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UK Geoenergy Observatories, Glasgow Environmental Baseline Surface Water Chemistry Dataset 1

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Open Report OR/20/061



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UK GEOENERGY OBSERVATORIES PROGRAMME

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UK Geoenergy Observatories, Glasgow Environmental Baseline Surface Water Chemistry Dataset 1

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Summary

The United Kingdom Geoenergy Observatory (UKGEOS) in Glasgow comprises 12 environmental baseline/mine water characterisation and seismic monitoring boreholes drilled into the superficial deposits and bedrock in Dalmarnock in the east of Glasgow City and the Cuningar Loop area of Rutherglen, South Lanarkshire. The aims of the Observatory include de-risking key technical barriers to low-temperature shallow mine water heat energy and heat storage from groundwater in former coal mine workings; and providing environmental characterisation and monitoring to assess any change in ambient conditions.

Prior to and during borehole construction and testing, monitoring of the chemical quality of surface water was carried out to aid understanding of the hydrological/hydrogeological system in the area and to determine the pre-operational environmental baseline, against which future change can be assessed.

Surface water chemistry is temporally variable and changes over short timescales in response to factors such as season, weather, precipitation and anthropogenic inputs. For this reason, it was necessary to carry out chemical monitoring for at least a year to capture seasonal and temporal trends.

This report provides information on the sampling and analytical methods and summary statistics for the environmental baseline surface water chemistry dataset collected at the Glasgow Observatory between February 2019-March 2020. Preliminary discussions of the spatial and temporal trends evident in the dataset are presented, based on visual inspection of the data distributions and time-series plots. Detailed investigations into the factors controlling surface water chemistry and statistical assessments of these relationships are beyond the scope of this initial data release. The report accompanies the release of the UKGEOS Glasgow Surface Water Chemistry Dataset 1.

Monthly surface water sampling was carried out at six sampling locations in the area. These comprised five on the River Clyde, which borders the Glasgow Observatory, and one on the Tollcross Burn, which is the only smaller surface water stream in the area. On the River Clyde, three samples were collected proximal to the Observatory at the Cuningar Loop and two control samples were taken at approximately 1.5 km upstream and 2 km downstream. At each location the following samples splits were collected:

- FA – filtered acidified sample for inorganic cation chemical analysis
- FUA – filtered unacidified sample for inorganic anion analysis
- CrVI – filtered unacidified sample for chromium (CrVI) speciation analysis
- NPOC – filtered sample for non-purgeable organic carbon analysis
- TPH – unfiltered sample for total petroleum hydrocarbon analysis
- PAH – unfiltered sample for polycyclic aromatic hydrocarbon analysis
- $\delta^{13}\text{C}$ – unfiltered sample for stable carbon isotope analysis
- $\delta^{18}\text{O}/\delta^2\text{H}$ – unfiltered sample for deuterium and stable oxygen isotope analysis

This resulted in a set of 98 samples (84 samples and 14 field duplicates) collected over 14 months (February 2019 – March 2020) that underwent chemical analysis to determine the concentration of 71 inorganic parameters and 10 organic substances. In addition, surface water pH, conductivity (SEC), redox potential (Eh), dissolved oxygen (DO), temperature and alkalinity (as field bicarbonate (HCO_3)) were measured at each sampling location.

The resultant chemical data are made available in the baseline UKGEOS Glasgow Surface Water Chemistry 1 dataset along with descriptive information about the waters, such as location, land use, weather conditions and presence of any contaminant material. The data are presented in Excel® table format in the file:

Filename: UKGEOSGlasgow_SurfaceWaterChemData1_Release.xlsx

Any use of the data should be cited to:

British Geological Survey (2021). UKGEOS Glasgow Surface Water Chemistry Dataset1 Release (2019 – 2020). DOI: 10.5285/b65716f4-4f4c-4070-8539-b796c4bf8796

and

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The UKGEOS monitoring programme determined the spatial and temporal variability of surface water chemistry under various seasonal conditions.

The chemical data show that the UKGEOS surface waters are primarily calcium-bicarbonate (Ca-HCO₃) dominated and range from circum-neutral to alkaline pH (7.44 – 8.23). This is as expected, given the calcareous nature of the underlying geological parent materials and presence of anthropogenic carbonate-rich materials, such as building rubble, in the urban environment of Glasgow and Rutherglen.

Stable isotope data indicate that the surface waters are of recent origin. The $\delta^{13}\text{C}$ values are typical for surface waters ($\delta^{13}\text{C}$ -10.5 to -25.6 ‰). The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ data are within ranges reported previously for surface waters in the west of Scotland ($\delta^2\text{H}$ -66.9 to -39.3 ‰; $\delta^{18}\text{O}$ -9.5 to -6.6 ‰). The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ data plot slightly above the global meteoric water line (GMWL), but this is likely because waters in the west of Scotland are known to be more enriched, especially in $\delta^2\text{H}$, as a result of the predominance of moist-Atlantic weather fronts and higher rainfall. There is some evidence of seasonal control on the isotopic signatures, with marginally more enriched $\delta^2\text{H}$ (> -47 ‰) and $\delta^{18}\text{O}$ (> -7.5 ‰) values reported in the summer months (June – September 2019). Heavy rainfall events, such as in February 2020, are characterised by more depleted values, indicating the greater influence of rainwater/runoff on surface water chemistry (Tollcross Burn $\delta^2\text{H}$ -66.9 and $\delta^{18}\text{O}$ -9.5 ‰; River Clyde SW06 $\delta^2\text{H}$ -53.7 and $\delta^{18}\text{O}$ -8.3 ‰).

Based on visual inspection of the data distributions (minimum, maximum, median) at each sampling location and in time-series plots, the majority of parameters determined in the UKGEOS surface water dataset demonstrate similarities in ranges and temporal behaviour at each of the sampling locations on the River Clyde. Hence, the results for the River Clyde samples are discussed as a group, except where deviations from these general trends are noted at individual sampling locations.

The dissolved organic carbon (DOC, as NPOC) concentrations in the River Clyde waters range from 3.0 to 17.3 mg/L. They are higher between July and November 2019, peaking in August, than during the rest of the year. This likely reflects greater quantities of organic matter in runoff during the vegetation growing season and leaf fall in the autumn. By contrast, the Tollcross Burn waters show little seasonal variation in DOC content (2.5 – 4.4 mg/L) for most of the year, but a marked spike in values (6.9 mg/L) corresponds to heavy rainfall in February 2020, that may indicate cross-contamination from the sewerage-storm drain system.

Minimum water temperatures in the River Clyde were recorded in winter and maximum values in summer months (3.6 and 21.9 °C) and in the Tollcross Burn (5.8 and 16.8 °C) as expected. By contrast, concentrations of DO are lower in summer and higher in winter in the River Clyde (6.1 – 13.2 mg/L) and Tollcross Burn (6.3 – 10.1 mg/L), as DO solubility increases in colder waters. The Eh values of 301 – 523 mV in the River Clyde and 279 – 512 mV in the Tollcross Burn indicate that the waters are generally oxic, with marginally higher values during winter, reflecting the greater DO content of cooler waters.

Specific electrical conductance values reported in the Tollcross Burn waters are generally higher (442 – 1026 $\mu\text{S}/\text{cm}$) than those in the River Clyde (174 – 532 $\mu\text{S}/\text{cm}$) demonstrating that the Tollcross Burn has a higher total dissolved solid content, and is chemically distinct from the River

Clyde. This is to be expected as the Tollcross Burn is a small partially culverted urban stream. The results suggest that the River Clyde waters are low-salinity freshwaters, whereas the Tollcross Burn waters are slightly saline.

Concentrations of the major ions in the River Clyde samples are within the following ranges:

- Calcium (Ca 13 – 46 mg/L), magnesium (Mg 3 – 14 mg/L), sodium (Na 13 – 30 mg/L) and potassium (K 2.0 – 5.9 mg/L)
- Field-HCO₃ (40 – 153 mg/L), chloride (Cl 16 – 40 mg/L) and sulphate (SO₄ 9 – 43 mg/L)

Major ion concentrations were higher in the River Clyde during periods of lower rainfall (April – June 2019), when baseflow was likely more dominant. Several trace elements show similar temporal behaviour in the River Clyde including arsenic (As), antimony (Sb), barium (Ba), caesium (Cs), cobalt (Co), rubidium (Rb), strontium (Sr) selenium (Se), tin (Sn) and uranium (U).

Total phosphorus (P-Total 0.037 – 0.220 mg/L), orthophosphate (HPO₄ <0.03 – 0.50 mg/L) and nitrate (NO₃ 2.8 – 14.9 mg/L) also follow this pattern, but with more variation in the concentrations recorded at each of the River Clyde sampling locations. This may partly reflect phosphate and nitrate fertiliser inputs in the catchment during the growing season.

By contrast, lower concentrations of silicon (Si < 1 mg/L), aluminium (Al < 30 µg/L) and iron (Fe < 180 µg/L) are reported in the River Clyde during either of April and May 2019, likely reflecting lower weathering inputs during this drier period. Lead (Pb), titanium (Ti), zirconium (Zr) and the lanthanide-series elements show a similar temporal trend.

Concentrations of PAH indicator compounds (< 0.0005 – 0.035 µg/L), PAH-Total (<0.005 – 0.104 µg/L) and TPH (C8 – 40) (<0.045 – 0.866 mg/L) are broadly lower in April and May 2019 than in the rest of the year also.

Whilst the majority of parameters show broadly overlapping ranges in concentration between the different sampling locations on the River Clyde, there are some exceptions. Cobalt, Fe and manganese (Mn) concentrations, which range between 0.14 – 0.34 µg/L; 31 – 748 µg/L and 20 – 201 µg/L respectively, are generally higher in waters collected from SW03 than the other River Clyde locations for the majority of months of the year. Boron concentrations are higher (58 µg/L) at SW03 in April 2019 also. Conversely, field-HCO₃ contents at SW03 in May 2019 are lower (84 mg/L) than at the other river water sample locations. The river is shallower at SW03 and these variances may reflect greater influence of local bank seepage at this location.

Aluminium, Ti, Sb, Zr and zinc (Zn) concentrations at both or either of SW06 and SW10 are higher than those reported at the other River Clyde sampling locations in February 2020 during heavy rainfall that month. Polycyclic aromatic hydrocarbon concentrations are elevated at these locations during the same weather event, which may indicate increased contaminant mobilisation under the wetter conditions.

Total chromium (Cr-Total), trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)) concentrations are notably higher in SW10 waters than at the rest of the River Clyde sampling locations. This sampling location is proximal to the Shawfield Business Park, where Cr-contamination of soil, groundwater and surface water with Cr(VI) from the former JJ Whites chromite ore processing works has been documented. The concentrations of Cr(VI) reported at SW10 (0.45 – 7.4 µg/L) are comparable to results in previous studies of the River Clyde at Shawfield (<0.05 – 10 µg/L). The elevated Cr-Total, Cr(VI) and Cr(III) concentrations in the River Clyde reported in the current study may reflect shallow groundwater – surface water interactions, as this is a known issue at the site, which is the subject of extensive remediation.

There is no evidence in the UKGEOS dataset of elevated Cr(VI) concentrations at any of the other sampling locations on the River Clyde or the Tollcross Burn.

To place the results of the present study in the wider context, comparisons were made between the UKGEOS surface waters and existing BGS surface water chemistry datasets collected from the River Clyde and urban streams within the Glasgow area in 2002 and 2003. These reveal that for the majority of parameters, the concentrations recorded in current study are within or similar to the ranges reported previously.

Regulatory authorities class the River Clyde in Glasgow as a highly modified water body with moderate rather than good ecological status. Initial comparisons here with the good river environmental quality standard (EQS) annual average (AA) and maximum allowable concentrations (MAC) show that the majority of parameters are within these limits with the following exceptions, which indicate the influence of the urban environment on surface water chemistry:

- Mean HPO_4 concentrations in the River Clyde waters of 0.19 mg/L versus the AA guideline of 0.069 mg/L.
- Mean HPO_4 concentrations in the Tollcross Burn of 0.08 mg/L versus the AA guideline of 0.069 mg/L.
- Mean NO_3 concentrations in the River Clyde and Tollcross Burn are 7.5 mg/L and 6.4 mg/L respectively, versus the EU AA guideline of 5.7 mg/L (there is no UK standard for NO_3 in surface water).
- The mean Al content in the River Clyde waters is 48 $\mu\text{g/L}$ versus the AA guideline of 15 $\mu\text{g/L}$ for good river status, and is greater than the MAC of 25 $\mu\text{g/L}$ at all the River Clyde sampling locations, except during the drier period between April and June 2019 and at SW06 and SW10 in February 2019.
- Mean Cu concentrations are 1.26 $\mu\text{g/L}$ in the River Clyde and 1.27 $\mu\text{g/L}$ in the Tollcross Burn versus the AA guideline of 1 $\mu\text{g/L}$ for Tier 1 risk assessment.
- Mean benzo(ghi)perylene and indeno(1,2,3-cd)pyrene contents in the River Clyde are 0.003 $\mu\text{g/L}$ and 0.004 $\mu\text{g/L}$ respectively versus the AA guideline of 0.002 $\mu\text{g/L}$ for these compounds. In the Tollcross Burn, mean concentrations are 0.010 $\mu\text{g/L}$ and 0.015 $\mu\text{g/L}$ respectively.
- Peak benzo(a)pyrene concentrations just above the MAC of 0.1 $\mu\text{g/L}$ are reported in the Tollcross Burn (0.106 $\mu\text{g/L}$) during heavy rainfall in 2020.

These results are to be expected in a city like Glasgow, where increased weathering in the urban environment, cross-contamination from the sewerage network and pollution of soil, shallow groundwater and urban runoff likely contribute to the loading of these substances into surface water bodies.

It is not anticipated that the operation of the Glasgow Observatory will cause any substantial change to surface water chemistry in the River Clyde or Tollcross Burn. To help check for this, the initial phase of surface water monitoring presented here has established a pre-operational baseline surface water chemistry dataset over a 14-month period.

The results reveal that the water chemistry of the River Clyde and Tollcross Burn in proximity to the Observatory displays significant temporal variability, related to seasonal/climatic patterns, rainfall and contaminant inputs.

Visual comparison of parameter values and temporal trends observed at River Clyde sampling locations SW03, SW04 and SW05 during/after Observatory borehole construction at the Cuningar Loop between June 2019 and February 2020 show similar ranges to those in the distal control surface waters at SW06 and SW10 where no drilling was taking place. Additionally, parameter values at SW05 are similar to those reported at the other River Clyde sampling locations during controlled discharges of wastewater to SW05 from borehole cleaning and test pumping. Therefore, there is little evidence of any significant impact on River Clyde water chemistry from either the borehole drilling or wastewater discharges during installation of the Observatory.

From the limited information provided by the current surface water dataset, there is some evidence of shallow groundwater – surface water interaction from the carbon stable isotope data, which suggest that the surface waters are derived from a mixture of soil and shallow carbonate aquifer sources. Shallow groundwater to surface water inputs are evident also from the Cr(VI) results at SW10 and from the possible bank seepage noted at SW03 on the River Clyde.

The current surface water dataset shows little sign of mine water – surface water interaction. For example, there is no evidence of acid mine drainage impact on surface water quality. However, it is only once mine water chemistry monitoring data are generated by the UKGEOS Glasgow project that surface water – mine water relationships can be explored using possible mine water indicator parameters such as stable isotopes, pH, Eh, DO, SEC, SO_4 , Fe and Mn.

1 Introduction

In 2015, the British Geological Survey (BGS) and the Natural Environment Research Council (NERC) were tasked with developing new centres for research into the sub-surface environment to aid the responsible development of new low-carbon energy technologies in the United Kingdom (UK) and internationally.

Glasgow is one of two UK Geoenery Observatories (UKGEOS) (Figures 1 and 2). The aims of the UKGEOS Glasgow Observatory include de-risking technical aspects of extracting/storing shallow mine water heat energy in an urbanised former coal mine setting (Monaghan et al. 2017; Monaghan et al. 2018; Monaghan et al. 2019).

The initial phase of the UKGEOS Glasgow project entailed installing a network of boreholes into superficial deposits and bedrock. These comprise a seismic monitoring borehole located in Dalmarnock in the east of Glasgow City (Site 10), and clusters of mine water characterisation and environmental monitoring boreholes at Sites 1, 2, 3 and 5 at the Cuningar Loop in Rutherglen, South Lanarkshire on the River Clyde (Figure 2).

These were designed to characterise the geological and hydrogeological setting as a research infrastructure to de-risk key technical barriers to low-temperature shallow mine water heat/storage in former coal mine workings. The borehole network is intended also for baseline monitoring to assess the environmental status before and during the lifetime of the project.

The Observatory is located in the former industrial heartland of east-Glasgow and Rutherglen, in an urban setting with extensive artificial ground. Previous work has shown that contaminants are present in the ground in the east-Glasgow and Rutherglen. These have had a detrimental impact on both surface and groundwater quality in the area (Bearcock et al. 2019; Farmer et al. 1999; Fordyce et al. 2004; Fordyce et al. 2019; Jones et al. 2004; Ó Dochartaigh et al. 2019; Palumbo-Roe et al. 2017; Smedley et al. 2017; Whalley et al. 1999).

The history and complexity of human activities (including coal mining) affecting the subsurface at the Glasgow Observatory mean that surface water – groundwater interactions are currently poorly understood.

Whilst the premise is that development of a mine water heat/storage observatory should not instigate any material change in surface water conditions, the potential for changes in sub-surface fluid flow to alter surface flow is unknown in such a complex environment. Equally, there is little information on the connectivity between surface water and groundwater in the area, and the potential for surface water ingress to influence the sustainability of the thermal resource.

The Glasgow Observatory provides an opportunity to monitor surface water chemistry as an exemplar, to provide reassurance for similar schemes in complex settings, in the many UK urban areas, where main centres of population and fuel poverty coincide with a potential former coal mine heat/storage resource.

As part of the environmental monitoring programme, a monthly survey of surface water chemical quality was carried out between February 2019 and March 2020 at the Glasgow Observatory to establish the pre-operational environmental baseline, against which future change can be assessed. The surface water quality monitoring programme aims to:

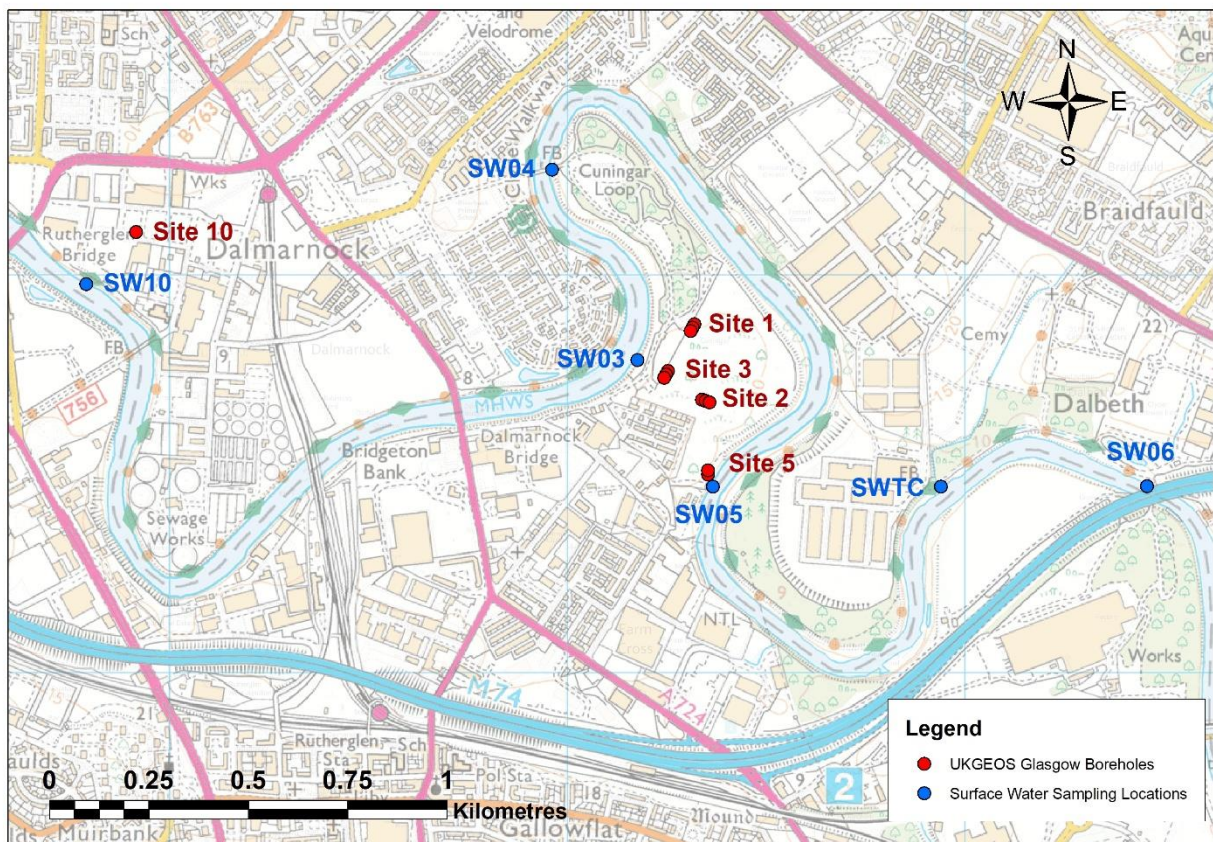
- Improve the scientific understanding of the surface water environment and any groundwater – surface water interactions to aid hydrogeological model characterisation
- Establish a surface water sampling network to generate benchmark information for at least a 12-month baseline period, including spatial and temporal variability. Against this benchmark, any future research results can be compared, to identify any environmental change(s) resulting from the proposed activities.
- Contribute to the assessment and management of risks associated with heat/storage resource development and help to meet regulatory requirements.

This report documents the methods used to carry out the surface water survey and analyse the samples and presents summary statistics and spatial and temporal trends to describe the data, as a guide to the release of the UKGEOS Glasgow Surface Water Chemistry Dataset 1.



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Figure 1 Map of Great Britain, showing Glasgow, where the UK Geoenergy Observatory is located.



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Figure 2 Map showing the location of the UKGEOS Glasgow boreholes and the baseline monitoring surface water sample locations in east-Glasgow and Rutherglen.

2 Surface Water Chemistry Baseline Rationale

Surface water chemistry is temporally variable and changes over short timescales in response to weather and precipitation events (Neal et al. 1999). In urban settings such as Glasgow and Rutherglen, it is also impacted by anthropogenic activity, including urban surface runoff, cross-contamination from the sewerage network and controlled discharges (Fordyce et al. 2013). Therefore, the surface water chemistry monitoring programme was designed to account for the inherent spatial and temporal variability of the parameters to provide a year of baseline data before the Observatory was in operation. Sampling was carried out monthly between February 2019 and March 2020, including during the period that the Glasgow Observatory boreholes were being constructed and tested (June 2019 – February 2020). The aim was to establish the ambient physicochemical conditions, against which any future change can be identified, and to help inform future studies into groundwater – surface water interactions.

The samples were analysed for a variety of parameters to characterise the chemical quality of the surface water as well as to aid determination of groundwater inputs to surface water bodies and flow pathways in the hydrological system. This included determination in the field of temperature, pH, alkalinity, conductivity (SEC), dissolved oxygen (DO) and redox potential (Eh). In addition, samples were collected for laboratory analysis of major and minor ions, trace elements, stable isotopes, and a range of organic compounds including dissolved non-purgeable organic carbon (NPOC). Laboratory analyses were carried out using the same procedures as for groundwater samples, so that the two datasets will be directly comparable. Stable isotopes are a useful tool to aid determination of the different sources of water in hydrological investigations and give indications of groundwater – surface water interactions (Kendall and McDonnell 1998). Organic compounds that may be present in waters arising from the Coal Measure strata present under Glasgow and Rutherglen, such as total petroleum hydrocarbons (TPH) and polycyclic aromatic hydrocarbons (PAH) were determined also. Chromium speciation to establish hexavalent chromium (Cr(VI)) content was included in the sampling suite because there is a history of chromite-ore processing, and contamination of surface/ground water with Cr(VI) in the area (Bearcock et al. 2019; Farmer et al. 1999; Fordyce et al. 2004; Fordyce et al. 2019; Palumbo-Roe et al. 2017; Smedley et al., 2017; Whalley et al. 1999). Table 1 outlines the surface water samples collected at each sampling location. Sampling conformed to BS-ISO standards (or other industry/regulator-approved best practice) and analysis was carried out where possible by United Kingdom Accreditation Service (UKAS) accredited laboratories/procedures. The analytical methods are outlined in Appendix 1. The BGS has existing surface water chemistry datasets in the surrounding area of Glasgow from the Geochemical Baseline Survey of the Environment (G-BASE) project (Bearcock et al. 2019; Fordyce et al. 2004; Smedley et al. 2017) and the River Clyde Estuarine Contamination project (Jones et al. 2004). The UKGEOS Glasgow baseline surface water chemistry survey used similar methods to previous BGS studies, so that the Glasgow Observatory can be placed in the context of these previous studies.

In terms of sampling design, 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. The locations on the River Clyde were chosen proximal to the mine water characterisation and environmental monitoring boreholes at Sites 1, 2, 3 and 5 at the centre of the Observatory in the Cuningar Loop. In addition, far-field control sample locations on the River Clyde were selected approximately 1.5 km upstream of the Cuningar Loop boreholes at location SW06 and approximately 2 km downstream adjacent to the Site 10 seismic monitoring borehole. Figure 2 shows the six locations chosen for surface water sampling. Sample locations were constrained by safe access points to the river/stream banks and locations immediately downstream of bridges and drain outlets etc. were difficult to avoid, given the limited safe access and urban setting.

The intention for the monitoring programme is that surface water chemistry samples will continue to be collected in combination with the planned groundwater chemistry sampling, once the Observatory is operational. The combined baseline groundwater and surface water chemistry datasets should allow surface water – groundwater interactions to be assessed.

3 Sample Collection Methods

The surface water sampling methods for the current project were based on BGS hydrogeological sample collection methods (Smedley et al. 2015) and the rigorous field-based control procedures developed by the BGS Geochemical Baseline Survey of the Environment (G-BASE) project, and were designed to minimise error (Bearcock et al. 2012; Johnson 2005).

Samples were collected in random number order but analysed in sequential order, so that any within-batch analytical instrument drift could be distinguished from genuine geographic/temporal variances (Plant 1973).

For each monthly sampling round, samples were collected by teams of two BGS members of staff from six target sample locations.

3.1 AVOIDING CONTAMINATION

- Jewellery was not worn during sample collection, to avoid metal contamination of the samples.
- Use of sun-cream and other skin products was avoided during sample collection.
- Gloves were worn during sample collection, for protection and to avoid contamination of the samples.
- Sampling equipment was cleaned in sample water between each sampling location and before the start of measurement and sampling.
- With the exception of pre-dosed containers, sample bottles were thoroughly rinsed in sample water prior to sample collection.
- Samples for inorganic analysis were collected using plastic sampling equipment and in trace-element free high-density polyethylene bottles (HDPE) to avoid metal contamination
- Samples for organic analysis were collected using metal or glass sampling equipment and in glass bottles to avoid plastic/organic contamination.

3.2 SURFACE WATER SAMPLING

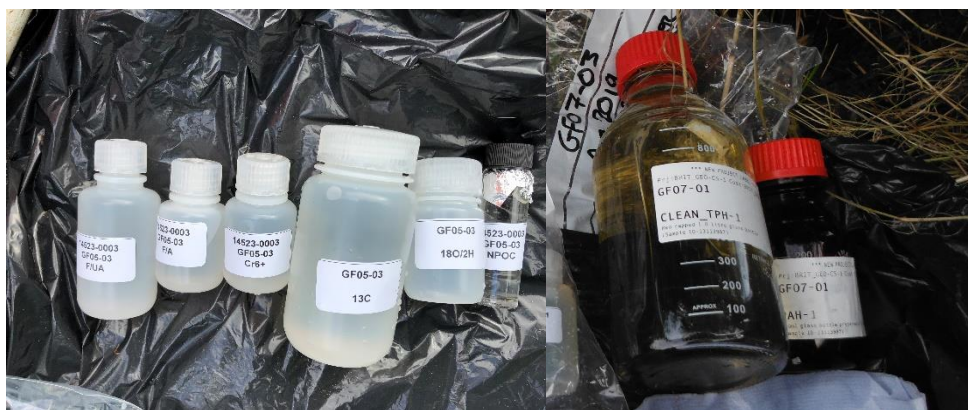
At each of the six locations, eight different bottles (or splits) of surface water were collected. Key water quality parameters were measured at each sampling location using portable meters. The various sample splits collected for chemical analyses and water characterisation parameters are summarised in Table 1. Examples of the sample splits collected are shown in Figure 3.

For quality control (QC) purposes, each sample was allocated a unique sample identifier (ID) for each monthly sampling round. The order in which the samples were collected from each location varied for each sampling round. In this way, samples from the same location were allocated different sample IDs for each round, so that the location of the samples was 'blind' to the laboratories.

Table 1 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 (SEC)	No sample - measured in field	Portable meter	
Dissolved oxygen (DO)	No sample - measured in field	Portable meter	
Alkalinity (CaCO ₃)/Bicarbonate (HCO ₃)	No sample - measured in field	Portable meter	
Laboratory Measurements:			
Non Purgeable Organic Carbon and Total Inorganic Carbon (TIC)	Ag-filtered unacidified foil capped 14 mL glass vial (NPOC)	Carbon analyser	BGS
Oxygen and deuterium isotopes $\delta^{18}\text{O}/\delta^2\text{H}$	30 mL unfiltered unacidified HDPE Nalgene® bottle ($\delta\text{O-H}$)	Isotope ratio mass spectrometry (IRMS)	BGS
Carbon isotopes $\delta^{13}\text{C}$	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	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)	Filtered unacidified 60 mL HDPE Nalgene® bottle (FUA)	Ion chromatography (IC) and ICP-MS	BGS
Cr(VI,III) speciation	Filtered unacidified 30 mL HDPE Nalgene® bottle, (CrVI)	High performance liquid chromatography (HPLC)-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

All laboratory tests UKAS accredited except $\delta^{18}\text{O}$, Cr(VI,III), Ag (and TPH/PAH in certain monthly sampling rounds).
HDPE: high density polyethylene



Photos © BGS, NERC, UKRI

Figure 3 Examples of the eight surface water sample splits taken for analyses at each sampling location.

3.3 SURFACE WATER SAMPLE COLLECTION

Due to the steepness of the banks on the River Clyde and Tollcross Burn and presence of invasive species such as giant hogweed, safe direct access to the water was not possible. Therefore, sample water was collected using an extendable telescope (Figure 4). At the Tollcross Burn, water was collected from the middle of the stream. On the River Clyde, water was collected c. 2 – 3 m from the river bank.



Photos © BGS, NERC, UKRI

Figure 4 Collecting surface water samples using an extendable telescope.

3.3.1 Collection of filtered water samples for inorganic anion, cation and Cr-speciation analysis

All sampling equipment including the telescope, beakers, syringes and filters was pre-rinsed in sample water prior to sample collection. Water for inorganic analysis was transferred from the plastic telescope into a plastic beaker (Figure 4), from which three sample bottles were filled with filtered water for cation (FA), anion (FUA) and Cr(VI) analysis. This was done using a plastic syringe and disposable cellulose nitrate filter with a pore size of 0.45 μm (bottles were pre-rinsed with filtered water before samples were collected). A new filter was used for each sampling location to avoid cross-contamination between locations (Figure 5). The filtered acidified (FA) sample for cation analysis, was acidified with 1 % (v/v) concentrated nitric acid (HNO_3) on return to the office at the end of each day of sampling. On submission to the laboratory, these samples were acidified further with 0.5 % (v/v) concentrated hydrochloric acid (HCl). Samples were acidified to prevent metal precipitation and sorption onto the container walls, and to minimise post-sampling microbial activity.



Photo © BGS, NERC, UKRI

Figure 5 Collecting a filtered surface water sample for inorganic analysis.

3.3.2 Collection of filtered water samples for NPOC analysis

All sampling equipment including telescope, beakers, syringes and filters were pre-rinsed in sample water prior to sample collection. Sample water for NPOC analysis was transferred from the metal telescope into a metal beaker, from where an acid-washed glass vial was filled with filtered water using a glass syringe and 0.45 μm silver filter (Figure 6). The silver filter was thoroughly flushed and cleaned between sampling locations and was changed regularly to avoid clogging.



Photo © BGS, NERC, UKRI

Figure 6 Collecting a silver-filtered surface water sample for NPOC analysis.

3.3.3 Collection of unfiltered water samples for TPH and PAH organic analysis

The metal telescope was pre-rinsed in sample water prior to sample collection. Water from the telescope was transferred directly into glass bottles, which were pre-dosed with sodium thiosulphate to preserve the samples. Samples for PAH analysis were collected in brown glass bottles to minimise ultraviolet light degradation of the samples (Figure 7).



Photo © BGS, NERC, UKRI

Figure 7 Collecting a surface water sample for PAH analysis.

All water samples were stored in a cool box upon collection and refrigerated at the end of each sampling day. Samples were transferred to the analytical laboratories within 48 hours, to avoid degradation of the samples prior to analysis. Analytical methodologies are outlined in Appendix 1.

3.4 SURFACE WATER FIELD MEASUREMENTS

3.4.1 Surface water pH, Eh, DO, SEC and temperature

Key water quality parameters including pH, redox potential (Eh), dissolved oxygen (DO), specific electrical conductance (SEC) and temperature were measured in the field using portable meters. The meters were calibrated/checked according to manufacturer instructions each day as follows:

- Surface water pH was determined using a Mettler Toledo® SevenGo pro pH meter and Jenway® gel probe calibrated with commercially available buffer solutions (pH 4, 7, 9).
- Redox potential was assessed using a Mettler Toledo® SevenGo pro ion meter and VWR® Eh probe checked with commercially available Zobell's solution of known Eh. The field Eh measurements were translated to the standard hydrogen electrode (SHE) using temperature-dependent conversion tables appropriate to the VWR® probe.
- Specific electrical conductance was measured using a Mettler Toledo® Seven2Go Pro conductivity meter and probe calibrated with commercially available buffer solutions 0.01 M KCl (1413 $\mu\text{S}/\text{cm}$) and 0.005 M KCl (718 $\mu\text{S}/\text{cm}$).
- Dissolved oxygen was determined using a Mettler Toledo® Seven2Go Pro DO meter and InSitu®. The DO probe was calibrated with commercially available saturated sodium sulphite solution (0% DO).
- Water temperature was recorded using a Hanna® waterproof thermistor thermometer.

At each sampling location, the plastic telescoop and a plastic beaker were rinsed in sample water. Sample water was then collected in the plastic telescoop and transferred to the plastic beaker. 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 (Figure 8).



Photo © BGS, NERC, UKRI

Figure 8 Recording surface water portable meter measurements on a standard field-sheet.

3.4.2 Surface water field alkalinity measurement

Surface water alkalinity was determined at each sampling location using the bromocresol green indicator acid titration method. This involves adding acid to the sample to neutralise the alkaline compounds present to an end-point of pH 4.5. This is denoted by a colour change of the bromocresol indicator from blue to green.

A known volume (100 mL) of sample water was collected in a plastic flask and a few drops of bromocresol green pH indicator added to the flask. The water was titrated with 1.6N sulphuric acid delivered from a cartridge loaded into a Hach® digital titrator. The titration was repeated until at least two readings were within 5% of each other, and was verified by the second sampler carrying out a titration without knowing the outcome of the first sampler's results (Figure 9). The field total alkalinity measurements were reported as field bicarbonate (HCO_3) concentrations.



Photo © BGS, NERC, UKRI

Figure 9 Field-based titration to determine surface water total alkalinity.

3.5 FIELD OBSERVATIONS

Information about each location and surface water sample was recorded on a standardised field-sheet at the time of sampling. Table 2 outlines the data recorded at each location.

Sample locations were recorded using a portable global positioning system (GPS). Other observations about each location were noted, as these can affect surface water chemistry. These included qualitative assessments of water colour and visible suspended solids; river/stream flow, the land use and the presence of any contaminating materials such as metal, brick and plastic in the river/stream.

Any rainfall on the day of sampling was noted also. Longer-term local weather records for Dalmarnock monitoring station were consulted following fieldwork, to assess if conditions had been dry at the field-location for at least a week before sampling (SEPA 2020a).

On return to the office, the portable meter measurements and field observations recorded on the field-sheets were transferred into an Excel® database and the data entries were independently checked.

Table 2 Summary of information recorded at each surface water sample location.

Data Type	Description																						
Sample Location	The sample location name SW03, SW04 etc.																						
Round Number	Monthly sampling round number 1, 2, 3 etc.																						
Surface Water Sample ID	Comprises the round number GF01, GF02 etc and the sample ID each month e.g. GF02-01 is round GF02, sample 01																						
Sample Grid Co-ordinates	12-figure British National Grid Co-ordinates (Easting and Northing) determined using a portable global positioning system (GPS)																						
Date	Date of sample collection																						
Water Source	Whether surface water/groundwater etc.																						
Water Type	River/stream etc.																						
Stream Flow	Based on the G-BASE qualitative visual inspection classification scheme (Johnson 2005): low, moderate, high																						
Water Colour	Based on the G-BASE 3-colour classification scheme (Johnson 2005): clear, brown, yellow																						
Suspended Solids	Based on the G-BASE qualitative visual inspection classification scheme (Johnson 2005): low, moderate, high																						
Source Condition	Based on the BGS qualitative visual inspection classification scheme: <table border="1"> <thead> <tr> <th>Code</th> <th>Source Condition</th> </tr> </thead> <tbody> <tr> <td>0</td> <td>no comment</td> </tr> <tr> <td>1</td> <td>clear</td> </tr> <tr> <td>2</td> <td>visible suspended matter</td> </tr> <tr> <td>3</td> <td>possible oil contamination</td> </tr> <tr> <td>4</td> <td>possible casing contamination</td> </tr> <tr> <td>5</td> <td>possible agricultural contamination</td> </tr> <tr> <td>6</td> <td>H₂S (hydrogen sulphide) smell</td> </tr> <tr> <td>7</td> <td>other odours</td> </tr> <tr> <td>8</td> <td>strong degassing</td> </tr> <tr> <td>9</td> <td>iron oxidation</td> </tr> </tbody> </table>	Code	Source Condition	0	no comment	1	clear	2	visible suspended matter	3	possible oil contamination	4	possible casing contamination	5	possible agricultural contamination	6	H ₂ S (hydrogen sulphide) smell	7	other odours	8	strong degassing	9	iron oxidation
Code	Source Condition																						
0	no comment																						
1	clear																						
2	visible suspended matter																						
3	possible oil contamination																						
4	possible casing contamination																						
5	possible agricultural contamination																						
6	H ₂ S (hydrogen sulphide) smell																						
7	other odours																						
8	strong degassing																						
9	iron oxidation																						
Contamination	Types of gross visible contamination present in the water such as brick, metal, glass, crockery, plastic, oil, etc.																						
Weather at location	Based on the G-BASE rainfall record scheme (Johnson 2005): rainfall within categories of 12 hours, 24 hours, 48 hours, 2-7 days, 1 week, > 1 week. Noted in the field and checked against local weather records (SEPA 2020a) following fieldwork																						
Method of Collection	Whether direct or using telescoop, buckets etc.																						

3.6 DESCRIPTION OF THE SAMPLE LOCATIONS

A brief description of the surface water sampling locations is provided in Figures 10 – 15 . Marked changes in vegetation cover were observed between the winter and summer seasons during sampling, making access more difficult in the summer months. Water levels on the River Clyde were noted to vary by c. ± 2 m over the course of the sampling year, and this is corroborated by river level data from the nearby Scottish Environment Protection Agency (SEPA) Daldowie river level monitoring station (See Figure 16, Chapter 5).

3.6.1 Cuningar Loop sampling locations

Surface water sampling locations SW03, SW04 and SW05 (Figures 10, 11 and 12) are located on a large meander on the River Clyde known as the Cuningar Loop; within what is today a woodland park in Rutherglen. These sampling locations are adjacent to the main UKGEOS mine water characterisation and monitoring borehole cluster (Figure 2).

Examination of historical maps reveals that the area has an interesting past. It was first developed in the early 1800s with the installation of a water pump and holding reservoirs for the Glasgow Waterworks, at the northern end of the Cuningar Loop adjacent to SW04. This provided water to Glasgow from the River Clyde, before the advent of the Loch Katrine water supply system in 1859. The Glasgow Waterworks closed in the mid-1800s, but the reservoirs, devoid of water, remained in place and are marked as earthworks by 1900. From the early 1900s, sand and gravel extraction were carried out in the northern half of the Cuningar Loop, resulting in open pits and a pond, which was present in the centre of the Loop until the 1990s. The south-west of the Cuningar Loop, adjacent to SW05, was home to the Old Farme Colliery, which operated between 1805 and 1931 and had a mineral railway to the west of SW05. Coal spoil mounds associated with the colliery were present in the area of SW05 from the 1930s. During the 1960s, the old sand and gravel pits, colliery workings and the former Glasgow Waterworks were infilled using material that included demolition rubble from the clearance of the Gorbals and other areas of the city. The land was then moribund until the regeneration of the area as a public park in 2014. The regeneration included construction of a public footbridge across the River Clyde adjacent to SW04 (Ramboll 2018a).

On the opposite bank of the river from SW03 and SW04 is a residential housing area that was formerly the 2014 Commonwealth Games athletes' village, created during a major urban regeneration project of former industrial land, that was previously home to the Glasgow Waterworks and large printing and dye works (CFA 2014). The opposite bank of the river from SW05 comprises an industrial area of distillery warehouses.



Figure 10 Description of surface water sampling location SW03.



Figure 11 Description of surface water sampling location SW04.

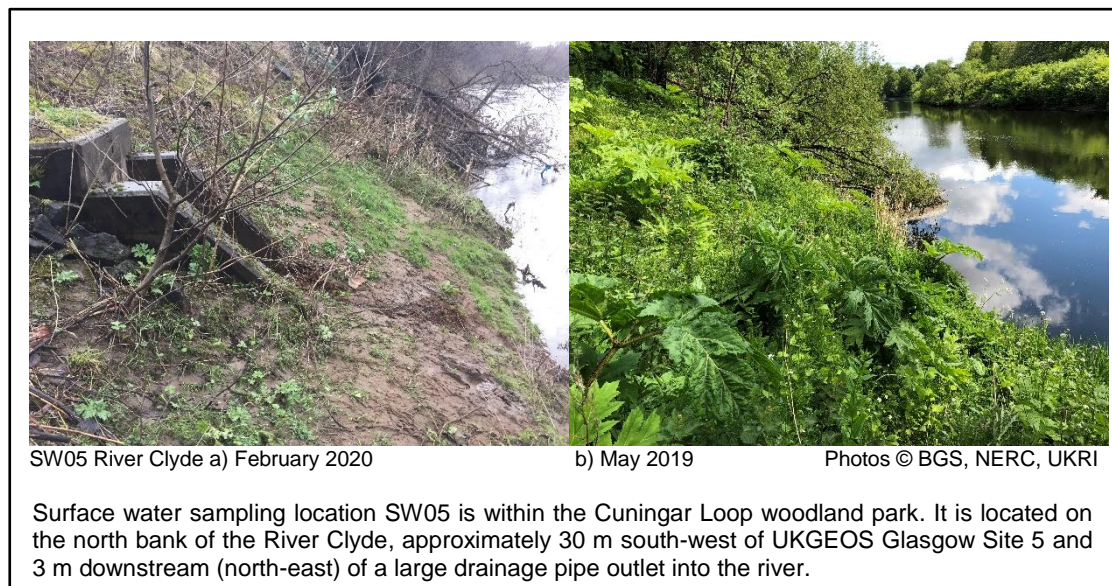


Figure 12 Description of surface water sampling location SW05

3.6.2 SW06 sampling location

SW06 (Figure 13) is a control sampling location on the River Clyde, c. 1.5 km upstream of the UKGEOS Observatory at the Cuningar Loop.

Historic maps reveal that the area was parkland of Easterhill House country estate, with a small lodge present to the north of the site between the mid-1800s until the 1940s. Two commercial properties were located to the north of the site in the 1950s until the early 2000s, when the site was cleared to make way for the current business park. Apart from these buildings, the site remained largely undeveloped and was used as a football pitch from the 1950s. However, the site lies immediately to the north and west of the former Easterhill Colliery and Clyde Iron Works. The surrounding site was used as an unofficial landfill for building rubble and other waste between the 1970s and 1990s. As part of the recent business park development, the site has been landscaped including the installation of a sustainable urban drainage swale pond system on the north bank of the river adjacent to SW06 (Ramboll 2018a).

The opposite bank of the river houses the Liberty steel works industrial site.

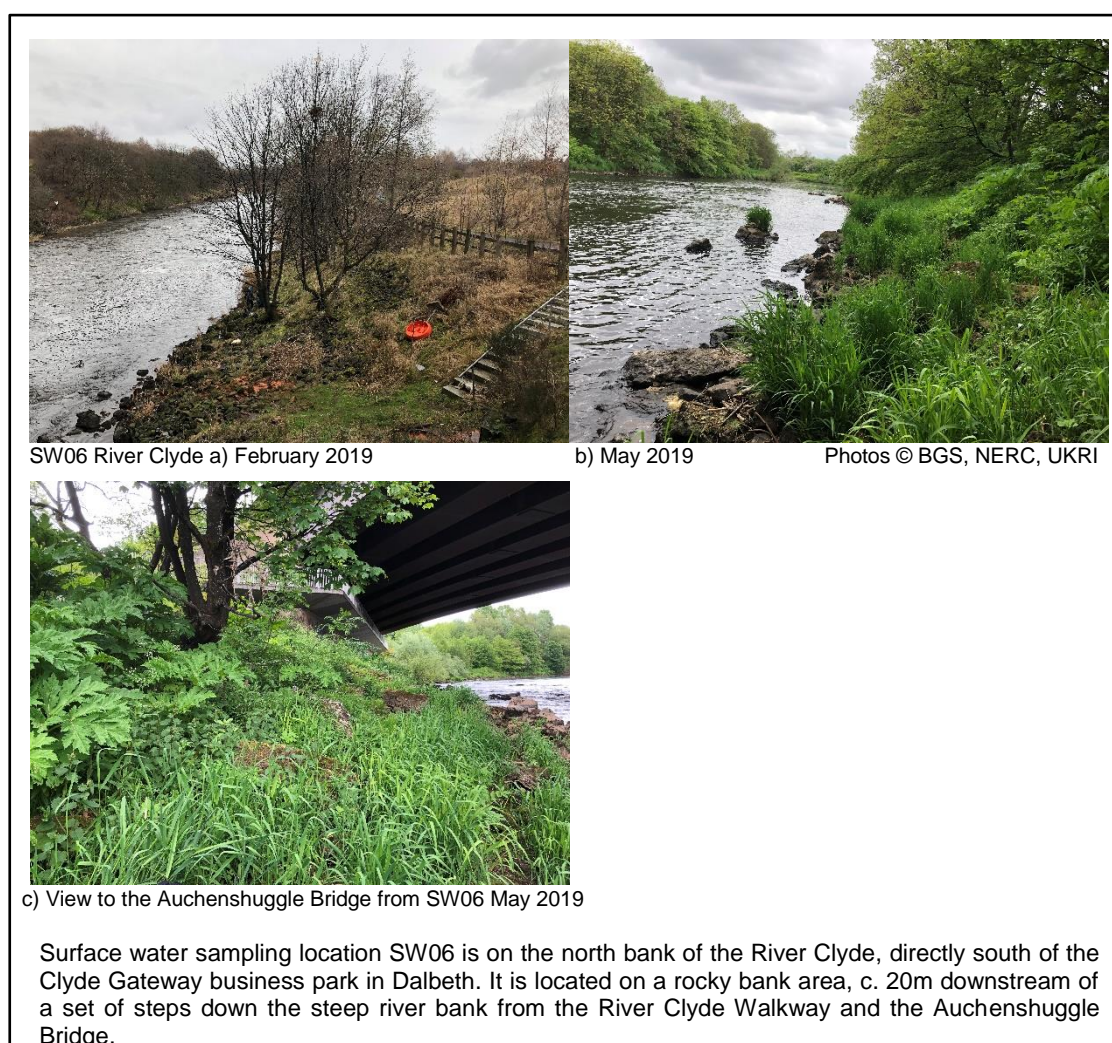


Figure 13 Description of surface water sampling location SW06.

3.6.3 SW10 sampling location

SW010 (Figure 14) is a control sampling location on the River Clyde, c. 2 km downstream from the UKGEOS Observatory at the Cuningar Loop. It is proximal to the UKGEOS seismic monitoring borehole at Site 10.

Historical maps reveal that from the mid-1800s this was an area of intense industrial activity. The Barrowfield Print and Dye works with associated cotton bleaching grounds were located to the north of the sampling location. The dye works were redeveloped as an iron foundry, chemical works and leather works before the turn of the 20th century, and the site was surrounded by cotton and carpet weaving mills until the mid-20th century.

The Dalmarnock gas works was located to the north of the sampling location from the mid-1800s. However, between the end of the 1800s and the 1950s, the area comprised tenement housing, which was cleared in the 1950 and 60s. The area was then largely empty, and within recent years, soil and shallow groundwater contamination from the former gas works and surrounding former industries has been remediated and the site has been cleared for development (Ramboll 2018b).

Immediately opposite the sample location, on the south side of the river, is the Shawfield Business Park, a major redevelopment site on the ground of the former JJ Whites chromium chemical works, where Cr(VI) contamination of soil, groundwater and surface water from chromium ore processing residue (COPR) has been the subject of extensive remediation in recent years (Bewley and Sojka 2013; Farmer et al. 1999).

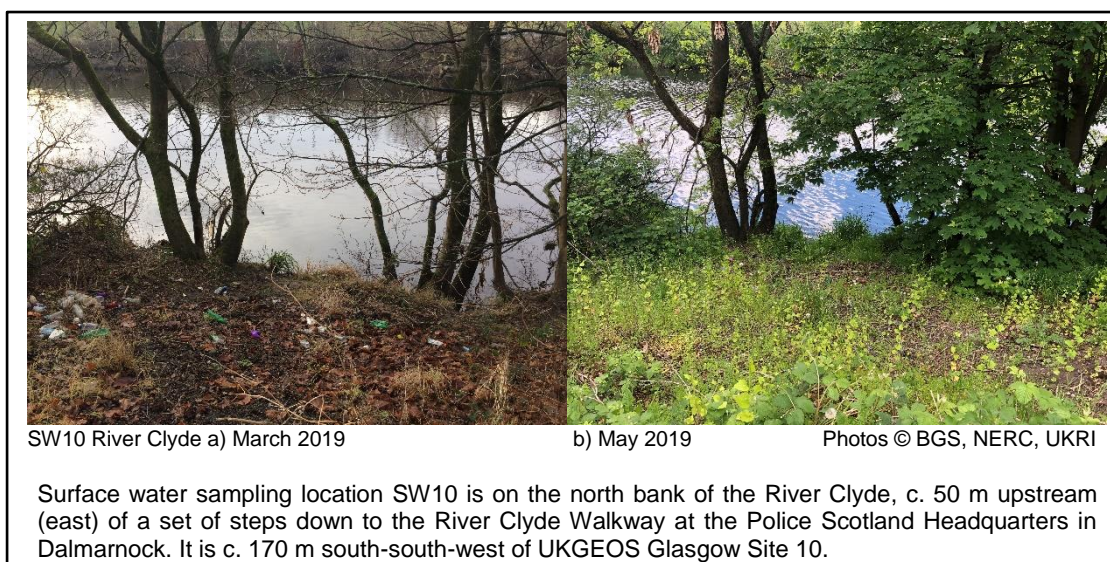


Figure 14 Description of surface water sampling location SW10.

3.6.4 Tollcross Burn sampling location

The Tollcross Burn is the nearest small stream to the UKGEOS Observatory (Figure 15). The burn is sampled c. 0.6 km east-south-east of the main UKGEOS borehole cluster at the Cuningar Loop (location SWTC, Figure 2). Water from the Tollcross Burn enters the River Clyde c. 1.3 km upstream of UKGEOS Cuningar Loop borehole cluster.

The Tollcross Burn is a small (first order stream) tributary of the River Clyde that rises in Springhill in north-east Glasgow. It is culverted for much of its length, appearing at surface only in short sections in the Mount Vernon area of north-east Glasgow. It emerges at the surface in the St Peter's Cemetery in Dalbeth, immediately upstream of the sampling location. The burn has been heavily altered, and like many surface water bodies in Glasgow, is linked to the 19th century sewerage storm-overflow system (Fordyce et al. 2004).

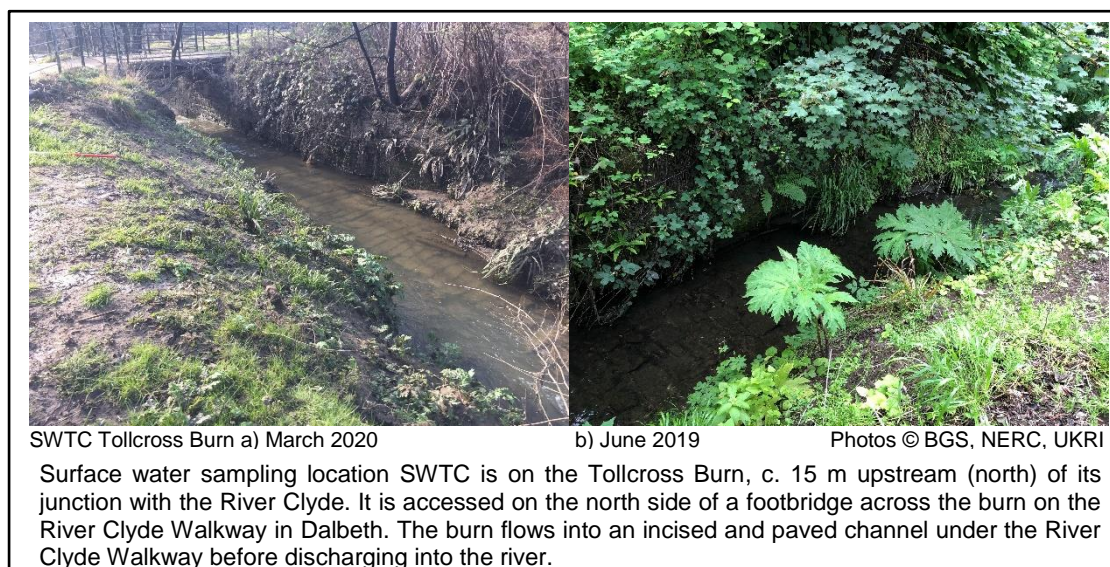


Figure 15 Description of surface water sampling location SWTC.

3.7 FIELD DATA QUALITY CONTROL

As a quality control (QC) measure, one field duplicate sample set was collected in every monthly 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. The purpose of a field duplicate sample is to check on the robustness of the sampling method. Samples collected from the same location should be more similar in their chemistry than samples collected from different locations (Johnson 2005). Bottles for the field duplicate samples were labelled with random sample identities in the same way as the primary samples and submitted 'blind' to the laboratories. The results are presented in Appendix 1 and Table A2.1 (Appendix 2).

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). Bottles for these samples were labelled with random sample identities also, and sent 'blind' to the laboratories. These comprised:

- Blank A: an analysis blank whereby the cation (FA), anion (FUA), Cr speciation (CrVI), NPOC, TPH and PAH sample bottles were filled directly with unfiltered UP water. The cation (FA) sample was acidified in the same way as the field samples.
- Blank P: a procedural blank to check on the filtering process, whereby the cation (FA), anion (FUA) and Cr speciation (CrVI) and NPOC bottles were filled with filtered UP water using the same set of syringes and batch of filters that had been used in the field. The cation (FA) sample was acidified in the same way as the field samples.

Following collection of the samples and field data, the samples were sent to the laboratories for chemical analysis according to the methods described in Appendix 1.

4 Data Presentation

The UKGEOS Glasgow Surface Water Chemistry_1 dataset is presented in Excel® table format:

Filename: UKGEOSGlasgow_SurfaceWaterChemData1_Release.xlsx

Any use of the data should be cited to:

British Geological Survey (2021). UKGEOS Glasgow Surface Water Chemistry Dataset1 Release (2019 – 2020). DOI: 10.5285/b65716f4-4f4c-4070-8539-b796c4bf8796

and

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

It contains the results of inorganic and organic chemical analyses for each of the 98 surface water samples (84 samples and 14 field duplicates) collected over 14 months from six sampling locations. The first sheet in the workbook contains 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, surface water body condition and the presence of any contaminant material at the sampling locations (See Table 2 for explanation).

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

The inorganic chemical data are reported in alphabetical order by chemical symbol in parts per million (mg/L) for the major and minor cations and anions, followed by trace element data in parts per billion (µg/L). Stable isotope data are then reported in ‰ Vienna Pee Dee Belemnite (VPDB) for δ¹³C and ‰ Vienna Standard Mean Ocean Water (VSMOW2) for δ¹⁸O and δ²H. Total inorganic carbon data are reported in mg/L following the isotope data. Finally, data for organic parameters are reported in mg/L for NPOC and TPH and µg/L for PAHs.

For the purposes of calculating summary statistics and presenting example graphs in this report, data below the LLD were set to half the long-term LLD. With the exception of the Piper diagram in Figure 17, field duplicates were removed from the dataset prior to statistical presentation. Summary statistics and graphs for this report were prepared in Excel® and Statview® software packages. The box and whisker plots in Appendix 4 show the 10th, 25th, 50th, 75th and 90th percentiles of the data distributions, with outliers plotted as points.

The Piper diagram to assess surface water type was generated using the Geochemist's Workbench® software package.

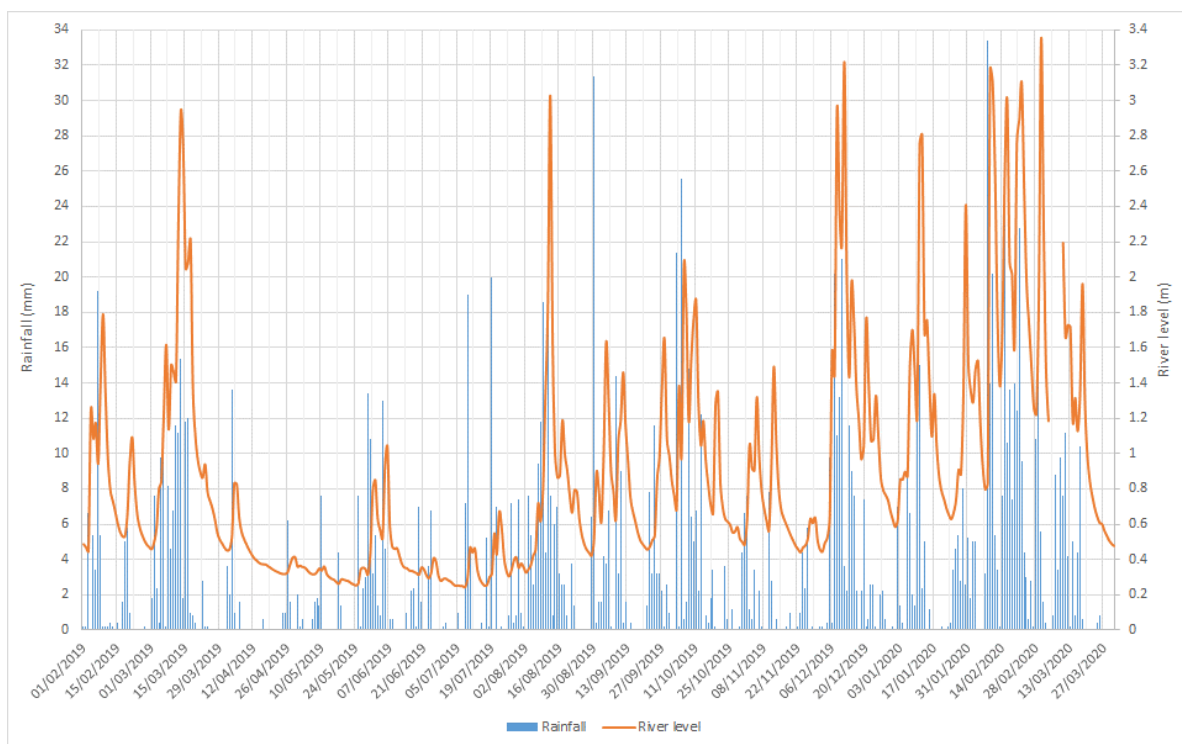
5 Results

Summary statistics of parameter concentrations in the UKGEOS Glasgow Surface Water Chemistry_1 dataset are shown in Table A2.2 (Appendix 2). Time-series plots of the chemistry data for selected parameters for each of the sample locations are presented in Appendix 3. Box and whisker plots of selected parameter distributions at each sampling location are shown in Appendix 4. Elements where the majority of data are below the LLD are not displayed. These include silver (Ag), beryllium (Be), bismuth (Bi), gallium (Ga), hafnium (Hf), lutetium (Lu), tantalum (Ta), thorium (Th), thallium (Tl), thulium (Tm) and tungsten (W).

In most circumstances, river and stream waters are derived from two main sources, the runoff from rainfall and baseflow. Baseflow comprises the discharges from both shallow (superficial deposit) and bedrock aquifers, over which the rivers and streams flow. The proportion of these inputs to rivers and streams depends partly on the geology and typology of the catchment and the weather, which can vary markedly between seasons. In drier periods of the year, river and stream flow can be low, and dominated by baseflow. The water chemistry is influenced by these different sources, and reflects the balance between rainwater/runoff inputs and the extent of groundwater – surface water interactions. In addition to these inputs, surface water chemistry is influenced directly by other factors such as how readily the water can penetrate the ground, soil type, land use, vegetation, biogeochemical weathering processes and human activities such as agriculture, waste disposal, industrialisation and urbanisation (BGS 1999; Darling et al. 2003; Hem 1992; Smedley et al. 2017). A detailed statistical exploration of these relationships in the UKGEOS surface water dataset is beyond the scope of this initial data presentation. Preliminary discussions of spatial and temporal trends evident in the data are provided here, based on visual inspection of summary statistics, the time-series graphs in Appendix 3 and the box and whisker plots in Appendix 4, only.

The relationship between rainfall/surface water flow and surface water chemistry is shown by plotting selected time-series data against rainfall records. These are the total volume of rainfall over the seven days prior to sampling, taken from the nearest monitoring station on the banks of the River Clyde at Dalmarnock (SEPA 2020a;) (Appendix 3). The rainfall records are compared to river level data taken from Daldowie, which is the closest river level monitoring station, located c. 6 km upstream of the Glasgow Observatory (SEPA 2020b). Rainfall and river level show broad concurrence, with some time-lag effects (Figure 16); but rainfall is taken as a proxy for river flow in the time-series graphs in Appendix 3.

These charts and graphs show that the Tollcross Burn has a markedly different chemistry to that of the River Clyde, as it is a smaller more mineralised urban stream. By contrast, the majority of parameters demonstrate similarities in concentration and temporal behaviour at each of the sampling locations on the River Clyde. Hence, the River Clyde results are discussed together, highlighting where spatial differences are evident between the sample locations for some parameters.



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Figure 16 Time-series plot of daily rainfall (© SEPA 2020a) and daily average river level (© SEPA 2020b) on the River Clyde during the surface water sampling period February 2019 March 2020.

5.1 UKGEOS SURFACE WATER PHYSICO-CHEMICAL PARAMETER RESULTS

The surface water field parameter results for SEC, pH, temperature, DO and redox potential (Eh) are shown in Table A2.2 (Appendix 2) and Figures A3.1 (Appendix 3) and A4.1 (Appendix 4).

5.1.1 Specific electrical conductance

The SEC of waters is controlled by the concentrations of ions in solution and is; therefore, a measure of the total dissolved solid (TDS) or mineral content of the water (Drever 1997).

Specific electrical conductance shows the following temporal and spatial trends in the UKGEOS dataset.

5.1.1.1 RIVER CLYDE

Ranges of 174 – 532 $\mu\text{S}/\text{cm}$ SEC are reported in the River Clyde samples, indicating that these are low-salinity freshwaters, (SEC < 700 $\mu\text{S}/\text{cm}$; Rhoades et al. 1992).

Specific electrical conductance shows little spatial variation in values between the river sample locations (Figures A3.1, Appendix 3 and A4.1, Appendix 4). However, it shows notable temporal variability, with higher values recorded during the drier months of April - June 2019 at all the sample locations. This probably reflects less input and dilution of the River Clyde water with rainfall/runoff and greater dominance of baseflow sources from groundwater in this period.

5.1.1.2 TOLLCROSS BURN

The SEC (442 – 1026 $\mu\text{S}/\text{cm}$) values reported in the Tollcross Burn are markedly higher than those in the River Clyde, indicating that the Tollcross Burn has a higher mineral content. Indeed, the results suggest that the Tollcross Burn waters are slightly saline (SEC 700 – 2000 $\mu\text{S}/\text{cm}$; Rhoades et al. 1992). This is not unexpected, given that the Tollcross Burn is a small urban stream with a limited and partly culverted catchment area, likely to be subject to potentially contaminated runoff and sewerage overflow.

Temporal trends in SEC are not so evident in the Tollcross Burn, but values broadly reflect changes in the concentrations of the major ions as expected. The higher value of 1026 $\mu\text{S}/\text{cm}$ reported in February 2019 possibly corresponds to the use of road salt, as it is concurrent with higher sodium (Na) and chloride (Cl) concentrations in the burn waters (See Sections 5.2.1 and 5.2.2). The SEC of the Tollcross Burn waters drops markedly in February 2020 (442 $\mu\text{S}/\text{cm}$) in response to heavy rainfall, indicating dilution of the burn water.

5.1.2 Surface water pH

Surface water pH in the UKGEOS samples shows a relatively narrow range of circum-neutral to alkaline values (River Clyde 7.44 – 7.99; Tollcross Burn 7.49 – 8.23) with little temporal variability. The River Clyde waters show only slight variation in pH also. The circum-neutral to alkaline values likely reflect the carbonate-rich nature of the underlying Carboniferous-age bedrock in the Glasgow area (Hall et al. 1998) and the presence of alkaline materials, such as building rubble, in urban soil and superficial deposits, which tend to elevate the pH in urban environments relative to the surrounding rural hinterland (Fordyce et al. 2017; Smedley et al. 2017).

As a smaller stream more sensitive to rainfall events, the Tollcross Burn shows a drop in pH to 7.49 in February 2020 during a period of heavy rainfall, with concurrent drop in field- HCO_3^- content (146 mg/L) (Figures A3.1 and A3.4, Appendix 3 and A4.1 and A4.4, Appendix 4).

5.1.3 Temperature, dissolved oxygen and redox potential

Temperature values are lowest in winter and highest in summer months in the River Clyde (3.6 – 21.9 °C) and Tollcross Burn (5.8 – 16.8 °C) waters as expected.

Dissolved oxygen solubility varies inversely with temperature in waters (Wilson 2010). Consequently, observed concentrations of DO are lower in summer and higher in winter in the River Clyde (6.1 – 13.2 mg/L) and Tollcross Burn (6.3 – 10.1 mg/L).

The Eh values of 301 – 523 mV in the River Clyde and 279 – 512 mV in the Tollcross Burn indicate that the waters are generally oxidic.

The River Clyde water samples show broadly similar temperature, DO and Eh ranges at all the sampling locations. Redox potential values are relatively consistent throughout the year, but follow a similar seasonal trend to DO, with marginally higher values in the winter months, reflecting the greater DO content in colder waters.

Deviations in Eh values from the general seasonal trend at SW03 and SW04 between April and July 2019 possibly reflect river morphology, (both have shelf areas and the river is shallower at SW03), which may result in slower flow at these locations and relatively limited dispersion of near-bank seepage and less agitated; hence, less oxygenated water.

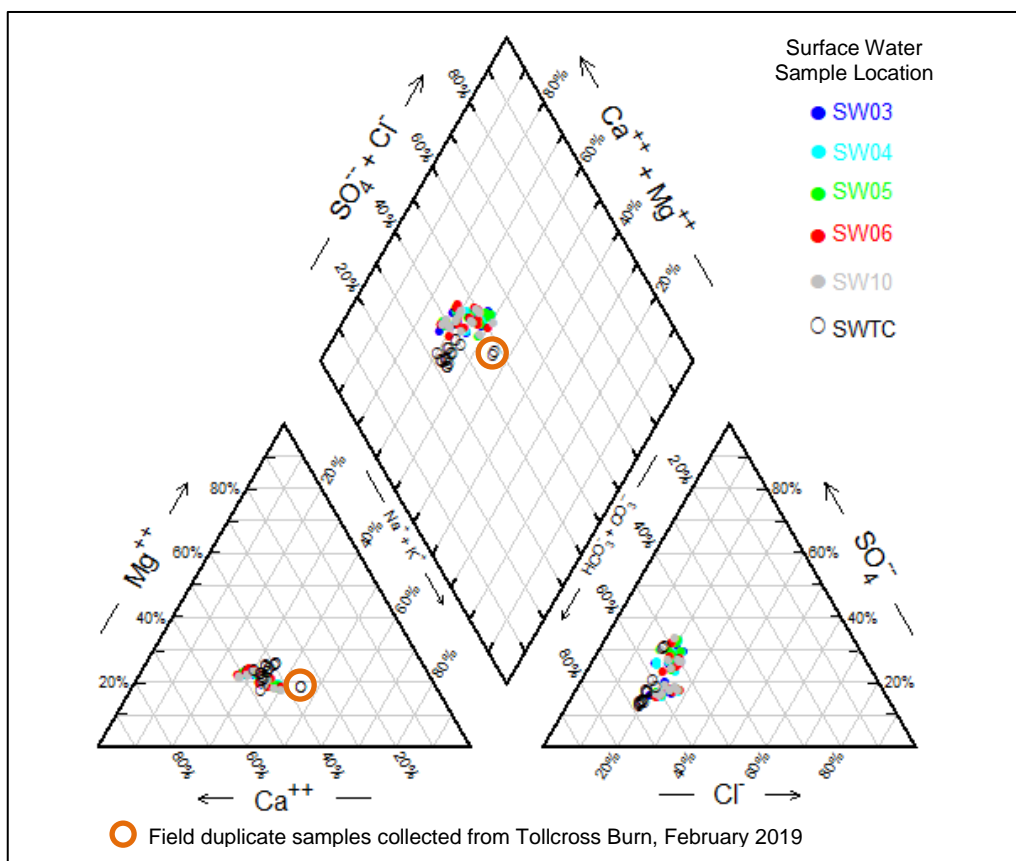
5.2 UKGEOS SURFACE WATER INORGANIC CHEMISTRY RESULTS

5.2.1 Water type

To assess water type, the surface water data were plotted on a trilinear Piper diagram (Piper 1944) showing the relative concentrations of major cations and anions to determine the hydrochemical facies (Figure 17). Results show that the surface water samples are largely calcium-bicarbonate (Ca-HCO_3^-) dominated, with the exception of a field duplicate pair of samples collected from the Tollcross Burn during February 2019, which are more sodium-bicarbonate (Na-HCO_3^-) dominated. The fact that the field duplicate samples show similar chemistry, is further validation of the sampling method.

Evidence that the surface waters are predominately of bicarbonate type is typical of areas underlain by carbonate-rich bedrock (BGS 1999) and Ca-domination is likely due to the dissolution of calcite in the Carboniferous-age sandstones, siltstones and limestones underlying Glasgow and Rutherglen (Hall et al. 1998) as well as carbonate-rich superficial and anthropogenic deposits in the urban environment (Fordyce et al. 2017). The greater dominance of Na in the samples collected from the Tollcross Burn in February 2019, is coincident with the highest Cl concentration (138 mg/L) reported in the burn (Figure A3.4, Appendix 3). This may reflect the use of road salt during February 2019, being washed off into the local drainage system. Such changes

in chemistry are likely more noticeable in a small stream like the Tollcross Burn, than in the River Clyde, where such inputs are probably diluted quickly in the much larger volume of water.



Note: field duplicates were included in the Piper plot, as a check on the results.

Figure 17 Trilinear Piper plot of the relative concentrations of major cations and anions in the UKGEOS Glasgow surface water samples, showing water facies.

5.2.2 Major and minor ions

The surface water results for major and minor cations and anions are shown in Table A2.2 (Appendix 2) and Figures A3.2 – A3.5 (Appendix 3) and A4.2 – A4.5 (Appendix 4). The graphs show that for the majority of months of the year, major and minor ion concentrations in the Tollcross Burn are similar to or higher than the River Clyde waters, with the exception of total phosphorus (P-Total) and orthophosphate (HPO_4), as follows.

5.2.2.1 RIVER CLYDE

Major cation and anion ranges in the River Clyde are reported respectively as:

- Ca (13 – 46 mg/L), magnesium (Mg 3 – 14 mg/L), Na (13 – 30 mg/L) and potassium (K 2.0 – 5.9 mg/L)
- Field- HCO_3 (40 – 153 mg/L), Cl (16 – 40 mg/L) and sulphate SO_4 (9 – 43 mg/L).

These parameters and bromide (Br <0.04 – 0.05 mg/L), fluoride (F 0.018 – 0.077 mg/L) and silicon (Si 0.68 – 3.58 mg/L) show little variation in concentration range between the different sampling locations on the River Clyde (Figures A4.2 – A4.5, Appendix 4).

For field- HCO_3 , the exception is sample SW03 in May 2019, which has a lower alkalinity value (84 mg/L) than the other river water samples. The river is shallower at SW03 and this result may reflect local bank seepage at this location.

The major ions, share the same temporal trend in the River Clyde, with higher concentrations in April – June 2019, during a period of lower rainfall, when baseflow was likely more dominant, with less dilution by rainwater, resulting in greater mineral content of the river water (Figures A3.2 and A3.4, Appendix 3). Baseflow inputs likely have higher mineral content given the carbonate-rich geological setting of Glasgow and Rutherglen and longer residence times of these waters as opposed to surface runoff (BGS 1999; MacDonald et al. 2017). In addition, evaporation (hence, concentration of the mineral content) may be greater from a large water body such as the River Clyde under these dry weather conditions. This seasonal pattern is typical of many surface water bodies, and can be influenced also by the increased amount of biological respiration during spring/summer months leading to greater generation of CO₂ (Norton et al. 2001).

Conversely, Si concentrations fall in the River Clyde samples in April – May 2019 relative to the rest of the year. This may reflect lower soil-water runoff inputs during this drier period. These can be an important source of Si to lowland rivers in carbonate-dominated weathering systems (such as the River Clyde), as a result of the biogeochemical cycling of Si in the soil environment (Georg et al. 2006).

Total phosphorus (0.037 – 0.220 mg/L), HPO₄ (<0.03 – 0.50 mg/L) and nitrate (NO₃ 2.8 – 14.9 mg/L) contents in the River Clyde samples show a broadly similar temporal pattern, with generally higher concentrations reported between April and July 2019. During this period, concentrations of these parameters and of nitrite (NO₂) show more marked variation between the different sample locations on the River Clyde than in the rest of the year (Figures A3.3 and A3.5, Appendix 3). These variations are rather sporadic and not consistent between the sampling locations. They may, in part, reflect phosphate and nitrate fertiliser inputs in the catchment during the growing season.

5.2.2.2 TOLLCROSS BURN

Major cation and anion ranges in the Tollcross Burn are reported respectively as:

- Ca (40 – 87 mg/L), Mg (9 – 33 mg/L), Na (32 – 99 mg/L) and K (4.5 – 13.2 mg/L)
- Field-HCO₃ (146 – 405 mg/L), Cl (41 – 138 mg/L) and SO₄ (28 – 75 mg/L)

Peak contents of K, Mg and SO₄ occur in April 2019, likely due to less dilution of the burn water by rainfall in this relatively dry month. Sodium concentration (78 mg/L) is higher in April 2019 than in the rest of the months also, with the exception of the high concentration (99 mg/L) recorded in February 2019. As outlined in Section 5.2.1, this is coincident with elevated Cl content (138 mg/L) and may reflect road salt inputs from surface runoff.

Concentrations of Si and NO₃ range between 3.61 – 6.94 mg/L and 4.1 – 9.6 mg/L respectively, and are generally lower in either or both of April and May 2019 than the rest of the year. This likely reflects lower runoff inputs to the Tollcross Burn during this drier period.

Total-P (0.244 mg/L) and HPO₄ (0.44 mg/L) contents peak in the Tollcross waters during heavy rainfall in February 2020, possibly reflecting cross-contamination from the storm-drain sewerage network. Conversely, concentrations of the major ions and most of the minor ions fall in February 2020, probably as a result of rainfall dilution of the burn water.

Bromide and F contents in the Tollcross Burn waters range between <0.04 – 0.19 mg/L and 0.071 – 0.220 mg/L respectively, peaking in October 2019.

The Br/Cl weight ratio, can be used to indicate sources of salinity in natural waters (Edmunds 1996). The Br/Cl ratios in both the Tollcross Burn (0.15^{10³} – 3.52^{10³}) and River Clyde (0.53^{10³} – 2.9^{10³}) waters are depleted relative to rainfall values reported by Edmunds (1996) (4.19^{10³} – 6.30^{10³}). This is further evidence that the waters are likely subject to contaminant inputs, which are known to cause Br/Cl ratios to vary widely in urban environments (Davis et al. 2005).

5.2.3 Trace elements

Surface water results for trace elements are shown in Table A2.2 (Appendix 2) and Figures A3.6 and A3.7 (Appendix 3) and A4.6 and A4.7 (Appendix 4). The graphs demonstrate that for the majority of months of the year, trace element contents in the River Clyde are similar to or higher

than in the Tollcross Burn waters, with the exception of boron (B), lithium (Li), rubidium (Rb), strontium (Sr), molybdenum (Mo), antimony (Sb), selenium (Se) and uranium (U).

5.2.3.1 RIVER CLYDE

Spatial and temporal trends in trace element concentrations are evident in the River Clyde waters as follows.

Temporal trends

Barium (Ba), Rb and Sr contents vary between 40 – 106 µg/L; 1.8 – 6.5 µg/L and 64 – 274 µg/L respectively in the River Clyde waters. These elements and arsenic (As), caesium (Cs), cobalt (Co), tin (Sn), Se, Sb and U show a similar temporal pattern in the River Clyde, with higher concentrations at all the sampling locations between April and June 2019 than in the rest of the year, corresponding to the period of drier weather when dilution of the river waters from rainfall was likely less (Figure A3.6, Appendix 3). Conversely, concentrations of the rest of the trace elements are generally lower in River Clyde waters in this period, with the exception of Mo, cadmium (Cd), manganese (Mn), nickel (Ni), and zinc (Zn).

The highest concentrations of iron (Fe 569 – 748 µg/L), copper (Cu 1.98 – 2.55 µg/L), lead (Pb 0.95 – 1.06 µg/L) and vanadium (V 0.80 – 0.97 µg/L) and the lanthanide series elements at each of the River Clyde sampling locations are reported in August 2019. These are coincident with highest dissolved organic carbon (DOC as NPOC 9.6 – 17.3 mg/L) concentrations also (Figure A3.8 and Section 5.3.1). August 2019 was a relatively wet month (Figure 16), and these results may reflect increased mobilisation of organic matter during the peak growing season. Dissolved organic matter can exert a significant control on the concentrations of these parameters in natural waters (Drever 1997; Gruau et al. 2004; Hem 1992; Smedley et al. 2017).

Spatial relationships

Lithium concentrations in the River Clyde waters are all below the LLD. The rest of the trace elements show broadly overlapping ranges in concentration between the different sampling locations on the River Clyde, with the following exceptions.

Cobalt, Fe and Mn concentrations range between 0.14 – 0.34 µg/L; 31 – 748 µg/L and 20 – 201 µg/L in the River Clyde waters respectively and are higher in samples collected from SW03 than the other River locations for the majority of months of the year (Figure A3.6, Appendix 3). The association between these elements reflects the fact that Fe and Mn oxides exert a significant control on the mobility of Co in natural waters (BGS 1999; Hem 1992; Saito and Moffett 2002; Smedley et al. 2017). Boron concentrations are below the LLD in the River Clyde waters except for a value of 58 µg/L at SW03 in April 2019 also. The higher concentrations of B, Co, Fe and Mn at SW03 possibly relate to shallower river morphology, resulting in slower flow at this location and relatively limited dispersion of near-bank seepage.

Niobium contents are generally close to the LLD in the River Clyde waters but a higher value (0.07 µg/L) is reported at SW04 in January 2020.

Aluminium (Al) titanium (Ti), zirconium (Zr) and Zn concentrations show good consistency between the sampling locations in River Clyde waters, except for markedly higher values at SW06 (Al 147 µg/L; Ti 6.9 µg/L; Zr 0.28 µg/L; Zn 23.7 µg/L) reported in February 2020, suggesting increased runoff during the heavy rainfall experienced that month (Figure A3.6, Appendix 3).

Similarly, Al (97 µg/L), Sb (0.27 µg/L), Ti (5.1 µg/L) and Zr (0.22 µg/L) concentrations are higher at SW10 than in waters from the other River Clyde sampling locations during heavy rainfall in February 2020. Antimony contents in May – July 2019 (0.29 – 0.39 µg/L) and Cd concentrations in July 2019 (0.3 µg/L) are higher in SW10 waters than the other sampling locations also. This may relate to the proximity of metal-rich waste at this location as follows.

The SW10 sampling location is on the opposite bank of the River Clyde to the Shawfield Business Park. This is the former home of the JJ Whites chromium chemical works, where Cr(VI) pollution of soil, groundwater and surface water from COPR waste is a known issue (Farmer et al. 1999; Fordyce et al. 2004; Fordyce et al. 2019; Palumbo-Roe et al. 2017; Smedley et al. 2017; Whalley

et al.1999). Hexavalent chromium occurs in trace amounts only in most natural environments, and elevated concentrations are largely a product of industrial contamination (Farmer et al. 1999).

Total chromium (Cr-Total > 0.95 µg/L) and Cr(VI) (> 0.40 µg/L) concentrations are markedly higher at SW10 than in the rest of the UKGEOS River Clyde samples (Figures A3.7, Appendix 3 and A4.7, Appendix 4). Trivalent-Cr (Cr(III)) concentrations are elevated at this location also, but to a lesser extent. Hexavalent-Cr is the dominant constituent of Cr-Total in the SW10 samples. Hence, these parameters show the same temporal pattern and are typically higher (Cr(VI) 4.16 – 7.40 µg/L; Cr-Total 4.91 – 8.47 µg/L) in April to June and September 2019, when rainfall is lower. This may indicate less dilution of continuous subsurface Cr-rich discharges at this location. Trivalent-Cr concentrations at SW10 show a similar temporal trend to the rest of the River Clyde samples with the exception of higher values (0.49 – 0.63 µg/L) in June and July 2019, which again may relate to variations in Cr-rich discharges from the Shawfield site.

Whalley et al. (1999) reported very high Cr(VI) concentrations (1100 µg/L) in the River Clyde at the confluence with the Polmadie Burn, the main stream draining the Shawfield site, located c. 700 m downstream of SW10. This burn is a significant contributor of Cr(VI) to the River Clyde. However, Cr(VI) entering the Clyde is quickly diluted. The concentrations of Cr(VI) at SW10 in the UKGEOS dataset (\leq 7.40 µg/L) are much lower than these values, but are comparable to concentrations noted downstream of Shawfield (10 µg/L) in the Walley et al. (1999) study.

Similarly, Palumbo-Roe et al. (2017) reported very high concentrations of 470 – 2060 µg/L Cr(VI) in the Polmadie Burn, but contents of < 0.05 µg/L only, in the River Clyde at the confluence with the Polmadie Burn. The concentrations of Cr-Total at SW10 (0.96 – 8.47 µg/L) are of a similar magnitude to those determined by Jones et al. (2004) in the River Clyde at the confluence with the Polmadie Burn (5 µg/L).

However, SW10 is upstream of the Polmadie Burn and it will not account for the higher Cr concentrations noted in the River Clyde at this location. The Shawfield site has been the subject of major remediation in recent years, including extensive surface sealing, in-situ chemical treatment of the COPR waste and emplacement of channel culverts and water retention bunds, to improve the quality of shallow groundwater, as this is known to be the major source of Cr contamination to the River Clyde and Polmadie Burn (Bewley and Sojka 2013). These shallow groundwater – surface water interactions likely explain the elevated Cr-Total, Cr(VI) and Cr(III) concentrations at SW10.

There is no evidence that COPR-waste affects surface water chemistry at the other sampling locations on the River Clyde or the Tollcross Burn.

5.2.3.2 TOLLCROSS BURN

Concentration ranges of B (< 53 – 130 µg/L), Li (< 7 – 15 µg/L), Rb (5.3 – 20.2 µg/L), Sr (327 – 1365 µg/L) and U (0.21 – 0.46 µg/L) are reported in the Tollcross Burn waters. These elements show a marked drop in content in February 2020, probably as a result of dilution of burn water with heavy rainfall that month (Figure A3.6, Appendix 3).

By contrast, concentrations of several trace elements peak in February 2020 likely reflecting greater runoff in the wetter conditions (Figure A3.6, Appendix 3). These include Al (20 µg/L), Fe (69 µg/L), Pb (0.20 µg/L), V (0.85 µg/L) and the lanthanide-series elements. Total-Cr, Cr(III) and Cr(VI) show similar behaviour with respective peaks of 0.5 µg/L, 0.22 µg/L and 0.26 µg/L in the Tollcross Burn waters (Figure A3.7, Appendix 3).

Similarly, the highest Se content (0.85 µg/L) in the Tollcross Burn dataset, corresponds to higher rainfall in March 2019. However, sporadic peaks in concentration of As (2.22 µg/L, May 2019) and Cu (2.02 µg/L, February 2019) in the burn waters are not related to greater rainfall and may indicate contaminant inputs.

Cobalt and Mn concentrations in the Tollcross Burn range from 0.19 to 0.53 µg/L and 44 to 157 µg/L, respectively. These elements show a similar temporal trend in the waters, and are higher in concentration between October 2019 and March 2020 than in the rest of the year.

5.3 UKGEOS SURFACE WATER ORGANIC PARAMETER RESULTS

5.3.1 Dissolved organic carbon

The results for DOC (as NPOC) are presented in Table A2.2 (Appendix 2) and Figures A3.8 (Appendix 3) and A4.8 (Appendix 4).

The Tollcross Burn waters show little temporal variation in DOC content (2.5 – 4.4 mg/L) for most of the year, but a marked spike in values (6.9 mg/L) corresponds to heavy rainfall in February 2020, that may indicate cross-contamination from the sewerage-storm drain system, as pollution by sewage is another source of DOC in surface waters (Smedley et al. 2017).

With the exception of the sample in February 2020, DOC concentrations are higher in the River Clyde (3.0 – 17.3 mg/L) than in the Tollcross Burn. The DOC concentrations in the River Clyde show marked seasonal variability with higher values during the summer and autumn months peaking in August 2019. This probably reflects greater quantities of organic matter in runoff during the vegetation growing season and leaf fall in the autumn. Decaying vegetation in soil is a major contributor to DOC in surface waters (BGS 1999; Smedley et al. 2017).

5.3.2 Organic pollutants

Concentrations of the PAH-indicator compounds benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene (BaP), benzo(ghi)perylene, indeno(1,2,3-cd)pyrene, PAH-Total and of TPH (C8-C10), TPH (C10-C40) and TPH (C8-C40) determined in the surface water samples are given in Table A2.2 (Appendix 2). The results for these parameters are shown in time-series graphs and box and whisker plots in Figures A3.9 (Appendix 3), A4.9 and A4.10 (Appendix 4). However, the combined TPH (C8-40) results are plotted only.

The concentrations of these parameters are generally close to or below the LOQ in the UKGEOS surface water samples.

Concentrations of the PAH indicator compounds, PAH-Total and TPH (C8 – 40) in the River Clyde waters vary between < 0.0005 – 0.035 µg/L; <0.005 – 0.104 µg/L and <0.045 – 0.866 mg/L respectively.

Similarly, contents of < 0.002 – 0.106 µg/L (PAH-indicators); 0.007 and 0.305 µg/L (PAH-Total) and <0.045 - 0.279 mg/L (TPH C8 – 40) are recorded in the Tollcross Burn.

Clear temporal patterns are difficult to determine, but broadly lower concentrations are associated with the dry spring period in 2019, probably as a result of less runoff, whereas concentrations are generally higher in the wetter autumn and winter months in both the River Clyde and Tollcross Burn. The PAH compounds show marked spikes in concentration in the Tollcross Burn and at sampling locations SW06 and SW10 on the River Clyde in February 2020 suggesting greater mobilisation of contaminants during heavy rainfall that month. Similarly, marked spikes in TPH (C8-40) concentration 0.263 mg/L in February 2019 in the Tollcross Burn and at SW06 on the River Clyde (TPH (C8-40) 0.866 mg/L), likely reflect contaminant inputs. SW06 is located immediately downstream of a drain outlet and busy road bridge.

5.4 UKGEOS SURFACE WATER STABLE ISOTOPE RESULTS

5.4.1 Carbon stable isotopes

Dissolved inorganic carbon (DIC) in natural waters is primarily derived from the weathering of carbonate and silicate minerals by (i) acid rain and (ii) carbonic acid in infiltrating waters derived from the dissolution of biogenically derived soil CO₂ gas. The δ¹³C signature of DIC can be used to provide an indication of surface water sources as different carbon sinks in catchments tend to have characteristic δ¹³C values. Atmospheric CO₂ generally has a δ¹³C signature of -6 to -8 VPDB ‰ (hereafter in this Section ‰). In temperate regions, the δ¹³C signature of bulk soil carbon is generally between -23 to -30 ‰ and that of soil CO₂ gas -27.5 to -23 ‰. Carbonate minerals have δ¹³C values between 8 and 0 ‰ (the latter for marine carbonates). As carbonate minerals dissolve, the DIC δ¹³C signature of the water evolves to more enriched values. Therefore, waters that are recent and shallow, primarily derived from soil, tend to have depleted DIC δ¹³C signatures, whereas deeper groundwaters that have had greater residence time to allow for

mineral dissolution and weathering display more enriched $\delta^{13}\text{C}$ signatures. The $\delta^{13}\text{C}$ signature in surface waters is generally in the range of -5 to -25‰ broadly representing a mixture of biogenic soil CO_2 and mineral dissolution sources, but the relationship between in-stream processes and $\delta^{13}\text{C}$ DIC signatures is complex and can be influenced by other factors such as CO_2 degassing and uptake of carbon by aquatic organisms (Bottrell et al. 2019; Bullen and Kendall 1998; Clark and Fritz 1997).

The results for DIC $\delta^{13}\text{C}$ ‰ in the UKGEOS surface water samples, are presented in Table A2.2 (Appendix 2) and Figures A3.10 (Appendix 3) and A4.11 (Appendix 4).

As a much smaller stream, the Tollcross Burn has a generally higher mineral content than the River Clyde. Despite this, a plot of DIC $\delta^{13}\text{C}$ values versus alkalinity (field- HCO_3) shows that the majority of River Clyde and Tollcross Burn waters display similar $\delta^{13}\text{C}$ signatures in the range -10.5 to -14.1 ‰ (Figure 18). The values are within typical extents for surface waters, provisionally suggesting that the waters are from a mixture of soil and shallow carbonate aquifer sources. The $\delta^{13}\text{C}$ signatures are marginally more enriched in the drier months of April – May 2019 in both the River Clyde (> -11.3 ‰) and Tollcross Burn (> 11.7 ‰), which likely implies greater influence of a groundwater component containing DIC derived from carbonate mineral dissolution during baseflow conditions.

Surface water samples collected from locations SW03, SW04 and SW05 on the River Clyde during August 2019 show marginally more depleted $\delta^{13}\text{C}$ values c. 16 ‰, as does the Tollcross Burn sample in February 2020. These samples, and a more depleted sample (-25.6 $\delta^{13}\text{C}$ ‰) from SW06 on the River Clyde in November 2019, likely indicate a greater contribution of DIC from a different pool such as soil water associated with storm runoff in these months (Figure 18; Figure A3.10, Appendix 3). SW06 is located immediately downstream of a shallow drain outlet into the River Clyde.

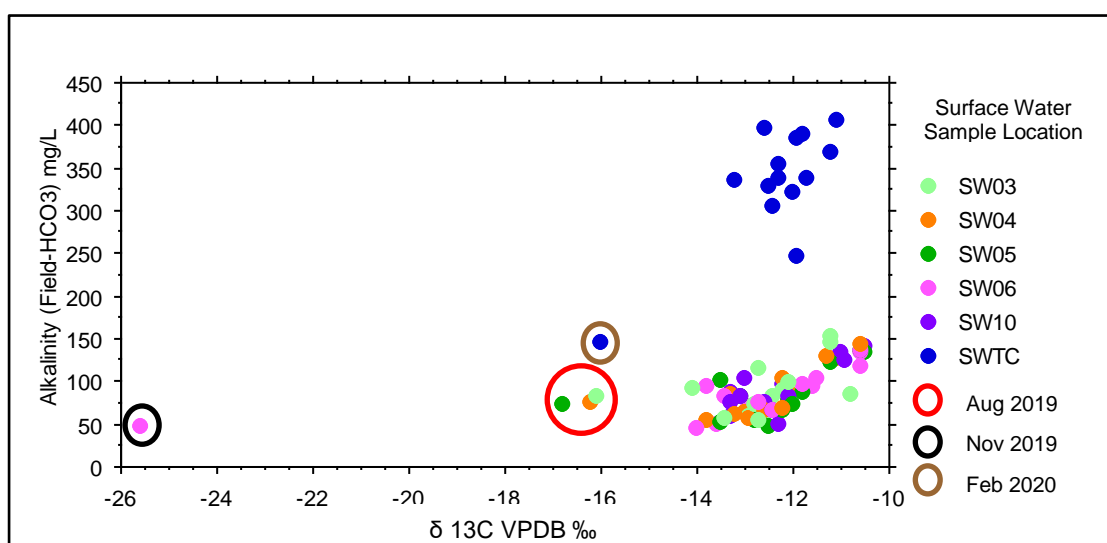


Figure 18 Plot of surface water alkalinity expressed as field- HCO_3 content versus $\delta^{13}\text{C}$ isotopic signature.

5.4.2 Deuterium and oxygen stable isotopes

Based on the premise that the isotope ratios deuterium $\delta^2\text{H}$ and oxygen $\delta^{18}\text{O}$ show a linear relationship in unevaporated precipitation, using world precipitation data, this relationship can be plotted as a global meteoric water line (GMWL) (Craig 1961). Natural water data can be assessed with respect to the GMWL. As precipitation falls and infiltrates the ground to become surface water and groundwater, natural processes can affect the isotopic signature of the waters causing them to deviate from the GMWL. Water that has evaporated or mixed with evaporated water typically plots below the GMWL, whereas low-temperature silicate diagenesis can raise the $\delta^2\text{H}$ and $\delta^{18}\text{O}$

values in natural waters. The isotopic signature of precipitation varies locally and temporally, influenced by the temperature and amount of water vapour in the atmosphere. These and other factors such as altitude, amount of rainfall, latitude, distance from the coast and interaction with vegetation also cause fractionation of the isotopes, as rain falls and infiltrates the ground surface. Hence, $\delta^2\text{H}$ and $\delta^{18}\text{O}$ isotopic signatures can be used to distinguish water sources and processes (Darling et al. 2003; USGS 2004).

The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values in the UKGEOS surface water dataset range from -66.9 to -39.3 VSMOW2 ‰ (hereafter ‰ in this Section) and -9.5 to -6.6 ‰ respectively (Table 2.2, Appendix 2; Figures A3.10, Appendix 3 and A4.11, Appendix 4). These are within typical ranges for Scottish surface water of -80 to -40 ‰ $\delta^2\text{H}$ (Birkel et al. 2018) and -10.6 to -1.3 ‰ $\delta^{18}\text{O}$ (Soulsby et al. 1999) and of UK surface waters c. -54 to -16 ‰ $\delta^2\text{H}$ (Darling et al. 2003). The $\delta^{18}\text{O}$ values are within ranges reported by Tyler et al. (2016) for UK rainwater (-18.5 to 0.6 ‰) and more specifically for rainwater within the west of Scotland (16.4 -6.0 ‰). They are also similar to values suggested by Darling et al. (2003) of -50 to -45 ‰ $\delta^2\text{H}$ and -7.6 to -7.0 ‰ $\delta^{18}\text{O}$ for groundwaters within a western zone of the UK including Glasgow and Rutherglen.

The waters generally plot along the GMWL, but are slightly above it suggesting that they are relatively unevaporated and closely related to rainwater (Figure 19). Water resources in the west of Scotland are known to be more enriched, especially in $\delta^2\text{H}$, due to the influence of moist isotopically-enriched Atlantic weather fronts and higher rainfall (Birkel et al. 2018; Darling et al. 2003; Tyler et al. 2016). Therefore, it is likely that the local meteoric water line plots above the GMWL. Summer rainfall is known to be generally more isotopically enriched than winter rainfall primarily as a result of variances in temperature and air-moisture sources (Clark and Fritz 1997; Darling and Talbot 2003). There is some evidence of seasonal control on the isotopic signatures of the UKGEOS surface waters as they plot in monthly groups on the GMWL (Figure 19). Similarly, marginally more enriched $\delta^2\text{H}$ (> -47 ‰) and $\delta^{18}\text{O}$ (> -7.5 ‰) values are evident in the surface water samples during the summer months (June – September 2019) on the time-series plots in Figure A3.10 (Appendix 3). During the period of high rainfall in February 2020, markedly more depleted $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values were reported in the Tollcross Burn (-66.9 and -9.5 ‰ respectively) and to a lesser extent at SW06 on the River Clyde (-53.7 and -8.3 ‰ respectively) suggesting a greater influence of recent rainfall at these sampling locations. SW06 is located immediately downstream of a shallow drain. As a much smaller stream, the Tollcross Burn is likely much more responsive to rainfall events than a large river like the Clyde.

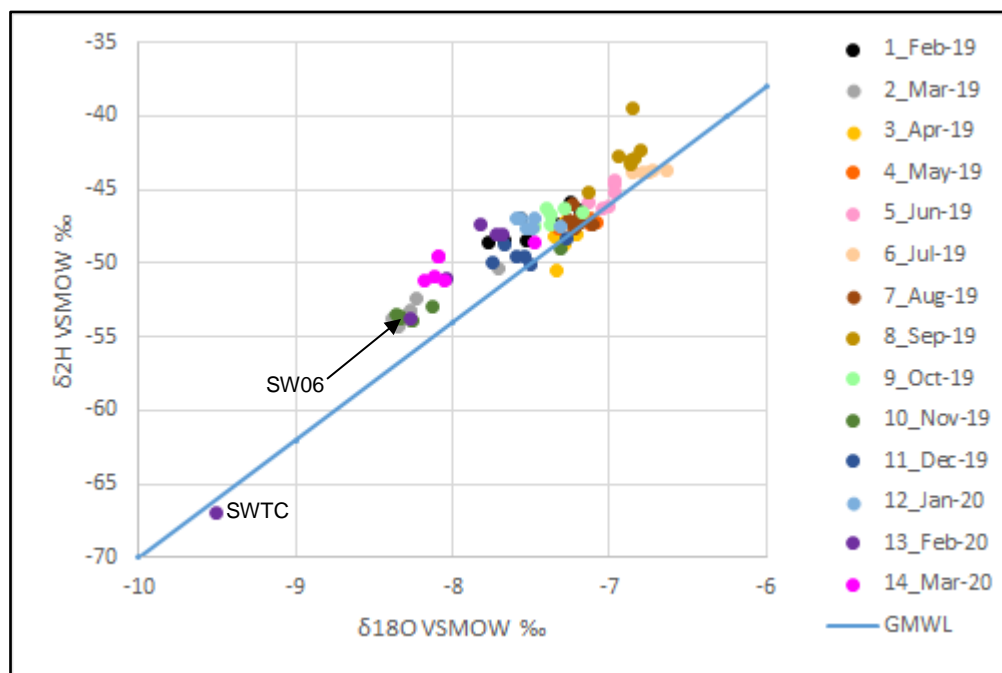


Figure 19 Plot of surface water $\delta^2\text{H}$ versus $\delta^{18}\text{O}$ stable isotope data with reference to the GMWL

5.5 COMPARISONS WITH PREVIOUS BGS GLASGOW SURFACE WATER DATA

To place the UKGEOS Glasgow surface water chemistry results in a wider historical context, they were compared to the city-wide BGS surface water chemistry geochemical baseline survey of the environment (G-BASE) dataset and the BGS Clyde Estuary dataset. The G-BASE dataset comprises one-off spot samples that were collected from every 1.5 km length of surface water tributaries draining into the River Clyde within the Glasgow city area in 2003 (Fordyce et al. 2004; Smedley et al. 2017). The BGS Clyde Estuary dataset comprises eight spot water samples that were collected from the River Clyde and its inner estuary in 2002 and 2003 (Jones et al. 2004). Six of these samples were selected for comparison with the present study as they span the stretch of river under consideration in this project. They were collected within the urban area of Glasgow along a section of the River Clyde between Carmyle (c. 2.2 km upstream of the UKGEOS sample locations) and the junction with the River Kelvin (c. 6.3 km downstream of the UKGEOS locations).

Summary statistics of parameter concentrations in UKGEOS Glasgow surface water samples, and BGS Clyde surface water datasets are presented in Table A2.2 (Appendix 2).

5.5.1 River Clyde

The results for the majority of parameters measured in the UKGEOS River Clyde waters are within or similar to the maximum ranges reported previously from the River Clyde by Jones et al. (2004) within the Glasgow area (Table A2.2, Appendix 2) with the exception of the following, which are markedly (more than 1.5 times) the maximum reported in the previous dataset:

- A value of 0.3 µg/L Cd recorded at SW10 in July 2019, which markedly exceeds the previous River Clyde maximum value (0.05 µg/L). This sporadic high value in the UKGEOS dataset may relate to contaminant ingress from the Shawfield COPR-waste site at this location (See Section 5.2.3.1).
- A Zn concentration of 23.7 µg/L at SW06 reported during high rainfall in February 2020, which is markedly higher than the previous River Clyde maximum (14 µg/L).
- A value of 17 mg/L NPOC at SW03 in August 2019 that is markedly higher than the previous maximum of 10 mg/L reported in the River Clyde.
- Aluminium contents recorded in November 2019 at SW05 (96 µg/L) and SW06 (98 µg/L) and at SW06 (147 µg/L) and SW10 (97 µg/L) during heavy rainfall in February 2020 that are more than 1.5 times the previous maximum (64 µg/L).
- Nitrate concentrations (14.3 – 14.9 mg/L) at sampling locations SW03, SW04 and SW10 in May 2019, that are more than 1.5 times greater than the maximum value (9.5 mg/L) recorded in the River Clyde previously.
- Concentrations of Pb (0.75 – 1.06 µg/L) at all River Clyde sampling locations in August 2019, SW05 in September 2019 and SW05 and SW06 in November 2019 and January 2020 that are more than 1.5 times above the maximum value (0.5 µg/L) reported by Jones et al. (2004) in the River Clyde.

The higher concentrations of Al, NO₃, NPOC, Pb and Zn reported in the current dataset likely reflect more varied seasonal changes and runoff inputs during the full year of data collection for UKGEOS compared to the spot sampling of the BGS Clyde Estuary dataset that was carried out during the months of December and June only.

5.5.2 Tollcross Burn

The results for all the parameters measured in the UKGEOS Tollcross Burn surface waters are within or comparable to the maximum ranges reported previously from urban streams in Glasgow by Fordyce et al. (2004).

5.6 SURFACE WATER CHEMICAL QUALITY

To evaluate surface water quality, the UKGEOS results were compared to surface water environmental quality standards (EQS) for good river status (SEPA 2014; 2019; UKTAG 2013). It should be noted that there is no UK river water nitrate standard, so assessment was made against commonly used European Union standards (Poikane et al. 2019). The SEPA class the River Clyde in Glasgow as a heavily modified water body with moderate, rather than good ecological

status (SEPA 2020c). However, comparisons here are made with the good river environmental quality standard (EQS) annual average (AA) and maximum allowable concentrations (MAC), as an indication of urban impacts on surface water chemistry.

Summary statistics of parameter concentrations in UKGEOS Glasgow surface water samples, BGS Clyde surface water datasets and the EQS are presented in Table A2.2 (Appendix 2). The EQS AA are shown on the time-series plots of the chemistry data in Appendix 3 also.

Mean concentrations of parameters in the UKGEOS River Clyde and Tollcross Burn water samples over the sampling period are generally within the EQS recommended AA limits for good river status. Similarly, individual values reported in the UKGEOS surface water dataset rarely exceed the recommended MAC for good river status. However, there are a few exceptions:

- Mean HPO_4 concentrations in the River Clyde waters of 0.19 mg/L versus the AA guideline of 0.069 mg/L.
- Mean HPO_4 concentrations in the Tollcross Burn of 0.08 mg/L versus the AA guideline of 0.069 mg/L.
- Mean NO_3 concentrations in the River Clyde and Tollcross Burn are 7.5 mg/L and 6.4 mg/L respectively, versus the EU AA guideline of 5.7 mg/L (there is no UK standard for NO_3 in surface water).
- The mean Al content in the River Clyde waters is 48 $\mu\text{g/L}$ versus the AA guideline of 15 $\mu\text{g/L}$ for good river status, and is greater than the MAC of 25 $\mu\text{g/L}$ at all the River Clyde sampling locations, except during the drier period between April and June 2019 and at SW06 and SW10 in February 2019.
- Mean Cu concentrations are 1.26 $\mu\text{g/L}$ in the River Clyde and 1.27 $\mu\text{g/L}$ in the Tollcross Burn versus the AA guideline of 1 $\mu\text{g/L}$ for Tier 1 risk assessment.
- Mean benzo(ghi)perylene and indeno(1,2,3-cd)pyrene contents in the River Clyde are 0.003 $\mu\text{g/L}$ and 0.004 $\mu\text{g/L}$ respectively versus the AA guideline of 0.002 $\mu\text{g/L}$ for these compounds. In the Tollcross Burn, mean concentrations are 0.010 $\mu\text{g/L}$ and 0.015 $\mu\text{g/L}$ respectively.
- Peak benzo(a)pyrene concentrations just above the MAC of 0.1 $\mu\text{g/L}$ are reported in the Tollcross Burn (0.106 $\mu\text{g/L}$) during heavy rainfall in 2020.

These water quality results are not unexpected in a city like Glasgow, where greater weathering and runoff in the urban environment than in natural river waters; pollution of soil, surface runoff and shallow groundwater and cross-contamination from the sewerage network likely contribute to the loading of these parameters into surface water bodies.

5.7 MONITORING SURFACE WATER – GROUNDWATER INTERACTIONS

It is not anticipated that the operation of the UKGEOS Glasgow Observatory will cause any substantial change to surface water chemistry in the River Clyde or Tollcross Burn. Significant interaction between these surface water bodies and the underlying mine water aquifers targeted by the Observatory is thought unlikely given the substantial thickness of superficial deposit cover overlying the bedrock in the River Clyde valley (> 30 m; Kearsley et al. 2015).

However, given limited existing information on the hydrogeological regime in Glasgow and Rutherglen, two of the main aims of the surface water chemistry monitoring programme are:

- (i) To provide reassurance that the operation of the UKGEOS Glasgow Observatory will not cause significant change to the chemical quality of adjacent surface water bodies.
- (ii) To check for surface water – groundwater interactions and improve understanding of the hydrological system at the UKGEOS Observatory.

To assess if there was any change in River Clyde water chemistry during construction of the Observatory, an initial visual inspection of the time-series plots in Appendix 3 was carried out. Activities associated with installation of the Observatory included borehole drilling and casing and borehole cleaning and test pumping.

Borehole drilling and casing took place in December 2018 and February 2019 at Site 10 (proximal to surface water sampling location SW10) and between June 2019 and February 2020 at Sites 1, 2, 3 and 5 at the Cuningar Loop (proximal to SW03, SW04 and SW05) (See the borehole data

packs on the UKGEOS website for exact dates: <https://ukgeos.ac.uk/data-downloads>). The time-series plots in Appendix 3 show similar surface water parameter values at SW10 to the other River Clyde sampling locations in February 2019 despite the borehole casing activities being carried out at Site 10 that month. Parameter values and temporal trends at SW03, SW04 and SW05 between June 2019 and February 2020 during borehole drilling activities at the Cuningar Loop are similar to those reported at the distal control locations SW10 and SW06 on the River Clyde, where no drilling was taking place.

Borehole cleaning and test pumping at the Cuningar Loop Sites between October 2019 and February 2020 resulted in wastewater that was collected into temporary settling tanks and then disposed of under licence to an existing drain, which discharges to the River Clyde at surface water sampling location SW05 (exact dates of these activities are available in the borehole data packs on the UKGEOS website: <https://ukgeos.ac.uk/data-downloads>). It was not expected that these relatively small discharges (up to a maximum of 369 m³ in one day) would have a significant impact on surface water quality, as they would be diluted very quickly in the River Clyde. These discharging activities coincided with the dates of surface water sampling at SW05 on 16th October 2019, 12th November 2019 and 15th January 2020. A review of the time-series plots (Appendix 3) shows that parameter values recorded at SW05 are similar to those reported at the other River Clyde sampling locations for these dates.

Therefore, there is little evidence of any significant impact on River Clyde water chemistry from either the borehole drilling or wastewater discharges during installation of the Observatory.

The initial phase of surface water monitoring presented here has established a pre-operational baseline surface water chemistry dataset over a 14-month period, at the Observatory. Once the Observatory is in use, future research and monitoring results can be compared to this benchmark to help identify any substantive change in surface water chemistry that may result from the Observatory activities. In particular, changes in parameter concentrations outside of the ranges reported in the current dataset at Observatory sampling locations SW03, SW04 and SW05, but not evident also at the distal control locations SW06, SW10 and SWTC would indicate that further investigations should be carried out to assess whether changes in surface water quality relate to the operation of the Observatory.

However, it will only be possible to assess surface water – groundwater interactions fully once the planned simultaneous monthly groundwater chemistry monitoring data are available and the two datasets can be evaluated together.

From the limited information provided by the current surface water dataset, there is some evidence of shallow groundwater – surface water interaction from the carbon stable isotope data, which suggest that the surface waters are derived from a mixture of soil and shallow carbonate aquifer sources. Shallow groundwater to surface water inputs are evident also from the Cr(VI) results at SW10 on the River Clyde and from the possible bank seepage noted at SW03.

The current surface water dataset shows little evidence of mine water – surface water interaction. Coal mine waters in the UK fall into three main chemical categories (Banks et al. 1997):

- (i) saline type
- (ii) acid mine drainage - due to the to the oxidation of the iron sulphide mineral pyrite (Fe₂S) commonly contained within coalbed resources. This is an acid-generating weathering reaction that can lower the pH of natural waters in the unsaturated zone and release Fe and SO₄ into solution. Hence, acid mine waters are often enriched in SO₄, Fe and several other metal elements that are more readily dissolved under low-pH conditions including Mn and to a lesser extent Al.
- (iii) alkaline mine drainage - under saturated anoxic conditions, bacterially mediated reduction of sulphate may lead to generation of reducing, sulphide-rich alkaline coal mine waters with low metal content.

Mine waters may also contain elevated concentrations of organic compounds derived from the coal deposits (Banks et al. 1997).

Therefore, depending on the mine water chemistry present at the Glasgow Observatory, parameters that may be used to assess any linkages between mine water and surface water bodies include the following:

- stable isotope data: to indicate water source and residence times
- Alkalinity and pH: there is no evidence in the current dataset of acid mine drainage ingress at the UKGEOS surface water sampling locations. Preliminary results collected at the Glasgow Observatory suggest that groundwaters are of alkaline rather than acid mine water type.
- Redox potential and DO: may indicate any discharge of reducing mine water at surface, depending on how quickly oxygenation and mixing of the two water bodies occurs.
- SEC: may point to ingress of saline mine water into surface water bodies depending on how quickly the waters are mixed.
- Sulphate, metal elements (Fe and Mn in particular) and organic compounds: depending on the composition of the mine water, the concentrations and distribution of these parameters may provide insights into surface water – mine water interactions.

In addition to the chemistry, mine water – surface water comparisons will take account of factors such as groundwater level, likely groundwater flow and prevailing weather conditions to examine possible linkages between the two water types, once this information is available for the Glasgow Observatory.

6 Conclusions

A baseline survey of surface water chemistry was carried out in proximity to the UK Geoenergy Observatory in east-Glasgow and Rutherglen over 14 months between February 2019 and March 2020. The survey involved the monthly collection of surface water samples from six locations, comprising five on the River Clyde, and one on the Tollcross Burn, the nearest small stream to the Observatory.

The resultant set of 98 samples (84 samples and 14 field duplicates) were analysed to determine surface water pH, alkalinity, SEC, DO, Eh, and temperature and the concentrations of 71 inorganic parameters and 10 organic substances.

The chemistry results reveal that the UKGEOS surface waters are primarily Ca-HCO₃ dominated and range from circum-neutral to alkaline pH (7.44 – 8.23). This is as expected, given the calcareous nature of the underlying geological parent materials and presence of anthropogenic carbonate-rich materials, such as building rubble, in the urban environment of Glasgow and Rutherglen.

Stable isotope data indicate that the waters are of recent origin and are within typical extents for surface waters for $\delta^{13}\text{C}$ and the ranges reported previously for surface waters in the west of Scotland for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ ($\delta^{13}\text{C}$ -25.6 to -10.5 ‰; $\delta^2\text{H}$ -66.9 to -39.3 ‰; $\delta^{18}\text{O}$ -9.5 to -6.6 ‰). The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ results plot slightly above the global meteoric water line (GMWL), but this is likely because waters in the west of Scotland are known to be more enriched, in $\delta^2\text{H}$ in particular, as a result of the predominance of moist-Atlantic weather fronts and higher rainfall. There is some evidence of seasonal control on the isotopic signatures in the UKGEOS dataset, with marginally more enriched $\delta^2\text{H}$ (> -47 ‰) and $\delta^{18}\text{O}$ (> -7.5 ‰) values reported in the summer months (June – September 2019). Heavy rainfall events, such as in February 2020, are characterised by more depleted values, indicating the greater influence of rainwater/runoff on surface water chemistry (Tollcross Burn $\delta^2\text{H}$ -66.9 and $\delta^{18}\text{O}$ -9.5 ‰; River Clyde SW06 $\delta^2\text{H}$ -53.7 and $\delta^{18}\text{O}$ -8.3 ‰).

Based on visual inspection of the data distributions, the majority of parameters demonstrate similarities in concentration and temporal behaviour at each of the sampling locations on the River Clyde. Hence, the results for the River Clyde samples are considered as a group, except where deviations from these general trends are noted at individual sampling locations.

The River Clyde and Tollcross Burn water samples show broadly similar temperature, DO and redox potential ranges at all the sampling locations, that vary with the season. Temperature values are lowest in winter (3.6°C) and highest in summer months (21.9 °C) as expected. By contrast, concentrations of DO are lower in summer (6.1 mg/L) and higher in winter (13.2 mg/L), as DO solubility increases in colder waters. The Eh values range between 279 – 523 mV indicating that the waters are generally oxidic.

The DOC concentrations at all River Clyde sampling locations are higher between July and November 2019, peaking in August. This likely reflects greater quantities of organic matter in runoff during the vegetation growing season and leaf fall in the autumn. By contrast, the Tollcross Burn shows little temporal variation in DOC content for most of the year, but a marked spike in values (6.9 mg/L) corresponds to heavy rainfall in February 2020, that may indicate cross-contamination from the sewerage-storm drain system.

The SEC values reported in the Tollcross Burn are generally higher (442 – 1026 $\mu\text{S}/\text{cm}$) than those in the River Clyde (174 – 532 $\mu\text{S}/\text{cm}$) indicating that the Tollcross Burn has a higher TDS content, and is chemically distinct from the River Clyde. This is to be expected as the Tollcross Burn is a small partially culverted urban stream. The results suggest that the River Clyde waters are low-salinity freshwaters, whereas the Tollcross Burn waters are slightly saline.

In general, major element concentrations, surface water pH and alkalinity in the Tollcross Burn are higher than in the River Clyde.

The major ions Ca, Mg, Na, K, HCO₃, Cl and SO₄ show little spatial variation in values between the River Clyde sample locations. However, these parameters show a marked temporal trend in the River Clyde, with higher values reported in April – June 2019. Several of the minor and trace elements show similar behaviour in the River Clyde including, As, Sb, Ba, Cs, Co, Rb, Sr, Se, Sn

and U. In the Tollcross Burn, peak contents of K, Mg and SO₄ occur in April 2019, also. These results correspond to a period of lower rainfall, when baseflow was likely more dominant, with less dilution by rainwater, resulting in greater mineral content of the surface water.

Total-P, HPO₄ and NO₃ contents in the River Clyde waters show a broadly similar temporal pattern, with generally higher concentrations reported between April and July 2019. This may in part reflect phosphate and nitrate fertiliser inputs in the catchment during the growing season.

By contrast, lower concentrations of Al, Fe and Si are reported in the River Clyde in either of April and May 2019, likely reflecting lower weathering inputs during this drier period. Lead, Ti, Zr and the lanthanide-series elements show a similar temporal trend.

Temporal trends are less evident for the organic pollutant PAH indicator compounds and TPH, but concentrations are broadly lower during the dry spring period in 2019 than in the rest of the year in both the River Clyde and Tollcross Burn waters.

The majority of parameters show broadly overlapping ranges in concentration between the different sampling locations on the River Clyde. However, Co, Fe and Mn are generally higher in waters collected from SW03 than the other locations on the River Clyde for the majority of months of the year. Boron concentrations are higher (58 µg/L) at SW03 in April 2019 also. Conversely, field-HCO₃ contents at SW03 in May 2019 are lower (84 mg/L) than at the other river water sample locations. The river is shallower at SW03 and these variances may reflect greater influence of local bank seepage at this location.

Aluminium, Ti, Sb, Zr and zinc (Zn) concentrations at both or either of SW06 and SW10 are higher than those reported at the other River Clyde sampling locations in February 2020 during heavy rainfall that month. Polycyclic aromatic hydrocarbon concentrations are elevated at these locations during the same weather event, which may indicate increased contaminant mobilisation under the wetter conditions.

Heavy rainfall in February 2020 results in marked spikes in concentration of several trace metals, P-Total, HPO₄, PAH and TPH (C8 – 30) in the Tollcross Burn also.

Total-Cr, Cr(III) and Cr(VI) concentrations are notably higher in SW10 waters than at the rest of the River Clyde sampling locations. This sampling location is proximal to the Shawfield Business Park, where Cr-contamination of soil, groundwater and surface water with Cr(VI) from the former JJ Whites chromite ore processing works has been documented. The concentrations of Cr(VI) reported at SW10 are comparable to results in previous studies of the River Clyde at Shawfield. The elevated Cr-Total, Cr(VI) and Cr(III) concentrations in the River Clyde reported in the current study may reflect shallow groundwater – surface water interactions, as this is a known issue at the site, which is the subject of extensive remediation.

There is no evidence in the UKGEOS dataset of elevated Cr(VI) concentrations at any of the other sampling locations on the River Clyde or the Tollcross Burn.

Comparisons between the UKGEOS surface waters and existing BGS surface water chemistry datasets collected in 2002 and 2003 from the River Clyde and urban streams within Glasgow reveal that for the majority of parameters, the concentrations recorded in current study are within or similar to the ranges reported previously.

Regulatory authorities class the River Clyde in Glasgow as a highly modified water body with moderate rather than good ecological status. Initial comparisons with the good river EQS AA and MAC show that the majority of parameters are within these limits with the following exceptions, which indicate the influence of the urban environment on surface water chemistry:

- Mean HPO₄ concentrations in the River Clyde waters of 0.19 mg/L versus the AA guideline of 0.069 mg/L.
- Mean HPO₄ concentrations in the Tollcross Burn of 0.08 mg/L versus the AA guideline of 0.069 mg/L.
- Mean NO₃ concentrations in the River Clyde and Tollcross Burn are 7.5 mg/L and 6.4 mg/L respectively, versus the EU AA guideline of 5.7 mg/L (there is no UK standard for NO₃ in surface water).
- The mean Al content in the River Clyde waters is 48 µg/L versus the AA guideline of 15 µg/L for good river status, and is greater than the MAC of 25 µg/L at all the River Clyde

sampling locations, except during the drier period between April and June 2019 and at SW06 and SW10 in February 2019.

- Mean Cu concentrations are 1.26 µg/L in the River Clyde and 1.27 µg/L in the Tollcross Burn versus the AA guideline of 1 µg/L for Tier 1 risk assessment.
- Mean benzo(ghi)perylene and indeno(1,2,3-cd)pyrene contents in the River Clyde are 0.003 µg/L and 0.004 µg/L respectively versus the AA guideline of 0.002 µg/L for these compounds. In the Tollcross Burn, mean concentrations are 0.010 µg/L and 0.015 µg/L respectively.
- Peak benzo(a)pyrene concentrations just above the MAC of 0.1 µg/L are reported in the Tollcross Burn (0.106 µg/L) during heavy rainfall in 2020.

It is not anticipated that the operation of the Glasgow Observatory will cause any substantial change to surface water chemistry in the River Clyde or Tollcross Burn. To help check for this, the initial phase of surface water monitoring presented here has established a pre-operational baseline surface water chemistry dataset over a 14-month period.

The results reveal that the water chemistry of the River Clyde and Tollcross Burn in proximity to the Observatory displays significant temporal variability, related to seasonal/climatic patterns, rainfall and contaminant inputs.

Visual comparison of parameter values and temporal trends observed at River Clyde sampling locations SW03, SW04 and SW05 during/after Observatory borehole construction at the Cuningar Loop between June 2019 and February 2020 show similar ranges to those in the distal control surface waters at SW06 and SW10 where no drilling was taking place. Additionally, parameter values at SW05 are similar to those reported at the other River Clyde sampling locations during controlled discharges of wastewater to SW05 from borehole cleaning and test pumping. Therefore, there is little evidence of any significant impact on River Clyde water chemistry from either the borehole drilling or wastewater discharges during installation of the Observatory.

From the limited information provided by the current surface water dataset, there is some evidence of shallow groundwater – surface water interaction from the carbon stable isotope data, which suggest that the surface waters are derived from a mixture of soil and shallow carbonate aquifer sources. Shallow groundwater to surface water inputs are evident also from the Cr(VI) results at SW10 and from the possible bank seepage noted at SW03 on the River Clyde.

The current surface water dataset shows little sign of mine water – surface water interaction. For example, there is no evidence of acid mine drainage impact on surface water quality. However, it is only once mine water chemistry monitoring data are generated by the UKGEOS Glasgow project that surface water – mine water relationships can be explored using possible mine water indicator parameters such as stable isotopes, pH, Eh, DO, SEC, SO₄, Fe and Mn.

Appendix 1 Analytical Methods

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

A.1 INORGANIC ANALYSIS

Surface water samples were sent to the BGS Inorganic Geochemistry Laboratories for:

- Major/minor cation and trace element analysis by inductively coupled plasma mass spectrometry (ICP-MS),
- Major and minor anion analysis by ion chromatography (IC),
- Chromium (VI and III) speciation by high performance liquid chromatography (HPLC)-ICP-MS

A.1.1 Major/minor cation and trace element analysis by ICP-MS

A.1.1.1 INSTRUMENTATION

The determination of major/minor cations and trace elements in surface water samples was carried out using an Agilent 8900 series quadrupole ICP-MS with an octopole reaction system (ORS), in combination with an autosampler. The system was controlled by a computer through dedicated software (Agilent MassHunter), which also controlled the autosampler.

A.1.1.2 METHODOLOGY

The instrument was calibrated at the beginning of every analytical run using at least three standards and a laboratory blank for each trace element and three standards and a laboratory blank for major cations. Calibration ranges for the elements determined are summarised in Table A1.1. A mixed internal standard solution containing scandium (Sc), germanium (Ge), rhodium (Rh), indium (In), tellurium (Te), rhenium (Re) and iridium (Ir) was added to the samples at a fixed ratio of approximately 1:10 via a T-piece. Any suppression of the instrument signal caused by the matrix is corrected by the software using the response of an internal standard.

A.1.1.3 DATA QUALITY CONTROL

Multi-element quality control (QC) check standards, containing the trace elements of interest (c. 5 µg/L) and separate major element standards at varying element concentration were analysed at the start and end of each run and after no more than every 30 samples. Quality control data are assessed using Shewhart Charts. Accuracy was monitored also by regular participation in the Aquacheck inter-laboratory proficiency testing scheme for waters, in which approximately 350 laboratories participate worldwide.

Each analytical run is independently verified by a different analyst, including post processing of the data for drift, dilution and collation.

The method is fully accredited by UKAS to the requirements of BS EN ISO/IEC 17025:2017 and the validation report details performance at accreditation (Barlow et al. 2018). Run-specific detection limits (LLD) were calculated as five times the standard deviation of the 1% nitric plus 0.5% hydrochloric acid laboratory blanks inserted at regular intervals during the analysis. Longer term method LLD obtained during method validation were calculated based on 4.65 times the total standard deviation of 20 laboratory blank samples. The limit of quantification (LOQ) is a conservative value, approximately 10 times the standard deviation of the same blanks. Measurement uncertainties are defined in Barlow et al. (2018). Table A1.2 outlines the long term LLD and LOQ for the method.

Repeat measurements of the standards and the analytical replicate results showed good precision of the data with relative standard deviation (RSD) of $\leq 5\%$, except where values were

close to the LLD or present in low concentration. This affected the following analytes, which should be treated with caution: beryllium (Be), cadmium (Cd), lithium (Li), lead (Pb), vanadium (V), uranium (U) and zinc (Zn). The RSD results for some of the lighter elements including aluminium (Al), silicon (Si) and titanium (Ti) were marginally higher (RSD 6-8%), probably as a result of tuning the ICP-MS to optimise heavier elements. This is normal and a necessary compromise.

Accuracy was assessed by comparison of the measured results for analytical QC standards with the accepted or target values. The percentage recovery of each QC check standard was calculated as $((\text{mean of measured values} \div \text{target value}) \times 100)$. All recoveries were $100 \pm 5-6\%$, except where element concentrations were close to the LLD or present in low abundance for Be, Cd, Mo, V and Zn; or conversely in very high concentration (Si, recovery 90%), and these results should be treated with caution.

Assessment of field blank Type 1 ultrapure (UP) water samples demonstrated the robustness of the sampling and analytical methodology with cation values generally below or very close to the long-term LOQ. However, Zn contents were above the LOQ in nine out of 28 of the field blank samples. Therefore, the Zn results should be treated with caution as there may be some contamination from the sample containers. This is a known problem with Zn, even using trace-element free sample bottles (Reimann et al. 2007).

Results for field duplicate samples showed good robustness of the sampling method, with acceptable variability between sample-pairs ($\text{RSD} \leq 20\%$) with the exception of cerium (Ce), erbium (Er), europium (Eu), lanthanum (La), gadolinium (Gd), samarium (Sm), yttrium (Y), ytterbium (Yb), tin (Sn), Cd and Pb where concentrations were close to the LOQ. Therefore, these results should be treated with caution. Cadmium, manganese (Mn) and Zn show more variability between some sample pairs, again in some cases due to low concentrations, even though the values are above the LOQ, so these data should be treated with care also (Table A2.1, Appendix 2).

Table A1.1 Calibration ranges for major/minor cations and trace elements determined by ICP-MS

Element	Isotope	Units	Top Calibration Std	Element	Isotope	Units	Top Calibration Std
Li	7	µg/L	4000	Ag	107	µg/L	100
Be	9	µg/L	100	Cd	111	µg/L	100
B	11	µg/L	4000	Sn	118	µg/L	100
Na	23	mg/L	400	Sb	121	µg/L	100
Mg	24	mg/L	40	Cs	133	µg/L	100
Al	27	µg/L	1000	Ba	137	µg/L	1000
Si	28	µg/L	20 000	La	139	µg/L	100
P	31	mg/L	20	Ce	140	µg/L	100
S	34	mg/L	400	Pr	141	µg/L	100
K	39	mg/L	40	Nd	145	µg/L	100
Ca	42	mg/L	200	Sm	147	µg/L	100
Ti	47	µg/L	100	Eu	153	µg/L	100
V	51	µg/L	100	Gd	157	µg/L	100
Cr	52	µg/L	100	Tb	159	µg/L	100
Mn	55	µg/L	1000	Dy	163	µg/L	100
Fe	56	µg/L	4000	Ho	165	µg/L	100
Co	59	µg/L	100	Er	166	µg/L	100
Ni	60	µg/L	100	Tm	169	µg/L	100
Cu	63	µg/L	100	Yb	172	µg/L	100
Zn	66	µg/L	1000	Lu	175	µg/L	100
Ga	71	µg/L	100	Hf	178	µg/L	100
As	75	µg/L	100	Ta	181	µg/L	100
Se	78	µg/L	100	W	184	µg/L	100
Rb	85	µg/L	100	Tl	205	µg/L	100
Sr	88	µg/L	4000	Pb	208	µg/L	100
Y	89	µg/L	100	Bi	209	µg/L	100
Zr	90	µg/L	100	Th	232	µg/L	100
Nb	93	µg/L	100	U	238	µg/L	100
Mo	95	µg/L	100				

Std: standard

Table A1.2 Long-term measurement and analytical limits of detection and limits of quantification.

Symbol	Parameter	Units	LLD	LOQ	Analytical Method
Field Parameters:					
DO	Dissolved oxygen	mg/L	0.1	NA	Meter
Eh	Redox potential (Corrected)	mV	0.1	NA	Meter
Field-HCO ₃	Field bicarbonate	mg/L	1	NA	Titration
pH	pH	log [H ⁺]mol/L	0.01	NA	Meter
T	Temp	°C	0.1	NA	Meter
SEC	Conductivity	µs/cm	0.1	NA	Meter
Major & Minor Anions:					
Br	Bromide	mg/L	0.01	0.04	IC
Cl	Chloride	mg/L	0.05	0.15	IC
F	Fluoride	mg/L	0.005	0.010	IC
Lab-HCO ₃	Lab bicarbonate	mg/L	5	NA	Lab-Titration
HPO ₄	Orthophosphate	mg/L	0.01	0.03	IC
NO ₂	Nitrite	mg/L	0.005	0.010	IC
NO ₃	Nitrate	mg/L	0.03	0.10	IC
SO ₄	Sulphate	mg/L	0.05	0.20	IC
Major & Minor Cations:					
Ca	Calcium	mg/L	0.3	0.6	ICP-MS
K	Potassium	mg/L	0.04	0.07	ICP-MS
Mg	Magnesium	mg/L	0.003	0.005	ICP-MS
Na	Sodium	mg/L	0.4	0.7	ICP-MS
P-Total	Total Phosphorus	mg/L	0.005	0.020	ICP-MS
S-Total	Total Sulphur	mg/L	0.03	0.06	ICP-MS
Si	Silicon	mg/L	0.04	0.09	ICP-MS
Trace Elements:					
Ag	Silver	µg/L	0.04	0.07	ICP-MS
Al	Aluminium	µg/L	0.6	2	ICP-MS
As	Arsenic	µg/L	0.04	0.08	ICP-MS
B	Boron	µg/L	53	114	ICP-MS
Ba	Barium	µg/L	0.05	0.10	ICP-MS
Be	Beryllium	µg/L	0.08	0.20	ICP-MS
Bi	Bismuth	µg/L	0.08	0.20	ICP-MS
Cd	Cadmium	µg/L	0.005	0.010	ICP-MS
Ce	Cerium	µg/L	0.004	0.007	ICP-MS
Co	Cobalt	µg/L	0.006	0.020	ICP-MS
Cr-Total	Total Chromium	µg/L	0.04	0.07	ICP-MS
Cr(VI)	Chromium VI	µg/L	0.05	NA	HPLC
Cr(III)	Chromium III	µg/L	0.04	NA	HPLC
Cs	Caesium	µg/L	0.04	0.08	ICP-MS
Cu	Copper	µg/L	0.05	0.20	ICP-MS
Dy	Dysprosium	µg/L	0.003	0.007	ICP-MS
Er	Erbium	µg/L	0.003	0.006	ICP-MS
Eu	Europium	µg/L	0.003	0.007	ICP-MS
Fe	Iron	µg/L	0.4	0.80	ICP-MS
Ga	Gallium	µg/L	0.04	0.09	ICP-MS

Table 1.2 cont.

Symbol	Parameter	Units	LLD	LOQ	Analytical Method
Gd	Gadolinium	µg/L	0.005	0.020	ICP-MS
Hf	Hafnium	µg/L	0.006	0.020	ICP-MS
Ho	Holmium	µg/L	0.003	0.006	ICP-MS
La	Lanthanum	µg/L	0.003	0.006	ICP-MS
Li	Lithium	µg/L	7	15	ICP-MS
Lu	Lutetium	µg/L	0.003	0.006	ICP-MS
Mn	Manganese	µg/L	0.2	0.30	ICP-MS
Mo	Molybdenum	µg/L	0.2	0.40	ICP-MS
Nb	Niobium	µg/L	0.01	0.03	ICP-MS
Nd	Neodymium	µg/L	0.005	0.010	ICP-MS
Ni	Nickel	µg/L	0.01	0.03	ICP-MS
Pb	Lead	µg/L	0.02	0.05	ICP-MS
Pr	Praseodymium	µg/L	0.003	0.007	ICP-MS
Rb	Rubidium	µg/L	0.05	0.20	ICP-MS
Sb	Antimony	µg/L	0.04	0.07	ICP-MS
Se	Selenium	µg/L	0.07	0.20	ICP-MS
Sm	Samarium	µg/L	0.005	0.010	ICP-MS
Sn	Tin	µg/L	0.08	0.20	ICP-MS
Sr	Strontium	µg/L	0.2	0.30	ICP-MS
Ta	Tantalum	µg/L	0.006	0.020	ICP-MS
Tb	Terbium	µg/L	0.004	0.008	ICP-MS
Th	Thorium	µg/L	0.03	0.05	ICP-MS
Ti	Titanium	µg/L	0.06	0.20	ICP-MS
Tl	Thallium	µg/L	0.02	0.04	ICP-MS
Tm	Thulium	µg/L	0.003	0.007	ICP-MS
U	Uranium	µg/L	0.009	0.02	ICP-MS
V	Vanadium	µg/L	0.02	0.03	ICP-MS
W	Tungsten	µg/L	0.06	0.02	ICP-MS
Y	Yttrium	µg/L	0.006	0.020	ICP-MS
Yb	Ytterbium	µg/L	0.004	0.009	ICP-MS
Zn	Zinc	µg/L	0.2	0.40	ICP-MS
Zr	Zircon	µg/L	0.009	0.020	ICP-MS
Inorganic Carbon:					
TIC	Total inorganic carbon	mg/L	NA	NA	From CaCO ₃
Organic Parameters:					
NPOC	Non-purgeable organic carbon	mg/L	0.5	NA	Carbon Analyser
Benzo(b)fluoranthene	Polycyclic aromatic hydrocarbons	µg/L	0.001	0.004	HPLC-FD
Benzo(k)fluoranthene		µg/L	0.001	0.003	HPLC-FD
Benzo(a)pyrene (BaP)		µg/L	0.0005	0.0016	HPLC-FD
Benzo(ghi)perylene		µg/L	0.001	0.004	HPLC-FD
Indeno(1,2,3-cd)pyrene		µg/L	0.002	0.005	HPLC-FD
PAH-Total		µg/L	0.005	0.012	HPLC-FD
TPH (C8-C10)	Total petroleum hydrocarbons	mg/L	0.003	0.003	GC-FID
TPH (C10-C40)		mg/L	0.042	0.042	GC-FID
TPH (C8-C40)		mg/L	0.045	0.045	GC-FID

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

A.1.2 Major and minor anion analysis by ion chromatography

A.1.2.1 INSTRUMENTATION

The analysis of the major and minor anions chloride (Cl), bromide (Br), fluoride (F), nitrite (NO₂), nitrate (NO₃), orthophosphate (HPO₄) and sulphate (SO₄) was carried out on a Dionex ICS5000 ion chromatograph system using reagent-free eluent generation and a conductivity detector. Separation is performed with AG19 guard and AS19 high-capacity analytical microbore (2 mm diameter) columns using a typical injection volume of 10 µL. System control and data capture is achieved by a dedicated computer running Dionex Chromeleon Software (currently version 7.2.9).

A.1.2.2 METHODOLOGY

The instrument was calibrated at the beginning of every analytical run using six manually prepared standards. Calibration uses a linear algorithm on all six standards for the major ions (Cl, SO₄, NO₃), but quadratic fits to five standards for F, and four for NO₂, Br, HPO₄. This combination has been demonstrated during method validation to provide the best performance in terms of analytical sensitivity and bias at over typical sample concentration ranges. A laboratory blank sample was analysed at the start of each run with QC samples analysed at the start and end of each run and after no more than every 20 samples.

The longer-term LLD and LOQ are outlined in Table A1.2. The LLD were based on three times the standard deviation of laboratory blank samples whereas the LOQ was calculated as 10 times the standard deviation of the laboratory blanks. The upper calibration limit (UCL) prior to any dilutions, and overall estimated expanded uncertainty, based on a coverage factor of 2, are given in Table A1.3.

A calibration drift check standard was run at the end of each run and after no more than every 50 samples. The analysis followed a pre-programmed schedule and the software collected the data with peaks identified by retention time.

For higher total concentration loads, the analytical column can become overloaded, causing poor peak shapes, variable retention times and thus unreliable results. To overcome this problem, more concentrated solutions were diluted. In addition, where necessary, sample dilution was also used to bring the analyte concentration within the concentration range covered by the standards.

Table A1.3 Upper calibration limits for ion chromatography analysis.

	Br	Cl	F	HPO ₄	NO ₂	NO ₃	SO ₄
UCL (mg/L)	1.25	100	2.5	2.5	1.25	60	50
Uncertainty (%)	20	10	20	20	20	20	10

UCL: upper calibration limit

A.1.2.3 DATA QUALITY CONTROL

The method is fully accredited by UKAS to the requirements of BS EN ISO/IEC 17025:2017 and the validation report details performance at accreditation (Harrison et al. 2012). Most anions are stable in solution for an appreciable length of time, and certainly within the period between sampling and analysis. Nitrite, HPO₄ and, to a lesser extent, NO₃, may, however, be modified by microbial activity. To minimize this, the samples were filtered to 0.45 µm and stored in a refrigerator between 1 and 5°C. The laboratory also makes every effort to carry out analyses as soon as possible after receipt.

Repeat measurements of the QC standards and the analytical replicate results showed good precision of the data with RSD of ≤ 5%. Similarly, the measured results for analytical QC standards demonstrated good recovery (100 ± 5%), relative to the target values, with the exception of F (93%) at low concentration in one standard.

Assessment of field blank UP water samples demonstrated the robustness of the sampling and analytical methodology with anion values below the long-term LOQ.

Results for field duplicate samples also showed good robustness of the sampling method, with acceptable variability between sample-pairs ($RSD \leq 20\%$), with the exception of HPO_4 , where concentrations were close to the LOQ. Fluoride, HPO_4 and NO_2 showed more variability between some sample pairs, again likely due to low concentrations, even though the values were above the LOQ. In the case of HPO_4 and NO_2 this may reflect post-collection microbial activity also, so these data should be treated with caution (Table A2.1, Appendix 2).

As a further check on the quality of the inorganic water chemistry analysis, the ionic balance of the samples was assessed. The ionic balance is based on the principle of electrical neutrality in natural water, meaning that the equivalent concentration of positively charged cations is equal to the concentration of negatively charged anions. Therefore, the sum in milliequivalents of major cations and anions should be nearly equal, adding to approximately 0 (Hem 1992). The ionic balance was $\pm 5\%$ for all the surface water samples, demonstrating the robustness of the analytical methods.

A.1.3 Chromium speciation analysis by high performance liquid chromatography (HPLC) – ICP-MS

A.1.3.1 INSTRUMENTATION

The determination of trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)) was carried out using an Agilent 1260 Infinity II Bio-Inert High-Performance Liquid Chromatography (HPLC) system coupled to an Agilent 8900 ICP-MS.

A.1.3.2 METHODOLOGY

The HPLC mobile phase (40 mM ammonium nitrate (NH_4NO_3)/50 mM TRIS Buffer/5 mM ethylenediaminetetraacetic acid-diammonium salt (NH_4 -EDTA), corrected to pH 7.0 with aqueous ammonia) was prepared fresh on the day of analysis. The analytical column (Hamilton® PRP-X100) was conditioned with the mobile phase at a flow rate of 1.2 mL/min until the baseline for m/z 52 was stable. The outflow from the analytical column was connected directly to the nebuliser of the ICP-MS using a length of PEEK tubing. The samples were diluted two-fold with 50 mM NH_4 -EDTA (pH 10.0) and placed in an oven at 70°C to complex the Cr(III) in the sample and allow retention on the anion-exchange column as a Cr(III)-EDTA complex; calibration standards at 1, 10 and 50 µg/L were prepared in the same matrix and subjected to the same complexation method. Analysis was carried out by ICP-MS.

Each analytical run was independently verified by a different analyst, including post processing of the data for dilution and collation.

A.1.3.3 DATA QUALITY CONTROL

Data quality was verified through the use of QC check standards containing both species of Cr at 5 µg/L, analysed at the start and end of the analytical run and after no more than every 10 samples. The percentage recoveries of each QC check standard were $100 \pm 5\%$ demonstrating good accuracy of the technique. Similarly, analytical replicate measurements showed good precision of the data ($RSD \leq 5\%$) (Table A1.4). The efficiency of the chromatographic separation was assessed through calculating the recovery of the sum of the measured Cr species against the total chromium (Cr-Total) measured in the FA sample. All recoveries were $100 \pm 15\%$ except in cases where either the Cr-Total or Cr species were below the detection limit. However, in samples GF02-05, GF02-08, GF09-01, GF09-08, GF11-01, GF12-07, GF14-02 values are above the LLD but have recoveries of $<85\%$. This could be due to the efficiency of the NH_4 -EDTA complexation in the presence of competing cations, or the presence of organic acid complexes of Cr, which are not resolved through the chromatographic setup, and results should be treated with caution. The lower limits of detection were reported as 0.05 (Cr(VI)) and 0.04 (Cr(III)) µg/L (Table A1.4).

Assessment of field blank UP water samples demonstrated the robustness of the sampling and analytical methodology with Cr(VI and III) values below the long-term LOQ.

Results for field duplicate samples showed good robustness of the sampling method also, with acceptable variability between sample-pairs ($RSD \leq 20\%$), with the exception of Cr(VI) where values were close to the LLD. Trivalent-Cr showed more variability between some sample pairs, again likely due to low concentrations, or the issues with efficiency of the NH_4 -EDTA complexation described earlier in this Section, so these data should be treated with care also (Table A2.1, Appendix 2).

The determination of Cr(VI and III) by the BGS laboratories is not UKAS accredited, but is an established method (Hamilton et al. 2020).

Table A1.4 Results for quality control standards included in the Cr(VI and III) speciation HPLC-ICP-MS analysis.

Standard	Number of Measurements	Results	Cr(VI) µg/L	Cr(III) µg/L
QC1	51	Target value	5	5
		BGS mean	5.10	5.05
		% RSD	3	3
		% recovery	102	101

RSD: relative standard deviation

A.1.4 Laboratory total alkalinity and total inorganic carbon analysis

A.1.4.1 INSTRUMENTATION

This method describes the UKAS-accredited BGS laboratory determination of alkalinity. The analytes determined are total alkalinity (expressed in terms of bicarbonate ($lab-HCO_3$)). Determination of alkalinity speciation (hydroxide, carbonate and bicarbonate) is outside the scope of accreditation.

Alkalinity is measured titrimetrically by monitoring the change in pH of the solution as a function of the volume of titrant added on a Radiometer TIM 865 TitraLab with accompanying PC software, TitraMaster 85 Data Collector.

A.1.4.2 METHODOLOGY

Calibration of the pH electrodes was performed using commercial high-resolution pH 4 and pH 10 buffers (Inorganic Ventures) by transferring a subsample of each buffer from the stock to 30 mL HDPE bottles and allowing them to equilibrate to approximately room temperature for at least 30 minutes prior to analysis.

Titration was performed using 0.005M sulphuric acid prepared from VWR Prolab Convolve Normadose 0.1N solution made up to volume with freshly prepared 18 MOhm deionised water in a volumetric flask according to the manufacturer's instructions.

Sample bottles were allowed to equilibrate to approximately room temperature for at least 30 minutes prior to analysis. Both electrodes and the burette dispenser were rinsed with 18 MOhm deionised water and dried by gently wiping with a clean tissue before commencing analysis and between each new sample. Neat sample (2 mL) was pipetted into a plastic receptacle to measure the pH. Alkalinity was measured by entering the volume of sample into the software (i.e. 1 or 2 mL) when prompted before commencing the titration by placing the electrodes and the burette dispenser into the plastic receptacle and commencing analysis.

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

A.1.4.3 DATA QUALITY CONTROL

To allow the QC to be measured before each sample run, a QC standard for the measurement of alkalinity was made up from a 200 mg/L bicarbonate solution, prepared from 0.275 ± 0.001 g (VWR Prolab) sodium bicarbonate (NaHCO_3), made up to volume with freshly prepared 18 MOhm deionised water in a 1000 mL volumetric flask. The pH QC check standard is a commercially purchased Merck® high resolution pH 7 buffer independent of that used for calibration.

The limit of detection for laboratory total alkalinity was 5 mg/L (Table A1.2). The percentage recoveries for the QC check standard were $100 \pm 5\%$ demonstrating good accuracy of the method. Analytical replicate measurements showed good precision of the data ($\text{RSD} \leq 5\%$) (Table A1.5).

Results for field duplicate samples showed good robustness of the sampling method also, with acceptable variability between sample-pairs ($\text{RSD} \leq 20\%$) (Table A2.1, Appendix 2).

As a further check on data quality the field and laboratory alkalinity measurements were compared. These showed broad agreement with $\text{RSD} \leq 20\%$ with the exception of sample GF04-07 ($\text{RSD} 41\%$), where the disparity between field- and lab- HCO_3 reflects inaccuracy of the field- HCO_3 measurement. This is possibly due to light conditions affecting detection of the indicator colour change at the time of sampling, 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 this sample should be treated with caution.

Table A1.5 Results for quality control standards included in the laboratory total alkalinity/bicarbonate analysis.

Standard	Number of Measurements	Results	HCO_3 mg/L
QC200	53	Target	200
		BGS mean	200
		% RSD	1
		% recovery	100

RSD: relative standard deviation

A.2 ORGANIC PARAMETER ANALYSIS

A.2.1 Non-purgeable organic carbon analysis by carbon analyser

A.2.1.1 INSTRUMENTATION

The analysis of non-purgeable organic carbon (NPOC) was carried out on a Shimadzu TOC-L CPH total organic carbon analyser fitted with an ASI-L autosampler, utilising a VWR Peak40-10-40 TOC gas generator as a carbon-free air supply at the BGS Inorganic Geochemistry Laboratories.

A.2.1.2 METHODOLOGY

The instrument was calibrated across a single concentration range: 0 – 50 mg/L using six organic carbon (OC) standards for the calibration (1, 2.5, 5, 10, 25 and 50 mg/L). Quality control standards containing 5, and 25 mg/L OC were analysed at the beginning and end of each run and after not more than 10 unknown samples. Samples exceeding the top calibration standard were diluted to bring them into the calibration range. Results were calculated automatically and stored in data files by the instrument software.

A.2.1.3 DATA QUALITY CONTROL

The method is fully accredited by UKAS to the requirements of BS EN ISO/IEC 17025:2017.

The laboratory makes every effort to analyse sample promptly after receipt in order to minimize the possibility of sample degradation, although evidence suggests that samples are stable for an extended time if the sample is filtered to 0.45 µm stored between 1 and 5°C. Stability checks using repeat analysis of stored samples over a several months period showed that NPOC concentrations in samples, which had been correctly filtered and stored were stable within analytical error during this time. The method is essentially interference free, as any inorganic carbon in the sample is removed prior to analysis by the instrument, and any OC is fully converted to carbon dioxide (CO₂) during the oxidation procedure. To all intents and purposes, NPOC data are equivalent to dissolved organic carbon (DOC).

The overall expanded uncertainty was estimated to be 10%; based on an average value across all validation samples (Kelly et al., 2018). Results for QC standards showed good accuracy (recoveries 100 ± 5%) and precision (RSD < 5%) of the data. The LLD reported for NPOC was 0.5 mg/L (Table A1.2).

Assessment of field blank UP water samples demonstrated that 17 of 28 measurements were above the long-term LOQ. However, this reflected problems reported by the laboratory supplying UP, with carbon removal from their UP system during the sampling period, rather than an issue with contamination due to the sampling or analytical methods.

Results for field duplicate samples also showed good robustness of the sampling method, with acceptable variability between sample-pairs (RSD ≤ 20%) (Table A2.1, Appendix 2).

A.2.2 Total petroleum hydrocarbon analysis by GC-FID

A.2.2.1 METHODOLOGY

Total petroleum hydrocarbon (TPH) concentrations were determined by gas chromatography flame ionisation detector (GC-FID) at the Scottish Water testing laboratory. A known volume of sample was acidified, then extracted by the use of liquid extraction, using a hexane extraction solvent with a known level of internal standard in it. Once extracted, the extract was centrifuged, the excess water was removed, then the extract was dried using anhydrous sodium sulphate, and florisil was added to clean it. A known volume of this extract was concentrated by evaporation. The extract is analysed by gas chromatography using a FID. Quantification was carried out using the combined areas of hydrocarbon peaks present within each hydrocarbon range to give separate 'TPH C8 – C10' and 'TPH C10 – C40' contents, the sum of which is expressed as 'TPH C8 - C40'.

A.2.2.2 DATA QUALITY CONTROL

Between February and December 2019, LLD were reported with the data (based on three times the standard deviation of laboratory blanks), but from January 2020 onwards, the more precautionary LOQ (based on 10 times the standard deviation of laboratory blanks) were stated, due to a change in legislation affecting Scottish Water laboratory operating protocols (Table A1.2). Analysis was carried out following UKAS accredited method ISO 17025. However, UKAS accreditation was withheld from TPH analysis dating from March 2019 onwards due to issues with method performance. None-the-less, results for QC check standards and repeat measurements show good accuracy (recovery 100 ± 5%) and precision (RSD < 10%) of the data (Table A1.6), given that a significant proportion of the data are close to or below the detection limit/limit of quantification.

Assessment of field blank UP samples demonstrated the robustness of the sampling and analytical methodology with TPH values below the long-term LOQ.

Results for field duplicate samples showed good robustness of the sampling method also, with acceptable variability between sample-pairs (RSD ≤ 20%) except where values were close to the LOQ. Therefore, these results should be treated with caution (Table A2.1, Appendix 2).

Table A1.6 Results for quality control standards included in the GC-FID TPH analysis.

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

RSD: relative standard deviation

A.2.3 Polycyclic aromatic hydrocarbon analysis by HPLC-FD

A.2.3.1 METHODOLOGY

Polycyclic aromatic hydrocarbon (PAH) contents were analysed using high performance liquid chromatography fluorescence detection (HPLC-FD) at the Scottish Water testing laboratory. Concentrations of the PAH indicator compounds benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene (BaP), benzo(ghi)perylene, indeno(1,2,3-cd)pyrene and PAH-Total were determined in the surface water samples as follows. A known volume of sample was extracted by the use of liquid extraction using pentane with a known level of internal standard in it. The resulting extract was dried using anhydrous sodium sulphate before being evaporated to dryness. The extract was reconstituted to a volume of 0.5 mL in acetonitrile. The prepared extract was analysed using HPLC with programmable fluorescence detection. The response for the sample with respect to the internal standard was compared with those from extracted standards.

A.2.3.2 DATA QUALITY CONTROL

Between February and December 2019, LLD were reported with the data (based on three times the standard deviation of laboratory blanks), but from January 2020 onwards, the more precautionary LOQ (based on 10 times the standard deviation of laboratory blanks) were stated, due to a change in legislation affecting Scottish Water laboratory operating protocols (Table A1.2). Analysis was carried out according to UKAS accredited method ISO 17025. However, UKAS accreditation was withheld from PAH analysis of samples GF09-02 and GF09-06 from the October 2019 sampling round, due to issues with method performance. The results for QC check standards and repeat measurements show good accuracy (recovery $100 \pm 10\%$) and precision (RSD $< 10\%$) of the data (Table A1.7), given that a significant proportion of the data are close to or below the detection limit/limit of quantification. The results for benzo(k)fluoranthene and benzo(ghi)perylene show poorer recoveries ($< 90\%$) again because the majority of the data are below the detection limit and should be treated with caution.

Assessment of field blank UP water samples demonstrated the robustness of the sampling and analytical methodology with PAH values below the long-term LOQ.

Results for field duplicate samples showed good robustness of the sampling method also, with acceptable variability between sample-pairs (RSD $\leq 20\%$) with the exception of benzo(b)fluoranthene, benzo(k)fluoranthene, BaP, benzo(ghi)perylene, indeno(1,2,3-cd)pyrene and PAH-Total, where concentrations were close to the LOQ. Therefore, these results should be treated with caution (Table A2.1, Appendix 2).

Table A1.7 Results for quality control standards included in the HPLC-FD PAH analysis.

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

RSD: relative standard deviation

A.3 STABLE ISOTOPE ANALYSIS

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

A.3.1 Carbon stable isotope analysis

A.3.1.1 METHODOLOGY

After precipitation of the bicarbonate using 1M BaCl_2 + 0.9M NaOH solution, the resultant barium carbonate was filtered, washed with deionised water three times and dried at 40°C and ground in agate. The carbonate was reacted with anhydrous phosphoric acid *in vacuo* overnight at a constant 25°C. The CO_2 liberated was separated from water vapour under vacuum and collected for analysis. Measurements were made on a VG Optima isotope ratio mass spectrometer (IRMS).

Samples from rounds GF09 (October 2019) and GF12 (January 2020) had low carbonate concentrations, too small to run by the standard analysis. Therefore, these samples underwent a multiprep method as follows. Approximately 50 – 100 μg of carbonate were used for isotope analysis using an IsoPrime dual inlet IRMS plus Multiprep device. Samples were loaded into glass vials and sealed with septa. The automated system evacuated the vials and delivered anhydrous phosphoric acid to the carbonate at 90°C. The evolved CO_2 was collected for 15 minutes, cryogenically cleaned and passed to the mass spectrometer. The calcite-acid fractionation factor applied to the gas values was 1.00798 (Kim et al. 2007; McCrea 1950; Rosenbaum and Sheppard 1986; Sharma and Clayton 1965).

A.3.1.2 DATA QUALITY CONTROL

Isotope values ($\delta^{13}\text{C}$) are reported as per mil. (‰) deviations of the isotopic ratio ($^{13}\text{C}/^{12}\text{C}$) calculated to the Vienna Pee Dee Belemnite (VPDB) scale using within-run laboratory standards (MCS, for all runs and KCM for the Multiprep analysis). These within-run standards were calibrated against NBS-19 - the International Atomic Energy Authority (IAEA) certified reference material (CRM) that defines the VPDB scale. A secondary in-house standard (CCS) was also run to verify the correction procedure. The Craig (1957) correction was applied to account for ^{17}O interference.

For the Multiprep analysis, due to the long run time of 21 hours, a drift correction was applied across the run, calculated using the standards that bracket the samples. The average analytical reproducibility of the standard calcite (KCM) was < 0.1‰ for $\delta^{13}\text{C}$.

Repeat measurements carried out during the sample runs on samples and standards show that overall analytical reproducibility for these samples was typically better than 0.1‰ for $\delta^{13}\text{C}$ (1σ)

(RSD ≤ 6%). Similarly, the measured results for the secondary in-house standard (CCS) demonstrated good recovery (100 ±5 %) relative to the preferred value (Table A1.8).

Results for field duplicate samples also showed good robustness of the sampling method, with acceptable variability between sample-pairs (RSD ≤ 20%) (Table A2.1, Appendix 2).

Table A1.8 Results for quality control standards included in the $\delta^{13}\text{C}$ stable isotope IRMS analysis.

$\delta^{13}\text{C}$ ‰ VPDB	MCS primary lab standard	KCM standard calcite	CCS secondary lab standard
Number of measurements	52	24	31
NIGL mean	-0.7	2.0	-22.4
% RSD	6	3	<1
In-house preferred value			-22.3
% recovery			100

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

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

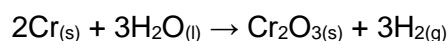
CCS: in-house secondary laboratory standard

RSD: relative standard deviation

A.3.2 Deuterium stable isotope analysis

A.3.2.1 METHODOLOGY

Samples were analysed using a continuous flow EuroPyrOH-IsoPrime IRMS with liquid autosampler. Each sample was injected (0.5 μL) into a heated septa-sealed injector port (160°C). The resulting water vapour was flushed through into a chromium-packed reactor (980°C) by helium carrier gas. The chromium reduces the water, resulting in the quantitative conversion to hydrogen gas:



The hydrogen gas entered the IRMS generating simultaneous peaks for H_2 at m/z 2 and hydrogen deuteride (HD) at m/z 3. The peaks were integrated and corrected for H^{3+} contribution, and the areas compared to those of a reference H_2 pulse introduced prior to the arrival of the sample peak. The data are reported as δ -values ‰ against the Vienna Standard Mean Ocean Water (VSMOW) reference material.

A.3.2.2 DATA QUALITY CONTROL

Each sample was analysed in triplicate, and the system can perform an automated run on up to 72 samples at a time. In each run, two laboratory standards (CA-HI and CA-LO) were analysed several times. The value of these laboratory standards was accurately determined by comparison with international calibration and CRM (VSMOW2, SLAP2 and GISP); hence, the $\delta^2\text{H}$ ratios (versus VSMOW2) of the unknown samples can be calculated. Errors were typically +/- 1.0 per mil. Repeat measurements show good precision of the data (RSD ≤ 5%) (Table A1.9).

Results for field duplicate samples also showed good robustness of the sampling method, with acceptable variability between sample-pairs (RSD ≤ 20%) (Table A2.1, Appendix 2).

Table A1.9 Results for repeat measurements on quality control standards included in the IRMS $\delta^2\text{H}$ stable isotope analysis.

$\delta^2\text{H}$ VSMOW2 (‰)	CA-LO calibration IAEA CRM SMOW2/SLAP	CA-HI calibration IAEA CRM SMOW2/SLAP
Number of measurements	38	46
NIGL mean	-311.1	-48.5
% RSD	<1	2

RSD: relative standard deviation

A.3.3 Oxygen stable isotope analysis

A.3.3.1 METHODOLOGY

Oxygen isotope ($\delta^{18}\text{O}$) measurements were made using the CO_2 equilibration method with an IsoPrime 100 IRMS plus Aquaprep device. 90 samples (200 μL of water) were loaded into Labco Limited® exetainers and placed in the heated sample tray at 40°C . The exetainers were then evacuated to remove atmosphere, then flushed with CO_2 and left to equilibrate for between 12 (first sample) and 37 (last sample) hours. Each individual gas sample was then admitted to the cryogenic water trap where any water vapour was removed. The dry sample gas was then expanded into the dual inlet mass spectrometer for analysis. The data are reported as δ -values ‰ against the VSMOW reference material.

A.3.3.2 DATA QUALITY CONTROL

In each run, two laboratory standards (CA-HI and CA-LO) were analysed several times. The value of these laboratory standards was determined by comparison with international calibration and reference materials (VSMOW2, SLAP2 and GISP) and the $^{18}\text{O}/^{16}\text{O}$ ratios (versus VSMOW2) of the unknown samples were calculated and are expressed in delta units, $\delta^{18}\text{O}$ (‰, parts per mil.).

Repeat measurements show good precision of the data ($\text{RSD} \leq 5\%$) (Table A1.10).

Results for field duplicate samples show good robustness of the sampling method also, with acceptable variability between sample-pairs ($\text{RSD} \leq 20\%$) (Table A2.1, Appendix 2).

Table A1.10 Results for repeat measurements on quality control standards included in the IRMS $\delta^{18}\text{O}$ stable isotope analysis.

$\delta^{18}\text{O}$ ‰ VSMOW2	CA-LO calibration IAEA CRM SMOW2/SLAP	CA-HI calibration IAEA CRM SMOW2/SLAP
Number of measurements	58	70
NIGL mean	-39.3	-7.3
% RSD	<1	<1

RSD: relative standard deviation

Appendix 2 Surface Water Chemistry Analytical Data Tables

Table A2.1 Results for surface water field duplicate analyses

Field Duplicate		DupA	DupB	Mean	RSD	DupA	DupB	Mean	RSD	DupA	DupB	Mean	RSD	DupA	DupB	Mean	RSD
Sample ID		GF01-03	GF01-07		%	GF02-03	GF02-07		%	GF03-05	GF03-08		%	GF04-08	GF04-01		%
Sample Round		1	1			2	2			3	3			4	4		
UKGEOS Location		SWTC	SWTC			SW04	SW04			SW03	SW03			SWTC	SWTC		
Analyte	Units																
Field Parameters																	
pH	log [H+]mol/L	8.15	8.15	8.15	<1	7.69	7.69	7.69	<1	7.54	7.58	7.56	<1	8.07	8.09	8.08	<1
Temp	°C	8.0	8.0	8.0	<1	8.9	8.9	8.9	<1	15.1	16.2	15.7	5	12.1	12.7	12.4	3
Eh	mV	438	438	438	<1	493	493	493	<1	310	319	314	2	345	356	351	2
DO	mg/L	10.1	10.1	10.1	<1	11.3	11.3	11.3	<1	9.2	10.1	9.63	6	7.8	8.1	7.93	2
SEC	µs/cm	1026	1026	1026	<1	267	267	267	<1	451	451	451	<1	853	846	849	1
Field-HCO ₃	mg/L	245	245	245	<1	63	65	64	2	153	151	152	1	338	342	340	1
Major & Minor Anions																	
Br	mg/L	<0.1	<0.1	nd	nd	0.03	0.03	0.03	4	0.05	0.06	0.05	9	0.12	0.14	0.13	7
Cl	mg/L	138	138	138	<1	31	31	31	<1	34	35	35	2	61	60	60	1
F	mg/L	0.071	0.072	0.072	1	0.038	0.030	0.034	18	0.044	0.048	0.046	6	0.098	0.116	0.107	12
Lab-HCO ₃	mg/L	305	294	300	3	69	66	67	3	149	152	150	2	358	354	356	1
HPO ₄	mg/L	<0.1	<0.1	nd	nd	0.22	0.10	0.16	51	0.12	0.03	0.08	81	<0.1	<0.1	nd	nd
SO ₄	mg/L	58	58	58	<1	18	18	18	<1	41	41	41	1	62	62	62	<1
NO ₂	mg/L	<0.05	<0.05	nd	nd	0.02	0.02	0.02	<1	0.44	0.47	0.45	4	0.12	0.06	0.09	45
NO ₃	mg/L	7.7	7.8	7.8	1	7.0	7.3	7.1	3	13.0	13.5	13.3	3	4.1	4.6	4.4	7
Major & Minor Cations																	
Ca	mg/L	72	72	72	<1	22	22	22	1	45	46	45	1	73	75	74	1
K	mg/L	8.8	8.8	8.8	<1	2.1	2.1	2.1	<1	5.2	5.2	5.2	1	11	11	11	1
Mg	mg/L	22	22	22	1	6	6	6	1	14	14	14	<1	26	26	26	2
Na	mg/L	99	99	99	<1	21	21	21	<1	28	29	28	2	62	62	62	1
P-Total	mg/L	0.035	0.033	0.034	4	0.087	0.086	0.087	1	0.090	0.084	0.087	5	0.070	0.067	0.069	3
S-Total	mg/L	22	22	22	1	7	7	7	<1	15	15	15	1	21	21	21	1
Si	mg/L	4.34	4.30	4.32	1	3.14	3.15	3.15	<1	0.89	0.93	0.91	3	3.61	3.78	3.70	3
Trace Elements																	
Ag	µg/L	<0.04	<0.04	nd	nd	<0.04	<0.04	nd	nd	<0.04	<0.04	nd	nd	<0.04	<0.04	nd	nd
Al	µg/L	8	7	7	7	41	40	41	2	16	15	15	2	8	9	9	7
As	µg/L	0.25	0.26	0.26	3	0.25	0.24	0.25	3	0.38	0.40	0.39	4	2.22	2.20	2.21	1

RSD: relative standard deviation nd: no data

Table A2.1 cont.

Field Duplicate		DupA	DupB	Mean	RSD	DupA	DupB	Mean	RSD	DupA	DupB	Mean	RSD	DupA	DupB	Mean	RSD
Sample ID		GF01-03	GF01-07		%	GF02-03	GF02-07		%	GF03-05	GF03-08		%	GF04-08	GF04-01		%
Sample Round		1	1			2	2			3	3			4	4		
UKGEOS Location		SWTC	SWTC			SW04	SW04			SW03	SW03			SWTC	SWTC		
Analyte	Units																
Trace Elements																	
B	µg/L	87	87	87	<1	<53	<53	nd	nd	58	62	60	5	102	110	106	5
Ba	µg/L	59	58	58	1	63	63	63	<1	100	101	100	<1	48	49	49	2
Be	µg/L	<0.08	<0.08	nd	nd	<0.08	<0.08	nd	nd	<0.08	<0.08	nd	nd	<0.08	<0.08	nd	nd
Bi	µg/L	<0.08	<0.08	nd	nd	<0.08	<0.08	nd	nd	<0.08	<0.08	nd	nd	<0.08	<0.08	nd	nd
Cd	µg/L	0.02	0.01	0.02	25	0.01	0.01	0.01	11	<0.006	0.01	0.01	nd	0.01	0.01	0.01	34
Ce	µg/L	0.01	0.00	0.00	16	0.14	0.14	0.14	1	0.01	0.01	0.01	8	<0.004	<0.004	nd	nd
Co	µg/L	0.23	0.23	0.23	<1	0.16	0.17	0.17	3	0.30	0.30	0.30	1	0.19	0.18	0.19	4
Cr-Total	µg/L	0.15	0.14	0.15	5	0.48	0.49	0.49	1	0.28	0.25	0.27	8	0.16	0.18	0.17	8
Cr(VI)	µg/L	0.14	0.15	0.15	5	0.28	0.28	0.28	<1	<0.05	<0.05	nd	nd	0.09	0.11	0.10	14
Cr(III)	µg/L	<0.04	<0.04	nd	nd	0.15	<0.04	nd	nd	<0.04	<0.04	nd	nd	0.06	0.06	0.06	<1
Cs	µg/L	<0.04	<0.04	nd	nd	<0.04	0.05	nd	nd	0.13	0.15	0.14	10	0.06	0.05	0.06	13
Cu	µg/L	2.02	1.94	1.98	3	1.23	1.19	1.21	2	0.91	0.87	0.89	3	1.07	1.03	1.05	3
Dy	µg/L	0.004	<0.003	nd	nd	0.02	0.03	0.03	17	<0.003	<0.003	nd	nd	<0.003	<0.003	nd	nd
Er	µg/L	<0.003	0.003	nd	nd	0.02	0.01	0.01	5	<0.003	<0.003	nd	nd	<0.003	<0.003	nd	nd
Eu	µg/L	<0.003	<0.003	nd	nd	0.01	0.01	0.01	11	<0.003	<0.003	nd	nd	<0.003	<0.003	nd	nd
Fe	µg/L	13	14	14	3	215	214	214	<1	319	354	336	7	20	15	17	20
Ga	µg/L	<0.06	<0.06	nd	nd	<0.08	<0.08	nd	nd	<0.05	<0.05	nd	nd	<0.04	<0.04	nd	nd
Gd	µg/L	<0.004	<0.004	nd	nd	<0.004	<0.004	nd	nd	0.006	0.006	0.006	<1	<0.005	<0.005	nd	nd
Hf	µg/L	<0.006	<0.006	nd	nd	<0.006	<0.006	nd	nd	<0.006	<0.006	nd	nd	<0.006	<0.006	nd	nd
Ho	µg/L	<0.003	<0.003	nd	nd	0.004	0.004	0.004	<1	<0.003	<0.003	nd	nd	<0.003	<0.003	nd	nd
La	µg/L	<0.003	0.003	nd	nd	0.099	0.103	0.101	3	0.005	0.006	0.006	13	0.004	<0.003	0.004	nd
Li	µg/L	10	11	11	7	<7	<7	nd	nd	<7	<7	nd	nd	12	12	12	<1
Lu	µg/L	<0.003	<0.003	nd	nd	<0.003	<0.003	nd	nd	<0.003	<0.003	nd	nd	<0.003	<0.003	nd	nd
Mn	µg/L	57	57	57	nd	35	35	35	1	145	153	149	4	59	60	59	1
Mo	µg/L	0.60	0.60	0.60	<1	0.30	0.30	0.30	<1	0.40	0.50	0.45	16	0.50	0.60	0.55	13
Nb	µg/L	<0.01	<0.01	nd	nd	<0.01	<0.01	nd	nd	<0.01	<0.01	nd	nd	<0.01	<0.01	nd	nd
Nd	µg/L	<0.005	0.01	nd	nd	0.15	0.13	0.14	10	0.01	0.01	0.01	20	0.01	<0.005	0.01	nd
Ni	µg/L	1.4	1.4	1.4	1	1.4	1.4	1.4	<1	1.8	1.8	1.8	<1	1.2	1.2	1.2	2
Pb	µg/L	0.10	0.07	0.09	25	0.51	0.50	0.51	1	0.07	0.07	0.07	<1	0.03	0.03	0.03	<1
Pr	µg/L	<0.003	<0.003	nd	nd	0.03	0.03	0.03	2	<0.003	<0.003	nd	nd	<0.003	<0.003	nd	nd
Rb	µg/L	13.4	13.4	13.4	<1	2.1	2.0	2.0	2	5.6	5.4	5.5	2	17.3	17.4	17.4	1

Table A2.1 cont.

Field Duplicate		DupA	DupB	Mean	RSD	DupA	DupB	Mean	RSD	DupA	DupB	Mean	RSD	DupA	DupB	Mean	RSD
Sample ID		GF01-03	GF01-07		%	GF02-03	GF02-07		%	GF03-05	GF03-08		%	GF04-08	GF04-01		%
Sample Round		1	1			2	2			3	3			4	4		
UKGEOS Location		SWTC	SWTC			SW04	SW04			SW03	SW03			SWTC	SWTC		
Analyte	Units																
Sb	µg/L	0.36	0.37	0.37	2	0.12	0.14	0.13	11	0.34	0.33	0.34	2	0.34	0.36	0.35	4
Se	µg/L	0.47	0.40	0.44	11	0.20	0.21	0.21	3	0.13	0.13	0.13	<1	0.20	0.19	0.20	4
Sm	µg/L	<0.005	<0.005	nd	nd	0.04	0.02	0.03	29	<0.005	<0.005	nd	nd	<0.005	<0.005	nd	nd
Sn	µg/L	<0.08	<0.08	nd	nd	0.21	0.09	0.15	57	0.10	0.13	0.12	18	<0.08	0.11	0.11	nd
Sr	µg/L	911	912	911	nd	111	110	111	<1	271	277	274	2	1130	1136	1133	<1
Ta	µg/L	<0.006	<0.006	nd	nd	<0.006	<0.006	nd	nd	<0.006	<0.006	nd	nd	<0.006	<0.006	nd	nd
Tb	µg/L	<0.005	<0.005	nd	nd	0.03	0.04	0.03	16	<0.004	<0.004	nd	nd	<0.004	<0.004	nd	nd
Th	µg/L	<0.03	<0.03	nd	nd	<0.03	<0.03	nd	nd	<0.03	<0.03	nd	nd	<0.03	<0.03	nd	nd
Ti	µg/L	<0.06	<0.06	nd	nd	1.2	1.1	1.2	9	<0.2	<0.2	nd	nd	0.08	<0.06	0.08	nd
Tl	µg/L	<0.02	<0.02	nd	nd	<0.02	<0.02	nd	nd	<0.02	<0.02	nd	nd	<0.02	<0.02	nd	nd
Tm	µg/L	<0.003	<0.003	nd	nd	<0.003	<0.003	nd	nd	<0.003	<0.003	nd	nd	<0.003	<0.003	nd	nd
U	µg/L	0.34	0.35	0.34	1	0.10	0.10	0.10	<1	0.22	0.22	0.22	<1	0.34	0.33	0.34	2
V	µg/L	0.36	0.35	0.36	2	0.54	0.48	0.51	8	0.31	0.35	0.33	9	0.79	0.73	0.76	6
W	µg/L	<0.06	<0.06	nd	nd	<0.06	<0.06	nd	nd	<0.06	<0.06	nd	nd	<0.06	<0.06	nd	nd
Y	µg/L	0.02	0.03	0.03	18	0.14	0.14	0.14	1	0.02	0.03	0.02	35	0.02	0.01	0.01	30
Yb	µg/L	0.008	0.004	0.006	47	0.01	0.01	0.01	6	<0.004	<0.004	nd	nd	<0.004	<0.004	nd	nd
Zn	µg/L	6.7	6.0	6.4	8	3.8	4.3	4.1	9	2.9	2.7	2.8	5	2.1	2.4	2.3	9
Zr	µg/L	0.03	0.03	0.03	<1	0.10	0.10	0.10	1	0.02	0.02	0.02	3	0.02	0.03	0.02	9
Inorganic Carbon																	
TIC	mg/L	60	58	59	3	14	13	13	3	29	30	30	2	70	70	70	1
Organic Parameters																	
NPOC	mg/L	2.9	2.5	2.7	9	4.5	4.8	4.6	3	4.1	4.2	4.2	1	3.0	2.5	2.7	11
Benzo(b)fluoranthene	µg/L	0.0118	0.0090	0.0104	19	0.0037	0.0050	0.0044	21	<0.0011	0.0022	0.0022	nd	0.0070	0.0076	0.0073	6
Benzo(k)fluoranthene	µg/L	0.0047	0.0035	0.0041	21	0.0011	0.0017	0.0014	30	<0.0010	<0.0010	nd	nd	0.0021	0.0025	0.0023	12
Benzo(a)pyrene (BaP)	µg/L	0.0127	0.0096	0.0112	20	0.0024	0.0043	0.0034	40	0.0008	0.0009	0.0009	8	0.0050	0.0053	0.0052	4
Benzo(ghi)perylene	µg/L	0.0067	0.0068	0.0068	1	0.0014	0.0035	0.0025	61	<0.0011	0.0013	0.0013	nd	0.0021	0.0029	0.0025	23
Indeno(1,2,3-cd)pyrene	µg/L	0.0050	0.0038	0.0044	19	0.0064	0.0125	0.0095	46	<0.0015	<0.0015	nd	nd	0.0050	0.0047	0.0049	4
PAH-total	µg/L	0.0282	0.0230	0.0256	14	0.0126	0.0228	0.0177	41	<0.0047	<0.0047	nd	nd	0.0162	0.0177	0.0170	6
TPH (C8-C10)	mg/L	<0.003	<0.003	nd	nd	0.003	0.004	0.004	20	<0.0030	<0.0030	nd	nd	<0.003	<0.003	nd	nd
TPH (C10-C40)	mg/L	0.263	0.387	0.325	27	<0.042	<0.042	nd	nd	0.060	0.060	0.060	<1	<0.042	0.052	0.052	nd
TPH (C8-C40)	mg/L	0.263	0.387	0.325	27	<0.045	<0.045	nd	nd	0.060	0.060	0.060	<1	<0.045	0.052	0.052	nd
Stable Isotopes																	
δ13C	VPDB ‰	-11.9	-11.7	-11.8	1	-13.0	-12.8	-12.9	1	-11.2	-10.9	-11.0	2	-11.7	-12.3	-12.0	3
δ18O	VSMOW2 ‰	-7.3	-7.2	-7.2	1	-8.3	-8.3	-8.3	1	-7.3	-7.3	-7.3	<1	-7.3	-7.2	-7.3	1
δ2H	VSMOW2 ‰	-45.9	-46.4	-46.1	1	-53.8	-53.9	-53.9	<1	-48.2	-48.4	-48.3	<1	-47.6	-47.9	-47.7	<1

Table A2.1 cont.

Field Duplicate		DupA	DupB	Mean	RSD	DupA	DupB	Mean	RSD	DupA	DupB	Mean	RSD	DupA	DupB	Mean	RSD
Sample ID		GF05-06	GF05-08		%	GF06-03	GF06-05		%	GF07-02	GF07-05		%	GF08-02	GF08-07		%
Sample Round		5	5			6	6			7	7			8	8		
UKGEOS Location		SW10	SW10			SW04	SW04			SW04	SW04			SW05	SW05		
Analyte	Units																
Field Parameters																	
pH	log [H+]mol/L	7.60	7.58	7.59	<1	7.56	7.57	7.57	<1	7.77	7.75	7.76	<1	7.86	7.86	7.86	<1
Temp	°C	15.1	15.1	15.1	<1	20.7	20.4	20.6	1	15.8	15.9	15.9	<1	13.3	13.0	13.2	2
Eh	mV	442	451	447	1	320	322	321	<1	359	347	353	2	356	356	356	<1
DO	mg/L	7.2	7.8	7.5	6	6.4	6.6	6.5	2	9.0	8.4	8.7	5	9.5	9.6	9.5	1
SEC	µs/cm	413	412	413	<1	311	308	309	1	237	237	237	<1	273	272	273	<1
Field-HCO ₃	mg/L	124	127	125	2	102	103	103	1	76	75	75	<1	87	88	87	1
Major & Minor Anions																	
Br	mg/L	0.05	0.04	0.04	2	0.02	0.02	0.02	12	0.03	0.03	0.03	17	0.03	0.04	0.04	13
Cl	mg/L	31	31	31	<1	22	22	22	<1	17	17	17	<1	19	19	19	<1
F	mg/L	0.046	0.045	0.046	2	0.042	0.044	0.043	3	0.054	0.052	0.053	3	0.030	0.050	0.040	36
Lab-HCO ₃	mg/L	130	131	131	1	105	104	105	1	79	80	79	<1	94	94	94	<1
HPO ₄	mg/L	0.36	0.43	0.40	13	0.48	0.48	0.48	<1	0.12	0.19	0.15	34	0.29	0.19	0.24	29
SO ₄	mg/L	34	34	34	<1	24	24	24	1	17	17	17	1	22	22	22	1
NO ₂	mg/L	0.11	0.20	0.16	42	<0.005	<0.005	nd	nd	0.05	0.04	0.05	2	0.04	0.04	0.04	4
NO ₃	mg/L	11.0	11.0	11.0	<1	6.6	7.4	7.0	8	4.4	4.3	4.3	1	6.2	6.3	6.2	2
Major & Minor Cations																	
Ca	mg/L	37	37	37	<1	31	31	31	<1	24	24	24	<1	27	27	27	1
K	mg/L	4.4	4.5	4.4	1	3.1	3.1	3.1	<1	2.5	2.6	2.5	4	2.7	2.8	2.7	1
Mg	mg/L	11	11	11	<1	9	9	9	<1	7	7	7	<1	8	7	7	2
Na	mg/L	26	26	26	1	20	20	20	<1	14	14	14	<1	16	16	16	<1
P-Total	mg/L	0.157	0.160	0.159	1	0.170	0.180	0.175	4	0.077	0.081	0.079	4	0.080	0.083	0.082	3
S-Total	mg/L	12	12	12	<1	9	9	9	1	6	6	6	<1	8	8	8	3
Si	mg/L	2.74	2.76	2.75	1	2.70	2.83	2.77	3	3.46	3.43	3.45	1	3.34	3.31	3.33	1
Trace Elements																	
Ag	µg/L	<0.04	<0.04	nd	nd	<0.04	<0.04	nd	nd	<0.04	<0.04	nd	nd	<0.04	<0.04	nd	nd
Al	µg/L	15	17	16	6	49	49	49	1	78	79	79	1	43	42	43	2
As	µg/L	0.40	0.41	0.41	2	0.50	0.47	0.49	4	0.48	0.46	0.47	3	0.43	0.39	0.41	7

Table A2.1 cont.

Field Duplicate		DupA	DupB	Mean	RSD	DupA	DupB	Mean	RSD	DupA	DupB	Mean	RSD	DupA	DupB	Mean	RSD
Sample ID		GF05-06	GF05-08		%	GF06-03	GF06-05		%	GF07-02	GF07-05		%	GF08-02	GF08-07		%
Sample Round		5	5			6	6			7	7			8	8		
UKGEOS Location		SW10	SW10			SW04	SW04			SW04	SW04			SW05	SW05		
Analyte	Units																
Trace Elements																	
B	µg/L	<53	<53	nd	nd	<53	<53	nd	nd	<53	<53	nd	nd	<53	<53	nd	nd
Ba	µg/L	83	83	83	<1	85	84	85	<1	66	66	66	1	73	72	72	1
Be	µg/L	<0.08	<0.08	nd	nd	<0.08	<0.08	nd	nd	<0.08	<0.08	nd	nd	<0.08	<0.08	nd	nd
Bi	µg/L	<0.08	<0.08	nd	nd	<0.08	<0.08	nd	nd	<0.08	<0.08	nd	nd	<0.08	<0.08	nd	nd
Cd	µg/L	0.01	0.01	0.01	18	0.01	0.01	0.01	<1	0.02	0.01	0.01	43	0.01	0.01	0.01	7
Ce	µg/L	0.03	0.04	0.03	2	0.16	0.16	0.16	2	0.32	0.31	0.32	2	0.14	0.12	0.13	8
Co	µg/L	0.23	0.24	0.23	4	0.26	0.27	0.26	2	0.19	0.19	0.19	3	0.14	0.13	0.14	6
Cr-Total	µg/L	8.47	8.31	8.39	1	0.35	0.35	0.35	<1	0.61	0.63	0.62	2	0.38	0.37	0.38	2
Cr(VI)	µg/L	7.29	6.97	7.13	3	0.13	0.08	0.11	34	0.07	0.09	0.08	18	0.12	0.11	0.12	6
Cr(III)	µg/L	0.49	0.46	0.48	4	0.25	0.25	0.25	<1	0.43	0.43	0.43	<1	0.22	0.23	0.23	3
Cs	µg/L	0.04	<0.04	0.04	nd	<0.04	<0.04	nd	nd	<0.04	<0.04	nd	nd	<0.04	<0.04	nd	nd
Cu	µg/L	1.02	1.08	1.05	4	1.46	1.38	1.42	4	2.20	2.12	2.16	3	1.16	1.04	1.10	8
Dy	µg/L	0.007	0.006	0.007	11	0.03	0.02	0.02	19	0.05	0.05	0.05	3	0.03	0.03	0.03	3
Er	µg/L	<0.003	0.004	0.004	nd	0.01	0.01	0.01	13	0.02	0.02	0.02	9	0.02	0.01	0.02	18
Eu	µg/L	<0.003	<0.003	nd	nd	0.009	0.007	0.008	18	0.01	0.01	0.01	12	0.01	0.01	0.01	25
Fe	µg/L	176	195	185	7	364	356	360	2	578	570	574	1	456	447	452	2
Ga	µg/L	<0.05	<0.05	nd	nd	<0.08	<0.08	nd	nd	<0.04	<0.04	nd	nd	<0.04	<0.04	nd	nd
Gd	µg/L	0.02	0.01	0.01	26	0.04	0.03	0.03	9	0.07	0.06	0.06	9	0.04	0.04	0.04	7
Hf	µg/L	<0.006	<0.006	nd	nd	<0.006	<0.006	nd	nd	0.007	0.009	0.008	18	<0.006	<0.006	nd	nd
Ho	µg/L	<0.003	<0.003	nd	nd	0.004	0.004	0.004	<1	0.009	0.008	0.009	8	0.004	0.005	0.005	16
La	µg/L	0.03	0.03	0.03	5	0.09	0.09	0.09	2	0.24	0.22	0.23	7	0.09	0.09	0.09	1
Li	µg/L	<7	<7	nd	nd	<7	<7	nd	nd	<7	<7	nd	nd	<7	<7	nd	nd
Lu	µg/L	<0.003	<0.003	nd	nd	<0.003	<0.003	nd	nd	0.004	0.003	0.004	20	<0.003	<0.003	nd	nd
Mn	µg/L	67	68	68	2	102	97	99	3	37	40	38	5	26	26	26	<1
Mo	µg/L	0.40	0.40	0.40	<1	0.40	0.40	0.40	<1	0.40	0.40	0.40	<1	0.30	0.30	0.30	<1
Nb	µg/L	<0.01	<0.01	nd	nd	<0.01	<0.01	nd	nd	0.01	0.01	0.01	<1	<0.01	<0.01	nd	nd
Nd	µg/L	0.04	0.04	0.04	15	0.12	0.11	0.11	6	0.30	0.22	0.26	20	0.13	0.10	0.12	18
Ni	µg/L	1.4	1.4	1.4	1	1.7	1.6	1.6	3	2.1	2.4	2.3	11	1.5	2.0	1.8	19
Pb	µg/L	0.30	0.34	0.32	9	0.46	0.46	0.46	<1	0.98	0.96	0.97	1	0.76	0.75	0.76	1
Pr	µg/L	0.006	0.007	0.007	11	0.03	0.03	0.03	<1	0.06	0.06	0.06	2	0.03	0.03	0.03	<1
Rb	µg/L	4.9	4.9	4.9	<1	3.7	3.8	3.7	1	2.7	2.6	2.6	3	2.9	3.0	2.9	1

Table A2.1 cont.

Field Duplicate		DupA	DupB	Mean	RSD	DupA	DupB	Mean	RSD	DupA	DupB	Mean	RSD	DupA	DupB	Mean	RSD
Sample ID		GF05-06	GF05-08		%	GF06-03	GF06-05		%	GF07-02	GF07-05		%	GF08-02	GF08-07		%
Sample Round		5	5			6	6			7	7			8	8		
UKGEOS Location		SW10	SW10			SW04	SW04			SW04	SW04			SW05	SW05		
Analyte	Units																
Sb	µg/L	0.29	0.27	0.28	5	0.21	0.20	0.21	3	0.18	0.21	0.20	11	0.14	0.14	0.14	<1
Se	µg/L	0.14	0.13	0.14	5	0.14	0.15	0.15	5	0.21	0.17	0.19	15	0.14	0.17	0.16	14
Sm	µg/L	0.006	0.007	0.007	11	0.02	0.02	0.02	15	0.07	0.06	0.07	12	0.03	0.03	0.03	5
Sn	µg/L	0.12	<0.08	0.12	nd	<0.08	<0.08	nd	nd	<0.08	<0.08	nd	nd	<0.08	<0.08	nd	nd
Sr	µg/L	216	219	217	1	177	176	176	<1	120	121	121	<1	148	147	148	1
Ta	µg/L	<0.006	<0.006	nd	nd	<0.006	<0.006	nd	nd	<0.006	<0.006	nd	nd	<0.006	<0.006	nd	nd
Tb	µg/L	<0.004	<0.004	nd	nd	<0.004	0.004	0.004	nd	0.009	0.008	0.009	8	<0.004	0.004	0.004	nd
Th	µg/L	<0.03	<0.03	nd	nd	<0.03	<0.03	nd	nd	<0.03	<0.03	nd	nd	<0.03	<0.03	nd	nd
Ti	µg/L	0.2	0.2	0.2	4	1.4	1.5	1.4	2	2.7	2.6	2.6	1	1.0	0.9	0.9	13
Tl	µg/L	<0.02	<0.02	nd	nd	<0.02	<0.02	nd	nd	<0.02	<0.02	nd	nd	<0.02	<0.02	nd	nd
Tm	µg/L	<0.003	<0.003	nd	nd	<0.003	<0.003	nd	nd	0.004	0.004	0.004	<1	<0.003	<0.003	nd	nd
U	µg/L	0.17	0.17	0.17	1	0.13	0.13	0.13	3	0.12	0.11	0.12	4	0.12	0.12	0.12	<1
V	µg/L	0.51	0.54	0.53	4	0.72	0.71	0.72	1	0.88	0.88	0.88	<1	0.62	0.59	0.61	4
W	µg/L	<0.06	<0.06	nd	nd	<0.06	<0.06	nd	nd	<0.06	<0.06	nd	nd	<0.06	<0.06	nd	nd
Y	µg/L	0.04	0.04	0.04	11	0.13	0.11	0.12	8	0.30	0.27	0.28	8	0.15	0.15	0.15	2
Yb	µg/L	<0.004	0.004	0.004	nd	0.009	0.007	0.008	18	0.02	0.02	0.02	7	0.02	0.01	0.02	23
Zn	µg/L	4.4	4.4	4.4	<1	2.9	2.9	2.9	<1	3.5	9.0	6.3	62	5.2	4.5	4.9	10
Zr	µg/L	0.03	0.04	0.03	6	0.11	0.11	0.11	1	0.22	0.23	0.23	3	0.12	0.12	0.12	2
Inorganic Carbon																	
TIC	mg/L	26	26	26	1	21	20	21	1	16	16	16	<1	18	18	18	<1
Organic Parameters																	
NPOC	mg/L	5.6	4.8	5.2	11	8.7	9.0	8.9	3	10.6	10.1	10.4	3	6.9	6.8	6.8	1
Benzo(b)fluoranthene	µg/L	0.0027	0.0025	0.0026	5	0.0055	0.0062	0.0059	8	0.0031	0.0038	0.0035	14	0.0022	0.0018	0.0020	14
Benzo(k)fluoranthene	µg/L	<0.001	<0.001	nd	nd	0.0017	0.0025	0.0021	27	<0.001	<0.001	nd	nd	<0.001	<0.001	nd	nd
Benzo(a)pyrene (BaP)	µg/L	0.0015	0.0014	0.0015	5	0.0043	0.0074	0.0059	37	0.0024	0.0026	0.0025	6	0.0016	0.0012	0.0014	20
Benzo(ghi)perylene	µg/L	<0.0011	<0.0011	nd	nd	0.0035	0.0025	0.0030	24	<0.0011	0.0032	0.0032	nd	<0.0011	<0.0011	nd	nd
Indeno(1,2,3-cd)pyrene	µg/L	<0.0015	<0.0015	nd	nd	0.0042	0.0047	0.0045	8	<0.0015	<0.0015	nd	nd	<0.0015	<0.0015	nd	nd
PAH-total	µg/L	<0.0047	<0.0047	nd	nd	0.0149	0.0159	0.0154	5	<0.0047	0.0070	0.0070	nd	<0.0047	<0.0047	nd	nd
TPH (C8-C10)	mg/L	<0.003	<0.003	nd	nd	0.003	<0.003	0.003	nd	<0.003	<0.003	nd	nd	<0.003	<0.003	nd	nd
TPH (C10-C40)	mg/L	0.045	<0.042	0.045	nd	<0.042	0.053	0.053	nd	<0.042	<0.042	nd	nd	<0.042	<0.042	nd	nd
TPH (C8-C40)	mg/L	<0.045	<0.045	nd	nd	<0.045	0.053	0.053	nd	<0.045	<0.045	nd	nd	<0.045	<0.045	nd	nd
Stable Isotopes																	
δ13C	VPDB ‰	-10.9	-11.8	-11.4	6	-12.2	-12.5	-12.4	2	-16.2	-16.7	-16.4	2	-11.8	-12.0	-11.9	1
δ18O	VSMOW2 ‰	-7.0	-7.1	-7.0	1	-6.9	-6.8	-6.8	1	-7.1	-7.3	-7.2	1	-6.8	-6.9	-6.8	1
δ2H	VSMOW2 ‰	-44.3	-45.1	-44.7	1	-43.8	-43.5	-43.6	<1	-47.3	-46.2	-46.8	2	-42.2	-43.1	-42.7	2

Table A2.1 cont.

Field Duplicate		DupA	DupB	Mean	RSD	DupA	DupB	Mean	RSD	DupA	DupB	Mean	RSD	DupA	DupB	Mean	RSD
Sample ID		GF09-03	GF09-07		%	GF10-08	GF10-02		%	GF11-02	GF11-01		%	GF12-06	GF12-03		%
Sample Round		9	9			10	10			11	11			12	12		
UKGEOS Location		SW10	SW10			SW04	SW04			SW03	SW03			SW03	SW03		
Analyte	Units																
Field Parameters																	
pH	log [H+]mol/L	7.93	7.87	7.90	1	7.77	7.81	7.79	<1	7.82	7.77	7.80	<1	7.81	7.75	7.78	1
Temp	°C	10.1	9.9	10.0	1	5.5	5.6	5.6	1	4.7	4.7	4.7	<1	5.1	5.1	5.1	<1
Eh	mV	301	303	302	<1	458	473	466	2	443	380	411	11	399	377	388	4
DO	mg/L	10.3	9.9	10.1	3	12.2	11.6	11.9	4	11.1	11.1	11.1	<1	11.6	11.4	11.5	1
SEC	µs/cm	251	249	250	1	235	205	220	10	278	284	281	1	210	211	211	<1
Field-HCO ₃	mg/L	83	85	84	2	57	58	57	2	73	75	74	2	53	56	55	4
Major & Minor Anions																	
Br	mg/L	0.05	0.05	0.05	8	0.03	0.03	0.03	11	0.04	0.04	0.04	1	0.02	0.02	0.02	3
Cl	mg/L	19	18	18	4	21	22	22	2	33	33	33	<1	23	23	23	1
F	mg/L	0.077	0.076	0.077	1	0.051	0.019	0.035	64	0.063	0.060	0.061	4	0.054	0.053	0.053	<1
Lab-HCO ₃	mg/L	86	86	86	<1	61	61	61	<1	77	78	77	<1	59	60	59	1
HPO ₄	mg/L	0.12	0.10	0.11	13	0.11	0.09	0.10	13	0.08	0.06	0.07	20	0.05	0.04	0.04	24
SO ₄	mg/L	20	18	19	6	11	11	11	<1	18	18	18	2	14	14	14	1
NO ₂	mg/L	0.06	0.05	0.05	15	0.03	0.02	0.03	5	0.02	0.02	0.02	11	0.02	0.02	0.02	1
NO ₃	mg/L	6.0	6.2	6.1	2	3.8	3.8	3.8	<1	5.9	5.9	5.9	<1	5.1	5.0	5.1	1
Major & Minor Cations																	
Ca	mg/L	25	26	25	<1	18	18	18	2	24	24	24	2	19	18	18	3
K	mg/L	2.9	3.0	2.9	<1	2.1	2.0	2.1	1	2.5	2.6	2.6	3	2.2	2.2	2.2	2
Mg	mg/L	6	6	6	<1	5	5	5	2	6	6	6	3	5	5	5	2
Na	mg/L	14	14	14	1	14	14	14	<1	22	23	22	2	15	14	15	3
P-Total	mg/L	0.065	0.068	0.067	3	0.037	0.037	0.037	<1	0.057	0.057	0.057	<1	0.050	0.040	0.045	16
S-Total	mg/L	7	7	7	<1	4	4	4	2	6	7	7	2	5	5	5	1
Si	mg/L	3.40	3.32	3.36	2	2.77	2.63	2.70	4	3.26	3.32	3.29	1	2.95	2.87	2.91	2
Trace Elements																	
Ag	µg/L	<0.04	<0.04	nd	nd	<0.04	<0.04	nd	nd	<0.04	<0.04	nd	nd	<0.04	<0.04	nd	nd
Al	µg/L	68	69	68	1	83	83	83	<1	72	63	67	10	78	78	78	<1
As	µg/L	0.40	0.41	0.41	2	0.32	0.31	0.32	2	0.30	0.31	0.31	2	0.28	0.26	0.27	5

Table A2.1 cont.

Field Duplicate		DupA	DupB	Mean	RSD	DupA	DupB	Mean	RSD	DupA	DupB	Mean	RSD	DupA	DupB	Mean	RSD
Sample ID		GF09-03	GF09-07		%	GF10-08	GF10-02		%	GF11-02	GF11-01		%	GF12-06	GF12-03		%
Sample Round		9	9			10	10			11	11			12	12		
UKGEOS Location		SW10	SW10			SW04	SW04			SW03	SW03			SW03	SW03		
Analyte	Units																
Trace Elements																	
B	µg/L	<53	<53	nd	nd	<53	<53	nd	nd	<53	<53	nd	nd	<53	<53	nd	nd
Ba	µg/L	73	73	73	<1	61	58	59	4	63	64	64	1	57	55	56	3
Be	µg/L	<0.08	<0.08	nd	nd	<0.08	<0.08	nd	nd	<0.08	<0.08	nd	nd	<0.08	<0.08	nd	nd
Bi	µg/L	<0.08	<0.08	nd	nd	<0.08	<0.08	nd	nd	<0.08	<0.08	nd	nd	<0.08	<0.08	nd	nd
Cd	µg/L	0.02	0.01	0.01	51	0.01	0.01	0.01	16	0.02	0.01	0.01	10	0.01	0.01	0.01	13
Ce	µg/L	0.23	0.24	0.24	1	0.23	0.28	0.25	13	0.21	0.21	0.21	1	0.28	0.25	0.26	10
Co	µg/L	0.19	0.18	0.18	5	0.19	0.18	0.18	3	0.22	0.25	0.23	8	0.19	0.19	0.19	<1
Cr-Total	µg/L	2.89	2.89	2.89	<1	0.50	0.49	0.50	1	0.54	0.54	0.54	<1	0.46	0.44	0.45	3
Cr(VI)	µg/L	2.38	2.37	2.38	<1	<0.05	<0.05	nd	nd	0.24	0.23	0.24	3	0.18	0.19	0.19	4
Cr(III)	µg/L	0.25	0.12	0.19	50	0.35	0.42	0.39	13	0.26	0.19	0.23	22	0.21	0.21	0.21	<1
Cs	µg/L	<0.04	<0.04	nd	nd	<0.04	<0.04	nd	nd	<0.04	<0.04	nd	nd	<0.04	<0.04	nd	nd
Cu	µg/L	1.39	1.49	1.44	5	1.42	1.30	1.36	6	1.28	1.32	1.30	2	1.27	1.21	1.24	3
Dy	µg/L	0.03	0.03	0.03	7	0.04	0.03	0.04	6	0.03	0.03	0.03	12	0.04	0.04	0.04	6
Er	µg/L	0.02	0.02	0.02	<1	0.02	0.02	0.02	14	0.01	0.02	0.02	9	0.02	0.02	0.02	11
Eu	µg/L	0.01	0.01	0.01	12	0.01	0.01	0.01	7	0.01	0.01	0.01	8	0.01	0.01	0.01	<1
Fe	µg/L	438	450	444	2	401	394	398	1	347	395	371	9	274	279	276	1
Ga	µg/L	<0.04	<0.04	nd	nd	<0.09	<0.09	nd	nd	<0.04	<0.04	nd	nd	<0.08	<0.08	nd	nd
Gd	µg/L	0.05	0.05	0.05	<1	0.05	0.04	0.04	5	0.05	0.04	0.04	16	0.05	0.04	0.05	14
Hf	µg/L	0.008	<0.006	0.008	nd	<0.006	0.006	0.006	nd	<0.006	<0.006	nd	nd	0.007	<0.006	0.007	nd
Ho	µg/L	0.009	0.007	0.008	18	0.006	0.007	0.007	11	0.005	0.005	0.005	<1	0.007	0.007	0.007	<1
La	µg/L	0.17	0.15	0.16	9	0.16	0.15	0.15	4	0.12	0.12	0.12	1	0.17	0.16	0.16	3
Li	µg/L	<7	<7	nd	nd	<7	<7	nd	nd	<7	<7	nd	nd	<7	<7	nd	nd
Lu	µg/L	<0.003	<0.003	nd	nd	<0.003	<0.003	nd	nd	<0.003	<0.003	nd	nd	0.004	<0.003	0.004	nd
Mn	µg/L	29	29	29	<1	22	22	22	2	76	105	91	22	26	30	28	11
Mo	µg/L	0.40	0.40	0.40	<1	0.30	0.30	0.30	<1	0.40	0.40	0.40	<1	0.30	0.30	0.30	<1
Nb	µg/L	0.01	0.01	0.01	<1	0.01	<0.01	0.01	nd	<0.01	<0.01	nd	nd	<0.01	<0.01	nd	nd
Nd	µg/L	0.18	0.23	0.21	17	0.19	0.20	0.19	3	0.15	0.15	0.15	1	0.22	0.20	0.21	7
Ni	µg/L	2.0	2.0	2.0	1	1.6	1.6	1.6	1	1.5	1.5	1.5	2	1.5	1.5	1.5	<1
Pb	µg/L	0.58	0.58	0.58	<1	0.53	0.55	0.54	3	0.50	0.52	0.51	3	0.61	0.62	0.62	1
Pr	µg/L	0.05	0.04	0.04	5	0.04	0.04	0.04	<1	0.04	0.03	0.03	10	0.04	0.05	0.05	6
Rb	µg/L	2.8	2.8	2.8	1	2.2	2.1	2.1	3	2.3	2.4	2.3	2	2.2	2.0	2.1	6

Table A2.1 cont.

Field Duplicate		DupA	DupB	Mean	RSD	DupA	DupB	Mean	RSD	DupA	DupB	Mean	RSD	DupA	DupB	Mean	RSD
Sample ID		GF09-03	GF09-07		%	GF10-08	GF10-02		%	GF11-02	GF11-01		%	GF12-06	GF12-03		%
Sample Round		9	9			10	10			11	11			12	12		
UKGEOS Location		SW10	SW10			SW04	SW04			SW03	SW03			SW03	SW03		
Analyte	Units																
Sb	µg/L	0.16	0.16	0.16	<1	0.12	0.11	0.12	6	0.13	0.12	0.13	6	0.12	0.12	0.12	<1
Se	µg/L	0.19	0.20	0.20	4	0.11	0.11	0.11	<1	0.18	0.19	0.19	4	0.13	0.13	0.13	<1
Sm	µg/L	0.04	0.04	0.04	2	0.05	0.04	0.05	20	0.04	0.04	0.04	6	0.05	0.05	0.05	1
Sn	µg/L	<0.08	<0.08	nd	nd	<0.08	<0.08	nd	nd	<0.08	<0.08	nd	nd	<0.08	<0.08	nd	nd
Sr	µg/L	132	133	132	1	85	83	84	2	114	117	116	2	88	87	87	1
Ta	µg/L	<0.006	<0.006	nd	nd	<0.006	<0.006	nd	nd	<0.006	<0.006	nd	nd	<0.006	<0.006	nd	nd
Tb	µg/L	0.007	0.007	0.007	<1	0.006	0.006	0.006	<1	0.005	<0.004	0.005	nd	0.006	0.007	0.007	11
Th	µg/L	<0.03	<0.03	nd	nd	<0.03	<0.03	nd	nd	<0.03	<0.03	nd	nd	<0.03	<0.03	nd	nd
Ti	µg/L	2.3	2.1	2.2	4	3.2	3.4	3.3	4	2.6	2.5	2.6	3	3.0	3.3	3.1	5
Tl	µg/L	<0.02	<0.02	nd	nd	<0.02	<0.02	nd	nd	<0.02	<0.02	nd	nd	<0.02	<0.02	nd	nd
Tm	µg/L	0.004	0.004	0.004	<1	<0.003	<0.003	nd	nd	<0.003	<0.003	nd	nd	0.003	<0.003	0.003	nd
U	µg/L	0.14	0.14	0.14	<1	0.07	0.07	0.07	8	0.11	0.11	0.11	<1	0.08	0.08	0.08	2
V	µg/L	0.77	0.80	0.79	3	0.59	0.57	0.58	2	0.64	0.67	0.66	3	0.60	0.60	0.60	<1
W	µg/L	<0.06	<0.06	nd	nd	<0.06	<0.06	nd	nd	<0.06	<0.06	nd	nd	<0.06	<0.06	nd	nd
Y	µg/L	0.23	0.20	0.21	9	0.21	0.20	0.20	6	0.18	0.17	0.17	7	0.23	0.21	0.22	6
Yb	µg/L	0.02	0.02	0.02	7	0.01	0.01	0.01	5	0.02	0.02	0.02	<1	0.02	0.02	0.02	17
Zn	µg/L	4.3	4.4	4.4	2	2.6	3.8	3.2	27	4.6	5.5	5.1	13	2.1	2.5	2.3	12
Zr	µg/L	0.21	0.20	0.20	4	0.20	0.19	0.19	3	0.15	0.16	0.15	5	0.17	0.17	0.17	1
Inorganic Carbon																	
TIC	mg/L	17	17	17	<1	12	12	12	<1	15	15	15	<1	12	12	12	1
Organic Parameters																	
NPOC	mg/L	8.1	8.3	8.2	1	7.8	7.8	7.8	<1	5.3	5.3	5.3	<1	5.9	6.6	6.3	8
Benzo(b)fluoranthene	µg/L	0.0019	0.0037	0.0028	45	0.0097	0.0110	0.0104	9	0.0033	0.0036	0.0035	6	0.0186	0.0164	0.0175	9
Benzo(k)fluoranthene	µg/L	<0.0010	0.0013	0.0013	nd	0.0046	0.0052	0.0049	9	0.0015	0.0015	0.0015	<1	0.0059	0.0057	0.0058	2
Benzo(a)pyrene (BaP)	µg/L	0.0016	0.0028	0.0022	39	0.0110	0.0123	0.0117	8	0.0039	0.0040	0.0040	2	0.0144	0.0136	0.0140	4
Benzo(ghi)perylene	µg/L	<0.0011	0.0017	0.0017	nd	0.0050	0.0057	0.0054	9	<0.0011	0.0014	0.0014	nd	0.0095	0.0093	0.0094	2
Indeno(1,2,3-cd)pyrene	µg/L	<0.0015	<0.0015	nd	nd	0.0082	0.0081	0.0082	1	0.0033	0.0018	0.0026	42	0.0118	0.0093	0.0106	17
PAH-total	µg/L	<0.0047	0.0066	0.0066	nd	0.0275	0.0299	0.0287	6	0.0082	0.0082	0.0082	<1	0.0457	0.0407	0.0432	8
TPH (C8-C10)	mg/L	<0.003	<0.003	nd	nd	<0.003	<0.003	nd	nd	<0.003	<0.004	nd	nd	<0.003	<0.003	nd	nd
TPH (C10-C40)	mg/L	0.046	0.053	0.050	10	0.050	0.043	0.047	11	<0.042	0.088	0.088	nd	0.055	0.078	0.067	24
TPH (C8-C40)	mg/L	0.046	0.053	0.050	10	0.050	<0.045	0.050	nd	<0.045	0.088	0.088	nd	0.055	0.078	0.067	24
Stable Isotopes																	
δ13C	VPDB ‰	-13.1	-13.7	-13.4	3	-12.9	-12.9	-12.9	<1	-12.8	-13.0	-12.9	1	-12.7	-13.5	-13.1	4
δ18O	VSMOW2 ‰	-7.4	-7.4	-7.4	<1	-8.3	-8.2	-8.2	<1	-7.8	-7.7	-7.8	<1	-7.5	-7.5	-7.5	1
δ2H	VSMOW2 ‰	-46.2	-47.0	-46.6	1	-53.9	-53.8	-53.9	<1	-49.9	-50.0	-50.0	<1	-46.9	-47.0	-46.9	<1

Table A2.1 cont.

Field Duplicate		DupA	DupB	Mean	RSD	DupA	DupB	Mean	RSD
Sample ID		GF13-01	GF13-08		%	GF14-01	GF14-05		%
Sample Round		13	13			14	14		
UKGEOS Location		SW05	SW05			SWTC	SWTC		
Analyte	Units								
Field Parameters									
pH	log [H ⁺]/mol/L	7.66	7.72	7.69	1	8.04	8.09	8.07	<1
Temp	°C	4.4	4.3	4.4	2	6.5	6.4	6.5	1
Eh	mV	496	496	496	<1	512	519	515	1
DO	mg/L	12.3	12.3	12.3	<1	10.0	10.3	10.2	2
SEC	µs/cm	257	256	256	<1	860	860	860	<1
Field-HCO ₃	mg/L	52	49	51	4	337	333	335	1
Major & Minor Anions									
Br	mg/L	0.03	0.03	0.03	1	0.13	0.13	0.13	3
Cl	mg/L	33	32	32	1	70	71	70	<1
F	mg/L	0.048	0.056	0.052	11	0.155	0.151	0.153	1
Lab-HCO ₃	mg/L	59	61	60	3	341	342	341	<1
HPO ₄	mg/L	0.11	0.09	0.10	11	<0.1	<0.1	nd	nd
SO ₄	mg/L	15	15	15	<1	61	61	61	<1
NO ₂	mg/L	0.01	0.01	0.01	2	0.13	0.14	0.13	7
NO ₃	mg/L	4.4	4.4	4.4	<1	5.8	5.8	5.8	<1
Major & Minor Cations									
Ca	mg/L	19	19	19	1	80	81	80	1
K	mg/L	2.2	2.2	2.2	2	9.6	9.7	9.6	1
Mg	mg/L	5	5	5	<1	24	24	24	<1
Na	mg/L	20	19	19	1	61	62	61	1
P-Total	mg/L	0.055	0.055	0.055	<1	0.038	0.040	0.039	4
S-Total	mg/L	6	6	6	1	23	23	23	<1
Si	mg/L	2.64	2.65	2.65	<1	5.96	6.12	6.04	2
Trace Elements									
Ag	µg/L	<0.08	<0.08	nd	nd	<0.08	<0.08	nd	nd
Al	µg/L	55	53	54	2	9	11	10	12
As	µg/L	0.25	0.25	0.25	<1	0.29	0.29	0.29	<1

Table A2.1 cont.

Field Duplicate		DupA	DupB	Mean	RSD	DupA	DupB	Mean	RSD
Sample ID		GF13-01	GF13-08		%	GF14-01	GF14-05		%
Sample Round		13	13			14	14		
UKGEOS Location		SW05	SW05			SWTC	SWTC		
Analyte	Units								
Trace Elements									
B	µg/L	<53	<53	nd	nd	100	100	100	<1
Ba	µg/L	54	54	54	<1	64	64	64	<1
Be	µg/L	<0.08	<0.08	nd	nd	<0.08	<0.08	nd	nd
Bi	µg/L	<0.08	<0.08	nd	nd	<0.08	<0.08	nd	nd
Cd	µg/L	0.02	0.01	0.01	35	0.01	0.02	0.01	47
Ce	µg/L	0.17	0.17	0.17	<1	0.01	0.02	0.01	55
Co	µg/L	0.17	0.17	0.17	2	0.53	0.53	0.53	<1
Cr-Total	µg/L	0.50	0.52	0.51	3	0.11	0.12	0.12	6
Cr(VI)	µg/L	0.26	0.25	0.26	3	<0.05	<0.05	nd	nd
Cr(III)	µg/L	0.26	0.28	0.27	5	<0.04	<0.04	nd	nd
Cs	µg/L	<0.04	<0.04	nd	nd	<0.04	<0.04	nd	nd
Cu	µg/L	1.22	1.22	1.22	<1	1.01	1.00	1.01	1
Dy	µg/L	0.02	0.03	0.03	14	0.003	<0.003	0.003	nd
Er	µg/L	0.01	0.01	0.01	<1	0.005	0.003	0.004	35
Eu	µg/L	0.005	0.01	0.008	47	<0.003	<0.003	nd	nd
Fe	µg/L	170	175	173	2	21	17	19	16
Ga	µg/L	<0.08	<0.08	nd	nd	<0.08	<0.08	nd	nd
Gd	µg/L	0.04	0.03	0.03	13	<0.005	<0.005	nd	nd
Hf	µg/L	<0.006	<0.006	nd	nd	<0.006	<0.006	nd	nd
Ho	µg/L	0.005	0.004	0.005	16	<0.003	<0.003	nd	nd
La	µg/L	0.10	0.11	0.11	6	0.01	0.01	0.01	31
Li	µg/L	<7	<7	nd	nd	10	10	10	<1
Lu	µg/L	<0.003	<0.003	nd	nd	<0.003	<0.003	nd	nd
Mn	µg/L	25	25	25	1	157	159	158	<1
Mo	µg/L	0.20	0.20	0.20	<1	0.60	0.60	0.60	<1
Nb	µg/L	<0.01	<0.01	nd	nd	<0.01	<0.01	nd	nd
Nd	µg/L	0.14	0.15	0.15	2	<0.007	0.02	0.02	nd
Ni	µg/L	1.4	1.4	1.4	<1	1.8	1.7	1.7	2
Pb	µg/L	0.62	0.64	0.63	2	0.04	0.04	0.04	<1
Pr	µg/L	0.03	0.03	0.03	4	<0.003	<0.003	nd	nd
Rb	µg/L	2.1	2.0	2.1	3	12.9	12.8	12.8	1

Table A2.1 cont.

Field Duplicate		DupA	DupB	Mean	RSD	DupA	DupB	Mean	RSD
Sample ID		GF13-01	GF13-08		%	GF14-01	GF14-05		%
Sample Round		13	13			14	14		
UKGEOS Location		SW05	SW05			SWTC	SWTC		
Analyte	Units								
Sb	µg/L	0.12	0.11	0.12	6	0.29	0.29	0.29	<1
Se	µg/L	0.16	0.15	0.16	5	0.77	0.76	0.77	1
Sm	µg/L	0.04	0.03	0.03	20	<0.005	0.007	0.007	nd
Sn	µg/L	<0.08	<0.08	nd	nd	<0.08	<0.08	nd	nd
Sr	µg/L	94	94	94	<1	921	924	923	<1
Ta	µg/L	<0.006	<0.006	nd	nd	<0.006	<0.006	nd	nd
Tb	µg/L	0.006	<0.004	0.006	nd	<0.004	<0.004	nd	nd
Th	µg/L	<0.03	<0.03	nd	nd	<0.03	<0.03	nd	nd
Ti	µg/L	1.6	1.9	1.7	11	0.1	0.1	0.1	9
Tl	µg/L	<0.02	<0.02	nd	nd	<0.02	<0.02	nd	nd
Tm	µg/L	<0.003	<0.003	nd	nd	<0.003	<0.003	nd	nd
U	µg/L	0.09	0.08	0.08	5	0.40	0.41	0.41	1
V	µg/L	0.61	0.64	0.63	3	0.48	0.47	0.48	1
W	µg/L	<0.06	<0.06	nd	nd	<0.06	<0.06	nd	nd
Y	µg/L	0.14	0.13	0.14	7	0.05	0.05	0.05	5
Yb	µg/L	0.01	0.01	0.01	6	0.01	0.01	0.01	13
Zn	µg/L	3.7	4.1	3.9	7	8.8	9.4	9.1	5
Zr	µg/L	0.10	0.09	0.10	10	0.03	0.03	0.03	<1
Inorganic Carbon									
TIC	mg/L	12	12	12	3	67	67	67	<1
Organic Parameters									
NPOC	mg/L	4.7	4.5	4.6	3	2.8	2.5	2.6	7
Benzo(b)fluoranthene	µg/L	0.0047	0.0049	0.0048	3	0.0457	0.0445	0.0451	2
Benzo(k)fluoranthene	µg/L	<0.0030	<0.003	nd	nd	0.0198	0.0197	0.0198	<1
Benzo(a)pyrene (BaP)	µg/L	0.0063	0.0061	0.0062	2	0.0503	0.0483	0.0493	3
Benzo(ghi)perylene	µg/L	<0.0036	0.0037	0.0037	nd	0.0281	0.0288	0.0285	2
Indeno(1,2,3-cd)pyrene	µg/L	0.0065	0.0056	0.0061	11	0.0318	0.0437	0.0378	22
PAH-total	µg/L	<0.0121	0.0142	0.0142	nd	0.1253	0.1366	0.1310	6
TPH (C8-C10)	mg/L	<0.003	<0.003	nd	nd	<0.003	<0.003	nd	nd
TPH (C10-C40)	mg/L	0.053	<0.042	0.053	nd	0.054	0.049	0.052	7
TPH (C8-C40)	mg/L	0.053	<0.045	0.053	nd	0.054	0.049	0.052	7
Stable Isotopes									
δ13C	VPDB ‰	-13.5	-13.5	-13.5	<1	-12.3	-12.4	-12.4	1
δ18O	VSMOW2 ‰	-7.7	-7.8	-7.8	1	-7.5	-7.5	-7.5	<1
δ2H	VSMOW2 ‰	-48.0	-47.4	-47.7	1	-48.5	-48.6	-48.5	<1

Table A2.2 UKGEOS Glasgow surface water chemistry analysis summary statistics

	Field Parameters						Major Cations				Minor Cations			Major Anions			Minor Anions				
	pH log [H+]mol/L	Temp °C	Eh mV Corr.	DO mg/L	SEC µs/cm	Field- HCO3 mg/L	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	P-Total mg/L	S-Total mg/L	Si mg/L	Cl mg/L	Lab- HCO3 mg/L	SO4 mg/L	Br mg/L	F mg/L	HPO4 mg/L	NO2 mg/L	NO3 mg/L
UKGEOS Glasgow Surface Water Dataset All																					
Min	7.44	3.6	279	6.1	174	40	13	2.0	3	13	0.031	4	0.68	16	43	9	<0.04	0.018	<0.03	<0.010	2.8
Max	8.23	21.9	523	13.2	1026	405	87	13.2	33	99	0.244	28	6.94	138	423	75	0.19	0.220	0.50	0.50	14.9
Mean	7.79	10.4	417	9.8	400	127	36	4.3	11	28	0.086	11	3.18	34	134	29	0.05	0.062	0.17	0.09	7.3
Median	7.79	9.9	431	10.0	299	87	27	2.9	8	20	0.069	8	3.17	30	94	22	<0.04	0.051	0.12	0.05	6.4
SD	0.16	4.9	62	1.8	225	100	21	3.1	8	19	0.049	6	1.35	19	104	17	0.04	0.038	0.14	0.12	3.1
Count	84	84	84	84	84	84	84	84	84	84	84	84	84	84	84	84	84	84	84	84	84
UKGEOS Glasgow River Clyde:																					
Min	7.44	3.6	301	6.1	174	40	13	2.0	3	13	0.037	4	0.68	16	43	9	<0.04	0.018	<0.03	<0.010	2.8
Max	7.99	21.9	523	13.2	532	153	46	5.9	14	30	0.220	15	3.58	40	153	43	0.05	0.077	0.50	0.50	14.9
Mean	7.75	10.4	421	10.0	310	86	27	3.0	8	20	0.091	8	2.73	27	91	23	<0.04	0.048	0.19	0.10	7.5
Median	7.77	9.5	435	10.5	280	81	25	2.7	7	19	0.078	7	2.97	28	85	20	<0.04	0.050	0.14	0.04	6.4
SD	0.13	5.2	60	1.8	87	29	9	1.1	3	5	0.047	3	0.86	7	30	10	0.01	0.013	0.13	0.13	3.3
Count	70	70	70	70	70	70	70	70	70	70	70	70	70	70	70	70	70	70	70	70	70
UKGEOS Glasgow Tollcross Burn:																					
Min	7.49	5.8	279	6.3	442	146	40	4.5	9	32	0.031	11	3.61	41	150	28	<0.04	0.071	<0.03	<0.010	4.1
Max	8.23	16.8	512	10.1	1026	405	87	13.2	33	99	0.244	28	6.94	138	423	75	0.19	0.220	0.44	0.14	9.6
Mean	7.99	10.3	399	8.9	853	332	77	10.4	25	66	0.061	22	5.44	69	349	61	0.13	0.132	0.08	0.08	6.4
Median	8.03	11.0	415	9.5	872	338	80	10.1	25	66	0.045	23	5.83	65	355	62	0.14	0.125	<0.03	0.08	6.3
SD	0.18	3.5	70	1.2	137	68	12	2.4	6	15	0.054	4	1.08	22	68	11	0.05	0.046	0.12	0.05	1.4
Count	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14
BGS Clyde Surface Water Dataset																					
Urban Stream:																					
Max	9.28	nd	nd	9.9	1064	451	179	14.9	39	85	4	nd	10	163	nd	222	0.67	0.680	nd	nd	42
Count	121			122	122	121	122	122	122	122	122	122	122	122	122	122	122	122	122	122	122
Clyde Estuary (River Samples):																					
Max	7.65	nd	nd	11.1	431	nd	40	5.6	13	28	0.45	nd	3.51	63	nd	48	nd	0.158	nd	nd	9.5
Count	6			3	6		6	6	6	6	6	6	6	6	6	6	6	6	6	6	6
Typical Rainwater																					
Mean	5.30				27	<1	0.2	0.1	0.4	2.9	0.010		0.13	5.4	1.70			0.02			0.79
River EQS																					
AA	5.95			4.5							0.069				400			5	0.069		5.7
MAC																		(>50 mg CaCO3/L)			15
95th%ile		*28																(>50 mg CaCO3/L)			

Table 2.2 cont.

	Trace Elements																	
	Ag µg/L	Al µg/L	As µg/L	B µg/L	Ba µg/L	Be µg/L	Bi µg/L	Cd µg/L	Ce µg/L	Co µg/L	Cr(III) µg/L	Cr(VI) µg/L	Cr-Total µg/L	Cs µg/L	Cu µg/L	Dy µg/L	Er µg/L	
UKGEOS Glasgow Surface Water Dataset All																		
Min	<0.04	7	0.22	<53	40	<0.08	<0.08	<0.005	<0.004	0.14	<0.04	<0.05	0.11	<0.04	0.82	<0.003	<0.003	
Max	<0.04	147	2.22	130	106	<0.08	<0.08	0.30	0.38	0.53	0.63	7.40	8.47	0.14	2.55	0.06	0.02	
Mean	<0.04	42	0.37	40	71	<0.08	<0.08	0.01	0.13	0.22	0.20	0.65	0.90	<0.04	1.26	0.020	0.011	
Median	<0.04	38	0.34	<53	66	<0.08	<0.08	0.01	0.12	0.19	0.21	0.18	0.46	<0.04	1.19	0.021	0.011	
SD	<0.01	29	0.22	30	15	<0.01	<0.01	0.03	0.10	0.07	0.14	1.44	1.52	0.03	0.35	0.015	0.007	
Count	84	84	84	84	84	84	84	84	84	84	84	84	84	84	84	84	84	
UKGEOS Glasgow River Clyde:																		
Min	<0.04	7	0.22	<53	40	<0.08	<0.08	<0.005	<0.004	0.14	<0.04	<0.05	0.13	<0.04	0.85	<0.003	<0.003	
Max	<0.04	147	0.61	58	106	<0.08	<0.08	<u>0.30</u>	0.38	0.34	0.63	7.40	8.47	0.14	2.55	0.055	0.023	
Mean	<0.04	48	0.34	<53	73	<0.08	<0.08	0.01	0.15	0.20	0.23	0.76	1.05	<0.04	1.26	0.023	0.012	
Median	<0.04	44	0.33	<53	69	<0.08	<0.08	0.01	0.15	0.19	0.22	0.20	0.50	<0.04	1.20	0.023	0.012	
SD	<0.01	27	0.09	4	16	<0.01	<0.01	0.03	0.10	0.05	0.14	1.55	1.63	<0.04	0.36	0.014	0.007	
Count	70	70	70	70	70	70	70	70	70	70	70	70	70	70	70	70	70	
UKGEOS Glasgow Tollcross Burn:																		
Min	<0.04	7	0.25	<53	48	<0.08	<0.08	<0.005	<0.004	0.19	<0.04	<0.05	0.11	<0.04	0.82	<0.003	<0.003	
Max	<0.04	20	2.22	130	69	<0.08	<0.08	0.02	0.11	0.53	0.22	0.26	0.50	0.06	2.02	0.010	0.006	
Mean	<0.04	9	0.51	103	62	<0.08	<0.08	0.01	0.01	0.30	0.06	0.08	0.16	<0.04	1.27	0.003	0.003	
Median	<0.04	9	0.36	104	62	<0.08	<0.08	0.01	0.01	0.27	<0.04	<0.05	0.13	<0.04	1.18	0.003	0.003	
SD	<0.01	3	0.50	26	6	<0.01	<0.01	0.01	0.03	0.09	0.06	0.07	0.10	0.02	0.32	0.002	0.001	
Count	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	
BGS Clyde Surface Water Dataset																		
Urban Stream:																		
Max	nd	335	149	nd	254	0.29	0.01	0.30	0.84	4.26	nd	nd	903	0.20	9.99	nd	nd	
Count		122	122		122	122	122	122	122	122			122	122	122			
Clyde Estuary (River Samples):																		
Max	nd	64	5	40	84	1.25	nd	0.05	nd	0.45	nd	nd	6	1.49	3	nd	nd	
Count		6	6	3	6	6		6		6			6	6	6			
Typical Rainwater																		
Mean		7.1	0.1		1			0.19										
River EQS																		
AA	0.05	15 (pH>6.5)	50	2000				0.09 (class 3 > 50 mg/L CaCO ₃) to 0.25 (class 5 ≥ 200 mg/L CaCO ₃)			3	4.7	3.4		1			
MAC	0.1	25 (pH>6.5)						0.6 (class 3) to 1.5 (class 5)			100							
95th%ile																		32

Table 2.2 cont.

	Trace Elements cont.																		
	Eu µg/L	Fe µg/L	Ga µg/L	Gd µg/L	Hf µg/L	Ho µg/L	La µg/L	Li µg/L	Lu µg/L	Mn µg/L	Mo µg/L	Nb µg/L	Nd µg/L	Ni µg/L	Pb µg/L	Pr µg/L	Rb µg/L	Sb µg/L	Se µg/L
UKGEOS Glasgow Surface Water Dataset																			
Min	<0.003	13	<0.04	<0.005	<0.006	<0.003	<0.003	<7	<0.003	20	<0.2	<0.01	<0.005	1.2	<0.02	<0.003	1.8	0.10	0.11
Max	0.02	748	0.04	0.07	0.008	0.010	0.24	15	0.004	201	0.80	0.07	0.30	2.2	1.06	0.06	20.2	0.49	0.85
Mean	0.007	250	<0.04	0.02	<0.006	0.004	0.08	5	<0.003	57	0.41	<0.01	0.11	1.6	0.44	0.02	5.1	0.20	0.21
Median	0.006	233	<0.04	0.03	<0.006	0.004	0.09	4	<0.003	39	0.40	<0.01	0.11	1.6	0.50	0.03	3.0	0.17	0.17
SD	0.004	176	<0.01	0.02	0.001	0.002	0.07	3	<0.001	41	0.16	0.01	0.08	0.2	0.28	0.02	4.8	0.09	0.14
Count	84	84	84	84	84	84	84	84	84	84	84	84	84	84	84	84	84	84	84
UKGEOS Glasgow River Clyde:																			
Min	<0.003	31	<0.04	<0.005	<0.006	<0.003	<0.003	<7	<0.003	20	<0.2	<0.01	<0.005	1.2	<0.02	<0.003	1.8	0.10	0.11
Max	0.017	748	0.04	0.066	0.008	0.010	0.24	<7	0.004	201	0.80	0.07	0.30	2.2	<u>1.06</u>	0.06	6.5	0.39	0.25
Mean	0.008	295	<0.04	0.029	<0.006	0.005	0.10	<7	<0.003	50	0.36	<0.01	0.13	1.6	0.51	0.03	3.2	0.18	0.16
Median	0.008	274	<0.04	0.033	<0.006	0.005	0.09	<7	<0.003	35	0.40	<0.01	0.13	1.5	0.52	0.03	2.7	0.15	0.15
SD	0.004	158	<0.01	0.018	0.002	0.002	0.06	0	<0.001	40	0.12	<0.01	0.08	0.2	0.25	0.02	1.3	0.07	0.04
Count	70	70	70	70	70	70	70	70	70	70	70	70	70	70	70	70	70	70	70
UKGEOS Glasgow Tollcross Burn:																			
Min	<0.003	13	<0.04	<0.005	<0.006	<0.003	<0.003	<7	<0.003	44	0.50	<0.01	<0.005	1.2	<0.02	<0.003	5.3	0.20	0.17
Max	0.004	69	<0.04	0.012	<0.006	<0.003	0.05	15	<0.003	157	0.70	<0.01	0.07	1.8	0.20	0.014	20.2	0.49	0.85
Mean	<0.003	26	<0.04	<0.005	<0.006	<0.003	0.01	11	<0.003	88	0.65	<0.01	0.01	1.6	0.06	0.003	14.8	0.32	0.44
Median	<0.003	21	<0.04	<0.005	<0.006	<0.003	0.005	11	<0.003	84	0.70	<0.01	<0.005	1.6	0.04	<0.003	14.2	0.31	0.43
SD	0.001	14	<0.01	0.002	<0.001	<0.001	0.01	3	<0.001	33	0.07	<0.01	0.02	0.2	0.05	0.003	4.0	0.08	0.23
Count	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14
BGS Clyde Surface Water Dataset																			
Urban Stream:																			
Max	nd	7580	nd	nd	nd	0.015	0.39	68	nd	1480	214	nd	nd	7.4	6	nd	23.7	10.7	3.88
Count		122				122	122	122		122	122			122	122		122	122	122
Clyde Estuary (River Samples):																			
Max	nd	560	nd	nd	nd	nd	nd	5.2	nd	1400	1.76	nd	nd	3	0.5	nd	5.18	0.40	0.27
Count		6						6		6	6			6	6		6	6	6
Typical Rainwater																			
Mean		5						0.07		1	0.17			0.7	6.8				
River EQS																			
AA		1000								123				4(Bio)	1.2(Bio)				
MAC														34	14				
95th%ile																			

Table 2.2 cont.

		Trace Elements cont.															
		Sm µg/L	Sn µg/L	Sr µg/L	Ta µg/L	Tb µg/L	Th µg/L	Ti µg/L	Tl µg/L	Tm µg/L	U µg/L	V µg/L	W µg/L	Y µg/L	Yb µg/L	Zn µg/L	Zr µg/L
UKGEOS Glasgow Surface Water Dataset																	
Min		<0.005	<0.08	64	<0.006	<0.004	<0.03	<0.06	<0.02	<0.003	0.05	<0.02	<0.06	0.01	<0.004	2.1	0.01
Max		0.07	0.31	1365	<0.006	0.0410	<0.03	6.9	<0.02	0.004	0.46	0.97	0.07	0.30	0.023	23.7	0.28
Mean		0.02	<0.08	292	<0.006	0.0063	<0.03	1.3	<0.02	0.002	0.17	0.56	<0.06	0.12	0.011	4.3	0.10
Median		0.03	<0.08	149	<0.006	0.0040	<0.03	1.0	<0.02	0.002	0.13	0.55	<0.06	0.13	0.010	3.7	0.09
SD		0.02	0.05	340	<0.001	0.0079	<0.01	1.3	<0.01	<0.002	0.11	0.16	0.01	0.08	0.006	2.8	0.07
Count		84	84	84	84	84	84	84	84	84	84	84	84	84	84	84	84
UKGEOS Glasgow River Clyde:																	
Min		<0.005	<0.08	64	<0.006	<0.004	<0.03	<0.06	<0.02	<0.003	0.05	<0.02	<0.06	0.01	<0.004	2.1	0.01
Max		0.07	0.31	274	<0.006	0.04	<0.03	6.9	<0.02	0.004	0.22	0.97	0.07	0.30	0.02	23.7	0.28
Mean		0.03	<0.08	150	<0.006	0.01	<0.03	1.5	<0.02	<0.003	0.13	0.57	<0.06	0.14	0.01	4.0	0.11
Median		0.03	<0.08	130	<0.006	0.01	<0.03	1.2	<0.02	<0.003	0.12	0.57	<0.06	0.14	0.01	3.6	0.11
SD		0.02	0.06	59	<0.001	0.01	0.00	1.3	<0.01	<0.001	0.04	0.16	0.01	0.08	0.01	2.5	0.07
Count		70	70	70	70	70	70	70	70	70	70	70	70	70	70	70	70
UKGEOS Glasgow Tollcross Burn:																	
Min		<0.005	<0.08	327	<0.006	<0.004	<0.03	<0.06	<0.02	<0.003	0.21	<0.02	<0.06	0.01	<0.004	2.1	0.02
Max		0.017	<0.08	1365	<0.006	<0.004	<0.03	1.5	<0.02	<0.003	0.46	0.85	<0.06	0.05	0.008	12.5	0.07
Mean		<0.005	<0.08	1003	<0.006	<0.004	<0.03	0.2	<0.02	<0.003	0.39	0.54	<0.06	0.03	0.005	6.2	0.04
Median		<0.005	<0.08	968	<0.006	<0.004	<0.03	0.1	<0.02	<0.003	0.39	0.54	<0.06	0.03	0.006	6.3	0.04
SD		0.004	<0.01	255	<0.001	<0.001	<0.01	0.4	<0.01	<0.001	0.06	0.20	<0.01	0.01	0.002	3.3	0.01
Count		14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14
BGS Clyde Surface Water Dataset																	
Urban Stream:																	
Max		nd	0.41	1550	nd	nd	0.04	nd	0.13	nd	1.24	18.1	nd	0.444	nd	177	0.8
Count			122	122			122		122		122	122		122		122	122
Clyde Estuary (River Samples):																	
Max		nd	0.40	240	nd	nd	nd	nd	nd	nd	0.22	1.25	nd	nd	nd	14	nd
Count			6	6							6	6				6	
Typical Rainwater																	
Mean				2								0.13				5	
River EQS																	
AA		25															Bio
MAC																	
95th%ile																	
																	20 (class 1 ≤200 mg/L CaCO3) to 60 (class 2>200 mg/> CaCO3)
																	10.9

Table 2.2 cont.

	Organic Parameters											Stable Isotopes		
	TIC mg/L	NPOC mg/L	Benzo(b) fluoranthene µg/L	Benzo(k) fluoranthene µg/L	Benzo(a) pyrene µg/L	Benzo(ghi) perylene 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	δ13C VPDB ‰	δ18O VSMOW2 ‰	δ2H VSMOW2 ‰
UKGEOS Glasgow Surface Water Dataset														
Min	8	2.6	<0.001	<0.001	<0.0005	<0.001	<0.002	<0.005	<0.003	<0.042	<0.045	-25.6	-9.5	-66.9
Max	83	17.3	0.102	0.052	0.106	0.061	0.091	0.305	0.004	0.866	0.866	-10.5	-6.6	-39.3
Mean	26	5.6	0.008	0.003	0.007	0.004	0.005	0.019	<0.003	0.061	0.061	-12.6	-7.5	-48.1
Median	18	4.7	0.003	0.002	0.003	0.002	0.002	0.006	<0.003	0.047	0.047	-12.4	-7.3	-47.5
SD	20	2.5	0.013	0.006	0.013	0.008	0.011	0.038	0.001	0.099	0.099	1.9	0.5	3.7
Count	84	84	83	83	83	83	83	83	84	84	84	83	84	84
UKGEOS Glasgow River Clyde:														
Min	8	3.0	<0.001	<0.001	<0.0005	<0.001	<0.002	<0.005	<0.003	<0.042	<0.045	-25.6	-8.4	-54.4
Max	30	<u>17.3</u>	0.035	0.016	0.034	0.021	0.033	0.104	0.004	0.866	0.866	-10.5	-6.6	-39.3
Mean	18	6.1	0.005	0.002	0.005	0.003	0.004	0.012	<0.003	0.058	0.057	-12.7	-7.5	-48.0
Median	17	5.2	0.003	0.001	0.003	0.002	<0.002	0.006	<0.003	0.046	<0.045	-12.5	-7.4	-47.4
SD	6	2.5	0.006	0.002	0.006	0.004	0.005	0.018	<0.001	0.102	0.102	2.0	0.5	3.3
Count	70	70	69	69	69	69	69	69	70	70	70	69	70	70
UKGEOS Glasgow Tollcross Burn:														
Min	30	2.6	0.003	0.001	0.002	0.002	<0.002	0.007	<0.003	<0.042	<0.045	-16.0	-9.5	-66.9
Max	83	6.9	0.102	0.052	0.106	0.061	0.091	0.305	<0.003	0.279	0.279	-11.1	-7.0	-45.2
Mean	69	3.5	0.019	0.008	0.019	0.010	0.015	0.053	<0.003	0.080	0.081	-12.4	-7.5	-49.0
Median	70	3.2	0.011	0.004	0.010	0.005	0.006	0.027	<0.003	0.054	0.054	-12.2	-7.3	-47.6
SD	13	1.1	0.026	0.013	0.028	0.016	0.023	0.078	<0.001	0.085	0.085	1.2	0.6	5.4
Count	14	14	14	14	14	14	14	14	14	14	14	14	14	14
BGS Clyde Surface Water Dataset														
River:														
Max	nd	8.9	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Count		60												
Urban Stream:														
Max	nd	48.8	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Count														
Clyde Estuary (River Samples):														
Max	nd	10	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Count		6												
Typical Rainwater														
Mean														
River EQS														
AA			∑B(b+k)F 0.03	∑B(b+k)F 0.03	0.05	∑B(ghi)PI+ I(123-cd)Py 0.002	∑B(ghi)PI+ I(123-cd)Py 0.002							
MAC					0.1									

Table 2.2 cont.

Rainwater mean: from BGS (1999) and Smedley et al. (2017)

BGS Clyde Surface Water Dataset: from Fordyce et al. (2004), Jones et al. (2004) and Smedley et al (2017)

EQS: Environmental quality standard for good river status from SEPA (2014) and SEPA (2019)

Nitrate: no UK river water standard. Commonly used EU standard from Poikane et al. (2019)

Phosphorus: typical lowland high alkalinity standard from UKTAG (2013)

Bio: generic 100% bioavailable limit for Tier 1 risk assessment

Italic text: UKGEOS maximum exceeds maximum in BGS Clyde river or urban stream dataset, but is of similar range

Italic underline text: UKGEOS maximum is more than 1.5 times the BGS Clyde river or urban stream dataset maximum

Bold text: UKGEOS mean exceeds EQS AA and/or UKGEOS maximum exceeds EQS MAC

B(b+k)F: Benzo(b+k)fluoranthene

B(ghi)PI: Benzo(ghi)perylene

I(123-cd)Py: Indeno(1,2,3-cd)pyrene

AA: annual average

MAC: maximum allowable concentration

95%ile: 95th percentile limit

* 98th percentile limit

Min: minimum

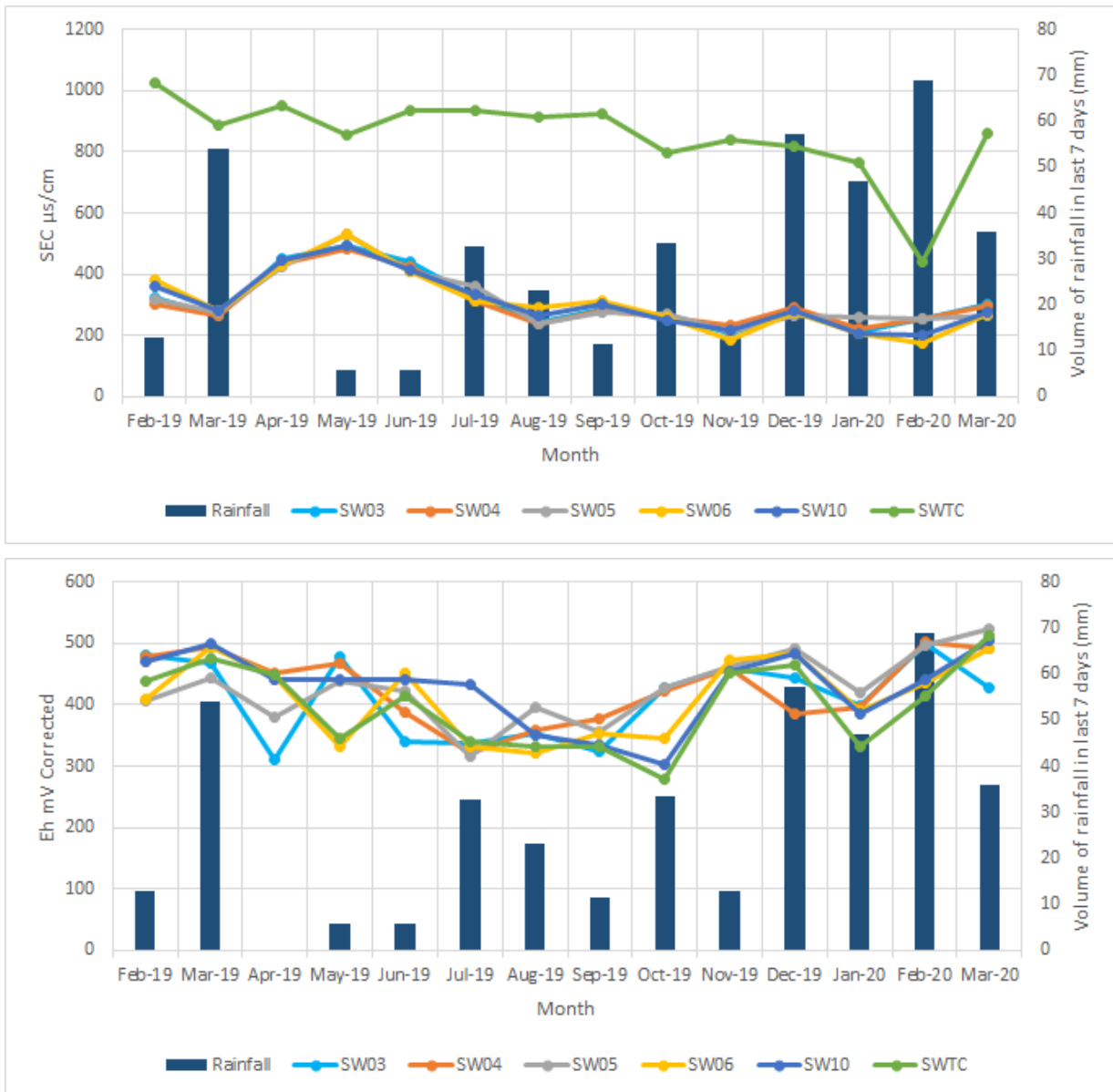
Max: maximum

SD: standard deviation

nd: no data

Appendix 3 Surface Water Chemistry Time-series Plots

Time-series plots of the UKGEOS surface water chemistry data are presented in Figures A3.1 to A3.10. The chemical parameters measured in each monthly round of water samples for each sampling location (shown in different colours) are plotted against the total amount of rainfall that fell within the seven days prior to sampling in each case. Rainfall is shown as bars on the plots. Where an environmental quality standard (EQS) is defined for a parameter, the annual average (AA) for good river status (SEPA 2014; SEPA 2019) is plotted on the graphs for comparison with the data.



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Figure A3.1 Time-series plots of surface water physico-chemical parameters: specific electrical conductance (SEC), pH, temperature, dissolved oxygen (DO) and redox potential (Eh), shown in different colours for each sampling location.

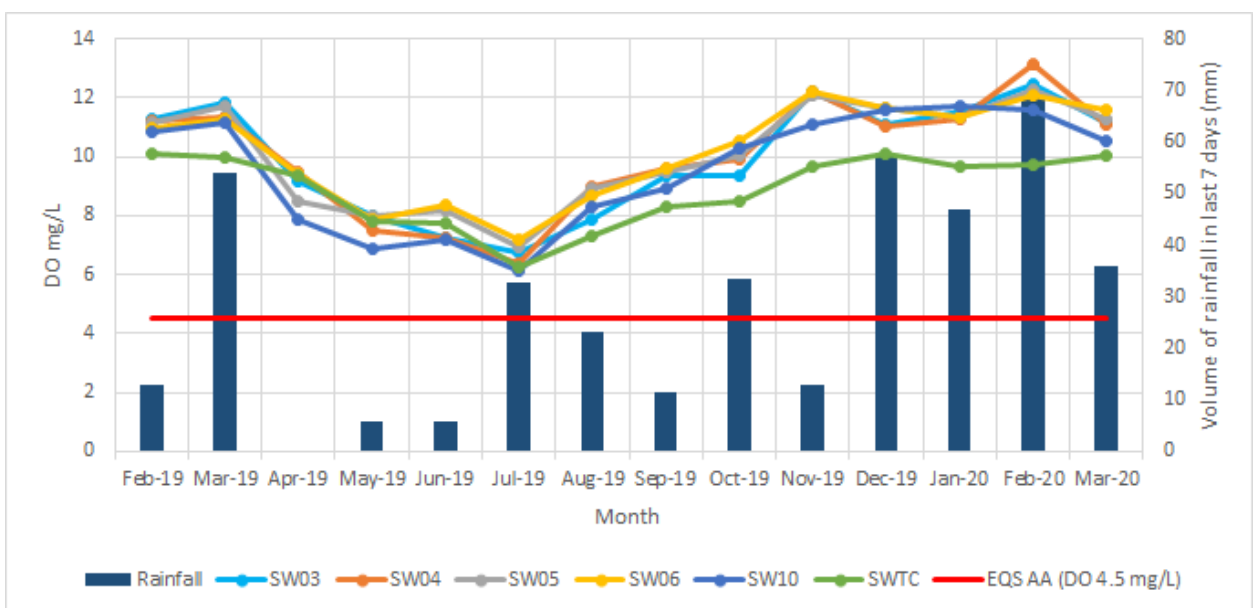
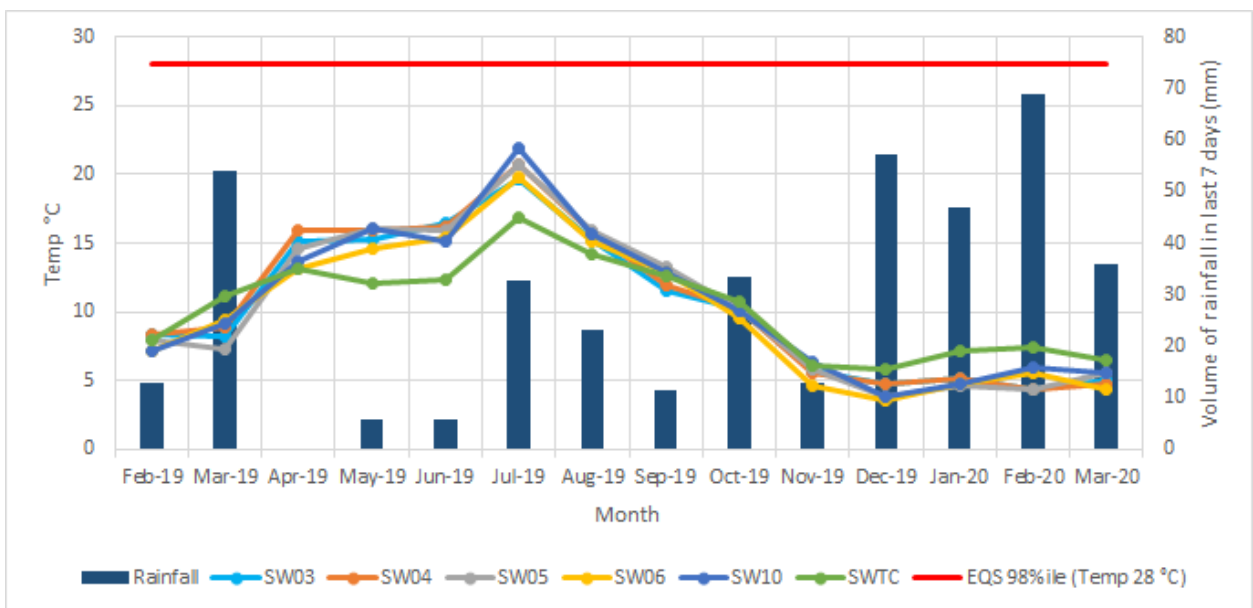
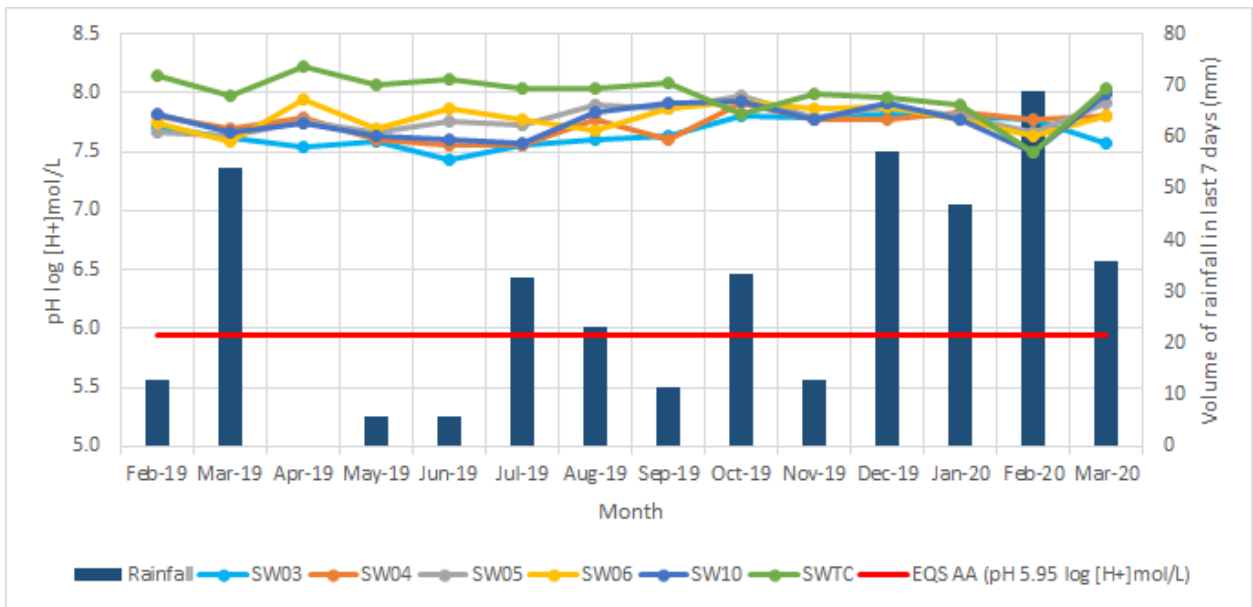
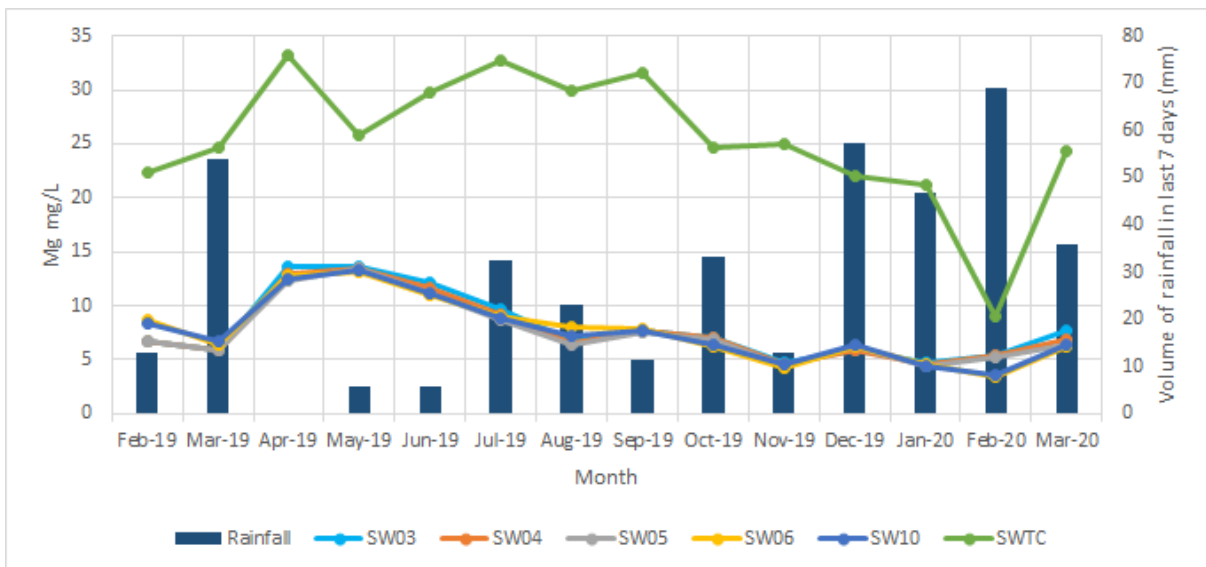
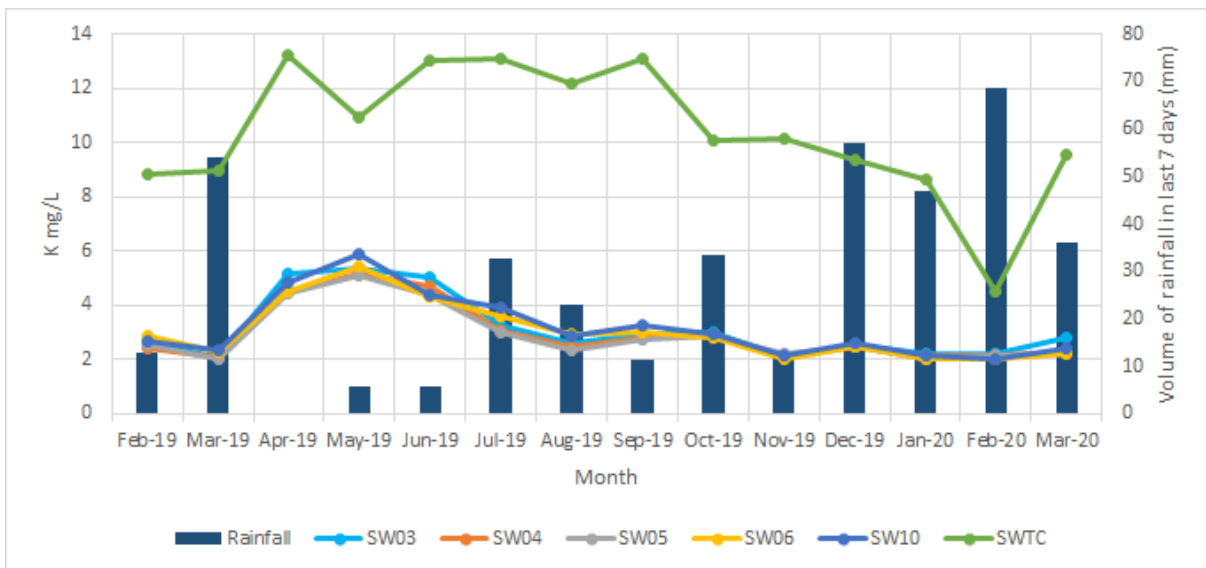
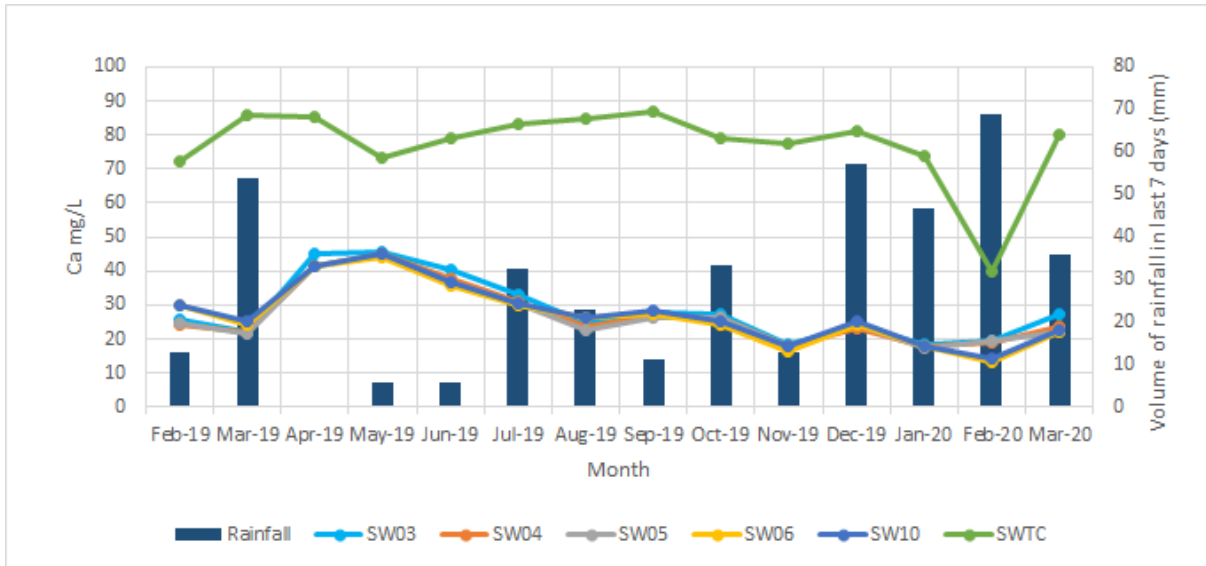


Figure A3.1 cont.



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Figure A3.2 Time-series plots of surface water major cation concentrations: Ca, K, Mg and Na, shown in different colours for each sampling location.

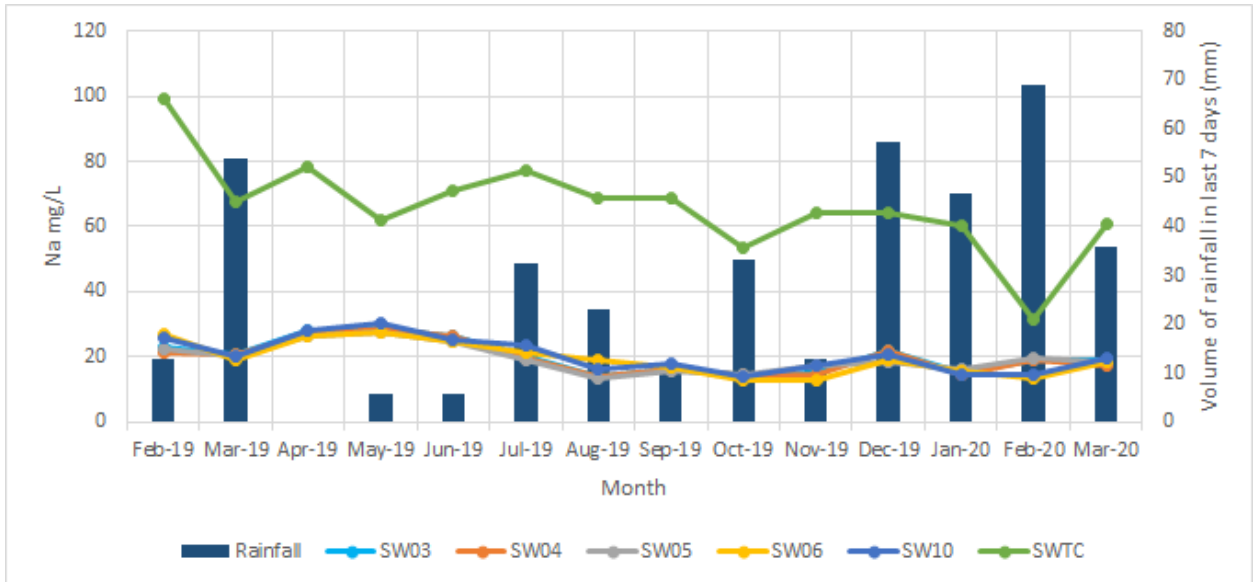
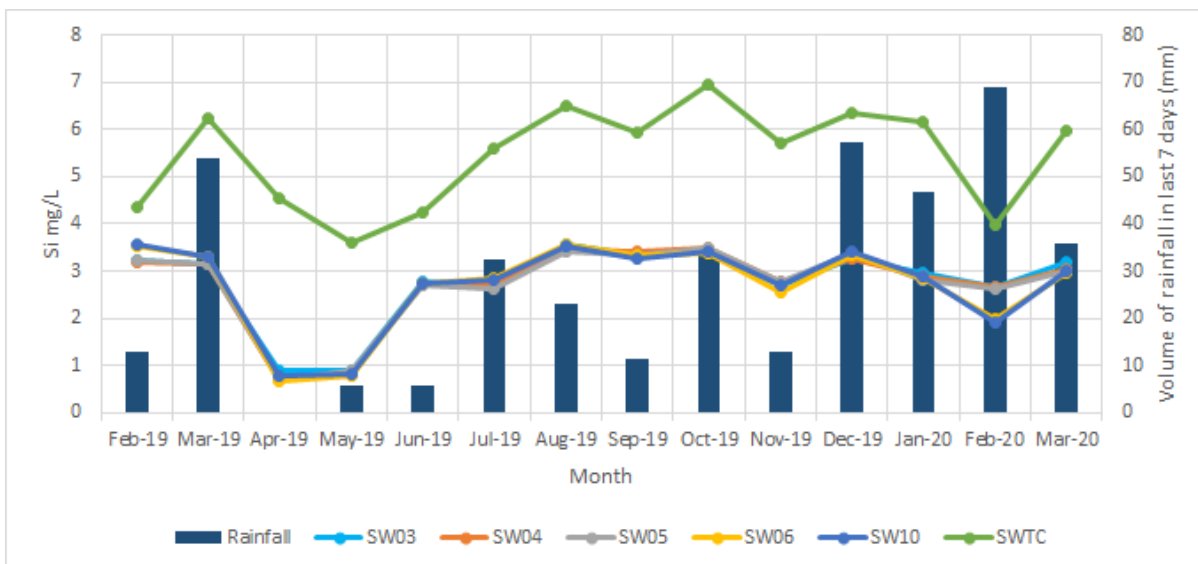
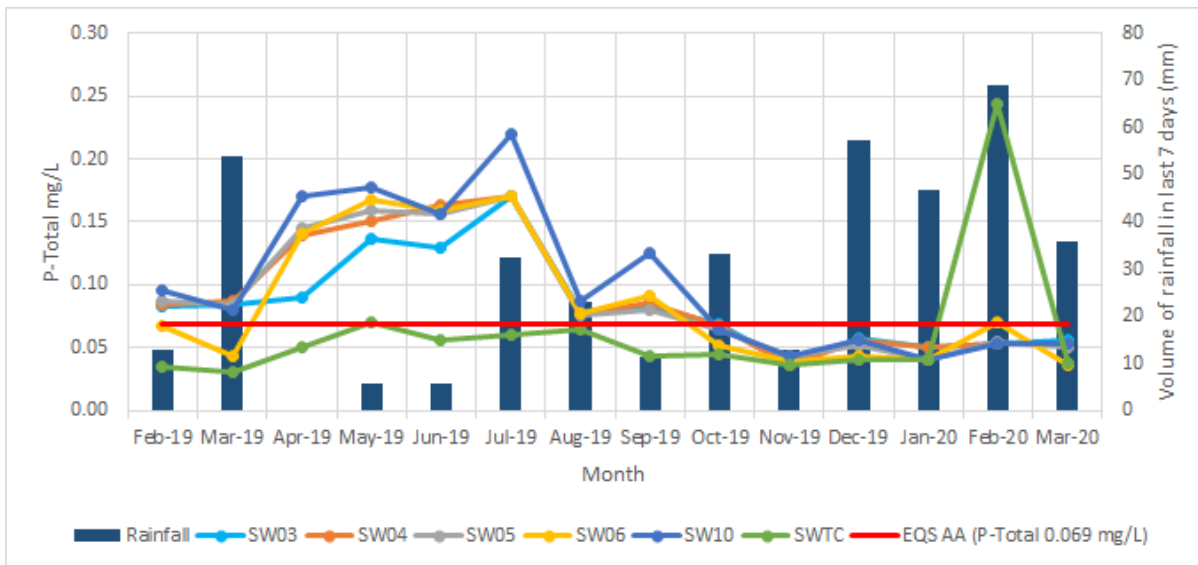
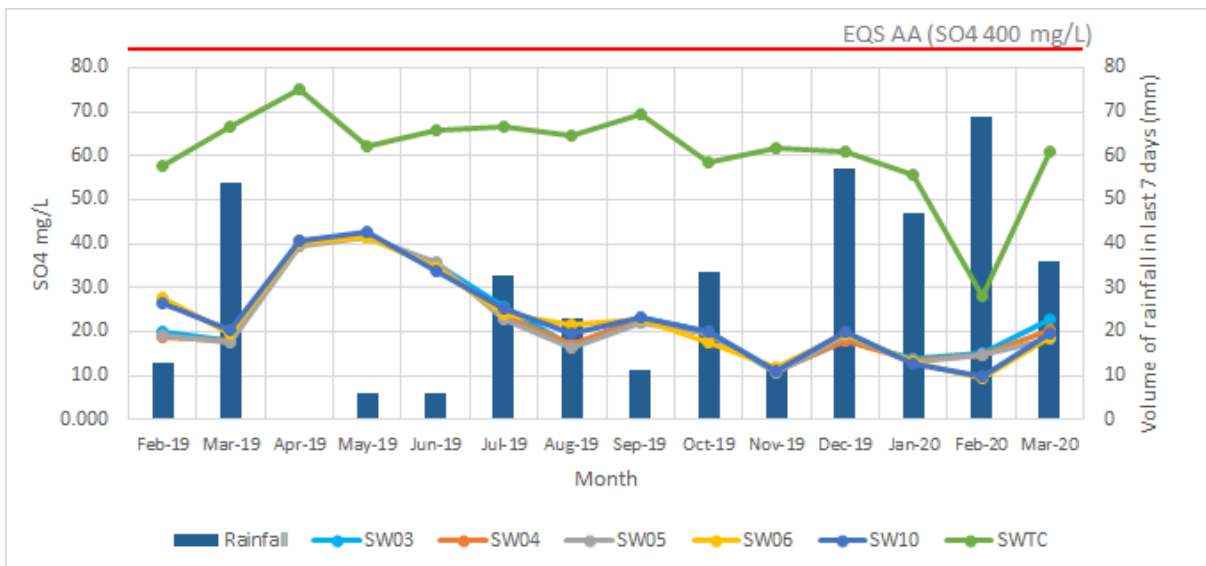
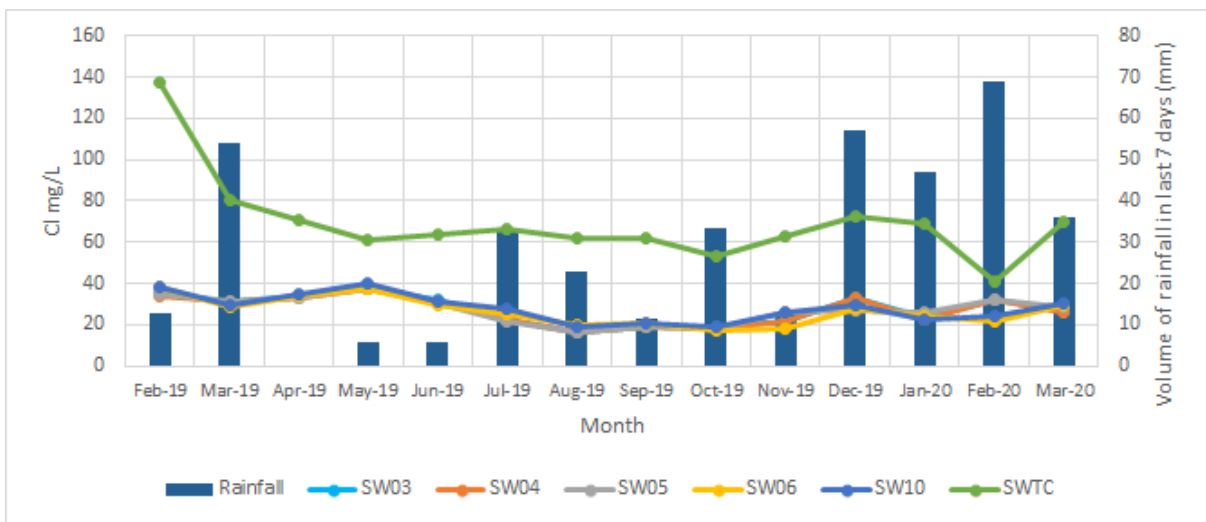
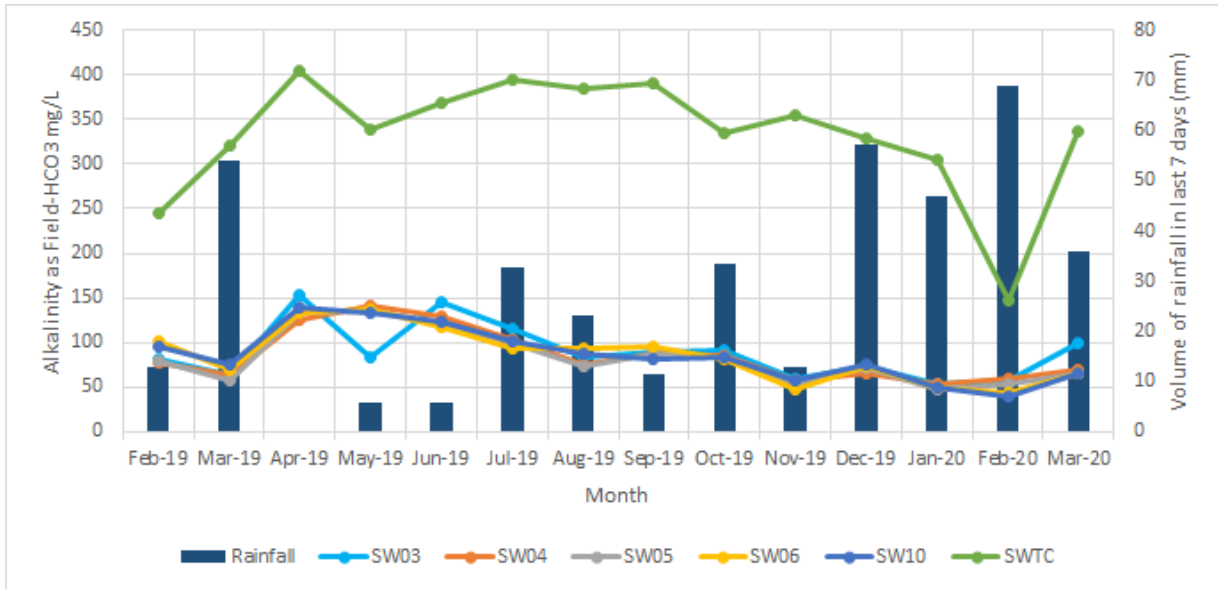


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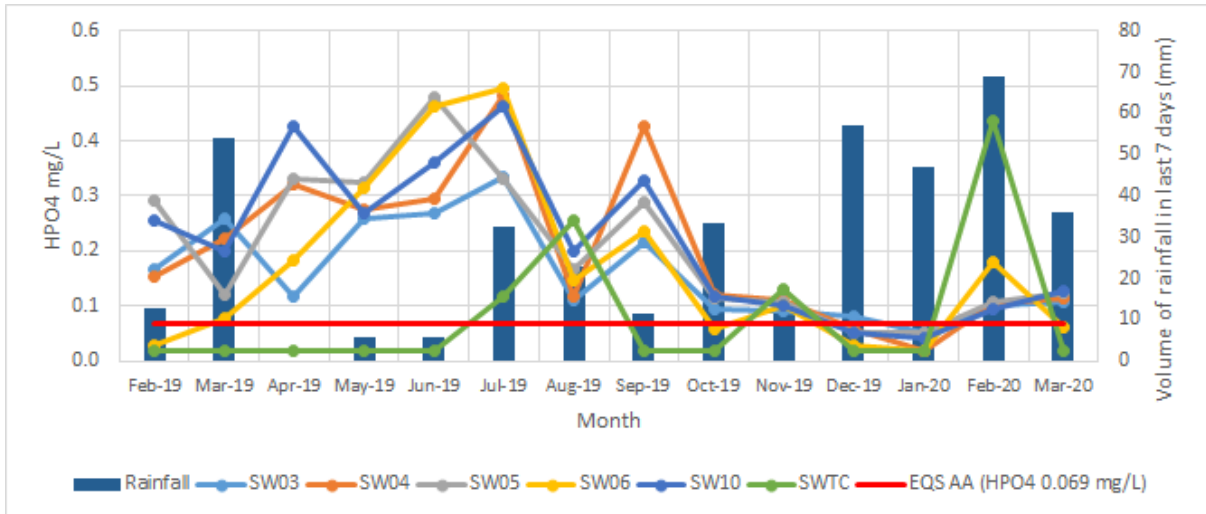
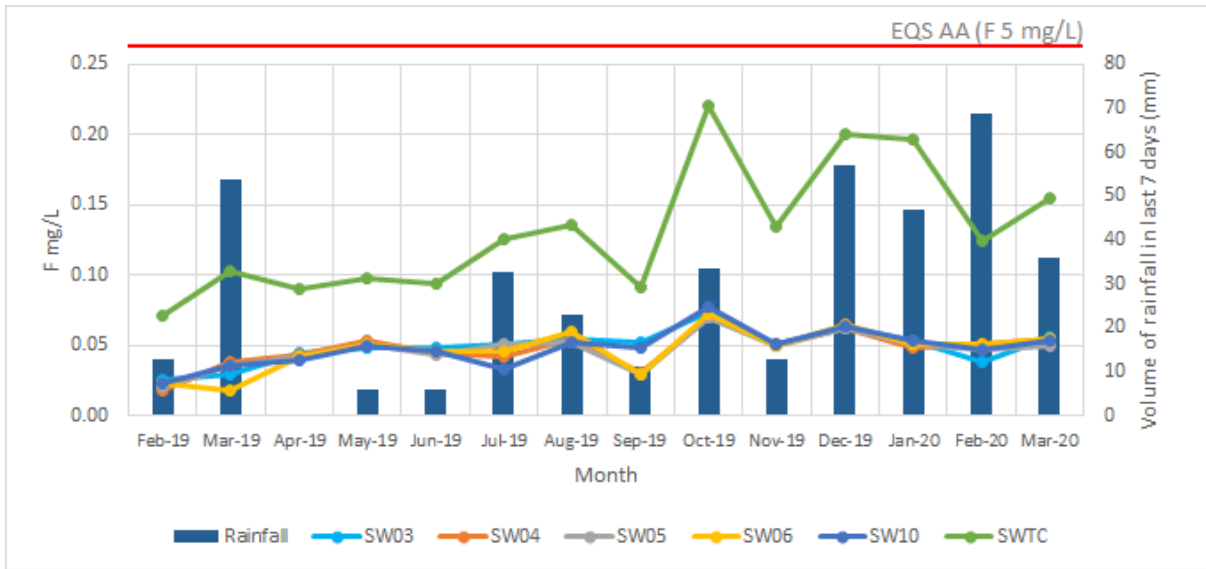
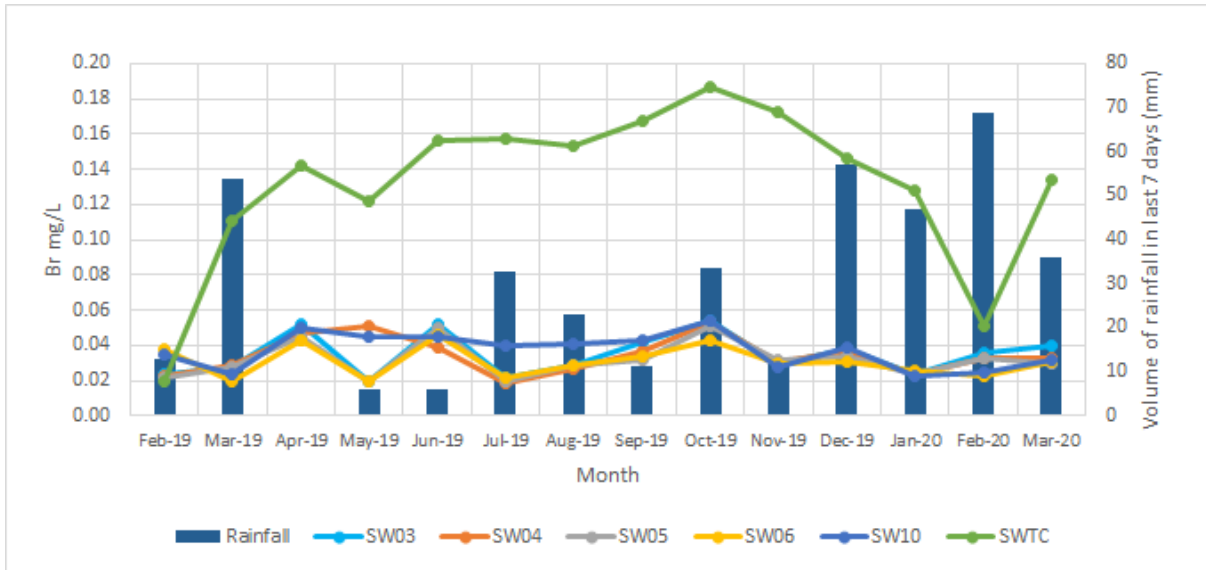
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Figure A3.3 Time-series plots of surface water minor element cation concentrations: P-Total and Si, shown in different colours for each sampling location.



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Figure A3.4 Time-series plots of surface water major element anion concentrations: field-HCO₃, Cl and SO₄, shown in different colours for each sampling location.



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Figure A3.5 Time-series plots of surface water minor anion concentrations: Br, F, HPO₄, NO₂ and NO₃, shown in different colours for each sampling location.

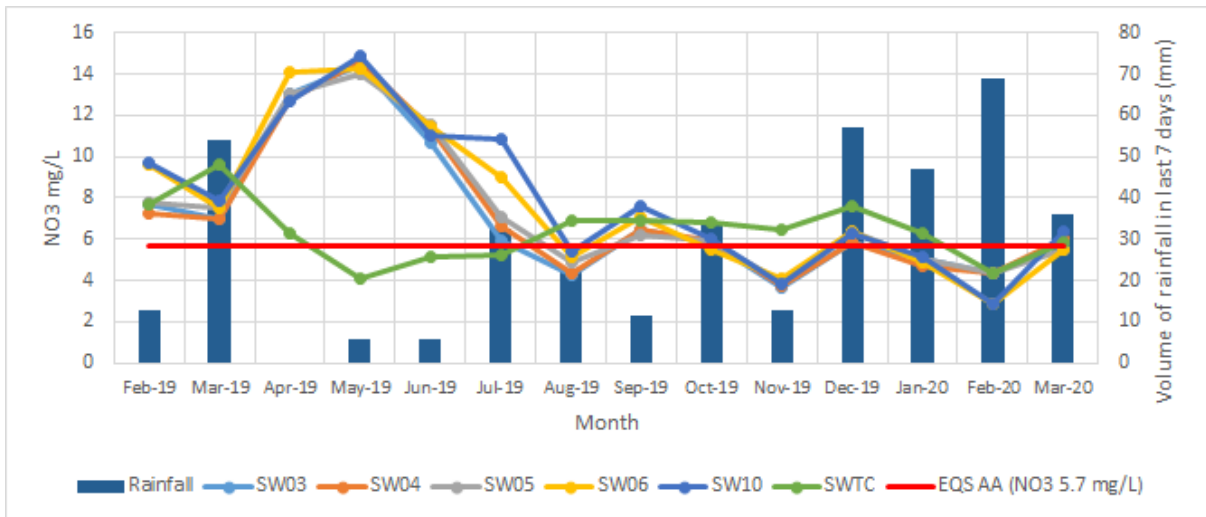
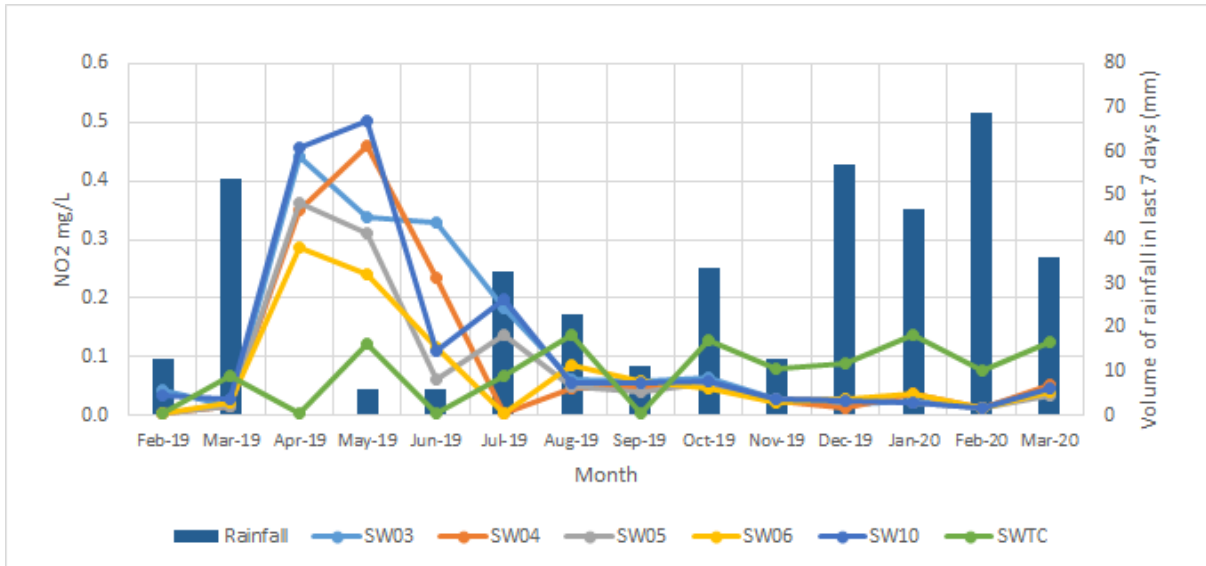
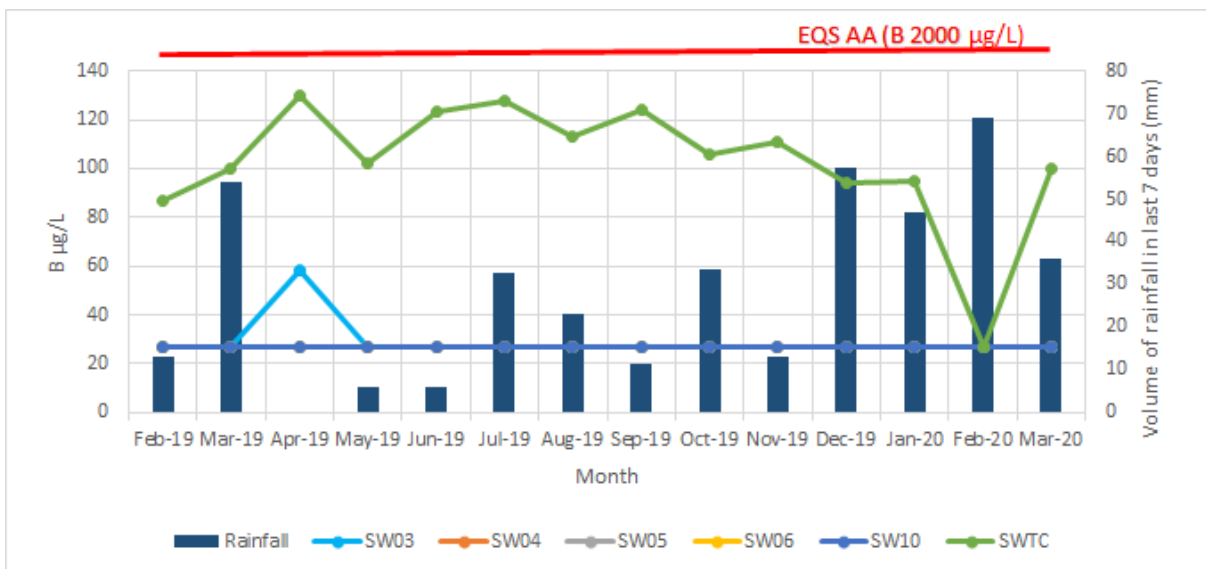
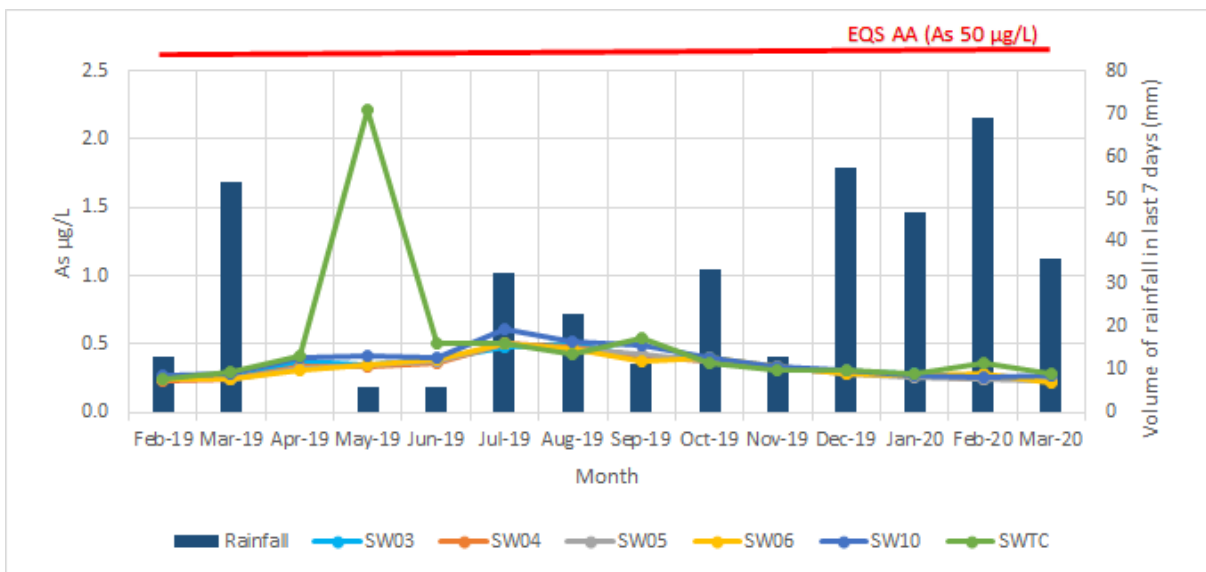
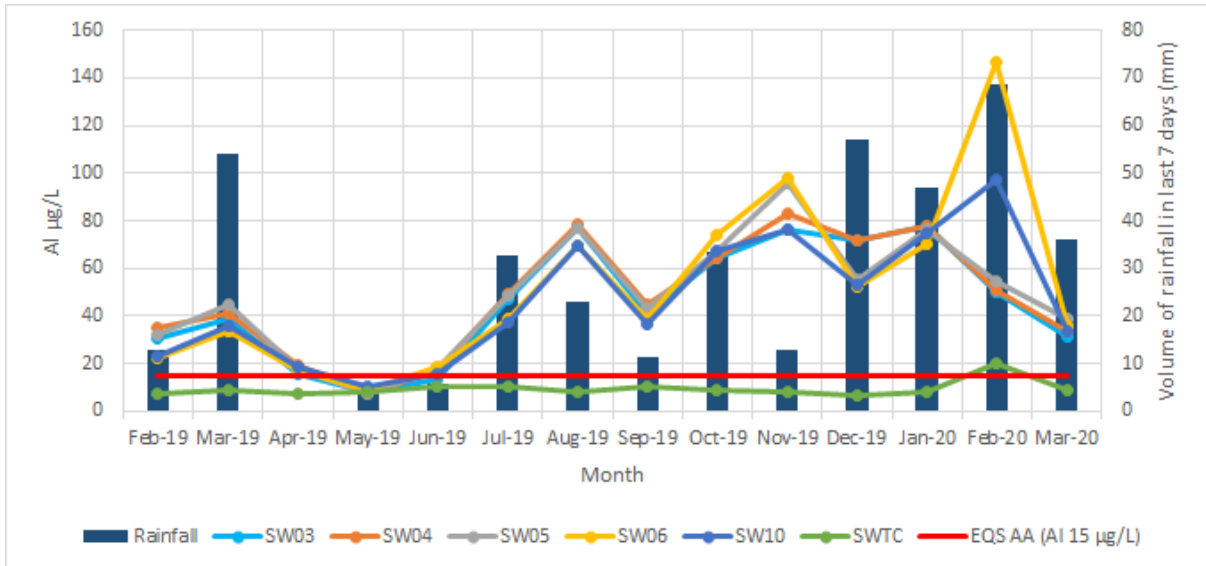


Figure A3.5. cont.



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Figure A3.6 Time-series plots of selected surface water trace element concentrations, shown in different colours for each sampling location.

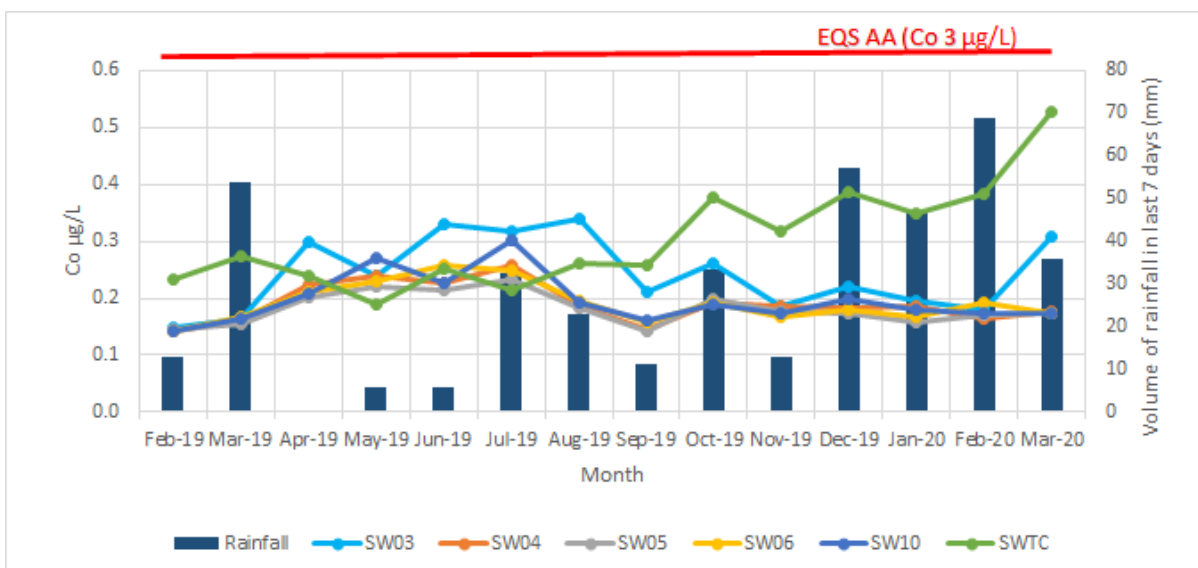
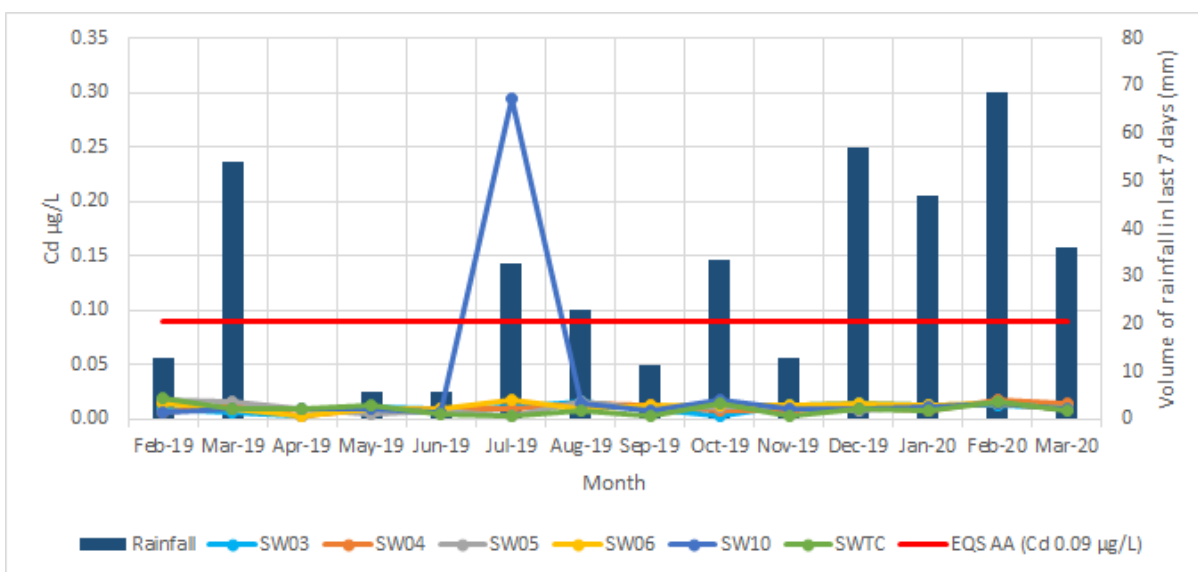
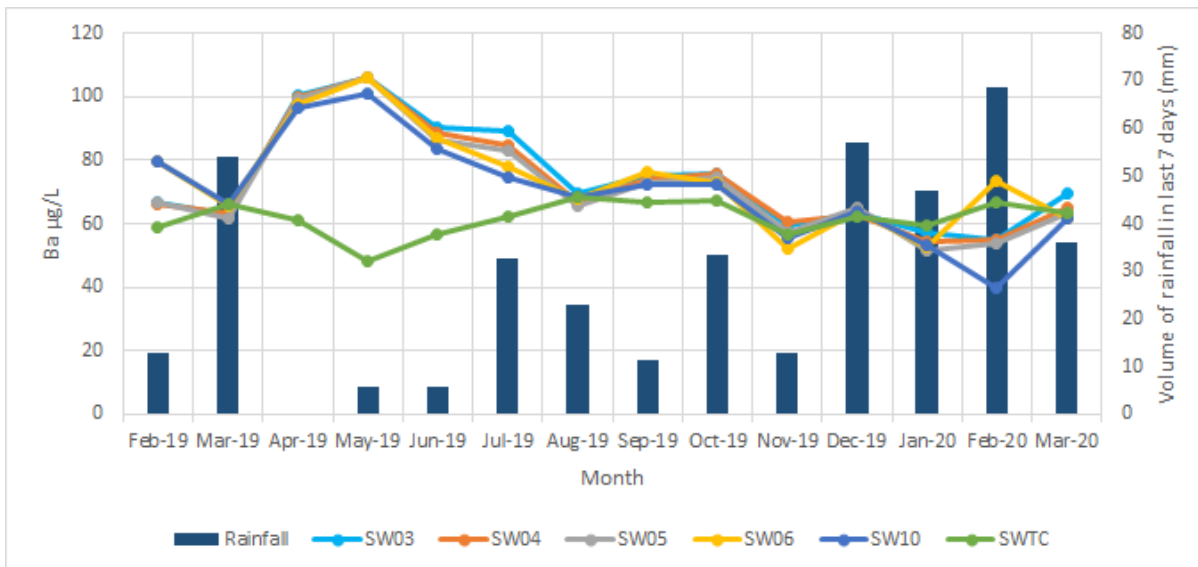


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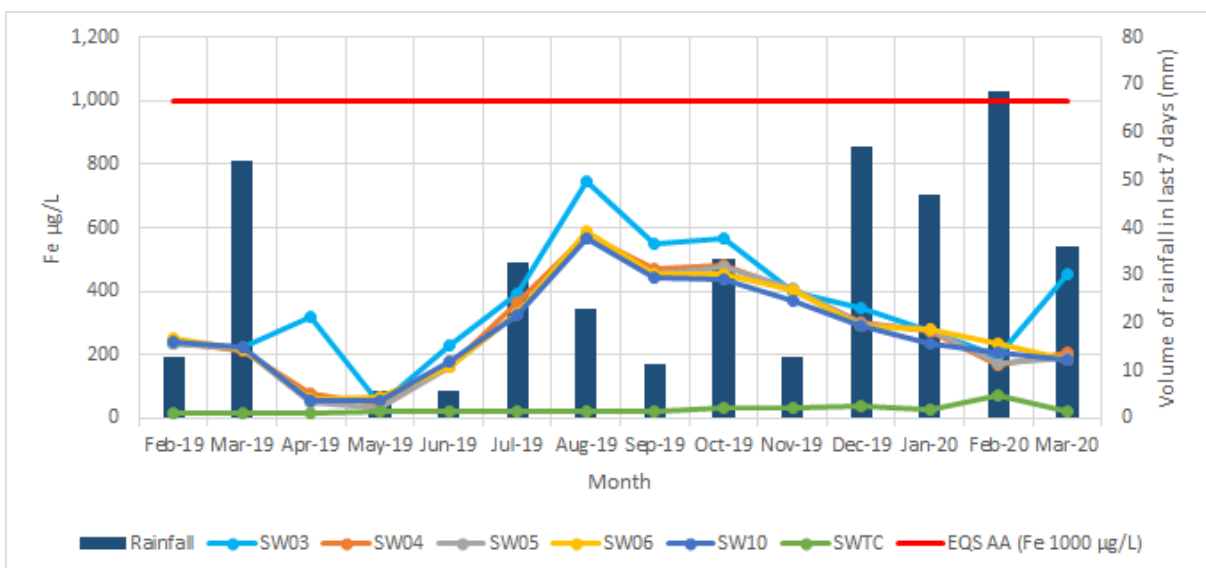
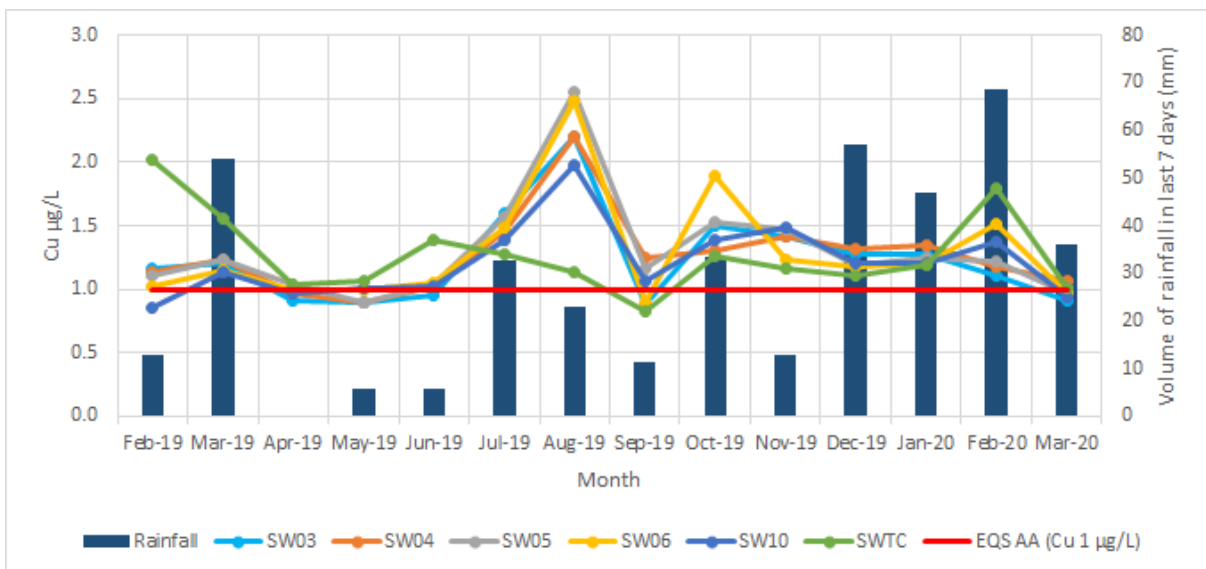
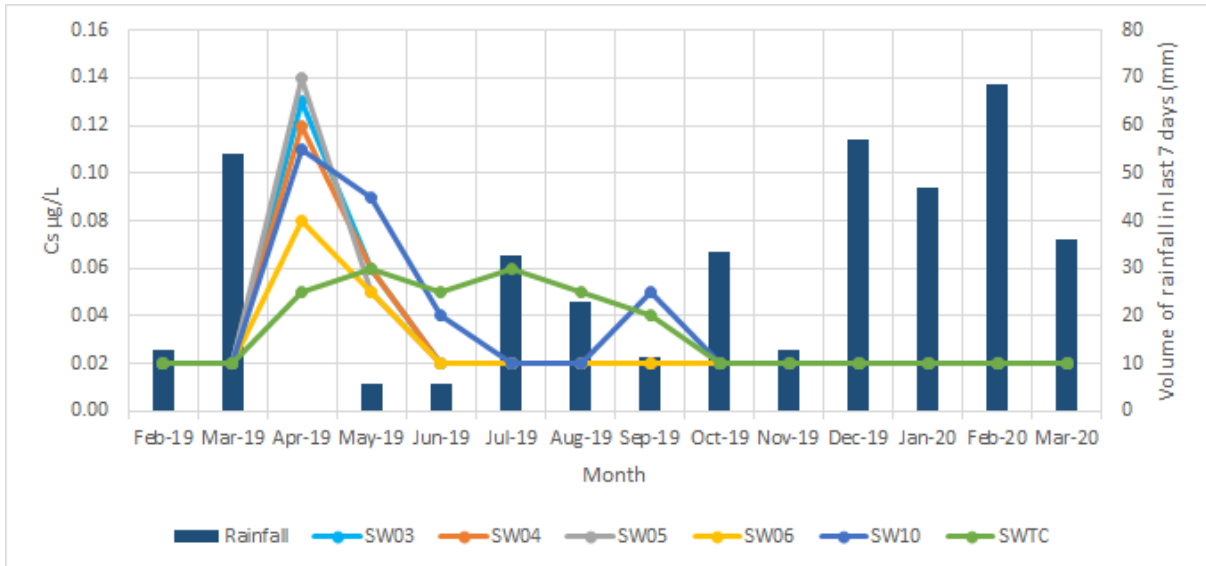


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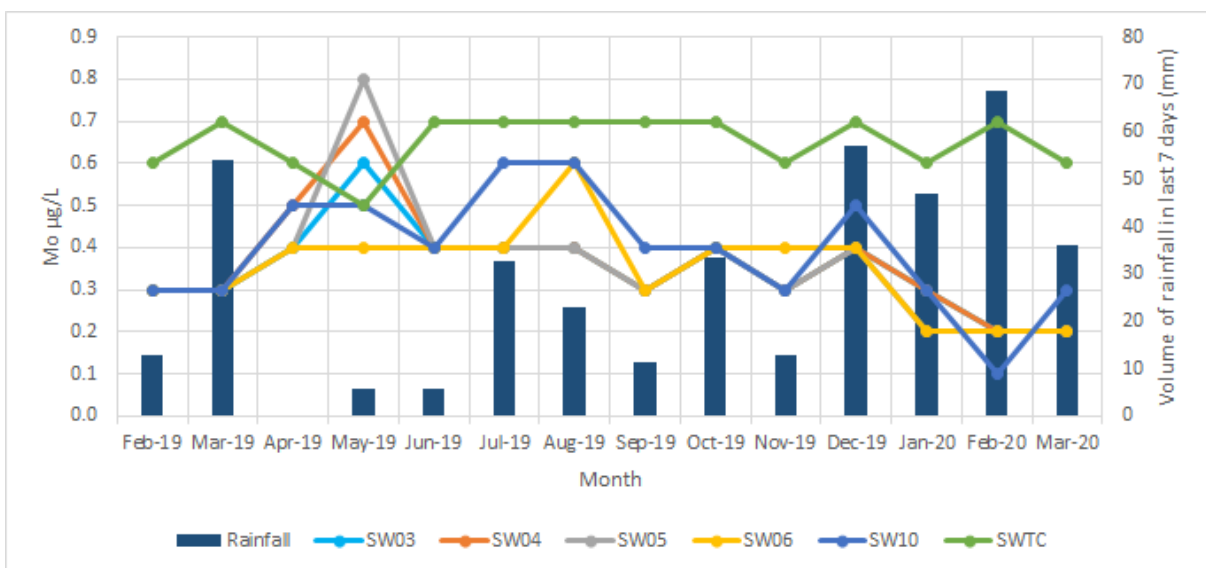
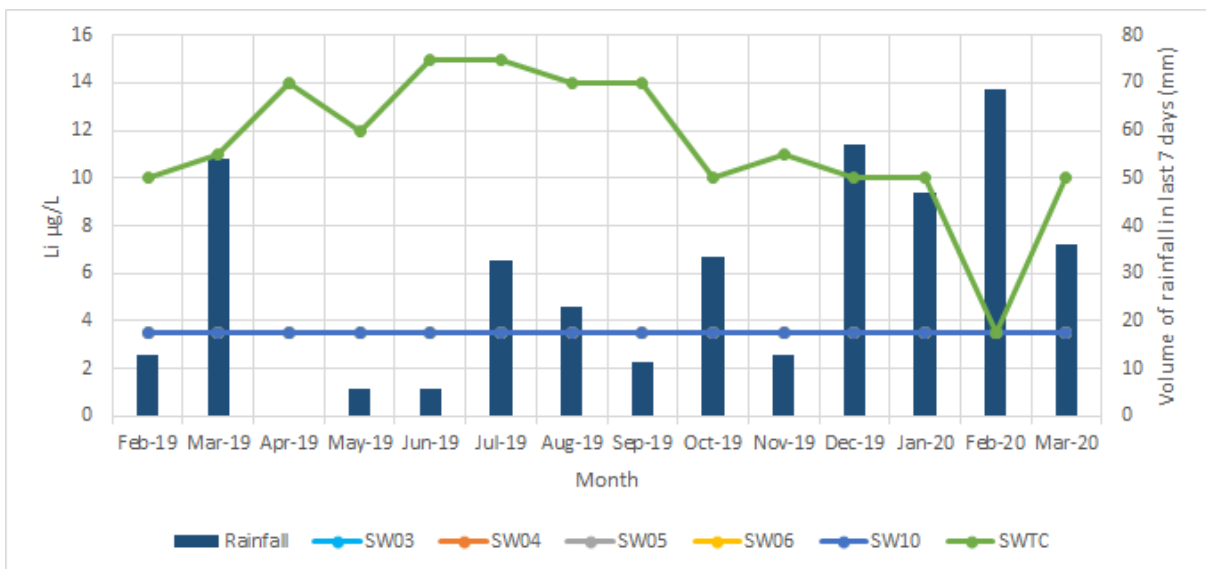
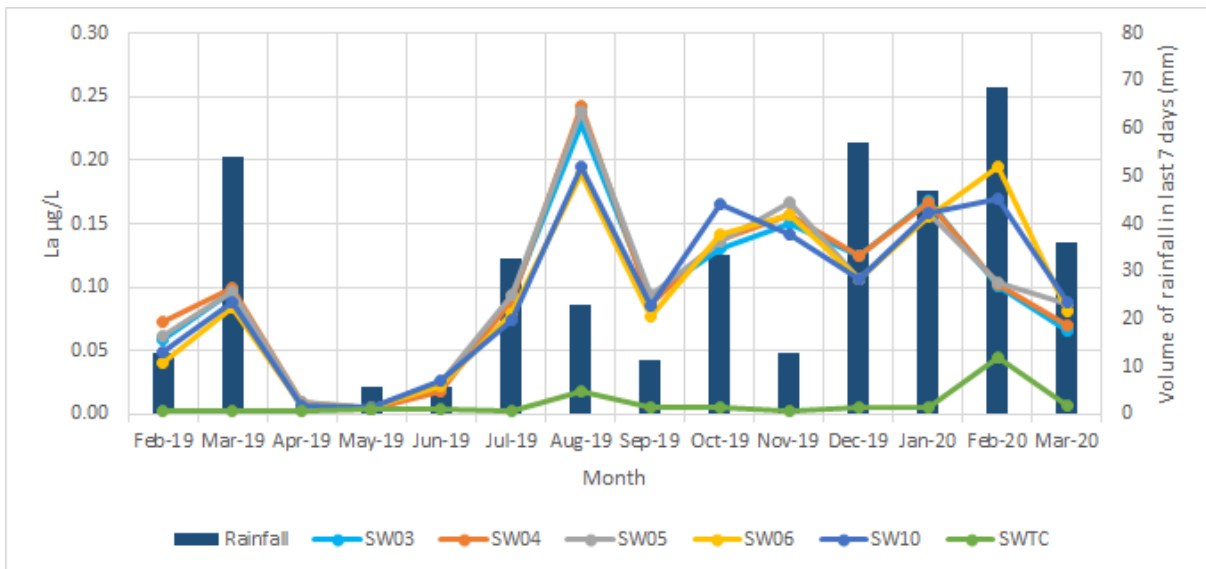


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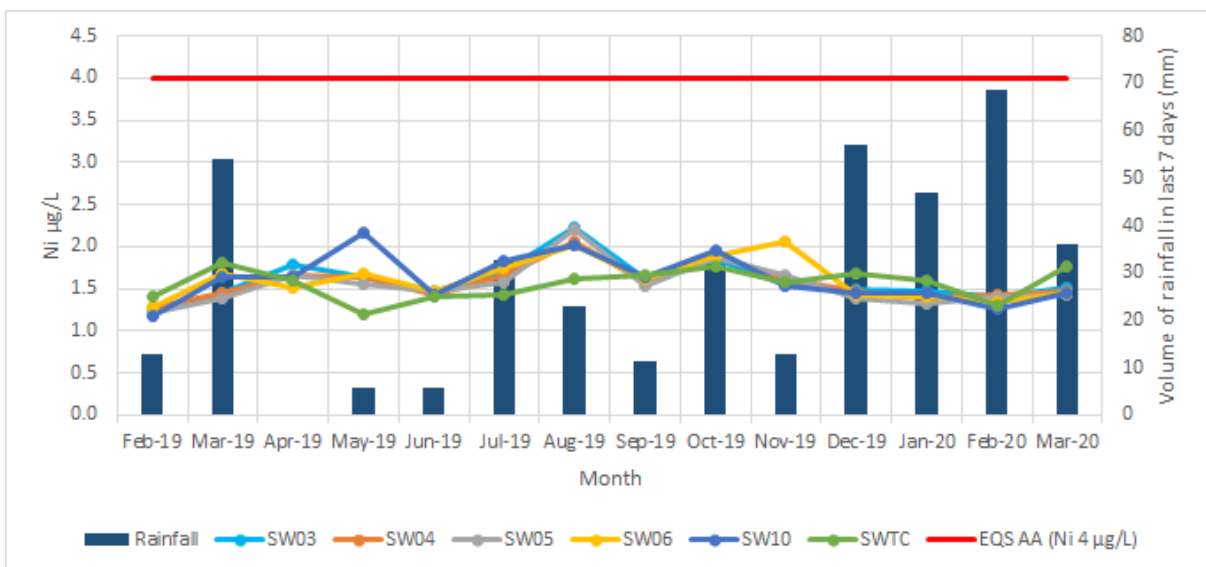
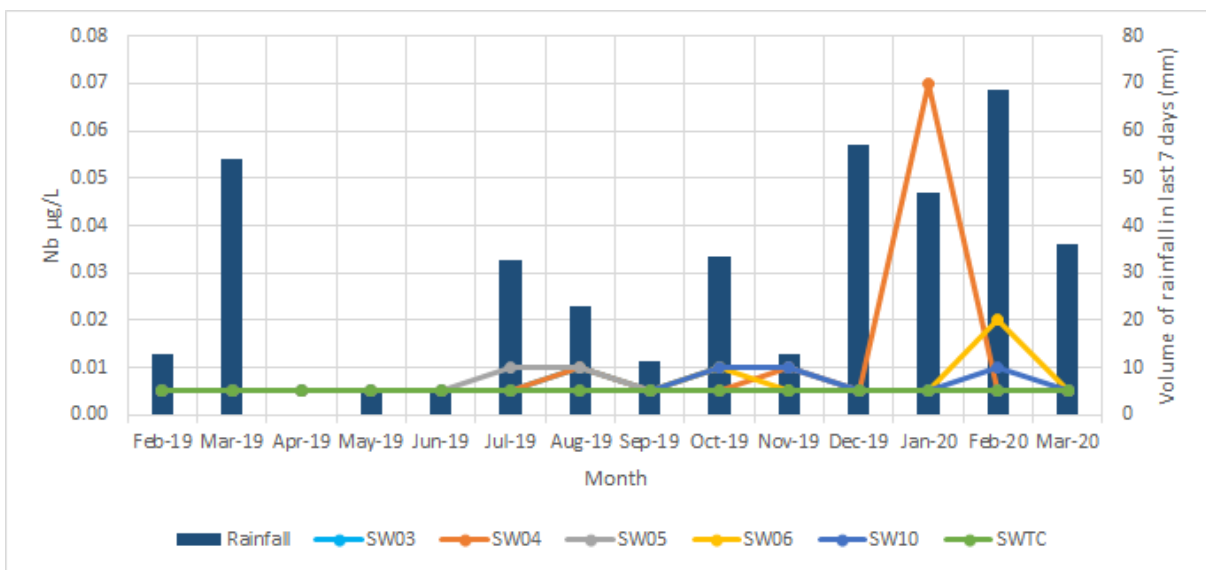
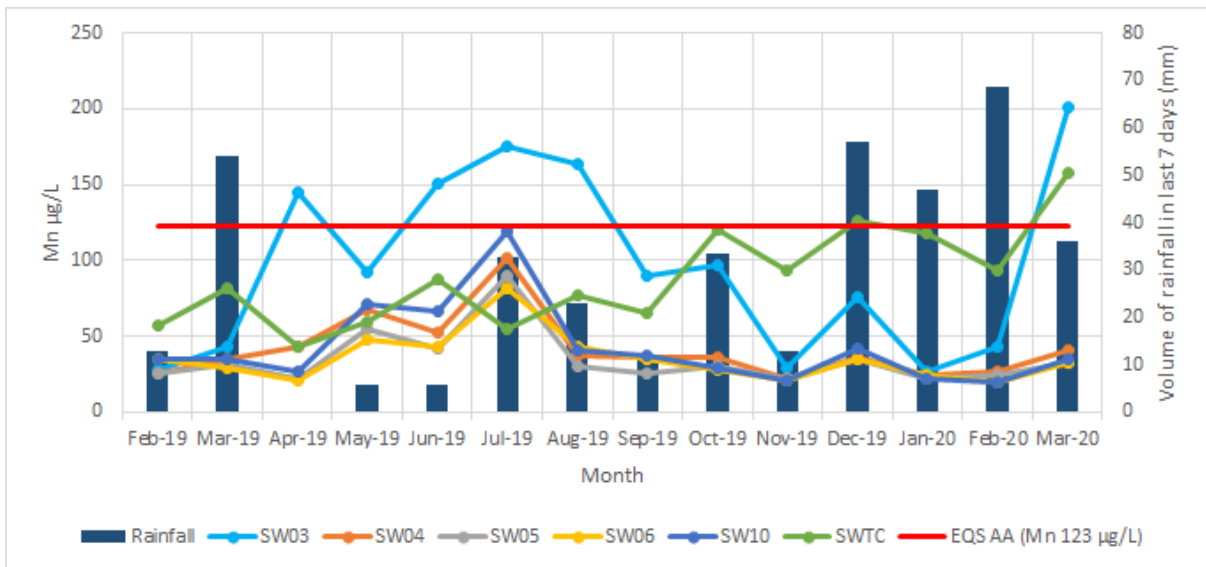


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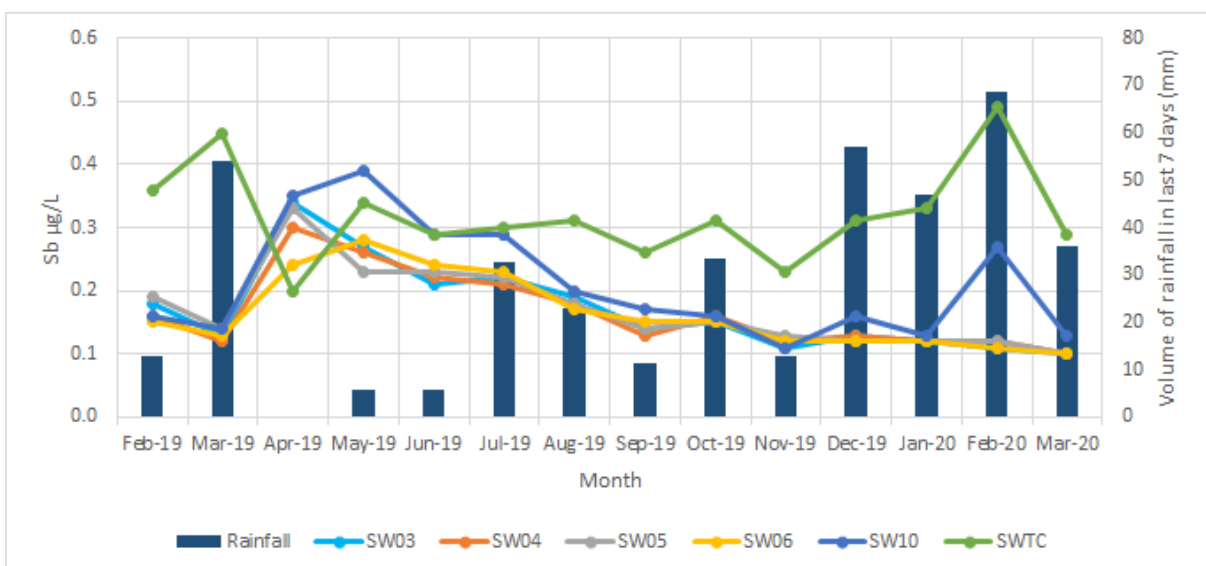
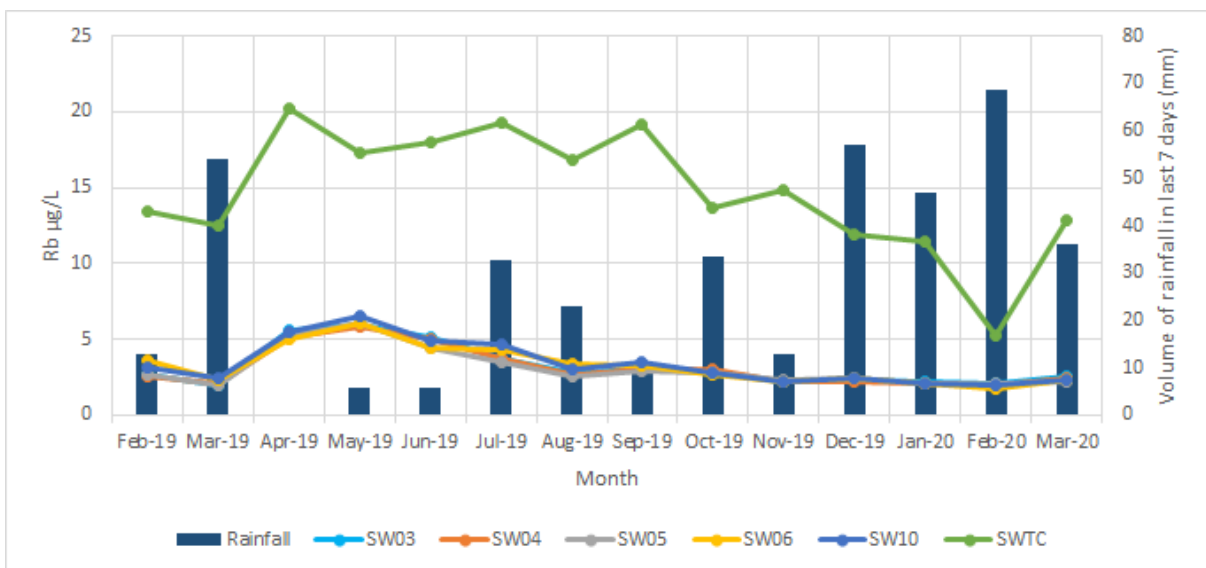
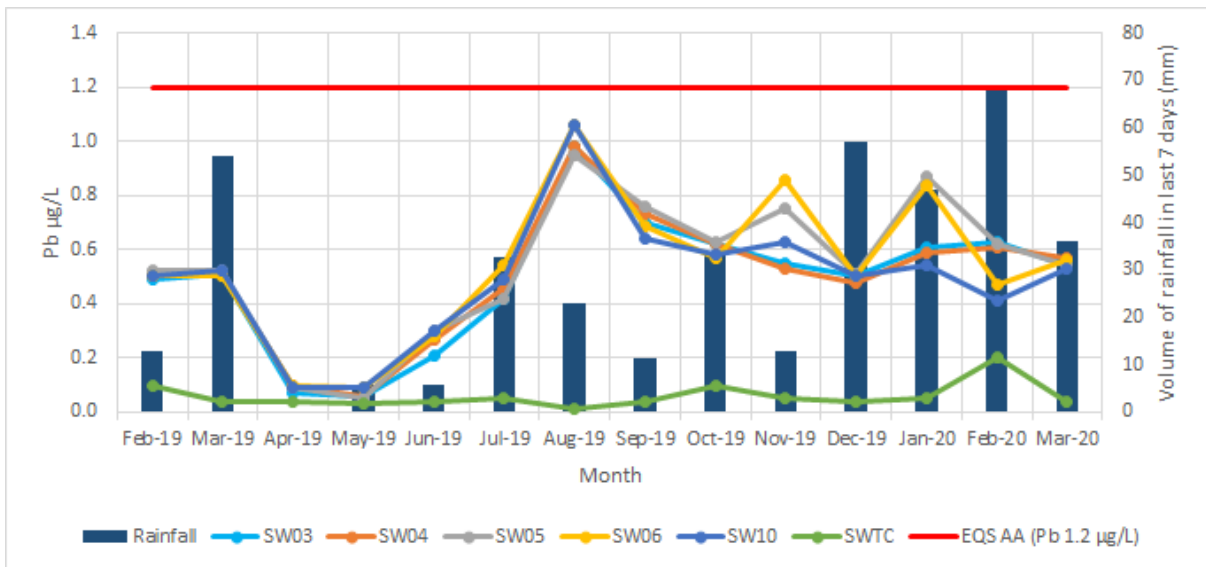


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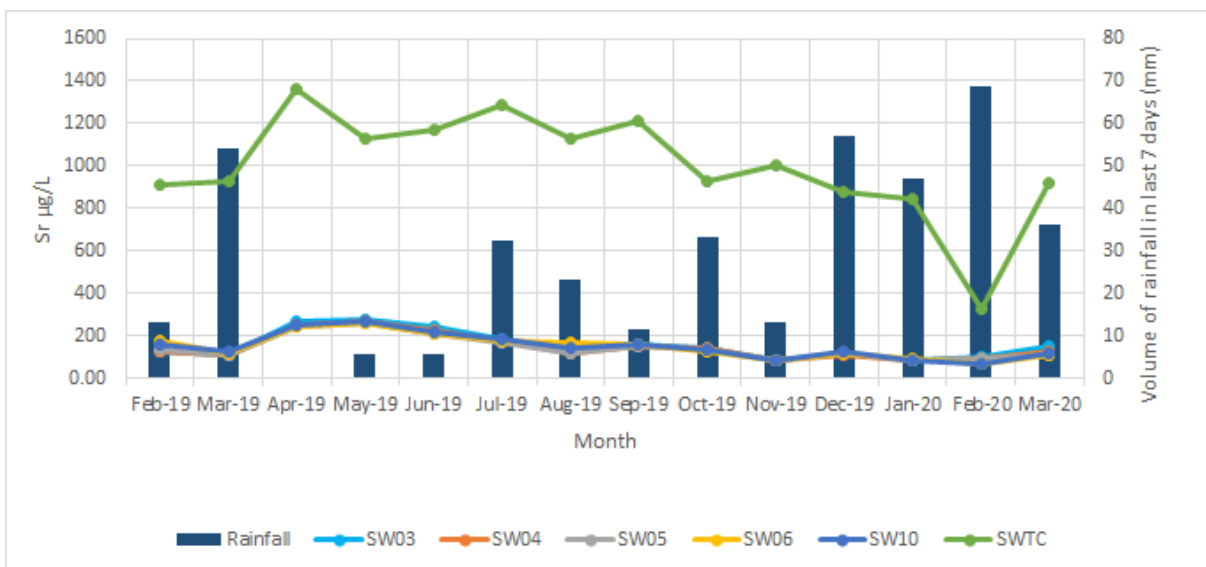
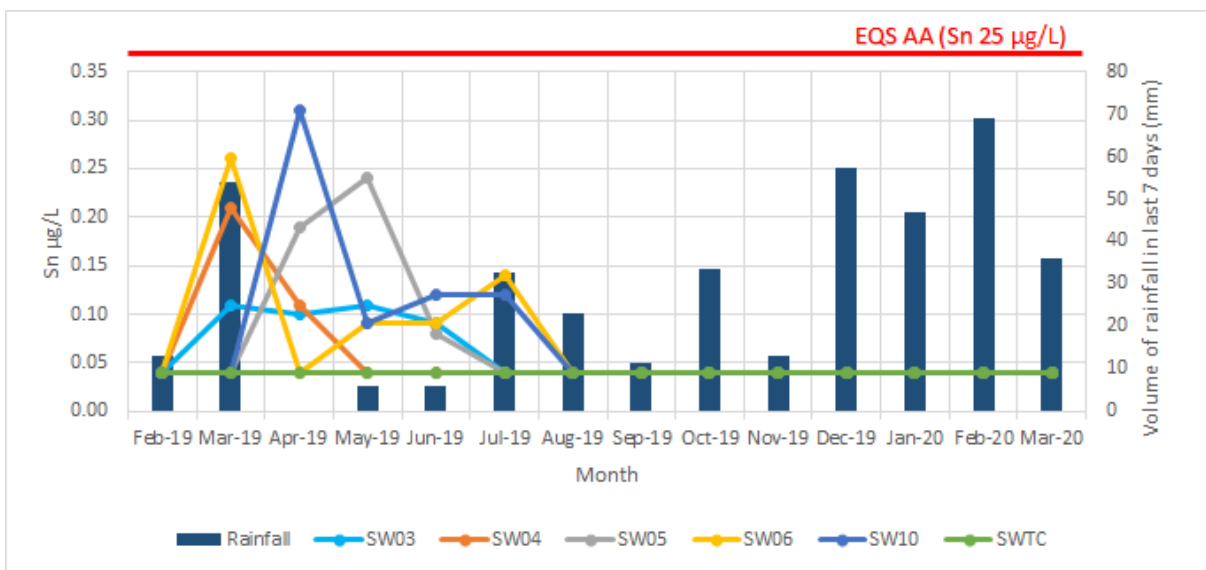
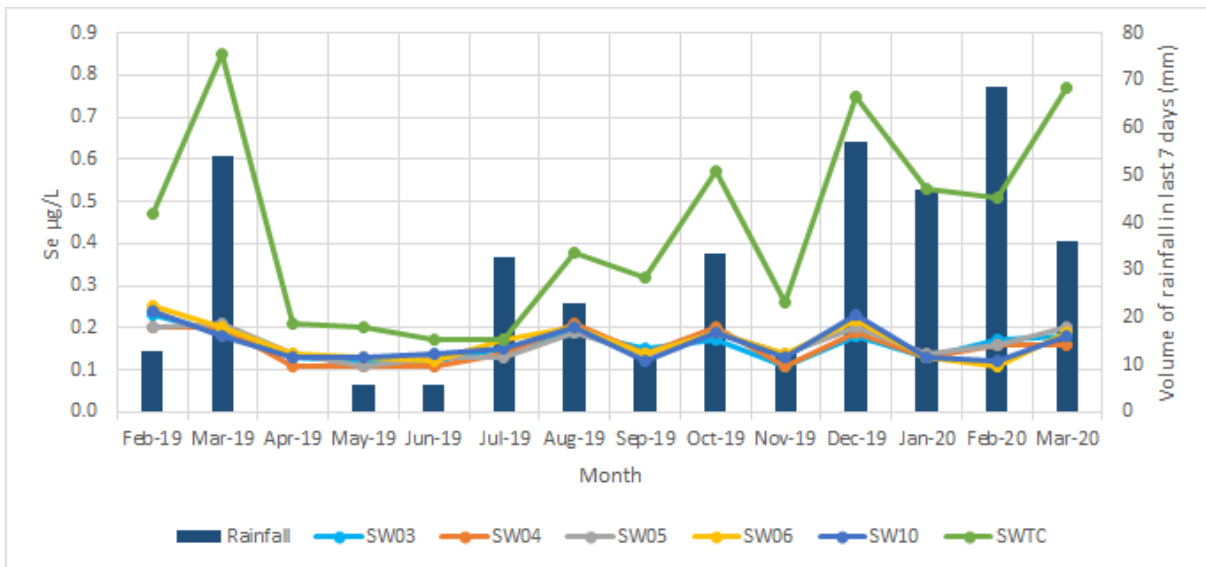


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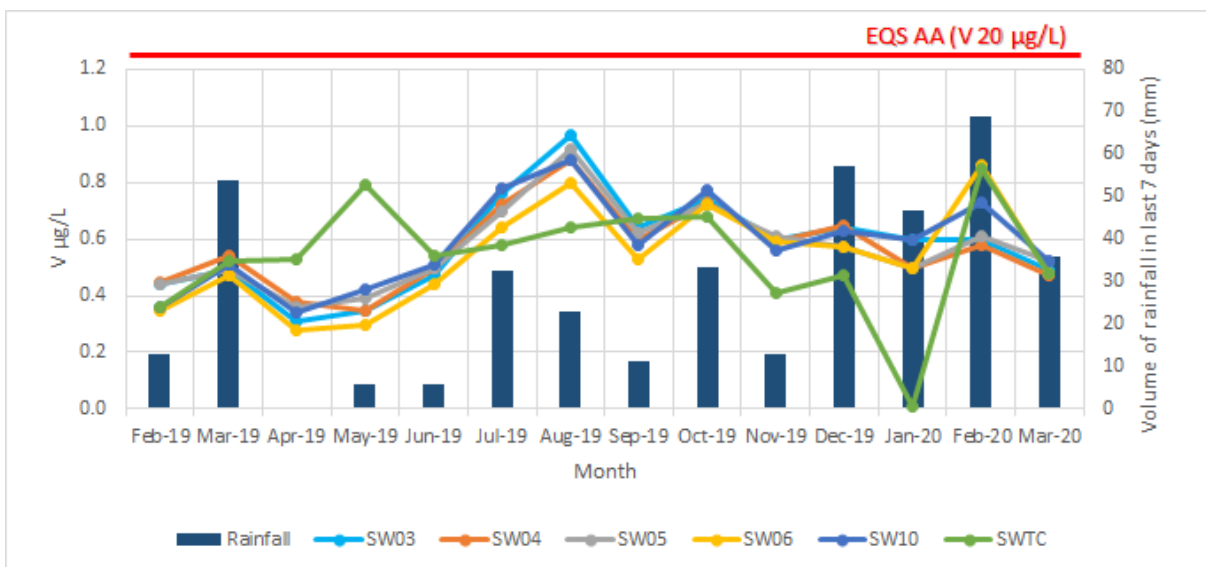
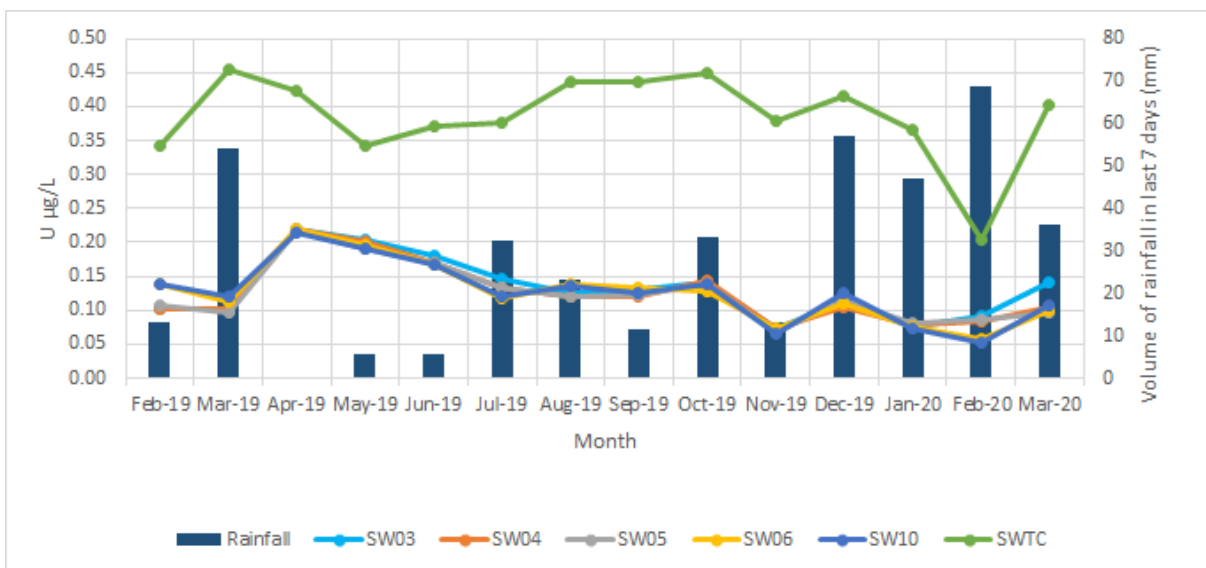
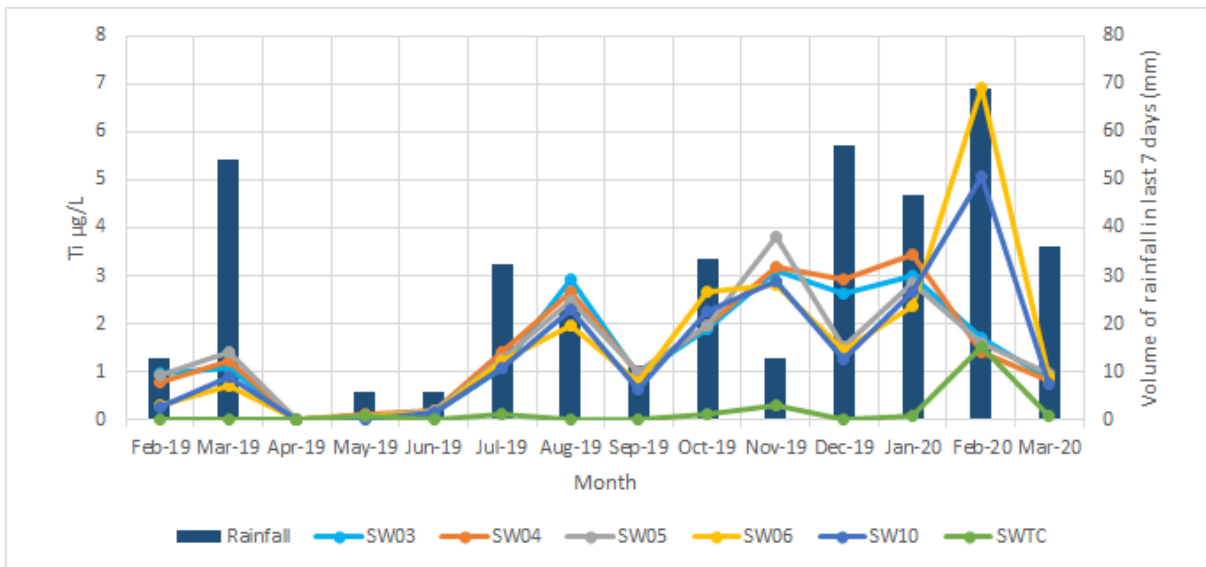


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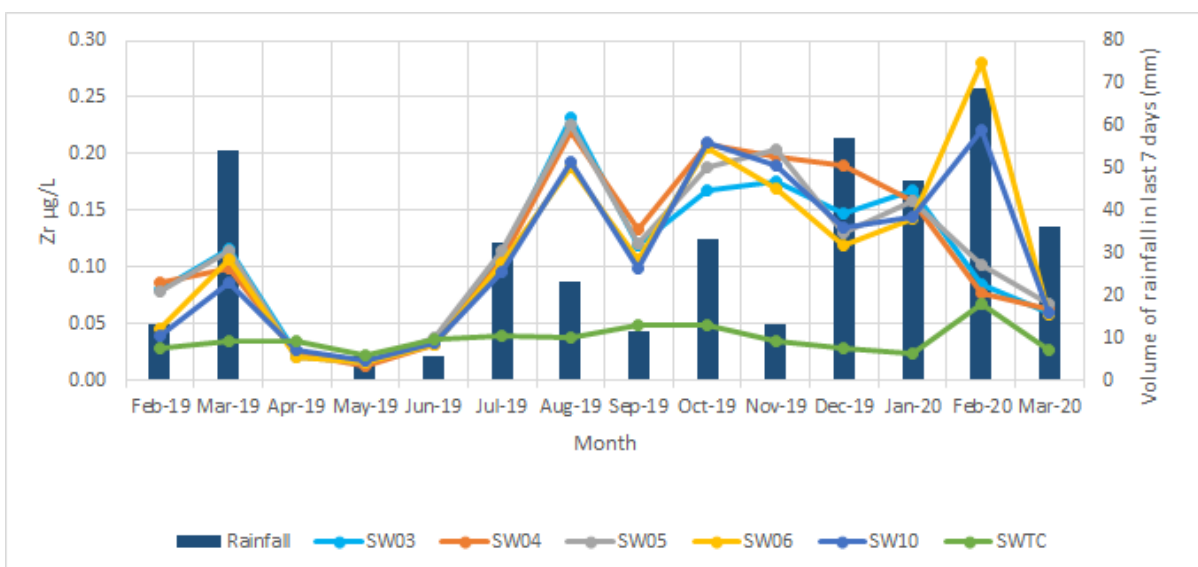
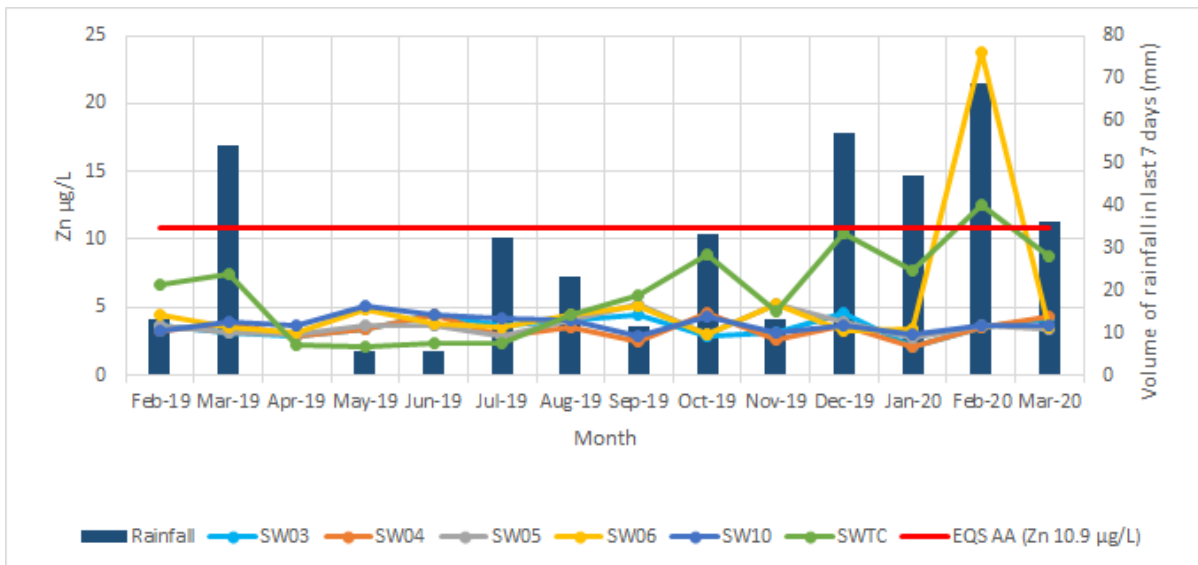
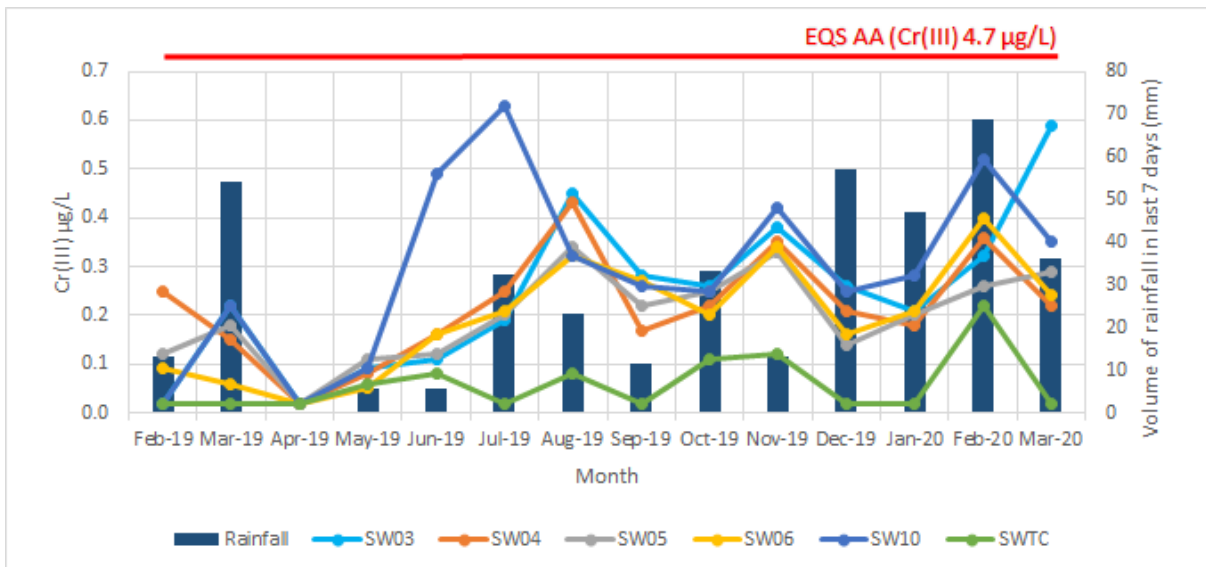
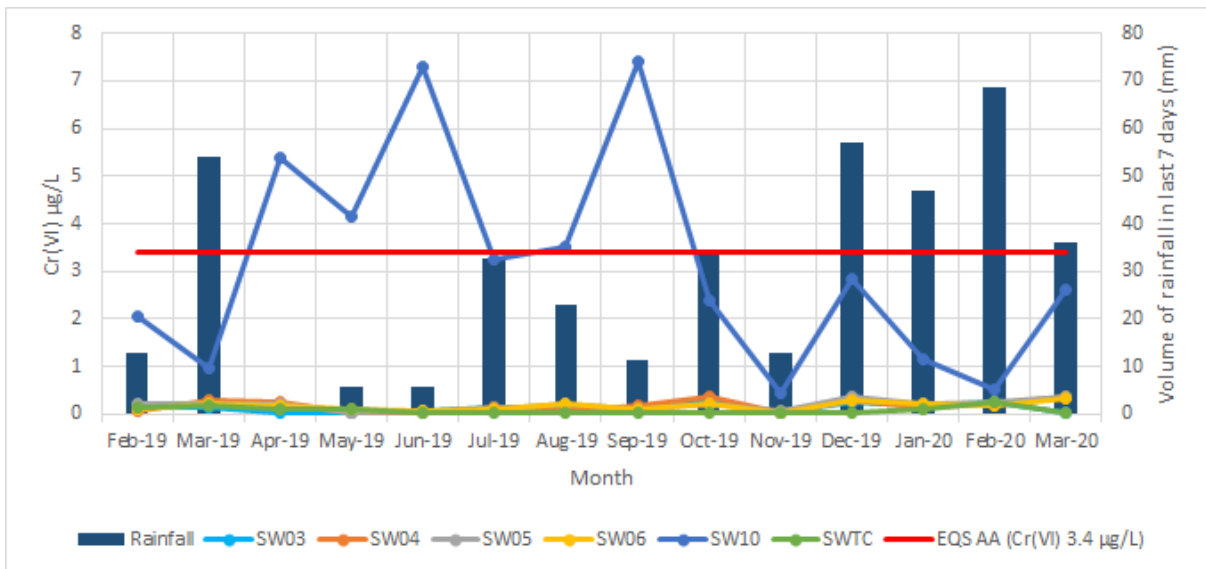
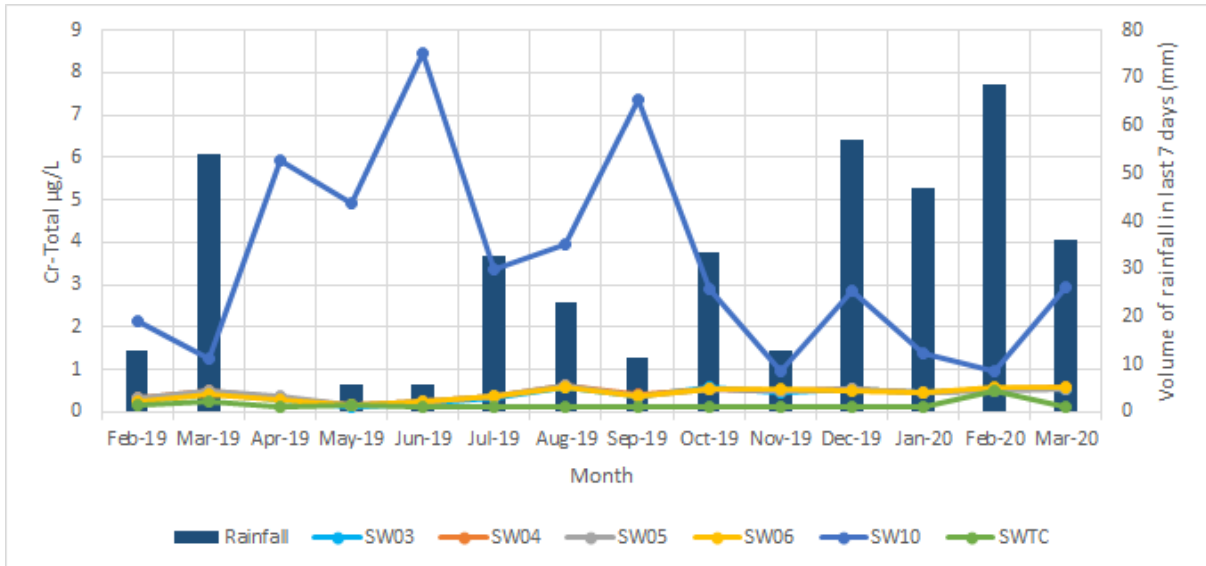
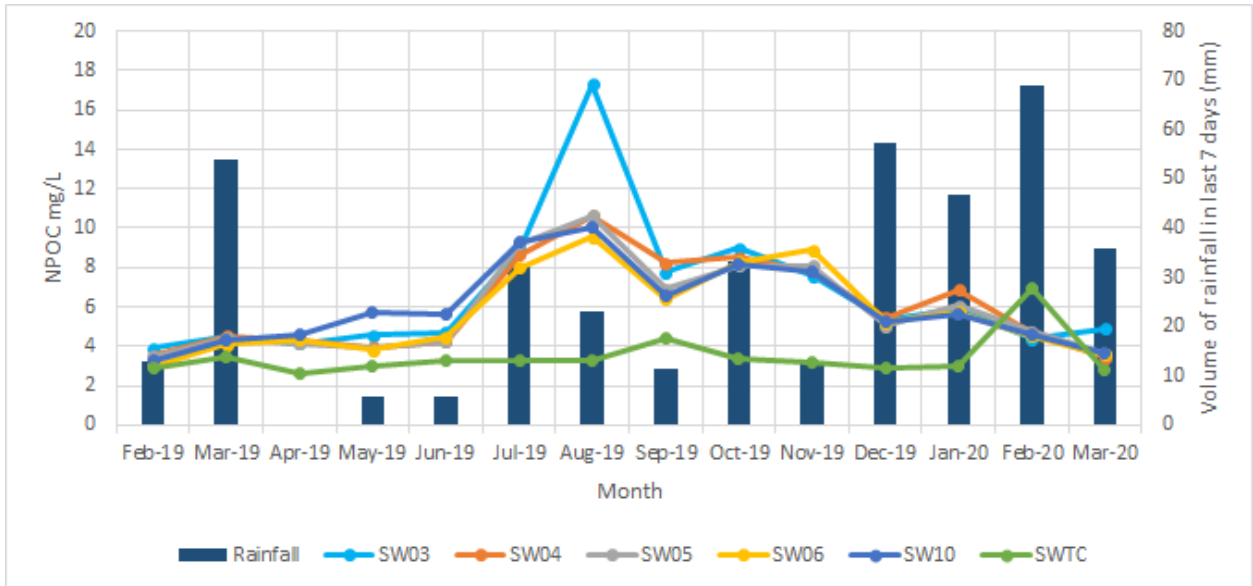


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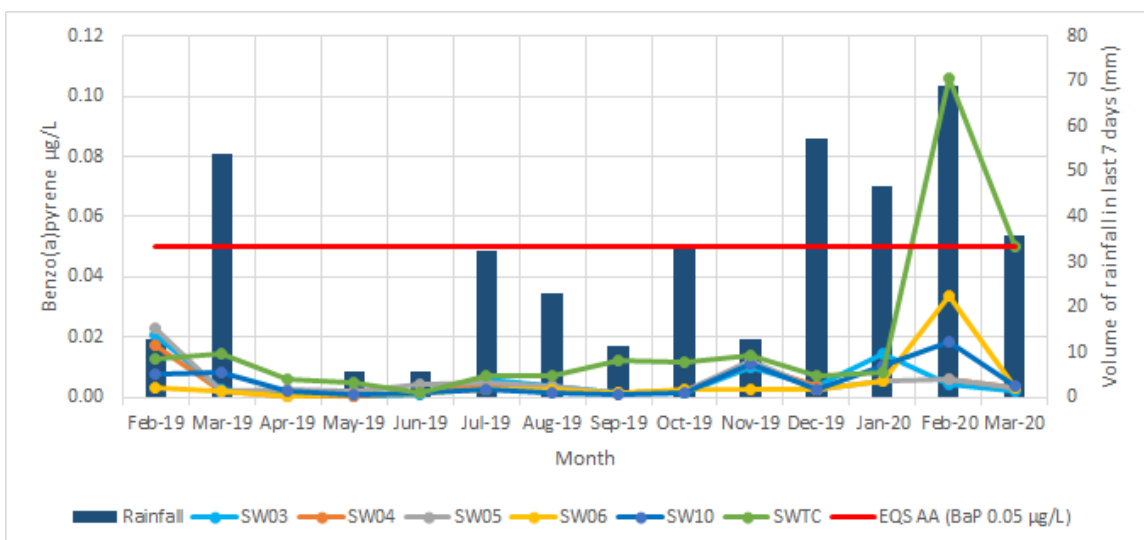
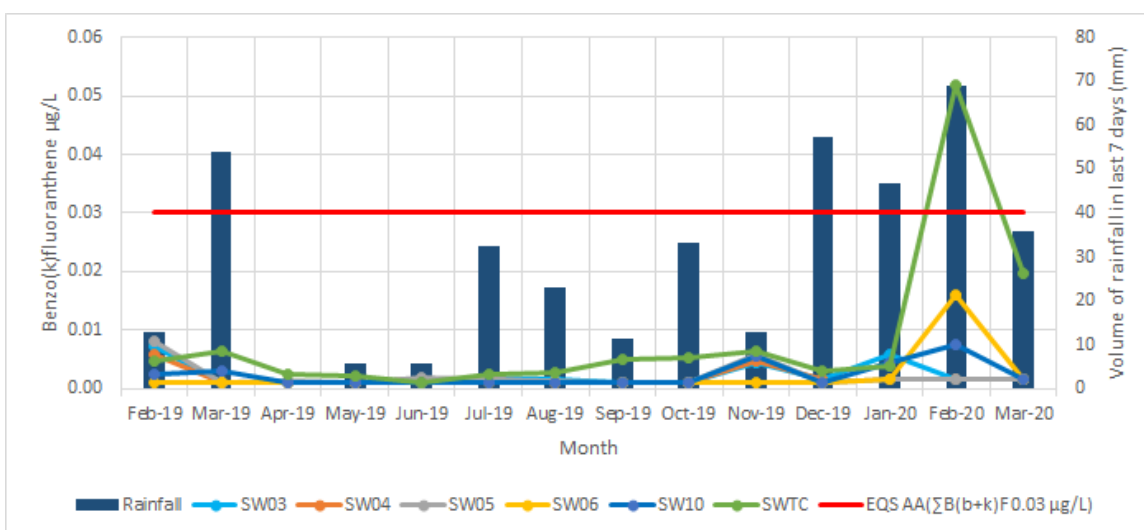
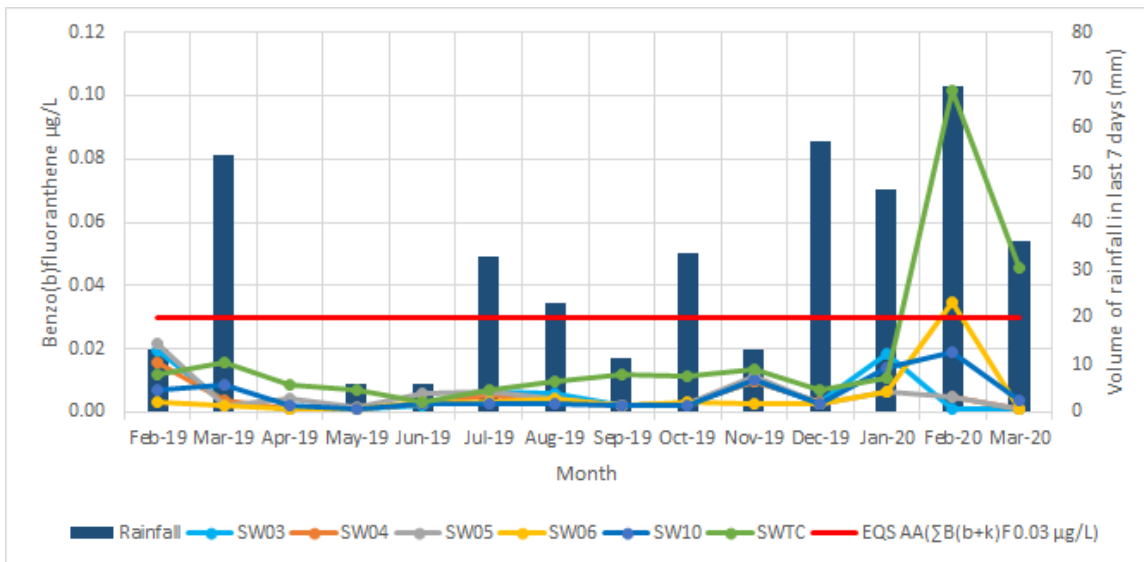
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Figure A3.7 Time-series plots of surface water Cr-Total, Cr(VI) and Cr(III) concentrations, shown in different colours for each sampling location.



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Figure A3.8 Time-series plots of surface water dissolved organic carbon (NPOC) concentrations, shown in different colours for each sampling location.



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$\Sigma\text{B(b+k)F}$: combined EQS for benzo(b)fluoranthene and benzo(k)fluoranthene

BaP: benzo(a)pyrene

Figure A3.9 Time-series plots of surface water organic parameter concentrations for benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene, indeno(1,2,3-cd)pyrene, PAH-Total and TPH (C8-C40), shown in different colours for each sampling location.

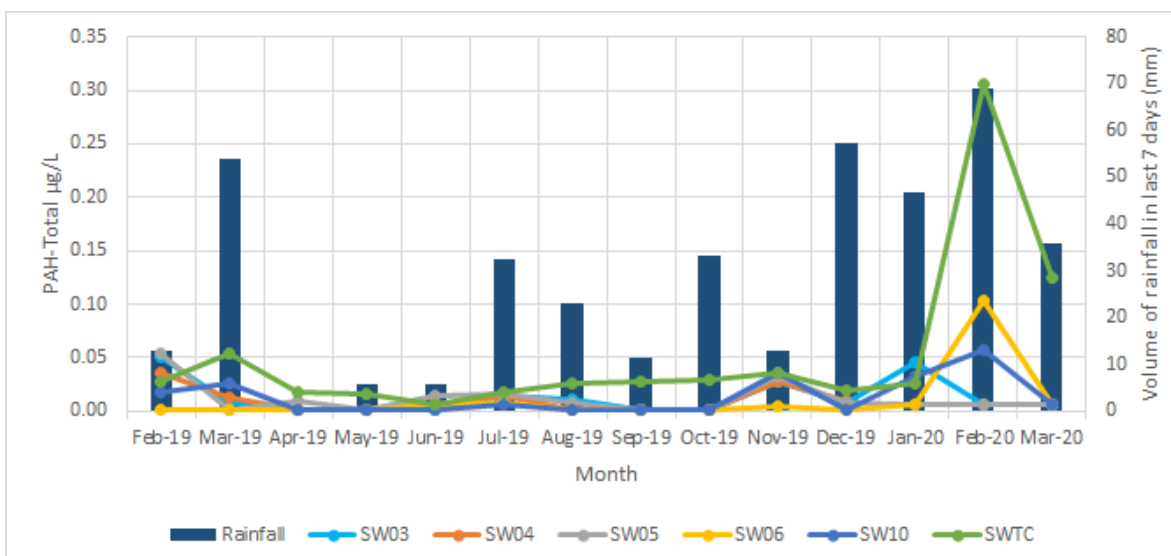
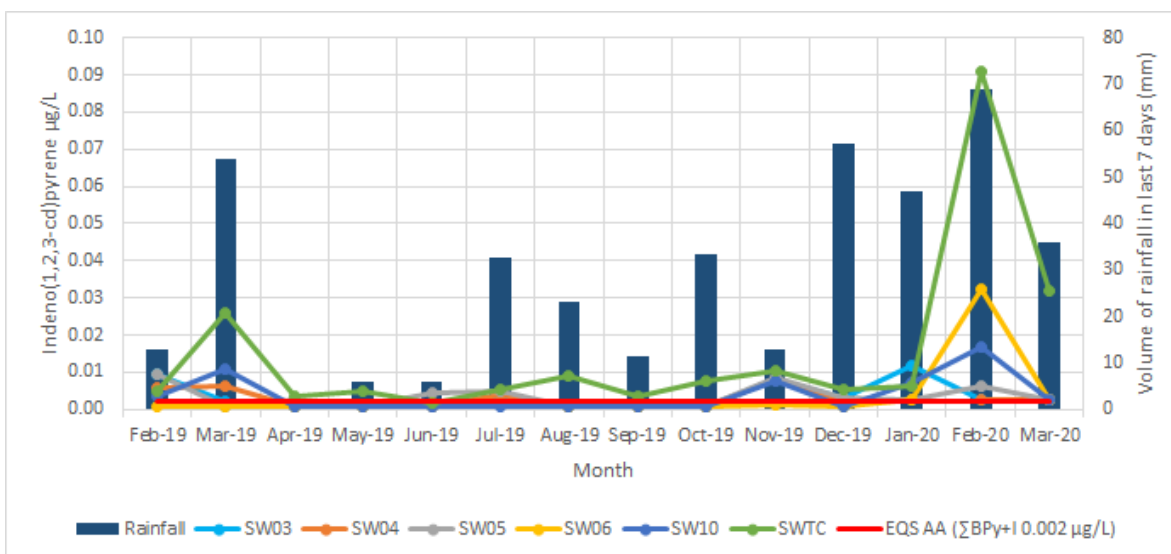
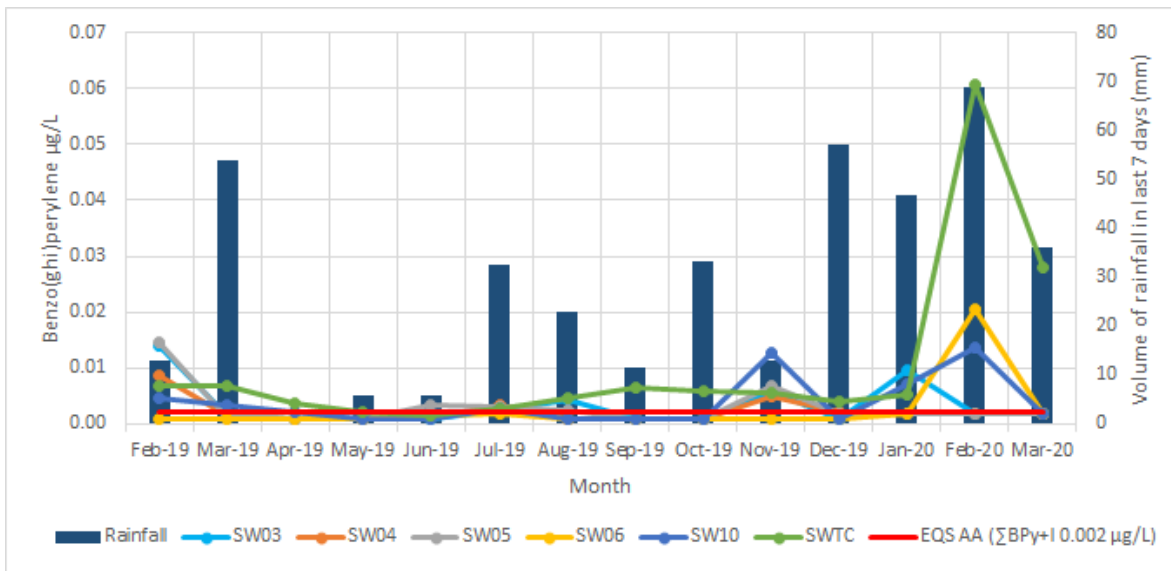


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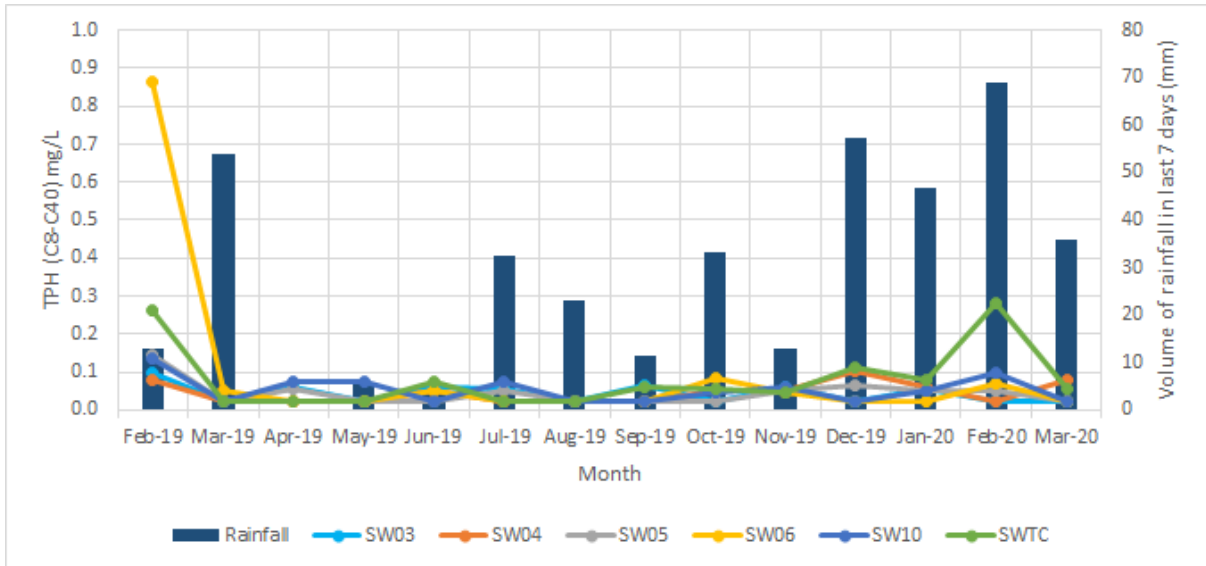
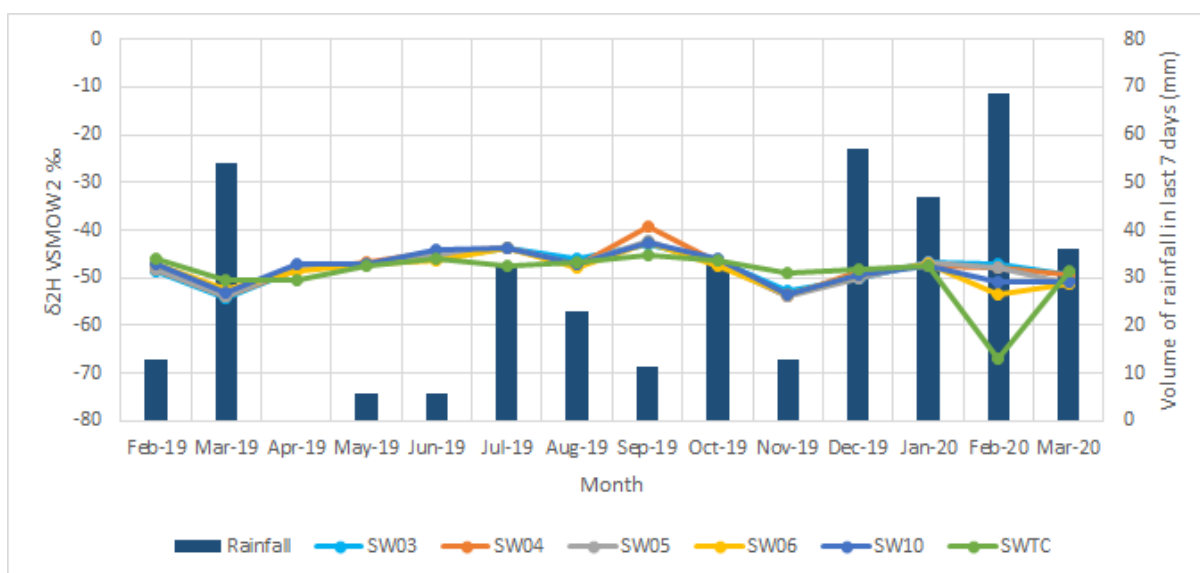
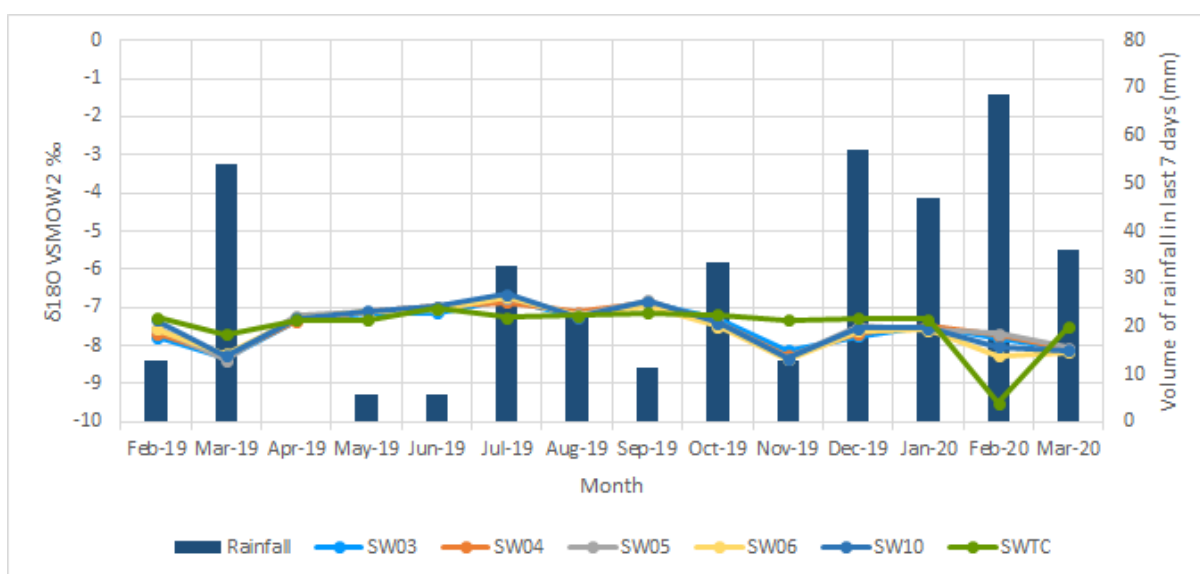
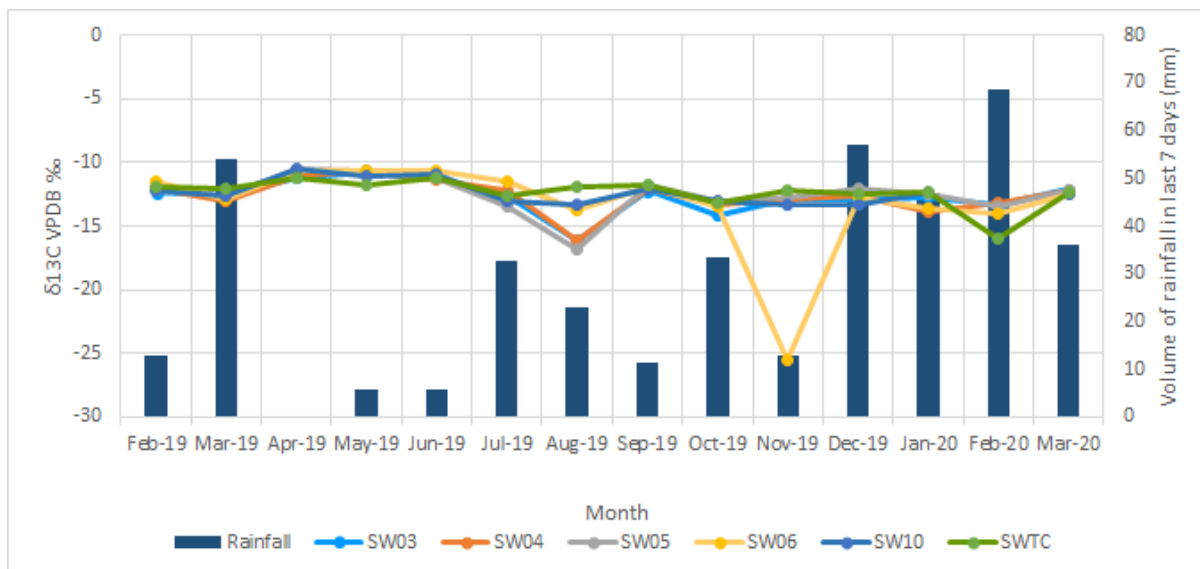


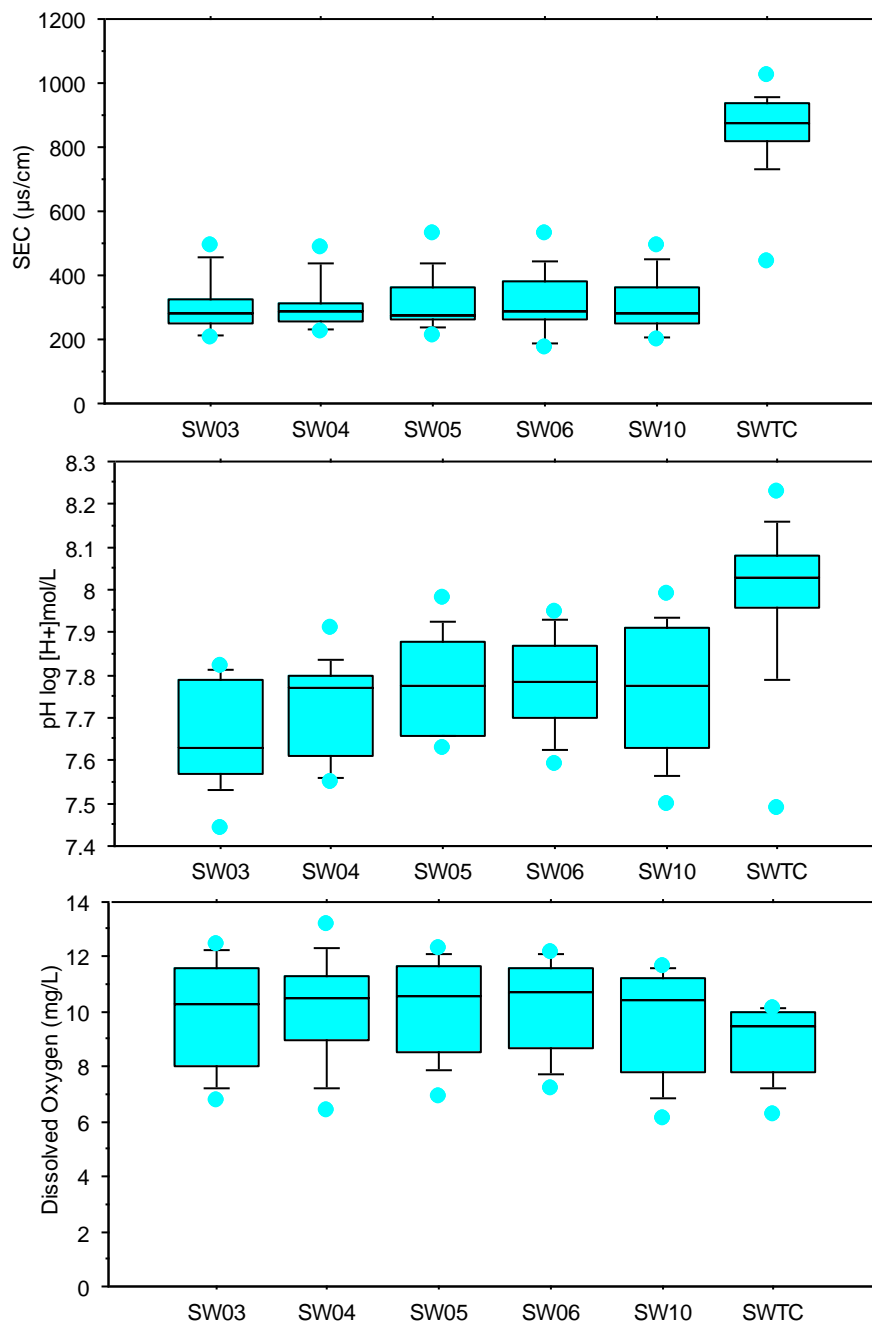
Figure A3.9 cont.



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Figure A3.10 Time-series plots of surface water $\delta^{13}\text{C}$, $\delta^2\text{H}$ and $\delta^{18}\text{O}$ stable isotope ratios, shown in different colours for each sampling location.

Appendix 4 Surface Water Chemistry Box and Whisker Plots



Number of samples at each location: 14

Figure A4.1 Box and whisker plots of physico-chemical parameters in surface water samples at each sampling location.

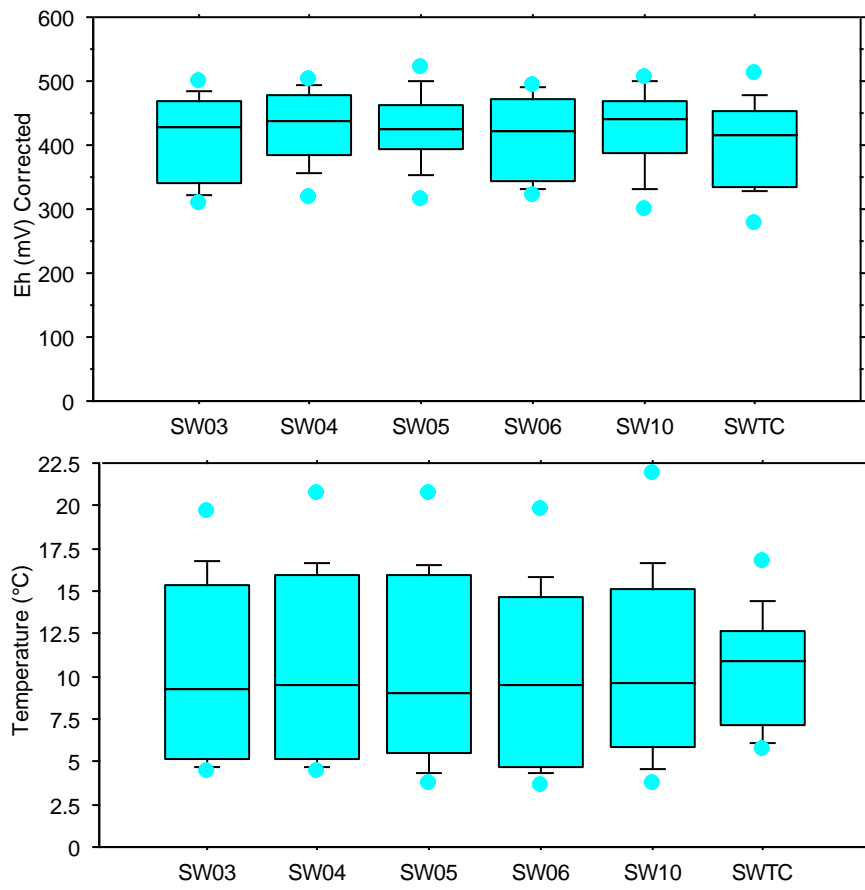
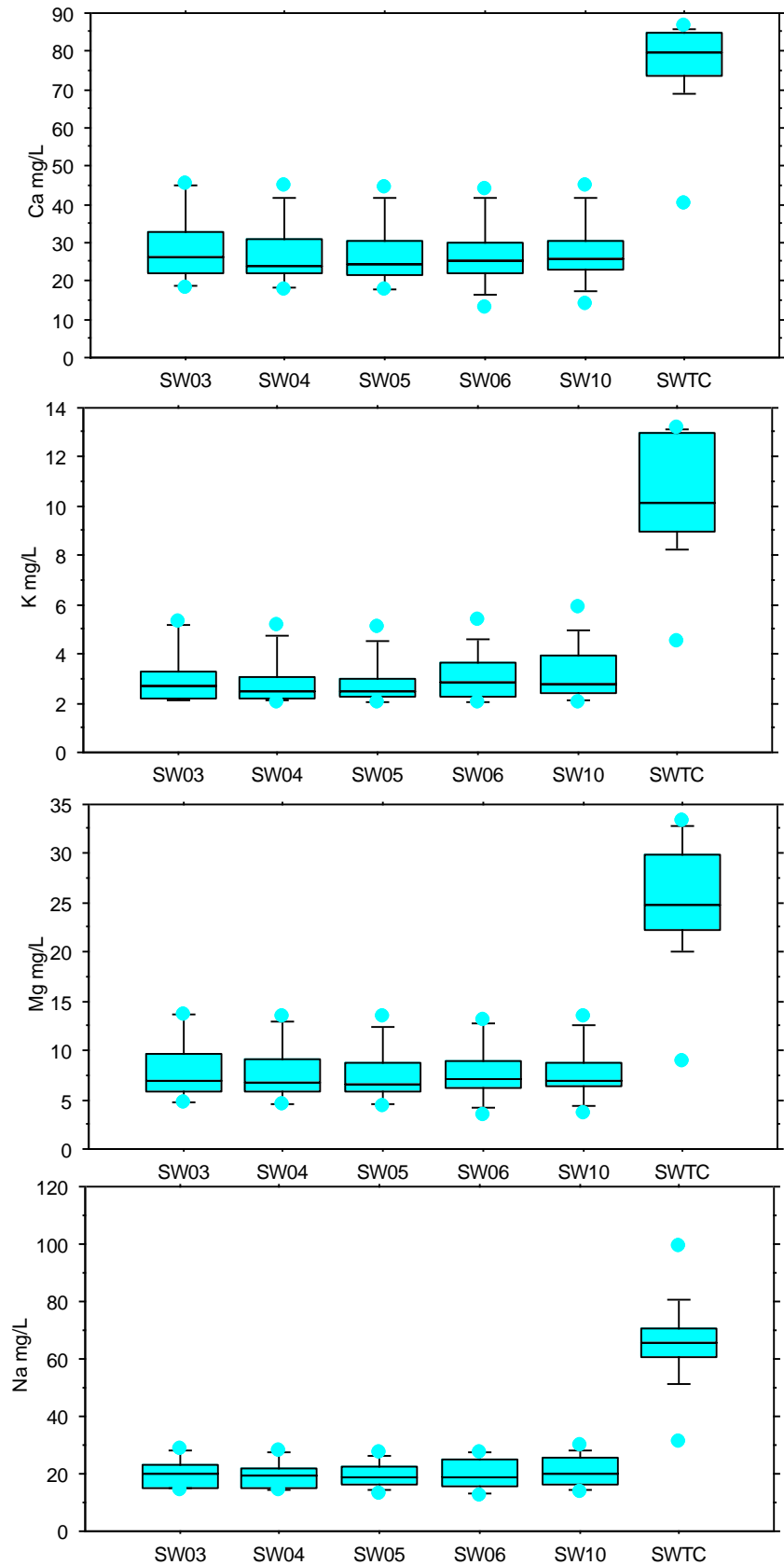
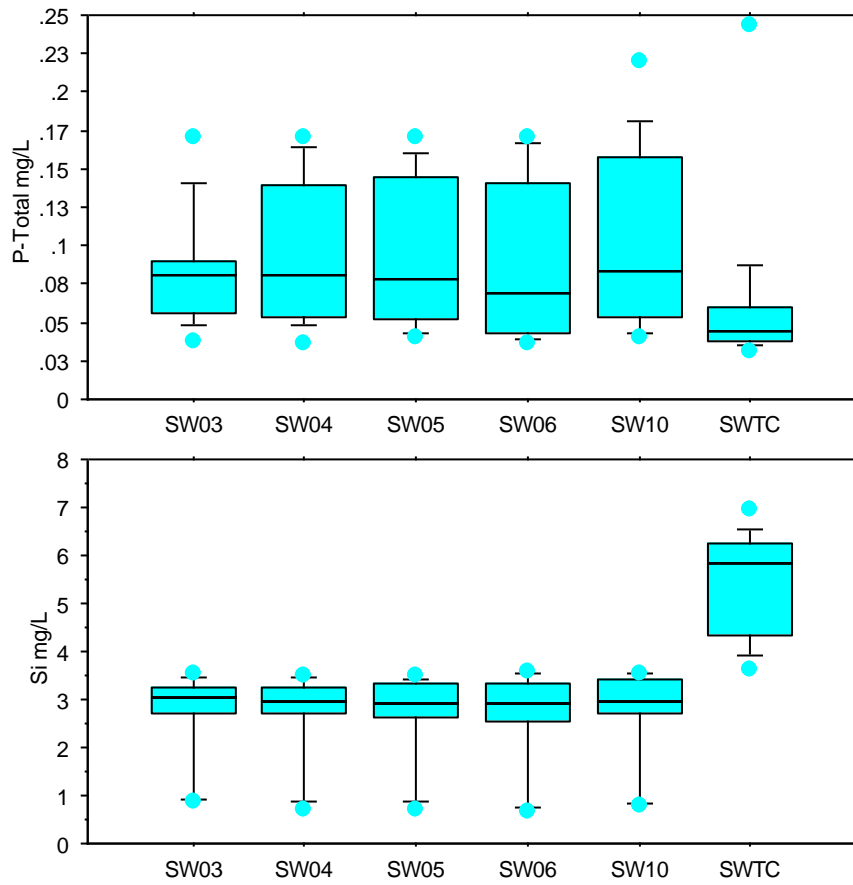


Figure A4.1 cont.



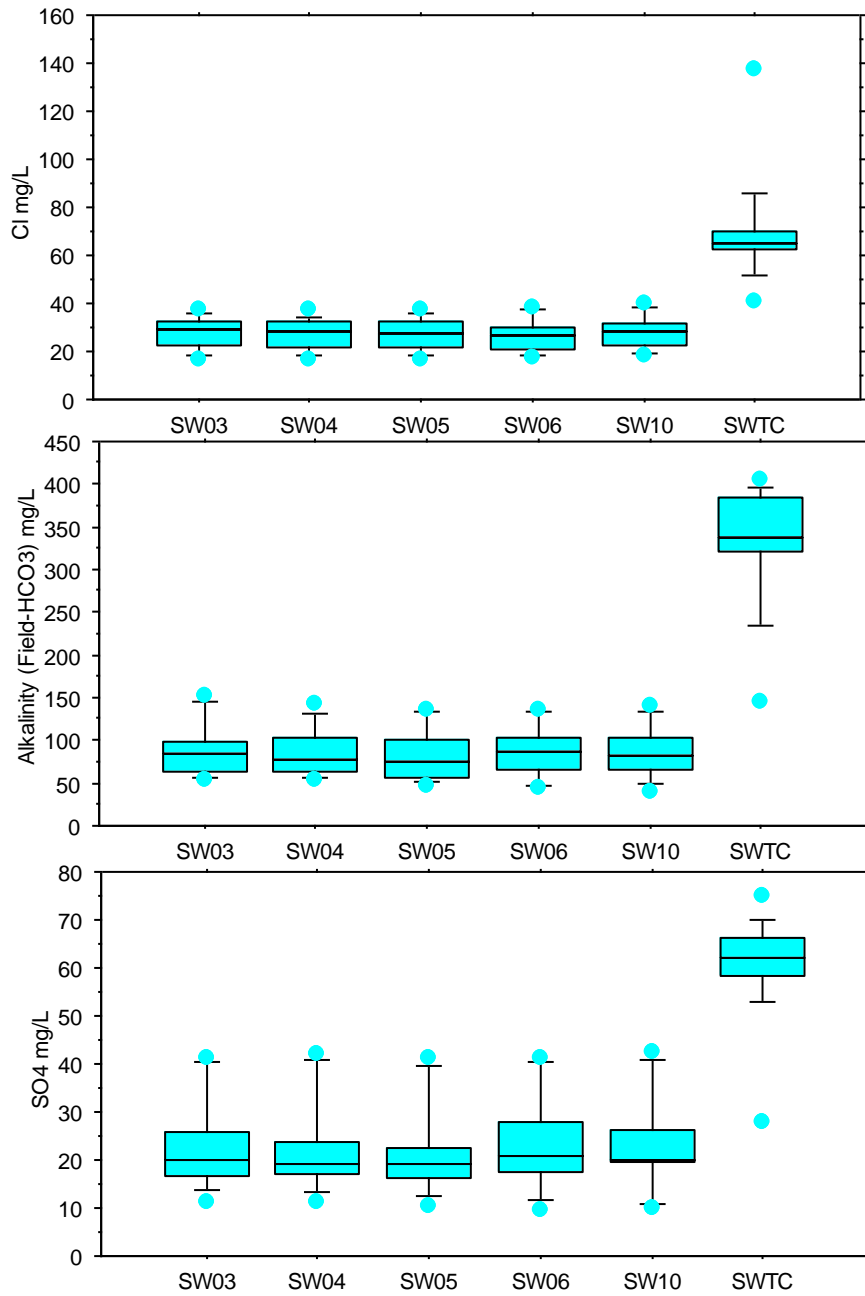
Number of samples at each location: 14

Figure A4.2 Box and whisker plots of major cation concentrations in surface water samples at each sampling location.



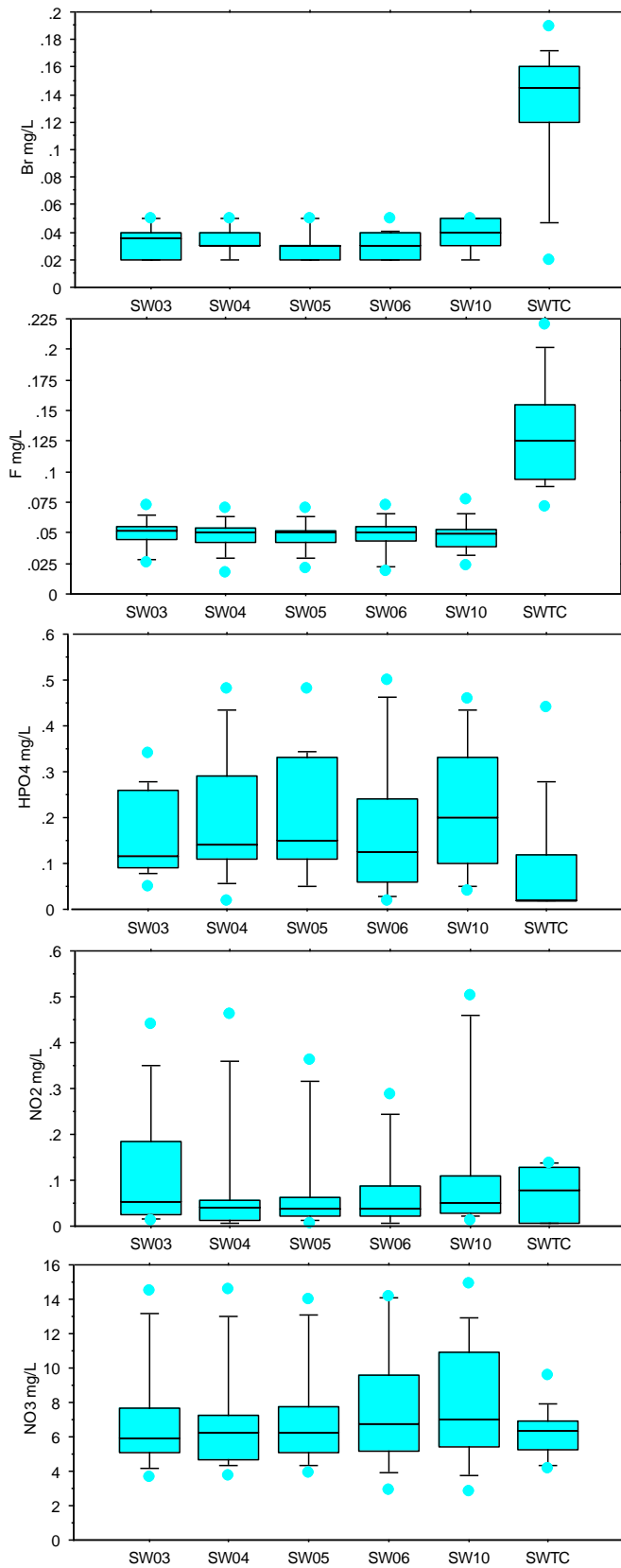
Number of samples at each location: 14

Figure A4.3 Box and whisker plots of minor cation concentrations in surface water samples at each sampling location.



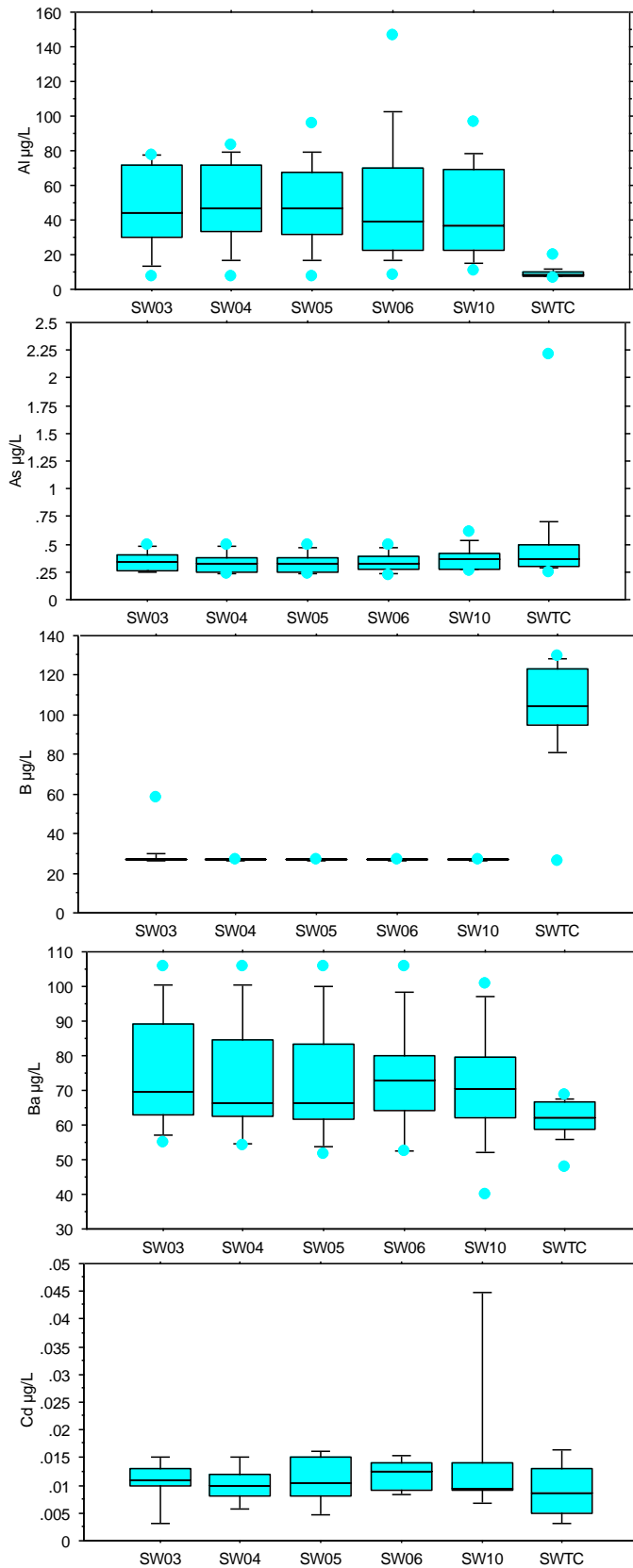
Number of samples at each location: 14

Figure A4.4 Box and whisker plots of major anion concentrations in surface water samples at each sampling location.



Number of samples at each location: 14

Figure A4.5 Box and whisker plots of minor anion concentrations in surface water samples at each sampling location.



Number of samples at each location: 14

Note that outliers are not shown for Cd, due to one high value (0.3 $\mu\text{g/L}$) at SWTC

Figure A4.6 Box and whisker plots of selected trace element concentrations in surface water samples at each sampling location.

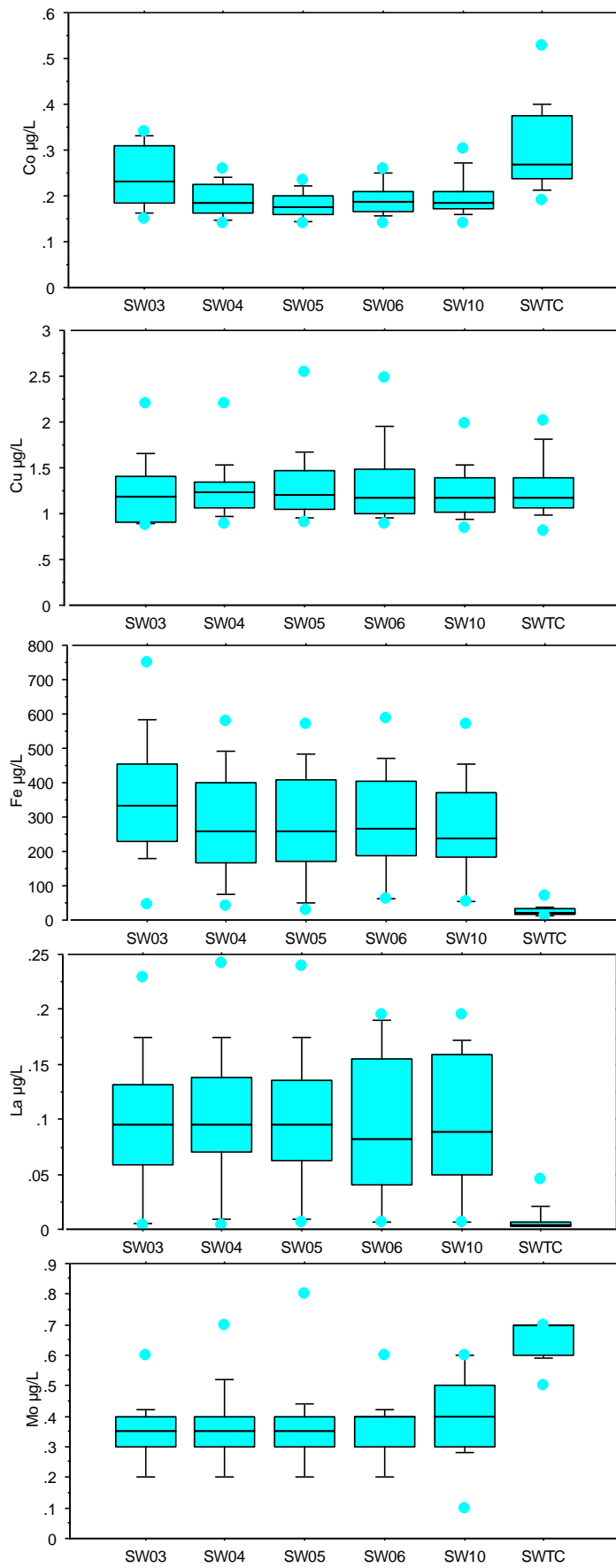


Figure 4.6 cont.

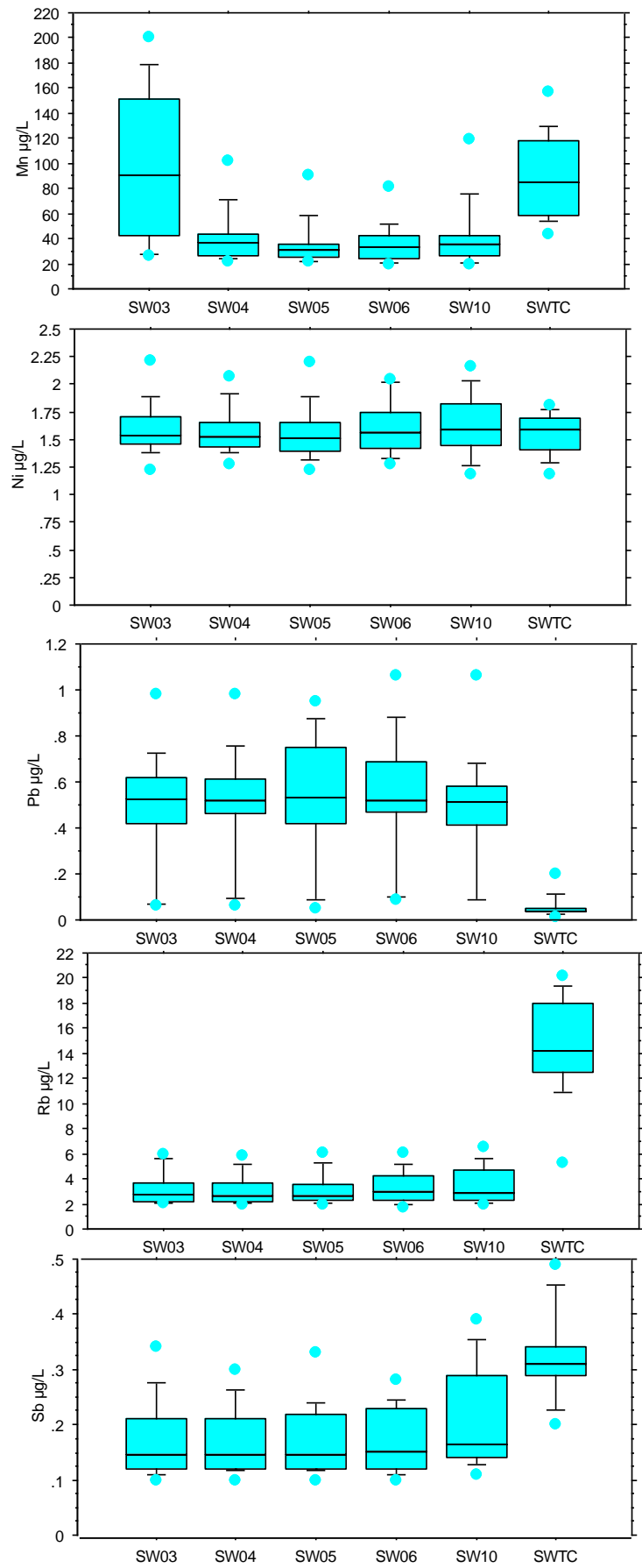


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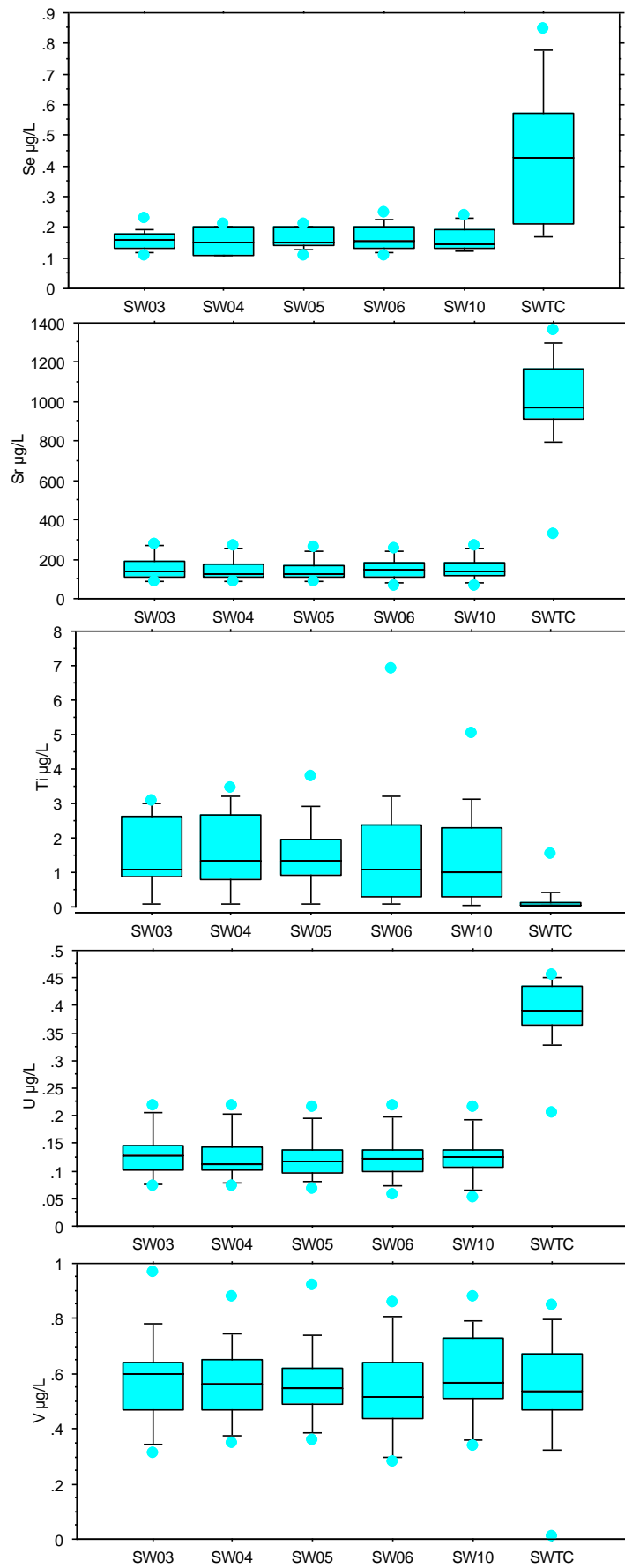


Figure A4.6 cont.

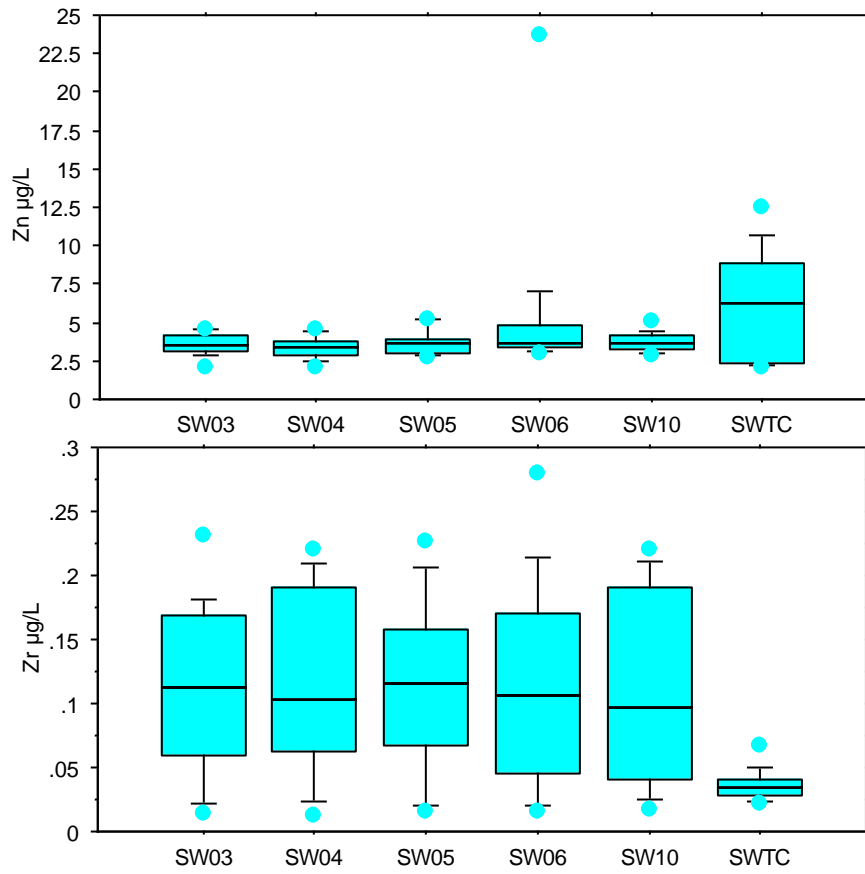
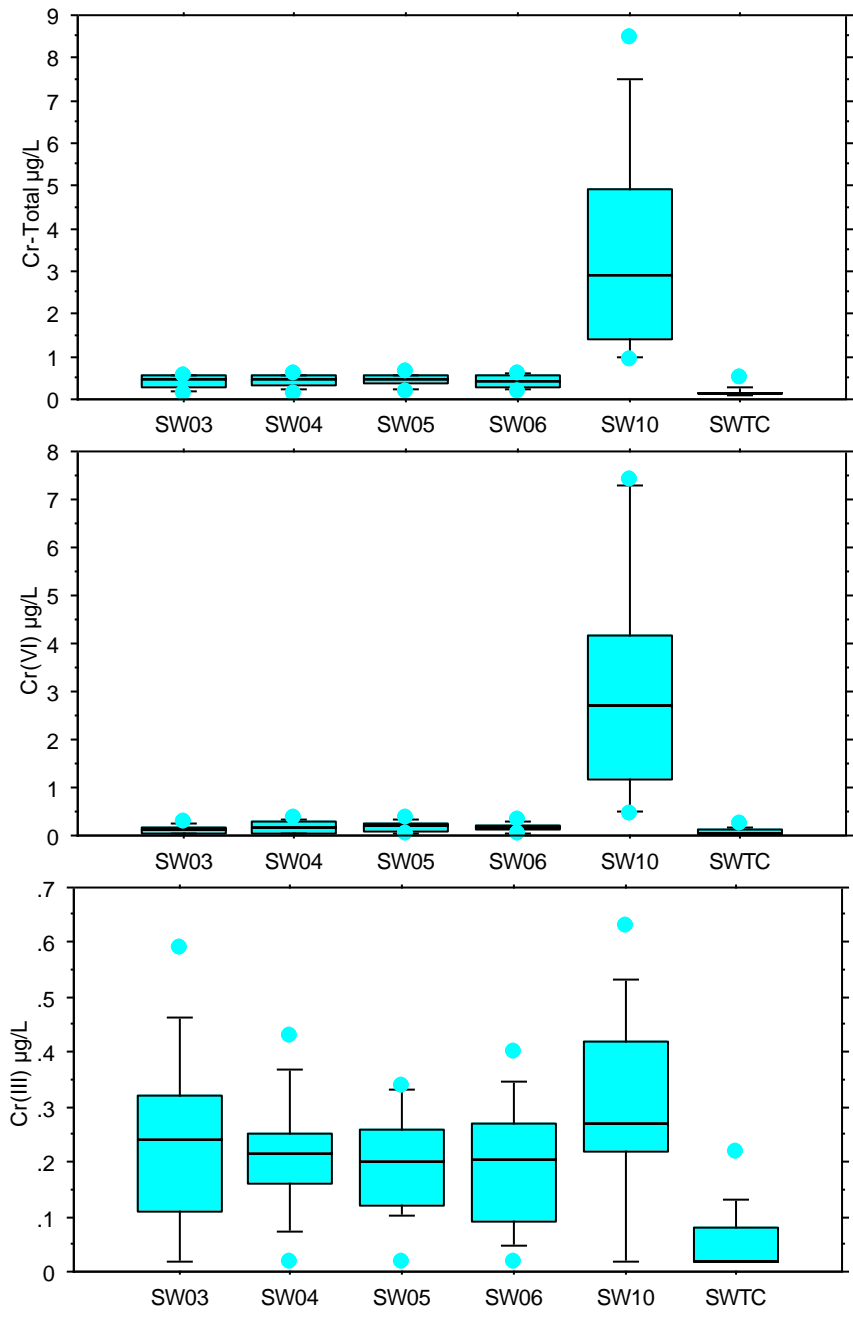
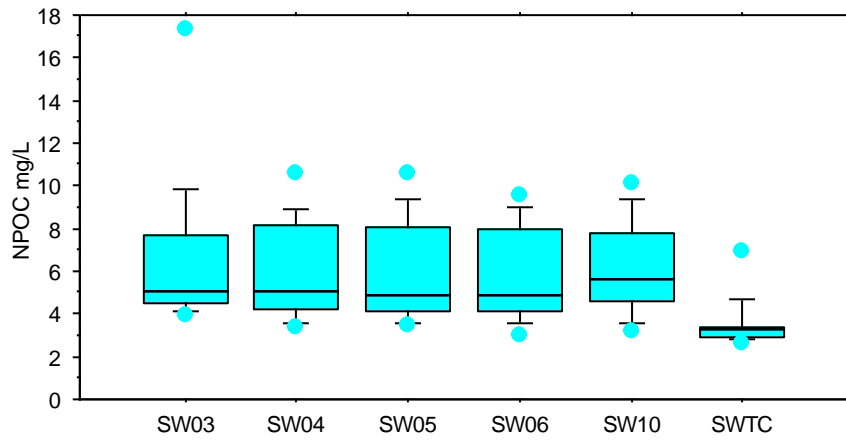


Figure A4.6 cont.



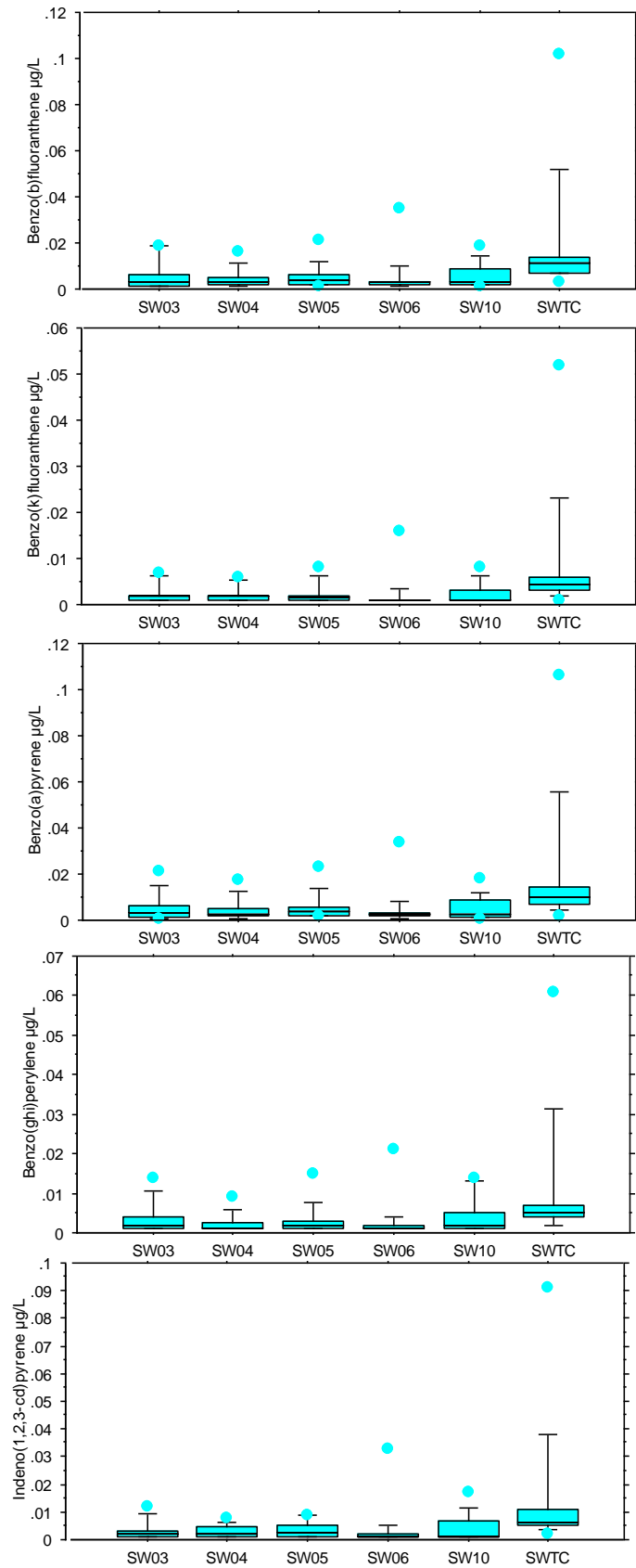
Number of samples at each location: 14

Figure A4.7 Box and whisker plots of Cr-Total, Cr(VI) and Cr(III) concentrations in surface water samples at each sampling location.



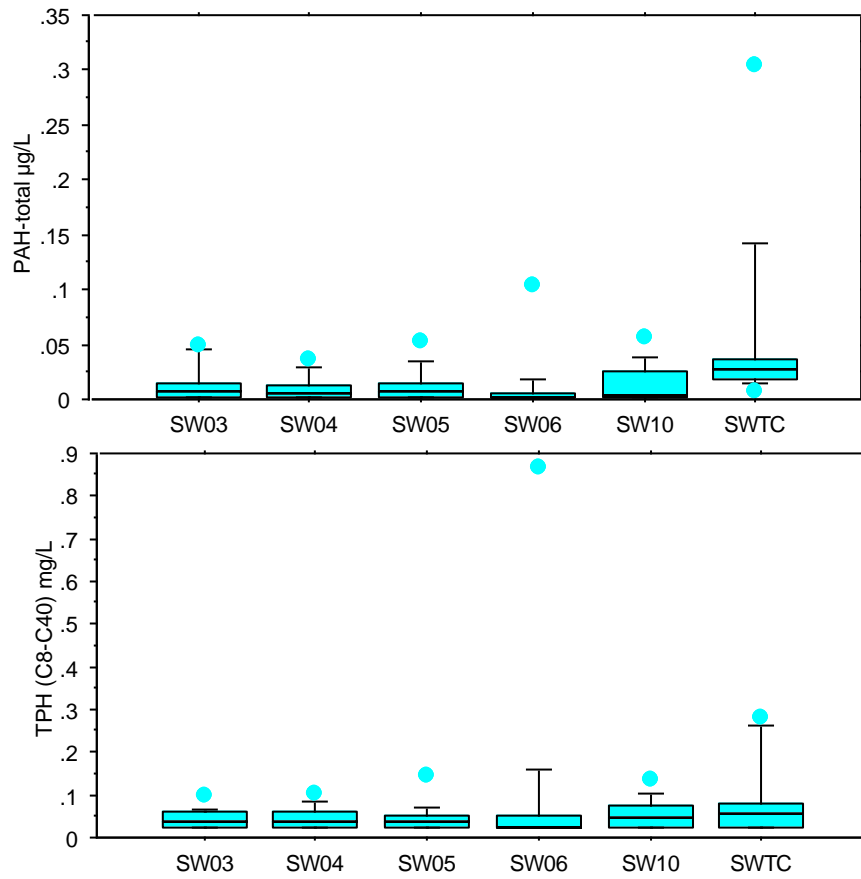
Number of samples at each location: 14

Figure A4.8 Box and whisker plots of dissolved organic carbon (NPOC) concentrations in surface water samples at each sampling location.



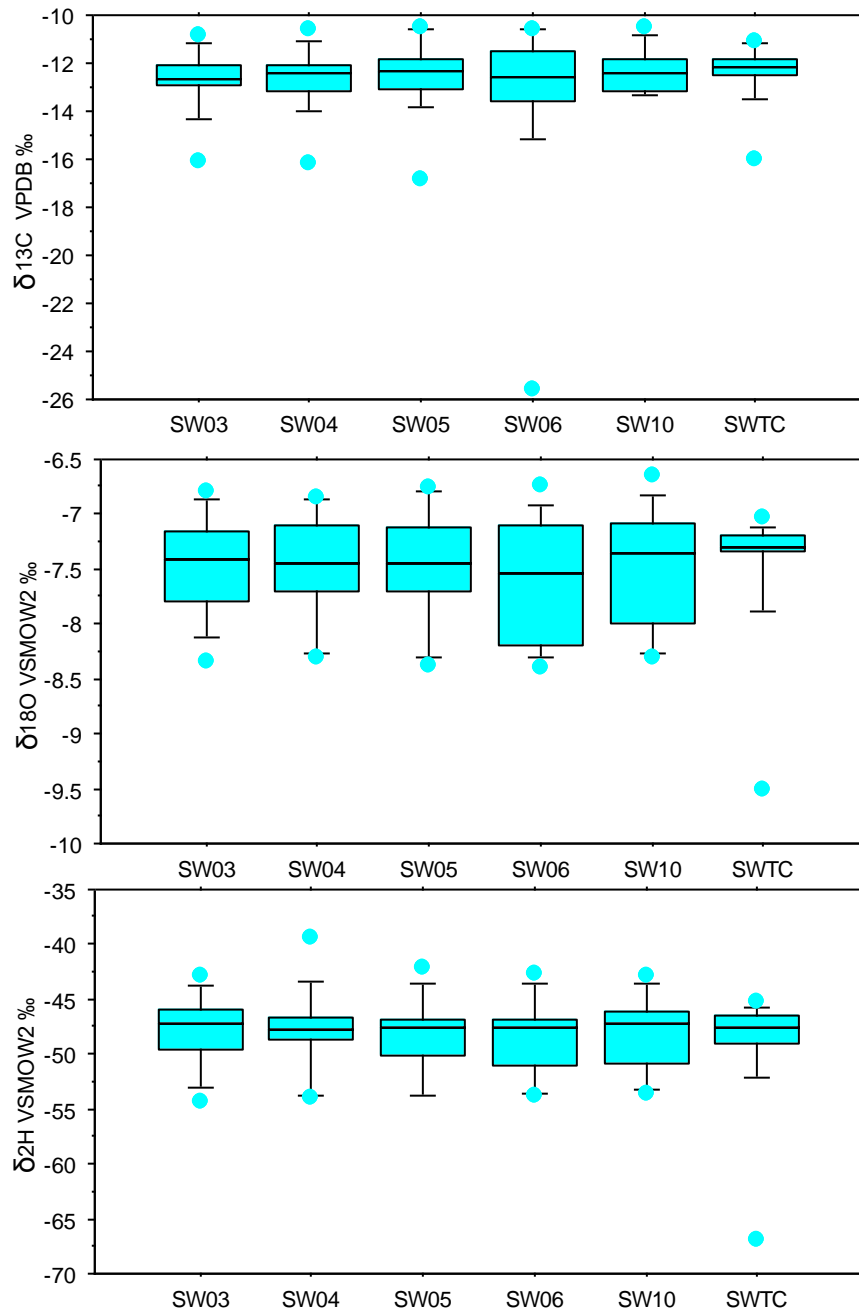
Number of samples at each location: 13

Figure A4.9 Box and whisker plots of PAH concentrations in surface water samples at each sampling location.



Number of samples at each location: PAH-Total 13; TPH 14

Figure A4.10 Box and whisker plots of PAH-Total and TPH concentrations in surface water samples at each sampling location.



Number of samples at each location: $\delta^2\text{H}$ and $\delta^{18}\text{O}$ 14; $\delta^{13}\text{C}$ 13

Figure A4.11 Box and whisker plots of stable isotope values in surface water samples at each sampling location.

Glossary

AA	annual average
BaP	benzo(a)pyrene
BGS	British Geological Survey
BS-ISO	British Standard International Organisation for Standardisation
CaCO ₃	calcium carbonate (alkalinity)
CCS	isotope laboratory in-house secondary standard
CO ₂	carbon dioxide
COPR	chromite ore processing residue
Cr(III)	trivalent chromium
Cr(VI)	hexavalent chromium
CRM	certified reference material
δ ¹³ C	ratio of stable isotopes ¹³ carbon: ¹² carbon
δ ¹⁸ O	ratio of stable isotopes ¹⁸ oxygen: ¹⁶ oxygen
δ ² H	ratio of stable isotopes ² hydrogen: ¹ hydrogen
DIC	dissolved inorganic carbon
DO	dissolved oxygen
DOC	dissolved organic carbon
Eh	redox potential
EQS	environmental quality standard
FA	filtered acidified water sample
FD	fluorescence detection
FUA	filtered unacidified water sample
G-BASE	Geochemical Baseline Survey of the Environment
GCC	Glasgow City Council
GC-FID	Gas chromatography flame ionisation detector
GIS	geographic information system
GMWL	global meteoric water line
GPS	global positioning system
HCl	hydrochloric acid
HD	hydrogen deuteride
HDPE	high density polyethylene
HMSO	Her Majesty's Stationery Office
HNO ₃	nitric acid
HPLC	high performance liquid chromatography
H ₂ S	hydrogen sulphide
IAEA	International Atomic Energy Authority
IC	ion chromatography
ICP-MS	inductively coupled plasma mass spectrometry
ID	identity number
IRMS	isotope ratio mass spectrometry

KCl	potassium chloride
KCM	Keyworth Carrera marble in-house calcite standard
LLD	lower limit of detection
LOQ	limit of quantification
MAC	maximum allowable concentration
MCS	isotope laboratory primary standard
NaHCO ₃	Sodium bicarbonate
NERC	Natural Environment Research Council
NH ₄	ammonium
NH ₄ NO ₃	ammonium nitrate
NH ₄ -EDTA	ethylenediaminetetraacetic acid-diammonium salt
NIGL	NERC Isotope Geoscience Laboratory
NPOC	non-purgeable organic carbon
ORS	octopole reaction system
PAH	polycyclic aromatic hydrocarbons
PEEK	poly-ether ether ketone
OC	organic carbon
QC	quality control
RSD	relative standard deviation
SEC	specific electrical conductance
SEPA	Scottish Environment Protection Agency
SHE	standard hydrogen electrode
SRM	secondary reference material
SUDS	sustainable urban drainage system
TDS	total dissolved solid
TIC	total inorganic carbon
TPH	total petroleum hydrocarbons
UCL	upper calibration limit
UK	United Kingdom
UKAS	United Kingdom Accreditation Service
UKGEOS	United Kingdom Geoenergy Observatories project
UKTAG	UK Technical Advisory Group on the Water Framework Directive
UKRI	United Kingdom Research and Innovation
UP	Type 1 ultrapure water
USA	United States of America
USGS	United States Geological Survey
VPDB	Vienna Pee Dee Belemnite
VSMOW	Vienna Standard Mean Ocean Water

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