

We thank the reviewer for their time and constructive comments on our manuscript. We have addressed all concerns raised below.

### M. Currell (Referee)

Iverach et al. present a novel approach to the determination of methane sources in shallow groundwater in the Condamine Alluvium aquifer, Australia. I think the study is of high scientific significance, for two main reasons:

1. The use of combined geochemical and microbiological indicators to study the origins of methane in groundwater is novel. Studies of this kind are relatively rare in the literature, and the microbiological analysis provide insight about the methane sources and degradation processes that couldn't otherwise be gained from the isotopic analyses alone
2. The topic and research question(s) are of high importance, given the current debate about environmental impacts of coal seam gas (and other unconventional gas), both in this particular area of Australia, and worldwide.

There are some minor issues and corrections needed, and some areas where additional information could be included to make the paper more solid. However, overall I think this is a high quality manuscript.

#### Specific comments

**Abstract Line 33-34:** Which data? I like to see some actual data values or description of the particular aspects of the data set of greatest significance (and supporting the conclusions described) included in the abstract. If more space is needed in order to do this, I suggest removing the second sentence of the abstract, as this is background information that can be included in the introduction.

A description of the particular data that provide the greatest significance (no methanogenesis *in-situ*) has been included in the abstract. We mention the isotopes of DIC and DOC and the concentration of  $\text{SO}_4^{2-}$  as being the pertinent geochemical data, and the absence of methanogenic archaea being the important microbial data presented to support the conclusions in the manuscript.

**Introduction Line 50:** I suggest adding the term 'in situ' when discussing biological production of methane in the shallow groundwater. This makes it clear that you are distinguishing two different potential gas sources- one produced in the shallow aquifer itself, and another whereby gas from another unit has migrated to the aquifer.

We have added 'in situ' when discussing biological production of methane in the shallow groundwater.

**Line 81:** 'Therefore' is not really the best word here. It does not follow logically from the preceding discussion that combining geochemistry/microbiology can discriminate the relevant processes; rather you could say that microbiological indicators have the potential to resolve some of the uncertainties just mentioned (e.g. methanogenesis and methane degradation processes), that can't be otherwise determined on the basis of geochemical data alone. Here you could also note the general absence of published studies which have combined geochemical and microbiological indicators to look at methane sources and degradation in an applied setting (an important point to make in your introduction).

'Therefore' has been removed and sentence has been rewritten following the suggestion

above. We have also mentioned that there are no studies using geochemical and microbiological indicators to assess CH<sub>4</sub> production and degradation processes in a freshwater aquifer and that this study aims to fill this gap in the literature.

**Line 103:** See previous comment; this could be clarified by adding 'in situ methanogenesis' to distinguish from gas migration from another unit.

As above, the term 'in situ' has now been added.

**Line 104-108:** I think you should expand this paragraph and include some of the actual data, e.g. the observed ranges and mean/median values of d13CCH<sub>4</sub> and d13CDIC found in the WCM from other published studies. This can be included in the text (e.g. ranges, mean values etc), as well as in a table. This would help to strengthen your isotopic lines of evidence to support the hypothesised migration mechanism later in the manuscript. Note that Baublys et al 2015 (Int. J. Coal Geol v.147-8, pp85-104) have also reported extensive data on isotopic composition of gases and water in the WCM, which should be included along with other recent published studies.

This paragraph has been expanded to include some actual data reported for the WCM. Data ranges have been provided in text as well as in a table. Isotopes for DIC weren't available for all of the studies, but included where possible. Baublys et al. 2015 has been added to the references here.

**Study area Line 146-47:** Try to avoid repetition (primary/primarily)

Primarily has been removed from the second sentence.

**Line 151:** Suggest adding 'including methane concentrations' at the end of this sentence, to highlight the significance of what you are looking at (mostly the methane in groundwater).

We have added 'especially with respect to CH<sub>4</sub> concentrations' after groundwater quality to highlight that it is the methane in groundwater that we are concerned with.

**2.1 Hydrogeological setting.** Could you include a cross section or at least a stratigraphic column to go with your description of the geological units?

We have included a cross section to go with the description and provided a reference to the literature.

**Line 160:** 'The CRAA sits within the Surat Basin, which is a major sub-province of the Great Artesian Basin'. Perhaps refer to one of the Geoscience Australia and/or CSIRO hydrogeology reports on the GAB (e.g. Ransley and Smerdon, 2012).

We have now referenced the abovementioned report, as well as the extensive work by Radke et al. 2000 on the hydrodynamics and hydrochemistry of the GAB (Radke et al. Hydrochemistry and implied hydrodynamics of the Cadna-owie Hooray Aquifer Great Artesian Basin, 2000).

**Line 188:** The recent studies by the Office of Groundwater Impact Assessment (OGIA) may have more detail about the connectivity between the CRAA and the WCM and the extent of the aquitard(s), e.g. the Surat Underground water impact report (OGIA, 2016).

This reference has been included in the connectivity section of the hydrogeology, with a sentence explaining their more recent findings on the connectivity between the WCM and the CRAA (lines 229-233).

**Line 203:** Connectivity for gas? water? both?

This has been clarified in the manuscript. It is connectivity for both gas and water.

**Method Line 212:** Here you should refer to a figure and/or table which includes your sample depths and locations

Figure 1 has been referred to in the methods for the locations of the samples and a small table has now been included to show the slotted interval depth of each bore that was sampled.

**Line 233-34:** Were the physico-chemical parameters (EC, pH, DO) monitored during the second round of sampling? If so, you could report these and use as evidence that the water composition between the two sampling events did not change substantially (if this is true).

Unfortunately, the physico-chemical parameters were not monitored during the second round of sampling. However, thirty years of studies have shown that the groundwater chemistry has remained fairly consistent (Huxley 1982).

**Line 238-239:** What about cations?

Our groundwater samples were analysed for cations, however we don't use any cation data in this manuscript. For completeness, we have now added the analysis method that the groundwater underwent for cations.

**Line 242-243:** Can you refer to a published paper where the same method was used? Same for the DIC isotopes (line 245).

Published papers have now been referred to for all of the analytical techniques used for the geochemical analyses.

**Results & Discussion Line 371:** Suggest writing 'in situ within the CRAA' instead of 'locally' to be clearer.

This has been changed.

**Line 377:** Do you mean the major ion data? Which particular aspects (e.g. sulfate and nitrate concentration data)?

At this point the discussion is just on the DIC and DOC isotopic data. The beginning of the sentence has been changed to "Our isotopic geochemical data" to make it clearer.

**Line 396:** Suggest changing to: 'major processes resulting in CH<sub>4</sub> in the CRAA' rather than 'producing CH<sub>4</sub> in the CRAA' (or you could say 'responsible for the presence of CH<sub>4</sub>').

This has been changed.

**Line 398:** Suggest changing 'coming from' to 'derived from'.

This has been changed.

**Line 406-411:** This paragraph is a bit confusing and needs re-writing. Is the gas in the WCM really 'typically thermogenic'? All of the isotopic data for <sup>13</sup>CCH<sub>4</sub> I have seen for gases and water in the WCM indicates a bacterial source of methane (e.g. <sup>13</sup>CCH<sub>4</sub> values around -50permil) rather than thermogenic (which should have values higher than -40permil). Is there anything else distinctive about the samples with more depleted <sup>13</sup>CCH<sub>4</sub>, such as a much lower CH<sub>4</sub> concentrations or differences in the major ions that could explain the isotopic difference?

Stating that the gas from the WCM was thermogenic was a large oversight and this sentence has now actually been completely removed in the re-write of the paragraph. A new reference that was published after this manuscript was originally submitted has been added (Owen et

al., 2016). This paper describes an isotopic signature for a ‘shallow WCM’ – a unit between the WCM ‘gas reservoir’ and the overlying alluvium. This signature is between -80permil and -65permil. Therefore, the -69.1permil that these three samples exhibit (despite no methanogens) could be a result of CH<sub>4</sub> from this ‘shallow WCM’, rather than the deeper ‘gas reservoir’. This is discussed in text now.

**Line 431-432:** Yes, and further, the evidence about the presence of sulfate and conditions favouring SRB is a further line of evidence that in situ methanogenesis is unlikely to be responsible for the CH<sub>4</sub> in the shallow aquifer

This further line of evidence has been included to strengthen the manuscript.

**Line 434 - 476:** The section on methane oxidation is insightful; good use of the microbiological methods to combine with the isotopic data and yield some new insights.

Thank you.

**Line 478:** Use the full name for AOM in the title.

The full name for AOM is now used in the title

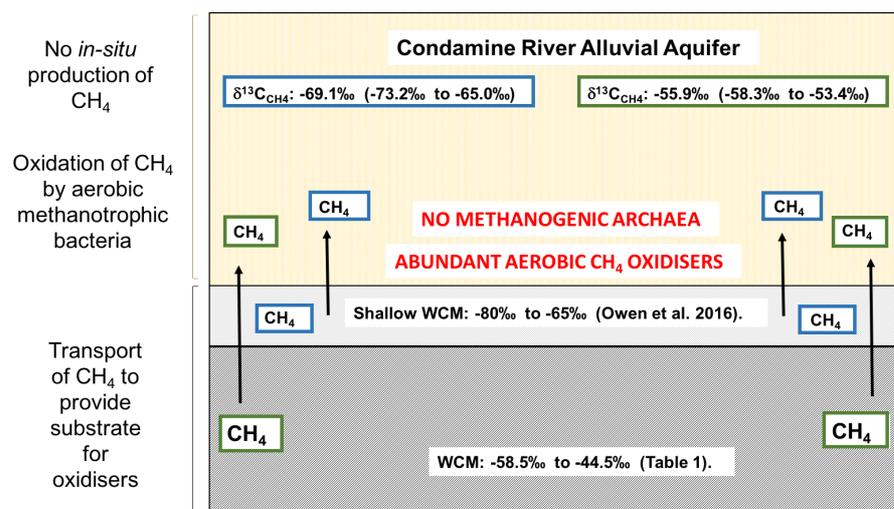
**Line 499-500:** Relative to what? Other water in the CRAA?

It was relative to groundwaters that have the potential for AOM to occur via denitrification.

This has been clarified in text with the appropriate reference.

**General comment** I think including a figure showing your isotopic compositions (<sup>13</sup>CCH<sub>4</sub>) and concentrations of methane, (using the data from Iverach 2015) and comparing with other published data on isotopic characteristics of WCM gases would be helpful, to strengthen the evidence for the proposed hypothesis (together with the microbiological indicators).

A conceptual figure has been included that highlights that there is no *in situ* CH<sub>4</sub> production in the aquifer, there is the presence of CH<sub>4</sub> in the aquifer and there are abundant CH<sub>4</sub> oxidisers in the aquifer. Hence, there is CH<sub>4</sub> migrating upwards to provide the substrate for those oxidisers. Isotopic signatures from the literature provided for the WCM, as well as the signature for the more depleted shallow WCM and measured isotopic signatures for the CRAA (from Iverach et al. 2015) have been included.



**Conclusions Line 536:** You could also note your other lines of evidence here (e.g., that this is supported by the co-existence of CH<sub>4</sub> with sulfate in the groundwater, and the isotopic

composition of the methane).

The isotopic signature of CH<sub>4</sub> and the concentration of SO<sub>4</sub> have been added as further evidence (on top of the microbial data) that methane is being oxidised (hence needs a source to oxidise) and is not being produced *in-situ*.

**Line 547-548:** Your study does not really provide information about the precise pathway(s) by which methane migrates from the WCM to the CRAA, only strong evidence that such migration occurs. Hence, the statement about 'through natural faults and fractures' is really just speculation. Unless you can support it with some geological evidence, other mechanisms may also be responsible (such as transport along wells that are not fully sealed, direct leakage of gas between the units where the aquitard is absent). I suggest either talking about all possible path ways (including these), or simply leaving out the discussion of the pathway altogether and sticking to what your data shows.

We have included all pathways that the gas could be taking to migrate upwards.