Applying ground gas and gas flux monitoring techniques to low-enthalpy, shallow geothermal energy exploration

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Applying ground gas and gas flux monitoring techniques to low-enthalpy, shallow geothermal energy exploration

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Abstract

Ground gas and gas flux testing has been undertaken in a variety of situations including volcanic and geothermal activity, landfill and carbon storage monitoring. However, there are no documented studies of its application to shallow geothermal investigations, particularly where the water in disused mines will be used as the conduit for heat and the overlying ground has a complex industrial heritage. Background ground gas and gas flux measurements from three separate campaigns at a mine water heat research site in Glasgow, UK did not reveal any concerns regarding mine gas or other potentially harmful gases from previous land uses. The detected CO_2 was found to be predominantly of biological origin and reflected the expected quantities based upon land use, seasonal and weather fluctuations and was consistent with other UK sites. One location is recommended for further investigation due to higher-than-expected nitrogen and lower oxygen measurements. Some hydrogen gas was detected, albeit well below explosive limits, which may be present as a result of past industrial site uses, highlighting the need for more investigation into the presence of hydrogen at ex-industrial sites. Apart from this there was very little evidence of the industrial site history in the gas characterisation.

A process-based analysis, based upon the stoichiometric relationship of CO_2, CH_4, O_2 and N_2, was applied to the results. This complemented, but was not a substitute for, the background survey. There were limitations with the process-based approach when there was not a clear anomalous CO_2 signal or where potentially more than one process was occurring simultaneously.

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Keywords (max 6)

Shallow geothermal energy, mine gas, industrial site, background gas survey , process-based analysis

1 Introduction

Measuring ground gas and gas flux at the surface or in the near-surface environment can be a requirement, or simply responsible management, for subsurface energy or disposal activities. It has been used in a variety of situations, such as detection of volcanic and geothermal activity, monitoring landfill sites and for the investigation of the impacts related to shale gas extraction (Cardellini et al., 2003; Zhang et al., 2017; Li et al., 2020 and Ward et al., 2019). It has also been extensively considered and employed in monitoring the effects of carbon capture and storage (CCS) (Beaubien et al., 2013; Carman et al., 2014; Pearce et al., 2014; Beaubien et al., 2015; Jenkins et al., 2015; Jones et al., 2015 and Tarakki et al., 2018). However, there is no record of it being applied to shallow geothermal energy production, particularly where the water in disused mine workings provide the conduit for the heat source; an immature but emerging technology in the UK (Athresh et al., 2015; Banks et al., 2017; Farr et al., 2020; Coal Authority, 2021). This paper analyses the efficacy of ground gas and gas flux measurements in determining the ground gas landscape and establishing whether there are any pre-existing issues, such as the lensing or escape of mine gases, as a result of the complex industrial history at the UK Geoenergy Observatory in Glasgow UK ('Glasgow Observatory'); circumstances that are likely to recur if other mine workings are to be utilised in this fashion.

The major gases associated with mine workings are methane (CH_4) and carbon dioxide (CO_2) which, as well as being significant greenhouse gases, can accumulate to create asphyxiation hazards, change the chemistry of ground water, affect biological processes, or explode (Pearce et al., 2014; Jones et al., 2015; Blackford et al., 2014 and Appleton, 2011). Methane that is adsorbed to the surface of coal is released when a coal seam is decompressed. In mines the mix of methane with other gases, known as firedamp, can be explosive and has resulted in a number of incidents. However, where present in sufficient quantities, coalbed methane (CBM) can be recovered from coal seams and disused mines and used as an additional source of hydrocarbons such as in USA, Australia, China and India (Jones et al., 2004; Moore, 2012 and DECC, 2013). Jones et al. (2004) estimate that the coal in central Glasgow has a methane content of 4.9 $m^3\ t^{-1}$, however, they note that this area had been extensively mined so the potential for viable CBM is low. Flooding in the mines will also

prevent the desorption reducing the prevalence of free CH_4 gas (Jones et al., 2004). In addition, the coal workings utilised for the Observatory are not sufficiently deep for CBM to be feasible. Nonetheless, other potentially harmful trace gases associated with the mining industry and other industrial uses, such as hydrogen sulphide (H_2S) and hydrogen (H_2), may also be present (Young and Lawrence, 2001; Wilson et al., 2010). It is therefore important to monitor for the presence of these gases throughout the development of the Observatory, and of minewater geothermal activities more broadly.

1.1 Use of gas surveys in geo-energy projects

To understand gas in the near-surface environment, it is helpful to measure a number of related parameters: firstly, ground gas concentrations, at a depth (c.70-100 cm below ground level) that minimises or eliminates interference from the atmosphere. These measurements correspond directly to concepts of 'soil gas' or 'near surface soil gas' discussed elsewhere in the literature (for example, Ball et al., 1992; Beaubien et al., 2013); secondly, gas flux measurements between soil and the lower atmosphere, a negative flux indicates migration from the atmosphere into the soil; finally, if possible, measurement of gas concentrations in the lower atmosphere, near to the ground surface.

These measurements are used, along with others, such as downhole, groundwater, soil and surface water chemistry and seismic measurements, to construct an overall environmental baseline that provides a picture of the typical conditions at a particular site (Pearce et al., 2014). Within this comprehensive assessment, investigation of the normal gas environment defines the site-specific geo-bio-chemical landscape, indicating the source of gas, distinguishing gases produced by biological and chemical processes in soils and artificial ground deposits and determining useful indicators of uncharacteristic behaviour (Beaubien, 2013; Jones et al., 2015 and Tarakki et al., 2018). This is often referred to as a 'baseline' or 'background' study and these terms are occasionally used interchangeably (e.g. Beaubien et al., 2015). However, baseline implies a fixed level of environmental noise, which has allowed this approach to be criticised as circumstances, such as climate change, will affect baseline measurements throughout the life of a project (Dixon and Romanak, 2015). We believe the term 'background' allows for such environmental fluctuations and is generally preferred in

relation to the activities described by this paper, however, the term baseline will still be used when referring to other studies that define their inquiries as such.

Gas conditions fluctuate daily and seasonally and may also alter with changes in climate (Beaubien et al., 2013; Dixon and Romanak, 2015). To capture the range of these cycles, measurements are ideally taken through a combination of multiple discrete surveys, preferably reflecting seasonal fluctuations, and continuous monitoring which allows diurnal and seasonal patterns in gas to be accounted for. One of the most comprehensive baseline studies was conducted at the Weyburn oil field, Saskatchewan, Canada where ground gas was sampled on seven campaigns over a ten-year period to form a picture of daily and seasonal fluctuations and, in doing so, developing many of the current techniques used to monitor ground gas (Beaubien et al., 2013). Similar techniques have commenced at the Glasgow Observatory and will be verified by comparing the results with those from previous background gas studies (Beaubien et al., 2013; Carman et al., 2014; Ward et al., 2019; Li et al, 2020 and results compiled by Jones et al., 2014). Signal to noise ratio (SNR) techniques can then be used to determine which measurements are most likely to provide strong indications of anomalies once investigation into the viability of using shallow geothermal heat commences (Nickerson and Risk, 2013; Risk et al., 2015 and Tarakki et al., 2018).

Dixon and Romanak (2015) advance an alternative method, initially proposed by Romanak et al. (2012), of identifying the source of ground gas and flux. They state that a site can be characterised with one set of measurements using a process-based approach that indicates the source of the gas based upon the stoichiometric relationship of the major gases so that a tailored monitoring regime can then be established based upon this characterisation taking into account the potential sources of ground gas. Further, they argue that baseline studies are not appropriate in attributing gas leakage at every site and assert that the process-based approach provides a suitable method for characterising anomalous gas. As evidence of this Dixon and Romanak (2015) maintain that the baseline studies were not useful in dealing with a gas leakage claim at Weyburn and that the process-based approach was one of the only methods that successfully characterised the detected gas as originating from a biological source.

Ground gas and gas flux measurements were collected during three discrete campaigns in August 2018, May 2019 and October 2019 at four environmental baseline sites at the Glasgow Observatory (**Figure 1**). The measurements were taken prior to research activities and during preliminary site preparation (May 2019) and borehole drilling/construction activities (October 2019). These measurements constitute the pre-operational background gas values. This paper analyses the sampling techniques and results of the background gas surveys, released as open data (National Geoscience Data Centre, 2021), in relation to the site complexity and their applicability to low-enthalpy, shallow geothermal exploration and compares them with the outcomes from the process-based analysis.

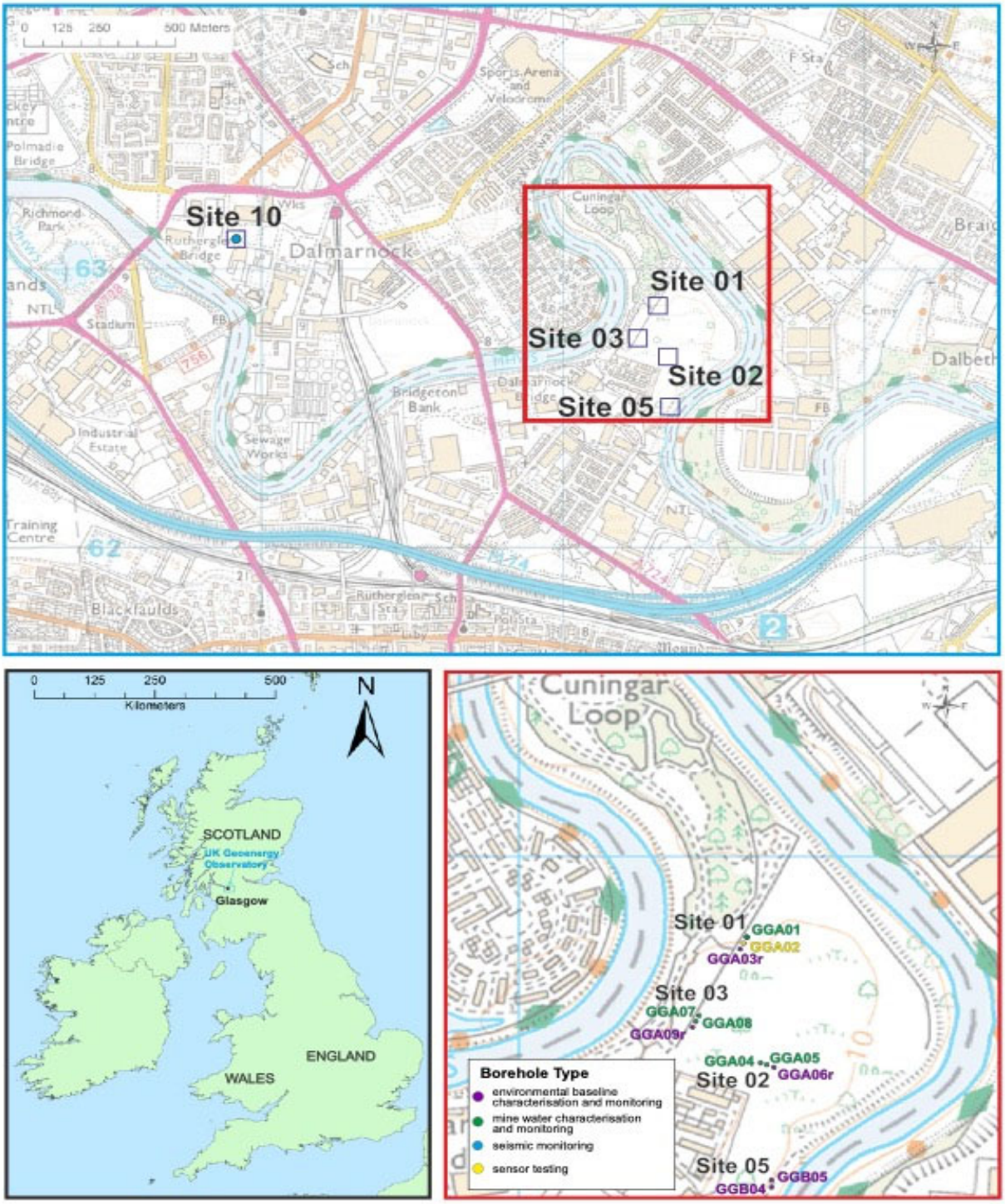

Figure 1 Location of the Glasgow Observatory including boreholes situated in the Cuningar Loop of the River Clyde (see red box). Contains Ordnance Survey data © Crown copyright and database rights. All rights reserved [2020] Ordnance Survey [100021290EUL]. Adapted from Monaghan et al. (2020).

2 Study Site

The Glasgow Observatory is one of three UK Geoenergy Observatories (UKGEOS) developed to substantially improve our understanding of the subsurface environment and determine the feasibility of carbon neutral technologies that harness geothermal energy resources as well as investigating the potential for other low carbon energy technologies (UKGEOS, 2021). Investigations at the Glasgow Observatory will explore the processes and impacts of using flooded, disused mines to extract geothermal heat (Monaghan et al, 2017).

The site is predominantly located in a meander of the River Clyde, named the Cuningar Loop (**Figure 1**). It is now a public open space, but it has a complex history of industrial use. In this area, the Upper Carboniferous sedimentary bedrock of the Scottish Coal Measures contains a series of stacked coal seams that were mined between 1810 and 1934. The coal measures are overlain by Quaternary glacial and post-glacial superficial deposits of variable thickness, to about 35 m below surface level, and by a further 10-15 m of anthropogenic deposits, made, filled and landscaped ground, relating to the various industrial uses of the site (Monaghan et al., 2019a). The superficial deposits in the Cuningar Loop, from top down, predominantly consist of alluvial sand and gravel from the River Clyde, part of the Gourock Sand Member, then a layer of the Paisley Clay Member, or Broomhouse Sand and Gravel Formation, depending on the location within the Loop, which sits upon glacial till of the Wilderness Till Formation, see **Figure 2** (Monaghan et al., 2019a). Detailed post-drill data can be viewed in various publications on the UKGEOS website (2021).

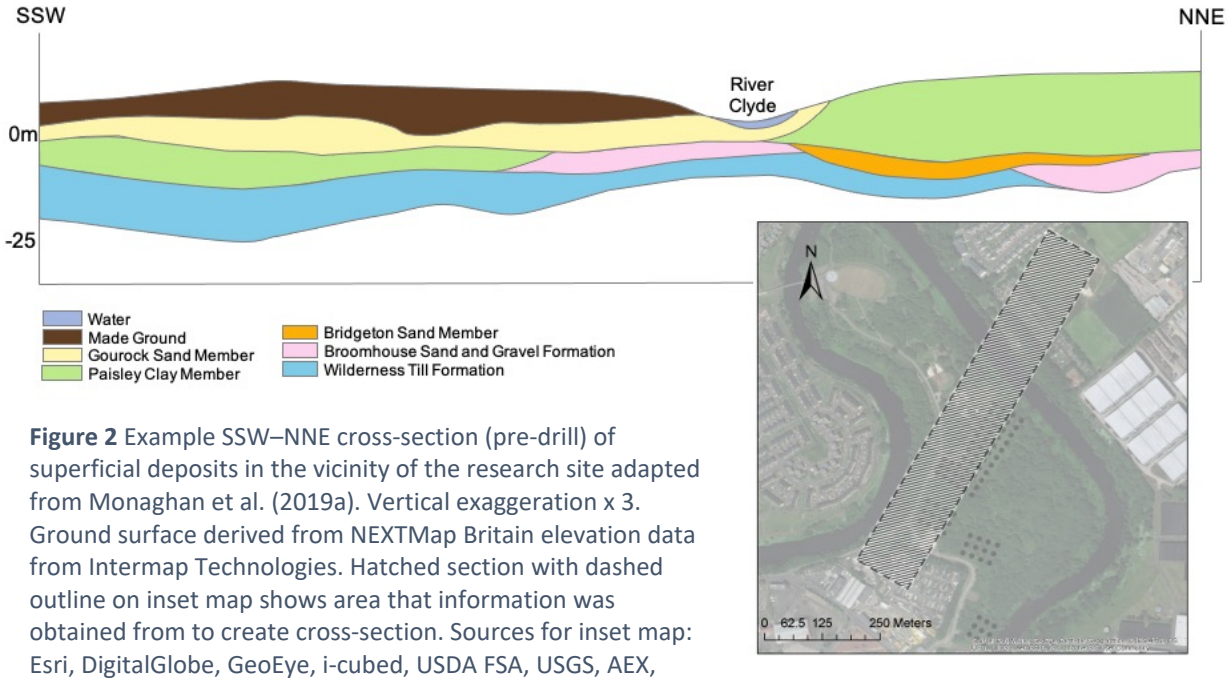

Figure 2 Example SSW–NNE cross-section (pre-drill) of superficial deposits in the vicinity of the research site adapted from Monaghan et al. (2019a). Vertical exaggeration x 3. Ground surface derived from NEXTMap Britain elevation data from Intermap Technologies. Hatched section with dashed outline on inset map shows area that information was obtained from to create cross-section. Sources for inset map: Esri, DigitalGlobe, GeoEye, i-cubed, USDA FSA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community.

There are eleven boreholes across the four Cuningar Loop sites; six that targeted the mine workings, a selection of which are planned to be part of a shallow mine water thermal heat loop, and five environmental baseline monitoring boreholes (**Figure 1** and **Figure 3**). There is also an additional seismic monitoring borehole about 1.5 kilometres to the west on the north bank of the River Clyde (Site 10 in **Figure 1**). The heat loop will be used to explore the ability to harness heat from within the shallow subsurface.

The surface character varies significantly across the four sites at Cuningar Loop. Some areas, at least superficially, appear relatively natural with more mature woodland, whereas in other areas the previous industrial and waste disposal land use is more apparent in an early succession landscape. Pictures of the sites showing the level of succession in the surface vegetation at the time of the soil chemistry survey can be seen in Fordyce et al. (2020). An industrial history of a waterworks, sand and gravel extraction, colliery workings and a mineral railway, all of which was infilled with demolition debris mean that rubble, coal spoil mounds and other buried waste material close to the surface is widespread across the entire site (Ramboll, 2018). In less complex settings, it is most likely that any migrating gas will use either natural or artificial preferential pathways, such as faults, boreholes or disused

wells (IPCC, 2005). The complexity of the shallow subsurface will affect these pathways, for instance, there may be reservoirs of escaped mine gas trapped below soils, natural and artificial, with low permeability (Jones et al., 2015), or there may be additional gas migration pathways through the shallow deposits to the surface. The process of drilling may have also created the potential for new gas migration pathways to surface.

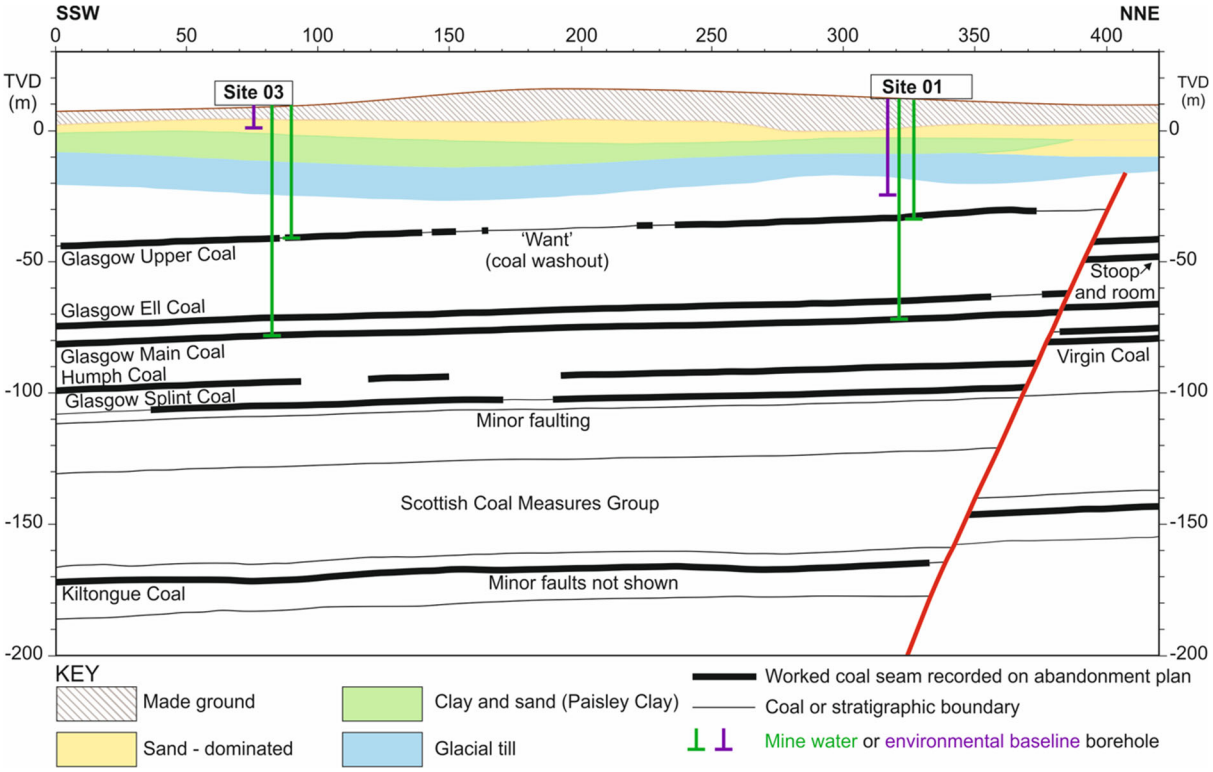

Figure 3 A pre-drill cross-section of part of the Glasgow Observatory illustrating how the mine water characterisation boreholes (green) intersect the mine workings and the relative position of the environmental boreholes (purple). The red line indicates an inferred fault (also see **Figure 4**) The depths are shown as True Vertical Depths (TVD) relative to Ordnance Datum. The horizontal axis is in metres (m) (Monaghan, 2019b).

3 Methods

3.1 Survey design

Point samples of ground gas and gas flux were taken at 83 locations in 20 m-spaced grids across the four sites (Site 1, Site 2, Site 3 and Site 5), taking into account faulted bedrock, superficial and made ground geology, particularly encompassing key locations such as, faults, legacy and new boreholes. 20 m-spaced grids were decided upon to balance the demands between covering a meaningful surface area at each of the sites and being of high enough resolution to offset the unpredictable impact that the made ground can have on the gas pathways. The idealised locations for the point measurements at each of the Glasgow Observatory sites are shown in **Figure 4**.

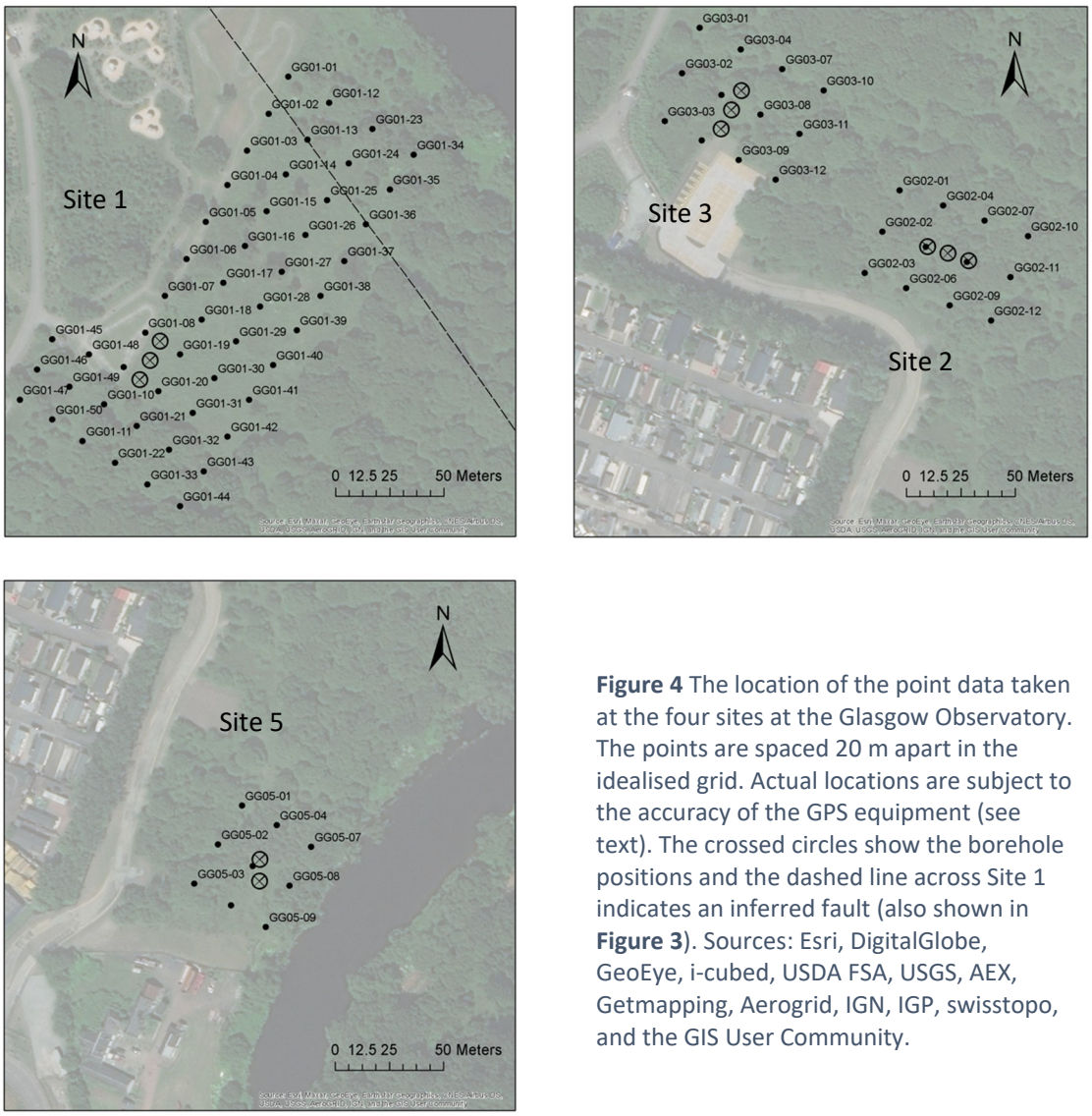

Figure 4 The location of the point data taken at the four sites at the Glasgow Observatory. The points are spaced 20 m apart in the idealised grid. Actual locations are subject to the accuracy of the GPS equipment (see text). The crossed circles show the borehole positions and the dashed line across Site 1 indicates an inferred fault (also shown in **Figure 3**). Sources: Esri, DigitalGlobe, GeoEye, i-cubed, USDA FSA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community.

3.2 Ground gas concentrations

Ground gas was sampled using thick-walled, stainless steel probes, with external diameter of 8 mm, that were driven into the ground to a maximum depth of 80 cm below ground level to avoid the dilution of ground gas by atmospheric air.

Samples of ground gas were pumped directly to a Geotechnical Instruments GA 5000 portable gas analyser which was attached to the probes to determine the major components of ground gas. The instrument produces CO_2, CH_4 and O_2 concentration data (volume percentage, %) and a H_2S concentration (parts per million, ppm). It is also adapted to measure H_2 concentration (ppm) and calculates a 'residual balance' as a percentage concentration, such that:

$$\text{Residual balance} = 100\% - (\%CH_4 + \%CO_2 + \%O_2)$$

The residual balance is roughly equivalent to nitrogen (N_2) concentrations in most circumstances and is used in this study as a proxy for N_2.

In addition, a Huberg Laser One analyser was used to measure the CH_4 concentration directly from the probe in ppm.

Instrument specifications can be found at the relevant manufacturer websites (Geotech, n.d.; QED, 2020) and Appendix A. The ground gas instruments are serviced and calibrated regularly by the manufacturer and additional quality control checks are made before deployment using in-house methods, as well as in the field, as required, to maintain data quality. The data reported is taken directly from these instruments without further manipulation.

3.3 CO_2 and CH_4 flux

Gas flux was measured at the ground surface using a closed-loop accumulation chamber (net volume 2.756 x 10^{-3} m^3) attached to a West Systems flux meter, equipped with a Li-

COR® model LI820 analyser (Li-COR, n.d. and Appendix A). The gas flux data reported is converted from mol m^{-2} d^{-1} to g m^{-2} d^{-1}.

3.4 Stable isotopes of carbon in CO_2 ($\delta^{13}C_{v\text{-}PDB}$)

Where measured ground gas parameters were notably different to neighbouring samples, additional ground gas samples were collected for $\delta^{13}C$ isotope analysis. The analysis was by Iso-Analytical Limited, UK using their documented GC-IRMS method to calculate a per mille $\delta^{13}C$ ratio normalised to the V-PDB (Vienna Pee Dee Belemnite) standard.

In all, isotope samples were taken at two of the probe locations as part of the August 2018 campaign and four locations during the May 2019 campaign. Research by Flude et al. (2017) attributing isotope results to biogenic and geogenic sources was used to help with the interpretation of these measurements.

3.5 Data interpretation

Given the subsurface complexity at the Glasgow Observatory due to the various previous uses of the location, referred to in section 2, it is possible that each environmental baseline site 1-5 has a significantly different gas profile. To establish whether the site results should be treated separately a one-way analysis of variance (ANOVA) evaluation was used to identify whether there was a statistical difference between the measurements at each site. This test was applied to the groups of CO_2 concentration and CO_2 flux measurements from each site and compared between the four sites. A statistical difference is identified by comparing the *F*-value, a value measuring the separation between the distributions of each sample group, with an *F*-critical value that identifies that there is a difference between the groups at the 95% confidence level. This same test was used to determine if there was a significant difference between the campaigns for the same two gas measurements. If a statistical difference was identified then pairwise comparisons were made between the sites and campaigns using the post-hoc, Tukey-Kramer analysis, also at the 95% confidence level, to establish where the differences lay. These analyses were chosen because they establish whether there is a difference between the means of unrelated, categorical groups

of measurements; this analysis was applicable for both the geographical (sites) and temporal (campaigns) groups.

In addition to comparing the range, mean, median and standard deviation of the ground gas concentrations and fluxes, a process-based approach (Romanak et al., 2012) was also applied to ground gas concentrations to assist in determining the origin of CO_2. The process-based analysis is a stoichiometric approach that evaluates ground gas concentrations of CO_2 against O_2, the N_2/O_2 ratio against CO_2 and CO_2 against N_2 to determine the biological or geological origin of CO_2 (**Figure 5**). Datapoints falling in the orange (lowest) area suggest that the reduced level of detectable CO_2 is due to CO_2 dissolution, whereas datapoints falling within the areas above the top, biological respiration line suggest an additional CO_2 input. Datapoints falling between the two lines are considered normal background levels of CO_2 as a result of biological and geological processes.

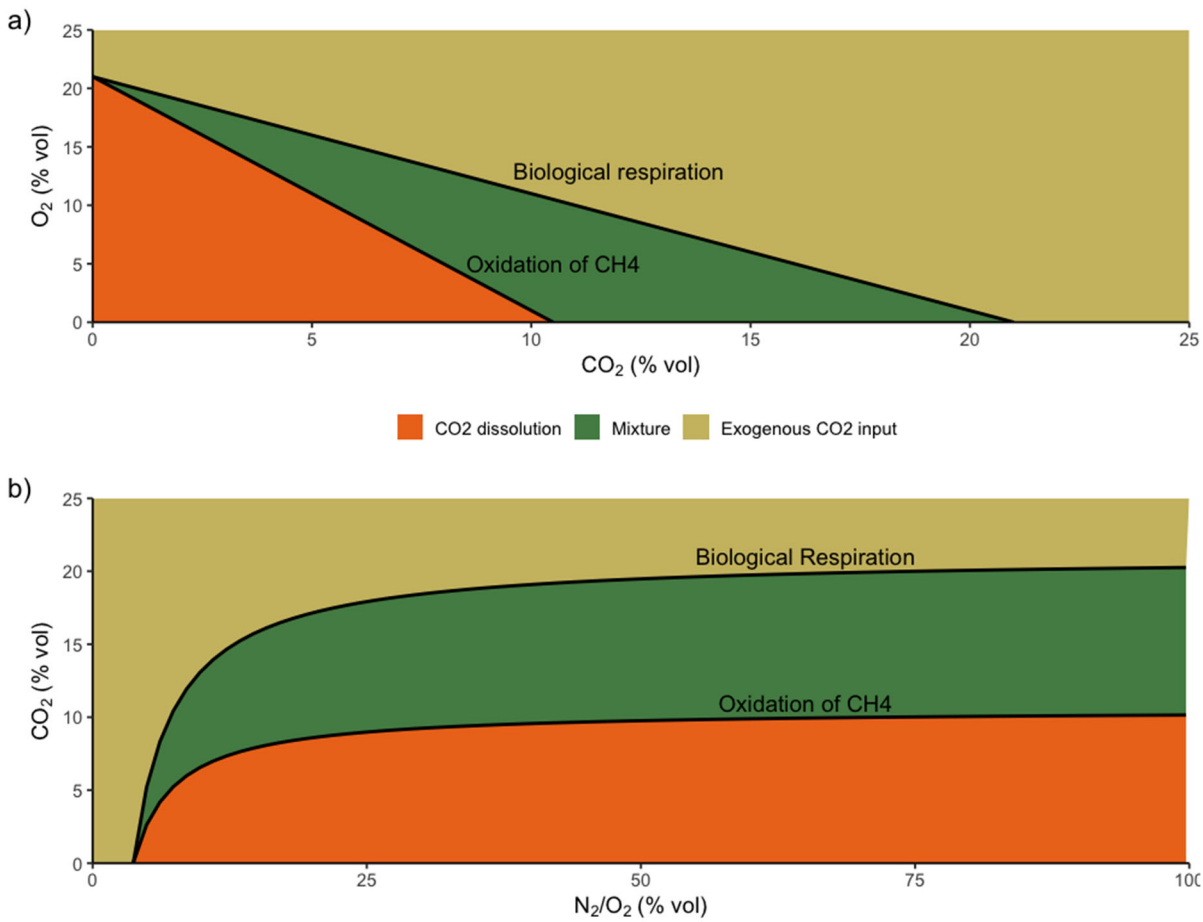

Figure 5 Interpretation of a) the O_2 and CO_2 data and b) CO_2 and N_2/O_2 developed by Romanak et al. (2012). The plotted lines are created by the stoichiometric relationship for biological respiration and oxidation of CH_4, respectively.

4 Results and Analysis

4.1 Results

Details of the measurements obtained in each survey and a summary of data are given in **Tables 1** to **3**; the complete datasets are available at the National Geoscience Data Centre (2021). Across the four Glasgow Observatory sites, the idealised grids totalled 83 sample points. In practice, it was sometimes not possible to obtain data for all parameters at all sample points due to prevailing ground conditions e.g., buried material, made ground, ongoing works or saturated ground. A handheld Garmin GPS was used to locate the British National Grid coordinates and locations are accurate to 5 m in ideal conditions. Where it was not possible to obtain a GPS signal because of obstruction by vegetation/tree canopy etc, grid coordinates were located using measuring tape. CH_4 flux is not reported as we were unable to detect any quantifiable CH_4 flux across the three surveys, apart from one measurement of 0.282 g m^{-2} day^{-1} recorded at GG01-40 in October 2019 (**Figure 6**); all other measurements were below the instrument's lower detection limit of 0.08 g CH_4 m^{-2} day^{-1}.

Table 1 Summary of August 2018 survey data. n=number of sample points. Reference to "<0.5" or "<1" denotes that the measurements were below the instruments' detection limits.

Gas Measured	n	Mean	Median	Standard Deviation	Maximum	Minimum
CH_4 (ppm)	67	1.9	1.9	0.5	3.8	<0.5
CO_2 (% vol)	68	3.3	2.6	2.7	12.4	<0.5
O_2 (% vol)	68	17.6	18.7	4.2	22.7	0.9
H_2 (ppm)	68	2.0	1.0	3.9	23.0	<1
H_2S (ppm)	68	<1	<1	0.1	1.0	<1
Balance (N_2) (% vol)	68	79.1	78.6	1.8	88.9	76.3
N_2/O_2	68	6.2	4.2	11.6	98.8	3.4
CO_2 flux (g m^{-2} day^{-1})	74	30.5	28.1	14.9	81.7	10.9

Table 2 Summary of May 2019 survey data. n=number of sample points. Reference to "<0.5" or "<1" denotes that the measurements were below the instruments' detection limits.

Gas Measured	n	Mean	Median	Standard Deviation	Maximum	Minimum
CH_4 (ppm)	58	1.4	1.6	1.1	8.2	<0.5
CO_2 (% vol)	58	4.0	3.2	3.2	17.9	<0.5
O_2 (% vol)	58	16.5	17.4	3.6	20.5	1.6
H_2 (ppm)	58	12.9	6.0	17.2	65.0	<1
H_2S (ppm)	58	0.4	<1	0.5	1.0	<1
Balance (N_2) (% vol)	58	79.5	79.3	1.0	83.5	76.8
N_2/O_2	58	5.8	4.6	6.1	50.3	3.8
CO_2 flux (g m^{-2} day^{-1})	59	22.7	21.9	16.1	79.0	-7.2*

*negative flux implies net transfer of CO_2 from atmosphere to soil.

Table 3 Summary of October 2019 survey data. n=number of sample points. Reference to "<0.5" or "<1" denotes that the measurements were below the instruments' detection limits.

Gas Measured	n	Mean	Median	Standard Deviation	Maximum	Minimum
CH_4 (ppm)	62	4.7	2.4	20.5	163.0	<0.5
CO_2 (% vol)	62	5.1	4.9	3.6	18.0	<0.5
O_2 (% vol)	62	16.0	16.2	4.1	21.8	2.8
H_2 (ppm)	62	3.7	<1	10.1	60.0	<1
H_2S (ppm)	62	0.9	<1	5.0	38.0	<1
Balance (N_2) (% vol)	62	78.9	78.4	1.5	86.4	76.6
N_2/O_2	62	5.7	4.9	3.9	28.3	3.6
CO_2 flux (g m^{-2} day^{-1})	65	12.6	11.6	5.8	35.6	3.5

Ranges of ground gas concentrations of CO_2, H_2 and O_2, along with CO_2 flux, are shown in **Figure 7**a to d. **Figures Figure 8** and **Figure 9** show the spatial distribution of CO_2 concentrations and CO_2 flux at each of the four sites in August 2018, May and October 2019. **Figure 10** shows the spatial distribution of H_2 for the three campaigns.

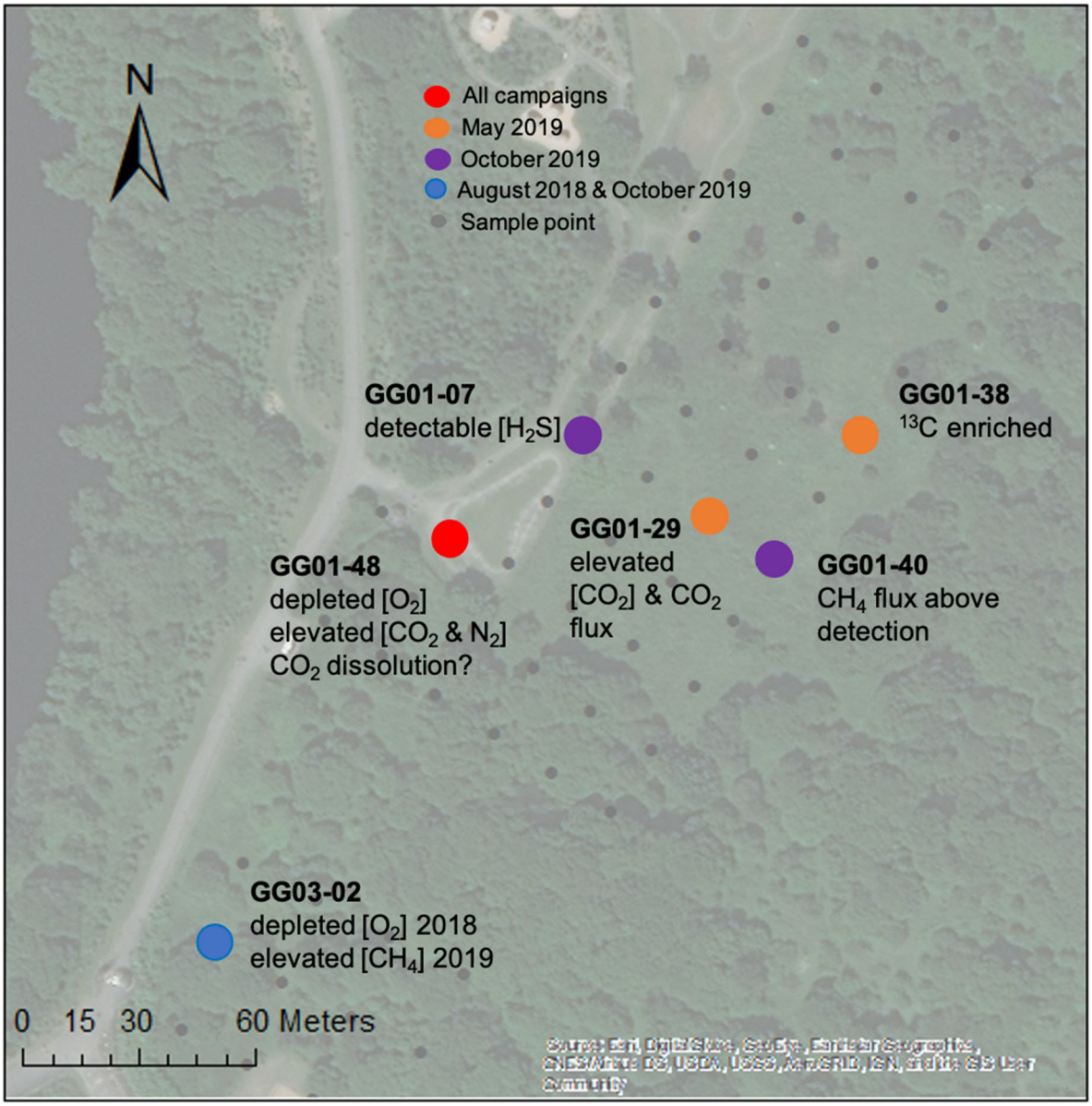

Figure 6 Individual sample points highlighted in the text. Square brackets indicate the values for gas concentrations. This summary figure is provided for convenience, it is not intended to convey any significance other than where explicitly stated in the text. Sources: Esri, DigitalGlobe, GeoEye, i-cubed, USDA FSA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community.

305

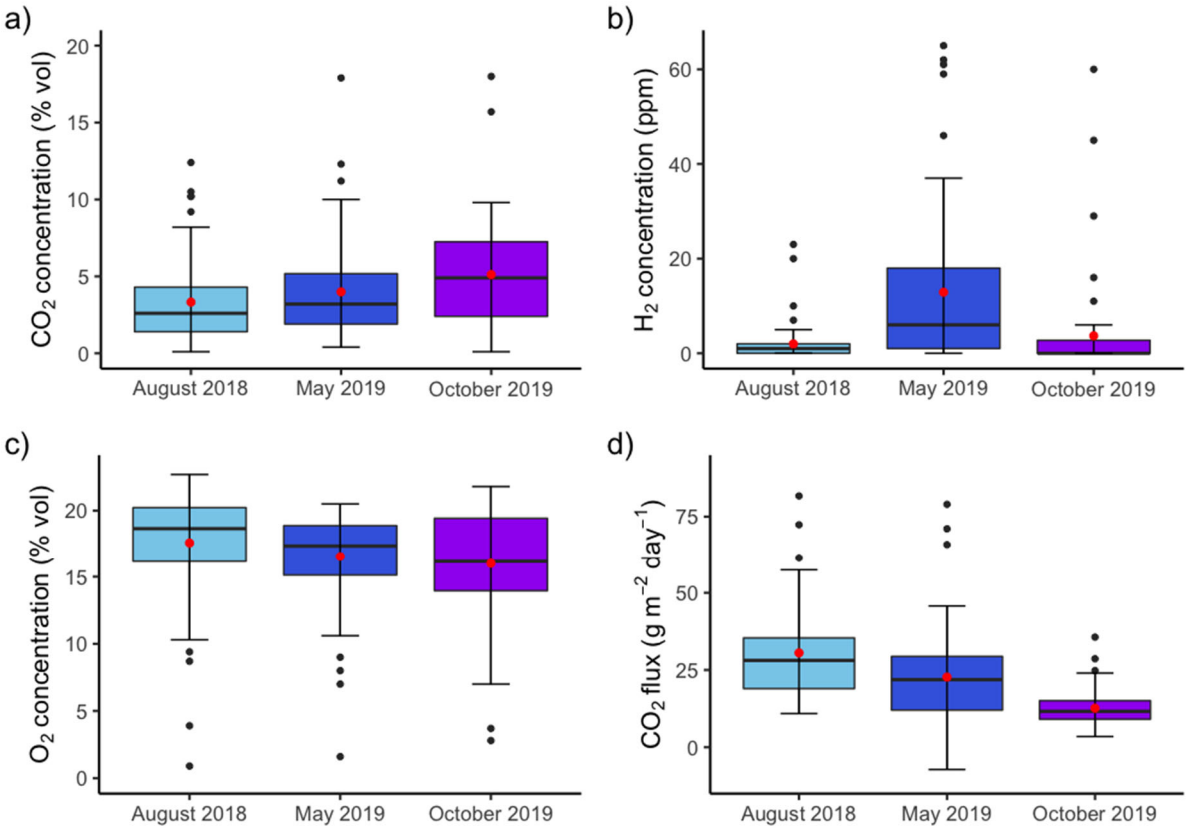

Figure 7 Boxplots comparing the range of baseline observations for August 2018, May and October 2019 for a) CO_2 concentration, b) H_2 concentration, c) O_2 concentration and d) CO_2 flux. The red point shows the mean of each set of observations, the black horizontal line shows the median value, the black points show outlier observations and the whiskers represent 1.5 times the standard deviation. The CO_2, H_2 and O_2 concentrations were analysed by the GA5000 gas analyser, the CO_2 flux was were measured by West Systems flux meter.

$\delta^{13}C$ stable isotope values for CO_2 in ground gas samples taken in August 2018 at GG01-07 and GG01-48 were -23.82 and -26.31‰ $\delta^{13}C_{V\text{-}PDB}$, respectively. Four further measurements taken in May 2019 at GG01-10, GG01-38, GG02-11 and GG03-06 were -23.59, -16.76, -25.00 and -26.10‰ $\delta^{13}C_{V\text{-}PDB}$, respectively (**Figure 11**).

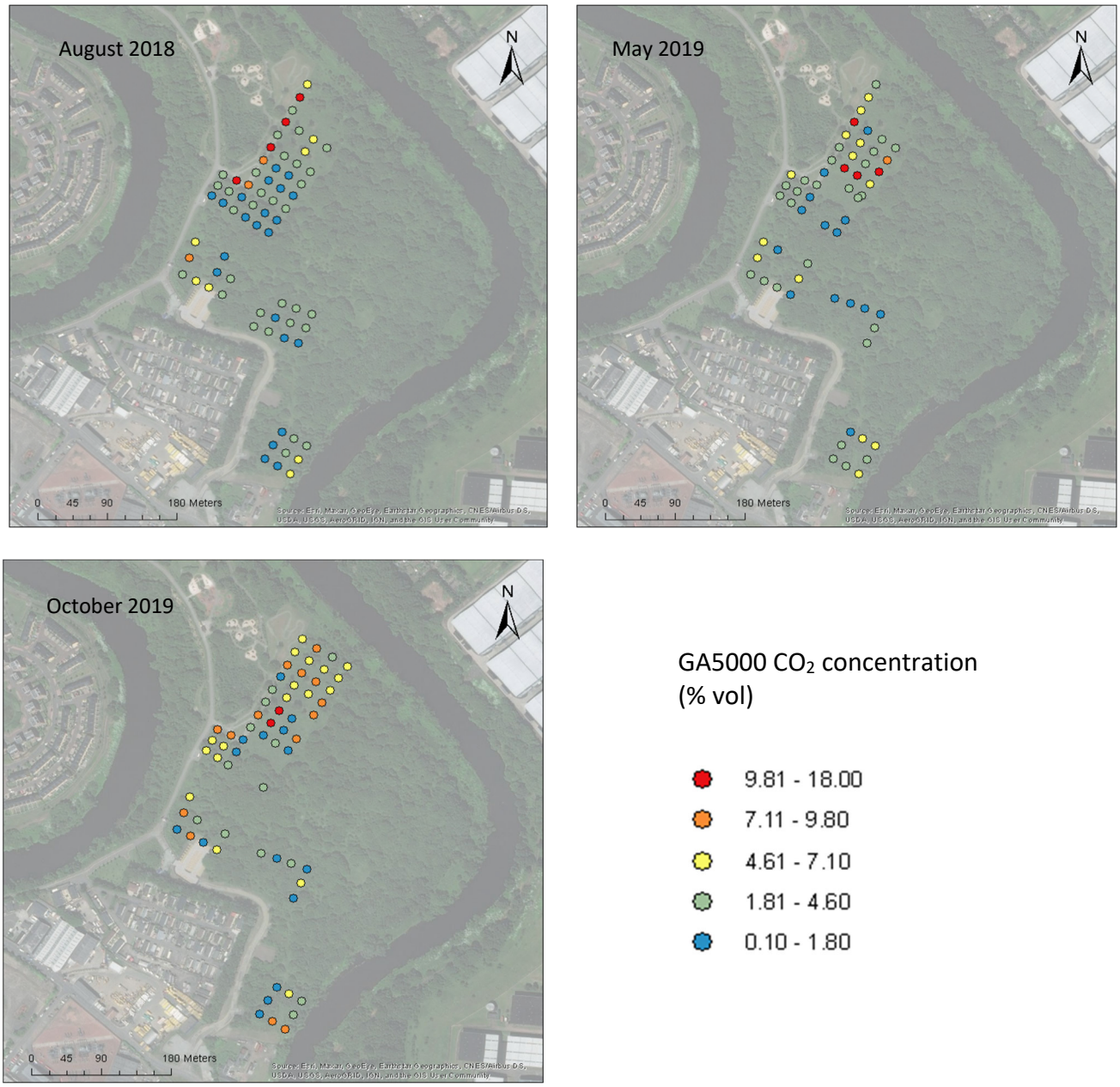

Figure 8 The CO_2 concentration measurements taken at Sites 1, 2, 3 and 5 by GA 5000 for August 2018, May and October 2019. Sources: Esri, DigitalGlobe, GeoEye, i-cubed, USDA FSA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community.

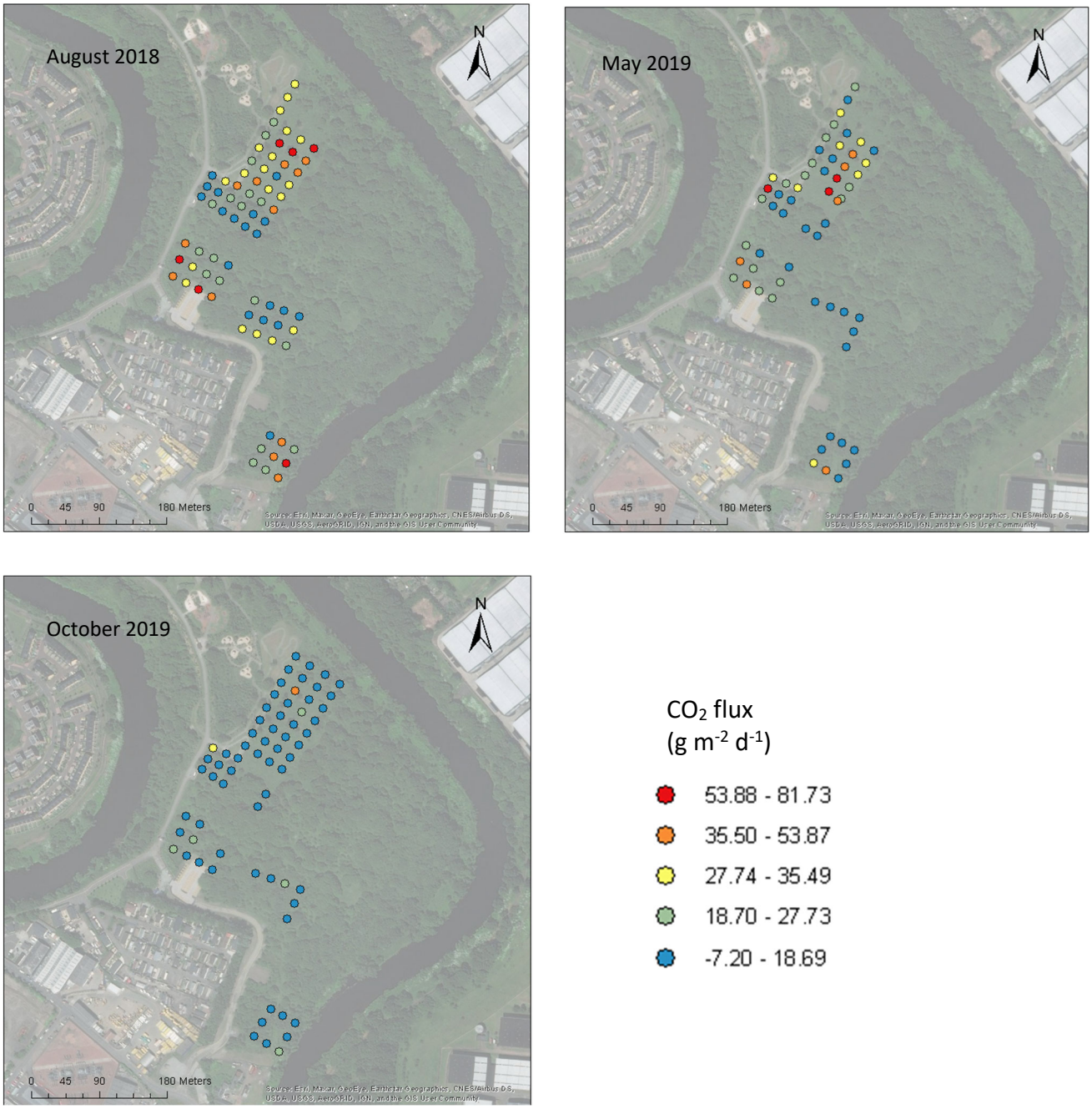

Figure 9 The CO_2 flux measured at Sites 1, 2, 3 and 5 by the West Systems flux meter for August 2018, May and October 2019. Sources: Esri, DigitalGlobe, GeoEye, i-cubed, USDA FSA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community.

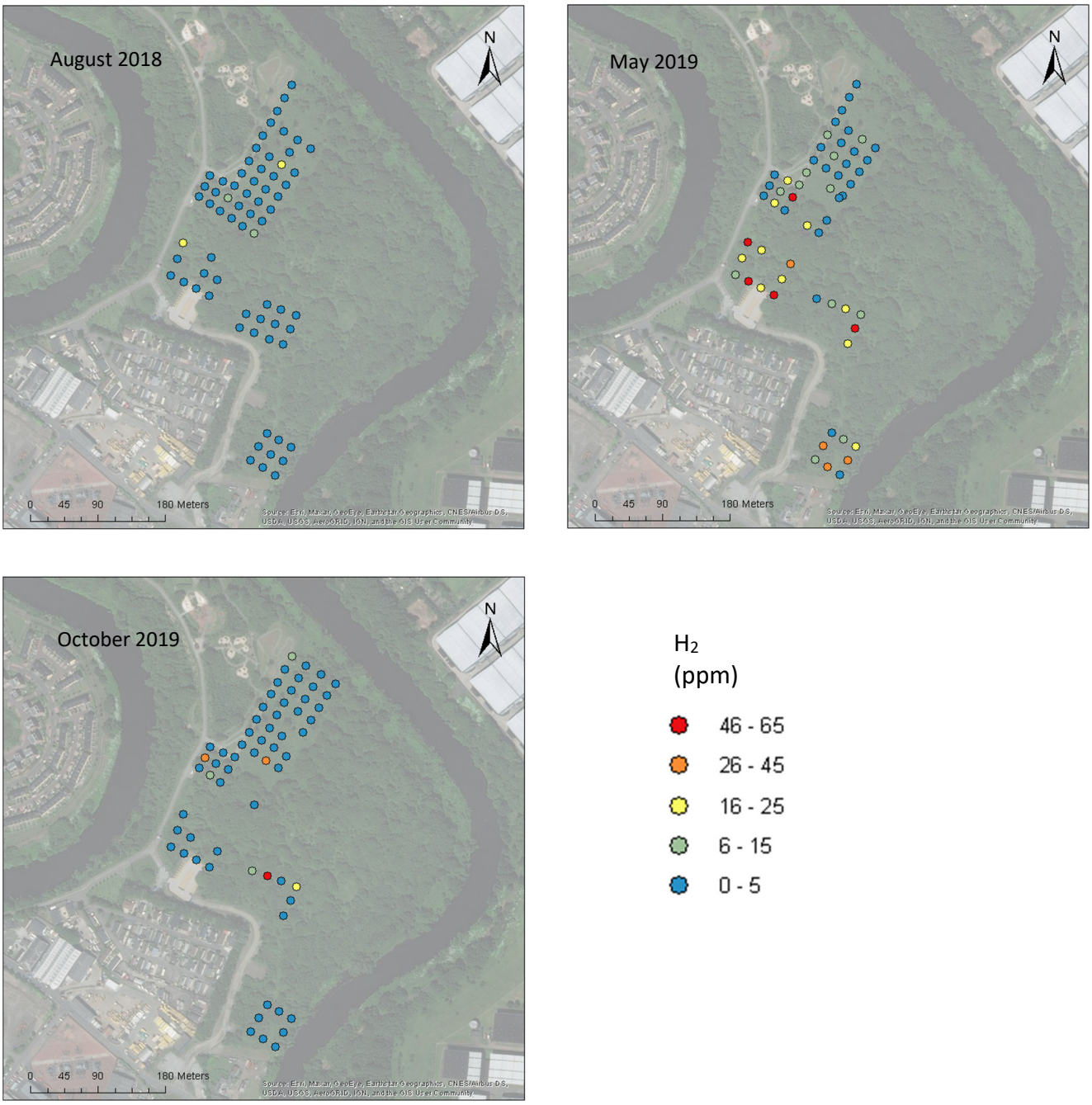

Figure 10 The H_2 measurements taken at Sites 1, 2, 3 and 5 by GA 5000 for August 2018, May and October 2019. Sources: Esri, DigitalGlobe, GeoEye, i-cubed, USDA FSA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community.

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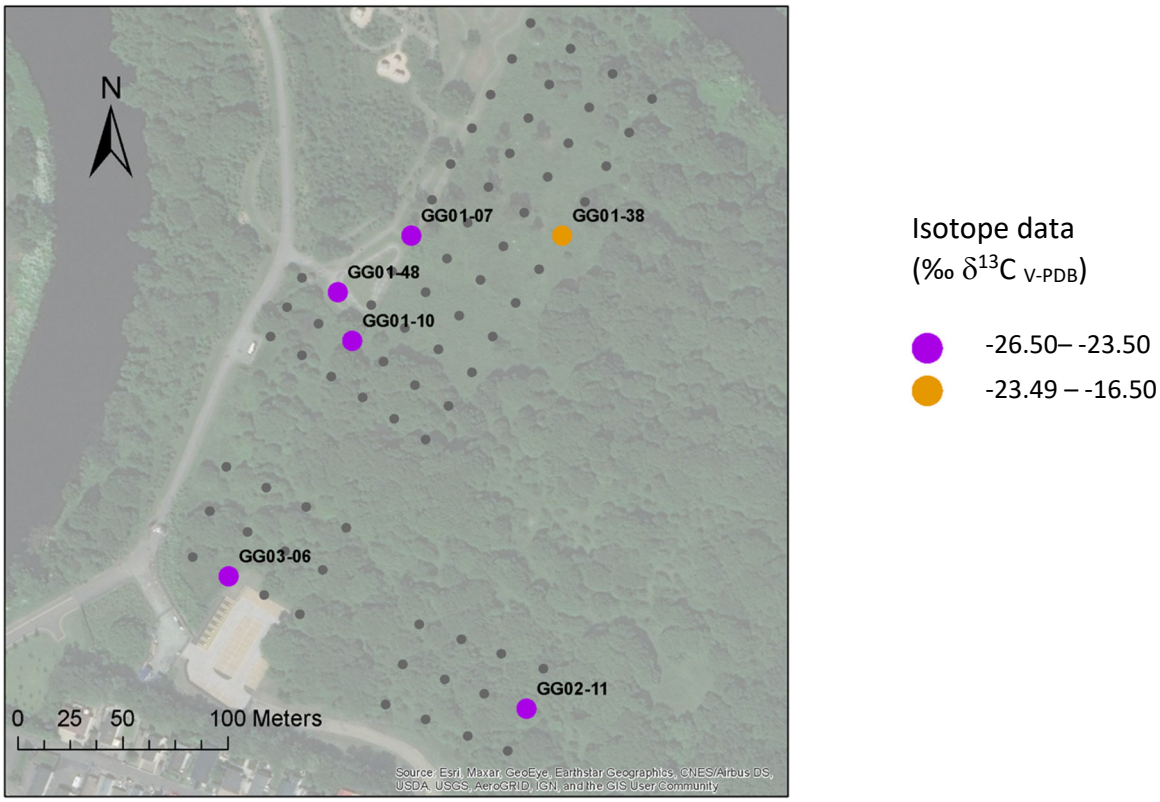

Figure 11 Spatial distribution of the six stable isotope samples. Samples from locations GG01-07 and GG01-48 were taken during the August 2018 campaign and samples GG01-10, GG01-38, GG02-11 and GG03-06 were taken during the May 2019 campaign. The grey circles indicate the position of the sample points. Sources: Esri, DigitalGlobe, GeoEye, i-cubed, USDA FSA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS

4.2 Analysis

4.2.1 CO_2 comparison between sites

Using the ANOVA analysis for each of the campaigns, August 2018, May 2019 and October 2019, *F*-values comparing the ground gas CO_2 concentration data between the four sites were 0.61, 1.74 and 1.79 with corresponding *F*-critical values of 2.75, 2.78 and 2.76 at a 95% level of confidence, respectively. *F* values comparing the CO_2 flux data between the four sites for the three campaigns were 2.67, 2.09 and 0.12 compared with *F*-critical values of 2.74, 2.77 and 2.75 for a 95% level of confidence. This analysis indicates the absence of a statistical difference for the between-site data. Therefore, the measurements for CO_2 concentration and CO_2 flux can be treated as single populations for each of the campaigns from this point, although notable measurements will be highlighted.

4.2.2 CO_2 comparison between campaigns

The ranges of the CO_2 ground gas concentrations across the three campaigns are similar, i.e. 0.1– 12.4% vol for August 2019, 0.4– 17.9% vol for May 2019 and 0.1– 18.0% vol for October 2019, although the latter campaign has a slightly wider spread across the central 50% of the data (**Figure 7**a). The mean and median CO_2 concentrations increase stepwise from August 2018 to October 2019, from 3.3 to 5.1 % vol and medians from 2.6 to 4.9 % vol (**Tables 1**, **2** and **3** and **Figure 12**). One-way ANOVA analysis suggests that there is a statistical difference between the CO_2 concentrations for the campaigns (*F*-value of 5.19 compared with an *F*-critical value of 3.04 for a 95% confidence level) but the post-hoc Tukey-Kramer test, shows that only the August 2018 and October 2019 data are statistically different.

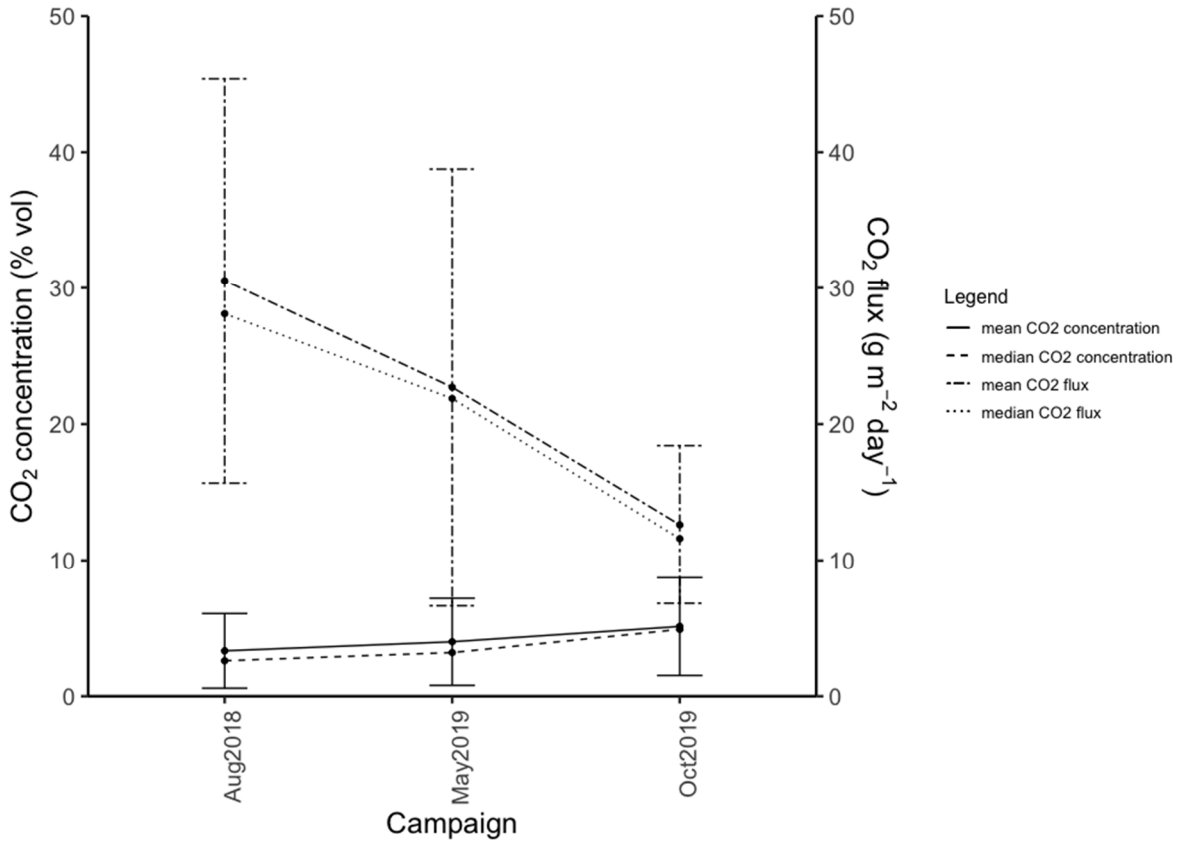

Figure 12 The mean and median CO_2 concentration and flux for the three campaigns. The CO_2 flux data was analysed using the West Systems flux meter equipped with a Li-COR® model LI820 analyser. The CO_2 concentration data was analysed using Geotechnical Instruments GA 5000. The error bars show 1 s.d.

Inversely to the ground gas CO_2 concentrations, the overall mean and median values for CO_2 flux reduce progressively from August 2018 to October 2019 (means 30.5 – 12.6 g m^{-2} day^{-1}; medians 28.1 – 11.6 g m^{-2} day^{-1} (**Figure 7**a and d and **Tables 1**, **2** and **3** and **Figure 12**).

There is some similarity between the upper end of the range of values and the middle 50% of the spread for the CO_2 flux measurements between the first two campaigns with ranges of 10.9 – 81.7 g m^{-2} day^{-1} for August 2018 and -7.2 – 79.0 g m^{-2} day^{-1} for May 2019, but the October 2019 campaign has a tighter spread of measurements, between 3.5 – 35.6 g m^{-2} day^{-1} (**Figure 7**d). Analysis using ANOVA shows that there is a statistically significant difference in the data across the three campaigns for a 95% confidence level with an *F*-value of 33.03 compared with an *F*-critical value of 3.04. Post-hoc Tukey-Kramer analysis shows a statistical significance between each pairing of campaigns.

Although the ground gas and gas flux data does not neatly fit the assumption for ANOVA, that the data is normally distributed, the test does have some tolerance to non-normality (Glass et al., 1972). In addition, all the data that shows a statistical difference does so at the higher 99% confidence level, so it was not considered necessary to interrogate the results from this statistical approach further.

4.2.3 Ground gas

Apart from a small number of measurements, most notably one at GG03-02 of 163 ppm in October 2019 (**Figure 6**), CH_4 concentrations in ground gas were found to be low in all three campaigns with means of 1.9, 1.4 and 4.7 ppm for the August 2018, May 2019 and October 2019 campaigns, respectively. If the one outlying measurement was excluded from the latter campaign, the mean for the October 2019 would be 2.1 ppm with a standard deviation of 1.2 ppm. This is more consistent with other findings, nonetheless the measurement has been retained in the dataset. These results are within the range expected for atmospheric dry air, and do not suggest significant mine gas inputs to the ground gas. It is likely that any CH_4 that had been present has since been oxidised or, if still present in the subsurface, it was trapped beneath an impermeable layer, such as rock, clay, water or waste material, that prevents its migration to the near surface measurement points (Dixon and

Romanak, 2015). Similarly, there was almost no H_2S detected at the Glasgow Observatory over the three campaigns, apart from one value of 38 ppm in October 2019 at GG01-07 (**Figure 6**).

There was some detection of H_2 in ground gas, particularly in May 2019 (**Figure 10**), where the measurements were distributed across the four sites, although Site 2 showed the highest concentration of measurements above 26 ppm. There were only three other measurements in this category, and they were all taken in October 2019 at Sites 1 and 3. Molecular hydrogen is highly prevalent in nature, usually from deep geological processes (Zgonnik, 2020), however, it is unusual to detect molecular hydrogen in soils as it is usually sorbed by the soil or consumed by microorganisms. Anthropogenic sources include the interaction of water with finely ground metal, such as aluminium (Wilson et al., 2010), which is possible given the history of the site. Hydrogen is also produced in the charging of lead acid batteries, used for activities such as haulage in the mining industry, and from the corrosion of other metals, such as magnesium or steel, particularly in acid. At present the provenance of H_2 is uncertain, but although the highest levels of H_2 detected, at 65 and 60 ppm in May and October 2019, respectively, are more than 100 times that of the atmospheric concentration for dry air, they are nearly three orders of magnitude below the lower explosive or flammable limit in air, which is between 5% and 15% (Appleton, 2011; Wilson et al., 2010).

Given that the concentrations of these three 'coal mine gases' (CH_4, H_2S and H_2) were low it is unlikely that their presence in ground gas is due to migration from the former coal mines.

In relation to the stable carbon isotopes of CO_2, $\delta^{13}C_{v\text{-}PDB}$, five of the six sample values range from -23.59 to -26.31‰ $\delta^{13}C_{v\text{-}PDB}$, consistent with the values for soil respired CO_2 (Flude et al., 2017). The apparent outlier, -16.76‰ $\delta^{13}C_{v\text{-}PDB}$ for GG01-38 in May 2019 (**Figure 6**), is still consistent with background soil CO_2 measurements for Carbon Capture and Storage (CCS) pilot sites according to the index developed by Flude. Interpretation of carbon isotope analysis can cause confusion when viewed in isolation due to the overlap between $\delta^{13}C_{v\text{-}PDB}$ signatures (Flude et al., 2017). This is highlighted by Dixon and Romanak (2015), particularly

in respect of the confusion at Weyburn. Therefore, the results from the Glasgow Observatory samples were used in conjunction with other evidence, particularly as the original isotopic signature (e.g. of mine gas) is not known.

All three campaigns exhibit a wide range of O_2 measurements, although they have similar mean values, albeit declining chronologically (**Figure 7**c). The comparable spread of the data across the campaigns is also confirmed by the size of the standard deviations, ranging from 3.6% vol to 4.2% vol. Most of the low ground gas O_2 concentrations (less than 10% vol) occur at Site 1. This indicates that Site 1 is the most active area in terms of oxidation, which is borne out by the CO_2 concentration data. The exception is one measurement of O_2 at GG03-02 in August 2018 (**Figure 6**), which was 8.7% vol, where the highest CH_4 measurement was obtained.

Tables 1, **2** and **3** and **Figure 13** also show that the balance of the unaccounted ground gas (proxy N_2) concentration ranges and means are similar for the three surveys. The mean values were slightly above atmospheric concentration of N_2 for dry air.

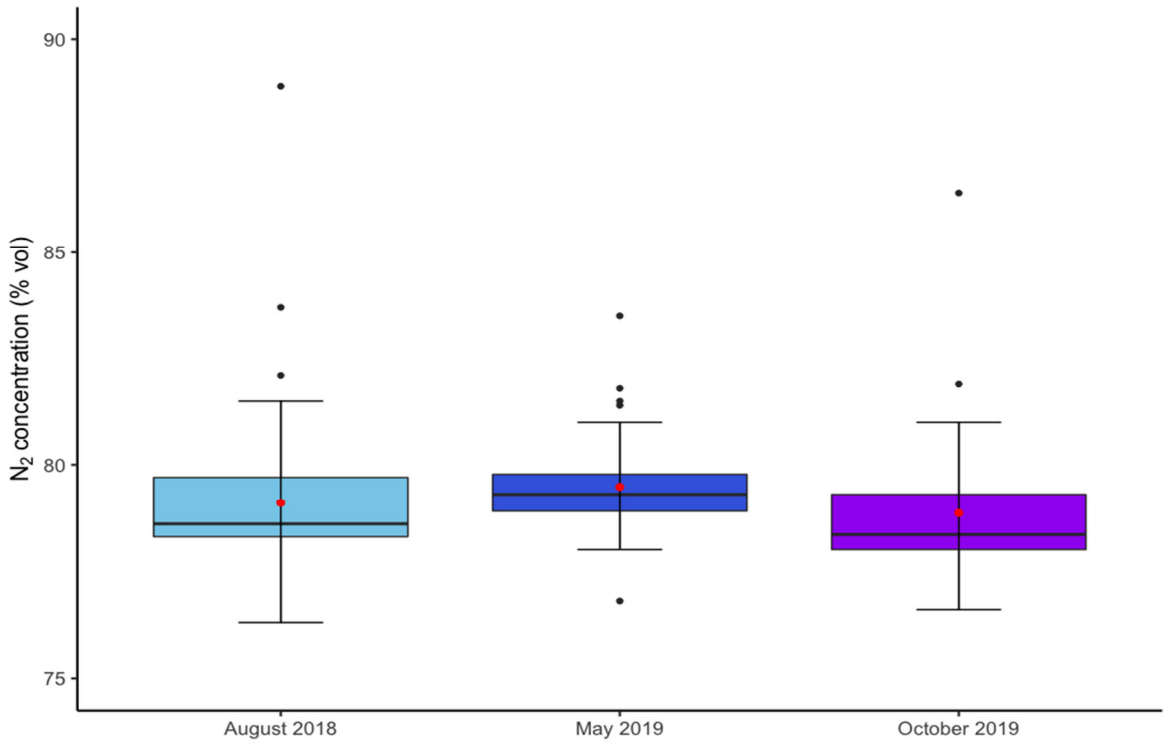

Figure 13 Boxplot comparing the range of baseline observations for August 2018, May and October 2019 for N_2. The red point shows the mean of each set of observations, the black horizontal line shows the median value, the black points show outlier observations and the whiskers represent 1.5 times the standard deviation. The N_2 concentrations were analysed by the GA5000 gas analyser.

One location of note is GG01-48, one of the more westerly locations in Site 1, next to the bicycle track (**Figure 4** and **Figure 6**). This location consistently saw the highest ground gas N_2 concentration for each of the campaigns: 88.9% vol for August 2018, 83.5% vol for May 2019 and 86.4% vol for October 2019. This is coupled with low O_2 concentrations, 12.9 and 7.0% vol for May and October 2019, respectively, and very low O_2, 0.9% vol, in the August 2018 campaign. The CO_2 concentrations at this point were 10.2%, 3.3% and 7.3% for the August 2018, May and October 2019 campaigns, respectively. Stable isotope analysis of the sample from this location suggests that the CO_2 is of biological origin (-26.31‰ $\delta^{13}C_{V\text{-}PDB}$). The presence of CO_2, low O_2 and a high proportion of N_2 may indicate that oxidation of CH_4 is occurring at this point. Another hypothesis is that denitrification, under anoxic conditions, is occurring as this is an acceptable alternative to sustain microbial metabolic processes, where oxygen is in short supply, (Castaldi, 2000; Beaubien et al., 2015 and Chapin et al., 2012). As a result, elevated levels of N_2 would be observed in these areas, particularly if the gas was not able to escape. However, there is a greater degree of uncertainty in the N_2 values because its presence is inferred from the balance after other major gases are accounted for. It is possible this assumption does not hold for such a complex site, and that other gases could be present.

The three adjacent point measurements (**Figure 4**) do not register the same high levels of N_2 or consistently low levels of O_2. Although 10.3% vol O_2 and 8.2% vol CO_2 were recorded at GG01-09, to the east of GG01-48, in August 2018 and 9.3% vol O_2 and 9.8% CO_2 at GG01-45, to the west of GG01-48, in October 2019. Therefore, it seems that location GG01-48 is an isolated anomaly and it should be investigated further in future surveys.

4.2.4 Gas flux

For the majority of measurements, CH_4 flux was below the limit of detection. This is consistent with low CH_4 concentrations in the shallow subsurface, it suggests that there is very little CH_4 actively migrating from depth.

Apart from the trends referred to in Section 4.2.2, there were no CO_2 flux measurements of note. Some of the individual measurements for CO_2 flux are discussed below where they help describe processes in specific locations.

4.2.5 Process-based analysis

Applying Dixon and Romanak's (2015) process-based analyses to the Glasgow Observatory data indicates that the detected CO_2 was predominantly biological in origin (**Figure 14**). However, there are also a number of instances where the values are just to the right of the biological respiration guideline, particularly in August 2018 and October 2019 (**Figure 14**a and g). Romanak et al. (2012) state that this is an indication of an external source of CO_2 or oxidised methane, however, they also acknowledge that an accuracy of ± 2% can have a significant effect on the datapoints, particularly when the O_2 values are above 18%, and therefore this analysis should be used in conjunction with the other two methods. The use of the relationship between the N_2/O_2 ratio and CO_2 potentially dilutes the effect of higher N_2, particularly if O_2 is close to atmospheric concentrations, so that only more pronounced effects are displayed outside of the respiration and oxidation lines. This plot seems to confirm that the CO_2 is predominantly biological in origin and does not indicate any exogenous input of CO_2 or significant CO_2 dissolution (**Figure 14**b, e and h).

On the CO_2 vs O_2 plot there is only one datapoint that is clearly to the left of the methane oxidation line (**Figure 14**d), indicating CO_2 dissolution (Dixon and Romanak, 2015). This occurred at location GG01-48 in May 2019, discussed above (section 4.2.3 and **Figure 6**). CO_2 dissolution would also be inferred based on the higher-than-atmospheric N_2 data at this location (Romanak et al., 2012), see **Figure 14**c, f and i), although it would be expected to see this as part of a more general trend either across several points or campaigns. However, as stated, the N_2/O_2 vs CO_2 plot does not indicate CO_2 dissolution but suggests that there is some oxidation of CH_4 occurring at GG01-48 as all three datapoints are either on or just over the CH_4 oxidation (**Figure 14**b, e and h). It may be that both these processes are occurring at this point, alternatively these explanations may not be suitable as a significant proportion of the total gas is CO_2 and O_2 levels are low, particularly in August 2018 and other gases, not detectable with the current instruments, may be present.

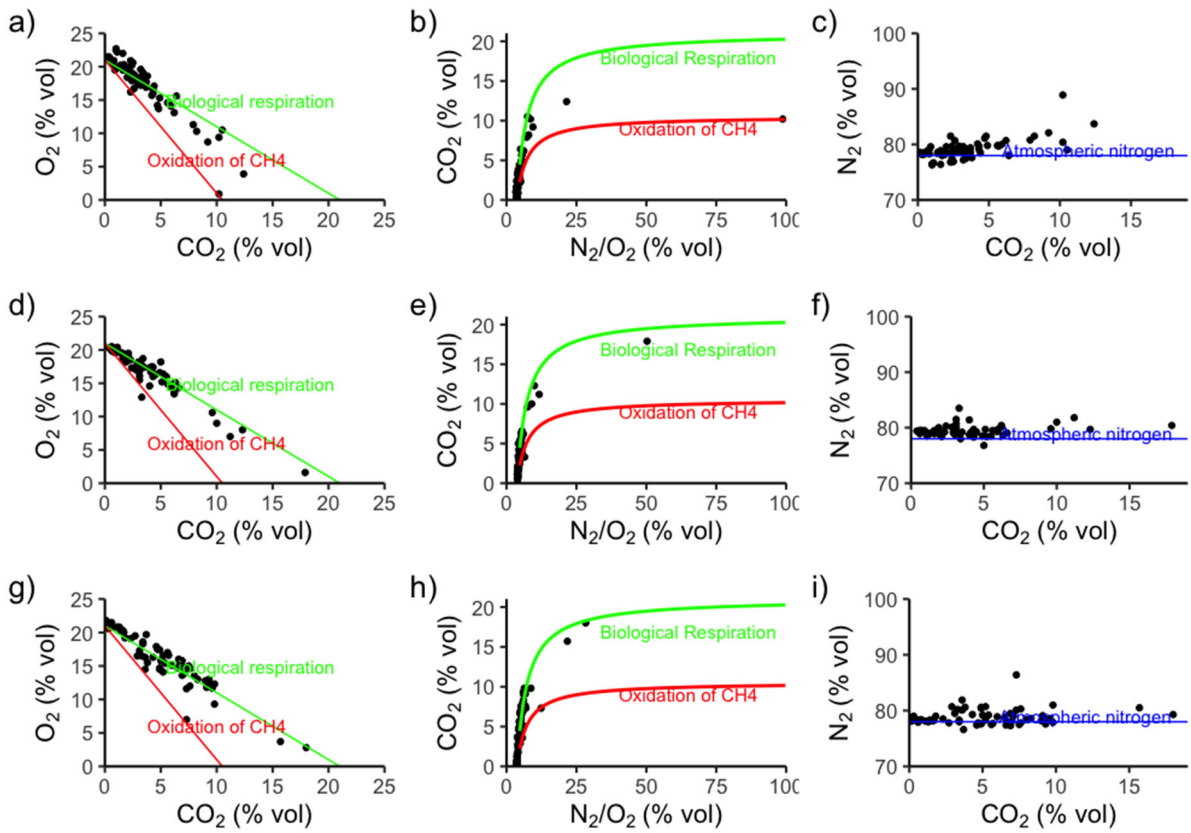

Figure 14 Comparison of the August 2018 (plots a), b) and c)), May 2019 (plots d), e) and f)) and October 2019 (plots g), h), i)) data using the visualisation developed by Romanak et al. (2012) to characterise the sources of the ground gas. The green and red lines in plots a), b), d), e), g) and h) reflect the reaction stoichiometry relating to biological respiration and oxidation of methane, respectively. All measurements were taken using the GA 5000. See **Figure 5** for further explanation of the data visualisation.

5 Discussion

5.1 Background gas data – overall indications and comparisons with other sites

The data obtained for the Glasgow Observatory strongly suggest that the detected CO_2 is from biogenic sources and is consistent with other background gas data based upon land use, seasonal patterns, weather fluctuations and geography, as shown in the following sections.

5.1.1 Land use

Previous studies have looked at the role of land use. At a large-scale carbon capture project in Decatur, Illinois, Carman et al. (2014) tested the difference between CO_2 flux from bare

ground, where natural processes had been inhibited by the addition of herbicide, and that from natural ground, where plants and microorganisms were left unfettered. They found that from 2009 to 2013 the latter consistently produced, on average, more than twice the levels of flux over the course of the year and the annual mean difference between the treatments ranged from 2.7 to 13.7 g m^{-2} d^{-1}. The summer flux levels at the Glasgow Observatory are slightly higher than at Decatur but this is probably due to the increased levels of vegetation at Glasgow, particularly as 70% of the data at Decatur came from bare ground measurements.

The question of whether land use affects background gas measurements was also considered by a study in Hobe, Denmark (Jones et al., 2014; Beaubien et al., 2015). It was found that three land uses, cultivated, heath and forest, did not seem to have an impact on CO_2 flux, which averaged about 15 g m^{-2} d^{-1} for May 2012 with measurements up to 75 g m^{-2} d^{-1}; similar to values recorded at Glasgow. There was, however, an observed difference in the CO_2 concentrations, which were higher for the cultivated and heath sites, indicating that overall CO_2 production was higher for these land uses. It was hypothesised that the lower concentrations for the forest were due to the lower soil temperatures caused by the shade of the trees. The overall mean CO_2 concentration was between 1 – 1.5% vol but the cultivated site recorded concentrations of about 6% vol by the end of summer, which is typical of soils in temperate zones, particularly if CO_2 production is aided by fertilisers stimulating the biological processes.

In terms of a site with a more industrial history, Li et al. (2020) reported on CO_2 flux from a sealed landfill site in Beijing in which they studied seasonal fluctuations in the transfer of gases and identified hotspots for the escape of the gases. The CO_2 flux data at the Glasgow Observatory is lower than the mean at the non-hotspot and intermediate sites, which included winter data, and significantly below the hotspot measurements.

5.1.2 Seasonal pattern and weather

Seasonal CO_2 concentration and CO_2 flux measurements at the Glasgow Observatory appear to have an inverse relationship (**Figure 12**). An explanation for this is that escaping CO_2,

creating the flux, cannot also accumulate to produce a high concentration. However, this does not match observations in other studies. At Kirby Misperton and Preston New Road (UK), Decatur (USA), the non-hotspots in Beijing and most markedly at Weyburn (Canada), overall CO_2 levels, both as flux and ground gas concentration, were at their highest in summer, followed by spring and then autumn with almost no detectable flux, if it was measured, during winter (Ward et al., 2019; Carmen et al., 2014; Li et al., 2020 and Beaubien et al., 2013). The CO_2 flux measurements at the Glasgow Observatory were consistent with these observations, and at other UK sites (see below, Jones et al., 2014), but the CO_2 concentration were not, increasing over the three seasonal campaigns.

The reason for the apparent inconsistency may be that CO_2 flux and ground gas concentration are often decoupled (Beaubien et al., 2015; Jones et al., 2014). The dissociation between different manifestations of CO_2 is due to biological CO_2 production at different depths. Biological processes are predominantly located in the top 2.5 cm of the soil and do not significantly affect accumulation at depth (Risk et al., 2002). If the pathways to the surface exist, this leads to higher CO_2 flux. If they are impeded, usually by precipitation, then the deeper, relatively weaker, biological CO_2 production will accumulate due to its inability to escape, as seen at Kirby Misperton (Maier, 2010; Ward et al., 2019). These factors must therefore be overlain on seasonal fluctuations, where it would be expected that biogenic CO_2 is at its highest when there is more metabolic activity.

This more intricate situation is seen at the Glasgow Observatory when the point measurements for CO_2 concentration and flux are compared (see **Figures 8** and **9**). In August 2018, three out of four of the highest concentrations coincided with medium flux levels. Additionally, most instances of medium to high concentration and flux are found in specific localities: the north and northwest edge of Site 1, northwest and southwest edges of Site 2 and southeast edge of Site 5. This indicates that total CO_2 is higher in these areas. In May 2019 the higher CO_2 values are generally to the northeast side of Site 1 and there is one location (GG01-29) that has both a high CO_2 concentration and flux (**Figure 6**). Overall CO_2 is less pronounced at Site 2 and 5. Finally, in October 2019 the highest CO_2 concentrations are again in Site 1 with more modest levels at Sites 2, 3 and 5. In this campaign, CO_2 flux is in the lowest category (less than 18.69 g m^{-2} d^{-1}) in all but seven out of

the 59 measurements reflecting the difficulty CO_2 has of escaping the sub-surface, probably due to the soil water content or some other physical barrier (**Figure 9**).

The Met Office weather data (2019) for Glasgow provides further context to the overall CO_2 flux and concentration levels at the Observatory (**Figure 15**). It shows that August 2018 experienced higher temperatures than May and October2019, creating conditions for higher levels of respiration. Incidentally, May 2019 experienced the most hours of sun, 193.2 compared with 110.6 for August 2018 and 106.4 for October 2019, and therefore may have experienced the most consistent conditions for higher levels of respiration. This could mitigate the potential difference in biological CO_2 production between summer and spring, indicating why the difference in overall CO_2 is not larger.

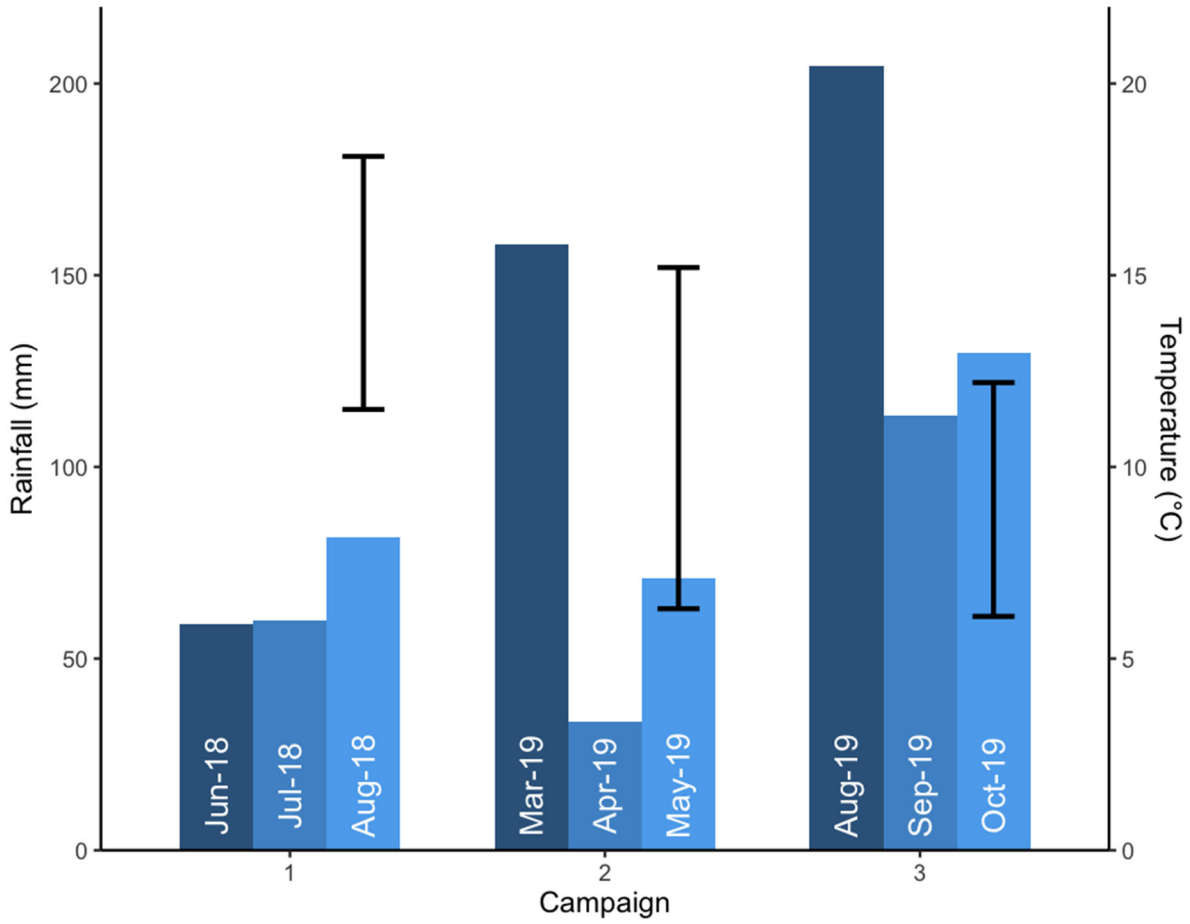

Figure 15 Rainfall data (blue bars) and temperature range (black lines) for the month of each campaign. The rainfall data for each of the two proceeding months is also shown (Met Office, 2019).

It is suggested that precipitation has more impact on short-term biological CO_2 flux and concentrations than soil temperature because of its wider variability (Tarakki et al., 2018; Beaubien et al., 2013). This is particularly true at shallower depths, although changes in CO_2 concentration have also been seen at depths of 85 cm (Maier et al., 2010). This corresponds to some extent with the findings of Carman et al. (2014). They observed that flux was inhibited by soil moisture levels above saturation level or below wilting point and that as soil moisture content reduced after heavy precipitation, flux levels significantly increased. However, outside these confines Carman et al. (2014) found that soil temperature correlated more closely with flux levels. This indicates that the relationship between temperature, precipitation, biogenic CO_2 production and CO_2 expression is complex. For instance, there is a moisture level sweet spot, where precipitation is not too high to create anoxic conditions or prevent any CO_2 from escaping and not too low to prevent biological activity. In Glasgow there does not seem to be a great variation in the rainfall between August 2018 and May 2019 (**Figure 15**), however, October 2019 experienced significantly more rainfall potentially preventing some biological activity and creating a barrier to CO_2 flux. In addition, there is a hysteretic effect on metabolic activity and CO_2 expression, so that preceding moisture availability, coupled with temperatures, affects the abundance of living matter, the soil's ability to absorb additional moisture and the ease with which gas can escape. October 2019 is most impacted by previous rainfall (**Figure 15**) and, as expected, the hysteretic effects on soil moisture are most apparent in the third campaign.

The difference in the seasonal weather is reflected statistically in the CO_2 data with the greatest statistical difference in CO_2 flux and the only statistical difference in CO_2 concentration arising between the August 2018 and October 2019 campaigns. The statistical difference between the CO_2 flux was smaller between the May and October 2019 campaigns, with the smallest difference between the August 2018 and May 2019 surveys. With only one set of measurements for each season the results from the three campaigns can only be suggestive of the general seasonal pattern, although they are consistent with seasonal findings elsewhere, particularly when precipitation levels leading to impermeable soils are taken into account (Beaubien et al., 2013; Carman et al., 2014; Jones et al., 2014 and Li et al., 2020). This indicates that the most likely significant factors affecting the

localised concentration and expression of background CO_2 is aggregate seasonal CO_2 production and the availability of CO_2 migration pathways.

5.1.3 Geography – other UK sites

Finally, taking into account land use and seasonality the results at the Glasgow Observatory are consistent with three other UK sites: ASGARD, Nottingham; Kirby Misperton, north-east England; and Preston New Road, north-west England (Jones et al., 2014; Ward et al., 2019). **Figure 16** demonstrates the similarity of Glasgow's results with the other sites; most notably the consistency of the seasonal pattern of CO_2 flux measurements with Kirby Misperton.

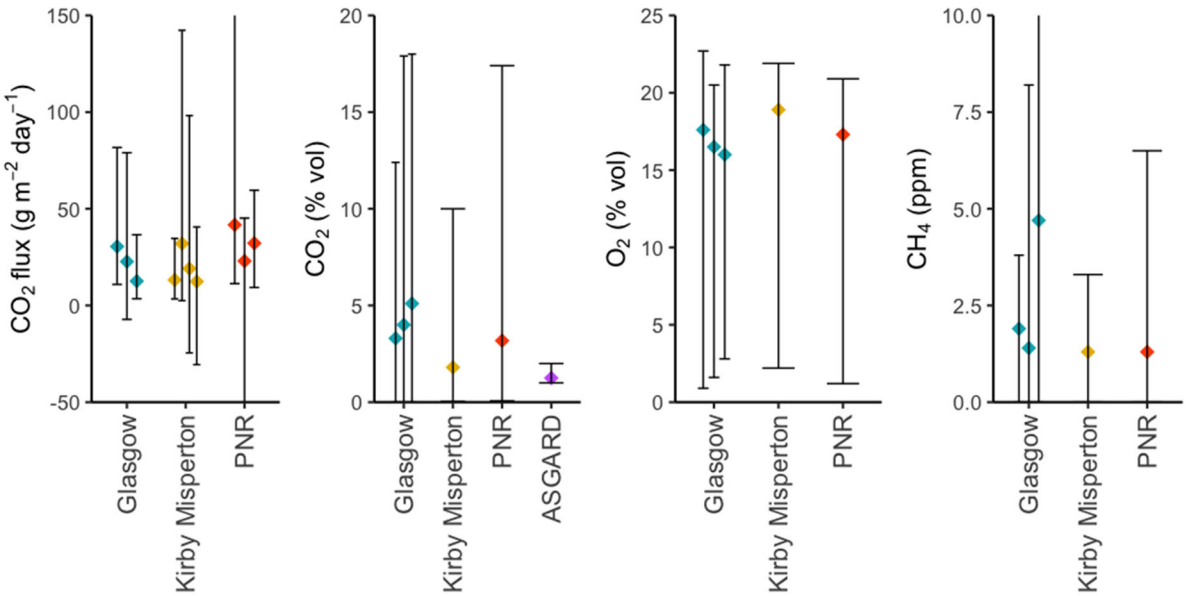

Figure 16 Comparing the three Glasgow campaigns with other UK sites. Black lines display the reported ranges and the coloured diamond indicate the mean values. CO2 flux can be negative if the net transfer is from the atmosphere to the soil. Where the 't' bars are not visible then the range is outside of the plot. Measurements at Kirby Misperton and Preston New Road (PNR) were taken over multiple campaigns (Ward et al., 2019). For Kirby Misperton they were in November 2015, June, August and October 2016 and for Preston New Road they were in August 2015, September 2016 and September 2018, however, the measurements for CO_2, O_2 and CH_4 concentrations at both Kirby Misperton and Preston New Road (PNR) sites were reported as compiled data across the surveys.

As the other three sites were all pastures, it may be expected that they would display higher overall levels of CO_2 but what is most notable is that the measurements at the Glasgow Observatory are unremarkable considering the complex site history. The only result that is incongruous is CH_4 for the October 2019 at Glasgow, that has already been discussed. A

caveat to this is that there are limitations to the grid sampling method in relation to detecting hot spots and more mobile surveys, such as using a quad bike or cart, would be beneficial in this respect (see Barkwith et al., 2020a). However, site conditions prevented the use of the ground-based, mobile, continuous sampling methods and it was necessary to use a sampling grid that balanced the proximity of sampling points but still covered a meaningful area.

5.2 Background gas vs Process-based approach

The above results demonstrate that background gas techniques are relevant and useful in a novel setting, both in terms of their applicability to shallow geothermal investigations and at sites with a complex industrial history. However, as seen, the results must be interpreted in the context of factors including land use, seasonal patterns and weather; although, in relation to the seasonal patterns, autumn campaigns are generally preferred to reduce the biological noise (Beaubien et al., 2013; Ward et al., 2019). The background gas approach provides the most comprehensive representation of the ground gas landscape as it allows investigators to document a wider range of relevant gases than the four that are the focus of the process-based approach. In this respect, better understanding of the occurrence and causes of the less prevalent gases, such as H_2, is needed for a more thorough understanding of the gas environment.

Collecting data for a background survey is a ceaseless task, particularly when set against a shifting backdrop of local and global environmental changes. These surveys can be labour intensive, although compared with other monitoring techniques, ground gas and flux measurement costs are relatively inexpensive. As the process-based approach analyses relative gas concentrations it is less affected by environmental change. It is an attractive alternative as it requires fewer resources and bases its analysis on scientific principles. However, each background gas survey, with its absolute measurements, assists in increasing understanding of the developing global gas landscape and adds to the catalogue of reference sites. This is particularly pertinent for subsurface activities below industrial sites as there seems to be very few comparable published studies. The surveys also provide a degree of reassurance to local communities through their visibility and by providing

confirmation that there is a safety net with regard to detecting any anomalies (Jenkins et al., 2015).

The current work shows the process-based approach can easily be incorporated into a background gas study, so that the benefits can be employed alongside a more comprehensive view. However, even using the process-based tools it has been difficult to characterise the anomaly at GG01-48. This is because this analysis does not provide clear indications when there are two or more processes occurring simultaneously and it may be that it does not account for all the processes that can affect the results. Care also needs to be taken with the process-based approach as instrument accuracy or lack of sensitivity at low CO_2 concentrations can affect the environmental characterisation, a common occurrence during background surveys where scientists are trying to identify pre-existing anomalies amongst the general background gas landscape. Instrument-based anomalies are more likely to be detected in repeated background gas surveys. The process-based approach seems to provide more effective results in relation to attribution where there is a clear signal, but the source is uncertain. As such, it is a useful tool in relation to CO_2 storage, where Dixon and Romanak (2015) assert anomalous gas should be attributed to a leakage before quantification and reporting.

In some circumstances a background gas survey is required before subsurface work can commence, however, it seems valuable and prudent to perform a background gas study in novel situations or where there is likely to be a complex history of land use. Both novelty and complexity are present at the Glasgow Observatory.

5.3 Future gas surveys

This background gas survey data will now be used as a comparison for results from future gas surveys, including from an installation that will provide continuous monitoring for part of the site. The continuous monitoring will include ground temperature measurements, which have currently been inferred from local weather reports, allowing for a more accurate understanding of the conditions for biological activity. If a wide range of variables continues to be monitored, it is likely that one of the elements will display an unusual result and so it

is sensible to refine the array of variables measured to the ones that are most likely to identify consequences from the investigations into low enthalpy heat from the mine workings. In this respect it may be possible to adapt the signal to noise ratio (SNR) technique employed to make the measurement, monitoring and verification (MMV) of CO_2 storage more robust (Risk et al., 2013; Nickerson and Risk, 2013 and Risk et al., 2015). In this setting the technique is used when the signature of the injected gas is known, however, it can be adapted so that the post-operational measurements can be compared with background gas measurements. From the results at the Observatory, it is apparent that the most consistently similar means and distribution are the N_2 measurements, potentially providing the clearest signal to noise ratio, although issues may arise because they are proxy measurements.

6 Conclusions

Background ground gas and gas flux surveys were employed in three campaigns, undertaken in three different seasons, across four sites as part of establishing an environmental baseline at a geoenergy observatory for mine water heat in Glasgow, UK. The research infrastructure is located at a site with complex former land use but as there was no statistical difference in the results between the sites, each campaign was treated as a single sample.

Overall, the results showed some seasonal fluctuations but background gas characteristics were consistent with a biogenic origin and were typical when compared with other sites taking into account land use, seasonal fluctuations and geography. Considering the historical industrial uses of the site the results were unremarkable with only one anomaly for CH_4, some sample points of interest for future campaigns, particularly GG01-48, and several elevated measurements of H_2, albeit well below the explosive limit. This highlighted the lack of published studies about H_2 in the shallow subsurface at former industrial sites that would improve our understanding of potential H_2 sources detected in this work. There was some evidence of oxidation of CH_4, particularly at Site 1, but low values of mine gases, CH_4, H_2S and H_2, indicate it was unlikely that the mine workings were a significant source of CH_4.

In addition to contributing to the catalogue of background environmental evidence, particularly of sites with substantial anthropogenic land-use, the survey results also illuminate the benefits and short-comings of the baseline and process-based approaches. Although the process-based method did assist in characterising the gas origin, and indicated that the CO_2 was biogenic, it did not replace the benefits of a background gas surveys, which enabled a more detailed picture. There were limitations with the process-based approach in relation to determining the origin of gas when there was not a clear signal and when there were potentially more than one process occurring simultaneously. The techniques used in background gas surveys are relevant for the exploration of low-enthalpy, shallow geothermal energy and it seems prudent to utilise them in novel situations, either due to the innovative technologies involved or the complexity of the subsurface environment.

Using an adaption of the SNR technique in future post-operational analysis may assist in distinguishing true anomalies from the normal background variations in data.

7 Data Availability

Further details about the data release for the three campaigns are contained in Barkwith et al. (2020b) and the data can be found at National Geoscience Data Centre (2021) or using https://doi.org/10.5285/2f98e806-1713-4ac9-8c91-bbf8e1a5ee7d. All data relating to the UKGEOS observatories can be found at https://ukgeos.ac.uk.

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10 Appendix A – Instrument specifications

Instrument	Gas	Measurement range	Accuracy
GA 5000	CH_4 concentration	0-100%	0-70% : ±0.5% (vol), 70-100% : ±1.5% (vol)
	CO_2 concentration	0-100%	0-60% : ±0.5% (vol), 60-100% : ±1.5% (vol)
	O_2 concentration	0-25%	0-25% : ±1.0% (vol)
	H_2S concentration	0-1,000 ppm	±2.0% FS
	H_2 concentration	0-1,000 ppm	±2.5% FS
Laser One	CH_4 concentration	1-10,000 ppm	+/-0.7ppm for [1: 10ppm] +/-10% relative up to 10,000
Li-COR® model LI820 analyser	CO_2 flux	0 – 20000 ppm with 5 cm optical bench	4% of reading with 5 cm bench

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