The Baseline Concentrations of Methane in Great British Groundwater - the National Methane Baseline Survey

Groundwater Science Programme

Open Report OR/15/071

BRITISH GEOLOGICAL SURVEY

GROUNDWATER SCIENCE PROGRAMME

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The Baseline Concentrations of Methane in Great British Groundwater - the National Methane Baseline Survey

R A Bell, Darling, W G, K Manamsa, B É Ó Dochartaigh

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Keywords

Groundwater, Aquifer, Methane.

Front cover

Methane sampling in Lancashire.

Bibliographical reference

R A BELL, DARLING, W G, K Manamsa, B É Ó Dochartaigh. 2016. The Baseline Concentrations of Methane in Great British Groundwater - the National Methane Baseline Survey. *British Geological Survey Open Report*, OR/15/071. 45pp.

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Acknowledgements

We are extremely grateful to BGS members of staff for their help and support during fieldwork, in particular Debbie White, Lindsay Holowka and Mick Strutt. Thanks also go to Pauline Smedley, Marianne Stuart and Rob Ward for their direction and technical advice. In addition to the BGS staff, a large number of individuals in the Environment Agency, Natural Resources Wales (NRW), public water supply companies and private residents have contributed to the project through their assistance with sampling and collection of data. Of the many individuals who have contributed to the project we would particularly like to thank the following:

Environment Agency: Laura Pender and Suze Southern (North West); Diane Steele and Andrea Lancaster (North East); Jan Hookey, Lucy Roberts, Polly Wallace (South East); Paula Awty (South); Stephanie Robson (South West); Andrew Pearson (Midlands); Dave Jones (formerly Wales).

Natural Resources Wales: Gemma Harris, Kay Roberts, Cath Rees, Jim Hawker

Southern Water: Sian Evans, Anthony Anderton, Dave West, Terry Smithson, Meyrick Gough

South East Water: Jeanette Sheldon, Christopher Taylor, Harry Shotter

Bristol Water: Rebekah Rice, Natasha Clements

Sembcorp Bournemouth Water: Tony Read, Tony Primmer, Tim Latcham

Portsmouth Water: Jonty Stead, Mark Botterill

Wessex Water: Paul Stanfield

Yorkshire Water: Mark Morton

Northumbrian Water: Dave Kippling

Severn Trent: Sid Priestley, Richard Winstanley

Sutton and East Surrey Water: Nicola Houlahan

Thames Water: Mike Jones, Estelle Ferschneider, Gary Holton, Rose Wilkinson

United Utilities: Phil Merrin

Affinity (Veolia Water): John Simpson

We would also like to thank the owners of privately owned boreholes who allowed us to sample and the University of Birmingham, especially Leon Halwa, for their contributions to the investigation of boreholes in South Wales.

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Executive summary

This report describes the BGS research programme evaluating the baseline concentration of methane in groundwater which ran from November 2011 to completion in March 2016. The aim of the survey has been to improve knowledge of conditions in aquifers overlying potential shale gas source rocks present at depth, thus providing baseline knowledge relevant to the management of future exploration of new hydrocarbon sources. The necessity for doing this has been prompted by evidence from elsewhere (notably the USA) which has revealed very high methane concentrations in groundwater in some areas of shale gas extraction. Although this has often been directly attributed to shale gas operations, there have generally been no pre-development data on methane concentrations available to test this.

Before the start of the current survey, BGS held some 170 analyses of methane in groundwaters from aquifers across Great Britain, acquired from the 1980s onwards. These data have been combined with new survey data, to give a total of 439 methane data points. In this combined dataset, 96% of samples show methane concentrations of less than 100µg/l and indicate that methane is rarely present at concentrations high enough to be potentially explosive (there are no health limits for methane in groundwaters). In the minority of samples with elevated concentrations, this was generally considered to be due to the proximity of organic rich coal seams or peats. The highest concentrations were found in the Cretaceous aquifers of the Weald Basin, a known area for occurrences of methane gas in the shallow subsurface.

The new survey covers the majority of principal aquifers in Great Britain, including the Chalk, Permo-Triassic Sandstones, Carboniferous Limestone, and the Lower Greensand. Samples from over twenty different aquifers have been collected. In general, methane concentrations in carbonate aquifers (Chalk, limestones, Oolites etc.) are low, similar to those seen in the Permo-Triassic sandstone aquifers, although methane is widely present above detection limit (approximately 1µg/L) in all these aquifers. The Coal Measures of South Wales have the highest median value across Great Britain and this aquifer also shows the greatest temporal variability. Methane concentrations in the Carboniferous sediments of Scotland are also elevated, likely due to the impact of mining and the presence of coal seams. While little temporal variability is generally seen in aquifers used for public water supply or otherwise regularly pumped, further work is required to understand the impact of borehole use, pumping regime and aquifer type on the variability of the methane baseline of Great British aquifers.

It should be noted that the Survey is not intended to replace any oil and gas operator's local monitoring as required by the regulators. This is a national scale survey to enable a broad understanding of the distribution of methane in aquifers across relevant areas of Britain and cannot replace an understanding of groundwater quality at a local scale.

1 Introduction

Methane, CH_4, is ubiquitous in the environment, including groundwater in which it is commonly found at trace concentrations. Methane is released both by natural processes and anthropogenic activities. While it has no known effects on human health, its presence at high concentrations can lead to explosions under specific conditions in confined spaces. It is also a significant greenhouse gas with a warming capability almost two orders of magnitude higher than carbon dioxide.

Evidence from the USA has shown very high methane concentrations in some aquifers in areas where shales are being commercially exploited for gas. However, there is considerable uncertainty and argument over the source(s) of methane and how it has entered the aquifers, either through natural processes or anthropogenic impacts. Crucially, there was no consistent collection of baseline data on methane concentrations in groundwater in the USA before shale gas exploitation began, making it difficult to correctly identify and attribute the reasons for the existence of the high-methane groundwaters.

The need for a methane baseline in the UK was recognised in the 2012 report on shale gas extraction published by the Royal Society and Royal Academy of Engineering. The methane *baseline* is defined for this project as the background range of methane concentrations in British groundwaters before any significant exploitation of unconventional hydrocarbons, such as shale gas, has taken place. It should be noted that the measured dissolved methane may not necessarily originate *naturally* from geological sources - in some cases it may have been produced or released because of human activities such as coal mining or landfill operations. It may also simply result from equilibration between groundwater and the small amount of methane in the atmosphere (currently ~1800 parts per billion by volume).

The British Geological Survey (BGS) has since 2011 been surveying the current distribution of methane concentrations in Great British (GB) groundwater, focusing on areas where aquifers are underlain by shale units that may have shale gas potential. The National Methane Baseline Survey (hereafter the 'Survey') will provide a dataset against which any future changes in groundwater methane concentrations can be compared. The Survey builds on previous methane-related work by BGS but has widened the scope both geographically and in terms of aquifer type. It is likely to be of particular interest to energy companies, the general public and environmental regulators, but also to environmental researchers more generally.

1.1 PROJECT BACKGROUND

The British Geological Survey (BGS) has been studying methane in GB groundwaters since the 1980s to investigate the potential for methane emissions from groundwaters, and sources of and hydrogeochemical controls on methane. Before the start of the current survey, BGS held some 170 analyses of methane in groundwaters from aquifers across GB, almost all separate sites sampled only once, at various times over the past three decades (Figure 1). Most of these have been reported in scientific publications (principally Darling and Gooddy (2006)) or in project reports (e.g. Ó Dochartaigh et al., 2011). In this dataset, 99% of samples show methane concentrations of less than 500µg/l and the remaining 1% have concentrations between 500 and 1680µg/l. These samples were collected using the same sampling procedures and analysed by the same method as for the current survey. These data have been combined with new Survey data.

Following on from this previous work, the BGS commenced the new Survey in November 2011 to determine the concentrations of methane in groundwaters of specific aquifers overlying potential shale gas source rocks. The present report serves as an extension to the report of Stuart (2012) who reviewed the potential risks to UK groundwater from the exploitation of shale gas, and as an update to Ó Dochartaigh et al.(2013).

The Survey is designed to supplement existing BGS groundwater methane data discussed previously to collectively create a nationwide baseline of methane concentrations in areas underlain by formation of potential unconventional hydrocarbon interest. The existing data available before the project began is shown in Figure 1, along with the areas that were made available in 2014 as part of the Department of Energy and Climate Change (DECC) 14th Licensing round.

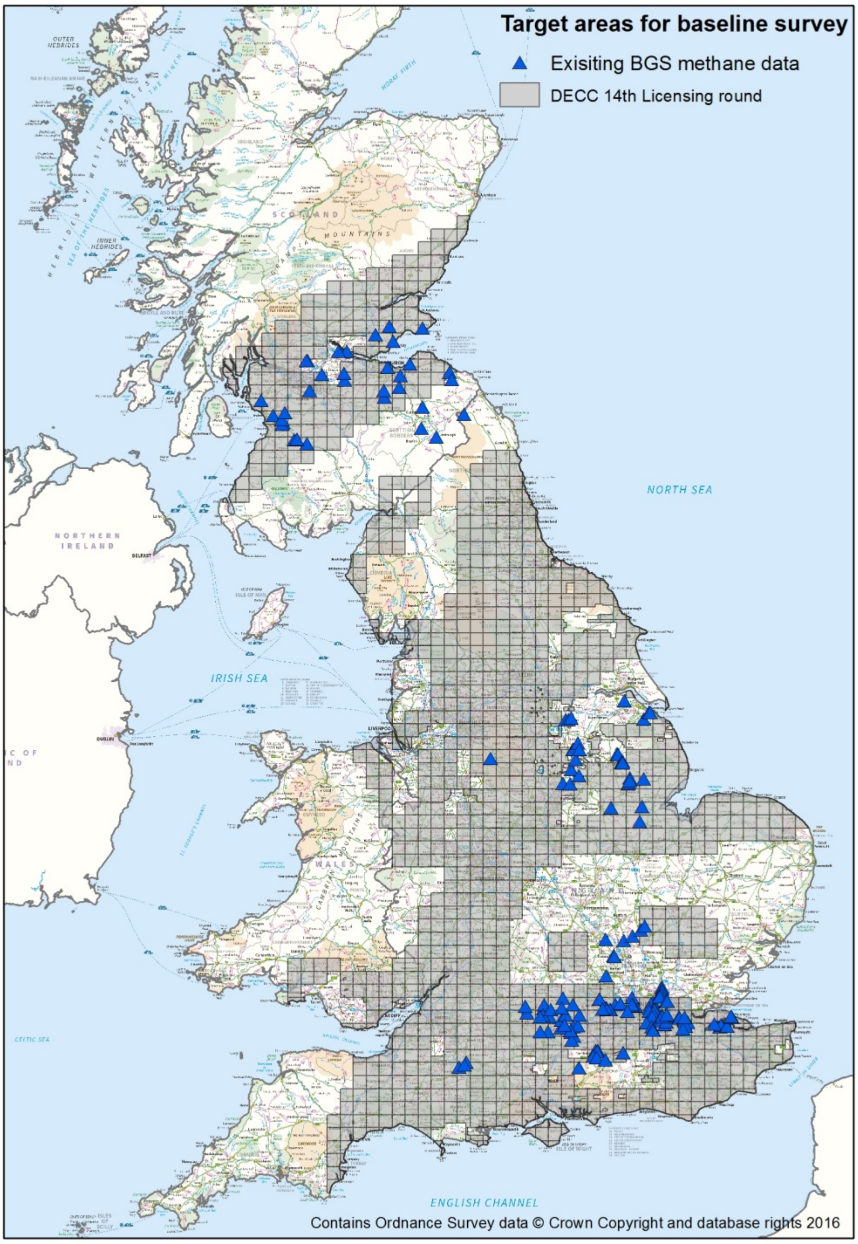

Figure 1 Existing BGS methane data and the areas available for the DECC 14th Licensing round. Contains public sector information licensed under the Open Government Licence v3.0.

This Survey focuses on assessing the methane concentrations in aquifers lying above zones of mature shale gas rock and in areas where exploration is a possibility. The baseline will be an important resource against which future groundwater quality can be compared, especially with regard to methane, but also for inorganic chemical quality which is an integral part of the present survey. This will permit an assessment of any impacts of shale gas exploitation on the water quality of relevant aquifers. For the purpose of this baseline the origin of the methane is of secondary importance. It may be naturally occurring or introduced by human activity such as coal mining and landfills.

2 Methane and GB Groundwater

2.1 METHANE AND ASSOCIATED RISKS

Dissolved methane when ingested has no known human health impacts and there is therefore no water quality standard for methane in the UK or internationally. Except under pressures exceeding hydrostatic due to in-situ production or leakage from underlying formations (unlikely in most water supply aquifers), methane is present exclusively in the dissolved phase until water is pumped to the surface. If methane concentrations exceed the equilibrium solubility at ambient pressure (approximately 0.05µg/l under the open atmosphere), methane will de-gas from the water until the system re-equilibrates. This de-gassing 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, resulting in the establishment of standards for the potential explosive limits of methane in air. More information on this and the calculation of the potential hazard for water degassing in confined spaces is provided in Hooker and Bannon (1993).

2.2 SOURCES OF METHANE IN GROUNDWATER

Methane in groundwater is derived from two main sources; *biogenic* methane, which is bacterially produced and *thermogenic methane*, which is formed during thermal decomposition of organic matter (Figure 2).

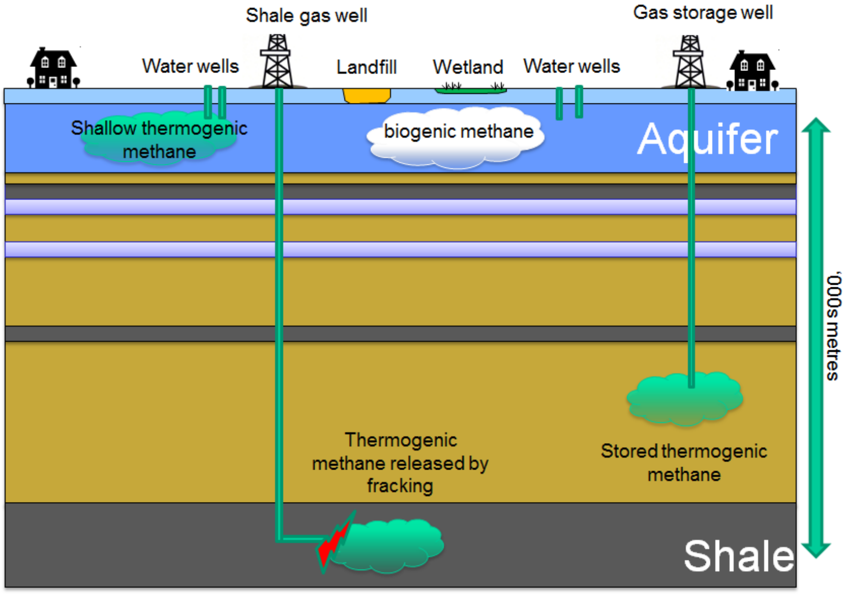

Figure 2 **The location of thermogenic and biogenic methane in the sub-surface.**

Biogenic methane 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 the work by Darling and Gooddy (2006), dissolved methane in the UK was widely considered only likely to be found in groundwaters that were sufficiently reducing, limiting occurrences to zones in confined aquifers with dissolved oxygen concentrations <0.1mg/l. Instead, methane was found to be ubiquitous throughout the aquifers studied: Chalk, Lower Greensand, Lincolnshire Limestone and Sherwood Sandstone. The source of this biogenic methane derives from two alternative mechanisms; acetate fermentation and carbon dioxide reduction. In groundwater environments it is likely that acetate fermentation is the dominant process for methane formation (Darling and Gooddy, 2006).

Thermogenic methane, 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. Thermogenic methane is generally present at depth in the sub-surface, stored in conventional gas reservoirs; these conventional reservoirs are created when hydrocarbons migrate from a source rock (organic rich shales or mudstones) into a formation with suitable porosity and permeability characteristics that make extraction possible, e.g. Permo-Triassic sandstones or Permian limestones. Unconventional exploration is where the source rock for this thermogenic methane is directly targeted, but these shales or mudstones tend to have much lower permeability. This low permeability is why hydraulic fracturing is required to extract the gas from these tight formations.

Gas ratio (C_1/C_{2+}) and stable isotope analysis ($\delta^{13}C$ and $\delta^{2}H$) of dissolved gases can be used to identify the potential origin of methane (thermogenic or biogenic), although isotope ratios can also be affected by in-situ oxidation. In general, biogenic methane tends towards lighter $\delta^{13}C$ and $\delta^{2}H$, due to the preferential usage of ^{12}C by microbial communities. The presence of C_{2+} hydrocarbons (lower gas ratio), is more indicative of a thermogenic methane source, as these hydrocarbons are typically associated with oil and gas reservoirs. As aerobic methane oxidation by methanotrophs can alter these ratios to leave residual methane with a more thermogenic signature, isotopic identification methods should not be done in isolation.

In the UK most methane in groundwater is likely to be biogenic in 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. The lower explosive limit (LEL) for methane in air is 5% by volume; the lowest dissolved methane concentration that theoretically could give rise to a 5% mixture in a confined space is 1,600µg/l. This concentration will therefore be used in this report as a level, above which there is the potential for explosive conditions, given a confined space and total methane degassing at the surface. The concentration of methane required for isotopic investigation into the potential source is >1,000µg/l.

3 Survey Methodology

The start of the Survey, in 2011, was prior to any major investigations into the shale gas resources in the UK and the target areas for the Survey have expanded over time (Figure 3). In 2011, the main target areas were based on expert geological knowledge of unconventional hydrocarbon resources and the regional geology based on available geological maps, 3D models, borehole data and geophysical data. Account was also taken of the locations of current hydrocarbon licenses and known operator interest in particular areas. Further information on the geological and geophysical basis for delineating these areas can be found in the DECC report on unconventional hydrocarbons in the UK (2010) and Smith et al.(2010). Survey target areas were based on this state of knowledge, with the focus being on areas where resources were considered to exist but there were limited or no groundwater methane data. These initial target areas were then refined in 2013 with the DECC/BGS assessment of Britain's unconventional resources (Harvey and Gray, 2013). In 2014, the DECC regional specific reports detailing prospective areas were released, in addition to the release of maps produced by BGS/Environment Agency (EA) which mapped the vertical separation distance between principal aquifer and shale gas source rocks (Bloomfield et al, 2014). As such the target areas have been refined over time to account for emerging information. Samples have only been collected from areas where the shales are deep enough to have achieved sufficient maturation to be a potential shale gas resource. No samples were collected from Northern Ireland; the baseline evaluation of groundwater quality in Ireland and Northern Ireland is being co-ordinated by the Irish Environmental Protection Agency as part of a joint research project on unconventional gas exploration and extraction (UGEE).

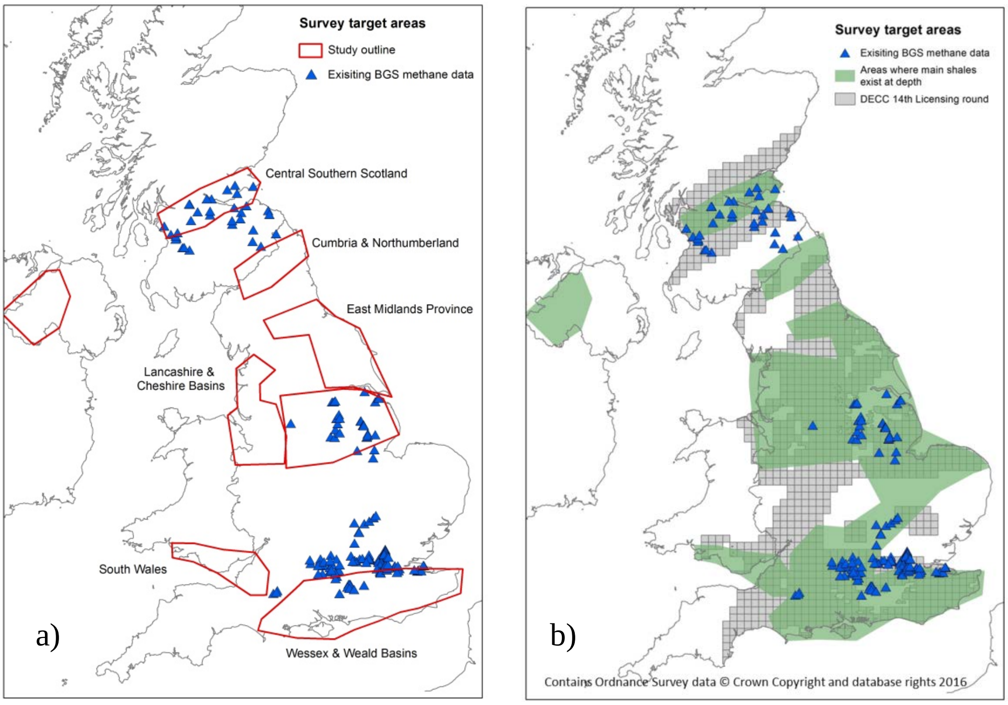

Figure 3 Target areas for the Survey a) in 2012 when the Survey started and b) after the work of Bloomfield et al (2014) and the 14th Licensing round.
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To collect methane data from the target areas, sample sites were selected by contacting the appropriate water companies and EA Regional offices, with the aim of having a good spatial distribution of sites and including a variety of aquifers utilised in the specific region. For ease of sampling only sites served by a borehole, not a spring or catch-pit, were chosen.

Sample sites near known high concentrations of methane such as landfill sites were avoided to prevent biased results. The number of samples that were collected per year as part of the Survey is reported in Table 1; the total number of samples collected over the 3 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 the area; and the resources available. Finding suitable sampling points was only possible with extensive assistance from public water supply companies and the EA. The majority of Survey sample sites are either water supply boreholes or EA monitoring boreholes (either from the Groundwater Quality Monitoring Network or private supply boreholes). However, assistance from the private supply borehole owners has also been invaluable. In the Wessex and Weald Basin 17 samples were collected by Thames Water and 11 by the Environment Agency; these data have been included in the summary.

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
Southern England	17	20	87	16
East Midlands Province	-	16	26	23
Northumberland	-	-	16	-
Totals	**42**	**24**	**134**	**48**

As mentioned in the Summary, this is a national scale survey to enable a broad understanding of the distribution of methane in aquifers across relevant areas of GB and cannot replace an understanding of groundwater quality at a local scale. It is also not intended to replace any oil and gas operator's local monitoring as required by the regulators.

3.1 SAMPLING METHODOLOGY

To obtain representative concentration measurements, groundwater has to be sampled before it has contact with the atmosphere so that no gases can exsolve. This entails collecting a pumped sample directly from a borehole, either by attaching a hose with a gastight connection to the wellhead for an installed pump, or directly to the outlet for a portable pump (Figure 4a). If an installed pump has no suitable wellhead, the nearest access point should be used. This must be situated before the pumped water enters a storage tank or is treated in any way. Samples collected using a portable pump were purged until field parameters were stable, with the pump placed at the mid-point of the screen, where details were available.

The methane samples are collected into double-valved steel cylinders of known volume, range 47–55cm^3 (Figure 4b). Ideally the samples are obtained at pump pressure via suitable clamped tube connections, but in cases where no suitable offtake point is available other arrangements may have to be extemporised and the sample taken at less than pump pressure. Unless the water is visibly degassing, this should have little or no effect on the dissolved gas concentration.

Water parameters including pH, temperature, specific electrical conductivity and alkalinity are measured in the field at the wellhead or other outlet. Samples for inorganic chemical analysis (ion chromatography and ICP-MS) were collected on site, filtered through a 45µm cellulose nitrate membrane; a sub-sample preserved with 0.5% HCl and 1% HNO_3, then analysed in the BGS Keyworth Laboratories.

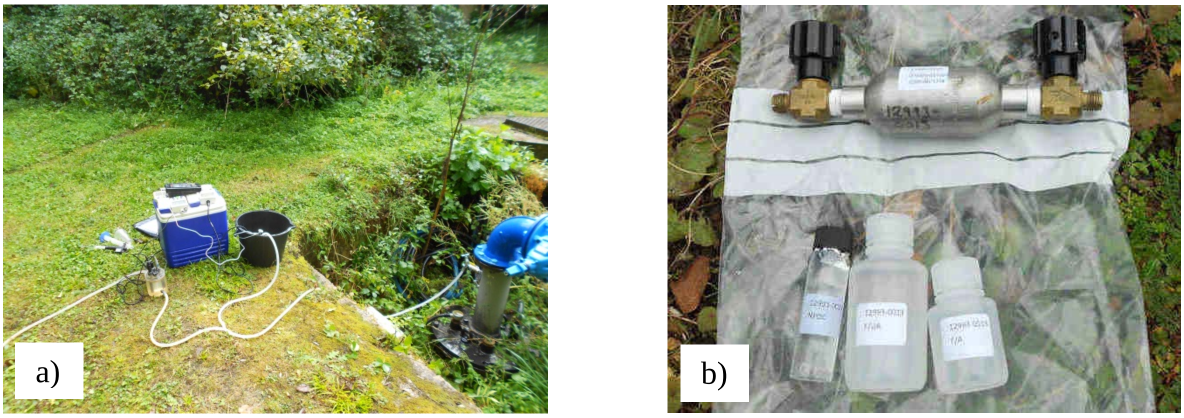

Figure 4 a) Collecting unstable parameters during sampling and b) gas collection cylinder and samples for inorganic and organic carbon analysis.

3.2 ANALYSIS METHODOLOGY

The dissolved gas samples are analysed in batches of approximately 20 at the BGS Wallingford laboratories. A headspace technique is used. This involves the transfer of the water and gas in the sampling cylinder to an evacuated glass bulb of known volume (range 117–123cm^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 Porapak-Q packed column at room temperature. Eluting methane and ethane (if present) are detected by a flame ionisation detector (FID). Co-eluting CO_2 is detected by a thermal conductivity detector (TCD). The detection limit for methane varies between 1 and 0.1µg/l depending on GC conditions during batch analysis. Measurement precision is estimated to be ±5% RSD.

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

3.3 QUARTERLY MONITORING

Quarterly monitoring was established with the aim of checking for possible temporal changes in dissolved methane concentrations over the course of a year. This initiative was intended to demonstrate whether a one-off sampling, conducted at any particular site, could be regarded as representative of conditions at that point in the aquifer over time, or whether methane concentrations were more of a ‘moving target’ in seasonal terms. It was considered unlikely that most groundwaters would show such fluctuations, so in the context of the resources available to the Survey the decision was made to monitor only a representative subset of sites amounting to about 10% of the total. Methane data from the repeat monitoring are included in both the national and regional summary data as additional samples.

3.3.1 Selecting the quarterly sites

In March 2014 a total of 17 sites were chosen for repeat sampling, from sites previously visited, to give a representative geographical spread of the aquifers in GB. The number of quarterly sites in each survey area was proportional to the size of the area, so the larger the target area the more sample sites selected. Within each survey area the quarterly sites represent a range of different aquifers and geographical separation. As the quarterly monitoring involved several visits to the same site, ease of sampling (e.g. a sample tap rather than an *ad hoc* tubing connection, and logistical constraints due to the nature of the borehole owner) was taken into account. Greatest preference was water company boreholes, followed by Environment Agency boreholes, followed by private sites.

4 Results

During the three year Survey, 248 samples were collected from a variety of aquifers across GB. The location of these sites shown in Figure 5, including the legacy data collected during earlier studies. The summary data (Table 2) highlight the differences in methane concentration seen in the target areas.

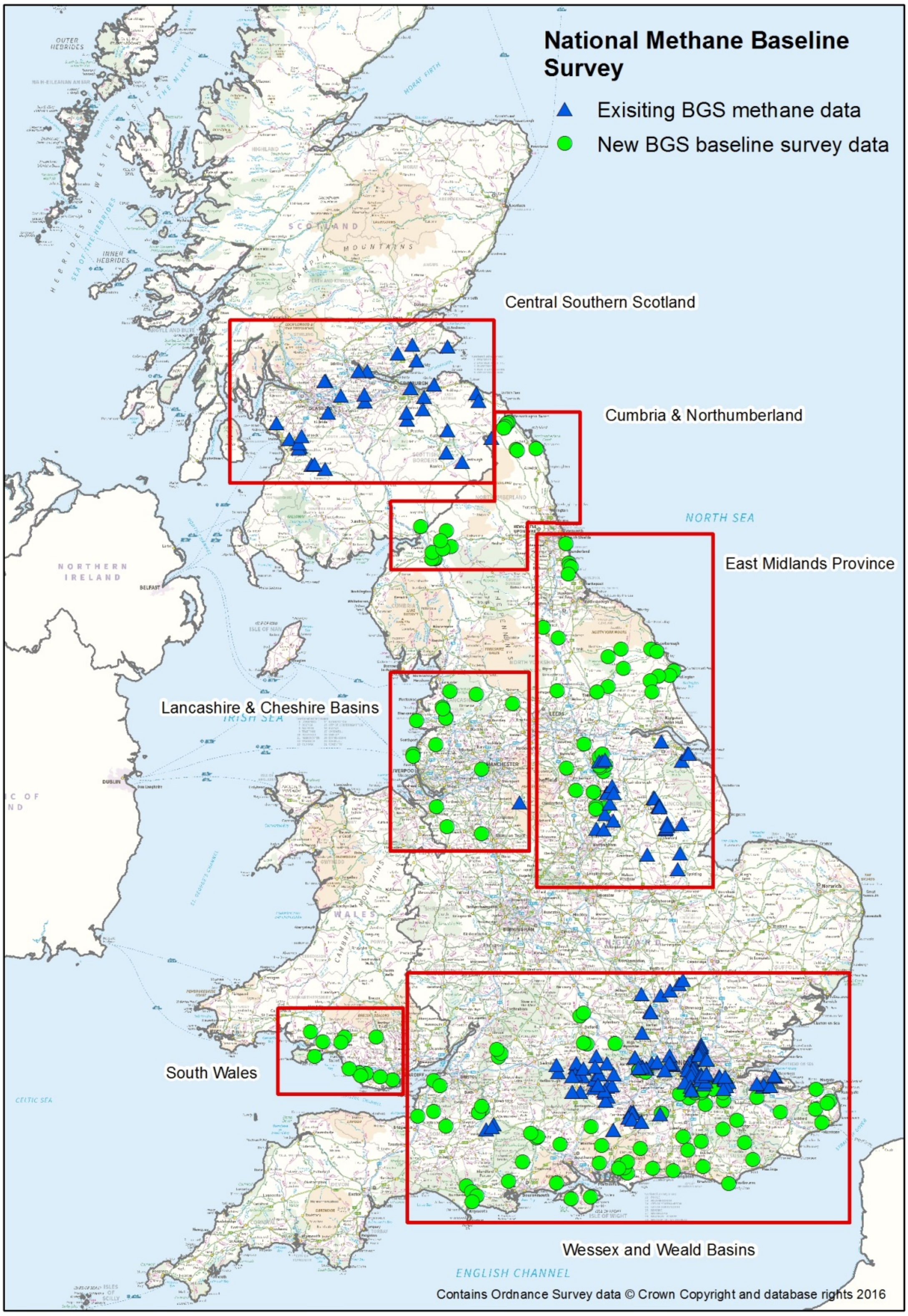

Figure 5 Samples collected as part of the National Methane Baseline Survey.

Table 2 Summary results of the Survey per target area.

Area	CH_4 Concentration (μg/l)				Number of Samples
	Minimum	***Median***	***Average***	***Maximum***	
Central Southern Scotland	<0.1	3.6	132	1,680	31
Lancashire & Cheshire Basins	0.2	2.5	9.3	91	23
East Midlands Province	<0.05	0.9	31	1,320	93
Southern England	<0.05	1.3	39	4,720	251
South Wales	0.1	32	58	483	25
Cumbria and Northumberland	0.2	0.65	93	1,434	16

*samples below the detection limit have been reported as the limit concentration.

Most of the groundwaters sampled by BGS during this sampling campaign have low methane concentrations; ~80% of sites have concentrations below 10µg/l and ~45% have concentrations below 1µg/l. All median values are far below the LEL of 1,600µg/l; this limit has only been exceeded three times (twice at one site after repeat sampling) and neither of these sites is a public drinking water supply. The results are described further on a regional basis in Section 4.1.

4.1 REGIONAL SUMMARIES

The natural quality of groundwater varies depending on geology, land use and distance from the sea. BGS, jointly with the EA, have produced a series of Baseline Reports summarising the natural water quality of different aquifers (Shand et al., 2007) across England and Wales. Another series of reports produced by BGS, jointly with the Scottish Environment Protection Agency, as part of the Baseline Scotland project are available and a summary of Scottish groundwater bodies and aquifers is in Ó Dochartaigh et al (2015). The sections below summarise our current understanding of the aquifers sampled and the methane data collected in the various regions.

4.1.1 Lancashire and Cheshire Basins

The geology of Lancashire and Cheshire target area is shown in Figure 6 with the locations of the Survey samples. In this region, four aquifers were sampled as part of the Survey (Table 3), 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 and one from the Millstone Grit. The targets for unconventional oil and gas exploration in this area are the organic rich mudstones of the Bowland Shale Group, which is prospective at depth (Andrews, 2013). The exploration company Cuadrilla have previous drilled into the Bowland Shale at Preese Hall (Green et al., 2012).

A summary of the methane data collected as part of the Survey is in Table 4; a total of 23 samples were collected, 13 of those in the SSG and 8 in the Superficial Deposits. Where adequate data were available, summary statistics have been collated per aquifer, in addition to the regional information. The methane data per aquifer are compared in Figure 7.

Table 3 Stratigraphy of the aquifers sampled in the Lancashire/Cheshire Basin.

	Lancashire/Cheshire
Quaternary	Superficial Deposits
Permian-Triassic	Sherwood Sandstone Group (SSG)
Carboniferous	Millstone Grit
	Bowland Shale Group

* Blue shaded aquifers as designated as Principal aquifers.

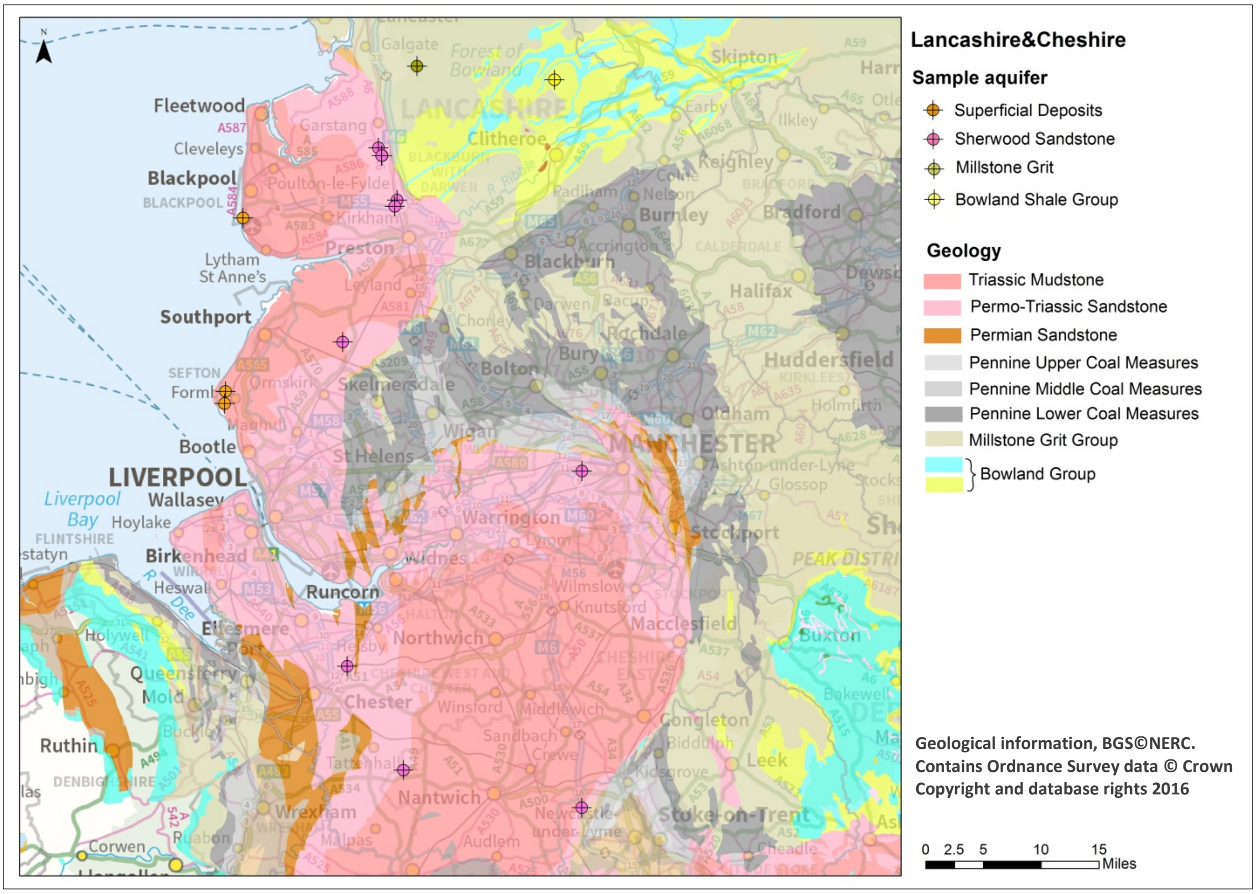

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Figure 6 Bedrock geology of the Lancashire & Cheshire region

The Superficial Deposits are of substantial thickness, up to 40m, and consist of glacial sands, gravels, and boulder clay; in places the boulder clay acts as a confining layer. The sands and gravels are discontinuous and supplies can be unpredictable. These Superficial Deposits are classified as a 'Secondary B aquifer' and are generally not used for public water supply, although they may be used for local scale private supplies such as irrigation and farming. The groundwater tends to be reducing with consequent elevated concentrations of iron, manganese and arsenic.

Less than half the samples collected in this region were from the unconfined SSG aquifer which is used for public water supply and numerous other private supplies. To both the east and west of the study area the SSG is confined by the Mercia Mudstone Group but there are very few boreholes that penetrate the confined zone.

Baseline hydrogeochemical data is available for the SSG in two parts of the region; West Cheshire and the Wirral (Griffiths et al., 2002) and Manchester and East Cheshire (Griffiths et al., 2003). The baseline conditions of the SSG in this area are known to be highly variable due to anthropogenic inputs to the aquifer, including both point and diffuse sources. The presence of thick, poorly permeable Superficial Deposits, mentioned above, can create reducing environments which also impact on quality.

The two samples collected from the Carboniferous formations were from small scale farming operations; very little is known about the construction of these boreholes.

Table 4 Summary results for Lancashire/Cheshire.

Lancashire and Cheshire	CH_4 Concentration (µg/l)				Number of Samples
	Minimum	Median	Average	Maximum	
All samples	0.2	2.5	9.3	91	23
Superficial Deposits	0.5	7.2	9.7	21	8
Sherwood Sandstone	0.2	1.8	8.5	91	13

Methane concentrations in both the SSG aquifer and the Superficial Deposits are consistently above the detection limit, highlighting the ubiquitous presence of methane in baseline groundwater environments. The magnitude of methane concentrations are well below the LEL and also lower than that required for further investigation (1,000µg/l). As shown in Figure 7, methane concentrations are typically lower in the SSG than those in the Superficial Deposits; 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 methane 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.

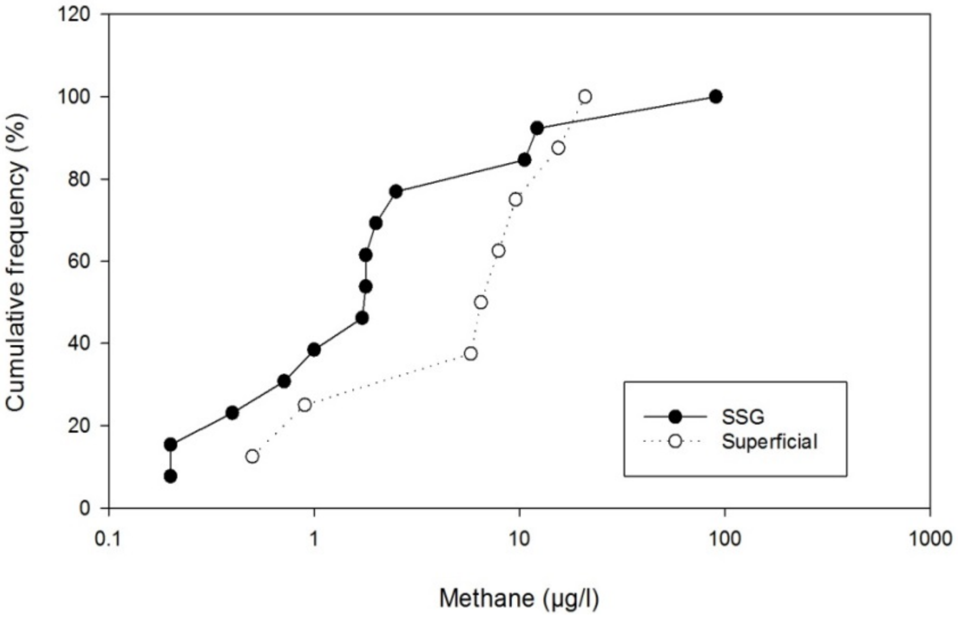

Figure 7 Methane data from the SSG and Superficial aquifers in the Lancashire & Cheshire Basins.

Figure 8 illustrates the distribution of methane concentrations in the basin. The highest methane concentration was recorded at a site in the SSG; this site is close to central Manchester and the borehole log for this site reports a 6m overburden of boulder clay which could create reducing groundwater conditions. In relation to other regions the maximum recorded methane concentration is well below that of other areas, 73% of samples have methane concentrations less than 10µg/l.

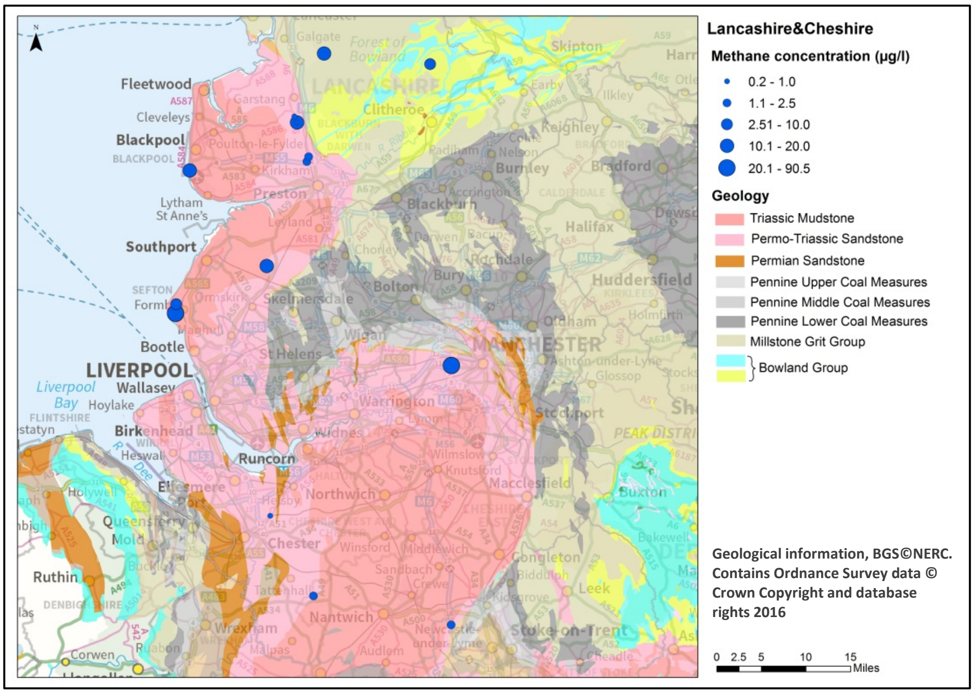

Figure 8 Methane data from the Lancashire & Cheshire region, dots are proportional to the CH_4 concentration.

4.1.2 East Midlands Province

In the East Midlands Province, groundwater supplies are mostly from the four Principal aquifers in the area, the Cretaceous Chalk, Lincolnshire Limestone, Permo-Triassic Sandstone and the Magnesian Limestone. In addition, more localised Principal aquifers including the Corallian and Carboniferous Limestones were sampled. Additional samples were collected from Secondary aquifers; West Walton Formation, Coal Measures and the Millstone Grit Group (Table 5). The geology of the region and the location of these samples are shown in Figure 9. The Namurian Bowland Shale Group is also the target formation for unconventional gas exploration in this area (Andrews, 2013).

Table 5 Stratigraphy of the aquifers sampled in the East Midlands Province.

	Midlands/Yorkshire
Cretaceous	Chalk
	Spilsby Sandstone
Jurassic	Corallian Limestone
	West Walton Formation
	Lincolnshire Limestone
Permian	Permo-Triassic sandstone (SSG)
	Zechstein Group (Magnesian Limestone)
Carboniferous	Pennine Middle Coal Measures Formation
	Millstone Grit Group
	Carboniferous Limestone

* Blue shaded aquifers as designated as Principal aquifers.

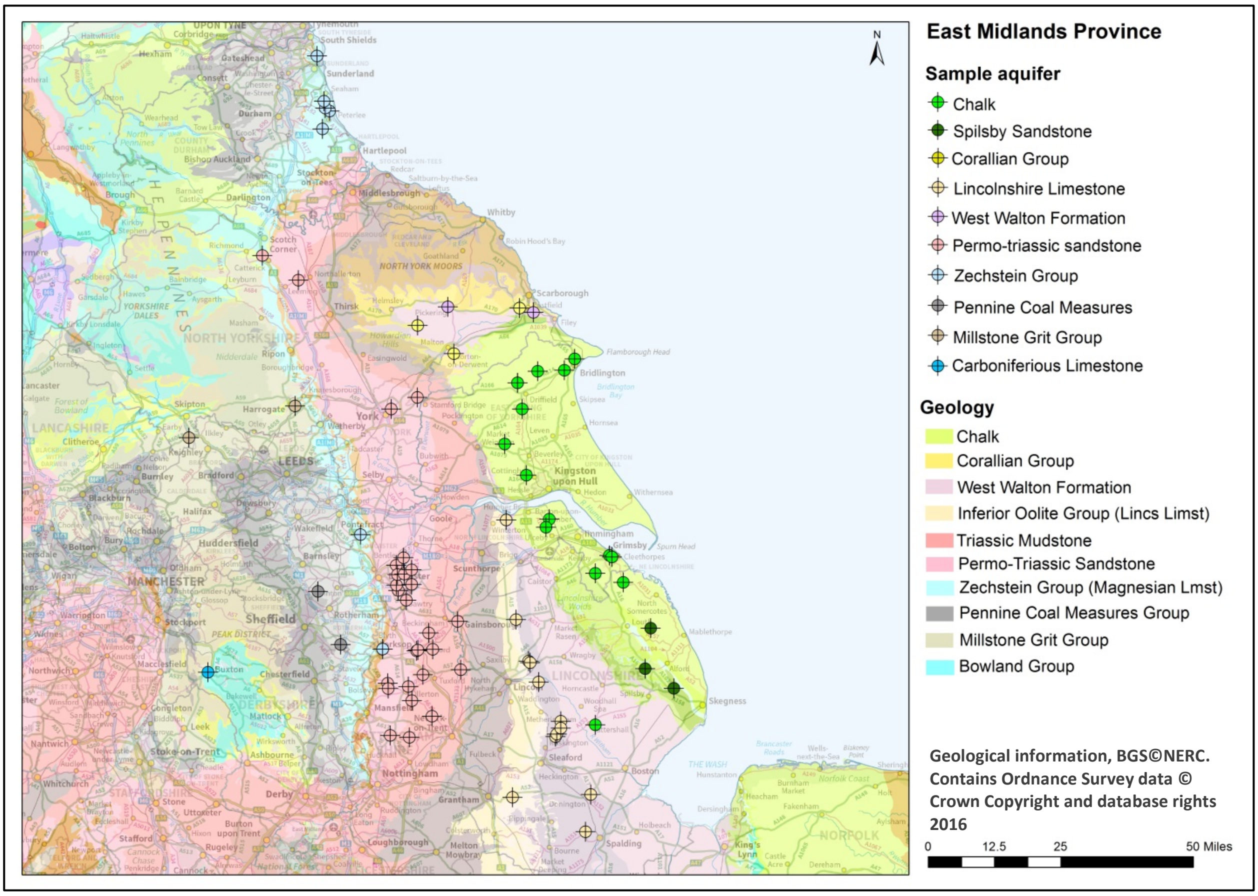

Figure 9 Location of Survey samples in the East Midlands Province.

A summary of the methane data collected as part of the Survey is in Table 6; a total of 93 samples were collected. Where adequate data were available, summary statistics have been collated per aquifer, in addition to the regional information. The methane data per aquifer are compared in Figure 10a.

The Chalk in this Northern Province has a total thickness in excess of 430m and is unconfined in the upland Wolds. Further east the Chalk becomes semi-confined, then fully confined, where it is overlain by glacial till deposits of varying permeability. The groundwater quality in the unconfined and semi-confined sections of the aquifer is of good status generally and oxidising, although with obvious impacts on quality from agricultural pollution. In the confined section, especially the Holderness Peninsula, the groundwater is reducing and of poor drinking water quality. Of the 23 samples collected, the majority were from the unconfined aquifer; 15 are from the Yorkshire Chalk and 8 from the Lincolnshire Chalk. Baseline hydrogeochemical data is available for this northern chalk province from Smedley et al (2004).

A total of 13 samples were collected from the Jurassic Lincolnshire Limestone, the majority from private water supplies. The aquifer is relatively thin (~30m) and localised but is used for public water supply. The majority of the samples collected as part of the Survey are from the shallow confined section of the aquifer where the aquifer is overlain by the clays of the Upper Estuarine Series. The baseline quality of the Lincolnshire Limestone is covered by Griffiths et al (2006).

The Permian rocks in this region include the SSG and the Magnesian Limestone. A third of the samples collected from this region were collected from the SSG, used extensively in the region for public water supply. The baseline groundwater quality of the SSG in this region is covered by Shand et al (2002). The SSG is at outcrop in the west, although overlain by thick glacial deposits, and confined by the Mercia Mudstone to the east. Of the 34 samples collected, nearly one quarter (8 samples) are from the confined section of the aquifer.

The Magnesian Limestone, comprising thinly bedded dolomitic limestone and dolomite, has a thickness between 21m in Northern England to 35m in Yorkshire. A total of ten samples were collected, with some of these being quarterly repeats; the majority of these samples were from public water supplies.

Table 6 Methane data from the East Midlands Province.

East Midlands Province	CH_4 Concentration (µg/l)				Number of Samples
	Minimum	Median	Average	Maximum	
All samples	<0.05	0.9	31	1,320	93
Cretaceous Chalk	0.07	0.9	1.0	4.7	23
Lincolnshire Limestone	0.05	2.6	6.7	32	13
Sherwood Sandstone	<0.05	0.5	15	465	34
Zechstein Group	0.2	0.4	0.8	2.1	10

Similar to other areas, methane concentrations in all aquifers are consistently above the detection limit. No samples exceed the LEL and have therefore not required further investigation. In general, methane concentrations are highest in the Lincolnshire Limestone and lowest in the SSG, although very few samples exceed 10µg/l. The majority of the samples collected from the Lincolnshire Limestone are from the confined zone, in contrast to the samples from both the Chalk and SSG, which could account for this difference.

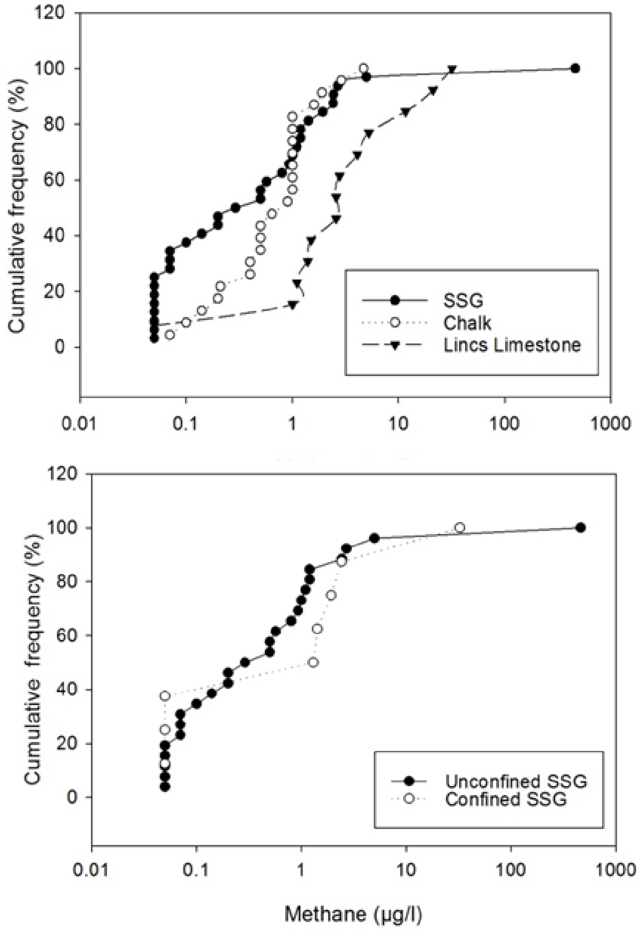

Figure 10 a) Methane data from the East Midlands Province, for the SSG, Chalk and Lincolnshire Limestone. b) Comparison of methane data between the confined and unconfined zones of the SSG in the East Midlands Province.

In Gooddy and Darling (2005) methane data were collected from both the SSG and the Lincolnshire Limestone. Methane concentrations in the Lincolnshire Limestone varied between 0.05µg/l to 2,300µg/l, a range within which the new Survey samples fit.

The study also investigated the impact of aquifer confinement on methane concentrations; as almost all samples from the Lincolnshire Limestone in the current Survey were from confined sections, it wasn't possible to assess this. It was however possible to assess the impact of confinement for the SSG; in the 2005 study, methane concentrations in the confined zone were similar to those in the unconfined zone. Figure 10b, using data from the Survey, illustrates slightly elevated methane concentrations in the confined zone, 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 zone may be relatively reducing, increasing the potential for elevated methane concentrations. Figure 11 illustrates the distribution of methane concentrations in the region. The highest methane concentrations were recorded at the two samples taken from the Carboniferous Millstone Git. Both boreholes logs record the presence of organic rich shales at intermediate depths which could be the source of this additional methane. The SSG sample close to Doncaster with elevated methane concentration was collected during the 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.

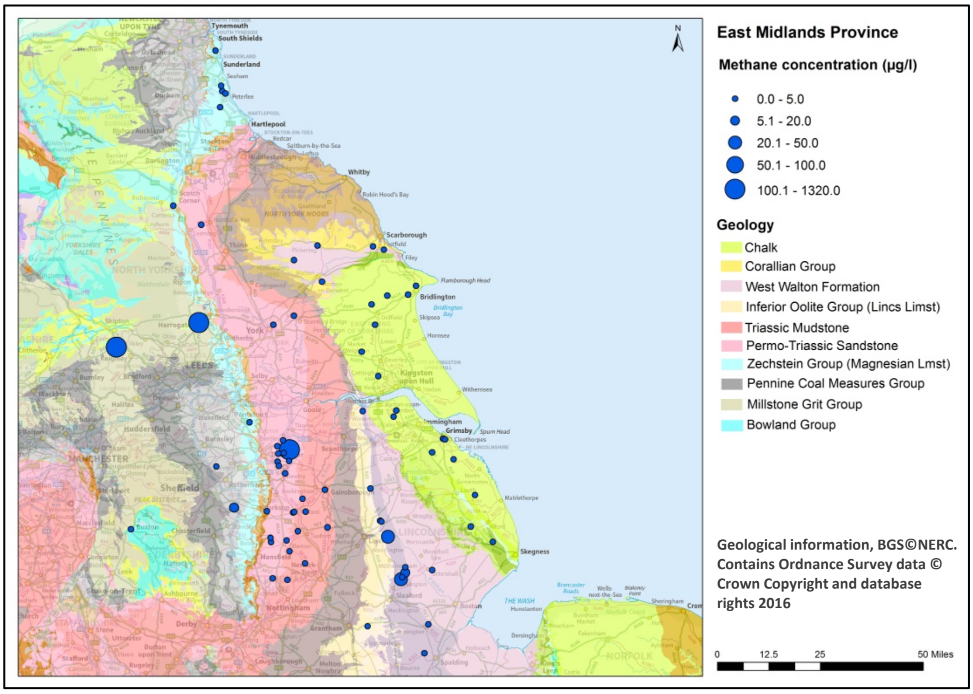

Figure 11 Methane data from the East Midlands Province, dots are proportional to the CH_4 concentration.

4.1.3 Southern England

The geology of Southern England is shown in Figure 12 with the locations of the Survey samples. This region encompasses the Weald Basin, Hampshire Basin and the area around Bristol and Gloucester. In this region, numerous different aquifers were sampled as part of the Survey (Table 7), including the Principal aquifers, Chalk and Lower Greensand. 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).

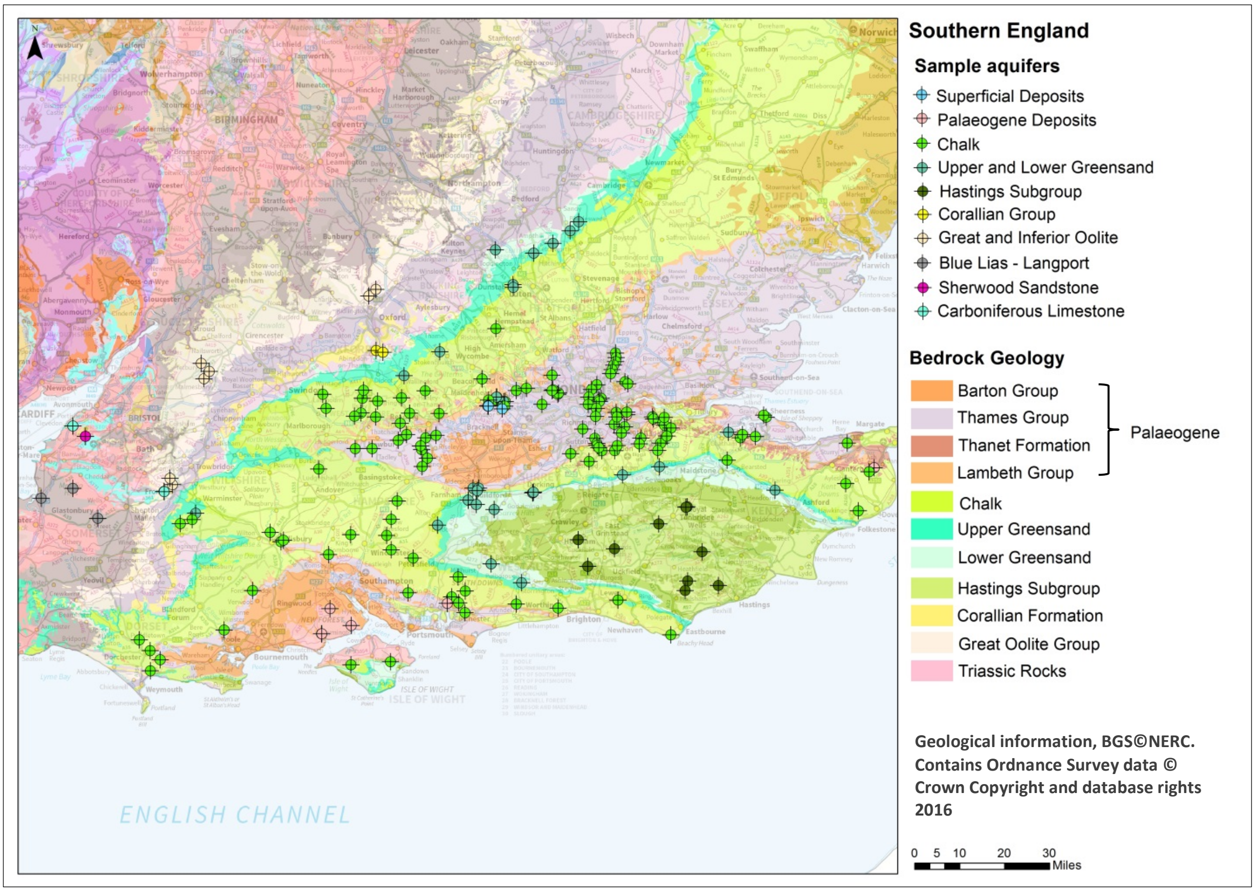

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Figure 12 **Bedrock geology of Southern England.**

Table 7 **Stratigraphy of the aquifers sampled in Southern England.**

	Southern
Quaternary	Superficial Deposits – gravels
Palaeogene	Barton Group, Harwich Formation, Lambeth Group, Thanet Formation
Cretaceous	Chalk
	Upper and Lower Greensand
	Hastings Subgroup – Tunbridge Wells Sand, Ashdown Formation
Jurassic	Corallian Group
	Greater and Inferior Oolite
	Blue Lias - Langport
Permian	Sherwood Sandstone
Carboniferous	Carboniferous Limestone

* Blue shaded aquifers as designated as Principal aquifers.

A summary of the methane data collected as part of the Survey is shown in Table 8; a total of 251 samples were collected. Where adequate data were available, summary statistics have been collated per aquifer, in addition to the regional information. The methane data per aquifer are compared in Figure 13.

In Southern England, a total of 251 sites have been sampled for methane from a number of different aquifers. The majority of samples came from four main aquifers; Chalk, Greensand, Wealden Group and Greater and Inferior Oolites. The additional aquifers can be important locally and are used for private supplies. In this southern province, the Chalk is used extensively for public water supply and outcrops in the Chilterns, North and South Downs, Salisbury Plain, Wessex Downs and on the south coast. It reaches a maximum thickness of 200m.

Over half the samples in the region are from the Chalk aquifer and almost half of those from public water supplies; the remainder are from EA observation boreholes. Baseline hydrogeochemical data is available for the Chalk in Edmunds et al (2002) and Smedley et al (2003).

The Lower Greensand aquifer consists of sands and sandstones, and groundwater flows preferentially where the sand is unconsolidated. The Lower Greensand is at outcrop around the edge of the Wealden anticline and has a maximum thickness of 220m. Where confined, it is separated from the Chalk by the Gault Clay. Groundwater from this aquifer is used for public water supply. Over 50 samples have been collected from the Greensand aquifer; 51 from the Lower Greensand and 3 from the Upper Greensand. Baseline hydrogeochemical information is available for the Lower Greensand in Shand et al (2003).

The Great and Inferior limestones are highly permeable Jurassic limestones, separated by the mudstones of the Fullers Earth Formation. To the north of the region both formations are at outcrop and unconfined. Both aquifers are used moderately for public and private water supply, Of the 12 samples collected, half were from the Great Oolite and half from the Inferior Oolite. The majority of samples are from the unconfined sections of the Great Oolite and confined sections of the Inferior Oolite. Baseline hydrogeochemical information is available for the Great and Inferior Oolite in Neumann et al (2003).

The aquifers of the Hastings Subgroup include the Tunbridge Wells Sand (TWS) and the Ashdown Formation; the two aquifers are separated by the Wadhurst Clay Formation which confines the underlying Ashdown Formation (Allen et al., 1997). Away from outcrop, the TWS is confined by the Weald Clay. Both aquifers are complex and thought to be multi-layered, with the additional complication of major faulting which affects groundwater flow. Although complex, both these aquifers are used privately and by water companies and almost 20 samples have been collected as part of the Survey.

Table 8 Summary methane data from Southern England.

Southern England	CH_4 Concentration (µg/L)				Number of samples
	Minimum	Median	Average	Maximum	
All samples	<0.05	1.3	39	4,720	251
Chalk	<0.05	0.5	3.6	83	137
Greensand	<0.05	4.9	8.0	105	54
Hastings Subgroup	0.4	19	461	4,720	19
Oolites	<0.1	0.5	1.3	7.6	12

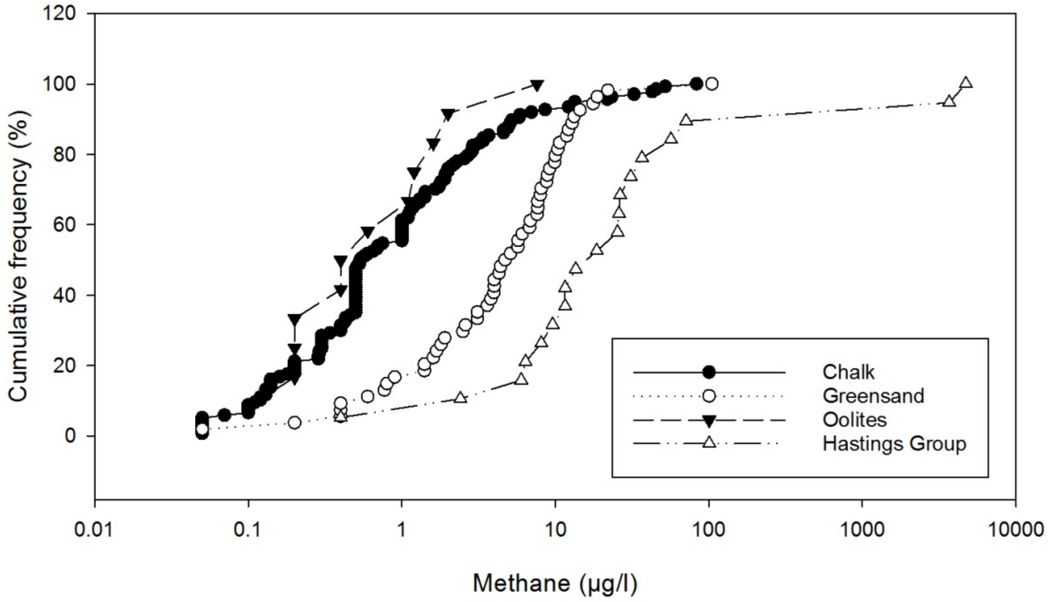

Figure 13 **Methane data from the Chalk, Greensand, Oolites and Hastings Subgroup.**

Methane concentrations at all sample sites are consistently above the detection limit; 98% of samples are below 100µg/l and 45% below 1µg/l. As shown in Figure 13, methane concentrations are typically lowest in the Oolites which show similar concentrations to the Chalk. 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 Greensand; this observation is echoed in the Darling 2005 study where methane concentrations in the Greensand were an order of magnitude above those in the Chalk. Methane concentrations in the Hastings Subgroup are higher than those in the other aquifers, and the two highest values were from the TWS.

The two samples over the LEL were taken from the same borehole; the sample was repeated after the initial analysis. There is a known zone of shallow methane in this region (Selley, 2012) and hydrocarbon well logs from the area report significant gas in the shallow Cretaceous sandstones in the area. Additional analysis of the dissolved gas content of this sample implied a thermogenic source, although isotope investigation was not possible due to access issues with the sample site. Given the shallow nature of the gas, the source could be either thermogenic gas migrated 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 ~1km depth; Upper Jurassic rocks are thought to be too shallow for hydrocarbon generation (Trueman, 2003). The spatial distribution, source and hydrogeological controls on this potentially thermogenic methane are as yet, poorly understood.

Figure 14 illustrates the distribution of methane concentrations in the region. The higher methane concentrations in the Hastings Subgroup and the Greensand can be seen in the Weald Basin and the lower methane concentration samples from the Chalk.

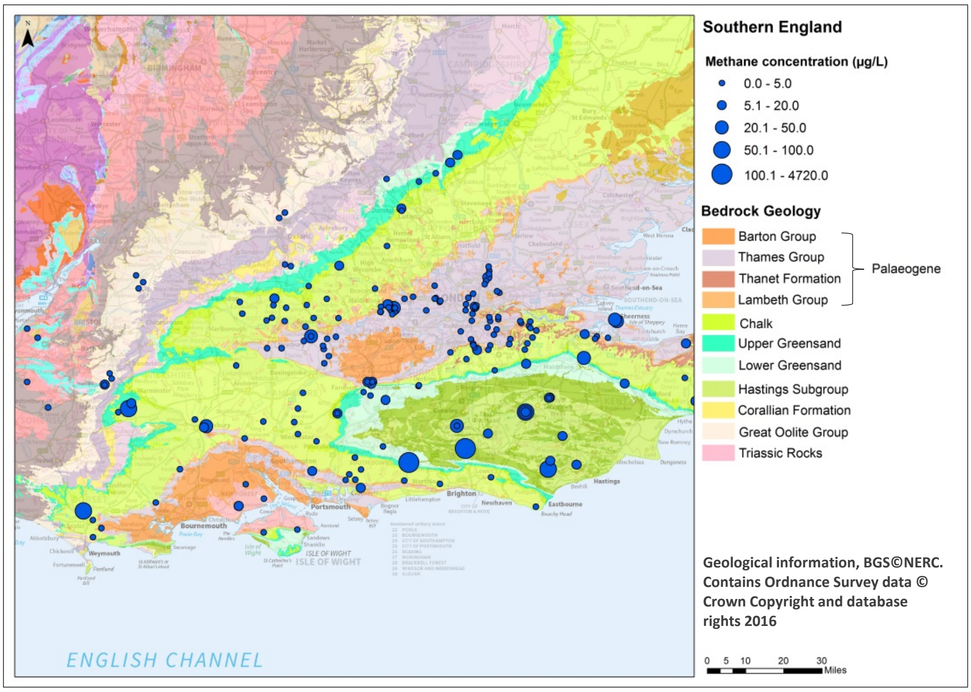

Figure 14 Methane concentrations in Southern England.

4.1.4 South Wales

The geology of South Wales is shown in Figure 15 with the location of the Survey samples. In this region 25 samples were analysed for methane from two main aquifers, the Carboniferous Limestone and the Coal Measures sandstones (Table 9). The target formation for unconventional gas development in this area is the Marros Group, with siliceous mudstones and local quartz rich sandstones.

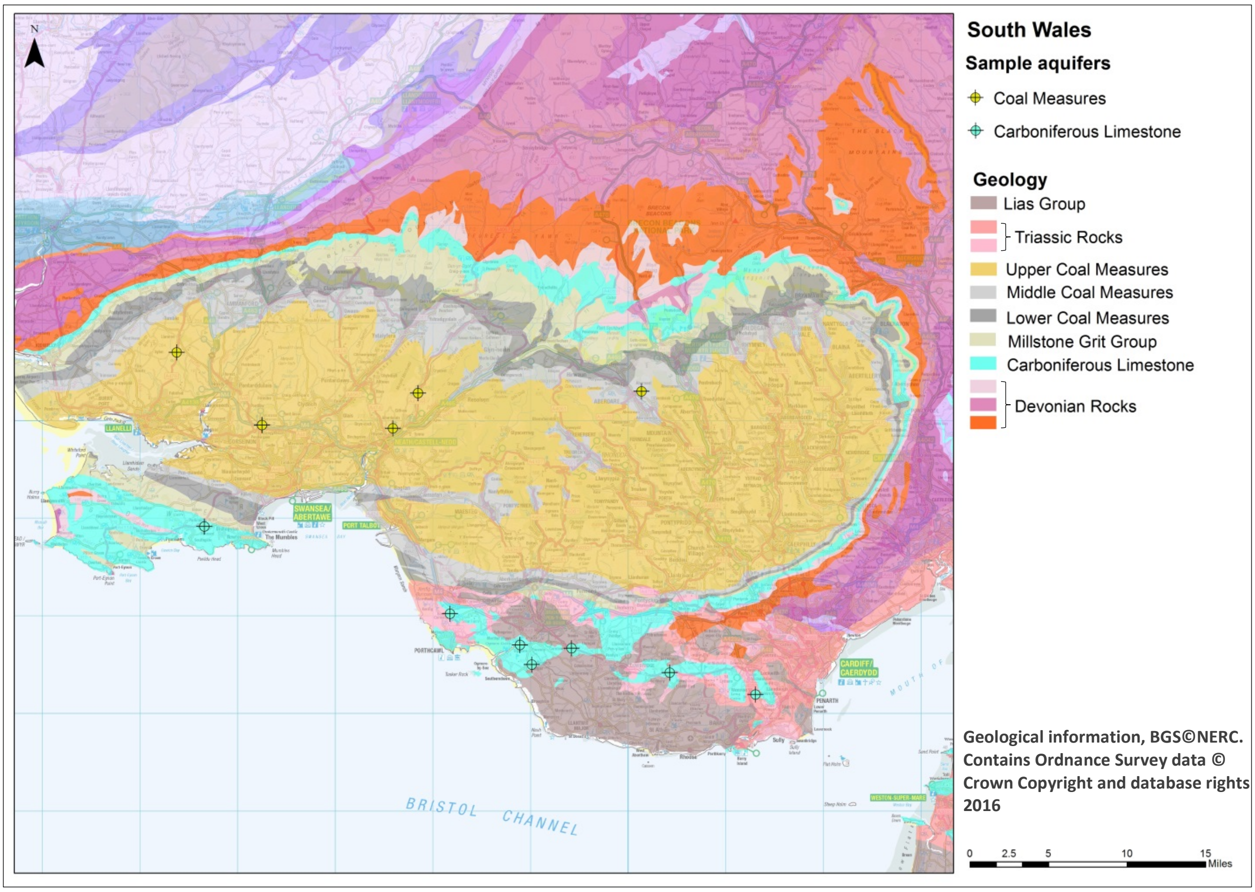

Figure 15 Bedrock geology and methane samples in South Wales.

Table 9 **Stratigraphy of the aquifers in South Wales.**

	South Wales
Carboniferous	Upper Coal Measures sandstones
	Carboniferous Limestone

* Blue shaded aquifers as designated as Principal aquifers.

A summary of the methane data collected as part of the Survey is in Table 10; a total of 25 samples were collected, almost half from both the Carboniferous Limestone and Coal Measures. Where adequate data were available, summary statistics have been collated per aquifer, in addition to the regional information. The methane data per aquifer are compared in Figure 16.

The coal measures sandstones in South Wales are very hard and dense, and groundwater will only tend to flow through fractures. Due to mining subsidence, there are zones of increased fracturing, and therefore increased water storage and flow. This aquifer is classed as Secondary A aquifer and is not used for public water supply. Only one sample collected can be attributed specifically to the Pennant Sandstone. All the samples collected as part of the Survey are from private supplies or Natural Resources Wales (NRW) monitoring boreholes.

In the southern UK, the Carboniferous Limestone is a Principal aquifer and groundwater flows rapidly through a network of fractures, conduits and caves. In South Wales, this aquifer has no public water supply sources, although it is used for many private supplies. The Carboniferous Limestone outcrops discontinuously between Porthcawl and Cardiff and has a maximum thickness of 425m. All the samples collected from this aquifer as part of the Survey were from Natural Resources Wales monitoring boreholes.

Table 10 **Summary methane data for South Wales.**

South Wales	**CH_4 Concentration (µg/l)**				**Number of Samples**
	Minimum	**Median**	**Average**	**Maximum**	
All samples	<0.10	32	58	483	25
Coal Measures	<0.10	34	53	216	13
Carboniferous Limestone	<0.10	32	69	483	11

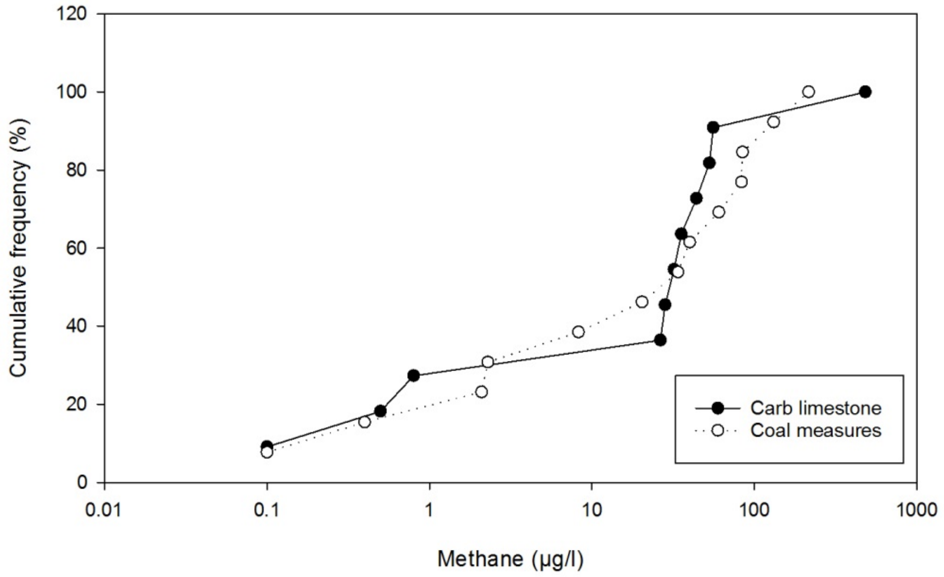

Figure 16 **Methane data from the Coal Measures and Carboniferous Limestone in South Wales.**

Methane concentrations in the Coal Measures and Limestone appear to be relatively similar, although elevated compared to the average concentrations in other areas of the UK. This could be due to the impact of methane adsorbed to the coal within the Coal Measures sequence and the stratigraphic position of the Carboniferous Limestone, directly below the Millstone Grit which contains layers of shales. In other carbonate aquifers the methane concentrations tend to be lower, reflecting the lack of organic matter and high degree of mixing. The absence of correct environmental conditions for methane production in the Carboniferous Limestone implies that the methane source is more likely to be a contiguous formation. Only 20% of samples have methane concentrations below 1µg/l, fewer compared to other regions, although 88% of samples are less than100µg/l. Although in general the methane concentrations are above those in other regions, with aquifers such as the Chalk and the SSG, no samples collected from South Wales have exceeded the LEL.

Figure 17 illustrates the distribution of methane concentrations in the region. The highest methane concentration was from a borehole in the Carboniferous Limestone; the borehole log for this site is unavailable, although logs from sites close by suggest that the aquifer is confined in this location, under an impermeable clay unit. This site was chosen as a quarterly site and the temporal data collected from all boreholes in South Wales showed large variations in the methane concentrations, including this one. This is discussed further in Section 4.2.

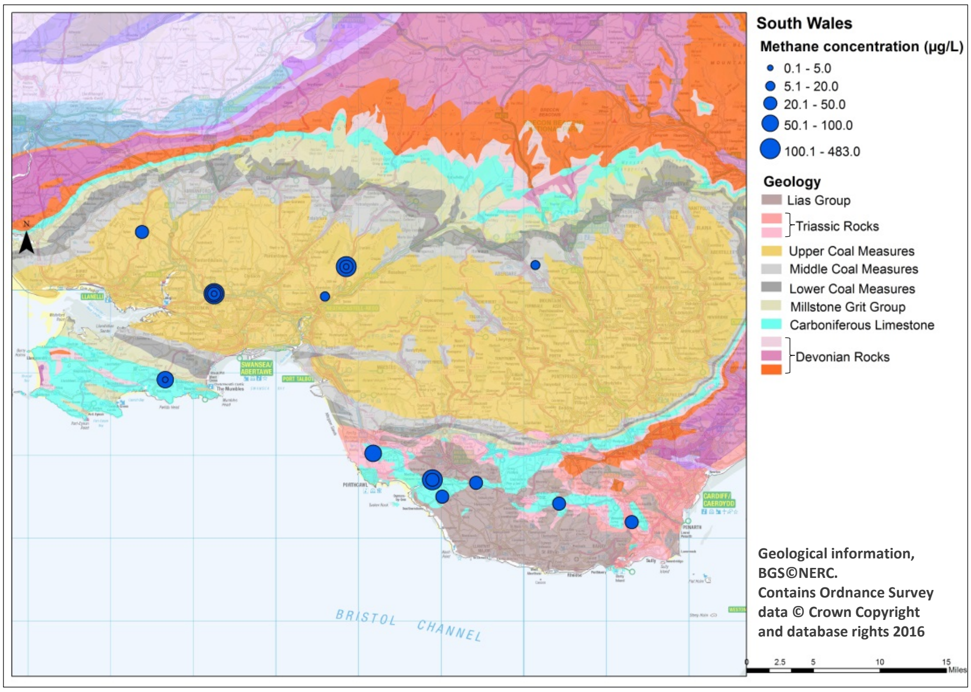

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Figure 17 **Methane data for South Wales, dots are proportional to methane concentration.**

4.1.5 Carlisle Basin and Northumberland Trough

In the Carlisle Basin and Northumberland Trough, 16 sites have been sampled for methane in a number of different aquifers. The two main aquifers are Permo-Triassic sandstone and the Fell Sandstone and Border Group (Table 11). The geology of the region and the methane samples are shown in Figure 18. The shale units present in the Northumberland Trough are the Bowland Shale and other black shales of Visean-Tournaisian age that are typically inter-bedded with sandstone, siltstone and mudstone. These shales are thinner, shallower and not laterally extensive when compared to the Bowland Shale Formation in Lancashire and Yorkshire. Over in Cumberland the coal seams of the Pennine Coal Measures Group are reported to have potential for coal bed methane.

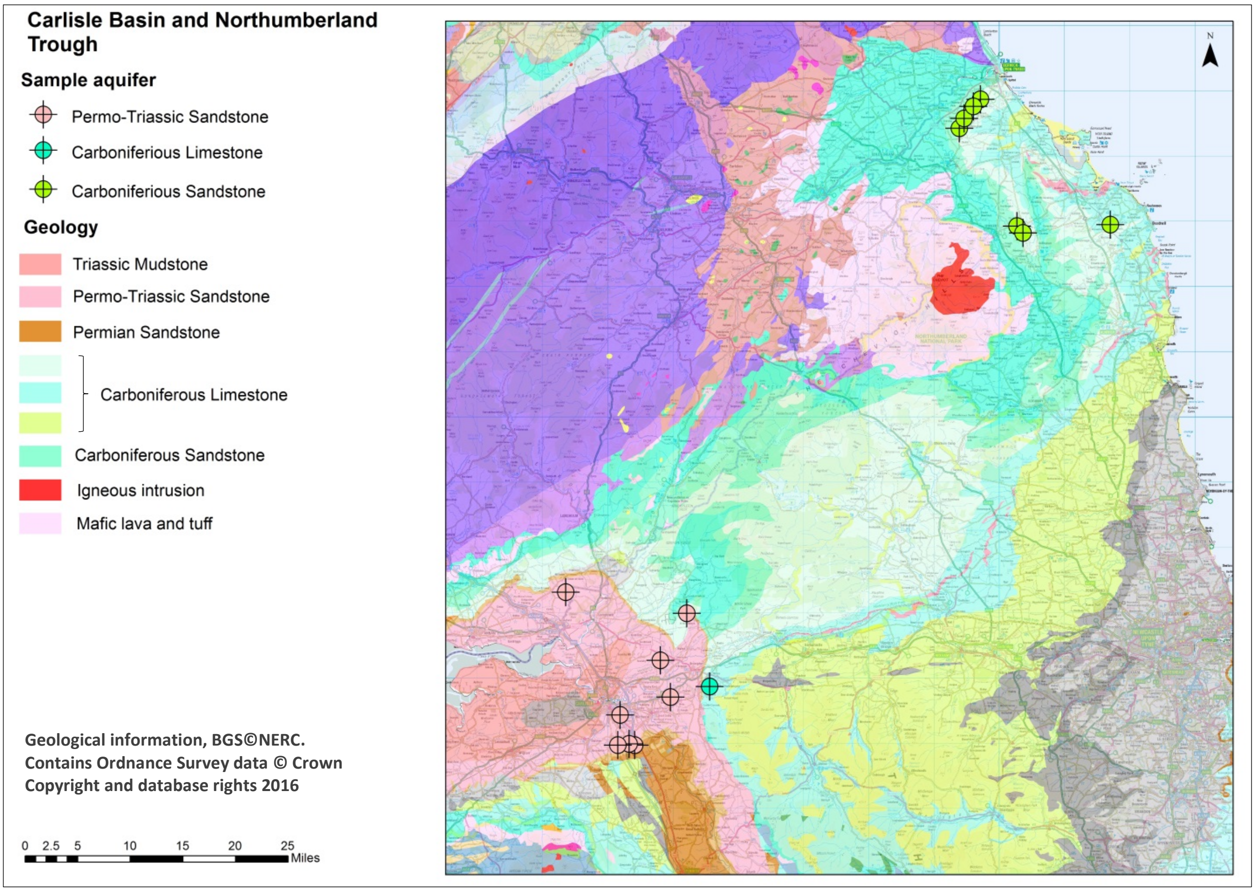

Figure 18 Bedrock geology and methane samples in the Carlisle Basin and Northumberland Trough.

Table 11 Stratigraphy of aquifers in the Carlisle Basin and Northumberland Trough.

	Carlisle Basin and Northumberland Trough
Permian-Triassic	Sherwood Sandstone Group (Undiff)
	Penrith Sandstone Formation
Carboniferous	Carboniferous Limestone (Undiff)
	Carboniferous Sandstone (including Border Group)

* Blue shaded aquifers as designated as Principal aquifers.

A summary of the methane data collected as part of the Survey is in Table 12; a total of 16 samples were collected with half of those in the Permo-Triassic Sandstone. Where adequate data were available, summary statistics have been collated per aquifer, in addition to the regional information.

To the west of the target area is the Carlisle Basin, the majority of which is comprised of Triassic sandstone; this can be up to 600m thick and is made up of sandstone, conglomerates and marls. The southern part of the Carlisle Basin is Permian sandstone consisting of sandstone, marls and breccias. Both the Triassic and Permian sandstones are classed as Principal aquifers. All Permo-Triassic sandstone samples in this region are from the Carlisle Basin and all are from private, agricultural supplies. Only one sample from the Carlisle Basin was collected from the Carboniferous limestone.

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 300m thick and is made of laterally extensive quartz rich sandstones with silty or pebbly bands. Low permeability shales or marl units can be present within the sequence which effectively isolates individual sandstone units from one another (Turner et al., 1993).

Where the Fell Sandstone is overlain by the mudstones of the Scremeston Coal Group, it is reported to be artesian (Hodgson and Gardiner, 1971). Due to the low matrix porosity and permeability of the Fell Sandstone, fractures have a significant impact on groundwater flows (Jones et al., 2000). All seven samples from the Northumberland Trough are from the Fell Sandstone and Border Group.

Samples were difficult to locate in the centre of the target area, around the Northumberland National Park and the Kielder Water reservoir. Instead, samples were collected from the western and eastern extremes in the Carlisle Basin and across the Northumberland Trough, where boreholes could be located.

Table 12 Summary methane data for the Carlisle Basin and Northumberland Trough.

Carlisle&Northumberland	CH_4 Concentration (µg/l)				Number of samples
	Minimum	Median	Average	Maximum	
All samples	<0.2	0.65	93	1,434	16
Sherwood Sandstone	<0.2	0.8	6	30	8
Carboniferous Sandstone	<0.2	0.6	205	1,434	7

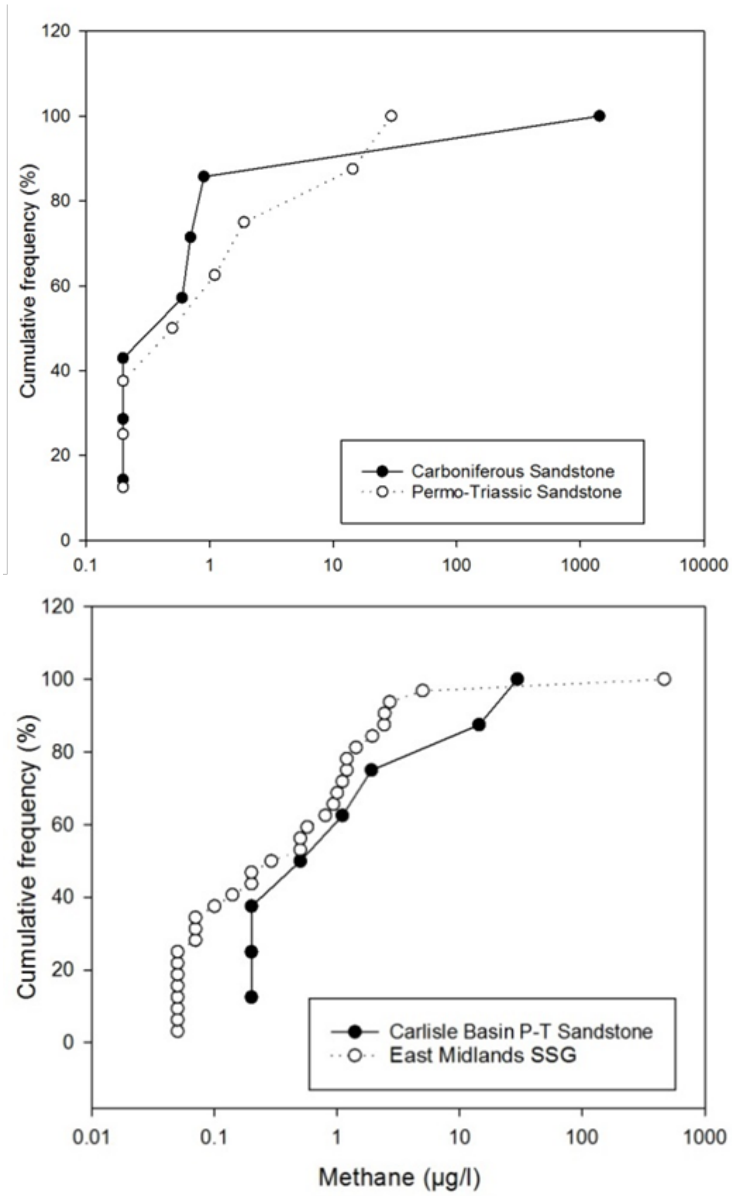

Figure 19 a) Methane data from the Permo-Triassic sandstone and Carboniferous Sandstone. b) Methane data for the Permo-Triassic sandstone in the Carlisle Basin in comparison to the SSG methane data in the East Midlands.

From the data collected, the methane concentrations are comparable between the two aquifers (Figure 19a). The one elevated methane concentration in the Northumberland Trough was from a borehole located in a fen, classed as a Special Area of Conservation; additional analysis of the dissolved gas content of this sample implied a biogenic source, which would correlate with the presence of peat rich soils. Nearly 70% of all the samples have methane concentrations <1µg/l and ~ 94% have concentrations <100µg/l.

Although the Fell Sandstone succession in the Northumberland Trough is known to contain some shale groups and thin coal seams, the baseline methane concentrations in the groundwater are all below 1µg/l, with the exception of the fen sample. In comparison to the methane 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 (Figure 19b).

Figure 20 illustrates the distribution of methane concentrations in the region; overall the concentrations are orders of magnitude below the LEL, with the one outlier being the sample from the peat rich fen.

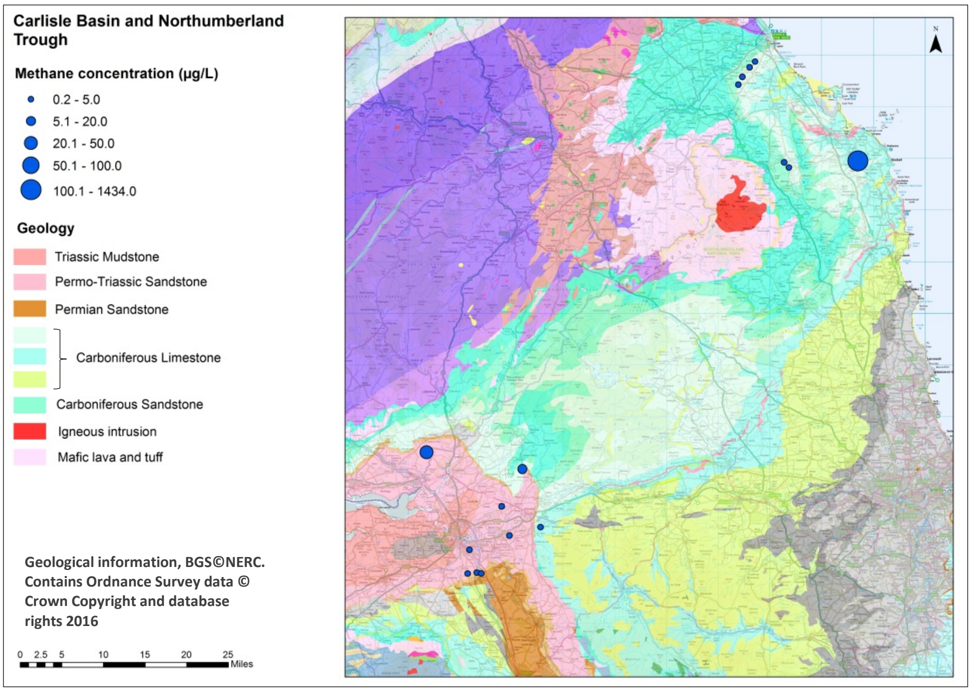

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Figure 20 Methane data for Cumbria and Northumberland, dots are proportional to methane concentration.

4.1.6 Central and Southern Scotland

In Central and Southern Scotland 31 sites have been sampled for dissolved methane from a number of different aquifers, mostly from Carboniferous sediments (Table 13). These data were collected as part of the Baseline Scotland project and reported in Ó Dochartaigh et al (2011). Four of the samples collected were from mine shafts or adits, the rest from boreholes. The geology of the region and the methane samples are shown in Figure 21. In this area the formation most likely to have potential for shale gas and/or oil is the West Lothian Oil-Shale Formation, which lies stratigraphically immediately below the Clackmannan Group in the eastern part of central Scotland.

Table 13 Stratigraphy of the aquifers sampled in Central-Southern Scotland.

	Central-Southern Scotland
Carboniferous	Coal Measures
	Clackmannan Group
	Strathclyde Group
	Inverclyde Group
Devonian	Devonian sandstone
Ordovician/Silurian	Siltstones

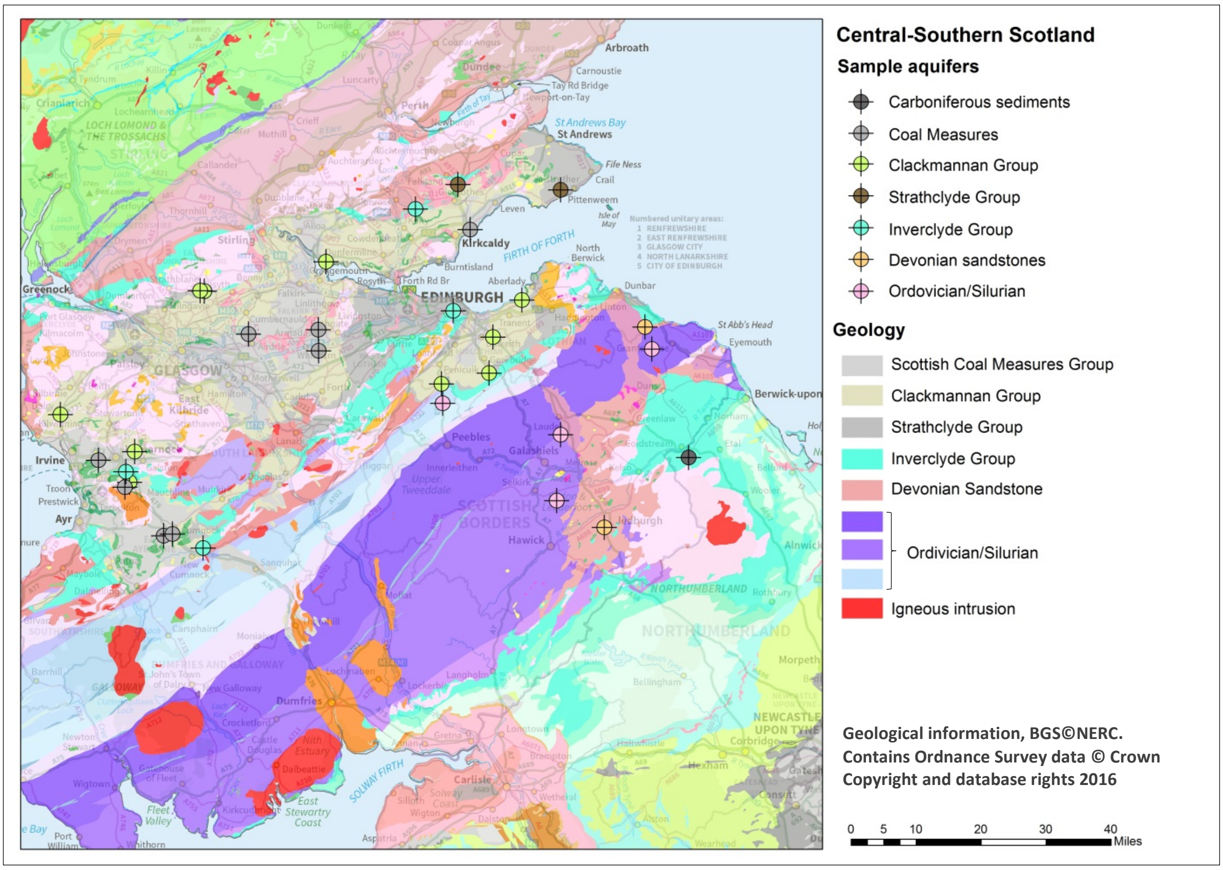

Figure 21 Bedrock geology and methane samples in Central-Southern Scotland.

A summary of the methane data collected as part of the Baseline Scotland project is in Table 14; of the samples collected within the study area, 25 are from Carboniferous sedimentary aquifers (Clackmannan, Inverclyde, Strathclyde and Coal Measures Groups), two from the Devonian sandstones and four from Ordovician/Silurian fractured aquifers.

In this region, groundwater was historically an important resource for industry, but today is not widely used; in southern Scotland there is local groundwater abstraction for agriculture and domestic use. 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 separated by lower permeability siltstones, mudstones and coals (Ó Dochartaigh et al., 2011). Groundwater may be present at various depths under unconfined or confined conditions, and different groundwater heads are seen in different aquifer layers.

The thickness of the Carboniferous sedimentary aquifers varies from less than 500m in southern Scotland to 3,000m in central Scotland. Groundwater from the Clackmannan and Coal Measures groups in this area is typically reducing and contains a high proportion of old water, recharged more than 35-60 years ago. Mining activity in this area has had a major impact on groundwater quality (MacDonald and Ó Dochartaigh, 2005).

Table 14 Summary results for Central-Southern Scotland.

Central-Southern Scotland	**CH_4 Concentration (µg/l)**				**Number of samples**
	Minimum	**Median**	**Average**	**Maximum**	
All samples	<0.1	3.6	132	1,680	31
Carboniferous aquifers	<0.1	4.6	178	1,680	25

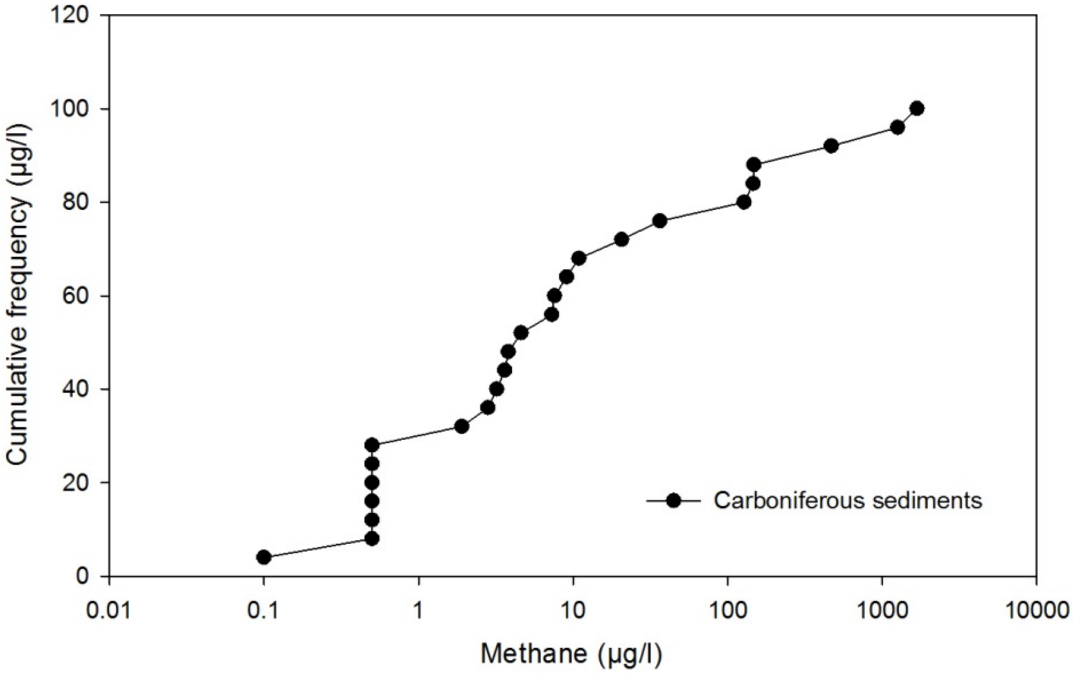

Figure 22 Methane data from the Carboniferous aquifers of Central-Southern Scotland.

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 less than 1µg/l and 77% are less than 100µg/l (Figure 22). Of the higher methane concentrations in the area, the highest was from a borehole in the Clackmannan Group and others were from the Coal Measures, sometimes where known, or suspected to be impacted by mining. One sample in the Ordovician siltstones had a concentration of 150µg/l. These elevated concentrations are most likely a consequence of high organic carbon content within the aquifers, specifically within the coal seams. Figure 23 illustrates the distribution of methane concentrations in the region.

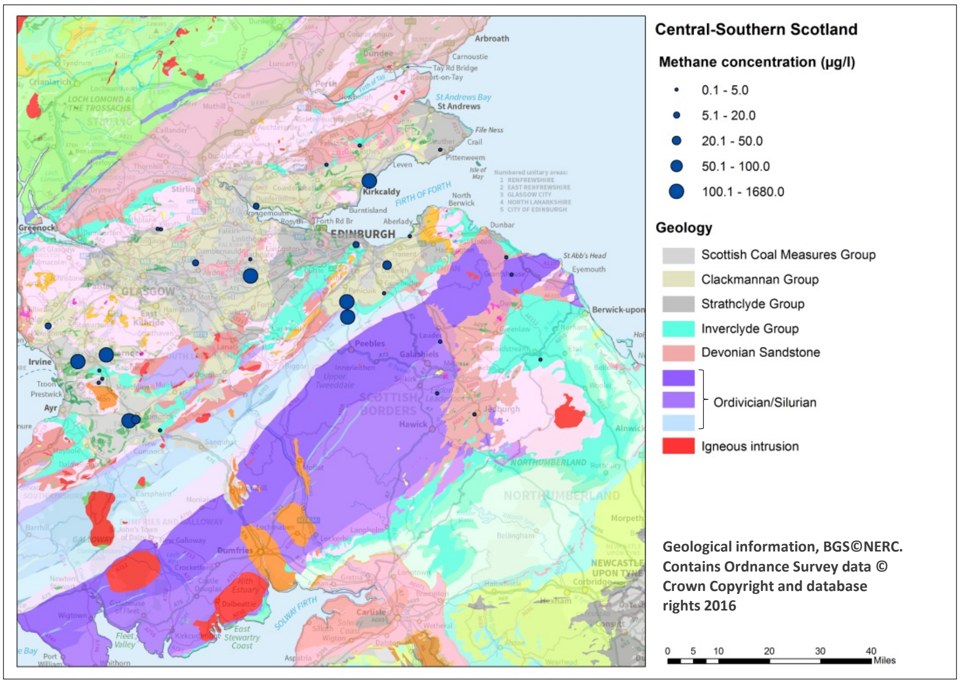

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Figure 23 Methane data for Central-Southern Scotland, dots are proportional to methane concentrations.

4.2 TEMPORAL VARIATION IN METHANE CONCENTRATIONS

To investigate the possibility of seasonal or other medium-term changes in groundwater methane concentration, a subset of sites was selected for quarterly monitoring. A total of 17 sites were chosen (Table 15) to give a geographical spread and range of aquifers (Figure 22). At some sites a complete data set was impossible to collect due to operational issues or significant declines in water levels (specifically South Wales).

Table 15 Summary of quarterly samples in each region.

Region	*Aquifers sampled quarterly*
Lancashire & Cheshire Basin	Superficial Deposits Sherwood Sandstone
East Midlands Province	Chalk Sherwood Sandstone Zechstein Group
South Wales	Coal Measures Carboniferous Limestone
Southern England	Barton Group Chalk Lower Greensand Tunbridge Wells Sand Ashdown Formation Sherwood Sandstone Carboniferous Limestone and Inferior Oolite Dolomitic conglomerate/Carboniferous Limestone

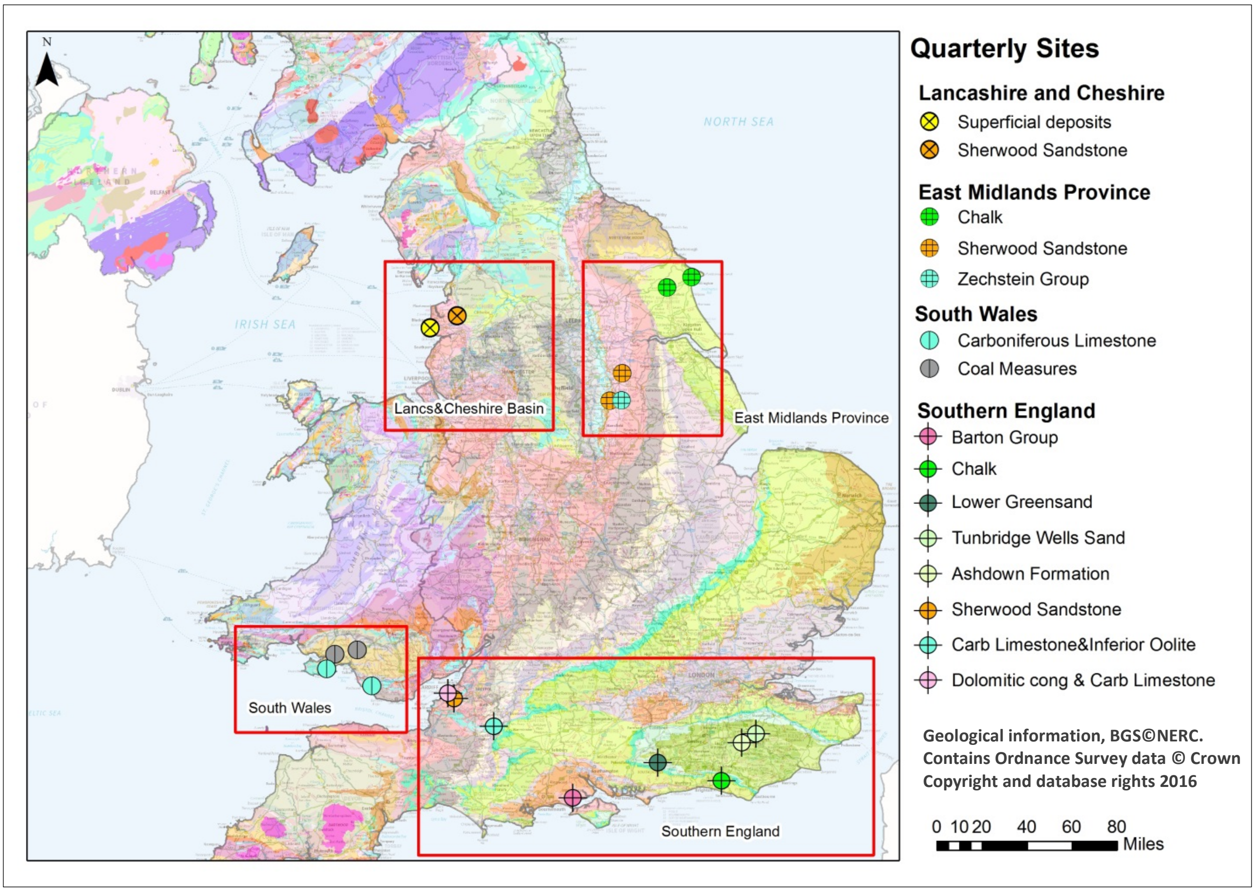

Figure 24 **Quarterly sample locations and aquifer types.**

Assessment of methane concentrations in US aquifers has shown variability over time in low methane concentration boreholes (<1,000µg/l) of ~1µg/l and in high methane boreholes (4,000–6,000µg/l) of between 20-40% (Senior, 2014). Little is currently known about changes with time in methane concentrations in UK groundwater; previous work has usually involved only a single sample to determine methane concentration at a particular location. A number of potential sources of variability exist: barometric fluctuations, changes in microbiological communities or nutrient inputs, sampling error, analytical error and complex hydrogeology i.e. fractured or karstic aquifers. Duplicates done as part of the Survey both within the BGS laboratory and also between different labs were within the expected 10% precision so would appear to rule out analytical error as a significant contributor to variation. The data collected from the various regions are summarised below.

4.2.1 Results

The quarterly results are shown in Figure 25 and discussed per region in the sections below. The data collected show that in the majority of cases the annual variability of methane concentrations in groundwater is minimal. Exceptions appear to be when the aquifer is karstic (Lower Magnesian Limestone or Carboniferous Limestone) or organic-rich (Coal Measures). Compared to data in the US, concentrations are much lower and show much less variability (Humez et al., 2016).

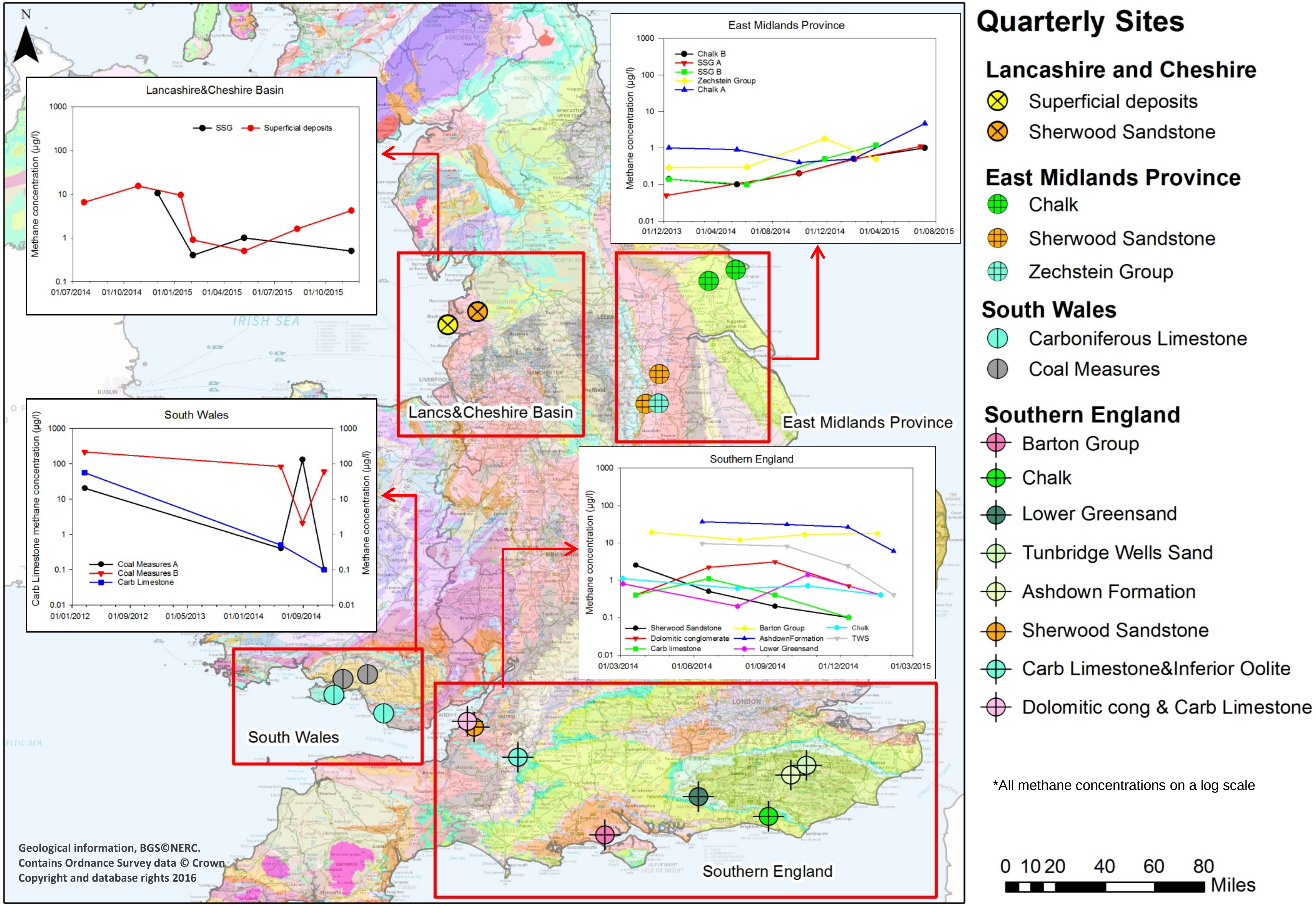

Figure 25 Regional results for quarterly methane monitoring.

LANCASHIRE AND CHESHIRE BASIN

Two quarterly monitoring sites were selected in the Lancashire and Cheshire Basins, one in the SSG and the other in the Superficial Deposits. Additional sites had been identified, but proved impossible to access regularly over the course of the project. The two boreholes were initially sampled in March 2012 then re-visited in 2014 at the start of the quarterly monitoring. The SSG samples are from a public water supply borehole and the Superficial Deposit samples are from an EA groundwater level monitoring borehole. This EA borehole had no installed pump so was sampled using a submersible pump following stability of wellhead parameters. The quarterly data for Lancashire and Cheshire have been collected over a longer time period than other regions due to additional baseline monitoring work in the area. After initial elevated levels in both aquifers, the concentrations methane concentrations have stayed low. The range of concentrations for the SSG is <0.5 – 10.6µg/l and <0.5 – 15.5µg/l for the Superficial Deposits. Although these ranges show changes of up to 97%, the concentrations remain very low.

EAST MIDLANDS PROVINCE

Five quarterly monitoring sites were selected in the East Midlands Province; two in the Chalk, two in the SSG and one in the Lower Magnesian Limestone. All samples were from public water supply boreholes; at one pumping station two boreholes were present abstracting from two different aquifers (SSG and Lower Magnesian Limestone). Although in close proximity, this represented an opportunity to investigate temporal variations in two aquifers at the same location. All these boreholes were initially sampled in December 2012 and then again in May 2014 for the start of the quarterly monitoring.

All the boreholes show very little change in concentration over the course of a year. The range for the SSG is 0.05 – 1.2µg/l, Chalk 0.1 – 4.7µg/l and 0.29 – 1.8µg/l for the Lower Magnesian Limestone. These ranges show the limited variability in methane concentrations in these regularly pumped public water supply boreholes in carbonate aquifers and Permo-Triassic sandstones.

SOUTHERN ENGLAND

In total, eight quarterly monitoring sites were selected in Southern England, all from different aquifers covering Paleogene, Cretaceous, Triassic, Permo-Triassic and Carboniferous formations. Samples from the Wealden Basin were initially collected in 2012; those in Bristol/Bath were originally sampled in the spring of 2014. All boreholes were then re-sampled as part of the quarterly monitoring in June 2014. Gaps exist for some of the public water supply boreholes due to operational issues. All samples were collected from public water supply boreholes.

Concentrations from boreholes in the LGS, SSG (Keuper Sandstone), Carboniferous Limestone and the Chalk are all consistently low (all < 5µg/l), again with very little variability. Higher concentrations were found in the Wealden Group aquifers (TWS and Ashdown Formation) and the Barton Group, the latter in particular showing very little variation around 15µg/l.

SOUTH WALES

Three quarterly monitoring sites were chosen for South Wales, two in the Carboniferous Upper Coal Measures Sandstones and one in the Carboniferous Limestone. Originally one additional borehole in the Carboniferous Limestone was included, but was removed on the second round owing to logistical reasons. The boreholes were initially sampled in February 2012 and then from May 2014 as part of the quarterly monitoring. All these boreholes are part of the NRW groundwater level observation network and have no pumps installed. For consistency between sampling rounds, the pump was placed at the same point within the screen and the same volume of water purged for each sample collected. No sample was collected from the Carboniferous

Limestone in August 2014 as the water level had dropped below 30m, which was beyond the capability of the submersible pump.

After the first two rounds of monitoring at the three sites, it was observed that the variation in methane concentrations was far greater than in any of the other regions, especially in the Coal Measures. This could be for a number of reasons. Within the Coal Measures, methane is often adsorbed to the matrix of the coal; during pumping, the hydrostatic head is lowered, potentially drawing in these gases. In both the boreholes, the records report thin coal seams within the main sandstone aquifer, which could be the source of the methane. Another potential reason for the fluctuation is the impact on dissolved gases from the submersible pump itself; there is some evidence that centrifugal pumps can cause pressure changes and disturbance of the water column if the flow rate is too high (Nielsen and Yeates, 1985; Parker, 1994). The Coal Measures aquifer is also highly fractured; during the different seasons (therefore changing water levels), different fractures could be contributing more or less to the borehole inflows, potentially changing the chemistry of the water.

To help investigate this further, additional work was done in collaboration with the University of Birmingham and NRW, targeting the impacts of purging time on methane concentrations. From an initial assessment of the data already gathered it was identified that vertical flows and hydraulic heads appear to impact on methane concentrations, but had opposite effects in the two Coal Measures boreholes (Halwa, 2015). A drop in water level at one borehole corresponded with the lowest methane concentration and as water levels increased with rainfall, the methane levels also rose; the opposite pattern occurred in the other Coal Measures borehole. New samples collected as part of the study were taken at different stages of the purging; at one of the boreholes as purging time increased, methane concentrations increased, while at the other, the opposite occurred. It was suggested that where methane concentrations increased during purging, this could be due to the borehole location, between an old colliery and a landfill, plus the potential for water to be drawn in from thin coal seams within the sequence. Where the concentrations reduced, flow could be sourced instead predominately from fractures in the sandstone, the quality of the mixed waters being dominated by this fracture flow. Although the rate of vertical flows in these boreholes is unknown, McMillan et al (2014) have identified that in boreholes where ambient up flows increase to ~50% of the pumping rate and the ambient flow rates vary seasonally, the sample origin may vary, even with consistent purge times and pump depth. The conclusion from the work in South Wales is that an understanding of in-well mixing and vertical head gradients is essential to understanding the variability of methane in occasionally-pumped groundwater boreholes. This work therefore highlights a knowledge gap on how sampling methodologies, vertical flows and in-well mixing affect methane concentrations.

5 Summary and recommendations

5.1 SUMMARY

The BGS has undertaken a national baseline survey of methane in groundwater, concentrating attention on areas where a shale gas resource is thought likely to exist and which could be developed in the future. The Survey has tried to capture the natural baseline conditions of methane in groundwaters of GB at a regional scale (Figure 26 and 27). The Survey has collated past methane data and merged with these new samples to create a database containing 439 methane data points (Table 16). Approximately 96% of the data have methane concentrations under 100µg/l, 80% are under 10µg/l and 43% are under 1µg/l. Less than 1% of the boreholes sampled had methane concentrations over the LEL of 1,600µg/l and none of these sites are public water drinking supplies. The average concentration across GB in the aquifers sampled is 45µg/l. From the different regions sampled as part of the Survey, South Wales has the highest methane concentrations, followed by Central-Southern Scotland and Lancashire/Cheshire. Although there are a few outliers in the other regions, the methane concentrations are lower in the East Midlands, Northumberland/Cumbria and the Wessex/Weald Basin. In general, methane concentrations in carbonate aquifers (Chalk, limestones, Oolites etc.) are low, similar to those seen in the Permo-Triassic sandstone aquifers, although methane is ubiquitous across all these aquifers. From the temporal data, little variation in methane concentrations has been observed, except in South Wales, where further investigations are needed to determine whether these variations are intrinsic to the aquifer type or are related to the mode of sampling used there.

Table 16 Summary methane concentration data for GB.

Area	CH_4 Concentration (µg/L)				Number of samples
	Minimum	***Median***	***Average***	***Maximum***	
UK	<0.05	1.2	45	4,720	439

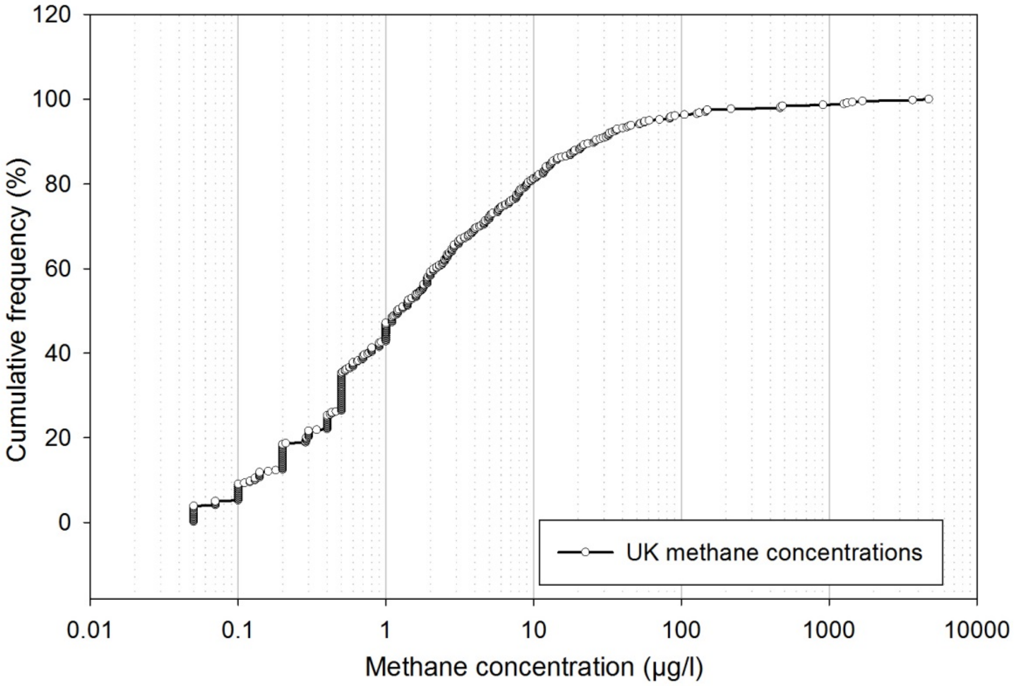

Figure 26 GB methane concentrations.

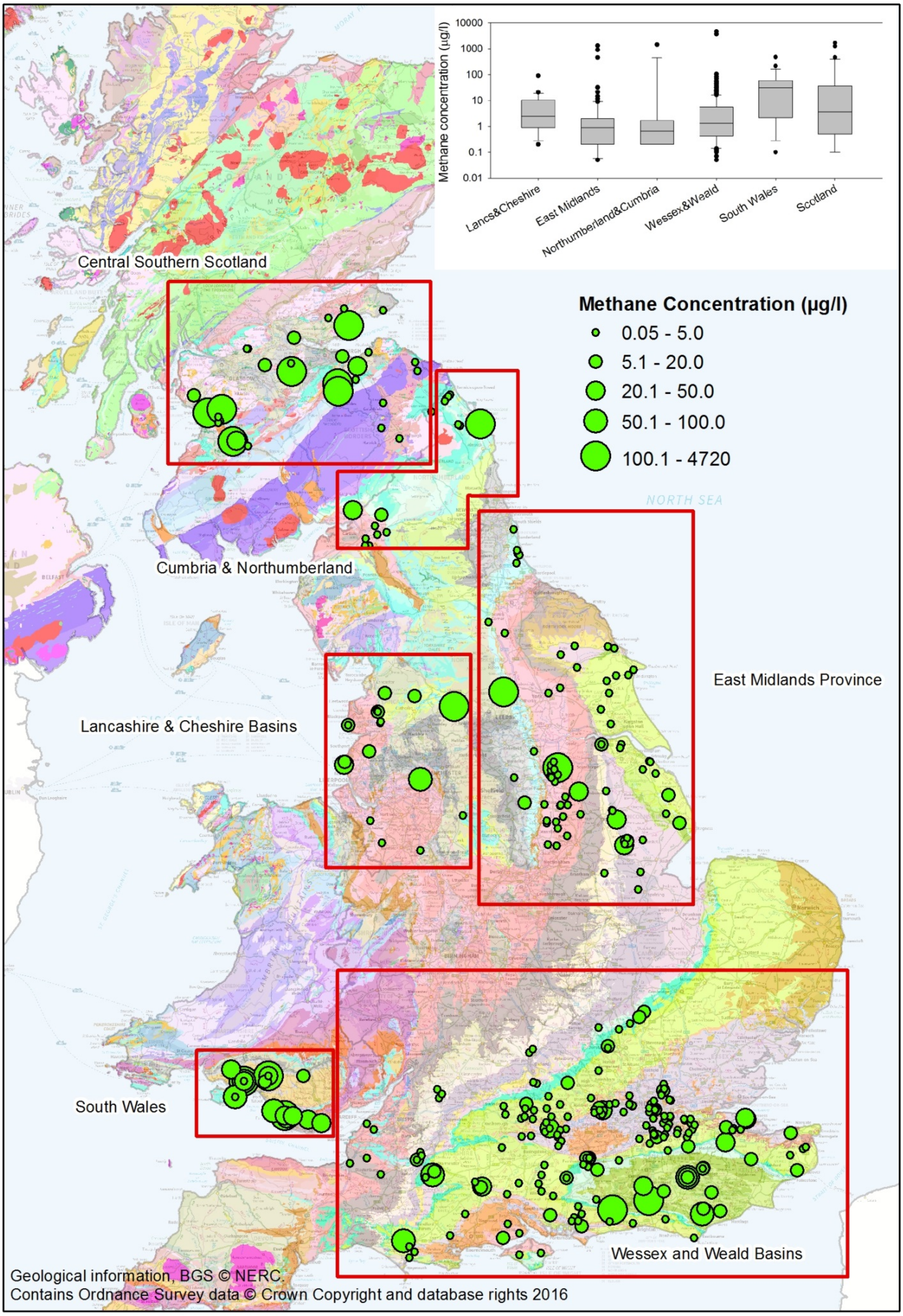

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Figure 27 **Summary methane data for GB.**

5.2 RECOMMENDATIONS FOR FURTHER WORK

Examination of the data collected as part of the Survey has revealed three main knowledge gaps that warrant further research to develop our understanding of methane in groundwater. The first is the need for a comprehensive study into the impact of different sampling methods on dissolved gas concentrations; this is pertinent for the baseline monitoring of methane and other volatile compounds around potential shale gas sites. There is the potential for certain types of pump (in particular, suction-lift pumps) to impact on dissolved gas concentrations; this is a known issue from sampling carried out in contaminated land settings and the potential degassing of Volatile Organic Compounds (VOC's) (Nielsen and Yeates, 1985; Parker, 1994; U.S EPA, 2010). This could also therefore impact on methane concentrations in groundwater. In Halwa (2015), a duplicate sample was also collected using a peristaltic pump, rather than the submersible centrifugal pump, the results of which showed a dramatic reduction in apparent methane concentration. The second area of research is the need for further investigation of the elevated concentrations of methane found in parts of the Weald and Wessex basin, to characterise its spatial distribution and develop an understanding of its source(s). An understanding of this is critical to determine how groundwater chemistry and microbiology are affected by these inputs. Thirdly, there is the need to develop techniques for dissolved methane monitoring at a high frequency, as this will be required to effectively monitor the possible effects shale gas operations on aquifers.

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