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.

<table>
<thead>
<tr>
<th>Area</th>
<th>CH$_4$ Concentration (µg/l)</th>
<th>Number of Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Central Southern Scotland</td>
<td>Minimum 0.1</td>
<td>Median 3.6</td>
</tr>
<tr>
<td>Lancashire &amp; Cheshire Basins</td>
<td>0.2</td>
<td>2.5</td>
</tr>
<tr>
<td>East Midlands Province</td>
<td>Minimum &lt;0.05</td>
<td>Median 0.9</td>
</tr>
<tr>
<td>Southern England</td>
<td>Minimum &lt;0.05</td>
<td>Median 1.3</td>
</tr>
<tr>
<td>South Wales</td>
<td>Minimum 0.1</td>
<td>Median 32</td>
</tr>
<tr>
<td>Cumbria and Northumberland</td>
<td>Minimum 0.2</td>
<td>Median 0.65</td>
</tr>
</tbody>
</table>

* 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 Regional summaries.

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[1]) 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)[2]. The sections below summarise our current understanding of the aquifers sampled and the methane data collected in the various regions.

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[3]). The exploration company Cuadrilla have previous drilled into the Bowland Shale at Preese Hall (Green et al., 2012[4]).

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
The Superficial Deposits are of substantial thickness, up to 40 m, 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[5]) and Manchester and East Cheshire (Griffiths et al., 2003[6]). 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.

<table>
<thead>
<tr>
<th>Lancashire and Cheshire</th>
<th>CH₄ Concentration (µg/l)</th>
<th>Number of Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Minimum</td>
<td>Median</td>
</tr>
<tr>
<td>All samples</td>
<td>0.2</td>
<td>2.5</td>
</tr>
<tr>
<td>Superficial Deposits</td>
<td>0.5</td>
<td>7.2</td>
</tr>
<tr>
<td>Sherwood Sandstone</td>
<td>0.2</td>
<td>1.8</td>
</tr>
</tbody>
</table>

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 6 m 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.
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[3]).

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

<table>
<thead>
<tr>
<th>Midlands/Yorkshire</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cretaceous</strong></td>
</tr>
<tr>
<td>Chalk</td>
</tr>
<tr>
<td>Spilsby Sandstone</td>
</tr>
<tr>
<td>Corallian Limestone</td>
</tr>
<tr>
<td><strong>Jurassic</strong></td>
</tr>
<tr>
<td>West Walton Formation</td>
</tr>
<tr>
<td>Lincolnshire Limestone</td>
</tr>
<tr>
<td><strong>Permian</strong></td>
</tr>
<tr>
<td>Permo-Triassic sandstone (SSG)</td>
</tr>
<tr>
<td>Zechstein Group (Magnesian Limestone)</td>
</tr>
<tr>
<td>Pennine Middle Coal Measures Formation</td>
</tr>
<tr>
<td><strong>Carboniferous</strong></td>
</tr>
<tr>
<td>Millstone Grit Group</td>
</tr>
<tr>
<td>Carboniferous Limestone</td>
</tr>
</tbody>
</table>

*Blue shaded aquifers as designated as Principal aquifers.*
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 430 m 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)\[7\].

A total of 13 samples were collected from the Jurassic Lincolnshire Limestone, the majority from private water supplies. The aquifer is relatively thin (~30 m) 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)\[8\].

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)\[9\]. 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 21 m in Northern England to
35 m 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>
<thead>
<tr>
<th>East Midlands Province</th>
<th>CH$_4$ Concentration (μg/l)</th>
<th>Number of Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Minimum</td>
<td>Median</td>
</tr>
<tr>
<td>All samples</td>
<td>&lt;0.05</td>
<td>0.9</td>
</tr>
<tr>
<td>Cretaceous Chalk</td>
<td>0.07</td>
<td>0.9</td>
</tr>
<tr>
<td>Lincolnshire Limestone</td>
<td>0.05</td>
<td>2.6</td>
</tr>
<tr>
<td>Sherwood Sandstone</td>
<td>&lt;0.05</td>
<td>0.5</td>
</tr>
<tr>
<td>Zechstein Group</td>
<td>0.2</td>
<td>0.4</td>
</tr>
</tbody>
</table>

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)[10] 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 Grit. 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](image-url)  

**Figure 11**  Methane data from the East Midlands Province, dots are proportional to the CH₄ concentration.

**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

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**  Upper and Lower Greensand

**Jurassic**  Greater and Inferior Oolite

**Permian**  Blue Lias — Langport

**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 200 m.

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)\(^\text{[12]}\) and Smedley et al (2003)\(^\text{[13]}\).

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 220 m. 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)\(^\text{[14]}\).

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)\(^\text{[15]}\).

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\(^\text{[16]}\)). 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.

<table>
<thead>
<tr>
<th>Southern England</th>
<th>CH₄ Concentration (µg/L)</th>
<th>Number of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>All samples</td>
<td>Minimum: &lt;0.05  Median: 1.3  Average: 39  Maximum: 4,720</td>
<td>251</td>
</tr>
<tr>
<td>Chalk</td>
<td>Minimum: &lt;0.05  Median: 0.5  Average: 3.6  Maximum: 83</td>
<td>137</td>
</tr>
<tr>
<td>Greensand</td>
<td>Minimum: &lt;0.05  Median: 4.9  Average: 8.0  Maximum: 105</td>
<td>54</td>
</tr>
<tr>
<td>Hastings Subgroup</td>
<td>Minimum: 0.4  Median: 19  Average: 461  Maximum: 4,720</td>
<td>19</td>
</tr>
<tr>
<td>Oolites</td>
<td>Minimum: &lt;0.1  Median: 0.5  Average: 1.3  Maximum: 7.6</td>
<td>12</td>
</tr>
</tbody>
</table>
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[17]) 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[17]). 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[18]). 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.
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 14** Methane concentrations in Southern England.
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 425 m. All the samples collected from this aquifer as part of the Survey were from Natural Resources Wales monitoring boreholes.
<table>
<thead>
<tr>
<th>South Wales</th>
<th>CH₄ Concentration (µg/L)</th>
<th></th>
<th></th>
<th></th>
<th>Number of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>All samples</td>
<td>Minimum</td>
<td>Median</td>
<td>Average</td>
<td>Maximum</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>&lt;0.10</td>
<td>32</td>
<td>58</td>
<td>483</td>
<td></td>
</tr>
<tr>
<td>Coal Measures</td>
<td>&lt;0.10</td>
<td>34</td>
<td>53</td>
<td>216</td>
<td>13</td>
</tr>
<tr>
<td>Carboniferous Limestone</td>
<td>&lt;0.10</td>
<td>32</td>
<td>69</td>
<td>483</td>
<td>11</td>
</tr>
</tbody>
</table>

**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 than 100µg/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 **Temporal variation in methane concentrations**.
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-bededded 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.
Table 11    Stratigraphy of aquifers in the Carlisle Basin and Northumberland Trough.

**Carlisle Basin and Northumberland Trough**

*Perman-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 600 m 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 300 m 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[19]).
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.

<table>
<thead>
<tr>
<th></th>
<th>CH(_4) Concentration (µg/L)</th>
<th>Number of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Minimum</td>
<td>Median</td>
</tr>
<tr>
<td>All samples</td>
<td>&lt;0.2</td>
<td>0.65</td>
</tr>
<tr>
<td>Sherwood Sandstone</td>
<td>&lt;0.2</td>
<td>0.8</td>
</tr>
<tr>
<td>Carboniferous Sandstone</td>
<td>&lt;0.2</td>
<td>0.6</td>
</tr>
</tbody>
</table>

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.

**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)[22]. 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

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 500 m in southern Scotland to 3,000 m 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[21]).

Table 14  Summary results for Central-Southern Scotland.

<table>
<thead>
<tr>
<th>Central-Southern Scotland</th>
<th>CH₄ Concentration (µg/L)</th>
<th>Number of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>All samples</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Carboniferous aquifers</td>
<td>&lt;0.1</td>
<td>4.6</td>
</tr>
</tbody>
</table>

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[10]). 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.
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.

<table>
<thead>
<tr>
<th>Region</th>
<th>Aquifers sampled quarterly</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lancashire &amp; Cheshire Basin</td>
<td>Superficial Deposits, Sherwood Sandstone, Chalk</td>
</tr>
<tr>
<td>East Midlands Province</td>
<td>Sherwood Sandstone, Zechstein Group</td>
</tr>
<tr>
<td>South Wales</td>
<td>Coal Measures, Carboniferous Limestone, Barton Group, Chalk, Lower Greensand, Tunbridge Wells Sand</td>
</tr>
<tr>
<td>Southern England</td>
<td>Ashdown Formation, Sherwood Sandstone, Carboniferous Limestone and Inferior Oolite, Dolomitic conglomerate/Carboniferous Limestone</td>
</tr>
</tbody>
</table>
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.

**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[26]; Parker, 1994[27]). 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[28]). 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.

References


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- OR/15/071 The baseline concentrations of methane in Great British groundwater - the National Methane Baseline survey