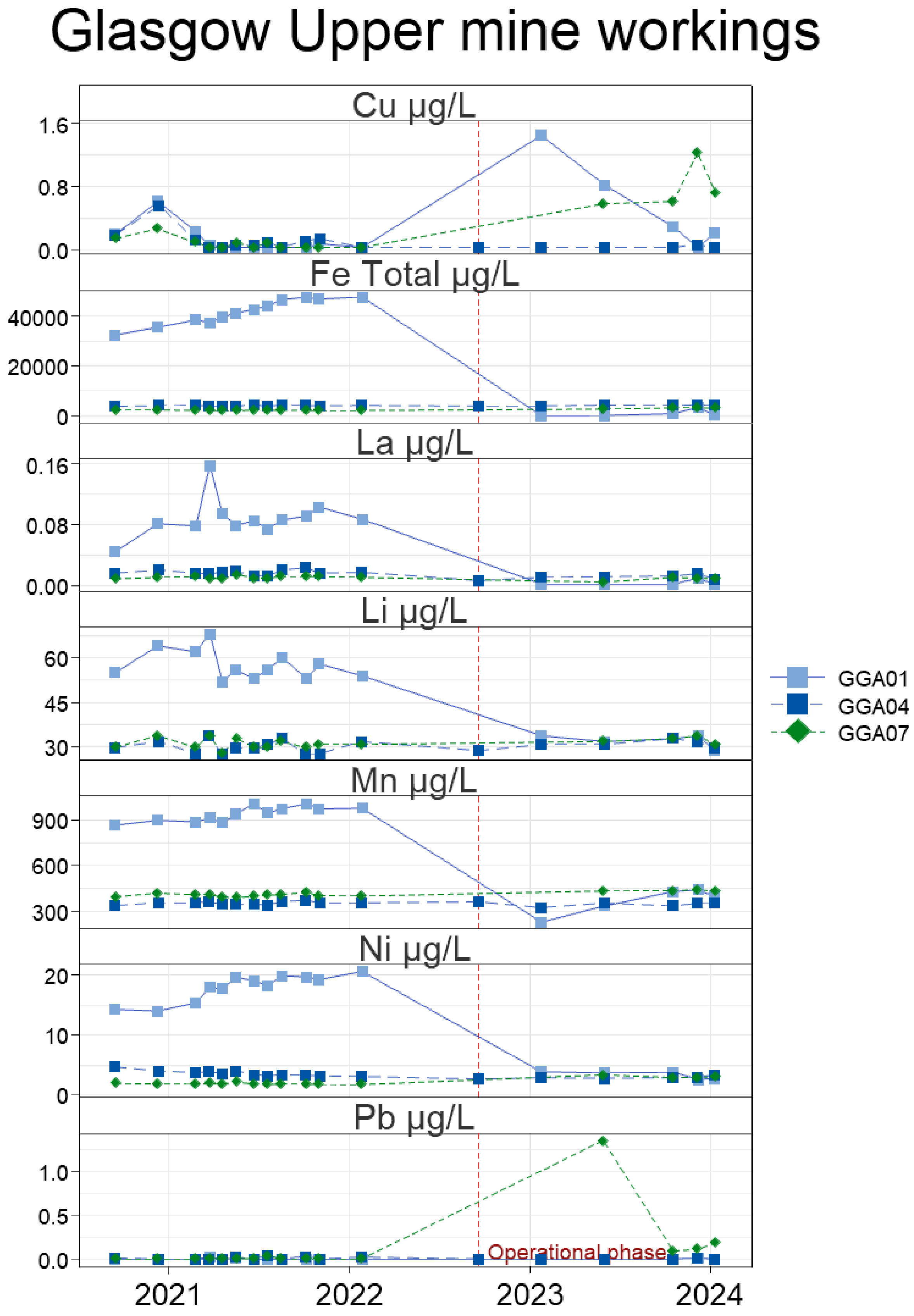

Glasgow Upper mine workings
DO (mg/L)
1.0
0.5
0.0
Eh (mV)
400
200
0
pH
7.8
7.2
6.6
SEC (µS/cm)
3200
2400
1600
Temp (°C)
14
12
10
Operational phase
2021
2022
2023
2024
GGA01
GGA04
GGA07

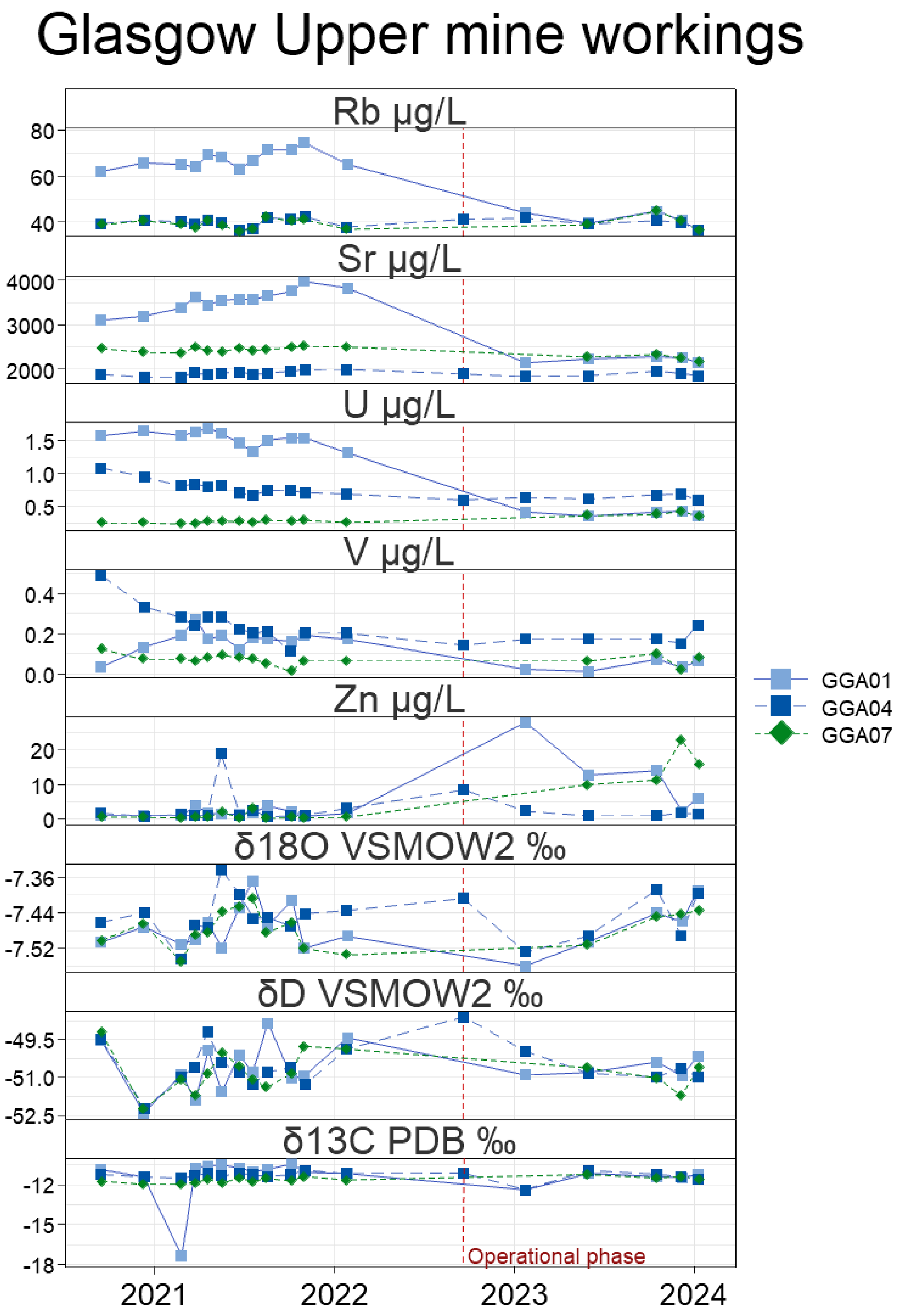

Glasgow Upper mine workings
Ca mg/L
500
300
100
Mg mg/L
80
60
40
Na mg/L
220
200
180
K mg/L
30
25
20
HCO3 mg/L
800
600
400
SO4 mg/L
1500
1000
500
Cl mg/L
90
75
60
Operational phase
2021
2022
2023
2024
GGA01
GGA04
GGA07

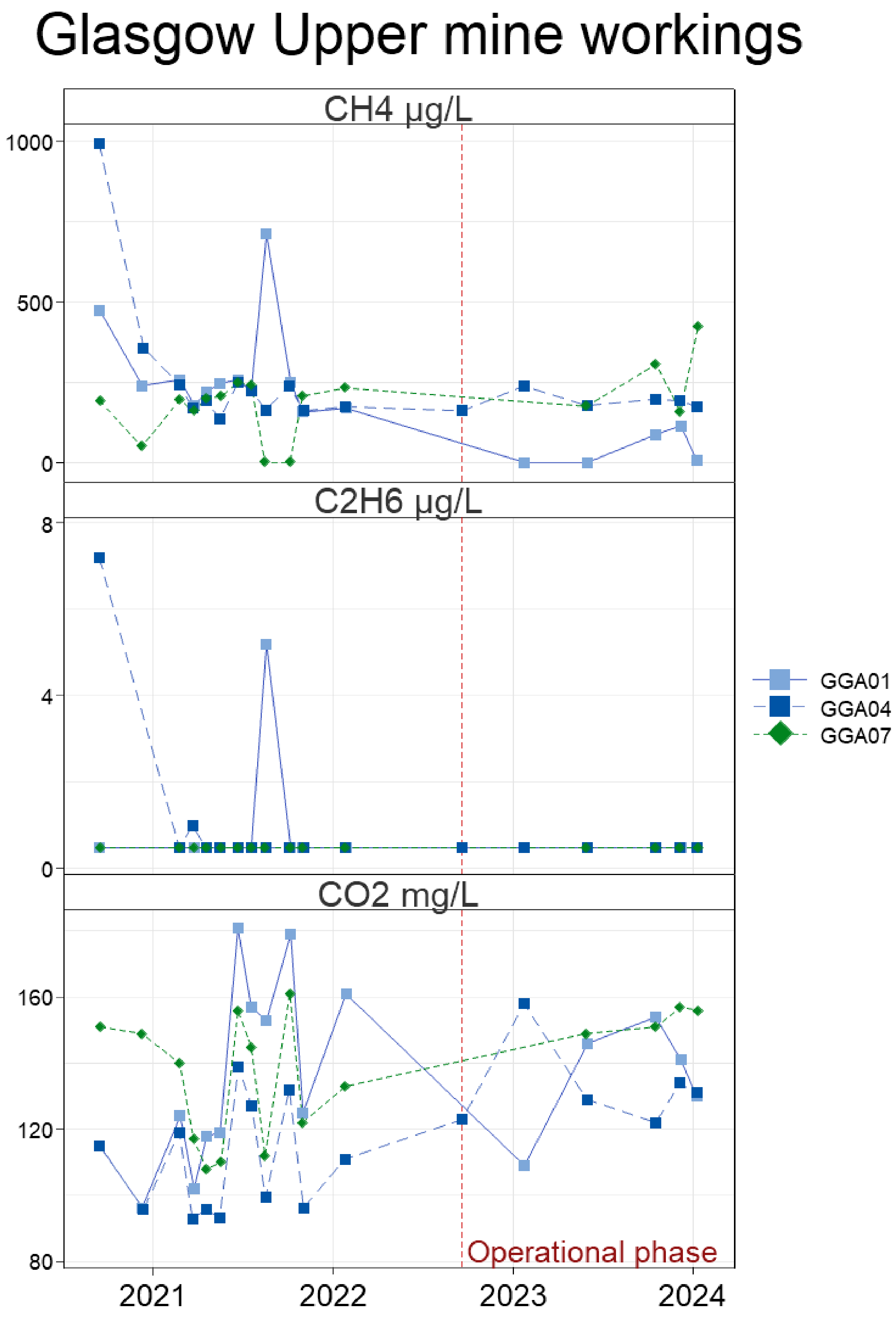
GLASGOW UPPER MINE WORKINGS MINOR ELEMENTS, TOTAL SULPHUR AND DISSOLVED ORGANIC CARBON

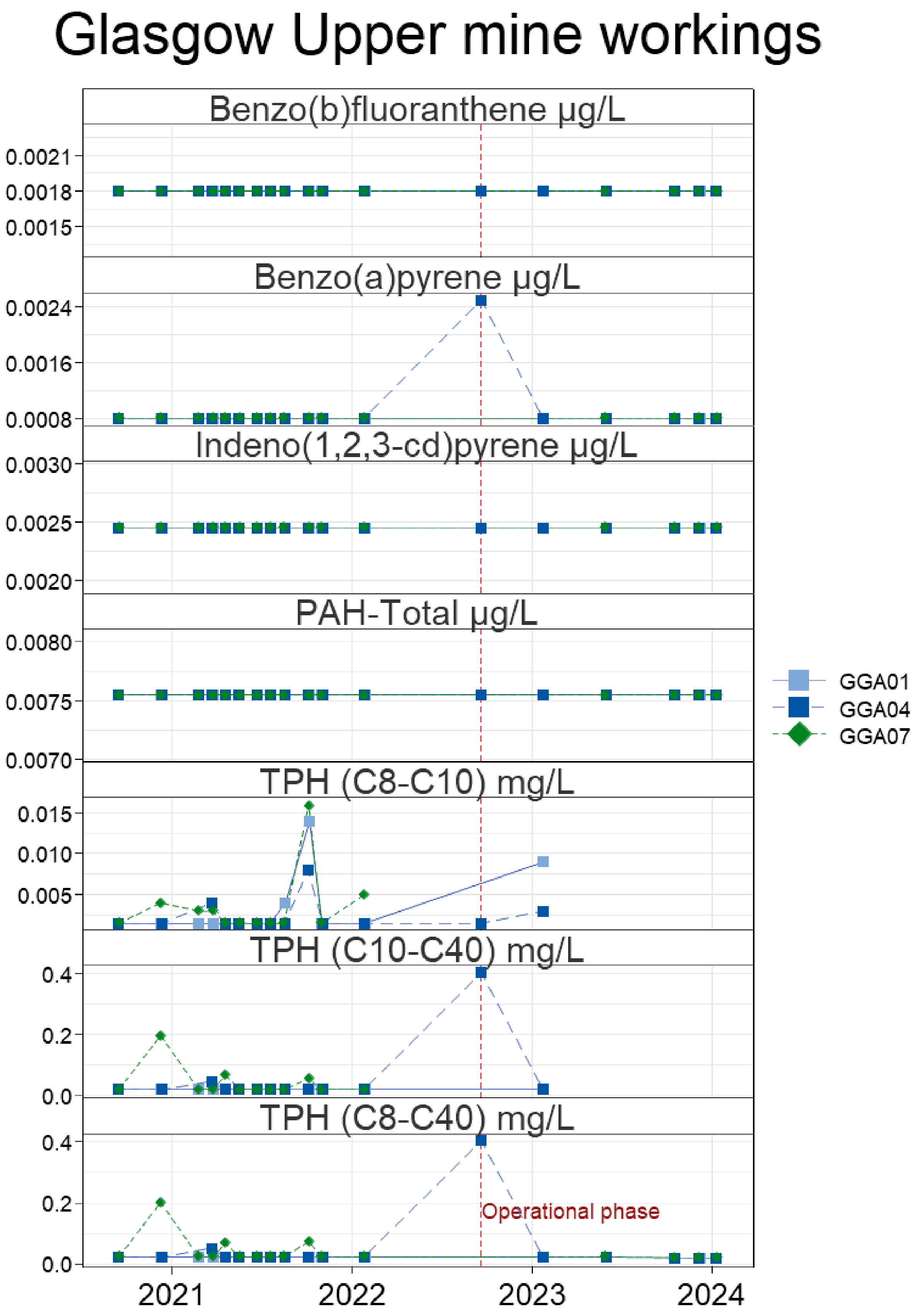



Glasgow Upper mine workings
Al µg/L
20
10
0
As µg/L
10
5
0
B µg/L
450
400
350
Ba µg/L
60
50
40
Cd µg/L
0.015
0.010
0.005
Co µg/L
10
5
0
Cr Total µg/L
0.3
0.2
0.1
Operational phase
2021
2022
2023
2024
GGA01
GGA04
GGA07

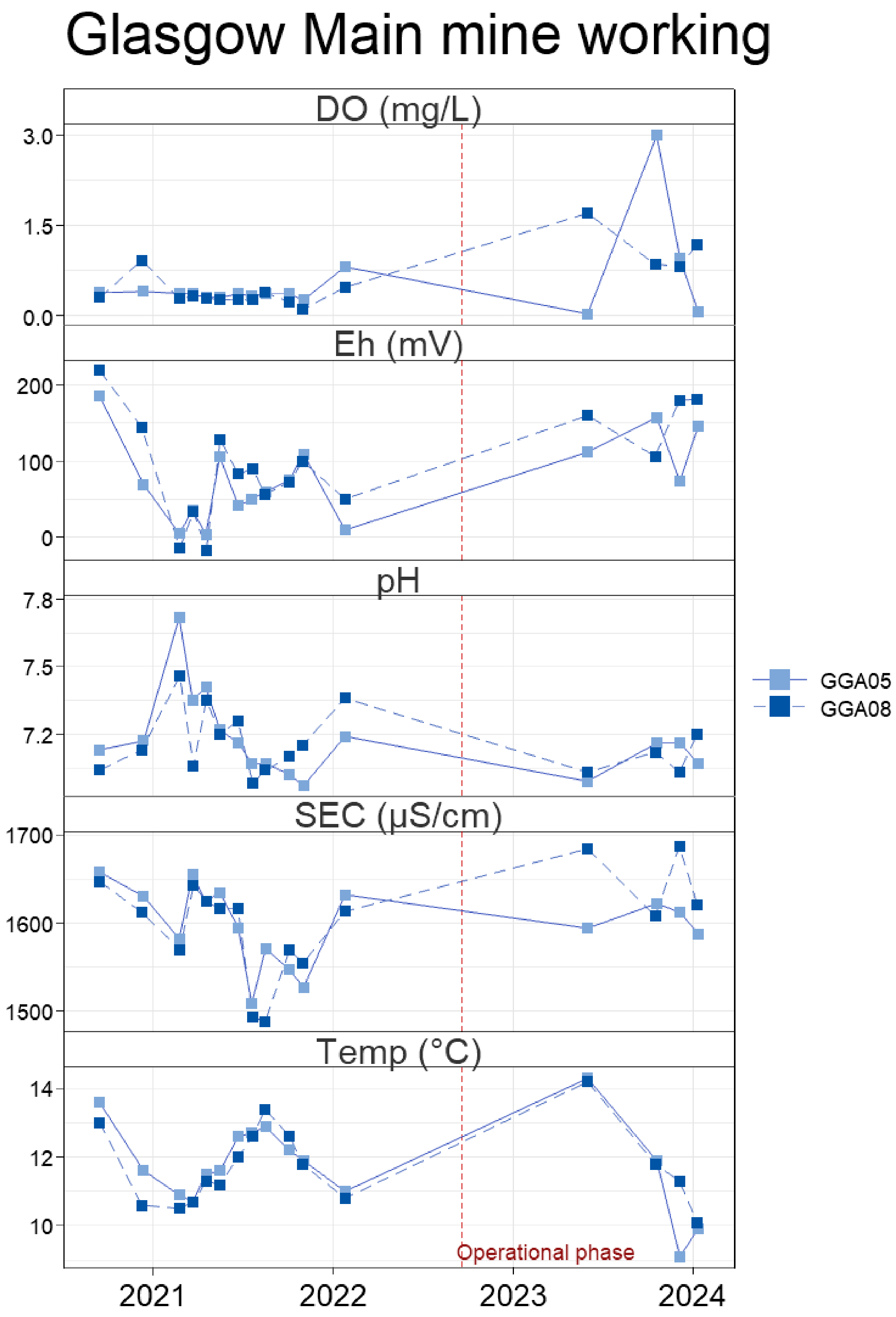

Glasgow Upper mine workings
Cu µg/L
1.6
0.8
0.0
Fe Total µg/L
40000
20000
0
La µg/L
0.16
0.08
0.00
Li µg/L
60
45
30
Mn µg/L
900
600
300
Ni µg/L
20
10
0
Pb µg/L
1.0
0.5
0.0
Operational phase
2021
2022
2023
2024
GGA01
GGA04
GGA07


Glasgow Upper mine workings
Rb µg/L
80
60
40
Sr µg/L
4000
3000
2000
U µg/L
1.5
1.0
0.5
V µg/L
0.4
0.2
0.0
Zn µg/L
20
10
0
δ18O VSMOW2 ‰
-7.36
-7.44
-7.52
δD VSMOW2 ‰
-49.5
-51.0
-52.5
δ13C PDB ‰
-12
-15
-18
Operational phase
2021
2022
2023
2024
GGA01
GGA04
GGA07

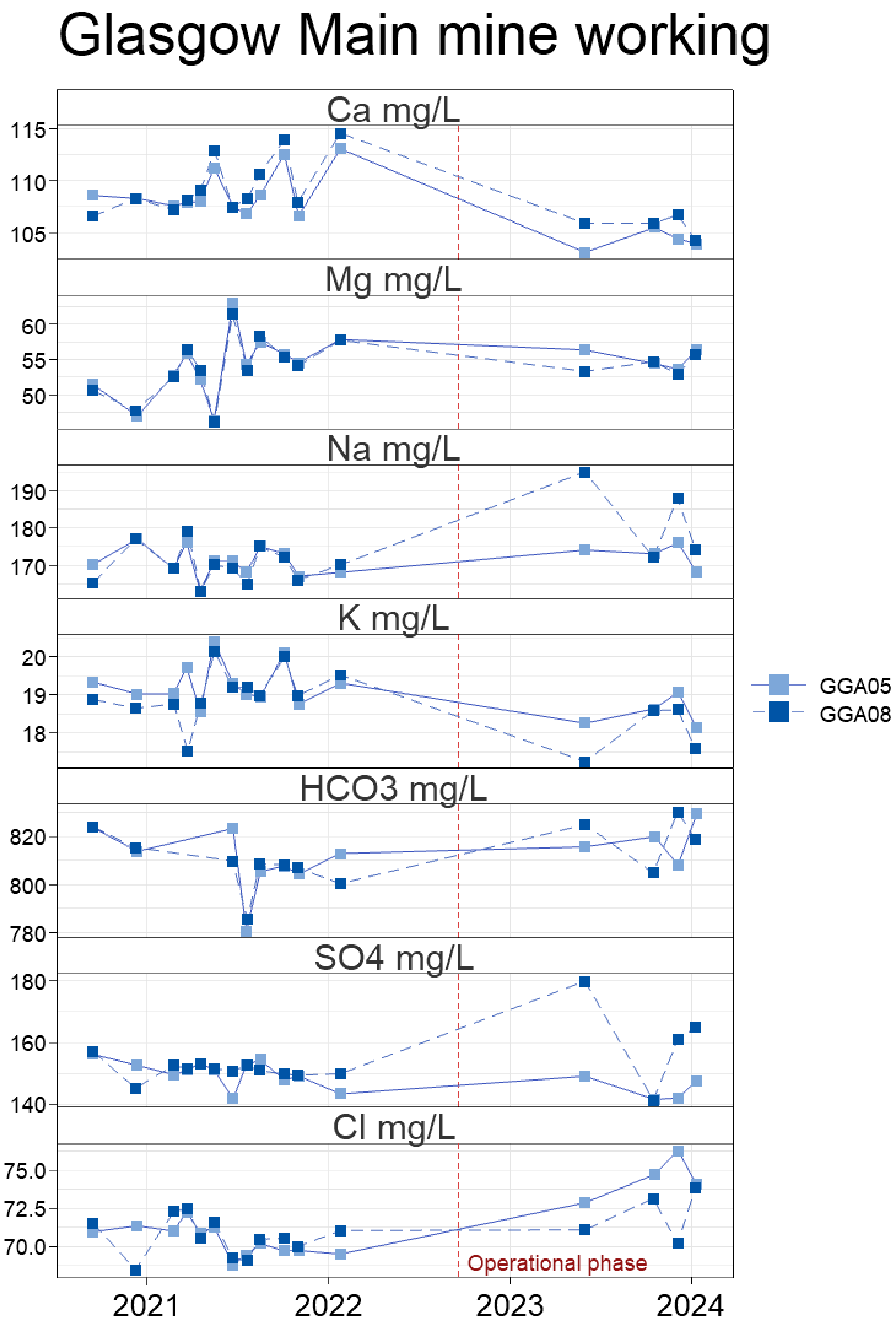

Glasgow Upper mine workings
CH4 µg/L
1000
500
0
C2H6 µg/L
8
4
0
CO2 mg/L
160
120
80
Operational phase
2021
2022
2023
2024
GGA01
GGA04
GGA07

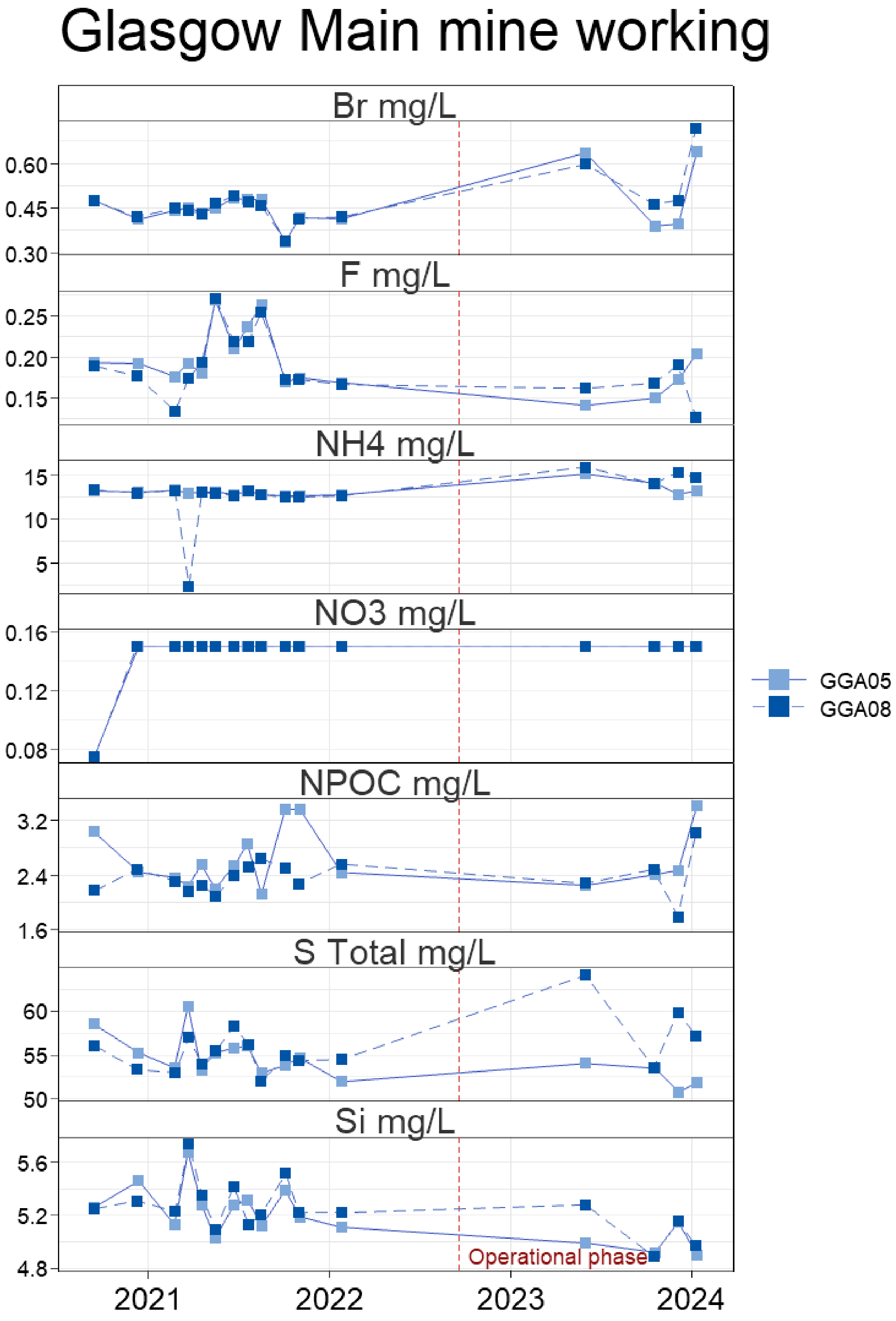

Glasgow Upper mine workings
Benzo(b)fluoranthene µg/L
0.0021
0.0018
0.0015
Benzo(a)pyrene µg/L
0.0024
0.0016
0.0008
Indeno(1,2,3-cd)pyrene µg/L
0.0030
0.0025
0.0020
PAH-Total µg/L
0.0080
0.0075
0.0070
TPH (C8-C10) mg/L
0.015
0.010
0.005
TPH (C10-C40) mg/L
0.4
0.2
0.0
TPH (C8-C40) mg/L
0.4
0.2
0.0
Operational phase
2021
2022
2023
2024
GGA01
GGA04
GGA07

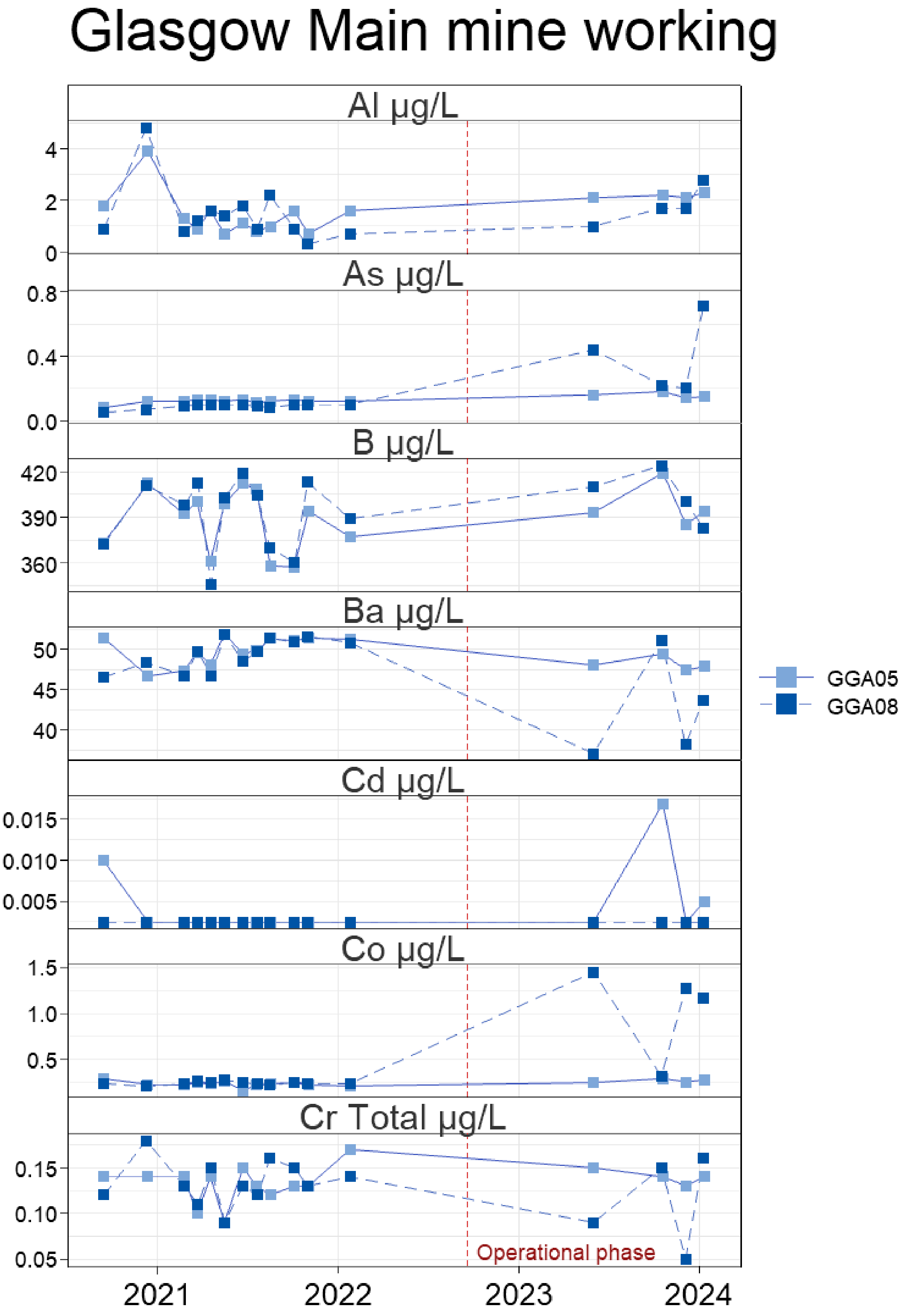
GLASGOW MAIN MINE WORKINGS FIELD PARAMETERS

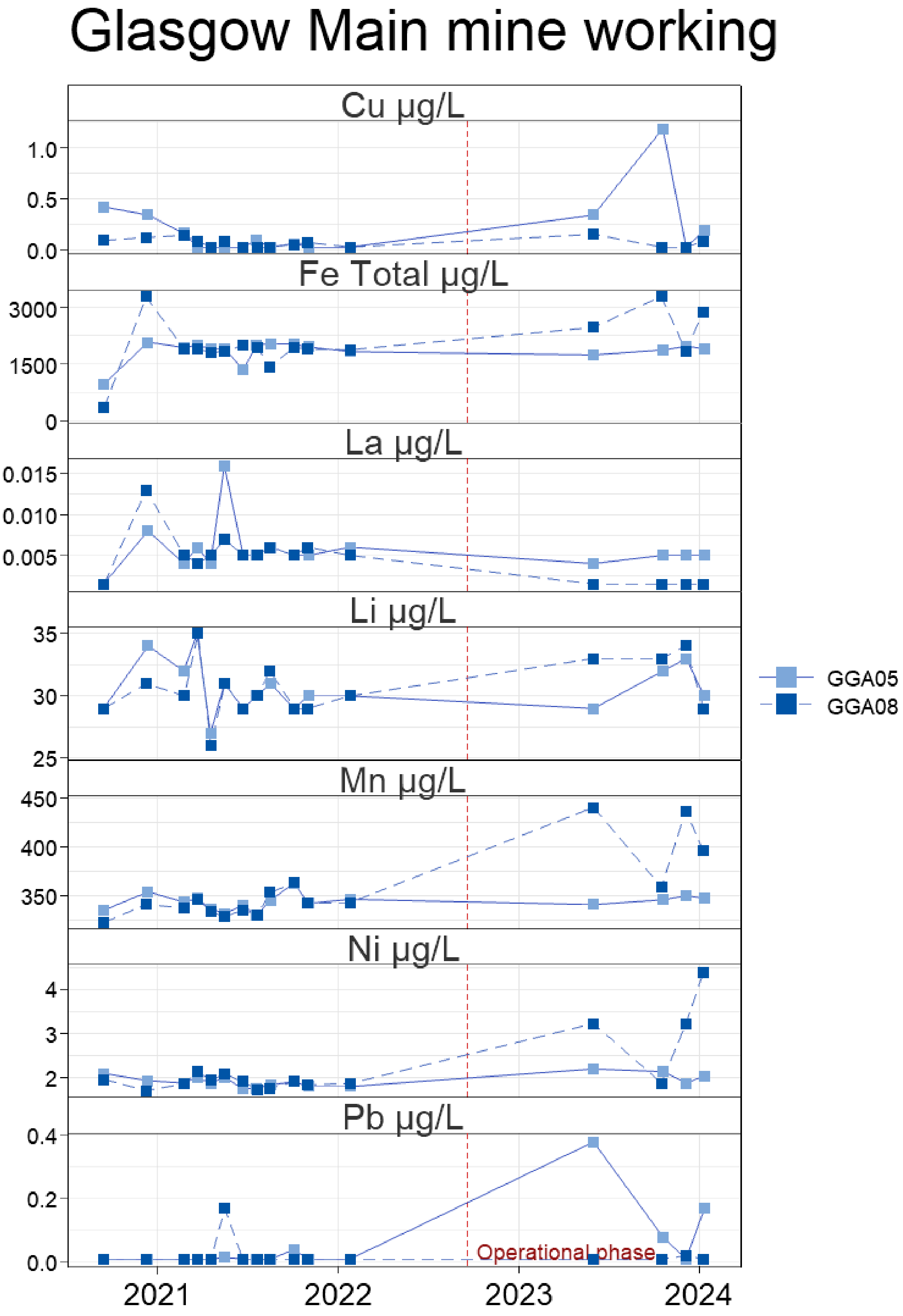


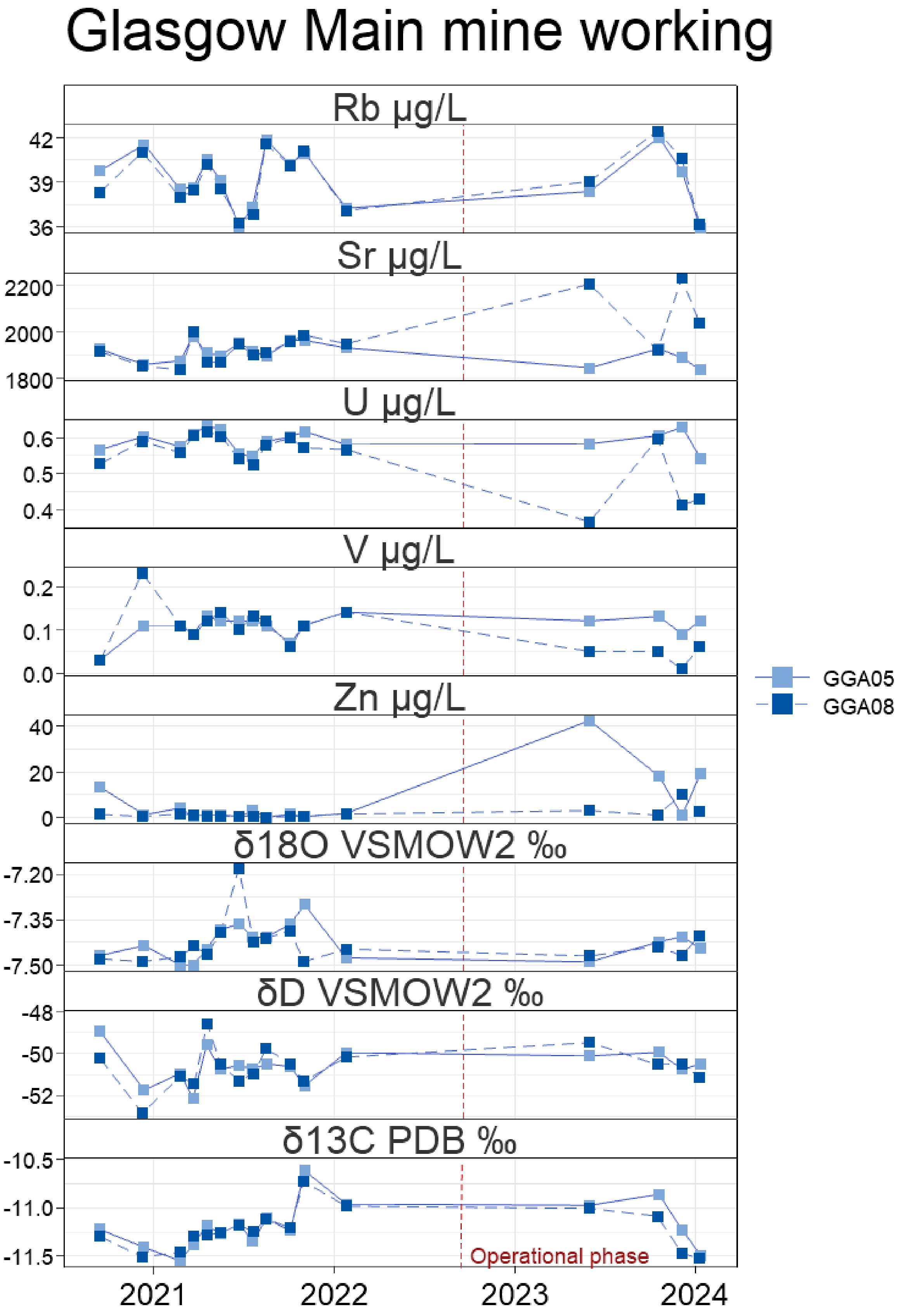
GLASGOW MAIN MINE WORKINGS MAJOR ELEMENTS

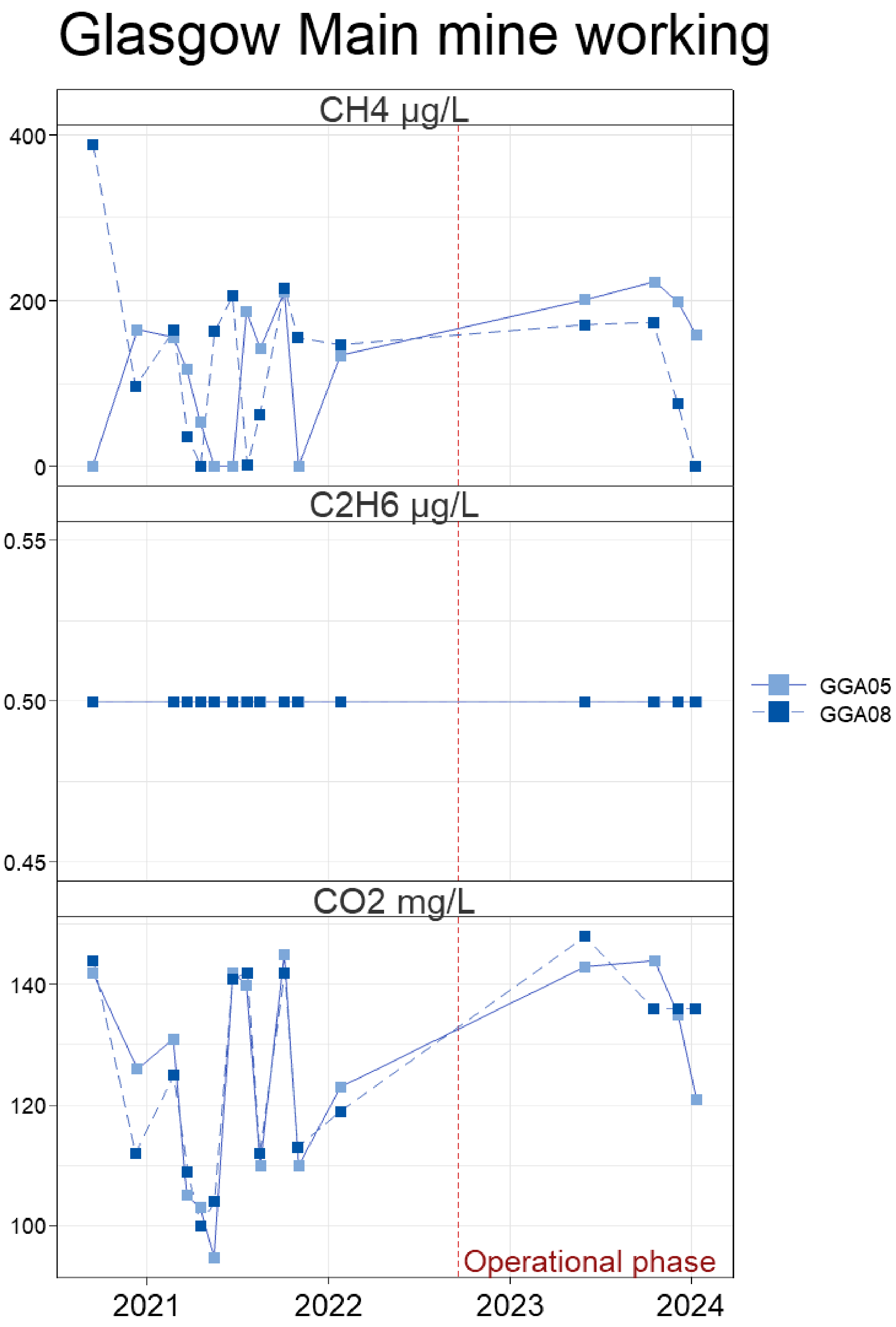



Glasgow Main mine working
Br mg/L
0.60
0.45
0.30
F mg/L
0.25
0.20
0.15
NH4 mg/L
15
10
5
NO3 mg/L
0.16
0.12
0.08
NPOC mg/L
3.2
2.4
1.6
S Total mg/L
60
55
50
Si mg/L
5.6
5.2
4.8
Operational phase
2021
2022
2023
2024
GGA05
GGA08

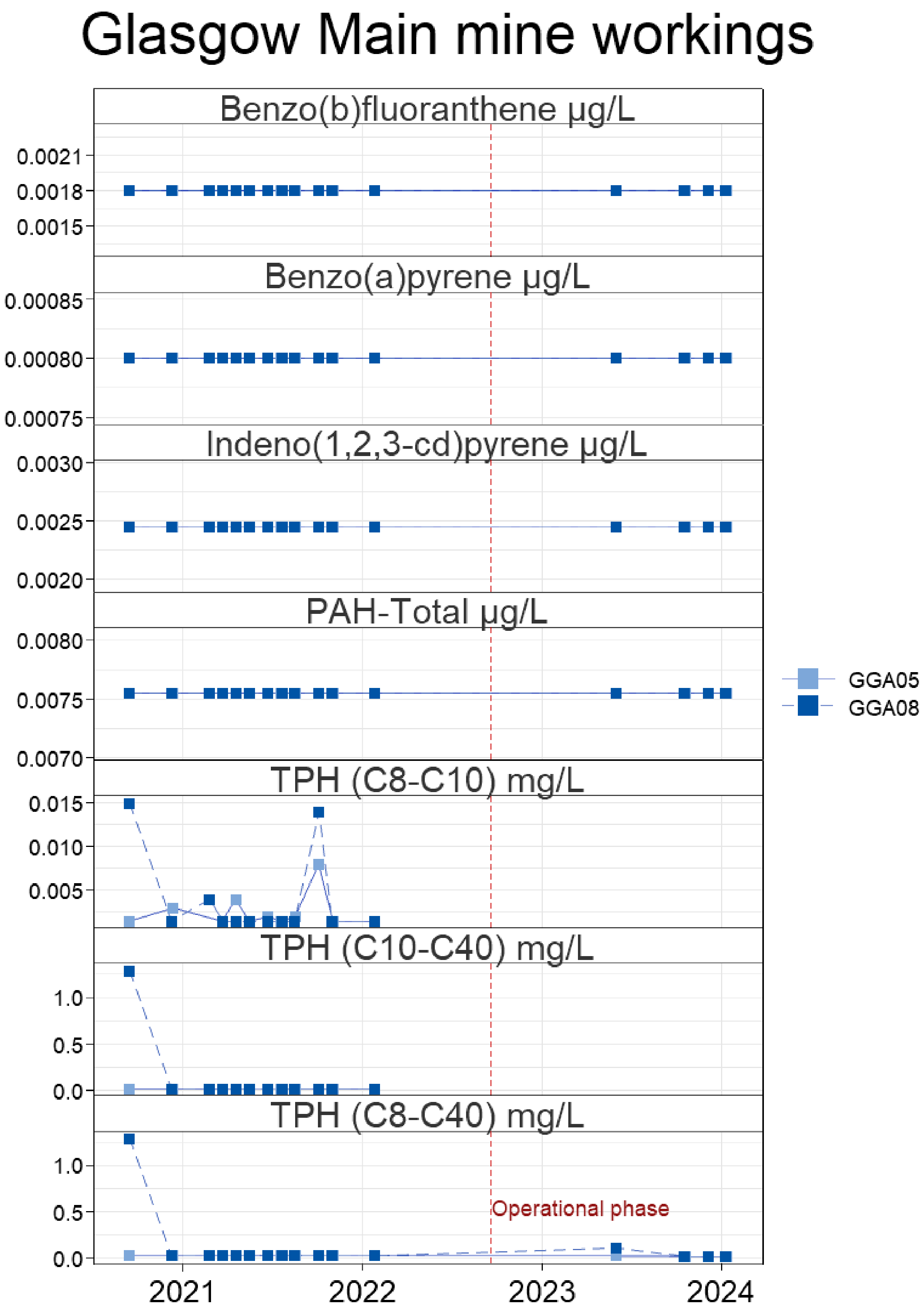

Glasgow Main mine working
Al µg/L
4
2
0
As µg/L
0.8
0.4
0.0
B µg/L
420
390
360
Ba µg/L
50
45
40
Cd µg/L
0.015
0.010
0.005
Co µg/L
1.5
1.0
0.5
Cr Total µg/L
0.15
0.10
0.05
Operational phase
2021
2022
2023
2024
GGA05
GGA08


Glasgow Main mine working
Cu µg/L
1.0
0.5
0.0
Fe Total µg/L
3000
1500
0
La µg/L
0.015
0.010
0.005
Li µg/L
35
30
25
Mn µg/L
450
400
350
Ni µg/L
4
3
2
Pb µg/L
0.4
0.2
0.0
Operational phase
2021
2022
2023
2024
GGA05
GGA08


Glasgow Main mine working
Rb µg/L
42
39
36
Sr µg/L
2200
2000
1800
U µg/L
0.6
0.5
0.4
V µg/L
0.2
0.1
0.0
Zn µg/L
40
20
0
δ18O VSMOW2 ‰
-7.20
-7.35
-7.50
δD VSMOW2 ‰
-48
-50
-52
δ13C PDB ‰
-10.5
-11.0
-11.5
Operational phase
2021
2022
2023
2024
GGA05
GGA08


Glasgow Main mine working
CH4 µg/L
400
200
0
C2H6 µg/L
0.55
0.50
0.45
CO2 mg/L
140
120
100
Operational phase
2021
2022
2023
2024
GGA05
GGA08

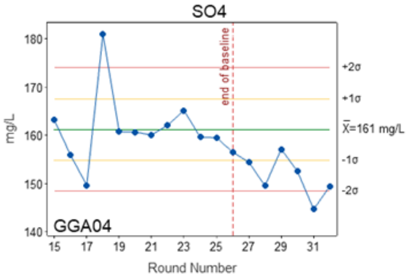
GLASGOW MAIN MINE WORKINGS PAH AND TPH

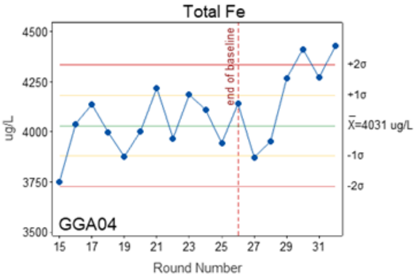


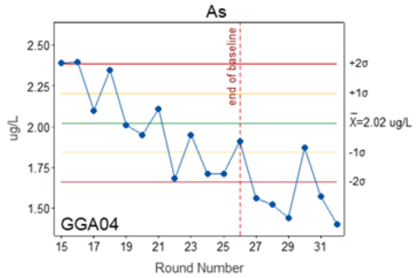
Appendix 3 Control charts

The graphs include data from the outset of groundwater monitoring activities in September 2020/sampling round 15 (prior to round 15 only surface water samples were collected). The graphs display reference lines at ±1 and ±2 standard deviations (σ) above and below the centre line representing the average of the baseline data (x̄) (September 2020/round 15 – January 2022/round 26). These baseline lines extend in the graph through the operational phase (from September 2022/round 27 to January 2024/round 32), as reference; by analysing the variations and mean and comparing the baseline and the operational monitoring phase, possible changes can be inferred.

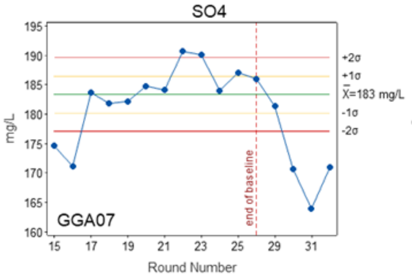
GLASGOW UPPER MINE WORKING GGA04

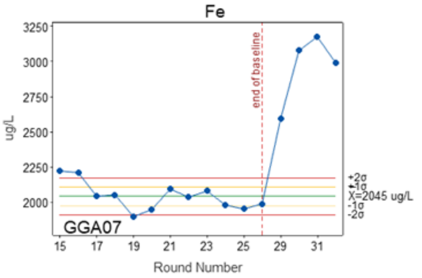


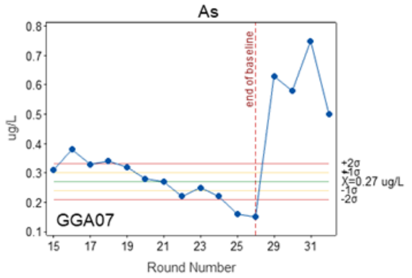




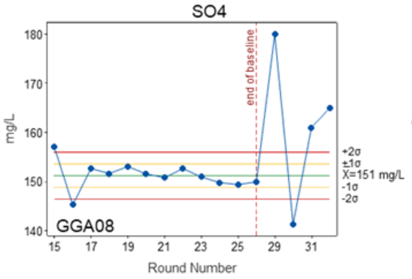
GLASGOW UPPER MINE WORKING GGA07

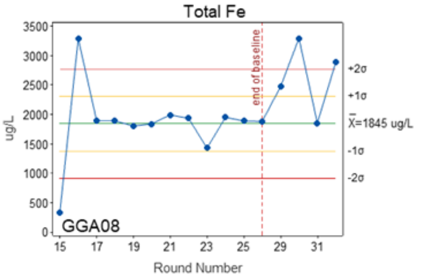


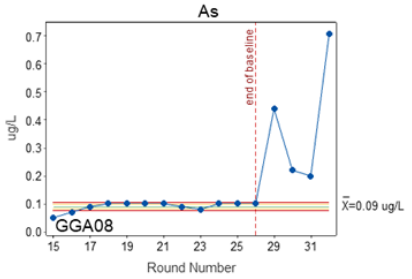




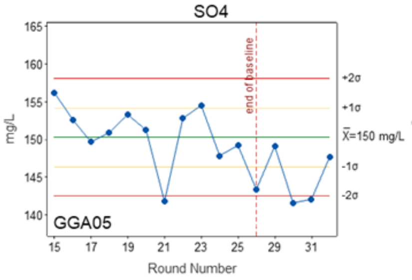
GLASGOW MAIN MINE WORKING GGA08

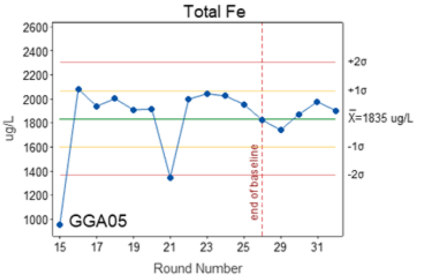


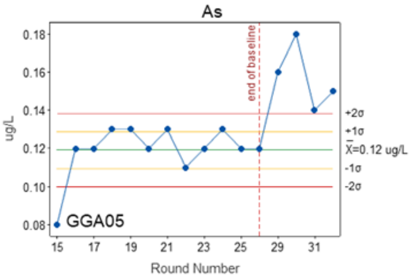




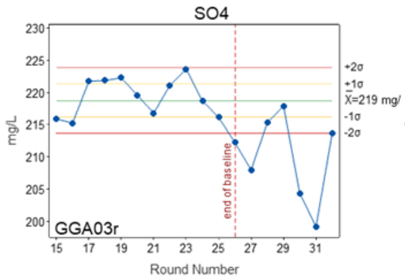
GLASGOW MAIN MINE WORKING GGA05

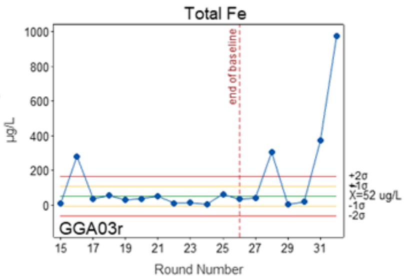


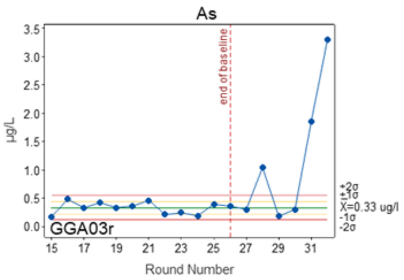




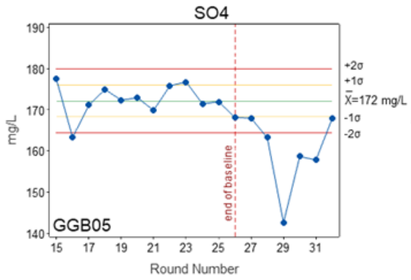
BEDROCK GGA03R

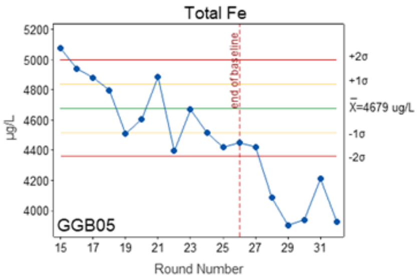


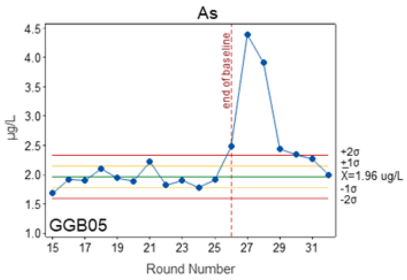




BEDROCK GGB05







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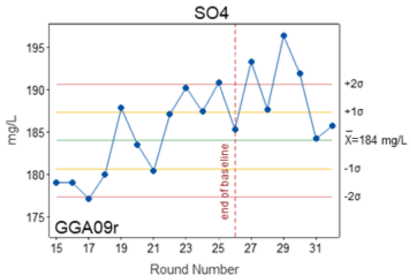

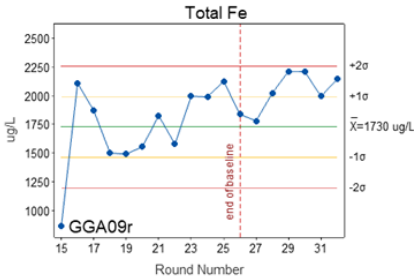

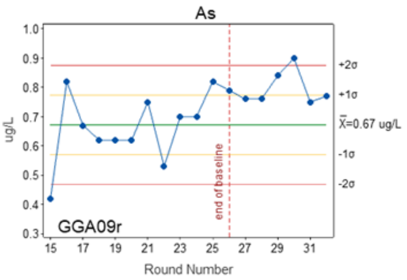

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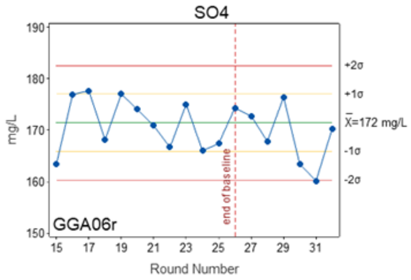

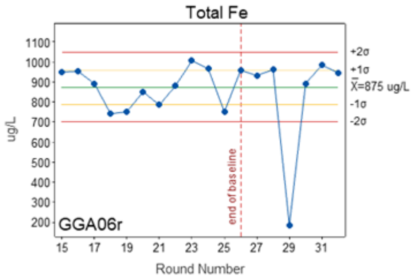

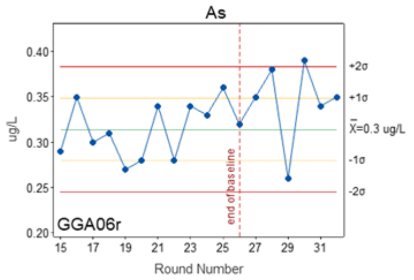

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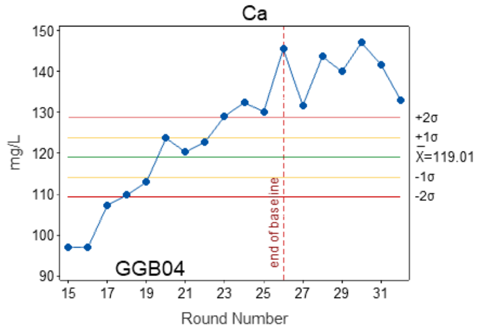

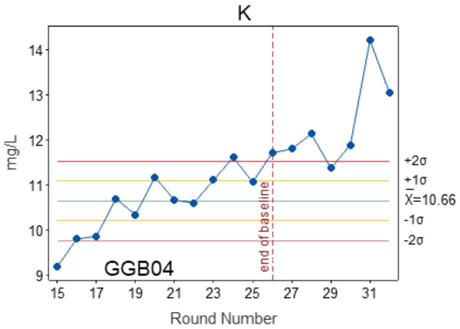

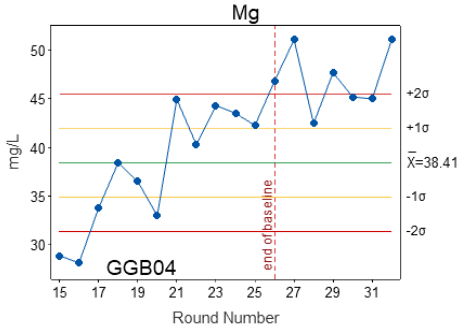

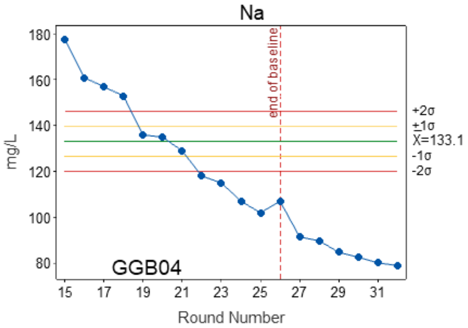

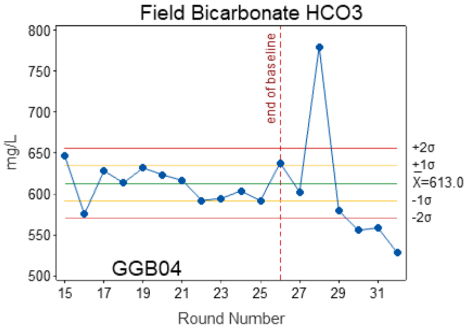

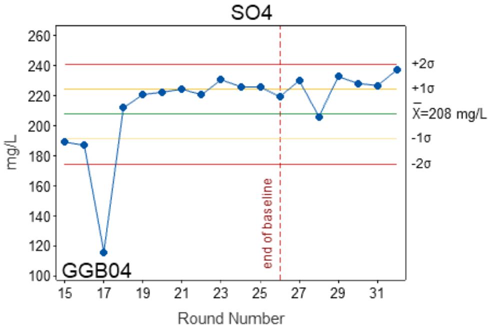

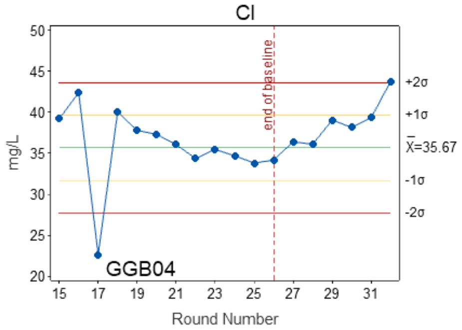

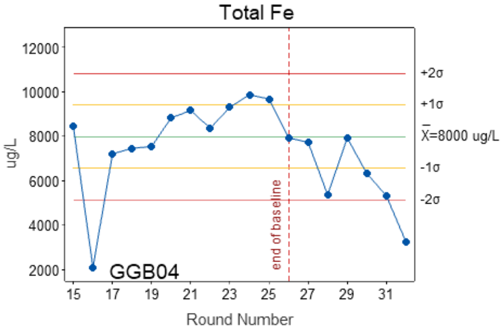

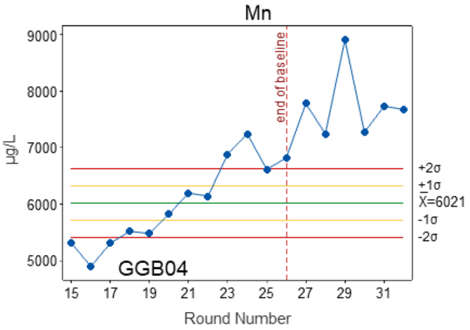

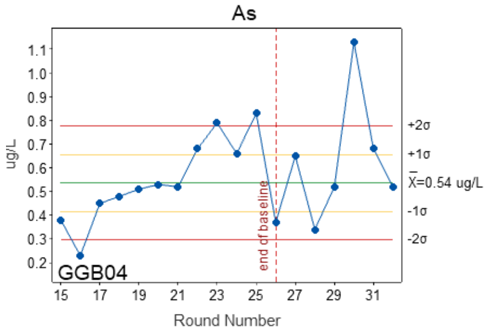

References

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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*, OR/23/029 (Nottingham, UK).

BEARCOCK, J M, WALKER-VERKUIL, K, MULCAHY, A, PALUMBO-ROE, B, MACALLISTER, D J, GOODDY, D C, AND DARLING, W G. 2022. UK Geoenergy Observatories : Glasgow baseline groundwater and surface water chemistry dataset release September 2020 - May 2021. *British Geological Survey*, OR/22/038 (Nottingham, UK).

CRAIG, H. 1961. Isotopic variations in meteoric waters. *Science*, Vol. 133, 1702-1703.

DREVER, J I. 1997. *The Geochemistry of Natural Waters (third edition).* (New Jersey, USA: Prentice Hall.)

FORDYCE, F M, SHORTER, K M, WALKER-VERKUIL, K, BARLOW, T, SLOANE, H, ARROWSMITH, C, HAMILTON, E M, EVERETT, P A, AND BEARCOCK, J M. 2021. UK Geoenergy Observatories, Glasgow Environmental Baseline Surface Water Chemistry Dataset 1. *British Geological Survey*, OR/20/061 (Edinburgh, UK).

JOHNSON C. 2005. 2005 G-BASE Field Procedures Manual*. British Geological Survey Internal Report,* IR/05/097. http://nora.nerc.ac.uk/id/eprint/5190/

MONAGHAN, A A, BARRON, H F, STARCHER, V, SHORTER, K M, AND WALKER-VERKUIL, K. 2020. Mine water characterisation and monitoring borehole GGA01, UK Geoenergy Observatory, Glasgow. *British Geological Survey*, OR/20/21 (Keyworth, Nottingham).

MONAGHAN, A A, STARCHER, V, BARRON, H F, SHORTER, K, WALKER-VERKUIL, K, ELSOME, J, KEARSEY, T, ARKLEY, S, HANNIS, S, AND CALLAGHAN, E. 2022. Drilling into mines for heat: geological synthesis of the UK Geoenergy Observatory in Glasgow and implications for mine water heat resources. *Quarterly Journal of Engineering Geology and Hydrogeology*, 55 (1): qjegh2021-033.

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

PARKHURST, D L, AND APPELO, C A J. 1999. User's guide to PHREEQC (Version 2)—A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. *U.S. Geological Survey*, U.S. Geological Survey WaterResources Investigations Report 99-4259. .

PIPER, A M. 1944. A graphic procedure in the geochemical interpretation of water analyses. *Eos, Transactions American Geophysical Union*, Vol. 26, 914-928.

POLIKANE, S, KELLY, M G, HERRERO, F S, PITT, J-A, JARVIE, H P, CLAUSSEN, U, LUEUJAK, W, SOLHEIM, A L, TEIXEIRA, H, AND PHILLIPS, G. 2019. Nutrient criteria for surface waters under the European Water Framework Directive: Current state-of-the-art, challenges and future outlook. *Science of the Total Environment*, Vol. 695, 133888.

RYVES D B, LENG M J, BARKER P A, SNELLING A M, SLOANE H J, ARROWSMITH C, TYLER J J, SCOTT D R, RADBOURNE A D, ANDERSON N J. 2020. Understanding the transfer of contemporary temperature signals into lake sediments via paired oxygen isotope ratios in carbonates and diatom silica: problems and potential. *Chemical Geology*, 552, 119705.

SEPA. 2014a. Position Statement (WAT-PS-10-01) :Assigning Groundwater Assessment Criteria for Pollutant Inputs. *Scottish Environment Protection Agency* (Stirling).

SEPA. 2014b. The Scotland River Basin District (Standards) Directions 2014. *Scottish Environment Protection Agency* (Stirling).

SEPA. 2020a. Environmental Quality Standards and Standards for Discharges to Surface Waters. Supporting Guidance (WAT-SG-53). *Scottish Environment Protection Agency* (Stirling).

SEPA. 2020b. Water Classification Hub. [cited 29/3/22]. https://www.sepa.org.uk/data-visualisation/water-classification-hub/

SHAND, P, EDMUNDS, W M, LAWRENCE, A R, SMEDLEY , P L, AND BURKE, S. 2007. The natural (baseline) quality of groundwater in England and Wales. *Environment Agency & British Geological Survey*, NC/99/74/24 & RR/07/06.

SHORTER, K M, PALUMBO-ROE, B, FORDYCE, F M, Ó DOCHARTAIGH, B E, WALKER-VERKUIL, K, 2021 UK Geoenergy Observatories Glasgow : groundwater chemistry data collected during the borehole construction phase. Edinburgh, UK, *British Geological Survey,* OR/21/015 (Edinburgh, UK).

UKTAG. 2013. Updated Recommendations on Phosphorus Standards for Rivers (2015 – 2025). *UK Technical Advisory Group on the Water Framework Directive* (London).