

Interactive comment on “Biogeochemical constraints on the origin of methane in an alluvial aquifer: evidence for the upward migration of methane from a coal seam” by Charlotte P. Iverach et al.

D.D.R. Owen

des.owen@nrra.science

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This paper uses geochemical data, microbial DNA analyses and $\delta^{13}\text{C}\text{-CH}_4$ of free gas measured in well headspaces to investigate potential production, degradation and migration processes of CH_4 in the Condamine Alluvium (CRAA), which is a large agriculturally-important groundwater resource. This alluvium overlies a coal-bearing formation, the Walloon Coal Measures, which contains commercial quantities of coal seam gas (CSG) in some areas.

The paper is generally well written and the microbial DNA data is novel for this study

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area. However, there are some shortfalls both with respect to information and interpretations (or lack thereof) of existing published work, as well as the interpretations of the authors' data set, some of which carry over from a preceding study (Iverach et al. 2015).

As a result, my opinion is that the major finding of the study, “that a combination of geochemical data ($[\text{CH}_4]$, $[\text{SO}_4^{2-}]$, $[\text{NO}_3^-]$, $[\text{NO}_2^-]$, $\delta^{13}\text{C}\text{-CH}_4$, $\delta^{13}\text{C}\text{-DIC}$, $\delta^{13}\text{C}\text{-DOC}$ and $\delta^2\text{H}\text{-H}_2\text{O}$), as well as characterisation of microbiological communities present, can inform the discussion surrounding the occurrence of CH_4 , and its potential for upward migration in the groundwater of the CRAA”, has not been achieved in the paper. In its current form, the broader interpretations of aquifer connectivity are not supported by existing data sets. This has potential to cause confusion not only in the scientific disciplines but also in the public arena (aquifer connectivity in this catchment is controversial). I suggest the discussion points below are worth considering and that some of the interpretations are revisited. I have provided additional references that may help the authors with this.

I also suggest the publication title needs revising: “. . .methane from a coal seam”. The authors actually mean the coal measures, which contain multiple discontinuous coal seams.

1. Addressing a recent paper published in the study area.

Another paper, which I co-author (Owen et al., 2016), was very recently published (31 August) in the same journal as the co-authors' more recent paper (Iverach et al., 2015), just after Iverach et al. submitted this Biogeosciences paper (25 August). This recent paper by Owen et al. provides some discussion and alternative thinking on the interpretations made by Iverach et al. (2015). This is relevant because Iverach et al. maintain some of these interpretations from the earlier paper in this Biogeosciences paper. While the Owen et al. (2016) paper was published after the Iverach et al. submission of this Biogeosciences paper, some issues raised in the Owen et al. (2016)

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paper should be addressed by Iverach et al. in this Biogeosciences paper in a revision going forward.

Owen et al. (2016) made an attempt to develop a conceptual model of CH₄ in this system which could be built upon. I also encourage the authors to contribute to the conceptual understanding of this system so that an improved understanding of this system can be built upon over time as more studies are performed.

2. Thermogenic vs biogenic CH₄.

Generally, the authors maintain that there is a significant thermogenic CH₄ component in the coal measures. However, this is at odds with published work in this basin (Draper and Boreham, 2006; Hamilton et al., 2012; Golding et al., 2013; Hamilton et al., 2014; Baublys et al., 2015). Similarly, the recent Owen et al. (2016) paper presents high and positive $\delta^{13}\text{C-DIC}$ for CH₄ in the CSG reservoir which is indicative of CO₂ reduction via microbial activity. I encourage the authors to familiarise themselves with this body of work and references therein.

Two other references (Papendick et al., 2011; Hamilton et al., 2012) (lines 399 – 402, page 19) are not really supporting the authors claim of thermogenic CH₄ and should be removed. In the abstract, and other parts, Hamilton et al. (2014) make clear statements about microbial CH₄. Papendick et al. (2011) provides some literature review of the $\delta^{13}\text{C-CH}_4$ from the basin, and in this section Papendick et al. make a clear statement that Walloon CH₄ is mainly biogenic (see section, 1.2, page 124 of Papendick et al. (2011)).

There is value in understanding CH₄ origins (biogenic vs thermogenic) in CSG studies that are concerned with the gas reservoir itself because this can inform us about a number of hydrogeological characteristics. Outside the gas reservoir, however, if it is not possible to accurately distinguish thermogenic vs biogenic sources then attempts to describe thermogenic vs biogenic components are not helpful for understanding potential gas migration and it can become a distraction. This underpins the next point.

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The Iverach et al. data set does not lend itself to distinguishing between thermogenic and biogenic CH₄ components. While the $\delta^{13}\text{C-CH}_4$ are within a thermogenic or mixed range, it is not possible to determine thermogenic vs biogenic components solely using $\delta^{13}\text{C-CH}_4$ data. Whiticar (1999) (which Iverach et al. have referenced) provides the well-known $\delta^2\text{H-CH}_4$ vs $\delta^{13}\text{C-CH}_4$ plot – from the boundaries on this plot you can see that the biogenic CH₄ can occur across a wide range of depleted and enriched $\delta^{13}\text{C-CH}_4$ values. However, Kotelnikova (2002), which Iverach et al. have also referenced, states in the abstract “Literature data shows that CH₄ as heavy as -40‰ or -50‰ can be produced by the microbial reduction of isotopically heavy CO₂”; therefore, this Whiticar plot alone is still insufficient to determine thermogenic components. Whiticar (1999) also goes into some examples of additional techniques that need to be used to identify thermogenic vs biogenic components, including the use of the Bernadi parameter, which is the ratio of C₁ / C₂ + C₃ gases. The Whiticar paper also discusses how other processes such as oxidation and acetate fermentation can also produce $\delta^{13}\text{C-CH}_4$ that is within a similar range to thermogenic CH₄. There is an excellent paper by Golding et al. (2013) that specifically reviews and discusses techniques for understanding CSG CH₄ origins, including the use of isotope fractionation factors, isotopes and the Bernadi parameter. The Iverach et al data set does not lend itself to any of these analytical techniques because they have only measured $\delta^{13}\text{C-CH}_4$ and CH₄ ppm in free gas samples. While the $\delta^{13}\text{C-DIC}$ in water is measured, I am not sure that a carbon isotope fractionation factor between dissolved carbon and free CH₄ would make much sense here (what’s needed is the $\delta^{13}\text{C-CH}_4$ of the intermediate, i.e. the $\delta^{13}\text{C-CH}_4$ of the CH₄ in the water prior to any degassing).

By reconsidering the initial position on thermogenic CH₄ in the study, as per the references above, then it could be argued that significant changes to data interpretations and conclusions in this paper are required. Since the authors do not have the data to assess thermogenic vs biogenic components, descriptions and interpretations on thermogenic vs biogenic CH₄ should be avoided in their paper.

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3. Limitations on using $\delta^{13}\text{C-CH}_4$ as “signatures”.

There is a dependency in this paper on the $\delta^{13}\text{C-CH}_4$ results to interpret CH_4 origins. This includes the claim that $\delta^{13}\text{C-CH}_4$ provides a “signature” of CH_4 origin and source (for example, lines 105 – 108, page 5; lines 114-116 page 5; lines 199-2-1, page 9; lines 333-341, page 14-15; lines 399-401, page 19; lines 406-407, page 19). The use of the term “signature” implies a unique identifier that is distinct from all others. However, the notion of a $\delta^{13}\text{C-CH}_4$ “signature” of CH_4 is not valid because there are numerous influences that can affect the isotope and associated fractionation processes. Thus, similar $\delta^{13}\text{C-CH}_4$ values can be produced coincidentally, and they are not necessarily an indication of related origins/sources. The authors acknowledge this to a small degree at lines 65-67 page 3, but the issue is later ignored in their interpretations. The $\delta^{13}\text{C-CH}_4$ can behave non-conservatively under many scenarios. I suggest the authors remove all instances of the word “signature” as it is misleading, particularly to the public.

I recommend the authors familiarise themselves with Golding et al. (2013) and Owen et al (2016) and references therein, when revising their interpretations of $\delta^{13}\text{C-CH}_4$. Figure S1 in Owen et al. (2016) provides a graphical example of overlapping $\delta^{13}\text{C-CH}_4$ based on examples from published literature; these papers and their results would also be of value to these authors.

4. Identifying the $\delta^{13}\text{C-CH}_4$ coal measure end member.

Iverach et al. claim that “the $\delta^{13}\text{C-CH}_4$ of the underlying WCM in the study area has been characterised (Papendick et al., 2011; Hamilton et al., 2012; Hamilton et al., 2014).” This is a very misleading statement and it is not supported by the references provided.

Papendick et al. assessed microbial growth from samples, and do not report $\delta^{13}\text{C-CH}_4$ data. Hamilton et al. (2012) assessed gas content trends and do not report $\delta^{13}\text{C-CH}_4$ data. In any case, the Hamilton et al. (2012) study only took a handful of samples that

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are possibly underlying the western alluvial edge, all of which are downstream (at least 50 km) of the Iverach et al study area.

Hamilton (2014) is the only reference used above that reports $\delta^{13}\text{C-CH}_4$ data. Based on the map provided in that study, the wells sampled for that study do not appear to be underlying the alluvium.

Commercial quantities of gas only occur in certain areas; usually geological structures where conditions support gas trapping; some useful references are (Exon, 1976; Day et al., 2006; Day et al., 2008; Day, 2009; Hamilton et al., 2012; Cook and Draper, 2013; Golding et al., 2013; Hamilton et al., 2014; Baublys et al., 2015). Generally, the gas reservoirs, where commercial quantities of gas occur, are much deeper (300-500 m+) than the alluvial-coal measures interface (~160-180m).

Importantly, the entire Walloon Coal Measures is not one big gas reservoir with homogenous $\delta^{13}\text{C-CH}_4$ and gas content. Inside gas reservoirs, where gas is trapped, conditions support enriched $\delta^{13}\text{C-CH}_4$ values. Outside the gas reservoir, conditions are different and so are the influences on $\delta^{13}\text{C-CH}_4$ fractionation. CH_4 is not consistent within the coal measures, and in some places it is absent altogether (or at least below DL). Owen et al. (2016) found that many shallow coal measure wells, including some directly underlying the alluvium, contain no $\text{CH}_4 > \text{DL}$ (10 $\mu\text{g/L}$).

To my knowledge, Owen et al. (2016) presents the only published $\delta^{13}\text{C-CH}_4$ data for the coal measures that directly underlie the alluvium so far (i.e. that are outside the gas reservoirs). This shows a depleted $\delta^{13}\text{C-CH}_4$ value (-80‰ to -65‰ in the coal measures directly underlying the alluvium, which is very different to the enriched $\delta^{13}\text{C-CH}_4$ range (~ -55‰ to -47‰ that Iverach et al. are using as the coal measure end member. Owen et al. (2016) has a discussion on the changes in $\delta^{13}\text{C-CH}_4$ throughout the coal measures, and presents a conceptual model based on that data. Based on this data, I suggest that the interpretations of aquifer connectivity using $\delta^{13}\text{C-CH}_4$ in this paper need reviewing.

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5. Microbial activity in the alluvium.

The novel microbial DNA data are interesting and provide a valuable addition to the data in this study area. The absence of methanogenic archaea is also interesting and supports Owen et al. (2016) which found very limited occurrence of CH₄ in the alluvium.

Regarding sample collection, were the water samples collected for microbial DNA filtered through 0.2 micron filters during collection (Line 232, page 10)? If so, then it is possible that this filtration has resulted in sample sterilisation. Or, is the 0.2 micron filtering referring to the biomass filtering as per line 262, page 12? As it currently reads, the 2L of water collected for DNA filtering, was pre-filtered in the field using 0.2 micron filters, which would have removed microbes.

Are the DNA data for potential methanogenic archaea focussing on acetoclastic archaea only? In other words, were archaea that are responsible for CO₂ reduction potentially ignored in this study? CO₂ reduction is the dominant methanogenic pathway in these aquifers (Golding et al., 2013; Hamilton et al., 2014; Baublys et al., 2015; Owen et al., 2016).

It would also be beneficial to attempt to grow microbes from alluvial water samples in the laboratory: until this research is performed at sites where CH₄ is measured in the water then conclusions about the general absence of methanogenic activity in this aquifer are premature.

I also wonder if the DNA data are useful for understanding aquifer connectivity. The authors use the microbial DNA data to show the absence of methanogens in the alluvium, but in Iverach et al. (2015) the authors use the same $\delta^{13}\text{C-CH}_4$ data to infer hydraulic connectivity between the aquifers at some sites. If hydraulic connectivity is occurring, wouldn't the alluvium contain the microbial consortia from the coal measures? In this Biogeosciences paper, the authors only refer to CH₄ migration, which may occur independently of water migration. Are the authors revising, or suggesting a

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change to, interpretations of hydraulic connectivity made in Iverach et al. (2015) in this new paper?

In order to support the claim that there is no methanogenic activity in the alluvium, Iverach et al. also use the absence of $\delta^{13}\text{C-DIC}$ enrichment and $\delta^{13}\text{C-DOC}$ depletion (Kotelnikova, 2002) to support the conclusion that there is no in situ methanogenesis in the alluvium. However, in this heterogeneous aquifer there are likely to be multiple sources of DIC and DOC. A relationship between $\delta^{13}\text{C-DIC}$ and $\delta^{13}\text{C-DOC}$ under methanogenic conditions would only be obvious in areas where high rates of methanogenesis are occurring and/or in discrete zones where single sources of DIC and DOC occur. The wells sampled by Iverach et al. are screened at multiple intervals over relatively large depth profiles. These samples can be expected to have variable (mixed) $\delta^{13}\text{C-DIC}$ based on the source/depth origin of the water and other hydrochemical conditions. Carbonates and calcretes are also common in this aquifer, and their dissolution and precipitation would affect the $\delta^{13}\text{C-DIC}$, as would different recharge sources and any connate water. In addition, Owen et al (2016) provide a discussion on the possibility of multiple sources of DOC in the alluvium.

The authors claim "Our geochemical data also showed no evidence for the occurrence of methanogenesis in the groundwater" (Line 376-377 page 17). Arguably, this is because their geochemical data set is not capable of making this assessment conclusively. There are no CH₄ measurements taken from the water itself, so how can the microbial response in the water be compared to a potential methanogenic pathway? Samples taken from wells with multiple screens over different depth profiles are likely to mask any depth-related methanogenic/redox conditions (e.g. changes in SO₄ concentrations). Owen et al. (2016) showed an inverse relationship between SO₄ and CH₄ in the water for alluvial samples in the same aquifer where CH₄ was detected. This is typical of methanogenic activity. Iverach et al. only have allegedly degassed, free CH₄ data. Humez et al. (2016) provides a very good methodological approach for investigating if CH₄ has potentially migrated from somewhere else or was generated in

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6. $\delta^{13}\text{C}$ -CH₄ are similar to background atmospheric CH₄.

The CH₄ ppm and $\delta^{13}\text{C}$ -CH₄ measured by Iverach et al. (2015) which are used in this study are similar to background, atmospheric CH₄ ppm and $\delta^{13}\text{C}$ -CH₄ (Dlugokencky et al., 2011; Stalker, 2013). Iverach et al. (2015) reference these references. Owen et al. (2016) raise the issue that Iverach et al. (2015) have possibly only measured atmospheric CH₄ that has been sucked into the well head during pumping. Iverach et al. are referred to that discussion in that paper.

What is missing in the Iverach et al. $\delta^{13}\text{C}$ -CH₄ data set is the crucial CH₄ in the water (end member), i.e. what is the $\delta^{13}\text{C}$ -CH₄ prior to any degassing? What is the concentration of CH₄ in the water? What is the flux of any degassing CH₄ from the water and how does this affect concentration and isotope fractionation, and how does this compare between samples? Without this additional data it is not possible to confidently determine where the measured free CH₄ presented by Iverach et al. (2015), and which is used again by Iverach et al. in this paper, has come from. The fact that the values are similar to background atmospheric free gas provides a plausible argument against both the findings of Iverach et al (2015) and Iverach et al. presented in this paper. Iverach et al. (2015) and Iverach et al. in this paper claim that the CH₄ must be coming from the underlying coal measures; however, this is an assumption that is not yet supported by any data. The authors should be careful not to open themselves up to criticism of subjective bias, i.e. a preconception that aquifer connectivity/gas migration must be occurring. Owen et al. (2016) proposes a minimum set of parameters required to make assessments of CH₄ migration. This includes discussion on the value of $\delta^2\text{H}$ -CH₄ in assisting with determining CH₄ origins.

7. Inferred vs. measured $\delta^{13}\text{C}$ -CH₄ values.

At times throughout the paper, Iverach et al. report $\delta^{13}\text{C}$ -CH₄ values, not as the measured values but as the values taken from a regression line as reported in Iverach

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et al. (2015); for example, lines 406-407, page 19. This is very misleading for the reader.

The keeling-style plot used in Iverach et al (2015) is inappropriate because; 1) there are three potential sources of CH₄ (alluvial, coal measure and atmospheric) and a keeling-style plot cannot be used to differentiate the mixing components between these three sources; 2) one of the regression lines relies on a single outlying point (removing this outlier would invalidate the regression line); 3) most of the data are clumped around similar values (is the variability in the data set significant/relevant?); 4) the method used (a combination of DOC and 3H) to categorize samples is questioned. Iverach et al. are referred to this discussion in Owen et al. (2016) for more detail.

The discussion by Iverach et al. on CH₄ origins tends to be assumptive and at times not logical. For example, at one point the authors claim that three samples “have a typically biogenic isotopic source signature (-69.1‰” (lines 406-407 page 19): recall that this is not the measured $\delta^{13}\text{C}$ -CH₄, but the $\delta^{13}\text{C}$ -CH₄ inferred from the regression line in Iverach et al. (2015); the measured values are \sim -47‰. The possible biogenic sources are explained as being coal measure-derived CH₄ from an area where biogenic CH₄ has replaced thermogenic CH₄ in the coal measures. Biogenic CH₄ can replace thermogenic CH₄, but then this discussion point is inconsistent with the authors' earlier thermogenic descriptions of the basin/coal measure CH₄. If thermogenic and biogenic CH₄ components change throughout the coal measures, then it would be reasonable to expect the proportion of biogenic vs thermogenic CH₄ in any migrating gas to also vary, and mixing would then also occur in the alluvium. Acknowledging this adds a great deal of complexity to this type of study which is not addressed in this paper.

In this paper, it would be more transparent for Iverach et al. to report the actual measured $\delta^{13}\text{C}$ -CH₄ values at all times. Given that Owen et al. (2016) raise discussion points about the use of the Iverach et al. (2015) methods, this Biogeosciences paper should either address those points, or avoid relying on the Iverach et al. (2015)

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$\delta^{13}\text{C-CH}_4$ results altogether. Given the isotopic data of the shallow coal measures underlying the alluvium (a biogenic, depleted $\delta^{13}\text{C-CH}_4$ range) presented in Owen et al. (2016), the interpretations made by Iverach et al. (2015) and by Iverach et al. in this paper could be questioned (see discussion point 4 above).

8. No samples were taken from the allegedly discharging aquifer.

A major shortfall of this paper and of Iverach et al. (2015) is that not a single sample was taken from the allegedly discharging aquifer, the Walloon Coal Measures. Samples have only been taken from the alluvium. It is without precedent that conclusions regarding hydraulic connectivity and aquifer interactions have been drawn in two successive hydrogeological studies without using appropriate reference samples from both the allegedly interacting aquifers.

In order to make valuable use of their data within the appropriate scientific limitations, I would encourage Iverach et al. in this paper to avoid jumping to conclusions about aquifer connectivity. I would recommend the authors assess the data that they have, play to its strengths with respect to the data limitations, and focus on contributing to the understanding of this system rather than resolving broader questions about aquifer connectivity, which cannot be confidently made from this data set.

9. Incorrect referencing.

In addition to the incorrect references regarding $\delta^{13}\text{C-CH}_4$ and thermogenic vs biogenic CH_4 identified in the above discussion points, there are other cases where Iverach et al. have incorrectly referenced material or have misrepresented quotes or statements from referenced material. This lets the paper down. I have provided some examples below, with discussion points and recommendations for new references in places. I encourage the authors to revise their work and check references carefully and present transparent, objective discussion based on all available literature.

Geological/hydrogeological references: In a number of places incorrect references are

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used when discussing background information. For example Hillier (2010) (Line 170-172, page 8) and KCB (2011) (Line 174-176, page 8) are non-peer-reviewed consultant reports that did not present the background information being referred to. Similarly, Kelly and Merrick (2007) (Line 178-181, page 8), is also not peer-reviewed and summarises other published work. Authors are referred to appropriate literature that provides the background information for referencing (e.g. Lane, 1979; Huxley, 1982; Cook and Draper, 2013).

Inappropriate references: Kelly et al. (2014) (Line 178-181, page 8) and Duvert et al. (2015) (Line 197-199, page 9) pertain to studies in two different catchments (the Namoi and Teviot Brook catchments, respectively). These references are inappropriate to reference here.

Misleading referencing: "Huxley (1982) and Hillier (2010) both suggest that the general decline in water quality downstream is due to some net flow of the more saline WCM water into the CRAA." (Line 193-195, page 9).

The theory that a general decrease in water quality downstream is due to an influx of more saline water from the coal measures has been examined in Owen and Cox (2015). That paper found that evapotranspiration was the dominant influence on salinity in the alluvium, and that the most saline water occurs in the shallowest alluvial wells. An increase in clay content and decrease in hydraulic conductivity downstream of Cecil Plains, which are characteristics identified by Huxley (1982), would be helping to drive these processes. Since Iverach et al. (2015) and Iverach et al. in this paper both reference Owen and Cox (2015) already, it is not clear why that paper is ignored in this context. Non-peer reviewed material (e.g. Hillier, 2010) should not be used in place of more recent peer-reviewed material.

"Duvert et al. (2015) and Owen and Cox (2015) both used hydrogeochemical analyses to show that there was limited movement of water between the two formations." (Line 197-199, page 9)

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Owen and Cox (2015) did not explicitly assess water movement between the two aquifers: the statement above is misleading. It is frustrating to see this material referenced in this way, particularly as Iverach et al. (2015) already also misquote this paper. The aims of Owen and Cox (2015) were to investigate hydrochemical evolution within the alluvium, with a focus on the origins of Na and Cl and Na-HCO₃ water types. This is clearly outlined in the introduction of that paper. The conclusions were that the dominant water types in the alluvium were the result of other processes not related to bedrock discharge, however the paper also noted in the conclusions that “The persistence of Na–HCO₃–Cl water types in some deep alluvial wells at the alluvial–WCM interface from Cecil Plains to Dalby provides the most likely indication of any alluvial–WCM interaction; however, these water types also occur in shallower alluvial zones.” Clearly this paper does not make definitive conclusions regarding aquifer connectivity, and it even highlights areas where potential aquifer interaction could be occurring. It appears that Iverach et al. have not read Owen and Cox (2015) properly. It is not appropriate to continue to misrepresent this published work, and to continue to rely on earlier, non-peer reviewed work (e.g. Hillier, 2010) to support particular angles/arguments.

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