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Field-scale evaluation of collection methods for dissolved methane samples in groundwaters

Environmental Change, Adaptation and Resilience Programme
Open Report OR/22/035



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ENVIRONMENTAL CHANGE, ADAPTATION AND RESILIENCE
PROGRAMME

OPEN REPORT OR/22/035

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Field-scale evaluation of collection methods for dissolved methane samples in groundwaters

M J Bowes¹, M O Rivett² & R A Bell³

Contributors:

S Loveless⁴, W G Darling¹, D Ashton⁴, G Edwards⁴, J Hookey⁴,
S Scott⁴, P L Smedley¹, S Smith⁴ & R S Ward¹

Reviewed by:

B É Ó Dochartaigh¹

¹British Geological Survey

²GroundH2O Plus Ltd.

³Formerly British Geological Survey

⁴Environment Agency

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British Geological Survey offices

**Nicker Hill, Keyworth,
Nottingham NG12 5GG**

Tel 0115 936 3100

BGS Central Enquiries Desk

Tel 0115 936 3143

email enquiries@bgs.ac.uk

BGS Sales

Tel 0115 936 3241

email sales@bgs.ac.uk

**The Lyell Centre, Research Avenue South,
Edinburgh EH14 4AP**

Tel 0131 667 1000

email scotsales@bgs.ac.uk

**Natural History Museum, Cromwell Road,
London SW7 5BD**

Tel 020 7589 4090

Tel 020 7942 5344/45

email bglondon@bgs.ac.uk

**Cardiff University, Main Building, Park Place,
Cardiff CF10 3AT**

Tel 029 2167 4280

**Maclean Building, Crowmarsh Gifford,
Wallingford OX10 8BB**

Tel 01491 838800

**Geological Survey of Northern Ireland, Department of
Enterprise, Trade & Investment, Dundonald House,
Upper Newtownards Road, Ballymiscaw,
Belfast, BT4 3SB**

Tel 01232 666595

www.bgs.ac.uk/gsni/

**Natural Environment Research Council, Polaris House,
North Star Avenue, Swindon SN2 1EU**

Tel 01793 411500

Fax 01793 411501

www.nerc.ac.uk

**UK Research and Innovation, Polaris House,
Swindon SN2 1FL**

Tel 01793 444000

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Executive Summary

This report presents the findings of a jointly funded project by the British Geological Survey (BGS) and Environment Agency (EA project SC210014) that addresses some of the research needs identified in the EA project SC190007 “Methods for sampling and analysing methane in groundwater: a review of current research and best practice”. Primary field sampling allowed comparison of sample collection techniques for dissolved methane in groundwaters, to provide a field evidence base to help establish good practice guidelines (or protocols). This included evaluation of purging protocols, groundwater sampling devices, surface collection protocols, and the influence of methane concentration.

The field study used two boreholes previously shown to have groundwater of contrasting low methane concentration (~1mg/l) ‘Site A’, and high methane concentration (~25 mg/l) ‘Site B’ in close proximity in the Vale of Pickering. The boreholes were previously used for hydrochemical baseline monitoring and were similar in construction and hydrogeological setting, each having shallow (~ 1 m depth) water table and a conventional 3-m long well screen sampling a fractured Kimmeridge Clay unit with methane naturally present from elevated organic matter contents. A stage 1 zero-purge passive sampling device was used to obtain initial samples, followed by a low-flow methodology with parallel use of submersible, bladder and peristaltic pumped samples, with stage 2 sampled after purging a single screen volume, and stage 3 sampled after purging to hydrochemical parameter stabilisation over 5.7 – 7.5 pumped screen volumes. Finally, a post-purge stage 4 sample was obtained with the same passive sampling device. Sample collection protocols tested were open (direct fill vial), semi-closed inverted (submerged-inverted vial), semi-closed upright (submerged-upright vial) and closed (double valve cylinder closed to atmosphere). All samples were obtained in triplicate from each pump during stages 2 and 3, but in stages 1 and 4 only open samples were possible from the passive sampling device. Data interpretation was supported by logged hydrochemical borehole groundwater depth profiles before and after the sampling programme, and by the historical methane baseline record.

Methane concentrations measured at Site A are challenging to interpret: they are highly sensitive to purging volume, with a decrease in mean concentration of 72% over the purging stages. This, and the time required to obtain multiple samples, obscured specific sensitivity of methane concentration to pump and sample collection protocol variables at Site A. Although the differences in concentrations seen between pumps and between collection protocol are not statistically significant, the high variability in Site A data overall, 52-117% relative standard deviation (RSD), mean these data are generally not useful for developing good practice proposals.

Site B, with high methane concentration, provided more consistent data that allowed meaningful comparisons of methane sensitivity between purging volume, pump type and collection methods with findings that are generally consistent with existing literature. Methane concentrations had a lower sensitivity to purging than at Site A (21% mean concentration declines with ~30 % RSD). Most of the conclusions made from Site B data can reasonably be expected to also apply to sites with lower concentrations.

In isolation, pump selection - bladder, submersible or peristaltic pump - makes little difference to sampled methane concentrations. The Hydasleeve™ passive sampler consistently produced the lowest concentrations, but is very likely to have sampled different water in the borehole to that sampled mid-screen by the active pumps. However, bladder and peristaltic pump closed samples yield higher concentrations, which is attributed to their capacity to provide increased pressure at low flow, thereby reducing degassing potential. The bladder pump is preferred for this use, due to its lower closed sample concentration variability, which is attributed to the controllability of the bladder pump pressure. The peristaltic pump was tested under favourable shallow water table conditions, and a negative concentration bias that is generally expected from suction pressure was not evident, but this is acknowledged as a concern, especially for deeper water tables, where its use may need more caution.

Closed sampling at Site B consistently yielded the highest methane concentrations across all pumps with lowest variability, and is the recommended sample collection protocol. Commercial availability of closed sample analysis is, however, limited. The semi-closed (inverted and upright) methods yielded intermediate concentrations between closed and passive samples, with inverted methods generally giving higher concentrations than semi-closed. When using the inverted protocol, exsolving gas headspace accumulation leads to uncertainties in concentration measurements, meaning that the semi-closed upright protocol is often preferred, especially where degassing is evident or expected although results in this study do not directly support this. Open samples consistently produced the lowest concentrations and should only be used where other protocols are impractical, e.g. sampling from a non-pumped collection device. Switching protocols from open sampling to upright sampling requires minimal investment, and is likely to produce more robust concentration data and/or reduced variability, although results from this study do not provide undisputable evidence of this.

The observed sensitivities of measured methane concentrations to different parts of the sampling methodology underline the central importance of using an identical protocol with specific pumps, similar deployments, identical purging volumes or stabilisation criteria, and specific sample collection protocol, in order to generate robust temporal records. Reliable cross comparison of data produced by different organisations requires sampling protocols to be as identical as possible. Any protocol change should be done using an overlap period in which both old and new protocols are used simultaneously, to prevent a sampling-related step change in data.

This study also indicates that extended purging of any borehole leads to lower concentration samples over time, which critically has the potential to underestimate methane risk.

Combining the findings of this study and wider literature reviewed under EA project SC190007, a concise 'lookup' sheet is presented as a non-prescriptive aid to assist practitioners in 'Groundwater methane sampling protocol development'. It covers: site selection, pump/sampler selection/deployment, supporting reconnaissance measurements, sample collection and protocol, data management and wider use.

Finally, outstanding field research needs are indicated. The foremost of these is comparative field testing of down-hole devices for obtaining closed system samples at in-situ groundwater pressure.

1 Introduction

1.1 BACKGROUND

Reliable and accurate measurement of methane concentration in groundwater is key to understanding the fate and transport of this dissolved gas. Accurate quantification of methane fluxes throughout the environment is important due to its potency as a greenhouse gas and due to explosion risks. Robust data are required to assess *in-situ* controlling processes, assess spatial trends (e.g. national baselines), demonstrate regulatory compliance (e.g. of anthropogenic activities including landfill and hydrocarbon extraction monitoring), and to enable management of any risks posed. Monitoring of methane in the sub-surface will be vital in developing industries such as mine water geothermal and the re-purposing of former hydrocarbon reservoirs (e.g. hydrogen and CO₂ storage). Methane sampling undertaken by different organisations and operators needs to be reproducible and comparable across all these activities.

To reliably evaluate groundwater methane concentration records and discern trends and baseline conditions, establishing the degree to which observed methane variability is an artefact of sampling and analysis techniques is important. This may be related to different techniques used to sample groundwater (different pumps and sampling protocols), or, for a specific technique, variable implementation by different personnel or organisations involved, or different laboratory analysis procedures. It is essential to differentiate ‘real’ observed changes in concentration over time - those reflecting true variations in monitored groundwater methane concentration because of changing methane source inputs or fate and transport in groundwater – from those that are artefacts of sampling and analysis techniques.

A recent review carried out by the BGS in collaboration with the Environment Agency, covering both methane sampling and analysis practice and the international literature (EA 2021), identified large uncertainties that may be associated with sampling and analysis practices. This study recognises that there may be further scope for assessing the uncertainties related to methane analysis in different laboratories, but concludes that the greatest uncertainties are associated with field sampling procedures, which are often unknown or at best poorly constrained compared to those related to laboratory analysis. There are no established UK-wide protocols and no formal best practice guidance for methane sampling in groundwater in the UK, and in consequence a range of measurement practices has been adopted by practitioners. A key concern is methane’s high volatility, and the inappropriate use of sampling procedures routinely used for other chemical determinants that fail to consider volatility losses. Methane losses during sampling or analysis may cause negative bias in measured methane concentrations, leading to underestimation of risks.

1.2 AIMS AND OBJECTIVES

The project aims were to:

- better understand sources of uncertainty associated with typical protocols used by practitioners to sample monitoring wells (boreholes) for dissolved methane in groundwater; and,
- develop accessible decision-making resources for practitioners, enabling good practice.

These were addressed through the following objectives:

- a) Using the SC190007 review (EA, 2021), short-list and prioritise key field sampling variables that may influence methane concentrations in sampled groundwater.
- b) Using the Vale of Pickering borehole infrastructure with established groundwater methane baseline records (Ward et al., 2020), design a series of field experiments to establish the significance of identified key variables and their contribution to sampling uncertainty.

- c) Identify suitable protocols/methodologies for sampling methane in groundwater.
- d) Make key projects findings accessible to practitioners (e.g. develop a decision-making tool/flow chart).
- e) Identify outstanding knowledge gaps and research priorities.

2 Methane sampling in groundwater experimental design

2.1 KEY UNCERTAINTIES IN METHANE SAMPLING

Potential sources of uncertainty when sampling for dissolved gases in groundwater are summarised in Figure 1. Based on review of previous work (EA, 2021), and discussions with the project steering committee, a short-list of key field sampling variables likely to influence methane concentrations in groundwater was adopted as a basis for the field study design. A field study was selected instead of a laboratory study because, although a laboratory environment offers greater control, it is difficult and expensive to reproduce real-world borehole-scale settings under a representative range of hydrogeological, hydrochemical and sampling conditions. The short-listed variables allows systematic evaluation of the entire field sampling process:

- Groundwater methane concentration in sites of both low and high dissolved methane concentration (the latter has increased potential for methane degassing),
- Pump/sampler type used to retrieve and bring a groundwater sample to surface,
- Purging protocol governing when to take a sample,
- Sample collection protocol used to transfer groundwater from pump to sample vessel.

Inter-laboratory comparison did not form a component of this study, but two laboratories were required due to differing capabilities of sampling different collection vessels (see Section 2.5).

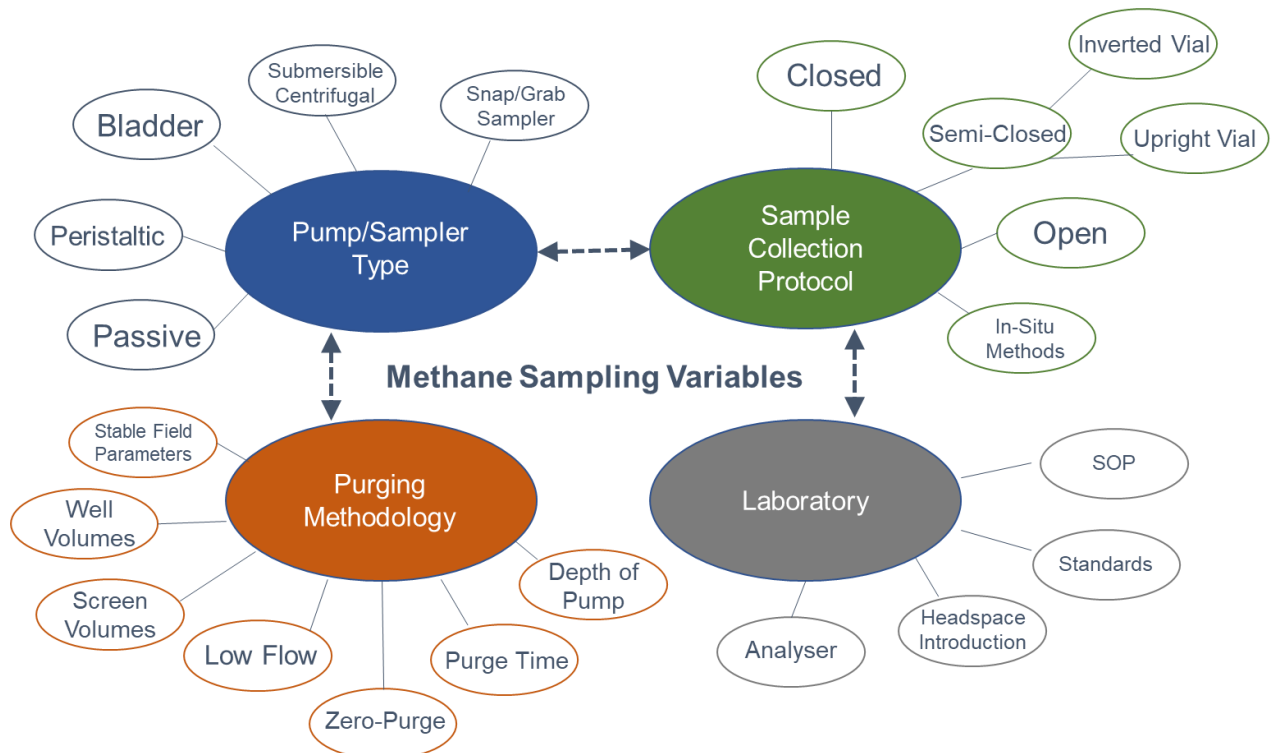


Figure 1 - Methane sampling variables. Dashed arrows indicate inter-variable reliance in certain combinations (e.g. closed samples require a specialist sample extraction method).

The key rationale for comparing boreholes with contrasting methane concentrations is due to greater uncertainties associated with sampling higher methane concentrations. Of particular interest is assessing uncertainties when concentrations are approaching, or above, methane solubility, with degassing thresholds from c. 25 mg/l upwards¹. This project focused on variability across common sampling protocols utilised by practitioners: *purging mode*, *sampler/pump type* and *surface collection protocols*. The main protocol tested was a very commonly used method, low flow purging with stabilisation of indicator parameters; the other methods tested were zero-purge and fixed-volume purge sampling.

The groundwater pump/sampler types tested, all of which are commonly used by practitioners, were:

- HydraSleeve™ passive system (HydraSleeve, 2020)
- Peristaltic pump,
- Bladder pump and,
- Small Submersible Centrifugal pump.

The Hydrasleeve™ discrete (passive) sample system was selected as the zero-purge option, and was used before, and also after, sampling by the various pumping methods.

The sample collection protocols used were (see Section 2.5 for more details):

- Open or 'Direct-Fill' (vial filled whilst open to the atmosphere),
- Semi-closed – inverted (vial filled whilst inverted underwater),
- Semi-closed – upright (vial filled whilst submerged underwater) and
- Closed (double valve steel cylinder not open to the atmosphere).

These protocols are all used by practitioners in the UK, although the closed system is least common. The key rationale for comparing these collection methods is that the potential volatile loss of methane may vary across these protocols. Samples for the four different sample collection protocols were collected in triplicate for each combination of different pump type and purging time.

To compare boreholes with different methane concentrations, two boreholes were selected based on the following criteria:

- One borehole having sampled methane concentrations approaching or above methane solubility thresholds,
- One borehole having sampled methane concentrations of <5 mg/L,
- Both boreholes possessing a time series of dissolved methane data,
- Both boreholes possessing short screen sections (3 m) typical of standard monitoring wells/boreholes,
- Both boreholes possessing a shallow depth to water (<5 mbgl) permitting the effective use of all pump types,
- Both boreholes screened across a similar geological unit.

Detail of the purging and sampling process are in Sections 2.3, 2.4 and 2.5.

2.2 VALE OF PICKERING STUDY AREA

The Vale of Pickering was chosen as the area of study due to a high concentration of BGS groundwater monitoring points utilised for baseline monitoring (>5 years data) and the range of methane concentrations found across the study site (<0.001 mg/l - >70 mg/l). Background

¹ Smith et al. (2016) indicate saturated (solubility) concentrations of methane in the absence of other dissolved gases vary from around 28mg/l (1.75mmol) at the water table (1atm) up to 55mg/l (3.44mmol) at 10m depth and 96mg/l (6mmol) at 25m depth (calculated at 25°C and a typical groundwater salinity). (Smith, B., Becker, M., Siegel, D., 2016. Temporal variability of methane in domestic groundwater wells, north-eastern Pennsylvania. Environmental Geosciences, 23, 49-80.)

information on the geographical, geological and hydrogeological setting of the Vale of Pickering is given by Newell et al. (2015), Ford et al. (2015) and Bearcock et al. (2015). In summary, the Vale comprises a broad flat-lying plain bordered by higher ground extending towards the North York Moors in the north, Howardian and Hambleton Hills in the west and Yorkshire Wolds in the south-east.

The uppermost geological formations of the Vale of Pickering form a minor aquifer of superficial Quaternary sediments and a thick sequence of weathered Upper Jurassic clays (the Amphill and Kimmeridge Clay formations) (Figure 2). Quaternary deposits are mainly of glaciolacustrine origin, with alluvial fan deposits at the margins. Much of the Quaternary material was deposited by proglacial Lake Pickering (Evans et al., 2017), which formed in the Vale following the post Devensian ice retreat at 10 ka BP. Sediments are of a variable thickness up to 40m (Ford et al., 2015), but absent in the centre of the Vale. Discontinuous glacial till deposits form local topographic highs around Kirby Misperton (Bell et al., 2021). The underlying Upper Jurassic Kimmeridge Clay Formation thickness varies greatly across the Vale due to faulting and is up to at least 340m thick (Bearcock et al., 2015). The organic-rich Kimmeridge Clay Formation is of marine origin but, at this location is too immature and shallow for oil production (Williams, 1986). Some groundwater flows occur through fractures in the shallow weathered Kimmeridge Clay. The Quaternary and Kimmeridge Clay aquifers are used mostly for small local private abstractions. Results of previous baseline studies of groundwater chemistry (Smedley et al., 2017; Ward et al., 2020; Ward et al., 2017) indicate strong anoxic conditions, high concentrations of iron, manganese and ammonium, increasing salinity with depth in the Kimmeridge Clay, and dominant Na-HCO₃ type groundwaters. Dissolved methane (CH₄) concentrations vary spatially, from below detection limit up to 30 mg/l generally (Figure 2), but to a maximum of 78 mg/l at a deep Kimmeridge Clay site.

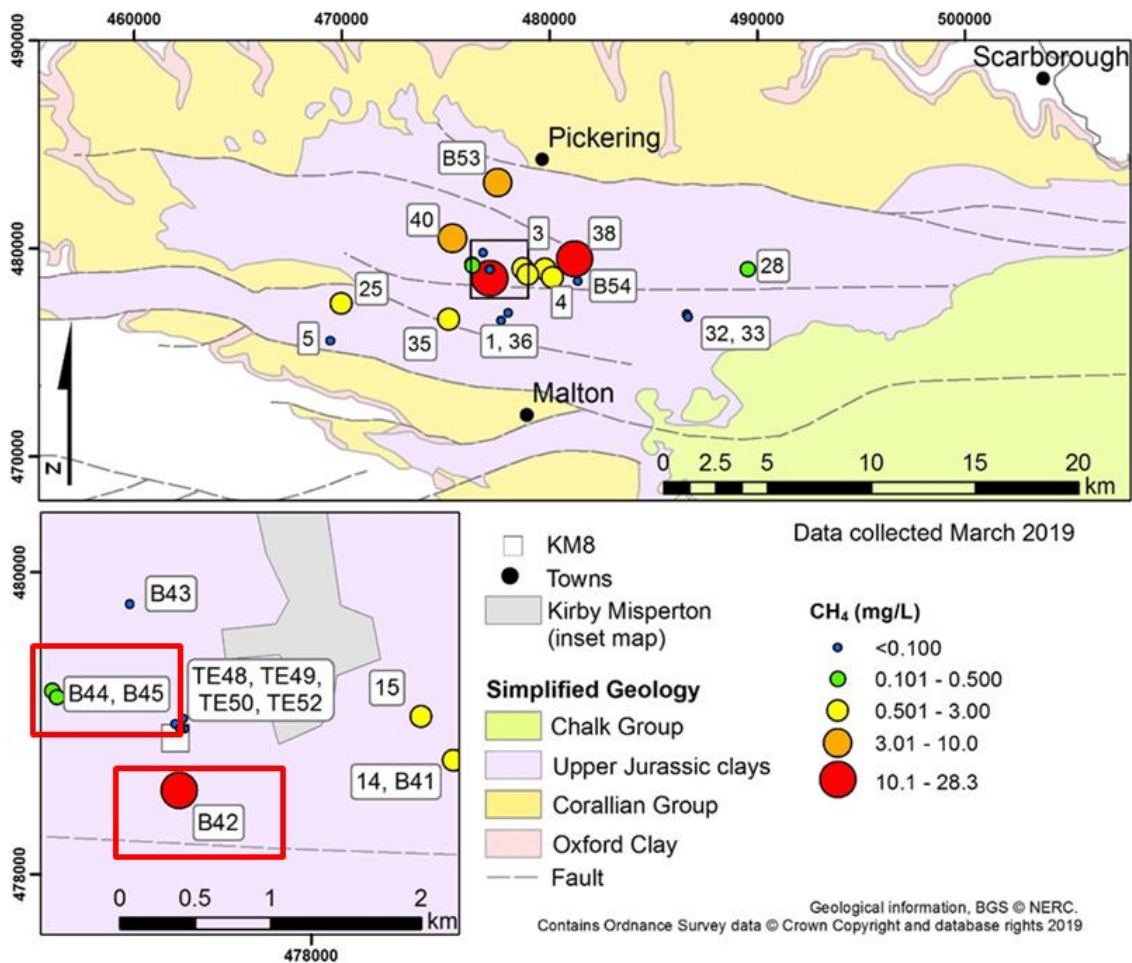


Figure 2 - Vale of Pickering study area simplified geology, methane concentrations and sample locations shown in red boxes (Ward et al., 2020).

The Ampthill & Kimmeridge Clay confine limestones of the underlying Jurassic Corallian Group in the Vale, which forms a primary aquifer. Public supply abstractions from this aquifer are only made at outcrop, towards the margins of the Vale, as groundwater is typically highly mineralised in the confined aquifer. Samples from the confined Corallian Group in the centre of the Vale show groundwater with high pH (up to pH 12) and with dissolved CH₄ concentrations of 13 – 60 mg/l (Ward et al., 2020).

Baseline concentrations of CH₄ in the shallow aquifer are highly variable. In earlier work, a basic comparison of CH₄ collection methods and analytical laboratories was made during BGS groundwater baseline sampling to explore discrepancies between sampling protocols (Ward et al., 2019; 2020). The comparison involved 159 samples, both closed steel cylinder type samples (BGS Wallingford analysed) and open 40ml vial type samples (ALS Environmental analysed) that were collected during baseline sampling rounds in 2020 and 2021 from 63 groundwater sites, including both boreholes tested in this study (Figure 3). Although not a formal study, the samples were taken consecutively from the same sampling points using the same pumps at each site, with purging to parameter stabilisation used for all samples. The data suggest generally good agreement between the two collection methods, although open samples showed higher methane concentrations than closed samples for concentrations less than 4 mg/l, and the reverse for high concentrations greater than 40 mg/l. However, the lack of experimental design and the sampling constraints doesn't allow robust conclusions from these data, and provided little detail of the exact protocols, pump and purging volumes used at each sample point.

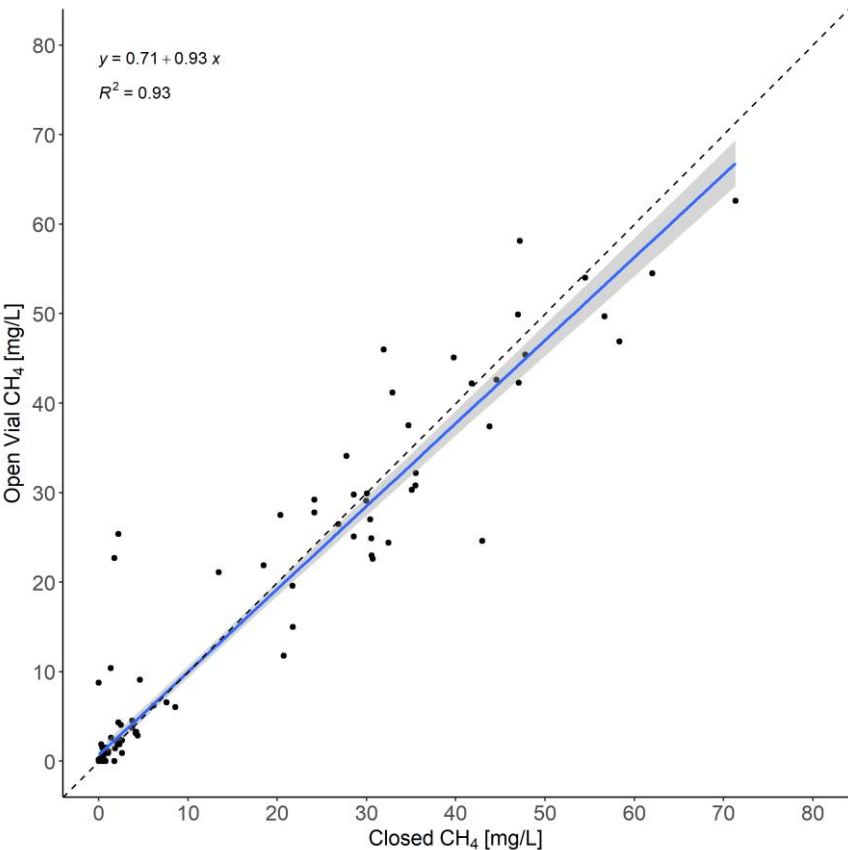


Figure 3 - Closed steel cylinder (x-axis) and open vial (y-axis) sampling of dissolved methane during Vale of Pickering baseline activities with linear fit (blue line) and 95% confidence interval band. Dashed line indicates 1:1. Data from Ward et al. (2020).

2.2.1 Sample Site Selection

Two contrasting boreholes for dissolved CH₄ sampling were selected from the baseline monitoring network. One has high groundwater CH₄ concentration, typically 20-45 mg/l, which is approaching/above methane solubility thresholds; the other has low concentration at <1 mg/l. The low methane site is still well above the analytical detection limits of 0.001 mg/l and 0.0001 mg/l for the ALS and BGS laboratories, respectively. However, it is elevated compared to most UK groundwater methane concentrations (Bell et al., 2017).

Sites were selected from the BGS operated monitoring network that were in close proximity and of similar depth and geology. Borehole B42 was the 'high methane' and Borehole B45 the 'low methane' site (Table 1). The two boreholes have similar depth and rest water levels, and therefore comparable hydrostatic pressure and methane solubility limits at the well screen. Both boreholes are in the same geological fault block and both screened in the shallow Kimmeridge Clay Formation, in which fracture flow dominates groundwater flow. Borehole construction and geology logs are presented in Appendix 1. Both boreholes were drilled using rotary open hole methods, and high-resolution geological log detail is unavailable. The boreholes were both sampled on a monthly to twice-yearly basis between 2015 and 2021. They are only used for groundwater monitoring – not abstraction – and are fitted with telemetered multiparameter sondes measuring pH, specific electrical conductance (SEC), oxidation-reduction potential, temperature, dissolved oxygen (DO) and groundwater level.

Figure 4 and Figure 5 show the time series of dissolved methane values collected at the sites throughout the previous BGS baseline study. Additional samples for comparison were taken during the latter stage of the baseline period only. A BGS supported thesis project estimated the aquifer transmissivity at Site A as 674 – 984 m²/d². No aquifer properties data are available for Site B.

Table 1 - Sample site information

Site	Sampling Identifier	Methane Conc. Range 2015-2020 (mg/l)	Borehole Depth (mbgl)	Screen depth (mbgl)	Casing diameter (mm)	Groundwater level 2015-2021 (mbgl)	Screened Geology Description
B45	Site A	0.0004 – 1.5	30	27 - 30	100	0.73 – 2.20	Weak fractured dark grey shale/mudstone
B42	Site B	9 - 45	30	24 - 27	100	0.85 – 1.83	Hard dark grey fractured shale

² Rahil, L. 2017. Aquitard Parameterisation and Flow Characterisation as a Baseline for the Vale of Pickering Shale Gas Site. Unpublished Thesis, University of Birmingham, UK.

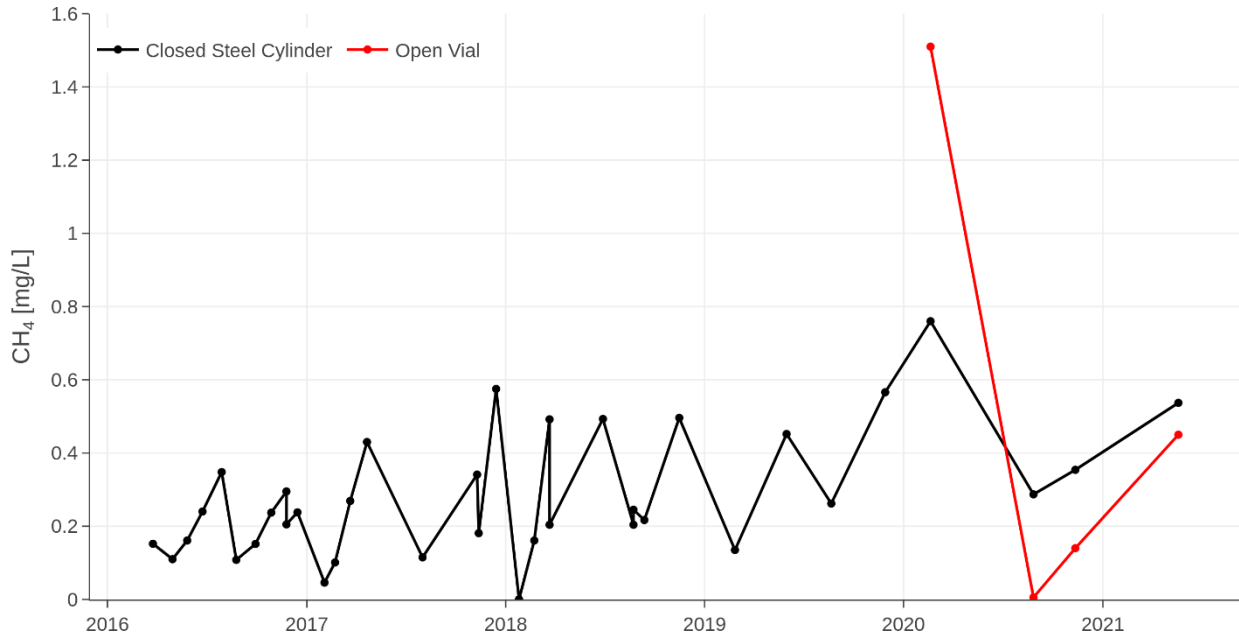


Figure 4 - Dissolved methane time series for Site A (data from Ward et al., 2020).

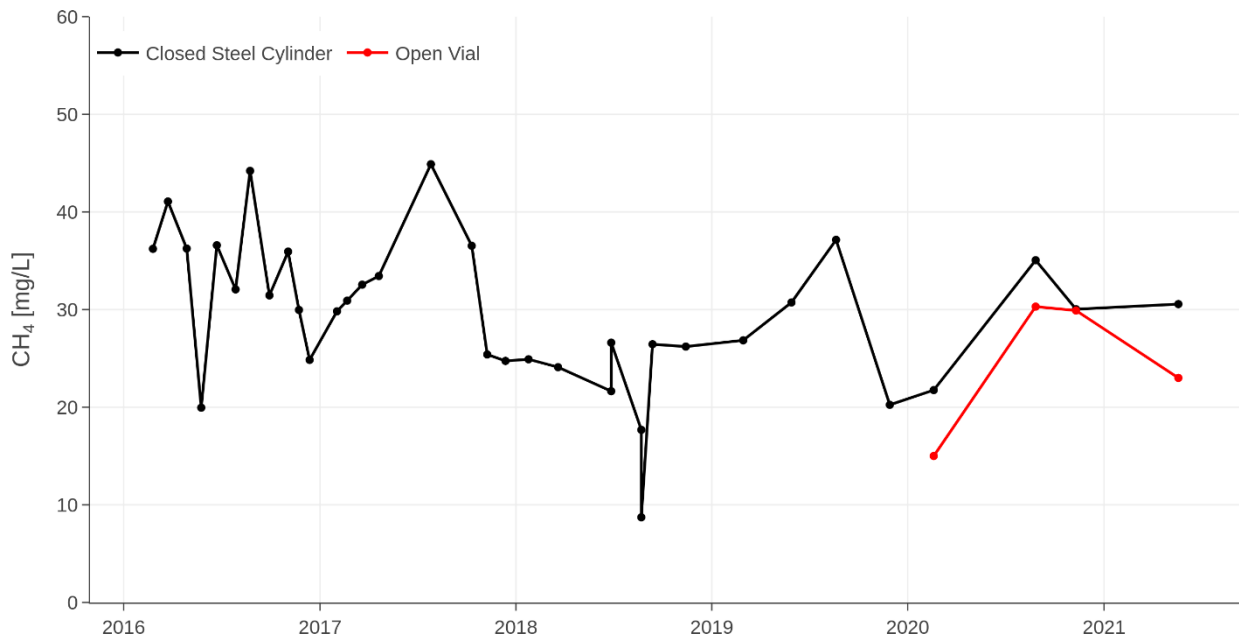


Figure 5 - Dissolved methane time series for Site B (data from Ward et al., 2020).

2.3 PURGING METHODS

There is much research on purging techniques used in groundwater quality sampling, but little specific to dissolved methane sampling. There is evidence that relatively high fixed volume purging – e.g. 3-5 well volumes at a moderate to high flow rate (> 1 l/min) before sampling - can result in “over-purging” and lowering of groundwater levels, with possible dewatering and aeration of the sampled aquifer (CL:AIRE, 2008). A methane-specific issue arising from lowered groundwater level is reduced downhole hydrostatic pressure, attendant reduction in gas

saturation, and possible methane (and other gas) bubble formation, with degassing in the borehole water column.

Purging protocols have been classified as (McMillan et al., 2018; EA, 2021):

(i) 'zero/minimal-purge' protocols using grab or passive diffusion-based samplers removing none or very small water volumes prior to sampling, obtaining a grab sample of the ambient flow regime at a point within the well screen

(ii) 'low-flow' (or low stress) protocols that purge and sample at low flow rates (typically <0.5 l/min) until indicator parameter stabilisation (pH, SEC etc.), which may involve low to moderate volumes of water being extracted (<100 l)

(iii) 'well-volume/screen-volume purging' (fixed volume purge) protocols that are based on purging a specified number of well (or screen) volumes prior to sampling

Low-flow purging and sampling (Nielsen and Nielsen, 2006; Puls and Barcelona, 1996), defined as a flow rate of 0.1-0.5 l/min, has become widely used in recent decades, particularly for sampling volatile compounds. By keeping groundwater level near constant, it avoids drawdown of potentially stagnant casing water and maintains hydrostatic pressure, therefore, may avoid induced degassing, which is clearly advantageous to dissolved gas/methane sampling.

The low flow sampling protocol (ii) with stabilisation of indicator parameters was the primary study protocol in this project, due to its widespread use and appropriateness to methane sampling. Protocol (i) 'zero purge' sampling was done to provide the initial borehole methane concentration. Abstracted volumes were noted during the low flow purge and allowed assessment of protocol (iii) screen volume purging by sampling at a set screen volume (specifically at one screen volume).

Different pumps could be compared by either (a) deployment of all three pumps in the test borehole at an identical mid-screen depth with simultaneous pumping and sampling of each at a similar low flow rate, or (b) separate deployment of each pump with dedicated pumping and sampling of each, with tests conducted in series and time allowed for borehole recovery and methane stabilisation between tests. However, the length of time needed for stabilisation, and therefore a reliable comparison between pump types, was unknown. The tri-pump option (a) was selected as it enabled each pump sampling groundwater that entered the borehole as close to the same time as possible, facilitating comparison. It was also much more time efficient than option (b), which was not considered viable in the time available, especially given uncertainty in the stabilisation times needed.

Using multiple pumps made it challenging to maintain standard low flow rate parameters (0.1-0.5 l/min). Puls and Barcelona (1996), however, note that strict adherence to these flow rates is not necessarily required and that drawdown of <10cm should primarily be used as the main adherence criteria for low-flow sampling. The approach adopted was to keep each of the three pumps at a flow rate of <0.5 l/min with the borehole water level used to demonstrate achievement of low-flow/low-drawdown conditions. Flow rates were adjusted in the initial stages of the purge to maintain a <10cm drawdown.

The experimental design consisted of the following purge and sampling stages to evaluate each protocol:

- **Stage 1** - zero-purge protocol, deploying a passive sampler and retrieving a sample from the centre of the well screen prior to purging.
- **Stage 2** – fixed volume purge protocol, with deployment of three active pumps in a tri-pump assembly and purging under low-flow criteria, taking samples after an aggregate one screen volume purged
- **Stage 3** low-flow protocol, with samples taken using three active pumps after indicator parameter (SEC, temperature, pH, ORP, DO) stabilisation, but still recording purged screen volumes as a point of reference

- **Stage 4** post-purge protocol, deploying a passive sampler and retrieving a sample from the centre of the well screen following termination of active pumping and retrieval of tri-pump assembly.

The screen volume was equal for both test boreholes and calculated at 23.55 litres based on internal borehole diameters (ID) of 100 mm and a screen length of 3 m. This compares to a total standing water borehole volume calculated from pre-test water level data of 226 litres for site A and 267 litres for Site B.

2.4 PUMP TYPES

Three common pump types and a passive sampling device available to the industry were selected for comparison. All of the selected pumps use a different mechanism to retrieve groundwater from the screen to the surface (Figure 6).

Submersible Centrifugal Pump – uses multiple impellers and motors built into the downhole body to drive a groundwater sample through the rising main to surface. Flow rate is altered by changing the voltage to the motors driving the impellers allowing both low and high flow application with control. Too high-powered pumps can cause turbidity issues and even scour borehole wall/screens due to the high speed of the impellers. This study used a 5-stage (5 motors/impellers) WaSP P5 12V submersible pump with a flow controller to vary flow rates, which is widely used for groundwater sampling. The pump polyvinyl chloride (PVC) outer shroud had a diameter of 46 mm and length of 610 mm, fitted with a 10 mm ID low density polyethylene (LDPE) tube rising main.

Bladder Pump – uses a positive displacement compressed gas mechanism to drive slugs of groundwater to surface. A Teflon (PTFE) bladder within the pump body fills with formation water through a screen. Pressurised air is then applied to the bladder via a compressor at the surface, closing a check valve at the bottom of the bladder and forcing the groundwater through the rising main. Pressure is then released, closing a check valve at the top of the bladder and re-opening the check valve at the base allowing the next slug of groundwater into the bladder. This cyclical process gradually purges the borehole and brings the sample to the surface. Cycle pressure and timings are adjusted to achieve desired flow rates. Importantly, there is no direct contact of the compressed air with the sample, preventing sample aeration and losses from partitioning to gas phase. Due to pressure and venting cycles, a continuous water flow is not achievable. This study used a stainless steel Geotech 42 mm diameter bladder pump with a PTFE bladder. The bladder volume of the pump used in this test was 325 ml meaning this was the maximum volume that could be pushed through each cycle. A 6mm ID discharge LDPE line was used as the rising main.

Peristaltic Pump – uses a surface-based pumping mechanism to retrieve groundwater samples. A small diameter tube is installed in the borehole and acts as the rising main connected to a flexible silicon tube at surface squeezed by a multi-roller turbine. The tubing squeeze creates a vacuum pulling groundwater from the rising main into the mechanism before being pushed through the outlet tubing by the next roller. The fluid in the tubing is therefore subject to negative suction pressure on the inlet line and positive pressure on the outlet line. Peristaltic pumps require shallower water tables than other pumps, theoretically up to around 10 m suction limit at sea level, but usually reducing to around 7 m owing to friction losses and elevation. The flow rate can be accurately altered by changing the frequency of the pump head. Flow is not “continuous” but occurs as near-continuous packets of water pushed through the tubing in rapid succession. This study used a Solinst 410 12V peristaltic pump with a 4 mm ID rising main. Water levels in both test boreholes were well within the theoretical maximum suction lift limit (Table 1).

Hydrasleeve™ (passive sampler) – uses a passive sampling method to collect a slug of water from a target depth (HydraSleeve, 2020). The simple device is made up of an evacuated high-density polyethylene (HDPE) bag, sealed with a HDPE Reed-Check valve at the top. The evacuated bag is lowered into place on a weighted Kevlar line. The bag is kept deflated by the surrounding water pressure. Once at the required depth, a swift upward pull on the Kevlar line opens the check valve allowing the bag to fill. The check valve closes once the bag is full and

the sample is retrieved to surface (Figure 7). A HDPE straw is used to pierce the bag and transfer the sample into a sample container. A HDSS-1.5L Hydrasleeve™ was deployed in this study (50mm diameter, 1168mm length) having a maximum sample volume of 1.5 l. The intake of the bag was placed as close to the centre of the borehole screens as possible without disturbing the sediment at the base. With this method of extraction, it is only possible to obtain open samples.

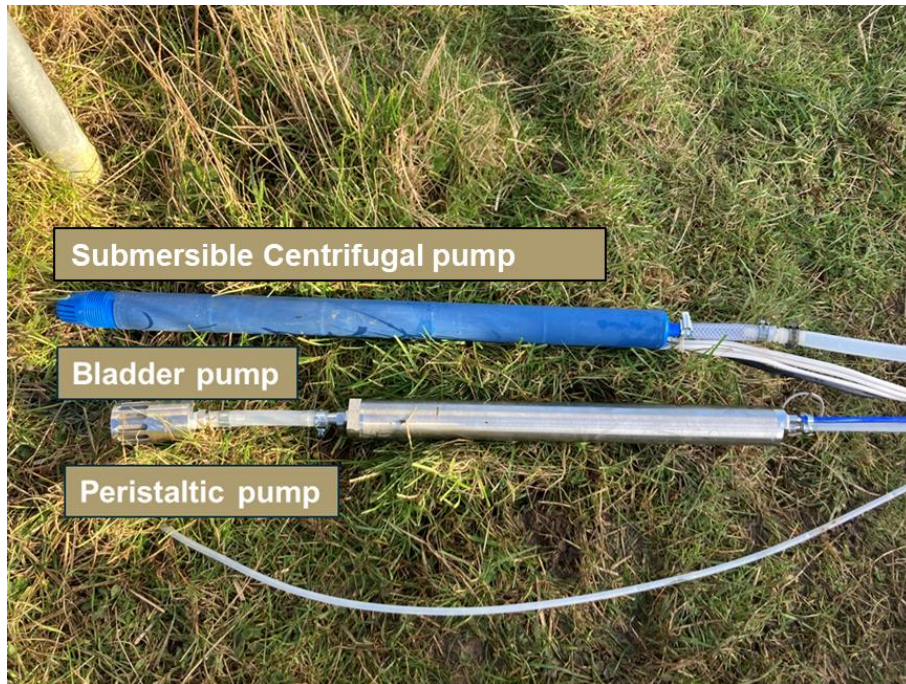


Figure 6 – The three active pump types used as part of the experimental methodology.

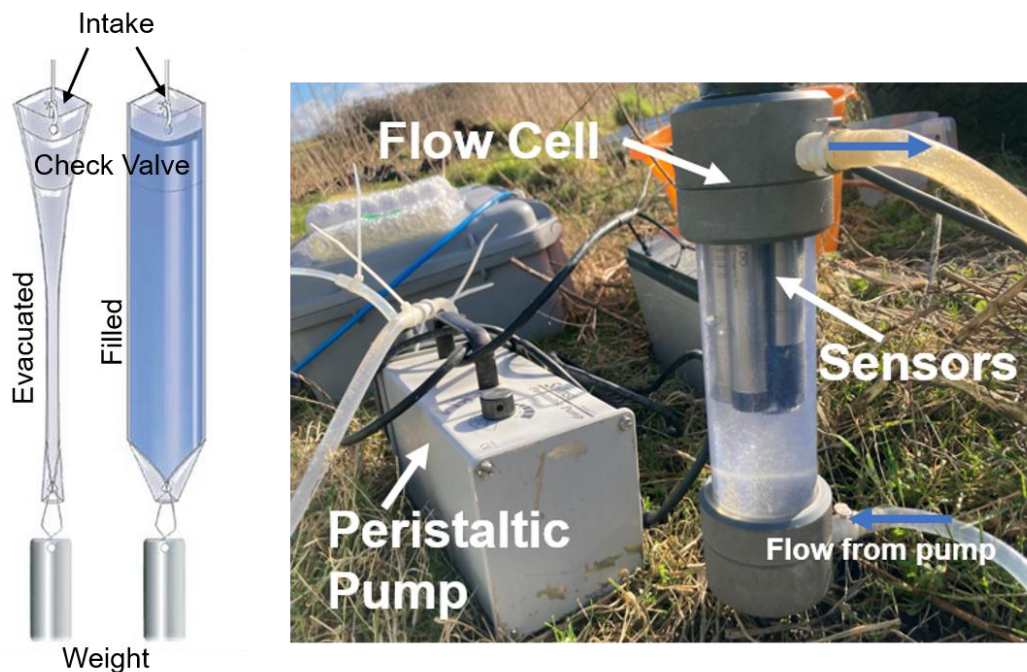


Figure 7 - Passive/zero purge sample collected using a Hydrasleeve (from HydraSleeve (2020)) (left). Flow cell set up for determining stable field parameters (right).

2.5 SAMPLE COLLECTION PROTOCOL

The four sample collection protocols evaluated in the study, which were introduced in Section 2.1, were:

- Open or 'Direct-Fill' (VOA vial filled open to the atmosphere),
- Semi-closed – inverted (VOA vial filled whilst inverted underwater),
- Semi-closed – upright (VOA vial filled whilst submerged underwater) and,
- Closed (double valve steel-cylinders).

The **open or 'Direct-Fill'** method is a common, convenient approach used for dissolved-phase volatile organic compound (VOC) sampling. The sample is open to the atmosphere for a few seconds during collection. The sample is subject to Henry's law partitioning of contaminants where dissolved gases partition from sample water into air, meaning rapid sampling is needed to limit exposure to the atmosphere. Methane has a higher Henry's constant compared to other VOCs and thus more rapidly transferred from dissolved to gas phase. In samples above the methane saturation point, bubbling has the potential to greatly enhance the rate of dissolved gases lost to the atmosphere (Banks et al., 2017; Roy and Ryan, 2013). All open samples were analysed at ALS laboratories.

The **semi-closed 'inverted VOA method'** sample collection system is widely used for methane sampling (Figure 8a). It was considered better than the open method because it was thought to minimise loss of gases exsolving to the atmosphere. However, recent literature questions its appropriateness (Molofsky et al., 2016; Rivard et al., 2018; Environment Agency, 2021). Degassing from groundwater during purging may cause gas to accumulate in the inverted vial headspace, potentially affecting the dissolved phase concentration analysed in the laboratory (Molofsky 2016). More recent studies adopt a semi-closed **non-inverted (or upright)** vial with the sample collected submerged under purge-water in a larger vessel (e.g. beaker), as is done for the collection of CFC's (USGS, 2020). Comparison between the two semi-closed methods was a key part of this research. All samples collected via both semi-closed methods were analysed at the ALS laboratory. They were stored in vials at 1-8°C to limit degassing within the vial in transit to the laboratory as exsolved gas is not analysed.

Closed system sampling is not as widely used, because it needs specialist sample collection equipment that is not routinely available, and samples can only be analysed at specialist laboratories (Figure 8b). Its benefits are to reduce potential for degassing during sampling by collecting and retaining groundwater samples downhole, at the in-situ pressure at depth. Some alternative methods (Bell et al., 2017; Isotech, 2019a, b) involve collecting 'closed' samples using standard pump types, but modified approaches at surface to either: maintain 'pump-pressure' in sealed, double valve steel cylinders, or collect samples in flexible plastic containers (IsoFlasks®) that enable the analysis of both free and dissolved gases. Closed samples using the double valve steel cylinder container were collected using the British Geological Survey (BGS) method and analysed at the BGS Wallingford Laboratories. These samples do not require specific storage conditions as samples are transferred to the analysing apparatus via a closed system with no loss of headspace (see Section 2.6.1).

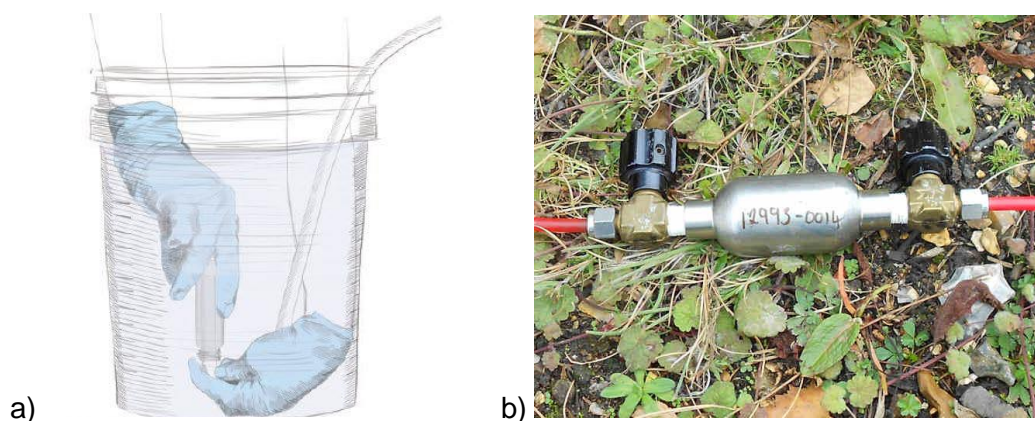


Figure 8 - Two surface sample collection methods: a) semi-closed - inverted (from Molofsky et al., 2016 – released under <https://creativecommons.org/licenses/by-nc/4.0/>) and b) closed (BGS steel sampling cylinder).

2.6 LABORATORIES AND QUALITY ASSURANCE

2.6.1 BGS Wallingford laboratory methodology

Closed samples were analysed at the BGS Wallingford laboratories via headspace gas chromatography (GC). This involved displacement transfer by helium gas of the water and gas from the sampling cylinder (of known volume, range 47–55 cm³) to an evacuated glass bulb of known volume (range 117–123 cm³) at a laboratory temperature maintained at 21±0.5°C. Aliquots of the headspace gas were then expanded into a sampling loop (volume 0.25 cm³) attached to the evacuated inlet system of the GC unit and admitted via a 6-port gas-sampling valve to a 1/8th-inch (3.175 mm) Porapak-Q packed stainless-steel column maintained at 100°C. Eluting CH₄ was detected by flame ionisation detection (FID). The system permits closed sample analysis separated from the atmosphere throughout.

Canned gas standards (Air Products Ltd) covering orders of magnitude intervals from 100 ppm to 100,000 ppm (10%) CH₄ were used for calibration before and after each batch, with the selected standard at the top of the same order of magnitude as the maximum concentration sample. A linear FID response over six orders of magnitude permitted a single-point calibration. Two consecutive standard gas aliquots must agree to within ±5% in the peak area to be acceptable, before and after each run. Dissolved gas concentrations were calculated (in ccSTP/l) by comparing headspace compositions with gas standards and using the relevant Ostwald partition coefficient values for the lab temperature, while also considering the volumes of the individual sampling cylinders and receiving bulbs. Results were recalculated to give concentrations in mg/l or µg/l as required. The dissolved-phase detection limit for CH₄ is 0.1 µg/l.

Further details of the method are available in Darling and Milne (1995).

2.6.2 ALS Environmental commercial laboratory methodology

Samples were collected for ALS in 40 mL VOA vials, filled without headspace by the open and semi-closed methods, sealed with a septum and stored at 1 – 8°C (ALS, 2012). The aqueous sample was heated to drive the volatile components into the headspace. A known volume of the headspace was introduced into the gas chromatograph via the gas sample loop within the injection system and analysed by temperature programmed gas chromatography using a GC. The gas components were separated according to their boiling points and/or affinity for the stationary phase and identified from their retention times. Methane and ethane were resolved on a capillary column and quantified against a 4-point calibration curve.

Flame ionisation and thermal conductance are non-specific means of detection, and therefore any substances that co-elute from the chromatographic column with any of the components of interest will interfere with analysis. Bias and precision data from this batch of analysis was 4.7% and 3.1%, respectively, which is within the 5% deemed acceptable by the BGS Wallingford laboratory.

2.6.3 Quality Assurance/Quality Control (QA/QC)

All samples were collected in triplicate in order to calculate standard deviation and assess variability of single point samples. Each sample for the ALS laboratory comprised a set of two vials for duplicate purposes – i.e., six vials were collected for each groundwater sample. Three steel cylinder samples were taken for each groundwater sample submitted to the BGS laboratory. Taking samples simultaneously was not possible due to the low flow rates, but samples were taken consecutively and as rapidly as possible in the same sequence.

Blank samples were also collected for laboratory QC analysis, and to ensure pumps and sample lines had been adequately flushed between sites. De-ionised Milli-Q® was used to fill a set of 40ml vials for ALS analysis (open method only) and a syringe used to fill a steel cylinder for BGS Wallingford analysis. To flush pumps and sample lines, a large bucket was filled with de-ionised water and all pumps flushed through for 10 minutes. Once flushed, fresh Milli-Q® was pumped into a set of 40ml vials (open method only) and a steel cylinder sample taken. All pumped blank samples were taken from the peristaltic pump tubing, as this presented the smallest overall volume of the three pumps, ensuring that flush water was completely absent on sampling of the blanks. Blank samples were taken as single samples and not in triplicate.

2.7 SUMMARY OF EXPERIMENTAL SAMPLING

Sampling was undertaken at Site A on 8th February 2022 and Site B on 9th February 2022. Weather conditions ranged from overcast to sun with temperatures ranging from 7 – 12 °C and strong breezes.

Prior to deployment of sampling equipment, long term downhole sensors were carefully removed from the boreholes trying not to disturb the water column. Not disturbing the water column was a primary aim throughout all activities in the study.

A pre-deployment standing water physicochemistry profile in each borehole was carried out using a YSI EXO1 multiparameter sonde fitted with specific electrical conductance (SEC), Temperature, Depth, Dissolved Oxygen and combined pH/oxidation-reduction potential (ORP) sensor. This provided information on water chemistry across the full length of the well screen and water column and provided a baseline from which to compare indicator parameters during purging.

The EXO1 was then deployed again downhole with sensors within the lower 1m of the screen to avoid the pumps which were installed at mid-screen (Figure 9b). Sensor readings were logged at 1-minute intervals before, throughout and after the pumped sampling phase, permitting comparison with surface-based indicator parameters. A downhole water level logger and surface mounted barometric pressure logger were installed to record drawdown.

The pre-purge passive sampler was deployed and left downhole for ~30mins, retrieved and sampled ('Open' only) to complete Stage 1 sampling. (Figure 9c).

Following Stage 1 passive sampling, pumps were installed at mid-screen with all pump intakes at the mid-point of the 3-m well screen (1.5m - Figure 9b). Pumps were lashed together with electrical tape ensuring pump intakes were uncovered (Figure 9a).

Following set-up of surface-based sensors, pumps were started at the same time and their flow rates set to as close to 0.5 l/min as possible. Groundwater level was frequently monitored during the initial 5 minutes to verify groundwater level variation, and pump rates were reduced if drawdown approached 10 cm. Each pump outlet was connected to a flow cell with YSI ProDSS sensor logging pH, SEC, ORP, DO and temperature at 1-minute intervals. These measurements were also noted manually at 5-minute intervals, in-line with standard BGS

groundwater sampling procedures to assess stability of parameters. Manual water level measurements were also taken regularly (10-15 minutes) to monitor any drawdown.

Purged water was collected in buckets to track purge volumes (Figure 10).

Stage 2 sampling was started after a total purge of 23.55L (1x screen volume). Samples were taken progressively from each pump in the following order: 'open', 'upright', 'inverted', 'closed'. The same order was used throughout all sampling at both sites.

Stage 3 was started when stable parameter readings were reached for all pumps and the same procedure followed as for Stage two. Purged (screen) volumes for each stage can be found in Sections 3.2 and 4.2.

The active pump assembly was then retrieved and Stage 4 sampling was done using the post-purge passive sampler, leaving it downhole in the same position as the pre-purge sampler for ~30mins before retrieval and sampling ('Open' only).

A post-sampling up profile was taken following completion of all sampling, during retrieval of the sonde that was deployed downhole.

The full schedule of sample collection is given in Table 2.

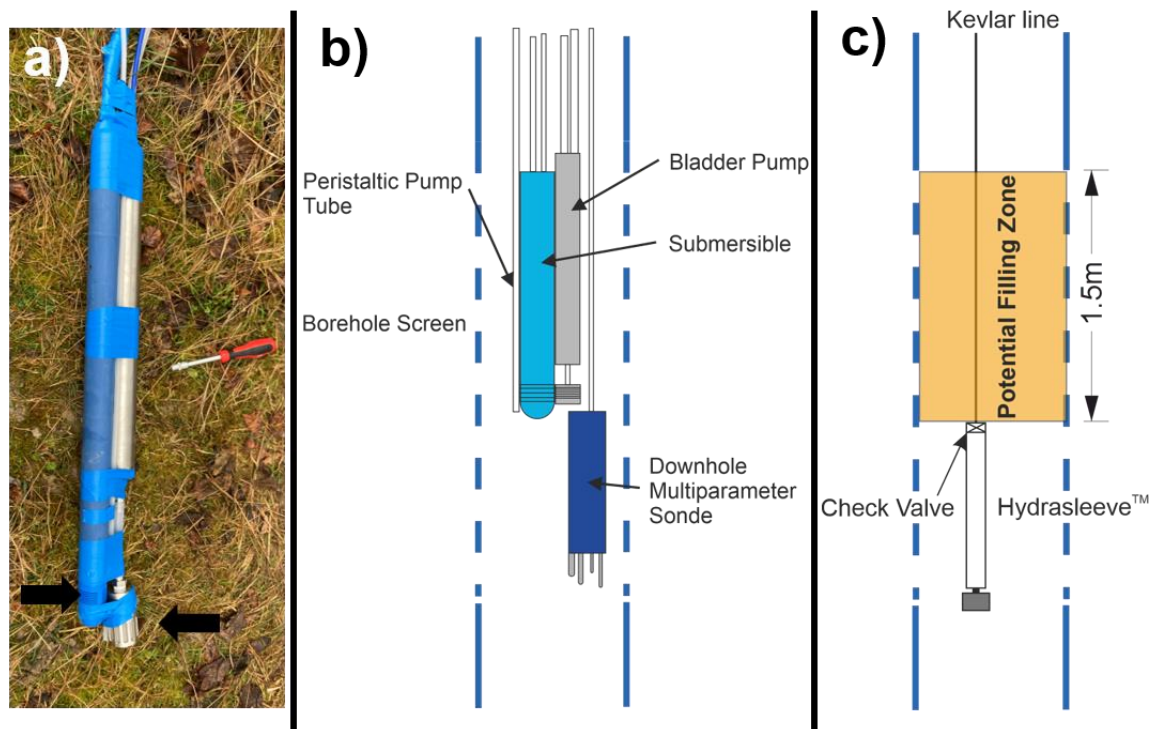


Figure 9 – a) Pump intakes set at the same depth as indicated by arrows (peristaltic not visible). b) downhole configuration showing tri-pump assembly placed at mid-screen and multiparameter sonde placed in lower screen. c) Hydrasleeve deployment with potential filling zone.

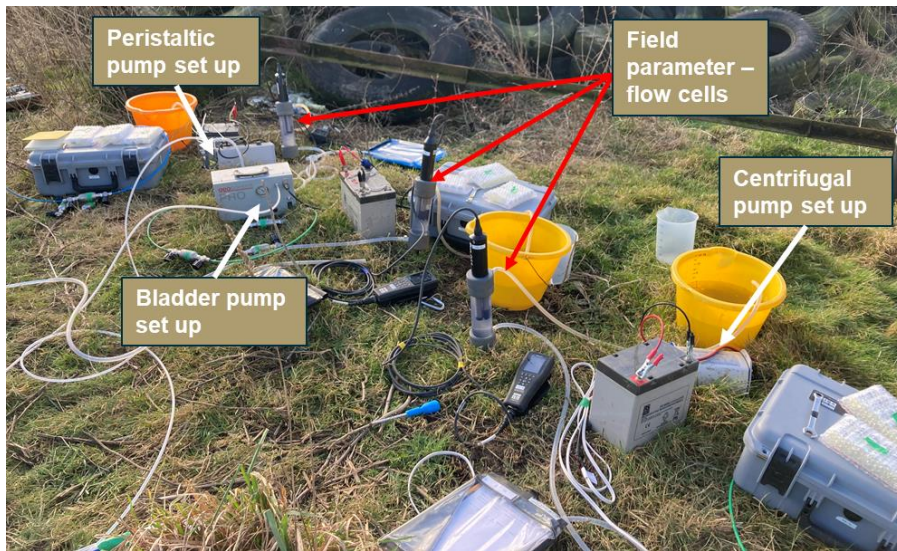


Figure 10 - Field set up at one borehole with three pumps set up to purge through in-line multi-parameter sensors - one for each pump.

Table 2 - Schedule of sample collection

Stage (Site A)	Stage (Site B)	Purge	Pump	Surface Sample Mechanism
A1	B1	Pre-purging	Hydrasleeve (passive)	Open
			Submersible Centrifugal pump	Open Semi-closed - upright Semi-closed - inverted Closed
A2	B2	1x Screen Volume (23.55L)	Bladder pump	Open Semi-closed - upright Semi-closed - inverted Closed
			Peristaltic pump	Open Semi-closed - upright Semi-closed - inverted Closed
			Submersible Centrifugal pump	Open Semi-closed - upright Semi-closed - inverted Closed
A3	B3	Stable Field Parameters	Bladder pump	Open Semi-closed - upright Semi-closed - inverted Closed
			Peristaltic pump	Open Semi-closed - upright Semi-closed - inverted Closed
A4	B4	Post-purging	Hydrasleeve (passive)	Open

3 Physico-chemical Profiles and Time Series

3.1 SITE A - LOW METHANE BOREHOLE PROFILES

Results of the pre- and post-sampling hydrochemical borehole profiles collected using the downhole sonde (screen logger) for Site A are presented in Figure 11. The water column is relatively stratified with SEC at 1200 – 3300 $\mu\text{S}/\text{cm}$, pH 6.8 – 7.4, temperature 9 – 10.7 $^{\circ}\text{C}$, dissolved oxygen 0 – 8 mg/l and ORP -138 – 70 mV. Some water column mixing effects induced by the movement of the sonde (or possibly some water retention in the sonde guard) are apparent in the pH and DO down and up profiles. The post sampling profile shows the effect of pumping water into the borehole through the screen with distinct pre-/post- differences around the screened section (27-30 mbgl). The decrease in SEC in the mid- to upper section of the screen and the cased section immediately above suggests inflows of lower conductivity groundwater in that screen section and hence stratified flows into the well screen.

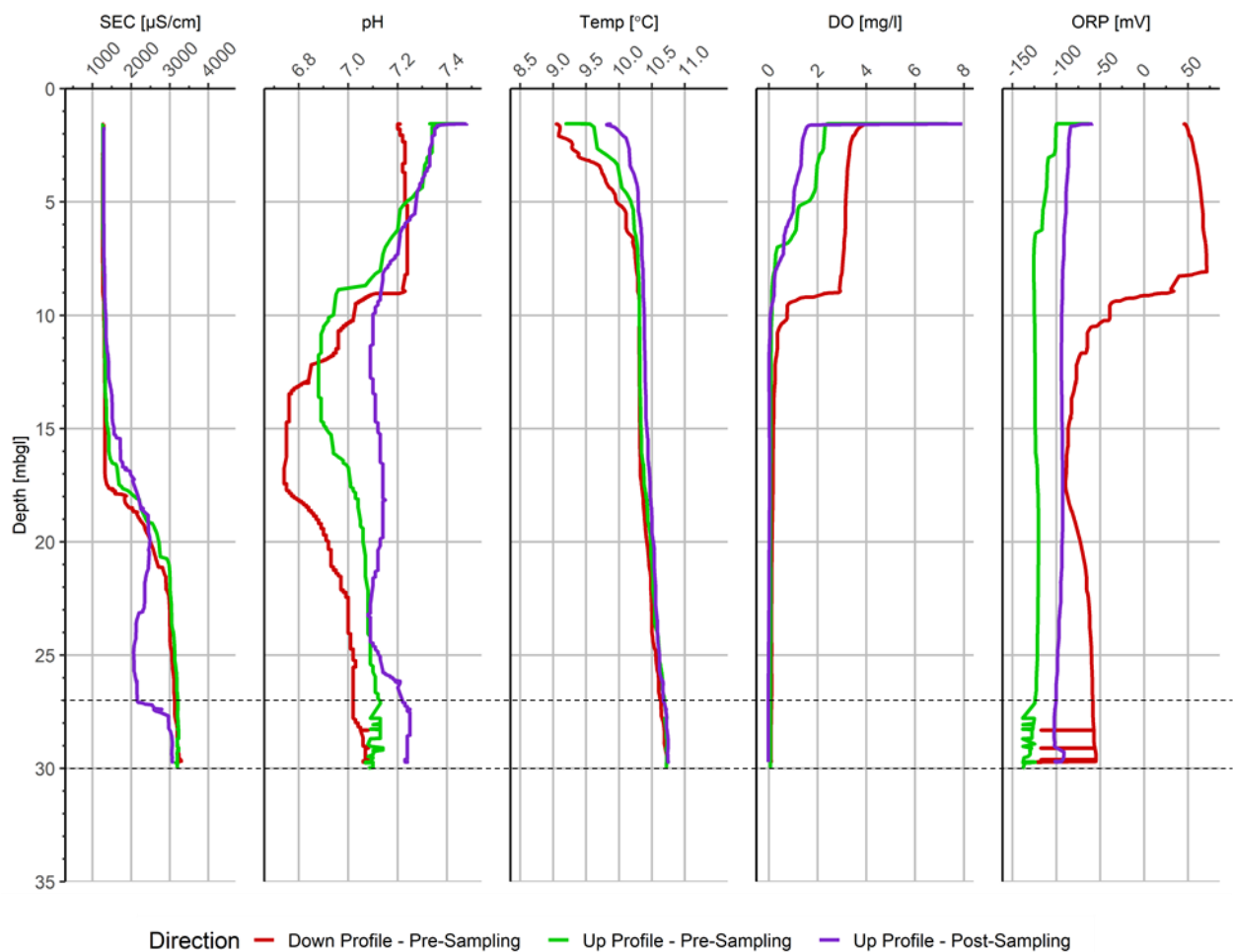


Figure 11 – Site A (low methane) pre-sampling and post-sampling hydrochemistry profiles. Screen position between dashed lines.

3.2 SITE A WATER LEVEL AND INDICATOR PARAMETERS

Figure 12 shows the groundwater level timeseries for Site A alongside the sampling timeline. Groundwater level remains relatively stable throughout the pumping stages, varying by less than 10cm. If single point peaks/troughs are discounted, this reduces to less than 3cm variation, showing a successful adherence to the low flow methodology criteria (<10cm drawdown).

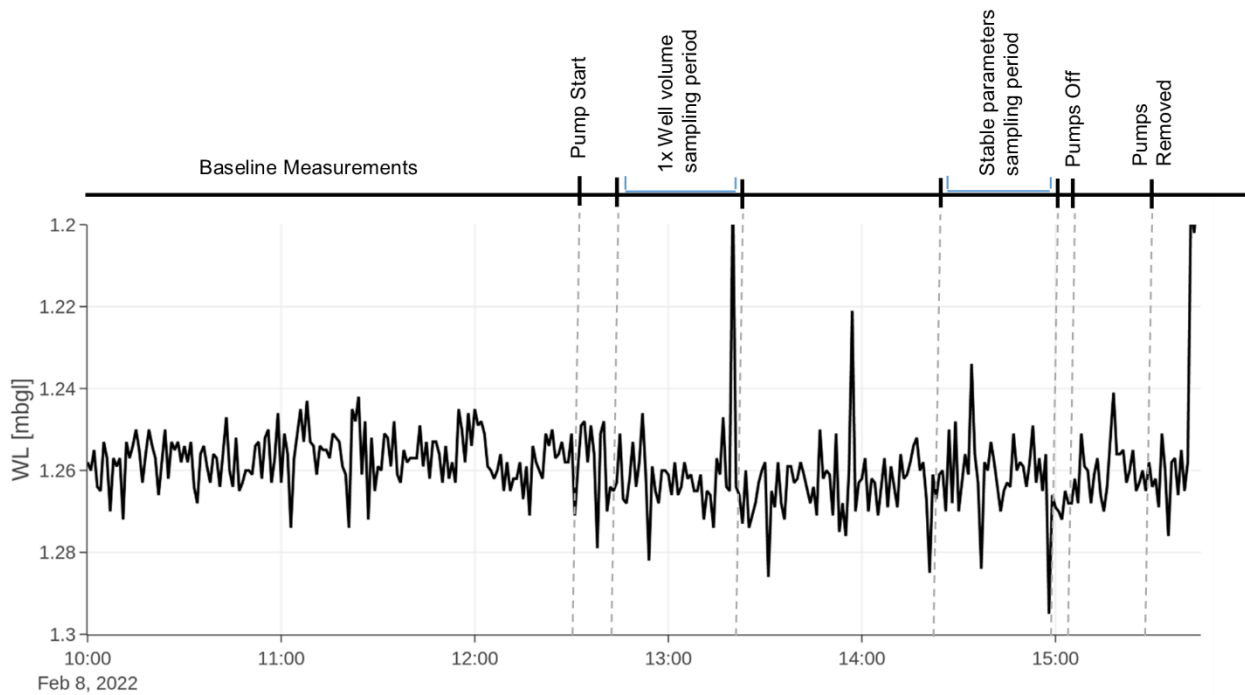


Figure 12 - Site A (low methane) barometric corrected groundwater level measurements from downhole logger with timeline.

Figure 13 shows the time series of hydrochemical parameters monitored from each pump and the downhole screen logger sonde, alongside the activity timeline. Occasional data gaps occur during sampling when the sondes were disconnected from the sample line or due to sensor issues. Hydrochemical parameters change immediately upon pump start, which is attributed to stagnant water clearance from the sample lines. Initially, the screen logger appears to stabilise relatively quickly, within 2-3 mins. However, during Stage A2 (1x well screen volume sampling), parameters continue to change with SEC (3000 – 2500 $\mu\text{S/cm}$), pH (7.15 – 7.05) and dissolved oxygen ($\sim 0.5 - 1$ mg/l) decreasing and ORP (-120 – -60 mV) increasing. This suggests that a one screen volume purge is not sufficient to obtain stable parameters. Parameters across all pumps were generally in good agreement during this period.

pH and DO surface parameters begin to stabilise following 80-90 minutes of purging, with SEC and ORP stabilising around 110mins after pump start. This was the start of Stage A3 of sampling.

Temperature varies throughout the time series and between pump types, attributed to variable solar radiation levels during the test that heated or cooled the sample lines and flow cells at the surface. A significant heating event can be seen at 14:10. The contrast between pumps is attributed to the volume and velocity of groundwater within the sample lines at surface. The submersible pump, with the largest diameter sample line, had the lowest velocity for a given flow rate and hence the longest exposure to temperature influences at surface.

Surface parameters in the pumped water tended to diverge from the downhole screen logger over time. This was attributed to the location of the downhole logger sensor 1.1m deeper than the pump intakes, and could indicate that there is little mixing within this borehole under low flow conditions with stratification of flow horizons within the mid to lower screened section.

An average flow rate of 1.5 l/min was achieved over the purging period (combined pump flow rate). Table 3 shows the volumes purged at the various stages of sampling, including equivalent screen volumes and well volumes. It took around 45 minutes to complete the sampling for each stage. In terms of screen volumes, completing Stage 2 sampling was done after purging 1 to 3.8 screen volumes and Stage 3 sampling after purging 7.5 to 10.9 screen volumes.

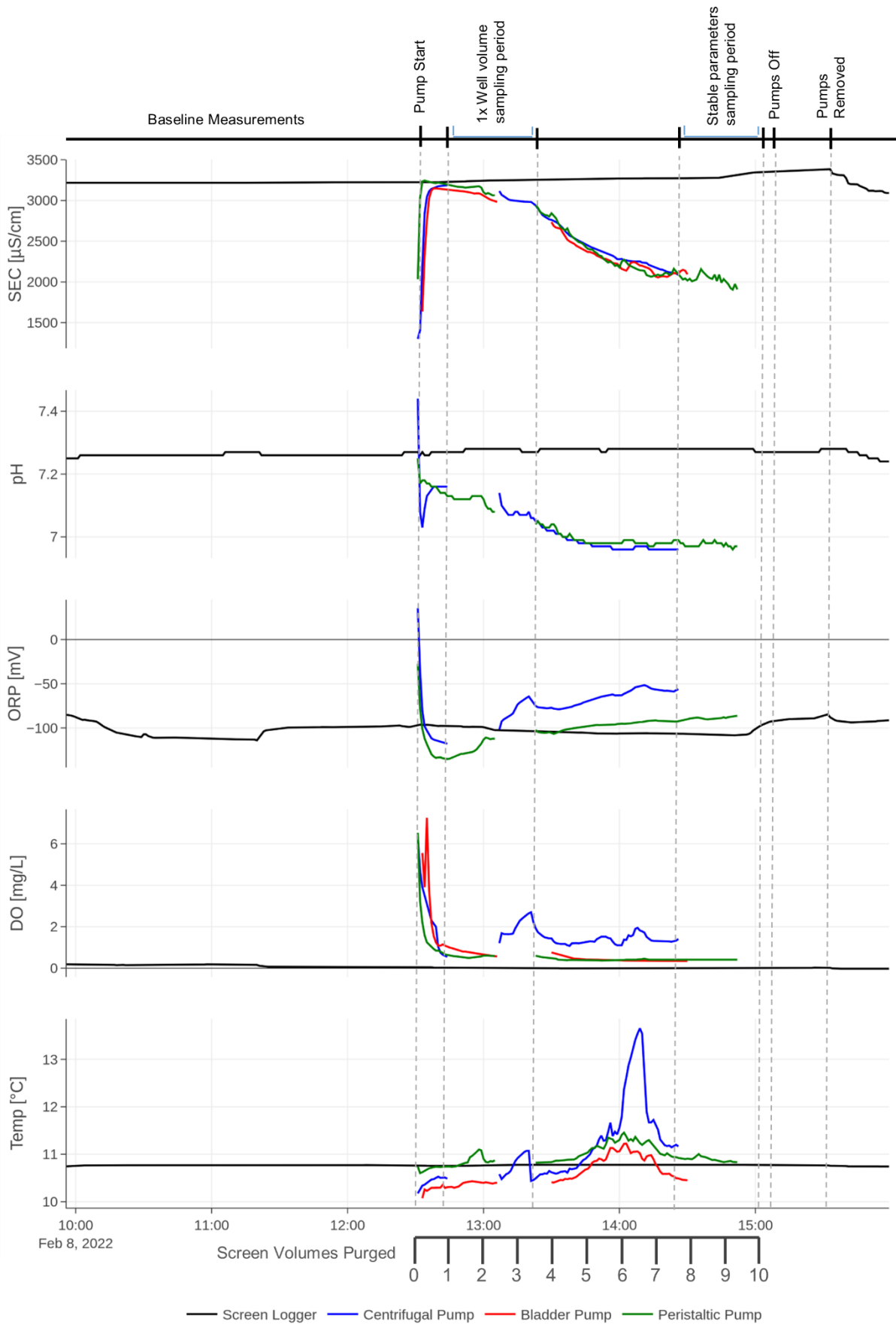


Figure 13 - Site A (low methane) hydrochemical parameter time series.

Table 3 - Site A purge volumes

Site A - mean flow rate 1.5 l/min				
	Time since purge start (mins)	Vol. Purged (l)	Screen Volumes (SV)	Well Volumes (WV)
Stage 1 (Pre-Purge)	0	0	0	0
Stage 2 (1x SV)	15 – 59	23 – 89	1.0 – 3.8	0.1 – 0.4
Stage 3 (Stable Params)	117 – 171	176 – 257	7.5 – 10.9	0.7 – 1.1
Stage 4 (Post-Purge)	171	257	10.9	1.1

3.3 SITE B - HIGH METHANE BOREHOLE PROFILES

Pre- and post-sampling hydrochemical borehole profiles collected using the downhole sonde (screen logger) for Site B (Figure 14) show a uniform profile within the water column to the base of the screened section (24-27 mbgl) and sump (27-29 mbgl). SEC ranges over 1700 – 2200 $\mu\text{S}/\text{cm}$, pH 7.4 – 8.2, temperature 8.7 – 11.2 $^{\circ}\text{C}$, dissolved oxygen 0 – 10 mg/l and ORP -180 – -22 mV. ORP and DO parameters in general have longer stabilisation times due to probe response and are, therefore, less useful as indicators of stabilisation than the more sensitive parameters SEC and pH. The effect of possible mixing due to probe movement is much less obvious than Site A. There is an obvious case of stagnant water collecting in the borehole sump with higher SEC and pH waters than seen in the screened and upper casing sections. The post profile SEC and pH profiles show that fresher water has been brought into the borehole water column uniformly across the screen and extending in influence across around 5 m height of the overlying cased section. The upper section of the cased water column remains stable throughout due to the methodology of low flow of pumping with limited drawdown, except for temperature close to surface that is influenced by atmospheric conditions.

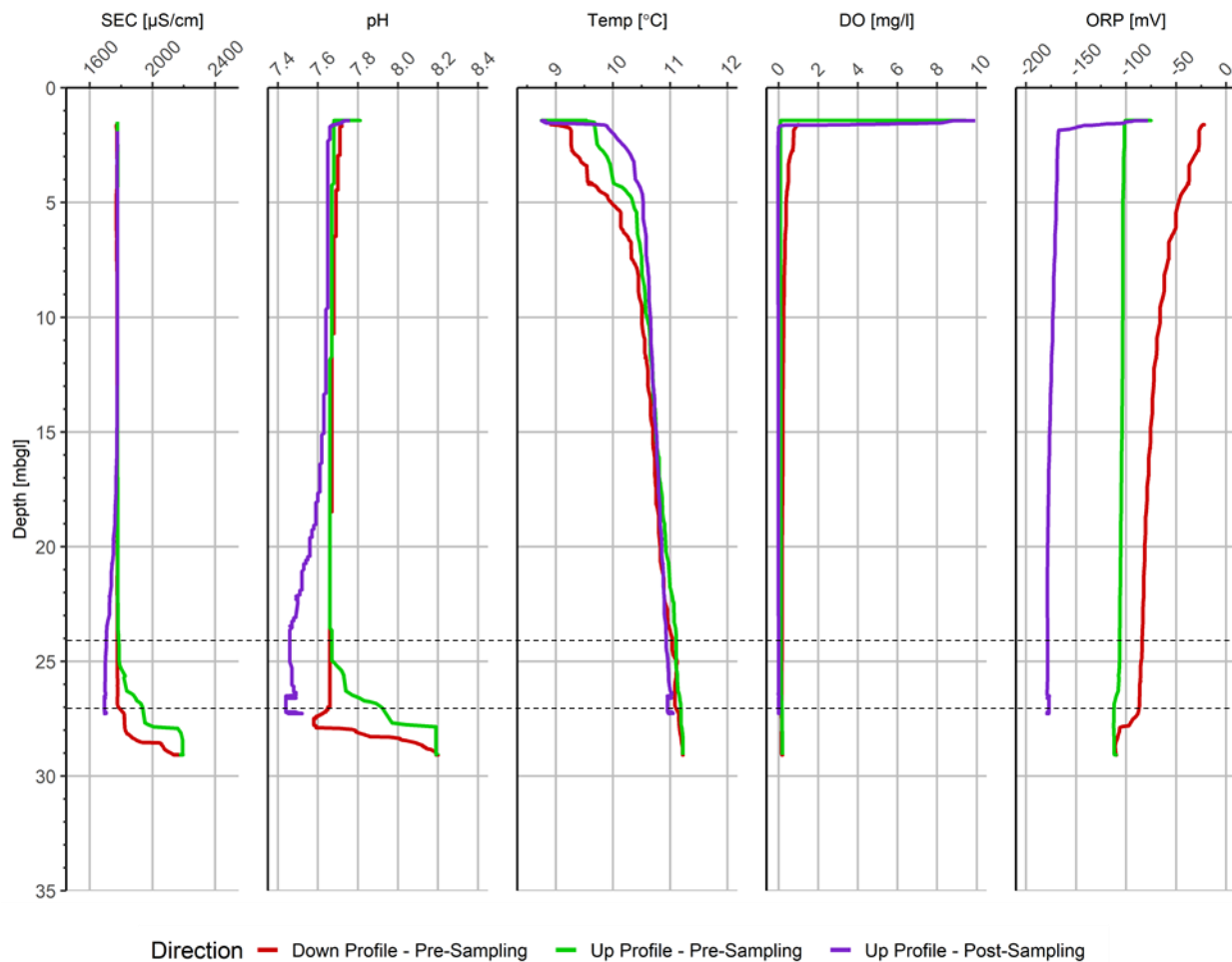


Figure 14 - Site B (high methane) pre-sampling and post-sampling hydrochemistry profiles. Screen position shown between dashed lines.

3.4 SITE B WATER LEVEL AND INDICATOR PARAMETERS

Figure 15 displays the groundwater level time series for Site B alongside the sampling timeline. Groundwater level data from the downhole screen logger placed at 26.65 mbgl was used as the In-Situ LevelTroll 700 failed. The data clearly reflect features such as a slight decrease in water level on pump start and recovery on pump shutoff. Water level changed by less than 5cm throughout the pumping phase, adhering to the low flow <10cm drawdown flow criterion.

Figure 16 shows the time series of hydrochemical parameters measured at each pump and the downhole screen logger. As for Site A, Site B shows a short apparent initial stabilisation time during flushing of sample lines, but true stabilisation taking longer. Parameters appear to have stabilised during stage B2 (SEC 1780 – 1850 $\mu\text{S}/\text{cm}$, pH 7.4 – 7.6, DO 0.1 mg/l). ORP for the submersible centrifugal pump shows significantly greater (>150 mV) values than other pumps and the downhole screen logger. Calibration data were checked and show no obvious discrepancies and the reason for the disparity is unexplained.

SEC begins to decrease following stage B2, with a final stabilisation around 120 minutes after pump start, which allowed the start of stage B3.

Parameters measured from pumps at the surface align closely with the downhole screen logger, indicating a more homogenous flow profile into the well screen in Site B than Site A.

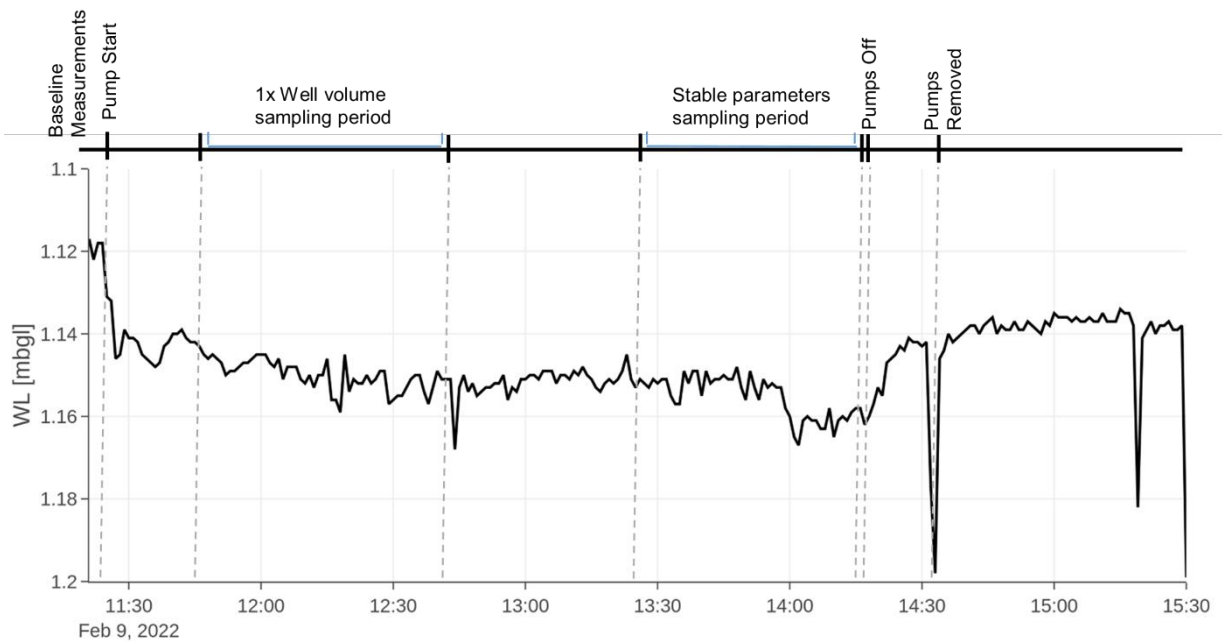


Figure 15 - Site B (high methane) barometric corrected groundwater level measurements from downhole screen logger with timeline.

An average flow rate of 1.05 l/min was achieved over the purging period (combined pump flow rates). Table 4 shows the volumes purged at the various stages of sampling including equivalent screen volumes and well volumes. It took around 57 minutes to complete the sampling for each stage. Stage 2 sampling was done after purging 1 to 3.3 screen volumes and Stage 3 sampling after purging 5.7 to 7.8 screen volumes.

Table 4 - Site B purge volumes.

Site B - mean flow rate 1.05 l/min				
	Time since purge start (min)	Vol. Purged (l)	Screen Volumes (SV)	Well Volumes (WV)
Stage 1 (Pre-Purge)	0	0	0	0
Stage 2 (1x SV)	23 – 74	24 – 78	1.0 – 3.3	0.1 – 0.3
Stage 3 (Stable Params)	128 – 174	134 – 183	5.7 – 7.8	0.6 – 0.8
Stage 4 (Post-Purge)	174	183	7.8	0.8

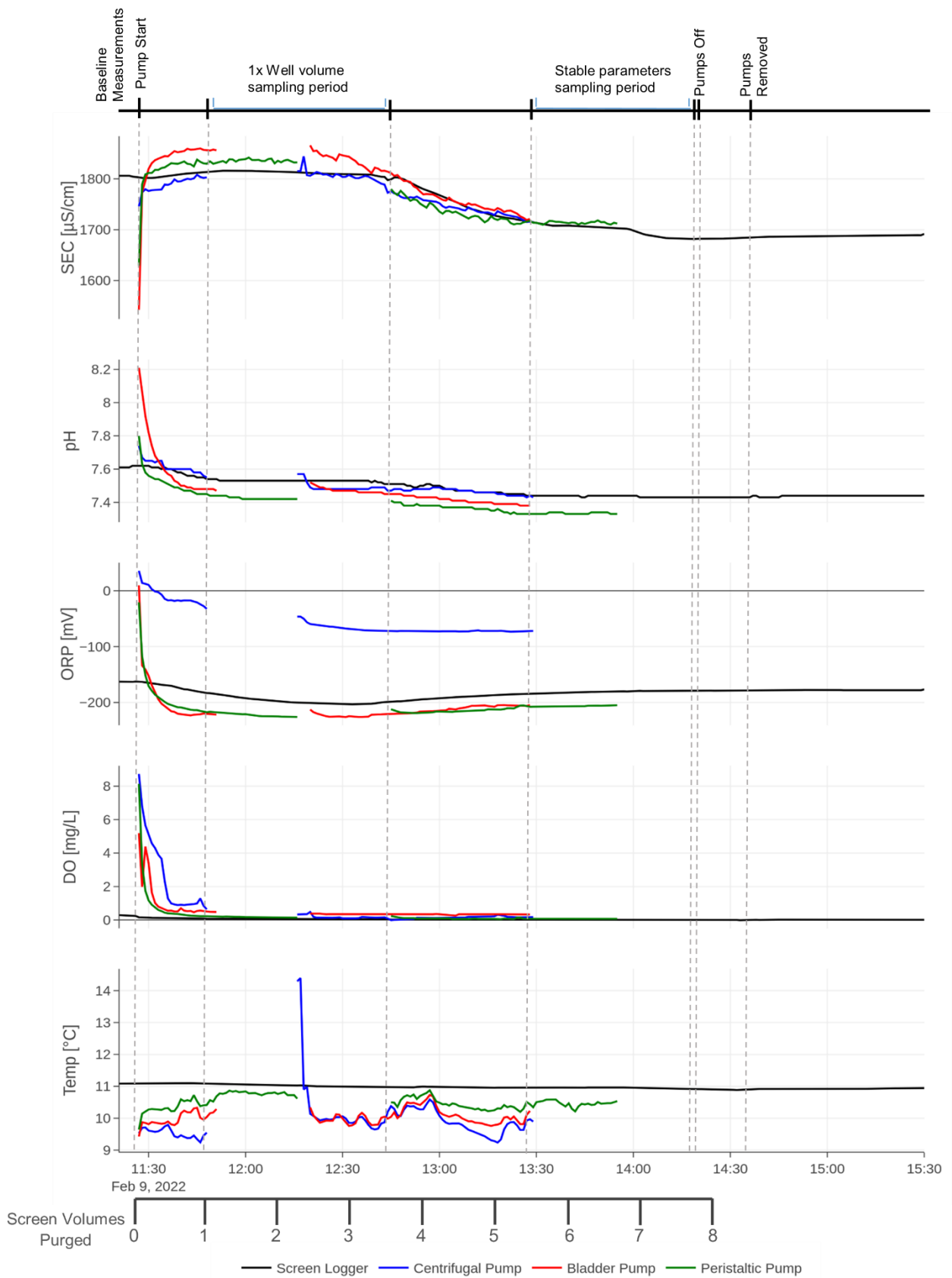


Figure 16 - Site B (high methane) hydrochemical parameter time series.

4 Methane Concentration Results

4.1 SITE A – LOW METHANE OVERVIEW

The entire dissolved methane dataset obtained from sampling the Site A low methane borehole is shown in Figure 17. Methane concentrations span a wide range from below detection limit (<0.0001 mg/l) to 2.6 mg/l. Mean and standard deviation (sd) were 0.59 ± 0.60 mg/l (n=78) with a large relative standard deviation (rsd) of 103%. Summary statistics for the complete dataset can be found in Table 5.

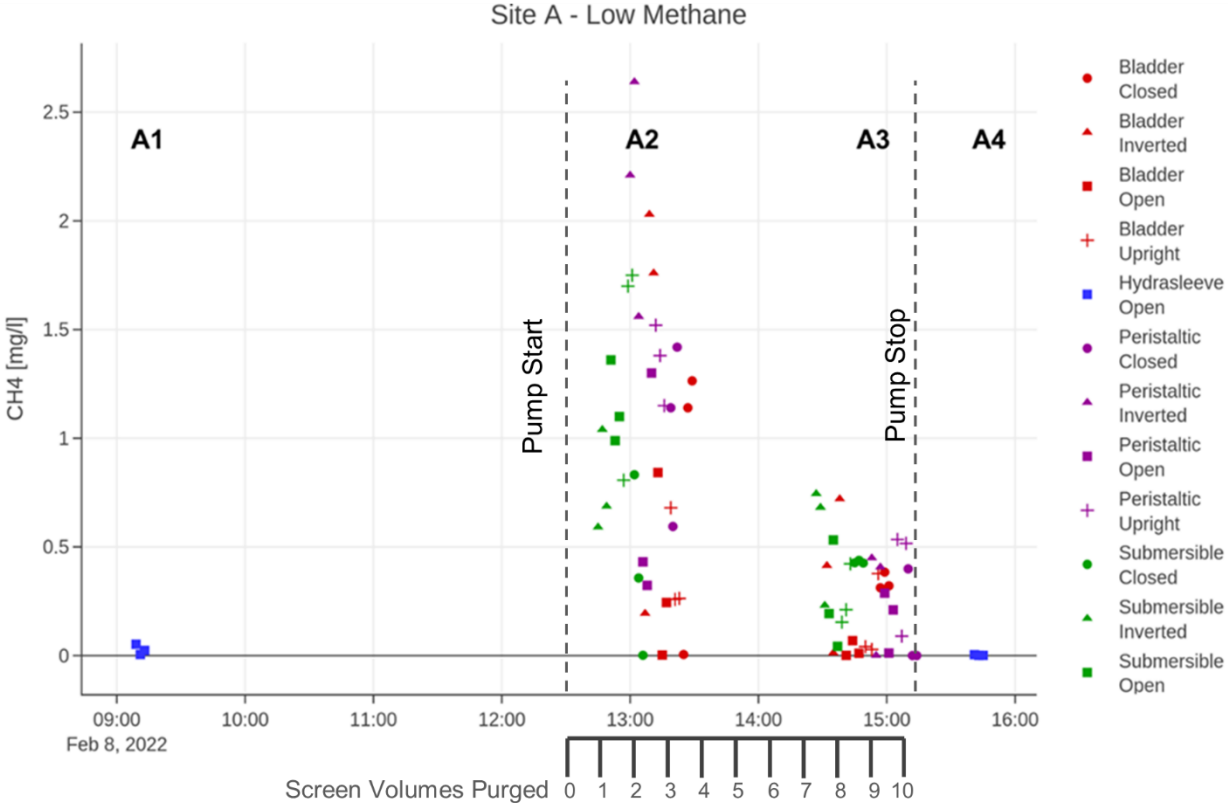


Figure 17 - Site A (low methane) methane concentrations with elapsed time and pump and sample collection protocol indicated.

4.1.1 Site A – Methane concentration sensitivity to purging method

A statistical summary of methane concentration data for Site A by stage shows that overall data variability is very high (Table 5). All stages exhibit greater than 65% rsd. A marked decline of 72% in mean methane concentration occurs between stage A2 (1 screen volume) and A3 (parameter stabilisation) with an attendant small increase in rsd from 67% to 80%. Mean concentrations for stages A1 and A4 are 1 and 2 orders of magnitude (respectively) lower than for stages A2 and A3, and appear anomalous. Only open samples taken with a Hydrasleeve passive sampler were collected at A1 and A4. The contrast between the pre- and post-purge methods and active pumped stages here suggests that the differences are a function of pump and/or sample methodology, rather than the degree of purging.

Table 5 - Site A methane concentration summary statistics by purging method.

	Mean mg/l	SD mg/l	RSD %	n	Percentiles				
					5 th mg/l	25 th mg/l	50 th mg/l	75 th mg/l	95 th mg/l
Stage A1 Zero purge	0.027	0.024	88	3					
Phase A2 1 screen volume purge	0.99	0.66	67	36	0.004	0.41	1.01	1.39	2.08
Stage A3 Parameter Stabilisation	0.28	0.23	80	36	<0.001	0.04	0.30	0.43	0.69
Stage A4 Post purge	0.0021	0.0017	82	3					
Stage A1-A4 Complete dataset	0.59	0.60	103	78	0.001	0.07	0.41	0.84	1.75

4.1.2 Site A – Methane concentration sensitivity to pump type

The sensitivity of methane concentration to pump type and purging stage is shown as a statistical summary in Table 6 and graphically in Figure 18.

Key points are:

- Measured concentrations from passive sampling in stages A1 and A4 are much lower (1 and 2 orders of magnitude, respectively) than those from the active pump types.
- Stage A2 shows the high variability in measured concentrations among all pump types. The peristaltic pump produces the highest measured concentrations and lowest rsd, followed by the submersible pump and then bladder pump with the lowest concentrations and a very high rsd. Rsd for peristaltic and submersible pumps are comparable.
- Concentrations measured in stage A3, for all pumps, have increased variability relative to the mean compared to A2. The submersible pump produces the greatest concentrations and lowest rsd, followed by peristaltic pump and bladder pump, which both produce the lowest concentrations.
- Two anomalous points below detection limit were produced by peristaltic pump closed samples in A3. This may account for lower concentration and higher rsd compared to A2. Removing these points results in a mean concentration of 0.29 ± 0.20 (69% rsd). Whilst increasing concentration and lowering rsd, it is not of sufficient magnitude to replicate the hierarchy found in A2.
- The mean measured concentration is inversely related to rsd for all pumps in stages A2 and A3: i.e., a higher mean concentration is accompanied by lower rsd.

Table 6 - Site A summary statistical data by pump type.

	Mean mg/l	SD mg/l	RSD %	Conc. decrease %	n
<i>Zero purge sample</i>					
Hydrasleeve™ A1	0.026	0.023	89	-	3
<i>1 screen volume purged</i>					
Bladder A2	0.72	0.69	95	-	12
Submersible A2	0.94	0.51	55	-	12
Peristaltic A2	1.31	0.68	52	-	12
A2 (all)	0.99	0.66	67	-	36
<i>Purged to parameter stabilisation</i>					
Bladder A3	0.22	0.23	103	69	12
Submersible A3	0.38	0.22	57	60	12
Peristaltic A3	0.24	0.22	92	82	12
A3 (all)	0.28	0.23	80	72	34
<i>Post-purge sample</i>					
Hydrasleeve A4	0.0021	0.0017	82	92	3

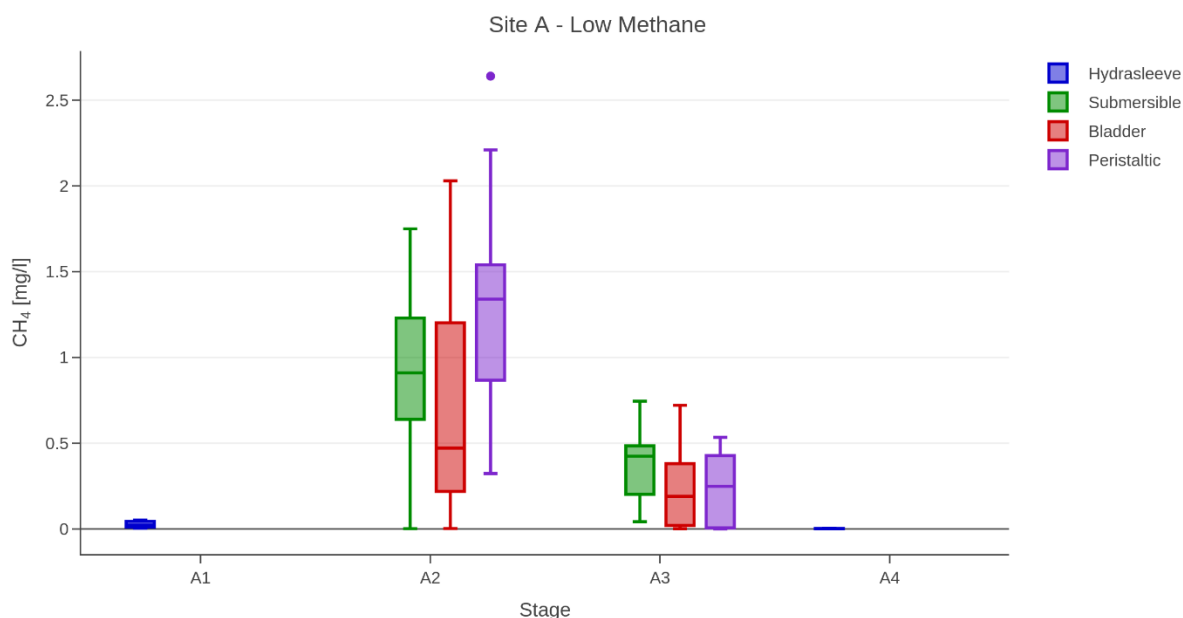


Figure 18 - Site A box plot of CH₄ conc. by pump type. Median and interquartile range (IQR) and outliers at ± 1.5 IQR (same metrics applied to subsequent boxplots).

4.1.3 Site A – Methane concentration sensitivity to sampling protocol

The sensitivity of methane concentration to sampling protocol and purging stage has been summarised statistically (Table 7) and graphically (Figure 19). A hierarchy of mean methane

concentration and accompanying rsd, from highest to lowest values, for each sampling protocol at stages A2 and A3 is given in Table 8 (comparative magnitude indicated).

Key points are:

- Samples collected by all protocols at all stages show high variability with a range of 55-107% rsd
- Open samples collected in A1 compared to A2 and in A4 compared to A3 show lower concentrations (1-2 orders of magnitude), suggesting that lower measured concentrations are related to passive sampling as opposed to active pumping, rather than related to sample collection protocol.
- Samples using the inverted collection protocol give highest methane concentrations in both A2 and A3 stages, with modest rsd values.
- Samples using the upright collection protocol give greater concentrations than those using the closed collection protocol in stage A2, with the lowest rsd. Closed samples result in marginally greater concentrations than upright samples at stage A3, and show the lowest rsd of stage A3.
- Closed samples give moderate to low concentrations in both A2 and A3 stages.
- Open samples consistently give the lowest methane concentrations and high rsd at all stages.
- Measured concentrations fall noticeably between A2 and A3, with similar decreases for upright, inverted and open samples (71-79% decrease), with closed samples seeing a fall in concentration of 60%.

Table 7 - Site A summary statistical data by sampling protocol.

	Mean mg/l	SD mg/l	RSD %	Conc. decrease %	n
<i>Zero-purge Hydrasleeve</i>					
Open A1	0.027	0.024	89	-	3
<i>1 screen volume purged</i>					
Closed A2	0.75	0.54	72	-	9
Upright A2	1.06	0.58	55	-	9
Inverted A2	1.41	0.83	59	-	9
Open A2	0.73	0.49	68	-	9
A2 (all)	0.99	0.66	67	-	36
<i>Purged to parameter stabilisation</i>					
Closed A3	0.30	0.18	59	60	9
Upright A3	0.26	0.20	76	75	9
Inverted A3	0.41	0.28	70	71	9
Open A3	0.15	0.18	117	79	9
A3 (all)	0.28	0.22	80	72	36
<i>Post-purge Hydrasleeve</i>					
Open A4	0.0021	0.0017	82	92	3

Table 8 - Site A hierarchy of methane concentration and rsd

Mean CH₄ Hierarchy	CH₄ RSD Hierarchy
A2 : Inverted > Upright > Closed > Open	A2 : Upright < Inverted < Open < Closed
A3 : Inverted > Closed > Upright > Open	A3 : Closed < Inverted < Upright < Open

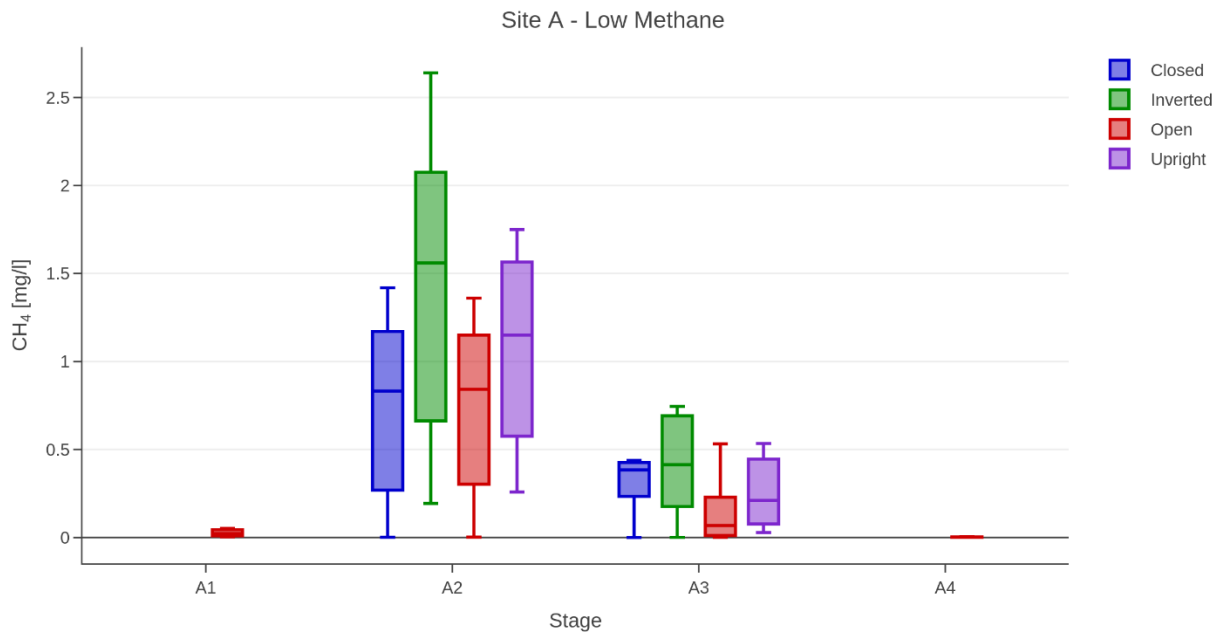


Figure 19 - Site A boxplot for sampling protocol by stage

4.2 SITE B – HIGH METHANE OVERVIEW

The entire dissolved methane dataset obtained from sampling the Site B high methane borehole is shown in Figure 20. Methane concentration across the testing period spans a relatively wide range from 5.4 mg/l to 36.47 mg/l. Mean and sd was 19.10 ± 5.79 mg/l (n=78) with a more conservative rsd of 30% compared to Site A. Summary statistics for the complete dataset can be found in Table 9.

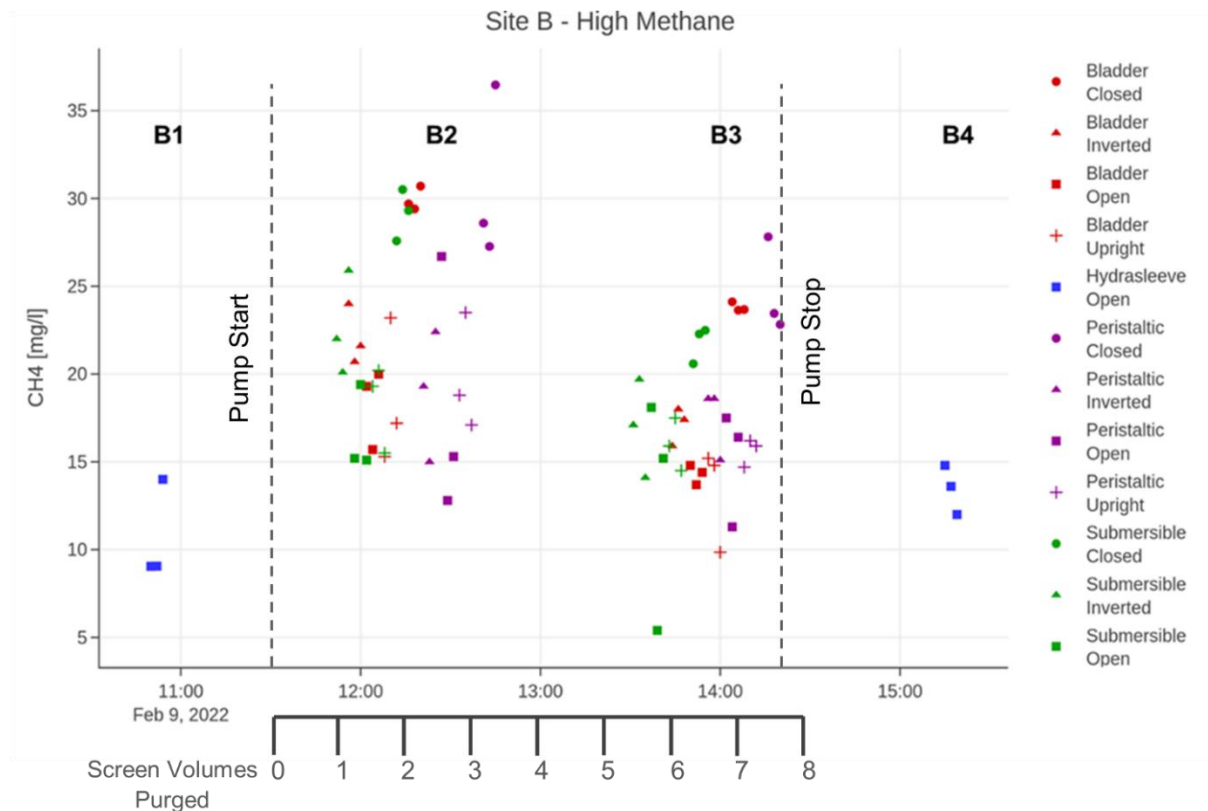


Figure 20 - Site B (high methane) individual point time series plot for all results

4.2.1 Site B - Methane concentration sensitivity to purging method

A statistical summary of methane concentration data for Site B by stage (Table 9) shows moderate variability. Methane concentrations in stage B2 (1 screen volume) are 21% higher than in B3 (parameter stabilisation), a smaller difference than at Site A. Rsd remains constant at 26% between the active pumping stages B2 and B3, indicating that purge volume has little effect on data spread. Stages B1 and B4 give somewhat lower mean concentrations than stage B2 and B3, but the difference is more modest compared to Site A (Site B within the same order of magnitude). There is a surprising 26% increase in concentration between stages B1 and B4 with a reduced rsd of 10% for the latter stage. The trend in decreasing methane concentration with purge volume suggests a lower concentration was expected at B4. Overall, results from Site B show similar trends to Site A in stages B2 and B3, but at Site B measured methane concentrations are much less sensitive to purged volume than at Site A. This makes it easier to differentiate other influencing variables, i.e. pump type and sample collection protocol.

Table 9 - Site B summary statistics for complete dataset and stages.

	Mean mg/l	SD mg/l	RSD %	n	Percentiles				
					5 th mg/l	25 th mg/l	50 th mg/l	75 th mg/l	95 th mg/l
Stage B1 Zero purge samples	10.70	2.86	27	3					
Stage B2 1 screen vol. purge	21.95	5.78	26	36	15.10	17.20	20.40	26.80	30.60
Stage B3 Param. Stabilisation	17.41	4.45	26	36	10.90	14.80	16.80	19.90	23.80
Stage B4 Post purge samples	13.47	1.41	10	3					
Stage B1-B4 Complete dataset	19.10	5.79	30	78	11.08	15.13	18.05	22.74	29.45

4.2.2 Site B – Methane concentration sensitivity to pump type

The sensitivity of methane concentration to pump type and purging stage is shown as a statistical summary (Table 10) and graphically (Figure 21).

Key points are:

- Concentrations measured by passive sampling, stages B1 and B4, are lower than those from other pump type open samples.
- Concentrations from all pump types in stage B2 are moderately variable and have similar mean values. The bladder pump produces the highest measured concentration with lowest rsd, followed by the peristaltic pump, which had highest rsd, and the submersible pump gave the lowest concentrations and had a similar rsd to the bladder pump.
- Stage B3 also gave similar mean concentrations and very similar data variability for the different pump types. The peristaltic pump produces the highest concentrations, followed by the bladder pump, with the submersible pump producing the lowest concentrations.
- However, one anomalously low measurement (5.4 mg/l) was observed in a submersible pump open sample in B3, which significantly affected the mean values. Removal of this point results in an overall mean concentration for submersible pump samples of 17.95 ± 2.98 (17% rsd), which gives the submersible pump the highest mean measured concentrations and lowest rsd.
- The hierarchy of mean concentration is inversely related to rsd for all pump types in stages B2 and B3: i.e., higher mean concentration is accompanied by lower rsd.

- Aside from the noted anomalous point in stage B3, there are relatively insignificant differences in concentration and variability in stages B2 and B3.
- A decrease in concentrations in B3 compared to B2 is also similar for all pump types.

Table 10 - Site B summary statistical data by pump type

	Mean mg/l	SD mg/l	RSD %	Conc. decrease %	n
<i>Zero purge sample</i>					
Hydrasleeve™ B1	10.70	2.86	27	-	3
<i>1 screen volume purged</i>					
Bladder B2	22.23	5.36	24	-	12
Submersible B2	21.68	5.46	25	-	12
Peristaltic B2	21.94	6.91	32	-	12
B2 (all)	21.95	5.78	26	-	36
<i>Purged to parameter stabilisation</i>					
Bladder B3	17.12	4.50	26	23	12
Submersible B3	16.91	4.61	27	22	12
Peristaltic B3	18.20	4.52	25	17	12
B3 (all)	17.41	4.45	26	21	36
<i>Post-purge sample</i>					
Hydrasleeve™ B4	13.47	1.41	10	-26	3

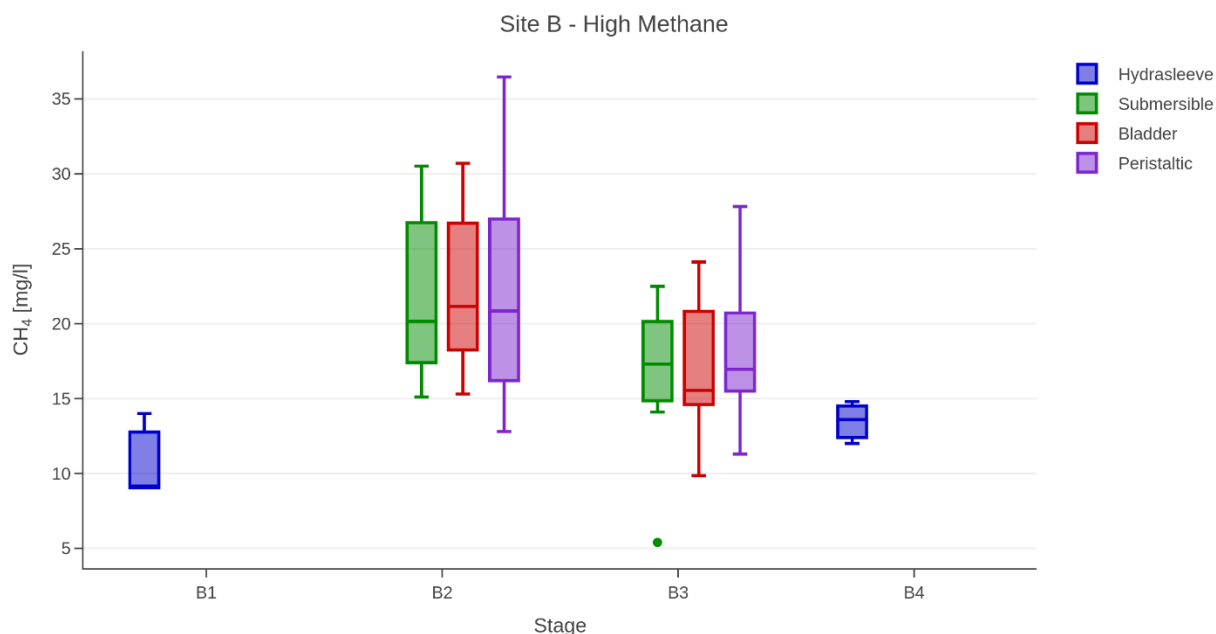


Figure 21 - Site B box plot of CH₄ conc. split between pump type

4.2.3 Site B – Methane concentration sensitivity to sampling protocol

The sensitivity of methane concentration to sampling protocol and purging stage is shown as a statistical summary (Table 11) and graphically (Figure 22). A hierarchy of mean methane

concentration from high to low and the accompanying rsd for each sampling protocol at stages B2 and B3 is given in Table 12 (comparative magnitude indicated).

Key points are:

- Open samples in all stages yield the lowest observed methane concentrations with largest rsd values
- The hierarchy of methane concentrations and rsd is consistent in both B2 and B3 stages with closed samples giving significantly greater concentrations than other sampling protocols and the lowest variability (<10% rsd)
- Inverted samples give ~2 mg/l greater mean concentration than upright samples in both B2 and B3 stages with comparable rsd
- Observed mean concentrations for upright samples are ~1 mg/l higher than for open samples, with variability ~10% greater amongst open samples.
- Rsd values follow the inverse of mean concentration (i.e. higher concentrations have lower rsd)
- Changes in measured concentrations between B2 and B3 stages are similar for all methods (~21% decrease).
- Open passive samples show a 26% higher concentration in stage B4 than stage B1 that appears anomalous compared to the decline in concentration generally seen with purging time. This may be due to variations in the positioning of the passive sampling device and, therefore, the exact location of sample collection within the borehole between stages: the samples in stage B1 and B4 could quite likely have been collected from slightly different horizons/flow inputs.

Table 11 - Site B statistical summary of methane concentration by stage and sample collection protocol

	Mean mg/l	SD mg/l	RSD %	Conc. decrease %	n
<i>Zero-purge Hydrasleeve</i>					
Open B1	10.70	2.86	27	-	3
<i>1 screen volume purged</i>					
Closed B2	29.95	2.71	9	-	9
Upright B2	18.90	3.00	16	-	9
Inverted B2	21.22	3.08	15	-	9
Open B2	17.72	4.16	24	-	9
B2 (all)	21.95	5.78	26	-	36
<i>Purged to parameter stabilisation</i>					
Closed B3	23.43	1.95	8	22	9
Upright B3	14.95	2.13	14	21	9
Inverted B3	17.17	1.82	11	19	9
Open B3	14.09	3.85	27	21	9
B3 (all)	17.41	4.45	26	21	36
<i>Post-purge Hyrdasleeve</i>					
Open B4	13.47	1.40	10	-26	3

Table 12 - Site B methane concentration and rsd hierarchy

Mean CH ₄ Hierarchy	CH ₄ RSD Hierarchy
B2 : Closed > Inverted > Upright > Open	B2 : Closed < Inverted ~ Upright < Open
B3 : Closed > Inverted > Upright > Open	B3 : Closed < Inverted ~ Upright < Open

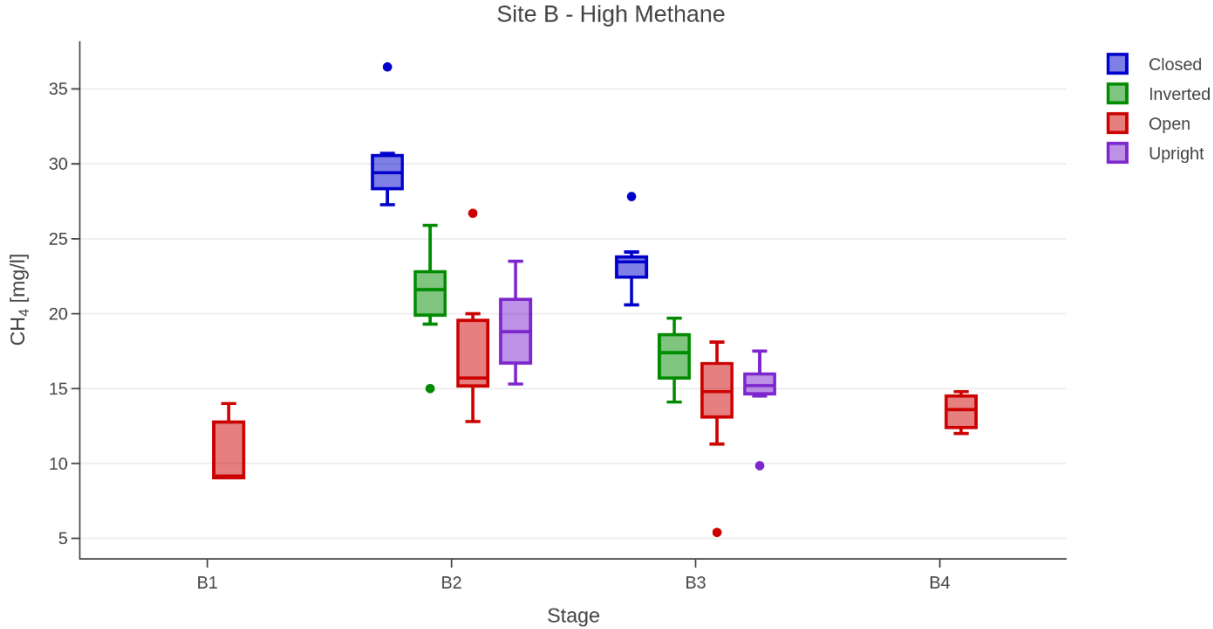


Figure 22 - Site B boxplot of methane concentration split between sample collection protocol

4.3 SAMPLE COLLECTION PROTOCOL CROSS-PLOT COMPARISONS

Cross-plot comparisons of the sample collection protocols are presented below comparing the various sample collection protocols against the closed samples (Figure 23, Figure 24 & Figure 25) followed by cross comparison of the two semi-closed methods (Figure 26). Points are shown as ‘cross-hair’ mean and standard deviations. The low number of sample points (n = 3 for each point) may make statistical inferences weak, but the plots overall nevertheless are indicative of emerging trends. Linear model fits using Pearson’s correlation were carried out for each dataset and also on datasets split by site, with equations for model fit lines given with proportion of variation (R²) and significance value. Significance values of <0.05 were deemed to be statistically significant.

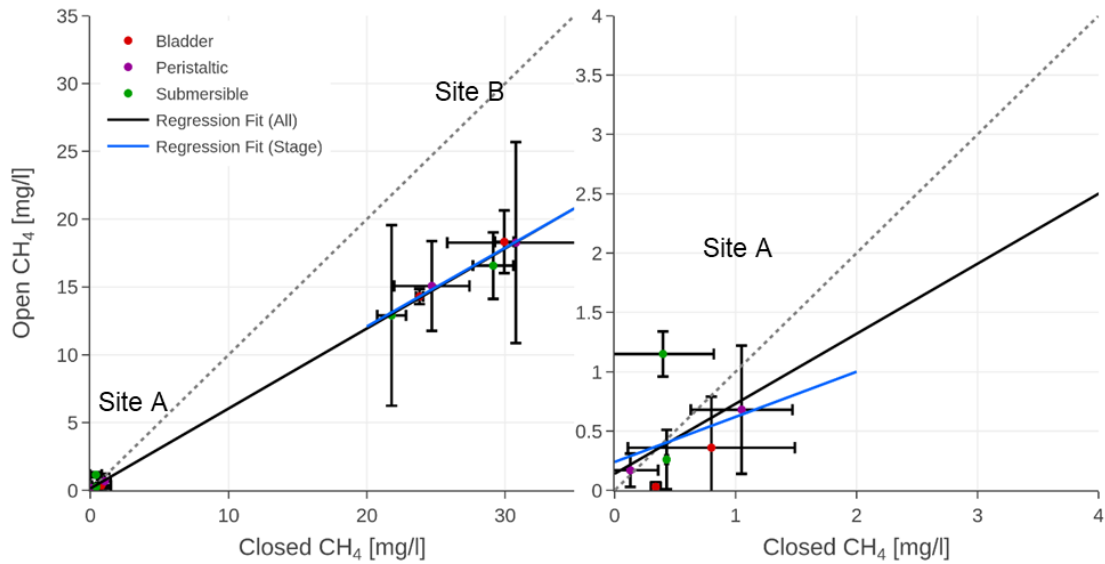


Figure 23 - Cross-plot of closed samples against open samples showing cross-hair mean and standard deviations of data from each pump type at each stage. Left plot shows all data, right plot shows scaled down axes to display Site A data in detail. Dashed line indicates 1:1.

A comparison of closed to open sampling protocols (Figure 23) reveals consistently higher closed concentrations across the measured methane concentration ranges. Linear model fits for the whole dataset and for the individual Site A and Site B sample cohorts gave equations for methane concentration of:

- All Data: $[\text{Open}] = 0.59 [\text{Closed}] + 0.14$, $R^2=0.99$, sig. <0.001 ($n=12$)
- Site A: $[\text{Open}] = 0.38 [\text{Closed}] + 0.24$, $R^2=0.97$, sig. = 0.59 ($n=6$)
- Site B: $[\text{Open}] = 0.58 [\text{Closed}] + 0.48$, $R^2=0.94$, sig. <0.001 ($n=6$)

This relationship weakens as low concentrations are approached, due to high variation in the data.

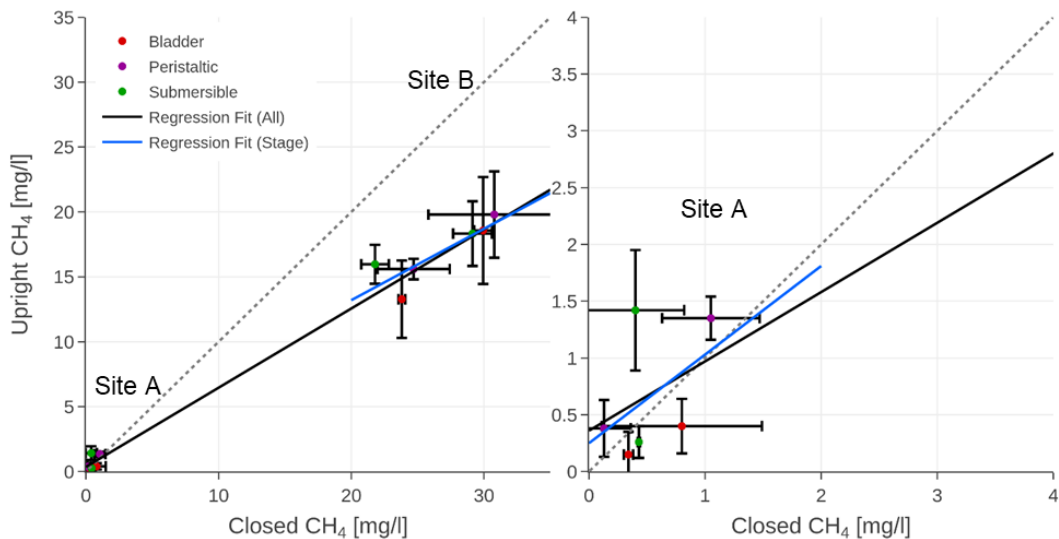


Figure 24 - Cross-plot of closed samples against upright samples showing cross-hair mean and standard deviations of data from each pump type at each stage. Left plot shows all data, right plot shows scaled down axes to display Site A data in detail. Dashed line indicates 1:1.

A comparison of closed to upright sampling protocols (Figure 24) indicates concentrations from both are generally similar at low methane concentrations, but closed samples result in greater concentrations in the group of high concentrations. Linear model fits for the whole dataset and the individual Site A and Site B sample cohorts gave equations for methane concentration of:

- All Data: $[Upright] = 0.61[Closed] + 0.36$, $R^2=0.99$, sig. <0.001 (n=12)
- Site A: $[Upright] = 0.78[Closed] + 0.25$, $R^2=0.21$, sig. =0.36 (n=6)
- Site B: $[Upright] = 0.55[Closed] + 2.20$, $R^2=0.73$, sig. <0.05 (n=6)

This relationship weakens as low concentrations are approached, due to high variation in the data, such that Site A fails to produce a statistically significant result. The whole dataset relationship is very similar to that of the closed and open samples relationship.

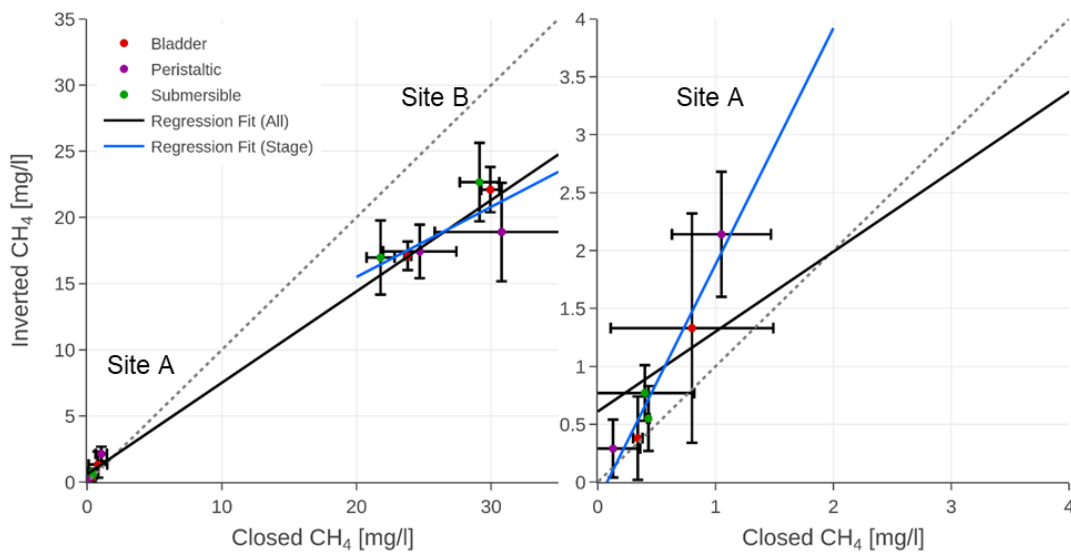


Figure 25 - Cross-plot of closed samples against inverted samples showing cross-hair mean and standard deviations of data from each pump type at each stage. Left plot shows all data, right plot shows scaled down axes to display Site A data in detail. Dashed line indicates 1:1.

Figure 25 shows a comparison of closed to inverted sampling protocols and reveals significantly higher values from inverted protocol samples at low methane concentrations, but noticeably higher concentrations from closed sample protocols at high concentrations. Linear model fits for the whole dataset and the individual Site A and Site B sample cohorts gave equations for methane concentration of:

- All Data: $[Inverted] = 0.69[Closed] + 0.61$, $R^2= 0.99$, sig. <0.001 (n=12)
- Site A: $[Inverted] = 2.04[Closed] - 0.16$, $R^2= 0.94$, sig. <0.01 (n=6)
- Site B: $[Inverted] = 0.53[Closed] + 4.9$, $R^2= 0.60$, sig. = 0.07 (n=6)

There is a strong significant relationship at Site A, but Site B is just over the significance level, possibly because of skewed results from highly variable peristaltic pump data at stage B3.

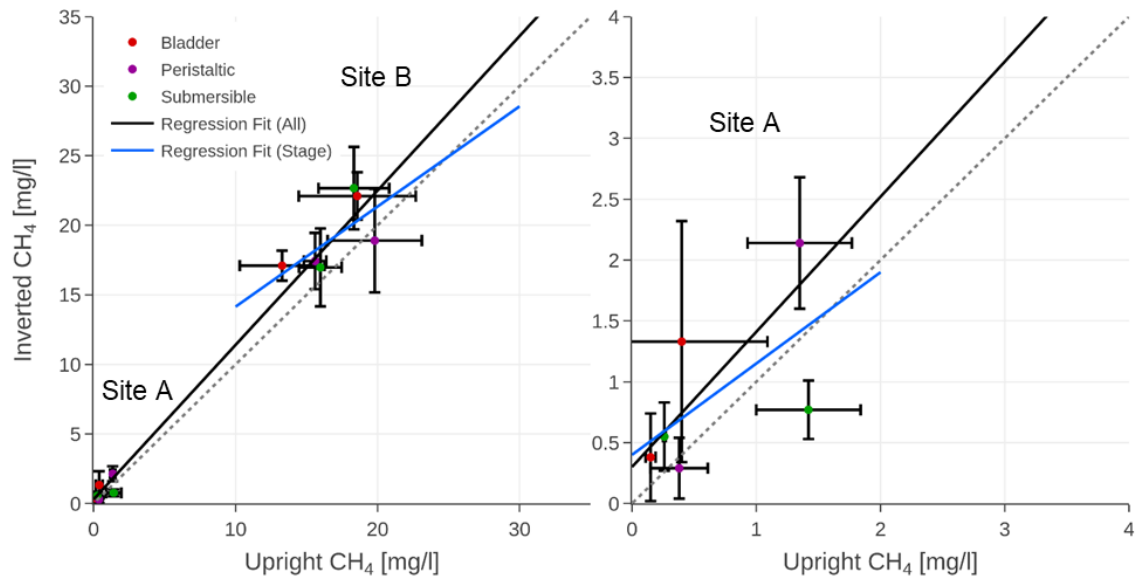


Figure 26 - Cross-plot of upright samples against inverted samples showing cross-hair mean and standard deviations of data from each pump type at each stage. Left plot shows all data, right plot shows scaled down axes to display Site A data in detail. Dashed line indicates 1:1.

A comparison of the semi-closed protocols - inverted VOA and upright VOA - (Figure 26) confirms a generally very close relationship for the entire dataset with linear model fits as follows:

- All Data: $[\text{Inverted}] = 1.11[\text{Upright}] + 0.30$, $R^2=0.98$, sig. <0.001 ($n=12$)
- Site A: $[\text{Inverted}] = 0.75[\text{Upright}] + 0.40$, $R^2=0.37$, sig. = 0.202 ($n=6$)
- Site B: $[\text{Inverted}] = 0.72[\text{Upright}] + 6.95$, $R^2=0.46$, sig. = 0.14 ($n=6$)

Model fits for individual Site A and Site B data perform relatively poorly with specific pump types (e.g. submersible at A2 and peristaltic at B2) pulling site data away from the overall fit. A significant relationship is seen in the entire data fit where inverted samples show elevated concentrations across the concentration range compared to upright samples.

4.4 BLANKS

Table 13 displays analytical results from blank samples. Although detects of methane were found in all blank samples, the concentrations reported were not of concern as all detections were orders of magnitude below that of any samples from Sites A and B. There may have been some latent dissolved methane in water within the pumps following the first round of testing at Site A, although this is not of a magnitude that would skew results.

Table 13 - Blank sample results

Blank Type	Fill Method	Laboratory	CH ₄ Conc. (mg/l)	Detection Limit (mg/l)
Static (direct from MQ Container)	Direct-Fill (Open)	ALS Environmental	0.0024	0.001
	Closed	BGS Wallingford	0.0001 (detected)	0.0001
Pumped (peristaltic)	Direct-Fill (Open)	ALS Environmental	0.0038	0.001
	Closed	BGS Wallingford	0.0101	0.0001

5 Discussion

5.1 COMPARISON OF PURGING METHODOLOGIES

The results presented in Sections 4.1.1 and 4.2.1 demonstrate an overall decrease in measured methane concentrations from stage 2 (sampled after one screen volume purged) to stage 3 (sampled after stable parameters reached) at both sites. Site A exhibits a much larger mean percentage decline (~72%) than Site B (~21%). An independent samples t-test reveals the decrease at both sites to be very significant (Site A: $t(70) = 6.0926$, $p < 0.0001$, Site B: $t(70) = 3.7332$, $p < 0.001$), where a significance level of < 0.05 is applied. Although the spread of data appears to reduce between stages 2 and 3 at both sites, %rsd increases (13% greater) at Site A, due to the large decrease in concentration between A2 and A3, but remains relatively constant at Site B. Stage 1 and Stage 4 passive samples appear anomalously very low for Site A compared to open samples in stages 2 and 3, and somewhat low for Site B sample data, and have possibly failed to sample screen-area groundwater and instead sampled stagnant casing waters. Based on the pumped sample trends of declining concentrations over stages 2 and 3 it is possible that had near-zero purge pumped samples been taken at stage 1 these could have returned a study maximum concentration.

A number of factors may contribute to the observed decrease in methane concentrations during the active pumping stages. A borehole with low ambient groundwater through flow may be acting as a 'sink' for methane in the surrounding aquifer, with, for example, diffusion from surrounding aquifer units of dissolved-phase methane, or possibly discrete gaseous phase migration of methane from some strata. The observed methane concentration decline when pumped suggests that even under low flow sampling conditions the fluxes of methane into the well screen under ambient flow conditions cannot be sustained, i.e. is flow rate limited. Groundwater flow into the borehole screened section from the fractured clay units at both sites dominantly occurs through fracture networks. The declining methane concentrations with purging indicate lower concentration groundwater inflow contributions become increasingly important with time and suggest there is flow rate-limited mass transfer of methane into the predominant fracture flow groundwater entering the borehole. The greater concentration decline with purging at low methane Site A may be explained by the presence of more stratified groundwater, which is suggested by both the parameter time series and downhole profiles.

The evolution of methane concentration throughout purging shown in detail in this study is not usually seen at individual sampling sites, as time-series methane sampling is rarely undertaken. Both site A and B datasets support such time-series data are both valuable for understanding methane presence and behaviour around individual boreholes, and can support decision making on appropriate purging times for routine monitoring. Such data can help decide whether a stable methane concentration can be reasonably reached for a specific borehole, or if there is likely to be significant sensitivity of measured concentrations to purging.

The observed sensitivity of measured concentrations to purging also raises the question as to what a representative (or otherwise appropriate) dissolved methane sample is, and at what point in a purge sampling should be done. At both sites, sampling after parameter stabilisation resulted in lower measured concentrations than sampling earlier at lower purge volumes. This could underestimate any risks present, particularly at sites with low methane concentrations such as Site A. The data from both Site A and Site B reinforce the importance of maintaining a consistent purging protocol designed to optimise repeatable sampling and like-for-like comparison of monitoring data over time. Monitoring of both parameter values and purged screen volumes during purging would provide more information and context when assessing concentrations over time. For example, observed variations in time series data could be explained by the number of screen volumes purged or the time taken to reach parameter stabilisation, rather than interpreted as real changes in methane in the groundwater environment.

It is difficult to make conclusions about the applicability of the zero-purge method, as only one collection method was available to be tested, and it proved to obtain the lowest methane

concentrations. Based on the stage 4 results, in which concentrations were lower at both sites than in stage 3 despite little or no additional purging between these stages, the main reason for low concentrations from passive sampling may be the lack of control on precise sampling depth, which may enhance the effect of groundwater stratification over the borehole screened section. It is not possible to control when the top valve of the passive sampler opens over a 1.5 m length of borehole, so the passive samples may be collected from different depths each time and at different depths than the active pump intakes. They may also have been collected from above the screen, in the cased section of borehole if this valve failed to open adequately in the screened section. To reduce uncertainty in sampling depth and further assess the no purge method, a quasi-passive sample could be collected using a low volume pump (e.g. peristaltic), to retrieve a slug of water with minimal to no purging.

5.2 COMPARISON OF PUMP TYPES

Based on the results presented in Section 4.1.2 for Site A, it is difficult to make firm conclusions on the influence of pump type. The observed range in mean and median values suggests that pumped methane concentrations are sensitive to the pump used, with the peristaltic giving the highest concentrations and the lowest (rsd) variability for stage A2 but the submersible for A3. The bladder pump gives the lowest mean and median concentrations in both stages A2 and A3, which is surprising as its bladder-based pump design seems the most suited of the pumps tested to minimising loss of volatile or dissolved gas constituents. The bladder pump also gives the greatest rsd and variability of concentrations. A possible reason for these results is that it was the last pump of the three sampled in stage A3, and as such was most likely to return lower concentrations (and therefore show negative concentration bias) due to the general trend of declining concentrations with purging. However, this was not seen in stage A2 where the peristaltic pump was the last of the three sampled.

A one-way ANOVA test shows that there is no significant difference between pumped sample groups in stage A2, although this result is borderline ($F(2, 33) = [2.617]$, $p = 0.088$), where a significant p value is considered to be <0.05 . In stage A3 there is no significant difference between pumped group concentration data ($F(2, 33) = [1.685]$, $p = 0.201$). Tukey's HSD analysis shows no significant pairwise differences between pumps.

Site B results, presented in Section 4.2.2, show that methane concentrations between pump types are very similar in stages B2 and B3. The range in pump mean concentration in stage B2 is ~2% with rsd 25-32%. This suggests that measured concentrations are not particularly sensitive to pump type at Site B and would on average give similar results. The bladder pump gives a marginally greater mean methane concentration in stage B2, although the peristaltic pump gives the greatest (and smallest) single point observations, evident from the 5th – 95th percentiles.

A one-way ANOVA test confirms that there was no statistically significant difference between the three active pump types in either stage B2 ($F(2, 33) = [0.026]$, $p=0.974$) or B3 ($F(2, 33) = [0.28]$, $p = 0.758$). Further Tukey's analysis shows no significant pairwise differences between pumps.

Site B results could indicate that any of the active pump types will give similar results when sampling for dissolved methane at high methane concentration sites. However, the shallow groundwater level at Site B means that the peristaltic pump was tested under very favourable conditions, as it does not need a great deal of suction pressure in order to retrieve a sample. With deeper groundwater levels, an increased suction pressure is needed to lift groundwater to surface for sampling, which could increase the probability of a negative concentration bias in measured methane concentrations.

All passive grab (Hydrasleeve™) samples had lower concentrations at Site B and substantially lower at Site A than any of the active pump sample concentrations. As discussed above, this may be because the depth at which the passive sampler collects samples can't be closely controlled, depending both on where the top valve is and on when the sampler is completely filled. By contrast, the depth of the active pump intakes was fixed at the mid-screen depth. The passive samples may therefore have been collected from different depths each time from the

mid-screen upwards, possibly extending into the cased off section of the borehole. The sampler filling procedure may also not be consistently repeatable. Measured concentrations may also be affected by volatility losses in the open and unpressurised passive sampler, especially as its retrieval to surface is relatively slow with progressively decreasing hydrostatic pressure, allowing increased degassing potential as the sample is brought to the surface. There may be further volatility loss during the relatively slow transfer to sampling vessels compared to active pumps.

In summary, this study suggests that reported methane concentration has little sensitivity to active pump type used when considered in isolation to sample collection protocols (i.e. closed, inverted etc.). Particularly at Site B, variability in measured concentrations is consistent between pumps and the observed variability in concentration within stages primarily relates to the sample collection protocol. The evidence from Site A is less convincing, but may be explained by the high sensitivity of Site A to a declining methane concentration with purge time, meaning intra-stage comparisons of pumps may offer negative bias towards pumps sampled later within the stage. The passive sampler appears to be an ineffective method for obtaining no purge samples, possibly because it is subject to significant volatility loss. However, it is also probable that the passive sampler did not sample the same mid-screen groundwater as that sampled by the active pumps, and hence a like-for-like comparison of sampled groundwater between the passive sampler and active pumps was not possible.

5.3 COMPARISON OF SAMPLE COLLECTION PROTOCOLS

The results in Sections 4.1.3 and 4.2.3 show differences between Site A and Site B. They suggest the closed sampling system results in the highest dissolved methane concentrations of all the protocols tested in most cases, with consecutively decreasing concentrations from inverted samples, upright samples and open samples. This pattern is not as clear at Site A, with low concentrations, where concentrations from inverted and upright samples are similar or higher than from closed samples, although inverted samples display significant variability. However, these low concentration relationship trends should be interpreted cautiously, because of the significant sensitivity shown at Site A in this study to purge volume and, in consequence, the increased likelihood that sample collection protocols later in the test are subject to negative bias. Collecting closed samples last at each pump may account for the notably lower and variable concentrations from closed samples at Site A compared to Site B. Open samples gave the lowest methane concentrations. One-way ANOVA analysis suggests there is no statistically significant difference between sample collection methods in stages A2 or A3, although the very large variability observed in the datasets suggests that none of the methods are adequate to produce reliable point results at Site A, with low methane concentrations. In contrast, Site B shows statistically significant differences between means of sample collection protocols (ANOVA – $p < 0.05$):

- A2 – $F(2, 32) = 2.363$, $p = 0.0896$
- A3 – $F(2, 32) = 2.196$, $p = 0.108$
- B2 – $F(2, 32) = 25.51$, $p < 0.001$
- B3 – $F(2, 32) = 24.23$, $p < 0.001$

Tukey's multiple mean comparison of the Site B data suggests that the closed sampling method produces statistically greater concentrations than other methods for both B2 and B3 stages. Whilst the other protocols do not show statistically significant pairwise differences, a hierarchy is apparent across the range of observed concentrations which is consistent at both B2 and B3: Closed > Inverted > Upright > Open, which is followed by an inverse rsd hierarchy (i.e. high concentration is accompanied by low rsd).

The above order is what would be expected based on the literature. Whilst it is difficult to replicate the hydrostatic pressure of the sample point with pumps during surface sampling at low flow, the closed protocol benefits from applying back-pressure to samples and thereby minimising degassing. The pressure applied is pump dependent, and is likely to influence measured concentrations. The semi-closed methods, collecting samples under water at surface, will be close to atmospheric pressure and subject to degassing: this was obvious in the sample

lines and accumulation of headspace gas in the Inverted VOA vials at Site B, but not Site A, consistent with their high and low methane concentrations. However, semi-closed methods have reduced water-air interfacial surface area contact with the atmosphere compared to open samples, where exsolution and volatilisation are expected to be greatest, which is consistent with the study results with the lowest concentrations measured in open samples.

When comparing both semi-closed methods, inverted samples give higher concentrations than upright, with comparable rsd values. This is not consistent with the existing literature or with reported practitioner concerns with inverted sampling protocols (EA, 2021). These concerns related to exsolution into the inverted vial and the accumulation of headspace containing exsolved methane building over time that could potentially lead to positive or negative bias in samples. This is in part dependent on how samples are handled in the laboratory (if any submitted gas is analysed) and the temporal profile of concentrations passing through the vial during collection and partitioning back of gaseous methane into the aqueous phase. Whilst degassing into the headspace was observed at Site B, it does not seem to impact the methane concentrations measured compared to the upright method in this study.

Upright sample concentrations are similar to open sample concentrations, but consistently slightly higher, with significantly lower variability. This presents a quick-win opportunity to improve the quality of data collected by switching from the open to the upright method.

The rapid change in methane concentration with purging at Site A means that it is not well suited to the experimental design of this study, in particular the relatively long time (45 - 55 minutes) required to take the series of multiple comparative samples. This may not be an issue for ongoing monitoring where only a single sample need be taken, but within this study it means it is not possible to draw reliable conclusions on preferred sampling protocol, and it is difficult to make comparisons about sampling protocols at low methane concentration (i.e. Site A) versus high concentration (i.e. Site B) sites.

The expanded boxplot (Figure 27) for Site B shows possible sensitivity of measured results to the combination of sample collection protocol and pumping method selection. Closed samples collected using the bladder and peristaltic pumps give higher mean concentrations in both B2 and B3 stages than closed submersible samples. This could be due to the greater pressure that can be applied by bladder and peristaltic pumps than submersible pumps under low flow conditions, with a greater capacity to minimise exsolution of dissolved gas. There is also an obvious increased concentration spread from closed samples obtained with the peristaltic pump than the bladder pump, which could be due to the degree to which applied sample pressure is controllable. A peristaltic pump will continue to build pressure, but the user does not have a quantifiable way of measuring this and is unable to keep it constant between samples. We also recognise that variability in results from the peristaltic pump may be caused by both the negative and positive pressure applied to the sample and the time needed for dissolved and gaseous methane to re-equilibrate. The bladder pump is controlled by a compressor allowing the user to set the pressure applied during each pump cycle. Taking a sample at the same point during the pumping cycle allows for increased repeatability. In summary, the selection of pump type may be important in Closed sample collection.

Site A does not show any discernible patterns between pump methods and sample methods. Any relationships are likely to be masked by the sensitivity of methane concentrations to purging and the high variability of data.

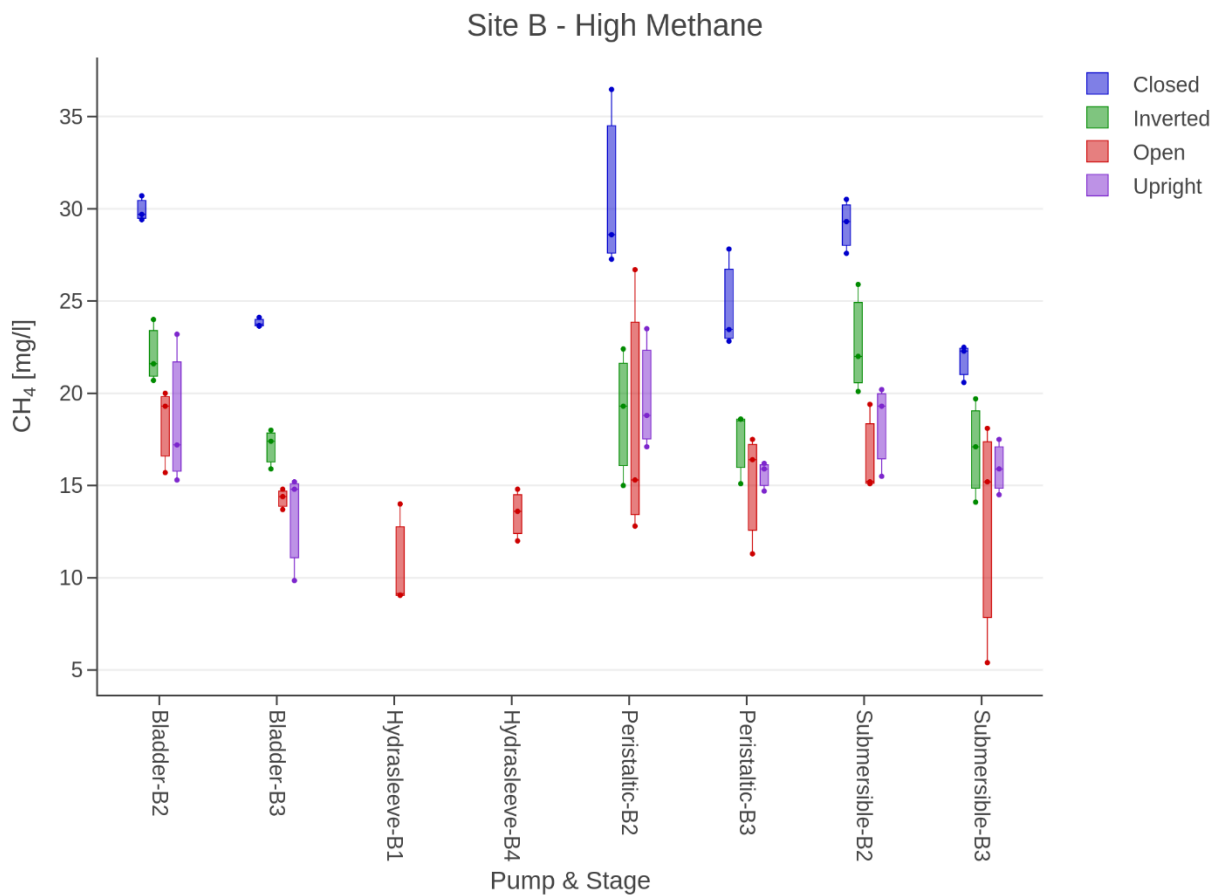


Figure 27 - Site B expanded boxplot of pump method and sample collection protocol between purging stages

5.4 COMPARISON WITH PREVIOUS MONITORING DATA

The vast majority of historical baseline dissolved methane data for Sites A and B (Figure 4 and Figure 5) were collected using the closed sampling protocol and a submersible centrifugal pump. Stable physico-chemical parameters were used as an indicator for sampling representative groundwater. A low-flow purge was not used and pumping rates varied between 3 and 5 l/min, which is 2 – 3.3 times the aggregate test rate for Site A and 2.9 – 4.8 times the aggregate test rate for Site B in the current study. In the current study, the closest results to the baseline data are from the equivalent sampling methodology, using submersible pump and closed sampling protocol sampled when chemical parameters had stabilised, i.e at stages A3 and B3 (Table 14). Given this, the study results may provide insight into variations in the historical monitoring record, including reasons for dissolved methane variability: i.e., whether the majority of historic variation is a result of naturally occurring variability in methane concentrations in groundwater or induced by sampling protocol or personnel variability.

The historic mean concentration at Site A of 0.28 mg/l (Table 14) is 0.12 mg/l lower than the stage A3 study mean of 0.40 mg/l. The rsd of the study A3 triplicate data of 2.5% is an order of magnitude lower than the baseline record rsd of 60.7%. This suggests that the majority of variation in dissolved methane concentration over time is 'real', the result of in-situ natural process variation controlling methane fluxes to the borehole, rather than due to the sampling process. The data from Site B also indicate that natural processes may be the main control on historical variability in concentrations.

However, this study resulted in a very wide range of concentrations from both sites from different pumps, purging timeframes/criteria and sample collection protocols. The overall variability is largest at Site A and underlines the critical importance of maintaining a consistent

sampling protocol as variations in protocol can result in significantly altered methane observations. The range of concentrations historically observed at Site A (c. 0.05 - 0.8 mg/l) is significantly exceeded by the range of concentrations (0.001 - 2.5 mg/l) observed in test sampling at Site A over a few hours of pumping in this study. It is possible that even relatively small changes in sampling protocol, such as the criteria for stabilised parameters or slightly varying execution by different personnel or sampling organisations, may lead to variability in concentrations sampled that is not 'real'.

Table 14 - Statistical data for the historical baseline methane record at Sites A and B and study data for samples collected using a closed sampling procedure and submersible pump with Stage 3 stable parameter purging.

	Mean (mg/l)	sd	%rsd	n
Site A				
Historic record 2016-21	0.28	0.17	60.7	36
A3	0.40	0.01	2.5	3
Site B				
Historic record 2016-21	29.59	7.60	25.7	35
B3	21.80	1.04	4.8	3

5.5 DISSOLVED METHANE MONITORING IN GROUNDWATER

The sensitivity of sampled methane concentrations to sample collection protocol, pumping method selection and purging demonstrate the importance of sampling campaigns using a consistent methodology with specific pumps deployed in a consistent way, identical purging volumes or stabilisation criteria, and a specific sample collection protocol, in order to generate robust, representative temporal records. Valid cross comparison of concentration data from different organisations requires overall sampling protocols to be as similar as possible. Any change in protocol should be done with an overlap period of simultaneous application of old and new protocols, as far as is practically possible, to enable reliable continuation of the historical record.

Both sites tested in this study showed declining methane concentration with time and purging and it is possible that a more effective pre-purge passive sampling would have shown even higher concentrations, making the decline even more significant. It could be argued that more extended purging results in samples with lower methane concentrations, which would underestimate assessments of representative local methane levels and any risks posed by methane present. As with all environmental monitoring, the specific objectives of methane sampling should be clearly identified to enable appropriate protocol selection, especially where it is known that sampled methane concentrations are significantly sensitive to the selected purging protocol.

6 Conclusions and Application

6.1 CONCLUSIONS

Analysis of the study data presented a significant challenge, in part due to significant and surprising variation in dissolved methane concentrations measured at the low methane site (Site A). This was attributed to some flow stratification within the well screen, with discrete inputs of varying methane concentration leading to significant sensitivity of sampled methane to purging and hence the purging protocol adopted. This was also seen at Site B, but to a lesser extent. Both sites exhibited obvious declining methane concentration trends with purging, which may be because both boreholes are acting as local methane sinks or provide environments conducive

to methanogenesis. From the observed declining concentration trends in the study data with purging, an unpurged methane sample from the well screen could potentially return a maximum dissolved-phase concentration (although zero purge samples appeared anomalously low in this study, likely a result of the passive sampling mechanism). Such sensitivities endorse the wider need for increased reconnaissance use of time-series sampling of methane concentrations with purging (rarely undertaken at sites) to discern purging sensitivities and inform decision making on purging protocol adoption for long-term monitoring.

The high methane concentration Site B presented more consistent data that allowed meaningful comparisons between purging, pump and collection methods and the sensitivity of sampled methane to these variables. Although the complexity of the low methane concentration Site A data makes it difficult to compare the sensitivity of methane results at low versus high methane concentration sites, it is likely that most conclusions drawn from Site B could also apply to lower concentration sites such as Site A. Higher concentration sites are more likely to have the added complexity of increased potential for methane exsolution. The following main study conclusions are hence primarily drawn from the results at Site B:

Pump selection:

- The Hydrasleeve passive sampler consistently give the lowest methane sample concentrations, possibly due to a combination of filling mechanism (which makes the exact sample point unknown) and sample exposure to atmospheric pressure as only open samples are possible.
- The different active pumps tested resulted in no statistical difference in sampled methane concentrations – noting though the nuances below.
- Sampled methane concentrations were sensitive to the combination of pump type and sample collection protocol - closed samples are particularly sensitive to pump type, giving higher concentrations when sampled with bladder and peristaltic pumps, which is ascribed to their ability to provide high back-pressure to samples at low flow, reducing exsolution losses, unlike the submersible pump.
- The bladder pump is preferred for closed sample acquisition as it delivered samples of very low variability that may be reasonably attributed to the bladder pumping mechanism and controllability of the applied back pressure.
- The peristaltic pump was tested under very favourable low depth to water conditions and hence, recognising the wider literature, is best used where groundwater level is shallow. It may not be appropriate for use where groundwater level is deeper, where there is increased potential for degassing from the increased suction pressures required to bring the sample to surface.

Sample collection protocol selection:

- The closed sample collection protocol consistently produced the highest concentrations of dissolved methane with the lowest variability across the pumping methods tested.
- Closed sample collection is hence the preferred collection protocol of choice although it is recognised that its commercial availability is limited (in the UK).
- The semi-closed inverted and upright methods yielded concentrations lower than closed samples, with inverted samples resulting in slightly greater methane concentrations than upright.
- Previous literature concerns around the accumulation of exsolving gas in inverted samples were not supported by the results of this study, although these concerns remain valid. Where degassing at surface is apparent, the upright method is recommended.
- Open samples consistently produced the lowest observed methane concentrations and should only be used where closed or semi-closed sampling is impractical.
- Switching protocols from open sampling to upright sampling is widely commercially supported, requires minimal or no investment but is likely to produce more robust, representative dissolved methane concentration data, with reduced variability.
- The observed sensitivity of methane concentrations to the various aspects of sampling procedure shows that comparing methane data not collected using identical

methodologies is not straightforward. The details of sampling protocols should be considered when comparing different datasets.

6.2 APPLICATIONS

The study findings reasonably align with the wider literature on sampling dissolved concentrations of methane in groundwater collated in a forerunner review (EA, 2021). Combining this study findings and the previous review, a concise 'lookup' document is presented to assist practitioners in their 'Groundwater methane sampling protocol development'. The document is not intended to be prescriptive, but an aid to development of a robust groundwater sampling protocol. The document provides a logical, numbered flow of thirteen areas of consideration under the headings:

- Site selection
- Pump/sampler selection – deployment
- Supporting – reconnaissance measurements
- Sample collection
- Protocol – data management and wider use

The document is intended to have generic value applicable to the variety of sites where groundwater sampling for methane might be undertaken, including the monitoring of oil and gas sites, landfill sites, petroleum hydrocarbon contaminated land, near coal mines, geothermal sites and in strata naturally containing high levels of organic matter.

The document is provided in Appendix 2.

6.3 RECOMMENDATIONS FOR FURTHER FIELD-BASED RESEARCH

Two possible field-based research studies are briefly outlined below that would provide suitable follow-on studies to further support the development of groundwater methane sampling protocols, along with other suggested areas of possible further study.

Pressurised closed sample acquisition

An acknowledged research gap in this study design was the lack of collection of pressurised closed samples that retain the at-depth, in-situ groundwater pressure. Such samples provide the best - 'gold standard' - approach to minimising sample degassing and would ideally be used when groundwater is sampled from moderate to great depth below the water table (>20m), especially at sites thought to have high methane concentrations that are prone to bubble formation and degassing. Pressurised closed sample acquisition is very rarely undertaken by the groundwater methane sampling community. A research study on pressurised closed system acquisition could be conducted at with differing hydrogeological settings to provide a broad evidence base. Such a study could comprise:

- Development of an in-situ sampling device capable of pressurising and sealing a groundwater sample in a sampling container at depth, based on a modified version of a device developed by Banks et al. (2017) that was modelled on an oil industry device;
- Comparative testing of the developed in-situ sampling device against the closest available commercial device, which is likely to be the Solinst discrete interval sampler. A particular challenge would be to compare sample transfer methods from the sample device(s) to the sample vessel while retaining pressurised sample conditions;
- Comparative testing against closed sample acquisition via conventional pumps (bladder etc.) as used in the study presented.

Zero-purge – borehole initial methane condition sampling

Effective zero-purge / passive / grab sampling of methane under ambient groundwater flow conditions in the screened section of a borehole and the cased water column above, in order to establish initial methane borehole conditions before active sampling, remains an outstanding research need. The rationale for understanding this includes:

- zero purge is widely used by practitioners due to its ease and cost effectiveness;
- boreholes may act as a local sink for methane and zero purge concentrations may be higher than any purged concentrations;
- methane degassing in the water column may lead to a varying methane profile with depth;
- borehole methane short-circuiting;
- pressurised closed system samples are zero-purge samples;
- borehole initial methane condition informs both zero purge and active purged protocols;
- the presented study failed to provide a confident initial condition zero-purge sampling assessment.

A research study on zero-purge borehole initial methane condition could valuably be undertaken at both Site A and Site B and other sites and may comprise:

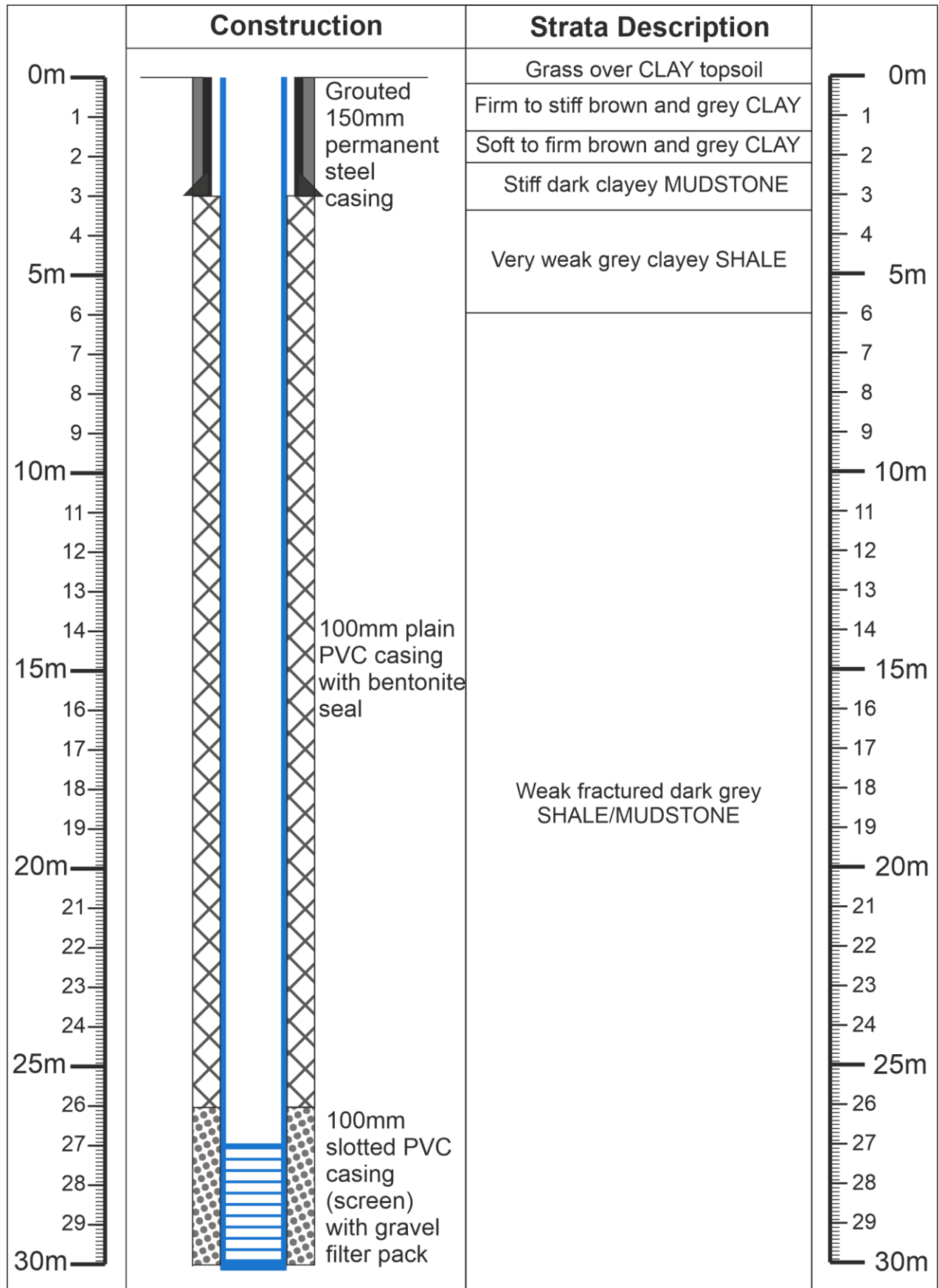
- Initial borehole condition assessment of methane occurrence and distribution in borehole standing water column via a combination of approaches to compare their suitability:
 - TDGP (total dissolved gas pressure) probe sensor log
 - methane-specific down-hole probe.log
 - passive (grab) samplers, e.g. Hydrasleeve™
 - pumped samples from different depths, with purging only done to clear sample discharge lines
- (Optional) Re-assessment during/post purge pumping to assess perturbation of the initial monitored condition and possible return to initial borehole methane condition

Other areas of possible field research study

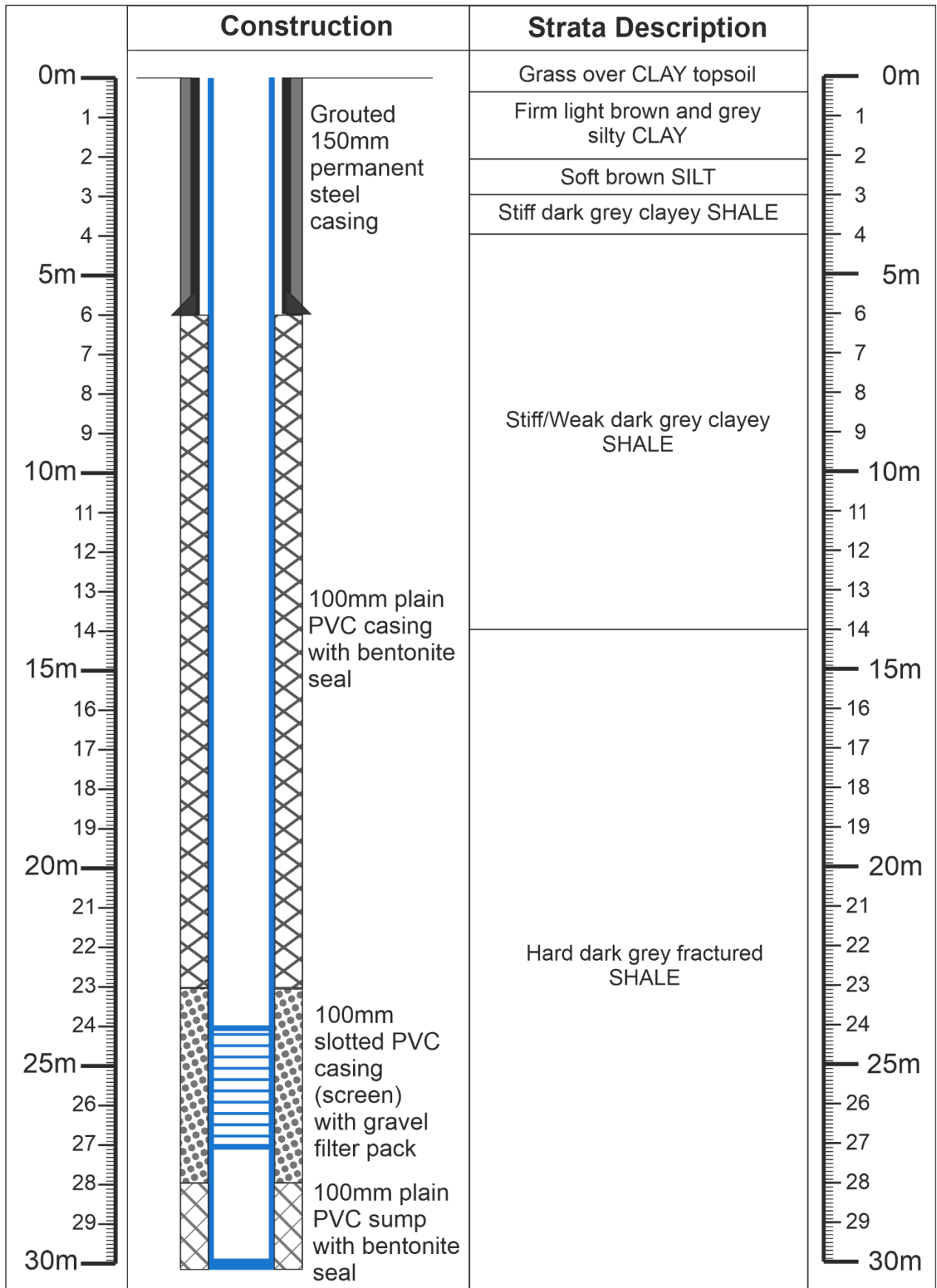
- **Low methane concentration site testing** – the low methane Site A data interpretation was restricted by the significant sensitivity of methane concentrations to purging. An alternative low concentration borehole site less sensitive to purging could be tested repeating the sampling conducted here to assess whether the Site B high concentration findings do generally apply to lower concentration sites as proposed. Testing further sites with moderate (5-15mg/l) and very high (40+ mg/l) methane concentrations would help to assess overall trends and whether correlations are consistent at all concentrations.
- **Peristaltic pump limit testing** – the comparable performance of the peristaltic pump in this study to other pumps was not expected (in terms of magnitude of methane concentration achieved) and attributed to the very shallow water table. As peristaltic pumps are used frequently by practitioners, quantification of acceptable conditions that these pumps could legitimately be used to produce acceptably accurate methane concentrations could be carried out, rather than discourage their use entirely.
- **Time series sampling with purging and sensitivity of time series to hydrogeological and methane occurrence conditions** – this study demonstrated significant methane concentration sensitivity to purging in a specific hydrogeological – methane occurrence environment. Time series methane concentration data with purging could be obtained from other borehole hydrogeological – methane occurrence environments to evaluate whether methane sensitivity to purging was the norm or unusual and its relationship to the tested environments to better conceptualise sampling interaction with the environment measured.

Appendix 1 Borehole Construction and Geology

Site A – Low Methane



Site B – High Methane



Appendix 2 Practitioner Look-up Sheet

Guidelines for developing a dissolved methane (CH₄) sampling protocol in groundwater

Dissolved methane may commonly occur in groundwater naturally, and at landfill, contaminated land, coal mine and oil & gas sites. The purpose of this guidance is to aid development of robust sampling protocols for the collection of dissolved methane in groundwater. Losses stemming primarily from methane's volatility necessitate sampling protocols that are carefully considered.

Monitoring point selection

1. Monitoring point suitability for sampling dissolved CH₄/gases, including availability of borehole construction and geological log data, water level and quality records (including dissolved CH₄) ensuring metadata support the monitoring objective e.g. sampling the groundwater body/interval of interest.

2. Monitoring scale suitability (screen length) to address monitoring objectives:

Short-screen (≤3 m) - usually preferred for greater certainty of sample origin. Maximum length chosen should meet objectives

Multilevel samplers - preferred where point concentration depth profile data are required (isolates monitoring zones)

Long-screen (>6 m) - discouraged due increasing uncertainty of sample origin and their potential to act as a conduit for vertical flow, mixing and pressure changes causing physical and chemical alteration to the water column, including buoyant gas bubble transport arising from degassing

Data interpretation, conceptual models and decision making should be appropriate for the scale of monitoring employed.

Pumping Protocol

3. Pump/sampler type selection should consider performance specifics tabulated below - a pressurised in-situ sampler or bladder pump may be preferred, although other devices may be used for practical reasons.

Pressurised in-situ sampler	Bladder	Submersible	Peristaltic	Non-pressurised in-situ sampler
Key features				
Maintains sample at hydrostatic pressure – advised for high dissolved CH ₄ concentrations and, or samples from depth	Bladder design and operation aims to minimise gas/VOC partitioning losses to air	Convenient for high-volume purging, but difficult to control for low-flow sampling	Convenient for shallow groundwater narrow tubing / monitoring. Limited to practical suction depth limit c. <8 m	Convenient for shallow zero-purge sampling but prone to degassing losses for samples retrieved from depth
Degassing potential				
Minimal degassing and should combine with surface closed sampling for optimal pressurised closed-system sample	Controllable and repeatable pressure enables repeatable closed samples. Reliably delivers low flow rates	Impeller can impart turbulence/cavitation and degassing exacerbated at higher flow rates	Used with caution only at small (few metres) depth to water due to increased degassing with increased suction depth	Slow retrieval with decreasing pressure causes increased degassing, especially of samples from depth
Deployment considerations				
Can be used at deep-water-table sites. Relies on slow deployment and retrieval to avoid mixing of water column	Wide range of deployment including deep-water-table sites	Wide range of deployment including deep-water-table sites if high-capacity pump	Limited to water-table depths less than practical suction limit (c. <8 m) and for reliable gas sampling much less	Uncertainty in sampling depth and zone of sample collection. High degassing losses if sampling from depth
Other				
Delivers zero-purge sample unless advanced purging with other pump type	Non-continuous flow causes increased sampling time and increased degassing at surface	May be used as advance purging device to enable use of other pump types for sampling	Non-continuous flow causes increased sampling time and increased degassing at surface	Limited surface collection options. Delivers zero-purge sample unless pre-purged with other pump type

4. Pump/sampler deployment depths should be kept constant and positioned within the screened section. A default position is mid-screen, or near a transmissive layer identified in the well screen area from geological or geophysical logging (e.g. a flowing fracture, or a more permeable lithology). Where vertical flows exist, the sampler intake position may reasonably be moved to the top (upward flow) or base (downward flow) of the screened interval.

5. Purging protocol selection may exert a primary control over dissolved CH₄ concentration in the sample collected and hence requires supporting rationale justifying its selection over other protocols. The following options are established protocols suitable for use in short-screened monitoring wells with the objective of delivering a flow-weighted average sample representative of inflow across the whole of the well screen (other protocols may be employed for differing objectives):

'zero/negligible-purge' protocol:	use of grab or passive diffusion samplers to sample ambient groundwater flow
'low-flow' (low-stress) protocol:	sample after purging at low flow rates (typically < 0.5 L/min) until indicator physical and chemical parameter stabilisation occurs; record indicator parameters, time and volume purged
'fixed-volume purge' protocol:	sample after purging a specified number of screen volumes at pumping rates maintained below 3 L/min; record purged volume and indicator parameters as supporting information (allows more confident comparison of data collected by different sampling protocols); conventional fixed-volume purging requiring high pumping rates and removal of ≥3 well volumes is discouraged due to increased degassing potential and large volume of potentially contaminated purge water for disposal

The suite of selected protocols (pump, depth and purging) should be followed consistently to produce a robust temporal record of dissolved CH₄

Sample Collection

6. Sample collection protocol choice may have a strong influence on sampled dissolved CH₄ concentrations. The following is the order of preference for protocol selection:

Closed samples sealed from the atmosphere are the preferred ideal, especially at sites with elevated dissolved CH₄ concentrations in groundwater, nominally > 10 mg/l, with increased prospects of sample degassing.

Semi-closed samples collected water-submerged are preferred if closed samples are not possible, with **Upright** preferred over **Inverted** due to the potential for accumulated headspace and increased uncertainty in measured concentrations for Inverted samples, especially at elevated dissolved CH₄ concentrations.

Open samples – collected open to atmosphere are not recommended and should only be collected where semi-closed/closed systems are not possible, for instance sampling from an unpressurised passive grab sample device.

Supporting data

7. Water-table depths should be recorded in sampled boreholes and archive records obtained to:

- Assess dissolved CH₄ degassing potential in the standing and drawn-down borehole water column during sampling
- Support low-flow sampling by allowing the planning and implementation of minimal drawdown protocols
- Assess pump viability and performance, especially for pumps where performance reduces with greater water-table depth
- Evaluate dissolved CH₄ concentration sensitivity to water-table changes – short term, seasonal or anthropogenic induced changes.

8. Reconnaissance dissolved CH₄ profile in standing water column is recommended via passive or grab / limited-pumped samples from different depths (with discharge lines purged), or else via Total Dissolved Gas Pressure or dissolved CH₄ downhole probe data. This may help assess zero or limited-purge volume options and the potential for the borehole to act as a natural dissolved CH₄ sink or conduit.

9. Reconnaissance indicator-parameter borehole-depth-profile logs for specific electrical conductance (SEC), oxidation-reduction potential (ORP), pH, dissolved oxygen (DO) and temperature form a recommended pre- and post-sampling reconnaissance tool. They should show ambient water quality in cased and screened sections, can help identify in/out-flows and may be valuably co-interpreted with well-head parameter stabilisation monitoring of pumped flows during purging and sampling. Parameters may also be related to dissolved CH₄ concentration.

10. Reconnaissance time-series dissolved CH₄ sampling is recommended, retrieving an initial zero-purge sample followed by a time series of samples with purging until parameter stabilisation or a fixed number of screen volumes purged. The time series of dissolved CH₄ may help:

- Determine sampled dissolved CH₄ concentration sensitivity to purging protocol (several protocols could be used in the test)
- Aid selection of final purging protocol and its justification
- Facilitate cross-comparison of different purging protocols
- Progress development of conceptual models of groundwater dissolved CH₄ in the aquifer
- Provide a snapshot of dissolved CH₄ concentration variability in a single visit that may provide useful context for long-term dissolved CH₄ records collected.

Data management and wider use

11. Comparative sampling between different stakeholders (consultants, regulators, or other organisations) should be undertaken using identical sampling protocols as far as possible, with any differences recorded. Compared samples should be obtained using a split pumping/sampling procedure, or at minimum close in time to enable like-for-like comparison.

12. Review and change of dissolved CH₄ sampling protocols: Periodic review should be undertaken to ensure continued good practice. Protocol changes should be supported by parallel overlap of old and new protocols to maintain continuity of the temporal monitoring record.

13. Dissolved CH₄ sampling and analysis protocol documentation should be provided with obtained datasets.

This document was developed from results obtained through BGS report OR/22/035 and EA Review SC190007. It does not serve as an exhaustive assessment of groundwater collection methods and does not replace good hydrogeological and hydrochemical practices and techniques.

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