



Methods for sampling and analysing methane in groundwater: a review of current research and practice

Chief Scientist's Group report

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Email: research@environment-agency.gov.uk

Author(s):

Rivett, M.O., Bell, R.A., Ward, R.S.

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Research contractor:

British Geological Survey, Environmental Science Centre, Nicker Hill, Keyworth, Nottingham, NG12 5GG

Environment Agency's Project Manager:
Gary Edwards/Sian Loveless

Collaborator(s):

GroundH2O plus Ltd

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Professor Doug Wilson
Chief Scientist

Executive summary

Accurately measuring methane in groundwater is essential to understanding the fate and transport of this dissolved gas in the environment and to identifying both in situ processes and human inputs. Methane in groundwater may be derived from both natural sources of organic matter in the shallow and deep subsurface and human inputs such as landfill. As there are no known harmful effects on human health of ingesting methane, there is currently no water quality standard for this gas. However, methane is a significant greenhouse gas, with a global warming potential almost 20 times higher than carbon dioxide (Bell and others, 2017, IPCC, 2018). Methane is highly mobile in groundwater, therefore if detected, it can also be an indicator of the presence, or increased risk, of other pollutants that could impact groundwater resources, drinking water supplies and human health.

Sampling and analysing dissolved methane in groundwater requires a robust method to accurately determine concentrations of methane (CH_4) and associated volatile gases such as ethane (C_2H_6). This project has identified factors that affect the reliability of measurements of concentrations of methane in groundwater and provides evidence to establish good practice guidelines (or 'protocols') and recommendations for further work. Recommendations address critical gaps in knowledge and uncertainties in sampling and analysis of methane in groundwater. The project comprised 2 parts; a literature review of current practices and guidelines, and a questionnaire survey of practitioners to understand practical application of methods and experience.

The main conclusions and recommendations are presented in this report as a table, indicating good practice and recommendations for further research. These primarily reflect the current state of knowledge informed by the literature, but are also supported or qualified, as appropriate, by the survey findings. The conclusions highlight that this subject is technically demanding, involving complex multi (gas/aqueous) phase systems with the need to appreciate, for instance, methane saturated (solubility) concentrations and the thresholds for free-gas (bubble) formation. The physiochemical processes controlling methane concentrations in groundwater have a significant influence on sampling and analysis and require an in-depth understanding to support sampling design and development and therefore good practice.

The recommendations to develop and communicate good practice and further research should help develop formal sampling and analysis protocols, which are essential for producing robust dissolved methane in groundwater data sets.

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1 Introduction

Understanding the fate and transport of methane in the environment is essential to identifying both natural and human inputs.

Previous monitoring of groundwater has shown that a range of substances, including methane, associated with landfills and onshore oil and gas (OOG) activities are already present in UK groundwater as a result of natural processes or human inputs (Smedley and others, 2017). In the case of methane, while concentrations are generally low in UK groundwater, they are variable, and significantly elevated concentrations have been found in some locations (Ward and others, 2017). Methane in groundwater may be derived from both in situ decay of organic material naturally present in the shallow or deep subsurface such as hydrocarbon deposits and from human inputs such as landfills and leaking gas pipelines. Methane is also highly mobile in groundwater (Cahill and others, 2018, Cahill and others, 2017) and for OOG operations it could therefore be an early warning indicator of subsurface infrastructure failure and/or migration of gas from depth.

There are no known harmful effects on human health of ingesting methane, therefore there is currently no water quality standard for this gas. There is, however, a risk of explosion related to elevated methane levels; the lower explosive limit (concentration) for methane in air is 5% (volume of gas/volume of air), the lowest dissolved methane concentration which could cause such a concentration in air in a confined space is 1.6mg/l (Gooddy and Darling, 2005). Methane is also a significant greenhouse gas, with a global warming potential almost 20 times higher than carbon dioxide (Bell and others, 2017, IPCC, 2018). Detecting methane in groundwater can also be an indicator of the presence, or increased risk, of other pollutants from the same source that could impact groundwater resources, drinking water supplies and human health.

Reliable measurements of methane in groundwater are therefore required for regulatory decision-making across a range of OOG, contaminated land and waste management activities. To compare methane data both spatially and temporally to determine trends, and to compare data from different practitioners and laboratories, means reliable sampling and analysis protocols that generate accurate and reproducible methane results are needed. For instance, establishing a robust environmental baseline ahead of any OOG development is useful in helping to identify future adverse changes that might occur as a result of new industrial activities. Low methane concentrations often expected in baselines may challenge protocols (as may high concentrations under methane-saturated conditions). In the USA, the absence of baseline data for water and air has resulted in significant criticism due to the difficulty in distinguishing industrial impacts from pre-existing natural and human-influenced environmental conditions. Where baselines do exist, uncertainties introduced from the sampling and analysis process may still hinder such differentiation, with knock-on challenges to effective environmental protection and remediation

(Jackson and others, 2013, Llewellyn and others, 2015, Osborn and others, 2011).

Measuring methane concentrations in groundwater therefore requires a robust sampling method and analysis to accurately determine concentrations of methane (CH₄) and associated volatile gases such as ethane (C₂H₆). It is also important for other characteristics of methane that can be used to support the diagnosis of its source(s) such as CH₄/ C₂H₆ concentration ratios and by measuring methane stable isotope ratios ($\delta^{13}\text{C}$ and $\delta^2\text{H}$). These methods attempt to identify the mechanism through which the methane has been produced, although these are also not without issues (Ward and others, 1996, Whiticar, 1999).

The objectives of this project were to identify factors that affect the reliability of methane concentration sampling and analysis in groundwater and to provide evidence to establish good practice guidelines (or 'protocols'). The report provides recommendations for further work, specifically aimed at addressing critical gaps in knowledge and uncertainties in sampling and analysis for methane in groundwater. The project comprised 2 complementary parts; a literature review of current practices and guidelines, and a stakeholder questionnaire to identify practical application of methods and practitioner experience. This enabled a scientific and experiential evidence base to be established.

Section 2 of this report presents the main conclusions and recommendations of the project, with protocol development needs. Section 3 outlines the methods used for the literature review and practitioner survey. Section 4 details the literature review findings. Section 5 presents the practitioner survey results. Each of the technical sections cover field sampling initially followed by laboratory analysis.

2 Summary and recommendations

A summary of the main conclusions and recommendations is presented below. It considers both the literature review and questionnaire survey findings, but primarily reflects the current state of knowledge informed by the literature as this generally provides a more robust evidence base and has usually been peer reviewed. The conclusions (section 2.1) are supported or qualified, as appropriate, by the practitioner survey findings. The survey provides supporting, practitioner-oriented evidence based on experience. Recommendations are presented in Table 1 (section 2.2), starting with general recommendations, and then focusing on good practice with respect to sampling and analysis of methane in groundwater. The conclusions and recommendations are number linked ([1] to [20]). Recommendations for further research and investigation are also identified and these are linked to the sections elsewhere in the report that provide greater detail and justification.

2.1 Conclusions

2.1.1 Literature review

There is a large, expanding body of literature on the sampling and analysis of methane in groundwater. This has been driven in recent years by the growth of onshore oil and gas operations, especially shale gas, in North America and concerns over pollution of private water supplies. There is comprehensive coverage of both field sampling and laboratory analysis literature, with much of the information diffusely scattered and with little collation evident. The literature review in this report provides an extensive, albeit incomplete, evidence base for good practice development [1]. It is augmented by the questionnaire responses which provide confirmation of practices and perceived needs [2].

Most of the recent literature is from North America, with some contributions from the UK, together with other international input. Despite the bias in geographic source, most study conclusions can be generally applied.

There are few targeted studies assessing groundwater methane sampling and analysis protocols and sources and characteristics of their uncertainties, but they are considered vital by a number of authors [3]. For example, Ryan and others (2015) conclude: “the lack of verified, standard approaches for the combined sampling, storage, manipulation and analysis of dissolved groundwater gases challenges our research community” and “the use of a wide range of practices that have not been rigorously tested or compared”.

The subject is technically demanding, involving complex multi (gas/aqueous) phase systems with the need to appreciate, for instance, methane saturated (solubility) concentrations and the thresholds for free gas (bubble) formation. Solubility increases with increasing pressure and therefore depth below the water table, and decreases with increased temperature and salinity. Although

the physicochemical equations and processes controlling methane distributions are well known, their complexity and various expression in the literature can be confusing. Their influence on sampling and analysis of methane in groundwater is very significant and requires understanding to support sampling design and development and therefore good practice [4].

2.1.2 Analytical capability

The questionnaire provided valuable information on current analytical practices; methane concentration samples are routinely collected, although detection limits in commercial labs can be high. In the UK, there is limited commercial capability for dissolved methane analysis, and there is currently no commercial lab that can carry out methane isotope analysis. Therefore, where isotope analysis is required the samples are typically sent to the USA.

Although widely circulated, Part B of questionnaire (Analytical Techniques and Capability) was not completed by as many laboratories as hoped (8 out of 15). However, many of the practitioners were amenable to future contact and more in-depth discussions on the technical detail, with some indicating a willingness to participate in future collaborations.

2.1.3 Field sampling

It is generally recognised, albeit not often shown in the literature, that field sampling variability accounts for greater uncertainties in the methane concentration measurements than laboratory analysis. Quantification of uncertainties is routinely provided in the literature for laboratory analysis, but not field sampling [4,12]. Questionnaire responses reveal similar findings. Methane is usually one of many substances sampled and can potentially be 'piggybacked' on sampling methodologies of varying appropriateness without due consideration [6].

It is generally expected and observed that the greatest uncertainties are associated with sampling and analysis of higher methane concentrations, especially where gas-saturated conditions may occur and effervescence (bubble formation) or degassing losses cause a negative bias in measured concentrations. In the presence of other gases, methane effervescence may occur below its solubility concentration and this possibility can be overlooked. Questionnaire responses from practitioners suggest moderate, but variable awareness of issues associated with sampling high methane concentrations [6]. Greater understanding is evident in the research organisations surveyed.

Practitioners questioned during the survey identified one of the main gaps in knowledge as being which system (closed, semi-closed) should be used when methane concentrations are known to be high.

Most groundwater methane sampling reported in the literature and reinforced by the questionnaire responses is either from available supply wells (63% of practitioners surveyed), or site-specific monitoring/observation wells (94% of

practitioners). Multilevel samplers appear to be rarely used, and when they are, it is mainly in research studies. Depth concentration profile detail revealed by multilevel samplers could, however, provide critical understanding about sites, and their targeted use could ultimately prove cost-effective [8].

Sampling pre-existing supply boreholes [7] typically uses existing sample taps at the ground surface, positioned as close to the well head as possible. The preference is also to sample before water reaches pressure tanks (vessels), storage (header) tanks or treatment facilities that may compromise a sample [11]. The influence of the prevalent pressure tank design in the USA appears insignificant on samples taken downstream. The single UK study looking at the influence of pressure tanks had limited scope, sampling just a few sites and inferring dissolved gas behaviour from other substances sampled.

Questionnaire responses indicated pressure tanks are common in private supply boreholes. A third of respondents have collected methane samples post treatment/tank, although there is an awareness that this might not be considered good practice.

Supply well purging protocols are varied [10], but often involve a fixed-volume purge, with samples taken after removing a set number of borehole/screen volumes and/or piped infrastructure and pressure tank volumes. They also generally involve measurement and stabilisation of 'field parameters' such as temperature, pH, dissolved oxygen (DO) and specific electrical conductivity (SEC). Protocols may be pragmatic, for instance, considering prior supply use to reduce the need for purging. A recent study in the USA observed no clear benefit to purging large volumes, and that this fails to represent normal residential use and concentration exposure. They advocated that, in this case, a representative sample can be obtained by purging <1 screen volume, together with parameter stabilisation, but emphasising temperature stabilisation may helpfully indicate when water from the pump intake reaches the sample tap and therefore lines/tanks had been flushed. Questionnaire responses confirm that pragmatic decisions are taken in relation to borehole purging, with 67% using low flow methods together with field parameter stabilisation (87%) to inform purge volumes/timings.

For sampling monitoring/observation wells, the wide range of possible purging protocols and sampling devices is likely to be a primary cause of variability in sampled methane concentrations [10]. 'Zero/minimal-purge' protocols using grab or passive diffusion-based samplers, 'low-flow' (low stress) protocols that purge and sample at low flow rates until indicator parameter stabilisation occurs, and 'multiple well-volume purging' (fixed volume purge) are all considered to be valid purging methods, but each has advantages and disadvantages.

There are literature studies on sampling device/pump influence on methane sampling, or with volatile organic carbon (VOC) analogue contaminants, albeit noting their lower volatility. Legitimate concerns of concentration negative bias from suction (peristaltic) pump sampling of shallow water-table systems are commonly raised [9]. Also, many devices/pumping setups will fail to retrieve

samples at in situ pressure, leading to potential degassing and methane loss. A study to evaluate the influence of sampling devices on groundwater methane concentrations back in 1984 remains the most comprehensive study to date.

Part A of the sampling survey (21 responses out of 37) found that the peristaltic pump is most commonly used for sampling despite issues with its use for sampling dissolved gases and it not being recommended by BS:ISO 5667-11. However, there is also a lack of clarity as to which pump types/sampling methodology are appropriate, both when methane concentrations are low and above or approaching possible saturation [5].

Sampling protocols for both supply and monitoring wells need to recognise their sensitivity to degassing losses. In particular, when sampling elevated methane concentrations, retrieving samples from a depth where significant depressurisation might occur as hydrostatic pressure reduces, or where there are dissolved gases that could lead to degassing of methane below its normal saturation concentration (that is, as an individual gas component). Protocols could be improved by using specialised depth samplers that maintain samples at in situ depth pressures and interface with closed-system, pressurised sampling procedures at the surface. Low purging rates could minimise drawdown and therefore depressurisation at the same time as allowing sufficient volumes of water to be purged in order to sample 'fresh' wellbore water and minimise in-well degassing. These systems/protocols appear underused in the literature. This is also confirmed in questionnaire responses, with use of in situ pressure sampling devices largely restricted to research-oriented studies. Issues related to low-yielding boreholes were noted in the questionnaire responses, including rapid reduction in water levels when purging, and with 'no-purge' methods there can be difficulties filling sample containers at ground surface.

Sample collection protocols from supply-well taps, pump-discharge lines or retrieved downhole sample devices are usually described as (in order of reduced volatile loss): i) open (to atmosphere), ii) semi-closed, or iii) closed systems. However, provided that sample collection is rapid, the literature suggests that for low concentrations of dissolved methane, there are likely to be only small differences between protocols, although semi-closed or closed systems are still preferred. These methods are definitely preferred in the literature where methane concentrations are high and prone to effervescence. The literature also indicates growing concern about the previously widely used semi-closed method of volatile organic analysis (VOA) sample collection using an inverted vial that is water-submerged. This is due to gas accumulation from degassing of the water stream in the vial headspace (air space above the water in the vial). This gas is not usually analysed, leading to concentration negative bias. Where awareness exists, and in the more recent literature, this protocol is being modified by using a semi-closed VOA protocol with a non-inverted (upright) vial. Questionnaire responses from UK participants indicate that approximately half use the semi-closed inverted method, but appear unaware of the emerging concern over that protocol [11]. Questionnaire responses suggest that there is ambiguity over the definitions of the different approaches, in

addition to uncertainty over a methane concentration 'limit', over which sample collection protocols should be amended to avoid degassing.

The collection of samples for $\delta^{13}\text{C-CH}_4$ and $\delta^2\text{H-CH}_4$ stable isotope measurement has become more widespread according to the research case literature and is now frequently included in North American studies to establish methane provenance in the shale gas context. However, questionnaire responses from UK participants indicated stable isotope ratio measurement in UK studies is limited; some (~70%) were collecting samples for $\delta^{13}\text{C-CH}_4$ as required by environmental permits, but none for $\delta^2\text{H-CH}_4$.

Collecting samples to measure $\delta^{13}\text{C-CH}_4$ and $\delta^2\text{H-CH}_4$ appears to be less sensitive to sampling protocol than for measuring methane concentration, as degassing losses are largely expected to affect each isotopic form in the same way, that is, with little or no isotopic fractionation occurring, thereby leaving the isotopic ratios largely unchanged.

The availability of relevant isotope analysis laboratories is a limiting factor for field sampling [13]. Most of those available are university or research institute specialised laboratories, with exporting samples abroad for analysis quite common. Currently, there are no commercial laboratories in the UK to perform this analysis. Using IsoFlasks® to collect and analyse isotope samples at IsoTech laboratories in the USA is now one of the main commercial laboratory options. This was reflected both in the published research literature and the questionnaire responses.

Provided that protocols are followed (correct sample containers used with properly sealed enclosures with cold storage, sample holding times adhered to, and sample preservation appropriately implemented), losses of methane during sample storage should be insignificant [14,15]. A precautionary approach is generally taken by adding preservatives or bactericide to inhibit microbial reactions within the sample container during transit/storage; or to demonstrate that they are not necessary where they are not used, through controlled testing of the protocol being used. Questionnaire responses indicate that the majority (60%) of participants are not using preservatives. These participants are typically researchers who use their own laboratories, with fast sample turnarounds with minimal holding times to justify this approach. A number of preservatives are reported: benzalkonium chloride capsules (IsoTech laboratories), hydrochloric acid and sodium azide. There is no consensus as to which is the most effective [14]. Responses also generally recognise the need to adhere to protocols provided by their analysing laboratories as a matter of course.

'Total dissolved gas pressure' (TDGP) is very rarely measured at sites detailed in the literature. However, some researchers present a compelling case for routinely using this, especially where sampling of high dissolved gas concentration, gas-charged water is suspected. Where a mixture of gases is present, effervescence of methane may occur at concentrations lower than its solubility as other gases contribute to the TDGP. Measurements would also be generally supportive of groundwater methane sampling, analysis and data

interpretation regardless of concentration. TDGP measurements are relatively easy to make, however, their use and significance to date has been largely overlooked. Evidence of their use in the UK was not found in the literature or in the questionnaire responses.

2.1.4 Laboratory analysis

Variability between different laboratories, even with 'identical' methods, can be high. The method widely used, since the 1980s at least, to analyse dissolved methane concentrations in (ground)water samples has been headspace – gas chromatography/flame ionising detector (GC/FID) analysis. Of foremost concern has been the long-term lack of a standard published methodology. This has resulted in a variable implementation of the headspace methodology typically built around several 'semi-formal' published methods. The most frequently cited is a US Environmental Protection Agency (EPA) laboratory Standard Operating Procedure (and related journal publication), although this is not an official EPA approved method.

Differences in sample transfer, headspace creation, equilibration conditions, use of gas- or aqueous-phase standard calibrations (respectively requiring or not requiring Henry's Law constants to calculate concentrations) among other factors have contributed to variability in laboratory implementation of the headspace methodology evident in the literature. These may largely account for discrepancies in analysed concentrations between laboratories found where comparative studies have been published or experiences (without data) relayed [16]. Too few laboratory questionnaire responses were received to substantiate the above, although it is likely to be applicable.

A significant recent step was taken to address the need for a standard headspace methodology with the publication by the ASTM (American Society for Testing and Materials) in 2017 of its 'Standard Test Method for Measurement of Dissolved Gases Methane, Ethane, Ethylene, and Propane by Static Headspace' - ASTM D8028-17. The method is perceived to provide detail, with guided flexibility that will ensure it can easily be reproduced. It remains too early to judge uptake, but it is anticipated that given time, it will provide a benchmark with international reach [16]. Interestingly, knowledge of the ASTM method was not found in any questionnaire response (noting it was not mentioned specifically in the questions posed), and is yet to emerge as a cited method in the literature.

The main caveat in applying ASTM D8028-17 and many headspace analysis methods used to date is their applicability to samples collected at a nominal ambient pressure, but not closed-system samples obtained (in situ, at depth) at pressures greater than 1 atmosphere (atm) or potentially containing free methane gas. Although most methods note the presence of free gas (methane or other) within a sample received, that free gas is generally not analysed and 'lost' in the analytical process [17,18]. This is confirmed by the literature published by laboratory practitioners largely from North America. Commercial headspace methods are typically not set up to analyse and report the total mass

of methane present in both the dissolved phase and any gas phase present, and therefore just report dissolved-phase mass. The notable commercial exception is the IsoFlask® system that allows closed-system analysis of the closed-system groundwater sample received.

The Henry's Law constant is commonly used to describe equilibration of methane concentrations in water with concentrations in an overlying air (or gas) phase. It strongly favours methane transfer to the gas phase. It may therefore cause field sampling methane losses, but also underpins the headspace analysis method for which Henry's Law constant values need to be selected if gas-phase standard calibration is used. Provided temperature and salinity influences are recognised, errors associated with selecting Henry's Law constant values for calculations are generally not thought to arise from variation in the actual constant values, which appear relatively well constrained in the database literature [19]. Rather, the confusing array of definitions of the Henry's Law constant, some of which are the direct inverse of each other, and the accompanying array of different units are perceived to be the main concern. Confused use of 'wrong' Henry's Law constants and unit errors in calculated methane concentrations analysed can therefore arise if there is not due care or there is a lack of knowledge [19]. From a laboratory analysis perspective, the need for Henry's Law constants may be short-circuited by using water-based calibration standards that would not require them to be used, as advocated by the recent ASTM method.

Although until the advent of the ASTM method there have only been 'semi-formal' methods for methane concentration analysis, these are even rarer for methane isotope analysis ($\delta^{13}\text{C-CH}_4$ and $\delta^2\text{H-CH}_4$), with no ASTM (or similar) method statements available [13]. Despite becoming more routine in the USA, questionnaire responses confirm analysis of the isotopic composition of methane is very limited in the UK, even though environmental permits for extracting hydrocarbons (such as shale gas) can require such analyses.

2.1.5 Protocol development needs

The literature review and practitioner survey have highlighted the need to develop sampling and analysis protocols and recommendations for good practice on an international level. Improved protocols will allow greater standardisation of methods and therefore reproducibility and accuracy of methane concentration measurements in groundwater. This will enable greater confidence in inter/intra-site comparison and compliance with regulatory criteria.

The breadth and detail of issues considered in this report confirm that protocol development is an important undertaking, given that it will take several years to develop the ASTM D8028-17 headspace analysis methodology and the level of detail that will be included. Protocol development would require underpinning research, for instance, into sample preservation methods and sample container integrity to enable reliable sample holding times to be specified prior to analysis.

While publication of the ASTM D8028-17 protocol by an international standards organisation might avoid the need for development of a UK headspace analysis methodology for methane concentration (subject to being tested in the UK context), there remains a need to develop protocols and standard methods in other areas of the methane sampling and analysis process, including for isotopes [20]. The existing literature provides reasonable, albeit not full, support in doing so. The questionnaire responses likewise provide justification for protocol development and highlight areas of variable practice or lower knowledge where guidance or protocol development is considered necessary.

2.2 Recommendations for good practice and further research

Recommendations for good practice for methane sampling and analysis in groundwater are summarised in Table 1 together with associated recommendations for further research. Both may further the development of formal sampling and analysis protocols.

Table 1. Recommendations for good practice and further research for methane sampling and analysis in groundwater. Numbered recommendations are cross referenced to section 2.1 ([1] to [20] labels).

[Link No.]	Good practice	Recommendations for further research and/or study	Section
General			
[1]	Ensure guidance and protocols are informed by published literature and relevant case studies.	The literature review carried out was extensive, but not exhaustive. There would be merit in extracting further detail from the literature in some areas, for example, the analysis of samples collected under pressure (> 1 atmosphere) and revisiting literature published in the 1980s and early 1990s on methane hazards and measurement techniques.	4.1
[2]	Enhance and maintain UK knowledge base by sharing experience and transferring knowledge to establish good practice.	There would be merit in: <ul style="list-style-type: none"> a. re-distributing the project questionnaire to commercial UK laboratories with further targeted follow-up interviews on important technical areas, including discussions about collaborative opportunities to strengthen UK capability 	5.1 5.2

		b. publishing any UK research or case experience revealed in the survey to support protocol development	
[3]	Investigate and understand the sources and characteristics of uncertainty in sampling and analysis.	It is recommended that a coordinated investigation and quantification of uncertainties associated with different elements of field sampling and laboratory analysis is carried out.	4.2
[4]	Improve understanding of physicochemical processes (gas solubility, gas bubble formation) and influence on sampling, analysis and reproducibility of results.	There would be merit in collating the relevant theory and equations relating to physicochemical processes (gas solubility, gas bubble formation) within a convenient user-friendly toolbox to allow a quantitative sampling-and-analysis conceptual model framework to help good practice.	4.2
[5]	<p>It is strongly recommended that ISO 5667 Part 11: 'Guidance on sampling of groundwaters' is used to inform sample programme design and sample collection.</p> <p>It is strongly recommended that ISO 5667 Part 18: 'Guidance on the design and installation of groundwater monitoring points' is used to inform monitoring point selection and design and information requirements.</p> <p>Environment Agency guidance should also be considered, including science report SC020093 (2006).</p>	Actively participate in design/revision of UK and international standards for groundwater sampling and monitoring to ensure that they are informed by good practice and are fit for purpose.	
[6]	Adequately trained staff are required. They should have experience in sampling different types of monitoring point, using a range of different purging	Consider the requirement for a personnel competency standard such as MCERTS accreditation for samplers.	

	methods and sampling devices, be able to carry out field chemistry measurements and provide accurate records.		
Sample collection			
[7]	Pre-existing boreholes should be evaluated carefully to ensure they are suitable for sampling dissolved gases. Good records should be available for borehole construction and there should be a reliable geological log.	To support establishing, reinforcing and improving good practice, targeted, comparative and combined field and laboratory research is recommended to underpin sampling and protocol development, address current specific knowledge gaps, and identify and characterise areas of uncertainty. Further details of potential research are given below.	4.4
[8]	Boreholes with long open sections should be avoided where possible when collecting samples for dissolved gases, unless sample horizons can be isolated and purged, for example, with packers. The use of multilevel samplers is recommended where depth profiling is required and where significant temporal variability in dissolved methane is observed in boreholes with a long open section.	Comparative research into nested scales of monitoring, including open boreholes (pumped/observation), piezometers and multilevel samplers, are required to better understand the influence of monitoring scales on samples taken.	4.3
[9]	Suction pumps such as peristaltic pumps are not recommended for sampling boreholes (see ISO 5667-11).	Experimental research to identify where degassing losses occur, especially during field sampling and within common/conventional sampling approaches (for example, pump types, tubing materials, sampling protocols).	4.5, 4.5.2

[10]	<p>An appropriate purging method suitable for the monitoring infrastructure being sampled needs to be selected. Different approaches should be considered on a case-by-case basis and in relation to the specific objectives of monitoring.</p>	<p>Investigation into the effects of well/borehole purging protocols on dissolved gas concentrations; including differences between methods and reproducibility of result for each.</p>	<p>4.4.2 4.5.3</p>
[11]	<p>Samples collected at the well head should be collected from taps as close as possible to the point that the rising main reaches ground level and prior to pressure and especially storage vessels.</p> <p>A semi-closed upright VOA vial protocol should replace the inverted VOA protocol.</p> <p>Samples collected from depth should be collected in situ and at hydrostatic pressure.</p> <p>Samples should be collected with no headspace.</p>	<ol style="list-style-type: none"> 1. Investigation of pumped borehole headworks configuration (for example, supply well) to determine effects of sample point/tap location and optimisation of design. 2. Comparative testing of different sample collection methods (including at in situ pressures) for groundwater with both high and low methane concentrations and for different sample point design; to understand where methane losses occur within the sampling device, during sample transport to surface and during acquisition at surface. 3. Revise existing groundwater sampling protocols specifically for dissolved gas sampling and incorporate any new findings and recommendations as they emerge. Engage with UK standards authorities, practitioners and industry to share findings and establish good practice. 	<p>4.4 4.5 4.6</p>
[12]	<p>Supporting measurements such as TDGP should be taken for QA/QC purposes and to help interpretation.</p>	<p>Investigate the role of TDGP measurement to optimise selection of sample collection protocols and support sample analysis and interpretation of results to help QA/QC.</p>	<p>5.1.3 4.10</p>

Sample handling and analysis			
[13]	Establish effective UK-based laboratory capability, especially for carbon and hydrogen stable isotope analysis.	Investigate the reasons for the lack of commercial laboratory interest in stable isotope analysis and encourage UK development if there is to be an ongoing regulatory need, for example, condition of an environmental permit.	4.7
[14]	Minimise sample degradation through effective sample preservation and storage protocols, including using preservative or bactericide in sample bottles.	Investigate the need for, and effectiveness of, sample preservation to address degradation of methane arising from microbial action during sample transit and storage.	4.8
[15]	Sample containers (and valves) should be made from materials that are reliable for sample storage, that is, they are not susceptible to gas diffusion or leakage. Stainless steel canisters, FlexFoil bags and Tedlar bags have all been shown to be reliable with adherence to stipulated holding times. The laboratory carrying out the analysis should also be consulted.	Investigate the suitability and reliability of different sample containers for measuring dissolved methane concentrations and stable isotope ratios in relation to length of storage.	
[16]	Inter-laboratory comparison of analysis methods.	Comparison of laboratory analyses to assess variability in measured methane concentrations; comparability with the ASTM D8028-17 method; identify deficiencies; and develop standard analysis method protocols that represent good practice.	4.11 4.11.5
[17]	If a headspace is present in the sample bottle, then this should always be reported by field and laboratory staff. Where at all possible, both headspace and dissolved gas concentrations should be measured to	Assessment of the field sampling conditions and protocols used that most commonly result in sample headspace to enable design modification of sampling protocols that avoid headspace and, or improved	4.9 4.11.6

	determine the total mass of methane. Further sampling of the site monitored should be carried out to establish the source and repeatability of headspace occurrence and to ascertain if improved sampling and analysis methods are required, for example, closed-system collection and analysis of pressurised samples.	guidelines on selecting appropriate protocols suited to the prevailing site conditions.	
[18]	Develop capability to measure dissolved gases in pressurised samples taken (in situ) from depth.	Develop cost effective and reliable laboratory closed-system analysis protocols that effectively interface with closed-system groundwater samples at pressure to be able to report total methane mass, dissolved and gas phase components.	4.5.4 4.11.6
[19]	Although a recommendation can be made to use water-based standards for headspace analysis thereby avoiding the use of a Henry's Law constant, this does not excuse the need to recognise their central significance and control in the entire sampling and analysis process and on methane environmental fate that requires Henry's Law constants to be considered transparently and correctly.	Encourage an improved understanding of the role and significance of Henry's Law constants in the entire sampling and analysis process and on methane environmental fate. Develop a toolbox facilitating Henry's Law constant use with example calculations linked to reliable database values that illustrates the constant sensitivity to temperature, salinity and errors arising from headspace volumes and bubble formation.	4.2.1 4.11.8
[20]	Development of an approved method statement for methane stable isotope analysis.	Develop a formal method statement for methane isotope analysis that parallels recent development of the ASTM D8028-17 method statement for methane concentration analysis.	4.12

3 Methods

3.1 Literature review

A literature review related to monitoring methane in groundwater covering sampling and analysis was carried out. It included UK and international peer-review and grey literature. A primary search using Science Direct and World Cat yielded 42 peer-reviewed studies. This was supplemented by searches in Science Direct, World Cat and Google Scholar for literature with related methodologies, aims or study regions. The primary searches undertaken were as follows:

- Groundwater+methane
- Groundwater+dissolved+methane
- Groundwater+methane+sampling
- Groundwater+methane+sampling+headspace
- Groundwater+dissolved+methane+sampling
- Groundwater+methane+isotopes+monitoring
- Methane+aquifer
- Methane+groundwater+shale

Selected grey literature was used to identify existing methodologies for purging/sampling wells and sample collection. These included best practice guidance, academic theses and reports from consultancies and government bodies (for example, United States Geological Survey (USGS)). An EndNote library was compiled of all literature sources. Details on borehole design, sampling method and objective, environmental conditions, type of analysis (concentration/stable isotopes) and the intended data application were compiled. Literature themes informed the review structure.

3.2 Questionnaire

3.2.1 Questionnaire design

To supplement the literature review, a questionnaire was designed to gain an understanding of stakeholder experiences of carrying out both methane sampling and laboratory analysis (concentrations and stable isotopes), in the UK and internationally. A systematic approach was taken which focused on questions pertaining to the project's objectives. The questions were focused around a number of topics, including:

- **monitoring site type and design** – purpose of borehole/sampling, presence of pressure tanks/treatment, depth of the borehole, screen length and design, depth of sampling, any information on geology or physical aquifer properties

- **groundwater sampling protocols** – information on pump type, purging method, methane sampling method and information on groundwater levels
- **sample transport and storage** – container types used, sample preservation, holding times before analysis, and storage conditions
- **laboratory sample analysis method** – method and equipment used, expected/reported accuracy, precision and limit of detection, assumptions about gas partitioning during the analytical process and calibration
- **quality assurance/quality control** – what measures are in place?

In order to constrain the scope and length of the questionnaire, it was divided into 2 sections. This was because the topic is wide-ranging, involves different types of practitioner (monitoring experts and laboratory analysts), and to ensure as many responses as possible could be obtained in a relatively short period of time.

Part A of the questionnaire focused on methane sampling techniques (65 questions) and Part B focused on laboratory analysis of methane in groundwater (55 questions). A targeted approach was used, with stakeholder practitioners asked to answer questions in their field. However, respondents were encouraged to look at both parts if appropriate and complete either section if they were able to.

The questionnaire was provided to all potential respondents as an online version (using Microsoft Forms) and also as a Microsoft Word document (Appendix A). Recipients were also encouraged to contact the project team by phone or email if they preferred a telephone interview. Respondents were encouraged to share any relevant supplementary information where possible, including method statements and guidelines.

The questionnaire was sent out to a variety of practitioners identified as being involved in either methane sampling or analysis. This included government bodies, universities, environmental consultants and laboratories, both national and international.

3.2.2 Questionnaire responses

In total, questionnaires were sent out to 37 organisations and 51 individuals. The majority of recipients answered only one part of the questionnaire, although some individuals had expertise to answer both the sampling and analysis parts. Some of the responses recorded were 'null' responses, which have been captured in the survey results, as they provide an indication that certain stakeholders are not carrying out this type of work, and this is in itself a valuable finding.

The survey was carried out between 6 and 20 March 2020 and was time limited due to the short duration of the project. There is scope for further responses from practitioners who were unable to complete the questionnaire in time, but are interested in contributing.

For Part A, 21 individual responses were received; 50% from UK based organisations and 50% from international ones. The largest percentage of these were from environmental consultancies (Figure 1). For Part B, 8 responses were received, with 3 of these from UK based organisations. As anticipated, the largest number of responses for Part B was from commercial laboratories (Figure 1).

Part A responses (%)

- Operator
- Universities
- Government bodies
- Consultants

n = 21



Part B responses (%)

- Universities
- Government bodies
- Laboratories

n = 8



4 Literature review

4.1 Literature overview

There is a large and growing body of literature concerning the sampling and analysis of methane and other light hydrocarbon dissolved gases in groundwater. Much recent literature has arisen from assessing fugitive methane release impacts to groundwater from onshore oil and gas operations, especially shale gas (Cahill and others, 2017, Forde and others, 2019, Humez and others, 2016b, Nicot and others, 2017b, Roy and Ryan, 2010, Smith and others, 2016), but also coal bed methane exploitation (Atkins and others, 2015, Banks and others, 2019). Sampling extends from low dissolved-concentration 'baseline' conditions (Bell and others, 2017, Humez and others, 2015, Schloemer and others, 2018) up to methane-saturated conditions where methane gas may occur (Banks and others, 2017, Molofsky and others, 2016, Smith and others, 2016, Tamamura and others, 2017). Sampling and analysis detail may be found in studies examining the many human and natural sources of methane in groundwater (Avrahamov and others, 2015, Humez and others, 2016a, Iverach and others, 2020, Moritz and others, 2015) and the expanding array of studies applying geological, hydrogeological and biogeochemical lines of evidence to assess methane provenance (Barker and Fritz, 1981, Bordeleau and others, 2018b, Harkness and others, 2017, Iverach and others, 2020, LeDoux and others, 2016, Thomas, 2018). $\delta^{13}\text{C}$ and $\delta^2\text{H}$ stable isotopes in methane (and ethane), perhaps with other isotopic or noble gas tracers also found in groundwater, are increasingly used to help differentiate microbial production biogenic methane from thermogenic (thermocatalytic) methane from non-biological, chemical processes (Bordeleau and others, 2018a, Darrah and others, 2014, Osborn and McIntosh, 2010, Zhu and others, 2018).

Growth in modern literature is based on earlier work on subsurface methane natural occurrence (Coleman and others, 1988, Schoell, 1988), contamination cases involving methanogenesis, notably landfill sources (Barber and Davis, 1986, Barber and others, 1990, Lyngkilde and Christensen, 1992, Williams and others, 1992) and more latterly, hydrocarbon fuel/oil or other chemical release sites (Barker and others, 1987, McAllister and Chiang, 1994, Salanitro, 1993), including recent drives to better quantify methanogenesis significance within emerging natural source zone depletion (NSZD) management options (Garg and others, 2017, Rivett and Sweeney, 2019). Methane sampling and analysis methods used today may still derive from this earlier period of interest (Barker and Fritz, 1981, Busenberg and others, 1998, Kampbell and Vandegrift, 1998, Lewin and others, 1989, US EPA, 2002).

Standard protocols still, however, lack and require development (Banks and others, 2017, Molofsky and others, 2016, Roy and Ryan, 2013). Ryan and others (2015) summarise the needs: "the lack of verified, standard approaches for the combined sampling, storage, manipulation and analysis of dissolved

groundwater gases challenges our research community” and “the use of a wide range of practices that have not been rigorously tested or compared”.

Literature was examined based on assessing factors likely to cause variability and uncertainties in reported methane concentrations, in particular methane loss (negative bias), arising from the sampling and analysis process. The literature may be subdivided into:

- research studies specifically examining or developing aspects of the groundwater methane sampling and analysis process and factors controlling concentrations reported - these studies are not plentiful, but are perceived to be the most useful and form an important focus (examples include Banks and others (2017), Houben and others (2018), McLeish and others (2007), Molofsky and others (2016, 2018), Rivard and others (2018a), Smith and others (2016))
- case or research studies where methane sampling and analysis has been used in site assessment or survey of a region – these studies have become plentiful and are of most interest where investigative or critical of the sampling and analysis process, (examples include Cahill and others (2018), Moritz and others (2015), Nicot and others (2017b), Schloemer and others (2016))
- guidelines and protocols directly relevant to the groundwater methane sampling and analysis process (for example, Alberta Environment, 2006) – these largely refer to references rather than being detailed, but are expected to inform development of good practice documentation

Some citation is made to the wider body of supporting literature. For instance, guidance in the US Geological Survey (USGS) National Field Manual for the Collection of Water-Quality Data – an introductory overview is provided by USGS (2018) with the manual found at <http://water.usgs.gov/owq/FieldManual/> (USGS, 2006) and Koterba and others (1995). Both, for instance, are applied within the context of groundwater methane sampling by Dillon and others (2016) and Wright and others (2019).

The literature review is novel, with little prior collation and critique of the groundwater methane sampling and analysis literature published. The closest example appears to be the now somewhat dated grey literature review of Hirsche and Meyer (2009). Their main conclusion was: “the highest potential for introducing large uncertainties on concentration data for free and dissolved methane in groundwater is in all likelihood associated with the sampling procedures in the field. Future research should evaluate the influence of sampling procedures and sampler design on the obtained concentration and isotope data for free and dissolved gas”.

4.2 Physiochemical controls relevant to sampling and analysis

4.2.1 Physiochemical controls

It is important to understand the physiochemical controls on methane occurrence in groundwater and outline any implications they may have on sampling and analysis. To this end, and to contextualise the review, a brief introduction is provided.

The solubility of methane gas in natural waters follows Henry's Law, which describes the equilibration of gases (or other solutes) dissolved in the aqueous phase with an adjacent gas phase. Henry's Law constants for methane are high compared to typical volatile organic compounds (VOCs) of concern in groundwater and favour partitioning from the aqueous to the gas phase (section 4.11.8). Therefore, methane may be readily lost from groundwater (samples) into an adjacent air/gas phase when present.

The maximum solubility (saturation) concentration of methane in water is a function of water pressure, temperature, and salinity. It can be calculated theoretically using complex Pitzer thermodynamic formulations (Duan and others, 1992, Smith and others, 2016). In summary, the solubility of methane will:

- decrease with increasing temperature
- linearly increase with increasing water pressure
- therefore, linearly increase with increasing hydrostatic pressure and linearly with depth below the water table
- decrease with increasing salinity of the groundwater, the so-called 'salting-out effect' (Yamamoto and others, 1976)

Some of these relationships are illustrated in Figure 2 (after Banks and others (2017)) depicting variation in gas pressure and saturated/unsaturated conditions versus depth below water table, and also methane solubility as a function of temperature and salinity. Increasing hydrostatic pressure of the overlying water column with depth permits more dissolved gas to be retained in solution (Banks and others, 2017; Pankow, 1986). Smith and others (2016) also show methane saturation conditions with depth, illustrating 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).

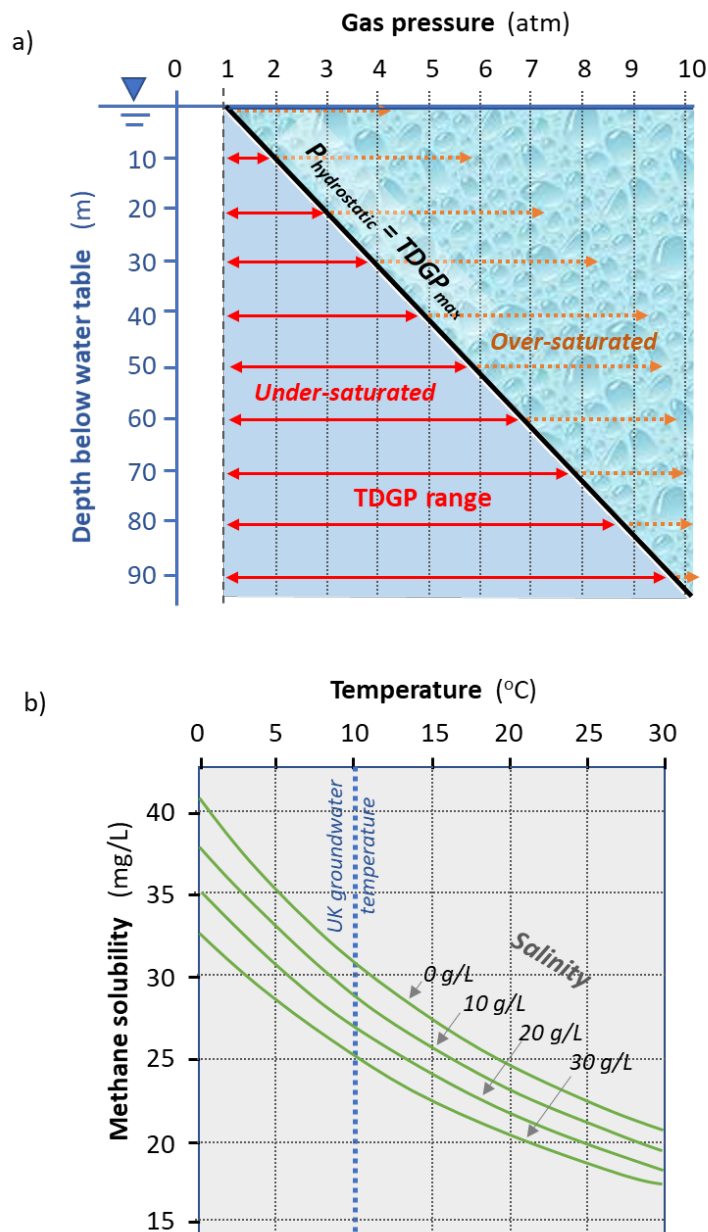


Figure 2. (a) Relationship between total dissolved gas pressure (TDGP) and depth below the water table showing oversaturated and undersaturated gas conditions in groundwater; (b) Solubility of methane as a function of temperature and salinity (plots adapted from Banks and others (2017)).

Where methane gas pressure reaches the sum of atmospheric and hydrostatic pressures for the particular depth of interest, bubble formation (gas effervescence) occurs (Pankow, 1986). In other words, when dissolved methane reaches its saturated solubility concentration for a particular water depth, 'excess' methane when oversaturation occurs will exist as 'free' methane gas that may 'exsolve' (come out of the aqueous phase and exist as a gas phase). This manifests in the formation of bubbles of methane in well water or in the geological formation. In greater volumes, these may coalesce to gaseous ganglia connecting across the geological pore network and undergo (buoyant

migration) of free methane if pore capillary forces (entry pressures) are overcome (Cahill and others, 2017, 2018).

Other gases may often co-exist with methane, for example, carbon dioxide (CO₂) in deep formations rich in coal seams. The total dissolved gas pressure (TDGP or P_{TDG}) (section 4.10) should then be considered, to which methane will contribute a partial pressure alongside other gases present (Roy and Ryan, 2010, 2013; Banks and others, 2017). A gas dissolved in water exerts a set partial pressure (p_i) to a gas phase with which it is in equilibrium, as described by the Henry's Law solubility constant. Following the terminology of Sander (2015) and recognising Henry's constant are variously defined (section 4.11.8):

$$H_i(T, S) = C_i / p_i$$

where H_i is Henry's Law constant for gas i and is a function of temperature (T) and salinity (S); and C_i is the concentration of dissolved gas i . H_i is assumed independent of hydrostatic pressure (or depth of water). TDGP is the sum of all partial pressures of each individual gas species present in the groundwater:

$$P_{TDG} = \sum p_i$$

per Dalton's Law of partial pressures. In other words, the amount of dissolved gas is proportional to its partial pressure in the gas phase (partial pressures (Sander, 2015) may be calculated from the ideal gas law, $p_i = n_i RT/V$ (where n_i is the number of moles of gas component i , R is the ideal gas constant, and V and T are the volume and temperature of the gas respectively (Ryan and others, 2015)).

The methane solubility estimates above are therefore maximum values and may only occur when other gases are absent. In the presence of other gases, methane solubility is reduced in direct proportion to its molar proportion (partial pressure) within the free gas. It is therefore important if degree-of-saturation, percent methane, calculations are made, that the contributions of other common groundwater gases (nitrogen (N₂), O₂, N₂O, hydrogen sulphide (H₂S) and CO₂) are measured to allow accurate partial pressure estimations (Ryan and others, 2000).

Therefore, more gas can dissolve in groundwater at greater depths. Any 'gas-charged' groundwater will tend to degas (form bubbles or effervesce) when the water pressure is reduced, for example, when groundwater at depth is brought to ground surface or when the water table is lowered, such as by pumping (Roy and Ryan, 2013). As other dissolved gases may contribute to the gas pressure, methane can effervesce from samples below its individual saturation value (solubility), significantly so if at low mole fraction compared to other gases. An alternative expression of the above concept using Banks and others' terminology (2017) is that the concentration at which gas would start to effervesce at a certain depth, the 'critical concentration', (or 'bubbling pressure') is reached when the sum of gas partial pressures corresponds to the sum of atmospheric and hydrostatic pressure. Pankow and others (1986) also express similar concepts in their quantitative consideration of bubble formation and headspace loss errors due to Henry's Law partitioning.

4.2.2 Sampling and analysis implications

Recognising the above physiochemical controls is central to understanding the various reasons for methane loss in the sampling and analysis process. Implications include the following, and more.

Henry's Law partitioning and ready loss of dissolved methane into a gas/air phase at an interface or via bubble formation (effervescence) allows:

- potential for significant methane loss from groundwater samples and negative bias in concentrations at both sample collection and sample analysis stages
- opportunity as Henry's Law partitioning is the basis of the 'headspace' gas analysis methodology widely used for methane analysis

Sensitivities of methane solubility (and Henry's Law constants) to pressure, temperature and salinity may have important consequences on the sampling and analysis of groundwater in that samples may:

- have different temperature, albeit typically of fairly limited variation within site or regional groundwater systems
- be from different depths, frequently both shallow and very deep monitoring points are sampled that have contrasting in situ pressures
- have different salinities, with salinity often naturally increasing with depth or groundwater age, and perhaps locally increased by contamination sources
- commonly contain varying amounts of other dissolved gases that also contribute partial pressures to the total dissolved gas pressure

Water pressure reduction, leading to possible exsolving of gas and formation of bubbles and effervescence losses of methane, may occur due to:

- pumping during sampling or by bringing a groundwater sample to surface from depth unless the in situ pressure existing at depth is maintained – this may be evident as gas bubbles in pump tubing
- lowering the water level during well purging, leading to degassing within the borehole
- collecting a groundwater sample from depth under open conditions that allows sample exposure to the atmosphere with consequent degassing
- inappropriate sample handling during laboratory analysis with, for instance, a sample collected from depth at in situ pressure inappropriately opened to the atmosphere with consequent degassing

Overall, the implications from physiochemical considerations alone are that sample recovery from depth, sample collection and handling at surface, sample transport and storage and, finally, laboratory analysis are all prone to degassing and therefore methane losses and negative concentration bias (McLeish and others, 2007). The sampling of groundwaters with high concentrations of methane where effervescence is observed or probable would in particular

require careful sampling and analysis protocols due to their enhanced susceptibility to losses.

4.3 Groundwater monitoring approaches

Scales of groundwater assessment differ depending on the monitoring facility chosen. The sampled subsurface volume decreases and resolution of the local subsurface detail increases in the following order of groundwater monitoring options:

- water supply wells – typically existing wells used for supply from which pumped samples provide an ‘integrated’ measure of groundwater quality from the well’s capture zone
- long-screen observation boreholes – typically existing boreholes from which a sample may provide a moderately local, but still integrated flow-weighted average sample from (multiple) units screened
- monitoring well/short-screen observation well – wells usually specifically installed for a project from which a sample may be drawn locally from a discrete unit, but still recognising the sample will be a flow weighted average sample from the often still heterogeneous permeability field screened
- ‘multilevel sampler’ (MLS) installations – a multi-port monitoring device specifically installed for a project and appropriately sealed to provide high resolution multi-depth (multilevel) discrete sampling of adjacent units resolving a vertical profile of point samples with depth

We focus on the first 3 scales of assessment as these are more commonly used to monitor groundwater methane. The broad similarity of sampling approaches allow us to consider monitoring and observation wells together unless otherwise specified. From this point, these are collectively termed ‘monitoring wells’. Use of MLS appears to be largely restricted to research-oriented studies (Barber and Briegel, 1987, Cahill and others, 2018, Cahill and others, 2017, Cheung, 2019, Dumble and others, 2006, Houben and others, 2018, Schout and others, 2018, Ward and others, 2020). Their use, though, should not be overlooked. Comparatively few, even one MLS installation, can reveal differences in methane concentrations with depth, accounting for previously unexplained variability of concentrations monitored at larger observation scales. High resolution profiles could also be obtained during the drilling process, as exemplified by the high-resolution concentration and isotope profiles obtained for methane, C_2H_6 , and propane (C_3H_8) to some 1,500m depth in the sampling of directional drilling cuttings at a site in Saskatchewan, Canada (Dominato and others, 2018).

Depth profiling of in situ methane does not need to be restricted to conventional multilevel approaches. For instance, Barber and Briegel (1987) used a string of 10 diffusion samplers within a borehole backfilled with grout. Individual diffusion cells simply comprised a 2m length of thin-walled (0.4mm) Teflon tubing (id 1.7mm) permeable to methane (Vieth and others, 1976) coiled with 8mm

separations around a 100mm length of PVC pipe (50mm od). Tubing ends were attached to small diameter (2mm od) nylon lines (impermeable to methane) which passed through the PVC pipe and connected the cells to the surface within the PVC tube. In situ measurement of groundwater methane was achieved via sampling of purge gas (air/inert) passed through the tubing. Calibration with ground temperature correction permitted sampling up to 25,000ppm_v (around 1atm partial pressure) of methane and likely much higher concentrations (but not tested).

Studies locally comparing different scales of assessment of groundwater methane such as Houben and others (2018) appear rare. A few research-based regional studies offer some comparison. For instance, Bordeleau and others (2018a) compare groundwater from 30 residential wells with 14 project drilled observation wells in the Saint-Édouard area, Quebec. In the UK, the Vale of Pickering baseline study compares supply well, purpose drilled observation well and multilevel samplers (Ward and others, 2020). Conclusions, though, on using different monitoring scales are typically quite restricted as the spatial heterogeneity of methane may dictate that the different scales are very locally nested to allow meaningful comparisons. This would necessitate a suitably designed research and drilling programme.

4.4 Sampling supply wells

Sampling existing water supply wells for methane assessment in the shale gas context is becoming internationally common to establish pre-operational baseline conditions and to provide verification monitoring of possible impacts of existing shale gas operations on their surroundings. It may allow direct monitoring of risks to people if wells are used to supply drinking water. Wells chosen for sampling may be influenced by their geographic coverage, protection of populations at risk, aquifer type or depth coverage, access, suitability of sample collection point, proximity to shale gas operations, and suitability for baseline monitoring.

Liabilities from possible damage associated with temporary removal/handling of existing pump assemblies or well infrastructure usually prevents downhole sampling devices being used, thereby restricting sampling to using existing above-ground access points, such as taps at the wellhead (Hirsche and Mayer, 2009). Sampling at surface increases the likelihood of degassing losses. These may occur within the well, surface infrastructure pipe network and tanks, and in association with the chosen sample collection approach (Ryan and others, 2015).

Current protocols for sampling supply wells have largely evolved from those used for monitoring wells. There are important differences though (Molofsky and others, 2018; Ryan and others, 2015; USGS, 2006). Supply wells are typically in regular (daily) use, have long screens or open borehole sections, are equipped with high capacity pumps at a specific depth, and leave the practitioner with limited options to control flow rates. Usually practitioners are unable to replicate low-flow sampling rates downhole, have poor or no access

for downhole sampling or sensor deployment, and variable access for water level measurement (Ryan and others, 2015). This contrasts with monitoring wells that are infrequently pumped (just for sampling), are short screen, have wide flexibility over pump and sampling device choice, its position and flow rates used, and where downhole sampling and water level monitoring are routine (Molofsky and others, 2018).

As the fundamental purpose of supply wells is to provide water, screen or open borehole lengths tend to be long. Screens may be particularly long in high-volume public water supply wells, for example, in the the UK Permo-Triassic sandstones and, for instance, screens in wells surveyed by Wright and others (2019) close to a Californian oilfield, ranged from around 20 to 170m. The result is an integrated, aquifer volume averaged water quality sample, with greater aquifer volumes sampled with increased supply abstraction rates and greater aquifer thicknesses sampled with longer screen lengths. These may differ greatly between different supply well types, even locally, for example, compare a < 20m³/d (0.02Ml/d) domestic household supply with a water utility 10Ml/d public water supply well.

Obtaining detail on supply well construction, performance and operation of selected monitoring sites is important for designing and implementing well sampling protocols. This information also supports meaningful groundwater methane data interpretation. Supporting supply well data should include the following (developed from USGS (2018)):

- borehole depth, casing, screened interval detail, and diameters – to allow screen volume and purging calculations
- lithological log, or at least summary data – to assess probable geological units sampled and inform geological conceptualisation
- identification of screened aquifers and main aquitard units – to allow reasonable hydrogeological conceptualisation locally and within the wider context (ideally with interpreted pumping test aquifer parameters)
- water level data, including the typical seasonal range of rest and pumped water levels – to inform hydrogeological conceptualisation and possible degassing issues
- typical water supply usage detail including pump type, capacity, installation depth, abstraction rates (daily/monthly and annual), periods of use, pump-cycling detail – to inform well purging requirements, aquifer volumes sampled and hydrogeological conceptualisation

Literature examples of good supporting data include Thomas (2018) and Dillon and others (2016), that are guided by USGS (2018).

Variables and uncertainties associated with supply well sampling include the following:

- supply well sample collection point influence

- supply well purging protocols adopted
- sample collection protocols adopted: open, semi-closed and closed systems (section 4.6)
- sample sensitivity to water levels and in-well degassing (section 4.4.3)
- practitioner experience, proficiency and individual interpretation of protocols
- quality assurance – quality control (QA-QC) checks implemented

The first 2 variables listed are discussed below.

4.4.1 Collection points in supply wells

Poor choice of sample collection points may lead to bias in sampled methane concentrations (Molofsky and others, 2018; Ryan and others, 2015). Samples are ideally obtained as close to the well head as possible, avoiding lengthy pipework, and prior to any pressure tanks (vessels), storage (header) tanks or treatment facilities that could compromise a sample. Many UK private supplies have pressure/storage tanks (Environment Agency, 2004) as do supplies in the US. Pressure tanks were encountered at 86% of Eastern Kentucky supply wells sampled by Zhu and others (2018).

Unavoidable sampling from taps immediately downstream of pressure tanks has been a concern in the US. They often represent the closest access point to the wellhead and are usually found prior to filtration or water treatment (Molofsky and others, 2018; Zhu and others, 2018). Permission to install sample taps upstream of pressure tanks from owners is not always forthcoming (Molofsky and others, 2018). Where taps are downstream of pressure tanks, the protocol used by Zhu and others (2018) for supply wells in regular use was to pump at a rate of around 0.2l/s to flush 2 pressure tank volumes with rates then lowered at the tap to ~0.03l/s for sample collection.

UK research on sampling downstream of tanks/facilities has been limited. A study of small groundwater sources observed supply wells sampled with pressure vessels that exhibited no significant change in inorganic water chemistry and bacteria levels before and after the vessel (Environment Agency, 2004). Limited change in alkalinity and DO suggested loss of dissolved gases in the pressure vessel would be insignificant, but these were not sampled for. The study also sampled 3 supply wells before and after storage header tanks. Slight DO increases were associated with water aeration, although there was little change in major ion and metal concentrations. Dissolved gases and VOCs were not analysed.

Molofsky and others (2018) specifically evaluated pressure tank influence on methane sampled at supply wells in the US. Samples were taken after purging 3 well casing volumes in line with the USGS (2006) default protocol. Sampling before versus after the pressure tank did not significantly influence methane concentrations. The median directional percent variability between pre- and

post-tank samples was very small, at just -3% (n = 31). The most common type of pressure tank was a bladder or diaphragm-type pressure tank where water is stored and flows through an air-tight bladder or diaphragm chamber surrounded by pressurised air. Since this is a sealed environment expected to result in minimal, if any, loss of dissolved gases, the minimal influence of the tank in this study was consistent with expectations.

One exception tested a well with an air-over-water pressure tank, which yielded much lower and variable post-tank methane concentrations. The differences, from -13 to -44%, were attributed to gas exchange loss to the compressed air in contact with water. These configurations are not common in the US (Molofsky and others, 2018).

Despite the apparent lack of pressure tank influence, Molofsky and others (2018) recommend sample collection from upstream of tanks and as close to the wellhead as possible. If it is not possible to achieve this, they recommend sampling at a consistent location to minimise variability between sampling events.

4.4.2 Purging in supply wells

Different volumes of water purged and flushed to waste prior to sampling could influence sampled methane concentrations. As well as water withdrawn during well-purging, the volume of water pumped recently for water supply should be considered (Smith and others, 2016; USGS, 2006). This 'prior contribution' could potentially account for substantial variations in methane concentrations found at supply wells pumped frequently, but intermittently (Gorody, 2012, Harder and others, 1965, Ryan and others, 2015). Prior pumping conditions may be relatively constant or vary from visit to visit, for example, water levels could be particularly low due to a recent increase in use, or sampling visits to wells only occasionally pumped for supply may be soon after, or a long time after, that operation. Generally, protocols purging smaller volumes may be expected to be more sensitive to previous well operations.

Purging aims to flush groundwater that is not representative of the aquifer from the borehole. This may include standing water from pipework, tanks or the wellbore. For volatile determinands such as methane and VOCs, this water may be prone to degassing loss to the wellbore 'headspace' (air space above the water table) (Powell and Puls, 1993, Smith and others, 2016). There has been much contention surrounding the degree of purging necessary for groundwater quality sampling of both supply or monitoring wells (Martin-Hayden, 2000, Martin-Hayden and others, 2014, McMillan and others, 2014, Puls and Barcelona, 1996, Robin and Gillham, 1987). The possibility of groundwater flow naturally flushing the screened section of the well, vertical flows in the wellbore, and turnover of wellbore water through operational use need considering when evaluating purging protocols.

Purging protocols for most supply wells usually involve a fixed-volume purge with sampling after removal of a set number of borehole, or well screen volumes

(USGS, 2006) and/or pipe infrastructure and pressure tank volumes (Zhu and others, 2018). Protocols typically also require stabilisation of water quality indicators (field parameters, for example, SEC, pH, temperature). The purging protocol set out in the USGS National Field Manual (USGS, 2018) is illustrative of standardisation needs, but also pragmatic flexibility and expert judgment required. The manual states, “As a rule of thumb, the standard USGS purge procedure removes three or more well volumes of standing water while monitoring the water level and the stabilization of routine field measurements as a function of time, pumping rate, and the volume of water being removed” (USGS, 2006). It goes on to state, “When standard purge volumes cannot be removed, sufficient water must be withdrawn from the well to evacuate at least one borehole volume and to field rinse the sampler and sample tubing - alternatively, flush the pump and tubing system with the equivalent of three tubing volumes”. And continues, “when a supply well to be sampled is being pumped continuously or daily at regular intervals and long enough to have removed three casing volumes of water - go directly to monitoring field properties”.

Molofsky and others (2016) present the most relevant recent research focusing on groundwater methane sampling at supply wells. They address the important question, “what is the effect of purging larger versus smaller volumes of water prior to sample collection?” in their evaluation of 10 supply wells in Pennsylvania within fracture-flow dominated interbedded sandstone, siltstone and shale units. Samples were collected from a tap post-pressure tank using IsoFlask™ containers (section 4.6.4). Commonly used purging protocols were tested. These were in decreasing volume purged (the low-volume pair may reverse):

- high-volume purge of 3 (well) casing volumes
- medium volume purge of one casing volume
- low-volume purge of 2 pressure tank volumes
- low-volume purge, with purge to initial parameter stabilisation comprising 3 successive readings of pH: ± 0.2 , temperature ± 0.2 °C, SEC $\pm 5\%$
- minimal purge of just 2 litres (not a common protocol, but a very minimal approach)

Molofsky and others’ (2016) main findings and recommendations are paraphrased below:

- There was no clear benefit to purging large volumes of water (3 casing volumes) prior to sampling; and, in any case, it was noted that these volumes tend to be much larger than those representative of normal residential use and therefore concentration exposure.
- Regardless of the volume purged and time between sampling events, the maximum change in methane concentration for most wells was less than a factor of 2 (that is, $\pm 100\%$).

- Changes in methane concentration with increasing purge volume are commonly predictable at individual wells and may display increasing or decreasing trends.
- Changes in dissolved methane concentration with increasing purge volume correlated with changes in SEC, Na, Cl, Br, SO₄ and salinity indicators, suggesting that methane concentrations in these cases were linked to changes in the relative volumes of sodium-rich fluids entering the wellbore. This could influence the degree of purging that should be undertaken and shows the value of accompanying major ion monitoring to understand purging influences and methane variability and provenance.
- There was typically little difference (less than $\pm 10\%$) in dissolved methane concentrations between samples after purging just 2 litres of water versus low-volume purging to initial parameter stabilisation.
- Purging to initial parameter stabilisation was nevertheless recommended to remove water present in lines and the pressure tank, that are subject to loss of small volumes of methane. It was especially important to monitor until temperatures stabilised, that is, the point at which water from the pump intake reaches the sample tap/port.
- If a sample should be representative of the typical water quality consumed from a residential well, it can usually be obtained by purging <1 casing volume of water prior to sampling. This allows rapid recovery of water levels in wells with on-off pump cycling during usage, which means that a large drawdown from a high-volume purge is unlikely to occur during routine supply well use. Therefore, a 3-casing volume purge was not recommended, although could be considered appropriate for the sampling of higher volume supply wells (e.g. irrigation wells).
- Regardless of the chosen purge volume, as recommended widely by others, protocol and purge volume should remain as consistent as possible between sampling events and surveyed locations.

The above is judged to provide a data-informed, reasoned and pragmatic approach to the purging of supply wells.

4.4.3 Degassing in supply wells

Samples taken for methane concentration analysis may be sensitive to water levels and in-well degassing, in supply well or observation/monitoring well contexts. Methane and other dissolved gases may be subject to in-well degassing (effervescence) due to bubble formation and migration (effervescence (or ebullition)). Effervescence may manifest as buoyant bubble migration and result in gas loss from the wellbore water surface and accumulation in the well headspace (and may constitute a flammable or asphyxiating gas hazard) (Pankow, 1986; Smith and others, 2016). Gas concentrations within the well water will therefore decline. Since gas effervescence is a rapid process (Walsh and McLaughlan, 1999), wellbore water that is standing or slow moving with a long residence time is prone to

increased gas loss. Moreover, gas losses will be further increased by water depressurisation; significant water table lowering during purging and sampling that may permit increased rates of bubble formation and gas loss (Pankow, 1986; Roy and Ryan, 2010; Ryan and others, 2015; Banks and others, 2017; Smith and others, 2016). Sampled well water concentrations will therefore be impacted by the purging and sampling protocol chosen and its sensitivity to any in-well degassing that might take place. This sensitivity needs to be considered in designing protocols, especially for sampling sites with higher concentrations of dissolved gases sufficient to result in effervescence over the relevant pressure variations envisaged (Banks and others, 2017; Pankow, 1986).

Lowering water levels in a well causes a decrease in groundwater hydrostatic pressure and therefore, at a given depth below surface, consequent decrease in the methane saturation threshold and risk of methane exsolving and bubble formation (Pankow, 1986). For instance, given a methane saturation of 28mg/l at the water table (1atm) and a saturation of 55mg/l methane at 10m depth, lowering the water table by 10m may exsolve 27mg/l (= 55 – 28mg/l) of methane previously dissolved under pressure (Smith and others, 2016). Methane releases have been observed in wells, for instance, by Tsunomori and Notsu (2008) induced by rapid groundwater level decline and by Siegel and others (2001) in peatland degassing to the atmosphere when the water table is lowered. Concerns of in-well degassing impacting methane concentrations in the shale gas monitoring context have recently been evaluated by Smith and others (2016) for supply wells and Roy and Ryan (2010) for shallow monitoring and deeper observation wells as summarised below.

Smith and others (2016) examined 12 domestic supply wells within a fracture-flow dominated interbedded sandstone, siltstone, and shale unit in Pennsylvania. the main findings were that:

- methane gas was observed during pumping to be exsolving from the groundwater and accumulating in the wellbore headspace due to pressure changes caused by drawdown during water supply well pumping, or regional seasonal declines in the water table
- short-term pumping from both purging and routine domestic use prior to sampling probably had a minor effect on sampled dissolved methane concentration variability in wells testing moderate (>5 to 15mg/l) to high (> 15mg/l) methane concentrations, with no consistent correlation with concentration
- the maximum drawdown during purging (up to around 10m in some cases) may have had a minor effect on dissolved methane in some wells, but varying drawdown during well purging or sampling could still contribute to the variability of dissolved methane. However, there was no consistent correlation to the dissolved methane concentrations in groundwater
- dissolved methane concentrations from most wells with initial dissolved methane > 6mg/l correlated with natural changes in regional groundwater levels - methane concentrations were highest when regional groundwater levels were at seasonal lows. Exsolved methane occurred at this, apparently

low threshold concentration, with methane accumulation observed in the well headspace

- in some wells with large drawdown or sustained water use, methane in the headspace of water wells could rapidly increase, reach ignitable concentrations, and remain elevated for days
- therefore overall, although methane exsolution and in-well degassing does not appear to be particularly influential on methane concentration variability during purging (especially if purging caused only small drawdowns), it was a significant control on the methane concentration variability monitored in the medium to long term

Roy and Ryan (2010) used TDGP sensors (section 4.10) within screened sections of 4 to 72m deep wells to compare dissolved gas under open and sealed conditions where in-well water was isolated from the atmosphere by a hydraulic packer under non-pumping and pumping scenarios. The study is novel in that while degassing of groundwater pumped or otherwise brought to surface has been addressed in various studies, there was an absence (that largely continues) of studies assessing in-well degassing, apart from Smith and others (2016) above. Roy and Ryan's (2010) main findings and recommendations include the following:

- When groundwater is gas charged, the background aquifer TDGP, and likewise the dissolved gas concentrations, may be substantially higher than initially measured in open wells, indicating significant in-well degassing.
- Furthermore, groundwater TDGP values are much greater than reported in the literature (up to 4atm observed when pumping methane gas-charged wells), which raises concerns that reported dissolved gas concentrations (and TDGPs if measured) may have been underestimated in some cases within the literature.
- Degassing from open wells could affect nearly all current methods of determining dissolved gas concentrations in groundwater, including water and gas samples collected in the well and sealed during the removal (including copper tubes, gas diffusion devices, grab sample devices, see section 4.6), those collected while pumping (including gas stripping methods (Hersche and Meyer, 2008)), and TDGP measurements.
- Recommendations made to remedy the above were adopting additional procedures to obtain representative measurements from some wells, including:
 - installing in-well hydraulic packers to seal the well
 - pumping to bring in fresh groundwater
- That said, observed decreases in TDGPs during pumping, attributed to gas bubble formation induced by drawdown in the well below a critical pressure (relative to TDGP), may disrupt measurements made during or after pumping recovery. Monitoring TDGP while pumping gas-charged wells was therefore recommended (section 4.10).

General recommendations arising from well degassing concerns would be that:

- protocols need to be carefully considered, especially where methane and, or other dissolved gasses are at elevated concentrations where degassing may be probable under the site pressure (change) conditions envisaged
- where degassing is shown or suspected as an issue:
 - sampling of ‘fresh’ wellbore water is carried out, meaning that a protocol minimum of one screen volume is purged prior to sampling (or else the wellbore is shown to flush rapidly by natural groundwater flows)
 - purging (and sampling) pumping rates are kept sufficiently low to result in insignificant well drawdown and insignificant degassing
 - supporting measurements are taken, for example, water levels, flow rates, well headspace gas sampling, TDGP measurements, pumping tests to determine drawdown characteristics (some time prior to avoid sample interference)
 - relevant health and safety aspects are adequately covered

4.5 Sampling monitoring wells

4.5.1 Sampling protocols in monitoring wells

There have long been many options for sampling groundwater from monitoring wells and observation boreholes, including for dissolved methane (Barcelona and others, 1984). Using different purging protocols and sampling devices is often suspected to be a primary cause of variability in methane concentrations that arise from the sampling process. Samples may be collected at the surface from pumped water following purging to remove standing well water. Alternatively, groundwater can be collected from within the screened section of the wellbore via a zero-purge downhole sampling device. This may be with or without prior purging, usually by another device capable of removing larger volumes.

A range of now conventional (commercially available) suction, inertial-lift, impeller, or bladder pumps may, in principle, be used to pump groundwater to the surface for methane sampling (Barcelona and others, 1984). The various pumping mechanisms involved may influence methane concentrations differently and vary in possible losses of dissolved gases (Pankow, 1986). At the surface, a range of possible open, semi-closed and closed sample collection options may then be used (section 4.6.1).

Similarly, a range of commercially available downhole, no-purge, grab samplers may be used. At their simplest, these comprise bailers that are typically designed for sampling groundwater in wells that are screened across the water table, but not for wells screened below the water table (McHugh and others, 2016, Newell and others, 2000). For sampling below the water table, downhole devices are preferred, in which the fill depth interval is within the well screen

either at or below the water table (Britt and others, 2010; McHugh and others, 2016; Parker and Clarke, 2004).

Many downhole devices have been developed over the years, some specifically designed for dissolved gas/methane sampling and retrieving a sample at its in situ pressure, aiming to minimise degassing losses that may occur in other sampling approaches (Barker and others, 1987, Hirsche and Mayer, 2009, Johnson and others, 1987, McLeish and others, 2007, Nurmi and Kukkonen, 1986, Simpkins and Parkin, 1993). To date, these tools appear largely only to be used in research settings.

Commercially available downhole sampling methods for both general groundwater and methane sampling include:

- devices that may be triggered to sample at a specific depth discrete interval, for example, the Snap Sampler (ProHydro, 2015), electro-mechanical depth samplers
- passive diffusion samplers – these may comprise plastic tubing or bags that are permeable to methane. Methane diffuses across the plastic into clean water or a gas stream in the container, equilibrating with the surrounding groundwater. This can then be analysed (Barber and Briegel, 1987). For instance, a dialysis sampler comprises a deionized water-filled tube of high-grade regenerated-cellulose dialysis membrane inside an outer protective layer of low-density polyethylene (LDPE) mesh, for example, (Gardner and Solomon, 2009, ITRC, 2007, Vroblesky and Praveck, 2002)
- grab check-valve sample bag systems, specifically the HydraSleeve™ system (HydraSleeve, 2020) – a plastic sample bag fitted with a check valve to take in water over a 1 to 2m interval via an upward pulling motion (McHugh and others, 2016) (noting the HydraSleeve™ may also be used as a passive diffusion sampler)

Reviewing the case literature confirms widespread use of the above conventional pumped and downhole sampling approaches for methane used with a range of purging protocols. The latter may be categorised, according to McMillan and others (2018), as:

- ‘zero/minimal-purge’ protocols using grab or passive diffusion-based samplers that remove none or a very small water volume prior to sampling, and effectively obtain a grab sample of the ambient flow regime occurring at the point or interval monitored within the well screen
- ‘low-flow’ (low stress) protocols that purge and sample at low flow rates until indicator parameter stabilisation occurs, and may involve low to moderate volumes of water being extracted to achieve this condition
- ‘multiple well-volume purging’ (fixed volume purge) protocols that are based on a specified number of well volumes being purged prior to sampling

It is challenging to completely separate the sampling approaches (pumps, devices) from purging protocols discussed in the literature. Acknowledging

some crossover, the subject area is nevertheless approximately split in the following section on comparative studies of sampling approaches; purging protocols; and, downhole samplers maintaining in situ pressure. The sections 4.5.2 and 4.5.3 cover the approaches more typically used in sampling groundwater methane.

4.5.2 Comparisons of sampling protocols in monitoring wells

While a significant amount of literature describes sampling methane in groundwater, few field studies have reported in detail the influence of sampling method and protocol adopted on methane concentrations measured (Rivard and others, 2018a). However, previous comparative work for measuring VOCs is of some relevance because of their similar volatility (Barker and Dickhout, 1988, Devlin, 1987, McHugh and others, 2015, Parker and Clark, 2004). The notable exception specifically addressing dissolved methane sampling (alongside VOCs) is the pioneering study of Barcelona and others (1984). This is related in some detail below due to its continuing relevance and the lack of studies since.

Barcelona and others (1984) present a controlled large-scale laboratory study examining the influence of sampling device type and mechanism. A test rig was built to replicate a shallow monitoring well and recovery of dissolved methane with concentrations between 0.1 and 18mg/l (below effervescence levels) by 11 commercial sampling devices tested. Their results are summarised in Table 2 and reveal the accuracy of samplers was consistently poor, with negative bias (underestimations) ranging from -7% up to -36%. Bias was reduced with the dual check valve bailer (similar to the control), positive displacement bladder pumps, gas displacement and syringe samplers. A larger negative bias and concentration losses were caused by peristaltic and mechanical pumps and conventional bailers. However, the sampling precision (shown by RSD (relative standard deviation) ratio) of the devices with less bias was poor, with an RSD of a factor of 2 or more than the controls, apart from the bladder pumps.

Table 2. Summary of dissolved methane (0.1 to 18 mg/l) sampling device testing results of Barcelona and others (1984).

Sampler type	Mean percent bias	Mean precision RSD _{sample} / RSD _{control}	Number of triplicate runs
	%		n
Dual check valve bailer	-7	2	1
Positive displacement, bladder (3 designs)	-15	1	4
Gas displacement (2 designs)	-18	3	4
Syringe sampler	-20	3	1
Suction sampler (peristaltic pump)	-23	1	2
Conventional bailer	-35	1	1

Positive displacement, mechanical pump (2 designs)	-36	1	4
Control samples (relative to standards)	-8		9

The main conclusions drawn from these results by Barcelona and others (1984) were that:

- methane losses resulting from the sampling mechanism can produce inaccurate results with negative bias (underestimations) of methane concentration. This can be 2 to 3 times greater than the analytical bias (conventional headspace – GC/FID analysis was used)
- poor precision arises from the actual operating conditions during sample collection – the sampling mechanism and the expertise of the sampling technician are regarded as the main source of imprecision. The critical variables were identified as time, temperature, reproducibility of flow rates and the technique used for filling the storage vessel

The pioneering study of Lewin and others (1989) of the UK Water Research Centre (WRC) that specifically set out to develop a sampling and analysis method for groundwater methane compared 2 types of depth sampler devices at observation boreholes. The BAT 'Hydroprobe' (BAT Envitech, Sweden) sampled at in situ pressure. Samples were taken in an evacuated vial at depth using a spring mounted needle assembly sampler that was sealed with a septum when the pressure differential was zero. From this, a headspace gas sample could be directly taken for analysis. This was compared to an electro-mechanical depth sampler (Wuidart sampler) (not dissimilar to double-valve bailer), then widely used by the water industry. Dissolved methane concentrations were found to be 2 to 8 times lower from the Wuidart sampler than the BAT sampler. This was attributed to some degassing of samples retrieved from depth and open system sample transfer from the depth sampler to analysis vials. Supporting laboratory experiments by Lewin and others (1989) demonstrated that 5 to 50% of the dissolved methane was lost in the open system transfer to vials. These losses were effectively avoided using the BAT sampler, however, the precision of that sampling method was poor. This was largely due to the variation of headspace-to-water ratio obtained within the BAT vials retrieved in the field that was recognised to require greater control (a water-headspace sample was expected as the BAT vial was not fully evacuated).

Some literature compares sampling methodologies, but does not necessarily report original data. Parker (1994) carried out a literature review of the early VOC work and the main conclusions were consistent with the Barcelona and others (1984) findings; that bladder pumps gave best overall recovery of VOCs, and recovery by suction-lift pumps such as peristaltic pumps was poor due to the vacuum application causing depressurisation and sample degassing. The effects of bubble formation and volatiles/gas loss due to sample depressurisation during pumping (section 4.2.1) is considered quantitatively by Pankow (1986) who briefly considers the impact of pump types. In particular,

suction-lift pump samples may be exposed to overlying pressures as low as 0.37atm when the limit of suction lift is reached and bubble formation with concomitant volatilisation losses may be exacerbated greatly. Pankow (1986) indicates that although samples retrieved with bailers and pumps typically experience a minimal pressure at surface of 1atm, some (submersible) pumps may expose the sample to lower pressures within the pump body. While any bubbles formed may be able to re-collapse before the sample reaches the surface (the at-depth pump outlet pressure will be greater than the in situ water column pressure to enable water lift to the surface), some bubbles may perhaps not collapse completely, subsequently allowing bubbles to nucleate at the surface. Pankow (1986) further surmises that because sample (summed gas/volatile partial) pressures substantially larger than 1atm are usually required to nucleate bubbles either heterogeneously (on say suspended silt/clay particles) or homogeneously, therefore relevant to open-system sampling (section 4.6.2), a sample can probably be sealed in its container before the bubble formation process is complete (that is, undertaken rapidly due to awareness of possible losses).

The US Interstate Technology & Regulatory Council (ITRC 2007) provides guidance on no-purge groundwater sampling, including for volatile gases (but no testing data). It recommended using the grab sample HydraSleeve™ bags and Snap Samplers® for sampling volatile gas, including methane. Still, both samplers were criticised for the small sample volume retrieved compared to the large water demand now common for multiple analyses that may include isotope analysis. Further criticism is levelled at HydraSleeve™ sampling though by McHugh and others (2016) based on their comparative VOC sampling with Snap Samplers, standard low-flow purge sampling and some high-volume purge sampling. They report a negative bias and more variability in HydraSleeve™ VOC concentrations, especially for wells with over 3m of water above the monitoring screen interval. Their expressed concern is that the HydraSleeve™ check valve may not always perform as expected, with potential to collect water from an incorrect depth interval, possibly compromised standing water above the well screen.

Rivard and others (2018a) and supporting works (Bordeleau and others, 2018b, Rivard and others, 2018b) are the most recent studies comparing conventional methods for sampling groundwater methane. Impeller and bladder pumps and HydraSleeve™ sampling bags were evaluated before and after purging and pump sampling within 30 to 60m deep fractured bedrock open observation boreholes in the Quebec's St. Lawrence lowlands where spatially variable dissolved methane naturally occurs. Samples were retrieved from 7 to 54m depth, with sampling devices located close to the most productive fractures, previously identified via downhole geophysics. Rivard and others (2018a) were dismissive of, but did not test, inertial pumps, stating based on their operating principle, that they were expected to lead to excessive degassing, per reporting of Barker and Dickhout (1988), Devlin (1987), and others cited in Parker (1994).

Preliminary tests with a peristaltic suction pump were discontinued by Rivard and others (2018a) when confirming that samples yielded significantly lower

methane concentrations compared to impeller pump samples (consistent with expectations above). They noted a well with the water table near the ~8m suction limit exhibited degassing very evident from “numerous bubbles visible in the sampling tube”. However, they found that $\delta^{13}\text{C-CH}_4$ and $\delta^2\text{H-CH}_4$ values from sampling with a peristaltic pump sample were similar to those obtained with impeller and bladder pumps. In their recent comparison of depth-specific methods for sampling methane in shallow groundwater (2.5m depth), Houben and others (2018) observed similar negative bias from using a peristaltic pump to sample narrow tubing (3mm internal diameter) multilevel samplers compared to pumped observation well and direct push probe samples obtained with a foot-valve (inertial) pump. They noted that the pulsed flow and local under-pressure in the tube produced by the peristaltic pump induces significant degassing (for example, Barcelona and others, 1984) and possible, albeit smaller, losses via gas diffusion through the plastic sample tubing that has a high surface area to volume ratio due to its narrow diameter. They also noted that peristaltic pump sampling of narrow multilevel sample tubing is common in VOC/methane research studies due to the impracticality of alternative pumping arrangements on many sample ports (Cahill and others, 2017; Houben and others, 2018; Schout and others, 2018). Whether samples are taken after or before the peristaltic pump head via a valving arrangement to try to minimise methane/VOC losses is often not indicated.

Some brief comments from Rivard and others (2018a) on the practicalities of the devices used include the sturdiness and ease of use of the impeller (Redi-Flo2) pump, but its inability to provide low enough flow rates in some less permeable wells to meet the US EPA low-flow purge minimum pre-sample drawdown of 10cm prior to stabilisation of field parameters (Puls and Barcelona, 1996); the average drawdown was $0.52\text{m} \pm 0.41\text{m}$ for which induced degassing influences would have been fairly low. While the bladder pump could overcome the above low-flow issue, it was criticised regarding the need for some delicate fine-tuning, its less sturdy nature, and requirement for an air compressor. Noted advantages of the HydraSleeve™ bags were their usefulness in extremely low hydraulic conductivity boreholes, where purging would otherwise lower the water level by several metres. They allowed sampling of a very deep (147m depth) well not accessible by the pumps used, and the option to sample with bags before and after purging to test the impact of purging on wellbore quality. The main negative was the need for 6 HydraSleeve™ bag volumes of water to fulfil analysis sample demands, partially overcome by a methodology outlined allowing limited bag reuse.

Rivard and others' main findings (2018a) include:

- Methane stable isotope composition ratios were not sensitive to the selected sampling techniques, with impeller, bladder and peristaltic pumps and HydraSleeve™ bags usually providing similar results.
- Methane concentrations were comparatively more sensitive, and significant differences were observed in a few wells, but no systematic technique-related bias was identified.

- The no-purge approach was appropriate in some wells but not in others, depending on the hydrogeological conditions, in particular in the presence of vertical hydraulic or salinity gradients within the well.
- Dissolved methane concentrations could sometimes vary quite significantly (up to 3.5 times) for a given well and sampling event.

Protocol recommendations by Rivard and others (2018a), directly quoting, were to:

- “carry out a purging period until stabilization of groundwater physicochemical parameters at the depth where flowing fractures are documented
- pump the well at a low flow that will keep drawdown to a minimum, to avoid groundwater pressure changes that result in degassing
- remain consistent in sampling depth and bottle-filling procedure, as well as for the sampling device
- preferably use a low-flow impeller submersible pump, such as the Redi-Flo2pump, as this kind of device is simple to use and very reliable and does not involve the use of disposable materials”

It is emphasised that it appears necessary for there to be knowledge about the flowing fracture zones via borehole-geophysical logging before sampling. It is assumed that placement elsewhere in the wellbore due to a lack of this knowledge would have led to greater discrepancy in concentrations obtained by the approaches tested. It is noted that it is typically more difficult to determine primary inflow zones to open boreholes in non-fractured sedimentary rock or unconsolidated sediment aquifer environments where inflows may be much less focused and vertical in-well velocities perhaps low and less easily discerned (McMillan and others, 2014).

4.5.3 Purging in monitoring wells

There is a range of commonly used purging protocols, but these have not been explored in detail in the literature. The comparative literature mostly applies to groundwater contaminant sampling in general rather than being methane specific (Britt and others, 2010; ITRC, 2007; McHugh and others, 2016; Puls and Barcelona, 1996; US EPA, 2010; 2017; Vroblesky, 2001). The methane sampling literature indicates that a range of protocols are used in practice. There have been some comparisons of these protocols.

The purging of 3 well (or casing) volumes remains quite common in groundwater methane sampling (Avrahamov and others, 2015; Schout and others, 2018; Wright and others, 2019). It is probably at or towards the upper limit of a fixed volume purge amount and is often accompanied by stabilisation of field parameters. For instance, Moritz and others (2015) indicate for methane (and other) sampling “a volume equivalent to 3 times the water volume in the wellbore was purged for observation wells” ... “the water was sampled once the physicochemical parameters of the water (pH, conductivity and temperature)

had stabilized". Some methane sampling studies have purged larger relative volumes as standard, but these appear to be shallow low-volume observation/monitoring wells. Houben and others (2018), for instance, purged 5 well volumes followed by field parameter stabilisation, but also note the parallel requirement to minimise drawdown to less than 20% of the height of the initial water column to avoid degassing losses of volatiles due to lowering of water pressures (section 4.4.3).

The other extreme, a zero/minimal-purge protocol may be used, whereby a 'grab' sample is retrieved directly from the wellbore within the screened section. The underlying justification for using this protocol is that natural groundwater flow through the well screen is sufficient to continually purge the borehole of standing water. This can in part justify low-flow (low stress) protocols that purge and sample at low flow rates until field parameters stabilise with frequently low volumes of water being extracted. Zero-purge sampling has been mostly tested for contaminants other than methane, VOCs being the most common (Britt and others, 2010; Vroblesky 2002; Parker and Clark 2002; ITRC 2007; Parker and Mulherin 2007; Adamson and others, 2012).

There has been some criticism of using zero-purge or passive sampling approaches to sample dissolved gases. For instance, passive diffusion samplers or HydraSleeve™ bags left to equilibrate for a period of time, due to the considerable in-well variability of methane concentration over time, even for short periods (Hirsche and Mayer 2009; Gorody 2012). This is especially apparent where methane concentrations are sufficiently elevated to cause in-well degassing losses (Humez and others, 2015; Smith and others, 2016; section 4.2.1). Zero-purge downhole grab sampling for methane may therefore involve pre-purging the well, often of 3 well screen volumes (Banks and others, 2017; Rivard and others, 2017a). Without this purging, zero-purge and low-flow (low stress) protocols, with low volumes of water extracted to achieve parameter stabilisation may be vulnerable to variability in concentrations from in-well degassing losses.

The well purge volumes required before taking pumped groundwater samples from monitoring/observation wells remains controversial. A pumped sample should converge to a steady-state 'flow-weighted average concentration' of a determinand; an average of the formation's vertical heterogeneous concentration distribution weighted by the vertical distribution of flow rates (or formation hydraulic conductivity) (Martin-Hayden and others, 2000; McMillan and others, 2014; Puls and Barcelona, 1996). Modelling based on this premise typically suggests that while concentration variability may persist up to at least 3 screen volumes, most variability occurs during the first screen volume purged and, to a lesser extent, during the second (Martin-Hayden and others, 2014; McMillan and others, 2018). Therefore, relatively low fixed volume purging of one to 2 screen volumes can be reasonably justified. Ideally, concentration time-series trends with purge volume should be validated at regularly monitored sites (McMillan and others, 2018). Where studies wish to reasonably guarantee removal of in-well standing water influences by high-volume purging, then 3 screen volumes may represent a useful default target. There may be

impracticalities of doing this for deep/wide high-volume observation boreholes and an added expense of contaminated waste water disposal.

4.5.4 Downhole samplers in monitoring wells

Downhole samplers maintain in situ pressure at depth and can avoid methane loss from degassing that can occur when groundwater is pumped to the surface. Degassing may occur within the pump head or the sampling tube or else the groundwater at depth may already contain both liquid and gas phases.

Conventional downhole samplers, for instance passive diffusion samplers, snap-samplers and dual-valve bailers do not form a sufficient seal to preserve gas in the sample fluid when the TDGP exceeds 1atm and bubbles form (Banks and others, 2017; Lewin and others, 1989; Paknow 1986). However, Banks and others (2017) noted that commercially available samplers that maintain pressure, such as the positive displacement samplers (for example, Leutert Positive Displacement Sampler-PDS Sampler, or One Phase Sampler), are designed to be used in large wells typically only used in the oil industry. These samplers are long (3.5 to 4.5m) and require significant financial investment. They are also not practical for sampling narrower diameter wells.

The above provided the rationale for Banks and others (2017) to develop a cost-effective downhole sampler that samples in-well dissolved gas (methane) in groundwater at the in situ pressure at depth. Figure 3 shows the sampler and provides a summary of the sampler operation. The sample is collected using flushing cycles and pressurised at depth. The sample is retrieved at the surface by piercing a butyl-rubber septum on the sampling port with a double-ended needle-valve assembly, allowing sample entry into a pre-evacuated sealed serum bottle that is partially (half) filled. Gases that were dissolved because of the sustained sample pressure rapidly degas from the water within the serum bottle, allowing separation of the gas and water phase to occur in a closed system without gas loss. Samples may then be analysed for methane concentration and isotope composition, and dissolved gas content determined using Henry's Law.

Banks and others (2017, 2019) demonstrated the use of this sampler in coal-seam gas monitoring wells (50 to 100mm diameter) to 230m depth in New South Wales, Australia. Before taking the samples 3 well volumes were purged to ensure sampled water represented formation water and it was uncontaminated by contact with the atmosphere. Purging rates were low enough to keep the hydrostatic pressure above the level needed to keep in-well gas in solution. Banks and others (2017) usefully illustrate the importance of maintaining pressure in samples in their data (their Figure 4) that notes many samples would have been expected to effervesce when brought to surface had the sample pressure not been maintained.

The value of depth samplers maintaining in situ pressure is obvious in high methane concentration environments, and/or sampling at depth, to manage depressurisation sampling losses.

Adapted text from Banks et al. (2017)

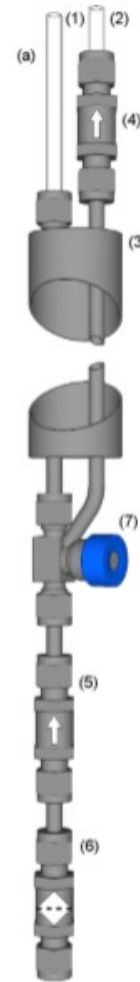
Purging - The well is purged of three well volumes before sampler use with pumping rates adjusted to minimize drawdown and water levels measured to ensure drawdown-induced in-well degassing is insignificant.

Sampler flushing - The sampler is lowered to the screened interval. Increase in external (hydrostatic) pressure causes the check valves to open, allowing water to fill the sampler, as well as the nylon tubing to the standing water level in the well. Pressurisation (nitrogen gas) of the inlet tube forces water down through the sampler, closes off the bottom check valve and then lifts water toward the surface via the outlet tube. Releasing the pressure at surface allows water to refill the inlet tube and the sampler, with the outlet tube remaining filled as the top check valve prevents backflow. This pressurisation and release pumping cycle is repeated until water is discharged at surface and then repeated. The cycle is repeated at least three times to ensure that the sampler is filled with fresh formation water only.

Sample collection - To collect a sample, the sampler, along with the inlet and outlet tubing is allowed to fill with groundwater after purging. Both the inlet and outlet valves are closed and the entire assembly is then pressurized to 7-9 atm (~ 70-90 m of water column equivalent). The sampler is then returned to the surface under pressure, preventing sample effervescence/loss of gas.

Sample transfer for analysis - At the well head, a sample is collected by piercing the butyl-rubber septum on the sampling port with a double-ended needle-valve assembly. For methane and methane isotope samples, the free end of the needle is flushed for a few seconds and then inserted into the septa of a crimp-sealed, pre-evacuated 100 mL serum bottle and filled approximately halfway with the sample water (~50 mL), leaving a head space in the bottle that is at a partial vacuum. Gases that were dissolved because of the sustained sample pressure rapidly degas from the water as it is released into the serum bottle, thereby allowing separation between the gas and water phase to occur in a closed system with no gas lost.

Lab analysis - The sample is taken to a lab for concentration and isotope analysis. The concentration of the dissolved gas can be determined using Henry's Law, from the known headspace (calculated from the known bottle volume and weight of water sample) – water volume ratio and the solubility of methane, which varies with sample temperature and salinity.



- (1) nylon inlet tube to surface
- (2) nylon outlet tube to surface
- (3) sampler (shown as cutaway)
- (4) top and (5) bottom check valves (arrow indicates direction of flow)
- (6) 140 micron filter screen
- (7) butyl-rubber septa sample port

Figure 3. Design and operation of downhole sampler of Banks and others (2017) used to sample dissolved gases (including methane) in groundwater at in situ pressure at depth (drawing and text adapted from Banks and others, 2017).

4.6 Sample collection protocols

4.6.1 Volatility and protocol choice

A range of sample collection protocols are available for sampling groundwater brought to ground surface, either from supply wells, observation boreholes, monitoring wells or multilevel samplers. Protocols for dissolved methane (and other hydrocarbon gases) have largely evolved from those used for sampling VOCs due to common volatility concerns (Molofsky and others, 2016). However, dissolved methane is generally more volatile, with greater Henry's Law partitioning to the gas phase (Pankow, 1986; Sander, 2015). Volatility related losses and consequent negative bias in sampled concentrations drives a sample collection process that typically aims to:

- take place quickly, therefore minimising time for losses to occur
- minimise or avoid open contact of sampled water with the atmosphere (air)
- minimise or avoid exposing the sample to a lower pressure
- keep samples cool to avoid increased Henry's Law partitioning to the air phase with increased temperature (Pankow, 1986)
- if headspace is not included in the sample analysis, samples are collected without leaving a headspace in sample vials (for exceptions, see section 4.6.4 and section 4.11.6)

Regarding the last point, Pankow (1986) set out equations to calculate the errors from the negative bias arising from partitioning losses into varying amounts of headspace inadvertently left in sample vials. The Henry's Law constant for methane (section 4.11.8) drives significant methane partitioning into the headspace. Using the equations presented in Pankow (1986), leaving a 1ml headspace in a 40ml vial at 20°C results in a calculated error of -42%, compared to only -1% for trichloroethene, a commonly encountered groundwater VOC of concern.

Protocols for dissolved methane sampling are categorised as closed, semi-closed and open systems depending on the degree to which water sample exposure to atmosphere occurs during the sample collection process (Molofsky and others, 2016; Rivard and others, 2018a; USGS, 2020). These systems are introduced below and illustrated in Figure 4 to provide context to the comparative study findings of Molofsky and others (2016) that follow. The section concludes with a revised semi-closed system method (USGS, 2020) arising from recent concerns raised over the previously widely used inverted volatile organic analysis (VOA) semi-closed method described below (Molofsky and others, 2016).

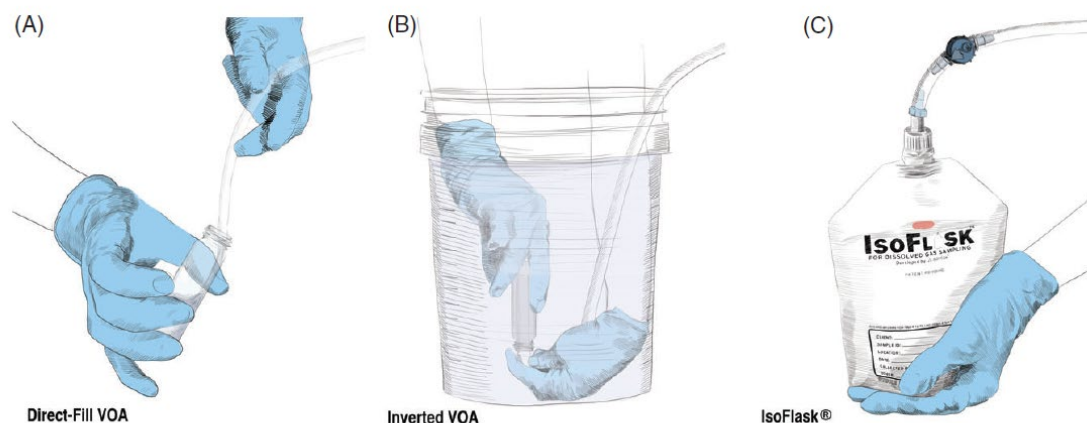


Figure 4. Illustration of sample collections methods: a) the direct fill VOA method, b) the inverted VOA method, and c) the closed system Iso-Flask® method (from Molofsky et al. 2016). © Creative Commons Attribution-Non-Commercial License.

Closed, semi-closed and open systems may, in principle, be applied across the range of groundwater monitoring scales, with appropriate plumbing arrangements at ground surface linked into groundwater discharge. However, options may be constrained by, for instance, pump type and flexibility of pumping rates, discharge pipe/tubing diameters, sample point (tap) access and modifications possible at the wellhead. Choice of sample collection protocol may also be influenced by the time and budget available.

Regardless as to whether sample collection is under open, semi-closed or closed conditions, pumping rates during sampling are usually adjusted to a typical 'low-flow' sampling method rate, allowing an even flow with minimal sample collection turbulence. It might be more difficult to achieve low rates for supply wells when these are constrained by the resident (submersible) pump, although sample tap flows can usually be adequately adjusted.

Effervescence at ground surface under open sampling conditions is expected when methane concentrations exceed their saturated concentration of around 25 to 35mg/l (dependent on water temperature, salinity and elevation (atmospheric pressure)), or at lower concentrations where other gases are present, contributing to the TDGP. For instance, CO₂ is co-produced with methane in equimolar concentrations during methanogenesis (Banks and others, 2017; Molofsky and others, 2016) (section 4.10). Under open system conditions methane may therefore be lost from effervescing samples to the atmosphere. This may be countered by using semi-closed or closed systems where sampled water is kept under sufficient (back) pressure to prevent the low-pressure conditions developing in the sample system that would permit effervescence occurrence and potential methane loss (Banks and others, 2017; Molofsky and others, 2016; Smith and others, 2016; Tamamura and others, 2017). Sample collection protocols need to therefore recognise the potential for both effervescent and non-effervescent groundwater that may require different sampling collection approaches within individual surveys.

4.6.2 Open systems

In open systems glass VOA vials (40ml or more) are filled directly from tubing or a tap at the surface leaving no headspace. The vial is closed with a Teflon-faced silicone septum. This 'Direct-Fill VOA method' is the most common approach used for dissolved-phase VOC sampling. The sample is open to the atmosphere for just a few seconds during the collection and vial closure process. Tap flows are set low to avoid unnecessary turbulence and splash to minimise volatile loss. The potential, however, for low concentration bias associated with dissolved gas open system sampling is well recognised (Beyerle and others, 2000, Molofsky and others, 2016). Still, the rationale for using open systems is that although when samples are exposed to the atmosphere dissolved gases will begin to equilibrate with the atmosphere and dissolved gas concentrations of methane (or VOC) decrease, the exposure time is sufficiently low that mass transfer across the water–air interface can be assumed to be insignificant. This is much more likely to be true for non-effervescent samples where slow (compared to air) diffusion in the aqueous-phase will be the limiting factor for mass transfer across the water-air interface. In effervescent samples, however, bubbling would greatly enhance the rate of dissolved gas loss across that interface to atmosphere (Banks and others, 2017; Roy and Ryan, 2013). However, as Pankow (1986) pointed out bubbles do take a finite time to form and nucleate which would buy some time (section 4.5.2).

Semi-closed and closed collection systems both aim to minimise or eliminate contact with the atmosphere during sample collection to minimise gas losses.

4.6.3 Semi-closed systems

The 'Inverted VOA method' for sampling gases including methane is a widely used semi-closed system that involves the filling of VOA vials while they are submerged and inverted in a bucket of purge water (American Water Works Association, 1957, Aravenaa and others, 1995, Bolton and Pham, 2013, Coleman and others, 1988, Humez and others, 2015, Molofsky and others, 2016, Moritz and others, 2015, Smith and others, 2016). Here Molofsky and others' (2016) viewpoint is adopted that "the Inverted VOA method is considered a semi-closed system because, although the sample is not directly exposed to the atmosphere, the liquid in the bucket is still in contact with the atmosphere during sample collection". Humez and others (2015) provide a typical description of its use – a semi-closed Inverted VOA sample collection was adopted from a bladder pump with flow rate reduced to $< 0.003\text{l/s}$ and flushing of 3 VOA sample bottle volumes through the bottle before capping. There has been increasing criticism of the vial inversion protocol, causing more recent studies to now adopt a semi-closed system with a non-inverted VOA vial (section 4.6.6).

4.6.4 Closed systems

If a water sample is exposed to the atmosphere, the dissolved gas composition will begin to equilibrate with the atmosphere. Dissolved gas concentrations will eventually, given time, reflect the solubility and atmospheric concentration of each gas species (Banks and others, 2017). The equilibration is typically described by Henry's Law constants. Continuing with the convention indicated by Molofsky and others (2016), a closed system method may be defined as occurring when the sample is collected without direct contact with purge water or the atmosphere. Therefore, while an 'open system' for sample collection may allow dissolved gases to escape to the atmosphere, in principle, a closed system traps all gases, both dissolved and effervescing, providing that the back-pressure during sampling is sufficient (Molofsky and others, 2016). In the absence of maintaining at-depth pressures, effervescence may occur as the sample is pumped or brought to the surface with accompanying hydrostatic pressure reduction. As degassing may occur within the pump head or the sample tubing as the sample approaches surface, a closed sample system at surface does not guarantee that this free gas will be completely captured or that its influence on sample integrity will be negated. It provides motivation for downhole sampling obtaining samples retaining in situ pressures at depth (section 4.5.4).

Closed system methods commonly used to collect groundwater samples at surface have involved crimp-sealable copper tubes connected to the pump outlet (Beyerle and others, 2000, Weiss, 1968). Beyerle and others (2000), recognising the potential for gas oversaturation and degassing, emphasise the need to keep the groundwater under pressure during sampling to avoid degassing and that "sufficient pressure can usually be achieved by the use of submersible pumps and tight connections". They also state that "to avoid any air bubbles being generated or captured during sampling the copper tube is rinsed [flushed] thoroughly" after which stainless steel pinch-off clamps are closed to seal off the copper tube. In the laboratory, the sample tube is typically connected to a high vacuum extraction and purification line to accomplish quantitative analysis.

Dillon and others (2016) describe a similar process for sampling dissolved (noble) gases collected in 9.53mm-diameter copper tubes by using reinforced-nylon (impermeable) tubing connected to the hose bib tap at the wellhead. Groundwater was flushed through the tubing to dislodge bubbles before the flow was restricted with a back-pressure valve. Clamps on either side of the copper tube were then tightened, trapping a sample of groundwater for analyses of dissolved noble gases.

However, Molofsky and others (2016) described the crimped-tube methods as challenging to implement. Also, they noted that commercial laboratories are often not equipped to process these samples.

A closed-system method used by the British Geological Survey (BGS) (for example, Bell and others, 2017) uses a 50ml (nominal) stainless-steel flow-through cylinder sampler fitted with valve taps at either end. The cylinder is

connected in-line to the groundwater sample tube discharge at surface with airtight connections, allowing groundwater flow through the device (Figure 5). Closing the downflow tap first creates back pressure to minimise any losses due to effervescence.

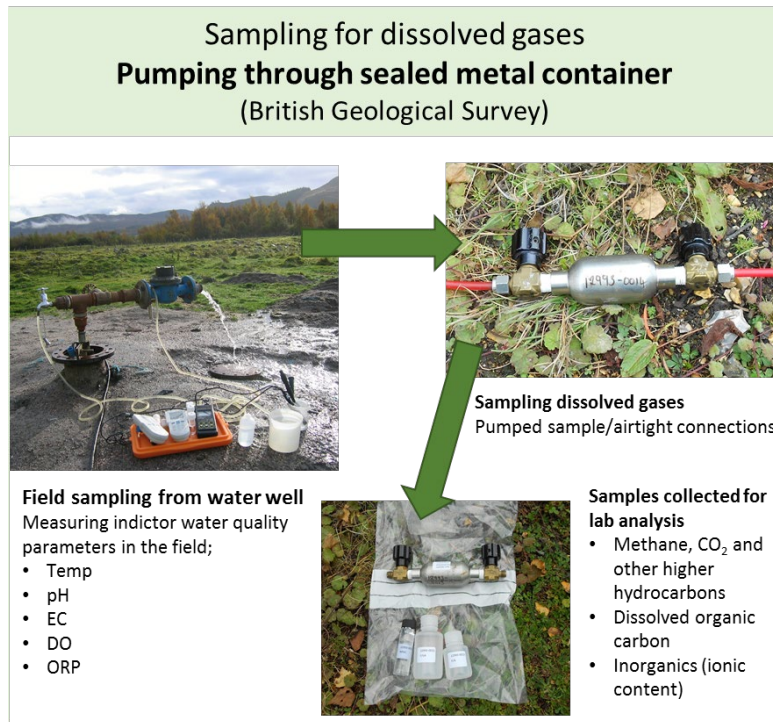


Figure 5. BGS closed system sampling methodology for dissolved gases (modified from Bell and others, 2017).

Closed samples may also be collected via pre-evacuated bags or containers tapped into a discharge line at the surface that may allow both water and any gas phase to be captured at the sample pressure (Figure 6). A pressure gauge is inserted ahead of the sampling valve T-point. After suitable well purging, the sampling valve is opened and the container filled to a specified level, often leaving a specific headspace volume in which any free gas accumulates.

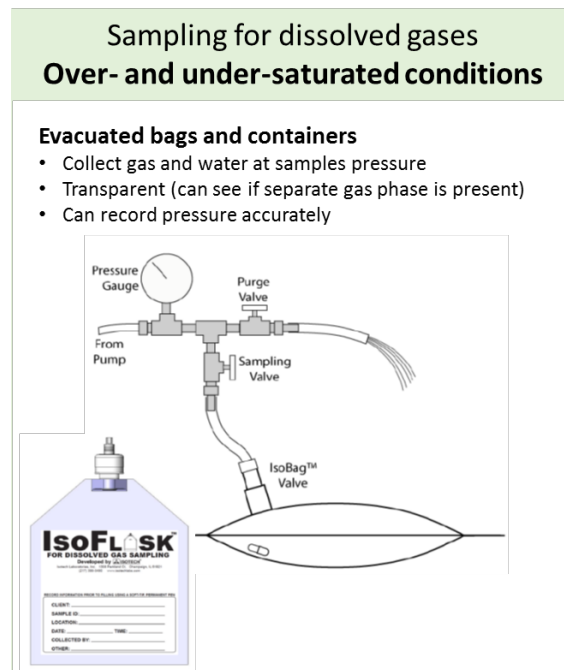


Figure 6. Evacuated container closed system sampling (images from Isotech, 2013).

Closed-system evacuated container sampling has become commercially available since 2013 via the IsoFlask® system (Isotech Laboratories, Champaign, Illinois) (Isotech, 2019a, Isotech, 2019b). The approach is becoming quite widely used (Schout and others, 2018; Molofsky and others, 2016, 2018; Zhu and others, 2018). The IsoFlask® system comprises a flexible, evacuated 750ml plastic container that comes preloaded with a benzalkonium chloride bactericide capsule. It is constructed with a Luer® valve that enables it to be directly connected to a sampling manifold or sample location, for example, a tap at the well head or tapped into discharge lines associated with pumped monitoring wells. Their plumbed combination allows the IsoFlask® and sampling line to serve as a closed system, designed to collect bulk samples of water and any exsolving gases drawn into the evacuated container after the valve is opened after appropriate purging of the borehole and sampling lines.

4.6.5 Comparative studies of sample collection

The recent work of Molofsky and others (2016) provides systematic testing of methane sampling using open, semi-closed and closed systems at supply well sites in the US. This testing included 2 variants of the Inverted VOA method:

- low-flush: water was flushed through the inverted VOA vial at a rate of 0.008l/s for 10 seconds (~2 VOA vial volumes) before capping the submerged vial near the base of the filled bucket. The aim was to minimise entrapment of bubbles within the VOA vial (following the Marcellus Shale Coalition (2012) protocols cited by Molofsky and others (2016))
- high-flush: water was flushed through the inverted VOA vial at a rate of 0.03l/s for one minute (equal to ~40 VOA volumes) before capping the submerged vial near the base of the filled bucket

Molofsky and others' (2016) main findings, relevant to both supply and observation well sampling, were as follows:

In the absence of effervescence corresponding to study area methane concentrations < 20mg/l:

- concentration differences between open, semi-closed and closed systems tested were relatively small, with most matched sample concentrations comfortably within a relative percent difference (RPD) of 30% (a typical laboratory duplicate quality assurance goal set)
- closed system IsoFlask® samples recorded consistently higher concentrations. The median concentration difference between IsoFlask® and Direct-Fill VOA samples in this concentration range was +16%, compared to 0% (no consistent difference) between Direct-Fill VOA and Inverted VOA (high-flush or low-flush) samples

With effervescence (at methane concentrations over approximately 20mg/l in the study area):

- closed system IsoFlask® samples yielded significantly higher methane concentrations than open system Direct-Fill VOA samples, and semi-closed Inverted VOA samples (both high-flush and low-flush). The median concentration difference between IsoFlask® and Direct-Fill VOA samples in this concentration range was +32%
- high-flush Inverted VOA samples yielded lower methane concentrations than low-flush samples, with significant differences between the volume of headspace gas in these vials (several high-flush samples contained >40% headspace within the container compared to at most 10% in low-flush Inverted VOA samples)
- regardless of the flushing volume, both variants of the Inverted VOA method showed negative bias relative to the Direct-Fill VOA method – an important finding
- divergence of open Direct-Fill VOA and closed IsoFlask® method concentrations below theoretical methane saturation (that is, 25 to 35mg/l) is consistent with the concept that the combined partial pressures of all dissolved gases (such as CO₂) is driving effervescence, not just methane

Important implications Molofsky and others (2016) indicated were that:

- open and semi-closed system sample collection methods are adequate for non-effervescing samples
- a closed system collection method, however, provides the most accurate means of measuring dissolved hydrocarbon gases under all conditions
- the Inverted VOA sampling method provides no advantage relative to Direct-Fill VOA sampling in non-effervescing conditions, and reports lower methane concentrations when bubbles of exsolved gases are present (explained in section 4.6.6)
- dissolved gas concentration data previously obtained using the Direct-Fill VOA or Inverted VOA sample collection methods should be considered valid unless effervescence is known or suspected

4.6.6 Revised semi-closed system

A synopsis of the Molofsky and others' (2016) discussion regarding exsolved gases, headspace and subsequent analysis is informative. The IsoFlask® method allows a headspace to form, however, the laboratory analysis accounts for both dissolved and exsolved gases, allowing the original dissolved gas concentration to be calculated prior to exsolution. In open Direct-Fill VOA sample collection, gases exsolving during sample collection are lost to the atmosphere, causing measured methane to be lower than the original dissolved concentration. Finally, absence of headspace in the sample vial prevents any further gas loss after the vial is sealed.

Despite the intent of the Inverted VOA method to minimise loss of gases exsolving to the atmosphere, exsolved gases trapped in the Inverted VOA vials contribute to greater loss of dissolved gases than found in Direct-Fill VOA samples and lower measured dissolved methane concentrations. Trapped headspace originates from water captured in the vial and flushed through prior to capping, causing the high-flush, rather than low-flush, variant to have greater accumulation of exsolved gases. If dissolved gas pressure remains greater than atmospheric pressure, then gases will continue to exsolve into the headspace after vial capping until equilibration of headspace and dissolved gas pressures, therefore reducing dissolved concentrations present in the sample.

Dissolved methane concentration analysis in the laboratory often does not account for methane accumulated in the vial headspace, therefore analysed Inverted VOA method concentrations are lower than the Direct-Fill VOA method. Modifying the analytical procedure to account for the methane in the vial headspace only partly corrects the deficiencies of the Inverted VOA method as some of the gas collected originates from water flushed through the vial, but not retained for analysis. Using helium (He) displacement on Inverted VOA samples could result in higher reported methane concentrations than those found in Direct-Fill VOA samples.

Recognising these problems, more recent works are replacing the semi-closed Inverted VOA protocol with a semi-closed Upright VOA vial protocol. For instance, Rivard and others (2018a) reason “the upright position was selected because the inverted (upside-down) position seemed more prone to trap gas and create a headspace while being filled with groundwater highly charged with methane”, citing Molofsky and others (2016). Rivard and others (2018a) cite the USGS protocol ‘CFC Bottle Sampling Method’ that details the upright use of the VOA vial under purge-water submerged semi-closed conditions (USGS, 2020); a diagram of their filling procedure is reproduced below (Figure 7). This should overcome the trapped headspace problems and it is anticipated that the semi-closed Upright VOA vial protocol should replace the Inverted VOA protocol.

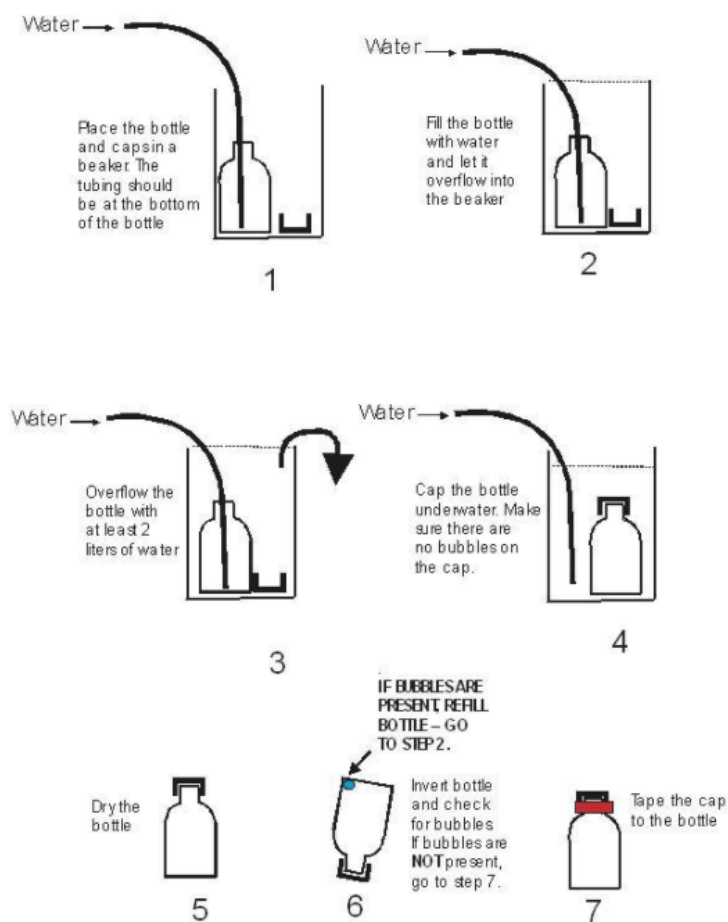


Figure 7. CFC bottle sampling method, USGS (2020).

4.7 Stable isotope sampling

Collecting samples for measuring the stable isotopes carbon-13 ($\delta^{13}\text{C-CH}_4$) and hydrogen-2 ($\delta^2\text{H-CH}_4$) of methane in groundwater has become widespread within the research case literature. In particular, it is used in surveying the baseline occurrence of methane or establishing methane provenance within the shale gas context. This is due to the potential of $\delta^{13}\text{C-CH}_4$ and $\delta^2\text{H-CH}_4$ signatures, together with other isotopes/tracers and hydrochemical evidence, to assess methane sources and differentiate biogenic versus thermogenic origins (McIntosh and others, 2019). Examples of studies acquiring $\delta^{13}\text{C-CH}_4$ and $\delta^2\text{H-CH}_4$ data in the shale gas context (unless otherwise noted) are proliferating across the international community, including regional methane surveys at localities within the following countries, for instance:

- **Australia** (coal bed methane assessment): Atkins and others (2015), Banks and others (2019), Iverach and others (2020)
- **Canada**: Bordeleau and others (2018), Humez and others (2015, 2016), Lemieux and others (2019), McIntosh and others (2014), Meyer and others (2015), Moritz and others (2015)
- **China** (natural methane emissions from groundwater): Wang and others (2018)
- **Estonia** (natural methane origins and formation): Raidla and others

- (2019)
- **Germany:** Schloemer and others (2016, 2018)
 - **Israel** (natural methane origins and formation): Avrahamov and others (2015)
 - **The Netherlands** (conventional gas source incident) Schout and others (2018)
 - **UK:** Basava-Reddi (2018), Bell and others (2017)
 - **USA:** Darrah and others (2014), Dillon and others (2016), Harkness and others (2017), LeDoux and others (2016), Nicot and others (Nicot and others, 2017a, Nicot and others, 2017b, Nicot and others, 2017c), Osborn and McIntosh (2010), Thomas (2018), Wright and others (2019), Zhu and others (2018)

The above listing is not exhaustive but nevertheless illustrative of how widespread acquisition and use of methane stable isotope data has become. Of the papers listed, the following are highlighted due to their prominent emphasis on using or developing isotope tracer techniques that may include other tracer tools such as noble gases: Banks and others (2019), Bordeleau and others (2018), Humez and others (2015, 2016), Basava-Reddi (2018), Darrah and others (2014), Harkness and others (2017), LeDoux and others (2016), Osborn and McIntosh (2010) and Thomas (2016). The intent below is not to provide an exhaustive critical review of this literature, but rather to highlight aspects that are relevant to significant isotope sampling protocols.

Isotope sample collection – Typically, the groundwater sample for isotopes analysis is collected immediately after taking the sample for dissolved methane concentration analysis. It adopts the same open, closed or semi-closed technique as far as possible to allow equivalence of samples. A large sample volume for $\delta^{13}\text{C-CH}_4$ and $\delta^2\text{H-CH}_4$ analysis is typically required. For instance, Humez and others (2015) collect samples using a semi-closed Inverted VOA 40ml vial for dissolved methane concentrations immediately followed by collecting a sample for isotope analysis by filling a 250ml amber glass bottle with a Teflon septum cap using the same Inverted VOA technique. Sometimes the laboratory may use the same field sample collected for both dissolved methane and methane isotope analysis. For instance, Moritz and others (2015) collected a single 60ml vial sample under semi-closed conditions and the headspace created in the vial is used for both dissolved methane and methane isotope analysis. Another common approach is to use IsoFlasks for isotope sample collection, as IsoTech is now one of the main commercial laboratories that carries out stable isotope analysis on dissolved methane.

Availability of isotope laboratories - Despite the widespread and increasing acquisition of $\delta^{13}\text{C-CH}_4$ and $\delta^2\text{H-CH}_4$, the availability of relevant isotope analysis laboratories appears largely limited to a moderate number of university or research institute specialised laboratories. Analysis may sometimes involve exporting samples abroad. For instance, the recent Australian study by Banks and others (2019) used both Australian university laboratories, but also exported some samples for $\delta^{13}\text{C-CH}_4$ and $\delta^2\text{H-CH}_4$ analysis to the UC Davis

Stable Isotope Laboratory at the University of California. In the UK, there are currently no commercial laboratories carrying out this type of analysis.

Methane threshold concentrations triggering isotopic analysis - Sampling and analysis of $\delta^{13}\text{C-CH}_4$ and $\delta^2\text{H-CH}_4$ stable isotopes is often triggered by a threshold concentration of detected methane. This may be a consequence of both analytical detection limits and interest to assess the provenance of more significant concentrations and costs of analysis. For example, Zhu and others (2018) adopted a dissolved methane concentration threshold of 1mg/l to trigger $\delta^{13}\text{C-CH}_4$ and $\delta^2\text{H-CH}_4$ analysis of samples. Laboratories in the UK that have previously had the capability to carry out isotope analysis required a minimum methane concentration of 1mg/l before they could carry out the $\delta^{13}\text{C-CH}_4$ analysis. Bell and others (2017) suggested that isotope analysis of concentrations below 0.5 to 1mg/l was of limited value as an indicator of methane origin, owing to the unpredictability of oxidation effects at low concentrations.

Sensitivity of isotope samples to purging and sampling technique - Collection of samples to measure isotopic composition for determining $\delta^{13}\text{C-CH}_4$ and $\delta^2\text{H-CH}_4$ signatures appears less sensitive to the purging and sampling methodology used. For instance, Rivard and others' (2018a) previously mentioned study found similar methane isotopic ratios for HydraSleeve™ and impeller, bladder and peristaltic pumped samples despite the negative bias of methane concentrations observed in the peristaltic pump due to degassing. This is attributed to the factors causing methane loss (notably degassing) and methane concentration reduction affecting each isotopic form of methane equally without isotopic fractionation occurring. Therefore, their composition ratio within the water sample remains largely unchanged. As such, $\delta^{13}\text{C-CH}_4$ and $\delta^2\text{H-CH}_4$ signatures are relatively insensitive to sampling methods used despite a negative bias in methane concentrations sampled.

Sample preservation – bactericide addition - A bactericide is usually added in the field to samples taken for isotopic analysis to prevent microbial degradation, which would be expected to alter $\delta^{13}\text{C-CH}_4$ signatures as a result of methane oxidation and preferential metabolism of carbon-12 ($\delta^{12}\text{C}$).

Complexity and costs of isotopic approaches - It is recognised that the complexity and costs of isotopic sampling and analysis can become a significant burden to a study. Decisions will need to be taken on the degree to which supporting isotopic and other tracer data should be obtained (see Table 5 of Humez and others, 2016a). The figure illustrates the increasing sophistication of a study approach, the increasing value of the information obtained, but also the increasing costs and complexity involved. These range from a simple approach to assessing dissolved methane concentration alone through various levels of approach examining dissolved and free-gas methane, alongside CO_2 and water isotopes in conjunction with measurements of other gases.

4.8 Sample handling, preservation and storage

4.8.1 Sample containers

It is important to select an appropriate sample container to ensure that the sample is not compromised before its analysis at a laboratory. The reviewed literature suggests holding times prior to analysis vary from as little as one to 2 days, up to typically one to 2 weeks. It is therefore important that the sample container provides effective sample containment for at least this long under typical storage conditions (that is, refrigeration in the dark).

Water samples submitted for analysing the chemical and isotopic compositions of dissolved gases are typically taken and stored in glass vials or bottles, without headspace, and capped by a septum closure (Amos and others, 2005; Hirsche and Meyer, 2009; Johnson and others, 1990; Pankow, 1986). Most studies use approximately 40ml VOA vials for dissolved methane/gases with a larger, up to one litre, volume bottle used for methane (and other) isotopes to accommodate larger analytical volume requirements. The approach of Bordeleau and others (2018b) is typical: a 40ml glass (VOA) vial with Teflon-faced septum closure for methane/alkane concentration analysis alongside methane isotope sample collection in one litre amber glass bottles capped with a butyl rubber septum.

Non-glass sample containers may be used, but more typically for collecting gas or water samples at pressure. Plastic bottles are not normally used, but flexible, evacuated plastic-based containers may be used to allow closed system evacuated fill of a gas/water sample at pressure. Demonstration of device integrity to diffusive losses through gas-permeable plastic polymer materials would be necessary. Low density plastics of low thickness may be more susceptible to diffusion losses, for example, thin-walled LDPE. Samples are therefore not stored long-term in HydraSleeve™ sample bags used for collection, but immediately transferred to glass vials once at the surface. The commercially available IsoFlask® flexible plastic sample container system used for sampling and sample storage comprises a material designed to enable long-term storage. It has demonstrated stability of methane and other gas concentrations over 150 days, of dissolved concentrations with natural headspace over 90 days and methane isotope signatures over 60 days (Isotech, 2019a).

Metal (copper, stainless steel) canisters/tubes may be used to allow storage with crimp or valve closure of pressurised samples, as used by the BGS and others (section 4.6.4). Glass vessels with sufficient thickness have been used for evacuated sampling and hold some advantage in being able to observe samples and identify signs of effervescence in particular. However, these are fragile and now rarely used. Hirsche and Meyer (2008) conclude that electro-polished stainless-steel air sampling canisters ensure the longest holding times for free gas samples. FlexFoil grab bags and Tedlar bags, however, constitute

cheaper alternatives for gas storage holding times of several days rather than months. Humez and others (2015) collect free gas samples from their gas-separator device via a gas sampling port closed-system connection to Summa canisters (US EPA, 1995) (for 60 seconds) or FlexFoil bags half-filled at a separator device pressure of 34kPa.

It is generally presumed that a sampling container provided by the laboratory would be fit for purpose and not exhibit significant losses over mandated protocol storage times. Provided sample bottles are properly closed and sealed, container-related losses should be minimal and not a cause significant negative concentration bias or variability.

4.8.2 Improperly sealed sample losses

Volatile losses of dissolved gases from improperly sealed containers arising from poor sampling practice may be rapid and lead to significant negative bias in measured concentrations. This may arise from a cross-threaded screw-cap on a vial, or perhaps sand-grains within the thread, or a poorly fitting septum during crimp-cap closure. Sampled gas losses in these instances are exacerbated by any headspace inadvertently left, into which methane may partition and equilibrate. The errors associated with gas loss into a static headspace may be quantified by Henry's Law and are significant for methane due to its high Henry's Law constant compared to VOCs (Pankow, 1986 and section 4.11.8). The losses, however, are even worse if a vial closure is not air tight and leaks gas with air entry. A dynamic headspace is created in such a scenario with a turnover of headspace air that may completely strip methane from the sample into the surrounding atmosphere beyond the vial.

To help mitigate the above, and recognising water contact (rather than air/gas phase contact) with closure openings may reduce loss rates by wet sealing, some protocols advocate precautionary storage of vials inverted or on their side. Such positioning allows any headspace present to contact non-permeable glass rather than a gas-leaky poorly closed septum vial top closure. Nicot and others (2017c) and Basava-Reddi (2018) for instance adopt inverted vial storage at 4°C until analysis. Bordeleau and others (2018a,b) and Rivard and others (2018a,b) store 40ml VOA samples upside down and larger one litre sample bottles (for isotopes) on their side.

4.8.3 Sample preservation

Sample preservation is important where samples contain naturally occurring bacteria that may metabolise methane and analytes of interest, thereby lowering chemical concentrations and altering isotopic composition. Precautions are therefore often taken to minimise microbial conversions (Hirsche and Meyer, 2008). Keeping samples in cool boxes and refrigerated in laboratories to enable storage of samples below 4°C is easily carried out as a matter of course in most, if not all, studies. Low temperature storage will reduce, rather than

completely eliminate, microbial activity (Hirsche and Meyer, 2008; Vroblesky and Chapelle, 1994).

Adding bactericides to samples at field collection or laboratory receipt to prevent microbial conversions is adopted in many, although not all, protocols.

Historically, bactericides such as copper chloride, mercury chloride or acids, were recommended. Benzalkonium chloride is now often used as a more environmentally acceptable alternative (Gorody, 2007; Hirsche and Meyer, 2008; Isotech, 2019b). Preservative may need to be carefully chosen to avoid interferences with isotope analyses, for example, avoiding acidification that may compromise carbon isotope measurements.

Example sample collection and storage protocols from studies in North America, Europe and Australia are provided below. Although not exhaustive, they are indicative of the cross section of practices adopted:

- McLeish and others (2007) stored samples (no headspace) without preservative at 4°C for less than 48 hours before analysis.
- Bordeleau and others (2018a) kept bottles/vials refrigerated at all times, with preservation of samples for volatile alkane (and metals, nutrients, and VOC) analyses ensured by the presence of acid in the bottles, resulting in a pH <2. Sample preservation times prescribed by the laboratories were respected; samples for alkanes were always analysed within 7 days of sampling, but the vast majority were analysed within 2 to 3 days.
- Nicot and others (2017c) “used a flow-through sampling approach to collect samples for dissolved gas analysis in a 70ml serum vial. Serum vials were first capped and crimp-sealed and subsequently filled using two flow-through syringes (fill and vent). At least 5 serum vial volumes were flushed through the serum vial to ensure that a representative groundwater sample was collected and that no gas bubbles remained. Samples were stored upside down in an ice-cooled container, shipped to the laboratory and acidified at pH<2 with 0.1 ml of 12N hydrochloric acid upon reception of the samples.”
- Schloemer and others (2018) indicate “For hydrocarbon gas analysis 122 ml serum flasks were filled air-free through a thin by-pass tube between wellhead and flow-through cell at low filling speeds to avoid disturbances and subsequent degassing. All bottles were allowed to overflow for several minutes. Samples taken by NLWKN were acidified with 2 ml concentrated hydrochloric acid before capping with aluminium crimps and Teflon coated butyl rubber septa. Acidification was necessary to suppress any further microbial alteration, since these samples had to be stored for longer time spans before shipping to the laboratory. For samples provided by LBEG, where analytical treatment was done the day after sampling, acidification was not necessary. As a consequence, determination of $\delta^{13}\text{C-CO}_2$ was only possible in the sample set of LBEG as the acidification might result in dissolution of particulate carbonate

matter. All samples were kept stored in a refrigerator at ~4°C until analytical work up.”

- Banks and others (2017) indicate for their sample preparation for methane and methane isotope analysis on samples obtained from their downhole in situ pressure sampler (section 4.5.4): “Pre-evacuated (<0.001 atm) serum bottles (100 ml clear glass Wheaton bottle) with 20 mm aluminium crimp caps and grey butyl-rubber stoppers were used to collect groundwater samples from the downhole sampler in triplicate. A saturated solution of mercuric chloride was used as a sample preservative to prevent bio-degradation and injected into the serum bottle (0.2 ml) following pre-evacuation. Shortly after the 50 ml sample was collected, the serum bottle was injected with zero air (i.e., laboratory air containing no measurable methane) to re-equilibrate the bottle to atmospheric pressure.”
- The IsoFlask® sample system (Isotech, 2019b) uses a flexible, evacuated plastic container preloaded with a benzalkonium chloride bactericide capsule.
- The recently issued ASTM (2017) standard analysis method (section 4.11.5) indicates (paraphrased): storage in 40ml glass vials with Teflon-lined chlorobutyl septa with no headspace, placed on ice within 15 minutes of collection, transported and kept cooled (not frozen) between 0 and 6°C, any visible headspace to be noted in results, and samples may be preserved with sulphuric acid (H₂SO₄) to extend expiration date to 2 weeks from the sampling date.

A few studies have examined storage conditions and sample preservatives that may facilitate longer and more convenient holding times. Gorody (2007) demonstrated that the chemical and isotopic composition of dissolved gas samples preserved with benzalkonium chloride did not change over 30 days. Moritz and others (2015) used a semi-closed sample collection method, ensuring air bubbles were purged from the bottle. They added 1ml of 6N hydrochloric acid to the submerged bottle that was sealed with a 20mm Teflon-lined crimp cap, while under water. Samples were stored at 4°C until analysis. A comparison with a sample series analysed in the laboratory on the same day revealed that the samples could be stored for as many as 117 days without significant variation in dissolved gas concentrations. However, an increase in the standard deviation was observed for samples analysed after 83 days of storage.

Molofsy and others (2016) used open system Direct-Fill VOA sampling to obtain 54 samples that were preserved using hydrochloric acid, and 16 samples that were unpreserved. They compared 9 pairs of the preserved and unpreserved VOA samples and found the variability in methane concentrations between paired samples was similar to that observed for field duplicate samples. Tested concentrations from 2 to 40mg/l exhibited an RPD of less than 11% for 7 of the pairs, and the remaining 2 exhibited an RPD of 26% and 32% in opposing directions. It was concluded that there was no statistical difference ($p=0.55$) in

methane concentration between the preserved and unpreserved samples, that is, the use of preservative had no measurable effect on the methane concentrations analysed.

Samples with an O₂-containing headspace, inadvertently or intentionally left, could be compromised as bacterial methane oxidation could occur if no preservative is used. Ryan and others (2015) emphasise this and criticise McIntosh and others' (2014) approach, which involved collecting partially filled samples, deliberately leaving headspace (600ml water with 575ml of headspace) without preservative, albeit with holding times of just 24 hours before analysis. Calculations made via the ideal gas law of methane lost if all O₂ in the headspace was consumed by bacterial methane oxidation indicate this loss can be considerable where modest to large headspace proportions are left (Ryan and others, 2015). In their defence, McIntosh and others (2015) provide evidence (isotopic and other) that negative bias in their analysed concentrations was not significant due to either the headspace approach, or lack of preservatives – they demonstrate their “protocol of testing within 24 hours of sampling is effective in avoiding biases by both organic and inorganic oxidation of methane without the requirement for poisons to ‘preserve’ the sample”.

The recent ASTM (2017) documentation includes detailed results of its preservation study that underpins its protocol paraphrased above, indicating samples may be preserved with H₂SO₄ to extend the expiration date to 2 weeks from the sampling date. With such preservation, methane losses after 2 weeks were $6.10 \pm 3.71\%$ compared to $21.59 \pm 5.77\%$ for unpreserved samples.

It is recognised that microbial conditions and potential for sample bias vary from site to site and within sites. Therefore, the precautionary approach would be to add preservatives, or where not used, to demonstrate they are not necessary through controlled testing of the protocol adopted (McIntosh and others, 2015; Molofsky and others, 2016).

4.9 Free gas versus dissolved gas samples

Sampling free gas instead of, or as well as, dissolved gas is an option. There are contrasts in jurisdictional legislative requirements regarding free gas versus dissolved gas sampling, highlighted by Humez and others (2015). Analysis of free gas obtained from selected well water samples has been mandatory in Alberta since 2006 (Alberta Environment, 2006), whereas dissolved gas sampling is required, for instance, in Colorado and the UK (Colorado Oil and Gas Association, 2011, Environment Agency, 2015, Infrastructure Act, 2015). The former has prompted development of free gas samplers and their use in Alberta's Groundwater Observation Well Network (GOWN) comprising 250 observation wells within areas of significant groundwater use and established conventional/unconventional energy exploitation (Humez and others, 2015). The standardised free gas sampler developed uses a valved arrangement to draw off accumulated headspace gas during sampling (Humez and others, 2015).

Sampling both dissolved gas and free gas (where obtainable) from GOWN wells has allowed their relative benefits to be compared (Humez and others, 2015). Sampling protocols comprised a submersible pump for collecting free gas and a bladder pump for retrieving dissolved gas samples. The bladder pump was suspended below the submersible at mid-screen, with a transducer used to record drawdown. Constant flow rates varying from 0.6 to 1l/s for 60 to 120 minutes allowed sufficient headspace accumulation for free gas draw-off to Summa canisters or FlexFoil bags. The submersible pump was then stopped and bladder pumped at a low flow rate of < 0.003l/s to collect the dissolved gas sample. Henry's Law calculations of methane partitioning in free and dissolved gas phases were used to quantify conditions under which gas may exsolve from water and create a free gas phase. Low groundwater DO contents generally expected in this field setting meant samples exhibiting increased O₂ partial pressure were typically taken as evidence of collection device leakage and sample compromise. These could be compensated by applying an air-contamination-correction factor (Humez and others, 2015).

Humez and others' (2015) main findings were that:

- combined sampling, sample handling and analytical uncertainties assessed via triplicate sampling coefficients of variation were $19 \pm 9\%$ for free-gas and $12 \pm 13\%$ for dissolved-gas methane concentrations
- free and dissolved gas samples yielded comparable methane concentration patterns, but sampling operations and pumping rates had a marked influence on methane concentrations in free gas
- a linear positive correlation was found between methane concentrations in dissolved and free gas
- but, geochemical modelling (PHREEQC) revealed most samples plot close to or below the free and dissolved methane equilibrium line with the former overestimated – the inference is the free gas sampling approach captures some exsolving dissolved gas
- water-table lowering resulted in degassing and increased free gas concentrations and therefore overestimates when purging significantly lowered water levels
- therefore, the protocol recommendation for free gas sampling was to operate the gas separator at the same constant flow rate and at the same groundwater drawdown level each time a well is sampled to achieve comparable methane concentration results, ensuring the well is sufficiently purged to obtain representative samples
- it is cautioned that if supply well sampling is carried out using existing pumps (as typical), the usual lack of control over some factors such as water-level drawdown or flowrates may especially influence free gas samples
- stable isotope analyses are easier to carry out using free gas samples, especially if methane concentrations are low
- dissolved gas sampling yields methane concentrations that are less dependent on sampling and pumping operations. However, if the recommendations made are incorporated into best practices, variability of methane concentrations during free gas sampling can also be minimised

Humez and others (2015) conclude free gas sampling, if carried out carefully and consistently, is a feasible approach for baseline groundwater sampling, but will be improved by additional dissolved gas sampling. For comparison between wells and regions, dissolved gas sampling with concentration and stable isotope analyses of methane is preferable as sampling approaches are less complicated.

4.10 Total dissolved gas pressure measurements

Roy and Ryan (2013) make a case for increased field measurement of groundwater total dissolved gas pressure (TDGP), supported by Ryan and others (2015), Roy and others (2017), Banks and others (2017) and further citations below. The main motivations are to avoid errors in groundwater methane concentration reporting due to other gases commonly present (section 4.2.1), and to recognise the influence of degassing during sampling of gas-charged water (section 4.4.3). In 2013, Roy and Ryan reported that TDGP measurements were mostly restricted to research studies (Manning and others, 2003, McLeish and others, 2007, Roy and Ryan, 2010, Visser and others, 2006, Solomon and others, 2011), with limited use in the wider groundwater community. This appears still to be the case despite its simple measurement by either commercial or simple in-house probes. The probes comprise a gas-permeable silicon membrane isolating a gas-filled chamber that contains a pressure transducer recording measurements typically with 5 to 20-minute equilibration times, although longer in the absence of some water movement past the probes (Manning and others, 2003; Roy and Ryan, 2013).

Specific reasons for measuring TDGP include (Roy and Ryan, 2013):

- TDGP can be used as a screening tool to identify whether wells i) may contain elevated dissolved gas, or ii) whether dissolved-gas conditions have changed since previous measurement(s):
 - concerning i), in gas-charged waters, monitoring TDGP during sampling helps inform pumping rates and sampling timing in order to avoid excessive drawdown causing pressure reduction and sample degassing
 - concerning ii), this knowledge permits targeting of wells for sampling that exhibit varying concentrations, therefore saving time and money
- more accurate (and potentially simpler) dissolved gas concentrations may be obtained, especially for gas-charged groundwater:
 - recognising here, degassing losses associated with sample collection, transport and analysis are likely to have a greater effect on concentration than gas composition (or mole fraction, that is, molar ratio of gases present), that is, accurate concentrations are more difficult to estimate than gas composition

- the influence of degassing effects can be limited by more accurately calculating dissolved gas concentrations from in situ TDGP (P_{TDG}) values (subtracting the vapour pressure of water) (Pankow, 1986), Henry's Law coefficients, and the gas composition (mole fractions). This approach is required for passive diffusion gas samplers (Sanford and others, 1996), but is applicable to any sampling method measuring gas composition (Visser and others, 2006; Solomon and others, 2011)
- analysis should account for any gas-charging, via measurement of a gas-water volume ratio (ensuring total mass analysis), or by incorporating in situ TDGP (P_{TDG}). The latter is advocated in that it is often simpler, potentially provides more accurate results, and could 'field check' other method results. Failure to account for the above in gas-charged samples may lead to substantial concentration errors, up to a fivefold underestimation for, say, a sample from 41m depth below the water table. The complexities of the former, gas-water ratio include:
 - although measured in the field when using gas-water separators (Browne, 2004), complete degassing separation can be difficult to achieve
 - although required for headspace extraction of groundwater samples for example, (Böhlke and Denver, 1995, Britt and others, 2010), headspace expansion must be accommodated and accurately measured (recognising near-complete water sample extraction with mass spectroscopy analysis (Andrews and others, 1991, Klump and others, 2007) avoids this ratio, but requires highly-specialised equipment)
- noting too, in the absence of the measurement of other common groundwater gases present (N_2 , O_2 , nitrous oxide (N_2O), CO_2 , H_2S), the percent methane saturation cannot be accurately calculated (Ryan and others, 2015)
- TDGP provides confirmation of 'free gas' (gas ganglia and bubbles) existence in the aquifer when TDGP values are recorded at, or exceeding, the bubbling (critical) pressure (Banks and others, 2017; Manning and others, 2003). TDGP is easily determined in the field by comparing atmospheric pressure (measured with a barometer) with water pressure at depth (measured using a pressure transducer) (Pankow 1986; Roy and Ryan, 2013). This is important because:
 - groundwater gas sampling techniques determine only dissolved concentrations
 - changes in methane concentrations in groundwater would be masked when methane bubbles are present. Therefore, it would not be possible to identify changes in dissolved methane concentrations

over time as the mass change is just in the free gas and dissolved concentrations remain unchanged

- TDGP can provide continuous measurements of background gas or stray-gas migration via downhole probe data collection, or a data logger at surface. It allows relatively inexpensive, high-resolution temporal groundwater data to be obtained. These data are considered impractical to obtain with conventional dissolved gas sampling and analysis on labour and analytical cost grounds

A related opinion expressed by Ryan and others (2015), somewhat controversial but not unreasonable from an accuracy point of view, is the need to report dissolved gas concentrations as 'estimates' unless either:

- "the total mass of gas molecules is fully captured and preserved (that is, under in situ water pressure) and included in the analytical approach
- in situ TDGP is measured and combined with robust gas composition analyses"

Overall, Roy and Ryan (2013), supported by citations above, present a compelling case for measuring TDGP, labelling it as "a master variable for dissolved gas that is analogous to what specific conductance is to major ions, or pH is for geochemical systems". TDGP measurements are essential where sampling of gas-charged water is suspected to allow accurate concentration reporting and interpretation. They would also generally support groundwater methane sampling and analysis and data interpretation arising regardless of concentration. Their use and significance to date, however, appear to have been overlooked.

4.11 Laboratory analysis of dissolved methane

4.11.1 Analytical factors causing concentration discrepancies

Many factors may cause differences in analysed dissolved methane concentrations. Laboratories may use different methodologies, but even when applying a similar methodology, interpretation and execution of protocols can vary. Discrepancies or variability may arise from (expanding Neslund (2014):

- appropriateness of field sample interface with the laboratory and laboratory sample storage practices
 - sample types/containers received and laboratory capability to analyse:
 - conventional VOA (40ml) sample vials, versus,
 - unconventional closed system samples perhaps at in situ pressure where a laboratory may not be suitably equipped to handle samples (but possibly still analyse samples anyway)

- preservative use or not (and need for preservative under particular site sample conditions to inhibit losses)
- sample containers used and integrity over holding times
- holding time duration prior to analysis
- sample handling
 - sample transfer (open or closed) in the analysis laboratory environment
 - method used to induce/create headspace for analysis
 - temperature at which the analysis is performed
 - sensitivity to methane loss – varying with method and concentration and potential for effervescence
 - pressurised sample handling capability
- calibration procedures
 - calibration procedure based on gas or water standards
 - calibration standard preparation
 - calibration range covered
 - frequency of calibration standards (with concentration and time)
- surrogate standard use
 - surrogate (internal) standard use or not
 - mode of surrogate standard introduction
- specifics of sample analysis
 - effective chromatographic system and discrimination of methane from other dissolved gases
 - specifics of how dilutions are performed
 - sample injection manual or automated/syringe or gas sample loop
- concentration calculations required
 - assumptions on partitioning parameters
 - use of Henry's Law constant or not, numeric value of constant selected
 - corrections for temperature or salinity influences
 - calculation method assumptions and inadvertent errors
- quality assurance – quality control procedures

The intent here is not to address all of these issues, but rather to outline a range of the main issues and provide an indicative overview of the literature status.

4.11.2 Static headspace analysis background

Static headspace methods are very commonly used to analyse dissolved methane concentrations in groundwater. They are based on analysis by gas chromatography of an aliquot (defined portion volume) of induced 'headspace' gas equilibrated above a contained water sample. The equilibration is typically described by Henry's Law partitioning (Pankow, 1986; Sander, 2015) and depending on the calibration carried out, Henry's Law constants may be needed to quantify dissolved phase concentrations from the gas concentrations analysed. The analysis of methane and other light hydrocarbon gas concentrations frequently uses gas chromatography with flame ionisation

detection (GC/FID). Dynamic headspace methods are also possible where, instead of equilibration with a static fixed volume of headspace, gas is continually flushed across the water sample and hydrocarbon gas concentrations dynamically stripped into that mobile headspace phase and concentrated downstream for analysis, for example, purge-and-trap type analysis. Use of static headspace – GC/FID methods to analyse methane in groundwater and other waters has been predominant though and dates from at least the 1980s (Barber and Briegel, 1987; Barcelona and others, 1984; Barker and Fritz, 1981; Lewin and others, 1989; Martens and Klump, 1980).

In the UK, prompted by concerns of methane degassing in boreholes and accumulating at hazardous (explosive) levels in (public) water supply pump houses, Lewin and others (1989) of the Water Research Centre (WRc) specifically sought to develop and evaluate sampling and analysis of methane in groundwater (reported in full in WRc Report CO 1911-M and as indicated, but not cited, by Lewin and others (1989)). Their work appears among the earliest globally to do so and included both laboratory and field testing. Although seemingly overlooked in the literature since, it nevertheless offers insights into sampling and analysis still relevant today and illustrates some of the analytical issues despite being carried out 30 years earlier. Findings or accomplishments of Lewin and others (1989) include:

- development of a GC/FID – headspace method to analyse both controlled laboratory and depth samples from boreholes
- sample manipulation to interface with headspace gas analysis requirements from both open system and closed system samples, demonstrating the advantage of eliminating transfer steps in the latter. While not now recommended, (Ryan and others, 2015) headspace for analysis was taken from the headspace within the BAT hydrophobe vials filled in situ at depth in the field
- evaluation of method optimisation and influential factors, including:
 - analysis of dissolved methane concentrations from below the detection limit (<0.005mg/l) up to very high levels >100mg/l (at 50m depth) (including free methane gas captured in closed system sampling)
 - prior to analysis, headspace – water sample equilibration time of just 5 minutes, implying methane degassing potential requires recognition and appropriate allowance in all sampling and analysis procedures
 - headspace method validation in distilled water up to ionic strengths typical of groundwater had no influence on methane determination
 - carry-over concentrations after high methane concentrations analysed, recommending the need for N₂ blank flush of sample injection loops (used in preference to gas-tight syringe injection to the GC system)

- provision of analysis method detail and testing, for example, equilibration of water and headspace, calibration procedures and options
- quantification of analytical precision (coefficient of variation) generally found to be better than 4% (at 95% confidence) and demonstration of accuracy improvement by using calibration standards within an order of magnitude of the anticipated sample concentrations

Further information regarding the specific analytical detail and sensitivities tested is included in Lewin and others (1989) and many of the analysis reports referenced later.

4.11.3 Primary headspace-GC/FID analysis background

The headspace-GC/FID method for groundwater methane analysis primarily cited in the scientific literature is the journal publication of Kampbell and Vandegrift (1998) on the 'Analysis of dissolved methane, ethane, and ethylene in ground water by a standard gas chromatographic technique'. The method originated from the US EPA National Laboratory (now RS Kerr Laboratory) and is sometimes cited as the 'US Environmental Protection Agency (EPA) method 'RSK-175' (Kampbell and Vandegrift, 1998)', by Bordeleau and others (2018a). This is in recognition of the common basis of Kampbell and Vandegrift (1998) and the 'RSKSOP-175' EPA Laboratory standard operating procedure (SOP) 'Sample preparation and calculations for dissolved gas analysis in water samples using a GC headspace equilibration technique'. Various versions of RSK-175 are referenced, for instance the US EPA archive document, Hudson (2004), and the earlier US EPA (1994).

As emphasised by Neslund (2014), the RSK-175 and para-versions is an EPA Lab SOP. Each version of the procedure contains the following disclaimer: "This standard operating procedure has been prepared for the use of the Ground Water and Ecosystems Restoration Division of the US EPA and may not be specifically applicable to the activities of other organizations. This is not an official EPA approved method". Despite this, RSK-175 is often cited by the commercial analysis sector (Jurek, 2016) and RSK-175 or Kampbell and Vandegrift (1989) cited in the scientific literature. Recent citing studies include Bordeleau and others (2018a), Molofsky and others (2016), Moritz and others (2015), Nicot and others (2017), Schloemer and others (2016a) and Dillon and others (2016) and other USGS publications.

Often though, the headspace method used in practice may be slightly modified. For instance, Moritz and others (2015) provide details of their methodology which differs slightly from Kampbell and Vandegrift (1989) in headspace extraction and GC analysis detail. Variants may, for instance, alter (or explore sensitivity of), vial size, water-to-headspace ratio, extracted sample salinity, temperature, time allowed for equilibration, aliquot volumes taken for analysis, mode of headspace generation or sample/aliquot transfer, and specifics of GC type of analysis conditions. These may be carried out to improve or optimise a

methodology to achieve increased detection limits, adjust ranges of concentrations detected, increase sample throughput and other reasons.

Given the widespread adoption of Kampbell and Vandegrift (1998) (or as RSK-175), the original methodology is summarised here to provide a benchmark against which variants or other approaches may be compared. The method entails generating a He headspace within a water-filled sample bottle, allowing gases dissolved in the water to partition and rapidly equilibrate between gas and aqueous phases. An aliquot of this headspace is analysed by GC to determine methane-gas concentration in the headspace. The gas concentration dissolved in water is then calculated based on its partitioning properties predicted by its Henry's Law constant. Received sample bottles will have typically been filled by open, or semi-closed sampling. Closed system sample containers usually demand a dedicated, tailored interface of the sample container with the laboratory analytical facility to maintain closed-system conditions, but would still usually involve gas-phase concentration analysis by GC methods.

Specifics of the method, according to Kampbell and Vandegrift (1998), include:

- samples received for analysis comprised 60ml serum bottles completely filled with water containing several drops of 1:1 H₂SO₄ to act as a preservative, capped and crimp-sealed with a 20mm diameter Teflon-faced rubber septum (40ml VOA vials are typically used nowadays)
- samples were kept at 4°C and analysed within 14 days of collection
- samples were allowed to reach room temperature prior to analysis
- a headspace was prepared by replacing 10% of the bottled sample with He achieved by closed system injection of He gas (at 8 x10⁻⁵ ml/s or less) into the sample via an 8cm 20-gauge needle attached to Teflon tubing and a needle valve inserted through the septum up to the bottom of the inverted sample bottle. Water was displaced into a 20-gauge needle previously inserted through the septum attached to a 10ml Luerlok glass syringe set for dead volume. When the volume of water in the syringe reached 6ml (10% headspace), the 8cm needle was pulled out, followed by the syringe
- the sample bottle was shaken on a rotary shaker at 1,400rpm for 5 minutes to allow the gases to equilibrate between the headspace and aqueous phase
- a 500µl gas-tight syringe equipped with sideport needle withdrew 300µl of headspace that was injected into the GC/FID for analysis on a packed column
- the temperature of the analysis (used in partitioning calculations) was confirmed from the remaining sample water

- the actual volume of the sample bottle was measured by filling the bottle with water and pouring the contents into a graduated cylinder (to allow accurate determination of aqueous volumes for calculations)
- a multi-point calibration with gas standards, comprising commercial gas standards of He, methane, ethane (C₂H₆), and ethene (C₂H₄) at 10, 100, and 1,000ppm together with standards of methane at 1, 10, and 20%. The GC was calibrated by injecting 300µl of each gas standard sampled from cylinder outlet flows at atmospheric pressure
- methane, C₂H₄ and C₂H₆ were identified by GC retention times and GC/FID peak area counts, generated for each sample. These were then compared with a calibration standard curve to allow estimation of the gas-phase concentration (partial pressure) of methane, C₂H₄ and C₂H₆ in the sample headspace
- the concentrations of the gases dissolved in the water sample were calculated using the partial pressure of the gas, Henry's Law constant, the temperature of the sample, the volume of the sample bottle, and the molecular weight of the gas. Values for Henry's Law constant were obtained from Perry's Chemical Engineer's Handbook (Perry, 1963)

The relevant equations and an example calculation of the concentration of dissolved gas in water obtained from headspace analysis is set out in Kampbell and Vandegrift (1998).

Regarding quality control used by Kampbell and Vandegrift (1998) and evaluation of precision and accuracy:

- field blanks were included with samples
- 10% of samples were collected in duplicate and analysed
- prior to analysis and at the end of the day, calibration of the GC was checked by analysing at least one of the gas standards for each analyte. The GC was considered to be in calibration if the analysed value was within 15% of that expected
- calibration standards for at least one of the gases were analysed with a frequency of 10% and variability monitored
- a method blank consisting of a serum bottle of deionised, boiled water was analysed on a daily basis (and was deemed necessary to correct for background levels of methane)
- quantification limits for methane, C₂ and C₂H₄ in water were 0.001, 0.002, and 0.003 mg/l, respectively
- determination of precision and accuracy was achieved by preparing saturated solutions of methane and C₂H₄ in water (from pure gases) with expected concentrations of 22.7 and 131mg/l, respectively:

- for methane, an average recovery of 87% was obtained for 6 replicates, the standard deviation was 0.64mg/l, and the RSD was 3.25%
- for C₂H₄, the average recovery for 3 replicates was 90%, the standard deviation was 8.8mg/l, and the RSD was 7.5%

4.11.4 Summary of semi-formal methods

The absence of an approved ‘standard’ method of analysis (and sampling) of dissolved methane or gases is lamented by Ryan and others (2015) and Roy and Ryan (2013), and for the analysis of methane by Neslund (2014), Vitale (2015) and Jurek (2016). Neslund (2014), commenting from a US commercial laboratory provider perspective, notes that although there are several published procedures, or ‘semi-formalised’ analytical approaches that have been used for analysing methane (and dissolved gases), there are both differences between the methods and differences between laboratories performing the ‘same’ method; quoting Neslund: “Dissolved methane results from water samples collected from the same source at the same time are comparable when analyzed within an individual laboratory but are not comparable when analyzed by different laboratories”. This is exemplified in their comparative study of 10 samples spanning 4 orders of magnitude concentration range analysed by RSK-175 versus PA-3686 methods (see below), with percent differences ranging from -46 to +48%.

Summary comments on the various ‘semi-formal’ methodologies compiled by Neslund (2014) are useful and replicated below to illustrate similarities and differences in laboratory methods used, at least in the US. These cover the previously mentioned RSK-175 as well as PA DEP 3686, PA DEP 9243 and EPA 8015 (together with EPA 5021). Within these, as emphasised by Jurek (2016), the lack of formal methods has caused inconsistent interpretations of these individual semi-formal methods. These inconsistencies have been a prime motivator for the recently completed development of a formal methodology under ASTM Committee D-19 (Jurek, 2016) (section 4.11.5).

Headlines on the above semi-formal methods are as follows (modified from Neslund (2014):

RSK-175 (Hudson (2004) based on Kampbell and Vandegrift (1998))

- Developed by RS Kerr Laboratory of the US EPA
- EPA laboratory ‘SOP’ method uses headspace for sample introduction
- GC/FID is the determinative step (that is, analytical instrumentation used to measure concentrations)
- Samples collected in serum bottles of unspecified volume, practice is to use 40ml VOA vials with 10% headspace volume induced
- Multi-point calibration with gas standards (dilutions of a pure gas injected onto the GC column)

- Since the calibration curve is a gas standard and injected samples are the water matrix headspace, dissolved gas concentrations must be calculated using Henry's constant
- Analysis technique set-up to accommodate several dissolved gases in addition to methane, including C₂H₆, C₂H₄, C₃H₈, butane (C₄H₁₀) and acetylene (C₂H₂)
- Recommends use of acid treated vials, which allows a sample holding time of up to 14 days
- Sample handling by helium displacement
- Samples warmed to room temperature for analysis

PA DEP 3686 (PA DEP, 2012a)

- PA DEP (Pennsylvania Department of Environmental Protection) method developed by Pennsylvania Bureau of Laboratories (PA BOL)
- Revision 0, April 2012, in-house version in use for several years prior
- Headspace GC/FID method
- Multi-point calibration with aqueous standards prepared by bubbling gas into laboratory water until water is saturated
- Only a single compound can be calibrated at a time
- Listed as applicable to methane, C₂H₆ and C₃H₈
- Holding time of 7 days in unpreserved 40ml vial
- Samples handled/transferred by opening 40ml sample vial (that is, open system)
- Dilutions prepared in headspace vials (diluted water sample with headspace gas present), able to be stored up to 7 days at <6°C

PA DEP 9243 (PA DEP, 2012b)

- Developed by PA BOL in conjunction with an instrument (Purge and Trap) manufacturer (Tekmar)
- Revision 0 from October 2012
- Uses Purge and Trap (P&T) with GC/FID (as opposed to headspace)
- Multi-point calibration using aqueous standards prepared similar to PA DEP 3686
- Only a single compound can be calibrated at a time
- Method makes several references to 'sequestering' of methane within the system
- As written, method applicable to methane, C₂H₆, C₂H₄ and C₃H₈
- Requires maintaining sample temperature at <10°C while handling for analysis
- Holding time of 7 days in an unpreserved 40ml vial

EPA 8015/5021 (US EPA, 2003, US EPA, 2007)

- Very generic EPA method based on US EPA 8015 gas chromatography methodology combined with US EPA 5021 headspace methodology
- Headspace GC/FID
- Multi-point calibration

- Preparation of calibration standards defined by laboratory SOP
- Based on use of gas standards, or gas injected into water standards, multiple compounds calibrated for at same time

Other cited methods exist in addition to the above. For instance, USGS publications such as Thomas and others (2018) and others such as Dillon and others (2016), cite the USGS dissolved gas methodology (USGS, 2016) that is similar to the above methods. It comprises analysis of VOA sample bottles equilibrated to room temperature, 10 to 12ml of water is removed from each bottle to create a headspace via a syringe needle attached to a vacuum pump. GC/FID analysis with sample-loop injection is used with minimum reporting levels of 1µg/l and precision of 0.5µg/l.

4.11.5 ASTM D8028-17: a recent standard test method

The draft D-19 ASTM method mentioned by Neslund (2014) and tested by Jurek (2016) during development was published in 2017 as ASTM D8028-17, 'Standard Test Method for Measurement of Dissolved Gases Methane, Ethane, Ethylene, and Propane by Static Headspace' (ASTM, 2017). The summary description of the method, paraphrasing ASTM (2017) indicates:

- headspace is made in the vial under closed-system conditions without exposure to the atmosphere
- the sample is then stirred or agitated and brought to a constant temperature to facilitate headspace partitioning
- quoting the central requirement, "Once temperature control and stirring or agitation parameters are established, EVERY sample, standard, and blank need to be temperature controlled and stirred or agitated in the exact same way in order to ensure reproducibility"
- a portion of the headspace is then injected on to the GC/FID for analysis
- calibration is based on using aqueous standards that avoid using Henry's Law constants and calculations

The method involves a closed system transfer step from the 40ml field sample vial to a separate 40ml instrument sample vial pre-purged with inert gas (helium recommended) and incorporated with a surrogate standard and stir bar, unless shaken. Transfer may be either manual via a Luer-lock valve fitted gas-tight syringe, or with a sealed automated device/system as long as that system meets the manual system requirements (Jurek, 2016).

ASTM (2017) flags interferences to be aware of and counter, paraphrasing these are:

- impurities in air contacting water samples, impurities in field sample vials and septa used, impurities in preservatives, and improper sealing and sample exposure in transport and holding can each cause contamination – these may be countered by the use of various method blanks
- carry over in the analysis process from high concentration samples analysed -this may be countered by blank runs and carry over studies
- non-selectivity of the FID detector and problems of matrix interference due to sample contamination or compound co-elution (on GC) - countered by an experienced analyst

- analyte loss due to poor sample handling and storage - countered by following the protocol outlined (section 4.11.5); ASTM (2017) provides the results of its detailed preservation study that underpins their protocol

Some further specifics of the ASTM method and results of its test application carried out under the D-19 ASTM development period are indicated by Jurek (2016). Some of these, or similar, are also detailed in the actual ASTM (2017) method. They include (Jurek, 2016):

- the ASTM method avoids the use of Henry's Law noted by Jurek (2016) to "sometimes be confusing. The calculation is complicated and if interpreted incorrectly, the concentration of the dissolved gas in the sample would be incorrect". The analysis process removes the need for calculation by diluting a saturated gas solution in order to prepare a five-point calibration curve with the sampling of the dissolved gases in both water standards and samples similar to that described in RSK-175 procedure (that is, calibration and field sample testing are now achieved in exactly the same way)
- four different gases (methane, ethane, propane, ethene) may be similarly calibrated via this common method. Calibration dissolved methane standards used by Jurek (2016) were: 5.8µg/l, 23µg/l, 116µg/l, 232µg/l, 1.16mg/l, 5.8mg/l, 11.6mg/l. Dissolved gas calibration curves obtained for all gases were linear, with a regression of 0.997 or better. An analytical range from 10µg/l to 11mg/l dissolved methane concentrations (and to 5mg/l for other gases above) is indicated by ASTM (2017), with samples above requiring dilution
- manual sample handling may be used for the sample transfer and headspace analysis. However, Jurek (2016) uses its EST Analytical patented autosampler for the sample handling affixed with a (1ml) headspace loop that automates the entire process of testing the headspace of dissolved gas samples. This ensures sample integrity as there is no need to open the samples during the entire sampling procedure (and it meets the ASTM (2017) handling requirements)
- the surrogate (internal standard - deuterated methyl tert-butyl ether (MtBE-d3)) requirement of the ASTM method can be added during the sample transfer to the analysis instrument vial, therefore ensuring accurate, reproducible surrogate recoveries
- a sample temperature of 60°C and equilibration time of 10 minutes were used for sample/standard headspace partitioning
- method detection limits (MDLs) were obtained by preparing and sampling 7 replicate low standards. Dissolved concentration MDLs quantified were 2.68µg/l methane, 1.47µg/l ethane, 1.17µg/l propane and 1.08µg/l ethene
- Demonstration of Capability (DOC) tests were carried out to evaluate the limits and the precision and accuracy of calibration curves by running 4 replicate standards - a precision percent recovery of 90% was obtained for all gases at the curve mid-point (97.8% for methane) and an accuracy of better than 8% RSD (relative standard deviation) (4.07% for methane)
- a series of 20 blank samples were run in order to test the surrogate addition precision and accuracy at 500ppb - an average percent recovery of 100% was obtained with a precision better than 6% RSD

The results of the Jurek (2016) application of the ASTM (2017) method bear out its conclusion that a diligently followed ASTM method may provide an “excellent system for the sampling of dissolved gases”. It is too early to conclude on the uptake of ASTM D8028-17 and whether it becomes the formal method of choice for headspace analysis of methane in the US and elsewhere. Citation of the method in the literature is yet to emerge. Critically though, ASTM D8028-17 provides a modern benchmark against which the performance of other current/past practices may be compared. Critically, it is a highly-detailed methodology that runs to 16 pages of core and supporting methodologies. These offer preciseness, but also guided flexibility in execution, allowing them to be reproduced, something which appears to have been lacking previously in the semi-formal analysis methods. Given time, methodology uptake is anticipated to become high.

The principal qualifier of the ASTM D8028-17 methodology indicated is that the headspace method applies to samples collected at a nominal ambient pressure, but not to samples collected under high pressures, (above ambient) that may not be accurately analysed. This means that closed system groundwater samples obtained at an in situ pressure greater than 1atm from depth may, or may not, contain free methane gas.

4.11.6 Methods for total mass (dissolved and free gas) analysis

It is important to recognise that many laboratory headspace analysis methods for dissolved methane are designed to simply report the dissolved methane in the water sample received. While (commercial) implementation of the methods outlined above such as RSK-175 or PaDEP 3686 (and ASTM, 2017) may note the presence of free gas, methane within that free gas is generally not analysed (Molofsky and others, 2016). In other words, any headspace present in the water sample received, when not expected to be there, may not be included and analysed by the analytical methodology used; it is ‘lost’ to the analytical process. Therefore, headspace methods routinely used do not typically report the total mass of methane present in both the dissolved phase and any gas phase present, just the dissolved phase mass.

Although this is irrelevant if samples contain no headspace gas as received, it becomes highly significant when they do and would include field samples impacted by depressurisation and effervescence where methane and, or other gas concentrations are elevated, that is, methane at around 20mg/l upwards. It is then crucial to know whether the laboratory analytical sample handling and analysis procedures capture received sample headspace and provide a total mass estimate of dissolved phase and free methane gas, or more likely a dissolved phase gas estimate that will be perhaps much lower.

Due to the easy loss of any headspace methane, total methane mass methods are only achieved by laboratory analytical methodology of intentional design. Moreover, that design will typically include suitable alignment with the sample collection methodology in the field to allow a collected sample to interface with the laboratory total mass analysis setup, that is bespoke designed sample

collection that can interface with the bespoke designed laboratory analysis (Banks and others, 2017). Commercially available systems of total methane mass sampling and analysis are rare. The one most widely used for total methane analysis is the previously mentioned IsoFlask® system (Isotech, 2019a,b).

Isotech's analytical procedure, as recounted by Molofsky and others (2016), used to analyse closed system field IsoFlask® samples (section 4.6.4) quantitatively accounts for the volume and composition of exsolved gas in the sample container. This allows for determining original dissolved gas concentrations prior to any exsolution, that is, it accounts for gases that are both dissolved in the water portion of a sample and present as free gas in the headspace of a sample container. If the IsoFlask® sample arrives at the laboratory with a headspace of less than 30ml, additional headspace is created by injecting 30 to 60ml of helium into the IsoFlask®. After the headspace volume is verified, the sample is placed on a shaker for a minimum of 2 hours to achieve equilibration between the water and headspace gas. An aliquot (5ml) of the headspace gas sample is then introduced into the GC/FID/TCD, which determines the concentrations of hydrocarbons (via FID) and fixed gases (argon, N₂, carbon dioxide, carbon monoxide, hydrogen, helium, and O₂) (via TCD (thermal conductivity detector)) in the headspace by comparing them to free gas standards. Dissolved concentrations of methane, ethane, propane, argon, N₂, and O₂ in the water portion of the sample are then determined by Henry's Law, based on the water temperature and atmospheric pressure. Dissolved gas concentrations prior to exsolution are calculated using the weight of the sample (by which the volume of water may be determined), the volume of the headspace, and the concentrations of hydrocarbons in the water and headspace, respectively.

Although the IsoFlask® is presently only commercially available through Isotech (Isotech, 2019a), Molofsky and others (2016) note that others could replicate the design of the sampling device and analytical procedures. The above illustrates the need to coordinate field sampling and laboratory analysis procedures to develop a fully closed system of sampling and analysis of hydrocarbon gases accounting for, and allowing quantification of, the total mass of dissolved and free gas.

4.11.7 Studies comparing analysis methods

Published studies comparing methane analysis methods or cross-comparing laboratories using similar methods appear quite sparse. Two recent examples are discussed below.

It is recognised that there are likely to be unpublished studies, for instance inter-laboratory comparisons supporting site studies that may underpin generalisations in the literature. For instance, it is not uncommon for different laboratories to report methane concentration results that differ by as much as 25% (for example, McHugh and others, 2011). Therefore, differences between measurements reported by different laboratories of 30% or less are not

unexpected (Molofsky and others, 2016). Hirsche and Mayer (2007) summarise, “Reproducibility of the obtained GC results for repeated injections from the same headspace sample are typically better than $\pm 5\%$. Therefore, the uncertainty introduced by the headspace equilibrium method ($< \pm 30\%$) is significantly larger than that of the GC analysis”. The general sentiment is that GC analysis reproducibility is a few percent and the laboratory variability is in the sample handling procedures prior. Single laboratory reproducibility of dissolved methane/gas analysis can be shown to be relatively high even in carefully controlled studies. For instance, (Schloemer and others, 2016) with split samples treated identically in storage, headspace extraction and GC analysis achieved a relative percent difference of dissolved methane concentrations of around $\pm 10\%$ and for methane isotope measurements around $\pm 1.5 \text{ ‰}$. Jurek (2016) achieved high reproducibility using the ASTM (2017) method (section 4.11.5).

Regarding comparative studies, a fairly recent initiative outlined by Vitale (2015) has been the setting up of the ‘Marcellus Shale Coalition (MSC) Dissolved Methane Method Study’. A working group was set up in 2013 to investigate and address analysis method issues and better understand sources of variability in order to provide recommendations on best practices for analysing dissolved methane in groundwater. The study, carried out by Environmental Standards, Inc. involved surveying 15 analysis laboratories with a questionnaire, a review of SOPs and an inter-laboratory comparison study on split field samples (but not sample collection procedures).

Their ‘Laboratory Key Elements Questionnaire’ comprised 102 questions identifying critical laboratory variables and detailed preparation and analytical procedures. SOPs reviewed included sample receiving, sample and standard storage, dissolved gases sample preparation, dissolved gases analytical methodology, and integration of chromatographic peaks. The field sampling involved sampling 2 domestic wells, using a simple direct fill method with nearly 400 vials (butyl rubber-Teflon faced septa) collected and preserved and unpreserved samples taken. Effervescence was observed during sampling. The study outcomes and preliminary conclusions drawn by Vitale (2015) were:

- a very broad range of laboratory approaches were found across the 15 laboratories surveyed (14 commercials, 1 government) and evidenced from the reviewed SOPs and questionnaire responses
- a significant range of reported concentrations were found in the 15 inter-laboratory sample analysis study. This affirmed previous concerns about applying regulatory standards to groundwater. Analysis results showed:
 - well 1 methane concentrations (n = 46): average of 21.071mg/l, standard deviation of 7.053mg/l, a %RSD of 33.47%, and range of 7.0 to 34.0mg/l
 - well 2 methane concentrations (n = 49): average of 23.565mg/l, standard deviation of 8.533mg/l, a %RSD of 36.21%, and range of 8.0 to 44.0 mg/l

- no significant difference apparent between preserved and unpreserved samples
- no 'smoking gun' existed to explain the variability of reported concentrations – details were, however, not presented on any attempts made to find controls
- recommendations were made to repeat a study at lower methane concentrations (avoiding the influence of effervescence in particular), carry out a sample collection study, and carry out an interlaboratory test 'round-robin study' using a controlled dissolved gases analytical procedure developed by the MSC

Methodology recommendations included:

- developing procedures specific for instrument calibration, sample handling/preparation, analysis, and calculations
- seeking collaboration from MSC laboratory members to develop a consensus procedure
- developing a certified performance sample that each laboratory can use to gauge their analysis

Molofsky and others (2016) carried out a study comparing residential supply well duplicate, replicate and matched samples, including high, > 30mg/l methane. They compared Eurofins Lancaster Laboratories Environmental 'Lancaster' analysis that adopts a slightly modified version of the RSK-175 method with the in-house Pennsylvania Department of Environmental Protection Bureau of Laboratories (PaDEP BOL) PaDEP 3686 (Rev. 1) method (PADEP, 2012a). Both methods report dissolved gas concentrations within the water portion of a sample with free gas noted, but not analysed. Both use static headspace GC/FID analysis with aqueous calibration solutions, thereby avoiding the use of Henry's Law calculations. Sample handling procedures differ. In the Lancaster RSK-175 method, 5ml of the water sample was extracted from the 40ml VOA vial using helium displacement via a gas-tight syringe and transferred to a 10ml headspace vial. This was subsequently agitated at a constant temperature for a specified period of time, with subsequent analysis of an aliquot. The PA DEP 3686 method uses cold samples (stored at 4°C). Each vial is opened, and a 10ml aliquot quickly transferred to a 20ml headspace vial using a volumetric pipette. Headspace vials were immediately capped, and the samples were agitated and heated to a constant temperature for a specified period of time in an automatic headspace sampler.

Despite these differences (that is, opening the vial and removing the water aliquot with a pipette versus removing it with displacement through the septum with a syringe), the differences between PaDEP BOL and Lancaster results were minor. Methane results reported by the 2 laboratories for replicate samples were quite similar. Of the 16 matched PaDEP BOL and Lancaster Direct-Fill VOA samples, none exhibited a RPD over 30%. Of the 16 matched

Inverted VOA samples, only 2 pairs exhibited an RPD greater than 30%. The median RPD for all matched samples analysed by the 2 laboratories was 6.5%. This difference is comparable to the median RPD of 6.3% for all field duplicates collected by the same sampling method. The difference was no larger than that found between field duplicates analysed at the same laboratory.

Molfsky and others (2016) compared results of replicate IsoFlask® samples analysed at the PaDEP BOL and Isotech Laboratories and used the difference in results to illustrate the influence of closed system sampling and analysis on the capture of free methane gas. Eight replicate IsoFlask® samples were analysed at the PaDEP laboratory for dissolved methane concentrations. These samples were obtained via a gas-tight Luer Lok syringe attached to the IsoFlask® port that withdrew a 10ml aliquot of water. This was quickly transferred to a 20ml headspace vial and analysed using the standard PaDEP 3686 method. Up to approximately 20mg/l, samples analysed by the PaDEP method reported comparable methane concentrations to samples analysed by Isotech using the standard IsoFlask® analysis method. Above 20mg/l, concentrations in the PaDEP BOL samples were notably lower (23mg/l versus 36mg/l, and 30mg/l versus 73mg/l). Differences were attributed to the expected missing free gas component using the PaDEP 3686 procedure at these higher concentrations where effervescence was expected.

4.11.8 Henry's Law constant: use and issues arising

Henry's Law states that the amount of dissolved gas in a liquid is proportional to its partial pressure above the liquid in the overlying gas phase. The proportionality factor is called Henry's Law constant (or coefficient) (Sander, 2015). With reference to the analysis of methane and other volatile gases by headspace analysis, the liquid is the water sample and the introduced headspace of inert gas (for example, helium) or air forms the overlying gas phase. The ensuing equilibration of methane between the water sample and gas phase may be described by the Henry's Law constant for methane. The value of the Henry's Law constant value is sensitive to both temperature and salinity (section 4.2.1). Increased temperatures and increased salinities each increase the dissolved methane transfer into the overlying gas phase. Increased sample equilibration temperature or the addition of salt are variously used in analysis protocols to enhance the partitioning of methane into the analysed gas phase headspace to improve detection limits.

Calibration of GC instrumentation based on gas-phase standards allows the headspace concentration of methane to be estimated. From this, the concentration of methane present in the water sample is calculated using Henry's Law constant. The use of Henry's Law constant is avoided where GC instrumentation is calibrated using water standards with known amounts of dissolved methane that are treated identically to actual water samples (that is, similar headspace volume, temperature and timeframes allowed for equilibration). The need for Henry's Law constant in the various analysis protocols therefore depends on the calibration approach adopted. For example,

it is required in the RSK-175 - Kampbell and Vandegrift (1998) method (section 4.11.3), but not in the recent ASTM (2017) method (section 4.11.5).

There are several areas of possible discrepancy in analysed methane concentrations that may relate to use of Henry's Law constant. These include:

- confusion arising from the multiple definitions of Henry's Law constant in the literature (Sander, 2015); these vary within and between subject disciplines, with different units depending on the definition. Errors may arise from the mis-application of a selected constant and lead to, sometimes substantially, incorrect calculated methane concentrations
- different literature values of Henry's Law constant may be selected from the choice of constants found in the literature, leading to differences in calculated dissolved methane concentrations
- failure to recognise Henry's Law dependency on temperature (Humez and others, 2015; Pankow, 1986; Sander, 2015) and, or, use of appropriate temperatures within some of the calculations using Henry's Law coefficients. For instance, use of the laboratory temperature under which samples equilibrated for headspace analysis of the gas phase (Ryan and others, 2015). A 1°C error in the temperature used in a headspace calculation causes approximately a 2% difference in dissolved methane concentration (Colt, 2012; Schloemer and others, 2018) (equations set out in Pankow (1986) may be used to examine temperature sensitivity)
- failure to recognise Henry's Law constant dependency on salinity (Sander, 2015). This may lead to errors where water samples vary significantly in salinity (Banks and others, 2017) and is not compensated for by appropriate selection of salinity dependent values of Henry's Law constant, or else adjustment of all samples and standards to a fixed salinity prior to headspace analysis
- poor transparency in the laboratory analysis procedure and use of Henry's Law constant that does not allow the correctness of the method used to be verified and may 'hide' some of the above issues

Expanding on some of these concerns, confusion arises over the definition and use of Henry's Law constant describing the partitioning of dissolved gas (or any solute) between water and air that has been defined in different ways. As noted by Ryan and others (2015), there are multiple definitions in the literature, two of which are the inverse of each other. The aqueous phase may be put as the numerator and the gaseous phase as the denominator, 'aq./gas', resulting in a so-called Henry's Law solubility constant (H). Alternatively, the numerator and denominator may be switched, 'gas/aq.', resulting in a Henry's Law volatility constant (K_H) (Sander, 2015). When working in a groundwater context (bubble formation and partitioning) Pankow (1986), uses K_H formulated as aq./gas in units of M/atm, in line with common practice for dissolved gases (including methane), but uses H as gas/aq. in units of atm.m³/mol for VOC partitioning from groundwater use.

The range of definitions, together with the interchangeable use of partial pressures and concentrations, and different expressions of concentration, leads

to a range of possible units for Henry's Law constants. This includes 2 unitless versions which can become muddled in their use unless well defined by users. This mire of definition and unit complexity is concisely explained by Sander (2015) who tabulates all the various solubility and volatility constant definitions of Henry's Law, their units and conversion factors. As the latter span several orders of magnitude, incorrectly applying Henry's Law constants may lead to large errors in some cases. Henry's Law constants are increasingly specified with superscripts denoting pressure, concentration or mole fraction to help denote the definition adopted and therefore help allay confusion, for example, H^{cc} , H^{cp} , K_H^{px} .

The user is faced with a choice of Henry's Law constant values that they may select from the literature and use in calculations. Sander's compilation (2015), available at <http://www.henrys-law.org>, contains some 17,350 values of Henry's Law constants for water for 4,632 species, collected from 689 references. It includes the conversion factors between different types of Henry's Law constants. Most data were measured at ambient conditions (at 1atm and between 20°C and 25°C (or extrapolated to the latter). Values for methane (<http://satellite.mpic.de/henry/casrn/74-82-8>), ignoring an (old) outlier, comprise a data set of $n = 28$ measured values of Henry's constant (H^{cp}) that have an arithmetic mean of $1.47 \times 10^{-5} \text{ mol m}^{-3}\text{Pa}^{-1}$ and median of $1.40 \times 10^{-5} \text{ mol m}^{-3}\text{Pa}^{-1}$ with a standard deviation of ± 0.30 representing $\pm 20\%$ of the mean.

Workers using Henry's Law constants for methane in groundwater tend to indicate the variation in constants between databases is not that significant. For instance, Humez and others (2015), based on comparing K_H values from 3 sources (in mol/L/atm: 2.58×10^{-3} (Parkhurst and Appelo, 1999), 2.57×10^{-3} (US EPA, 2002), 2.47×10^{-3} (Duan and Mao, 2006), concluded that the differences were negligible. Therefore, achieving correct calculations is a greater concern. Example calculations using Henry's Law constants in headspace analysis protocols and manipulation of constants and their sensitivities (for example, to temperature) may be found within Humez and others (2015), Kampbell and Vandegrift (1998), Lewin and others (1989), McLeish and others (2007), Pankow (1986), Ryan and others (2015) and the reply by McIntosh and others (2015) and Sander (2015).

4.12 Methane isotope analysis

Although there are only 'semi-formal' methods for methane concentration analysis, there appear to be even fewer for methane isotope analysis ($\delta^{13}\text{C-CH}_4$ and $\delta^2\text{H-CH}_4$), with no ASTM (or similar) method statements available. Although more routinely carried out in the USA, analysis of the isotopic composition of methane is rarely carried out in the UK, even though permits for hydrocarbon extraction can require such analyses. Methods of headspace generation are typically the same as methane concentration analysis and some laboratories use the same headspace gas for both methane concentration and methane isotope analysis, for example, Moritz and others, 2015 and Lemieux and others, 2019. Yarnes (2013) describes in detail the issues of using commercially available equipment for $\delta^{13}\text{C}$ and $\delta^2\text{H-CH}_4$ analysis (predominately matrix

interferences) and suggests a methodology for making minimal modifications to the equipment to eliminate these issues.

Many of the references identified as carrying out methane isotope analysis use the commercial Isotech Laboratories in the USA (McIntosh and others, 2014, Schout and others, 2018, Darrah and others, 2014, Dillon and others, 2016, Jackson and others, 2013, Osborn and others, 2010, Thomas, 2016 and Zhu and others, 2018), including the scientific investigation reports by the USGS. Work done by Bordeleau and others (2018) includes detailed information on the use of 4 different commercial laboratories for $\delta^{13}\text{C-CH}_4$ and $\delta^2\text{H-CH}_4$. Four labs were used due to limited instrument availability, and duplicate analyses were carried out to ensure comparable data. Both Schloemer (2016) and Basava-Reddi (2018) developed new methods for carrying out isotopic analysis on low methane concentration waters. Schloemer (2016) developed a single preparation line for GC- Isotope Ratio Mass Spectrometry (IRMS) to analyse $\delta^{13}\text{C-CH}_4$ at CH_4 concentrations as low as $0.7\mu\text{l/l}$ by using cryo-focusing. Basava-Reddi (2018) developed a field method of onsite water sparging as a technique for analysing $\delta^{13}\text{C-CH}_4$ and $\delta^2\text{H-CH}_4$ in waters with CH_4 concentrations $\sim 2\mu\text{g/l}$. UK laboratories historically carrying out $\delta^{13}\text{C-CH}_4$ analyses required CH_4 concentrations $>1\text{mg/l}$.

Final isotope data are expressed relative to the international standards V-PDB (Vienna PeeDee Belemnite) for carbon and V-SMOW (Vienna-Standard Mean Ocean Water) for hydrogen. Reference materials used include National Institute of Standards and Technology (NIST) and Natural Gas Standards (NGS) 1 and 2, plus NBS19 standard, and LSVEC (Carbon and Lithium Isotopes in Lithium Carbonate). The standards used vary between labs as described in the section below.

4.12.1 Laboratories and methods for analysing methane isotopes

Isotech Laboratories (Illinois, USA)

- Not much information online or in papers.
- GC-IRMS.

Duke Environmental Stable Isotope Laboratory

- $\delta^{13}\text{C-CH}_4$ is determined by cavity ring-down spectroscopy (CRDS) (Busch and Busch, 1997) using a Picarro G2112i or newer generation G- or gas chromatographic separation using a Trace Ultra ThermoFinnigan followed by combustion and dual-inlet isotope ratio mass spectrometry using a Thermo Fisher Delta XL.

University of California, Davis Labs, USA

- Gas samples are purged from vials through a double-needle sampler into a helium carrier stream.
- The CH_4 is separated from residual gases by a GC column.

- After CH₄ elutes from the separation column, it is either oxidised to CO₂ by reaction with nickel oxide at 1,000°C ($\delta^{13}\text{C}$), or pyrolysed in an empty alumina tube heated to 1,400°C ($\delta^2\text{H}$) and subsequently transferred to the IRMS.
- A pure reference gas (CO₂ or H₂) is used to calculate provisional delta values of the sample peak.
- Laboratory reference materials are commercially prepared CH₄ gas diluted in helium or air and are calibrated against NIST 8559, 8560, and 8561.
- Yarnes (2013) list the working standards at UC Davis SIF (Table 3).

Table 3. $\delta^{13}\text{C}$ and $\delta^2\text{H}$ measurements of methane from working standards and ambient air at the Stable Isotope Facility at the University of California, Davis. All d-values (‰) are reported at $\pm 1\text{s}$ (from: Yarnes, 2013).

Sample	n	$\delta^{13}\text{C}$	$\delta^2\text{H}$
NGS-1 (IAEA)	3	-29.02 \pm 0.38	-138.09 \pm 2.03
NGS-2 (IAEA)	3	-44.31 \pm 0.51	-177.12 \pm 0.39
Mamm Creek	3	-41.29 \pm 0.40	-223.69 \pm 2.67
B-iso1 (Isometric Instruments)	3	-54.29 \pm 0.26	Not measured
H-iso1 (Isometric Instruments)	3	-23.88 \pm 0.27	Not measured
L-iso1 (Isometric Instruments)	3	-66.44 \pm 0.42	Not measured
UCDM1 (Airgas)	4	-36.59 \pm 0.13	-131.86 \pm 2.19
UCDM2 (Airgas)	12	-36.78 \pm 0.27	-146.96 \pm 1.09
Scott (Scott Specialty Gases)	3	-41.63 \pm 0.47	-176.65 \pm 1.23
Air (Davis, CA, USA)	4	-45.21 \pm 0.45	-84.09 \pm 2.96

Delta-lab of the Geological Survey of Canada

- Between 10 to 1,200ml of gas is extracted from the headspace using an airtight syringe and manually injected into a GC equipped with a column interfaced with an IRMS via a GC IsoLink system.
- For $\delta^{13}\text{C}$ analyses, samples pass through a high-temperature (1,050°C) combustion furnace, where all hydrocarbon gas species are converted to CO₂. An internally calibrated CO₂ reference (monitoring) gas with known $\delta^{13}\text{C}$ values is used for computing the isotopic composition of samples. The $\delta^{13}\text{C}$ value of this reference gas is determined using CO₂ calibrated against international carbonate standards (NBS 18, NBS 19, and LSVEC).
- For $\delta^2\text{H}$ analyses, samples pass through a high-temperature (1,420°C) pyrolysis furnace, where all hydrocarbon gas species are converted to H₂. For computing the isotopic composition of samples, a commercial H₂ isotopic reference gas is used (Oztech Trading Corporation, Safford, Arizona), which was calibrated against the Vienna Standard Mean Ocean Water (VSMOW) international standard. Both reference gases were introduced into the system via bellows.

- All sample measurements are corrected using calibration curves made from isotopically distinct methane standards (Isometric Instruments, Victoria, British Columbia, Canada): B-iso1 ($\delta^{13}\text{C} = -54.5\text{‰}$, $\delta^2\text{H} = -266\text{‰}$), L-iso1 ($\delta^{13}\text{C} = -66.5\text{‰}$, $\delta^2\text{H} = -171\text{‰}$), and H-iso1 ($\delta^{13}\text{C} = -23.9\text{‰}$, $\delta^2\text{H} = -156\text{‰}$). Precision is less than or equal to 0.5‰ for $\delta^{13}\text{C}$ and less than or equal to 3.0‰ for $\delta^2\text{H}$.
- QC – standards are injected at the beginning, middle and end of the day to verify lack of instrument drift. Every sample is injected a minimum of 2 times for $\delta^{13}\text{C}$ and 3 times for $\delta^2\text{H}$ to ensure method precision.

Isotope Science Laboratory at the University of Calgary, Canada

- 600 μl of gas volume is withdrawn from the IsoJar headspace using an airtight syringe and manually injected into a GC IsoLink system interfaced to an IRMS.
- For $\delta^{13}\text{C}$ analyses, samples pass through a high-temperature ($1,000^\circ\text{C}$) combustion furnace, where all hydrocarbon gas species are quantitatively converted to CO_2 .
- For $\delta^2\text{H}$ analyses, samples pass through a high-temperature ($1,420^\circ\text{C}$) reactor, where all hydrocarbon gas species are quantitatively converted to H_2 .
- In both analyses, the CO_2 and H_2 gas pulses are swept by helium carrier gas through a water trap (Nafion®) before entering the ConFlo IV open split interface to the IRMS.
- The $\delta^{13}\text{C}$ and $\delta^2\text{H}$ values of the unknowns are determined using single-point calibration against CO_2 and H_2 reference gases, respectively, whose $\delta^{13}\text{C}$ and $\delta^2\text{H}$ values have been calibrated against international carbonate standards (NBS 18, NBS 19, and LSVEC) and H_2 gases (Oztech Trading corporation I, II and III), respectively (Tables below).

Table 4. $\delta^2\text{H}$ standards used by ISL Calgary

ID	$\delta^2\text{H}$
Oz-Tech-I	$+2.80 \pm 0.13 \text{‰}$
Oz-Tech-II	$-364.01 \pm 0.10 \text{‰}$
Oz-Tech-III	$-761.86 \pm 0.20 \text{‰}$

Table 5. $\delta^{13}\text{C}$ standards used by ISL Calgary

ID	$\delta^{13}\text{C}$
NBS 18	$-5.01 \pm 0.06\text{‰}$
NBS 19	1.95‰ (by definition)
IsoMetric(CH4-239)	$-23.9 \pm 0.2 \text{‰}$
IsoMetric(CH4-383)	$-38.3 \pm 0.2 \text{‰}$
IsoMetric (CH4-545)	$-54.5 \pm 0.2 \text{‰}$
Messer CO2 I	$-0.29 \pm 0.20 \text{‰}$
Messer CO2 II	$-40.13 \pm 0.17 \text{‰}$

- QC - Instrument stability and linearity range are measured daily using an in-house methane mix of 5% CH₄ (balance helium). Accuracy and precision are less than or equal to 0.2‰ for δ¹³C and less than or equal to 2‰ for δ²H based on long-term monitoring of these daily injections. Measurements of Isometric Instruments (Victoria, British Columbia, Canada) gases (B-iso1 [δ¹³C = -54.5‰, δ²H = -266‰], L-iso1 [δ¹³C = -66.5‰, δ²H = -171‰], and H-iso1 [δ¹³C = -23.9‰, δ²H = -156‰]) agree within analytical error.

Concordia University, Canada

- 500ml of headspace gas is extracted using an airtight syringe and manually injected into a GC fitted with a column coupled to a combustion interface and an IsoPrime IRMS. The various compounds of the gas (air, CO₂, alkanes) are separated on the GC column.
- For δ¹³C analyses, samples pass through a high-temperature (950°C) combustion furnace.
- Samples are normalised using 3 in-house standards (methane, -40.90‰–0.17‰; ethane, -29.79‰ – 0.19‰; and propane, -34.33‰ – 0.23‰). precalibrated with the certified international standards NBS 19 and LSVEC (δ¹³C = 1.95‰ and -46.6‰, respectively).
- Precision for the 3 in-house standards injected during the day is between 0.2‰ and 0.4‰ for δ¹³C.
- QC – three-point calibration curve using alkane standards. The standards are injected at the beginning of the day and after every 10 to 12 samples. Each sample is injected twice or three times.

G.G. Hatch Stable Isotope Laboratory at the University of Ottawa, Canada

- Between 10 and 100ml of headspace gas (dilution 1:10 for more concentrated samples) is extracted using an airtight syringe and manually injected into a GC.
- The CH₄ is separated from residual gases by a GC column which is interfaced with a IRMS via a GC IsoLink system.
- For δ¹³C analyses, samples pass through a high-temperature (1,000°C) combustion furnace, where all hydrocarbon gas species are quantitatively converted to CO₂.
- For δ²H analyses, samples pass through a high-temperature (1,420°C) pyrolysis furnace, where all hydrocarbon gas species are quantitatively converted to H₂.
- Samples were normalised using NGS1 (δ¹³C = -29.1‰, δ²H = -138‰) and NGS2 (δ¹³C = -44.8‰, δ²H δ²H = -172‰) international methane standards. Precision is 0.2‰ for δ¹³C and 2‰ for δ²H.
- QC – standards injected at the start and end of every day, plus after every 10 samples, one is injected twice.

Geological Survey of Israel

- $\delta^{13}\text{C}$ analysis performed by GC-IRMS.
- The $\delta^{13}\text{C}$ values are measured relative to the CO_2 reference gas and reported relative to PDB. The sample of the standard methane gas with known isotope composition is analysed after each 5 samples to ensure accuracy.
- $\delta^{13}\text{C}$ QC - All the samples are analysed at least twice and analytical precision (1sd) does not exceed 1.2‰.
- The $\delta^2\text{H-CH}_4$ analyses of selected samples are performed in the Hydroisotop GmbH laboratory (Germany) by the following procedure. An aliquot of the liberated gas is transferred in a vial filled with He. The content of the bottle is flushed with He for 20 minutes and trapped on the absorption material at 120°C (Purge and Trap autosampler). After that, the trap is heated to 200°C for transferring the analytes into the GC-MS-IRMS system. Conversion of the analyte into H_2 was performed at 1,400 °C.
- $\delta^2\text{H-CH}_4$ was recalculated against isotope ratios $13/12R_{\text{sample}}$ or $2/1R_{\text{sample}}$ against VSMOW, and the analytical precision (1sd) for all the samples is $\pm 10\text{‰}$.

GNS Labs (New Zealand), Intertek Geotechnical Services (worldwide) –
limited information.

5 Questionnaire survey results

5.1 Methane sampling

There was a 57% response rate to this part of the questionnaire (21 responses in total), with the largest proportion of responses coming from UK consultancies (36%) and international universities (27%), including the USA and Canada. Around 15% of the responses indicated that the organisation contacted no longer carries out methane sampling. Although there were 21 responses to the initial contact, some of these responses were null, and others sent through information (papers, method statements). These are therefore not included in the questionnaire data below but are incorporated into the discussions.

The results have been split into the sections used in the questionnaire.

5.1.1 Reasons for sampling dissolved methane

Practitioners gave mixed reasons for sampling dissolved methane (Figure 8a), but they were predominately for research (63%), with 25% carrying out regulatory monitoring and 13% involved in both areas. Regarding the type of methane samples actually collected (Figure 8b), 100% of the respondents had collected samples for methane concentration analysis, with this number dropping to 69% for $\delta^{13}\text{C-CH}_4$ and 31% for $\delta^2\text{H-CH}_4$. Of the organisations collecting $\delta^{13}\text{C-CH}_4$ samples, only 3 were from the UK, and no UK respondents were collecting $\delta^2\text{H-CH}_4$.

In the UK, the onshore oil and gas regulatory permits for many operators specify the need to monitor methane concentrations in groundwater to create a baseline understanding and ongoing assessment. Permits also specify the need to monitor $\delta^{13}\text{C-CH}_4$ to help determine if methane is biogenic or thermogenic in origin. The use of $\delta^2\text{H-CH}_4$ analysis is typically not required in the UK, although it is also useful for determining methane provenance. There are, however, only limited capabilities in the UK for carrying out such analysis. There are currently multiple commercial UK laboratories that can provide methane concentration analysis (with variable method detection limits), but no commercial laboratory offering either $\delta^{13}\text{C-CH}_4$ or $\delta^2\text{H-CH}_4$ analysis. The NERC Isotope Geosciences Laboratory (NIGL) is in the process of developing $\delta^{13}\text{C-CH}_4$ and $\delta^2\text{H-CH}_4$ analysis, but currently this is for internal research purposes only and not offered on a commercial basis. Previously, Hall Analytical Laboratories Limited in the UK carried out $\delta^{13}\text{C-CH}_4$ analysis commercially, although this ended in 2019. All respondents carrying out $\delta^2\text{H-CH}_4$ sampling and analysis are international researchers.

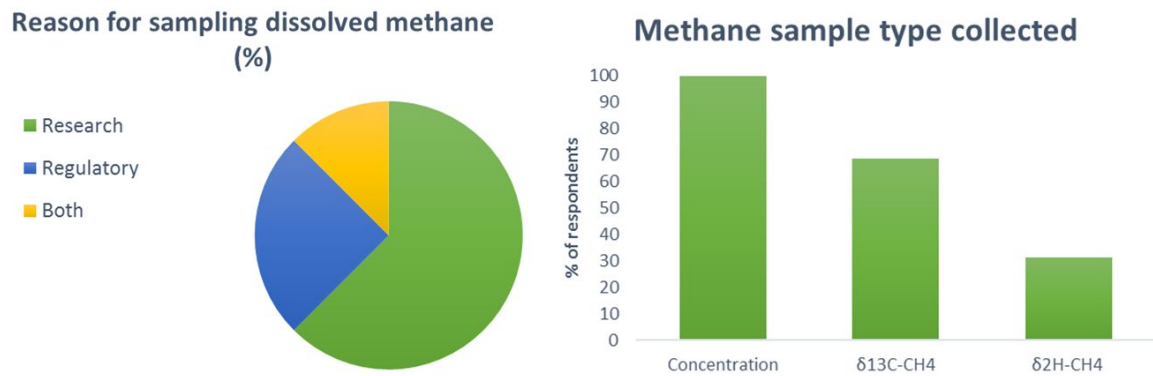


Figure 8. a) Reasons for sampling dissolved methane and b) type of methane sample collected as part of this work.

5.1.2 Monitored site types

Questions on the types of sites being monitored were designed to extract information on the types of boreholes typically sampled for dissolved methane. This included the borehole purpose (monitoring, water supply), number of sites sampled, depth of boreholes and borehole design. In terms of site types, most respondents were involved in contaminated land, onshore oil and gas, landfill and industrial sites where hydrocarbons were a potential issue. Responses on the types of monitoring points sampled were highly varied, ranging from project-specific monitoring boreholes (94%) and multilevel samplers, for example, Continuous Multichannel Tubing (CMT) wells (69%), to private supplies and water company boreholes (62%) (Figure 9a). The depth of boreholes being sampled is varied, from <10m to >50m and screen lengths vary between 1m on experimental site monitoring boreholes to long (>10m) open sections for water company boreholes. This variety applied to both research and regulatory work. Only 25% of respondents said that they exclusively sampled boreholes specifically installed for methane sampling (Figure 9b); the majority (~50%) are using a combination of project-specific monitoring boreholes (not always installed just for methane) and supply boreholes.

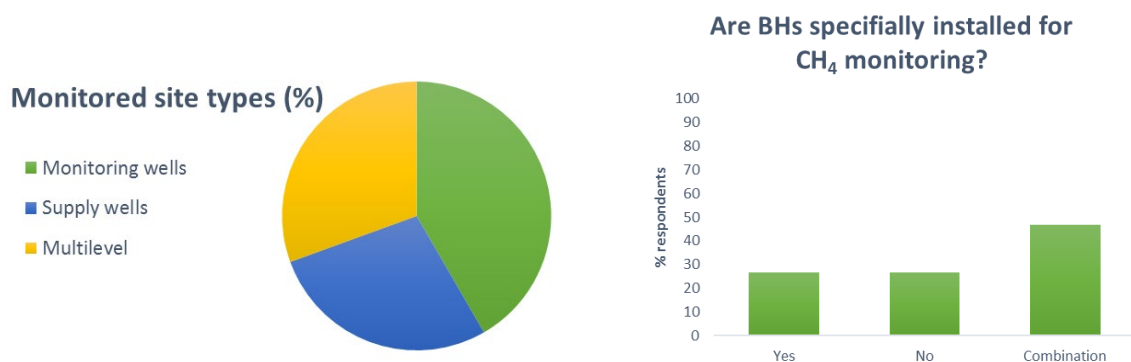


Figure 9. a) Site types monitored by practitioners, b) Responses to question “are boreholes (BH) specifically installed for methane monitoring?” ‘Combination’ means a project sampling network incorporates both project-specific monitoring boreholes and private supplies.

5.1.3 Methane monitoring and sampling

Methane sampling protocols

These questions were designed to understand how frequently dissolved methane samples were being collected and other procedures related to this (recording groundwater levels, barometric pressure). The frequency of monitoring for regulatory work typically depends on the phase of activity (for example, baseline, during drilling, post drilling, in relation to unconventional gas sites), the result of an Environmental Impact Assessment (EIA), and previous data availability. For research, the frequency depends on the scope of the research. For practitioners, the most common (63%) sampling frequency was monthly (Figure 10).

Regarding sampling protocols, 56% of respondents confirmed that they measured groundwater levels during sampling. Accompanying comments suggest low-flow sampling is predominantly used, consistent with low-flow sampling protocol guidelines to keep drawdown to a minimum (<1% of the water column) and to avoid ingress of stagnant water from above the borehole screen. Just over 30% of respondents did not routinely measure groundwater levels while collecting dissolved methane samples. However, it was unclear if respondents recognised the importance of minimising drawdown to prevent reduction in hydrostatic pressures and possible attendant degassing losses. Some reported only recording groundwater level changes if large variations were anticipated – typically if wells are known to be low yielding. Some practitioners, but just 2 researchers in North America, also use total dissolved gas pressure (TDGP) sensors to assess the impact of purging on in-hole gas pressures (including one of the researchers who advocates this approach in the literature review (section 4.10)).

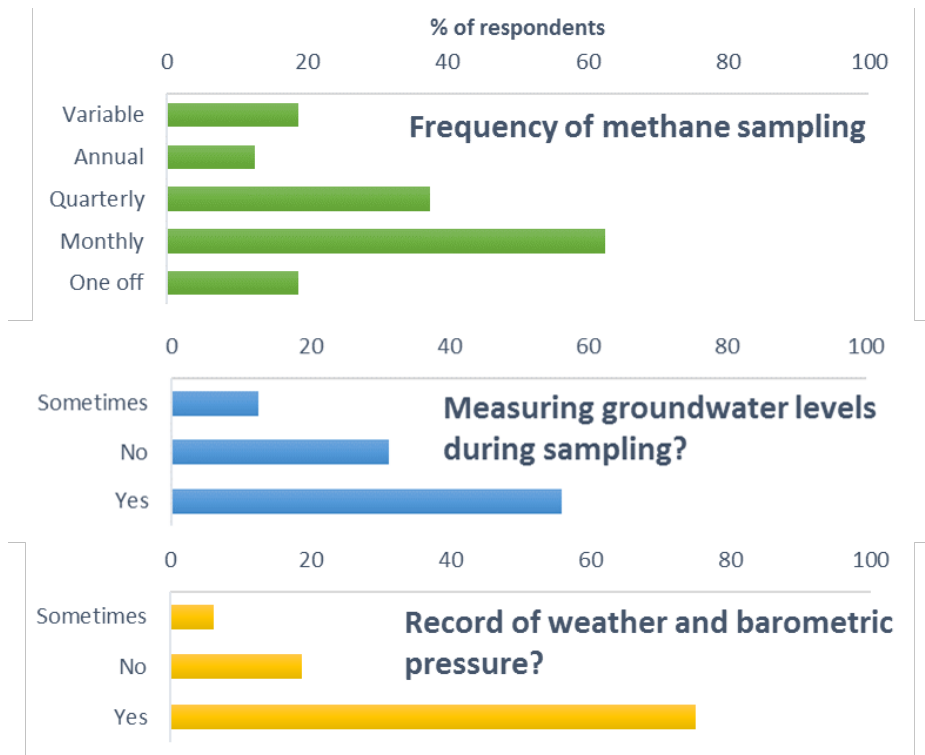


Figure 10. Responses to questions on dissolved methane sampling protocols.

The majority of participants (75%) record the weather or barometric pressure during sampling, especially if they are also collecting samples for borehole headspace analysis or free phase gas. In situ borehole headspace gas monitoring is carried out as standard around landfill and other industrial sites in the UK, whereas free phase gas samples are only typically collected in Alberta, Canada where it is required by law. There are no UK examples of practitioners collecting free phase gas samples.

Methane sampling methods

This section of the questionnaire contained the most questions, as it covered many topics related to methane sampling methods, including types of pump used, purging protocols, sample tubing material and the use of sensors.

Many of the participants had used a variety of pump types to sample for dissolved methane (Figure 11), with 75% having used peristaltic pumps, 68% having used centrifugal and bladder pumps and 30% having used inertial pumps. As some samples are collected from existing supply borehole infrastructure and not from monitoring boreholes, the type of pumps used in these cases are typically constrained to the installed pump used for supply. There does not appear to be a consensus on which type of pump is best for dissolved gases. In some cases, methane is not the main contaminant of concern, therefore the sampling design and pump chosen is not necessarily specifically selected with dissolved gas sampling fully considered. When using peristaltic pumps, 83% of respondents said that dissolved gas sampling would be carried out after the water has passed through the pump head, with only

researchers collecting beforehand as standard equipment is not set up for this. Many practitioners appear to underestimate the impact of negative pressure changes induced by these suction pumps.

The types of materials being used for sampling tubing are varied, but include HDPE, LDPE, Teflon and silicon, often chosen primarily due to their chemical resistance. Generally, dissolved methane is not sampled in isolation and priority is given to other parameters. It is surmised that practitioners have little appreciation of the potential for methane transmission via diffusion through some plastics, although care is taken to avoid reactive tubing for inorganic sampling.

The position of the pump in relation to the screened section of the borehole was variable depending on the borehole construction and water levels, but predominately (62%) mid-screen and consistent between monitoring rounds. As low-flow methods are often used, mid-screen pump positioning is standard, but the yield of the borehole and known inflow zones are also taken into account (and the pump located appropriately) if they have been previously geophysically logged. Where practitioners have used downhole samplers, which don't also allow for borehole purging, one methodology is to first purge from above the well screen (to avoid the likelihood of water levels being lowered into the screen section), which limits the impact on gas pressures within the screen section.

Borehole purging methods used by practitioners for sampling dissolved methane are predominately low flow (67%), with field parameter stabilisation (87%). Low flow purge volumes reported were variable and included both 3 times screen volume and 3 times sample tubing volume. With other methodologies, the volume purged is of secondary importance and is instead dependent on field parameter stabilisation or time constrained. Canadian researchers reported that if monitoring in situ TDGP, this would generally take longer to stabilise than other field parameters (for example, pH, SEC, temperature). Approximately 25% of respondents purge a fixed volume and 20% have carried out zero purge methods (Figure 11). Participants reported only using zero-purge methods (for example, HydraSleeve™, bailers) when other methods were not available. They were perceived to have limited use if their aim was to understand dissolved gas concentrations. If the monitoring is designed for sampling methane, then respondents have recommended purging while monitoring water levels. For instance, one response stated:

“Pumping with water level monitoring to ensure minimal change to water pressure at sampling point and minimal in situ free phase gas exsolution during sampling”.

Once again, there is no clear consensus as to which method is the best for sampling dissolved gases.

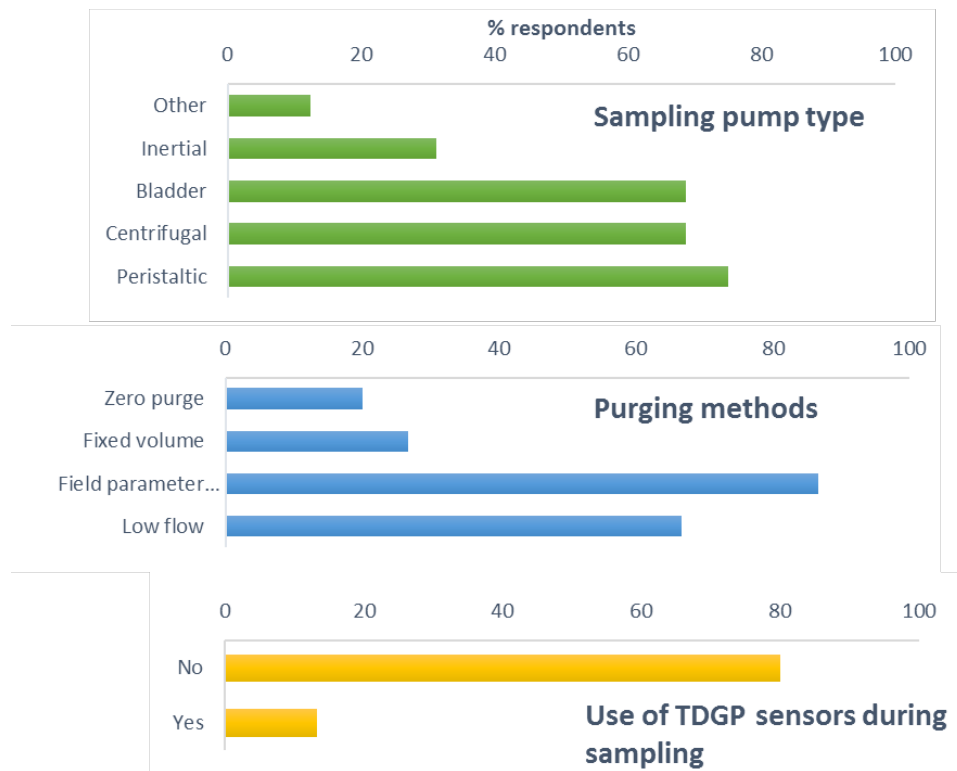


Figure 11. Questionnaire responses to methane sampling methods used.

From the survey, only 2 of the respondents were using TDGP sensors during sampling for dissolved methane and these were both international researchers. There are no reports of TDGP sensors being used for regulatory monitoring. A recent MSc thesis from the University of Calgary (Evans, 2017), which was sent through as supporting material for the questionnaire, involved multiple experiments on known high methane concentration wells using TDGP sensors to identify how different purging/sampling methods impacted on in situ gas pressures. Both dissolved methane samples and free gas samples were collected. The conclusions were that all gas sampling methods were susceptible to a certain degree of atmospheric contamination, but the most robust approach was to use passive diffusion samplers in combination with TDGP data. The research also investigated the impact of pumping at a low flow rate to maintain in situ gas pressures versus pumping at a much higher rate to assess the impact of changes in hydrostatic head on methane concentrations. These drawdown effects were seen to have an impact on methane concentrations, but were not consistent across all the wells tested.

Methane sample collection

The use of different sample collection systems for sampling dissolved gases has been studied for many years in relation to VOCs, and guidance exists for these types of samples. The questions asked as part of this survey relate to how sample containers are filled up once groundwater has been brought to the surface via one of the purging methods described above. Responses for collecting dissolved methane samples revealed 80% had used closed systems, 47% semi-closed and 33% open (Figure 12). Canadian researchers reported

using a combination of systems depending on whether they were sampling for methane concentration or isotopic composition. The supporting text for those responses identifying the use of a closed system suggest that the methodology may actually be classed as semi-closed, and some using inverted VOA vials submerged in a bucket of water. Responses did not reveal any awareness of the emergent concerns in the literature on the use of the inverted VOA vial semi-closed system and modification to use non-inverted vial for sample collection.

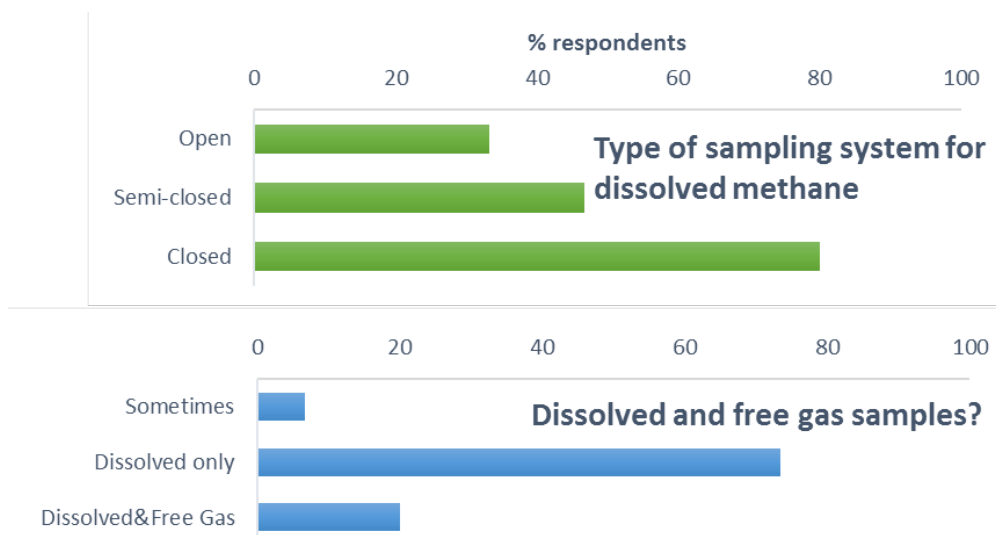


Figure 12. Responses to questions on the types of sampling system for dissolved gases and whether free gas samples are also collected.

Over 70% of participants were collecting dissolved gas samples only (Figure 12), and 20% were collecting free gas samples as part of their monitoring; these 20% were all international researchers. Free gas samples are required in Canada for baseline monitoring around coalbed methane wells. In the UK, there is no such requirement and no UK based respondents had carried out free gas sampling as part of their monitoring. The majority of participants also said that their methodology would not change if they knew that the methane concentrations in the borehole were >20mg/l (that is, approaching methane saturation).

In terms of sample containers for methane concentration, 81% of participants used 40ml glass VOA (Teflon septa) vials, with some using the inverted vial semi-closed method (as per section 4.6.3 literature definition, but called closed system by many in the responses) and 30% using IsoFlasks (Figure 13) under closed system sampling conditions.

For methane isotope analysis, participants were either using clear glass or IsoFlasks, although there are far fewer people carrying out isotopic analysis. In the UK, consultants are using IsoFlasks and shipping them to the US, due to a lack of options for $\delta^{13}\text{C-CH}_4$ analysis in this country. There is also no laboratory method commercially offered in the UK similar to IsoTech’s method for dissolved methane sample collection or isotopic analysis, and no commercial

lab currently carrying out analysis for either $\delta^{13}\text{C-CH}_4$ or $\delta^2\text{H-CH}_4$ in dissolved methane.

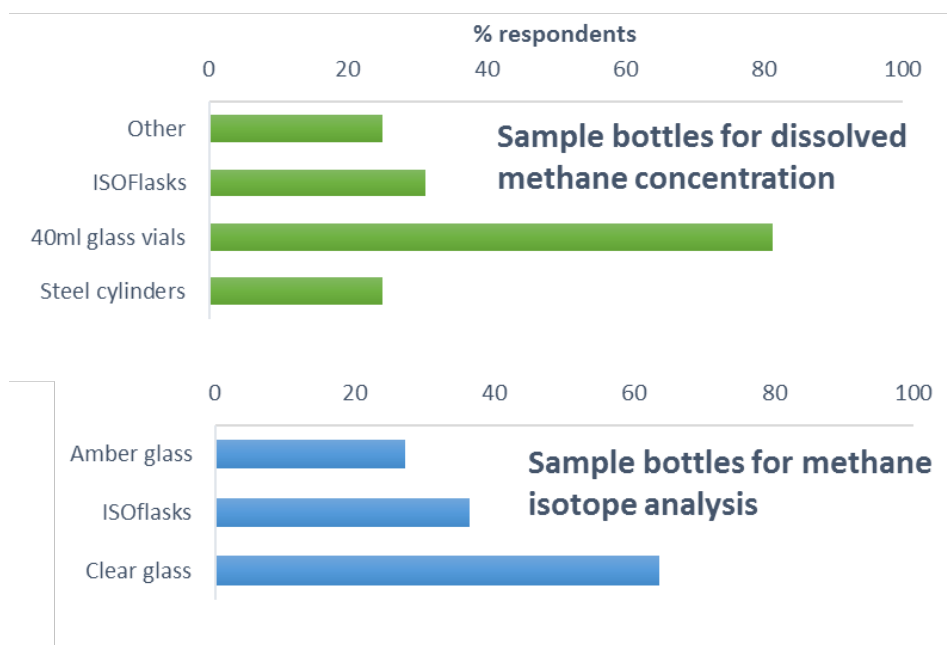


Figure 13. Responses to questions on sample containers used for dissolved methane concentrations and isotope analysis.

Sample storage

Preservation of dissolved methane samples was not used by 63% of participants responding. Only 25% of participants used preservative for both dissolved gas concentration and isotope analysis (Figure 14). Some of this use is accounted for by participants using IsoFlasks for sampling that come 'pre-dosed' with a benzalkonium chloride preservative capsule with a single IsoFlask container being used for both methane concentration and isotope analysis. These capsules were also recommended by other participants (in preference to using HCl). If using a direct fill method for dissolved methane sampling, the VOA vials can be pre-dosed with the preservative. For a variety of semi-closed/closed methods (inverted vial, steel vessels), the sample containers require flushing through, therefore the addition of a preservative is difficult and, if used, needs to be added once the sample has been sealed. This in itself creates other issues related to sample integrity. The 'other' category (13%) was for respondents indicating their use of preservatives varied. Also, they were unsure of the impact that preservatives had on the analysis. Some participants justified not using preservatives based on completing sample analysis within 24 hours. This may not always be feasible.

Most, 93% of participants, stored dissolved methane samples in the dark. 87% refrigerated them, except where steel vessels were used which were kept at ambient temperatures. The manufacturers of the IsoFlasks advise that with the addition of the bactericide there is no requirement to store the samples in the cold/dark and that holding times are longer than unpreserved samples. 20% of respondents inverted their samples, although the understanding of the impact of

this appears to be uncertain (per section 4.8.2; this is to bring any headspace gas into contact with impermeable glass rather than a septum or possible gas leaky closure).

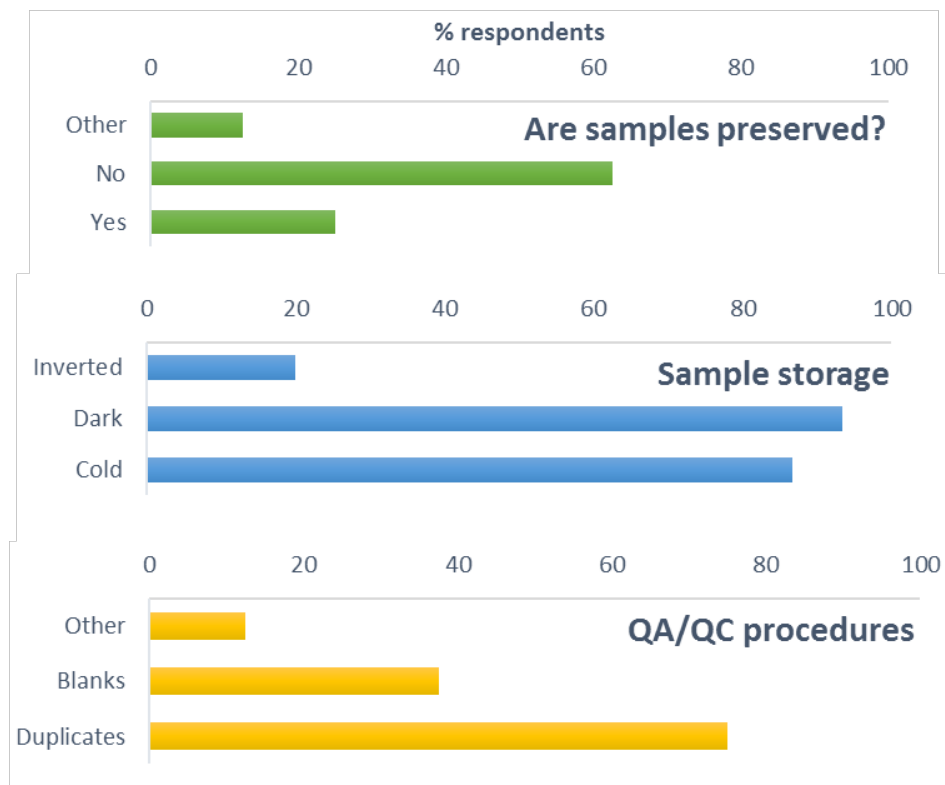


Figure 14. Responses to questions on sample storage and QA/QC.

Responses on quality assurance and quality control (QA/QC) procedures indicate 75% of participants collected dissolved methane sample duplicates and 36% were using blanks. 'Other' responses included submission of control samples of known methane concentrations and isotopic compositions to the laboratory. The chain of custody procedure is also identified as being important to ensure the integrity of the samples.

5.1.4 Dissolved methane data

When asked how repeatable or variable methane concentrations have been in their work, participants in the survey reported changes between sampling rounds were site dependent and could be as little as 0% to greater than 100%. Around half the respondents also mentioned a high level of variability between different laboratories carrying out methane concentration analysis, even when samples were collected consecutively and with the same methodology. It is generally appreciated that variability may arise from both the sampling and analysis process, but also there could be 'real' variation of groundwater methane due to changing physio-hydrogeochemical conditions and methane migration. The typical range of dissolved methane concentrations that have been encountered by the participants is from less than the method detection limit (usually around 1µg/L) up to ~60mg/l. The variability in methane

concentrations is attributed to a number of factors in the responses. These are summarised below:

- Low yielding wells with multiple inflows and long open hole zones.
- Sampling issues –
 - “if free gas loss occurs, it will bias against the dissolved species that are least soluble”.
 - “Duration of purging before sampling, sampling equipment, water level changes”.
- “Actual groundwater changes – physiochemical changes, groundwater flow and their impacts on methanogenesis”.
- “Barometric pressure changes”.
- “Different geology”.

Several respondents identified variation in sampling protocols used as a major contributing factor to dissolved methane variability.

5.1.5 Laboratory interaction

Around 60% of participants are using different laboratories for dissolved methane concentrations and methane isotopes. As discussed in section 5.1.1, there are no laboratories in the UK that can do all of these analyses. Participants have reported the need to change laboratories for several reasons such as laboratory closure and issues with QA/QC. On the whole though, participants indicated that regularly used laboratories provide good interaction and feedback on the analysis data provided.

There appears to be no typical time taken for samples to be submitted to a laboratory. Times vary between participants from 24 hours to a week and depend to some extent on the location of the field area with respect to the laboratory location.

Regarding costs, isotope analysis can be around 10 times more expensive than a standard dissolved methane sample analysis from a commercial UK lab, although this is to be expected as they currently have to be exported to the US.

5.1.6 Overall perception of methane sampling issues

Some main comments from questionnaire responses on methane sampling are collated below. These summarise understanding of the reasons for variable methane concentrations:

- “Multiple inflow zones/fracture flow, long screen sections.”
- “Semi-closed and closed system differences – at high methane concentrations.”
- “Sampling issues/methods, especially with free phase gas – bias against dissolved gas species that are least soluble.”
- “Actual changes in methane generation due to shifts in groundwater flow.”

- “If methane is present [gas], then in situ TDGP is above atmospheric pressure and free phase gas loss is very difficult to avoid.”
- “Methane isn’t particularly variable in situ, but affected by sampling methods.”

There are many stages in the methane sampling process through which methane losses could occur, and practitioners appreciate that this is the case. However, it is not clear (due to a lack of specific protocol guidance) what methods are most appropriate for sampling dissolved gases. It appears that other analyte suites are taking priority over the decision of what sampling methods are chosen, as methane is in some cases, a minor analyte, within the suites sampled. Where sampling methane is a priority focus (that is, shale gas, landfill gas migration), then sampling methods may be expected to be geared specifically to this, more so than when methane data may be seen to be supporting, for example, assessment of contaminated land conditions.

When asked about the main areas of uncertainty, questionnaire responses included:

- pump type
- purging methodology
- sampling system (open, closed, semi-closed)
- sample bottle type
- sample preservative/storage
- should sampling methodology change in effervescing sample conditions?
- is it useful to measure TDGP?

5.1.7 Summary of sampling methods used

A summary of sampling methods used by questionnaire respondents (Table 6) confirms a variety of borehole purging, water collection (pumping), sample collections system at ground surface and sample containers used.

Table 6. List of current sampling methodologies and collection techniques for dissolved methane.

BH purging methods	Water collection method	Sampling system	Sample container
<ul style="list-style-type: none"> - 3 x well volume - low flow - field parameter stabilisation - dependent on groundwater levels/drawdown 	Pump types: <ul style="list-style-type: none"> - peristaltic (suction) - centrifugal (impeller) - bladder pumps - inertial-lift (Waterra) No-purge: <ul style="list-style-type: none"> - in situ sensors - grab samplers (for example, HydraSleeve™) - downhole samples 	Handling at ground surface: <ul style="list-style-type: none"> - open system (direct fill) - semi-closed (inverted bottle) - closed system (IsoFlask, stainless steel cylinder (BGS)) 	<ul style="list-style-type: none"> - Glass vials - IsoFlasks - BGS 'gas bombs'

Methods not recommended by some questionnaire responses include:

- peristaltic pumps
- open and semi-open sampling systems
- delayed laboratory submission and measurement
- sampling for methane concentration without an estimation of in situ TDGP
- long lengths of tubing at the surface – water can warm up, and outgas more as longer at atmospheric pressure

5.2 Methane analysis

A total of 8 responses were received to Part B of the questionnaire from 15 practitioners approached, with 2 of these indicating that they no longer carry out either dissolved methane concentration or methane isotope analysis. The responses were from a variety of practitioners; 2 international universities, one international commercial lab, 2 UK based research labs and one UK commercial lab. All the labs that participated in the questionnaire were carrying out dissolved methane analysis, half were carrying out $\delta^{13}\text{C-CH}_4$ analysis, and this dropped to a third for $\delta^2\text{H-CH}_4$ analysis.

Survey response results are again presented using the sectioning adopted in the questionnaire.

5.2.1 Methane sample containers and preservatives

Questionnaire responses reveal a surprisingly wide variety of sampling containers being used for dissolved methane analysis, listed below:

- glass vials with septa within crimp or screw cap enclosures, for example, VOA vials commonly used for VOC analysis
- 150ml glass bottles with septa screw caps
- IsoFlasks
- 250ml PET bottle with screw caps
- 1L plastic bottles with screw caps
- double-valve 50ml steel cylinders

The first two on this list are fitted with septum-enclosure caps, the others rely on other forms of sample transfer. Half (50%) of the respondents use the same containers for the methane concentration and isotope analysis and the other half are using separate containers for the 2 different types of analysis.

A third (33%) of respondents confirmed that they routinely used preservatives, while the remainder did not use preservatives. For some of the sampling methodologies adding a preservative is difficult and sometimes impossible as discussed in section 5.1.3. The laboratories that require a preservative typically pre-dose the bottles with capsules. For the IsoFlasks closed sampling system, for instance, there is no flush through required, so these bottles are simply filled up with the preservative preloaded. For some sampling systems that involve a flush through of groundwater in the field, preservative is added through preservative capsules glued to the inside of the bottle caps. After the vials have been flushed and filled, they are capped underwater and therefore preserved.

5.2.2 Sample storage and holding times

Responses indicated that sample storage and holding times depend primarily on the types of sample containers being used and whether a preservative had been added. For glass vial samples that are not preserved, storing in the dark/refrigerated is standard and these labs require analysis as soon as possible, ideally within 24 hours. This rapid turnaround is possible for research projects, but unlikely to be typical for other types of sampling. Where a preservative is used, these labs do not tend to specify a holding time or require the samples to be refrigerated.

In some cases, methane samples may be collected before researchers/consultants have decided if this analysis needs to be done. In these cases, samples could be held for days/weeks before eventually being submitted for analysis. The adequacy of storage condition and suitability of these samples for analysis is questionable.

Respondents gave several reasons why samples may be judged unfit for analysis. These include excessive headspace not attributable to oversaturated samples, not enough sample volume in the container, and any defects found or suspected in the sample container.

5.2.3 Methane analysis

All participants in this survey carried out analysis for dissolved methane concentrations via headspace - GC (gas chromatography) analysis typically with a flame ionisation detector (FID) or more occasionally a thermal conductivity detector (TCD). Only 2 of the survey responses named a particular method, both indicated a modification of the Kampbell and Vandegrift (1998) method. This is alternatively referred to a 'US EPA method' but meaning the RSK-175 US EPA laboratory Standard Operating Procedure; that is, the primary semi-formal method referred to in the literature survey (section 4.11.3). Other methods for dissolved methane concentration analysis (apart from the analysis of closed system samples (for example, IsoFlasks)) appeared, on the basis of the described detail, to be variants of this or the other semi-formal headspace – GC methods indicated in the literature review (section 4.11.4).

The volume of water removed to create a headspace for these analyses depends on the lab specific methodology, but ranges between 5 and 10% of the total sample volume. From the participants surveyed, the majority of labs inject either zero-grade air or helium to create the headspace. Two of the laboratories (one UK research lab) reported that if, when the samples are submitted, they already contain a headspace, this would be taken into consideration, and if the headspace volume was less than required for analysis, more helium would be added. As there were no responses from commercial UK labs on how they deal with sample headspace and the transfer steps, this needs further consultation.

Once the headspace has been created, this needs to be equilibrated with the remaining sample – all of the variables related to the sample equilibrium (time, agitation, heating) depend on the specific procedures for individual laboratories. The majority of labs do not use heating for sample equilibrium – most leave the samples at room temperature and the time for equilibrium can vary between 10 seconds to overnight. Two-thirds of the respondents agitate the samples to facilitate equilibrium, although some do this by hand and others use a shaker bath set to specific repetitions per minute. The volume of this headspace gas is then used for the analysis of methane concentrations or isotopes.

All of the lab procedures, for concentration and isotope analysis, make an effort to minimise sample transfer and handling, and design procedural steps that minimise methane loss. These include using gas-tight syringes and avoiding creating pressure gradients in bottles during headspace creation. All methods, apart from one, involve needles piercing septa and the use of gas-tight syringes. The exception is the use of the double-valved steel-cylinders.

The only analysis method or protocol for methane concentration referred to by UK laboratories analysis was the US EPA standard operating procedure (2004), which describes the creation of a sample headspace for analysis. None of the respondents referred to the ASTM D8028-17.

5.2.4 Calibration procedures

All the laboratories that responded to the survey carried out dissolved methane concentration analysis using gas-based standards for calibration. Therefore, all used Henry's Law constants to calculate dissolved concentrations. IsoFlask closed system samples, although using a different extraction approach, also relied on gas-based standards and a Henry's Law constant. The BGS uses the Ostwald Coefficient of Gas Solubility approach to calculate dissolved concentrations from the gas standard-based calibrations (that is expected to yield essentially similar results to a Henry's Law based calculation). None of the laboratories used water-based standards advocated by the recent ASTM D8028-17 method nor mentioned the method in their responses. Various databases are indicated to source the Henry's Law constant, although some responders could not recall the source when completing the questionnaire.

All the laboratories that responded to the survey carry out calibration procedures, typically with at least 3 gas standards over a wide range of concentrations. These calibrations are all carried out using gas standards and not dissolved methane water-based standards. Half the respondents use multiple certified gas calibration standards and the other half dilute a single calibrated gas to produce known standards. The same split in respondents is seen when asked about multiple injections of a single point concentration; half take consecutive aliquots of gas and obtain an average, and others will only do this if there appear to be issues with the calibration linearity. The typical linear range of the calibrated analysis varies between different laboratories, with some suggesting the entire range between atmospheric to 100% is useful. Some laboratories require a sample dilution once methane concentrations are over a certain limit (that is, where they exceed the calibration standard range used). These tend to be done by diluting the original sample with zero-grade air. If the samples are re-run later, the laboratory recognises the sample could potentially be compromised.

5.2.5 Data reporting

When reporting dissolved methane concentrations, half the labs use parts per million (although it was not explicit whether this is dissolved or gas phase) and the other half report as weight per litre (mg/l) to make it clear that it is a dissolved concentration. One of the international research laboratories indicated that, provided it had in situ total dissolved gas pressure (TDGP), it would report methane in mg/l, otherwise it would report in percent methane (a relative concentration). For isotope analysis, the standard notation of per-mil versus the appropriate standard is used.

Method detection limits (MDLs) for the different labs are reported in both ppm and µg/l and range between 1 to 2ppm methane for the headspace analysed and 0.1 to 10µg/l for dissolved concentrations. These MDLs are essentially invariant over time (they have not changed or improved for years). Standard

errors tend to be reported on the gas phase from multiple analysis of certified gas standards, for both methane concentration and isotopes.

5.2.6 Overall perception of analysis issues

Some main comments drawn from the questionnaire on methane laboratory analysis are shown below. These highlight an appreciation that methane concentrations between laboratories are likely to be variable and that the reasons for this could partly be due to varying laboratory protocol implementations. Quotations include:

- “Variability is likely to be higher where methane is present above the saturation limit due to various sampling and analysis techniques that essentially de-gas the water.”
- “Variability is potentially due to the accuracy of calibration and in transfer of sample from sample bottle to auto-sampler vial.”
- “Sampling and analytical protocols - mostly involving losses in sampling, incomplete yields in analysis, failure to maintain equilibration of dissolved and headspace gas.”
- “There are various potential sources of variability in apparent dissolved methane concentration, from field sampling procedures right through to the calculated results. I don’t think it is possible to identify ‘key sources’ – these will vary between the approach used by individual organisations.”
- “The key source of variability is not measuring and considering in situ total dissolved gas pressure.”
- “An understanding of other common dissolved gases in groundwater is key and can enable the detection of atmospheric contamination if O₂ is present.”

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Appendix A: Blank Questionnaire

Dissolved methane in groundwater sampling and analysis survey

*****Instructions for questionnaire completion*****

Our anticipation is that most organisations would be primarily completing either Part A – Site sampling, OR Part B – Laboratory Analysis, rather than both parts that may be completed by a few organisations. However, please review both Parts A and B in case you wish to make some input to both Parts, even if limited. If you would prefer to send through your method statements instead of completing the questionnaire, this would also be welcome.

A partially completed questionnaire is of value.

The questionnaire has an open format and hence do please be encouraged to type in follow up comments below questions in response to not only the prompts such as ‘other?’, but also to more fully explain any answer you provide.

Additionally, we provide an ‘Any other comments?’ at the end of both Parts for you to add anything not already said. If you have any further comments or to send through method statements etc, please contact the BGS project manager.

Your organisation details

If possible, please complete your organisation questions below:

- Job position/role:
- Name of organisation:
- Type of organisation:
 - *University, OOG operator, Commercial laboratory, Government body, other?*
- Country of work:
- Contact details for follow up clarification (if applicable):

Part A - Site sampling

for organisations primarily involved in field site monitoring and sampling

Monitored site types

- Type of site(s) monitored:
- Number (approx.) of groundwater monitoring points at a site(s):
- Number (approx.) of dissolved methane samples taken during a site survey:
- Frequency of site surveys for methane sampling:
 - *Monthly, 3-monthly, annual, other?*

Monitoring and sampling

- What is the main reason for your sampling of dissolved methane/gases in groundwater?
 - *Regulatory, Research, Other?*
- Have you collected samples for methane concentration and methane isotopes?
 - *Concentration, $\delta^{13}\text{C-CH}_4$, $\delta^2\text{H-CH}_4$*
- Have you also collected samples for other dissolved hydrocarbons e.g. ethane and propane?
 - *Yes, no, other*
- What type of monitoring points have you used for sampling dissolved methane?
 - *Monitoring wells (~3 m screen), observation boreholes (long screen), water company borehole, private supply, multilevel-sampler, other*
 - *Were they installed specifically for the site / methane monitoring?*
- Have dissolved methane samples ever been taken post treatment or pressure tank?
 - *Yes, No, Comments*
- When is the methane sample taken relative to other samples (e.g. for inorganics etc)?
- What depth of borehole etc. have you collected these samples from?
 - *<10m, 10 – 50m, >50m*
- What slotted screen length do your monitoring wells or boreholes etc. typically have?
 - *Screen length(s):*
- What is the position of the pump / sampling device in relation to well screen?
 - *Mid-screen or other?*
 - *Does it vary with different visits?*
 - *Does positioning depend on water level?*
 - *Main reasons for decisions made are:*
- Do you routinely measure changes in groundwater level as you collect dissolved methane samples?
 - *Yes, No, Comments*
- Do you know the geology or yield of the borehole before sampling?
 - *Comments?*
- Do you take note of the weather and barometric pressure when sampling?
 - *Comments?*
- What type of pumps have you used in the past to collect dissolved methane samples?
 - *Peristaltic, centrifugal (e.g. Whale or Wasp), Bladder pump, inertial (e.g. Waterra), Other*
 - *If peristaltic, is sample collection before or after groundwater passes through the pump?*
- Typical types of sample tubing (or device) material used?
 - *HDPE etc.?*
 - *Is material choice an important consideration to you?*
- What purging methods do you typically employ for methane sampling?

- *Fixed volume purge – how many well or screen volumes?, low flow – what flow rate?, with field parameter stabilisation – what parameters?, zero purge,*
- *Brief description of protocol used (incl. values where useful):*
- *Typical time taken for purging and sample collection is?*
- Have you ever used zero-purge/passive methods in the list below for sampling dissolved gases?
 - *HydraSleeves, In-situ sensors, downhole samplers, passive diffusion samplers, Other*
- If you have used zero-purge methods, what is your experience with them?
 - *Comments*
- Have you ever used Total Dissolved Gas Pressures (TDGP) sensors as part of your dissolved methane monitoring?
 - *Yes, No, Comments*
- Are your samples collected as part of a closed (no exposure to air), semi-closed (e.g. inverted vials) or open system (direct fill)?
 - *Closed, Semi-Closed, Open, Other*
 - *Other sample handling measures taken to avoid volatile methane losses?*

Methane monitoring

- Have you monitored methane as part of a one off survey, or repeat sampling?
 - *One off survey*
 - *Repeat sampling*
- Have you had to change monitoring/sampling protocols at a site?
 - *Brief description of change:*
 - *Main reasons for change?*
 - *How did you evaluate the influence of this change (e.g. overlap of protocols?)?*
- If you have carried out repeat sampling, how repeatable or variable are methane concentrations?
- What do you typically ascribe observed methane concentration variability to?
- Are there sampling methods you would not recommend (based on your experience?)?
- Have you tried to compare different monitoring and sampling methods? (would you be interested to share such findings in a follow-up study?)

Methane sample collection

- Would you as standard, collect both dissolved and free phase gas samples?
 - *Yes, No, Comments*
- Would this change if you knew that dissolved methane concentrations were >20 mg/l?
 - *Yes, No, Comments*
- What is the typical range in methane concentrations you have observed?
 - *Typical range observed:*
 - *Approx. maximum methane concentrations you have observed:*

- For dissolved methane concentration analysis, what sample bottles have you used?
 - *40ml glass (Teflon septa) vials, ISOFlasks, other glass bottles, steel cylinders, other*
- For dissolved methane isotope analysis, what sample bottles have you used?
 - *Amber glass, clear glass, ISOFlasks, foil polymer bags, other*
- Were any of these bottles pre-evacuated?
 - *Yes, No, Comments*
- Are samples pre-filtered in the field before collection or not? If so, brief details:
- Do you sometimes/frequently have occurrence of head-space (air) in samples?
 - *Main cause? (eg sample degassing)*
 - *What do you do about it?*
- Do submitted samples have other non-ideal issues sometimes?
 - *Comment (e.g. suspended solids)?*
- Are the samples preserved?
 - *Yes, No*
- If so, what is used to preserve the samples?
 - *Comments box*
- If used, how is the preservative added?
- How are the samples stored before analysis (e.g. cold, dark, inverted)?
 - *Comment box*
- What QA/QC procedures do you employ in the field to ensure integrity of dissolved methane samples?
 - *e.g. duplicate samples, blanks etc*

Laboratory interaction

- Do you typically use the same laboratory for methane concentration and isotope analysis?
 - *Yes, No, Other*
- What are the typical and upper limit of times taken for samples to reach the labs?
- What is the typical cost for dissolved methane analysis?
- What is the typical cost for methane isotope analysis?
- Have you had cause to change labs (and what was the main reason?)?
- Have you had any other concerns over lab methane concentration data provided? If so, what?
- Do you have good interaction and feedback from your methane analysis laboratory?
 - *If so, key examples:*
 - *Could this interaction be improved and prove valuable (and in what way?)?*

Overall perception of issues

- **Overall**, what would you perceive to be the key sources of dissolved methane concentration variability arising from the groundwater monitoring, sampling and analysis process?
 - *Open response:*

Section A – Any other comments

- Any other comments?
- Please attach any supporting documents that you believe may provide useful background to your response (e.g. a sampling protocol)
- Would your organisation be interested in later follow-up research studies (e.g. field comparison of sampling protocols etc.)? Please state main interest:

Part B - Laboratory analysis

for organisations primarily involved in laboratory analysis

Methane sample containers and preservatives

- What methane analysis do you carry out?
 - *Dissolved methane concentrations, $\delta^{13}\text{C-CH}_4$, $\delta^2\text{H-CH}_4$*
- For dissolved methane sample analysis, what sampling containers do you request samplers use?
 - *Comments?*
 - *Do you provide these containers?*
 - *Are your containers pre-cleaned? If so, briefly state cleaning protocol*
 - *Are these containers just used for methane analysis or for analysis of other parameters (is sample split)?*
- Do you require a preservative to be used?
 - *Type used?*
 - *Do you provide it?*
 - *Do you advise how to add preservative to samples in field avoiding methane loss?*
- What key guidelines do you provide to clients for sampling dissolved methane (gases)

Sample storage and holding times

- In the laboratory, how do you store the samples before analysis?
 - *Comments box*
- Does your laboratory specify a holding time for dissolved methane analysis?
 - *Maximum holding time is:*
 - *Typical holding time is:*
- Would you judge some samples unfit for analysis?
 - *If so, main issues are (e.g. sediment, head-space etc)?*
 - *What criteria used to reject sample as unfit for analysis?*
- Do clients provide you with supporting sample information that is useful

- *e.g. Methane concentrations are likely very elevated?*
- *Samples is possible compromised due to...?*
- *Would such information help you?*

Methane analysis

- When analysing for dissolved methane concentrations, what method and equipment do you use? (Please describe in reasonable detail and/or attach a methods document if preferred)
 - *Description of method of analysis:*
 - *Description of equipment used:*
- When analysing for dissolved methane isotopes, what method and equipment do you use? (Please describe in reasonable detail and/or attach a methods document if preferred)
 - *Description of method of analysis:*
 - *Description of equipment used:*
- What dissolved methane concentration is required before methane isotope analysis can be carried out?
- If there is headspace already present in the sample upon receipt, what happens to this headspace gas?
 - *Actions:*
 - *Would it matter to the analysis method used and result obtained?*
- Are there any transfer steps that could lead to volatile methane loss in the lab analysis procedure?
 - *If so, please detail steps (e.g. sample vial opening, pipette transfer etc.)*
- If a headspace is required in the analysis:
 - *how is the headspace added?*
 - *what volume of water (percentage of sample) is removed to create a headspace?*
- What time is allowed for equilibration between the water and the created headspace?
 - *Is sample heating used? – Temperature? etc*
- Are the samples agitated to facilitate equilibrium?
 - *If so, how long?*
- What volume of the headspace gas is then used for analysis?
 - *Volume?*
 - *How is this introduced – by syringe or valve?*

Calibration procedures

- Description of typical calibration procedure for dissolved methane analysis:
- Methane calibrant used (gas canister? conc? etc)
- Single point calibration or a range of concentrations (please be specific)
- Are internal standards used? If so brief details?
- Other standards used to ensure equipment calibration?
- Multiple injections of a single point concentration to obtain average (and errors)?

- Typical linear range of calibrated analysis?
- Is there an upper methane concentration limit requiring sample dilution?
- What procedures are used when methane concentrations are above the linear analysis range?
- Is the sample then compromised for a diluted re-run?
- What are your limits of detection for methane (and, ethane, propane and butane)?
 - *Values: LOD? Reporting LOD?*
 - *Have these changed over time? – brief details:*
- What are the (standard) errors for your dissolved methane analysis?
 - *Values:*
 - *How are these determined (briefly):*
- How are the dissolved methane concentrations calculated and reported?
 - *Are there any key assumptions made?*
 - *Is the calculation dependent using a Henry's constant? If so, where is this sourced?*
- Is there any potential for unit errors in methane concentrations reporting?
 - *Eg conversions in the concentration calculation process?*
 - *Reporting units used for dissolved methane are:*
- Are there additional QA/QC procedures in place for these analyses not covered above?

Client interaction and feedback

- Do you assist clients in their understanding of dissolved methane results provided?
 - *If so, in what way:*
- Would there be benefit to you in increasing this technical interaction?
 - *Comments*

Overall perception of issues

- **Overall**, what would you perceive to be the key sources of dissolved methane concentration variability arising from the groundwater monitoring, sampling and analysis process?
 - *Open response:*

Section B – Any other comments

- Any other comments?
- Please attach any supporting documents that you believe may provide useful background to your response (e.g. a dissolved methane analysis method)
- Would your organisation be interested in later follow-up research studies (e.g. laboratory analysis experiments etc.)? Please state main interest:

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