

Monitoring of methane in groundwater from the Vale of Pickering, UK: Temporal variability and source discrimination

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ABSTRACT

Groundwater abstracted from aquifers in the Vale of Pickering, North Yorkshire, UK and monitored over the period 2015–2022, shows evidence of variable but commonly high concentrations of dissolved CH₄. Sampled groundwater from the Jurassic organic-rich Kimmeridge Clay Formation (boreholes up to 180 m depth) has concentrations up to 57 mg/L, and concentrations up to 59 mg/L are found in groundwater from underlying confined Corallian Group limestone (borehole depths 50–227 m). The high concentrations are mainly from boreholes in the central parts of the vale. Small concentrations of ethane (C₂H₆, up to 800 µg/L) have been found in the Kimmeridge Clay and confined Corallian groundwaters, and of propane (C₃H₈, up to 160 µg/L) in deeper boreholes (110–180 m) from these formations. The concentrations are typically higher in groundwater from the deeper boreholes and vary with hydrostatic pressure, reflecting the pressure control on CH₄ solubility. The occurrences contrast with groundwater from shallow Quaternary superficial deposits which have low CH₄ concentrations (up to 0.39 mg/L), and with the unconfined and semi-confined sections of the Corallian aquifer (up to 0.7 mg/L) around the margins of the vale. Groundwater from the Quaternary, Kimmeridge Clay formations and to a small extent the confined Corallian aquifer, supports local private-water supplies, that from the peripheral unconfined sections of Corallian also supports public supply for towns and villages across the region.

Dissolved methane/ethane (C1/C2) ratios and stable-isotopic compositions ($\delta^{13}\text{C-CH}_4$, $\delta^2\text{H-CH}_4$ and $\delta^{13}\text{C-CO}_2$) suggest that the high-CH₄ groundwater from both the Kimmeridge Clay and confined Corallian formations derives overwhelmingly from biogenic reactions, the methanogenesis pathway by CO₂ reduction. A small minority of groundwater samples shows a more enriched $\delta^{13}\text{C-CH}_4$ composition (–50 to –44 ‰) which has been interpreted as due to anaerobic or aerobic methylotrophic oxidation in situ or post-sampling oxidation, rather than derivation by a thermogenic route.

Few of the existing groundwater sites are proximal to abandoned or disused conventional hydrocarbon wells that exist in the region, and little evidence has been found for an influence on groundwater dissolved gases from these sites. The Vale of Pickering has also been under recent consideration for development of an unconventional hydrocarbon (shale-gas) resource. In this context, the monitoring of dissolved gases has been an important step in establishing the high-CH₄ baseline of groundwaters from Jurassic deposits in the region and in apportioning their sources and mechanisms of genesis.

1. Introduction

Investigations of the occurrence and distributions of CH₄ in groundwater have long been carried out in the context of landfills, mine gas and tunnel safety. In recent years, many studies have also focused on the occurrence and mobility of CH₄ in groundwater in response to

hydraulic fracturing and the unconventional hydrocarbons industry. In North America where shale-gas extraction is an established industry, increased CH₄ concentrations have been linked with such activities. Methane is seen as a key potential contaminant (Osborn et al., 2011), as are compounds present in hydraulic fracture fluids (e.g. Jackson et al., 2013; Lewelllyn et al., 2015; Osborn et al., 2011). However, without a

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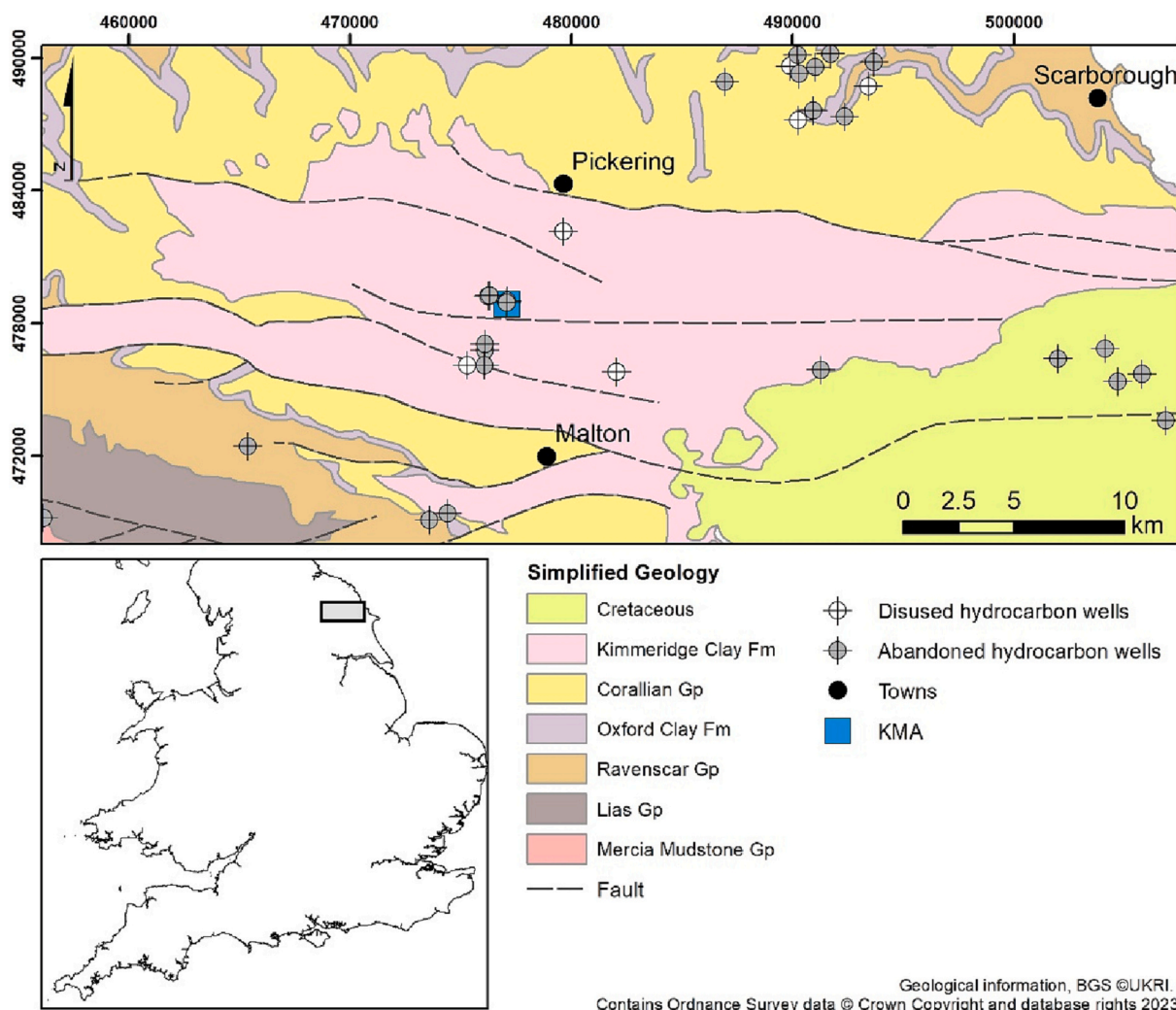


Fig. 1. Bedrock geology of the Vale of Pickering showing faults, locations of former conventional hydrocarbon wells and the KMA (Kirby Misperton A) site which hosts a conventional hydrocarbon well and unconventional hydrocarbon exploration well; inset map of study location also given.

thorough understanding of the baseline conditions pertaining in an aquifer before shale-gas development takes place, proving an unequivocal link is difficult. Hence the recognised need to measure CH₄ and other dissolved gases, along with other diagnostic solutes and indicators, to establish baselines and to set against any future changes. This provides the context for recent investigations of CH₄ in groundwater in regions of the UK.

The development of a shale-gas industry in the UK has long been the subject of controversy (Mackay and Stone, 2013; The Royal Society and The Royal Academy of Engineering, 2012). Arguments in favour of development have cited the potential to provide greater national energy security, those against cite the environmental cost of fossil-fuel proliferation, degradation of groundwater and air quality and induced seismic activity (Jackson et al., 2014; Vidic et al., 2013), as well as financial cost (Cooper et al., 2018) and uncertainties over the viability of the resource (Whitelaw et al., 2019). Concerns for groundwater quality include uncertainty over contamination with solutes and gases from deep rock formations through faulty well casings, deep reactivated faults and surface spills.

The last 15 years or so have seen large changes in the fortunes of the nascent shale-gas industry in the UK. There have been in total nine applications for shale-gas exploration in England since 2014. In 2016, two operators held licences for shale-gas exploration in England. These were for sites at Preston New Road (Lancashire) and Kirby Misperton, Vale of

Pickering (North Yorkshire). Approval for high-volume hydraulic fracturing at Kirby Misperton (Fig. 1) stalled in January 2018 pending a requirement for the operator to report its financial resilience to government. Subsequent sale of the operator's onshore business signalled a change in direction with the new operator moving from unconventional hydrocarbons towards geothermal exploration in the Vale of Pickering. To date (July 2023), wells at only two sites in England (Preese Hall and Preston New Road in Lancashire) have undergone exploration hydraulic fracturing. At each, operations ceased because of concerns from, or threshold exceedances of, induced seismicity. Seismicity concerns led to the imposition in November 2019 of a moratorium on hydraulic fracturing for shale gas in England. This placed England in line with existing moratoria imposed in Wales and Scotland and a similar position proposed for Northern Ireland. Following significant increases in global gas prices in 2022 and with two changes of UK prime minister, the moratorium on high-volume hydraulic fracturing in England was lifted briefly in September 2022, but reinstated a month later. No valid exploration licences for shale gas currently exist in England and the prospect for future shale-gas exploration looks unlikely.

Against this backdrop, in 2015 the British Geological Survey (BGS) began an investigation of groundwater quality in the aquifers of the Vale of Pickering, North Yorkshire, one of the two areas then earmarked for shale-gas exploration. Groundwater monitoring continued there until 2021, with minor targeted measurements in 2022. The investigation

formed part of a wider environmental baseline monitoring programme, including air quality, seismicity, soil gas and ground motion (Ward et al., 2017). This was independent of the shale-gas operator's statutory environmental monitoring activities at and around the Kirby Misperton (KMA) exploration site (Raper et al., 2022).

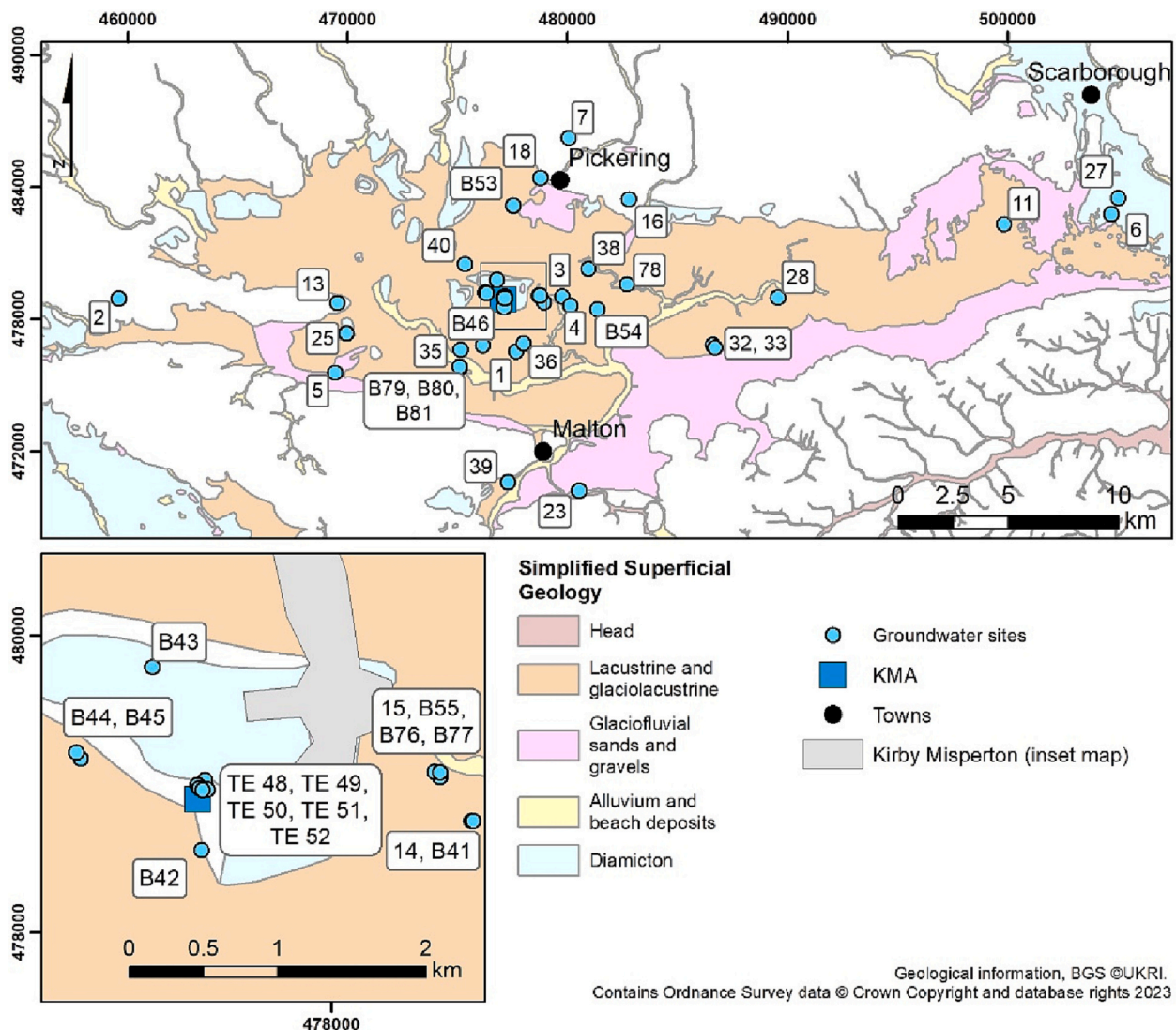
This paper concerns the baseline characterisation of dissolved methane in groundwater from the shallow aquifers (≤ 60 m depth) of the Vale of Pickering, which comprise minor superficial Quaternary deposits and Jurassic strata of the Kimmeridge Clay Formation and Corallian Group. Some deeper boreholes in the Kimmeridge Clay (to 180 m depth) and Corallian which underlies the Kimmeridge Clay Formation are also represented (to 227 m depth). The KMA site and surrounding parts of the Vale of Pickering have existing disused or abandoned conventional gas extraction boreholes, with past activities at some sites spanning >20 years. As such, groundwater quality is discussed here in the context of a baseline with respect to hydraulic fracturing rather than a pristine natural and pre-industrial condition.

2. Methane sources and hazard

Observed concentrations of methane in groundwater are low, in the $\mu\text{g/L}$ or sub $\mu\text{g/L}$ range, under oxic and sub-oxic conditions (Deirmendjian et al., 2019; Jurado et al., 2018). Concentrations may be

higher under strongly reducing (low- SO_4 , anoxic) conditions (Whiticar, 1999; Zhang et al., 1998), and may reach the mg/L range. Solubility in water is a function of temperature, partial pressure and salinity. In pure water, solubility reaches around 28 mg/L at 25°C , 1 bar pressure; 32 mg/L at 10°C , 1 bar; and some 175 mg/L at 25°C , 5 bar at equilibrium (Duan and Mao, 2006). Degassing from groundwater will occur on increasing temperature and/or reduction of partial pressure as water is pumped to the surface. An aqueous concentration in equilibrium with atmospheric CH_4 (1910 ppb, Dlugokencky, 2022) would be ca. $0.06 \mu\text{g/L}$ at 10°C (Henry's Law constant from Wilhelm et al., 1977), consistent with the typical ranges observed in shallow oxic groundwaters.

Methane gas is known to form naturally via distinct biogenic or thermogenic pathways, the former in near-surface environments (e.g. peat bogs, wetlands, other organic-rich sediments) via activity of methanogenic archaea, the latter at depth by thermally-activated breakdown of larger organic molecules (kerogen, crude oil) (Stolper et al., 2015; Whiticar et al., 1986), associated with hydrocarbon sources and reservoirs. Methanogenic microorganisms produce methane via fermentation of acetate (or formate, ethanol, benzoate) or via CO_2 reduction by H_2 (Whiticar, 1999; Whiticar et al., 1986). Methanogenic microorganisms and SO_4 -reducing bacteria have been found to coexist in SO_4 -reducing conditions, although SO_4 -reducing bacteria out-compete for acetate or H_2 and restrict CH_4 production (Lovley and Chapelle,



1995; Lovley et al., 1982; Whiticar et al., 1986).

Biogenic and thermogenic origins of CH₄ have been well-categorised by the C1/C2+ gas ratio (CH₄/C₂H₆ and higher alkanes) or simple C1/C2 ratio, and by analysis of stable-isotopic signatures of CH₄ ($\delta^{13}\text{C-CH}_4$ and $\delta^2\text{H-CH}_4$). However, the hydrocarbon ratios and isotopic compositions are prone to alteration by in-situ aerobic or anaerobic CH₄ oxidation reactions, controlled by gas diffusion rates and microbial activity (Alperin and Hoehler, 2009; Kuloyo et al., 2020; Tyler et al., 1994; Whiticar, 1999; Zhang et al., 1998). Oxidation of CH₄ is known to result in a preferential loss of the lighter C and H isotopes and enrichment of the isotopic compositions of the residual CH₄ (Vigneron et al., 2017; Whiticar, 1999). Methane oxidation has commonly been attributed to coupled SO₄ reduction under anaerobic conditions (Alperin and Hoehler, 2009; Alperin and Reeburgh, 1985; Timmers et al., 2016). Generation of microbial CH₄ by alteration of primary thermogenic CH₄ has also been documented in petroleum reservoirs (Milkov and Etiope, 2018; Pearce et al., 2023).

For parts of the UK, observed concentrations of dissolved methane in shallow groundwater have been reported in the range <0.00005–4.7 mg/L (343 samples), though 96% were <0.1 mg/L (Bell et al., 2017). A concentration of 2.3 mg/L was reported for groundwater from an unused observation borehole in confined Jurassic Lincolnshire Limestone from eastern England (ca. 90 m depth) (Bishop and Lloyd, 1990); a concentration of 7.8 mg/L was also reported in groundwater from a 2 km deep geothermal well (75 °C) in the Sherwood Sandstone of southern England (Darling and Goody, 2006).

Elsewhere, much higher concentrations have been reported in groundwater from deep and/or organic-rich formations. In North America especially, large numbers of studies of drinking-water aquifers overlying areas of unconventional and conventional hydrocarbons have identified large concentration ranges of methane in groundwater. Osborn et al. (2011) reported concentrations up to 64 mg/L in groundwater from drinking-water wells above Marcellus and Utica shales in north-eastern Pennsylvania and upstate New York, USA. Molofsky et al. (2013) reported a range of <0.00005–43 mg/L for groundwaters from a similar area in north-eastern Pennsylvania. Concentrations of <0.001–28 mg/L were found in private-supply wells in aquifers overlying the Eagle Ford, Fayetteville and Haynesville shale plays of Texas, Arkansas and Louisiana (McMahon et al., 2017). A range of <0.0006–46 mg/L was found in groundwater from public and private supply wells (depths 6–120 m) overlying Utica shale in St Lawrence Lowlands, Quebec, Canada (Moritz et al., 2015). Groundwater from the Los Angeles Basin had a reported range of 0.002–150 mg/L (the highest from a borehole at 466 m depth) (Kulongoski et al., 2018). Also, concentrations in the range 0.001–23 mg/L were found in shallow groundwater from Texas overlying Barnett Shale (Wen et al., 2016). The high observed methane concentrations have been variably associated with influx of deep stray thermogenic gases from shale (Osborn et al., 2011), derivation of thermogenic or mixed compositions from other strata (e.g. Devonian formations, Molofsky et al., 2013; Wen et al., 2016) or generation of biogenic methane by shallow in-situ reactions (Kulongoski et al., 2018; McMahon et al., 2017).

Methane is a greenhouse gas. It is not toxic but is an asphyxiant in air at high concentrations. It also constitutes an explosion hazard in the approximate range 5–15% v/v in air. Release of CH₄ into confined spaces can therefore pose a safety hazard. For groundwater, the state of Pennsylvania, USA, has imposed an action level for dissolved CH₄ of 7 mg/L in recognition of this potential degassing hazard. The US Department of the Interior also offers advice to US residents for further investigation at dissolved concentrations >10 mg/L and action to reduce concentrations at >28 mg/L. Several US states have also adopted a threshold of 10 mg/L for CH₄ in water supplies for reporting to the regulator and potential action (Molofsky et al., 2021). Similar precautions for UK water-supply boreholes are appropriate, along with precautions against installations involving confined spaces where high CH₄ concentrations occur.

3. Regional setting

The Vale of Pickering, North Yorkshire, is an east-west-trending graben structure which forms part of the Cleveland Basin of north-east England (Williams, 1986). The vale is fault-bounded and defined by the east-west Asenby–Coxwold–Gilling graben, Helmsley–Filey fault belt and the Howardian–Flamborough fault belt (Powell, 2010). The Vale of Pickering forms a flat-lying plain with an elevation of <60 m OD, bounded by the lower slopes of the North York Moors to the north, the Howardian and Hambleton Hills to the south-west, and to the south by the escarpment of the East Yorkshire Wolds (Fig. 1). At its eastern extremity, the plain is cut off from the sea by moraine (Wilson, 1948). The Vale of Pickering forms the catchment of the River Derwent. Land use is dominated by arable farming, the clay-rich soils supporting mostly cereal crops in the west and root crops and oil seed rape in the east (Bearcock et al., 2015).

Quaternary superficial deposits cover much of the plain especially in the eastern part (Fig. 2). The sediments are predominantly of Late Devensian lacustrine origin, with alluvial fan deposits at the margins. Much of this material was deposited by a former proglacial lake, Lake Pickering, which occupied the plain during the Devensian until ice retreat some 10,000 years ago (Evans et al., 2017). These sediments are of variable thickness, typically up to 40 m thick (Ford et al., 2015), but are thin or absent around the north-west of the plain, and around Kirby Misperton in the central part (Ward et al., 2017). Isolated patches of till occupy topographic highs near Kirby Misperton and around the northern margins of the plain. Discontinuous lenses of sand and gravel occur elsewhere within the Quaternary sediments (Ford et al., 2015) (Fig. 2). The Quaternary sediments are underlain by thick deposits of marine Jurassic strata.

On the valley floor, uppermost Jurassic deposits comprise the Upper Jurassic Kimmeridge Clay Formation. The northern boundary, defined by the Helmsley–Filey fault, has a downthrow of around 150 m on the south wall (Williams, 1986). Kimmeridge Clay thicknesses vary due to faulting, but some 305 m of organic-rich mudstone of the Kimmeridge Clay Formation was proved in the Fordon No 1 borehole [505,834 475,713] (Powell, 2010). The Kimmeridge Clay is marine, formed in a shelf sea (Gallois, 2021) during a major transgression that began in the Callovian (Powell, 2010). The formation is dominated by mudstone, with grey calcareous mudstone and black fissile organic-rich units and occasional siltstone. Occurrences of pyrite or weathered gypsum are sporadic (Cope, 1974). The strata are consistent with deposition in anoxic bottom-water conditions. Kerogen, mainly of type II marine algal origin (Herbin et al., 1991), is abundant in the Kimmeridge Clay of the Cleveland Basin, with high organic content even in the calcareous horizons, although vitrinite reflectance measures (0.39–0.51%R_o) (Williams, 1986) suggest that organic horizons are immature for hydrocarbon production and burial history too shallow for oil production (Powell, 2010; Williams, 1986). Reconstruction of burial history (Williams, 1986) has suggested burial of the Kimmeridge sequence to a depth of around 1.8 km by the Palaeogene, insufficient for extensive oil generation. A 48 m thickness of mudstone with sideritic nodules, equivalent to the Ampthill Clay Formation of southern England, underlies the Kimmeridge Clay Formation in the Vale of Pickering (Powell, 2010).

The Upper Jurassic mud-dominated deposits signalled a rise in sea level which drowned a pre-existing shallow marine carbonate platform that had controlled the deposition of the Corallian Group. Depth of deposition of the Kimmeridge Clay was likely in the range 50–200 m (Gallois, 2004).

Upper Jurassic (Oxfordian) limestones of the Corallian Group total some 70–150 m thick in the area. These are found at outcrop in areas including the Hambleton Hills, the Howardian Hills, and the North York Moors and form the northern and south-western boundaries of the Vale of Pickering (Newell et al., 2016; Tattersall and Wilkinson, 1974) (Fig. 1). The Corallian Group formed in a shallow epeiric sea with a

carbonate platform, interrupted by periods of clastic supply (Wright, 2009). The sequence comprises the Upper Calcareous Grit (12–15 m thick), the Coralline Oolite Formation (60–70 m thick) and Lower Calcareous Grit (22–50 m thick). The Upper Calcareous Grit is a sand-dominant unit, with silt, marl and clayey micritic limestone, formed in nearshore to offshore conditions during a period of rising sea level. The underlying Coralline Oolite strata comprise grey, ooidal limestone and buff-yellow, fine calcareous sandstone, with additional micritic limestone (Powell, 2010), with minor horizons of mud, oolite, bioclastic limestone and interbeds of silt and sand (Cope, 2006; Reeves et al., 1978; Wright, 2009). The Coralline Oolite formed during marine regressive (sea-level lowstand) conditions. The Lower Calcareous Grit formed in shallow offshore conditions and comprises yellow calcareous sandstone with ooidal limestone and beds of chert. Beneath the valley floor, the Corallian underlies the Kimmeridge Clay Formation, its top reaching depths down to 295 m in sections due downfaulting (Kent, 1980).

Underlying the Corallian Group, the Oxford Clay of Oxfordian age comprises 0–44 m of grey-green silty mudstone and calcareous mudstone and siltstone, also deposited under marine transgressive conditions (Powell, 2010). In cores from Scarborough, the Oxford Clay is described as a grey calcareous siltstone and silty mudstone with berthierine ooids and pyritised and/or limonitised burrows, formed in a lower shoreface depositional environment (Powell and Riding, 2016). The Oxford Clay is underlain in turn by the sandstone-dominated Callovian Osgodby Formation, described as a bioturbated, lower to upper shoreface, silty sandstone deposit (Powell and Riding, 2016).

The permeable units of the Quaternary and underlying Kimmeridge Clay deposits are exploited by small-scale groundwater abstractions for agricultural and domestic use, albeit not for drinking water. Local sandy horizons and weathered sections at the interface with the lacustrine deposits can host locally important supplies of groundwater. Some of the boreholes lack logs and others have insufficiently detailed logs to be able to distinguish units, so in a few cases screened or open-hole depths and lithologies are unclear. Rest-water levels in these units are deepest (up to around 40 m) towards the north-west of the plain, and flow follows the surface drainage, that from the central part flowing southwards towards the lower part of the River Derwent catchment (Tattersall and Wilkinson, 1974; Ward et al., 2017) (Fig. 2). Several boreholes in the central part of the vale are artesian (Sites 1, 3, 4, 36, 38, 54 and 78).

Major extensional faulting during the Jurassic to Cenozoic has resulted in a number of east-west normal faults across the Vale of Pickering (Fig. 1). Extensional faulting started in the mid Oxfordian, and continued into the Cretaceous, with some reactivation during the Cenozoic (Wright, 2009). Block faulting has resulted in large variations in the depths of the Cenozoic and older formations across different blocks.

The Corallian Group at outcrop and subcrop is defined as a principal aquifer and is used for public and private drinking-water supply, agriculture and industry. Beneath the plain, the aquifer is confined and the depth and brackish chemistry preclude its use for water supply. Deep confined Corallian boreholes in the central low-lying part of the plain are also artesian.

The Vale of Pickering has a recent history of conventional hydrocarbon development, with around 10 disused or abandoned wells located in the Vale of Pickering and further wells beyond the periphery (Fig. 1). These extracted gas from the reservoir rock of the Zechstein Kirkham Abbey Formation (Haarhoff et al., 2018). The location of the former planned unconventional (shale-gas) exploration borehole, KM8, is co-located with one of these conventional wells at the KMA site in Kirby Misperton (Fig. 1). KM8 was drilled by Third Energy in 2013. The topmost part of this vertical borehole penetrates Quaternary lacustrine sediments and Kimmeridge Clay, with the top of the Corallian Group located at 190 m depth. The top of the Kirkham Abbey Formation is located at 1300 m and the borehole terminates at 3110 m in the Viséan Lower Bowland Shale.

4. Methods

4.1. Groundwater survey design

A groundwater monitoring network consisting of three pre-existing third-party boreholes penetrating to the Quaternary lacustrine deposits, 12 into the Kimmeridge Clay and 10 to the Corallian Group was established across the Vale of Pickering and periphery in 2015 (Fig. 2). For boreholes where drillers' logs were not available and borehole depths and lithology were uncertain, best estimates were made of likely aquifer completion based on evidence from local geology, borehole age and landowner knowledge.

The third-party boreholes were supplemented in 2016 by eight newly-drilled boreholes into the Kimmeridge Clay Formation, located mostly within 2 km of the KM8 hydrocarbon exploration borehole (Fig. 1) (Smedley et al., 2015). These were all 30 m or less total depth, with typically ca. 3 m of screened section in the lower part of the borehole. In addition, five water monitoring boreholes installed at KMA in 2015 by the shale-gas operator (Third Energy) were monitored from 2016. These consist of three shallow boreholes (11.5 m depth: BHA, BHB, BHC) to target the shallowest parts of the weathered Kimmeridge Clay, one intermediate (38 m depth: BHD) to target deeper sections of the Kimmeridge Clay, and one deep (ca. 220 m: BHE) to target the upper section of limestone of the Corallian Group. Full details of borehole construction are given by Envireau Water (2017).

The 33 boreholes were each monitored monthly for a year initially, and mostly quarterly thereafter until monitoring stopped in 2020–2022 (varying for different sites). A further two piezometers were installed into a borehole in the deeper Kimmeridge Clay (130 m, 180 m) and three further boreholes, one containing two piezometers, were installed into the confined part of the Corallian (50–150 m depth) in the central part of the plain for occasional sampling.

4.2. Groundwater sampling and analysis

At each site, groundwater was pumped using either a dedicated pump if installed, or mobile submersible pump or, in the case of the operator boreholes, dedicated bladder pump. Each site was sampled using the same pump type and procedure on each monitoring round. The only exception was for six pre-2017 samples collected from Site 15, where the pump was deployed in error at 20 m depth in contrast to the more usual chosen depth of 30 m. At each site, pumped groundwater was monitored until stable readings were obtained for temperature, pH, redox potential, dissolved oxygen and specific electrical conductance, each measured in a flow cell. The monitoring before sampling took typically 30–60 min at each site. Samples for analysis of dissolved gases (CH_4 , CO_2 and C_2H_6) were collected after completion of sampling for groundwater chemistry. Additional samples for dissolved-gas analysis were collected in 2016 from Site 15 at the start of pumping as well as at the end in order to check for pumping-related variability.

Dissolved-gas samples were collected via a tube with a gas-tight connection to the well head or pump outlet. Samples were collected into doubled-valved steel cylinders (47 to 55 cm^3 capacity) at pump pressure with care taken to avoid degassing in the tubing (Bell et al., 2017). Higher alkanes were not investigated.

Groundwater samples for analysis of $\delta^{13}\text{C}\text{-CH}_4$ and $\delta^2\text{H}\text{-CH}_4$ were collected at a selected number of sites during the course of the monitoring. Two different methods and laboratories were used for measurement of $\delta^{13}\text{C}\text{-CH}_4$. In the earlier stages of monitoring (pre-2019), groundwater samples for $\delta^{13}\text{C}\text{-CH}_4$ analysis were collected by filling a sample bottle submerged within an overflowing container and crimping a septum cap on top. From 2019, samples for both C and H isotopic analysis were collected into glass bottles with septum screwcap. To avoid air entry and maintain back pressure, two needles were inserted into the septum, one connected to the water pump outlet, the other used as an exit. The bottle was flushed through before slowly removing the

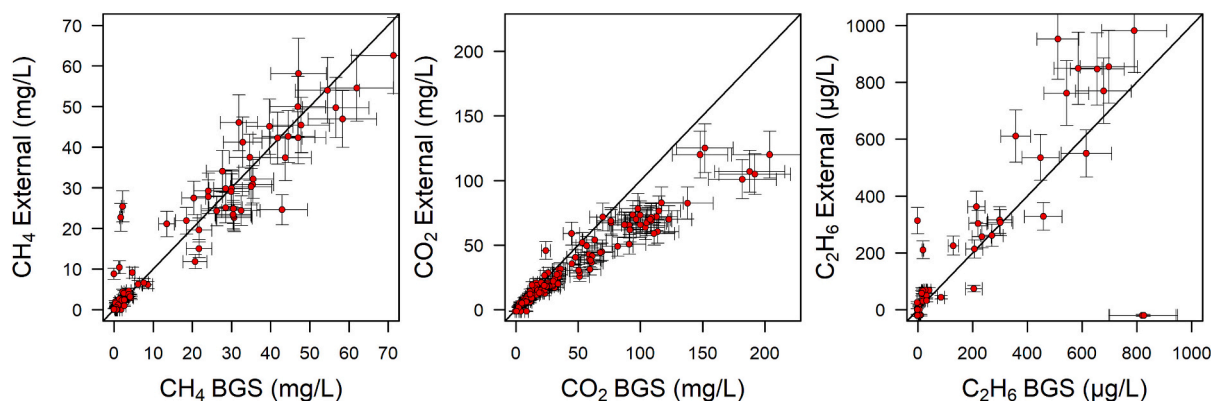


Fig. 3. Comparison between dissolved gas compositions (CH_4 , CO_2 , C_2H_6) from two laboratories (BGS and external laboratory: ALS Ltd) with uncertainty (15% expanded) and 1:1 line.

exit needle followed by the entrance needle. All bottles were transported in a cool box before refrigeration in the laboratory.

Samples for dissolved-gas analysis were transported to the BGS Wallingford laboratory for analysis by headspace gas chromatography (GC). This involved transfer of the water and gas from the steel cylinder to an evacuated glass bulb of known capacity (range 117–123 cm^3) using GC helium. Aliquots of the headspace gas were expanded into the evacuated inlet system of the GC and introduced to a Porapak-Q packed column at room temperature to February 2019 and 100 °C thereafter. CH_4 and C_2H_6 were detected by flame-ionisation detector (FID) and CO_2 by thermal conductivity detector (TCD). The detection limits for dissolved CH_4 were ca 1 $\mu\text{g/L}$, CO_2 ca. 1 mg/L and C_2H_6 ca. 1 $\mu\text{g/L}$. Canned gas standards (Air Products Ltd., in decadal steps from 100 ppm to 10% CH_4) were used for calibration. Measurement precision for CH_4 is estimated to be $\pm 5\%$ RSD. Details are provided in Darling and Milne (1995).

Pre-2019 samples for $\delta^{13}\text{C}\text{-CH}_4$ analysis were measured by Hall Analytical Laboratories Ltd., UK, by isotope ratio mass spectrometry (IRMS). These samples were not analysed for $\delta^2\text{H}\text{-CH}_4$. Samples for both $\delta^{13}\text{C}\text{-CH}_4$ and $\delta^2\text{H}\text{-CH}_4$ analysis from 2019 were analysed by the NERC Environmental Isotope Facility at BGS, Keyworth, also by IRMS. Each laboratory measured concentrations of dissolved CH_4 by helium displacement and GC detection beforehand. Analysis of $\delta^{13}\text{C}\text{-CH}_4$ by Hall laboratory involved manual syringe injection of an aliquot from the equilibrated helium layer into the IRMS, with internal calibration using a CO_2 reference gas and analysis in duplicate (averaged). Analysis of $\delta^{13}\text{C}\text{-CH}_4$ at the Keyworth laboratory was performed using a Sercon

20–22 Continuous-Flow (CF) IRMS coupled to a Sercon CryoGas sample preparation module, using a method reported by Smith et al. (2021). Gas samples were introduced to the CryoGas via a Cetac ASX-7400 autosampler in a flow of laboratory-grade (99.9%) helium. Any CO , H_2O and CO_2 were removed using a series of cryogenic and chemical traps, before combustion of CH_4 to CO_2 and H_2O . H_2O and non-condensable gases such as O_2 and N_2O were removed before passing the sample via GC column to the 20–22 CF-IRMS. Analysis of $\delta^2\text{H}\text{-CH}_4$ was undertaken in the same way but with a slightly modified configuration. Sample gas was introduced via the Cetac autosampler with removal of CO_2 and H_2O and then pre-concentrated using Hayesep D and GS-Q GC columns, each held at liquid-nitrogen temperature (-196 °C). These concentrated the sample CH_4 and enabled less-condensable gases to pass. The pre-concentrated CH_4 was then passed through a pyrolysis furnace to retain C and H detected by 20–22 CF-IRMS. All carbon isotopic values are reported relative to Vienna-PDB and hydrogen relative to Vienna-SMOW. Typical precision for Keyworth analyses is <0.3 ‰ and <3.0 ‰ for $\delta^{13}\text{C}\text{-CH}_4$ and for $\delta^2\text{H}\text{-CH}_4$ respectively (Smith et al., 2021). Fewer analyses of $\delta^2\text{H}\text{-CH}_4$ were determined as the laboratory method was set up more recently than for $\delta^{13}\text{C}\text{-CH}_4$.

Additional samples were collected for analysis of dissolved gases by a commercial laboratory (ALS Ltd., Hawarden, UK) during the final four regular groundwater monitoring rounds in order to check reproducibility. Samples for these were collected at approximately the same time as the inline steel cylinder samples by filling to the brim 40 mL glass vials with septum lids. These were transported on ice in a cool box to the

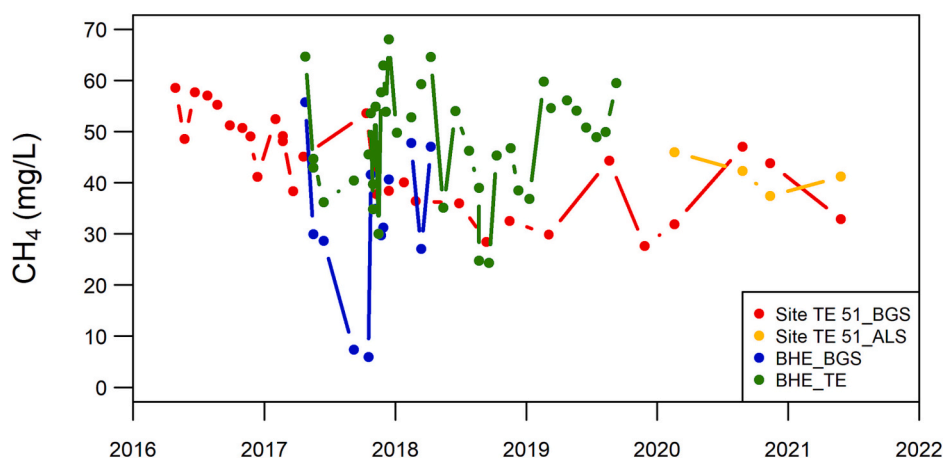


Fig. 4. Comparison of monitoring data for dissolved methane in groundwater from Site TE 51 (BHE), Kirby Misperton; Site TE51_BGS data are BGS samples and analyses; Site TE51_ALS are BGS samples analysed by ALS laboratory; Site BHE_BGS are Third Energy samples analysed by BGS; Site BHE_TE are Third Energy samples and analyses.

Table 1

Summary data for monitoring of dissolved CH₄, CO₂ and C₂H₆ in groundwater from borehole sites in the Quaternary, Kimmeridge Clay and Corallian aquifers, Vale of Pickering, determined in the BGS laboratory.

Site	No.	CH ₄ (mg/L)				CO ₂ (mg/L)				C ₂ H ₆ (µg/L)			
		ncens	min	Mean	max	ncens	min	mean	max	ncens	min	mean	max
<i>Quaternary</i>													
Site 5	26	0	0.0026	0.0642	0.387	0	3.6	33.9	61.3	26	<2		<2
Site 32	30	2	<0.0005	0.0239	0.291	0	9.0	12.5	16.7	30	<2		<2
Site 33	30	1	<0.0005	0.0294	0.365	0	8.5	14.7	60.3	30	<2		<2
<i>Kimmeridge Clay</i>													
Site 1	25	0	0.00029	0.033	0.332	0	13	29.6	43.4	25	<2		<2
Site 3	29	0	2.49	4.02	5.81	0	2.8	9.15	140	2	<1	7.85	19
Site 4	32	0	0.011	0.496	0.759	0	7.7	12.4	42.5	28	<0.5		3.0
Site 14	26	1	<0.0005	1.37	2.70	0	16.6	35.7	57.0	6	<1.5	4.2	10.4
Site 15	35	0	2.30	18.2	46.1	0	10.8	103	230	0	45.6	237	600
Site 25	29	0	0.53	0.993	1.99	0	10.4	26.2	40.0	8	<1	2.56	7.8
Site 28	32	1	<0.0005	0.144	0.535	0	6.9	12.9	61.4	31	<2		8.4
Site 35	29	0	0.0014	1.89	3.17	0	25.8	38.8	106	1	<2	9.00	16.2
Site 36	28	0	<0.0004	0.0232	0.51	0	20.4	32.4	44.8	28	<2		<2
Site 38	34	0	11.66	26.6	48.8	0	2.8	7.26	45.0	0	18.8	106	271
Site 40	27	0	1.36	2.97	5.02	1	<2	5.60	11.3	0	5.5	26.1	50.2
Site 78	5	0	24.6	32.0	36.4	0	1.50	1.76	2.40	0	4.42	6.70	9.5
Site BGS 41	33	0	0.13	2.52	23.1	0	24	63.1	78.5	17	<0.5	17.6	170
Site BGS 42	35	0	17.7	30.2	44.9	0	51.2	90.7	138	24	<0.5		3.75
Site BGS 43	33	0	0.0004	0.0808	0.617	0	6.0	10.3	22.1	33	<1		<1
Site BGS 44	33	2	<0.0004	0.274	1.76	0	48.0	73.9	90.1	33	<1		<1
Site BGS 45	36	0	0.0004	0.28	0.76	0	57.0	91.4	131	34	<0.5		2.1
Site BGS 46	7	2	<0.0008	0.0577	0.194	0	25.8	29.6	37.3	7	<2		<2
Site BGS 53	35	0	2.25	10.2	24.0	0	25.6	48.6	74.9	13	<0.5	2.89	26.7
Site BGS 54	32	2	<0.0005	0.0237	0.165	0	9.6	12.1	16.9	32	<2		<2
Site BGS 76	5	0	28.5	40.6	56.7	0	23.2	25.8	29.8	0	175	518	791
Site BGS 77	5	0	39.2	45.3	54.5	0	30.0	35.3	45.4	0	206	460	592
Site TE 48	31	3	<0.0005	0.0472	0.562	0	118	167	223	30	<1		6.0
Site TE 49	28	6	<0.0004	0.051	0.626	0	123	169	244	27	<2		5.9
Site TE 50	31	1	<0.0005	0.0577	0.482	0	85.3	134	243	31	<1		<1
Site TE 52	30	4	<0.0005	0.0532	0.443	0	16.6	25.6	42.8	29	<1		5.8
<i>Corallian</i>													
Site 2	22	1	<0.0005	0.0296	0.454	0	27.0	38.9	52.1	22	<2		<2
Site 6	24	11	<0.0005	0.052	0.579	0	11.1	15.5	40.3	23	<1		0.7
Site 7	26	10	<0.0005	0.0237	0.438	0	6.21	14.4	34.5	26	<2		<2
Site 11	4	1	<0.0005	0.0326	0.123	0	3.70	5.47	6.40	4	<2		<2
Site 13	24	11	<0.0005	0.0458	0.702	0	15.3	22.3	35.6	23	<2		2.4
Site 16	29	11	<0.0004	0.0205	0.257	0	13.0	18.6	29.4	28	<2		1.3
Site 18	24	5	<0.0004	0.0493	0.624	0	0.90	22.0	43.3	22	<2		2.5
Site 23	22	12	<0.0004		0.698	0	8.1	29.5	40.0	21	<2		8.4
Site 27	23	13	<0.0004		0.444	0	13.9	21.5	54.9	23	<2		<2
Site 39	21	2	<0.0005	0.00744	0.0231	0	11.6	18.5	24.0	21	<2		<2
Site TE 51	29	0	27.6	43.6	58.6	21	<0.5		32.9	3	<1	4.53	20.0
Site BGS 55	6	0	13.45	17.8	29.2	5	<0.1		<0.1	0	8.0	23.4	43.4
Site BGS 79	4	0	2.21	21.3	43.0	0	4.4	11.7	29.9	0	16.2	130	459
Site BGS 80	4	0	28.6	34.0	47.8	0	4.7	10.0	23.9	0	19.8	231	679
Site BGS 81	3	0	24.7	26.5	28.6	0	2.0	4.37	5.80	0	14.9	20.0	26.9

No.: number of analyses, ncens: number censored (non-detects); TE 48 = BHB, TE 49 = BHC, TE 50 = BHA, TE 51 = BHE (cf. Raper et al., 2022).

laboratory. Analysis of dissolved gases was also carried out by headspace GC-FID or GC-TCD. Analytical detection limits for dissolved methane, ethane, ethene and propane were typically 1 µg/L; 1 mg/L for dissolved CO₂. Laboratory documentation for the method for CH₄ quotes a precision of ca. ±5% RSD, with expanded uncertainty of 14% (95% confidence).

5. Results

5.1. Comparisons between sampling protocols

Comparisons of results for dissolved gases between the BGS and the external laboratory (Fig. 3) indicate a large variability. For methane the values fall mainly along the 1:1 line and therefore indicate no systematic bias. For CO₂, analyses from the BGS laboratory appear to be higher overall and for ethane, lower overall at concentrations greater than ca. 600 µg/L.

Data for CH₄ from one borehole site on the KMA well pad (TE 51/BHE) from four sets of sampling and analysis are shown in Fig. 4.

Analyses include samples collected from the regular monitoring network and analysed by BGS using closed steel cylinders (Site TE 51_BGS) and four samples analysed by the ALS laboratory from vials (Site TE 51_ALS). Samples were also collected separately on different dates by Envireau Water (on behalf of Third Energy) using closed steel cylinders and analysed by BGS (BHE_BGS) and collected in open vials with analysis by another external laboratory (BHE_TE). The data show large variability in concentrations of methane between samplers. Samples collected in vials by Envireau Water and analysed by the external laboratory have the highest observed concentrations on average. Samples in steel cylinders have overall more comparable ranges, though lower concentrations than the vial samples. The four BGS samples from vials analysed by ALS also show broadly comparable concentrations to those from steel cylinders (Site TE 51_BGS/Site TE 51_ALS). Two BHE_BGS steel cylinder samples have anomalously low concentrations <10 mg/L (Fig. 4). The reasons for these discrepancies are unclear, but differences in timing of sampling relative to borehole purging and differences in sampling technique between teams are possibilities. Anomalously low concentrations in samples collected by Envireau Water from steel containers could be due to

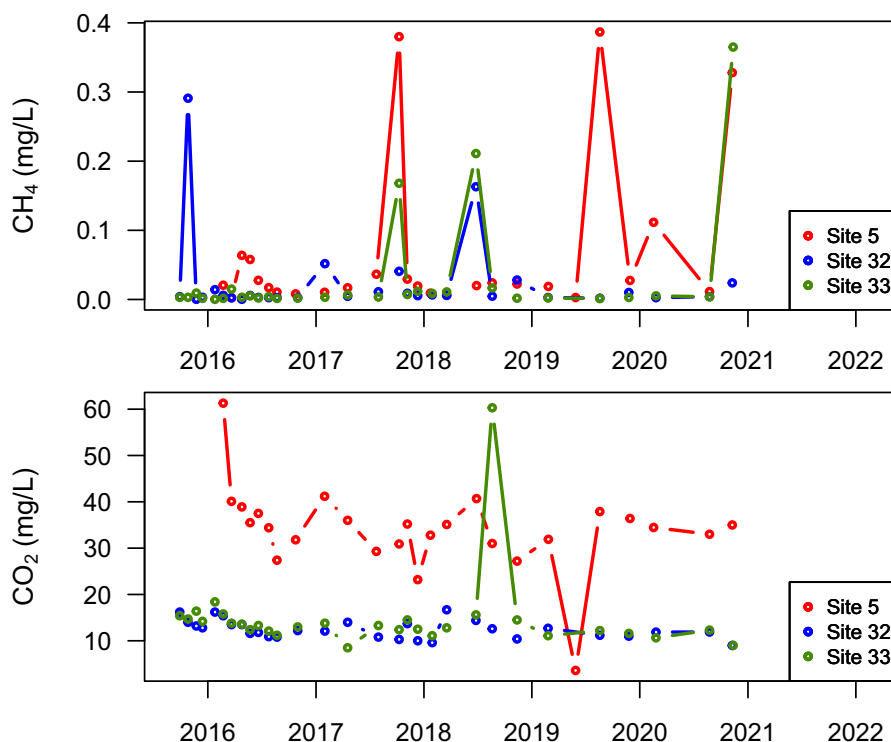


Fig. 5. Temporal variation in concentrations of CH₄ and CO₂ in groundwater from the Quaternary aquifer.

inconsistencies in timing of the cylinder fill due to pulsating flow of the bladder pump installed at the site. The cause of discrepancies is difficult to pin down because of the numerous uncertainties involved in disparate sampling and analytical protocols as well as different sampling times. The data indicate the large variability in concentrations with time, even within a given sampling/analytical method and the challenges therefore in collecting representative dissolved-gas samples.

Analyses of other alkanes by the ALS laboratory showed that ethene was below detection limits in all analysed samples (171 analyses). Propane was also undetected in groundwater from all but five sites; in these, concentrations were in the range 12–158 µg/L. The detections were all in deeper boreholes, three from the confined Corallian Group (Sites BGS 55, 79, 80; depths 130–180 m) and two from the Kimmeridge Clay (Sites BGS 76, 77; depths 110–150 m).

5.2. Distributions of dissolved gases

Summary statistical data for dissolved CH₄, CO₂ and C₂H₆ concentrations in groundwater from the monitored boreholes from the Quaternary, Kimmeridge Clay and Corallian aquifers are given in Table 1. Time-series plots for CH₄ and CO₂ are also shown for sites in the Quaternary aquifer in Fig. 5. Measured dissolved CH₄ concentrations are low, up to 0.39 mg/L, in the Quaternary groundwater with CO₂ up to 61 mg/L and dissolved C₂H₆ all below detection limits.

Concentrations of dissolved CH₄ are much higher in the groundwater from the Kimmeridge Clay, with observed maxima above 40 mg/L at five of the sampled sites (Table 1). Concentrations of dissolved CO₂ and C₂H₆ are also much higher at some Kimmeridge Clay sites, up to 230 mg/L and 790 µg/L respectively. Time-series variations in CH₄, C₂H₆, C₁/C₂ ratio (CH₄/C₂H₆) and CO₂ in groundwater from selected sites are also shown in Fig. 6. The plots indicate considerable temporal variability in gas concentrations although notable consistency in C₁/C₂ ratios. Greatest temporal variability is shown in sites with higher concentrations and is most notable at Site 15. This can partially be explained by an inconsistent depth of installation of the portable pump at the time of sampling, being mostly inserted at 30 m below ground level but in error

at 20 m depth for some of the early sampling rounds (these are indicated for CO₂ in Fig. 6). The data for CH₄ and C₂H₆ show lower concentrations at the shallower sampling depth, possibly due to a smaller hydrostatic pressure at 20 m relative to 10 m deeper (groundwater level at the site typically 1–2 m below ground level). The higher CO₂ concentrations at these shallower sampling depths are likely a function of varying redox conditions (greater oxidation of CH₄ at shallower levels) as well as potential spatial variations in solid organic carbon content.

Temporal variability of dissolved CH₄ concentrations at Site 15 can also be partially explained by variations over the course of pumping. Formal experiments were not set up to test CH₄ concentrations over time, but samples at the start and end of sampling were taken on two occasions in 2016 (Table 2). Concentrations were significantly higher at the initiation of pumping than after about an hour of pumping. This may be due to drawing in groundwater from subtly different levels in the open-hole section of borehole over time or to reduced hydrostatic pressure with pumping.

The argument for influence of inflows of groundwater with differing dissolved-gas concentrations from different horizons at Site 15 is supported by observed relationships between CH₄ concentrations and groundwater major-ion chemistry (Fig. 7). Monitored concentrations of CH₄ correlate positively with Na and HCO₃ and negatively with Cl. Concentrations of Na and HCO₃ are also lower and Cl higher in groundwater from 20 m depth compared with 30 m depth. Chemical stratification of groundwater has been observed from profiling of a neighbouring borehole (distance <40 m, not shown). The associations indicate that temporal variations in CH₄ (and C₂H₆, CO₂) at Site 15 are related to variations in composition of pumped groundwater and are not simply an artefact of sampling. Large variability in CH₄ concentration of pumped groundwater and its relation with major-ion variation has also been noted in other high-CH₄ groundwaters (Molofsky et al., 2018).

Time-series data for dissolved gases in groundwater from the confined Corallian aquifer in the central part of the plain are shown in Fig. 8. Data for the unconfined Corallian aquifer around the periphery are not shown as concentrations of CH₄ and C₂H₆ were typically low or undetected (Table 1). Our data showed that of the confined sites

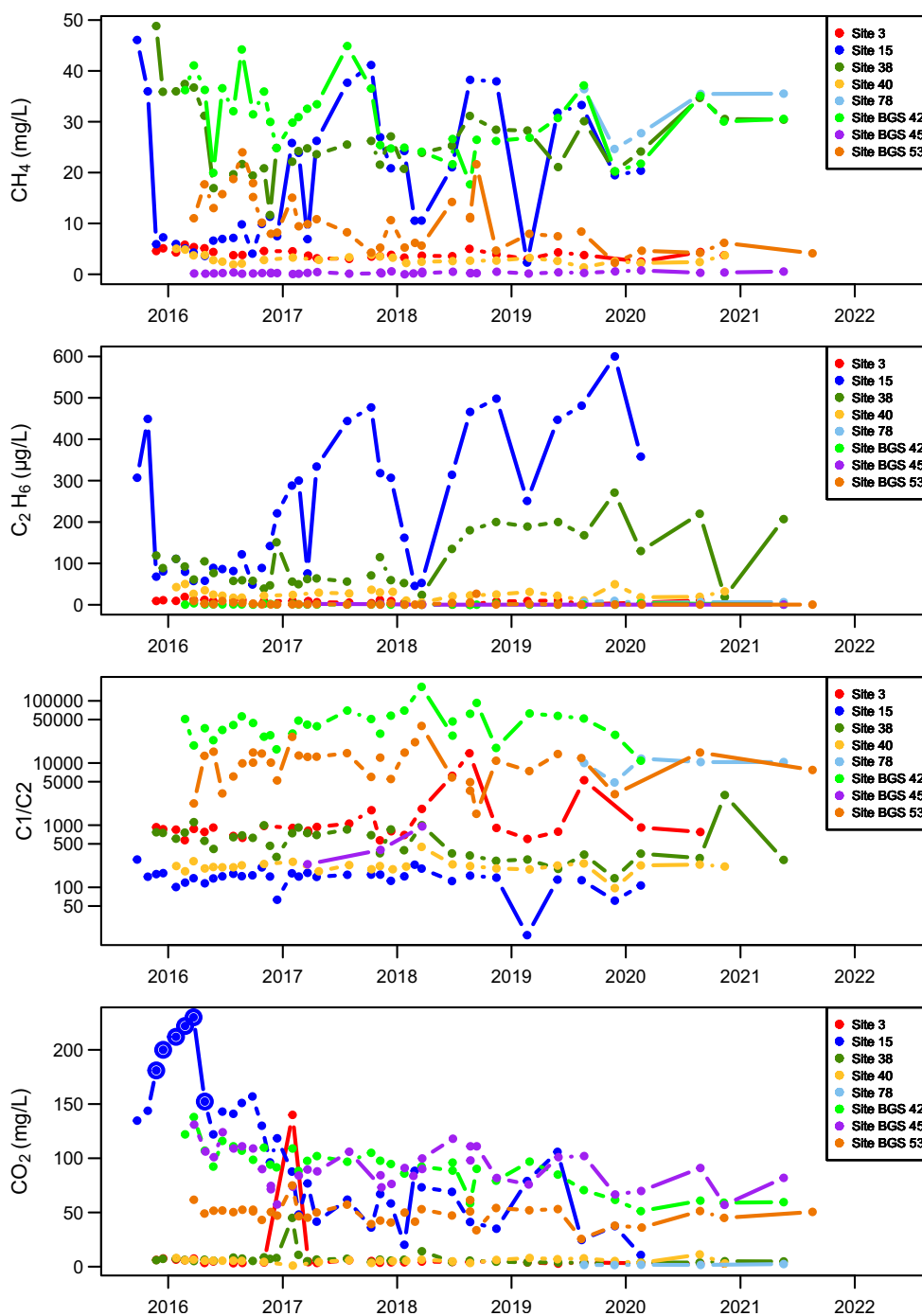


Fig. 6. Temporal variation in compositions of dissolved CH₄, C₂H₆ and CO₂ and C1/C2 molar ratios in groundwater from selected sites in the Kimmeridge Clay; larger circles in the CO₂ plot for Site 15 indicate samples that were collected from a pump depth of ca. 20 m (also applies for CH₄ and C₂H₆); other samples from the site were collected from a pump depth of 30 m below ground level.

sampled, Site TE 51 (located at KMA) had the highest overall CH₄ concentration (up to 59 mg/L) and this occurred at the start of the monitoring in 2016. Concentrations steadily declined to 2019 with no clear trend subsequently. As noted above, the data show some

inconsistencies with trends observed by Third Energy (Raper et al., 2022) (Fig. 4). The BGS data for several other sites also show initially high dissolved-gas concentrations with subsequent decline. This is interpreted as an artefact of new drilling before groundwater conditions

Table 2

Variation in concentration of dissolved CH₄ in groundwater from Site 15 over the course of pumping for sampling purposes (submersible pump installed at 30 m below ground level (bgl)).

Sample date	Pump duration (mins)	RWL start (mbgl)	Drawdown (m)	CH ₄ start (mg/L)	CH ₄ finish (mg/L)
22/05/2016	50	1.36	1.43	46.3	6.61
23/06/2016	70	1.51	0.87	63.4	6.94

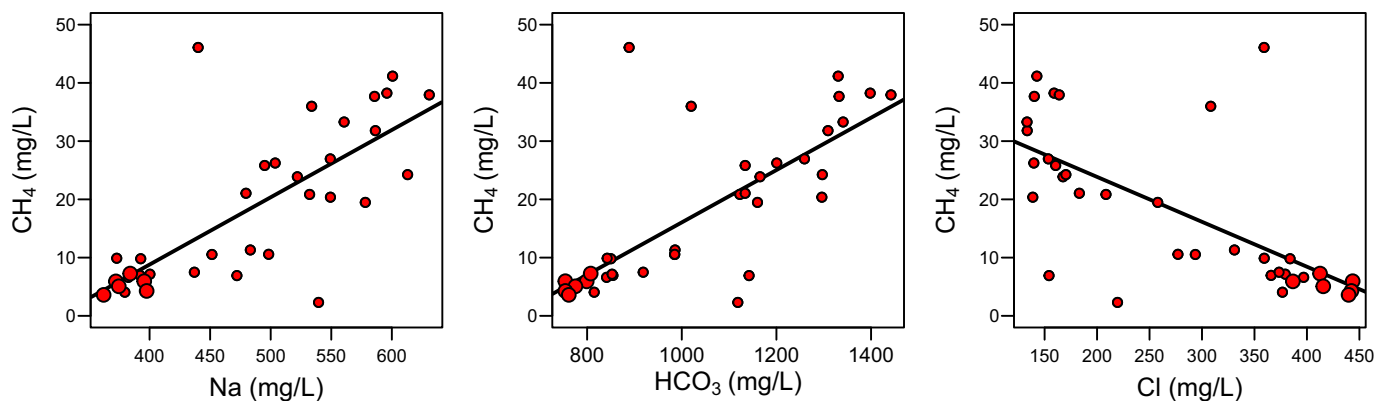


Fig. 7. Variation in concentrations of major ions (Na, HCO₃, Cl) with CH₄ in groundwater from Site 15; larger circles indicate samples that were collected from a pump depth of ca. 20 m (best-fit regression lines also shown, $p < 0.05$ in all cases).

transition towards a steady state following periods of pumping.

Spatial distributions of dissolved CH₄ are shown for groundwater samples collected in August 2019 in Fig. 9. Sites abstracting groundwater from Quaternary deposits with low CH₄ concentrations occur at locations in the southern periphery or the eastern part of the plain where Quaternary deposits are relatively thick (Section 3). Groundwater from the unconfined Corallian or at the feather edge of confined conditions around the periphery also shows low CH₄ concentrations. Highest CH₄ concentrations are predominantly in groundwater from the central parts of the plain, in both the Kimmeridge Clay and confined Corallian strata.

There is little convincing evidence to suggest that conventional hydrocarbon wells in the Vale of Pickering have had an impact on dissolved-gas compositions in the shallow groundwaters from the area. However, only two groundwater monitoring sites are located within 1 km lateral distance of a conventional hydrocarbon well and so there has been little opportunity to test the association with certainty. The two closest are Site 35 and Site TE 51, in the Kimmeridge Clay and confined Corallian respectively. Neither indicates anomalously high CH₄ concentrations when compared to other groundwater boreholes at similar depths in the respective aquifers. Average CH₄ concentration for Site 35 was 1.89 mg/L, that from Site TE 51, located at KMA, was 43.6 mg/L (Table 1). Further, shallow boreholes in the Kimmeridge Clay at KMA have groundwater with uniformly low dissolved CH₄ concentrations (≤ 0.6 mg/L; Table 1).

There is likewise little evidence to suggest that the high CH₄ concentrations observed in the groundwaters have been influenced by upward flows of deep gases via faults. Although the Mesozoic strata of the Vale of Pickering have a recognised history of extensional faulting which could provide pathways for upward movement of gases, only Site 35 and Site 38 are close to (within 1 km of) marked faults (Fig. 1). Most high-CH₄ groundwaters in the study area appear not to be linked to the surface expressions of identified faults.

5.3. Variations in stable-isotopic compositions

Data for $\delta^{13}\text{C-CH}_4$ and $\delta^2\text{H-CH}_4$ in groundwater from the Kimmeridge Clay and confined Corallian aquifers are given in Table 3. Only samples with sufficient dissolved CH₄ (ca. 1 mg/L or more) were measured/reported.

Isotopic compositions and relations with molar C1/C2 ratio are also given in Fig. 10. Fields for discriminating origins and pathways of methanogenesis/methanotrophy are also given, based on a data review by Milkov and Etiope (2018). These show a cutoff between biogenic and thermogenic CH₄ at C1/C2 close to 100 which has reduced from the 1000 cutoff recommended originally by Bernard et al. (1976). From the discriminant fields, the plot of C1/C2 against $\delta^{13}\text{C-CH}_4$ (Fig. 10a) shows

the strong dominance of a biogenic signature in Kimmeridge Clay groundwater samples, albeit with a large range of C1/C2 ratios which reflects the relatively high C₂H₆ concentrations of some samples. The consistency of compositions at many of the sites is notable.

The samples with reduced C1/C2 ratios (≤ 100 ; Fig. 10a) range into the early mature thermogenic (EMT) field and their presence was tentatively suggested by Smedley et al. (2017) as potentially due to mixing between groundwaters with hydrocarbons of biogenic and thermogenic origin. However, alternative explanations for the low ratios observed include generation of C₂H₆ under anoxic conditions by methanogenic bacteria (Hinrichs et al., 2006; Oremland, 1981; Schloemer et al., 2016). Generation of small quantities of C₂+ gases together with $\delta^{13}\text{C-CH}_4$ ratios intermediate between biogenic and thermogenic compositions have also been attributed to radiolysis of organic matter in immature organic-rich shales (Yin et al., 2023). Reduced C1/C2 ratios together with enriched $\delta^{13}\text{C-CH}_4$ have also been attributed to methanotrophic oxidation, under either aerobic or anaerobic conditions (McIntosh et al., 2019; Van Stempvoort et al., 2005; Whiticar, 1999). Either way, the groundwaters with reduced C1/C2 ratios \pm relative $\delta^{13}\text{C-CH}_4$ enrichment observed are not necessarily attributable to a thermogenic or EMT origin.

Only two Kimmeridge Clay groundwater samples have $\delta^{13}\text{C-CH}_4$ compositions greater than -50 ‰. One, from Site 35, is anomalous (Fig. 10a) compared to four other samples collected from the site at other times. The sample composition is interpreted as more likely due to CH₄ oxidation than to mixing with thermogenic gases. Evidence for oxidation of CH₄ by SO₄ reduction is lacking as the concentrations of SO₄ are not distinctive between the enriched and depleted samples. A post-sampling degradation of the water sample by oxidation is an alternative explanation (Humez et al., 2016b). The other sample with relative $\delta^{13}\text{C}$ enrichment is from Site BGS 76. This has a marginal $\delta^{13}\text{C-CH}_4$ composition of -49.8 ‰, not so different from the more depleted samples from the site and shares consistent C1/C2 ratios. The sample composition is interpreted as a continuum of the biogenic signature.

Fewer samples are available for $\delta^2\text{H-CH}_4$ but from those investigated, Fig. 10b indicates that the mechanism of methanogenesis in the Kimmeridge Clay groundwaters was by CO₂ reduction rather than by acetate fermentation. Compositions of $\delta^{13}\text{C-CO}_2$ for the Kimmeridge Clay groundwaters are in the range 32 to -10 ‰ (Table 3). The $\delta^{13}\text{C-CO}_2$ compositions (Fig. 10c) are not able to discriminate further between different mechanisms but are consistent with inferring a biogenic signature, with the exception of the one anomaly from Site 35. This has a $\delta^{13}\text{C-CO}_2$ composition at the depleted end of the observed range and is consistent with the sample showing microbial oxidation of CH₄ and associated generation of CO₂.

Isotopic compositions and C1/C2 ratios in the confined Corallian

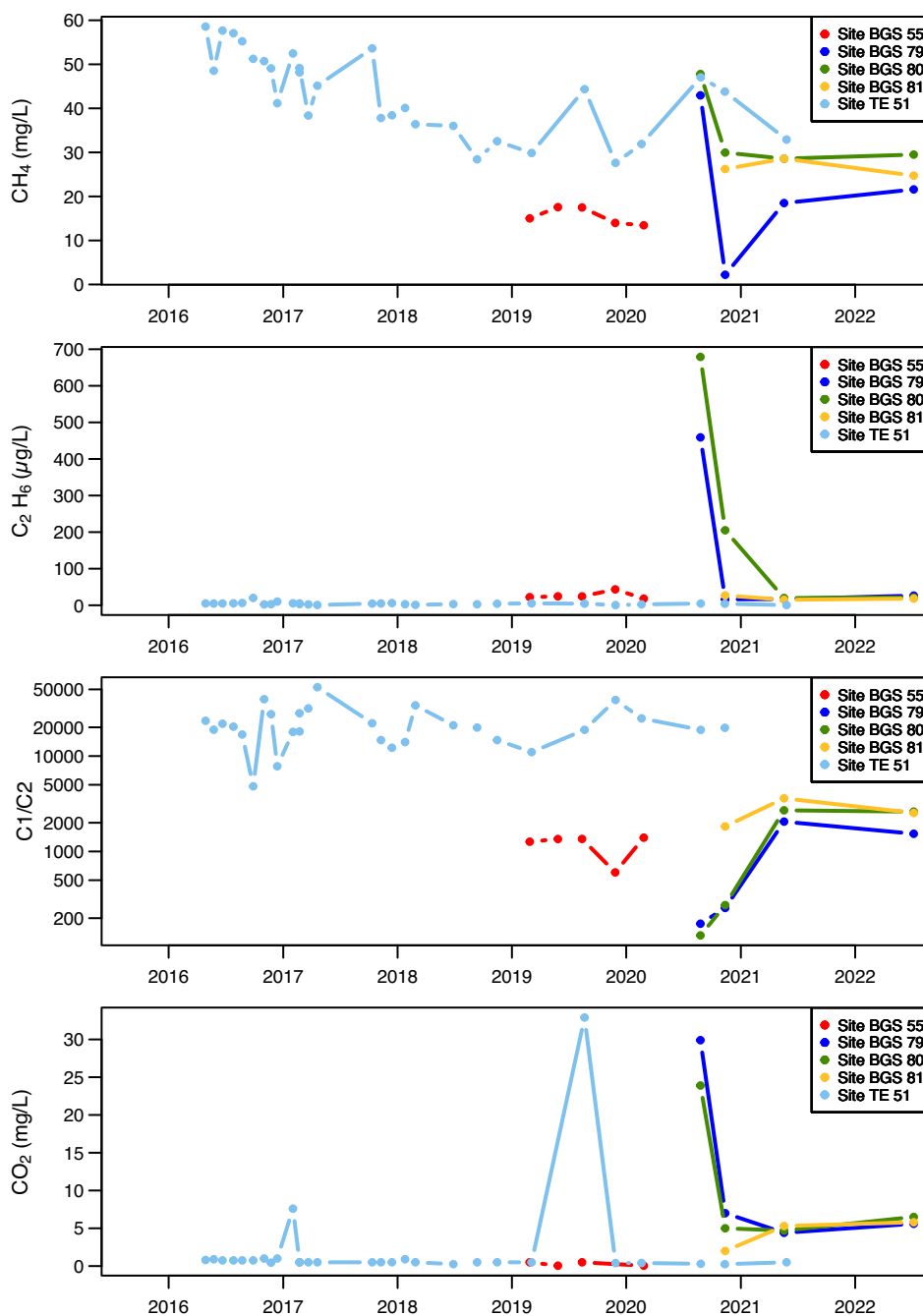


Fig. 8. Temporal variation in concentrations of CH_4 , C_2H_6 , CO_2 and ratio of C1/C2 in groundwaters from the confined Corallian aquifer.

groundwaters (Fig. 10d) show similar dominance of a biogenic signature but with a C1/C2 molar ratio usually >1000 . The largest observed C1/C2 ratios are consistently found in the groundwater from Site TE 51, located at KMA. This suggests that lateral proximity to the deep conventional hydrocarbon well at KMA (<100 m distant) has not had an impact on the C–H isotopic composition of the Corallian groundwater.

As for the Kimmeridge Clay groundwaters, the few samples with lower C1/C2 could also be derived by methanotrophic oxidation or microbially-generated C_2H_6 . Two samples also have $\delta^{13}\text{C}\text{-CH}_4$ compositions at the enriched end of the biogenic field (close to -50 ‰). As other samples from these two sites (sites BGS 80, 81) were more depleted, the compositions are inferred to have undergone CH_4 oxidation. Chemical compositions of these samples (e.g. SO_4 , NO_3 both below detection limits) indicate that if formed in situ, such oxidation would have been under anoxic conditions. Alternatively, the more enriched

compositions could be due to post-sampling oxidation. From the available data, the depleted $\delta^{13}\text{C}\text{-CH}_4$ and relatively enriched $\delta^2\text{H}\text{-CH}_4$ compositions (Fig. 10e) of the Corallian groundwaters show a methanogenesis pathway also determined overwhelmingly by CO_2 reduction.

Groundwater compositions from both rock types suggest that methanogenesis was produced by shallow microbial rather than thermogenic processes but with subsequent oxidation having likely modified the isotopic compositions.

6. Discussion

The ranges of concentrations of dissolved CH_4 in groundwater from the Kimmeridge Clay and underlying Corallian aquifer compare with those observed in shallow groundwater from well-documented high- CH_4 locations elsewhere. These are principally in organic-bearing

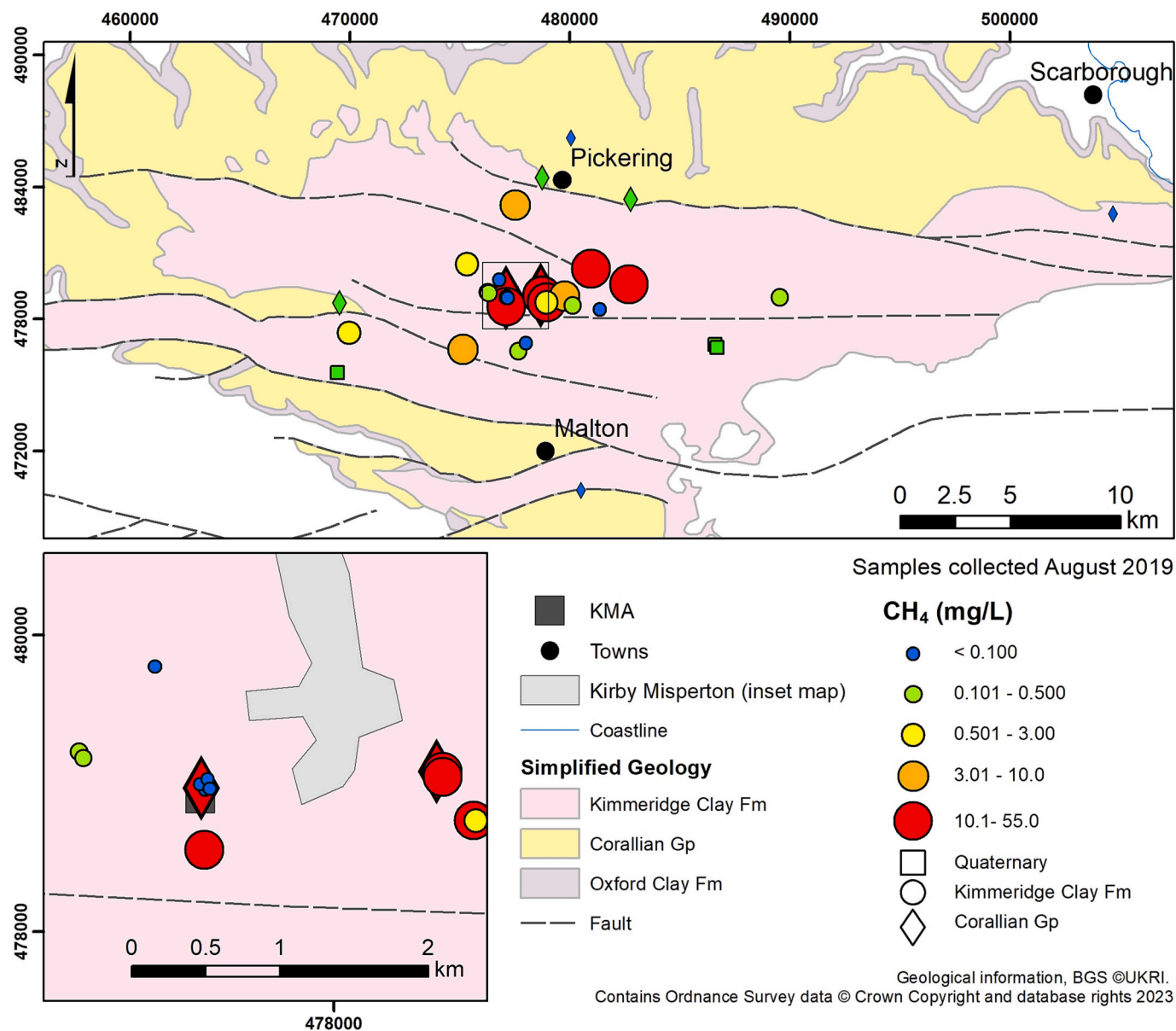


Fig. 9. Bedrock geology of the Vale of Pickering showing the spatial distribution of dissolved CH₄ in groundwater, sampled in August 2019 from the Quaternary, Kimmeridge Clay and Corallian aquifers.

sedimentary aquifers, examples including Upper Devonian sandstones and shales of Pennsylvania, USA (Molofsky et al., 2013; Osborn et al., 2011; Siegel et al., 2015), shale and coal-bearing formations of Nova Scotia, Alberta and Quebec, Canada (Humez et al., 2016a; Moritz et al., 2015; Taylor et al., 2021) and coal-bearing Cenozoic sediments of south-east Australia (Currell et al., 2017).

The observed concentrations in the Vale of Pickering groundwaters are also much higher than those found from a national survey of CH₄ in English groundwater (up to 4.7 mg/L) (Bell et al., 2017), although these were collected mainly from shallow principal water-supply aquifers which contrast with the poorly-permeable Kimmeridge Clay and confined Corallian aquifer (to 230 m depth) discussed in the current investigation. The concentrations of CH₄ in groundwater from the Quaternary deposits are much lower (concentrations up to 0.39 mg/L) than for the Kimmeridge Clay and confined Corallian aquifers although they are higher than national survey samples for Quaternary aquifers (up to 0.02 mg/L, 7 samples) (Bell et al., 2017). This reflects the dominance of permeable glacial sand and gravels represented in the national survey, in contrast to the (glacio)-lacustrine clay-sand-

dominant lithology of the Quaternary of the Vale of Pickering.

The overall biogenic signature of the dissolved CH₄ in the Kimmeridge Clay groundwater points towards a methanogenesis process occurring in situ rather than through migration from deeper strata. Such deep strata include for example the Viséan–Namurian Bowland Shale which was to be the target source for shale gas in the basin and which has some 2000 m of separation from the base of the Kimmeridge Clay.

The presence of small quantities of C₂H₆ in some of the shallow Kimmeridge Clay groundwaters and detection of C₃H₈ (propane) within a small number of the deeper boreholes from the formation are also inferred to have been likely generated by microbial processes. While, presence of these gases is conventionally associated with thermogenic origins, other studies have also detected them in biogenic settings (Hinrichs et al., 2006; Oremland, 1981; Schloemer et al., 2016). The organic-rich Kimmeridge Clay of the Cleveland Basin is established to have had a history of burial that was insufficiently deep to promote oil or gas production (Section 3), although thermally mature oil-producing units of the Kimmeridge Clay are well known to occur in southern England and the North Sea (Gallois, 2021; Gautier, 2005).

Table 3Stable-isotopic data for $\delta^{13}\text{C}$ (‰ VPDB) and $\delta^2\text{H}$ (‰ VSMOW) in dissolved CH_4 and CO_2 from the Kimmeridge Clay and Corallian formations.

Site	Sample date	$\delta^{13}\text{C}\text{-CH}_4$	$\delta^{13}\text{C}\text{-CO}_2$	$\delta^2\text{H}\text{-CH}_4$	Site	Sample date	$\delta^{13}\text{C}\text{-CH}_4$	$\delta^2\text{H}\text{-CH}_4$
Kimmeridge Clay					Confined Corallian			
Site 3	26/01/2016	-87.0			Site TE 51	24/05/2016	-69.4	
Site 3	24/05/2016	-90.1			Site TE 51	14/12/2017	-69.6	
Site 3	21/03/2018	-86.9			Site TE 51	15/11/2018	-71.8	
Site 3	19/02/2020	-86.3			Site TE 51	28/11/2019	-70.1	
Site 3	10/11/2020	-58.5			Site TE 51	26/08/2020	-67.9	-199.7
Site 4	10/11/2020	-60.1			Site TE 51	11/11/2020	-66.2	-195.5
Site 5	09/11/2020	-62.4			Site TE 51	27/05/2021	-63.1	-163.0
Site 14	24/05/2016	-75.8	-24.1		Site BGS 55	13/08/2019	-69.4	
Site 14	14/11/2018	-73.4	-19.0		Site BGS 55	26/02/2020	-70.3	
Site 14	10/11/2020	-51.9		-60.51	Site BGS 79	25/08/2020	-63.0	-167.7
Site 15	26/01/2016	-80.4	-19.4		Site BGS 79	12/11/2020	-67.1	-195.1
Site 15	24/05/2016	-81.8	-20.8		Site BGS 79	19/05/2021	-66.1	-195.3
Site 15	20/03/2018	-80.5	-32.1		Site BGS 79	07/07/2022	-65.8	
Site 15	14/11/2018	-76.9	-17.3		Site BGS 80	25/08/2020	-62.6	-186.8
Site 15	18/02/2020	-77.7		-203.9	Site BGS 80	12/11/2020	-67.0	-164.4
Site 25	27/01/2016	-77.0	-24.8		Site BGS 80	19/05/2021	-64.5	-188.8
Site 25	23/05/2016	-77.6	-24.7		Site BGS 80	07/07/2022	-49.9	
Site 25	09/11/2020	-60.9			Site BGS 81	12/11/2020	-68.9	-153.4
Site 33	12/11/2020	-55.5		-210.9	Site BGS 81	19/05/2021	-64.5	-169.4
Site 35	27/01/2016	-43.7	-30.1		Site BGS 81	07/07/2022	-51.0	
Site 35	26/05/2016	-80.3	-23.1					
Site 35	19/03/2018	-72.8	-23.5					
Site 35	14/11/2018	-76.3	-20.2					
Site 35	11/11/2020	-71.5						
Site 38	26/01/2016	-77.0						
Site 38	25/05/2016	-77.2						
Site 38	21/03/2018	-72.6						
Site 38	13/11/2018	-70.0						
Site 38	26/11/2019	-69.6		-210.9				
Site 38	24/08/2020	-58.1		-122.0				
Site 38	12/11/2020	-64.7		-146.3				
Site 38	19/05/2021	-62.4		-173.5				
Site 40	24/05/2016	-76.5						
Site 40	14/11/2018	-78.0						
Site 40	18/02/2020	-73.4		-187.9				
Site 40	24/08/2020	-75.7		-158.8				
Site 40	12/11/2020	-72.7		-169.6				
Site BGS 41	14/11/2018	-73.8	-14.4					
Site BGS 41	25/08/2020	-62.0		-158.1				
Site BGS 42	24/05/2016	-81.2	-16.8					
Site BGS 42	20/03/2018	-73.8	-27.5					
Site BGS 42	13/11/2018	-78.9	-10.9					
Site BGS 42	28/11/2019	-73.7		-203.6				
Site BGS 42	18/02/2020	-71.7		-134.0				
Site BGS 42	26/08/2020	-69.9		-167.1				
Site BGS 42	09/11/2020	-73.3		-191.0				
Site BGS 42	19/05/2021	-68.9		-184.9				
Site BGS 43	20/08/2019	-58.3						
Site BGS 53	25/05/2016	-87.6	-18.0					
Site BGS 53	20/03/2018	-85.1						
Site BGS 53	13/11/2018	-79.5	-15.1					
Site BGS 53	21/02/2020	-65.3		-173.6				
Site BGS 53	10/11/2020	-75.5						
Site BGS 55	26/02/2020	-70.3						
Site BGS 61	26/09/2017	-82.5						
Site BGS 68	27/09/2017	-70.1						
Site BGS 69	27/09/2017	-73.6						
Site BGS 71	27/09/2017	-71.6						
Site BGS 71	14/08/2019	-70.3						
Site BGS 72	27/09/2017	-72.7						
Site BGS 73	13/08/2019	-72.8		-167.5				
Site BGS 73	27/09/2017	-73.5						
Site BGS 73	18/05/2021	-76.5		-198.6				
Site BGS 74	27/09/2017	-84.9						
Site BGS 74	13/08/2019	-65.9						
Site BGS 75	27/09/2017	-84.6						
Site BGS 75	13/08/2019	-60.1						
Site BGS 69	14/08/2019	-68.7		-205.7				
Site BGS 68	14/08/2019	-75.0		-192.0				
Site BGS 68	26/08/2020	-74.3		-172.0				
Site BGS 71	26/08/2020	-74.1		-235.1				
Site BGS 72	27/02/2020	-72.4		-244.9				
Site BGS 73	26/02/2020	-78.1		-226.5				

(continued on next page)

Table 3 (continued)

Site	Sample date	$\delta^{13}\text{C-CH}_4$	$\delta^{13}\text{C-CO}_2$	$\delta^2\text{H-CH}_4$	Site	Sample date	$\delta^{13}\text{C-CH}_4$	$\delta^2\text{H-CH}_4$
Kimmeridge Clay					Confined Corallian			
Site BGS 73	25/08/2020	-70.6		-158.2				
Site BGS 76	14/08/2019	-49.8		-174.8				
Site BGS 76	10/11/2020	-59.7		-156.4				
Site BGS 76	20/05/2021	-55.9		-161.1				
Site BGS 77	14/08/2019	-59.7						
Site BGS 77	10/11/2020	-60.2		-170.8				
Site BGS 77	19/05/2021	-63.0		-190.6				
Site 78	21/08/2019	-55.4						
Site 78	19/02/2020	-63.2						
Site 78	27/08/2020	-61.6		-181.6				
Site 78	12/11/2020	-64.8		-200.9				
Site 78	19/05/2021	-61.3		-183.3				

In the underlying Corallian aquifer, groundwater likely owes its high CH_4 concentrations to the higher solubility afforded by the higher hydrostatic pressures at greater depth. High artesian heads are typical of the confined Corallian in the low-lying central part of the Vale of Pickering. The higher piezometric surface of the Corallian groundwater compared to that in the Kimmeridge Clay is illustrated for the KMA site in Fig. 11, albeit the piezometric surface for the Corallian borehole is non-artesian (some 3 mbgl) at the site. As pressure gradients in the Corallian are consistent with upward groundwater movement, the groundwater is unlikely to have derived its dissolved CH_4 by migration from the overlying Kimmeridge Clay. A possible alternative mechanism is via the upward migration of dissolved CH_4 from the underlying Oxford Clay although no direct evidence for this exists. The organic content of the limestone and sandstone units of the Corallian Group as a source of C for CH_4 generation is lower than the sandwiching mudrocks of the Kimmeridge and Oxford Clay formations, but in-situ methanogenesis (dissolved CH_4 concentration of the order of 50–60 mg/L with overwhelmingly biogenic signature) is inferred as the most likely origin at the depths of the groundwaters tested (to 227 m).

The large variability in concentrations of monitored CH_4 in groundwater has been similarly observed in other studies of high- CH_4 groundwater. Humez et al. (2016c) found a 56% (CV) variation around average CH_4 concentration in groundwater from an eight-year monitoring study. The variation was greatly in excess of that attributable to sampling and analytical error and was inferred to be due to pumping-related changes in groundwater level, with resultant changes in hydrostatic pressure leading to degassing. As with the current study, the concentration variations were noted to be accompanied by much less variability in respective stable-isotopic compositions (Humez et al., 2016b; Humez et al., 2016c), a factor cited as valuable in CH_4 source discrimination in aquifers.

The dominant biogenic signatures of the high- CH_4 groundwaters in both the Kimmeridge Clay and Corallian argue against migration along deep fractures in locations where groundwater samples do exist.

The dominance of the carbonate (CO_2) reduction methanogenic pathway of both Kimmeridge Clay and Corallian groundwaters presumably lies in the strongly reducing, SO_4 -reduced conditions characteristic of the CH_4 -rich groundwater of the area (Raper et al., 2022; Smedley et al., 2017) and the likely paucity of remnant acetate and other organic substrates under these conditions for fermentation reactions to proceed (Whiticar, 1999).

The minority of groundwater samples with enriched $\delta^{13}\text{C-CH}_4$ isotopic compositions (ca. -50 ‰) may be due to secondary microbial oxidation because multiple samples taken from the same sites more usually show a depleted (biogenic) signature. Under the strongly reducing conditions of the CH_4 -rich groundwater in both the Kimmeridge Clay and Corallian strata, this could proceed via an anaerobic pathway, potentially coupled with SO_4 reduction (Humez et al., 2019; Van Stempvoort et al., 2005; Yoshinaga et al., 2014). However, there is a lack of direct evidence for a reduction of SO_4 relative to the depleted

(biogenic) samples and the enriched representatives could equally reflect oxidation (degradation) following sampling (Humez et al., 2016b).

The original purpose of the groundwater CH_4 investigation of the Vale of Pickering was to establish the baseline conditions ahead of the proposed development of shale gas from the Bowland Shale Formation. The high observed concentrations of CH_4 (up to 59 mg/L) and the detection of small quantities of higher alkanes in a number of the water boreholes emphasise the requirement for this to be carried out in order that hydrocarbon sources and pathways in the groundwater can be understood and attributed appropriately.

7. Conclusions

Groundwater from the Vale of Pickering shows a large variability in the concentrations of dissolved CH_4 and higher alkanes, both spatially and temporally. Shallow groundwater from Quaternary superficial deposits has low concentrations of CH_4 (up to 0.39 mg/L) and undetectable C_2H_6 (<2 $\mu\text{g/L}$), as does groundwater from the peripheral unconfined and marginally-confined sections of the Corallian aquifer (CH_4 concentrations up to 0.70 mg/L, C_2H_6 <10 $\mu\text{g/L}$). On the other hand, groundwater from the Kimmeridge Clay Formation and underlying confined Corallian in the central part of the plain shows a large variation but commonly high concentrations (up to 57 mg/L and 59 mg/L respectively) and with presence of sub-mg/L quantities of C_2H_6 in some (up to 790 $\mu\text{g/L}$ and 680 $\mu\text{g/L}$ respectively) and C_3H_8 in a few of the deeper groundwater samples (up to 159 $\mu\text{g/L}$). The high concentrations in the Kimmeridge Clay are related to its high organic-matter content, a feature well-recognised in thermally mature oil-producing units of the formation elsewhere in the UK. However, the formation is thermally immature in the Vale of Pickering, likely precluding the generation of in-situ thermogenic hydrocarbon gases. High concentrations of CH_4 in the confined Corallian are also likely linked to organic-rich horizons as well as to increased depth of abstraction and hence increased pressure.

The large temporal and depth variability in CH_4 concentrations especially at Site 15 demonstrates the influence of pressure, with higher dissolved concentrations typically recorded from a greater pumping depth and reduced concentrations over time resulting from pumping-related drop in hydrostatic pressure. Variations in the contribution of inflowing horizons from different depths over the course of pumping are also evident from the associations between dissolved-gas content and major-ion chemistry. The variability demonstrates the common difficulties in obtaining consistent and representative monitoring data for CH_4 and other dissolved gases over time.

Carbon and deuterium stable-isotopic compositions of the both the Kimmeridge Clay and confined Corallian groundwaters show an overwhelmingly biogenic origin for the dissolved CH_4 and a methanogenesis pathway by CO_2 reduction. A minority of samples show more enriched $\delta^{13}\text{C-CH}_4$ isotopic compositions which are inferred to be due to oxidation rather than upward migration of deeper thermogenic gases.

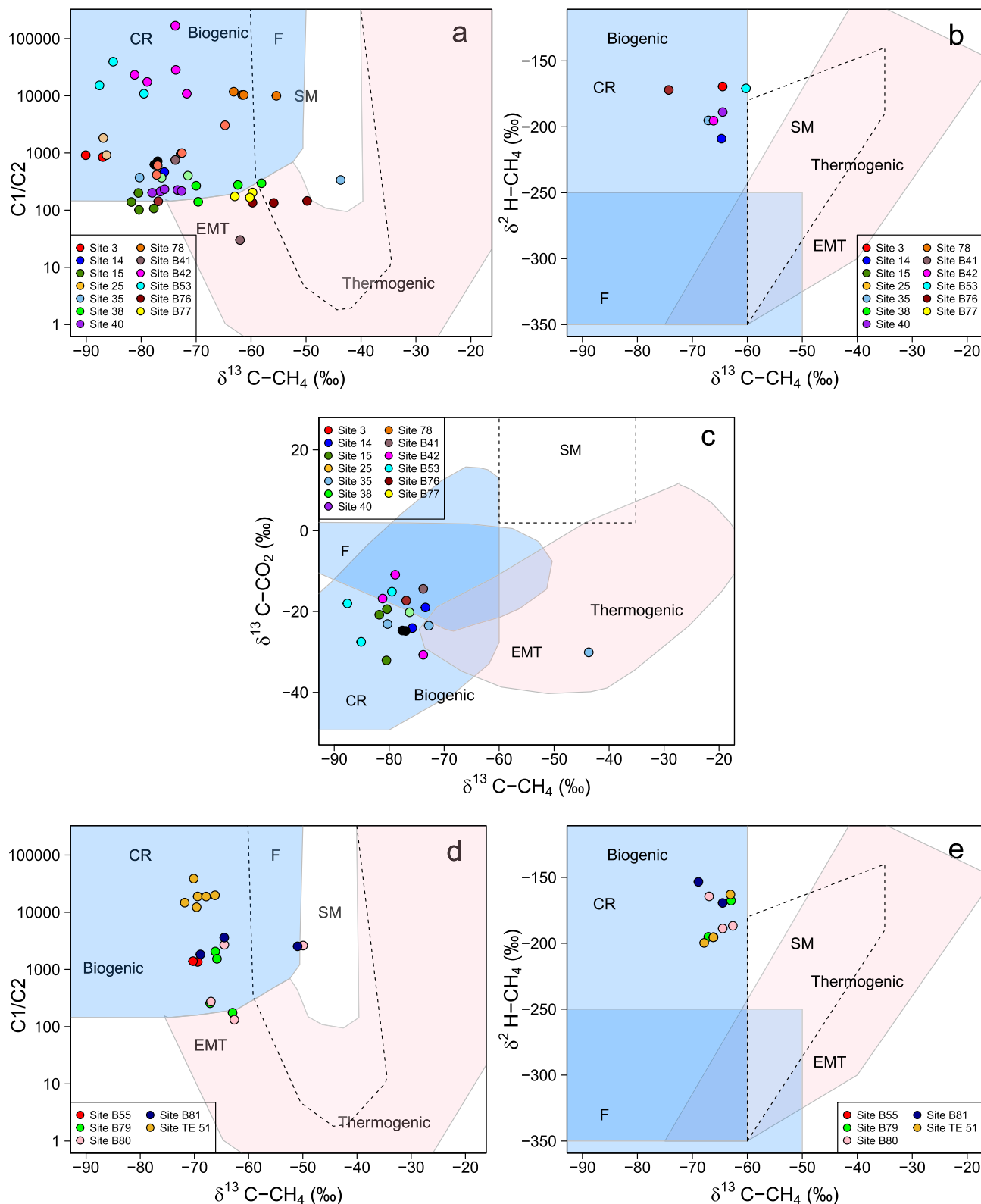


Fig. 10. Relationships among CH_4/C_2H_6 ($C1/C2$) ratio and isotopic compositions of $^{13}C-CH_4$, $^{13}C-CO_2$ and $^2H-CH_4$ for groundwater from the Kimmeridge Clay (a, b, c) and confined Corallian (d, e) aquifers; $C1/C2$ represent molar ratios. $\delta^{13}C-CH_4$ and δ^2H-CH_4 variables (b and e) have been switched contrary to most published studies in order to place $\delta^{13}C-CH_4$ consistently as the abscissa for comparison purposes. Background fields taken from Milkov and Etiope (2018): Biogenic field incorporates CR: CO_2 reduction and F: fermentation; Thermogenic field includes EMT: early mature thermogenic; SM: secondary microbial (petroleum biodegradation).

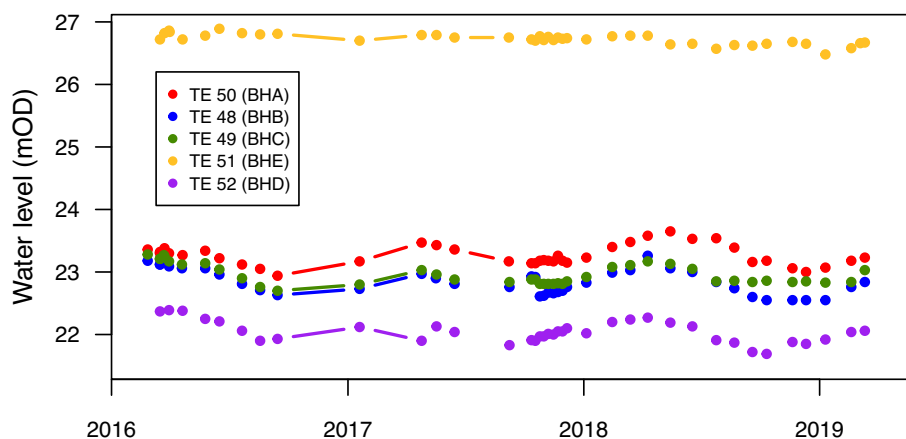


Fig. 11. Piezometric surface (metres above OD) of groundwater as measured by Envireau Water from the KMA boreholes (February 2016 to March 2019; data from Envireau Water, with permission).

Whether the oxidation is via an anaerobic or aerobic pathway is unclear, but compositions may be an artefact of sampling for the small number of samples concerned.

Few groundwater sites are in close proximity to existing conventional hydrocarbon wells, and there appears to be little evidence from dissolved-gas concentrations or isotopic compositions that these have had an impact on the dissolved-gas content of the shallow groundwaters investigated. The closest conventional hydrocarbon site to a monitored groundwater borehole occurs at KMA, where deep Corallian groundwater shows a strongly biogenic CH_4 signature and shallow Kimmeridge Clay groundwaters at the site have consistently low CH_4 concentrations, insufficient to provide a reliable CH_4 stable-isotopic measurement.

The high concentrations of dissolved CH_4 and detectable concentrations of C_2H_6 and C_3H_8 in the Kimmeridge Clay and confined Corallian groundwaters provide a baseline for the Vale of Pickering and augment the database and extend the range for concentrations of dissolved hydrocarbons in UK groundwaters. This baseline forms an important starting point for assessing the impacts from any future deep subsurface industrial development.

Declaration of Competing Interest

The authors declare the following financial interests which may be considered as potential competing interests:

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Data availability

Data are included

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References

- Alperin, M.J., Hoehler, T.M., 2009. Anaerobic methane oxidation by archaea/sulfate-reducing bacteria aggregates: 2. Isotopic constraints. *Am. J. Sci.* 309 (10), 958–984.
- Alperin, M.J., Reeburgh, W.S., 1985. Inhibition experiments on anaerobic methane oxidation. *Appl. Environ. Microbiol.* 50 (4), 940–945.
- Bearcock, J.M., Smedley, P.L., Milne, C.J., 2015. Baseline Groundwater Chemistry: The Corallian of the Vale of Pickering, Yorkshire OR/15/048. British Geological Survey, Keyworth, Nottingham.
- Bell, R.A., et al., 2017. A baseline survey of dissolved methane in aquifers of Great Britain. *Sci. Total Environ.* 601, 1803–1813.
- Bernard, B.B., Brooks, J.M., Sackett, W.M., 1976. Natural gas seepage in the Gulf of Mexico. *Earth Planet. Sci. Lett.* 31, 48–54.
- Bishop, P.K., Lloyd, J.W., 1990. Chemical and isotopic evidence for hydrogeochemical processes occurring in the Lincolnshire Limestone. *J. Hydrol.* 121 (1), 293–320.
- Cooper, J., Stamford, L., Azapagic, A., 2018. Economic viability of UK shale gas and potential impacts on the energy market up to 2030. *Appl. Energy* 215, 577–590.
- Cope, J.C.W., 1974. New information on the Kimmeridge Clay of Yorkshire. *Proc. Geol. Assoc.* 85 (2), 211–221.
- Cope, J.C.W., 2006. Jurassic: The Returning Seas. In: Brenchley, P.J., Rawson, P.F. (Eds.), *The Geology of England and Wales*. The Geological Society, London, p. 559.
- Currell, M., Banfield, D., Cartwright, I., Cendón, D.I., 2017. Geochemical indicators of the origins and evolution of methane in groundwater: Gippsland Basin, Australia. *Environ. Sci. Pollut. Res.* 24 (15), 13168–13183.
- Darling, W.G., Goody, D.C., 2006. The hydrogeochemistry of methane: evidence from English groundwaters. *Chem. Geol.* 229, 293–312.
- Darling, W.G., Milne, C.J., 1995. Quantitative Analysis of Dissolved Gases: Preparation and Calculations, British Geological Survey, WD/95/10, Wallingford, UK.
- Deirmendjian, L., et al., 2019. Importance of the vegetation-groundwater-stream continuum to understand transformation of biogenic carbon in aquatic systems – a case study based on a pine-maize comparison in a lowland sandy watershed (Landes de Gascogne, SW France). *Sci. Total Environ.* 661, 613–629.
- Dlugokencky, E., 2022. Global CH_4 monthly means. In: NOAA/ESRL. Global Monitoring Laboratory: Earth System Research Laboratories.
- Duan, Z., Mao, S., 2006. A thermodynamic model for calculating methane solubility, density and gas phase composition of methane-bearing aqueous fluids from 273 to 523K and from 1 to 2000bar. *Geochim. Cosmochim. Acta* 70 (13), 3369–3386.
- Evans, D.J.A., et al., 2017. Glacial Lake Pickering: stratigraphy and chronology of a proglacial lake dammed by the North Sea Lobe of the British-Irish Ice Sheet. *J. Quat. Sci.* 32 (2), 295–310.
- Ford, J., Hughes, L., Burke, H., Lee, J., 2015. The Vale of Pickering: An Initial Summary of the Quaternary/Superficial Geology and Data Holdings. Open Report, OR/15/064. British Geological Survey, Keyworth, UK.
- Gallois, R., 2004. The Kimmeridge Clay: the most intensively studied formation in Britain. *Open Univ. Geol. J.* 25, 33–38.
- Gallois, R., 2021. The stratigraphy of the Kimmeridge Clay Formation (Jurassic) of the Vale of Pickering, Yorkshire, UK. *Proc. Yorks. Geol. Soc.* 63 (4) pygs2021-004.

- Gautier, D.L., 2005. Kimmeridgian Shales Total Petroleum System of the North Sea Graben Province, Bulletin 2204-C. United States Geological Survey, Reston, Virginia, p. 24.
- Haarhoff, M.Q., et al., 2018. The history of hydrocarbon exploration and development in North Yorkshire. In: History of the European Oil and Gas Industry. Geological Society of London, p. 0.
- Herbin, J., Muller, C., Geysant, J., Melieres, F., Penn, I., 1991. Heterogeneity of organic matter distribution in relation to a transgressive systems tract: Kimmeridge Clay (Jurassic), England. *Aapg Bull. - AAPG BULL* 75, 593–594.
- Hinrichs, K.U., et al., 2006. Biological formation of ethane and propane in the deep marine subsurface. *Proc. Natl. Acad. Sci. U. S. A.* 103 (40), 14684–14689.
- Humez, P., et al., 2016a. Occurrence and origin of methane in groundwater in Alberta (Canada): Gas geochemical and isotopic approaches. *Sci. Total Environ.* 541, 1253–1268.
- Humez, P., et al., 2016b. Redox controls on methane formation, migration and fate in shallow aquifers. *Hydrol. Earth Syst. Sci.* 20 (7), 2759–2777.
- Humez, P., et al., 2016c. An 8-year record of gas geochemistry and isotopic composition of methane during baseline sampling at a groundwater observation well in Alberta (Canada). *Hydrogeol. J.* 24 (1), 109–122.
- Humez, P., Osselin, F., Kloppmann, W., Mayer, B., 2019. A geochemical and multi-isotope modeling approach to determine sources and fate of methane in shallow groundwater above unconventional hydrocarbon reservoirs. *J. Contam. Hydrol.* 226.
- Jackson, R.B., et al., 2013. Increased stray gas abundance in a subset of drinking water wells near Marcellus shale gas extraction. *Proc. Natl. Acad. Sci. U. S. A.* 110 (28), 11250–11255.
- Jackson, R.B., et al., 2014. The environmental costs and benefits of fracking. In: Gadgil, A., Liverman, D.M. (Eds.), *Annual Review of Environment and Resources*, vol 39. Annual Review of Environment and Resources, pp. 327–362.
- Jurado, A., et al., 2018. Occurrence of greenhouse gases in the aquifers of the Walloon Region (Belgium). *Sci. Total Environ.* 619–620, 1579–1588.
- Kent, P.E., 1980. *British Regional Geology: Eastern England from the Tees to the Wash*. HMSO for the British Geological Survey, London.
- Kulogoski, J.T., et al., 2018. Origin of methane and sources of High Concentrations in Los Angeles Groundwater. *J. Geophys. Res. Biogeosci.* 123 (3), 818–831.
- Kuloyo, O., et al., 2020. Methane oxidation and methylotroph population dynamics in groundwater mesocosms. *Environ. Microbiol.* 22 (4), 1222–1237.
- Lewellyn, G.T., et al., 2015. Evaluating a groundwater supply contamination incident attributed to Marcellus Shale gas development. *Proc. Natl. Acad. Sci. U. S. A.* 112 (20), 6325–6330.
- Lovley, D.R., Chapelle, F.H., 1995. Deep subsurface microbial processes. *Rev. Geophys.* 33 (3), 365–381.
- Lovley, D.R., Dwyer, D.F., Klug, M.J., 1982. Kinetic analysis of competition between sulfate reducers and methanogens for hydrogen in sediments. *Appl. Environ. Microbiol.* 43 (6), 1373–1379.
- Mackay, D.J.C., Stone, T.J., 2013. *Potential Greenhouse Gas Emissions Associated with Shale Gas Extraction and Use*. Department of Energy & Climate Change, London.
- McIntosh, J.C., et al., 2019. A critical review of state-of-the-art and emerging approaches to identify fracking-derived gases and associated contaminants in aquifers. *Environ. Sci. Technol.* 53 (3), 1063–1077.
- McMahon, P.B., et al., 2017. Methane and benzene in drinking-water wells overlying the Eagle Ford, Fayetteville, and Haynesville Shale hydrocarbon production areas. *Environ. Sci. Technol.* 51 (12), 6727–6734.
- Milkov, A.V., Etiope, G., 2018. Revised genetic diagrams for natural gases based on a global dataset of >20,000 samples. *Org. Geochem.* 125, 109–120.
- Molofsky, L.J., Connor, J.A., Wylie, A.S., Wagner, T., Farhat, S.K., 2013. Evaluation of methane sources in Groundwater in Northeastern Pennsylvania. *Ground Water* 51 (3), 333–349.
- Molofsky, L.J., et al., 2018. Purging and other sampling variables affecting dissolved methane concentration in water supply wells. *Sci. Total Environ.* 618, 998–1007.
- Molofsky, L.J., et al., 2021. A review of physical, chemical, and hydrogeologic characteristics of stray gas migration: Implications for investigation and remediation. *Sci. Total Environ.* 779, 146234.
- Moritz, A., et al., 2015. Methane baseline concentrations and sources in shallow aquifers from the shale gas-prone region of the St. Lawrence Lowlands (Quebec, Canada). *Environ. Sci. Technol.* 49 (7), 4765–4771.
- Newell, A.J., Ward, R.S., Fellgett, M.W., 2016. A 3D Geological Model of Post-Permian Aquifers and Aquitards in the Vale of Pickering, North Yorkshire, UK. OR/15/068 (in press). British Geological Survey, Keyworth, UK.
- Oremland, R.S., 1981. Microbial formation of ethane in anoxic estuarine sediments. *Appl. Environ. Microbiol.* 42 (1), 122–129.
- Osborn, S.G., Vengosh, A., Warner, N.R., Jackson, R.B., 2011. Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing. *Proc. Natl. Acad. Sci. U. S. A.* 108 (20), 8172–8176.
- Pearce, J.K., et al., 2023. Methane in aquifers and alluvium overlying a coal seam gas region: gas concentrations and isotopic differentiation. *Sci. Total Environ.* 861, 160639.
- Powell, J.H., 2010. Jurassic sedimentation in the Cleveland Basin: a review. *Proc. Yorks. Geol. Soc.* 58 (1), 21–72.
- Powell, J.H., Riding, J., 2016. Stratigraphy, sedimentology and structure of the Jurassic (Callovian to lower Oxfordian) succession at Castle Hill, Scarborough, North Yorkshire, UK. *Proc. Yorks. Geol. Soc.* 61, 109–133.
- Raper, E., Banks, D., Shipperbottom, J., Ham, P., 2022. Baseline surface- and groundwater monitoring prior to an onshore shale gas operation in the Vale of Pickering, UK. *Q. J. Eng. Geol. Hydrogeol.* 55 (3).
- Reeves, M.J., Parry, E.L., Richardson, G., 1978. Preliminary investigation of the groundwater resources of the western part of the Vale of Pickering. *Q. J. Eng. Geol.* 11, 253–262.
- Schloemer, S., Elbracht, J., Blumenberg, M., Illing, C.J., 2016. Distribution and origin of dissolved methane, ethane and propane in shallow groundwater of Lower Saxony, Germany. *Appl. Geochem.* 67, 118–132.
- Siegel, D.I., Azzolina, N.A., Smith, B.J., Perry, A.E., Bothun, R.L., 2015. Methane Concentrations in Water Wells Unrelated to Proximity to existing Oil and Gas Wells in Northeastern Pennsylvania. *Environ. Sci. Technol.* 49 (7), 4106–4112.
- Smedley, P.L., et al., 2015. Site Selection Strategy for Environmental Monitoring in Connection with Shale-Gas Exploration: Vale of Pickering, Yorkshire and Fylde, Lancashire. Open Report, OR/15/067. British Geological Survey, Keyworth, UK.
- Smedley, P.L., Ward, R.S., Bearcock, J.M., Boves, M.J., 2017. Establishing the baseline in groundwater chemistry in connection with shale-gas exploration: Vale of Pickering, UK. In: Marques, J.M., Chambel, A. (Eds.), *15th Water-Rock Interaction International Symposium, WRI-15*. Procedia Earth and Planetary Science, pp. 678–681.
- Smith, A.C., Welsh, S., Atkinson, H., Harris, D., Leng, M.J., 2021. A new automated method for high-throughput carbon and hydrogen isotope analysis of gaseous and dissolved methane at atmospheric concentrations. *Rapid Commun. Mass Spectrom.* 35 (11), e9086.
- Stolper, D.A., et al., 2015. Distinguishing and understanding thermogenic and biogenic sources of methane using multiply substituted isotopologues. *Geochim. Cosmochim. Acta* 161, 219–247.
- Tattersall, K.H., Wilkinson, W.B., 1974. *Groundwater Investigation in the Vale of Pickering: Final Report on Preliminary Investigation*. Yorkshire River Authority and Water Resources Board.
- Taylor, K.A., Risk, D., Williams, J.P., Wach, G.D., Sherwood, O.A., 2021. Occurrence and origin of groundwater methane in the Stellarton Basin, Nova Scotia, Canada. *Sci. Total Environ.* 754, 141888.
- The Royal Society and The Royal Academy of Engineering, 2012. *Shale Gas Extraction in the UK: A Review of Hydraulic Fracturing*. The Royal Society and The Royal Academy of Engineering, London.
- Timmers, P.H.A., et al., 2016. Anaerobic oxidation of methane associated with sulfate reduction in a natural freshwater gas source. *ISME J.* 10 (6), 1400–1412.
- Tyler, S.C., Crill, P.M., Brailsford, G.W., 1994. 13C12C fractionation of methane during oxidation in a temperate forested soil. *Geochim. Cosmochim. Acta* 58 (6), 1625–1633.
- Van Stempvoort, D., Maathuis, H., Jaworski, E., Mayer, B., Rich, K., 2005. Oxidation of fugitive methane in ground water linked to bacterial sulfate reduction. *Groundwater* 43 (2), 187–199.
- Vidic, R.D., Brantley, S.L., Vandenbossche, J.M., Yoxheimer, D., Abad, J.D., 2013. Impact of Shale Gas Development on Regional Water Quality. *Science* 340 (6134).
- Vigneron, A., et al., 2017. Microbial and Isotopic evidence for methane Cycling in Hydrocarbon-Containing Groundwater from the Pennsylvania Region. *Front. Microbiol.* 8.
- Ward, R.S., et al., 2017. Environmental Baseline Monitoring Project: Phase II - Final Report. Open Report, OR/17/049. British Geological Survey, Keyworth, UK.
- Water, Envireau, 2017. KM8 monitoring boreholes as built construction report; KM8 well. In: Kirby Misperton A wellsite, North Yorkshire, Envireau Water.
- Wen, T., et al., 2016. Methane sources and Migration Mechanisms in Shallow Groundwaters in Parker and Hood Counties, Texas—a Heavy Noble Gas Analysis. *Environ. Sci. Technol.* 50 (21), 12012–12021.
- Whitelaw, P., et al., 2019. Shale gas reserve evaluation by laboratory pyrolysis and gas holding capacity consistent with field data. *Nat. Commun.* 10 (1), 3659.
- Whiticar, M.J., 1999. Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane. *Chem. Geol.* 161 (1), 291–314.
- Whiticar, M.J., Faber, E., Schoell, M., 1986. Biogenic methane formation in marine and freshwater environments: CO₂ reduction vs. acetate fermentation—Isotope evidence. *Geochim. Cosmochim. Acta* 50 (5), 693–709.
- Wilhelm, E., Battino, R., Wilcock, R.J., 1977. Low-pressure solubility of gases in liquid water. *Chem. Rev.* 77 (2), 219–262.
- Williams, P.F.V., 1986. Petroleum geochemistry of the Kimmeridge Clay of onshore Southern and Eastern England. *Mar. Pet. Geol.* 3 (4), 258–281.
- Wilson, V., 1948. *East Yorkshire and Lincolnshire*. British Regional Geology, HMSO, London, 94 pp.
- Wright, J., 2009. The geology of the Corallian ridge (Upper Jurassic) between Gilling East and North Grimston, Howardian Hills, North Yorkshire. *Proc. Yorks. Geol. Soc.* 57, 193–216.
- Yin, M., Snowdon, L.R., Silva, R.C., Huang, H., Larter, S., 2023. Impacts of natural irradiation on sedimentary organic matter—a review. *Org. Geochem.* 180, 104602.
- Yoshinaga, M.Y., et al., 2014. Carbon isotope equilibration during sulphate-limited anaerobic oxidation of methane. *Nat. Geosci.* 7 (3), 190–194.
- Zhang, C., Grossman, E.L., Ammerman, J.W., 1998. Factors influencing methane distribution in Texas Ground Water. *Groundwater* 36 (1), 58–66.