A baseline survey of dissolved methane in aquifers of Great Britain

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HIGHLIGHTS

- Pre-development investigation of methane in drinking water aquifers of Great Britain
- Methane detected in all the aquifers sampled, but typically only at low concentrations (<10 µg/l)
- No samples above the methane 'action level' of 10,000 µg/l
- Unique dataset for detection of future changes and regulatory monitoring

GRAPHICAL ABSTRACT
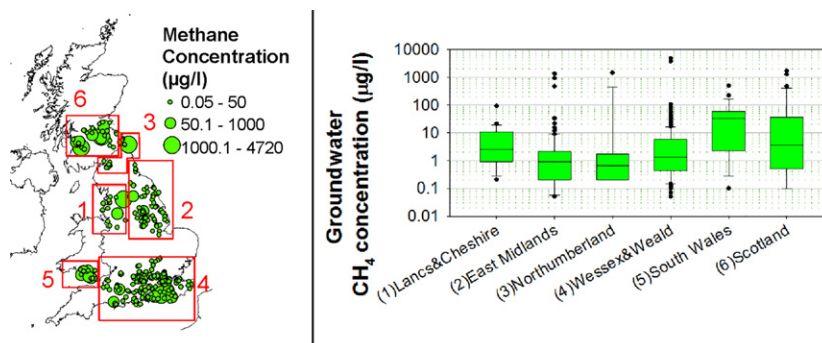
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ABSTRACT

Interest in dissolved methane (CH_4) concentrations in aquifers in England, Scotland and Wales ('Great Britain' or GB) has grown concurrently with interest in the exploitation of unconventional gas sources (UGS). Experience, mainly from North America, has shown the importance of a pre-production baseline against which changes possibly due to UGS extraction can be compared. The British Geological Survey, aided by water utilities, private users and regulators, has compiled a unique dataset for CH_4 in groundwaters of GB. This focuses principally on areas where UGS exploration is considered more likely, as indicated by the underlying geology.

All the main water supply aquifers (Principal aquifers) were targeted, plus Secondary aquifers where locally important. The average dissolved CH_4 concentration across GB in the aquifers sampled was 45 µg/l. Out of a total of 343 sites, 96% showed dissolved CH_4 concentrations <100 µg/l, 80% <10 µg/l, and 43% < 1 µg/l. No site had a CH_4 concentration above the US Department of the Interior suggested risk action level of 10,000 µg/l.

While most sites were sampled only once, a subset was monitored quarterly to determine the magnitude of seasonal or other variations. Generally these variations were minor, with 84% of sites showing variations within the range 0.5–37 µg/l, but some aquifers where the porosity was primarily fracture-related showed larger changes (0.5–264 µg/l). This may have been due to the nature of sampling at these sites which, unlike the others, did not have installed pumps. Since the regulatory compliance monitoring attending UGS operations will include the measurement of parameters such as dissolved CH_4, it is essential that sampling methods are tested to ensure that reliable and comparable datasets can be obtained.

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1. Introduction

Methane (CH$_4$) is released to the environment both by natural processes and anthropogenic activities, the latter conceivably including the exploitation of unconventional gas sources (UGS) such as shale gas or coal-bed methane. In addition to being potentially explosive, CH$_4$ is also a significant greenhouse gas with a global warming potential about 20 times higher than that of carbon dioxide (IPCC, 2013). The current widespread development of UGS energy has therefore led to renewed interest in the possibility of water supply aquifers being affected by 'stray' or 'fugitive' CH$_4$ from extractive operations.

Evidence from the USA has shown that very high dissolved CH$_4$ concentrations may be found in some aquifers in areas where shales are being commercially exploited for gas, but there is considerable uncertainty and debate over the source(s) of the CH$_4$ and how it has entered the aquifers and drinking water wells, whether through natural processes or anthropogenic impacts (Molofsky et al., 2016a and references therein). Crucially, there was no consistent collection of baseline data on CH$_4$ concentrations in groundwater in the USA before shale gas exploitation began, making it sometimes problematic to correctly identify and attribute the reasons for the existence of high-methane groundwaters. This has been identified as a key data gap and uncertainty in investigations into the impact of UGS exploitation (USEPA, 2016).

The need for a pre-development methane baseline in the UK was recognised in the report on shale gas extraction published by the Royal Society and Royal Academy of Engineering (RS/RAE, 2012). The *methane baseline* is defined for the current study as the range of background CH$_4$ concentrations in British groundwaters before any significant exploitation of unconventional hydrocarbons, such as shale gas, has taken place. The origin of this background methane is of secondary importance, whether naturally occurring or introduced by human activity such as coal mining and landfills.

The aim of the present paper is to make a substantial contribution to establishing this baseline, by reporting the results of methane measurements from 343 sites from a range of aquifers across England, Scotland and Wales. The results are considered likely to be of particular interest to energy companies, the general public and environmental regulators, but also to environmental researchers more generally.

2. Background

2.1. Methane and associated risks

Dissolved CH$_4$ when ingested has no known human health impacts (indeed, it is produced in the human gut) and there is accordingly no formal water or environmental quality standard for methane. However, if dissolved CH$_4$ concentrations exceed the equilibrium solubility at the ambient partial pressure of ~1850 parts per billion by volume (NOAA, 2016), which is ~0.05 μg/l under the open atmosphere, methane will degas from the water until the system re-equilibrates. This degassing may create a potential explosion hazard or asphyxiation risk if it occurs in a confined space, and therefore constitutes the main risk of methane to human health. Methane in confined spaces has caused problems in mines, tunnels and landfills (e.g. Williams and Aitkenhead, 1991; Wilson et al., 1989), resulting in the establishment of standards for the potential explosive limits of methane in air. The lower explosive limit (LEL) for CH$_4$ in air is 5% by volume; the lowest dissolved concentration that theoretically could give rise to this mixture in a confined space is 1600 μg/l (Hooker and Bannon, 1993). In practice a CH$_4$ risk 'action level' of 10,000 μg/l is considered realistic (Eltschlager et al., 2001).

2.2. Previous methane baseline studies

A number of shallow aquifer methane baseline studies covering areas comparable in size to the present survey have been reported. Some of these are in areas where UGS are already being exploited (e.g.

Humez et al., 2016; Li and Carlson, 2014; Molofsky et al., 2013), some in areas where conventional gas production is already taking place but prior to possible UGS extraction (e.g. McPhillips et al., 2014; Schloemer et al., 2016), and some in areas without conventional gas production but with shale gas prospects (e.g. Moritz et al., 2015) and therefore most similar to the areas of the UK covered by the present study. Most of the studies use isotopic characterisation in addition to measuring methane and ethane concentrations.

Typically these studies found dissolved methane concentrations covering several orders of magnitude, but with a bias towards low concentrations of ≤10 μg/l CH$_4$ (McPhillips et al., 2014; Molofsky et al., 2013; Schloemer et al., 2016). They also found a tendency for δ^{13}C-CH$_4$ values to peak in the range −60 to −70‰ (Humez et al., 2016; Li and Carlson, 2014; Moritz et al., 2015; Schloemer et al., 2016) typical of biogenically produced CH$_4$, though the overall spread in isotope values tended to be large (up to 130‰ in the case of Schloemer et al., 2016) and therefore not always diagnostic of likely origin.

2.3. Potential sources of methane in groundwater

Methane in groundwater is derived from two main sources: biogenic CH$_4$, which is produced by microbial metabolism and thermogenic CH$_4$, which is formed during thermal decomposition of organic matter (Fig. 1). Biogenic CH$_4$ is mainly associated with shallow anaerobic groundwater environments, such as peat bogs, wetlands, lake sediments and landfills, although it is detectable in nearly all groundwater. Prior to work by Darling and Gooddy (2006), dissolved CH$_4$ in the UK was typically considered only likely to be found in groundwaters that were sufficiently reducing, limiting occurrences to zones in confined aquifers where no dissolved oxygen is detectable (e.g. Edmunds et al., 1984). However, Darling and Gooddy (2006) showed that biogenic CH$_4$ was ubiquitous throughout the aquifers studied: Chalk Group, Lower Greensand Group, Lincolnshire Limestone and Sherwood Sandstone Group. This biogenic CH$_4$ derives from either fermentation of acetate (organic salts present in most groundwater) or carbon dioxide reduction; in shallow groundwater environments it is likely that the former process predominates (Chapelle, 2000).

Thermogenic CH$_4$, formed during thermal decomposition of organic matter (kerogen) at depth, is usually associated with coal, oil and gas fields and is not typically found in shallow groundwater environments. It is generally found, if at all, at depths of several hundred metres to kilometres in the subsurface, trapped in conventional gas reservoirs. These reservoirs are created when hydrocarbons migrate from a source rock (organic rich shales, mudstones or coal seams) into a porous reservoir rock overlain by a low permeability cap-rock, which inhibits further upward fluid migration and allows gas to accumulate in the reservoir. The porosity and permeability characteristics of the reservoir are such that conventional hydrocarbon extraction is possible, as is the case with typical UK onshore Carboniferous and Mesozoic reservoirs (e.g. Gluyas and Hichens, 2003). In contrast, UGS exploration directly targets the source rock for this thermogenic CH$_4$, but these shales or mudstones tend to have much lower permeability, requiring hydraulic fracturing to extract the gas (e.g. Selley, 2012). In the UK, the main target shale gas source rocks are the Carboniferous Bowland and Craven Groups (Andrews, 2013), Carboniferous West-Lothian Oil Shales (Monaghan, 2014) and the Jurassic clays and mudstones of the Weald Basin (Andrews, 2014). There are, however, other older (Cambrian) units with the potential for exploration.

3. Methods

3.1. Setting up the new baseline survey

The current survey builds on previous work by the British Geological Survey (BGS). The ~170 analyses obtained before the current survey (Gooddy and Darling, 2005; Darling and Gooddy, 2006; Ó Dochartaigh
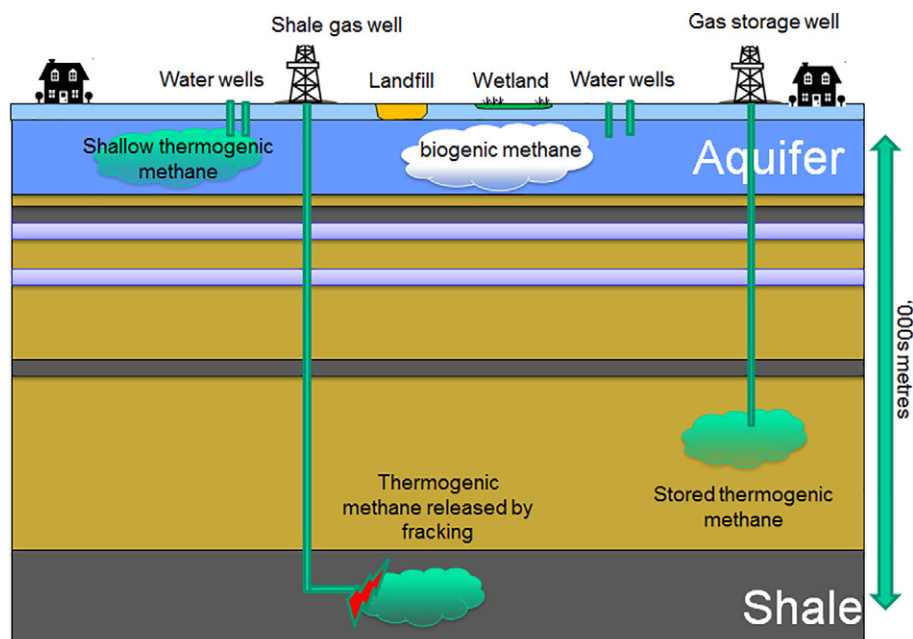
Fig. 1. Sources of methane in groundwater environments.

et al., 2011) were collected using the same sampling procedures and analysed by the same method as for the current survey, so the two datasets have been combined for the purposes of this study. The existing data points available before the present survey began are shown in Fig. 2, together with the areas currently licensed for hydrocarbon exploration by the Oil and Gas Authority (OGA). Target areas for the new survey were primarily focussed on areas where UGS are considered likely to exist but there were limited or no groundwater CH_4 data. Areas were initially selected by using a combination of expert knowledge, available geological maps, 3D models, borehole and geophysical data (Smith et al., 2010). Account was also taken of the locations of current hydrocarbon licences and known operator interest in particular areas. The target areas were then refined as new information became available; the DECC/BGS assessment of Britain's unconventional resources was released (DECC, 2013) followed up by the DECC regional specific reports detailing prospective areas (Fig. 2). Also in 2014, maps produced by BGS and the Environment Agency (EA) showed the vertical separation distance between Principal aquifers and shale gas source rocks (Loveless et al., 2017).

Northern Ireland, part of the UK, is also considered to have UGS potential. However, it was decided that the BGS survey would not proceed in this area as the baseline evaluation of groundwater quality in Ireland and Northern Ireland is being co-ordinated by the Irish environmental protection agency (Teagasc) as part of a joint research project on UGS exploration and extraction in the island of Ireland. The methane baseline defined in this paper therefore relates exclusively to Great Britain.

Samples for the present survey were only collected from areas where the shales are thought to be mature enough to be a potential shale gas (or shale oil) resource (e.g. Andrews, 2013 and Andrews, 2014). All the new Survey sites were in England and Wales. Sites were selected by contacting the appropriate water utilities and EA regional offices, with the aim of having a good spatial distribution of sites and including a variety of aquifers, both Principal and Secondary (for definitions see Carey and Thursten, 2014) utilised in the specific region. For consistency of sampling only borehole sources rather than springs or catch-pits were chosen.

The number of samples collected per year as part of the survey is reported in Table 1; the total number of samples collected over the three-year survey period was 248. The number and distribution of sites was influenced by: the national scale of the survey; the size of

each of the target areas; the availability of sampling points in each area; and the resources available. The majority of survey sample sites are either water supply boreholes or EA monitoring boreholes (either from their Groundwater Quality Monitoring Network or Level Network), though assistance from private borehole operators was also sought to enhance coverage in some areas. Approximately 70% of all sites were water company boreholes, with the remaining 30% divided between EA and private sites, some of the latter forming part of the EA monitoring networks. In the Wessex and Weald Basin 17 samples were collected by Thames Water and 11 by the EA; these data have been included in the summary.

To investigate the possibility of seasonal or other short-to-medium-term changes in groundwater CH_4 concentration, a subset of sites was monitored quarterly, usually over one year. From sites previously sampled a total of 18 were chosen, to give a representative geographical spread of aquifers. The number of quarterly sites in each survey area was proportional to the size of the area. Within each survey area the quarterly sample sites represent a range of different aquifers and areal separations.

3.2. Geology and hydrogeology

Of the 12 Principal aquifers in the UK, nine were included in this Survey. For simplicity during survey design, the target areas were divided into the regions below, rather than aquifer types (Bell et al., 2016). However, the hydrogeological characteristics of each aquifer type (yields, flow type, etc.) are outlined in Table S1 (Supplementary data) and summarised below.

3.2.1. Central-southern Scotland

All the CH_4 samples from this region were collected as part of the Baseline Scotland project, completed in 2011. The main aquifers are the Carboniferous sedimentary formations (Clackmannan, Inverclyde, Strathclyde and Coal Measures Groups), the Devonian sandstones and the Ordovician/Silurian fractured aquifers. In this region, groundwater was historically an important resource for industry, but today is not widely used. The Clackmannan and Coal Measures Groups form multi-layered and vertically segmented aquifers, in which fine grained, well-cemented sandstone layers act as discrete aquifer units in which groundwater flow is predominantly through fractures, and which are
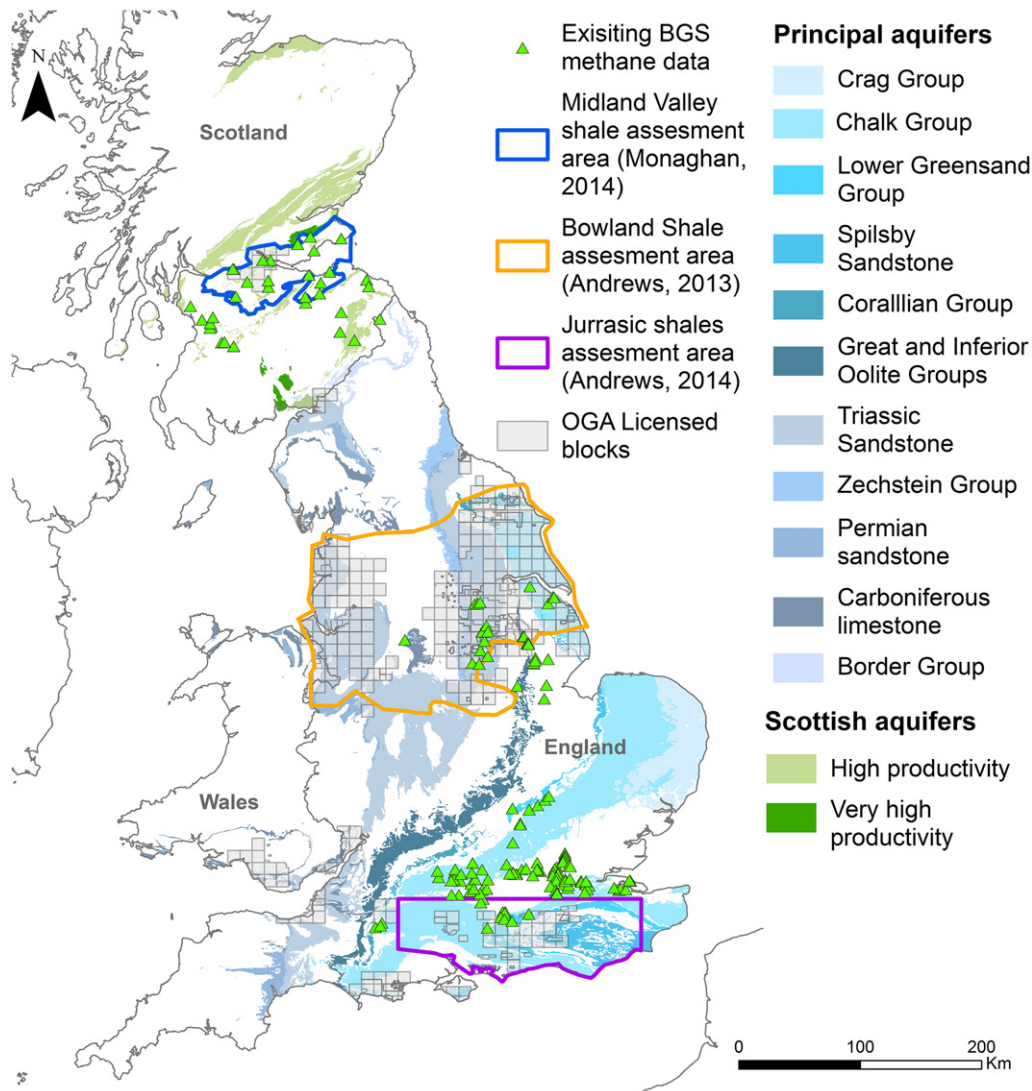
Fig. 2. BGS groundwater methane datapoints prior to the current survey, shown with the location of the Oil and Gas Authority licensed areas. Contains Ordnance Survey data ©Copyright and database rights 2017.Ordnance Survey Licence 100021290. Contains public sector information licensed under the Open Government Licence v3.0. Geological information, BGS © NERC.

separated by lower permeability siltstones, mudstones and coals (Ó Dochartaigh et al., 2011). In this area, the formation most likely to have potential for shale gas and/or oil is the West Lothian Oil-Shale Formation, in the eastern part of central Scotland (Monaghan, 2014).

3.2.2. Lancashire and Cheshire Basins

Within the Lancashire and Cheshire Basins four aquifers were targeted as part of the survey including the Permo-Triassic Sherwood Sandstone Group (SSG) and the shallow Quaternary Superficial Deposits. In addition, two samples were collected from the Carboniferous; one from the Namurian Bowland Shale Group and one from the Millstone Grit Group. The targets for unconventional oil and gas exploration

Table 1
Summary of methane samples collected per year (including quarterly repeats) per target area.

Survey area	2012	2013	2014	2015
Lancashire & Cheshire Basins	13	–	5	5
South Wales	12	–	9	4
Wessex & Weald Basins	17	20	87	16
East Midlands Province	–	16	26	23
Northumberland	–	–	16	–
Totals	42	24	134	48

in this area are the organic rich mudstones of the Bowland Shale Group, which is prospective at depth (Andrews, 2013).

3.2.3. East Midlands Province

In the East Midlands Province, groundwater supplies are mostly from the four Principal aquifers in the area, the Cretaceous Chalk Group, Lincolnshire Limestone, Permo-Triassic Sandstone and the Zechstein Group limestones. In addition, more localised Principal aquifers including the Corallian Group and Carboniferous Limestones were sampled. Additional samples were collected from Secondary aquifers; West Walton Formation, Coal Measures Group and the Millstone Grit Group. The Namurian Bowland Shale Group is the target formation for unconventional gas exploration in this area (Andrews, 2013).

3.2.4. Wessex and Weald Basins

In this region, numerous different aquifers were sampled as part of the survey, including the Principal aquifers; Chalk Group, Lower Greensand Group, Sherwood Sandstone Group, Carboniferous Limestone and Great and Inferior Oolite groups. In this southern province, the Chalk Group is used extensively for public water supply and as such, half the samples in this region were from the Chalk aquifer. In addition, many samples from formations classed as Secondary aquifers were collected. The targets for unconventional exploration in this region are the

Jurassic, organic-rich, marine shales that have the potential for shale oil (Andrews, 2014).

3.2.5. South Wales

In this region samples were collected from two aquifers, the Carboniferous limestone and the Coal Measures Group sandstones. Although the Coal Measures Group is not a Principal aquifer, groundwater flows through fractures in the hard dense sandstones within the Group and groundwater levels are monitored by Natural Resources Wales. The target formation for unconventional gas development in this area is the Namurian Marros Group, with siliceous mudstones and local quartz rich sandstones (DECC, 2013).

3.2.6. Cumbria & Northumberland

The two main aquifers in this area are the Permo-Triassic sandstone and the Fell Sandstone and Border Group. At shallow depths, the Carboniferous Fell Sandstone and Border Group is an important aquifer for the north east of England, used for both small, local supplies and public water supply. It is a Principal aquifer up to 300 m thick and is made of laterally extensive quartz rich sandstones with silty or pebbly bands. The shale units present in the Northumberland Trough are the Bowland Shale Group and other black shales of Visean-Tournaisian age that are typically inter-bedded with sandstone, siltstone and mudstone (DECC, 2013).

3.3. Sample collection

To obtain representative gas concentration measurements over the maximum range, groundwater has to be sampled before contact with the atmosphere so that gases cannot exsolve (e.g. Molofsky et al., 2016b). This entailed collecting pumped water samples directly from a borehole, by attaching tubing with a gas-tight connection either to the wellhead for an installed pump, or directly to the pump outlet for a portable pump. If an installed pump had no suitable wellhead tap or valve, the nearest access point was used, provided this was situated before the pumped water entered a storage tank or was treated in any way. Samples from boreholes with installed pumps were taken after purging 2–3 well volumes, if the boreholes were not continuously pumped, or more usually, immediately if the installed pump was running continuously. Where samples were collected using a portable pump, this was placed if possible at the mid-point of the screen (where borehole construction details were available), and the borehole purged until field parameters were stable.

Samples for CH_4 analysis were collected into double-valved steel cylinders of known capacity, mean volume 50.9 cm^3, range 47–55 cm^3 (Fig. 3). Ideally the samples were obtained at pump pressure via suitable clamped tube connections, but in cases where no suitable offtake point was available other arrangements were improvised and the sample taken at less than pump pressure. Samples collected in this way were not observed to be degassing within the connecting tubing, so it is considered this mode of sampling will have had little or no effect on the measured dissolved gas concentration. Groundwater samples for $\delta^{13}C$-CH_4 analysis were transported from field sites to the University of Bristol laboratory in 3 l Marvel® foil polymer bags containing 30 ml of a 5% solution of the preservative benzalkonium chloride.

3.4. Sample analysis

The dissolved gas samples were analysed in batches of approximately 20 at the BGS Wallingford laboratories. A headspace technique was used. This involves the transfer of the water and gas in the sampling cylinder to an evacuated glass bulb of known capacity (mean volume 121.1 cm^3, range 117–123 cm^3). The displacement process uses helium gas from the same source as used by the gas chromatograph (GC). Aliquots of the headspace gas are then expanded into the evacuated inlet system of the GC, from where they are admitted to a 1/8th-inch

Fig. 3. Steel cylinders used for methane sample collection.

(3.2 mm) od Porapak-Q packed column at room temperature. Eluting methane and ethane (if present) are detected by a flame ionisation detector (FID). The detection limit for dissolved CH_4 was ~0.5 µg/l depending on GC conditions during batch analysis. Canned gas standards (Air Products Ltd.) covering the decades from 100 ppm to 10% CH_4 were used for calibration. Measurement precision is estimated to be ±5% RSD. Further details of the method are available in Darling and Milne (1995).

For the $\delta^{13}C$-CH_4 analysis at the University of Bristol, the methane was extracted from the water by sparging with 'zero' air containing <1 part per billion CH_4. The zero air was prepared by circulating a fixed volume of air through a quartz tube packed with CuO pellets heated at a temperature of 950 °C. The extracted CH_4 was transferred to Wheaton vials sealed with Belco® rubber stoppers. Stable isotope analysis was conducted using a ThermoElectron XP continuous flow isotope ratio mass spectrometer equipped with a trace gas pre-concentrator (PreCon®), which was used to remove CO_2 and H_2O prior to combustion of CH_4 and cryo-focusing of the resulting CO_2. The PreCon® was modified according to the approach of Fisher et al. (2006), which uses palladium powder on quartz wool at 780 °C for quantitative conversion of CH_4 to CO_2. Stable isotope ratios are reported in the standard delta (δ) notation in units of permil (‰) relative to Vienna Pee Dee Belemnite (VPDB). The accuracy of analysis was verified using the ISO series (H, B, T and L) of $\delta^{13}C$-CH_4 standards (Isometric Instruments, Victoria, BC Canada). Analytical precision (±0.1‰) was determined via replicate analysis of a 2 ppmv CH_4 alpha-gravimetric standard (BOC Ltd.).

4. Results and discussion

Results for individual sites are reported in Table S2 (Supplementary data). These include location, date of sampling and CH_4 concentration, plus C_2H_6 concentration and $\delta^{13}C$-CH_4 where these have been measured. Repeat measurements are included in Table S3.

4.1. The methane baseline of Great Britain

The combined survey results from the baseline regions (central-southern Scotland, Cumbria and Northumberland, East Midlands province, Lancashire and Cheshire basins, Wessex and Weald Basins, and South Wales) are summarised in Fig. 4. Twelve Principal and Secondary water supply aquifers, from Recent to Lower Palaeozoic, are represented. Measured dissolved CH_4 concentrations ranged from 0.5 to 4700 µg/l. Only three samples exceeded the minimum possible hazard concentration of 1600 µg/l, and none exceeded the risk action level of 10,000 µg/l. Approximately 80% of sites yielded concentrations below 10 µg/l, while ~45% had concentrations below 1 µg/l. The inset to Fig. 4

shows basic statistics (min, max, median) for each of the regions; these are presented numerically in Table 2.

Methane concentrations are also shown as cumulative frequency plots for aquifers in each target area (Fig. 5).

4.1.1. Central southern Scotland

Methane concentrations in the Carboniferous sediments are similar to those seen in the Carboniferous Limestones of South Wales, and elevated concentrations have been found in previous work on Carboniferous sediments (Gooddy and Darling, 2005). Approximately 40% of the samples had a concentration <1 µg/l and 77% are <100 µg/l. Of the higher CH$_4$ concentrations in the area, the highest was from a borehole in the Clackmannan Group and others were from the Coal Measures Group, sometimes where known, or suspected to be impacted by mining. These elevated concentrations are most likely a consequence of high organic carbon content within the aquifers, specifically within the Carboniferous coal seams.

4.1.2. Lancashire & Cheshire Basins

Methane concentrations in both the SSG aquifer and the Superficial Deposits are consistently above the detection limit, highlighting the ubiquitous presence of CH$_4$ in baseline groundwater environments.

The magnitude of CH$_4$ concentrations are well below that required for further investigation (1000 µg/l) and also the risk action level. Methane concentrations are typically lower in the SSG than those in the Superficial Deposits (Fig. 5). Groundwater in the Superficial Deposits is generally relatively reducing, although it is unlikely that conditions are such that sulphate reduction and ultimately methanogenesis are occurring. The source of this additional CH$_4$ could be from small scale reducing 'pockets' around organic matter in the Superficial Deposits. A combination of oxic conditions and a lack of organic carbon in the SSG could be responsible for lower methane concentrations, although this is very site dependent. The site with the highest CH$_4$ concentration was recorded at a site in the SSG; the borehole log for this site reports a 6 m overburden of boulder clay which could create reducing groundwater conditions. In relation to other regions the maximum recorded CH$_4$ concentration is well below that of other areas, 73% of samples have CH$_4$ concentrations <10 µg/l.

4.1.3. East Midlands Province

Similar to the other target areas, CH$_4$ concentrations in all aquifers are consistently above the detection limit. No samples exceed the risk action level and have therefore not required further investigation. In general, CH$_4$ concentrations are highest in the Lincolnshire Limestone
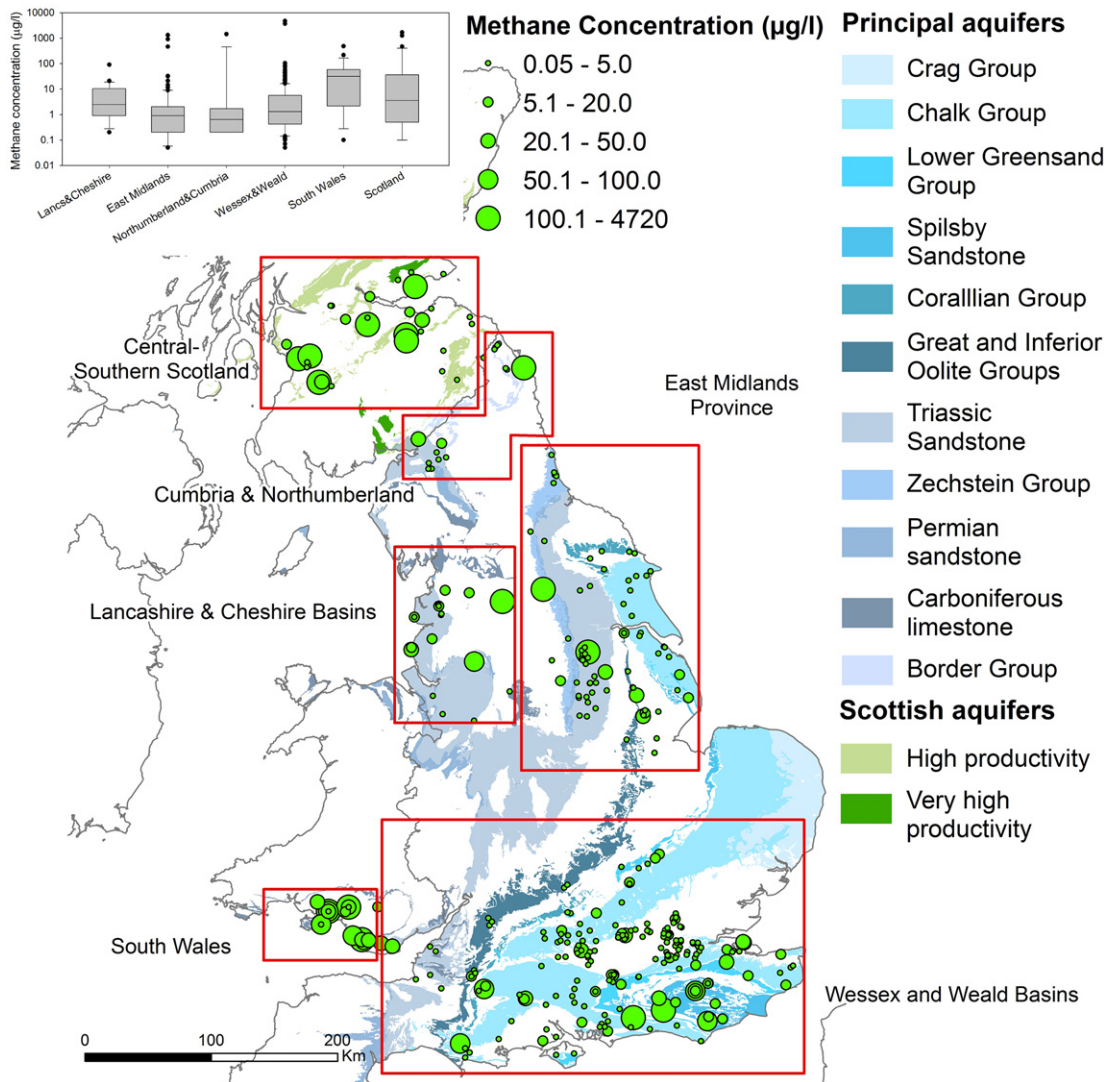

Fig. 4. Dissolved methane concentrations in groundwater in selected aquifers and areas of Great Britain, with geology at 1:625,000 scale (see also Table S2). For more detail on aquifers at individual sites see Tables S2 and S3 (Supplementary Data). Contains Ordnance Survey data © Copyright and database rights 2017. Ordnance Survey Licence 100021290. Geological information, BGS © NERC.

Table 2
Methane baseline result statistics.

Area	CH$_4$ concentration (µg/l)				Number of samples
	Minimum	Median	Average	Maximum	
Central southern Scotland	<0.5	3.6	132	1680	31
Lancashire & Cheshire Basins	<0.5	2.5	9.3	91	23
East Midlands Province	<0.5	0.9	31	1320	93
Wessex & Weald Basins	<0.5	1.3	39	4720	251
South Wales	<0.5	32	58	483	25
Cumbria and Northumberland	<0.5	0.65	93	1434	16

and lowest in the SSG, although very few samples exceed 10 µg/l. The majority of the samples collected from the Lincolnshire Limestone are from the confined zone, in contrast to the unconfined samples collected from both the Chalk Group and SSG, which could account for this

difference. The impact of confinement on the SSG appears to be a general increase in CH$_4$ concentrations, although the maximum value was from a sample in the unconfined section. Due to the thick nature of the glacial drift deposits in the area, the groundwater in the unconfined
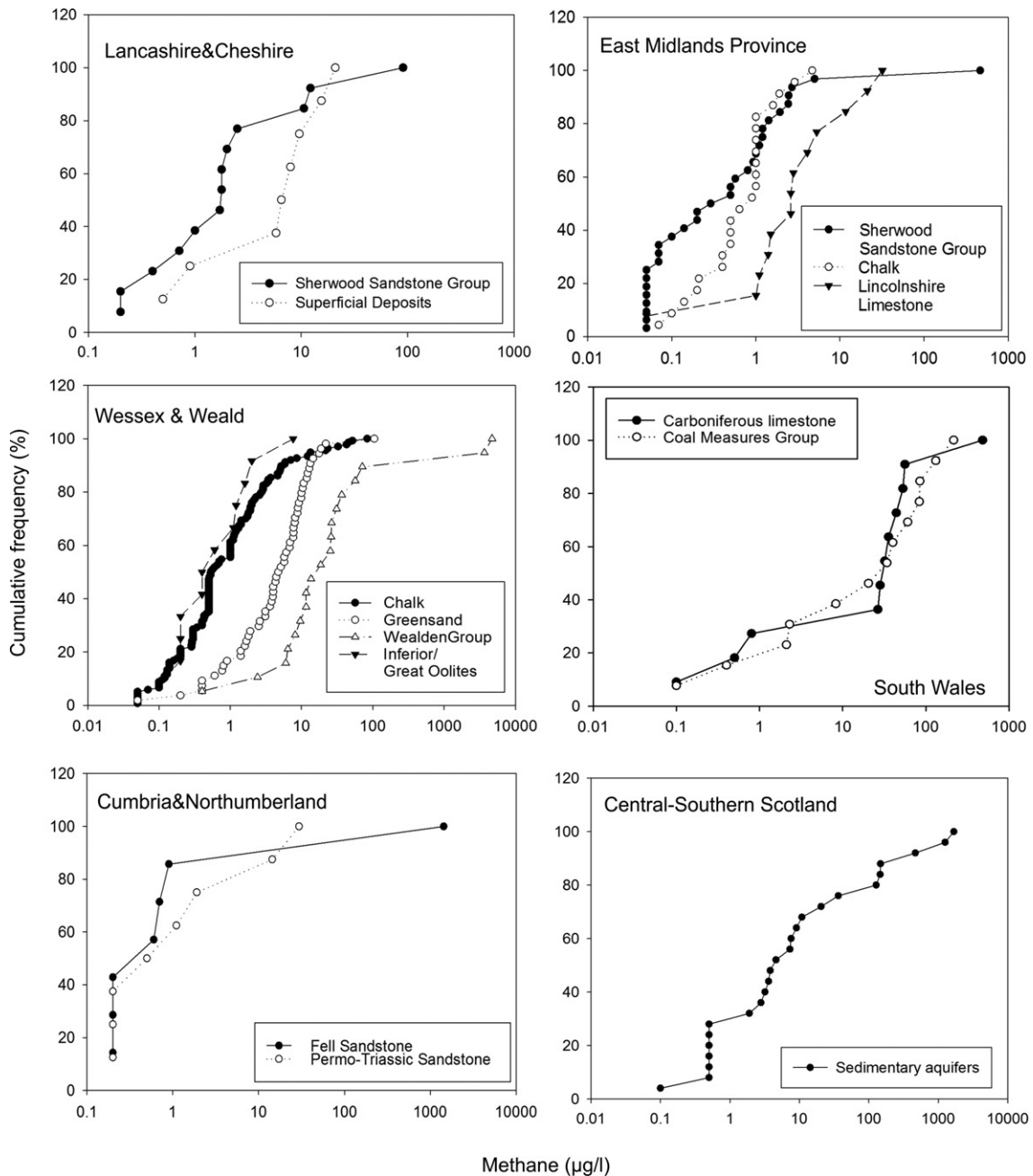
Fig. 5. Cumulative frequency plots of dissolved CH$_4$ for the regions studied as part of the baseline survey.

zone may be relatively reducing, increasing the potential for elevated CH_4 concentrations. The SSG sample with elevated CH_4 concentration was collected during the Gooddy and Darling (2005) study and it was suggested that the complex drift cover could be a reason, with the abstracted groundwater being a mixture of reducing and oxic waters. The highest CH_4 concentrations were recorded at the two samples taken from the Carboniferous Millstone Grit Group. Both boreholes logs record the presence of organic rich shales at intermediate depths which could be the source of this additional CH_4.

4.1.4. Wessex and Weald Basins

Methane concentrations at all sample sites are consistently above the detection limit; 98% of samples are below 100 μg/l and 45% below 1 μg/l. Methane concentrations are typically lowest in the Great and Inferior Oolite groups which show similar concentrations to the Chalk Group (Fig. 5). These low concentrations are typical of high purity carbonate aquifers containing little organic carbon, required for the process of methanogenesis. Elevated concentrations are consistently seen in the Upper and Lower Greensand Groups; this observation is echoed in the Gooddy and Darling (2005) study where CH_4 concentrations in the Lower Greensand Group were an order of magnitude above those in the Chalk Group. Methane concentrations in the Cretaceous Wealden Group are higher than those in the other aquifers, and the two highest values for this region were from these fractured sandstones.

4.1.5. South Wales

Methane concentrations in the Coal Measures Group and Carboniferous limestone appear to be relatively similar (Fig. 5), although elevated compared to the average concentrations in other areas of GB. This could be due to the impact of CH_4 adsorbed to the coal within the Coal Measures sequence and the stratigraphic position of the Carboniferous limestone, directly below the Millstone Grit Group which contains layers of shales. In other carbonate aquifers the CH_4 concentrations tend to be lower, reflecting the lack of organic matter and high degree of mixing. The highest CH_4 concentration in this region was from a borehole in the Carboniferous limestone, although the repeat data from this aquifer was variable (Fig. 6). The absence of suitable environmental conditions for CH_4 production in the Carboniferous limestone implies that the methane source is more likely to be a contiguous formation. Only 20% of samples have CH_4 concentrations below 1 μg/l, fewer compared to other regions, although 88% of samples are <100 μg/l. Although in general, the CH_4 concentrations are elevated compared to those in other regions, no samples collected from South Wales have exceeded the risk action level.

4.1.6. Cumbria and Northumberland

The CH_4 concentrations are comparable between the two sandstone aquifers (Fig. 5). The one elevated CH_4 concentration in the Carboniferous Fell Sandstone was from a borehole located in a peat fen; additional analysis of the dissolved gas content of this sample implied a biogenic source, perhaps related to the presence of peat-rich soils above the sandstone. Although the Fell Sandstone succession in the Northumberland Trough is known to contain some shale groups and thin coal seams, the baseline CH_4 concentrations in the groundwater are all below 1 μg/l, with the exception of the fen sample. In comparison to the CH_4 concentrations seen in the Permo-Triassic sandstone in the East Midlands, the samples from the Carlisle Basin are slightly elevated, but otherwise show a similar distribution. Nearly 70% of all the samples have methane concentrations <1 μg/l and ~94% have concentrations <100 μg/l.

4.1.7. Methane baseline summary

In general, CH_4 concentrations in carbonate aquifers (Chalk, limestones, oolites, etc.) are low, similar to those seen in Permo-Triassic sandstone aquifers (Sherwood Sandstone Group), although CH_4 is widely present above detection limit in all these aquifers. The samples collected from two study areas, South Wales and central southern Scotland are predominately from Carboniferous sedimentary aquifers (e.g. sandstones of the Coal Measures Group) and these tend to have higher CH_4 concentrations, which may be due to the impact of mining and the presence of coal seams. The Coal Measures of South Wales have the highest median value of all the target areas, and samples from the sedimentary aquifers of Scotland also have higher concentrations. However, the highest individual concentrations were found in Lower Cretaceous aquifers of the Weald Basin, specifically, the Hastings Group; a complex, multi-layered, fractured sandstone aquifer. The Weald Basin is an area known for accumulations of methane gas in the shallow (<100 m) subsurface (Selley, 2012). Given the shallow occurrence of the gas, the source could be either thermogenic gas migrating up from depth, or of biogenic origin, sourced from the thin lignite layers within the Weald Clay (Selley, 2012). The reservoir for established oil fields in this area is the Middle Jurassic Great Oolite at ~1 km depth; Upper Jurassic rocks are thought to be too shallow for hydrocarbon generation (Trueman, 2003). The spatial distribution, source and hydrogeological controls on this shallow methane remain to be fully understood.

4.2. Monitoring results

Out of the 151 sites visited in the new survey, 18 (12%) were selected for quarterly monitoring. For the majority of sites samples were taken over at least four quarters, though in South Wales monitoring was only carried out over three quarters, with one not consecutive. Repeat sampling was only performed in the southern half of GB for logistical reasons, but in this area 11 different aquifers were targeted. The sources chosen for England all had installed pumps and were in regular use; for South Wales no such sources were available and so it was necessary to use portable pumps. The sources are shown in Fig. 6, with a summary of the observed variations in dissolved methane over the repeat sampling.

In the target areas within England (East Midlands Province, Lancashire and Cheshire Basins, Wessex and Weald Basin), dissolved methane concentrations rarely showed variations of more than one order of magnitude during quarterly monitoring; the highest concentration during monitoring (in Wessex and Weald) was <50 μg/l.

However, the three sources chosen in South Wales showed variations in concentration of up to three orders of magnitude, with a maximum measured concentration 264 μg/l.

4.3. Source characterisation

Gas ratio and stable isotope analysis of dissolved gases can potentially be used to identify the origin of CH_4. Molar CH_4/C_2H_6 ('C_1/C_2') ratios >1000 are associated with biogenic CH_4, while $C_1/C_2 < 100$ suggests a thermogenic origin (Schoell, 1983). Ratios between 100 and 1000 indicate possible mixing between the two types of gas. Analysis of $\delta^{13}C$ can help to confirm the likely source: biogenic CH_4 tends towards more depleted $\delta^{13}C$ values due to the preferential usage of ^{12}C by microbial communities (Fuex, 1977). However, C_1/C_2 and $\delta^{13}C$ data need to be interpreted with caution since their ratios can also be affected by aerobic methane oxidation mediated by methanotrophs, leading respectively to relative C_1 depletion and ^{13}C enrichment and therefore possibly masking the true origin of the gas (Coleman et al., 1981; Schoell, 1983; Ward et al., 2015). Studies suggest that at dissolved CH_4 concentrations below 500–1000 μg/l, source attribution is not reliable owing to the scatter induced by oxidation effects (Schloemer et al., 2016; Warner et al., 2013).

Ethane concentrations measured during the survey were generally below detection and therefore C_1/C_2 characterisation could rarely be attempted. However, ten of the new survey sites yielded measurable C_2H_6 in addition to CH_4, two of them more than once (Table S2). Molar C_1/C_2 ratios varied between ~15 and ~3350. A co-plot of gas
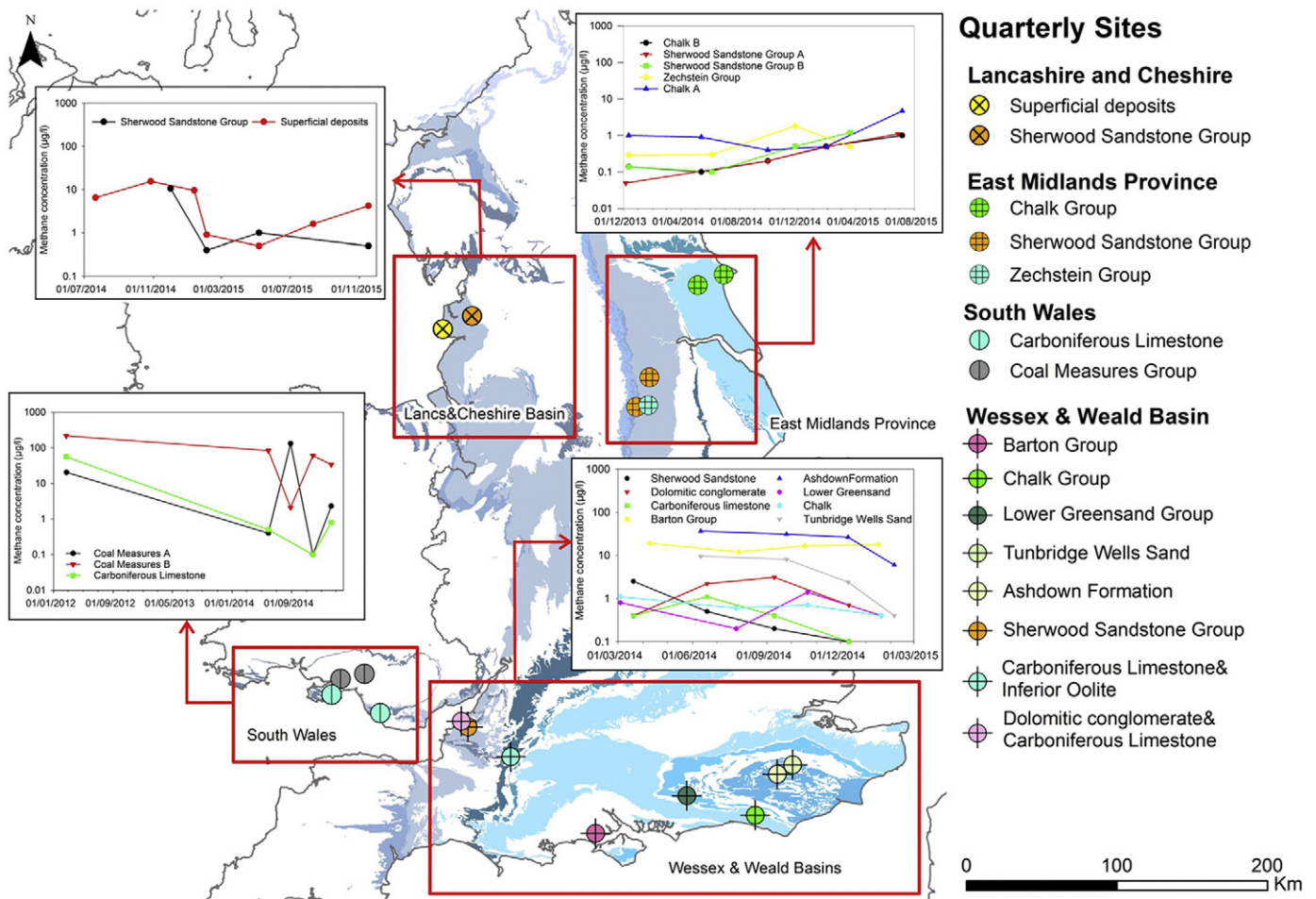
Fig. 6. Results of quarterly methane monitoring (see also Table S3). Contains Ordnance Survey data ©Copyright and database rights 2017.Ordnance Survey Licence 100021290.

concentrations (Fig. 7a) indicates a certain amount of scatter in the data, even for repeat samplings. While most samples appear to lie in the 'mixed gas' category, i.e. between C_1/C_2 ratios of 100 and1000, other evidence suggests that a biogenic origin is more likely, with C_1/C_2 ratios originally ≫ 1000. These may have been lowered by oxidation (see above). Measurements of δ^{13}C-CH$_4$ from a similar number of sites broadly bear this out (Fig. 7b), showing a wide range from ~ −30 to −80‰. As with the C_1/C_2 data, it is likely from other evidence that most of the CH$_4$ is of biogenic origin and would therefore be expected to have δ^{13}C values more negative than −50‰. At the low (<1000 μg/l) concentrations involved, oxidation effects as a cause of isotopic enrichment cannot be ruled out.

Notwithstanding the ambiguous results from these techniques, it is likely that most CH$_4$ in these shallow (<100 m deep) GB groundwaters is of biogenic origin, although thermogenic contributions may be locally important where gases have migrated from depth or there is slow release from previously deeply buried, low permeability, organic-rich rocks (Darling and Gooddy, 2006). In this respect the findings are typical of those of other CH$_4$ baseline studies such as those referred to in Section 2.2 above.

If the GB baseline is further developed in future, source characterisation could be aided by additional techniques including measurement of δ^2H-CH$_4$ (e.g. Schoell, 1983), clumped isotopes (e.g. Stolper et al., 2014) and noble gases (e.g. Darrah et al., 2014).

4.4. Applicability of the results

How representative is the methane baseline presented here? All the samples from English sites in the new survey, and also most in the older

dataset, were taken from boreholes with permanently installed pumps and generally producing good quality water suitable for drinking. It is possible that zones of poorer-quality water existing within the same aquifer have naturally elevated CH$_4$ concentrations (see for example the case of the Lincolnshire Limestone aquifer considered in Bishop and Lloyd, 1990), but since such waters are not usually abstracted, the opportunities for sampling them are limited. In any case, it must be assumed that the interest in the CH$_4$ baseline lies mainly in the possible future risk to groundwater used for domestic and/or industrial purposes. However, this risk applies to any groundwater (as defined by the EU Water Framework Directive; UK TAG, 2011) and although the surveying of all aquifers is outside the scope of this work, the contamination of poorer-quality groundwater with methane could still lead to the release of CH$_4$ to the atmosphere, which has implications for the wider environment. We do however consider that for practical purposes, the present baseline is representative for the areas surveyed.

There are, of course, limitations to this kind of study: the number of datapoints defines a relatively coarse grid, and the range of measured CH$_4$ concentrations may be large enough within a particular region (see Table 2) to effectively conceal possible UGS-related impacts if viewed on a regional scale. The baseline information therefore needs to be applied with care, with a particular focus on local geology and hydrogeology; for example, on the basis of the present data from Southern England (Wessex and Weald Basins), a CH$_4$ concentration of 500 μg/l in the Upper Cretaceous Chalk Principal aquifer would be regarded as anomalously high, while in the Lower Cretaceous Wealden Group minor aquifers it would not be. It is therefore essential that the CH$_4$ aquifer baseline be considered in the context of other relevant material such as resource information (DECC, 2013; Andrews, 2013; Andrews,
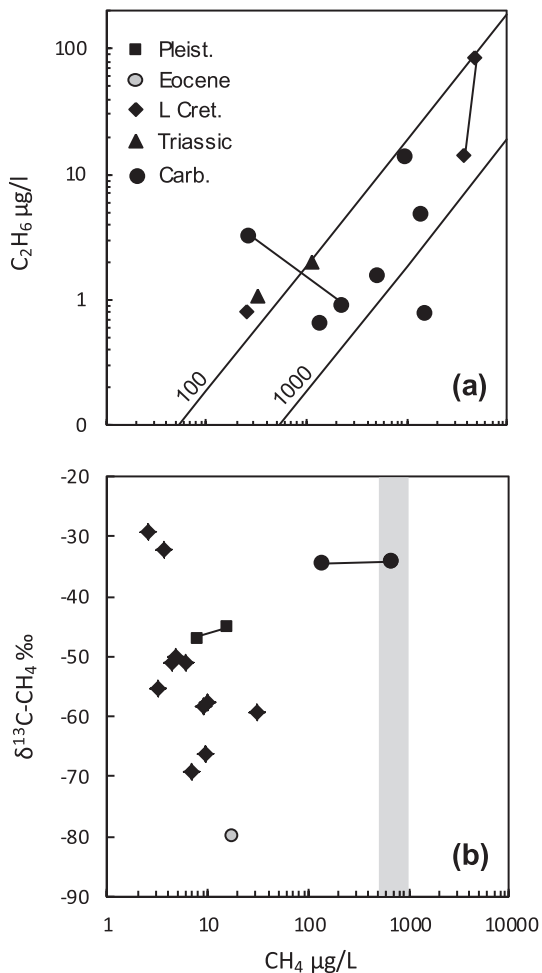
Fig. 7. Plots of (a) C_2H_6 and (b) $\delta^{13}C$-CH_4 versus CH_4 for selected groundwater samples from the methane baseline study. Legend applies to both (a) and (b). Sites sampled more than once are linked. Included in (a) are lines representing C_1/C_2 ratios of 100 and 1000. Also shown in (b) is the 500–1000 µg/l lower limit for effective CH_4 source attribution (see Section 2.2 above).

2014 and Monaghan, 2014) and aquifer–shale gas separation data (Loveless et al., 2017).

Another possible limitation is that most sites were sampled only once, on the supposition that groundwaters are not likely to vary much over time in their dissolved gas content, since seasonal or other transitory phenomena are not likely to be significant. In the majority of cases this has been borne out by the minor-to-very-minor (10s of µg/l to <1 µg/l) fluctuations in dissolved CH_4 observed in the subset of sites sampled quarterly over a period of a year (Fig. 6). We therefore consider the survey data to be representative of the dissolved CH_4 baseline in regularly pumped boreholes and aquifers. Most notably, the risk action level of 10,000 µg/l (or 10 mg/l) was not found to be exceeded at any baseline site.

The dissolved methane fluctuations observed in the Carboniferous aquifer in South Wales, however, require consideration. It had previously been suggested by Darling and Gooddy (2006) that pumping regime might be a controlling factor on measured dissolved CH_4 concentrations in fractured aquifers, insofar as a high-yield water utility pumping station would have a much larger zone of contribution and therefore tend to homogenise the water quality of the output. The opposite of this may have occurred at the three South Wales boreholes sampled, which were drilled for observation purposes in fractured Carboniferous aquifers: they are not regularly pumped and were sampled using temporarily installed low-capacity portable pumps. A detailed investigation of these three boreholes (Halwa, 2015) revealed varying behaviour,

particularly between two of the sites: for example, during a short pumping test, CH_4 concentrations rose in one borehole but fell in the other. Variations are most likely to be linked to different natural vertical groundwater flow directions within the boreholes and the source of groundwater drawn in during pumping (from fractured sandstones or coal beds) which are different for each individual borehole. The presence of an upward head gradient has been linked to higher CH_4 concentrations at high borehole water levels and low CH_4 concentration at low borehole water levels. Where a downward head gradient was present, the opposite pattern was observed in CH_4 concentrations. By contrast, boreholes in similar Carboniferous aquifers in England with permanent pumps showed much less variation. It is therefore conceivable that had water been regularly abstracted from the South Wales boreholes using large pumps, the observed range in dissolved CH_4 concentration would have been much reduced. Future site-specific studies and monitoring activities should bear this in mind. This is particularly important as the UK Government has introduced new legislation, the Infrastructure Act (2015), with a requirement for the shale gas industry to undertake at least 12 months of baseline monitoring for methane in groundwater before any operations start, with monitoring continuing as part of the Environmental Permit conditions (http://www.legislation.gov.uk/ukpga/2015/7/section/50/enacted). Representative monitoring will be essential to ensure that environmental risks are properly identified and managed.

5. Conclusions

A baseline for methane (CH_4) in the drinking water aquifers of Great Britain has been compiled using analyses from 343 borehole sites in England, Wales and Scotland. Aquifer coverage is concentrated in areas of assessed UGS (unconventional gas sources) potential. While this baseline will serve as a benchmark against which any future changes in dissolved CH_4 possibly due to UGS operations can be compared, it should not be regarded as any kind of UGS prospecting tool.

On the basis of the data collected, dissolved CH_4 is ubiquitous across all the aquifers sampled, typically present at low levels (<1000 µg/l). In such cases, further investigation of the CH_4 source is generally not warranted. Of the samples collected from Principal aquifers, 99% had CH_4 concentrations <100 µg/l, compared with 96% of all samples collected as part of the survey. The average dissolved CH_4 concentration across all aquifers was 45 µg/l. No samples exceeded or even approached the risk action threshold concentration of 10,000 µg/l.

While the majority of sites were sampled only once, a subset was sampled quarterly over a period of a year. Observed variations in dissolved CH_4 were generally insignificant in boreholes with installed pumps which were regularly purged (such as public water supplies), leading to the conclusion that single samples from such boreholes are a valid basis on which to compile a baseline. However, in boreholes that are not regularly pumped, greater fluctuations in CH_4 were seen. Future site-specific studies should take this into consideration. A similar approach to the monitoring used in this study is likely to be taken for regulatory compliance purposes associated with any future UGS sites in Great Britain. It is therefore essential that suitable methods are applied and tested to ensure reliable measurement of dissolved CH_4 (and other parameters) in groundwater.

An appreciation of the geological and hydrogeological setting is also essential for interpreting CH_4 data. This is especially pertinent in situations where aquifers have a complex groundwater flow system, such as the Carboniferous aquifer in South Wales.

This was a national scale survey designed to enable a broad understanding of the distribution of dissolved CH_4 in water-supply aquifers across specific target areas of Great Britain. It is not intended to replace the more detailed investigations needed to establish an understanding of groundwater quality at a local scale.

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